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NATO/CCMS Pilot Study

Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater

PHASE II
FINAL REPORT

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Phase II Final Report
NATO/CCMS Pilot Study

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NOTICE

This *Phase II Pilot Study Final Report* was prepared under the auspices of the North Atlantic Treaty Organization's Committee on the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United States Environmental Protection Agency (U.S. EPA). Production of the document was funded by U.S. EPA's Technology Innovation Office under the direction of Michael Kosakowski. Michael A. Smith of Berkhamsted, U.K., served as the principal editor for the report. Final editing and formatting services were provided by Environmental Management Support, Inc., of Silver Spring, Maryland, under U.S. EPA contract 68-W6-0014. Mention of trade names or specific applications does not imply endorsement or acceptance by U.S. EPA.

Chapter 1: INTRODUCTION

Michael A. Smith
M.A. Smith Environmental Consultancy

1.1 BACKGROUND

Groundwater and soil contamination are among the most complex and challenging environmental problems faced by many countries. The problems involve a number of technical issues, including the means of identifying contamination, understanding contaminant behavior in the environment, and mitigating the potential adverse affects to human health and the environment. There are also a number of non-technical issues to be considered, such as the social, economic, and psychological impacts of contamination on individuals and communities, and the need to rejuvenate old urban and industrial areas.

The NATO Committee on the Challenges to Modern Society (NATO/CCMS) has organized a number of pilot studies on the technical aspects of contaminated land. The first pilot study (Box 1.1), which ran from 1980-1984, included an assessment of available remediation methods and a number of other topics. This led to the Phase I Pilot Study (Box 1.2) from 1986-1991 for the purpose of identifying and evaluating innovative, emerging, and alternative technologies and transferring the technical performance and economic information to potential users.

Twenty-nine demonstration projects were shared by the pilot study participants. A specific and important objective of this study was to identify “lessons learned” from the technology demonstrations—not only the successes but also those lessons that illustrated technology failures or limitations. Attention was paid not only to the technologies themselves, but to the practical, operational, and organizational aspects of implementation. Information on limitations and practical aspects of implementation is rarely presented at conferences or discussed in the technical literature, but is very important for making informed decisions involving critical time and monetary requirements. It is also useful for defining priorities in research and development.

The success of the Phase I Pilot Study led to the inception of the Phase II Pilot Study in 1992. Phase II was conducted similarly to Phase I, but was extended in scope to include technologies at an earlier stage of development.

This report provides:

- the background and organization of the Phase II Pilot Study;
- a short description of each of the more than 50 projects included in the study;
- characterization of the projects in a variety of ways including, for example, by the technologies used, their development status, and contaminants treated;
- a critical review of the project results in a series of technology-based chapters; and
- the conclusions and recommendations arising from the study.

The organization of the pilot study, a summary of its achievements, key conclusions, and recommendations to the NATO/CCMS have also been published in a separate *Overview Report (1)*.

Technologies are frequently classified as emerging, innovative, or demonstrated. *Emerging* technologies are at a stage where successful bench-scale testing has been conducted and pilot-scale evaluation is required to determine its potential for use in remediation. *Innovative* technologies are at the stage where pilot- or field-scale testing is being conducted and performance or cost information is incomplete. In general, innovative technologies require field testing to prove their effectiveness before they can be considered proven and available for use in remediation. Finally, *demonstrated* technologies have undergone properly designed independent field evaluation to determine their performance under carefully monitored conditions.

What is viewed as an innovative technology in one country may be regarded as established in another. What is considered as established in one country may not be used widely in others because of doubts about its effectiveness[1]. The term "innovative" often applies to the application of a technology rather than to the principles underlying it. While truly innovative technologies remain a goal, there is also a need for better information and understanding of established processes or means of ensuring that their capabilities are fully realized in practice.

Box 1.1: The First NATO/CCMS Pilot Study on Contaminated Land (1980-84)

The first NATO/CCMS Pilot Study on contaminated land was conducted from 1980 to 1984. Seven countries participated in the study: Canada, Denmark, the Federal Republic of Germany, France, the Netherlands, the United Kingdom (U.K.), and the United States (U.S.).

The Pilot Study culminated in publication of a report (2), which provided a state-of-the-art review of measures available for dealing with contaminated sites and of a number of related topics. It also provided the participating countries with a common basis for understanding the problems posed by contaminated sites and how they might be addressed. A chapter entitled "Long-Term Effectiveness of Remedial Measures," provided the basis for three principal conclusions of the Pilot Study:

- *Systems based on isolation of the contamination (*e.g.*, covering systems) are vulnerable to loss of effectiveness with time; like many other engineered projects they have a finite life;*

- *The development of on-site and* in situ *processes resulting in the removal or destruction of contaminants is to be encouraged as providing a one-time final solution; and*

- *Very few of the technologies described have been sufficiently proven in applications specific to the treatment of contaminated land.*

The initial NATO pilot study led to an extensive exchange of information between participants, the formation of a professional and scientific network that continues to this day, and the initiation of bilateral programs of cooperation.

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[1] An example is stabilization/solidification. While widely applied in the United States, it has only limited application to date in Western Europe.

Box 1.2: The Phase I Study (1986-1991)

The formal title of the Phase I Pilot Study was "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater." This Pilot Study was intended to be a practical, rather than a desk-based exercise, although it continued to provide a forum for the exchange of information on policy developments in the participating countries. It was co-piloted by Germany, the Netherlands, and the United States. and ran from 1986 to 1991. Seven countries participated formally throughout the study. A number of other countries attended at least one meeting on a less formal basis or through the CCMS Fellowship Program.

The objectives of the Phase I Pilot Study were to:

- *identify and evaluate innovative, emerging, and alternative remediation technologies and to transfer technical performance and economic data to potential users; and*
- *identify "lessons learned" from the technology demonstrations, including not only the successes, but lessons illustrating technology failures or limitations.*

A total of 29 demonstration projects from several countries were included in the Phase I Pilot Study. The results of demonstration projects were critically reviewed at the pilot study meetings so that "lessons learned" could be distilled.

The final report (3) published by the U.S. Environmental Protection Agency (USEPA) comprises a principal volume, which presents the lessons learned and technology classifications, and supporting volumes, which contain the individual project reports, reports by CCMS Fellows, papers presented by expert speakers, and other supporting material arising from the Pilot Study.

1.2 STRUCTURE OF THE STUDY

The Phase II Pilot Study was intended to provide a means for information and technology exchange between participating countries; information was also exchanged on regulatory and policy developments. The primary vehicles for the exchange were the Pilot Study members' critical review of projects submitted by the participating countries (Table 1.1), and technical presentations and themed discussions at the meetings of the Pilot Study members. The technical work of the Pilot Study members was enhanced by work on special topics by a number of CCMS Fellows[2] (Section 1.4).

The Phase II Pilot Study was modeled on the Phase I study but included technologies that were in an early stage of development, as well as those that were ready for full-scale demonstration.

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[2] The CCMS awards a number of Fellowships each year to meet travel and subsistence costs for projects related to on-going Pilot Studies. Fellows (*i.e.*, the recipients of fellowships) are encouraged to attend meetings of the Study Group. Fellows have made important contributions to all three CCMS projects on contaminated land.

Table 1.1: List of Projects Included in CCMS Study on Remediation Technology

Country	Project Number	Title
Australia	1	Trial of air-sparging of a petroleum-contaminated aquifer
	2	Bioremediation of petrochemicals following a major fire
	3	Bioclogging of aquifers for containment and remediation of organic contaminants
	4	Remediation of methyl ethyl ketone contaminated soil and groundwater
Austria	5	*In situ* bioremediation, bioavailability, and process control with different soil types
Canada	6	*In situ*/on-site bioremediation of industrial soil contaminated with organic pollutants: elimination of soil toxicity with DARAMEND®
	7	Demonstration of thermal gas-phase reduction process
	8	Biodegradation/bioventing of oil-contaminated soils
	9	Field demonstration of an *in situ* process for soil remediation using well points
	10	Integrated treatment technology for the recovery of inorganic and organic contaminants from soil
Czech Republic	51	Sobéslav, South Bohemia wood treatment plant
	56	Spolchemie a.s.—mercury-contaminated site
Denmark	11	On-site biological degradation of PAHs in soil at former gasworks site
	12	Groundwater and soil remediation at former manganese sulfate production plant
	13	Rehabilitation of a site contaminated by tar substances using new on-site techniques
France	14	Ozone treatment of contaminated groundwater
	15	Combined chemical and microbiological treatment of coking sites/bioremediation of soils from coal and petroleum tar distillation plants
	16	Combined vacuum extraction and *in situ* stripping of chlorinated vapors
	17	Treatment of polluted soil in a mobile solvent extraction unit
	45	Bioremediation of soils from coal and petroleum tar distillation plants
Germany	18	Biological *in situ* remediation of contaminated gasworks
	19	Cleaning of mercury-contaminated soil using a combined washing and distillation process
	20	Fluidized bed soil treatment process—*BORAN*
	21	Mobile low-temperature thermal treatment process
	52	Permeable treatment beds
Hungary	22	Environmental evaluations of former Soviet military bases in Hungary

Country	Project Number	Title
Netherlands	23	Modeling and optimization of *in situ* remediation
	24	Combined remediation technique for soil containing organic contaminants: Fortec®
	25	Slurry reactor for soil treatment
	53	*In situ* bioremediation of chloroethene-contaminated soil
Norway	26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)
	27	Soil washing and chemical dehalogenation of PCB-contaminated soil
	28	Use of white-rot fungi for bioremediation of creosote-contaminated soil
Sweden	54	Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors
Switzerland	49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil
Turkey	29	Sorption/solidification of selected heavy metals and radionuclides onto unconventional sorbents
United Kingdom	30	Using separation processes from the mineral processing industry for soil treatment
	31	Decontamination of metalliferous mining spoil
	32	Cacitox™ soil treatment process
	33	In-pulp decontamination of soils, sludges, and sediments
	34	Chemical fixation of soils contaminated with organic chemicals
	35	*In situ* soil vapor extraction within containment cells combined with *ex situ* bioremediation and groundwater treatment
	36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles
United States	37	Bioventing of hydrocarbon-contaminated soils in the subarctic environment
	38	Demonstration of Peroxidation Systems, Inc., Perox-Pure™ advanced oxidation technology
	39	Management of soil vapors at the Basket Creek site
	40	An evaluation of the feasibility of photocatalytic oxidation and phase transfer catalysis for destruction of contaminants from water (*in situ* treatment of chlorinated solvents)
	41	*In situ* microbial filters
	42	*In situ* pneumatic fracturing and *in situ* bioremediation
	43	Multi-vendor bioremediation technology demonstration project
	44	Enhanced *in situ* removal of coal tar: Brodhead Creek Superfund Site
	47	*In situ* electro-osmosis (Lasagna™ project)
	50	Integrated rotary steam stripping and enhanced bioremediation for *in situ* treatment of VOC-contaminated soil (cooperative approach to application of advanced environmental technologies)
	55	Czechowice oil refinery project

NOTE: There are no Project Nos. 45, 46 or 48. Project 5 from Austria was withdrawn.

The objectives were to:

- exchange technical information on demonstrated technologies;
- exchange information on the development of emerging and innovative technologies; and
- recommend, develop, and adopt uniform data reporting methods for results of technology studies (demonstrations, bench, pilot, and other technology studies).

The third objective was intended to facilitate evaluation of the probable performance of a technology, based on a country's environmental, health, or risk standards. The need for better reporting standards was identified during the Phase I Pilot Study. However, the nascent stage of technical developments in many countries did not permit this need to be fully addressed. It is anticipated that the development of better reporting standards will be addressed further during the planned Phase III Pilot Study.

A number of the conclusions drawn from the Phase I Pilot Study report were addressed during the Phase II Pilot Study. For example, Fellowship projects addressed the costs and the design of demonstration projects. The organization of the Phase II Pilot Study is described in Box 1.3.

1.3 HOW THE INFORMATION IS PRESENTED

Chapter 2 presents an overview of the Phase II Pilot Study. It lists the 52 projects included in the study and classifies them in several ways, including by their development status and whether *in situ* or *ex situ* methods were employed.

Chapter 3 provides an overview of process-based remediation methods and is intended to show how the different technologies discussed in later chapters relate to one another. The terminology used here and elsewhere in the report generally corresponds to with that being developed by the International Organization for Standardization (ISO) *(4)*.

Chapters 4 to 9, which are generally organized as shown in Box 1.4, present the results of the Pilot Study by technology area as follows:

- Chapter 4, *In Situ* Treatment;
- Chapter 5, Physical-Chemical Treatment;
- Chapter 6, *Ex Situ* Biological Treatment;
- Chapter 7, Thermal Treatment;
- Chapter 8, Stabilization/Solidification; and
- Chapter 9, Other (includes all projects not easily dealt with in the other chapters).

The broader topic of integrated treatment systems is addressed in:

- Chapter 10: Integration of Technologies.

Box 1.3: Organization of the Phase II Pilot Study

Formal members of the Pilot Study held either "participant" or "observer" status. Each country nominated a representative to attend Pilot Study meetings[3]*, and these representatives invited others from their countries to take part in meetings and activities. The major part of the Phase II Pilot Study was completed during international meetings attended by:*

- *country representatives;*
- *technical experts representing Pilot Study projects;*
- *leading international experts invited to speak on topics of interest to the Pilot Study;*
- *nominated guests of the host country; and*
- *Pilot Study Fellows.*

Individual country representatives nominated projects of potential interest to the Phase II Pilot Study, and the representatives as a group voted whether or not to accept them. The Pilot Study strived to maintain a balance between long-term and short-term projects[4] *across a range of technologies. Projects that were accepted were expected to produce interim reports and a final project report within the Pilot Study's lifetime. Throughout the Pilot Study, project presentations were open to technical scrutiny and critical review. These discussions have been used in conjunction with each project's interim and final presentations as the basis for information presented in this report.*

Each country was limited to a maximum of four active projects within the Pilot Study at any one time, although during the course of the study, countries could replace completed projects with new ones. Germany, the United Kingdom, and the United States all had more than four projects accepted over the lifetime of this study.

The Phase II Pilot Study was at the forefront of technology development and application. Hence, projects that might be regarded in some countries as state-of-the-art or innovative, such as applications of thermal treatment, may not have been accepted into Phase II if they were previously considered in Phase I. Where an established technology was accepted, it was generally because the project focused on a novel application or involved a fundamental investigation that offered potentially significant improvements in process optimization.

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[3] "Participants" are countries that had a technical project accepted within the Pilot Study while "observers" are formal members of the Pilot Study, but did not contribute projects. Some countries have been represented by individuals, such as the CCMS Fellows, and were not formal members of the Pilot Study.

[4] Long-term projects involve technologies that are being developed in the laboratory and might not be commercially available for another 5-10 years. Short-term projects involve technologies being evaluated in full field-scale trials and are therefore near-market applications.

Box 1.4: Organization of Technology Chapters

Introduction: A description of the technology including basic principles of the process and its potential application. A fuller description is provided in Chapter 3.

Case studies included: A brief summary of the projects evaluated, including why the project was chosen for evaluation. More detailed summaries of each project are provided in Appendix IV (Volume 2).

Background of the case studies as a group: A synthesis of pertinent information from the projects to help the reader understand the range of applicability of the technology. This includes the type, concentration, and sources of contamination, as well as the type of media that can be treated. The lessons learned in the application of the technology are also presented.

Performance results: An assessment of the results of the case studies, including whether project objectives were met, whether the technology was effective, and lessons learned in site preparation and operational testing.

Residuals and emissions: A discussion of the residual materials and emissions, if any, associated with the technology that should be considered when evaluating the potential application of these processes to contaminated sites.

Factors and limitations to consider for determining the technology's applicability: Identification of both technical and non-technical aspects.

Costs: An overview of major capital, operating, and maintenance cost factors that need to be considered by remediation planners. Typical costs or costs specific to case studies are provided in some chapters.

Prognosis for technology: A summary of the state of the technology and its expected role in future site remediation, including an identification of future research needs.

Conclusions and recommendations

1.4 RELATIONSHIP TO OTHER CCMS PROGRAMS

1.4.1 Contributions by CCMS Fellows

The CCMS Fellowship Program made an important contribution to the success of the Phase II Pilot Study, as it did to the earlier studies on the remediation of contaminated soil and groundwater. It enabled the participation of a number of experts from countries that would not otherwise have had a presence in the Pilot Study. It also enabled a wider range of topics to be covered.

Ten NATO Fellows participated in the Phase II Pilot Study. Nine Fellows conducted associated studies and submitted reports to the Pilot Study under the guidance of the Pilot Study Directors. One acted as the editor of this report, and two others contributed to its preparation. The Fellows came from private, university, and governmental organizations in Germany, Portugal, the Netherlands, Turkey, the United Kingdom, and United States. Their activities examined a range of topics, including national approaches to environmental problems, costs and economics, quality management, innovative approaches to large-scale remediation projects, and performance assessment of *in situ* treatment methods. The Fellows and the subjects of their studies are listed in Appendix II. The Fellows' summary reports are provided in Appendix V.

1.4.2 CCMS Study Visit Program

Participation of a number of individuals, particularly expert speakers, was made possible by travel funds provided under the CCMS Study Visit Program.

1.5 CONTRIBUTIONS BY EXPERT SPEAKERS

Invited expert speakers (see Appendix III) attended all of the meetings, which often lead to an in-depth discussion of a particular subject area. Where relevant, these discussions have been taken into account in the preparation of this report.

1.6 CONCLUSIONS AND RECOMMENDATIONS

One of the major achievements of the Phase II Pilot Study is that it has demonstrated the benefits of exchanging technical and economic information on the remediation of contaminated land and groundwater. Conclusions regarding specific technologies, remediation in general, technology transfer, and research needs were drawn from the Pilot Study. The conclusions and recommendations are based on an analysis of the results of Pilot Study projects, and on the contributions of expert speakers, CCMS Fellows, and the numerous other participants in the Study Group meetings.

The conclusions and recommendations reflect both the achievements to date in devising effective treatment technologies and the gaps in the methods available to treat some of the more difficult problems. The conclusions are presented in Chapter 12, which also includes the recommendations made to the CCMS/NATO Council following the Study Group's deliberations.

1.7 REFERENCES

1. U.S. Environmental Protection Agency, *Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-up of Contaminated Land and Groundwater: Overview Report*, EPA/542-R-98-001b, 1998.

2. Smith, M. A. (editor), *Contaminated Land: Reclamation and Treatment*
Plenum (London) 1985.

3. U.S. Environmental Protection Agency, *NATO/CCMS Pilot Study: Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater, Final Report*, Volume 1, 1993, EPA/600/R-93/012a.

4. International Organization for Standardization, *ISO DIS 11074-4: Soil Quality - Vocabulary: Part 4: Terms and Definitions Relating to the Rehabilitation of Soils and Sites*

Chapter 2: TECHNICAL OVERVIEW

Michael A. Smith
M.A. Smith Environmental Consultancy

2.1 INTRODUCTION

While the objective of the Pilot Study was to evaluate applications of particular technologies, a large proportion of the projects involved more than one technology. For example, some involved the use of integrated treatment systems combining more than one technology type, and others involved the application of different more than one technology to address different aspects of site contamination (*e.g.*, more than one contaminated medium). Other projects involved:

- large-scale remediation projects for which the remediation strategy had yet to be developed (*e.g.*, Projects 51 and 56);
- theoretical studies (*e.g.*, Project 23); and
- strategic scientific studies (*e.g.*, Project 49).

Because the projects are classified below in a variety of ways, they may be counted two or three times, and not all projects may be included in each analysis. Furthermore, the categorization of projects is, in part, at a matter of judgment, and alternative categorizations to those presented here are possible.

The projects have been classified as follows:

- by the development status of the technology;
- whether they are *in situ*, *ex situ* technologies, or a combination of both;
- by the type of technology used;
- by the contaminants treated; and
- whether they involve a single technology, mixed technologies, or integrated treatment systems.

Table 2.1 summarizes the 52 “active” projects in the Pilot Study. Additional information can be obtained from the project summaries, which are provided separately (Appendix IV). The project summaries contain a technical abstract providing a synopsis of the author’s written and oral reporting, but are not a critical review of the material presented. The technical contact for the project is also provided in each summary.

2.2 DEVELOPMENT STATUS

Forty-nine of the 52 pilot study projects were technology based. The Pilot Study accepted technical projects in two stages of development: emerging and demonstration. For the purposes of this report an emerging technology is defined (see Chapter 1) as being at bench- or pilot-scale, while a demonstrated technology is one implemented at field- or full-scale. Demonstrated technologies are usually at or near to commercial application. There was almost an even split of projects within the Pilot Study examining emerging and demonstrated technologies.

2.3. *IN SITU* VS. *EX SITU*

There were 18 projects using *in situ* technologies, 26 projects using ex *situ* technologies, six projects using both *in situ* and *ex situ* technologies, and two projects for which the remediation strategy has yet to be decided.

2.4 TECHNOLOGIES EMPLOYED

For the purposes of this report,the technologies described in each technical project were broadly classified as one of five types: biological, chemical, physical-chemical, stabilization/solidification, and thermal. The additional categories of "integrated" and "mixed" are used to describe combinations of technologies used as part of an overall remediation strategy. Integrated refers to approaches where two or more technologies are used simultaneously or in series to treat a specific site problem. "Mixed" projects involved two or more technologies to treat different contaminated areas or media across a site as part of an overall remedial strategy.

The classification of projects was as follows (Note that some projects are counted more than once.):

Technology	Number of Projects	Examples of Technologies
Biological	24	bioventing, biopiles, slurry reactors, white rot fungi
Physical-chemical	29	soil vapor extraction, soil washing, solvent extraction, ultraviolet treatment
Chemical	4	photochemical oxidation, ozone treatment, sorption, leaching
Thermal	5	thermal desorption, incineration, thermal vitrification
Stabilization/Solidification	2	chemical fixation, grouting
Other	4	site characterizations, free-product recovery systems

There were 23 projects that relied upon a single technology, 19 that used integrated technologies, seven mixed technologies, and three that did not involve treatment.Typical combinations were soil vapor extraction with *in situ* biotreatment, soil washing followed by biotreatment, and soil washing followed by thermal treatment.

2.5 CONTAMINANTS TREATED

Forty of the 52 projects were concerned only with the treatment of organic contaminants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). Six projects dealt exclusively with metals, while six dealt with both inorganic and organic contaminants. One project focused on remediation of inorganic sulfates and cyanides. A matrix showing the contaminants treated for each project is presented in Table 2.2.

Table 2.1: Projects Included in NATO/CCMS Pilot Study, Classification by Technology (February 1997)

Project	Title (Chapter in which Project is Addressed)	Technology	*In situ/ ex situ*	Single/ integrated/ mixed
1	Trial of air-sparging of a petroleum-contaminated aquifer (Chapters 4 & 10)	Physical-chemical	*In situ*	Integrated
2	Bioremediation of petrochemicals following a major fire (Chapter 4)	Biological	*Ex situ* *In situ*	Single
3	Bioclogging of aquifers for containment and remediation of organic contaminants (Chapter 4)	Biological	*In situ*	Single
4	Remediation of methyl ethyl ketone contaminated soil and groundwater (Chapter 4)	Physical-chemical	*In situ*	Integrated
6	*In situ*/on-site bioremediation of industrial soils contaminated with organic pollutants: elimination of soil toxicity with DARAMEND® (Chapters 4 & 6)	Biological	*In situ* *Ex situ*	Single
7	Demonstration of thermal gas-phase reduction process (Chapter 7)	Physical-chemical Thermal	*Ex situ*	Single
8	Biodegradation/bioventing of oil-contaminated soils (Chapter 6)	Biological	*Ex situ*	Single
9	Field demonstration of an *in situ* process for soil remediation using well points (Chapters 4 & 10)	Physical-chemical	*In situ*	Integrated
10	Integrated treatment technology for the recovery of inorganic and organic contaminants from soil (Chapters 5 & 10)	Physical-chemical	*In situ*	Integrated
11	On-site biological degradation of PAHs in soil at a former gasworks site (Chapter 6)	Biological	*Ex situ*	Single
12	Groundwater and soil remediation at a former manganese sulfate production plant (Chapter 4)	Physical-chemical	*In situ*	Mixed
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique (Chapters 7 & 10)	Thermal Physical-chemical	*Ex situ*	Integrated
14	Ozone treatment of contaminated groundwater (Chapter 5)	Chemical	*Ex situ*	Single
15	Combined chemical and microbiological treatment of coking sites/ bioremediation of soils from coal and petroleum tar distillation plants (Chapters 4, 6, & 10)	Chemical Biological	*Ex situ*	Integrated
16	Combined vacuum extraction and *in situ* stripping of chlorinated vapors (Chapter 4)	Physical-chemical	*In situ*	Integrated
17	Treatment of polluted soil in a mobile solvent extraction unit (Chapter 5)	Physical-chemical	*Ex situ*	Single
18	Biological *in situ* remediation of contaminated gasworks (Chapter 4)	Biological	*In situ*	Single
19	Cleaning mercury-contaminated soil using a combined washing and distillation process (Chapters 5, 7, & 10)	Physical-chemical Thermal	*Ex situ*	Integrated
20	Fluidized bed soil treatment process—*BORAN* (Chapter 7)	Thermal	*Ex situ*	Single
21	Mobile low-temperature thermal treatment process (Chapter 7)	Thermal	*Ex situ*	Single
22	Environmental evaluations of former Soviet military bases in Hungary (Chapter 9)	-	-	Integrated
23	Modeling and optimization of *in situ* remediation (Chapter 4)	Physical-chemical Biological	*In situ*	Research

Project	Title (Chapter in which Project is Addressed)	Technology	*In situ/ ex situ*	Single/ integrated/ mixed
24	Combined remediation technique for soil containing organic contaminants: Fortec® (Chapters 5, 6, & 10)	Physical-chemical Biological	*Ex situ*	Integrated
25	Slurry reactor for soil treatment (Chapter 6)	Biological	*Ex situ*	Single
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor) (Chapters 5, 6, & 10)	Physical-chemical Biological	*Ex situ*	Integrated
27	Soil washing and chemical dehalogenation of PCB-contaminated soil (Chapters 5 & 10)	Physical-chemical Chemical	*Ex situ*	Integrated
28	Use of white-rot fungi for bioremediation of creosote-contaminated soil (Chapter 6)	Biological	*Ex situ*	Single
29	Sorption/solidification of selected heavy metals and radionuclides onto unconventional sorbent (Chapter 8)	Stabilization/solidification	*Ex situ*	Single
30	Using separation processes from the mineral processing industry for soil treatment (Chapter 5)	Physical-chemical	*Ex situ*	Single
31	Decontamination of metalliferous mine spoil (Chapters 5, 6, & 10)	Physical-chemical Biological	*Ex situ*	Integrated
32	Cacitox^{TM} soil treatment process (Chapters 5 & 10)	Physical-chemical	*Ex situ*	Integrated
33	In-pulp decontamination of soils, sludges, and sediments (Chapters 5 & 10)	Physical-chemical	*Ex situ*	Integrated
34	Chemical fixation of soils contaminated with organic chemicals (Chapter 8)	Stabilization/solidification	*In situ*	Single
35	*In situ* soil vapor extraction within containment cells combined with *ex situ* bioremediation and groundwater treatment (Chapters 4 & 6)	Physical-chemical	*In situ* *Ex situ*	Mixed
36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particle (Chapters 5, 6, & 10)	Physical-chemical	*Ex situ*	Integrated
37	Bioventing of hydrocarbon-contaminated soils in the subarctic environment (Chapter 4)	Biological	*In situ*	Single
38	Demonstration of Peroxidation Systems, Inc., Perox-Pure^{TM} advanced oxidation technology (Chapter 5)	Physical-chemical Chemical	*Ex situ*	Single
39	Management of soil vapors at the Basket Creek site (Chapter 9)	Physical-chemical	*Ex situ*	Single
40	An evaluation of the feasibility of photocatalytic oxidation and phase transfer catalysis for destruction of contaminants from water *(in situ* treatment of chlorinated solvents) (Chapter 5)	Physical-chemical	*Ex situ*	Single
41	*In situ* microbial filters (Chapter 4)	Biological	*In situ*	Single
42	*In situ* pneumatic fracturing and *in situ* bioremediation (Chapters 4 & 10)	Biological Other	*In situ*	Integrated
43	Multi-vendor bioremediation technology demonstration project (Chapters 4 & 6)	Biological	*In situ* *Ex Situ*	Mixed
44	Enhanced *in situ* removal of coal tar: Brodhead Creek Superfund Site (Chapter 5)	Physical-chemical	*Ix situ*	Single

Project	Title (Chapter in which Project is Addressed)	Technology	*In situ/ ex situ*	Single/ integrated/ mixed
47	*In situ* electro-osmosis (Lasagna™ project) (Chapters 4, 5, & 10)	Physical-chemical Biological	*In situ*	Integrated
49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil (Chapter 6)	Biological	*Ex situ*	Research
50	Integrated rotary steam stripping and enhanced bioremediation for *in situ* treatment of VOC-contaminated soil (Cooperative approach to application of advanced environmental technologies) (Chapter 9)	Physical-chemical Biological	*In situ*	Mixed
51	Sobéslav, South Bohemia wood treatment plant (Chapter 9)	Biological Containment	*Ex situ* *In situ*	Mixed
52	Permeable treatment beds (to be addressed in the Phase III report)	Physical-chemical Chemical	*In situ*	Integrated
53	*In situ* bioremediation of chloroethene-contaminated soil (Chapter 9)	Biological Physical-chemical	*Ex situ*	Mixed
54	Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors (Chapter 6)	Biological	*In situ*	Single
55	Czechowice oil refinery project (Chapter 9)	Biological Physical-chemical	*Ex situ*	Mixed
56	Spolchemie a.s.— mercury-contaminated site (Chapter 9)	-	-	Other

Table 2.2: Projects Included in NATO/CCMS Phase II Pilot Study, Classification by Media and Contaminants

PROJECT NO.	**MEDIUM**		**CONTAMINANT**					**NOTES**
	Soil	Groundwater	VOCs	SVOCs	Pesticides/PCBs	PHCs	Inorganics	
1	•	•	•					benzene, xylene, petroleum hydrocarbons
2	•	•	•	•				benzene, phenol, acrylonitrile
3		•	•					BTEX
4	•	•	•			•		MEK, oil, gasoline, turpentine, kerosene
5	•							*project withdrawn*
6	•		•	•				aliphatic and aromatic hydrocarbons, phthalates, chlorophenols
7	•	•	•	•	•			TCE, 1,2-DCE, methylene chloride, toluene, ethylbenzene, PCBs, benzidine, benzene, vinyl chloride, chlorobenzene, PAHs, lindane, dieldrin, chlordane, DDT metabolites
8	•		•	•		•		BTEX, PAHs, mineral oil, grease, pentachlorophenols
9	•		•					BTEX, aliphatic hydrocarbons
10	•			•			•	PAHs, lead, copper, zinc
11	•			•				PAHs
12	•	•					•	sulfate, cyanide
13	•		•	•			•	coal tar, PAHs, BTEX, phenols, cyanides, heavy metals, ammonium compounds
14		•	•	•		•		phenols, aliphatic and aromatic hydrocarbons, BTEX, acetone, ethanol, chlorinated solvents, petroleum hydrocarbons
15	•			•			•	PAHs, phenols, cyanides
16	•	•	•					PCE
17	•		•	•	•			BTEX, PAHs, PCBs
18	•			•				PAHs, extractable lipophilic organics
19	•						•	mercury
20	•			•	•			PAHs, PCBs
21	•		•	•		•	•	BTEX, PAHs, mineral oils, lignite tar oil, mercury, TNT
22		•				•		jet fuel, including DNAPL
23	•	•	•					VOCs
24	•			•	•	•		mineral oils, PAHs, chlorophenol, lindane
25	•			•		•		mineral oil, PAHs
26	•			•				PAHs
27	•				•			PCBs
28	•			•				PAHs
29		•					•	lead, cadmium, copper, cesium-137, strontium-90
30	•			•			•	PAHs, phenols, heavy metals, cyanides
31	•						•	lead, zinc
32	•						•	heavy metals, radionuclides
33	•						•	copper, zinc, chromium, arsenic
34	•		•	•	•			chlorinated hydrocarbons, PAHs, benzene and benzene derivatives, phenolics, PCBs, organophosphorus/sulphurous compounds
35	•	•	•	•			•	BTEX, PAHs, phenols, heavy metals, cyanides
36	•			•		•		PAHs, diesel fuel
37	•	•				•		jet propellant #4
38		•	•					TCE, PCE, 1,1,1-TCA, 1,1-DCA
39	•		•				•	TCE, PCE, toluene, MEK, MIBK, lead, mercury
40		•	•					BTEX
41		•	•					TCE
42	•		•					benzene, toluene, xylenes
43	•		•					TCE, PCE, DCE, acetone, MEK, toluene
44	•	•	•	•				BTEX, PAHs, coal tar

PROJECT NO.	**MEDIUM**		**CONTAMINANT**					**NOTES**
	Soil	Groundwater	VOCs	SVOCs	Pesticides/PCBs	PHCs	Inorganics	
45								*accidental replication of project #15*
46								*project withdrawn*
47	•	•	•					TCE
48								*project withdrawn*
49	•		•	•	•	•		unspecified hydrocarbons
50		•	•					unspecified VOCs
51	•	•		•			•	PAHs, phenols, heavy metals
52		•	•	•	•	•	•	various contaminants
53	•	•	•					TCE, PCE
54	•			•				PAHs, PCP
55	•	•				•		oil refinery organics
56	•	•					•	mercury

NOTES:

BTEX = benzene, toluene, ethylbenzene, and xylenes
DCE = dichloroethene
DDT = dichlorodiphenyltrichloroethane
DNAPL = dense, non-aqueous phase liquid
MEK = methyl ethyl ketone
MIBK = methyl isobutyl ketone
PAHs = polycyclic aromatic hydrocarbons
PCBs = polychlorinated biphenyls
PCE = tetrachloroethene
PCP = pentachlorophenol
PHCs = petroleum hydrocarbons
SVOCs = semivolatile organic compounds
TCE = trichloroethene
TNT = trinitrotoluene
VOCs = volatile organic compounds

Chapter 3: PROCESS-BASED REMEDIATION METHODS

Michael A. Smith
M.A. Smith Environmental Consultancy

3.1 INTRODUCTION

A risk assessment is usually used in deciding whether or not to eliminate or reduce the risks posed by a contaminated site. If the risks need to be reduced, a remediation strategy must be developed to address them. For sites designated for development, the remediation strategy also must address engineering requirements, such as minimum load-bearing capacities, and management objectives, such as making a profit.

This chapter provides an overview of the available process-based remediation methods for controlling risk. It draws extensively on the lessons learned from the Phase I Pilot Study *(1)*, which also contributed to the development of the primary reference for this chapter *(2)*. Descriptions of specific methods are provided in subsequent chapters.

In general, the suitability of a remediation method depends on many factors including: contaminated media, contaminants, remediation objectives, current status of the site, location of the site, time available to complete the treatment, and money available to pay for the treatment.

3.2 BASIC OPTIONS AND CLASSIFICATION OF METHODS

The three basic approaches to remediation are:

- risk avoidance by changing the intended use of the land, re-routing a sewer, *etc.*;
- elimination of the risks by removing or destroying contaminants; and
- control of risks to an acceptable level by reducing contaminant concentrations or by containing the contaminants, such as installing barriers between the contaminants and potential receptors.

The remediation strategy developed for a particular site may combine all three approaches and several different methods.

The methods may be classified as[1] civil engineering-based methods, such as excavation, containment using cover systems and vertical barriers, and hydrogeological controls; or process-based methods.

Process-based methods can be further classified on the basis of the underlying physical-chemical principles involved. For the purposes of this report, they are classified according to the following generic processes: thermal, chemical, biological, physical, and stabilization/solidification.

This allocation is a matter of judgment. For example, vitrification, considered a thermal method in this classification scheme, may be viewed by others as a solidification process. The generic processes are

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[1] The terminology employed throughout this report is generally consistent with that proposed by the International Organization for Standardization (ISO) in its draft document: CD11074-4: Soil Quality Vocabulary — Part 4 Terms and definitions relating to rehabilitation of soils and sites.

frequently combined in treatment trains so that, for example, soil washing becomes the prelude to chemical or biological treatment.

Process-based methods may be applied *ex situ*—after contaminated soil or groundwater has been removed from the ground for treatment—or *in situ*—without removing the contaminated media from the ground. *Ex situ* treatment may be performed onsite or offsite.

Although civil engineering approaches are discussed only briefly in this chapter, often they are used in conjunction with process-based methods.

3.3 CIVIL ENGINEERING-BASED METHODS

Civil engineering-based methods, may be an essential precursor to the application of a process-based method involving *ex situ* treatment. Furthermore, civil engineering-based methods, such as vertical barriers and lowering the water table, can also be essential to the application of an *in situ* treatment, such as soil vapor extraction. Issues to be addressed during the excavation of contaminated media for subsequent treatment include:

- delineation of the volume of material to be removed;
- compliance with excavation specifications to ensure that all material that should be removed has been removed;
- control of potential environmental impacts as well as other impacts, such as emissions to the atmosphere and traffic movements;
- engineering support, such as controlling water levels, required for excavation to proceed;
- ancillary support, such as the treatment of contaminated groundwater;
- facilities required for temporary storage;
- source and specification of clean replacement material, including chemical composition; and
- planning and permissions, including permits.

Careful consideration must be given to pre-treatment requirements of civil-engineering-based methods, such as particle size and moisture content of the contaminated media. In addition, hydraulic measures are often essential components of remediation systems. The extraction or infiltration of groundwater may be used to:

- control groundwater levels, enabling excavation to take place;
- control groundwater levels in conjunction with physical barriers as part of a long-term remediation strategy;
- control groundwater levels and flow directions so that *in situ* treatment, such as soil flushing or soil vapor extraction, can be applied;

- extract groundwater for *ex situ* treatment (pump-and-treat) and return the treated water to the ground; and

- infiltrate water as part of an *in situ* treatment process.

Extracted groundwater may be contaminated and require either disposal to the local sewer system or on-site or off-site treatment.

Vertical barriers, which can be designed in a number of ways *(3, 4, 5, 6)*, are used to control the migration of contaminated groundwater and soil gas. They are frequently used in conjunction with hydraulic measures to control the groundwater plume or with an active or passive system to control gas emissions. When used as the primary remediation method, vertical barriers must be designed to last, sometimes for decades. When used as an adjunct to another treatment method (for example, to control the groundwater flow rate, flow direction, and level), they usually need to last for a much shorter time.

As a permanent solution, vertical barriers have several disadvantages. No matter how well designed and installed, barriers perform satisfactorily only for a limited time, albeit possibly several decades. Eventually, they have to be replaced unless steps have been taken to remove the original hazard or the potential for migration decreases with time as can occur at gas-producing sites. Because experience is limited in the use of vertical barriers under all environmental conditions, predicting performance is difficult.

3.4 PROCESS-BASED METHODS

3.4.1 *Ex Situ* Methods for Solids and Liquids

Several generic methods are available for the *ex situ* treatment of solids (*e.g.*, soils, sediments, sludges, and filter cakes) and liquids (*e.g.*, groundwater, surface water, and wastewater). Treatment aims to remove, destroy, or modify contaminants, rendering them unavailable to potential human and environmental targets. Whether an *ex situ* method can be applied at a site is determined by the nature and distribution of the contaminants, and by the physical, chemical, and in some cases, biological properties of the media to be treated.

Many generic methods generate waste streams that may require further treatment or disposal. This may take place onsite, using for example mobile or transportable treatment systems, or at off-site fixed treatment facilities. The decision to treat contamination onsite or offsite depends on a number of factors, including availability and cost of on- and off-site facilities; available time scales; and site-specific factors, such as the location of the site relative to off-site treatment centers, space available for on-site treatment and temporary storage, and availability and capacity of local services, such as power, drainage, and water supply.

On-site treatment generally requires:

- appropriate approvals for operating the treatment equipment;

- preparation of the site to receive the treatment plant and equipment;

- appropriate site services and support facilities to protect occupational and public health and safety and the environment;

- installation and commissioning of the treatment plant; and
- temporary storage and materials-handling facilities for feedstocks, products, and wastes.

When the use off-site facilities is expected, it is important to:

- comply with legal requirements on the transfer of controlled wastes and the discharge of hazardous effluents;
- make arrangements for temporary storage and pre-treatment requirements prior to transfer;
- ensure adequate protection of the workforce, public, and environment during transfer operations; and
- agree on transport routes and permissible shipping rates.

Factors requiring special attention during the selection, design, and implementation of any remedy include:

- properties of the material to be treated in relation to potential applicability, effectiveness, and constraints;
- need for treatability studies;
- materials handling requirements;
- engineering aspects, such as ancillary engineering support;
- operational aspects, such as electrical and water services required;
- testing for compliance and performance to demonstrate that target concentrations and other specifications can be achieved;
- potential for integration with other remedial measures; and
- compatibility with engineering and management objectives.

To assess the applicability and potential performance of *ex situ* treatment methods, information is required on the contaminants present (*e.g.*, types, concentrations, speciation, and distribution) and the physical, chemical, and biological properties of the material to be treated. The data on applicability and performance should be tailored to meet the specific requirements of the method, or methods, intended for use. In most cases, this involves collecting supplementary data beyond that necessary for the risk assessment and initial remedy selection. Treatability studies are likely to be required to select, design, and implement the remedy.

Many *ex situ* treatment methods are specific to particular types of contaminants and are sensitive to variations in feedstock composition. Comprehensive data on the composition of the material are needed to ensure:

- applicability to the contaminants present;

- applicability to the material to be treated;
- applicability to the contaminant concentration range that needs to lie within the range that can be treated;
- absence of any interfering or inhibitory substances;
- feedstocks in the correct physical form for processing;
- maintenance of optimal processing conditions; and
- accurate predictions of the waste stream composition so that appropriate pollution control measures can be provided and suitable disposal and discharge arrangements can be made.

Several factors determine how effective the treatment method will be in producing material that consistently achieves pre-defined remedial objectives, such as residual contaminant concentrations. These factors include the composition, physical condition, and homogeneity of the feedstocks; presence of inhibitory or interfering substances; and conditions that affect the ability to maintain the process at optimal levels. Factors that can limit the effectiveness of *ex situ* methods of treatment include:

- inappropriate particle size preventing effective contact between treatment reagents and contaminants;
- heterogeneous feedstocks leading to variable performance and quality of the treated product;
- inappropriate matrix types, such as clay or humic soils in soil washing technologies or overly coarse material in thermal treatment technologies;
- complex contaminant mixtures leading to antagonistic or unproductive reactions, or interference in the main process reaction; and
- sub-optimal processing conditions leading to poor or variable performance.

When selecting, designing, or implementing remedial strategies that include *ex situ* treatment methods, effectiveness must be defined. The potential effectiveness of the method should always be considered in the context of its ability to meet the prescribed standard, such as allowable residual concentrations of contaminants in treated material or compliance with leachability criteria.

Although low residual contaminant concentrations may appear to provide the most direct means of assessing effectiveness, they may not always be a sufficient measure of the ecological quality of soil or other treated material. A number of treatment methods, including biological and chemical methods, can produce toxic intermediates or fail to adequately treat low concentrations of highly toxic substances. Thus, direct measures of toxicity may be required.

All *ex situ* treatment operations should be subject to compliance and performance testing. Typically, such tests include assessing the potential for exposure of personnel to hazardous materials and measuring the composition of emissions to the atmosphere, discharges to the sewer, and any material landfilled onsite or offsite. Performance evaluations include:

- On-going monitoring of treatment performance, measured, for example, as interim quality inspections on samples of processed material; and

- Final validation of the quality of the treated product to confirm that it conforms to pre-defined remediation objectives. Validation may include a variety of measurements, such as total concentrations of residual contamination in the treated product, concentrations of hazardous substances in leachates prepared under standard conditions, and measurements of the physical condition (*e.g.*, strength development) of the treated product.

Post-treatment validation programs vary depending on the methods used, contaminants treated, volume of material handled, and variability of the feedstocks.

Long-term testing of material processed in *ex situ* systems is unlikely to be required although long-term monitoring may be necessary where stabilized/solidified material has been returned to the site. Long-term monitoring may involve periodic removal and chemical/physical analysis of cores of treated material. In addition, groundwater monitoring wells may have to be installed to determine long-term changes in water quality.

3.4.2 *Ex Situ* Treatment of Groundwater and Other Contaminated Liquids

Where soils are treated using *ex situ* methods, such as soil washing, the treatment and/or disposal of process waters and effluents usually form part of the overall treatment system. Contaminated waters requiring *ex situ* treatment include:

- surface waters, such as ponds and lagoons;

- groundwater collected during pump-and-treat operations;

- groundwater removed incidentally as a result of excavation and other engineering operations;

- effluents from the pre-treatment of solids (*e.g.*, dewatering of dredged sediments or industrial sludges);

- aqueous liquids extracted from contaminated soil and waste;

- leachates collected from waste deposits and contaminated sites;

- contaminated water from *in situ* soil flushing or washing, and chemical treatment operations;

- process effluents from *ex situ* treatment of solids (*e.g.*, soil washing and chemical treatment); and

- effluents from the decontamination of plant and equipment, using, for example, high pressure water jets.

Contaminated waters may contain only one or a small number of contaminants present over a relatively narrow concentration range, or they may contain complex mixtures of contaminants at wide-ranging or very high concentrations. In addition, these concentrations may fluctuate over time, and the volumes of liquid to be treated and time scales may vary considerably. For example:

- Process and decontamination effluents associated with the *ex situ* treatment of solids arise only during the operational phase of remediation, and the total volumes of effluents to be treated may be relatively small; and

- Treatment of large volumes of contaminated groundwater may be necessary over extended time periods, particularly where source control measures are not possible and groundwater remediation is the only feasible means of reducing contamination hazards.

Options other than on-site treatment of contaminated water may be available. Two examples are discharge to an existing sewage treatment plant, possibly after some initial pre-treatment, or transfer by tanker to a central treatment facility.

Treatment methods developed for drinking water, process water, sewage treatment, and industrial effluent can be adapted, provided that the physical, chemical, and biological properties of the liquid to be treated and the design and operational requirements of the treatment system have been considered. Several methods have been specially developed for the treatment of contaminated groundwater.

Contaminated waters from land remediation projects usually require treatment in an integrated treatment train in order to overcome variations in contaminant types and concentrations, flow rates, and physical properties. Treatment trains usually conform to the following basic sequence: pre-treatment, primary treatment, secondary treatment, and tertiary treatment or polishing. As liquid moves through the treatment train, it becomes progressively cleaner. Trace levels of contamination are removed in the tertiary treatment stage. In conventional applications, treatment trains are normally constructed as permanent installations.

A number of treatment methods or options may be available at each stage of the treatment train. The methods selected depend on their compatibility; the physical, chemical, and biological properties of the liquid; and quality of the water to be achieved on completion of treatment.

The liquids must be well characterized at the outset in order to provide for appropriate treatment stages and adequate capacity for expected variations in concentration and flow. In modern industrial plants, care is taken to ensure that effluents from processes having different treatment requirements are not unnecessarily mixed in, thereby adding to the technical difficulties and costs of downstream treatment. For instance, effluents with inorganic and organic contaminants are not mixed because they have different treatment requirements. Particular attention should be given to the potential for biological and mineralogical fouling of treatment systems.

The information needed to design a treatment system for a contaminated land application is similar to other systems. However, the system design must take into account the:

- variable nature of water;

- common presence of contaminant mixtures and the inability to control for them;

- range of contaminant concentrations frequently present;

- temporary status of the treatment plant (with the exception of some groundwater treatment operations); and

- the fact that systems often have to be installed in less than optimal physical conditions, such as working space, services, terrain, and access.

The relatively short-term nature of many contaminated land projects, compared to conventional water and wastewater treatment applications, presents a number of potential design problems. The conventional treatment plant is usually designed and constructed to last for 20 years or more depending on the life expectancy of the equipment. Contaminated land projects are typically much shorter. The shorter time scales have implications for the commercial availability and operational efficiency of the treatment plant, and for the cost of designing the treatment system. For instance:

- Appropriate plants may not be available “off-the-shelf;”

- Commercially available plants may not operate as effectively on a small scale due to design constraints; and

- Cost may be very high relative to the volume of material to be treated.

During the life cycle of a groundwater treatment project, significant changes may occur in the basic parameters that determined the selection and design of the initial treatment system. When designing groundwater treatment systems, it must be understood that:

- Management of the hydraulic regime, including the extraction and recharge rates, should be considered an integral part of the overall design of a pump-and-treat system;

- Flow rates may be controllable within limits (allowing for a choice of plant size) or dictated by hydrogeological factors, such as the pumping rate required to control plume migration—all of which may change during the lifetime of the project;

- Because contaminant concentrations decrease with time, different treatment processes may be required at different stages of a project in order to maintain technical effectiveness and economy of operation;

- Relatively small plant sizes may mean high operating costs compared to capital costs; and

- A point probably will be reached when *ex situ* treatment ceases to be more effective than natural degradation or dispersion processes—this point may occur before target concentrations are reached. If this occurs, a period of passive management, such as monitoring, will be required until target concentrations are achieved.

3.4.3 *In Situ* Methods for Soils

In situ treatment methods avoid the above-ground environmental impacts and costs associated with excavation and extraction. Some methods are particularly attractive for application on operating sites and other sites where buildings and structures need to be preserved.

In situ technologies for treating soil and similar materials can be classified like their *ex situ* counterparts on the basis of the underlying treatment principle, such as physical separation and biological degradation. In addition, a distinction can be made between those methods that seek to remove, destroy, or stabilize contaminants by introducing a treatment agent into the ground, and those that act directly on the ground, such as electroremediation and *in situ* vitrification.

Typically, the aim of *in situ* remediation is to treat the saturated or unsaturated zones, although some integrated systems are capable of treating both. Methods for the treatment of soil and soil-like materials (including soil water and gas) and methods intended to treat groundwater and associated strata may be used separately or in an integrated system. *In situ* treatment methods may be combined with pump-and-treat methods to treat contaminated groundwater. Soil flushing, *in situ* bioremediation, and soil vapor extraction may be combined in an integrated remediation scheme. Heat may be introduced to aid bioremediation or vapor extraction, and electrokinetic techniques may be used to enhance penetration of chemical or stabilization agents.

Typical *in situ* systems:

- deliver a treatment agent or agents in liquid, gas, or energy form;
- recover products; and
- dispose of or treat products, although the aim of many methods is to produce only non-harmful products or safely “lock-up” contaminants *in situ*.

The engineering, legal, and operational issues that must be addressed in all *in situ* applications are generally the same as those for *ex situ* treatment:

- site characterization and pilot studies to determine potential applicability, effectiveness, and constraints;
- testing for compliance and performance; and
- compatibility with engineering objectives.

Thorough characterization of the chemical contaminants and physical properties of the contaminated matrix is essential for a proper evaluation of the feasibility of particular *in situ* treatments. Also, the mode of action, which usually involves in-ground treatment, often at significant depths, imposes unique constraints on treatment applicability and feasibility. Site characterization should be tailored to meet the specific requirements of the method, or combination of methods, that may be applied. This almost certainly requires supplementary investigations beyond those that estimate risk. Bench and pilot-scale treatability studies are frequently required.

Accurate identification of all contaminants present, combined with treatability data, is essential because of the danger that a treatment adopted to remedy some contaminants could lead to adverse or counter-productive reactions with other contaminants. This may result in increased toxicity or mobility. An understanding of the physical characteristics of a site is essential for all *in situ* techniques, especially those requiring infiltration of treatment agents. Information on the engineering properties of the ground is required, especially if heavy equipment is used or if the remedial action itself could lead to unfavorable ground changes, such as increased soil density, volume, or instability.

The effectiveness of *in situ* treatment methods is determined by a variety of factors, including:

- nature, extent, and distribution of contaminants;

- contact achieved between contaminants and treatment agents, and often the extent to which the contaminants can be solubilized (Conductivity and penetration can be enhanced by a variety of means);

- accessibility of the contaminants on a micro- and macro-scale;

- control over processing conditions in the ground which are not visible, especially when working at considerable depth;

- extent to which treatment agents can be delivered to the site of action;

- ability to effectively remove treatment products and excess agents from the ground; and

- time available for treatment in terms of access to the site and natural factors, such as groundwater flow rates.

Minimal information is available on the long-term effectiveness of *in situ* treatment methods that do not remove or destroy contaminants. Effectiveness is limited by the actual contamination as well as the perception of contamination. A system design based on an inadequate understanding of the contamination and site characteristics may not be sufficient to treat the actual situation. Flexible and robust designs that can be modified as treatment proceeds are essential.

In situ techniques are likely to be most effective when applied to specific types of contaminants in homogeneous ground conditions or at least well defined heterogeneous ground conditions. Monitoring undertaken during processing and for a considerable time after treatment is likely to be required to fully demonstrate effectiveness over time.

Often engineering or hydraulic measures must be employed to contain *in situ* methods of treatment or to increase the volume of soil available for treatment. For instance, if the groundwater table needs to be lowered, consideration must be given to whether the mobility of contaminants will increase. This can occur when a floating layer of contaminants enters the saturated zone. In addition, lowering the groundwater table may adversely affect trees and other vegetation, and alter the level and flow of surface water bodies. *In situ* treatment may have significant implications on the engineering properties of the ground and hence on any subsequent construction works. For example:

- Infiltration/extraction operations may affect the stability of the neighboring buildings, plant, and services;

- Density and volume increases may result from the addition of solidification/stabilization reagents or grouts; and

- Changes in load-bearing capacity must be taken into account in designing foundations.

The delivery systems used to deliver treatment agents to the sub-surface and to recovery systems may be propelled by gradients, such as hydraulic, pressure, chemical, temperature, and electrochemical/ electrokinetic gradients. Systems based on air or gas are driven by similar potentials.

Where aqueous fluids are to introduced into the ground, facilities for preparing, storing, and “reconditioning” recirculated extraction solutions must be provided. Treatment agents may be hazardous and potentially polluting and thus require appropriate storage and handling arrangements. Also, recovered treatment solutions or gases, and incidental emissions, such as those from heat treatment, require appropriate treatment or disposal.

The site geology and hydrogeology may be such that treatment agents are diverted away from target areas, thereby limiting effectiveness and possibly leading to the contamination of surrounding ground. For water-based systems, an initial test of the delivery system using water only or water with a tracer usually is necessary to make sure the recovery system is adequate.

Delivered materials are typically liquids but may be gases (such as those used in soil vapor extraction and bioremediation), vapors, slurries, or solids. Recovery systems involve fluid flows (gases, liquids, and emulsions) and may require enhancement by modifying the physical or chemical attributes of the contaminants or pathways.

Problems associated with installing and operating delivery and recovery systems include:

- presence of structures, plant, and services;
- presence of physical obstacles, such as boulders, drums, concrete debris, and hard rock;
- depth restrictions that affect the integrity and performance of the system;
- ensuring the penetration of aqueous fluids where hydraulic conductivity is less than about 10^{-6} to 10^{-5} m/sec;
- presence of contaminants with low solubilities;
- adsorption of contaminants onto clay minerals or organic matter;
- existence of fractures or other secondary porosity that create paths of high conductivity in bedrock of otherwise low conductivity;
- absence of an underlying low-permeability layer that precludes migration of delivered materials and treatment products;
- whether remedial action is progressing as planned;
- whether remediation targets (standards) have been achieved;
- whether any contaminants or treatment agents have migrated beyond the operational area;
- composition of extracted fluids or emissions, which could provide information on progress and treatment/disposal requirements;
- presence and nature of any fugitive emissions to the atmosphere;
- validating that treatment has been fully effective; and
- determining whether the engineering properties of the ground have been affected by the treatment.

Procedures for monitoring soil and groundwater are likely to be required in most applications of *in situ* technologies. The basis for deciding compliance in terms of pre-defined remediation criteria, and the statistical basis for accepting that compliance has been achieved, should be decided before monitoring is carried out. Although most *in situ* methods affect both solid and liquid media, these media can be affected separately when parallel treatment processes are used. Monitoring procedures vary depending on the purpose of the testing and the methods used, but they typically include *(7)*:

- installing monitoring wells for collecting groundwater samples as well as assessing groundwater and contaminant movement at the site;

- monitoring recovery streams to determine the quantity of contaminants removed;

- analyzing cores of treated material to determine residual concentrations or other properties, such as leachability of stabilized/solidified soils; and

- monitoring process streams, such as treated groundwater or air from soil vapor extraction systems, to determine quality prior to discharge.

Monitoring data can be used in making process stream and mass balance calculations, which are used to establish how effective *in situ* treatment is in removing contaminants. Such calculations are important because demonstrating the effectiveness of *in situ* treatment can be difficult in the presence of heterogeneous ground conditions, poor accessibility of contaminants, low degree of mixing, and migration of contaminants away from the zone of treatment due to the remedial action itself. Experience has shown that concentrations of contaminants in groundwater recovery streams may decrease initially, but then increase after a period of inaction as contaminants move back into the groundwater system from the fine pore structure or other locations in the ground. Similar behavior can be observed when soil vapor extraction is applied to ground containing zones of low gas permeability within strata of higher permeability. Long-term monitoring, well beyond the point at which remedial action appears to be complete, is often required to confirm that remediation has been fully effective.

3.4.4 *In Situ* Treatment of Groundwater

In situ treatment of groundwater requires water to pass through a treatment zone where injection of agents in solution or in gaseous form cause degradation or promote natural degradation of contaminants; or a solid substrate exists that supports physical separation of the contaminants by adsorption, chemical or biological degradation, or reduction in toxicity.

These two processes may be used in combination. *In situ* treatment of groundwater may be combined with *in situ* treatment of the unsaturated zone. Soil vapor extraction coupled with microbial treatment is an example of this type of combination. *In situ* groundwater treatment also may be combined with pump-and-treat operations. The flow of groundwater through or to the treatment zone may be the result of natural gradients; induced by pumping from vertical or horizontal wells, or by infiltration of water; or achieved through injection of heated water or steam.

Regulatory authorities should always be consulted prior to applying such methods to obtain relevant permissions for installing and operating injection and extraction wells, and for deliberately introducing chemical agents into the environment.

In situ groundwater remediation requires a thorough understanding of the hydrogeology of the site and its environs, and usually requires the prior removal or containment of the source of the contamination and removal of free product. As for all *in situ* methods, ensuring contact between contaminants and the treatment agent is the major practical difficulty. Contaminants may be adsorbed onto mineral surfaces and held in capillary pores. Effective long-term treatment requires that these contaminants be released into the groundwater. A variety of means may be used to promote the movement of contaminants through the subsurface. These include hydrofracturing, electrokinetic techniques, injection of steam or hot water, and surfactant flushing.

Because contaminant mobility is different at each site, any *in situ* treatment method must take into account the characteristics of the contaminants present. Contaminants partition between liquid, soil, and vapor phases in amounts characteristic of the contaminants, aquifer materials, organic content, and other geochemical factors. For many contaminants, these associations vary and may not be completely reversible. Modeling groundwater and contaminant movement is often required to design the treatment system.

Significant amounts of groundwater flow—both horizontally and vertically—may occur through limited parts of the aquifer, and the direction and rate of flow may be markedly different at different depths. This can result from spatial variability in the permeability of water, or as a result of density or other contaminant characteristics. Thus, neither the bulk water flow nor the distribution of contaminants can be assumed to be homogeneous.

Principal treatment methods for *in situ* groundwater contamination include:

- oxidation of contaminants by introducing oxidizing agents, such as oxygen, ozone, hydrogen peroxide, and permanganate;
- enhancement of natural biological degradation processes;
- air-stripping of volatile organic compounds;
- adsorption on, or reaction with, reactive materials, such as those in a chemical barrier; and
- biological degradation within an active barrier.

Planning and management requirements typically associated with these methods include:

- obtaining appropriate approvals to install and operate extraction and infiltration wells and to introduce treatment agents into the groundwater;
- obtaining appropriate approval to install and operate a treatment plant;
- preparing the site to receive the installation, including preparing any reagent storage or handling facilities; and
- monitoring to measure boundary effects, check progress, and determine the completion point.

Technical specifications should ensure:

- appropriate controls over treatment agents and other materials used during treatment;

- proper provisions for locating, installing, operating, and maintaining injection wells, barrier systems, and associated storage facilities; and
- satisfactory monitoring arrangements, particularly to determine the end point of treatment.

Care is required in the selection and design of an *in situ* groundwater treatment system to ensure that:

- any chemical introduced into the ground during treatment does not itself become a pollutant;
- mobilization of contaminants other than those that are the primary object of the treatment or are naturally present is prevented; and
- treatment end products are not more harmful than the original compound.

A full understanding of the contamination and the geological, hydrogeological, and geochemical characteristics of the site is required to effectively design and implement the remedy. Detailed information is necessary on a range of physical-chemical properties of the contaminants, including sorption characteristics, volatility, partitioning, and chemical and microbial degradability.

A range of laboratory investigations, such as treatability studies, development of sorption isotherms, and column and microcosm experiments, are necessary to determine contaminant transport and transformation parameters, assist in developing a full understanding of site conditions, and enable evaluation of alternative methods of treatment. When microbial treatment is used, laboratory studies usually are required to determine if the native populations of microbes can degrade the contaminants, and if minerals are present to promote maximum activity at ambient groundwater temperature and under aerobic conditions. Natural conditions may be anaerobic or only slightly aerobic. Data on the quantity of contaminants present and the porosity of the aquifer can be used to calculate theoretical oxygen requirements for degradation and the volumes of air or water (saturated with air or oxygen) needed to supply the oxygen. Similar calculations can be made for the unsaturated zone.

Relatively scarce information is available on the long-term effectiveness of most *in situ* groundwater methods, and much of it originates only from field trials. However, the use of hydrogen peroxide as an oxygen source at petroleum contaminated sites to enhance biological degradation rates, and sparging to strip volatile contaminants and encourage biological degradation, are established techniques.

Effectiveness may be enhanced by using techniques, such as hydrofracturing or pneumatic fracturing, surfactant flushing, electrokinetics, and hot water and steam flushing, to promote the movement or penetration of treatment agents or contaminants. However, many of these systems are themselves at an early stage of development.

Chemical and other forms of treatment requiring the introduction of agents into the ground are limited by the fact that groundwater flows within an aquifer in a plug flow manner, providing very minimal natural mixing. Therefore, introduced agents tend to be pushed ahead of water entering the treatment zone. Such difficulties may be overcome by using systems designed to induce mixing, such as the UVB system (Project 43).

Precipitation and polymerization may lower hydraulic conductivities near the injection wells making closely spaced wells necessary for effective treatment. Microbial growth close to points of nutrient and oxygen injection may have a similar effect.

In general, permeable barriers can be used only in relatively shallow aquifers because the trench must be excavated to a layer of low permeability. However, it may be possible to design fence-and-gate systems to operate effectively where contamination is restricted to the upper portion of an aquifer. In 1992, the Technology Innovation Office (TIO) of the USEPA identified *in situ* groundwater treatment as a critical area requiring research and development. TIO surveyed available technologies and ongoing research and development on chemical, biological, and physical treatments that alter the toxicity of contaminants, enhance their removal, or improve the mobility of non-aqueous phase liquids *(8)*. The report concluded that the range of techniques available was very limited; at the present rate of development, alternative technologies may not be available for three to five years; and of the 15 technologies under development, most were at the bench- or pilot-scale stage.

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Chapter 4: IN SITU *TREATMENT*

Mark Smith
European Office of Aerospace Research and Development

Cathy Vogel and Alison Thomas
Tyndall Air Force Base

4.1 INTRODUCTION

Environmental remediation technologies can be broadly divided into two categories: *ex situ* and *in situ*. *Ex situ* technologies treat contaminated materials after gross removal and transport of contaminated media to the treatment facility. Actual treatment often occurs onsite—reducing costs, risks, and administrative burden incurred with hazardous material portage. In contrast, *in situ* technologies apply the remediation process directly to the contaminants, with little or no gross movement of hazardous material.

The cost of environmental remediation is, to a large degree, directly proportional to the amount of material handled in the process. When large masses of earth or water are removed and cleaned, costs are incurred for both the physical handling of the material—large fractions of which may be uncontaminated—and for application of the treatment process in order to ensure complete decontamination. Deep contamination can involve extensive excavation of uncontaminated overburden. In addition to direct costs, excavation of contaminated soil is often impractical due the presence of overlying structures.

In situ processes attempt either to destroy the contaminants where they are found or, at the very least, to remove the contaminants from the contaminated matrix. Post-extraction physical separations are avoided or minimized, even if destruction or recovery is necessary. The technical challenge common to all of these processes involves moving mass to some desired area, moving reagents (oxygen, nutrients, oxidants, *etc*.) to the contaminants, or moving the contamination to some subsurface treatment zone.

In general, *in situ* processes require less capital outlay than *ex situ* treatments. Material handling requirements are lower, transportation costs are avoided, and post-process treatment (*e.g.*, landfilling) is avoided. *In situ* processes are also less invasive, which is often the reason for their use, as in the case of treatment under a building. On the other hand, *in situ* treatments, especially biotreatments, are generally slower and require longer implementation. In many circumstances, such as in the sale of property, the need to act quickly can outweigh the lower capital costs.

In situ strategies frequently use biological processes to destroy contaminants. Bioremediation uses microorganisms to transform the hazardous organic contaminants into harmless products, such as carbon dioxide and water. Microorganisms require mineral nutrients and a carbon and energy source (food) to carry out these biodegradation processes. Ideally, the target contaminant will be the food source, and sometimes a treatment process can be designed around fortuitous incidental biochemical reactions. Microbes also require a terminal electron acceptor to complete the circuit of reactions by which they survive. The most familiar electron acceptor is oxygen, but certain other oxidized ionic species, such as nitrate, sulfate, or ferrous iron, can support bacterial growth. Several other factors (*e.g.*, temperature and pH) affect the efficiency of these processes. Degradation capabilities of microorganisms have been used for decades to treat municipal and industrial wastes. Recent advances in biotechnology allow these processes to be applied to hazardous chemicals *in situ*.

In general, petroleum hydrocarbons can serve as primary growth substrates for bacteria. The ease of biodegradability of a hydrocarbon is inversely proportional to its molecular weight and complexity. Short-chain aliphatic hydrocarbons and simple aromatic molecules are fairly readily consumed, while large, polycyclic aromatic hydrocarbons (PAHs) are more recalcitrant. Synthetic organic compounds, such as chlorinated solvents (tetrachloroethene [PCE], trichloroethene [TCE], carbon tetrachloride, *etc*.), are much more resistant to biodegradation. Chlorinated solvents cannot serve as growth substrates for most microorganisms, but can nonetheless be degraded or transformed by populations that grow on other substrates. TCE, for example, can be transformed and even mineralized by a variety of microorganisms growing on different organic compounds, including methane, phenol, toluene, propane, methanol, and n-butane. The current challenge for bioremediation is the encouragement of microorganisms to degrade these manufactured compounds.

Bioremediation can be very effective for removing contaminants that serve as growth substrates, particularly if low concentrations of the contaminants are present in an appropriate environment. Bioremediation can provide a cost-effective alternative to traditional technologies (*e.g.*, air stripping, carbon sorption, and excavation) for a wide range of natural organic compounds, such as motor or jet fuel. Biological treatment offers a permanent and often less expensive solution than strictly physical treatments, because microorganisms convert toxic organic compounds to environmentally benign products. However, bioremediation is no panacea. *In situ* bioremediation systems are often integrated with other remediation technologies to effect total cleanup.

Physical processes will also be considered as *in situ* for purposes of this study if the intent of the process is to physically remove only the contaminant from the contaminated media. As an example, air sparging is intended to remove volatile organic compounds (VOCs) from groundwater. This judgment could be debated, as such a process still merely transfers contamination from water-saturated soil to air, which often still requires post treatment. However, as opposed to the pumping and treating of groundwater, air sparging promises several advantages in material handling, as well as certain challenges associated with the physical transfer of matter at the contaminated area, and it is appropriate to discuss these processes here.

Knowledge of contaminant location and physical state in the subsurface is critical in implementing *in situ* remediation techniques. In the vadose or unsaturated zone, contamination may exist as a vapor phase, adsorbed to particles, dissolved in the thin film of water surrounding soil particles, or as a non-aqueous phase liquid (NAPL). Contamination in the saturated zone might consist of residual saturation or material trapped within the soil matrix, matter sorbed to solids, a pool of NAPL, or dissolved material in the groundwater. Each situation can pose unique challenges to the remediation engineer.

Each of the technologies examined by the Phase II Pilot Study offers innovations over more traditional, mass-intensive approaches to remediation. As they are implemented, a greater understanding of the dynamic interaction of contamination with the subsurface is gained. Comparing and contrasting the results of these demonstrations suggests further innovations, as well as contextual evaluation of the technologies themselves.

4.2 CASE STUDIES

Of the 52 remediation projects examined by the pilot study, 18 were either fully *in situ* implementations or involved partial *in situ* treatment. Of these 18, 11 provided sufficient detail by the end of the pilot study from which to draw conclusions. These projects consisted mainly of biological treatments of organic contaminants. Table 4.1 shows those projects considered to be totally or significantly *in situ* in nature, with country of origin and a basic description. More information is provided in the sections that

Table 4.1: *In Situ* Projects

Project Number	Title	Description
1	Trial of air-sparging of a petroleum-contaminated aquifer	Field trials of air sparging combined with soil vapor extraction (SVE) to determine the increase of extracted VOCs.
2	Bioremediation of petrochemicals following a major fire	*In situ* flushing/bioremediation process substantially reduced the total soil contamination burden at the site and, as a consequence, greatly reduced the potential migration of contamination offsite. Phenol-degrading microorganisms were encouraged to proliferate. *In situ* application was only part of overall cleanup strategy.
3	Bioclogging of aquifers for containment and remediation of organic contaminants	Strategy entails using biomass, polysaccharide and gas production to decrease soil permeability. Pilot Study report is limited to laboratory studies and modeling.
4	Remediation of methyl ethyl ketone contaminated soil and groundwater	Strategy includes a combination of pump and treat for free-phase product and SVE for volatile and adsorbed contamination. *In situ* bioremediation is planned to treat residual contamination within the basalt aquifer after pumping operations are complete.
6	*In situ*/on-site bioremediation of wood treatment soils	Daramend® process. Land farming with amendments. Highly effective for relatively shallow contamination (*in situ*) or for excavated soils (*ex situ* application)
9	Demonstration of an *in situ* process for soil remediation using well points	Field demonstration of a combined *in situ* soil flushing and bioremediation technology for BTEX and other petroleum hydrocarbons.
12	Groundwater and soil remediation at a former manganese sulfate production plant	*In situ* treatment involving accelerating the leaching process with an aggressive leachant, and collecting leachate in a drainage system.
15	Combined chemical and microbiological treatment of coking sites	Bench-scale microbiological treatment of aromatic hydrocarbons with and without oxidizing pretreatments (bench-scale)
16	Combined vacuum extraction and *in situ* stripping of chlorinated vapors	NOVOC™ wells and SVE wells and blowers remove contamination as a gas stream for treatment above ground by carbon adsorption.
18	Biological *in situ* remediation of contaminated gasworks	Large-scale injection and extraction of water through a contaminated zone leached contaminants. This process was later used to introduce nutrients into the ground and to raise soil temperature by preheating the infiltration water.

23	Modeling and optimization of *in situ* remediation	Investigation of several aspects of remediation models including economic and time constraints as well as technical considerations.
35	*In situ* SVE within containment cells combined with *ex situ* bioremediation and groundwater treatment	Partial *in situ* application for dual-phase vacuum extraction. On-site treatment of materials in lagoons and biopiles.
37	Bioventing of hydrocarbon-contaminated soils in the sub-arctic	Study investigating economic viability of soil heating to promote bioventing in cold soils. Considerable detail is available including an economic analysis.
41	*In situ* microbial filters	Resting-state methanotrophic bacteria can degrade TCE. Exploiting this capability, the bacteria are raised in a bioreactor, and the biomass is injected into the subsurface through a borehole where they attach to the solid rock matrix creating an inoculated subsurface zone. After an attachment period to allow fixation and establishment of the microbiological community, groundwater is extracted from the borehole resulting in the flow through the impregnated zone.
42	*In situ* pneumatic fracturing and *in situ* bioremediation	Tight soils hamper *in situ* technologies such as SVE, bioventing, air sparging, and other air and nutrient injection techniques. Hydraulic and pneumatic fracturing are enhancement technologies to increase treatment efficiency of *in situ* techniques by increasing the permeability of the soils.
43	Multi-vendor bioremediation technology demonstration project	Three technologies were tested, including two aquifer stripping wells and a co-metabolic bioventing process using added methane and ammonia.
47	*In situ* electroosmosis (Lasagna™ process)	Contaminants are directed through treatment zones under the influence of electroosmosis.
49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil	Bioremediated soil was chemically characterized, and its environmental behavior was evaluated by cultivating various plant species.

follow. The project number corresponds to extended project summaries found in Appendix IV. Note that Project 47, which is discussed in this chapter, is also discussed in Chapter 5, Physical-Chemical Treatment.

4.2.1 Project 1: Trial of Air-Sparging of a Petroleum-Contaminated Site

Leaking pipes beneath a gas station in Adelaide, South Australia, contaminated the soil and groundwater with up to 2,100 mg/L petroleum hydrocarbons, up to 1.5 mg/L benzene, and up to 20 mg/L xylene. Contamination occurred as dissolved, adsorbed, vapor, and minor free phases. The adsorbed phase occurred as a relatively thin and widespread zone above the water table at a depth of 7.5 m. Three trials were conducted to determine the effectiveness of air sparging in combination with vapor extraction at this site.

The study found that air sparging substantially increased the amount of VOCs that could be removed by vapor extraction from soil and groundwater. The initial increase in extraction rate was short-lived, however, and slowed dramatically after only a few days operation. The zone of influence and rate of recovery of VOCs were highly dependent on local geology. Air sparging also produced mounding of the water table around the sparge well, which may have forced contaminants away from the extraction wells. Based on the results of the trials, air sparging was abandoned as a remediation strategy at this site.

4.2.2 Project 2: Bioremediation of Petrochemicals Following a Major Fire

A major fire at a petrochemical facility near Melbourne, Australia resulted in the widespread contamination of soil and groundwater with phenol, benzene, and acrylonitrile from damaged storage tanks. A site investigation found phenol concentrations as high as 24,000 mg/kg in near-surface soils and 700 mg/L in the groundwater, making bioremediation problematic due to the toxicity of phenol to bacteria. Following extensive laboratory studies, a flushing-biotreatment system was investigated at field scale.

A field study was undertaken on a 1,600-m^2 area of soil. The site was prepared by plowing gypsum and slow-release nutrients into the soil. Contaminated water was flushed through the soil, recovered, and treated in a bioreactor. Phenol concentrations decreased rapidly in the top 0.6 m of soil after treatment commenced. Monitoring of soil microbiology showed high concentrations of phenol-degrading bacteria (up to $5x10^7$/g) were being maintained. Two months after *in situ* treatment began, phenol concentrations in the groundwater rose to 1,000 mg/L, and then gradually declined to about 1 mg/L.

In situ treatment was only one aspect of this project. The overall remediation scheme for the site also included disposal of some contaminated fire water, storm water, and groundwater to local sewage works for aerobic lagoon biotreatment; ultraviolet (UV) peroxidation of fire water and storm water; and soil vapor extraction (SVE) and sparging of VOCs.

4.2.3 Project 3: Bioclogging of Aquifers for Containment and Remediation of Organic Contaminants

Recent studies have suggested a correlation between increased microbial biomass density in aquifer materials and reduced saturated hydraulic conductivity of aquifers. This process, termed "bioclogging," is believed to result from several different processes, such as the production of low solubility gaseous end products, the excretion of extra-cellular polysaccharides, and the increase in bacterial cell numbers. The objective of this project was to investigate the potential benefits of bioclogging to provide a temporary partial subsurface containment of contaminated areas, and to act as a site for enhanced biodegradation of organic contaminants. Only laboratory results were reported to the Phase II Pilot Study, and no bioclogging in the field had yet been attempted.

Test leachate containing growth medium, glucose, and sodium nitrate was passed through a 0.5-m long, by 0.08-m diameter column at a constant volume flux density of 0.11 m^3/day. Results showed that polysaccharide production can lead to at least one order of magnitude reduction in column hydraulic conductivity. The study also suggested that after initial delivery of amendments (*e.g.*, nutrients), the reduction in hydraulic conductivity appeared to be long-lived. The most rapid change in K_{sat} occurred in the first 18 hours of the experiment, with further slow reductions after 50 hours.

4.2.4 Project 4: Remediation of Methyl Ethyl Ketone Contaminated Soil and Groundwater

This Pilot Study project reports on the development and implementation of a site remedial strategy that incorporates *in situ* recovery of free product and contaminant vapors. Geology at the site consists of a thin layer of clay and reworked soil overlying basaltic lava flows to a depth of 30 m. The basalt is an extremely heterogeneous aquifer comprising discontinuous, very low to moderately permeable layers with occasional interconnecting joints and fractures. There are three free product contaminant plumes present in the aquifer: a lubrication oil plume, a methyl ethyl ketone (MEK) plume, and a mixed plume containing benzene, toluene, ethylbenzene, and xylene (BTEX), motor fuel, turpentine, and kerosene. The plumes cover an area of greater than 7 ha.

The initial remedial strategy consisted of a combination of pump-and-treating free phase product and SVE for volatile and adsorbed contamination. Since contaminant distribution can be distinguished as three separate plumes, the remediation plan addressed separate recovery and treatment systems for each of them. Floating free product was recovered from a network of boreholes with specially designed "top loading" pumps. These modified displacement pumps use compressed air to pump the recovered fluid to the surface. Uncontaminated water was injected around each plume to force free product towards the recovery wells. Vapor extraction was conducted simultaneously to take advantage of the dewatered ground.

Recovered vapor, free product, and groundwater were treated at the surface in a treatment compound comprising a three-stage oil/water separator, a heated air stripper for groundwater treatment, discharge of treated wastewater to a municipal sewer, and a thermal destruction system (using a methane gas carrier to ensure full product combustion) to treat all hydrocarbon waste streams from the air stripper as well as the vacuum manifold system. When operated at 760°C and a retention time of 0.5 seconds, the system ensured total destruction of hydrocarbons. Emissions met the 10 mg hydrocarbon/m^3 objective.

