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U.S. EPA Workshop on Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal

Proceedings and Summary Report

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

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List of Acronyms

AMD	Acid Mine Drainage
ATP	Adenosine Triphosphate
AVS	Acid Volatile Sulfide
BDAT	Best Demonstrated Achievable Technology
BRS	EPA Biennial Report System
CAA	Clean Air Act
CCA	Chromated Copper Arsenate
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CWA	Clean Water Act
DMAA	Dimethylarsinic Acid
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
EM	Electron Microprobe
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right to Know Act
FDA	Food and Drug Administration
GPS	Global Positioning System
HGMS	High Gradient Magnetic Separation
ISCF	In-Situ Chemical Fixation
LDR	Land Disposal Restriction
LRPCD	Land Remediation and Pollution Control Division (NRMRL)
MCL	Maximum Contaminant Level
MEP	Multiple Extraction Procedure
MMAA	Monomethylarsonic Acid
MPW	Mineral Processing Waste
NCEA	National Center for Environmental Assessment
NERL	National Exposure Research Laboratory
NHEERL	National Health and Environmental Effects Research Laboratory
NPL	National Priorities List

List of Acronyms (Cont.)

NRMRL	National Risk Management Research Laboratory
NURE	National Uranium Resource Evaluation (a program)
ORD	Office of Research and Development
ORP	Oxidation-Reduction Potential
OSW	Office of Solid Waste
PAH	Polynuclear Aromatic Hydrocarbons
PIG	Peat, Iron, and Gypsum
PRB	Permeable Reactive Barrier
RCRA	Resource Conservation and Recovery Act
RME	Risk Management Evaluation
ROD	Record of Decision
S/S	Solidification/Stabilization
SMZ	Surfactant-Modified Zeolite
SPLP	Synthetic Precipitation Leaching Procedure
SPRD	Subsurface Protection and Remediation Division (NRMRL)
TCLP	Toxicity Characteristic Leaching Procedure
TRI	Toxics Release Inventory
TSD	Treatment, Storage, and Disposal
TTSD	Technology Transfer and Support Division (NRMRL)
USGS	U.S. Geological Survey
WET	Waste Extraction Test
WTP	Water Treatment Plant
ZVI	Zero-Valent Iron

1.0 Executive Summary

1.1 Introduction

1.1.1 Purpose and Goals of the Workshop

A workshop titled "Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal," was held on May 1 – 3, 2001, in Denver, Colorado. This workshop was sponsored and facilitated by the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) and Office of Solid Waste (OSW), Emergency Response. The purpose of the workshop was to achieve three goals:

1) Examine the chemical fundamentals related to arsenic chemistry, speciation, and analytical issues;
2) Examine the state of practice of existing and emerging technologies that treat and properly dispose of arsenic wastes; and
3) Identify/characterize sources of arsenic.

The workshop was not designed to cover issues related to drinking water; rather, to focus on characterization of wastes, arsenic speciation, and treatment and disposal practices. To facilitate discussion of these issues, the workshop featured a series of speaker presentations at a plenary session, and moderated technical breakout sessions with additional speaker presentations and participant discussions. Topics for the 12 presentations during the plenary session included arsenic waste, chemistry, and treatment and disposal, as well as regulatory perspectives and information management. Technical breakout sessions looked more closely at arsenic chemistry, source identification, and treatment and disposal issues: presentations during these sessions were more specific to the session topics.

Presenters were from the EPA, U.S. Geological Survey (USGS), Government of Canada, state agencies, academia, federal laboratories, consulting firms, and technology developers. Presenters and other workshop participants were known for their knowledge and involvement in the field of arsenic waste and management.

This report provides a summary of the key issues pertaining to managing arsenic risks to the environment, followed by plenary speaker abstracts, breakout session discussion review and speaker abstracts, and lastly, appendices with the workshop agenda, attendees, and a selected arsenic publications bibliography. It is hoped that this information will be useful to anyone involved with managing arsenic issues, and will prompt additional work and research to resolve outstanding arsenic issues.

1.1.2 Background

It is well known that arsenic, especially the inorganic forms, is very toxic and is a carcinogen. The chemical nature of arsenic compounds, in particular their tendency to change valence states or chemical form under a wide range of pH and redox conditions, makes it difficult to assess their fate and mobility in the environment. Furthermore, case studies show that arsenic wastes that have been treated to U.S. regulatory standards are found to leach out of landfilled waste. A key issue for this workshop was, therefore, effective treatment and stabilization of arsenic wastes to minimize risk to health and the environment.

Arsenic wastes are generated from several industries such as mining and smelting operations. Currently in the U.S., arsenic contaminated wastes are subject to the Resource Conservation and Recovery Act (RCRA) land disposal restrictions and must be treated to meet Toxicity Characteristic Leaching Procedure (TCLP) limits. A RCRA hazardous waste is defined as a waste that produces an extract containing more than 100 times the maximum contaminant level (MCL) in drinking water for that specific chemical. The MCL for arsenic (50 ppb) was recently subjected to a critical review due to concerns about the association of long-term exposure to arsenic and serious health problems such as skin and internal cancers and cardiovascular and neurological effects. As a result of this review, a change in the arsenic MCL from 50 ppb to 10 ppb was promulgated. This new, lower MCL may have implications related to public perception of the risks associated with arsenic waste and contamination, treatment standards and effectiveness, and cost issues.

EPA funded several arsenic treatment studies throughout the 1990s and has research ongoing. Containing and minimizing arsenic contamination has been a priority for ORD. Projects have included mine waste technology, groundwater treatment using permeable reactive barrier (PRB) technology, transport and fate in sulfidic systems, and drinking water research including MCLs. OSW has been reviewing and re-evaluating solid waste treatment standards and evaluating the effectiveness of land disposal restrictions for management of arsenic waste.

Challenges and research opportunities for arsenic include:

- Arsenic chemistry and mobility at contaminated sites
- Risk assessment
- Public perception and trust in the science
- Long-term stability of treated arsenic wastes
- Stabilization design issues and organics interference
- Measurement of treatment effectiveness
- Disposal of residuals from drinking water plants

The following technical session discussion summaries speak to these challenges and other issues. Additional information is available in the speaker abstracts and detailed session discussions.

1.2 Summary of Breakout Session Discussions

1.2.1 Source Identification

In this technical session, researchers presented information about natural and anthropogenic (influence of man) sources of arsenic; characterizing and identifying arsenic in soils and sediments, coal deposits, and mining environments; and management of arsenic risk in marsh environments and the mining and wood treating industries. Arsenic data were presented from research at natural and industrial sites, and approaches for best communicating arsenic contamination and risk data to the public were discussed. Group discussions centered around three general questions:

1) What are the primary sources that contribute to arsenic releases to the environment?
2) What are the significant data gaps and information needs for characterizing and identifying arsenic sources and waste forms?
3) What are the important insights to be conveyed regarding the management of arsenic risks for decision makers?

Primary Sources. Arsenic in the environment occurs from both natural and anthropogenic sources. There has been an effort to differentiate between natural and anthropogenic impacts, particularly in areas where expansion and development is occurring and with limited water supplies. There is also a growing appreciation of the regional nature of residual arsenic contamination from agricultural and other anthropogenic sources such as copper and sodium-based arsenicals from herbicides and pesticides. Based on the information presented in this session, the primary natural sources of arsenic releases to the environment are: hot springs (geothermal), igneous rock (basalt), sedimentary rock (organic/inorganic clays, shale), metamorphic rock (slate), seawater, mineral deposits, and volcanoclastic materials/releases. The primary anthropogenic sources of arsenic releases to the environment include: historic mining sites, pesticide/herbicide use, combustion byproducts from burning fossil fuels, animal feeds/waste byproducts, historic wood preserving sites, medicinal uses, fertilizer use, landfill leachate, glass production, and tanneries.

Information Needs for Identifying and Characterizing Arsenic Sources and Wastes. Information is needed on anthropogenic and natural sources to identify parameters that affect treatment and to assess effects from anthropogenic constituents such as petroleum hydrocarbons from leaky pipelines. Site characterization techniques (e.g., oxidation, species concentration) and guidance are also needed for collecting and analyzing data. It may be possible to determine the source of the arsenic based on the presence of other source-specific anthropogenic chemicals/elements (tracers) or to understand the history of a pollution source by examining reservoir sediment samples, dendrochronological (tree wood) samples, and local records. Soil characterization information is needed that defines “natural” arsenic concentrations and conditions in different types of soils, and the impacts that arsenic introduction can have on different types of soil. More information is needed on arsenic mineralogy, bioavailability, leachability, and speciation, particularly for As(III) and As(V). Generic guidance is needed that can be used to help identify impacted media, characterize contamination, and assess potential impacts. Finally, information or techniques are needed which can be used to predict the future impacts of an arsenic release, including fundamental kinetics/thermodynamics.

Management of Arsenic Risks. Some of the primary conclusions from this session concerning management of arsenic risks are: 1) it is important to monitor arsenic releases and provide this information to the public; 2) the risk from an arsenic release needs to be well defined, and it is also important to differentiate real versus perceived risk; 3) during a risk characterization, the environmental effects of the arsenic release should be predicted; and 4) it is important to understand how to fix an arsenic contamination/release problem, and then monitor the performance of the selected corrective action.

There was a general consensus in this technical session that there is not enough information, either nationally or regionally, on background arsenic concentrations in soils. Since this information is very important, a national database/map is needed to address metals in soils. It is important, however, to identify criteria for collecting these samples, such as depth and the analytical method to use, before proceeding any further with this effort. There are also a number of sample libraries that could be used to develop the background information needed to assess human health and environmental impacts from arsenic. Efforts to set standards are complicated by difficulties determining the difference between "pristine" background concentrations and anthropogenic inputs after contamination has occurred. Although MCLs are used to protect human health, it is necessary to define how they relate to natural sources with high variability. Analytical methods must have low enough method detection limits (typically 10 to 20% of the MCL) to provide quantitative arsenic MCL results. The issues raised in this summary are discussed in greater detail in the Discussion Review section. As part of this discussion, important conclusions concerning the current state of the science are listed as well as recommendations and research needs for improving our technical capability to resolve arsenic source identification issues.

1.2.2 Treatment and Disposal

There was a series of 11 presentations in the arsenic treatment and disposal breakout session. Speakers from Australia and Canada as well as the U.S. provided the arsenic issues and the challenges to assess the chemical fundamentals, as well as the treatment choices that are utilized to minimize arsenic's impact on the environment.

Group discussions centered around these general questions:

1) What are the long-term stability issues with regard to land disposal (i.e., on-site storage or landfills) of arsenic stabilized wastes?
2) How do current advances (i.e., molecular chemistry, leaching mechanisms) impact the areas of arsenic treatment and disposal?

The highest priority research needs in advancing arsenic treatment and disposal were also identified.

In 1996, the U.S. demand for arsenic in market products was estimated at 22,000 metric tons, making the U.S. the world's largest consumer. Most arsenic is used in wood preservatives, but significant use also occurs in agricultural chemicals, glass production, and metal alloys. These industrial practices and metals mining and smelting operations generate arsenic-bearing wastes. In 1998, the metal mining industry managed the most arsenic waste, over 617 million pounds or 96% of the total mass of arsenic waste managed. Gold mining accounted for about 93% of the arsenic mining wastes. Several federal cleanup programs, such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and RCRA, manage the remediation of contaminated sites that may contain arsenic. Most of the detailed data are available due to the cleanup of Superfund sites.

Long-term Stability. There are a number of test methods used to predict the performance of stabilized arsenic wastes, including the TCLP, Synthetic Precipitation Leaching Procedure (SPLP), and Multiple Extraction Procedure (MEP). In California, the Waste Extraction Test (WET) is used. There are issues with all of these test methods that make it difficult to predict the effects of time on the stability of treated wastes. Although EPA requires the use of TCLP for predicting the performance of stabilized arsenic wastes in a landfill, several concerns have been raised about the ability of this method to predict long-term stability. In addition, the other methods give different kinds of performance results and are not truly comparable between sites. Models that predict thermodynamic and kinetic variables can also be used to simulate long-term conditions and determine treated arsenic waste stability. The disposal environment of the waste must also be considered. For example, avoid placing wastes in saturated zones, and utilize capping materials to protect waste and minimize contact with leaching agents.

Current Advances. In research and development, advances in techniques and instrumentation have allowed for greater site investigation. For example, X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) often provide a better understanding of a material's microstructure. However, these advances have not yet transferred into field performance specifications. Researchers are investigating the toxicity of different arsenic forms such as As(III) and As(V). This research may result in developing different regulations for different species of arsenic.

Research Needs. Important research needs for arsenic treatment and disposal are: 1) improved understanding of long-term stability and protocols for simulating long-term conditions and performance, 2) improved understanding of waste chemistry, speciation, and biogeochemistry, 3) improved understanding of waste microstructure and mineralogy,

4) evaluation of biological processes (bacteria, fungi, plants) on arsenic mobilization, and 5) improved understanding of arsenic toxicity issues.

The change in the arsenic MCL from 50 ppb to 10 ppb could prompt EPA to change the required treatment standard to a value that is at or below the current TCLP regulatory level of 5 mg/L. If this is the case, then it is important to assess whether or not the current array of treatment options could achieve the potentially more stringent treatment requirements. However, treating high-concentration arsenic wastes is difficult and treatment costs associated with these technologies can be high. The key question is: are the high treatment costs justified by the incremental reduction in potential risk associated with arsenic in treated wastes? The issues raised in this summary are discussed in greater detail in the Discussion Review section. As part of this discussion, important conclusions concerning the current state of the science are listed as well as recommendations and research needs for improving our technical capability to resolve arsenic waste treatment and disposal issues.

1.2.3 Arsenic Chemistry

The basis for the reliable prediction of arsenic mobility and treatment in subsurface systems is dependent on an adequate understanding of the chemical processes that control arsenic partitioning between the aqueous and solid phase. While significant effort has been expended to study the factors controlling arsenic fate and transport in environmental systems, the ability to predict arsenic mobility and exposure in a regional or ecosystem context is still inadequate. This inadequacy derives both from an incomplete compilation of the necessary chemical information and the application of inappropriate methods to collect these data. The goal of this session was thus to task a panel of experts to establish the current state of knowledge and to identify future areas of research and the most reliable pathways to fill existing data gaps.

Group discussions centered around three general questions:

1) Is our knowledge of arsenic speciation and transformation adequate to identify pathways and routes of mobility?
2) Are current collection, preservation, and analytical techniques sufficient for defining arsenic chemistry in natural and engineered systems?
3) Are existing leaching procedures adequate for characterization of arsenic-bearing waste materials?

Arsenic Mobility. Since arsenic is a redox-sensitive element, its chemical speciation is dependent on changes in system redox parameters that are driven by biotic and abiotic processes. The mobility of arsenic is tied to the cycling of major elements such as carbon, iron, and sulfur between the solution and solid phase in natural and engineered systems. While there is generally a sound phenomenological understanding of arsenic mobility, the ability to provide a quantitative assessment is limited. This limitation is due, in part, to the complexities of coupling chemical and hydrodynamic models in complex heterogeneous systems. This limitation is compounded by the existence of knowledge gaps, including: 1) coupling of arsenic chemical speciation to the cycling of redox-sensitive nutrients such as nitrogen, 2) knowledge of aqueous arsenic speciation in anoxic environments, 3) protocols for applying sorption models to describe arsenic solid phase partitioning, and 4) predictive tools and modeling approaches to describe the influence of microbial activity on arsenic mobility.

Analytical Tools. In general, existing analytical tools are satisfactory for quantification of arsenic chemistry in aqueous systems. However, attempts to apply these tools in a uniform manner for evaluation of all sample matrices are problematic. A matrix was developed to point out the strengths and limitations of the various analytical tools, and this information can be used as a guide for developing the most appropriate analytical protocol on a site- or case-specific basis. This limitation also applies to attempts to apply a single technique for preservation of arsenic chemistry prior to analysis. While there was agreement that filtration, acidification, and light exclusion are generally adequate for preservation of most aqueous samples, this approach must be validated and modified as required to achieve desired site-specific data quality objectives.

Waste Form Characterization. Leach tests have been developed to provide guidance as to the stability of solid waste forms prior to or following land disposal. Limitations have been identified for the application of existing test procedures for evaluation of arsenic stability (or mobilization potential) in waste solids. In particular, research indicates that the TCLP provides results that do not reflect the in-situ leaching behavior of arsenic for municipal solid waste. Design of leach tests should be governed both by the application of the test results and/or the in-situ chemistry anticipated for the disposal environment. For example, tests designed to assess differences in treatment process effectiveness may differ from those employed to assess the post-disposal leach potential of a solid waste form. Assessment of in-situ leach potential should focus on critical geochemical parameters that are characteristic for the disposal environment.

A re-occurring theme for all of the topics addressed in this session was that a degree of flexibility is required for application of the knowledge and tools employed to resolve arsenic waste problems. The complexity of arsenic chemistry is sufficiently high to preclude rigid protocols for site assessment and waste characterization. The issues raised in this summary are discussed in greater detail in the Discussion Review section. As part of this discussion, important conclusions concerning the current state of the science are listed as well as recommendations and research needs for improving our technical capability to resolve arsenic waste chemistry issues.

2.0 Plenary Session

The following extended abstracts are provided for the oral presentations made by invited speakers during Day One of the Workshop, Plenary Session. Speakers were selected by the Steering Committee, and the topics were intended to provide some foundation for subsequent discussions that occurred both formally and informally during the balance of the Workshop. The Plenary Session presentations covered a range of arsenic topics from regulatory to scientific issues. EPA researchers discussed the ORD and OSW perspectives on contamination issues, treatment efforts, treatment standards, and testing issues. Other EPA topics included arsenic sources, research on microbial activity, and the Toxics Release Inventory (TRI). Other researchers discussed arsenic issues for mining, groundwater and drinking water, and arsenic geochemistry, leaching, and treatment options.

Additional oral presentations were made on Day Two during the Breakout Sessions. These presentations were intended to complement the session topics and provide a basis for discussion for each session. The extended abstracts for these oral presentations are presented in Section 3.0, Breakout Sessions.

It should be noted that the abstracts were not part of the formal peer-review process which the remainder of this document underwent, and may represent opinions or personal points of view in some cases. Any references cited in the abstracts are the responsibility of the authors.

Presentation materials (visuals) for the Plenary Session and Breakout Session speakers are not included in this Proceedings document, only abstracts. A few speakers did not prepare abstracts, only presentation materials. However, speaker presentation materials can be viewed online at the EPA Technology Transfer website. The website address for these materials is www.epa.gov/ttbnrmrl/arsenictech.htm. Or, for further information regarding this Technology Transfer product, please contact Doug Grosse via email at: grosse.douglas@epa.gov.

The Current Status of Arsenic Research in the U.S. EPA's Office of Research and Development

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Notice

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's (EPA's) peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abstract

The mission of EPA's Office of Research and Development (ORD) is "to conduct leading-edge research and foster the sound use of science and technology in fulfilling EPA's mission to protect human health and safeguard the natural environment" (USEPA, 2001). ORD researchers have examined how metabolic processes affect arsenic (As) speciation in humans as well as carcinogenic effects of As (USEPA, 1999). An epidemiological study conducted by ORD researchers in Utah, regarding long-term exposure to As in drinking water, has provided essential data to compare with studies concerning non-US populations (Smith et al., 1992; Nickson et al., 1998; Karim, 2000). Other studies have been initiated by ORD scientists and engineers examining As treatment and management in solid wastes and soils. This abstract will briefly discuss the current status of As research within ORD.

Drinking Water Issues

EPA recently decreased the maximum contaminant level (MCL) for As in drinking water from 50 mg/L to 10 mg/L. Two significant issues arise from the lowering of the arsenic MCL in drinking water. The first issue concerns improvement of existing water treatment methods for water treatment plants (WTPs) to cost-effectively meet the new arsenic MCLs. Researchers in ORD's National Risk Management Research Laboratory (NRMRL) address this issue by coordinating studies on chemical and physical removal of As from water. One study found that the removal of natural iron significantly reduced soluble As (USEPA, 2000a). Another study examined WTPs that employed ion exchange and activated alumina systems. Both systems were found capable of reducing arsenic concentrations from 50 to 70 μg/L to 5 μg/L providing that proper media regeneration (or change-out of exhausted media) was followed (USEPA, 2000b). A third study analyzed the long-term performance of two coagulation/filtration plants and a lime softening plant (USEPA, 2000c). The coagulation/filtration plants consistently achieved low levels of As in treated water (< 5 μg/L). The study suggested that the primary mechanism of As removal was by co-precipitation with metal hydroxides. The lime softening plant did not consistently reduce As levels in treated water to low levels. This study determined that As removal from the water was low because of competition for binding sites by carbonate species and/or pH effects. The second significant issue that would result from reducing the As MCL in drinking water concerns As in WTP residuals. Research funded by NRMRL has provided fundamental data describing As in residuals from water treatment processes (USEPA, 2000d). This research compares As concentrations in residuals from five different water treatment processes and also illustrates some differences in state policies concerning disposal of As containing residuals.

Closely tied with NRMRL's research on drinking water issues is research that is currently underway in ORD's National Exposure Research Laboratory (NERL). NERL is currently working on methods for preserving As species in drinking water samples and the development of As speciation methodologies for separation of arsenite and arsenate. This work provides data to support water treatment decisions in utilities affected by changes in the As MCL. NERL researchers are also developing analytical methods for As speciation analysis in foods (e.g., seafood) and urine. NERL works in conjunction with the Food and Drug Administration (FDA) on projects that examine methods for speciation of As in daily diets. This work will aid in assessing risk of As exposure associated with diet. On-going NERL research will examine the bioavailability of As species in water, soils, and food constituents (USEPA, 1998).

Health and Toxicological Issues

ORD's National Health and Environmental Effects Research Laboratory (NHEERL) currently conducts research that can be broadly divided into three categories: 1) mechanisms/modes of As as a carcinogen and toxicant; 2) biomarkers and population studies; and 3) modifiers of susceptibility to toxic and carcinogenic effects. Research performed by the NHEERL on the mechanisms and modes of As toxicity has provided critical insight concerning the nature of As toxicity.

For example, NHEERL researchers have shown that methylated trivalent arsenicals appear to be direct-acting genotoxicants, which distinguishes them from other forms of As previously studied (Mass et al., 2001). Research conducted in the area of mechanisms and modes of As toxicity include biomethylation effects, interspecies (rat, mouse, guinea pig, human) comparisons of As carcinogenicity, uptake and fate in living organisms, and protein binding and effects on human cell DNA methylation. Work on biomarkers and population studies include epidemiological studies on human exposure to As, both in the US and abroad, and identification of biomarkers (e.g., heme oxygenase and urinary porphyrins) that could adequately indicate exposure to As species. NHEERL conducts leading-edge research in the area of As susceptibility modifiers. Studies into the characterization and behavior of the enzyme human As methyltransferase will lead to a better understanding of the ability for human populations to develop resistance to As toxicity. Research on modifiers of As behavior in organisms also includes studies on heat shock proteins, selenium and dietary folate deficiencies.

ORD's National Center for Environmental Assessment (NCEA) focuses on human health issues and works in conjunction with NHEERL to advance our understanding of As related exposure and risk assessment. Current NCEA activities include assessment of chronic As exposure from drinking water sources and the effects of As exposure on human reproduction. This long-term study examines data from exposed and control populations in Chile (Hopenhayn-Rich, et al., 2000). The NCEA works closely with the National Cancer Institute and the National Institute of Environmental Health Sciences in the establishment and maintenance of the International Tissue and Tumor Repository on Chronic Arsenosis. This repository holds tissues and fluids from cases of As poisoning and environmental samples (e.g., coal). The repository also safeguards data and literature and develops databases for protocols and methods of specimen handling, storage, transportation and analysis.

Groundwater Issues

NRMRL's Subsurface Protection and Remediation Division (SPRD) leads research pertaining to groundwater issues. Though inextricably linked with solid waste and soil, groundwater will be considered separately here. The SPRD currently conducts research regarding As mobilization in groundwater, oxidation-reduction reactions of As species in groundwater, and remediation of As contaminated groundwater. SPRD researchers perform these studies in both the laboratory and field. For example, work evaluating permeable reactive barriers (PRBs) will examine the efficacy of this remediation technique on As removal (and other contaminants) from groundwater. Pilot-scale PRB studies will be used to identify effective reactant media for successful, long-term uptake of inorganic contaminants, examine metal uptake mechanisms, and evaluate barrier longevity and long-term PRB stability.

Solid Waste/Soil Issues

SPRD also provides essential research in the area of subsurface As fate and transport issues. Research includes attenuation/stabilization of As on solid phases in soil/vadose zone systems, measurement procedures and protocols for sampling of soils for As studies, and geochemical controls on As speciation in soils. In addition to studies in oxic environments, research regarding the fate and transport of As in anoxic systems is underway in the SPRD. Laboratory studies will provide key data for identification of mechanisms and rates of As sorption/precipitation reactions in sulfidic media. This work will provide a better understanding of As behavior in anoxic systems and lead to improved practices for field monitoring in these geochemically complex systems.

