AD-A201 244

FILE COPY

ESL-TR-87-17

IN SITU IMMOBILIZATION OF HEAVY-METAL CONTAMINATED SOIL

G. CZUPRYNA, R.D. LEVY, A.I. MACLEAN, H. GOLD

FOSTER-MILLER, INC.
350 SECOND AVENUE
WALTHAM, MA 02254

JUNE 1988

FINAL REPORT

SEPTEMBER 1984 - FEBRUARY 1987

DTIC
ELECTE
OCT 1 9 1988
S D
H

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

AFESC

ENGINEERING & SERVICES LABORATORY
AIR FORCE ENGINEERING & SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

88 10 18 061

NOTICE

The following commercial products requiring Trademark (TM) and/or Registered (R) are mentioned in this report. Because of the frequency of usage, the Trademark and/or Registered was not indicated. If it becomes necessary to reproduce any segment of this document containing any of these names, this notice must be included as part of that reproduction.

Amberlite	Duolite
Attasorb	Satintone
BEN	Teflon
Dowex	Valfor

Mention of the products listed above does not constitute Air Force endorsement or rejection of this product, and use of information contained herein for advertising purposes without obtaining clearance according to existing contract agreements is prohibited.

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM HQ AFESC/RD (ENGINEERING AND SERVICES LABORATORY). ADDITIONAL COPIES MAY BE PURCHASED FROM:

NATIONAL TECHNICAL INFORMATION SERVICE
5285 PORT ROYAL ROAD
SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22314

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release. Distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) AFE-0302-FMI-8472-68	5. MONITORING ORGANIZATION REPORT NUMBER(S) ESL-TR-87-17
6a. NAME OF PERFORMING ORGANIZATION Foster-Miller, Inc. 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Air Force Engineering and Services Laboratory
6c. ADDRESS (City, State and ZIP Code) 350 Second Avenue Waltham, MA 02254	7b. ADDRESS (City, State and ZIP Code) Headquarters, Air Force Engineering and Services Center Tyndall AFB, FL 32403
8a. NAME OF FUNDING/SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State and ZIP Code)	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT NO.
11. TITLE (Include Security Classification) In Situ Immobilization of Heavy-Metal Contaminated Soil	
12. PERSONAL AUTHOR(S) G. Czupryna, R.D. Levy, A.I. MacLean, and H. Gold	
13a. TYPE OF REPORT Final 13b. TIME COVERED FROM 9/11/84 TO 2/4/87	14. DATE OF REPORT (Yr., Mo., Day) June 1988 15. PAGE COUNT 162
16. SUPPLEMENTARY NOTATION Availability of this report is specified on reverse of front cover.	

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	In Situ Immobilization, Hazardous Waste, Heavy Metals, Treatment, Contaminated Soil
07	02		
11	07		

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Many waste solutions and sludges contaminated with heavy metals are generated during aircraft maintenance operations at various Air Force Air Logistics Centers. The disposal of these waste streams by previously acceptable means has led to problems with the contamination of both soil and groundwater. Available technologies for treating contaminated soils are expensive. In situ immobilization of heavy metals is a cost-effective treatment alternative to alleviate the environmental and health hazards associated with contaminated soils.

The objective of the program was the laboratory evaluation of various treatment chemicals for the in situ immobilization of hexavalent chromium, cadmium, nickel, copper and zinc in soils from Air Force facilities in the United States. The test program consisted of batch and column testing for measuring

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL [illegible]	22b. TELEPHONE NUMBER (Include Area Code) (904) -28-4628 22c. OFFICE SYMBOL HQ AFESC/RDVW

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

19. Abstract (concluded)

the leachability and subsequent immobilization of single and multiple heavy metals in soils. The batch equilibrium tests were used to screen 25 chemical additives for their ability to react with contaminated soils. Lime and Valfor 200 (a molecular sieve), in conjunction with ferrous sulfate, were selected for further column studies.

Dynamic-flow column studies were conducted to obtain detailed data on the maximum capacity and mobility of the metal contaminants in soil with and without the addition of the best treatment chemicals. Long-term column tests on the stability and leachability of the best treatment chemicals with and without the effects of acid rain and solvent addition were also carried out. Finally, tests were performed in a Hazardous Waste Site Simulator over a 4-month period to determine the immobilization of hexavalent chromium, cadmium and nickel in treated soil against a dynamically-changing environment. The results of the column studies showed that the use of the Valfor 200/ferrous sulfate combination for the immobilization of hexavalent chromium, cadmium, and nickel proved very effective in treating soils from McClellan AFB and Robins AFB. Specifically, hexavalent chromium and in particular Ni, were so tightly bound to the treated soil that a total digestion of the soil (using concentrated acids) was required to determine the total metal distribution with the soil columns. Long-term stability tests with soils contaminated with only hexavalent chromium showed that very little, if any, leaching occurred with simulated acid rain (pH 5.3), deionized water, and water saturated with a solvent (toluene) leachate solutions, indicating that the treatment chemicals and the metal complexes they formed were stable over the test period (25 days).

The primary cost of in situ immobilization treatment is the cost of the chemical treatment additive; the application costs are less than 5 percent of the chemical costs. The estimated chemical costs to treat soil contaminated with 30 milliequivalents of total metal per g soil ranged from $33,300/acre-ft to $81,200/acre-ft, or $13.9/ton to $33.8/ton. As a basis for comparison, the costs of transporting the contaminated soil to, and disposing the contaminated soil in a secured landfill is estimated to be in the range of $150/ton to $250/ton, depending upon the distance to the secured landfill and the disposal and/or treatment costs.

Future research should be directed towards:(1) laboratory tank studies to understand the interactions between soil dynamics and metal immobilization and (2) pilot field-scale studies in which the actual soil and environmental conditions are required to give a complete evaluation of immobilization processes applied to hazardous waste sites.

EXECUTIVE SUMMARY

A. INTRODUCTION

Various industrial operations are carried out on behalf of the U.S. Air Force at five Air Logistics Centers and at a number of Government-Owned, Contractor-Operated facilities throughout the United States. These facilities conduct a variety of aircraft maintenance operations, including aircraft paint stripping, parts degreasing, and electroplating, which generate many waste solutions and sludges contaminated with heavy metals. The disposal of the waste solutions and sludges by previously acceptable means has led to problems with the contamination of both soil and groundwater.

Available technologies for treating soils contaminated with heavy metals are expensive and include excavation of the contaminated soil and transport and disposal in a landfill, or excavation, treatment and disposal in a landfill. The treatment could include washing of the soil and subsequent pH adjustment and precipitation.

In situ immobilization of heavy metals will avoid the requirement for excavation of contaminated soils or pumping of contaminated groundwater. Immobilized metals will not migrate through the soil to groundwater and will not hydrolyze or be desorbed from exposure to varying conditions in the soil, such as a low pH or varying oxidation-reduction potential which tends to solubilize the metals. The immobilized metals will present no adverse environmental or health hazards in their treated state. In situ treatment also provides a cost-effective treatment alternative to alleviate these hazards.

The objective of the program was the laboratory evaluation of various treatment chemicals for the in situ immobilization of chromium, cadmium, nickel, copper and zinc in soils typical of those found at Air Force facilities throughout the United States.

n For
A&I
od
ation
By
Distribution/
Availability Cod
Dist | Avail and/or Special
A-1
DTIC COPY INSPECTED 1

B. TEST RESULTS

1. Overview of Test Program

The laboratory test program consisted of batch and column testing for measuring the leachability and subsequent immobilization of single and multiple heavy metals in soils. The soils used for testing were obtained from three Air Logistics Centers. Batch equilibrium methods were used to screen a large number of chemical additives for their ability to react with contaminated soils. The two best treatment chemicals for each soil-metal combination were selected for more detailed column studies. Dynamic flow studies were conducted to obtain detailed data on the capacity and mobility of metal contaminants in soil with and without the addition of the best treatment chemicals. Long-term column tests on the stability and leachability of the best treatment chemicals with and without the effects of acid rain and solvent addition were also carried out. Tests were also carried out in a Hazardous Waste Site Simulator to determine the immobilization of the heavy metals, chromium, cadmium and nickel, in treated soil against a dynamically changing environment.

Effluent and supernates generated during the testing program were analyzed for the heavy metal contaminants (Cd, Cr, Ni, Cu and Zn). The total metal contaminants were determined on a Perkin-Elmer Model 2380 Atomic Absorption (AA) Spectrophotometer. Metal ion concentrations in test solutions that exceed the sensitivity of the AA were determined on an EG&G PARC 364 Polarographic Analyzer.

2. Soil Collection and Characterization

Soil types vary radically throughout the United States and soils typical of those contaminated by heavy metals are difficult to define. The approach taken in the test program was to use soils representative of those contaminated at Air Force Air Logistics Centers (ALC) through the United States. Soils were characterized onsite and collected at three ALCs: Sacramento ALC, McClellan AFB, CA; Warner Robins ALC, Robins AFB, GA; and Oklahoma City ALC, Tinker AFB, OK. Samples of uncontaminated soil, taken in

the vicinity of the contaminated metal disposal areas, were collected from several locations at each site from the wall of shallow excavations.

Approximately 1500-2100 pounds (680-950 kg) of uncontaminated soil were collected at each ALC and shipped to Foster-Miller in three 55-gallon plastic or plastic-coated drums. Soil from McClellan and Robins AFB was mixed by screening the entire sample through an ASTM 2-foot standard sieve shaker. The Tinker AFB soil was mixed in a 1500-pound capacity roller mill because the clay would not pass through the sieve shaker and could not be mixed by hand.

Table ES-1 summarizes the more important physical and chemical properties of each soil. The Tinker AFB soil has the lowest permeability and highest organic content of the three soils.

TABLE ES-1. SOIL PROPERTIES.

Soil Property	McClellan AFB	Robins AFB	Tinker AFB
Description	Sandy loam	Loamy Sand	Clay Loam
Dry Density (lbs/ft^3)	118.0	107.6-109.2	99.7-117.7
(Specific Density)	1.89	(1.73-1.75)	(1.60-1.89)
Moisture (percent)	14.0	7.32-8.08	15.5-20.0
Permeability (in/hr)	1.5	1.6	0.66-1.0
(cm/hr)	3.8	4.1	1.7-2.5
Soil pH	5.8	5.3	6.6
Buffer pH	7.0	6.7	7.3
Conductivity (10^{-4} milliohms)	1.3	1.2	7.0
Cation Exchange Capacity (mequiv/100 grams)	4.4	5.2	15.9
Readily Oxidizable Organics (percent)	1.04	0.93	2.70

3. Treatment Chemical Additives

Many chemical additives are used in the treatment of wastewaters to reduce heavy metal concentrations. Many of these chemical additives can

reduce the metal concentrations to levels below federal and state effluent discharge limits, and, in some cases, to below drinking water standards. Twenty-one candidate materials that have been used in the treatment of metal-containing wastewaters and have the potential to be used as immobilizing agents in contaminated soils were identified and screened in a batch test program. These materials fell into the following classes: standard cation exchange resin (1 type); chelate ion-exchange resins (3 types); Devoe-Holbein metal scavenging molecules (3 types); natural materials such as clays (5 types), molecular sieves (2 types) and greensand (2 types); and other additives consisting of hydrated lime, silylated silica gel, insoluble starch xanthate, Metal Sorb-7 and ferrous sulfate; for a total of 21 chemical additives. Since the four ion-exchange or chelate resins could be conditioned in two different ways, a total of 25 chemical additives were available for use in the test program.

4. Batch Screening Test Program

Batch testing was carried out in 18 - 1,000 mL Erlenmeyer flasks in which soils were placed in an uncompacted, unconfined state and to which treatment chemicals and/or contaminant metals were added. The mixtures were reacted by mechanical shaking on reciprocal shakers. The mixtures reached chemical equilibrium within 24 hours. Aliquots of the solutions were taken after the tests and analyzed for each of the six contaminant metals on an AA. The difference between the original and the measured metal values correspond to the amount of metal adsorbed and/or complexed by the chemical additive and the soils.

In the initial series of screening tests, each one of the 25 chemical additives was reacted with a metal salt solution containing all five metals at a concentration of 30 milliequivalents (mequiv)/L each. Twelve chemical additives generally having the highest capacities were selected for further testing.

Subsequent testing involved using both the soils and chemical additives. As a control case, the uptake capacity of the three soils contaminated with both single and multiple metals were first determined.

The total capacities (soil and chemical additive combined) of the 12 chemical additives for each soil contaminated with a single metal at a concentration of 30 mequiv/L were determined in another series of tests. The differential capacity of each chemical additive was then calculated by subtracting the total capacity from the control capacity (contaminated soil with no chemical additive). The chemical additives were ranked on the basis of their cost per unit weight of heavy metal removed from the soil.

The data for all single metal contaminants, with the exception of hexavalent chromium revealed:

- Lime and Valfor 200 (synthetic molecular sieve) consistently outranked all the other additives.
- The treatment chemicals generally having the lowest treatment cost also had the highest differential capacities. A notable exception was the bentonite clays which had low differential capacities and low unit costs.
- The treatment costs were lower and the differential capacities were higher for the McClellan and Robins AFB soils than for the Tinker AFB soil. This is consistent with the higher soil capacity of the Tinker AFB soil.
- For the two best chemical additives, the treatment costs ranged from $0.01/equiv to $0.23/equiv for the McClellan and Robins AFB soils, and with the exception of copper, from $0.03/equiv to $0.55/equiv for the Tinker AFB soil.

Lime ranked first for the McClellan AFB and Robins AFB soils as a cost-effective treatment for hexavalent chromium at $0 13/equiv, but did not appear to be an effective treatment chemical for hexavalent chromium for the Tinker AFB soil. The most cost-effective treatment for hexavalent chromium in the Tinker AFB soil is the synthetic chelating resin Duolite CS-346 at $4.45/equiv. Since Duolite CS-346 is so expensive, ferrous sulfate was investigated as an alternative treatment chemical. In the preliminary screening tests, ferrous sulfate addition with pH adjustment by lime, was found to be very effective in immobilizing hexavalent chromium.

Hexavalent chromium, Cr^{+6}, can be reduced to the less toxic, less mobile trivalent chromium state, Cr^{+3}, with ferrous sulfate. Ferrous sulfate is a nontoxic, inexpensive reducing agent. Theoretically, once in the Cr^{+3} form, it can be precipitated with lime as chromium hydroxide, $Cr(OH)_3$, or adsorbed onto Valfor 200 by ion exchange. Lime/ferrous sulfate and Valfor 200/ferrous sulfate combinations were tested on the three soils to determine their effect on hexavalent chromium immobilization.

The test results showed clearly that lime/ferrous sulfate and particularly Valfor 200/ferrous sulfate are viable alternatives for Cr^{+6} immobilization relative to the other expensive treatment chemicals discussed above. The costs of the two best treatments for Cr^{+6} immobilization for each soil ranged from $0.08/equiv to $0.27/equiv, consistent with the treatment costs for the immobilization of the four other metals. The test data showed that the combination of soil and lime/ferrous sulfate treatment immobilized 50 percent of the total Cr^{+6} found in the soil, while soil and Valfor 200/ferrous sulfate immobilized 100 percent of Cr^{+6}, making this latter immobilization method exceptionally effective and inexpensive.

For soils contaminated with only Cr^{+6}, Valfor 200/ferrous sulfate was more effective in immobilizing Cr^{+6} than lime/ferrous sulfate at the highest dosage tested.

Lime and Valfor 200, with and without the addition of ferrous sulfate, were tested with multiple metal solutions and at various dosages. Lime and Valfor 200, by themselves, appear to be viable for immobilizing Cu, Ni, Cd and Zn, singly and in multiples, but do not immobilize hexavalent chromium. However, hexavalent chromium can be immobilized with the addition of ferrous sulfate to either lime or Valfor 200.

With multiple metal solutions, all of the five metals were virtually immobilized at the highest lime/ferrous sulfate dosage tested. At a given lime dosage, the effect of increasing the ferrous sulfate dosage reduces the immobilization efficiency of Cd, Ni, Cu and Zn, but decreases the mobility (increases the immobilization efficiency) of Cr^{+6}. Cr, Cd and Ni were all virtually immobilized with Valfor 200/ferrous sulfate, but Cd and Zn were not

fully adsorbed on Valfor 200 at the dosage tested. Ferrous sulfate addition at a fixed Valfor 200 dosage also decreased the immobilization efficiency of Cd, Ni, Cu and Zn and increased the immobilization efficiency of Cr^{+6}.

5. Dynamic-Flow Column Test Program

Dynamic-flow column studies were conducted to obtain detailed data on the maximum capacity and mobility of the metal contaminants in soil columns with the addition of the treatment chemicals, lime or Valfor 200/ferrous sulfate. Control tests were carried out by packing only the soil in the columns. Twelve test columns were constructed of polyvinyl chloride, each with an inside diameter of 2.0 inches (5.1 cm) and a length of 30 inches (76.2 cm). The apparatus was constructed without any metal components contacting the fluid or soil. The soil columns were packed to the in situ density of each soil and the total weight of soil used in each column was 600 grams.

Single and multiple metal solutions containing a total metal concentration of 30 mequiv/L and a natural pH of approximately 4.2 were passed through the columns and small aliquots of the effluent were gathered at periodic intervals and analyzed for the contaminant metals on an AA. In the case of multiple metal solutions all of the individual metal concentrations had the same mequiv/L concentration. The tests were terminated when the effluent concentration equaled the influent concentration.

Only the McClellan and Robins AFB soils were used in the soil columns; the Tinker AFB soil was incompatible with soil column testing because of its very low permeability. Each soil was treated with lime and Valfor 200/ferrous sulfate at three different dosages. The amount of lime added to the soil correlates to soil pHs 7.0, 8.5 and 10.0. Valfor 200 ferrous/sulfate was added at a weight ratio of 1:1 and at soil-to-Valfor 200 weight ratios of 200:1, 100:1, and 50:1.

The test data show that the total metal capacities generally increase as the dosage is increased. At the two highest dosages, the

immobilizing action of Valfor 200/ferrous sulfate exceeds that of lime. The multiple metal tests with Valfor 200/ferrous sulfate generally showed chromium is selectively adsorbed relative to the four other contaminant metals. Chromium, nickel and copper are selectively adsorbed relative to cadmium and zinc.

6. Long-Term Stability Column Test Program

Long-term stability column tests were carried out to determine the leachability of Cr^{+6} - contaminated soils treated with lime and Valfor 200/ferrous sulfate. Twelve (12) PVC columns similar to the dynamic flow columns were constructed; the inside diameter was 2.0 inches (5.1 cm) with a length of 12 inches (30.5 cm). The columns were packed to the *in situ* density of each soil.

Six columns were prepared for each of the test soils. For each soil, two columns were treated with lime to bring the soil pH to 10, while three other columns were treated with the same dosage of Valfor 200/ferrous sulfate (Valfor 200/ferrous sulfate = 1:1 by weight; soil/Valfor 200 = 100:1 by weight). The sixth column was used as a control and was packed with soil without a treatment chemical. Each column contained 600 grams of soil contaminated with 18 milliequivalents of Cr^{+6}, for a metal loading of 3 mequiv/100 grams soil.

Different leachate solutions were passed through the soil columns for periods ranging from 24 days to 53 days. The leachate solutions included deionized water, applied to the soil to bring it to both a saturated and unsaturated condition; simulated acid rain, which was deionized water adjusted to a pH 5.3 with sulfuric acid; and water saturated with toluene. The test data show that Valfor 200/ferrous sulfate is responsible for complete immobilization of chromium in the soil, with the chromium concentrations generally less than the analytical detection limit of 0.25 ppm. The metal concentrations in these leachates are considerably less than the concentrations in the deionized water leachate from the corresponding control columns. This indicates that the three leachate

solutions are ineffective in desorbing Cr^{+6} from the contaminated soils treated with a combination of Valfor 200/ferrous sulfate.

Lime treatment was ineffective in immobilizing Cr^{+6} in the soil. The metal concentrations in the simulated acid rain and deionized water leachates were equivalent to or greater than the metal concentrations in the deionized water leachate of the corresponding control columns. The shape of the removal curves indicates that most of the metal is removed in the first two to five leachate pore volumes.

7. Hazardous Waste Site Simulator Test Program

Soil can pick up specific metal ions from waste solutions and later give them up because of intervening conditions in the soil acting on the passage of liquid containing the metallic waste. The hazardous waste site simulator test program was carried out to determine the immobilization efficiency of treated soil in a dynamically-changing soil environment.

Four columns were constructed. Each column consisted of four sections, each having an inside diameter of 2.0 inches (5.1 cm), that were mounted on top of each other after being packed with soil to its native density. Sampling ports were placed between each section of the column to monitor the passage of Cr, Cd and Ni from one section on the column to the next section. The first or top section (Section A) was 2 feet long and each of the three successive sections (Sections B, C, D) were 1 foot long. Leachate fluid was gravity fed through the columns.

Two columns were filled with McClellan AFB soil and two with Robins AFB soil. The top section of each column was packed with 1800 grams of soil contaminated with 18 mequiv each of Cr, Cd and Ni. The total metal contamination of 3 mequiv/100 grams soil was the same as in the long-term stability test. In one column, the contaminated soil was treated with Valfor 200/ferrous sulfate soil in the same dosage as in the long-term stability tests (Valfor 200/ferrous sulfate = 1:1 by weight; soil/Valfor 200 = 100:1 by weight). The other column was used as a control, i.e., the soil was not treated. All of the bottom three 1-foot sections in each column were

filled with uncontaminated, untreated soil and represented the virgin soil below the contaminated soil on a hazardous waste site. The columns were continuously leached with deionized water for 114 days at a flow rate equal to their as-packed permeability.

All effluents were analyzed for Cr, Cd and Ni; the iron concentrations were also analyzed in the soil columns treated with Valfor 200/ferrous sulfate. The distribution of Cr, Cd and Ni retained by the soil columns were determined after the leachate test was concluded by analyzing the soil columns. Initially, the metal content in the soils was measured by determining the concentration of readily extractable metals. Cadmium was accounted for using this method in all four columns; nickel was also determined in the two control columns by this method. However, in the other columns, specifically the two treated columns for Ni and Cr^{+6}, and to some extent, in the control columns for Cr^{+6}, only a fraction of the original doped metal values were observed. It was concluded that these metals were bound tightly to the soil as a result of treatment with Valfor 200/ferrous sulfate. A soil digestion method was used to analyze for Ni and Cr^{+6} in the treated soil columns.

Immobilization of Cr, Cd and Ni in contaminated soils treated with Valfor 200/ferrous sulfate was enhanced relative to the untreated control columns. The immobilization effects of the treatment chemicals are more pronounced in the lower metal capacity Robins AFB soil, when compared to the higher metal capacity McClellan AFB soil. Most of the chromium, cadmium and nickel in the Robins AFB soil was immobilized in the treated top section compared to the control column. With the exception of cadmium, excellent immobilization of these metals in the top section resulted in less metal available to challenge the lower soil sections.

Cadmium appears to be very mobile with 21.2 percent of the total cadmium in the Robins AFB control column leachate effluent. The mobility of cadmium was further corroborated by the results of the dynamic flow and long-term stability column tests.

These results indicate that in situ treatment may be a viable solution for the immobilization of Cr, Cd and Ni in contaminated soil. The use of Valfor 200/ferrous sulfate mixtures as a treatment additive for the immobilization of heavy metals proved effective in the McClellan and Robins AFB soils. The treatment additives provided immobilization efficiencies superior to the continuously leached columns.

