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EDGEWOOD ARSENAL CONTRACTOR REPORT

EC-CR-76076

STATE-OF-THE-ART SURVEY
OF
LAND RECLAMATION TECHNOLOGY

May 1976

ARTHUR D. LITTLE, INC.
Acorn Park
Cambridge, Massachusetts
02140

Contract No. DAAA 15-75-C-0188

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DEPARTMENT OF THE ARMY
Headquarters, Edgewood Arsenal
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report focuses on absolute removal of contaminants from soil. A combination of downgradient ground and surface water collection and treatment with soil activation is recommended. The first method aims at eliminating leaching to ground (surface) water. The second stimulates natural degradation processes by way of soil activation. One method works on low-lying contaminants, the other works on the upper foot of soil. ↑		

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PREFACE

The work reported in this document was authorized by contract number DAAA15-75-C-0188, State-of-the-Art Survey of Land Reclamation Technology. It was carried out from June, 1975 to June, 1976.

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EXECUTIVE SUMMARY

Although there are many well documented incidences of land contamination due to burial or dumping of hazardous manufacturing wastes, we were not able to identify a single instance where an effort was made to handle the problem by actually removing the contaminants from the soil. In the vast majority of cases, land contamination is manifested by leaching of toxic materials to ground or surface water. This often represents a serious threat to public health, requiring prompt ameliorative steps. The most common approaches have been to condemn contaminated wells and provide a new water supply, or to divert surface and ground water away from the contaminated area through the use of trenches, barrier wells and pumps. Small areas of contaminated soil have on occasion been dug up and reburied in a secure, lined sanitary landfill. In cases where lateral migration of contaminants through the soil have been shown to be negligible, the contaminated area is frequently paved over with an impermeable material. None of these alternatives permits return of the contaminated land to unrestricted use.

This report focuses on approaches for absolute removal of contaminants from a land area half-a-square-mile in extent and 25 feet deep, the approximate size of Basin A at Rocky Mountain Arsenal (RMA). Three general types of approaches are considered: excavation and treatment; in-situ treatment; and ground water treatment. Specific implementation methods considered are listed below.

- A. Excavation and Treatment
 - 1. Incineration and revegetation
 - 2. Wet chemical processing

- B. In-Situ Treatment
 - 1. Soil Activation
 - 2. Vegetational Uptake
 - 3. Inoculation
 - 4. Fixation

- C. Ground Water Treatment
 - 1. Upgradient diversion
 - 2. Downgradient collection and treatment

A summary description of each method and its major characteristics is given in tables 1-7.

The various methods are compared with respect to technical and economic feasibility in table 8. Considering the state of the art (R&D time required to fill in gaps in the data base and to firmly establish technical feasibility), costs, and chance of success, we would recommend a combination of (1) downgradient ground and surface water collection and treatment, with (2) soil activation. The first method is directed towards the critical problem of leaching to ground water and should eventually result in removal of all leachable components

from the contaminated land mass. If in addition reagents and/or solvents were percolated through the land mass, using techniques developed for solution mining, removal of all toxic components could be accelerated. Simultaneously with ground water treatment, we recommend stimulation of natural degradation processes via soil activation. While the degree of detoxification achievable cannot be predicted, there is a moderate possibility of success for relatively little investment, and an added bonus in developing a strong and healthy soil for subsequent growth of vegetation. The two processes are compatible, the one working on low-lying contaminants, the other working on the upper 12 inches of soil. The one addresses the groundwater contamination problem, the other the phytotoxicity problem, both of which are tangible manifestations of land contamination.

Table 1. Incineration and Revegetation

Process Description

The contaminated area would be excavated, and the soil, after coarse screening, would be fed into a rotary kiln incinerator, 16 ft. in diameter and 300 ft long, with a capacity of 3000 tons/day. The incinerated and sterilized soil would be returned to the test site area, and restored to a condition where vegetation could again be supported.

Characteristics

State-of-the Art	Rotary kilns used by the cement industry have the necessary soils handling capability, temperatures and residence times. Techniques for revegetating sterile soils are well known.
Depth of Soil Treatable	No restrictions
Degree of Detoxification	Complete destruction of organics Partial volatilization of As, Hg, Zn, and B Will not remove Cr, Mn, or Fe
Time for Treatment of a 1/2 sq. mi. area, 25 ft. deep (Basin A analog)	15 years
Costs of Treating Basin A analog	Capital investment - \$10 million Operating costs - \$4.5 million/yr Revegetation costs - \$120,000

Conclusions

The method has potential for complete removal of organic contaminants. A separate treatment step might be necessary to remove heavy metals. The environmental impact of the excavation operation could be significant. Emissions of HCl from decomposition of chlorinated hydrocarbons, toxic vapors and particulates, must be controlled and could present disposal problems. Costs are high and the project time is long.

Table 2. Wet Chemical Processing

Process Description

The contaminated area would be excavated, and the soil after coarse screening, would be slurried with water and passed through a two-stage chemical reaction and/or solvent extraction train. The treated slurry would be dewatered by thickeners and rotary vacuum clarification filters, and returned to the test site area.

Characteristics

State-of-the Art	The unit processes involved in ore beneficiation and hydrometallurgy are closely analogous to those required for wet chemical processing of contaminated soils.
Depth of Soil Treatable	No restriction
Degree of Detoxification	Complete, in principal, but much R&D would be required to develop specific methods for detoxifying all contaminants present.
Time for Treatment of a 1/2 sq. mi. are, 25 ft. deep (Basin A analog)	15 years
Costs of Treating Basin A analog	Capital investment - \$10-25 million Operating Costs - \$3.5 million, exclusive of chemical reactants and effluent treatment train.

Conclusions

The method has potential for complete removal of all contaminants, but specific chemical detoxification methods (e.g., hydrolysis, neutralization, oxidation, reduction, solvent extraction, etc.) for the contaminants found to be present will have to be developed and tested. Water usage is expected to be of the order of 7000 tons/day, and the effluent control and waste disposal problems could be very severe. Costs are at least as high as those for incineration, and project time is comparable. The properties of the soil would be affected far less by wet chemical processing than by incineration.

Table 3. Soil Activation

Process Description

The properties of the soil (e.g., pH, oxygen content, moisture content, organic content, and temperature) would be adjusted to maximize its inherent capacity to degrade toxicants via chemical and biological mechanisms.

Characteristics

State-of-the Art	Natural soil degradation processes are well documented for many contaminants. Accelerated rates of degradation of a number of pesticides have been achieved by manipulation of single soil parameters. The method has not been applied on a large scale, and has not been tested for soils contaminated with a wide variety of chemical species.
Depth of Soil Treatable	Probably only the top 12 inches, at most.
Degree of Detoxification	Largely unknown. Organophosphates and carbamates do degrade to non-toxic products. Some contaminants may be converted to equally or more toxic products
Time for Decontamination	5-20 years
Costs of Treating a 1/2 sq. mi. area	\$1.4 million

Conclusions

Since the method involves stimulation of natural processes, the environmental impact should be minimal. Laboratory and small field plot tests will be necessary to determine optimum conditions for degradation of each contaminant present, and to establish technical feasibility for the particular contaminated area under consideration. If the method is demonstrated to have real potential for converting the contaminants present to non-toxic products, then it has the advantage of relatively low implementation costs. The method, if it works at all, would probably not be capable of degrading contaminants lying much below a depth of 12 inches.

Table 4. Vegetational Uptake

Process Description

Crops capable of concentrating toxic residues from soil would be repeatedly planted, harvested, and hauled away for disposal (most safely by incineration).

Characteristics

State-of-the Art	Root crops and soybeans have been shown to concentrate residues of arsenic, lead, and a number of pesticides. The method has not been applied on a large scale, or for multiple contaminants.
Depth of Soil Treatable	Removal is probably limited to the upper twelve inches of soil, although some crops, such as alfalfa are much more deeply rooted.
Degree of Detoxification	Largely unknown. A few field studies have shown of the order of 5% removal of certain pesticide soil residues per harvest.
Time for Decontamination	At 5% removal per harvest, independent of concentrations present, 60 harvests would be needed to achieve 95% removal of the original contaminants present.
Costs of Treating a 1/2 sq. mi. area	\$60,000/harvest (exclusive of disposal costs for the contaminated vegetation).

Conclusions

It is very questionable whether a soil contaminated with a multitude of toxic compounds could be cleaned up to any significant extent by planting and harvesting vegetation. Even for those contaminants that would be taken up and translocated into the crops selected, times of the order of 60 years would be required for 95% removal. Furthermore, it is not highly likely that the most effective crops, from the point of view of contaminant uptake, will be ideally suited for growth in any given contaminated area. There are also environmental risks in deliberately growing contaminated crops. Promising candidates, such as sugar beets, carrots, soybeans and alfalfa, are used for food and forage by various domestic and wildlife species. The vegetables are eaten by man. Thus, the utmost care would be required to assure that harvested crops are disposed of properly, and are not accidentally used as food for animals or man. Although the costs of planting and harvesting are lower than for any other alternative, the method also has a very low probability of success

Table 5. Inoculation

Process Description

Large quantities of microorganisms with known ability to degrade the contaminants of concern would be incorporated into the soil.

Characteristics

State-of-the Art	Appropriate microorganisms are not known for every contaminant likely to be present. Lab studies are few in number and generally show slow degradation, often to products that are still toxic. Field tests have failed due to inability of the microorganisms to survive in competition with endogenous species.
Depth of Soil Treatable	Upper twelve inches
Degree of Detoxification	Unknown
Time for Decontamination	Unknown
Costs	Higher than soil activation, since appropriate microorganisms would have to be isolated, and then incorporated into the soil much as in the activation process.

Conclusions

The method is judged technically infeasible for the foreseeable future.

Table 6. Upgradient Ground and Surface Water Diversion

Process Description

A bentonite slurry trench, barrier wells or an infiltration gallery, and a surface drain would be installed to divert water from the contaminated land mass or leachate source.

Characteristics

State-of-the Art	The method has been applied and represents well established technology.
Depth of Soil Treatable	Not a treatment method, but only a containment technique.
Degree of Detoxification	Close to 100% eventually for the water; zero for the land. Leaching of land contaminants is prevented, but contaminants are neither removed nor treated
Treatment Time	Infinite
Costs of Diversion away from Basin A	Capital Investment - \$1.2 million (with barrier wells) - \$2.2 million (with an infiltration gallery) Operating Costs - \$130,000/yr (with wells) - \$230,000/yr (with gallery)

Conclusions

If the problem is containment of contaminated ground water, the method could be implemented relatively rapidly, following hydrogeological analysis, determination of cross sections, pumping tests, and dye studies. Once a sound data base has been obtained, the design of a system to do the job should be relatively straightforward.

Table 7. Downgradient Ground and Surface Water Collection and Treatment

Process Description

A barrier system would be installed to intercept contaminated waters. Collected water would be pumped to a treatment plant, and clean water would be recharged to the aquifer. A possible treatment sequence might include filtration to remove suspended solids, carbon adsorption to remove organics, and reverse osmosis to remove inorganic ions.

Characteristics

State-of-the Art	Technology to design an appropriate barrier system is available. Treatment of the water and subsequent recharge has been talked about a lot, but has seldom been implemented.
Depth of Soil Treatable	From ground surface to top of the first impermeable unit.
Degree of Detoxification	Eventually, all leachable components should be removed. Leaching of insoluble or strongly adsorbed contaminants might be promoted through use of appropriate reagents or solvents (as in solution mining).
Time for Decontamination	Unknown but probably of the order of 50 years.
Costs for Clean-up of Basin A	Capital Investment - \$5.9 million (with barrier wells) - \$9.7 million (with an infiltration gallery) Operating Costs: ~ \$1 million/yr.

Conclusions

Although this method is comparable in cost to incineration or wet chemical treatment, and the project lifetime is longer, it is the only state-of-the-art method that can handle both organic and inorganic contaminants. It also avoids the rather severe environmental impacts that could be associated with an excavation operation in contaminated soil. The preliminary lab and field test data required for implementation is less than for incineration, and far less than for wet chemical treatment. The degree of detoxification achievable through interception and treatment of the groundwater should eventually approach that for treatment of excavated soils, although the times for detoxification would be vastly longer.

Table 8. Summary of Treatment Methods Examined
(half sq. mi. contaminated land area, 25 ft. deep)

Decontamination Method	Project Time (yrs)	Capital Investment (\$)	Annual Operating Costs (\$/yr)	R&D Time Prior to Implementation	Chance of Success	Notes
Inclination and Revegetation	15	10,000,000	4,500,000	1-2 years	Very high for organics	Heavy metals may require separate treatment
Wet Chemical Processing	15	10,000,000-25,000,000	>3,500,000	3-5 years	Very high in principle	Specific chemical steps are yet to be worked out.
Soil Activation	5-20	-	1,400,000(a)	2-4 years	Moderate(b)	(a) Costs of a single treatment, which might suffice (b) No really hard data are available (c) Exclusive of disposal of harvest
Vegetational Uptake	60	-	60,000(c)	3-5 years	Low	
Inoculation	Unknown	-	Greater than soil activation	>10 years	Very low	
Upgradient Ground and Surface Water Diversion	Infinite	1,200,000-2,200,000	130,000-230,000	<2 years	High for containment; zero for land decontamination	
Downgradient Ground and Surface Water Collection & Treatment	>50	5,900,000-9,700,000	~1,000,000	2-3 years	High, but very slow	

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I. INTRODUCTION

A. Scope of Work

On July 1, 1975, Arthur D. Little, Inc. entered into a contract with Edgewood Arsenal to prepare a state-of-the-art survey of methods potentially applicable to restoring large contaminated land areas for unrestricted use. Two tasks, as described below were carried out:

Task 1 - Identification of Methods

- a. The literature was reviewed to identify methods of large scale land reclamation.
- b. Information was solicited through personal contact with experienced industry, government and university representatives.
- c. Consideration was given to allied processes dealing with mining; toxic and hazardous waste handling and disposal; reclamation of dredge spoil areas; spill cleanup; and commercial handling of large amounts of soil like material (e.g., cement manufacture).
- d. A listing and description of potentially applicable methods was prepared.

Task 2 - Classification of Land Areas for Decontamination

- a. Arthur D. Little, Inc. was provided with a description of contaminated areas by Edgewood Arsenal, with an emphasis on conditions prevailing at Rocky Mountain Arsenal (RMA).
- b. The technical feasibility of using the methods identified in Task 1 for various types of contaminated land areas was assessed.
- c. Rough estimates of economic feasibility were prepared for the technically promising methods, and data needed to refine these estimates were specified.

B. Nature of the Problem

Throughout history, waste products from industrial production and other activities have been disposed of on land. Only relatively recently has it been recognized that indiscriminate use of land disposal sites for certain types of chemical wastes can give rise to a variety of adverse environmental effects. In the vast majority of documented incidences of improper land disposal, the problem has been manifested by leaching of toxic substances to groundwater or discharge of contaminants to surface waters. (1) The problem of land contamination is quite universal in highly industrialized nations, and has been associated with industrial plants, commercial laboratories, public and private landfill sites, commercial waste disposal facilities, etc.

A historical survey of official data relating to the missions of DARCOM installations suggests that large tracts of land may have become contaminated over the years since 1942 with a variety of toxic substances, as a result of deliberate waste disposal procedures or as a result of continuous functioning and field testing of weapons. A list of suspected contaminants is given in Table 9. Levels are not known precisely but probably range from one to 1000 ppm, with not every contaminant present in every area. Such chemically contaminated areas were originally intended to be permanently denied to civilian populations. There is now reason to consider converting these areas to unrestricted civilian use. Furthermore, some of the contaminated areas are in close proximity to shallow aquifers and hence represent a potential threat to public water supplies. This report provides a survey of the current state of the art of land decontamination, with specific reference to the applicability of existing methods to DARCOM problems.

C. Basic Approach

Adverse environmental effects due to contaminated land areas are generally manifested in one or more of the following ways:

1. Groundwater contamination due to leaching from the land
2. Surface water contamination due to run-off from the land
3. Inhibited plant growth, if the contaminants have reached phytotoxic levels in the soil
4. Uptake of contaminants by vegetation and transfer through the food chain
5. Air pollution due to evaporation, sublimation and wind erosion from contaminated soils
6. Poisoning via direct contact
7. Fire and explosion

Due to the very complex and often slow mechanisms of transport and degradation of contaminants in the soil, adverse environmental effects may not become apparent until 40 or 50 years after the initial contaminant deposition. Leaching, for example, may go on continuously, but it will generally go unnoticed until the contaminated leachate has reached the ground water. The rate of movement of leachate through the soil is a function of the contaminants present, the soil type, rainfall, temperature, etc.; it cannot be predicted accurately. In contrast, the dispersion of a contaminant in the air or water environment is typically quite rapid, and can be modeled reasonably well.

Clearly, absolute physical removal of all toxic materials from the soil would solve environmental problems that may have already developed, and also provide complete safeguard against the possibility of such problems developing in the future. On the other hand, the process of digging up the soil for treatment can in itself create adverse environmental impacts, such as noise, dust, and destruction of existing habitats. Furthermore, if the treatment process selected removes essential soil nutrients or microorganisms as well as undesirable contaminants, the

Table 9. List of Suspected Contaminants

<u>Highly Toxic Contact Hazards</u>		
Mustard	Lewisite Oxide	Lewisite
VX	GB	White Phosphorous
<u>Metals and Metal Salts</u>		
Arsenic	Chromium	Mercury
Boron	Copper	Sodium
Cadmium	Iron	Zinc
Calcium	Manganese	Potassium
<u>Insecticides, Pesticides</u>		
Aldrin	Phosdrin	Dicyclopentadiene (DCPD)
Chlordane	Ciodrin	Bicycloheptadiene
Dieldrin	Bidrin	Dibrom
Endrin	Planavin	Landrin
Nudrin	Bladex (Formulate)	Cardonal (Rabon)
Azodrin	Vapona (DOVP)	Nemagon
<u>Other</u>		
Arsenic Oxide	Phenolics	
Chloride	Diisopropyl methylphosphonate (DIMP)	
Fluoride	Sodium isopropyl Methylphosphonate (SIMP)	

High Salt Content as Result of the Above

essential elements would have to be replaced before the soil could be considered suitable for unrestricted use. Incineration, for example, would yield a completely sterile soil.

As a practical matter, immobilization of contaminants in the soil, detoxification in situ, and/or cleanup of groundwater might provide more optimal alternatives to absolute removal of contaminants. In other words, it may prove more cost effective to mitigate against the toxic effects of soil contaminants without actually removing the contaminants.

In the civilian sector, where there have been many reported incidents of ground and surface water contamination, phytotoxicity, poisoning, air (1-3) pollution, fires and explosions due to improper land disposal of toxic substances, we are not aware of any instances where an attempt was made to clean up the land by actual physical removal of the contaminants. The most common "decontamination" approaches have included:

1. Digging up of the contaminated soil and reburying it in a secure, lined sanitary landfill (This is applicable only when small areas are contaminated.)
2. Condemnation of contaminated wells and extension of public water supplies into the area. (This amounts to abandonment of the contaminated area.)
3. Diversion of surface and ground water away from the contaminated area. (This also is abandonment in a sense.)
4. Capture and treatment of contaminated ground and surface water. (This must usually be done essentially forever, but should eventually remove all leachable contaminants from the soil.)
5. Paving over the contaminated area with an impermeable material. (This can only be effective if there is no lateral motion of contaminants through the soil, and of course does not return the land to unrestricted use.)