The Land Remediation and Pollution Control Division (LRPCD) works in conjunction with the SPRD on As soils/solid waste issues. Researchers in the LRPCD are currently researching As source contamination issues. These studies will focus on As contamination of solids (soils, mine tailings, sediments) from agricultural sources, mine wastes and treated lumber sources. The researchers will examine desorption of As from solids (effects of pH and dissolved organic matter), solution speciation, and As bonding at the molecular level. Research will also be carried out by LRPCD in the application of thermodynamic theories to leaching studies in order to better characterize specific scenarios and provide more focused direction on methods to minimize As mobilization. Other projects include work on As leaching from mineral processing waste (MPW). The researchers will examine several leaching methods on MPW and compare these data with that from the toxicity characteristic leachate procedure (TCLP- EPA Method 1311). These engineers and scientists will also examine the relationships between leachate chemistry data and TCLP data from landfills.

Risk Management

NRMRL's Technology Transfer and Support Division (TTSD) provides a cohesive, cooperative environment where experts in specific fields can meet and formulate Risk Management Evaluations (RMEs). RMEs play a crucial role in providing a balanced approach to policy formulation and regulation based on sound science and engineering research. Findings from ORD's research activities combined with other important aspects such as cost-of-compliance issues and health/economic benefits from risk reduction aid in focusing future research efforts within the ORD.

In addition to the projects mentioned previously, ORD strives to work closely with EPA regional offices. This ensures that certain aspects of research projects focus on site-specific issues. By working closely with regional offices, ORD aids in addressing immediate, site-specific needs while gaining fundamental knowledge for contribution to our understanding of As and its effects on human health and the environment.

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Arsenic Cycling in the Mining Environment

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Occurrence of Arsenic in a Metal Mine

Over 200 As-containing minerals have been identified in nature. Of these 60% are arsenates, 20% sulfides and sulfosalts, 10% are oxides, and the remainder are arsenides, native elements and metal alloys. Arsenic naturally occurs in chalcophile hydrothermal mineral deposits and is more rarely associated with volcanic or magmatic rocks. Rare arsenic phases are also known to occur in fumaroles and geothermal systems. Occasionally arsenic can also occur associated with sedimentary pyrite in sedimentary rocks and in this environment has been considered to be the source for anomalous concentrations of arsenic in drinking water in Wisconsin, Maine and Bangledesh. Within the United States the largest occurrences of arsenic minerals occur associated with the Carlin-type mines of northern Nevada in the form of realgar (AsS), orpiment (As_2S_3) and arsenic-bearing pyrite (up to 5wt%,) and the rare mineral, Galkhaite, a complex sulfosalt with the chemistry ($[Cs,Tl][Hg,Cu,Zn]_6[As,Sb]_4S_{12}$) which also occurs in the belt at the Getchell mine. Within Carlin ores, the arsenic minerals are intimately associated with the ore elements or adjacent host rock.

The most common arsenic mineral, globally, is arsenopyrite. Arsenopyrite is common in many vein gold deposits, such as those of Yellowknife, Canada or Homestake, South Dakota. It also occurs in granite hosted Cu-Sn veins such as those of Cornwall, England.

Arsenic has long been used as an excellent “pathfinder element” because of its low abundance in most rock types and concentration in hydrothermal deposits, as well as its generally low mobility. This coupled with sensitive analytical protocols by conventional methods makes the element extremely useful in mineral exploration. For example, the average concentration of As in hydrothermal ore deposits ranges from 500 ppm up to 10-wt% of an ore or altered host rock. In unmineralized rocks the average concentration is less than 10 ppm, but can be up to 20 ppm in argillaceous sediments.

Release of Arsenic In a Mine Site

Mining does not produce arsenic although it can be liberated when exposed to conditions in which the primary host mineral is unstable and thus oxidises or weathers, for example when placed on a heap or waste rock dump. Alternatively when an As-hosting ore is chemically treated prior to liberation of the ore element such as during smelting, the arsenic mineral may also be liberated from its matrix and in this form become mobile.

The concentration of arsenic liberated from such reactions is dependent on several factors:

- Total concentration available; this in turn is related to geology of the original hydrothermal deposit.
- The Eh-pH regime of the environment in which the arsenic is liberated.
- The chemistry of natural waters in promoting release or attenuation of arsenic.

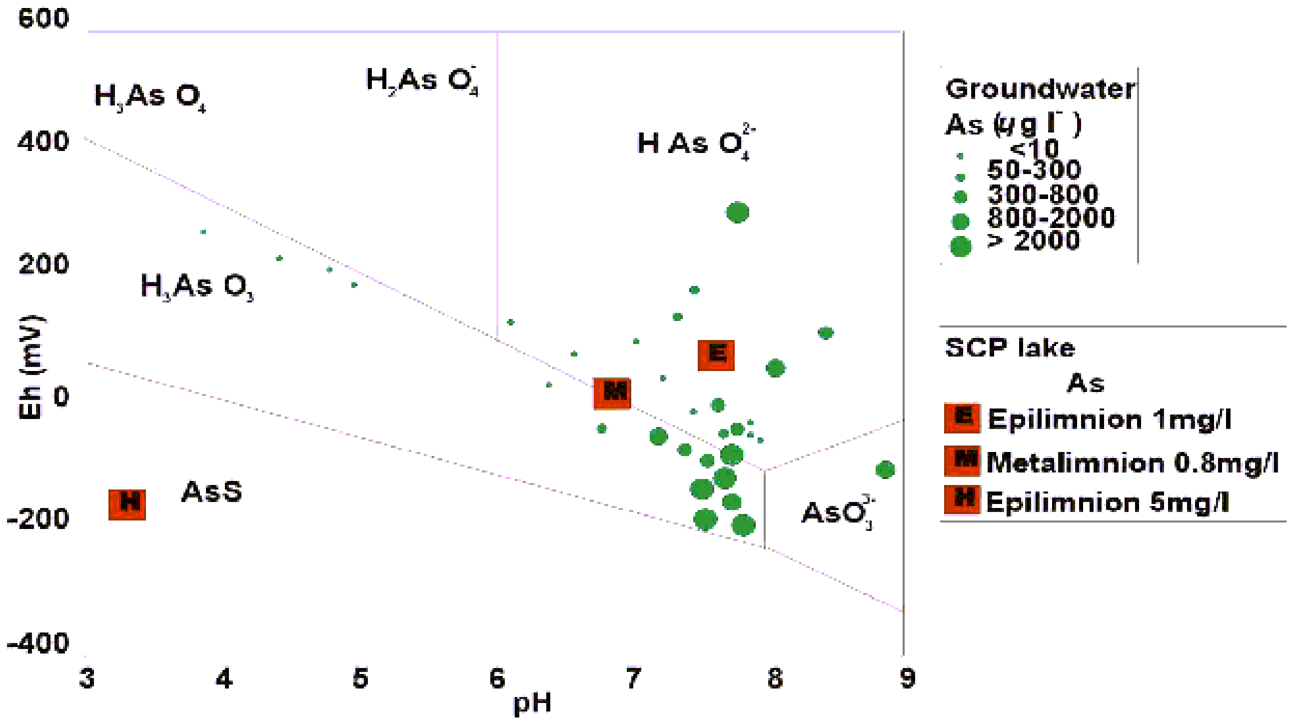
The total amount of arsenic available is entirely dependent on the proportion of arsenic minerals available in the deposit. So for example, for a volcanogenic massive sulfide, high sulfide-gold deposit, or a Carlin deposit, high concentrations of arsenic would be anticipated.

Control on the release of this arsenic is then dependent on environmental conditions. Typically in very acidic environments, for example those of Iron Mountain in California, arsenic mobility would be high. Equally, in high pH environments high arsenic mobility would be anticipated as the major control would be adsorption onto mineral phases, and this would be predicted to be low at higher pH for arsenic oxyanions. Within ambient systems arsenic can occur as arsenate ($H_nAsO_4^{3-n}$) or arsenite ($H_nAsO_3^{3-n}$) complexes or in the presence of methylating agents as Monomethylarsonic acid (MMAA) or Dimethylarsinic acid (DMAA).

Over the natural pH range of most soils and waters the principal species of As (V) is $H_2AsO_4^{2-}$ and of As (III) is H_3AsO_3, of which the reduced form is the more mobile. For example, the speciation of arsenic in the principal reactions retaining arsenic in soil, sediment and water are in acidic solutions, adsorption by ferric oxyhydroxides and to a lesser extent Al-Mn oxides, clays and organic matter, and in alkaline solutions co-precipitation of As as arsenate and arsenite salts.

However, the rate of change in the oxidation state of arsenic is not rapid, so the predicted proportions of arsenic species based on thermodynamic calculations do not always correspond to actual analytical results.

Due to the strong adsorption effect exerted on As in mildly acidic soils, As uptake by plants tends only to be significant in alkaline soils or where extremely high As levels (>10000 mg/kg As) occur in the substrate.



GROUNDWATER ARSENIC CONCENTRATION
FROM GETCHELL ON Eh - pH DIAGRAM

In the Bau area of Sarawak, Malaysia, high As levels in the soil (15-50000 mg/kg As) coupled with an alkaline soil pH (7.5-8.4) has led to high As uptake in bamboo species (up to 4500 mg/kg in roots and 2650 mg/kg in leaves). In the Kelly Basin in northern Nevada, Great Basin Sagebrush shows a similar tolerance and uptake of arsenic that is precipitated out as oxide phases within the vascular part of the plant.

Options for the Control of Arsenic Dispersion

The metals industry is faced with the necessity of disposing of waste material in an *environmentally safe manner*. Over the last two decades significant advances have been made in the design of waste facilities, and in stabilization and treatment of mining effluents.

Arsenic waste disposal generally involves one of four options:

- Physical stabilization through the use of engineered disposal facilities and institutional controls
- Chemical stabilization of arsenic containing waste
- Chemical treatment of effluents to produce saleable products, such as white arsenic oxides by the El Indio or Warox processes or production of an insoluble arsenate such as ferric arsenate
- Chemical stabilization of the arsenic waste by fixing it within an inert material such as cement, slags or silica material

Currently all options are utilised in the mining industry, and all will be illustrated with examples of use. Future application of such technologies will be discussed in terms of key parameters of cost, environmental stability of products and risks associated with each.

Arsenic in Groundwaters of the United States

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The U.S. Geological Survey has collected and analyzed arsenic in potable (drinkable) water from 18,850 wells in 595 counties across the U.S. during the past two decades. These wells are used for irrigation, industrial purposes, and research, as well as for public and private water supplies. Arsenic concentrations in samples from these wells have been shown to be similar to those found in source waters for nearby public supplies. Arsenic concentrations in groundwater are generally highest in the West. Parts of the Midwest and Northeast also have arsenic concentrations that exceed 10 μg/L, the World Health Organization's provisional guideline for arsenic in drinking water. Arsenic concentrations appear to be generally lowest in the Southeast. The large number of samples, broad geographic coverage, and consistency of methods produce an accurate and detailed picture of arsenic concentrations across the U.S.

Managing Arsenic Occurrence Information in Drinking Water

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With the advent of the new Drinking Water maximum contaminant level (MCL) for arsenic set at 10 μg/L on January 22, 2001, many states are reviewing their drinking water data for compliance with the new rule. The State of Utah has had a computerized water quality database since 1978. This flat file format was gradually changed to a multiple-table relational database in the mid 1990s. This new database linked an inventory of public water supply sources with global positioning system (GPS) locations, source production, and other data. This data was exported to Microsoft Access in the mid-90s and used to summarize arsenic occurrence in Utah. Detection limits have varied from certified laboratories submitting data since 1978, but an attempt was made to review all available data for each potentially regulated drinking water source under the new rule. Data which obviously did not agree with subsequent analyses results were flagged for exclusion. The remaining data were counted for the number of measurements made, averaged, and a standard deviation of arsenic concentration for each source was computed. This approach allows a confident statement of arsenic concentration where the data allow. Fifty water systems in Utah will need to provide treatment or dilution for eighty sources to meet the new arsenic MCL by 2006. A statewide "compliance" list has been developed to begin working with systems needing treatment. Utah's system, the findings produced from using it thus far, and management of this occurrence information will be presented as a possible model for use by others.

Arsenic Hazardous and Remediation Waste: Sources and Treatment

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Introduction

In 1996 U.S. demand for arsenic was estimated at 22,000 metric tons, making the U.S. the world's largest consumer of arsenic (USEPA, 2001a). Most arsenic is used in wood preservatives, but significant use also occurs in agricultural chemicals, glass production, and metal alloys. These industrial practices, and metals mining and smelting operations, generate arsenic-bearing waste. In addition, past waste disposal practices have resulted in sites containing arsenic-contaminated soil, groundwater, and other media that may pose a risk to human health and the environment. Many additional sites contain naturally-occurring arsenic that may impact drinking water supplies.

Arsenic, especially inorganic forms, is very toxic and a known carcinogen (ATSDR, 1993). The chemical nature of arsenic compounds, in particular their tendency to change valence or chemical form, makes it difficult to assess their fate and mobility in the environment, and to immobilize arsenic effectively for ultimate disposal. Even wastes that have been treated to existing federal standards are found to leach out of landfilled waste (USEPA, 2000d). To support the future study of these and other arsenic-related issues, this paper presents the current state of arsenic waste generation and management. It summarizes the sources and estimated quantities of arsenic industrial and remediation wastes, regulatory treatment standards, and treatment technologies currently used.

Arsenic Industrial Applications

Arsenic metals and compounds have not been produced domestically since 1986. The U.S. imports arsenic primarily from China, Chile, and Mexico at about 30¢ per pound. Of the total 22,000 metric tons of arsenic imported in 1996, almost 20,000 metric tons of arsenic were used in wood preservatives, followed by 1,100 metric tons in agricultural chemicals, 440 metric tons in glass production, and 440 metric tons in metal alloys. The most common wood preservative is chromated copper arsenate (CCA), used at 88% of wood preserving facilities. Agricultural applications of arsenic compounds include feed additives, animal dips, and herbicides. Arsenic metal is consumed in the manufacture of nonferrous alloys, principally lead alloys for use in lead-acid batteries. Small amounts are also found in alloys used in other applications, such as bearings, lead ammunition, and solders. Other uses include electronics and semiconductors, pyrotechnics, and antifouling paints (USEPA, 2001a).

Sources and Quantities of Arsenic Waste

Hazardous Waste

Hazardous waste in the U.S. is regulated under the Resource Conservation and Recovery Act (RCRA). For 29 listed hazardous wastes, EPA has identified arsenic as a hazardous constituent, or has established a land disposal restriction (LDR) standard. Arsenic is also a characteristic waste. A hazardous waste exhibits the toxicity characteristic for arsenic if the arsenic concentration is greater than 5 mg/l when analyzed using the Toxicity Characteristic Leaching Procedure (TCLP). Wastes are listed for arsenic if the arsenic poses a risk; its concentration does not have to exceed 5 mg/l TCLP. Also, there are often higher-concentration constituents present in the waste.

The EPA Biennial Report System (BRS) contains information reported by hazardous waste large quantity generators, and by treatment, storage, and disposal (TSD) facilities. An analysis of BRS data submitted for 1997 was conducted for the 29 hazardous waste codes that can contain arsenic, and for arsenic characteristic waste. For this analysis the conservative assumption was that all of the waste generated in each waste code contained arsenic. In 1997 industry generated a total of 519 million short tons of wastewaters (USEPA, 2000b). Of this total, 55 million tons (11%) can contain arsenic. (One photographic facility accounts for 40 million tons.) The largest generators of arsenic wastewaters are the photographic (74%), plastics (12%), and organic chemicals (9%) industries. Half of this waste is in the form of multi-source leachate, which has over 200 regulated constituents, including arsenic. The analysis includes all of the data submitted, including wastewaters managed in systems that are not RCRA-permitted; these wastes are not included in the national BRS numbers.

In 1997 industry generated 15 million tons of hazardous nonwastewaters. Of this 4 million tons (27%) can contain arsenic. The largest generators are organic chemicals (23% of 4 million tons); steel and iron works (20%); aircraft parts/equipment

(10%); commercial hazardous waste management (13%); national security (i.e., metals, ammunition, explosives) (10%); and copper smelting/refining (7%). The most common forms of these wastes are solvent mixtures (27%), ash and slag (20%), and other waste inorganic solids (12%).

Non-hazardous Waste

The EPA's Toxic Release Inventory (TRI) tracks toxic chemicals manufactured and used at facilities nationally, and amounts of chemicals released and managed on- and off-site. Both hazardous and nonhazardous waste are reported; however, RCRA-exempt (i.e., nonhazardous) waste from the metal mining industry accounts for the vast majority of the arsenic releases reported. The TRI considers arsenic and arsenic compounds to be metals; only the metal portion of the metal compound is considered in TRI calculations, and quantities are reported by mass, not volume.

Arsenic wastes are generated from mining and smelting operations, particularly those involving copper, silver, and gold. Because of the large volume of rock that must be moved as part of the mining operations, even low concentrations of naturally-occurring arsenic that may be present will yield very large TRI reported quantities. Most of the reported metals remain in the waste rock that is returned to the land at mine sites or returned underground as backfill. In 1998 the metal mining industry managed most arsenic waste, over 617 million pounds, or 96% of the total mass of arsenic waste managed (643 million pounds)(USEPA, 2000c). Gold mining accounts for 93% of the arsenic mining waste, followed by copper ores (4%) and silver (3%). Lead, zinc, and iron mining wastes, combined, make up less than 1% of the total.

The other top industries managing arsenic waste are the primary metals industry, 11 million pounds (17% of total arsenic managed); electric utilities, 7 million pounds (1%); and RCRA/solvent recovery, 6 million pounds (1%).

Remediation Waste

Several cleanup programs manage the remediation of contaminated sites that may contain arsenic, including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, also known as Superfund), RCRA corrective action, and the Departments of Energy (DOE) and Defense (DOD). The most detailed data available concern Superfund sites:

1) Almost half (48%) of the1500 Superfund National Priorities List (NPL) sites have arsenic as a contaminant of concern that must be addressed. These data are extrapolated from an analysis of 1177 NPL sites with Records of Decision (RODs) through fiscal year 1998 (USEPA, 2000a). By comparison, lead is of concern at half of NPL sites.
2) For media, 32% of NPL sites have arsenic in groundwater, 32% in soil, and 13% in sediment.
3) Activities at NPL sites with arsenic include wood preserving, municipal and industrial landfills, metal ore mining and smelting, machine shops, battery recycling/disposal, and pesticide/herbicide manufacturing and use.

In addition, about 5% of 137 DOE installations and other DOE cleanup locations, or about 500 sites, contain arsenic. An estimated 20% of RCRA facilities contain arsenic in groundwater, and 13% in soil (USEPA, 1996). Data on DOD sites are not available; however, it is expected that a large number of sites contain arsenic from machine shops, ammunition, and explosives.

Treatment of Arsenic Waste

The chemical nature of arsenic compounds makes them difficult to treat effectively. Arsenic is a semi-metallic element and is labile, readily changing chemical form in the environment (and in waste treatment processes). Arsenic mobility is affected by environmental conditions including acid-base equilibria and overall pH; oxidation-reduction potential and electron activity; the presence of complexing cations and anions (such as sulfides, calcium, and iron); and adsorption/desorption reactions. (USEPA, 2001a)

Arsenic can be readily precipitated from aqueous waste (including As-generated waste and groundwater) if the form of the arsenic and other waste characteristics are considered. Oxidation of arsenic to its less soluble As^{+5} state can increase the effectiveness of precipitation. Ion exchange, carbon adsorption, and membrane filtration are also used. According to the 1997 BRS, 240,000 tons of aqueous hazardous waste can contain arsenic and are managed offsite. The treatment methods used are chemical precipitation (31% of the aqueous waste), other aqueous organic treatment (8%), and incineration of solids or liquids (13%) (USEPA, 2000b).

Of the 1.84 million tons of nonaqueous arsenic hazardous waste managed offsite, 400,000 tons (22%) are treated via stabilization/chemical fixation using cement or pozzolans. Thermal technologies (incineration, energy recovery, or fuel blending) are used for 36% of the wastes, most likely to address the organic fraction of the waste. An additional 11% are subjected to recovery technologies (high temperature metals recovery or secondary smelting), but these data do not indicate whether arsenic is being recovered.

EPA tracks the application of cleanup technologies, primarily at Superfund sites (USEPA, 2001b). Based on this information, stabilization is the most common technology for disposing of nonaqueous remediation waste containing arsenic. At least 45 NPL sites are using stabilization to treat arsenic-contaminated soil, sediments, sludge, and other solids. Cement, lime, and phosphate are the most common stabilization binders used at these sites. Other technologies used at contaminated sites include: soil washing (6 sites), chemical treatment (4), acid extraction with hydrochloric acid (2), in situ soil flushing (2), vitrification (3), and electrical separation (1). Chemical treatment agents used include a combination of ferrous iron/lime/potassium permanganate, oxygenated water with an iron catalyst, and phosphate.

Groundwater contaminated with arsenic usually contains other contaminants, such as chromium or pentachlorophenol, and other wood treating chemicals. Pump-and-treat is typically used to remediate groundwater at these sites. Data are available on nine sites applying pump-and-treat for arsenic-contaminated groundwater. Filtration, carbon adsorption, and chemical precipitation are commonly used to remove both the inorganic and organic groundwater contaminants. A permeable reactive barrier has been installed at two Superfund sites (Monticello Mine Tailings, UT and Tonolli Site, PA) to treat groundwater contaminated with arsenic and metals (USEPA, 2001b; Remediation Technologies Development Forum, 2000).

The RCRA LDRs specify the technologies or treatment levels that must be achieved prior to land disposal of hazardous wastes. The LDR treatment standard for arsenic in wastewater is 1.4 mg/l, based on the performance achievable by chemical precipitation. The standard for nonwastewaters is 5 mg/l as measured by the TCLP, based on slag vitrification of wastes up to almost 25% arsenic. Any technology that is not defined as impermissable dilution under RCRA can be used to achieve these standards. In evaluating arsenic treatment performance, EPA had inconclusive performance data for stabilization of arsenic in three different wastes using nine different binders. EPA found that the effectiveness of any particular stabilization binder appeared to be highly dependent upon the waste type (USEPA, 1990). However, based on the BRS and remediation data, stabilization appears to be the treatment of choice for arsenic in nonaqueous waste, and the technology can meet the 5 mg/l TCLP standard (USEPA, 2001a; USEPA, 2000b; USEPA, 2001b).

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Treatment Options for Arsenic Wastes

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Since recycling of arsenic-containing materials is technically challenging and cost prohibitive, there is a great demand for the development of effective treatment technologies for the safe disposal of arsenic-contaminated hazardous wastes. The industrial use of arsenic has been curtailed in recent times; however, historic operations have led to significant contamination at some industrial sites where arsenic compounds were previously used to produce pesticides, herbicides, or veterinary pharmaceuticals. Current uses of arsenic are more limited and include the use of chromated copper arsenate for wood-preserving operations and the use of gallium arsenide in the development of semiconductor material for the electronics industry. In addition, mining operations often involve the smelting of ores with high arsenic concentrations.

Currently, arsenic contaminated hazardous wastes are subject to land disposal restrictions under the Resource Conservation and Recovery Act (RCRA) and must be treated to meet toxicity characteristic leaching procedure (TCLP) limits. A RCRA hazardous waste is defined as a waste that produces an extract containing more than 100 times the maximum contaminant level (MCL) in drinking water for that specific chemical. The MCL for arsenic (50 μg/L) was recently subjected to critical review due to concerns about a potential association between long-term exposure to arsenic and serious health problems such as skin and internal cancers and cardiovascular and neurological effects. As a result of these concerns, and after further review of the relevant scientific data by the U.S. Environmental Protection Agency (EPA), a change in the arsenic MCL from 50 to 10 μg/L was promulgated.

Due to these potential changes, there is a need to investigate the impact that a revised rule would have on the treatment and disposal of arsenic-contaminated hazardous wastes under the RCRA program. This presentation assumes that, if EPA changes the TCLP regulatory level, it would also change the required treatment standard (40 CFR 268.40 and 268.48) to a value that is at or below the TCLP regulatory level. It is important to perform an assessment of whether or not the current array of treatment options, both innovative and conventional, will be able to achieve the potentially more stringent treatment requirements.

Due to the existence of alternate treatment standards for soils (40 CFR 268.49), the potential changes to the TCLP limit should not have a major effect on the treatment and disposal of arsenic-contaminated soils. However, the potential changes would alter the treatment cap for soils and the definition of RCRA hazardous waste for arsenic (D004). With these changes, more soils would be considered hazardous than at the current TCLP regulatory level. The existing alternate treatment standards for soil should minimize the impact of any MCL or TCLP revisions. In setting the alternate treatment standards, EPA already reviewed and compiled treatability data to determine cost-effectively achievable treatment goals for arsenic-contaminated soils. Thus, this presentation focuses primarily on arsenic-contaminated wastes, but will briefly review recent innovations in soil treatment technologies.

