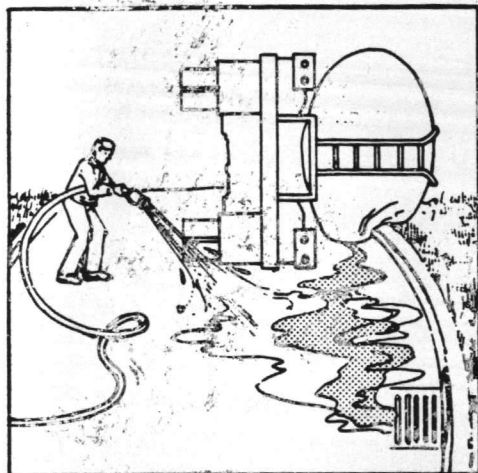
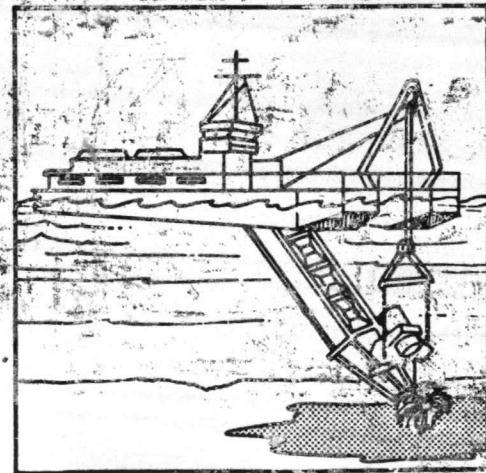
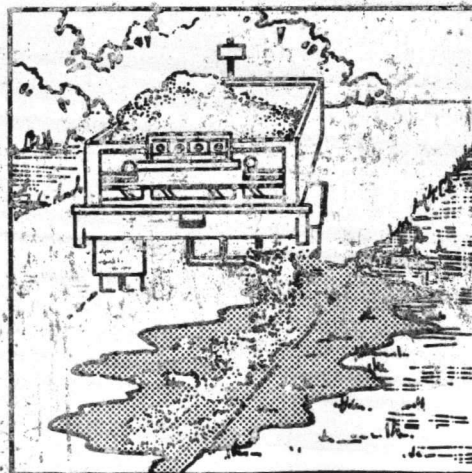
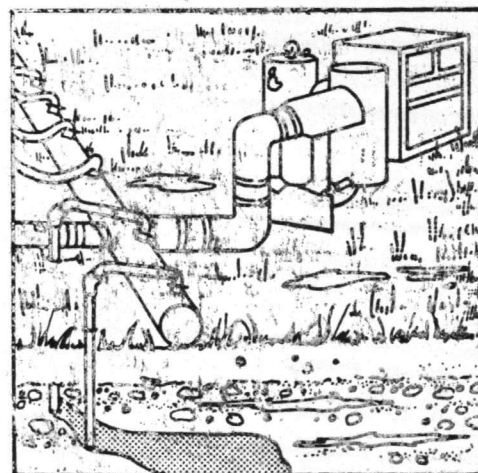
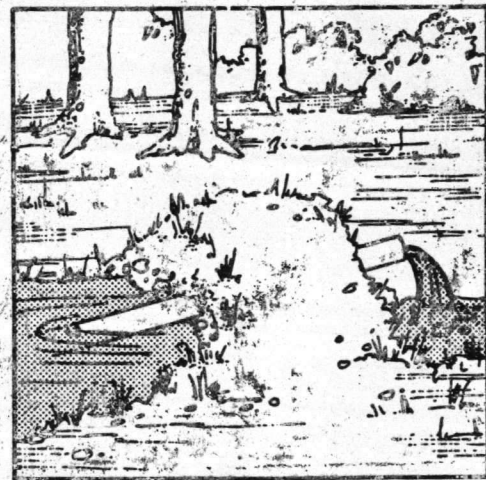
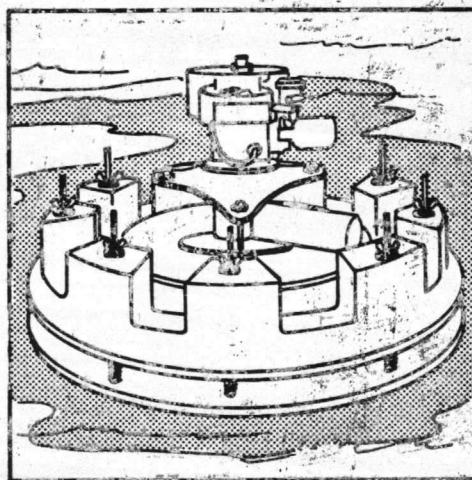
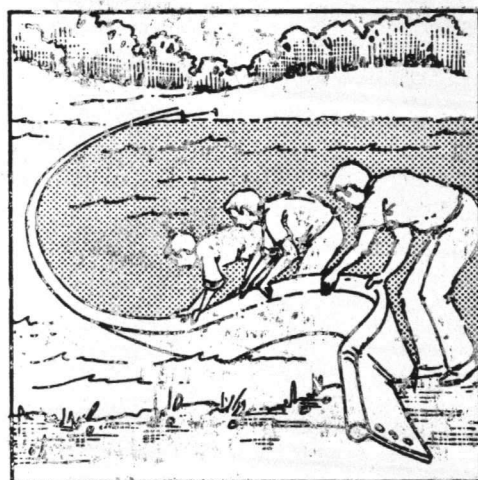
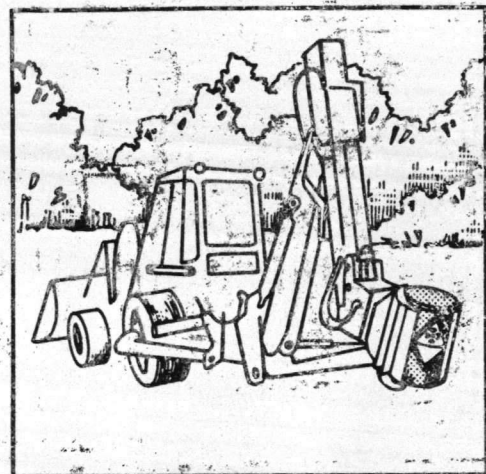
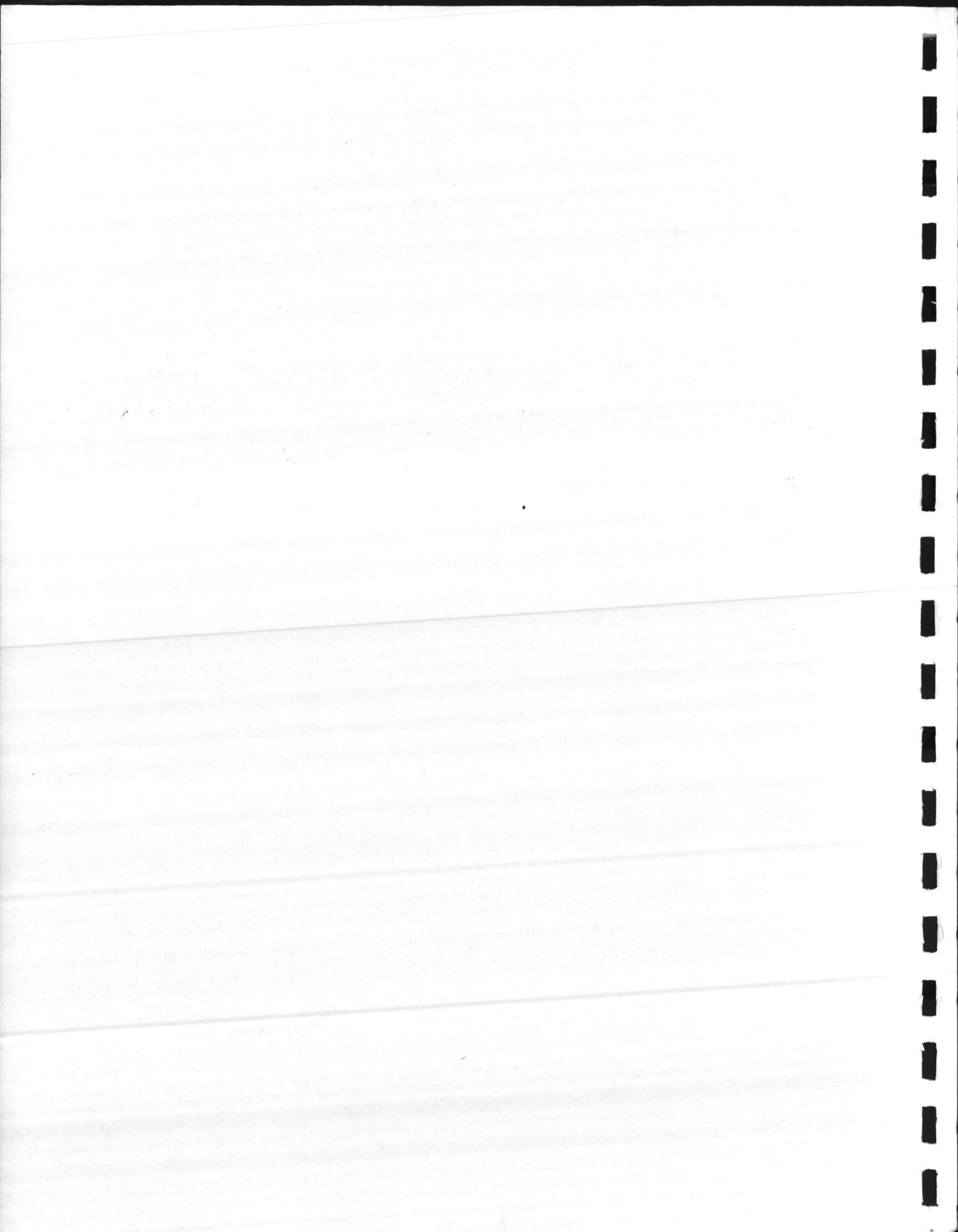


# TECHNIQUES FOR HAZARDOUS CHEMICAL AND WASTE SPILL CONTROL

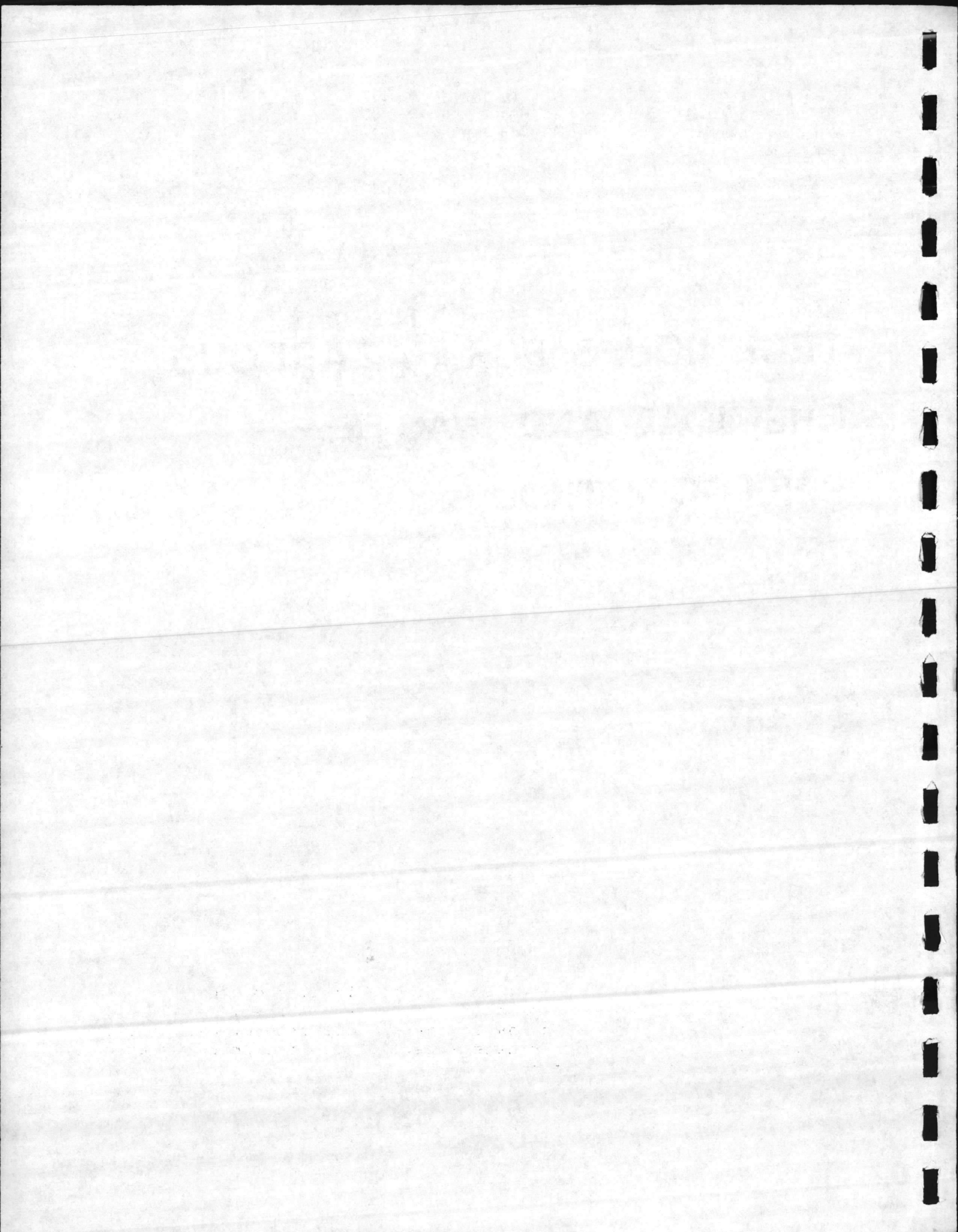


L. Albert Weaver III,  
CSP





**TECHNIQUES FOR HAZARDOUS  
CHEMICAL AND WASTE  
SPILL CONTROL**



\$39.95

Library of Congress Cataloging in Publication Data

Weaver III, L. Albert

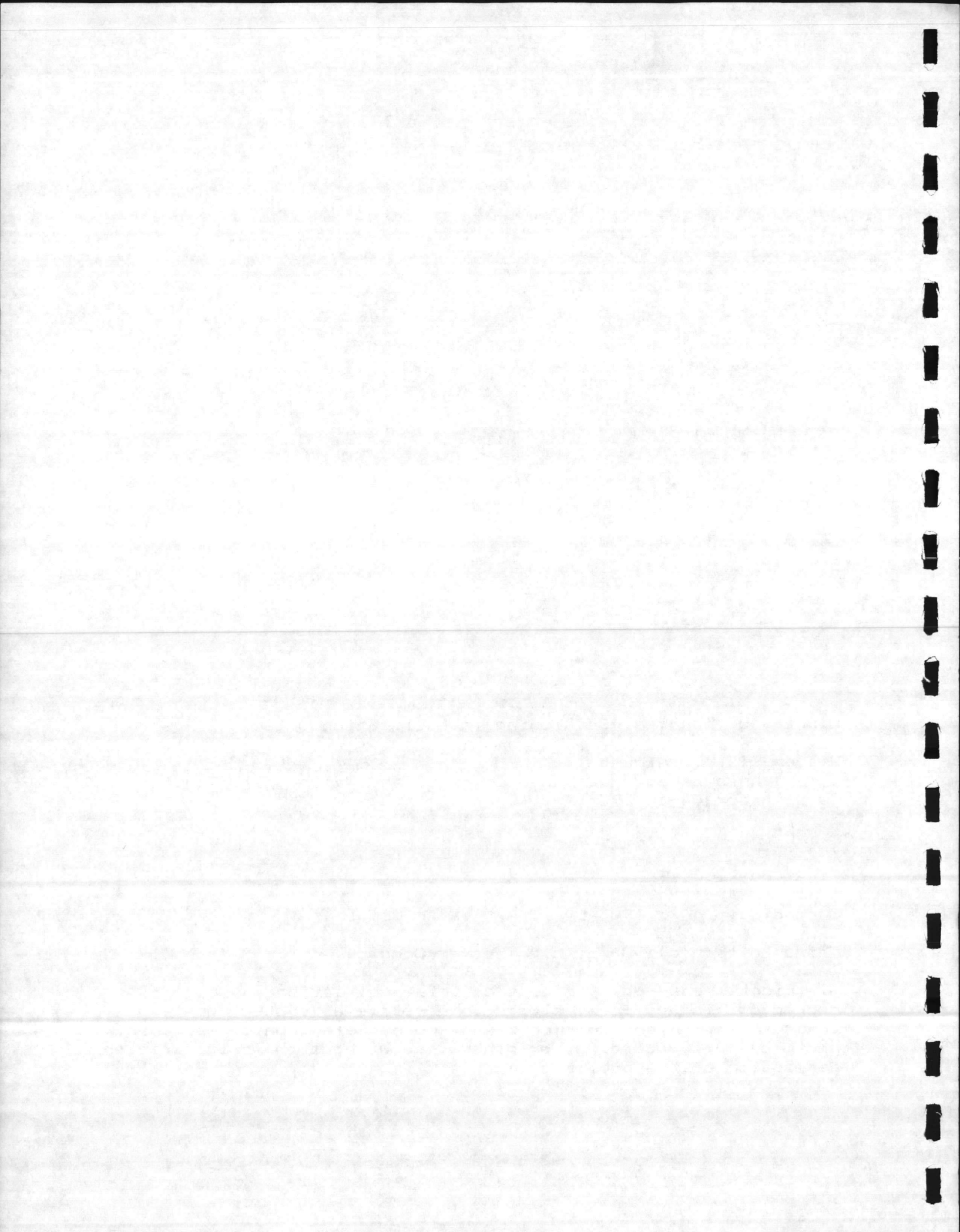
Techniques for Hazardous Chemical and Waste Spill Control  
Card Number 84-115573

First Edition 1982

Second Edition c 1983 by L. A. Weaver Company

Third Edition © 1986 by L.A. Weaver Company

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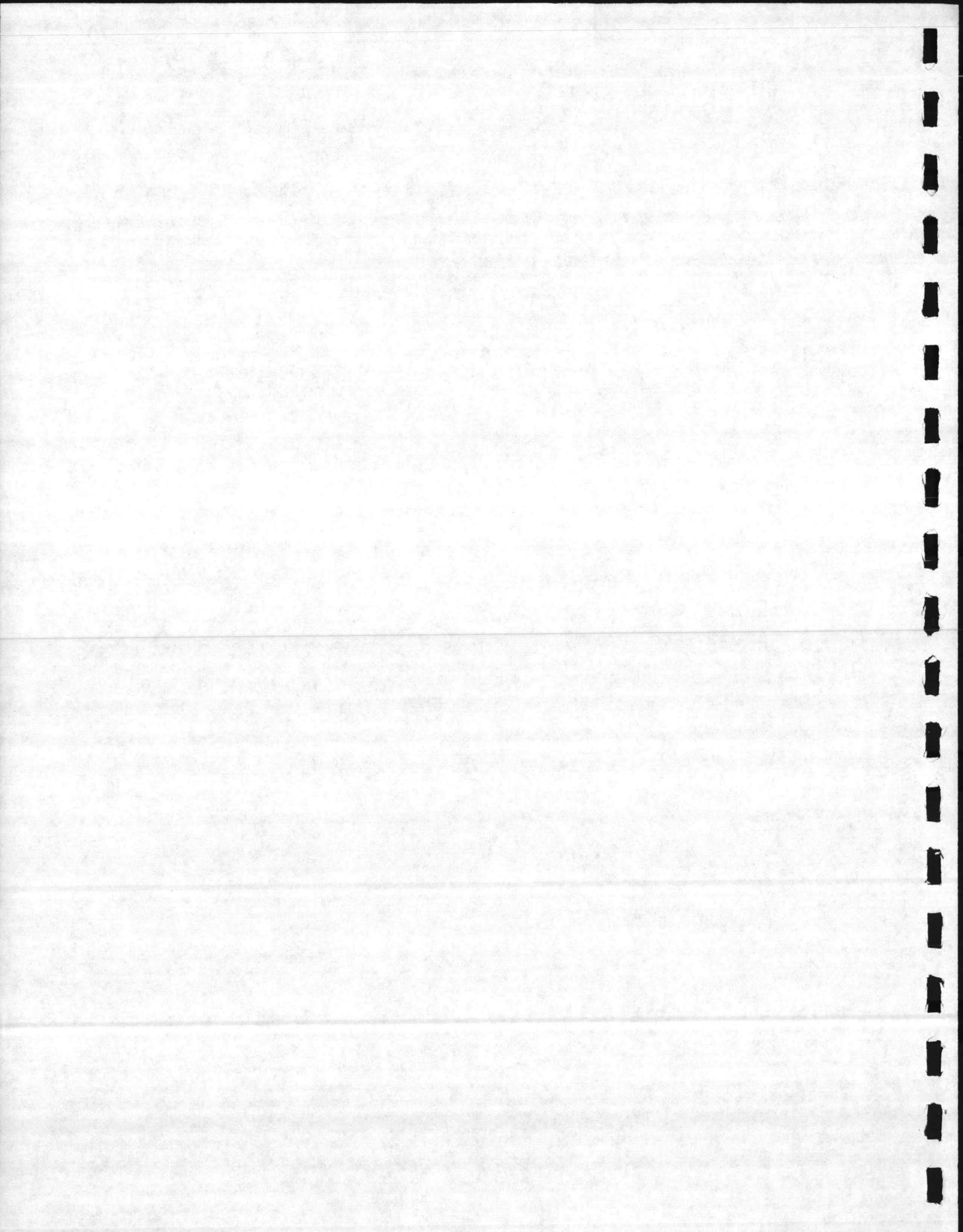
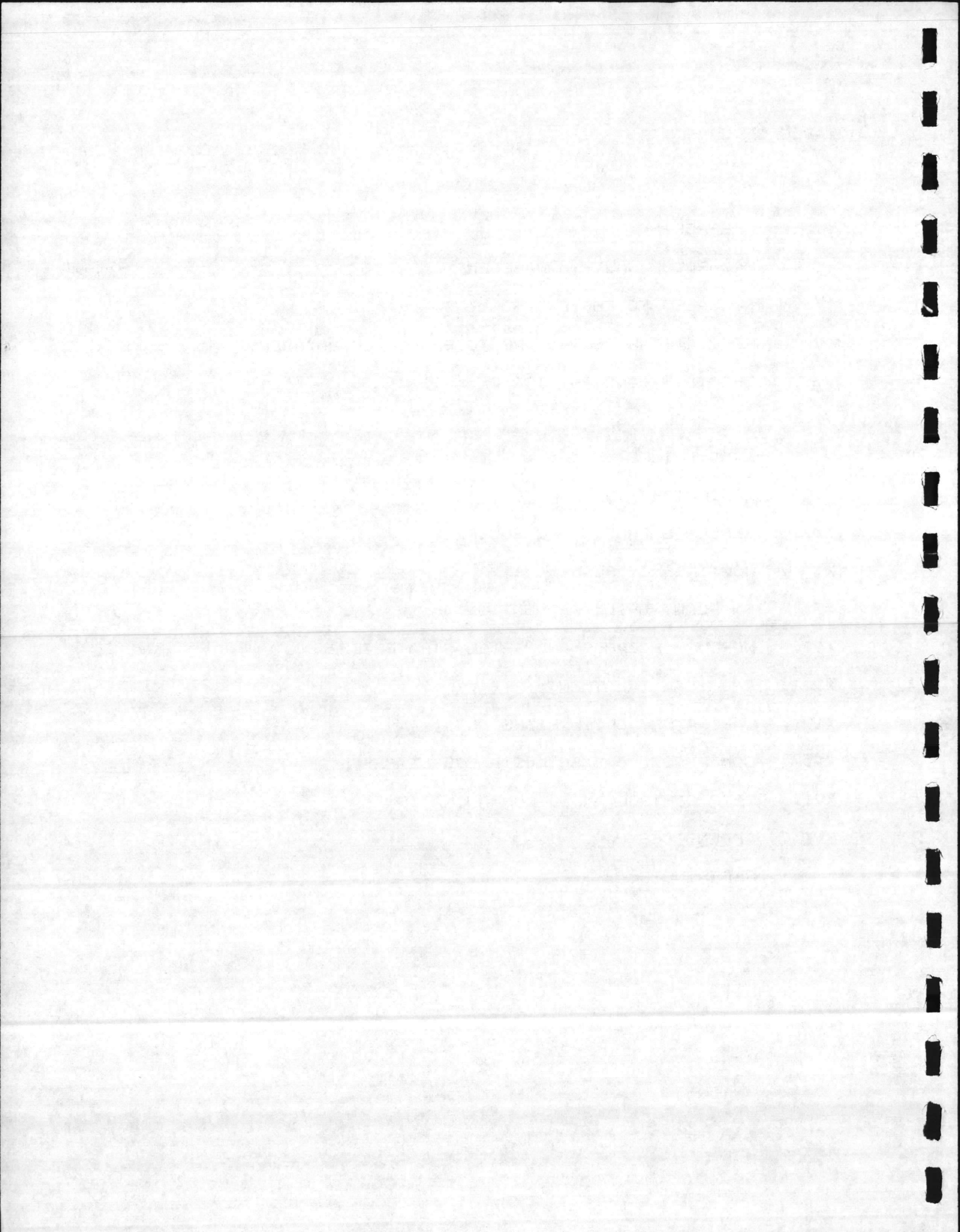




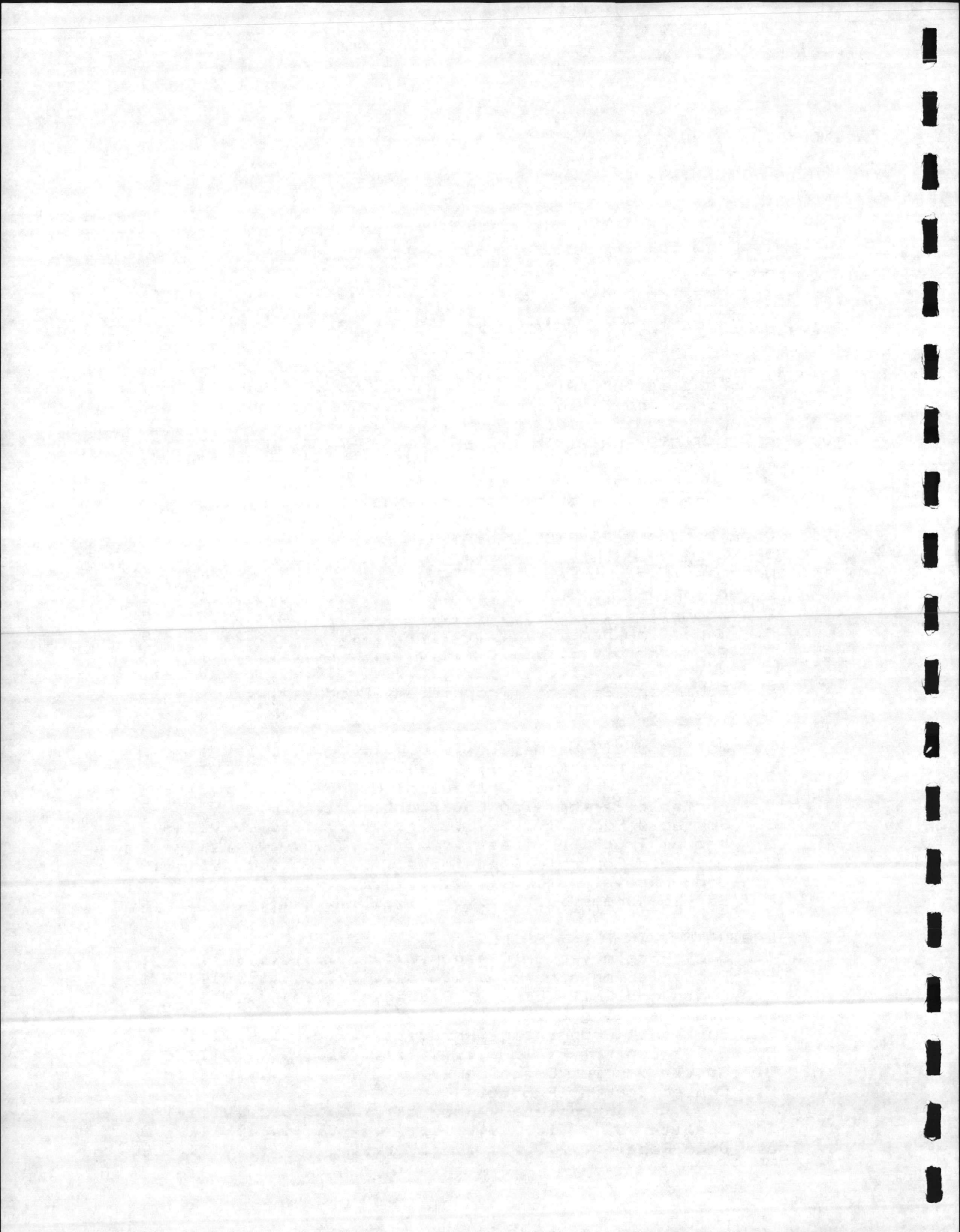
TABLE OF CONTENTS

- I. PREFACE
  - II. HAZARDOUS WASTE MANAGEMENT
  - III. RELEASES TO THE ENVIRONMENT
  - IV. REGULATIONS PERTAINING TO SPILLS OF HAZARDOUS MATERIALS
  - V. CHEMISTRY AND PHYSICS OF MATERIALS
  - VI. WATER SPILLS
  - VII. LAND SPILLS
  - VIII. LABORATORY/IN-PLANT SPILLS
  - IX. PERSONAL PROTECTIVE EQUIPMENT
  - X. CONTINGENCY PLANS
  - XI. IN-PLANT SPILL PREVENTION
  - XII. MERCURY HAZARDS AND SPILL STRATEGIES
  - XIII. CHEMICAL TREATMENT
  - XIV. LABORATORY SPILL RISKS
  - XV. COMPRESSED GAS SPILLS AND RELEASES
  - XVI. SITE CONTROL AND DECONTAMINATION
  - XVII. APPENDICES
- REFERENCES

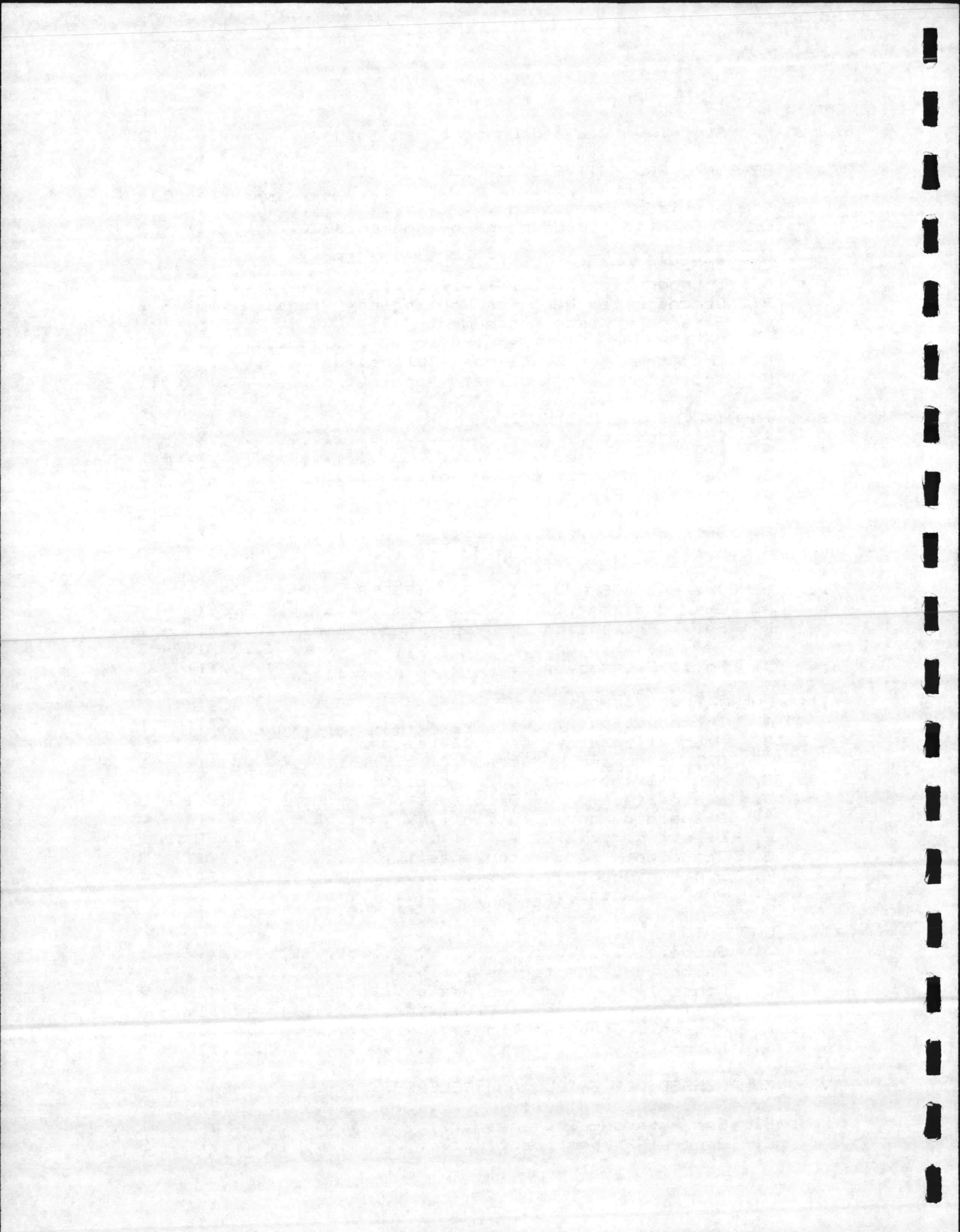


# INDEX

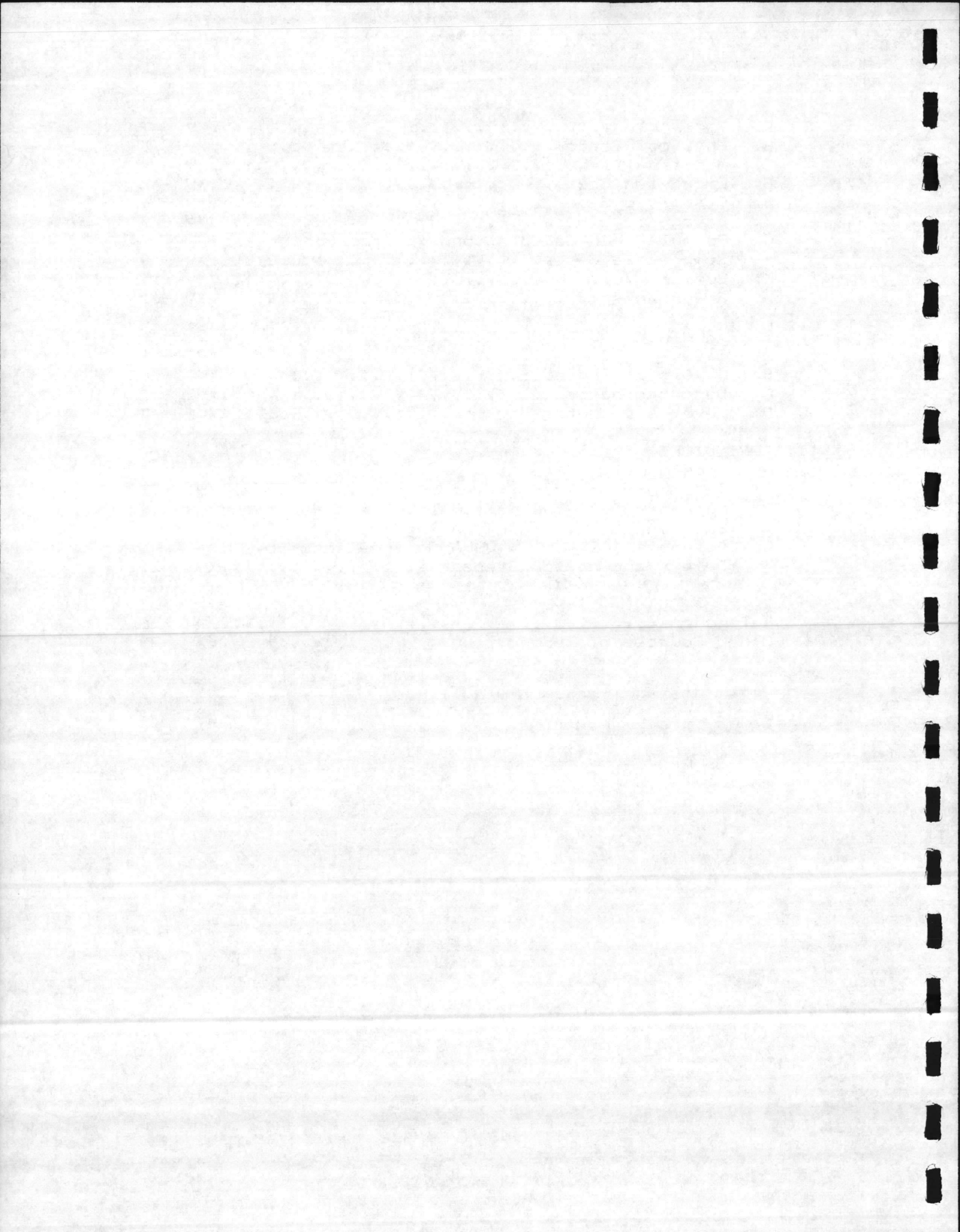
I.	PREFACE	
II.	HAZARDOUS WASTE MANAGEMENT	
	A. Systems Analysis.....	II - 2
III.	RELEASES TO THE ENVIRONMENT	
	A. Release into the Water.....	III - 1
	B. Release onto Land.....	III - 1
	C. Release into Air.....	III - 2
	D. Fires and Explosions.....	III - 2
IV.	REGULATIONS PERTAINING TO SPILLS OF HAZARDOUS MATERIALS	
	A. Department of Transportation.....	IV - 1
	B. Environmental Protection Agency.....	IV - 4
	C. General Inspection Requirements.....	IV - 5
V.	CHEMISTRY AND PHYSICS OF MATERIALS	
VI.	WATER SPILLS	
	A. Dredging.....	VI - 1
	B. Booms.....	VI - 5
	C. Underflow Dams.....	VI - 9
	D. Skimming.....	VI -11
	E. Weirs.....	VI -12
	F. Fiberperl Sorbent (Proprietary Product).....	VI -13
VII.	LAND SPILLS	
	A. Well-Point Systems.....	VII - 1
	B. Urethane Foam Control.....	VII - 2
	C. Emergency Material Collection System.....	VII - 3
	D. Portable Earthmoving Equipment.....	VII - 7
	E. Portable Pumps.....	VII - 8
	F. Vacuum Truck Services.....	VII - 9
	G. In-Field Portable Containers.....	VII -10
	H. Land Excavators.....	VII -12
	I. Salvage Drums.....	VII -14
VIII.	LABORATORY/IN-PLANT SPILLS	
	A. Small-Scale Vacuum Cleanup.....	VIII - 1
	B. Portable Containers.....	VIII - 1
	C. Contained Spill Control Packages.....	VIII - 2
	D. Drum-Handling Units.....	VIII - 4
	E. Spilkart (Proprietary Product).....	VIII - 4
	F. Spill Control Pillows.....	VIII - 5
	G. Bottle Carrier Containers.....	VIII - 6
	H. Conwed Sorbent Products (Proprietary Product).....	VIII - 7
	I. Opalite .....	VIII - 8
	J. Drum Repair.....	VIII - 8



	K. Pipes, Valves and Control Manifolds.....	VIII	-12
IX.	PERSONAL PROTECTIVE EQUIPMENT		
	A. Introduction.....	IX	- 1
	B. Levels of Protection.....	IX	- 2
	C. Protection in Unknown Environments.....	IX	- 8
X.	CONTINGENCY PLANS		
	A. Introduction.....	X	- 1
	B. Demonstrated Need for Contingency Plans.....	X	- 2
	C. Hazardous Waste Management Facility Contingency Plan Requirements.....	X	- 5
	D. Key Items for Contingency Plans.....	X	- 9
	E. Training Needs and Their Application.....	X	-11
XI.	IN-PLANT SPILL PREVENTION		
	A. Introduction.....	XI	- 1
	B. Plant Drainage.....	XI	- 2
	C. Monitoring Process Variables.....	XI	- 2
	D. In-Plant Piping.....	XI	- 3
	E. Solid Material Storage.....	XI	- 5
	F. Bulk Storage.....	XI	- 5
	G. Spill Prevention During Transport.....	XI	- 8
XII.	MERCURY HAZARDS AND SPILL STRATEGIES		
	A. Introduction.....	XII	- 1
	B. Spill Prevention and Vapor Reduction.....	XII	- 1
	C. Personal Hygiene.....	XII	- 3
	D. Spill Cleanup.....	XII	- 3
XIII.	CHEMICAL TREATMENT		
	A. Introduction.....	XIII	- 1
	B. Neutralization - Acids/Bases and Oxidation and Reduction.....	XIII	- 1
	C. Neutralization Steps - Acids/Bases.....	XIII	- 9
	D. Neutralization of Oxidizers and Reducers.....	XIII	- 5
	E. Dispersion and Dilution.....	XIII	-10
	F. Dilution.....	XIII	-11
	G. Coagulants and Flocculants.....	XIII	-12
	H. Sinking Agents.....	XIII	-14
	I. Precipitants.....	XIII	-14
XIV.	LABORATORY SPILL RISKS		
	A. Scope.....	XIV	- 1
	B. Laboratory Strategies.....	XIV	- 2
	C. Controls on Hazardous Wastes.....	XIV	- 2
	D. Spill Prevention.....	XIV	- 3
	E. Hygienic Considerations.....	XIV	- 5
	F. Laboratory Spill Kits.....	XIV	- 5
XV.	COMPRESSED GAS SPILLS AND RELEASES		
	A. Gas vs Liquid.....	XV	- 1
	B. Gas Hazards--Extremes.....	XV	- 1
	C. General Properties.....	XV	- 2



D.	Terminology.....	XV	- 3
E.	Physical States.....	XV	- 3
F.	Non-liquified.....	XV	- 4
G.	Liquified Gases.....	XV	- 5
H.	Dissolved Gases.....	XV	- 6
I.	Cryogenic Liquids.....	XV	- 7
J.	Formulas and Calculations for Compressed Gases.....	XV	- 9
K.	Summary.....	XV	-11
L.	References.....	XV	-12
XVI.	SITE CONTROL AND DECONTAMINATION		
A.	Site Work Zones.....	XVI	- 1
B.	Levels of Protection.....	XVI	- 1
C.	Decontamination.....	XVI	- 2
D.	Level A Decontamination.....	XVI	- 7
XVII.	APPENDICES		
A.	Appendix I. Subpart D -- Vehicles and Shipments in Transit; Accidents.....	XVI	- 1
B.	Appendix II. The National Oil and Hazardous Substances Pollution Contingency Act.....	XVI	-10
C.	Appendix III. U.S. OSHA General Industry Safety and Health Standards.....	XVI	-21
	References.....	XV	-26
	Other Sources of Information.....	XV	-29





## I. PREFACE

"Techniques for Hazardous Chemical and Waste Spill Control" first appeared last year and has now been revised and expanded in order to meet growing needs and ever changing technology. This second edition (1983) now includes an additional five sections, X through XIV, which provide greater in-depth information about the problems and solutions of hazardous wastes and chemical spills today.

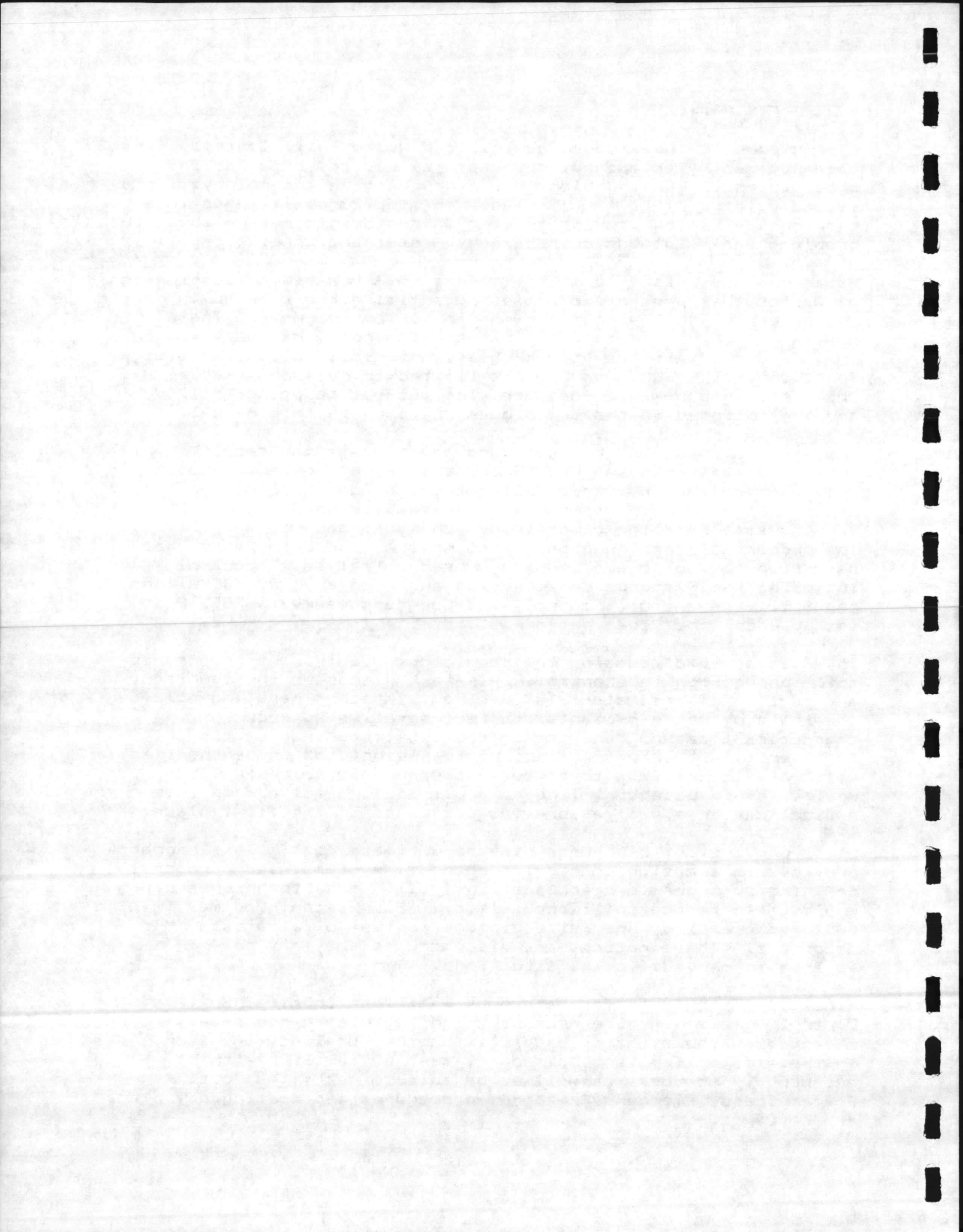
Hazardous waste is a term that refers to any waste or combination of wastes that presents or poses potential dangers to human health and safety or to living organisms in our environment. These wastes may be biological, explosive, flammable, radioactive, or toxic and may take the form of gases, liquids, solids, or sludges. Spill control techniques are not limited to hazardous wastes; chemicals in non-waste form are also subject to being spilled and are included in the techniques reviewed in this manual.

The mismanagement of chemicals and their waste may result in serious damage to human health and to the environment. Due to this danger, the Environmental Protection Agency (EPA) and the Department of Transportation (DOT) have both set up guidelines for the safe handling of hazardous chemical and waste spills. The purpose of this handbook is to review the guidelines that have been set up to aid in hazardous chemical spill control, including the Resource Conservation and Recovery Act (RCRA) and the Spill Prevention, Control, and Countermeasures (SPCC) Plan set up under the Clean Water Act.

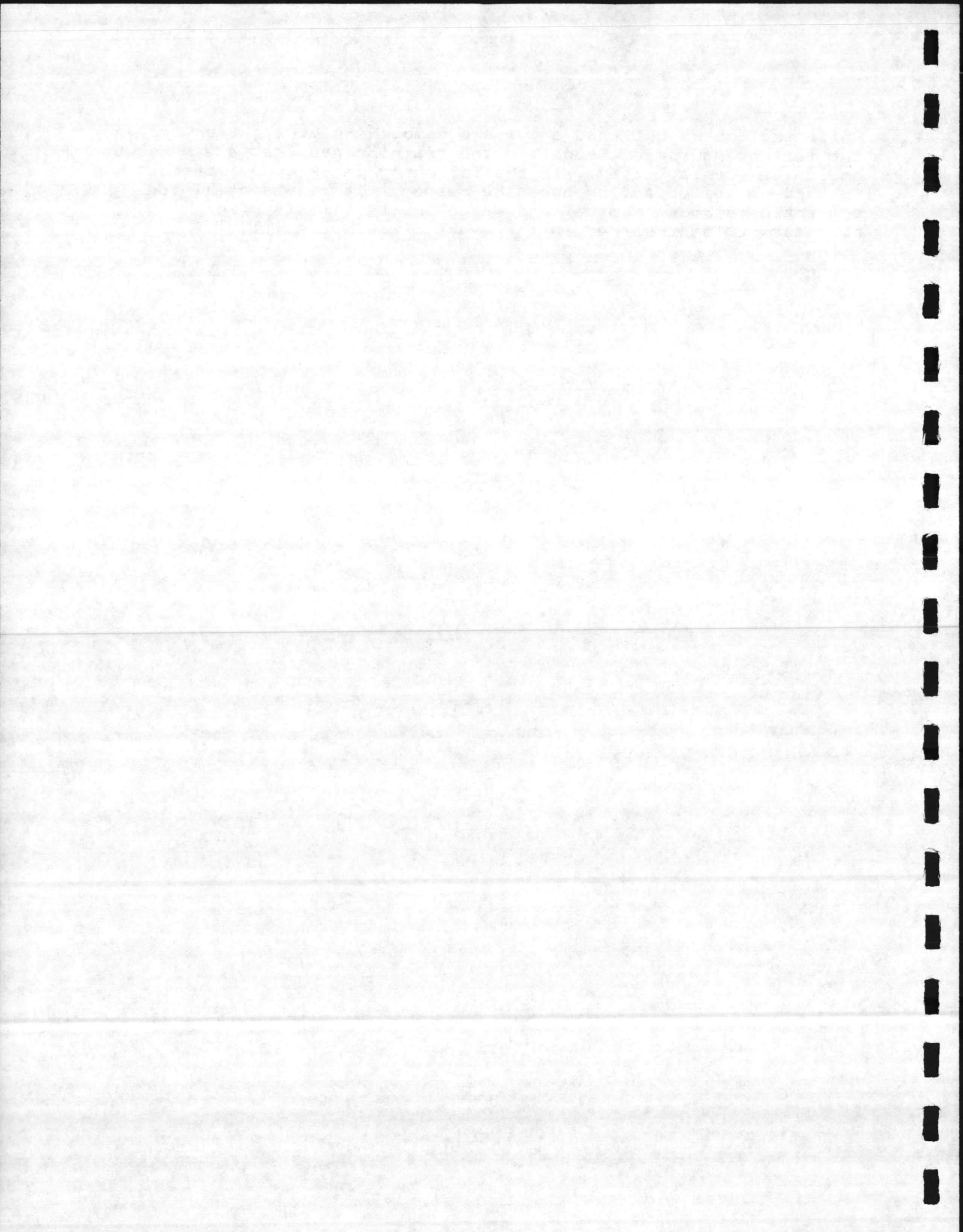
In addition to discussing the regulatory requirements concerning spill prevention and control, this text discusses the chemistry and physics of the materials involved. Whether handling pure chemicals or waste products, it is imperative to know the characteristics and behavior of the substances. Unquestionably, familiarity with chemicals and wastes being used or synthesized will make it possible to properly cleanup and/or neutralize spills; avoid potential fire hazards; and provide appropriate medical care; as well as prevent accidents in the first place.

Spill prevention, of course, is the ultimate goal. This handbook provides information concerning methods, systems, and personnel training in order to reach just this aim. Many techniques can be employed to reduce spill probability. Such techniques may involve employee training, special equipment, or use of alternate materials. These options are discussed as they may be applied in many different situations.

Finally, "Techniques for Hazardous Waste and Chemical Spill Control" deals with the necessary and legislated responses expected in the event of a spill. Whether on land, in water, in the air, or in-plant, personnel must be familiar with emergency procedures as well as be able to carry them out. Preparedness, emergency response procedures and contingency plans are reviewed.



While the topics outlined above are simple and straightforward, the various equipment, supplies and training required are numerous and quite sophisticated. In the following pages every attempt is made to advise and prepare the reader. It is essential to prevent hazardous chemical and waste spills; it is also necessary to be prepared in the event of such a spill.



## **II. HAZARDOUS WASTE MANAGEMENT**

Congress enacted the Resource Conservation and Recovery Act (RCRA) in 1976. Although the Act has several objectives (including the promotion of resource recovery and the proper management of non-hazardous solid waste), Congress' "over-riding concern" in enacting RCRA was to establish the statutory framework for a national system that would insure the proper management of hazardous waste.

That framework is contained in Subtitle C of the statute. It requires EPA to establish a Federal "cradle to grave" management system for hazardous waste, including standards for generators of hazardous waste (Section 3002), standards for transporters of hazardous waste (Section 3003), standards and permit requirements for owners and operators of facilities that treat, store, or dispose of hazardous waste (Sections 3004 and 3005), and a manifest system that will track the movement of the waste from the point of disposal.

Spill prevention and control programs are mandated by RCRA in Subpart C entitled "Preparedness and Prevention" and Subpart D entitled "Contingency Plan and Emergency Procedures" of Part 265 of the standards. The requirements in Subpart C deal with the required equipment which can be summarized as follows:

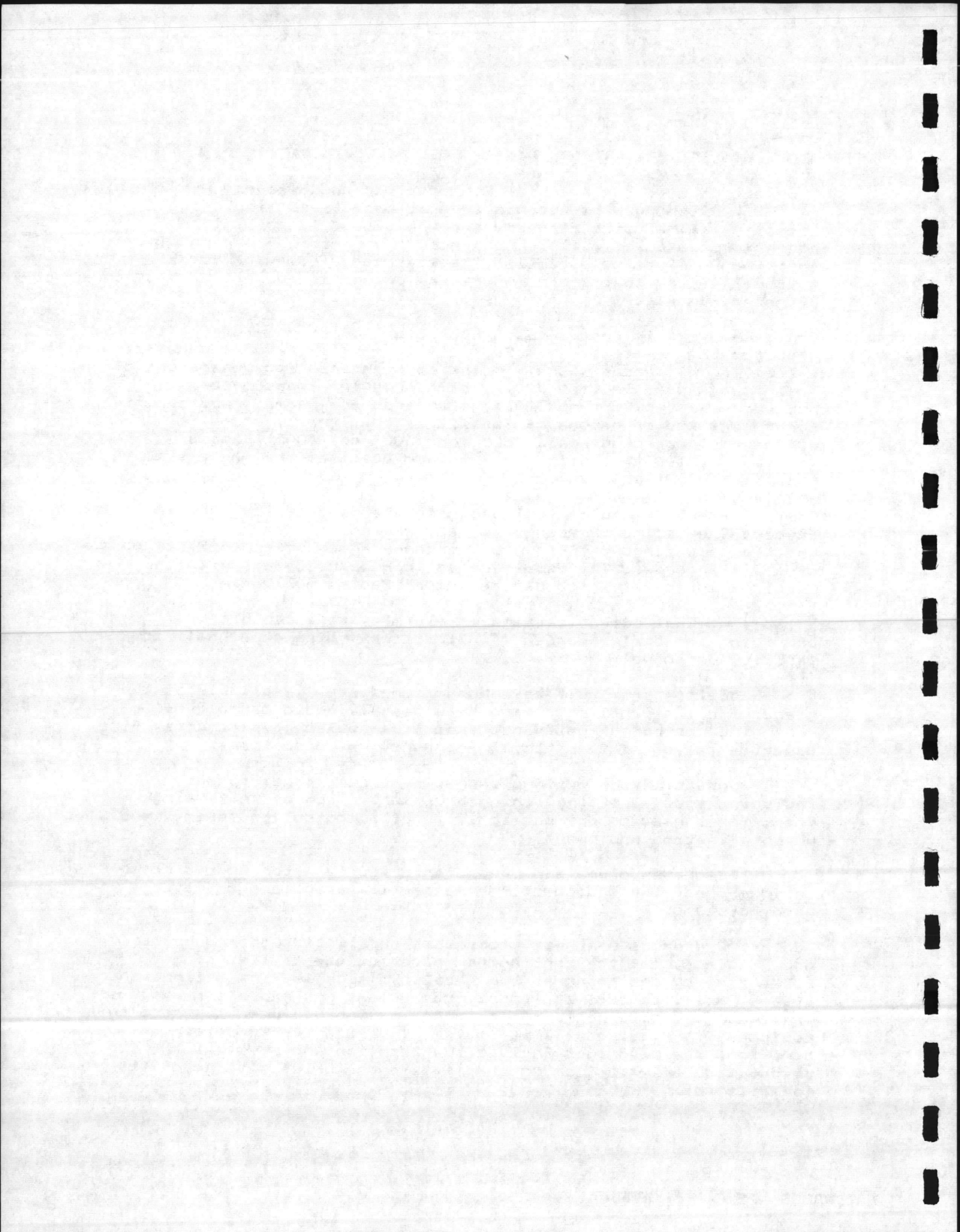
- internal communications or alarm systems capable of providing immediate emergency instruction (voice or signal) to facility personnel.

- devices such as a telephone (immediately available at the scene of operations) or a hand-held two-way radio capable of summoning emergency assistance from local police departments, fire departments, or state or local emergency response teams.

- portable fire extinguishers, fire control equipment including special extinguishing equipment (such as that using foam, inert gas, or dry chemicals), spill control equipment, and decontamination equipment.

- adequate volume and pressure to supply water hose streams or foam-producing equipment for automatic sprinklers or water spray systems.

Subpart D expands on these items that are listed under Subpart C and requires that the contingency plan include "a list of all emergency equipment at the facility (such as fire extinguishing systems, spill control equipment, communications and alarm systems (internal and external), and decontamination equipment), where this equipment is required. This list must be kept up-to-date. In addition, the plan must include the location and physical description of each item on the list, and a brief outline of its capabilities."



The requirements of Subpart C and Subpart D do not specify the exact type of equipment that is needed for spill control. The preamble to the standard does indicate that the rules are "...intended to minimize the possibility of and effect of a release, fire, or explosion which could threaten human health or the environment." The preamble also indicates that the equipment, where required, must be routinely tested and maintained in a proper operating condition. It was stated to be the intent of the RCRA contingency and emergency response plans to include steps to respond to both internal and external threats. The preamble to the standard does acknowledge, however, that the primary responsibility for regulating workplace health and safety rests with the Occupational Safety and Health Administration of the Department of Labor, more commonly known as OSHA.

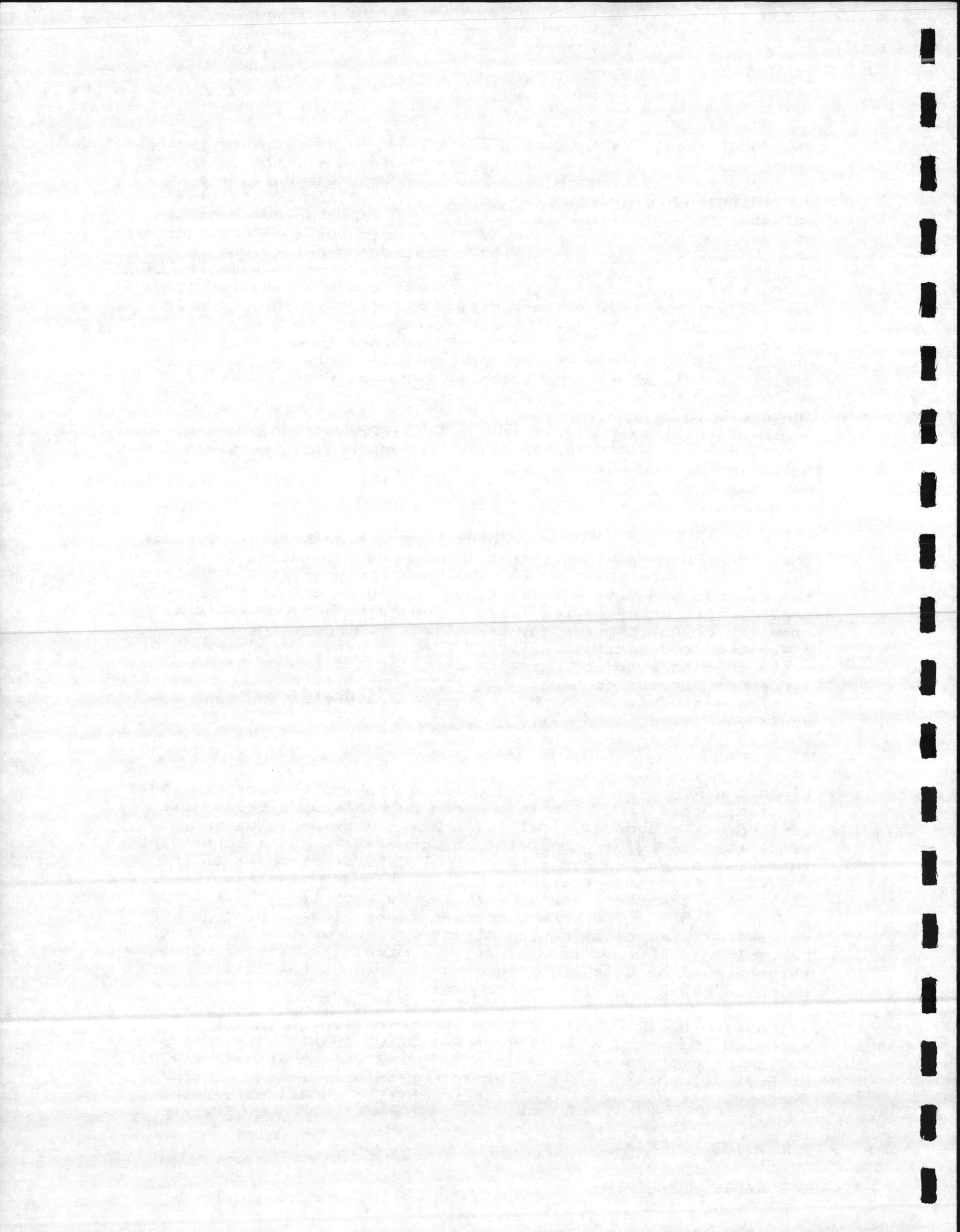
The preamble also acknowledges that much of the spill prevention program can be assembled from the Spill Prevention, Control, and Countermeasures (SPCC) plan which is required by the Clean Water Act. The history of the rules indicates, however, that EPA does not feel that the SPCC plan is identical to the type of plan that is necessary for the RCRA requirements.

Another important point presented in the preamble to the rules is that the EPA acknowledges that it was not its intent to require that contingency plans be invoked when insignificant amounts of the hazardous wastes are released. Examples are given of very small spills or a leaking valve. The rules and regulations, however, do not provide any exemption from providing spill prevention and control equipment that is based on an amount of waste that an owner or operator or generator has on hand. Therefore, it is incumbent upon the owner, operator, or generator to have available the necessary spill prevention and control equipment.

#### A. SYSTEMS ANALYSIS

Since the RCRA rules do not provide a listing of equipment that is required, this type of standard can properly be labeled as a performance standard. That is, a measure of performance is required of an owner, operator, or generator. As a consequence, there is no real way to make a final determination as to the suitability of the equipment unless an emergency actually occurs. It becomes a matter, then, of trying to ascertain the type of emergency that might occur, whether it be fire, explosion, or release. The type of equipment and procedures that will need to be employed in order to adequately control the fire, explosion, or release must be determined in order to reduce the hazard to human health and the environment.

One possible way of making this determination is through a technique known as a Fault Tree Analysis. Fault Tree Analysis is a type of systems safety engineering analysis that was developed by Bell Telephone Laboratories and refined by Boeing Aircraft Company. It begins with a catastrophic or undesired event and,



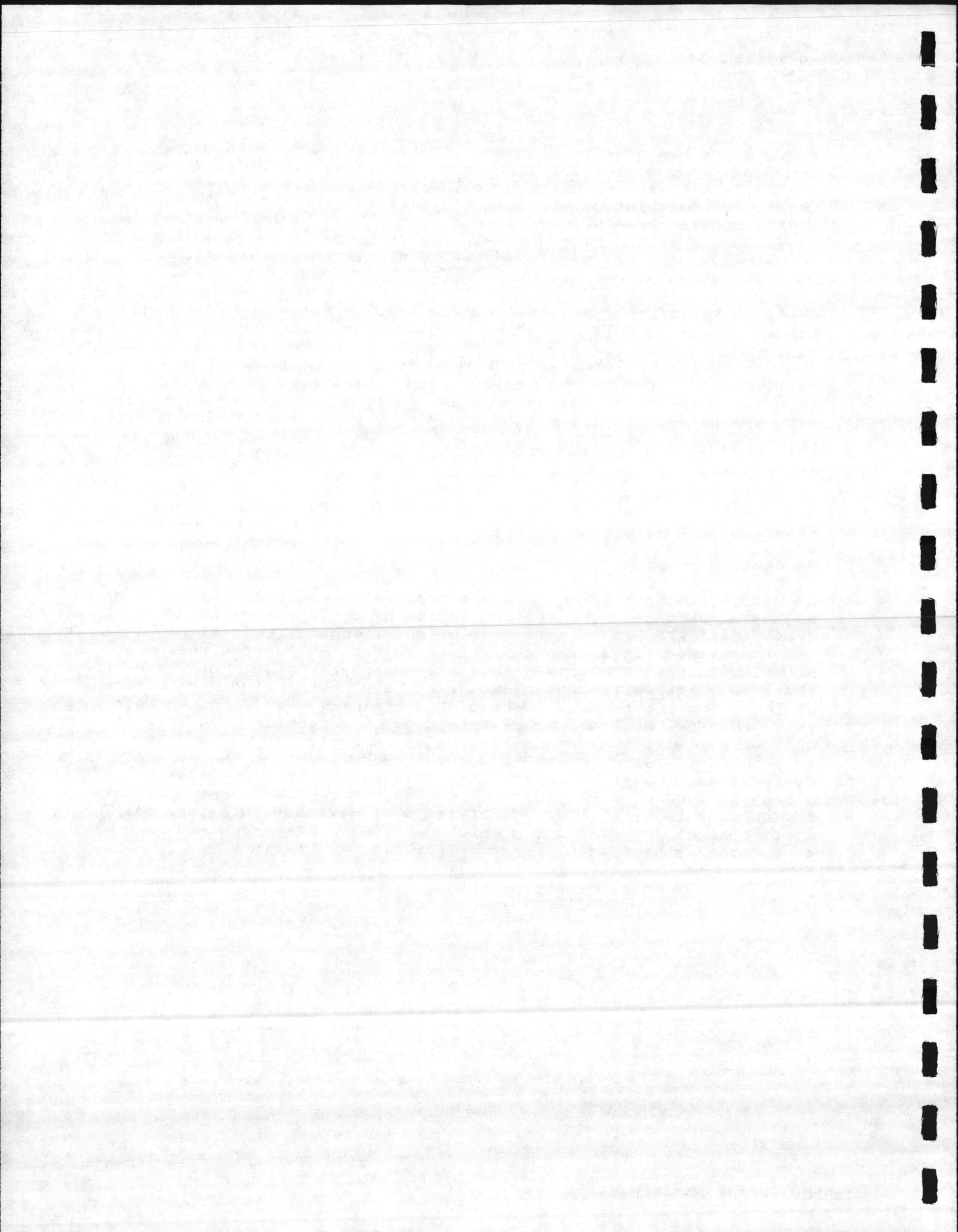


through the use of flow diagrams, traces preceding events that might have caused the catastrophe. The diagrams provide for probability that each pathway to the final undesired event will occur. By calculating the probabilities of each pathway occurring, a determination can be made as the most likely method or manner of failure. If the hazard is capable of occurring from a number of pathways, the use of a computer to aid in the calculations would be advantageous, if not an absolute necessity.

Another type of analysis that can be made to determine how a spill control program would be implemented, and thus the type of equipment necessary, is the system employed by the nuclear industry which is known as an Event Tree. As contrasted to a Fault Tree, an Event Tree depicts each separate event that might occur from any given operation being performed. It does not begin with the catastrophic event or undesired event, but it begins with any particular function.

Other methods exist within the field of system safety engineering. Whatever method is used, someone, based on engineering analysis, or a review of historical data, or a review of existing literature, must make a determination as to the type of events that could occur and then specify the type of spill control equipment necessary.

Some spill control techniques are readily acknowledged as being an essential part of the operating equipment or layout of the facility. Examples of this type of spill control consist of dikes provided for aboveground tanks as well as lagoons that are normally located downstream from a tank area. In both of these instances, the spill control measures have been included as part of the operating layout. Most of the measures overviewed in this text, however, will not be of this type of preconstructed spill control but will instead be of the type expected to be used in an emergency. As an example, vacuum trucks or honey wagons are reviewed as a means of controlling a spill that has occurred onto a body of land or water such as in a lagoon or diked area. Most of the permanently installed facilities will have had this type of spill control provided and probably will have been required to do so by other governmental codes or building regulations.



### III. RELEASES TO THE ENVIRONMENT

One particular way of categorizing the type of event that might occur is in terms of release to the environment. It is possible that the spill could be released to the air; that is, become airborne. Secondly, the possibility exists that the release could occur onto land. Thirdly, the release could possibly occur into a body of water. Releases either into the air or onto the land could eventually end up in a body of water. A release onto land could go into underground aquifers and hence migrate into a body of water. Releases into the air could, with some degree of possibility, end up condensing and then falling back to earth, and through migration through the ground, end up in the water table and into the drinking water supply. For the most part, the initial

spill prevention and control program will probably be designed around the possibilities of the release occurring either to the air, to a land mass, or to a body of water. If the release does occur to either of the three, specific types of spill control equipment are available and should be employed.

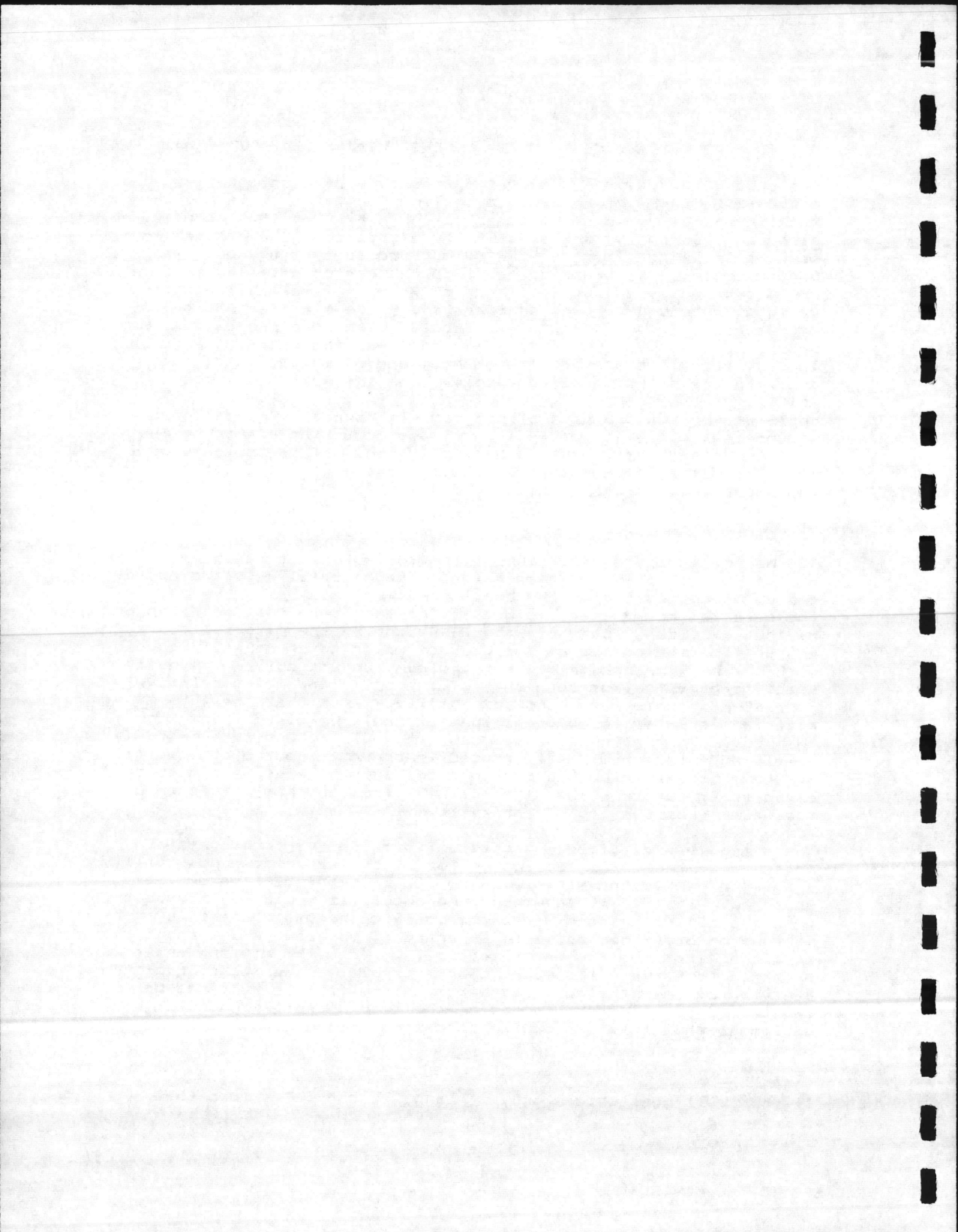
#### A. RELEASE INTO THE WATER

If the release does occur into a body of water, it is assumed that one of several possibilities exist. The material released could end up on the bottom of the body of water, this being the case if the material has a specific gravity greater than that of water or of that particular body of water. Secondly, the material could end up floating on top of the body of water, such as will occur with oil or kerosene or other petroleum product spills having a specific gravity less than that of the water and being relatively non-water-soluble. A third possibility exists that the material is water soluble and that it could be mixed throughout the body. In the three instances, it would necessitate that vastly different equipment be used in order to control the spill. If the material is on the bottom, some type of equipment must be employed to remove either the material from the body of water or the water from the top of the spill.

There are several different possibilities for performing this action. If the spill remains on top of the water, the possibility exists to remove the material from it, or remove the water from underneath it. If it is mixed throughout, it would be incumbent upon the person responding to the spill to remove the entire mixture or use a mechanism to separate it in place and then remove it either from the top or the bottom, or from the mixture as it exists. It is very important that a complete understanding of the behavior of the particular material which might be released be maintained for a determination of the type of spill control equipment that this particular operation will employ.

#### B. RELEASE ONTO LAND

If the spill goes onto a body of land, it can be assumed that



either it will remain on top of the land body for a specified period of time, or that it will immediately go through the land body, or that it will mix with the land body to a specified depth. What actually occurs depends first on the type of material that has been released and, specifically, whether it exists as a liquid, as a sludge, or as a solid, and second, and equally as important, the type of soil on which the material is spilled. As an example, a material that is spilled onto a sandy soil would, for the most part, pose a far greater hazard than a material which is spilled onto a clay soil. Therefore, in determining the type of response equipment necessary, one would need to determine the physical state of the material being released as well as the land body onto which it might be released. If the material is, for example, in a state of low viscosity and quick migration into the water table could be expected, then the equipment capable of removing the land body itself might be necessitated. If the material is of a low viscosity and remains viscous in a state not combining with the land body, then a type of equipment to remove the liquid material (without actually removing the soil) might be necessitated. In any of the examples given here, the key point is that the person who is making the determination as to the type of equipment necessary for a response needs to have an understanding of the physical properties of the waste being handled. It is also imperative that the person know the type of environment onto or into which the spill might occur; that is, onto the land, into the air, or into a body of water. These would be the two key parameters that the designer would need to take into consideration.

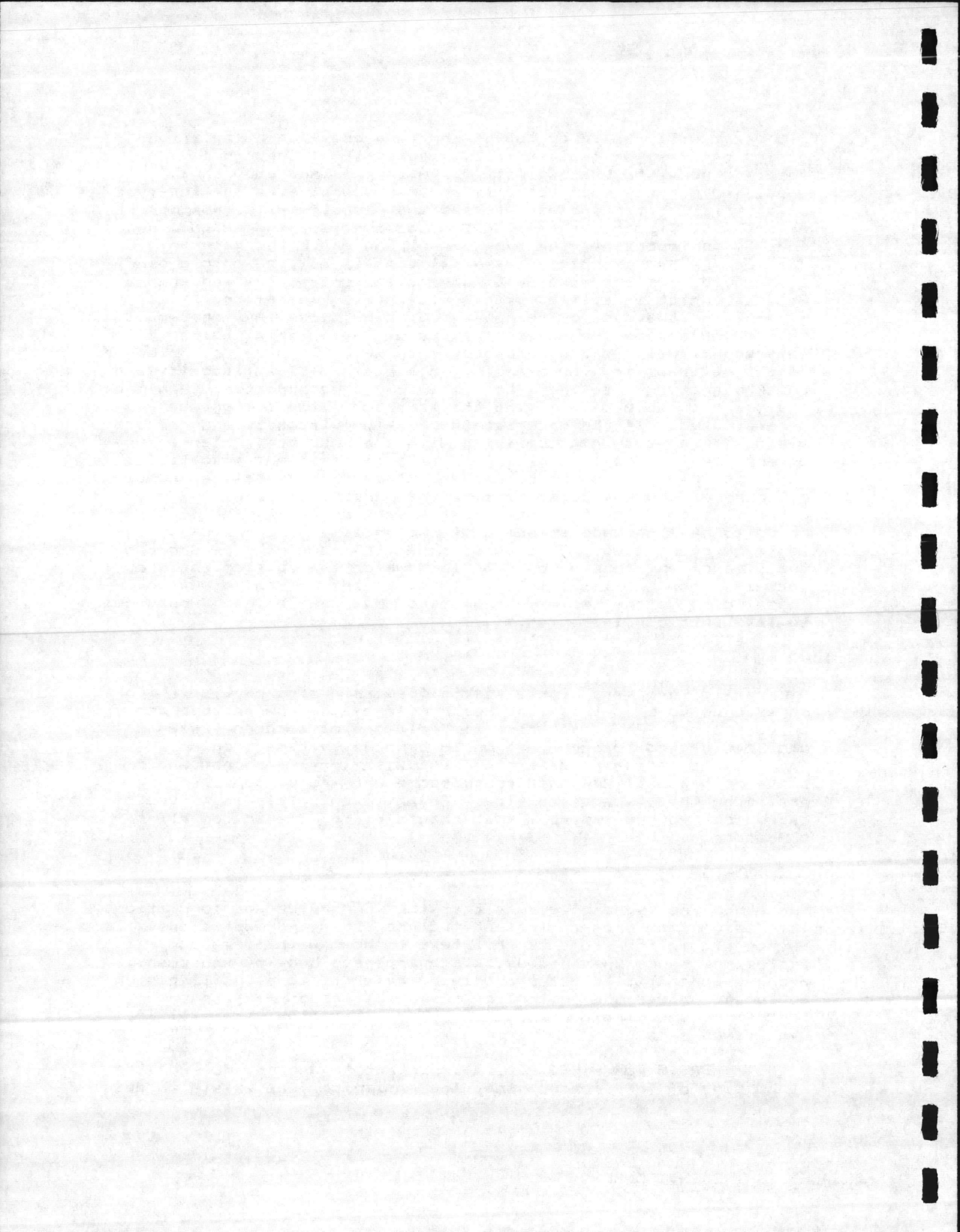
#### C. RELEASE INTO AIR

Air spills involve a highly specialized area of expertise which is considered to be outside the realm of the local owner, operator, or generator. In cases where air releases or airborne releases can be expected to occur, it would behoove that particular facility to make a prior arrangement with local response and/or state or national response contractors who are capable of providing that type of service. In any event, this is a type of backup or redundant system that should be considered for all operators.

#### D. FIRES AND EXPLOSIONS

The other two types of events that the RCRA rules and regulations are designed to protect against include fires and explosions. It is not within the scope of this text to deal with fires and explosions since they necessitate a separate body of equipment. Such equipment would not properly be referred to as spill control equipment unless the control of the spill was primary to the control of the fire or explosion. They, nevertheless, will be overviewed here.

1. BASIS FOR FIRE. It is important to understand from the standpoint of fire control that the basis for fire exists through

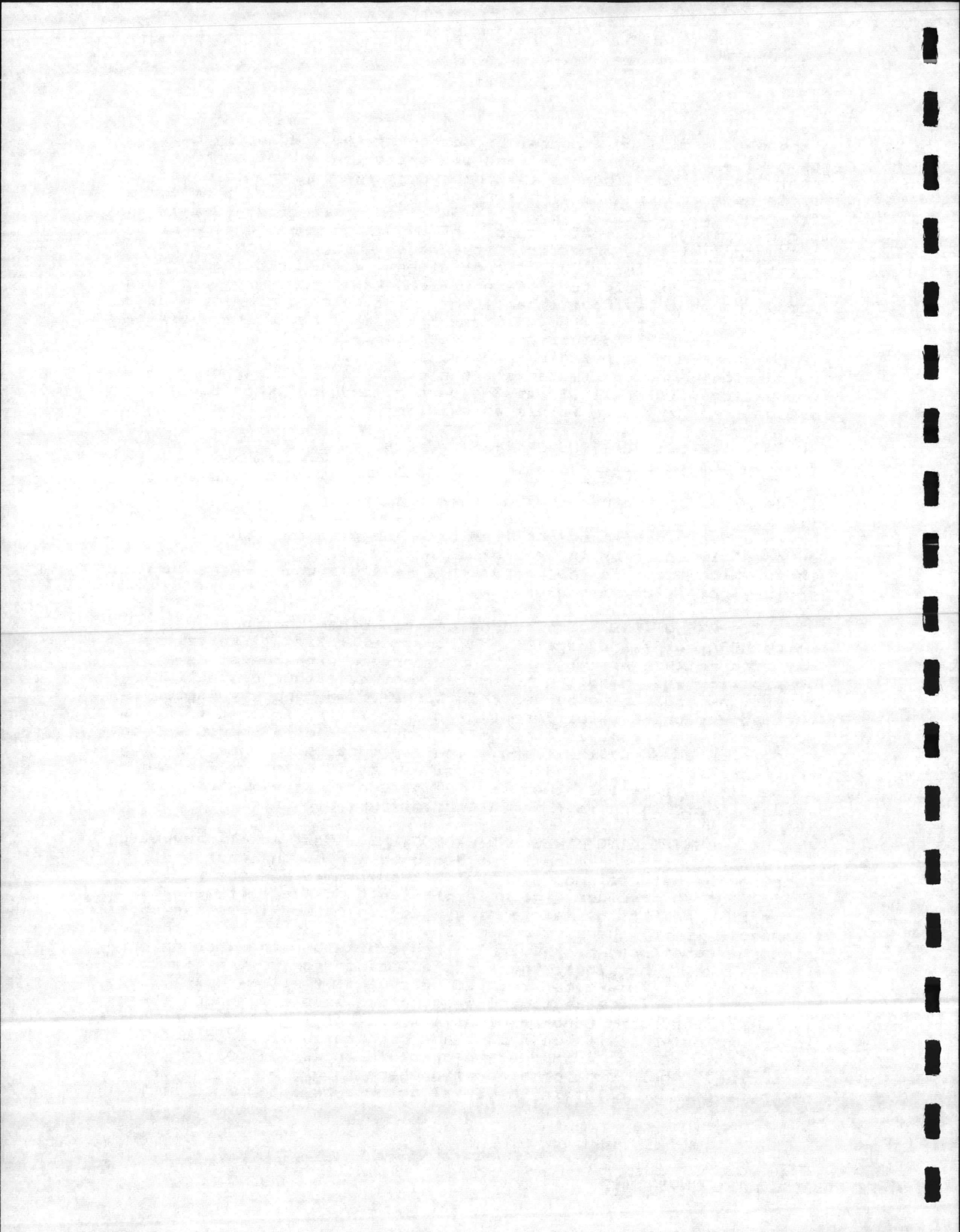


combination of four aspects: a source of fuel, a supply of oxygen, an ignition source, and the establishment of combustion chain reactions. This is the theory upon which fire is based and it is referred to as a fire tetrahedron. It presumes that for a fire to exist that the fuel will exist in a vaporized form (with one exception) and that a supply of oxygen somewhat greater than 16 percent will be provided. It further recognizes that fires exist in one of two modes of combustion: either glowing or flaming. An example to differentiate between the two would be a wood fire that may have embers, which indicates a glowing mode of combustion, and that also may have flames and hence would exist in a flaming mode of combustion. Most materials will need at least 16 percent oxygen in order to exist in a flaming mode of combustion. However, materials can exist in a glowing mode of combustion with as little as 3-4 percent oxygen. This does not presume that the material is an oxidizer.

2. CLASSIFICATIONS OF FIRE. Fires are also classified by the type of material in which they occur. These are referred to as classes of fire and are labeled A, B, C, and D. Class 'A' fires occur in ordinary combustible materials; 'B' fires occur in flammable liquids, vapors, and gases; and 'C' fires occur either as an underlying 'A' or 'B' fire with the exception that it is in, or possibly could be in, energized equipment. Class 'D' fires are those which occur in the combustible metals such as magnesium, sodium, potassium, and aluminum.