Valfor 200 is a sodium aluminosilicate that has a high sorption capacity for divalent and trivalent heavy metals. The high distribution of exchangeable sodium cations in Valfor 200 accounts for its high sorptive capacity for Cd and Ni. Valfor 200 is not selective for chromium in the hexavalent state. The addition of ferrous sulfate reduces Cr^{+6} to the less toxic, less mobile trivalent species, Cr^{+3}, which is readily sorbed onto the Valfor 200 surface or precipitated as insoluble chromium hydroxide. Co-precipitation of iron and contaminant metal sulfides also occurs in the top section of the treated columns. Contaminant metal immobilization is also derived not only from simple ion exchange consideration, but also strong covalent bonding responsible for precipitation and chemisorption of metal contaminants.

C. COST ANALYSIS

The total costs of in situ immobilization consist of the chemical additive costs and the soil application costs. The chemical costs to treat soil contaminated with 30 mequiv/kgram of total metal (consisting of Cr^{+6} and/or Cd and/or Ni) with Valfor 200/ferrous sulfate was estimated to be in the range of $33,300/acre-ft to $81,200/acre-foot, or $23.9/ton to $33.8/ton. The chemical dosage, i.e. soil-to-Valfor 200 was taken to be 100:1 and Valfor/ferrous sulfate = 1:1. Experimentally, this dosage was found to completely immobilize the contaminant metals in soil columns under varying leachate conditions. More precise estimates can be made only after field tests.

The costs of tilling dry chemicals into the soil has been estimated at $1,000/acre-foot or $0.42/ton and is based on the rental of tilling equipment and labor costs. The tilling equipment would be able to apply the treatment

chemicals to a depth of about 5 feet. The application costs can be neglected relative to the chemical treatment costs for the illustrative example given.

As a basis of comparison, the costs of transporting the contaminated soil to, and disposing the contaminated soil in, a secured landfill is estimated to be in the range of $357,000/acre-foot to $595,000/acre-foot, or $150/ton to $250/ton, depending upon the distance to the secured landfill and the disposal and/or treatment costs. Thus, for the particular example given here, the costs of in situ immobilization are substantially less than the costs of transporting and securing the contaminated soil in a secured landfill.

D. RECOMMENDATIONS

Future research work should be directed at verifying the laboratory test results on larger laboratory scale and on pilot scale. Laboratory tank studies should be carried out to begin to understand the interaction between the soil dynamics and metal immobilization. Pilot field studies are required to give a complete evaluation of immobilization/stabilization procedures applied to a given hazardous waste site. In particular, the degree of mixing between the treatment chemicals and the contaminated soil to achieve complete immobilization and the required dosages should be evaluated.

PREFACE

This report was prepared by Foster-Miller, Inc., 350 Second Avenue, Waltham MA 02254, under Contract No. F08635-84-C-0302. The work was sponsored by the Air Force Engineering and Services Center, Engineering and Services Laboratory (HQ AFESC/RDVW), Tyndall AFB FL 32403-6001. The Air Force project officers were Captain Jack Jeter and Captain Raymond A. Peters.

The report presents the results of laboratory investigations on the use of inexpensive chemical additives for the treatment of soils contaminated with hexavalent chromium, cadmium, nickel, copper, and zinc. The study was performed between 11 September 1984 and 4 March 1987. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Air Force, nor can the report be used for advertising the products.

The authors acknowledge the assistance and contributions of Dr John C. Swallow, Consultant; Dr Calvin Calmon, Consultant (deceased); Mr Jay Hildreth (Soil and Plant Tissue Testing Laboratory, Suburban Experiment Station, University of Massachusetts, Waltham MA); Mr Gerald W. Finn (Terracon Consultants, Inc., Oklahoma City OK); Mr Ronald J. Perisho (J.H. Kleinfelder & Associates, Sacramento CA); Mr Steven Shugart (Law Environmental Associates, Marietta GA); and Mr Rene Batista and Mr Paul Zerner (Foster-Miller, Inc.).

The report has been reviewed by the Public Affairs Office (PA) and is releasable to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

RAYMOND A. PETERS, Capt, USAF, BSC
Environmental Research Engineer

LAWRENCE D. HOKANSON, Colonel, USAF
Director, Engineering and Services Laboratory

THOMAS J. WALKER, Lt Col, USAF, BSC
Chief, Environics Division

(The reverse of this page is blank.)

TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION	1
	A. OBJECTIVE	1
	B. BACKGROUND	1
	C. SCOPE	2
II	SOIL CHARACTERISTICS	4
	A. BACKGROUND	4
	B. INTERACTION OF SOIL AND CONTAMINANT METALS	9
	C. SOIL COLLECTION	11
	D. SOIL ANALYSIS	15
	1. Permeability Testing	15
	2. Elemental Analysis and Organic Content	15
III	TREATMENT CHEMICAL ADDITIVES	22
	A. IN SITU IMMOBILIZATION	22
	B. TREATMENT CHEMICALS	23
	1. Characteristics	23
	2. Standard Cation Exchange Resin	24
	3. Chelate Ion Exchange Resins	26
	4. Devoe-Holbein Metal-Scavenging Molecules	28
	5. Natural Materials	29
	6. Other Additives	32
IV	TEST APPARATUS AND ANALYTICAL TECHNIQUES	37
	A. EQUIPMENT AND OPERATION	37
	1. Laboratory-Scale Batch Equipment	37
	2. Laboratory-Scale Column Operation	38
	B. ANALYTICAL TECHNIQUES	42
V	TEST APPROACH AND RESULTS	45
	A. PLAN OF APPROACH	45
	B. BATCH SCREENING TEST PROGRAM	46
	1. Chemical Additives:Multiple Heavy Metal Contaminant Interactions	50
	2. Soils:Single and Multiple Heavy Metal Contaminant Interactions	58
	3. Soils:Chemical Additives:Single Heavy Metal Contaminant Interactions	60

TABLE OF CONTENTS (CONCLUDED)

Section	Title	Page
V	B. BATCH SCREENING TEST PROGRAM (CONCLUDED).....	
	4. Effect of Chemical Dosage on Metal Immobilization.....	76
	5. Soils:Chemical Additives:Multiple Metal Contaminant Interactions.....	80
	C. DYNAMIC FLOW COLUMN TEST PROGRAM.....	86
	D. LONG-TERM STABILITY COLUMN TEST PROGRAM.....	93
	1. McClellan AFB Soil.....	96
	2. Robins AFB Soil.....	96
	3. Test Results and Discussion of Results....	96
	E. HAZARDOUS WASTE SITE SIMULATION TEST PROGRAM...	101
VI	IN SITU TREATMENT COSTS.....	113
VII	CONCLUSIONS AND RECOMMENDATIONS.....	117
	A. CONCLUSIONS.....	117
	B. RECOMMENDATIONS.....	118
VIII	REFERENCES.....	120
APPENDIX		
A	BATCH SCREENING TEST DATA AND ANALYSIS.....	123
B	LONG-TERM STABILITY COLUMN TEST DATA.....	136

LIST OF FIGURES

Figure	Title	Page
1	Soil Classification Based on Grain Size.....	5
2	Photographs of Sampling Test Pit at Robins AFB, GA (Supplied by Law Environmental Associates, Marietta GA).....	14
3	Diagram of Air Entry Permeameter.....	16
4	Reciprocal Shaker Apparatus for Batch Screening Testing.....	37
5	Dynamic Flow Column Apparatus.....	39
6	Schematic of Dynamic Flow Column.....	40
7	Hazardous Waste Site Simulator.....	41
8	Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer.....	43
9	Overview of Laboratory Test Program.....	47
10	Overview of Batch Screening Test Program.....	49
11	Overview of Dynamic Flow Column Test Program.....	89
12	Overview of Long-Term Stability Column Test Program....	95
13	Effluent Leachate Concentration from Long-Term Stability Soil Columns. McClellan AFB Soil.....	98
14	Effluent Leachate Concentration from Long-Term Stability Soil Columns. Robins AFB Soil.....	98
15	Total Capacity and Immobilization Efficiency for Long-Term Stability Soil Columns.....	100
16	Overview of Hazardous Waste Site Simulation Test Programn.....	102
17	Schematic of Hazardous Waste Site Simulator.....	103
18	Concentration Profiles of Hazardous Waste Site Simulator for McClellan AFB Soil.....	106
19	Concentration Profiles of Hazardous Waste Site Simulator for Robins AFB Soil.....	107

LIST OF TABLES

Table	Title	Page
1	Adsorption Potential of Minerals	6
2	Soil Collection Sites and Soil Types	11
3	Soil Specialist Subcontractors	12
4	Soil Properties	17
5	Chemical Soil Testing Parameters	18
6	Chemical Analysis of Test Soils	20
7	Total Elemental Analysis of Test Soils (in ppm)	21
8	Candidate Treatment Chemical Additives	25
9	Solubility of Metal Hydroxides when Precipitated at pH 8.0	33
10	Solubility Product Constants (K_{sp}) for Methyl-Ethyl Xanthates	35
11	Standard Conditions for Heavy Metal Contaminants with Perkin-Elmer 2380 AA Spectrophotometer	43
12	Half-Wave Potentials	44
13	Composition of Metal Salt Solutions	50
14	Treatment Chemical Chromium Capacity (mequiv metal/gram additive) and Immobilization Efficiency	52
15	Treatment Chemical Cadmium Capacity (mequiv metal/gram additive) and Immobilization Efficiency	53
16	Treatment Chemical Nickel Capacity (mequiv metal/gram additive) and Immobilization Efficiency	54
17	Treatment Chemical Copper Capacity (mequiv metal/gram additive) and Immobilization Efficiency	55
18	Treatment Chemical Zinc Capacity (mequiv metal/gram additive) and Immobilization Efficiency	56

LIST OF TABLES (CONTINUED)

Table	Title	Page
19	Treatment Chemical Total Metal Capacity (mequiv metal/gram additive) and Immobilization Efficiency	57
20	Soil Capacity (mequiv/100 grams soil) and Immobilization Efficiency (percent) for Single and Multiple Metal Contaminants	61
21	Total Capacity (mequiv/100 grams soil) and Immobilization Efficiency for McClellan AFB Soil-Treatment Chemical System (100 Percent Dosage)	64
22	Total Capacity (mequiv/100 grams soil) and Immobilization Efficiency for Robins AFB Soil-Treatment Chemical System (100 Percent Dosage)	65
23	Total Capacity (mequiv/100 grams soil) and Immobilization Efficiency for Tinker AFB Soil-Treatment Chemical System (100 Percent Dosage)	66
24	Total Capacity (mequiv/100 grams soil) and Immobilization Efficiency for McClellan AFB Soil-Treatment Chemical System (100:1 Dosage Rate)	67
25	Total Capacity (mequiv/100 grams soil) and Immobilization Efficiency for Robins AFB Soil-Treatment Chemical System (100:1 Dosage Rate)	68
26	Total Capacity (mequiv/100 grams soil) and Immobilization Efficiency for Tinker AFB Soil-Treatment Chemical System (100:1 Dosage Rate)	69
27	Unit Cost ($/kg) of Chemical Additives	71
28	Ranking of Treatment Chemicals for McClellan AFB Soil	72
29	Ranking of Treatment Chemicals for Robins AFB Soil	73
30	Ranking of Treatment Chemicals for Tinker AFB Soil	74
31	Ranking of Treatment Chemicals for Chromium (+6) Immobilization	77
32	Effect of Chemical Dosage on Total Capacity (mequiv/100 grams) and Immobilization Efficiency for Soil Contaminated with Single Metals and Treated with Lime	78

LIST OF TABLES (CONTINUED)

Table	Title	Page
33	Effect of Chemical Dosage on Total Capacity (mequiv/100 grams) and Immobilization Efficiency for Soil Contaminated with Single Metals and Treated with Valfor 200	79
34	Effect of Chemical Dosage on Total Capacity (mequiv/100 grams) and Immobilization Efficiency for Soil Contaminated with Multiple Metals (Cr, Cd, Ni) and Treated with Lime and Valfor 200	81
35	Effect of Chemical Dosage on Total Capacity (mequiv/100 grams) and Immobilization Efficiency for Soil Contaminated with Multiple Metals (Cr, Cd, Ni, Cu, Zn) and Treated with Lime	82
36	Effect of Chemical Dosage on Total Capacity (mequiv/100 grams) and Immobilization Efficiency for Soil Contaminated with Multiple Metals (Cr, Cd, Ni, Cu, Zn) and Treated with Valfor 200	83
37	Effect of Ferrous Sulfate Addition on Total Capacity (mequiv/100 grams) and Immobilization Efficiency for Soils Contaminated with Chromium (+6)	84
38	Effect of Ferrous Sulfate Addition on Total Capacity (mequiv/100 grams) and Immobilizaton Efficiency for Soils Contaminated with Multiple Metals (Cr, Cd, Ni, Cu, Zn)	85
39	Soil Capacity (mequiv/100 grams soil) for Multiple Metal Contaminants	89
40	Effect of Dosage on Total Soil Column Capacity (mequiv/100 grams soil) for Multiple Metal Contaminants	90
41	Effect of Dosage on Differential Column Capacity (mequiv/100 grams chemical additive) for Multiple Metal Contaminants	92
42	Effect of Dosage on Total Capacity (mequiv/100 grams soil) for Hexavalent Chromium and Five Metal Contaminants	93
43	Long-Term Stability Column Test Conditions	97
44	Differential Capacity of Treatment Chemicals in Long-Term Stability Soil Columns	101
45	Hazardous Waste Site Simulator Test Conditions	104

LIST OF TABLES (CONCLUDED)

Table	Title	Page
46	Hazardous Waste Site Simulator Contaminant Metal Mass Balance (As Percent of Individual Contaminant Metal Species Initially Added to Section A)	109
47	Metal Loading in Soils	114
48	Summary of Differential Capacity Data for Valfor 200/Ferrous Sulfate Addition	115
49	Chemical Costs	116
A-1	Test Data and Analysis for McClellan AFB Soil, 100 Percent Dosage	124
A-2	Test Data and Analysis for Robins AFB Soil, 100 Percent Dosage	126
A-3	Test Data and Analysis for Tinker AFB Soil, 100 Percent Dosage	128
A-4	Test Data and Analysis for McClellan AFB Soil, 100:1 Dosage	130
A-5	Test Data and Analysis for Robins AFB Soil, 100:1 Dosage	132
A-6	Test Data and Analysis for Tinker AFB Soil, 100:1 Dosage	134
B-1	Effluent Concentrations from McClellan AFB, Long-Term Stability Test Columns	137
B-2	Effluent Concentrations from Robins AFB, Long-Term Stability Test Columns	138

(The reverse of this page is blank.)

SECTION I
INTRODUCTION

A. OBJECTIVE

This report summarizes an experimental study to determine the feasibility of using in situ chemical additions for the treatment of soils contaminated with heavy metals. The objective of the laboratory test program was the evaluation of various treatment chemicals for the in situ immobilization of chromium, cadmium, nickel, copper and zinc in soils from Air Force facilities in the United States.

The test program consisted of batch and column testing for measuring the leachability and subsequent immobilization of single and multiple heavy metals in soils. Batch equilibrium methods were used to screen a large number of chemical additives for their ability to react with contaminated soils. The two best treatment chemicals for each soil-metal combination were selected for more detailed column studies. Dynamic-flow column studies were conducted to obtain detailed data on the capacity and mobility of metal contaminants in soil,with and without the addition of the best treatment chemicals. Long-term column tests on the stability and leachability of the best treatment chemicals with and without the effects of acid rain and solvent addition were also carried out. Tests were also carried out in a Hazardous Waste Site Simulator to determine the immobilization of treated soil in a dynamically changing soil environment.

B. BACKGROUND

Various industrial operations are carried out on behalf of the U.S. Air Force at five Air Logistics Centers and at a number of Government-Owned, Contractor-Operated facilities throughout the United States. These facilities conduct a variety of aircraft maintenance operations, including aircraft depainting, parts degreasing and electroplating, which generate many waste solutions and sludges contaminated with heavy metals. The disposal of the waste solutions and sludges by previously acceptable means has led to problems with the contamination of both soil and groundwater.

The mobility of heavy metals in the soil and groundwater environment is affected by the soil organic matter content, hydrous metal oxides, cation exchange capacity, pH, oxidation-reduction potential (E_h), particle size, and permeability. Surface soils typically retain the heavy metal cations in the upper few feet of strata, which contain the highest organic matter. The various heavy metal species have different mobilities under different pH conditions. For example, under alkaline conditions, divalent cadmium has low mobility but hexavalent chromium has much higher mobility. These variations of mobility under different pH conditions have considerable impact under multiple metal contamination conditions. Once the toxic heavy metals reach the saturated zone, their transport in the groundwater is an environmental and health hazard.

Available technologies for treating contaminated soils include excavation of contaminated soil for drumming or soil washing and subsequent treatment of the washwater. Purged groundwater can be treated for heavy metal removal by pH adjustment and precipitation.

In situ immobilization of heavy metals will avoid the requirement for excavation in soils or pumping of groundwater. The immobilized metals will present no adverse environmental or health hazards in their treated state. In addition, in situ treatment provides a cost effective treatment alternative to alleviate these hazards.

C. SCOPE

This report is written in eight sections:

- Section I - Introduction.
- Section II - Soil Characteristics. The problems created by introducing contaminant metals into soils are discussed, along with the methods used for soil collection and soil analysis.

- Section III - Treatment Chemical Additives. Methods for the in situ application of treatment chemicals are briefly described, together with a detailed discussion of the characteristics of each of the chemicals used in the laboratory test program.

- Section IV - Test Apparatus and Analytical Techniques. The components and operation of the laboratory scale batch and column test apparatus are described, together with the analytical techniques used for determining the concentrations and valence states of the contaminant metals in the influent and effluent streams.

- Section V - Test Approach and Results. The rationale for the test approach is described, along with the results of the laboratory scale test program.

- Section VI - In Situ Treatment Costs. The costs of the treatment chemicals and their application are estimated and compared to existing methods of cleaning up hazardous waste sites.

- Section VII - Conclusions and Recommendations.

- Section VIII - References.

SECTION II
SOIL CHARACTERISTICS

The problems created by introducing metal contaminants into soils are discussed in this section. The first subsection presents information on the soil properties, while the second subsection defines the potential for remobilization and migration of the contaminant metals through soil. The last two subsections discuss the methods used for soil collection and soil analysis.

A. BACKGROUND

Soils are composed of the natural aggregate of mineral grains derived from chemical and physical weathering processes combined with constituents derived from organic origin. Soils are generally not homogeneous and may be stratified due to historical variations in the formation process. Stratification is typified by several soil horizons reflecting interactions of the soil with groundwater, atmospheric conditions and vegetation. The nature and extent of the upper horizons are a direct function of the growth and decay of vegetation and soil organisms which in turn are influenced by soil chemistry, moisture content, and climatic conditions. The continual external changes, combined with the continual process of weathering, are reflected in the dynamic nature of the soil properties.

There are numerous systems for classifying the soil type and constituents. The primary physical parameter used to distinguish soil constituents is grain size and the principal constituents are gravel, sand, silt and clay. The relative sizes of these constituents and some classification conventions that have been developed are summarized in Figure 1.

The void structure within the soil has a major impact on both the transport and immobilization potential of the contaminant metals. The void structure depends on the distribution of grain size (or soil gradation) and degree of compaction (or consolidation), which is a function of the soil history. The size and continuity of voids determine the migration paths

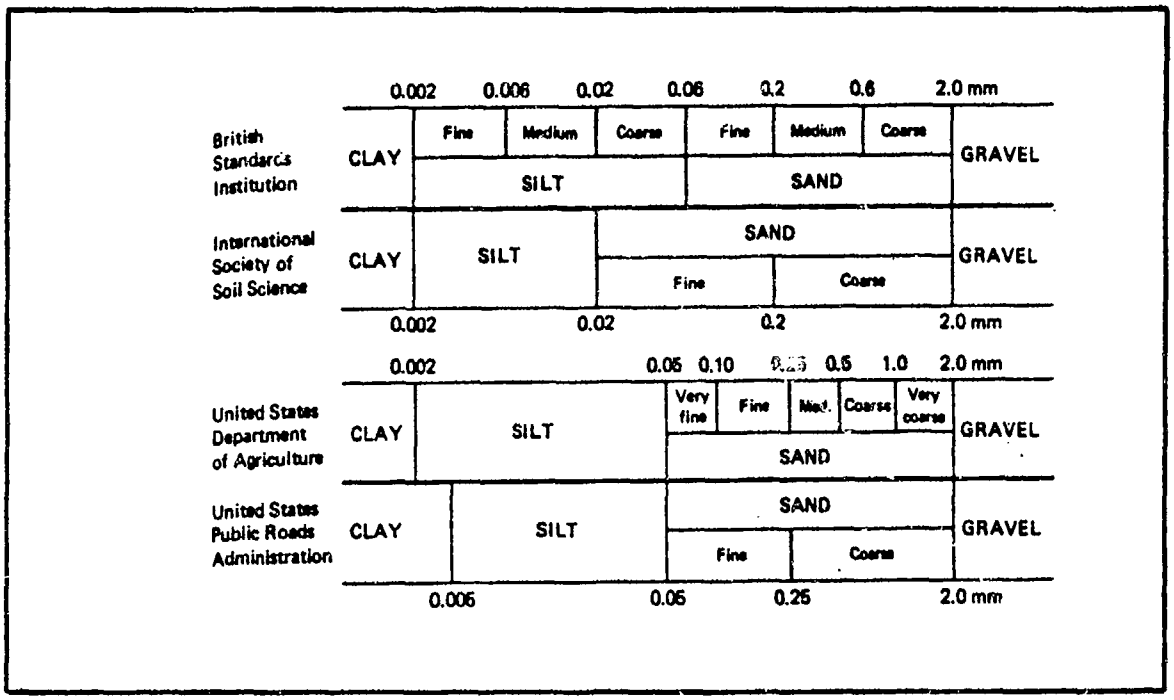


Figure 1. Soil Classification Based on Grain Size.

through the soil. The resistance of the migration paths to soil water flow is called the permeability of the soil. The migration of the heavy metal ions and the treatment chemicals is dependent on the transport paths. The understanding and measurement of soil water movement in the soils is a necessary part of the experimental program.

The voids can be categorized as connected macrovoids, microvoids and isolated macrovoids. Solutions and gases within the soil move easily through connected macro voids but require a disruption in the soil and/or a driving force to enter or pass through microvoids or isolated macrovoids. Variation in the soil environments and weathering with time can liberate potentially mobile constituents trapped in these isolated voids, such as cations, which are temporarily in solution .

Clay particles, the finest fraction of soils, are composed of both mineral and organic constituents. Clay minerals exhibit physiochemical properties similar to those of plate- or sheet-like crystalline structures. Minerals with sheet-like structures can be subdivided into the following groups: kaolinites, illites, and montmorillonites. These minerals are

characterized by a negative electric charge on the flat surface of the crystal and by either a positive or negative charge on the disrupted crystal edge. This gives the plate-like minerals the ability to weakly adsorb cations inherently present in the soil water. This weak bond plays a role in the overall chemical interaction of cations, organic content and hydrous oxides present in the soil. The relative cation adsorption potential of these minerals is given in Table 1.

TABLE 1. ADSORPTION POTENTIAL OF MINERALS

Mineral	Number of Positive Charges Adsorbed per 100 grams (x 10^{20})
Montmorillonite	360 to 500
Illite	120 to 240
Kaolinite	20 to 90

The organic content varies widely between soils. Sandy soils may contain less than one percent organics; the upper 5 inches of a grassland soil (Mollisol) contain 5 to 7 percent organics; soils in poorly drained areas (Aquepts) up to 10 percent organics; and soils near saturation for most of the time (Histosols) have greater than 20 percent organics in the top 2.5 feet of soil. Many factors affect the accumulation of organic matter. As a rule of thumb, the order of importance of environmental conditions affecting the organic content in loamy soils in the United States is climate > vegetation > topography = parent material > age.