Full-scale remediation commenced with recovery of a large volume of free product with an associated high concentration of dissolved contamination. Two years later, remediation was on-going with an average rate of groundwater recovery on the order of 50,000 L/day. The rate of hydrocarbon recovery declined significantly over time. *In situ* bioremediation was being considered to treat the residual contamination within the basalt aquifer after pumping operations were completed.

4.2.5 Project 6: *In Situ*/On-Site Remediation of Wood Treatment Soils

DARAMEND® bioremediation carefully cultivates desirable microorganisms through soil preparation and addition of nutrients. Soil amendments are incorporated into the contaminated soil and homogenized to supply biologically available water, nitrogen, phosphorous, micronutrients, and oxygen to support biodegradation of the contaminants. The amendments also reduce the acute toxicity of the soil's aqueous phase by transiently adsorbing contaminants and providing surfaces for microbial adhesion and development of biofilms. The composition of DARAMEND® organic amendments is soil-specific and based upon the results of a thorough physical and chemical characterization (*e.g.*, texture, moisture retention, carbon:nitrogen ratio, nutrient profile, and concentrations of target compounds) and treatability studies of the soil or waste. Soil moisture content is also strictly controlled.

The process was applied *ex situ* to excavated, PAH-contaminated harbor dredgings; *in situ* to petroleum hydrocarbon-contaminated soil in the Arctic, and *in situ* to soil at a wood treatment plant.

Harbor sediments were treated for 46 days, which resulted in an 84% reduction in total PAH, from 1,146 mg/kg to 187 mg/kg. A control plot (tillage only) showed a 40% reduction. Benzo(a)anthracene reduction for unpretreated sediment, pretreated sediment, and control sediment was 60%, 58%, and 30%, respectively.

At the Arctic site, pilot *in situ* plots were covered by temporary greenhouses to control soil moisture content and to increase soil temperatures through solar heating. Three DARAMEND® formulations were tested, and after 10 days, 89%, 62%, and 75% reductions in total petroleum hydrocarbons (TPH) were observed. No TPH reduction was observed in the control plot.

After 254 days in the *ex situ* demonstration at the wood treatment plant, PAHs were reduced 94%, from 1,710 mg/kg to 98 mg/kg; chlorophenols 96%, from 352 mg/kg to 13.6 mg/kg; and TPH by 87%. The control area showed a reduction of 41%, but no reduction in either chlorinated phenols or TPH was observed. Toxicity, as measured by earthworm mortality and seed germination, was eliminated or greatly reduced only in the treated soil.

4.2.6 Project 9: Demonstration of an *In Situ* Process for Soil Remediation Using Well Points

The treatment process consisted of a recirculation system with injection and extraction wells. A surfactant/co-surfactant solution is injected into the well points to mobilize soil contaminants. The extracted contaminated soil washings were sent to an effluent treatment plant. Biodegradation of the remaining hydrocarbon residual located in the subsurface was stimulated by injecting nutrients and air or hydrogen peroxide via the well points. The project scope included laboratory-scale selection of surfactants, *in situ* soil washing tests using the selected surfactant, *in situ* biodegradation testing of residual hydrocarbons and the contaminated washing solution, and subsequent monitoring to verify contaminant removal. Over 50 types of surfactants and co-surfactants were tested to establish pairings and concentrations required to extract over 95% of the hydrocarbons from the contaminated soil.

4.2.7 Project 12: Groundwater and Soil Remediation at a Former Manganese Sulfate Production Plant

On-site disposal of about 45,000 m^3 of hazardous waste at a former manganese sulfate plant in the municipality of Tinglev, Denmark, left severe contamination of the soil and groundwater. Groundwater was contaminated with high concentrations of manganese, sulfate, and cyanide. Solid wastes, leachate, and contaminated groundwater all required treatment. Traditional remediation of the solid waste by off-site incineration and off-gas treatment was estimated to cost 8-13 million ECU (U.S.$9-10 million). Paper to pilot scale studies were used to investigate alternatives.

Conceptually, the leachate and most contaminated groundwater could be collected for treatment by constructing drains beneath the wastes. Leaching of wastes could be accelerated by installing a system at the top of the wastes to distribute suitable treatment agents. It was estimated that leaching at a liquid/solid ratio of 2-3 annually (40-60 times the natural rate) would leach contaminants from the solids in 7-10 years. Between 160,000 and 240,000 m^3 of leachate would have to be treated and cleaned each year.

Ex situ batch processing of the wastes was also investigated. Sodium hydroxide was shown in pilot studies to leach sulfate and cyanide effectively from the production waste. Another waste material, which had been used to clean the coal gas, contained fine particles that did not allow for efficient flow of leachant.

Five possible methods for treating the leachate and contaminated groundwater were considered: biodegradation, chemical precipitation, chemical oxidation, evaporation, and reverse osmosis. Evaporation and reverse osmosis were not evaluated experimentally because economic analysis indicated they would be too expensive. Pilot-scale tests of leachate biodegradation required continuous supervision and were laborious, and the biomass was insensitive to fluctuations in pH. Therefore, bioremediation was not evaluated further. Precipitation of the sulfate with barium chloride was determined to be impractical because high residual barium levels would result in precipitation and aquifer clogging if reinjected, or require expensive post-treatment if disposed of elsewhere. Thus, precipitation was also rejected for technical and economic reasons. Laboratory experiments showed that UV light destroyed complex cyanides in the range of 1-25 parts per billion (ppb) within 10 minutes.

Both *ex situ* batch and *in situ* remediation processes were proposed for the sulfate-rich solid waste. In the *ex situ* batch process, solid waste would be mixed with water in an impoundment to leach the sulfate. Effective leaching required retention times as high as 120 hours. An improved design consisted of a fluidized bed batch treatment.

In situ treatment would involve accelerating the leaching process by using pH neutral groundwater or an aggressive leachant containing sodium hydroxide on the waste, and collecting leachate in collection drains. It was suggested that at a liquid/solid ratio of 20, the leachate derived from pH-neutral water would have a concentration acceptable for being returned to the groundwater. A pilot-scale treatment facility was constructed onsite consisting of heaped waste that was leached using a sodium hydroxide solution. Objections to this technology are due to the use of chemicals during treatment.

It was concluded that batch treatments are unlikely to be feasible due to high treatment costs, long treatment times, and costly effluent disposal. *In situ* treatment may be more viable although it will take a long time.

Treatment of the cyanide-contaminated waste was evaluated using accelerated *in situ* leaching and an *ex situ* batch process. *In situ* treatment was unsuccessful at pilot-scale because the waste heap was clogged by fine particles. *Ex situ* batch processing was evaluated at bench-scale using both sodium hydroxide solution and neutral water. Solid/liquid separation from the alkali leach proved extremely difficult, and cyanide was incompletely leached by the neutral water. It was therefore concluded that treatment of the cyanide wastes was not feasible due to lengthy treatment times and high costs.

In conclusion, the sulfate-contaminated wastes could be treated by an *in situ* method although the treatment times could be lengthy and disposal of effluent costly. Viable options include leaving the wastes on the site, covering it with clean soil and planting vegetation. Another option may be to cover the wastes with a protective membrane. The cyanide-contaminated wastes are not suitable for on-site treatment and should be excavated and removed for incineration or other treatment. Final disposition of the site was not reported to the Pilot Study.

4.2.8 Project 15: Combined Chemical and Microbiological Treatment of Coking Sites

Disposal sites of wastes (including coal tars) from the petroleum refinery industry are often characterized by high concentrations of total hydrocarbons (up to 2,200 mg/kg in soil and 4,800 mg/kg in settling ponds), phenols (3-10 mg/kg), PAHs (850-1,500 mg/kg), and cyanides (10-300 mg/kg). In this project, PAH-degrading bacteria were identified and the practical bioremediation of PAHs within the contaminated soils was evaluated. The ability of an oxidation pretreatment to enhance subsequent bioremediation was also assessed.

Pilot-scale assessments were conducted with five different fungi and nine bacterial isolates in a recirculating bioreactor. Biopiles were continuously mixed and aerated with amendments of straw, saw dust, and uncontaminated soil. Inorganic nutrients were added to the system using a proprietary time-release nutrient. Three oxidizing pretreatments (hydrogen peroxide, sodium hypochlorite, and ozone) were assessed by mixing them as amendments into the biopiles during their construction.

The results after 2 months of the trial showed that only four of the bacterial isolates and none of the fungi significantly degraded PAHs in the soil tested. The high concentrations of tar present in the soil made it difficult to turn and mix the material which may have reduced contaminant accessibility. Despite these difficulties, degradation rates of 75% for PAHs after 12 months, 75% for phenols after 7 weeks, and 50% for cyanides after 2-3 months were reported. No information was provided on the relative efficacy of each organism.

Considerable additions of oxidizing agents were required to observe any enhanced decrease in PAH concentrations. The addition of a catalyst, such as ferrous sulfide, was found to reduce the amount of nutrient necessary. In 19 weeks, 1,000 mg/kg PAH was reduced to 50 mg/kg with pretreatment by hydrogen peroxide and ferrous sulfide catalyst.

4.2.9 Project 16: Combined Vacuum Extraction and *In Situ* Stripping of Chlorinated Vapors

NOVOC^{TM}, an *in situ* VOC removal system, is based on an air-lift pumping technology that uses air injection. A remediation system installed at a former pigment manufacturing facility consisted of a series of NOVOC^{TM} wells and SVE wells and blowers. Contaminants included PCE and heavy metals. Initial PCE concentrations ranged from 0.085-3.7 mg/L in groundwater and from 10 mg/kg to greater than 5,000 mg/kg in soil. The negotiated cleanup level for PCE was 1 mg/L in groundwater and 50 mg/kg in soil.

The NOVOC^{TM} system operated for a period of 22 months. System efficiency was controlled quarterly and consisted of collecting water samples from monitoring wells adjacent to the remediation wells. Results from the final soil and groundwater sampling showed that the target concentration of 1 mg/L in groundwater was achieved. PCE concentrations measured in the NOVOC^{TM} wells after the system had been turned off for a 1-month period ranged from 200-565 mg/L.

4.2.10 Project 18: Biological *In Situ* Remediation of Contaminated Gasworks

This Pilot Study project followed the progress of a 3-year *in situ* bioremediation project of a former gasworks site. The specific test area was located beneath a tar/ammonia separating sump, where spills and leaks had contaminated the ground beneath. Maximum contamination was located at a depth of 5-7 m. Soil recovered from this zone contained up to 55,000 mg/kg of extractable, lipophilic organics and 14,000 mg/kg of PAHs. The intent of this project was to optimize natural degradation processes by controlled addition of oxygen and nutrients.

The test area was sealed off from its surroundings by constructing walls into an impervious clay aquiclude at 17 m depth, forming a test cell. The water level in the test cell was lowered below the level of contamination to enhance air flow and promote aerobic degradation of hydrocarbons. A network of lances was sunk into the ground to serve as injection and extraction points for oxygen, with the goal of achieving homogeneous horizontal subsurface air flow. Above ground, an irrigation system was installed for vertical seepage of inorganic nutrients and moisture into the soil.

An objective of the project was to chart changing concentrations of leachable contaminants during the course of the experiment. This was achieved by using a dedicated infiltration and extraction well to flush the soil at long intervals during the test period. This process was later used to introduce nutrients into the ground and to raise soil temperature by preheating the infiltration water.

Using 4-ringed PAHs as conservative tracers to compare initial to final organic contents, the researchers reported that 54% of total PAHs present in the soil were degraded after 2.5 years of remediation. Assuming that the hydrocarbons consumed were predominantly aromatic, the oxygen consumed and carbon dioxide produced (which were monitored) account for 2,400 kg of organic material mineralized. Maximum degradation rates were seen when the soil was warmed either by flushing with warm air or water, or by natural warming during the summer months. Rapid degradation was also supported by supplying oxygen by air flushing, rather than as dissolved oxygen in water. This latter observation reinforced the desirability of lowering the water table below the level of contamination to facilitate aeration of the contaminant zone.

Assessing exactly the efficiency of bioremediation in the field was difficult due to the extreme heterogeneity of the subsoil. Analysis of contaminant composition suggested that the most available components of the tar oil were readily biodegraded. Water was repeatedly flushed through the contaminant zone (10-20 fold flushing of mobile soil pore water volume) approximately every three months to extract elutable contaminants. During the 3 years of bioremediation, the chemical oxygen demand (COD) levels thus recovered were reduced by about 83%, while dissolved organic carbon (DOC) dropped about 76%. Over the same period, there was a parallel decrease of 97% in the concentration of PAH.

The main limitation to biodegradation appeared to be the bioavailability of contaminants. Although in some places the soil still contains relatively high concentrations of PAHs, the hazard potential of the contaminated site was reduced considerably.

4.2.11 Project 23: Modeling and Optimization of *In Situ* Remediation

In situ remediation of contaminated soil and water is widely perceived to offer the greatest potential for enhancing performance and reducing treatment cost. However, its commercial implementation has been limited by the perception that current methods are unreliable and their treatment duration unpredictable. The unpredictability of full-scale *in situ* treatment is not solely due to the heterogeneity of field sites, but also due to economic and time constraints on the preliminary collection of field data. Treatment design and predicted performance are often based on bench-scale studies used in combination with models incorporating subjective default data values. The results are often misleading and overly optimistic. This Pilot Study project reported on several aspects of an investigation into the modeling of *in situ* treatment with an overall goal of enhancing and optimizing treatment performance.

A literature survey indicated that although several groundwater models existed, soil air models for predicting the performance of SVE were relatively immature. A spreadsheet model to predict SVE performance for sites contaminated with up to three VOCs linked differential equations to a mass balance maintained on the spreadsheet. Model outputs included the cumulative amount of contaminants extracted and soil contaminant concentration, both as a function of time. Parameters and expressions within the model accounted for equilibrium sorption to organic matter, transfer from liquid to vapor phase, and contaminant interactions, diffusion, biodegradation, and time dependence. The model output was used to determine expected treatment durations. Four case studies were evaluated using the predictive model with one laboratory-based study, two on-site studies, and another conducted *in situ*.

Another model examined changes in contaminant concentration in extracted water as a function of time to predict the treatment duration of *in situ* soil flushing. The model combined a simple predictive model with statistical simulation to account for variabilities and uncertainties in the input parameters. Assuming a homogeneous distribution of site parameters, soil flushing duration was predicted to achieve the remedial target for groundwater contaminant concentration in three years. A more realistic scenario accounting for site heterogeneity resulted in treatment times on the order of decades. The authors stressed that a higher quality of soil investigation was necessary in order to generate a realistic prediction of remediation duration and cost.

A mechanistic model of *in situ* bioventing, dubbed ECOSAT, was developed and calibrated with data from laboratory batch and column bioventing tests. Mechanistic models allow for scenario calculations, which may help to develop site-specific soil investigation strategies, to evaluate different combinations of remediation techniques, and to design and optimize the process control of the selected techniques. The calibrated model was used to predict bioventing performance, and the predictions were compared to ten full-scale soil venting projects. Comparison of idealized geology with field data revealed that predictions based on averaged properties are too optimistic—the observed duration of the remediation is longer than predicted. The deviation between estimated and observed duration of remediation differ by up to one order of magnitude. The stagnation of biotreatment suggests that a significant fraction of contamination is unavailable to the treatment process.

The ECOSAT model was used to more fully investigate the “stagnation” phenomenon. The study concluded that nonequilibrium phenomena, particularly diffusion-controlled mass transfer from areas of the soil where convective flow was absent, were the dominant factors in treatment stagnation. The model was also used to compare continuous vapor extraction with intermittent extraction. Results showed that treatment times for either method were approximately the same since they were dependent upon the slowly diffusing contaminant fraction. However, the intermittent extraction technique provided oxygen to the bioavailable water-soluble contaminants much more efficiently, promoting biodegradation as the dominant contaminant removal process. In contrast, the continuous extraction method rapidly reduced the concentration of available contaminants through volatilization, not through biodegradation.

4.2.12 Project 35: Combined *In Situ* Soil Vapor Extraction Within Containment Cells and Subsequent *Ex Situ* Bioremediation

An area of 7.9 ha was significantly contaminated with coal carbonization wastes from a cokeworks plant. Contaminants included BTEX, PAHs, phenols, heavy metals, and cyanides. The site is underlain by reworked soil, sand and gravel to a depth of 2-4 m, and groundwater was encountered within this interval. The original site investigation indicated that both soil and groundwater were highly contaminated. In particular, the groundwater was found to be contaminated across the entire site with phenol, oil, and PAHs. NAPL was evident at certain locations, and oil was seeping into the nearby river. Benzene and other VOCs were also detected in significant concentrations.

A deep cut-off slurry wall was installed to allow safe excavation up to 5 m and to prevent discharges of contaminants directly into the river. Following dewatering, solid material was excavated. Solids unsuitable for treatment were placed directly into an on-site encapsulation facility. The remaining material was then screened and either air dried and reused or treated by *ex situ* bioremediation to remove oil and PAH contamination. Treated materials were used as backfill to reinstate the excavated contaminated area.

Dual-phase vacuum extraction (DVE) was implemented by dividing the area into a series of treatment cells. The DVE system used an applied subsurface vacuum to draw contaminant vapors and free product to the surface for separation and treatment. At the surface, free product was separated from the groundwater in a separator tank, and volatile organic vapors were adsorbed onto activated carbon filters. In order to facilitate free product removal, dewatering trenches were dug in some areas of the site. The DVE process was operated for 46 weeks. Severe weather conditions often caused problems during DVE treatment because of freezing of supporting pipes and equipment. The goal of the treatment was to remove free product and reduce VOC concentrations (particularly benzene) to safe levels for excavation, rather than as a complete remedial treatment in itself.

Extracted groundwater was treated as follows in a succession of holding lagoons and reactors: (1) floating product are removed by skimming reception/buffer lagoons; (2) heavy metals are removed by hydroxide precipitation; (3) cyanide is treated by oxidation; (4) sulfide is treated by oxidation; (5) pH is corrected; (6) filtration using sand filters and activated carbon filters; (7) ammoniacal nitrogen is oxidized in a biological treatment plant. Inoculum from a local sewage works was found to perform far better than commercially available inocula. Treated groundwater was discharged to a soakaway along the river.

Treatment beds (biopiles) to treat some of the solids were constructed over a high density polyethylene (HDPE) membrane and clay liner. Runoff was collected in an HDPE-lined ditch and was reapplied to the treatment beds. Aeration was provided continuously via a network of air injection pipes. Effectively treated material was re-used on site.

A reed bed has been planned to treat any residual contamination following site reinstatement. It is envisioned that the reed bed will need to accommodate a groundwater flow of 30-50 m^3/day.

4.2.13 Project 37: Bioventing of Hydrocarbon-Contaminated Soils in the Sub-Arctic

This technology demonstration was carried out on a 0.4-ha area at an arctic air base that had been contaminated with JP-4 jet fuel to a depth of nearly 3 m. The site is underlain by a mixture of sand and gravel, with increasing silt content to 3 m, the depth of the water table. Total petroleum hydrocarbon (TPH) levels ranged from 100-3,000 mg/kg. A field evaluation of bioventing was undertaken to determine whether and to what degree soil warming can enhance the effectiveness of bioventing of JP-4 and to determine whether soil warming promoted a higher rate of biodegradation all year round.

The demonstration area was divided into four test plots, which were used to test four different soil warming techniques:

(1) warm water system: Groundwater collected via an extraction well was pumped through an electrical heater and warmed to around 35˚C before re-infiltration. Insulation was placed over the ground surface to retain heat;

(2) heat tape system: Strips of heat tape were buried to a depth of 1 m in the test plot and warmed at a rate of 16 W/m^2. Insulation was placed over the plot to retain heat;

(3) solar test: Insulation placed over the ground during the winter months was replaced with plastic mulch sheeting during the spring and summer to capture solar heat and passively warm the soil;

(4) control test: Both the warm water and heat tape systems were operated for two years from summer to summer over the demonstration period. The solar and control plots were monitored for 3 years. No soil warming.

Soil temperatures in the warm water and heat tape plots were consistently 10˚C higher than in the solar-heated and control plots, resulting in average biodegradation rates three- to four-times higher in the warmer plots than in the solar and control plots. After the heating systems were switched off, biodegradation rates in these plots decreased below that of the control, suggesting that the microorganisms may have adapted to the higher temperatures. TPH removal in the warmed plots was an order of magnitude higher than in the solar heated and control plots. Warm water was most effective, followed by heat tape. In all cases, soil TPH and BTEX levels dropped dramatically, indicating that bioventing resulted in significant contaminant removal. In general, air emissions of benzene vapor in the control plot were higher when the bioventing system was on than when it was off, but were still well below regulatory limits.

From demonstration data, the estimated costs per volume of soil treated were comparable in all cases, ranging from U.S.$31.67-$34.16 per m^3 for a 5,000 m^3 site with an average TPH level of 4,000 mg/kg. Soil heating significantly decreased treatment time (from nearly 20 years to about three), however, so that the decision to use soil heating in conjunction with bioventing becomes a choice about project duration and budget allocation. Doubling initial TPH level increased the cost estimates by only 13-26%

4.2.14 Project 41: *In situ* Microbial Filters

Cultured methanotrophic bacteria injected into the subsurface through a borehole attach to the solid rock matrix creating an inoculated subsurface zone. After an attachment period to allow fixation and establishment of the microbiological community, groundwater is extracted from the borehole therefore drawing the flow through the impregnated zone. It was concluded that a 100-mm thick biofilter established at the site provided complete breakdown of TCE for a period of eight weeks, and had a reduced degradation capacity for an additional eight weeks. The demonstration was reported to be successful, although regulatory guidelines for TCE were not met in the treated water. The authors concluded that this was due to a high concentration of co-contaminants, including chlorofluorocarbon and methane, which were degraded preferentially to TCE. Remedial costs were claimed to be up to 50% lower than pump-and-treat, with applicability problems being associated with large fast-flowing plumes with contaminant concentrations less than 10 mg/L.

4.2.15 Project 42: *In Situ* Pneumatic Fracturing and Bioremediation

By increasing the permeability of the soil to liquids and vapors, removal of contaminants by SVE and biodegradation can be accelerated. Hydraulic and pneumatic fracturing increase treatment efficiency of *in situ* techniques by creating fissures in the soil, which act as conduits for air and water. Hydraulic fracturing utilizes pressurized water while pneumatic fracturing utilizes pressurized air to create cracks in low permeability and highly consolidated sediments. Aerobic processes dominate at the fracture interfaces and, to a limited distance, into the soil away from the fracture.

Initial characterization of the test site revealed low permeability soils and benzene, toluene, and xylenes (BTX) contamination. Over a one-year period, the site was pneumatically fractured, and nitrate and ammonium salt were periodically injected to enhance aerobic and anaerobic biodegradation. Off-gasses from monitoring wells were analyzed for BTX, carbon dioxide, methane, and oxygen to monitor the progress of treatment. Additional soil corings were analyzed to measure the change in extent of site contamination during remediation. Carbon mass balances were also performed to evaluate treatment efficiency.

Fracturing increased subsurface permeability by a factor of 40 within an effective radius of approximately 6 m. Results from soil sampling at the end of the demonstration showed a 79% reduction in BTX concentrations in the soil. Cores from three distinct depths taken before and after remediation showed a 22-kg decrease in BTX. Biodegradation accounted for over 82% of total BTX mass removal during the 12-month study period. Based on periodic soil-gas sampling, 14% of BTX was removed by SVE. Other mechanisms accounted for 4% of the BTX loss.

4.2.16 Project 43: Multi-Vendor Bioremediation Technology Demonstration

This comparison of three treatment technologies took place at an abandoned hazardous waste disposal site containing very high concentrations of chlorinated and non-chlorinated solvents such as TCE, PCE, MEK, and toluene. Specific technical objectives of this study included determining whether the use of naturally-occurring microorganisms can effectively remediate VOCs present in the unsaturated zone, generating field data for simultaneous evaluation of different biological processes, and evaluating the ability of the *in situ* and *ex situ* approaches to meet site specific remedial objectives.

The site consisted of a clay cap over mixed fill, which was comprised of hazardous waste and soil fill. Beneath the mixed fill is a thin silty-clay layer with numerous fine silty-sand lenses. Beneath the fill is sandy silt glacial till. Work during the trial revealed that a plastic liner was present between the fill material and the natural soil creating a perched water table.

The first technology was a co-metabolic bioventing approach, consisting of extraction wells linked to a central blower. The output of the blower was connected to the injection wells via ports to allow inputs of ambient air, methane, and anhydrous ammonia. The methane was intended to boost co-metabolic processes degrading chlorinated VOCs. The ammonia was intended as a bioavailable nitrogen source. The blower operated for approximately 2 hr/day for nearly 5 months. The material treated turned out to be relatively lightly contaminated, with many samples meeting treatment targets in advance of treatment. The installation of the technology was complicated by the plastic liner and perched water, which were not expected based on the available site investigation information. The system achieved the compliance target; however, contaminant levels were already low in the test area—particularly for methyl isobutyl ketone (MIBK) and PCE—and data for acetone and MEK could not be interpreted because of difficulties with their detection limits. Using demonstration data, the treatment cost was U.S.$52/m^3, and the duration of treatment was 12 months[1].

The second technology consisted of biopiles constructed on twin layers of high density polyethylene (HDPE) supported by earthen berms. The HDPE was covered by a layer of sand for protection and drainage. The surface of the pile was covered by a similar felt, sand, and HDPE construct. Aeration was via extraction pipes in the lower sand layer connected to a fan with passive air injection pipes in the upper sand layer. Liquids could be percolated into the biopile via a sprinkler system. Air and liquid movement was intended to optimize conditions for biological activity within the piles. Two piles were set up: one with continuous aeration, and the other with discontinuous aeration to allow the development of alternating periods of aerobic and anaerobic activity within the piles. The materials treated within the piles were the most grossly contaminated site materials. The treatment was made more difficult by the fine texture of the soil, which impeded aeration and water movement. The intermittent aeration pile possibly did not achieve conditions suitable for aerobic activity. Neither the continuously nor intermittently ventilated biopiles achieved compliance, although both substantially degraded the VOCs. Based on demonstration data, the treatment cost was U.S.$71/m^3, and the duration was 9 months[1].

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[1] The cost bases for each of three technologies were not the same. For instance, the co-metabolic bioventing estimate included costs associated with permitting, while the UVB estimate did not.

The third technology was a vacuum vaporization (UVB™) well. The basic unit was a 400-mm diameter steel water well with upper and lower screens inserted to a depth of 8 m below the ground surface. A submersible pump in the bottom zone of the well pumped groundwater through an in-line bioreactor packed with granular activated carbon. The treated water was discharged back into the soil through the upper screen. The bioreactor unit was integrated with an air stripping function, both to remove VOCs and to oxygenate the groundwater prior to discharge. The extraction of groundwater from the lower zone and discharge to the upper zone was intended to circulate water around the well to create a zone of enhanced stripping and biodegradation activity. Installation of the well was complicated by the plastic liner and an unexpectedly shallow water table. After 5 months, when the other trials were completed, samples from the UVB treatment area indicated little significant contaminant reduction; compliance was achieved for PCE only. A longer treatment period was recommended for this type of technology. After 14 months, compliance was also achieved for MIBK and TCE (based on 45 usable data points). Using demonstration data, the treatment cost was U.S.$240/m^3, and the duration was 14 months[1].

4.2.17 Project 47: *In Situ* Electroosmosis (Lasagna™ Process)

The Lasagna™ process is intended to deliver treatment agents to contaminants in low permeability soils and to render *in situ* treatments more feasible. The process depends on electroosmosis, whereby low voltage electrical current applied to electrodes creates an electric field to mobilize contaminants through low-permeability soil toward treatment zones. These zones, installed in close proximity through the contaminated material, contain materials (*e.g.*, sorbents, catalytic agents, microbes, oxidants, buffers, *etc*.,) to sorb or degrade contaminants. Placing the treatment layers close to each other minimizes the time needed for electroosmotic transport. Intermittent reversal of electrical polarity reverses liquid flow and appears to increase the efficiency of contaminant removal as well as allowing complete sorption/degradation by passing contaminants several times through the treatment zones. Reversed flow minimizes the pH extremes that occur at the electrodes when the system is operated in one direction.

Various configurations of the technology are possible. The Pilot Study project used a vertical configuration at a site contaminated with TCE. The case study was carried out in two phases: Phase I evaluated the overall effectiveness of coupling electrokinetics and carbon adsorption treatment zones, and Phase II examined the use of iron filings in the treatment zone to dehalogenate TCE in a commercial-scale demonstration .

The demonstration site covers an estimated area of 557 m^2 and extends to a depth of 15 m. TCE concentrations in soil are as high as 1,523 mg/kg, but average around 84 mg/kg. Concentrations increase with depth, and the highest concentrations are believed to occur at depths from 6-9 m. The test site was about 4.6 m x 3 m on the surface and 4.6 m deep. A control area was built next to the test area and was isolated from it hydraulically. The vertical configuration tested at the site consisted of steel panel electrodes and treatment zones made of wick drains containing granular activated carbon. A direct current of approximately 40 volt/m applied to the electrodes caused groundwater to flow from the anode to the cathode at about 13 mm/day. The induced pH gradient caused problems such as soil drying and cracking and the formation of metal and mineral deposits at the cathode. Pumping water from the cathode to the anode reduced these problems.

Soil samples collected at the demonstration site before and after the test showed that the process removed 98%-99% of the TCE from the tight clay (a reduction from 100-500 mg/kg to an average of 1 mg/kg). Carbon canisters used to collect soil vapors accounted for around 50% of the original TCE. The remaining removal of TCE may be attributed to passive diffusion, evaporation, *in situ* degradation, non-uniform distribution of the contaminant in the soil, or incomplete extraction of the compound from the activated carbon before analysis.

Results suggest the process is also effective for removing residual dense non-aqueous phase liquid (DNAPL). At most soil sampling locations with TCE concentrations greater than 225 mg/kg (which is indicative of residual DNAPL) the Lasagna™ process reduced these levels to less than 1 mg/kg.

A more extensive field investigation incorporated reactive treatment zones, such as iron filings, to destroy TCE *in situ*. Preliminary results show that the iron filings can dechlorinate TCE, producing relatively innocuous end-products such as chloride ion, ethane, and ethene. Potential intermediate products, like dichloroethene and vinyl chloride, are associated with the surface of the filings.

An engineering evaluation and cost analysis for the vertically-configured process estimates a treatment cost of U.S.\$52-118/m^3 of clay soil containing TCE at a depth of 12-15 m and over an area of 0.4-0.8 ha. With optimized electrode spacing, improved ability to install treatment zones and electrodes at closer spacing, and mass-produced prefabricated materials resulting from wider use of the technology, costs are expected to fall to U.S.\$26-52/m^3. These costs exclude those for analyses, waste disposal, *etc*.

4.2.18 Project 49: Characterization of Residual Contaminants in Bioremediated Soils and Reuse of Bioremediated Soils

The emission levels expected during the reuse of remediated soil were estimated by means of laboratory and field tests. For all investigations, hydrocarbons were extracted by Soxhlet extraction using tetrachloromethane, and hydrocarbon content was evaluated by infrared spectroscopy. In further discussion, total petroleum hydrocarbon (TPH) content is defined as the total solvent extractable material (TSEM) after removing polar compounds with alumina.

The remediated soil used for all tests contained 780 mg/dry kg TSEM and 430 mg/dry kg TPH, the hydrocarbon originating from EL heating oil. The content of PAH was below 2.8 mg/kg and was not subsequently measured.

Most of the residual contaminants remaining in bioremediated soil consisted of apolar, low-volatility compounds (boiling points >280˚C). Small quantities of polar compounds (*e.g.,* fatty acids and long-chain alcohols) were also detected in individual fractions. On the whole, however, the compounds were very hydrophobic, with octanol/water distribution coefficients greater than 10^6.

The second phase of the project involved investigating the environmental behavior of residual contaminants in the bioremediated soil after being applied as topsoil. The processes investigated were biodegradation, leachability due to precipitation, and volatilization. The leachability of the residual contaminants to percolating water was investigated in laboratory tests by means of shake and column leachate tests and by means of a lysimeter test outdoors. The initial total hydrocarbon content was of the order of 0.09 mg total hydrocarbons (THC) per liter, but rapidly declined thereafter. After less than one average annual precipitation throughput, the THC content in the percolating water was already below the drinking water limit of 0.02 mg/L. The leached quantity of contaminants corresponded to 0.1% of the total hydrocarbon content in the soil material. Extrapolation of these measurements indicated that only about 1% of the residual contaminants would leach out, even after 100 years' precipitation. DOC, which includes all the polar and apolar organic compounds dissolved in the water, ranged from 4.3-15 mg/L in the leachate from bioremediated soil, which is comparable to that of gravel. In comparison, the DOC of garden soil is about 107 mg/L.

Further biodegradation of the residual contaminants was observed when the soil was used to cultivate red clover or rye-grass, or left fallow or regularly plowed. Over 28 months, residual contamination declined about 13%, with no significant differences between the cultivation types. Since only small quantities of residual contaminants leached out or were emitted into the air over the whole trial period, the reduction in the TSEM/THC contents can be attributed to biodegradation.

The germination and growth of 36 plant species on both remediated soil and garden soil (control) were investigated in greenhouse trials. The plants developed normally on both soil materials and showed no phenotypical changes of any kind. Eight crops and eight wild herbs grown in deliberately contaminated soil showed a slightly increased plant yield over the controls after 30 days. The effect was not statistically significant, but these results clearly show that the contaminants added to the soil did not inhibit growth.

DIN-S4 leachates showed no significant acute toxic effects on the water-flea (*Daphnia magna*). The residual contaminants in successfully bioremediated soil are slightly soluble, difficult to volatilize, and undergo further biodegradation only over prolonged periods. Since the anticipated emissions are very low, no risks to humans or the environment are expected.

4.3 REVIEW OF CASE STUDIES AS A GROUP

As discussed in Chapter 2, Pilot Study projects were nominated and selected by a vote of Country Representatives. The selections, therefore, reflect a desire of a particular panel of experts to review representative or interesting new technologies available at that time, and should in no way be construed as either a random sampling of available technologies or representing any relative abundance or popularity of technologies. The *in situ* technologies chosen range from modeling efforts, to laboratory studies, to field studies and full-scale remediation projects.

The period of the Pilot Study saw the rapid development and deployment of bioventing as a remediation strategy for hydrocarbons in the vadose zone. Bioventing is similar to vacuum extraction, but whereas vacuum extraction is used as a means to remove contaminant vapors from the soil for recovery or disposal, bioventing is aimed at promoting microbial destruction of the contaminants before they reach the atmosphere. Variables affecting the effectiveness of bioventing are the capacity of microorganisms in the soil to metabolize hydrocarbons; the bioavailability of the hydrocarbons; temperature; and proper control of air flow to supply sufficient oxygen while minimizing venting of volatilized contaminants. While in some ways epitomizing “innovative” technology, bioventing had by 1993 become a widely-accepted alternative to traditional excavate-and-dispose solutions. Extensions to the technology were being sought to apply bioventing to hydrocarbon contamination in cold climates, to tight soils, and to the cleanup of more recalcitrant contaminants, like chlorinated hydrocarbons.

The demonstration of arctic region bioventing (Project 37) and the demonstrations of co-metabolic bioventing (Project 43) both achieved these to some degree. In Project 37, soil warming was applied to promote biodegradation, and the economics of the use of soil warming were evaluated. It was shown that the cost of bioventing with or without soil warming was about the same, but that soil warming significantly accelerated cleanup. The decision to use soil heating in conjunction with bioventing then becomes a choice about project duration and budget allocation, in the context of government imposed or negotiated cleanup agreements. The estimated cost of less than U.S.\$35/m^3 is still significantly less than typical dig-and-haul rates of U.S.\$100/m^3 or more.

Project 43 showed some promise as well, but the validation of co-metabolic bioventing based on the one demonstration presented is equivocal. *In situ* concentrations of contaminants decreased, but some of the target chlorinated compounds were already within regulatory limits at the demonstration site, and degradation of other compounds, (*e.g.*, toluene) was disappointing.

Project 18 assessed the applicability of bioventing to the contaminated soils on a pilot scale at a former gasworks site. Assessing exactly the efficiency of bioremediation in the field was difficult due to the extreme heterogeneity of the subsurface. Analysis of contaminant composition suggested that the more available tar oil components were readily biodegraded. The main limitation to biodegradation appeared to be the bioavailability of contaminants.

Similar to bioventing are land farming and "biopile" technologies (Projects 6 and 15). These technologies depend upon soil microbiology to perform the transformations necessary for cleanup, but are applied to relatively shallow depths and depend upon air diffusion, natural convection, or plowing for aeration. Several successes for the Daramend® process (Project 6) were reported to the Pilot Study, including one at an arctic site and demonstrations involving a variety of soil types and contaminants. The successes of this technology are attributed to the application of proprietary amendments to the soil, which improve the bioavailability of contaminants and meet coincident microbial nutritional requirements. A similar effort (Project 15) attempted to apply this kind of treatment on PAHs in a biopile. Partial success was reported for PAH degradation, but significant difficulties were encountered due to the tarry nature of the contaminated soil. A biopile was also part of the overall strategy in Project 35.

Soil flushing was attempted in two demonstrations to avoid more invasive efforts. A former manganese sulfate plant in Denmark was severely contaminated with sulfate and cyanide (Project 12). While sodium hydroxide solution was shown in laboratory studies to effectively leach sulfate, limited soil porosity prevented effective *in situ* application, necessitating further disposal or treatment of the leachate. The cyanide contamination was found to be unsuitable for on-site treatment. Final resolution of the treatment plan was not reported to the Pilot Study, but the project was illustrative of practical limitations encountered in the field. Project 9 reported attempts at flushing contaminants with surfactant and co-surfactant aqueous solutions, but final outcome of these efforts were not reported.

One of the Pilot Study projects was a hybrid between land farming and leaching. Project 2 leached water through amended soil and recovered the leachate for treatment in a bioreactor. Successful destruction of the contaminating phenolic compounds occurred in both the soil and the bioreactor.

The delivery of treatment to the contaminants is an alternative to remote treatment. Project 41 involved a conceptual demonstration that created a subterranean zone of resting-stage methanotrophic bacteria known to dechlorinate TCE. This "biofilter" provided a treatment zone capable of dechlorinating TCE in eight weeks at a cost approximately half that for a pump and treat system. Operational limitations include interference by other substances such as methane and chlorofluorocarbon and difficulty in capturing a fast-moving plume, given the necessarily slow draw rate of contaminated water through the biofilter.

Aquifer stripping and SVE are regarded in this report as *in situ* treatments, although the actual treatment of the contaminants occurs *ex situ*. Project 4 applied SVE after dewatering, to take advantage of the increased unsaturated volume. Project 1, applied air sparging to a petrol-contaminated site, in conjunction with SVE. The amount of volatile hydrocarbons removed by vapor extraction when sparging commenced initially increased, but the increase was short-lived and slowed dramatically after only a few days operation. Two competing and patented aquifer stripping technologies were introduced during the early 1990's, and examples were included in the Pilot Study inventory. NOVOC™ (Project 16) is based on an air-lift pumping technology using air injection. NOVOC™ was demonstrated for 22 months at a PCE-contaminated site and reduced the PCE concentration in the aquifer from up to 3.7 mg/L to less than 1 mg/L. In Project 43, a UVB™ well pumped water from the aquifer, aerated to remove VOCs, and discharged it back to the subsurface. The system of extracting water from the lower zone and discharging it to the upper zone was intended to circulate water around the well and create a zone of enhanced stripping biodegradation activity. Compliance at the site was achieved in 14 months for both MIBK and TCE, at a cost of U.S.$240/m^3. Project 35 applied a subsurface vacuum to draw contaminant vapors and free product to the surface for separation and treatment in a process called DVE. Applied after dewatering, DVE in this instance was intended to reduce the benzene concentration at the site to a level safe for excavation.

Remediation is the removal of a mass of contamination from a mass of natural materials, and the energy and effort applied to separate these two masses are the fundamental problems requiring both technological and economic solutions. The technology becomes more intensive and the costs increase when the contaminated soil has low porosity, either because of inherent soil properties or due to fouling by the contaminant. Two Pilot Study technologies addressed the subject of these “tight” soils. Bioventing can be used in tight soils once pneumatic fracturing has been applied to increase their porosity. An increased porosity makes contaminants more accessible and facilitates the introduction of air into the subsurface. In Project 42, the site was pneumatically fractured, and nitrate and ammonium salt were periodically injected to enhance aerobic and anaerobic biodegradation. Fracturing increased subsurface permeability up to 40 fold within an effective radius of approximately 6 m. Biodegradation accounted for over 82% of the total BTX mass removed; the remaining loss was accounted for by SVE and other losses. Project 47, dubbed the Lasagna™ process, used electroosmotic transport to move contaminated groundwater through treatment zones. In the Pilot Study demonstration, TCE was dehalogenated in a treatment zone of iron filings. TCE concentrations in the soil were reduced from 100-500 mg/kg to an average of 1 mg/kg.

An unusual application of biological processes is bioclogging. The combination of cells, polysaccharide, and gases produced can reduce the hydraulic conductivity in an area for temporary partial subsurface containment of contamination and to act as a site for enhanced biodegradation of organic contaminants. In Project 3, biomass was made to grow in particular regions. However, only laboratory results were reported to the Pilot Study, and no bioclogging in the field had yet been attempted.

Project 23 took a detailed look at technical and economic models of *in situ* remediation. In one of the studies, the anticipated duration of remediation was three years, assuming homogeneous distribution of site parameters, and several decades when accounting for site heterogeneity. Similar calculations changed duration projections by an order of magnitude, just by accounting for heterogeneity. Modeling of bioventing through a diffusion-controlled region suggested that intermittent convection promoted biodegradation over vapor extraction as the dominant means of mass removal.

4.4 ENVIRONMENTAL IMPACTS AND HEALTH AND SAFETY

For the most part, those sites that selected *in situ* technologies are those with hydrocarbon contamination ranging from lighter petroleum fractions to PAHs. In some cases, chlorinated hydrocarbons were present. The typical strategy was to destroy the contaminants in the subsurface, reducing the chance for toxic exposure to workers or the general public compared to traditional methods. Vapor extraction methods involve plumbing that carries contaminants directly to treatment, which also reduces the risk of exposure. Fugitive emissions are typically very low, providing for very little adverse environmental impact.

Project 49 found that the risk from the bioremediated soils was extremely low. Extensive tests of bioremediated soils originally contaminated with EL heating oil showed very low leachability, no toxicity to a number of different plants, and leachates non-toxic to *Daphnia* water fleas. These studies strongly support the idea that residual limits should be based upon toxicological data and not upon analytical capabilities.

4.5 COSTS

Costs for the five Pilot Study *in situ* technologies that provided an economic analysis ranged from U.S.\$26-\$240/m^3, and these costs were estimated based on limited field data and operating assumptions. Actual costs of any technology at any given site are notoriously dependent on actual site parameters, but the data in Table 4.2 indicate that the costs of *in situ* technologies are likely to be competitive for a number of applications. In Project 12, the *in situ* technologies evaluated were deemed too expensive, lengthy, or inadequate to apply. However, neither was an excavation-and-incinerate or landfill strategy deemed suitable. The final disposition of the site is not known, but some type of impermeable cap was being considered.

Table 4.2. Estimated Costs of Technology Application

Project Number	Project	Technology Costs (U.S.$)
6	*In situ*/on-site bioremediation of wood treatment soils	\$46/m^3 (*in situ*) or \$96/m^3 (*ex situ*), excluding treatability studies and disposal of hazardous oversize screenings. \$92/m^3 (*in situ*) or \$140/m^3 (*ex situ*) including disposal.
12	Groundwater and soil remediation at a former manganese sulfate production plant	deemed too expensive
37	Bioventing of hydrocarbon-contaminated soils in the sub-arctic	\$31.67-34.16/m^3 See Appendix IV for assumptions and other details.
43	Multi-vendor bioremediation technology demonstration project	Co-metabolic *in situ* bioventing: \$52/m^3 biopiles: \$71/m^3 UVB™ well: \$240/m^3 See Appendix IV for assumptions and other details.
47	*In situ* electroosmosis (Lasagna™ process)	\$26-52/m^3 expected with mass-produced prefabricated equipment. Otherwise, \$52-118/m^3

4.6 APPLICABILITY OF *IN SITU* TECHNOLOGIES

The most successful *in situ* technologies were those directed toward simple hydrocarbons in the vadose zone, *i.e.*, some form of bioventing or land farming. Complicating factors involve mass transfer and bioavailability because tight clayey soils or tarry deposits prevent the intimate contact of microbes, oxygen, water, contaminants, and other nutrients necessary to carry out the destruction of the contaminant. Cold temperatures pose no great threat to implementing bioremediation—provided one is willing to heat the soil or wait longer for success.

SVE has also come into its own during this period, with several enhancements being demonstrated. Extension of bioventing and SVE through pneumatic fracturing of tight soils is notable.

Aquifer stripping entered the remediation scene during this Pilot Study period and met with mixed success. These technologies appear to be most effective in relatively homogeneous aquifers contaminated with highly volatile contaminants. Microbial filters, as demonstrated to the Pilot Study, show promise in chlorinated hydrocarbon contamination, but still require further development. Electroosmotic transport of contaminants through treatment zones is also promising.

Attempts to extend bioremediation to PAHs have met with mixed success, due to the recalcitrance of the substrate. Land farming was somewhat more successful than bioventing toward these contaminants.

Chapter 5: PHYSICAL-CHEMICAL TREATMENT

Alex Lye and Robert Booth
Water Technology International Corporation, Burlington, Ontario, Canada

5.1 INTRODUCTION

5.1.1 Overview of Chapter

This chapter presents information for 16 projects that investigated physical-chemical techniques to treat soils, sediments, other solid media, and groundwater containing a variety of chemicals. Most of the chapter deals with soil washing, because it was the most frequently used technology for pretreating solid contaminated media. Contaminated concentrates that resulted from soil washing were subsequently treated by biological and physical-chemical technologies. Only six projects investigated physical-chemical technologies without soil washing as a pretreatment.

To make meaningful comparisons of data reported for the projects, the projects were grouped as follows:

- Group 1: Typical soil washing;
- Group 2: Soil washing and biological treatment;
- Group 3: Soil washing and physical-chemical treatment;
- Group 4: Physical-chemical treatment (no soil washing); and
- Group 5: Photo-oxidation treatment.

The project summaries presented in Section 5.2 provide an overview of the projects but do not contain all information, such as performance data and criteria achieved. This excluded information is discussed elsewhere in the chapter and in the project summaries (Appendix IV). However, key points of the technologies are contained in Table 5.1.

For the purposes of this chapter, soil washing includes unit processes such as screening, attrition scrubbing, hydrocycloning, *etc.*, as well as enhancements such as flotation, magnetic separation, and gravity separation.

Finally, it must be noted that the authors of this chapter summarized and compared data contained in available reports. Data are presented as they were reported for the various projects. Final reports were not available for some projects, while documents for others did not provide detailed information. As a result, there are limitations to the data comparisons and observations made by the authors.

5.1.2 Generic Description of Technology Group

Typical Soil Washing

As a pretreatment for excavated material, soil washing exploits the fact that contaminants are often preferentially adsorbed to the fine particles. This approach relies on physical processes to separate a small volume of contaminated material from the bulk of relatively uncontaminated material. Current commercial soil washing processes remove mainly fine fractions (<0.063 mm) containing the highest concentrations of contaminants. The remaining coarse fraction (>0.063 mm) is relatively clean. The clean material is often reused as “inert” fill.

Separating the contaminated fines often results in lower costs for overall treatment, because it is only this smaller volume of contaminated material, not all the original material, that requires further treatment or disposal. The contaminated material is shipped to a controlled landfill or treated further by a variety of processes that destroy, immobilize, or recycle the contaminants.

Soil washing is economically feasible only if the volume reduction is large enough to provide financial benefits. According to a report (*1*) on an extensive review of commercial and pilot-scale soil washing systems, soil washing is most effective on soils containing less than 30-35% clay and silt, *i.e.*, particles smaller than 0.063 mm. At higher percentages of these fines, the volume reduction is not large enough for the process to be economical. In addition, difficulties arise in handling these materials, separating the contaminated and uncontaminated materials, and handling the products.

Despite these problems for soils rich in fines, soil washing may be seen as a cost-effective treatment if the technology overcomes difficulties presented by the high levels of silt and clay. Possible solutions include enhancing soil separation techniques and developing processes to treat the fine fractions downstream.

Soil Washing Combined with Other Technologies

With some soils, physical treatment alone will not reduce the absolute concentration of contaminants to acceptably low levels. For soils containing more than 30% clay and silt by weight, physical pretreatment could reduce the volume of contaminated material requiring downstream treatment. Pretreatment may also present the separated contaminant concentrate in a form suitable for the downstream process, *e.g.*, bioslurry, solvent extraction, and vacuum distillation. Case studies in this chapter illustrate soil washing combined with biological or physical-chemical treatment such as vacuum distillation, photo-oxidation, biodegradation, and chemical dehalogenation.

Physical-Chemical Treatment (No Soil Washing)

Some of the downstream processes mentioned above may be used directly on contaminated material that was not previously washed. Some of the case studies in the chapter examine processes such as:

- solvent extraction and treatment of extracts by stabilization (for heavy metals);
- leaching and treatment of leachate; and
- *in situ* electro-osmosis and adsorption.

Like soil washing, these conventional technologies experience difficulties in treating contaminated materials where the fines exceed 30-35%. When the levels of fines are this high, methods such as thermal treatment and solvent extraction become more expensive, while others such as biological treatment take a longer time.

Photo-Oxidation Treatment

This chapter restricts the discussion of photo-oxidation treatment to ultraviolet (UV) radiation and hydrogen peroxide (H_2O_2) to treat groundwater.

5.2 CASE STUDIES CHOSEN

This section summarizes each of 14 projects as a case study. The projects are discussed in groups as follows:

- Group 1: Typical soil washing (Project 30);
- Group 2: Soil washing and biological treatment (Projects 24, 26, and 36);
- Group 3: Soil washing and physical-chemical treatment (Projects 10, 17, 19, 27, 31, and 33);
- Group 4: Physical-chemical treatment (no soil washing) (Projects 32, 44, and 47); and
- Group 5: Photo-oxidation treatment (Projects 14, 38, and 40).

Some of the projects are also discussed in other chapters: Project 47 in Chapter 4; Projects 24, 26, and 31 in Chapter 6; Project 19 in Chapter 8; and Projects 10, 24, 26, 31, 32, 33, and 47 in Chapter 11.

5.2.1 Group 1: Typical Soil Washing (Project 30)

Project 30: Using Separation Processes From The Mineral Processing Industry For Soil Treatment

Investigators evaluated the applicability of particle separation techniques from the mineral processing industry to treat contaminated soil from sites in the U.K. This technique of soil washing by physical separation used established and innovative mineral processing equipment to separate soil into fractions of varying contaminant concentrations. The majority of tested soils contained clay and fines at high levels normally considered uneconomical for soil washing. These soils contained arsenic, complexed cyanides, and metals such as Hg, Cr, Cu, Pb, Ni, and Zn. Organics in the samples included polycyclic aromatic hydrocarbons (PAHs) and petroleum hydrocarbons.

Laboratory studies assessed the potential of physical processes to separate the contaminated soils into various fractions. These processes consisted of grain-size separation, attrition scrubbing, specific gravity partitioning, froth flotation, and magnetic separation. The studies confirmed that contaminants in the tested soils appeared to occur preferentially in particular soil fractions. Unfortunately, this preferential distribution was not always sufficient, so that fractions with the lowest concentrations of contaminants could be reused as inert landfill.

A pilot-scale investigation with the Warren Spring Laboratory’s National Environmental Technology Centre’s (WSL/NETCEN) soil washing plant examined soils from a former metal processing works and gasworks. Both soils were included in the laboratory studies. Material from the former gasworks consisted of building rubble, wastes and soil. A relatively high clay content (around 30%) made handling difficult. To exploit the physical properties of the soil and contaminants, the WSL/NETCEN soil washing plant was designed to transfer contaminants from the soil to a water-based suspension. This plant, with a throughput of 0.5-1.0 tonne/hr, compared froth flotation and a multi-gravity separator (MGS) for separating fine particles. Altogether, treatment processes consisted of coarse sizing, further sizing, attrition scrubbing and classification, and contaminant concentration.

The effectiveness of the process was measured by comparing the levels of contaminants in treated and untreated soil. In the pilot-scale tests using froth flotation, residues with low levels of contaminants (*i.e.*, treated material) made up around 48% by weight of the original feed. For similar tests with an MGS instead of froth flotation, the residues with low levels of contaminants totaled around 50% of the original feed. Compared to the rest of the feed, these residues contained markedly lower levels of PAHs, petroleum hydrocarbons, cyanide, Pb, and As. Comparing data on contaminants in the two types of residues (*i.e.*, froth flotation and MGS) revealed that the flotation residues contained higher levels of PAHs and petroleum hydrocarbons, but lower levels of Pb and cyanide. Arsenic levels did not differ much between the two residues.

Samples from the former metal reprocessing works produced a small proportion of dense material (specific gravity >2.8) with very marked concentrations of contaminants. Despite this separation of contaminants into the dense fraction, the remaining bulk of treated material contained unacceptable levels of contaminants. According to a project report, researchers re-assessed results of the Toxicity Characteristic Leaching Procedure (TCLP) of the soil and then re-considered the role of physical treatment in a treatment train to reduce the hazard.

For the soil from the former gasworks, the researchers suggested improving separation of fractions then destroying concentrated contaminants in the fine clay and silt fraction as a cheaper option to treating the entire soil. The recommended approach could consist of an enhanced soil washing process to improve separation, an in-line bioslurry reactor to destroy contaminants, or a combination of the two. The resulting treated fines may form a sludge that could be disposed of as a contaminant-free waste.

The pilot-scale soil washing plant featured process water containment and recirculation, and carbon filters to extract volatile contaminants from emissions. Wastes and sludges from the plant received further treatment at downstream processes or were shipped to a licensed landfill. The reports did not contain information on costs.

5.2.2 Group 2: Soil Washing and Biological Treatment (Projects 24, 26, and 36)

Project 24: Combined Remediation Technique for Soil Containing Organic Contaminants: FORTEC®

Developed by Heidemij Realisatie of the Netherlands, the Fortec® (Fast Organic Removal Technology) process combines hydrocyclone separation, photo-oxidation, and bioslurry technologies to treat soils contaminated with heavy aliphatic hydrocarbons (oils) and PAHs. A multi-staged configuration of hydrocyclones selects specific soil fractions that contain the majority of the contaminants. A clean sand fraction and heavily contaminated sludge result. The technology has been developed through bench- (25 m^3) and pilot- (50 m^3) scale to its current demonstration-scale of 300 m^3/batch.

Depending on the composition of the feed material, the sludge may be pretreated before it enters the slurry bioreactor. Pretreatment involves photo-oxidation (using high-pressure mercury UV lamps and H_2O_2) or a physical process in a batch reactor. This step transforms contaminants that are difficult to biodegrade into readily biodegradable ones.

The batch slurry bioreactor has a retention time of 3-20 days depending on the matrix being treated. Nutrients (nitrogen and phosphorus) are added as required. Once biotreatment is complete, the slurry is allowed to settle. The resulting effluent is recycled, while a belt filter press dewaters the sludge.

While photo-oxidation pretreatment enhances the biodegradation of PAHs, it is not required for more readily biodegradable contaminants. Initial studies showed that concentrations of 400-5,000 mg/kg mineral oil in contaminated soil could be reduced to the objective of 100 mg/kg in eight days without photo-oxidation pretreatment. In contrast, data showed that photo-oxidation helped degrade PAHs in soil and chlorophenol in groundwater. The pretreatment reduced PAHs from 30 mg/kg to 5-10 mg/kg in 15 days and chlorophenol from 200 µg/L to approximately 50 µg/L in 25 hours. It was suggested that the enhanced degradation resulted from the breakdown of soil organic matter and subsequent release of sorbed PAHs rather than to the oxidation of PAH molecules themselves. Without photo-oxidation pretreatment, PAHs were not degraded, while chlorophenols were reduced to only 100 µg/L.

Two demonstration tests were undertaken: one on sandy soil contaminated with heavy crude oil and one on sediment contaminated with mineral oil and PAHs. Soil washing was used as the pretreatment step to separate the fines from the larger soil or sediment fractions. Fines rich in organics were then treated in the 300-m^3 bioslurry reactor designed to maintain a minimum dissolved oxygen concentration of 2 mg/L and a set temperature between 15-30°C.

The results of these demonstrations showed that soil contaminated with up to 14,500 mg/kg of crude oil was treated to less than 3,000 mg/kg (in recombined fractions). Sediment contaminated with up to 2,000 mg/kg PAHs and 20,000 mg/kg mineral oil was treated to levels of 150 and 2.5 mg/kg respectively.

Project 26: Treatment of Creosote-Contaminated Soil (Soil Washing and Slurry Phase Bio-reactor)

The project investigated combining soil washing (especially using froth flotation) and slurry-phase bioremediation to remediate soils contaminated with 3- and 4-ring PAHs. The project consisted of bench-scale treatability studies and pilot-scale remediation.

The bench-scale biotreatability studies involved first isolating and screening soil microorganisms to evaluate their tolerance to PAHs and their ability to degrade these contaminants. Subsequent experiments with selected microorganisms provided optimum conditions for biodegradation of these compounds in slurry reactors.

The pilot-scale plant set up at the Norwegian State railways site in Lillestrom, Norway, combined froth flotation as a pretreatment for soil washing, a 1-tonne/hr soil washing plant, and a 454-L bioslurry reactor. This phase of work tested four excavated soils made up of sand, silt, clay, and sawdust/sand from the railway site, as well as two soils from another location. Investigators evaluated single and blended commercial anionic and cationic surfactants used with a foamer at water temperatures between 10-50°C and pH of 7-11. The biotreatment phase of the study tested indigenous microorganisms as well as patented PAH degraders. Parameters for biostimulation included nitrogen (N) and phosphorous (P), pH, aeration, surfactant, and temperature.

Bench-scale investigations of soil washing revealed that the most effective combination of one of the cationic collectors and a foamer removed 90-95% of PAHs from sandy soils. Increasing water temperature or pH provided no significant benefits and was incompatible with the downstream biological treatment. At the pilot-scale, soil washing at a loading rate of 550-859 kg/hour removed 20-90% of PAHs from two clay soils. The cleaned soil fraction contained 15-1,500 mg/kg PAHs. Clayey soils impaired the efficiency of soil washing and resulted in less than optimum performance.

The pilot-scale bio-reactor tested five 60 L batches of sludge resulting from soil washing two clayey soils. During treatment of the sludges, which contained 14-20% solids, PAH concentrations fell by up to 97% after 6 days. Oxygen uptake decreased during this time corresponding to a decrease in bioavailable PAHs in the bioslurry. An interim report noted that the native populations of PAH degraders "appeared to be sufficient to achieve residual PAH concentrations ranging from 55-200 mg/kg after a 6-day retention time."

A Microtox 15-minute bioassay revealed that the combined soil washing and biological treatment reduced toxicity by a factor of 10. Soil washing itself reduced the relative toxicity only slightly. The bioslurry treatment accounted for most of the reduced toxicity. Costs for various aspects of the remediation approach for the site were estimated at U.S.\$160/m^3 for excavation, sorting and backfilling, U.S.\$300/m^3 for washing, and U.S.\$530/m^3 for biological treatment.

Project 36: Enhancement Techniques for Ex Situ Soil Separation Processes, Particularly with Regard to Fine Particles

This pilot study examined the feasibility of extending soil washing processes to soils containing a high proportion of fine particles. The investigation focused on physical separation techniques and equipment used to treat fine mineral ores and industrial minerals. Tested soils contained a high proportion of fines and were contaminated with organic compounds. The studies investigated a variety of processes that included disaggregation, sizing, and classification of particles, attrition scrubbing, dewatering, and integration with slurry-phase biological treatment.

For the laboratory- and pilot-scale studies, two tested soils were both rich in clays. One soil from a former industrial site contained 62% soil particles less than 0.063 mm and was contaminated with diesel fuel. The other soil from a former gasworks facility had up to 43% soil particles less than 0.063 mm and contained PAHs, total petroleum hydrocarbons (TPH), and complexed cyanides. Laboratory tests served to characterize the soils and help design the pilot-scale studies. The tests evaluated disaggregation, screening, classifying at fine sizes, attrition scrubbing, and removal of misplaced or “entrained” particles. For the pilot plant tests, investigators used small-scale commercial separation and concentration equipment. Tests were conducted as a number of batch processes, with material from one process being collected and used as feed for further processes.

Contaminated fines were sometimes treated by froth flotation and specific gravity separation. The froth flotation approach, seen as an alternative to ultrafine hydrocycloning, consisted of a coal collector and frother. A part of the study tested 10 common organic flocculants and three inorganic coagulants to choose a flocculant/coagulant that produced relatively large compact flocs that settled rapidly. Work included settling tests and capillary suction tests.

Ten-liter air-sparged reactors provided a temperature-controlled environment for biological treatment. These investigations evaluated the biodegradability of different contaminated fine fractions at different temperatures, and with and without nutrients.

The bulk of contamination in the diesel-contaminated soil occurred in the fraction smaller than 0.002 mm. Pretreatment with a rotary ball mill partially filled with steel balls or pebbles disaggregated the soil particles and produced a slurry amenable for separation. Up to four additional sequential stages of hydrocycloning substantially reduced the concentration of contaminants in the coarse fraction. The resulting contaminant-reduced fraction accounted for 68.7% of the original soil.

Froth flotation, tested on the fraction smaller than 0.01 mm, did not significantly reduce contamination in the non-floating product. Of the 13 organic and inorganic coagulants/flocculants examined, calcium hydroxide at a dose rate of 100 g/tonne of solids produced a floc with the lowest moisture content after filtration.

After 28 days of treatment in the slurry reactor, fines separated from the diesel-contaminated soil retained only 20% of their original contamination. Despite this reduction, treated fines contained relatively high levels (2,300 mg/kg) of TPH, down by 80% from the original 12,000 mg/kg.

Despite their success with diesel-contaminated soil, physical separation and slurry phase biological processes experienced difficulties treating fines in the gasworks soil. Disaggregating this soil involved a tumbling mill system, sometimes preceded by a high pressure water-sprayed screen. Laboratory studies revealed that attrition scrubbing had little benefit because fine aggregated particles and contaminant-coated particles were minimal.

Froth flotation and specific gravity separation, unlike sizing and multi-staged classification, were able to concentrate contaminants in specific fractions. Froth flotation proved best on the 0.01-0.063 mm fraction, producing a non-floating fraction that accounted for 69% of the original untreated material. Three stages of froth flotation reduced PAH contamination by 61%, petroleum hydrocarbons by 54%, and cyanide by 39%. Specific gravity separation on the 0.01-0.063 fraction reduced PAHs, petroleum hydrocarbons, and cyanide contamination by 68%, 76%, and 14%, respectively. Despite these reductions, treated fractions could not be reused because they still contained unacceptable levels of contaminants.

Biological slurry treatment of the fine fractions failed to significantly reduce levels of the contaminants. After 28 days of treatment, PAHs fell by 40-50%, and petroleum hydrocarbons by up to 20%. Cyanide remained unchanged.

Residuals include clean treated soil materials and others that did not achieve remediation guidelines. Clean material could be reused onsite, while partially clean materials have to be dewatered and disposed. Water from soil washing and bioslurry treatment would also have to be treated before disposal.

For treatment to be more cost-effective than disposal of the untreated soil, the cost for transporting and disposing of such material must exceed £40-60 (U.S.$65-100) per tonne. Total operating costs were estimated at £23-37 (U.S.$38-60) per tonne of treated material.

The results of the study suggested that *ex situ* separation processes may be cost-effective for soils containing more than 30-35% of particles smaller than 0.063 mm. However, further work should assess the extent of application of this approach. This work may examine the mineralogy of clay particles, as well as how the exchange capacity of these particles influences adsorption/desorption of contaminants and subsequent dewatering.

5.2.3 Group 3: Soil Washing and Physical-Chemical Treatment (Projects 10, 17, 19, 27, 31, and 33)

Project 10: Integrated Treatment Technology for the Recovery of Inorganic and Organic Contaminants from Soil

This technology uses an integrated process to recover metals and organic compounds from soils and sediments. The process combines physical and hydrometallurgical steps to recover metals, and physical-chemical methods for organics. The combination provides a technology capable of recovering organic and inorganic contaminants simultaneously.

The first step involves separating the finer fraction of material, normally associated with contaminants, for further treatment. Coarse screens remove the fraction greater than 75 mm, which is usually clean and normally returned to the site. Material less than 75 mm goes through sequential soil washing separation methods, which break down soil aggregates, separate ferrous metal, and produce fractions of different sizes.

The resulting slurry, free of coarse metal fractions, is then treated with proprietary reagents and conventional flotation equipment to extract a product rich in organic contaminants. If further treatment is required, the organic-depleted slurry passes to a hydrometallurgical circuit where fine metal contaminants that were not recovered physically are leached into solution then extracted with Vitrokele™ metal-selective absorbents. The resulting metal-rich filtercake is recycled, while the remaining slurry is washed, dewatered, and disposed as a clean material.

The intended uses for treated materials govern the degree of treatment required to satisfy the relevant criteria and the consequent overall costs. For example, sediments to be used as lake-fill may require an extra hydrometallurgical leach and counter-current Vitrokele™ adsorption unit to achieve lake-fill guidelines. Sediments for on-shore use as fill may not require this step.

Tallon Metal Technologies, Inc. conducted bench-scale tests with sediments from Hamilton Harbour, Ontario, Canada. The sediments contained high concentrations of organic contaminants (PAHs, oil and grease), metals such as Pb, Zn, Cd, Cu, and Ni, as well as a total organic carbon (TOC) load that exceeded 10%. A 20-kg test sample was made up of approximately 92% material smaller than 100 µm and 75% smaller than 50 µm. Metals such as Cd, Cr, Fe, Mn, Ni, Pb, and Zn exceeded the “severe effect level” base on Ontario’s sediment quality guidelines. The bench-scale treatment approach included flotation, magnetic separation, and gravity separation techniques.

The results showed that cleaned tailings represented around 40% of the original sediment feed, but contained only 4.1% of the total oil and grease, 4.9% of the PAHs, less than 2% of the total Pb, and 11% of the total Zn. In contrast, Cd, Ni and Fe were also reduced but remained at 24-30% of the original load.

The organic product contained 27% of the total mass and captured 62% and 74% of the original oil and grease and PAHs, respectively. It was also enriched in Pb, Zn, Cd, Ni, and Fe at 81%, 60%, 54%, 54%, and 32%, respectively, of the original content.

Based on the bench-scale investigation, the treatment process for Hamilton Harbour sediments would consist of screening, magnetic separation, concentration of organics by flotation, and a hydrometallurgical extraction if required to remove residual Zn, Cu, Ni, and Pb from feeds to the leach circuit. For this treatment, the contractor estimated a cost of Cdn$75-100 (U.S.$52-69)/tonne, assuming at least 20,000 tonnes require treatment.

The technology was tested on soils from two industrial sites: the Ataratiri site in Toronto, Ontario, Canada, and a site in Longue Pointe, Quebec, Canada. The soils exceeded industrial guidelines for reuse for some heavy metals and inorganics. Ataratiri soils contained PAHs, while those from Longue Pointe were contaminated with metals such as Pb, Cu, and Zn.

Pretreatment of Ataratiri soils resulted in a metal concentrate, suitable for recycling, containing as much as 55% by weight iron. “Clean” fractions that made up around 95% by weight of the feed material were within Ontario’s residential criteria for some contaminants, but within industrial criteria for PAHs. The treatment reduced benzo(b)fluoranthene from 14 mg/kg to 4 mg/kg, a value that exceeds residential guidelines. Treatment reduced Zn from 4,026 mg/kg to 360 mg/kg, but Cu remained unchanged at 100 mg/kg. An added hydrometallurgical step proved effective for treated soils that still exceeded industrial guidelines. When soils were treated by this extra recovery step, higher percentages of the original feed material achieved industrial or residential guidelines.

For Longue Pointe soils, the technology incorporated hydrometallurgical extraction and Vitrokele™ adsorption because most of the Pb contamination occurred in fine particles in the soil. Soil treated this way contained as little as 7% of its original Pb content (as high as 11,800 µg/g), and met regulatory limits for industrial or residential use.

At Ataratiri and Longue Pointe, recovered contaminant metal products were of low mass, rich in metals and suitable for recycling off-site in the steel or base metal industries. Recovered organic contaminants were low in mass, enriched in oil and grease and PAHs, and suitable for on-site or off-site treatment by a secondary technology.

According to the technology vendor, the integrated approach for organic and inorganic contaminants is economically attractive over one that uses two independent treatments.

Project 17: Treatment of Polluted Soil in a Mobile Solvent Extraction Unit

The ORG-X mobile solvent extraction unit, originally designed to remove viscous non-aqueous phase liquids (NAPLs), such as PAHs and tars, from excavated soils at manufactured gas plants, is modular and usually mounted on five trailers. Under this NATO/CCMS Pilot Study, the ORG-X process was combined with other technologies to treat PAHs, polychlorinated biphenyls (PCBs), petroleum hydrocarbons, and heavy metals in different soil types.

After first screening contaminated soil to remove a coarse clean fraction (>#4 mesh), contaminated fines are mixed with a non-chlorinated, non-toxic, biodegradable solvent at ambient temperature. An extraction auger enhances dissolution of organics from soil in the resulting slurry and partially separates the cleaned fines from the solvent laden with organics. The solvent then passes to a decanter where the entrained fines settle. After settling, fines are returned to the initial mixing tank, and spent solvent is decanted and sent to a vaporizing recovery unit. Solvent recovered from this unit is recycled to the initial mixing tank while organics form a concentrated contaminated oil, which requires subsequent treatment.

Soil from the extraction auger goes to a dryer that evaporates residual solvent, condenses it, and sends it to the vaporizing unit. The treated dry soil is then either stabilized if contaminants such as heavy metals are present, or is reused. Traces of solvent in cleaned soils are claimed to be innocuous and biodegradable.

The feed rate depends on the soil type and ranges from two to five tonnes/hour. Treatment costs vary from U.S.$75-200/tonne depending on the volume of material to be treated.

Tests were conducted with 12-200 tonnes of media (silty sand, loamy soil, and sediment) contaminated with PAHs, coal tar, petroleum hydrocarbons, heavy metals, and PCBs. Extraction reduced levels of PAHs from 250-2,000 mg/kg to 6-30 mg/kg, and PCBs from 200-500 mg/kg to 1-6 mg/kg (98% reduction). Treated materials were used as fill or treated further to stabilize metals.

The solvent formulation, protected by trade secret, which is non-specific and thus provides excellent extraction for a wide range of organic contaminants. These include crude oil, machining oils, PCBs, pesticides, and herbicides. A key feature of the system’s design is its ability to treat finer particles with adsorbed contaminants.

The ORG-X mobile solvent extraction unit operates best under optimum moisture content and grain size. In one case study, the soil moisture content of 20% made the soil more difficult and costly to treat. The process achieves higher efficiency on sandy material, but is being improved for fine-grained soils.

The technology vendors reported that cost savings increase as the volume of material to be treated increases, for example:

- 2,000 tonnes: approximately U.S.$200/tonne
- 20,000 tonnes: just under U.S.$100/tonne
- 100,000 tonnes: about U.S.$60/tonne

Project 19: Cleaning of Mercury-Contaminated Soil Using a Combined Soil Washing and Distillation Process

The large-scale Harbauer soil washing and vacuum distillation plant was evaluated at a site in Marktredwitz, Germany. The site contained 57,000 metric tonnes of soil and debris contaminated with mercury, solvents, chemical waste, and treatment residuals. Mercury occurred at concentrations of 300-5,000 mg/kg. The project's remediation goal was to clean the contaminated soil and debris to meet criteria for landfilling.

This was reported as the first full-scale application of vacuum distillation technology. This unit is containerized, transportable, and equipped with systems to treat process water and off-gas. During the 3-year period of operation, the unit processed 57,000 tonnes at the rate of 150 tonnes/day.

Vacuum distillation eliminates drawbacks associated with conventional thermal processes. For example, the moderate heating does not change the mineral structure of treated soils.

In this technology, soil washing first concentrates mercury in a fine fraction (as small as 0.1 mm to as large as 8 mm). During subsequent vacuum distillation, the fines concentrated with mercury are heated in a rotating drum to 350-450°C under reduced pressures of 50-150 hPa. Reduced pressures (rather than higher temperatures) lower the boiling points of contaminants and result in lower energy costs. Also, vacuum distillation releases only 1/20 to 1/30 of emissions normally encountered with incineration. Volatile mercury is recovered by condensation. Treated soils containing more than 50 mg/kg mercury are passed through the process again.

In addition to soil washing and vacuum distillation, the system incorporates processes to treat water and off-gases. Water treatment consists of thickeners, flocculants, a sand filter, and activated carbon filters. The sand filter removes very fine particles while the carbon adsorbs organic contaminants that may be present in the process water. An ion exchanger completes treatment before water may be discharged to a sanitary sewer.

In the remediation project, 15,000 tonnes were treated at a rate of 150 tonnes daily during the first year of operation. Soil containing mercury up to 1,900 mg/kg achieved levels below the target of 50 mg/kg, and often reached 10 mg/kg. Treated off-gases and water also achieved relevant target levels.

Monitoring the plant revealed that the operation met emission standards. Under the low-oxygen environment of vacuum distillation, secondary oxidation does not occur, so dangerous organic residues like dioxin are not formed.

Residuals to be disposed of or recycled were condensed mercury, spent ion-exchange resin, and a fine-grained precipitation sludge from the water treatment unit.

Costs for treatment, according to results from a U.S. SITE demonstration project, were estimated at U.S.$320/tonne.

In addition to its application for mercury in the remediation project, the combined process can be used to treat crude oil fractions, halogenated hydrocarbons, PAHs, cyanides, and metal compounds that can be vaporized.

Project 27: Soil Washing and Chemical Dehalogenation of PCB-Contaminated Soil

Soil washing and chemical dehalogenation were used to treat 1,288 tonnes of excavated material contaminated with PCBs. This material came from a site in Oslo, Norway, where insulator oils containing PCBs had leaked from transformer equipment and contaminated soil with up to 2,000 mg/kg PCBs.

The three-year project included bench-scale studies on soil washing followed by pilot-scale and full-scale washing. Dehalogenation investigations were conducted at bench-scale and full-scale. The Pilot Study focused on a combined system of water-based soil washing and dehalogenation, because this combination had not been applied before in Norway. Both processes were novel in that country, and reductive dehalogenation was itself innovative.

Duplicate bench-scale soil washing treatability experiments with a laboratory-scale flotation cell tested these variables: water temperature, pH, five surfactants, and a foamer (methylisobutylcarbanol). The additives and soil were mixed for a fixed conditioning period, then aerated for a fixed period. The foam and remaining clean soil were collected and analyzed for PCBs.

Soil washing involved first separating and sorting debris, then treating the soil in a soil washing plant. For this treatment, the plant consisted of three processes to separate the remaining contaminated materials into two size fractions (>0.1 mm and <0.1 mm) and to surface-wash them. The contaminated fines (<0.1 mm), having passed through a conditioning mixing tank and a double flotation cell, were trapped in a foam in the cell. The trapped material, laden with contaminants, was coagulated and flocculated with an organic polymer, then thickened and dewatered.

The full-scale soil washing operation did not achieve its performance target for volume reduction because the levels of fine particles were higher than expected. Washing reduced the volume of material by 60%, not 70% as expected. The excess particles overloaded the system with solids, and soil that should have been clean after one washing had to be washed again. As a result of the reduced performance, washing produced 780 tonnes of clean soil and around 400 tonnes of sludge containing PCBs to be destroyed.

The dehalogenation technology tested at the pilot-scale involved first drying soil to 10% moisture, then adding a reducing agent and exposing the mixture to a reducing environment. The final report documenting results of the pilot-scale dehalogenation investigation was not available for this review.

In terms of performance for PCBs, the duplicate bench-scale soil washing experiments on samples with around 1,000 mg/kg PCBs achieved 80-95% removal of PCBs. The remaining soil (clean fraction) contained residual PCBs at 40-50 mg/kg.[1] The full-scale soil washing operation treated 1,400 tonnes of soil containing 50-300 mg/kg PCBs (dry weight). All batches achieved the performance criterion of less than 10 mg/kg PCBs.

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[1] Authors' note: In the absence of mass balance data, the percent removal cannot be verified. It is possible that the laboratory work aimed to achieve a specific concentration of PCBs in the clean fraction rather than a targeted percent removal.

The report did not contain information on performance in terms of discharged water. This water could contain no more than 10 µg/L PCBs, that translates to a loading of less than 200 mg/day.

The interim report did not contain information on the full-scale dehalogenation studies, or on the eco-toxicological tests to evaluate the risk associated with clean and treated soil to be redeposited at the site. Leachates from TCLP tests of treated material provided information on the toxicity of the biphenyl by-products.

The soil washing operations generated residuals, but no gaseous emissions. Coarse material and treated fines were returned to the original excavation and capped. All wash water was collected, analyzed for PCBs, and treated if required before discharge to a sewer.

Treated soil contained residual PCBs, by-products formed during treatment, and chemicals used to promote dehalogenation of the PCBs. All of these compounds posed possible environmental hazards. To evaluate these hazards, a suite of eco-toxicological tests was conducted on leachate generated from samples treated according to the TCLP.

For the full-scale soil washing operations, equipment costs were estimated at U.S.$75,000 and operations at U.S.$380/tonne. These amounts include handling materials, and analyses (approximately U.S.$76/tonne). Costs for dehalogenation were not available.

Project 31: Decontamination of Metalliferous Mine Spoil

The Water and Environment Division of the Welsh Office commissioned a study to evaluate methods for decontaminating metalliferous spoil from abandoned mines in mid and north Wales. This study aimed to determine if current metal-processing could be used to reprocess old metalliferous spoil materials to recover metals of some value and to reduce the environmental impact of the spoil.

Laboratory-scale studies evaluated the mineral processing techniques on lead-zinc mine spoil materials from five unreclaimed former metal mines. This evaluation, the first phase of a two-part study, set out to identify promising treatment options for detailed examination in the second phase. Researchers first characterized spoil material then examined techniques involving gravity separation, froth flotation, chemical leaching and biological extraction.