Basically, there are three generic approaches with potential for restoring contaminated land areas to unrestricted use. These are listed below together with a number of specific variants.

- A. Decontamination by Treatment of Excavated Soil
 1. Incineration and Restoration of Soil Properties
 2. Wet chemical and/or Solvent Extraction Processes
- B. Decontamination by In-Situ Treatment
 1. Soil Activation
 2. Vegetational Uptake
 3. Inoculation
 4. Fixation

C. Decontamination of the Land by Capture and Treatment of Contaminated Ground and Surface Water

1. Barrier wells or infiltration galleries and pumps
2. Water treatment facility
3. Percolation of solvents and chemical reactants through the soil to promote release to the water treatment system.

The state of the art, technical and economic feasibility, and advantages and disadvantages of each of these approaches is discussed in the sections that follow.

II. DECONTAMINATION BY TREATMENT OF EXCAVATED SOIL

Two methods are considered in this section for removing contaminants from soil, following excavation. These are rotary kiln incineration, and wet chemical treatment. They are analogous to thermal processing and hydrometallurgical processing respectively in the mining, metallurgical and mineral industries. Both are fairly expensive with capital investment requirements of the order of \$10 million for a plant capable of treating 1×10^6 tons of soil per year. Minimum operating costs are estimated to be in the neighborhood of \$4-5 million/yr. The throughput time for a half square mile contaminated area 25 feet deep is estimated to be about 15 years. Since incineration results in a sterile soil, microorganisms and soil nutrients would have to be restored to the treated soil in order to render it suitable for the growth of vegetation (i.e., for unrestricted use).

A. Land Reclamation via Incineration

1. State of the Art - Incineration as a method of thermal destruction of waste streams containing toxic and hazardous organic compounds is well established industrial practice. A number of companies which have installed incinerators to handle their own chemical wastes are listed in Table 10. There are also a number of facilities which accept industrial wastes for contract disposal via incineration. Some of these are listed in Table 11. In addition, there are many companies in the business of manufacturing incinerators for industrial plants. Most of these incinerator manufacturers, some of which are listed in Table 12, have test facilities for demonstration purposes. Additional information is provided in Reference 4.⁽⁴⁾ All of these facilities handle bulk waste streams, such as liquid still bottoms, tars, resins, sludges, solids, etc. None have had experience in detoxification of small concentrations of hazardous materials adsorbed in an essentially inert matrix. Some types of incinerators, such as liquid injection units would clearly not be applicable at all.

There are industries which thermally process large quantities of soil-like material as part of a manufacturing operation, but they are of course not concerned with detoxification of hazardous waste.

The portland cement industry, in particular, uses thermal processing equipment analogous to that which might be applicable to incineration and detoxification of large quantities of contaminated soil. In the United States today, approximately 80 million tons of portland cement are produced in 172 separate plants. The product is made by pyro-processing approximately 150 million tons of crushed and finely ground limestone, clay, shale, and other raw material mineral species, in 435 separate rotary kilns. Thus, 1,000 tons per day of finely ground raw material is processed in the average rotary kiln in the cement industry today.

Table 10. Industrial Companies Using Incineration for Detoxification of Organic Chemical Wastes (partial listing)

<u>Company</u>	<u>Type of Incinerator</u>
Rohm and Haas	Liquid injection
Eastman Kodak	Liquid injection
du Pont	Liquid injection
General Electric	Liquid injection
B. F. Goodrich	Catalytic
Dow Chemical	Liquid injection; rotary kiln
Monsanto	Liquid injection; pyrolysis
Union Carbide	Catalytic
3-M	Rotary kiln
Georgia Pacific	Catalytic
Eli Lilly	Catalytic
General Motors	Fluidized bed
Ford Motor Co.	Catalytic
American Oil	Fluidized bed

Table 11. Facilities Engaged in Contract Disposal via Incineration
(partial listing)

<u>Facility</u>	<u>Type of Incinerator</u>
Pollution Abatement Services	Liquid injection
Chem-Trol Pollution Services	Liquid injection
Hyon Waste Management	Rotary kiln; liquid injection
Pollution Controls, Inc.	Rotary kiln
Solvent Recovery Services	Open pit
Hazen Research	Fluidized bed
Systems Technology	Fluidized bed

Table 12. Manufacturers of Incinerators for Industrial Management
(partial listing)

<u>Company</u>	<u>Type of Incinerator</u>
Babcock and Wilcox	Liquid injection
Prencor	Liquid injection
Combustion Power, Inc.	Fluidized bed
Torrax (Carborundum)	Pyrolysis
Surface Combustion	Pyrolysis
Eimco/BSP	Multiple hearth; liquid injection
Atomics International	Molten salt
Barber-Colman	Wet air oxidation
Zimpio	Wet air oxidation

The dimensions, and hence, capacity of the rotary kilns used by the cement industry varies over a wide range. The largest rotary kiln operating in the United States today is located at the Clarksville, Missouri plant of the Dundee Cement Company. This plant has a production capacity of 1.2 million tons per year of cement, produced by a single kiln which is 25 ft. in diameter and almost 800 ft. long.

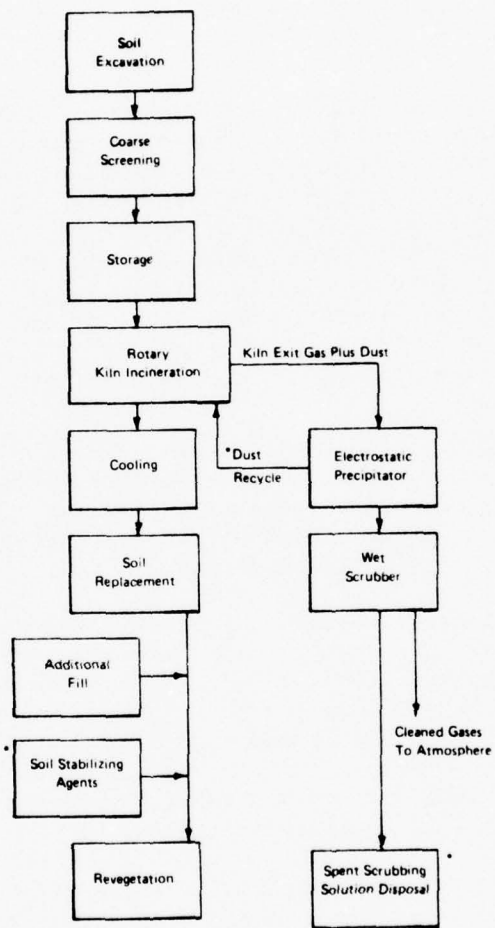
The technology and equipment utilized by the portland cement industry today certainly has a demonstrated capability which exceeds the actual requirements for soil detoxification, and therefore constitutes a technically viable candidate process alternative.

The unit thermal energy, the maximum processing temperature, and the residence time of raw materials in the rotary kiln in portland cement manufacture are all considerably higher than presently appear necessary for soil detoxification. Therefore, the throughput of soil to the kiln would be significantly higher than indicated by its portland cement productive capacity. The differences are:

- Portland cement raw materials are heated to a maximum temperature of 2800°F, compared with approximately 1800°F for soil detoxification.
- The residence time of raw materials in a portland cement rotary kiln is approximately 4 to 5 hours, compared with probably only a few minutes necessary in the high temperature zone of a soil detoxification operation.
- The chemical reactions involved in portland cement manufacture are highly endothermic, and require approximately 5 to 7 million Btu's per ton of cement produced. In contrast, soil detoxification probably involves sensible heat effects only, and should require only about 1 million Btu's per ton of soil treated.

Among the incinerators which handles solids at all, only the rotary kiln and fluidized bed are in widespread use for the treatment of hazardous wastes. The gas flow requirements for the fluidized bed precludes its economical use for contaminated soil, and hence the remainder of the discussion centers around the rotary kiln.

2. Incinerator System Description - Figure 1 is a simplified schematic process flow diagram of a possible incineration system suitable for pyro-processing of large quantities of soil. The soil would be excavated, using the appropriate combination of scraper-loaders, dozers, and front-end loaders. Scraper-loaders would excavate the soil and transport it to the processing plant. Dozers and front-end loaders would be used to excavate and load trucks for transport. This could be done on a contract basis, which would simplify the project and reduce the fixed capital requirements.



*Potential Problem Areas

Figure 1. Schematic Process Flow Sheet Rotary Kiln Soil Detoxification

The soil received at the processing plant would be dumped into a Hopper feeding a grizzly for removal of any material considered too large to be handled by the rotary kiln (probably material within the range of 2-12 inches). The coarsely-screened soil would next go to a covered storage area. This probably would be necessary to prevent the wind from producing a dusting condition. The storage area would feed one or more feed bins from which the soil would be fed at a metered rate to the rotary kiln.

A kiln 16 ft. in diameter and 300 ft. long, complete with attached planetary coolers would have a processing capacity of 3,000 tons per day of soil feed, and would be capable of heating the soil to a maximum temperature in the range of 1800°F-2000°F. The total retention time in the kiln should be approximately 45-60 minutes at 4.5% loading and 2 rpm kiln speed. The exact residence time for complete combustion should be determined empirically, since it will impact on the design of the kiln, and hence on costs. There is not, however, any single relationship between retention time and project time or operating costs. A 6-inch standard brick lining should be sufficient refractory for this application.

The kiln would be fired with pulverized coal fuel. The fuel energy requirements would be on the order of 1.1 million Btu's per ton of soil fed. If it is necessary to pass the kiln exit gas into a stationary incinerator, requiring additional separate fuel firing, then the total energy requirements would be greater.

The hot soil leaving the kiln would pass through the planetary coolers attached to the kiln shell. This is a standard means of cooling in the minerals pyro-processing industries. The soil discharged from the coolers would be sufficiently low in temperature to be handled by conventional equipment and transported back to the test site area for replacement. At this point, it may be necessary to add additional soil fill, and possibly a minor amount of one or more soil stabilizing agents, along with top soil as described below.

The hot combustion gases should leave the kiln at approximately 400-500°F. With no further treatment, they can go to an electrostatic precipitator for dust removal. This dust would probably be contaminated, and in the best case would be reintroduced to the kiln, perhaps along with a fluxing agent such as coal ash, to encourage the retention of this dust by the kiln.

The dust-free gases, leaving the electrostatic precipitator should next be treated by a wet scrubbing system, probably operating with a caustic solution. If this system could capture and neutralize or chemically destroy the harmful vapors and gases coming from the pyrolysis and/or vaporization of the organic compounds contained in the raw soil, then there should be no need for a stationary fired incinerator interposed between the rotary kiln exit and the electrostatic precipitator inlet.

The disposal of the spent scrubbing solution from this system could constitute a problem. The use of a stationary separately fired incinerator after the rotary kiln could relegate a wet scrubbing system

to a backup role only. This would then justify the use of such an auxiliary incinerator.

3. Degree of Detoxification Achievable

(a) Organic Contaminants

In a TRW study of the thermal degradation of military standard pesticide formulations,⁽⁵⁾ it was reported that the full roster of pesticides incinerated were completely destroyed at temperatures above 1845°F, with minimum residence time of 0.4 seconds, and with excess combustion air in the range of 45-60%. Since the conditions of temperature and residence time for soil being treated in the kiln exceeds all the minimum values for these parameters, the probability is extremely high that all of the organic compounds contained within the soil will be thermally destroyed.

(b) Metals and Metal Salts

Probably arsenic, mercury, zinc and boron will form oxides, chlorides, and fluorides in the hot zone of the kiln, and be volatilized to a considerable extent. However, such materials as chromium, manganese, and iron will probably remain in the final cooled treated soil. Without actual experimental work on field samples, however, it is not possible to predict the actual concentration of these metal values in the treated soil.

4. Process Economics - Cost estimates were based on treatment of a half-square mile contaminated area, 25 feet deep, corresponding roughly to Basin A at Rocky Mountain Arsenal. The cost implications of incinerating smaller or shallower contaminated areas are discussed briefly, but cost estimates should be carried out specific to such areas as they are identified and prioritized.

(a) Fixed Capital Investment

The amount of soil (density 1.2-1.6 g/ml) contained in a half-square mile area contaminated to a depth of 25 feet is approximately 15-million tons. The fixed capital requirement for processing this material in a rotary kiln incinerator with a capacity of one million tons per year is of the order of \$10-million. This excludes excavation and soil transportation equipment. Excavation and transport are assumed to be done on a contract basis and hence, have been represented as an operating expense. The fixed capital investment estimate is based on available data on the size and mix of many pieces of processing equipment used in minerals pyro-processing facilities.

(b) Operating Costs

Table 13 shows the estimated operating costs of the proposed facility. The fixed capital and operating costs for the electrostatic precipitator and scrubbing sections are estimated and included separately.

Table 13. Estimated Cost of Operating Rotary Kiln Soil Detoxification Facility (RMA)

Physical Investment: \$10 MM
 Capacity : 1 x 10⁶ Tons/Year; 15 x 10⁶ Tons Total
 Operating Factor : 3 Shifts/Stream Day
 345 Stream Days/Year

	<u>Quantity/Ton</u>	<u>\$/Unit</u>	<u>\$/Ton</u>	<u>\$/Year</u>
<u>Variable Costs</u>				
<u>Utilities</u>				
Fuel (Coal)	1.1 mm Btu	0.70	0.77	797,000
Power			0.10	104,000
Soil (Excavation & Replacement)			1.00	1,035,000
<u>Semi-Variable Costs</u>				
Operating Labor	2 men/shift	\$5/man-hr		83,000
Supervision	1 supervisor	\$16,000/year		16,000
Maintenance	5% of investment/year			500,000
Labor Overhead	60% of labor & supervision			60,000
<u>Fixed Costs</u>				
Plant Overhead	40% of labor & supervision			40,000
Depreciation	6.67% per year			667,000
Taxes & Insurance	1.5% of investment/year			150,000
Interest	8% per year of principal balance			<u>400,000</u>
Annual cost excluding electrostatic precipitator and scrubber				3,852,000
Annual cost of electrostatic precipitator and scrubber				<u>600,000</u>
Total annual operating cost				<u>\$4,452,000</u>
15-year total project cost (1975 dollars)				\$66,780,000

The individual items shown on Table 13 are broken down only for the facility, excluding the particulate and gaseous emission handling systems. The most important unit operating cost items are shown individually.

The main variable cost is fuel, which has been assumed to be coal in this example. From a current issue of the federal power commission news, the United States average price of contract coal, of all types, delivered at steam-electric plants, is 70 cents per million Btu's and this is the number that has been used in the analysis.

(c) Parametric Analysis

The base cost estimates in Table 13 are based on processing of 15 million tons of soil over a period of 15 years. Figure 2 shows the variation of project costs as a function of quantity of soil to be treated, for project lifetimes of 5 and 15 years.

The fixed capital investment was scaled from the \$10 million base case estimate, for the fifteen year total project life case, by applying an exponential scaling factor of 0.6 to the ratio of annual productive capacities. For the five-year project life, an exponential scaling factor of 0.6 was used for annual capacities less than 1×10^6 tons/yr, and an exponential scaling factor of 0.8 was used for capacities greater than 10^6 ton/yr. This is based on the assumption that any productive capacity greater than the base case of one million tons/year would require additional processing lines.

The operating costs were developed in the same way as shown in Table 13, assuming that the IRS would permit the fixed capital investment to be depreciated over a five-year period in that accelerated rate case. The same interest rate of 8% per year of the outstanding principal was applied in order to determine the total capital recovery cost.

Figure 2 suggests that as the total quantity of soil to be processed decreases, it becomes increasingly more economic to process that soil over progressively shorter periods of time. There is probably minimum processing capacity (in tons/year) for any given sized job.

5. Problem Areas for R, D. and D - Incineration has in fact not been used to treat soils containing relatively low levels of adsorbed contaminants. Prior to any large scale implementation therefore, a number of laboratory, pilot and field studies should be done to verify the estimates of technical and economic potential presented above. Some of the more critical study areas include:

- Experimental test of the temperatures and residence times needed to thermally destroy organic contaminants adsorbed on soil. Temperatures of 1800-2000°F and residence times

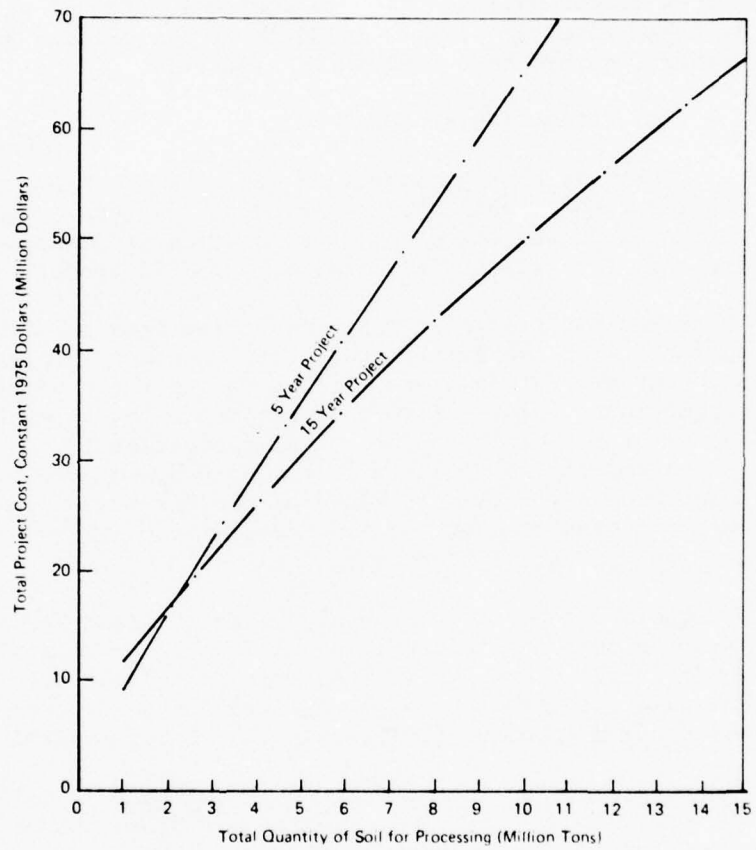


Figure 2. Sensitivity Analysis
 Total Project Cost Versus Soil Quantity,
 Parametric in Project Life

of 45-60 minutes were assumed in the analysis above, based on data for thermal destruction of bulk hazardous materials. The lower the temperature and the shorter the necessary residence time, the lower the costs.

- Experimental test of the fate of heavy metals in incineration. We believe that arsenic, boron, mercury and zinc will form volatile compounds that might be captured by an electrostatic precipitation or baghouse filter. We think that chromium, manganese, and iron will remain in the treated soil. These hypotheses must be checked experimentally, and supplemental methods devised for handling heavy metals if removal by incineration is insufficient. The efficiency of air pollution control equipment for the removal of volatile metal compounds, as well as other toxic vapors and particulate matter, must be checked experimentally.
- Analysis of the physical, chemical and biological properties of the incinerated soil. While the soil after incineration will be sterile and will not support vegetation, the steps necessary to restore it for unrestricted use cannot be prescribed until the texture, pH, particle size, and mineral content of the incinerated soil are known.