The chemical nature of the organic phase in soils is extremely complex. It contains most, if not all, of the the organic chemicals or their degradation products synthesized by living organisms. Two major categories of organic compounds which differ in their soil-chemical cation interactions are present in soils: high molecular weight humic substances containing aromatic nuclei in complex polymers, and nonhumic substances of low molecular weight containing organic acids and bases.

Humic substances have been fractionated into three general substances. The humin fraction is insoluble in alkali and acid and has the highest

molecular weight. The humic acid fraction is a dark-colored extract which is soluble in alkali but insoluble in dilute acid. The fulvic acid fraction remains in solution after removal of humic acid by acidification. Total acidity for the humic acids ranges from 500 to 900 mequiv (milliequivalents) per 100 grams soil and for fulvic acids from 900 to 1400 mequiv per 100 grams of soil.

Nonhumic substances found in the soil are of lower molecular weight and of recent biological origin and result from plant or animal biosynthesis or their degradation products. Nonhumic substances include aliphatic, sugar, amino and lichen acids, carbohydrates and lipids.

An important factor in the chemical nature of soils is the presence of hydrous oxides and cations in soil water. The predominant, naturally occurring exchangeable cations in soil water are Ca, Mg, K, Na, Al, H, Fe and Mn. The first four cations are termed exchangeable bases. In acid soils Ca, Mg, K and Al predominate, while in calcareous soils Ca and Mg are found at most of the exchange sites. The sodium ion predominates in salty soils.

The degree of attraction or affinity of cations to the exchange sites on fine soil particles varies between cations. The cation exchange capacity (CEC), or the capacity of the soils to chemically adsorb cations, is measured by displacing the exchangeable cations with neutral ammonium acetate (NH_4 OAc) and then determining the amount of ammonia (NH_4) bound on the exchange sites. The cation exchange capacity is determined by an analysis of the extract and is expressed as milligram equivalents per 100 grams of soil.

Contaminant metals in the soil water can be removed by adsorption and/or precipitation. Adsorption in soils is defined as the adhesion of dissolved substances to the surface of soil solids with which they are in contact. Precipitation involves the formation of a solid phase which has low solubility in the soil water.

Different mechanisms can be operative for the removal of an ion from the soil water onto a solid surface: physical adsorption, chemical adsorption and penetration onto a solid surface. Physical adsorption occurs through weak

atomic and molecular attractive forces (van der Waal forces). This process is important for metal retention in soils because it can lead to other stronger attractions, such as chemical adsorption. Chemical adsorption occurs when chemical bonds form that are more ionic in nature between an ion in the soil solid phase and an ion that was formerly in the soil solution. Insertion or penetration of an ion into the solid mineral phase may occur as a consequence of chemical adsorption. This reaction is frequently irreversible and time-dependent.

The factors affecting the interrelation between adsorption and precipitation are the cation concentration in the soil water, pH, cation-anion pairing and complexation by organic molecules.

The hydrous oxides of Fe, Mn and Al are common in soils and occur as crystalline minerals or as surface coatings on other minerals. They are characterized by a very high surface area to weight ratio and are frequently amorphous. The Fe and Mn hydrous oxides are very labile because they form in oxidizing conditions and dissolve under reducing conditions. This phenomenon is very important when interpreting the role of organic matter in its interaction with heavy metals.

The processes of soil genesis and the subsequent development of soil horizons define zones within the soil profile that have highly distinguishable behavior. The so-called upper A and B horizons typically contain the greatest concentration of organic content and consequently are responsible for the adsorption of most of the metals that are introduced into the soil. Superimposed on these horizons are four major soil zones associated with ground moisture. The upper two zones (or the pendicular and funicular zones), contain unsaturated voids within the soil and thus tend to be aerobic. However, the lower two zones (or capillary purge and phreatic zones), contain voids which are completely filled with water and are anaerobic.

The extent of aeration directly affects the oxidation-reduction status of the soils. The oxidation-reduction potential, E_h, impacts the composition and concentration of ionic species in the soil water. Fluctuations in soil

saturation because of climatic cycles and groundwater elevation changes create regions of leaching and precipitation of various ions within the soil. This cyclic behavior can result in a slowly undulating concentration of temporary cations through the soil. Furthermore, the rate of latent migration of highly soluble constituents can be maximized within the capillary zone due to the combined effects of favorable moisture and anaerobic conditions.

B. INTERACTION OF SOIL AND CONTAMINANT METALS

Heavy metals added to soils react with the soil components in a variety of ways. These reactions can be generally classified as ion exchange, adsorption, precipitation and complexation. The reaction mechanisms and rates are dependent upon the type and amount of the organic matter, clay and hydrous oxides present in the soil. Additional factors are the exchangeable cations, soil reaction (pH), oxidation-reduction potential (E_h), soil water composition, and concentration. These additional factors are dynamically affected by the physical and biological properties of the soil and any meaningful investigation of soil-heavy metal interactions must consider the whole soil continuum, as discussed in the previous subsection.

Metal ions may be bound to soil particulates by a combination of forces ranging from electrostatic to covalent forces. When stronger covalent bonding dominates, certain cations are specifically bound and the reversibility of exchange decreases. This type of bonding occurs in organic matter, clays and hydrous oxides.

Hydrous metal oxides are important to the retention of heavy metals in soils. The fact that hydrous oxides of Fe and Mn tend to dissolve in reducing conditions is very important when interpreting the role of organic matter in its interaction with heavy metals. Experimental results which point to the action of organic matter with heavy metals can alternatively be interpreted as evidence of the influence of hydrous oxides as a function of pH and E_h (References 1, 2).

Most heavy metals become less mobile in soils with an increase in pH. This observation can be explained by the precipitation of heavy metal hydroxides, changes in the carbonate and phosphate concentrations in the soil water, adsorption and desorption of metals by hydrous oxides and organic matter, and the formation and dissolution of Fe and Mn oxides. The heavy metals, Cd and Zn, illustrate the effect of pH on mobility. Cadmium exists in the divalent form to pH 7.8 and only 50 percent is converted to the precipitate $Cd(OH)_2$ at pH 11. On the other hand, 50 percent of zinc is in the $Zn(OH)_2$ form at pH 7.5. This comparison suggests that, at a given soil pH, zinc will be less mobile than cadmium in a soil system.

Metals are bound to organic molecules by complexation and chelation. A complex is formed when an electron-rich atom (such as O, S, N or P) in an organic molecule shares a pair of electrons with a metal ion having an empty outer shell. The molecule combining with the metal is called a ligand and the resulting combination is called a coordination compound.

Chelation occurs when two or more coordination positions around the metal ion are occupied by two more more donor groups from the same organic molecule. The resulting internal organometallic ring gives the complex a high degree of stability.

Functional organic groups which serve as electron donors in metal complexes are enolates, alkoxides, carboxylates, phenoxides, alkyl amino, heterocyclic N, mercaptides, phosphates, phosphonates, hydroxyalkyls, carbonyls, ethers, esters, amides, and thioethers.

As discussed in the previous subsection, the organic phase of soils is composed of two major compounds: humic and nonhumic. The high-molecular-weight humic substances have a high affinity for metals and are largely insoluble in the soil water. Nonhumic substances of low molecular weight, such as organic acids and bases, are relatively soluble when complexed with metals.

The humic and fulvic acid fractions account for most of the metal immobilization attributed to the organic matter in soil. Complexation and

chelation with metals occur through the acidic functions and, less importantly, at the amide and heterocyclic nitrogen centers in these complex polymers (Reference 3). The low molecular weight nonhumic compounds are usually very good complexing agents with metal ions. The resulting complexes are far more soluble than the humic-metal complexes. The nonhumic complexes generally mobilize heavy metals in soils.

C. SOIL COLLECTION

One of the objectives of the test program was to determine the mobility of contaminant metals in various types of soils with and without the addition of treatment chemicals. However, soil types vary radically throughout the United States and soils typical of those contaminated by heavy metals are difficult to define. The approach taken in the test program was to use soils representative of those contaminated at three Air Force Logistics Centers (ALC) in the United States. Table 2 identifies the Air Force bases used as soil collection sites. These sites were based on geological site data supplied by the Air Force Project Officer.

TABLE 2. SOIL COLLECTION SITES AND SOIL TYPES.

Air Force Base	Soil Type
Sacramento ALC McClellan AFB, CA	Sand, Gravel Sand, Sandy Loam
Warner Robins ALC Robins AFB, GA	Loamy Fine Sand, Sandy Clay Loam
Oklahoma City ALC Tinker AFB, OK	Sandy Loam, Silty Loam, Silty Clay Loam

These soil types have the greatest potential for possible metal contamination because heavy metals are fairly mobile in soils that do not contain much clay and are fairly permeable. For example, clay, which is the finest fraction of soil, consists of mineral and organic constituents that have a natural

affinity to chemically adsorb metallic cations making the mobilization of heavy metal contaminants very difficult. For example, the soil at San Antonio ALC, Kelly AFB, Texas, was omitted from the above list because the contaminated soil consisted of clay, silty clay, and clay loam soil types. Analysis of the groundwaters at this base showed very slight traces of contamination and supports our soil selection criteria.

Soil scientists were identified in the vicinity of each selected site. Table 3 lists each Air Force base, together with the corresponding soil specialist subcontractor. The soil specialists coordinated the collecting of the various soil samples, performed onsite characterization tests, and shipped the soil samples back to Foster-Miller, Inc. A soil sampling Scope of Work defining how the samples were to be collected, analyzed and shipped to Foster-Miller was sent to each subcontractor. At the conclusion of the sampling program, each subcontractor submitted a detailed field engineering report that described the sampling location and the results of all tests performed on site and in the laboratory.

TABLE 3. SOIL SPECIALIST SUBCONTRACTORS.

Air Force Base	Subcontractor
Oklahoma City ALC Tinker AFB, OK	Mr. Gerald W. Finn Terracon Consultants, Inc. 832 Northwest 67th Street, Suite 1 Oklahoma City, OK 73116
Sacramento ALC McClellan AFB, CA	Mr. Ronald J. Perisho J.H. Kleinfelder & Associates 9795 Business Park Drive, Suite A, Sacramento, CA 95827
Warner Robins ALC Robins AFB, GA	Mr. Steven Shugart Law Environmental Associates 2749 Delk Road Marietta, GA 30067

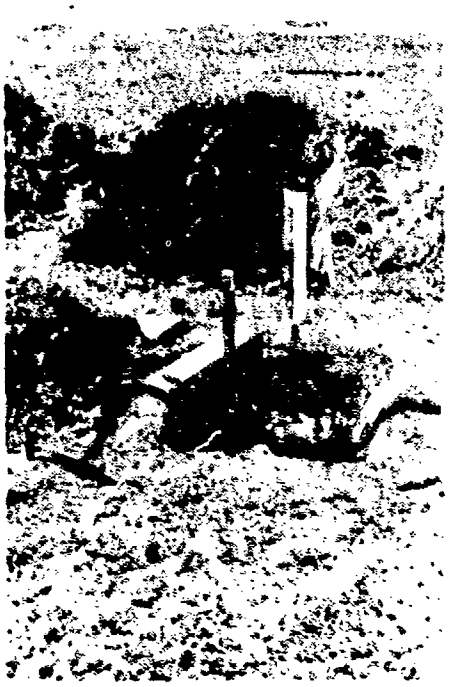
Street maps of each selected Air Force base were obtained from the Air Force Project Officer. These maps were used in conjunction with U.S. Geological Survey maps, local soil surveys and the subcontractor's knowledge of the area in determining the exact location of the soil sampling site. Permission to access each base and to use Air Force personnel and heavy machinery (backhoe/front-end loader) to assist the subcontractors in collecting the soil were obtained by the Air Force Project Officer. All visits by the subcontractor to the Air Force base were coordinated with the appropriate Air Force liaison contact.

Samples of uncontaminated soil, taken near the contaminated metal disposal area, were collected from several locations at each site from the wall of shallow excavations. Care was taken to avoid highly disturbed zones such as artificial fill or landscaped areas. At each sampling location, the in-place soil was inspected and classified in conformance with U.S. Department of Agriculture procedures (see Figure 1). At each site where a soil sample was taken, sand funnel tests were carried out to determine the natural density of the collected soil. Figure 2 shows photographs of the soil collected and tested at Robins AFB.

Approximately 1500 - 2100 pounds (680 - 950 kg) of uncontaminated soil were collected at each Air Force base. Soil from each base was shipped to Foster-Miller in three 55-gallon plastic or plastic coated drums. Each soil from Robins AFB and McClellan AFB was mixed by screening the entire base sample through an ASTM 2-foot standard sieve shaker. Coarse soil fractions were removed with a 0.25-inch screen. The entire soil sample was mixed uniformly on a clean canvas tarp by repeatedly raking and folding. The soil samples were repacked into the original three drums. The coarse fractions were stored in separate containers and saved.

The above mixing procedure was not applied to the Tinker AFB soil because the clay would not pass through the sieve shaker and could not be mixed by hand. Instead, the clay samples were uniformly mixed in a 1500-pound (680 kg) capacity roller mill.

a. Soil Sampled from Test Pit



b. Air Permeameter used to Determine Hydraulic Conductivity of Undisturbed Soil

c. Longitudinal Section of Test Pit Showing the A(top) and B(bottom) Soil Horizons

Figure 2. Photographs of Sampling Test Pit at Robins AFB, GA (Supplied by Law Environmental Associates, Marietta, GA).

D. SOIL ANALYSES

1. Permeability Testing

At each site the natural density of the collected soil was determined by a sand funnel test. The test involved weighing a small sample of the soil and measuring the volume of the cavity created by removing the sample. The volume is measured by filling the cavity with sand using a sand core apparatus as specified in the ASTM D-2937 standard (Reference 4).

The grain size distribution on coarser soil fractions (>2 microns) was obtained by a sieve analysis. Particle size distributions of the finer constituents (<2 microns) was derived by correlating the particle size to the rate of sedimentation. The fine fraction of soil was mixed with water and a hydrometer was used to determine the weight of material remaining in suspension and correlated to time. The hydrometer test procedures are described in the ASTM D-422 standard (Reference 5).

In situ soil permeability (hydraulic conductivity) was measured at each sampling site using an air-entry permeameter (Figures 2 and 3). Water is applied under a relativity high head to a covered infiltration cylinder. A wetted zone is created with a predominantly positive water pressure and a distinct wet front. When this front has reached a depth approximately equal to the cylinder penetration, the water supply valve is closed. The flow conditions in the wetted zone during infiltration are assumed to follow well-established flow laws and the saturated hydraulic conductivity is calculated using Darcy's equation.

Table 4 summarizes the soil properties at each of the three Air Force bases. The range of values represents data taken from several pits at each location.

2. Elemental Analysis and Organic Content

The test procedures and parameters for soil analysis are summarized in Table 5. Both elemental analysis and organic content testing were

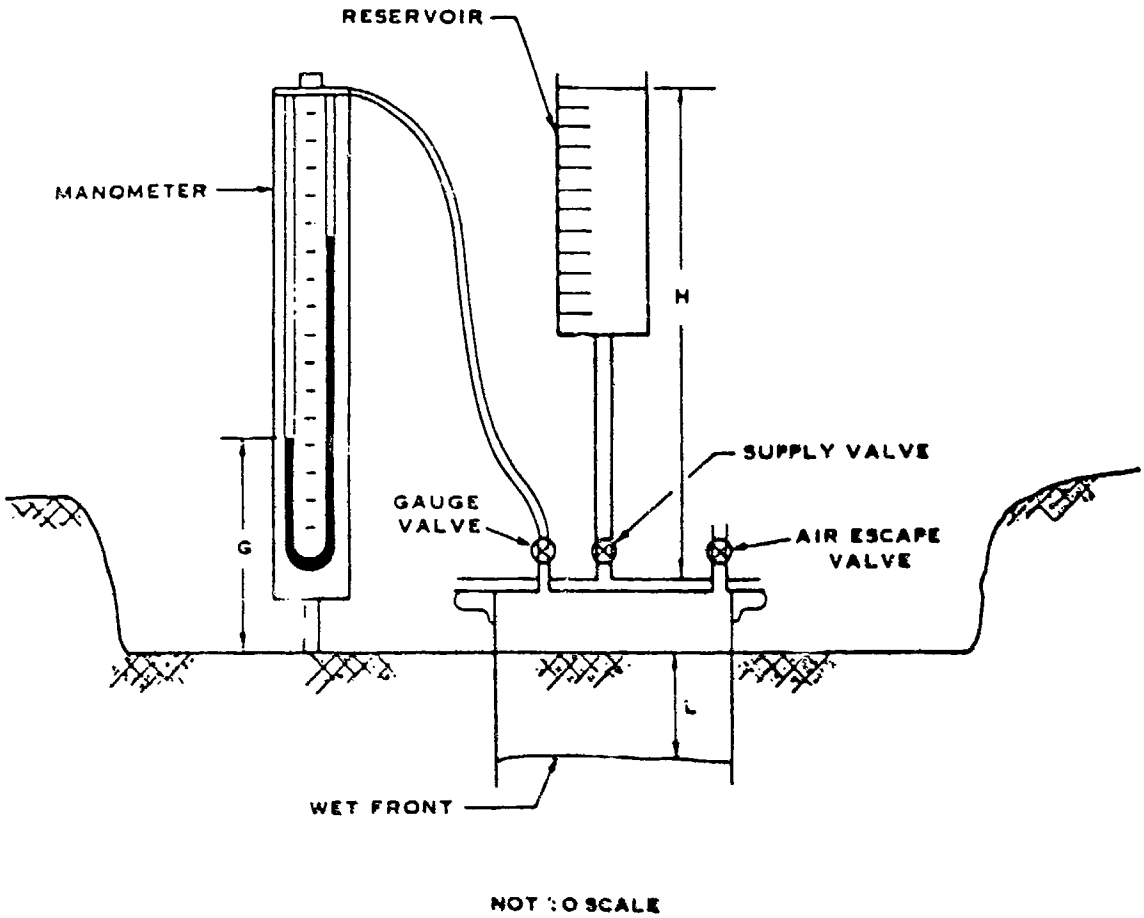


Figure 3. Diagram of Air Entry Permeameter.

carried out. Elemental analyses were carried out in two ways to determine both the total elements and the extractable elements.

The total elemental analysis was carried out using a total digestion method. The method involved taking 10 grams of soil previously dried overnight at 50 °C and sieved through a 12-mesh screen and transferring it to a quartz crucible. Each soil sample was covered and burned to ashes at 450 °C for 12 hours. This was followed by digestion with 10 mL of concentrated nitric acid and evaporation to dryness. The sample was then refluxed with 10 mL of hydrochloric acid for 2 hours. The soil sample was cooled and filtered through Whatman 934-AH filter paper and diluted to 50 mL

TABLE 4. SOIL PROPERTIES.

Soil Property	McClellan AFB	Robins AFB	Tinker AFB
Description	Sandy loam	Loamy Sand	Clay Loam
Dry Density (lbs/ft^3)	118.0	107.6 - 109.2	99.7 - 117.7
(Specific Density)	1.89	(1.73 - 1.75)	(1.60 - 1.89)
Moisture (percent)	14.0	7.32 - 8.08	15.5 - 20.0
Permeability (in/hr)	1.5	1.6	0.66 - 1.0
(cm/hr)	(3.8)	(4.1)	(1.7 - 2.5)

in a volumetric flask with 1N HCl. Metals from both the mineral and organic constituents were determined by measuring the weight percent for each element by atomic absorption.

An analysis of extractable metals was performed for each soil sample. This involved treating 100 grams of soil with 200 mL of an extractable solution of 10 percent sodium acetate in 3 percent acetic acid at pH 4.8. The extract was analyzed with an atomic emission spectrometer.

Readily oxidizable organic matter was characterized by determining the weight loss of the soil sample after a 30 percent hydrogen peroxide digestion treatment. The total organic carbon (TOC) determinations were based on the oxidation of organic carbon and thermal decomposition of carbonates in a furnace. The carbon dioxide that was liberated was trapped and measured and correlated to the original total carbon.

In addition to the elemental and organic content analyses, a mineralogy assay was carried out to determine the composition of the soil clay fraction. Scanning electron microscopy (SEM) combined with energy-dispersive spectroscopy (EDX) was utilized to semiquantitate the mineralogy and composition of the clay-sized fraction of each native test soil.

TABLE 5. CHEMICAL SOIL TESTING PARAMETERS.

Test Method	Parameter Tested
In water (1:1) soil paste	E_h
in 0.01 M $CaCl_2$ (1:1)	pH
SMP	Buffered pH
Conductivity	EC_5, EC^2
Calculated	Cation Exchange Capacity
Colorimetrically	Ammonium Nitrate Phosphorous
Measured[a,b] by Plasma Emission Spectroscopy and Atomic Absorption	Aluminum, Arsenic, Boron, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Manganese, Magnesium, Molybdenum, Nickel, Potassium, Zinc
Thermal H_2O_2	Organic matter
Dry Combustion	TOC
SEM EDX	Mineralogy

---

[a] Extracting solution: 10 percent sodium acetate in 3 percent acetic acid at pH 4.8.

[b] Second extracting solution: 1N HNO_3/HCl.

Table 6 shows the analyses of the three soils for various chemical parameters including readily extractable trace metals. The data show that the soils are not contaminated and are safe to work with. The chemical parameters are typical of each soil type. The total elemental analysis for the three soils are shown in Table 7. The analysis represents the total elemental composition of the inorganic soil matrix.

TABLE 6. CHEMICAL ANALYSIS OF TEST SOILS.

Chemical Parameter	McClellan AFB	Robins AFB	Tinker AFB
Soil pH	5.8	5.3	6.6
Buffer pH	7.0	6.7	7.3
Conductivity (10^{-4} milliohms)	1.3	1.2	7.0
Cation Exchange Capacity (mequiv/100 grams)	4.4	5.2	15.9
Readily Oxidizable Organics (percent)	1.04	0.93	2.70
Nutrient Elements (ppm)			
Ammonium, NH_4	3	3	3
Calcium, Ca	709	299	1769
Magnesium, Mg	162	38	899
Nitrate, NO_3	15	15	15
Phosphorus, P	2	3	0
Potassium, K	65	45	23
Trace Elements (ppm)			
Arsenic, As	0.2	0.4	0.3
Aluminum, Al	11	58	47
Boron, B	0.2	<0.1	1.0
Cadmium, Cd	<0.2	<0.2	<0.2
Chromium, Cr	<1.0	<1.0	<1.0
Copper, Cu	1.7	0.1	<0.1
Iron, Fe	2.2	5.1	1.4
Lead, Pb	<2.0	<2.0	<2.0
Manganese, Mn	4.1	0.4	3.4
Molybdenum, Mo	<0.1	<0.1	<0.1
Mickel, Ni	<0.7	<0.7	0.7
Zinc, Zn	2.9	3.3	0.6

TABLE 7. TOTAL ELEMENTAL ANALYSIS OF TEST SOILS (IN PPM).

Chemical Parameter	McClellan AFB	Robins AFB	Tinker AFB
Aluminum, Al	16765	27750	31305
Arsenic, As	31.65	58.9	64.70
Boron, B	8.55	1.69	8.04
Cadmium, Cd	0.5	0.41	0.92
Calcium, Ca	1152	328	2141
Chromium, Cr	3.4	2.0	3.3
Copper, Cu	11.99	3.8	7.93
Iron, Fe	12780	7995	17910
Lead, Pb	7.21	8.08	13.96
Magnesium, Mg	1172	504	4082
Manganese, Mn	343	24.5	434
Molybdenum, Mo	2.01	2.17	3.06
Nickel, Ni	1.60	1.10	3.01
Phosphorous, P	266.2	237.1	281.6
Potassium, K	1098	507	3497
Sodium, Na	101.6	22.3	411.4
Zinc, Zn	30.8	23.9	31.8

SECTION III
TREATMENT CHEMICAL ADDITIVES

A. *IN SITU* IMMOBILIZATION

One remedial action option available to mitigate the leaching potential of contaminant metals into groundwater and their subsequent transport through underground aquifers is *in situ* immobilization. *In situ* immobilization can be carried out by introducing treatment chemicals into the ground by various means. If soluble chemicals are used, they can be applied by saturating the soil with the chemical in solution. This fluid application may be carried out at a high rate by surface flooding the site or more gradually by spraying and allowing the solution to drain freely into the soil. The variation in application rate will affect the period of soil exposure to the treatment material, the degree of void filling accomplished, and the amount of air present in the soil during the treatment period. A complementary confinement or pumping system may be appropriate if the soluble treatment chemical has undesirable environmental effects or is worth recycling due to high chemical costs.