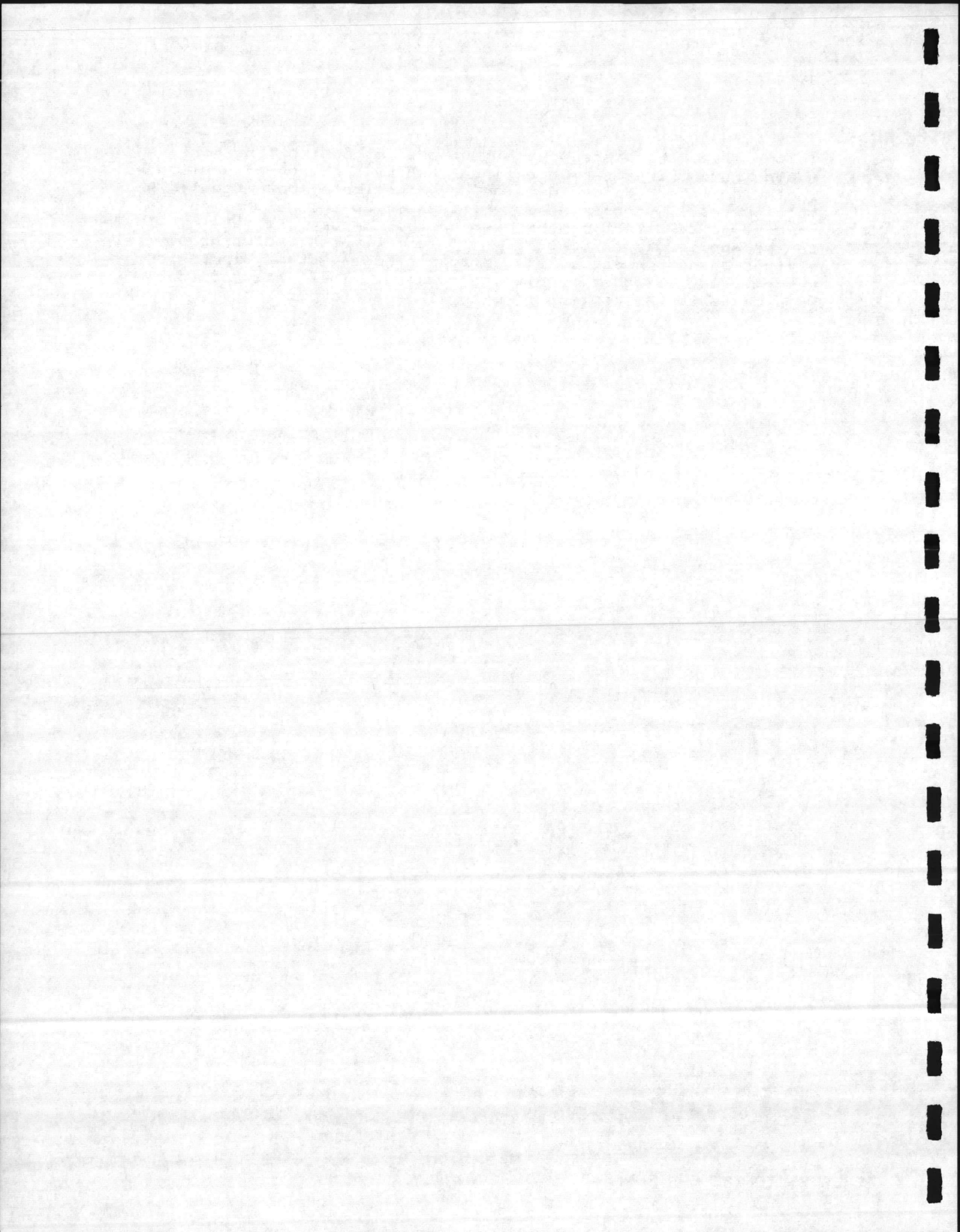
3. EXPLOSIONS. Explosions are the other contingency to which RCRA rules and regulations direct attention. Explosions may occur either without gases and vapors or with dusts; as a possibility when handling hazardous wastes, either of the two conditions could be expected. In either case, the key factor is that an explosion is differentiated from a fire in that there is either total or partial confinement in order for a pressure front to develop ahead of the flame. The key factors in understanding the explosions of gases and vapors have to do with the flammable range of the material; that is, the percent of the mixture by volume in air which is flammable by mixture with air.

4. CONTROLLING FIRES AND EXPLOSIONS. Most spill prevention and control procedures could be designed around the fact that keeping the material above or below the flammable range would be sufficient to preclude fire or explosion. However, it must be borne in mind that by maintaining a concentration above the upper flammable limit, there is quite likely a possibility that the airborne substance, particularly, could be above the threshold limit value. Therefore, the accepted method for control is to maintain it at no greater than 25 percent of the lower explosive limit. With dusts, the same consideration exists although there is no corresponding upper explosive limit for a dust. Once the lower explosive limit for a dust has been reached, it is not possible to get too much dust to preclude an explosion from occurring. Again, the consideration here should be in the design of the system to maintain the level below a predetermined amount.





In any case, there are several methods for controlling fires and explosions. Fires can be extinguished by a number of substances including water, carbon dioxide, dry chemicals (both regular and multipurpose), vaporizing materials such as the halons, and special powders that can be used on the combustible metals. These can be applied in a number of different manners including portable extinguishing apparatus, standpipe and hose systems, sprinkler systems, and fixed extinguishing systems. These are applicable in some cases to the control of both fires and explosions.



## IV. REGULATIONS PERTAINING TO SPILLS OF HAZARDOUS MATERIALS

### A. DEPARTMENT OF TRANSPORTATION

One particular document that provides a great deal of information on hazardous waste in the transportation process is the EPA/DOT: HAZARDOUS WASTE TRANSPORTATION INTERFACE -- GUIDANCE MANUAL. This particular document summarizes in a table the pertinent hazardous material spill incident regulations as they are governed by the sections in 49 CFR. The table provides information for accidents as they may exist by categories of explosives, which is governed by Section 49 CFR 177.855, flammable liquids in Section 177.856, flammable solids and oxidizing materials in 177.857, corrosive materials in 177.858, compressed gases in 177.859, poisons (either by leakage or accidents) in 177.860, and radioactive material accidents in 177.861. The sections discuss in general the procedural requirements that the individual is required to meet.

1. REGULATIONS CONCERNING DISABLED VEHICLES. Section 177.854, entitled "Disabled Vehicles and Broken or Leaking Packages; Repairs," indicates in 177.854(b), entitled "Disposition of Containers Found Leaking or Broken in Transit" that "When leaks occur in packages or containers during the course of transportation subsequent to initial loading, disposition of such package or container shall be made by the safest practical means afforded by paragraphs (c), (d), and (e) of this section." Paragraph (c) provides requirements for repairing or overpacking packages:

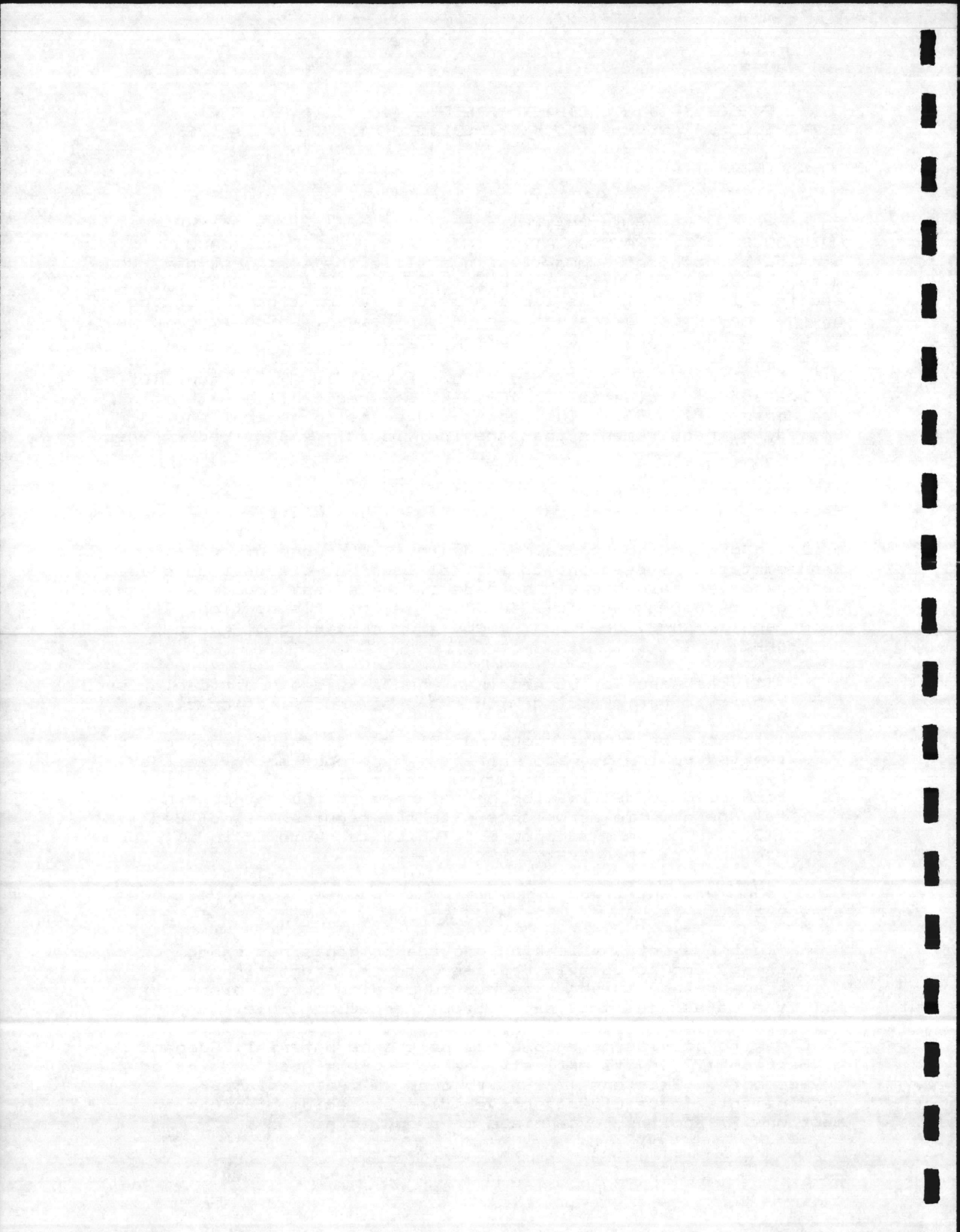
"(1) Packages may be repaired when safe and practicable, such repair to be in accord with the best and safest practice known and available.

(2) Packages of hazardous materials that are damaged or found leaking during transportation or hazardous materials that have spilled or leaked during transportation, may be forwarded to destination or returned to the shipper in a salvage drum in accordance with the requirements of Section 173.3(c) of this subchapter" (which is reviewed in a later section of this text).

Paragraph (e), entitled "Disposition of Unsafe Broken Packages" states that:

"In the event any leaking package or container cannot be safely and adequately repaired for transportation or transported, it shall be stored pending proper disposition in the safest and most expeditious manner possible."

In order to provide more complete reference material, Subpart D, of Section 177 in its entirety, has been reprinted and included as an appendix. Sections 177.853 through 177.861 include the requirements for accidents on vehicles and shipments in transit, Section 177 applies to carriage on a public highway.



Other modes of transportation might also be appropriate to examine if there is going to be transportation of a hazardous waste. There are, in addition, requirements for accidents as they may occur for transportation by rail, which is governed in Part 174 of the DOT rules and regulations given in the CFR. Data are given for aircraft requirements in Part 175 and by vessel in part 176.

2. TRANSPORTATION BY RAIL. Section 174.50 pertains to general requirements for leaking tank cars. The general requirements that are specified in this section provide in six separate items under 174.50 (a) through (f) the following:

"(a) A tank car discovered in a leaking condition in transit may not be unnecessarily moved until the unsafe condition has been corrected. In the case of a small leak, short movements may be made if a receptacle is attached under the leak to prevent the spread of the liquid over tracks.

"(b) Each leaking tank car must be protected against ignition of the liquid or vapor by flame from sources such as lanterns, torches, flares, fuses, switch lights, switch-thawing flames, fires on sides of tracks, hot coals, lighted pipes, cigars, or cigarettes. All spectators should be kept at a safe distance.

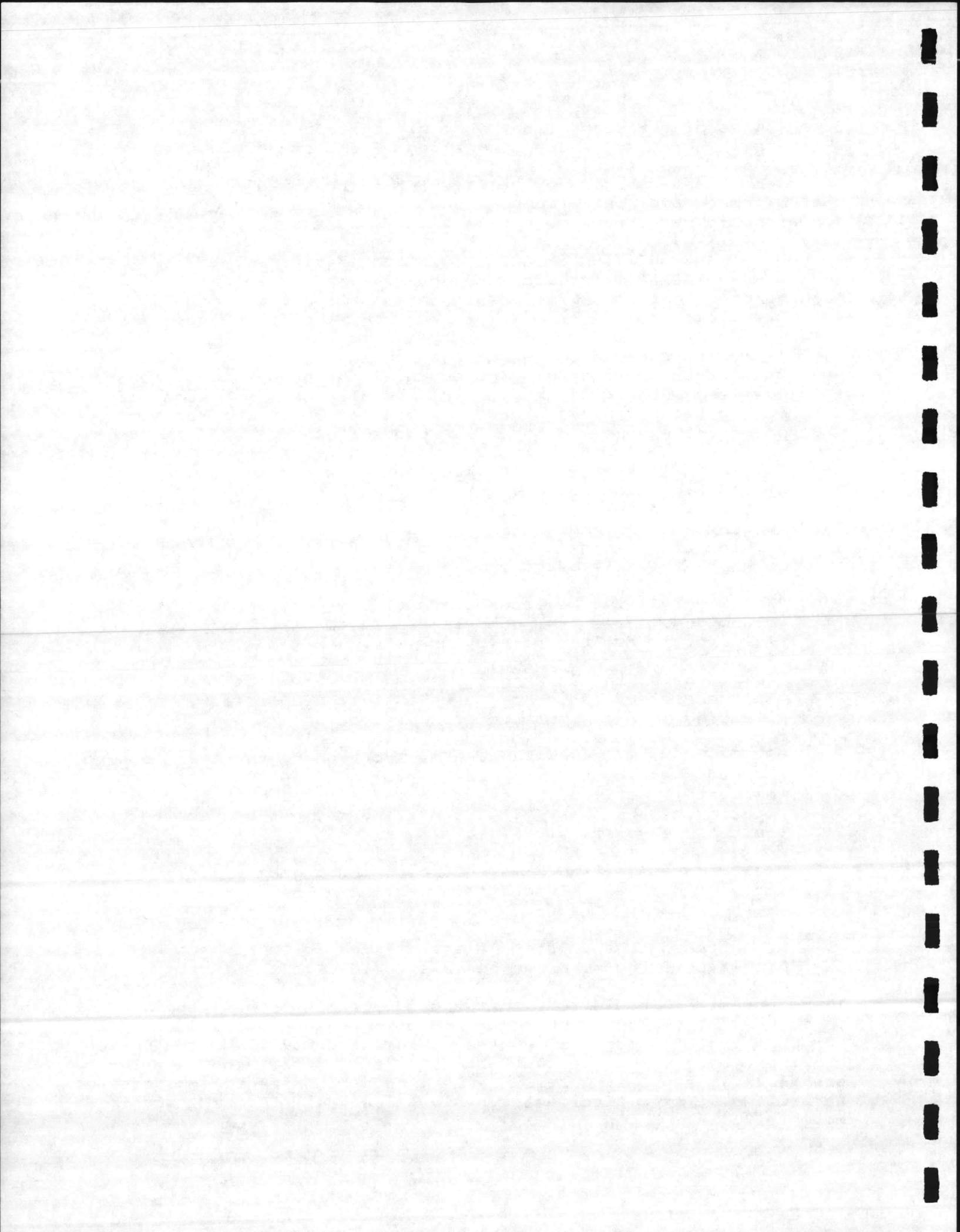
"(c) Highly volatile liquids cannot be transferred by a vacuum pump unless the pump is placed so that the liquid flows to it from the tank by gravity.

"(d) Whenever the leaking condition of a tank car requires the transfer of lading or makes that tank unfit for reloading, the car must be stenciled on both sides in letters three inches in size, adjacent to the car number, LEAKY TANK. DO NOT LOAD UNTIL REPAIRED. The location of the leak must be indicated and marked with the symbol X. The owner must be immediately notified by telegram and advised of the exact location of the leak. The stenciling may not be removed until the tank is repaired.

"(e) Open-flame lights may not be brought near a placarded empty or partially loaded tank car.

"(f) A leaking tank car containing any hazardous material may be switched to a location distant from habitation and highways if the move can be safely made."

There are other regulations that are applicable to rail spill incidents. These are contained in Section 49 CFR 174.103 for the "Disposition of Damaged or Ashtray Shipment's, 174.290 for "Poison A Shipped by, for, or to the Department of Defense" and specifically addressing leaking container requirements for poison A; and 174.750 for "Incidents Involving Leakage" [of radioactive material].



These paragraphs should be consulted for additional requirements which may be applicable for incidents or spills that could occur during the transportation by rail.

3. TRANSPORTATION BY AIRCRAFT. The next section that addresses transportation, specifically spills that may occur in transportation by aircraft, is contained in Part 175. The basic requirements that pertain to incidents that may occur during air transportation are governed by Section 175.90 entitled "Damaged Shipments." In this section, it states that:

"Except as provided for in Section 175.700, the operator of an aircraft shall remove from the aircraft any package subject to this subchapter that appears to be damaged or leaking. No person shall place or transport a package that is damaged or appears to be damaged or leaking aboard an aircraft subject to this Part."

4. TRANSPORTATION BY VESSEL. The requirements that pertain to transportation by vessel are contained in Section 176 entitled "Carriage by Vessel." The two specific standards that address Carriage by Vessel are Sections 176.45 and 176.50. Section 176.45 is entitled "Emergency Situations" and provides in paragraph (a) that:

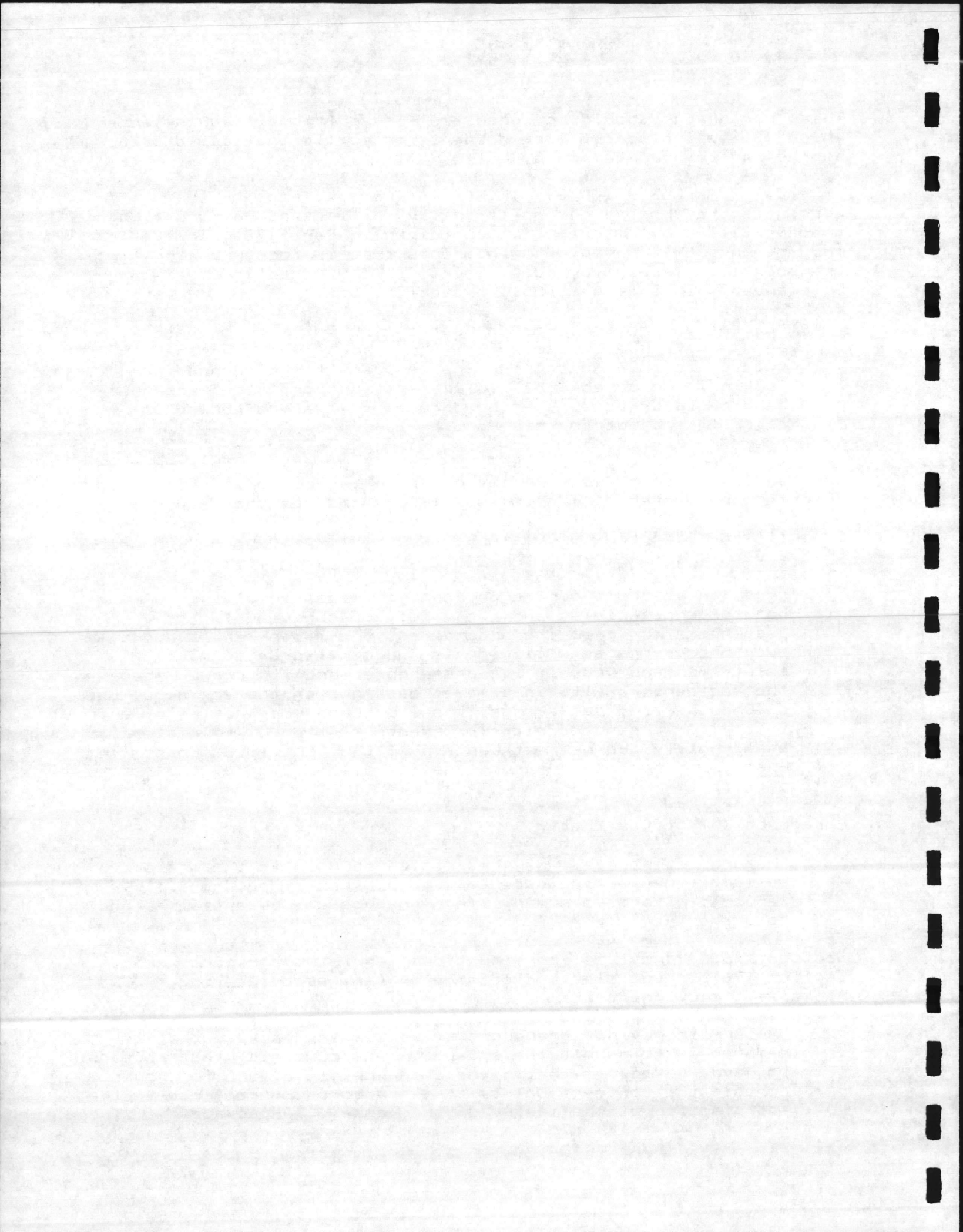
"When an accident occurs on board a vessel involving hazardous materials, and the safety of the vessel, its passengers, or crew are endangered, the master shall adopt such procedures as will, in his judgment, provide maximum safety for the vessel, its passengers, and its crew. When the accident results in damaged packages or the emergency use of unauthorized packagings, these packages may not be offered to any forwarding carrier for transportation. The master shall notify the nearest Captain of the Port, U.S. Coast Guard, and request instructions for disposition of the packages."

Paragraph (b) states that:

"Hazardous materials may be jettisoned only if the master believes this action necessary to prevent or substantially reduce a hazard to human life or reduce a substantial hazard to property."

Section 176.48 provides for situations requiring a report. Section 176.50, entitled "Acceptance of Damaged or Leaking Packages," provides that:

"A carrier may not transport by vessel any package that is so damaged as to permit the escape of its contents, that appears to have leaked, or that gives evidence of failure to properly contain the contents unless it is restored or repaired to the satisfaction of the master of the vessel. A package





containing radioactive materials (other than low specific activity materials) may not be repaired or restored.

For any of these applications, reference prior to shipment ought to be made to the complete requirements that are contained in 49 CFR governing the transportation of hazardous materials and hazardous wastes.

#### B. ENVIRONMENTAL PROTECTION AGENCY

The general facility EPA RCRA standards are contained in Part 264 entitled "Standards for Owners and Operators of Hazardous Waste Treatment Storage, and Disposal Facilities." These contain requirements for necessary equipment under Section 264.32. This appears under Subpart C for "Preparedness and Prevention." Section 264.32 provides that:

"All facilities must be equipped with the following, unless it can be demonstrated to the Regional Administrator that none of the hazards posed by waste handled at the facility could require a particular kind of equipment specified below; ..."

Item (c) includes:

"Portable fire extinguishers, fire control equipment (including special extinguishing equipment, such as that using foam, inert gas, or dry chemicals), spill control equipment, and decontamination equipment; ..."

The standards under Part 264, Subpart D entitled "Contingency Plan and Emergency Procedures" require that under the content of the contingency plan that:

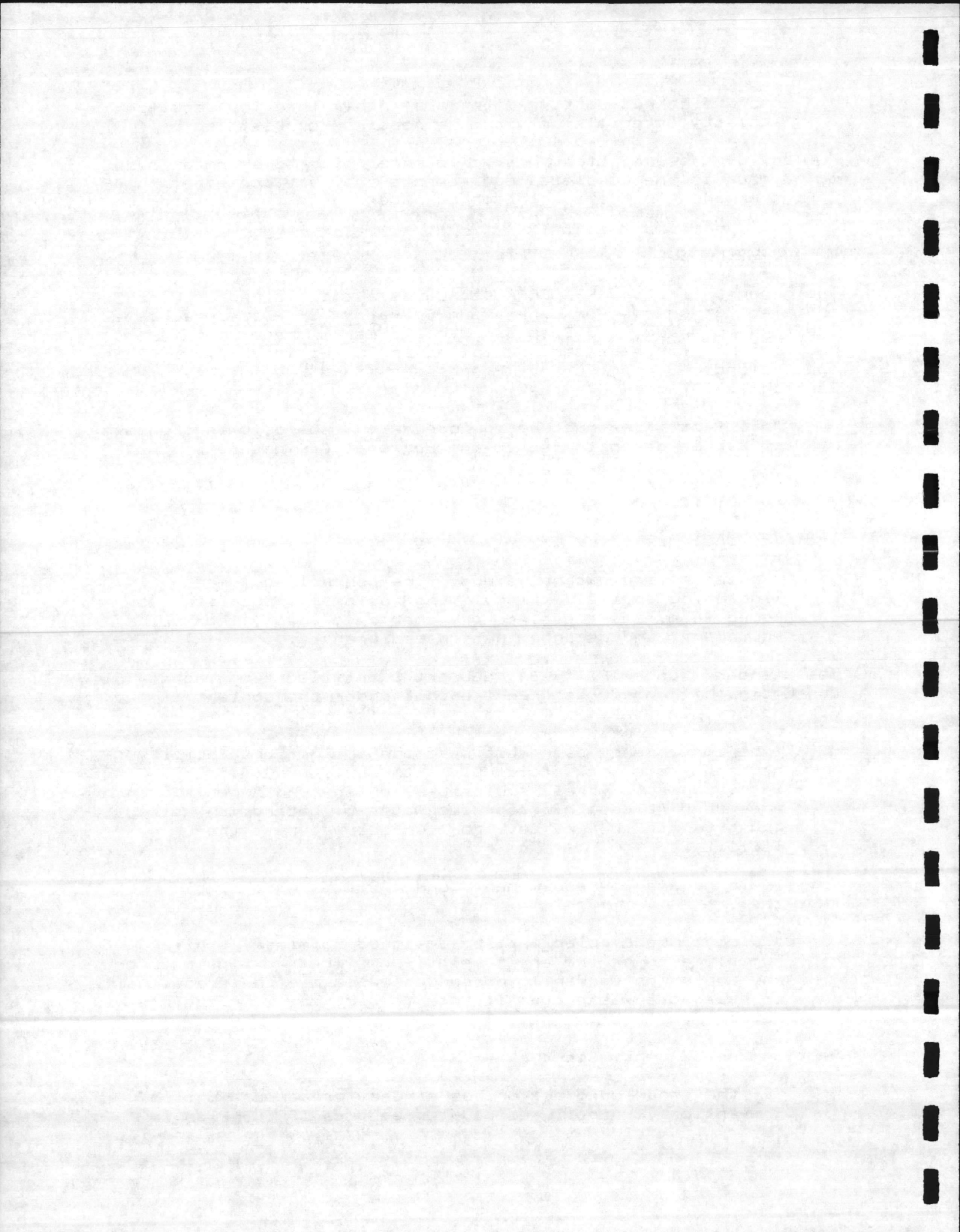
"The contingency plan must describe the actions facility personnel must take to comply with Sections 264.51 and 264.56 in response to fires, explosions, or any unplanned sudden or nonsudden release of hazardous waste or hazardous waste constituents to air, soil, or surface water at the facility."

This is in regard to requirements under 264.51 which indicates that the:

"...contingency plan must be designed to minimize hazards to human health or the environment from fires, explosions, or any unplanned sudden or nonsudden release of hazardous waste or hazardous waste constituents to air, soil, or surface water."

Section 264.52 continues that:

"If the owner or operator has already prepared a Spill Prevention, Control, and Countermeasures [SPCC] Plan in



accordance with Part 112 of Part 151 of this Chapter, or some other emergency or contingency plan, he need only amend that plan to incorporate hazardous waste management provisions that are sufficient to comply with the requirements of this Part."

Other items that are pertinent to the subject of spill control include Paragraph E of Section 264.52 which indicates that:

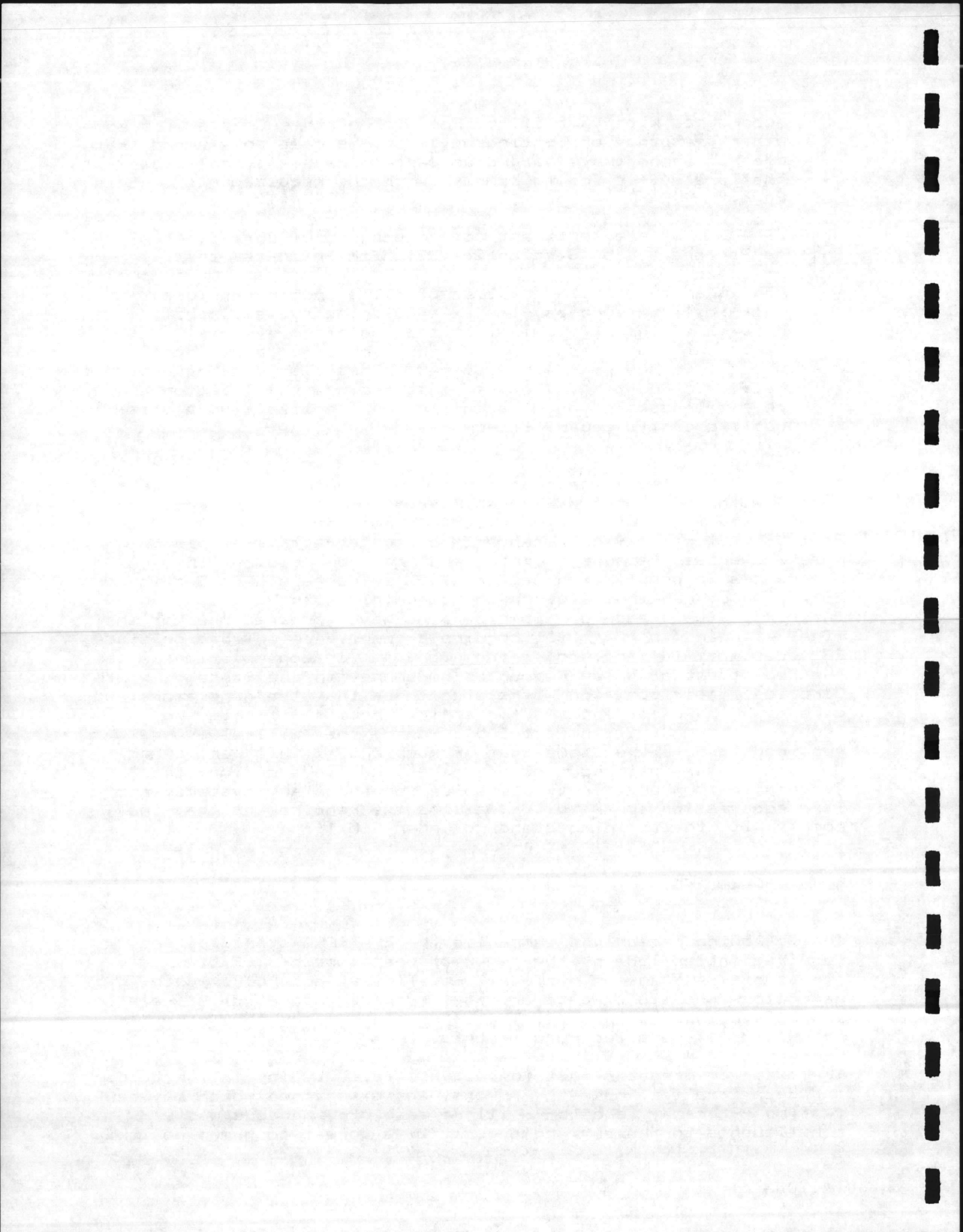
"The plan must include a list of all emergency equipment at the facility (such as fire extinguishing systems, spill control equipment, communications and alarm systems (internal and external), and decontamination equipment), where this equipment is required. This list must be kept up to date. In addition, the plan must include the location and a physical description of each item on the list, and a brief outline of its capabilities."

A specific question that has arisen concerns whether persons who are not classified as generators will be required to continue to comply with the standards for spill control prevention equipment, decontamination equipment, and other items that are outlined in Part 265 after the final standards become effective. This question arises because the standard that now requires the generators to comply with Section 2675 is contained in Section 262.32 which requires a generator to comply with Part 265, an interim status standard. Some persons have wondered whether the final standards of 264 will require a compliance obligation since 262 does not, in fact, refer them to 264. In conversations with the Department of Human Resources personnel in the State of North Carolina, their position was stated to be that the generators and others who have not applied for a final permit will also be required to comply with Part 265. Hence, they will always be required to have the items that are subject to this particular document under spill control equipment and, in addition, the decontamination equipment, communication and alarm systems, and fire suppression apparatus as well as the requirement that they comply with the training standard under 265.16.

### C. GENERAL INSPECTION REQUIREMENTS

The following paragraphs summarize the EPA/RCRA standards for required inspections by the owner or operators of T.S.D. (treatment, storage or disposal) facilities. Hazardous waste generators who store waste on-site for more than 90 days are also subject to these standards. The current standards should be consulted for detailed requirements.

The owner or operator must inspect his facility for malfunctions and deterioration, operator errors, and discharges which may be causing -- or may lead to -- (1) release of hazardous waste constituents to the environment or (2) a threat to human health.



The owner or operator must conduct these inspections often enough to identify problems in time to correct them before they harm human health or the environment.

- o The owner or operator must develop and follow a written schedule for inspecting monitoring equipment, safety and emergency equipment, security devices, and operating and structural equipment (such as dikes or sump pumps) that are important to preventing, detecting or responding to environmental or human health hazards.

- o The owner or operator keeps the schedule at the facility.

- o The schedule identifies the types of problems (e.g., malfunctions or deterioration) which are to be looked for during the inspection (e.g., inoperative sump pump, leaking fitting, eroding dike, etc.)

- o The frequency of inspection may vary for the items on the schedule. However, it should be based on the rate of possible deterioration of the equipment and the probability of an environmental or human health incident if the deterioration or malfunction of any operator error goes undetected between inspections. Areas subject to spills, such as loading and unloading areas, must be inspected daily when in use.

The owner or operator must remedy any deterioration or malfunction of equipment or structures which the inspection reveals on a schedule which ensures that the problem does not lead to an environmental or human health hazard. Where a hazard is imminent or has already occurred, remedial action must be taken immediately.

The owner or operator must record inspections in an inspection log or summary. These records are kept for at least three years from the date of inspection. At a minimum, these records must include the date and time of the inspection, the name of the inspector, a notation of the observations made, and the date and nature of any repairs or other remedial actions.

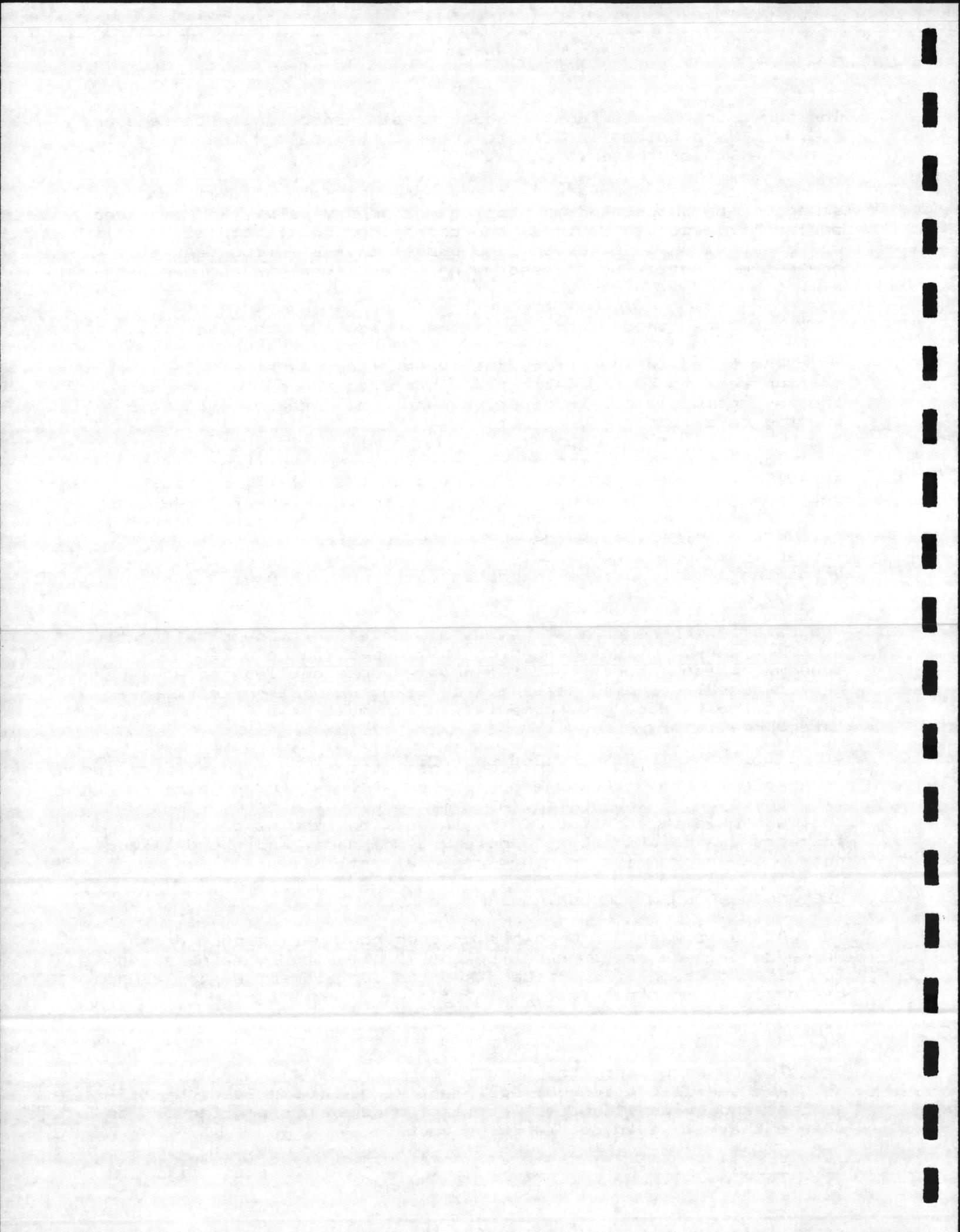
#### USE AND MANAGEMENT OF CONTAINERS

At least weekly, the owner or operator must inspect areas where containers are stored, looking for leaking containers and for deterioration of containers and the containment system caused by corrosion or other factors.

#### TANKS

The owner or operator must inspect:

- a. Overfilling control equipment (e.g., waste feed cut-off systems and by-pass systems) at least once each operating day to ensure that it is in good working order.



b. Data gathered from monitoring equipment (e.g., pressure and temperature gauges) where present, at least once each operating day to ensure that the tank is being operated according to its design.

c. For uncovered tanks, the level of waste in the tank, at least once each operating day.

d. The construction materials of the above-ground portions of the tank at least weekly to detect corrosion or erosion and leaking of fixtures and seams

e. The area immediately surrounding the tank, at least weekly, to detect obvious signs of leakage (e.g., wet spots or dead vegetation)

As part of the inspection schedule, the owner or operator must develop a schedule and procedure for assessing the condition of the tank. The schedule and procedure must be adequate to detect cracks, leaks, corrosion or erosion which may lead to cracks or leaks, or wall thinning to less than the thickness required.

Procedures for emptying a tank to allow entry and inspection of the interior must be established when necessary to detect corrosion or erosion of the tank sides and bottom. The frequency of these assessments must be based on the material of construction of the tank, type of corrosion or erosion protection used, rate of corrosion or erosion observed during previous inspections, and the characteristics of the waste being treated or stored.

a. As part of a contingency plan, the owner or operator must specify the procedures intended for use to respond to tank spills or leakage, including procedures and timing for expeditious removal of leaked or spilled waste and repair of the tank.

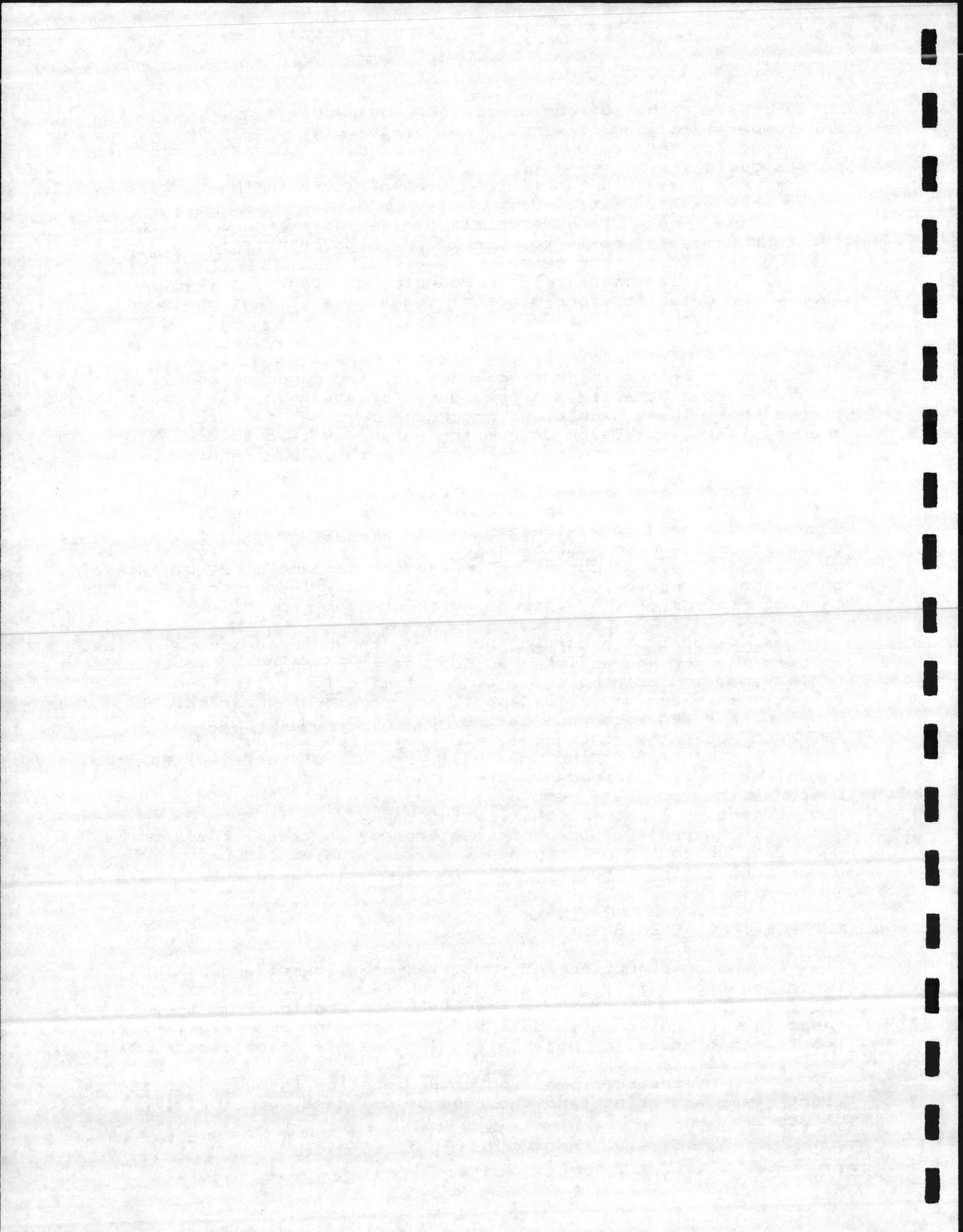
b. For EPA Hazardous Wastes Nos. F020, F021, F022, F023, F026 and F027, the contingency plan must also include the procedures for responding to a spill or leak of these wastes from tanks into the containment system. These procedures include measures for immediate removal of the waste from the system and replacement or repair of the leaking tank.

c. The owner or operator must remedy any leak, crack or wall thinning, or equipment or process malfunction violation discovered during inspections.

#### SURFACE IMPOUNDMENTS

During construction and installation, liners (except in the case of existing portions of surface impoundments) and cover systems (e.g., membranes, sheets, or coatings) must be inspected for uniformity, damage, and imperfections (e.g., holes, cracks, thin spots, or materials). Immediately after construction or installation:

o Synthetic liners and covers must be inspected to ensure tight seams and joints and the absence of tears, punctures, or blisters





o Soil-based and admixed liners and covers must be inspected for imperfections including lenses, cracks, channels, root holes, or other structural non-uniformities that may cause an increase in the permeability of the liner or cover.

While a surface impoundment is in operation, it must be inspected weekly and after storms to detect evidence of any of the following:

- o Deterioration, malfunctions, or improper operation of overtopping control systems
- o Sudden drops in the level of the impoundment's contents
- o The presence of liquids in leak detection systems, where installed.
- o Severe erosion or other signs of deterioration in dikes or other containment devices.

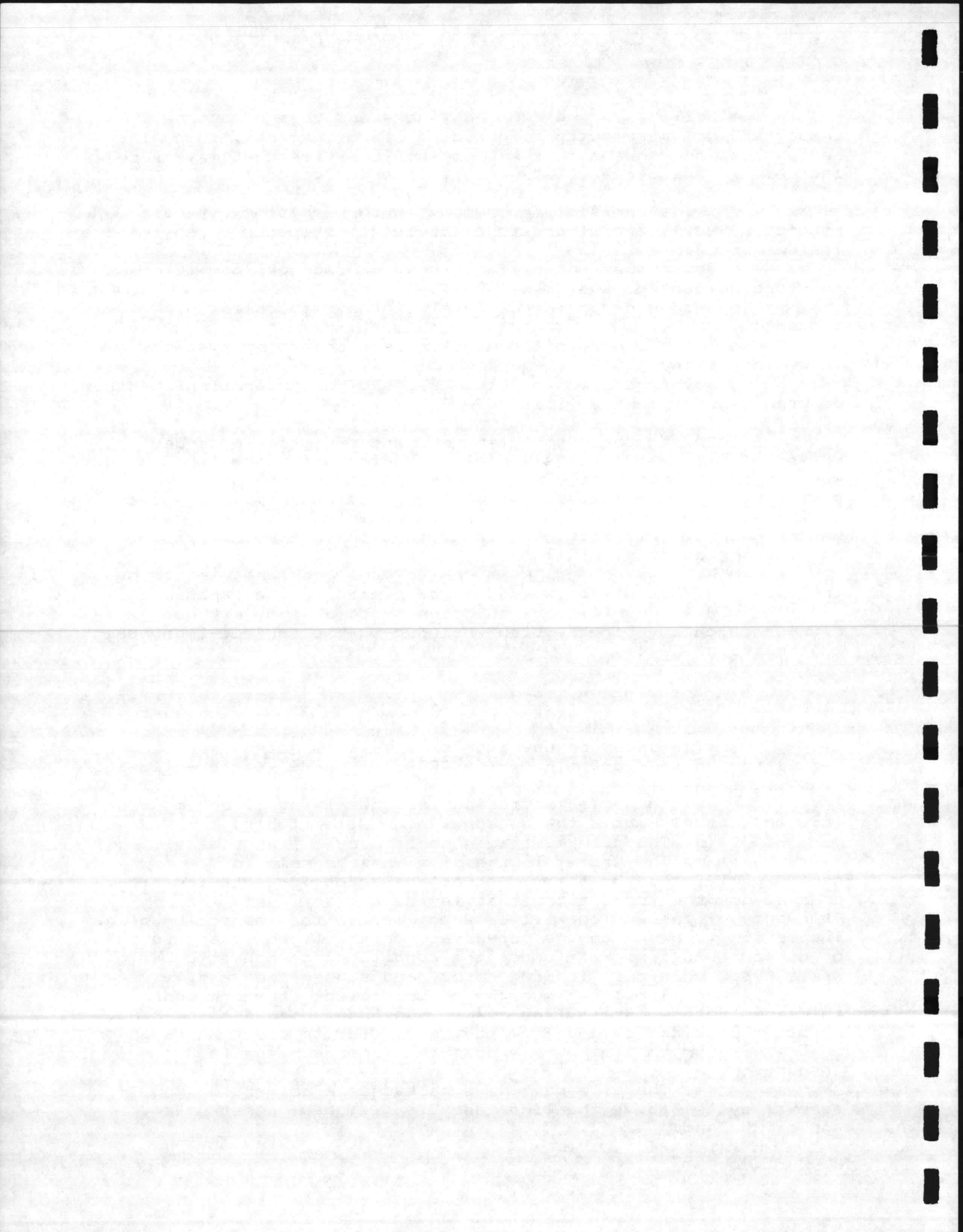
Prior to the permit issuing, and after any extended period of time (at least six months) during which the impoundment was not in service, the owner or operator must obtain a certification from a qualified engineer that the impoundment's dike, including that portion of any dike which provides freeboard, has structural integrity. The certification must establish in particular, that the dike:

- o Will withstand the stress of the pressure exerted by the types and amounts of wastes to be placed in the impoundment
- o Will not fail due to scouring or piping, without dependence on any liner system included in the surface impoundment construction.

## LINERS

The owner or operator of a pile is not subject to regulation under Subpart F of the RCRA standards if the following conditions are met:

- a. The pile (including its underlying liner) must be located entirely above the seasonal high water table.
- b. The pile must be underlain by a liner (base).
- c. The wastes in the pile must be removed periodically, and the liner must be inspected for deterioration, cracks, or other conditions that may result in leaks. The frequency of inspection will be specified in the inspection plan. Inspection is based on the potential for the liner (base) to crack or otherwise deteriorate under the conditions of operation (e.g. waste type, rainfall, loading rates, and subsurface stability).
- d. The liner must be of sufficient strength and thickness to prevent failure due to puncture, cracking, tearing, or other physical damage from equipment used to place waste in or on the pile or to clean and expose the liner surface for inspection.
- e. The pile must have a leachate collection and removal system above the liner that is designed, constructed, and maintained.



If deterioration, a crack, or other condition is identified that is causing or could cause a leak, the owner or operator must:

o Notify EPA Regional Administrator of the condition in writing within seven days after detecting the condition

i. Repair or replace the liner (base) and obtain a certification from a qualified engineer that, to the best of the engineer's knowledge and opinion, the liner (base) has been repaired and leakage will not occur, or:

ii. If a detection monitoring program has already been established in the permit (to be complied with only if a leak occurs), begin to comply with that program and any other other applicable requirements within a period of time specified in the permit.

The Regional Administrator will specify in the permit all design and operating practices that are necessary to ensure that the requirements of this section are satisfied.

#### WASTE FILES

During construction or installation, liners and cover systems must be inspected for uniformity, damage and imperfections. Immediately after construction or installation:

o Synthetic liners and covers must be inspected to ensure tight seams and joints and the absence of tears, punctures, or blisters

o Soil-based and admixed liners and covers must be inspected for imperfections including lenses, cracks, channels, root holes or other structural non-uniformities that may cause an increase in the permeability of the liner or cover.

While a waste pile is in operation, it must be inspected weekly after storms to detect evidence of any of the following:

o Deterioration, malfunctions, or improper operation of run-on and run-off control systems

o The presence of liquids in leak detection systems, where installed

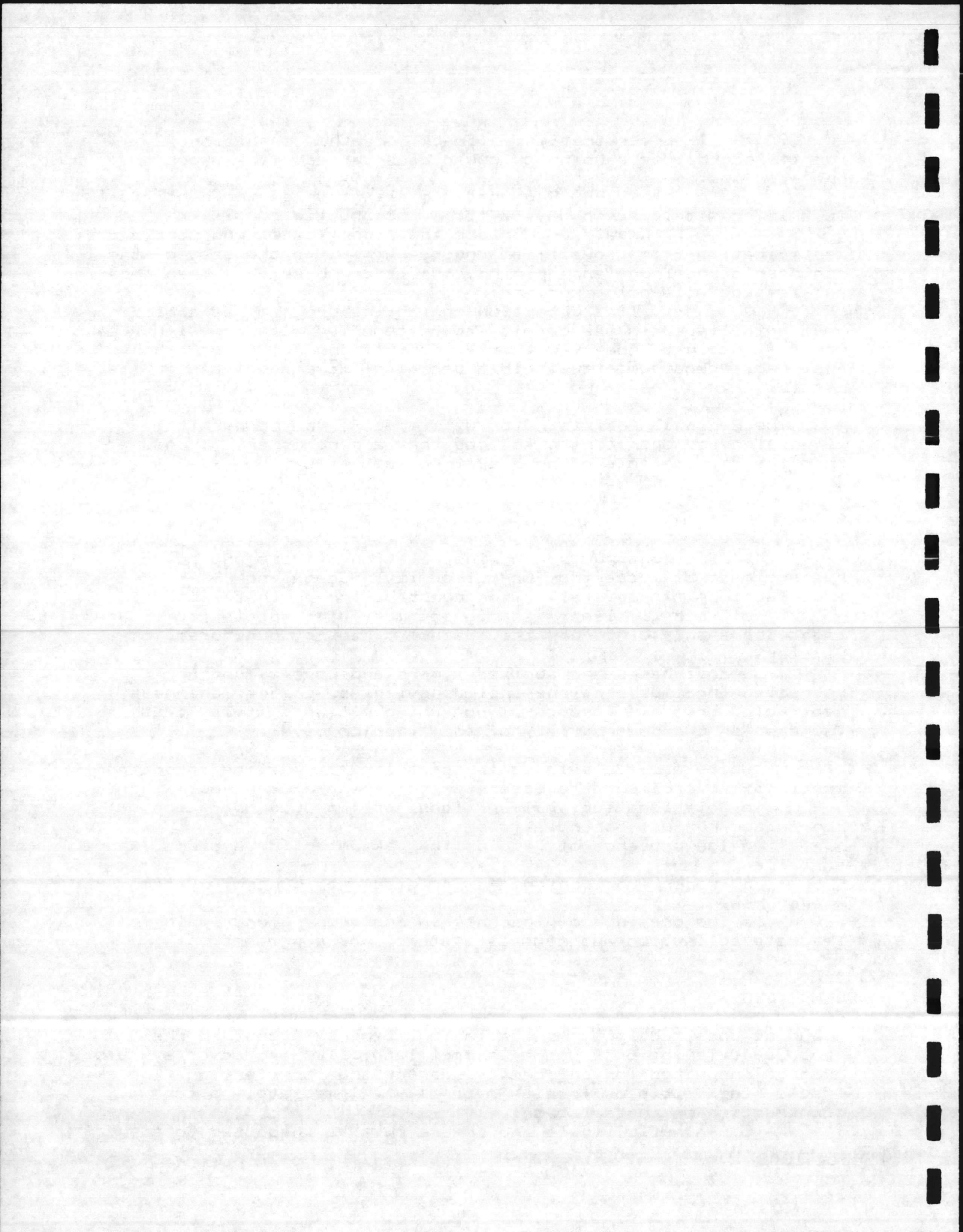
o Proper functioning of wind dispersal control systems, where present

o The presence of leachate in and proper functioning of leachate collection and removal systems, where present.

#### LANDFILLS

During construction or installation, liners (except in the case of existing portions of exempt landfills) and cover systems must be inspected for uniformity, damage and imperfections (holes, cracks, thin spots or foreign materials). Immediately after construction or installation:

o Synthetic liners and covers must be inspected to ensure



tight seams and joints and the absence of tears, punctures, or blisters

- o Soil-based and admixed liners and covers must be inspected for imperfections including lenses, cracks, channels, root holes, or other structural non-uniformities that may cause an increase in the permeability of the liner or cover.

While a landfill is in operation, it must be inspected weekly and after storms to detect evidence of any of the following:

- o Deterioration, malfunctions, or improper operation of run-on and run-off control systems

- o The presence of liquids in leak detection systems, where installed

- o Proper functioning of wind dispersal control systems, where present

- o Presence of leachate in and proper functioning of leachate collection and removal systems, where present.

## INCINERATORS

The owner or operator must conduct as a minimum the following monitoring while incinerating hazardous waste:

- o Combustion temperature, waste feed rate, and air feed rate must be monitored on a continuous basis.

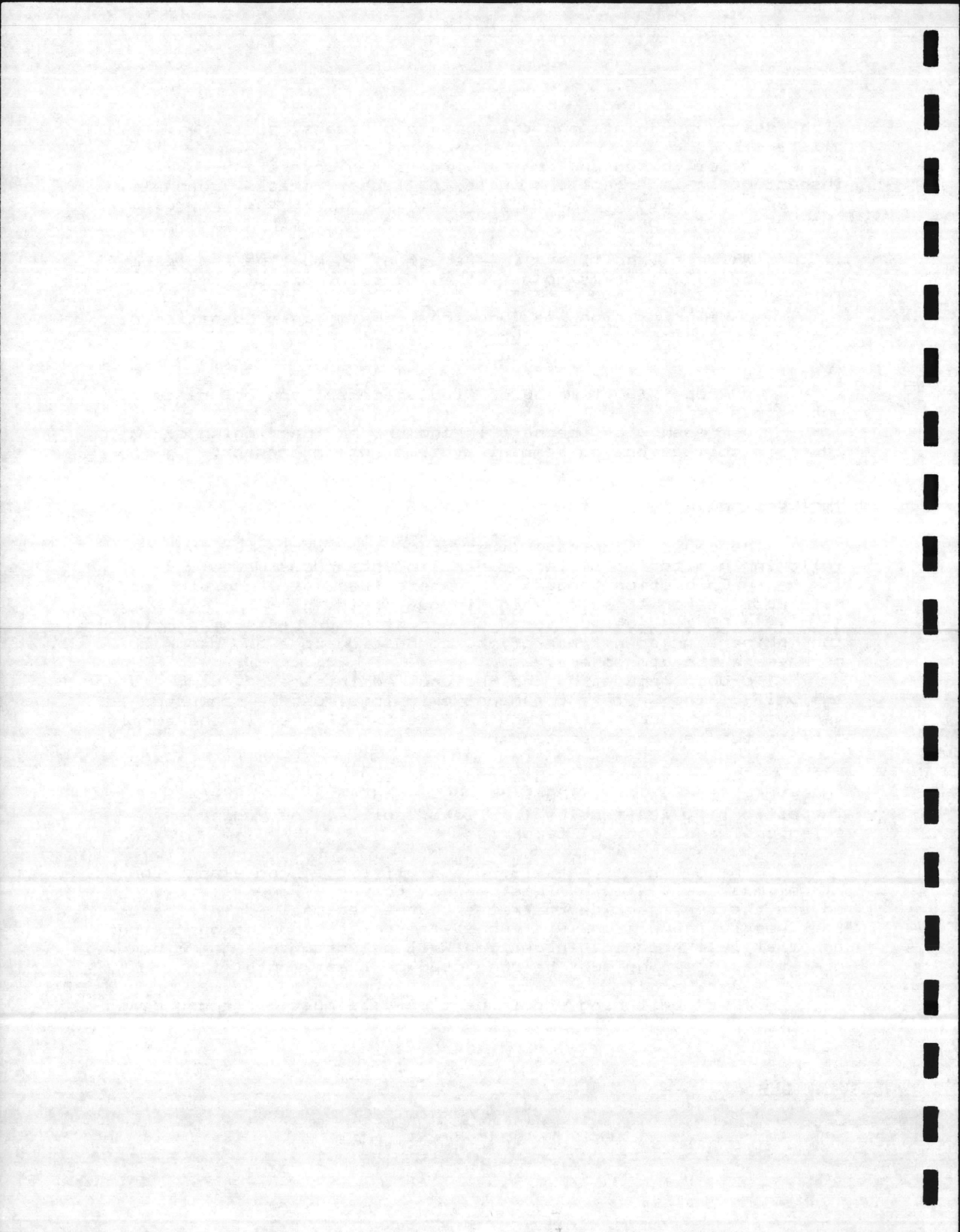
- o CO must be monitored on a continuous basis at a point in the incinerator downstream of the combustion zone and prior to release in the atmosphere.

- o Upon request by the Regional Administrator, sampling and analysis of the waste and exhaust emissions must be conducted to verify that the operating requirements established in the permit achieve the performance standards.

The incinerator and associated equipment (pumps, valves, conveyors, pipes, etc.) must be subjected to thorough visual inspection, at least daily for leaks, spills, and fugitive emissions, and signs of tampering.

The emergency waste feed cut-off system and associated alarms must be tested at least weekly to verify operability, unless the applicant demonstrates to the Regional Administrator that weekly inspections will unduly restrict or upset operations and that less frequent inspection will be adequate. At a minimum, operational testing must be conducted at least monthly.

This monitoring and inspection data must be recorded and the records must be placed in the operating log.

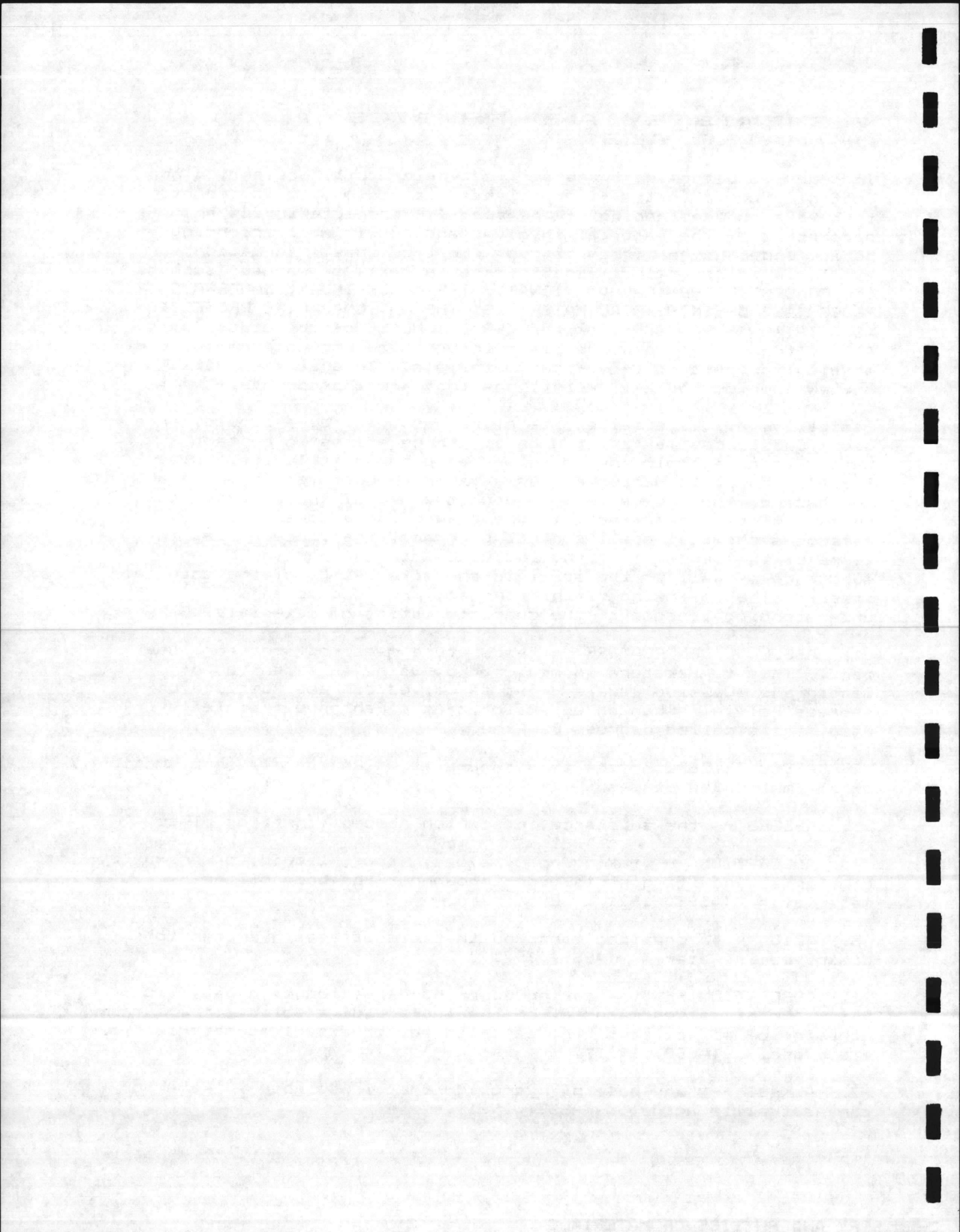


## V. CHEMISTRY AND PHYSICS OF MATERIALS

In order to determine the specific type of spill prevention and control program that a firm will need to employ, it is important to have an understanding of the specific characteristics and parameters of the material involved and how it will accordingly behave under given circumstances. Most of this information is available in several different forms in texts or manuals such as the CONDENSED CHEMICAL DICTIONARY, THE MERCK INDEX, DANGEROUS PROPERTIES OF INDUSTRIAL MATERIALS, THE NATIONAL FIRE PROTECTION ASSOCIATION'S HANDBOOK, or the CHRIS MANUALS of the Coast Guard. All of these texts provide basic information on the chemical and physical properties of various materials. This section will review some of the key definitions that are appropriate.

Basically, all material exists either as a solid, a liquid, or a gas. Substances may exist with all three states in contact. Water, as an example, may exist as a solid if it is ice, as a liquid when it is water, and as a vapor when it is fog or steam. The hazard, then, depends more upon the use of the material than on any of its properties. In the case of hazardous waste and hazardous chemical spill control programs, the concern lies in terms of the exposure of the individual to the particular substance as well as the specific characteristics of the material itself. The following definitions are provided as an understanding to some of the characteristics of materials.

1. ABSOLUTE TEMPERATURE -- temperature measured from absolute zero. This temperature is measured by using an extension of Centigrade (Celsius) scale -- it is called degrees Absolute or degrees Kelvin. When an extension of the Fahrenheit scale is used, it is called degrees Rankine.
2. ABSOLUTE ZERO -- the temperature at which translational motion of all molecules ceases.
3. ABSORB -- the substance into which absorption takes place.
4. ABSORPTION -- "taking up of a gas, vapor, liquid, or energy by a material and its distribution throughout the body of the material." (ASSE, 1971).
5. ACID -- "a chemical compound that dissociates hydrogen ions dissolved in water." (ASSE, 1971).
6. ADSORPTION -- "the taking up or condensation of a gas, liquid vapor, or dissolved material on the surface of a solid. The adhesion of molecules of the gas, liquid, or dissolved material to a surface." (ASSE, 1971).
7. ALKALI -- "any base of hydroxide that is soluble in water or can neutralize acids." (ASSE, 1971).





8. ATMOSPHERIC PRESSURE -- "the pressure exerted by the atmosphere at the surface of the earth due to the weight of air. The pressure of the atmosphere at sea level is about 14.7 pounds per square inch (760 mm or 30" of mercury)." (ASSE. 1971).

9. ATOM -- smallest particle in an element that retains the chemical characteristics of the element.

10. AUTO IGNITION TEMPERATURE -- temperature at which a flammable vapor will ignite without the application of a spark or flame.

11. AVOGARDO'S LAW -- equal volumes of different gases at the same pressure and temperature contain the same number of molecules.

12. BIOLOGICAL ADDITIVES -- microbiological cultures, enzymes, or nutrient additives that are deliberately introduced into an oil or hazardous substance spill for the specific purpose of encouraging biodegradation to mitigate the effects of a spill.

13. BOILING POINT -- "exists when the pressure on the surface of the material exceeds the atmospheric pressure. That pressure on the surface is known as vapor pressure." (NFPA Fire Protection Handbook, 1981).

14. BOYLE'S LAW -- at a constant temperature, the volume of a given quantity of any gas varies inversely as the pressure to which the gas is subjected.

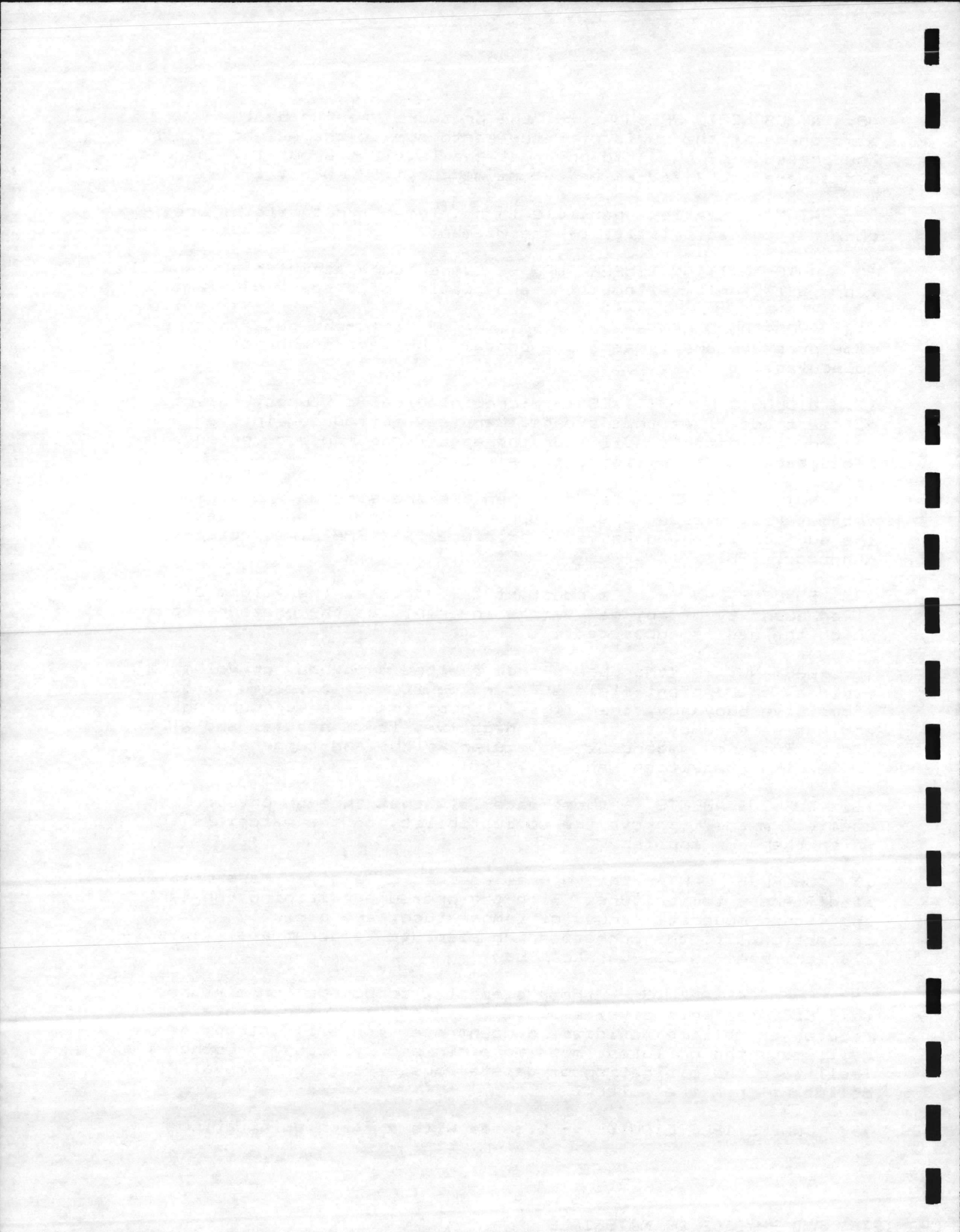
15. BUOYANCY -- "the upper force exerted on a body or volume of fluid by the ambient fluid surrounding it. If a volume of gas has a positive buoyancy, then it is lighter than its surrounding gas and has a tendency to rise; if negative, it is heavier and will sink. Buoyancy depends on molecular weight and temperature." (NFPA Fire Protection Handbook, 1981).

16. BURNING AGENTS -- those materials that through physical or chemical means, improve the combustibility of the materials to which they are applied.

17. CHARLES' LAW -- the volumes assumed by a given mass of a gas at different temperatures, with the pressure remaining constant and within moderate ranges of temperature, are directly proportional to the corresponding absolute temperatures. This is also the same as Gay-Lussac's Law.

18. CHEMICAL AGENTS -- those elements, compounds, or mixtures that disperse, dissolve, emulsify, neutralize, precipitate, reduce, solubilize, oxidize, concentrate, congeal, entrap, fix, gell, make the pollutant mass more rigid or viscous, or otherwise facilitate the mitigation of deleterious effects or removal of the pollutant from the water.

19. COMBUSTIBLE LIQUIDS -- Liquids with a flash point at, or



above, 100 degrees Fahrenheit and with a boiling point above 100 degrees.

20. CRITICAL PRESSURE -- the pressure required to liquefy a gas at its critical temperature.

21. CRITICAL TEMPERATURE -- that temperature above which a gas cannot be liquefied by pressure alone.

22. DEFLAGRATION -- "an exothermic reaction which propagates from the burning gases to the unreacted material by conduction, convection, and radiation. The combustion zone progresses through the material at a rate that is less than the velocity of sound in the unreacted material." (ASSE, 1971).

23. DENSITY -- the concentration of matter measured by the mass per unit volume. The units used in the English system are pounds per cubic foot at 32 degrees Fahrenheit, and one atmosphere (14.7 pounds per square inch).

24. DETONATION -- "an exothermic reaction that is characterized by the presence of a shock wave in the material that establishes and maintains the reaction. A distinctive feature is that the reaction zone propagates at a rate greater than sound velocity in the unreacted material." (ASSE, 1971).

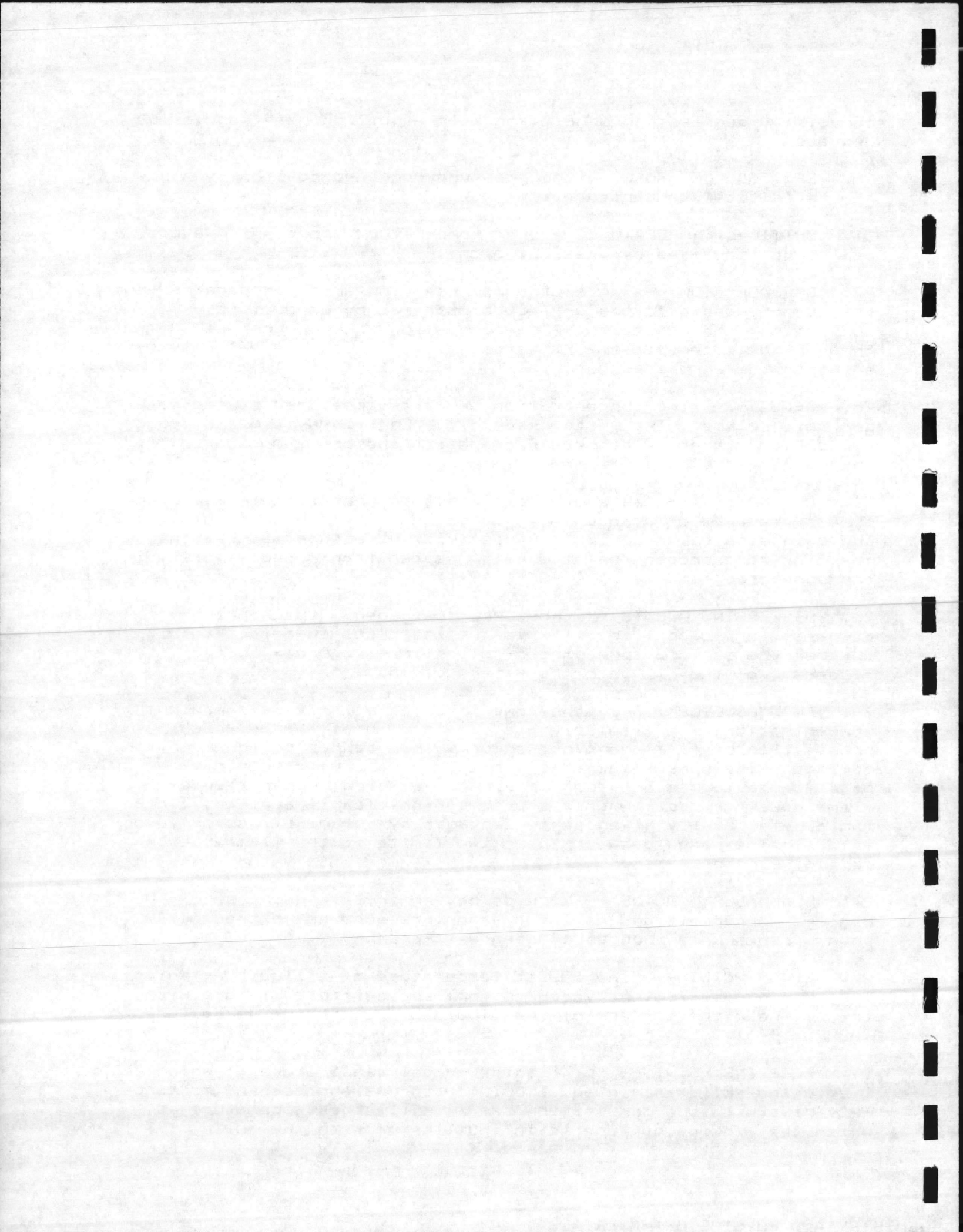
25. DISPERSING AGENTS -- those chemical agents that emulsify, disperse, or solubilize oil into the water column or act to further the surface spreading of oil slicks in order to facilitate dispersal of the oil into the water column.

26. FLAMMABLE LIMITS -- the lower flammable limit is a minimum concentration of a flammable gas or vapor in air below which propagation of flame does not occur when a source of ignition is applied. The upper flammable limit is a maximum concentration of a flammable gas or vapor in air above which propagation of flame does not occur when a source of ignition is applied. These limits are usually given as percentages by volume of gas or vapor in air. The range between these two limits is the flammable or explosive range.

27. FLAMMABLE LIQUIDS -- Liquids having a flash point below 100 degrees Fahrenheit and having a vapor pressure not exceeding 40 pounds per square inch at 100 degrees Fahrenheit.

28. FLASH POINT -- "the lowest temperature of a liquid at which it gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid or within the vessel used." (ASSE, 1971).

29. FREEZING POINT -- "of liquids -- the temperature at which the liquid and solid are in equilibrium with one another; of mixtures -- varies with the composition but is still the temperature at which the liquids mixture is in equilibrium with the solid



material that separates from it on cooling." (ASSE, 1971).

30. GRAHAM'S LAW -- the relative rates of diffusion of gases under the same conditions are inversely proportional to the square roots of the densities of those gases.

31. GAS SPECIFIC GRAVITY -- "the ratio of the weight of a gas to the weight of an equal volume of dry air at the same temperature and pressure." (NFPA Fire Protection Handbook, 1981).

32. GAY-LUSSAC'S LAW -- the volumes of two or more gases that combine to give a gaseous product are in the proportion of small whole numbers to each other and to the volume of the product. [This is the same as Charles' Law.]

33. IGNITION TEMPERATURE -- the minimum temperature to which a substance must be heated in order to cause self-sustained combustion independently of the heating or heating element.

34. INORGANIC -- "a term used to designate compounds that generally do not contain carbon. Exceptions are carbon monoxide and carbon dioxide." (ASSE, 1971).

35. LIQUEFACTION -- "the process of converting a gas or vapor into a liquid by cooling below its critical temperature usually accompanied by application of pressure." (ASSE, 1971).

36. MECHANICAL REMOVAL METHODS -- the use of pumps, skimmers, booms, earthmoving equipment, and other mechanical devices.

37. MISCIBLE -- having the capability of being mixed.

38. MOLECULAR WEIGHT -- the sum of the atomic weights of all the atoms in a molecule.

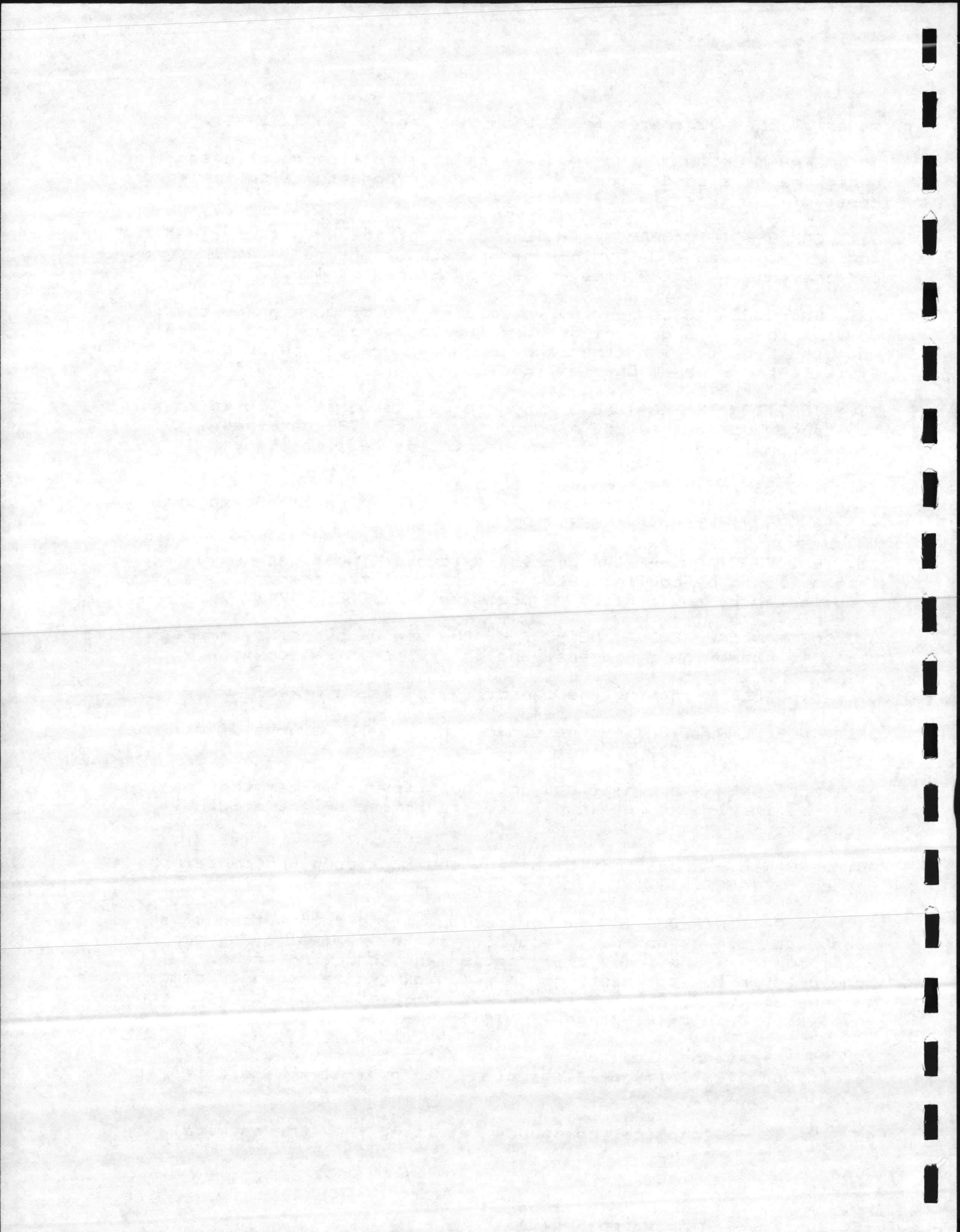
39. MOLECULE -- the smallest unit quantity of matter that can exist by itself and retain all the properties of the original substance.

40. ORGANIC -- "designation of any chemical compound containing carbon." (ASSE, 1971).

41. OXIDATION/REDUCTION -- "oxidation is the combination of a substance with oxygen; ... reduction is the removal of oxygen from a compound ... The terms of oxidation and reduction are not, however, limited to reactions in which oxygen is added or removed. In general, oxidation involves a loss of electrons and reduction involves a gain of electrons." (ASSE, 1971).

42. pH -- "means used to express numerically the degree of acidity or alkalinity of a solution with neutrality indicated at 7." (ASSE, 1971).

43. SALTS -- "chemical compounds resulting from the chemical



reaction between acids and gases. For example, hydrochloric acid reacts with sodium hydroxide to give sodium chloride, which is a salt, and water." (ASSE, 1971).

44. SINKING AGENTS -- those materials that are applied to oil and hazardous substance spills to sink floating pollutants below the water surface. This will include precipitants, coagulants and flocculants.

45. SOLUBLE -- capable of being dissolved by another substance.

46. SOLUTE -- the substance that is dissolved in a solution.

47. SOLVENT -- a substance, generally liquid, capable of dissolving other substances.

48. SORBANTS -- essentially inert and insoluble materials that are used to remove oil and hazardous substances from water through a variety of sorption mechanisms. Examples include: straw, expanded perlite, polyurethane foams, reclaimed paper fibers, and peat moss.

49. SPECIFIC GRAVITY -- the ratio of the weight of a given volume of a substance to the weight of an equal volume of a standard substance. Liquids and solids are generally compared to water, and gases and vapors are generally compared to air.

50. SPONTANEOUS IGNITION -- self-ignition that may occur when a chemical reaction produces enough heat to elevate the temperature of the material above its ignition temperature, causing a fire (as in the oxidation of oil in oily rags). This is often called spontaneous combustion.