6. Restoration of Incinerated Soil for Plant Growth

(a) Nature of Incinerated Soil

In the Denver, Colorado area the soil is believed to be sandy, with crystalline silica probably constituting the main mineral. This mineral should undergo no significant physical or chemical change during the relatively mild pyro-processing treatment proposed and should leave the rotary kiln in essentially the same form that it entered. Probably the second most important soil mineral present will be clay of various species. Most or all of any kaolinite clay present will probably be dehydroxylated during the pyro-processing.

The resulting amorphous alumina and silica might combine to form mullite and other alumino-silicates. If the metal cations present in the contaminated soil are adsorbed on the clay particles, it is possible that these cations will be incorporated into this alumino-silicate structure, possibly rendering them inert to aqueous leaching. However, this is difficult to predict without at least bench-scale testing.

Probably the particle size distribution of the soil will shift toward the finer end of the scale as a result of pyro-processing. This will increase the soil's propensity to become airborne by wind action. Consequently, it may be necessary to add some soil stabilizing agents to the upper layer as it is replaced into the excavated areas.

For purposes of analysis, it has been assumed that following incineration, the soil will be completely sterile, powdery in nature and devoid of toxic contaminants. (Although it is not clear whether or not incineration will remove the toxic metals, it is assumed that some method of removal will have been employed before the material is considered for reuse.) Tests need to be performed to confirm the assumption that the material will be powdery in nature. Tests to determine the pH of the incinerated material will also be needed.

(b) Restoration Procedure

To enable the incinerated material to support vegetation, only the top six inches needs to be treated. Therefore, the first step after incineration is to put the material back where it came from and grade the area to eliminate steep slopes and basins. Once the material is in place, the following steps need to be taken:

- i) The proper texture must be obtained by agglomerating or pelletizing the material.
- ii) The pH must be adjusted by the addition of FeSO_4 or limestone.
- iii) Organic material must be replaced by adding sewage sludge or cattle manure.
- iv) Nutrients must be added by fertilization.
- v) Vegetation must be established by seeding and watering.
- vi) Other treatments may be necessary depending on vegetation requirements and environmental conditions.

These steps are outlined in Figure 3 and discussed below.

i. Agglomerating or Pelletizing - In order to retain nutrients and the correct amounts of air and water, and to mechanically support plants, the soil must be of a particle size ranging from coarse (sand particles of various sizes) to very fine (clay particles).

Assuming that the incinerated materials will be powdery or highly colloidal, the material would have to be 'pelletized' or 'agglomerated'. The addition of 3-4% Peneprime (a commercial asphaltic bitumen product cut with white kerosene) will aid in formation of pellets which can then be mixed with the original material. Another method involves watering the soil and then raking the wet material to form small size agglomerates. These agglomerates can be sprayed with a commercial elastomeric polymer, such as Coherex or Soil Guard, to preserve their form. Both of the above methods have been tried successfully on mine tailings by the Bureau of

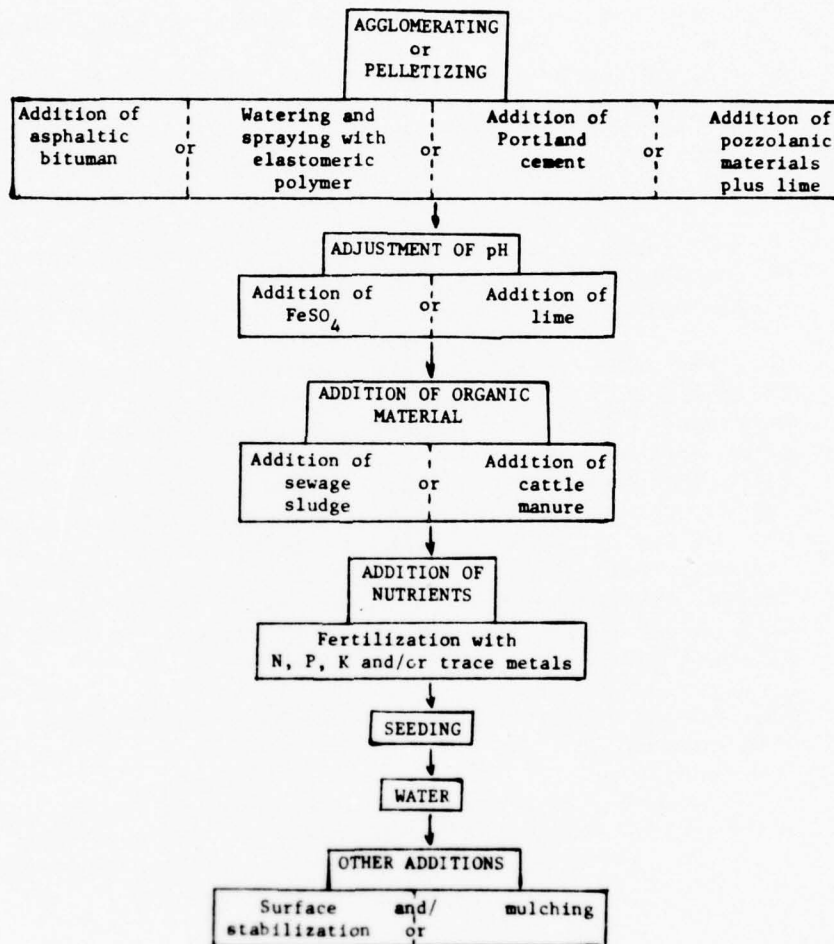


Figure 3. Steps for Reconstituting Soil from Incinerated Material

Mines.¹ Other examples of agglomerates are portland cement, or any one or combination of a large number of naturally occurring or artificially produced pozzolanic materials (e.g. fly ash plus lime).

Cost figures are available only for agglomeration with Coherex. Coherex costs about 30¢ per gallon with about 15¢ added for freight. At the recommended rate of application, 0.18 gallons/acre, the Coherex would cost about \$55 per acre. The water truck, applying about 1/4" water per acre and then the Coherex, would cost about \$73 per acre.¹ (ADL cost estimates based on 1967 Bureau of Mines figures.)

ii. Adjusting pH - For many plants, the pH of the soil, after the addition of organic material and fertilizers, should be in the pH 6-7 range, although pH requirements vary considerably with particular plants. (Plants which have established at RMA are tolerant of the slightly alkaline soil which exists there naturally.)

Acid-alkaline imbalances of the incinerated material, if any, may be corrected by the addition of ferrous sulfate (FeSO_4)² to reduce alkalinity, or the addition of crushed limestone to reduce acidity.

The rates of application required will depend on the particular pH imbalance. Rates involved in mine and other reclamation activities have ranged from 1-9 tons/acre of FeSO_4 ,² and from 3-30 tons/acre lime.³ Additional benefits from FeSO_4 include a reduction in chromate toxicity; additional benefits from liming include a precipitation of some metals and an encouragement of bacterial decomposition of organic solids. The cost of liming, is about \$9/ton, including the cost of limestone and the equipment and labor for spreading. A soil discing operation would follow, costing about \$1.50/acre. Costs of FeSO_4 treatment might be less, since FeSO_4 is produced in abundance as a waste in acid pickling of steel and titanium dioxide manufacture.

iii. Adding Organic Material - Organic matter must be added to the soil in order to:

- restore active bacterial populations and provide sufficient organic energy sources to keep the populations going until more organic material can accumulate in the soil from the decay of vegetation:
- increase the capability of soil to retain moisture;
- increase the likelihood of seed germination by improving the physical nature and moisture content of the soil substrate, and
- add trace elements, and some major nutrients.^{1,4}

Either cattle manure or sewage sludge can be added to the incinerated material to accomplish the above objectives.

Activated sludge has been proven effective in numerous land reclamation projects. Golden Gate Park in San Francisco was made from activated sludge effluent placed on a sand dune. Dried sewage sludge was used later for fertilizer. Sludge applied to two strip mines in Stark County, Ohio in 1956 was found to support vegetation even in one place where the soil was very acid (2.8-3.3). Apparently the sludge was able to neutralize the acid to some extent.

The amount of sludge which should be applied to soil varies with the end use of the area. Strip mines designated for use as sludge disposal areas have accommodated up to 500 tons/acre/year. As a fertilizer for corn, about 5 to 15 tons/acre/year are applied. Anywhere from 10 to 40 tons/acre/year are recommended, depending on the trace metal concentrations. "Averages" of some of the trace metal concentrations for activated sludge are (in ppm):⁴

molybdenum	16
boron	33
copper	916
zinc	2,500
manganese	134

Activated sludge may be available from a nearby sewage treatment plant (located about 4 miles from RMA). The costs for transporting the sludge are not readily available. Costs of land spreading range from \$5-30/acre.⁴ The safety of the sludge in terms of pathogens has been studied extensively and the results show that no known outbreaks of disease have occurred due to sludge disposal. However, long term effects are not known. The "cost" of public hesitance about health effects must be considered in addition to the monetary costs.

Possible long term effects from ground water contamination by heavy metals may also be a problem. The extent of contamination seems to depend on the rate of application and the nature of the soil (calcareous soils for instance are more apt to retain the toxic metals than acid soils). The uncertainty which surrounds this problem contributes to an overall hesitancy on our part concerning the use of sludge.

Cattle manure as an alternative to sewage sludge as a soil additive has some advantages. The application of cattle manure to farmlands is a well accepted present day agricultural practice, especially on small farms. Thus, existing machinery, expertise, cost estimates, etc., are presently available, and the method can be applied without further testing. Equipment can be rented from nearby dealers; no public acceptance problem exists. In the case of RMA, the other major advantage of using cattle manure is that feedlots exist around the perimeter of the arsenal.

A nominal fee for the manure may be involved: about \$1.50 to 2.00 per ton. The maximum cattle manure which should be applied (considering possible trace metal buildup) is about 20-30 tons/acre.⁵ A front end loader and trucks would be needed, along with a manure spreader rented from a local agricultural supply dealer (at about \$25-30/hr including operator, operating at about 506 acres/hr).

iv. Fertilization* - Although cattle manure provides a good supply of trace elements (see Table 14), its supply of major nutrients (nitrogen, phosphorous, and potassium) is inadequate. Minor nutrients (sulfur, calcium and magnesium) may also need to be added, depending on the concentrations found in the manure. Cultivation to incorporate the nutrients, (along with soil additives from previous steps) is necessary at this stage.

Commercial fertilizers can be added to the incinerated material to attain the proper balance of major and minor nutrients. Mixed fertilizers, containing various ratios of these nutrients, are readily available. The particular concentrations and rates of application depends on the needs of the particular plants to be grown.⁶ (For instances, grasses are stimulated by nitrogen additions, while legumes, which generate nitrates from free nitrogen, are inhibited by nitrogen additions.)¹

Super phosphate (phosphorous plus sulfuric acid to increase availability to plants) costs about \$12 per 20 lb. unit. Potassium costs about \$1.85 per 20 lb. unit, while nitrogen (ammonium nitrate) costs about \$5.10 per 20 lb. unit. Assuming about 40 lbs/acre of each, this would come to about \$38 per acre. The fertilizer would have to be bulk spread at a cost of about \$2.50/acre. Cultivation would follow (with a tractor) at a cost of about \$8/acre. Two or three cultivations may be necessary.

v. Seeding and Watering - Grasses are the most amenable to introduction in land reclamation projects since in normal vegetation they are one of the first plants to penetrate most unvegetated open areas. Grasses are highly productive and provide good cover for erosion control.

At RMA, grasses which presently cover uncontaminated areas include crested wheat grass and blue grama. Both these grasses have been used successfully in mine tailing reclamation. Both are resistant to drought and the blue grama does exceptionally well in sand or gravelly soils.³

* The following discussion on fertilization seeding and watering reflects standard general agricultural practices. Before proceeding with re-vegetation attempts, details on the particular needs of the area should be obtained from local county agents of state experimental stations.

Table 14. Trace Element Concentrations of Fresh Manures^{5*}

<u>Element</u>	<u>Minimum</u>	<u>Maximum</u>	<u>Average</u>
	ppm, dry-matter basis		
Boron	4.5	52.0	20.2
Manganese	75.0	549.0	201.1
Cobalt	0.25	4.70	1.04
Copper	7.6	40.8	15.6
Zinc	43.0	247.0	96.2
Molybdenum	0.84	15.83	2.37
Molybdenum +	0.84	4.18	2.06

* Data from 44 samples of farmyard manure, representing fresh cow, horse, swine, sheep, poultry, and mixed manures and composted cow and mixed manures

+ With one exceptionally high value omitted.

Since the present establishment of these plants attests to their ability to adapt to the surrounding temperature, rainfall, and growing season, these plants should be used for revegetating the area.

To assure the germination of a sufficient number of seeds, about 10 to 20 lbs/acre of seeds would be necessary at a cost of \$1/lb for either crested wheat grass or blue grama. A tractor pulling a grain drill with press wheels would have to be rented at a cost of about \$3.50/hr for 7 days for one square mile (about \$30/acre).

To encourage germination, water must be added after germination. Probably only 1-3 waterings are necessary to assure sufficient germination. The capital costs necessary for even a temporary irrigation system are very high (about \$50/acre fixed annual capital cost). For a 'one time' operation, the use of a water truck is probably more effective even though it is slower and less even in its application. Renting and operating a water truck would probably cost about \$60/acre for a 1/4" application.

vi. Other Additions - Sandblasting, rapid evaporation of moisture, and the reflection of sun's rays onto plants (which can 'burn' very young plants), are conditions which can develop with loose, sandy, light-colored soils and low rainfall. Although the addition of sludge or manure will hopefully prevent these problems from developing, additional soil treatment may be necessary if the problems are observed after seeding and watering. The surface application of Coherex was found to be effective in preventing sandblasting in revegetation tests on mine tailings in McGill, Nevada. The treatment was also successful in decreasing the loss of moisture through evaporation, absorbing heat needed for germination, and preventing reflection of sun's rays onto plants. No manure or sludge was added in this test.¹ Another method which has been found to be successful is the addition of mulching material to the seeded areas. About 1 ton of wood fiber/acre is needed. The mulching material decreases the loss of moisture through evaporation and prevents the reflection of the sun's rays onto plants.

To assure proper aeration after the addition of Coherex or mulching, bacterial growth promoters can be mixed in. These compounds cause flocculation of topmost layers facilitating the movement of air, water, and nutrients. Although these growth promoters have been successful in the laboratory, past experience in vegetating mine tailings has not demonstrated their success in the field.

(c) Summary of Restoration Costs

The total costs for the conversion of the incinerated material is given in Table 15. This estimate assumes the following conversion steps are taken: agglomeration of the soil through watering, discing, and spraying with Coherex; pH adjustment with the application of limestone; application of cattle manure; fertilization with major nutrients; seeding with a mixture of grasses, and watering.

Table 15. Soil Restoration Costs Following Incineration

<u>Restoration Components</u>	<u>Operating Cost (\$/acre)</u>	
<u>AGGLOMERATING</u>		
watering		
water truck	36.50	
racking		
tractor with disc and labor	1.50	
Coherex application		
Coherex (0.18 ga/acre @\$0.45/gal)	.08	
water truck and labor	<u>36.50</u>	74.58
<u>pH ADJUSTMENT</u>		
lime, equipment and labor for spreading (purchased together) (\$9.03/ton @10 tons/acre)	90.30	
discing	<u>1.50</u>	91.80
<u>ADDITION OF ORGANIC MATTER</u>		
cattle manure (\$4.00/ton @10 tons/acre) and transport for up to 5 miles	40.00	
spreading (\$30/hr @1/6 hr/acre)	<u>5.00</u>	45.00
<u>FERTILIZATION</u>		
super phosphate (\$12/20 lbs @40 lb/acre)	24.00	
potassium (\$1.85/20 lbs @40 lb/acre)	4.00	
NH ₄ NO ₃ (\$5.10/20 lbs @40 lb/acre)	10.00	
spreading	2.50	
cultivation	<u>8.00</u>	48.50
<u>SEEDING</u>		
seeds (mixed crested wheat grass and blue grama)		
\$1/lb @15 lbs/acre	15.00	
planting with drill and press	<u>30.00</u>	45.00
<u>WATERING</u>		
water truck and operator		<u>60.00</u>
	TOTAL	364.88
Total Cost for a Half Square Mile Area (320 acres)		\$116,762.00

B. Land Reclamation via Wet Chemical Processing

1. State of the Art - The mining, metals, and non-metallic minerals industry today extracts tens of billions of tons of rock and ore each year, for subsequent processing and conversion to a host of commodities and products. In the majority of these operations, the materials of value are the minerals which constitute a minor fraction of the total ore. The desired minerals are liberated by crushing and grinding the ore to a suitable fineness, thereby separating the mineral grains from the particles of host rock or gangue. This process is called beneficiation. Much of the beneficiation practiced by these industries is done in an aqueous medium using differences in the physico-chemical characteristics of the desirable minerals and the undesirable gangue.

The unit processes involved in the mixing of these large quantities of finely crushed ore (which in many industries truly resembles soil) with water; agitation of the resulting slurry; pumping, filtration; sedimentation in thickeners, etc., are all widely practiced and commonly used. These unit processes would be typical of the ones required for detoxification of excavated soil by chemical treatment and/or solvent extraction.

Although chemical methods have not been used in practice to remove low levels of contaminants in excavated soils, they have been tested to some extent for detoxification of bulk chemicals.

In a review of methods of chemical degradation of pesticides and herbicides, Dennis,⁷ in 1972, reported that no single chemical procedure exists for degrading the entire spectrum of pesticides and herbicides. He concluded that several approaches to chemical degradation will be needed due to the great variation in solubilities and chemical structures of these agents. He proposed four general methods for chemically degrading pesticides and herbicides, which he suggested might represent the entire universe of necessary generic chemical reactions which could effectively detoxify any compounds.

These four general methods are:

- Hydrolysis - Hydrolysis appears to be the most practical and reliable method of destroying organophosphorous and carbamate pesticides.

- Dechlorination - The polychlorinated pesticides appear to be best degraded by chemical dechlorination. Dennis believes that the most effective and non-specific system for dechlorination uses t-butyl alcohol, tetrahydrofuran and lithium or sodium metals. However, the hydrogen produced from the reaction of an alkali metal with the alcohol, plus the use of tetrahydrofuran (which is flammable) results in an inherent fire hazard. He suggests that a promising alternative method for dechlorination is a catalytic one, where he cites nickel oxide as a candidate catalyst worth investigating; however, this method presently appears conceptual.

- Photolysis - Dennis believes that photolysis is particularly useful in degrading 2,4-D and 2,4,5-T. However, the rates of degradation of pesticides and herbicides in both sunlight and ultraviolet light is not sufficiently well known, nor is an assessment of the toxicity of the photo products.

- Oxidation - Dennis recommends that this last method is worth study. 2,4-D and 2,4,5-T should be oxidized by chlorine dioxide, in an aqueous medium; however, at the time of his report, these reactions had not been investigated. He also states that oxidations of pesticides carried out in non-aqueous or partly aqueous solutions are poorly understood.

While in principle chemical removal methods can probably be devised for any specific contaminant, in practice problems are likely to arise due to the wide range of contaminants of different physico-chemical properties that may be present in the soil at various AMC sites. One of the most fundamental problems stems from the mixture of both water-soluble and water-insoluble contaminants in the soil to be detoxified. Water is the most convenient liquid medium in which to carry out chemical destruction reactions, but the entire family of water-insoluble toxic agents is not amenable to such treatment. Because of this, it is probable that a chemical treatment system will consist of at least two completely distinct sections, demarked by the use of water as the solvent and reaction medium in one section, and some non-aqueous solvent as the reaction medium and chemical raw material carrier in the other section.