Characterization of the mine spoil revealed that concentrations of Pb and Zn in the whole spoil samples were up to 20% and 15% by mass, respectively, but Cu and Cd were in the range of parts per million. Lead was concentrated in the finer particle sizes of the spoil. Results also showed that a fine-grained, compact, clay-like spoil saturated with water created anaerobic conditions, which inhibited oxidation and allowed minerals to retain their sulfide forms. In contrast, a sandy spoil allowed extensive oxidation to occur and convert Pb and Zn minerals to their more easily leached sulfate forms.

In this study, differences in particle density and surface chemistry for the separation of spoil particles were evaluated using dense media (so called “sink and float”) and froth flotation tests. An MGS was further examined for density separation at pilot-scale. Laboratory-based density separation consistently reduced metal concentrations (<2 weight %) in the lighter spoil fractions, which represented over 90% of the total sample weight. The heavier concentrate contained up to 32% Pb and 5% Zn by weight. Although treated material was significantly cleaner than original spoil, these levels still greatly exceeded U.K. soil guidelines. The pilot-scale MGS treatment produced similar results on the fraction of spoil less than 0.5 mm. Results showed that the MGS can concentrate almost 70% of the metals into a mass of less than 10% of the original spoil. The residue has a combined metal assay of 2.5%.

For most of the tested spoils, froth flotation performed poorly but achieved reasonable performance where spoils remained un-oxidized. Additives showed little promise in terms of producing marketable concentrates or significantly more acceptable (*i.e.*, low metal) tailings. The effectiveness of this technique depended critically upon the mineralogy of the spoil. Un-weathered material, rich in sulfides, showed better segregation of contaminants into the concentrate.

Leaching metal contaminants from the spoil by a variety of chemical agents, such as sulfuric acid, sodium hydroxide, diethylenetriamine, and by using ferric bacteria inoculum, was evaluated on unprocessed spoil and treated fractions from the density and froth flotation tests. Effective chemical leaching depended on the degree of spoil weathering. Generally, sulfuric acid and diethylenetriamine, leached 2-33% of the Pb and 12-64% of the Zn. Sodium hydroxide leaching of weathered spoil mobilized 25-92% of the Pb and 3-23% of the Zn in unprocessed spoil.

To evaluate the extent to which metals remaining in reprocessed (by gravity separation or froth flotation) residues would be leached and hence be of environmental concern, the residues were subject to chemical and biological leaching. This leaching removed 2-5% of the remaining contaminants, indicating a resistance to leaching in residual material. Bacterial leaching proved to be ineffective for Pb but removed significant amounts of Zn from the spoil.

Project 33: In-Pulp Decontamination of Soils, Sludges, and Sediments

This project consisted of bench-scale and demonstration-scale development of a treatment technology by Davy International Environmental Division of the U.K. and Kommunekemi of Denmark. The process combines conventional *ex situ* soil washing techniques with an innovative chemical treatment stage. A major expected advantage is the ability of the approach to remove contaminants from fine sized soil fractions such as silt and clay. Two measures used to extract contaminants are:

- leaching using acidic or alkaline reagents followed by adsorption to activated carbon or ion exchange resin; and

- adsorption by activated carbon or cation exchange resins in direct contact with a soil slurry.

Contaminating substances then may be desorbed from the recovered carbon or ion exchange resin that is then recycled.

Test materials consisted of contaminated soils and sediments. Soils came from a reclaimed site contaminated with arsenic from a catalyst; a gasworks facility containing Zn and Pb; a wood preserving site contaminated with Cu, Cr, and As; and chlor-alkali and gas metering sites with Hg contamination. A sediment sample containing Zn, Pb, and Fe was collected from Hamilton Harbour in Ontario, Canada. Zn, Pb, Fe, and Mn levels in the sediment exceeded Ontario’s “severe effect” guidelines, while Cu, Cr, and Ni levels ranged between the “severe effect” and “limited effect” levels. This summary highlights work done on samples from the wood preserving site, the chlor-alkali site, and the harbor. Project reports did not contain information on the other samples.

Small pilot-scale leaching experiments examined inorganic and organic acids, alkalis, and chelating reagents under various conditions. The results showed that mild leaching was inadequate for obtaining target contaminant concentrations in the solid residue. The most effective leachant, sulfuric acid, removed 90-97% of the contaminants from the soil. Cu, Zn, and Cr were removed to below target levels, but As exceeded the target of 30 mg/kg.

Adsorption tests on leachate from soils from the wood preserving site were carried out with ion exchange resins, activated carbon, and magnetite to treat the leachates. Compared with the other adsorbents, the ion exchange resins removed the most Cu, Cr, and Zn from the leachate. Acid resins adsorbed from 75-100% of the Cu, Cr, and Zn but only 20-60% of the As.

A 10-kg sample of the soil from the wood preserving site was treated at bench-scale using the unit operations of physical separation and chemical leaching which had been identified from the experimental studies. The treated soil had a lower metal content than the feed material. Copper fell from 360 mg/kg to 22 mg/kg, Cr from 621 mg/kg to 74 mg/kg, Zn 414 mg/kg to 68 mg/kg, and As from 1,204 mg/kg to 112 mg/kg. Only As exceeded its preliminary treatment target of 30 mg/kg. Further work focusing on protocols that take As speciation into account showed that chelating agents leached up to 52% of As. Combining flotation, screening, and hydrocycloning achieved 60% removal in 80% of a soil but the residual still exceeded target levels. Multiple acid leaching reduced As from 650 mg/kg to 22 mg/kg, but at a relatively high cost.

Trials with the Hg-contaminated soil used oxidative compounds and complexing agents such as nitric acid, hydrochloric acid, and sodium hypochlorite. To improve extraction of mercury, the approach included size separation to remove fines and was operated at higher temperatures. Ion exchange resins developed for mercury adsorbed the metal slowly. As a result of difficulties with this approach, a thermal option was investigated. Preliminary tests revealed that by heating contaminated materials to around 800°C, treated soils achieved regulatory targets for mercury.

Work with Hamilton Harbour sediment showed that the Ontario guidelines for sediment could be met. Leaching tests were conducted with mineral and organic acids. Strong mineral acids dissolved contaminants as well as Ca and Fe in 90 minutes. Since these two metals, as well as organic contaminants would compete with the metal contaminants during adsorption, a two-stage leaching approach was tested as a way to eliminate this competition. This involved a mild acid to dissolve iron first, followed by a strong acid to attack the contaminants. The presence of organic contaminants had little impact on the removal of metals.

Tests with several adsorbents pointed to chelating resins as the likely candidates. These resins proved to be more selective than activated carbon or magnetite for the contaminant ions over the other metal ions. The high level of Fe in solution inhibited the adsorption of contaminants, and thus required pretreatment such as magnetic separation to remove iron particles from the sediment before leaching. Precipitation to remove metals from the leachate was somewhat ineffective because some metal remained in solution and required further processing.

The process generates a variety of residuals and emissions some of which require further treatment or disposal. Decontaminated solids may require final treatment such as pH adjustment and dewatering before being disposed. For most metal extractions, acid is used to remove metals from the resin, resulting in a concentrated solution of metals which may be treated by precipitation, reduction or electrowinning to recover metals, or may be disposed of at a secure disposal site or encapsulated. In the case of sediments, the leach stage may produce gas emissions if anaerobic activity produces sulfides. These emissions, noted during leach tests with sediments from Hamilton Harbour, may require gas scrubbing in a scaled-up commercial plant. Decanted water from excavated sediment may also have to be treated.

Treatment costs are expected to be high (no data or expected costs were provided) if the process demands aggressive leaching with oxidative and complexing agents as well as elevated temperatures for enhanced leaching.

Although principally applicable to metal contamination, the technology may be adapted (by using carbon as an additional adsorbent) to handle organic contaminants. Plans to develop the technology further include investigating surfactants, solvents and other agents to extract organic contaminants and to combine this with adsorption by activated carbon. The applicability of the technology would depend on its ability to achieve regulatory requirements.

5.2.4 Group 4: Physical-Chemical Treatment (No Soil Washing) (Projects 32, 44, and 47)

Project 32: CACITOX™ Soil Treatment Process

This innovative technology aims to chemically treat soils containing significant silt and clay fractions for which conventional soil washing techniques are not cost-effective. The technology potentially can treat contaminated soils and sediments while not depositing unacceptable by-products into the matrix or destroying the matrix itself.

The CACITOX™ process involves soil leaching, soil/leachate separation, and leachate treatment. The proprietary leaching process uses a three-component mixture consisting of low concentrations of carbonate, oxidants, and complexing agents such as carboxylic acids. This mixture, which is used at near-neutral pH and ambient temperature, reacts with contaminated materials and converts insoluble or absorbed contaminants into soluble complexes. The oxidant helps dissolve certain metals that occur in their less soluble forms. As a result of its high selectivity, the leaching reagent minimizes secondary waste.

A combination of precipitation and ion exchange removes dissolved inorganic contaminants from the leachate. This stage of treatment may include innovative approaches such as electro-deposition/polishing to recover valuable by-products or to minimize the volume of secondary waste. Precipitated contaminants may be conditioned to ensure they meet requirements for disposal. This conditioning may involve dewatering, containerization, or encapsulation. Chemical processes destroy organic contaminants in the extract.

Treated soils can be used again because the leaching process uses low concentrations of the mild chemicals. Hydrocyclones or mixer settlers separate the leached soil from the leachate. A filter press or belt filter then dewaters separated soil, that was washed to remove residual reagent.

When used with a range of aqueous leaching reagents, CACITOX™ initially experienced more difficulty decontaminating soils with high clay content than those containing sand. As a result, further work focused on fine-grained soils to satisfy one of the aims of the project to treat soils with significant clay and silt content.

Experiments with soils containing “high” levels of heavy metals showed that the leaching process achieved Dutch B and Canadian Residential Values for all metals except Cd and As. A report claimed that optimizing the formulation and process variables could enable the technology to achieve target values for these two metals. Added organic contaminants reduced initial leaching efficiencies by 1-2%. However, leaching removed 98% of these organics. Leaching with CACITOX™ achieved removal efficiencies comparable to leaching with mineral acids. However, the proprietary reagent dissolved less than 10% of the soil matrix, while the mineral acids removed 40%.

During trials to leach radionuclides from test soils, a single contact with the CACITOX™ reagent mixture removed 52-76% of the Pu, Am, Np, Sr, and Ra, but only 2% of the Cs. Limited data for removal of radionuclides from a contaminated site show how repeated contacts could improve removal.

In summary, the CACITOX™ technology can process materials containing high levels of fines like silt and clay and can selectively dissolve actinides and heavy metals from other wastes. Because the CACITOX™ process treats inorganic contaminants, it requires other technologies for treating mixed wastes. The final report mentioned that using low concentrations of mild chemicals resulted in low costs, but did not provide supporting data. The pilot-scale transportable plant has a capacity of 10 kg/hour, but can be easily scaled up to 100 kg/hr.

Project 44: Enhanced **In Situ** ***Removal of Coal Tar: Brodhead Creek Superfund Site***

During the operation of a former gasworks plant from 1888 to 1944, waste coal tars were disposed onsite in an open pit. Over time, the coal tars migrated into the subsurface, where they collected 6-9 m below ground surface in a natural depression formed at the geological boundary between coarse gravels and silty sands. A layer of coal tar (dense non-aqueous phase liquid—DNAPL) was shown to be polluting 0.12-ha of the underlying aquifer and a nearby river. A larger 3-acre (1.22-ha) area of residual contamination is also present.

Remediation efforts focused on recoverable coal tar in an area with an estimated 22,700 L of DNAPL because it was believed to represent the major source of groundwater pollutants; however, the dissolved groundwater contaminants were not addressed. A slurry cut-off wall was constructed to protect the river from further pollution. Excavation of the contaminated soil was not considered practical, so an innovative *in situ* treatment known as Contained Removal of Oily Wastes (CROW) was selected. CROW is a thermally enhanced *in situ* recovery process that uses hot water injected at the perimeter of the contaminated area to reduce the density and viscosity of tar to a level where it can be pumped to the surface for further treatment and disposal. The rate at which the heated water is injected into the ground is is used to control the displacement and temperature of the tar material so that it is forced towards the of extraction wells. Lateral containment is achieved by carefully controlling injection and extraction rates to isolate the affected area hydraulically. A layer of cooler groundwater above the area of active recovery prevented mobilized fluids from migrating vertically and condensed contaminants that were volatilized by the heated water below.

Preliminary treatability studies on coal tar samples were used to determine the optimum temperature and injection/extraction rates required for full-scale operation. These studies indicated that coal tar in soils could be reduced to a residual saturation of 60-70%.

Full-scale operation was based on a pattern of six injection wells surrounding two extraction wells in the center of the contaminated area. Well screens focused injection and extraction flows at the depth of contamination. A greater amount of water was extracted than injected to hydraulically isolate the contaminated area. The design flow for injection of heated water was 378 L/min and 435 L/min for recovery of the water and coal tar mixture. However, much lower injection rates were actually attained because iron precipitate that formed around the injection well screens significantly reduced operational performance. This problem was partially solved by installing agitators in the injection wells, but flow rates remained low (114-132 L/min). The system operated at 71°C instead of the expected 93°C because the water heater was designed for high flows and could not heat the water to the required temperatures at the lower flows. The reduced flow rate and lower operating temperature extended the treatment time to 10 months, approximately twice the expected treatment time. A higher injection temperature of 96°C was achieved in January 1996 with the installation of the new heater.

At the ground surface, the initial treatment step was to separate the coal tar from the water. The coal tar was incinerated, and the water was treated by removing the dissolved inorganics (primarily iron and manganese) through oxygenation and pH adjustment of the water. The precipitated inorganics were removed by gravity separation. (The inorganics required removal because they were found to inhibit the coal tar separation process and foul the system.) The treated water was reheated and reinjected into the subsurface. A lesser amount was injected than was extracted to maintain hydraulic isolation. The overdraw of water was treated in a fluidized bed reactor followed by granular activated carbon units and then discharged into Brodhead Creek.

The performance standard for the CROW process was to continue operating the system until the cumulative recovery of coal tar dropped to 0.5% or less per pore volume of water flushed through the contaminated zone. This was based on previous operational experiences at a similar site where achieving this specification meant that 98.5% recovery of recoverable tar had been attained. Planned groundwater sampling will assess the overall effectiveness of the treatment. During December 1995, a cumulative flow of 3.1 pore volumes resulted in recovery of 602 L of tar. Over a 10-month period of operation, 29 pore volumes of hot water were flushed through the formation, and a total of 5,400 L of coal tar was recovered as pure tar.

Groundwater contaminants and residual coal tar remain at the site. A "No-Further Action" record of decision was issued for groundwater and residual coal tar contamination because of technical impractibility considerations.

Project 47: **In Situ** *Electro-Osmosis (Lasagna™ Project)*

In the Lasagna™ *in situ* treatment process, electro-osmosis moves dissolved contaminants to treatment zones, where they are degraded or adsorbed. This process can be operated in a horizontal or vertical configuration. The vertical configuration consists of outer layers that act as either positively or negatively charged electrodes and promote electro-osmosis. Sheet piling, trenching, and slurry walls can be used to create vertical treatment zones, in between the outer electrodes. In the horizontal configuration, which is installed by hydraulic fracturing or related methods, treatment layers occur between the upper and lower layers that make up the electrodes. These electrodes may contain graphite or other granular, electrically conductive materials.

Site characteristics and contaminants determine the configuration to use. In general, the vertical configuration is more applicable to contamination occurring within about 15 m (50 ft) of the surface. The horizontal configuration works best for deeper contamination.

The NATO/CCMS case study was limited to the field demonstration of electro-osmosis, using the vertical configuration to transport and adsorb trichloroethene (TCE) at the U.S. Department of Energy’s Paducah Gaseous Diffusion Plant in Kentucky. The case study was carried out in three phases. Phase I, conducted January-May 1995, evaluated the overall effectiveness of coupling electrokinetics and carbon adsorption treatment zones. In 1996, the Phase IIa commercial-scale demonstration examined iron filings in the treatment zone to dehalogenate TCE. This work was conducted to depths of about 14 m (45 ft) and with a wider spacing between the treatment zones. The full-scale Phase II cleanup will take place if the Phase IIa tests successfully reduce TCE levels in soil to 5.6 mg/kg.

The field study lasted for 120 days. A key objective was to successfully demonstrate coupling electro-osmosis to flush TCE from the clay soil (hydraulic conductivity $<10^{-9}$ m/sec) and adsorption to remove the contaminant from the pore water. The test site was about 4.6 m x 3 m (15 ft x 10 ft) on the surface and 4.6 m (15 ft) deep. A control area was built next to the test area and isolated from it hydraulically. The vertical configuration tested at the site consisted of steel panel electrodes and treatment zones made of wickdrains containing granular activated carbon.

A direct current of around 40 volt/m applied to the electrodes caused groundwater to flow from the anode to the cathode at about 13 mm/day. The induced pH gradient caused problems such as soil drying and cracking, and metal and mineral deposits at the cathode. Pumping water from the cathode to the anode reduced these problems. Operating parameters during this period were:

• Power requirements:	105 volts and 40 amperes
• Electro-osmotic flow rate:	4-5 L/hr
• Average soil temperature:	25-30°C

Soil samples collected throughout the demonstration site before and after the test showed that the process removed 98-99% of the TCE from the tight clay. TCE levels in the soil were reduced from 100-500 mg/kg to an average of 1 mg/kg. Sampling and analyzing the carbon revealed how much dissolved TCE was adsorbed in the treatment zones and provided mass balance data. These carbon samples accounted for around 50% of the original TCE. The remaining TCE reduction may be attributed to passive diffusion (5%), evaporation (5%), *in situ* degradation of TCE, non-uniform distribution of the contaminant in the soil, or incomplete extraction of the compound from the activated carbon before analysis.

The results suggest the process is effective for removing residual DNAPL as well. At most soil sampling locations with TCE concentrations of more than 225 mg/kg—indicative of residual DNAPL in soil pores—the process reduced these levels to less than 1 mg/kg.

A more extensive field investigation incorporated material such as iron filings in reactive treatment zones to destroy TCE *in situ*. The first part (Phase IIa) of this two-stage investigation, to be conducted on 20 times more soil than was treated in the preliminary field investigation, will try to resolve scale-up questions, verify cost estimates for treatment, and evaluate how the zero-valent iron performs. Preliminary results of the Phase IIa demonstration at the site in Kentucky show that treatment zones with iron filings can dechlorinate TCE, producing relatively innocuous end products such as chloride ion, ethane, and ethene. Other potential intermediate products like dichloroethene and vinyl chloride are associated with the surface of the filings.

Residuals and emissions include off-gases resulting from evaporation, and the treatment layers. At the test site in Kentucky, TCE losses by evaporation accounted for 5% of the mass balance. These off-gases did not require treatment. If treatment zones are determined to be a hazardous waste, removing and disposing them may be an issue.

An engineering evaluation and cost analysis for the vertically configured process estimates a treatment cost of U.S.\$52-118/m^3 of clay soil containing TCE at a depth of 12-15 m and over an area of 0.4-0.8 ha. With optimized electrode spacing, improved ability to install treatment zones and electrodes at closer spacing, and mass-produced prefabricated materials resulting from wider use of the technology, costs are expected to fall to U.S.\$26-52/m^3. These costs exclude those for analyses, waste disposal, *etc.*

The Lasagna™ process reportedly offers promise for treating water-soluble organic and inorganic contaminants, and mixed wastes in low-permeability soils as well as in groundwater. For highly non-polar contaminants, surfactants introduced into groundwater or incorporated into treatment zones will solubilize the organics. The process has been shown to be effective in treating residual DNAPL as well. Larger scale demonstrations need to be conducted to confirm the effectiveness of using zero-valent iron to degrade contaminants. The horizontal configuration using biological treatment zones also needs to be evaluated.

5.2.5 Group 5: Photo-Oxidation Treatment (Projects 14, 38, and 40)

Project 14: Ozone Treatment of Contaminated Groundwater

This project examined biological and advanced oxidation treatment of groundwater contaminated by leachate from an abandoned quarry located at Vaucelles, France. Between 1963 and 1972, this quarry served as a site for disposal of various chemical wastes.

After an initial site investigation to confirm the source and extent of contamination, the project focused on examining optional treatments for contaminated groundwater to achieve acceptable drinking water limits. The water contained a wide variety of organic compounds such as chlorinated and non-chlorinated solvents at concentrations of 0.8-360 mg/L.

The selected approach combined biological pre-treatment and a UV/ozone oxidation system. The biological process is seen as a way to degrade chlorinated contaminants into a form more amenable for photo-oxidation. A membrane filter that separates activated sludge from purified water was claimed to be better than the conventional process by producing five times less sludge. In the second treatment step, photo-oxidation degrades compounds remaining in the biologically purified water. Tested treatment combinations were:

- ozone, and ozone/UV without biological treatment; and
- ozone, ozone/UV, and ozone/H_2O_2 after biological treatment.

Pilot testing showed that the combined biological/photo-oxidation treatment was more effective than photo-oxidation alone. The combination reduced chemical oxygen demand (COD) by 90-95%, TOC by 80%, and volatile organic compounds (VOCs) by 100%. The report did not mention investigations to identify by-products.

In terms of costs, achieving the goal that treated water should achieve drinking water guidelines for VOCs was estimated to cost FF15 million (U.S.$2.5 million) in capital cost and FF23.7 million (U.S.$4 million) annually. Alternatively, discharge to a surface water body would cost FF10 million (U.S.$1.7 million) at first, and only FF1.7 million (U.S.$280,000) annually.

Project 38: Demonstration of Peroxidation Systems, Inc., Perox-Pure™ Advanced Oxidation Technology

The Perox-Pure™ UV/oxidation technology combines UV radiation and hydrogen peroxide to treat groundwater contaminated with a variety of organic compounds. Other components such as acid and base feed systems may be added to the treatment train to ensure successful treatment of the contaminants. Adding acid to the water feed reduces the pH (<5.5) to minimize interferences by bicarbonates and carbonates. Following treatment, adding a base increases the pH to normal levels (6.5-7.5) so that discharged water meets designated criteria.

The Perox-Pure™ UV/Oxidation treatment technology was evaluated under the USEPA Superfund Innovative Technology Evaluation (SITE) program at a site at the Lawrence Livermore National Laboratory in California. Evaluation of the technology’s performance at three other sites was used to support findings for the SITE demonstration.

At the Lawrence Livermore National Laboratory site, shallow groundwater was contaminated with TCE and tetrachloroethene (PCE) at concentrations around 1,000 µg/L and 100 µg/L, respectively. The SITE technology demonstration intended to:

- determine the ability of the technology to remove VOCs from groundwater under different operating conditions;
- find out if treated water achieved applicable disposal requirements at the 95% confidence level; and
- estimate treatment costs.

A secondary objective was to identify by-products formed during treatment.

The Perox-Pure™ system effectively achieved the California drinking water action levels and U.S. federal drinking water maximum contaminant levels for the five compounds studied. Quartz tube wipers kept the quartz tubes clean and prevented scaling, which is detrimental to contaminant removal efficiencies. Bioassay tests results demonstrated that the effluent was acutely toxic to freshwater test organisms. This toxicity may have been caused by the residual hydrogen peroxide rather than by treatment by-products.

The following three case studies summarize work and findings to demonstrate the technology for:

- wastewater containing acetone and isopropanol (IPA);
- groundwater contaminated with TCE; and
- groundwater contaminated with pentachlorophenol (PCP).

The first study, at the Kennedy Space Center in Florida, tested the photo-oxidation system as a replacement for the existing carbon adsorption treatment for wastewater. The replaced system could not achieve the required discharge level of 0.5 mg/L. In contrast, effluent from the new oxidation system met all of the discharge criteria, including the demineralization discharge standards, in less than the specified 24-hour maximum treatment time. The system was efficient enough to allow treatment of the wastewater in a flow-through mode rather than a batch mode at a flow rate of 18.9 L/min (5 U.S. gal/min), a hydrogen peroxide dosage of 100 mg/L, and 10 kilowatts of power for a period of 20 hours per day.

For the second study, the Perox-Pure™ technology was used to treat well water containing 50-400 mg/L of TCE. Because the well was located in the middle of a large residential area in Arizona, the treatment was chosen because of its low-visibility and quiet operation. When treatment was conducted at a flow rate of 510 L/min (135 U.S. gal/min) and 15 kW of power, TCE was consistently treated to a level below the analytical detection limit of 0.5 µg/L.

A full-scale Perox-Pure™ system treated groundwater contaminated with PCP at levels up to 15 mg/L for the third study conducted on the property of a chemical manufacturing company in Washington in 1988. Continued operation confirmed that the Perox-Pure™ system could destroy the PCP to below the target level of 0.1 mg/L. To obtain this result, the system operated at a flow rate of approximately 265 L/min (70 gal/min), a hydrogen peroxide concentration of 150 mg/L, and a power requirement of 180 kW. A pretreatment system oxidized and removed high levels of iron. To reduce the scaling tendency, acid was added to decrease the pH of water to about 5.0. The photo-oxidation system featured automatic devices to keep the reactors clear.

Treatment costs for three of the four tests were U.S.\$0.95-1.3/m^3 (U.S.\$3.60-5.00 per 1,000 U.S. gallons). Treating well water in the second case study cost only U.S.\$0.07/m^3 (U.S.\$0.28 per 1,000 U.S. gallons). These costs exclude those for capital.

*Project 40: An Evaluation of the Feasibility of Photocatalytic Oxidation and Phase Transfer Catalysis for Destruction of Contaminants from Water (***In Situ** *Treatment of Chlorinated Solvents)*

Photocatalysis is an emerging treatment technology that uses an advanced oxidation process based on generating hydroxyl radicals using UV light in the presence of a semi-conductor catalyst, such as platinum-coated titanium oxide. The Hand D process uses a fixed-bed catalyst with the semi-conductor fixed to a silica gel support. Pretreatment of groundwater by removing suspended matter and inorganic ions is conducted by a series of filters and ion-exchange columns. Dissolved oxygen levels are increased, as necessary, to supply oxidants for the destructive oxidation process. The UV light is provided by natural sunlight.

The project researched development of highly photoactive catalysts and a fixed-bed photocatalytic process to destroy toxics in air and water. It also researched development of a treatment process using adsorption to remove contaminants and advanced oxidation processes (AOPs) to regenerate spent adsorbents. The developed technologies were field tested at Tyndall Air Force Base (AFB), K.I. Sawyer AFB, and the Wausau Water Treatment Plant.

Some of the photocatalysts used in the laboratory studies were modified on their surfaces with noble metals, or changed by doping with transition metals to extend the photocatalyst’s response to visible light. Artificial light and UV sources and solar radiation were used to evaluate the photoactivities of these catalysts for destroying model compounds. Results showed that platinum-coated Aldrich titanium oxide (Pt-Aldrich-TiO_2)—a surface-modified catalyst—performed best for destroying hydrophobic compounds. The laboratory-developed, platinum-coated Michigan Technology University TiO_2 catalyst performed best for hydrophilic compounds.

The supports tested for fixed-bed photocatalysts consisted of random packing and structured materials. These supports were chosen for their adsorption capacity, UV transmission, and mass transfer properties. Silica-based materials were included to test how they performed at destroying organic compounds, and some of them were surface-modified to increase their adsorption capacity. Investigations excluded electron-rich materials that could scavenge reactive radicals and diminish the efficiency of photocatalysis. Researchers developed a unique procedure involving heating and annealing to prepare supported catalysts for fixed-bed reactors. During solar experiments, the fixed-bed processes were optimized with respect to the type of catalyst and dosage, support type and size, and preparation methods. Destruction of a model compound was tested under various UV irradiance, influent concentration, pH, and hydraulic loading. Tanning lamps tested on the same fixed-bed process tested the destruction of several other compounds in air and water. Two reactor designs consisted of a catalyst added as a slurry and passed through a lighted reactor, and a catalyst attached to a support in a lighted fixed-bed reactor.

Tests with the fixed-bed photocatalysts revealed that Pt-Aldrich-TiO_2 supported on silica gel completely mineralized TCE in water (8 mg/L) in one contact time of 1.3 minutes. This destruction rate was 16 times better than observed for an optimized slurry of a commercially-available photocatalyst (Degussa P25).

Increasing the adsorption capacity of a silica-based support improved the overall destruction kinetics. Silica gel modified to increase surface hydrophobicity and the adsorption capacity for non-polar organic water pollutants increased the adsorption capacity for trichloroethene (TCE) in water by more than a factor of five. When used as a support for Pt-TiO_2, the modified silica gel showed faster overall degradation kinetics for TCE than did the unmodified silica gel.

For experiments with contaminants in the gas-phase, results showed faster destruction kinetics than in the aqueous phase. This suggests the option to strip volatile compounds followed by gas-phase destruction by photocatalysis. For trichloroethane (TCA), a relative humidity of 25% yielded the best destruction rate. On the other hand, toluene destruction increased with increasing vapor content. The fixed-bed approach provided high light efficiency. The reported ratio of organic molecules destroyed to UV photons required was 40%—much higher than the 5% value commonly reported. Phosgene and carbon monoxide, two major toxic by-products in air-phase photocatalysis, were not found above regulated levels.

Developing the combined processes of adsorption followed by regeneration consisted of using a fixed-bed system adsorber to remove and accumulate organic compounds, and regenerate the spent adsorbent using homogeneous AOP, photocatalysis, or a combination of steam and photocatalysis. For homogeneous AOP, hydrogen peroxide/ozone and UV light/hydrogen peroxide were used for destructive adsorbent regeneration. Both of these options consumed three to six times more oxidants in the regeneration process than would be needed to destroy the contaminants in water directly by conventional AOP. Regeneration appeared to be limited by adsorbate desorption from the interior to the exterior adsorbent surface. Neither option is feasible because the desorption rate is too slow, and therefore too much oxidant is required to regenerate the adsorbents.

In testing photocatalysis for destruction of adsorbed contaminants and regeneration of adsorbents simultaneously, the catalysts were impregnated onto the adsorbent before being used to adsorb organics. The first test consisted of using UV illumination to test photocatalysis alone for regenerating the spent adsorbents and destroying the contaminants. Results showed that desorption of adsorbates from the interior to the exterior of an adsorbent limited the regeneration process. Thus, temperature played a leading role in photocatalytic regeneration, and increasing temperature enhanced regeneration rate much more effectively than increasing light intensity. Using heat to increase the desorption rate and match the photocatalytic oxidation rate is one way to maximize the photolytic regeneration efficiency.

Saturated steam was used to overcome this problem of slow desorption rates. Heating promoted the kinetics of photocatalysis and AOP processes by desorbing organic contaminants on the interior of the adsorbents and moving them to the exterior for oxidation. Thus, steam followed by photocatalysis was found to be an effective way to regenerate spent adsorbents and to clean up the regeneration fluid (off-steam or steam condensate).

At Tyndall AFB, a solar photocatalytic process was used to remediate fuel-contaminated groundwater containing BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) at greater than 2 mg/L. Two options were tested: (1) a solar photocatalytic fixed-bed process using Pt-TiO_2 supported on silica; and (2) fixed-bed process with Pt-TiO_2 impregnated adsorbents alone or combined with Pt-TiO_2 supported on silica gel. During option 1, ionic species fouled the catalysts and inhibited destruction, so the water was pretreated to remove suspended particulates and ionic species and to increase dissolved oxygen. Following pretreatment, catalyst photo-activity continued undiminished after 25 days of operation. The BTEX compounds were destroyed with 6.5 minutes of empty bed contact time on rainy days. Test results with various flow rates, reactor diameters, influent concentrations, solar irradiances and weather conditions confirmed the potential application of the process. Treatment cost was estimated at U.S.\$5.52/1,000 U.S. gallons (U.S.\$1.46/m^3).

During option 2, two different reactor design configurations were tested. The first design was a continuous flow configuration with three fixed-bed reactors in series. The first and third reactors were packed with platinum-coated TiO_2 supported on silica gel supports. The second reactor was packed with a photocatalyst-impregnated adsorbent. In daylight, the incoming organic compounds were destroyed in the first reactor. At night, the organics were adsorbed onto photocatalyst-impregnated adsorbent in the second reactor; the adsorbed organics were either mineralized or partially mineralized in the second reactor during daylight. The remaining organics or destruction by-products were destroyed in the third reactor. Because organic compounds can be adsorbed during periods of insufficient sunlight, the process can treat water continuously. Like option 1, option 2 was also affected by catalyst fouling. After four days of operation, the process was apparently unable to destroy any more BTEX compounds. An ion exchange unit was added to the system and satisfactory BTEX destruction was resumed; however, the third reactor still did not perform well, presumably due to fouling species desorbed from the second reactor.

In the second design, a reactor packed with photocatalyst-impregnated adsorbents was used to remove the organics during darkness. During daylight, the adsorbent was taken off-line and regenerated by passing heated water through the reactor. The hot water was then passed through a fixed-bed reactor packed with platinum-coated TiO_2 supported on silica gel supports to destroy any residual desorbed organics or by-products. The strategy behind this design was to have an 18-hour adsorption period followed by a 6-hour regeneration period during which the solar irradiance is strong enough to destroy most contaminants.

The spent adsorbents were regenerated in the presence of sunlight while passing hot water (90°C) counter-current to the flow direction during the adsorption process. The desorbed organics from the regeneration process were destroyed in the subsequent fixed-bed photoreactor. The process was examined for 10 adsorption and regeneration cycles. The efficiency (ratio of organics removed and destroyed to organics adsorbed) of the process to regenerate the adsorbents was examined for each cycle. Overall, 21% of the total influent BTEX was destroyed, and 98% of the BTEX was removed from the waste stream. The detention times required for 99.9% destruction of TCE (5 mg/L), TCA (5 mg/L), and toluene (115 mg/L) were 2.15 seconds, 11.2 seconds, and 40 seconds, respectively. While the process appears to be effective for 10 cycles, more cycles are required to determine whether steady-state is achieved.

At K.I. Sawyer AFB, the unit used a fixed-bed photocatalyst and a solar panel made up of 80 tubular reactors to treat chlorinated compounds in groundwater. The design included a water pretreatment unit, which included a turbidity filter, a bubble-less oxygen contactor, and ion-exchange columns. The reactor was a modified solar thermal reactor panel with 80 plastic tubes mounted in parallel. The capacity for each reactor panel was designed as 0.25 U.S. gallons per minute. On a sunny afternoon, the panel destroyed 95% TCE, which was present in groundwater at 100 µg/L, within a two-minute contact time.

At the Wausau Water Treatment Plant, fixed-bed adsorption removed and accumulated organic compounds. The spent adsorbents were regenerated off-line with steam followed by photocatalysis. The groundwater contained chlorinated compounds and BTEX. Direct photocatalytic oxidation was not effective for regenerating spent adsorbent loaded with contaminated groundwater because nuisance substances in the water fouled the catalyst. Tests combining steam regeneration followed by photocatalysis of steam condensate showed that carbon adsorbent was not effectively regenerated and lost a significant amount of capacity. Background organic matter in the water may have caused this loss of efficiency. Based on the results of chloride yield with all the tested adsorbents, steam regeneration did not appear to destroy significant amounts of the sorbed chlorinated compounds.

5.3 BACKGROUND OF CASE STUDIES AS A GROUP

Table 5.1 presents key information on the projects. In terms of media treated, Projects in Groups 1-4 dealt with contaminated solids, while Group 5 projects addresses groundwater contamination. Project 44, which is in Group 4, addressed DNAPL contamination in a gravel layer, but not the dissolved groundwater contaminants. In general, the contaminated solids consisted of soils and sediments containing a high content of fines. The fines made up 12.5-63% of the parent material. Metalliferous spoil examined for Project 31 also had a high proportion of fines.

Organic and inorganic compounds were present in some of the contaminated solid media. Typical concentrations of organic contaminants were 200–5,000 mg/kg petroleum hydrocarbons, 30–2,000 mg/kg PAHs, and around 120–1,000 mg/kg PCBs. One site contained a concentration of 100–500 ppm TCE, while another reported chlorophenols at 200 µg/L. Heavy metal contamination attributed to individual species included Pb (up to 12%), Zn (up to 5%), Cu (360 mg/kg), Cr (621 mg/kg), Hg (300–5,000 mg/kg), and As (1,204 mg/kg). At one site, total metals were detected at 32-650 mg/kg, while cyanides were detected at 2,000–3,000 mg/kg.

Treatment technologies generally consisted of soil washing and groups of other treatments that included biological or physical-chemical treatment. Soil washing usually involved screening, scrubbing and particle size separation. Specialized techniques such as flotation and density and gravity separation were sometimes used to obtain better separation of clean fractions and contaminated concentrates. Other groups of treatments that did not include soil washing relied upon physical-chemical or photo-oxidation technologies.

5.4 PERFORMANCE RESULTS

5.4.1 Analytical and Assessment Procedures

Common analytical and assessment approaches were adopted for all the projects regardless of the contaminants or media to be treated, the technology being used, or the targeted criteria.

For projects with a soil washing component, the contaminated soil or sediment was first characterized with respect to particle size distribution and the concentration of organic and inorganic contaminants in the various particle fractions. Soil washing products were also checked for distributions of mass and contaminants.

For all projects, the effectiveness of the processes was determined by comparing the levels of contaminants in treated and untreated materials. All streams were reportedly sampled to measure flows in the slurry, solids, and water. These data were sometimes used to provide a mass balance. Contaminant concentrates and products low in contamination were analyzed to determine the degree of contaminant reduction.

Agency-approved procedures were used to determine characteristics such as pH, moisture content, and organic and inorganic constituents. For example, analytical approaches included USEPA procedures for digesting samples, atomic absorption spectrophotometry (AAS) for metal content of aqueous samples, gas chromatography (GC) for mineral oil, and x-ray fluorescence (XRF) to determine the mineralogy of the soil and sediment. Specialized methods (*e.g.*, DEXSIL L2000 PCB/chloride analyzer) were sometimes required.

Table 5.1: Classification of the 14 Case Studies by Technology Used

Project Number	Media Treated	Contaminants Treated	Contaminant Concentrations	Technology Used	Treatment Process
Group 1: Soil Washing Only					
30	Soil (mainly clayey)	Heavy metals, inorganic cyanides, PAHs, petroleum hydrocarbons	Heavy metals (32-650 mg/kg); PAHs (184 mg/kg); petroleum hydrocarbons (200 mg/kg)	Soil washing	Particle size separation
Group 2: Soil Washing and Biological Treatment					
24	Soil, sediment	PAHs, heavy aliphatic hydrocarbons (oils), chlorophenols	400-5,000 mg/kg mineral oil; 30 mg/kg PAHs; 200 µg/L chlorophenol	Soil washing, bioslurry reactor, photo-oxidation	Particle size separation, biodegradation
26	Soil (sandy and clayey)	PAHs (3- and 4-ring) from creosote	180-3,500 mg/kg PAHs	Soil washing, bioslurry	Flotation, biodegradation
36	Soils with high fines content	Diesel, PAHs, TPH, complexed cyanides	2,000-4,000 mg/kg; TPH; 200-300 mg/kg PAHs; 2,000-3,000 mg/kg cyanides	Soil washing, bioslurry treatment	physical separation, bioremediation
Group 3: Soil Washing and Physical-Chemical Treatment					
10	Soil, sediment	Heavy metals (Pb, Zn, *etc.*), PAHs	11,800 µg/g Pb; 7,400 µg/g Zn; 12.15 µg/g pyrene	Soil washing, hydrometallurgy	Particle size separation, metal recovery, chemical destruction of organics
17	Soil, sediment	PAHs, PCBs, petroleum hydrocarbons, metals	250-2,000 ppm PAHs; 200-500 ppm PCBs	Soil washing, solvent extraction	Particle size separation, extraction (for organics), stabilization
19	Soil, debris	Solvents, chemical waste, Hg	300-5,000 mg/kg Hg	Soil washing, vacuum distillation	Particle size separation, distillation, condensation
27	Soil, other solids	PCBs	120-1,000 mg/kg PCBs	Soil washing, chemical dehalogenation	Particle size separation, dehalogenation
31	Metalliferous spoil	Pb, Zn, Cu, Cd	up to 12% Pb; up to 5% Zn; Cu and Cd in ppm range	Gravity separation, flotation, chemical leaching, biological extraction	Particle size separation, leaching and extraction
33	Soil with high fines, sediment	Heavy metals (Cu, Cr, Zn, As), Hg	360 mg/kg Cu; 621 mg/kg Cr; 414 mg/kg Zn; 1,204 mg/kg As	Combined soil washing and chemical treatment	Leaching and adsorption

Project Number	Media Treated	Contaminants Treated	Contaminant Concentrations	Technology Used	Treatment Process
Group 4: Physical-Chemical Treatment					
32	Soil with high clay and silt content	Heavy metals, radionuclides, organics		Leaching	Oxidation, complexing, precipitation, ion exchange
44	Gravelly soil and ground-water	Coal tar DNAPL	DNAPL over 0.12 ha	Thermally enhanced recovery of coal tar	Coal tar: *ex situ* incineration. Water: *ex situ* precipitation, fluidized bed reactor, and filtration
47	Soil (clay)	TCE	100-500 ppm TCE	Electro-osmosis, *in situ* treatment	Electro-osmosis, adsorption
Group 5: Photo-Oxidation Treatment					
14	Groundwater	Chlorinated solvents, esters, phenols, BTEX, *etc.*	0.8-360 mg/L	Combined biological and photo-oxidation	Activated sludge, ozone, UV/ozone, ozone/H_2O_2
38	Groundwater, wastewater	TCE, PCE, acetone, IPA, PCP	1,000 µg/L TCE; 100 µg/L PCE; 15 mg/L PCP	Advanced oxidation and chemical oxidation	UV radiation and O_3/H_2O_2 or H_2O_2
40	Groundwater	BTEX, TCE, other chlorinated solvents	100 µg/L TCE, others not given	Adsorption and advanced oxidation	Highly photo-active catalysts and fixed-bed photocatalysis

Treatability studies were often conducted on various contaminants and matrices. During these studies, measurements of the initial and final concentrations of the contaminants provided information to assess the probable performance of planned full-scale operations.

Full-scale treatment plants were monitored to ensure they met operational requirements. In some cases, concentrations of contaminants in emissions and discharges were measured and compared to specified target levels. For technology evaluations conducted under the SITE program, routine operation of a treatment plant followed SITE protocols.

Finally, treatments were assessed in terms of their ability to achieve regulatory targets and criteria or the hazards posed by treated materials. Microtox or a suite of ecological tests were sometimes used to assess hazards associated with contaminants, residual process additives, and by-products in treated materials.

5.4.1.1 Group 1: Typical Soil Washing (Project 30)

Comparing the levels of contaminants in treated and untreated soil showed the effectiveness of the process. All streams were sampled to measure flows in the slurry, solids, and water, and data were compiled to provide a mass balance. Contaminant concentrates and products low in contamination were analyzed to determine the degree of contaminant reduction.

Batch processes (for jigging coarse material and the MGS for separating sand and silt) were incorporated into the overall materials balance to determine how the entire circuit performed.

5.4.1.2 Group 2: Soil Washing and Biological Treatment (Projects 24, 26, and 36)

Soil Washing

Test materials were first characterized according to the approaches summarized above. Preliminary experiments first determined the percentages of sand, fines, and coarse material in soil and sediment test samples. Soil washing was evaluated with bench-scale and small-scale commercial equipment and a pilot plant. Following soil washing, test material and the resulting wash fractions were analyzed to determine initial and final concentrations, respectively, of contaminants. This information was used to determine if contaminants in these fractions were significantly reduced so that the fractions could be reused or discharged, or required further treatment.

Biological Treatment

To assess the biological phase of the treatment, researchers measured initial concentrations of contaminants in the soil wash concentrates and compared them with final concentrations of contaminants after a known treatment period. The final concentrations of contaminants in the recombined treated fractions (from soil washing and biological treatment) were also measured.

To assess the impact of biological activity, experiments focused on measuring contaminant degradation over time, comparing the carbon dioxide concentration in the headspace to the concentration in the atmosphere, and monitoring biological activity expressed as the respiration rate (mg O_2/g-hr).

Microtox was used in Project 26 to measure the acute toxicity of water-extractable components of the soils. Test results assessed hazards associated with the soils that could not be quantified by chemical analyses, and also the formation of possible toxic intermediates from the biological process.

5.4.1.3 Group 3: Soil Washing and Physical-Chemical Treatment (Projects 10, 17, 19, 27, and 31)

Characterization

Where mentioned in project reports, characterization of contaminated material involved determining particle size distribution and analyzing sub-samples of the separated fractions for organics and inorganics. Preparing materials consisted of screening soil samples at various sizes (*e.g.*, 20 mm, 6 mm, and 2 mm and with a standard set of screens) sometimes down to 45 µm. Yields at each screen size were calculated as dry weights and used to prepare particle size distribution curves.

Each major fraction was digested using standard USEPA procedures and analyzed for contaminants and other soluble species. For the content of inorganics, digested samples were analyzed by methods such as AAS. In the project on metalliferous spoil (Project 31), the mineralogy of the separated fractions was examined by XRF. For XRF, samples were subjected to a 0-100° scan against standard results for lead sulfide, lead sulfate, and lead carbonate. Analytical procedures for Project 33 consisted of USEPA Method 3010 for acid digestion of aqueous samples and extracts for total metals for analysis by FLAA or ICP spectroscopy, and Method 3050 for acid digestion of sediments, sludges, and soils. The investigators modified recommended procedures by using hydrochloric and nitric acids in the USEPA protocols, since the use of hydrofluoric acid in U.K. laboratories is restricted.

Soil Washing

Soil washing was conducted at bench-, pilot-, and full-scale. To assess this technology, feed material as well as contaminant concentrates and various separated fractions were weighed and analyzed for contaminants such as oil and grease, and metals. Samples were sometimes analyzed in duplicate or triplicate.

Physical-Chemical Treatment

In general, performance was assessed by checking mass and contaminant distributions in feed and recovered products. This approach was taken for investigations from bench-scale treatability to full-scale application. Analyses were usually conducted in a laboratory, but for Project 27, PCB analyses were done in the field with a DEXSIL L2000 PCB/chloride analyzer.

At full-scale, plants were sometimes monitored to ensure that they met operational requirements. For a technology evaluation conducted under the USEPA SITE program, routine operation of the plant work followed SITE protocols. As an example, instruments at the field site for Project 27 monitored air for particle-bound and free PCBs.

Because different technologies were used to treat soil wash fractions, different assessment procedures were applied during subsequent work with these wash fractions. In froth flotation tests (Project 31), for example, the technology was initially assessed in a 2.5-L Denver flotation cell under conventional conditions practiced widely in the base metal industry to recover sulfide minerals. Similarly, a preliminary leach program with several types of soils (Project 33) tested various inorganic and organic acids, as well as alkaline and chelating reagents under various conditions. Samples of the soil wash mixture, which were withdrawn and analyzed periodically, revealed concentrations of metals in both the solid and liquid fractions. Adsorption tests with the leachates involved first screening a variety of adsorbents then obtaining adsorption isotherms for candidate adsorbents.

Only one report documented quality assurance and quality control (QA/QC) procedures. For Project 33, where work was conducted on Hamilton Harbour sediment, Davy International Environmental Division and the Wastewater Technology Center (WTC) in Burlington, Ontario, agreed on a program of laboratory work and a QA program. As agreed with the WTC, a full USEPA quality assurance project plan was inappropriate for the laboratory work. However, to obtain quality data and have confidence in the pilot plant design, control actions included performing analyses in duplicate, testing blanks and spiked samples (approximately 10% of samples over the whole program), performing elemental mass balances for each test, and completing an independent audit.

Overall Assessment

This overall assessment concerns criteria/targets used to assess the performance of the technologies in this group.

In terms of targets, mercury emissions from vacuum distillation used for Project 19 were measured, and concentrations were compared to a specified level of 50 µg/dscm. Mercury was measured in the feed and treated stream to evaluate the performance of the technology and to determine if the residual had achieved the target of 50 mg/kg. Mercury in cleaned water for discharge to a sewer had to achieve a target level of 10 µg/L. For Project 27, the Norwegian Pollution Control Authority proposed the test methods and acceptance criteria for PCB reduction and eco-toxicological tests. A 70% guideline was set for volume reduction. This agency also recommended a suite of ecological tests (biodegradation, acute toxicity, and bioaccumulation) to evaluate risk associated with the clean soil and dehalogenated sludge that would remain onsite. These tests were conducted on leachate generated from samples treated according to the TCLP. The potential risks included residual PCBs as well as residual process additives and by-products of the chemical dehalogenation process. To assess performance, criteria for PCBs were less than 10 mg/kg for soils; less than 10 µg/L for water to be discharged; and less than 100 µg/100 cm^2 for non-porous scrap for landfilling.

Other regulatory agencies also established criteria or targets to assess performance. This applied to Project 31, which investigated reprocessing techniques such as gravity separation, froth flotation, chemical leaching, and biological extraction for metalliferous mine spoil. To determine the effectiveness of the treatments on various types of spoil, residual levels of metals in treated spoil were compared with U.K. soil guidelines for corresponding metals. To determine the extent to which metals in original spoil and reprocessed residues could be leached and hence be of environmental concern, both materials were subjected to chemical and biological leaching. The procedure for chemical leaching tests was a modified version of the shake-flask test described in the *Acid Rock Drainage Prediction Manual* published by the Canadian Center for Mineral and Energy Research (CANMET). Laboratory microcosms were set up to investigate how oxidative microbial activity affected metal leachability. These studies simulated natural biological processes that occur when the residues are exposed to air and water, and quantified losses of metals from such a weathered deposit.

Finally, for Project 33, the technology on in-pulp decontamination of soils, sludges and sediments was assessed in terms of its ability to achieve low absolute regulatory levels (*e.g.*, Danish, U.K., and Dutch) and leachability criteria recommended by the U.S.

5.4.1.4 Group 4: Physical-Chemical Treatment (No Soil Washing) (Projects 32, 44, and 47)

Characterization

For Projects 32 and 47, characterization of test material comprised determination of particle size distribution, mass distribution, and distribution of heavy metals (Project 32 only) across the size fractions. Project 44 involved initial laboratory studies on the coal tar and soil to obtain data for system design. The specific gravity of the coal tar was determined, and the optimum temperature for the injected water was determined to be 68°C. It was estimated that 60% of the coal tar in the soil could be removed with 98% of the removable tar being recovered after 19 pore volumes were flushed through the surface. Piezometers were installed to define the areal extent of the coal tar.

Treatment Assessment

For Project 32 (CACITOX™ treatment), differences in contaminant removal effectiveness for varying levels of heavy metal contaminants were determined using a range of tests, including tests on soils spiked at “high” (1,000-22,500 mg/kg) and “low” (10-450 mg/kg) concentrations of these metals. To assess the decontamination efficiency of the treatment for radionuclides, researchers spiked USEPA simulated soil matrices with individual radioisotopes of Pu, Am, Np, Sr, Cs, and Ra.

In Project 44, the recovery of coal tar was measured and compared to performance specifications. Performance specifications required treatment to continue until results showed that there was less than 0.5% additional recovery of coal tar per pore volume of water flushed through the contaminated zone.

To evaluate the performance of the *in situ* Lasagna™ technology (Project 47), soil samples and sampling cassettes were analyzed to assess the TCE removal efficiency. Twelve soil borings were completed before and after the demonstration. The soil samples collected from each boring were analyzed to assess how TCE concentration changed at each location. Also, cassettes from 12 treatment zones and from the control zone were analyzed to determine the amount of TCE they collected. The data were used to perform a mass balance.

Overall Assessment

To evaluate the success of a given formulation or process change in the leaching process (Project 32) for heavy metals, concentrations of these metals in the feed and product were compared against Dutch B values and Canadian Residential values for heavy metals in soil. The CROW process used in Project 44 was considered successful although it did not achieve expected operating conditions and recovery of contaminants. Groundwater sampling was planned to assess the overall effectiveness of the treatment. No overall assessment criteria were reported for the *in situ* demonstration of the Lasagna™ technology.

5.4.1.5 Group 5: Photo-Oxidation Treatment (Projects 14, 38, and 40)

Unlike the projects in the other groups, Group 5 projects solely involved technologies for treating groundwater. Biological treatment (Project 14), chemical treatment (Project 38), and adsorption (Project 40) accompanied photo-oxidation, the main technology for each project.

Characterization

Investigators characterized groundwater by analyzing samples for contaminants of concern and other parameters. For Project 14, concentrations of organic contaminants as well as COD, TOC and adsorbed organic halogens (AOX) were determined first for untreated groundwater. In addition to conducting gas chromatography/mass spectrometry (GC-MS) analysis of influent samples for VOCs, investigators working on Project 38 determined toxicity of influents by subjecting them to bioassay tests with waterfleas and minnows. As discussed in Section 5.2.5, a number of laboratory tests were conducted during Project 40 to optimize the photoactivities of photocatalysts and to optimize the supports for fixed-bed photocatalysts.

Treatment Assessment

To assess the biological pretreatment coupled with an ozone/UV combination process, researchers measured COD, TOC, VOC, and AOX levels as a function of ozone concentrations. For Project 38, samples were taken at several locations to evaluate the treatment system's efficiency. GC-MS analysis of influent and effluent samples for VOCs were used to indicate levels of intermediate organic compounds created during treatment. Other analyses included parameters such as total organic halogens (TOX), AOX, TOC, total carbon, and purgeable organic carbon. To obtain reliable data, USEPA-approved sampling, analytical, and QA/QC procedures were followed. For toxicity assessment, influents and effluents were subjected to bioassay tests with waterfleas and minnows.

Overall Assessment

Projects 14 and 38 were assessed in terms of their ability to achieve target levels of contaminants or toxicity limits. The combined biological and photo-oxidation treatment was required to achieve acceptable drinking water limits. The effectiveness of the Perox-Pure™ system was measured in terms of its ability to achieve the California drinking water action levels and U.S. federal drinking water maximum contaminant levels for the five compounds studied. However, neither project report listed the numerical values for the target limits. However, for a separate study involving treatment of groundwater containing TCE, the discharge level for the treatment was set at 0.5 mg/L. Bioassay tests also demonstrated whether the effluent was toxic to freshwater organisms.

The effectiveness of the systems tested at Tydall AFB and K.I. Sawyer AFB for Project 40 were assessed in terms the destruction rates of contaminants. The effectiveness of the system tested at the Wausau Water Treatment Plant was not measured because fouling of the catalyst inhibited destruction of the adsorbates.

5.4.2 General Effectiveness

This section of the chapter examines the performance of soil washing when it was used alone or in combination with other technologies. In the latter cases where soil washing was used as a pretreatment to provide a contaminant concentrate for further treatment, this review considers the performance of the pretreatment step only.

Unfortunately, some data on soil washing are not available for reporting or comparison here. Instead of documenting the effectiveness of soil washing and the add-on treatments separately, some investigators provided information on the overall performance for pretreating the feed and treating the concentrate. Another part of this chapter focuses on this overall performance.

It is somewhat difficult to compare reported performance of soil washing because the projects did not use the same unit processes. For example, one project examined hydrocycloning only, while others incorporated sizing, scrubbing, froth flotation, magnetic and gravity separation, *etc.* Thus, effectiveness will be measured in terms of targets and criteria mentioned in Section 5.4.1.

Table 5.2 provides data on contaminated material before and after soil washing and on the treatment processes used. Where results were not provided, a notation has been made. Performance data in Table 5.2 also identify if treated materials achieved their target criteria.

Data for these projects confirm reported observations that washing efficiency was dependent on the composition of the soil, and specifically that particle size distribution plays an important role in washing effectiveness. In general, the process is very efficient on sandy material, but fine-grained materials containing relatively high percentages of silt and clay were more difficult to treat. As reported in the Introduction, soil washing is most effective on soils containing less than 30-35% clay and silt.

As demonstrated in Project 36, additional treatments or several passes of the same unit process overcame treatment difficulties presented by materials high in fines. Investigators deliberately tested material containing up to 62% of particles less than 0.063 mm to test the feasibility of extending soil-washing processes to such materials. The results confirmed that three stages of froth flotation or gravity separation succeeded in significantly reducing levels of contaminants in the clean fraction. Despite these reductions, contaminants in the treated fraction were still significant making it unsuitable for reuse.

Table 5.2: Performance of Soil Washing Only

Project	Contaminant Levels[1]	Media	Treatment Processes	Performance[2]
10 (B)	TOC, >10%; high concentrations of PAHs and O&G; 92% metals in <100 µm fraction; 75% metals in <50 µm fraction	Sediment	Flotation, magnetic and gravity separation	Tailings: 40%; O&G, 4.1%; PAHs, 4.9%; Pb, 2.9%; Zn, 11%; Cd, Ni, and Fe, 24-30% Organic concentrate: 27%; O&G, 62%; PAHs, 74%; Pb, 81%; Zn, 68%; Cd, 54%; Ni, 54%; Fe, 32%)
10 (P)	4,026 mg/kg Zn; 100 mg/kg Cu	Soil		Clean: 95%: 360 mg/kg Zn; Cu unchanged. Achieved industrial guidelines for PAHs and residential guidelines for some contaminants. Metal concentrate: Fe, 55%
17 (F)	Not provided	Soil, sediment	Screening, solvent extraction	No data on screening.
19 (P)	Not provided	Soil, debris	Soil washing, vacuum distillation	No data on soil washing.
24 (F)	Crude oil up to 14,500 mg/kg	Sandy soil (77% sand, 12.5% fines, 10.5% coarse)	Multi-step hydrocyclone	Sand fraction: 87.5%; 130 mg/kg crude oil Coarse fraction, 10.5% Fine fraction: 12.5%; 110,000 mg/kg crude oil
24 (F)	High levels of mineral oil and PAHs (no data given)	Sediment (40% sand, 55% fines, 5% coarse)	Multi-step hydrocyclone	Sand fraction: no data; hydrocarbons, 100 mg/kg Fine fraction: no data; 20,000 mg/kg hydrocarbons; 1,000-2,000 mg/kg PAHs
26 (B)	180-3,500 mg/kg PAHs	Sandy soils	Screening, flotation	Washed fraction: 20-185 mg/kg PAHs Concentrate: no data
26 (P)	100-11,000 mg/kg PAHs	Clayey soils	Screening, flotation	Washed fraction: 24-1,250 mg/kg PAHs Concentrate: 480-6,000 mg/kg PAHs
27 (B)	up to 1,000 mg/kg PCBs	Soil	Screening; flotation	Clean fraction: 40-500 mg/kg PCBs
27 (P)	10-100 mg/kg PCBs	Soil	Screening, flotation	Clean fraction: 0.7-5.0 mg/kg PCBs

Project	Contaminant Levels[1]	Media	Treatment Processes	Performance[2]
27 (F)	50-300 mg/kg PCBs	1,288 tonnes soil; Fines, 63% (30% not expected)	Screening, flotation	780 tonnes clean fraction (60%) 400 tonnes PCB-enriched sludge
30 (P)	184 mg/kg PAHs; 937 mg/kg TPH; 2,332 mg/kg CN; 650 mg/kg Pb; 32 mg/kg As	Clayey soil	Sizing, scrubbing, flotation	Clean: 48%; 48 mg/kg PAHs; 250 mg/kg TPH; 1,242 mg/kg CN; 540 mg/kg Pb; 18 mg/kg As Fines: 29%; 170 mg/kg PAHs; 1,523 mg/kg TPH; 3,423 mg/kg CN; 1,000 mg/kg Pb; 54 mg/kg As Concentrate: 24%; 476 mg/kg PAHs; 1,694 mg/kg TPH; 3,191 mg/kg CN; 441 mg/kg Pb; 33 mg/kg As
30 (P)	163 mg/kg PAHs; 939 mg/kg TPH; 2,340 mg/kg CN; 733 mg/kg Pb; 32 mg/kg As	Clayey soil	Sizing, scrubbing, multi-gravity separation	Clean: 50%; 39 mg/kg PAHs; 188 mg/kg TPH; 1,651 mg/kg CN; 577 mg/kg Pb; 18 mg/kg As Fines: 29%; 170 mg/kg PAHs; 1,523 mg/kg TPH; 3,422 mg/kg; 1,001 mg/kg Pb; 54 mg/kg As Concentrate: 21%; 450 mg/kg PAHs; 1,931 mg/kg TPH; 2,494 mg/kg CN; 735 mg/kg Pb; 35 mg/kg As
31 (B)	Pb, 20%; Zn, 15%	Pb in fines; fine-grained material, anaerobic; coarse material, aerobic	Gravity separation	Light fraction: >90%; <2% metals; exceeded U.K. guidelines Concentrate: <10%; Pb, 32%; Zn, 5%
31 (P)	Not provided	<0.5 mm fraction of spoil	Multi-gravity separation	Light: 90%: metals, 2.5% Concentrate: 10%; metals, 70%
31 (B)	Pb, 9.8%; Zn, 2.3%	<180 µm fraction un-oxidized spoil	Froth flotation	Tailings: Pb, 3.0-3.5%; Zn, 0.1-1.1%
33	360 mg/kg Cu; 621 mg/kg Cr; 414 mg/kg Zn; 1,204 mg/kg As	Soil, sediment	Screening, hydrocycloning, flotation	No information on performance.
36 (P)	3,000-4,000 mg/kg TPH	Soil, 62% <0.063 mm	Sizing	Clean fraction: 68.7%; 200-210 mg/kg TPH Fines: 26-31%; 12,000 mg/kg TPH

Project	Contaminant Levels[1]	Media	Treatment Processes	Performance[2]
36 (P)	200-300 mg/kg PAHs; 2,000-3,000 mg/kg TPH; 2,000-3,000 mg/kg CN	Gasworks soil, 43% <0.063 mm	3 stages of froth flotation; gravity flotation. Applied to separate 0.01-0.63 mm fraction.	Clean fraction from froth flotation: 69%. PAHs reduced by 61%, TPH by 54%, and CN by 39%. Clean fraction from gravity separation: PAHs reduced by 68%; TPH reduced by 76%; and CN reduced by 14%.

Notes:

[1] Data are presented in the units that appeared in the various project reports.

[2] Washed media and concentrate provided as percentage of feed.

(B)= bench-scale (F)= full-scale

(P)= pilot-scale O&G= oil and grease

Project 27 demonstrates how an unanticipated high quantity of fines impaired soil-washing performance and required changes to the treatment. The higher than anticipated fines (63% rather than 30%) overloaded the system with solids and reduced performance. A volume reduction of 60%—not the targeted 70%—was achieved. Treated material often did not achieve target levels for PCBs and had to be washed again.

In summary, the projects demonstrated that soil washing may require several unit processes before treated materials can achieve target criteria. While this goal is desirable, it must be pointed out that performance should take into account the ability of the processes to produce a concentrate suitable for downstream treatment.

5.4.3 Overall Performance

To complement the discussion above on the performance of soil washing alone, this section of the report presents overall performance for the treatments, which may or may not have included soil washing. Data are presented for Group 2 on soil washing and biological treatment, Group 3 on soil washing and physical-chemical treatment, Group 4 on physical-chemical treatment, and Group 5 on photo-oxidation treatment.

5.4.3.1 Group 2: Soil washing and biological treatment (Projects 24, 26, and 36)

Table 5.3 summarizes data for projects conducted at the bench-scale to full-scale. Demonstration projects used soil washing as a pretreatment followed by bioslurry treatment of contaminant concentrates. To achieve better degradation rates, photo-oxidation was used as an added pretreatment in Project 24 to convert contaminants such as PAHs to readily biodegradable forms.

Materials tested in Project 24 consisted of a sandy soil contaminated with crude oil and a sediment contaminated with mineral oil and PAHs. In experiments conducted at the pilot scale, soil washing and biodegradation reduced mineral oil in soil from 400-5,000 mg/kg in the original feed to less than 100 mg/kg in the biologically-treated material. Biological treatment lasted 3-8 days. For treating soil contaminated with PAHs, pilot-scale investigations supplemented biological treatment with UV/H_2O_2 pretreatment. This combined photo-oxidation and biological treatment reduced PAH levels in soil wash concentrates from 30 mg/kg to 2-4 mg/kg in recombined soil in 15 days. PAH availability to UV/H_2O_2 pretreatment appears to be a rate-limiting factor. For soil washing and biological treatment at the full scale, crude oil levels in a soil fell from 14,500 mg/kg to less than 3,000 mg/kg (in recombined fractions). Similarly, soil washing a contaminated sediment resulted in a sludge with up to 2,000 mg/kg PAHs and 20,000 mg/kg hydrocarbons. After 30-32 days of treating the sludge biologically, residuals contained 2,000 mg/kg hydrocarbons and 200 mg/kg PAHs.

When the froth flotation fraction of a diesel-contaminated soil (Project 36) containing 12,000 mg/kg TPH was treated in a bioslurry reactor, the TPH concentration fell by 81%. However, treated solids still contained relatively high TPH (2,300 mg/kg). Similarly, biological treatment of fines generated by froth flotation and specific gravity separation of a gasworks soil failed to significantly reduce levels of contaminants. After 28 days of treatment, PAHs fell by 40-50%, and petroleum hydrocarbons by up to 20%. Cyanide remained unchanged.

Photo-oxidation pretreatment of soil-washed residues enhanced the subsequent biodegradation of PAHs, but was not required for more readily biodegradable contaminants such as mineral oil. As demonstrated in Project 24, pretreatment enhanced subsequent biological treatment which reduced PAHs from 30 mg/kg to 5-10 mg/kg in 15 days. PAHs were not biodegraded without this pretreatment. In contrast, the pilot-scale bioreactor tested batches of sludge resulting from soil washing two clayey soils in Project 26.

Table 5.3: Overall Performance of Soil Washing and Biological Treatment

Project	Treated Media and Contaminants	Soil Washing Performance	Biological Treatment		Treatment Time (days)
			(Before)	(After)	
24 (P)	400-5,000 mg/kg mineral oil in soil	Not provided	Not provided	<100 mg/kg mineral oil	3-8
24 (P)	30 mg/kg PAHs in soil	Not provided	Not provided	2-4 mg/kg PAHs in recombined soil	15
24 (F)	14,500 mg/kg mineral oil in sandy soil (77% sand, 12.5% fines, 10.5% coarse)	Fines: 110,000 mg/kg mineral oil; Clean: 130 mg/kg mineral oil	110,000 mg/kg mineral oil	22,000 mg/kg mineral oil in treated sludge; <3,000 mg/kg in recombined soil	40
24 (F)	Mineral oil and PAHs (concentrations not provided) in sediment (40% sand, 55% fines, 5% coarse)	Sand fraction: 100 mg/kg hydrocarbons; Sludge: 20,000 mg/kg hydrocarbons; 1,000-2,000 mg/kg PAHs	Sludge (see previous cell)	2,000 mg/kg hydrocarbons; 200 mg/kg PAHs	30-32
26 (B)	180-3,500 mg/kg PAHs in sandy soil	Clean fraction: 17-185 mg/kg PAHs	180-52,000 mg/kg PAHs	55-4,800 mg/kg PAHs	
26 (P)	41-12,000 mg/kg PAHs in clay soils	Clean fraction: 30-1,500 mg/kg PAHs; sludge: 2,400-3,750 mg/kg PAHs	2,400-3,750 mg/kg PAHs	55-200 mg/kg PAHs	6
36 (P)	Diesel fuel (3,000-4,000 mg/kg TPH) in fine-grained soil (62% <0.063 mm)	Clean fraction: 200-210 mg/kg TPH; fines: 120,000 mg/kg TPH	120,000 mg/kg TPH	2,300 mg/kg TPH	28
36 (P)	200-300 mg/kg PAHs; 2,000-3,000 mg/kg petroleum hydrocarbons; 2,000-3,000 mg/kg cyanide in fine-grained soil	Flotation clean fraction: 80-117 mg/kg PAHs; 920-1170 mg/kg TPH; 1,220-1,830 mg/kg CN	Not provided	Slurry reduced PAHs by 40-50%, hydrocarbons by 20%; CN unaffected	28
36 (P)	200-300 mg/kg PAHs; 2,000-3,000 mg/kg petroleum hydrocarbons; 2,000-3,000 mg/kg cyanide in fine soil	Gravity clean fraction: 62-93 mg/kg PAHs; 460-690 mg/kg TPH; 1,680-2,520 mg/kg CN	Not provided	Slurry reduced PAHs by 40-50% and hydrocarbons by 20%. CN unaffected.	28

Notes:
(P)= pilot-scale
(F)= full-scale

After 6 days of treatment, PAH concentrations fell by up to 97% (from 2,400-3,750 mg/kg to 55-200 mg/kg). A project report claimed that indigenous PAH degraders could achieve residual PAH concentrations ranging from 55-200 mg/kg after a 6-day retention time.

According to data collected during the biological treatment for Project 24, toxicity was reduced significantly. Since soil washing itself accounted for little of the reduced toxicity, it was concluded that bioslurry treatment accounted for most of the reduced toxicity.

5.4.3.2 Group 3: Soil Washing and Physical-Chemical Treatment (Projects 10, 17, 19, 27, and 33)

Table 5.4 summarizes data for projects conducted at the bench-scale to full-scale. Physical-chemical treatments applied to the soil wash concentrates were leaching and adsorption (Projects 10 and 33), solvent extraction (Project 17), vacuum distillation (Project 19) and chemical dehalogenation (Project 27). Because little similarity exists among these treatments, their performances will be assessed individually.

When used on concentrates containing heavy metals, leaching and adsorption reduced metal concentrations in treated materials by between 60-95%. In both cases, metal residuals fell within regulatory industrial and residential limits. However, the in-pulp leaching and adsorption method used in Project 33 appeared to be better than the approach used for Project 10. The metal content in the first case was lower, but the relative removal was higher than observed in the second case.

Materials treated by solvent extraction, vacuum distillation, and chemical dehalogenation reportedly achieved their regulatory targets. Solvent extraction removed almost 98% of PAHs and PCBs from soil that originally contained between 250-2,000 mg/kg PCBs and 200-500 mg/kg PCBs. Chemical dehalogenation achieved a similar level of success on soil wash concentrates with PCBs in the same concentration range. However, data suggest that when compared with these technologies, vacuum distillation achieved the highest removal. Treated soil contained less than 1% of the original organic contaminants and only around 3% of the mercury. Altogether, vacuum distillation will likely perform better than the others because it can remove volatile organic and inorganic contaminants from contaminated materials.

5.4.3.3 Group 4: Physical-Chemical Treatment (No Soil Washing) (Projects 31, 32, 44, and 47)

Table 5.5 summarizes data for projects conducted at the bench-scale to full-scale. The table identifies the NATO project number and the scale of the investigation, characteristics of the tested material, and overall performance of the treatment.

Physical-chemical treatments applied to unwashed contaminated material were leaching and adsorption (Project 31), leaching and extraction (Project 32), *in situ* thermally enhanced recovery (Project 40), and *in situ* electro-osmosis and adsorption (Project 47). Because little similarity exists among these treatments, their performances is assessed individually.

Of all the reprocessing techniques tested (others discussed for Project 31 under Group 3), leaching of oxidized Pb minerals with alkalis like sodium hydroxide displayed the highest potential for removing metals from spoil thereby resulting in the lowest concentrations of metals in the residue. Sodium hydroxide released 25-92% of the Pb and 3-23% of the Zn in un-reprocessed spoil containing 7.5% Pb and 0.1% Zn. These releases correspond to 1.5-5 tonnes Pb and 0.1-1.2 tonnes Zn per 100 tonnes spoil.

Table 5.4: Overall Performance of Soil Washing and Physical-Chemical Treatment

Project Number	Contaminants in Feed	Contaminants in Concentrate	Overall Performance	Treatment Processes
10 (P)	2,112 mg/kg Pb; 950 mg/kg Cu; 4 mg/kg Cd; 2,535 mg/kg Zn	Not applicable	Soil solids after leaching: 1,070 mg/kg Pb; 480 mg/kg Cu; 0 mg/kg Cd; 1,050 mg/kg Zn Soil solids after metal adsorption: 898 mg/kg Pb; 289 mg;kg Cu; <1 mg/kg Cd; 286 mg/kg Zn; Recovery= Pb, 57%; Cu, 70%; Cd, >90%; Zn, 67%. Metal residuals within regulatory industrial (1,000 mg/kg) and residential (500 mg/kg) limits	Leaching and adsorption
10 (P)	Pb as high as 11,800 µg/g	Not applicable	Clean material (7% original Pb) met regulatory industrial and residential criteria	Leaching and adsorption
17 (F)	Silty sand, loamy soil, and sediment (250-2,000 mg/kg PAHs; 200-500 mg/kg PCBs; 2,000 mg/kg heavy organics	Not provided	Treated material (6-30 mg/kg PAHs; 1-6 mg/kg PCBs; 20 mg/kg heavy organics	Solvent extraction
19 (P)	32,000 mg/kg PAHs; 102,000 mg/kg TPH; 1,728 mg/kg CN; 8,000 mg/kg HG; 100,000 mg/kg TNT; 3,400 mg/kg lindane	Not provided	Treated soil: <1 mg/kg PAHs; <10 mg/kg TPH; <10 mg/kg CN; 0.5-4.0 mg/kg Hg; 0.4 mg/kg TNT; 0.0002 mg/kg lindane	Vacuum distillation
19 (F)	Hg up to 1,900 mg/kg	100 µm - 8 mm; contaminant concentrations not given	Treated material (Hg 10-50 mg/kg); below target of 50 mg/kg.	Vacuum distillation
27 (B)	PCBs at unknown levels	250 mg/kg PCBs	Treated concentrate (PCBs <1 mg/kg); below target of 10 mg/kg.	Chemical dehalogenation
33 (B)	1,204 mg/kg As; 360 mg/kg Cu; 621 mg/kg Cr; 414 mg/kg Zn	Information not provided	Treated product: 112 mg/kg As; 22 mg/kg Cu; 74 mg/kg Cr; 68 mg/kg Zn. Corresponding targets are 30, 100, 160, and 100 mg/kg, respectively.	Leaching and adsorption

Notes:
(B)= bench-scale
(F)= full-scale
(P)= pilot-scale

Table 5.5: Overall Performance of Physical-Chemical Treatment Without Soil Washing

Project Number	Characteristics of Contaminated Media	Overall Performance	Treatment Processes
31 (P)	Un-reprocessed metalliferous spoil: Pb, 7%; Zn, 0.1%	Sodium hydroxide leached 25-92% Pb and 3-23% Zn. Sulfuric acid leached 2-33% Pb and 12-64% Zn.	Aggressive leaching
32 (F)	Soil with 46% silt/clay: total heavy metals 1,000- 22,500 mg/kg;	Treated material achieved Dutch B values and Canadian residential values for Cr, Ni, Cu, Zn, and PB, but not for As or Cd.	Mild leaching and extraction
32 (F)	Soil spiked with radionuclides	Treated material contained 24-48% of Pu, U, Ru, Am, Np, and Sr.	Leaching and extraction
44 (F)	Gravelly soil with coal tar DNAPL	5,400 L of pure coal tar was removed	DNAPL: thermally enhanced recovery, incineration Water: precipitation, fluidized bed reactor, filtration
47 (P)	Soil with TCE averaging 72.6 mg/kg	Treated soil contained 1.1 mg/kg TCE; removal efficiency 98%;	Electro-osmosis and adsorption

Notes:
(F)= full-scale (P)= pilot-scale

Other leach tests showed that sulfuric acid was more effective at leaching Pb from un-oxidized spoil than from oxidized material. The acid leached 2-33% Pb and 12-64% Zn. By comparison, tests with reprocessed spoil showed that the acid leached only 2-5% of the original Pb, suggesting that the residual Pb is resistant to acid leaching.

As demonstrated for Project 32, using the CACITOX™ reagent to leach a 46% silty clay soil containing a variety of heavy metals at concentrations in the range of 1,000-22,500 mg/kg resulted in simultaneous removal of metals. The treated material achieved Dutch B values and Canadian Residential values for Cr, Ni, Cu, Zn, and Pb, but not for As and Cd. The researchers reported that if the conditions were optimized, all metals would have met the criteria. In tests of soil spiked with radionuclides, a single leach removed between 52 and 76% of Pu, U, Ru, Am, Np, and Sr. Multiple contacts could have resulted in better removal of these radionuclides.

When the Lasagna™ technology was applied to a contaminated site (Project 47), TCE concentrations were reduced on average from 72.6 mg/kg to 1.1 mg/kg, which translates to an average removal efficiency of 98%. At sampling locations where the initial concentrations were as high as 225 mg/kg, indicative of residual DNAPL in soil pores, the process reduced these concentrations to less than 1 mg/kg in all but one sample. Upward diffusion of TCE from untreated soil may explain the single discrepancy of 17.4 mg/kg TCE. TCE reduction in a control area averaged at around 45%, falling from 89.9 m/kg to 49.5 mg/kg. These data, when compared to those from the demonstration area, confirm the effectiveness of the Lasagna™ process for removing TCE from soil.

Mass balance accounted for 50% of the pre-demonstration TCE. The remaining 50% may be attributed to passive diffusion (5%), evaporation (5%), *in situ* degradation of TCE, non-uniform distribution of TCE in the soil, or incomplete extraction of TCE from the activated carbon (taken from the treatment layer) before analysis.

5.4.3.4 Group 5: Photo-Oxidation Treatment (Projects 14, 38, and 40)

Table 5.6 summarizes the performance data for the Group 5 projects. The table identifies the scale of the investigation, characteristics of the tested groundwater and wastewater, and overall performance of the photo-oxidation treatment.

While all three projects used photo-oxidation, Project 14 included biological treatment with activated sludge to improve performance. The project report did not explain how the biological step improved performance, or why it was necessary. However, the combined approach reduced dissolved constituents by 80-85%, eliminated VOCs, and lowered COD from 239 ppm to undetectable levels.

For the three tests conducted under Project 38, the photo-oxidation technology generally achieved regulatory targets and reduced contaminants to below detection levels. For a technology demonstration conducted at the Lawrence Livermore National Laboratory facility, groundwater contained TCE and PCE at 1 mg/L and 0.1 mg/L, respectively. Treated water contained TCE and PCE at levels below detection limits, while TCA and chloroform occurred at levels slightly above detection limits. In another study where the technology was used to treat well water containing 50 to 400 mg/L TCE, effluents consistently achieved levels below the analytical detection limit of 0.5 µg/L. Also, at a full-scale treatment for groundwater containing PCPs as high as 15 mg/L, the system destroyed the contaminants to below the target level of 0.1 mg/L.