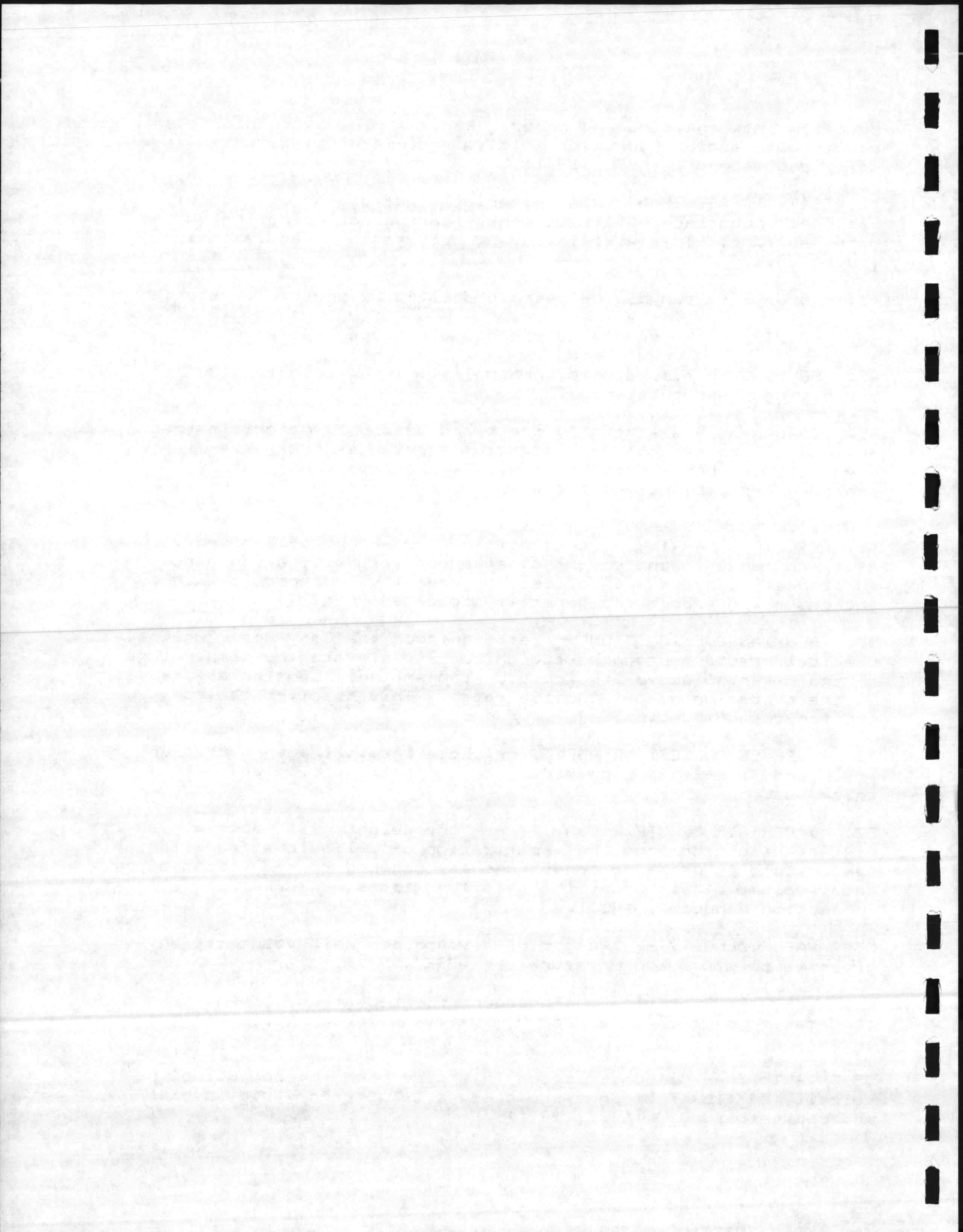
51. SURFACE COLLECTING AGENTS -- those chemical agents that are a surface-film-forming chemical for controlling oil layer thickness.

52. VAPOR-AIR SPECIFIC GRAVITY -- "the weight of a vapor-air mixture resulting from the vaporization of a liquid at equilibrium temperature at pressure conditions as compared to the weight of an equal volume of air under the same conditions." (NFPA Fire Protection Handbook, 1981).

53. VAPOR DENSITY -- "weight of a vapor per unit volume at any given temperature and pressure." (ASSE, 1971).

54. VAPOR PRESSURE -- "the pressure exerted at any given temperature by a vapor either by itself or in a mixture of gases."

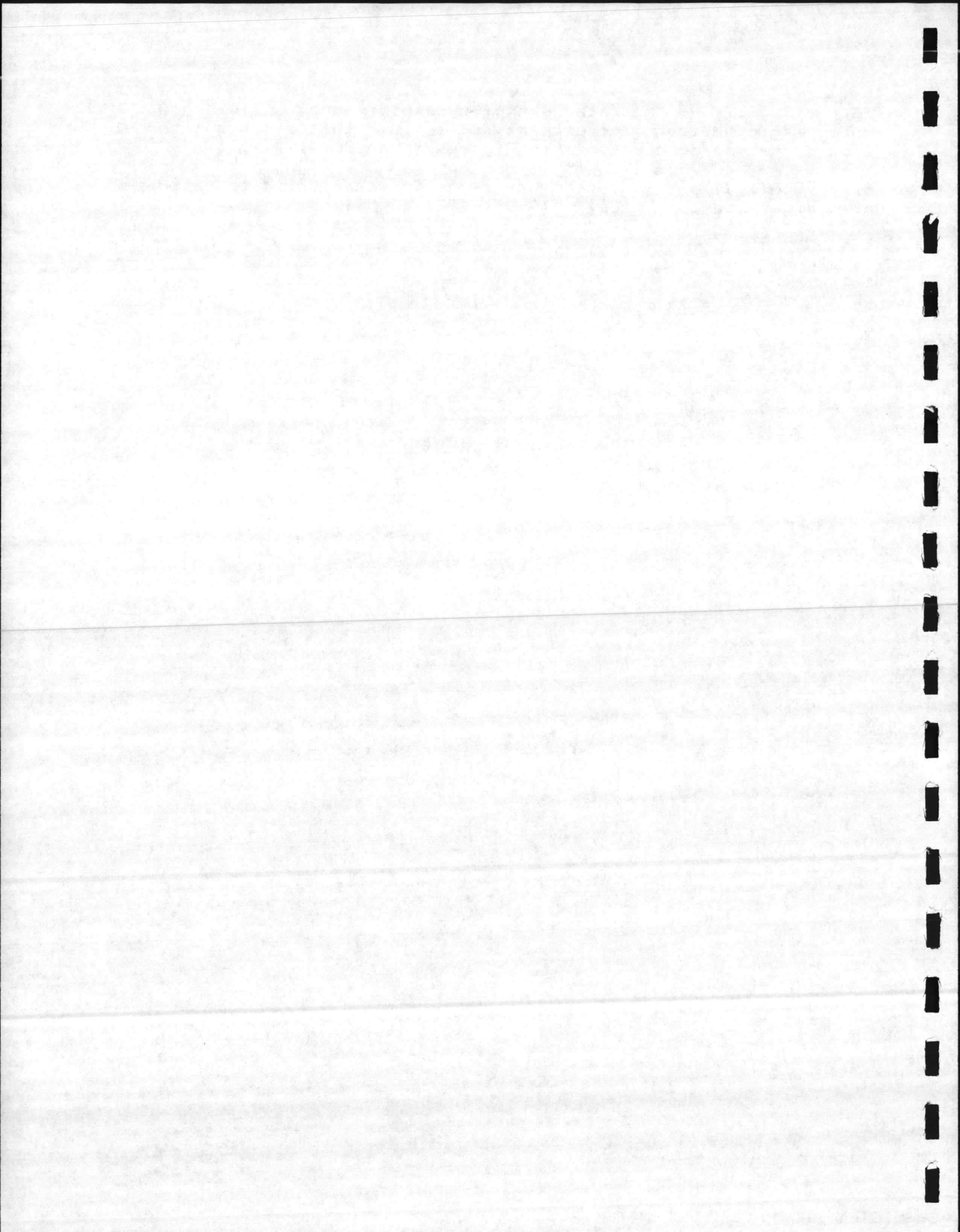
55. VENTURI -- "a constriction in a pipe used for computing the velocity of flow from pressure difference between fluid in pipe and constriction." (ASSE, 1971).





56. VISCOSITY -- "resistance to flow exhibited by a fluid due to molecular cohesion. The property of a fluid that resists internal flow by releasing counteracting forces." (ASSE, 1971).

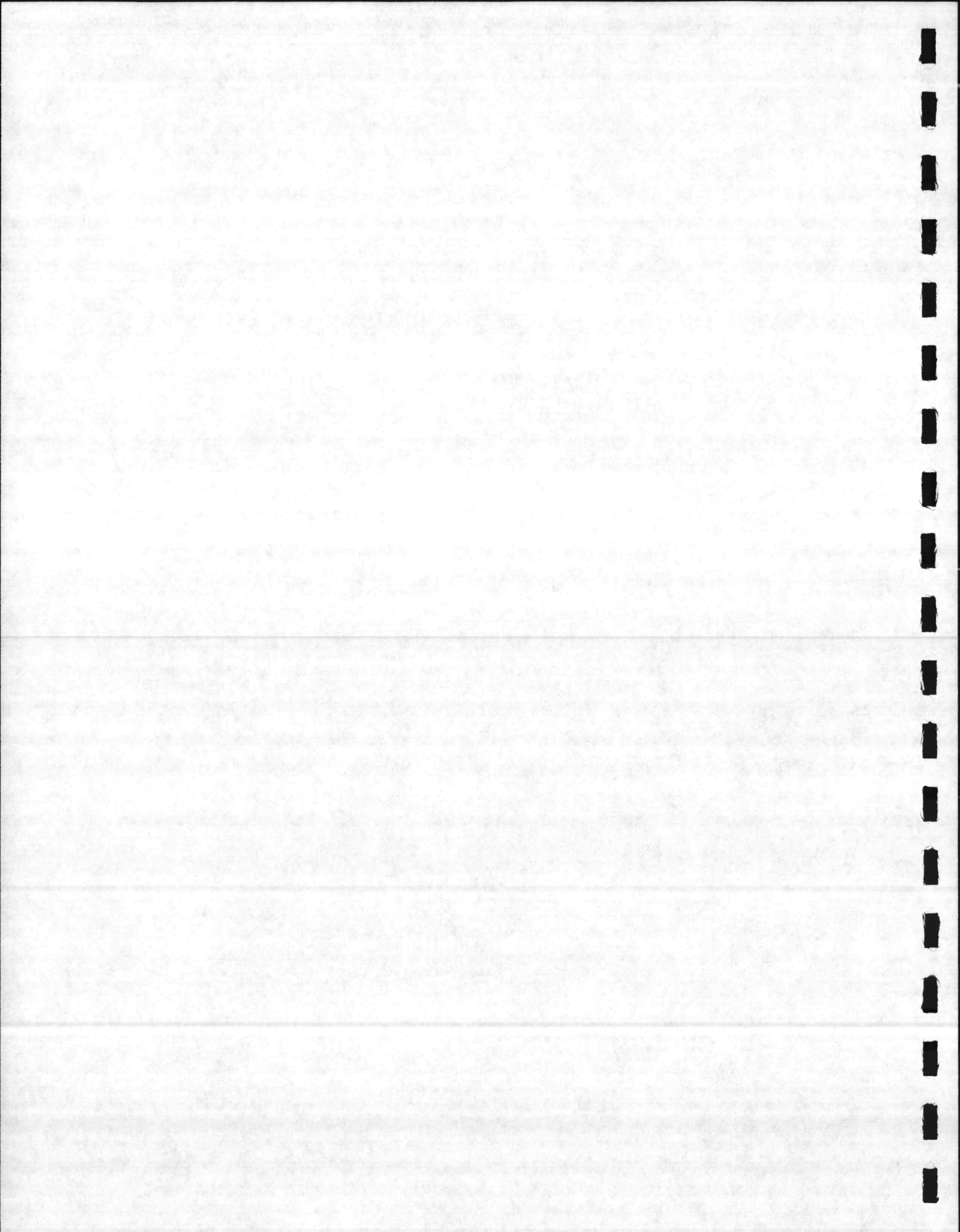
57. VOLATILITY -- "the tendency of a liquid or solid to vaporize at ordinary temperatures." (ASSE, 1971).



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## VIII. LABORATORY/IN-PLANT SPILLS

Another area where spills may occur, and which will behave somewhat differently from spills onto either the land or into a body of water is in the laboratory. The major distinguishing feature here is that the surface onto which the spill may occur is generally hard and nonporous, thereby eliminating the necessity for concern about migration into the water table or removal from a body of water.

The major method of spill control in the laboratory will be to contain the spilled chemical and then to place it into a holding vessel or place it back into the original container. This section will overview the methods for the containment aspect of this process.

It should be noted, however, that some of the methods and procedures reviewed for both land and water spills may have some applicability here; the reader is urged to carefully examine those sections for additional information.

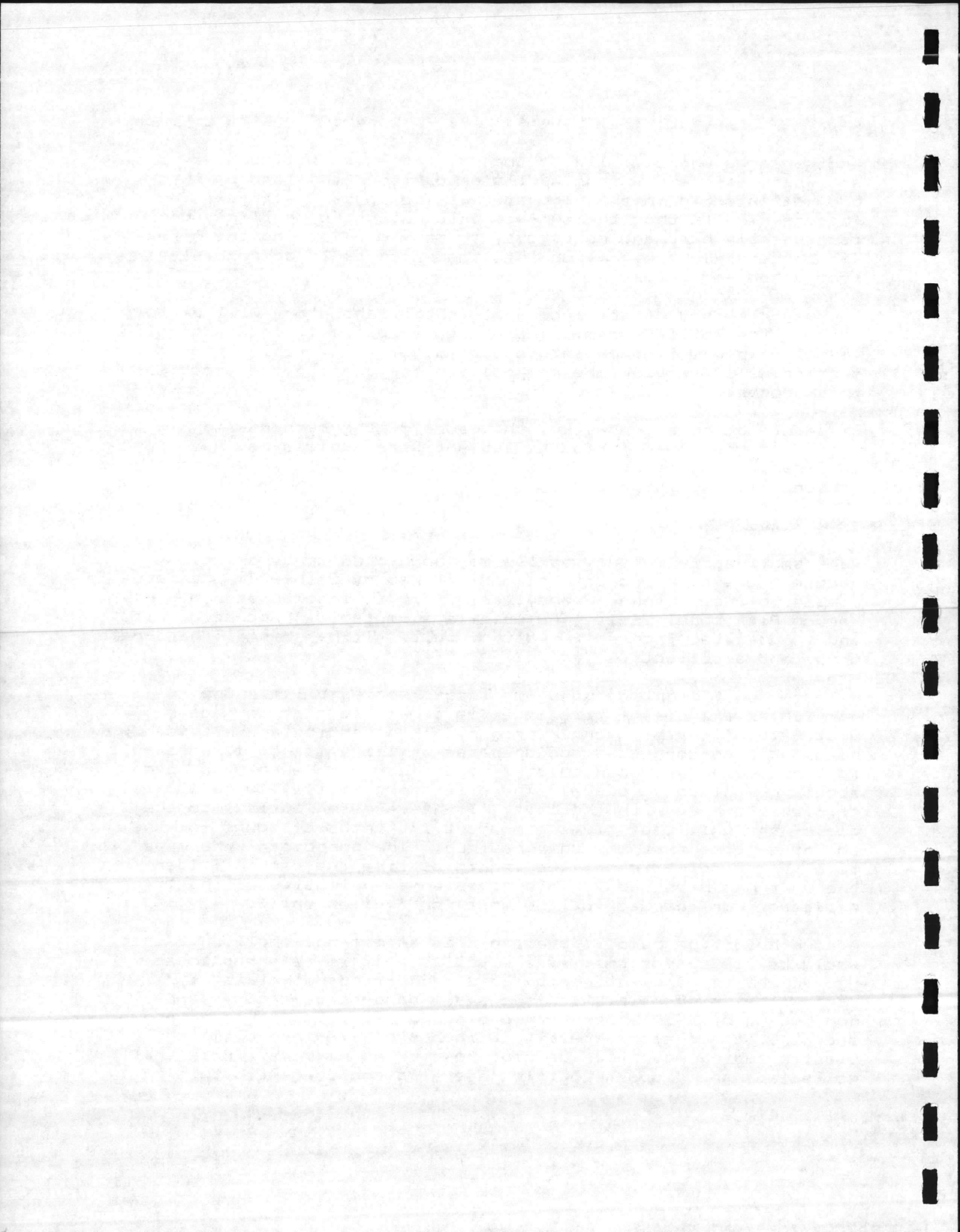
### A. SMALL-SCALE VACUUM CLEANUP

Very-small-scale mercury spills may be picked up by a mercury vacuum. One such product is manufactured by Bethlehem Apparatus Company of Hellertown, Pennsylvania. It is labeled as a Mercury Vacuum Pick model VP-2. The unit is a portable, hand-held unit and is operated from a 110-volt circuit. It has a small hand-held probe and a collection jar.

A larger unit might be used for larger scale spills. One particular example of this model is a Mer-Vac that is made by Scott-Ato of South Haven, Michigan. This particular unit is cord-and-plug-connected and operates at 115 volts on 12 amps. It is a portable unit mounted on a hand truck with wheels to move it about from place to place. There is approximately 10 to 12 feet of flexible hose with the unit. It has a meter built into the top of the unit that gives a readout in tenths of hours for the amount of time that the unit has run. The purpose of the meter is to give an indication of the length of time the carbon filter in the unit has been used. This gives some indication of the life expectancy or adequacy of the unit for a given spill.

A hand-held-type pump is available as an off-the-shelf unit that would be useful for small-scale spills. It is referred to as Hg-Vac and is manufactured by Science-Related Materials of Janesville, Wisconsin. It is a small hand-held mercury pump consisting of a cylinder with a piston. It establishes a vacuum and consists of approximately 18 inches of 1/8-inch-diameter plastic tubing which can be used to pick up mercury. Some small collection and disposal bottles are also included with this unit.

### B. PORTABLE CONTAINERS





Another type of portable container that might be useful for containing small chemical spills is the Protectoseal. This unit is produced by the Protectoseal Company of Chicago. It consists of a spring-loaded metal top with a large-mouth glass container on the inside which is housed in a metal jacket. It has insulation over approximately 2/3 of the container. It is suitable for use where materials might otherwise react with a metal-type safety can. This particular unit is approximately a 3-gallon container.

Another type of container is a large metal safety can which may be used for containing relatively large amounts of spills. These are a bit larger than the standard 5-gallon-size container which is the largest size approved by either NFPA or DOT regulations. This particular size is structurally similar to the smaller 5-gallon-size metal safety cans and includes a wide-mouth opening, a flame-arrester, and a spring-loaded top. Most are equipped with handles on either side and are similar in appearance to old milk containers.

#### C. CONTAINED SPILL CONTROL PACKAGES

Several manufacturers have spill control packages that are primarily designed to control small spills. As an example, Baker Chemical Company has a series of products including an acid spill cleanup kit, and spill cleanup kits for cyanide, mercury, and hydrofluoric acid spills. These kits are suitable for relatively small-scale spills. Baker uses several names to label their products. These include, along with their uses:

CINNASORB as an elemental mercury absorbent.  
Includes the activator and the base.

CN-PLEX as a cyanide neutralizer.

LIQUISORB as a liquid absorbent for the absorption of treated liquid chemical spills.

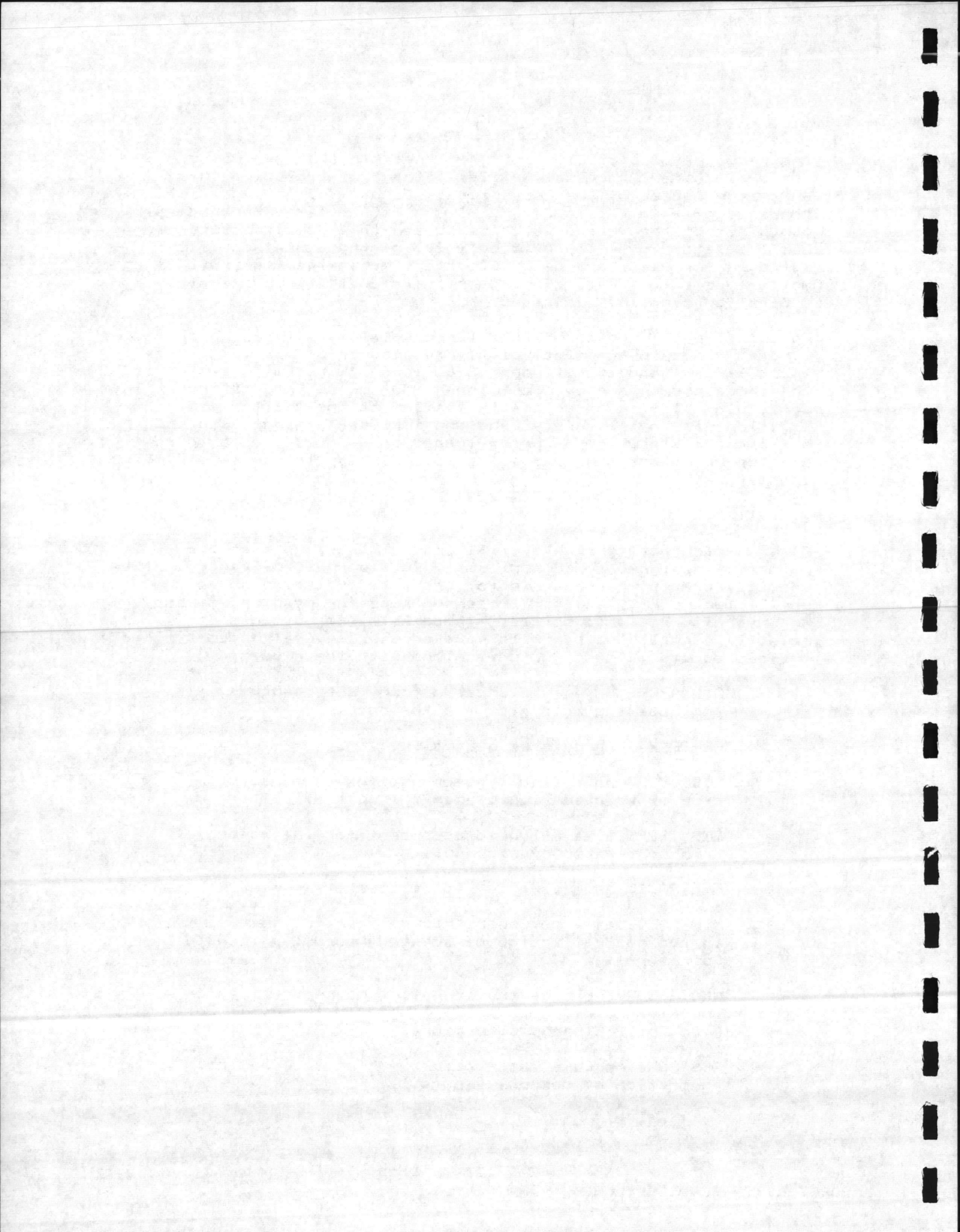
LIQUISORB S as a liquid absorbent for the absorption of treated cyanide spills.

NEUTRACIT as a caustic neutralizer.

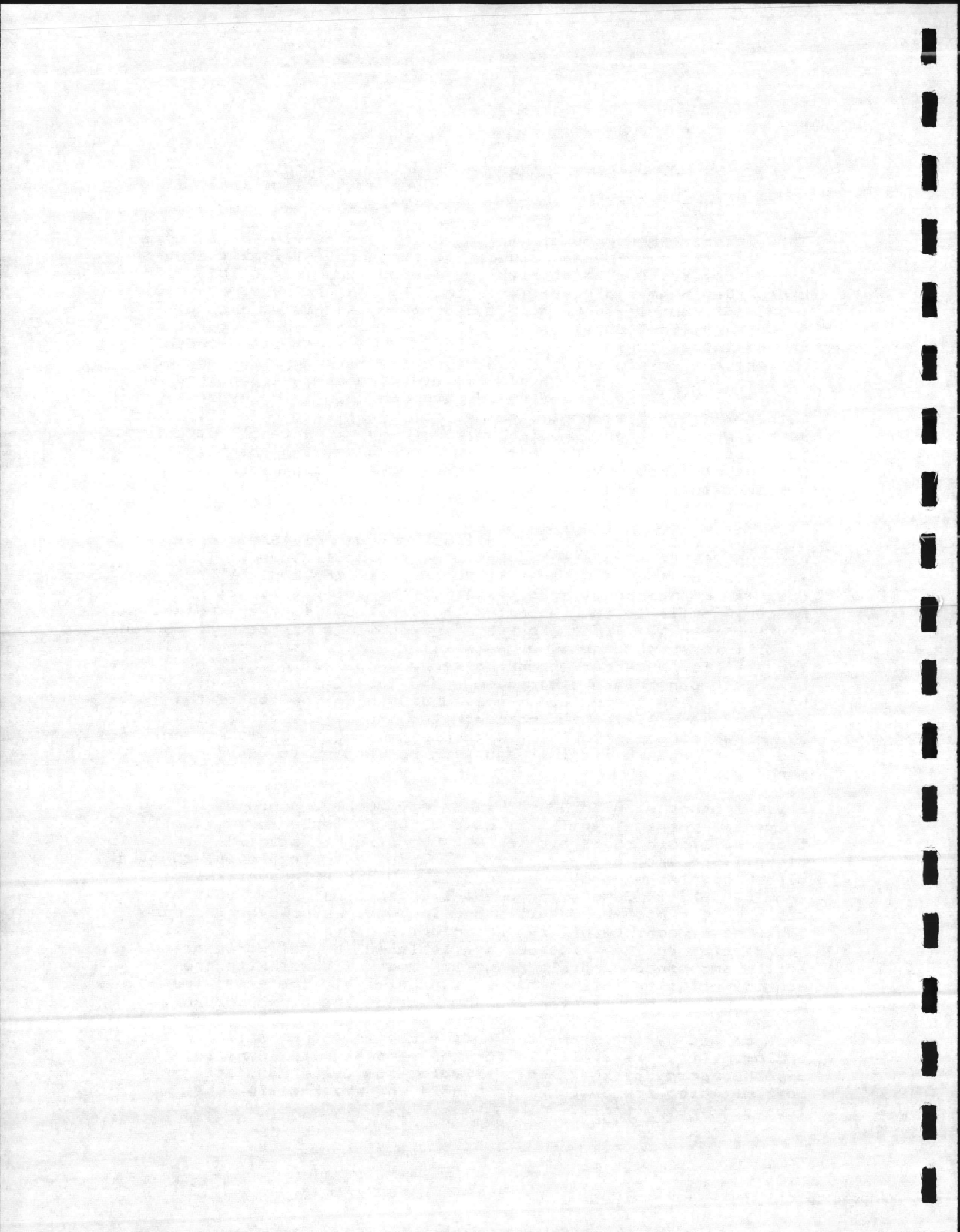
NEUTRASOL as a secondary neutralizer for the use in the neutralization of treated Hydrofluoric Acid Spills.

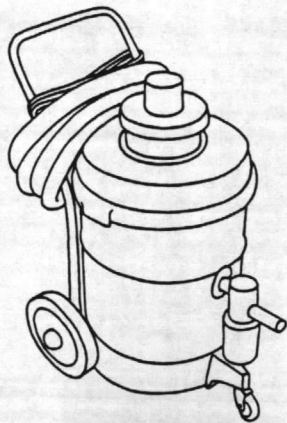
NEUTRASORB acid neutralizer for the neutralization and cleanup of those acids listed in the J. T. Baker Acid Spill Cleanup directions.

RESISORB mercury vapor absorbent for the chemical absorption of mercury vapors.

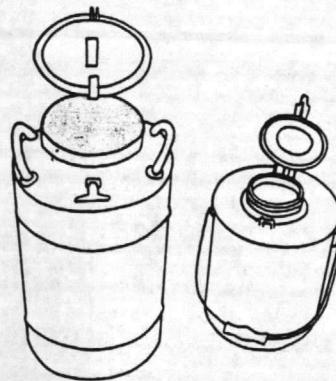




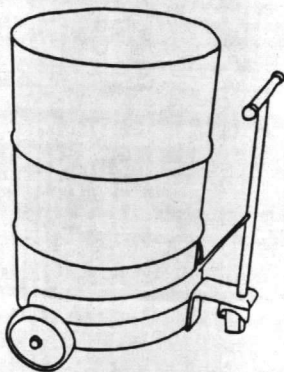




**Portable Vacuum**



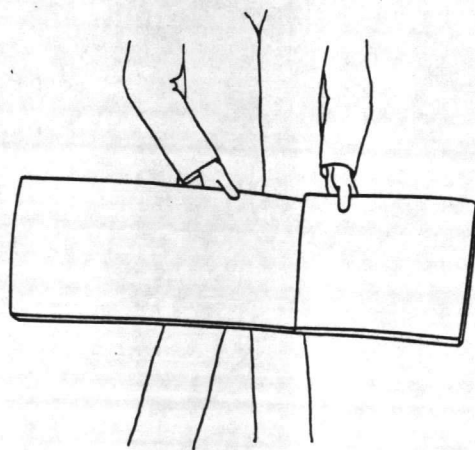
**Metal and Glass  
Safety Containers**



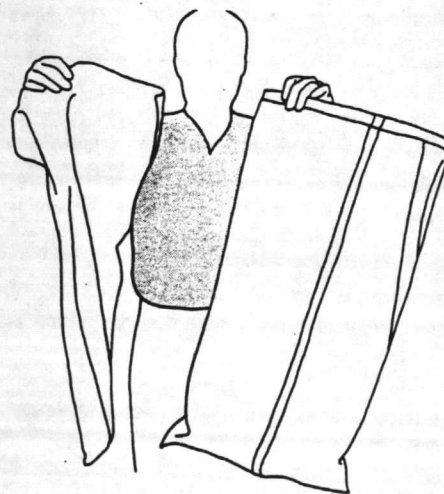
**Drum Handling Unit**



**Bottle Carrier**

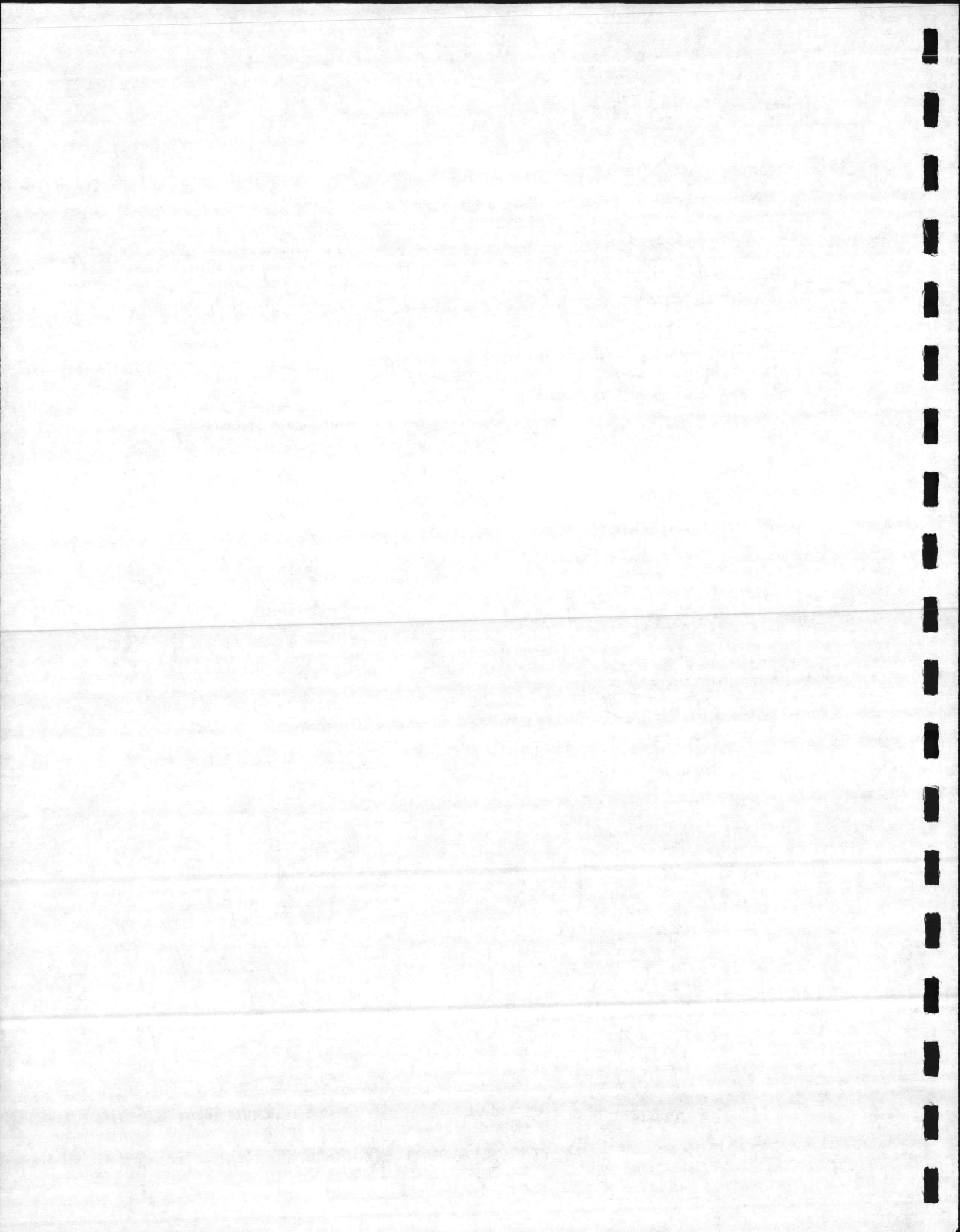


**Absorbent Sheet**



**Spill Control Pillow**

**SMALL-SCALE SPILL EQUIPMENT**



#### D. DRUM-HANDLING UNITS

To move spills from one location to another, a drum-handling unit may be needed. The drum-handling unit consists of a cart that is designed to wheel a 55-gallon drum from one location to another with a bottom draft or spigot on the 55-gallon drum so that the spill, once collected, can be drained or transferred from one location to another. The unit should also be equipped with a top since there could be a great deal of exposure to the material and its associated toxicity or from the standpoint of it being either a volatile or reactive material. In such cases, separation from the environment would be necessary. It would be quite advantageous to have some of these units in locations where there might be spills or leaks in a tank. The unit could be positioned underneath to catch the spill only or stop the leak as it is occurring until such time as the vessel in which the material is contained can be repaired.

#### E. SPILKART (PROPRIETARY PRODUCT)

Lab Safety Supply manufactures and markets a cart that is designed to contain several different types of spill control and cleanup equipment on the cart. Product literature indicates that the cart is constructed of a chemical-resistant structural foam and measures 39 inches high by 46 inches long by 21 inches wide. It is bronze with a gray rigid polyethylene liner. It is built to provide three trays for storing clean-up accessories and "... space to accommodate a 35-quart mop bucket and wringer (included)." It is equipped with a number of different types of equipment which may be suitable for spill control, particularly in a laboratory or on a small-scale basis. The items which are contained in this particular product include:

"30 Spill Control Pillows, 1-liter size

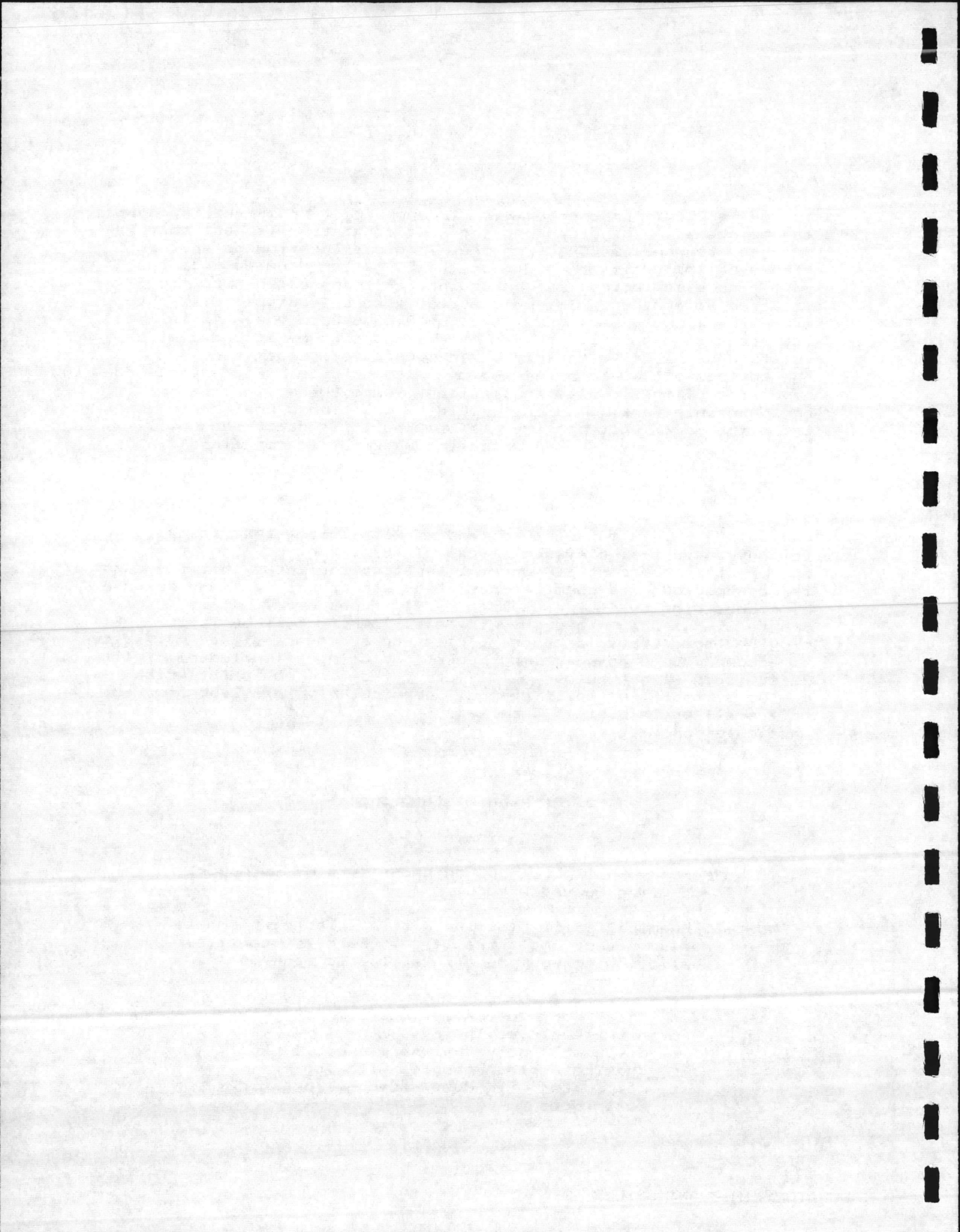
"Assortment of Printed Waste Disposal Bags

"HF Spill Cleanup Equipment

"Mercury Spill Cleanup Equipment (4 g of Hg Absorb,  
and 0.9 g Hg Vap/Absorb)

"2 Chemical Spill Clothing Kits available in small,  
medium, large and extra large. Each kit contains  
the following equipment in a plastic storage  
container:

- o total body coveralls, poly laminated Tyvek
- o nitrile gloves, pair
- o disposable polyethylene gloves, 1 pkg.
- o chemical splash goggles with fog-free lens
- o respirator with dust, acid gas/organic vapor  
cartridges





- o mercury vapor, hydrogen fluoride and dust/mist respirators
- o toxic and hazardous chemicals pocket chart
- o clothing container sealing tape

"Spill Squeegees (floor and bench models)

"35 qt. Mop Bucket with Wringer

"Mop, polypropylene broom and dust pan

"Tongs, Clorox, and Liquid Cleaner

"Bench Brush, pH paper

"Chem/Kleen-Ups (TM), Sponge

"Barricade Tape

"Printed Floor Sign

"Acid and Caustic Neutralizers

"Safety Flashlight with Batteries

"Instruction Booklet."

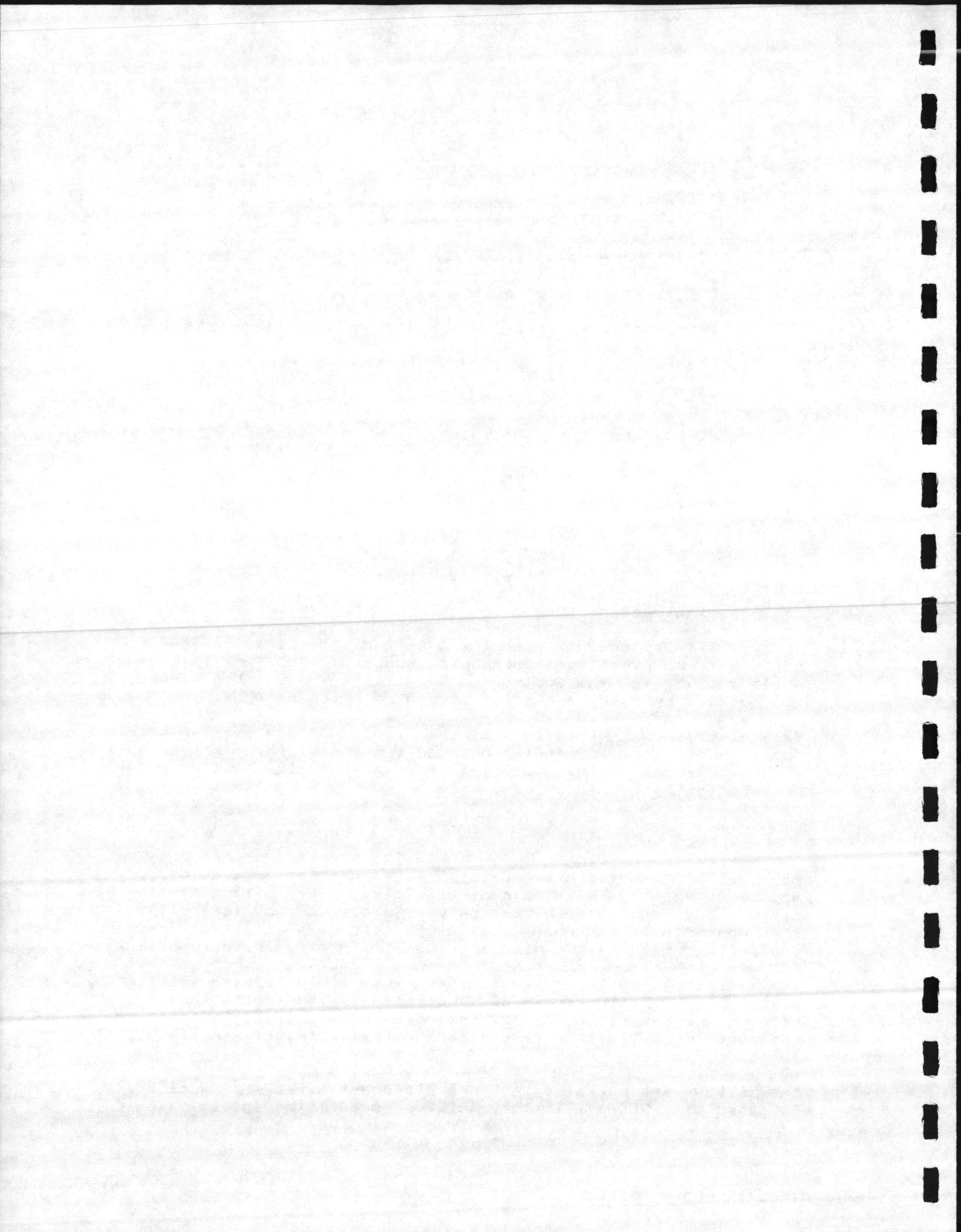
This particular product with the cart and all its associated equipment is advertised for a price range of \$750 for all the equipment, or for the SpilKart only with the disposable bucket, mop bucket, wringer, and floor sign at a price of \$354.

Several different variations of this equipment are available to a facility or firm. Depending on need, an individual might be able to assemble all of this material from various suppliers on a car or vehicle that would be adaptable or suitable for that particular firm's needs.

#### F. SPILL CONTROL PILLOWS

At least one manufacturer distributes an absorption type of apparatus known as a spill control pillow. The spill control pillow that is offered by Lab Safety Supply Company is a pillow that consists of amorphous silicate particles that act to absorb the spilled material. This particular firm markets these pillows for use with acids, caustics, and organic solvents, but it does indicate that the major exception for use would be with solutions containing hydrofluoric acid. The firm also indicates that the pillows are effective for absorption of hazardous biological and radioactive spills that cannot be chemically inactivated in-situ for safe handling.

The pillows are packaged in three different sizes with a capacity for absorbing 250-milliliter, 1-liter, or 4-liter spills. The



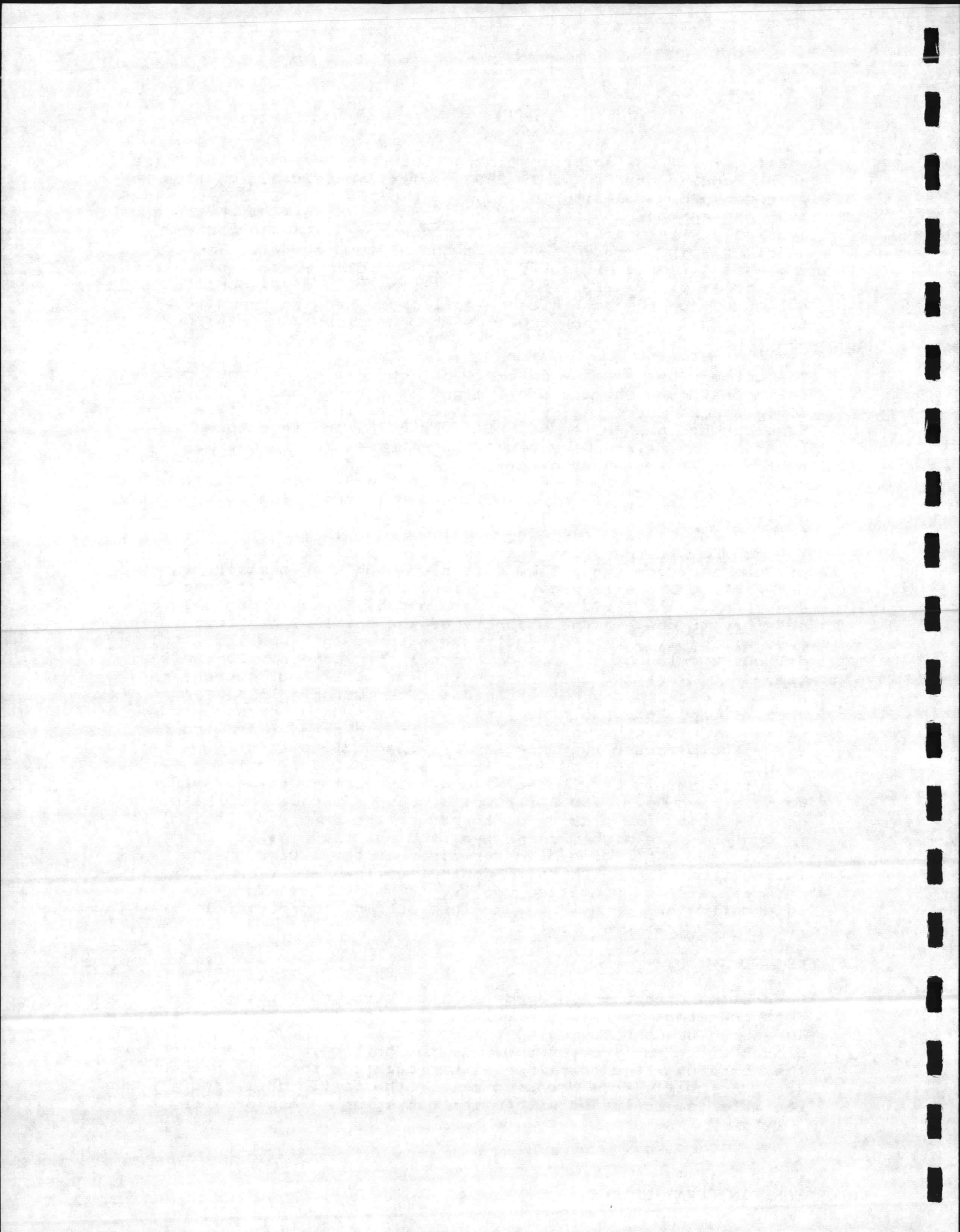
shelf life of the absorbent is indicated to be indefinite. The price range quoted in early 1982 varies from \$28.58 for a carton of twenty 250-milliliter pillows to a price of \$122.89 for 49 and over per carton for the 4-liter pillows. The pillows are also available with disposable bags for temporary storage and for handling a spill-saturated pillow prior to disposal. These bags are made of 1-1/4 mil polyethylene. The distributors of this particular pillow also indicate that the rate of evaporation of a liquid from the spill control pillow is reduced by polyolefin fabric and the entrapment of the absorbed liquid by millions of "falling particles."

The primary use of many of these pillows has so far been observed in laboratories where a spill might take place onto a floor surface area where the pillow can be used to fit the floor area. Some use has been noted of this type of pillow in outdoor locations as well. Many of the laboratories use this type of equipment in instances of a toxic or hazardous waste chemical spill. The carton size for the largest spill control pillow provides a capability of absorbing 480 liters which is about 127 gallons.

The general instructions that are given for the spill control pillows indicate that "they control a highly absorptive, inert material in a coarse bag that allows a flow of fluids into the absorbent. The fluid will be retained by the absorbent making it possible to contain the majority of the spill within the bag for easy disposal." The information continues that spill control pillows should not be used on hydrofluoric acid spills and that they should be used only on one type of spill, not reused, nor attempts made to dry out materials after using. This precaution is given because residues may remain which could react violently with other chemicals. It is indicated that with the exception of hydrofluoric acid "... chemical spill pillows can be used to pick up most of any liquid spills. Heavy oils or viscous materials should be diluted with an appropriate solvent before being picked up. Also spills of highly hazardous chemicals should be diluted before picking up to reduce the change of coming in contact with highly corrosive liquids, toxic gases, or chemicals." The types of materials that are listed on the instructions for which spill control pillows might be used include chemical spills, biohazard spills, or radioactive spills. The information also provides some instructions for disposal after the information has been collected.

#### 6. BOTTLE CARRIER CONTAINERS

Several manufacturers produce an insulated, cushioning-type container that is used for bottle handling or bottle carrying. These can be used to reduce the possibility of a bottle being broken and a spill occurring. If the bottle is dropped within the container, the container either cushions the fall enough to keep the bottle from breaking or, if the bottle does break, keeps the material contained within the packaging. This provides a



measure of prevention as well as some amount of control if the bottle does become broken. Bottle carriers exist both as plastic and as rubberized products. One consideration that should be taken into account when using this type of container is whether or not there will be any reaction between the the substance that is being carried within the container and the container material, should breakge occur.

#### H. CONWED SORBENT PRODUCTS (PROPRIETARY PRODUCT)

Conwed Corporation produces a range of absorbent products for use for petroleum spills. These products are made from a biodegradable natural fiber that is treated to repel water and absorb hydrocarbons. The fibers are also reinforced with a special plastic net that provides additional strength for handling the sorbents when completely saturated.

According to the product file on these products, "Conwed sorbents can absorb and hold up to 26 times their weight in water.... Disposal of saturated sorbents is convenient. They may be incinerated leaving less than 4% residual ash. They may be buried in an approved dumping site. Or, if inadvertently left on the job, they will degrade over time."

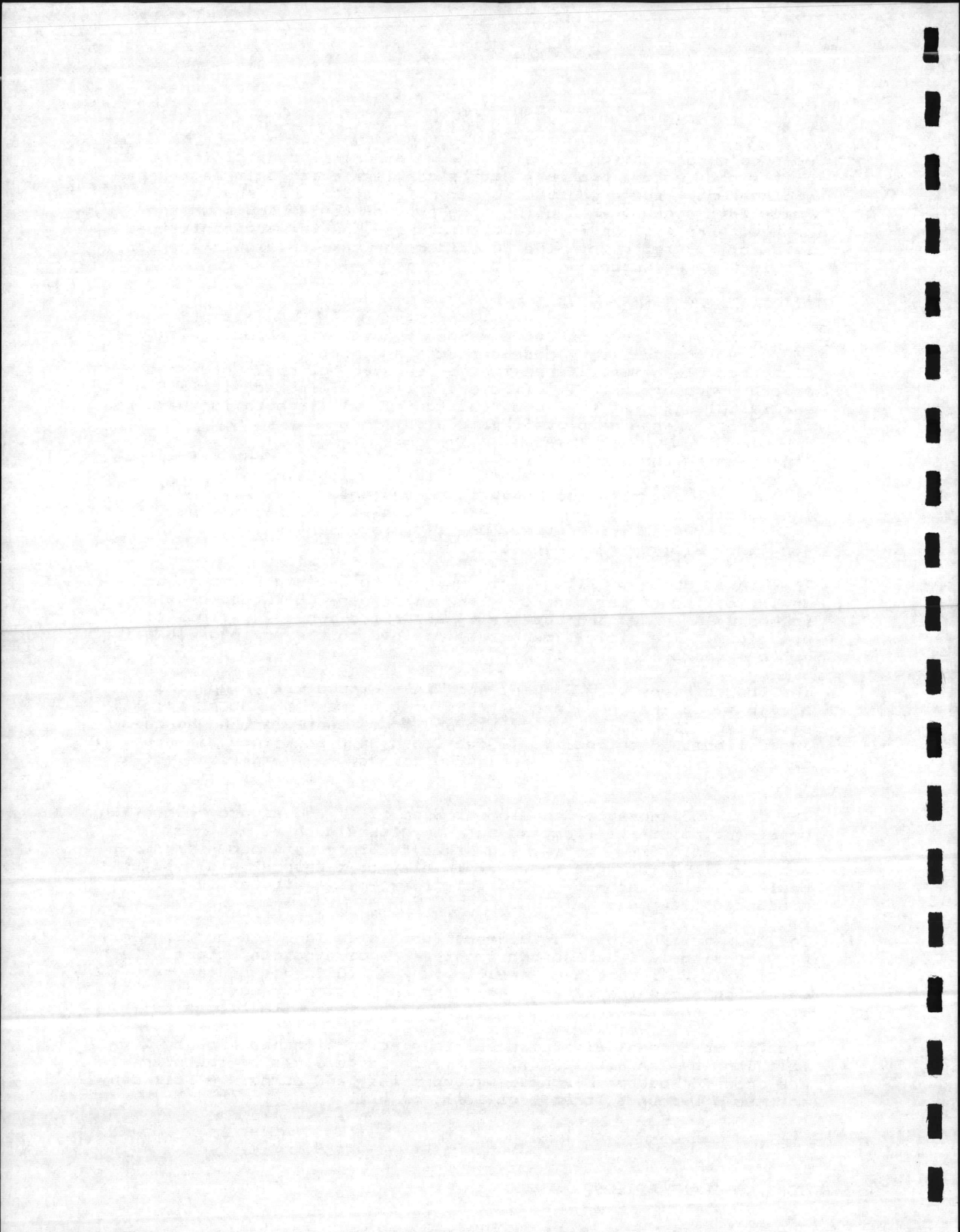
The Conwed Sorbent Pillows are designed to be used in sumps or drains of industrial plants. The pillows are 18 inches by 24 inches by 4 inches and capable of absorbing about 2 gallons of petroleum. The pillows can be maintained in the drain or sump for up to 4 weeks.

The Conwed Heavy Duty Sorbent Boom is equipped with a special olefin strip that provides extra flotation when the boom is fully saturated. The boom is flexible and forms easily around beaches and pilings. Each boom is 10 feet long with an 8-inch diameter. A carton of four booms can absorb 800 pounds, or 100 gallons, of oil.

The Conwed Disposable Containment Boom is "... designed to contain or divert polutants floating on quiet lakes such as marinas, lagoons, well pits, lakes, and dikes." Since this boom-type is produced in 7-foot sections, it is easy to transport and assemble onsite. As the boom is relatively inexpensive, it can be discarded after use.

The Conwed Disposable Containment Boom is designed so sections may be used singularly or joined together by sliding connectors. Each section is 20 inches high and floats with 10 inches of the boom extending above the water line. The boom is constructed of a generally chemical-resistant polyethylene foam with closed cells.

The Conwed Sorbent Blanket comes in a roll 35 inches wide by 200 feet long by 1/4 inch thick. Rolls or large pices of the blanket are good for use on beaches, ground areas, and sumps. A roll can soak up 900 pounds, or 113 gallons, of oil.



Conwed Sorbent Pads are used on small spills. The pads can be retrieved by a tool such as a pitchfork. They can then be wrung out for reuse. One square weighs about 4 pounds when fully saturated and measures 17-1/2 inches square with a 1/4-inch thickness. A carton of 10 pads should be capable of absorbing 460 pounds, or 58 gallons of oil.

#### I. OPALITE

Opalite is an absorbent and is indicated by the manufacturer to be a nonflammable, inert fuller's earth. It is said to be "...used safely to absorb liquids of almost any description." The directions further suggest that one "...spread absorbent over spilled area sufficiently to absorb liquid, allow enough time for absorption, and sweep up with a stiff broom." This particular product is packed in 50-pound bags.

#### J. DRUM REPAIR

1. INTRODUCTION. In many instances, drums that are used to transport or store hazardous or chemical wastes are damaged. Among other things, this may occur due to punctures resulting from fork lift accidents, the dropping of drums, or rupture due to overpacking of drums.

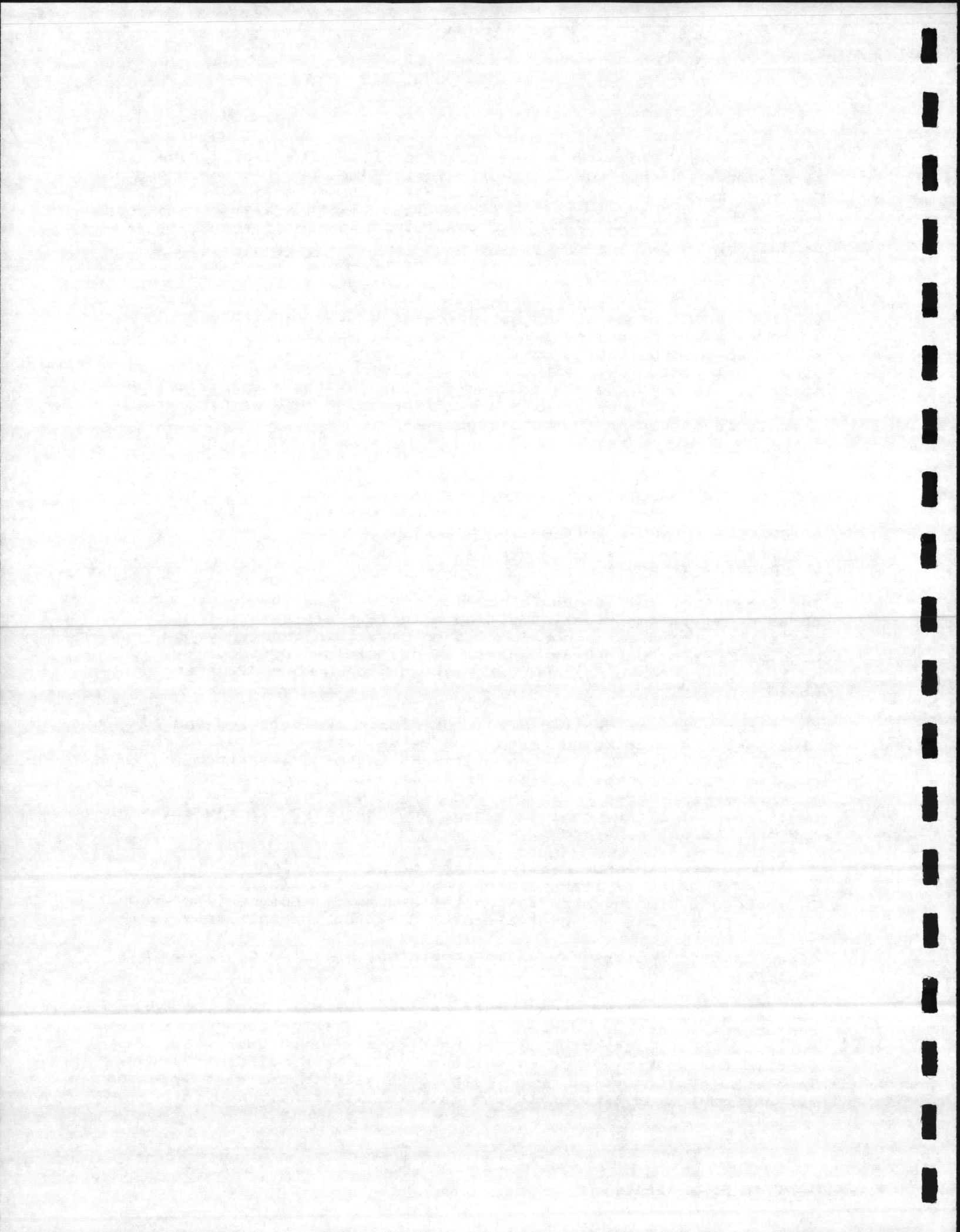
The cleanup of spills resulting from rupture and the repairing of these drums is important. Spilled materials may result in one's slipping due to poor footing or result in injury due to high amounts of dangerous vapor. If not cleaned up properly, spills may spread or accumulate making a dangerous situation worse.

Two techniques for dealing with drum repair are patching and plugging. Each technique requires the same steps preceding the actual repair and the same careful handling of drums after repairs. In some cases, a container may have to be moved or material transferred to another container before the drum can be repaired. If a drum cannot be repaired properly, all the material may have to be transferred.

The first step in drum repair is the proper positioning of the drum. The point of leakage should be above the liquid level. This prevents further leakage in the course of repair. The second step is to contain and neutralize or clean up the spilled material.

After these two steps have been completed, the drum can be safely repaired.

Following repair, the drum should be overpacked in a salvage drum and properly labeled, marked, and sealed. This procedure must be followed whether the drum is returned to the warehouse to be emptied and destroyed, or is shipped to its original destination. This should also be followed if the drum sits in the same location for any period of time or if the material is transferred into a





new drum.

2. PLUGGING METHODS. Wedging is the process used to repair wedge-shaped or round punctures made by fork lift tines or other hard objects. Wooden wedges or round-tapered plugs are used to seal these punctures.

In this procedure, a wedging action is used that helps hold a plug in place. Although given the name "wedging" to represent the wedge used for rectangular-shaped punctures and corner splits, round-tapered plugs are also included in this method.

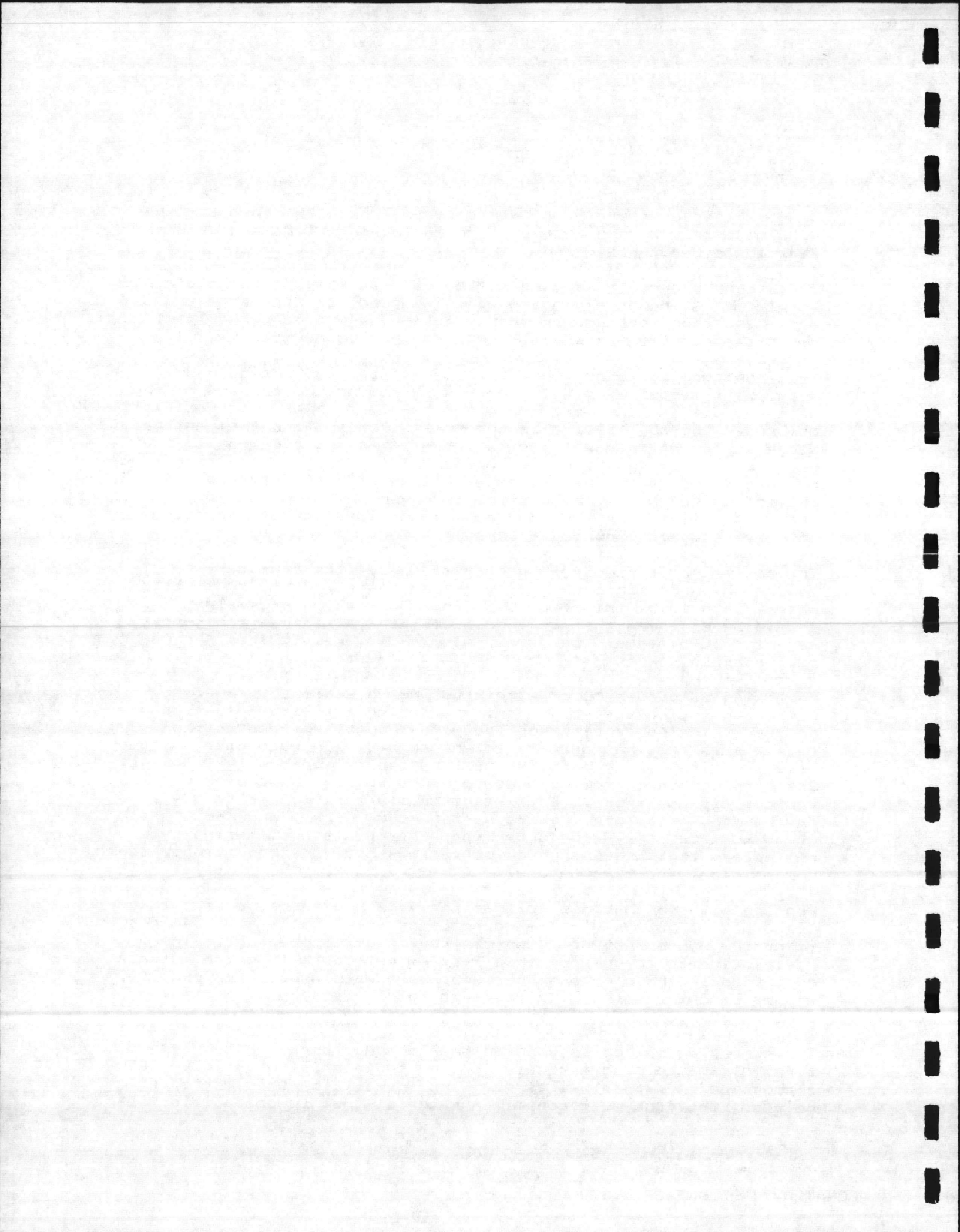
If a puncture is large, more than one wedge may be required. A wedge is inserted by placing lead wool around the corners of the hole and driving the wedge into the puncture. The lead wool will compress, thereby filling in the splits and sealing them as the wedge is driven in. Any protruding area is cut off that so the wedge is even with the outer surface of the drum. Next, aluminum or lead tape, depending on compatibility with the material, is applied. Enough must be applied to cover the wedge while remaining within the sanded area. Taped edges should be rounded to prevent snags that could cause tearing.

The next step is to wire-brush or sandpaper the drum surface around the wedge in order to remove any paint, dirt, or spilled material that may interfere with the application of sealant. It should be stressed that if a drum contains a flammable material, sandpaper ONLY should be used. A spark may result from the use of a wire-brush.

Following sandpapering or wire-brushing, a sealant is applied. Either epoxy, polyester, or self-hardening metalized plastics may be used. The sealant is applied with a putty knife over the entire area that has been taped and sanded. In each case, a resin base and catalyst or hardener must be applied before the sealant. Sealants can take from minutes to hours to dry, depending on various circumstances. Epoxies generally take longer to dry, and dry harder. Polyester resins harden more quickly and require a clean surface. Kits for drum repair may contain different types of sealers that are designed for various humidity conditions, drum composition, and temperatures.

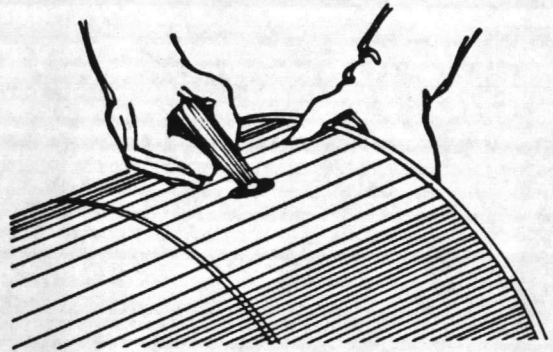
Wedging with round plugs follows the same procedure, except that lead wool is not used. The round plugs are usually made of soft to medium woods that will conform to irregular openings. The restriction to the use of this type of method is that the material contained in the drum must be compatible with wood. For example, wedges cannot be used with drums containing strong oxidizers and certain acids.

The tire plug method is used on smaller punctures. A tubeless tire vulcanized plug assembly is used to shoot a rubber plug into a puncture in a tubeless tire. First of all for this method to be used, the drum must contain a material that is compatible with

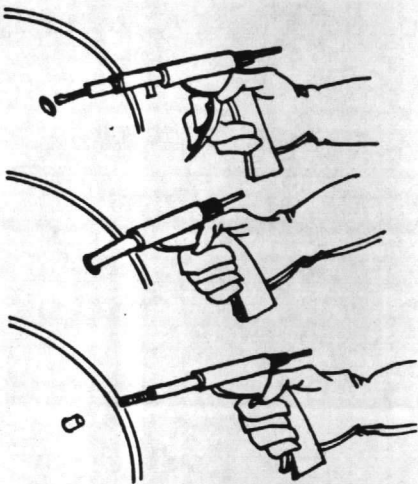




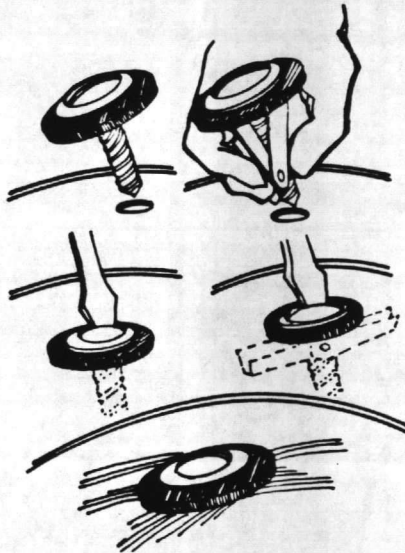
Sequential Wedge Plugging Steps



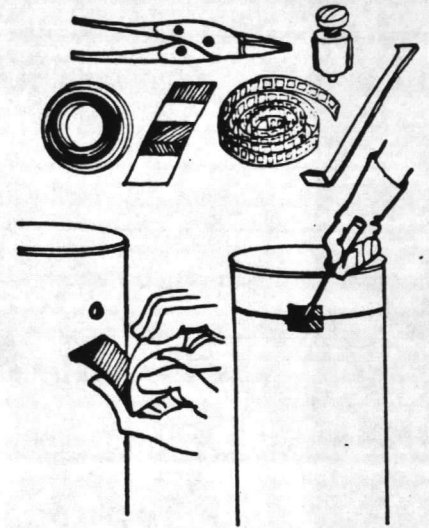
Dowell Plugging



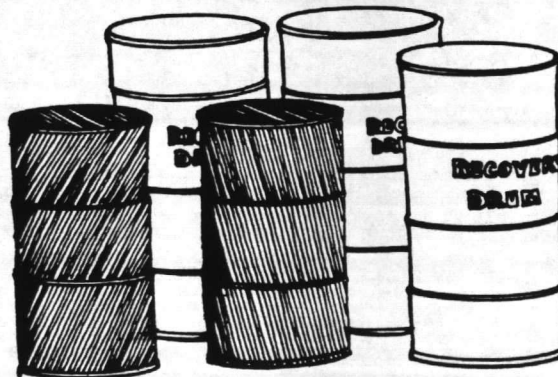
Sequential Tire Plug Steps



Sheet Metal Screw Toggle Bolt Sequential Steps

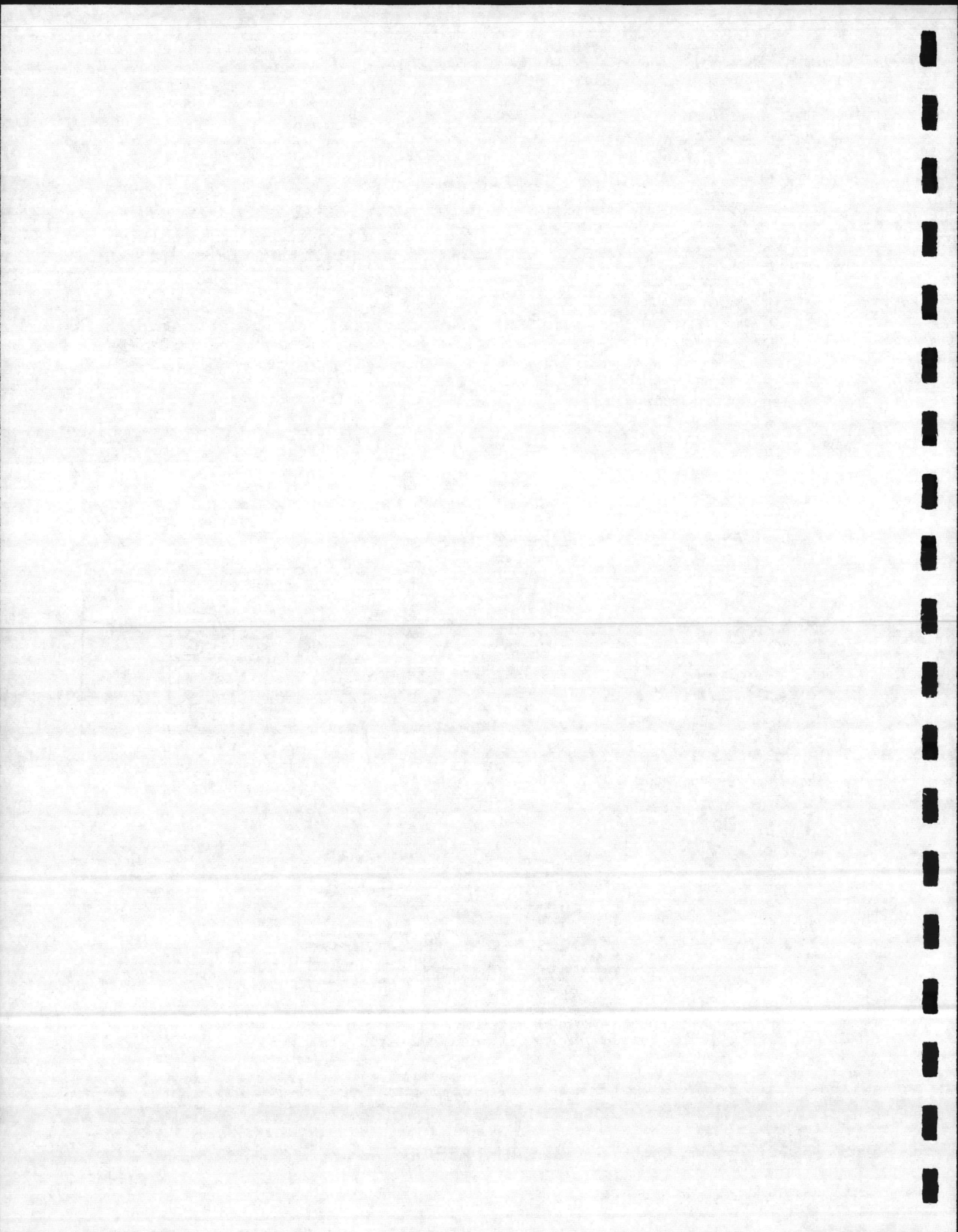


Band Patching



Salvage Drums

## DRUM REPAIR



the rubber plug. Second, the puncture must be large enough to admit the plug tip but also must be smaller than the actual plug. To insert a tire plug, a loaded gun is inserted into the puncture, the handle depressed, and the gun slowly withdrawn from the puncture. The plug does not have to be sanded flush with the drum surface.

Washer-screw plugs are also used on small punctures. These plugs consist of a sheet metal screw and a washer that are inserted in a piece of neoprene. The screw serves as a plug and a seal. These plugs can be assembled in various sizes in order to fit the puncture. The major advantage of using the washer-screw plug is that it creates a tighter seal on almost any contour due to the washer that is used. The precaution that must be taken when using this plug is not to tighten it too much. Such a practice would drive the screw completely through or tear the neoprene washer.

The expanding-foam-in-bag method can be used as a means of plugging, but is best used for temporary repairs. The seal created by this method is not very tight and will not withstand rough handling or long distance transport.

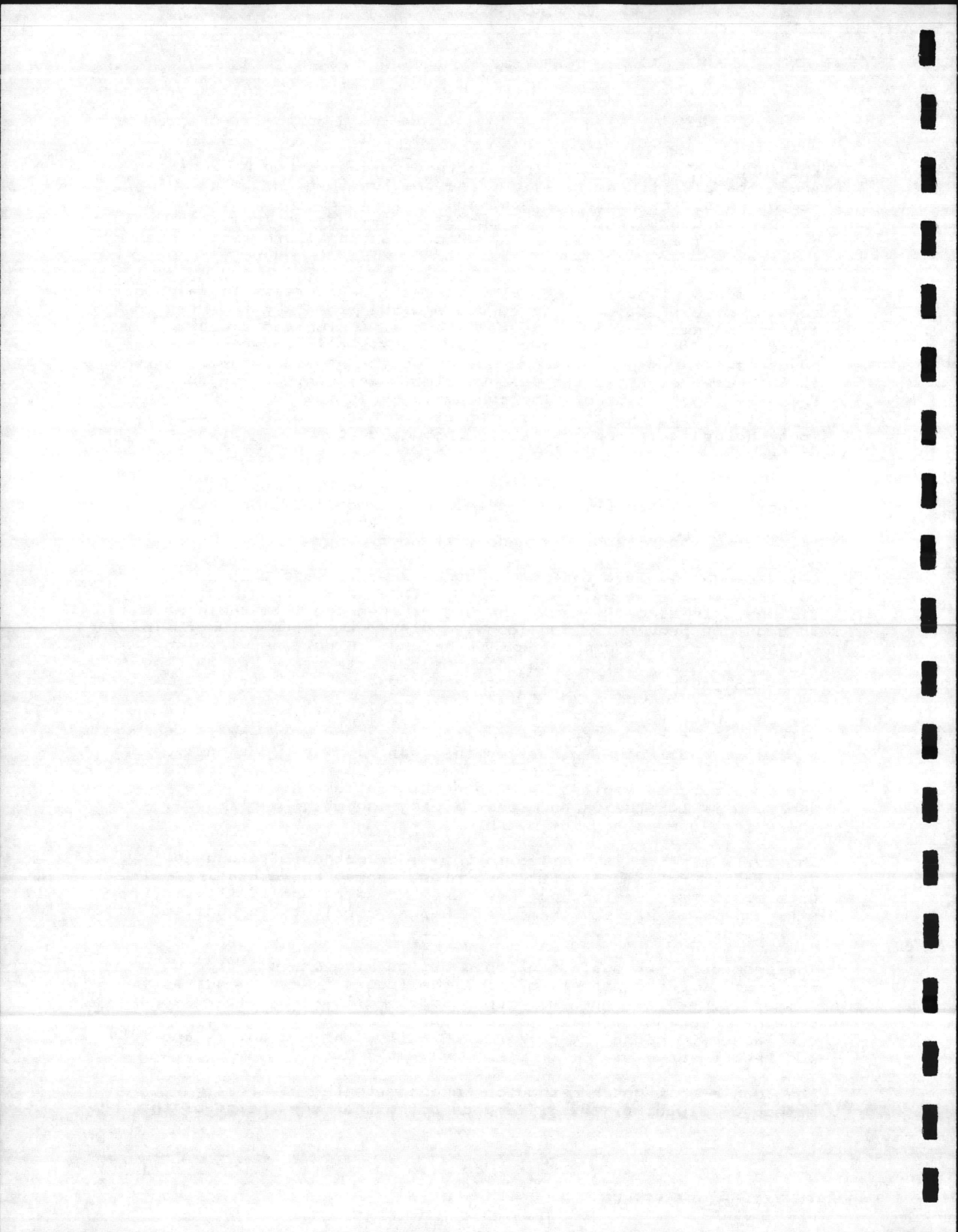
This method involves the use of bags, usually made of polyurethane. The bags are filled with a self-hardening foam dispensed in aerosol foam. The bag is inserted into the drum and through the puncture, then loosely twisted at the puncture. Thus, an inner and outer compartment is formed. Simultaneously, an expanding foam is dispensed into the compartments. Lastly, the outer compartment is twisted off and tied.

3. METHODS OF PATCHING. There are some instances in which patching is more desirable than plugging. One of these is when a drum is repaired within a confined space. Other instances for using patches include those when time is important, as they are more quickly applied, and when the contour on which the puncture is located is such that a plug cannot be applied. There are four methods of patching.

The sealant patch is similar to the wedge method of plugging. This method is used for patching rims, seams, and other irregular drum contours. Sealant patches have the advantage of flexibility, making it suitable for irregular shapes. Sealants include epoxy, self-hardening putty, and plastic metal.

The procedure for sealant patches begins with the positioning of the drum so the puncture is above the liquid. Next, a suitable hammer is used to knock out rough edges followed by either sanding or wire-brushing of the damaged area. Aluminum or lead tape is then added to round the corners. Finally, the sealant is applied and left to dry.

The toggle-bolt patch method corresponds to the washer-screw method of plugging, the difference being that the inside of the



toggle-bolt patch is only used to tighten and hold the patch; it does not plug the hole. The toggle-bolt patch works by the insertion of a central bolt through a neoprene washer/gasket with a backup metal washer. The turning of the bolt under pressure seals the washer against the puncture and exterior drum surface.

Magnetic tape patching is a quick method, and it can be applied in confined spaces. The tape may consist of either a plasticized metal composition or a plastic-metal sandwich. In some cases, the tape is cut to size, the adhesive backing peeled off, and the patch applied.

The magnetic tape patch is temporary since it can be loosened by heat, vibration, and friction. The patch is held in place by the backing and the magnetic attraction between the metal in the drum and the tape.

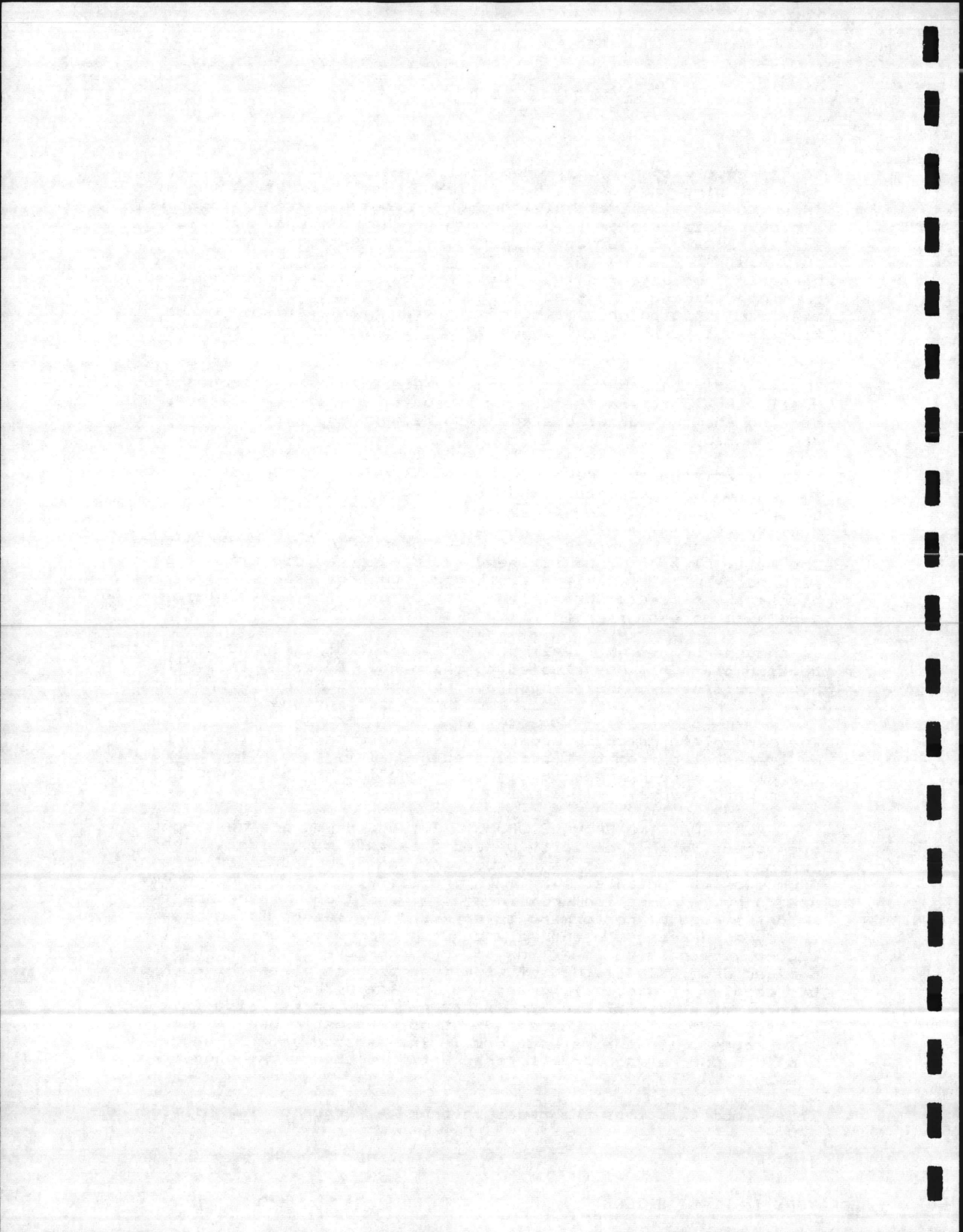
Four materials are necessary to install a band-plate patch. These include an indexed metal band with a screw tightener, a piece of rubber or neoprene, a metal plate or a piece of magnetic tape, and, optionally, a block of wood. This patch is applied by placing either the piece of neoprene or rubber over the puncture. The metal backing piece is then placed over the piece and a band slipped over the patch and tightened. On irregular surfaces, wood blocks are placed either to the side or over the metal plate, depending on the situation.