Insoluble chemicals can be introduced into the ground by spreading, filling, forced injection, suspension transport, or by placing it in a low-permeability encapsulation barrier. Spreading may suffice as a means of treating metals if the soil has a high moisture content and if the metal contaminants lie very close to the surface. This may be most applicable to soils with high organic content. Tilling is the most common method of introducing a soil treatment chemical into the ground. Routine tilling can mix dry chemical additives into the soil to a depth of 1 to 2 feet. Special deep tilling equipment is available which can reach as deep as 5 feet into the ground. Fine insoluble chemicals can be transported short distances through soil voids by placing them in suspension in water or in a weak solvent or acid. The suspended material is then injected in a fashion similar to chemical grouting or through nozzles in close-spaced probes. Typically, fine material can be transported several feet from the nozzle in this fashion. The particle size can be correlated to soil grain size, using traditional grouting guidelines. In formations with high permeability and

low organic content, where metals have migrated to depths greater than 10 feet, mixing insoluble treatment materials into the soil may be impractical. Under these circumstances, the treatment chemical can be made part of a barrier material, such as bentonite soil or asphalt emulsions used for slurry wall construction, jet grouting or block displacement.

B. TREATMENT CHEMICALS

1. Characteristics

In situ immobilization of heavy metals in contaminated soils can be accomplished by adding natural or synthetic chemicals to the soil. These additives must have certain desirable properties to successively immobilize heavy metals. Treatment additives fall into two classes of chemicals; strongly adsorbing and weakly adsorbing.

By their nature, once strongly adsorbing insoluble chemical additives are added and distributed throughout the soil, they will not migrate down through the soil to groundwater. The heavy metals must be adsorbed, complexed and/or chelated on the additive and must not hydrolyze nor be desorbed under exposure to varying conditions in the soils, such as a low pH or a varying E_h which tends to solubilize the metals. The chemical additives must resist chemical and microbial degradation in the soil environment so that metals are not released from the additives over long periods of time, say, for at least a few years. Finally, the chemical additives, themselves, must not leach any deleterious organic or inorganic substances that could contaminate groundwater.

For weakly adsorbing chemical additives to be effective in immobilizing heavy metals, they must either cause the metals to precipitate or complex and/or chelate the metals and then attach themselves to the soil structure. In either case, the metals must not migrate down through the soil. Complexation and/or chelation of the metals to the weakly adsorbing additive is not sufficient since there is the distinct possibility the complexed metal could migrate to and be transported in groundwater. In any event, after the metals are precipitated, they must not be resolubilized

under varying soil conditions, such as over a range of pH and E_h. Finally, as with the strongly adsorbing additives, the weakly adsorbing additives must be resistant to chemical and microbial degradation in the soil and must not leach out any deleterious organic or inorganic substances to the soil water.

Today, many chemical additives are used in the treatment of wastewaters to reduce heavy metals concentrations. Many of these chemical additives can reduce the metal concentrations to levels below federal and state effluent discharge limits, and in some cases to below drinking water standards. Table 8 identifies some candidate materials that have been used in the treatment of metal-containing wastewaters and have the potential to be used as immobilizing agents in contaminated soils. These materials were screened in a batch test program for their ability to immobilize metals. Each of the treatment chemical additives are discussed in the subsequent subsections.

2. Standard Cation Exchange Resin (References 6-8)

Amberlite IR-124, manufactured by Rohm and Haas, is a gelatinous, strong sulfonic acid cation exchange resin. Studies have shown that, as a result of 12 percent divinyl-benzene crosslinking, Amberlite IR-124 exhibits greater resistance to chemical oxidation and longer operating life relative to other commercial standard cation exchange resins. This resin has been successfully used to recover contaminant metals from harsh environments, such as chrome plating baths and rinse waters.

Amberlite IR-124 exhibits the greatest selectivity for ions of higher valence and smaller ionic radii that its Na^+ or H^+ counter ion. The adsorbing selectivity for this resin in dilute solutions is:

$$Cr^{+6} > Pb^{+2} > Ni^{+2} > Cd^{+2} > Cu^{+2} > Zn^{+2}.$$

Under ideal conditions, the equilibrium ion exchange capacity of Amberlite IR-124 is 2.20 equiv/L of wet resin. As with any resin, the operating capacity of Amberlite IR-124 is a function of the regenerating agent, regenerant concentration, regenerant dosage, flow rate and the composition of the solution to be treated by ion exchange.

TABLE 8. CANDIDATE TREATMENT CHEMICAL ADDITIVES.

Class	Chemical Additive
Standard Cation Ion Exchange Resin	Amberlite IR-124
Chelate Ion Exchange Resins	Amberlite IRC-718
	Duolite CS-346
	Dowex XFS-4195
Devoe-Holbein Metal Scavenging Molecules	DH 524
	DH 565
	DH 566
Natural Materials	
Clays	Slurry BEN 125 Bentonite
	325 Bentonite
	HPM 20 Microfine Bentonite
	Attasorb LVM
	Satintone 5
Molecular Sieves	Valfor Z84-326
	Valfor 200
Greensand	Raw Greensand
	Mn Greensand
Other Addititives	Hydrated Lime
	Silylated Silica Gel
	Insoluble Starch Xanthate (ISX)
	Metal Sorb-7
	Ferrous Sulfate

3. Chelate Ion Exchange Resins (References 9-11)

Chelating or specific ion exchangers are insoluble polymers that have complexing groups attached which, in turn, specifically attach or complex metal cations from solution within their structure, or form precipitates with the ion in question. Chelate resins can be synthesized to have a high selectivity for specific metal ions, depending on the complexing group used on the resin (References 9,10).

Chelate ion exchange was recently evaluated for removing low concentrations (1 to 10 mg/L) of heavy metal contaminants from plating baths containing 10,000 to 100,000 mg/L of plating metal ions (Reference 11) . The purpose of the test program was to determine the feasibility of using chelate ion exchange for the purification and reuse of the plating baths. The five heavy metals of interest in the present soils test program were the same as some of the metal contaminants in the plating bath evaluation. The capacities of the resins were in the range of 1 to 2 equiv/gram of resin. The test program demonstrated that chelate ion exchange is a viable process for plating bath purification and reuse.

In work more closely related to the present test program, selective cation exchangers were added to a number of soils for the purpose of immobilizing the heavy metal ions, zinc, lead and copper, and preventing their uptake by plants (Reference 12). The cation exchangers were applied in powder form and loaded with exchangeable calcium, magnesium and potassium ions; granular form exchangers with exchangeable calcium ions were also added. The capacity of the exchangers was 2.3 mequiv/gram of cation exchanger. Based on the capacity of the exchangers and the soil metal content (as determined by a soil analysis), varying doses of cation exchangers were added to the soil. Test data were taken over a 2-year period and the uptake of the heavy metals by various plants (radishes, strawberries and chervil) was measured. A mixture of powdered form exchangers having exchangeable calcium and magnesium ions in a proportion of 1:1 was the most effective combination. Test data showed a large decrease in the uptake of the heavy metals by the plants due to their bonding to the cation exchangers.

The field experiments showed the persistance of the bond and application of the exchangers did not result in additional residue problems.

a. Amberlite IRC-718 (Reference 13)

This resin, a product of Rohm and Haas Co., is a macroreticular chelate resin with a functional group of iminodiacetic acids. The molecule has two active groups, imino -N- and carboxylic. Its polymeric matrix consists of a copolymer of styrene and divinylbenzene. When the resin reacts with a divalent ion, it forms a ring structure.

The resin in the H^+ form is a weak electrolyte. The maximum degree of swelling occurs when the resin is in the salt form. Amberlite IRC-718 is manufactured in the macroreticular form to allow for the diffusion of larger, higher molecular weight molecules from solution. The selectivity of the resin for various metal ions at pH 4 is given as follows:

$$Hg > Cu > Pb > Ni > Zn > Cd > Co > Fe^{+2} > Mn > Ca$$

Since the resin is a complexing material, it must often compete for the metal ion with complexing anions in solution. Thus, the selectivity of the resin for mercury is very high when the mercury is a nitrate, but very poor when it is a chloride because the latt : form complexes with mercury.

b. Duolite CS-346 (Reference 14)

Duolite CS-346, a product of Diamond Shamrock (recently bought out by Rohm and Haas), is a unique macroporous chelating resin. It is a crosslinked copolymer whose functional groups are primarily amidoxime ($CNOHNH_2$) groups. These groups exhibit excellent chelate functionality in the lower pH (acidic) range. The resin also contains a small proportion of hydroxamic acid (RCONHOH) groups which function in the higher pH (basic) range. Because of its three-dimensional crosslinked structure, Duolite CS-346 is insoluble in all common organic and aqueous solvent systems.

Duolite CS-346 amidoxime groups form strong, stable complexes with many metals, especially in acidic solutions. Under alkaline conditions, the combination of the amidoxime and hydroxamic acid groups have proven useful in adsorbing certain metals. Duolite CS-346 does not form chelates with alkali or alkaline earth metal ions and will not interact with cations commonly found in soils, such as potassium, magnesium and calcium. Chelation properties of Duolite CS-346 have not been fully evaluated. The metals that have been studied are classified as follows:

Very Strong Chelation: Cu^{+2}, Au^{+3}, $V^{+2,+3,+4}$, $U^{+2,+4}$, Fe^{+3}, Ru^{+3}, Rh^{+3}, $Pd^{+2,+4}$, $Pt^{+2,+4}$, Mo^{+6}

Moderate Chelation: Zn^{+2}, Cd^{+2}, $Cr^{+2,+3}$, Th^{+4}, $Co^{+2,+3}$, $Ni^{+2,+3}$.

Duolite CS-346 is regenerated to the H^{+} form with a mineral acid, such as HCl or HNO_3. Duolite CS-346 also contains weak-base ion exchange capacity and when regenerated with a mineral acid must be converted to its salt form to avoid hydrolysis.

c. Dowex XFS-4195 (References 15, 16)

This resin, a product of the Dow Chemical Co., is a macroporous weak base chelate resin especially suited for copper and nickel removal. The resin is protonated in acid solutions and is converted to the free base form in alkali. The total capacity for copper is 1 equiv/L of resin. The adsorption of metal ions is dependent on pH and is more rapid at low pH than at high pH. The selectivity of the resin for divalent ions at pH 2 is as follows:

$$Cu > Ni > Fe^{+3} > Cd > Zn > Co > Fe^{+2} > Ca > Mg > Al$$

4. Devoe-Holbein Metal-Scavenging Molecules (References 17-19)

Recently, Devoe and Holbein of McGill University have synthesized molecules that have a high chelating affinity for metals. They modeled living-cell biological metal extraction and recovery mechanisms to create

metal-scavenging molecules without actually employing living cells. The Devoe-Holbein extractive agents, DH 524, DH 565, and DH 566, consist of proprietary-beaded synthetic compositions incorporated into insoluble polystyrene substrates. Varying porosity and active site composition determines the capacity and selectivity for individual metals and related metal groups. The extraction mechanism ensures that the metal-scavenging molecules convert mobile metal-laden waste to a stable state, where the toxic metal remains immobile. The Devoe-Holbein extractive agents have been reported to resist thermal, chemical and microbial degradation.

a. DH 524. This extracting molecule has a capacity of 20 mg Cr^{+6}/gram with sharp breakthrough curves. Swelling or compaction does not occur at throughput rates up to 50 bed volumes (BV)/hr in column operation. DH 524 requires only 1-2 BV of regenerant.

b. Dh 565. This extractive agent has been found effective for wastestreams containing Cd, Cu and Zn.

c. DH 566. This composition has been evaluated in the field for its ability to extract Cs, Sr and Co from nuclear wastewaters, as well as Ni in wastewater lagoons.

Other Devoe-Holvein extractive agents have demonstrated their utility for immobilizing Pb and Hg in a number of other wastestreams.

5. Natural Materials

a. Clays. In a series of papers, Pickering, Hatton and Farrah (References 3, 20-23) examined the sorption of many heavy metals on various natural clays, such as kaolin, illite and montmorillonite. Changes in pH and organic content and the presence of ligands (both the composition and concentration) influence uptake. Different theoretical models have been proposed to explain the adsorption behavior of the various clays. The test data indicate metals are adsorbed over a wide range of conditions. It would appear that the addition of natural clays would be a relatively inexpensive method to immobilize heavy metals in soils.

Slurry BEN 125 Bentonite (Reference 24). Slurry BEN 125 Bentonite, 325 Bentonite and HPM 20 Microfine Bentonite are sodium-montmorillonite clays of different particle sizes and purities. Na-montmorillonite clay is a three-layered mineral consisting of one octahedral trivalent aluminum sheet that shares oxygen atoms with two tetrahedral silica sheets. The presence of the sodium ion in these clays accounts for its ability to reach heavy metal contaminants by ion exchange mechanisms. The cation exchange capacity of the clay differs according to the amount and distribution of the exchangeable sodium cations. These parameters are determined according to the particle size and purity of the clay.

Slurry BEN 125 Bentonite has a dry particle size of 125 Mesh and a purity of 90 percent.

325 Bentonite (Reference 24). This clay is a powder of 325 Mesh and has a purity of 90 percent.

HPM 20 Microfine Bentonite (Reference 24). This is a microfine clay having a purity of 99.75 percent.

Attasorb LVM (Reference 25). Attasorb LVM (low volatile matter) is produced when a Hapulgus clay, commonly called attapulgite, is thermally activated and milled and screened to a fine powder, with an average particle size of 2.9 microns. Attapulgite derives two unusual characteristics from its unique hydrated magnesium aluminum silicate structure. First, because the structure consists of three-dimensional chains, the clay cannot swell like clays such as montmorillonite, which have three-layer sheets. Second, specific cleavage of the crystal structure yields a porous attapulgite clay that has a high specific surface area (125 m^2/g).

Satintone 5 (Reference 26). This clay is a calcined kaolin with a matrix consisting of thin flat plates. Typically, kaolin is a complex aluminum silicate whose constituents (SiO_2, Al_2O_3) do not exist as free oxides. Kaolins exhibit pH-dependent charged surfaces. For example,

Satintone 5 is positively charged at low pH values and has a cation exchange capacity of 27 mequiv/100 grams.

b. Molecular Sieves (References 27, 28). Valfor Z84-326 and Valfor 200, products of The PQ Corporation (Valley Forge, PA), are high-purity crystalline synthetic Type A aluminosilicates in the sodium form. The aluminosilicate portion of the structure is a three-dimensional open framework consisting of a network of AlO_4 and SiO_4 tetrahedra, linked to each other through sharing of all of the oxygen atoms. The ion exchange capacity of zeolite ion exchangers is a function of its SiO_2/Al_2O_2 mole ratio, since each AlO_4 tetrahedron in the zeolite framework provides a single cation exchange site.

Valfor Z84-326. This was an experimental product and is no longer available.

Valfor 200. Valfor 200, now designated as Valfor G100, has a capacity of 5.6 mequiv/gram, on an hydrate basis, and 7.0 mequiv/gram, on an anhydrous basis. Valfor 200 has the following selectivity for divalent ions:

$$Pb^{+2} > Cu^{+2} > Cd^{+2} > Zn^{+2} > Co^{+2} > Mn^{+2} > Ni^{+2} > Mg^{+2} > Fe^{+2}$$

This zeolite has a rigid strong framework stable to high temperatures and oxidation/reduction and not subject to physical attrition due to osmotic shock, as are many organic resin ion exchangers. Similarly, it does not adsorb organic molecules or ions and does not become fouled as readily as ion exchangers. Valfor 200 is a nonphosphate commercial detergent builder and is, therefore, compatible with soil and groundwater.

c. Greensand (Reference 6). Greensand, or glauconite, is a natural marine mineral deposit that consists of aluminum, silicon, iron, magnesium and potassium oxides. Greensand, found in New Jersey and Texas in the United States and in Australia, Italy and China, is distributed in the United States by Inversand Co., Inc., a division of Hungerford and Terry (Clayton, NJ).

Raw Greensand. Raw greensand consists of 46 percent SiO_2, 5 percent Al_2O_3, 8 percent K_2O, and 5 percent of MgO and CaO, with the remainder consisting of Fe_2O_3 and FeO. Greensand has fast reaction rates (equilibrium achieved within an hour), about equal selectivity for both calcium and magnesium, good regeneration efficiency, and good stability in neutral solutions. The cation exchange capacity of the raw greensand is about 0.14 equiv/L. The pH range of greensand is 6.2 to 8.4 with a maximum temperature of 150 ^{o}F. Greensand is regenerated with a 6 to 12 percent solution of salt.

Mn Greensand. The natural product, after being cleaned of fine and coarse material, is treated with solutions of aluminum sulfate and sodium silicate and kiln-dried. The treated product is called modified greensand. Mn greensand is produced by treating modified greensand with manganese sulfate and then with potassium permanganate, so that films of MnO_2 are formed on the greensand granules. The MnO_2 oxidizes iron and manganese in the water or wastewater to be treated, while at the same time the greensand filters out the hydroxides that are formed. After some period of time, it is necessary to regenerate the greensand with potassium permanganate.

6. Other Additives

a. Hydrated Lime

Hydrated lime changes the pH of the soil and acts as a precipitating agent for the contaminant metals in the soil. The best practical technology for treating wastewaters containing heavy metals has been pH adjustment with either lime or caustic soda to cause precipitation as a metal hydroxide sludge (Reference 29). The hydroxide process is often not capable of removing enough of the heavy metal contaminants to achieve specified discharge levels. The reason for this is that the contaminant metals have minimum solubility at a specific pH and further additions of hydroxide can cause the metals to become more soluble. In addition the metals require a different pH to achieve a minimum solubility so that it is

difficult to precipitate them to low levels. Table 9 shows the solubility of metal hydroxides when precipitated at pH 8.0.

TABLE 9. SOLUBILITY OF METAL HYDROXIDES WHEN PRECIPITATED AT pH 8.0.

Metal	Solubility (mg/L)
Iron	2.2 x 10-15
Tin	1.7 x 10-11
Mercury	6.0 x 10-9
Copper	1.4 x 10-3
Zinc	7.8 x 10-1
Nickel	1.2 x 10+2
Lead	2.5 x 10+2
Silver	2.2 x 10+3
Cadmium	2.8 x 10+3

b. Silylated Silica Gel (Reference 30)

A silica gel containing a number of immobilized complexing and chelating groups was synthesized for use in the removal of heavy metals from electroplating wastewaters. An immobilized diamine produced from silane was found to be relatively stable at room temperature. The capacity of the silica gel was 23 mg Cu/gram of silica gel. The optimum performance of the silica gels for a broad range of heavy metals was near pH 9. For the present test program, the silylated silica gel was synthesized by immmobilizing a monolayer of Dow Corning Z-6020 diamine onto a silica gel substrate.

c. Insoluble Starch Xanthate (References 31-33)

Insoluble starch xanthate (ISX) was originally developed by R.W. Wing at the Northern Regional Research Center of the U.S. Department of Agriculture and is used to remove heavy metal cations from various industrial wastewaters (References 3-4 and 3-4). It is presently being marketed by Pollution Technology Systems, Garland, TX.

Originally, water-soluble starch xanthates were used in combination with cationic polymers to form polyelectrolytic complexes that were effective in removing heavy metal cations from solution. However, Wing et al. (Reference 31) found the addition of the cationic polymer could be eliminated by xanthating a highly cross-linked starch to give a water-insoluble product. ISX, in the sodium form, although effective for heavy metal removal, was difficult to isolate in a room temperature stable form. The stability of ISX in room temperature increases if the product is converted to other salt forms. The present form of ISX uses magnesium sulfate, which not only aids in the processing of the product, but greatly increases room temperature stability.

ISX is a cereal grain-based product that is chemically cross-linked to make it insoluble in water and then xanthated to form an anionic polymer. When used to treat wastewaters, ISX acts like a cation exchange resin and, upon contact with the contaminant heavy metal cations, exchanges sodium or magnesium ions. Sodium and magnesium are relatively innocuous in groundwater, although there is a secondary drinking water limitation on sodium of 20 mg/L. In practice, the ISX containing the adsorbed heavy metals is removed from the process wastewater by gravity precipitation or filtration. The metal-ISX can be land-filled because the metal is bound very strongly to the xanthate and has less chance to be leached out than with an hydroxide sludge (Reference 33).

ISX contains a sulfur group that effectively attaches to the heavy metal. The higher the sulfur content of ISX the greater its capacity for heavy metal bonding. Sulfur with attached functional groups are the active sites on ISX. The sulfur-metal bonds are particularly strong, exspecially if the metal ion is bound to the ISX by more than one sulfur ion with the attached functional groups. The sulfur-bonding of the xanthate to the metal and probably multiligand complexing explains why a metal ISX sludge is more stable to leaching than an hydroxide sludge.

ISX has a heavy metal capacity of about 1.5 mequiv/gram ISX and an affinity for the five heavy metals of interest (cadmium, chromium, copper, nickel and zinc). For example, the capacity of ISX for chromium (+6) is

13 mg/gram ISX. ISX is effective over a pH range of 3 to 11 with a maximum capacity at approximately a pH 9. In typical industriial applications, ISX is used in a slurry form with batch treatment, or is used as a filter precoat. ISX gives over a 99.9 percent removal efficiency even at metal concentrations of less than 10 mg/L and reduces the effluent concentrations down to less than 0.01 mg/L. ISX is suitable for removing heavy metals from wastewaters when the heavy metals have different solubility characteristics as a function of pH, or in removing heavy metals in the presence of various metal complexing agents such as EDTA (Reference 33).

ISX contains a sulfur group that effectively attaches to the heavy metal cation. Table 10 shows the solubility product constants for several metal-ethyl xanthates. The solubility product values for ISX-metal complexes should correspond closely to those listed in the table; low values of the solubility product indicate good removal of the heavy metals. The higher the sulfur content of the ISX, the greater its capacity for heavy metal bonding. Sulfur-containing functional groups appear to be the active sites. The sulfur-metal bonds are particularly strong, especially if the metal ion is bound by more than one sulfur-containing functional group. The sulfur bonding of the xanthate to the metal and probably multiligand complexing explains why the metal-ISX sludge is more stable to leaching than hydroxide sludge.

TABLE 10. SOLUBILITY PRODUCT CONSTANTS (K_{sp}) FOR METHYL-ETHYL XANTHATES (REFERENCE 31).

Metal	Solubility Product	Metal	Solubility Product
Hg+2	1.7×10^{-35}	Cd+2	2.6×10^{-14}
Au+1	6×10^{-30}	Ni+2	1.4×10^{-12}
Cu+1	5.2×10^{-20}	Zn+2	4.9×10^{-9}
Ag+1	5×10^{-19}	Fe+2	8×10^{-8}
Pb+2	1.7×10^{-17}	Sn+2	1×10^{-8}

d. Metal Sorb-7

Metal Sorb-7 is a high molecular weight chelating agent to which are attached numerous complexing sites using various functional groups. The substance is derived from natural products originating from biosynthesis. The chelating groups complex the heavy metals in the soil and fix onto the soil itself, completely immobilizing the metal. Because it is derived from natural products the chelating agent is expected to be more resistant to chemical and microbial degradation in soil environments. Metal Sorb-7 was synthesized by Dr. J. Swallow, a consultant to Foster-Miller, Inc.

e. Ferrous Sulfate

Ferrous sulfate is a nontoxic, inexpensive reducing agent. The addition of ferrous sulfate reduces the very toxic, very mobile hexavalent chromium to its less toxic, less mobile trivalent form. In the trivalent form, chromium can be precipitated with lime as chromium hydroxide or can be adsorbed onto some of the ion exchangers or molecular sieves by ion exchange.