As an inorganic constituent, arsenic cannot be destroyed, but it can be converted into less soluble or leachable forms to inhibit migration into the environment and subsequent exposure by sensitive receptors. Vitrification was selected by EPA as the Best Demonstrated Achievable Technology (BDAT) for characteristic and listed wastes containing arsenic including D004, K031, K084, K101, K102, P10-12, P36, P38, and U36. Vitrification involves the use of a plasma torch, an electrical current, or other heat source to melt the contaminated material into a glass matrix at extremely high temperatures ranging from 2,900 to 3,650°F. The vitrified material is non-porous, has a high strength, and is much more resistant to leaching than the original feed materials. Although vitrification, as BDAT, would be considered the “conventional” approach to treatment, it is not widely used and has been selected as a treatment option for arsenic-contaminated waste at only one out of twelve Superfund sites identified. The remaining sites with arsenic-impacted soil or other wastes had Record of Decision (ROD) selected remedies that included solidification/stabilization (6), containment/capping (4), and soil washing (1). Vitrification is not used extensively for the following reasons: 1) the cost is prohibitive since the process requires complex, capital-intensive equipment; 2) wastes with elevated moisture content, high metal content, and/or inappropriate physical characteristics may be more expensive or difficult to treat; and 3) significant volatile losses of arsenic can occur unless the waste is properly pre-treated to produce less volatile forms of arsenic.

There are several other treatment options for arsenic-contaminated wastes, including the most commonly applied technology, solidification/stabilization (S/S) with cement, fly ash, sodium silicates, or other binders. S/S relies upon mobility reduction, resulting from a combination of physical entrapment (e.g., encapsulation) and chemical reaction (e.g., precipitation) mechanisms. Cement, silicate, and other S/S binder materials were evaluated by EPA, but not accepted as BDAT for arsenic wastes due to concerns about long-term stability and waste volume increases. However, EPA did not preclude the use of S/S methods for the treatment of arsenic wastes, but instead recommended site-specific treatability studies. Several studies have demonstrated that S/S can be successfully implemented for the treatment of arsenic-contaminated wastes, if pre-treatment methods are employed first to transform arsenic into the appropriate oxidation stage or species and then to decrease the solubility or availability of the arsenic compounds in the solid matrix prior to binding. The following is a list of alternate or innovative treatment technologies that can be applied to treat arsenic-contaminated hazardous wastes:

1. S/S with pretreatment by oxidation using hydrogen peroxide, potassium permanganate, and others
2. S/S with pretreatment by hydrated salt addition including ferric sulfate, ferrous sulfate, ferric chloride, and others
3. S/S with proprietary formulations
4. Slag incorporation
5. Encapsulation with polymer resins

The advantages and limitations of the above technologies will be discussed and their ability to meet potential revisions to the hazardous waste treatment standard will be evaluated in light of available literature and Battelle and ENVIRON’s project experience.

Treatability study results for K084 and D004 wastes will be discussed based on a case study from a veterinary pharmaceutical Superfund site. The waste consisted of iron-arsenic sludge and sludge generated from arsenic precipitated with lime. As part of the ROD selected remedy, an estimated 3,800 tons of these arsenic wastes, containing up to 260,000 mg/kg of arsenic, were removed and treated off-site with S/S before disposal at a RCRA Subtitle C landfill. The treatability study tested a total of 88 mixture designs to determine an effective method of treating the vault wastes. Table 1 lists the types of binders and pretreatment additives that were tested.

Table 1. List of Solidification/Stabilization Treatability Study Materials

Binders	Other Pre-Treatment Additives
Type I, II, V Portland Cements	Potassium permanganate (oxidation)
Class F Fly Ash	Hydrogen peroxide (oxidation)
Cement Kiln Dust	Calcium hypochlorite (oxidation)
Lime Kiln Dust	Potassium persulfate (oxidation)
Sodium Silicate	Sodium persulfate (oxidation)
HWT-25, Organophillic Clay With Additives	Calcium chloride (precipitation) Ferric chloride (precipitation)
pH Control Additives	Ferric sulfate (precipitation)
Sulfuric acid	Ferrous sulfate (precipitation)
Phosphoric acid	Magnesium oxide (adsorbent)
Buffer solution	Activated carbon (adsorbent)

The final formulation arrived at during the treatability study involved pretreatment with potassium persulfate and ferric sulfate, followed by binding with Type I Portland cement. Initial TCLP levels in the untreated waste were up to 6,900 mg/L for arsenic; post-treatment TCLP results with the final optimized formula ranged from 0.67 to 1.9 mg/L for arsenic. The full-scale system used a similar formulation with the substitution of sodium persulfate for oxidation of arsenic from As(III) to the less soluble and less toxic As(V) form. The final TCLP results from the full-scale system were 1.24 to 3.44 mg/L. The full-scale system experienced several challenges that were not anticipated based on the bench-scale studies including excessive heat production during mixing. The total cost for off-site S/S treatment and disposal of the arsenic-impacted vault wastes was over $900 per ton. The cost for S/S treatment alone was approximately $800 per ton.

Other arsenic-contaminated materials on-site included K101 or distillation tar residues and K102 or activated carbon residues. These materials contained a high enough organic content that incineration was determined to be the appropriate treatment method. The treatment and disposal cost for the 455 tons of K101 and K102 wastes was approximately $2,000 per ton.

These data show the difficulties in treating high-strength arsenic wastes and excessive treatment costs. It will be necessary to understand whether the high treatment costs can be justified by the incremental reduction in potential risk associated with arsenic in treated wastes.

Some Chemical Aspects Relating to Arsenic Remedial Technologies

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The information that is summarized here originates mostly from publications by well-known and established authors in the field, during their many years of research on this subject. Most of the material is mentioned only briefly, but is found in a publications list, which is available by e-mail from the author. Although there are many other excellent relevant references, the author has chosen the selected papers for their reliability and convenience, but they are not necessarily the earliest chronological references. There are many other statements here which originate from much unpublished work. This extended abstract is an abridged version of the paper (with the references) that is available by e-mail.

Introduction

The removal of arsenic from process solutions and effluents has been practiced by the mineral process industries for many years. Existing hydrometallurgical techniques are adequate for most present day product specifications, but the stability of solid and liquid waste materials for long-term disposal or discharge will not meet the regulatory requirements of the future. The removal and disposal of arsenic from metallurgical process and effluent streams will become a greater problem as minerals with much higher arsenic content are processed in the future, and as regulations become more stringent. Disposal of stable residues will be critical, and the testing methods for assessing stability will need thorough revision.

The various unit processes that have been considered to deal with arsenic in hydrometallurgical processes include: oxidation-reduction, precipitation and thermal precipitation, coprecipitation, adsorption, electrolysis and cementation, solvent extraction, ion exchange, membrane separations, precipitate and ion flotation, and biological processing. These methods are not considered here, but are detailed in some of the references in the e-mail version of this paper. Here only precipitation, adsorption and cementation are considered, as these are the processes that are presently being more generally adopted and need further investigation.

The aqueous solution chemistry of arsenic and the most common hydrometallurgical methods that have been applied commercially for arsenic removal, recovery, and disposal are only mentioned briefly here, as are some techniques which have been used only in the laboratory, and otherwise suggested as a means of eliminating or recovering arsenic from solution.

The aqueous solution chemistry of arsenic that relates to hydrometallurgical processes has been extensively covered in the literature, and the use of thermodynamic stability diagrams to describe the chemistry has been widely adopted. The important oxidation states of arsenic are -3, 0, +3, and +5, and all have been utilized in some way in hydrometallurgy. The removal of arsenic from solution has relied mostly on precipitation and adsorption processes, and it has been considered that arsenic(V) is the oxidation state that leads to the most effective removal by precipitation since the simple metal arsenates generally have lower solubility than the arsenites, and also arsenate is more strongly adsorbed on certain substrates, but this is pH dependent. The general assumption that arsenic(V) is more easily removed from solution, even by adsorption, is not correct. Current work has identified other compounds and also the element (formed by either cementation or electrolysis) to be appropriate low solubility materials for effective removal of arsenic from solution. Arsenic complexation in solution has had little attention, and it seems that only complexes of arsenic(V) with iron(III) have been studied to any extent. Oxidation of arsenic(III) in solution to arsenic(V), and reduction of arsenic(V) to arsenic(III) have been investigated as part of the overall chemistry relating to hydrometallurgy. Oxidants such as air and oxygen, chlorine and hypochlorite, hydrogen peroxide, permanganate, ozone, and SO_2/O_2 have been investigated, both with and without catalysts. Photochemical oxidation of arsenic (III) to arsenic(V) is a recent innovation. The removal of arsenic from gold process solutions has been of understandable interest over the years, and has perhaps been investigated more than other hydrometallurgical processes.

Precipitation

The insolubility of certain inorganic arsenic(V) compounds is the basis of many hydrometallurgical arsenic removal processes, and the insoluble product is often a disposal material. The most common methods of removing arsenic from aqueous process streams are by precipitation as arsenic(III) sulfide, calcium arsenate, or ferric arsenate, but it has been shown that all of these materials are unstable under certain conditions and therefore not suitable for direct disposal to uncontained sites as they will produce leachate containing arsenic.

The sulfide As_2S_3 has its lowest solubility below pH=4, but that solubility is significantly higher than has been generally accepted. The sulfide is not usually the form that is disposed in residues as it is easily oxidized and increasingly soluble above pH=4. There have been unsuccessful attempts to use As_2S_3 in landfills in which acidic-anaerobic conditions are maintained, and also in cement cast admixes. Recent work on biological formation of arsenic sulfides may have an application in treating process residues, but containment of waste material remains a problem.

There are a number of calcium arsenates that can be precipitated from arsenic(V) solutions by lime addition to high pH. Lime addition in excess can reduce arsenic concentrations in solution to <0.01 mg/L, but those calcium arsenates which are precipitated at pH>8 are not stable with respect to the CO_2 in the atmosphere which converts them into calcium carbonate, releasing arsenic to solution in balance with appropriate cations.

Arsenic(V) can be precipitated from aqueous solutions below about pH=2 with iron(III) to form ferric arsenate, $FeAsO_4.2H_2O$, which is white to very pale green in colour. At ambient precipitation temperatures the compound is very small in crystal particle size (<10nm) and is "2-Line X-ray amorphous," but these particles tend to agglomerate to about 100nm and the material is difficult to de-water by conventional operations. At temperatures above about 90°C the precipitated compound is crystalline (>100nm) and has a solubility about 2 orders of magnitude lower than the amorphous material (this is a particle size effect). The "amorphous" ferric arsenate exhibits incongruent solubility at about pH=1 (where [As] is about 500 mg/L) and at higher pH will convert very slowly to an arsenic bearing ferrioxyhydroxide, which initially forms around the surfaces of the ferric arsenate tending to stabilize the material and colouring it yellow to brown. Crystalline ferric arsenate (*scorodite*) has an incongruent solubility point at about pH=2 and is comparatively slow to convert to the arsenic bearing ferrioxyhydroxide, and for material of larger crystal particle size this may take some years. Crystals of $FeAsO_4.2H_2O$ do not grow to appreciable size (greater than about 1 mm) as they have a relatively high positive surface potential up to the pH of the incongruent point. Ferric arsenate of either form is not thermodynamically stable in the neutral to high pH region (the rate of decomposition being related to particle size and solution composition, and being controlled by diffusion through both the reactants and the product layer). The materials may pass conventional leach tests (such as the TCLP) and are not suited for direct uncontained disposal, but perhaps would satisfy a "slow release criteria" if regulatory authorities would give this option its deserved consideration. Ferric arsenate is also not stable in alkaline cement cast admixes.

There are other metal arsenates, such as those of Fe(II), Zn(II), Cu(II) and Pb(II), which are less soluble and more stable in the neutral pH region than the calcium arsenates or ferric arsenate, but these have not been seriously considered as disposal forms. Iron(II) arsenate has particular interest as a low solubility material, and this compound has recently been the basis of a process developed and successfully demonstrated in a variety of applications. Barium(II) arsenate was proposed as being an extremely insoluble arsenate, but this was shown to be incorrect. More complex compounds, such as the apatite structured calcium phosphate-arsenate have recently been demonstrated to be of low solubility and of appropriate stability (including being stable to atmospheric CO_2) for disposal considerations. Ferric arsenite sulfate is also of recent interest and may prove to be useful in stabilizing arsenic(III). One of the most insoluble arsenic compounds is lead(II) chloroarsenate, $Pb_5(AsO_4)_3Cl$, (the mineral form being *mimetite*) which has been studied in detail.

Very little attention has been given to mixed oxidation state materials (both Fe(II)-Fe(III) and As(III)-As(V) combination compounds have been tentatively identified, and the author is presently involved in a comprehensive study of these systems). The Fe(II)-Fe(III) hydroxy sulfate, $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4.8H_2O$, (known as "green rust") incorporates arsenic into the structure at pH<7, and is worthy of further study.

Adsorption of Arsenic on Ferrihydrite

Over many years there has been much attention directed to the removal of arsenic from hydrometallurgical process solutions and waste waters by precipitation and coprecipitation with iron(III). At relatively high concentrations of iron(III) and arsenic(V) (> about 0.001m) and at low pH, the precipitation results in the formation of ferric arsenate, $FeAsO_4.2H_2O$, as previously mentioned. At lower concentrations of arsenic(V) and higher iron(III) concentrations (where Fe/As>1), the coprecipitation of arsenic with ferrioxyhydroxide (*ferrihydrite*) which occurs is probably the most effective method of removal of arsenic from aqueous solutions, and leads to a solid phase which can be stable at least for a year or so. The solid coprecipitate has been referred to as "basic ferric arsenate," and in 1985 a controversy commenced, as to whether the coprecipitated material was in fact a compound of iron(III) and arsenic(V) or simply an adsorptive binding of arsenic with ferrioxyhydroxide (*ferrihydrite*). There was even at that stage sufficient evidence to support the latter contention, but the use of the term "basic ferric arsenate" still exists and formulae such as "$FeAsO_4.xFe(OH)_3$" are used.

A number of studies have indicated that various complexes are formed in the adsorption of As(V) on ferrihydrite. EXAFS studies on arsenic bearing ferrihydrite formed at pH>7, have shown that arsenic(V) is adsorbed to ferrihydrite as a strongly bonded inner-sphere complex with either monodentate or bidentate attachment. It has also been reported that monodentate attachment predominates near the optimal pH=4-5 for adsorption.

The adsorption of arsenic(III) on ferrihydrite has also been investigated, but the optimal adsorption in this case occurs at pH 8-9, and although it seems an efficient process, there is no evidence that the adsorbed species is in fact arsenic(III). It may be that during the process, oxidation of arsenic(III) will occur at the surface with some ease, being balanced by the reduction of Fe(III) to Fe(II) in the ferrihydrite structure, as has been shown in preliminary experiments by the author. It is well known that Fe(II) substitution in ferrihydrite does occur. Currently there is an investigation of the adsorption of As(III)-As(V) mixtures on ferrihydrite. Very little attention has been given to the possibility of modifying the ferrihydrite structure to improve its adsorptive capacity for arsenic in solution. It is well known that many cations will incorporate into the *goethite* structure, and therefore possibly into a precursor ferrihydrite. The author is aware of current work investigating the coprecipitation of both Al(III) and Mn(III) with Fe(III) to form an aluminic ferrihydrite and a manganic ferrihydrite respectively. Both materials are showing considerably better capacity for arsenic adsorption. The control of potential is important in this adsorption process. The effective oxidation of As(III) by manganese substituted goethite has been studied by XANES spectroscopy, and the implications are obvious in relation to adsorption mechanisms. There is little work reported on the adsorption of arsenic from solutions initially below say 50 μg/kg. This region of concentration is presently of immediate interest in relation to drinking water, where EPA announced a new standard of 10 ppb (10 μg/L) for the maximum level allowed.

Many substrates, other than ferrioxyhydroxide, have been investigated and used commercially for removing arsenic from solution by adsorption. Some of these have shown excellent adsorptive capacity, but there is not the scope here for any details. Of personal interest is “adsorption” on sulfide minerals and titanium oxyhydroxide.

Cementation

It is well known that iron and other metals will replace arsenic from solution to produce arsenic as the element or as an alloy. This method of removing arsenic from solution to levels <2 μg/L has been demonstrated on groundwater at a commercial site in California at a pilot scale of 1-5 US gallons per minute. Cementation has also been suggested, demonstrated, and may be appropriate for the removal of arsenic from drinking water.

Testing for Long Term Stability

Testing methods for evaluating the stability of hazardous waste residues have been defined by EPA in several “Background Document for Toxicity Characteristic Leaching Procedure” publications. The test methods do not adequately assess the long term stability of arsenical residues. Improved test methods must be designed which also include a characterization of physical properties and chemical components (mineralogy) so that predictions of behavior can be made.

Thermodynamic Modeling

The stability of arsenic species can be characterized by their standard free energies of formation ($\Delta_f G^o$). Many of the papers referenced in the e-mail version of this paper have free energy of formation data for arsenic species that have been invaluable to the author in producing thermodynamic stability diagrams to gain a better understanding of arsenic systems. None of the reputable thermodynamic databases have significant relevant data, but there are a number of publications where reasonable data can be obtained, and it is likely that these data will be evaluated and a compilation produced in the near future.

Conclusions

There have not been any significant and innovative improvements in the methods for removing arsenic from process and effluent solutions, or for stabilizing sludges and residues, in the last decade or so. The current need to remove arsenic from drinking water it seems is now a world problem, and so that too must be addressed.

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This paper is available with references from bobrobins@bigpond.com.au.

Arsenic Geochemistry: Overview of an Underhanded Element

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Arsenic is 38th in cosmic abundance but only about 52nd in earth and crustal abundance. The formation of the earth apparently discriminated against arsenic. In the ocean, however, it is 26th in abundance, suggesting accumulation in seawater over geologic time. Arsenic is preferentially concentrated in shales relative to other major rock types. Partitioning into shales reflects the strong adsorption tendency of arsenic for clay minerals. During high-temperature processes, arsenic can be expelled from sediments and volcanics and concentrated in the fluid phase, especially at low porosity. This phenomenon may explain high arsenic in hydrothermal fluids and their ore deposits.

The geochemical cycle of arsenic from magmatic-hydrothermal processes through weathering, sedimentation, and diagenesis transforms the element and produces an array of natural sources. Probably the single most abundant mineral source of arsenic is arsenian pyrite. Pyrite is ubiquitous in the earth's crust and arsenic has a strong affinity for the sulfur site in pyrite, substituting up to about 10wt. %. Arsenopyrite contains higher concentrations of arsenic (39-53%) but is a much rarer mineral. Other arsenic-rich minerals include orpiment, realgar, and enargite. Weathering of these minerals in oxidizing environments solubilizes arsenic as As(III) and ultimately as As(V). Arsenate, or As(V), has a strong adsorption affinity for hydrated iron oxides and in oxidized sediments iron oxides can be a source of soluble arsenic if they undergo reductive dissolution during early diagenesis. Geothermal springs are commonly enriched in arsenic, containing 0.1-5 mg/L dissolved arsenic as both As(III) and As(V).

Arsenic concentrations in groundwaters can range from less than a few μg/L to tens or even hundreds of mg/L in locally contaminated environments. Both anthropogenic and natural sources for arsenic in groundwaters occur in many locations worldwide. Natural sources cause or have caused poisoning of populations in India, Bangladesh, Chile, Argentina, Mexico, Taiwan, Mongolia, Japan, and China. Mining activities are responsible for arsenic poisoning in Thailand. Arsenic mass poisoning in Bangladesh is the largest known, affecting nearly 30 million people.

The primary source of industrial and commercial arsenic was arsenic trioxide, produced as a by-product of metal mining and processing. Stockpiles still exist and are releasing soluble arsenic to groundwaters. Several arsenic insecticides, herbicides, desiccants, wood preservatives, animal feed additives, drugs, chemical weapons, and alloys were produced for many years and sites are contaminated from these industries and their applications. Roxarsone, an organic arsenical, is still widely used today to clean parasites out of the stomachs of pigs and poultry.

Arsenic in surface and groundwaters occur dominantly as either arsenite, As(III), or arsenate, As(V). Reduction of arsenic can produce methylated forms of arsenic. Several microorganisms, including species of fungi, algae, and bacteria, catalyze the reduction of arsenic. Oxidation of As(III) is also catalyzed by microbes and it has been demonstrated that soluble As(III) and arsenic sulfide minerals such as arsenopyrite and orpiment can be catalytically oxidized to soluble As(V).

Impact of Microorganisms on Arsenic Geochemistry

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Introduction

Microbial activities are ubiquitous in the geochemical environment, and they can exert tremendous influences on the biogeochemical cycles of elements by interconverting species that display remarkably different behaviors. Arsenic is one such element, possessing a multi-dimensional biogeochemical cycle with important components contributed both directly, by microbial transformations of arsenic itself, and indirectly, by microbial transformations of elements with biogeochemical cycles that intersect that of arsenic.

Microbial Energy Generation by Catalyzing Redox Reactions

One of the primary tasks of a microorganism is to catalyze chemical reactions that will help it to obtain energy for metabolic growth from its environment, and as a result, many of the biogeochemically significant transformations that microorganisms catalyze are the result of energy-generating endeavors. The greatest energy-generating reactions available to the biosphere are those in which electrons are transferred from one element or compound to another, also known as oxidation-reduction or "redox" reactions (Stumm and Morgan, 1996). Redox reactions necessarily alter the electronic configurations of the compounds involved, and because electronic associations form the basis for much chemical reactivity, redox reactions frequently create dramatic alterations in the behaviors of their substrates (Schlesinger, 1997). In addition, because the microbial incentive to catalyze energy-generating reactions is so great, and because the abiotic rates of redox reactions are frequently so slow, such reactions frequently proceed much more rapidly and to a much greater extent in the presence of microbial catalysis than they would otherwise (Morel et al., 1993).

Aerobic and Anaerobic Respiration

Microorganisms catalyze redox reactions by means of "respiratory" processes, which are those that catalyze the transfer of electrons from one reactant to another. Aerobic respirations couple the oxidation of an electron donor such as organic carbon, H_2, or Fe(II) to the reduction of molecular oxygen, O_2, forming water. These processes necessarily occur in unsaturated soils or well-mixed or oligotrophic surface waters where oxygen is abundant (Brock and Madigan, 1991). In contrast, anaerobic respirations couple the oxidation of an electron donor to the reduction of an alternative electron acceptor such as nitrate, Fe(III), or sulfate, generating N_2, Fe(II), or sulfide, for example (Zehnder and Stumm, 1988). Aerobic and anaerobic respiratory processes form one central class of processes that strongly influences arsenic biogeochemistry, both directly and indirectly.

Respiratory Arsenic Transformations

Within the past seven years, microorganisms have been discovered in a great diversity of anoxic environments that are able to generate energy by coupling the oxidation of H_2 or organic carbon to the reduction of inorganic As(V), arsenate, forming inorganic As(III), arsenite (Ahmann et al., 1994; Cummings et al., 1999; Dowdle et al., 1996; Laverman et al., 1995; Macy et al., 1996; Newman et al., 1997; Newman et al., 1998). Arsenite behaves much differently than arsenate in natural environments; in particular, its sorption onto clay minerals and metal oxides appears to be less rapid and/or less stable, with the result that As(III) is generally much more mobile than As(V) in aqueous systems (Aggett and Kriegman, 1988; Kuhn and Sigg, 1993; Masscheleyn et al., 1991; Mok and Wai, 1994; Onken and Adriano, 1997; Seyler and Martin, 1989; Seyler and Martin, 1990; Spliethoff et al., 1995).

Because arsenate reduction is an energy-generating process for the microorganisms involved, and because arsenite is both more toxic and more mobile than arsenate, this process has the potential to influence greatly the geochemistry of arsenic in anoxic systems, particularly with respect to arsenic mobilization (Ahmann et al., 1997; Cummings et al., 1999). The converse respiratory process, the oxidation of arsenite to arsenate, coupled to the reduction of O_2 to water, has the theoretical potential to generate energy for microbial growth, but has been indicated in only one microorganism to date

(Ilyaletdinov and Abdrashitova, 1981). Nevertheless, a variety of other microorganisms have been shown to oxidize arsenite to arsenate by non-energy-generating mechanisms (Osborne and Ehrlich, 1976; Phillips and Taylor, 1976; Sehlin and Lindstrom, 1992; Wilkie and Hering, 1998).

Respiratory Iron, Manganese, and Sulfur Transformations

Sorption onto iron and manganese oxide solids and precipitation in sulfide solids in anoxic environments appear to be the two primary mechanisms governing arsenic mobility in aqueous, soil, and sedimentary environments (Bodek et al., 1988; Sadiq, 1997). Consequently, microbial activities that affect the abundances of iron or manganese oxides or sulfides have indirect, but potentially very important, influences on arsenic geochemistry. Respiratory iron and manganese reduction are ubiquitous and, in many cases, dominant redox processes in anoxic soils and sediments (Lovley, 1993; Nealson and Saffarini, 1994). Because the reduced forms of iron and manganese are highly soluble, their oxides dissolve readily upon microbial reduction, simultaneously releasing sorbed substances such as arsenic (Commings et al., 1999). When sufficient sulfate is present in an anoxic region, however, microbial sulfate reduction can potentially generate sufficient sulfide to precipitate the arsenic in solids such as amorphous arsenic sulfide, realgar, or orpiment (Moore et al., 1988). The corresponding oxidative processes, microbial oxidation of Fe(II), Mn(II), or S(-II), are known to occur, but are usually restricted to acidic environments (Schlegel, 1993) and have not been shown directly to promote arsenic sorption onto metal oxides nor to promote arsenic sulfide dissolution. While the geochemical significance of the reductive processes for arsenic cycling is well-established, the significance of the oxidative pathways is much less understood.