If enough room is not available for assembling the band-plate, the backing plate may be soldered to the band. By doing this, the band would need to be slipped over the drum, the plate positioned over the neoprene or rubber, and the plate tightened.

The band-plate patch is especially suitable on drums that are to be transported from the accident scene. This is due to the fact that it is more rugged and can withstand rougher handling than other patch types.

4. REPAIRING SALVAGE DRUMS. Salvage drums are heavy-duty, open drums, with a capacity of approximately 85 gallons. The purpose of these drums is to contain a damaged and/or repaired drum and its contents. The main problem with using these drums is how to put a 55-gallon drum into a salvage drum. There are two major methods of performing this task. One method is to insert the damaged drum into the salvage drum turned on its side. The second method is to lower the salvage drum over the upright damaged drum. The method of side insertion requires the work of two people. A piece of lumber and a piece of cardboard are also helpful to aid in sliding the punctured drum on its side into the salvage drum. To use the second method, a plastic bag is used which comes with the salvage drum. The damaged drum is bagged and then the salvage drum lowered until it covers the punctured drum.

It is important that the repaired drum be wedged or immobilized





inside the salvage drum with wood, cardboard, or some other packing material, and absorbent added. If there is enough space between the walls of the two drums to permit movement of the damaged drum, new ruptures may be created during their handling and transport. Wedging and proper absorption may prevent further damage.

#### K. PIPES, VALVES AND CONTROL MANIFOLDS

1. INTRODUCTION. Experts agree that the best way to control piping leaks, whether they be liquid or gas, is to stop the flow at its source whenever possible. Sometimes all that is needed is to close a valve, but other times it is more complicated as there may be ruptured or broken piping, leaking unions, valve packing leaks or other similar releases with which to contend.

Those responding to hazardous material spills should have some knowledge of basic plumbing and various plugging and patching techniques employed to handle unwanted releases from pipes, manifolds, valves, gauges and meters. As with other unplanned incidents one can greatly benefit from preplanning to control piping failures. A working, hands-on knowledge of the control manifolds for bulk storage tanks, plant process piping and delivery vehicles is needed of those chemicals expected to be encountered.

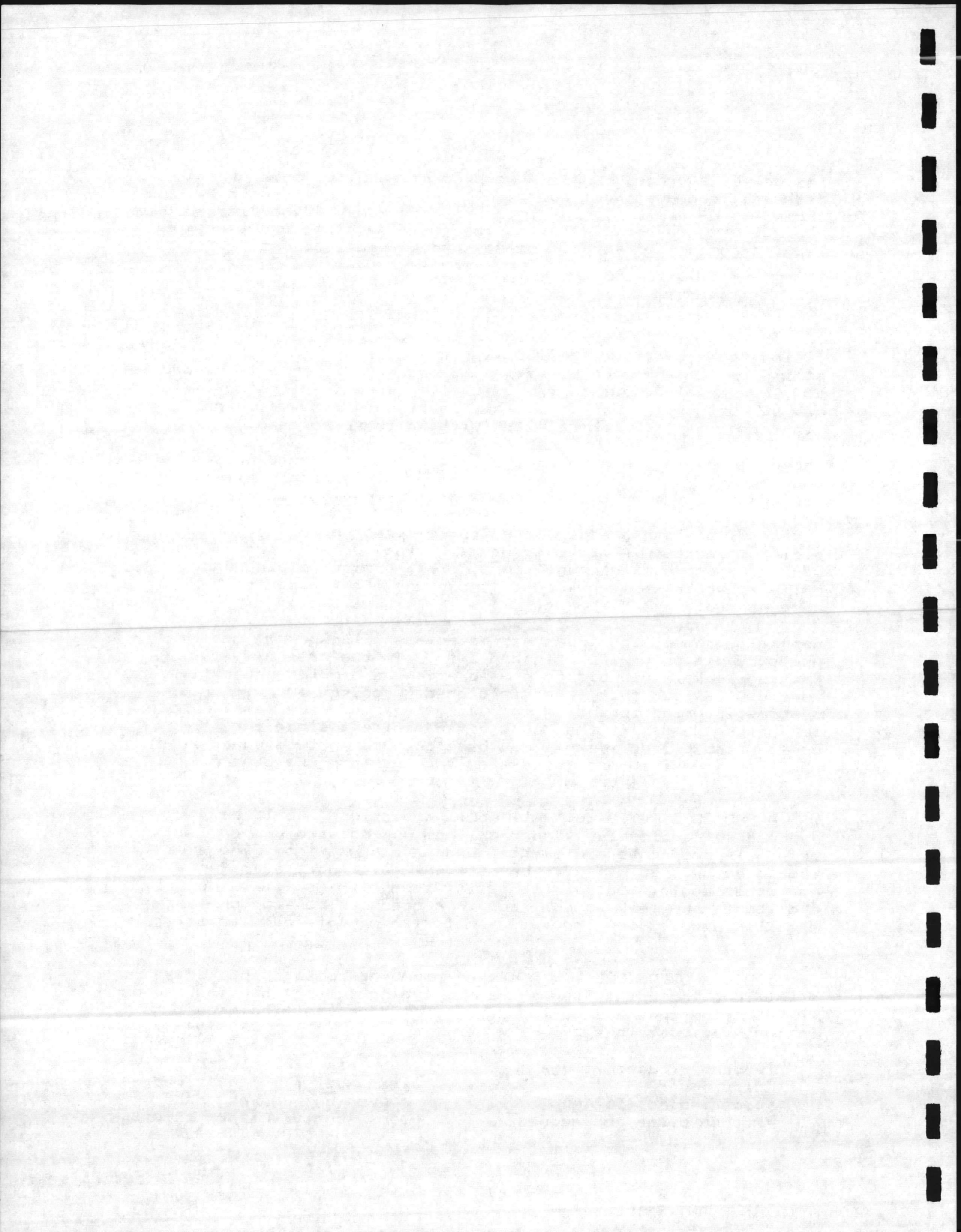
Generally these techniques and materials will work on medium pressure piping of 100 psig and less. In the case of valve packing leaks, much higher pressure can be handled prudently. It must be realized that there is stored up energy in pressurized systems with the potential for explosive sudden release. There is further danger at the scene of an accident since the pressurized piping systems may have been subject to shock loading that has stress loaded the system and weakened the piping.

2. APPROACH STRATEGIES. All spill situations should be approached cautiously. Approach from upwind with proper personal protective equipment. Evacuate down wind. The area should be secured off with barricades. Dike spilled material or use other containment strategies. Attempt to isolate, identify and locate the leak. Apply repair procedures to stop or lessen the flow and use countermeasure material on spilled material.

3. TOOLS AND EQUIPMENT. A set of plumbing tools should be maintained including pipe wrencher, tubing cutter, hacksaw, rubber mallet, pipe dope and teflon tape. Other specialized materials include various sizes of:

expander rubber plugs  
pipe plugs  
pipe and hose clamps  
wooden plugs and wedges

tubeless tire plugging kit  
lead wool & felt for wedges  
rubber or neoprene pads  
epoxy putty; ribbon or stick



screws and toggle bolts

cloth and metal duct tapes

Complete plugs and patch kits for leak sealing can be purchased already assembled. One source is: E & C Manufacturing, 12104 N. Oak Hills Parkway, Baton Rouge, Louisiana 70810.

Various piping breaks, discharges, releases and leaks can be stopped and flows reduced using techniques and materials that are relatively easy to apply. The following cases outline various situations that a responding emergency team might be confronted with. Each example assumes that the team is properly equipped with personal protective equipment before handling each piping problem.

Case 1. Leaking union, ell, tee or other pipe connections.

Control Measure: Tightening of these connections with a pipe wrench can often eliminate or reduce the flow to manageable rates. Actually, as any plumber will advise, two Stillson or pipe wrenches are needed; one to hold the connection steady while the other is used to tighten the leak. There is some danger in piping repair, especially in accidents, that the connection has been cracked. In that case, undue pressure can open the crack further or cause a complete break in the pipe and make matters worse.

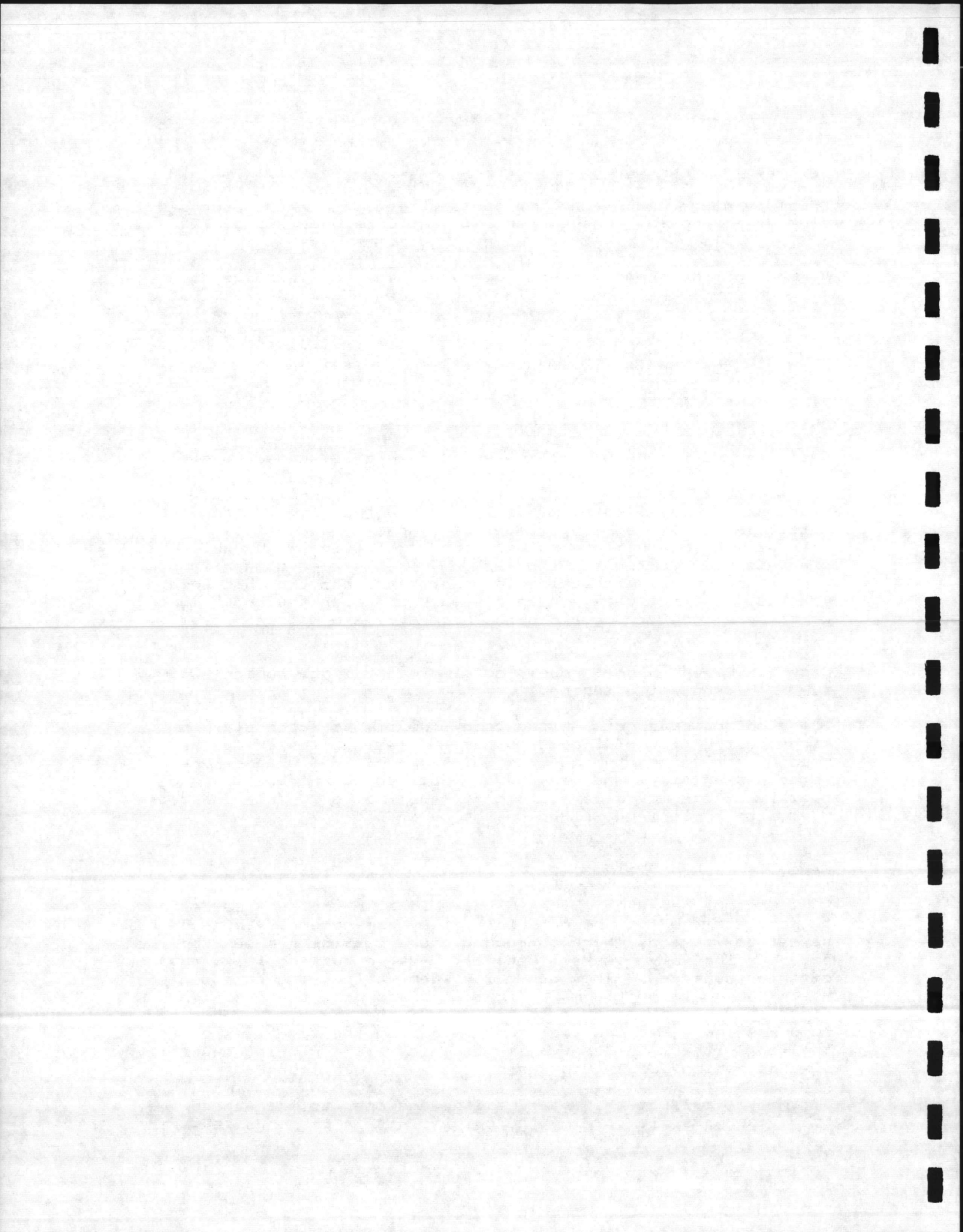
Case 2. Leaks in soft copper or aluminum tubing, rubber or plastic tubing.

Control Measure: A squeeze-off device is successful in stopping the flow of liquid or gas. Firemen often crimp the copper or aluminum tubing from LPG tanks on trailer and rural homes during fires and many have a tool to do this easily and quickly. A crimping device can be made from a "C" clamp and two pieces of angle iron welded on the jaws.

Case 3. Leaking Valves.

Control Measure: Since a valve is a control device designed to regulate the flow of materials, they are generally considered safest to work on. Work on much higher pressure can be done when encountering valve leaks. Generally, valve packing leaks are most often encountered. They can occur when the packing gets old and stiff and no longer forms a tight seal around the valve stem. One approach would be to turn the valve all the way open. This can compress the valve packing from the bottom and sometimes control the leak without the use of any tools at all. Packing leaks may also be controlled by tightening the valve packing nut.

If the valve is at the end of a line and open to the atmosphere, it may be possible to plug the opening with a proper size pipe



plug. In other cases, a proper size wooden plug may be driven into the opening.

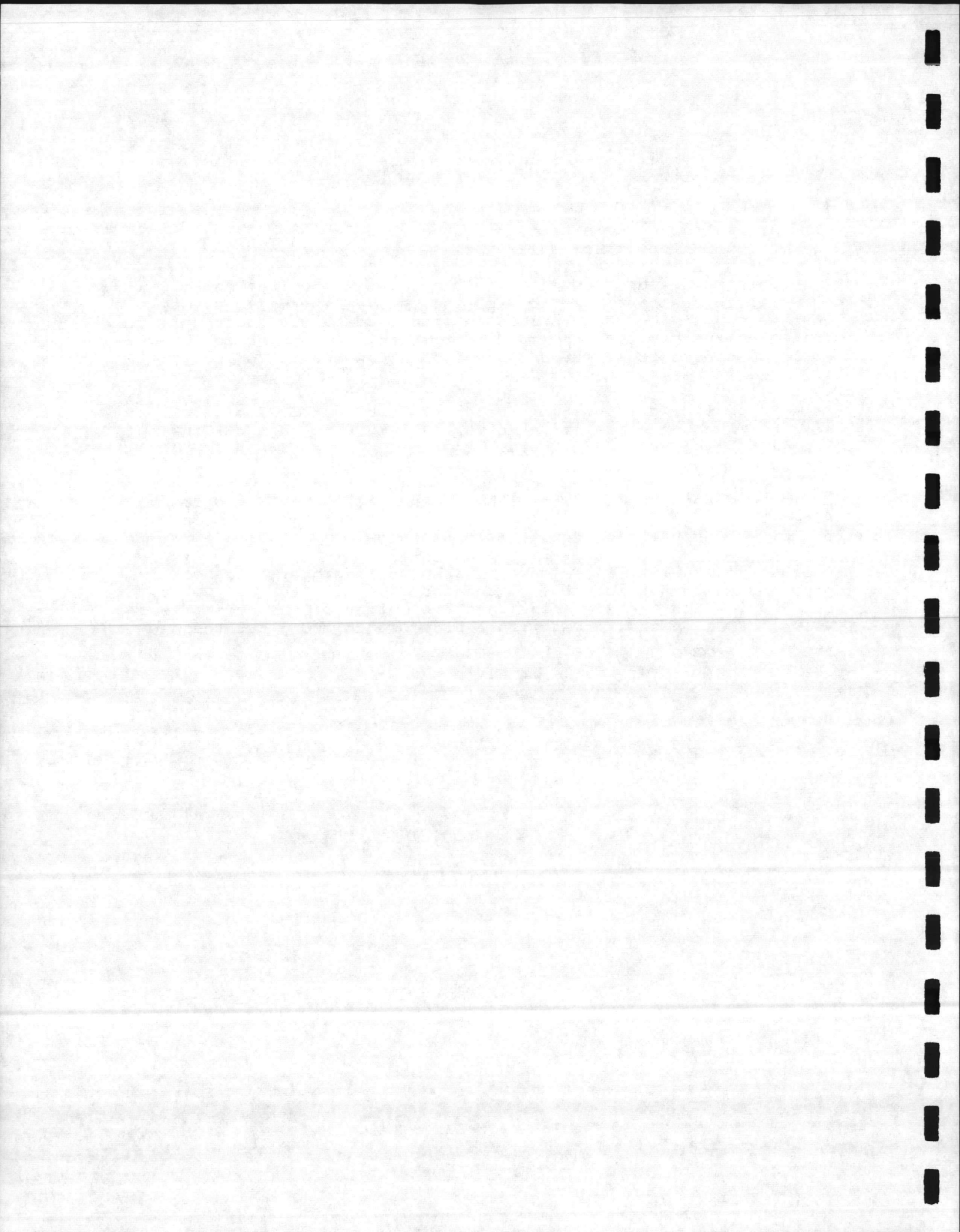
Case 4. A liquid is leaking through a hole in the sidewall of a 1" pipe.

Control Measure: Use a pipe clamp and rubberized gasket material to seal the hole to stop the leak. Other methods may involve the use of epoxy ribbon or sticks to make a right semi-permanent seal. For added protection, a clamping device would be needed to hold the epoxy in place while it cures.

Case 5. A liquid is gushing forth from a broken 3/4" pipe. It is down stream of a valve. Attempts to shut off the valve prove fruitless.

Control Measure: Use a pipe wrench to keep the valve from moving and another to unscrew the broken length of 3/4" pipe. After the broken pipe is removed, drive the proper size wooden plug into the valve outlet to stop the flow.

Another possibility is to make up a short length of threaded 3/4" pipe and screw a good valve on one end. Leaving the new valve open, screw the threaded pipe into the outlet of the defective valve. Snug up the thread with a pipe wrench and close the new valve to stop the flow.



# IX. PERSONAL PROTECTIVE EQUIPMENT

## INTRODUCTION

The following incident points up the need for proper selection of materials for fully encapsulating suits including plans for rescue and escape if the suits fail.

On August 12 and 13, 1983 outside of San Francisco four volunteer firemen were exposed to the vapors from leaking anhydrous dimethylamine (DMA) because of failure of totally encapsulating suits, suit facepieces, gloves and boots.

A 6600 gallon tank car of DMA sprung a leak in the sampling line inside the dome on top of the car. After donning encapsulating acid suits with breathing apparatus inside and being exposed for a total of approximately 43 minutes, the facepieces began to crack and shatter such that the persons involved could not see where they were going. Their gloves and boots became sticky and soft and unuseable. Because of the failure of the facemasks the vapors were able to get inside the suit and a quick-assisted escape from the suit in one case was necessary.

Butyl rubber coated encapsulating suits with fresnel facepieces were finally used by a contractor to stop the leak and transfer the tank contents.

Fully encapsulating does not necessarily mean fully protective. No one material is resistant to all chemicals. Hazardous materials response teams will require several different suit materials to cover the widest possible chemical exposures.

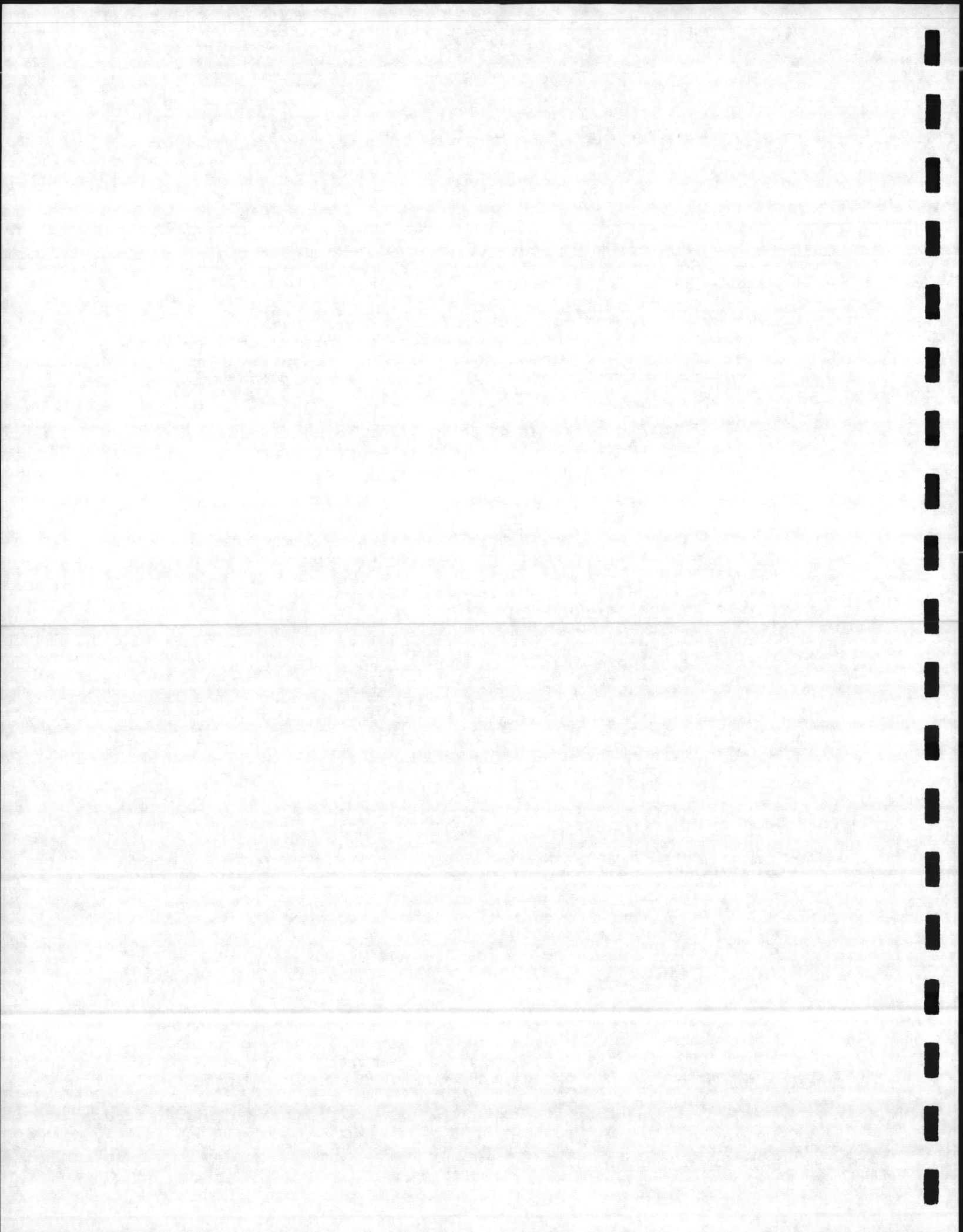
## TYPES OF ENCAPSULATING SUITS

### Type I - SCBA Inside Suit

This combination provides the protection of the SCBA itself, particularly the straps, rubber parts and other items. It provides maximum protection for the user. The biggest disadvantage includes problems with changing the air tanks.

### Type II - SCBA Outside the Suit

Type II suits are more form fitting allowing greater mobility in tight spaces. They also allow easy and quick changing of air tanks. The big disadvantage is the exposed breathing apparatus is being subject to direct contamination.





### Type III - Airline Supplied

Type III suits provide fresh air well beyond the time of an SCBA but are limited to the length of the hose, usually no more than 300 feet. It should be determined that the hose has the same chemical resistance as the suit. An airline hose has the much desired ability to add suit cooling.

### SUIT INTEGRITY

Some chemical compatibility information for suit material is available from the suppliers. Only a limited number of chemicals are usually listed. There is no material compatibility listing for mixtures of chemicals that may be found at a spill site.

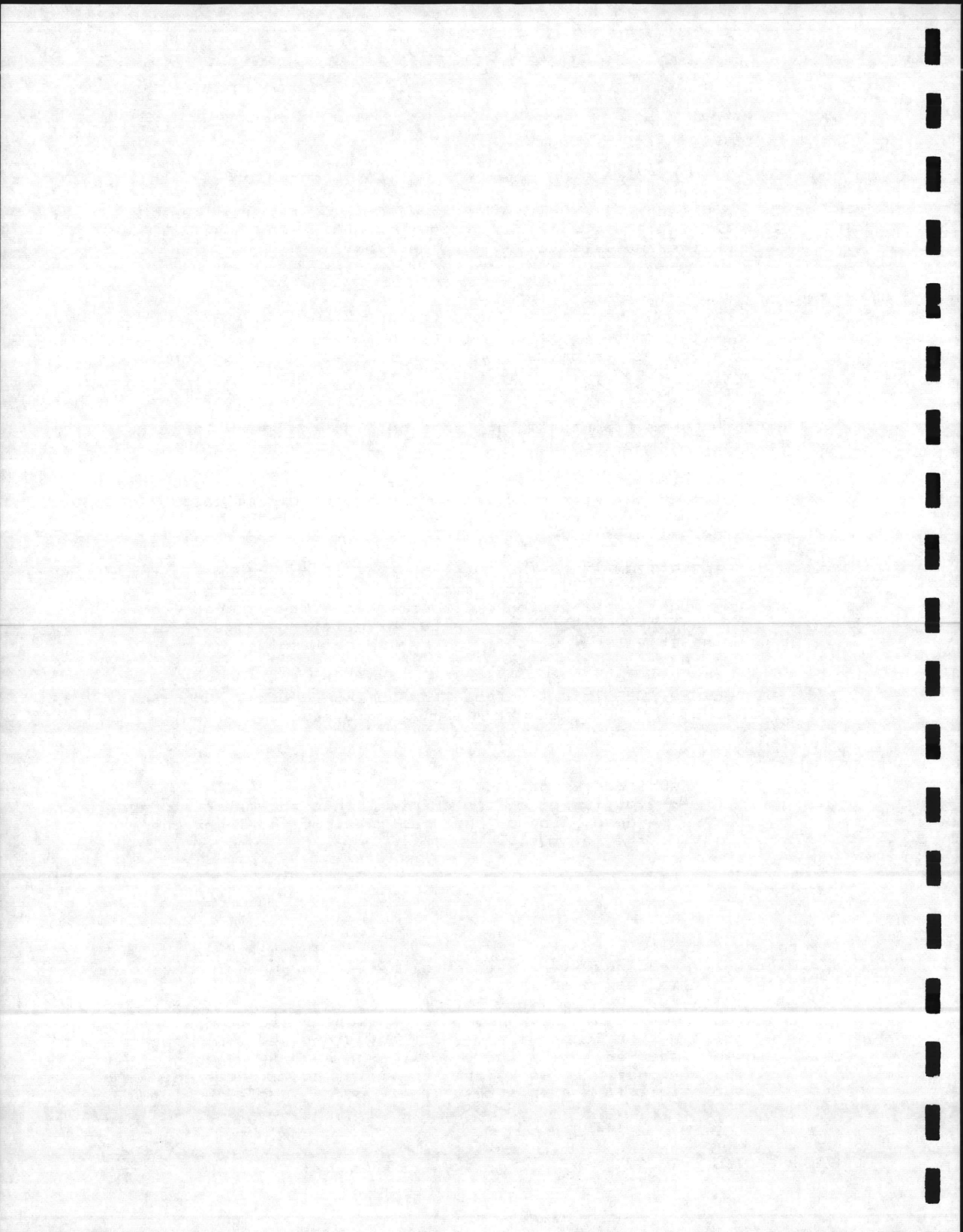
There are three important terms that help define suit material integrity. These include:

- (1) DEGRADATION--This is the physical destruction or decomposition of the suit material by incompatible chemicals. The failure may result in the material dissolving, swelling shrinking or burning.
- (2) PENETRATION--This involves the flow of hazardous liquids, gases or vapors through pinholes, zippers, stuck seams or other imperfections. Other leakage may occur at the facepiece, breathing apparatus, exhalation valves, suit exhaust valves, suit fasteners and particularly the gloves.
- (3) PERMEATION--This involves a phenomenon whereby a chemical moves through the suit material on a molecular level. It is a three step process.
  - (a) the adsorption of the chemical into the outer surface of the material
  - (b) the diffusion of the chemical into the material, and
  - (c) the desorption of the chemical from the inner surface of the material.

### SUIT LEAK TEST METHODS

A fully encapsulating suit should be tested after each use to confirm that its integrity is still intact. There are several quantitative and qualitative tests that can be used to determine if the suit is leak-proof.

- o Light Test. In a dark room, put a light inside the suit including the legs and arms. If any pinholes, small tears or other imperfections exist they will be readily apparent. Any type of light will work but ultraviolet and fluorescent work best. This is a simple test requiring no special equipment



and can be used in conjunction with other leak-test methods.

- o Carbon Monoxide Test. A sealed carbon monoxide (CO) indicator badge is sealed inside the suit and the suit is hung in a smokehouse for a specified period. This is a method of measuring the penetration of a colorless and odorless gas into the suit. A variation of this is to have a person with a CO badge and wearing the suit enter a smoke-filled environment. One of the problems with this variation is the expired air of the wearer may give a false reading.

The CO test requires a smokehouse which is not always available or in use and an instrument to read the CO badges. In some cases, they may be mailed to a center for analysis but that could take several days.

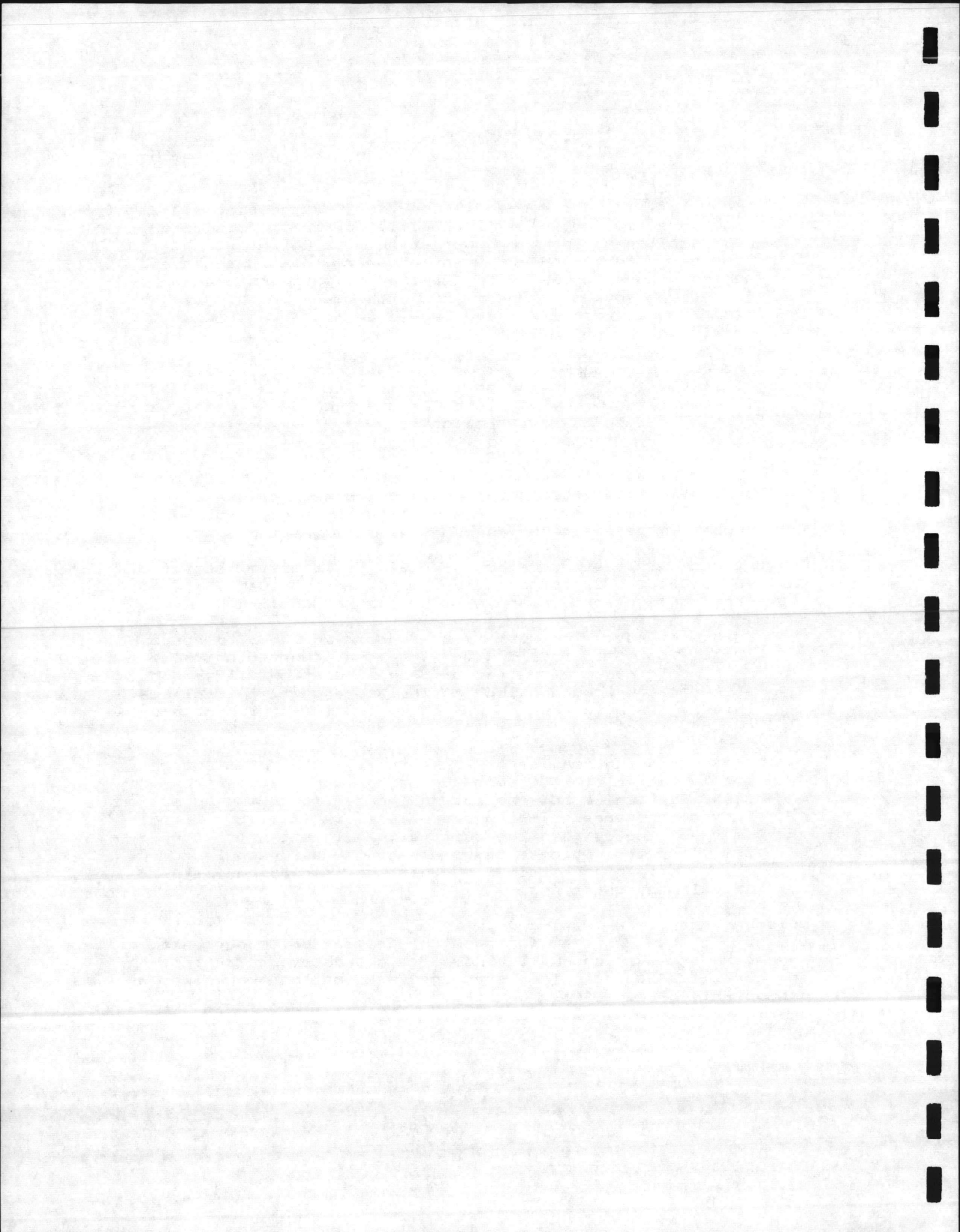
- o Shower Test. The wearer stands under a shower for a short period of time. The suit is examined while in the shower and internally after being removed for water leaks. The wearer's sweat may interfere with the test results. This is probably the least reliable of the leak testing methods.

These three leak testing methods are all qualitative tests that involve subjective decisions. The following two quantitative tests are more scientific and give better results.

- o Soapsuds Test. The suit is sealed and inflated to approximately 0.5 psig then tested with a soapsuds solution. This would require sealing off any exhalation valves and allowing the arms and legs to inflate and start to billow. This is a simple test requiring no special equipment and can be done almost anywhere.
- o Pressure Retention Test. The suit is inflated to approximately 180 mm of water pressure and after a 10 minute stabilization period the internal pressure is monitored for loss of pressure. If the pressure falls from 180 mm to 150 mm in 6 minutes then the suit fails. This test is used by some industry response teams and by the suit manufacturers. Gloves should be attached so that the test approximates actual use conditions.

Remember that leak testing only insures that the suit is air tight. It does not test for chemical permeation or degradation. When standards for encapsulating suits are developed by testing and certification agencies, standard leak testing procedures will undoubtedly be more fully developed.

LEVELS OF PROTECTION



Personnel must wear protective equipment when response activities involve known or suspected atmospheric contamination, when vapors, gases, or particulates may be generated, or when direct contact with skin-affecting substances may occur. Respirators can protect lungs, gastrointestinal tract, and eyes against air toxicants. Chemical-resistant clothing can protect the skin from contact with skin-destructive and -absorbable chemicals. Good personal hygiene limits or prevents ingestion of material.

Equipment to protect the body against contact with known or anticipated chemical hazards has been divided into four categories according to the degree of protection afforded:

Level A: Should be worn when the highest level of respiratory, skin, and eye protection is needed.

Level B: Should be selected when the highest level of respiratory protection is needed, but lesser level of skin protection. Level B protection is the minimum level recommended for initial site entries until the hazards have been further defined by on-site studies and appropriate personnel protection utilized.

Level C: Should be selected when the type(s) of airborne substance(s) is known, the concentration(s) is measured, and the criteria for using air-purifying respirators are met.

Level D: Should not be worn on any site with respiratory or skin hazards. Is primarily a work uniform providing minimal protection.

The Level of Protection selected should be based primarily on:

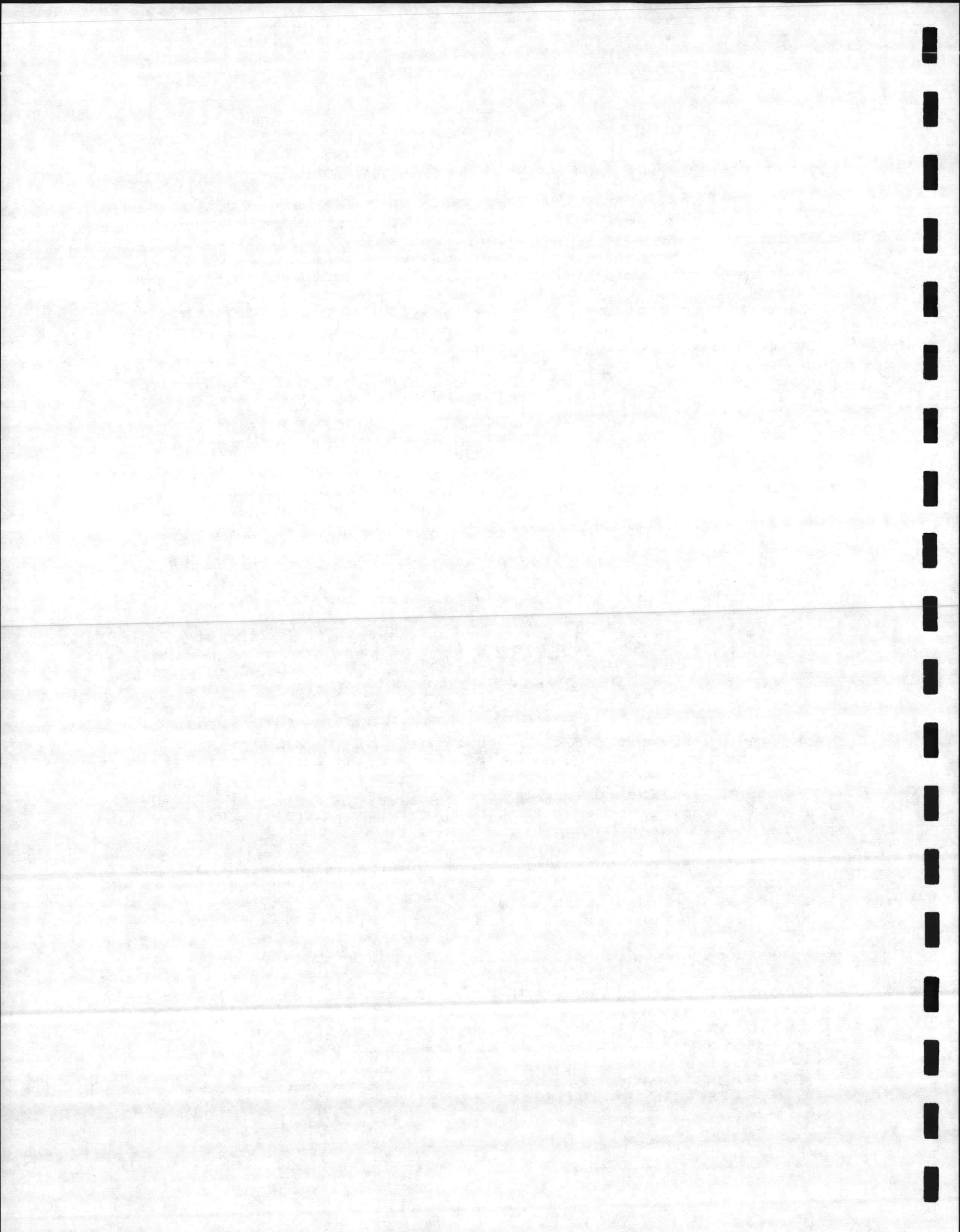
Type(s) and measured concentration(s) of the chemical substance(s) in the ambient atmosphere and its toxicity.

Potential or measured exposure to substances in air, splashes of liquids, or other direct contact with material due to work being performed.

In situations where the type(s) of chemical(s), concentration(s), and possibilities of contact are not known, the appropriate level of protection must be selected based on professional experience and judgement until the hazards can be better characterized.

While personnel protective equipment reduces the potential for contact with harmful substances, ensuring the health and safety of response personnel requires, in addition, safe work practices, decontamination, site entry protocols, and other safety considerations. Together, these protocols establish a combined approach for reducing potential harm to workers.

A. Level A Protection



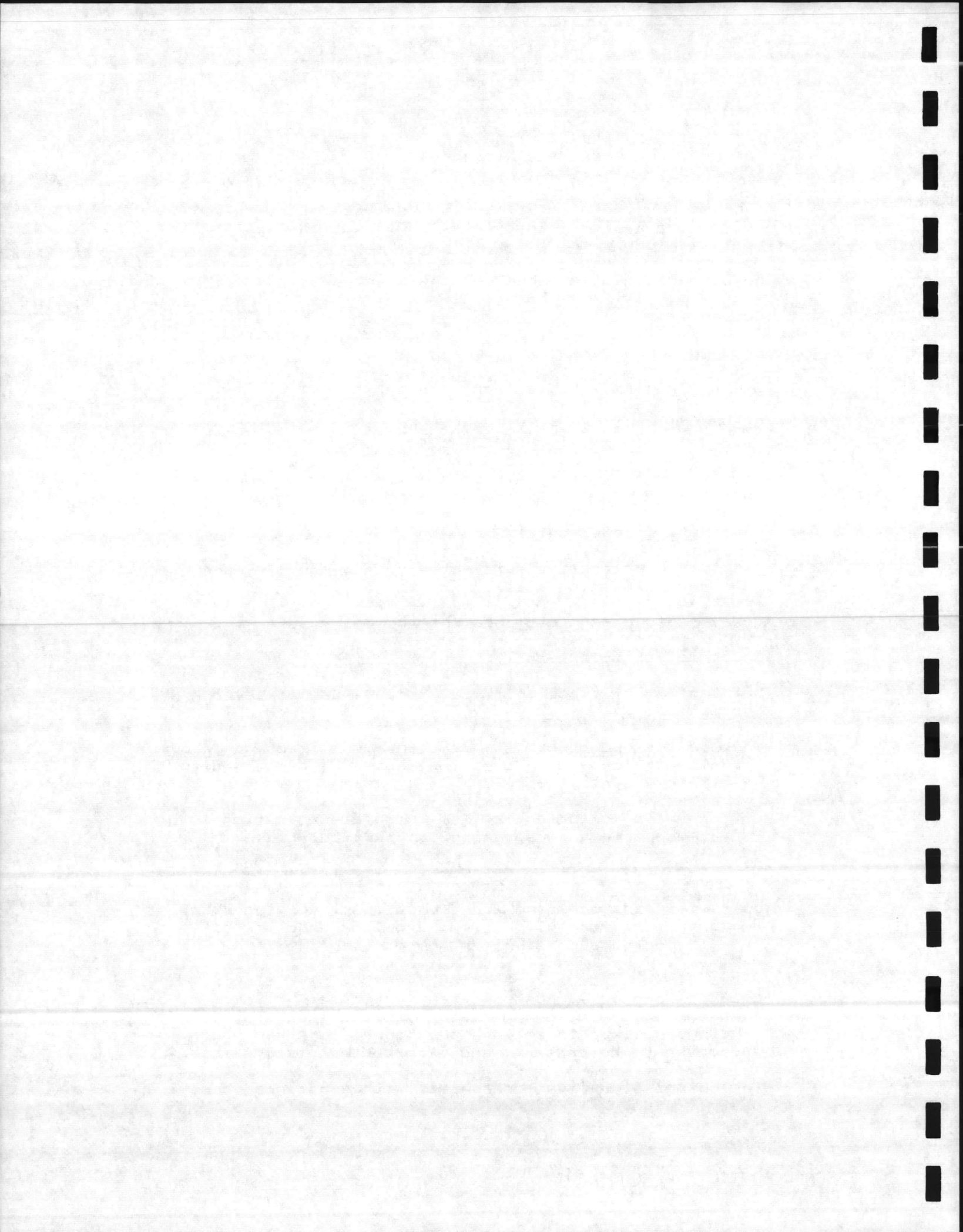
1. Personnel protective equipment

- o Pressure-demand, self-contained breathing apparatus, approved by the Mine Safety and Health Administration (MSHA) and National Institute of Occupational Safety and Health (NIOSH).
- o Fully encapsulating chemical-resistant suit
- o Coveralls\*
- o Long cotton underwear\*
- o Gloves (outer), chemical-resistant
- o Gloves (inner), chemical-resistant
- o Boots, chemical-resistant, steel toe and shank. (Depending on suit construction, worn over or under suit boot)
- o Hard hat\* (under suit)
- o Disposable protective suit, gloves, and boots\* (Worn over fully encapsulating suit)
- o 2-Way radio communications (intrinsically safe)

2. Criteria for selection

Meeting any of these criteria warrants use of Level A Protection:

- o The chemical substance(s) has been identified and requires the highest level of protection for skin, eyes, and the respiratory system based on:
  - oo measured (or potential for) high concentration(s) of atmospheric vapors, gases, or particulates
  - or
  - oo site operations and work functions involving high potential for splash, immersion, or exposure to unexpected vapors, gases, or particulates.
- o Extremely hazardous substances (for example: dioxin, cyanide compounds, concentrated pesticides, Department of Transportation Poison "A" materials, suspected carcinogens, and infectious substances) are known or suspected to be present, and skin contact is possible.
- o The potential exists for contact with substances that destroy skin.





### DONNING/HELPER

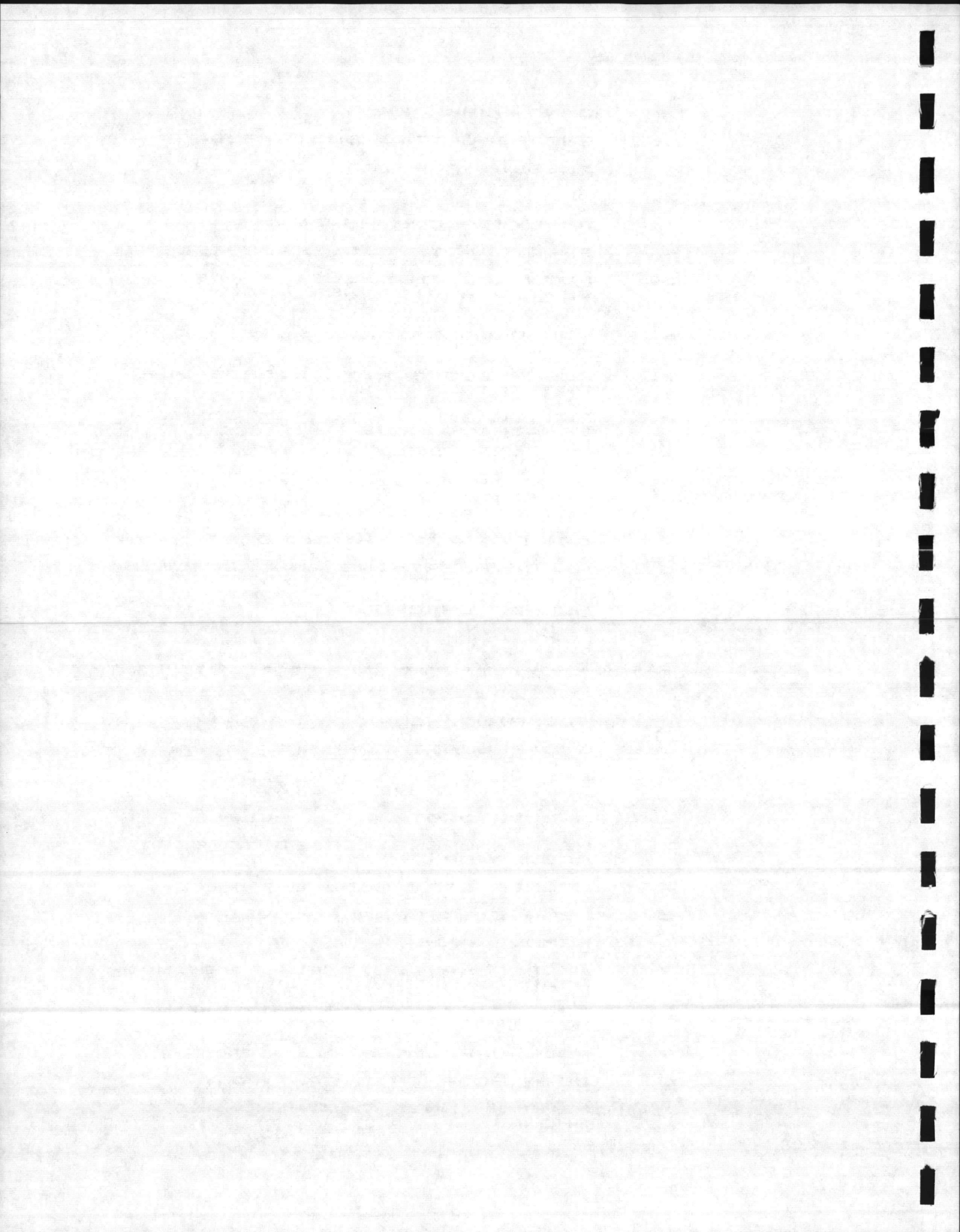
#### FULLY ENCAPSULATING SUITS/SCBA

1. INSPECT FOR DEFICIENCIES
  2. OPEN AND ADJUST
  3. APPLY TALCUM POWDER
  4. SPRAY ANTIFOG ON FACEPIECE
  5. PUT LEGS INTO SUIT WHILE SEATED AND GATHER AROUND WAIST
  6. PUT ON CHEMICAL RESISTANT SAFETY BOOTS
  7. COVER BOOTS WITH DISPOSABLE PROTECTORS
  8. PUT ON SCBA - DO NOT CONNECT BREATHING HOSE
  9. PUT ON GLOVES
  10. GET INTO SLEEVES OF SUIT
  11. SECURE ALL FASTENERS
  12. CONNECT BREATHING HOSE
  13. CHECK BREATHING AND COMPLETE CLOSING SUIT
  14. HELPER CHECKOUT
- 

### DOFFING/HELPER

#### FULLY ENCAPSULATING SUITS/ SCBA

1. REMOVE DISPOSABLE BOOT COVERS, GLOVES, ETC.
2. REMOVE BOOTS WITH HELPER
3. HELPER OPENS ACCESS TO SCBA REGULATOR
4. HELPER LIFT HOOD OFF HEAD
5. REMOVE EXTERNAL GLOVES
6. REMOVE ARMS
7. HELPER LAY SUIT FLAT BEHIND WEARER
8. REMOVE LEGS FROM SUIT WHILE SITTING
9. ROLL OFF INTERNAL GLOVES
10. DOFF SCBA IN CLEAN AREA
11. REMOVE INNER CLOTHING AND SHOWER



- o Operations must be conducted in confined, poorly ventilated areas until the absence of hazards requiring Level A protection is demonstrated.
- o Total atmospheric readings on the Century OVA System, HNU Photoionizer, and similar instruments indicate 500-1,000 ppm of unidentified substances.

### 3. Guidance on selection criteria

The fully encapsulating suit provides the highest degree of protection to skin, eyes, and respiratory system if the suit material is resistant to the chemical(s) of concern during the time the suit is worn and/or at the measured or anticipated concentrations. While Level A provides maximum protection, the suit material may be rapidly permeated and penetrated by certain chemicals from extremely high air concentrations, splashes, or immersion of boots or gloves in concentrated liquids or sludges. These limitations should be recognized when specifying the type of chemical-resistant garment. Whenever possible, the suit material should be matched with the substance it is used to protect against.

The use of Level A protection and other chemical-resistant clothing requires evaluating the problems of physical stress, in particular heat stress associated with the wearing of impermeable protective clothing. Response personnel must be carefully monitored for physical tolerance and recovery.

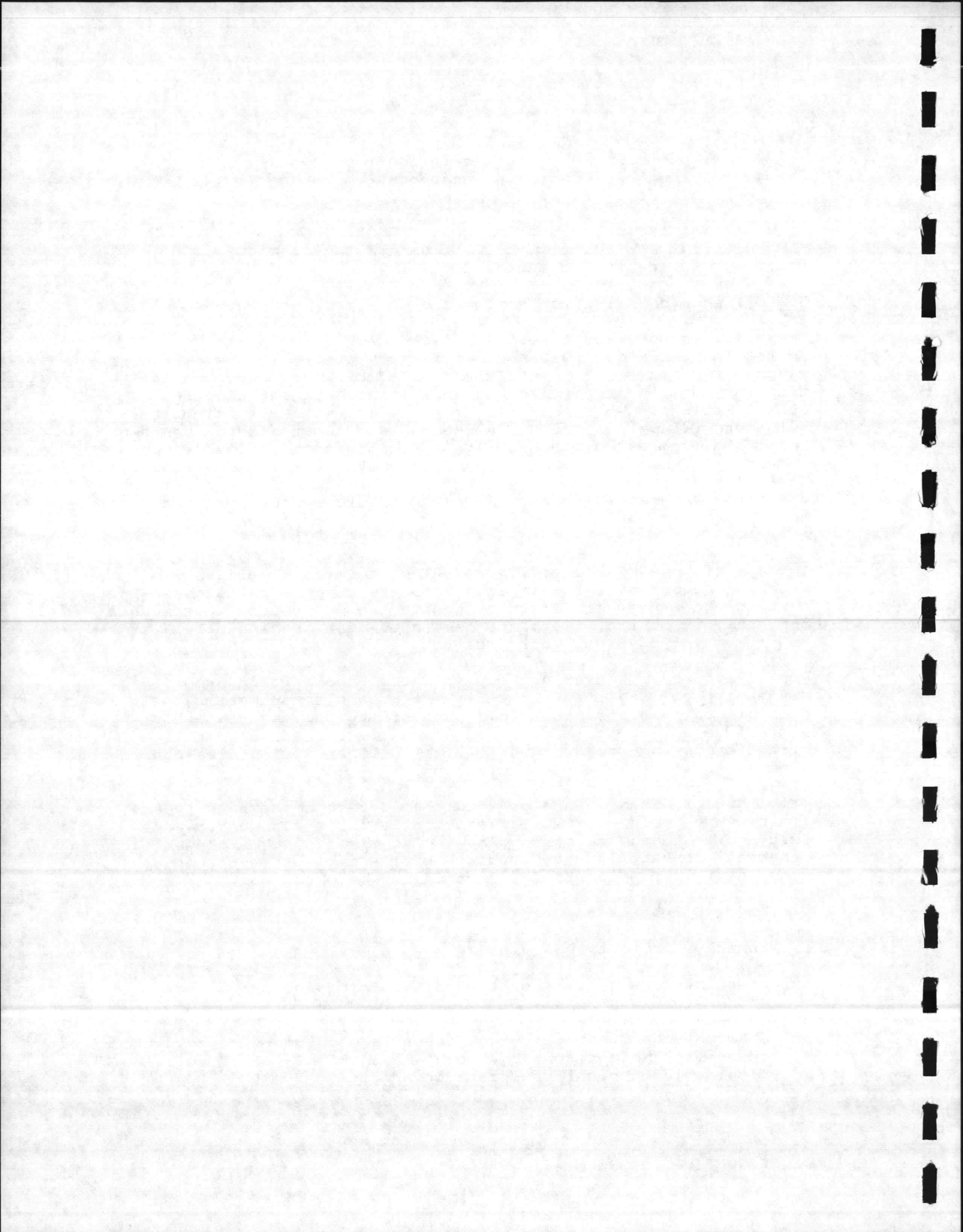
Protective equipment being heavy and cumbersome, decreases dexterity, agility, visual acuity, etc., and so increases the probability of accidents. This probability decreases as less protective equipment is required. Thus, increased probability of accidents increased probability of accidents should be considered when selecting a level of protection.

Many toxic substances are difficult to detect or measure in the field. When such substances (especially those absorbed by or destructive to the skin) are known or suspected to be present and personnel contact is unavoidable, Level A protection should be worn until more accurate information can be obtained.

### B. Level B Protection

#### 1. Personal protective equipment

- o Pressure-demand, self-contained breathing apparatus (MSHA/NIOSH approved)
- o Chemical-resistant clothing (overalls and long-sleeved jacket; coveralls; hooded, one or two-piece chemical-splash suit; disposable chemical-resistant coveralls)



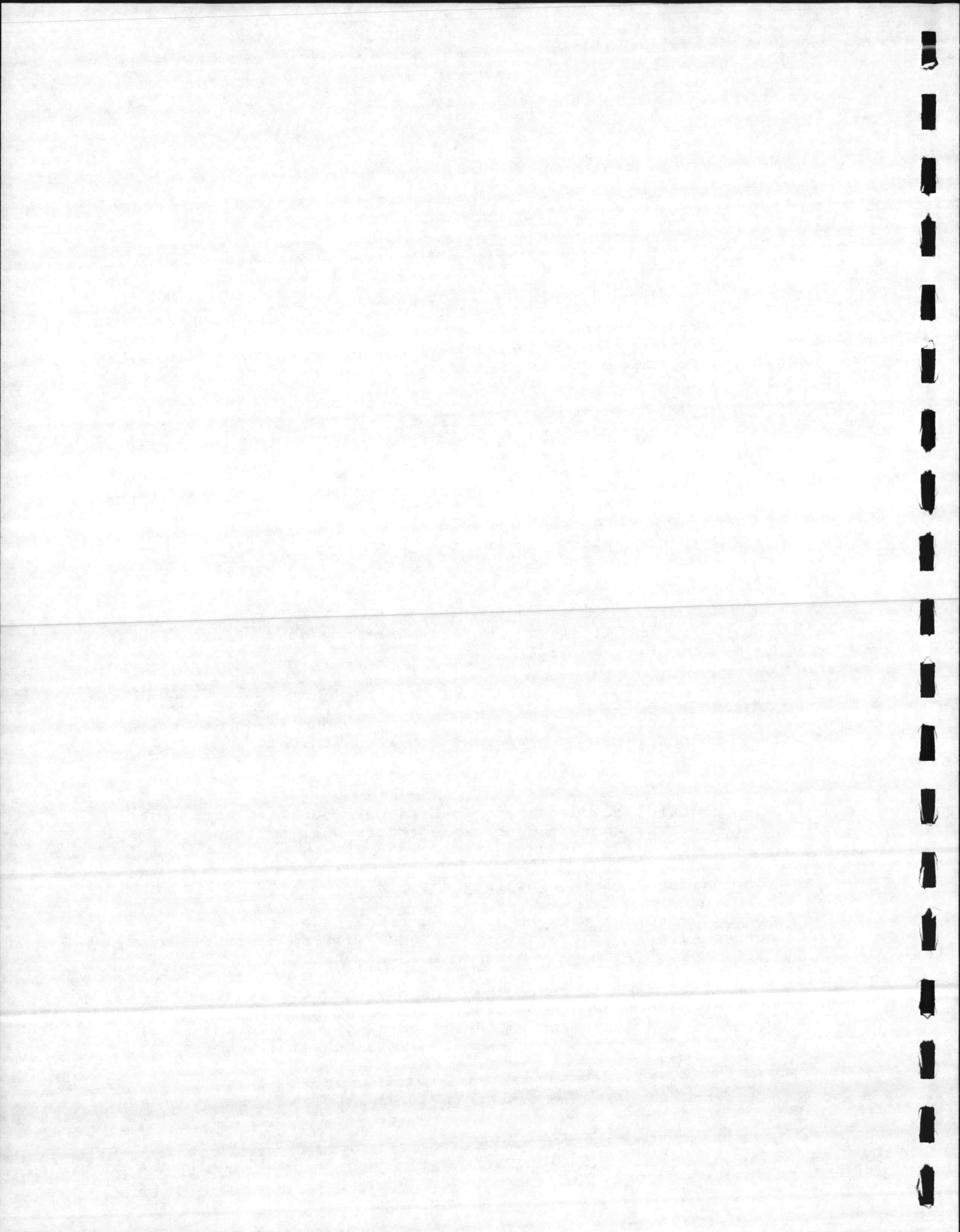
- o Coveralls\*
- o Gloves (outer), chemical-resistant
- o Gloves (inner), chemical-resistant
- o Boots (outer), chemical-resistant, steel toe and shank
- o Hard hat (face shield)
- o 2-Way radio communications (intrinsically safe)

## 2. Criteria for selection

Meeting any one of these criteria warrants use of Level B protection:

- o The type(s) and atmospheric concentrations (s) of toxic substances have been identified and require the highest level of respiratory protection, but a lower level of skin and eye protection. These would be atmospheres:
  - oo with contractions Immediately Dangerous to Life and Health (IDLH)
  - or
  - oo exceeding limits of protection afforded by a full-face, air-purifying mask
  - or
  - oo containing substances for which air-purifying canisters do not exist or have low removal efficiency
  - or
  - oo containing substances requiring air-supplied equipment, but substances and/or concentrations do not represent a serious skin hazard
- o The atmosphere contains less than 19.5% oxygen.
- o Site operations make it highly unlikely that the small, unprotected area of the head or neck will be contacted by splashes of extremely hazardous substances.
- o Total atmospheric concentrations of unidentified vapors or gases range from 5 ppm to 500 ppm on instruments such as the Century QVA System or HNU Photoionizer, and vapors are not suspected of containing high levels of chemicals toxic to skin.

## 3. Guidance on selection criteria



Level B equipment provides a high level of protection to the respiratory tract, but a somewhat lower level of protection to skin. The chemical-resistant clothing required in Level B is available in a wide variety of styles, material, construction detail, permeability, etc. These factors all affect the degree of protection afforded. Therefore a specialist should select the most effective chemical-resistant clothing (and fully encapsulating suit) based on the known or anticipated hazards and/or job junction.

Generally, if a self-contained breathing apparatus is required, Level B clothing rather than a Level A fully encapsulating suit is selected, based on the protection needed against known or anticipated substances affecting the skin. Level B skin protection is selected by:

- o Comparing the concentrations of known or identified substances in air with skin toxicity data.
- o Determining the presence of substances that are destructive to and/or readily absorbed through the skin by liquid splashes, unexpected high levels of gases or particulates, or other means of direct contact.
- o Assessing the effect of the substance (at its measured air concentrations or splash potential) on the small area of the head and neck unprotected by chemical-resistant clothing.

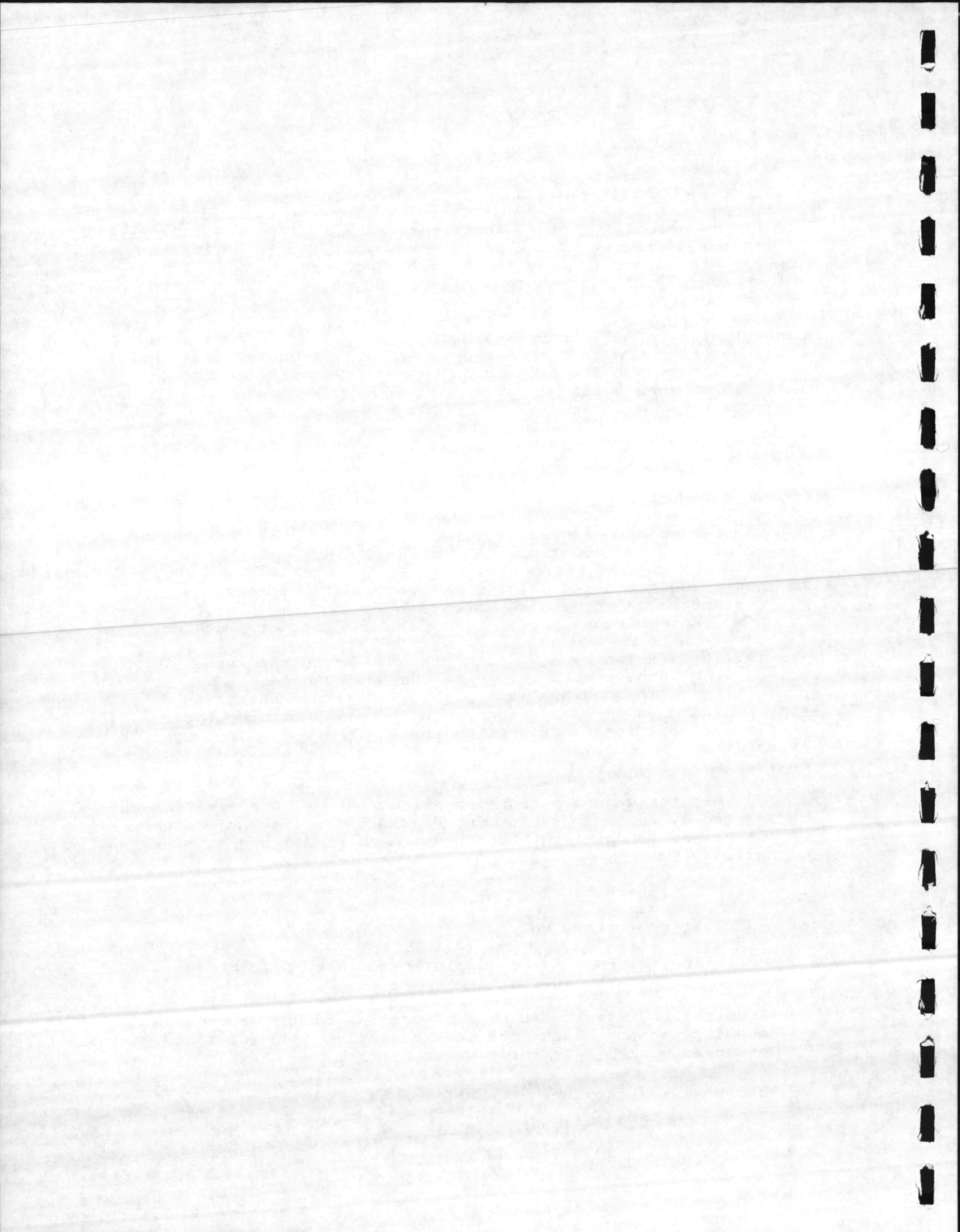
For initial site entry and reconnaissance at an open site, approaching whenever possible from the upwind direction, Level B protection (with good quality, hooded, chemical-resistant clothing) should protect response personnel, providing the conditions described in selecting Level A are known or judged to be absent. For continuous operations, the aforementioned criteria must be evaluated.

At 500 pm total vapors/gases, upgrading to Level A protection may be advisable. A major factor for re-evaluation is the presence of vapors, gases, or particulates requiring a higher degree of skin protection.

#### C. Level C Protection

##### 1. Personal protective equipment

- o Full-face, air-purifying, canister-equipped respirator (MSHA/NIOSH approved)
- o Chemical resistant clothing (coveralls; hooded, two-piece chemical splash suits; chemical-resistant hood and apron; disposable chemical-resistant coveralls)
- o Gloves (outer), chemical-resistant





- o Gloves (inner), chemical-resistant\*
- o Boots (outer), chemical-resistant, steel toe and shank\*
- o Boots (outer), chemical-resistant (disposable)\*
- o Hard hat (face shield\*)
- o Escape mask\*
- o 2-Way radio communications (intrinsically safe)

## 2. Criteria for selection

Meeting all of these criteria permits use of Level C protection:

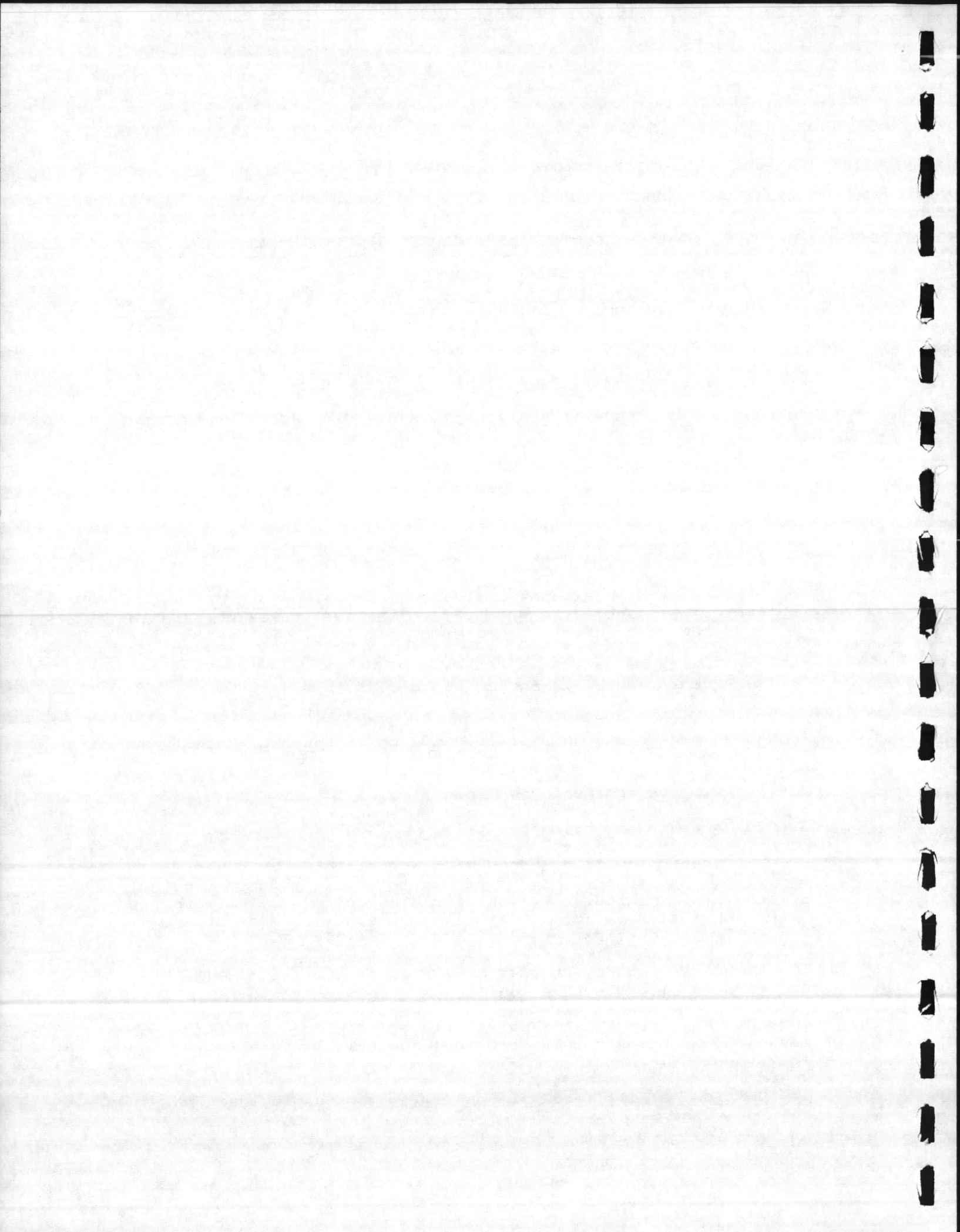
- o Measured air concentrations of identified substances will be reduced by the respirator to at or below the substance's exposure limit, and the concentration is within the service limit of the canister.
- o Atmospheric contaminant concentrations do not exceed IDHL levels.
- o Atmospheric contaminants, liquid splashes, or other direct contact will not adversely affect the small area of skin left unprotected by chemical-resistant clothing.
- o Job functions have been determined not to require self-contained breathing apparatus.
- o Total vapor readings register between background and 5 ppm above background on instruments such as the HNU Photoionizer and the Century OVA System.
- o Air will be monitored periodically.

## 3. Guidance on selection criteria

Level C protection is distinguished from level B by the equipment used to protect the respiratory system, assuming the same type of chemical-resistant clothing is used. The main selection criterion for Level C is that conditions permit wearing air-purifying devices.

The air-purifying device must be a full-face mask (MSHA/NIOSH approved) equipped with a canister suspended from the chin or on a harness. Canisters must be able to remove the substances encountered. Quarter- or half-masks or cheek-cartridge full-face masks should be used only with the approval of a qualified individual.

In addition, a full-face, air-purifying mask can be used only if:



- o Oxygen content of atmosphere is at least 19.5% by volume.
- o Substance(s) is identified and its concentration(s) measured.
- o Individual passes a qualitative fit-test for the mask.
- o Appropriate cartridge/canister is used, and its service limit concentration is not exceeded.

An air monitoring program is part of all response operations when atmospheric contamination is known or suspected. It is particularly important that the air be monitored thoroughly when personnel are wearing air-purifying respirators (Level C). Continual surveillance using direct-reading instruments and air sampling is needed to detect any changes in air quality necessitating a higher level of respiratory protection.

Total unidentified vapor/gas concentrations of 5 ppm above background require Level B protection. Only a qualified individual should select Level C (air-purifying respirators) protection for continual use in an unidentified vapor/gas concentration of background to 5ppm above background.

#### D. Level D Protection

##### 1. Personal protective equipment

- o Coveralls
- o Gloves\*
- o Boots/shoes, leather or chemical resistant, steel toe and shank
- o Boots (outer), chemical-resistant (disposable)\*
- o Safety glasses or chemical splash goggles\*
- o Hard hat (face shield)\*
- o Escape mask\*

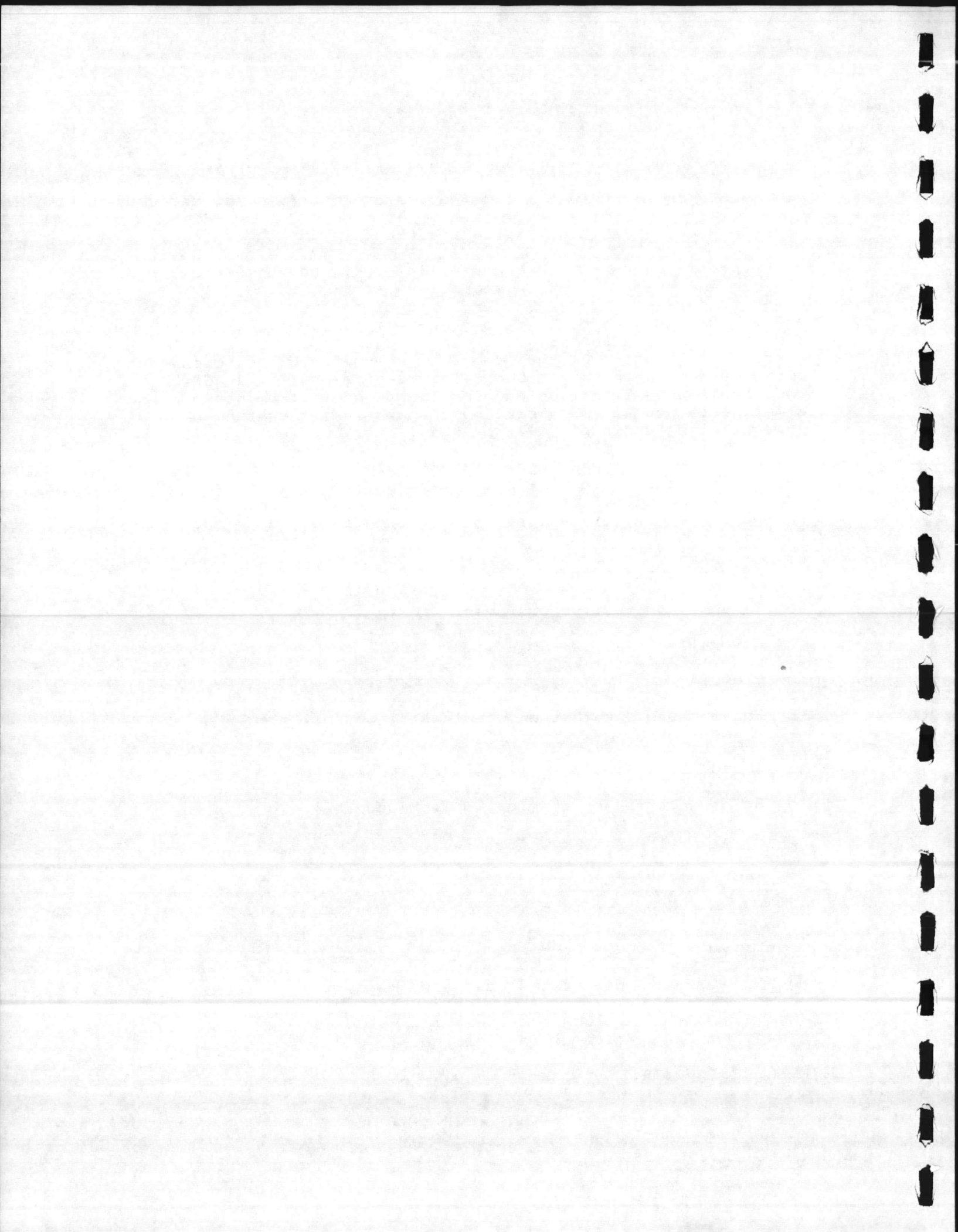
##### 2. Criteria for selection

Meeting any of these criteria allows use of Level D protection:

No hazardous air pollutants have been measured.

Work functions preclude splashes, immersion, or potential for unexpected inhalation of any chemicals.

#### PROTECTION IN UNKNOWN ENVIRONMENTS



In all site operations, selecting the appropriate personnel protection equipment is one of the first steps in reducing the potential for adverse health effects. Until the hazardous conditions presented by an environmental incident can be identified and personnel safety measures commensurate with the hazards--real or potential--instituted, preliminary measures will have to be based on applying experience, judgment, and professional knowledge to the particular incident at hand. Lack of knowledge concerning the hazards that could be encountered precludes selecting protective equipment by comparing environmental concentrations of known toxicants against protection afforded by each type of equipment.

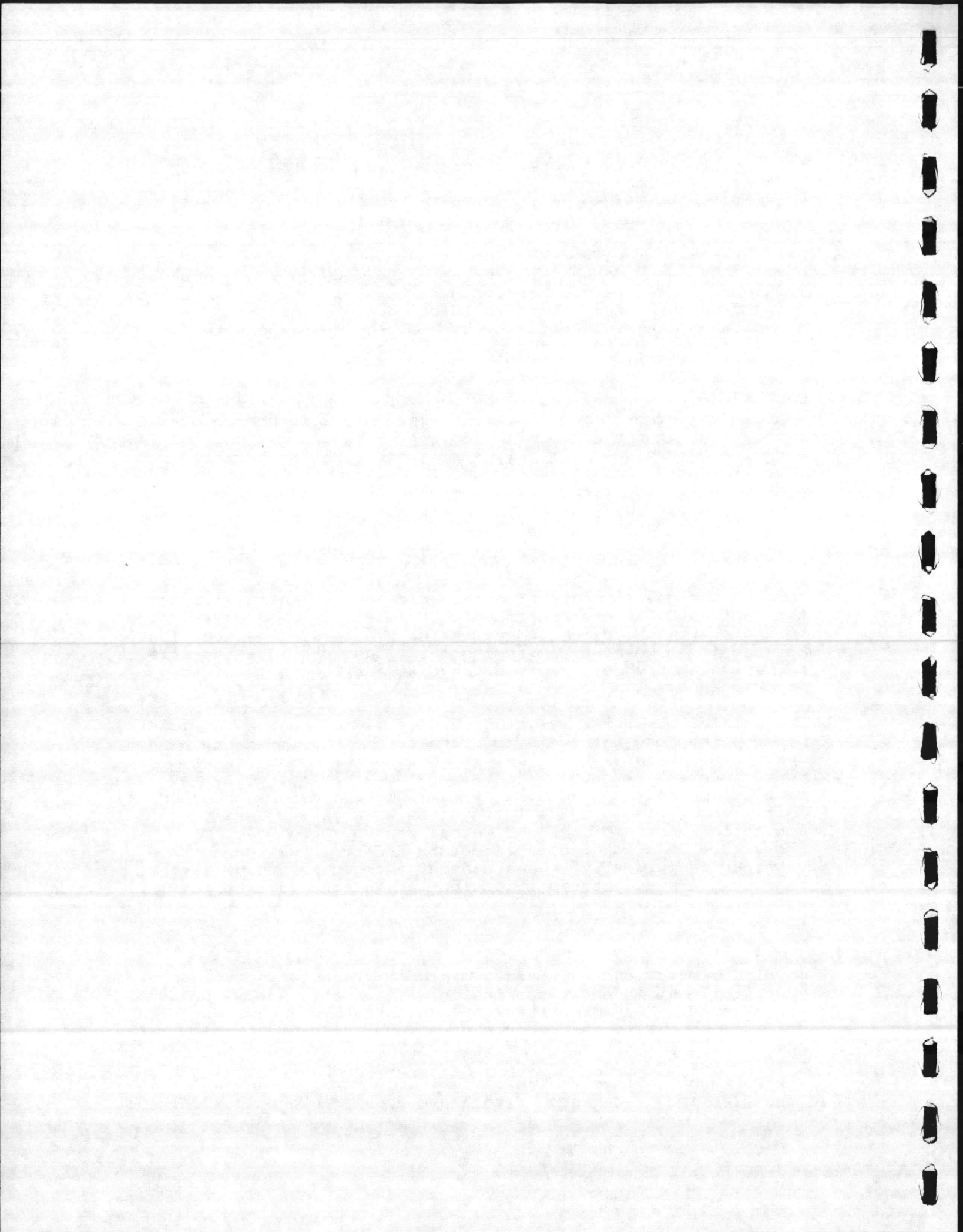
One of the first considerations in evaluating the risk of an unknown environment is to measure immediate atmospheric hazards such as the concentrations (or potential concentrations) of vapors, gases, and particulates; oxygen content of the air; explosive potential; and, to a lesser degree, the possibility of radiation exposure. In addition to air measurements, visual observation and/or evaluation of existing data can help determine the degree of risk from other materials that are explosive, have a high fire potential, are extremely toxic, or exhibit other hazardous characteristics that cannot be monitored by field instruments.

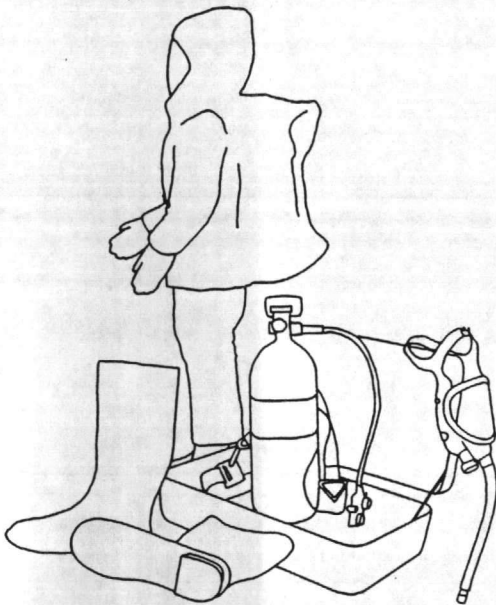
Total vapor/gas concentration as indicated by instruments such as the Century OVA System or the HNU Photoionizer is a useful adjunct to professional judgment in selecting the level of protection to be worn in an unknown environment. It should not be the sole criterion, but should be considered with all other available information.

The initial on-site survey and reconnaissance, which may consist of more than one entry, is to characterize the immediate hazards and, based on these findings, establish preliminary safety requirements. As data are obtained from the initial survey, the level of protection and other safety procedures are adjusted. Initial data also provide information on which to base further monitoring and sampling. No method can select a level of protection in all known environments. Each situation must be examined individually. Some general approaches can be given, however, for judging the situation and determining the level of protection required.

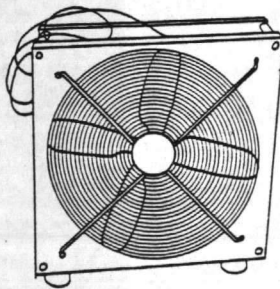
#### A. Level C

Level C protection (full-face, air-purifying respirator) should be worn routinely in an atmosphere only after the type(s) of air contaminant(s) is identified and concentrations measured. To permit flexibility in prescribing a level of protection at certain environmental incidents, a specialist could consider air-purifying respirators for use in unidentified vapor/gas concentrations of a few parts per million. The guideline of total vapor/gas concentration of background to 5 ppm above background should not



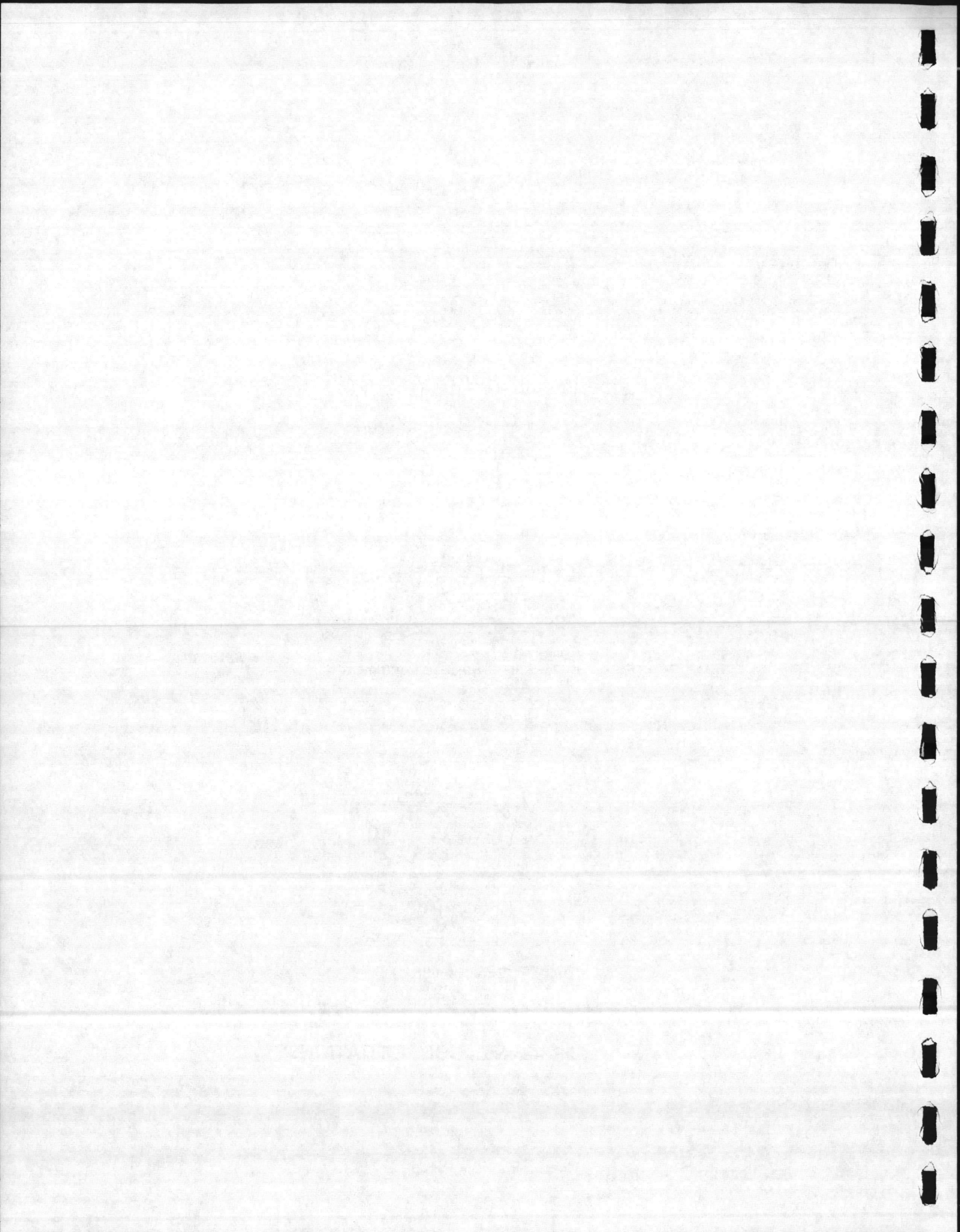


**Personal Protective Equipment**



**Explosion-Proof Fan**

## **PERSONNEL CONSIDERATIONS**





be the sole criterion for selecting Level C. Since the individual contributors may never be completely identified, a decision on continuous wearing of Level C must be made, after assessing all safety considerations, including:

- o The presence of (or potential for) organic or inorganic vapors/gases against which a canister is ineffective or has a short service life.
- o The known (or suspected) presence in air of substances with low TLV or IDLH levels.
- o The presence of particulates in air.
- o The errors associated with both the instruments and monitoring procedures used.
- o The presence of (or potential for) substances in air which do not elicit a response on the instrument(s) used.
- o The potential for higher concentrations in the ambient atmosphere or in the air adjacent to specific site operations.