5.5 RESIDUALS AND EMISSIONS

5.5.1 Soil Washing

Table 5.7 identifies residuals (*i.e.*, soil/sediment, water, and concentrates) and emissions (air) from soil washing only. For projects that used soil washing as a pretreatment to provide a concentrate for further treatment, residuals and emissions for the subsequent treatments are covered under the project groups to follow.

As seen in the examples in Table 5.7, soil washing residuals usually include the following:

- Wastewater from sizing and classifying material. This water is usually recycled, but may eventually require treatment before disposal.

- Concentrates that may be treated further to destroy or stabilize contaminants, or to extract useable products.

- Treated material that may be reused or recycled if it meets regulatory criteria, or disposed of at a landfill, incinerated, *etc.*, if it does not.

- Off-gases that may contain volatile contaminants, which may be removed by techniques such as adsorption by activated carbon.

5.5.2 Combined Treatments

Residuals from combined treatments consist of those identified for soil washing in Table 5.7, as well as others unique to the treatments used on contaminant concentrates. Residuals discussed below pertain mainly to treatment of the concentrates.

Table 5.6: Overall Performance of Photo-Oxidation Treatment of Contaminated Water and Wastewater

Project Number	Characteristics of contaminated water/wastewater	Overall Performance
14 (F)	239 ppm COD; chlorinated solvents, esters, phenols, BTEX, *etc.*, at 0.8–360 mg/L	COD undetected; dissolved organic constituents reduced by 80%-85%; VOCs eliminated.
38 (F)	Groundwater: TCE 1 mg/L; PCE 0.1 mg/L	TCE (99.9% removal) and PCE (98.7% removal) below detection limits in treated water; TCA and chloroform slightly above detection limits.
38 (F)	Drinking water: TCE 50–400 mg/L	Effluents below analytical detection of 0.5 µg/L.
38 (F)	Groundwater: PCPs up to 15 mg/L	PCPs in treated water below target level of 0.1 mg/L.
40 (F)	Groundwater: contained total BTEX compounds greater than 2 mg/L	Ionic species initially fouled the catalysts and inhibited destruction. Following treatment to remove suspended particulates and ionic species, catalyst photo-activity did not decrease after 25 days of operation. BTEX compounds were destroyed within 6.5 minutes of empty bed contact time on rainy days.
40 (F)	Groundwater: 100 µg/L TCE	>21% of total influent BTEX destroyed; 98% of BTEX removed from waste stream.
40 (F)	Groundwater: 100 µg/L TCE	>95% of TCE was destroyed within a 2-minute contact time.
40 (F)	Groundwater: contained chlorinated solvents and BTEX compounds at unspecified concentrations	Direct photocatalytic oxidation did not effectively regenerate spent adsorbent because nuisance substances in the groundwater fouled the catalyst. Tests combining steam regeneration followed by photocatalysis of steam condensate showed that carbon adsorbent was not effectively regenerated an lost a significant amount of capacity. Background organic matter in the water may have caused this loss of efficiency. Also, steam regeneration did not appear to destroy significant amounts of the sorbed chlorinated compounds.

Notes:
(F)= full-scale BTEX= benzene, toluene, ethylbenzene, and xylenes

5.5.2.1 Group 2: Soil Washing and Biological Treatment (Projects 24, 26, and 36)

The main residuals from biological treatment are process water and sludge. Table 5.8 identifies residuals (soil/sediment, water, and concentrate/other) associated with biological treatment of soil wash concentrates for the three Group 2 projects.

Only one of the three projects reported recycling of the process water, and it is not clear what was done for the other projects. Contaminants in treated concentrate achieved regulatory guidelines or remained at unacceptable levels. Clean material derived from Project 24 was described as having no residuals, while Microtox analysis of treated material from Project 26 revealed that toxicity had been reduced significantly. In contrast, unacceptable levels of contaminants remained in fines treated in Project 36.

Table 5.7: Residuals and Emissions Associated with Soil Washing

Project Number	Soil/Sediment	Water	Air	Concentrate/Other
10	Treated sediment material achieved industrial limits for Pb, Cd, and organics. Not suitable as off-shore fill.	Wastewater from sizing and classifying material	Not reported	Inorganic concentrates for disposal or recovery of metals; organic concentrate for secondary treatment
17	Treated material used as fill, or treated further to stabilize metals.	Not reported	Not reported	Concentrate treated by solvent extraction.
19	Not reported	Wastewater treated chemically to form a precipitation sludge. Disposed in a hazardous waste facility. Water polished with activated carbon.	Off-gases treated with activated carbon.	Light-weight particles and spent activated carbon treated by vacuum distillation.
24	Not provided	Not provided	Not provided	Concentrate treated biologically.
26	Not provided	Not provided	Not provided	Concentrate treated biologically.
27	Non-porous debris disposed in a landfill; porous debris registered as hazardous waste for incineration; coarse fraction (>0.1 mm) returned to excavation and capped	Wash water treated if it contained PCBs, then recirculated or discharged to a sewer.	No off-gases generated	Concentrate treated by chemical dehalogenation.
30	Not provided	Process water was contained and recirculated.	Carbon filters, which extracted volatile contaminants, created emissions.	Wastes and sludges received further treatment or shipped to a licensed landfill.
31	Residue contained total metals exceeding U.K. guidelines for soils. Metals are leachable.	Not provided	Not provided	Not provided
33	Provided for overall treatment, not for soil washing only.	Decanted water	Off-gases may be produced	Concentrate leached and metals adsorbed.
36	Residue contaminant-reduced, but unsuitable for reuse. Contamination levels still significant.	Not provided	Not provided	Concentrate treated biologically.

Table 5.8: Residuals Associated with Biological Treatment of Soil Wash Concentrates

Project Number	Soil/Sediment	Water	Concentrate/Other
24	Clean soil with no residuals; treated fractions recombined.	Effluent from biodegradation was recycled.	Not clear what was done with sludge treated biologically.
26	Not applicable	Not provided	Microtox analysis of water-extractable components of treated concentrate showed significantly reduced toxicity.
36	Not applicable	Not provided	Treated fines contained unacceptable levels of contaminants.

5.5.2.2 Group 3: Soil Washing and Physical-Chemical Treatment (Projects 10, 17, 19, 27, 31, and 33)

The type of physical-chemical treatment used on soil wash concentrates determined the nature and quality of residuals. Table 5.9 identifies residuals (soil/sediment, off-gases, and concentrate/other) associated with physical-chemical treatment of soil wash concentrates for five of the six Group 3 projects. For four of these projects in this group, treatment consisted of further concentrating the contaminants to provide a recoverable product or a smaller volume of contaminated material for disposal.

These treatments resulted in products such as a metal-rich filter cake, oil, and mercury. The treated materials were usually suitable for reuse or disposal. If carbon filters were used in the treatment, they contained captured volatile contaminants.

Only Project 27 examined chemical destruction of PCBs in the concentrate. Based on bench-scale studies only, the treated material contained acceptable residual PCBs.

5.5.2.3 Group 4: Physical-Chemical Treatment (No Soil Washing) (Projects 32, 44, and 47)

Like the Group 3 projects already discussed, the type of physical-chemical treatment used on contaminated materials treated by Group 4 projects determined the nature and quality of residuals. Table 5.10 identifies residuals (soil, sediment, water, off-gases, and concentrate/other) associated with physical-chemical treatment (no soil washing) for three projects.

In Projects 31 and 32, treated materials were reused or disposed. One of these materials had to be washed before disposal to remove residual leachant. In the case of Project 47 (*in situ* treatment of TCE contaminated soil), soil retained around 1 mg/kg TCE after treatment. The physical treatments concentrated the contaminants further rather than destroying them. Because of this, contaminant-rich products resulted. These consisted of metal-rich concentrates as well as treatment cartridges that captured TCE. Only Project 47 reported residuals in off-gases and water.

5.5.2.4 Group 5: Photo-Oxidation Treatment (Projects 14, 38, and 40)

When used to treat contaminated groundwater, photo-oxidation—with or without biological treatment—resulted in few residuals (water, off-gases, and concentrate/other) as noted in Table 5.11. Treated groundwater contained low levels of contaminants that could be discharged directly or treated further before being sent to a municipal treatment facility.

Table 5.9: Residuals Associated with Physical-Chemical Treatment of Soil Wash Concentrates

Project Number	Treatment Process	Soil/Sediment	Off-Gases	Concentrate/Other
10	Metal recovery, chemical destruction of organics	Treated sediment material achieved industrial limits for Pb, Cd, and organics. Could be used as fill on-shore or offshore.	Not applicable	Metal-rich filter cake for off-site recycling
17	Solvent extraction, stabilization	Traces of solvent in cleaned soils. Claimed to be innocuous and biodegradable	Carbon filters with recovered vapors	Oil concentrate requires treatment, recycling, or disposal.
19	Distillation	Not provided	Not provided	Spent ion-exchange resins for recycling; condensed mercury.
27	Chemical dehalogenation	Not applicable	Not provided	Treated concentrate contained <1 mg/kg PCBs.
33	Leaching, adsorption	Treated material was disposed.	Gaseous emissions may require scrubbing	Acid used to remove metals was recycled. Concentrated solution of metals may be treated by precipitation, reduction, or electrowinning to recover metals, or encapsulated or disposed. Precipitated residues may require fixation before disposal.

Photo-oxidation treatments normally do not result in sludge or spent media requiring further processing, handling, or disposal. Ideally, end-products include water, carbon dioxide, halides, and in some cases organic acids. However, although Project 14 included a biological step, the reports did not mention how a biological sludge was treated or the levels of residual contaminants.

GC/MS analysis of influent and effluent samples examined for Project 38 revealed no new target compounds or other tentatively identified compounds being formed during treatment. The report for Project 14 did not mention work to identify possible by-products resulting from the ozonation treatment. Finally, treated water may have retained unused hydrogen peroxide: investigators for the study at the Lawrence Livermore Laboratory (Project 38) reported residual hydrogen peroxide in the effluent.

5.6 FACTORS AND LIMITATIONS TO CONSIDER FOR DETERMINING THE APPLICABILITY OF THE TECHNOLOGY

Several factors determine the success of physical-chemical technologies. As most of the case studies dealt with in this chapter involved soil washing as a pretreatment stage, consideration is given below to this technology both when used alone and in combination with other technologies. The final part of this section examines the factors governing the applicability of physical-chemical treatment not involving soil washing.

Table 5.10: Residuals Associated with Physical-Chemical Treatment of Contaminated Materials (No Soil Washing)

Project Number	Treatment Process	Soil/Sediment	Water	Off-gases	Concentrate/Other
31	Froth flotation, gravity separation, density separation	Treated spoil was disposed or reused.	The effluent has to be addressed. Options include conventional metal adsorption filters.	Not reported	Compared to other treatments, alkali leaching provides the residue with the lowest concentration of metals.
32	Leaching, complexation, precipitation, ion exchange	Treated soil was washed to remove residual leaching agent, dewatered, then reused	Not reported	Not reported	Precipitated contaminants may be reconditioned (contained or encapsulated). Electro-deposition/ polishing the leachate may recover valuable products or minimize secondary waste.
44	Thermally enhanced recovery	Soil and ground-water concentrations were not provided. Recovered coal tar DNAPL was incinerated.	Groundwater was treated and was either reinjected or discharged to Brodhead Creek	Not reported	Sludge and spent carbon from treatment of groundwater and the recovered DNAPL must be disposed.
47	Electro-osmosis, adsorption	Soil treated *in situ* contained <1 ppm TCE.	Recycling water from the cathode to the anode eliminates effluent.	Evaporation produces contaminant vapors	Treatment layers with captured TCE may require disposal as a hazardous waste.

Table 5.11: Residuals Associated with Photo-Oxidation Treatment of Groundwater

Project Number	Water	Off-Gases	Concentrate/Other
14	Dissolved contaminants were reduced by 80-85%. Water was treated again before being sent to treatment plant or discharged to a stream.	Not provided	Sludge. No mention of the levels of residual contaminants.
38	Treated water has TCE and PCE below the detection limit of 0.5 µg/L. Chloroform slightly exceeds detection limits. Effluent may contain residual H_2O_2;	None generated	Not applicable
38	For a full-scale treatment, treated water contained 0.1 mg/L PCP.	None generated	Not applicable
40	Concentrations of residual contaminants varied, depending on the system tested.	Not provided	Not provided, but presumably sludge from water pretreatment and spent catalyst and support materials.

5.6.1 Typical Soil Washing

General Issues

This *ex situ* separation process could potentially be applied cost-effectively to materials with less than 30-35% of particles less than 0.063 mm. When the concentration of fines exceeds this range, conventional soil washing may have to include other treatments (*e.g.*, flotation, density and gravity separation), washed material will have to be reprocessed, or several cycles of the same treatment (*e.g.*, hydrocycloning) may have to be implemented. Another option includes using the CACITOX™ technology (Project 19) which is claimed to be effective for soils containing a high content of silt and clay, a characteristic that presents difficulties to other treatment technologies—including soil washing.

If low absolute standards cannot be achieved with a single technology, pretreatment by flotation or size separation may be used to complement a treatment process. Pretreatment may reduce the volume requiring downstream treatment and may also present the separated contaminant concentrate in a form suitable for the downstream process (*e.g.,* bioslurry).

For soil washing pretreatment and companion treatment technologies to be viable, the treatment process on the separated contaminated fines has to be rapid. Otherwise, long treatment periods will cause problems when matching commercially viable throughput of physical processes with relatively slow treatments such as biological processes.

Coarse-grained soils would not benefit much from soil washing and accompanying treatments. As explained for Project 33 which used soil washing and in-pulp extraction, coarse-grained soils containing metals can be easily leached, filtered and washed. Extracted metals can then be precipitated or adsorbed from the resulting wash and leachate. In contrast, the washing step becomes more difficult for soils high in fines.

Material Characteristics

When soil washing is used as a pretreatment for other technologies, accurate determination of feed material characteristics is a crucial step. These characteristics have a key influence on the choice of the most efficient technologies to treat soil wash concentrates, and on how the selected technology performs. Single unit operations can then be combined to provide tailor-made solutions to deal with the contamination. However, it is important to note that for complex sites with many sources of contamination, the contaminated material may not behave consistently during the separation process. Thus, the chosen technology should be able to cope with variations in the chemical and physical composition of the feed.

For example, the ORG-X solvent extraction unit (Project 17) operates best under optimum moisture content and grain size. Soil moisture content of 20% in one case made the soil difficult and more costly to treat. The process achieves higher efficiency on sandy material, but is being improved for fine-grained soils. Similarly, the mineralogy of clay particles in a soil matrix may influence the overall treatment process. The exchange capacity of different clay minerals affects the degree to which contaminants can be adsorbed or desorbed, and strongly influences the characteristics of subsequent dewatering.

In contrast, some treatment technologies are insensitive to variations in soil types. Vacuum distillation (Project 19), for example, can effectively treat materials such as gravel, sandy soils, fine-grained soils (up to 90% silt and clay although at a reduced throughput); slags, concrete and brick debris, *etc.*

Contaminant Characteristics

Physical and chemical properties of contaminants to be treated influence the applicability of technologies. For example, vacuum distillation (Project 19) is suitable for volatile contaminants with boiling points of 350-400°C at pressures of 50-150 hPa. In terms of biological treatment, candidate contaminants must be amenable to biological degradation. Other factors influencing the applicability of a technology are operating parameters and maintenance requirements of equipment used in the treatment processes.

Treatment Criteria and Characteristics of Residuals

With some soils, physical pretreatment alone will not reduce the absolute concentration of contaminants to acceptably low levels. However, by combining this pretreatment with other approaches such as biodegradation and chemical treatment, treated material may achieve the regulatory criteria. Thus, the applicability of a treatment system would depend on its overall ability to achieve regulatory requirements.

A technology that may not achieve absolute regulatory criteria should not necessarily be discounted as a treatment option. As shown in Project 33, in-pulp extraction provides an attractive option for removing metals from pulp generated by leaching a contaminated soil high in fines. The project's report notes that achieving low absolute levels can be difficult and costly. On the other hand, leachability criteria could be achieved easily.

Before using soil washing pretreatment and companion treatments, property owners should clarify the intended use or disposal of treated materials and soil wash concentrates. This is a key point because it determines which soil washing processes should be used to achieve this goal. For example, if treated material is to be disposed of at a secure landfill, the feed will require less rigorous treatment than a material for reuse on an industrial or residential property.

If destruction of a soil matrix is not desirable, strong acids should not be used for treatment because they can significantly impair the integrity of a soil matrix. In contrast, weak extractants such as those used in the CACITOX™ technology (Project 32) do not destroy the matrix and thus be potentially be used treat contaminated soils and sediments when this is an important consideration.

5.6.2 Soil Washing and Other Treatment

With some soils, soil washing alone will not reduce the absolute concentration of contaminants to acceptably low levels. Combining this treatment with other proven extraction, destruction, or concentration approaches may reduce contaminants in treated media to meet acceptable criteria. The proven technologies must be combined in such a way that each technique is properly integrated and the overall performance better than could be achieved with a single unit application alone.

An alternative approach, claimed to be more economically attractive than one using two independent treatments in sequence, is one that combines treatment of inorganic and organic contaminants in a single unit operation.

In a combined treatment approach that includes soil washing, the selectivity of the companion technology for contaminants determines its applicability to soil wash concentrates. Biological treatments, for example, can be applied only to contaminants that are biodegradable. Similarly, the CACITOX™

technology is claimed to selectively dissolve and extract heavy metals and transuranic elements from other wastes.

Soil Washing and Biological Technologies

This combination of technologies is restricted to soil and sediment with a low content of organic matter and contaminated with high concentrations of biodegradable organic compounds, such as mineral oil and PAHs. High molecular weight PAHs biodegrade slowly, and the limited bioavailability of these compounds restricts degradation to even lower rates. Limited bioavailability of PAHs results from adsorption of these compounds to the organic soil matrix. As seen in Project 24, using a UV/H_2O_2 pretreatment to break down the organic matrix and release the PAHs can increase this bioavailability.

The combination of soil washing and slurry-phase treatment provides a viable option for treating contaminated soil. The washing step reduces the volume of material requiring treatment by up to 80-90% and can function as the prerequisite mixing operation for microorganisms, nutrients, and contaminants. Under optimal conditions (*e.g.*, pH, temperature, and nutrients) during the bioslurry phase, indigenous degraders in the contaminated material may significantly increase removal of contaminants.

For the overall treatment to be viable, the degradation process on separated contaminated fines has to be rapid. Otherwise, long degradation periods will cause problems when coupling commercially viable throughput of physical processes with relatively slow biological processes.

Soil Washing and Physical-Chemical Technologies

Soil washing pretreatment should reduce the volume of material requiring downstream treatment and also present the separated contaminant concentrate in a form suitable for the downstream physical treatment. If the feed to soil washing contains organic and inorganic contaminants, the organic and inorganic concentrates should be separated for subsequent treatment.

To be applied successfully for treating a contaminant concentrate, physical-chemical technologies have to complement each other. For example, if a treatment involves leaching contaminated materials and subsequently adsorbing metals, the leached metals have to be in a form suitable for adsorption. As demonstrated in Project 33, ion exchange resins work well for Cu, Cr, and Zn. However, these resins experienced difficulties removing As because the metal forms un-dissociated arsenic acid, which is unavailable for ion exchange, at the low pHs needed to dissolve arsenates. At high pHs, the ion exists in solution but preferentially adsorbs onto iron precipitates formed under these conditions.

The degree to which physical-chemical treatments destroy a soil matrix may be significant. When this is a concern, other technologies may have to be considered. The CACITOX™ technology, for example, which employs "weak extractants," potentially can treat contaminated soils and sediments without destroying the matrix.

5.6.3 Physical-Chemical Technologies

Like biological treatments, physical-chemical technologies treat specific contaminants and media. The Lasagna™ process (Project 47) demonstrates this selectivity, because it offers promise for treating water-soluble organic and inorganic contaminants and mixed wastes in groundwater and low-permeability soils. For highly non-polar contaminants, surfactants introduced into groundwater or incorporated into treatment zones will solubilize the organics. The process has been shown also to be effective in treating residual DNAPLs. If contaminated soil has a relatively high permeability, other treatment processes may be more effective or more economical than the Lasagna™ process. The CACITOX™ process also demonstrates this selectivity by dissolving and extracting heavy metals and transuranic elements from other wastes.

For *in situ* treatment, the spatial distribution of contamination may influence how a technology is applied. Contaminated material within 10 m of the surface may be easily excavated for treatment on the surface. However, when contamination occurs at depths greater than 10 m, it is usually treated *in situ*. A similar rationale applies to using the Lasagna™ technology. The vertical configuration of the technology is more appropriate for contamination near the ground surface. For deeper contamination, installing horizontal treatment zones provides a better option. Finally, if contaminant concentrates are determined to be hazardous wastes, treating, removing and disposing of them may be an issue and may prove costly.

5.6.4 Photo-Oxidation Technologies

Photo-oxidation treatment does not transfer or concentrate contaminants that may require further treatment or costly disposal. Treated water can be disposed onsite or offsite. Options for on-site disposal include groundwater recharge or temporary on-site storage for sanitary use. Off-site disposal options include discharge into surface water bodies, storm sewers, and sanitary sewers. Depending on permit requirements, discharged water may have to be adjusted for pH. Factors influencing the applicability of photo-oxidation can be grouped into four categories: site characteristics, influent characteristics, operating parameters, and maintenance requirements.

Site Characteristics

Site characteristics can influence the application of the technology. Site-specific factors include support systems (*e.g.*, extraction wells, facility for treatment, and equalization tanks), site area and preparation, climate, utilities, and services and supplies.

Influent Characteristics

In general, minimal pretreatment is required. If needed, it usually consists of oil and grease removal, suspended solids removal, metals removal, or pH adjustment to reduce carbonate and bicarbonate levels. Under a given set of operating conditions, contaminant removal efficiencies depend on the chemical structure of the contaminants. Removal efficiencies are high for organic compounds with double bonds (*e.g.*, TCE, PCE, and vinyl chloride) and aromatic compounds (*e.g.*, benzene, toluene, xylene, and phenol) because these compounds are easily oxidized. Organic compounds without double bonds (*e.g.*, TCA and chloroform) are not easily oxidized and are more difficult to remove.

Contaminant concentration also influences the technology's effectiveness. The system is most effective for contaminant concentrations lower than 500 mg/L. At higher concentrations, the technology can be combined with others such as air stripping. For highly contaminated water, the system can be operated in a "flow-through with recycle" mode. In this arrangement, part of the effluent is recycled through the oxidation unit to improve overall removal efficiency.

Other chemical species in influents may consume oxidants and place an additional load on the system. These species, known as scavengers, include anions such as bicarbonate, carbonate, sulfide, nitrite, bromide and cyanide. Metals in reduced states (*e.g.*, trivalent chromium, ferrous iron, manganesian ion) are also likely to be oxidized. Under alkaline conditions, these reduced metal species can cause other concerns. For example, trivalent chromium can be converted to the more toxic hexavalent form, while ferrous and manganous ions can be converted to insoluble forms which precipitate to create suspended solids that can build up on the quartz tubes housing the UV lamps. Natural organic compounds such as humic acids (often measured as TOC) are also potential scavengers.

Suspended solids, oil, and grease pose potential problems because they can build up on the quartz sleeves, reduce UV transmission and so decrease treatment efficiency.

Operating Parameters

The main operating parameters are hydrogen peroxide dose, influent pH, and flow rate. Treatment unit configuration, contaminated water chemistry, and contaminant oxidation rates determine the hydrogen peroxide dose. A hydrogen peroxide splitter allows the operator to inject hydrogen peroxide to the oxidation unit influent and directly to any of the individual oxidation reactors. Influent pH controls the equilibrium among carbonate, bicarbonate, and carbonic acid. When carbonate and bicarbonate concentrations exceed 400 mg/L, lowering the influent pH to between 4 and 6 improves the efficiency by shifting the carbonate equilibrium to carbonic acid that is not a scavenger. In general, increasing the hydraulic retention time improves treatment effectiveness by increasing the time available for contaminant destruction.

Maintenance Requirements

Regular maintenance by trained personnel is essential for the successful operation of photo-oxidation systems. The lamp assembly is the only major system component requiring regular maintenance. Other components of the system can be checked monthly.

5.7 COSTS

Table 5.12 summarizes information on contaminants and media treated, pretreatment and other treatments used, reported treatment costs, and qualifiers regarding the costs. Some of these costs are based on actual remediation projects, while others are estimated from results of bench- and pilot-scale investigations. In another approach (Project 47), a cost model examined a contamination scenario and predicted treatment costs. The currencies used for costs are those used in project reports.

The costs in Table 5.12 should be treated with caution. The reports for some of the projects did not differentiate between capital and operating costs; and generally did not clearly state if the costs were for treatment only, exclusive of excavation, handling and disposal. However, for Project 26 the cost of excavation, sorting and backfilling was reported as U.S.\$160/m^3 and the cost of washing as U.S.\$300/m^3.

Cost-effectiveness and costs will be highly site-specific and will depend on factors that influence treatment. For example, the nature of the material determines the need for various types of specialized pretreatment processes such as magnetic separation, flotation, and density separation. If material contaminated with organic and inorganic compounds contains relatively high concentrations of fines, specialized treatments will require additional handling of material and result in higher costs. As demonstrated in Project 19, the rate of utilization of a soil washing plant influences treatment costs. Cost decreases as the rate of utilization increases. The size of a treatment plant also has an impact on cost. For example, for the groundwater treatment conducted during Project 38, a larger plant, if required, could offer lower treatment costs.

Table 5.12: Reported Costs for Different Options Used to Treat Contaminated Media

Project Number	Contaminants and Media Treated	Treatment Processes	Overall Cost (per m^3 unless other units given)	Comments
Group 1: Typical Soil Washing				
30	32-650 mg/kg metals; 184 mg/kg PAHs; 200 mg/kg TPH	Particle size separation, froth flotation, gravity separation	Not provided.	
Group 2: Soil Washing and Biological Treatment				
24	14,500 mg/kg crude oil in soil; PAHs in sediment	Hydrocycloning photo-oxidation, bioslurry	Not provided	Pretreatment by photo-oxidation and hydro-cycloning can be expensive, depending on the ratio of sand to fines and the organic matter content
26	180-3,500 mg/kg PAHs in sandy and clayey soil	Flotation, bioslurry	Excavation, sorting, backfilling (U.S.$160/$m^3$); washing (U.S.$300/m^3); biological (U.S.$530/$m^3$)	
36	2,000-4,000 mg/kg TPH; 200-300 mg/kg PAHs; 2,000-3,000 mg/kg CN in soils high in fines	Size separation, bioslurry	£23-£37 (U.S.$38-61)/tonne of treated material	Treatment is more cost-effective only if transporting and disposing of untreated Mattel exceeds £40-60 (U.S.$65-100)/tonne.
Group 3: Soil Washing and Physical-chemical Treatment				
10	4,026 mg/kg Zn; 100 mg/kg Cu in soil	Flotation, magnetic separation, leaching of metals and adsorption	U.S.$75/tonne	Estimated cost for treating 500,000 tonnes of soil containing PAHs and metals.
17	250-2,000 mg/kg PAHs; 200-500 mg/kg PCBs in soil and sediment	Size separation, solvent extraction, oil recovery	U.S.$200/tonne for 2,000 tonnes; U.S.$100/tonne for 20,000 tonnes; U.S.$60/tonne for 100,000 tonnes	
19	875 mg/kg Hg in sandy loam and loam soils	size separation, scrubbing, vacuum distillation	U.S.$320/tonne	Rate of utilization of the soil washing plant influences treatment costs. Soil wash treatment costs U.S.$221/tonne if utilization is 25%, but drops to $70/ tonne if utilization is 100%.
27	50-300 mg/kg PCBs in soil and other solids	Particle size separation, chemical dehalogenation	Soil washing alone cost U.S.$380/tonne	Costs for dehalogenation were not provided.

Project Number	Contaminants and Media Treated	Treatment Processes	Overall Cost (per m^3 unless other units given)	Comments
31	Metals in mine spoil	Particle size separation, flotation	Not available.	The project was not at the stage where meaningful costs could be calculated.
33	360 mg/kg Cu; 621 mg/kg Cr; 414 mg/kg Zn; 1,204 mg/kg As	Particle size separation, leaching, adsorption	For proposed scale-up plant, cost estimated at £70-£80 (U.S.$115-130)/tonne.	Treating Hg-contaminated soil by aggressive leaching and complexing agents requires costly unique construction materials for a treatment plant.
Group 4: Physical-Chemical Treatment (no soil washing)				
31	Metals in mine spoil	Leaching, adsorption	Not available.	The project was not at the stage where meaningful costs could be calculated.
32	Heavy metals and radionuclides in clay/silt soil	Oxidation, complexation, precipitation, ion exchange	Not provided.	Report noted that using low concentrations of mild chemicals for leaching yielded low costs, but did not provide supporting data.
44	Coal tar DNAPL in gravelly soil	Thermally enhanced recovery	Total cost: approx. U.S.$1.8M	Cost for removing 5,400 L of recoverable coal tar and treating groundwater before reinjection or discharge.
47	TCE in clay	Electro-osmosis	U.S.$52-118/$m^3$;	Costs obtained from a cost-optimization model; 1-2 acre site with TCE at depth of 12-15 m (40-50 ft) electrode installation accounts for 20-40% of the overall cost.
Group 5: Photo-Oxidation Treatment (no soil washing)				
14	0.8-360 mg/L chlorinated compounds in groundwater	Biodegradation, photo-oxidation	15 million FF (U.S.$2.5 million) capital costs; 23 million FF (U.S.$3.9 million) annual costs	Costs for achieving acceptable drinking water limits. To achieve surface water discharge, costs would be U.S.$1.7 million for capital, and U.S.12.9 million annually.
38	1,000 µg/L TCE; 100 µg/L PCE; 15 mg/L PCP in groundwater and wastewater	Chemical oxidation, photo-oxidation	U.S.$2-3/$m^3$ for a 190 L/min unit	Unit costs increase as the size of the treatment unit gets smaller and contaminants become more difficult to oxidize.
40	BTEX and chlorinated solvents (Tyndall AFB)	Adsorption and photocatalysis	U.S.$1.46/$m^3$	The unit cost is for treating BTEX-contaminated water using a solar photocatalytic fixed-bed process (Pt-TiO_2 supported on silica gel).

In summary, unit costs will vary from site to site. However, these costs may sometimes be offset by the sale of concentrate produced by treatments although none of the project reports provided evidence that recovered concentrates were actually sold for profit.

5.8 FUTURE STATUS OF THE CASE STUDY PROCESS AND THE TECHNOLOGY AS A WHOLE

5.8.1 General Remarks

Physical-chemical methods, used alone or in combination with other technologies in a treatment train, have proved capable of treating mainly fine-grained materials contaminated with organic and inorganic contaminants. Despite their successes, these technologies have limitations that restrict their ability to treat certain types of media and contaminants effectively. If planned investigations reveal ways to overcome these limitations, the future of physical-chemical technologies will lie in their ability to cost-effectively treat a wide range of contaminants in a wide variety of media. This section of the chapter presents some of the issues that could have an impact on the future of the technologies.

5.8.2 Characterizing Contaminated Material

Soil washing provides a reliable way to treat contaminated solids, and specialized treatments like flotation enhance the overall physical separation of clean and contaminated materials. For the approach to be most effective, material to be treated must be properly characterized. When feed material is properly characterized, unit processes can be tailored to site-specific contamination situations.

5.8.3 Optimizing Performance of Unit Processes

Unit processes have proven excellent for media such as sand and gravel, but need to be improved for fine-grained soils where more than 30-35% of particles are less than 0.063 mm. In terms of other physical characteristics of contaminated materials, future investigations should investigate the feasibility of treating sediments and sludges with high water content.

Improved performance in the separation methods is required to increase the weight of the clean fraction and reduce the volume of contaminated concentrate. Obtaining better effectiveness at this separation stage of treatment could improve the performance of downstream treatments.

Optimizing plant operation may lead to lower levels of contaminants, a key requirement if reuse of treated material is required, and residual contaminants are otherwise unacceptably high. For example, the pilot-scale MGS described in Project 31 achieved a combined metal assay of 2.5% in the residue. Optimizing the MGS could result in higher separation efficiencies. Similarly, for soil washing and bioslurry treatment demonstrated in Project 26, using longer retention times or adding special microbial cultures were proposed as ways to achieve further reductions in contaminant concentrations in treated materials.

5.8.4 Investigating Cost-Effectiveness of Treatment Combinations

Preliminary investigations conducted for some of the case studies identified specific treatments that may perform better if combined with others. This observation confirms that the future of physical-chemical technologies lies in their ability to be used both alone and in existing and new combinations for treating contaminated materials. For example, a proposed new combination consists of MGS physical separation and chemical leaching as a potentially effective two-stage process for decontaminating metalliferous mine spoil. This combination needs further investigation with larger volumes and varieties of spoil samples before being used in the field.

Some existing combinations have proved to be cost-effective in some situations, but investigations should confirm their full range of application. For example, further investigations should assess the extent of application of the combined soil washing/slurry biodegradation processes which can likely be applied cost-effectively. Long degradation periods will cause problems when combining commercially viable throughput of physical processes with relatively slow biological processes. To enhance the viability of the treatment, further work should investigate ways to achieve rapid biodegradation to a reusable product. As an example, further work for Project 36 could investigate if continuous biological treatment can reduce the contaminant levels in fewer than the reported 28 days.

Similarly, many water treatment systems combine the Perox-Pure™ technology with carbon adsorption, air stripping, and biological treatment. Depending on the influent water quality and treatment objectives, the technology can be paired with others to produce a more cost-effective solution than any single process.

5.8.5 Investigating Residuals

The physical and chemical characteristics of residuals from physical-chemical treatments are key attributes when considering the applicability and acceptability of the treatments for any particular application. For example, two key factors will be their ability to achieve regulatory requirements for the reuse and recycling of treatment chemicals, and the use or disposal of treated materials and concentrates. Projects 31 and 47 illustrate considerations of regulatory requirements for residuals.

Further investigations should focus on the feasibility of reprocessing metalliferous mine spoil (Project 31) by single-stage physical separation or two-stage physical-chemical treatment to achieve regulatory criteria for treated material to be redeposited onsite. Tests of treated material should examine the susceptibility of residual tailings to biological leaching. If this leaching does occur, leached metals may contaminate surface water and groundwater.

The formation of potentially harmful intermediates may limit the applicability of emerging technologies. In the Lasagna™ technology (Project 47), for example, result show that iron filings in treatment zones can decontaminate TCE resulting in innocuous end products such as chloride ion, ethane, and ethene. While the technology satisfies regulatory criteria for these compounds, more attention has to be paid to potential intermediate products such as dichloroethene (DCE) and vinyl chloride. These products tend to be associated with the iron surface.

5.9 REFERENCES

1. Pearl, Mike and Peter Wood (1994). *Review of Pilot and Full Scale Soil Washing Plants*. AEA Technology, National Environmental Technology Centre, Oxford, 113p.

Chapter 6: BIOLOGICAL TREATMENT PROCESSES: INTRODUCTION AND EX SITU *APPROACHES*

R. Paul Bardos
r^3 Environmental Technology Ltd.

6.1 INTRODUCTION

This chapter reviews the projects presented at the Pilot Study that focused on, or included in a significant way, *ex situ* biological treatments. These are listed in Table 6.1. All of these projects investigated the treatment of solid materials rather than groundwater. This chapter also provides a brief overview of biological treatment with particular regard to *ex situ* approaches and appropriate situations for their use. It summarizes the case studies and then discusses them with regard to:

- performance;
- residuals and emissions;
- applicability;
- costs; and
- prognosis for the future.

Where possible, project references that are in the public domain have been provided. Some of the projects dealt with in this chapter are also dealt with in other chapters: Projects 24, 26, 31 and 36 are dealt with in Chapter 5, and Projects 15, 24, 26, 31, and 36 are dealt with in Chapter 11.

6.2 GENERAL OVERVIEW

6.2.1 Biological Processes, In General

Innovative treatments are often described as *ex situ* or *in situ*. *Ex situ* refers to processes applied to excavated soil either onsite or offsite. *In situ* refers to processes occurring in unexcavated soil, which remains relatively undisturbed. Treatment processes can also be categorized according to their general operating principles *(5, 32)*, for instance: biological, chemical, physical, solidification or thermal.

For ease of discussion, materials are considered in this chapter as three basic types in the context of materials handling: groundwater, soil, and slurry, where slurry is some mixture of soil and groundwater or added water from another source. “Soil” is used to describe the solid phase material. However, in reality, the solid phase materials encountered and treated encompass a far broader range of materials, including, but not limited to topsoil, subsoil, and other natural regolith, fill, waste deposits and industrial process residues, sediment, demolition debris, vegetation, and refuse. In many cases, remediation of bedrock is required. Typically, treatment of bedrock—if it is attempted at all—is approached *in situ*, so it is not considered in this chapter. Some materials onsite are liquid or semisolid in nature, such as sludges and coal tars. So far as *ex situ* biological approaches are concerned, these are treated either by mixing with a solid material or by treatment in a bioreactor in some form of suspension or slurry treatment *(25)*. In some cases, the semi-solid material to be treated is a process residue from an earlier non-biological treatment process such as soil washing.

Table 6.1: Projects Reviewed and References

Project Number	Project Title
6	*In situ*/on-site bioremediation of industrial soils contaminated with organic pollutants: elimination of soil toxicity with DARAMEND® *(55, 57)*
8	Biodegradation/bioventing of oil-contaminated soils *(35, 45)*
11	On-site biological degradation of PAHs in soil at a former gasworks site *(33)*
15	Combined chemical and microbiological treatment of coking sites/bioremediation of soils from coal and petroleum tar distillation plants
24	Combined remediation technique for soil containing organic contaminants: Fortec
25	Slurry reactor for soil treatment *(30, 39)*
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactors) *(16, 17)*
28	Use of white-rot fungi for bioremediation of creosote-contaminated soil
31	Decontamination of metalliferous mining spoil *(59)*
35	*In situ* soil vapor extraction within containment cells and combined with *ex situ* bioremediation and groundwater treatment *(47)*
36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles *(43, 60)*
43	Multi-vendor bioremediation technology demonstration project *(24, 31)*
49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil
54	Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors

Biological processes for the remediation of contaminated land depend on one or more of four basic processes: (1) biodegradation; (2) biological transformation to a less toxic form (*e.g.*, for metals); (3) biological accumulation into biomass; or, conversely, (4) mobilization of contaminants for downstream recovery. In general, established commercial processes are limited to those based on biodegradation.

The vast majority of practical biological treatments exploit degradation *(5, 8, 13, 38, 56)* and are variously described as bioremediation, bioreclamation, biotreatment or biorestoration. Contaminated sites are also commonly revegetated to improve their stability and aesthetic appeal and to reduce windblow of contaminated dust *(18)*.

Concerns about current biological processes include:

- Their susceptibility to inhibition by toxic contaminants *(13)* (*e.g.*, for example heavy metals) although some biodegradation processes appear quite robust *(26)*;

- The low biodegradability and or bioavailability of some common organic pollutants, found with other more degradable contaminants *(34)*. (Current research includes the use of chemical pre-treatments to enhance biodegradability *(1)* and treatment of an increasing number of compounds is found to be feasible, for example chlorinated solvents *(11)*);

- Residual concentrations of contaminants after treatment, whose environmental significance is not known *(34, 44)*; and

- The mobilization and release of potentially toxic, partially degraded contaminants from *in situ* treatments *(12, 27, 40)*.

6.2.2 Main Process Variations (by Biological Process)

Degradation and Transformation

Biodegradation describes the decomposition of an organic compound into smaller chemical subunits through the action of organisms. Both aerobic and anaerobic degradation pathways exist, although there are some differences in the types of compound that will degrade under aerobic and anaerobic conditions *(3)*. Principally, soil microorganisms (bacteria, fungi, and actinomycetes) are responsible for bioremediation processes, but some researchers are interested in prospects for plants and algae *(13, 53)*. As summarized below, plants may be of more immediate use in the accumulation of contaminants or as a means of stimulating soil microbial activity. These approaches are known collectively as "phytoremediation" and are regarded as an important emerging technology for future research*(4, 34, 49)*.

Completely degraded compounds are said to be "mineralized," and the end products of the aerobic degradation of chlorinated hydrocarbon might be carbon dioxide, water, and chloride ions. Guthrie *(23)* describes this as "ultimate biodegradation." He defines "acceptable biodegradation" as breakdown to below toxic levels, and "primary biodegradation as a structural change in the parent molecule. Primary biodegradation is more commonly referred to as "biotransformation."

Biotransformation may be of use in biological treatment of contaminated soil, but has not been exploited. It has the drawback that further transformations could regenerate toxic forms. In addition, biotransformation can be accompanied by an enhancement in toxicity.

Biodegradation may proceed via enzymic activity on compounds adsorbed into cells or through the activity of extracelluar enzymes active outside the confines of the cell. Cells also use enzymes to generate free radicals or peroxide ions that attack organic compounds, particularly insoluble compounds *(2, 5, 13)*. In many cases, organic compounds do not readily enter microbial cells since the compounds are either sorbed to soil surfaces, are too large, or are physically incapable of being sorbed into cells. Bioavailability is regarded as one of the key limiting factors for bioremediation *(34)*.

More complex compounds may not be completely degradable by single organisms, but are degraded by consortia of organisms, or in some cases may not be completely degradable in any circumstance. Some organic compounds may be coincidentally degraded as a result of microbial activity against other substrates, a process called "cometabolism." An example of this is the use of methane oxidation to degrade some chlorinated solvents *(14)*. There are a number of organic compounds, such as tetrachloroethene (PCE), whose degradation is not energetically favorable to microorganisms. However, in some cases, under anaerobic conditions, these compounds may be biodegraded. The compound does not serve as an energy source or carbon source, but is used as an electron acceptor, *i.e.*, it is reduced during the conversion of other organic materials *(40)*.

It is likely that several of these processes may occur simultaneously in practical bioremediation treatments; however, some techniques are designed to capitalize on particular microbial processes, such as the use of fungal lignase systems to degrade recalcitrant organic contaminants like pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAHs) (*26*).

Inorganic compounds may also be changed by microorganisms, either by direct metabolism (as in the oxidation of sulfur or the methylation of mercury) or indirectly through the release of ligands or acids (*6*). These processes may mobilize inorganic contaminants such as heavy metals. There may be potential applications for mobilization as a means of stripping inorganic contaminants from soils, and several laboratory- and pilot-scale initiatives based on microbial mobilization are underway (*5*). Arsenic and some heavy metals may be converted into volatile methylated forms by microbial activity (also referred to as "biotransformation"). However, the toxicity of the methylated compounds may raise serious issues of operational safety and environmental emissions from such an approach.

Other Processes

Biological immobilization of contaminants is common, for example, the sorption of metals or organic compounds to plant roots. The bioavailability of sorbed compounds may be reduced by this process, but the effect is temporary, depending on the lifetime of the root. Contaminants would be mobilized as the supporting plant matter was degraded. There is some evidence that PAHs may be irreversibly adsorbed into soil humus (*51*); however, the usefulness of this in land remediation may be limited by current approaches to hazard assessment based on total soil concentrations of contaminants.

Biological accumulation of contaminants by plants and fungi is a well-known phenomenon. The potential use of plants that accumulate metals in their leaves and shoots is being investigated as a possible means of removing metals from contaminated soils (*7*). The approach seems particularly suited to shallow contamination arising, for example, from sewage sludge disposal or atmospheric deposition of metal-rich dusts. More recently, interest has emerged in combining accumulation of contaminants with energy forestry to achieve use of the land during the remediation process.

Commercially Available Processes

At present, the great majority of commercially available bio-remediation techniques assist the biodegradation of fairly readily degradable contaminants: mononuclear aromatics (*e.g.*, benzene toluene, ethylbenzene, and xylenes); simple aliphatic hydrocarbons (*e.g.*, mineral oils and diesel fuel) and lower PAHs (2-, 3- and 4-ringed) *(8)*. However, full-scale applications of bio-remediation to treat more complex contaminants (such as pentachlorophenol, chlorinated solvents and possible more difficult PAHs) are taking place, and some successes are being reported *(11)*. Recently, the use of metal accumulation by plants has also begun to be exploited in full-scale practical applications *(58)*.

6.2.3 Main Process Variations (by Mode of Application)

Ex situ application of biological processes allows better process control—in particular, the breaking down of soil material into small particles (*e.g.,* by cultivation, grading, or conversion into a slurry). This overcomes one of the major limitations of *in situ* processes, which is ensuring the accessibility of the contaminant to the treatment *(9)*. *Ex situ* processes can be divided into four basic groups *(8)*:

(1) Shallow cultivation, where contaminated soil is cultivated in a treatment bed or *in situ* by cultivating the surface layers of a specially prepared area of a contaminated site (*e.g.*, Project 6);

(2) Windrow turning, where piles of contaminated soil often mixed with organic materials such as bark are turned on a regular basis using processes akin to green waste composting (*e.g.*, Project 11);

(3) Biopiles, where static piles of contaminated soil are vented and irrigated using processes akin to static pile waste composting (*e.g.*, Project 8); and

(4) Bioreactors where groundwater or a soil slurry is treated in a reaction vessel (*e.g.*, Project 25).

Cultivation

The term "landfarming" has been used to describe cultivation processes, but is avoided here to avoid confusion with the treatment of oily sludges by cultivation on land, which is also known as landfarming. Methods vary from simple to advanced techniques—which are all largely based on agricultural practice. Contaminated soil is spread over a surface, typically to a thickness of about 0.5 m. The soil is regularly mixed and tilled to improve soil structure and oxygen supply. Water can be supplied to adjust the moisture content and supply inorganic nutrients to the system. In many applications the treatment bed is placed over an impermeable membrane to ensure complete collection of leachate. Spray irrigation/recirculation of leachate is also common practice. An example configuration is provided in Figure 6.1.

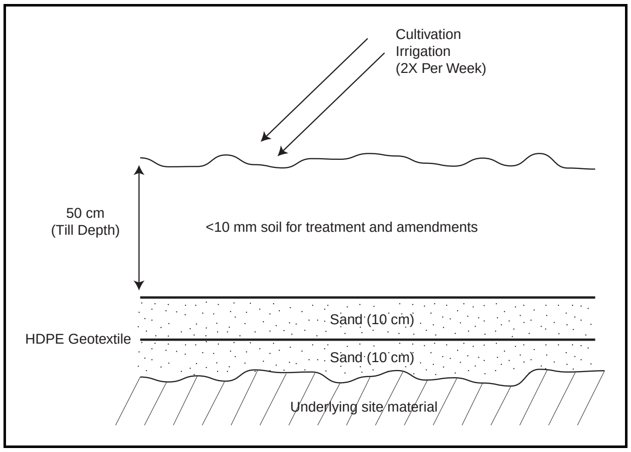

Figure 6.1: Section Through a Treatment Bed (based on Project 6)

Windrows

Treatment techniques using windrows are similar to approaches used for waste composting, for example, of urban and agricultural wastes. Soil is placed in thick layers or heaps (see Figure 6.2). Materials such as wood chips, bark, or compost are often mixed in to improve the soil structure and increase aeration. Regular turning and tilling is often carried out to further improve aeration. Specialized equipment using technology borrowed from the waste composting industry is typically used for this purpose. In most cases, true composting (*i.e.*, a controlled aerobic, solid-phase thermophilic process) does not take place. Furthermore, amendments tend to be added to condition the soil, rather than as part of an integrated waste management approach, which perhaps remains an under-exploited opportunity.

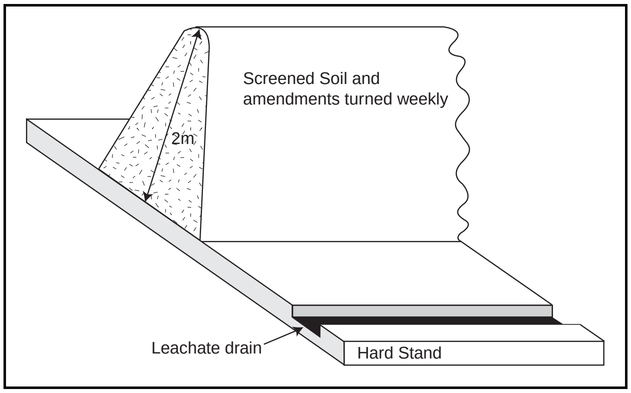

Figure 6.2: Windrow Treatment (schematic)

Biopiles

Excavated soil is placed in a static heap (*i.e.*, no mechanical turning or tilling is conducted). Nutrients and water are added to the contaminated soil by percolation or along a network of internal galleries. The conditions in the piles are monitored and optimized through aeration and water supply. An example schematic (based on Project 35) is provided in Figure 6.3. The principal distinction between biopiles and windrow-based systems is the use of active aeration and irrigation. Biopiles are closely allied to the aerated static pile technique for waste composting *(52)*, although refinements such as feedback control based on temperature, moisture, and partial pressure of oxygen (pO_2) are less frequent in soil treatment than aerated static pile composting. The technology has a longer history for waste composting, and there

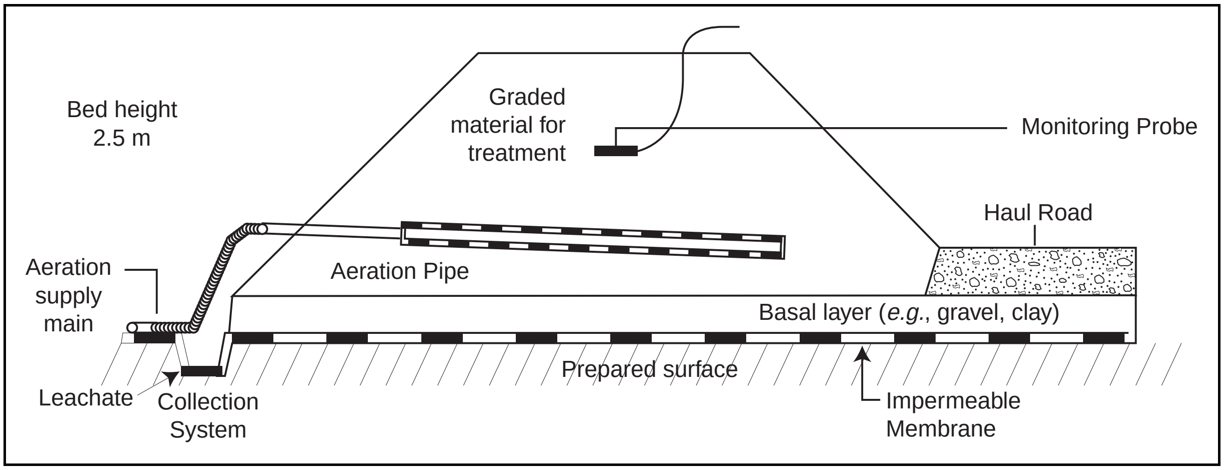

Figure 6.3: Example Biopile Configuration (based on Project 35)

would appear to be still some capacity for technology transfer to soil treatment (*e.g.*, combined aeration and turning technologies).

Bioreactors

Pre-treated soil (*e.g.*, soil with particles >4-5 mm removed) are slurried with water and treated in a purpose built reactor system with a mechanical agitation device. Within the reactor, controls on temperature, pH, nutrients, and oxygen supply can be amended to gain the maximum contaminant degradation rates using either microorganisms indigenous to the soil or specially added cultures.

Bioreactors can range from treatment lagoons *(38)* to contained in-vessel systems *(19)*, and the sophistication of engineering approach can vary accordingly. Bioreactors can also operate in the solid phase. Although infrequent for soil remediation, this is a common approach for waste treatment. Waste compost bioreactors often incorporate an ability to turn and mix materials, as well as to simply aerate. The technology is robust, and again there may be opportunities for technology transfer to soil remediation *(20, 48)*. An example slurry-phase bioreactor (based on Project 25) is illustrated in Figure 6.4.

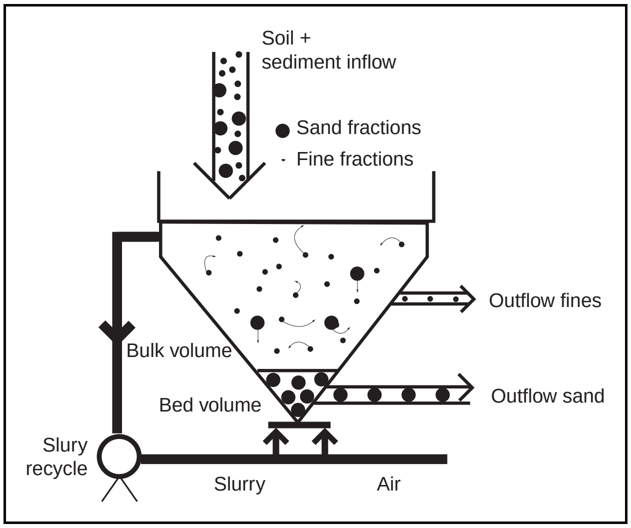

Figure 6.4: Principle of the DITS Reactor with the Dual Injection Manifold at the Bottom of the Reactor (based on Project 25)

6.2.4 Combinations with Abiotic Processes

The difficulties of remediating complex contamination problems with individual process technologies has led to the development of process integration, which combines unit process treatments to provide an effective overall treatment *(43, 54)*. Two examples follow:

- Bioventing, which can be applied *in situ* or *ex situ* in treatment beds, is an integrated technology that combines biodegradation and volatilization. A significant problem for biological treatment has been to supply the active microbial population with sufficient nutrients and oxygen to ensure rapid biodegradation. In bioventing, soil vapor extraction (SVE) is used to supply oxygen as well as a means of removing volatile organic compounds (VOCs) from soil. Bioventing is far more efficient at delivering oxygen to soil microorganisms than systems that use recirculated groundwater. Project 8 used bioventing to treat soil *ex situ.*

- Project 24 is a pilot-scale investigation that combined hydrocyclone treatment with separate "cleaned" sandy fractions from a process residue, which was then sequentially treated by photo-oxidation and biodegradation.

Treatment integration in general within the Pilot study projects is discussed in Chapter 11.

6.2.5 Extensive Approaches

Intensive treatments, such as soil washing or incineration, use relatively complex equipment and plants, and require a lot of resources for initiation, running, and support. Therefore, they tend to be costly. Extensive technologies operate over a longer period with low maintenance, cost, and energy requirements. Approaches being considered include reducing contaminant concentrations, environmental mobility, and availability and toxicity, or enhancing natural attenuation processes. Techniques include hyper-accumulator plants and enhanced rhizosphere-mediated biodegradation, and fixation by minerals. In addition to cost savings, they tend to have less impact on soil quality than their intensive counterparts. Indeed, biologically based extensive methods such as the promotion of *in situ* biological activity by plant roots actually may enhance soil structure and fertility. The development of extensive treatments is of particular interest to industrial holders of contaminated land as potential low cost treatments over the lifetime of existing industrial plant operation *(12, 44)*.

Extensive approaches considered to date are mostly *in situ* techniques *(11)*. However, *ex situ* approaches include techniques based on waste composting, and are particularly appropriate where there is a -possibility of synergy between the treatment of hazardous wastes and other organic wastes such as sewage sludge or green wastes.

6.2.6 Groundwater Treatment

Contaminated groundwater is treated in three main contexts:

(1) As part of a system where it acts as carrier to transport contamination from soil to the treatment process(es), for example, in pump-and-treat systems *(32)*;

(2) When it is removed to lower the water table for treatment of contaminated ground; and

(3) As effluent treatment prior to re-infiltration or discharge to surface water.

A permanent solution to groundwater contamination will always require the reduction of contamination in the aquifer and the source of contamination.

Where groundwater is treated above ground, biological approaches include:

- a variety of bioreactors *(5, 46)*;
- treatment within a soil mass (*e.g.*, through the irrigation of a biopile, windrow, or treatment bed); and

- combined treatment with solids in slurry bioreactors.

The majority viewpoint is that simple approaches to pump-and-treat, using groundwater as a carrier to effect an *in situ* treatment, are rarely effective; this has led to the emergence of more elegant approaches *(37)*. These can be divided into two broad and overlapping categories: treatment zones and active containment.

Treatment zones improve *in situ* remediation by treating contamination in a smaller, more clearly defined and better optimized subsurface volume to address typical limitations of *in situ* remediation, such as process and emissions control, and to ensure contaminant availability and accessibility. Treatment zones employ groundwater as a "carrier" for the contamination.

Contamination may be directed or mobilized to the *in situ* treatment technology by processes such as the natural groundwater flow, managed groundwater flow (*e.g.*, funnel and gate systems *(50)*), or by manipulation such as by using electroosmosis. This approach has a cross-over with *ex situ* techniques in several ways:

- The operating principle of the *in situ* treatment zone may be contained in some form of removable cartridge or cassette, in which case, it may be considered as a buried *ex situ* system;

- The treatment system may be entirely or partially above ground; and

- More complex permutations are possible, for example, where a fairly dispersed *in situ* technique is used to mobilize contaminants, which are then contained and collected for further treatment above ground.

Active containment, or use of treatment walls, is a special case of an *in situ* treatment zone that treats migrating contaminants, usually dissolved in groundwater or in the vapor phase, where the source cannot be treated. Active containment targets treatment of the pathway rather than the source. It aims to overcome the perceived limitations of passive containment measures (which physically restrict migration of contaminants) such as doubts over long-term barrier integrity and treatment of contaminants.

The control of the contaminant plume can be visualized in terms of a control surface or boundary beyond which contaminant levels are "acceptable." The treatment system may or may not act at this surface. For example, a treatment process may be remote from the boundary where subsequent natural degradation and attenuation also plays a part in contaminant destruction. Active containment deals with migrating contaminants. At its most elegant, active containment does not contain groundwater, but contains the contaminants by destroying them or removing them from the groundwater *(28)*.

6.2.7 Indications for Using *Ex Situ* Treatment Technologies

Within the process industries sector and among much of the research community, there is great interest in developing *in situ* treatment technologies because of their perceived advantages in terms of cost and environmental impact. These advantages are clearest when remediation can proceed over significant periods of time, and perhaps when *in situ* treatments are compared with excavation and transportation to the intensive *ex situ* treatment plants.

However, the availability of time is a critical limitation to the use of *in situ* treatments for many situations, for example, where an acute risk exists or a redevelopment is planned. Furthermore, *in situ* applications are limited by subsurface conditions. Even where *in situ* techniques are applied, many *in* *situ* treatment approaches still require the removal of concentrated hot spots. In addition, practical site reclamation for redevelopment often requires removal of debris and site materials. In such cases, *ex situ* treatment may be performed to reduce the volume of material requiring disposal offsite through materials recovery, or to render the materials more environmentally benign.

Ex situ treatment may take place onsite (*e.g.*, for minimization of material taken off site) or at a remote site (*e.g.*, to recycle re-usable components and render contamination "safe"). The costs of mobilizing a treatment plant usually means that on-site treatment is only cost effective above some threshold of volume of material to be treated. Many countries, including Canada, Denmark, Germany, and the Netherlands, have off-site biological treatment plants for contaminated site materials. However, an opportunity that has yet to be broadly exploited is synergy with recycling and reuse of contaminated site materials and other wastes, for example, construction wastes, civic amenity wastes, or compostable wastes. Indeed, the longer-term goals of sustainable waste management and sustainable approaches to dealing with contaminated land are seen not only as an opportunity for synergy, but requiring an integrated approach if the best opportunities for either are to be realized. An interesting illustration of this is where an old landfill must be excavated and removed for redevelopment. A particular interest may be the stationing of an off-site treatment plant at landfills where the opportunities for co-treatment with materials from different sites and waste streams is greatest *(21)*.

There also may be opportunities for synergy among the needs of sustainable waste management, recovery of materials from land remediation, and the improvement of marginal land. In this context, marginal land refers to land that could be remediated, but whose remediation is not possible from a strictly commercial viewpoint. An example is the possibility of linkage among land remediation, waste management, and sustainable energy forestry. The opportunity is the long-term reuse of waste (*e.g.,* as compost or site engineering materials such as gravel substitutes) in ongoing productive use of marginal land for non-food uses. This may be particularly appropriate for former coal fields, providing new jobs as well as environmental improvement and sustainable waste management into the long term. However, it could be appropriate for a wide range of marginal land types.

6.3 CASE STUDIES CHOSEN

The Pilot Study projects chosen as case studies for this chapter are listed in Table 6.1.

6.4 BACKGROUND OF CASE STUDIES AS A GROUP

Table 6.2 describes the Pilot Study projects involving *ex situ* treatment in terms of the type of technology configuration (as described in Section 6.2). Projects in the Pilot Study cover the four modes of treatment application described in Section 6.2.3. The majority of these projects examine exploiting biodegradation. However, one project examines bioleaching (mobilization of metals by reducing pH through the action sulfur-oxidizing bacteria). Another is an investigation of the risks posed by a variety of inorganic and organic contaminants. Table 6.3 outlines the process investigated for each project. Detailed project summaries are provided in Appendix IV.

Although site details are lacking for some projects, those sites for which details are reported are mainly wood preservation plants or other sites with PAH contamination, including gasworks and coking works. PAH and oil degradation are the main processes reported, although some projects also considered PCP degradation. One project considered treatment of chlorinated and non-chlorinated solvents.

Table 6.2: Overview of Selected Projects

Project		Technology Type	Input Material for Treatment	Site Details
6	*In situ*/on-site bioremediation of industrial soil contaminated with organic pollutants: elimination of soil toxicity with DARAMEND®	Cultivation (full-scale)	Screened soil (<100 mm) + proprietary amendment (a screen size of 250 mm was also mentioned)	Main results from Domtar Site, Toronto, Canada. Former wood preserving site that used PCP, and PAH-contaminated sediments from Hamilton Harbour
8	Biodegradation/bioventing of oil-contaminated soils	Biopile + monthly turning (full scale)	Screened soil + organic amendments	Boucerville (contaminated by transformer oils) Jonquiere (former rail station) Canada plus brief data from other sites
11	On-site biological degradation of PAHs in soil at former gasworks site	Windrow (+ "passive" aeration) (full-scale)	Screened soil (<80 mm) + organic amendments	Frederiksberg Gasworks, Denmark
15	Combined chemical and microbiological treatment of coking sites/bioremediation of soils from coal and petroleum tar distillation plants	Biopile ("pilot"-scale)	Soil + organic amendments / untreated soil	Not specified, France
24	Combined remediation technique for soil containing organic contaminants: Fortec	Bioreactor (part of a treatment train) (pilot-scale)	Soil slurry and sediment slurry contaminated with PAHs or hydrocarbons	Various, not specified, The Netherlands
25	Slurry reactor for soil treatment	Bioreactor (pilot-scale)	Clay-rich soil and harbor sediment contaminated with PAHs	Mijdrecht and Petroleumhaven, The Netherlands
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	Bioreactor (part of a pilot-scale treatment train)	Soil slurry (PAHs)	Former wood preserving facility (creosote contamination) , Lillestrom, Norway
28	Use of white-rot fungi for bioremediation of creosote-contaminated soil	Laboratory-scale R&D	Soil, examined degradation of higher PAHs	Former wood preserving facility (creosote contamination) , Southern Norway
31	Decontamination of metalliferous mining spoil	Laboratory-scale R&D on "bioleaching" of heavy metals	Mine spoil (metals)	Former metalliferous mine sites, Wales, U.K.
35	*In situ* soil vapor extraction within containment cells combined with *ex situ* bioremediation and groundwater treatment	Biopile (part of a full-scale integrated approach)	Screened and "vented" soil (various organinc and inorganic contaminants)	Derwenthaugh Cokeworks, U.K. (PAH contamination, cyanides, VOCs and metals)
36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles	Laboratory-scale bioreactors (part of a pilot-scale treatment train)	Soil slurries from a diesel contaminated soil, and a gasworks soil	Unspecified U.K. locations

Project	Technology Type	Input Material for Treatment	Site Details
43 Multi-vendor bioremediation technology demonstration project	Biopile (full-scale)	Soil contaminated with chlorinated and non-chlorinated solvents	Sweden 3-Chapman site, Sweden, New York, USA, an abandoned hazardous waste disposal area.
49 Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil	Laboratory-scale R&D	Soils treated at a full-scale *ex situ* biological treatment plant, various residual contaminants tested for.	Unspecified location(s), Switzerland
54 Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors	Bioreactor (pilot-scale)	Soil (PAHs, PCP)	A closed wood preservation plant (PAH contaminated), oil storage plant (PCP contaminated), Sweden

Table 6.3: Outline of Treatment Processes By Project

Project	Process Outline (see Project Summary for further Information)
6 *In situ*/on-site bioremediation of industrial soil contaminated with organic pollutants: elimination of soil toxicity with DARAMEND®	The technology is a proprietary system: DARAMEND® bioremediation. It is targeted at a range of organic contaminants including aliphatic and aromatic hydrocarbons, chlorinated phenols, and phthalates. The test results reported to the Pilot Study focused on PAH and PCP in the range of 1,000s and 100s of mg/kg. The treatment is based around a proprietary soil amendment. Its composition varies from site to site depending on soil analyses. The amendments are based on plant materials and increase the water holding capacity of the soil. They include slow-release nutrients and surfaces that sorb contaminants with the claimed effects of reducing their toxicity to microbial activity and also increasing their accessibility to degraders. Soil amendments are introduced at 1-5% by weight using conventional agricultural equipment followed by regular cultivation. For "*ex situ*" application, soil or sediment to be treated is transported to the treatment area and homogenized by tilling with a power take-off driven rotary tiller. During the remediation process, soil moisture content is maintained within a narrow range with drip irrigation. The DARAMEND® amendment is also cultivated directly into to the surface of the contaminated site, which is termed an "*in situ*" application. Pilot Study reports also suggest its use in biopile applications. It is conceivable that the amendments could also be applied in windrow and solid-phase bioreactor systems.
8 Biodegradation/bioventing of oil-contaminated soils	Biogénie has developed a biopile-based, *ex situ* bioremediation technique whereby soil is heaped in contained areas, such as on an asphalt pad with drainage collection, and supplied with oxygen, moisture, and nutrients to enhance natural degradation processes. The test results center on soils contaminated with oil and grease in the range of 10^4 mg-kg^{-1}. The project also discussed the use of biofilters for emissions control from the process (see project summary). Since the beginning of the Pilot Study the company has also carried out a large number of commercial remediation projects. Results from 24 of these projects were presented in 1996, total tonnage nearly 400,000 tonnes. On the basis of these projects, the company calculated average degradations of 75% for mineral oil and grease; 99% for BTEX; 95% for PCP; 90% for total PAH including 99% for naphthalene.

Project	Process Outline (see Project Summary for further Information)
11 On-site biological degradation of PAHs in soil at former gasworks site	Windrow-based treatments were tested for their ability to reduce PAH concentrations at pilot-scale (20-30 m^3) after laboratory and microcosm studies on <4-mm fraction. The soil was screened at 80 mm. The tests were performed on sandy soil containing total PAH at about 400 $mg\text{-}kg^{-1}$. After mixing soil was spilt into test windrows. Windrows tested different amendments (wood chips, compost, none) and the impact of adding nutrients (N, P, K) and Ca or detergent solution was examined.
15 Combined chemical and microbiological treatment of coking sites/bioremediation of soils from coal and petroleum tar distillation plants	Investigations encompassed the use of bioreactors and biopiles at pilot-scale to treat PAH & hydrocarbon contaminated soil (10^3 mg/kg. Biopiles were made of contaminated soil/wastes mixed with organic amendments (straw, sawdust, uncontaminated soil). The effect of adding oxidizing agents (hydrogen peroxide, sodium hypochlorite, and ozone) during biopile construction was also evaluated.
24 Combined remediation technique for soil containing organic contaminants: Fortec	Fortec® consists of three unit operations combined in series: multi-step hydrocyclone separations, UV/hydrogen peroxide photochemical pretreatment, and slurry-phase bioremediation. It deals with more recalcitrant contaminants in fine fractions (a common soil washing residual). The photo-chemical oxidation is designed to transform recalcitrant organic compounds into more readily biodegradable compounds. The bioreactor is slurry based and operates at mesophilic temperatures (10-25°C). Mixing is achieved by slurry recirculation and reactor operates on a batch-wise process, residence time 3-20 days. The reactor has been tested at up to 300 m^3 as part of an integrated soil washing process. Testing has been carried out on soils contaminated with diesel oil and PAH.
25 Slurry reactor for soil treatment	This project treats excavated clay soils and sediments contaminated with organic compounds, such as mineral oil and PAH. The treatment technology described is the Slurry Decontamination Process (SDP), which combines separation processes with a microbiological slurry reactor. The bioreactor is used to treat a <4 mm fraction produced by removal of debris (>60 mm), grinding, and sieving. The basic bioreactor configuration has been tested up to 4 m^3. The process uses a cascade of bioreactors. A key aspect of the configuration is the triangular base and the turbulent flow produced with the bioreactor to maintain the soil particles in suspension, mix and grade them by particle size. Coarse particles settle out in the first bioreactor. Subsequent bioreactors treat the finer fractions and the more recalcitrant contamination attached to them or remaining in solution or suspension. Testing has focused on mineral oils and PAHs.
26 Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	This project is an investigation into the remediation of three and four ring PAHs contaminated soils using a process that combines soil washing (especially froth flotation) with slurry-phase bioremediation. The project consisted of bench-scale treatability studies and pilot-scale remediation trials. Bioslurry testing was carried out initially at bench-scale (1 L), and at 454 L, using fines slurry from froth flotation in a tonne/hour soil washing plant. PAH degradation was determined.
28 Use of white-rot fungi for bioremediation of creosote-contaminated soil	Laboratory-scale testing was carried out to determine the potential of white and brown rot fungi to degrade PAHs in soil from an abandoned wood preservation site contaminated with creosote. Testing consisted of screening a limited number of fungal types for their capacity to degrade PAH and determine their requirements for optimal degradation performance at mesophilic temperatures (20°C), such ase lignin-rich substrates. Subsequently, 60-L batches were tested. Pilot-scale testing due in 1995/96 has been delayed.

Project		Process Outline (see Project Summary for further Information)
31	Decontamination of metalliferous mining spoil	This project investigated a variety of treatments for dealing with metalliferous mining wastes. Biological investigations centered on ferric bacterial leaching (*Thiobacillus* spp) of metals from metalliferous mine tailings and from a fine fraction residue from MGS (a particle separation process exploiting density—see Chapter 5). The investigations aimed to understand both the potential of "bioleaching" as a treatment, and as a factor causing the release of metals from tailings and residues in the environment. Investigations were carried out at bench-scale.
35	*In situ* soil vapor extraction within containment cells combined with *ex situ* bioremediation and groundwater treatment	Investigation of the former Derwenthaugh Cokeworks site identified an area of 7.9 ha that was significantly contaminated with coal carbonization wastes from the original plant including BTEX, PAHs, phenols, heavy metals, and cyanides. The remedial scheme involved four stages: (1) Installation of a cut-off wall to protect the adjacent river from further pollution and to allow safe excavation (to a depth of 5 m) of the contaminated ground; (2) Installation of wells for Dual Phase Vapor Extraction (DVE) to remove VOCs and free phase product; (3) Use of wells to abstract contaminated groundwater for surface treatment; and (4) Excavation and biological treatment of contaminated ground. A biopile technique was used to treat 28,000 m^3 of material in four batches using continuous forced aeration over 2-3 months. All material was screened at 100 mm, with oversize being crushed and then re-used on site if found acceptable.
36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles	Laboratory-scale, slurry-phase bioreactors (10-L) were used to test the potential for biodegradation of contaminants in fractions of soil from a gasworks site and from a site contaminated by diesel (locations not revealed). Fractions had been produced from a pilot-scale soil washing plant and had been stored briefly prior to testing. Two fractions of diesel-contaminated soil were tested: 0.002-0.01 mm and <0.002 mm. One fraction of gasworks soil was tested (<0.063 mm). Test periods were 10-14 days, and the bioreactor operated at mesophilic temperatures (15°C or 25°C). The effect of nutrient amendments was also evaluated.
43	Multi-vendor bioremediation technology demonstration project	The biopile treatment investigated was one of three technologies investigated at field-scale at the Sweden 3-Chapman site. The other two were *in situ* approaches and are discussed in Chapter 4. The site is an abandoned hazardous waste disposal area containing very high concentrations of chlorinated and non-chlorinated solvents such as trichloroethylene, tetrachloroethene, 2-butanone (MEK) and toluene. Materials were tested at pilot-scale (76 m^3 biopiles). Discontinuous and continuous forced aeration was tested. Irrigation was via a sprinkler system.
49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil	Mineral oil products are major pollutants found at contaminated sites in Switzerland. Certain residual pollutants remain after soils contaminated with oil products have been bioremediated. The emission levels to be expected during the reuse of remediated soil were estimated in laboratory and field tests. The remediated soil material used for all tests came from various minor oil spills (primarily involving EL heating oil) and was combined before being sent as a single batch to a bioremediation plant. The contaminant content in the fine material (<2 mm) was 780 mg (TSEM) and 430 mg/kg (TPH), in each case related to the dry content of the sample. The PAH content (according to EPA) was below 2.8 mg/kg and was not measured subsequently. The project was subdivided into the following operational stages: (1) physical and chemical characterization of the residual contaminants; (2) environmental behavior of the residual contaminants; (3) effects of the residual contaminants on the environment; and (4) evaluation of the environmental acceptability by means of a risk assessment.
54	Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors	Eko Tec has carried out several full-scale remedial actions at contaminated sites across Sweden. This project reports on the intended use of these reactors to treat 3,000 metric tons of creosote-contaminated soil containing 1,000-10,000 mg/kg PAHs and 100 metric tons soil contaminated with 500-1,000 mg/kg PCP. Small-scale bioreactors were used to treat approximately 1 m^3 of each contaminated soil. Pilot-scale testing was scheduled for 1996/97 but results have not yet been reported.

6.5 PERFORMANCE RESULTS

6.5.1 Project 6: *In Situ*/On-Site Bioremediation of Soils Contaminated with Organic Pollutants: Elimination of Soil Toxicity with DARAMEND®

A 216-m^2 test plot and a 12-m^2 control plot were compared using *ex situ* treatment beds (Table 6.3). Total PAH removal was in excess of 90%, and total chlorophenol removal was just below 90% using the DARAMEND® technology *(55)*. These removals were about double the removals found for the control plot, which was left unattended over the treatment period (254 days). Removals for individual PAH and chlorophenol compounds showed some variation, (from 41% to 98%). Higher-ring PAH compounds were more recalcitrant. Tests of toxicity to earthworms and seeding emergence also indicated amelioration through treatment. Total petroleum hydrocarbon (TPH) removal in the test plot was 87%. Interestingly, a zero value for the TPH removal was recorded for the control plot, despite the reported removals of PAHs and chlorophenols. The fate of compounds was not reported (*e.g.*, disappearance into humic materials versus degradation). The vendor has provided further case study information where similar treatment performances were achieved.

6.5.2 Project 8: Biodegradation/Bioventing of Oil-Contaminated Soils

Field tests at Boucherville and Jonquiere reported total hydrocarbon removals of around 70%. The contractor, Biogenie, also presented summary data from 25 practical remediation projects. The cumulative amount of material treated was around 400,000 "tons." (Note the exact unit of measurement was not specified). These case studies are listed in Table 6.4. Biogenie reports average removal efficiency for a variety of contaminant classes: mineral oil and grease, 75%; benzene, toluene, ethylbenzene, and xylenes (BTEX), 99%; PCP, 95%; and total PAHs, 90%, with 99% removal for naphthalene.

Table 6.4: Biogenie Case Studies

Type of Site	Number of Sites	Amount of Material Treated (tons[1])
Gas station (decommissioning and underground storage tank replacement)	8	174,800
Former diesel power station	5	78,200
Manufactured gas plant	1	75,000
Refinery	2	40,500
Former petroleum depot	3	10,000
Industrial yard and waste lagoon	2	7,000
Others (railroad yard, electrical substation, *etc.*)	4	4,700
TOTAL:	**25**	**390,200**

[1] The original reports do not specify whether "tons" refers to metric tons (tonnes), U.S. short tons (2,000 lbs), or Imperial long tons (2,240 lbs).

Aging has been suggested as a major factor in reducing the degradability of mineral oil and grease. Some projects were halted as soon as regulatory criteria were met. Pile temperatures may be on the order of 50°C, so some loss of organics through volatilization will take place. However, based on the tests at

Jonquiere, Biogenie believes that more than 99% of contaminant removal is due to degradation. No other information on fate of compounds was reported. Field-scale performance tends to be less than the potential treatment performance based on bench-scale test work. This indicates some potential for further optimization of the full scale treatment. The trade-off is whether such optimization is achievable at a reasonable cost and within a reasonable treatment duration.

6.5.3 Project 11: On-Site Biological Degradation of PAHs in Soil at a Former Gasworks Site

Ten turned-windrow configurations were tested (Table 6.5), and the authors compared: "ordinary" sampling with analysis shortly after sampling; freeze drying for sample preservation; and freezing of samples for sample preservation.

Table 6.5: Project 11 Treatments

Windrow [1]	**Amount of soil (m^3)**	**Aeration**[2]	**Treatment at initiation of test**	**Treatment in the test period**
IG Control	33	-	-	Addition, as required, of: - NPK fertilizer - calcium nitrate - water
IB Control	21	-	-	
2G	19	Turning	+ 11 m^3 wood chips	
2B	19	Aeration	+ 11 m^3 wood chips	
3G	20	Turning	+ 10 m^3 compost	
3B	20	Aeration	+ 10 m^3 compost	
4G	32	Turning	+ detergent solution	Addition of detergent solution to windrows 4G and 4B
4B	32	Turning	+ detergent solution	
5G	33	Turning	-	
5B	36	Turning	-	

Notes:

[1] (1G-5G): Windrows located outside.
(1B-5B): Windrows located inside.

[2] Aeration by turning of soil with excavator (a total of 10 times during the test period).
Aeration via air drains in the bottom of the windrow from where air is drawn (around 50 m^3/hour).

[3] A 5% detergent solution was added three times during the test period. A total of 1.6 g of detergent/kg of soil was added to test windrow 4G, and 2.6 g of detergent/kg of soil was added to test windrow 4B.