Arsenic Toxicity

In addition to energy generation, a second important task for microorganisms is to protect themselves from toxic substances. Arsenate, with its structural similarity to phosphate, enters microbial cells readily through phosphate-uptake proteins. Its primary mode of toxicity is then to displace phosphate in the production of adenosine triphosphate (ATP), the primary energy currency of the cell. The resulting molecules hydrolyze spontaneously, causing the cell to deplete its energy stores rapidly (Winship, 1984). Although this mechanism of toxicity is quite effective, many cells are able to induce highly phosphate-specific uptake proteins that improve the exclusion of arsenate (Rosenberg et al., 1977; Torriani, 1990; Willsky and Malamy, 1980). Arsenite, in contrast, is uncharged at neutral pH and appears to gain access to the cytoplasm by less specific mechanisms, possibly including diffusion across the membrane. Once inside, it crosslinks sulfhydryl groups on enzymes, forming stable adducts that permanently disable the enzyme. This mechanism is even more destructive to the cell than that of arsenate (Winship, 1984).

Arsenic Detoxification

To protect themselves against the toxic effects of arsenic, many microorganisms have evolved strategies for detoxification. The best-studied among these is the microbial reduction of arsenate to arsenite by means of the *Ars* system, an enzymatic process in which energy is actually consumed to drive the reduction. The *Ars* system is borne on plasmids that are easily transferred among both Gram-positive and Gram-negative bacteria, and it is induced at arsenic concentrations low enough to be relevant to contaminated environments, with the result that this process is potentially rapid, extensive, and ubiquitous in both oxic and anoxic environments (Ji and Silver, 1995; Silver et al., 1993).

Certain other bacteria and fungi appear to detoxify arsenicals by reducing them to arsine, As(-III), in both inorganic and methylated forms (Cheng and Focht, 1979; Cullen and Reimer, 1989). In addition, some algae have been shown to reduce arsenate to arsenite, presumably for detoxification purposes, but this purpose has not been confirmed (Sanders and Windom, 1980). Finally, certain bacteria and algae, as well as many higher organisms, may incorporate arsenic into organic compounds such as arsenocholine, arsenobetaine, and other arsenosugars (Andreae and Klumpp, 1979; Cullen and Reimer, 1989). Regardless of the utility to the microorganism, however, it is clear that many non-energy-generating microbial transformations of arsenic occur both rapidly and extensively in natural environments, and should be considered potentially important contributors to arsenic geochemistry.

Passive Nucleation

Microbial cell surfaces possess an abundance of surface functional groups that can form complexes with dissolved ions, including arsenic oxyanions, and such complexes have been shown to function as sites of nucleation in the precipitation of certain minerals (Beveridge, 1989). In the case of arsenic, it may be possible that microbial cell surfaces contribute to arsenic geochemical cycling in this passive manner as well, particularly in the instance of nucleating arsenic sulfide precipitation (Newman et al., 1997; Rittle et al. 1995).

Summary

In oxic environments, the dominant microbial influences on arsenic geochemistry appear to be the bacterial and algal oxidations of arsenite to arsenate, diminishing both toxicity and mobility of the arsenic, as well as confirmed detoxification processes, including the *Ars*-mediated reduction of arsenate to arsenite and fungal generation of arsines. In anoxic environments, in contrast, the dominant microbial roles are expected to be the respiratory reductions of arsenate, iron, and manganese, all of which promote arsenic desorption and enhance its mobility, and the respiratory reduction of sulfate, which promotes arsenic immobilization into sulfide solids. While the mechanisms underlying these processes are well understood in many cases, and their geochemical influences are potentially great, the ability to quantify and, more importantly, to predict the rates and extents of these processes in natural environments, remains a tremendous challenge for the future.

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A Framework for Assessing Arsenic Leaching from Soils and Wastes

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Estimating long-term release from wastes and soils by leaching requires a testing and interpretation framework that considers specific management scenarios. However, development of dedicated test methods to simulate the wide variety of environmental scenarios is impractical. An alternative approach, presented here, is to measure a common set of intrinsic leaching parameters and use models that reflect the anticipated environmental scenario to estimate release. Thus, a common set of testing results can be used to compare alternative management scenarios, including site-specific climate and design conditions. Alternatively, a set of default management assumptions can be used to compare the efficacy of different treatment processes. Important intrinsic leaching properties of the soil or waste include: (i) release potential, (ii) solubility and release as a function of pH, (iii) solubility and release as a function of liquid to solid ratio, and (iv) mass transfer rates.

A challenge is simplification of the approach to allow routine implementation. It is proposed to achieve the goal by carrying out testing at two levels: (i) material characterization, and (ii) verification. Initial characterization is carried out to define a class of materials, based on its behavior. Subsequently, simplified testing is carried out to verify that the material being evaluated has not varied significantly from the material class that was subjected to more extensive characterization. Evaluation is further enhanced by development of a multi-party database that facilitates comparison of the leaching behavior for a wide range of materials. This presentation will provide an overview of the leaching framework and comparison of results for arsenic leaching from a variety of wastes and secondary materials. For a soil contaminated with As caused by wood preservation, the geochemical modeling is presented. This illustrates the nature of the solubility controlling phases and the degree to which the model can predict the observed leaching behavior. A second paper presents the testing protocols in more detail (see Sanchez, et al. "Protocols for Estimating Arsenic Leaching from Soils and Solidified Wastes," 3.3 Arsenic Chemistry Session).

3.0 Breakout Sessions

3.1 Source Identification Session

This session was designed to encourage discussion that addressed methods for characterizing and identifying arsenic sources, and to develop recommendations for managing risk from arsenic releases/sources. The session co-chairs were:

- *Diana Bless - U.S. EPA, NRMRL*
- *Doug Grosse - U.S. EPA, NRMRL*
- *Carol Russell - U.S. EPA Region VIII*

The objective of the Source Identification session was to address the following three general questions:

1) What are the primary sources that contribute to arsenic releases to the environment?
2) What are the significant data gaps and information needs for characterizing and identifying arsenic sources and waste forms?
3) What are the important insights to be conveyed regarding the management of arsenic risks for decision makers?

Speaker Abstracts

Speaker presentations addressed a variety of source identification and fate and transport issues from a broad spectrum of sites/locations. Each presentation was followed by a brief question and answer period. A general discussion addressing the three questions occurred after all the presentations had been completed. A summary of some of the material discussed during the presentations and open discussion periods, including responses to the three questions, is presented in Section 3.1.1 of this report. The presentation abstracts are located in section 3.1.2 of this report.

3.1.1 Discussion Review

Primary Sources of Arsenic Releases

Natural vs. Anthropogenic Sources: Emphasis has been placed on differentiating between natural and anthropogenic arsenic sources. This is particularly important in the West. For example, in California, expansion and development is occurring in areas with naturally occurring arsenic in their water supplies. It is, therefore, important to focus characterization efforts and resources to protect the point of use rather than attempt to identify all of the source terms contributing to the contamination problem.

There is also a growing awareness of the wide-scale (regional) nature of residual arsenic contamination from agricultural and other anthropogenic sources such as copper and sodium-based arsenicals from herbicides and pesticides. Since it is difficult to identify point sources for this contamination it is important to understand the complex behavior of arsenic.

Information is needed on distinguishing anthropogenic and natural sources in order to identify parameters that affect treatment and to assess effects from other anthropogenic contaminants such as petroleum hydrocarbons from leaky pipelines and/or underground storage tanks (USTs). Site characterization techniques (e.g., oxidation, species concentration) and guidance are also needed for collecting and analyzing data. It may be possible to determine the source of the arsenic based upon the presence of other source-specific anthropogenic chemicals/elements (tracers) or to investigate the history of contamination by examining reservoir sediments, dendrochronological "data," and local records. (Note: Both sediments and wood can trap arsenic over time.)

Background sources can be differentiated by: using regional distributions (via geo-referenced databases); assessing local geochemical changes in arsenical type; and performing principal component analyses to determine chemometric statistics. Geo-referenced databases are useful tools for understanding the location of sources indicating where treatment should occur. Principal component analysis, which is a method of segregating and classifying samples (data) on the basis of similarities or differences within variables, can be used to extract the main relationships for data of high dimensionality. Outputs show similar components clustered together, while dissimilar components are shown as outliers. The international community varies in the manner in which arsenic contaminant limits are developed. For ex-

Note: Statements captured in the panel discussion are those of participants, not necessarily EPA.

ample, the United Kingdom relies on localized background arsenic concentrations in natural formations to establish contaminant levels. In the U.S., statewide and site-specific standards are used, complicated by naturally occurring and anthropogenic inputs.

Arsenic Mineralogy: Background arsenic concentrations pose regulatory challenges due to arsenic's tendency to occur naturally in soil, sediments, and minerals. According to Richard Glanzman, a large number of the background ranges have been established in the early 1970s and 1980s for arsenic concentrations in rocks (igneous and sedimentary), sediments, soils, and water sources. Much of the supporting information on how these background numbers were developed has not been reported or made readily available, including the statistical design. Methods used to determine arsenic concentrations (e.g., pulverization followed by the analysis of the whole sample) produced false negatives for materials in which the arsenic was merely adsorbed to the surface. An extraction technique is perhaps more accurate when arsenic is adsorbed to the surface of a material.

Based on the literature search performed by Mr. Glanzman, phosphorite and iron formations have the highest mean background arsenic concentrations found in the different types of sedimentary rock analyzed, both 41 mg/kg. Travertine, hot, and volcanic springs had the highest mean background concentrations of the different water sources analyzed; 304, 2,090, and 22,200 µg/L, respectively. Mine waters have also been measured at very high concentrations, from 3.0 to 400,000 µg/L.

Although some soil data are available, there is a paltry amount of information, of a national scale, on background arsenic concentrations in soils. A national database/map would be useful in addressing these types of constituents in soil. It is important to establish criteria for collecting these types of samples, including depth and the appropriate analytical method. There currently exists a number of sample libraries which could be used to develop the background information needed to assess human health and environmental impacts from arsenic.

Arsenic mobility, along with its ability to act as either a source or sink, is largely dependent on its natural form. Arsenic naturally occurs as a major element in hundreds of minerals. In addition to native arsenic, there are 276 known arsenic minerals including: 39 arsenides (X As), 64 arsenic sulfides (X AsS), 26 arsenites (X AsO_3Y), and 147 arsenates (X AsO_4Y). Below is a list of cations (X's) associated with the different species of arsenic minerals; the cations are listed according to their preference for each mineral type. For example, there are more arsenides containing nickel than arsenides containing copper. There is also an equal number of arsenides containing iron and arsenides containing lead. This information is relevant to principal component analyses.

Arsenides	Ni>Cu>Fe = Pd>Sb = Co>Se>Pb
Sulfides	Sb>Pb>Cu > Tl>Ag>Fe = Rare Earth Elements (REE)>Hg
Arsenites	(OH) = Mn = Pb>Fe>Ca = Cl>Mg = Cu=Zn=Si
Arsenates	(H_2O)>(OH)>Ca>Fe>Zn>Cu>
	Mn=Pb>Mg>UO_2>Cl>SO_4=PO_4>Co>Sb=Bi=F

Animal Feed: Arsenical feed amendments are used to promote weight gain in poultry, and the resultant manure containing arsenic is an issue. Soil, sediment, poultry litter, and water samples extracted from ditches, tributaries, and groundwater in the Pocomoke River Basin (a Chesapeake Bay watershed) yielded the following preliminary results:

- Measurable arsenic was detected from poultry intensive agricultural areas;
- Significant arsenic concentrations were also detected in the shallow pore water and groundwater;
- Storm events indicate surface runoff from an arsenic source; and
- More arsenic is transported in the particle bound phase than in the dissolved phase.

The degradation pathways of arsenical feed amendments (e.g., roxarsone) in the environment are still unknown, particularly the relationship between the organic forms in the feed and the observed forms in the environment. The transport of arsenic during storm events needs to be better defined; especially, the impact that high application rates and/or seasonal variation has on concentrations and transport due to overland and groundwater flows. It is particularly important to look at the initial surge when sampling storm events. More information is also needed on natural sources (background) of arsenic in the Pocomoke River Basin, as well as a variety of nutrients (i.e., ammonia in surface waters).

Characterizing and Identifying Arsenic Sources and Waste Forms

Soils/Sediments: One of the methods used to evaluate methods for removal of arsenic from groundwater, determine mobility of arsenic in surface water/sediments, and to assess arsenic mobility at an arsenical pesticide manufacturing site was an electron microprobe (EM). EMs were also used at a wood preserving site to determine the forms of arsenic in the soil and at a smelting site, to evaluate forms of arsenic in solid wastes, to determine solidification formulations (agents, ratios, etc.), and to evaluate treatment effectiveness.

Although some samples were analyzed from the area surrounding the contaminated zone at the arsenical pesticide manufacturing site, concerns were raised regarding whether the arsenic associated with biotite samples can be attributed to water adsorbed on the crystalline material rather than trace elements in the crystal. Ideally, more background samples should have been collected upgradient for comparison. Also, a lower solid to liquid ratio (e.g., 20 to 1) would probably have been warranted during SPLP leaching tests (with the Wester Formula) performed on samples from the smelting site because concentrations can be quickly diluted with this method, which uses 60 to 70 pore volumes.

Appalachian Basin Coals: The presentation on the potential impacts of localized arsenic enrichment in Appalachian Basin redirected the focus of the breakout session towards the impacts of large, diffusely impacted sites. Based on Mr. Goldhaber’s presentation, the presence and use of Appalachian Basin coal has resulted in significant depositions of arsenic to river sediments in the Appalachian region. This deposition has been associated with natural weathering, mining activities, mine waste deposition, and coal combustion/atmospheric impacts. Based upon the concentrations found in the sediment cores, arsenic concentrations in sediments increased until particulate controls were implemented in the mid 1970s. The advent of unleaded gasoline use in the 1970s may, also, have contributed to reductions in lead, arsenic, and zinc deposition. Further data may be used to help determine appropriate baselines for arsenic and also provide data for establishing future levels of emissions control for coal combustion.

Arsenic was introduced to the Appalachian Basin coal deposits during a large platonic collision that occurred during the formation of the Appalachian range. Mesothermal gold deposits (e.g., gold/arsenic deposits), which were formed at the distal end of a hydrothermal ore forming process, are also located to the east of the Appalachian basin. These deposits contain the same type of elements (e.g., arsenic, antimony, thallium, selenium, molybdenum, and mercury) as found in the Appalachian Basin coal deposits. Similar to gold deposits, this is the same grouping of elements that is transported in sulfite-bearing solutions.

Mercury deposition from the coal-fired power plants is also being investigated. Mercury is typically concentrated in pyrite at concentrations up to 220 ppm. There are certain elements such as germanium that are accumulated in fly ash particles that are not normally found in soils or the geology in the Appalachian Basin. These elements could theoretically be used to help track the arsenic concentrations in the soil and sediments to power plant emissions. Mr. Goldhaber also plans to analyze arsenic-contaminated sediment samples for specific polynuclear aromatic hydrocarbons (PAHs) associated with coal combustion in an attempt to link the arsenic deposition to power plant emissions.

Mining: Mr. Pantano supplemented his presentation with information provided in other presentations in order to highlight how different groups can reach different conclusions from the same or similar sets of data.

A review of arsenic data from samples in the Verde River watershed showed that: (1) water collected at the bottom of mine tailings exhibited the highest concentration (210 ppb); (2) a well from the nearby Montezuma Castle National Monument had the second highest arsenic concentration (94 ppb); and (3) concentrations in the Verde River were measured at 200 ppb. Very few samples obtained in the watershed had arsenic concentrations below 10 ppb. It can be inferred that the arsenic is due to the sulfide oxidation of the mine waste.

Specifically, water chemistry data from the oxidation of a sulfide mineral from a mine tailing near Tuzigoot National Monument are shown in Table 3.1-1. When sodium, potassium, calcium, and magnesium are present, usually one element is greatly exaggerated or increased due to dissolution of the host rock. In this case, magnesium, at 12,000 ppm, has been elevated as a result of the acidic water digesting the other minerals. The presence of an elevated sulfate concentration also illustrates Mr. Goldhaber’s point that an arsenic source can be identified by the presence of an associated byproduct or surrogate. In pyrite oxidation, sulfate is the natural byproduct.

Table 3.1-1. Water Chemistry Data from the Oxidation of a Sulfide Mineral

Parameter	Result
pH	2.6
Sodium	1.2 ppm
Calcium	280 ppm
Magnesium	12,000 ppm
Arsenic	0.21 ppm
Alkalinity	0
Chloride	22.3 ppm
Sulfate	10,000 ppm
Zinc	4 ppm
Iron	75 ppm
Copper	2 ppm
Aluminum	550 ppm
Acidity	198 ppm

When considering treatment for a waste stream with similar mineral composition, the recommended treatment approach will more likely target the removal of the aluminum, copper, iron, or zinc over the arsenic. It is also likely that the arsenic will be removed along with the key elements (e.g., aluminum, copper, iron, or zinc) specifically targeted by the treatment process. It should also be noted that in mine waters containing copper, nickel, and zinc, arsenic is usually present at concentrations between 1/100th and 1/200th of the composite elements.

While Stiff Diagrams, Horner Plots, and other thermodynamic modeling are good techniques for identifying arsenic sources, these are hard to convey to the nonprofessional. When source information needs to be communicated to the public, it may be preferable to present principal cation and anion data to identify the source of the arsenic. Master thesis data from creeks, lakes, mines, river, springs, and wells were presented during the session. Average arsenic concentrations, pH, and alkalinity data are shown for each water source (see Table 3.1-2). Although it is possible to conclude that the pH could be used as an indicator for elevated arsenic concentrations, this parameter can be very deceiving due to buffering capacities. As a result, the alkalinity data may provide a little more information on the bulk chemistry of the water and a better indicator for elevated arsenic concentrations since arsenic concentrations tend to increase with alkalinity, except when acidic conditions prevail. Sulfate and magnesium data can also be used to characterize arsenic impacts.

Table 3.1-2. Average Arsenic, pH, and Alkalinity Data

Parameter	Creek	Lake	Mine	River	Spring	Well
Average of Arsenic (ppb)	20	38	210	20	17	65
Average of pH	7.7	8.5	2.6	7.8	7.6	7.6
Average of Alkalinity (ppb)	230	220	—	245	197	303

Often, plots of sample frequency versus arsenic concentration can be log-normally distributed at different sites, as was shown by a plot of the National Uranium Resource Evaluation (NURE) Program sediment samples taken from the Walker Lake triangle. Thus, if a specific concentration (e.g., a background) with a very narrow range is chosen as the decision criterion for either sampling or excavation for a site with a similar distribution, it is very likely that excessive sampling or excavation will result. Therefore, a good understanding of concentration variation and background is very important.

Management of Arsenic Risk

Marsh Environments: When investigating a remedial scenario, it is important to understand the phase of the arsenic, the arsenic's mineralogic characteristics, and its solubility and bioavailability. When a reactive iron blanket is being considered for use in a tidal estuarine environment like Castro Marsh in the San Francisco Bay Region of California, it is important to: 1) identify the mechanism responsible for drawing the arsenic to the iron; 2) the longevity of this relationship; and 3) the long-term consequence of using the peat, iron, and gypsum (PIG) amendment. It is also important to consider the effects that the salinity in the water may have on the effectiveness of the barrier, such as possible kinetic impacts. Pitting and other severe geochemical conditions have also been observed in iron zones in saline environments.

Questions were raised regarding whether As(III) will be oxidized to As(V) before binding with iron in the surface water. Although arsenic was found in the bioavailable fraction using AVS (Acid Volatile Sulfide) in sediment, referenced in EPA 821/R-91-100, sulfate concentrations in saltwater may recreate reducing conditions. Although most of the published research on this issue does not, specifically, address iron's effect on arsenic, potentially useful information has been published on iron passivation/activation. Workgroup participants suggested investigating the long-term benefits associated with using different grain sizes when designing an adsorption/passivation system. They also suggested using more pore volumes of water per mass of solid in the next set of bench scale studies for the Castro Marsh site.

Mining: Arsenic can be found in nature in its elemental form but is more commonly found as an inorganic arsenic compound associated with other elements such as mercury, thallium, and selenium. Typically, natural arsenic levels in western U.S. soils vary widely from 1 ppm up to about 100 ppm with a mean value of 7 ppm. The mean concentration in typical soil ranges from about 4 to 9 ppm. Arsenic compounds from the Barrick Goldstrike Mines, Inc. and Placer Dome America mines are predominantly contained in naturally occurring minerals within the precious metal-bearing ore and associated waste rock. Arsenic is not added to any of the natural earth materials processed on site at the Barrick Goldstrike Mines and Placer Dome America mines.

In general, the indigenous arsenic compounds in waste rock are not altered by the mining process and remain as the naturally occurring minerals that were present in the rock before it was mined. The arsenic is managed as an integral constituent of the waste rock in engineered disposal facilities on-site. Thus arsenic and acid mine drainage (AMD) are main concerns during the design of the waste rock areas, tailing impoundments, and heap leach liner systems.

Ores from both the Barrick Goldstrike and Placer Dome America mines containing naturally occurring arsenic compounds requiring pretreatment (e.g., via pressure oxidation or roasting) are oxidized in an acidic pH environment and neutralized in an alkaline environment prior to beneficiation to form insoluble calcium or iron arsenates. Naturally occurring arsenic compounds are not affected by the beneficiation process and pass through the circuit as unchanged, inert materials under normal leach conditions. Certain copper-gold ores containing high values of naturally occurring arsenic compounds are roasted in an acidic pH environment, in which the arsenic is volatilized to form arsenic trioxide, which is subsequently collected in a bag house and either sold as arsenic trioxide product or disposed as a hazardous waste. Arsenic compounds resulting from the beneficiation of ore, including both tank leach and heap leach facilities, are managed in engineered containment structures.

Table 3.1-3 illustrates how the Barrick Goldstrike Mines, Inc. and Placer Dome America mines are prominently featured in the 1998 and 1999 public reports for the EPA Toxic Release Inventory (TRI) program. Fugitive dust emissions from the waste rock disposal areas resulting from dumping and wind effects are responsible for the majority of the fugitive arsenic releases to the air. The majority of the material responsible for the 33,000,000 (Barrick) and 28,009,300 pounds (Placer) of arsenic released to surface impoundments is managed in a composite tailing impoundment system with a liner and clay barrier. Arsenic releases associated with “Other Disposal” refers to non-contained/impoundment disposal scenarios, such as waste rock disposal.

According to Mr. Eurick and Mr. Schoen, the Barrick Goldstrike Mines, Inc. and Placer Dome America mines do not substantially contribute arsenic to the natural earth material; their operations utilize engineered and designed closure and reclamation of waste rock, tailing, and heap leach facilities, thus minimizing the potential for arsenic releases to the environment. They also stated that the reported TRI values for arsenic for both sites have not been demonstrated to represent a health or environmental concern.

It is important to clarify that TRI data, as reported, represent releases that are permitted by federal and state agencies, not exposures. TRI also does not report concentrations. TRI data are specific numbers calculated in accordance with guidance provided by the Emergency Planning and Community Right To Know Act (EPCRA). According to the mining industry, the relevance of releases has been somewhat confused by the issue of coincidental manufacturing. During coincidental manufacturing, naturally occurring mineral arsenic is converted/broken down during pretreatment (roasting) to render the sulfur and carbonaceous materials inert. Under the current guidance, a second set of arsenic releases is tallied for these new compounds. Thus, arsenic oxide formation is accounted for on top of the arsenic mineralization coming into the system and the arsenic in the waste rock. Also, TRI data have been used to set objectives for research and data needs. Other “numbers” besides TRI data should also be looked at, including Clean Air Act (CAA), CWA, and RCRA data.

Although a lot of emphasis has also been placed on reducing mercury emissions from mining sites, additional controls for mercury should not have an impact on arsenic compounds since mercury releases are relatively small compared to arsenic releases. These reductions are dwarfed by the huge arsenic releases at these sites. However, it may be useful to assess and compare how much arsenic was removed from the ore circuit following the addition of organic sulfide to reduce mercury throughout the circuit to achieve 90% reduction (Reference: Cortex Mine).

Wood Treating: Jim Basler from Osmose, Inc. gave a brief presentation as a representative of the wood treating industry. Wood treating is an older, more established industry associated historically with shipbuilding, railroads and utilities. In the mid 20th century, consumer use of treated wood became very popular (e.g., for decks and landscaping). In the 1980s, water based wood preservatives, like chromated copper arsenate (CCA), experienced a tremendous growth.

Currently, six to seven billion board feet of dimensional lumber are preserved each year using a variety of preservatives such as creosote solutions, pentachlorophenol systems, copper and zinc naphthalate, CCA, ammoniacal copper zinc arsenate, etc. Approximately 30 years ago, Osmose, Inc. began to research alternative preservatives. Although they introduced a non-arsenical system called copper citrate, this system has not been commercially successful largely due to costs, and it is not as effective.