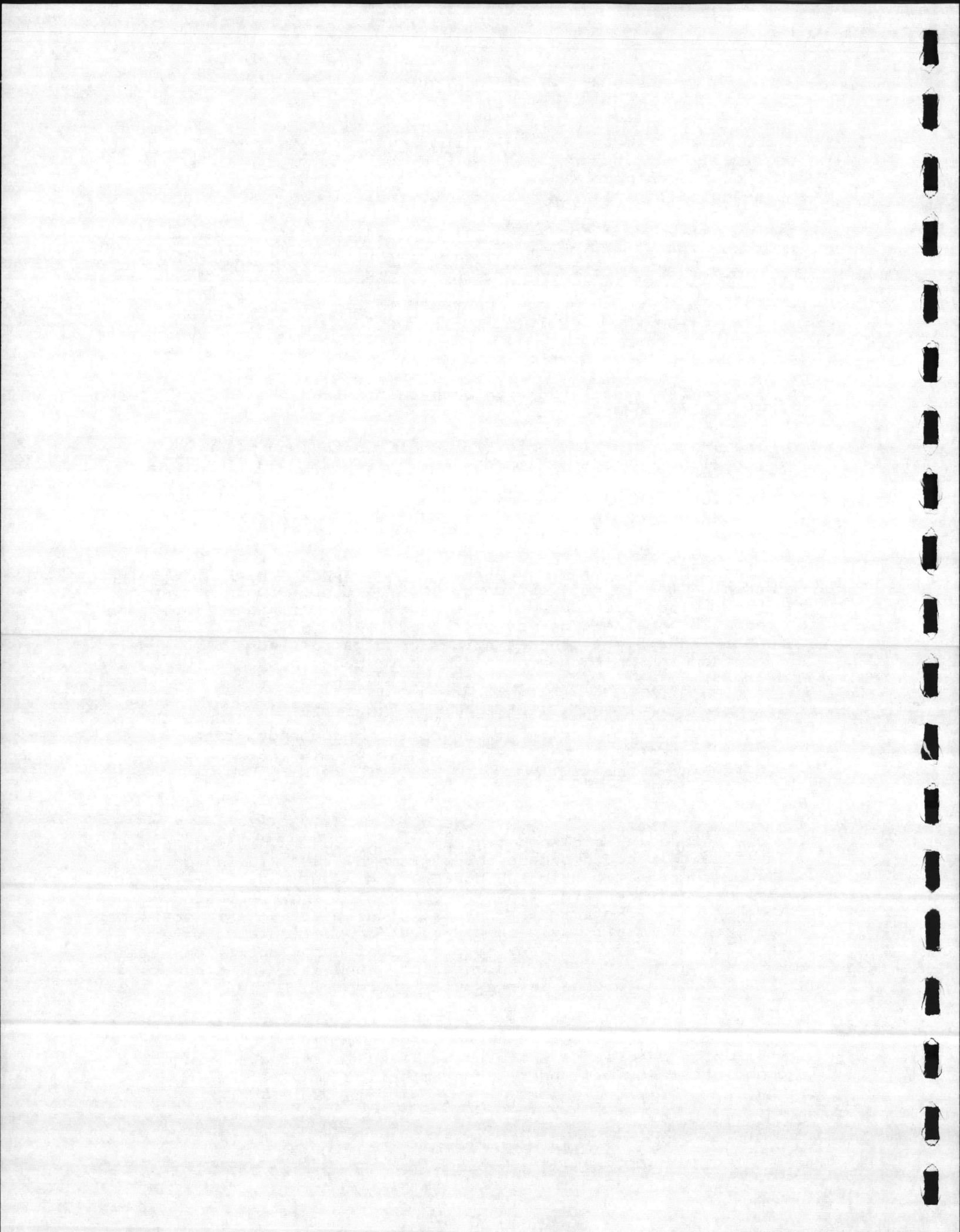
The continuous use of air-purifying respirators (Level C) should be based on the identification of the substances contributing to the total vapor/gas concentration and the application of published criteria for the routine use of air-purifying devices. Unidentified ambient concentrations of organic vapors or gases in air approaching or exceeding 5 ppm above background require Level B protection.

Individuals without appropriate training and/or experience should be discouraged from modifying upward the recommended total vapor/gas concentration guideline and associated levels of protection.

#### B. Level A

Level A should be worn when maximum protection is needed against substances that could damage the surface of the skin and/or be absorbed through the skin. Since Level A requires the use of a self-contained breathing apparatus, the eyes and respiratory system are also protected. For initial site entry, skin toxicants would exist primarily as vapors, gases, or particulates in air, with a lesser possibility of splash. Continuous operations at an abandoned waste site, for instance, may require Level A due to working with and around severe skin toxicants.

Until air monitoring data are available to assist in the selection of the appropriate level of protection, the use of Level A for initial site entries may have to be based on indirect evidence of the potential for atmospheric contamination or direct skin contact.

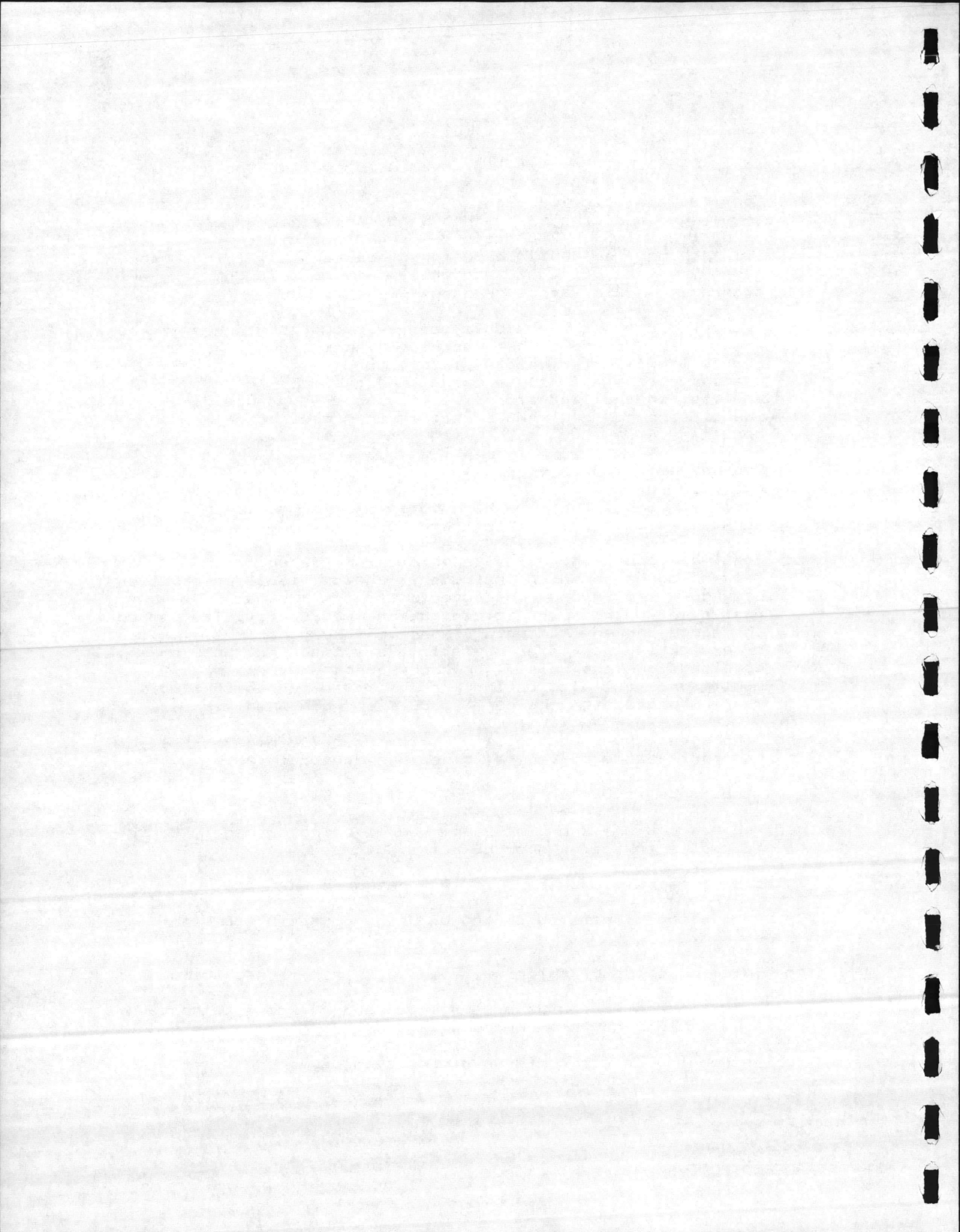


Considerations that may require Level A protection include:

- o Confined spaces: Enclosed, confined, or poorly ventilated areas are conducive to buildup in air of toxic vapors, gases, or particulates. (Explosive or oxygen-deficient atmospheres also are more probable in confined spaces. Low-lying outdoor areas--ravines, ditches, and gulleys--tend to accumulate any heavier-than-air vapors or gases present.
- o Suspected/known toxic substances: Various substances may be known or suspected to be involved in an incident, but there are no field instruments available to detect or quantify air concentrations. In these cases, media samples must be analyzed in the laboratory. Until these substances are identified and levels measured, maximum protection may be necessary.
- o Visible emissions: Visible emissions from leaking containers or railroad/vehicular tank cars, as well as smoke from chemical fires, indicate high potential for concentrations of substances that could be extreme respiratory or skin hazards.
- o Job functions: Initial site entries are generally walk-throughs in which instruments and/or visual observations provide a preliminary characterization of the hazards. Subsequent entries are to conduct the many activities needed to reduce the environmental impact of those hazards. Levels of protection for later operations are based not only on data obtained from the initial and subsequent environmental monitoring, but also on the probability of contamination. Maximum protection (Level A) should be worn when:
  - oo there is a high probability for exposure to high concentrations of vapors, gases, or particulates.
  - oo substances could splash.
  - oo substances are known or suspected of being extremely toxic directly to the skin or by being absorbed.

Examples of situations where Level A has been worn are:

- o Excavating of soil suspected of being contaminated with dioxin.
- o Entering cloud of chlorine released in a railroad accident.
- o Handling and moving drums suspected and/or known to contain substances that were destructive and absorbable.
- o Responding to accidents involving cyanide, arsenic, or undiluted pesticides.

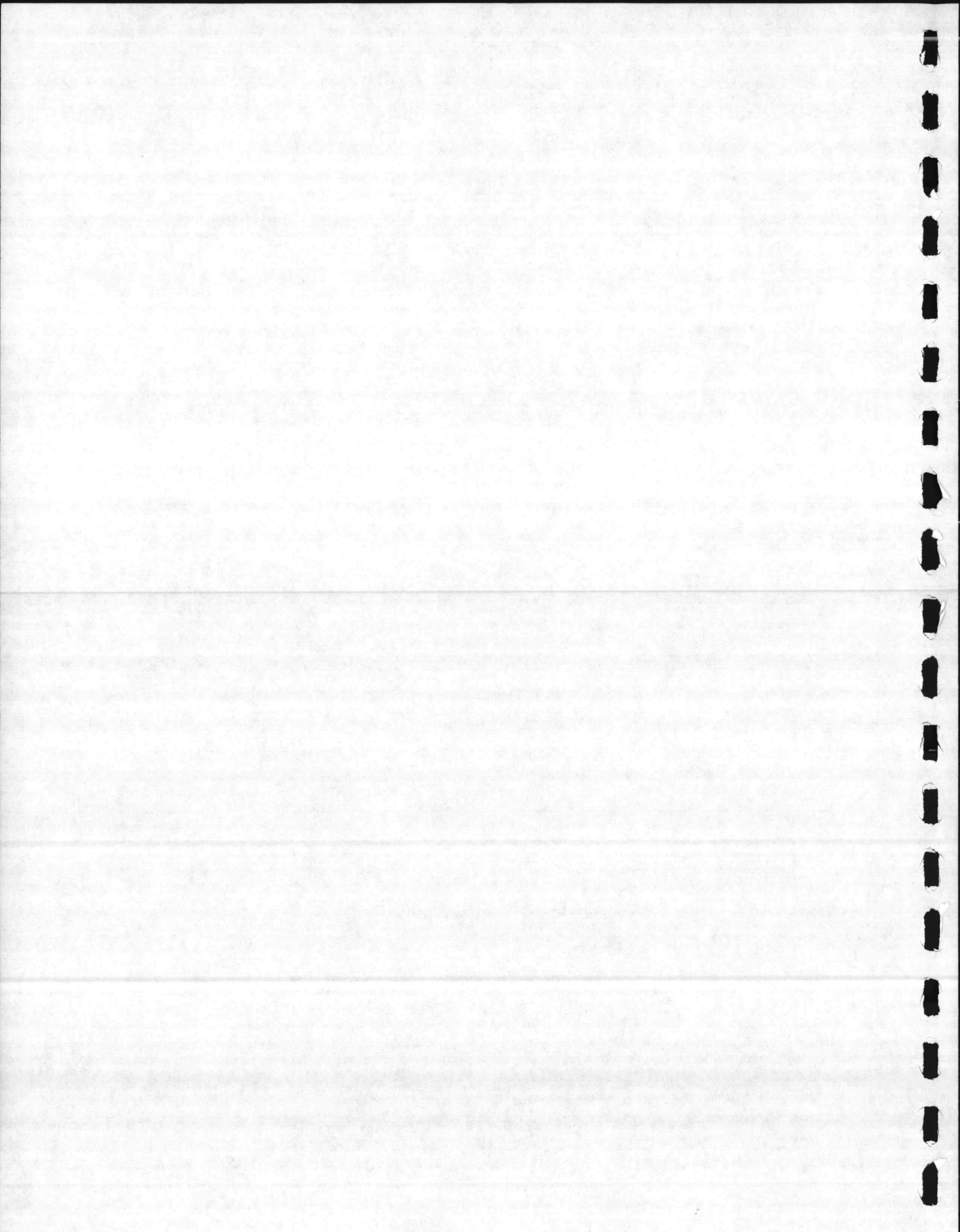


C. Level B

While Level B protection does not afford the maximum skin (and eye) protection as does a fully encapsulating suit, a good quality, hooded, chemical-resistant, one-or-two-piece garment, with taped joints, provides a reasonably high degree of protection. At most abandoned hazardous waste sites, ambient atmospheric gas/vapor levels have not approached concentrations sufficiently high to warrant maximum protection. In all but a few circumstances, Level B should provide the protection needed for initial entry. Subsequent operations require a re-evaluation of Level B based on the probability of being splashed by chemicals, their effect on the skin, or the presence of hard-to-detect air contaminants.

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## XI. IN-PLANT SPILL PREVENTION

### A. INTRODUCTION

The full utilization of proper plant design and effective control systems is essential for an effective spill prevention program. All control systems are of little value unless backed by management committed to utilizing these systems to their fullest extent. It is generally recognized that assignment of responsibility to the smallest supervisory unit practicable is an effective management approach to improve performance. In spill prevention this unit would be the smallest group of facilities that are physically separable from others in terms of measurable pollutional loadings.

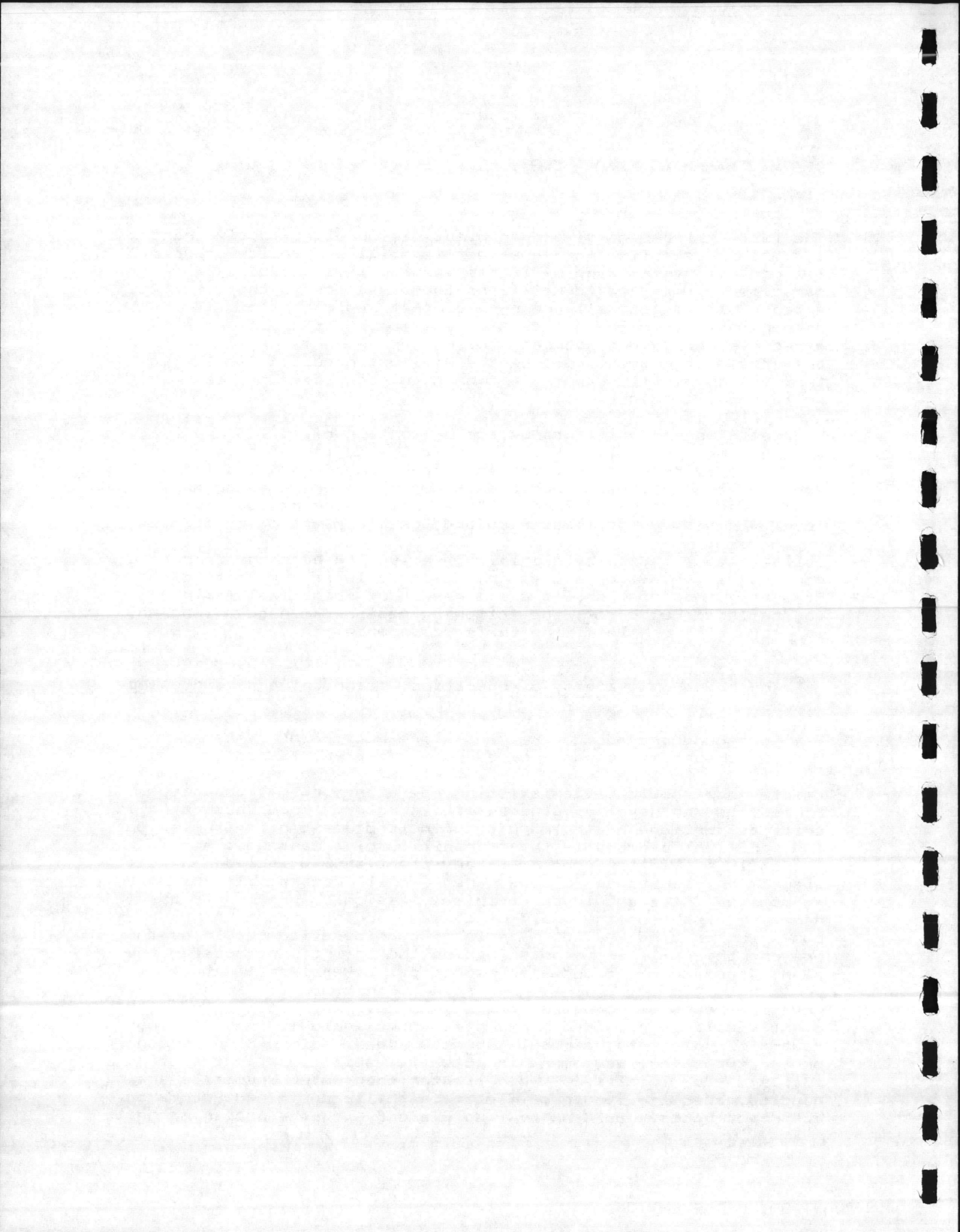
Management considerations for the prevention of spills are multitudinous. Spill prevention objectives, investigation of spills to avoid a repetition, and promotion of open and frank communication channels should be some of the prime management objectives. All of these objectives aid in the rapid identification of spill sources and the minimization of spills.

Spills may be caused by mechanical failure or personnel error, or more rarely, by fire, explosion, power failures, or "acts of God." However, since most spills are a result of mechanical failure and/or personnel error, the following measures can go a long way in preventing or minimizing their occurrence:

- o sound basic design
- o thorough training of operating, technical and maintenance personnel
- o strict job responsibility
- o sound process control and alarm monitoring systems
- o proper maintenance of equipment and facilities

Maintenance should review existing operating and maintenance procedures and develop vulnerability studies. From these studies critical portions of the manufacturing process can be singled out and modified to decrease the probability of a hazardous spill. The spill prevention program of any plant should include an action diagram or plan to be followed when a spill occurs. In this plan, responsibilities should be definitely assigned (preferably by name) to establish the chain of command so that there is no confusion or time wasted. A primary consideration should be to prevent the spill from contaminating the environment outside the plant (surface or groundwater, municipal sewers, soil, etc.).

Physical means of stopping spills from reaching areas outside the plant should be provided. Examples would include: maintaining neutralizing agents near bulk storage areas, maintaining personal protective safety equipment in potential spill locations so that spills may be localized. When lighter than water chemicals are handled, adequate length of flotation spill-contaminant booms or absorbent booms should be available along with the proper means to



deploy them. An adequate supply of dispersants (that have been approved by State authorities) should be stored at the plant for treatment of spills.

#### B. PLANT DRAINAGE

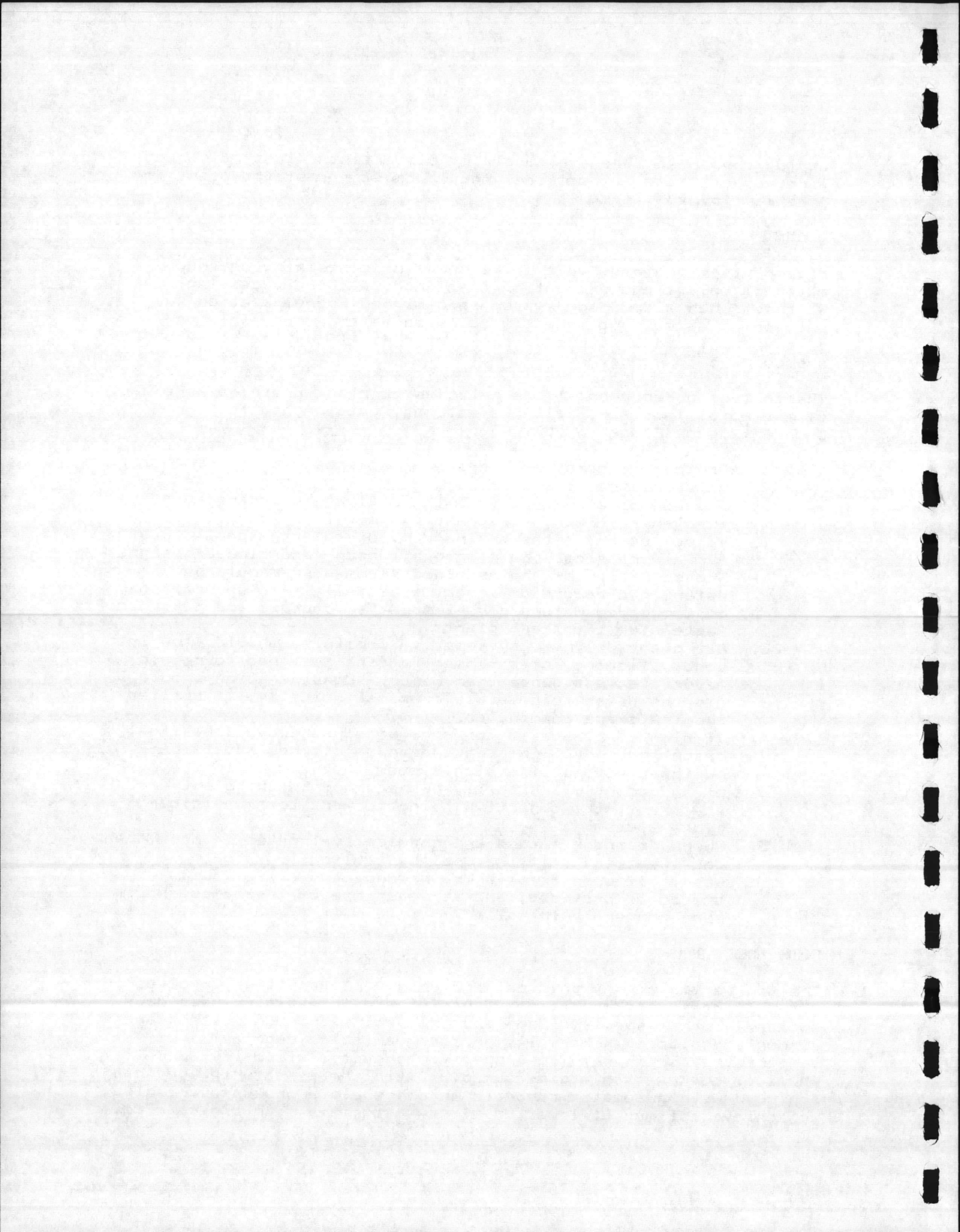
Proper plant drainage is a prime means of containing hazardous material spills and preventing them from reaching receiving waters. When a drainage system is designed, consideration to entrapping as much potentially polluted water as possible and diversion of these waters to the proper final destination are the predominant concerns.

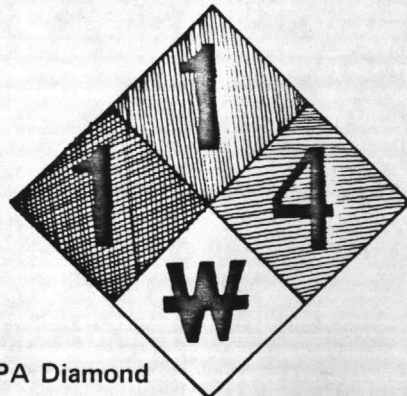
The following recommendations relative to plant drainage were part of the Guidelines for Spill Prevention, Containment, and Countermeasure Plans (SPCC).

1. Drainage from diked storage areas should be valve-restrained to prevent a spill or other excessive leakage of a product into the drainage discharge or in-plant effluent treatment system.
2. Valves used for the drainage of diked areas should, as far as practical, be of manual, open- and closed design. The condition of the retained stormwater should be determined before drainage, especially if such drainage of impounded waters goes into water courses and not into wastewater treatment plants.
3. All plant drainage systems, if possible, should flow into ponds, lagoons, or catchment basins designed to retain materials less dense than water. Consideration should also be given to possible chemical reaction, if spilled chemicals are commingled.
4. If plant drainage is not engineered as above, the final discharge of all in-plant drainage ditches should be equipped with a diversion system that could, in the event of an uncontrolled spill, be returned to the plant for treatment, the objective being to work toward a closed cycle system.
5. Where drainage waters are chemically treated in more than one treatment unit, natural hydraulic flow should be used. If pump transfer is needed, two "life" pumps should be provided, and at least one of the pumps should be permanently installed.

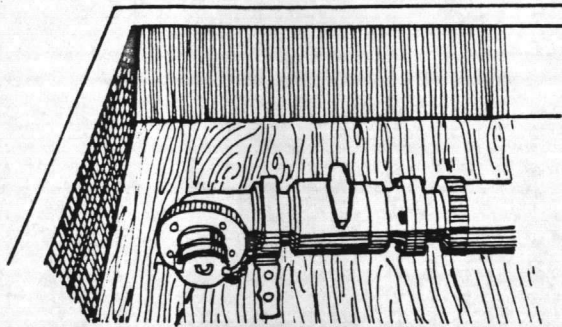
#### C. MONITORING PROCESS VARIABLES

The monitoring of any physical and chemical quantities involved in plant processes is an extremely useful aid in avoiding hazardous spills. Either specific apparatus or entire process systems are commonly monitored. Normally process variables such as temperature, pressure, flow, specific gravity, viscosity, and chemical composition are measured. Often these measuring devices are used with automatic controls which regulate process variables to achieve optimum utilization of raw materials. In order to do

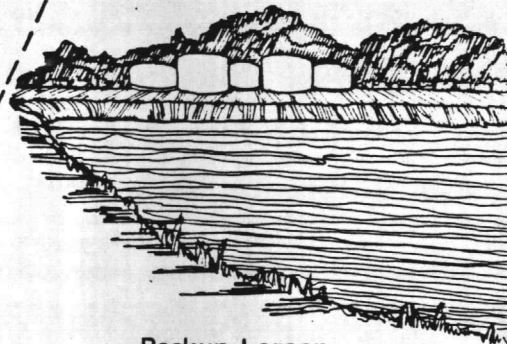
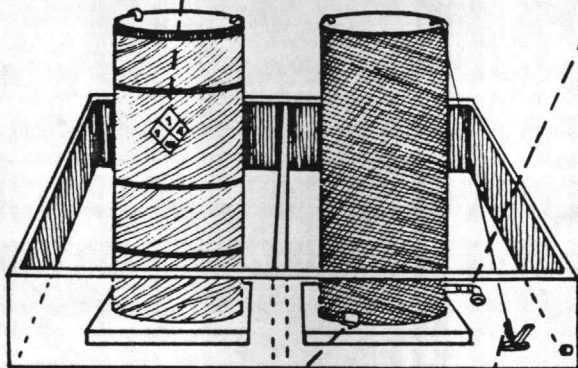




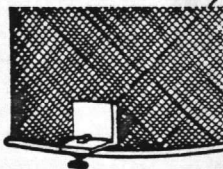
NFPA Diamond



Fill Pipe



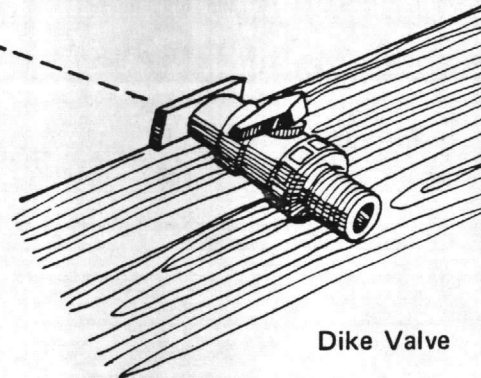
Backup Lagoon



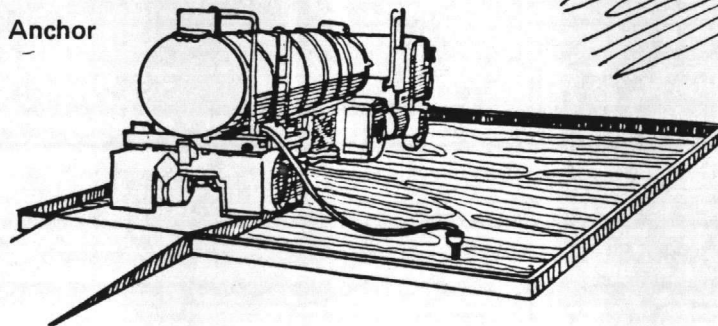
Tie Down Anchor



Tie Down Cable

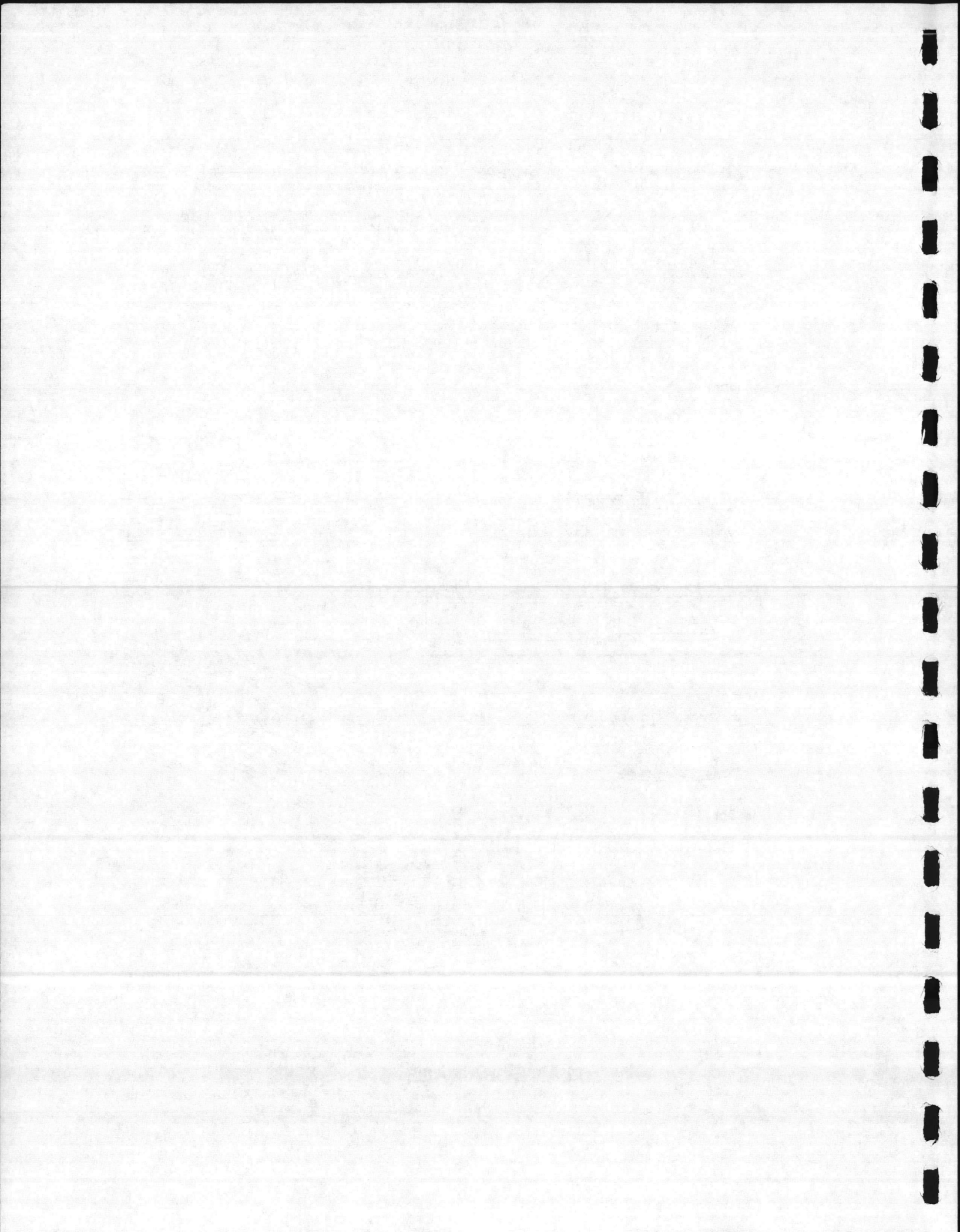


Dike Valve



Truck Diking

## PLANT DRAINAGE



this, the control keeps process variables within predetermined specifications. Under such control a device may also have a vital role during abnormal situations triggering corrective action, or, in extreme cases, in safely shutting down the system.

When monitoring hazardous materials, it is normal to use redundant or backup instrumentation. Because the sampling probe is in direct contact with the usually extreme condition of heat and corrosive vapors, it is the least reliable part of the system. Frequently it is desirable to use a device having a different principle of measurement as a backup unit. An example of this is the use of a resistance bulb to sense the operating temperature of a reaction vessel. The backup device could be a thermocouple.

After determining that something is wrong, the proper corrective action should be initiated. The corrective action depends entirely on the nature of the hazard and the consequences to the plant or operation. An electrical interlock system to shut down pumps and close valves leading to the process unit which is malfunctioning is a common device to prevent more material from being added to a potential spill.

Monitoring equipment should warn personnel that an operating abnormality has occurred. Commonly a flashing light and horn, that can be silenced by the operator, are used to attract the operator's attention to a particular control loop. Operation of the alarm should be independent of any control mechanism so that the alarm will still function properly even though a malfunction might occur in the control mechanism. Further monitoring equipment, such as a siren, should be employed to signal hazardous situations that might require evacuation of personnel from the area. Monitoring systems can also be obtained that use prerecorded messages to indicate the nature of the problem for the operator.

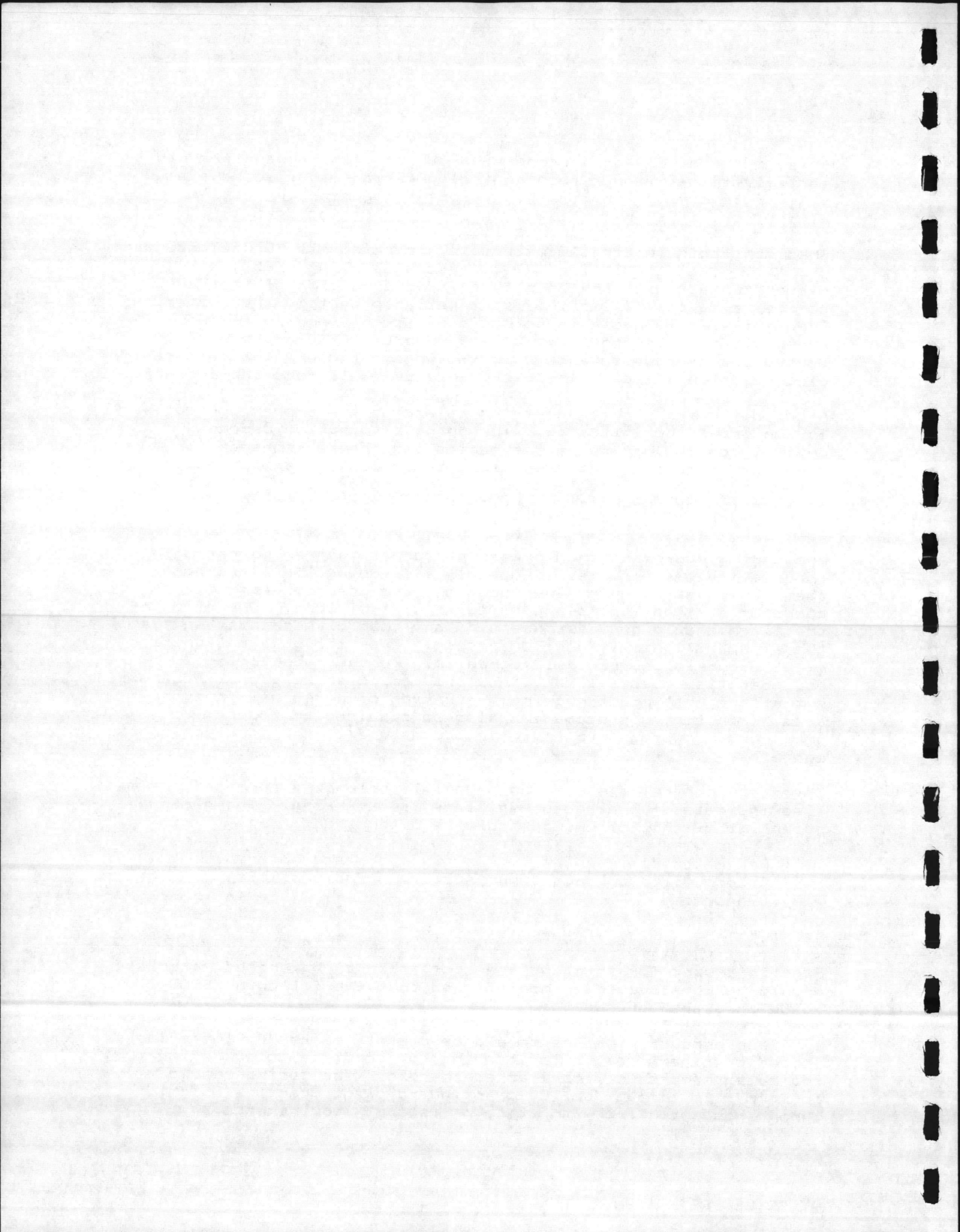
Inventory control systems and materials balance determinations may also indicate if leakage or spillage is occurring. The hazard potential of the following should be determined:

Raw materials	Waste materials
Intermediate process compounds	End products
Byproducts	

#### D. IN-PLANT PIPING

Pipelines used for in-plant transportation of hazardous materials should be constructed or modified so that the following SPCC guidelines are adhered to:

1. Each product pipeline should be clearly marked by lettering (coded or otherwise), color banding, or complete color coding to indicate the product transferred therein. The coding should conform with company policy or standard plant practice which, in turn, should conform with state or federal requirements.





2. Each oil or hazardous material product-fill line which enters a tank below the liquid level should have a one-way flow check valve located as closely as possible to the bulk storage tank. In addition to confining the product to the tank, in the event of valve or pipeline failure, the check valve should permit overhaul of the main shutoff valve and should aid in preventing shock loading of the pipeline and valves from a "slug" of the tank content caused by backflow into an empty fill line. As far as practical, the product flow in suction lines should be controlled by use of a positive displacement pump.

3. Buried pipelines should be avoided. However, buried installations should have a protective wrapping and coating and should be cathodically protected if soil conditions warrant. A section of the line should be exposed and inspected annually. This action should be recycled until the entire line has been exposed and examined on a regularly established frequency. An alternative would be the more frequent use of exposable pipe corridors or galleries.

4. When a pipeline is not in service, the terminal connection at the transfer point should be capped or blank-flanged, and marked as to origin.

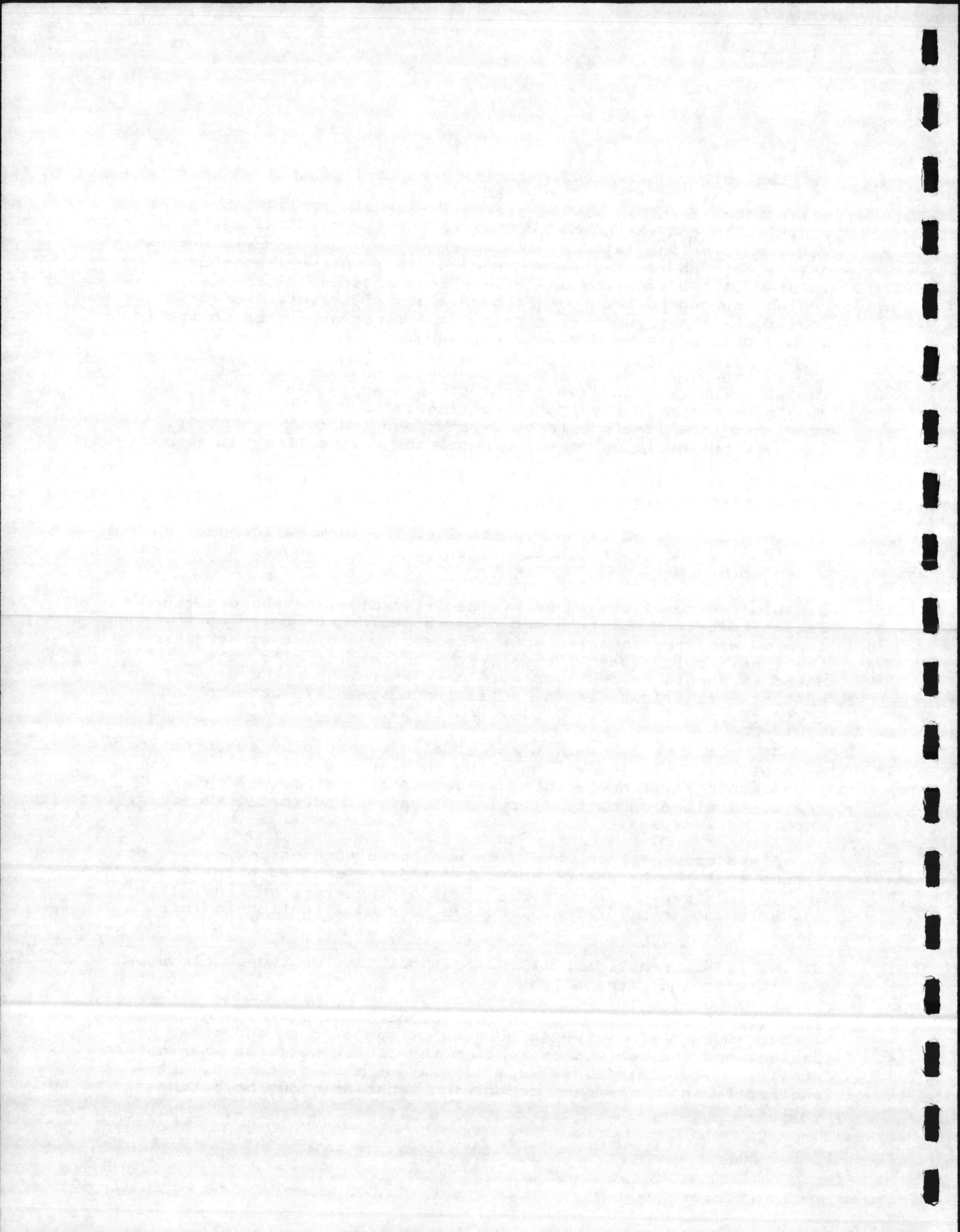
5. Wood-to-metal should be avoided as a pipeline support since it is apt to retain moisture and cause pipeline corrosion which, when coupled with the abrasive action caused by the pulsating action of the line, could cause line failure with resulting leakage. Supports should be designed with only a minimum point of surface contact that allows for the pulsating movement (expansion and contraction) of the line (i.e., rollers).

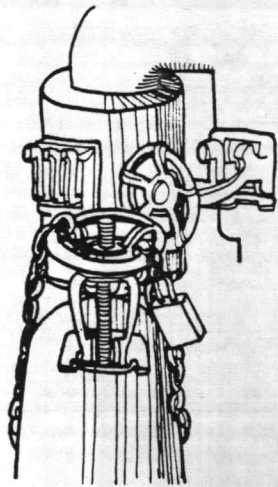
6. All above-ground valves and pipelines should be subjected to a regular monthly inspection at which time the general condition of items, such as flange joints, valve glands and bodies, catch trays, pipeline supports, locking of valves, and metal surfaces, should be assessed.

7. Elevated pipelines should be subjected to constant review to insure that the height of vehicular traffic granted plant entry does not exceed the lowermost height of the elevated line; gate check-in and in-plant travel routes warrant attention in this respect.

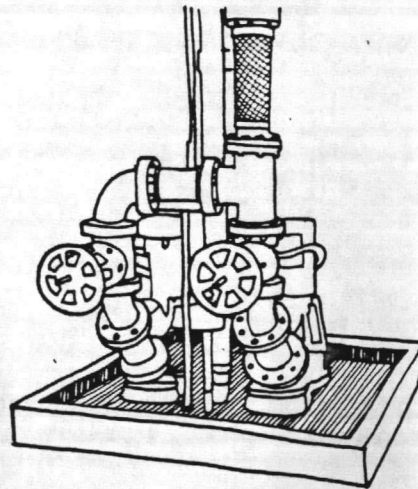
8. As far as practical, all pumps should be located as close as possible to the storage tank.

9. Flapper-type drain valves should not be used to drain diked areas. Such drain valves should be of manual open and close design, and they should be kept in the closed position when not in service. The drain lines from dike areas should drain directly or indirectly into treatment or holding tanks or ponds or catchment basins.

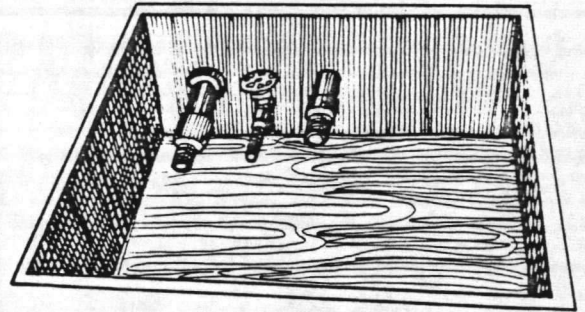




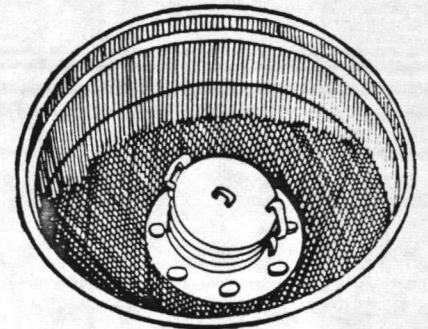
Locked O.S.Y. Valve



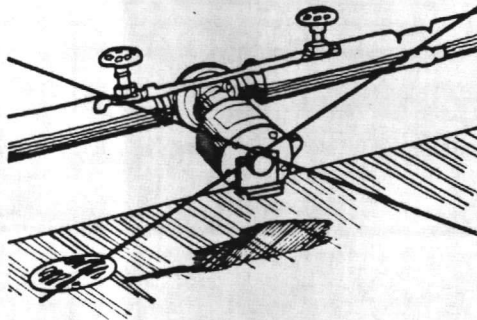
Valve Area Diking



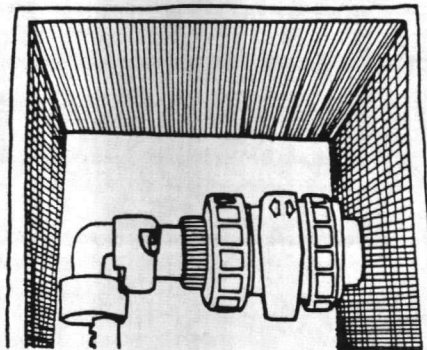
Fill Pipe Valve Diking



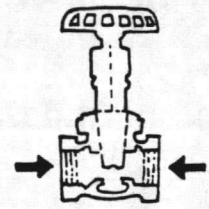
Fill Pipe Valve Diking



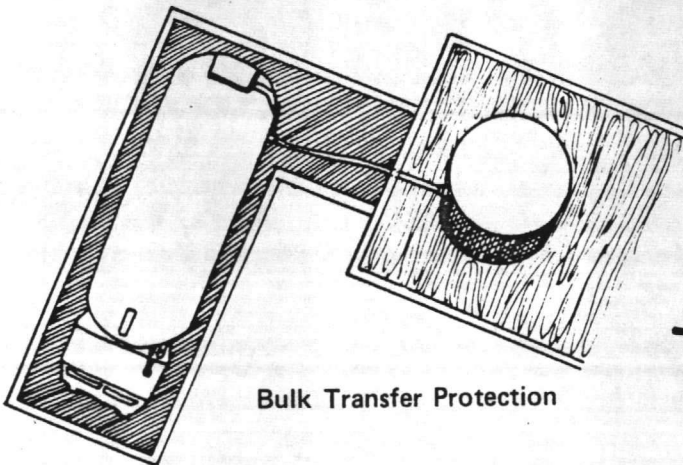
Valves Near Drain



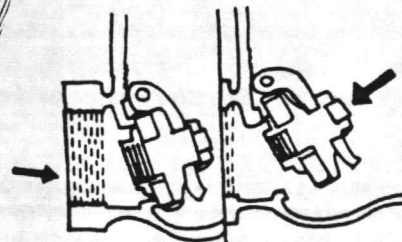
Open/Close Valve Design



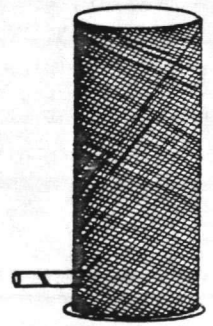
Gate Valve



Bulk Transfer Protection

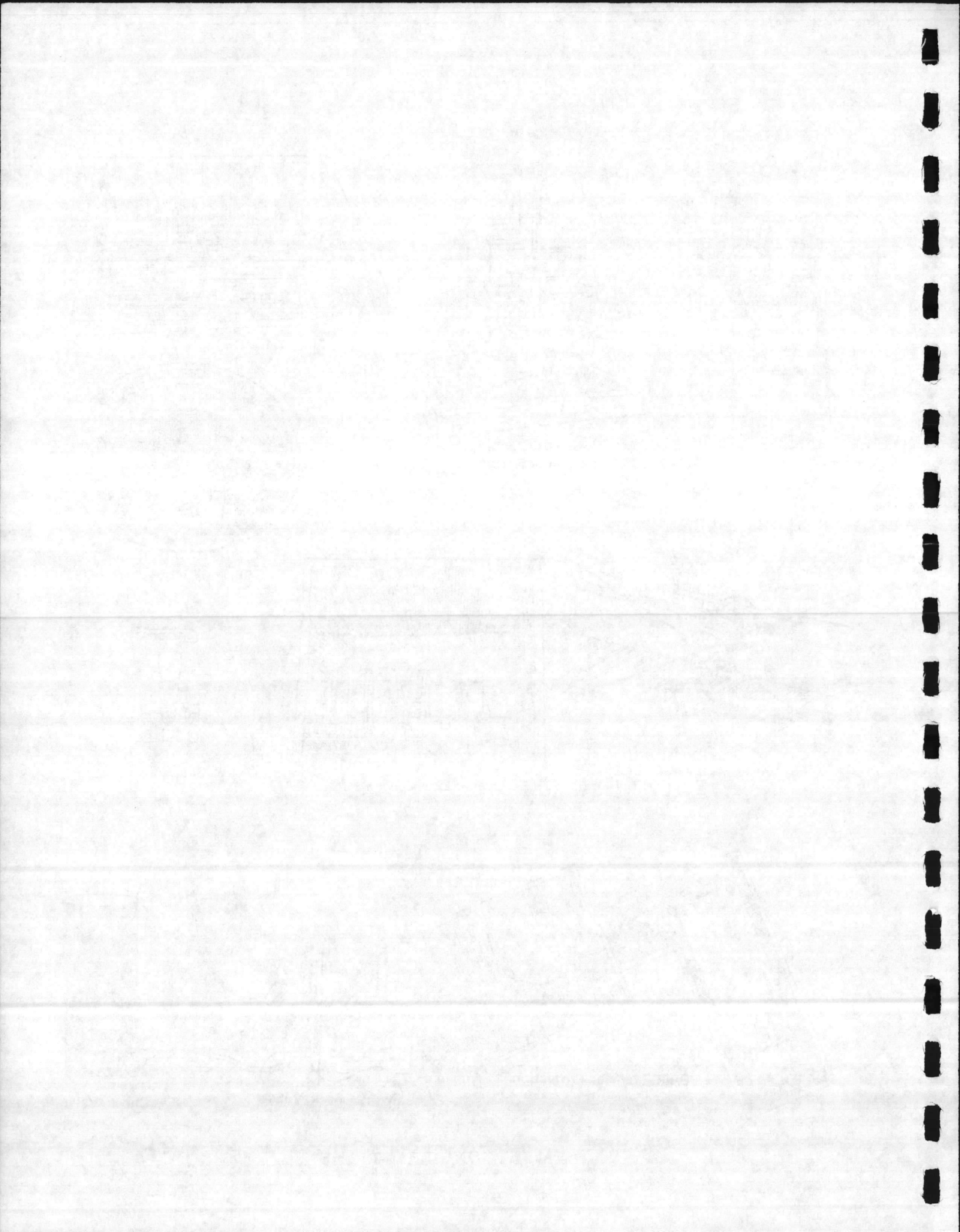


Swing Check Valves



Check Valve

## VALVE CONSIDERATIONS



#### E. SOLID MATERIAL STORAGE

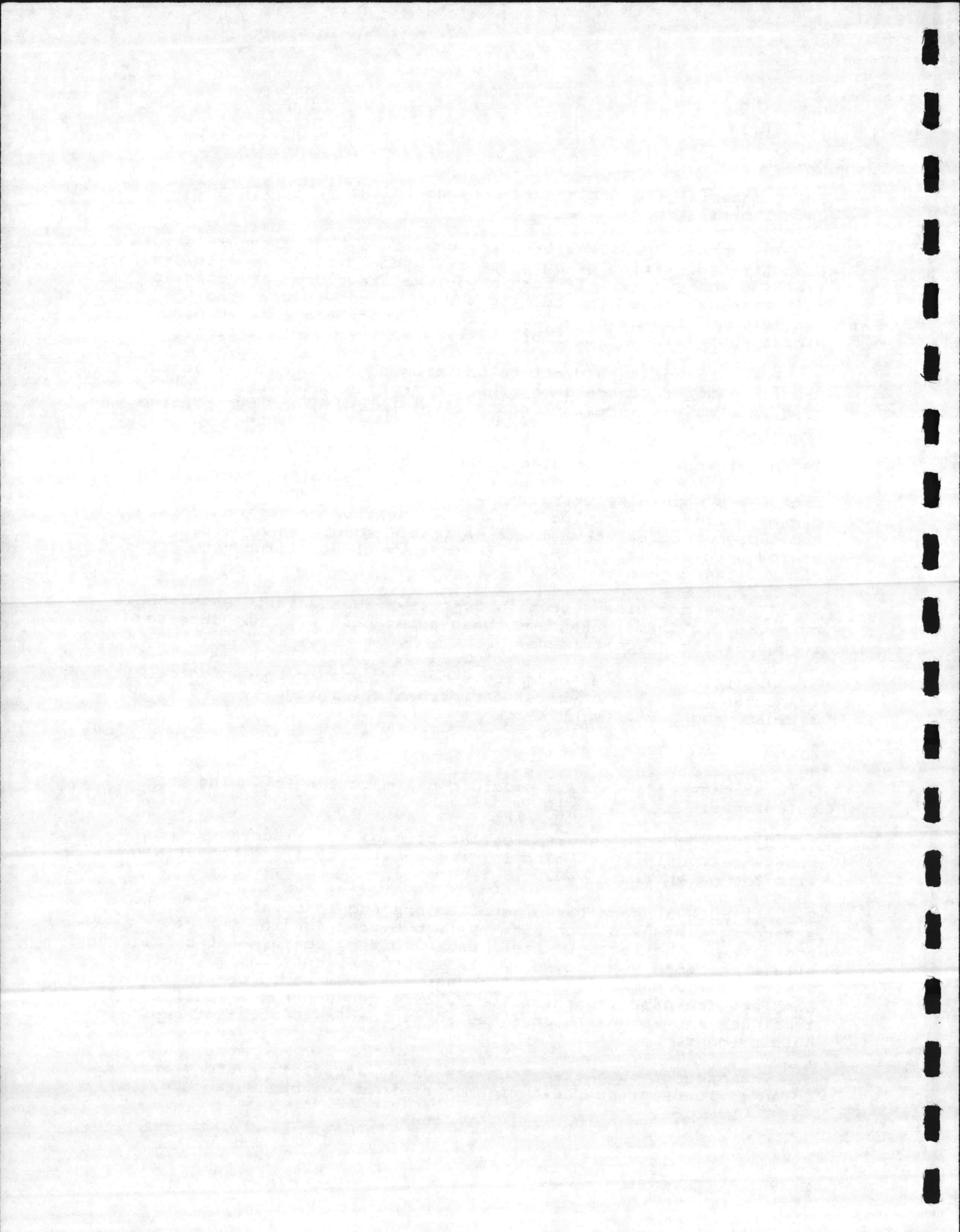
Solid material storage should conform to the following SPCC guidelines:

1. The open stockpiling of ores, chemicals, and minerals should be discontinued. Piles of bulk material should be covered to prevent leaching and runoff. If open shed-like structures are used for bulk storage, retention curbing should be provided around the perimeter of the pile, or perimeter drainage trenches should direct runoff into a suitable wastewater treatment facility.
2. Bulk storage should not be positioned on the natural earth. Storage pads of concrete or other impervious materials should be used as a base to prevent ground water leaching and percolation into the earth.
3. Metal and fiber containers should be loaded, stored, and unloaded so as to minimize possibility of container damage. The containers should be stored in a covered area, off the ground in a manner which will preclude damage and weathering to the container, and subsequent leakage. The area itself should be provided for drainage to a treatment facility in an analogous manner to diked storage tank areas.
4. If some containers contain corrosive substances, these should be stored so that leakage of these substances will not corrode through adjacent containers.
5. All items outlined under this heading should be periodically inspected to insure physical and mechanical integrity of the drainage and containment systems.

#### F. BULK STORAGE

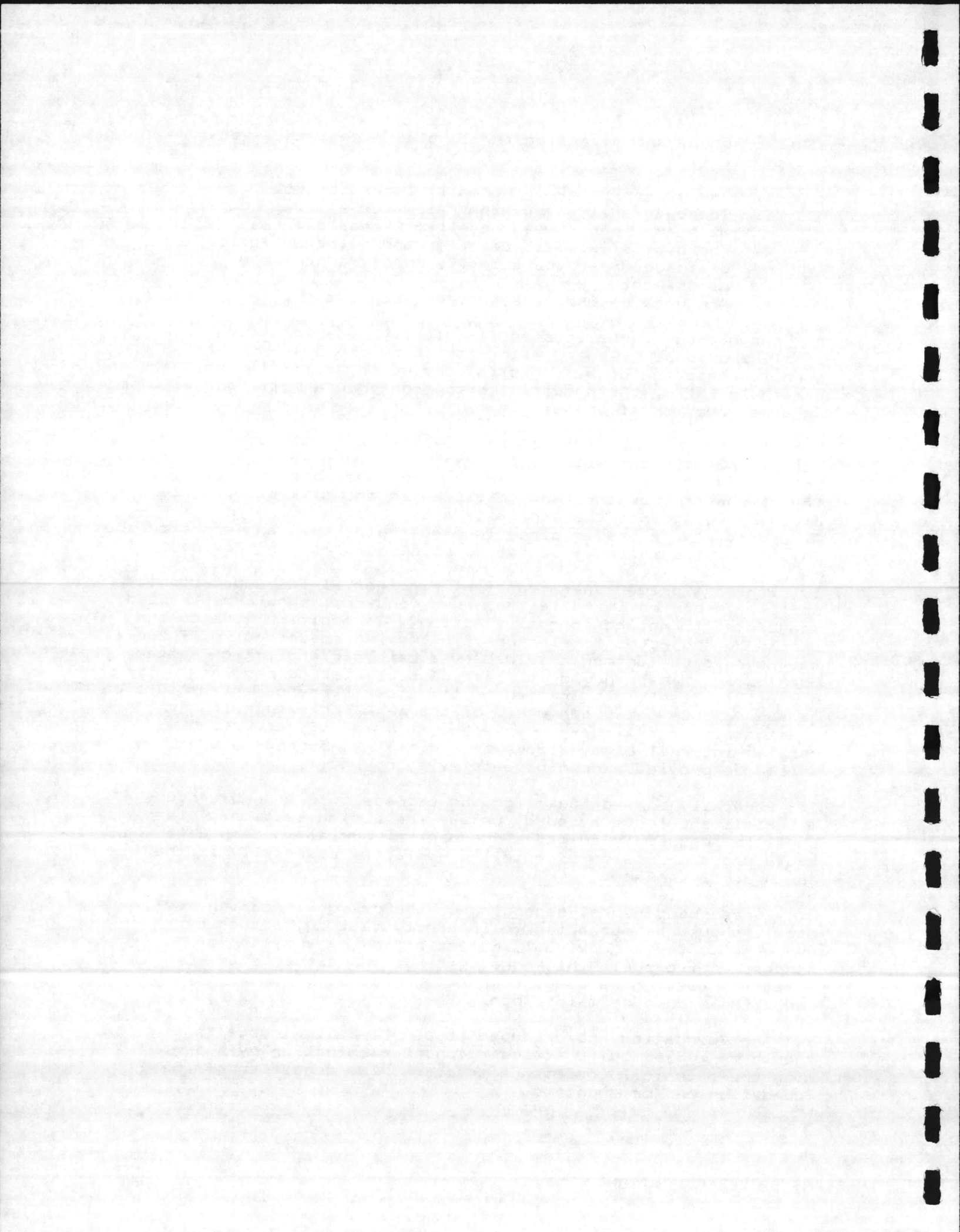
Bulk storage of materials should conform to the following SPCC guidelines:

1. No tank should be used for the storage of oil or hazardous substances, unless its material and construction are compatible with the material stored.
2. All bulk storage tank installations should be planned so that a secondary means of containment is provided for the entire contents of the largest single tank. Dikes, containment curbs, and pits are commonly employed for this purpose, but they may not always be appropriate. An alternative system would consist of a complete drainage trench enclosure arranged so that a spill could terminate and be safely confined in an in-plant catchment basin or holding pond.
3. Drainage of rainwater from the diked area into a storm drain or an effluent discharge that empties into an open watercourse,



lake, or pond, and bypassing the in-plant treatment system may be acceptable if:

1. The bypass valve is normally locked close.
  2. Thorough analysis of the rainwater ensures compliance with applicable water quality standards.
  3. The bypass valve is unlocked and relocked following drainage under the supervision of responsible management.
  4. Adequate records are kept of such events.
4. The storage tanks located immediately adjacent to the dike itself should be oriented with respect to the dike so that no manholes face the dike. This is considered desirable, so that if a manhole falls, the resulting discharge from a full tank will not be aimed over or at the dike.
5. If storage tanks located immediately adjacent to the dike itself are equipped with fill lines which enter the tank near the bottom and if the fluid pumped has suspended abrasive material, the discharge into the tank should be on the dike side, discharging against the tank side away from the dike. Alternatively, a baffle plate located inside the tank opposite the pump discharge in the area apt to be abraded may be provided.
6. Buried storage tanks represent a potential for undetected spills. A buried installation, when required, should be wrapped and coated to retard corrosive action. In addition, the earth should be subjected to electrolytic testing to determine if the tank should be further shielded by a cathodic protection system. Such buried tanks should at least be subjected to regular hydrostatic testing. In lieu of the above, arrangements should be made to expose the outer shell of the tank for external examination at least every 5 years. A means of conducting regular internal examinations of the tank at 5-intervals should be provided (down-hole television, etc.).
7. Partially buried tanks for the storage of oil or hazardous materials should be avoided, unless the buried section of the shell is adequately coated since partial burial in damp earth can cause rapid corrosion of metallic surfaces, especially at the earth/air interface.
8. Aboveground tanks, depending on the design (floating roof, etc.), should be subjected to integrity testing, either by hydrostatic testing, visual inspection, or by a system of nondestructive shell thickness testing. When the latter system of integrity testing is used, comparison records of shell thickness reduction should be maintained.
9. The foundation and/or supports of all bulk storage tanks should be subjected to at least annual examination by a person with the technical competence to assess the condition of the foundation and/or supports.





10. To control leakage through defective integral heating coils, the following factors should be considered and applied:

1. The past life span of internal steam coils should be determined, and a regular system of maintenance and replacement that does not exceed the anticipated life span should be established.
2. To reduce failure from corrosive action, prolong life, and reduce replacement costs, the temperature and environment have to be carefully considered when selecting heating coil materials.
3. The steam or exhaust lines from integral heating coils should be monitored for contamination, or passed through a settling tank or skimmer.
4. The feasibility of installing an external heating system should also be considered.

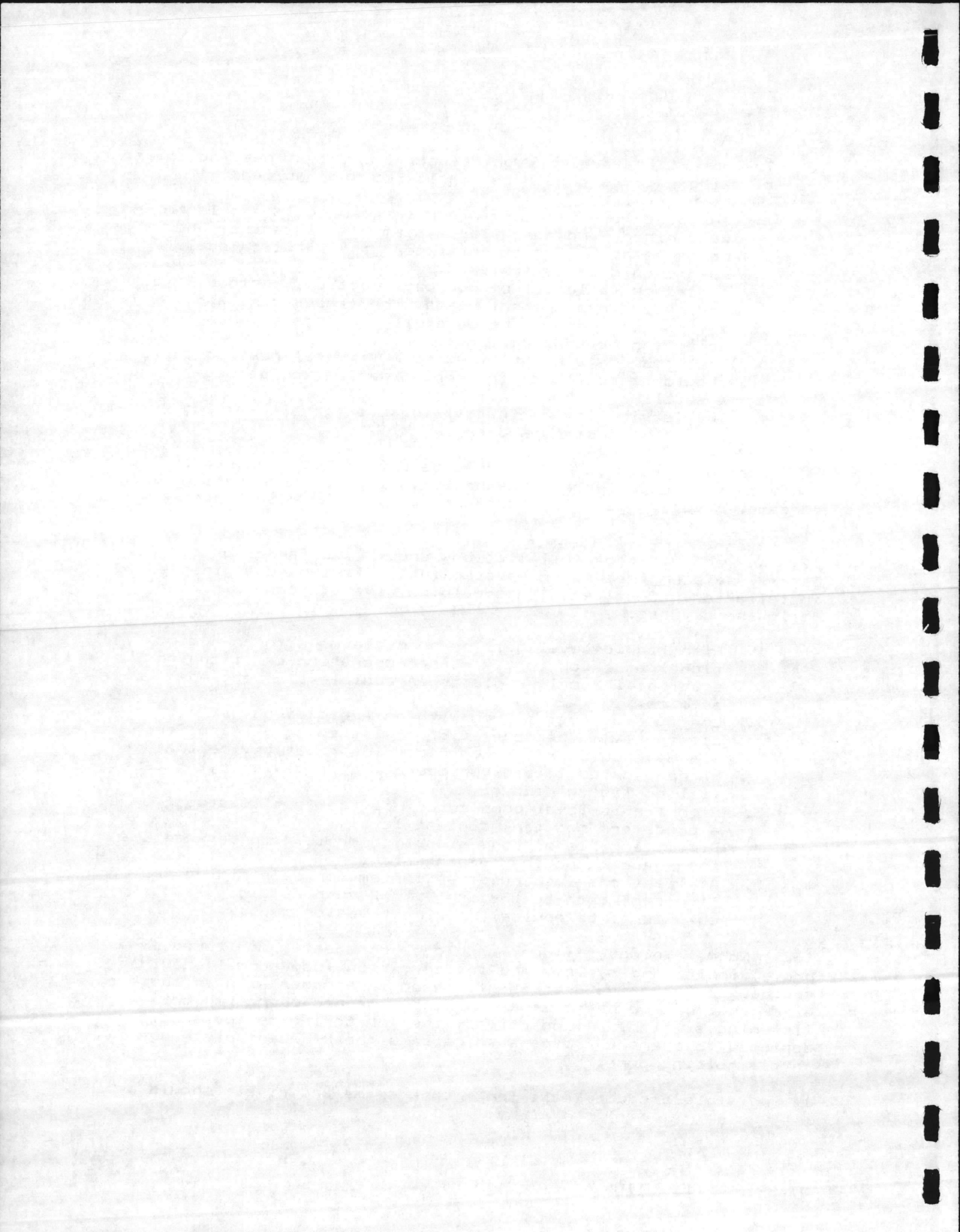
11. Each bulk storage tank should be externally examined at least every month. Each inspection should include an examination of streams, rivets, nozzle connections, valves, and pipelines directly connected to the tank.

12. New and old tank installations should, as far as practical, be fail-safe engineered or updated into a fail-safe engineered installation. Consideration should be given to providing the following devices:

1. High liquid-level bell or horn alarms with an audio signal at a constantly manned operating or listening station; in smaller plants an audible air vent may suffice.
2. Low liquid-level alarms with an audio signal at a constantly manned operation of listening station; such alarms should have a non-bypassing reset device that can be readjusted to a given operating level following tank fill or liquid removal.
3. High liquid-level pump cutoff devices set to stop flow at a predetermined tank content level.
4. Direct audible or code signal communication between the tank gauger and the pumping station.
5. At least one fast response system for determining the liquid of each bulk storage tank such as digital computers, telepulse, or direct vision gauges.

13. "Normal" plant effluent should be constantly monitored by a proven monitoring system, and any deviation from normal should be engineered to activate a visible readout recorder with an audible alarm that can be heard at a constantly manned operation or listening station. If practical, the monitoring device should be designed to operate a bypass to release the effluent discharge into a holding pond.

14. Visible product leaks from tank seams and rivets should be



promptly corrected.

15. Tanks should not be used with the knowledge that the "head" or top is in a corroded-through condition. Action should be taken to drain such tanks and repair the defective member as promptly as possible.

16. When practical, each bulk storage tank should be lettered (code or otherwise) or color coded to indicate its chemical content, the Manufacturing Chemists Association or Department of Transportation coding being preferred, and the coding should duplicate those used for chemical transportation identification.

17. The use of wooden tanks should be confined to water storage and should be avoided for liquid chemical storage.

The Manufacturing Chemists Association has developed a checklist to aid in developing spill prevention and control programs for chemical plants.

## 6. SPILL PREVENTION DURING TRANSPORT

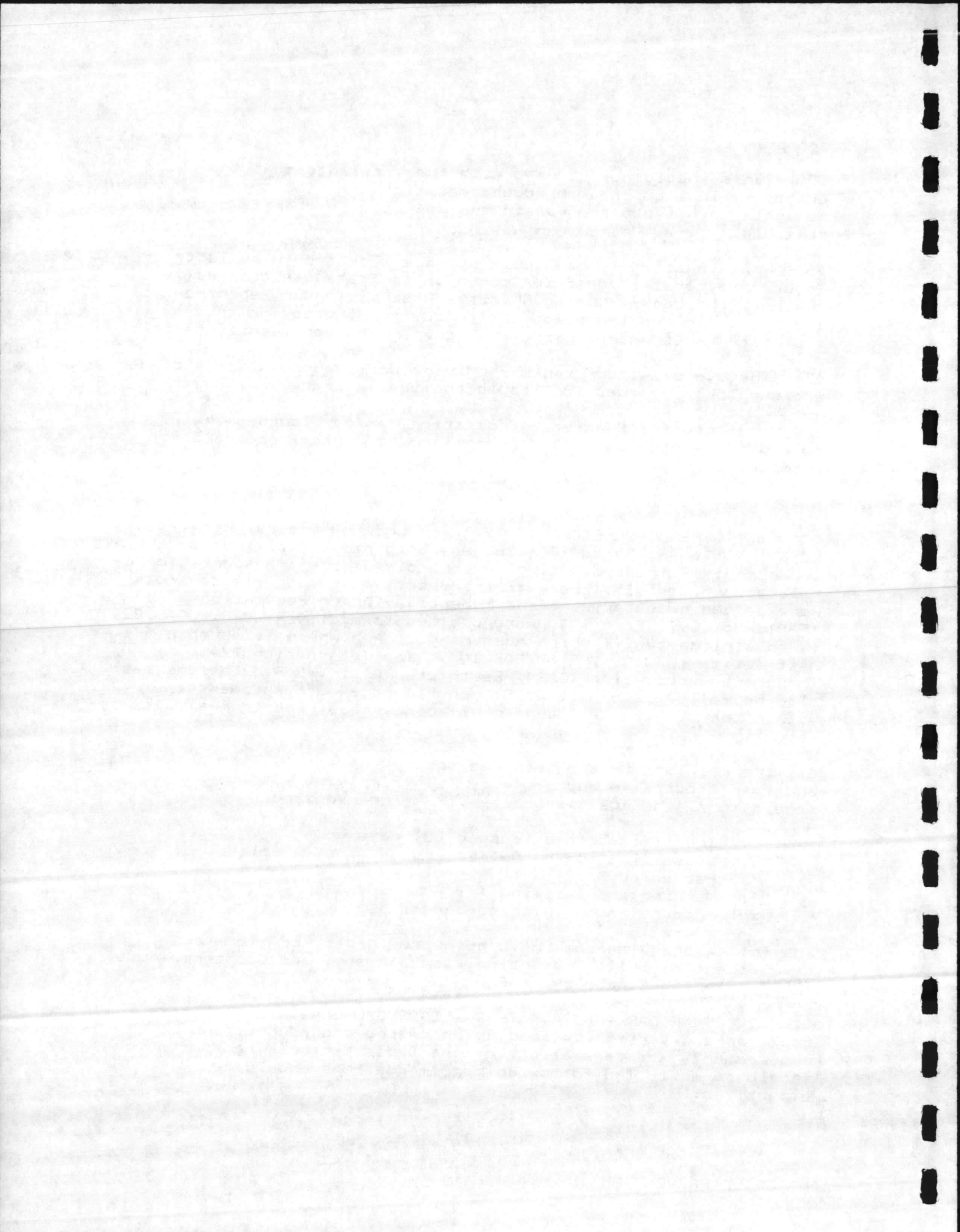
1. GENERAL CONSIDERATIONS. The Code of Federal Regulations (CFR), Title 49, Parts 170-178, was originally published by the Department of Transportation to control surface transportation of hazardous materials. For air transport, more specific controls were deemed necessary and the Federal Aviation Regulations (FAR), Vol. VI, Part 103, were drafted to modify 49 CFR. CAB 82 is an airline tariff which must be followed where it is more restrictive than 49 CFR or FAR 103. The International Air Transport Association (IATA) Restricted Articles Regulations must also be followed for all U. S. import and export shipments. Within the U. S., state and local agency requirements must also be met.

All the regulations are designed to prevent spills from occurring and to protect life and property. In complying with the regulations, the following activities are required:

1. Identification by proper DOT name
2. Classification by DOT hazardous material class
3. Packaging
4. Marking and labeling
5. Preparation of shipping papers

The following guidelines have been provided by EPA for the development of Spill Prevention, Containment, and Countermeasure (SPCC) Plans by Industry.

2. TANK CAR AND TANK TRUCK LOADING/UNLOADING. Relative to tank car and tank truck loading/unloading procedures, the requirements and regulations of the Department of Transportation should be met. The following recommendations should be emphasized:

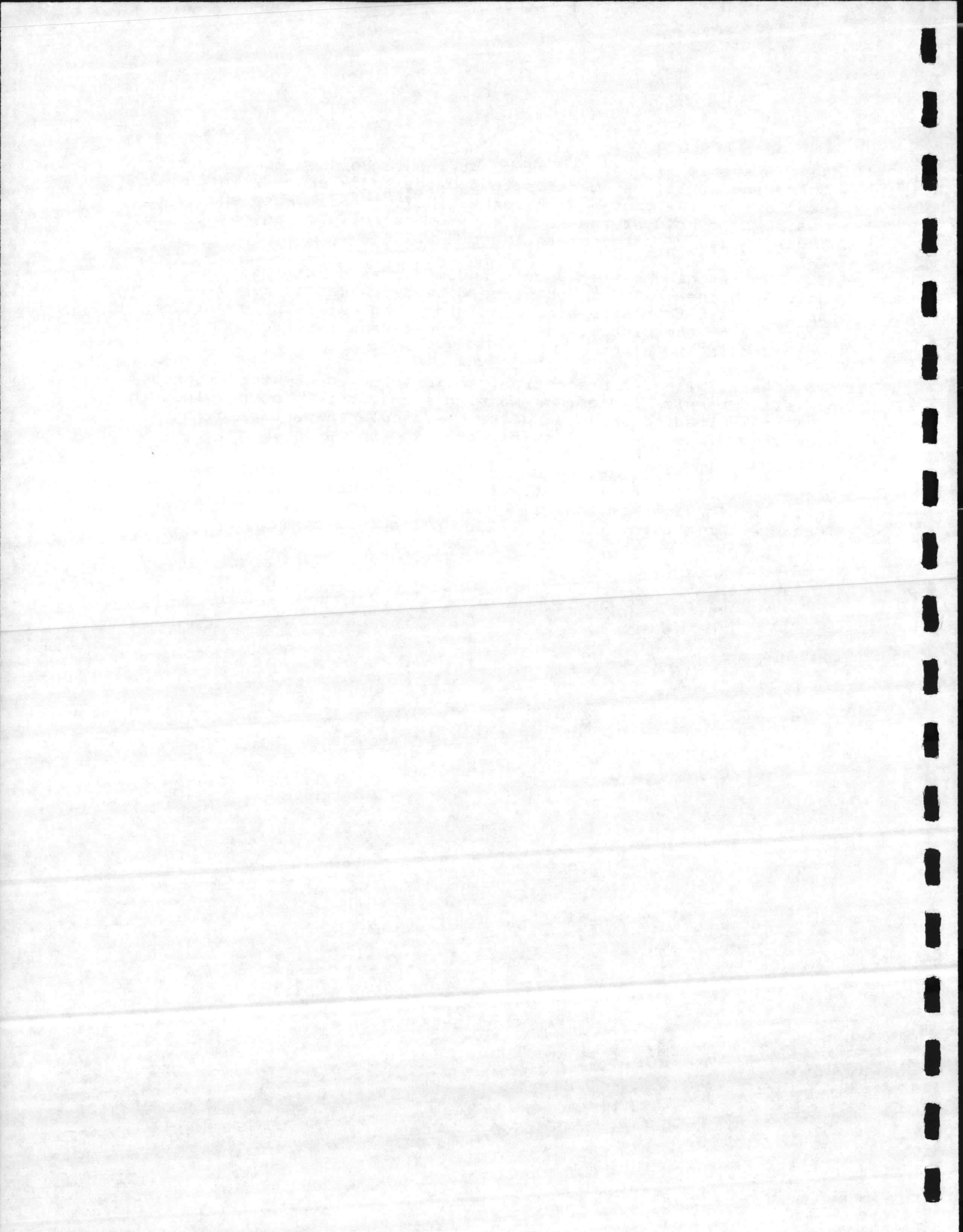


(1) A system of containment curbs should be used for tank truck unloading areas, using ramps to provide truck access into the confines of the containment curb. The curb enclosure should be designed to hold at least the maximum capacity of any single tank truck loaded or unloaded in the plant.

(2) A trenching system should encompass each railroad tank car unloading area. The trench should be designed to carry away any spill to a catchment basin or holding pond, at least equal in capacity to the capacity of the largest tank car loaded or unloaded in the plant.

(3) As a fail-safe precaution, an interlocked warning light or physical barrier system, or warning signs, should be provided in loading/unloading areas to prevent vehicular departure before complete disconnect of flexible or fixed transfer lines.

(4) Prior to filling and departure of any tank truck, the lowermost drain and all outlets of such vehicles should be closely examined for leakage, and if necessary, tightened, adjusted, or replaced to prevent liquid leakage while in transit.



## XII. MERCURY HAZARDS AND SPILL STRATEGIES

### A. Introduction

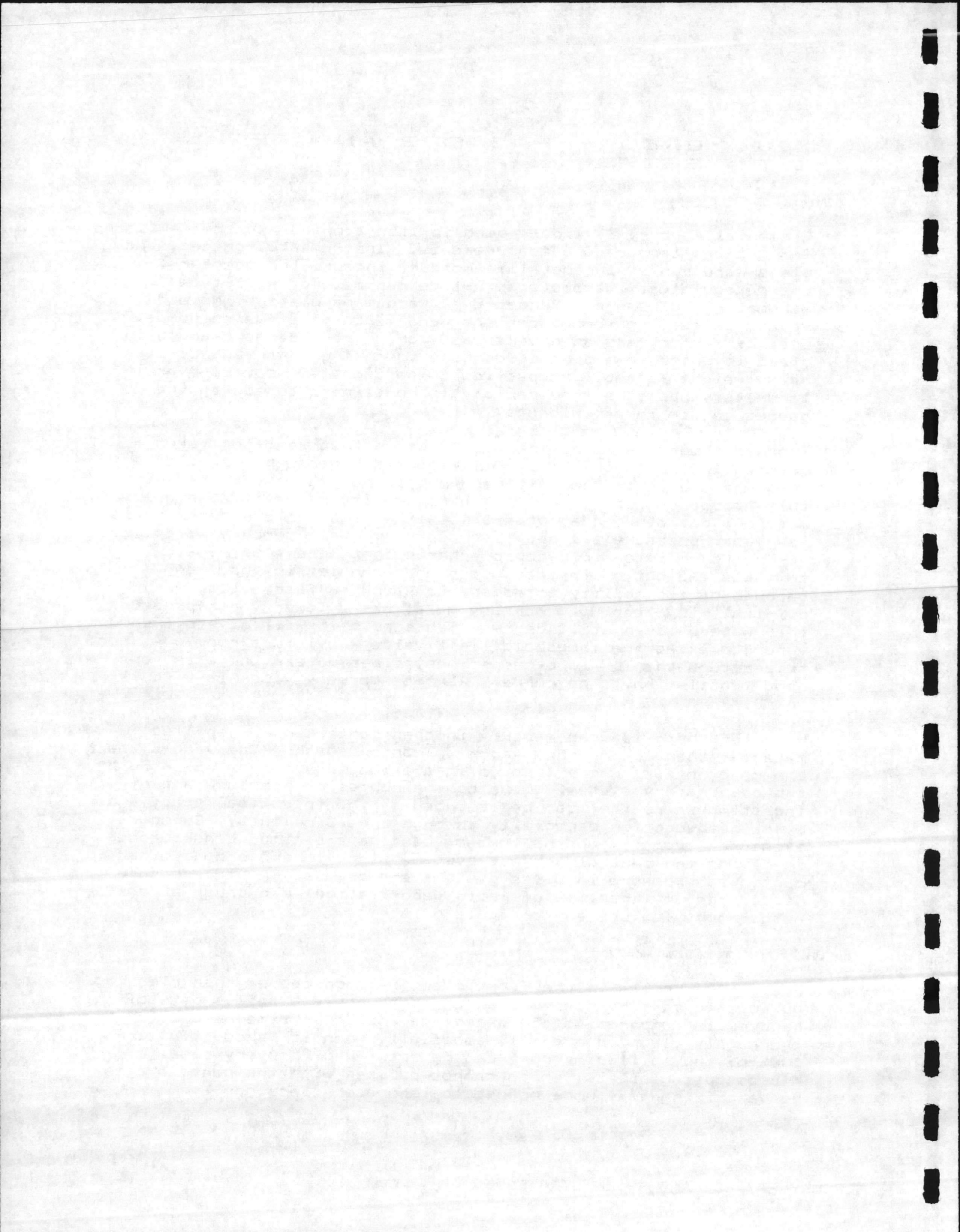
Elemental mercury is widely used in laboratories as a reagent, and for gas and temperature measurements. Instruments, gauges, and glass-ware containing metallic mercury include thermometers, thermoregulators, barometers, u-tube manometers, well-type manometers, closed-end Bennet-type vacuum manometers, McLeod vacuum gauges, sphygmomanometers, and mercury diffusion pumps. Uses of mercury are as diverse as storing rare gases trapped in glass inverted in a pool of mercury to taking advantage of its heavy weight for soil compaction comparison. Of course every laboratory has some free mercury in containers to add to the gauges or use in experiments.