The sample preservation route had a strong impact on reported findings. For freeze-dried samples no significant differences between PAH removal for the different treatments were found. However, some differences were found for analyses of ordinary samples. Significant degradation (at the 5% level) compared with the starting concentration was found for both indoor and outdoor control batches, and for batches that had detergent addition and were turned. In addition, the indoor batch with turning but not detergent addition also showed significant total PAH removal. The remaining piles, including piles with compost addition (turned or otherwise), showed no significant decrease in total PAH concentration. It appears that turning is beneficial except that the control batches that were not turned also showed significant decreases in total PAH concentration. This study shows the difficulties in interpreting biodegradation data. The data are strongly affected by the sample preservation and subsequent analytical approach. Furthermore, results vary greatly for individual PAHs. The authors suggest that bioavailability was a limiting factor for PAH removal and was affected by aging and sorption of the PAH to soil surfaces. It may also be that the relatively low initial levels of PAH in the soil (400 mg/kg in total) affected treatment performance, although this is not suggested by the authors. The low initial concentration may have meant a much smaller pool of available degradable PAHs, and hence a much slower initiation of biological action.

6.5.4 Project 15: Bioremediation of Soils from Coal and Petroleum Tar Distillation Plants

Biopiles and recirculating bioreactors were used to screen 14 fungal and biological isolates. However, no detailed results were provided for this project.

6.5.5 Project 24: Combined Remediation Technique for Soil Containing Organic Contaminants: Fortec

The process concept uses a hydrocyclone treatment to separate the sandy fraction from finer soil grains. The fines are then treated biologically in a batch mode slurry reactor (3% solids) with a retention time of 3-20 days. The test work investigated whether a photochemical treatment of the hydrocyclone-treated soil before biological treatment led to further reductions in residual contaminant concentrations in the treated residues. The photochemical pretreatment consisted of ultraviolet (UV) irradiation and addition of hydrogen peroxide.

The pilot-scale reactor had a capacity of 25 m^3, and its contents were mixed by air sparging and slurry pumping. The initial charge of biomass was 1 m^3 of activated sludge from sewage treatment. Subsequent batches were seeded with recycled biomass from earlier runs. Reactor effluent was recycled to a process water "buffer." Nitrogen and phosphorus amendments were made during processing, based on initial contaminant loadings. Processes were carried out at ambient temperatures (10-16°C).

Tests on mineral oil contaminated soil (input loadings 400-5,000 mg/kg) set a target residual concentration of 100 mg/kg. Treatment times to reach this target were found to be in the range 3-8 days. The sandy fractions separated by hydrocyclone treatment generally contained less than 50 mg/kg mineral oil. No detectable benefit of photochemical pretreatment was found.

Tests on PAH-contaminated soil (input loading 30 mg/kg) used target residual concentrations of 1 mg/kg and 20 mg/kg. Only slight PAH removal from the fines fraction took place in the absence of photochemical pretreatment. With pretreatment, PAH levels decreased to around 5-10 mg/kg after 15 days treatment in the bioslurry reactor. If the fines fraction and sandy fraction were recombined, final residual PAH concentrations would be in the order of 2-4 mg/kg, which is lower than 20 mg/kg and close to 1 mg/kg. The accumulation of organic effluents in the process effluent was not severe.

Further studies on high molecular weight PAH compounds concluded that degradation rates were limited by contaminant bioavailability, which decreased due to strong adsorption of these compounds to organic matter in the soil. The photochemical pretreatment appeared to act as a mechanism for destroying the soil organic matter and increasing contaminant bioavailability. Comparative results showed that pretreatment significantly increased slurry phase biological degradation of PAH compounds. Sixty-nine percent of the PAH compounds were degraded after 12 days for the pretreated sample compared with 26% for the sample without photochemical pretreatment. It was concluded by the authors that photochemical destruction of soil organic matter enhances subsequent degradation but the technique would be limited to soils with a naturally low soil organic matter content (tests of the 300-m^3 reactor were not reported in detail).

Tests on β-HCH (lindane), including chemical pretreatment, resulted in no biological degradation of the contaminant. It was concluded that the chemical stability of β-HCH was too high for this combined process.

6.5.6 Project 25: Slurry Reactor for Soil Treatment

Pilot-scale tests (1 m^3) were conducted, and removal rates of 95% for oil contamination (Petroleumhaven clay soil) and 90% for total PAH (Mijdrecht sediment) were achieved in under two weeks. Starting concentrations were 800 mg/kg and 300-400 mg/kg respectively. A lower removal of oil contamination was found for the Mijdrecht sediment (80%). Process losses to volatilization were checked using capture of VOCs in filters and found to account for 1% or less of contaminant removals.

6.5.7 Project 26: Treatment of Creosote-Contaminated Soil (Soil Washing and Slurry Phase Bioreactors)

Bench-scale tests indicated that:

- PAH degrading organisms could be isolated from the creosote contaminated soil, and under optimal culture conditions, 94% of PAHs was degraded in 7 days (after acclimation); and

- PAHs could be concentrated by froth flotation**.**

Pilot-scale test work using a 454-L bioslurry reactor examined the treatment of PAH concentrates from froth flotation. Process optimization was carried out for biostimulation using nutrient (nitrogen and phosphorous) addition, pH amendment, aeration, addition of surfactants and temperature control. Tests were carried out on five 600-L batches from two clay-rich soils of solids content 14-20%. These initial tests resulted in 97% PAH removal—better than the bench-scale finding. Residual PAH concentrations were 71-200 mg/kg, from starting concentrations of 480-6,000 mg/kg. The removal of PAHs was found to correspond with oxygen uptake indicating that aerobic biodegradation had taken place. Addition of commercially available inocula was not found to be necessary at pilot-scale.

6.5.8 Project 28: Use of White-Rot Fungi for Bioremediation of Creosote-Contaminated Soil

Screening tests were conducted using the white-rot fungi *Pleurotus ostreatus* and *Trametes versicolor* and the brown-rot fungus *Lentinus leptinus.* The tests were used to evaluate different lignin substrates, such as wheat straw, wood chips (birch or pine), and newspaper, and to determine the influence of pH, aeration, and addition of compost. Tests were carried out either on petri dishes or in 1-L Erlenmeyer flasks. Following these tests, *Pleurotus ostreatus* was investigated further using wheat straw as the lignin substrate.

Contaminated soils were incubated with straw and fungus for 8 weeks at 20ºC. A range of supplements was added (peat, compost, potato pulp). Degradation performance was dependent upon the number of aromatic rings in each PAH compound ranging from up to 70% degradation for 3-ring PAHs to less than 35% for 5-ringed PAHs.

Further bench studies (using 60-L batches) investigated the impact on degradation of indigenous microbial populations as a pretreatment, followed by fungal inoculation. The pre-inoculation incubation period was two months. After inoculation, samples were incubated for a further three months. Samples incubated with bark prior to fungal inoculation were found to show the greatest PAH degradation. This benefit was reduced if fertilizer was also added during the pre-inoculation incubation period. Degradation of PAH was greater at 20°C than at 8°C; however, the benefit of preliminary incubation with bark was greater for the lower temperature. Compared with controls, degradation of PAHs, but not heterocyclic compounds, was enhanced by the fungal inoculation.

Radiolabelling of the PAH compounds was used to enable tracing of treatment metabolites to be conducted. These produced the contradictory findings that no accumulation of intermediate metabolites was detected, yet mineralization rates were low.

6.5.9 Project 31: Decontamination of Metalliferous Mining Spoil

Biological leaching due to microbial generation of sulfuric acid from sulfide was investigated for a highly oxidized sandy spoil (Frongoch); fine particle size sulfitic material (Y Fan); and high metals content tailings (Cwmerfyn). Ten-gram samples were subjected to a standard bioleaching test (from the Canadian Centre for Mineral and Energy Research) which was not described. Aliquots were tested of untreated material (“head”); residues remaining after soil washing (as described in Chapter 4); and a heat-treated aliquot (500°C for 18 hours) intended to simulate oxidation through weathering in the long term. The residues remaining after soil washing tended to have a lowered content of lead, zinc, cadmium, and sulfur.

Heat-treated samples showed higher zinc leaching than untreated samples. In all cases, the initial rate of bioleaching of zinc was high but then declined. The authors concluded that bioleaching can lead to significant movement of zinc from the solid to the aqueous phase. In regards to using bioleaching as a treatment, the authors concluded that it would be ineffective for lead. Lead would be rapidly precipitated as sulfate and hence remain in the solid phase. It was also regarded as less suitable than chemical leaching for zinc removal. However, bioleaching may have a significant environmental impact for zinc spoils, even if reprocessed, in cases where iron sulfide is also present and conditions are aerobic.

6.5.10 Project 35: Combined *In Situ* Soil Vapor Extraction within Containment Cells Combined with *Ex Situ* Bioremediation and Groundwater Treatment

Initial laboratory-scale studies discounted the need for using inocula in the proposed biopile system. Nutrient addition and aeration were found to enhance biodegradation at this scale. However, at full-scale, attempts to reproduce optimization through nutrient addition were not found to be cost effective.

Following the main works, it was noted that the main factors affecting the degradation process were aeration and ambient temperature. Attempts to replicate the laboratory conditions indicated as beneficial showed no cost benefits at full-scale. Significant reductions in the contaminant levels were achieved through redistribution and volatilization. Often these processes alone were enough to achieve the specified criteria, with no further action required. A key contribution to success is careful management of material batches and the screening of materials before placement in the biopiles. Treatment targets were set by the local regulatory authorities to allow reuse of the treated material onsite. No additional information on removal rates was reported.

6.5.11 Project 36: Investigation of Enhancement Techniques for *Ex Situ* Separation Processes, Particularly with Regard to Fine Particles

Bench-scale (10 L) bioreactor degradation of organic contaminants produced from a pilot-scale soil washing plant was investigated. Soil washing treatment residues for a gasworks soil and a diesel contaminated soil were tested.

For the gasworks soil, the <0.063 mm fraction was tested. Management of pH was difficult, with large decreases in the first 4 days of operation requiring correction. In addition, CO_2 was consumed by the process over this period of time. The authors believe this was due to the stimulation of chemolithotropic organisms, such as *Thiobacillus*, metabolizing sulfide compounds in the gasworks material. Three bioreactor tests were carried out: one at 12°C, one at 12°C with added nitrogen (N) and phosphorous (P), 25°C operation with added N and P. The best performance came from the 25°C treatment, but still only 40-50% of PAHs and 20% of TPH were removed after 28 days. There was no indication of cyanide degradation. It was suggested that the initial problems with acidification reduced the potential for PAH degradation.

Greater success was achieved for the diesel-contaminated soil. The size fractions 0.002-0.01 mm and <0.002 mm were treated. (Note that the performance of the soil washing stages is discussed in Chapter 4). A single test of degradation in a bioreactor at 15°C with no additives was carried out for the 0.002-0.01 mm fraction. Three tests were carried out for the <0.002 mm fraction: 15°C no additions; 15°C plus N and P, 25°C plus N and P. Two flushes of activity were noted for the <0.002 fractions tested, the first over the initial three days of treatment, and a second less intense flush some 8 to 10 days later. The authors postulated that during the first flush microorganisms degraded readily available substrates, and then a period of acclimation took place to deal with more complex substrates, resulting in the second flush of activity (as measured by CO_2 release). The size of the flush was enhanced by both temperature and nutrient addition. Similar removal rates for TPH (80%) were observed for both the 15°C and 25°C treatments with N and P addition. The removal rate for the 15°C treatment was around 20% without nutrient addition, similar to the removal rate found for the <0.002 to 0.01 mm fraction, which was also tested at 15°C without nutrient addition. The duration of all four tests was 28 days.

6.5.12 Project 43: Multi-Vendor Bioremediation Technology Demonstration Project

Aeration of two 76-m^3 test piles (Table 6.3) was found to be difficult because of the fine texture of the soil being treated. Average removal percentages of VOCs by the biopile technologies ranged from 43-99%, depending on the compound.

Soil clean-up goals were set by the New York State Department of Environmental Conservation for six VOCs: acetone, 200; methyl ethyl ketone (MEK), 600; methyl isobutyl ketone (MIBK), 2,000; PCE, 2,500; trichloroethene (TCE), 1,500; and dichloroethene (DCE), 600 µg/kg. Ninety percent of the tested samples were to meet these targets to achieve compliance (success) in the test.

Only 79% of the samples from the biopile treatment met these limits, so on these grounds it was deemed unsuccessful. Stripping and volatilization accounted for some of the VOC removal. The treatment duration was nine months. The aeration used was negative forced aeration (*i.e.*, air was sucked through the piles). Evidence from conventional composting technology is that negative aeration tends to be less effective for process optimization, especially for finely-textured materials such as sewage sludges *(52)*. However, positive aeration would require containment of the process to prevent the release of VOCs.

6.5.13 Project 49: Characterization of Residual Contaminants in Bioremediated Soil and Reuse of Bioremediated Soil

The availability of residual contaminants remaining after biological treatment was tested by leaching tests. Biodegradability studies and bioassays of the residues' toxicity were also performed. The nature of the treatment process was not specified, only that it was a commercial treatment plant, presumably *ex situ* and offsite. Dissolved organic carbon levels in the leachate of the treated soil were comparable to those from gravel. The residual organic contaminant levels, while detectable, were found to be only slowly leachable and only slowly biodegradable. Only around 10% degradation was observed over a two-year period. No negative impact was found on the growth yield for a number of plant species compared with controls in growth trials. Indeed, a significant enhancement was reported. Patterns of plant growth were normal. Ecotoxicity tests (using *Daphnia* and *Vibrio ficheri*) did not detect significant toxicity from soil leachates. A qualitative risk assessment based on the experimental findings concluded only a low possibility of adverse effects on human health and the environment from residual contaminants in the treated soil.

6.5.14 Project 54: Treatment of PAH- and PCP-Contaminated Soil in Slurry Phase Bioreactors

A trial using a 1-m^3 Eko Tec bioreactor over 28 days was carried out at 24-28°C. Biostimulation and bioaugmentation were conducted. Input material was screened at 2-3 mm, and the total PAH concentration was 859 mg/kg. The residual concentration after treatment was 75 mg/kg. In a second trial, the Eko Tec bioreactor was evaluated in parallel with a 450-L EIMCO reactor. In this case, concentrations of total PAHs were 313 mg/kg and 164 mg/kg, respectively. Both bioreactors yielded total PAH levels of 48 mg/kg after 28 days. Emissions of VOCs were found to be negligible. Eko Tec also reported a PCP treatment trial, using soil with an initial PCP level of 630 mg/kg. Redox conditions were varied from anaerobic to aerobic over a 6-week period. The exact nature of the process was not described. The PCP level after treatment was reported to be 80 mg/kg. An unspecified composting treatment was also found to reduce PCP levels over a 4-month period, with initial and treated concentrations of 126 mg/kg and 75 mg/kg, respectively. The full-scale process will be included in the Phase III Pilot Study.

6.6 GENERAL DISCUSSION OF PROJECTS

The general level and quality of information provided in a number of projects is inadequate to support a detailed discussion. However, the following points were worthy of note.

Ex situ biological treatments, with the possible exception of bioslurry reactors, are rapidly becoming established technologies for contaminated solids. The number of full-scale demonstrations and commercial projects has increased for several of the treatment approaches included in the Pilot Study, in particular for biopile and cultivation-based approaches. These approaches appear to be robust and relatively simple treatments for organic contaminants including simple alkanes and aromatics, as well as for more recalcitrant compounds such as 3- and 4-ringed PAHs and PCP. However, this is not a uniform picture. Biological treatments may fail to reach desired targets, even where there are good experimental reasons to believe that they should succeed. The reasons for this often appear to be associated with the texture of the contaminated medium, its organic matter content, and its age (Section 6.8).

While it is hard to make a generalization, it does appear that the technical “know-how” of the remediation contractor is also a key factor to success. The likelihood of success for solid phase treatments appears to be related to the “ingredients” in the mix of materials used, and to relatively simple process changes. Examples of these simple changes include how to improve porosity for fine-grained soils, how to improve activity for low initial concentration or for aged contaminants, and how best to optimize the flow of air and water.

One issue that is well-known in waste composting but has been little reported in biopile projects is that of “edge effects.” Materials at the edge of a static pile or treatment bed may be affected by greater variations in process conditions such as temperature, moisture, or nutrient supply, but conversely have better access to oxygen. The significance of edge effects is that treatment effectiveness depends on where the contaminated material is in the pile, bed or windrow. The idea of zones of activity is recognized in composting *(22, 52)* as a particular problem for static systems. As a result, turning is commonly employed for windrows, for actively aerated “piles,” and in-vessel to ensure that edge effects have no lasting impact on overall treatment effectiveness and to reduce heterogeneity of the treated product through mixing.

Bioslurry reactors have not seen widespread adoption at a practical scale. However, treatment in bioslurry reactors, as indicated by some of the Pilot Study projects, may extend the range of biologically treatable contaminants, for example to include higher PAHs. However, this technology is also more expensive and creates a need for dewatering of the treated product and, as a result, process water handling. One application where bioslurry reactors may have a competitive edge is in situations where a material is already in a liquid or semi-liquid form. Examples examined by Pilot Study projects are treatment concentrates from soil washing.

The majority, if not all of practical *ex situ* biological treatments, rely on biodegradation processes mediated by bacteria—mostly as a direct carbon source for microbial growth. Fungal lignolytic activity has long been recognized as a possible means of extending the range of biologically treatable contaminants, to more insoluble and recalcitrant compounds (Section 6.2.2). Of course, many such contaminants may be biodegradable ultimately by bacteria, but the lignolytic attack mediated by nonspecific enzymes and free radicals may be faster. It may be conjectured that fungi may offer the opportunity to extend the range of contaminants treatable in simple solid phase systems, to include those currently regarded as being practically biodegradable only in bioslurry reactors.

As a final comment, there appear to be two sets of competing factors that fundamentally determine the effectiveness of an *ex situ* biological treatment:

- The competing needs to use pore space for air and water movement, discussed below in the context of forward and reversed aeration, but also evident in trying to supply solutions (*e.g.*, of nutrients or detergents) at the same time as supplying air; and

- The need to mobilize and render contamination available to facilitate biodegradation (which typically means moving it to gaseous or liquid phase), versus the need to limit process emissions of contaminants in vented air or in leachate.

6.7 RESIDUALS AND EMISSIONS

Residuals and emissions generated from the projects are summarized by project in Table 6.6. Whether collected or left to disperse, gaseous and aqueous phase emissions are likely for any biological treatment (*ex situ* or *in situ*) based on biodegradation. Gaseous emissions in process air or that leave the surface of treatment beds or windrows comprise VOCs that are stripped and not biodegraded. Forced aeration tends to increase the amount of VOCs stripped and volatilized. The amount of VOCs lost to volatilization is dependent on the nature of the contamination. Amounts recorded for semivolatiles such as PAHs were low, but were high for solvents.

Table 6.6: Residuals and Emissions

Project		Comments on Residuals and Emissions
6	*In situ*/on-site bioremediation of industrial soil contaminated with organic pollutants	No leachate generation was recorded. Oversize screenings were the main process residue.
8	Biodegradation/bioventing of oil-contaminated soils	Leachate is reportedly recirculated to irrigate the biopile, but no information on generation rates was provided. Vented air is treated by a biofilter card, which apparently removes 85% of the VOC's passing through it. Oversize rejects may also be a significant process residual.
11	On-site biological degradation of PAHs in soil at a former gasworks site	Pilot trial. No practical information reported.
15	Combined chemical and micro-biological treatment of coking sites	Not reported.
24	Combined remediation technique for soil containing organic contaminants: Fortec	Process and dewatering effluent not recycled elsewhere in the soil washing plant may be a significant emission. (For residues from the washing stage see Chapter 4.)
25	Slurry reactor for soil treatment	Process effluent and water from solids removal that are not recycled, oversize reject material, and process air emissions.
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	Process effluent and water from solids removal that are not recycled, process air emissions. (For residues from the washing stage see Chapter 4.)
28	Use of white-rot fungi for bioremediation of creosote-contaminated soil	Not applicable.
31	Decontamination of metalliferous mining spoil	See comments in text.
35	*in situ* SVE within containment cells combined with *ex situ* bioremediation and groundwater treatment	For the biopile process, vented air (significant VOC removals due to volatilization were reported) and leachate.
36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles	Presumably bioreactor and dewatering effluent. Presumably bioreactor process air.
43	Multi-vendor bioremediation technology demonstration project	VOCs in process air emissions.
49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil	Not applicable.
54	Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors	Screened oversize (>2-3 mm) and presumably excess water from bioreactor and dewatering operations.

Not all of the biopile or bioreactor studies reported here record the steps being taken to treat process air. Reversed aeration (suction) is a common approach to ensuring that process air from aeration of biopiles can be collected; for example for subsequent treatment in a biofilter (*e.g.*, a peat bed). Reversed aeration is not, however, optimal for enhancing the degradation process, particularly as particle size decreases. A recognized effect of reversed aeration in waste composting *(22)* is that the pile retains a higher moisture content and that moisture is drawn to the center of the pile to points of suction. This effectively clogs the system's air supply, reducing the amount of air that can be delivered to the system.

Steps to contain process water and leachate containment were reported for many trials. However, treatment of the process water was not typically described, but presumably relied on capture and recirculation.

Most biological processes are intended to destroy contaminants rather than collect them in a solid waste residual. Nonetheless, residual contaminants are commonly detected in treated soils after processing. It appears from Project 49, which deals with residuals from biological treatment, that such residuals can be effectively inert, at least in terms of risk management. However, that should not be taken as a blanket assumption.

The most common solid process residue is over-size material after screening prior to biological treatment. While this may not be important for an approach integrated with, for example, a soil washing plant, it could lead to large volumes of solid residues for approaches centered on a biological treatment such as a biopile. One possibility is to crush such materials and incorporate them in the biopile if testing indicates they require treatment.

6.8 FACTORS AND LIMITATIONS TO CONSIDER FOR DETERMINING THE APPLICABILITY OF THE TECHNOLOGY

The majority of *ex situ* treatment technologies with established track records are relatively simple to apply and relatively robust in the hands of an experienced operator. Table 6.7 lists key factors and limitations found for the various projects discussed in this chapter including:

- Biodegradability and bioavailability (which may be linked to the age and initial concentrations of the contaminants as well as the sorptive capacities of the solid matrix);
- Dewatering and water handling for slurry-based processes;
- Dealing with edge effects and heterogeneity and ensuring adequate process control (*e.g.*, air and water supply) for solid-phase technologies;
- The texture of the treated material (content of fine particles); and
- The distribution of contaminants by particle size for slurry-based systems.

Two other interesting observations were made:

(1) Project 36 postulated that interactions between different biological processes could limit the success of slurry-phase treatment of soil at gasworks sites. It was also suggested that sulfide oxidation leading to changes in slurry pH might have limited subsequent biodegradation of PAHs.

(2) Based on the results of several of the Pilot Study projects, laboratory-, bench-, and pilot-scale tests do not always predict the performance of full-scale treatment.

In the absence of an adequate fundamental understanding, know-how appears to be a key factor in process prediction: both in interpreting test data, and in knowing which tests to carry out. This comment links back to the earlier comment that in general treatment performance may be linked to empirical operational expertise of the practitioner.

Table 6.7: Key Factors Limiting Performance

Project		Comments on Factors Limiting Performance
6	*In situ*/on-site bioremediation of industrial soil contaminated with organic pollutants: elimination of soil toxicity with DARAMEND®	• Proportion of more recalcitrant organics (*e.g.*, higher PAHs). • Ambient conditions and their impact on possible leachate generation. • Maximum treatment depth (*in situ* application) of 0.6 m. • Proportion of oversize material.
8	Biodegradation/bioventing of oil-contaminated soils	• Biodegradability/availability. • Proportion of oversize material. • Temperature, although piles can be air heated. • Soil texture. Heavier soils are harder to treat, which increases costs because of their more difficult materials handling properties and often extended treatment time.
11	On-site biological degradation of PAHs in soil at a former gasworks site	• Aging, which was thought to have reduced the biological treatability of the PAHs, along with sorption to soil particles. • Turning the windrows? • Initial concentration of PAHs? (related to aging factor).
15	Combined chemical and microbiological treatment of coking sites	No relevant information provided.
24	Combined remediation technique for soil containing organic contaminants: Fortec	• Contaminant distribution by particle size. • Biodegradability/treatability by photooxidation. • Soil composition (texture and organic matter content).
25	Slurry reactor for soil treatment	• Contaminant distribution by particle size. • Contaminant bioavailability and biodegradability.
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	• Presumably contaminant distribution by particle size. • Contaminant bioavailability and biodegradability. • Optimization of the biodegradation process in the reactor.
28	Use of white-rot fungi for bioremediation of creosote-contaminated soil	No relevant information provided.
31	Decontamination of metalliferous mining spoil	Bioleaching was not recommended as a treatment option.
35	*In situ* soil vapor extraction within containment cells combined with *ex situ* bioremediation and groundwater treatment	• Treatment is more difficult for heavier, less porous fractions. • The main process factors affecting the degradation process at full scale were aeration and temperature. • Process optimization through nutrient addition was not found to be cost effective at full-scale.
36	Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles	• Dewatering the treated slurry. Up to 57% solids could be achieved after 10 minutes of filtration at 1,600 Kpa with calcium hydroxide as a coagulant. • Temperature and nutrient addition strongly affect bioreactor performance. • The nature of the contaminated matrix (*e.g.*, sulfide content. See text). • Bioavailability and biodegradability of contaminants.
43	Multi-vendor bioremediation technology demonstration project	• Soil texture affects aeration.

Project		Comments on Factors Limiting Performance
49	Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil	Not applicable (see text).
54	Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors	No relevant information provided. Limitations are presumably similar to bioreactors in general.

6.9 COSTS

Scant cost data could be compiled for most projects. What could be gleaned is summarized in Table 6.8. However, it would be wise to treat the data in Table 6.8 with a great deal of caution. Costs are strongly dependent on site specific factors, and cost data were reported in different years.

6.10 FUTURE STATUS OF THE CASE STUDY PROCESSES AND THE TECHNOLOGY AS A WHOLE

The pilot study projects discussed here as case studies are an interesting cross-section of the biological treatments applied to solid materials and slurries. Dealing with the technology overall first, it is clear that *ex situ* biological treatments are an effective means of dealing with many contamination problems and offer great advantages over *in situ* approaches in terms of process control, monitoring and assessment, and treatment duration. These advantages come at a premium. This premium encompasses the possibility of higher costs, a more intrusive response, and greater visible generation of process residuals and emissions. In some situations, the specific circumstances of a site's redevelopment make this premium worth paying for the *ex situ* treatment advantages.

Across Europe, great attention is being paid to the treatment of wastes in general, with a desire to reduce the volumes of material being landfilled, more specifically the disposal of biodegradable or chemically active wastes. These desires are manifest in the latest Landfill Directive draft and the intention for a Directive on composting. It would therefore seem likely that possibilities for synergy in the co-treatment of different waste types will be of increasing interest. It also seems likely that landfill operators and waste management companies will become more open to treatment-based waste management solutions. It may be that these two factors will extend to wastes arising from contaminated sites and offer new opportunities for offsite and integrated treatment plant. *Ex situ* treatment also offers the opportunity for on-site recycling, and it does seem likely that future redevelopment projects will take a more strategic and integrated view of risk reduction, waste minimization, and construction requirements.

Biopile, windrow, and treatment bed approaches are now well established approaches and because of their track record and the know-how acquired for them, these approaches seem set to be used more widely. So far as fundamental advances are concerned, the best place to look for these might be around the resolution of the two process conflicts outlined in Section 5: air *versus* water movement; and mobilization *versus* containment.

Bioslurry bioreactor technologies are under active development, but at present are not easily cost-competitive. However, bioreactors for slurries are likely to continue to be a useful approach for specific circumstances, such as the treatment of sludges from soil washing.

Table 6.8: Cost Information by Project

Project	Comment
6 *In situ*/on-site bioremediation of industrial soil contaminated with organic pollutants: elimination of soil toxicity with DARAMEND®	*In situ* unit costs are estimated to be U.S.$46-92/m^3, and *ex situ* process costs are estimated to be U.S.$96-140/m^3 (1995).
8 Biodegradation/bioventing of oil-contaminated soils	Based on the 24 case studies reported, 0-5,000 tons, $45-90/ton; 5,000-25,000 tons, $30-45/ton; and >25,000 tons, $15-30/ton. *The type of "ton" is not specified, nor is it stated whether Canadian or U.S. dollars are used.*
11 On-site biological degradation of PAHs in soil at a former gasworks site	Not applicable.
15 Combined chemical and microbiological treatment of coking sites	Not applicable.
24 Combined remediation technique for soil containing organic contaminants: Fortec	Cost data not provided.
25 Slurry reactor for soil treatment	Cost data not provided.
26 Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	Estimated to be U.S.$530/m^3 of froth flotation sludge (1993).
28 Use of white-rot fungi for bioremediation of creosote-contaminated soil	Not applicable.
31 Decontamination of metalliferous mining spoil	Not applicable.
35 *In situ* soil vapor extraction within containment cells combined with *ex situ* bioremediation and groundwater treatment	The biological treatment costs were not separately reported.
36 Enhancement techniques for *ex situ* separation processes, particularly with regard to fine particles	The authors felt that reporting treatment costs would be misleading as they depend on too many site-specific factors.
43 Multi-vendor bioremediation technology demonstration project	Estimated to be U.S.$71/m^3 (1996).
49 Characterization of residual contaminants in bioremediated soil and reuse of bioremediated soil	Not applicable.
54 Treatment of PAH- and PCP-contaminated soil in slurry phase bioreactors	Not reported.

Bioreactor technologies for the solid phase may be a suggestion for useful future development, taking advantage of existing waste composting technology and know-how. In-vessel treatments, particularly those involving mixing, offer advantages over cultivation, biopile, and windrow systems including better containment, process control and monitoring, as well as improved product homogeneity and elimination of edge effects. An opportunity for such enhanced process control is to make better use of fungal processes, which tend to be inhibited above 50°C, or to achieve sequential aerobic and anaerobic effects. More complex *ex situ* biological treatments may tend to be most easily installed as fixed plant, perhaps as part of an integrated wastemanagement system.

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6.12 DISCLAIMER

Reference to any individual or organization or mention of any proprietary name or product in this report does not confer any endorsement by the author, nor the Environment Agency, nor DETR.

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Chapter 7: EX SITU *THERMAL METHODS*

Michael A. Smith
M.A. Smith Environmental Consultancy, U.K.

7.1 INTRODUCTION

Thermal treatment methods use heat to remove or destroy contaminants *(1)*. Some methods also encapsulate contaminants that cannot be volatilized or burned. Processes vary with respect to:

- the heat source (*e.g.*, heated air or another gas, open flame, or liquid heat-transfer medium) and method of application (direct or indirect contact);
- operating temperature;
- phasing of the process (*i.e.*, one or more stages);
- the equipment used to contain the thermal process and provide heat and mass transfer (*e.g.*, a rotary kiln or fluidized bed reactor);
- the materials handling methods used both before and after treatment; and
- methods used to collect and contain and treat air and other emissions from the process.

7.2 MAIN PROCESS VARIATIONS

Three main types of thermal treatment can be identified for contaminated soils, sediments, sludges, filter cakes (*e.g.*, from soil washing) and similar materials:

(1) Thermal desorption in which contaminants are removed from the feedstocks at relatively low temperatures and then destroyed or collected from the gas stream in a subsequent stage;

(2) Incineration (thermal destruction) in which contaminants are destroyed at high temperature; and

(3) Vitrification in which very high operating temperatures destroy some contaminants and trap others in a glassy product.

The thermal process projects reviewed in this chapter involved either thermal desorption or incineration, and the introductory sections that follow concentrate on these forms of treatment. In practice, there is no clear technical distinction between thermal desorption and incineration, since thermal desorption of contaminants occurs during incineration of soils or other solids, and partial combustion of desorbed organic compounds often occurs within a desorber unit or downstream in a fume incinerator, depending on the design.

Existing industrial thermal processors, such as cement kilns and coal-fired boilers, are also sometimes used for organic-rich residues. Other thermal processes can be used for specific contaminants; for example, retorts have been specified by the USEPA for the treatment of mercury-contaminated soil.

7.3 DESCRIPTION OF MAIN PROCESS VARIATIONS

7.3.1 Thermal Desorption

Thermal desorption methods physically separate volatile and semivolatile[1] contaminants from soils, sludges, and sediments. They do not generally result in a high degree of thermal decomposition of contaminants, although temperature variations between different systems may allow for some localized oxidation or pyrolysis. The thermal desorption unit is only one part of a treatment train; some pretreatment of feedstocks and post-treatment of treated soil or separated contaminants is usually required.

Efficient separation can occur at temperatures of up to 600°C, although temperatures may reach 900°C during the primary stage in some specialized systems. In practice, many systems operate at relatively low solids temperatures; even polychlorinated biphenyls (PCBs) can be removed at 450-500°C. An important design parameter is the length of time that soils remain at the target temperature.

Separated contaminants, water vapor, and particulates must be collected and treated. Typically, this is done using conventional methods of condensation, adsorption, incineration, filtration, *etc*. The methods are selected according to the nature and concentration of contaminants, regulatory regime, and economics of the system employed. It may be possible to recover separated contaminants for reuse. Thermal desorption systems that employ combustion or other oxidation processes for treating the off-gas can accomplish the same goal as incineration—*i.e.*, destruction of contaminants.

Two basic configurations are available:

(1) Direct systems, in which heat is transferred by convection, radiation from heated air (or another gas), or an open flame to the contaminated feedstock; and

(2) Indirect systems, in which heat is transferred by conduction from the heat source to the contaminated feedstock.

Project 7, in which soil was floated on molten metal, can be regarded as a directly heated system, while Project 13 involved two indirectly heated stages. A classification of thermal desorption systems is shown in Figure 7.1. In practice some commercial types occupy a hybrid position and are capable of operating in different modes. Most systems of both types employ rotary kilns, although more innovative systems use various types of conveyors (*e.g.*, screw, paddle, mixing, or belt). Fluidized beds are also under development (see Project 20).

The achievable solids-treatment temperature is a function of the temperature of the heating medium as well as the heat transfer area and the heat burden posed by the feedstock. Both directly and indirectly heated desorbers can be classified as low- or high-temperature systems. High-temperature desorbers can achieve solids temperatures comparable to some incinerators, depending on the design, operating conditions, and the volatility and thermal characteristics of the contaminants. In the U.S., many thermal desorption units are regarded as low-temperature systems and are employed for soils contaminated with hydrocarbon fuel. Evolved water and volatile compounds may be swept from the processor using an inert gas such as nitrogen or oxygen-deficient (<4 % by volume) combustion off-gas (see Project 13).

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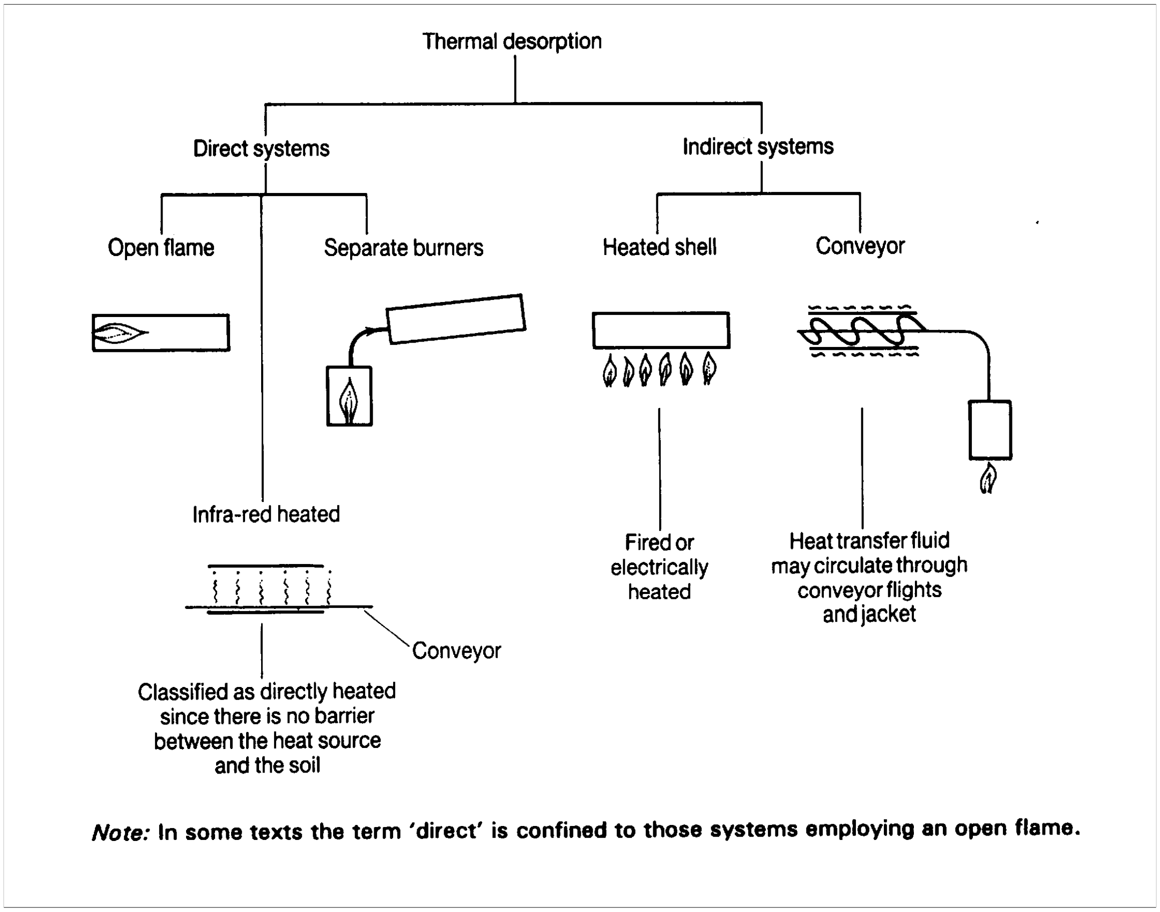
[1] What matters is whether the contaminants of concern are volatile under the conditions of temperature, *etc.*, in the desorber. The terms “volatile” and “semivolatile” are here used as in much USEPA literature.



Note: In some texts the term 'direct' is confined to those systems employing an open flame.

Figure 7.1: A Classification of Thermal Desorption Systems

Depending on the pretreatment handling processes used and the temperatures applied during treatment, thermal desorption may not significantly alter the physical properties of the soil or its ability to support vegetation, although resident microbial populations will have been affected. Provided the material conforms to all site-specific remediation standards, it may be returned for reuse onsite. At high operating temperatures, however, the natural organic constituents of the soil (*e.g.*, humic acids) are broken down. This reduces the utility of the treated product for landscaping. Furthermore, changes in mineral properties may lead to a loss of cohesiveness, and the loss of water from clay matrices may render them potentially reactive (pozzolanic).

Directly Heated Processes

Direct processes usually take place in a rotary kiln into which externally heated air or gas is introduced or an open flame provided. Energy requirements vary according to the moisture content of the contaminated feedstocks, the maximum bed temperature required, ambient temperatures, maximum gas combustion temperatures, and the extent to which heat is transferred and recovered from the kiln exhaust gases.

Indirectly Heated Processes

Indirect methods operate by transferring heat across a metal surface, either from a fired or electrical furnace adjacent to the desorber or from a heated fluid, such as steam, flue gas, air, heat transfer liquid or molten salt. Indirect heating can be carried out in a rotary unit (similar to a rotary calciner) with a furnace shell surrounding the rotating desorber, or in conveyor systems equipped with a travelling belt or pipes or hollow augers through which a heat transfer medium (such as steam, oil, or molten salts) is fed.

In the conveyor systems, screw conveyors or hollow augers are used to transport the soil or other feedstock, continuously through an enclosed trough. Hot oil or steam circulates through the conveyor or auger to heat the soil. Molten salts have seen limited use. A heat transfer fluid is commonly pumped through the walls of the trough for additional heat transfer. One, two, or four augers may be arranged in a trough to provide mixing during the heating and conveying process. More than one trough system can be run in series to achieve the bed temperature and residence time required. A clean sweep gas, such as nitrogen or steam, typically is used to convey the vaporized contaminants and water from the troughs. The sweep gas also may be used to minimize oxidation of the contaminants by reducing the availability of oxygen. The maximum bed temperature is limited by the properties of the heat transfer fluid and the materials used to construct the equipment. It also depends on the speed at which soils are conveyed through the trough(s) and the operating temperature of the heat transfer fluid. Advantages of this type of desorption unit include simplicity of operation and temperature control, as well as reduced generation of fines or dust.

A typical indirectly fired rotary unit consists of an outer furnace that is heated and a rotary inner drum that contains the contaminated soil. The soil is primarily heated by direct contact with the drum and by radiation from the drum walls. The efficiency of indirect systems relies on the provision of a large heat exchange area. Compared to directly heated rotary kiln systems, a much smaller volume of gas (approximately 300 m^3/tonne of treated soil) is discharged from the desorber. As a result, secondary combustion and gas cleaning systems are smaller and more economical to construct compared to those of direct systems. However, construction costs for indirect systems may be high due to the complexity of the heat exchanger.

Gas Collection and Treatment

Gas collection and treatment arrangements vary according to the design of the plant, whether it is directly or indirectly heated, its capacity and the type of contaminants being treated. Regulatory requirements on acceptable emissions are also important, as is the availability of a water supply and discharge facility. Gas collection and treatment systems in common use include:

- combustion of volatile contaminants at high temperatures (up to 1,400°C) in an afterburner followed by gas cleaning and discharge through a stack;

- thermal treatment at moderate temperatures (200-400°C) using catalysts (*e.g.*, nickel or zinc/ copper) to assist oxidation, followed by gas cleaning and discharge through a stack;

- for indirect heating systems, conventional low-temperature scrubbers using water or organic solvents, and activated carbon absorption; and

- for indirect systems, condensation of volatile compounds with possible recovery.

A combination of systems may be necessary to comprehensively treat all the constituents present in the gas phase exiting the primary desorber.

7.3.2 Incineration

Incineration (thermal destruction) destroys contaminants at high temperature (800-1,200°C). Specifically, incineration is a high-temperature oxidation reaction between combustible substances and oxygen under controlled conditions of retention time, temperature, and turbulence within a single- or multiple-stage combustion chamber[2]. Although organic contaminants are destroyed in the process, air pollution control equipment must be provided to collect and treat combustion products, particulates, and volatile metals present in exhaust gases. Incineration of soils and sediments involves volatilization and desorption of water and organic contaminants (and some inorganic contaminants), as in thermal desorption. A secondary combustion chamber to complete oxidation of the volatilized materials is generally required.

The high temperatures used during incineration have implications for the reuse of the treated soil due to changes to the physical, chemical, and biological properties of the material. Changes in soil texture together with the loss of natural organic constituents, reduce the ability of treated material to support vegetation and may affect engineering properties. The loss of soil structure and organic content also may increase the leachability of any heavy metals remaining in the treated product. Further treatment, *e.g.*, stabilization/solidification (Chapter 8), may therefore be required before the material is acceptable for reuse.

A wide range of incineration techniques have been developed for the treatment of contaminated soils, sediments, and sludges, including direct-fired rotary kilns, fluidized beds, and infrared belt conveyor systems.

Direct Fired Rotary Kiln Incinerators

Direct fired rotary kiln incinerators typically contain a primary and a secondary combustion chamber. The primary chamber is a cylindrical, sloping, rotating, refractory-lined shell in which the soil is dried and heated by firing fuel or liquid wastes with a high calorific value. The secondary combustion chamber provides additional capacity for any contaminants not destroyed at the primary stage. Soil may move with, or counter to, the direction of gas flow. The kiln can be designed to operate in an oxidation mode or pyrolysis (anoxic) mode, with the latter generating smaller volumes of flue gas. Rotation and inclination provide the necessary mixing and heat transfer functions. Gases exiting the secondary combustion chamber pass through a multi-stage gas cleaning plant.

Fluidized Beds

Fluidized beds have been used for the treatment of waste liquids and sludges and, on a more limited scale, of contaminated soils and sediments. In these systems, air or combustion gases are used to develop and maintain a fluidized bed of solid particles derived from sand or the inorganic residue from the soil or waste being treated. The continuous movement of the solids in the bed promotes rapid heat and mass transfer, and hence destruction of the contaminants. Continuous removal of bed solids is required for the treatment of soil or sediments. Additional fuel is added as necessary to maintain a bed temperature of between 700-1,200°C, although temperatures must be limited to prevent sintering. Particulates escaping the bed are generally recovered in a cyclone and returned to the combustion chamber if treatment is incomplete.

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[2] Thermal processors also can be operated at high temperatures under anoxic conditions, so that pyrolysis (reductive degradation) of organic substances occurs.

Infrared Incinerator Systems

Infrared systems use infrared radiant heat (generated by electrically powered silicon carbide elements) to heat organic wastes to combustion temperatures. A typical configuration comprises an infrared primary chamber, a gas-fired secondary combustion chamber, an emissions control system, and a control center. Mobile infrared incineration systems have been developed for use in the United States.

7.3.3 Vitrification

Vitrification destroys contaminants by oxidation and thermal decomposition and immobilizes residual contaminants in a vitreous product. The advantages of vitrification over other thermal treatment processes are that it produces fewer air emissions and a solid residue with favorable leaching characteristics.

Vitrification systems consist of a melter, heat recovery system, air pollution control system, and storage and handling for feedstock and raw materials. There are various configurations for melters, some of which are multi-chamber and others which use mechanical agitation. Energy requirements are significant where feedstocks have a high mineral content. The most common melters are heated by electrical currents passed through the melt mixture from electrodes. Variations between melters include the method of introducing feed, the degree and type of mixing, electrode design, and the means of achieving complete combustion of organic compounds. More recent melter designs utilize alternative methods of introducing heat and have different heat and mass transfer characteristics.

Typical melt temperatures are about 1,500°C. Sufficient glass-forming material (silicate) must be present to produce a proper melt that will result in a durable vitrified product. This may require the addition of fluxing agents. Molten product is continuously drawn off the melter either into containers for cooling, solidification, and handling, or through some type of cooling process to produce granular solids. Emissions of the more volatile metals is a potential concern, and air pollution control systems must be highly efficient. Process residues include glass/vitrified waste, molten metal (not produced as a separate phase in most processes), scrubbing and cooling liquors, and off-gases.

Commercial vitrification systems have been developed for the treatment of contaminated soils and sediments in the U.S. where a number of vendors have field-, bench- and pilot-tested the technology. Most of these systems were modifications of different types of glass-making furnaces, and development was directed initially towards radioactive or other highly hazardous solid wastes. One commercial facility in the United States was used to treat organic wastes for several years.

7.4 DETERMINATION OF EFFECTIVENESS

The effectiveness of both thermal desorption and incineration (thermal destruction) systems should be judged on the basis of their ability to achieve target residual concentrations while complying with emission limits to air, *etc.*

The primary technical factors governing the performance of thermal desorption processes are the maximum bed temperature achieved; the total residence time; the content of organic contaminants and water; contaminant characteristics; and medium (*e.g.*, soil) properties.

Since the basis of the processes is the physical removal of contaminants from the medium by volatilization, bed temperature directly determines end point concentrations. The degree of mixing and, where applicable, sweep gas rate will also affect the effectiveness of the process.

The primary technical factor affecting performance of thermal destruction (incineration) systems is also the maximum bed temperature of the solids. Overly large particle sizes lead to poor performance. A high proportion of fines leads to high dust loading in the downstream air pollution control system.

7.5 CASE STUDIES CHOSEN

The projects reviewed for this chapter are listed and described in Table 7.1. Brief descriptions of the projects are provided in Sections 7.5.2 to 7.5.6. Project summaries can be found in Appendix IV.

Table 7.1: Projects Involving *Ex Situ* Thermal Treatment

Project		Description
7	Demonstration of thermal gas-phase reduction process	Key feature is the high temperature (850°C) thermal reduction unit. Contaminants in soils are volatilized in a specially designed thermal desorber and then injected into the unit. Contaminated aqueous phases are vaporized before injection. Successfully demonstrated by USEPA's SITE Program in 1992.
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique	Integrated soil washing and two-stage thermal treatment employing ventilated tent to reduce atmospheric emissions.
19	Cleaning mercury-contaminated soil using a combined washing and distillation process	Integrated soil washing and vacuum distillation plant used to treat mercury-contaminated soil and debris. Started operation in 1993.
20	Fluidized bed soil treatment process—*BORAN*	Fluidized bed thermal desorption plant with high-temperature afterburner intended to treat soils and residues from soil washing plants. Full-scale, but regarded as test plant by the design/operating company. In September 1996, the plant was undergoing modifications to overcome feed problems.
21	Mobile low-temperature thermal treatment process	Low-temperature (<300°C) sealed processor employs steam injection. Pilot plant successfully operated in 1994 and 1995.

Three projects (Projects 7, 20 and 21) involved the use of *ex situ* thermal treatment as the main treatment element, and two (Projects 13 and 19) used *ex situ* thermal treatment as the second element of a treatment train. In both cases, the first element was a soil washing process.

7.5.1 Project 7: Demonstration of Thermal Gas-Phase Reduction Process

The ECO LOGIC thermo-chemical process employs hydrogen to chemically reduce organic compounds to mineral components at temperatures of about 900°C. Soils are treated with the aid of a novel thermal desorber involving use of a molten metal bath. A technology demonstration at the Middleground Landfill, Bay City, Michigan, U.S., was conducted in 1992 under the USEPA's Superfund Innovative Technology Evaluation (SITE) Program with partial funding from the Canadian and Ontario governments. The wastes processed were oily PCB contaminated water, high-strength PCB oils, and PCB-contaminated soil.

Background

The Middleground Landfill accepted municipal wastes for approximately 40 years. A 1991 investigation indicated elevated levels in groundwater of trichloroethene (TCE), PCBs, 1,2-dichloroethene, methylene chloride, toluene, and ethylbenzene. The groundwater contained lesser concentrations of benzidine, benzene, vinyl chloride, chlorobenzene, polycyclic aromatic hydrocarbons (PAHs), lindane, dieldrin, chlordane, and DDT metabolites.

Technical Concept

The ECO LOGIC thermo-chemical process employs hydrogen to chemically reduce organic compounds to mineral components at temperatures of about 900°C. Chlorinated hydrocarbons, such as PCBs and polychlorinated dibenzo-p-dioxins, are converted to methane and hydrogen chloride, while non-chlorinated organic compounds, such as PAHs, are reduced to methane and ethene. Incomplete reduction/combustion in the system may result in benzene formation (as noted below, residual benzene was a problem in the demonstration project. Ethene produced by contaminant breakdown may undergo additional conversion to methane. Methane reacts with water vapor to form hydrogen and carbon monoxide. The hydrogen chloride is removed in a caustic soda scrubber downstream of the processor. The reformed process gas can then be recirculated in the system or used as fuel in various stages of the process. The absence of free oxygen in the reactor inhibits dioxin and furan formation. The process employs automatic monitoring to maintain optimum operating conditions.

The reactor feed is dependent upon the soil or waste being treated. Aqueous streams, such as groundwater, are preheated in a vaporizer using steam from a boiler that is fired by propane or process gas, before injection. When soils or sediments are to be processed, they are first pretreated in a linked thermal desorption unit (TDU), in which the soil or sediment is floated on a bath of molten tin. Volatilized contaminants are sent to the reactor through a separate port. Contaminated solids, such as transformer parts, can be handled in sequencing batch vaporizer chambers. The process is shown schematically in Figure 7.2.

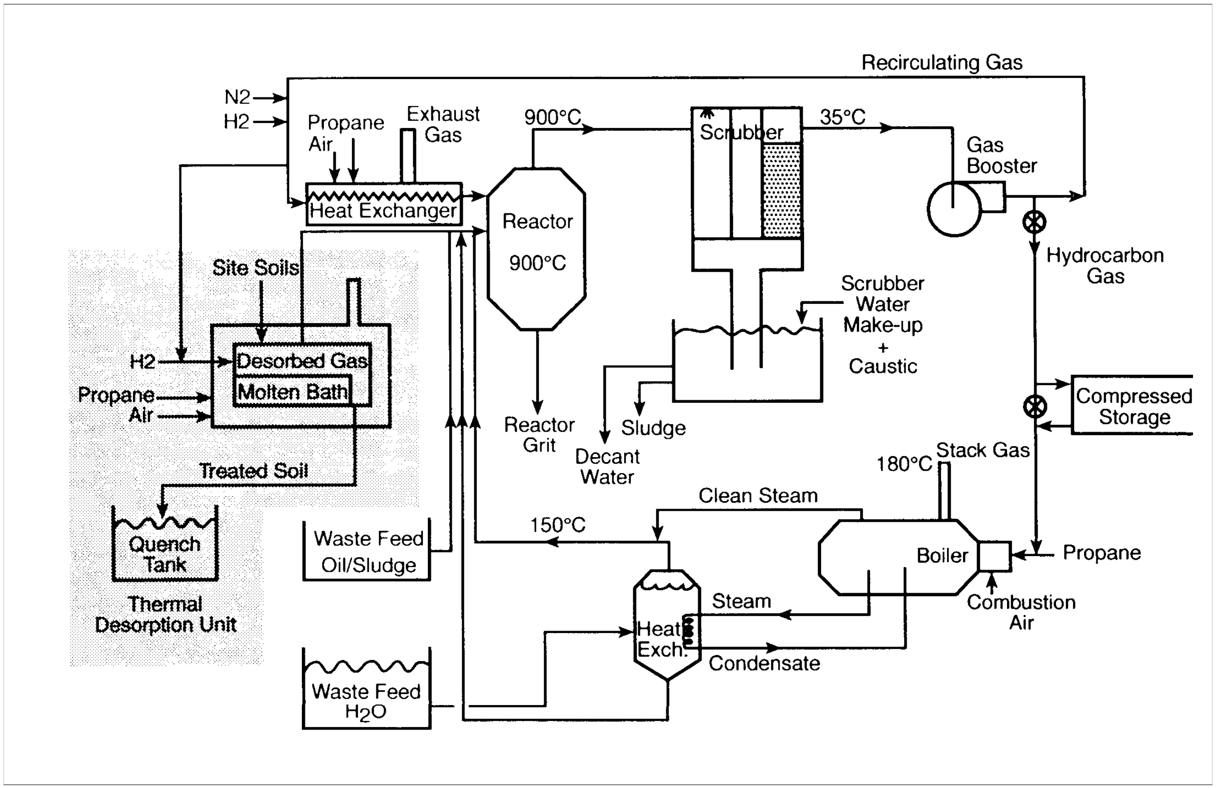

Figure 7.2: Reactor and Thermal Desorption Unit Schematic Diagram

The Demonstration Reactor

The demonstration-scale reactor (Figure 7.3) was 2 m in diameter and 3 m tall, mounted on a 15-m drop-deck trailer. This trailer carried a scrubber system, a recirculation gas system, and an electrical control center. A second trailer held a propane boiler, a waste preheating vessel, and a waste storage tank.

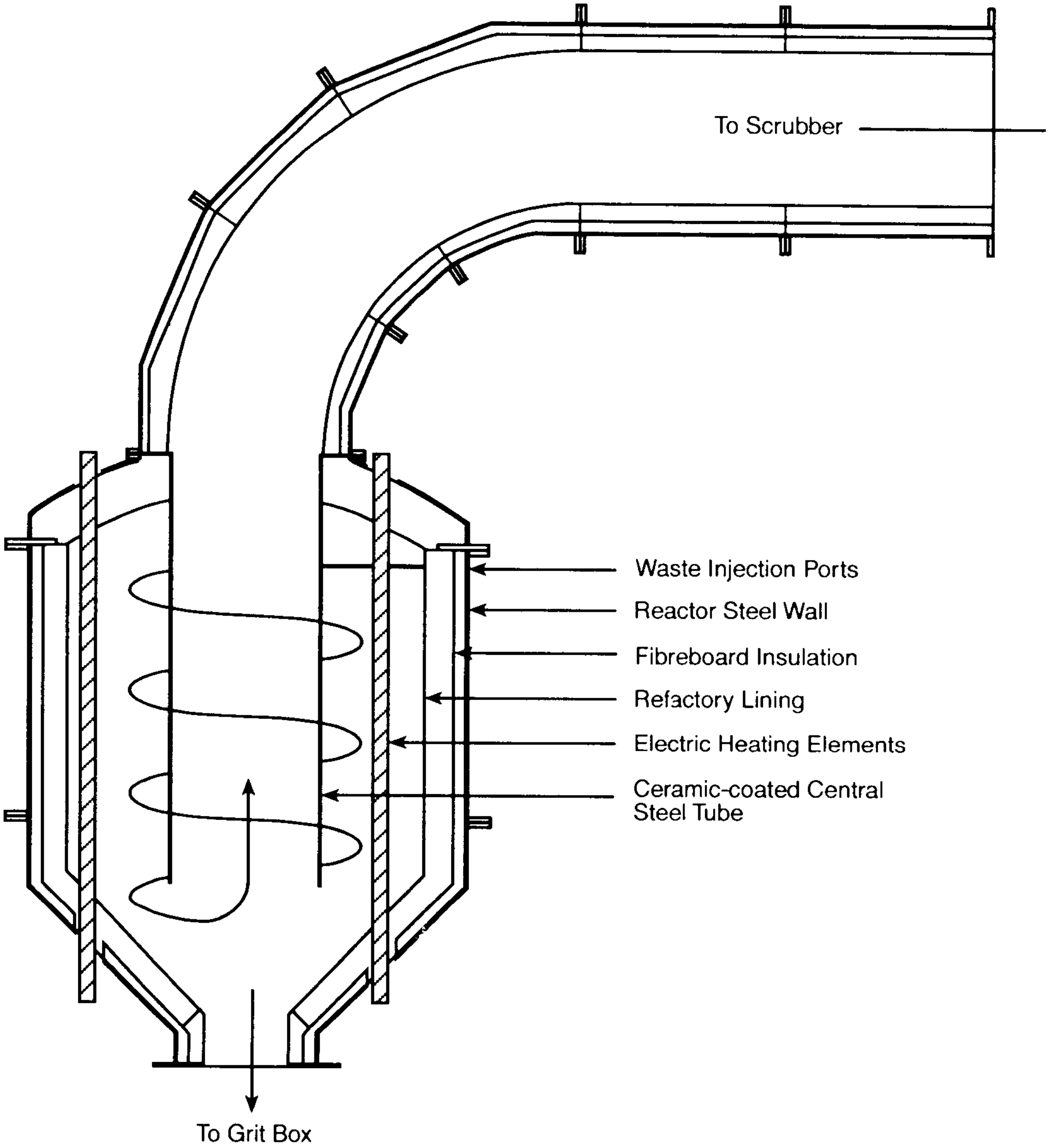

Figure 7.3: The ECO LOGIC Reactor

In the demonstration, a heat exchanger evaporated contaminated aqueous feedstock to form steam and a concentrated liquor. Atomizing nozzles sprayed the heated liquor and associated particulates into the reactor; a separate set of atomizing nozzles injected the PCB-rich oil directly into the reactor. Compressed hydrogen-rich recirculation gas passed through a gas-fired heat exchanger and entered the top of the reactor tangentially. The tangential entry swirled the fluids to provide effective mixing. As indicated in Figure 7.3, the swirling mixture travelled downwards in the annulus formed by the reactor wall and the central ceramic-coated steel tube, past electrically heated silicon carbide elements. These elements heated the mixture to 900°C. At the bottom of the reactor, the mixture entered the central tube and flowed upwards to the outlet of the reactor. The reduction reactions occurred as the gases travelled from the reactor inlets to the scrubber inlet.

Heavy particulates dropped out of the gas stream and collected at the base of the reactor in a grit box. The gas leaving the reactor was scrubbed using a caustic alkaline (pH 9) wet scrubber, which removes steam, particulates, and gases such as hydrogen chloride. Ninety-five per cent of the exhaust gases (reheated to 500°C) were recycled, and 5% were used as a supplementary fuel for the propane-fired boiler. The boiler produced steam, which was used in the heat exchanger and burned the reformed gas. The exhaust from this boiler was the only source of emissions to air from the process.

Thermal Desorption Unit

The TDU desorbs organic compounds at 500-600°C into a hydrogen-rich carrier gas from soil supported on a molten tin bath. Hydrogen and tin are used because they do not react. Tin offers favorable properties: high density, low vapor pressure, high surface tension (which means it does not “wet” the soil and enter the pores), high thermal conductivity, and good solvent properties for heavy metals such as lead, cadmium, and arsenic.

Some of each volatile metal present passes to the reactor, some dissolves in the molten tin bath, and the remainder stays in the soil. Non-volatile metals remain in the treated soil. Quench water cools the soil before disposal.

During the demonstration, a hopper with a screw feed dropped waste soil onto the tin bath. The screw feeder provided a gas seal between the hydrogen and the outside air. Once inside the TDU, the soil floated on the molten tin. A paddle wheel removed treated soil from the end of the tin bath and fed it to the quench tank.

Materials Processed

The wastes processed were oily PCB contaminated water, high-strength PCB oils, and PCB-contaminated soil extracted directly from the landfill. The tests on the two liquid wastes yielded information on reactor performance; the tests on the soil yielded information on the functioning of the complementary thermal desorption unit.

A liquid pool of waste within the landfill provided feedstock for the tests. Tetrachloroethene (PCE) was added to the feedstocks to serve as a tracer to determine destruction efficiencies (DEs)[3]. The reactor program treated approximately 2.6 tonnes of wastewater contaminated with 3,757 mg/L PCBs and 3,209 mg/L PCE at a rate of 1.73 kg/min, and 0.2 tonnes of waste oil containing 25.4% PCBs and 6,203 mg/kg PCE at a rate of 0.385 kg/min. Additional feedstock contaminants included fluoranthene,

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[3] DE is a measure of the system’s ability to destroy organic compounds, as measured around the system and all output streams. $DE(\%) = \{(1-Mass_{output})/Mass_{input}\}*100$.

naphthalene, phenanthrene, other PAHs, chlorobenzene, chlorophenol, methyl chloride, toluene, and various metals.

Two runs were conducted with the TDU on PCB-contaminated soil. The two runs treated 1 tonne of soil contaminated with 627 mg/kg PCB and 14,693 mg/kg hexachlorobenzene (HCB).

7.5.2 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using New On-Site Technique

This on-site remedial demonstration project combining excavation of tar-contaminated soil followed by on-site *ex situ* thermal desorption was carried out at an old gasworks site in a densely populated area of Copenhagen. The excavation was performed inside a ventilated tent. The project was regarded as a demonstration of a new on-site technique.

Background

The Valby Gasworks was one of the largest in Copenhagen with an operating capacity of up to 300,000 m^3 coal gas/day. Site investigation results showed a wide distribution of contaminants in the soil and groundwater including coal tars, phenols, ammonium compounds, cyanides, and heavy metals. One area of the site contained two tar reservoirs that had been partially filled with demolition debris after site closure. A large amount of tar was left at the base of the reservoirs. The upper part was filled with rainwater mixed with tar substances. The total amount of contaminated material in the two reservoirs was about 12,000 tonnes.

The objective of the demonstration project was to remediate the heavily contaminated soil and debris within and around the pits using an approach that minimized off-site migration (for example as air emissions) since the site was located in an urban area.

Technical Concept

Free-phase tar and heavily contaminated materials were excavated within the tent, which covered an area of 40 m by 50 m (with a height of up to 10 m). The air within the tent was cleaned using three powerful extraction ventilators connected to a two-stage filter system consisting of particle and active carbon filters. About 60% of ventilation air was blown in actively as fresh air at the end of the tent away from the extraction fans; the remaining 40% came from general leakages.

Although on-site thermal desorption is claimed to be suitable for treating tar contaminants, it was considered uneconomical to treat all of the excavated material in this manner. Therefore, a soil washing system was used to provide a volume reduction step by producing clean fractions in the particle size ranges of greater than 50 mm and 2-50 mm through screening and high pressure spray washing. All solid fractions were dewatered before further treatment or reuse, and the contaminated process effluent was recycled and treated before discharge. It was observed that tar removal efficiencies were increased through using recycled water. Elevated levels of ammonia in the recycled water (up to 20,000 mg/L) were believed to have assisted tar solvation. The contaminated fraction (<2 mm) was treated using the thermal desorption process.

The thermal treatment plant consisted of two separate indirect heat treatment units: the first operating at 250-300°C, while the second operated at 800-900°C. In the first stage water and volatile substances were evaporated from the contaminated materials The off-gas was treated using a particulate dust trap and an air/oil/water separator and condenser. The second stage was used to volatilize the heavier tar substances, which were then recovered in an air/tar condenser. Each treatment unit was transported in a standard 12 m x 9 m container and had a maximum operating capacity of 2.5 tonnes/hr. However, during operation, its practical operating capacity was only 1 tonne/hr—the limiting factor being the rate at which energy could be transferred from the reactor walls to the material. Treated material had a residence time of approximately 3 hours inside the reactors. After treatment, the decontaminated soil was cooled using a closed single axle screw conveyor with a box cover to prevent dust emissions.

The first stage desorber was a specially designed, indirectly heated rotary unit operated in a strictly controlled atmosphere, which was slightly over-pressurized and secured by inert gas. The processor was heated by a closed-loop thermal fluid (boiler). The slight excess pressure led the gaseous hydrocarbons and steam to the controlled condensation stage. Non-condensable gases (nitrogen, argon, methane, hydrogen, *etc.*) were removed from the condenser and fed to the oil-fired burner of the Stage-2 processor. Stage 2 employed an indirect rotary heat exchanger with an external shell temperature of 1,100°C produced by oil burners.

7.5.3 Project 19: Cleaning Mercury-Contaminated Soil Using Combined Washing and Distillation Process

The Marktredwitz Chemical factory in Germany, which was established in 1786, manufactured various mercury compounds (including agrochemicals) and mineral acids. Site investigations in the early 1980s found that the buildings, soil, and groundwater were heavily contaminated with mercury and other contaminants. Mercury concentrations ranged from 400-3,300 mg/kg on the surfaces of brickwork, from 1,000-4,000 mg/kg in the soil, and up to 200 mg/L in the wastewater. This led to closure of the factory in 1985. The Pilot Study project reported on the remedial operations employed including:

- Dismantling of the production plant, which involved removal of highly contaminated wall plastering and supporting pipework for disposal in a secure on-site facility (approximately 5,000 tonnes);

- Protection of the River Kösseine, which flows adjacent to the site, using a sheet piling wall and a pump-and-treat system;

- Demolition of the old factory building;

- Excavation of soil and debris to an average depth of 5 m across the entire site followed by refilling to prepare the entire site for further urban redevelopment. Contaminated material was transported offsite for treatment and disposal. A large off-site monofill waste disposal area was prepared where treated material and slightly contaminated material (<50 mg/kg mercury) was disposed.

- Treatment of excavated soil and debris at an off-site treatment plant, which was constructed as a semi-mobile (*i.e.*, transportable) operation consisting of several modularized containers. This project is the first full-scale application of vacuum distillation technology applied to debris and soil contaminated by volatile and semivolatile substances like oil, mercury, and the lighter fractions of tar.

The distillation unit is used in combination with a soil washing plant that separates out the highly contaminated silt and clay soil fractions to form a pretreatment concentrate for thermal treatment. The soil washing plant includes the following processes: crushing of material and screening at 0.05 m; wet screening and density separation of slurried contaminated material; attrition scrubbing to remove fine particles from coarser material; and dewatering and waste stream categorization. The sand and rubble fraction is discharged as clean fill. The fine fraction (<0.008 mm) is concentrated in thickeners, dewatered in a chamber filter press, and then transferred to the vacuum distillation unit.

The thermal treatment process is a two-stage system involving thermal desorption at 100°C to reduce material moisture content followed by vacuum distillation at the higher temperature. Treated material exiting Stage 1 has a reported moisture content of about 1%. Volatilized contaminants and steam are recovered from the off-gas using condensers. In the vacuum distillation reactor contaminated waste is heated to temperatures between 350-450°C at a pressure of 50-150 hPa and the volatilized contaminants recovered from the off-gas. By using reduced pressures rather than higher temperatures it is claimed that overall energy consumption is significantly reduced and that off-gas volume is less than 1/30th of that produced by an incineration plant. After treatment, the treated soil is water cooled in a rotating drum to an average temperature less than 50°C and is recombined with the coarse-grained material from the soil washing plant. Treated soil with residual concentrations greater than 50 mg/kg are treated again.

The Harbauer soil treatment plant is a full-scale, commercial, transportable plant. The plant is a modular system, and the process units are preassembled in about 60 containers (3-m wide, 3-m high, 10-14 m long). The plant is gas-sealed; internal air is kept and treated; noise-reduced equipment is used; and soil underlying the site is protected by a bottom-sealing system.

About 57,000 tonnes of soil were treated between 1993 and 1996, with an average daily throughput of 150 tonnes. Besides routine monitoring during operation, the technology demonstration was conducted according to the USEPA’s SITE Program protocols.

7.5.4 Project 20: Fluidized Bed soil Treatment Process—*BORAN*

The *BORAN* thermal fluidized bed soil treatment process plant has been designed primarily to treat slurry residues from soil washing plants. It is designed to treat contaminants such as PAHs and PCBs. The plant is operated by its designers and manufacturers, and while intended to be a commercial operation, is also intended to be used as a full-scale test bed for design modifications. The basic technology is in use for waste treatment and a number of other applications.

Before the contaminated soil is fed into the furnace, it is screened in a vibrating bar sizer with a cut-point at 20 mm. Material greater than 20 mm is transferred elsewhere for alternative treatment and safe disposal. Material less than 20 mm is fed into the furnace.

The furnace is fitted with two over-bed screw feeders for soils and four in-bed feed points for fine residues. A bed temperature of 900°C is maintained to ensure that the organic content of the soil is fully oxidized and destroyed. The combustion chamber is rectangular with one side wall being inwardly inclined to act as a deflector plate and a limit to bed expansion. Preheated air is injected into the chamber to ensure that feedstock (contaminated soil), combustion gases, and the bed materials are circulated rapidly in an elliptical path within the combustion chamber. The controlled circulation produces lateral mixing and turbulence, which reportedly enhances combustion efficiency.

Immediately downstream of the reactor is a hot gas cyclone, which is capable of removing up to 85% of the soil and fines expected to be carried by the fast moving off-gas stream. The cyclone is designed to remove up to 7.5 tonnes of particles per hour. This material is cooled from approximately 900°C to 180°C using water-cooled screw feeders before it is transferred to three storage silos as a clean product. The majority of the treated soil is collected at this stage, although some of the coarser particles sink to the base of the fluid bed within the furnace and are collected as a heavy ash product.

After the hot gas cyclone the off-gas stream passes to an afterburner where it is heated to 1,200°C by an oil-fired heater. The flue gas enters the treatment chamber at the top, passes down the center of the chamber, and exits at the base. The afterburner gases are directed at high velocity and tangentially to the flue gas stream to mix turbulently with the flue gas at the top of the chamber. At the base of the chamber, a water bath with an immersed screw feeder extracts any soft entrained material. When the afterburner is in use the following quench chamber reduces the temperature of the flue gas back to 900°C. A heat exchanger system uses the flue gases to preheat air about to be injected into the main furnace. The flue gas cleaning plant consists of a primary and a secondary system. Primary absorption of inorganic gases, such as hydrogen chloride and sulfur dioxide, is achieved by mixing finely powdered limestone into the flue gas stream. The limestone is subsequently collected in a baghouse. In the secondary absorption system any residual organic compounds, including dioxins and furans, are collected by activated brown coal coke filters. Fouled coke is incinerated in the furnace.

No performance data for this technology were available.

7.5.5 Project 21: Mobile Low-Temperature Thermal Treatment Process

Many commercially available thermal treatment plants for contaminated soil are based on rotary kilns operating at temperatures above 500°C, although some hydrocarbons are volatile at temperatures below 300°C. Use of lower operating temperatures, where appropriate, would reduce the environmental and economic cost of treatment significantly.

Ruhrkohle Umwelttechnik GmbH have been operating thermal treatment facilities for contaminated soil since 1986. In 1990, they began developing a mobile low-temperature treatment system for a range of soil contaminants (such as volatile hydrocarbons, chlorinated solvents, and various forms of mercury) with the following objectives: to reduce overall treatment costs compared with high temperature treatment; to reduce plant transport costs in order to increase applicability of on-site treatment to smaller remediation projects; to improve performance and cost effectiveness of thermal treatments for fine-grained (especially clay-rich) soils; and to shorten project initiation times by developing a process that did not require regulatory permitting for any off-gas or effluent emissions.

The process involves heating soil of less than 15 mm grain size in a gas-tight evaporator to 290°C under continuous agitation for 30-45 minutes. Direct heating is achieved by mixing the soil with a hot medium such as steam. Volatilized contaminants are collected from the off-gases by a multi-step condensation system. Contaminants such as chlorinated solvents and mercury are separated from the condensed steam which is cleaned and reused. Further contaminant separation may be carried out to produce low boiling point and high boiling point products to increase their recycling value. The cooled off-gas (at about 5°C) is cleaned further using an activated carbon filter for organic contaminants and an unspecified chemical adsorption unit for inorganics (such as mercury) before discharging to the atmosphere. The treated soil is cooled to about 60°C and water added to raise soil moisture content to 7-10%.

7.6 REVIEW OF CASE STUDIES AS A GROUP

Projects 7, 20 and 21 used *ex situ* thermal methods as the main element of treatment, while Projects 13 and 19 used *ex situ* thermal methods as the second element of a treatment train (the first element of which was a soil washing process). Project 20 (fluidized bed treatment) assumed that some enrichment of organic contaminants in the feedstock would take place elsewhere, for example, in a soil washing plant. Tables 7.2 and 7.3 describe the input materials and thermal treatment processes of the projects, respectively.

Table 7.2: Input Materials

	Project	Medium	Contaminants	Pretreatment/ Fraction treated
7	Demonstration of thermal gas-phase reduction process	Soil, groundwater, and oily waste.	Chlorinated hydrocarbons, including PCBs and HCB, PAHs, chlorobenzene, chlorophenol, methyl chloride, PCE, toluene, metals.	Soil homogenized to provide uniform feed. Volatile compounds in soil desorbed and subjected to gas-phase reduction. Oil injected directly into gas-phase reduction unit. Concentrate from pre-treatment of aqueous phases injected directly into reduction unit.
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique	Soil and demolition debris.	Coal tars.	First stage soil washing. The fraction <2 mm was subjected to thermal desorption.
19	Cleaning mercury-contaminated soil using a combined washing and distillation process	Soil and debris.	Mercury.	First stage soil washing. The fraction 0.1-8 mm was subjected to thermal desorption under vacuum.
20	Fluidized bed soil treatment process—*BORAN*	Designed for soil and slurry residues from soil washing plants.	Designed for PAHs, PCBs, *etc.*	Simple screening to remove >20 mm material for treatment elsewhere (plant does not have crushing equipment).
21	Mobile low-temperature thermal treatment process	Soil.	Volatile hydrocarbons and 5- and 6-ringed PAHs.	Fraction <15 mm subjected to steam injection.

7.7 PERFORMANCE RESULTS

Performance results of each project are summarized in Table 7.4 and discussed in more detail in the paragraphs that follow. There are no results for Project 20 as this plant had not become operational by the time the study ended.

7.7.1 Project 7: Demonstration of Thermal Gas-Phase Reduction Process

The runs employing liquid feeds confirmed the feasibility of the gas-phase reduction process for treating PCBs and other chlorinated organic compounds, producing a fuel gas from contaminated liquids that yielded environmentally acceptable air emissions. In general, the reactor system destroyed PCBs effectively, reducing them to lighter hydrocarbons.

Theoretically, the overall effectiveness of the destruction process could depend on the functioning of both the reactor system's gas phase reduction process (which produced the reformed gas), and the propane and reformed-gas fired boiler. Destruction and removal efficiencies (DREs)[4] for PCBs in the

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[4] DREs compare the mass flow rate of selected feedstock compounds, in this case PCBs, to their mass flow rate in the boiler stack gas. DRE(%)= $\{(1-\text{Mass}_{\text{stack}})/\text{Mass}_{\text{input}})\}*100$.

scrubbed reformed gas essentially were equal to the DREs at the boiler stack. This shows that combustion of the reformed gas in the boiler is not required to complete PCB destruction.

Stack emissions generally met stringent regulatory standards. However, average benzene concentrations in the stack gas (corrected to 7% oxygen) and scrubber liquor required close monitoring. Benzene emissions (73-113 µg per dry standard cubic meter [dscm]) exceeded the regulatory limit. The scrubber liquor required either disposal as a Resource Conservation and Recovery Act (RCRA) waste or recycling through the system for additional treatment.

Demonstrated DREs for PCBs ranged from 99.9999 to 99.99999%. Demonstrated DEs for PCE was 99.99%. There was no net formation of dioxin or furan.

The TDU did not operate to specification. The most important finding was inefficient desorption from soil during one of the runs. The DE for HCB ranged from 72.13 to 99.99%.

Table 7.3: Thermal Treatment Process

Project		Process	Temperature (°C)	Fate of contaminants	Fate of treated material
7	Demonstration of thermal gas-phase reduction process	Thermal desorber using molten metal bath for soil, *etc.* Gas-phase reduction	500-600 850	Degraded to hydrogen chloride, hydrogen, methane, ethene, *etc.*, depending on feedstock. Recirculated or removed by wet scrubbing.	Fate of treated water and soil not indicated in reports.
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique	Two-stage thermal desorption. Both stages employed indirect heating.	Stage 1: 250-300 Stage 2: 800-900	Condensed.	Coarse (>2 mm) washed material backfilled onsite. Fate of thermally treated material not clear.
19	Cleaning mercury-contaminated soil using a combined washing and distillation process	Two-stage thermal desorption: (1) to remove water; and (2) vacuum distillation at 50-150 hPa.	Stage 1: 100 Stage 2: 350-400	Condensed	Landfilled with untreated materials containing <50 mg/kg mercury.
20	Fluidized bed soil treatment process—*BORAN*	Fluidized bed Afterburner	900 1,200	Condensed, if not thermally degraded.	No operating results available.
21	Mobile low-temperature thermal treatment process	Sealed thermal desorption with steam injection.	270-290	Condensed.	No information available.