The chemical processing is completely heterogeneous since the toxic compounds are present:

- as solids themselves,
- on solid carriers, and
- adsorbed, or in some way physically and/or chemically attached to the individual grains of soil.

Therefore, the reaction medium must be either a gas or liquid. Although the use of a gaseous reaction medium might be necessary for the chemical destruction of one or more of the toxic compounds present in the soil, the equipment necessary for the appropriate contacting of particulate solids, such as soil particles and a gas, is usually more complex and costly than comparable equipment for the contacting of particulate solids and a liquid medium. Therefore, the use of a gaseous continuous phase for the reaction medium is to be avoided unless absolutely necessary.

In considering the roster of candidate liquid media as the reaction vehicle and carrier of the chemical reactants used in the chemical destruction processes, water is by far the most desirable. Any non-aqueous solvent presents a contamination problem of its own, in proportion to the residue of that solvent remaining in the processed soil. In addition,

the very high cost of organic solvents, and usual flammable nature of these materials, combined with the probable high inventory volumes of such a solvent required for a processing plant of the size necessary for treatment of one million tons per year of soil combines to mitigate very strongly against non-aqueous solvents.

2. Wet Chemical Processing System Description - Figure 4 is a simplified schematic process flow diagram of a possible chemical detoxification system suitable for processing large quantities of soil. Since the various candidate methods for chemical destruction of the toxic agents suspected to be present in the contaminated soil are only incompletely quantified at the time of writing, this flowsheet was developed using the following simplifying assumptions:

- Water is the only reaction medium and solvent used in the system.
- Only one chemical reaction step is necessary for detoxification.
- The products of chemical detoxification are in themselves non-toxic, and will not require a significant effluent control system.
- A wet filter cake (of approximately 30% water content) of processed soil and water is suitable for replacement into the excavated area, obviating the need for a final drying step.
- The method and costs for the excavation, hauling, and replacement of soil described in the above analysis of incineration is directly applicable to this chemical processing scheme, and is therefore included here by reference.

The contaminated soil would be excavated, conveyed to the chemical processing plant site, passed through a coarse screen, and conveyed to closed storage in the manner described in Section A above.

The next processing step, as shown on Figure 4, is that of chemical reaction, and/or solvent extraction. As described earlier, this is the least well known processing step involved in this approach to detoxification. Since the necessary solvent extraction and/or chemical reaction steps necessary for detoxification are not yet known, we have based this analysis on the use of an aqueous solution only.

The soil would therefore be mixed with a sufficient quantity of water to produce a slurry of sufficiently low viscosity to permit good mixing and pumping. These requirements should be met by a slurry containing approximately 30% solids by weight. A 3,000 ton/day soil processing facility would therefore require 7,000 tons/day of water (which is equivalent to about 1,200 gallons per minute of water flow).

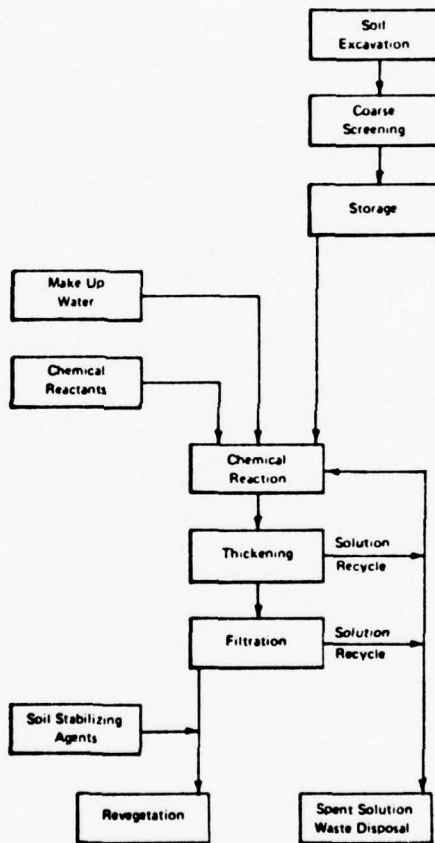


Figure 4. Schematic Process Flow Sheet
Chemical Soil Detoxification

We have assumed that a one-hour residence time for this slurry in a reactant or solvent extraction stage should be sufficient to carry out any reaction of practical value. Based on the volume of water only, this is equivalent to approximately 70,000 gallons of reactor volume.

A total of four agitated stainless-steel reactors were selected for the chemical reaction stage of this process flowsheet. Each of these reactors has an active working volume of 35,000 gallons. Therefore, a pair of these reactors operated either in series or in parallel (depending upon the residence time distribution appropriate for the specific chemical reaction or solvent extraction to be carried out in this stage) will constitute a one-hour residence time for a 1,200-gpm solution flow rate.

A second pair of reactors was included for an additional one-hour reaction or solvent extraction step, since it is probable that at least two separate reaction steps will be necessary. Each of these reactors is equipped with a stainless-steel agitator, driven by a 60-hp motor. These atmospheric pressure reactors are constructed completely of 304 stainless steel for corrosion resistance.

Four 30-hp, 1,000-gpm, 35-psig head pumps move the slurry through this stage of the process plant. Specific provisions have not been included for makeup water, nor chemical reactants, since these flowstreams can be defined only after the required chemistry has been developed.

After the chemical reactions have been completed in the reaction vessels, the resulting product slurry must be physically separated into the remaining (but now detoxified) soil particles, and the water (now containing the products of the chemical detoxification reactions) which is pumped from the reactors. It is common practice in the ore beneficiation and minerals processing industries to use thickeners, followed by vacuum filters to perform such a separation.

For the flowrates of slurry in this processing plant, two thickeners have been used, in series, to effect the first and major stage of separation by counter-current decantation. Each of these thickeners is 215 ft in diameter, with a nine-foot-high sidewall, lined with a vinyl plastic coating. Appropriately sized effluent surge tanks, repulp tanks, agitators and pumps complete this section of the processing facility.

Two rotary vacuum clarification filters have been included in the final filtration step for the ultimate separation of solution and processed soil. These 304 stainless-steel filters are 10' x 16' in drum dimensions, which is equivalent to a 500-square-foot filtering area. A single 45,000-gallon solution surge tank, of 304 stainless-steel construction, completes this final step.

3. Process Economics

(a) Fixed Capital Investment

We have estimated the fixed capital requirement to be \$10 million for the facilities excluding the excavating and soil transportation equipment. This excluded equipment is represented as an expense item, assuming that excavation and transportation will be done on a contract basis.

Table 16 gives costs (in 1975 dollars) for all of the major pieces of processing equipment required for this facility, excluding any specific chemical processing or solvent extraction equipment which might be necessary in addition to the two separate reactor stages included in the flowsheet development.

Since thickeners are constructed at the site, and are analogous to large concrete civil works, the thickener cost shown here is an installed cost, with piping attendant to the thickeners represented as 50% of the installed cost.

For the other section of the plant, items such as installation cost, piping, electricals, instrumentation, etc., are developed as percentages of the total purchased equipment cost, based on chemical process industry capital cost estimating techniques which are common to estimates of this order of accuracy. Engineering and construction costs were estimated at 25% of the physical plant cost. The contractor's fee was estimated as 8% of the direct plant cost, which along with a 20% of direct plant cost contingency item adds up to \$10 million for fixed capital costs in 1975 dollars.

This value, coincidentally, is essentially the same as the estimated fixed capital cost required for an incineration facility. However, this fixed capital cost estimate is actually on the low side, since the specific chemical processing steps have not been included, and have been represented simply by general conceptual reaction stages. The actual chemical processing or solvent extraction necessary for satisfactory detoxification could be significantly higher. Therefore, the actual fixed capital cost for a chemical and/or solvent processing plant would be in the range of \$10-25 million, depending on the chemical processing steps, and the waste disposal costs (waste treatment) actually necessary.

(b) Operating Costs

Table 17 shows the estimated operating costs of this facility. Just as the fixed capital costs were dependent upon several major unknown factors which relate to the actual chemical and solvent extraction steps necessary for detoxification, so too are the operating costs strongly dependent on:

- The specific chemical reactions or solvent extraction necessary for satisfactory detoxification. Following directly from this

Table 16. Estimate of Fixed Capital Costs, Chemical Soil Detoxification Facility

<u>Equipment</u>	<u>Cost</u>
1 Soil Conveyor	\$ 165,000
1 Soil Storage Bin	776,000
1 Bucket Elevator	8,000
1 Conveyor Belt (to digestors)	26,000
4 Surge Bins	10,000
4 Weigh Feeders	26,000
4 Air Locks	7,000
4 Reactors (35,000 gal. each - 304 ss)	264,000
4 Agitators (60 HP - ss construction)	91,000
4 Pumps (30 HP - 1,000 GPM - 35 psig heads)	15,000
2 Thickener Feed Tank (45,000 gal. - 304 ss)	63,000
1 Agitator (60 HP - ss)	21,000
2 Thickeners (216' dia. x 9' high - vinyl lined)	
1 Effluent Surge Tank (6,000 gal. - 304 ss)	18,000
1 Repulp Tank (6,000 gal. - 304 ss)	18,000
1 Agitator (5 HP ss)	5,000
1 Feed Pump (30 HP - 1,000 GPM - ss)	4,000
1 Recycle Pump (20 HP - 400 GPM ss)	3,000
1 Filter Surge Tank (15,000 gal. ss)	26,000
2 Clarification Filters [10' x 16' (500 ft ²) rotary vacuum - 304 ss with accessories]	201,000
1 Solution Surge Tank (45,000 gal. atmos. press. - ss)	63,000
 Purchased Equipment Cost (PEC) 1975 dollar value (excluding thickeners)	 1,810,000
 Installation (35% of PEC)	 634,000
Piping (65% of PEC)	1,177,000
Electricals (15% of PEC)	272,000
Instrumentation (15% of PEC)	272,000
Insulation (3% of PEC)	54,000
Painting (4% of PEC)	72,000
 Physical Plant Cost (excluding thickeners)	 \$4,291,000
 Thickeners (IEC)	 1,221,000
Piping, etc. (50% IEC)	611,000
 Total Physical Plant Cost (PPC)	 \$6,123,000
 Engineering and Construction (25% PPC)	 1,531,000
 Direct Plant Cost (DPC)	 \$7,654,000
 Contractors Fee (8% DPC)	 612,000
Contingency (20% DPC)	1,531,000
 Fixed Capital	 \$9,797,000

Table 17. Estimate of Operating Costs
Chemical Soil Detoxification Facility

Physical Investment: \$10 x 10⁶
Capacity : 1 x 10⁶ tons per year; 15 x 10⁶ tons total
Operating Factor : 3 shifts/stream day, 345 stream days/years

	Quantity/ton	\$/unit	\$/ton	\$/year
<u>Variable Costs</u>				
Utilities				
Fuel (Coal) ¹				
Power	30 kwh	1.5c/kwh	0.45	466,000
Soil (Excavation & Replacement)			1.00	1,035,000
Chemical Reactants ²				
<u>Semi-Variable Costs</u>				
Operating Labor	3 men/shift	\$5/man-hr		125,000
Supervision	1 supervisor	\$16,000/year		16,000
Maintenance	5% of investment per year			500,000
Labor Overhead	60% of labor & supervision			85,000
<u>Fixed Costs</u>				
Plant Overhead	40% of labor & supervision			56,000
Depreciation	6.67% of investment per year			667,000
Taxes & Insurance	1.5% of investment per year			150,000
Interest	8% per year of principal balance			400,000
	Annual cost of waste disposal and liquid effluent treatment ²			-
	Total annual operating cost			<u>\$3,500,000</u>
	15-year total project cost (1975 dollars)			\$52,500,000

¹Not necessary unless the detoxified soil filter cake produced by this plant must be dried before replacement.

²Not known without actual chemical treatment and/or solvent extraction conceptual flowsheet and exposition of the basic chemistry involved in the chemical processing.

is the effluent control problem. The costs attending this are a specific function of the actual nature and quantity of waste product generated by the chemical processing steps, and the techniques and equipment required for satisfactory environmental protection.

- The physical nature of the processed soil commensurate with satisfactory replacement and land rehabilitation. The costs for transportation and replacement of the detoxified soil are strongly dependent upon the physical nature of the soil produced by this plant.

- If a moist filter cake is suitable for replacement, then the semi-solid, but probably quite plastic, cake produced from the final filtering step of the process schematic flowsheet shown in Figure 4 can be transported by truck to the replacement area.
- If it is necessary to replace the soil in a dry condition, then a drying step must follow the filtering step. This would require additional fixed capital investment and a significant unit fuel operating cost for drying. A rotary dryer would probably be the best device for this processing step if necessary.
- If the moisture content of the soil being replaced presented no constraint at all, then transportation and soil replacement costs could conceivably be significantly reduced from truck haulage of filter cake by adding some water to the filter cake, repulping, and simply pumping the resulting slurry through a pipeline to the replacement area. Suitable dike construction would confine the slurry which should settle (probably aided by flocculants) with a recovery of the transport water from the water layer collected from the top of the settled solids. Proper logistics would permit drying of older diked areas followed by subsequent revegetation.

For purposes of cost estimation, it has been assumed that truck hauling of the moist filter cake will meet the necessary criteria of soil replacement. Therefore, no unit fuel cost has been included in the operating cost estimate shown in Table 17.

These examples have been cited to illustrate the rather wide spectrum of possibilities involved at the conceptual level in a wet chemical processing scheme. Detailed design plans will be dependent not only upon the specific chemistry involved in the chemical detoxification, but also upon site-specific criteria.

4. Problem Areas for R, D, and D - Although capital and operating costs for incineration and wet chemical processing are estimated to be of the same order of magnitude, considerably more research and development would be needed to design a wet chemical system.

From the available literature, it appears highly probable that simply heating the contaminated soil to a sufficiently high temperature and maintaining it in an oxidizing atmosphere for a sufficiently long period of time would thermally destroy most or all of the organic contaminants. This basis provided essentially all of the important requirements for the development of a conceptual process flowsheet, the design and sizing of all major pieces of processing equipment, and an estimate of the fixed capital requirements and operating costs of an incineration facility.

Unlike the incineration of contaminated soil which permitted the development of a single conceptual process flowsheet, the chemical and solvent extraction method has no simple, single, unifying process criterion. The available literature indicates that the broad spectrum of contaminants, embodied within several distinct and diverse generic groups, are not amenable to chemical destruction or solvent extraction through only one or two simple chemical routes. In fact, some of the chemical techniques reported for the destruction of certain families of organic contaminants may be too limited in applicability, and possibly too costly to include in a large-scale chemical detoxification process.

In view of the relative complexity of the prospective chemical and solvent extraction methods, the approach taken in the above analysis was to develop a process flowsheet, equipment sizing, and fixed capital and operating costs for all of the physical and materials-handling operations which are necessary regardless of the specific individual chemical processing steps actually required for the destruction of the toxic agents. Prior to implementation, however, a more detailed site-specific analysis will be required, based on the following kinds of experimental and field data:

- Identification and quantitative analysis of the contaminants to be removed
- Identification of potentially applicable wet chemical detoxification methods (e.g., hydrolysis, neutralization, oxidation, reduction, solvent extraction, etc.);
- Laboratory tests to determine the best method or series of methods for detoxification, and to identify operating parameters;
- Pilot test of the detoxification scheme worked out by the laboratory; and
- Design and test of a waste water and/or solvent recovery system.

IV. IN SITU TREATMENT OF CONTAMINATED SOIL

Decontamination based on incineration or wet chemical treatment of excavated soil is costly, involving capital costs of at least \$10,000,000 and operating costs of over \$3,500,000/yr. Furthermore, it would require about 15 years to process the soil in an area the size of Basin A at Rocky Mountain Arsenal, and the potential environmental impacts of excavation itself could be quite severe. The excavation and treatment methods, however, do have the conceptual advantage of physically removing toxic contaminants.

While in situ methods have a lower probability of destroying contaminants than the excavation and treatment methods, they are generally less costly and less destructive of the environment. In this chapter, four in situ decontamination methods are considered--soil activation, vegetational uptake, inoculation, and fixation.

A. Soil Activation

1. State of the Art - 'Soil activation' is used here to mean a maximization of the inherent capacity of the soil to degrade toxicants by chemical and biological mechanisms. It involves an identification of the soil conditions which promote the degradation of each toxicant, and a manipulation of the soil environment to bring about these conditions. Although each toxicant in general has a unique set of 'ideal' soil conditions for degradation, for some toxicants these ideal conditions overlap and more than one toxicant can be the focus of soil manipulation at one time. For other toxicants, however, the ideal conditions do not overlap and are sometimes even contradictory; these toxicants must be treated in series.

The manipulation of the soil environment to simulate the ideal set of conditions for degradation is not receiving much attention as a method of soil decontamination. Soil degradation itself, however, is a well known, well documented route of disappearance for many toxicants, and manipulation of single soil parameters, e.g., increasing organic content, has often been done as the most logical, cheapest way to bring toxicant concentrations below phytotoxic levels. To assess the current state of the art for this method is difficult: it has been used repeatedly on a small scale (in many cases without documented results) but has not been tried on a large scale with multiple toxicants and manipulation of multiple soil conditions.

The one exception has been a field test conducted by Dr. Walter Farmer at the University of California at Riverside. He flooded a 1.5 acre field which was heavily contaminated with DDT, added organic matter, and increased soil temperatures. His results showed complete transformation of all DDT to DDD in 18 days. In normal soil, the transformation of an equivalent amount would have taken over two years. However, DDD is about 1/30 as toxic as DDT.

USDA personnel recommended soil activation as an approach to AMC decontamination problems. Their basic approach, however, was to 'get the soil going' by cultivation, etc., without assessing the individual requirements of each toxicant. Their faith was strong that an active, healthy soil could detoxify most of the contaminants over a 5- to 20-year time frame. It would appear that actual manipulation of the soil environment to meet the specific requirements of the toxicants known to be present should shorten this detoxification time considerably.

Degradation or loss mechanisms in the soil include physical processes such as photodegradation and volatilization from the topmost surface, biological degradation by micro-organisms, and a number of chemical reactions catalyzed by various soil components and chemical adsorption. Soil activation as a method of decontamination rests on the assumption that these mechanisms, if actively promoted, are capable of degrading more contaminants, more rapidly. This assumption needs to be investigated before implementation of this method, especially for the phosphonates, CS, DM, and other relatively uncommon soil contaminants, for which few degradation data are available. The pesticide-related contaminants need much less investigation; reviews are available on the mechanisms of soil degradation for many insecticides and herbicides. Heavy metal contaminants, of course, cannot be eliminated except by transformation to volatile forms. Soil reactions can transform them to less toxic forms or make them unavailable to plants.* Organic arsenic, for example, undergoes two reactions in the soil--one to volatile arsines, and the other to inorganic arsenate, which is strongly adsorbed by clay particles in the soil.

It should be noted that soil reactions can also activate contaminants, i.e., change them to more toxic forms, or forms which are equally as toxic. For instance, in the soil, 2,4-dichlorophenoxyethanol sulfate is activated upon its conversion to 2,4-D. This potential for activation would need to be considered in the investigation which precedes the implementation of this method.