Some risk associated with using preserved wood has been identified. The wood treating industry recently performed a risk:benefit analysis that concluded that the benefits of using preserved woods far outweigh the risks. Although the wood preserving industry believes that when used properly, CCA is very safe, it is also very responsive to arsenic-related concerns and is investigating alternative preservatives systems. For example, the wood preserving industry has also been investigating heavy copper formulations that are comprised mostly of copper and have environmental tradeoffs, as compared to CCA. As of January 1, 2004, EPA will not allow CCA products to be used to treat wood intended for residential uses. The wood preserving industry voluntarily agreed to discontinue the use of CCA in consumer wood products by December 31, 2003.

Table 3.1-3 Arsenic and TRI in Select Gold Production Operations

RELEASED TO	QUANTITY (pounds)	% TOTAL	MAJOR SOURCES
Fugitive Air	4000	<0.01	Waste Rock/Roads/Ore
	12,500	***0.05***	
Stack Air	340	<0.01	Waste Rock/Ore/Process
	870	***<0.01***	
Water	12	<0.01	Humboldt River
	0	***0***	
Underground Injection Control	0	0	N/A
	0	***0***	
Other Landfill	0	0	N/A
	0	***0***	
Surface Impoundment	33,000,000	17	Tailing Impoundment
	28,009,300	***53***	
Other Disposal	160,000,000	83	Waste Rock/Spent Heap
	24,342,000	***46***	***Ore / Infiltration***
Publicly Owned Treatment Works	0	0	N/A
	0	***0***	
Other Offsite Transfer	1	<0.01	Transfer to TSDF
	0		
TOTAL	193,004,353 / ***52,364,670***		

References:

Barrick 1999 TRI Data (Goldstrike/Meikle Complex) As Compounds

Placer Dome 1999 TRI Data-NV Operations (Pipeline, Bald Mountain, Getchell) As and As Compounds (***bolded and in italics***)

3.1.1.1 Summary of Important Conclusions and Recommendations from the Source Identification Session

Primary Sources of Arsenic Releases

1. The following activities/processes are responsible for arsenic releases to the environment: oxidation/reduction, adsorption/co-precipitation, evapoconcentration, biodegradation, volatilization, photo-reactivity, ingestion/metabolism, irrigation, over-pumping of aquifers, and transport processes such as advection, dispersion, and diffusion.
2. Hot springs (geothermal), igneous rock (basalt), sedimentary rock (organic/inorganic clays, shale), metamorphic rock (slate), seawater, mineral deposits, and volcanoclastic materials/releases are the primary natural sources of arsenic releases to the environment.
3. Anthropogenic sources of arsenic include: historic mining sites, pesticide/herbicide use, combustion byproducts from burning fossil fuels, animal feeds/waste byproducts, historic wood preserving sites, medicinal uses, fertilizer use, landfill leachate, glass production, and tanneries.
4. Production sources typically have higher concentration, localized arsenic releases. Application sources typically have lower concentration, widespread arsenic releases.

Characterizing and Identifying Arsenic Sources and Waste Forms

1. Soil characterization information is needed that defines background arsenic concentrations/conditions in different types of soils and the impacts that arsenic introduction can have on different types of soils.
2. Arsenic mineralogy, geoavailability, bioavailability, and leachability should be characterized at each site in order to help identify the source of an arsenic release and determine whether it is natural or anthropogenic. Speciation data also need to be collected, particularly As(III) and As(V) data.
3. Characterization techniques need to be standardized. Generic guidance is needed that can be used to help identify impacted media, characterize contamination, and assess potential impacts. Sampling designs need to be developed that are capable of providing the data needed to address these issues.
4. Before characterizing the impacted media at a site and determining potential management approaches, it is important to first identify the temporal and spatial scale of the system, potential receptors, and potential physical, chemical, and biological transport processes. Methods and/or models need to be developed in order to perform multimedia integrations across spatial/temporal scales.
5. Information and techniques are needed which can be used to predict how natural or anthropogenic changes will impact arsenic fate and transport, both in the short- and long-term. Fundamental kinetic and thermodynamic data (e.g., the adsorption coefficients of both phosphate and arsenic on iron oxide) can be used to assess transformations between phases.

Management of Arsenic Risk

1. It is important to monitor arsenic releases and provide this information to the public.
2. It is important to identify an arsenic contamination/release problem, understand how to fix the problem, and then monitor the performance of the selected corrective action.
3. The risk from an arsenic release needs to be well defined. It is also important to differentiate real versus perceived risk.

It is important during a risk characterization to predict the environmental effects of the arsenic release

3.1.2 Source Identification Session Speaker Abstracts

Speaker abstracts from the Source Identification session are presented in this section.

Note: Statements captured in the panel discussion are those of participants, not necessarily EPA.

Distinguishing Natural and Anthropogenic Sources of Arsenic: Implications for Site Characterization

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Both anthropogenic and natural sources contribute to the presence of arsenic in soil and groundwater. Understanding both source types, as well as the geohydrochemical conditions for a given site should be considered important in developing and implementing an effective site characterization program, and ultimately, a technically feasible and cost-effective management or remediation program. Anthropogenic sources of arsenic, including mineral processing, glass manufacturing, wood preserving, pesticide production and application, landfill/waste pile leaching, and coal/oil production and processing, typically are localized and seldom result in regional increases in arsenic concentration with the possible exception of the widespread application of arsenical-pesticides/herbicides. Natural sources of arsenic, of which there are nearly 250 naturally-occurring arsenic-containing minerals, including volcanically-derived sediment, sulfide minerals, and metal oxides, can affect large areas. The "background" contribution of the natural sources creates additional complexity in assessing the impact of arsenic at a given site with respect to developing appropriate site solutions.

Arsenic is a redox-sensitive element, and its presence, distribution, and mobility is dependent on the interplay of several geochemical factors including reduction-oxidation reactions, pH conditions, microbial activity, the distribution of other ionic species, and general solution chemistry of pore-water or groundwater. These factors, which are influenced by both natural and human-based conditions and activities, in turn control the major adsorption/desorption and precipitation/dissolution reactions that influence arsenic mobility. The two primary redox forms of arsenic, arsenate and arsenite, can occur in almost any hydrogeochemical setting, although arsenate generally predominates under oxidizing conditions with arsenite predominating under reducing conditions. For waste site settings (e.g., anthropogenic sources), the type of arsenic present in the subsurface will be strongly affected by the contributions of other waste types, including hydrocarbon compounds, which tend to affect pH and redox conditions of the subsurface system, as well as the form in which the arsenic was released. Crude arsenic trioxides typically contribute to the presence of arsenates in near-surface, oxygenated soil and groundwater. Reduction due to the presence of hydrocarbon contributions can, in turn, result in the reduction and change of mobility of the arsenic ion. Local releases of sulfuric or nitric acids in waste streams, can in turn, reoxidize arsenite to arsenate. Because conditions can change greatly over short distances in such release sites, site characterization programs must involve a comprehensive understanding of the history of releases, as well as background information with respect to ambient site conditions.

This presentation will discuss issues associated with the types and conditions of arsenic sources and release scenarios, as well as the characterization techniques important to developing a representative interpretation of the site conditions.

Arsenic Background, Associated Elements and Factors Controlling Mobility

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This presentation includes representative arsenic multimedia background concentrations, and mineralogy and controls on arsenic mobility with case histories illustrating these controls. There is a rich history of background arsenic concentrations in most media that are readily sampled in the environment. These background values are strongly related to their origin but the physiochemical conditions where they originate are generally poorly described in tabulations from the literature. Background arsenic concentrations can be used to determine distribution, attenuation and bioaccumulation coefficients but the site-specific conditions within which the background concentrations were determined and for which one is interested need to be carefully evaluated before their use.

Arsenic naturally occurs as a major element in hundreds of minerals and is associated as a minor or trace element in hundreds of additional minerals. Fortunately, most of these involve sulfide and sulphosalt minerals or iron oxydroxide/oxide phases. This considerably simplifies the geochemical conditions one requires to estimate arsenic mobility and arsenic concentrations. From the above mineralogical relationships it is obvious that pH and closed-cell oxidation reduction potential measurements are required field measurements. Unfortunately, most regulatory data requirements collect laboratory instead of field pH values and dissolved oxygen instead of ORP values.

Ongoing geochemical research on arsenic has lead to the quantification of arsenic adsorption onto iron oxyhydroxide/oxide phases under natural conditions involving multiple competing ions. The specific rank of arsenic speciation with respect to commonly associated dissolved metals and other common ions has been developed along with the total adsorption capacity of iron oxyhydroxide/oxide phases. The kinetics of most of these reactions is generally very rapid, commonly less than a few seconds to a few hours, therefore, kinetics is not usually an issue, as it is for manganese. Current research defines the actual adsorption mechanisms and range of irreversible sorption characteristics under oxidizing conditions but not the range of probable arsenic release under reducing conditions. Reducing conditions need to be considered in the TCLP protocol for landfill disposal of arsenic adsorbed to iron oxyhydroxide.

Reconnaissance for Arsenic in a Poultry Dominated Chesapeake Bay Watershed - Examination of Source, Transport, and Fate

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The source, transport, and fate of several arsenic compounds are being investigated in water, soil, and sediment of the Pocomoke River Basin in Maryland and Delaware. This basin in the Chesapeake Bay Watershed has a high concentration of poultry-feeding operations where arsenic feed amendments are used extensively. Concentrations of total arsenic in fresh poultry manure collected from the Pocomoke River Basin were as high as 27 mg/kg, whereas older, composted manure contained less than 2 mg/kg total arsenic. Arsenic in composting manure may be volatilized, and during rain events, it is likely leached into water. Total arsenic in agricultural and forest soil of the Pocomoke River Basin was 1–2 mg/kg; these soils had similar concentrations of arsenic as the composted manure sample. Base-flow concentrations of total arsenic in suspended particles and in bed sediment in the Pocomoke River and its tributaries were 0.8–21.0 mg/kg in both 1997 and 1999. Concentrations of total dissolved (0.45 μm filtered) arsenic in water samples from the Pocomoke River did not exceed 1.6 μg/L during base-flow. Concentrations of total dissolved arsenic in agricultural ditches and in the Pocomoke River increased during high flow, presumably due to runoff.

Although the initial input of arsenic to the basin from poultry waste is in the form of organic arsenic compounds, we found mostly inorganic arsenic (As III and As V) and relatively low concentrations of methylated arsenic in pore water in cored sediments collected beside an agricultural field. Total arsenic in pore water in surface sediments and at depths to 8 feet ranged from below detection limits to as high as 29 μg/L. The As (V) concentrations were elevated in pore water from the near-surface sandy soil (29 μg/L) and from an iron-rich clay silt layer at depth (24 μg/L). As (III) was not detected in the near-surface sediments, but increased with depth to 11 μg/L.

Shallow groundwater from piezometers near agricultural fields, which had total dissolved arsenic concentrations as high as 23 μg/L, appears to be an important reservoir for arsenic cycling in the Pocomoke Basin. Water from a deeper, semi-confined part of the surficial aquifer system, which is a drinking water source, had total dissolved arsenic concentrations as high as 8 μg/L. This deeper groundwater also had relatively high concentrations of dissolved iron (25–29 mg/L) and did not contain any obvious signs of agricultural influence. These findings suggest two sources of arsenic in the basin: poultry waste spread on land, and a natural source associated with iron-rich sediments, particularly at depth. Elevated arsenic concentrations were observed in groundwater with low dissolved oxygen content, and under these reducing conditions, groundwater has the potential to mobilize arsenic from the reduction of metal oxides.

To understand all the potential sources and sinks of arsenic in the basin, total arsenic concentrations in soil and bed sediment samples representing varying intensities of agricultural land use will be analyzed. Core sediment collected from various locations and representing various land uses in the basin will be analyzed for total arsenic, carbon, and sulfur. In addition, grain-size analyses and sequential partial extractions will be performed to characterize the sediments. Storm-runoff samples will be measured for total arsenic and arsenic speciation in both whole water and dissolved (filtered) samples. Sampling also will be expanded to other tributaries in the Chesapeake Bay Watershed affected by high-density poultry operations, such as the Shenandoah Valley of Virginia.

Characterization of the Forms of Arsenic in Soil/Sediment To Evaluate Mobility and Treatment

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The chemical compositions or forms of arsenic in solid materials are typically evaluated using indirect methods such as sequential leaching procedures or elemental analyses. As opposed to indirect methods, electronmicroprobe (EM) techniques can determine the form, associations and morphology of individual particles of arsenic-containing materials. This information is extremely beneficial in evaluating the mobility and treatment of arsenic in solid materials.

Case Study No. One – Arsenical Pesticide Manufacturing Site

Waste materials from the manufacture of sulfuric acid and lead arsenate were disposed of at this site. Subsequent disposal of animal by-products and hides caused reducing conditions which mobilized the arsenic resulting in arsenic(3+) and organic (methylated) arsenic in groundwater. The contaminated groundwater is confined to the outwash deposits of a buried valley aquifer and discharges to a surface water pond. Even though elevated concentrations of arsenic enter the pond from the groundwater (490 ∝g/L) and pore water concentrations in the pond sediments are high (1,700 ∝g/L), concentrations of arsenic in water discharging from the pond are very low (<5 – 12.2 ∝g/L). EM studies of the pond sediments indicated that the arsenic had been removed by adsorption to natural iron-containing minerals (e.g., biotite). The adsorption capacity of the sediments was measured to be 3,350 mg As/Kg of sediment.

Case Study No. Two – Wood Treating Site

At this site, wood was treated with zinc meta-arsenite ($ZnAs_2O_4$) and resulted in contaminated soil. Batch leaching studies were performed to determine the mobility of the arsenic in the soil. Results indicated “reverse” isotherms with lower adsorbed concentrations in the soil at higher water concentrations. EM studies of the soil revealed arsenic-containing (e.g., 0.5 percent) iron oxyhydroxide solid phases. In addition, small particles of arsenic oxide (63 percent arsenic) were identified. Overall, the arsenic is present as arsenic oxide, in solid-solution with iron oxyhydroxide and adsorbed to iron containing minerals. The “reverse” isotherms are caused by dissolution of arsenic phases followed by adsorption onto the iron-containing minerals.

Case Study No. Three – Smelter Site

During the smelting of mineral concentrates to produce lead, zinc and other metals, a variety of waste materials were produced including calcine and bag house dust. These wastes and the associated contaminated soil contained large concentrations of arsenic (up to 20,900 mg/Kg). One alternative to treat the contaminated soil and solid waste was through solidification/stabilization (S/S) techniques. EM analyses were used to identify the form of the arsenic in the original waste materials and contaminated soil and in the treated materials from the S/S processes. The evaluations were used to determine the type and quantity of S/S agent to use and to determine the effectiveness of the treatment process. The calcine waste contained arsenic in the form of arsenopyrite, scorodite and arsenic-bearing oxyhydroxides. Due to the potential instability of scorodite at elevated pH values (caused by the cement S/S agent), ferrous sulfate was added to the mixture. The iron (2+) assisted in removing any arsenic leached from the solidified waste by coprecipitation with iron oxyhydroxides. EM studies indicated this process was effective with abundant iron oxyhydroxides present with up to 0.7 percent arsenic in the solidified materials.

Iron Amendments as Adjuncts To Constrain Arsenic Solubility in a Marsh Environment

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Upon remediation/removal of Castro Marsh sediments, there will be remnant arsenic (As) concentrations of up to 100 mg/kg. As an adjunct to removal, an amendment was developed to mitigate any remnant soluble arsenic that may possibly migrate to Castro Creek.

Peat, Iron and Gypsum (PIG) envisioned to be emplaced at the base and on the downgradient face of the sediment excavation were investigated. One set of experiments using Zero Valent Iron (ZVI) was remarkably successful, resulting in removal of >99% of soluble arsenic from the system. Phase II of the study (upcoming) is designed to determine the particle size and mass of ZVI necessary to provide a long-term solution to soluble As in the Castro Marsh, and also to optimize costs.

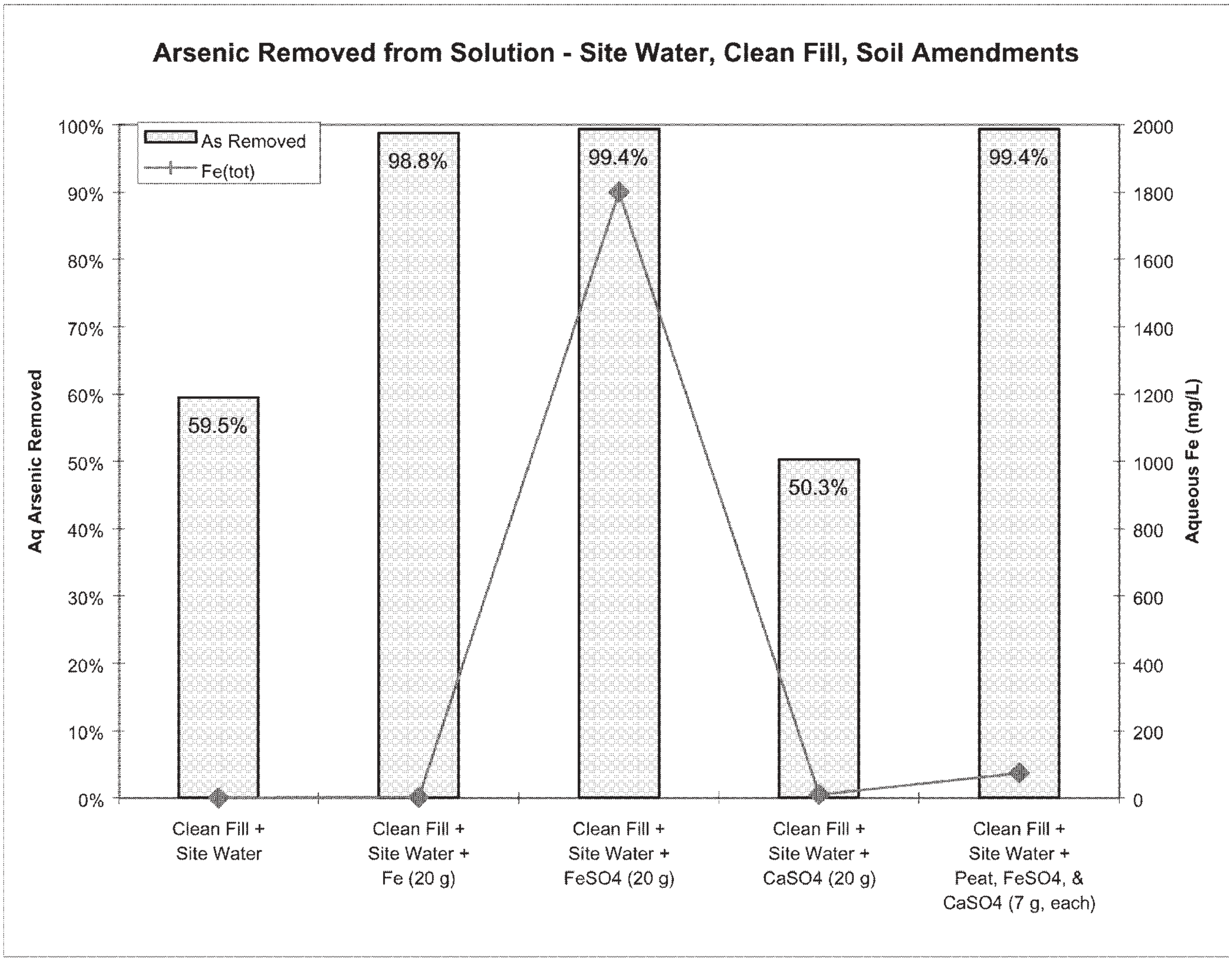
The release of arsenic into solution was investigated initially by combining site groundwater (~3 ppm arsenic), marsh soil (2000 – 3000 mg/kg arsenic), clean topsoil, and/or DI water with and without the addition of peat, iron, and/or gypsum as soil amendments. The soil amendments were incorporated into specific reaction vessels (along with the water and soil media) in order to determine if these amendments could augment the removal of arsenic from solution. In this experiment, three media combinations were used in the reaction vessels (either with or without amendments). They were:

1. Site Water + Clean Fill
2. Site Soil + DI Water
3. Site Soil + Site Water

Of these three combinations, only numbers 1 and 2 provided useful data, see Figure 1. The results from these two media combinations are summarized below.

1. Clean Fill + Site Water (no soil amendments) resulted in ~60 % removal of aqueous-phase As.
2. Clean Fill + Site Water + Iron (either Fe or $FeSO_4$) resulted in ~99 % removal of aqueous-phase As.
3. The amendments $CaSO_4$ and peat did little to remove As when combined with clean fill and site water.
4. Oxic and anoxic experiments produced comparable results for comparable media combinations.
5. The use of $FeSO_4$ as a soil amendment produces high levels of Fe and SO_4 in solution (1800 and 1400 mg/L, respectively).

Figure 1. Phase 1 Results for Site Water Combined with Clean Fill



Potential Environmental Consequences of Localized Arsenic Enrichment in Appalachian Basin Coals

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Coals from the Appalachian Basin in the eastern U.S. are locally quite enriched in arsenic. The highest arsenic concentrations for all U.S. coals, up to 2500 mg/kg on a whole coal basis, are found in Pennsylvanian bituminous coals of the Warrior Cahaba and Coosa coal fields, in northern Alabama. More generally, coals in the central and southern Appalachian Basin, may locally contain up to several hundred-ppm arsenic. Investigation by SEM, electron microprobe, and Laser-Ablation ICP Mass Spectroscopy demonstrates that the arsenic in Appalachian Basin coals is contained in the mineral pyrite. Pyrite in the Warrior Basin has up to 4.7 weight percent arsenic and is accompanied by elevated mercury, molybdenum and selenium contents.

To evaluate the possible environmental dispersion of arsenic from coals, three studies are underway. The first is in Alabama. Archived stream sediment samples from nearly 3000 sites in northern Alabama collected during the National Uranium Resource Evaluation (NURE) Program of the early 1970s were reanalyzed for arsenic. These data reveal that stream sediment arsenic is clearly enriched in Warrior Basin steam sediments (generally > 12ppm) compared to adjacent areas (<12ppm). A more geographically focused study of several abandoned coal mines documented that abandoned coal waste piles are a significant source of both acid and stream sediment arsenic. Stream waters from these sites are enriched in iron, aluminum, and zinc but not arsenic. However, stream sediments associated with these coal acid mine drainage sites did have elevated concentrations of arsenic ranging from 4 to 180 mg/kg with an arithmetic mean of 48 mg/kg. Streams adjacent to operating strip mines show no significant impact on either water or sediment.

A second study also involving reanalysis of NURE stream sediments in the eastern Kentucky coal field revealed detectible but much more subdued stream sediment arsenic enrichments than in Alabama. However, natural weathering of Devonian shale in rocks immediately west of the coal-mining region has produced significant stream sediment arsenic enrichments of up to 100 ppm.

The third study focused on West Virginia. NURE stream sediment geochemical data show elevated arsenic concentrations in the northwest portion of the state where coal mining does not occur. The arsenic-enriched area is south of a large concentration of coal-fired power plants. To test whether coal fly ash was a source of the observed stream sediment arsenic enrichment, a reservoir in the effected area was cored to determine the temporal evolution of arsenic in the catchment. Very preliminary results indicate an input of coal fly ash that peaked in about the mid 1970s, and has been declining since. The arsenic is accompanied by elevated contents of zinc and lead.

Arsenic Concentrations in Water at Mining Sites

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Hard rock mining occurs where metal concentrations are high. There are several different geological settings that are responsible for enrichment of metal concentration in ore bodies. Epithermal (volcanogenic massive sulfide deposits) and supergene (in hot, arid regions where surface waters tend to redistribute metals from an exposed porphyry system, concentrating it elsewhere) enrichments are two types of geological processes targeted for mining. Trace elements are usually elevated in these areas. Geographically these metal deposits coincide with the "Rim of Fire," the area of volcanism that rings the Pacific Ocean.

Predominately iron, magnesium, aluminum and calcium are the major cations of the minerals. Arsenic usually is present in trace amounts. Both mining processes and natural weathering of these materials releases the elements of minerals into the water phase. There are two main processes that transform the elements from solid phase to aqueous species. Biological mediated oxidation of sulfide minerals produces acid and iron in solution (Equation 1).

$$(1)\ FeS_2 + 7/2\ O_2 + H_2O \longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

The abiotic actions may further dissolve the solids, due to low pH and oxidation-reduction reactions *(Equations 2 & 3).*

$$(2)\ FeS_2 + 14\ Fe^{3+} + 8\ H_2O \longrightarrow Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

$$(3)\ Fe^{2+} + \breve{}\ O_2 + H^+ \longrightarrow Fe^{3+} + {}^{\circ}\ H_2O.$$

Under acidic conditions arsenic is co-dissolved with the major elements and transformed into an aqueous specie when pH is below 4.

The amount of arsenic in the water changes as the water interacts with its surroundings. Whether the changes in the water chemistry are due to interactions with geological materials, mining processes or water treatment, several trends have been observed and are consistent with known geochemical reactions. As the pH of the water is increased, iron and aluminum are precipitated out as oxy-hydroxides. Once above pH 5, because iron concentrations are usually 10–50 times those of arsenic, most of the arsenic is removed from the water and deposited with the iron oxy-hydroxide. A good deal of work has gone into investigating removal of arsenic with iron addition and reactions with much lower concentrations. My observations are that arsenic concentrations are reduced to below levels of concerns as a side benefit, because other elements (e.g., iron, copper, zinc, etc.) require more attention and arsenic is usually removed early on in the process to clean water.