SECTION IV

TEST APPARATUS AND ANALYTICAL TECHNIQUES

A. EQUIPMENT AND OPERATION

1. Laboratory-Scale Batch Equipment

For the purpose of batch screening a large number of chemical additives, the tests were carried out in a reciprocal shaker apparatus (Figure 4). The testing apparatus consisted of up to 18-1,000 mL Erlenmeyer flasks in which soils were placed in an uncompacted, unconfined state and to which treatment chemicals and/or contaminant metals were added. The bulk soils, saturated with solutions containing contaminant metals and/or treatment chemicals were reacted by mechanical skaking on two Eberbach (Ann Arbor, MI) 6000 Reciprocal Shakers at a speed of 120 cycles/min. One oscillating table had a capacity of six flasks and the other a capacity of 12 flasks, with the latter one modified by mounting two six-flask trays on top of each other in a two-tier configuration. The tables were equipped with a timer and relays to facilitate unattended shaking and settling cycles.

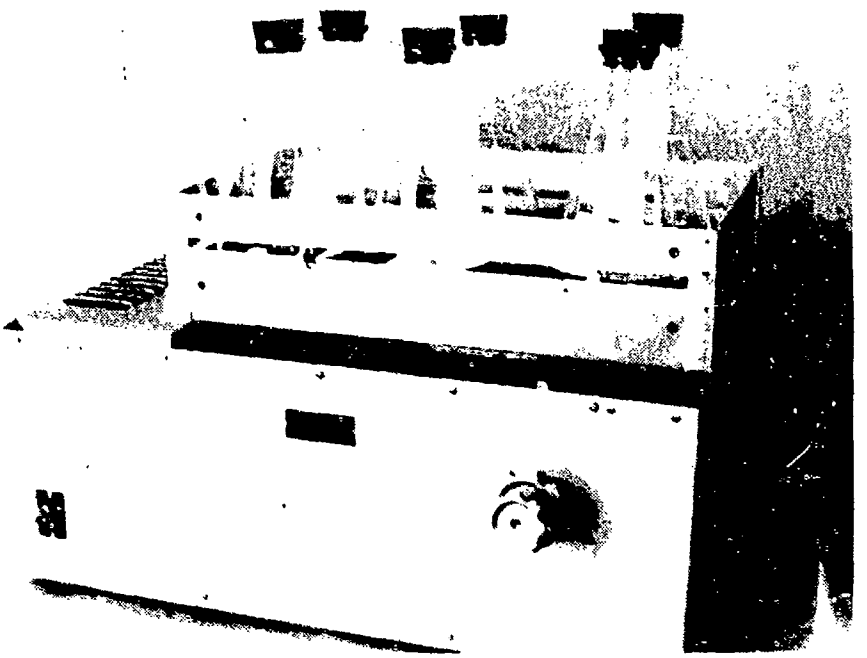


Figure 4. Reciprocal Shaker Apparatus for Batch Screening Testing.

2. Laboratory-Scale Column Operation

The majority of the test program was conducted in column apparatus. Three types of columns were used: dynamic flow test columns, long-term stability test columns, and hazardous waste site simulation columns. The dynamic flow column studies were conducted to obtain detailed data on the capacity and mobility of metal contaminants in soil with and without the addition of treatment chemicals. Tests on the long term stability of treatment chemicals in soil with and without the effects of acid rain and solvent addition were carried out in the long term test columns, while tests were carried out in the hazardous waste site simulator to determine the immobilization of treated soil in a dynamically changing soil environment.

Only the McClellan AFB and Robins AFB soils were used in the column test program. All soils were compacted in the dynamic flow and long-term columns and Hazardous Waste Site Simulator to their native density by means of a controlled-drop hammer. The inside diameter of each soil column was scored in concentric circles to reduce channeling and minimize wall effects. Once the soil columns were packed with soil, with and without treatment chemicals, they were saturated by pulling deaerated, deionized water through the bottom of the soil column with a vacuum pump. This procedure reduced channeling further by removing entrained air from the soil column.

Twelve (12) dynamic flow test columns were constructed of polyvinyl chloride (PVC). Each of the dynamic flow test columns had an inside diameter of 2.0 inches (5.1 cm) and was 30 inches (76.2 cm) long (Figure 5). The apparatus was constructed without any metal components contacting the fluid or soil. Both ends of the columns were fitted with PVC threaded caps with 0.5 in. (1.3 cm) diameter holes. Perforated plexiglass disks of 1.90 in. (4.8 cm) diameter and 0.25 in. (0.63 cm) thick, as well as a ball of glass wool, were placed at the base of each column to prevent the loss of soil during the tests. Teflon tubes connected to Teflon fittings threaded into the end caps allowed for the introduction of metal contaminant solutions and the collection of effluent samples (Figure 6). Simulated overburden pressures of 0 to 100 psi (0 to 0.69 MPa) can be obtained with this system. Totally independent fluid flow pressures of 0 to 100 psi are also obtainable.

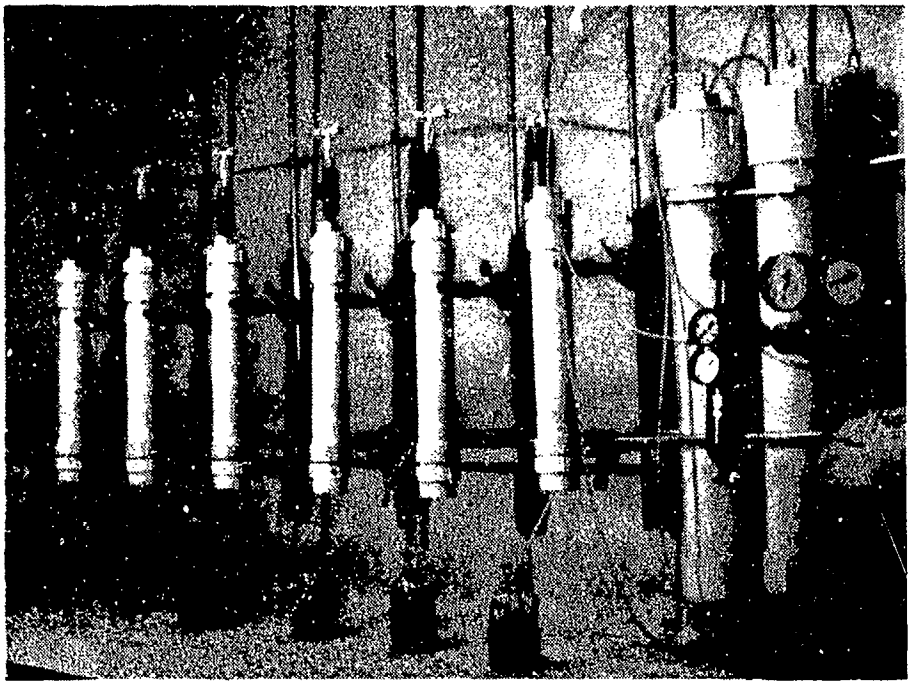


Figure 5. Dynamic Flow Column Apparatus

To avoid soil compaction in the columns caused by pressurizing the system, fluid was gravity fed through the columns at constant head pressures. Flow rates approximated native soil permeabilities. The flow rates were regulated with a peristaltic pump connected to the column's effluent stream.

The soil columns were packed to the in situ density of each soil. One hundred grams of each soil were packed to approximately 1 inch (2.54 cm) lifts using the custom-made controlled-drop hammer described above. The procedure was repeated for a total of six lifts per column to achieve a soil height of six inches (15.2 cm), a total volume of 18.85 cubic inches (308.9 cm^3), and a total weight of 600 grams. The soil weight, packing depth, and the number of taps required were recorded for each soil column. The columns were packed in this manner to achieve the desired density of 107-118 lb/ft^3 (1.72-1.89 gr/cm^3) and the desired permeability rates of approximately 0.66-1.66 in/hr (1.68-4.22 cm/hr) to simulate the original field conditions (Table 4). The soil column was repacked if the actual soil density varied to within ± 10 percent of the desired in situ soil density.

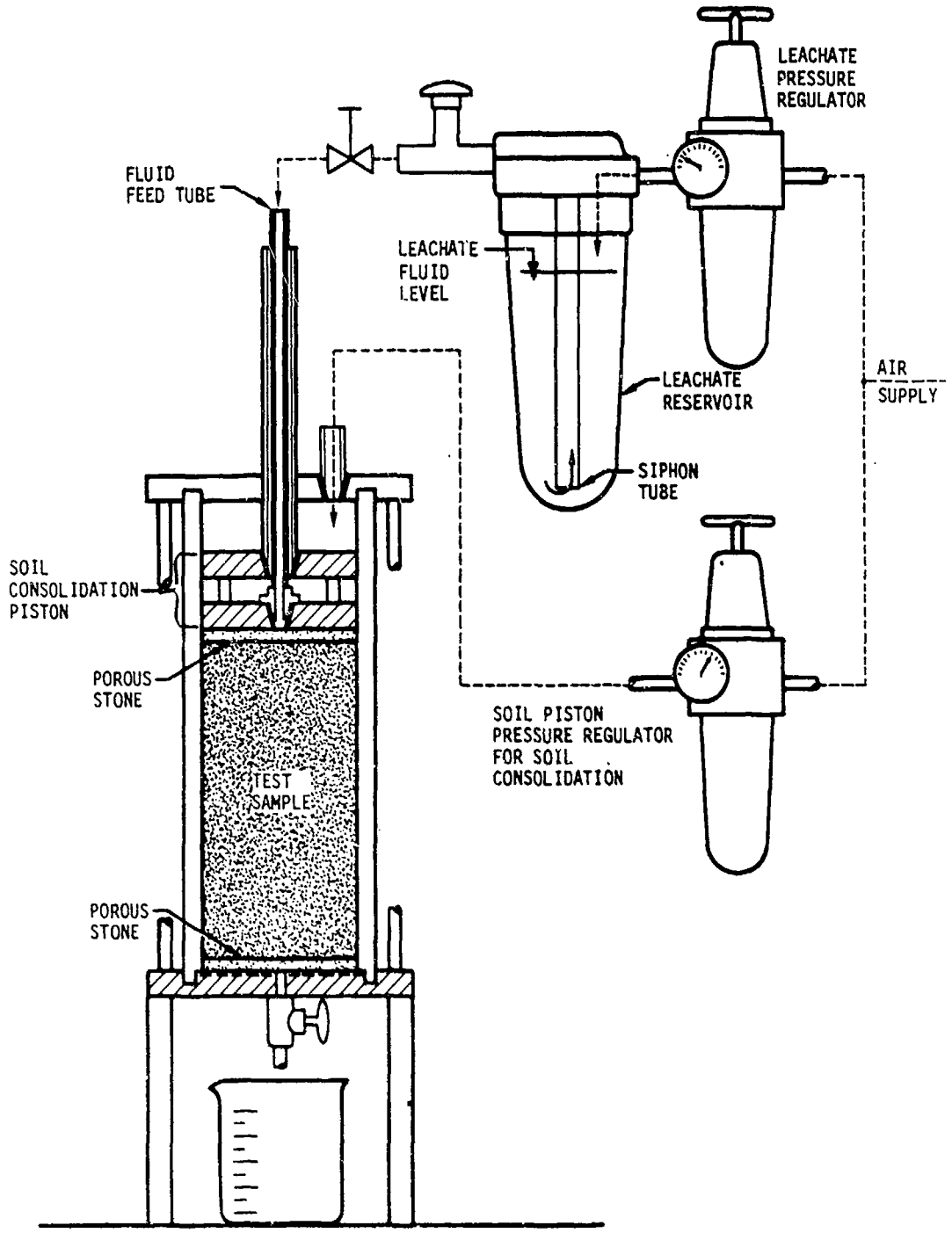


Figure 6. Schematic of Dynamic Flow Column.

To facilitate long-term stability testing, 12 columns similar to the dynamic flow columns, were constructed. The columns were made of the same PVC as the dynamic flow columns and each had an inside diameter of 2.0 inches (5.1 cm) and a length of 12 inches (30.5 cm). Fluid was gravity fed through these columns via a reservoir above the test columns.

A four column - Hazardous Waste Site Simulator (Figure 7) was also built. Each column consisted of four-2.0 inch inside diameter plexiglass sections that were stacked and mounted on top of each other after they were packed with soil. The first or top section was 2 feet long and each of the four successive sections was 1 foot long. The leadrate fluid was gravity fed through the columns. The soil in each section was compacted to its native density by the procedures already described.

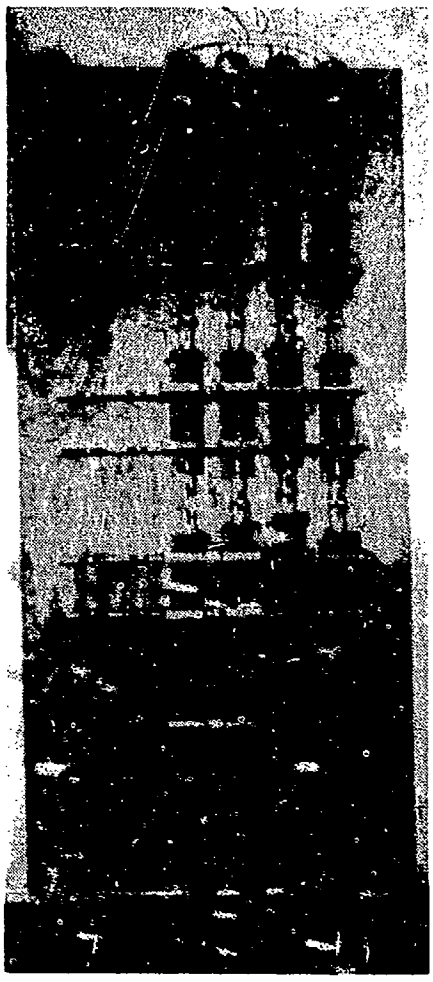


Figure 7. Hazardous Waste Site Simulator.

Both ends of the columns were fitted with a plexiglass cap with 0.5-inch diameter holes. A perforated plexiglass disk (0.44 inches diameter, 0.25 inches thick) and glass wool were fitted at the base of each column allowing passage of leachate to the next column while restraining soil migration. The top caps were held in place with four wing nuts attached to bolts runnning from a plastic collar glued to the top of the column along its outside diameter. The column was made watertight by inserting a butyl rubber gasket between the collar and cap. The bottom cap was cemented into place. Teflon tubes connected to plastic fittings threaded into the end caps allowed the introduction of water solutions. Three-way plastic valves located between the columns provided a method of collecting effluent samples. Tubes at the base of the columns were placed into a 500 mL glass flask for the collection of most of the total effluent passed through the column during the testing duration.

B. ANALYTICAL TECHNIQUES

Effluent and supernates generated during the testing program were analyzed for the heavy metal contaminants (Cd, Cr, Cu, Ni and Zn). The total metal contaminants were determined on a Perkin-Elmer Model 2380 Atomic Absorption (AA) Spectrophotometer (Figure 8). Relevant test parameters for each metal of interest are summarized in Table 11.

Metal concentrations in liquid samples above the linear range of the instrument were appropriately diluted before measurement. Recommended procedures for dilution, calibration, and measurement as given in the manufacturer's handbook and in Reference 34 were followed.

Free metal ions and metal concentrations in test solutions that exceed the sensitivity of the AA were determined on an EG&G PARC 364 Polarographic Analyzer. Half-wave potentials and several different electrolytes for each possible species of interest are found in Table 12. Data obtained by a polarographic scan were quantitated by preparing a standard curve or by the method of standard additions (Reference 34).

Figure 8. Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer.

TABLE 11. STANDARD CONDITIONS FOR HEAVY METAL CONTAMINANTS WITH PERKIN-ELMER 2380 AA SPECTROPHOTOMETER.

Metal	Wave Length (nm)	Sensitivity[a] (mg/L)	Detection Limit (mg/L)	Working Range (Max. Conc.) (mg/L)	Flame
Cadmium, Cd	228.8	0.025	0.1	2	Air-Ac
Chromium, Cr	357.9	0.1	0.003	5	Air-Ac
Copper, Cu	324.8	0.09	0.002	5	Air-Ac
Nickel, Ni	232.0	0.15	0.005	1	Air-Ac
Zinc, Zn	213.9	0.018	0.01	1	Air-Ac

[a] At 1 percent absorption.

The pH was determined by a specific ion electrode in conjunction with an Orion Model 901 Research Microprocessor Ionanalyzer. Purchased standard solutions and electrolytes were used for calibration and quality assurance of the analytical procedures.

TABLE 12. HALF-WAVE POTENTIALS.

Metal	Supporting Electrolyte	$E_{1/2}$(v)
Cation		
Cd^{+2}	0.2M NH_4 Citrate, pH 3	-0.62
Cd^{+2}	1M KCN	1.18
Cr^{+6}	1M NaOH	-0.85
Cr^{+6}	0.1M KCl	-0.30
Cr^{+3}	0.2M KSCN, pH 3	-0.85
Cr^{+2}	1M KCl	-0.40
Cr^{+2}	1M KSCN	-0.80
Cu^{+2}	0.2M NH_4 Citrate, pH 3	-0.07
Cu^{+2}	1M NH_3 - 1M NH_4Cl	-0.24
Ni^{+2}	1M NH_3 - 1M NH_4Cl	-1.0
Ni^{+2}	0.01M KCl	-1.1
Ni^{+2}	1M KSCN	-0.70
Zn^{+2}	0.2m NH4 Citrate, pH 3	-1.04
Anion		
NO_2^-	2M Citrate, pH 2.5	-1.06
S^{-2}	0.1M NaOH	-0.76
$S_2O_3^{-2}$	0.2M NaOAc Buffer, pH 5	-0.40
SO_3^{-2}	0.2M NaOAc, pH 5	-0.65

SECTION V
TEST APPROACH AND RESULTS

A. PLAN OF APPROACH

The objectives of the test program were to identify, characterize, and evaluate chemicals with the potential to immobilize contaminant metals in soil. Variability was the biggest obstacle in implementing a reasonable and meaningful test matrix. The major test parameters are:

- Soil type
- Variability of soil properties
- Type of metals, metal combinations and waste solutions associated with waste-generating process
- Composition of treatment chemicals
- Variability of post treatment events and processes impacting a given site

The large number of test parameters generated by combinations of soils, metal contaminants and treatment chemicals makes it economically unattractive to carry out a test program that would be required for a very rigorous evaluation of in situ immobilization. The following approach was taken to arrive at a reasonably sized test program that would focus on the specific problems of the Air Force and enable a feasibility evaluation of the treatment chemical immobilization concept:

- Three clean soils from three Air Force bases were used in the test program. The soils reflect the generic characteristics of actual contaminated soils of three Air Logistics Centers in the United States.
- The metal salt solutions used to simulate the wastestreams were limited to single metal solutions of Cr, Cd, Cu, Ni, and Zn and multiple metal solutions of Cr-Cd, Cr-Ni, Cr-Cd-Ni, and Cr-Cd-Cu-Ni-Zn. Except for a few isolated cases, the total metal concentration in solution was 30 mequiv/L. In the case of multiple metal

solutions, all of the metals had the same (milliequivalent) concentration with a total contaminant metal concentration of 30 mequiv/L.

- The test procedures were designed to screen a large number of treatment chemical additives to determine the best two to three chemicals for further evaluation. After each series of tests, the test data were reviewed and, if warranted, the number of parameteric variations were reduced for the next series of tests.

Batch and column test procedures for measuring the leachability and subsequent immobilization of heavy metals through contaminated soil were carried out. Batch equilibrium methods were used to rapidly screen the treatment chemical additives for their ability to react with contaminant metals in the soil. The two best treatment chemicals for each soil-metal combination were selected for more detailed column studies.

The data obtained by the column methods give a more realistic representation of the immobilization and leaching phenomena than the batch equilibrium methods because the soil structure, pore space distribution, and diffusion characteristics more closely mimic the natural field conditions. The dynamic column studies were conducted to obtain detailed data on the capacity and mobility of metal contaminants in soil with and without the addition of treatment chemicals. Long-term tests on the stability of the best treatment chemicals in soil with and without the effects of acid rain and solvent addition were also carried out in the columns. A Hazardous Waste Site Simulator was also constructed to determine the immobilization of treated soil in a dynamically changing soil environment. An overview of the test program is shown in Figure 9.

B. BATCH SCREENING TEST PROGRAM

Twenty-one (21) chemical additives were identified as being able to immobilize heavy metals in soils (Table 8). Since four of these are ion exchange or chelate resins which could be conditioned in two different ways, a total of 25 chemical additives were available for use in the test program. Because these additives were too numerous to carry through a full range of

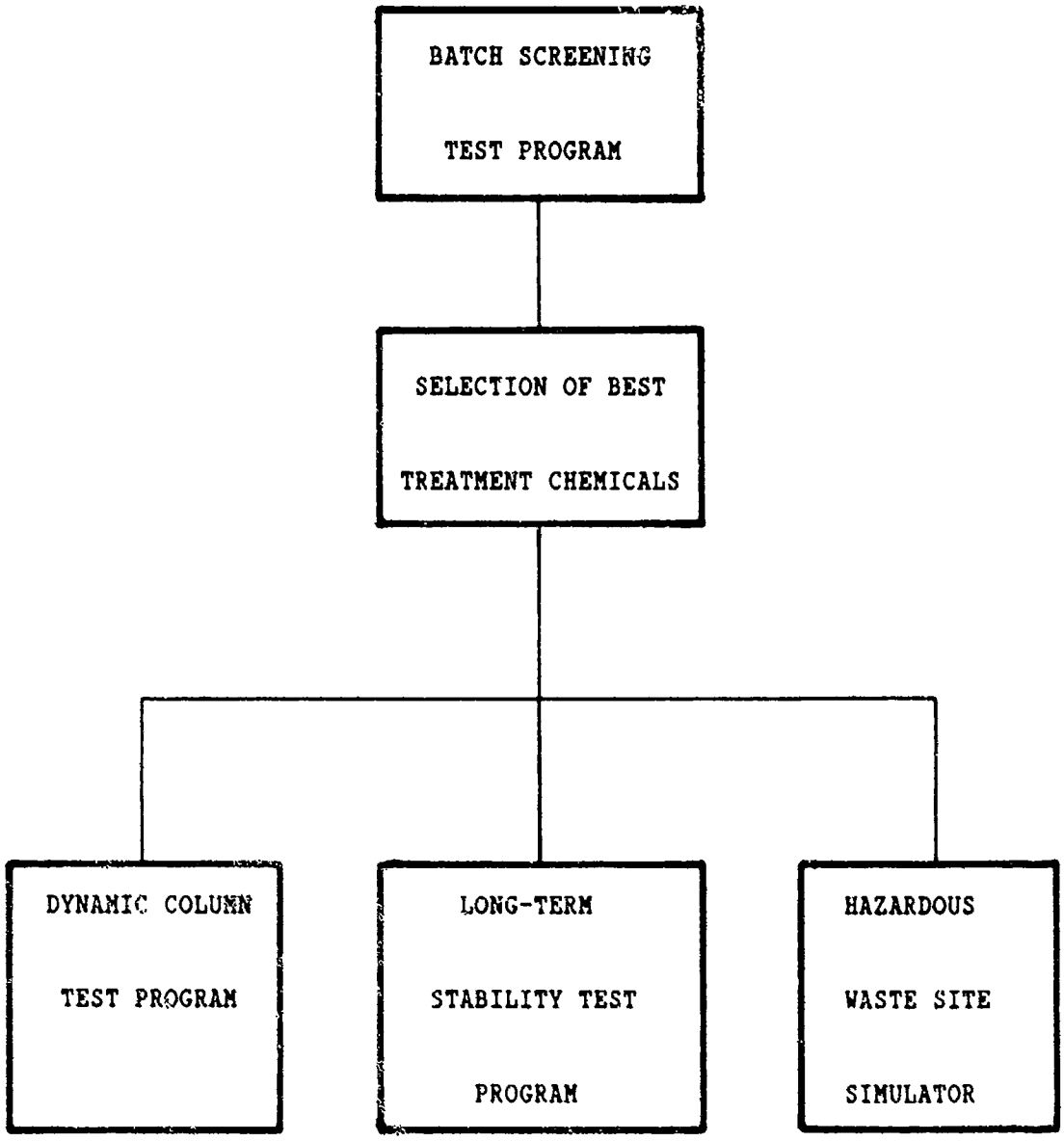


Figure 9. Overview of Laboratory Test Program.

testing, a batch screening test program was conducted and one or two of the best additives were selected for each combination of soil type and contaminant metal. In this way, if any one chemical additive could not immobilize all of the metals of interest in a given soil, it was anticipated that enough chemical additives could be found and, when mixed, could immobilize all of the five metals. A more detailed characterization of the best treatment chemicals was then carried out in column tests.