One of the uncertainties in soil activation is the lack of information on the extent of detoxification. This is partly due to the fact that many studies which have indicated soil degradation have merely tested for the 'disappearance' of the original toxicant, or have tested for initial, previously identified, degradation products. Kearney, Plimmer, and Helling¹³ state that, in general, soil is able to degrade and detoxify organophosphates and carbamates. Carbaryl, for example, is hydrolyzed to 1-naphthol, methylamine, and carbon dioxide. The organochlorines, however, may not be detoxified as readily as other contaminants. The cyclodienes are oxidized to form epoxides (e.g., heptachlor is oxidized to heptachlor epoxide) which are themselves insecticidal and toxic. DDT

*There is some question as to whether merely making undegradable toxicants unavailable to plants would be considered an acceptable form of the detoxification to the Army.

is dehydrohalogenated to DDE, or can be dechlorinated to form DDD. The route of further breakdown after conversion to DDD has been difficult to ascertain. In the soil, a number of 'polar materials' which cannot be recovered has been noted. The breakdown under anaerobic conditions of DDT by Enterobacter aerogenes has been reported to yield reduced dechlorinated compounds, as well as oxidized derivatives, and ultimately p,p-dichlorobenzophenones. Although this route of degradation was determined in vitro, it is likely that this route, or some similar route of degradation, is present in the soil since in many areas which have applications of DDT, DDT plus the initial degradation products, DDE and DDD, have been shown to be lost from the soil.

2. Soil Activation System Description - Assuming that laboratory and field investigations support the hypothesis that a significant number of the toxicants present in DARCOM soils can be degraded by natural soil processes, and that activation to more toxic compounds will not be a problem, the implementation would proceed accordingly to the following steps:

- Determination of optimum conditions for each of the contaminants;
- Integration of each set of optimum conditions into an overall plan of action considering sequencing of treatment process and the particular toxicants found together in particular areas;
- Manipulation of the environmental conditions (e.g., pH, oxygen, organic matter) according to the plan of action; and
- Monitoring of toxicant degradation.

(a) Soil Conditions Which Promote Degradation

Table 18 lists some toxicants believed to be present in Basin A at Rocky Mountain Arsenal and the soil conditions which promote their degradation. The toxicants listed (pesticides and heavy metals) along with the environmental conditions shown are the result of an initial literature search involving primarily pesticides (due to the availability of literature on these as opposed to other toxicants involved).

The following discussion addresses each of the manipulations shown in Table 18, i.e., increasing organic matter, decreasing soil oxygen content, increasing temperature, increasing soil moisture, and increasing and decreasing pH.

i. Increasing Organic Matter - Organic matter can be added in the form of synthetic commercial organics, cattle manure, sewage sludge, or crop residues. Commercial synthetic organics are expensive and their suitability for microbial growth is uncertain, although they have been used as an energy source in soil tests done by the Bureau of Mine Reclamation.

Table 18. Change in Soil Conditions which Promote Degradation

Organic Material	Moisture	Oxygen	Temp.	pH
Aldrin	increase	increase	increase	
DDT		decrease		
Lindane		decrease		
Heptachlor		decrease	increase	
Endrin		decrease	increase	
Mercury	increase		increase	increase
Arsenic		decrease		
Organophosphates		decrease		decrease
Methoxychlor		decrease		

Sewage sludge and cattle manure are probably the least expensive organic supplements available; however, their use for this purpose is limited by the fact that they contain variable quantities of trace elements which may disturb the expected soil mechanism for degradation. Additionally, they contain populations of organisms which, although they are usually enteric and do not survive long in the soil, may represent enough competition to slow the build-up of the desired soil micro-organisms. In the field experiment done by Dr. Farmer (referred to previously), both cattle manure and alfalfa meal was used. He found that 8 tons/acre of alfalfa meal was equally as effective in stimulating micro-organisms as 80 tons/acre of cattle manure. Dr. Farmer suggested that considerable energy source is removed in the digestive tract of the cattle.

Plant material, such as alfalfa meal, is the most common organic additive in laboratory work showing the stimulation of degradation mechanisms by organics. Alfalfa meal can be obtained from commercial animal feed manufacturers for a fee of approximately \$5.00 per 100-lb bag. Assuming that about 8 tons are required per acre, the cost of the plant material itself will be about \$800 per acre. Transporting the material by truck over a distance of (e.g.) 20 miles would cost about \$2.00 per ton. The plant material would have to be spread over the area at a cost of about \$3-5 per acre, followed by a discing operation at a cost of \$1.50 per acre. The total cost, therefore, of adding the plant material would equal about \$820.00 per acre.

ii. Decreasing Soil Oxygen Content - The only proven method of creating anaerobic conditions in the field is that used by Dr. Farmer in his efforts to degrade DDT. Dr. Farmer diked the 1.5 acre area into 1/10 acre plots. The dikes were about 15" high and about 18" wide. Each dike segment had a depression covered with polyethylene which served as a weir to allow water to flow between plots. Water was pumped in to a depth of 3-6" in the plots (depth varied due to an uneven soil surface). Anaerobic conditions were maintained throughout the 49-day experiment, monitored by pH measurement.

Diking is a common agricultural practice in areas where rice is grown and in many areas of the United States where salt must be periodically leached from the soil. A tool designed to do this is the disk ridger, a bordering tool which can be purchased for \$500-600. The disk ridger is attached to a tractor and operated by one man, diking about 2 acres/hr. Available soil is used for dike material; occasionally dikes must be repaired because of the instability of the dike material.

The size of the plots will depend on the slope of the ground: plots will have to be smaller for uneven areas. Assuming a reasonably even land, however, plots could range from 1/4 to 1/2 acre in size. An irrigation system could supply the water. Figuring a diking cost of about \$6 per acre for 1/2-acre plots, a maintenance cost of about \$8 per acre, and an irrigation cost of about \$60 per acre, the total cost for maintaining anaerobic conditions would be about \$68 per acre.

Another method for decreasing soil oxygen content, which has not been tried yet in the field, is the addition of water through irrigation with a simultaneous addition of organic matter. It is Dr. Guenzi's* belief that stimulated microbial populations can decrease the oxygen content of water more quickly than oxygen can be added from the water. However, according to Dr. Farmer, this tends to produce only partially anaerobic conditions, i.e., wide variations in oxygen content will occur among soil pore spaces.

iii. Increasing Soil Oxygen Content - The quickest and cheapest way of increasing the oxygen content is to aerate it through repeated discing. Assuming about 25 discing operations would be required over a treatment period, the cost per acre would be \$37.50.

iv. Increasing Temperature - No literature has been found which documents any attempt, successful or unsuccessful, to significantly increase the temperature of the soil in the field. Burnside¹⁴ suggested that black plastic, asphalt, or some other heat-absorbing material might be placed over the soil to increase temperatures and thus increase the rate of detoxification of pesticides. Dr. Guenzi suggested that black PVC sheeting be laid on the surface of the soil to decrease the reflective characteristics of the soil surface. Fairly simple field tests would need to be done to determine whether application of such material to the surface would increase the temperature enough to cause significant increases in degradation rates.* Black PVC sheeting, 10 mils thick, can be obtained from WaterSaver Co. in Denver at a cost of 6.5¢ per square foot. The sheeting, which comes in a variety of sizes up to 101' wide, can be specified for any length. It must be applied with a front end loader or similar vehicle and 6 to 10 men. (The sheeting, folded in an accordion manner, is pulled off the loader as it proceeds and laid down by men following behind the loader. Ten men can lay about 5 sheets a day. If the sheets are to be sealed together, it can be done by hand or with a hydraulic sealer, along with a team of 3 men. For this purpose, however, the sheets could be weighted down on the corners or edges with soil.)

The cost of the material would equal about \$2,831 per acre. The cost of laying the material would be about \$30 per acre, with about \$5 added for maintenance. After use, the sheeting could be disced into the soil at a cost of \$1.50 per acre. The total cost of raising the soil temperature

*The laboratory studies which have shown this increase in degradation with temperature have generally used a temperature differential of 20°C. Dr. Wayne Guenzi at Colorado State University in Fort Collins is currently studying the effects of temperature increases on the degradation of DDT and he has shown that degradation rates continue to increase with increases in temperature beyond 20°C.

would be about \$2,870/acre. Because of this high cost, it is very important to conduct field tests to thoroughly establish the importance of temperature (and ability of sheeting to significantly raise temperature) prior to implementation of any large-scale measures.

v. Increasing Soil Moisture - Probably the best method for adding moisture is to use existing irrigation methods. Temporary irrigation systems suitable for this program cost about \$50 per acre, fixed annual capital cost. Annual operating costs are about \$12-15 per acre, and assuming a two-year operation, this brings the cost to about \$62-65 per acre.

vi. Decreasing Soil pH - Ferrous sulfate (FeSO_4) can be added to the soil to decrease alkalinity. FeSO_4 is available from commercial sources at a cost of about \$24/ton when purchased by the carload (50 tons). Freight cost over a 100-mile distance would be about \$5/ton. Assuming that about 5 tons/acre are needed, the cost per acre would be about \$145/acre.

vii. Increasing Soil pH - To increase alkalinity, limestone should be added to the soil at a rate dependent upon the particular pH to be attained. The increased alkalinity of the soil that has a current pH of about 7 to a pH of 8 or 9 would take around 15 to 25 tons per acre. Since limestone costs about \$9 per ton (including the equipment and labor for spreading), and since a discing operation would follow at a cost of \$1.50 per acre, the total cost per acre will be approximately \$158 to \$263 per acre.

(b) Possible Sequencing of Activating Measures

If the toxicants of interest were those in Table 18, for example, a possible sequence of activating measures to increase their degradation is illustrated in Figure 5.

The first steps taken should be those that are common to the greatest number of toxicants. In this case, those steps are adding organic material, decreasing oxygen, increasing temperature, and decreasing pH (since this is important to the organophosphates in general). Logistically lowering the pH should come first, because the addition of ferrous sulfate should be done before irrigation mechanisms are put in place. The organic matter should be incorporated into the soil next, immediately preceding the implementation of irrigation measures. These last two should be done at the same time since the combined action will help produce anaerobic conditions. Application of a PVC sheeting, of course, should come last.

These measures should be kept in operation for about two to three years, depending on the time necessary for significant degradation to occur. Monitoring for the toxicants involved may indicate that a longer duration is necessary. After the level of toxicants has reached an acceptable level, conditions would be changed to degrade the next set of contaminants.

Table 19. Total Cost for Soil Manipulation

Decrease pH		
FeSO ₄ at \$24/ton		
\$5/ton transportation		
at 5 tons/acre		\$144/acre
Increase organic content		
Alfalfa meal at \$100/ton		
\$2/ton transportation		
at 8 tons/acre		\$820/acre
Decrease oxygen content		
Diking at \$8/acre		
Irrigation at \$60/acre		\$68/acre
Increase temperature		
PVC sheeting at \$2831/acre		
Application at \$30/acre		
Maintenance at \$5/acre		
Discing in at \$1.50/acre		\$2867.50/acre
Increase soil moisture		
fixed annual capital cost for		
irrigation \$50/acre		
operating cost \$12/acre		\$62/acre
Increase oxygen content		
25 discings at \$1.50/acre		\$37.50/acre
Increase pH		
limestone at \$9/ton		
20 tons/acre		
Discing at \$1.50/acre		\$181.50/acre
TOTAL COST	\$4180.50/acre	
320 acres (1/2-square mile)	\$1,337,760	

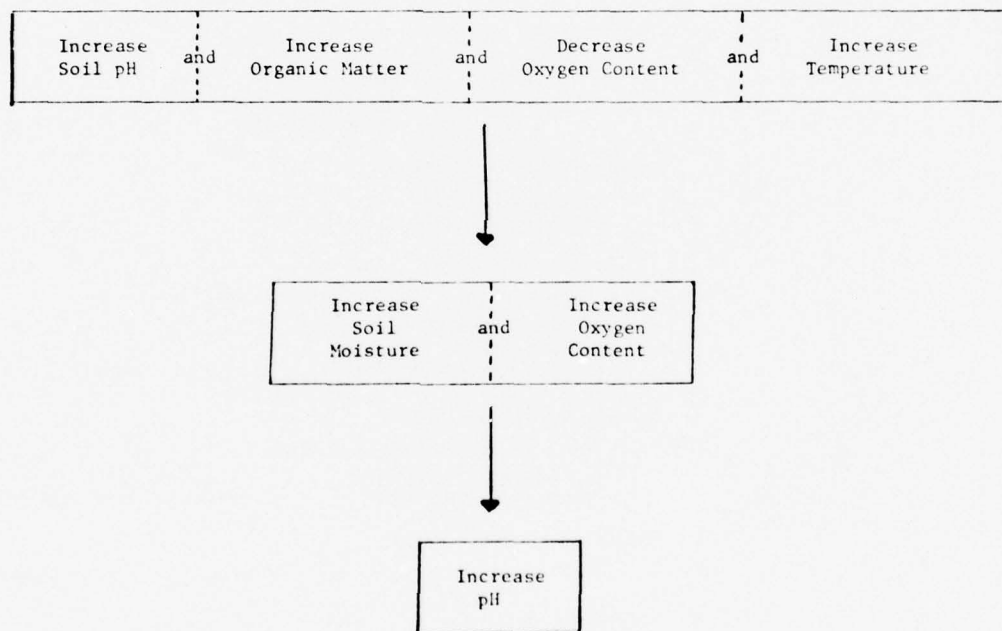


Figure 5. Possible Sequencing of Soil Manipulation

In this case, this would involve measures to increase the degradation of compounds like aldrin which need oxygenated soil and moisture. The irrigation measures can be kept in place, but the rate of application of water may need to be changed. Discing operations would proceed after removal of the PVC sheeting. Although aldrin is degraded more quickly at higher temperatures, the additional cost of replacing the polyethylene sheeting after discing operations may not be warranted.

Finally, efforts must be made to decrease the availability of heavy metals and other undegradable toxicants left in the soil, e.g., increasing the pH of the soil with an application of limestone, although this tends to be unreliable in areas of acidic rainfall.

3. Process Economics - Table 19 presents the total cost per acre if all soil manipulations were carried out.

4. Problem Areas for R, D, and D - Soil activation as discussed above is primarily based on the results of laboratory experiments which have indicated that degradation of toxicants is affected by a number of parameters. Some, but not all, of these results have been verified in field operations. Combining the conditions which maximize degradation into a purposeful effort to increase degradation has not been attempted in the laboratory or the field. However, these conditions are naturally combined in the field in many agricultural soils and other soils which have been shown to be capable of degrading a variety of toxicants. Since soil activation is essentially a method of enhancing natural soil degradation processes, it will have few, if any, adverse environmental impacts. It is also not very costly. Thus, if even modest benefits are demonstrated in preliminary laboratory and field tests, soil activation should certainly be included as part of an overall land decontamination effort. In order to develop an implementation plan for maximizing the inherent capacity of the soil to degrade the particular contaminants present, the following experimental data should be obtained:

- Analysis (qualitative and quantitative) of the contaminants present;
- Rates and products of degradation of each contaminant as a function of manipulable soil parameters;
- Rates and products of degradation of mixtures of contaminants as a function of soil parameters; and
- Extent of degradation achieved under field conditions.

B. Vegetational Uptake

1. State of the Art - The use of resistant grasses is common in land reclamation efforts, but not as a contaminant removal mechanism. It is possible that certain types of vegetation will remove contaminants from the top layers of the soil. Although some work has been done on this

Table 20. State of the Art of Plant Uptake and Translocation of Pesticides from Soils

<u>Insecticide</u>	<u>Absorbed by root</u>	<u>Translocated from root</u>	<u>Compounds Found After Translocation</u>	
			<u>Parent</u>	<u>Metabolite</u>
Aldrin	Yes	Yes	Yes	Yes
Dieldrin	Yes	Yes	Yes	Probable
Isodrin	Yes	Probable	Improbable	Yes
Endrin	Yes	Yes	Yes	Yes
Heptachlor	Yes	Yes	Yes	Yes
Heptachlor epoxide	Yes	Yes	Yes	Unknown
Chlordane	Yes	Improbable	Unknown*	Unknown
Endosulfan	Yes	Yes	Yes	Unknown
Toxaphene	Probable	Improbable	Unknown	Unknown
BHC	Yes	Yes	Yes	Yes
Lindane	Yes	Yes	Yes	Yes
DDT	Yes	Probable	Probable	Yes
Diazinon	Yes	Yes	Yes	Probable
Dimethoate	Yes	Probable	Unknown	Probable
Disulfoton	Yes	Yes	Yes	Yes
Phorate	Yes	Yes	Yes	Yes
Parathion	Yes	Probable	Probable	Unknown
Chloroneb	Yes	Yes	Yes	Yes
Arsenic	Yes	Yes	Yes	---
Lead	Yes	Yes	Yes	---

*None, or has never been investigated.

problem, additional preliminary studies must be completed before attempting large-scale treatment.

There is some evidence from residue studies that certain contaminants in the soil will be taken up and translocated into growing plants. Repeated growth, harvest, and disposal of the plants has the potential for eventually removing contaminants from the soil. There are, however, no known full- or pilot-scale applications. Some of the studies which suggest the technical feasibility of the method are cited briefly below.

Edwards (1873)⁵ predicted that a root crop yield of 20 tons per acre could remove from 0.01-0.1 lb per acre of insecticide (less than 5% removal).

Onsager, *et al.* (1970)⁶ reported removals of about the same magnitude. Removal from the soil by sugar beets averaged 8.4% for dieldrin, 5.5% for DDT, and 9.6% for chlordane.

On the other hand, Lichtenstein and Schulz (1965)⁷ reported that carrots grown in soil treated with dieldrin absorbed 37-64% of the applied dose. Lichtenstein (1959¹⁸, 1960¹⁹) previously reported on the uptake of lindane, DDT, and aldrin and reported residues in carrots ranging from 0 to 7.7 times the residues found in the soil.

Obviously, removal is highly variable and depends on the soil type, the specific toxicant and level, and the crop used. Nash (1974)²⁰ reviewed plant uptake of pesticides from soils. His results are summarized in Table 20. Much research is needed to determine if this method is useful for all of the toxicants present in a given contaminant and whether sufficient amounts of contaminants can be removed.

2. Vegetational Uptake System Description - The first steps in the development of a system are as follows:

- (a) Determine most effective plant for the areas to be treated. - Root crops appear to be quite effective, although soybeans may also concentrate toxic residues. Alfalfa is another possibility which should be explored since the crop is deeply rooted.
- (b) Determine optimum soil conditions for plant growth. - It is likely that these conditions are already known, or can be located in agricultural literature.
- (c) Small-scale field test.

Implementation would normally require the following steps:

- (a) Soil adjustment - The soil needs the adjustments suggested in the preliminary study (b above). Fertilizer will probably be necessary, and perhaps cattle manure application and pH adjustment. The cost of fertilizing and cultivating would be approximately \$50/acre for one cultivation.

- (b) Seeding - After the soil adjustment, the area can be seeded with the appropriate crops. The cost of seeding obviously depends on the crop chosen, but would range around \$20-35 per acre.
- (c) Watering - Irrigation may be necessary to insure germination and growth. Assuming only one application, the cost of a water truck would probably be about \$60/acre for a 1/4" application.
- (d) Harvesting and Disposal - Since the plants may contain toxic residues, they must be harvested and disposed of in a sanitary landfill, or by incineration. Costs for harvesting and transport would be \$40-65/acre for sugarbeets and about \$12-15 for soybeans for a distance of 20 miles.

Additional costs (of the order of \$20/ton) would be incurred if incineration is used as the disposal method, but these have not been included in the cost estimates.