After reviewing data at mine sites, I have observed that arsenic is:

1. Present at many sulfide deposits as a trace element;
2. Potentially in the water above level of concern, if pH is below 4; and
3. Removed from the water phase once pH goes above 5–6.

Arsenic and TRI in Select Nevada Gold Production Operations

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Gold deposits mined by Barrick Goldstrike Mines Inc. and Placer Dome America in Nevada are enriched in arsenic. Mining and processing of these deposits to recover gold currently creates a reporting requirement for arsenic and/or arsenic compounds under the Toxic Release Inventory (TRI) Program. Other pre-existing, media-specific environmental programs regulate processing, reclamation, and monitoring of all mined materials.

Arsenic values reported by these two Nevada mining interests for the calendar year 1999 TRI Program were calculated to be 217,397,023 pounds. Release categories of primary significance were surface impoundments, reflecting management of tailing in tailing impoundments, and other disposal reflecting management of waste rock in disposal areas.

This paper describes the occurrence of arsenic in our precious metals ores, how arsenic is accounted for and reported in the TRI Program, and the environmental protection technologies used at these U.S. gold mines to properly manage arsenic-bearing materials; thus minimizing releases of arsenic compounds to the environment.

3.2 Treatment and Disposal Session

This session was designed to promote discussion of the chemical fundamentals related to the treatment and disposal of arsenic wastes and to develop conclusions about the current state of knowledge and recommendations for further research. The session co-chairs were:

- *Paul Randall, Senior Chemical Engineer - U.S. EPA, NRMRL*
- *Robert Robins, Scientific Fellow - AquaMin Science Consortium International*
- *Christopher Impelliteri, Environmental Engineer - U.S. EPA, NRMRL*

The objective of the Treatment and Disposal Session was to address the following questions:

1) What are the long-term stability issues impacting the land disposal (i.e., on-site storage or landfills) of arsenic stabilized wastes?
2) How do current advances in molecular chemistry and leaching methodology impact the areas of arsenic treatment and disposal?

The highest priority research needs in advancing arsenic treatment and disposal were identified at the conclusion of the session.

Speaker Abstracts

The abstracts for presentations made during this session are located in section 3.2.2 of this report. The session began with an overview of arsenic treatment technologies. Several case studies of mining wastes sites were presented followed by several presentations on treatment technologies featuring phytoremediation, chemical fixation, cement stabilization, electrokinetics, and soil washing. The session participants then discussed the presentations and treatment and disposal issues in order to address the session questions. The discussion is reviewed in section 3.2.1.

3.2.1 Discussion Review

A variety of technologies can be used to treat arsenic-bearing materials. Table 3.2-1 presents these treatment technologies and the number of times they have been used to treat wastes and environmental media containing arsenic at full-, pilot-, and bench-scale levels. These data are taken from a recent “white paper” review by EPA and other investigators of technologies available to treat wastes and media containing arsenic and their usage.

These treatment technologies are used to stabilize and/or remove arsenic contamination in order to reduce its impact to the environment. Recycling uses pyrometallurgical or precipitation techniques that convert arsenic waste to a concentrated arsenic product. Vitrification, incineration, soil flushing, soil washing/acid extraction, electrokinetics, and phytoremediation are for the treatment of non-wastewaters. Chemical precipitation, ion exchange, carbon adsorption, membrane separation, foam floatation, and permeable reactive barriers are for the treatment of process wastewater, groundwater, and wellhead treatment. The following paragraphs present highlights and key points generated from the arsenic treatment and disposal case studies and current research efforts.

A large amount of arsenic contaminated media is generated from mining activities. A variety of treatment technologies are being developed and employed at mines, mining waste sites, and impacted environments to treat this material for beneficial reuse. For example, options for managing 265,000 tons of arsenic trioxide-bearing dust stored underground at the Giant Mine site, in Yellowknife, Northwest Territories, Canada are being assessed. At the Newmont gold mining site in Minahasa Raya, Indonesia, mine tailings are treated prior to submarine disposal on the sea floor.

EPA’s Mine Waste Technology Program researches the removal of arsenic from waters impacted by the mining industry. This program is evaluating a mineral-like (mineral-based) precipitation process from MSE Technology Applications Inc. (MSE), which compares favorably to other conventional technologies (i.e., alumina adsorption and ferrihydrite adsorption) for arsenic removal and stabilization of arsenic byproducts. Mineral-like precipitation along with reductive precipitation and catalyzed cementation are also effective in removing arsenic from groundwater.

The University of Florida discovered that the Brake fern is an extremely efficient arsenic-hyperaccumulating plant. The plant has a large capacity to uptake arsenic from the soil and translocate it to the aboveground biomass (i.e., fronds) in

Table 3.2-1 Frequency of Use of Treatment Technologies Used To Treat Wastes And Environmental Media Containing Arsenic

Treatment Technology	Full-Scale	Pilot-Scale	Bench-Scale
Solidification/stabilization	69	2	
Precipitation and Oxidation	35	10	
Adsorption	9	5	
Recycling	9	1	
Ion Exchange	5	0	
Vitrification	5	10	
Soil Washing	4	3	2
Permeable Reactive Barriers	2	0	2
Soil Flushing	2	0	
Electrokinetics	1	1	2
Membrane Filtration	1	23	6
Phytoremediation	0	0	2

a short period of time. The arsenic-rich biomass would then be treated as a hazardous waste. Brake ferns are tropical/subtropical plants that are hardy, sun tolerant, and easy to reproduce. They show great potential in phytoremediating arsenic contaminated sites in the southeastern U.S.

Southern Company is involved in several arsenic remediation projects. They are currently investigating in-situ chemical fixation. Batch and column tests were conducted with various mixtures of soil, water and reagents. Binding reagents/formulations used were: ferrous sulfate, ferrous sulfate and potassium permanganate, and ferrous sulfate, potassium permanganate, and calcium carbonate. Although all treated soils passed the Toxicity Characteristic Leaching Procedure, SW846 Method 1311 (TCLP), only soils treated with ferrous sulfate passed the Synthetic Precipitation Leaching Procedure (SPLP). Southern Company is also evaluating variables that influence arsenic mobility, as well as conducting an economic analysis of arsenic remediation treatment methods. Additional information can be found at the following website: www.eng.fsu.edu/departments/civil/research/arsenicremedia/index.htm.

Researchers at Victoria University in Australia treated arsenic wastes with several S/S formulations. They evaluated the effectiveness of treatment by three different leach tests. Their investigation showed that S/S formulations containing exclusively Portland cement were the most effective. Formulations incorporating additional iron were the least effective in preventing arsenic leaching from the treated waste. Clemson University is currently developing an inexpensive magnetic filtration/adsorption technology that can purify water supplies that may be contaminated with arsenic.

DuPont has developed a phased approach for evaluating the use of soil washing for treating arsenic contaminated soils. Results from a feasibility study demonstrated that adequate leaching was possible using soil washing with sodium hydroxide. The arsenate in the soil washing leachate was then sorbed onto surfactant-modified zeolite (SMZ) under a research program conducted by Los Alamos National Laboratory.

Long-term Stability

The technologies listed in the previous subsection have been used to treat wastes and environmental media containing arsenic; however, many of the following statements refer to the treatment of arsenic-bearing wastes using S/S.

Test Methods: Many test methods can predict the performance of stabilized arsenic wastes. Some of the more commonly used methods include the TCLP, SPLP, and Multiple Extraction Procedure (MEP). There are several issues associated with test methods used to demonstrate the long-term stability of arsenic wastes. First, long-term can be used to refer to 10, 20, 100, or 1000 years; thus, a specific evaluation time period needs to be defined before a project begins. While some test methods can attempt to "compress" a timeframe, there are problems associated with accelerated testing. The effects of time on the stability of the treated wastes (i.e., how arsenic in the waste gets bound to the material over time) can be difficult to predict with these test methods.

The regulatory test method used to determine the suitability of applying stabilized arsenic wastes into a landfill is the TCLP. Several concerns have been raised about the use of TCLP and the need for EPA to identify other tests that can simulate long-term performance. Currently, there is no regulatory protocol that accurately simulates long-term stability. There is a need for EPA to identify and provide test methods along with guidance protocols, which are not TCLP-based.

Follow-up from this workshop might include establishing a work group to investigate various leach methods that demonstrate long-term stability. Dr. David Kosson at Vanderbilt University is working with a multinational group investigating various leach procedures. This group is an important knowledge base that can be used as a valuable resource. New guidance protocols need to be established to address what works and does not work.

Data consistency can be challenging; comparing different test results from different sites can lead to misleading information and conclusions. Test results can also have more than one use. SPLP, a commonly used leach test method, does not have regulatory requirements, and there are no associated pass/fail criteria. However, SPLP results given in units of concentration can be used as a performance specification for determining releases of stabilized arsenic wastes back into the environment. The MEP is used to monitor long-term performance/stability and is typically not used as a field specification. MEP results can show how arsenic speciation evolves over time. Soil tests should be conducted in order to understand the soil characteristics of the site.

While long-term stability is an important concern, short-term effectiveness must also be considered. Short-term effectiveness is determined through monitoring and periodic sampling. For example, during S/S, it is important to show treatment effectiveness as soon as possible, requiring quick turnaround test results (i.e., in days).

Use of Models and Analogs: Models that predict thermodynamic and kinetic variables can also simulate long-term conditions and can be used to determine if and when the arsenic becomes unstable and can leach into the environment. Archiving samples at the start of the project for later testing for stability and leaching is another way of confirming technology effectiveness.

The use of analogs, such as ancient concrete made with arsenic rich ash and other past markers of arsenic stability, should be examined as a method for demonstrating the potential effectiveness of S/S treatment. Historic mine tailing piles can be used as a source for this kind of information. In Montana, core samples have been collected and groundwater wells installed in old mine tailing piles at abandoned mine sites.

Disposal Concerns: It is important to consider the ultimate disposal of arsenic wastes; particularly, future exposure to leaching agents. For example, decision makers remediating arsenic sites should, when possible, avoid placing stabilized wastes in saturated zones. However, this may be difficult in areas exhibiting shallow water tables, such as Florida.

In response to the posed question "How are ideal treatment conditions maintained in order to maintain long-term stability?" capping arsenic contaminated sites is a viable consideration. Common practice has shown that treated material above a certain action level is typically capped. There are many capping materials available now on the market. In addition, many manufacturing by-products or off-products also make good capping materials. Capping specifications may be an important issue when mining is eventually halted in Butte, Montana.

Current Advances

In order to understand how a technology works, it is important to understand how the contaminant reacts to its location (e.g., biogeochemistry of the site). In the research and development arena, advances in techniques and instrumentation have allowed for greater site investigation. For example, molecular chemistry and X-ray diffraction often provide a sound understanding of material microstructure. However, these advances have not yet been applied to field performance specifications.

Currently, regulations do not distinguish between As(III) and As(V) species. Historically, As(III) has been considered more toxic than As(V), and treatment strategies have focused on converting As(III) to As(V) which is more amenable to conventional treatment technologies. Arsenic toxicity is not well understood. Practitioners are still investigating the toxicity of the different speciated forms.

3.2.1.1 Summary of Important Conclusions from the Treatment and Disposal Session

Long-term Stability

There is a need to:

1. Establish a regulatory protocol to simulate long-term conditions/performance.
2. Examine other protocols for simulating long-term conditions/performance including internationally applied methods.
3. Examine analogs that would simulate long-term conditions/performance (i.e., ancient concrete made with arsenic rich ash, old mine tailing piles).
4. Examine mineral phases as arsenic speciation changes with time.
5. Consider the environment in which the waste/media will be ultimately disposed.
6. Consider both thermodynamics and kinetic issues with respect to long-term stability.

Current Advances

The EPA should:

1. Continue to develop and promote technology transfer
2. Develop and maintain a web-based bulletin board to facilitate the transfer of information
3. Form a partnership/consortium of stakeholders interested in arsenic-related issues
4. Establish cooperative links and partnerships with outside experts in academia, government agencies and public sector groups, and conduct more pilot- and field-scale demonstration projects.

3.2.1.2 Recommendations or Research Needs from the Treatment and Disposal Session

Long-term Stability

1. A potential outcome from this work group is a consensus document, which details the types of methods that are needed to demonstrate long-term stability for a waste.
2. EPA should revisit testing guidance and protocols.
3. EPA might consider conducting a comparative laboratory study of various test methods under a large number of conditions.

Current Advances

1. Continue to research molecular arsenic chemistry, and leaching mechanisms, in order to develop a better understanding of site characteristics and applicable treatment technologies.

2. Develop a better understanding of the following arsenic treatment and disposal research issues: arsenic chemistry, biogeochemistry, long-term stability, chemical speciation, microstructure/mineralogy, biological processes impacting the mobilization of arsenic: bacteria, fungi, and plants, phytoremediation mechanisms, and arsenic toxicity.

3.2.2 *Treatment and Disposal Session Speaker Abstracts*

Speaker abstracts from the Treatment and Disposal session are presented in this section.

Treatment Technologies for Wastes and Environmental Media Containing Arsenic

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Treatment of industrial wastes and environmental media containing arsenic has been conducted using a variety of technologies. This presentation will discuss the contents of a white paper that summarizes technologies available to treat wastes and media containing arsenic. The purpose of the white paper is to provide background material for a discussion of: (1) the current state of treatment of wastes and environmental media containing arsenic, and (2) areas where additional research may yield significant benefits.

The paper describes in broad terms the sources of waste and wastewater containing arsenic, with a focus on Resource Conservation and Recovery Act (RCRA) hazardous wastes, mining waste, and industrial wastewaters regulated under Clean Water Act (CWA) effluent guidelines. The treatment technologies selected for discussion include those most commonly used and innovative technologies that appear to offer promising alternatives. The technologies include solidification/stabilization, recycling, vitrification, incineration, in situ soil flushing, soil washing/acid extraction, electrokinetics, and phytoremediation for the treatment of non-wastewaters and chemical precipitation, ion exchange, carbon adsorption, membrane separation, foam flotation, and permeable reactive barriers for the treatment of wastewater, groundwater, and drinking water.

The paper summarizes the following information for each selected technology:

- Brief technology description
- How the technology is used for treatment of wastes and media containing arsenic
- Status of the technology and scale of its implementation (bench, pilot, or full)
- Vendors that have used the technology to treat wastes or media containing arsenic
- Available performance data (amount/type of wastes or media treated, and results of analyses for total and leach able arsenic concentrations in untreated and treated waste)
- Cost data for arsenic waste

The paper also compares the expected applicability and effectiveness of the selected technologies based on the type of wastes or media treated, the concentration of arsenic, the presence of other contaminants that may interfere with treatment, and other factors.

For more information about treatment technologies, see the following web site: http://www.clu-in.org/arsenic

Treatment Options for Arsenic Trioxide Bearing Dust at the Giant Mine, Yellowknife, Northwest Territories, Canada

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Background

The Giant Mine, located in Yellowknife, Northwest Territories, Canada, has been operating as a gold mine since 1948. Refractory ore containing arsenopyrite was mined from underground and roasted to facilitate the recovery of gold. The roasting process produced arsenic trioxide bearing dust as a waste product, which was placed into underground storage chambers at a rate of 10–13 tons per day. Fifty years of operation have resulted in approximately 265,000 tons of arsenic trioxide bearing dust, stored in 15 underground chambers.

In 1999, Royal Oak Mines, Inc., the owner of Giant Mine, was placed in receivership and the property was purchased by an existing Yellowknife mine operator. As a result, roasting operations were shut down and Giant Mine ore is now being processed at another local mine. In order to effect the sale, the federal government assumed liability for the pre-existing conditions of the site, including the arsenic trioxide bearing dust stored underground. The mine is located within city limits, and potentially significant environmental, public health and safety concerns exist.

Project Management

The Department of Indian Affairs and Northern Development, in its role as regulator and project manager, has been working independently and with the mine's current owner to assess options for managing the dust stored underground. Research has been initiated into: the hydrogeology and geochemistry of the mine; options for permanent underground storage (freezing technology, in-situ stabilization, preferential groundwater pathways); methods of extracting dust from the underground chambers; material re-processing for arsenic and gold recovery (hot water leach or sublimation); arsenic chemical stabilization (ferric arsenate using autoclave); and solidification/encapsulation (glass, bitumen or cement). By October 2001, the MacKenzie Valley Land and Water Board requires the submission of a Project Description outlining an arsenic trioxide management plan for the dust stored underground.

This presentation will examine the activities undertaken and issues faced in evaluating treatment processes for the Giant Mine arsenic trioxide project.

Removing Arsenic for Mining Industry Waters, Treatability Studies, and the EPA Mine Waste Program

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Three technologies were demonstrated and evaluated for arsenic removal and stabilization of arsenic byproducts. Each technology was evaluated treating two separate industrial waste water streams. The baseline technology was ferrihydrite precipitation with concurrent adsorption of arsenic onto the ferrihydrite surface. The two innovative technologies demonstrated were: 1) an integrated adsorption membrane filtration process that used activated alumina and micro filtration; and 2) a process called mineral like precipitation. Each of the technologies was evaluated for arsenic removal capabilities, long term stabilities of byproducts produced, and process costs. The overall results will be presented and discussed. MSE Technology Applications, Inc. managed the project and demonstrated these technologies through the U.S. Department of Energy (DOE) and Environmental Protection Agency's Mine Waste Technology Program under Interagency Agreement Number DW89938513-01-0. Work was conducted through the DOE Federal Energy Technology Center at the Western Environmental Technology Office under DOE Contract Number DE-AC22-96EW96405.

Characterization of Arsenic in Refractory Gold Ores Roasting-Cyanidation Processing

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PT Newmont Minahasa Raya, Indonesia operates a refractory gold-ore treatment plant. The deposit is predominately refractory in nature. Extensive studies were performed to develop a process for gold recovery as well as detoxification. The plant operation incorporates whole ore roasting followed by conventional cyanidation and carbon adsorption. The tailings are treated to remove arsenic and other deleterious elements before disposal by submarine tailings placement on the sea floor.

Development of the process for Minahasa was based on a detailed understanding of the ore characteristics. The gold is finely disseminated and associated with fine-grained pyrite enriched in arsenic. A significant fraction of this As-rich sulfide is fine-grained pyrite and is intimately intergrown with gangue minerals. Two different refractory ore types in the deposit were characterized: siliceous pyritic and carbonate pyritic. Blending of siliceous and carbonate ores as roaster feed gave two advantages: (1) the sulfur dioxide generated from roasting of the sulfides was captured by the decomposition products of carbonate minerals, especially dolomite, and (2) the fixation of arsenic in calcine during roasting.

In the roasting reaction, arsenic-bearing pyrite was oxidized to SO_2 and As_2O_5. With decomposition of dolomite, arsenic was fixed as magnesium (or calcium) arsenate in the calcine. Concentrations of arsenic in the gas stream directly after roasting measured from 1 to 10 mg/Nm^3, (equated as 0.03 to 0.30 % of the feed arsenic). The roaster off-gas was treated in a wet scrubber and over 99.9 % of the arsenic was removed. The concentration of arsenic in the scrubber outlet gas stream was below the detection limit. The soluble arsenic concentration in the calcine varied depending on the ore minerals and roaster temperature. Plant monitoring indicated the soluble arsenic in the roaster products decreased with increasing roaster temperature. Extensive studies in the laboratory and plant trials were performed to understand the chemistry and optimize the operation system for both gold recovery and arsenic fixation.

In the detoxification circuit, the low concentration of soluble arsenic was precipitated with ferrous sulfate. Ferrous sulfate is not the normal reagent of choice for precipitation of arsenic; ferric salt is more often used. However, the process being operated is in alkaline slurry. With due regard for the upstream effect of plant operations on the arsenic chemistry, the success of this treatment method can be explained by reference to well documented principles of precipitation of arsenic (V) compounds. Based on thermodynamic considerations and test results, a minimum solubility for ferrous arsenic at pH ~8 has been reported. In consideration of an operating plant, ferrous sulfate has two distinct advantages over ferric salts. Ferrous sulfate is cheaper on an available iron basis and is easier to handle, as it is less corrosive and toxic.

Tailings after detoxification are de-aerated and discharged on the sea floor below the natural ocean thermocline. The long-term stability of metal ions is a concern, especially arsenic in seawater. Extensive large-scale static leach tests on tailings in seawater have been studied. The static leach tests closely simulated the fluid dynamics of submarine disposal, and provided an indication of the long-term stability of the tailings deposited on the ocean floor. Since the plant startup, monitoring work, using sea floor coring methods, measurement of chemistry and turbidity in the water column and measurement of heavy metals uptake in the predominate fish species, has confirmed that the submarine tailing placement system is successful. No measurable changes in the seawater quality have been detected.

Phytoremediation of Arsenic Contaminated Sites Using Brake Fern Hyperaccumulator

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Arsenic is of great environmental concern due to its extensive contamination and carcinogenic toxicity. There is a great need for reliable and cost-effective technologies capable of reducing arsenic contaminated sites to environmentally acceptable levels. Phytoremediation, a plant-based green technology, has been successfully used to remove contaminants from soils. However, no arsenic hyperaccumulating plant was available until recently. We have discovered an extremely efficient arsenic-hyperaccumulating plant, Brake fern. A number of plant samples were collected from an arsenic contaminated soil and analyzed for arsenic concentrations. In addition, plants after growing in artificially contaminated soils for up to 8 weeks in a greenhouse were harvested and analyzed for arsenic concentrations. The highest arsenic concentration in the aboveground biomass in plants growing in the arsenic contaminated soil in the field was 7,500 ppm, with the arsenic concentrations in aboveground biomass being up to 200 times greater than those of soils. After 4 weeks, the arsenic concentration reached over 2.3% in the aboveground biomass of the plant growing in the soil spiked with 500 ppm arsenic. Obviously, this plant has an extraordinary capability to uptake a large quantity of arsenic from soils and translocate it to aboveground biomass (up to 90%). In addition to being effective in taking up a large amount of arsenic into its aboveground biomass in a relatively short period of time from soils containing arsenic of different concentrations and species, Brake fern also has many desirable attributes as a hyperaccumulating plant. This plant thus has a great potential to be used for phytoremediating arsenic contaminated sites.

In-Situ Chemical Fixation for Arsenic Remediation and Arsenic Mobility Studies

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The Electric Power Research Institute and the Southern Company are engaged in work that can significantly reduce arsenic risk to the environment. In-situ chemical fixation (ISCF) for remediation and factors affecting arsenic mobility are under investigation.

ISCF, an emerging technology, can render arsenic immobile at a reasonable cost. In ISCF, a liquid reagent (such as ferrous sulfate) is applied to contaminated soil or aquifer media in place. Processes such as adsorption and precipitation greatly reduce the solubility of the arsenic. The University of Alabama Department of Geological Sciences performed a series of batch treatability studies using various mixtures of soil, water, and reagents, followed by optimized column studies. Results from soil columns treated with ferrous sulfate showed dramatic decreases in leachable arsenic (both TCLP and SPLP) as compared to untreated control columns; specifically, total leachable arsenic was reduced by a factor of 200 to 1000 in the column studies. A field demonstration is currently underway to determine the effectiveness of ISCF in the field. Costs are expected to range from $20 to $40 per cubic yard treated.

The published arsenic literature indicates that many variables may influence arsenic mobility in soil and aquifer media. Significant parameters include pH, redox potential, carbon content, iron and other metal oxides and hydroxides, anion and cation exchange capacity, arsenic concentration, and grain-size distribution (particularly fines). These parameters will be tested in both batch and column studies in the laboratory, and the relative importance of each variable will be determined. In addition, distribution coefficients (Kds) necessary for fate and transport modeling will be calculated.

Arsenic Contamination in Soil and Groundwater: Review of Remediation Results

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Arsenic contamination is a prevalent problem throughout the world, including countries such as Bangladesh and the U.S. These problems exist in other countries due to naturally occurring arsenic and past use of arsenic for pesticides, herbicides, mining wastes and other miscellaneous uses.

Water and soil treatment methods exist to clean up these anthropogenic or natural sources of arsenic. Several successful methods for soil remediation consist of excavation, soil solidification/stabilization, and soil flushing/washing. Successful water treatment methods for arsenic consist of iron coprecipitation with soil flushing, lime precipitation, activated alumina and reverse osmosis. Promising technologies, which can be utilized for both soil and water contamination, are phyroremediation and electrokinetics.

In order to evaluate existing remediation methods, an economic analysis and performance evaluation was conducted. In addition, the final document entitled “Comparison and Economic Analysis of Arsenic Remediation Methods Used in Soil and Groundwater” discussed case histories utilizing various technologies as well as the initiation of a website for arsenic remediation. This website can be found on the FAMU-FSU College of Engineering webpage.

The Cement Stabilization and Leaching of Arsenic

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Arsenic has found widespread use in agriculture and industry to control a variety of insect and fungicidal pests. Most of these uses have been discontinued, but residues from such activities, together with the ongoing generation of arsenic wastes from the smelting of various ores, have left a legacy of a large number of arsenic-contaminated sites. To date a wide range of arsenic stabilization formulations have been used in an attempt to successfully fix arsenic. These have included mixing the arsenic waste with:

- Cement
- Lime
- Aluminum or iron hydroxides
- Silicates
- Fly ash
- Or combinations thereof.