An outline of the batch testing program is shown in Figure 10. The test program was divided into five distinct tasks:

- Task 1. Chemical Additives:Multiple Heavy Metal Contaminants Interactions. In the absence of the soils, the capacity and selectivity of each of 25 chemical additives were determined in a solution containing all five metals. A little less than one-half of the chemical additives generally having the highest capacities were selected for further testing.
- Task 2. Soils:Single and Multiple Heavy Metal Contaminant Interactions. As a control case, the uptake capacity of the soils contaminated with heavy metals both singly and in multiples, were determined.
- Task 3. Soils::Chemical Additives:Single Heavy Metal Contaminants Interactions. The capacities of the 12 best chemical additives (based on the results of Task 1) for each soil contaminated with a single metal were determined. The differential capacity of each chemical additive was then determined by subtracting the capacity of the soil-single metal system from the total capacity (soil-single metal-chemical additive system). The unit cost ($/gram) of each chemical additive was estimated and the cost per unit weight of heavy metal immobilized in the soil was then calculated. The two chemical additives having the lowest cost per unit weight of metal immobilized was selected for each soil-heavy metal combination.
- Task 4. Effect of Chemical Dosage on Metal Immobilization. The effect of changing the dosage on the total capacity and differential capacity of the two best chemical additives (for each soil-single metal combination) was then determined.
- Task 5. Soils:Chemical Additives:Multiple Metal Contaminants Interactions. The degree of immobilization, total capacity, and differential capacity were determined as a function of dosage for the two best chemical additives (for each soil-single metal combination) in soils contaminated with all five metals.

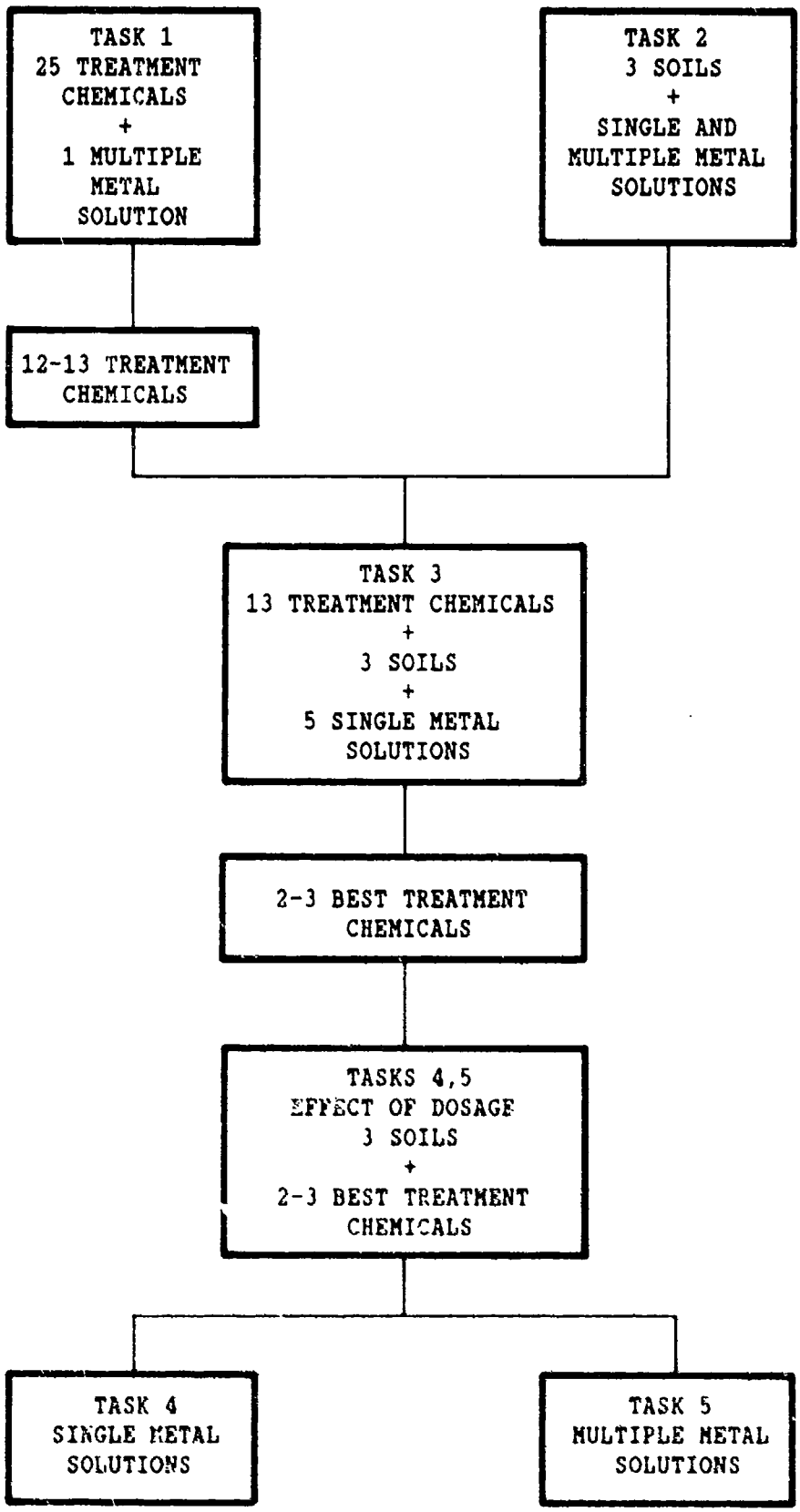


Figure 10. Overview of Batch Screening Test Program.

1. Chemical Additives:Multiple Heavy Metal Contaminant Interactions

All of the chemical additives were screened for their equilibrium capacity and relative selectivity in metal salt solutions. Two grams (dry weight) of each chemical additive were reacted with 400 cc of a metal salt solution in a 1-liter Erlenmeyer flask. The metal salt solution consisted of 30 mequiv/L each of Cr, Cd, Ni, Cu and Zn. The exact composition and the salts used in the solution are described in Table 13. Some of the chemical additives and metal salt solutions were mixed for 1 hour, 6 hours and 24 hours (elapsed time) on the reciprocal shaker. At the end of each time interval, 10-20 mL aliquots of the metal salt solution were taken and suction filtered on a Buchner funnel through a Whatman 934 AH glass microfiber filter having an effective retention of 1.5 microns. The filtrate was analyzed for each of the five contaminant metals on a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. The difference between the original concentration and the measured concentration corresponded to the amount of metal adsorbed and/or complexed by the chemical additive.

TABLE 13. COMPOSITION OF METAL SALT SOLUTIONS.

Metal	Reagent	Concentration (ppm)	Concentration (mequiv/L)
Ni^{+2}	$NiCl_2.6H_2O$	910	31.0
Cu^{+2}	$CuCl_2$	1000	31.5
Zn^{+2}	$ZnCl_2$	1040	31.8
Cd^{+2}	$CdSO_4.8H_2O$	1720	30.6
Cr^{+6}	CrO_3	252	29.1

Preliminary analyses showed that the chemical additives initially tested reached equilibrium at different rates, but all the chemical additives reached equilibrium within 24 hours. As a result, all the subsequent tests were run for 24 hours.

The screening procedure for the lime and ferrous sulfate additives were slightly modified. A magnetic stirrer was used instead of the

reciprocal shaker, making it easier to monitor pH during the precipitation reaction.

The metal capacity for each additive was defined by the quantity of metal removed from the metal solution divided by the weight of the additive (mequiv metal/gram chemical additive). The total metal capacity for each additive was determined by adding the chemical additive capacities for the individual metals. The capacities were calculated from Equation (1) as follows:

$$Cap = (C_o - C_f)\ V/W \qquad (1)$$

where:

Cap = Capacity of the chemical additive for single or total metal(s) in solution (mequiv/gram)

C_o = Initial concentration of single or total metal(s) in solution (mequiv/L)

C_f = Final concentration of single or total metal(s) in solution (mequiv/L)

V = Volume of metal salt solution (L)

W = Weight of chemical additive (grams).

The immobilization efficiency was defined as the quantity of metal(s) adsorbed on the additive divided by the metal(s) initially added in solution. The immobilization efficiency was calculated from Equation (2), as follows:

$$K = (Cap \times W)/(C_o \times V) = 1 - (C_f/C_o) \qquad (2)$$

Tables 14 through 18 show the capacities and the immobilization efficiencies of the 25 chemical additives for each of the contaminant metals. For each metal, the chemical additives were ranked according to their single metal capacity and immobilization efficiency (see Tables 14 to 18). In addition, on Table 19 each of the chemical additives have been ranked according to their total capacity (and immobilization

TABLE 14. TREATMENT CHEMICAL CHROMIUM CAPACITY (MEQUIV METAL/GRAM ADDITIVE) AND IMMOBILIZATION EFFICIENCY.

K	Cap (Cr) (mequiv/gram)	Chemical Additive
0.92	5.38	Duolite CS-346
0.83	4.89	Dowex XFS-4195
0.83	4.85	Dowex XFS-4195C
0.80	4.71	Duolite CS-346-C
0.77	4.52	Hydrated Lime
0.77	4.52	Ferrous Sulfate
0.71	4.17	ISX
0.50	2.91	Valfor Z84-326
0.45	2.65	Metal Sorb-7
0.18	1.08	Silylated Silica Gel
0.13	0.77	DH 565
0.13	0.77	BEN 1[illegible] Bentonite
0.13	0.74	Valfor 200
0.11	0.67	325 Bentonite
0.11	0.66	Raw Greensand
0.11	0.66	Attasorb LVM
0.10	0.57	DH 524
0.05	0.30	Amberlite IRC-718C
0.02	0.11	Amberlite IRC-718
0.01	0.07	Mn Greensand
0.00	0.00	DH 566
0.00	0.00	HPM 20 Bentonite
0.00	0.00	Amberlite IR-124
0.00	0.00	Amberlite IR-124C
0.00	0.00	Satintone 5

TABLE 15. TREATMENT CHEMICAL CADMIUM CAPACITY (MEQUIV METAL/GRAM ADDITIVE) AND IMMOBILIZATION EFFICIENCY.

K	Cap (Cd) (mequiv/gram)	Chemical Additive
1.00	6.53	Hydrated Lime
0.36	2.37	Ferrous Sulfate
0.06	0.37	Amberlite IR-124C
0.05	0.31	Valfor 200
0.04	0.28	HPM 20 Bentonite
0.03	0.21	Metal Sorb-7
0.03	0.19	Valfor Z84-326
0.03	0.18	BEN 125 Bentonite
0.02	0.14	DH 565
0.02	0.11	Amberlite IR-214
0.01	0.05	Dowex XFS-4195C
0.01	0.05	Satintone 5
0.00	0.02	Mn Greensand
0.00	0.01	Duolite CS-346C
0.00	0.00	DH 566
0.00	0.00	DH 524
0.00	0.00	ISX
0.00	0.00	Raw Greeensand
0.00	0.00	Attasorb LVM
0.00	0.00	325 Bentonite
0.00	0.00	Silylated Silica Gel
0.00	0.00	Amberlite IRC-718
0.00	0.00	Amberlite IRC-718C
0.00	0.00	Duolite CS-346
0.00	0.00	Dowex XFS-4195

TABLE 16. TREATMENT CHEMICAL NICKEL CAPACITY (MEQUIV METAL/GRAM ADDITIVE) AND IMMOBILIZATION EFFICIENCY.

K	Cap (Ni) (mequiv/gram)	Chemical Additive
1.00	6.25	Hydrated Lime
0.94	5.88	Ferrous Sulfate
0.13	0.82	Amberlite IR-124C
0.09	0.56	Amberlite IR-124
0.06	0.37	Valfor 200
0.04	0.23	Dowex XFS-4195C
0.04	0.22	BEN 125 Bentonite
0.03	0.20	Valfor Z84-326
0.02	0.14	HPM 20 Bentonite
0.02	0.12	Metal Sorb-7
0.02	0.12	Amberlite IRC-718C
0.01	0.09	Amberlite IRC-718
0.01	0.07	Raw Greensand
0.01	0.07	325 Bentonite
0.01	0.05	ISX
0.01	0.05	Satintone 5
0.01	0.05	Dowex XFS-4195
0.01	0.03	Mn Greensand
0.00	0.00	DH 566
0.00	0.00	DH 565
0.00	0.00	DH 524
0.00	0.00	Attasorb LVM
0.00	0.00	Silylated Silica Gel
0.00	0.00	Duolite CS-346
0.00	0.00	Duolite CS-346C

TABLE 17. TREATMENT CHEMICAL COPPER CAPACITY (MEQUIV METAL/GRAM ADDITIVE) AND IMMOBILIZATION EFFICIENCY.

K	Cap (Cu) (mequiv/gram)	Chemical Additive
0.98	6.00	Ferrous Sulfate
0.73	4.46	Valfor 200
0.66	4.02	Valfor Z84-326
0.46	2.83	ISX
0.27	1.65	Dowex XFS-4195C
0.24	1.49	Duolite CS-346
0.20	1.23	Dowex XFS-4195
0.20	1.19	Amberlite IRC-718
0.18	1.11	Amberlite IRC-718C
0.15	0.90	Duolite CS-346C
0.13	0.78	Amberlite IR-124C
0.11	0.64	Metal Sorb-7
0.10	0.61	Amberlite IR-124
0.04	0.24	HPM 20 Bentonite
0.03	0.21	BEN 125 Bentonite
0.03	0.19	Attasorb LVM
0.02	0.11	325 Bentonite
0.01	0.06	Raw Greensand
0.01	0.03	Hydrated Lime
0.00	0.00	DH 566
0.00	0.00	DH 565
0.00	0.00	DH 524
0.00	0.00	Silylated Silica Gel
0.00	0.00	Mn Greensand
0.00	0.00	Satintone 5

TABLE 18. TREATMENT CHEMICAL ZINC CAPACITY (MEQUIV METAL/GRAM ADDITIVE) AND IMMOBILIZATION EFFICIENCY.

K	Cap (Zn) (mequiv/gram)	Chemical Additive
1.00	6.23	Hydrated Lime
0.95	5.92	Ferrous Sulfate
0.12	0.73	Amberlite IR-124C
0.08	0.48	Valfor 200
0.07	0.46	Amberlite IR-124
0.03	0.18	HPM 20 Bentonite
0.02	0.15	Raw Greensand
0.02	0.12	Metal Sorb-7
0.01	0.09	Valfor Z84-326
0.01	0.06	BEN 125 Bentonite
0.01	0.03	325 Bentonite
0.00	0.00	DH 566
0.00	0.00	DH 565
0.00	0.00	DH 524
0.00	0.00	ISX
0.00	0.00	Attasorb LVM
0.00	0.00	Silylated Silica Gel
0.00	0.00	Dowex XFS-4195C
0.00	0.00	Amberlite IRC-718
0.00	0.00	Amberlite IRC-718C
0.00	0.00	Duolite CS-346
0.00	0.00	Duolite CS-346C
0.00	0.00	Mn Greensand
0.00	0.00	Satintone 5
0.00	0.00	Dowex XFS-4195

TABLE 19. TREATMENT CHEMICAL TOTAL METAL CAPACITY (MEQUIV METAL/GRAM ADDITIVE) AND IMMOBILIZATION EFFICIENCY.

	Cap (mequiv/gram)						
K	Total	Ni	Cr	Cd	Cu	Zn	Chemical Additive
0.77	24.69	5.88	4.52	2.37	6.00	5.92	* Ferrous Sulfate
0.74	23.56	6.25	4.52	6.53	0.03	6.23	* Hydrated Lime
0.23	7.41	0.20	2.91	0.19	4.02	0.09	* Valfor Z84-326
0.22	7.05	0.05	4.17	0.00	2.83	0.00	* ISX
0.21	6.87	0.00	5.38	0.00	1.49	0.00	* Duolite CS-346
0.21	6.78	0.23	4.85	0.05	1.65	0.00	* Dowex XFS-4195C
0.20	6.36	0.37	0.74	0.31	4.46	0.48	* Valfor 200
0.19	6.17	0.05	4.89	0.00	1.23	0.00	Dowex XFS-4195
0.18	5.62	0.00	4.71	0.01	0.90	0.00	Duolite CS-346C
0.12	3.74	0.12	2.65	0.21	0.64	0.12	* Metal Sorb-7
0.08	2.70	0.82	0.00	0.37	0.78	0.73	Amberlite IR-124C
0.05	1.74	0.56	0.00	0.11	0.61	0.46	* Amberlite IR-124
0.05	1.53	0.12	0.30	0.00	1.11	0.00	* Amberlite IRC-718C
0.05	1.44	0.22	0.77	0.18	0.21	0.06	* BEN 125 Bentonite
0.04	1.39	0.09	0.11	0.00	1.19	0.00	Amberlite IRC-718
0.03	1.08	0.00	1.08	0.00	0.00	0.00	Silylated Silica Gel
0.03	0.94	0.07	0.66	0.00	0.06	0.15	* Raw Greensand
0.03	0.91	0.00	0.77	0.14	0.00	0.00	DH 565
0.03	0.88	0.07	0.67	0.00	0.11	0.03	325 Bentonite
0.03	0.85	0.00	0.66	0.00	0.19	0.00	Attasorb LVM
0.03	0.84	0.14	0.00	0.28	0.24	0.18	* HPM 20 Bentonite
0.02	0.57	0.00	0.57	0.00	0.00	0.00	DH 524
0.00	0.12	0.03	0.07	0.02	0.00	0.00	Mn Greensand
0.00	0.10	0.05	0.00	0.05	0.00	0.00	Satintone 5
0.00	0.00	0.00	0.00	0.00	0.00	0.00	DH 566

* Chemical additives selected for further testing.

efficiency). Of the 25 chemical additives initially tested, 13 were selected for further batch testing. These additives are indicated by an asterisk in Table 19. The 13 chemical additives were selected on the basis of the following criteria:

- Each chemical additive must exhibit an affinity for at last three metal contaminants and have a capacity greater than or equal to 0.15 mequiv/gram for each metal

or

- Each chemical additive must have a capacity of at least 0.15 mequiv/gram for each of two contaminant metals and have a total metal capacity greater than or equal to 0.90 mequiv/gram.

Table 19 shows that ferrous sulfate and hydrated lime both exhibit exceptional capacity for most of the contaminant metals in the combined metal solution. However, this is not a true measure of capacity since the mechanism of metal removal is dependent solely on pH. The formation and precipitation of metal hydroxides occurs as a result of increasing the pH of the metal solution to 10.75 with the addition of 2 grams of hydrated lime. Metal sulfides precipitate with the addition of 2 grams of ferrous sulfate and a pH adjustment to 10.75. The pH adjustment causes the formation of ferrous sulfide and the coprecipitation of insoluble contaminant sulfides. Ferrous sulfate also reduces the very toxic hexavalent chromium (Cr^{+6}) to its less toxic trivalent form (Cr^{+3}). The mechanism of contaminant removal for the remaining chemical additives is that of adsorption and ion exchange.

2. Soils:Single and Multiple Heavy Metal Contaminant Interactions

The equilibrium capacity and immobilization efficiency of each of the three soils for the contaminant metals was determined by saturating 200 grams of soil (dry weight) with one pore volume (100-200 mL) of deionized water. Four hundred mL of a metal salt solution was combined with the saturated soil and agitated on the reciprocal shaker at 120 cycles/min for 24 hours. Preliminary experimentation indicated that all soils reached equilibrium within 24 hours. At the conclusion of the experiment, 10-20 mL

aliquots were filtered (as discussed in the previous subsection above) and in some cases centrifuged prior to filtration, and all the clear filtrates were analyzed by atomic absorption spectrometry to determine each metal ion concentration. The difference between the original metal concentration and the measured filtrate concentration corresponded to the amount of metal adsorbed by the soil.

In these experiments, the equilibrium capacities of the soils were determined for single and multiple metal contaminants. The capacity of the soil for single metal contaminants was determined by adding 30 mequiv/L of each metal contaminant (Cr, Cd, Ni, Cu and Zn) to each soil. The multiple metal capacity was determined by adding three multiple metal combinations (Cr-Cd, Cr-Ni, and Cr-Cd-Ni) to each of the three soils. In the case of the multiple metals, the total contaminant metal concentration was equal to 30 mequiv/L, with all of the metals having the same milliequivalent concentration. For example, for the Cr-Cd solution, the concentration of each metal was 15 mequiv/L for a total metals concentration of 30 mequiv/L.

In some cases emulsions resulted from contacting the soils with chromium and multiple metal combinations containing chromium. Polaragraphic techniques were successfully used to determine the free chromium in the emulsions.

The capacity (mequiv metal/100 grams soil) of each soil for single and multiple contaminants was calculated from Equation (3):

$$Cap = [(C_o \times V_o) - (C_f \times V_f)] \times 100/W_s \qquad (3)$$

where:

Cap = Capacity of the chemical additive for single or total metal(s) in solution (mequiv/gram)

C_o = Initial concentration of single or total metal(s) in solution (mequiv/L)

C_f = Final concentration of single or total metal(s) in solution (mequiv/L)

V_o = Initial volume of metal salt solution (L)

V_f = Initial volume of metal salt solution + pore volume added (L)

W_s = Weight of soil (grams).

The immobilization efficiency for this series of tests is defined as the quantity of metal(s) adsorbed by the soil divided by the quantity of metal(s) initially added in solution. The immobilization efficiency was calculated from Equation (4), as follows:

$$K = (Cap \times W_s)/100(C_o \times V_o) = 1 - (C_f V_f / C_o V_o)$$
$$= 1 - (C_f/C_o)[1 + V(p)/V_o] \qquad (4)$$

where V(p) is the pore volume added.

Table 20 shows the capacities and immobilization efficiencies for the Tinker AFB, Robins AFB, and McClellan AFB soils for single and multiple metal contaminants. The data shows that in many cases the capacity of the multiple metal test is not equal to the sum of the individual metals in the single metal capacity tests. This suggests that interaction of the multiple metals with the soils is very complex and is not just an additive effect. The soil capacities for the Tinker AFB soil were generally higher than the McClellan and Robins AFB soils because of its higher organic content (see Table 6).

3. Soils:Chemical Additives:Single Heavy Metal Contaminant Interactions

The objectives of this series of experiments were two-fold:

- To determine the capacity of the 12 best treatment chemicals for single heavy metals for each of the three soils.
- Based on the immobilization efficiency and cost tradeoffs, to select the two best treatment chemicals for each soil-metal combination

For these tests, 200 grams of soil were saturated with one pore volume (100-120 mL) of deionized water and then was spiked with 400 mL of a single metal salt solution containing a concentration of 30 mequiv/L of the

TABLE 20. SOIL CAPACITY (MEQUIV METAL/100 GRAMS SOIL) AND IMMOBILIZATION EFFICIENCY FOR SINGLE AND MULTIPLE METAL CONTAMINANTS.