The steps described above may be repeated until residues in soils reach acceptable levels. Assuming a removal of 5% per harvest, independent of contaminant concentration in the soil, and one harvest per year, it would take 59 years or harvests to reach a 95% removal.

$$0.95^n = 0.05$$

n = number of years required

3. Process Economics - A summary of costs for a single harvest using sugarbeets as an example is given in Table 21. At the 5% level of removal per harvest, the total cost for 95% removal could approximate \$3,500,000 over 59 harvests.

4. Problem Areas for R, D, and D - Some of the problems which require further investigation include.

- The costs and technical feasibility of obtaining optimum conditions for growth of the selected crop;
- The extent of uptake of the contaminants of concern by various candidate crops as a function of contaminant concentration in the soil; and
- The degree of movement of contaminants into plants in different soil types, which may bind or adsorb various contaminants differently.

Table 21. Cost of Vegetation Uptake* Using Sugarbeets

<u>Steps</u>	<u>Cost/A (max.)</u>
1. Soil adjustment, fertilizing, and cultivating	\$ 50
2. Seeding	35
3. Watering to 1/4"	60
4. Harvesting	30
5. Transport	<u>10</u>
	\$185/acre
Total cost for treatment of 320 acres (1/2 square mile)	\$59,200

*ADL estimates

C. Inoculation

1. State of the Art - 'Inoculation' as a method of decontamination involves the use of large quantities of micro-organisms incorporated into the soil in order to biologically degrade the toxic material. The organisms used must have shown degrading ability, at least in the laboratory.

The following discussion briefly reviews some of the literature on microbial degradation. This review is not meant to be complete in any sense; it is presented here to provide examples of the state of the art of this method in regard to various chlorinated hydrocarbons, organophosphates, and inorganic compounds.

Wedemeyer (1968)²² reported about 70% conversion of DDT in solution to DDD by Aerobacter aerogenes after overnight incubation. However, this was a laboratory experiment without the use of soil as a medium, and DDD is toxic.

Kearney, et al. (1969),²² found more rapid loss of DDT when soils in the laboratory were inoculated with Aerobacter aerogenes under flooded conditions. DDD was the major metabolite, but a net loss of DDT-DDD occurred in four weeks. The lost product could not be identified and was thought to be bound very tightly to soil particles.

The fungus Mucor alternans also can degrade DDT (Anderson, et al., 1970).²³ Cultures were treated with DDT and incubated for 6 days. After 2 days, only 42% of the applied DDT was recovered from the cultures, whereas 100% was recovered from the control (autoclaved mycelium). The product was an unidentified water-soluble metabolite. Although degradation of DDT occurred in culture by this fungus, it was not shown in soil after an 11-week incubation.

Dr. Philip Kearney (personal communication) at USDA laboratories in Beltsville, Maryland, has conducted field tests inoculating several pesticides, including DDT, with mixed cultures of micro-organisms which had been shown to degrade the pesticides in the laboratory. None of the micro-organisms survived in the soil long enough to significantly degrade the pesticides. The reason for the rapid die-off was apparently the strong competition by existing populations of micro-organisms for energy sources, nutrients, etc. (The existing populations are better adapted to the particular ecological parameters of that soil.)

Microbial degradation has been observed for few other compounds of interest. Tu, et al. (1968),²⁴ screened 92 pure cultures for aldrin-degrading activity in vitro. No one species dominated the conversion of aldrin to dieldrin. Of the fungi, Trichoderma were the most active converters. (Mucor was of minor importance.) It is of interest that some strains of several species of fungi including Trichoderma, Fusarium, and Aspergillus were able to metabolize dieldrin to other unidentified products. Some actinomycetes and bacteria also showed this ability. Unfortunately, this degradation has not been shown in soil.

Mucor alternans was tested for its ability to degrade in culture and soil. In culture, 74% of the applied dieldrin was recovered in 6 days, but no metabolites could be isolated. The addition of M. alternans spores to a dieldrin-contaminated soil had no effect of the degradation of dieldrin (Anderson, et al., 1970).²³

Degradation pathways have been identified for other chlorinated hydrocarbons. Some strains of fungi, bacteria, and actinomycetes have been shown to epoxidize heptachlor in culture (Miles, et al., 1969).²⁵ In addition, Matsumura, et al. (1971),²⁶ reported the degradation of endrin to ketones and aldehydes by a variety of micro-organisms in culture.

Microbial degradation of the organophosphorus insecticides and the phosphonates has not been extensively studied. Kaufman (1974)²⁷ stated that the role of micro-organisms in the initial degradation of organophosphorus is unclear. According to Kaufman's review (1974)²⁷ hydrolysis can be microbially mediated under in vitro conditions, but has not been shown for any of the contaminants of interest.

Some of the inorganic compounds are also affected by micro-organisms. For example, mercury compounds may produce free mercury which may be methylated (Kaufman, 1974).²⁷ Unfortunately, this is not a detoxifying step. Inorganic arsenicals are often inactivated in soil due to the formation of insoluble iron and aluminum salts (Woolson, et al., 1971).²⁸ Under anaerobic conditions, arsenic may be lost as a gas (A. E. Hiltbold, personal communication). Apparently little other information is available concerning the influence of micro-organisms on the detoxification of inorganics.

As this brief review indicates, most of the effort on microbial degradation is currently being directed at the preliminary work of identifying the micro-organisms capable of degrading the toxins. Even this preliminary work has not covered some of the toxins present at DARCOM sites, and there is no assurance that micro-organisms can be found to degrade all of them. Further, the preliminary work has shown that degradation is often not complete and may yield products which are themselves toxic.

The uncertainties indicated by this preliminary work, combined with the failures of the limited field work conducted, indicate that inoculation with micro-organisms is not a method which we feel is presently viable, or worth the large expenditures needed to explore it further.

2. Technical Feasibility - Overall, there appear to be a number of serious problems involved with this method. Our conclusion, after a brief period of review, is that it should not be considered as a viable treatment method for any contaminated site. Some of the major problems include:

- The time required for the completion of the necessary research and preliminary work is too extensive to be useful in the near future.

- There is no reason to believe that appropriate micro-organisms can be isolated to degrade each possible contaminant.

- Degradation has been far from complete, even in the laboratory studies. In many cases, degradation has not been to innocuous materials.

- If the method worked at all, it would only be a surface treatment. Other methods would have to be used for soils contaminated deeper than about 8 inches.

- Most importantly, field tests with known degraders have failed, largely because the micro-organisms introduced cannot compete with the indigenous populations.

IV. LAND RECLAMATION VIA HYDROGEOLOGIC TECHNIQUES

Introduction

The vast majority of documented damage incidents due to improper land disposal of toxic materials have involved contamination of ground water. The leaching of contaminants from a landfill or dump is often a very slow process, and in some cases groundwater pollution has only been manifested 40 or 50 years after the initial burial of the toxic or hazardous waste. Once the groundwater has become contaminated, however, particularly if a major aquifer or water supply is threatened, ameliorative action usually becomes a matter of considerable urgency. In the civilian sector, action has taken three forms: (1) abandonment of the contaminated area, closing of contaminated wells, and provision of a new water supply; (2) digging up of the contaminated soil and reburying it in a sanitary landfill; and (3) use of barrier wells and pumps to curtail the spread of contaminants, with or without provision for collecting and treating the contaminated water. The first two options are not likely to be either feasible or acceptable for contaminated Army lands. The third option, which falls generally into the category of hydrogeologic techniques, forms the subject of this chapter.

Hydrogeologic techniques for reclaiming contaminated land masses and their accompanying groundwater regimes include two fundamental concepts:

1. upgradient groundwater and surface water diversion;
2. downgradient groundwater and surface water collection.

The first concept derives from the assumption that polluted leachate from a contaminated land mass is generated as waters pass through that mass. Diverting waters away from the land mass isolates the mass and curtails leachate production. Use of impermeable materials (e.g., bentonite, asphalt, polyvinyl chloride, hypalon, chlorinated polyethylene) to either under-line or cap the contaminated zone further enhances the first concept of isolation.

The second concept involves downgradient collection of groundwaters and surface waters which have already been degraded by the contaminated land mass. The collected waters can then be treated to acceptable levels of concentration, and either discharged to surface waters or recharged to groundwaters. The concept is based on the ability to fully intercept the contaminated waters downgradient of the land mass and to employ long-term full-time treatment until the waste constituents being contributed by the land mass have considerably declined.

State of the Art

The use of barrier wells and pumps to curtail groundwater contamination is reasonably well-established technology, although systems

must be designed and engineered specifically for any given site and contamination problem.

At the Llangollen refuse landfill in Delaware, a barrier well system was installed to intercept groundwater downgradient of the 56 acre landfill. The landfill had an average depth of 25 feet of refuse, and the refuse, which was placed below the high groundwater table, was contributing to contamination of a public water supply. Forty well points, 60-80 feet deep, along a 2,000 foot line were installed to pump an average of 120,000 gallons per day. Each well has a capacity of 200-250 gpm. Infiltration galleries were placed within the landfill site. Capital costs for the containment system alone were estimated to be in excess of \$2,000,000 with annual operating costs exclusive of amortization in excess of \$300,000 per year.²⁹

A gasoline leak near the City of Los Angeles resulted in 250,000 gallons of gasoline seeping into the groundwater. Hydrogeologic techniques to reclaim the groundwater consisted of 70 wells skimming the gasoline off the upper levels of the aquifer. Aside from the cost of well drilling and pumping, there is, of course, the secondary cost of losing a public water supply well field.³⁰

An industrial company had for many years disposed of arsenic salts by land burial on their own property, leading eventually to groundwater contamination. A pumping system was installed and had to be operated continuously for five years before arsenic levels in the groundwater began to show a measurable decline.

Hydrogeologic Systems Descriptions for Rocky Mountain Arsenal

Land disposal of manufacturing and other wastes at Rocky Mountain Arsenal from about 1942 to 1955 may have contributed to a groundwater contamination problem.^{31, 32} In 1955, chloride contamination was estimated to cover a 6.5 square mile area (see Figure 6).³² More recently, low level concentrations of DIMP have been reported.^{34, *,**} Because of the areal extent of groundwater contamination, hydrogeologic reclamation alternatives cannot be confined to the same area as land based alternatives such as incineration and revegetation. Barrier systems of well points, infiltration galleries and bentonite slurry trenches would have to either intercept downgradient contaminated flow passing through former waste disposal areas (see Figure 7, basins A, C, D, and E) or intercept upgradient uncontaminated flow which would potentially flow through the disposal areas.

*Personal (telephone) communication, Stan Robson, November 6, 1975 and December 3, 1975, located at Denver's U.S.G.S. - (303)234-3815.

**Personal (telephone) communication, Robert Shukle, Colorado Public Health Department, December 3, 1975 (303)388-6111.

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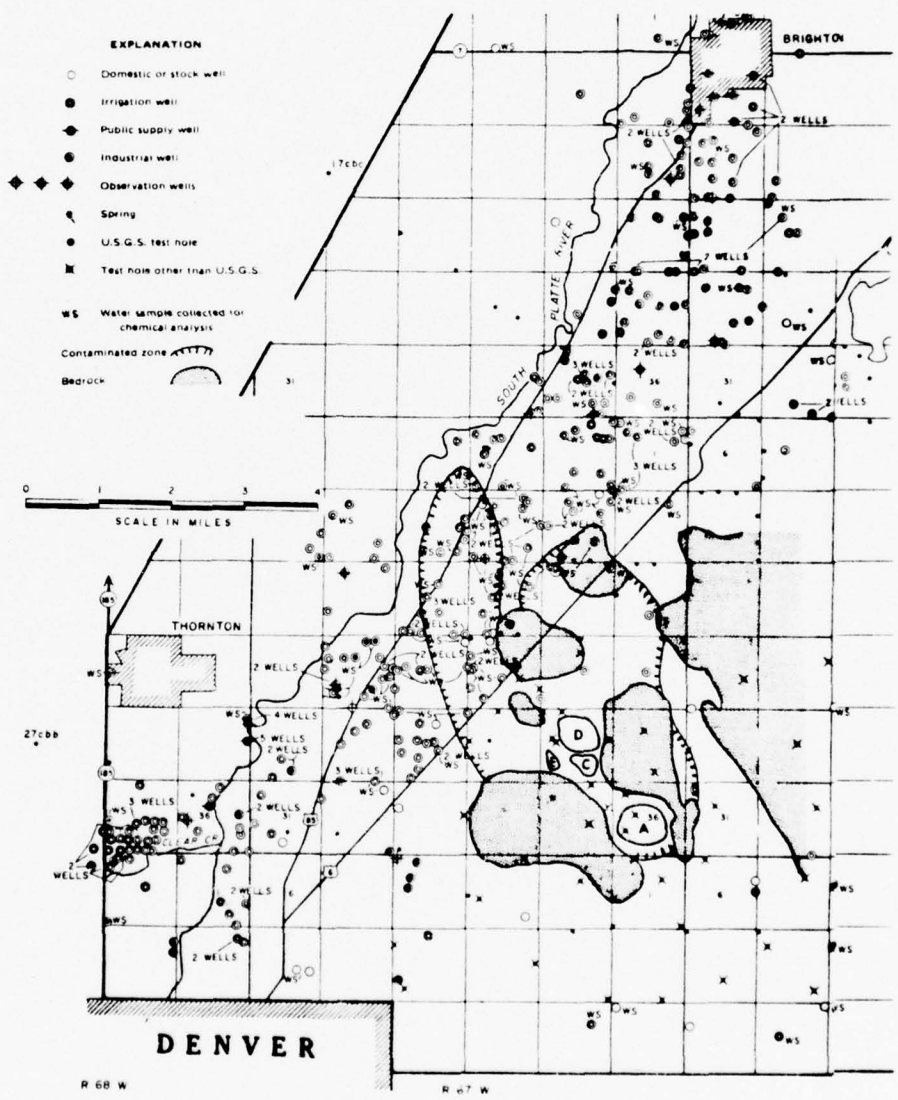


FIGURE 6 1956 AREAL EXTENT OF CHLORIDE CONTAMINATION

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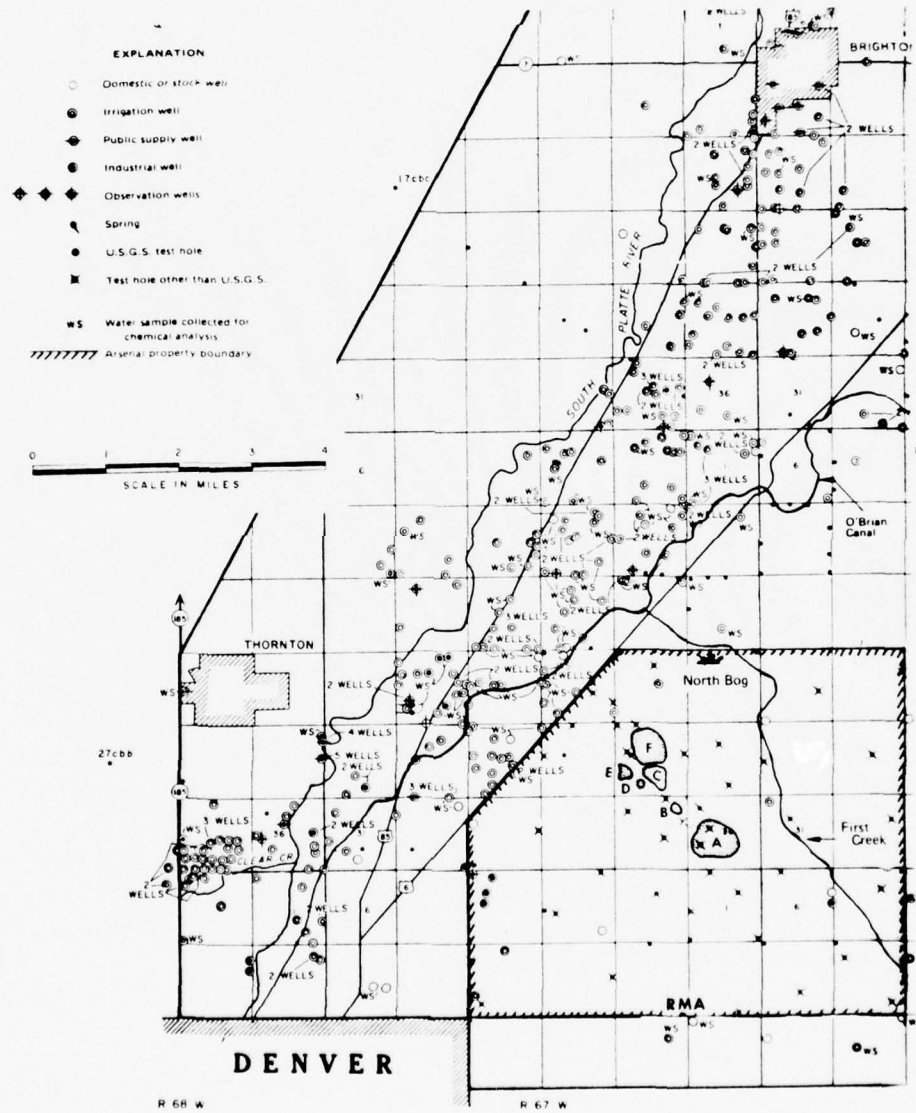


FIGURE 7 STUDY AREA

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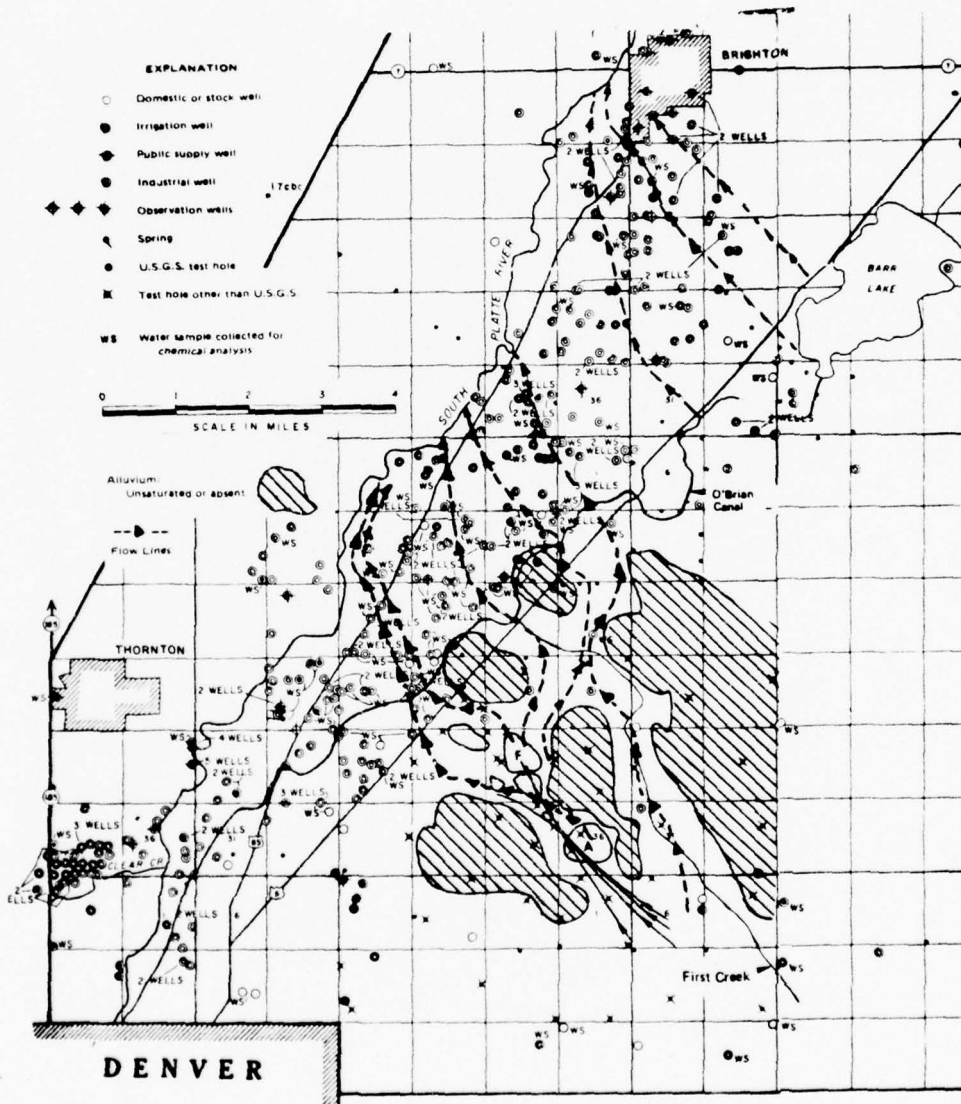