Despite the research that has been conducted, it is difficult at present to gauge just which of the stabilization formulations is the most effective. This is due to a number of factors that include:

- The diverse range of arsenic compounds and oxidation states that can be encountered as arsenic waste
- The varying additive-to-waste ratios that have been utilized
- The different leaching tests which researchers have used to access the leachability of the treated waste

In this study, arsenic compounds in both of the common oxidation states have been stabilized using various cement-based formulations. Each of the formulations investigated contained near identical arsenic loadings and their success was determined by utilizing a number of leaching tests, which have included:

- Bottle leach tests
- Sequential leach tests
- Column leach tests

The results of this research will lead to more appropriate waste disposal management by:

1) Providing conclusive results on the success of a range of solidification/stabilization procedures, which will be applicable to the hundreds of tonnes of arsenic containing wastes,
2) Comparing and contrasting the results obtained from the numerous leach tests.

Characterization and Treatment of Arsenic Contaminated Soils: The DuPont Experience

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Thorough characterization of complex soil matrices can provide information on chemical speciation, mobility, and distribution through the soil, thus enabling the project team to develop the most technically feasible, cost effective technologies that are protective of human health and the environment. Soil characterization studies can provide the fundamental information necessary to consider the feasible options for a site. The screening and final selection of remediation technology is impacted by many factors such as regulations, clean-up goals, final site end-use and other project strategies/goals. Scientific and engineering data generated through soil characterization can be very useful in guiding the technology screening and development process. Based on a solid foundation of information, carefully designed treatability and/or field pilot testing can be used to evaluate promising remediation technologies. Treatability studies should be used to examine the technology-specific design and operating conditions and develop preliminary cost/performance data.

This presentation will highlight a previous case study involving soil characterization and treatment of arsenic contaminated soils (Legiec et al., 1997). Detailed soil characterization studies included particle size distribution, sequential chemical soil extraction, leaching and mobility testing, scanning electron microscopy, and XRF analyses. Results indicated that the arsenic was primarily associated with the organic fraction and the iron oxide/manganese oxide fraction of the soil. A phased approach was developed to evaluate the feasibility of arsenic leaching. This preliminary treatability study demonstrated that alkaline leaching of arsenic was possible and provided information towards scale-up of the process.

Finally, a brief overview will be provided to highlight the current research and competency building activities within DuPont, such as metals fate and transport, including biogeochemical reactions, biogeochemical modeling, and treatment.

Reference

Legiec, I.A.; Griffin, L.P.; Walling, P.D.; Breske Jr., T.C.; Angelo, M.S.; Isaacson, R.S., and Lanza, M. B. “DuPont Soil Washing Technology Program and Treatment of Arsenic Contaminated Soils”, Environmental Progress, Vol. 16, No. 1, Spring 1997, pp. 29-34.

Sorption of Arsenate from Soil-Washing Leachate by Surfactant-Modified Zeolite

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Surfactant-Modified Zeolite

Surfactant-modified zeolite (SMZ) is an effective and economical sorbent for nonpolar organics, inorganic anions, and inorganic cations dissolved in water (Haggerty and Bowman, 1994; Bowman et al., 1995). Due to its low unit cost of about $400 per ton, SMZ is an attractive alternative to activated carbon and ion exchange resins. Oxyanions that are sorbed by SMZ include chromate, nitrate, selenate and sulfate (Bowman et al., 1995; Li et al., 1998). SMZ was tested in batch studies to remove arsenate from a leachate generated during a soil-washing treatability study. The SMZ was prepared from a pure clinoptilolite zeolite from the St. Cloud mine in Winston, New Mexico. The raw zeolite was treated with hexadecyltrimethylammonium bromide (HDTMA-Br) surfactant to a level of 150 meq/kg (42.6 g HDTMA per kg of zeolite). The surfactant forms a stable organophilic coating on the zeolite surface. Further details on the preparation and properties of SMZ are found in Haggerty and Bowman (1994).

Soil Leachate Characteristics and Treatment

Soil washing is an ex-situ remediation treatment technology that utilizes wet classification, mechanical separation, and chemical extraction processes to remove contamination from soil. Byproducts include fluids or a concentrated residue containing high concentrations of contaminants, fine particulates, and organic carbon. A synthetic soil leachate was prepared from Kennet “A” glacial till-type soil. Clean soil (5 x 150 g) was leached with 750 ml of 0.1N NaOH solution (pH >14) to yield a humate-rich solution. The leachate fractions were combined and diluted to 6 L with deionized water, filtered, then spiked with $As_2O_5^{2-}$ as the sodium salt to approximately 500 mg/L as arsenic. Batch isotherms using variable leachate:SMZ ratios from 40:1 to 4:1 were run at pH 12 and two temperatures, 25°C and 15°C, respectively. The supernatants and solids were analyzed using EPA methods 7060 (dissolved and total solution arsenic), EPA Method 7060 with digestion (total arsenic-solid fraction), and EPA Method 9060 (TOC).

Results

Dissolved versus total arsenic results were similar. At each temperature, sorption reached a plateau or maximum, then decreased at the highest solution concentration (corresponding to the lowest amount of zeolite added, 2.5 g). Sorption maxima of 5540 mg of arsenic per kg of SMZ were observed at 25°C, and 3150 mg at 15°C. Total arsenate recoveries varied from 74% to 125%. SMZ effectively decolorized the leachate solutions, proportional to the amount of SMZ. The maximum TOC removed varied from 94 to 97 percent. The linearized form of the Langmuir equation was fitted to the As data, with a coefficient of determination of 0.997 for the 25°C batch (0.906 for the 15°C batch). Sorption of arsenate likely results from two mechanisms: anion exchange with bromide on the external portion of the surfactant bilayer on the zeolite surface, and adsorption of organically complexed arsenate via hydrophobic interactions with the surfactant moiety at the zeolite surface.

References

Haggerty, G.M, Bowman, R.S., 1994. ES&T, 28, 452-458.

Bowman, R.S., Haggerty, G.M., Neel., D., Flynn, M., 1995. ACS Symposium Series 594, pp.54-64.

Li, Z., Anghel, I., and Bowman, R.S., 1998. J. Dispersion Science and Technology, 19(6&7), 843-857.

Adsorption and Nanoscale Magnetic Separation of Heavy Metals from Water

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One of the primary needs of mankind over the next millennium is improved and less expensive water treatment methods. Recent efforts by the U.S. Environmental Protection Agency (EPA) have focused on reducing the concentration levels of arsenic in drinking and wastewater treatment plants. Thus we are developing a new and inexpensive magnetic filtration/adsorption technology for purifying water supplies that is not only in line with mankind's future needs, but may also alleviate the problems with arsenic identified by EPA. This nanolevel high gradient magnetic separation (HGMS) process is based on the use of a supported surface complex adsorbent such as natural magnetite ($FeO \cdot Fe_2O_3$) in a fixed bed mode (Kochen and Navratil). Due to its ferromagnetic property, magnetite can be used not only as an adsorbent for removing toxic metals from solution, but also as a magnetically energizable element for attracting and retaining paramagnetic nanoparticles, thus removing them from solution. In such a system, the inexpensive magnetite serves as a metal ion adsorbent, high gradient magnetic filter, or both, depending on the characteristics of the aqueous stream to be purified.

Reference

Kochen, R.L. and Navratil, J.D. "Removal of Radioactive Materials and Heavy Metals From Water Using Magnetic Resin," U. S. Patent 5,595,666.

3.3 Arsenic Chemistry Session

This session was designed to allow further discussion of the chemical fundamentals related to arsenic chemistry, speciation, and analytical issues, and to develop conclusions about the current state of knowledge and recommendations for further research. The session co-chairs were:

- *Robert Ford, Environmental Scientist - U.S. EPA, NRMRL*
- *Kirk Nordstrom, Chemist - USGS*

The objective of the Arsenic Chemistry session was to address three general questions:

1) Is our knowledge of arsenic speciation and transformation adequate to identify pathways and routes of mobility?
2) Are current collection, preservation, and analytical techniques sufficient for defining arsenic chemistry in natural and engineered systems?
3) Are existing leach procedures adequate for assessing the stability of arsenic-bearing waste materials?

Speaker Abstracts

Speaker presentations were first made for the subject areas of arsenic (bio)geochemistry, analytical characterization of aqueous and solid phase arsenic, and leach procedures for arsenic solid waste. The abstracts for these presentations are located in section 3.3.2 of this report. The presentations and arsenic chemistry issues were then discussed by the session participants in order to address the three session questions. The discussion is reviewed in section 3.3.1.

3.3.1 Discussion Review

Identifying Pathways and Routes of Mobility

Geochemical Factors: A field case study was reviewed to highlight the importance of understanding the relationships between chemical cycling of elements such as carbon, iron, nitrogen and sulfur and the redox speciation of arsenic. The distribution of arsenic species [As(III) and As(V)] and aqueous and solid phase iron between lake sediments and lake water was investigated. Data showed that conversion of As(V) to As(III) was spatially and temporally correlated with zones of nitrate (NO_3) depletion (anoxic or reducing zones). Data also showed that either NO_3 or As(III) would dominate; they do not coexist. Spatial and temporal trends in NO_3 and As(III)/As(V) concentrations indicated that NO_3 (not O_2) was the primary oxidant of As(III). In addition, in this environment it was possible to predict the partitioning of arsenic to hydrous iron oxides precipitated in the water column using published sorption constants. However, biological activity can disrupt the chemical equilibrium.

This study determined that the aqueous and solid phase arsenic speciation was mediated by reaction with nitrate and iron precipitation-dissolution processes, respectively, in anoxic lake water. These observations are significant for waterlogged agricultural soils (oxygen deficient), where arsenic may remain in an oxidized and less mobile state due to the influence of high concentrations of NO_3. However, elevated phosphate levels introduced during agricultural operations will also influence arsenic mobility. Therefore, as part of any effort to understand arsenic fate and transport on a watershed scale, we need to consider the influence of nutrients such as nitrate in addition to the chemical relationships with iron and sulfur compounds that are commonly assumed.

Microbial Factors: The role of the microbial community in arsenic cycling is in the early stages of evaluation. The specific microbial community may have a large impact, but it is hard to extrapolate to a large-scale system. There is a need for better ways of measuring microbial activity in the field. Currently, redox parameters and carbon dioxide production are utilized, but these parameters are not enough to fully characterize the microbial activity. A “leave in place” measuring system would be very useful. Also, it may be possible to use RNA for identification of the microbial community. Our current scientific understanding indicates that microbial communities can exert both a direct and indirect influence on arsenic chemistry, but there is no quantitative foundation to aid prediction of this influence on spatial or temporal scales relevant to site assessment.

Modeling Fate and Transport: Applications for modeling chemical controls on arsenic solubility through solid phase precipitation were reviewed. Thermochemical analysis was used as a tool to evaluate potential routes for optimizing arsenic immobilization in treated solid wastes. Model chemical systems were constructed using relevant salt solutions in equilibrium with atmospheric carbon dioxide and assuming possible equilibrium with one or more minerals. The hypothetical chemical systems were allowed to approach equilibrium based on constraints imposed by the free energies of formation for all components, phase rule restrictions, and the balance of mass and charge. Arsenic solubility was evaluated as a function of various system chemical parameters. This analysis did not incorporate adsorption to other solids present at equilibrium as a possible control on arsenic solubility, and thus should be viewed as an initial approximation. The point was raised that many chemical equilibrium models do not have an adequate database that includes solubility data for relevant arsenic-bearing solids.

Computational chemical models can be used to help understand arsenic fate and transport. Two models that were discussed included MINTEQA2 and PHREEQC, which are supported by EPA and USGS, respectively. The MINTEQA2 model is a geochemical equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in natural aqueous systems, and the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases under a variety of conditions. However, MINTEQA2 does not handle species transport problems. PHREEQC is also a geochemical equilibrium model that can perform one-dimensional transport calculations and is also used for speciation, batch-reaction, and inverse geochemical calculations. It was emphasized that the user needs to determine what questions should be answered before selecting and applying a model. Also, data inputs need to be defined including relevant aqueous and solid phase parameters and the acceptable level of uncertainty in results.

One of the greatest shortcomings identified with the use of off-the-shelf computational chemical models was the inadequacies and inconsistencies in the associated database. For instance, a model database may lack data required to account for reactions between contaminants of concern and common aqueous and solid phase constituents in soil and sediment systems. Therefore, the users may have to add data or customize the model for their application. There is no “canned” package for arsenic modeling. In addition, existing model databases may need to be updated or revised to include more current thermochemical data. While most databases are generally complete with respect to the description of aqueous speciation and solid phase precipitation reactions, there is much less consistency in the data available to support calculation of reactions describing sorption of aqueous constituents to solid surfaces. The database associated with PHREEQC is considered to be good, but the USGS needs additional funding to improve this database. MINTEQA2 is a regulatory accepted model, but it is currently not well maintained by EPA and should be used with caution.

There is no scientific consensus on the appropriate use of existing models to quantitatively describe sorption reactions in complex systems. Data available in the literature may be derived either from: 1) whole soil/sediment experiments or 2) studies that approximate system behavior by employing a predominant reactive solid phase (e.g. an iron oxide mineral). Data derived using the first approach may result in the most reliable site-specific data, provided experiments are conducted on a statistically representative set of solid phase samples. This will likely require added time and cost associated with site or system assessment. There are much more data available in the literature derived using the second approach, but the application of these data to heterogeneous media (soils and sediments) is not reliable. It is recommended that the user employ site-specific conditional constants and evaluate model results in the context of soil/sediment characterization data, e.g., mineralogy, organic matter content, surface area. Since soils/sediments and engineered treatment systems rarely achieve a state of chemical equilibrium, it is also recommended that the user consider the kinetics of chemical reactions relevant to contaminant speciation in their system.

Quantifying Arsenic Exposure and Uptake: A case study was presented to evaluate issues of site characterization and risk assessment with respect to the potential exposure to and uptake of arsenic from anthropogenic sources. Principal components analysis was used to determine the origins of arsenic in soils and sediments related to historic and recent gold mine operations in Yellowknife, Northwest Territories, Canada, and to establish cleanup criteria. The cleanup guideline for arsenic in soil is 12 mg/kg, however, natural arsenic background levels in this area ranged from 3 to 150 mg/kg. Plants and fish were also analyzed for total, extractable, and water-soluble arsenic species. Significant arsenic levels were found in freshwater (lake) fish, which normally have much lower arsenic levels than marine fish. These data should be considered in establishing soil and sediment cleanup levels.

Extraction studies were performed to examine arsenic uptake and bioavailability in fish. Most of the arsenic was not extracted, and it was therefore not considered to be bioavailable. Acute arsenic toxicity is due to organic arsenic (arsenine), while carcinogenicity is primarily due to As(III) and As(V) species. Methylated forms of arsenic are generally genotoxic. There are currently no good animal carcinogenicity models. There is also a lack of knowledge of the true bioavailability of arsenic to human and other receptors. The standard uptake of arsenic in tissues has not been looked at closely.

Field-Scale Application: Site assessment of arsenic chemistry, cycling, and exposure was discussed. A site-by-site approach to evaluation/assessment may be needed because it is not realistic to use the same approach for every site due to hydrologic and chemical heterogeneities. An iterative approach to site evaluation may be practical. Arsenic mobility and transport must be understood, and there should be a focus on key parameters that control arsenic chemistry for different contaminated media. To obtain this information routinely, the use of standard and easy to implement sampling and analytical methods is needed. There is a lack of standard procedures for some methods, and some site characterization methods may require specially trained personnel.

It may not be necessary to do a detailed site assessment if the site contamination is well documented and remediation is straightforward. The evaluation of long-term implications of site contamination or a complex site is more difficult and may require the assistance of an expert. For example, to evaluate a landfill, it may be necessary to treat it as a bioreactor, do a simulation, and look at releases. These results could be compared to other landfill results to develop fate and transport patterns. Using only direct analytical parameter measurements may not be enough to characterize this type of site.

Sampling and Analytical Techniques

Three principal strategies currently employed for the measurement of arsenic speciation in waters were discussed: 1) field speciation using solid-phase cation and anion exchangers; 2) EPA Method 1632 using batch (selective) hydride generation (HG-CT-GC-AAS); and 3) ion chromatographic separation coupled with an element-specific detector (e.g., ICP-MS). All three methods have advantages and disadvantages concerning issues such as species quantification or exclusion, identification of inorganic versus organic species, interferences, and identification of additional elements. Sample dilution can be used to overcome analytical interference problems, but there is a possibility of changing the speciation either by addition of oxygen or other modifications to the sample chemistry. The field speciation technique works well for clean oxic waters and no additional specie-specific preservation is needed. However, this technique may be susceptible to As(V) breakthrough, potentially resulting in incorrect speciation patterns. Method 1632 is good for oxic waters. It provides low detection limits, but As(V) must be quantified by difference, an indirect approach. The chromatography method produces good speciation and direct quantitation of As(V). It has higher detection limits than Method 1632, but is usually adequate. Table 3.3-1 provides a comparison of the advantages and disadvantages of the three principal methods (Frontier Geosciences, Inc. 2001).

Preservation of water samples is important in order to maintain the natural distribution of arsenic species during sampling and storage. Preservation techniques include acidification and cryogenic freezing, although acidification is the most common and cryogenic freezing is not recommended if there is a potential for the dissolved phase to develop particulates from precipitation upon thawing. Sample oxidation can be a problem, but this factor can be minimized through acidification. Samples should be stored in the dark to prevent light-induced transformations, and filtered to remove microbes. Based on a recent study, there is some question about whether the EPA-specified 6-month holding period for metals is acceptable if oxidation is a concern. The general rule of thumb is to analyze samples as soon as possible, especially when samples are known to have low arsenic concentrations and/or a difficult sample matrix. Collection vessels for water samples should be of FEP teflon or low-density polyethylene materials.

Speciation of Toxicity Characteristic Leaching Procedure (TCLP) leachate samples may be problematic because of the complicated sample matrix. In addition, the leach process may modify the actual speciation; therefore, speciation of leaching samples may not be useful for evaluation of potential arsenic mobility. However, in-situ leachate fluid samples collected using devices such as soil lysimeters may be amenable to arsenic speciation by the principal methods.

For characterization of solid phase arsenic speciation, accurate identification of the arsenic solid phase association is dependent on the use of collection and storage techniques that preserve the in-situ physicochemical state of the sample. For example, samples collected from a reduced environment will react with oxygen in the atmosphere, thus altering sample mineralogy and arsenic phase association. The presence of arsenic within a discrete solid phase may be identified through evaluation of mineralogy using optical/electron microscopy and/or X-ray diffraction. More commonly, solid phase associations are established through identification of correlations in element composition. These associations may be established via characterization by X-ray fluorescence spectroscopy, a non-destructive method that is generally not as susceptible to matrix interference, or by determination of element content following chemical dissolution.

Table 3.3-1 Arsenic Speciation Method Comparison

Issues:	**Field Speciation**	**Method 1632**	**ICP-MS**
Detection limits	Good	Very good	Very good
Preservation issues	Storage?	Storage	Storage + analysis
Chemical interferences	Pre-concentration?	Few	Few
Chromatographic interferences	Probably	No	Yes
Spectroscopic interferences	Pre-concentration?	Yes	No
Direct quantification of As(V)	Possible	No	Yes
As(III)/As(V) Issues	No	Yes	No
Problems with methylated species	Maybe	Yes	No
Suitability For:			
Particulate speciation	No	Possible	No
Other As species	No	No	Yes
Sulfidic waters	No	No	Yes
Saline waters	No	Yes	No
Clean surface waters	Yes	Yes	Yes

Leaching Procedures for Characterization

This discussion focused on best methods to evaluate arsenic leachability from contaminated soil and treated solid water prior to and following disposal. Relevant applications for leaching procedures include:

- Hazard classification (TCLP)
- Evaluation of treatment process effectiveness
- Evaluation of waste management options
- Evaluation of remediation endpoints
- Evaluation of source term for contaminant release

Protocols for estimating arsenic leaching from soils and solidified wastes were evaluated to estimate impacts from different waste management scenarios and to compare treatment processes. These protocols included the use of percolation and flow-around models to assess the long-term release of the contaminant from the waste material. This approach provides a method to estimate long-term environmental impacts from leaching and to compare the efficacy of waste treatment processes. The site-specific liquid-to-solid ratio and mass release can be estimated with the percolation method. Local pH can be a limiting factor, however. With the flow-around method, mass transport within the solid matrix is rate limiting. Fundamental leaching parameters evaluated for equilibrium-based leaching tests include constituent availability, acid neutralization capacity of the waste, and liquid-solid equilibrium solubility. For mass transfer-based leaching tests, constituent release rates should be evaluated. Study results indicate that these fundamental leaching parameters can be used to compare the effectiveness of different waste treatment processes. A more robust evaluation can be used for waste management decisions and to reduce overall costs while maintaining environmental protection.

Other research that was reviewed included comparison tests that were conducted to evaluate the utility of the EPA Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (WET) for characterizing the leachability of municipal and hazardous solid waste. The primary difference between these two leach procedures is that the TCLP uses acetate (acetic acid) as the leaching medium, while the WET uses citrate (citric acid). (Citric acid chelates arsenic better than acetic acid, and thus makes arsenic more mobile.) Initial results showed higher leachate concentration results from the WET than the TCLP. WET is a more aggressive leach test for arsenic and other constituents. Comparison of measured arsenic concentrations for a municipal solid waste leachate database showed that arsenic leachabilty data derived from the WET correlated better than TCLP data.

For evaluation of site contamination, in-situ vadose zone sampling may be used as an alternative to performing simulated leaching tests on collected soil samples. This method involves use of pressure/vacuum lysimeters for collection of soil moisture (water) in the vadose zone. The lysimeters utilize ceramic cups and inert atmosphere sampling to help determine actual arsenic mobility. It has been found that core sample soil analysis can often show high levels of (adsorbed) arsenic or other metals, but collected interstitial soil pore water may still have very low concentrations. Arsenic in the interstitial water represents the highly mobile contaminant phase. The soil lysimeter approach is best for evaluating in-place source waste leaching. It is not as useful for characterizing treated waste leachability prior to disposal. Soil lysimeter sampling can be performed at various depths and under different site conditions (wet, dry, etc.) to account for variables that may affect soil water concentrations. Field research has shown that sites can have significant variability in spatial sampling results.

Parameters for Site Characterization

Based on information generated during discussion of the previous arsenic chemistry topics related to the three general questions, parameters for site characterization were evaluated for aqueous and solid phases. It is important to determine in advance the intended use of site characterization data and what level of characterization is needed to guide the field investigation. The required parameters will vary from site-to-site due to site history, site conditions, and questions to be answered. Some measurements may be needed to understand site conditions beyond the arsenic species present.

Table 3.3-2 presents a summary of recommended parameters that may be necessary to provide a general characterization of an arsenic contaminated site, to determine if arsenic is being mobilized into groundwater, and to determine what biogeochemical processes are controlling arsenic mobilization. Not all of these parameters may be necessary at a given site, but they provide a good starting point for site evaluation. Dependent on the availability of site data, a stepped approach that includes periodic re-assessment of the required characterization effort may prove most practical and cost-effective.

3.3.1.1 Summary of Important Conclusions from the Arsenic Chemistry Session

Identifying Pathways and Routes of Mobility

1. Arsenic speciation and partitioning are commonly coupled to the cycling of redox sensitive elements such as iron, sulfur and manganese.
2. Arsenic speciation and partitioning are apparently linked to nitrogen transformations. Therefore it may be important to examine nutrient cycling during site assessment.
3. Microbial activity may exert direct and indirect influence on arsenic speciation, but predictive tools and modeling approaches to determine this influence are in their infancy.
4. The sophistication of chemical models is generally greater than commonly available field data and existing thermodynamic and kinetic data. Sorption modeling is limited by lack of: 1) a consistent set of model parameters for oxic systems, and 2) data for sorbents common to anoxic environments.
5. There is uncertainty about potential soluble inorganic complexes of arsenic relevant to suboxic or anoxic systems,

Table 3.3-2 Recommended Site Parameters for Characterization of Arsenic Contamination and Mobility

Aqueous Phase	Solid Phase
pH temperature specific conductivity dissolved oxygen alkalinity (full titration curve) oxidation reduction potential (ORP) – an optional indicator measurement using platinum electrode arsenic speciation dissolved organic carbon (DOC) major anions – SO_4, NO_3, Cl, HCO_3/CO_3, PO_4, Fl major cations – Na, K, Ca, Mg, Al, Si (more anions and cations may be needed to provide charge balance, which is required for chemical modeling) redox indicators – Fe(II)/Fe(III), As(III)/As(V), arsine, $NO_3/NO_2/NH_4$, $HS/SO_2/SO_3$, CH_4, H_2, Mn(II) filtered and unfiltered trace metals – Cr, Cu Note: Aqueous samples should be tested as unfiltered and filtered (0.1um) for major anions and cations and the contaminant(s) of concern	<u>Natural</u> total arsenic organic carbon anion exchange capacity grain size distribution mineralogy lithology hydraulic conductivity extraction/leach test or solubility versus pH Note: If used, the leach test should mimic site geochemistry. The solubility versus pH assessment should use a pH range representative of site water. <u>Anthropogenic</u> total arsenic matrix identification site history (disposal, contamination, waste age, etc.)

such as complexes incorporating carbonate or sulfide.