Metal Solution	Parameter	Cr	Cd	Ni	Cu	Zn	Total
McClellan AFB							
Single Cr	Capacity[a]	0.21	2.41	2.77	3.40	2.61	
	K	0.04	0.40	0.48	0.58	0.44	
Multiple Cr-Cd	Capacity	0.51	0.94				1.45
	K	0.18	0.30				0.24
Multiple Cr-Ni	Capacity	0.17		1.89			2.06
	K	0.06		0.64			0.36
Multiple Cr-Cd-Ni	Capacity	0.29	0.95	1.30			2.54
	K	0.16	0.52	0.66			0.46
Robins AFB							
Single Cr	Capacity	1.79	1.23	1.46	1.87	1.31	
	K	0.32	0.20	0.26	0.32	0.22	
Multiple Cr-Cd	Capacity	1.31	0.94				2.25
	K	0.44	0.30				0.38
Multiple Cr-Ni	Capacity	1.23		1.87			3.10
	K	0.46		0.62			0.54
Multiple Cr-Cd-Ni	Capacity	1.19	0.50	0.75			2.44
	K	0.66	0.28	0.42			0.44
Tinker AFB							
Single Cr	Capacity	1.40	4.62	4.64	5.68	4.62	
	K	0.26	0.76	0.82	0.92	0.80	
Multiple Cr-Cd	Capacity	1.30	2.55				3.85
	K	0.44	0.86				0.66
Multiple Cr-Ni	Capacity	2.72		1.75			4.47
	K	0.90		0.58			0.74
Multiple Cr-Cd-Ni	Capacity	0.95	1.45	1.63			4.03
	K	0.52	0.84	0.96			0.76

[a] (mequiv/100 grams soil).

contaminant metal. A single treatment chemical was added to each soil/contaminant metal combination and then reacted on the reciprocal shaker for 24 hours. The samples were filtered, as described above, and the metal ion concentrations were determined by atomic adsorption spectrometry. The degree of immobilization was measured by determining the amount of contaminant metal retained by the soil-chemical additive system.

The primary problem encountered for the screening tests was to determine a suitable dosage for the treatment chemical. Preliminary tests showed the effect of dosage was not a linear relationship making it difficult to determine and compare the unit weight effect of each treatment chemical on the differential capacity.

A number of methods can be used to determine the dosage rate. These include:

- The dosage rate is based on the capacity of each treatment chemical for a single metal (see Tables 14 to 18) in the five multiple metal solution shown in Table 13. This is a problem for some metals because they were not adsorbed by the chemical additive and the differential capacity is zero.
- The dosage rate is based on the <u>total capacity</u> of each treatment chemical (see Table 19) in the same five multiple metal solution shown in Table 13.
- The dosage rate is based on a single metal capacity for a single metal solution. This would have involved repeating all of the tests described previously in Task 1 with five single metal solutions and 25 chemical additives. Since the batch tests were to be used primarily as a screening tool, it was felt that the effort to repeat all these tests was not cost-effective.
- The dosage rate is based on an equal weight dosage for each treatment chemical. This would enable a comparison of the degree of immobilization for the same weight of treatment chemical in the same quantity of soil.

The second and fourth approaches were used to further screen the treatment chemicals. In the second approach, a chemical dosage of 100 percent was used in one set of experiments. For example, a 100 percent dosage of Valfor Z84-326 was calculated in the following manner. Two hundred (200) grams of soil were spiked with a total single metal input of 12 mequiv (400 mL of a 30 mequiv/L single metal salt solution). Table 19 shows the total capacity of Valfor Z84-326 is 7.41 mequiv metal/gram additive, so a 100 percent chemical dosage is 12/7.41 = 1.62 grams and the soil-to-treatment chemical weight ratio is 200/1.62 = 123 or 0.81 grams Valfor Z84-326 per 100 grams of soil.

In the initial set of experiments, ferrous sulfate was not considered because this required pH adjustment (from 3.72 to 10.75) with hydrated lime. Some immobilization of the contaminant metals could also be achieved by the precipitation of metal hydroxides with just the addition of hydrated lime. Ferrous sulfate was used later in the test program to reduce chromium from the hexavalent state to the less toxic trivalent state.

The total soil:chemical additive system capacities and immobilization efficiencies for the three Air Force soils and 12 chemical additives are given in Tables 21 to 23 for 100 percent chemical dosage. The tables show the total metal immobilized by the soil-treatment chemical system per 100 grams of soil (mequiv/100 grams soil) and the fraction of the total metal in solution adsorbed by the soil-treatment chemical interaction. The capacity of each soil for each single metal contaminant is given in the last line of each table and is repeated from Table 20.

In the fourth approach, the soil-treatment chemical weight ratio was fixed at 114:1 (approximately 100:1), or 1.75 grams of treatment chemical per 200 grams of soil. Each soil-treatment chemical mixture was reacted with 400 mL of a 30 mequiv/L single metal salt solution. The results of these tests are summarized in Tables 24 to 26. Some of the data points are taken from the previous set of experiments for 100 percent dosage and approximately 100:1 soil-treatment chemical ratio. The capacity is given in terms of the weight of metal adsorbed by the treatment chemical per 100 grams of soil. A capacity of 6 mequiv/100 grams soil represents an immobilization efficiency

TABLE 21. TOTAL CAPACITY (MEQUIV/100 GRAMS SOIL) AND IMMOBILIZATION EFFICIENCY FOR MCCLELLAN AFB SOIL-TREATMENT CHEMICAL SYSTEM (100 PERCENT DOSAGE).

Treatment Chemical	Dosage (a)	Soil Chem (b)	Parameter (c)	Cr	Cd	Ni	Cu	Zn
Lime	0.26	392	Cap	0.00	5.29	5.83	5.71	6.25
			K	0.00	0.95	0.98	1.00	0.99
Valfor Z84-326	0.81	123	Cap	0.40	4.43	4.12	5.46	5.23
			K	0.07	0.79	0.70	0.96	0.83
ISX	0.85	118	Cap	0.36	3.45	4.21	5.12	5.00
			K	0.06	0.62	0.71	0.90	0.80
Duolite CS-346	0.88	114	Cap	3.81	2.34	3.03	4.08	3.93
			K	0.69	0.42	0.51	0.71	0.62
Dow XFS-4195C	0.89	113	Cap	3.82	3.54	3.16	4.77	4.63
			K	0.69	0.63	0.53	0.83	0.74
Valfor 200	0.95	106	Cap	0.06	4.83	5.13	5.71	6.02
			K	0.01	0.86	0.87	1.00	0.96
Metal Sorb-7	1.61	62	Cap	0.70	2.96	3.60	4.39	4.01
			K	0.13	0.53	0.61	0.77	0.64
Amberlite IR-124	3.45	29	Cap	0.69	5.38	5.85	5.63	5.17
			K	0.13	0.96	0.99	0.98	0.82
Amberlite IR-718C	3.92	26	Cap	2.61	3.27	4.11	5.47	4.39
			K	0.48	0.58	0.69	0.96	0.70
Ben 125 Bentonite	4.17	24	Cap	0.58	3.27	4.17	4.60	4.70
			K	0.11	0.58	0.70	0.80	0.75
Raw Greensand	6.39	16	Cap	0.42	1.81	2.73	3.45	3.32
			K	0.08	0.32	0.46	0.60	0.53
HMP 20 Bentonite	7.15	14	Cap	0.06	4.03	4.84	5.23	5.54
			K	0.01	0.72	0.82	0.92	0.88
Soil Only	0.00		Cap	0.21	2.41	2.77	3.40	2.61
			K	0.04	0.40	0.48	0.58	0.44

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) Capacity in mequiv metal/100 grams soil; K dimensionless.

TABLE 22. TOTAL CAPACITY (MEQUIV/100 GRAMS SOIL) AND IMMOBILIZATION EFFICIENCY FOR ROBINS AFB SOIL-TREATMENT CHEMICAL SYSTEM (100 PERCENT DOSAGE).

Treatment Chemical	Dosage (a)	Soil Chem (b)	Parameter (c)	Cr	Cd	Ni	Cu	Zn
Lime	0.26	392	Cap	1.56	5.01	5.74	4.79	6.22
			K	0.26	0.90	0.97	0.86	0.99
Valfor Z84-326	0.81	123	Cap	1.79	3.67	2.20	4.89	5.08
			K	0.30	0.66	0.37	0.88	0.81
ISX	0.85	118	Cap	3.06	2.21	2.84	2.72	3.78
			K	0.51	0.40	0.48	0.49	0.60
Duolite CS-346	0.88	114	Cap	5.19	1.58	1.56	2.65	2.48
			K	0.87	0.28	0.26	0.48	0.39
Dow XFS-4195C	0.89	113	Cap	4.95	3.38	2.22	3.61	3.85
			K	0.83	0.43	0.38	0.65	0.61
Valfor 200	0.95	106	Cap	0.98	4.25	4.22	4.99	5.54
			K	0.16	0.76	0.71	0.90	0.88
Metal Sorb-7	1.61	62	Cap	2.31	2.12	2.27	3.16	3.47
			K	0.39	0.38	0.38	0.57	0.55
Amberlite IR-124	3.45	29	Cap	2.02	5.39	5.03	4.97	6.19
			K	0.34	0.96	0.85	0.89	0.98
Amberlite IR-718C	3.92	26	Cap	3.70	2.30	3.12	4.90	3.10
			K	0.62	0.41	0.53	0.88	0.49
Ben 125 Bentonite	4.17	24	Cap	1.44	2.38	2.60	3.46	4.31
			K	0.24	0.43	0.44	0.62	0.69
Raw Greensand	6.39	16	Cap	1.90	1.54	1.68	1.95	2.63
			K	0.32	0.28	0.28	0.35	0.42
HMP 20 Bentonite	7.15	14	Cap	1.79	3.41	4.52	4.71	5.15
			K	0.30	0.61	0.76	0.85	0.82
Soil Only	0.00		Cap	1.79	1.23	1.46	1.87	1.31
			K	0.32	0.20	0.26	0.32	0.22

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) Capacity in mequiv metal/100 grams soil; K dimensionless.

TABLE 23. TOTAL CAPACITY (MEQUIV/100 GRAMS SOIL) AND IMMOBILIZATION EFFICIENCY FOR TINKER AFB SOIL-TREATMENT CHEMICAL SYSTEM (100 PERCENT DOSAGE).

Treatment Chemical	Dosage (a)	Soil Chem (b)	Parameter (c)	Cr	Cd	Ni	Cu	Zn
Lime	0.26	392	Cap	0.98	6.29	5.87	5.72	6.24
			K	0.17	0.97	0.99	1.00	0.99
Valfor Z84-326	0.81	123	Cap	0.33	6.01	5.42	5.71	5.90
			K	0.07	0.93	0.92	1.00	0.94
ISX	0.85	118	Cap	1.64	5.27	5.33	5.64	6.03
			K	0.29	0.81	0.91	0.99	0.96
Duolite CS-346	0.88	114	Cap	3.56	5.04	5.08	5.42	5.44
			K	0.62	0.78	0.86	0.95	0.86
Dow XFS-4195C	0.89	113	Cap	2.41	5.76	5.04	5.75	5.76
			K	0.42	0.89	0.86	1.00	0.92
Valfor 200	0.95	106	Cap	0.00	6.11	5.59	5.72	6.16
			K	-	0.94	0.95	1.00	0.98
Metal Sorb-7	1.61	62	Cap	2.07	5.46	5.06	5.47	5.68
			K	0.36	0.84	0.86	0.96	0.90
Amberlite IR-124	3.45	29	Cap	1.16	6.24	5.89	5.71	6.15
			K	0.20	0.96	1.00	1.00	0.98
Amberlite IR-718C	3.92	26	Cap	3.61	5.89	5.59	5.80	5.85
			K	0.63	0.91	0.95	1.00	0.93
Ben 125 Bentonite	4.17	24	Cap	0.56	5.50	5.33	5.49	5.76
			K	0.10	0.85	0.91	0.96	0.92
Raw Greensand	6.39	16	Cap	1.53	4.58	4.67	5.24	5.45
			K	0.27	0.70	0.79	0.92	0.87
HMP 20 Bentonite	7.15	14	Cap	1.04	5.78	5.58	5.70	6.06
			K	0.18	0.89	0.95	1.00	0.96
Soil Only	0.00		Cap	1.40	4.62	4.64	5.68	4.62
			K	0.26	0.76	0.82	0.92	0.80

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) Capacity in mequiv metal/100 grams soil; K dimensionless.

TABLE 24. TOTAL CAPACITY (MEQUIV/100 GRAMS SOIL) AND IMMOBILIZATION EFFICIENCY FOR MCCLELLAN AFB SOIL-TREATMENT CHEMICAL SYSTEM (100:1 DOSAGE RATE).

Treatment Chemical	Dosage (a)	Soil Chem (b)	Parameter (c)	Cr	Cd	Ni	Cu	Zn
Lime	0.88	114	Cap	1.54	5.80	6.18	5.62	5.70
			K	0.29	1.00	1.06	1.00	1.00
Valfor Z84-326	0.81	123	Cap	0.40	4.43	4.12	5.46	5.23
			K	0.07	0.79	0.70	0.96	0.83
ISX	0.85	118	Cap	0.36	3.45	4.21	5.12	5.00
			K	0.06	0.62	0.71	0.90	0.80
Duolite CS-346	0.88	114	Cap	3.81	2.34	3.03	4.08	3.93
			K	0.69	0.42	0.51	0.71	0.62
Dow XFS-4195C	0.89	113	Cap	3.82	3.54	3.16	4.77	4.63
			K	0.69	0.63	0.53	0.83	0.74
Valfor 200	0.95	106	Cap	0.06	4.83	5.13	5.71	6.02
			K	0.01	0.86	0.87	1.00	0.96
Metal Sorb-7	0.88	114	Cap	1.13	3.00	3.56	3.90	3.09
			K	0.21	0.52	0.61	0.69	0.54
Amberlite IR-124	0.88	114	Cap	0.38	3.84	4.21	4.31	4.01
			K	0.07	0.66	0.72	0.77	0.70
Amberlite IR-718C	0.88	114	Cap	1.54	3.04	3.58	3.68	3.24
			K	0.29	0.52	0.62	0.65	0.57
Ben 125 Bentonite	0.88	114	Cap	0.52	2.24	3.50	3.46	3.09
			K	0.10	0.39	0.60	0.61	0.54
Raw Greensand	0.88	114	Cap	0.50	2.38	3.16	3.30	2.63
			K	0.09	0.41	0.54	0.59	0.46
HMP 20 Bentonite	0.88	114	Cap	0.20	2.88	2.64	3.77	3.31
			K	0.04	0.50	0.45	0.67	0.58
Soil Only	0.00		Cap	0.21	2.41	2.77	3.40	2.61
			K	0.04	0.40	0.48	0.58	0.44

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) (mequiv metal/100 grams soil).

TABLE 25. TOTAL CAPACITY (MEQUIV/100 GRAMS SOIL) AND IMMOBILIZATION EFFICIENCY FOR ROBINS AFB SOIL-TREATMENT CHEMICAL SYSTEM (100:1 DOSAGE RATE).

Treatment Chemical	Dosage (a)	Soil Chem (b)	Parameter (c)	Cr	Cd	Ni	Cu	Zn
Lime	0.88	114	Cap	3.84	5.80	6.19	5.63	5.69
			K	0.71	1.00	1.06	1.00	1.00
Valfor Z84-326	0.81	123	Cap	1.79	3.67	2.20	4.89	5.08
			K	0.30	0.66	0.37	0.88	0.81
ISX	0.85	118	Cap	3.06	2.21	2.84	2.72	3.78
			K	0.51	0.40	0.48	0.49	0.60
Duolite CS-346	0.88	114	Cap	5.19	1.58	1.56	2.65	2.48
			K	0.87	0.28	0.26	0.48	0.39
Dow XFS-4195C	0.89	113	Cap	4.95	2.38	2.22	3.61	3.85
			K	0.83	0.43	0.38	0.65	0.61
Valfor 200	0.95	106	Cap	0.98	4.25	4.22	4.99	5.54
			K	0.16	0.76	0.71	0.90	0.88
Metal Sorb-7	0.88	114	Cap	1.88	1.88	2.42	2.70	2.55
			K	0.35	0.32	0.42	0.48	0.45
Amberlite IR-124	0.88	114	Cap	1.54	3.18	3.55	3.71	3.70
			K	0.29	0.55	0.61	0.66	0.65
Amberlite IR-718C	0.88	114	Cap	2.89	1.80	2.10	2.65	2.17
			K	0.54	0.31	0.36	0.47	0.38
Ben 125 Bentonite	0.88	114	Cap	1.59	1.71	2.30	2.37	2.33
			K	0.29	0.29	0.40	0.42	0.41
Raw Greensand	0.88	114	Cap	1.88	1.62	1.90	2.02	2.02
			K	0.35	0.28	0.33	0.36	0.36
TMP 20 Bentonite	0.88	114	Cap	1.81	1.88	2.64	2.73	2.82
			K	0.34	0.32	0.49	0.48	0.50
Soil Only	0.00		Cap	1.79	1.23	1.46	1.87	1.31
			K	0.32	0.20	0.26	0.32	0.22

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) (mequiv metal/100 grams soil).

TABLE 26. TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR TINKER AFB SOIL-TREATMENT CHEMICAL SYSTEM (100:1 DOSAGE RATE).

Treatment Chemical	Dosage (a)	Soil Chem (b)	Parameter (c)	Cr	Cd	Ni	Cu	Zn
Lime	0.88	114	Cap	0.90	5.80	5.86	5.63	5.69
			K	0.17	1.00	1.01	1.00	1.00
Valfor Z84-326	0.81	123	Cap	0.33	6.01	5.42	5.71	5.90
			K	0.07	0.93	0.92	1.00	0.94
ISX	0.85	118	Cap	1.64	5.27	5.33	5.64	6.03
			K	0.29	0.81	0.91	0.99	0.96
Duolite CS-346	0.88	114	Cap	3.56	5.04	5.08	5.42	5.44
			K	0.62	0.78	0.86	0.95	0.86
Dow XFS-4195C	0.89	113	Cap	2.41	5.76	5.04	5.75	5.76
			K	0.42	0.89	0.86	1.00	0.92
Valfor 200	0.95	106	Cap	0.00	6.11	5.59	5.72	6.16
			K	-	0.94	0.95	1.00	0.98
Metal Sorb-7	0.88	114	Cap	1.74	4.74	5.06	5.35	4.97
			K	0.32	0.82	0.86	0.95	0.87
Amberlite IR-124	0.88	114	Cap	0.30	5.01	5.26	5.42	5.13
			K	0.06	0.86	0.91	0.96	0.90
Amberlite IR-718C	0.88	114	Cap	2.10	4.69	5.24	5.27	4.97
			K	0.39	0.81	0.90	0.94	0.87
Ben 125 Bentonite	0.88	114	Cap	0.98	4.55	5.06	5.30	4.90
			K	0.18	0.78	0.87	0.94	0.86
Raw Greensand	0.88	114	Cap	1.32	4.41	4.99	5.33	4.82
			K	0.24	0.76	0.86	0.95	0.85
HMP 20 Bentonite	0.88	114	Cap	0.95	4.67	5.43	5.52	5.08
			K	0.17	0.81	0.93	0.98	0.89
Soil Only	0.00		Cap	1.40	4.62	4.64	5.68	4.62
			K	0.26	0.76	0.82	0.92	0.80

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) (mequiv metal/100 grams soil).

of 100 percent, providing the concentration of the metal salt solution was exactly 30 mequiv/L. As with the previous set of data, the capacity of each soil for each single metal contaminant is given in the last line of each table.

Based on total capacity and without considering unit treatment chemical costs, several chemical additives seem attractive. For example, lime immobilizes nearly 100 percent of all the single metals except hexavalent chromium. Valfor Z84-326 and Valfor 200 also has high immobilization efficiencies for all metals but hexavalent chromium. Two synthetic chelate ion exchangers, Duolite CS-346 and Dow XFS-4195C exhibit a high degree of chromium (+6) immobilization. The other chemical additives exhibit variable and somewhat lower degrees of immobilization for the single metal contaminants.

The total capacity or immobilization reflects the contributions from both the soil and the treatment additives. The treatment chemicals were ranked according to their net immobilization. The net immobilization effect of the chemical additive for a given metal was determined by calculating the differential capacity, which is defined as the difference between the capacity of the soil-chemical additive system and the capacity of the soil for the given metal (without the chemical additive). Each chemical additive was ranked and compared for their ability to immobilize single heavy metal contaminants according to their differential capacity and their treatment cost, which is defined as follows:

Treatment Cost ($/equiv)

= [Unit Cost ($/kg)]/[Differential Capacity (mequiv metal/gram)] (5)

The best treatment chemicals have low unit costs and/or high differential capacities.

The unit costs for the chemical additives given in Table 27 were obtained from vendor quotes. Tables 28 to 30 rank the four best chemical additives for each contaminant metal, for each soil type, and for each dosage level, according to the treatment cost. The differential capacities are also

shown in the second column for the four top-ranked chemical additives. The differential capacities and treatment costs for all of the treatment chemicals are given in Appendix A.

TABLE 27. UNIT COST ($/KG) OF CHEMICAL ADDITIVES.

Chemical Additive	$/kg
Lime	0.198
Ben 125 Bentonite	0.297
Lime/Ferrous Sulfate[a]	0.31
Valfor 200/Ferrous Sulfate[a]	0.48
Valfor 200	0.551
Greensand	0.617
HMP 20 Bentonite	0.705
Valfor Z84-326	2.20
Metal Sorb-7	2.32
Insoluble Starch Xanthate	3.74
Amberlite IR-124	6.61
Amberlite IRC-718	11.00
Duolite CS-346	11.00
Dow XFS-4195	11.00

[a] In a 1:1 ratio by weight.

The data shows for all single metal contaminants, with the exception of hexavalent chromium:

- Lime and Valfor 200 consistently outranked all the other additives.
- There was very little difference in the rankings between 100 percent dosage and equal dosage by weight.
- The treatment chemicals generally having the lowest treatment cost also had the highest differential capacity. A notable exception was the bentonite clays which had low differential capacities and low unit costs.

TABLE 28. RANKING OF TREATMENT CHEMICALS FOR MCCLELLAN AFB SOIL.

	100 Percent Dosage				Equal Dosage by Weight			
Rank	Treatment Chemical	Soil-Chem (a)	Dif Cap (b)	Cost (c)	Treatment Chemical	Soil-Chem (a)	Dif Cap (b)	Cost (c)
Chromium								
1	Duolite CS-346	114	4.11	2.67	Lime	114	1.52	0.13
2	Dow XFS-4195C	113	4.08	2.70	Ben 125 Bentonite	114	0.35	0.84
3	Ben 125 Bentonite	24	0.09	3.34	Greensand	114	0.33	1.86
4	Metal Sorb-7	62	0.31	7.60	Metal Sorb-7	114	1.05	2.21
Cadmium								
1	Lime	392	11.29	0.02	Lime	114	3.87	0.05
2	Valfor 200	106	2.56	0.22	Valfor 200	106	2.56	0.22
3	Valfor Z84-326	123	2.49	0.88	Valfor Z84-326	123	2.49	0.88
4	Ben 125 Bentonite	24	0.21	1.44	HMP 20 Bentonite	114	0.54	1.31
Nickel								
1	Lime	392	12.00	0.02	Lime	114	3.90	0.05
2	Valfor 200	106	2.50	0.22	Valfor 200	106	2.50	0.22
3	Ben 125 Bentonite	24	0.34	0.88	Ben 125 Bentonite	114	0.83	0.36
4	Valfor Z84-326	123	1.67	1.32	Valfor Z84-326	123	1.67	1.32
Copper								
1	Lime	392	9.06	0.02	Lime	114	2.54	0.08
2	Valfor 200	106	2.44	0.23	Valfor 200	106	2.44	0.23
3	Valfor Z84-326	123	2.54	0.87	Valfor Z84-326	123	2.54	0.87
4	Ben 125 Bentonite	24	0.29	1.03	HMP 20 Bentonite	114	0.42	1.67
Zinc								
1	Lime	392	14.27	0.01	Lime	114	3.53	0.06
2	Valfor 200	106	3.61	0.15	Valfor 200	106	3.61	0.15
3	Ben 125 Bentonite	24	0.50	0.59	Ben 125 Bentonite	114	0.55	0.54
4	Valfor Z84-326	123	3.23	0.68	Valfor Z84-326	123	3.23	0.68

(a) grams soil/gram treatment chemical.
(b) Differential capacity in mequiv metal/gram treatment chemical.
(c) ($/equiv).