FIGURE B GROUND WATER STEAM LINES

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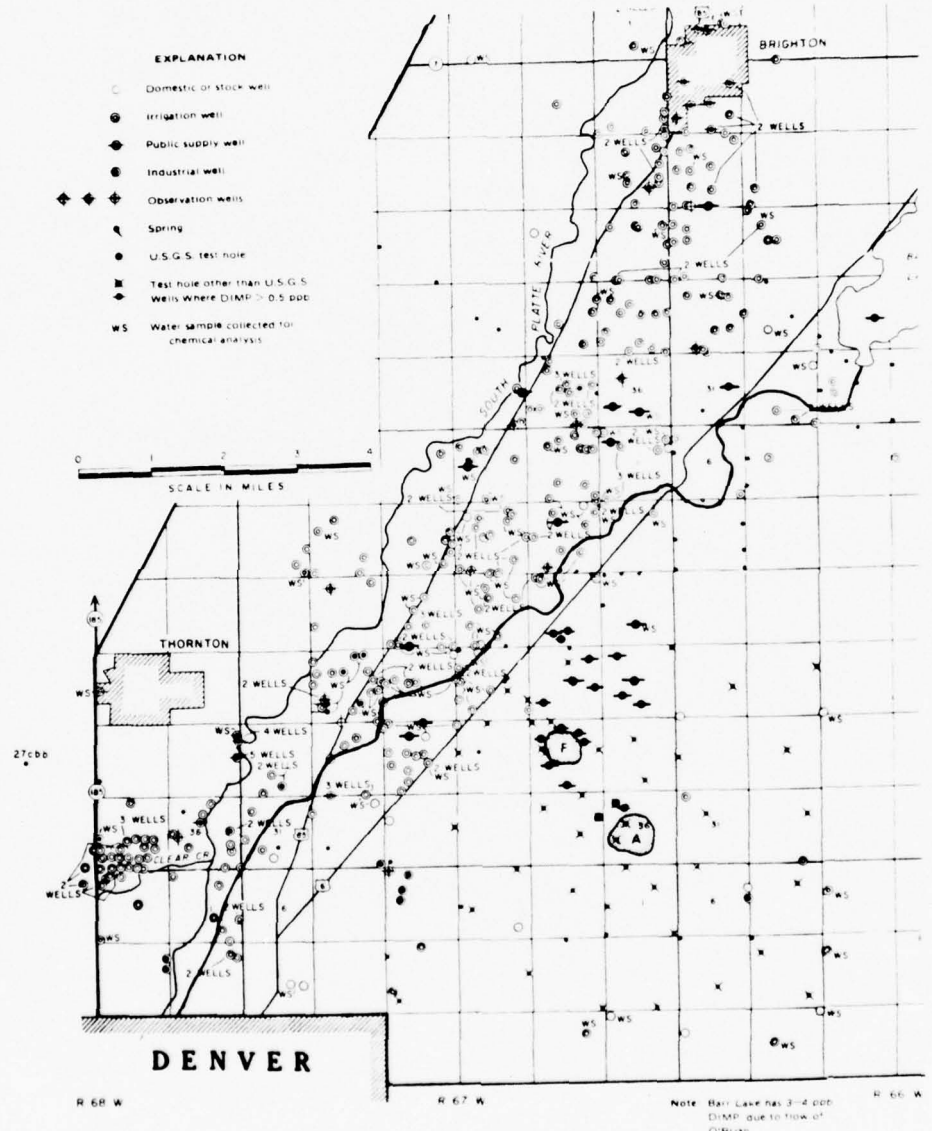


FIGURE 9 WELLS WHERE DIMP > 0.5 ppb

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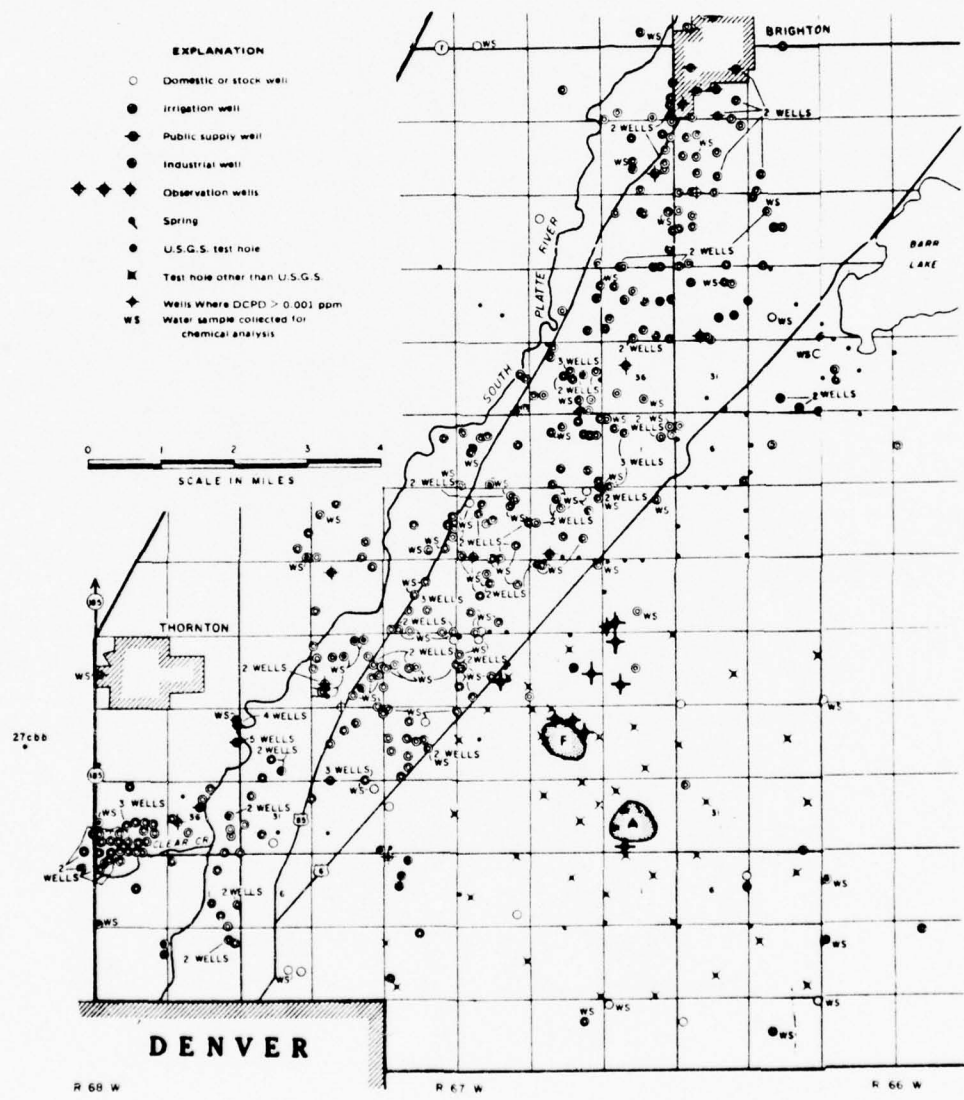


FIGURE 10 WELLS WHERE DCPD > 0.001 ppm

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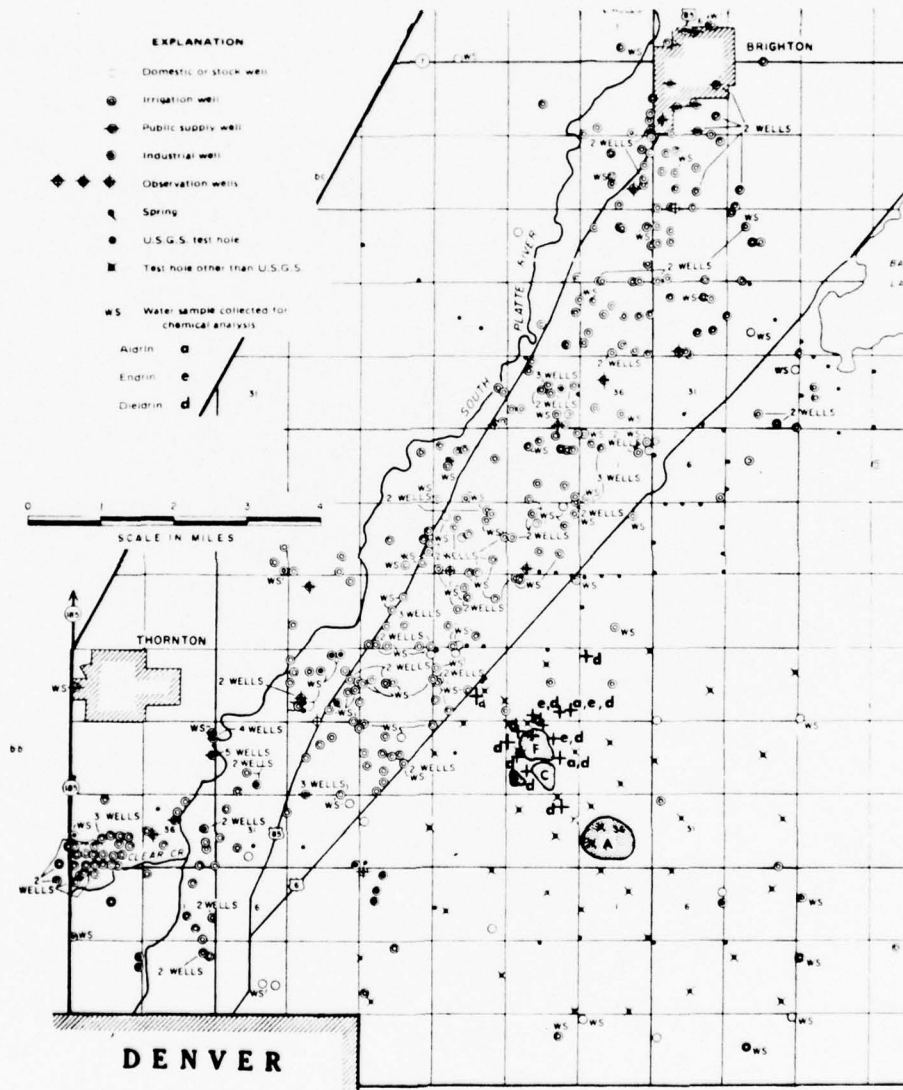


FIGURE 11 LOCATIONS OF ALDRIN, ENDRIN AND DIELDRIN EXCEEDING RECOMMENDED DRINKING WATER SUPPLY CRITERIA

For preliminary planning purposes, the U.S.G.S. hydrogeologic maps^{35,36} of 1975 were used to place the barrier systems. These maps show areas where alluvium is either absent (bedrock outcrops) or unsaturated (impermeable). These areas normally represent the boundaries of the groundwater flow region. Water table contours (not shown) meet these boundaries at right angles. Corresponding stream lines representing the direction of groundwater flow are drawn at right angles to the water table contours. (See Figure 8) For the purposes of this study, the area of "absent or unsaturated alluvium" immediately east and north of Basin A was not assumed a no flow boundary. Hence chloride contamination could have flowed to First Creek in the 1950's, and may be allowing DIMP and pesticide derivatives to contaminate the North Bog (See Figures 6 and 8 through 11) presently.

Two alternatives are proposed to address the groundwater contamination problems of Rocky Mountain Arsenal.

The first alternative involves upgradient groundwater and surface water diversion to circumvent the contaminated area. Leachate production from a contaminated land mass is a direct function of the amount of flow allowed to pass through that land mass. Since most of the flow passing through the contaminated waste disposal basins comes from underflow through the aquifer from outside the area and from surface runoff from the unsaturated alluvium upgradient of the unlined ponds, upgradient diversion of these waters would virtually eliminate leachate production.

The second alternative involves reclaiming the groundwater after it has been contaminated. Barrier systems are placed downgradient of the waste disposal basins to intercept the most highly contaminated groundwater and treat the groundwater to acceptable effluent concentrations.

Figure 12 shows the location of the upgradient elements making up alternative 1. The elements include:

- a 0.8 mile bentonite slurry trench southeast of Basin A;
- a line of well points or an infiltration gallery immediately upgradient of the bentonite slurry trench with discharge to the First Creek channel;
- a 2.7 mile surface drain to collect surface water runoff from the area of "absent or unsaturated alluvium" southwest of the disposal basins, with drainage discharge to the northwest of Basin E.

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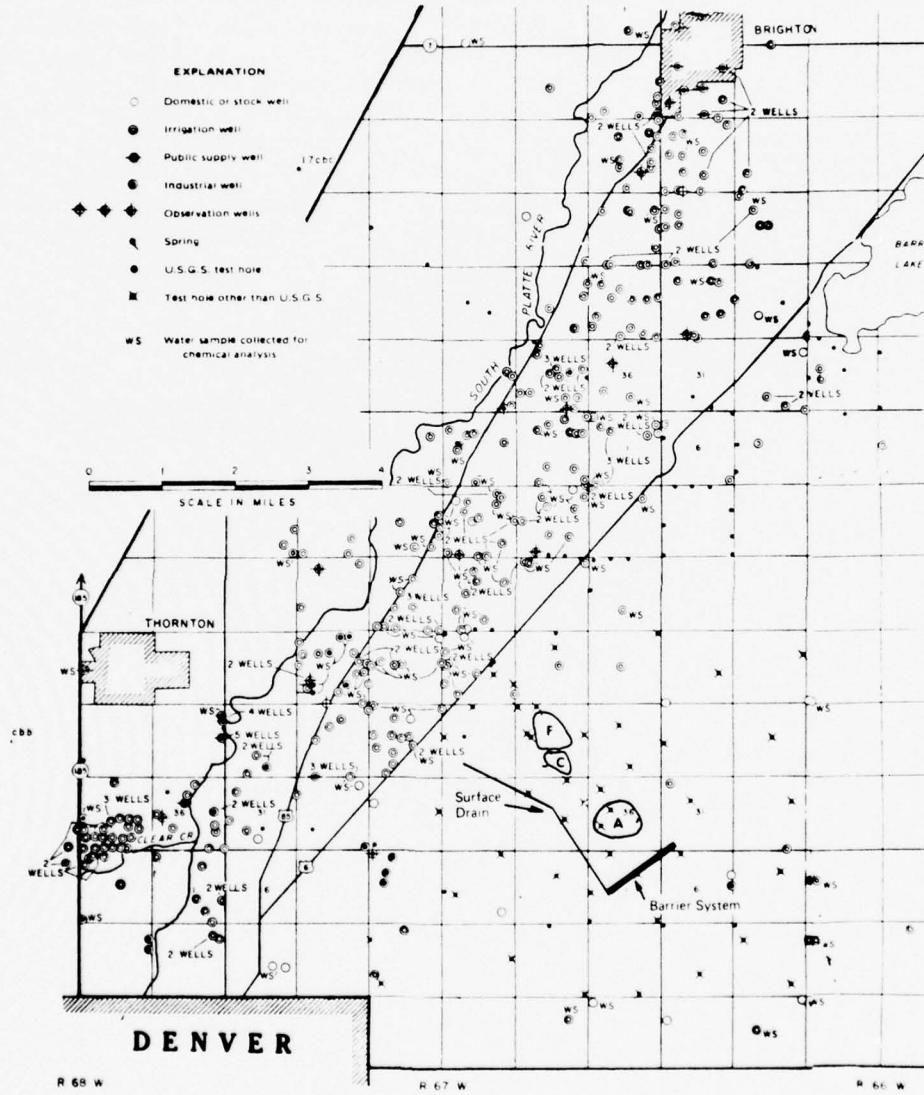


FIGURE 12 ALTERNATIVE 1

Figure 13 shows the location of the downgradient elements making up alternative 2, and Figure 14 shows the process diagram for alternative 2. The elements include:

- a 1.3 mile bentonite slurry trench across the First Creek flow region north of the contaminated basins;
- a line of well points or an infiltration gallery immediately upgradient of the bentonite slurry trench with discharge to a treatment plant;
- a 1.5 mile bentonite slurry trench across the flow region west of Basins F and E;
- a line of well points or an infiltration gallery immediate upgradient of the bentonite slurry trench with discharge to a treatment plant;
- a 1.5 MGD (rough estimate based on hydrogeologic maps) wastewater treatment plant containing facilities for degritting, filtration, activated carbon and reverse osmosis;
- treated effluent discharge to land immediately downgradient of the bentonite slurry trenches.