Inorganic mercury is an insidious poison that is often taken for granted in the laboratory. All laboratory personnel should be keenly aware of the toxicity and subtle hazards associated with this poisonous substance. Its high density makes it a unique material but other characteristics like high surface tension and low vapor pressure are negative aspects. When mercury is spilled it breaks up into microscopic spheres that adhere to vertical surfaces and out of the way nooks and crannies in the floor. Because of its ability to adhere to slick surfaces it is very difficult to clean up. Mercury metal has a lower vapor pressure than water. Even at 10 degrees Fahrenheit it will give off enough vapor to exceed the threshold limit value (TLV) in a room. At room temperature the TLV is exceeded many times unless there is very good ventilation. The current TLV for mercury vapor is 0.05 mg/m<sup>3</sup>.

Whenever there is free mercury in open containers or spilled material there is mercury vapor to contend with. The vapors are the major hazard where through inhalation they can be absorbed by the respiratory system. Less common routes of exposure are by ingestion where they can be absorbed by the intestinal tract and by skin absorption especially through breaks or cuts. Chronic exposures from six months to two years have serious consequences involving the central nervous system, kidneys, and brain; other continued exposure involves systems and organs. Acute exposure to heated mercury, because of rapid vaporization, can cause severe respiratory failure and/or acute poisoning.

### B. Spill Prevention and Vapor Reduction

Preventing spills in the first place is much easier than cleaning up spilled mercury. Effort expended to prevent spills pays off handsomely compared to the excessive amount of time needed to thoroughly clean up a spill, especially when it is doubtful if 100% of the spilled mercury can be retrieved in every case. Microscopic globlets, which cannot be seen with the naked eye may be vaporizing away unbeknownst to laboratory personnel.

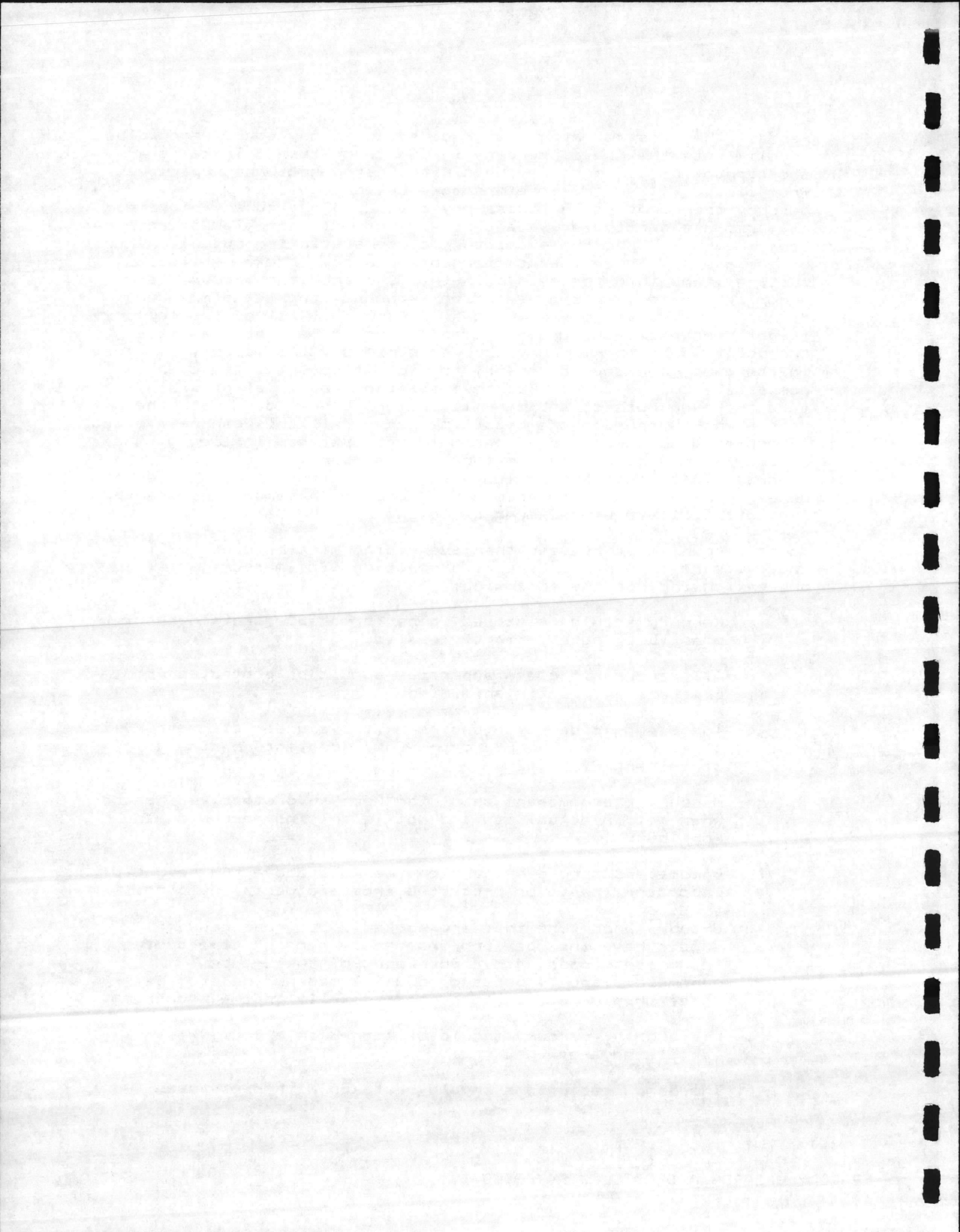




Perhaps the first strategy, as radical as it may sound, should be to eliminate the use of mercury in the laboratory. There is a substitute for all mercury-containing instruments and apparatus from liquid filled thermometers to electronic vacuum gauges. Mercury thermometers in laboratory ovens and heated environmental chambers are particularly dangerous. In most laboratories, one can look around and see the glass thermometers sticking out of the top of the ovens. These thermometers often become broken while putting items into the oven. In this instance the mercury is vaporized rapidly in the heated environment, the tests may be ruined and the oven may have to be scrapped if all of the mercury is not recovered. Laboratory ovens cannot always be dismantled to the point where the mercury can be retrieved. If mercury is loose in the oven, one should not try to pick it up until the oven is completely cooled down. Retrieve all the free metal possible, take the oven outside and turn it on for several days with the door open to vaporize the hidden mercury. All this can be avoided if non-breakable metal dial thermometers are used in lieu of the mercury-filled glass thermometers. If mercury is not around the laboratory it can't be spilled. Somewhere along the line the benefits of using a substance with a greater hazardous nature than its potential usefulness must be weighed in the balance.

Where mercury must be used then everything must be done to limit the exposure to vapors. General precautions for mercury spill prevention include the following:

- o Mercury should be stored in non-breakable containers of plastic or metal, tightly sealed.
- o All mercury in glass apparatus should be protected from breakage by plastic shielding.
- o There should be catch basins or trays under all mercury in glass which will capture the total contents of the containers if broken.
- o Mercury thermometers should be kept in protective sheaths when not in actual use and not left lying around on the work bench.
- o Barometers should be hung on the wall above the height of laboratory carts or protected from accidental bumping.
- o U-tube manometers that are hooked up to gas pressure should have the open end trapped by running some tubing to an open-topped jar. Both ends of the U-tube manometers should be stopped or closed during storage. These should not be stored horizontally in the stockroom.
- o Preferably, mercury should be stored in a cool, well ventilated area.
- o The same precautions should be taken with dirty used



mercury while awaiting cleaning, redistilling or disposal.

In cases where there are exposed surfaces of mercury, for one reason or another, pouring a one-sixteenth inch film of mineral oil will control the vapor. Water will do the same thing but evaporates too fast itself.

Heating of mercury should definitely be avoided because of the high rate of vaporization. If it must be done be sure to use a fume hood and filter the fumes through a special mercury absorbant to avoid contamination of the exhaust ducting.

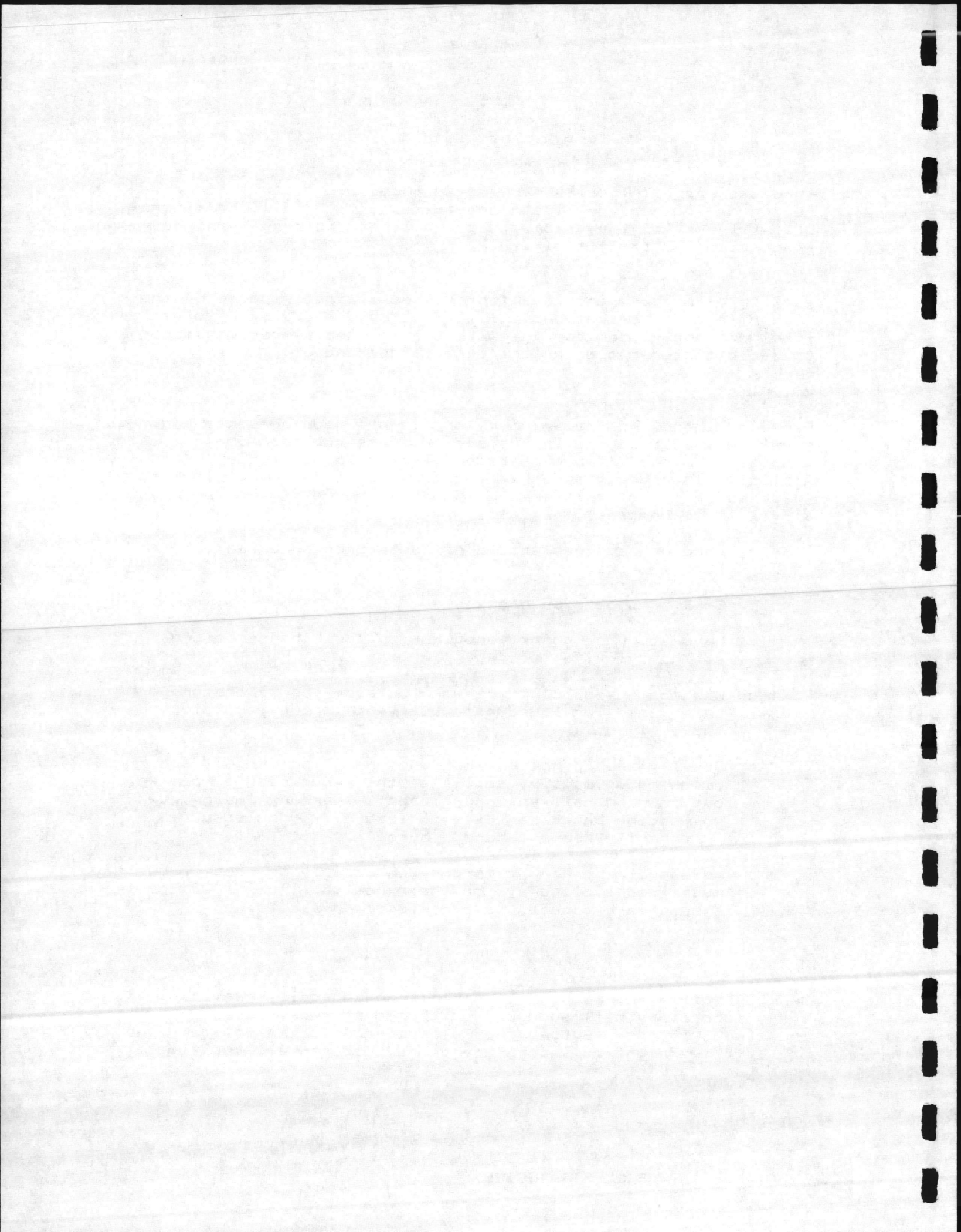
#### C. Personal Hygiene

Personnel handling free mercury should use good personal hygienic practices. Gloves should be used to avoid contact with the skin. Disposable mercury vapor masks are available for longer exposures. A plastic laboratory apron is also advisable as small globlets splashed onto wool sweaters, pants and other clothing is very difficult to remove, if at all.

- o Food or beverages should not be stored or eaten in laboratories.
- o Smoking should be prohibited.
- o Laboratory personnel should wash their hands before eating, smoking, etc.
- o Lab coats should not be worn outside the laboratory or taken home for laundering but kept in the laboratory lockers.
- o Jewelry should not be worn when handling mercury and cleaning up mercury spills as the vapor readily plates out on gold, silver, and copper. (Mercury amalgamated on wedding bands can be vaporized off by holding momentarily above a bunsen burner).
- o Personnel who handle mercury on a daily or routine basis must keep a close eye on their health. These personnel should make sure to have periodic physicals.

#### D. Spill Cleanup

Mercury spills are much more common than generally realized. Every laboratory has had a broken thermometer or vacuum gauge at one time or other. Spills should be cleaned up immediately and not left overnight as vapors are being produced all the time at room temperature.



When cleaning up a mercury spill be sure to wear the appropriate personal protective equipment. Gently scrape all the spilled globlets together to form one large pool of mercury. Do not sweep with a broom, as that breaks up the globlets into smaller particles. There are a number of devices that can be used to pick up the pool by employing a vacuum. They range all the way from a squeeze bulb and small diameter tube to a large industrial type vacuum machine made especially for mercury pick-up. For further information on these vacuums, see the section on LABORATORY/IN-PLANT SPILLS. Many laboratories have utilized an erlenmeyer flask with side outlet and a one-hole rubber stopper hooked up to a vacuum to trap the mercury globlets. Do not hook this device to the building vacuum system, as the mercury will ruin the vacuum pump as it readily amalgamates with copper or brass bearings and aluminum parts. The same holds true for portable vacuum pumps used with such a device. If a portable vacuum pump is used, hook up a hose to the exhaust and run it out the window. Otherwise you will be filling the room with poisonous mercury vapors.

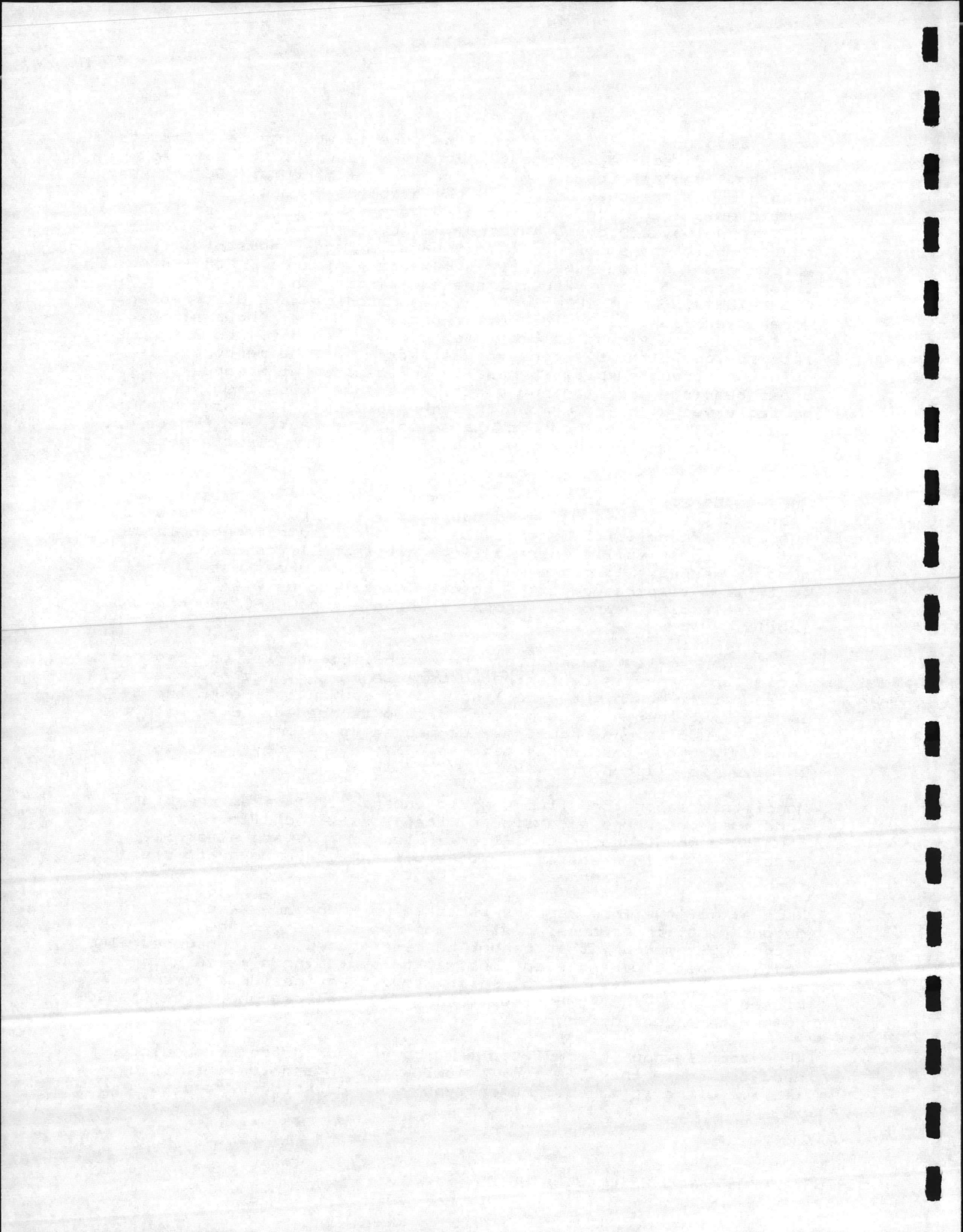
One of the most versatile devices that will work for most laboratory spills is the hand operated vacuum pump that comes in the SRM Mercury Spill Control Station. This pump can handle all but the largest spills where a large electrically operated vacuum pump is needed. It can even retrieve mercury under water in controlled temperature baths, etc. The kit comes with a disposable mask, vapor absorbing sponges and powder, and disposal labels.

For larger spills and multiple research laboratories or when a whole laboratory is contaminated because mercury was blown out of a manometer, has hit the ceiling and spread out all over the laboratory, then a large mercury vacuum is needed. Even with the large vacuum several hours may be needed to decontaminate the rooms. Without the larger size vacuum, several days may be involved in cleanup.

Monolithic laboratory floors would enhance cleanup as the pick-up wand must go around each side of the 12 x 12 inch floor tile usually encountered on the floor. Floor drains are a special problem as it is necessary to take off the drain cover to clean around it. A plumber may be needed to empty the drain trap.

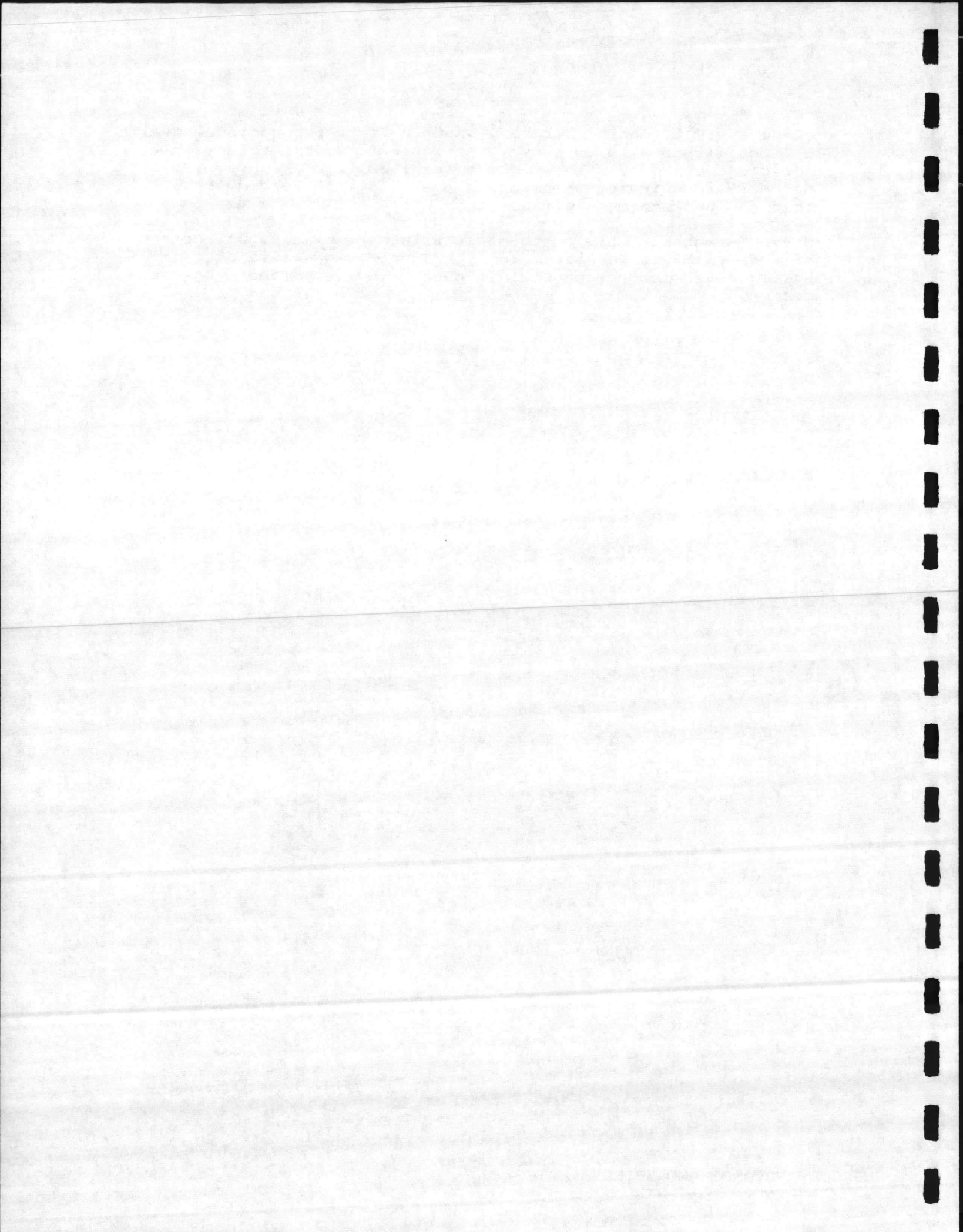
Once all of the free mercury is taken up there are several decontamination powders, pastes, and sponges to get the microscopic mercury that cannot be seen without a microscope. The next to last cleaning step consists of spreading a mercury vapor absorbant and leaving it overnight to fix any residual mercury missed by the first two steps. Finally, the area should be washed down with a good detergent.

When the cleanup is completed a mercury vapor detector should be used to assure that the room is below the threshold limit value (TLV). Ultraviolet absorbance type vapor detectors are used



effectively to monitor mercury vapor. State occupational health offices may be able to survey the laboratory for mercury or a detector may be available from a local college or university. Mercury vapor indicator badges are also available commercially that can be worn on the laboratory coat.

Given as much trouble as there is with mercury cleanup and the hazards involved for laboratory personnel, an active program of spill prevention and control is needed in every laboratory using mercury.





## XIII. CHEMICAL TREATMENT

### A. INTRODUCTION

The EPA, through the 1510 Plan (Oil and Hazardous Substances Contingency Plan) favors the development and utilization of sorbents, skimmers, booms and other mechanical control methods to remove or mitigate oil and remove, mitigate or neutralize hazardous substances discharges from the environment. The EPA acknowledges the use of chemicals and other additives to remove oil and hazardous substances discharges but cautions that it is EPA's intent that this be done with the least overall environmental impact.

In regarding the use of chemical treatments, the 1510 Plan addresses eight classes of materials or methods. These include chemical agents, dispersing agents, surface collecting agents, biological additives, burning agents, sinking agents, mechanical removal methods and sorbents. The section of this text entitled CHEMISTRY AND PHYSICS OF MATERIALS should be consulted for the definition of these terms.

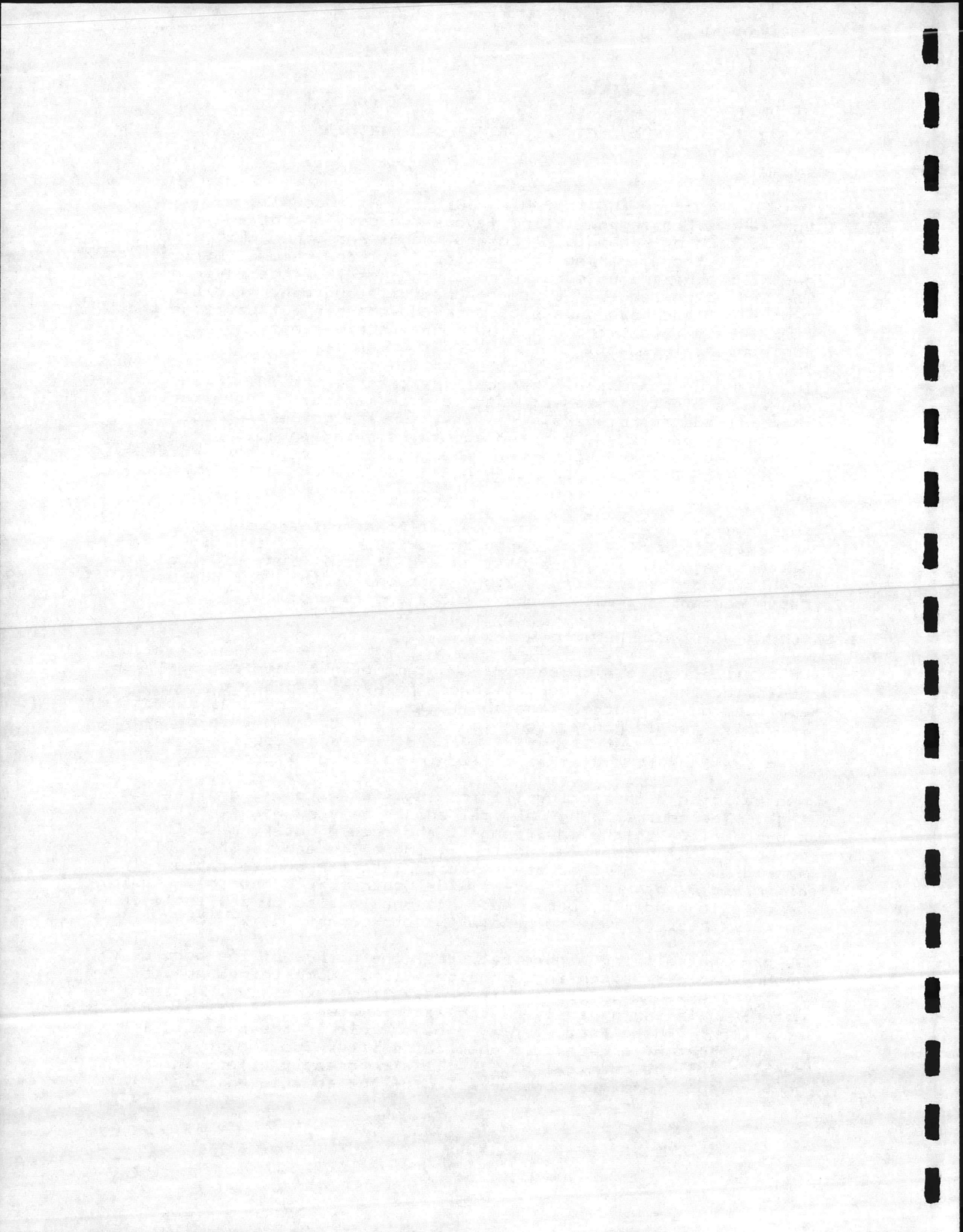
Included in this section on chemical treatment are subsections on neutralization of acids, bases and oxidation and reduction; dispersion; dilution; coagulation and flocculation; sinking agents; and precipitants. Other sections of the text address in depth mechanical removal and methods and absorption.

### B. NEUTRALIZATION - Acids/Bases and Oxidation and Reduction

Neutralization is a process of counteracting a chemical spill and restoring the neutral condition of the water rapidly by application of neutralizing chemicals. The term neutralization is commonly used in connection with acids and bases but is extended to include the neutralization of oxidizing and reducing agents when dealing with chemical spills in bodies of water.

Neutralizing a chemical spill in a body of water is a difficult task. The neutralizing chemical should be very weak and non-injurious to the environment, and should not form toxic compounds. The chemical and/or biological demand (COD < BOD) should be very small so as not to deplete the concentration of dissolved oxygen in the water. The neutralizing chemical should be safe to handle by personnel. It should also be available in bulk quantities, easy to handle and store, and low in cost.

Before neutralizing a chemical spill the nature of the body of water should be taken into consideration. Some things to consider are: natural pH level (acidic or alkaline); fresh vs. marine water; buffering capacity of the water; water movement; and rate of mixing. These factors play a major role in the biological consequences of a hazardous chemical spill. The amount and duration of the chemical spill will also greatly affect the environment. Another consideration of the aquatic environmental



damage due to a chemical spill is the season of the year, since this naturally determines the number and type of organisms present.

Chemical spills in a body of water cause considerable environmental damage. These damages include:

- o altered pH balance
- o cation exchange
- o hydrolysis
- o biochemical oxidation for some chemicals; evaporation for chemicals such as NH<sub>3</sub> and HCl
- o absorption onto colloidal particles and sediments, especially for weaker electrolytes
- o increase in water temperatures
- o increase in ionic strength
- o increase in COD
- o other changes in water chemistry

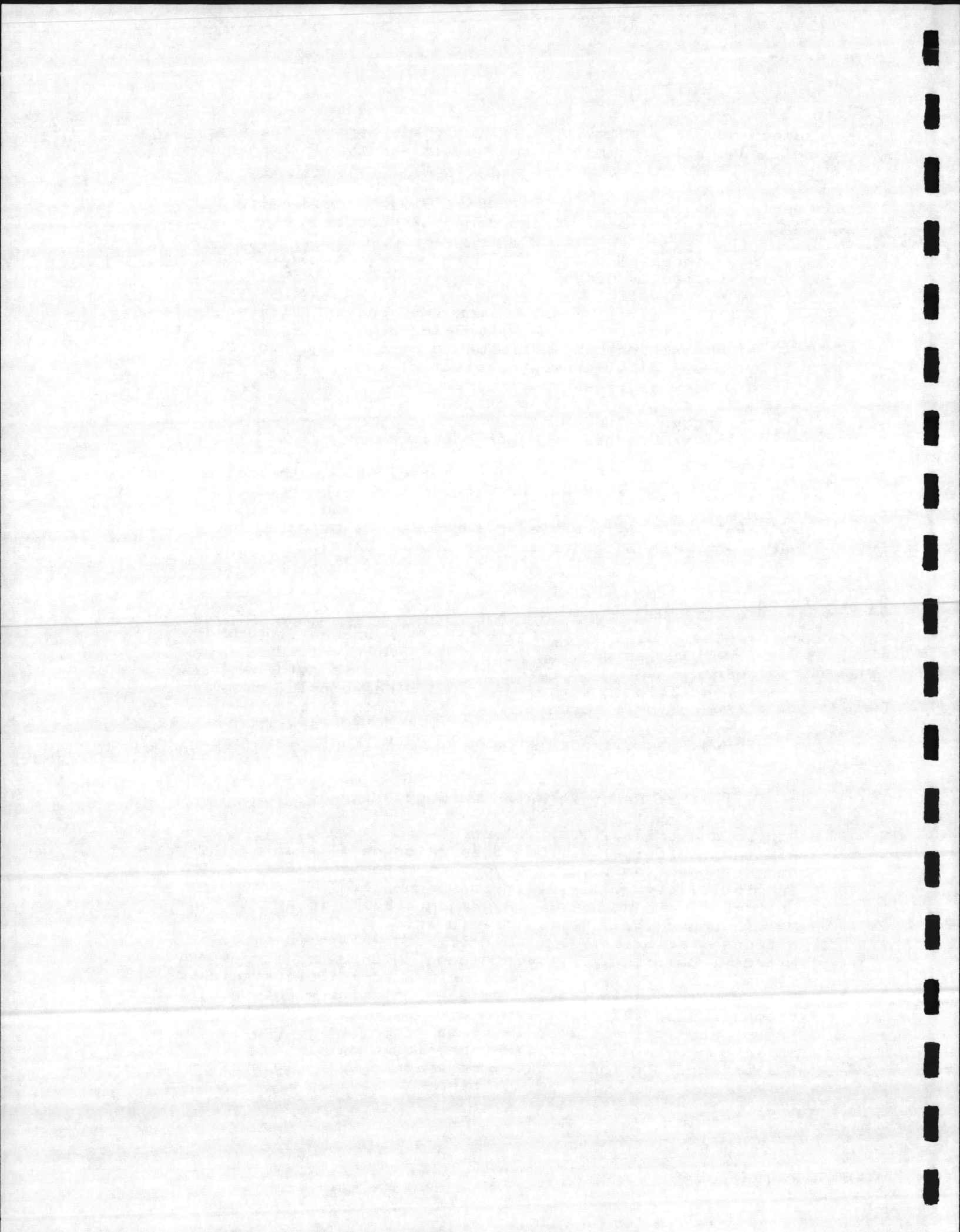
Most of the hazardous chemicals that can be neutralized are acids and bases, chemicals that react with water to form acids or bases, and oxidizing and reducing agents. Listed in the following table are chemicals that are classified as acids or bases and chemicals that react with water to form acids and bases.

#### Acids

Acetic acid	Hydrogen fluoride
Acrylic acid	Nitric acid
Formic acid	Oxalic acid
Hydrochloric acid	Phosphoric acid
Hydrofluoric acid	Propionic acid
Hydrogen chloride	Sulfuric acid
Hydrogen cyanide	Sulfuric acid (spent)

#### Chemicals that React in Water to Give Acids

Acetic/anhydride.....	Acetic acid
Aluminum chloride.....	Hydrogen chloride + (Aluminum hydroxide)*
Benzoyl chloride.....	Hydrogen chloride + Benzoic acid
Bromine.....	Hypobromous acid
Chlorosulfonic acid.....	Hydrogen + Sulfuric acid
Maleic anhydride.....	Maleic acid
Nitrogen tetroxide.....	Nitric acid + (Nitric oxide)*
Nitrosyl chloride.....	Hydrogen chloride + Nitrous acid
Oleum.....	Sulfuric acid + (Sulfur trioxide)*
Phosphorus oxychloride....	Hydrogen chloride + Phosphoric acid
Phosphorus pentasulfide...	Hydrogen sulfide + Phosphorous acid
Phosphorous trichloride...	Hydrogen chloride + Phosphorous acid
Polyphosphoric acid.....	Phosphoric acid
Sulfur monochloride.....	Hydrogen chloride + Sulfuric acid (+ others)*



Sulfuryl chloride.....Hydrogen chloride + Sulfuric acid  
 Titanium tetrachloride...Hydrogen chloride + (Ti-hydrochlorides)\*

\* are not acids

Bases

Aminoethanolamine	Hexamethylenetetramine
Ammonium hydroxide	Hydrazine
Aniline	Methylethylpyridine
Caustic potash solution	Monoethanolamine
Caustic soda solution	Monoisopropanolamine
Cyclohexylamine	Morpholine
Diethanolamine	Potassium hydroxide
Diethylamine	Pyridine
Diethylenetriamine	Sodium hydroxide
Diisopropanolamine	Triethanolamine
Dimethylformamide	Triethylamine
1, 1-Dimethylhydrazine	Triethylenetetramine
Ethylenediamine	Trimethylamine
Hexamethylenediamine	Urea

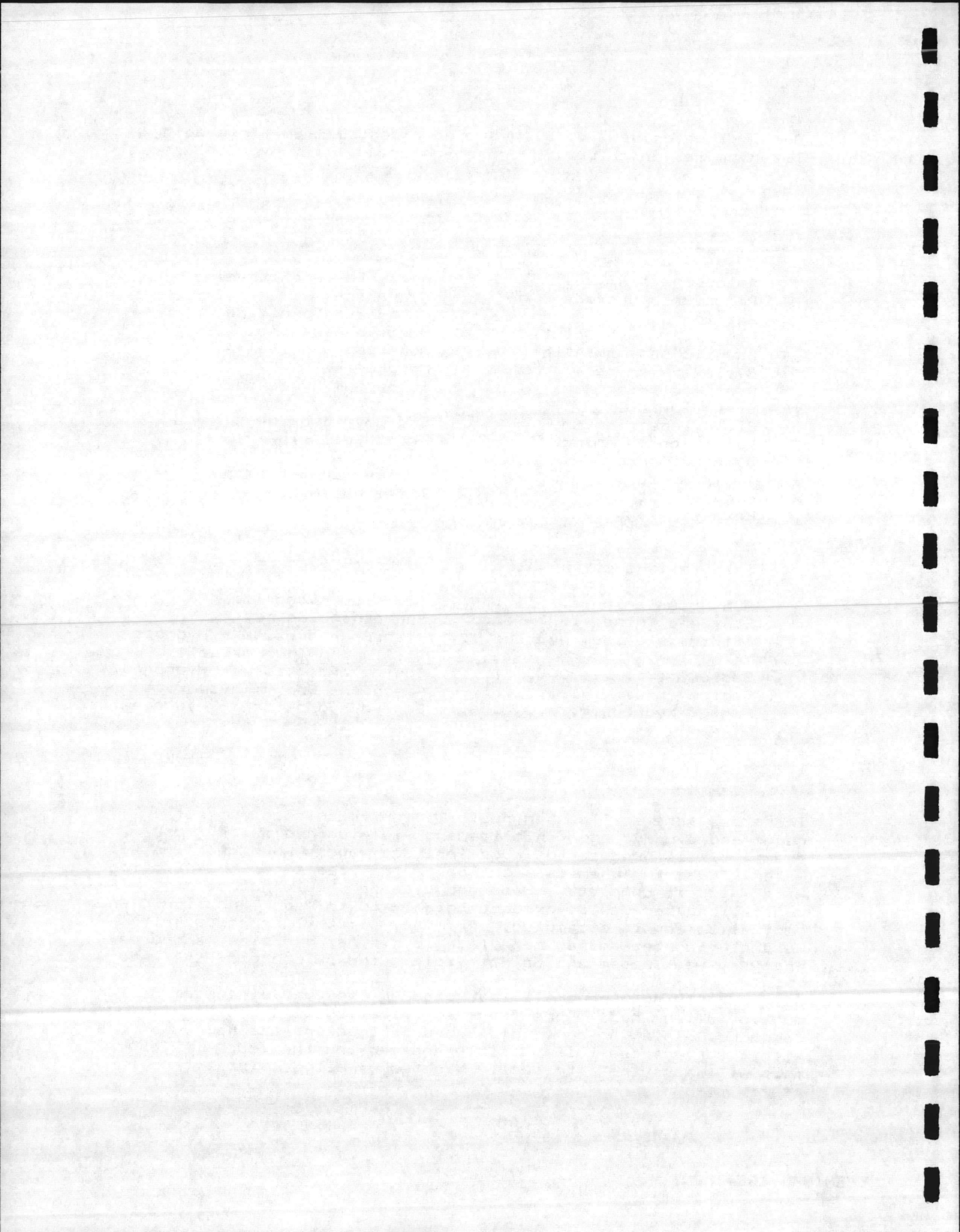
Chemicals that React in Water to Give Bases

Anhydrous ammonia.....	Ammonium hydroxide
Ethylene imine.....	Monoethanolamine
Lithium aluminum hydride.....	Lithium hydroxide(+ Hydrogen + Aluminum hydroxide)*
Sodium.....	Sodium hydroxide (+ Hydrogen)*
Sodium amide.....	Ammonia + Sodium hydroxide
Sodium hydride.....	Sodium hydroxide (+ Hydrogen)*

\* are not bases

There are some spills when neutralizing techniques are not recommended. Hydrogen chloride and ammonium hydroxide, for example, will produce toxic or irritant vapors when reacting with water. These two chemicals can be neutralized after the reaction with water is complete. Hydrogen cyanide should not be neutralized because it produces highly toxic vapor and liquid when neutralization is attempted. Aniline, dimethylformamide, hexamethylenetetramine, methylethylpyridine, pyridine, and urea are very weak bases and do not violate the pH range of the water.

Before applying a neutralizing compound the zone of contamination must be determined to prevent misapplication of the neutralizing compound. This can be accomplished by tracking the hazardous zone with a surface craft if possible and marking the zone with buoys. This will make the site easily sighted by either aircraft or marine craft.



Neutralizing chemicals should be available within the immediate vicinity and stored in easily moveable containers. Most neutralizing chemicals are stored as dry powders in 50 to 100 pound bags. This is important to facilitate the movement of the powder. The powder should not be dumped into the water since little mixing will take place and the dense powder will sink. The preferred application techniques are as follows:

- o to distribute powder over a wide area, mechanical slings or compressed air powder sprays are a possibility;
- o the powder can be mixed with water to form a slurry (for this procedure mixing and dumping equipment is needed).
- o the powder could be added in the region of maximum propeller turbulence to promote rapid solution and mixing.

When applying a neutralizing chemical in still water, the preferred strategy is to start beyond the periphery of the spill and spiral towards the center, using some type of scattering movement.

In flowing waters the discharged chemical moves downstream in a constantly growing, but diluting, sludge. The preferred strategy is to spread the chemical in a zig-zag pattern across the chemical spill. It is best to start downstream of the contaminated waters and work upstream. If this is not possible, the neutralizer can be added near the front end of the spill. If the chemical is added too far downstream it will not be very effective in neutralizing the spill. If the neutralizing agent is too heavy and not mixed well, it will sink to the bottom and the discharged chemical will pass over with no chance to neutralize.

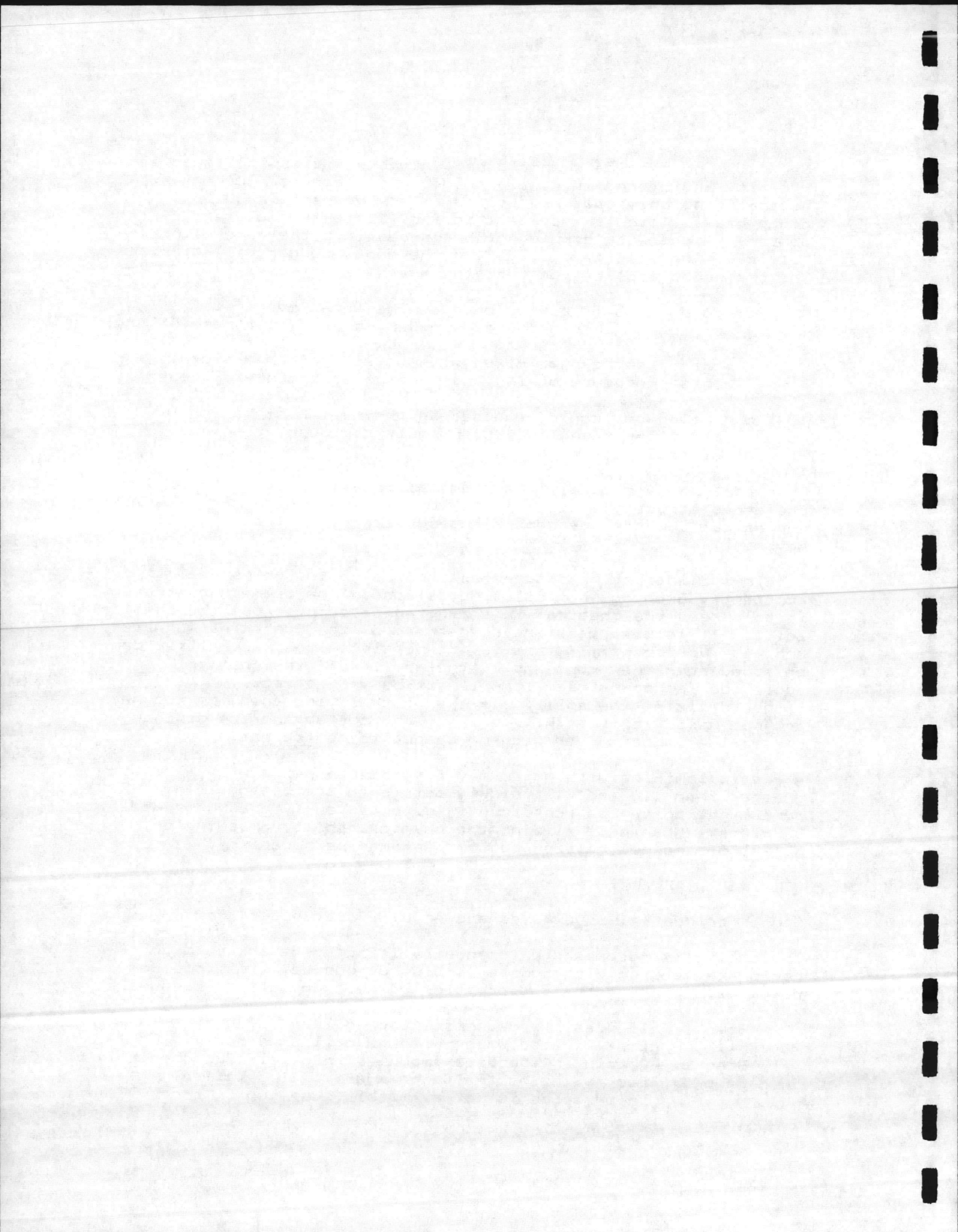
A chemical mixing with water may form a suspension with a density greater than 1.0 and will slowly settle to the bottom. The contamination can be contained if detected early enough by use of barriers. When neutralizing the chemical spill, dredging or burial of the neutralized contaminant may be necessary.

#### C. NEUTRALIZATION STEPS - ACIDS/BASES

Steps for Neutralizing Acids and Acidic Substances:

The chemicals recommended for neutralizing acids are calcium carbonate, sodium bicarbonate, sodium carbonate, limestone, or dolomite. Lime can cause formation of calcium sulfate sludges.

- Step 1: If possible determine the pH level of the contaminated water with pH or litmus paper.
- Step 2: Obtain an adequate amount of neutralizing chemical.
- Step 3: Deploy the neutralizing agent. If detailed information is not available, use two or three times





the weight and/or volume of neutralizing agent to the weight and/or volume of the chemical spill for concentrated acids. For dilute acids use a 1:1 ratio.

Step 4: Monitor the pH of the contaminated water until the pH is restored to normal range.

#### Steps for Neutralizing Bases and Basic Substances:

The chemicals recommended for neutralizing bases are sodium dihydrogen phosphate and dry ice, as well as dilute acetic acid (vinegar).

Step 1: Measure the pH of the contaminated water with a pH meter or litmus paper. Measure the pH at various locations and depths.

Step 2: Obtain an adequate amount of neutralizing agent. For bases use a weak acid as the neutralizing agent.

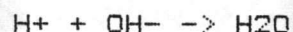
Step 3: Deploy the neutralizing agent in roughly equal amounts to discharged contaminant.

Step 4: Monitor the pH of the contaminated water as the neutralizing agent is added until the normal pH range is restored.

#### Acid and Base Neutralization: Method #2

A second method for neutralizing acids and bases is presented below. It is a more precise method than the previous one, and therefore also more complex, requiring an understanding of the chemistry and mathematics involved.

Acids are substances which donate a hydrogen ion, H<sup>+</sup>, in aqueous solutions. Bases are substances which donate an hydroxide ion, OH<sup>-</sup>, in aqueous solutions. The neutralization of acids and bases occurs by the following reaction:

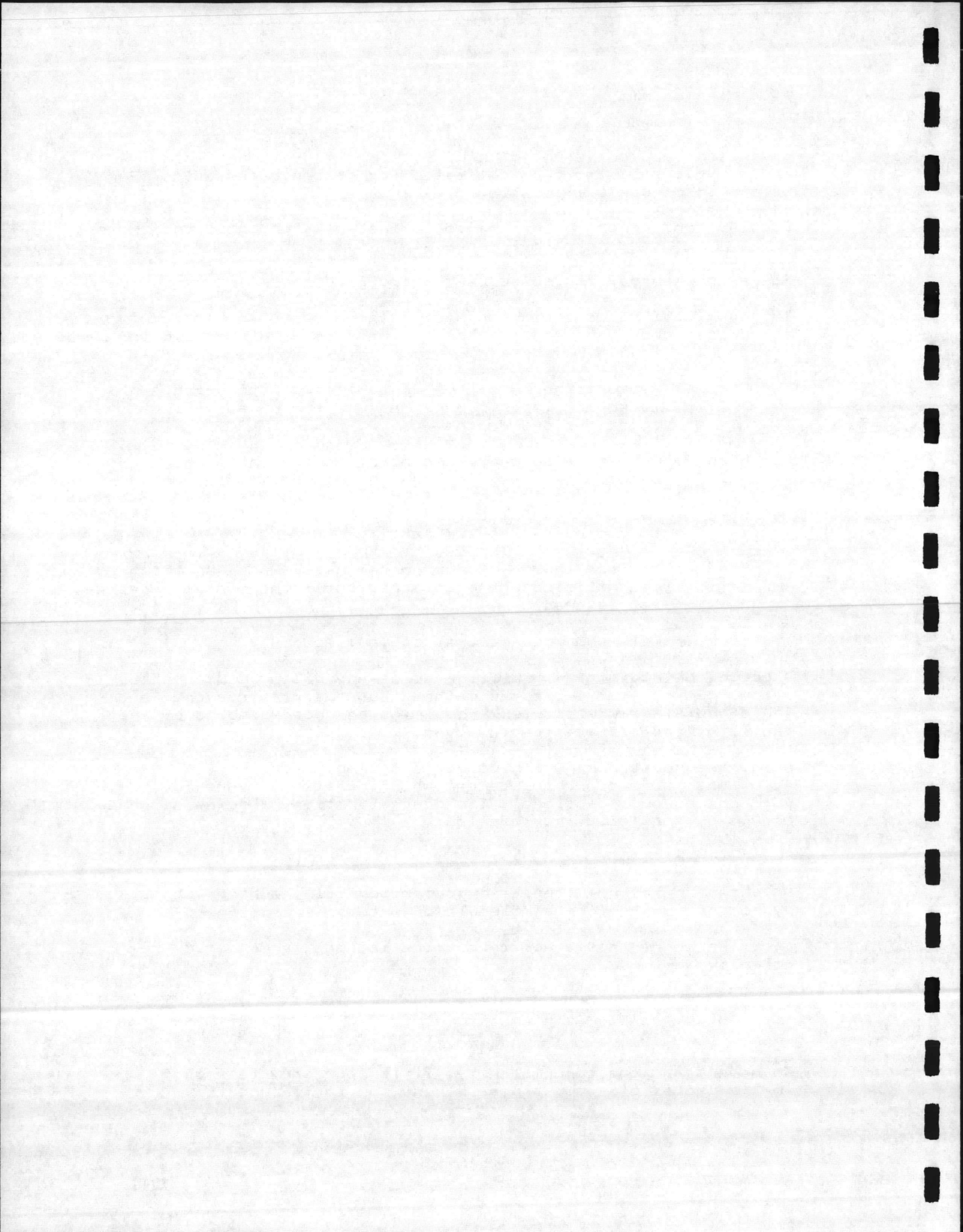


As shown in the reaction, a hydrogen ion will combine with a hydroxide ion to form a molecule of water.

The concentration of these ions is usually measured in molarity (M).

$$\text{Molarity (M)} = \frac{\text{moles}}{\text{liter of solution}}$$

To understand the term molarity, it is necessary to know what a "mole" of a substance is, and how to measure it.

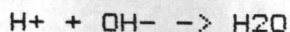


A mole can best be understood by relating it to the term, "dozen." A dozen of anything would have twelve items.

A "mole" of items would have  $6.02 \times 10^{23}$  items, or 602,000,000,000,000,000,000,000 items, a very large number.

A mole of a substance also has weight. The weight of a mole of atoms depends upon the atomic weight of the specific atom or molecule. For example, one atom of hydrogen, which is equal to one ion of hydrogen, has an atomic weight of 1.0. Therefore, 1.0 grams of hydrogen ions would have 1.0 "gram" - moles of hydrogen ions. Water has a molecular weight of 18. Therefore, 9.0 grams of pure water would have 0.50 or one-half "gram" - moles of water.

The term "mole" is also used when talking about chemical reactions. Going back to the water reaction:



The equation should be read, "1.0 moles of hydrogen ion combines with 1.0 moles of hydroxide ion to form 1.0 moles of water." In chemical reaction equations, ions and molecules with no number preceding them are understood to be 1.0 moles of substance. Take for example this next reaction:



This equation reads, "2.0 moles of NaOH combines with 1.0 moles of H<sub>2</sub>SO<sub>4</sub> to produce 2.0 moles of water and 1.0 moles of Na<sub>2</sub>SO<sub>4</sub>."

When moles and molarity are understood, it is possible to learn how to precisely neutralize a given amount of acid or base solution.

Pure water at 25 degrees C has an equal and constant concentration of hydrogen and hydroxide ions:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} M$$

(the symbol "[ ]" stands for "concentration of ")

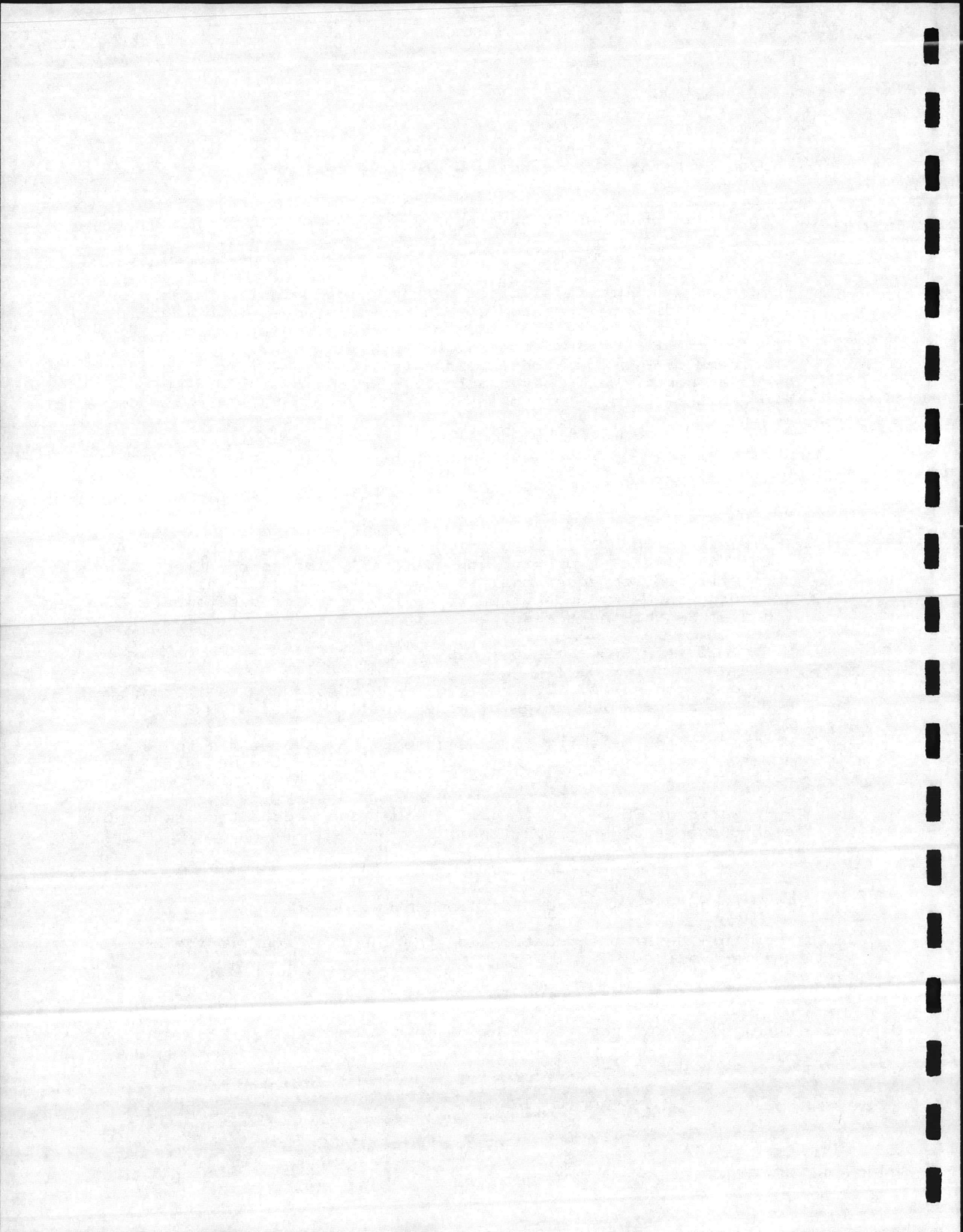
From this data, the equation for the chemical equilibrium of water was derived:

$$[H^+] [OH^-] = 1 \times 10^{-14}$$

then, by taking the logarithm of both sides:

$$pH + pOH = 14$$

$$\text{where } pH = -\log [H^+]$$



$$\text{pOH} = -\log [\text{OH}^-]$$

Therefore, by knowing the pH and amount of acid or base spilled, the exact amount of neutralizing acid or base can be determined.

For example, determine the amount of neutralizer needed to neutralize 1/2 liter of a basic solution.

Step 1: Determine the pH of the spilled solution using pH paper.

In this example, the pH was measured to be 13.0.

Step 2: Estimate the amount of the spill.

This might be difficult to do, particularly in cases of spills occurring in water. For ease of calculation, the spill occurred on land, and involved 1/2 liter of solution.

Step 3: Set up the equation to determine the number of moles of hydrogen or hydroxide ion to be neutralized.

$$\text{pH} = 13.0 \text{ (from pH paper)}$$

Take the antilog of both sides:

$$[\text{H}^+] = 1.0 \times 10^{-13} \text{ M}$$

Substitute this value into the equation:

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

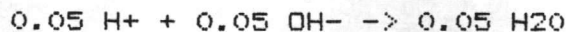
$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-13}}$$

$$[\text{OH}^-] = 0.1 \text{ M. or } \frac{0.1 \text{ moles OH}^-}{\text{liter}}$$

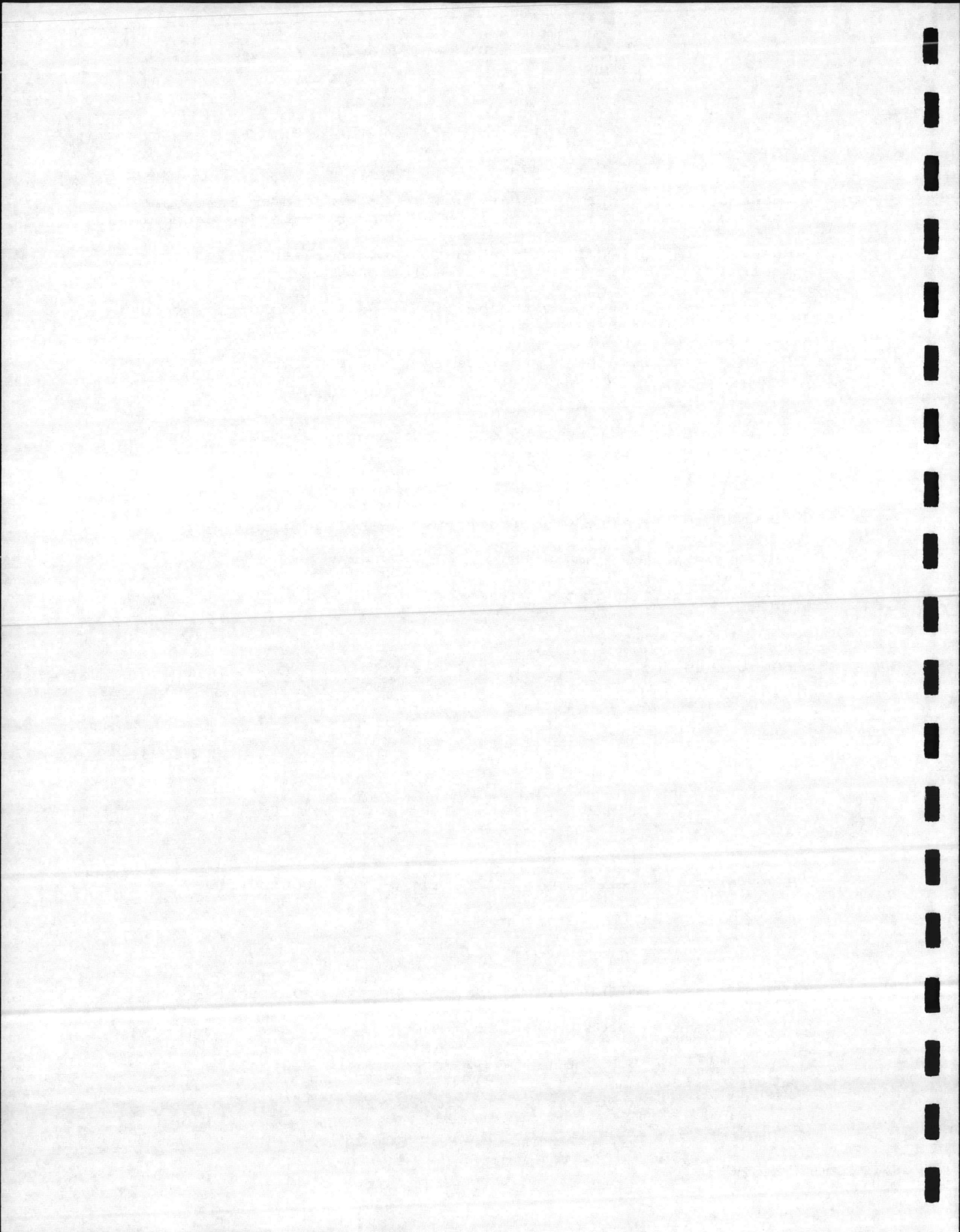
But, since there was only 1/2 liter of solution spilled.

$$\frac{0.1 \text{ moles OH}^-}{0.5 \text{ liters}} = \frac{0.05 \text{ moles OH}^-}{\text{liter}}$$

Therefore, from the neutralization reaction equation:



There must be 0.05 moles of hydrogen ion to neutralize 0.05 moles of hydroxide ion!



Step 4: Determine the pH and amount of neutralizer needed.

The neutralizer used should be weak, easy to handle, inexpensive, readily available, and with little or no environmental risks. For this example, there must be an acidic solution, such as acetic acid (vinegar).

Using pH paper, the pH of the vinegar is approximately 2.8.

$$\text{pH} = 2.8 = -\log [\text{H}^+]$$

Taking antilogs:

$$[\text{H}^+] = 0.00158 \text{ moles} \\ \text{liter}$$

$$(.00158 \text{ moles}) \\ \text{liter} \times \text{liters} = 0.05 \text{ moles}$$

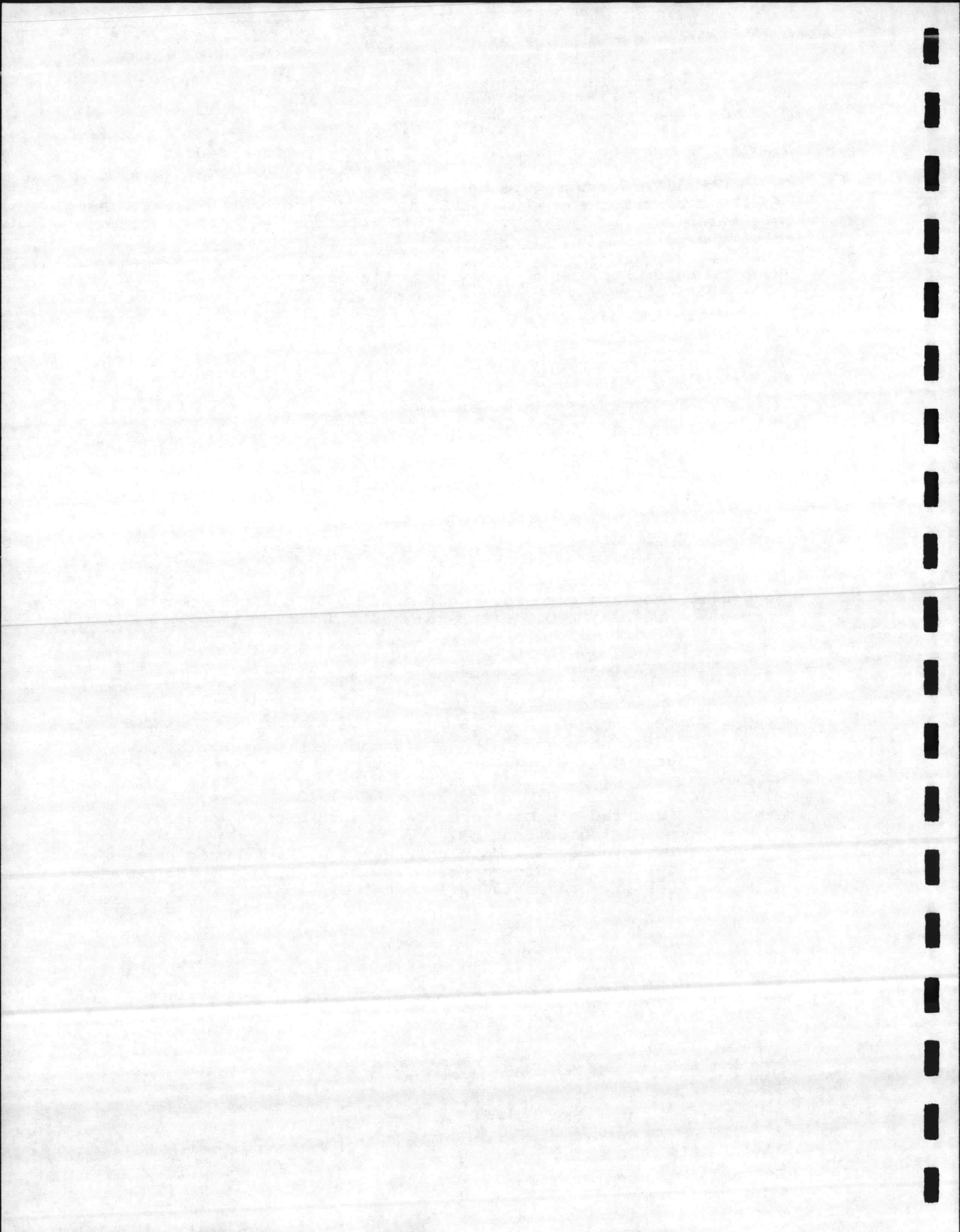
$$X = \frac{0.05}{0.00158} = 31.6 \text{ liters acetic acid needed.}$$

Therefore, from the example, there must be 31.6 liters of vinegar to neutralize 0.5 liters of basic solution to a pH of 7.0.

Listed below are some advantages and disadvantages of both methods.

Method #1 Advantages - Easy to follow, faster response method,  
Disadvantages - Can easily under or overshoot the pH desired. Can be more expensive, particularly in the case of very large spills.

Method #2 Advantages - Most precise method, better accuracy at obtaining desired pH.  
Disadvantages - Math and chemistry background needed to implement. Slower response than method #1. Calculator usually needed to perform calculations.





#### D. NEUTRALIZATION OF OXIDIZERS AND REDUCERS

Acids and bases can also act as oxidizers and reducers. It is important to monitor the dissolved oxygen level in a body of water with a dissolved oxygen probe when neutralizing an acidic or basic chemical spill, since these can cause a change in the COD and/or BOD of the water. The natural dissolved oxygen concentration is about 5 ml/l. If this level is reduced by more than one-half, serious problems may exist for the aquatic life present.

Oxidizing agents are neutralized by reducing agents. Reducing agents can be defined as anything that will burn in air. The best possible reducing agents for neutralizing oxidizers are the naturally occurring organic materials in water. Sodium thiosulfate and calcium sulfite are good reductants as well as sewage. The recommended chemicals for neutralizing oxidizing agents are carbon, vegetable oil, or corn syrup. The behavior of the discharged chemical should be matched to the behavior of the reducing agent, e.g. carbon sinks, vegetable oil floats, and corn syrup dissolves.

The best possible technique for neutralizing reducing agents which have depleted oxygen levels in water is with the use of oxygen or aeration of the water. Ozone, peroxides, or permanganates can be used as neutralizers. Care should be taken when using a powerful oxidant because fire and explosion can occur when in contact with combustible materials.

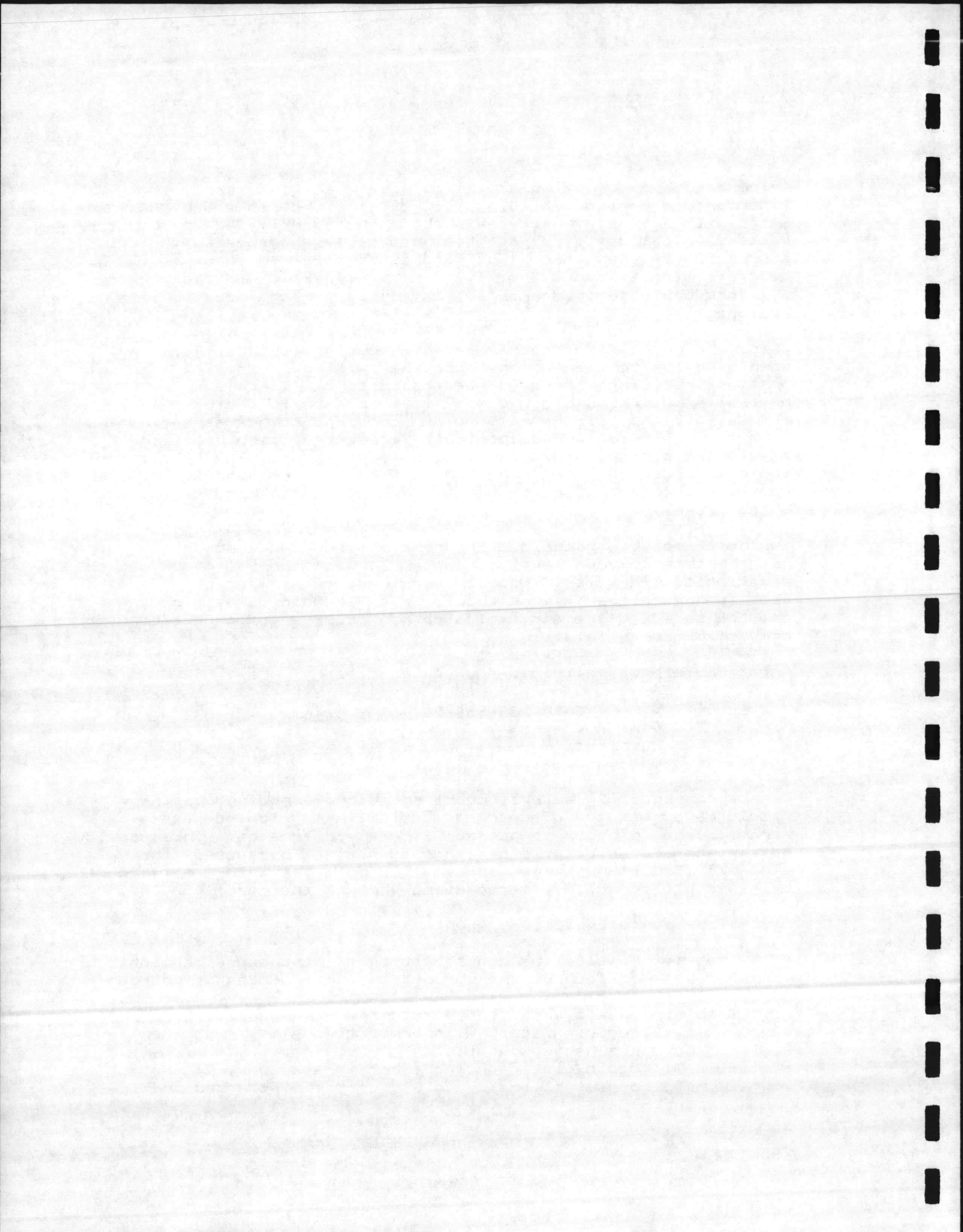
Aeration methods fall into four categories:

1. Stirring and agitating
2. Dams and weirs
3. Bubbling
4. Spray formation

When aerating still waters, bubbling is preferred. Bubbling should be across the discharged chemical. In flowing waters, aeration should begin downstream from the discharge. This should take place a considerable distance downstream because of the slowness of COD/BOD oxygen uptake. If not, the water will become oxygen depleted again after passing through the bubbling zone.

#### Neutralization of Oxidizing Agents

- Step 1: Measure the concentration of discharged chemical or look up the solubility limit of the discharged chemical.
- Step 2: Obtain an adequate amount of a naturally occurring reducing agent with properties similar to the discharged chemical.
- Step 3: Deploy the reducing agent in a roughly 2:1 ratio of weight and/or volume of the discharged chemical.



## Neutralization of Reducing Agents

- Step 1: Measure the concentration of discharged chemical or look up the solubility limit of the discharged chemical.
- Step 2: Select aeration method that is appropriate for the area of chemical contamination.
- Step 3: Aerate the water until the oxygen level has returned to normal.

## E. DISPERSION AND DILUTION

The main objective of the dispersion technique for hazardous spill cleanup is to spread out the spilled chemical so that the concentration of the contamination is below the recommended limits. Dispersion leads to rapid dilution of the chemical.

The use of a dispersant, as is with the use of water as a diluent, is a decision made on a case-by-case basis. The decision should be based on environmental conditions at the site, the amount of chemical spilled, the chemicals toxicity and similar considerations.

Chemicals which are lighter than water, non-soluble in water, and those with oil-like properties will disperse when discharged in water. The rate of dispersion of these chemicals depends on the chemical, currents, sea-state and other meteorological and environmental conditions. This dispersion is commonly so slow that ecological damage results before dispersion is complete. Listed below are some chemicals which are subject to dispersion.

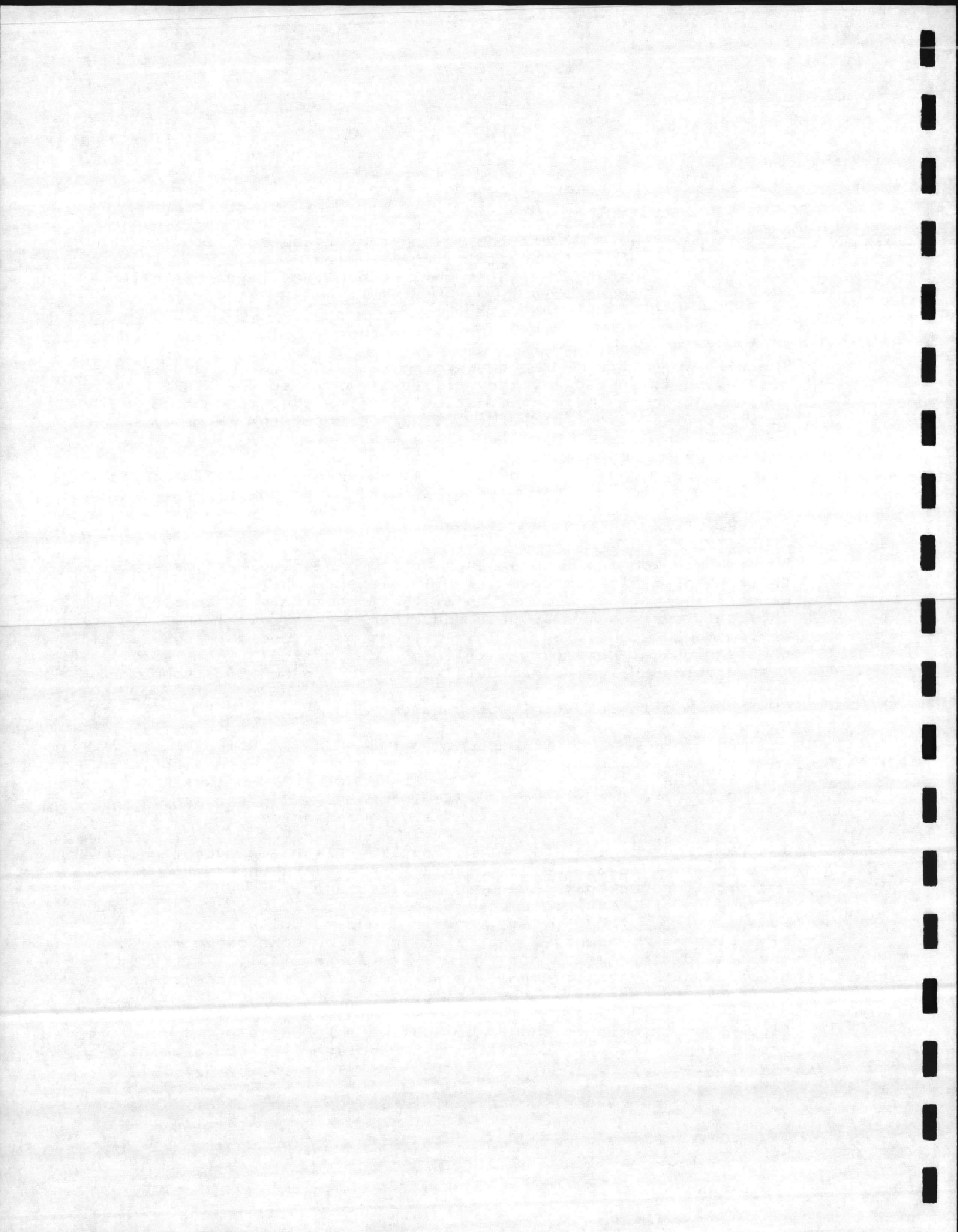
### CHRIS Chemicals Subject to Dispersion:

Aniline	Carbonic oil	Dimethyl sulfate
Benzoyl chloride	Cresols	Epechlorohydrin
Bromine	Dichloromethane	Furfural
Calcium oxide	2,4- Dichlorophenol	Toxaphene
	Lithium aluminum hydride	

The EPA, through the 1510 Plan, requires, with few exceptions, that chemical agents not be used as dispersants unless the technical product data has been provided and accepted by the EPA's Oil and Special Materials Control Division. This technical data is essentially the physical, chemical and toxicity characteristics of a dispersing agent. Dispersion should be considered when the chemical discharged is not a highly toxic chemical. To try to disperse highly toxic chemicals will result in an increase in environmental damage as the chemical spreads.

Dispersion techniques should be applied only where water conditions are appropriate. The conditions where disperison could be used are itemized as follows:

- o In open water, where rapid dilution might be



expected upon dispersion.

- o In small streams flowing into large rivers.
- o At the mouth of a harbor with fast tidal currents.

There are two possible ways for dispersing a discharged chemical; mechanical and chemical. Mechanical dispersion can be accomplished by water streams from fire hoses, propwash from a boat and compressed air.

Chemical dispersants are commercially available and are usually available in a liquid form. These chemicals can be applied to a chemical spill or oil slick by spraying from an aircraft, ship or from shore.

Chemical dispersants are surfactants and orient at an oil-water interface, reducing surface tension and promoting droplet formation. It should be noted that because dispersants are organic chemicals, dispersants increase the chemical and/or biological oxygen demand (COD and/or BOD). A good dispersant should contain no phosphates, halogens, or heavy metals and should be readily biodegradable. The flash point should also be high so as to not represent a fire hazard.

Dispersion should be used only as a last resort since most chemical spills should be contained, removed and/or neutralized.

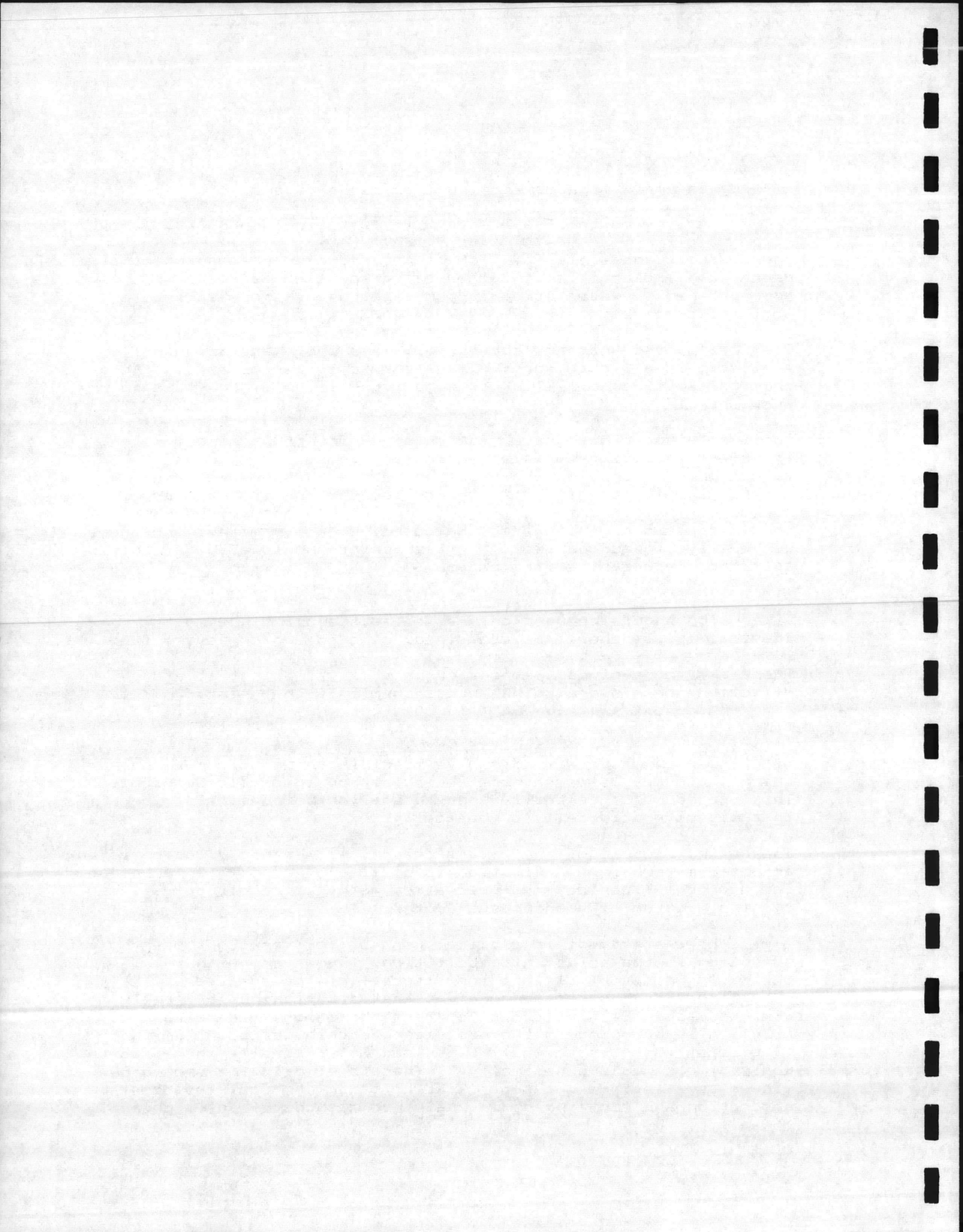
There are no developed methods currently available that are effective for dispersing hazardous chemicals that sink.

#### F. DILUTION

Dilution with water will dissolve miscible or soluble chemicals quickly and may disperse some immiscible or insoluble compounds. This procedure is generally used to ameliorize chemicals that dissolve acidically or basically.

The nature and use of the waters determines whether dilution is an acceptable technique. Dilution is considered a possible technique for hydrogen fluoride, sulfuric acid, methyl alcohol, potassium cyanide, sodium alkybenzenesulfonates.

A well used statement in chemical control for years has been "Dilution is the solution to pollution." However, with the increasing costs of cleanup and disposal of the spilled substances, it has become apparent that dilution has extremely limited uses. Perhaps a more current philosophy regarding dilution is embodied in the statements attributed to Al Smith -- "The least water is the best water and water usually increases the costs of cleanup exponentially." Therefore, dilution should be viewed as a last resort superceded by other chemical treatments, absorption and containment as preferred methods of spill control.



## 6. COAGULANTS AND FLOCCULANTS

Coagulants are materials which encourage aggregation of colloid matter to precipitate and/or flocculate. Flocculants are materials that precipitate themselves and in so doing will bring down the pollutants with them. The removal of pollutants by both coagulants and flocculants is by sedimentation.

\*Coagulation and flocculation are procedures often employed by waste water treatment plants. For chemical spills, the decision to utilize this procedure will be determined by the toxicity of the pollutant and the nature of the water. However, there are no clear-cut procedures for the use of coagulants and flocculants.

Alum (potassium aluminum sulfate) is the most widely used as a water treatment chemical. Listed below are other coagulants and flocculants.