Table 7.4: Performance Information

Project	Contaminant Concentrations		Removal Efficiency
	Input	Output	
7 Demonstration of thermal gas-phase reduction process	Soil: 1,000 mg/kg PCBs Oil: 25.4% PCBs, 0.6% PCE Water: 3,757 mg/kg, PCB 3,209 mg/kg, PCE (tracer)	0.6 mg/kg in soil from desorber	PCB DE[1] for soil up to 99.9% PCB DRE[2] 99.9999%+ PCB DE[1]
13 Rehabilitation of a site contaminated by tar substances using a new on-site technique	1,500-80,000 mg/kg total tars. Median value is 11,000 mg/kg.	22 mg/kg total tars	99.8%
19 Cleaning mercury-contaminated soil using a combined washing and distillation process	400-3,000 mg/kg Hg on surface of brickwork 1,000-4,000 mg/kg Hg in soil	Average from January 1995: 20 mg/kg Hg	No overall figures.
20 Fluidized bed soil treatment process—*BORAN*	No information	No information	No information.
21 Mobile low-temperature thermal treatment process	Mineral oil, 3.8% Heavy mineral oil, 2.2% Light tar oil (PAH $C_{2\text{-}6}$), 0.45% Tar oil ($C_{2\text{-}6}$), 0.5% TNT, 180 mg/kg Mercury, 11,000 mg/kg 900 mg/kg 300 mg/kg	60 mg/kg 1,000 mg/kg 2 mg/kg 20 mg/kg 4.5 mg/kg 85 mg/kg 25 mg/kg 5 mg/kg	No information.

Notes:

[1] Destruction efficiency (DE) is a measure of the system's ability to destroy organic compounds as measured around the system and all output streams. DE(%)= $(1-\text{Mass}_{output}/\text{Mass}_{input}) \times 100$

[2] Destruction and removal efficiencies (DREs) compare the mass flow rate of selected feedstock compounds to their mass flow rate in the boiler stack gas. DRE(%)= $\{(1-\text{Mass}_{stack})/\text{Mass}_{input})\} \times 100$

7.7.2 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using New On-Site Technique

Analysis of the "clean" products of the soil washing process proved difficult due to the heterogeneity of the coarse material, which comprised pieces of brick, concrete, and stones. Only limited chemical analysis of the coarse washed fraction (2-50 mm) was conducted. Reliance was largely placed on visual inspection. Ammonia in the recycled wash water enhanced washing efficiency. However, as tar concentrations in the recycled wash water built up, washing efficiency decreased because at high tar concentrations, the water lost its ability to emulsify the tar.

Concentrations of total tars in the fine concentrate (<2 mm) treated at the thermal treatment plant were found to range between 1,500 mg/kg and 83,000 mg/kg. The fine concentrate was regarded as of optimal grain size and homogeneity for the thermal treatment. Because of the variable nature of the feed material and the 3-hour plug-flow operation, it was difficult to match input and output samples. The characteristics were therefore expressed statistically; the distribution of values for both was approximately log normal.

Treatment efficiency was reported to be in the order of 99.8% with total tar concentrations reduced to 22 mg/kg from a median input of 11,000 mg/kg. Comparable performance was achieved for individual PAHs including benzo(a)pyrene, which was reduced from a median value of 100 mg/kg to less than 0.1 mg/kg.

7.7.3 Project 19: Cleaning of Mercury-Contaminated Soil Using a Combined Soil Washing and Distillation Process

Results of Routine Plant Monitoring

About 57,000 metric tons of soil were successfully treated between 1993 and 1996; the daily average throughput was about 150 metric tons. Thorough monitoring of the plant showed that all requirements were met during operation of the system. Emissions were found to be well below the specified criteria. Long-term plant monitoring has shown that residual concentrations are well below 50 mg/kg, even if peaks of very high input concentrations amount to more than 5,000 mg/kg mercury (Table 7.5). Trial runs done with mercury-contaminated soil from another site showed that a clean-up criterion of 2 mg/kg can be reliably met using an appropriate plant configuration.

Table 7.5: Mercury Concentrations in Waste Streams Treated in Project 19

Unit	Period	Average Concentration of Mercury		Treatment Criteria
		Feed Stream (mg/kg)	Treated Stream (mg/kg)	
soil washing plus vacuum distillation	Sept. 93-Oct. 94	average= 500 peaks up to 5,000	23	50 mg/kg
	Nov. 94-Oct. 95		19	
	Nov. 95-Feb. 96		7.9	
vacuum distillation	Oct. 95-Apr. 96	-	3.6	-
water treatment	1993-96	-	(see Section 3.2)	10 µg/L
stack gas	1993-96	-	(see Section 3.2)	50 µg/dscm

Results of a Technology Demonstration Under USEPA's SITE Program

The Harbauer Treatment System was the subject of a technology demonstration in a joint project of the German Federal Ministry of Science, Education, Research and Technology and the USEPA. The technology demonstration was done according to the SITE protocols during routine operation of the plant. Based on the SITE demonstration results, the following conclusions were drawn about the Harbauer soil washing and vacuum distillation soil treatment technology:

- Average total mercury concentrations in the treated sandy loam and loam soils were reduced from 875 mg/kg to less than 18 mg/kg (95% confidence level).

- Average total mercury removal efficiencies for the soils ranged from 98-99%.

- Average Toxicity Characteristic Leaching Procedure (TCLP) mercury concentrations in the soil leachates were reduced from 82 µg/L to less than 6 µg/L.

- The average mercury concentration in treated process water discharged to the municipal sewer was 5 µg/L.

- The average mercury concentration in the treated stack gas discharged to the atmosphere was 2.92 µg per normal cubic meter (However, these measurements were not made during the same test runs as the demonstration soil samples that were collected.).

7.7.4 Project 20: Fluidized Bed Soil Treatment Process—*BORAN*

There are no results for Project 20 because the plant was not operational by the time the Phase II Pilot Study ended.

7.7.5 Project 21: Mobile Low-Temperature Thermal Treatment Process

Pilot-scale trials (Table 7.6) were carried out during 1994 and 1995 to evaluate process performance and to aid design of a commercial scale plant. In many cases, the observed concentration of contaminants in the process water was low or below detection limits. Steam injection enhanced volatilization of certain contaminants at a particular temperature. The results showed that at 270°C, and at low steam injection rates, a treated soil sample still contained up to 35 mg/kg of 5- and 6-ringed PAHs. At higher injection rates but at the same temperature this residual concentration dropped to about 10 mg/kg.

Table 7.6: Summary Results of Pilot-Scale Trials

Contaminant	Temperature (°C)	Stripping Steam (kg/hr)	Input Concentration (mg/kg)	Output Concentration (mg/kg)
Mineral oil in clay soil	240	6	38,000	60
Heavy mineral oil	270	5	22,000	1,000
Light tar oil (PAH C_2-C_4)	270	6	4,500	2
Tar oil (PAH C_2-C_6)	240	6	5,000	50
Mercury in sandy soil in clay soil in clay soil	280 330 320	4 6 6	300 900 11,000	5 25 85
Trinitrotoluene (TNT)	210	8	180	4.5

7.8 ENVIRONMENTAL IMPACTS

7.8.1 Project 7: Demonstration of Thermal Gas-Phase Reduction Process

During the tests, continuous emission monitors measured the concentrations of the criteria air pollutants at the stack: nitrogen oxides (NO_x), sulfur dioxide (SO_2), total hydrocarbons (THC), and carbon monoxide (CO). Each of these pollutant concentrations were well under the level established in the Michigan Department of Natural Resources (MDNR) permit.

The demonstration boiler operated between high and low fire, depending on the system's steam requirements. The test analyses showed out-of-range spike concentrations of THC and CO, which are indicators of combustion efficiency, during low-fire operation, most notably during treatment of the wastewater when cycling between high- and low-fire conditions.

Hydrogen chloride emissions were well below the MDNR permitted level of 4 lbs/hr (1.81 kg/hr or 99% removal); average stack concentrations ranged from 0.66 mg/dscm at 109 mg/hr to 0.81 mg/dscm at 198 mg/hr. Removal efficiencies reached 99.98%.

Process residuals comprised reactor grit, scrubber sludge, scrubber decant, scrubber liquor, compressed tank condensate and stack gas—and when the TDU was used, treated soil. The reactor grit contained PCBs, PAHs, and other organic compounds. However, ECO LOGIC intend to recirculate the grit through the reactor in a full-scale plant. Scrubber residuals also contained metals and a variety of organic compounds, but again recycling through the plant should be possible.

7.8.2 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using a New On-Site Technique

Washed coarse material (>2 mm) was returned to the excavation. The disposal route for thermally treated fine materials is not clear from the report.

One of the key elements of the project was to avoid emissions to atmosphere by the use of a ventilated tent. Air emissions from the thermal treatment process were destroyed by feeding them to the Stage-2 oil burner.

One of the projects key conclusions concerned the noise associated with the remedial process. It was found that with a measured level of about 60 dB(A) at the working site it was difficult but practical to meet the maximum permitted noise level of 50 dB(A) at the site boundary.

Water from the tar reservoirs was used in the soil washing process and treated in a plant (1 m^3/hr capacity) comprised of an oil skimmer, cellulose filter for particulates and an active carbon filter.

7.8.3 Project 19: Cleaning of Mercury-Contaminated Soil Using a Combined Soil Washing and Distillation Process

Precipitation sludge from the water treatment system was disposed in subsurface hazardous waste storage facilities. Spent ion exchange resin was reactivated off-site for recycling. Condensed mercury was disposed off-site for reuse or proper disposal. During plant operation, nearly 30 tonnes of mercury were recovered. Treated wastewater and treated off-gas were subject to constant on-line monitoring. Treatment criteria of 10 µg/L and 50 µg/dscm, respectively, were achieved.

7.8.4 Project 20: Fluidized Bed Soil Treatment Process—*BORAN*

No performance data available because the plant was not operational by the end of the Phase II Pilot Study.

7.8.5 Project 21: Mobile Low-Temperature Thermal Treatment Process

No information on emissions was provided.

7.9 HEALTH AND SAFETY

7.9.1 Project 7: Demonstration of Thermal Gas-Phase Reduction Process

The principal health and safety concerns were the physical hazards common on construction and remediation sites, chemical use, equipment integrity, and process control.

The chemical hazards arise from the use of propane, liquified nitrogen and oxygen, hydrogen, industrial chemicals, and hazardous feed materials. In addition, the process generates methane. Standardized industrial procedures provided adequate guidance for storing, transporting and handling these materials.

There should be no undue concern associated with hydrogen usage in the process. Well-established and proven procedures are available for safe hydrogen storage and use. Hydrogen is no more or less dangerous than gasoline or methane, but it must be handled with regard to its unique properties. Verification of system integrity is essential for process safety. Hydrogen is more difficult to contain because of its small molecular size. Therefore, interfaces of equipment, instruments, and piping must be leak-free. To provide additional safeguards, the process is operated at a slight positive pressure to prevent oxygen ingress, internal oxygen concentrations are monitored, and gas feeds (propane and hydrogen) maintained at low pressure to minimize the likelihood of pipeline breaks. The plant is fitted with an automatic safety system which initiates plant shutdown in the event of a number of hazardous situations occurring.

7.9.2 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using a New On-Site Technique

During excavation, the release of volatile substances was very high. Although a ventilation rate of three air exchanges per hour was maintained, it was still necessary for workers within the tent to use personal protection. Two principal levels of protection were provided:

- chemically resistant suits with fresh-air supply through an air tube for manual work involving direct contact with heavily contaminated material; and

- fabric coveralls combined with a fresh-air mask with multi-filter in all other work operations.

Excavator operators either used a fresh-air mask with multi-filter or were supplied with a pressurized cabin with filtered air supply.

The effectiveness of the chemically resistant suits was checked. Volatile tar substances such as BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), phenols and naphthalene, could not be detected inside the suits.

Both of the desorber units were protected by two independent systems:

(1) Jets spraying water on the hot internal surface thereby producing steam. This steam has three functions: (a) as a start up procedure to remove air/oxygen from internal hot parts before feeding materials; (b) to keep the system over-pressurized relative to atmospheric pressure during operation; and (c) back-up in shutdown situations, when steam production from wet material decreased.

(2) Nitrogen was added automatically to the processor if the internal pressure dropped below atmospheric pressure.

7.9.3 Project 19: Cleaning of Mercury-Contaminated Soil Using a Combined Soil Washing and Distillation Process

No information was provided.

7.9.4 Project 20: Fluidized Bed Soil Treatment Process—*BORAN*

No information was provided.

7.9.5 Project 21: Mobile Low-Temperature Thermal Treatment Process

No information was provided.

7.10 FACTORS AND LIMITATIONS TO CONSIDER FOR DETERMINING THE APPLICABILITY OF THE TECHNOLOGY

7.10.1 Project 7: Demonstration of Thermal Gas-Phase Reduction Process

The SITE Program concluded that the ECO LOGIC process efficiently treated liquid wastes containing oily PCBs and other organic compounds, and water containing PCBs, other organic compounds, and metals. Stack emissions met stringent regulatory levels. The principal residual stream—the scrubber effluent—concentrated metals and some organic compounds (benzene, PCBs, PAHs), indicating that additional treatment, such as recycling through the process, might be required prior to disposal. However, throughput reliability was only 20-55% of design and system availability was 24% indicating that system reliability needs improvement. A number of technical problems were encountered during operation of the plant and are recorded in the SITE program report. The boiler should be operated at firing rates and air/fuel ratios that prevent the spikes of THC and CO observed during the trial.

The reactor system is best suited for processing liquids and TDU off-gases and water vapor. The waste's organic content limits the demonstration-scale system's feed rate because of the reformed gas generation. ECO LOGIC plans to improve throughput by storing excess reformed gas after compressing it. Future users should consider the implications, logistics, and costs of this approach.

The TDU did not perform to design specifications. The USEPA categorized the TDU test data as a system proof-of-concept rather than as a comprehensive evaluation of a fully developed unit. The TDU only achieved acceptable desorption efficiencies at the expense of throughput. In addition, ECO LOGIC experienced material handling problems with the TDU feed. The combination of feed problems and inadequate organics desorption showed a need for further development. Nevertheless, the demonstration did show that the TDU can desorb PCBs and that satisfactory treatment in the reactor system was possible.

Cold-weather operations may inhibit efficient destruction because of the incremental amount of energy required to heat the reactor. In addition, frozen feedstock liquids would require melting prior to treatment, and liquid residuals could freeze in the unheated storage tanks. Winterization, including heat tracing, is necessary to provide adequate feedstock and to ensure uninterrupted processing.

7.10.2 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using a New On-Site Technique

The only specific difficulty noted in the report was the reduction in effectiveness of the soil washing plant as the concentration of tarry substances built up in the recycled wash water. This could presumably be overcome by introducing a greater proportion of fresh water. This has also been noted as a limitation in other soil washing operations.

Operation within a tent successfully limited emissions to the atmosphere from soil handling although noise remained a potential problem. However, containment in this way, does increase the potential risks to workers compared to working in the open when emissions can rapidly disperse into the air. However, avoidance of weather extremes may help to reduce the potential for accidents due to difficult working conditions.

7.10.3 Project 19: Cleaning of Mercury-Contaminated Soil Using a Combined Soil Washing and Distillation Process

No specific limitation regarding the technology were noted in the report. However, it emerged during analysis of the results of the USEPA-German Bilateral project that the analytical method used to determine PAH concentrations in the untreated and treated soils is important. In particular, the extraction method used as some methods will tend to underestimate the proportion of the more volatile PAHs present, and other methods will tend to underestimate the less volatile fraction. Reliable assessment of effectiveness may, therefore, require use of more than one analytical method in parallel.

7.10.4 Project 20: Fluidized Bed Soil Treatment Process—*BORAN*

No performance data available because the plant was not operational by the end of the Phase II Pilot Study.

7.10.5 Project 21: Mobile Low-Temperature Thermal Treatment Process

No specific limitations were noted in the project reports.

7.11 COSTS

Cost data are summarized in Table 7.7.

Table 7.7: Cost Data

Project		Cost information
7	Demonstration of thermal gas-phase reduction process	Liquids: U.S.$1,840-2,205/ton Soil: U.S.$550-695/ton
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique	Total cost U.S.$2.6M, of which 70% is directly attributable to soil and ground water treatment.
19	Cleaning mercury-contaminated soil using a combined washing and distillation process	Total cost estimated to be DM 150M.
20	Fluidized bed soil treatment process—*BORAN*	Plant not operated.
21	Mobile low-temperature thermal treatment process	Costs of a full-scale plant are estimated to be about DM 150-250 (U.S.$90-160), depending on the contaminants (1996 prices). The report suggested the process would not be economical for remedial actions of less than 100 tonnes.

7.11.1 Project 7: Demonstration of Thermal Gas-Phase Reduction Process

The 12 categories established for the SITE Program[5] formed the basis for the cost analysis of the treatment of liquid wastes. Costs relate to the reactor system, processing an average 2.2 kg/min, as operated at the Middleground Landfill site. For this estimate it was assumed that 378 m^3 (100,000 U.S. gallons) of wastewater and 114 m^3 (30,000 U.S. gallons) of waste oil were stockpiled for treatment. Based on the economic analysis, the estimated cost (1994 U.S. dollars) for treating liquid wastes similar to those at the Bay City site ranged from U.S.$2,205/tonne (60% utilization factor) to U.S.$1,840 (80% utilization factor). The most important element affecting cost is labor (52%), followed by site preparation (15%), supplies (12%), and start up/mobilization (12%).

Demonstration site preparation costs were U.S.$127,400. Capital costs (for the reactor and immediately associated equipment, but excluding the TDU) for a commercial operation are estimated to be U.S.$585,000.

Similarly, the costs of treating contaminated soils were estimated. These were estimated at U.S.$695/tonne (at a 60% utilization factor) and U.S.$550/tonne (80% utilization factor). Important elements affecting cost are fuel (67%), equipment (11%), and labor (9%).

7.11.2 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using a New On-Site Technique

The total project cost was about 18M DKK (about U.S.$2.6M) of which 15M DKK (about 70%) was for contracted clean up costs. The total cost included:

Personnel costs (consultant and contractor)	13%
Operation and maintenance	7%
Establishment and rental of the tent	7%
Soil. air and water cleaning costs	70%
Analytical costs	1%
Miscellaneous	2%

7.11.3 Project 19: Cleaning of Mercury-Contaminated Soil Using a Combined Soil Washing and Distillation Process

The estimated treatment cost was 480 Deutsche Marks (DM) per tonne, which is approximately U.S.$320/tonne (assuming 1.5 DM= U.S.$1).

7.11.4 Project 20: Fluidized Bed Soil Treatment Process—*BORAN*

No projected costs for an operational process were provided.

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[5] Site preparation, permitting and regulatory, capital equipment, mobilization and start-up, operations labor, supplies, utilities, effluents, residuals, analytical, repair and maintenance, demobilization.

7.11.5 Project 21: Mobile Low-Temperature Thermal Treatment Process

According to Ruhrkohle, the costs of cleaning soil using a full-scale plant based on this process would be about 150-250 DM/tonne (U.S.$90-160), depending on the contaminant(s). The cost depends on the plant equipment required and waste disposal costs.

An important factor influencing costs is the quantity of soil to be treated at a particular site. Ruhrkohle accepts that a mobile plant cannot compete with stationary plants when only a small amount of soil is to be treated (for example, mobilization costs would be disproportionally high). However, for larger quantities of soil, treatment of the contaminants such as mineral oils and PAHs in the mobile plant should be less expensive, because on-site cleaning does not involve transport costs for the soil and does not require any expenditure for obtaining permits. It can be installed rapidly and operated under German law without the need for time-consuming applications for approvals to set up and operate.

7.12 CONCLUSIONS AND PROGNOSIS

As a group, the projects showed that thermal treatment plants can provide a technically satisfactory means of dealing with a wide range of organic contaminants and with mercury. They also showed that thermal treatment can be integrated well with pretreatment processes such as soil washing that are intended to reduce the volume of material to be treated. Unfortunately, the promising fluidized bed technology described under Project 20 did not become operational during the study.

Project 13 illustrated the benefits and practicality of operating even complex on-site operations under cover thereby limiting possible impacts from emissions within an urban area; however, noise may still remain a problem. Containing the operations under a tent may increase risks to workers from emissions that might otherwise rapidly disperse into the air.

The thermal processor employed in Project 11 appears to be uniquely versatile in being able to handle contaminated soils, waste waters and non-aqueous phase liquids (NAPLs).

Costs will remain a limiting factor for the technologies described here, hence pretreatment to reduce the amount of contaminated material to be treated is important. The cost of U.S.$550-695/tonne of soil quoted for the Eco Logic process (Project 7) is only likely to be justified for treatment of difficult contaminants such as PCBs. Costs for processing of less difficult materials such as PAHs and hydrocarbon oils are most likely to come from measures to reduce energy requirements, which are much more expensive in Europe than in the United States, and to increase throughput of mobile plants of a given size.

7.13 REFERENCES

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Chapter 8: STABILIZATION/SOLIDIFICATION PROCESSES

Michael A. Smith
M.A. Smith Environmental Consultancy

8.1 INTRODUCTION

Stabilization/solidification methods (sometimes called immobilization methods) change the physical state of a contaminated material, such as solidifying a contaminated sludge. In addition, chemical stabilization can reduce the “availability” of contaminants to potential targets, usually by containment within a solid product of low permeability. Harris *(1)* and the American Academy of Environmental Engineers *(2)* have recently reviewed stabilization/solidification methods.

Stabilization involves adding chemicals to the contaminated material to produce more chemically stable constituents, for example, is the formation of virtually insoluble metal hydroxides. Stabilization may not result in an improvement in the physical characteristics of the material. For instance, the material may remain as a relatively mobile sludge, but the stabilization process will have reduced the toxicity or mobility of the hazardous constituents within it.

Solidification involves adding reagents to the contaminated material to reduce the material’s fluidity or friability and to prevent access by external mobilizing agents, such as wind or water, to the contaminants contained in the solid product. Solidification does not necessarily require that chemical reactions occur between contaminants and the solidification agent, although such reactions may take place depending on the nature of the reagent.

In practice, many commercial systems and applications involve a combination of stabilization and solidification processes. Solidification follows stabilization to reduce exposure of the stabilized material to the environment through, for example, formation of a monolithic mass of low permeability.

Although volatile constituents may be driven off (because heat is often generated) and some hydrolysis of chlorinated organic compounds may occur during the application of some processes, the destruction or removal of contaminants is not the objective of stabilization/solidification.

Contaminants may become available once again if the physical or chemical nature of the treated product alters in response to changes in the external environment, such as exposure to an acidic discharge or leachate or physical breakdown of a compacted soil mass due to freezing and thawing. Solidified products also may be subject to internal degradation reactions over time (*e.g.,* the oxidation of sulfides to form expansive sulfates). Key points for selecting a stabilization/solidification method are therefore:

- its ability to achieve and retain the desired physical properties, chemically stabilize or permanently bind contaminants, and contain (physically entrap) contaminants over the long-term; and

- the methods to be used to determine treatability and short- and long-term performance.

The effectiveness of stabilization/solidification methods depends on:

- proper characterization of the material to be treated so that the most appropriate formulation can be selected;

- effective contact between the contaminants and treatment reagents—for many systems this can be achieved by ensuring a high degree of chemical and physical consistency of the feedstock, and the use of appropriate mixing equipment;

- control over external factors, such as temperature, humidity, and amount of mixing after gel formation, since these affect the setting and strength development processes and the long-term durability of the product; and

- absence of substances that inhibit the stabilization/solidification process and development of the required physical characteristics, or pretreatment to render such substances harmless, such as by sorbent addition.

Treatability studies are always required to establish anticipated effectiveness and materials handling requirements.

Because most stabilization/solidification methods involve the addition of solid reagents to the contaminated material, some increase in the final volume of the treated product can be expected. Increases in the range 30-130% are typical *(4)*. A major advantage of most stabilization/solidification methods is that they improve the handling characteristics of sludges and other high-water content materials, and may confer additional structural strength on contaminated material. Sometimes these are the primary reasons for their use, and they may be an important consideration for contaminated sites undergoing redevelopment. Stabilization/solidification methods are readily applied onsite using mobile mixing and blending equipment.

Most commercial stabilization/solidification systems are derived from established hazardous waste treatment techniques and use relatively simple equipment and conventional reagents (binders) to immobilize the contaminants. Systems may be classified according to the primary stabilization agent used: cement-based, pozzolan-based, silicate-based, thermoplastic-based, or polymer-based systems. In practice, a combination of these reagents may be employed. The formulations actually used on a commercial basis are often proprietary in nature.

In the U.S., stabilization/solidification is considered an established technology for the treatment of certain inorganic forms of contamination, and long-term monitoring data are available on the performance of solidified wastes in the field *(4, 5, 6)*. Stabilization/solidification techniques have also been used in Europe for the treatment of hazardous waste. However, doubts remain over their long-term performance. These doubts arise from the chemical and physical nature of the processes themselves and from observed deficiencies in the quality of application in the field (and in fixed plant). In addition, methods of testing and predicting performance are not well developed and are the subject of continuing debate *(7)*. Proprietary formulations for the treatment of organic contaminants prior to the use of conventional binders are available in the U.S., but practical experience in their application is limited.

8.1.1 Main Process Variations

Processes can be grouped according to the reagents used to achieve stabilization/solidification and conveniently categorized into three main groups:

(1) Those based on inorganic cementitious systems including Portland cement, pozzolans, hydraulic slags, and lime.

(2) Those using organic binders, including asphalt emulsions, bitumen, and other thermoplastics.

(3) Other systems, such as those using sulfur as a binder *(2)*.

Other materials used in cementitious systems include cement kiln dust, lime kiln dust, and steel slag fines. Depending on the source, cement kiln dust may contain variable proportions of reactive calcium silicates, free lime, partially reacted and possibly pozzolanic clay minerals, and alkali sulfates.

With the exception of proprietary lime and thermoplastic-based methods, which can be applied to solids contaminated with organic residues, one of the principal limiting factors associated with conventional stabilization/solidification systems is that even very low concentrations of organic contaminants may interfere with setting and hardening processes. Thus, recent research has addressed the development of methods that can treat materials contaminated with both organic and inorganic contaminants. One approach involves the use of organophilic clays to preferentially absorb organic contaminants (see discussion of Project 34 below). Treated material then undergoes conventional stabilization/solidification to immobilize the inorganic constituents and provide a secondary layer of protection around the clay-bound organics. Other potentially useful adsorbents include ion exchange resins, activated carbon, and zeolites.

8.1.2 *Ex situ* Methods of Application

Ex situ stabilization/solidification methods can be applied in three main ways:

(1) Plant processing, in which contaminated material is excavated and then mixed with stabilization/solidification reagents in a plant specifically designed for the purpose or adapted from other applications, such as concrete batching and mixing plants.

(2) Direct mixing, in which contaminated material is excavated and transported to a designated area of the site. The material is then spread out in layers, and the reactive ingredients are added and mixed in using a mechanical plant. Direct addition and mixing may be used to treat contaminated sludges and sediments present in lagoon areas and ponds.

(3) In-drum processing, in which binders are added to contaminated material contained in a drum or other container. After mixing and setting, the product is disposed in the drum.

Plant processing has considerable advantages: it ensures adequate mixing and reduces unacceptable environmental impacts due to the release of particulates and vapors. Three principal steps are employed in the application of plant processing:

- pretreatment, for example to dewater, grade, or homogenize the material to be treated, or to concentrate the contaminants (*e.g.*, by soil washing);

- mixing of waste with active ingredients either to form a pumpable slurry or a material that can be placed using standard earth moving/engineering equipment; and

- placement and curing.

Curing of pumpable material requires maintenance of appropriate temperature and humidity to promote stabilizing reactions and proper development of physical properties. Curing may take place in molds or in disposal lagoons. With low-moisture content material, curing occurs at the final disposal site. When treated material is placed in lagoons, care should be taken to prevent the formation of “cold joints,” which would allow water easy access and allow excessive accumulation of contaminated free water (bleeding).

Effective treatment usually requires a relatively high ratio of treatment agent to feedstock. The amounts used affect chemical stabilization capacity, permeability, and the long-term strength and durability of the product.

The required amount of water varies with the system and can be very important. For instance, in cement-based systems, the water:cement ratio is an important factor in the development of early and long-term properties of the system. Water is a reactive component of the system. Lower water contents are generally preferred.

The options for final disposal should be taken into account when deciding on the acceptability of a particular application. What is permitted depends on the nature of the product and may vary among countries. In some cases, a full containment landfill may be required. In contrast, there are reported cases *(8, 9)* where treated material has been used successfully as a construction base. In these cases, the material is placed and compacted in thin layers to agreed specifications using standard engineering procedures.

8.1.3 *In Situ* Methods of Application

Stabilization/solidification reagents may be introduced into the ground using soil mixing equipment (*e.g.*, contra-rotating hollow stem augers through which treatment agents are injected) or by pressure injection using techniques analogous to conventional grouting.

Only the former method has been developed on a commercial scale, and the discussion that follows is restricted to such systems. The latter concept was examined in a report for the U.K. Department of the Environment in 1982 *(10)*, and two principal disadvantages were identified:

- difficulty in ensuring even permeation of the treatment agent in the ground; and
- treatment depth limitations (in excess of about 2 m) because of a need for sufficient overburden pressure to withstand the injection pressures required (the report indicated that this might be overcome by temporary surcharging).

Stabilization/solidification, when applied to material in lagoons, is typically performed using conventional construction equipment, such as backhoe excavators and draglines. Effective mixing is very difficult to achieve. The primary purpose of these operations is usually to improve the physical characteristics of the material *(11)*.

The in-ground mixing process developed in the U.S. by International Waste Technologies and Geo Con, Inc., was evaluated under the USEPA Superfund Innovative Technology Evaluation (SITE) Program in 1988 *(12)*. Other *in situ* stabilization/solidification processes are under development and scheduled for demonstration under the SITE program *(13, 14)*. An established ground improvement (solidification) technique, using jet grouting, also has potential for application (see Box 8.1).

As with *ex situ* stabilization/solidification processes, the product obtained after treatment typically should comprise a dense, homogeneous material with favorable leaching and weathering characteristics, low permeability ($\leq 10^{-5}$m/s), and good (>0.34 MPa) unconfined compressive strength. Unlike *ex situ* systems, where the physical properties of the excavated material can be determined in advance of processing and some pretreatment preparation is possible, the effectiveness of *in situ* applications relies on adequate characterization of the ground at the treatment location to optimize the mixing conditions.

Box 8.1: Soilcrete® Jet Grouting

In this process, soil is loosened by the high pressure action of water, often sheafed in a cone of air (jet-cutting). The loosened soil is partially removed to the surface via air-lift pressure as the remaining soil is simultaneously mixed with cementitious or cement/bentonite grout. Columns can be made to overlap, thus treating all of the soil. The columns have diameters of 0.5-1.8 m, depending on soil type. Compressive strengths of up to 10 MPa can be achieved in granular soils and 5 MPa can be achieved in cohesive soils. Some binding of inorganic contaminants can be expected. Permeabilities in the range 10^{-6}-10^{-9} *m/s can be achieved.*

A variation of the jet-cutting process, in which the soil is displaced by clean material introduced at the base of the hole, has been applied to permit ex situ treatment of the displaced soil.

8.2 CASE STUDIES CHOSEN

Only two stabilization projects were included in the pilot study:

- Project 34 *Chemical fixation of soils contaminated with organic chemicals* (Envirotreat); and

- Project 29 *Sorption/solidification of selected heavy metals and radionuclides on to unconventional sorbents*.

Conventional stabilization/solidification methods, such as those based on cementitious and pozzolanic materials, have been applied with limited success to treat soils with organic contaminants. Project 34 involved the development of a range of modified organophilic clays with the goal of overcoming these limitations in an *in situ* stabilization/solidification application based on cementitious binders. Following laboratory trials to develop the optimum combination of modified clays and other ingredients, the technology was tested at field scale on a site contaminated with a variety of inorganic and organic substances.

Project 29 involved a laboratory-scale investigation of the use of solid wastes, such as red muds and coal fly ashes, to absorb toxic heavy metals and radionuclides from water (a fixation or stabilization process) followed by solidification of the metal-loaded solid wastes in a cement-based system.

Both projects focused on the pre-solidification stabilization stage with the intention of providing adsorptive media for organic and inorganic contaminants, respectively. Both are intended to be used with cement-based solidification processes.

The projects differ in that the:

- Project 34 uses a tailor-made (possibly expensive) organophilic clay, while Project 29 seeks to use readily available, inexpensive waste materials; and

- Project 34 is intended for the treatment of soils, while the Project 29 is intended for the treatment of effluents.

The projects are summarized below. Additional detail is provided in Appendix IV, Project Summaries.

8.2.1 Project 34: Chemical Fixation of Soils Contaminated with Organic Chemicals (Envirotreat Process)

The Envirotreat process uses modified smectite clays that contain reactive species. The process is primarily targeted at organic contaminants, but also has the capability to treat cationic and anionic heavy metal species by a combination of ion-exchange processes and chemical interaction with pillaring agents and other intercalatants. The technology uses modified continuous-flight auger drilling and injection techniques. The treatment materials are injected in slurry form into the ground and mixed with the contaminated soil *in situ*.

Commercially available organophilic clays are typically made by the substitution of quaternary ammonium salts into phyllosilicate clay matrices (*e.g.*, montmorillonite). The primary objective of this project was to modify these clays through intercalation (*i.e.*, substitution of the cations between clay layers) to improve stabilization of organic contaminants by:

- increasing the size of the interlamellar spacing within the clays to accommodate large molecules, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs); to increase the effective surface area; and to increase the potential reactivity by introducing selected pillaring agents;

- optimizing the polarity of the interlamellar environment to increase the absorption and adsorption of organic contaminants;

- providing a reactive environment on interlamellar clay surfaces to chemically bind contaminants permanently; and

- providing an active medium for effective treatment of heavy metals (both cationic and anionic) and other inorganics by cation exchange processes and/or interaction with the intercalated species (which then can be immobilized within the cementitious matrix following alkaline precipitation).

An advantage of using tailored organoclays is that a clay can be manufactured to treat a specific group of contaminants by manipulating the type and amount of intercalating agents used. Envirotreat's goal was to produce a range of clays with varying hydrophobicity and chemical composition to deal with five different groups of organic compounds.

Following laboratory trials to develop the clays and additional efforts to optimize the auger design, a field trial was carried out on a site occupied since the turn of the century by a variety of industrial operations, including a chemical waste “quarantine store,” chemistry laboratory, flammables store, battery bank, engine testing areas, underground storage tanks, and nucleonic laboratory. Likely contaminants included flammable materials, solvents, concentrated sulfuric acid, oils, gasoline, and radioactive species. Site characterization seems to have been very limited in terms of the range of contaminants analyzed and the number of samples *(3)* analyzed. The maximum value for PAHs (six carcinogenic compounds selected by the World Health Organization [WHO]) was 12 mg/kg—well below the U.K. threshold value for residential development (50 mg/kg for 16 USEPA PAHs). Maximum copper, lead, and zinc concentrations were 635, 3,330, and 785 mg/kg, respectively.

Prior to field operations, a laboratory program was conducted to determine the type of intercalated clay to be used; the proportions of cement, fly ash, and clay for the grout; and the optimum soil:grout ratio. The clay formulation used was Al^{3+} pillared and Fe^{3+} exchanged (spiked) and then treated with benzyl quaternary ammonium salt. The modified clay was produced as a suspension at Birmingham University and transported to the site in steel drums. The clay concentration was 20 g/L (2.5 times more dilute than that used in laboratory treatment trials).

The grout was injected using a prototype auger fitted to a conventional piling rig that produces 900-mm diameter columns either individually or overlapping. The columns were formed by advancing the auger into the soil to the required depth of the column, mixing the soil in place during the auger descent, and then injecting the grout slurry into the soil with simultaneous mixing on the auger withdrawal. The overall volume increase, measured at the end of the second day, was about 1 m^3, which represents an increase of about 6.5%. For this demonstration, columns with 50% overlap were chosen, and several different optimized mixes were evaluated in adjacent columns. An area of 6 m^2 to a depth of 2.5 m was treated in the trial. Cores aged 50 days (taken at 44 days), 70 days (taken at 57 days), and 1 year (presumed to have been taken at 57 days) from each column were tested in the laboratory against the treatment criteria outlined below.

The effectiveness of the various treatments in the laboratory and field was assessed based on:

- unconfined compressive strength by an American Society for Testing and Materials (ASTM) method (greater than 350 kPa after 28 days of curing);

- leachability, based on the USEPA Toxicity Characteristic Leaching Procedure (TCLP), which uses an aggressive acid leaching medium, with respect to six WHO PAHs (total PAHs less than 10 µg/L and benzo(a)pyrene less than 0.5 µg/L) and chromium, copper, lead, and zinc with target levels 50 times the U.K. drinking water limits; and

- a final leachate pH in the TCLP leachate (between 8-10 following 28 days curing) to ensure low metal solubility (this was later amended to a pH of 7-11).

Durability (freeze/thaw and wet/dry) and permeability tests (less than $1x10^{-9}$ m/s) were used as secondary evaluation criteria. ASTM test procedures were used for the initial freeze/thaw tests on laboratory prepared materials, but the test method was subsequently modified as it was judged too harsh in relation to typical U.K. weather conditions.

The results on the cores taken at 44 and 57 days were judged to be satisfactory. All unconfined compressive strength values exceeded the target value of 350 kPa and were greater than the equivalent (28-day) laboratory results. This was particularly true for the mixes containing quick lime. The total concentrations of the six WHO PAHs in the leachates were all below 2 µg/L and often below the 0.02 µg/L detection limit. Also, the individual leachate values for benzo(a)pyrene were within the target value of less than 0.5 µg/L. All results for chromium, copper, lead, and zinc were satisfactory. Subsequently, more detailed analyses showed satisfactory performance with respect to a wider range of metals. The samples survived a modified freeze-thaw test—the ASTM method being considered too aggressive following the laboratory trials for U.K. conditions. The wet-dry test results were also satisfactory. However, only one sample satisfied the permeability criterion of less than $1x10^{-9}$ m/s; this was probably due to the presence of natural bentonite.

Cored samples collected during the site trial were cured under laboratory conditions for 12 months. They were wrapped in wet cloth and kept in a humidity room. The cores were 75-150 mm in diameter and had a maximum length of 400 mm.

Samples from all mixes showed an increase in unconfined compressive strength for those cured for 12 months, compared to those cured for 70 days. Permeability values decreased as expected due to continuing cement hydration processes. Wet-dry durability testing gave similar results after 12 months, and freeze-thaw testing was largely inconclusive (all samples failed at very low temperatures as previously observed).

8.2.2 Project 29: Sorption/Solidification of Selected Heavy Metals and Radionuclides onto Unconventional Sorbents

Cadmium (II) (Cd^{2+}), lead (II) (Pb^{2+}) and copper (II) (Cu^{2+}) are toxic heavy metals that pose a serious threat to the ecology of receiving water bodies when discharged in industrial wastewater. Cesium-137 (^{137}Cs) and strontium-90 (^{90}Sr), with half lives of 30 years and 28 years, respectively, pose significant threats to the environment as a result of fallout from nuclear bomb tests and reactor accidents. In recent years, land burial of radioactive wastes has become a common practice, posing a radioactive contamination risk to groundwater. In Turkey, ^{137}Cs became a matter of public concern after the Chernobyl accident, especially due to contamination of tea-growing areas on the Black Sea coast. Milk products and other biological materials containing ^{137}Cs were also extensively investigated for possible ^{90}Sr contamination.

Various treatment technologies have been developed for the removal of these metals from water. They include ion exchange, electrodialysis, reverse osmosis, membrane filtration, sludge leaching, electrowinning, solvent stripping, precipitation, and common adsorption. The cost of adsorptive metals removal processes is relatively high when pure sorbents, such as activated carbon or hydrated oxides, are used. Consequently, there is an increasing trend towards substitution of pure adsorbents with natural byproducts or stabilized solid waste materials. Such materials may also be useful for constructing "natural barriers" around radioactive waste disposal sites, especially for facilities involving shallow burial of low-level wastes, to prevent the leakage of radionuclides from the facility to the environment.

The goal of this pilot study project was to develop cost-effective unconventional sorbents, preferably metallurgical waste solids, for the removal of heavy metals and radionuclides from contaminated water. The removal capacities of heavy metals (Cd, Pb, and Cu) and radionuclides (^{137}Cs and ^{90}Sr) and the sorption modeling of red muds and fly ashes were studied. The irreversible nature of sorption needs to be demonstrated to guarantee non-leachability of metals from the metal-loaded sorbents.

Metal uptake (sorption) and release (desorption) were investigated by thermostatic batch experiments on coal fly ashes and on red muds, which are alkaline leaching wastes of bauxite from the Bayer process for the manufacture of alumina. The materials were subjected to a variety of pretreatments prior to the introduction of the contaminated solutions. The distribution ratios of metals between the solid sorbents and the aqueous solution were determined as a function of sorbent type, equilibrium aqueous concentration of metals, and temperature. The breakthrough volumes of the heavy metal solutions were measured by dynamic column experiments to determine the saturation capacities of the sorbents. The sorption data were analyzed and fitted to linear adsorption isotherms.

The heavy metal solutions contained up to 10,000 mg/L of Cd, Pb, or Cu made from the corresponding nitrate salts. No further pH adjustment was made. Solutions containing ^{137}Cs and ^{90}Sr were made by diluting flacons of standard solutions supplied by Amersham International, Ltd.

The desorption studies were conducted using distilled water, saturated aqueous carbonic acid (pH=4.75), and $H_2CO_3/NaHCO_3$ buffer solutions (pH=7.0) to simulate carbonated groundwater conditions for the purpose of analyzing risks around waste disposal sites.

The sorbents may serve as effective fixation agents for removing heavy metals from water prior to solidification for disposal. Although stabilization tests were conducted on the fly ash and red muds, as well as on the adsorbents after they were loaded with contaminating metals, the detailed results were not described in the final project report. Solidification of the red muds and fly ash was accomplished by adding them to a mixture of cement, standard sand, and carefully measured water. When metal-loaded solid waste was added (up to 20% by mass) to Portland cement-based formulations, the fixed metals did not leach out from the solidified concrete blocks over extended periods with the exception of Cu^{2+}, which reached a concentration of 0.4 mg/kg after 8 months in water of pH 8-9. In solid-waste concentrations below 20%, the compressive strengths and shear strengths of the doped concrete did not significantly differ from the control concrete. However, there is a critical weight percentage of 10-20% additives above which the strength declines dramatically.

8.4 PERFORMANCE RESULTS

8.4.1 Project 34: Chemical Fixation of Soils Contaminated with Organic Chemicals (Envirotreat Process)

Regardless of the success of laboratory trials, the field trial suffered from a number of deficiencies that make it difficult to evaluate the effectiveness of the process. The characterization of the site in terms of the contaminants present and their distribution was poor. The maximum PAH concentration (the total of six WHO carcinogens) was 12 mg/kg compared to a threshold trigger value of 50 mg/kg (16 USEPA compounds) for residential development and 1,000 mg/kg for commercial developments, suggesting that the site was in no need of PAH treatment. In contrast, the metal concentrations were high relative to the threshold trigger values. The greatest weakness, however, was the lack of any control mixes not containing the modified clay; thus, the possibility that a similar satisfactory performance could have been achieved in the absence of the clay cannot be ruled out. The detailed leaching results for metals are not provided in the reports but it should be noted that the criteria applied (50 times U.K. drinking water limits) were quite generous.

A calculation shows that the six WHO PAHs in the treated soil would be reduced to about 8.5 mg/kg compared to 12 mg/kg in the soil due to dilution by the other ingredients. The concentration of modified clay is about 500 mg/kg. Given the low solubility of the PAHs, the insolubility of the clay, and the probable inefficient mixing, it seems unlikely the clay could have a profound effect on binding the PAHs.

8.4.2 Project 29: Sorption/Solidification of Selected Heavy Metals and Radionuclides onto Unconventional Sorbents

The laboratory study showed that:

- Bauxite wastes of alumina manufacture (*i.e.*, red muds) are capable of removing the radionuclides ^{137}Cs and ^{90}Sr as well as other heavy metals from water. Acid- and heat-treated red muds are more effective in Cs removal than water-washed red muds, but heat treatment is detrimental to the surface hydroxyl sites, which are important for ion-exchange sorption of ^{90}Sr. Cesium uptake is predominantly irreversible and exothermic and increases with the specific surface area of the sorbent. A rise in pH favors the exchange sorption of Sr, while the specific adsorption of Cs is negatively affected.

- Coal fly ashes from thermal power plants are capable of removing ^{137}Cs and ^{90}Sr, as well as other heavy metals from water. Although acid treatment of fly ash did not result in an improved adsorption capacity, acid treatment is recommended to prevent trace pollutant leach-out from the adsorbent into water.

Red muds and especially fly ashes were shown to exhibit a high capacity for heavy metals. The sorption sequence was Cu > Pb > Cd in accordance with the order of insolubility of the corresponding metal hydroxides. The metals were held irreversibly and would not leach out into carbonic acid or bicarbonate-buffered solutions.

Metal-loaded solid wastes could be solidified to an environmentally safe form thereby serving the two-fold objective of water treatment and solid waste disposal. Thus, the two-fold objective of heavy metal fixation and metallurgical solid waste disposal could be achieved with the constraint that fly ashes better serve the purpose of heavy metal fixation than red muds.

Red muds and fly ashes, along with other metallurgical solid wastes and clay minerals, may be utilized for constructing “natural barriers” (active permeable barriers) around shallow-land burial sites of low-level radioactive wastes and heavy metal-containing products.

8.5 RESIDUALS AND EMISSIONS

8.5.1 Project 34: Chemical Fixation of Soils Contaminated with Organic Chemicals (Envirotreat Process)

No information on residuals or emissions was provided. Likely emissions would be dust that presents similar hazards to any cement-based system, and possibly volatile organic compounds if temperatures in the mixed material rise too high (the hydration of cement and lime are exothermic processes).

8.5.2 Project 29: Sorption/Solidification of Selected Heavy Metals and Radionuclides onto Unconventional Sorbents

No information on emissions was provided, but as noted above, prior treatment of the fly ash is recommended to reduce the possibility that trace elements already present in the ash will leach into the environment.

8.6 HEALTH AND SAFETY

8.6.1 Project 34: Chemical Fixation of Soils Contaminated with Organic Chemicals (Envirotreat Process)

No specific information was provided on health and safety. However, the likely hazards are those associated with any cement- or lime-based system and are primarily those that result from contact with highly alkaline materials and from chrome in cement. If volatile organic compounds are emitted due to heating of the mix, additional hazards would be expected.

8.6.2 Project 29: Sorption/Solidification of Selected Heavy Metals and Radionuclides onto Unconventional Sorbents

No specific issues of health and safety are related to this process, other than those that would ordinarily attend pretreatment processes. The reports provided no indication of the specific activity of fully loaded wastes and whether these activities might pose a health hazard, but the purpose of the treatment is, after all, to concentrate radionuclides on the solid adsorbent.

8.7 COSTS

No information was provided on costs for either project.

8.8 FUTURE STATUS OF CASE STUDY PROCESSES AND TECHNOLOGY AS A WHOLE

The Envirotreat Process (Project 34) clearly has potential but needs to be employed in better designed studies that are more likely to reveal the claimed benefits of the active ingredient. The findings of the pilot field study fail to demonstrate that the technology can bind PAHs or other organic compounds.

The use of wastes as adsorbents needs to be followed up by larger-scale studies, leading in due course to field trials under practical conditions.

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Chapter 9: OTHER REMEDIATION TECHNOLOGIES

Diane Dopkin
Environmental Management Support, Inc., Silver Spring, MD, U.S.

9.1 INTRODUCTION

The projects included in this chapter (22, 39, 50, 51, 53, 55, and 56) were not covered in previous chapters for the following reasons: (1) the project is still in the site investigation stage; (2) remedial options have been selected, but not implemented; or (3) the selected remedial option does not fit into the categories of technologies highlighted in the other technology chapters (*in situ* treatment, physical-chemical treatment, *ex situ* biotreatment, thermal treatment, or stabilization/solidification). The following sections summarize the findings of these projects. Additional information on these projects is contained in Appendix IV.

9.2 PROJECTS IN THE SITE INVESTIGATION STAGE

Projects 51 and 56 involve site investigations at contaminated industrial and military properties in the Czech Republic and will continue into the remediation stage during Phase III of NATO/CCMS Pilot Study.

9.2.1 Project 51: Sobéslav, South Bohemia Wood Treatment Plant

Since the 1870s, a wood processing plant has been operating on the outskirts of the town of Sobéslav, located 120 km south of Prague, Czech Republic. Wood products such as railway sleepers and telegraph poles were treated at the Sobéslav wood processing plant by immersion in boiling tar ("black" impregnation) or by coating with a mixture of heavy metal salts ("white" impregnation).

In 1990, following a decision to install and upgrade existing process equipment, a site investigation was performed to determine the extent of soil and groundwater contamination resulting from industrial operations at the plant. This investigation was completed in December 1996. Soil and groundwater contaminated with polycyclic aromatic hydrocarbons (PAHs) and metals were identified in an area of approximately 1-2 km^2. The contamination resulted from on-site disposal of tar sludges in poorly lined pools, discharge of untreated effluent into the Lužnice River, and discharges of chemicals from treated products staged at the site prior to transportation.

Initial concerns about site pollution centered on the foul odors emanating from local drinking water wells. The odors prompted an investigation by the local environmental health authority, which examined the results of biological oxygen demand (BOD), chemical oxygen demand (COD), and non-polar extractable organic analyses of surface water and groundwater samples. The more comprehensive investigation initiated in 1990 included a detailed site walkover survey, aerial imaging, inspection of plant life, installation and logging of monitoring wells, chemical sampling of soil and groundwater, and pump testing to determine subsurface permeability. Although originally intended to be completed in 14 months, the investigation was extended to 35 months because of financial, analytical, and regulatory difficulties.

During the walkover survey, the principal sources of contamination were identified as a leaking creosote oil storage tank and seepage from unlined disposal lagoons in the southeast part of the site. Nearly 100 boreholes were drilled, and sandy to sandy clay soils overlying sedimentary clays were found to underlie the site. Monitoring of the groundwater indicated a light non-aqueous phase liquid (LNAPL) layer up to 0.7 m thick at the site. Extensive analysis of soil and groundwater samples confirmed elevated concentrations (unspecified) of PAHs, heavy metals, and phenols.

An initial investigation of remedial options was carried out by a German consultancy, which studied the effectiveness of biotreating the contaminated soils. Results showed that an initial decrease in PAH concentrations was followed by a greater increase in concentrations, which destroyed the degrading micro-organisms. The study concluded that microbial activity had caused rapid desorption of contaminants and increased bio-available concentrations to intolerably high levels. Although more success was achieved during bench-scale testing using *in situ* groundwater biotreatment, the technique was unsuccessful during field-scale testing. As a result, it was concluded that soil encapsulation, in combination with pumping and treating groundwater with gravel filters, was the most cost-effective remediation solution.

9.2.2 Project 56: Spolchemie a.s.—Mercury-Contaminated Site

The town of Űsti nad Labem lies in the a region of North Bohemia known as the “black triangle” because of the severity of its environmental problems. The *Spolek pro chemické a hutni vyroba* (Company for Chemical and Industrial Production), also known as “Spolchemie,” is one of the most contaminated sites in this region. Spolchemie was founded in 1856 for the production of chlorinated lime and sodium bicarbonate. The company has since produced pesticides, including DDT and “Agent Orange,” and a variety of other chemicals. More than 30 separate production facilities are known to have operated at the site, which occupies over 1,000 x 5,000 m^2 (>500 hectares or 1,000 acres).

Mercury has been used in electrolysis operations at Spolchemie since 1890. Based on an environmental audit of the site, it is estimated that the total release of mercury at the site has been greater than 500 metric tons. Liquid mercury has been observed during soil excavations.

Site investigations have been conducted near the electrolysis plant to assess mercury contamination in soil and groundwater. Mercury concentrations in nine groundwater samples collected in January 1996 ranged from <0.1 µg/L to 154.1 µg/L, and concentrations in 39 soils samples ranged from <0.0001 mg/kg to 707 mg/kg. Concentrations of all but one of the groundwater samples exceed 0.1 µg/L, which is the Ministry of Environment's Category A threshold concentration for mercury; four samples exceed 5 µg/L, which is the Category C threshold. Furthermore, nine of 39 soil samples exceed the Category A threshold concentration of 0.3 mg/kg for mercury in soil; six samples exceed the Category C threshold of 10 mg/kg.

Up to several hundred micrograms per liter of chlorinated hydrocarbons and slightly elevated concentrations of zinc and copper were also detected in samples at Spolchemie. Remedial options are being studied.

9.3 PROJECTS FOR WHICH REMEDIAL OPTIONS HAVE BEEN SELECTED, BUT NOT IMPLEMENTED

The site characterization and risk assessment stages of Project 55 have been completed, and bioventing and biosparging have been selected to remediate the site.

9.3.1 Project 55: Czechowice Oil Refinery Project

This project involves a working partnership between the U.S. Department of Energy (DOE) and the Institute for Ecology of Industrial Areas (IETU), an independent organization under the Polish Ministry of Environmental Protection. Each phase of the project aims to demonstrate the technology and decision-making processes involved in site remediation.

The first project initiated by the partnership was the environmental characterization, risk assessment, and remediation of the Czechowice Oil Refinery, which has operated for nearly 100 years near the city of Katowice in southern Poland. The refinery uses a catalytic cracking process to refine crude oil. Wastes from the cracking process were deposited in site lagoons, which are now filled with a thick viscous sludge. Leakage of the lagoons has contaminated soil and groundwater with several organic compounds.

Environmental characterization of the refinery will consist of a two-phased expedited site characterization approach using low-cost, simple rapid-response technologies to obtain general site information, followed by quantitative sampling using direct push technologies for data collection. Risk assessment will involve the development and refinement of potential exposure scenarios. The scenarios will be combined with the expedited site characterization results to quantify potential risks from the site to humans and the environment. The estimates of risk will be compared to appropriate benchmark concentrations for the contaminants.

Based on preliminary site information, bioventing and biosparging have been proposed to remediate the lagoons. Bioventing involves the injection of oxygen and nutrients into the subsurface to aerobically stimulate the indigenous microorganisms to degrade hydrocarbons to carbon dioxide and water. Vertical injection wells will be installed around the perimeter of the lagoons to aerate and remediate the contaminated vadose zone. Biosparging will be conducted to treat the lagoon sludge. Biosparging is similar to bioventing except that the air and nutrients are injected into a liquid, in this case a lined basin filled with process water. Sludge that has been pH-adjusted or mixed with a surfactant will be added to the basin in batches. In the implementation of both remediation technologies, the level of microbial activity, pH, contaminant concentrations, and rate of degradation will be carefully monitored.

9.4 PROJECTS FOR WHICH THE SELECTED REMEDIAL OPTION DOES NOT FIT IN THE CATEGORIES OF TECHNOLOGIES HIGHLIGHTED IN THE OTHER TECHNOLOGY CHAPTERS

Projects 22, 39, 50, and 53 involved remedial options not covered by the technologies detailed in the previous chapters of this report. Project 22 describes the recovery of jet fuel from contaminated groundwater; *in situ* bioremediation is proposed to treat residual contamination in the unsaturated zone, but has not yet been implemented. Project 39 involves the *ex situ* treatment of groundwater contaminated with dissolved organic compounds using a chemical oxidation technology.

Project 50 involved demonstration of a groundwater pump-and-treat system coupled with a pervaporation system to treat groundwater contaminated with dissolved organic contaminants. In addition, *in situ* rotary steam and air stripping were demonstrated for the treatment of contaminated soil. *In situ* bioremediation has been proposed for further treatment of soil; however, the demonstration has not yet been conducted.

Project 53 involved both laboratory- and pilot-scale studies of *in situ* biotreatment, using aerobic and anaerobic zones to mineralize tetrachloroethene (PCE) to ethene.

9.4.1 Project 22: Environmental Evaluations of Former Soviet Military Bases in Hungary

After the withdrawal of the Soviet army from Hungary in 1990, the Hungarian Ministry for Environment conducted an environmental assessment and damage survey following a method acceptable to both the Hungarian and Soviet governments. Tököl airbase was one of the sites identified as needing prompt remediation because it is located just 600 m from the Danube River and lies atop of the aquifer that supplies the village of Halasztelek with about 5% of its municipal drinking water. Site investigations determined that the groundwater was contaminated by free phase and dissolved hydrocarbons from a jet fuel storage area. Contaminated groundwater from the airfield was migrating slowly towards the Halasztelek water supply wells.

Recovery operations at Tököl began in August 1991. Recovery of free product from groundwater was accomplished by depressing the water table to accelerate the flow of groundwater toward large diameter recovery wells where product was separated using 150 mm diameter Filter Scavenger pumps. By June 1993, approximately 224,000 liters of jet fuel were recovered from 279,000 m^3 of pumped groundwater. By April 1994, the volume of recovered jet fuel was about 700,000 liters.

Remediation at Tököl was accomplished in cooperation with the Danish Agency of Environmental Protection. The total cost was estimated at U.S.$600M (1994). The study concluded that although immediate risks to the Halasztelek water supply was reduced, jet fuel sorbed to soil in the unsaturated zone is still present and poses a long-term source of groundwater contamination. Pilot scale *in situ* bioremediation was successful and was recommended as an effective method for further reducing risks to groundwater quality.

9.4.2 Project 39: Management of Soil Vapors at the Basket Creek Site

The Basket Creek Site, located in Douglassville, Georgia, is an abandoned surface impoundment used in the 1960’s for the disposal of industrial wastes. The disposed wastes were ignited accidently and burned for several days in 1970. The USEPA initiated emergency action at the site in 1991. Analyses of soil samples revealed concentrations of toluene, methyl ethyl ketone, methyl isobutyl ketone in concentrations exceeding 30%; concentrations of trichloroethylene and tetrachloroethylene of up to 8,000 mg/kg; and concentrations of mercury and lead of 400 mg/kg and 5,000 mg/kg, respectively. Approximately 765 m^3 of contaminated soil was present with total organic concentrations ranging from 5-10%.

An *in situ* soil vapor extraction (SVE) treatability study determined that the soil was not sufficiently permeable for *in situ* SVE to be viable, and low temperature thermal desorption was rejected due to the low flash point of the soil vapor (150°C), which resulted in ignition of a soil sample during the treatability study. Based on the treatability results, *ex situ* SVE was selected to treat the contaminated soil.

Contaminated soil was excavated from the site within a 60-foot by 120-foot (18.3 m by 36.6 m) ventilated metal enclosure to prevent the escape of untreated vapors. The excavated soil was screened to remove rock and debris; the screened soil was stockpiled, and ambient air was pumped through the stockpile via 4-inch (10-cm) diameter slotted horizontal well screens.

Extracted vapors from excavation and SVE were passed through a bag-house for the removal of particulates and treated with a thermal oxidizer. The thermal oxidizer operated at temperatures of 816-871°C and had a greater than 95% removal efficiency.

In total, approximately 1,500 m^3 of soil were excavated and treated. In addition, 100 tons of screened rocks and debris, 18 yd^3 (13.8 m^3) of excavated metal and crushed drums, and 4,250 gallons (16,086 liters) of decontamination water were disposed at appropriate off-site facilities.

The total cost of the project was $2 million (1993), which was $1 million less than the original estimate in 1992. The project was interesting in that the soil was not treatable by SVE *in situ*, but could be treated by venting *ex situ* after excavation and screening.

9.4.3 Project 50: Integrated Rotary Steam Stripping and Enhanced Bioremediation for *In Situ* Treatment of VOC-Contaminated Soil (Cooperative Approach to Application of Advanced Environmental Technologies)

This project involves technology demonstrations at the Department of Energy's Pinellas Northeast Site, located in Largo, Florida, USA. Concentrations of chlorinated volatile organic compounds (VOCs) in the sandy surficial aquifer at the site range from 10-1,000 mg/L. In January 1995, the following three technologies were selected for pilot tests at the Pinellas site:

(1) groundwater pump and treat with a pervaporation system to remove VOCs from the pumped groundwater while eliminating air emissions and the need for costly groundwater pre-treatment;

(2) *in situ* rotary steam and air stripping to treat the highest concentrations of VOCs in soil and reduce them to a level of 100 mg/kg; and

(3) nutrient injection to enhance *in situ* anaerobic bioremediation of soil with VOC concentrations of 100 mg/kg or less.

A potential cost savings of U.S.$5-10 million was anticipated over the proposed baseline remedial design, which was a standard 30-year pump-and-treat system using groundwater recovery wells and an air stripper. Furthermore, the proposed baseline remedial design was not expected to reduce the most concentrated areas of VOCs to below drinking water standards.

Pervaporation Technology Evaluation

Evaluation of the pervaporation pilot test was conducted from 1995-1996. Two recovery wells pumped groundwater to the system, which used membranes to allow VOCs to preferentially permeate. Transport of VOC vapors through the membrane was induced by maintaining a lower vapor pressure on the permeate side of the membrane than on the side of the influent groundwater. This pressure difference was achieved by cooling the permeate vapor to make it condense.

The pilot system was capable of treating 1-2 gallons of groundwater per minute. Approximately 6,250 gallons of groundwater with VOC concentrations ranging from 500-1,000 parts per million (ppm) were treated during the pilot test. Effluent contaminant concentrations were reduced to 1-4 ppm under optimum operating conditions; however, the efficiency of the system was lowered due to membrane fouling caused by the precipitation of iron gel. Moderate success was achieved by modifying the system and adding chemicals to reduce membrane fouling. The only wastes produced during the pilot test were the permeate and the spent filters used to inhibit membrane fouling. VOCs were successfully concentrated in the permeate, eliminating air emissions. Full-scale system capital costs for the pervaporation system to treat 20 gallons per minute are expected to range from U.S.$200,000-275,000; operating costs are expected to range from U.S.$10-20 per 1,000 gallons (3,785 liters) of treated water.

Rotary Steam and Air Stripping Technology Evaluation

Evaluation of the rotary steam and air stripping pilot test is currently being conducted. The stripping system injects steam and hot air through a rotating auger to volatilize VOCs sorbed onto soil particles.

The off-gases are transported by the injected steam and air to a metal hood at the ground surface where they are treated using a catalytic oxidation system for the destruction of contaminants and an acid-gas scrubber to eliminate air emissions.

Thus far, the system has effectively reduced the concentrations of chlorinated VOCs in soil from 1,000-6,000 ppm, to 100-300 ppm, which was the goal for this site. However, several operational problems were experienced with the total system. In particular, the catalytic oxidation system was unable to handle the quantity of the vapors generated by the stripping system. As a result, some vaporized VOCs initially escaped from the metal hood. This problem was subsequently controlled by reducing the injection pressures. The only wastes generated by the system were from the scrubber. The initial results of the pilot test indicate that the operational costs will range from U.S.$70-200/yd^3 (U.S.$92-260/m^3).

Nutrient Injection to Enhance In Situ *Anaerobic Bioremediation*

The *in situ* anaerobic bioremediation system recently began operation and has not yet been evaluated. The system involves a series of horizontal wells and infiltration galleries to control the hydraulic gradient and supply nutrients to the contaminated zone.

9.4.4 Project 53: *In Situ* Bioremediation of Chloroethene-Contaminated Soil

In the Netherlands, between 20-30% of heavily contaminated sites have chlorinated hydrocarbons—in particular, trichloroethene (TCE) and PCE—as a principal constituent. On some sites, the depth to contamination makes *ex situ* treatment technically difficult and uneconomical. Therefore, there is a need to develop *in situ* remedial techniques for this type of contamination. Biotreatment is particularly attractive since it offers the potential for remediation without generating any secondary hazardous waste for further treatment or disposal. However, biodegradation of chloroethenes is technically and microbiologically complex, and might prove difficult to achieve under field conditions. This Pilot Study project reports on the development of an *in situ* biotreatment for chloroethenes from bench-scale studies to a pilot-scale field application.

Technical Concept

The *Tauw Milieu* approach to treating chloroethenes exploits both aerobic and anaerobic microbial processes. Although chloroethenes such as PCE are persistent under aerobic conditions, they can be dechlorinated sequentially by anaerobic bacteria to TCE, dichloroethene (DCE), vinyl chloride, and ultimately to ethene. Since the dechlorination of DCE and vinyl chloride are the rate-limiting steps, these compounds are accumulated under anaerobic conditions as intermediate breakdown products of PCE. In contrast to PCE, however, less-chlorinated ethenes can be co-metabolically mineralized by aerobic bacteria. The *Tauw Milieu* process degrades PCE through stimulation of bacteria in spatially separated aerobic and anaerobic zones. PCE is degraded anaerobically to TCE and DCE, which are transported downstream to an aerobic zone where they are mineralized to ethene.

Laboratory Studies

By February 1996, the process had been demonstrated and verified for PCE at the bench scale. These studies showed that under anaerobic conditions, using formate and methanol as carbon and electron-donor sources respectively, PCE and TCE were readily dechlorinated to DCE and other intermediaries. In addition, using toluene or phenol as a co-substrate, TCE, DCE, and vinyl chloride were readily degraded aerobically. Flask studies with indigenous bacteria from a proposed pilot-scale test site had similar results.

In order to evaluate degradation kinetics, a series of column experiments were performed using 0.7-L columns of site soil through which 200 mL of site groundwater was recirculated. The soil column was operated anaerobically, spiked with PCE, and supplied with formate or methanol as a carbon source and electron donor. PCE concentrations initially decreased due to sorption onto column material, but dechlorinated breakdown products were noted approximately three weeks after start-up. Although degradation was observed using both formate and methanol, it was concluded that methanol would be used for the pilot-scale system because of its lower cost and more stable pH profile. The aerobic column was set up in a similar way to the anaerobic column. It was spiked with PCE and its breakdown products (TCE, DCE, and vinyl chloride). The daughter products were readily degraded with the addition of phenol to the column, but PCE degradation was not observed.

Pilot-Scale Study

The pilot-scale remediation study was conducted from August 1995 to September 1996 at a former dry cleaning facility near the town of Breda. Soil and groundwater was contaminated with PCE over an area of 1,800 m^2 to a depth of 10 m. Concentrations of PCE in groundwater ranged up to 10,000 µg/L. The unsaturated zone was remediated using soil vapor extraction, and the saturated zone and groundwater were remediated by a combination of aerobic and anaerobic biodegradation.

The anaerobic biodegradation zone was created by the extraction and injection of groundwater (up to 250 m^3 per day) to which methanol and nutrients were added. A total of about 1,100 kg of methanol was injected. By carefully controlling the hydrogeological environment, anaerobic conditions were created within the recirculating "groundwater loop." Downstream of this loop, aerobic biodegradation was supported by slow infiltration of phenol (acting as a co-metabolite) through a series of wells. A well downstream of the anaerobic treatment zone was used to extract up to 150 m^3 of groundwater per day, in order to prevent the contamination spreading and to provide water for the phenol infiltration process. Extensive monitoring was conducted to determine the effectiveness and kinetics of the degradation processes and to mitigate the migration of the contamination plume. Methanol was detected in all monitoring wells in the anaerobic zone, in concentrations ranging from 120 to 800 µmol/L. As soon as the methanol was detected, anaerobic degradation was observed. PCE was degraded rapidly to DCE; TCE, vinyl chloride, and ethene were present but did not accumulate significantly.

Under anaerobic conditions, PCE was dechlorinated at rates comparable to those found in the laboratory, and evidence of complete anaerobic degradation to ethene was found. The aerobic process also proved successful, with complete degradation of phenol and DCE. The limiting factor associated with *in situ* biodegradation of chloroethenes appears to be the availability of suitable electron donors rather than the presence of microorganisms.

Prognosis

The pilot study proved so successful that the site owner is continuing the remediation, which is expected to take two to three years.

Chapter 10: INTEGRATION OF TECHNOLOGIES

Kai Steffens
Probiotec GmbH

10.1 INTRODUCTION

Experience shows that contaminated sites frequently cannot be remediated by a single technology. Complex contamination problems require the combination of different technologies for either different contaminated areas and media or for a specific medium exhibiting complex contamination.

However, remediation strategies employing a single treatment technology and those employing a combination of technologies are commonly more complicated and more expensive than is removal to a landfill. Consequently, not only technical effectiveness (in terms of ability to achieve remediation objectives, time requirements, potential environmental impacts, and cost), but also “political” (policy) factors will influence the choice of strategy. These policy considerations may lead to adoption of complex treatment systems that otherwise might be rejected in terms of short term costs alone (assuming comparable technical effectiveness).

In Chapter 2, the terms “integrated” and “mixed” are used to describe combinations of technologies that are used as part of an overall remediation strategy. In the Phase II Pilot Study, 23 projects used a single technology, 19 involved an integration of technologies, and seven used different technologies in parallel (“mixed”).

The term “integrated” refers to approaches involving process integration where two or more technologies are used simultaneously or in series to treat a specific problem. The term “mixed“ refers to projects involving two or more technologies to treat different contaminated areas or media at a site as part of an overall remedial strategy. The individual technologies applied in both the integrated and the mixed projects are discussed in detail in the other chapters in this report.

This chapter focuses on projects in which treatment technologies were integrated to treat a contaminated material in two or more stages. The goal is to discuss identified benefits, problems, and general constraints.

The Pilot Study projects involving integration of treatment technologies are listed and briefly described in Section 10.3. The general characteristics of the projects are summarized in Section 10.4 Performance results of the integration are discussed in Section 10.5, while factors and limitations to consider for determining the applicability of technology integration are dealt with in Section 10.6. Cost information is provided in Section 10.7. Finally, general conclusions are discussed in Section 10.8.

10.2 BASIC OPTIONS AND CLASSIFICATION OF APPROACHES

Effective and efficient treatment of environmental contamination requires tailor-made solutions meeting the specific requirements of the media to be treated, of the contaminants to be removed or destroyed, and of the policy framework within which the project is to be implemented. In many projects, the contamination problem can be adequately addressed by applying a single treatment technology. However, problems may occur due to one or more technical or organizational factors:

10.2.1 Technical Factors

- Difficult-to-treat media, such as soil with high proportion of fine-grained material; mixed solids (soil, ashes, slags, brick, debris, concrete, plastics, wood, *etc.*); solids with a high proportion of organic matter (*e.g.*, peat); low-permeability soils and sediments; fine or uneven distribution of contaminants (*i.e.*, giving rise to low bioavailability); or large volumes of contaminated material requiring treatment.

- Contaminants that are difficult to treat due, for example, to physical properties (*e.g.*, low solubility); chemical properties (*e.g.*, not biodegradable); presence of complex contaminant mixtures (*e.g.*, metals and organic compounds).

10.2.2 Organizational Factors

- Policy (*e.g.*, generation of secondary waste that would have to be landfilled)

- General project constraints, such as budget; time constraints; space constraints; or lack of community acceptance (*e.g.*, due to high emissions).

The limitations of the "single" technologies are discussed under their respective chapters in this report. Frequently, combinations of technologies can overcome these limitations. In many cases, efforts are made to reduce the amount of material requiring expensive treatment by separating fractions of materials that can be reused without further treatment or with limited effort. In other cases, materials or contaminants are difficult to treat, which means that the limitations of a single technology are evident early in the development of the remediation strategy. In these cases, means of modifying the material's physical and chemical conditions have to be identified and evaluated in order to allow treatment at all, or to optimize cost and results.

The organizational factors mentioned above are commonly reduced to the "policy" requirement to avoid generating secondary wastes that would have to be landfilled.

Technology integration can be generally classified into methods involving

- separation of fractions for volume reduction or to apply different downstream treatments; or

- increasing the availability of contaminants for treatment by mobilizing of contaminants in the medium to be treated; modifying the chemical or physical properties of contaminants; or employing treatment trains for sequential removal/treatment of different types of contaminants.

In practice, a combination of these options may be employed in an integrated treatment system to deal with particularly complex contamination.

Separation of different fractions may be carried out to reduce the volume to be treated using a more expensive technology or to be treated at all; to separate out fractions that need to be treated differently. Separation is usually achieved through dry physical separation (*e.g.*, crushing or sieving) or wet physical separation (*e.g.*, soil washing or other wet mechanical separation processes or flotation with or without chemical pretreatment). Besides separating out the more contaminated fine grained concentrate, creating a "clean" coarse fraction may be intended when applying wet mechanical separation processes. One group of integration options is based on the principle of washing off the contaminants and the (highly) contaminated fine particles from the surfaces of the coarser particles, leaving the coarse fraction relatively “clean.” A second group of options uses physical techniques to separate fractions by exploiting differences in the physical properties (*e.g.*, specific gravity or surface hydrophobicity).

Mobilization of contaminants may be achieved by altering the medium to be treated. Examples include

- *in situ* methods, such as through fracturing, steam injection, air sparging, or soil flushing with agents; and
- *ex situ* methods, such as crushing clay-clumps.

Mobilization may also be achieved by modifying the contaminants to increase availability to microbial degradation by concentrating or pretreating the contaminants (*e.g.*, partial oxidation of organics).

Treating combinations of different contaminants (*e.g.*, organics and metals) usually will require application of different processes in sequence. Table 10.1 lists the factors limiting effective treatment with only one technology and the options to overcome these limitations.

Table 10.1: Factors Limiting Effective Treatment with Only One Technology and the General Options to Overcome the Limitations

Limiting Factor	Options to Overcome Limitation		
	Separation	**Mobilization of Contaminants**	**Sequential Treatment**
Soil with high fines	✓	✓	
Mixed solids	✓		
Solids with high proportion of organic material	✓		
In situ treatment of low-permeability sediments		✓	
Fine or uneven distribution of contaminants (low bioavailability)	✓	✓	
Large volumes to treat	✓		
Low solubility contaminants		✓	
Non-biodegradable contaminants		✓	
Complex mixtures of contaminants	✓	✓	✓

10.3 CASE STUDIES CHOSEN

The 15 Pilot Study projects reviewed for this Chapter are listed in Table 10.2. Additional information on the projects is provided in the brief descriptions that follow. Further information is available in the project summaries found in Appendix IV.

This Chapter focuses on the integration of technologies. The individual technology elements, which make up the integrated technologies discussed in this chapter, are described and analyzed in detail in the respective technology-based chapters.

Table 10.2: Projects Involving Integration of Treatment Technologies

	Project	Description	Goal of Integration
1	Trial of air sparging of a petroleum-contaminated aquifer	Field trials of air sparging combined with soil vapor extraction to determine the increase of extracted VOCs	Mobilization of contaminants
9	Field demonstration of an *in situ* process for soil remediation using well points	Field demonstration of a combined *in situ* soil flushing and bioremediation technology for BTEX and petroleum hydrocarbons	Mobilization of contaminants
10	Integrated treatment technology for the recovery of inorganic and organic contaminants from soil	Integrated *ex situ* classification and solvent enhanced soil washing process for metals and PAHs; separation of metal particles by classification; solvent extraction of PAHs and hydrometallurgical leaching of metals from a slurry (pilot-scale)	Mixed contaminants requiring different treatment
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique	Integrated soil washing and two-stage thermal treatment of highly tar-contaminated fines (full-scale, thermal unit: 1 ton/hr operating capacity)	Volume reduction
15	Combined chemical and microbiological treatment of coking sites/ bioremediation of soils from coal and petroleum tar distillation plants	Microbiological treatment of aromatic hydrocarbons with and without oxidizing pretreatments (bench-scale)	Increase availability of contaminants
19	Cleaning of mercury-contaminated soil using a combined washing and distillation process	Integrated soil washing and vacuum distillation plant used to treat mercury contaminated soil and debris (full-scale, 150 tonnes/day)	Volume reduction
24	Combined remediation technique for soil containing organics: Fortec®	Combined hydrocyclone separation, photochemical treatment, and bioremediation (demonstration-scale, 300 m^3 reactor)	Increase availability of contaminants
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	Combined soil washing and slurry phase bioreactor (pilot-scale, 1 ton/hr washing, 600 dm^3 reactor)	Volume reduction
27	Soil washing and chemical dehalogenation of polychlorinated biphenyl (PCB)-contaminated soil	Combined soil washing and chemical dehalogenation (pilot/bench scale, 1.5 ton/hr washing, bench-scale reactors)	Volume reduction
31	Decontamination of metalliferous mining wastes	Laboratory tests of a combination of flotation and metal-leaching processes (pilot-scale)	Volume reduction
32	Cacitox™ soil treatment process	Tests of combined application of soil washing (for physical separation) and metal leaching (pilot-scale, 10 kg/hr)	Volume reduction
33	In-pulp decontamination of soils, sludges, and sediments	Tests of combined application of soil washing (for physical separation) and metal leaching (bench-scale)	Volume reduction
36	Enhancement techniques for *ex situ* separation processes particularly with regard to fine particles	Tests of combined application of wet soil separation techniques and biological treatment of the contaminated fines fraction (bench-scale)	Volume reduction

	Project	Description	Goal of Integration
42	*In situ* pneumatic fracturing and biotreatment	Pneumatic fracturing in low-permeability and over-consolidated sediments increases permeability and improves the conditions for *in situ* remediation (SITE demonstration)	Increase availability of contaminants
47	*In situ* electro-osmosis (Lasagna™ Project)	Fracturing in low-permeability and over-consolidated sediments increases permeability and improves the conditions for *in situ* remediation, *e.g.*, by electro-osmosis (demonstration-scale)	Increase availability of contaminants

10.3.1 Project 1: Field Trial of Air Sparging of a Petroleum-Contaminated Aquifer

Goal: *Mobilization of contaminants to increase removal rate.*

Three field trials were carried out at a gas station site in Adelaide, Australia, to determine the effect of air sparging when applied in combination with soil vapor extraction (SVE). Air sparging caused a substantial increase in the amount of extracted contaminants in the short term. However, the rate slowed down within just a few days. This effect probably resulted from a mobilization of contaminants from the immediate vicinity of the boreholes. The areas and layers with higher permeability were assumed to exhaust fairly quickly, while the lower permeability layers were only slightly affected by sparging. The zone of influence was limited to between 3 m and 9 m from the sparging well.

10.3.2 Project 9: Field Demonstration of an *In Situ* Process for Soil Remediation Using Well Points

Goal: *Mobilization of contaminants to increase removal rate. Treatment of residual concentration with second technology.*

The field demonstration was carried out at a site contaminated with benzene, toluene, ethylbenzene, and xylenes (BTEX) and aliphatic hydrocarbons. The treatment process consisted of a recirculation system with injection and extraction wells. During soil flushing, a surfactant/co-surfactant solution was used to mobilize the contaminants, which were separated in an above-ground effluent treatment plant. The remaining hydrocarbon contamination was to be subjected to microbial degradation enhanced by the injection of nutrients and air or hydrogen peroxide into the well points.