Sampling and Analytical Techniques

1. Existing analytical instrumentation appears adequate for determination of aqueous arsenic speciation; however, no single method for preservation and analysis is appropriate for all sample matrices.
2. Filtration, acidification, and light exclusion are the most critical issues for sample preservation and handling. The techniques used should be customized to the type of sample and analytical needs, such as speciation.
3. Sample matrices that can cause analytical problems include high dissolved organic carbon, ferrous iron, and sulfide.
4. Current analytical approaches may inadequately describe inorganic arsenic speciation in anoxic environments.
5. Analytical limitations of EPA Method 1632 are a potential source of inaccurate species identification or quantitation. This method requires very good laboratory expertise to get correct results.
6. Strategies for preservation and species separation need to consider the sample matrix. For example, acidification may be beneficial with Fe(II), but detrimental with sulfide.

Leaching Procedures for Characterization

1. TCLP may be inappropriate as a stand-alone test for evaluation of arsenic bearing materials. Sometimes, however, a combination of leach tests may be desirable.
2. The most appropriate leaching method to use may differ for the pre- and post-disposal setting.
3. The influence of waste material age with respect to long-term arsenic stability and partitioning to natural solids is poorly understood.

3.3.1.2 Recommendations or Research Needs from the Arsenic Chemistry Session

Identifying Pathways and Routes of Mobility

1. Initiate an effort to develop and disseminate a consolidated thermochemical database with consistent parameters for use in modeling applications.
2. EPA has a responsibility for providing adequate computer models to evaluate arsenic mobility. EPA should update and maintain the MINTEQA2 model database and develop a website to provide users with access to arsenic chemical speciation models and application information.
3. Produce guidance outlining uniform strategies for implementation of sorption modeling.
4. Produce guidance on uniform approaches for site assessment.
5. Evaluate methods for measuring microbial activity in the field. Determine what measures are valuable for interpreting the impacts of microbial activity on arsenic mobility.

Sampling and Analytical Techniques

1. Operational protocols tailored towards specific sample matrices need refinement and development.
2. Document limitations and strengths of various analytical approaches relative to different sample matrices and the desired data output.
3. Evaluate and provide guidance for approaches to preserve speciation for oxic and anoxic sample matrices during sampling and storage (holding time).
4. Develop a more comprehensive understanding of analytical requirements in anoxic or suboxic environments representative of many disposal scenarios.

Leaching Procedures for Characterization

1. Design leach procedures based on information needs, such as waste classification versus source term evaluation.

2. For assessment of leach potential, design the leach procedure to be more representative of the in-situ environment, including:
    - Solubility over a range of pH inclusive of natural pH of material and pH range of in-situ environment
    - Consistent with site geochemistry (based on site characterization)
    - Measure in-situ concentrations in contact with the source (e.g., pressure/vacuum lysimeter)

3.3.2 *Arsenic Chemistry Session Speaker Abstracts*

Speaker abstracts from the Arsenic Chemistry session are presented in this section.

Interactions of Arsenic Speciation with the Nitrogen Cycle

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The speciation of As in freshwaters is strongly influenced both by redox potential and by the presence or absence of iron oxyhydroxides. Recent work in Upper Mystic Lake, located on the Aberjona River watershed near Boston, MA has shown that these characteristics can both be controlled by nitrogen during a substantial part of the year. In this eutrophic urban lake, total nitrogen (nitrate plus ammonium) concentrations typically exceed 100 micro-equivalents per liter, and nitrification represents a major hypolimnetic oxygen demand following onset of seasonal stratification. Later during the period of stratification, following oxygen depletion, nitrate controls the redox potential of the bottom waters and is responsible for reoxidizing ferrous iron as it diffuses from the lake sediments into the hypolimnion. It is also suspected that nitrate is concurrently responsible for the reoxidation of As(III) to As (V). Consequently, As is present chiefly in particulate form, its speciation dominated by surface complexation of As(V). The conclusion that nitrogen is the controlling factor is supported by clear spatial and temporal correlations, as well as by thermodynamic arguments, mass balance data, and microcosm results. We argue that in eutrophic freshwaters, nitrogen can thus take on a chemical role analogous to that played by molecular oxygen as a key controlling factor in the cycling and speciation of As and probably many trace metals.

Arsenic Immobilization: Thermochemical Analyses

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The possibility of putting arsenic into slightly soluble minerals is examined by thermodynamic methods and is the subject of this paper. The equilibrium states of several systems are described from free energies of formation, the phase rule, and the balances of mass and charge. Each model system has one or more minerals, a solution containing soluble salts such as NaCl and KCl and CO_2 from the atmosphere. A number characteristic of each mineral and called the pK_{sp}^0 is calculated from the dissolution of that mineral according to the following rules. The mineral is on the left side of the equation, written with one mole of the principal metal. The species on the right side are the neutral species, and common oxidation states are used for each element, namely, Fe(III), S(-II), As(V), and Mn(II). The value of pK_{sp}^0 is then computed from the free energies. When oxidation or reduction is required to achieve the common oxidation state, pe + pH is used. For example:

$$\text{haematite: } Fe_2O_3,\ pK_{sp}^0 = pFe(OH)_3^0 = 11.943$$

$$\text{siderite: } FeCO_3,\ pK_{sp}^0 = pFe(OH)_3^0 + pCO_2^0 + (pH + pe) = 16.723$$

The activities of all other solute species may then be calculated if the pe and pH of the solution are known. (The activity of CO_2 is found by assuming an atmosphere with 270 ppm.) A spreadsheet is calculated with (pH + pe) constant, with each solute species on a row, and with each column being a fixed pH. The phase rule is used to find the degrees of freedom, and these are satisfied by using STP, the fixed (pH + pe), and trial and error to reach mass balances. The charge balanced is achieved at a single pH only.

Two example systems will be discussed. The first has the components Fe_2O_3, H_2S, CO_2, Na_2O, K_2O, HCl, H_2 and O_2. If any two minerals of iron are present with the solution and the atmosphere, there will be six degrees of freedom. Three tests on stoichiometry will be required, and these will be found by testing pCl(t), pK(t), and pNa(t) in each column against preset values. The charge balance is found by plotting pQ(+) and p(abs(Q(-))) vs. pH and noting where the lines meet. Twenty-seven minerals of the components are possible, and the chemical potentials of their precipitations are found by comparing pK_{sp}^0 to pQ_{sp}^0, which has the same form with the actual activities. The customary game is to find the pair of minerals which gives $(pQ_{sp}^0 - pK_{sp}^0) > 0$ for all the others. The system so found is the stable one, under the conditions.

The second system will be like the first with the added components As_2O_5 , MnO, P_2O_5, and CaO. There will be six minerals or seven, and the game will be played. Graphs of arsenic solubility under several sets of circumstances will be shown.

Arsenic in Yellowknife, Canada

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Elevated levels of arsenic are found in a variety of environmental compartments in Yellowknife, NWT, Canada. Much of this arsenic may be the consequence of historic and recent gold mine operations. The criteria for cleanup of the mine sites and the surrounding land are currently being formulated but there are problems in determining what are the natural, pre-mining concentrations that could be considered to be the remediation objective. The use of principal components analysis to determine the origins of the arsenic in soils and sediments and to establish cleanup criteria will be described.

Plants and fish in the Yellowknife area were analyzed for total arsenic and for extractable, water-soluble, arsenic species by using HPLC-ICP-MS methodology. The plant extracts contained mainly inorganic species although some methylated species and arsenosugars were present. However, in general most of the arsenic, less than 50%, was not extracted. Model gastric fluid studies suggest that the extracted arsenic represents the bioavailable arsenic. The arsenic species in fish are more varied and probably reflect their diet. Unlike their marine counterparts, arsenobetaine is not the dominant arsenic species.

Measuring Arsenic Speciation in Waters — Choosing the Right Analytical Technique for Your Geochemical Problem

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Measuring arsenic (As) speciation in environmental and industrial waters is very important for accurate risk assessment, understanding of hydrogeochemical processes, and for the design of efficient treatment strategies. Traditionally, four As species have been determined in waters by most speciation techniques, namely arsenite [As(III)], arsenate [As(V)], monomethyl arsenate [MMAs(V)] and dimethylarsenate [DMAs(V)]. Different types of analytical approaches have been employed, and a wide variety of speciation methods has been published, each of which has its inherent advantages and disadvantages. This presentation will compare the three principal strategies currently employed for the measurement of As speciation in waters, and discuss their strengths and weaknesses with respect to their applicability in certain geochemical environments.

Preservation is a key problem in the analysis of As speciation in waters, due to the instability of As(III) towards oxidation. Two approaches are commonly used to stabilize As(III) between sample collection and analysis, namely acidification and cryofreezing, but both lead to specific problems in certain types of waters. To overcome this whole problem area, operationally-defined speciation approaches have been developed that use separation of As(III) and As(V) in the field (immediately after sample collection), and then only require total As measurements afterwards. Separation of As(III) and As(V) is achieved by selective adsorption on or desorption from solid phase extraction cartridges. However, the separation conditions are usually optimized in aqueous standard solutions, and complex matrices may alter the adsorption/desorption behavior, thereby introducing speciation artifacts. Also, this approach is not suitable for the analysis of MMAs(V) and DMAs(V).

EPA Method 1632 uses batch hydride generation (HG) to convert the four As species to their corresponding hydrides, which are purged from the sample, cryogenically trapped, and then analyzed by gas chromatography with AAS detection. As(III) and As(V) yield the same derivatization product, so they can only be distinguished by operationally-defined selective HG at different pH. Due to the large possible sample volume, the technique has excellent detection limits around 1 ng L^{-1}. It works very well in most waters; only samples with high dissolved metal concentrations give chemical problems. Due to the fairly unspecific detection, artifactual signals have been observed in sulfidic waters and in petroleum-contaminated samples. The main problems of the method arise from the quantitation by difference for As(V), which results in higher uncertainty, and sometimes in “negative” results, and often leads to issues regarding total vs. dissolved concentrations. For MMAs(V) and DMAs(V), problems with de- and transmethylation have been widely reported, unless pH during HG is controlled carefully.

Hyphenated speciation methods coupling liquid chromatography to atomic spectrometry detection are state-of-the-art for As speciation. Each species yields a separate signal, eliminating problems arising from the indirect quantification of As(V). HG-AFS detection yields detection limits around 0.1 ∝g L^{-1}, and problems with chemical interferences during the HG are eliminated by the preceding separation. ICP-MS detection yields detection limits around 1 ng L^{-1}, which is comparable to EPA Method 1632. The big advantage of hyphenated speciation techniques is the ability to detect other As species than the four pre-conceived compounds. The importance of this capability is demonstrated for the analysis of anoxic waters, where currently unidentified species may constitute the majority of the total as present.

Approaches to Characterizing Solid Phase Arsenic Speciation

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The partitioning of arsenic to solid matrices is an important process controlling the stabilization of arsenic wastes and mobility of arsenic in the environment. Identification of the physicochemical characteristics of the partitioning mechanism(s) is an important step towards optimization of treatment processes and assessment of the stability of arsenic-bearing solids in environmental systems. Arsenic may reside in the solid phase as a discrete precipitate, a minor constituent coprecipitated within the structure of a separate phase, or as a sorbed ion bound to surface sites of a separate phase. Each of these solid phase partitioning mechanisms will possess a unique stability relative to the chemical conditions of the treatment or disposal environment. It is critical to understand that a partitioning mechanism that is stable under pre-disposal conditions may become unstable after disposal due to differences in system chemistry such as pH and oxidation-reduction (redox) potential.

Accurate identification of the arsenic solid phase association is dependent on the use of collection and storage techniques that preserve the in-situ physicochemical state of the sample. In soils and sediments, inorganic forms of arsenic are commonly associated with solid phases composed of redox sensitive elements such as iron, manganese, and sulfide. Samples collected from a reduced environment will react with oxygen in the atmosphere, thus altering sample mineralogy and arsenic phase association. This type of sample alteration may not be critical if the primary task of characterization is demonstration of patterns in element distribution. However, sample preservation is critical if the goal of characterization is demonstration of arsenic partitioning to specific mineral phases.

Various methods are available for identification of the arsenic solid phase association. The presence of arsenic within a discrete solid phase may be identified via optical/electron microscopy and/or X-ray diffraction provided there is sufficient abundance of the discrete phase. It may be possible to increase the relative abundance of a discrete phase through physical means such as particle size or density separations. More commonly, solid phase associations are established through identification of correlations in element composition. These associations may be established via characterization by X-ray fluorescence spectroscopy or by determination of element content following chemical dissolution. Chemical extraction procedures designed to target specific solid phase associations are frequently employed to aid identification of the arsenic partitioning process. However, two major limitations to the universal acceptance of proposed extraction schemes are 1) the lack of standard reference materials appropriate for near surface environments, and 2) the acceptance and application of a quality assurance protocol to verify data obtained for the various solid matrices present in environmental systems.

Protocols for Estimating Arsenic Leaching from Soils and Solidified Wastes

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A framework for evaluation of leaching from soils and wastes has been presented in a preceding paper (see van der Sloot, et al. “A Framework for Assessing Arsenic Leaching from Soils and Wastes,” 2.0 Plenary Session). The specific objectives of this talk will be to: (i) describe specific testing protocols and interpretation approaches for estimating the leaching behavior of pollutants from solid wastes, and (ii) show how the integrated use of equilibrium and mass transfer leach tests in conjunction with appropriate mass transfer models can provide more realistic release estimates for both direct comparison of different treatment processes under diverse potential environmental conditions (e.g., over a range of field pHs) and impact from different management scenarios. This approach has potential for use to estimate long-term environmental impacts from leaching and to compare the efficacy of waste treatment processes.

We will discuss arsenic solubility as a function of pH and low liquid-to-solid ratio and arsenic release rate information of (i) a soil contaminated with arsenic from a pesticide production facility (“untreated As soil”), and (ii) the same soil subsequently treated by a Portland cement stabilization/solidification process (“S/S treated As soil”). As an example, we will provide and compare long-term arsenic release estimates (100-year time frame) for different management scenarios (disposal under percolation and flow-around contact mode) including consideration of local conditions (e.g., infiltration and site-specific design).

The Best Analog to the Real World Is the Real World: Vadose-Zone Sampling as an Alternative to Core Sampling and Leaching Protocols

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Shortcomings with Conventional Approach

The conventional approach to evaluating the presence and potential mobility of metals and metalloids such as arsenic in a soil is to collect core samples of the soil, assay the core for metal content, and perhaps to run some sort of synthetic leach protocol designed to simulate the mobility of the metal under field conditions. The analysis of the core determines a total of three component concentrations:

1) Metals present in the soil or rock at the time of deposition, with little or no potential mobility
2) Metals sorbed onto the soil material, with variable mobility
3) Metals dissolved in the interstitial void moisture

This last component is the one that presents the greatest potential for migration into the underlying groundwater. Cullen, Kramer, Everett and Eccles (1995) noted the failings of not considering such migration as the greatest threat to the groundwater.

The various leach protocols commonly use some form of organic acid as a lixiviant. In some cases, the selected lixiviant is capable of mobilizing the metal of concern to a much greater extent than real world soil moisture. For example, lead acetate is one of the few mobile forms of lead, so use of acetic acid in the TCLP overstates the geochemical "hazard" of lead, compared to observations of actual ground-water contamination with lead. Vinegar is not a common component of rainfall.

Alternative Approach

An alternative that has proven useful is to utilize the real-world conditions that obtain at the sites of metal contamination of soil and sludges, by obtaining samples of actual soil moisture by the installation and sampling of pressure/vacuum lysimeters. Such p/v lysimeters were originally developed for soil moisture sampling in agricultural applications, but have proven highly useful in the determination of the concentrations of contaminants in soil moisture (Wilson, Dorrance, Bond, Everett, and Cullen, 1995) (Bond and Rouse, 1985). Such lysimeters are capable of collecting samples of actual soil moisture, in remote locations such as under heap-leach facilities or ponds, on a periodic basis to monitor for the development of leaks and an advancing front of contaminated moisture.

Case Histories

A number of cases are discussed, where there was little relationship between the soil moisture and total or leachable metals content. In many cases, the conventional approach severely overstated the hazard, but in some cases it understated the hazard, which potentially could lead to a false sense of security.

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Appendix A – Workshop Agenda

US EPA Workshop on Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal

WORKSHOP GOALS

The goals of the workshop are: (1) to examine the chemical fundamentals related to arsenic chemistry, speciation, and analytical issues, (2) to examine the state of practice of existing and emerging technologies that treat and properly dispose of arsenic wastes, and (3) to identify/characterize sources of arsenic.

TUESDAY, MAY 1 – PLENARY SESSION

Capitol Rooms

8:45 AM	Welcome Remarks, *Max Dodson, US EPA Region 8*
8:55 AM	Opening Remarks, *Doug Grosse, US EPA, National Risk Management Research Laboratory (NRMRL)*
9:05 AM	ORD Perspective, *Paul Randall, US EPA, National Risk Management Research Laboratory (NRMRL)*
9:30 AM	Hazardous Waste Treatment/Regulatory Issues, *Jim Berlow, USEPA, Office of Solid Waste (OSW)*
9:55 AM	Break
10:10 AM	Arsenic Cycling in the Mining Environment, *Rob Bowell, SRK Consulting*
10:35 AM	Arsenic in Groundwaters of the United States, *Dennis Helsel, U.S. Geological Survey*
11:00 AM	Managing Arsenic Occurrence Information in Drinking Water, *Larry Scanlan, Utah Department of Health*
11:30 AM	Lunch
1:00 PM	TRI: What It Is. Where to Find It. And How to Use It., *Joyel Dhieux, US EPA, Region 8*
1:25 PM	Arsenic Hazardous and Remediation Waste: Sources and Treatment, *Linda Fiedler, US EPA, Technology Innovation Office (TIO)*
1:50 PM	Treatment Options for Arsenic Wastes, *Godage Wickramanayake, Battelle Memorial Institute*
2:15 PM	Some Chemical Aspects Relating to Arsenic Remedial Technologies, *Robert Robins*, *AquaMin Science Consortium International*
2:40 PM	Break
3:00 PM	Arsenic Geochemistry: An Overview of an Underhanded Element, *Kirk Nordstrom*, *U.S. Geological Survey*

TUESDAY, MAY 1 – PLENARY SESSION

Capitol Rooms

(Continued)

3:25 PM	Impact of Microbial Activity on Arsenic Geochemistry, *Dianne Ahmann, Colorado School of Mines*
3:50 PM	A Framework for Assessing Arsenic Leaching from Soils and Water*, David Kosson, Vanderbilt University*
4:30 PM	Q & A
5:00 PM	Adjourn

WEDNESDAY, MAY 2 – CONCURRENT BREAKOUT SESSIONS

8:00 AM	Concurrent Breakout Sessions
10:00 AM	Break
10:30 AM	Concurrent Breakout Sessions
Noon	Lunch
1:30 PM	Concurrent Breakout Sessions
3:00 PM	Break
3:30 PM	Concurrent Breakout Sessions
5:00 PM	Adjourn
7:30 - 9:00 PM	Meeting to plan Day 3 Reports

BREAKOUT SESSION SPEAKERS AND PARTICIPANTS

Source Identification Breakout Session

Capitol Room 2

Co-Chairs
Diana Bless, US EPA NRMRL
Doug Grosse, US EPA NRMRL
Carol Russell, US EPA Region VIII

Speakers

Scott Warner, Geomatrix Consultants, Inc.	Distinguishing Natural and Anthropogenic Sources of Arsenic: Implications for Site Characterization
Richard Glanzman, CH2M Hill	Arsenic Background and Associated Elements Controlling Mobility
Tracy Connell Hancock, USGS	Reconnaissance for Arsenic in a Poultry Dominated Chesapeake Bay Watershed – Examination of Source, Transport and Fate
Roger Olsen, Camp Dresser & McKee, Inc.	Characterization of the Forms of Arsenic in Soil/ Sediments to Evaluate Mobility and Treatment
Andy Davis, Geomega, Inc.	Iron Amendments as Adjuncts to Constrain Arsenic Solubility in a Marsh Environment
Martin Goldhaber, USGS	Potential Environmental Consequences of Localized Arsenic Enrichment in Appalachian Basin Coals
John Pantano, ARCO Env. Remediation	Arsenic Concentrations in Water at Mining Sites
Stephen Schoen, Placer Dome America and Glenn Eurick, Barrick Management Corporation	Arsenic and TRI in Select Nevada Gold Production Operations

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Tim Eastep, Phelps Dodge Corporation
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Treatment and Disposal

Capitol Room 3

Co-Chairs
Paul Randall, US EPA NRMRL
Robert Robins, AquaMin Science Consortium International
Chris Impellitteri, US EPA NRMRL

Speakers

Peter Shields, Tetra Tech EMI	Treatment Technologies for Wastes and Environmental Media Containing Arsenic
Neill Thompson, Government of Canada	Treatment Options for Arsenic Trioxide Bearing Dust at the Giant Mine, Yellowknife, Northwest Territories, Canada
Jay McCloskey, MSE Inc.	Removing Arsenic for Mining Industry Waters, Treatability Studies, EPA Mine Waste Program
Rong-Yu Wan, Newmont Mining Corporation	Characterization of Arsenic in Refractory Gold Ores Roasting - Cyandation Processing
Lena Ma, University of Florida	Phytoremediation of Arsenic Contaminated Sites Using Brake Fern Hyperaccumulator
James Redwine, Southern Company Services, Inc.	In-Situ Chemical Fixation for Arsenic Remediation and Arsenic Mobility Studies
Richard Markey, Southern Company Gulf Power Company	Arsenic Contamination in Soil and Groundwater: Review of - Remediation Methods
Michael Leist, Varian Inc.	The Cement Stabilization and Leaching of Arsenic
Irene Legiec, DuPont	Characterization and Treatment of Arsenic Contaminated Soils: The Dupont Experience
Jeri Sullivan, Los Alamos National Laboratory	Sorption of Arsenic from Soil-Washing Leachate by Surfactant-Modified Zeolite
James Navratil, Clemson University	Adsorption and Nanoscale Magnetic Separation of Heavy Metals from Water

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David Kosson, Vanderbilt University
Juan Parra, US EPA OSW
Florence Sanchez, Vanderbilt University
Larry Scanlan, Utah Department of Health
Godage Wickramanayake, Battelle Memorial Institute

Arsenic Chemistry

Capitol Room 4

Co-Chairs
Robert Ford, US EPA NRMRL
Kirk Nordstrom, USGS

Speakers

Harry Hemond, Massachusetts Institute of Technology	Interactions of Arsenic Speciation with the Nitrogen Cycle
Spencer Porter, US EPA ORD	Arsenic Immobilization: Thermochemical Analyses
William Cullen, University of British Columbia	Arsenic in Yellowknife, Canada
Dirk Wallschlaeger, Frontier Geosciences, Inc.	Measuring Arsenic Speciation in Waters - Choosing the Right Analytical Technique for Your Geochemical Problem
Robert Ford, US EPA NRMRL	Approaches to Characterizing Solid Phase Arsenic Speciation
Barton Simmons, California Department of Toxic Substances Control	Comparative Extractions of Arsenic Containing Wastes for Waste Classification
Florence Sanchez, Vanderbilt University	Protocols for Estimating Arsenic Leaching from Soils and Solidified Waste
Jim V. Rouse, Montgomery Watson	Alternative Methods to Assessing Leach Potential

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THURSDAY, MAY 3 – BREAKOUT SESSION REPORTS – SINGLE SESSION

8:30 AM	Source Identification
9:15 AM	Arsenic Chemistry
10:00 AM	Break
10:30 AM	Treatment and Disposal
11:15 AM	Q & A
Noon	Closing Remarks
12:15 PM	Adjourn

QUESTIONS FOR BREAKOUT GROUPS

Source Identification

1. What are the primary waste forms that contribute to Arsenic contamination?
2. What are the major problems encountered with characterization of Arsenic impacted media or sources?
3. What significant data gaps and information needs exist for characterizing and identifying Arsenic sources and waste forms?
4. What are the two or three important insights to be conveyed regarding the management of Arsenic risks from industry?

Treatment and Disposal

1. What are the long term stability issues with regard to land disposing (i.e., on-site storage or landfills) arsenic stabilized wastes?
2. How do current advances (i.e., molecular chemistry, leaching mechanisms) impact the areas of arsenic treatment and disposal?
3. What are the top five research needs in arsenic treatment and disposal?

Arsenic Chemistry

1. Is our knowledge of arsenic speciation and transformation adequate to identify pathways and routes of mobility?
2. Are current collection, preservation, and analytical techniques sufficient for defining arsenic chemistry in natural and engineered systems?
3. Are existing leaching procedures adequate for characterization of arsenic-bearing waste materials?

Appendix B – Steering Committee and Attendees

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May 1-3, 2001
Denver, Colorado
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USA

Appendix C – Selected Publications Bibliography

NHEERL Publications on Arsenic

U.S. Environmental Protection Agency
Office of Research and Development

National Health and Environmental Effects Research Laboratory
Drinking Water Research Program
1998 to Present

(April 2001)

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