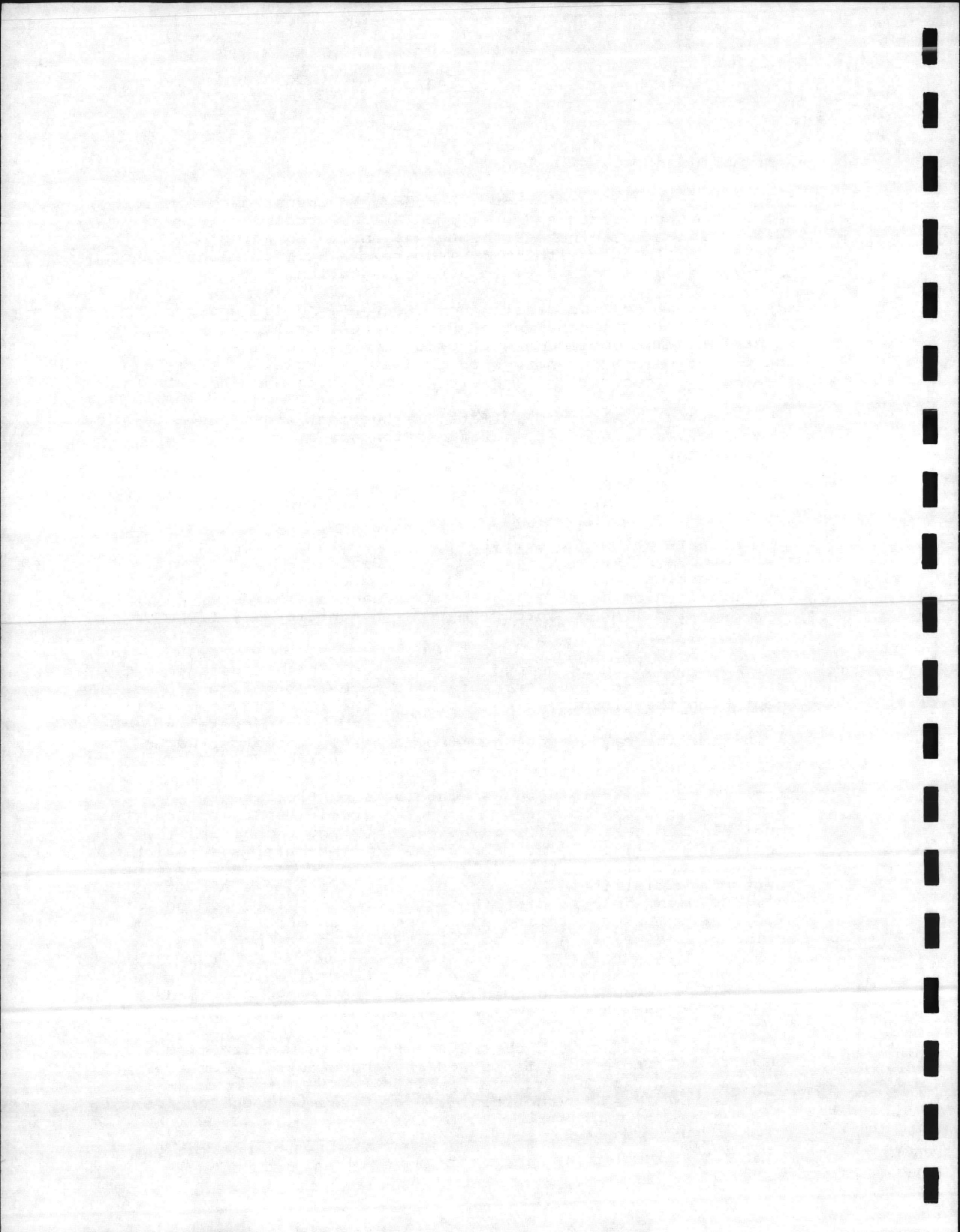
Coagulants	Flocculants
Bauxite (aluminum sulfate)	Aluminum ammonium sulfate
Ferrous sulfate	Bentonite
Ferric sulfate	Calcium carbonate
Sodium aluminate	Carbon dioxide
Hydrated lime or Quick lime	Synthetic acrylic polymers

Before coagulation is deemed necessary as a hazardous chemical remover, it is advisable to obtain as much information as possible about both the discharged chemical and the intended coagulant or flocculant. This information may be found on the container labels or information may be obtained from a nearby industry, water treatment plant, or from water treatment engineers.

Most of the chemicals used as coagulants or flocculants are available in a dry powder or granular form. Deployment of these chemicals can be accomplished by crop dusting techniques from airplanes or helicopters. For granular chemicals, a rotating disk-type granular fertilizer spreader can be used. When fine powders are distributed from a ship the ship's wake and other water movement help to distribute the powder. Too much agitation will impede the coagulation and flocculation process, prevent settling, and maintain the pollutant in suspension.

The steps given below may be used as a general guide to be used when this procedure is deemed necessary to remove a hazardous chemical. These are guidelines established in the CHRIS manuals:

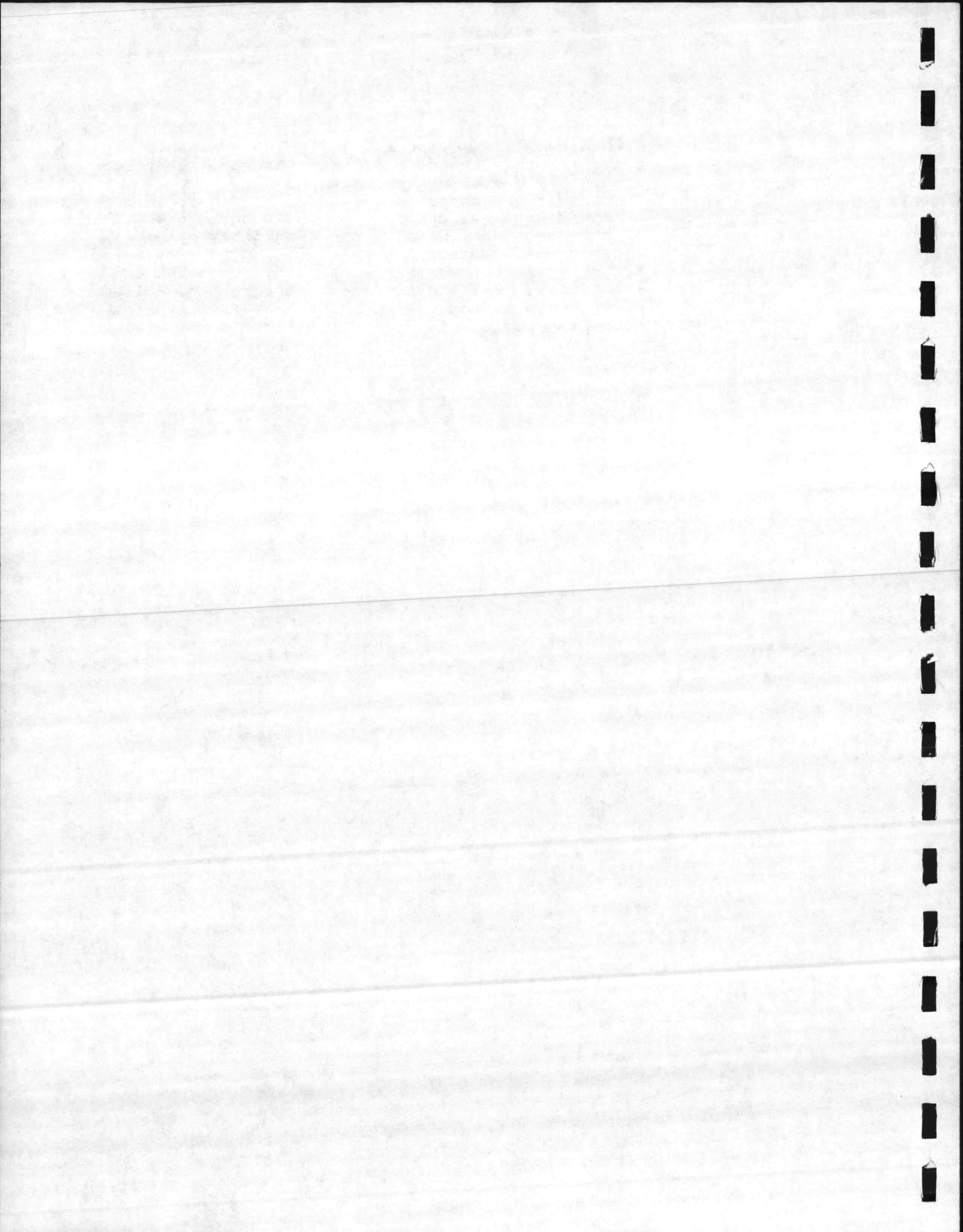
- Step 1: Select and obtain a sufficient quantity of one or more coagulants and/or flocculants. (Consider economy and availability.)
- Step 2: Prepare the agent(s) for dispersal, dry or premixed





with water. The dispersal equipment available may determine this choice. If more than one agent is used, they may be mixed together.

- Step 3: Disperse the agent(s) evenly over the whole area of the discharged chemical. Add 10 to 50 grams of the agent (dry weight) for each cubic meter of water to be treated.
- Step 4: Mix or agitate the water vigorously for about one minute immediately after adding the agents, follow with gentle mixing for an additional five minutes.
- Step 5: Allow the coagulants and/or flocculants to settle.



## H. SINKING AGENTS

Sinking agents are those materials which are applied to oil and hazardous substance spills to sink the floating pollutants to the bottom. The hazardous material is then destroyed by bacteria and other natural processes.

There are no established guidelines for the use of sinking agents in response to hazardous chemical spills. Finely ground chalk is most often used as a sinking agent. Other materials include treated and untreated sand, carbon powder, kaolin, calcite, other mineral substances, treated ground fuel, and gypsum. Gypsum is used most often for settling material in sea water. This forms a hard crust preventing the release of oil pollutants.

### 1. Recovery of Chemicals That Have Been Treated With Sinking Agents

Recovery of a chemical that has settled on the bottom is determined by the toxicity of the discharged chemical. If removal of the chemical is necessary, knowing the area of the underwater pollutant is a must. To find this, surface sampling is necessary using a small grab sampler. Suction dredging techniques should be applied to recover and safely dispose of the chemical. Wire-line bucket techniques are not recommended because they are prone to reactivate the suspension of the chemical.

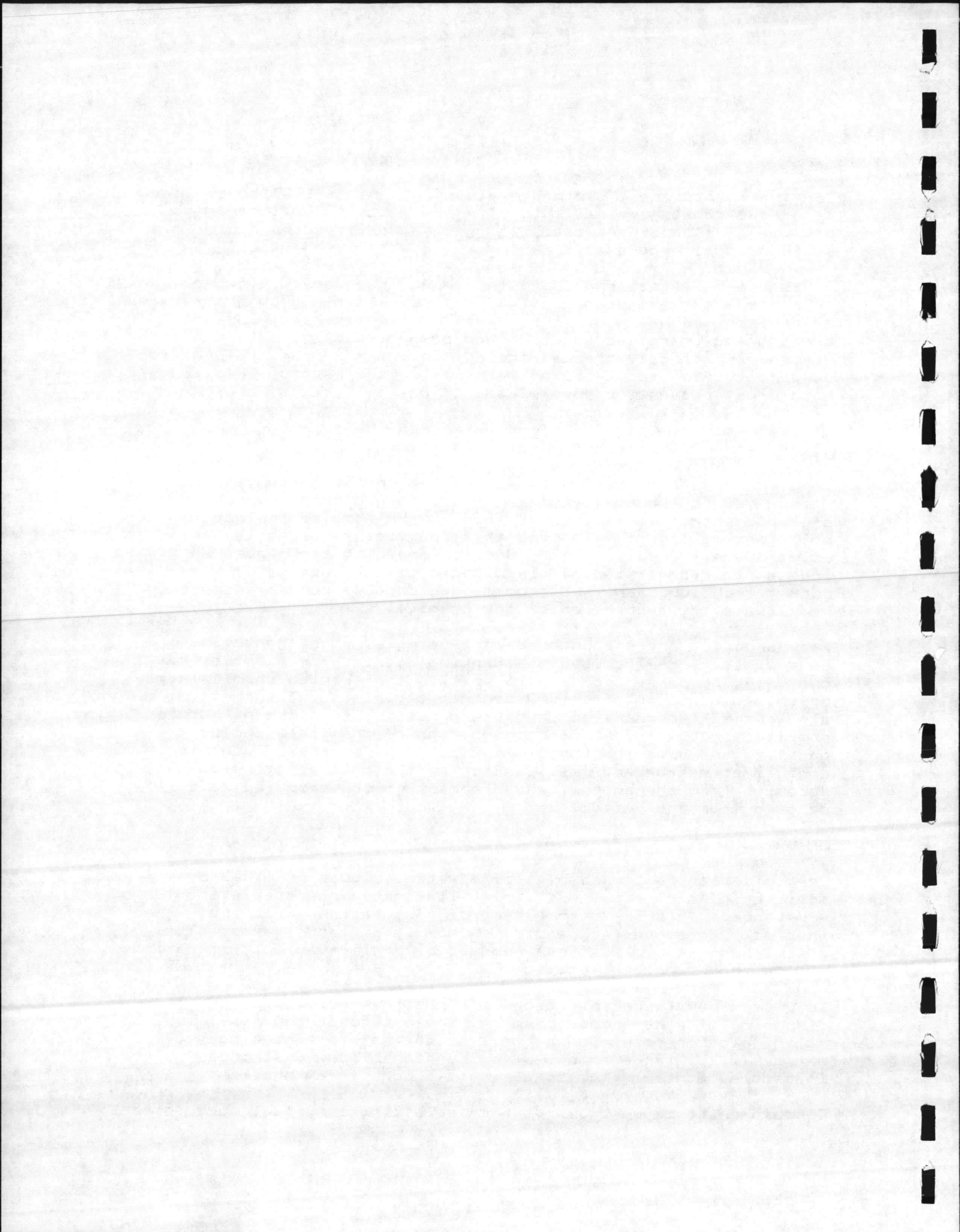
Many problems are encountered when using sinking agents, coagulants, and flocculants. Sinking agents, for example, may only sink 50 percent of an oil spill. The settled chemicals may be injurious to the fish and benthic organisms. The chemical may also become incorporated into the predatory food chain. Other problems associated with sedimentation of chemicals include handling and distribution of fine powders, burial of benthic organisms, escape and resuspension of the pollutant, removal of deposits from the bottom, and disposal of contaminated material removed from the bottom.

## I. PRECIPITANTS

Precipitation is the removal of a water soluble chemical by the addition of a chemical with which it forms a new stable insoluble substance. This leads to a type of coagulation where the insoluble compounds aggregate to form larger aggregates. The discharged chemical is then removed by sedimentation, filtration, floatation, or centrifugation.

To determine if precipitation is a possible procedure for disposing of a hazardous chemical the nature of the spill must be taken into consideration as well as the nature of the body of water. (i.e., large amount of suspended solids, a strongly insoluble, contaminant, or a sensitive downstream process).

Certain criteria must be met when selecting a suitable precipitant



for use in treatment of a hazardous chemical spill. The reagent to be used must reduce the toxic chemical in a solution to within an acceptable limit. The reagent must be soluble in water. Any reagent remaining in the solution after treatment must be at a nonharmful level and should not cause any biological changes in the environment, nor should it alter the chemical balance of the water, e.g., pH changes. Misapplication of the reagent to be used should not cause toxic effects. The reagent to be used should also be economical, readily available, easy and safe to handle.

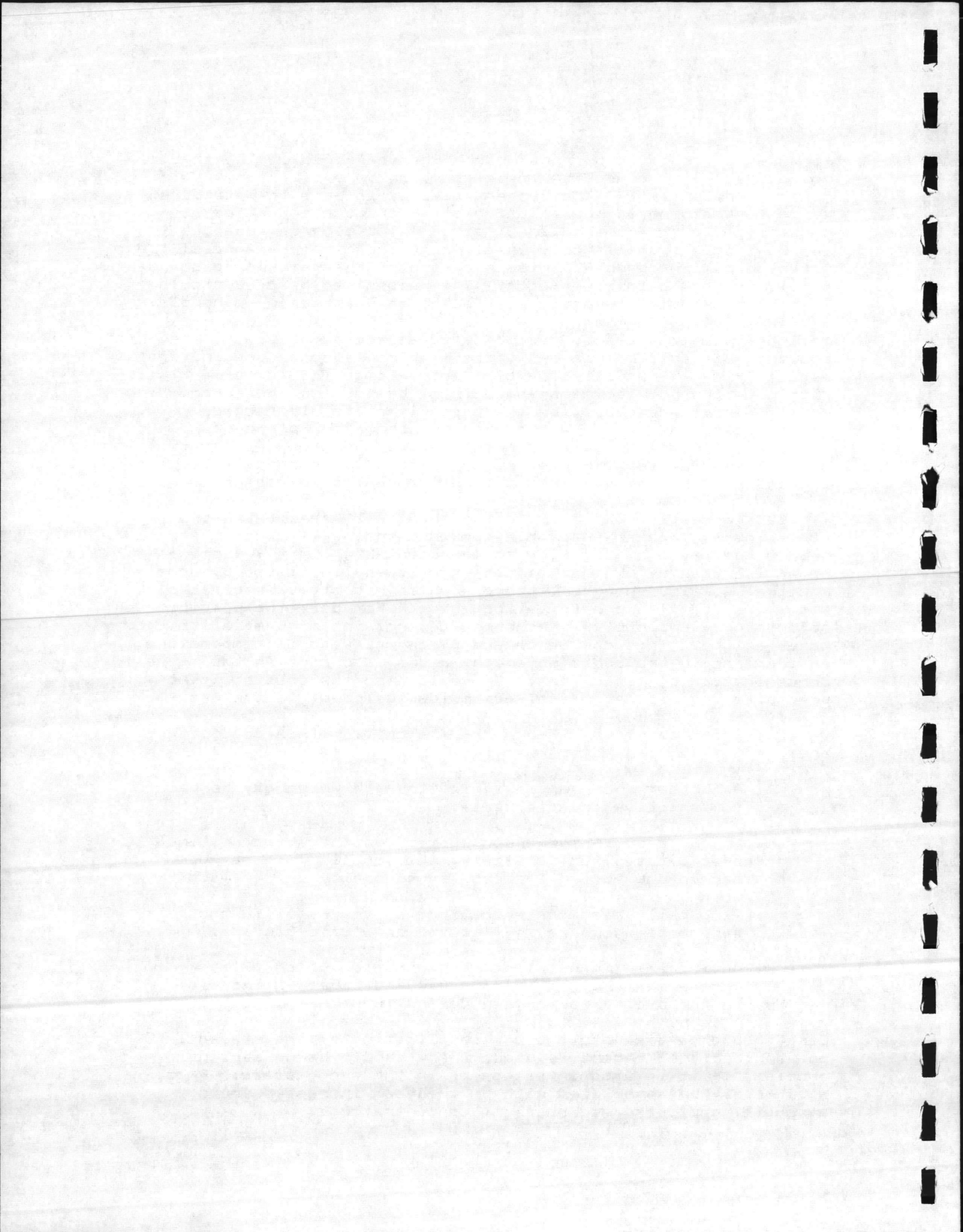
Most heavy metals can be precipitated as the hydroxide by the addition of caustic soda or lime. They can also be precipitated as a sulfide. Precipitation of a metal to an insoluble form will eliminate the problem of seepage into the soil or the surrounding environment. When applying the precipitant to discharged chemicals the pH of the water must be within the proper range necessary for the reagent to properly precipitate. Application is accomplished as is with most other powders. The precipitated chemical may be removed from the environment by dredging.

If used correctly, a precipitating agent will react with the contaminant, form an insoluble compound that will precipitate, and reduce the level of toxicity to an acceptable limit. There may be an increase of pH that offsets the low pH initiated by some chemical spills. However, there are many problems associated with the use of a precipitating agent. For one, the precipitated material may redissolve, returning the hazardous chemical to the water column. This can be caused by an increase in temperature, an increase in the ionic strength, and by a change in the concentration of toxic ions. There is also the possibility of precipitating natural dissolved solids (calcium) in the water.

Other effects caused by treatment of a spill with a precipitant are:

- o A further increase in ionic strength which may be harmful to sensitive aquatic biota.
- o An increase in suspended solids concentration; if the precipitates settle slowly, the aquatic life may be harmed due to the increase in turbidity of the water.
- o Abnormally high concentrations of the metal in the sediments which may effect the benthic organisms.
- o An increase in nutrient concentration which will accelerate the growth of algae and cause an increase in the biological oxygen demand (BOD).

Care should be taken to avoid misapplication of the reagent. If the appropriate reagent is used, there should be no serious problems if it is used in excess or in the wrong place. Problems will mainly be associated with pH changes, increased ionic strength, and increased nutrient concentrations.



## XIV. LABORATORY SPILL RISKS

### A. SCOPE

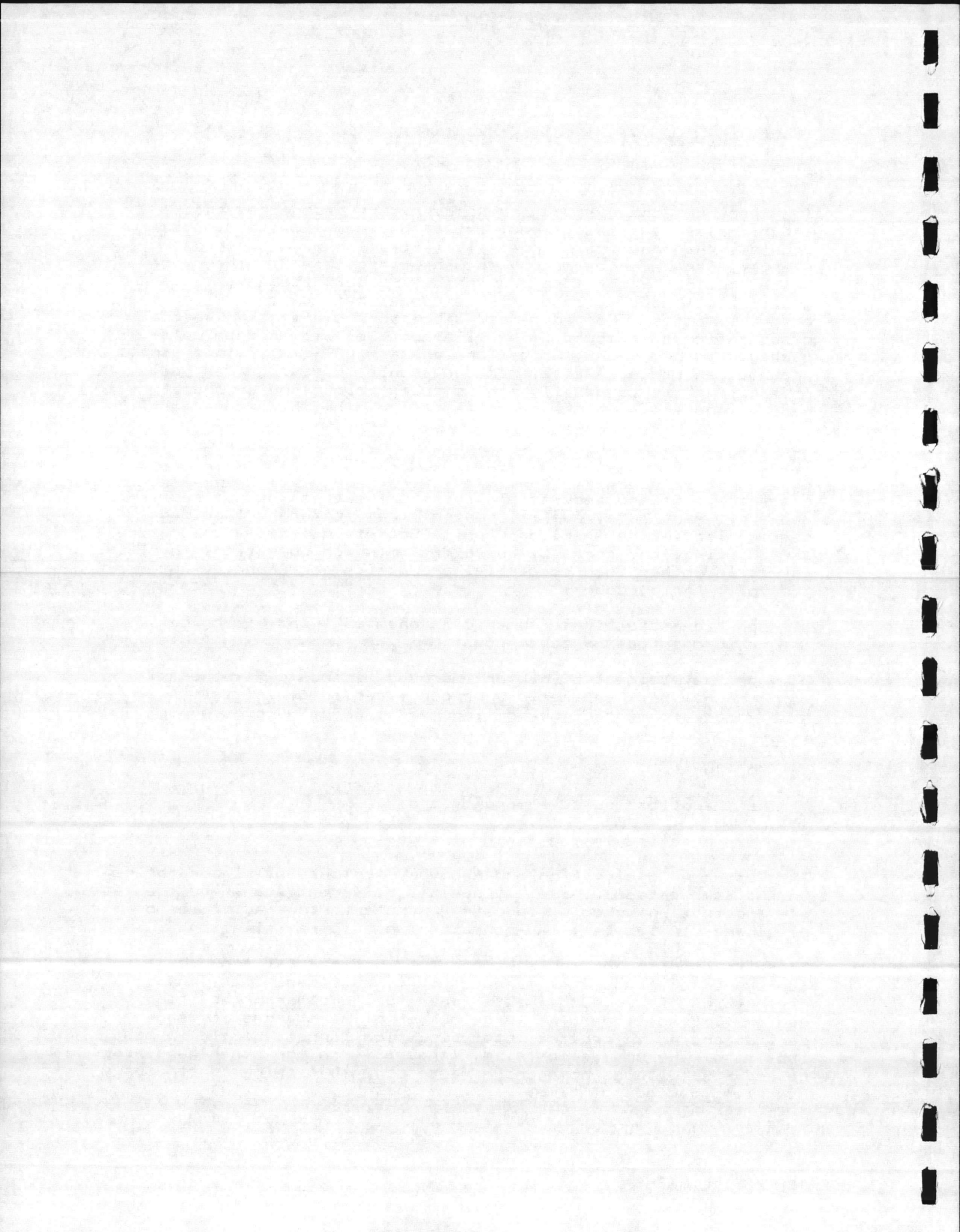
The Resource Conservation and Recovery Act recognizes that laboratories have a different set of hazardous waste disposal problems than chemical process facilities or manufacturing plants. Laboratories occupy an unusual position in the overall waste chemical program in that there are definite advantages and greater latitudes in laboratory disposal methods than with other chemical wastes. For instance, laboratories are given special dispensation to dispose of small amounts of liquid chemicals packaged in LAB PACKS (55 gallon drums - DOT 17H). These small amounts can range in size from one ampule to five gallon pails. In addition, it is usually more cost efficient for a laboratory to handle laboratory wastes separately from other hazardous waste.

Various types of laboratories include instructional laboratories found in high schools, colleges and universities; medical laboratories such as in hospitals, clinics and pharmaceutical research labs; and industrial laboratories that include research and development labs, quality control labs, standard labs, and testing labs. The American Chemical Society defines a laboratory as "Buildings and areas of buildings in which operations involving chemicals, other than commercial production, are carried out for the following purposes:

- o "investigation of physical, chemical, and biological properties of substances;
- o "development of new or improved methods of synthesis, analysis, separation, or purification of initial development of new or improved chemical processes or products;
- o "quality assurance;
- o "application development; and
- o "practice in the field of study."

The Resource Conservation and Recovery Act puts all laboratories in the same category, i.e. it doesn't differentiate where the labs are located; in schools, industry, manufacturing facilities or elsewhere. A lab is a lab no matter what its affiliation.

There is good reason why labs are put in a special group because there are fundamental differences in types, quantities, and diversities of hazardous waste generated. Research labs tend to use small quantities of a large number of substances for short periods and at infrequent intervals. The largest bottle in most labs is of the one gallon size. Industry, on the other hand, is geared toward large homogenous waste streams flowing continuously over long periods of time.





Researchers have problems in predicting the need for, and use of, particular substances in advance of actual use, making it difficult to establish prudent procedures for the disposal of the chemicals before the fact. Laboratories are not penalized excessively by regulations aimed at industrial uses.

There are some limitations involving the use of LAB PACKS, namely incompatibles cannot be packed in the same drum and reactives are forbidden. There is one exception in the reactive category that allows cyanide and sulfide bearing wastes to be packed in a separate LAB PACK used exclusively for that particular waste. For the full regulations on LAB PACKS, check the November 17, 1981 Federal Register.

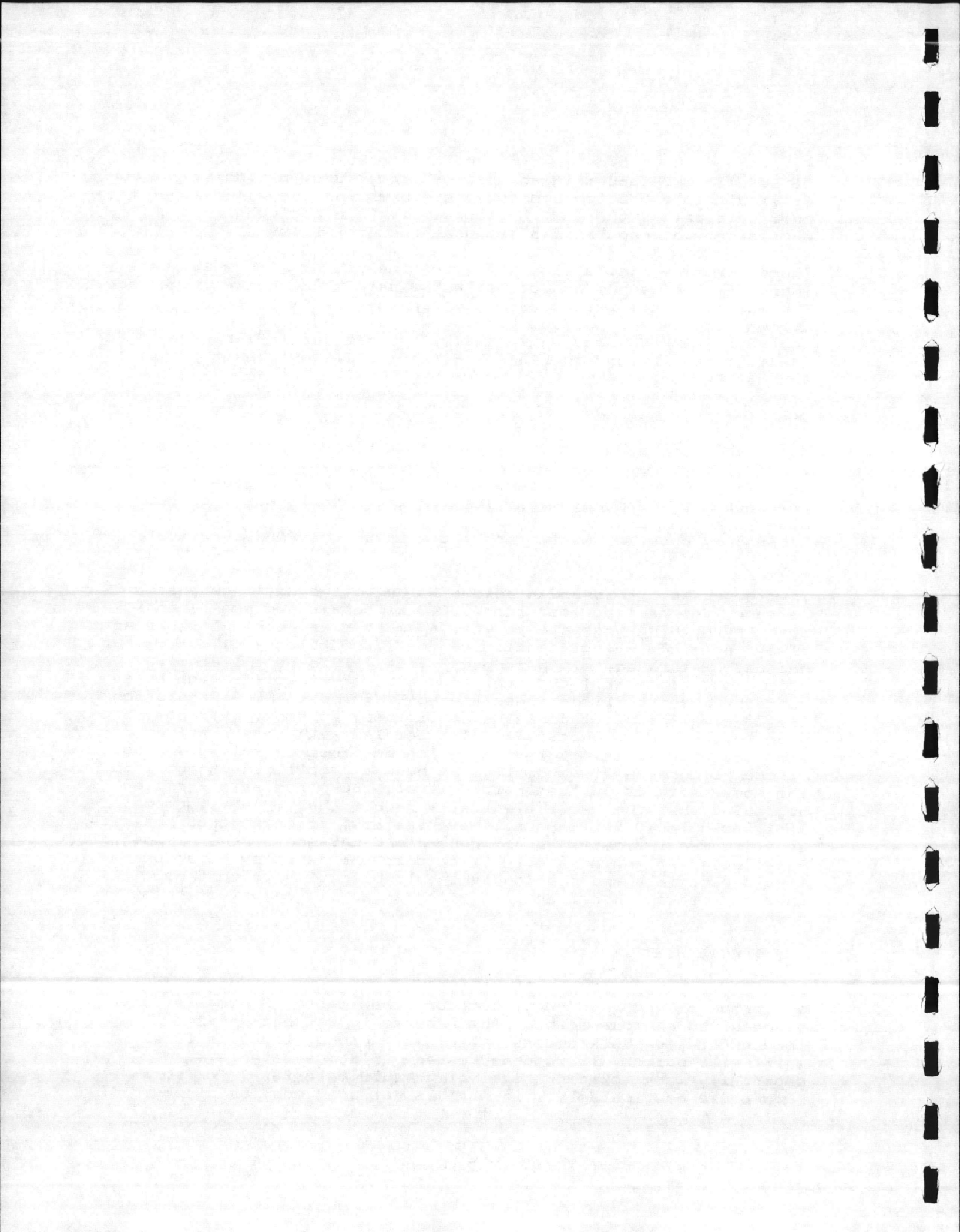
#### B. LABORATORY STRATEGIES

Many laboratories are a small part of a larger plant that is already listed as a generator or even may have interim status as a treatment, storage, and disposal facility. Wastes generated by the laboratory can have an effect on the overall waste disposal plan. Prudent practices should be in effect to minimize laboratory chemical waste and handle it in LAB PACKS particularly if an outside contract service is used.

In other cases it is advantageous to be in the small generator category (generating less than 1,000 kilograms per month) and doing everything possible to stay a small generator. This is not always possible -- not because of the 1,000 kilogram limit -- but because of the "acutely hazardous" list. This is a list of "discarded commercial chemical products, off-specification series, containers and spill residues thereof", found in RCRA Regulation 261.33(e). This list contains pesticides, poisons, cyanides, and other highly toxic chemicals. The problem with this list, aside from acute toxicity, is the one kilogram limit on spills. A spill of one kilogram will automatically push a "small generator" into the more restrictive "generator" level. RCRA has said from the beginning that they will eventually reduce the 1,000 kilogram limit down to 100 kilograms. Nevertheless, it makes good business sense to remain in the "small generator" category whenever possible. Particular attention should be paid to the "acutely hazardous" listed materials and procedures should be set up to control inventory so as to prevent a 1 kilogram spill of any of these materials.

#### C. CONTROLS ON HAZARDOUS WASTES

Laboratory personnel should always consider the methods of storage and disposal required for laboratory chemicals. Minimal amounts of required chemicals should be ordered in spite of price inducements for bulk orders. The less around, the less likely a spill will occur. It is unnecessary to store materials, especially very toxic or highly flammable materials, for some future use particularly when what is not used must be disposed of



at a high cost.

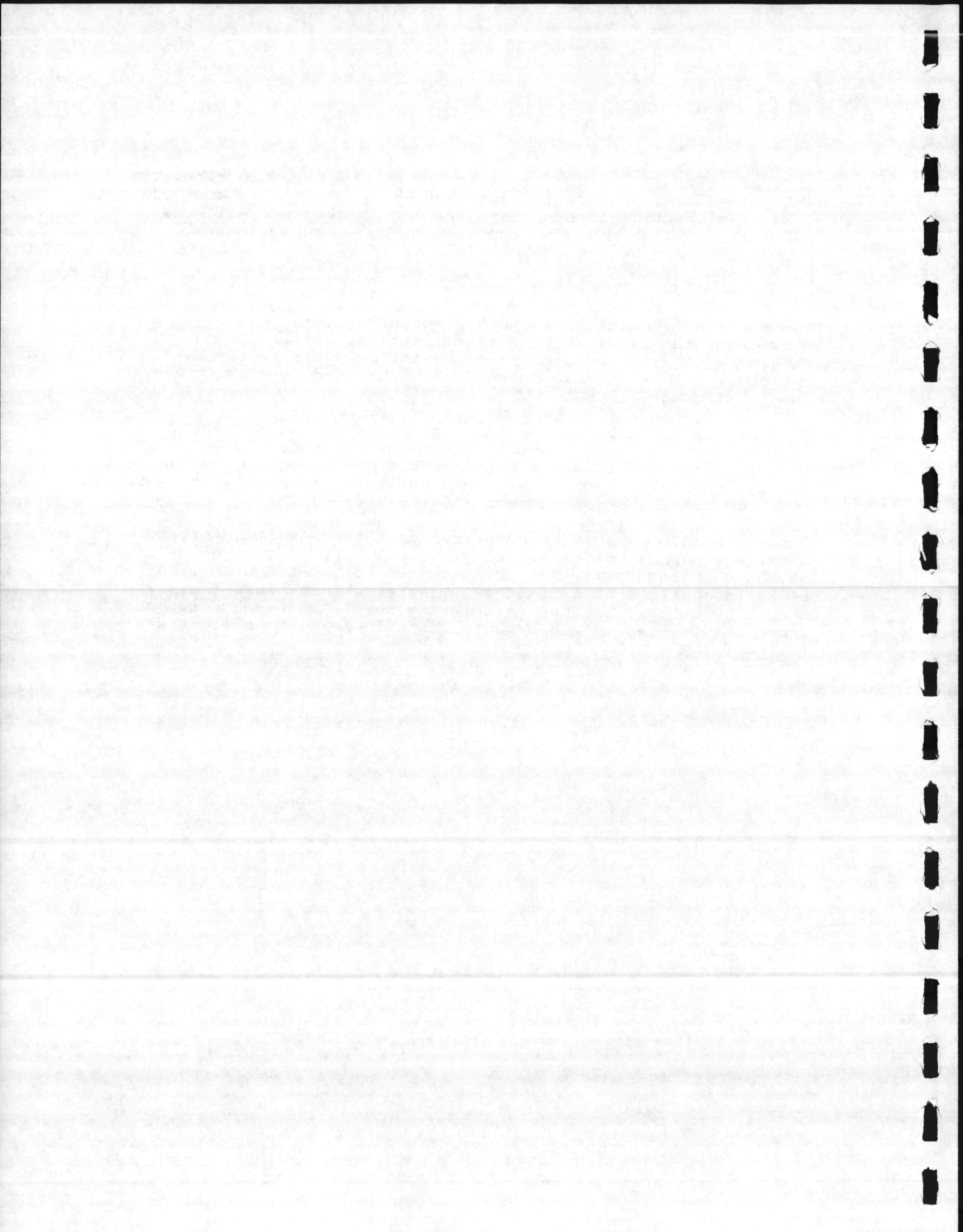
In some instances, prior to disposing of left-over chemicals, laboratories will check if other labs may want to use them. This is a wise practice though there are "rat packs" who will hoard chemicals whether or not there is a current need. These hoarders should be avoided.

#### D. SPILL PREVENTION

"An ounce of prevention is worth a pound of cure" was never more true than when considering chemical spills. Often it will cost many more times the original cost of the chemical to dispose of it. Obviously, it is best to prevent all laboratory spills in the first place.

A structured laboratory safety program must exist where the avoidance of accidental spills is stressed. Laboratory technicians should have formalized training programs in chemical safety and health and be part of a periodic laboratory inspection team utilizing a prepared check-list.

Close attention should be paid to proper storage of chemicals. Chemicals should not be stored alphabetically on shelves -- this may pair up chemicals that could dangerously react with each other if accidentally broken together. Instead, compatible groups should be stored together on the same shelf. One suggested scheme separates inorganics and organics into 20 separate shelf spaces as follows:



### Inorganics

sulfure, phosphorus, arsenic,  
phosphorus pentoxide

halides, sulfates, sulfites,  
thiosulfates, phosphates, etc.

amides, nitrates (not ammonium  
nitrate), nitrites, etc.

metals and hydrides (store  
away from any water)

hydroxides, oxides, silicates,  
etc.

arsenates, cyanides, etc.  
(store above acids)

sulfides, selenides, phosphides,  
carbides, nitrides, etc.

borates, chromates, manganates,  
permanganates, etc.

chlorates, perchlorates, chlorites  
perchloric acid, peroxides, etc.

acids, EXCEPT nitric

### Organics

alcohols, glycols, etc.

hydrocarbons, esters, etc.

ethers, ketones, etc.

epoxy compounds, isocyanates

sulfides, polysulfides, etc.

phenol, cresols

peroxides, azides, etc.

acids, anhydrides, peracids,  
etc.

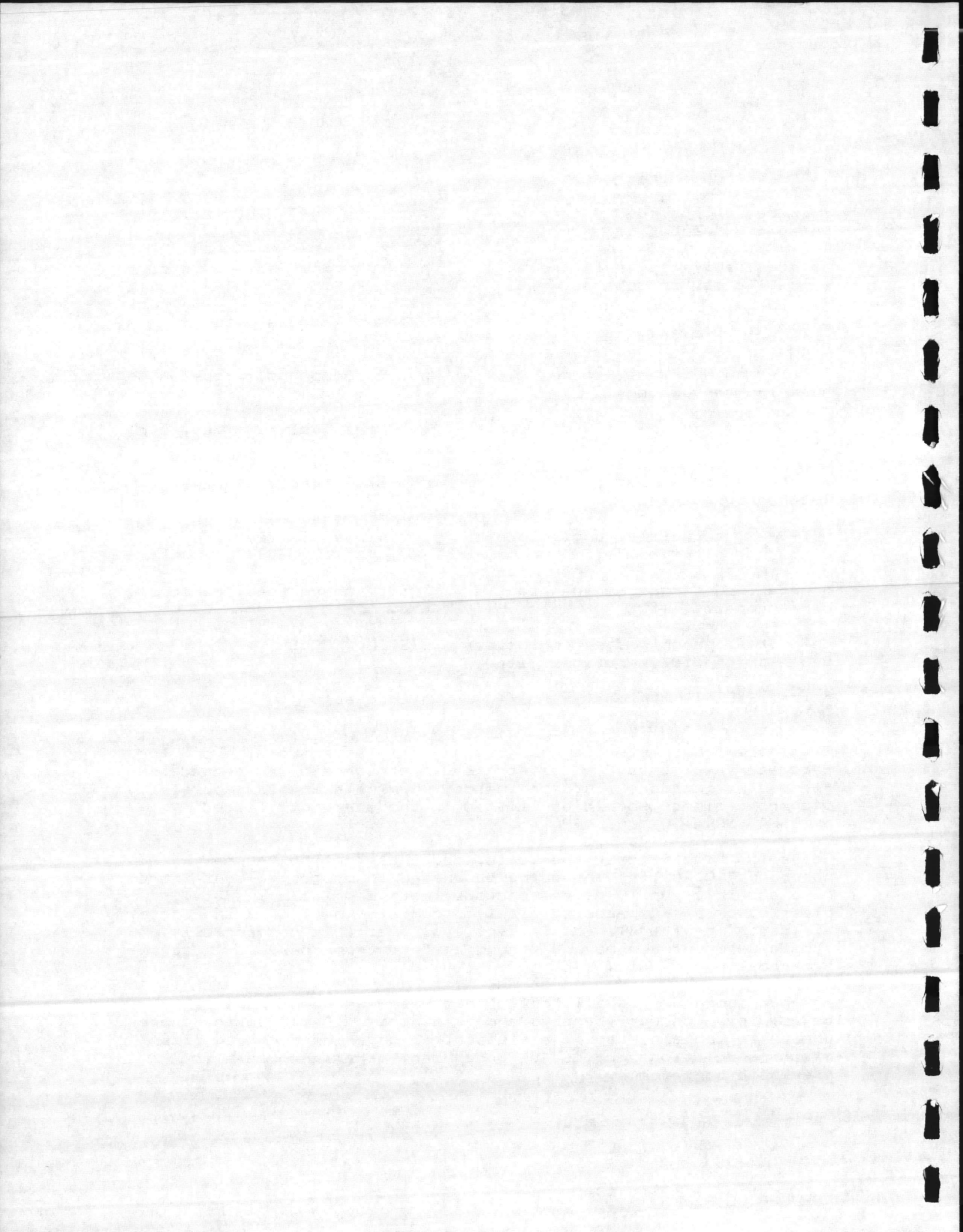
### MISCELLANEOUS

nitric acid

Flammable liquid storage cabinets and safety cans are needed for laboratory solvents. A "safety" type refrigerator is needed if flammable liquids are stored inside. Chemicals in glass outside storage cabinets should be limited to those amounts listed by OSHA, NFPA 30 and NFPA 45.

Solvents, highly toxic chemicals, and those on the "acutely hazardous" RCRA list should be purchased in protected containers. Most chemical supply houses package their chemicals in metal, plastic, or plastic coated glass to contain the liquid in case of accidental breakage. Bottle carriers, available commercially, should be used when moving strong acids, strong bases, or "acutely hazardous" chemicals.

In the laboratory, spill trays lined with absorbent paper should be used even on work benches and fume hoods. Catch basins large enough to contain a spill are essential under mercury and glass cleaning solutions and useful under many other chemicals in breakable containers.



#### E. HYGIENIC CONSIDERATIONS

After having taken all the spill prevention precautions a chemical spill still has to be cleaned up in the laboratory. Lab personnel need to be made aware and trained concerning the specific exposures they can encounter day by day or during a spill emergency. Hazardous waste means that there is a potential hazard requiring special handling. Accident statistics reveal that 30 percent of serious lab injuries are related to chemical spills. These can involve burns, loss of eyesight, pulmonary edema, and other bodily harm.

A contingency plan for chemical spills needs to be devised before you start a research project. This is especially true in the laboratory since in many cases only the researcher and the technician have any idea of what is being used or produced in the way of waste reaction products. Depending on what chemicals are being used -- whether they be acids or caustics, oxidizers or reducers, poisons, carcinogens, mutagens or teratogens, flammables or explosives, bio-hazards or radioactives -- proper emergency personnel protective equipment must be available to deal with the spill. These can range from safety glasses, rubber gloves, and rubber aprons to cannister respirators, self-contained breathing apparatus (SCBA), supplied air respirators, or complete chemical suits.

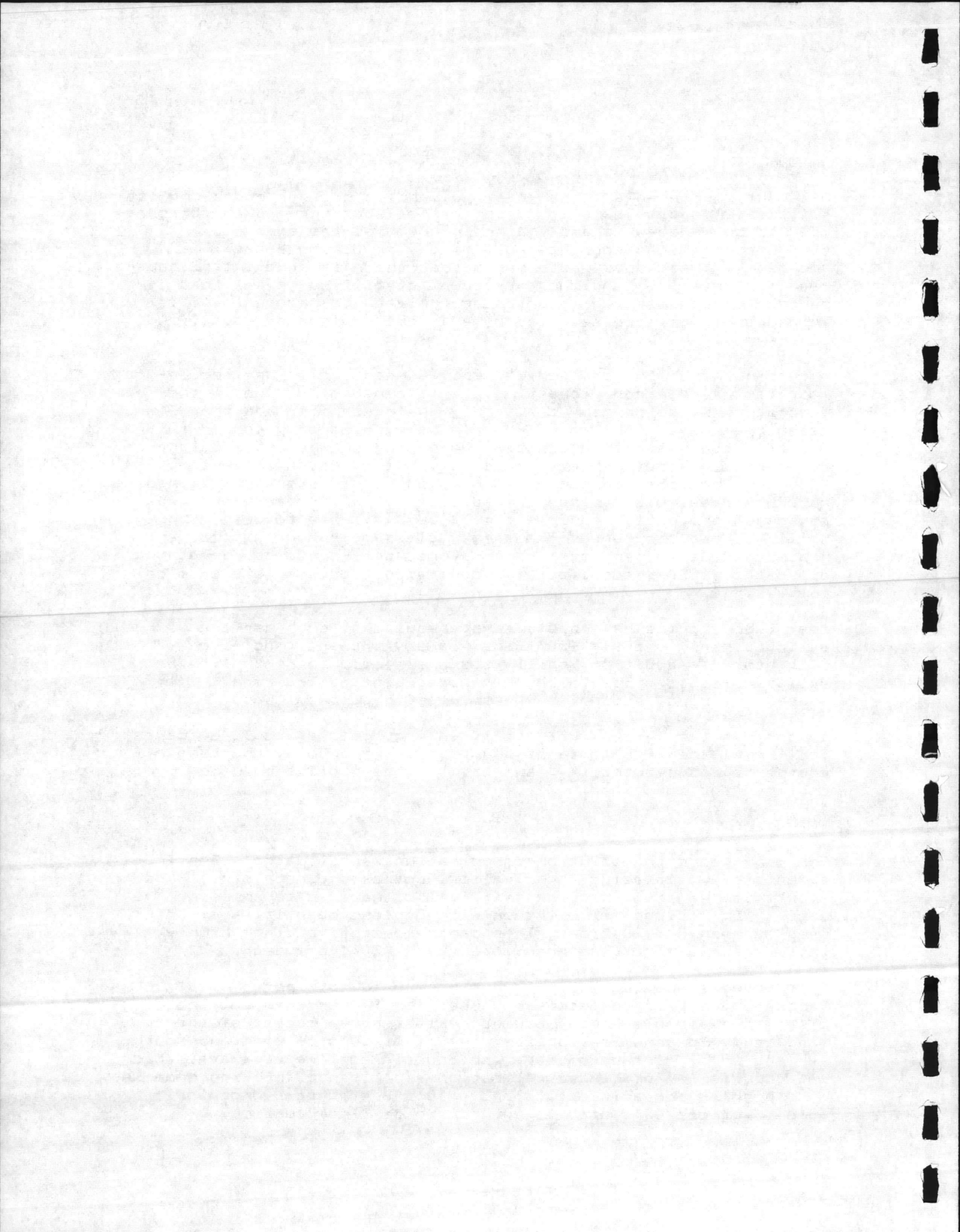
Most laboratories have basic safety equipment such as fire extinguishers, eyewash fountains, safety showers, and fire blankets. In addition, spill kits are needed to neutralize or solidify liquid spills along with absorbent paper, rags, squeegees, mops, scoops, buckets, plastic disposal bags, etc.

In the event of a chemical spill, injured people should be cared for first, then fire hazards should be tended to by shutting off equipment and electricity, and lastly, the spill should be confined and contained.

#### F. LABORATORY SPILL KITS

For many years the solution to pollution was dilution. Small amounts of waste acids and alkalies, not exceeding a pint, were slowly poured into the sink half full of water after opening the drain. Directions for dilution with copious quantities of water usually mean 50:1 ratios. This can be deceptive since highly toxic materials require much more than a 50:1 dilution.

Paper towels and rags have always been used to wipe up small laboratory spills and sometimes used for larger spills if nothing else was available. Many chemistry labs had a bucket of inert sand handy for chemical spills. A 9:1 mixture of sand and soda ash and a 1:1 mixture of soda ash and slaked lime were available and popular for spill neutralization and cleanup. Baking soda was also popular for acid spills and dilute acetic or hydrochloric acid solutions were used to neutralize spilled caustics.





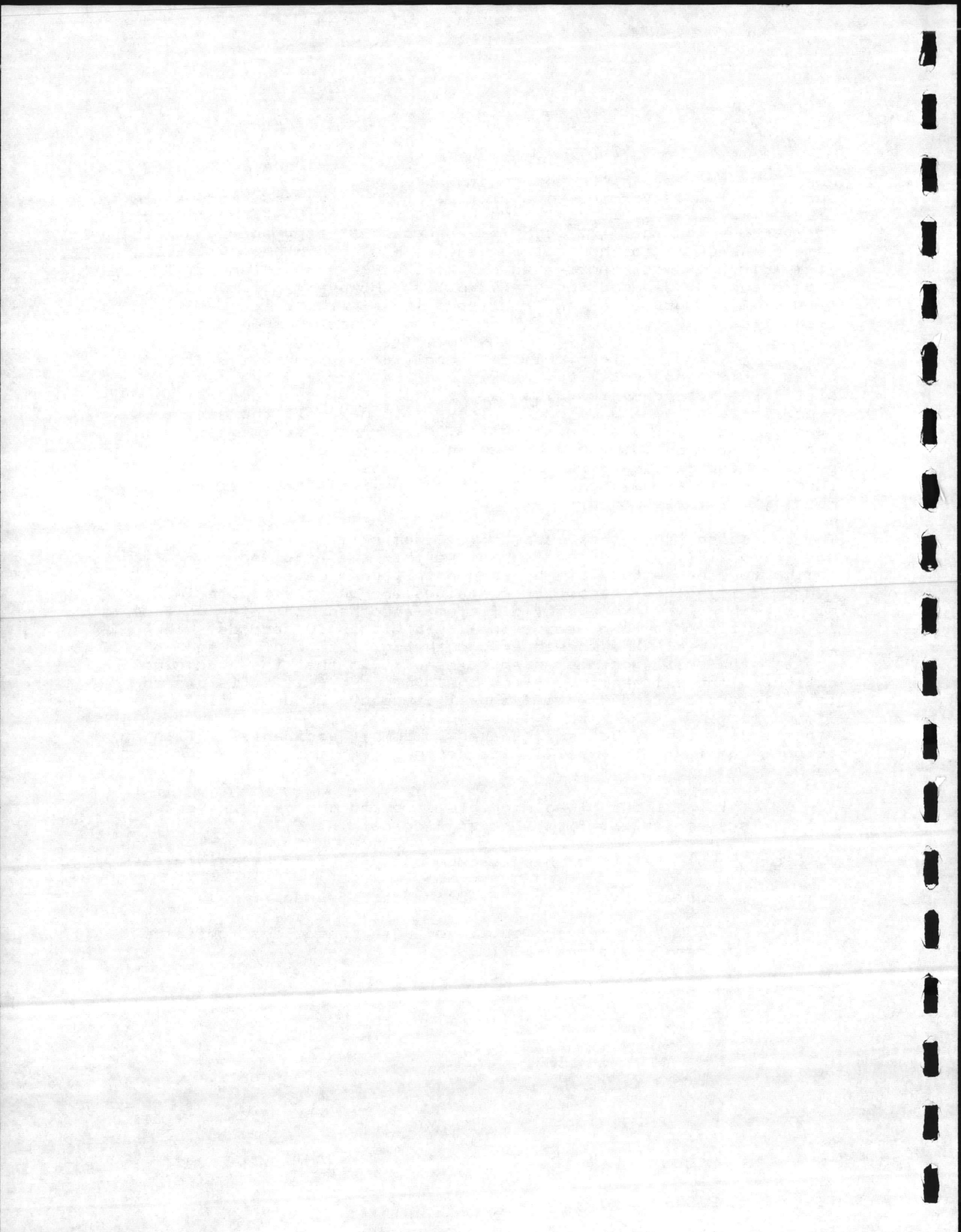
For large spills various absorbents were used to contain the spill and soak it up. Vermiculite, diatomaceous earth, and absorbent clays like Oil-Dry, Zorb-All and kitty litter have all been used for various chemical spills. The absorbents listed above have the same drawback of not controlling the vapors from highly volatile flammable solvents. Activated charcoal will absorb flammable vapors and may be used for small spills. However, at an absorbent rate of 2-1/2 pounds of charcoal per pint of liquid, larger quantities of spilled material would soon become uneconomical.

In recent years, various chemical supply companies have made up package spill control kits. Baker Chemical Company has separate kits for acids, caustics, flammables, solvents, cyanides, hydrofluoric acid, and mercury. These kits have all the materials needed, even safety glasses for small laboratory spills. They are expensive but do the job when needed. Several sizes of packages and refills give flexibility to users. Other chemical supply companies have come out with comparable kits so they are readily available for purchase.

The latest spill control product for chemicals is the spill control pillow. It is less expensive than the kits and much easier to use, as they can be used on all chemicals except hydrofluoric acid. The pillow contains amorphous silicate in a polyolefin bag. This highly efficient absorbent can pick up from 10 to 20 times its own weight in liquid within 30 seconds. The pillows can easily be spread around the spill to confine and contain the spill and has an added benefit in that the absorbing action is not exothermic. After the pillow is full it is placed in a plastic bag and tied off and it is ready for disposal.

Laboratories can be better prepared to combat accidental spills by using a combination of spill kits depending on the specific needs.

- o Spill pillows of appropriate size and the best universal system (except for hydrogen fluoride).
- o A separate kit or hand vacuum pump for mercury spills.
- o A separate kit for hydrofluoric acid if used.
- o A bag or two of vermiculite or absorbent clays for large volumes or viscous spills.



## XV. COMPRESSED GAS SPILLS AND RELEASES

### A. Gas vs Liquid

Flammable gases generally have a much wider flammable range in air than flammable liquids do. Hydrogen and acetylene gases have flammable ranges over 70% wide while gasoline vapors only have a 6% flammable range in air.

Most liquids and solvents in particular have vapors heavier than air and will tend to hug the ground and seek the lowest level. Gases on the other hand may be lighter or heavier than air and may more readily diffuse over a much wider area and be more affected by wind conditions.

Failure of flammable liquified gas containers can cause a disastrous phenomenon known as a BLEVE--Boiling Liquid--Expanding Vapor Explosion with resultant fireball and vessel shrapnel.

Gas releases are more hazardous than liquid spills in many ways. Much attention and training are given to handling flammable liquid incidents while less planning is focused on compressed gases; in many cases this may involve more devastating consequences during accidents.

### B. Gas Hazards--Extremes

If only one term could be used to highlight the hazards involved with compressed gases, it would be the word EXTREMES, such as

- o Very high pressures with compressed gases in cylinders, regulators and piping;
- o High vacuums used in construction of cryogenic containers;
- o Chemical hazards including flammables, corrosives, reactives, poisons, oxidizers, and toxic gases;
- o Extremely low temperatures hundreds of degrees below zero, e.g., liquid nitrogen at minus 320 degrees Fahrenheit;
- o Oxygen deficiencies and oxygen enrichment both involving behavior foreign to our usual expectations;
- o Abnormally large amounts of gas at atmospheric pressure resulting from a many fold expansion from its compressed state when released by accident.

All these conditions contribute to dangerous spill situations that have to be approached with extreme caution. In addition the physical and chemical characteristics of the gases must be known to deal effectively with the releases. One should not lose sight of the fact that gases are chemicals. There are eleven gases found in the chemical periodic chart and of course these combine with many other chemicals to produce hundreds of more complex gas

The boiling point of gases are extremely low—oxygen -297 degrees

also as they directly affect the properties of the gases.

and wind conditions at the scene have to be taken into account conditions for the diffusion rates; in actual practice temperatures the ceiling corners. It should be mentioned that these are ideal a molecular weight of 28 diffuses slowly and tends to pocket at

lightest of gases will diffuse very rapidly while acetylene with readily than the heavier gases. Hydrogen and helium being the

is heavier or lighter than air. The lighter gases diffuse more molecular weights in the same manner to determine whether a gas

but a good ball park estimate can be made by simply using the as well as the gas densities. The formula may be very precise,

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a formula for the Law of Diffusion or Graham's Law. It states know whether the gas will dissipate slowly or rapidly. There is

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gases—hydrogen at 2 and helium at 4—are much lighter than air. is slightly lighter than air at 29. Of course the two lightest

including gases. For instance, the molecular weight of oxygen is reference material will give one the molecular weight of chemicals

building or simply dissipate overhead. A periodic chart and most down and seek a low point or go up into the upper stories of the

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minimum requirement. Self-contained breathing apparatus operated in pairs would be a

written plan or procedure covering the situation. should enter a reduced oxygen atmosphere without following a

one's ability to think and affects physical coordination. No one perform with fatigue setting in faster than usual. It also slows

effect on humans. All physical activity becomes harder to the amount of oxygen available to breathe can have an adverse

oxygen in the air is a hazardous atmosphere. Small decreases in Any deviation of more than plus or minus one percent from the 21%

gases found in trace amounts only. Neon, krypton, and xenon are other atmospheric

being inert gases. The air we breathe is a mixture of gases. The principal constitu-

3. General Properties

formulas.

formulas.

### C. General Properties

The air we breathe is a mixture of gases. The principal constituents are 21% oxygen, 78% nitrogen, and 1% argon, the latter two being inert gases. Neon, krypton, and xenon are other atmospheric gases found in trace amounts only.

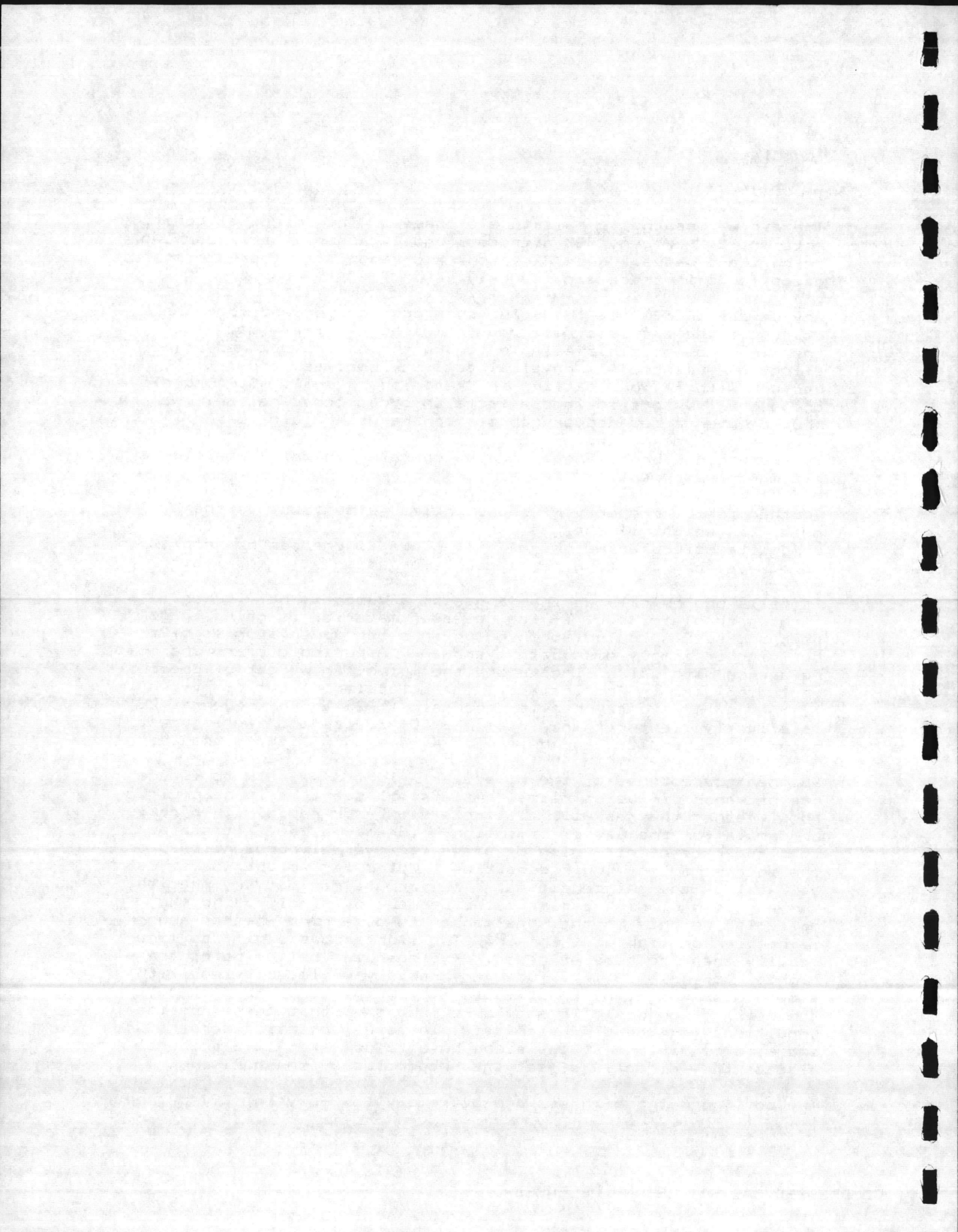
Any deviation of more than plus or minus one percent from the 21% oxygen in the air is a hazardous atmosphere. Small decreases in the amount of oxygen available to breathe can have an adverse effect on humans. All physical activity becomes harder to perform with fatigue setting in faster than usual. It also slows one's ability to think and affects physical coordination. No one should enter a reduced oxygen atmosphere without following a written plan or procedure covering this situation. Self-contained breathing apparatus operated in pairs would be a minimum requirement.

Another useful property of gases in leak situations is the molecular weight of the gas. Memorize the figure 29 as the composite molecular weight of air. This figure can be helpful in more ways than one to give needed information at a spill site.

It tells one quickly whether a gas or a vapor is heavier or lighter than air, e.g. if the released material is going to go down and seek a low point or go up into the upper stories of the building or simply dissipate overhead. A periodic chart and most reference material will give one the molecular weight of chemicals including gases. For instance, the molecular weight of oxygen is 32 making it slightly heavier than air at 29 and nitrogen at 28 is slightly lighter than air at 29. Of course the two lightest gases--hydrogen at 2 and helium at 4--are much lighter than air.

Another prudent use of the molecular weight of air is to figure gas or vapor diffusion rates. At a spill scene it is helpful to know whether the gas will dissipate slowly or rapidly. There is a formula for the Law of Diffusion or Graham's Law. It states that the rate of diffusion of gases is inversely proportional to the square root of their densities. Molecular weight works just as well as the gas densities. The formula may be very precise, but a good ball park estimate can be made by simply using the molecular weights in the same manner to determine whether a gas is heavier or lighter than air. The lighter gases diffuse more readily than the heavier gases. Hydrogen and helium being the lightest of gases will diffuse very rapidly while acetylene with a molecular weight of 26 diffuses slowly and tends to pocket at the ceiling corners. It should be mentioned that these are ideal conditions for the diffusion rate; in actual practice temperature and wind conditions at the scene have to be taken into account also as they directly effect the properties of the gases.

The boiling point of gases are extremely low--oxygen -297 degrees



F, nitrogen -320 degrees F, air -318 degrees F. Those gases that have a boiling point below -150 degrees F are called cryogenic liquids--meaning extremely low temperatures. It is important to note that the liquid nitrogen boiling point is below that of air. Therefore, if liquid nitrogen is left in an open container, it will liquify the air it comes in contact with. If left this way over several hours, the nitrogen tends to evaporate off faster being the coldest component, and leave the oxygen behind. Now instead of a inert nitrogen liquid there is an oxygen-nitrogen mixture that could create a hazardous situation.

Another unique property of cryogenic gases is the volume expansion from liquid to gas. The ratio for oxygen is 861 to 1. That means that one unit of liquid produces 861 units of gas. That gives a hint as to why the gases are shipped as liquids.

#### D. Terminology

The terms "gas, vapors, and fumes" are used rather loosely when describing conditions. Actually these terms are defined more precisely by industrial hygienists and various standard setting organizations. Usually vapors are used to describe flammable liquid vapors or water vapor. The vapors act like gases, but if they come in contact with a cold surface, they will recondense into liquid form at close to ambient temperatures. A pure gas will not recondense into a liquid except at much lower temperatures.

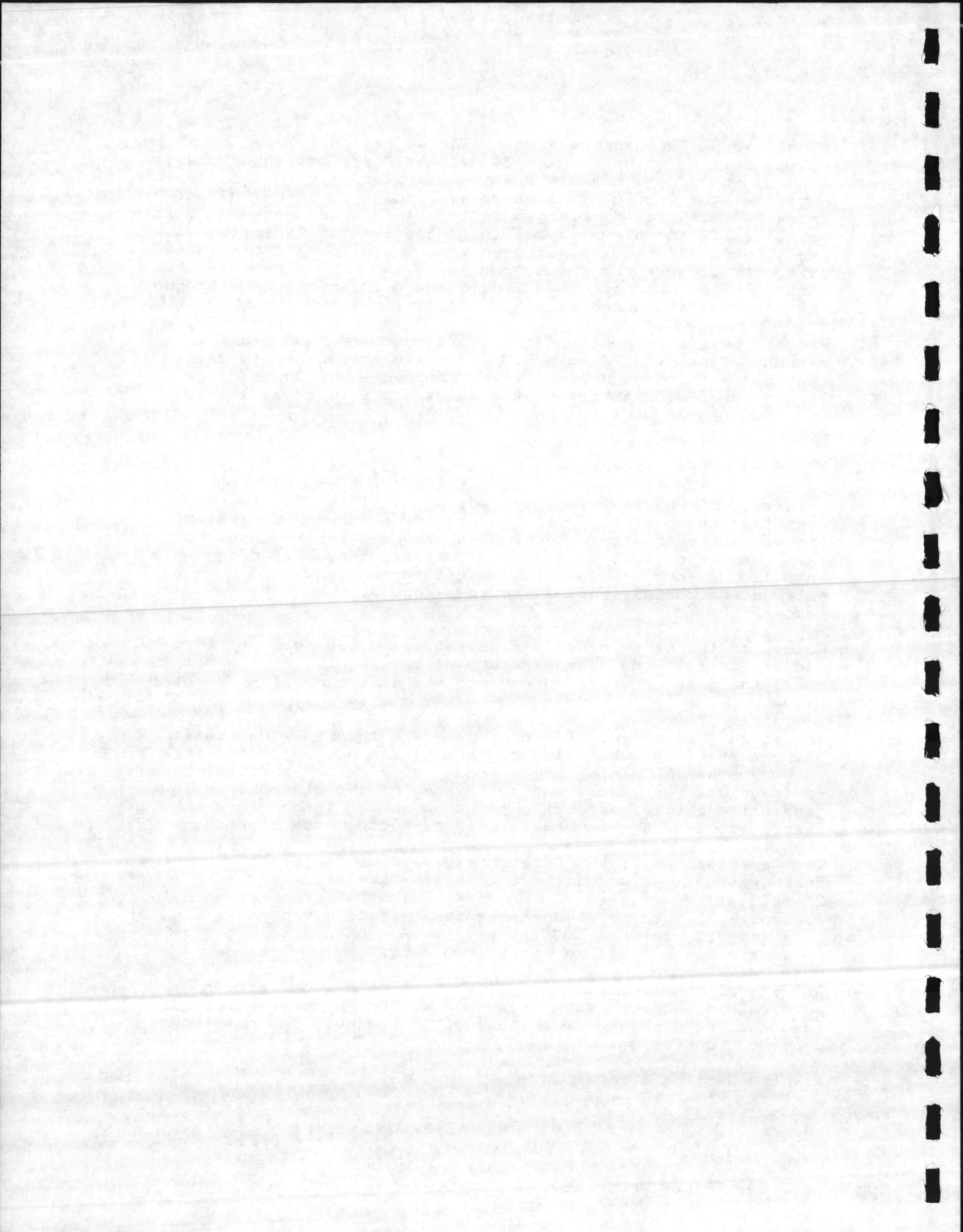
Fumes, on the other hand, are usually produced from molten metal and are in fact the gaseous state of the metal. As the hot fumes cool, the gaseous state returns to its parent metal or a metal oxide.

The scientific definition for a gas is a material that boils between absolute zero (-459 degrees F) and normal temperature 40 to 80 degrees F. This ranges from liquid helium which boils a few degrees from absolute zero to some of the liquid petroleum gases like butane that boils close to normal temperature. Butane exerts about 8 psig in a plastic butane cigarette lighter.

The Department of Transportation (DOT) uses one definition of a compressed gas as a substance that exerts a vapor pressure above 25 psig at 100 degrees F. One definition DOT uses for a flammable liquid is a substance that exerts a vapor pressure of less than 25 psig at 100 degrees F. A high pressure gas is considered at a pressure above 1000 psig.

As with all chemicals, one is always safer using a proper name when talking about a specific gas. Welders often ask for gas when they mean oxygen or acetylene. This could and has led to dangerous confusion.

#### E. Physical States





Compressed gases can be received by the customers in four different physical states. When dealing with compressed gas releases and spills, it is essential to understand the difference between each type of container and how they are expected to behave. The gases are usually grouped as (1) non-liquified gas; (2) liquified gas; (3) dissolved gas; and, (4) cryogenic liquids.

#### F. Non-liquified Gases

High pressure or non-liquified gases are shipped at high pressure in heavy steel cylinders. They are filled to a certain settled pressure at 70 degrees F. Oxygen, nitrogen, argon, and helium are examples of high pressure gases normally shipped at 2200 psig. The hazards of high pressure always exist when handling this type of highly compressed gas.

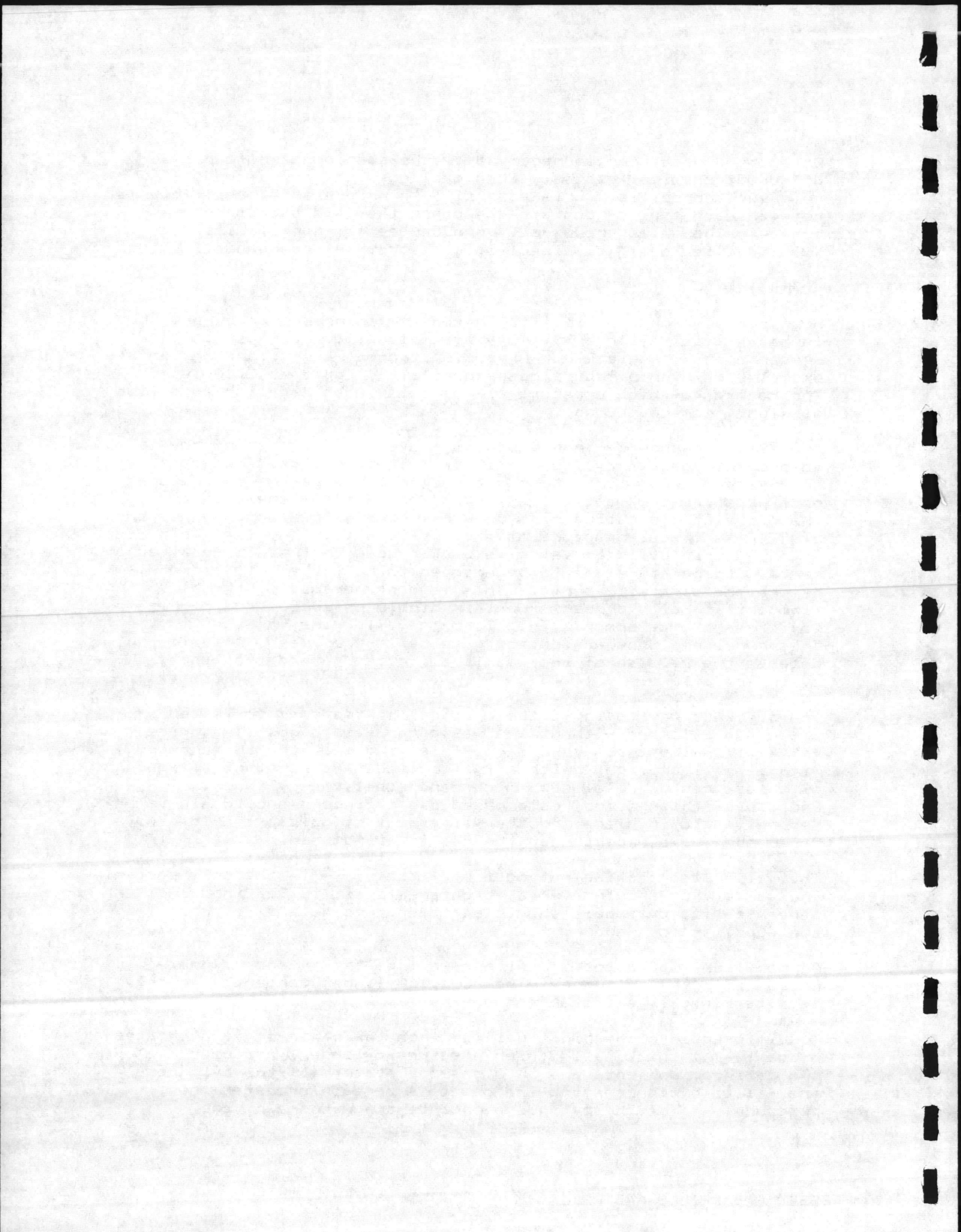
The high pressure cylinders usually have a safety relief device to protect against cylinder failure. These devices are set to relieve pressure with either a 100 degree F rise in temperature or a pressure 150% above the working pressure of the cylinder. Therefore, the bursting disk on a cylinder with a working pressure of 2200 psig would rupture at about 3400 psig. The frangible disc on a hydrogen cylinder valve is backed up with fusible metal so a certain temperature has to be reached to melt the fusible metal before the disc will burst. This is done because of the high flammability of hydrogen. Certain highly poisonous and highly toxic gases like ammonia, nitric oxide, fluorine, arsine, phosphine, and phosgene do not have relief devices. This is because the release of the gas is a greater hazard than the cylinder failure.

The quickest way to loose the cylinder contents is to let an unsecured cylinder without its valve cap fall over. The brass valve will almost always shear off leaving only the thread spud with a small orifice. With a full cylinder, a substantial amount of thrust can be developed which can propel the cylinder. Because of this hazard, compressed gas cylinders should always be securely held in place and the valve protecting cap should always cover the valve except when the gas is being used.

The valve stem packing nut on top of the valve is the only part of the valve that should ever be tightened if it is leaking. All other leaking cylinders should be taken outside and returned to the supplier for repair.

As non-liquified gases are withdrawn from the cylinder, the pressure in the cylinder is reduced. Cylinder contents can only be determined by a pressure gauge.

To differentiate the non-liquified from the other physical states of gas: (1) thick walled high pressure cylinders are used, (2) the cylinder contents are in a gaseous state, (3) the cylinders are filled by compressing the gas to a certain predetermined pressure, (4) as the cylinder contents are withdrawn, the



pressure is reduced accordingly.

## 6. Liquefied Gases

As the name states, there is both a liquid and a gas in the cylinders. The gas is liquified under its own vapor pressure. Each gas has a different vapor pressure so the cylinder pressure is different for each gas. Common liquified gases are carbon dioxide, chlorine, ammonia, liquid petroleum gases, propane and butane and nitrous oxide.

Some examples of liquified gas cylinder pressures are:

o Chlorine . . . . .	86 psig
o Ammonia . . . . .	114 psig
o Hydrogen Sulphide . . . . .	253 psig
o Hydrogen Chloride . . . . .	613 psig
o Carbon Dioxide . . . . .	839 psig

Generally the working pressure is not as high as with the non-liquified gases so lighter walled cylinders are used in most cases.

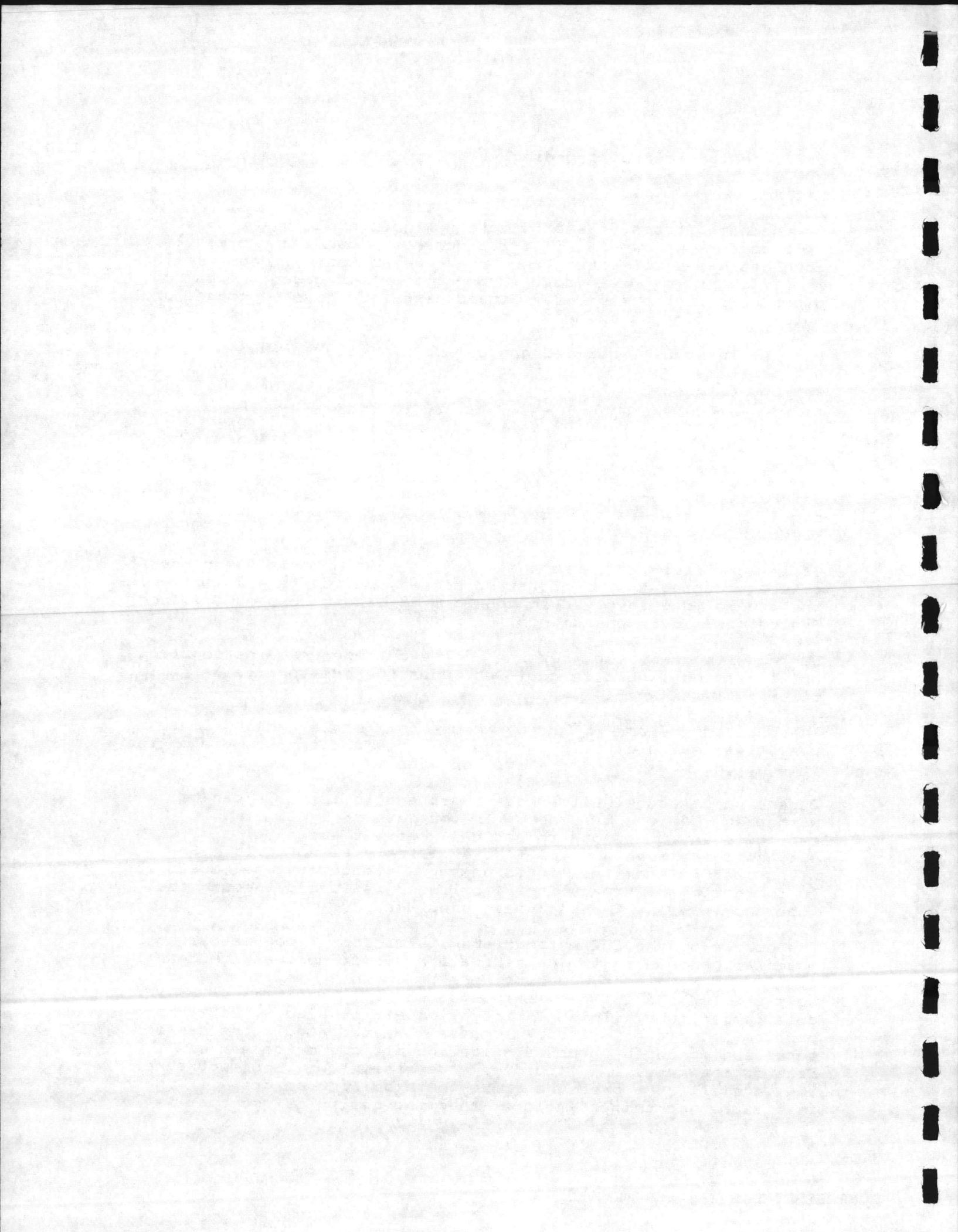
It is the liquified gases that get the most notoriety and press coverage during train wrecks and highway accidents. This is also the type of gas involved in the Boiling Liquid--Expanding Vapor Explosion (BLEVE) phenomenon.

During withdrawal the pressure in the cylinder remains constant until all the liquid is gasified, then the pressure falls rapidly to empty.

These cylinders are filled by weight on a scale and the contents can be estimated by weighing the cylinder and taking note of the tare weight stamped on the cylinder head.

Depending on usage, either gas phase or liquid phase can be withdrawn from the cylinder. In the case of a CO<sub>2</sub> fire extinguisher, one wants to get the greatest amount of extinguishing agent on the fire as quickly as possible. So withdrawal is from the liquid phase. An eductor tube runs almost to the bottom of the cylinder so liquid is forced through the tube and valve by the gas phase pressure.

The nozzle on the CO<sub>2</sub> extinguisher is made of a non-metallic material because of the refrigeration effect during withdrawal. If it were metal and a person were to put his hand on the nozzle, he might leave a layer of skin that would adhere because of the cold temperature. This refrigeration effect also gives withdrawal problems at higher withdrawal rates. Heated regulators can be purchased for both carbon dioxide and nitrous oxide gases. Because the gases are liquified under their own vapor pressure, they are all at a pressure above their boiling points. If there is a sudden container failure, then the gas phase pressure is



reduced and the liquid will start to boil very rapidly. If it is a flammable gas and there is an ignition source around, then a BLEVE could occur. This explosion will hurl the container parts long distances and produce a large fireball as the flammable gases are consumed.

Liquified gases use a variety of relief devices. Most of the flammable gases have a spring loaded safety device that will open on pressure rise and close again on falling pressure. Sometimes the discharge will light off and produce a torch type flame pattern. When the pressure in the tank is reduced and the valve closes, the source of gas is interrupted and the flame goes out. Toxic or poisonous liquified gases are likely to have frangible metal discs as a relieving device or in the larger size containers fuse plugs are used as with ton size chlorine containers.

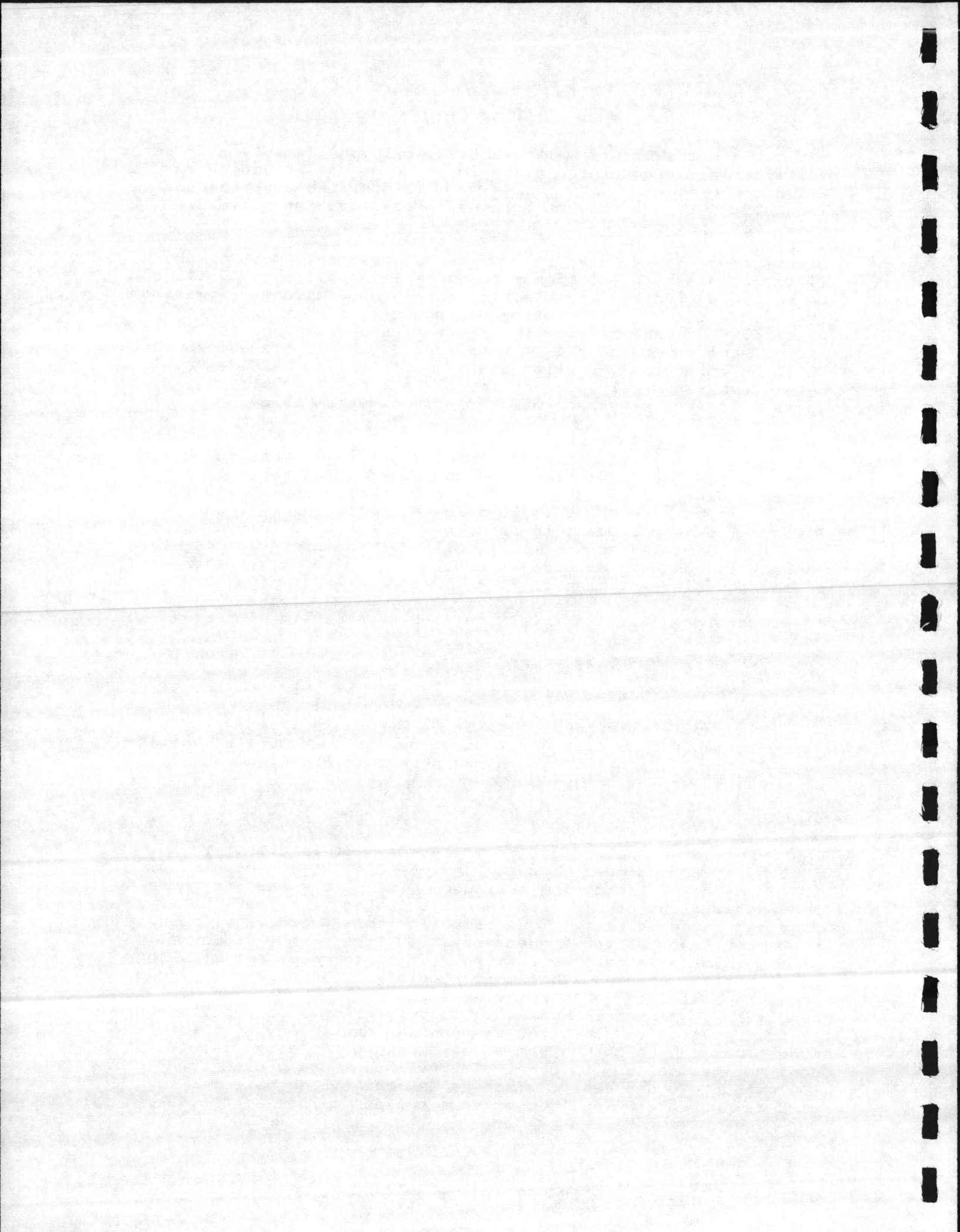
The Chlorine Institute has developed a series of kits to repair leaks in chlorine cylinders, ton containers, and railroad/highway tanks. These are designated A, B, and C kits respectively. At normal temperature there is 86 psig in a chlorine cylinder. These kits have a means to clamp over a valve, a fuse plug, or a hole in the container sidewall. All chlorine distributors have these kits as well as some fire departments and city waterworks or sewage treatment plants.

The conditions that identify liquified gases are:

- (1) Both liquid and gas phase in the cylinder.
- (2) Cylinders are filled by weight.
- (3) Withdrawal pressure is steady as long as there is any liquid in the cylinder.
- (4) The gas is refrigerated as it is withdrawn.
- (5) Flammable liquified gases use a spring loaded safety device.
- (6) Flammable liquified gases can produce a BLEVE during container failure.

#### H. Dissolved Gases

The principal dissolved gas is acetylene. It is dissolved in acetone for shipping purposes. The acetone is saturated in a filler material inside the cylinder. The porous mass is there to provide millions of microscopic cells to keep the gas from forming large pockets. The reason for this special cylinder is that acetylene has the highest positive free energy of formation of any chemical except explosives. It is thermodynamically the most unstable compound that most people ever encounter. High pressure acetylene is 15 psig. The delivery gauge on an acetylene regulator is marked in red above 15 psig. Above 15 lbs pressure it is sensitive to sharp impact and high heat. Any of these conditions can cause the gas to decompose or "disassociate." It does not need oxygen to burn. The cylinders are pressurized to 250 psig at 70 degrees F. That is why the filler material is used to prevent the buildup of free pockets of gas at the very



high pressure. At 250 psig, acetone will absorb large volumes of acetylene gas. The gas goes into solution just like CO<sub>2</sub> is dissolved in water to make soda water. When the valve is opened, the gas comes out of solution just like the bubbles in soda water.

Acetylene has the widest flammable range of all the gases 2.5% - 82% mixture in air. So practically all air mixtures are flammable. It also has a low ignition temperature of 571 degrees F.

Copper tubing should not be used with acetylene as in the presence of water a copper acetylide can form that is about as sensitive as a match head. It is also reactive with silver, mercury, and chlorine.