10.3.3 Project 10: Recovery of Inorganic and Organic Contaminants from Soil

Goal: *Integration of different physical and chemical separation steps suitable for different contaminants in a treatment train.*

A bulk soil sample from two industrial sites in Canada was collected for a pilot-scale evaluation of this integrated technology. After breaking down clay clods in a wet scrubber, the slurried soil was sorted by particle size, density, or magnetic susceptibility to produce a contaminant concentrate that was to be recycled off site. The remaining slurry was subjected to a leaching process involving solvent extraction for polycyclic aromatic hydrocarbon (PAH) removal and a hydrometallurgical treatment involving leaching metals selectively and recovering them using metal-selective adsorbents. The pilot tests were reportedly successful in producing a soil suitable for further use. Full-scale remediation of one of the sites was decided on using a 600 tonnes/day plant. Estimated costs are U.S.$75/tonne.

10.3.4 Project 13: Rehabilitation of a Site Contaminated by Tar Substances Using a New On-Site Technique

Goal: *Volume reduction of the material treated thermally, and application of different treatment technologies suitable for different grain size fractions of soil.*

This on-site remedial demonstration project combining excavation of tar-contaminated soil followed by on-site *ex situ* thermal desorption was carried out at an old gasworks site in a densely populated area of Copenhagen. Soil and debris surrounding two tar reservoirs were excavated in a tent and subsequently treated in a combined soil-washing and thermal-desorption system. Soil washing was used to provide a volume reduction step by producing clean fractions in the particle size ranges >50 mm and 2-50 mm through screening and high-pressure spray washing. The contaminated fraction (<2 mm) was treated using a two-stage thermal desorption process. In the first stage water and volatile substances were evaporated from contaminated materials. The off-gas was treated using a particulate dust trap and an air/oil/water separator and condenser. The second stage, operating at higher temperatures, was used to volatilize the heavier tar substances, which were recovered in an air/tar condenser

10.3.5 Project 15: Combined Chemical and Microbiological Treatment of Coking Sites/ Bioremediation of Soils from Coal and Petroleum Tar Distillation Plants

Goal: *Pretreatment of contaminants to optimize biodegradation rates.*

PAH-degrading bacteria were identified and the practicality of using bioremediation for PAHs in soil was evaluated. Furthermore, an oxidation-based pretreatment was examined to assess whether subsequent bioremediation was enhanced. Very limited information was provided on this project and on the success of the oxidizing pretreatments. Considerable additions were required to observe any increased degradation of PAHs. There are indications that ferrous sulfide was used as an oxidizing catalyst.

10.3.6 Project 19: Cleaning Mercury-Contaminated Soil Using a Combined Washing and Distillation Process

Goal: *Volume reduction of the material that was to be treated thermally, and application of different treatment technologies suitable for different grain size fractions of soil.*

The Marktredwitz Chemical factory in Germany was established in 1786 and manufactured various mercury compounds (including agrochemicals) and mineral acids. Buildings, soil, and groundwater were heavily contaminated with mercury. A distillation unit was used in combination with a soil washing plant that separated the highly contaminated silt/clay soil fractions to form a pretreatment concentrate for thermal treatment. The sand and rubble fraction was disposed as clean fill. The fine fraction (grain size ranging from <100 µm to <8 mm) was transferred to the vacuum distillation unit. The treated soil was water cooled in a rotating drum to an average temperature of <50°C and recombined with the coarse-grained material from the soil washing plant.

10.3.7 Project 24: Combined Remediation Technique for Soil Containing Organics: Fortec

Goal: *Volume reduction of material that is to be treated in downstream steps, and pretreatment of contaminated concentrate to optimize biodegradation rates.*

The system combines hydrocyclone separation of soil fractions resulting in separated coarse fractions, which are either “clean” or can be subjected to additional soil washing. The slurry carrying the fine fraction can be treated in a photochemical (UV/H_2O_2) treatment step if persistent organic contaminants (*e.g.*, PAHs) are to be treated. The UV/H_2O_2 treatment partially oxidizes the organics and transforms these compounds into biodegradable fragments. This photochemical pretreatment may be skipped if organics are present, since they are more easily biodegraded. The final treatment step of the slurry is a slurry-bioreactor, which is operated in batch mode.

10.3.8 Project 26: Treatment of Creosote-Contaminated Soil (Soil Washing and Slurry Phase Bioreactor)

Goal: *Volume reduction of the material that is to be treated in downstream steps.*

Pilot-scale testing was done using a 1 tonne/hr soil washing unit. “Clean” coarse material was removed. Soil washing was used as a pretreatment for froth flotation studies, which showed that a cationic collector and frother removed high percentages of PAHs from the soil. PAH-contaminated slurry was subjected to a subsequent bioreactor treatment in a pilot-scale unit.

10.3.9 Project 27: Soil Washing and Chemical Dehalogenation of PCB-contaminated Soil

Goal: *Volume reduction of the material that is to be treated in downstream steps.*

A soil washing unit with an operating capacity of 1.5 tonnes/hr was used for cleaning and separation of a coarse grain-size fraction. The fines were treated further in a double air flotation cell. The contaminated sludge from the flotation process was used for bench-scale testings of chemical dehalogenation. Systems from three different vendors were tested, two of which (both closed reactors) were successful. Detailed information on the dehalogenation testings was not presented.

10.3.10 Project 31: Decontamination of Metalliferous Mining Wastes

Goal: *Volume reduction of the material that is to be treated in downstream steps.*

Laboratory-scale studies of mineral processing techniques were carried out on lead- and zinc-containing spoils from abandoned mine sites in Wales. Separation testing was conducted using dense media (“sink-and float”) and froth flotation cells. Subsequently, leaching tests were done using various chemical agents. Results show that leaching of unprocessed material is significantly more effective than leaching of processed material.

10.3.11 Project 32: Cacitox™ Soil Treatment Process

Goal: *Volume reduction of the material that is to be treated in downstream steps.*

The proprietary reagent converts insoluble or adsorbed contaminants into soluble complexes. Pilot-scale studies used a plant with a capacity of 10 kg/hr to leach heavy metals and radionuclides from soil. During application of this technology, soil washing should be applied as a pretreatment step to reduce the volume by separating out a fine-grained contaminant concentrate.

10.3.12 Project 33: In-pulp Decontamination of Soils, Sludges, and Sediments

Goal: *Volume reduction of the material that is to be treated in downstream steps.*

Laboratory- and bench-scale studies of metal leaching processes were carried out using a 10-kg sample of soil contaminated with copper, chromium, zinc, and arsenic. It is indicated that a preliminary soil washing process should be used for initial volume reduction by separation of a fine-grained concentrate. The results of the leaching tests show that arsenic was the contaminant most difficult-to-treat, requiring multiple acid leaching to achieve low residual concentrations. Other trials were done with mercury-contaminated soil, including the investigation of a thermal option (heating the material to around 800°C) to achieve regulatory targets.

10.3.13 Project 36: Enhancement Techniques for *Ex Situ* Separation Processes Particularly with Regard to Fine Particles

Goal: *Volume reduction of the material that requires further treatment or is to be landfilled.*

Laboratory- and pilot-scale tests were done with two soils contaminated with organics. The study focused on the fate of highly contaminated fine particles in a wet separation processes. Subsequent tests were conducted using a laboratory-scale slurry bioreactor for treatment of the fines. The study concludes that wet separation techniques (“soil washing”) can be beneficially applied if a substantial fraction of the soil of grain size >0.002 mm is contaminant free, and if material <0.002 mm is less than 30-35% by weight of the original feed soil.

10.3.14 Project 42: *In Situ* Pneumatic Fracturing and Biotreatment

Goal: *Improvement of conditions for subsequent* in situ *treatment.*

A field-scale pilot study was done under the USEPA’s Superfund Innovative Technologies Evaluation (SITE) Program. Low-permeability and over-consolidated sediments were subjected to pneumatic fracturing (by pressurized air) to increase the permeability of the soil to liquids and vapors. In the field demonstration, permeability was increased by up to 40 times within an effective radius of about 6 m. This technology can improve the conditions for *in situ* treatment of low-permeability sediments by SVE or biodegradation, for example. The results of the field test combining fracturing and bioremediation are promising.

10.3.15 Project 47: *In Situ* Electro-Osmosis (Lasagna™ Project)

Goal: *Improvement of conditions for subsequent* in situ *treatment.*

The overall concept of the Lasagna™ technology is to introduce treatment zones (zones of high permeability containing treatment agents) into contaminated areas. Electro-kinetic mechanisms carry water and contaminants through these zones for treatment *in situ* or after extraction. To improve conditions for *in situ* treatment in low-permeability sediments, hydraulic or pneumatic fracturing may be employed.

10.4 REVIEW OF CASE STUDIES AS A GROUP

In eight of the 15 Pilot Study projects employing integrated technologies, the primary goal of integration was to reduce the volume of the material requiring expensive treatment, such as thermal treatment of organics and mercury (in two projects) or leaching of metals (in three projects). In other cases, wet physical separation processes were applied to form a fine-grained contaminant concentrate that was subjected to further treatment: microbial degradation in bioreactors (in two projects) and chemical dehalogenation of PCBs. Information on various aspects of the projects is summarized in Table 10.3.

Table 10.3: Goal of Combination, Input Materials in Terms of Medium Treated, Contaminants Present, Types of Technologies Combined and Scale of Project

Project	Input Materials	Contaminants	Technologies Combined	Scale
Separation of Fractions				
13 Rehabilitation of a site contaminated by tar substances using a new on-site technique	Soil and debris (fraction <2 mm)	Tar	Soil washing and two-stage thermal treatment	Full-scale, thermal unit: 1 ton/hr operating capacity
19 Cleaning of mercury-contaminated soil using a combined washing and distillation process	Soil and debris (fraction 0.1-8 mm)	Mercury	Soil washing and vacuum distillation	Full-scale, 150 tonnes/day
26 Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	Sandy soil	PAHs	Soil washing and slurry-phase bioreactor	Pilot scale, 1 ton/hr washing, 600-dm^3 reactor
27 Soil washing and chemical dehalogenation of PCB-contaminated soil	Soil and debris (fraction <0.1 mm)	PCBs	Soil washing and chemical dehalogenation	Pilot/bench-scale, 1.5 ton/hr washing, bench-scale reactors
31 Decontamination of metalliferous mining wastes	Mine spoils	Pb, Zn	Flotation and metal leaching	Laboratory tests
32 Cacitox™ soil treatment process	Most testings with fine particle soils	Heavy metals, radionuclides	Soil washing and metal leaching	Pilot-scale, 10 kg/hr
33 In-pulp decontamination of soils, sludges, and sediments	No data	Cu, Cr, Zn, As, Hg	Soil washing and metal leaching	Bench-scale
36 Enhancement techniques for *ex situ* separation processes particularly with regard to fine particles	2 Soils with fines (<0.063 mm) contents of 43% and 62%	Diesel fuel, PAHs	Wet soil separation and biological treatment	Laboratory- and pilot-scale
Mobilization of Contaminants to Enhance Treatment				
1 Trial of air sparging of a petroleum-contaminated aquifer	*In situ* (water table at 7.5 m depth)	VOCs, gasoline	Air sparging and SVE	Field trials
9 Field demonstration of an *in situ* process for soil remediation using well points	*In situ*	BTEX, petroleum hydrocarbons	Soil flushing and bioremediation	Field demonstration
Increase Availability of Contaminants to Treatment				
15 Combined chemical and microbiological treatment of coking sites/bio-remediation of soils from coal and petroleum tar distillation plants	Soil	Aromatic hydrocarbons	Oxidizing pretreatments/ microbiological treatment	Bench-scale

24	Combined remediation technique for soil containing organics: Fortec	Sandy soil/fines	PAHs, chlorophenol	Hydrocyclone separation and photochemical treatment and bioremediation	Demonstration scale, 300-m^3 reactor
42	*In situ* pneumatic fracturing and biotreatment	Low permeability sediments	Benzene, toluene, and xylene	Pneumatic fracturing and biotreatment	SITE demonstration
47	*In situ* electro-osmosis (Lasagna™ Project)	Low permeability sediments	-	Fracturing and electro-kinetics	Field demonstration
Sequential Removal of Different Types of Contaminants					
10	Integrated treatment technology for the recovery of inorganic and organic contaminants from soil	Soil	Cu, Pb, Zn, PAHs	Classification and solvent enhanced soil washing and leaching	Pilot-scale

Mobilization of contaminants was the goal in two projects. Both were *in situ* processes targeting an increase of the amount of contaminants extracted by conventional methods like SVE and groundwater pump-and-treat approaches. Both technologies were applied at field demonstration scale.

Low availability of contaminants to treatment was the reason that four projects modified the physical-chemical properties of the contaminants. Two of these involved an oxidizing pretreatment process for organics in slurries. In one of these cases, the slurry had been generated by using a wet mechanical separation process. Unfortunately, the reported data are rather limited in both cases. An evaluation of the pretreatment effect is therefore restricted to some global assumptions.

Only one of the reviewed projects involved a combined technological approach to a matrix containing mixed contaminants (organics and metals). The pilot-scale tests of these integrated technologies were reported to be successful, although the reported data sets are limited.

10.5 PERFORMANCE RESULTS

10.5.1 Overview

The effectiveness of integrating treatment technologies should be judged on the basis of their ability to achieve the goals of the overall treatment system. However, the primary technical factor for evaluating the performance of the integration is the degree to which the goals of the integration itself (*e.g.*, reduction in the volume of material to be subjected to downstream treatment) are achieved. Table 10.4 lists the categories of the projects reviewed in this chapter together with criteria that can be employed for the performance evaluation of integration. The costs of integrating the technologies are also discussed below. Tables 10.5 to 10.8 show the key data for the performance evaluation for the categories. Information was very limited for some projects.

10.5.2 Separation of Fractions

The integrated technologies involving separation of fractions succeeded in reducing the volume of the material requiring treatment in more expensive or technically more complicated downstream treatment processes. In Projects 19, 27, 31, and 36, a significant portion of the soil was separated in soil washing

Table 10.4: Categories of Integration of Technologies and Respective Criteria

Category	Example criteria
Separation of fractions	• Volume reduction achieved • Concentration in separated fractions
Mobilization of contaminants to enhance treatment	• Increase of contaminant mobilization in the medium
Increase of availability of contaminants for treatment	• Increase of destruction caused by pretreatment
Sequential removal of different types of contaminants	• Interferences reducing different treatment effects

Table 10.5: Performance Data of the Separation of Fractions Category

Project		Contaminants	Volume Reduction (%)	Contaminant Concentrations (mg/kg)			
				Input for Pretreatment	**Output of Pretreatment**	**Input for Downstream Treatment**	**Output of Downstream Treatment**
13	Rehabilitation of a site contaminated by tar substances using a new on-site technique	Tar	No data	No data	Coarse: 13-35 mg/kg "total tars"	Fines: 1,500-83,000 mg/kg "total tars," median value 11,000 mg/kg (1.1 wt %)	median value 22 mg/kg "total tars"
19	Cleaning of mercury-contaminated soil using a combined washing and distillation process	Mercury	About 30%	Average: 500 mg/kg Hg peaks: 5,000 mg/kg Hg	7.9-23 mg/kg Hg	1,000-4,000 mg/kg Hg in soils	Average in January 1995: 20 mg/kg Hg
26	Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	PAHs	No data	No data	No data	No data	Flotation: 90-95% PAH removal (sandy soil), 20-90% PAH removal (clay soil); bioreactor: 97% PAH reduction after 6 days
27	Soil washing and chemical dehalogenation of PCB-contaminated soil	PCB	60%	50-300 mg/kg	Coarse: <10 mg/kg; fines (<0.1 mm): no data	250 mg/kg	< 1 mg/kg
31	Decontamination of metalliferous mining wastes	Pb, Zn	90%	20 wt% Pb, 15 wt% Zn	<2 wt% metals in light fraction; 32 wt% Pb, 5 wt% Zn in heavy concentrate	No data	Removal rates from untreated material: NaOH: 25-92 % Pb, 3-23% Zn; H_2SO_4: 2-33% Pb, 12-64% Zn; much lower removal from pretreated material: 2-5% "metals" removed

				Contaminant Concentrations (mg/kg)			
32	Cacitox™ soil treatment process	Heavy metals, radionuclides	No data	No data	No data	No data	Metals exceeded Dutch “B” values; 98% removal of organics
33	In-pulp decontamination of soils, sludges, and sediments	Cu, Cr, Zn, As	No data	No data	No data	Cu: 360, Cr: 621, Zn: 414, As: 1,204 mg/kg	Cu: 22, Cr: 74, Zn: 68, As: 112 mg/kg; multiple acid leaching: As 650 down to 22 mg/kg
36	Enhancement techniques for *ex situ* separation processes particularly with regard to fine particles	Two samples: 1) Diesel 2) PAHs	1) fraction >0.01mm, 68-72% 2) fraction >0.01mm, 78%	1) 3,000-4,000 mg/kg TPH, 4 mg/kg PAHs 2) 2,000-3,000 mg/kg TPH, 200-300 mg/kg PAHs	1) fraction >0.01 mm: 200-290 mg/kg TPH (3-4 hydro-cyclone repasses) 2) fraction >0.01 mm, 4,200 mg/kg TPH, 320 mg/kg PAH	1) Fraction <0.01 mm, 12,000 mg/kg TPH 2) fraction 0-0.063 mm, 413 mg/kg PAH	1) fraction <0.01 mm, 2,300 mg/kg TPH 2) fraction 0-0.063 mm, 214 mg/kg PAH

or flotation processes. The flotation tests in Project 31 resulted in a potentially recyclable metal-rich concentrate leaving the “light” fraction as an input material for further processing in a metal-leaching process. This process needs to be optimized to increase contaminant removal. The same is true for Projects 32 and 33, which also involved leaching processes as a downstream treatment.

The volume reduction effects of the soil washing processes are critically dependent on the fines content of the original feed soil and the distribution of contamination in the different grain size fractions. In Projects 19 and 27, volume reduction did not reach the anticipated level. In Project 19, this was caused by higher-than-expected contamination of the fine-to-medium size fraction, which therefore could not be treated with the required effect by soil washing alone; it had to be subjected to thermal treatment together with the fines. The “cutting grain size” of the soil washing had to be increased, resulting in a larger amount of separated fines.

In Project 27, the fine-grained portion of the feed soil was reported to be much higher than anticipated. Nonetheless, the reduction by 60% in this case would result in significant savings of costs and effort during the downstream treatment.

The target volume reduction, or “separation of fractions,” was achieved by the different approaches. However, in the soil washing projects, removing contaminants from the coarse fraction was an additional goal. It was difficult to achieve cleaning levels and analytically determine the extent of contaminant removal. Although the reported data sets in this respect are limited, it can be stated that in Projects 13, 19, 27, and 36 (total petroleum hydrocarbon [TPH] sample), a significant cleaning effect was achieved. In other cases, either no data were reported or the coarse fraction still showed elevated levels of contaminant concentrations (*e.g.*, Project 36, sample 2).

10.5.3 Mobilization of Contaminants

Performance data for this category are provided in Table 10.6. Only for one of the two projects of this category were data reported that can be evaluated regarding the effect of combination of technologies. The field trials of *in situ* air sparging in Project 1 showed that preferred flow paths of air in the subsurface were exhausted very rapidly when SVE was supplemented with air sparging. After additional

Project **Contaminants** **Volume Reduction (%)**

air sparging was applied, the contaminant yield of SVE increased very rapidly and significantly, but dropped after about 30 hours to very low values.

Table 10.6: Performance Data of the "Mobilization of Contaminants to Enhance Treatment" Category

Project		Contaminants	Status Before Mobilization	Status After Mobilization	Degree of Increase
1	Trial of air sparging of a petroleum-contaminated aquifer	volatile organic compounds (VOCs), gasoline	Total hydrocarbons: initially: 0.5-0.8 kg/day, before sparging: 0.1-0.2 kg/day	Total hydrocarbons: 0.8-1.5 kg/day dropped after 30 hours to <0.1 kg/day	About ten times for about 30 hours. After 30 hours, drop due to exhaustion of preferential flow paths
9	Field demonstration of an *in situ* process for soil remediation using well points	BTEX, petroleum hydrocarbons	No data	No data	No data

From the projects results, it cannot be determined if preferred flow paths were created by air sparging, or if they were also present and active during the "conventional" SVE. In both cases, air sparging was beneficial:

- If the preferred flow paths are caused by air sparging, it can be concluded that air sparging is not a suitable method to enhance an evenly distributed removal of contaminants from a sedimentary formation by SVE.

- If these flow paths are present no matter if air sparging is applied or not, SVE would be a longer lasting effort to exhaust these paths and not more. Thus, the trials would have shown in a very short period of time that SVE does not affect the entire subsurface but only parts of it.

In the future, air sparging could be an option to check the effectiveness of long-term SVE efforts under the conditions of the particular project.

10.5.4 Increase of Availability

Performance data for projects involving an increase of availability are given in Table 10.7. The effect of technology combinations in this category is very difficult to evaluate based on the reported data. Projects 42 and 47 involved site or medium pretreatment. In these cases, fracturing was used—or should be used—as a method to allow *in situ* treatment of densely packed sediments with low permeability. It is unlikely that *in situ* treatment of these sediments without fracturing would be possible. Therefore, given that *in situ* treatment is the only way to handle the problem, the pretreatment by fracturing can be assumed successful if there is any treatment effect at all. In Project 42, pneumatic fracturing was shown to increase permeability by up to 40 times. Thus, this appears to be a useful means to apply *in situ* processes to a much wider range of cases than in the past.

The oxidizing pretreatment in Project 24 showed a significant increase in biodegradability of PAHs. PAHs were partly oxidized by physical-chemical treatment (UV/H_2O_2) and were thus more available for microbial degradation in a slurry-bioreactor process. Test results for chlorophenol were interpreted as showing the same effect as the PAH results. It is remarkable that the pretreatment process-step is an

Table 10.7: Performance Data of the "Increase of Availability of Contaminants to Treatment" Category

	Project	Contaminants	Without Pretreatment	With Pretreatment	Degree of Increase
15	Combined chemical and microbiological treatment of coking sites/bioremediation of soils from coal and petroleum tar distillation plants	PAHs, phenols, cyanides	No data	PAH decreased from 800 to 200 (after 12 months); phenols: 75% degradation (after 7 weeks); cyanides: 50% removal (after 2-3 months)	no data; info that considerable additions were required to observe increased degradation
24	Combined remediation technique for soil containing organics: Fortec	Petroleum hydrocarbons	Petroleum hydrocarbons decreased from 400-5,000 mg/kg down to 100 mg/kg in 3-8 days	Petroleum hydrocarbons: same as without pretreatment	Petroleum hydrocarbons: no difference detectable
		PAHs	PAHs: no degradation observed	PAHs: decreased from 30 mg/kg to 5-10 mg/kg in 15 days	PAHs: pretreatment allowed degradation
		Chlorophenol	Chlorophenol: decreased from 200 to 100 mg/kg in 24 days	Chlorophenol: decreased from 160 to 60 mg/kg in 24 days	Chlorophenol: increase unclear
42	*In situ* pneumatic fracturing and biotreatment	BTEX	No treatment possible	79% reduction in soil-phase BTEX	Fracturing increased permeability by up to 40 times within 6 m radius
47	*In situ* electro-osmosis (Lasagna™ Project)	trichloroethene (TCE)	Vertical electrodes were used. Control plot (no treatment): TCE decreased from 89.9 to 49.5 mg/kg	TCE decreased from 72.6 to 1.1 mg/kg	In the future, horizontal electrodes will be placed by fracturing

optional part of the capabilities of the soil treatment center in this project. This combination is a beneficial way to improve flexibility in soil treatment and to overcome impediments to microbial degradation of PAHs.

10.5.5 Sequential Removal of Contaminants

Performance data for projects involving sequential treatment are given in Table 10.8. In Project 10, an *ex situ* classification was combined with a solvent-enhanced soil washing process for metals and PAHs. The separation of metal particles by sorting resulted in a metal-rich concentrate of the fine particles. Unfortunately, the concentrate was not characterized in deeper detail in the project report. After this treatment, the remaining soil contained only 7% of the initial lead content, meeting the regulatory limits of either 1,000 mg/kg for industrial use or 500 mg/kg for residential use.

Table 10.8: Performance Data of the "Sequential Removal of Different Types of Contaminants" Category

	Project	Contaminants	Removal in Step 1	Removal in Step 2
10	Recovery of inorganic and organic contaminants from soil	Cu, Pb, Zn, PAHs	Metal concentrates for potential recycling contained 55% by weight of iron lead was reduced to 7% of the initial content	Benzo(b)fluoranthene: decreased from 14 to 4 mg/kg, Zn from 4,000 down to 360 mg/kg, Cu was not affected by treatment

The solvent extraction of PAHs from the remaining slurry resulted in significant removal of benzo-(b)-fluoranthene and a successful hydrometallurgical leaching of zinc. Further optimization should focus on improving removal of other metals. This project is an example of treatment of different types of contaminants in sequential steps. The composition and other properties of the treated material were not reported.

10.6 FACTORS AND LIMITATIONS OF INTEGRATED TECHNOLOGIES

10.6.1 Separation of Fractions

In this category, technologies like soil washing and flotation are included as pretreatment processes. Important factors to consider, limitations, and integration into treatment trains are discussed below.

Separation by Soil Washing

The portion of fines present in the feed soil and the distribution of contaminants in different grain sizes determine the volume reduction that can be achieved. If contaminants mainly adhere to fine particles, and the soil washing process minimizes "misplaced" fines, the volume reduction can be significant. Minimizing misplaced fines, (in the coarse fraction) together with the efficiency of washing contaminants off the surface of coarser particles, are the critical factors for the residual contamination in the coarse fraction.

Separation by Flotation

The portion of material to be removed by exploiting the differences in physical-chemical properties must be significant. The separated "heavy" material—*i.e.*, metal concentrates—must be very suitable for metallurgical processes. The flotation process should not hinder downstream processes like leaching of metals from the "light" fraction, solvent-extraction, or microbial degradation of organics. An example of interferences between the pretreatment and the downstream treatment of the light fraction by metal-leaching was given in Project 31. No information was given on the suitability of recycling of concentrates.

10.6.2 Mobilization of Contaminants to Enhance Treatment

The examples for this category show a potential to improve the treatment of proven technologies like *in situ* SVE and groundwater pump-and-treat systems. The effect itself and the duration of the effect may promote clean-up efficiency and may provide information on conclusions about the future course of the chosen remedial approach.

The critical factors for applying SVE in combination with air sparging are the degree to which the contaminant yield can be increased and the development of this increase. If low soil permeability is the reason for low yields of extracted contaminants, air sparging might not improve extraction. Project 1 shows that the presence (or formation) of preferred flow paths governs the conditions for this approach.

The other example of an attempt to mobilize contaminants and increase extraction by groundwater pumping by using surfactants or co-surfactants (Project 9) raises two issues:

- whether increase in solubility from the introduction of the surfactant into the aquifer is always desirable—this particular issue is of critical importance in discussions with water-control authorities; and

- the possibility of impediments to microbial degradation caused by the surfactant enhanced extraction pretreatment should be evaluated in laboratory trials at a reasonable investment of resources.

10.6.3 Increase of Availability of Contaminants to Treatment

The main characteristic of the technology combinations in this category is that without the preliminary treatment of the subsurface or contaminants, contaminant removal would not be possible. Therefore, the evaluation of the factors and limitations of the combination of the technologies applied can be limited to the respective issues brought up in the discussions of the single technologies in the other chapters of this report.

10.6.4 Sequential Removal of Different Types of Contaminants

This category is represented by Project 10, in which a solvent-enhanced soil washing process for metals and PAHs was the downstream treatment for the separation of metal particles by sorting. The main factor is the hindering of the downstream extraction or leaching caused by the flotation process's effects. The example shows that different leaching process steps probably have to be applied for different metals. Another factor is the extent to which the pretreatment process can lower the contaminant concentration levels. Because of the high cost of downstream treatment agents and the severe damage they cause to the soil structure, the largest potential for optimization of this technology combination is considered to be the preliminary wet separation process.

10.7.5 General and Concluding Aspects Regarding Integration of Technologies

Factors and Limitations for Ex Situ *Treatment*

In the projects involving *ex situ* treatment, thermal treatment, microbial degradation, and chemical treatment were applied as downstream processes to the wet, mechanically separated fine fractions. Thus, one of the main characteristics of the wet mechanical separation processes, the generation of highly contaminated concentrates was matched with technologies targeting these secondary waste streams. Other *ex situ* projects involved pretreatment to enhance microbial degradation of organics and sequential treatment of metals and organics.

Besides the general critical factors for the pretreatment of the soil stated above, the following factors are important for integrated technology application in practical clean-up projects:

- Interference of physical and chemical pretreatment that hinder or complicate downstream treatment.

- Availability of two or more compatible technologies in terms of their technological “readiness.”

- Throughput capacities per time unit of the technologies must match as well as possible to allow smooth handling of materials on the site and to avoid interim storage and multiple handling of materials.

- Condition and properties of materials that have undergone thermal treatment or multiple solvent- and acid-leaching.

Factors and Limitations for In Situ *Treatment*

The *in situ* projects reviewed involved enhancement of treatment by mobilizing contaminants or improving the subsoil conditions. The critical factors for the application of the *in situ* pretreatment technologies of this group are discussed above and in the respective chapter of this report. For the integration of technologies, the following factors and limitations are important:

- availability of two or more compatible technologies in terms of their technological “readiness.”

- cost-effect ratio of the enhancing technology.

- duration of the positive effect.

- environmental impact of substances introduced into the subsurface.

- control of the process, increasingly complicated in combinations of *in situ* technologies.

In the projects reviewed, a combination of technologies has been shown to make treatment possible, to increase treatment efficiency, and to adapt the remedial approach to policy requirements such as the avoidance of secondary wastes that would have to be landfilled.

Especially in the latter respect, the requirement to minimize residues is promoting the application of integrated technologies. The cost of additional pretreatment or downstream-treatment, however, can be considered to be the main hurdle for integrated technologies application. Additional cost factors include additional investigation of treatment options, investment cost for additional plants or equipment, cost for longer project duration, cost for interim storage and additional handling of material, and fees for treatment of material in treatment centers.

The policy framework in a region or a country for the decisions in a particular remedial project can be considered the critical factor for having a real option either to landfill or to treat residues. In some cases of site clean-up, contaminated soil is disposed at municipal waste landfills. In these cases, prices range from U.S.$80-150/tonne. If contaminated soil or treatment residues are to be handled as hazardous wastes, landfilling in state-of-the-art hazardous waste landfills costs about U.S.$ 500-800/tonne. In Project 27, costs for incineration of PCB-contaminated material was reported to be U.S.$5,000-7,500/ tonne. In the last two cases, many efforts of integrating remedial technologies would be competitive. If the decision either to treat the soil or to dispose it in a low-cost landfill is more or less left to the responsible project personnel, in most cases no expensive treatment will be carried out.

In the international remedial marketplace, two factors are under discussion:

- How many follow-up costs (*e.g.*, monitoring and maintenance of closed landfills) should be included in the landfilling fees (what is “maintenance” and for how long must it be continued)?

- Should contaminated soil be disposed at municipal waste landfills or at hazardous waste landfills?

The policy decisions made in these respects set the framework for soil treatment. Costs for integrating technologies in site cleanup, in most cases, are higher than landfilling. Therefore, policy decisions must support decontamination by establishing a policy for minimizing disposed wastes by treatment.

10.7 COSTS

As shown in Table 10.9, only very limited information was provided on the costs of the studied or applied technologies. One of the reasons may have been that most of the technologies were only applied in bench- or pilot-scale testing. In the two full-scale applications of wet mechanical soil separation and subsequent thermal treatment of the fines fraction (Projects 13 and 19), cost data were reported for the entire clean-up project. A breakdown of cost showing the relative portions of the two treatment steps was not reported.

10.8 GENERAL CONCLUSIONS

The examples of technology integration in the Phase II Pilot Study show that significant progress has been achieved by efforts to:

- optimize cost and energy consumption by reducing materials volumes to be treated thermally;

- improve the conditions for microbial degradation of contaminants;

- improve the conditions to permit treatment of difficult-to-treat media *in situ*;

- achieve higher removal rates; and

- avoid landfilling of residues.

Although many of the technological approaches to integration of remedial technologies are still at bench- or pilot-scale, there is a broad spectrum of promising approaches and technologies. The review of application factors has shown that the limitations inherent in many single technologies can be compensated for by using integrated technologies. Therefore, it can be stated that integrated treatment technologies are needed to handle complex projects of site remediation better, faster, and (in the long-term) more cheaply.

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Table 10.9: Cost Data (to the extent available)

Project	Information on Costs
Separation of Fractions	
13 Rehabilitation of a site contaminated by tar substances using a new on-site technique	Project costs are discussed in Chapter 7 of this report; no breakdown of costs for soil washing and thermal treatment were provided.
19 Cleaning of mercury-contaminated soil using a combined washing and distillation process	Treatment costs were reported by vendor to be about U.S.$320/tonne, no further breakdown of costs for soil washing and thermal treatment provided.
26 Treatment of creosote-contaminated soil (soil washing and slurry phase bioreactor)	Cost estimates per cubic meter for the remediation of the site: U.S.$160 for soil handling; U.S.$300 for soil washing; U.S.$530 for biological treatment.
27 Soil washing and chemical dehalogenation of PCB-contaminated soil	Bench- and pilot-scale washing tests: U.S.$70,000; 2 tonnes/hr washing plant: capital cost U.S.$750,000, operation (including materials handling and analytical costs) U.S.$380/tonne; cost of dehalogenation: not yet presented.
31 Decontamination of metalliferous mining wastes	No data available.
32 Cacitox™ soil treatment process	No data available.
33 In-pulp decontamination of soils, sludges, and sediments	No data available.
36 Enhancement techniques for *ex situ* separation processes particularly with regard to fine particles	Based on a bench-scale test sample; treatment cost for a diesel-contaminated soil was estimated roughly to be U.S.$50-80 in a 20-tonne/hr plant.
Mobilization of Contaminants to Enhance Treatment	
1 Trial of air sparging of a petroleum-contaminated aquifer	No data available.
9 Field demonstration of an *in situ* process for soil remediation using well points	No data available.
Increase Availability of Contaminants to Treatment	
15 Combined chemical and microbiological treatment of coking sites/bioremediation of soils from coal and petroleum tar distillation plants	No data available.
24 Combined remediation technique for soil containing organics: Fortec	No data available.
42 *In situ* pneumatic fracturing and biotreatment	No data available.
47 *In situ* electro-osmosis (Lasagna™ Project)	Estimate: U.S.$52-118/m^3 for TCE at an approx. 0.5-km^2 site with contamination 12-15 m deep (direct costs of application only).
Sequential Removal of Different Types of Contaminants	
10 Integrated treatment technology for the recovery of inorganic and organic contaminants from soil	Estimate for full-scale plant (500,000 tonnes to treat): Cdn$100/tonne

Chapter 11: REMEDIATION TECHNOLOGY RESEARCH NEEDS

Michael A. Smith
M.A. Smith Environmental Consultancy

11.1 INTRODUCTION

In preparing this report, the authors identified several technology research needs that would be beneficial to:

- countries in the formulation of national research programs;
- the Phase III CCMS study in scoping its future work; and
- the selection of individual projects for a Phase III study.

Technologies are frequently classified as emerging, innovative, or established. However, what is viewed as innovative in one country may be regarded as established in another, and what is considered established in one country may not be used widely in others because of doubts about effectiveness.[1] The term "innovation" often applies to an application of a technology rather than to the principles underlying the technology. While developing truly innovative technologies remains an important goal, such a focus should not divert attention from the need for better information and understanding of established processes and for ensuring that their capabilities are fully realized in practice.

A great wealth of knowledge is available on many technologies, such as soil vapor extraction, bioventing, bioremediation, and stabilization/solidification, enabling authoritative guidance to be provided on good practice for many situations. The difficulty is getting this knowledge applied to the myriad of small projects where these technologies are used. This is not to say that continued research is not required, but that the barriers to the application of research results must also be tackled. This is not unique to contaminated land. In areas such as construction, there is a constant battle to ensure that good practice, established on the basis of past research, is adhered to by practitioners.

As in all areas of research, a variety of topics such as the following need to be recognized:

- Basic scientific research, not directed specifically to solving problems posed by contaminated land—basic science researchers may have an idea of the potential relevance of their work, but relevance is not the immediate driving force;
- Strategic applied research of a fairly basic nature into such things as biodegradation mechanisms and the behavior of contaminants in soil;
- Strategic research leading to a better understanding of how a process works so that improvements can be made;
- Feasibility testing of concepts derived from basic research;

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[1] An example is stabilization/solidification. While widely applied in the United States, this technology has only limited application to date in Western Europe.

- Pilot-scale and field testing of potentially useful technologies; and
- Development of a new concept or process as a result of a problem discovered during site investigation for which no adequate technology exists.

Soil and groundwater remediation industries have been established in a number of countries, and in some cases, as in soil washing in Germany and the Netherlands, some of the plants can be regarded as third generation. Innovation can be driven by operators seeking to extend the physical and chemical range of materials that can be treated and effectiveness of treatment, and to lower processing costs so that they can compete in an increasingly challenging market. Such research by commercial interests is of a proprietary nature and will only slowly reach the wider scientific and technical community.

Promising technologies can sometimes find rapid application before fullly understanding the processes involved, and subsequent improvements can follow after initial application. Soil vapor extraction, electro-remediation, and more recently, active treatment barriers, are examples of such technologies.

In practice, some research needs represent very broad concepts, whereas others relate to improvements or extensions required for particular technologies. For example, the USEPA identified in 1993 a lack of technologies for *in situ* treatment of contaminated groundwater *(1)*.

More recently, a general need has been identified for treatments that are less costly and extensive, which means they are less dependent on technology and energy, and are likely to have less impact on other costs. Ideally, treatments should harness time and natural processes to the wheel of remediation. Such treatment methods have been discussed by Bardos and van Veen *(2)*. These considerations are particularly appropriate to the large-scale pollution problems in Central and Eastern European countries. Existing methods are generally too costly for the pollution problems in these countries. Similarly, in many developing and less developed countries, existing technologies are too expensive. Owners and operators of industrial facilities, also have a need for similar methods once they have taken the measures necessary to avoid immediate legal liabilities.

It is important to recognize that scale has a major influence on the costs of any process. The size of many treatment plants has been limited by the need to be transportable, or at least mobilizable. Even the largest soil washing plants only handle about 150,000 tonnes/year. This capability is small compared to, for example, mineral processing plants, where capabilities of 1 million metric tons/year are not uncommon. This brings into play several factors, such as how remediation is organized and the relative importance of the costs and environmental impacts of transportation (*e.g.,* to a central transport facility), compared to those of the actual treatment process.

Cement kilns are used for disposal of hazardous wastes, used oil, and even vehicle tires in parts of Europe (the energy content is the attraction). In Canada, waste foundry sands and power station fly ash are used as silica sources. In the United Kingdom, colliery wastes have been used as sources of fuel, silica, and aluminum. The possibility of using cement plants as a means of treating contaminated soils merits further investigation, taking into account that the process usually requires large volumes of reasonably consistent material to ensure product quality and that performance is very sensitive to low concentrations of some metals in the cement clinker. Obviously, limits on atmospheric emissions would have to be met and it is important to recognize that the burning of hazardous wastes in cement kilns is controversial in some countries.

In Western Europe the use of a fast-fix, intensive treatment approach is often driven by the need to redevelop an area. Remediation is a step in the redevelopment process rather than the end objective. For instance, the need to rejuvenate brownfield sites is becoming increasingly important in policy and research in the United States and has always been a driver in parts of Canada (*e.g.*, the greater Toronto area of Ontario). In these cases, the overall costs and value of the development can have a greater influence on the selection of a remedial strategy than the direct remediation costs alone. Time (a costly commodity to developers) is often an overriding factor leading to the use of off-site strategies, such as simply excavating and disposing off site, rather than on-site *in situ* or *ex situ* treatment.

Although a great range of technologies now exists, many technologies such as bioremediation will only work on a limited group of contaminants and may be hindered by the presence of other substances (*e.g.*, metals hindering the bioremediation of organic compounds). Few technologies can deal with such mixed contamination, and increasingly, integrated treatment systems are being used. These may involve sequential treatment in a treatment train or parallel treatment of different fractions following an initial separation step. This trend is apparent in the Phase II study—20 projects involved the use of integrated technologies.

Some contamination problems occur on such a scale and are so complex that containment is the only technically and economically viable solution. However, the effectiveness of containment systems (*e.g.*, cover systems, vertical barrier walls) can be reduced with time and require long-term monitoring, repair, replacement during operation. Containment systems would be more attractive if low cost, minimal methods could be found to reduce the pollution potential of the contained materials during the lifetime of the containment system. This situation is very similar to the deliberately constructed mixed waste landfill that has a finite lifetime. Although highly controversial in other countries, the concept of the "flushing landfill bioreactor," which is gaining acceptance in the United Kingdom, is relevant. Research that brings this concept to practical use will in turn aid the development of methods for dealing with old "problem" hazardous waste sites.

11.2 LESSONS FROM PREVIOUS NATO/CCMS STUDIES

An objective when preparing the final reports of the CCMS Pilot Studies on remediation technologies has been to identify research and development requirements as well as the general lessons learned. For the report on the Phase I Pilot Study *(3)*, the authors of individual chapters initially took on this task and then met to further refine their ideas. Their conclusions are:

- There is a continuing need for development of new technologies and use of common research protocols;
- Scientific understanding of processes is essential in order to ensure against formation of harmful end products;
- Standardization of analytical methods is needed; and
- Techniques are required to remove contamination beneath urban structures without significant disturbance to on-going activities.

The conclusions that were technology specific are listed in Box 11.1 (note that variants of some of these appear in Chapter 12 as conclusions of the Phase II Pilot Study, together with supporting reasons for their inclusion).

Several technologies, especially *in situ* treatments, either fail to destroy or remove contaminants or are based on principles of immobilization or transformation (*e.g.*, stabilization/solidification processes). The long-term performance of these technologies needs to be better understood in terms of risk management and appropriate environmental quality criteria to be applied during monitoring.

Box 11.1: Conclusions from Phase I Study Indicating a Need for Research[2]

- *The long-term effectiveness of solidification/stabilization processes has not been proven, especially when these processes are applied under field conditions;*
- *Electro-reclamation deserves to be extensively investigated—no other technology currently shows the same potential for treating clay soils;*
- *Pump and treat is a limited technology for remediating aquifers;*
- *Scaling up the bioremediation process from the laboratory to the field is difficult;*
- *Further research is needed on bioavailability and residual concentrations achievable in bioremediation;*
- *A mass balance approach to remediation is desirable;*
- *Uniform data collection is needed to enhance technology transfer; and*
- *Continuation of the current NATO/CCMS Pilot Study should also include cleanup criteria, project design methodologies, and documentation of completed remediation projects.*

11.3 THE PRESENT STUDY

The projects included in the Phase II Pilot Study do not necessarily provide a true reflection of research and development needs. However, they do have certain characteristics that possibly provide some indication of where current interest lies. For example, interest can be identified in:

- coal carbonization sites and the chemicals typically associated with them, such as polycyclic aromatic hydrocarbons (PAHs), and mixtures of coal-tar chemicals such as creosote;
- *in situ* treatment methods;
- methods to treat chlorinated solvents;
- *ex situ* methods for treating metal contamination;
- residuals left after biotreatment;
- all forms of bioremediation; and
- active barriers.

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[2] The wording in the report has been slightly amended for clarity.

There are, however, significant gaps in the coverage of the projects. For example, there are very few projects on groundwater cleanup (although a number of projects dealt with groundwater as part of an overall remediation strategy). This may, of course, simply be a reflection of a lack of innovative technologies and their practical applications.

Taking discussions at meetings into account, the general areas where research might be directed are:

- *In situ* methods for soil treatment, particularly for metals and mixed contaminants;
- *In situ* methods for groundwater treatment;
- Means for improving the effectiveness and speed of operation of pump-and-treat systems;
- Extensive treatments, requiring fewer resources, but possibly taking more time to achieve a given level of risk reduction;
- Means of reducing the pollution potential within a contained site through low intensity processes for the purpose of extending the life of the overall system and achieving an overall environmental improvement in the long term;
- Test facilities where technologies, considered to have potential negative environmental impacts, can be tried out at field scale under controlled conditions;
- Improved methods for stabilization/fixation or solidification of organic chemicals;[3]
- Long-term studies of stabilized/solidified materials, especially the products of *in situ* treatment; and
- Better techniques to characterize sites before remediation and to perform evaluations, particularly of *in situ* treatments.

The discussion at the Berlin meeting regarding the proposed Phase III study indicated an interest in including containment systems (*e.g.*, cover systems or vertical barrier walls) within the scope of the study. There remains a dearth of information on long-term performance, and laboratory and field studies are required. However, it is important to recognize that these studies must be long-term in nature and might require 20 or more years to complete. Despite the widespread use of covers in the United Kingdom, and some research in the early 1980s and currently at the Building Research Establishment, there is little or no long-term field monitoring.

Additional areas of study that might merit attention include:

- A feasibility study on the use of cement kilns to dispose or treat contaminated soils in Eastern and Central Europe (Note: As stated above, there is controversy about the burning of hazardous wastes in kilns in some countries);

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[3] A conclusion of the Phase I study and various U.S. studies is that the performance of cement-based stabilization/ solidification processes is one of physical occlusion only, which means there is no chemical change or fixation of organic species. Project No. 34 tests a method of binding organic chemicals to organophilic clay minerals before solidification.

- Investigation of the importance of time (for equilibrium reactions to occur) and the intensity of mixing in the treatment of soils contaminated with organic chemicals using organophilic clays and other adsorbents as a prelude to solidification; and

- Development of cost-effective technologies (including sorption and solidification) applicable in less developed countries as well as highly developed NATO-member countries (*e.g.*, using readily available wastes as treatment agents).

11.4 REFERENCES

1. U.S. Environmental Protection Agency, *In Situ Treatment of Contaminated Ground Water: An Inventory of Research and Field Demonstrations and Strategies for Improving Ground Water remediation*, 1993.

2. Bardos R.P. and H.J. van Veen, “Review of longer-term or extensive treatment technologies,” *Land Contamination and Reclamation*, 1996, **4**(1), pp 19-36.

3. U.S. Environmental Protection Agency, *NATO/CCMS Pilot Study: Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater, Final Report, Volume 1*, 1993, EPA/600/R-93/012a.

Chapter 12: CONCLUSIONS AND RECOMMENDATIONS

Michael A. Smith
M.A. Smith Environmental Consultancy

Stephen P. James and Walter W. Kovalick, Jr.
U.S. Environmental Protection Agency

12.1 INTRODUCTION

The Phase II Pilot Study once again demonstrated the benefits of exchanging technical and economic information on technologies for the remediation of contaminated land and groundwater. This chapter presents the conclusions and recommendations of the Phase II Pilot Study and contains:

- general conclusions arising from the Pilot Study (12.2);
- general conclusions about remediation and technology transfer (12.3);
- research needs (12.4—see also Chapter 11); and
- the formal recommendations to CCMS arising from this Pilot Study (12.5).

The conclusions are based on the deliberations of the Study Group, results of case studies, expert speaker presentations, special studies carried out by Fellows of the Pilot Study, and the experience and expertise of the individual chapter authors.

A number of the conclusions closely parallel those of the previous phase of the Pilot Study *(1)*, further affirming their importance.

12.2 GENERAL CONCLUSIONS

1) *Involvement of more countries led to better and wider awareness of the problems posed by contaminated land.*

   A total of 23 countries were involved in the Pilot Study, and 14 contributed projects. The increased number of countries participating in Phase II undoubtedly increased the overall value and impact of the technology exchange process. Although more countries took part largely as recipients of technology information rather than as contributors, the representatives of these countries brought new insights and priorities to the Pilot Study and were able to make valuable contributions to the discussions.

2) *Presentation of additional full-scale experiences was helpful.*

   A number of the participants found the case studies involving full-scale remediation, as opposed to demonstration-, pilot- or bench-scale studies, to be particularly valuable.

3) *In a number of countries, remediation strategies are moving from technology-intensive treatment processes to greater recognition of land use management and extensive approaches, such as natural attenuation. Further research into these approaches is needed.*

It was apparent during the Pilot Study that there is increasing interest in land use management and extensive approaches to remediation. While these approaches can be as effective as more intensive methods, they may take longer to complete. Extensive approaches demand fewer resources and are less costly; thus, they can be viewed as more sustainable. Extensive remediation options, which are less dependent on technology and energy inputs, *etc*., and are likely to have less impact on other aspects of economic activity, are needed. Cost considerations are particularly appropriate for less-developed countries having pollution problems that would be prohibitively expensive to treat using technology-intensive processes.

Consideration of the overall potential environmental, social, and economic impacts of planned remedial actions are of increasing interest and the subject of formal study in some countries. It should be noted that taking these issues into account can both increase the level of clean up required (*e.g.,* in situations where "fit for current or immediate future use" is a prime criterion) and lessen the level of clean up required (*e.g*., in a situation where multi-functional land use might otherwise be required or where groundwater has no economic value).

4) The intended future use of a site is increasingly a determining factor when setting clean-up objectives and selecting a remediation strategy.

This conclusion reflects the convergence in thinking between those countries that have always seen land use as an important factor and those that have tended to set clean-up requirements irrespective of the future use of the land. Consideration of future land use can lead to a better allocation of scarce resources.

5) All remediation activities require proper operation and management.

The success of field demonstration and treatability studies is not enough to ensure success of the remediation activities. The overall effectiveness of a remediation scheme, which may include many interrelated elements of civil engineering works and soil and groundwater clean-up technologies, will depend heavily on the care with which the individual technologies are operated in the field. Site and operating conditions may change over time, and skilled people are needed to adjust technologies to these changes or discontinue them if they do not meet expectations. Similarly, a strong quality assurance program needs to be in place, and activities must be carried out by a dedicated and effective management team.

6) Whenever possible, the wider environmental impacts of a chosen remedial strategy should be considered during remedial selection.

Short-term performance goals should not be the sole factor in technology selection when developing a remediation strategy. Some remediation strategies may only be effective over a longer time frame, but may have lower environmental impacts during implementation *(e.g.*, reduced traffic, lower emissions, and lower energy requirements) .

12.3 GENERAL TECHNICAL CONCLUSIONS

7) Integrated treatment systems are frequently needed for site remediation.

Contamination at many sites can be complex, with different contaminants in different media and areas. Multi-technology solutions are required for the effective remediation of such sites. Many of the Phase II projects involved the use of integrated or mixed technologies (see Chapters 2 and 10).

Modular integrated treatment systems can provide system flexibility by allowing optimization of specific process units to treat different contaminants of varying concentrations within various media. This modular arrangement also allows the addition or withdrawal of processing units within the system and the opportunity to insert and evaluate new or upgraded technologies as they become available. Modular systems require additional up-front design, but may result in lower capital and operating costs than conventional one-technology approaches.

The integrated systems approach also applies to sites where there are multiple areas of contamination and where it is more practical to use specific technologies on each area, rather than trying to make one technology solve all of the contamination problems (see Chapter 2).

8) *Energy efficiency practices influence plant design resulting in varying processing costs between countries. This may make cost comparisons between countries difficult and leads to the choice of different technologies to address similar problems.*

Variable factors, such as the cost of energy and labor, not only influence operating costs, but also plant design and associated capital costs. These factors must be taken into account when considering the application of a technology in a country other than the one in which it was developed.

9) *Independent evaluation and verification of technologies and uniform data collection are needed for effective technology transfer.*

The NATO/CCMS Pilot Studies have shown the benefits to be gained from well-designed, supported, executed, and documented field demonstrations of treatment technologies that are independently evaluated and verified. Such field demonstrations not only help to confirm the strengths and limitations of a technology, but also provide a credible basis for technology transfer and application.

There is a critical need for the establishment of a uniform data reporting methodology for demonstration projects, *etc*. Various database systems are available and in use; however, input of consistent data into these systems and easy access to them will benefit all users. Critical information needed in these databases includes:

- a minimum data set concerning the site's geological and hydrological setting, the types and concentrations of contaminants present, *etc*.
- the clean-up standards used to provide the basis for selecting remediation strategies and for assessing their effectiveness. The clean-up standards are important because there are currently no internationally adopted standards or guidelines, and those applicable in one nation or state may not be pertinent in another.

The identification and/or development of standard protocols for demonstration projects was one of the objectives of the Phase II Pilot Study. This objective was not achieved, but it was addressed, in part, by one of the CCMS Fellows and will be considered further in the Phase III Pilot Study.

10) *Consensus on analytical methods and quality assurance is needed.*

There is a lack of consensus on analytical methods used within the worldwide contaminated-land community and often within individual countries. As a result, there can be confusion between or within countries about meaning of the data and how the data were obtained and analyzed. Under such circumstances, data can be misinterpreted or appear inconclusive. A greater level of confidence in the interpretation of data could be established if there were worldwide acceptance of analytical methods.

In addition, greater attention is needed in the areas of experimental design and quality assurance and quality control (QA/QC) for identifying data needs and data quality, which in turn determine the analytical methods. Programs to evaluate new analytical techniques and update analytical standards would further benefit the contaminated-land community. One forum addressing this issue is the International Organization for Standardization (ISO) Technical Committee 190 for soil quality.

11) Scientific understanding of processes is essential to avoid forming harmful end-products and byproducts, ensure process optimization, avoid unwanted transfer of contaminants to other media, and understand the limits of technical performance.

The demonstrated removal of contaminants from contaminated media is not a sufficient basis for implementing a treatment technology because toxic intermediates, byproducts, and residuals may be formed during treatment. A thorough understanding of the treatment process mechanisms involved is required in order to avoid such undesirable occurrences.

12) Field treatability/pilot studies should be conducted under the range of potential field conditions they might be realistically applied. Test facilities are required where technologies considered to have potential negative environmental impacts can be field-scale tested under controlled conditions.

The complex physical and chemical nature of the subsurface environment makes both laboratory testing and pilot-scale field evaluations (treatability studies) essential elements of a successful approach to remediation. Generally, either bench-scale or pilot-scale studies in the laboratory need to be followed by pilot-scale or full-scale field evaluations. These evaluations should indicate whether the technology is applicable to the contaminated medium and should provide information on the optimal level of treatment effectiveness that the technology can achieve. Bench-scale and pilot-scale evaluations must be tailored to each specific application in order to obtain the maximum amount of credible data at a minimum cost and establish the basis for follow-on field evaluations.

13) Field-scale studies aimed at understanding phenomena such as transport of contaminants and natural attenuation are needed. International collaboration on this effort would increase the value and diversity of conditions studied and lead to quicker application of results.

Studies of this type are already taking place, particularly in North America. Field laboratories in which controlled release of contaminants is permitted would be particularly valuable.

14) Technology scale-up problems need to be addressed in design and testing.

Care must be taken in translating technologies from bench- to pilot-scale to demonstration-scale or full-scale so that all aspects of the scale-up are taken into account. The scale-up of pilot-scale systems to full-scale operating systems can often result in unforeseen difficulties that need to be addressed in the design. For instance, design variables (*e.g.*, wall effects, mixing efficiencies, flow patterns, fugitive emissions, and retention times) can change as a result of system scale-up. To overcome some of these problems (particularly for technologies that are not widely used), operating flexibility can be built into the system by modular design, by providing the ability to vary feed rates, and by providing surge capacity at various points throughout the system.

15) *Long-term monitoring of assumed permanent remediation may be necessary to ensure that clean-up goals are met.*

    Construction of soil and groundwater remedies is not the endpoint for determining whether environmental protection concerns have been satisfied. Focused, long-term monitoring is essential to ensure that the required remedies are properly implemented, operated, and maintained and ultimately are successful. This, in turn, requires that long-term oversight is provided by well-trained personnel and that the necessary institutional controls are put in place to ensure that monitoring is conducted and appropriate responses to the results of monitoring are taken.

    Limiting monitoring to the period in which remediation goals and objectives are first achieved may yield misleading results. It has been demonstrated both in "pump-and-treat" groundwater systems and soil vapor extraction systems that "bounce back" can occur as contaminants held in less permeable zones diffuse out to re-contaminate the apparently clean (and more permeable) zones. Monitoring must be continued until such phenomena no longer occur to a significant extent.

16) *Assessment, remedy selection, and implementation records should be preserved.*

    A major challenge in evaluating the effectiveness of current and emerging technologies is that there are usually insufficient data available to evaluate them (particularly for *in situ* remediation strategies). Therefore, it would be advantageous to remediation planners if site investigation and assessment records and the rationale for selecting the remediation strategy are preserved for future reference and evaluation. Such records are valuable in property transactions and in determining the suitability of land for a particular use subsequent to remediation. It is also important that the records reflect "as-built" or "as-operated" systems, rather than just the design intentions.

17) *Although treatment and permanent solutions are widely sought, some contamination problems occur on a scale and complexity for which containment may be the preferred technical and economically-viable solution. Further information sharing among countries is needed to determine the long-term effectiveness and state of development of containment systems.*

    Containment systems can be expected to decline in effectiveness with time, require long-term monitoring, and possibly require repair or replacement.

18) *Studies related to stabilization/solidification processes are required in respect to:*

    - improved methods for stabilization/solidification of organic chemicals;

    - long-term performance of stabilized/solidified materials, especially the products of *in situ* treatment;

    - the importance of time (to permit equilibrium reactions to occur) and the intensity of mixing in the treatment of soils contaminated with organic chemicals using organophillic clays and other adsorbents as a prelude to solidification; and

    - development of cost-effective technologies applicable in less-developed countries as well as highly-developed NATO-member countries (*e.g.*, using readily available wastes as treatment agents).

12.4 RESEARCH NEEDS

19) *Future work on the NATO/CCMS Pilot Study should include the formulation of the overall scope of a Phase III CCMS study and the selection of individual projects for inclusion in a Phase III study.*

20) *As in all areas of research, it is necessary to recognize that research of a variety of types is required.*

    For example:

    - basic scientific research not directed specifically to solving the problems posed by contaminated land—although the researchers may have an idea of potential relevance, this is not the immediate driving force;
    - strategic applied research on such topics as biodegradation mechanisms and the behavior of contaminants in soil;
    - strategic research leading to a better understanding of how a process works so that improvements can be made;
    - feasibility testing of concepts derived from more basic research;
    - pilot-scale and field testing of possible technologies; and
    - development of a new concept or process as a result of a problem discovered during site investigation for which no adequate technology exists.

21) *Further research is required into the remediation of coal carbonization sites and the chemicals typically associated with them, such as polycyclic aromatic hydrocarbons (PAHs) and mixtures of coal tar chemicals.*

22) *Further research is required into:*

    - *in situ* methods for soil treatment particularly for metals and mixed contaminants;
    - *in situ* methods for groundwater treatment, including active barriers;
    - improving the effectiveness and speed of pump-and-treat systems; and
    - better techniques for site characterization before remediation and for performance evaluation—particularly of *in situ* treatments.

12.5 RECOMMENDATIONS TO CCMS

1) *The CCMS is invited by the Pilot Study Directors to commend this Phase II Pilot Study Final Report to the NATO Council for approval.*

   All the participants in this phase of the study are commended for their professionalism, technical expertise, and cooperation. The Pilot Study Directors particularly thank the two co-pilot countries, Germany and The Netherlands, for their assistance. The CCMS Fellows are complimented on their technical quality and personal input to the Pilot Study. The Expert Speaker activities were a major success in stimulating discussion among participants. Over and above the technical successes of the Pilot Study, a camaraderie was established between participants leading to extensive exchanges of information outside of the Pilot Study. The progress of the Study was reported via formal interim reports and numerous papers published in technical journals, and conference proceedings published in North America, Europe, and Australia. Consequently, the CCMS is invited to commend the Final Report to member governments and to the governments of the North Atlantic Cooperation Council (NACC) countries drawing their attention to the technical information, conclusions, and recommendations it contains.

2) *The CCMS is requested to encourage participation of NATO and non-NATO countries in the continuation study (Phase III Pilot Study).*

The participation of NACC and other non-NATO countries has been a feature of the Phase II Pilot Study with mutual benefit to all involved. The Pilot Study co-pilots will continue to elicit formal participation by additional countries known to have contaminated land and groundwater programs.

CCMS is requested to draw the attention of member countries to the way in which formal participation can open doors for researchers, regulators, and others from within and outside government to high quality technology and information exchange activities and to an extensive network of professional contacts. The CCMS is asked to encourage member countries to adopt formal observer status, even if the countries wish to have only minimal active participation at an official level.

3) *The Phase III Pilot Study should maintain liaison with related international activities on contaminated land.*

The benefits to all participants has been enhanced by the parallel activities in policy-orientated areas (*e.g.*, the International Working Group on Contaminated Land and the Common Forum on Contaminated Land) and technical areas such as risk assessment through the European Union’s (EU) Coordinated Action on Risk Assessment for Contaminated Sites (CARACAS) and soil quality through the ISO Technical Committee 190. Liaison should be extended in the Phase III study to include the EU’s Network for Industrially Contaminated Land (NICOLE), the European Environment Agency’s Soil Topic Centre, the World Health Organization’s European Centre for Environment and Health and others involved in this technical area. Close liaison should be continued with NATO/CCMS Pilot Studies dealing with contamination of military installations.

4) *The Phase III Pilot Study should publish an annual progress report and, as appropriate, periodic technical reports on selected topics.*

Preparing a technical report summarizing several years' work requires a considerable effort on the part of all concerned. It involves not only critical review of submitted information, but also the gathering of additional technical information and liaison with country representatives and project authors. Furthermore, there is a considerable editorial effort required to combine the individual contributions into a coherent final report. Preparation of the Final Report for this and the preceding Pilot Studies *(1,2)* has been possible because of the efforts of the volunteer writing teams.

The remediation of contaminated soil and groundwater is a rapidly evolving field so that there is a risk that much of the information provided in the Pilot Study report will already be out of date by the time of publication. It is therefore recommended that this issue be addressed by:

- preparation of an annual report that could be widely distributed and serve as a working tool for participants to monitor the progress of the Pilot Study, including the introduction and completion of individual projects;
- the publication from time to time of technical and non-technical reports on specific topics as seems appropriate; and
- the use of other channels of publication, such as technical journals and conference publications, to ensure rapid dissemination of the results of individual projects and of the Pilot Study as a whole.

12.6 REFERENCES

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2. Smith, M.A. (editor). *Contaminated Land: Reclamation and Treatment,* Plenum (London) 1985.

Appendix I
COUNTRY REPRESENTATIVES

Country Representatives (1998)

COUNTRY	CONTACT
AUSTRALIA	Gillian King Rodda Manager, Contaminated Sites Environment Protection Group Environment Australia PO Box E305 Kingston ACT 2604 tel: 61-2-6274-1114 fax: 61-2-6274-1164 E-mail: gillian.king.rodda@ea.gov.au
AUSTRIA	Nora Auer Federal Ministry of Environment, Youth and Family Affairs Dept. III/3 Stubenbastei 5 A-1010 Vienna tel: 43/1-515-22-3449 fax: 43/1-513-1679-1008 E-mail: Nora.Auer@bmu.gv.at
BELGIUM	Jacqueline Miller Groupe d’Étude Habitat/territoire Brussels University Avenue Jeanne 44 1050 Bruxelles tel: +32/2-650-3183 fax: +32/2-650-3189 E-mail: jmiller@resulb.ulb.ac.be
CANADA	Harry Whittaker Emergencies Engineering Division Environment Canada 3439 River Road Ottawa, Ontario, K1A OH3 tel: 613/991-1841 fax: 613/991-1673 E-mail: harry.whittaker@etc.ec.gc.ca

COUNTRY	CONTACT
CZECH REPUBLIC	Jan Švoma Aquatest a.s. Geologicka 4 152 00 Prague 5 tel: 420/2-581-83-80 fax: 420/2-581-77-58 E-mail: aquatest@aquatest.cz
DENMARK	Inge-Marie Skovgård Contaminated Land Division Danish Environmental Protection Agency 29 Strandgade DK-1401 Copenhagen K tel: 45/3-266-0100 - direct 45/32660397 fax: 45/3-296-1656 E-mail: ims@mst.dk
FRANCE	René Goubier Polluted Sites Team ADEME BP 406 49004 Angers, Cedex 01 tel: +33/41-204120 fax: +33/41-872350
GERMANY	Volker Franzius Umweltbundesamt Bismarkplatz 1 D-14193 Berlin tel: +49/30-8903-2496 fax: +49/30-8903-2285 or -2103
HUNGARY	Pál Varga National Authority for the Environment Fö u.44 H-1011 Budapest tel: 36/1-457-3530 fax: 36/1-201-4282 E-mail: vargap@kik.ktm.hu

COUNTRY	CONTACT
NETHERLANDS	H. Johan van Veen The Netherlands Integrated Soil Research Programme P.O. Box 37 NL-6700 AA Wageningen tel: 31/317-484-170 fax: 31/317-485-051 E-mail: anneke.v.d.heuvel@spbo.beng.wau.nl
NEW ZEALAND	Raymond Salter Resource Management Directorate Ministry for the Environment 84 Boullcott Street P.O. Box 10362 Wellington tel: 64/4-917-4000 fax: 64/4-917-7523 e-mail: rs@mfe.govt.nz
NORWAY	Bjørn Bjørnstad Norwegian Pollution Control Authority P.O. Box 8100 Dep N-0032 Oslo tel: 47/22-257-3664 fax: 47/22-267-6706 E-mail: bjorn.bjornstad@sftospost.md.dep.telemax.no
REPUBLIC OF SLOVENIA	Branko Druzina Institute of Public Health Trubarjeva 2-Post Box 260 6100 Ljubljana tel: 386/61-313-276 fax: 386/61-323-955 E-mail: branko.druzina@ivz.sigov.mail.si
SWEDEN	Ingrid Hasselten Environmental Protection Agency Biekholmsterrassen 36 S-106 Stockholm tel: +48/8-698-1179 fax: +48/8-698-1222 E-mail: inh@environ.se

COUNTRY	CONTACT
SWITZERLAND	Bernhard Hammer Federal Office of the Environment, Forests and Landscape Federal Department of the Interior Buwal Laupenstrausse 20 3003 Bern tel: +41/31-322-6961 fax: +41/31-382-1546
TURKEY	Resat Apak Instanbul University Faculty of Engineering Avcilar Campus Avcilar 34840 Instanbul tel: 90/212-5911-998 fax: 90/212-5911-997 E-mail: rapak@istanbul.edu.tr
UNITED KINGDOM	Ian D. Martin Environment Agency Olton Court 10 Warwick Road Olton, West Midlands tel: 44/121-711-2324 fax: 44/121-711-5830 E-mail: ianmartin@environment-agency.gov.uk

COUNTRY	CONTACT
UNITED STATES	Stephen C. James U.S. Environmental Protection Agency National Risk Management Engineering Laboratory 26 Martin Luther King Drive Cincinnati, OH 45268 tel: +1/513-569-7877 fax: +1/513-569-7680 E-mail: james.steve@epa.gov Walter W. Kovalick, Jr. U.S. Environmental Protection Agency Technology Innovation Office 401 M Street SW (5012W) Washington, DC 20460 tel: +1/703-603-9910 fax: +1/703-603-9135 E-mail: kovalick.walter@epa.gov

Appendix II
CCMS FELLOWS

NATO/CCMS Fellows[1]

FELLOW	**SUBJECT**
Robert M. Bell Technical Director Hyder Consulting c/o Ty Isa Farm Garth Road Glan Conway LL28 5TE Colwyn Bay United Kingdom tel: +44/(0)1492-580-950 (home) +44/(0)1928-579-955 ext. 53015 (work) E-mail: bob.bell@hyder-con.co.uk	Quality management systems in the remediation of contaminated land
Maria Teresa Chambino INETI ITA/DTA Azinhaga dos Lameiros a Estrada do Paco do Lumiar 1699 Lisboa Codex Portugal tel: +35/1-1-716-4211 fax: +35/1-1-716-0901	Important issues about the Portuguese situation
Domenic Grasso Department of Civil Engineering University of Connecticut Storrs, CT 06269-3037 USA tel: +1/860-486-2680 fax: +1/860-486-2298 E-mail: grasso@eng2.uconn.edu	Hazardous waste site remediation
Mary R. Harris Monitor Environmental Consultants Ltd. Blakelands House 400 Aldridge Road Birmingham B44 8BH United Kingdom tel: +44/(0)121-356-5533 fax: +44/(0)121-356-5222 E-mail: mary.harris@monitorec.co.uk	Economic/cost data issues related to innovative environmental restoration technologies

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[1] *For information about the CCMS Fellowship Programme, contact NATO's Scientific and Environmental Affairs Division in Brussels at Tel: +32/2-707-4111 or FAX: +32/2-707-4232. Information can be found on the World Wide Web at http://www.nato.int/science. Invitations for applications are extended each year through national NATO coordinators.*

FELLOW	SUBJECT
Merten Hinsenveld TSM Business School University of Twente P.O. Box 217 7500 AE Enschede The Netherlands tel: +31/53-489-8009 fax: +31/53-489-4848 E-mail: m.hinsenveld@tsm.utwente.nl	Changing approaches to remediation
Maria Jose Macedo Hovione - Sociedade Quimica SA Qt. S. Pedro Sete Casas Loures Portugal tel: +35/1-1-982-9000 fax: +35/1-1-983-6801-1406	Use of remedial clean-up technology in Portugal
Robert Siegrist Colorado School of Mines Environmental Science and Engineering Division 1500 Illinois Avenue Golden, CO 80401-1887 USA tel: +1/303-273-3490 fax: +1/303-273-3413 E-mail: rsiegris@mines.edu	*In situ* remediation of organics: process design, treatment efficiency, and performance assessment
Michael A. Smith 68 Bridgewater Road Berkhamsted Hertfordshire HP4 1JB United Kingdom tel: +44/1442-871500 fax: +44/1442-870152 E-mail: Michael.A.Smith@BTinternet.com	Contributed to preparation of the final report
Kai Steffens PROBIOTEC gmbh Schillingsstrasse 333 D 52355 Düren-Güzenich Germany tel: 49/2421-69090 fax: 49/2421-690961 E-mail: info@probiotec.ac-euregio.de	Concepts of quality management in testing and monitoring of innovative technologies for remedial actions on contaminated land and groundwater

FELLOW	SUBJECT
Hans-Joachim Stietzel Bundesministerium für Umwelt, Naturchutz und Reaktorsicherheit Postfach 120629 D-53048 Bonn Germany tel: 49/228-305-3432 fax: 49/228-305-2398 E-mail: Hans-Joachim.Stietzel@metronet.de	Innovative approaches used on large remediation projects in Germany

Appendix III
GUEST SPEAKERS

During the Phase II Pilot Study, meetings were held at which numerous experts were invited to make presentations related to the overall objectives of the study. Most of these invitees and the titles of their presentations are listed below.

Guest Speakers

GUEST SPEAKER	**TITLE OF PRESENTATION**	**YEAR**
Jens Nonboe Andersen Rambøl, Hannemann & Højlund Denmark	Danish assistance in the remediation of Tököl Airbase (Hungary)	1994
Baldur Barczewski Grundwasser u. Germany	Research facility for subsurface remediation	1994
James Barker Waterloo Centre for Groundwater Research Ontario, Canada	Controlled *in situ* groundwater treatment	1994
Prof. Harald Burmeier WCI Umwelttechnik GmbH, Germany	Permeable treatment beds	1997
David Cooper U.S. EPA Office of Emergency and Remedial Response USA	Risk Assessment in Superfund	1997
Patrick Davoren Department Primary Industries and Energy Canberra, Australia	Rehabilitation of former British nuclear test sites at Maralinga, South Australia	1996
Dr. Wolfgang Dott Institut fur Hygiene und Umweltmedizin, Aachen Germany	Strategies for *in situ* bioremediation	1996b
Marco Estrela Instituto de Soluadura e Qualidade, Centro de Technologias Ambientais Portugal	Use of remedial clean-up technology in Portugal	1997
Ayse Filibei Dokuz Eylul University Turkey	Solidification of fly ash samples coming from a solid waste incineration plant	1993
Jan Freijer University of Amsterdam The Netherlands	Prediction and optimization of the abiotic environment in landfarms to enhance biodegradation of hydrocarbons	1994
Karsten Hupe Technical University of Hamburg-Harburg Germany	Biological soil remediation	1996b

GUEST SPEAKER	TITLE OF PRESENTATION	YEAR
Steven Hutchins U.S. EPA Office of Research and Development Ada, Oklahoma USA	Field demonstration of bioremediation under anaerobic conditions of a fuel-contaminated aquifer	1997
Rune Dyre Jespersen Technical Soil Cleaning Denmark	Electrodialiytic soil remediation (EDSR)	1996
Harald Kasamas CARACAS Office Vienna, Austria	CARACAS—The Concerted Action on Risk Assessment for Contaminated Sites (in the European Union)	1996b 1997
Nic Korte, Gary Jacobs, and Tony Palumbo Oak Ridge National Laboratory USA	*In situ* remediation employing redox processes in reactive barriers and zones	1997
Walter Kovalick, Jr. U.S. EPA Technology Innovation Office USA	Overview of *in situ* treatment options for metals-contaminated soils	1996b
Walter Kovalick, Jr. U.S. EPA Technology Innovation Office USA	Treatment walls	1996
Andrew Langley Environmental Health Branch Australia	The interface between risk assessment and remediation: choosing a method of risk assessment appropriate for Australia	1996
Andrea Leeson Battelle-Columbus USA	Results of bioventing studies at over 100 field sites	1994
James Mantle Rust PPK Australia	Oil terminal remediation: integration of free product, dissolved phase and soil vapor recovery and treatment	1996
Dr. Ewa Marchwinska IETU Poland	Environmental issues in Poland	1997
Igor Marvan Grace Dearborn, Inc. Canada	Evaluation of six near-real-time analytical methods	1996
Mark McNamara Clough Engineering Group Australia	Introduction to the Homebush Bay regeneration project	1996
Annemieke Nijhof TAUW Milieu bv. The Netherlands	The NOBIS project	1996b

GUEST SPEAKER	TITLE OF PRESENTATION	YEAR
Annemieke Nijhof TAUW Milieu bv. The Netherlands	Risk assessment bottlenecks	1996b
Mark Noll Applied Research Associates, Inc. Dover AFB USA	Groundwater remediation field laboratory	1996b
Anna Orlova University of Maryland USA	Soil contamination in Russia	1996b
Paul Richter New Jersey Department of Environment and Energy USA	Selection of remedial technologies	1993
Inge-Marie Skovgård Environmental Protection Agency Denmark	The new Danish assistance to Central and Eastern Europe	1994
Thomas Stauffer U.S. Air Force USA	Natural attenuation/degradation of aromatic hydrocarbons	1996
Brian Ullensvang U.S. EPA, Region 9 USA	Design and construction of an on-site leachate treatment plant at the Operating Industries, Inc., landfill	1992
Paul Van der Heidje Colorado School of Mines USA	The role of modeling in risk assessment and site remediation engineering	1997
Vilma Wisser Tauw Milieu bv. The Netherlands	Contaminated land in industrialized countries	1993
Ken Wangerud U.S. EPA, Region 8 USA	On-site risk assessment and remediation planning at lead-contaminated sites in Romania	1997
Geoffrey Williams British Geological Survey United Kingdom	Natural attenuation at the U.K. Villa Farm	1997

Appendix IV
PROJECT SUMMARIES

These summaries are published in a separate document
available on the Internet from:
http://clu-in.com
http://www.nato.int/ccms

Appendix V
FELLOW STUDIES

PREFACE

This Volume of the Final Report of the Phase II Pilot Study on the remediation of contaminated land and groundwater contains contributions from CCMS Fellows who took part in the study. They are reproduced directly from the texts provided by the authors: they have not been edited other than to put them into a common format. Contact addresses for the Fellows are provided at the end of the volume.

These papers do not represent the entirety of the contribution of the Fellows to the Pilot Study. Each Fellow attended one or more of the international meetings and played an active part in discussions at the meetings. In addition, a number of the Fellows have contributed to the preparation of the Final Report by writing technology-related chapters (see Volume 1) and preparing extended project summaries (see Volume 2).

The CCMS Fellowship Programme provides grants towards the travel and subsistence costs of individuals conducting small studies related to on-going CCMS Pilot Studies. Recipients are encouraged to attend meetings of the study group with which they are associated. Fellwoships are awarded annually in response to applications through national CCMS coordinators. For more information on this and other CCMS programmes, such as the Study Visit Programme, please contact:

CCMS Secretariat
NATO Scientific Affairs Division
B-1110 Brussels
Belgium

tel. +32/2-707-4619
fax. +32/2-707-4232

Information can also be obtained through national CCMS coordinators and on the World Wide Web at: http://www.nato.int/science.

Quality Management Systems and the Remediation of Contaminated Land

Dr. R.M. Bell, Hyder Consulting, and Mr. Richard Failey, SGS Environment,
Colwyn Bay, U.K.

1. INTRODUCTION

Quality Management Systems (QMS) are required to be established for the remediation of contaminated land and waste containment in the expectation that the system will provide a consistent, and maintainable operation which results in a piece of land that is fit for use and that all information upon which decisions are made is reliable.

Quality Management Systems (QMS) are used where a contract between two parties requires the demonstration of capability and assurance to provide the design and supply of a product or service. The aim is to prevent nonconformity by using a system comprising components and elements subject to Quality Control and Quality Assurance.

QMS like any system requires a policy, set of objectives and a method of measurement and review to ensure targets are being met. QMS in the remediation of contaminated land requires a plan giving the methods used, responsible parties and a system for identifying a non-conformance and implementation of corrective action.

Quality Assurance (QA) is achieved through planned auditing/inspection of components of the system against predetermined targets to give confidence that product or service requirements are being met, *i.e.*, it is prevention rather than detection of non-conformance.

Quality Control (QC) is the ongoing measurement of conformance to ensure objectives and targets set by the system are being reached. QC aims to achieve conformity through quantified measurement against predetermined specifications which may include product standards, *etc*.

The most common method of ensuring QA/QC is by auditing which determines whether activities comply with planned arrangements through the assessment of objective evidence. This is discussed later under verification.

For the remediation of contaminated land a QMS will comprise a three phase system:

- Pre-works design and specification;
- On site operations including materials testing, site sampling and analysis; and
- Post works verification, ongoing monitoring, and guarantees.

Environmental Management Systems (EMS) are a method by which organisations can demonstrate environmental performance through controlling the impact of their products and services. Many organisations conduct environmental reviews or audits, but an EMS gives assurances that environmental performance is in accordance and will continue to meet with the organisations environmental policy and objectives. Examples include the ISO 140001; and the European Eco-Management and Auditing Scheme (EMAS) which requires the publication of an auditable statement on the organisations concerns with the environment.