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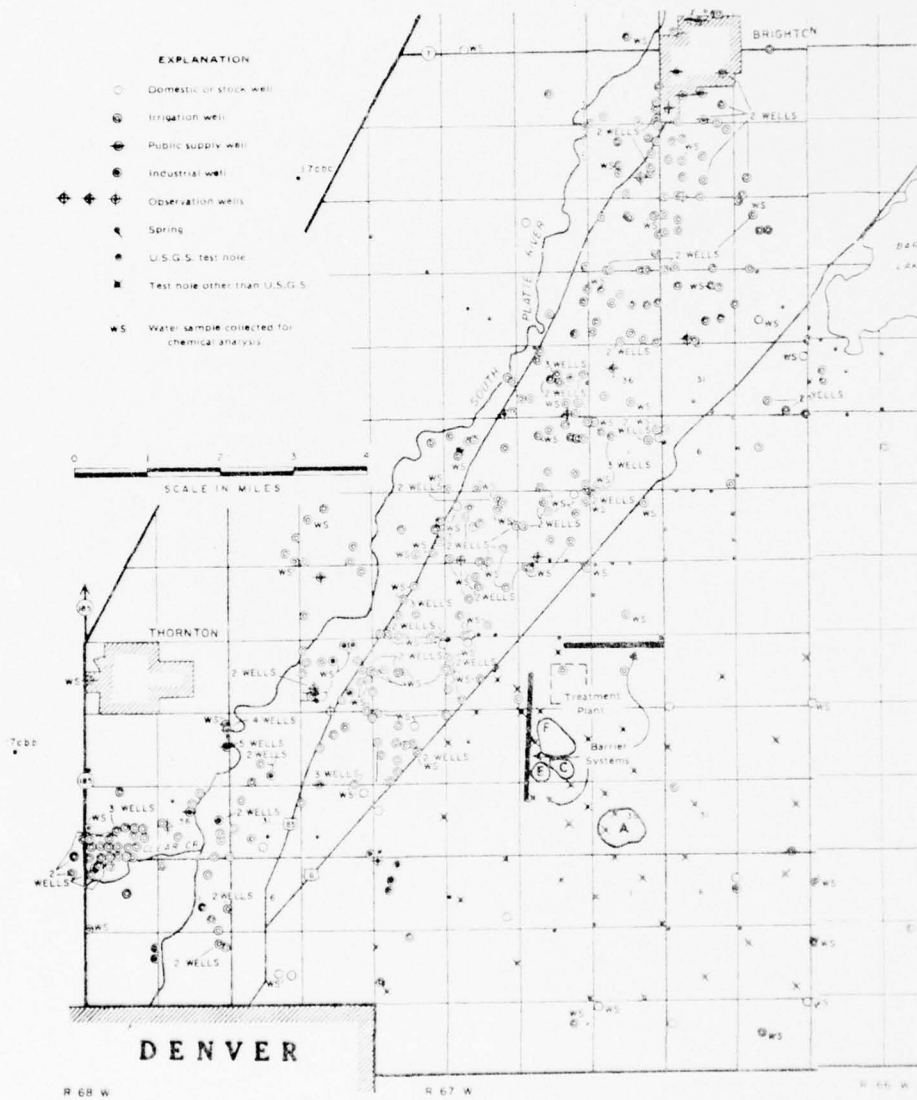


FIGURE 13 ALTERNATIVE 2

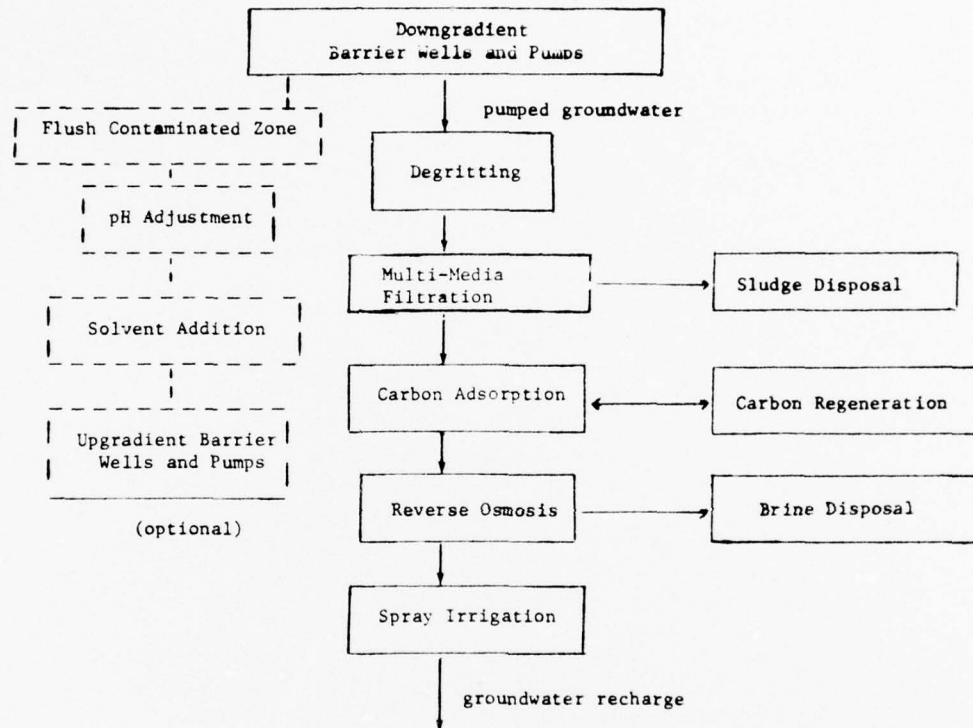


Figure 14. Schematic Process Flow Diagram Groundwater Decontamination, Alternative 2

The optional units shown on Figure 14 include collection of groundwaters upgradient of the contaminated zone, adjustment of the waters' pH to an acid condition and/or addition of a solvent, and discharge of these adjusted waters to the contaminated basin areas. The purpose of this optional measure is to encourage dissolution and desorption of heavy metals and other chemicals from the basin soils, thereby accelerating the period of reclamation. The optional measures are not included in the cost estimates presented below. Further study is needed on the type of solvent and acid feasible and the impact of these additives on the treatment processes and treated effluent quality.

Information for the development of well, trench, and pump costs was provided by Lucas Aguirri, Ron Halley and Ralph Beatty, respectively, each from the Denver area.^{36,*} ** Well screen and "revert" costs were provided by Al Smith.⁺ Insight on the technical feasibility of the proposed alternative was received from each of the above specialists, as well as Thom Neff.[§]

Bentonite slurry trenches are recommended in alternative 1 as impermeable boundaries blocking all groundwaters from reaching the waste disposal areas. Bentonite trenches in alternative 2 dam the groundwaters and augment the ability of the well system or infiltration gallery to intercept all flow. In both cases they provide a simple monitoring system; i.e., when the trenches overflow, the pump systems are not functioning adequately.

The recommended bentonite slurry trenches extend from the ground surface to the top of the impermeable claystone bedrock, an average depth of 40 feet. They cross flow regions bounded by areas where alluvium is either unsaturated or absent. During trench digging, upper portions of the unconsolidated sediment are removed by scrapers; once the water table is reached, draglines are used to remove the remaining portion of the unconsolidated sediment. The width of the trench will be about 5 1/2 feet, created by the pass of 4-foot wide dragline bucket. Bentonite slurry, generally obtained from Wyoming for the Denver region, is pumped into the excavated area; and the excavated soils (if appropriate) are backfilled into the slurry. The final trench is a moist impermeable boundary to groundwater flow (complete drying of the trench should not be allowed, otherwise cracking may occur). The trenches will not be easy to construct. The primary difficulty will be keeping the hole open until the bentonite slurry is injected (when digging at elevations below the water table, water bearing soils tend to slough into the trench).

*Personal (telephone) communication, Ron Halley, President of Hydro-triad, Limited, December 19, 1975, Denver, Colorado area, (303)934-2477.

**Personal (telephone) communication, Ralph Beatty, President of Ralph Beatty and Associates, December 19, 1975, Denver, Colorado area (303) 232-5370

+Personal (telephone) communication, Al Smith, December 19, 1975, located at Johnson Division, Universal Oil Products, St. Paul, Minnesota, (612) 636-3900.

§Personal (telephone) communication, Thom Neff, December 19, 1975, geotechnical consultant associate with T. William Lambe, Marshfield, Massachusetts, (617)837-1515.

Continual pumping of a well forms a conical drawdown curve of the water table elevation with a circular area of influence determined by the soil transmissivity, the boundary conditions, type of aquifer system, and the rate of pumping. A barrier well system is designed to allow a series of wells with intercepting circles of influence to sufficiently lower the water table so that no flow occurs between wells. The series of wells would be spaced so that a hydraulic no-flow boundary would be implemented; the pumping rates of the individual wells would be adjusted so that their depression cones would balance at the mid-point. Because pumping data are not available for the proposed barrier locations, we assume a distance of 30 feet between wells. Each well will have a 5 foot long well screen, with an average length of 35 feet of PVC casing. The method for well placement currently used on Arsenal property is recommended here: a truck-mounted hollow-stem well auger which leaves a 5-6 inch diameter casing in place.

The Denver area, including the Arsenal, has erratic soil conditions. Soils consist of mixtures of sands, silts and clays. Soils within the Arsenal's contaminated zone appear to be very silty or clayey with low permeabilities. There are sand lenses throughout the arsenal soils which account for much of the groundwater flow. It is difficult to intercept the sand lenses, and to insure that a barrier well system will provide a hydraulic no-flow boundary. If, upon field investigation and pumping tests, the barrier well system appears infeasible, an infiltration gallery is proposed.

The infiltration gallery, like the bentonite slurry trench might be excavated with scraper and dragline equipment to the top of the bedrock strata. For excavation below the water table, special steps would have to be taken to maintain side slope stability. Substances such as "Revert" used in the well drilling industry, might find application. If this drilling fluid additive proves suitable, it should temporarily seal the trench and wash out within three days. After the trench reopens, a horizontal well screen could be laid, downward sloping to the pump, and the trench could be filled with gravel. At the collection point, a line shaft vertical turbine pump (plus a standby pump) might be placed within a vertical casing to lift the water to the surface and pressure pump it through the filtration and activated carbon units.

Groundwater pumped from the barrier systems would be directed to a treatment plant consisting of filtration, carbon adsorption and reverse osmosis units. The filtration system allows for the filter media to trap suspended solids within the pore spaces. After the filter media becomes clogged with solids, the flow direction is reversed and the media is backwashed. A carbon adsorption unit provides for the removal of dissolved organic constituents of high molecular weight onto a carbon adsorbent with high surface area. The unit must be preceded by filtration because suspended solids would coat or clog the adsorbent and decrease its efficiency. Reverse osmosis provides for the removal of dissolved inorganics; it relies upon membranes

which are permeable to water and impermeable to salts. The filtration unit might remove up to 92% of the influent suspended solids; carbon adsorption might remove up to 90% of the chemical oxygen demand; and reverse osmosis might remove up to 95% of the total dissolved inorganics. Carbon adsorption can handle influents with chemical oxygen demands as high as 300 mg/l; while reverse osmosis can handle total dissolved solids up to 5000 mg/l. Filtration units result in a clarified effluent and a sludge obtained during filter backwash; carbon adsorption units result in a relatively organic-free effluent and a spent adsorbent material requiring regeneration (e.g., by thermal means in a multiple-hearth furnace); reverse osmosis units result in an effluent nearly free of dissolved solids and a low volume waste stream (brine) containing high concentrations of the original materials and requiring evaporation and ultimate disposal. Both the filtration sludges and the reverse osmosis brines may be disposed in suitably engineered basins.

We recommend consideration of on-land discharge of treated effluent immediately downgradient of the bentonite slurry trenches so that natural hydraulic processes will dilute and encourage micro-biological assimilation of the contamination already existing off arsenal property.

Process Economics

Tables 22 and 23 present capital and operating costs for Alternatives 1 and 2. Capital costs for Alternative 1 (upgradient groundwater and surface water diversion) are estimated at 1.2 million dollars if barrier wells prove to be technically feasible, and at 2.1 million dollars if an infiltration gallery proves necessary. Annual operating costs are expected to be of the order of \$130,000/yr for the wells, and \$230,000/yr for the infiltration gallery.

For Alternative 2 (downgradient groundwater and surface water collection and treatment), estimated capital costs are 5.9 million dollars with wells and 9.7 million dollars with an infiltration gallery. Corresponding operating costs would be of the order of \$1,000,000/yr in either case.

UPGRADIENT HYDROGEOLOGIC
TECHNIQUES

Table 22 - Alternative 1

<u>Capital Costs</u>	<u>Total 1975 dollars</u>
- Excavation equipment mobilization	55,000
- Excavation of trench (0.8 mile x 40 ft. x 5.5 ft.) with scraper and dragline	120,000
- Wyoming bentonite slurry - installed	80,000
- Soil backfill into slurry trench	25,000
- Excavation of surface drain (2.7 mile x 2 ft x 4 ft) with scraper	5,000
- Asphalt drain lining - installed	20,000
- Discharge pipe to First Creek - installed	120,000
- Site clean-up	15,000
- Field investigation and tests	10,000
- Engineering and Design	30,000
<hr/>	
Total applicable to alternative 1A and 1B	\$480,000

Table 22 - Continued

<u>Capital Costs</u>	<u>Total 1975 dollars</u>
<u>Barrier Wells - Alternative 1A</u>	
. Hollow stem augering of 135 wells (35 ft casing, 5 ft well screen)	30,000
. Submersible pumps - installed*	610,000
. Engineering and design	40,000
	<hr/> \$680,000
* assumes average depth of 40 ft, although cheaper suction lift systems may apply for shallower depths	
<u>Infiltration Gallery - Alternative 1B</u>	
- Excavation of trench (0.8 mile x 40 ft x 5.5 ft)	120,000
- Revert - installed	750,000
- Well screen (0.8 miles-type 304 stainless steel) - installed	230,000
- Gravel Pack - installed	460,000
- 2-line shaft vertical turbine pumps and casing (60 hp - 1000 gpm) - installed	15,000
- Engineering and design	90,000
	<hr/> \$1,665,000
Total capital for Alternative 1A	
480,000 + 680,000 =	\$1,160,000
Total capital for Alternative 1B	
480,000 + 1,665,000 =	2,145,000

HYDROGEOLOGIC TECHNIQUES WITH BARRIER
WELLS UPGRADIENT

Table 22a - Alternative 1A

	<u>\$/Year</u>
Capital Recovery (8% over 20 years)	120,000
Operating Cost of Wells (1.2¢/Kwh, \$6,000/ person year)	10,000
Total Annual Cost	<u>\$130,000</u>

HYDROGEOLOGIC TECHNIQUES WITH INFILTRATION
GALLERY UPGRADIENT

Table 22b - Alternative 1B

	<u>\$/Year</u>
Capital Recovery (8% over 20 years)	220,000
Operating Cost of Gallery (1.2¢/Kwh \$6,000/ person year)	<u>10,000</u>
Total Annual Cost	\$230,000

DOWNGRADIENT HYDROGEOLOGIC
TECHNIQUES

Table 23 - Alternative 2

<u>Capital Costs</u>	<u>Total 1975 Dollars</u>
- Excavation equipment mobilization	55,000
- Excavation of trenches (2.8 miles x 10 ft x 5.5 ft) with scraper and dragline	450,000
- Wyoming bentonite slurry - installed	290,000
- Soil backfill into slurry trench	90,000
- Site clean-up	30,000
- Field investigation and tests	30,000
- 1.5 MGD multimedia filtration processes	260,000
- 1.5 MGD carbon adsorption and regeneration	610,000
- 1.5 MGD reverse osmosis	1,360,000
- Discharge pipes and ground recharge	400,000
- Engineering and design	245,000
<hr/>	<hr/>
Total applicable to Alternatives 2A and 2B	\$3,820,000

Table 23- Continued

<u>Capital Costs</u>	<u>Total 1975 dollars</u>
<u>Barrier Wells - Alternative 2A</u>	
. Hollow stem auger of 420 wells (ave. 35 ft casing, 5 ft well screen)	75,000
. Submersible pumps - installed	1,890,000
. Engineering and design	130,000
	<u>\$2,095,000</u>
<u>Infiltration Gallery</u>	
- Excavation of trenches (2.8 mile x 40 ft x 5.5 ft)	450,000
- Revert - installed	2,670,000
- Well screen (2.8 miles - type 304 stainless steel) - installed	750,000
- Gravel pack- installed	1,620,000
- 2-line shaft vertical turbine pumps and casing (60 hp - 1000 gpm) - installed	30,000
- Engineering and design	360,000
	<u>\$5,840,000</u>
Total capital cost for Alternative 2A 3,820,000 + 2,095,000 =	5,915,000
Total capital cost for Alternative 2B 3,820,000 + 5,840,000 =	9,650,000

HYDROGEOLOGIC TECHNIQUES WITH BARRIER
WELLS DOWNGRADIENT

Table 23a - Alternative 2A

	<u>\$/Year</u>
<u>Capital Recovery</u> (8% over 20 years)	600,000
<u>Operating Cost</u>	
Barrier Wells (electricity, labor)	20,000
Filtration (electricity, labor, materials, maintenance)	45,000
Carbon adsorption (electricity, fuel, make-up carbon, labor, materials, maintenance)	45,000
Reverse osmosis (membrane replacement, power labor, materials)	230,000
<u>Total Annual Cost</u>	<u>\$940,000</u>

HYDROGEOLOGIC TECHNIQUES WITH INFILTRATION
GALLERIES DOWNGRADIANT

Table 23b- Alternative 2B

	<u>\$/Year</u>
<u>Capital Recovery</u> (8% over 20 years)	985,000
<u>Operating Cost</u>	
Infiltration Gallery	15,000
Filtration	50,000
Carbon adsorption	40,000
Reverse Osmosis	230,000
<u>Total Annual Cost</u>	<u>\$1,320,000</u>

Problem Areas for R, D, and D

The barrier systems proposed above represent preliminary plans derived without the benefit of field investigations, cross-sections, soil borings and pumping tests in the locations designated on Figures 12 and 13. We have not proposed to collect all contaminated groundwaters and surface waters because the areal extent is too great. Rather we have confined our plans to isolating and reclaiming areas reported as having the highest concentrations of pollutants within the arsenal property boundaries. We expect that discharging treated water near the arsenal boundaries will allow natural hydraulic processes to flush and dilute the existing contamination found outside arsenal boundaries.

Additional compilation and review of existing information is required for more definitive hydrogeologic plans to be derived. For example, review of climatic and infiltration data is needed to determine whether significant leachate results from precipitation on the waste disposal area. For the foregoing analysis, it was assumed that most leachate production comes from groundwater flow through the disposal area and from surface run-off recharging Basin C. As a result, no capping of waste disposal areas with an impermeable material was proposed or costed. Furthermore, the proposed placement of barriers was based on a review of hydrogeologic maps. Additional review with U. S. G. S. water resources personnel responsible for the solute-transport model³⁷ is essential, as well as dye studies to confirm the dispersion of seepage from waste disposal areas.

Field investigations required include soil borings and pumping tests in the proposed barrier system location. Wells pumped for a specified rate and time should be placed to observe drawdown of the water table and estimate transmissivity and groundwater flow rates. If technically feasible, a barrier well system is to be favored over an infiltration gallery due to the construction difficulties and additional costs of the latter. Pumping tests would establish the feasibility of the barrier well system in RMA's erratic soils.

Cross-sections of proposed barrier locations are needed to determine the true dimension of the systems and establish the completeness of the barrier. Where the cross-sections show relatively short distances to bedrock, suction lift pumping systems might be used to lower cost. Our preliminary cross-sections, drawn for working purposes at two barrier locations, show that bedrock did not outcrop at the so-called groundwater flow boundaries of "unsaturated or absent alluvium". It is our impression that these flow boundaries, therefore, represent relatively impermeable unconsolidated sediment. If this impression is confirmed, it may be well to change the straight line barriers now proposed to a horse-shoe barrier.

Additional alternatives for constructing barriers should be investigated and tested in the field. Methods of driving sheet piles and pressure-pumping grout into the soil may work to create an

impermeable barrier. Hydraulic fracturing should be explored for improving groundwater yield.

To determine the capabilities for detoxification of the contaminated grounds by water percolation and its subsequent collection and treatment, it will be necessary to obtain certain data for estimating the efficacy of the procedure, the size and type of the treatment system and the length of time required for achieving detoxification. The data which should be obtained as a minimum are:

1. Measurements on soil cores of the types of contaminants and their concentration profiles within the area of concern.
2. Leaching behavior of soil samples from the core location; i.e., measurements of the rate and degree of detoxification achievable by percolating water or other solvents through the soil.
3. Assessment of the capabilities of alternative treatment processes for removing the pollutants by tests on leachate from Item (2) as well as samples of groundwater from the area. The type of tests selected would depend upon the data obtained in (2). Foremost among these would be the development of activated carbon absorption isotherms, preferably by column tests simulating the probable contact times expected in a water treatment plant. Other tests might encompass reverse osmosis, biological systems or other physio-chemical methods.
4. Pilot plant or mini-plant operating experience directed toward establishing final design parameters for a full-scale plant.

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