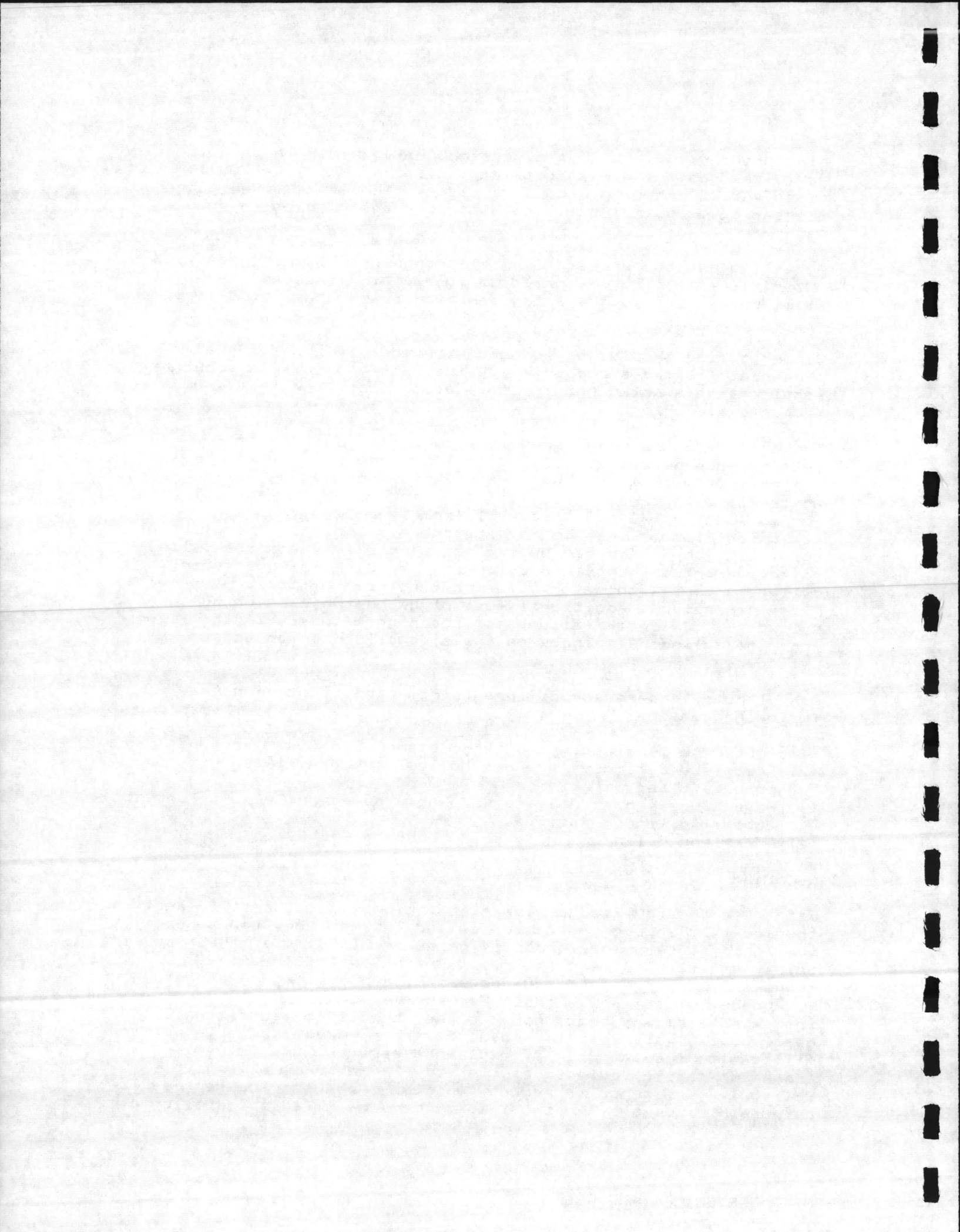
The safety device on an acetylene cylinder consists of low melting fuse plugs set to melt at 212 degrees F. When this happens, it will more than likely ignite, producing a long narrow white flame that may be 15 feet in length. This flame will burn for as long as 1/2 hour and will finally recede to a shorter yellowish flame. This is the acetone starting to burn off. At this point the flame can be extinguished safely and the cylinder moved. Fight an acetylene cylinder fire by keeping adjacent cylinders cool with water. The radiant heat of the acetylene flame can release additional fuse plugs on the same or adjacent cylinders. Cylinder failure can occur prematurely if the flame from one cylinder impinges on the sidewall of an adjacent cylinder.

Acetylene cylinders are different from other types for the following reasons:

- (1) Acetylene is dissolved under pressure in liquid acetone.
- (2) Acetylene cylinders are not hollow, but are filled with a porous filler material.
- (3) Fuse plugs set at 212 are used as a safety release to protect against cylinder failure.
- (4) Acetylene cylinders will not produce a BLEVE.

#### I. Cryogenic Liquids

Gases can be liquified by lowering their temperature. If kept in thermos type vacuum containers called dewars, they can be kept in the liquid state. This group of gases are liquids at their boiling points at very low temperatures. Oxygen is liquid at -297 degrees F, nitrogen at -320 degrees F, hydrogen at -423 degrees F, and helium at -452 degrees F. The cryogenics have to be insulated from any heat input to keep them from vaporizing into a gas. Double wall vessels are used with a vacuum space in between filled with insulation. As explained earlier, the volume expansion rate--liquid to gas is very large. For oxygen it is 861 to 1. Cryogenic transport vehicles pressures are kept as low as possible, usually in the 1-20 psig range. Tanks installed at





industrial locations usually are in the pressure range of 110-130 psig.

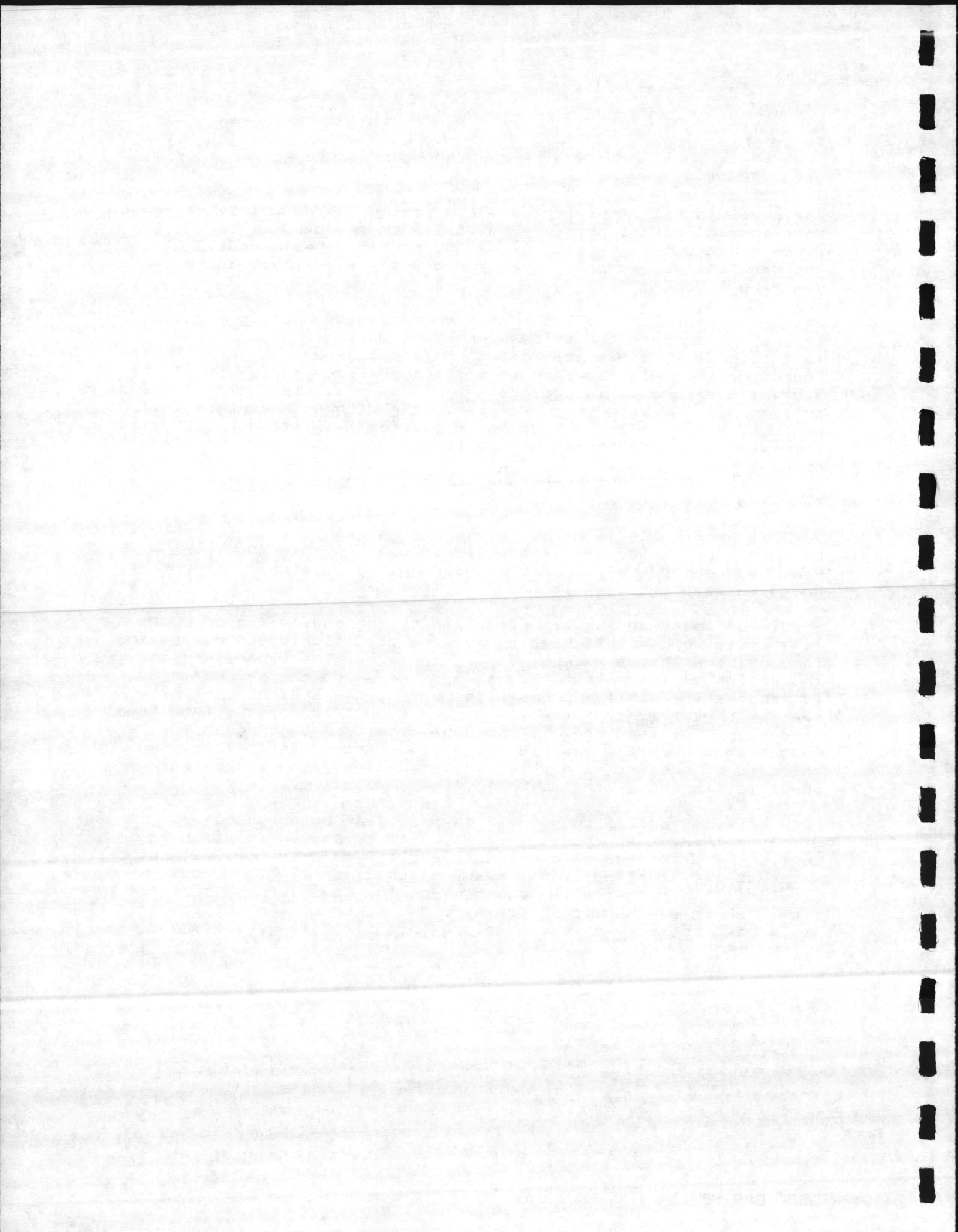
The pressure relief devices are the spring loaded safety valve to take care of normal pressure buildup with a backup of bursting discs to take care of loss of vacuum or large heat input. At accident scenes, keep water away from safety devices, as they could be frozen shut.

Because of the extremely cold temperatures involved, personal protective equipment must be worn when handling these liquids. A full face mask, preferably one that is designed with an extension under the chin, is required to protect the face and eyes. In fact, all exposed skin surfaces should be protected against the cold liquid. Severe frostbite can occur with skin contact that produces a burn similar to a hot flame that will take a long time to heal. Burns of this type should not be rubbed or subjected to strong streams of water as frozen skin could be washed away. Simply let the skin temperature return to ambient temperature by itself or use luke-warm water.

Very loose fitting gauntlet gloves and chucka type boots that can be thrown or kicked off if any liquid gets in them should be worn. Pant legs should, of course, be worn on the outside or over the boots to keep out the liquid.

Spills or leaks during transfer operations produce fog or smoke like white vapors that result from the cold liquid and gas coming in contact with the water vapor in the air. The vapors are an indication of where the cold gas has been. As the gas warms up, it becomes invisible and disipates beyond the area of the white vapors. The area of the white vapors should be roped off to keep persons out of the area. If someone were to walk through the vapors, their clothing would become saturated with the gas. In the case of oxygen, an act as careless as lighting a cigarette could ignite the clothing.

Liquid oxygen spills on asphalt pavement can be hazardous as simply walking over the surface may produce enough friction to ignite the saturated pavement with explosive force. Do not use water to try to speed up the evaporation of spilled cryogenic liquids. The result will be water forming ice over the pools of liquid which will build up pressure and forcefully eject the ice. It is best to let everything return to ambient temperature naturally.



## J. Formulas and Calculations For Compressed Gases

There are several useful formulas that can be applied to compressed gases under "ideal" conditions for the calculation of various physical properties. Ideal conditions for gases refer to conditions where the chance for condensation of the gas back to its liquid phase is slight. These conditions are found in gases at high temperatures and low pressures, and different gases at the same T and P will vary in other physical properties, such as the volume they occupy, due to the nature of that specific gas. However, even though these formulas are not exact, they are good approximations for the quantities they represent.

To be able to use the gas formulas, the following symbols need to be defined:

T = Absolute Temperature  
T degrees C = Temperature (degrees Celsius)  
T degees F = Temperature (degrees Farenheith)  
P = Pressure  
n = Moles of gas  
R = Ideal Gas Law Constant

When working with calculations involving the gas laws, the temperature used is always the absolute temperature.

T = T degrees C + 273 (in degrees Kelvin)  
or T = T degrees F + 460 (in degrees Rankine)

The first law presented is called Boyle's Law. It is expressed mathematically as:

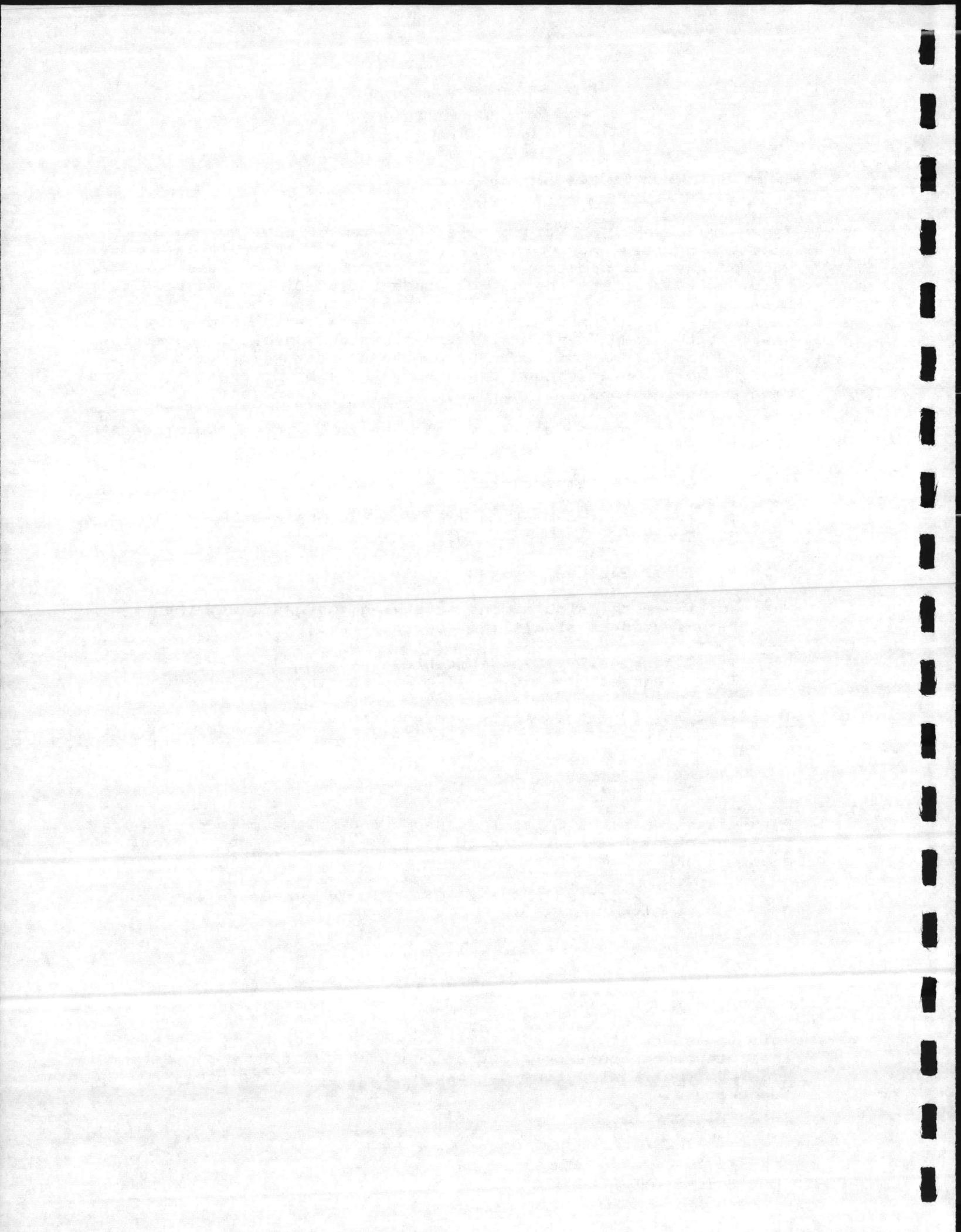
$$P_1 V_1 = P_2 V_2$$

This states that the initial pressure and volume of a gas at constant quantity and temperature is equal to the gas's final pressure and volume.

The next law is called Charles' Law. It is expressed as:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This law states that the initial volume divided by the initial absolute temperature of a gas at constant quantity and pressure is equal to the final volume divided by the final absolute temperature.



Thirdly, the Gay-Lussac law, which states that the initial pressure of a gas at constant quantity and volume divided by the initial absolute temperature is equal to the final pressure divided by the final absolute temperature, or:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

This law is particularly useful because its conditions apply to containers of constant volume, such as compressed gas cylinders.

By combining all three equations, the Ideal Gas Law is formulated:

$$PV = nRT$$

Example of a Gas Law calculation:

Most compressed gas cylinders are equipped with a safety device known as a bursting disc, which will rupture to avoid violent cylinder explosions at 1.5 times the service pressure of the cylinder.

A 2200 psi cylinder of oxygen at 70 degrees F is heated by fire. At what temperature will the cylinder's disc rupture?

Solution

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

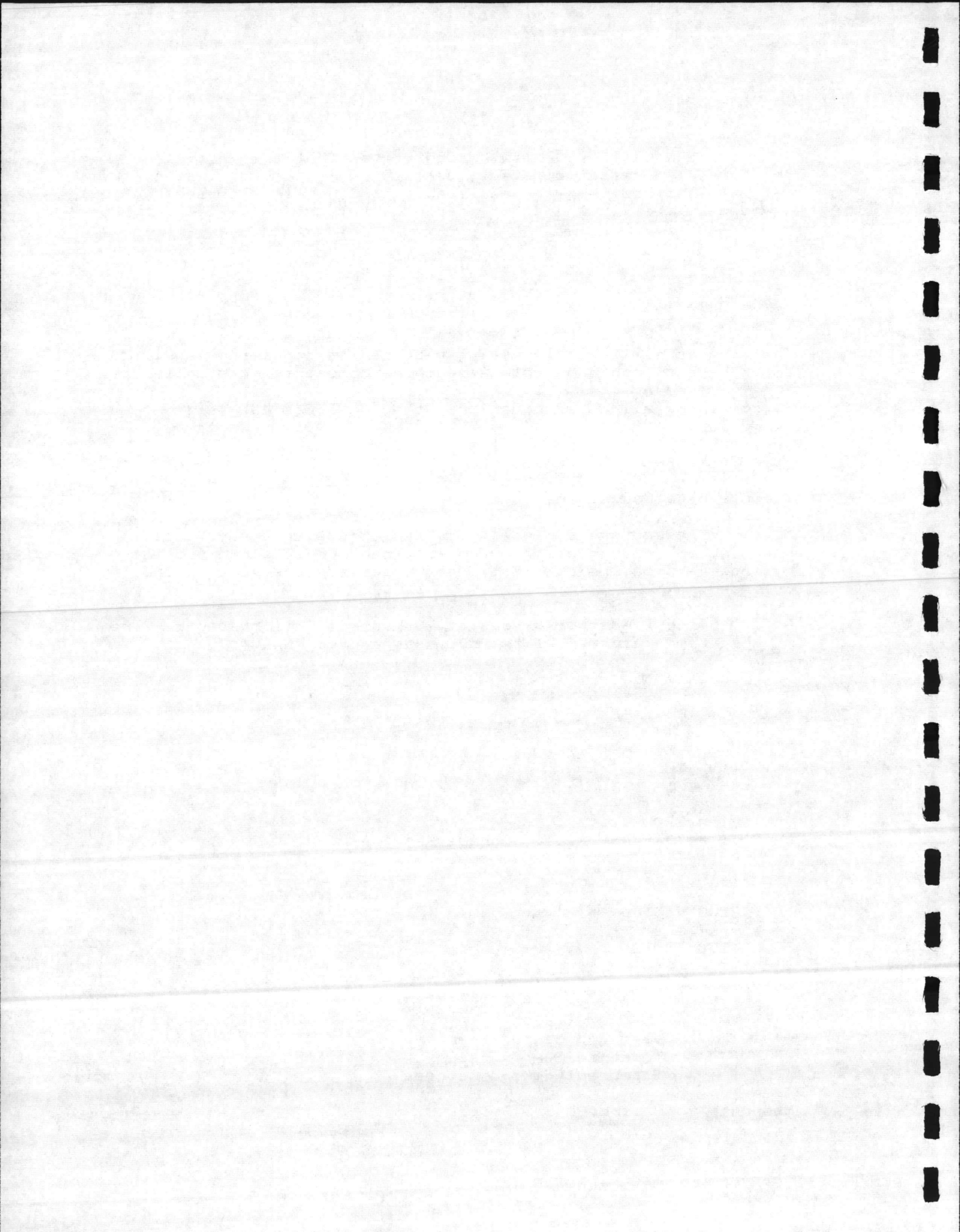
$$\begin{aligned} P_1 &= 2200 \text{ psi} \\ T_1 &= 70 + 460 = 530 \text{ degrees Rankine} \\ P_2 &= (1.5)(2200) = 3300 \text{ psi.} \\ T_2 &= ? \end{aligned}$$

$$\frac{2200}{530} = \frac{3300}{T_2}$$

$$\text{Solving for } T_2 = \frac{(3300)(530)}{(2200)}$$

$$\begin{aligned} T_2 &= 795 \text{ degrees Rankine} \\ T \text{ degree F} &= 795 - 460 \\ T \text{ degree F} &= 335 \text{ degrees F} \end{aligned}$$

Response to Hazardous Gas Releases



The Department of Transportation through the U.S. Coast Guard has published tables which list:

- 1) The maximum downwind distance over which gases may be harmful, and
- 2) The maximum width of the cloud that may be harmful for several different gases.

These tables divide the gases into two groups: toxic gases and flammable gases. The gases are listed in alphabetical order, and the data is listed for 1 ton, 10 ton, and 100 ton cylinder releases. The hazards calculated assume worst case weather conditions (steady low wind), and that the discharge occurred instantaneously. For cases when the release occurs over an extended period of time, the time which the gas is hazardous is considered the same period over which the release occurs.

From these tables, two useful formulas can be derived. First, the formula for time of the cloud arrival:

$$\begin{array}{l} \text{Time of Arrival} \\ \text{(min. after spill)} \end{array} = \frac{60 \times \text{Distance Downwind } V \text{ (miles)}}{\text{Wind Speed (MPH)}}$$

And secondly, a formula for the maximum duration of the cloud after reaching a point of measureable concentration:

$$\begin{array}{l} \text{Maximum Duration} \\ \text{(min)} \end{array} = \frac{\text{Maximum Width (ft.)}}{\text{Wind Speed (MPH)} \times 88}$$

Example: An instantaneous release of a 1 ton cylinder of chlorine gas occurs under worst weather conditions. What is the time of the cloud's arrival one mile away and the maximum duration if the wind is blowing at 5 MPH?

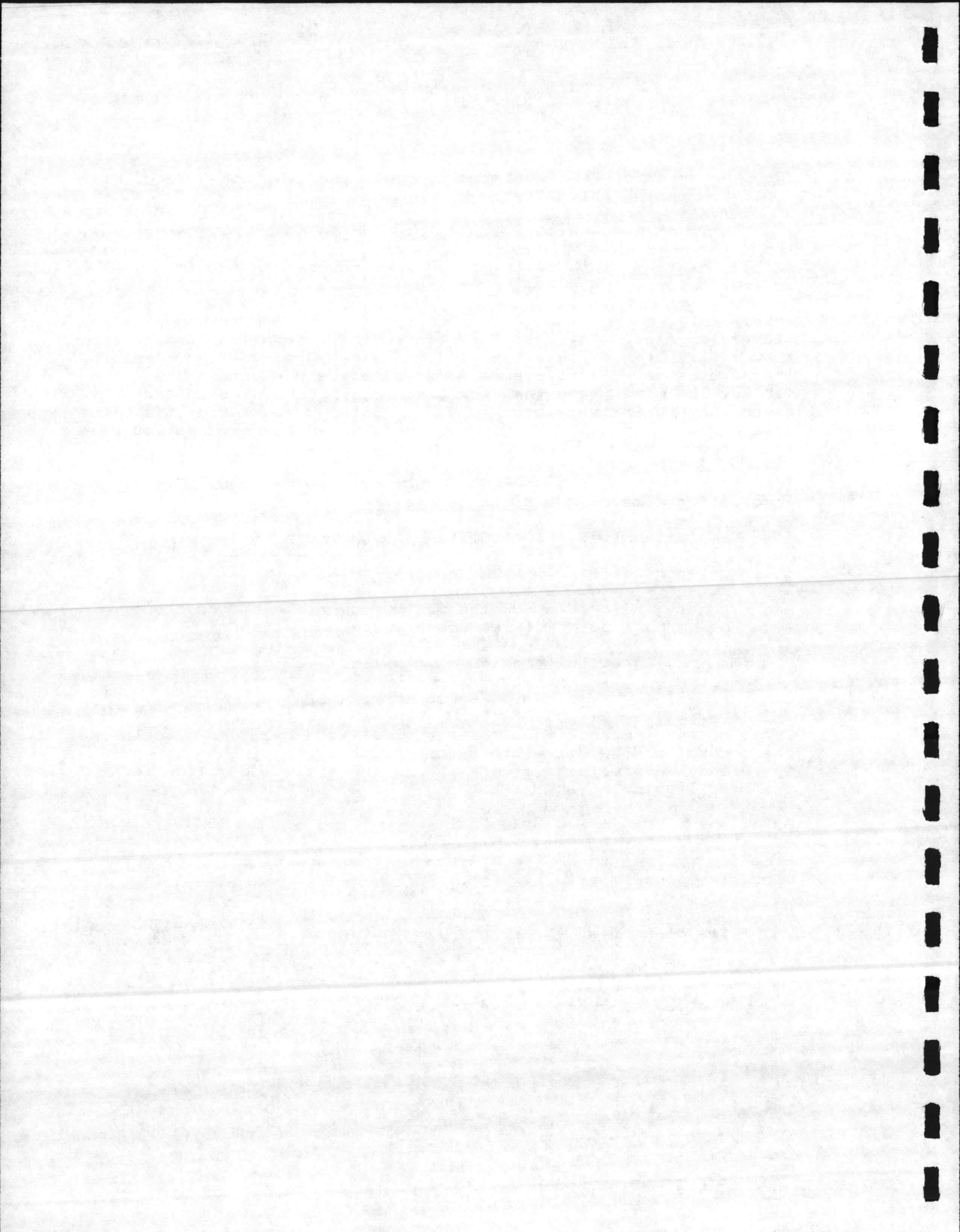
Solution:

From the tables, the maximum width of the harmful chlorine gas cloud is approximately 5000 ft.

$$\text{Time of Arrival} = \frac{60 \times 1}{5} = 12 \text{ minutes}$$

$$\text{Maximum Duration} = \frac{5000}{5 \times 88} = 11.4 \text{ minutes}$$

#### K. Summary





In summary the primary hazards associated with handling compressed gases and cryogenic liquids during spill incidents are the extremes of using high pressures, high vacuums, cryogenic temperatures, chemical hazards including flammables, corrosives, reactives, poisons, toxics, and oxidizers, oxygen deficiencies or enrichment and abnormally large volumes of gases.

In order to avoid injury, it is imperative to know the physical and chemical characteristics of the gases involved. This includes the containers peculiarities used for non-liquified, liquified, dissolved, and cryogenic gases.

Proper personal protective equipment such as gas masks, self-contained breathing apparatus, monitoring instruments and rescue equipment should be available for immediate use in hazardous atmospheres produced by unexpected releases of compressed gases.

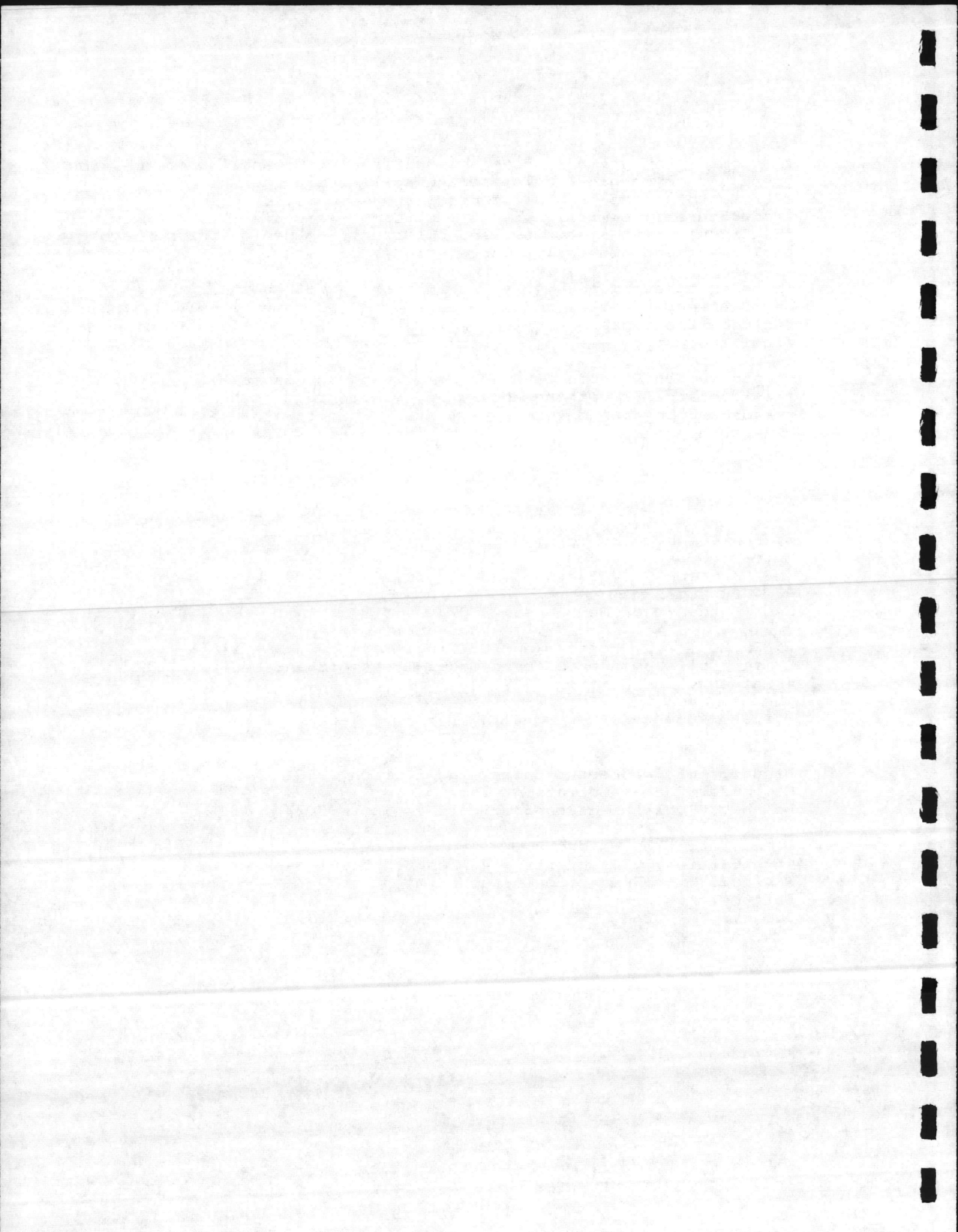
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## XVI. SITE CONTROL AND DECONTAMINATION

### INTRODUCTION

Two recent incidents involving chemical releases dramatically point out the need for decontamination procedures and systems.

In February 1982, an incident involving pentaborane "...killed one man, left another permanently blind and paralyzed, and caused minor to serious permanent damage to sixteen other people, including twelve members of the rescue squad." The victims and the rescue squad members were put into the ambulances without any decontamination. Subsequently, doctors and nurses at the hospital and family members exposed to the clothing experienced the same symptoms.

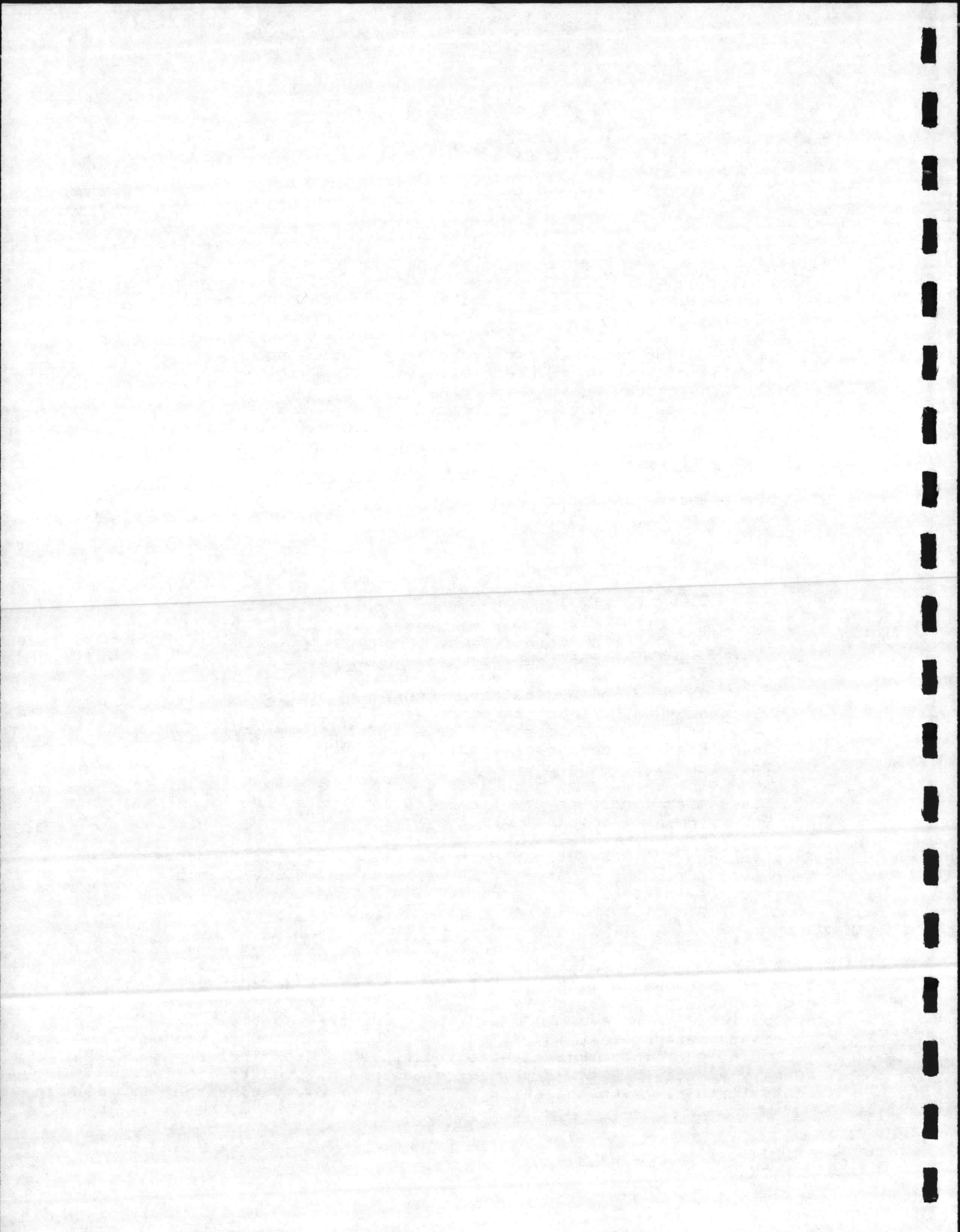
The above incident explains the need for hospitals at one extreme and rescue personnel at the other to have had decontamination training.

In April 1984, a manufacturer of printed circuit boards experienced a chemical release and mixing of sulfuric acid, sodium hydroxide, cupric sulfate, peroxydisulfuric acid and manganese dioxide. The materials were contained, sent through a neutralizing tank not designed for these products and into the sanitary sewer. A decontamination line was used for the firefighters but the runoff was not contained. Sewer plant operators were forced to evacuate the sewer plant, rescue squad and medical personnel not decontaminated experienced breathing difficulties among the other symptoms noted, and the fire department's hazardous materials team has been recommended to receive perpetual monitoring of their respiratory and pulmonary systems.

This incident points out the need for all persons to be decontaminated following exposures, as well as the need to contain the decontamination water runoff.

### SITE WORK ZONES

Once a hazardous substance spill has occurred and has been reported the response team should make a preliminary on-site evaluation. The primary interest is in identifying the immediate hazards that may effect the public and the environment. Depending upon the circumstances the situation is sized up as quickly as possible and a plan of attack is devised to contain, control and clean up the release. In almost every case the



immediate area of the spill is cordoned off in some fashion for the protection of the public from fire, explosion, radiation or air-borne contaminants.

Once the size of the spill has been determined, a buffer zone is required around the spill to establish a safety zone for additional public protection and to use for staging of equipment and supplies and to monitor the spill zone. Support equipment and a command post should also be established around the outside of the safety zone.

In work with abandoned hazardous waste sites and spill incidents, EPA has delineated three zones essentially as above. These are called the "exclusion zone" for the contaminated spill area and the outer perimeter of that zone is called the "hot line". Around the exclusion zone is an area called the "contamination reduction zone". This is a transition buffer zone between the contaminated zone and the clean zone. The contamination reduction zone is where decontamination of personnel and equipment takes place. In this middle zone, a "contamination reduction corridor" is set up to clean up the spill site workers as they leave the area for whatever reason. A wider corridor through this zone would be needed to move large equipment such as a forklift truck or backhoe.

The outermost zone or "support zone" is a clean area and has the command post, a dress-out and redress facility and parking area.

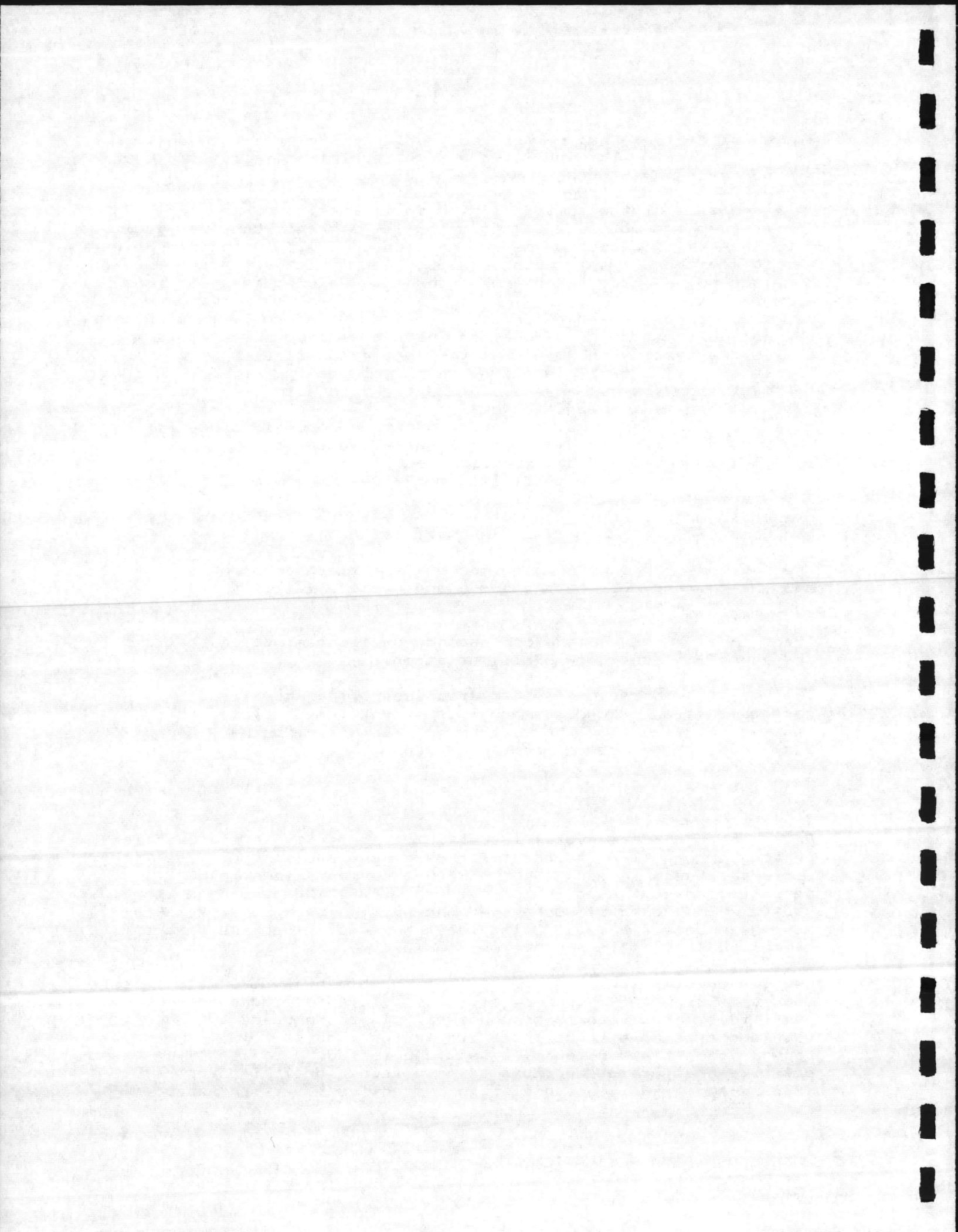
These three zones and the corresponding decontamination stations are shown in the following illustration.

The use of a three-zone system with controlled access and decontamination procedures provides a containment system that lessens the chance of the spilled material leaving the site and widening the area of contamination.

#### LEVELS OF PROTECTION

Once the three-zone system is set up it makes it easier to assign personal protective equipment for each zone and in some cases for different tasks in each zone. EPA has set up a four level personal protective equipment system (A,B,C,D) depending on the hazard encountered by workers at the spill site. Level A is the most hazardous and level D the least hazardous from the perspective of respiratory, skin and eye exposures.

Level A denotes a worst-case spill of highly hazardous materials such as a cloud of chlorine, arsenic, or cyanide compounds, pesticides, acid vapors, or unknowns. In these cases the lungs, skin and eyes have to be protected to the highest level. Depending on the substance, this might include a positive-pressure demand type self-contained breathing apparatus (SCBA), and a fully-encapsulating protective suit with expanded



back for the SCBA. Level A protection is suitable for oxygen deficient atmospheres and atmospheres having from 500 to 1000 ppm of the contaminant. Both conditions could be immediately dangerous to life or health (IDLH).

Level B has almost the same level of respiratory exposure but the skin exposure is less. Therefore a SCBA is still needed but light-weight suits such as raingear or disposable suits will probably give sufficient skin protection. Contaminants here are present in the air in a range from 5 to 500 ppm. Oxygen deficiency may still be a problem in level B areas. Level B protection is the minimum level required for the initial spill site survey.

Level C denotes areas where cartridge-type respirators can be used since there is no problem with lowered oxygen content in the air. Those contaminants that are present are at a low level and give adequate warning properties. Therefore, when the cartridge is beginning to lose its effectiveness, it can be detected. Contaminants here are present in the air at 5 ppm or below and would not be IDLH.

Level D does not require respiratory protection because the contaminants are below the threshold limit value (TLV) or short time exposure limit (STEL). Of course some kind of protective outwear like a plastic apron is needed as well as a full face mask or chemical goggles. It would also be a good idea to have a 5 minute escape mask available in case of a sudden release or a change in direction of the wind.

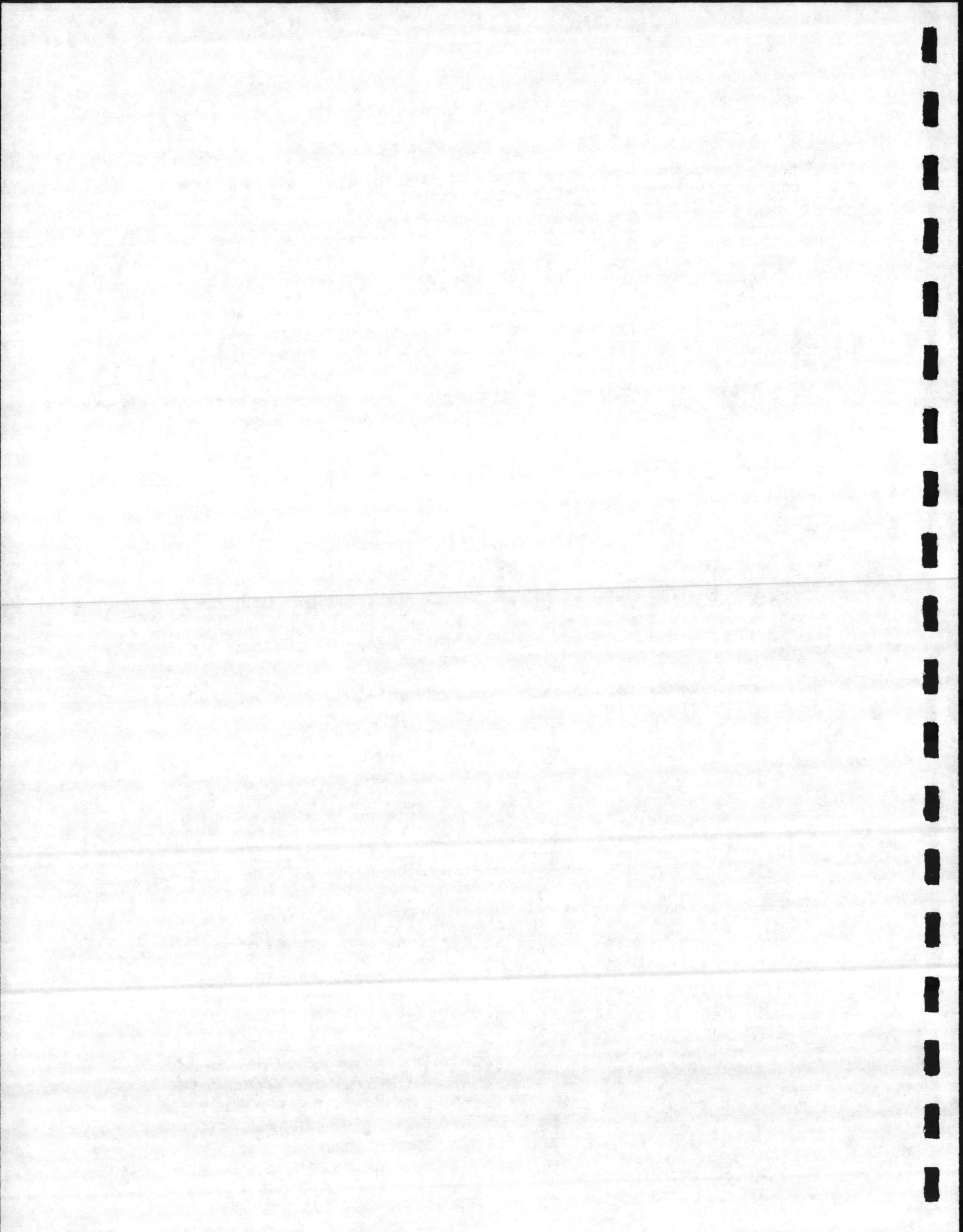
The following table provides a summary of the levels of protection discussed above.

#### DECONTAMINATION

Persons at a spill site become contaminated from exposures to hazardous chemicals. This may occur from: (1) contact with gases, vapors, mists or particulates in the air; (2) being splashed by materials while opening containers or sampling; (3) walking through puddles of liquids or on contaminated soil; or, (4) using contaminated instruments or equipment.

Although splash suits and other personal protective gear protects the person, it almost always becomes contaminated. As the response personnel leave the site they take this contamination off the site and further contaminate items they contact. A system needs to be established at the site to decontaminate the response team upon leaving the contaminated area.

Only general advice can be given on decontamination because it depends upon the chemicals encountered as to the methods that are used. In some cases the contaminant can be physically removed;





in other cases it may be chemically changed to an innocuous substance.

Using site work zones and combining decontamination with the correct method of doffing gear helps to control any further spread of the spilled material.

All personnel and equipment leaving the exclusion zone and crossing the hot line should be treated as dirty and in need of cleaning. A series of wash and rinse stations, each separated by several feet, is set up for pieces of personal protective garments worn. By having the first wash handle the most contaminated items (like gloves or boot covers) and the last station the least contaminated items (like underclothing) the contamination decreases as one moves farther down the line. This wash and rinse line is called the "contamination reduction corridor (CRC)".

As each piece of clothing is removed it is washed and scrubbed in a detergent solution and rinsed. Whether each piece is cleaned is visually determined in most cases. Wipe swabs may be used that can be analyzed at an on-site lab. If oils are involved a black light may be used to determine the extent of cleanliness.

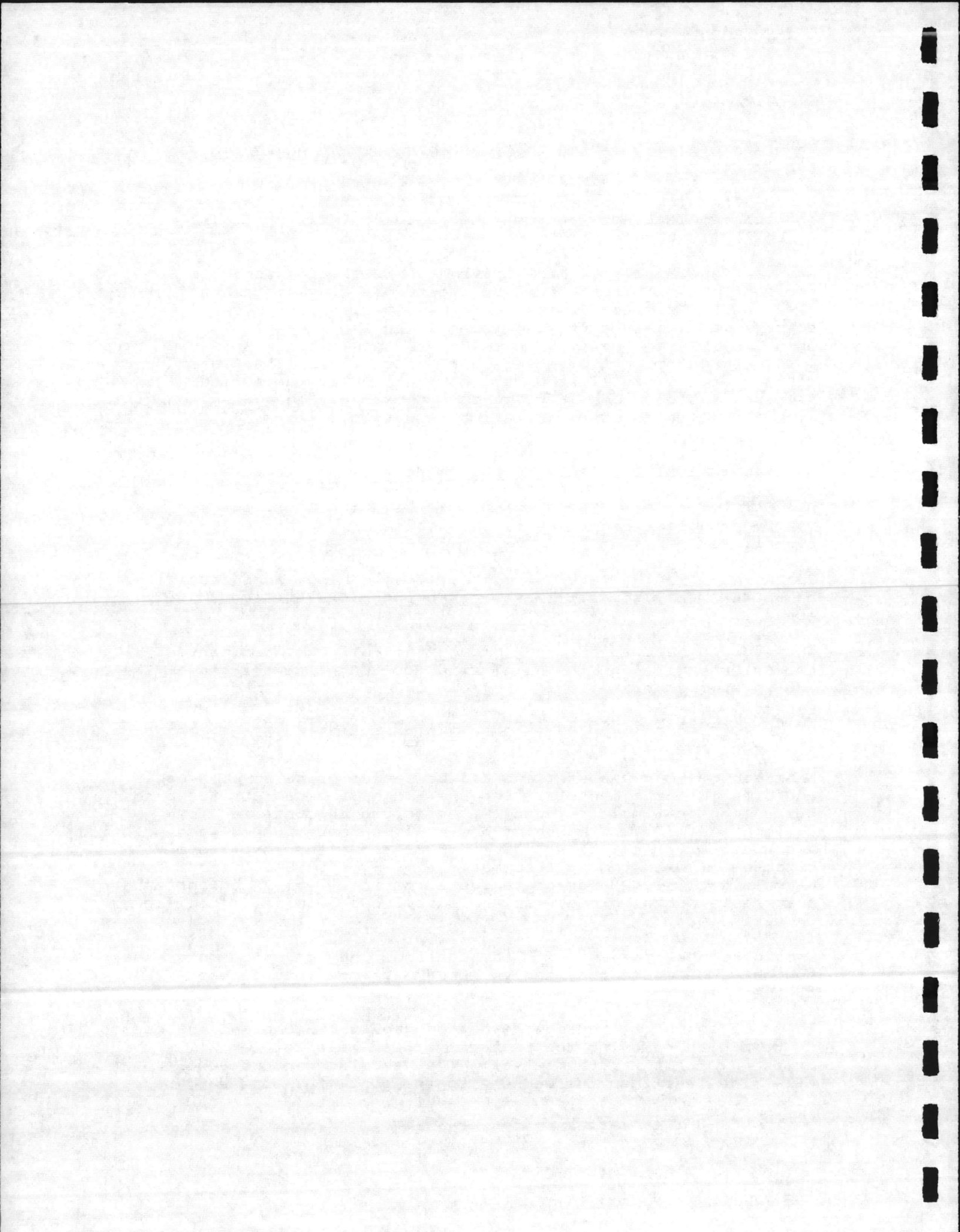
Depending upon the level of protective clothing worn there may be up to twenty separate wash, scrub and rinse stations established.

Individuals need to proceed through the full decontamination process when leaving the spill site for lunch, at the end of the day, and in similar situations. Persons changing air tanks or respirator canisters need only go through part of the line. Wherever possible, contaminated monitoring equipment and tools left overnight should be stored in the exclusion zone.

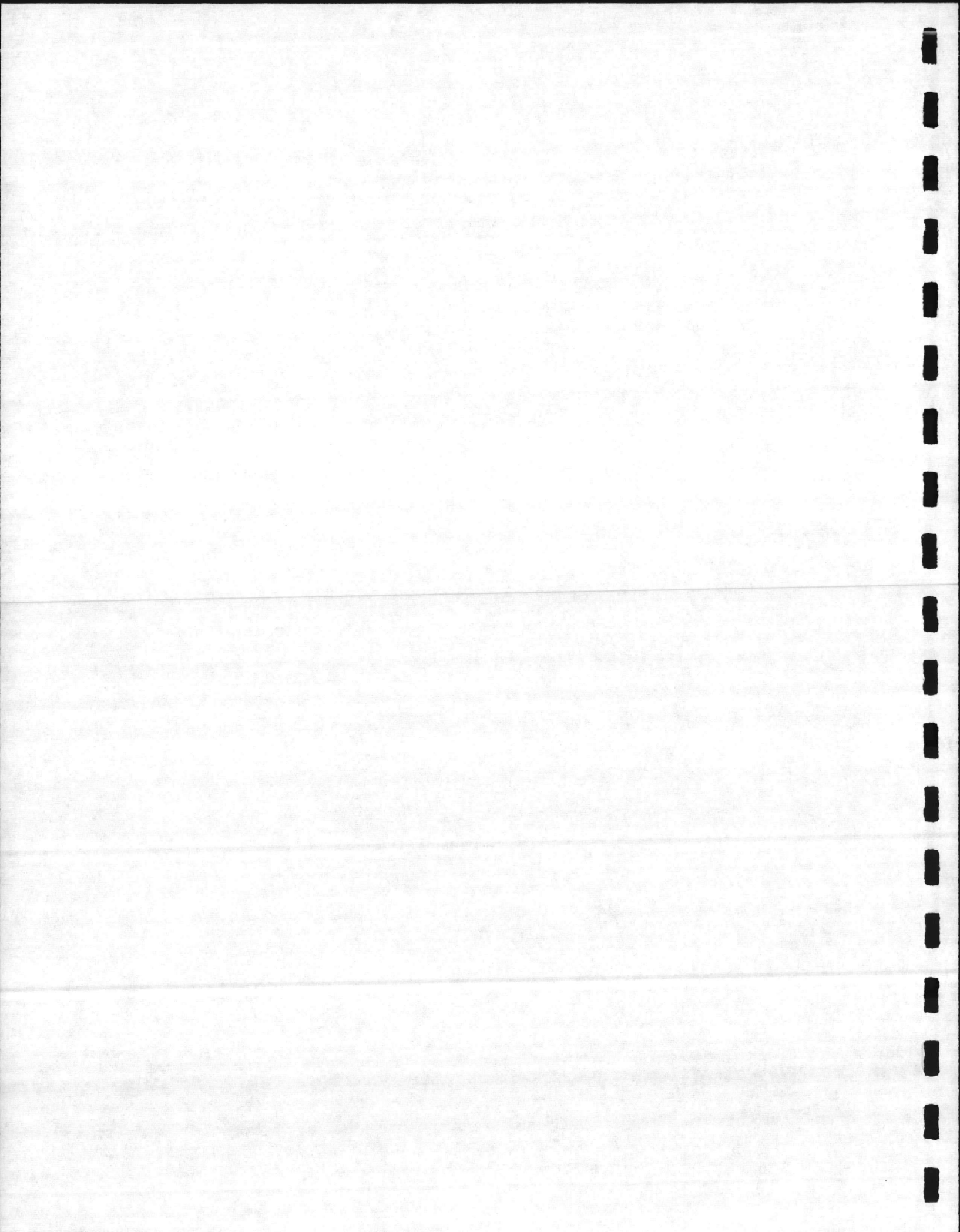
Wash scrub and rinse stations can be set up using scrub brushes, and plastic trash barrels. Showers and sprays can utilize garden hoses and spray nozzles, and the water can be contained in childrens' inflatable wading pools. The contaminated wash solution and rinse water can be stored in drums and either treated or disposed of with the spilled material. Plastic bag lined trash barrels can be used for contaminated drying towels, sealing tape, disposable boots, gloves, splash suits, and respirator canisters or cartridges.

Once personnel traverse all the stations they can then enter the support zone where they can shower and change into street clothes.

Those personnel in the contamination reduction zone who are needed to help with removing the protective gear need to wear protective clothing themselves. They should wear one level of attire less than the persons in the contaminated areas are wearing.



The following pages provide the proper protocol for level A decontamination.



## LEVEL A DECONTAMINATION

### A. EQUIPMENT WORN

The full decontamination procedure outlined is for workers wearing Level A protection (with taped joints between gloves, boots, and suit) consisting of:

- Fully encapsulating suit with integral boots and gloves.
- Self-contained breathing apparatus.
- Hard hat (optional).
- Chemical-resistant, steel toe and shank boots.
- Boot covers.
- Inner and outer gloves.

### B. PROCEDURE FOR FULL DECONTAMINATION

#### Station 1: Segregated Equipment Drop

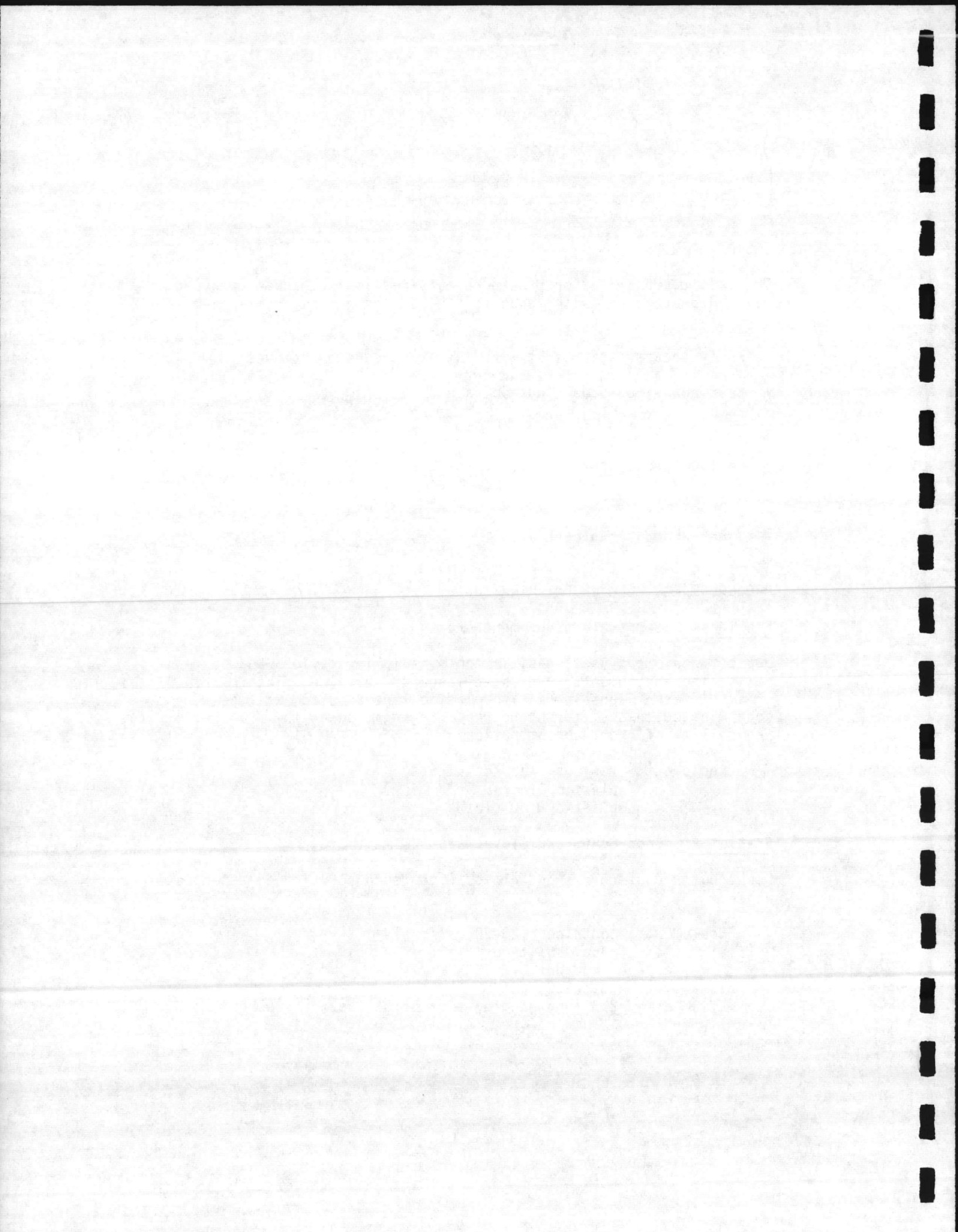
Deposit equipment used on-site (tools, sampling devices and containers, monitoring instruments, radios, clipboards, etc.) on plastic drop cloths or in different containers with plastic liners. Each will be contaminated to a different degree. Segregation at the drop reduces the probability of cross-contamination.

Equipment: various size containers  
plastic liners  
plastic drop cloths

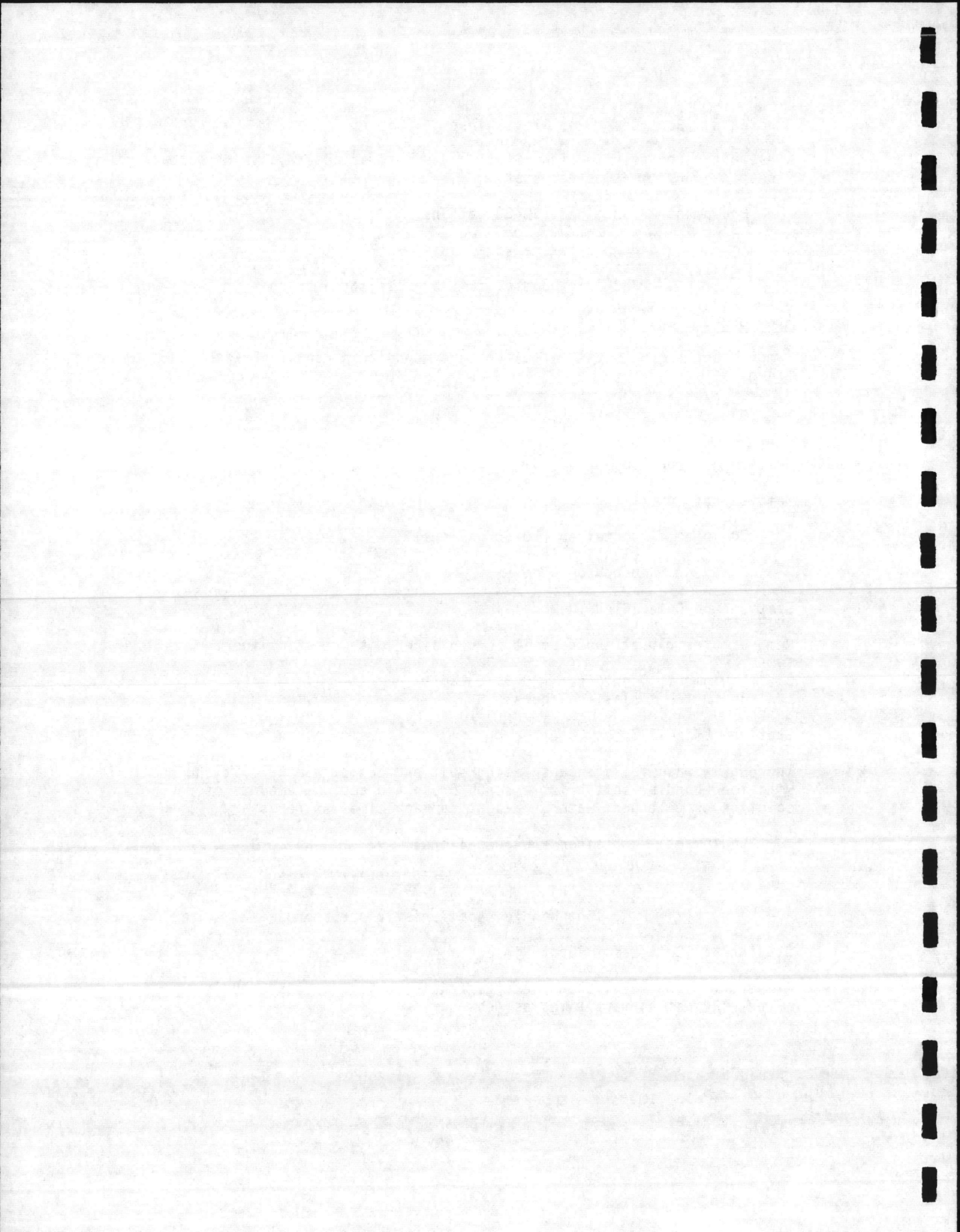
#### Station 2: Boot Cover and Glove Wash

Scrub outer boot covers and gloves with decon solution or detergent/water.

Equipment: container (20-30 gallons)  
decon solution  
or  
detergent water  
2-3 long-handle, soft-bristle scrub brushes

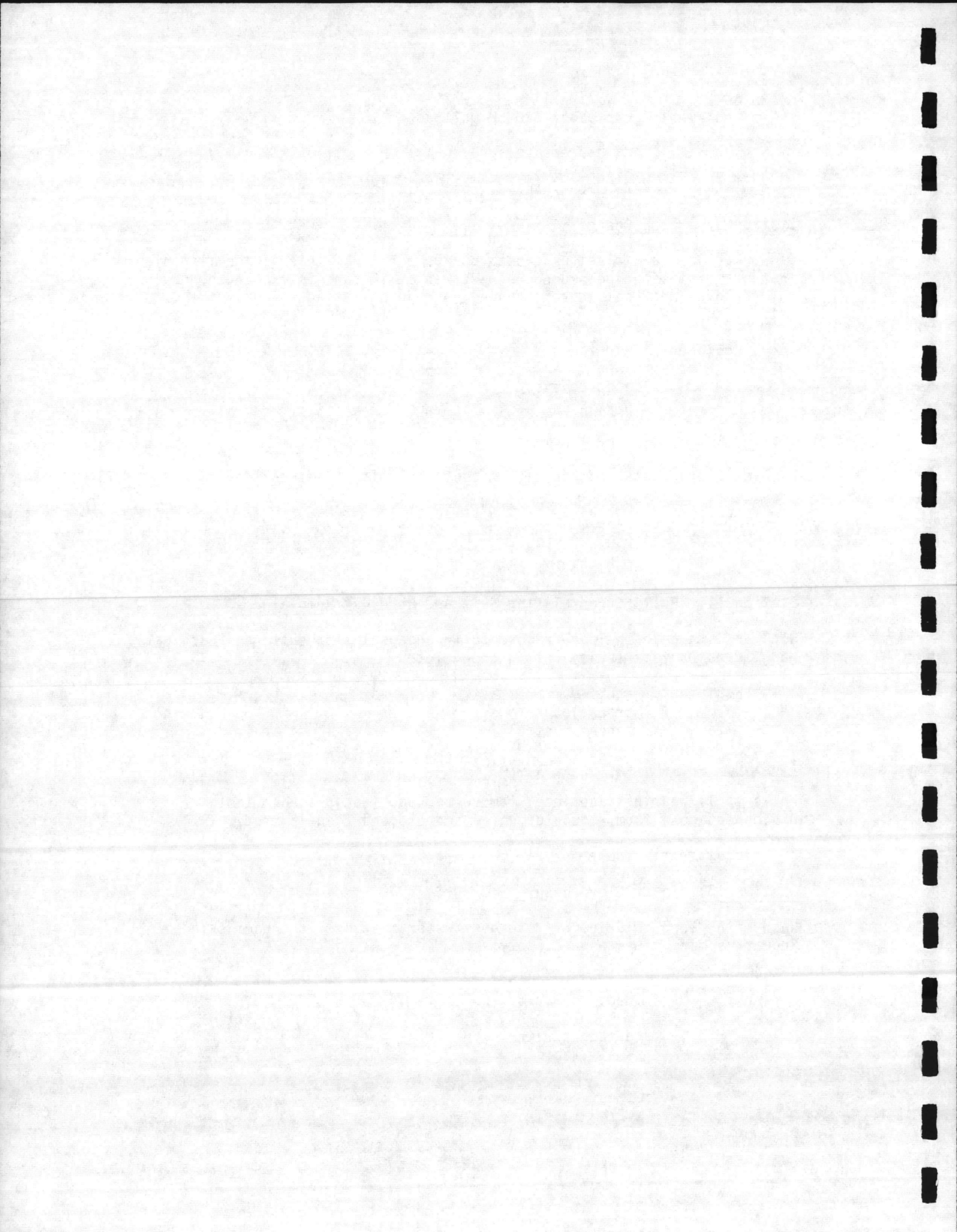












Station 14: Inner Glove Rinse

Rinse with water. Repeat as many times as necessary.

Equipment: water  
basin or bucket  
small table

Station 15: Facepiece Removal

Remove facepiece. Deposit in container with plastic liner. Avoid touching face with fingers.

Equipment: container (30-50 gallons)  
plastic liners

Station 16: Inner Glove Removal

Remove inner gloves and deposit in container with plastic liner.

Equipment: container (20-30 gallons)  
plastic liners

Station 17: Inner Clothing Removal

Remove clothing soaked with perspiration. Place in container with plastic liner. Do not wear inner clothing off-site since there is a possibility that small amounts of contaminants might have been transferred in removing fully encapsulating suit.

Equipment: container (30-50 gallons)  
plastic liners

Station 18: Field Wash

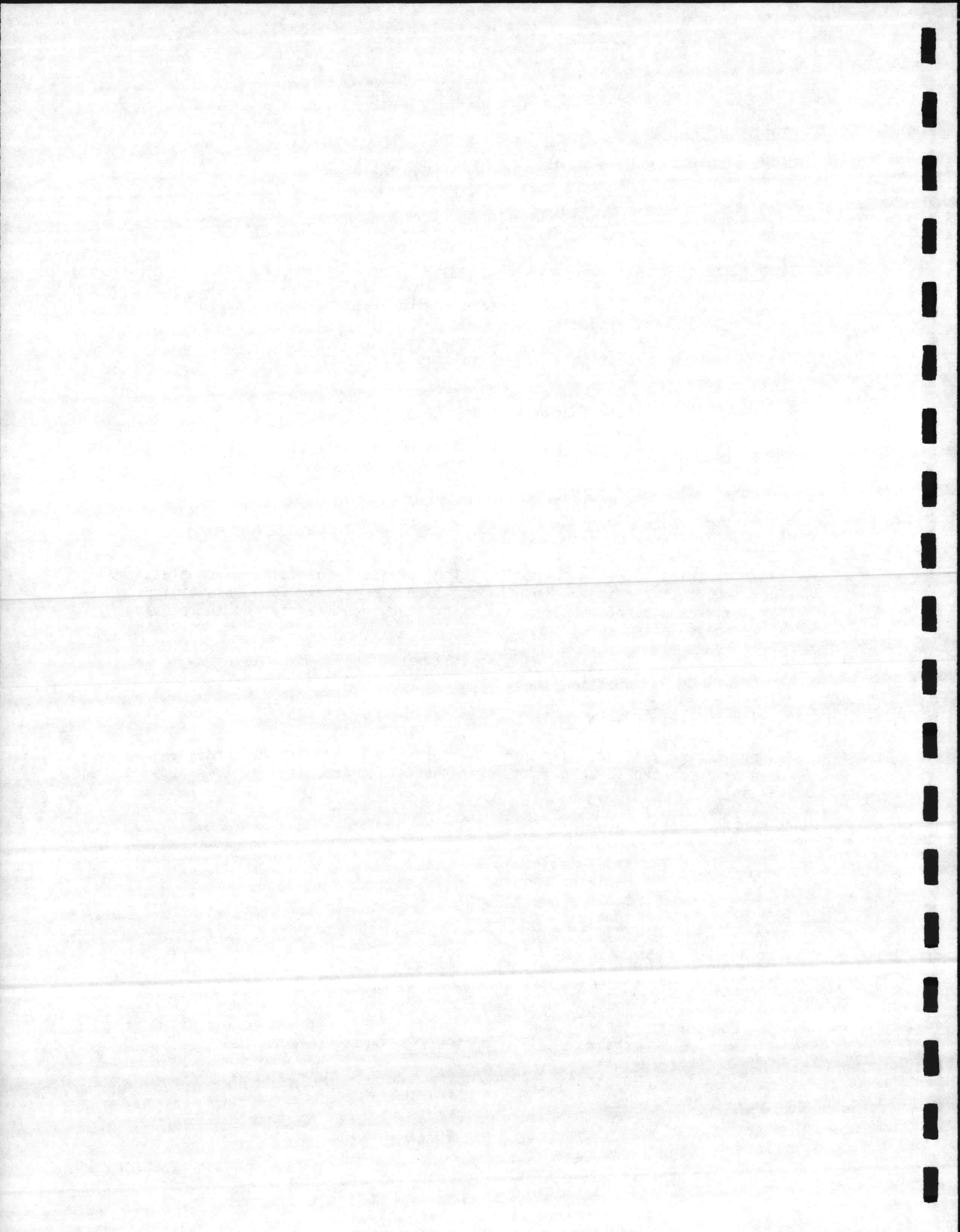
Shower if highly toxic, skin-corrosive or skin-absorbable materials are known or suspected to be present. Wash hands and face if shower is not available.

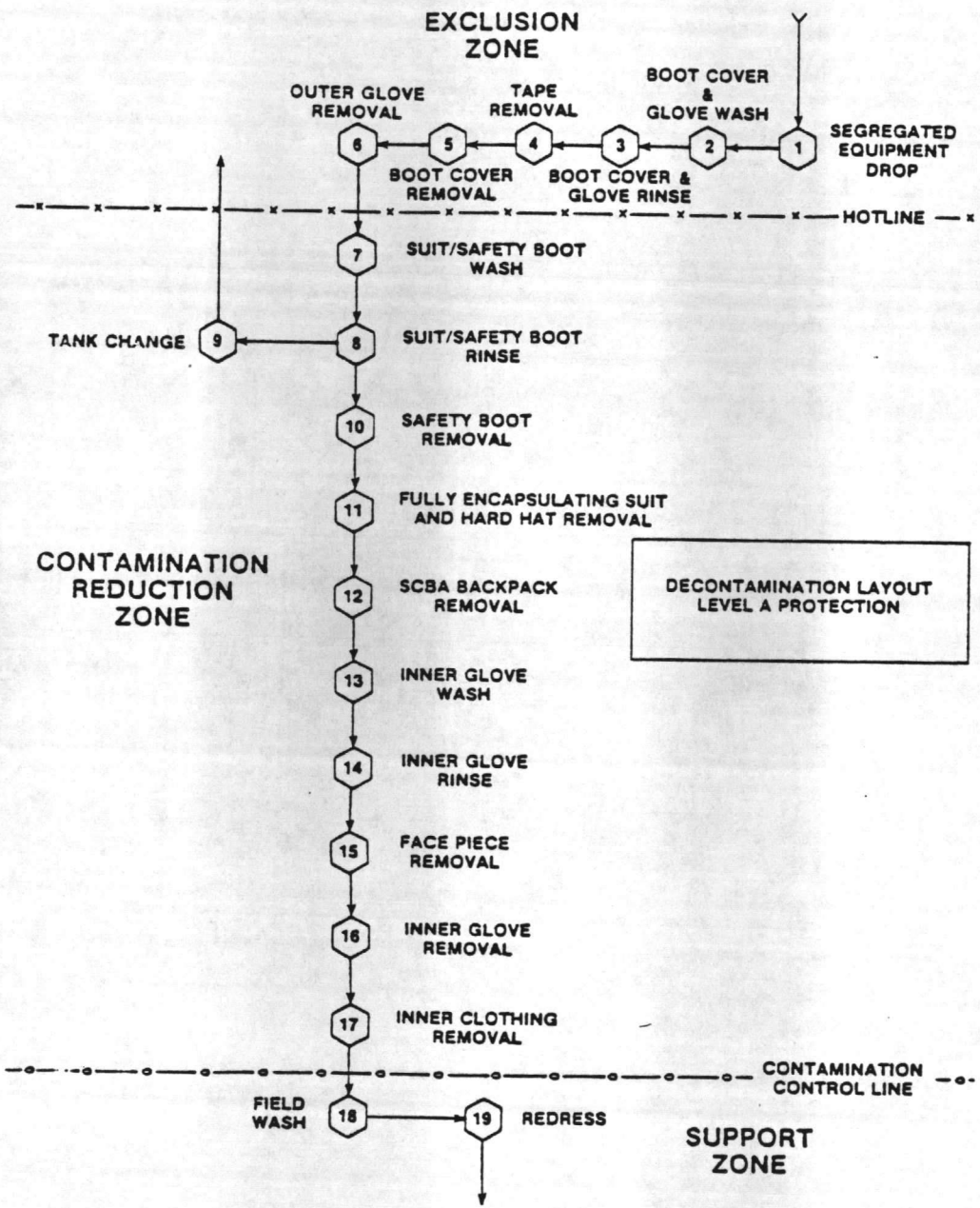
Equipment: water  
soap  
small table  
basin or bucket  
field showers  
towels

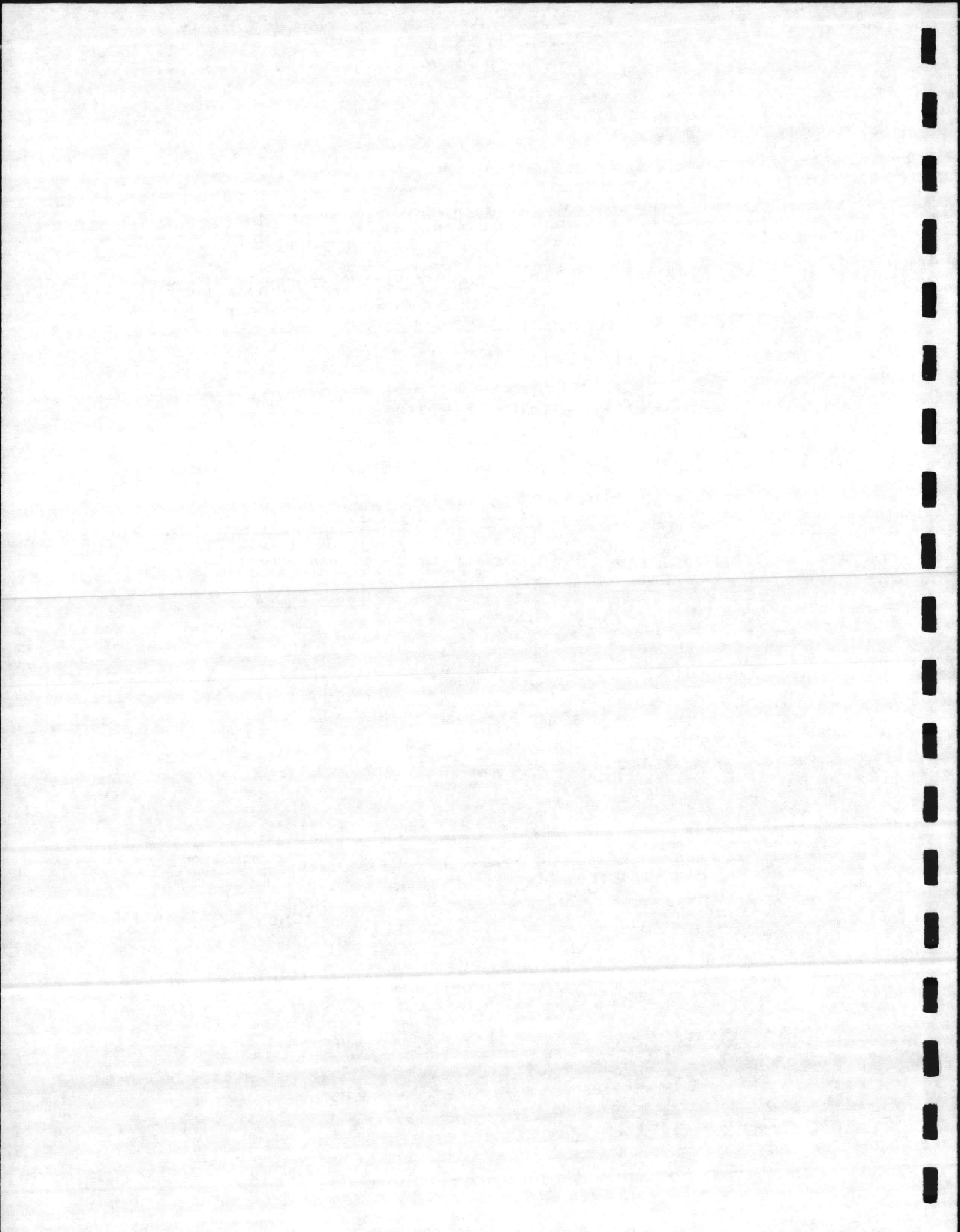
Station 19: Redress

Put on clean clothes. A dressing trailer is needed in inclement weather.

Equipment: tables  
chairs  
lockers  
clothes







C. FULL DECONTAMINATION (SIT. 1) AND THREE MODIFICATIONS

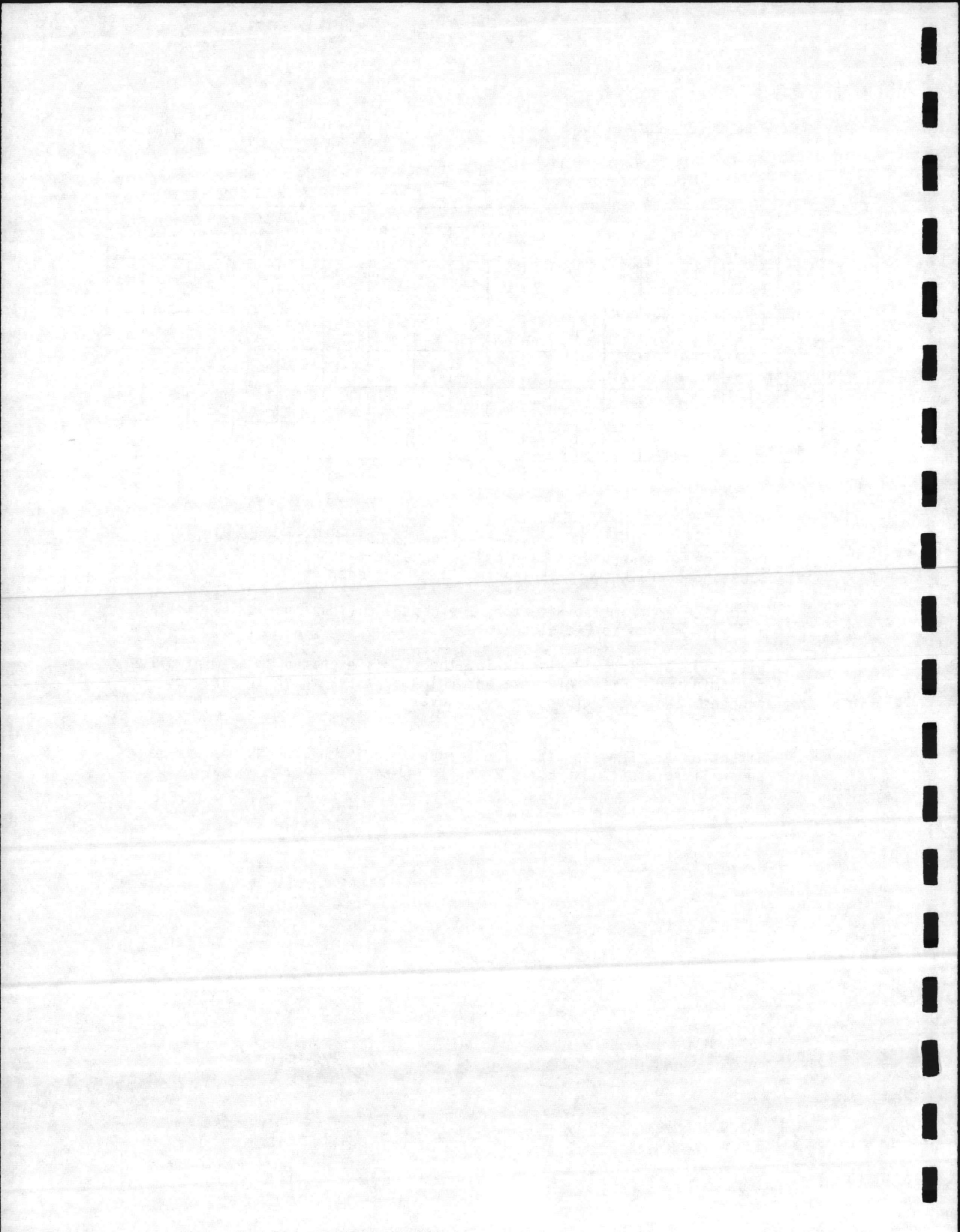
S I T	STATION NUMBER																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
2	X	X	X	X	X	X	X	X	X										
3	X						X	X		X	X	X			X	X	X	X	
4	X						X	X	X										

Situation 1: The individual entering the Contamination Reduction Corridor is observed to be grossly contaminated or extremely toxic substances are known or suspected to be present.

Situation 2: Same as Situation 1 except individual needs new air tank and will return to Exclusion Zone.

Situation 3: Individual entering the CRC is expected to be minimally contaminated. Extremely toxic or skin-corrosive materials are not present. No outer gloves or boot covers are worn. Inner gloves are not contaminated.

Situation 4: Same as Situation 3 except individual needs new air tank and will return to Exclusion Zone.





XVII OMITTED FOR THIS PRINTING