The essential elements of an EMS are that the system is based upon the evaluation of environmental effects, from which all policies, targets, and procedures are based, and that the system is auditable. An EMS follows QMS principles of control, calibrate, and verify, but also requires continual improvement in environmental performance.

2. LAND REMEDIATION

EMS in land remediation allows for effective site management and policing of issues and allows the site manager to pre-empt future problems. One assumes the land remediation process itself is a measure of continual improvement. The first step in establishing an EMS is a preliminary environmental review which needs to cover four key areas:

- Legislative requirements of proposed operations; Evaluation of significant effects;
- Examination of existing management practices;
- Assessment of feedback systems in dealing with incidents.

These key areas are considered in relation to internal site management issues, as well as external factors such as neighbouring land use, road network, planning constraints, *etc*.

Important elements of any EMS relating to land remediation and waste containment include:

- *Policy* documents must incorporate principles of Economically Viable of Application of Best Available Technology (EVABAT). In the U.K., this would include adoption of the waste management hierarchy outlined in Department of Environment Waste management Paper No.28, 1991.
- *Procedures* for waste containment sites will be those outlined in the site working plan and licensing conditions. For proprietary processes, the procedures relating to site controls are usually outlined in an Environmental Impact Assessment required as part of planning permission.
- *Responsibility* includes the identification of management representatives, training of personnel, and instructions to subcontractors. Current U.K. legislation requires the nomination of a ’Fit and Proper Person’ as representative of waste management expertise; the EMS, however, requires demonstration of appropriate training at all levels of staff which critically impinge on day to day operations.
- *Evaluation of Environmental Effects* requires the operator to identify, evaluate, and control all significant environmental effects. These are to be registered in a “live” document that will be auditable. Effects to be evaluated include direct effects from operations which may have already been assessed using risk management principles during the site investigation or site licensing. There also needs to be consideration of indirect effects which are generally more esoteric and may include unmanageable issues such as nearest neighbours, or site location and access. The effects from abnormal operations and accidents also need to be identified and evaluated. This is normal for sites subject to an EIA under U.K. planning regulations.

The aim of the EMS is to manage significant environmental effects; however, there is guidance as to what is meant by ’significant’ in any current certified system. The determination of a significant effect is relative in all cases and can only be adjudged through transparent reasoning.

- *A Management Programme* will be progressive and a chance to emphasise the positive aspects of site management and evidence of the application of EVABAT.

- *Operational Control* is required on an activity from which a significant effect arises and that any control mechanism is verified. Clear recognition of non-conformance is therefore required for controls to be effective. For site remediation, operational controls are incorporated in the first phase of site remediation, site design and construction/remediation methods. This also includes the establishment of acceptance criteria for each activity that causes a significant effect.

- *Verification and corrective actions* are to ensure that operational controls are effective. This usually comprises regular sampling and monitoring regimes during the second and third phase of site remediation.

- *Management Review* principles are adopted for EMS as a normal part of QMS to ensure performance reaches targets. It is the system that is reviewed and not the *raison detre* for the operation or site works, since this will have been established in the Environmental Effects Evaluation.

3. U.K. EXPERIENCE

There are currently no formal systems for QMS in the U.K. for site remediation; we still rely largely on caveat emptor as a means of absolving responsibility. Out of fifteen remediation contractors in the U.K., only two specifically stated that they have an identifiable QMS in place to ensure the site remediation process is reliable and that reliability can be demonstrated.

Planning legislation and licensing generally provide checks in the quality of site remediation, although this can result in major differences in the reasoning for adopting site remediation techniques and the interpretation of what is acceptable. In many cases, site remediation may be dictated by local politics and the understanding of local council officers and not necessarily EVABAT/BATNEEC or a proper evaluation of risk.

For large scale remediation schemes, an Environmental Impact Assessment and accompanying statement are required. There are obvious and numerous licensing and regulation requirements, particularly for waste containment as a means of site clean up which will soon be subject to taxation.

Section 78 of the Environment Act 1995, to be implemented in April 1996, allows the regulator to serve a remediation notice and establishes responsible parties and the means by which remediation will be undertaken. The courts, however, are not the best place to start the remediation process and the quality of site remediation may not be uppermost in the polluters mind when paying court fines.

Some contractors and consultants operate a QMS system in accordance with IS09000 and there are numerous product standards for materials used in the site remediation process.

However, for the U.K. there is currently no standard procedure for documentation for verification of remedial action.

The Welsh Development Agency (WDA) (the government agency in Wales for remediation and redevelopment) have produced a Manual on the Remediation of Contaminated Land with the purpose of outlining its policy and objectives on the quality of land remediation projects.

The WDA's aim of land remediation is to ensure economic regeneration and environmental improvement can take place using appropriate technical procedures, the effectiveness of which are confirmed through appropriate management procedures. This will demonstrate to investors and regulators that remediation has been carried out to a sufficiently high standard.

It is the WDA's principal policy that remediation schemes comply with legislation and present residual environmental health risks that are low as are reasonably practicable according to existing and proposed site use, local setting, and technical and financial constraints. That is, the quality of land remediation is based upon the principles of risk management and provides a complete record of site remediation.

The manual sets out guidance on procurement associated with site investigations, design and selection criteria for technologies and materials, and gives guidance for requirements for detailed design and verification.

The main documentation are the Outline Strategy Document (OSD) and Final Strategy Document (FSD). The aim of the OSD is to ensure that site design considers and incorporates Best Practicable Environmental Options and should fulfil those planning requirements for an Environmental Statement, particularly the review of alternatives and the assessment of risks through accidents and abnormal operations. In establishing the best practicable environmental option for remediation, the OSD will also fulfil[those requirements for an effects evaluation identified in ISO 14000. The FSD sets out the requirements for auditing mechanisms to verify the quality of remediation with the eventual aim of providing a Certificate of Completion that can be substantiated.

The site remediation process typically involves a consultant undertaking site investigations and designing remedial works; a contractor undertaking the remedial works; regulatory authorities ensuring regulatory compliance; a site owner/operator for whom the works are carried out; financial institutions or funding bodies and solicitor to ensure contractual obligations are met. Further to this, an independent verifier of works is often employed. These parties require a clear understanding of the remediation process and their liabilities as well as clarification of any future obligations. A standard documented procedure is therefore warranted.

Elements for documentation of verification procedures include:

- Description of site conditions and contamination;
- Hazard identification and risk assessment;
- Definition of remedial objectives and standards;
- Selection of preferred strategy;
- Site design for preferred technique;
- Tender preparation and contract documents;
- Variations to works; and
- Certificate of completion and warranties.

The above elements need to be part of, or referenced in a Verification Report which should provide a clear understanding of:

- The rationale for remedial action;
- Nature of works carried out;
- Key decisions and responsibilities;
- Regulatory compliance;
- Post remediation status of site; and
- Performance of site works.

The environmental performance of site works will be measured against objectives and standards established in the first phase of remediation. The first phase of the remediation process also needs to demonstrate:

- BATNEEC
- Practicality
- Guarantees of performance through demonstration on other sites
- Acceptance of technique by statutory authorities

For the second and third phase of the remediation quality controls will be implemented through an agreed sampling and monitoring programme. Where a documented EMS has been established, verification can be limited to an appraisal of whether commitments have been carried out. Otherwise specific sampling programmes and protocols are required to ensure predetermined standards have been met.

Most financial and funding institutions require independent measurement to ensure the quality of site remediation. The establishment of a standard documented procedure will almost certainly provide substantiated evidence that controls were in place during the entire remediation process and therefore site warranties can be accepted as collateral.

4. CONCLUSIONS

In the U.K., QMS for site remediation is informal and variable and there is currently no consistent system by which developers, regulators and funders can have confidence in. Pressure from developers, legal and financial institutions has resulted in the issue being addressed by government agencies such as the WDA and the Department of Environment.

By adopting QMS principles, this allows us to build in consistency, reliability, and independent verification of the remediation process. Such principles may be set out in an EMS which brings together all phases and elements of site remediation into a reasoned, documented, and measurable or auditable system that gives objective evidence of verification. This in turn allows all parties in the remediation process to have a clear understanding of their obligations and can give value to site warranties.

Groundwater Contamination in Portugal: Overview of the Main Problems

Maria Teresa Chambino, Instituto Nacional de Engenharia e Tecnologia Industrial (INETI),
Instituto de Tecnologias Ambientais/Dep. Tecnologias Ambientais, Portugal

1. INTRODUCTION

Nowadays in Portugal, there is a progressive degradation of soils and groundwater, mainly as a consequence of the population growth and industrial development of the last decades. Quite often waste and wastewater treatment plants are not created according to the new needs and industrialists and farmers are not yet conscious of the dangers of the uncontrolled deposition of wastes or use of excessive amounts of fertilizers and pesticides.

Nevertheless soil and groundwater contamination are not yet a priority in Portugal compared to other european countries. To overcome these problems the creation of a national program of characterization of soil and groundwater contaminated sites and also the intervention of local authorities is of great importance.

This paper presents a national overview of the main groundwater contaminated problems. The case of the industrial site of Estarreja is specifically mentioned because it is a very important one and the most systematically characterized .

2. MAIN POLLUTION SOURCES

2.1 Industry

The principal industries causing major pollution problems are food processing, pulp and paper, chemistry, textile, and cattle breeding. These together account for 90% of the total pollution produced.

The major contributions are from pulp and paper (20.9%), textile (12.4%), olive oil (10.6%), pig breeding (10.2%), wine and derivatives (4.7%), synthetic resins (4.5%), yeast (4.2%), and oil refineries (3.4%).

Industry is responsible for the consumption of around 16% (800 million m^3) of the total water consumed. Around 80% of this water is consumed in North region and Lisbon area.The sectors consuming most are textiles and tanning (≅ 45%) and pulp and paper, and printing (≅ 25%). The slaughter houses, tanning, extractive industry and steel works are not important at a national level, but may be important regionally.

2.2 Agriculture

Agriculture is an important pollution source due to the intense activity in certain areas and the excessive use of pesticides and fertilizers that contribute to the degradation of superficial and groundwater.

The total yearly water consumption in agriculture is around 3,800 million m^3 (≅ 77% of total consumption). Of this, the North region has 31%, Lisbon area 35%, Centre 17%, Alentejo 14%, and Algarve 3%.

2.3 Urban Areas

The public water supply is ≅ 7% of total consumption or 360 million m^3. 67% of this water is for domestic consumption, 20% for industrial consumption, and 13% for public sector. Portugal has a consumption of 100 L/inhab/day, which is less than most other european countries. The dependency of domestic and industrial water supply on groundwater is indicated in Figure 1.

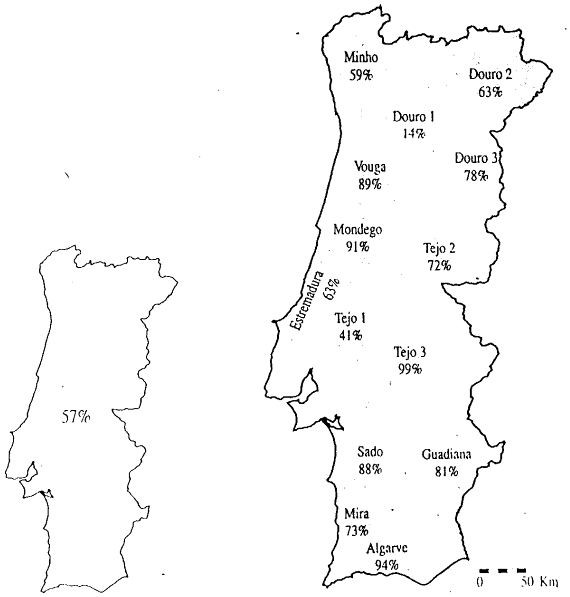

Figure 1: Dependency of domestic and industrial supplies on groundwater

3. MAIN PORTUGUESE REGIONS WITH SERIOUS PROBLEMS OF GROUNDWATER POLLUTION AND OVEREXPLOITATION

The main problems are presented here. Due to its relevance the Estarreja case, in centre region, is described in detail in Section 4 below. A general problem is the groundwater contamination by most of the landfills, in particular in Estarreja, Almada/Seixal and Sines.

3.1 North Region

3.1.1 Organic and Industrial Pollution in River Cávado Sediments

This is an important industrial area. The main activity is textiles but paper, ceramics, food processing, and slaughter houses are also important.

The water from the Borralha mines contaminates the river with cadmium and copper. Some urban areas also dispose of their domestic effluents to the river.

An investigation of the river sediments revealed high levels of cadmium, copper, lead, chromium, nickel, and zinc.

The groundwater revealed organic contamination. In the nearby urban area of Barcelos 69% of the water is bacteriologically unsuitable and only 11.5% is chemically unsuitable. This means the water has good quality in the origin, but becomes contaminated along the way.

3.1.2 Domestic and Industrial Pollution in the Sediments of the Rivers Ave and Affluent

The same situation as the previous one. Contamination by cadmium, chromium, copper, lead, and zinc. The main industry is textiles, which absorbs around 70% of all the people employed in industry in the area.

Most of the industrial wastewaters are discharged directly and without any treatment into the rivers. The situation with regard to sewage discharges the situation is quite similar.

3.2 Centre Region

3.2.1 Lowering of Piezometric Levels in the Baixo Vouga Aquifer

During recent decades, piezometric levels have fallen by tens of meters. From only 1989 to 1993, the level decreased 5.5 m. Chloride levels over 500 mg/L were detected in the part of the area closer to the sea.

3.2.2 Industrial Pollution in Caldas de S.Jorge

Toys industrial units, with chromium and nickel plating operations have disposed around 500 L/week of their effluents, over the years, into wells and on land near the industries. The main pollutants were chromium, nickel, cyanide, copper, and zinc, and the contamination reached the groundwater.

3.2.3 River Sediments

Near Águeda there are about 120 industrial units with anodizing surface treatments mainly chromium, nickel, and zinc plating. Around 80-90% of these units have infiltrated their effluents in the soil. The sediments of river Águeda are contaminated with heavy metals. The sediments of the river Criz (Tondela) are polluted by effluents of aviculture.

3.3 Lisbon Area

3.3.1 High Nitrate Concentrations

Nitrate levels between 74 and 471 mg/L have been detected in river Sizandro valley. High nitrate levels were detected in Rio Maior (325 mg/L), Seixal (274.5 mg/L), Almeirim (226.1 mg/L), and Torres Vedras (203.5 mg/L).

3.3.2 Disposal Area of Almada

Domestic and industrial wastes were disposed in the old disposal site, with no impermeabilization. The groundwater are contaminated with heavy metals of industrial origin.

3.3.3 Ridge of Mountains of Aires and Candeeiros

Over the years domestic waste was thrown in pits and this contaminated the groundwater.

3.3.4 Alcanena

The tanning industry is concentrated in Alcanena, representing 75% of the national production.The wastewater rejection over the years has contaminated the aquifers near the water lines. A wastewater treatment plant has now been installed, but there remains the problem of sludges and wastes highly saturated with chromium.

Due to the industry concentration in this area, it was decided to install a collective treatment plant to treat the domestic and industrial effluents of almost all the industrial units. The sludges from the treatment have been deposited on the soil, with no control for over six years.

A new landfill is being built consisting of three impermeable pools. Some sludges are being transferred to the first pool with 61,000 m^3, located 100 m from the treatment plant. This plant is going to be enlarged to produce 60 m^3/day of sludges that will be deposited in the two lagoons with 122,000 m^3. This sludge and waste transfer to the landfill has created atmospheric pollution problems with chromium acid, hydrogen sulphide, and methylmercaptan.

3.4 Alentejo Region

The main problem in this region is nitrate contamination of groundwater. In the Évora area, around 50% of the groundwater analysis performed indicate values exceeding the limit value of 50 mg/L. The nitrate level is also high in Beja.

3.5 Algarve Region

3.5.1 Nitrate

Nitrate levels over the limits were detected in several river sediments, due to agriculture and effluent disposal.

3.5.2 Groundwater salinization

Several areas around the south coast have problems of groundwater salinization. Besides the problems of salinization by overexpoitation of the aquifers, salinization also occurs due to the leaching of saliferous rocks. The main contaminated (saline ?) aquifers are shown in the map in Figure 2.

4. GROUNDWATER CONTAMINATION IN ESTARREJA

4.1 Main Chemical Units

4.1.1 The general situation

This area is one of the most industrialized in the country and presents serious problems of soil and groundwater contamination due to over forty years of presence of an important chemical complex, with precarious methods of effluent and waste disposal.

The chemical industrial area of Estarreja includes mainly the following industrial concerns: Quimigal, Uniteca, and Cires. The first unit to be installed was Quimigal, in 1952, followed by Uniteca in 1959 and Cires in 1963. There is a great interdependence among these units, with exchanges of raw material and subproducts.

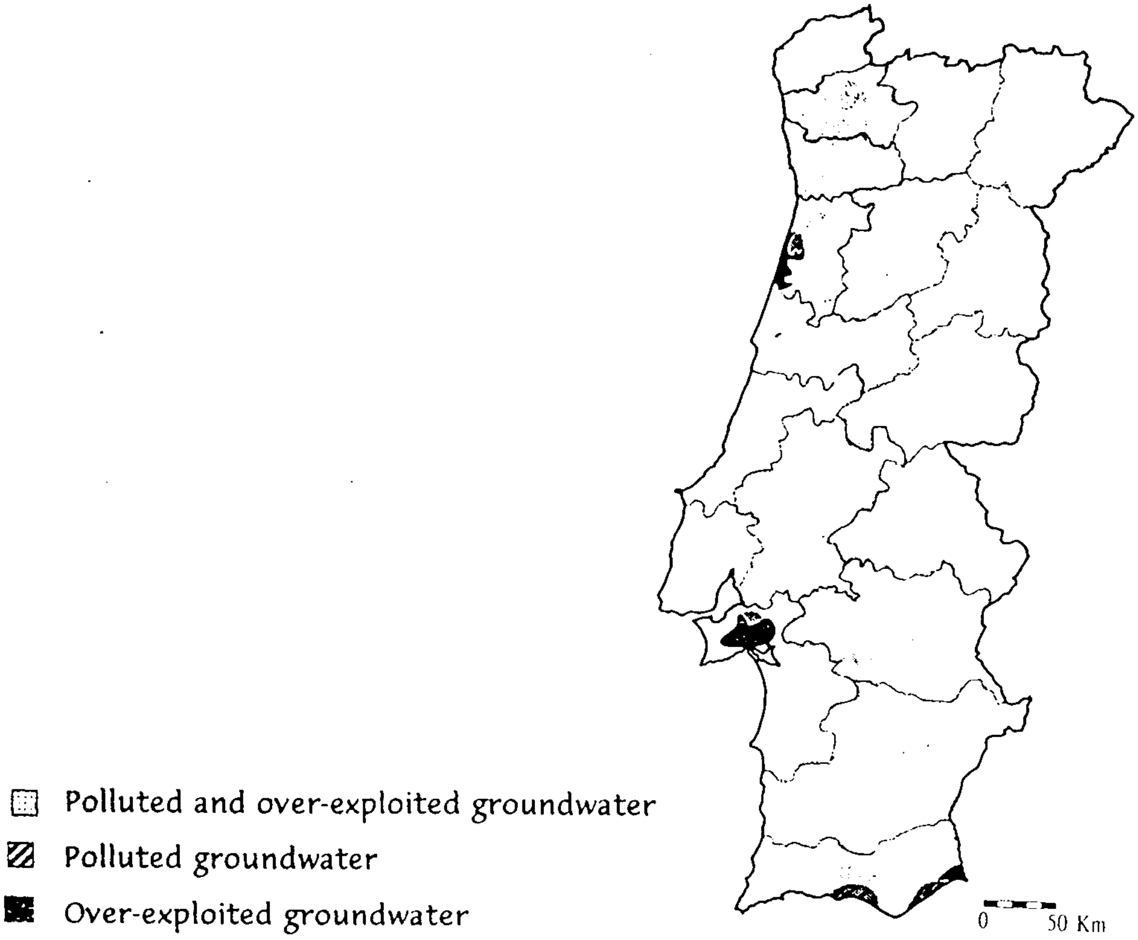

Figure 2: Main contaminated aquifers

This industrial area is regarded as a threat to the environment due to the wastes and effluents produced. Furthermore, it is located on highly permeable soils with a groundwater level that is periodically high, and near an area of intense agricultural activity highly dependent on groundwater.

Over the years these units have been rejecting large quantities of waste directly on the soil: Uniteca sludge deposit, 60,000 tonnes; Cires sludge deposit, 300,000 tonnes; and the Quimigal sludge deposit, 80,000 tonnes. These wastes were deposited with no impermeabilization measures.

Until recently, the effluents were disposed to a not impermeable ditch, transporting over several kilometers arsenic, mercury and other heavy metals and inorganic compounds to the Estarreja river branch. Some compounds infiltrated through the bottom of the ditch have contaminated the local groundwater. In addition, during periods of with heavy rain or disposal of large effluent volume, the effluents have overflown the agricultural land near the ditch.

A few years ago, a pipe was built for effluent transport. Although the ditch has officially ceased to be used for effluent rejection, effluents with nitrobenzene were detected during a sampling campaign performed in 1992.

The atmospheric pollution and the deposition on the soil of several metals and sulphur dioxide from gaseous emissions will increase the soils acidification.

The effects of this industrial area are felt until the Aveiro estuary, 20 km away, where high levels of mercury were detected.

The groundwater contamination has reached such a level in many wells that the municipality has been forced to distribute water for domestic use. Nevertheless the water distribution is not enough for agricultural purposes.

The volume of groundwater withdrawn over the years has lowered the piezometric level and induced a gradual salinization. So the industrial units were forced to capture water from the river nearby (corresponding to 90% of their needs), and use groundwater during summertime.

4.1.2 Quimigal

This plant has been producing, ammonium sulphate since 1952, nitric acid and ammonium nitrate since 1974 and aniline from mononitrobenzene since 1978. The main raw material was pyrites for sulphuric acid production. This production is now stopped for economic reasons.

Over the working decades, we can foresee the impact of the atmospheric emissions of sulphur dioxide and sulphuric anhydride, arsenic, mercury, and other metals and the effluents and waste rejection. Some years ago, a gas treatment system was installed but no protection was made for soil or groundwater. The dust from the treatment was gathered with the other sludges and wastes.

Waste Production

Around 80,000 tonnes of wastes and sludges were produced over the years—mainly dusts from gaseous effluents treatments with heavy metals, and sludges from primary treatment contaminated with arsenic and ashes.

Main Contaminants

- In liquid effluents: aniline, ammonia, arsenic, mononitrobenzene, and benzene
- In wastes: arsenic, lead, zinc, vanadium, other heavy metals

Effluent Treatment

- Incineration for effluent rich in organic matter and activated carbon for inorganic effluents.
- Settling

Raw Materials

- Ammonia, potassium chloride, pyrite, solid sulphur, phosphates, benzene

4.1.3 Uniteca

This plant produces sodics and chlorates from rock salt through electrolytic cells, using graphite anodes and mercury cathodes. Some mercury goes to the environment, mainly due to cleaning of the cells, cleaning of the pavements near the electrolysis area, and wastewater treatment sludges

Nowadays in the European Community, the most important producers of alkaline chlorides no longer use mercury cells. Nevertheless in Uniteca they are still being used, although there exists a new line with membrane technology that avoids pollution with mercury.

<u>Main Contaminants</u>

- Liquid effluents with mercury, suspended solids, and sulphuric acid
- Sludges with mercury
- Atmospheric pollutants: sulphur dioxide, nitrogen oxide, particles, mercury, and hydrochloric acid

<u>Raw Materials</u>

Raw materials include sodium chloride, mercury, sodium carbonate, and sulphuric acid. There is a plan to install a process for mercury removal from the liquid effluents, lowering the mercury level from 25 mg/L to 0.025 mg/L. In the Portuguese legislation, the mercury level allowed in wastewaters is 0.001 mg/L.

4.1.4 Cires

This plant produces synthetic resins, mainly PVC (polyvinyl chloride).

<u>Main Contaminants</u>

- Liquid effluents with vinyl chloride and mercury
- Sludges with calcium hydroxide, wastewater sludges

<u>Effluents Treatment</u>

The effluents are stored in two lagoons before going to the treatment plant. The lagoons are not impermeabilized and so vinyl chloride can contaminate the groundwater.

<u>Raw Materials</u>

- Hydrochloric acid, vinyl chloride, mercury chloride, and sodium hydroxide

4.2 Sampling

Two different sampling campaigns were performed for groundwater and soil characterization, from 1992 to 1994. In the first campaign, in 1992, samples were collected only from 37 wells and three ditches covering an area of 15 km^2 around the industrial units. In the second campaign, in 1993/94, samples were collected in 39 monitoring holes. The depth of sampling was in average 5.5 m.

These data allowed the characterization of the groundwater and the identification of the major pollution plume, only with season concentration changes.

4.3 Results

4.3.1 Overview

The main concentration values were detected near the industrial units, in the ditches and in the sludges deposition areas. This concentration flows in the direction of the quaternary aquifer flow, from east to west. So the highest concentrations are found west of the industrial area. The concentration levels found in monitoring holes are higher than those found previously in wells. Due to the nonexistence of legislation for groundwater in Portugal, the comparison is made with legislation for water for human consumption.

4.3.2 Heavy Metals

Mercury

High values of mercury were found reaching 745 µg/L (the legislation value is 1 µg/L). The areas where this happened are near the effluent rejection ditches and west of the industrial area.The total mercury concentration is higher than the dissolved mercury, revealing that mercury is adsorbed by small particles. A map of mercury concentrations is provided in Figure 3.

The origin of the mercury is mainly the sludge disposal area of Uniteca. Those sludges have mercury levels from 100-500 mg/kg. In the area where these high mercury levels were detected, the water cannot be used for human consumption.

Arsenic

High concentrations in groundwater were found, reaching 6,760 µg/L, compared the legislation level was 50 µg/L. The high levels of arsenic come from the sludge disposal area of Quimigal. Also the effluents from Quimigal presented high levels of arsenic. From 1987 to 1991, the industry effluent had maximum levels of arsenic of 38,000 µg/L. The average values were 8,355 µg/L and the effluent value allowed in legislation is 1,000 µg/L.

Zinc

The origin of the zinc is the sludge disposal area. The main pollution area is west of this area and reaches 204 mg/L, compared to the limit of 0.1 mg/L. Also, near the ditches the values are important.

Iron

The higher concentrations are near the ditches, reaching values of 61 mg/L (legislation value of 0.2 mg/L). So we can see that the heavy metals reach high contamination levels in groundwater.

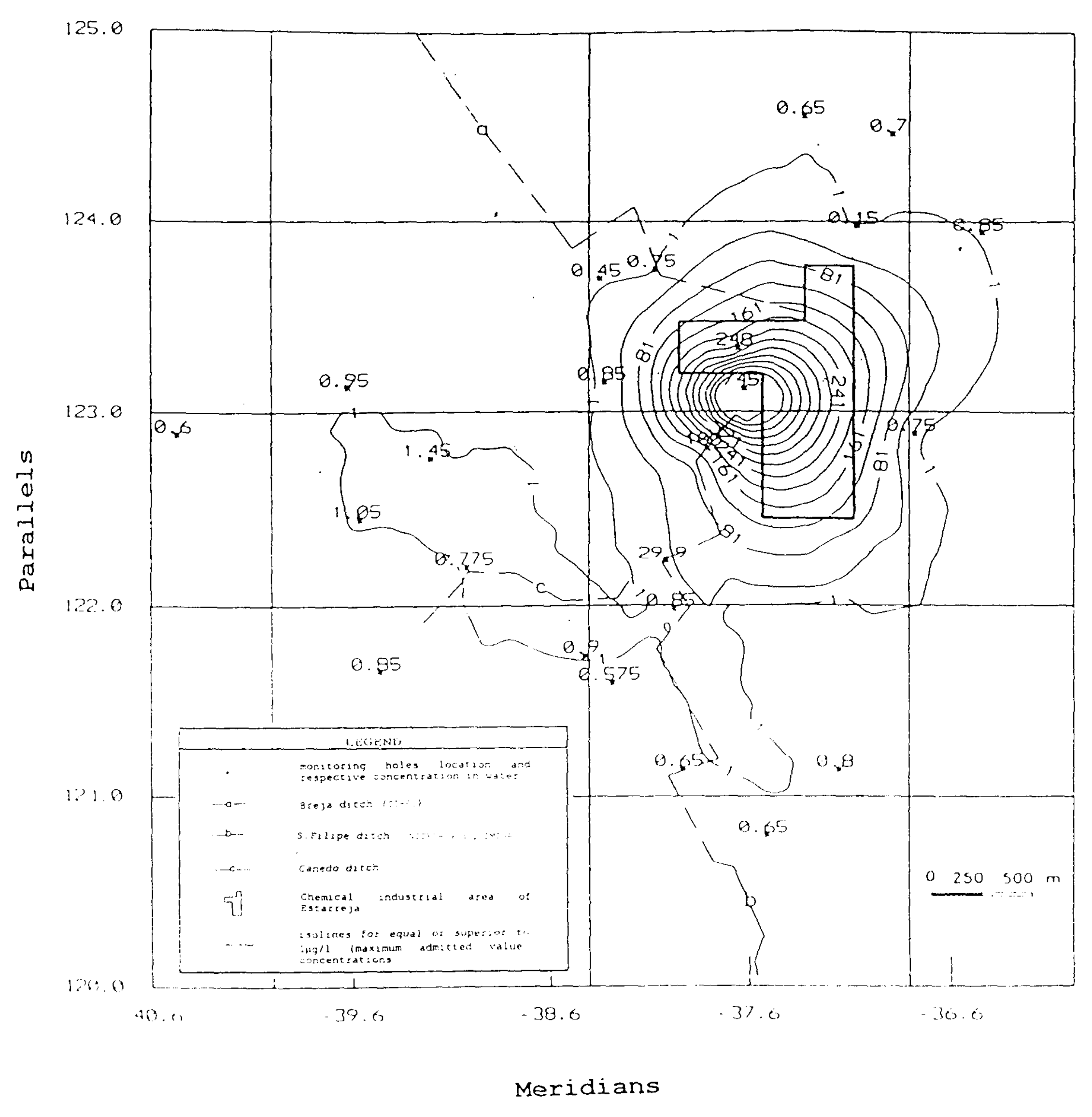

Figure 3: Groundwater mercury contamination

4.3.3 Anions

<u>Chlorides</u>

The chloride concentrations reach higher values (highest value = 36,540 mg/L) than the legislation permits (25 mg/L) all over the sampling area. The origin is probably the sludges from Uniteca, which present chloride values of 7 to 11% in the 60,000 tonnes of sludges. Also, the effluents from Quimigal present high chloride values, reaching an average between 1987 and 1991 of 630 mg/L.

Sulphates

Values over three times the legislation limit were found: values of 900 mg/L compared to the limit of 250 mg/L. The origin is the sludge from Uniteca, where calcium sulphate is 10 to 14% of the sludges, and the effluents from Quimigal that reach values of 2,300 mg/L, compared to the legislation limit of 2,000 mg/L. Some of the sulphate might have been reduced to sulphide and be responsible for the smell characteristic of the waters in this area.

Nitrates

Values exceeding the legislation value (50 mg/L) were found near the ditches, reaching values of 325 mg/L. Their origin is the effluent rejection and also the fertilization for agriculture. The effluent rejection between 1987 and 1991 reached values of 5,116 mg/L, hundred times the legislation value.

4.3.4 Organic compounds

There is no mention of organic compounds in the Portuguese legislation for water for human consumption so reference is made below to international legislation.

Nitrobenzene

In three of the monitoring holes, the level was higher than the U.S.legislation limit for groundwater (20 µg/L), reaching the high value of 2,520 µg/L. This hole is very near to the ditches, indicating the importance of effluents disposal as a source.

Benzene

The high value of 85.7 µg/L was reached in the same hole where nitrobenzene also reached the maximum (the limit in USA legislation is 5 µg/L). These two compounds are present in Quimigal effluents. The sampling campaigns allowed the detection of the area where contaminant concentrations are higher than the legislation permits. This area is illustrated in Figure 4.

4.4 Solutions Proposed

The Estarreja problem is a complex one due to the long time over which disposals have taken place (over forty years) and the dispersion of contaminants over a large area. Before the decontamination of the area, the first step should be the removal and treatment of the main pollution sources: *i.e.*, the sludges disposal area of Quimigal and Uniteca and the liquid effluent disposal to the ditches.

For the moment, the sludges disposal area should be covered to prevent the rain entering and consequent leaching and a physical isolation of the area through the injection, in the land and until near the aquifer, of walls preventing the pollutants migrating. Also, effluent disposal through the ditches should be stopped and wastewater treatment should also be installed.

There is a project from the Estarreja Municipal Government to treat the wastes by “Chemical Fixation and Solidification.” The sludges from Quimigal and Uniteca would be mixed with Cires sludges, which are more inactive (mainly calcium hydroxide) and would be used as material for encapsulation.The sludges and wastes would finally be deposited in a landfill.

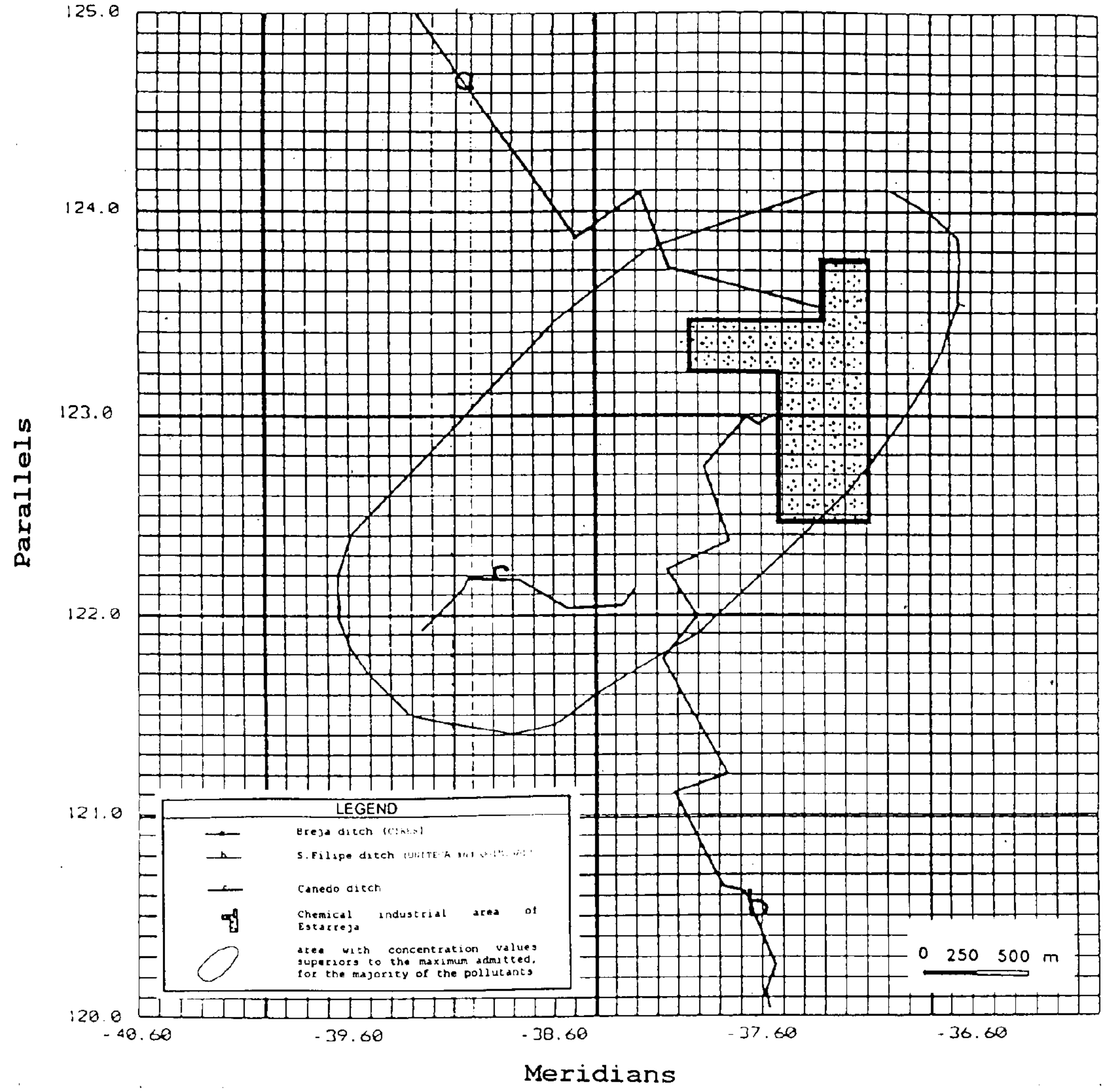

Figure 4: Main polluted areas

In addition to the measures listed above, decontamination of the groundwater is essential. The polluted groundwater should be removed and should be treated, to prevent the pollution spreading. Through the method developed by Javandel and Tsang (1986) the volume and extraction flow and number and position of capture holes were established. The volume to be removed should be 7 x 10^6 m^3, and the extraction flow should be 17,797.5 m^3/day

The time necessary to perform this operation will be around 400 days. This decontamination will remove the elements not adsorbed in the surrounding soil. The groundwater should be treated in wastewater treatment plants and afterwards be reintroduced again in the aquifer or used in agriculture or industry.

This groundwater pollution case is the most important and also the most studied one in Portugal. In 1995 a governmental law (DR 19/7/95) established that Estarreja was a critical area for pollution and industrial security. For management of industrial wastes, an Integrated System of Waste Treatment (SITRI) was programmed for the country.

In Estarreja should be installed an incineration unit, together with a project for soil and groundwater decontamination (Project ERASE) and a project for industrial and domestic wastewater treatment (Project AMRIA). Also, priority should be given in Estarreja to the installation of clean technology industries.

The incineration installation is somewhat delayed because the NIMBY mentality (not in my backyard) arrived quickly in Portugal, and through 1995 great opposition was made by the population to the installation of incineration units or landfills.

5. RESEARCH PROJECTS

In Portugal, very few research projects are dedicated to the problems of groundwater and soils contamination, and those there are mainly are master theses in the universities. One of the few existing projects is a European Community project “Experimental Evaluation of Remediation Techniques for Contaminated Coke Oven Sites.” The partners are Siderurgia Nacional, Instituto de Ciência e Tecnologia dos Materiais (ICTM) and Deutshe Montan Tecnologie (DTM).

INETI is subcontracted by ICTM, one of the partners. INETI’s activities concern characterization of the contamination of soils and groundwater in the coke oven site of Siderurgia Nacional by the Institute of Environmental Technologies (ITA); and strategies for microbial remediation of coke oven contaminated sites by the Institute of Biotechnology, Chemistry and Food Technologies (IBQTA).

The contamination of soil at operational coke oven sites is due to organic and inorganic toxic compounds such as mono-aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), phenols, cyanides, heavy metals, and ammonia. This contamination may be a source of groundwater pollution, especially when the water table is at shallow depths. Due to the fact that the contaminated site is located near an estuary, the tide effect can cause a groundwater gradient towards the surface water and cause superficial water pollution problems.

The objective of this research project is to select the most effective biological treatment technology to remove phenols, PAHs, and cyanides from contaminated coke oven plant sites still in operation and also to analyse the groundwater contamination. The program of work was:

- Identification of organic contaminated areas;
- Development of sampling program for soils and groundwater;
- Characterisation of soils and groundwater; and
- Determination of biological treatment efficiencies.

Regarding ITA’s activities, the characterisation of soil contamination as well as the mapping of the extent of pollution was carried out. Individual samples of soil representative of each geological layer were collected in order to obtain information about the lithology and the contamination of the area. Twelve trenches were dug with a mechanical excavator, almost all were dug until groundwater level was reached.

The contamination found in the coke oven site is mainly due to tar at the top of the first layer. Coke oven tar is an extremely complex mixture, the main components of which are polycyclic aromatic hydrocarbons (PAHs), highly toxic. Fluoranthene, phenanthrene, and pyrene have been detected as major contaminants.

Due to their high chemical stability and low water solubility, the PAHs have low mobility and persist as soil contaminants. The PAHs were identified by reverse phase high performance liquid chromatography, and values exceeding 1,000 mg/kg of fluoranthene, phenanthrene and pyrene were detected. The phenols and total cyanides reached 25.3 mg/kg and 1,420 mg/kg, respectively.

The tar contamination was mapped. In most places tar contamination is only at the surface, but in some sampling points, it has reached deeper layers down to groundwater level.

In lower soil layers the presence of ammonia was detected in the groundwater in all the trenches. This contamination is due to ancient accidental spillage and probably also to pipe leaks. In the next project phase, groundwater contamination is going to be characterised.

Regarding the bioremediation studies, the objective was to determine the potential for bioremediation of the microbial communities indigenous of the coke oven site through the evaluation of their abilities to degrade PAHs, particularly those detected as major contaminants. Tests already performed indicate that mixed culture selected and enriched from soil native microbial populations have the ability to degrade the predominant PAHs contaminants fluoranthene, phenanthrene, and pyrene.

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Critical Review of Air Sparging and *In Situ* Bioremediation Technologies

Domenic Grasso, The School of Engineering, University of Connecticut, Kenneth L Sperry,
Envirogen, Lawrenceville, NJ, and Susan Grasso, Environ, Princeton, NJ

1. INTRODUCTION

This review consists of the identification, classification, and analysis of issues of concern (or "critical issues") frequently encountered during the application of *air sparging/biosparging*, *bioventing, biostimulation*, and *biorestoration* remediation technologies. This review was prepared for the NATO Committee on the Challenges of Modern Society, which is evaluating emerging environmental remediation technologies, in an effort to facilitate future applications of these technologies.

The review utilized a case study approach and included more than 400 sites located in the United States, Australia, Canada, and Europe. Case studies included bench-, pilot-, and full-scale applications of these technologies, and explored remediation at a wide variety of sites including:

- petroleum processing/handling facilities;
- wood preserving plants;
- manufactured gas plants;
- military installations; and
- industrial/chemical manufacturing facilities.

At a majority of the sites reviewed, organic compounds in soil and groundwater were the target of remediation. Elevated levels of heavy metals and inorganic compounds were, however, also present at many of the sites reviewed. In general, seven classes of compounds were frequently encountered: (1) aliphatics; (2) substituted benzenes; (3) polycyclic aromatic hydrocarbons; (4) polychlorinated biphenyls; (5) pesticides/insecticides/herbicides; (6) inorganics; and (7) metals.

Critical issues identified in the case studies were categorized according to scale (macro, meso or micro). A macroscale issue was generally defined as a factor that may complicate the selection and administration of a remedial technology. Meso- and microscale issues were generally defined as factors that may adversely affect the performance of a remedial technology. More specifically, mesoscale issues were related to the physical geologic and hydrogeologic properties of the subsurface, and microscale issues pertained to biological and physicochemical processes. The review focused primarily on the detailed evaluation of meso- and microscale critical issues most frequently associated with the remediation technologies of interest.

Overall, critical issues (macro, meso, and micro) were reported in approximately 35% of all cases reviewed. More specifically, critical issues were observed with the following frequency for each technology:

Technology	Total Number	Sites with	Percentage of Sites
Air sparging/biosparging	87	18	21%
Bioventing	101	31	31%
Biostimulation	67	29	43%
Biorestoration	104	47	45%

The actual number of case studies where critical issues were encountered may be much greater as there may be reluctance to report such information. The primary types of critical issues observed for each technology are summarized below.

2. AIR SPARGING/BIOSPARGING

Air sparging/biosparging consists of injecting air (or other gases) under pressure directly into groundwater-saturated aquifer materials. The objective is to facilitate contaminant transfer from an aqueous phase (groundwater) to a gaseous phase (*in situ* air stripping) which is subsequently transported to the overlying unsaturated zone and removed by traditional soil vapor extraction (SVE) techniques. In addition to volatilization, air sparging fortuitously stimulates microbial degradation of contaminants by increasing the concentration of dissolved oxygen in the subsurface (biosparging).

Mesoscale critical issues were observed most frequently followed by macro-scale critical issues. Reported macroscale issues were associated with regulatory acceptance of these technologies due to their limited use. A very limited number of air sparging and biosparging case studies reported microscale issues.

While some of the mesoscale issues observed were related to contaminant distribution and site hydrogeology, those relating to site geology were observed to most severely compromise air sparging and biosparging performance. In these cases, geologic stratigraphy (such as lenses of low or high permeability material), and small variations in soil permeability resulted in preferential air channeling and poor air distribution through tortuous and asymmetrical air flow pathways.

> *Preferential air flow reduced the effectiveness of air sparging and biosparging because large portions of the targeted remediation zone were bypassed by the sparge air.*

3. BIOVENTING

Bioventing induces air movement through the unsaturated soil to enhance aerobic biodegradation of contaminants by supplying oxygen to soil microorganisms. Air movement is usually induced by forced (active) aeration using injection and extraction wells.

Similar to air sparging/biosparging, mesoscale critical issues were observed most frequently followed by macro-scale critical issues. Reported macroscale issues were associated with regulatory approval and acquisition of regulatory permits. Relatively few of the bioventing case studies provided information detailed enough to accurately identify microscale critical issues. Where microscale critical issues were observed, however, they were likely associated with biological and/or physicochemical limitations that adversely affected biodegradation kinetics.

Mesoscale critical issues observed to most adversely affect system performance were related to site geology and hydrogeology. More specifically, the effectiveness of bioventing was reduced when the delivery of oxygen to indigenous microorganisms was hindered by: (1) low permeable soils; and (2) excessive soil moisture content.

> *Fine-grained soils (silts and clays) which have a low intrinsic soil gas permeability and a high field capacity (potential for high soil moisture content) were found to be especially problematic in the application of bioventing. The combination of these factors decrease effective soil gas permeability and increase the potential for oxygen diffusion limitations.*

4. BIOSTIMULATION

Biostimulation refers to the enhancement of aerobic biodegradation of contaminants in the unsaturated zone (above the water table) through the addition of electron acceptors, electron donors, and nutrients. In the case studies reviewed, these amendments were typically delivered to the subsurface using water or air as a carrier fluid.

Macroscale and microscale critical issues were observed with equal frequency in biostimulation case studies, while mesoscale critical issues were observed to a lesser degree. Macroscale critical issues included: (1) difficulty in obtained regulatory approval for use of the technology; and (2) difficulty obtaining discharge to groundwater permits. The primary mesoscale issue observed involved the non-uniform delivery of components required to enhance aerobic biodegradation as a result of geologic heterogeneity.

Microscale critical issues were most often associated with biological and physicochemical processes, however, in many case studies differentiating between these mechanisms was not possible. The following were observed:

(1) Biological microscale issues were related to contaminant biodegradation potential, microorganism metabolic requirements, and contaminant toxicity.

(2) Physicochemical critical issues were related to reduced contaminant bioavailability deriving from either mass transfer kinetics or dissolution rate limitations.

The predominance of microscale critical issues in the biostimulation case studies reviewed was a reflection of the contaminant type targeted for remediation. In contrast to the majority of the air sparging/biosparging and bioventing case studies reviewed, a wide range of large polycyclic aromatic hydrocarbons (PAHs) were the target of remediation at the majority of biostimulation case studies reviewed.

> *The insoluble and nonvolatile nature of PAHs targeted for remediation in many of the biostimulation case studies makes them more recalcitrant to biodegradation (and volatilization) than the lower weight aliphatic and aromatic hydrocarbons that were typically the target of remediation in the air sparging/biosparging and bioventing case studies discussed.*

5. BIORESTORATION

Biorestoration refers to the injection of fluids containing electron acceptors, electron donors, or nutrients into the saturated zone (below the water table) to stimulate *in situ* aerobic or anaerobic biodegradation.

Macroscale critical issues were observed most frequently in the biorestoration case studies reviewed, and typically involved: (1) difficulty in obtained regulatory approval for use of the technology; and (2) difficulty in monitoring biorestoration performance.

Mesoscale critical issues were most often related to site hydrogeology. Groundwater flow velocity, as determined by hydraulic conductivity and hydraulic gradient, was an important factor in the successful application of biorestoration, as expected.

> *In formations with low groundwater velocities, the areal extent of biodegradation was limited because electron acceptors, electron donors, and nutrients were quickly consumed within the immediate vicinity of injection wells.*

Microscale critical issues were most often associated with biological processes in many of the biorestoration case studies reviewed. Specific hindrances to system performance included:

(1) The biodegradation kinetics of some components of coal tar waste were observed to be rate limiting.

(2) Microbial inhibition due to elevated levels of arsenic, lead, chromium, and dioxins was also observed to potentially limit biodegradation.

> *The slow biodegradation rate of components of coal tar wastes was observed to limit system performance in some of the biorestoration case studies reviewed. The biodegradation kinetics of these compounds were potentially limited by contaminant bioavailability. In addition, microbial inhibition due to elevated concentrations of arsenic, lead, chromium, and dioxins was suspected of limiting biodegradation rates in some biorestoration case studies discussed.*

6. MASS TRANSFER LIMITATIONS—A UBIQUITOUS CRITICAL ISSUE

Although many critical issues were observed to be specific to either air sparging/biosparging, bioventing, biostimulation, or biorestoration, all the reviewed technologies have one at least one critical issue in common: diffusion limited mass transfer. The theory and ramifications of diffusion limited mass transfer were therefore explored in depth. The discussion focused on diffusion limitations:

(1) in bulk aqueous solution where advective flow is minimal or absent; and

(2) from within soil matrices to the surrounding bulk aqueous solution (sorption retarded diffusion).

6.1 Diffusion Limitations in Bulk Solution

In situ technologies discussed herein are inherently susceptible to diffusion limited mass transfer in the bulk aqueous phase because each technology relies upon fluid flow to either:

(1) deliver components required to enhance biodegradation (electron donors, electron acceptors, and nutrients); or

(2) to extract contaminants (such as volatilization in air sparging).

Fluid flow in most subsurface environments, however, is not uniform and heterogeneities in the subsurface can result in preferential flow pathways. Outside these flow pathways, advective fluid flow may be minimal or absent. As a result, the primary mechanism for delivering components required to enhance biodegradation or contaminant extraction in these areas may be governed by molecular diffusion. A mathematical model was used to explore diffusion times required for oxygen and contaminants under various subsurface conditions encountered in this review.

> *Modeling results indicated that extensive diffusion times (ca. years) are required for oxygen and common contaminants to diffuse short distances (less than 1 m) in regions of the subsurface where advective fluid flow is minimal or absent.*

6.2 Sorption Retarded Diffusion

A sorption retarded diffusion limitation (*i.e.*, diffusion from within the soil matrix to the surrounding bulk aqueous solution) has been proposed as the primary mechanism responsible for the significant "tailing effect" in contaminant concentrations which was observed in many of the case studies reviewed. A bi-modal theory describing desorption from the soil matrix was combined with a radial diffusion model of transport in an aqueous solution to simulate the tailing effect phenomena. Model simulations assessed the effects of:

- tortuous and constricting soil pores;
- intra-particle porosity;
- soil fraction organic carbon;
- particle size; and
- contaminant chemical properties.

> *Model simulations demonstrated that considerable time (ca. years) may be required to desorb some contaminants from the soil matrix to the surrounding bulk aqueous solution. In addition, the use of a Freundlich isotherm to represent non-linear sorption in select portions of a soil matrix resulted in the prediction of significantly higher desorption times.*

The ability to uniformly distribute fluid in the subsurface was frequently encountered as a limitation in the application of the *in situ* technologies under review due to heterogeneous conditions commonly present in the subsurface. Without this ability, accomplishing uniform and complete remediation is such an environment can be difficult, due to diffusion limitations that may exist in the bulk fluid. Additionally, in most of the case studies reviewed, soils had been contaminated for many decades prior to remediation, suggesting that sorption retarded diffusion may be responsible for tailing phenomena commonly observed. As previously discussed, this may severely limit the long-term performance of the *in situ* remedial technologies reviewed.

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The Cost of Remedial Action

Dr. Mary R. Harris, Monitor Environmental Consultants Ltd, Birmingham, U.K.

1. INTRODUCTION

Considerable efforts have been made over recent years to identify and develop new technologies for the treatment of contaminated soil and groundwater and to demonstrate their technical performance in the field. Many of these technologies have the potential to transfer across international boundaries. Some appear to offer the prospect of dealing with contamination on a “once-and-for-all,” as opposed to “contain and control,” basis.

With some notable exceptions, however, there seems to be relatively little reliable information available to landowners, regulators and practitioners on:

- the cost of different technologies, and how they may compare against more established or traditional approaches;
- the key cost components of different technologies; and
- how the cost of treatment may be distributed over time.

A lack of reliable cost information can be as important as technical uncertainty in discouraging the wider uptake and application of new technologies. For example:

- it encourages users to favour the selection of established methods and approaches, where technical capabilities and costs are already well established and understood;
- it makes it difficult for users to predict at the outset (and with any acceptable degree of accuracy) what the financial implications of a remedial project may be; and
- it makes it difficult for users to gauge short versus long-term costs and benefits when making selection decisions, and to justify them financially.

Finally, a lack of information on the cost characteristics of new technologies can hamper their transfer across international borders because users are unable to make the essential financial adjustments needed to translate technology costs into a specific national context.

There are, of course, a number of practical difficulties in obtaining reliable financial information. Examples include:

- commercial confidentiality (on the part of both clients and contractors) on the actual “value” of the work done, rather the estimated or predicted cost;
- local or temporal cost variations due, for example, to fluctuations in local demand for remedial goods and services; and
- other site specific factors, such as the nature of the contamination, scale of operations, duration of the works, extent of other ground improvement or construction activities and their relationship with remedial action.

However, opportunities do exist for the systematic collection of financial information. Examples include national and international research and demonstration programmes, such as this NATO/CCMS study, and other publicly-funded remedial works, *e.g.*, regulatory-led action and grant-aided redevelopment schemes.

The development of standardised data collection and reporting procedures can help to ensure that financial information is consistent, objective and informative. The aim of this Fellowship was to assist in the development of reliable information on remedial costs and to improve the ability of technology users to interpret and apply cost information.

2. OBJECTIVES

The main objective of the Fellowship was to develop a standardised framework for reporting information on the costs of remediation that will:

- help to expand the currently relatively limited information base on remedial costs;
- assist in the international transfer of information on remedial costs;
- allow potential users of different remedial technologies to identify where the main cost burden is likely to fall;
- alert potential users to the trade-offs (*e.g.*, high capital/low aftercare versus low capital/high aftercare costs) which may have to be made when selecting particular technologies; and
- help potential users of overseas technologies to identify those cost items (*e.g.*, waste disposal, energy, labour, *etc.*) which may vary significantly as a result of country-specific factors.

3. APPROACH

Draft guidance on reporting remedial costs has been developed (see Annex I) based on:

- the cost framework developed in support of the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation (SITE) Program;
- research on remedial costs commissioned by the German Federal Environment Ministry; and
- work carried out by the U.S. Federal Remediation Technologies Roundtable *Ad Hoc* Working Group on Cost and Performance.

The draft guidance was circulated to Pilot Study Country Representatives for comment. Some comments have been received and have been incorporated into the current draft. This will be circulated to Pilot Study members with a request for submission of cost information.

4. ANALYSIS AND REPORTING

It is hoped that sufficient cost data on individual Pilot Study Projects will be available to allow a simple analysis of the broad cost characteristics of different types of technologies. The responses of Project Leaders will also be used to refine the cost framework where necessary and to identify the key issues to be addressed when attempting to interpret or apply cost information.

It is intended that the findings of the Fellowship will be incorporated into the final Pilot Study report in the form of a separate chapter on Remedial Costs.

5. ACKNOWLEDGEMENTS

The work reported here was carried out by means of written correspondence with other members of the Pilot Study and through participation at the following Pilot Study Meetings:

Quebec City, Canada	September 1993
Oxford, U.K.	September 1994
Nottingham, U.K.	May 1995

The assistance of other members of the Pilot Study, and the financial support of NATO and the U.K. Department of the Environment are gratefully acknowledged.

ANNEX I: Guidance on Reporting Information on Remedial Costs

A.1. INTRODUCTION

One of the aims of the Pilot Study is to provide information on the cost of remediating contaminated soil and groundwater. This guidance has been prepared to assist project leaders in collecting and presenting cost data on their technologies. The information obtained will be used to prepare a Chapter on costs for inclusion in the Final Pilot Study Report. The guidance supplements that produced by Mike Smith (see notes of the September 1994 Pilot Study meeting in Oxford) on overall reporting requirements.

The guidance has been developed with reference to the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation (SITE) programme cost framework, research on remediation costs commissioned by the German Federal Environment Ministry and work carried out by the Federal Remediation Technologies Roundtable *Ad Hoc* Working Group on Cost and Performance. Comments from the Pilot Study Country Representatives have also been taken into account.

It is recognised that not all the projects in the Pilot Study programme will be able to provide cost data at the level of detail shown; some projects are only just under way, and others are too remote from commercial realisation to provide meaningful data. Nevertheless, the aim is to provide actual or estimated costs for the full-scale operation of the technology.

A.2 OBJECTIVES

The main aims of providing cost data on remediation technologies through the NATO/CCMS Pilot Study are to

- expand the relatively limited information base currently available;
- assist in the international transfer of information on remedial costs;
- inform potential users where the main costs are likely to fall when applying a particular technology; and
- alert potential users to the trade-offs (*e.g.*, high capital costs/low aftercare costs vs low capital cost/high aftercare costs) that will have to made when selecting particular types of remedial technology for use.

It has been suggested that the provision of cost data is of relatively limited value because actual remedial costs are highly site-specific and some cost items (*e.g.*, energy, labour, waste disposal) can vary significantly from country to country. However, potential technology users can be made aware of the limitations associated with the cost data and the need to make appropriate adjustments when attempting to apply them in individual cases.

It is important therefore to document any important limitations applying to the cost data provided. All assumptions used to derive cost estimates and any other information essential to the correct interpretation of the data should be reported.

To facilitate the presentation and analysis of the data, costs should be in national currency and dated. SI units (*e.g.*, quantities of material treated) should be used throughout.

A.3 COST BREAKDOWN

Where possible, data should be provided according to the generic cost breakdown provided in Table A.1. This shows the different activities that might be carried out during the course of remedial action (left hand column) against various cost elements (top row). It may be necessary to add activities/cost elements when submitting data for individual technologies.

Sections A.4 and A.5 give a brief description of the intended scope of the activities/cost elements to be covered in project submissions. A brief explanation of the items covered by the cost data actually submitted should be provided.

Table A.1. Actual/Estimated Full-Scale Remediation Costs

Stage	Activity	Plant &	Materials	Laboratory	Other
Pre-operational	Legal approvals Site Preparation Mobilisation				
	Sub-total				
Operational	Excavation/extraction Pre-treatment Processing Waste treatment/disposal Monitoring I. process control I. legal compliance Modification and repair Public relations				
	Sub-total				
Post-operational					
	Sub-total				
	TOTAL				

A.4 ACTIVITIES

A.4.1 Pre-Operational Stage

Legal approvals: Costs involved in obtaining regulatory approval for the installation/operation of the remedial technology. Requirements are likely to vary widely depending on the (national) regulatory framework, the technology involved and site-specific factors but they will typically include: approval for installing/constructing items of plant & equipment; consents to make permitted discharges (*e.g.*, to air, water, sewer); permission to abstract water (*e.g.*, for groundwater remediation work); provision of environmental impact statements, *etc*.

Site preparation: Costs involved in preparing the site to receive all necessary plant & equipment. Typical items to be included are: provision of site security/access; site leveling; provision of hardstanding/storage areas; ground and surface water protection measures; provision of site services, *etc*.

Mobilisation: Costs involved in transferring, setting up and commissioning all necessary plant and equipment.

A.4.2 Operational Stage

Excavation/extraction: Cost of removing contaminated solids/liquids from the ground prior to treatment in on or off-site facilities.

Pre-treatment: Costs associated with storing/preparing material for treatment where this can be identified as a separate part of the process. Typical pre-treatment activities include storing/conditioning, size classification, grinding, dewatering, drying, *etc*., of feedstocks.

Processing: The cost of processing/treating contaminated material using physical, chemical, biological techniques.

Waste treatment/disposal: Cost of transporting/treating/disposing of solid, liquid or gaseous wastes from the process, including pollution control residues (*e.g.*, spent activated carbon, scrubbing liquors, *etc.*).

Monitoring: All operational monitoring costs including that required to optimise/control the process (*e.g.*, to maintain temperatures, mixing conditions, pH conditions) and ensure legal compliance (*e.g.*, with respect to atmospheric discharge limits, to protect the health and safety of the workforce).

Modifications/repair: Cost of modifying/repairing plant and equipment.

Public relations: The costs of informing/liaising with third parties, such as the local community.

A.4.3 Post-Operational Stage

Demobilisation/reinstatement: Cost of dismantling, decontaminating and removing items of plant and equipment, and reinstating the site (where appropriate).

Monitoring: The cost of demonstrating that remedial objectives have been met including one-off validation (*e.g.*, demonstrating the quality of a product from a soil washing plant) and long-term monitoring (*e.g.*, demonstrating that an *in situ* treatment process has reached completion).

A.5 COST ELEMENTS

Plant and equipment: Plant and equipment costs may be reported as capital items (amortisation period to be specified) or as plant hire costs.

Materials costs: These include all materials consumed during the course of remedial action. Typical items include treatment chemicals, energy (electricity, diesel), water, health protection equipment, monitoring equipment not otherwise specified.

Labour costs: These should be reported for all personnel involved in setting-up, operating and completing the remedial operation. Consultancy and contracting labour costs should be reported separately where possible. Travel and subsistence costs should be reported under the “other costs” activity heading.

Analysis: All laboratory analytical support used before, during and after remedial action.

Other costs: All costs not otherwise specified. The items covered under this heading should be specified and may include permitting/legal fees, travel and subsistence costs, loan charges, insurance, *etc*.

Changing Approaches to Remediation[1]

Merten Hinsenveld, TSM Business School, University of Twente, Enschede, The Netherlands

In the 1980s, large differences existed amongst the various countries in their approach towards contaminated sites. By looking at the concentrations in their supposedly clean soils, the Dutch took a straight forward approach and derived a single concentration per contaminant for a clean soil (so-called A-value) and a concentration of a polluted soil for which prolonged exposure might lead to health effects (so-called C-value). The Americans on the other hand choose a more site specific, but cumbersome and disputable, risk approach. Both approaches were developed on the assumption that the problem of contaminated sites was limited.

Initially, various countries adopted—with or without modifications—one of these extreme examples. Experience made two points clear:

(1) the problem was not limited, and

(2) concentration based approaches as well as risk based approaches each have their specific advantages and disadvantages.

Mixed approaches in various forms and the study of exceptions to the rule is now more common practice.

Improved understanding of the mechanisms with which the subsoil and the groundwater can and does cope with a contamination, is changing the approach towards remediation rapidly. With particular reference to intrinsic bioremediation, the scientific and the regulatory world are both changing from a problem-solution approach towards a process-oriented approach. Contamination in this approach is more a process that might be altered, stopped or monitored, than it is a problem.

Finally, the realisation that the tremendous cost of remediation may not be in balance with its benefit, has provided a growing incentive to the development and use of methods that can weigh the various cost/benefit elements (economy, environment, health, spacial use) of contaminated sites to provide a tool for integrated decision making.

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[1] *This fellowship is still in progress and will be extended into the new Pilot Study on remediation starting in 1998.*

Use of Remedial Clean-Up Technology in Portugal

Maria José Macedo, Hovione - Sociedade Quimica SA, Loures, Portugal

1. INTRODUCTION

Until recently there was no experience of remedial clean-up of industrial sites in Portugal. Lisbon is organizing the 1998 World Exposition (EXPO'98) and a site located East of the city was chosen to host the exposition. This site was formerly occupied by the Petrogal, BP, Mobil and Shell petroleum companies. Principal activities at the site included petroleum refining and storage, causing soil and groundwater contamination in several distinct areas. Prior to the existence of the petroleum companies at the site, there was a sulphuric acid producing plant that caused, in a determined area, contamination of the soil by arsenic.

ISQ made an audit to the decontamination of this site. A brief description of the decontamination work is presented.

2. SOIL REMEDIATION AT THE EXPO'98 SITE

The soil was contaminated by several petroleum originated pollutants (benzene, toluene, ethylbenzene, and xylenes and total petroleum hydrocarbons [TPH]) and arsenic from a previously existent sulphuric acid plant.

For the site clean-up, several techniques were considered, namely:

- thermal treatment;
- stabilisation;
- soil-vapour extraction;
- biological treatment; and
- excavation and landfilling.

Excavation and deposition in a controlled landfill was finally chosen since it was the technique that presented a better cost/benefit ratio. Prior to the start of the excavations an excavation plan was prepared. In this excavation plan, excavation activities to be carried out were described area by area, completed with drawings and cross-sections. Each excavation area was staked out first, based on the results of the delineation investigation and the modifications that were included in the excavation plan.

Excavation was done in two phases. After completing a first topographical survey of the area, the non-contaminated soil was excavated. The limits of the non-contaminated soil were determined during excavation by means of an oil detection pan. The excavated non-contaminated soil was placed in stockpiles in the vicinity of the excavated area.

The quantity of excavated non-contaminated soil was determined after doing a second topographical survey. Excavation of contaminated soil proceeded according to the remediation goals.

In general, the extent of contamination was quite similar to the expected extent. A total of approximately 300,000 m^3 of soil was excavated and landfilled.

The contaminated soil was transported to a landfill. The new designed landfill was situated at the eastern part of the existing Beirolas landfill in Moscavide, Lisbon. The landfill was constructed with recompacted clay layers, geotextiles, geonets and liners, to provide a secure storage facility for contaminated soil. The contaminated soil was transported to the landfill by truck.

There were also large amounts of free product and a large quantity was removed. In total approximately 400 m^3 of free product was recovered and removed by tanker truck.

In order to properly excavate to the required depth dewatering of certain excavated areas was necessary. The water was pumped into a temporary water treatment plant.
The water treatment plant consisted of the following components:

- collection sump with pumps;
- oil/water separator;
- aeration container;
- compost container for treatment aeration air;
- buffer basin for temporary storage;
- sandfilters;
- active-carbon filters;
- end buffer container;
- watermeter; and
- discharge hose to existing sewer.

The contaminated groundwater entered into the oil/water separator, where free product and groundwater were separated. The free product accumulated in the separator was removed regularly by tankertruck.

The groundwater then entered the aeration container, in which the volatile compounds were dispersed into the air. The contaminated air was led into the compost container for bio-cleaning. The treated groundwater was discharged into the buffer basin.

From the buffer basin the water was pumped through the sand filters and the active carbon filters and then discharged via the end buffer container into the existing sewer. The discharged water was regularly sampled and analysed. The concentrations of TPH and volatile organic compounds (VOCs) never exceeded the allowed concentrations.

In total, approximately 5,200 m^3 groundwater was treated in the temporary plant.

3. CONCLUSIONS

This is the only case of soil remediation of a previously industrial site in Portugal.

There are some studies being made for the assessment of soil and groundwater contamination in industrial sites but no remedial actions have been made. One example of a study area is the chemical complex of the Estarreja industrial area, in Oporto district.

The processing industry, namely the chemical industry, is, in Portugal, the major source of industrial contamination. Until recently, the solid wastes originating from there were deposited, without any control or protective measures in municipal landfills or in landfills belonging to the companies, as was the case of the Estarreja chemical complex. Thus, there is a large contaminated area with solid wastes from several production processes.

In 1991, the Environment Ministry started a project aiming to study an adequate methodology for remediation of contaminated groundwater and soil. The objectives of this study were:

- selection of a study area with problems of soil contamination by industrial wastes
- assessment of present situation, in terms of soil and water quality: (1) elaboration of hydrogeological studies; and (2) risk analysis
- elaboration of recommendations for the resolution of the problems of the selected area

This study has been made but no remedial actions have started.

At present, there are two factors that make the adoption of state of the art technologies slower in Portugal than in more industrialised countries:

- the difficult financial situation of Portugal—made worse by the recession in all Europe—does not allow large investments in remedial projects; and
- the awareness level of the Portuguese population is still extremely low.

The delay that Portugal suffered in its economic development can, however, in the long term become an advantage, because, due to the low industrialisation in this century, there are not contaminated sites in such a large number and proclivity (throughout the country) as for instance in Germany. In addition, it is still possible to avoid strategic errors (future problems) by applying appropriate legislative, administrative and technological measures.

Experiences with the Performance of *In Situ* Treatment Technologies

Dr. Robert L. Siegrist, Environmental Science & Engineering Division, Colorado School of Mines

1. INTRODUCTION

The overall goal of this study is to explore international experiences gained with the performance of *in situ* treatment technologies for contaminated soil and groundwater and to determine the cleanup achieved as related to time and cost expended compared to predictions made when the *in situ* technology was selected. The types of sites of interest include those commonly encountered and where *in situ* technologies have been employed. These sites include those contaminated with petrochemicals such as benzene and/or chlorocarbons such as trichloroethylene. The types of technologies commonly applied include soil vapor extraction and air sparging for source treatment and increasingly treatment barriers for interception and plume migration control. As originally conceived, this work is being accomplished by literature review and critical analysis complemented by interactions with delegates at NATO Pilot Study meetings and through personal inquiries and correspondence.

While performance of *in situ* treatment technologies can be assessed with regard to various measures, one critical question relates to how well did the technology achieve the cleanup goal initially prescribed in terms of time and cost predictions that were made initially when the technology was selected. This question is a critical one. The selection, design, and implementation of *in situ* technologies requires knowledge of their ability to achieve various cleanup goals and at what cost over what time. If large expenditures in terms of cost and time are made but the technology does not achieve the goal, then it could be speculated that savings could have been realized with no loss in risk reduction actually achieved, if a more realistic goal had been initially prescribed. In so doing, the savings in cost and time could have been allocated to other sites and overall the reduction in risk in a jurisdiction might have been greater.

Work on the project started with attendance at the Adelaide meeting of the Phase II Pilot Study held in February 1996 and will continued into the Phase III Pilot Study.

2. PROJECT SCOPE AND CONCEPTS

For contaminated sites, a conceptual model for risk is generally considered to include several key elements:

(1) a source of contamination,

(2) transport/fate in the soil and ground water environment, and

(3) the receptors and their exposure pathways and dose-response properties (Figure 1).

If the risk is deemed unacceptably high, risk management is often implemented to reduce or eliminate the source, beneficially modify the transport/fate properties, or cut-off the exposure of receptors. For these purposes, *in situ* remediation technologies are often preferred because they can be implemented over larger areas with lower site disruption, with lower worker exposure, and generally at lower cost. Achieving risk reduction via *in situ* technologies often requires a reduction in concentration and/or mass of contaminants somewhere prior to exposure occurring.Figure 2 presents a graphical illustration of contaminant concentration as related to time and cost.

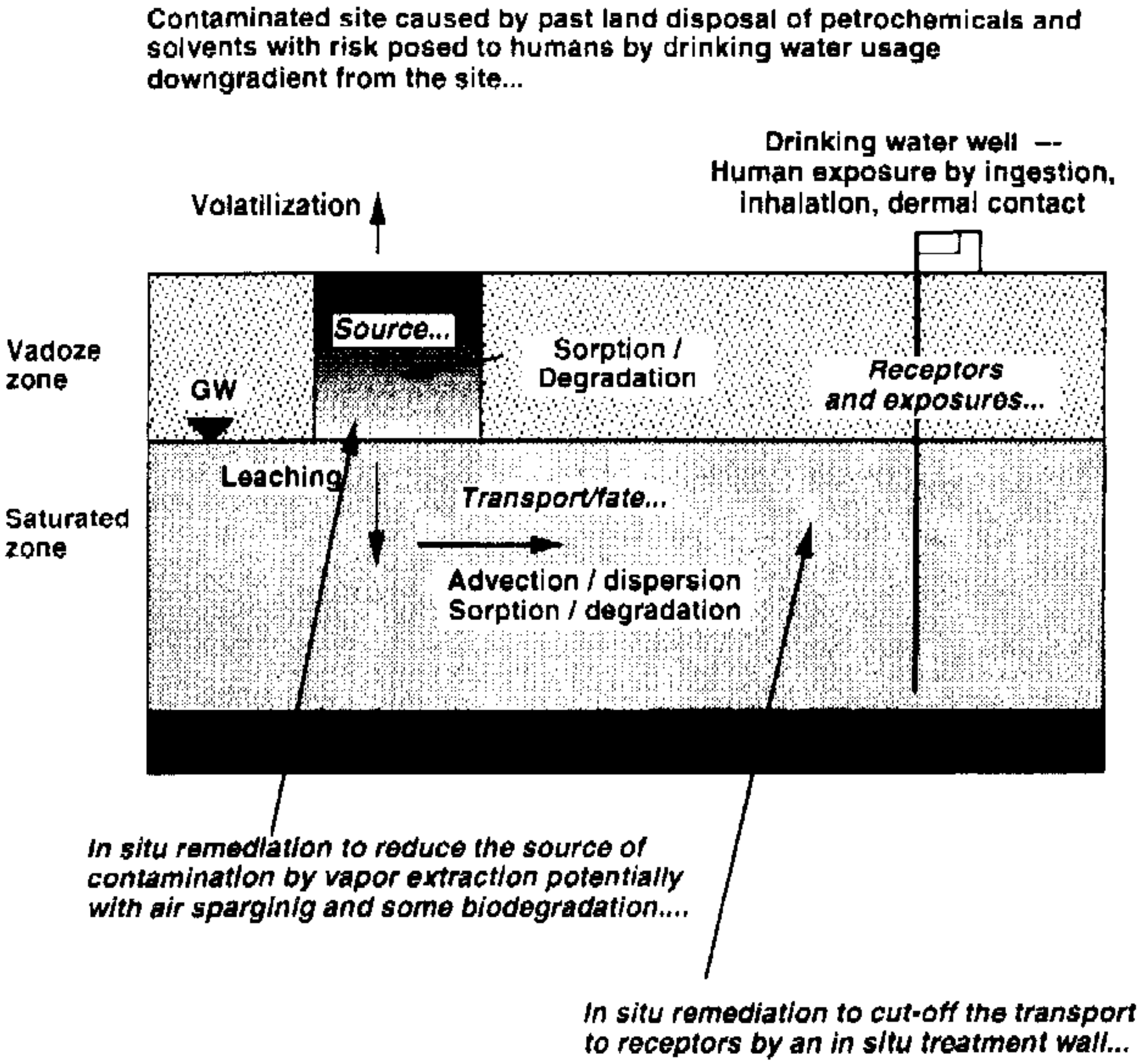

Figure 1: Conceptual Model Components for an Organically Contaminated Site and *In Situ* Remediation to Achieve a Reduction in Risk

In most remediation cases, extensive time and expense are devoted to characterizing a site, assessing the risk associated with the nature and extent of contamination present, and selecting and implementing a remedial action to achieve a prescribed cleanup goal. However, less effort is often expended to evaluate technology performance over time and to document cleanup goal achievement versus the time and cost incurred. Such a critical review of technology performance is needed however, to ascertain whether investments made in characterization, assessment, and remedial action implementation are justified by the benefits achieved.

Information is being gathered on *in situ* technologies to enable a critical evaluation of the treatment efficiency and the risk reductions that have been claimed to be achieved and whether there is adequate information to support these claims. Moreover, the study will attempt to determine whether the initially established cleanup goals were in fact achieved at the cost and time predicted. The study will also explore whether resources could have been more effectively expended by treating more sites to less stringent goals that were in fact all that was achieved even when more stringent goals were initially established.

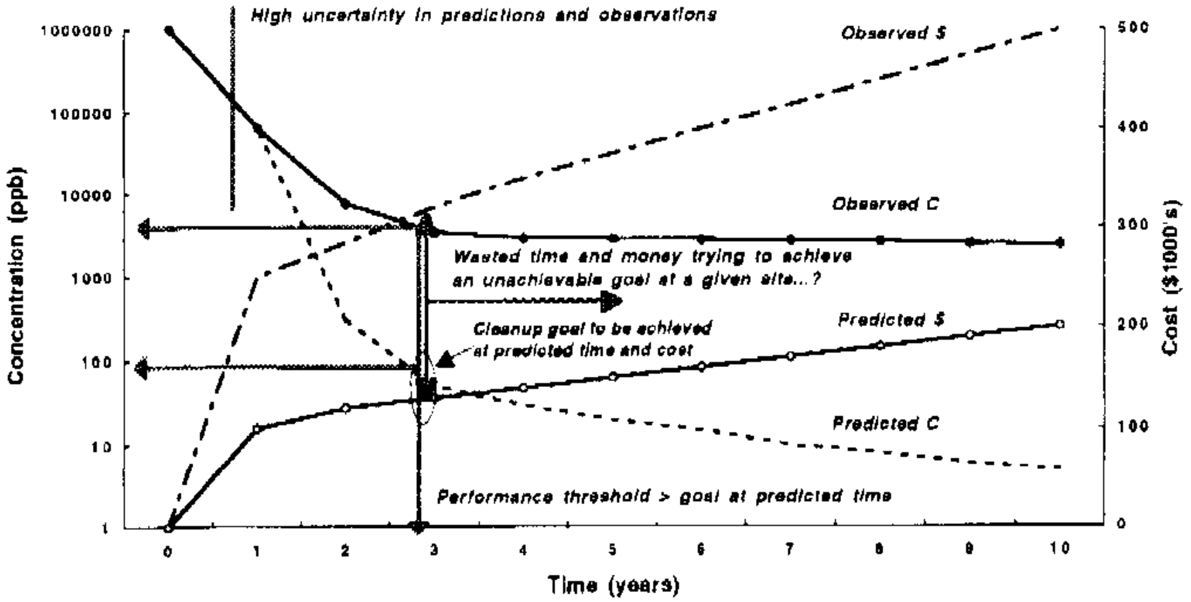

Figure 2: Illustration of the Relationship Between In Situ Remediation Performance Predictions versus Actual Achievement as Related to Time and Cost of Remediation

The project will contribute to the objectives of the Pilot Study by providing an independent and critical understanding of the use of *in situ* treatment technologies, methods used for their process control, and their true performance in achieving cleanup goals and associated risk reductions.

Editorial Note:

In addition to the CCMS Fellowship study described here, Dr. Siegrist hosted the meeting of the Phase II Pilot Study held in Golden, Colorado in March 1997. In addition, during the meeting he made a guest speaker presentation on *In situ remediation of DNAPLs in low permeability media*.