TABLE 29. RANKING OF TREATMENT CHEMICALS FOR ROBINS AFB SOIL.

	100 Percent Dosage				Equal Dosage by Weight			
Rank	Treatment Chemical	Soil-Chem (a)	Dif Cap (b)	Cost (c)	Treatment Chemical	Soil-Chem (a)	Dif Cap (b)	Cost (c)
Chromium								
1	ISX	118	1.49	2.50	Lime	114	2.34	0.08
2	Duolite CS-346	114	3.89	2.83	ISX	118	1.49	2.50
3	Dow XFS-4195C	113	3.57	3.08	Duolite CS-346	114	3.89	2.83
4	Metal Sorb-7	62	0.32	7.16	Dow XFS-4195C	113	3.57	3.08
Cadmium								
1	Lime	392	14.82	0.01	Lime	114	5.22	0.04
2	Valfor 200	106	3.20	0.17	Valfor 200	106	3.20	0.17
3	Valfor Z84-326	123	3.01	0.73	Ben 125 Bentonite	114	0.55	0.54
4	Ben 125 Bentonite	24	0.28	1.08	Valfor Z84-326	123	3.01	0.73
Nickel								
1	Lime	392	16.78	0.01	Lime	114	5.41	0.04
2	Valfor 200	106	2.92	0.19	Valfor 200	106	2.92	0.19
3	Ben 125 Bentonite	24	0.27	1.09	Ben 125 Bentonite	114	0.96	0.31
4	HMP 20 Bentonite	14	0.43	1.65	HMP 20 Bentonite	114	1.35	0.52
Copper								
1	Lime	392	11.45	0.02	Lime	114	4.30	0.05
2	Valfor 200	106	3.30	0.17	Valfor 200	106	3.30	0.17
3	Valfor Z84-326	123	3.73	0.59	Ben 125 Bentonite	114	0.57	0.52
4	Ben 125 Bentonite	24	0.38	0.78	Valfor Z84-326	123	3.73	0.59
Zinc								
1	Lime	392	19.25	0.01	Lime	114	5.01	0.04
2	Valfor 200	106	4.48	0.12	Valfor 200	106	4.48	0.12
3	Ben 125 Bentonite	24	0.72	0.41	Ben 125 Bentonite	114	1.17	0.25
4	Valfor Z84-326	123	4.65	0.47	HMP 20 Bentonite	114	1.73	0.41

(a) (grams soil/gram treatment chemical).
(b) Differential capacity in mequiv metal/gram treatment chemical.
(c) ($/equiv).

TABLE 30. RANKING OF TREATMENT CHEMICALS FOR TINKER AFB SOIL.

	100 Percent Dosage				Equal Dosage by Weight			
Rank	Treatment Chemical	Soil-Chem (a)	Dif Cap (b)	Cost (c)	Treatment Chemical	Soil-Chem (a)	Dif Cap (b)	Cost (c)
Chromium								
1	Duolite CS-346	114	2.47	4.46	Duolite CS-346	114	2.47	4.46
2	Metal Sorb-7	62	0.42	5.56	Metal Sorb-7	114	0.39	5.97
3	Dow XFS-4195C	113	1.14	9.64	Dow XFS-4195C	113	1.14	9.64
4	ISX	118	0.28	13.25	ISX	118	0.28	13.25
Cadmium								
1	Lime	392	6.55	0.03	Lime	114	1.35	0.15
2	Valfor 200	106	1.58	0.35	Valfor 200	106	1.58	0.35
3	Valfor Z84-326	123	1.72	1.28	Valfor Z84-326	123	1.72	1.28
4	Ben 125 Bentonite	24	0.21	1.41	ISX	118	0.76	4.89
Nickel								
1	Lime	392	4.82	0.04	Lime	114	1.39	0.14
2	Valfor 200	106	1.01	0.55	Valfor 200	106	1.01	0.55
3	Ben 125 Bentonite	24	0.17	1.79	Ben 125 Bentonite	114	0.48	0.62
4	Valfor Z84-326	123	0.96	2.28	HMP 20 Bentonite	114	0.90	0.78
Copper								
1	Lime	392	0.16	1.26	Valfor 200	106	0.04	13.02
2	Valfor 200	106	0.04	13.02	Valfor Z84-326	123	0.04	59.40
3	Valfor Z84-326	123	0.04	59.40	Dow XFS-4195C	113	0.08	139.07
4	Dow XFS-4195C	113	0.08	139.07				
Zinc								
1	Lime	392	6.35	0.03	Lime	114	1.22	0.16
2	Valfor 200	106	1.63	0.34	Valfor 200	106	1.63	0.34
3	Ben 125 Bentonite	24	0.27	1.09	Ben 125 Bentonite	114	0.32	0.93
4	Valfor Z84-326	123	1.58	1.39	HMP 20 Bentonite	114	0.53	1.34

(a) (grams soil/gram treatment chemical).
(b) Differential capacity in mequiv metal/gram treatment chemical.
(c) ($/equiv).

- The treatment costs were lower and the differential capacities were higher for the McClellan and Robins AFB soils than for the Tinker AFB soil. This is consistent with the higher soil capacity of the Tinker AFB soil (see Table 20).
- For the two best chemical additives, the treatment costs ranged from $0.01/equiv to $0.23/equiv for the McClellan and Robins AFB soils, and with the exception of copper from $0.03/equiv to $0.55/equiv for the Tinker AFB soil.

Lime ranked first for the McClellan AFB and Robins AFB soils as a cost-effective treatment for hexavalent chromium at $0.13/equiv, but did not appear to be an effective treatment chemical for hexavalent chromium for the Tinker AFB soil. This latter effect could be related to the low dosages used; data on higher dosages for the Tinker AFB soil is given below. The most cost-effective treatment for hexavalent chromium in the Tinker AFB soil is the synthetic chelating resin Duolite CS-346 at $4.45/equiv.

The next best chemicals for the treatment of hexavalent chromium were BEN 125 Bentonite for the McClellan AFB soil at $0.81/equiv, insoluble starch xanthate (ISX) for the Robins soil at $2.48/equiv, and Metal Sorb-7 for the Tinker AFB soil at $5.95/equiv. Since these chemicals, as well as Duolite CS-346, are expensive relative to lime and Valfor 200 addition for the treatment of the other contaminant metals, ferrous sulfate was investigated as an alternative treatment chemical. In the preliminary screening tests, ferrous sulfate addition with pH adjustment by lime, was found to be very effective in immobilizing chromium (+6) (see Table 19).

Hexavalent chromium, Cr^{+6}, can be reduced to the less toxic, less mobile trivalent chromium state, Cr^{+3}, with ferrous sulfate. Ferrous sulfate is a nontoxic, inexpensive ($0.40/kg) reducing agent. Theoretically, once in the Cr^{+3} form, it can be precipitated with lime as chromium hydroxide, $Cr(OH)_3$, or adsorbed onto Valfor 200 by ion exchange. Lime/ferrous sulfate and Valfor 200/ferrous sulfate combinations were tested on the three soils to determine their effect on hexavalent chromium immobilization. A quantity of 1.75 grams of lime or Valfor 200 was added to 200 grams of soil, consistent with the other batch tests. Then 1.67 grams of ferrous sulfate heptahydrate

was added to the mixture of soil and lime (and soil and Valfor 200). This amount of ferrous sulfate represents the stoichiometric amount of Fe^{+2} needed to reduce 12 mequiv of Cr^{+6} to Cr^{+3}.

Table 31 ranks the treatment chemicals for chromium (+6) immobilization and includes the lime/ferrous sulfate and Valfor 200/ferrous sulfate test data. The results clearly show that lime/ferrous sulfate and particularly Valfor 200/ferrous sulfate are viable alternatives for Cr^{+6} immobilization relative to the other expensive treatment chemicals discussed above. The costs of the two best treatments for chromium (+6) immobilization for each soil ranged from $0.08/equiv to $0.27/equiv, consistent with the treatment costs for the immobilization of the four other metals. The test data showed that the combination of soil and lime/ferrous sulfate treatment immobilized 50 percent of the total Cr^{+6} found in the soil, while soil and Valfor 200/ferrous sulfate immobilized 100 percent of Cr^{+5}, making this latter immobilization method exceptionally effective and inexpensive.

The preliminary screening tests showed that lime and Valfor 200, either alone or in combination with ferrous sulfate, were the best chemical additives capable of immobilizing single metal contaminants in each of the three soils at the lowest treatment cost. The remainder of the test program focused on obtaining more detailed data on the use of these chemicals for treating contaminated soils on a batch basis and in soil columns.

4. Effect of Chemical Dosage on Metal Immobilization

The single dosage tests just described were extended to include a range of treatment chemical dosages. The single metal concentration was again set equal to 30 mequiv/L. The dosages used in the test program corresponded approximately to soil-to-chemical additive weight ratios of 800:1, 400:1, 100:1 and 75:1. Tables 32 and 33 show the total capacities and immobilization efficiencies for both lime and Valfor 200 addition as a function of the dosage rate for soils contaminated with single metals. Baseline data showing the capacity of the soil without the addition of any treatment chemicals is also given. The results clearly indicate at 400:1 or less soil-to-lime weight ratios, the contaminant metals Cd, Cu, Ni and Zn are

TABLE 31. RANKING OF TREATMENT CHEMICALS FOR CHROMIUM (+6) IMMOBILIZATION.

Rank	Treatment Chemical	Tot Cap (mequiv/100 grams)	K	Diff Cap (mequiv/gram)	Cost ($/equiv)
McClellan AFB Soil		0.21	0.04		
1	Lime[a]	1.54	0.29	1.52	0.13
2	Valfor 200/$FeSO_4$[b]	6.00	1.00	3.39	0.14
3	Lime/$FeSO_4$[c]	3.06	0.51	1.67	0.19
4	Ben 125 Bentonite[a]	0.52	0.11	0.35	0.84
Robins AFB Soil		1.79	0.32		
1	Lime[a]	3.84	0.71	2.34	0.08
2	Valfor 200/$FeSO_4$[b]	6.00	1.00	2.46	0.20
3	Lime/$FeSO_4$[c]	3.15	0.53	0.80	0.39
4	ISX[d]	3.06	0.51	1.49	2.50
Tinker AFB Soil		1.40	0.26		
1	Valfor 200/$FeSO_4$[b]	6.00	1.00	2.69	0.18
2	Lime/$FeSO_4$[c]	3.38	0.56	1.16	0.27
3	Duolite CS-346[a]	3.56	0.62	2.47	4.46
4	Metal Sorb-7[a]	1.74	0.32	0.39	5.97

[a] 114 grams soil/gram treatment chemical.
[b] 114 grams soil/gram Valfor 200; 1.67 grams $FeSO_4$/1.75 grams Valfor 200.
[c] 114 grams soil/gram lime; 1.67 grams $FeSO_4$/1.75 grams lime.
[d] 118 grams soil/gram ISX.

over 90 percent immobilized (except for Robins AFB soil contaminanted with copper). The data on chromium immobilization with lime addition is not as consistent. Both the Robins AFB and Tinker AFB soils exhibit a high capacity for chromium relative to the McClellan AFB soil without lime addition. However, for the Robins AFB soil, the chromium capacity is generally enhanced with increased lime dosage, while the addition of lime to the Tinker soil enhances chromium mobility. The addition of lime to the McClellan AFB soil generally increases chromium immobilization.

Each data point shown in Tables 32 and 33 correspond to generally one test point taken per dosage. Approximately 10 percent of the tests were

repeated for quality control. Tests were also repeated if there were any apparent inconsistencies in data trends.

The test results for the effect of Valfor 200 dosage (Table 33) for the immobilization of Ni, Cu, Cd and Zn are consistent with those for lime (Table 32). However, at the same value of the chemical dosage, metal immobilization appears to be better with lime than with Valfor 200.

TABLE 32. EFFECT OF CHEMICAL DOSAGE ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOIL CONTAMINATED WITH SINGLE METALS AND TREATED WITH LIME.

			Soils					
			McClellan AFB		Robins AFB		Tinker AFB	
Metal	Dosage (a)	Soil-Chem (b)	Cap (c)	K	Cap (c)	K	Cap (c)	K
Cr	0.00		0.21	0.04	1.79	0.32	1.40	0.26
	0.13	800	0.02	0.01	4.33	0.79	1.24	0.23
	0.26	392	0.00	0.00	1.56	0.26	0.98	0.17
	0.88	114	1.54	0.29	3.84	0.71	0.90	0.17
	1.30	77	2.74	0.50	5.26	0.96	0.60	0.11
Cd	0.00		2.41	0.40	1.23	0.20	4.62	0.80
	0.13	800	4.44	0.75	3.42	0.58	5.37	0.91
	0.26	392	5.29	0.95	5.01	0.90	6.29	0.97
	0.88	114	5.80	1.00	5.80	1.00	5.80	1.00
Ni	0.00		2.77	0.48	1.46	0.26	4.64	0.93
	0.13	800	5.10	0.88	3.61	0.62	5.48	0.94
	0.26	392	5.83	0.98	5.74	0.97	5.87	0.99
	0.88	114	6.18	1.06	6.19	1.06	5.86	1.00
Cu	0.00		3.40	0.58	1.87	0.32	5.68	0.97
	0.13	800	4.87	0.93	3.83	0.73	5.21	0.99
	0.26	392	5.71	1.00	4.79	0.86	5.72	1.00
	0.88	114	5.62	1.00	5.63	1.00	5.63	1.00
Zn	0.00		2.63	0.41	1.31	0.22	4.62	0.80
	0.13	800	4.77	0.80	4.01	0.67	5.69	1.00
	0.26	392	6.25	0.99	6.22	0.99	6.24	0.99
	0.88	114	5.70	1.00	5.69	1.00	5.69	1.00

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) (mequiv metal/100 grams soil).

TABLE 33. EFFECT OF CHEMICAL DOSAGE ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOIL CONTAMINATED WITH SINGLE METALS AND TREATED WITH VALFOR 200.

			Soils					
			McClellan AFB		Robins AFB		Tinker AFB	
Metal	Dosage (a)	Soil-Chem (b)	Cap (c)	K	Cap (c)	K	Cap (c)	K
Cr	0.00		0.21	0.04	1.79	0.32	1.40	0.26
	0.25	400	0.00	0.00	1.35	0.25	1.12	0.20
	0.95	106	0.06	0.01	0.98	0.16	0.00	0.00
	1.30	77	1.06	0.19	0.00	0.00	0.20	0.03
Cd	0.00		2.41	0.40	1.23	0.20	4.62	0.80
	0.25	400	3.63	0.62	2.57	0.44	5.02	0.85
	0.95	106	4.83	0.86	4.25	0.76	6.11	0.94
	1.30	77	5.69	0.96	5.55	0.94	5.80	0.98
Ni	0.00		2.77	0.48	1.46	0.26	4.64	0.93
	0.25	400	3.54	0.61	2.47	0.43	5.15	0.89
	0.95	106	5.13	0.87	4.23	0.71	5.60	0.95
	1.30	77	5.25	0.90	5.37	0.93	5.64	0.97
Cu	0.00		3.40	0.58	1.87	0.32	5.68	0.97
	0.25	400	4.14	0.79	2.76	0.53	5.13	0.98
	0.95	106	5.71	1.00	4.99	0.90	5.72	1.00
	1.30	77	5.21	0.99	5.21	0.99	5.21	0.99
Zn	0.00		2.61	0.41	1.31	0.22	4.62	0.80
	0.25	400	4.08	0.61	3.01	0.50	5.54	0.92
	0.95	106	6.02	0.96	5.54	0.88	6.16	0.98
	1.30	77	5.89	0.98	5.84	0.97	5.97	0.99

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) (mequiv metal/100 grams soil).

The effect of Valfor 200 dosage on the capacity (and mobility) of hexavalent chromium is different for the three contaminated soils. Chromium immobilization in the McClellan AFB soil first decreases and then gradually increases with increasing Valfor 200 dosage. However, for the Robins AFB soil, the addition of Valfor 200 enhances the mobility of hexavalent chromium, while for the Tinker AFB soil the mobility of hexavalent chromium also increases but then decreases as the dosage is increased. The difference in the mobility of hexavalent chromium may be explained by the difference in the soil pH. Chromium immobilization in soil is a function of soil pH.

Chromium is amphoteric and will precipitate under certain alkaline conditions, but will resolubilize when the pH of the environment exceeds its isoelectric point. Valfor 200 is an alkali compound and will increase the pH of the soil in a manner very similar to that of lime; this may account for its ineffectiveness to immobilize hexavalent chromium. However, this explanation was not confirmed experimentally because soil pH was not measured as a function of dosage.

5. Soils:Chemical Additives:Multiple Metal Contaminant Interactions

The single metal tests using Valfor 200 and lime were extended to include multiple metal solutions and the effect of ferrous sulfate addition. For the multiple metal solutions, the total contaminant metal concentration was equal to 30 mequiv/L with all of the metals having the same mequiv/L concentration. Multiple metal solutions of Cr-Ni-Cd and Cr-Ni-Cd-Cu-Zn were mixed with 200 grams of soil and the treatment chemicals in various dosages. The capacities and immobilization efficiencies were obtained for each treatment chemical and for each metal in solution. The test results for the three soils contaminated with Cr-Ni-Cd and treated with lime and Valfor 200 are shown in Table 34. The test results for the soils contaminated with Cr-Ni-Cd-Cu-Zn and treated with lime are shown in Table 35 and with Valfor 200 in Table 36. The dosages corresponded approximately to soil-to-chemical additive ratios of 800:1, 400:1, 100:1 and 75:1. The two dosages of 400:1 and 100:1 were applied to both lime and Valfor 200 so that a direct comparison of the capacity and immobilizaton efficiency as a function of dosage could be made between the two treatment chemicals and to the results for the soils contaminated with the single metals.

The test results for the multiple metal solutions are consistent with those of the single metal solutions. The multiple metal tests with lime addition indicates that chromium immobilization is greatest when the McClellan AFB soil is slightly "sweetened" at a 800:1 soil-to-lime ratio. Any increase in lime dosage causes a decrease in chromium capacity similar to the Tinker soil. Lime and Valfor 200 appear to be a viable treatment chemical for immobilizing Cu, Ni, Cd, and Zn singularly and in combination

TABLE 34. EFFECT OF CHEMICAL DOSAGE ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOIL CONTAMINATED WITH MULTIPLE METALS (Cr, Cd, Ni) AND TREATED WITH LIME AND VALFOR 200.

			Soils					
			McClellan AFB		Robins AFB		Tinker AFB	
Metal	Dosage (a)	Soil-Chem (b)	Cap (c)	K	Cap (c)	K	Cap (c)	K
Lime								
Cr	0.00		0.29	0.16	1.19	0.66	0.95	0.52
	0.13	800	1.90	0.99	1.39	0.73	1.41	0.74
	0.26	392	1.39	0.73	1.13	0.59	0.79	0.42
	0.88	114	1.13	0.59	1.43	0.75	0.36	0.19
Cd	0.00		0.95	0.50	0.50	0.28	1.45	0.84
	0.13	800	1.63	0.80	1.21	0.59	1.94	0.95
	0.26	392	2.01	0.99	1.99	0.98	2.01	0.99
	0.88	114	2.13	1.00	2.03	2.03	2.03	1.00
Ni	0.00		1.30	0.66	0.75	0.44	1.63	0.96
	0.13	800	1.80	0.91	1.67	0.84	1.96	0.98
	0.26	392	1.98	0.99	1.97	0.99	1.98	0.99
	0.88	114	1.98	0.99	1.98	0.99	1.98	0.99
Valfor 200								
Cr	0.00		0.29	0.16	1.19	0.66	0.95	0.52
	0.25	400	0.12	0.06	0.84	0.44	0.81	0.42
	0.95	106	0.00	0.00	0.42	0.22	0.37	0.20
	1.30	77	0.01	0.01	0.25	0.13	0.19	0.10
Cd	0.00		0.95	0.50	0.50	0.28	1.45	0.84
	0.25	400	1.52	0.75	0.98	0.48	1.89	0.93
	0.95	106	1.99	0.98	1.89	0.93	2.01	0.98
	1.30	77	2.02	0.99	2.02	0.99	2.02	0.99
Ni	0.00		1.30	0.66	0.75	0.44	1.63	0.96
	0.25	400	1.45	0.73	1.18	0.59	1.85	0.94
	0.95	106	1.84	0.93	1.80	0.91	1.94	0.98
	1.30	77	1.95	0.98	1.96	0.99	1.96	0.99

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(c) (mequiv metal/100 grams soil).

with the contaminant metals. However, lime and Valfor 200 by themselves, do not appear to immobilize hexavalent chromium.

The effect of ferrous sulfate addition, in combination with either lime or Valfor 200 treatment, on hexavalent chromium immobilization was also carried out. A fixed amount (0.5 grams) of ferrous sulfate was added to each soil contaminated with all five metals together and with hexavalent chromium alone. For the hexavalent chromium alone, the quantity of ferrous sulfate is lower than the stoichiometric amount theoretically required to reduce hexavalent chromium to its trivalent form. A ferrous sulfate dosage of 1.67 grams represents the stoichiometric amount of Fe^{+2} needed to reduce 12 mequiv of Cr^{+6} to Cr^{+3}. For the five metals together, the quantity of ferrous sulfate is 50 percent more than the stoichiometric amount (0.33 grams).

TABLE 35. EFFECT OF CHEMICAL DOSAGE ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOIL CONTAMINATED WITH MULTIPLE METALS (Cr, Cd, Ni, Cu, Zn) AND TREATED WITH LIME.

			Soils					
		Soil-	McClellan AFB		Robins AFB		Tinker AFB	
Metal	Dosage (a)	Chem (b)	Cap (c)	K	Cap (c)	K	Cap (c)	K
Cr	0.13	800	0.40	0.35	0.76	0.67	0.71	0.63
	0.25	400	0.24	0.21	0.70	0.62	0.47	0.42
	0.95	105	0.18	0.16	0.90	0.79	0.37	0.32
Cd	0.13	800	0.80	0.68	0.46	0.40	1.04	0.89
	0.25	400	1.15	0.98	1.13	0.97	1.15	0.87
	0.95	105	1.17	1.00	1.17	1.00	1.17	1.00
Ni	0.13	800	0.91	0.78	0.72	0.62	1.13	0.97
	0.25	400	1.16	0.99	1.16	0.99	1.16	0.99
	0.95	105	1.16	0.99	1.16	0.99	1.16	0.99
Cu	0.13	800	1.13	0.99	1.13	0.99	1.13	0.99
	0.25	400	1.13	0.99	1.13	0.99	1.13	0.99
	0.95	105	1.13	0.99	1.13	0.99	1.13	0.99
Zn	0.13	800	1.00	0.89	0.90	0.79	1.11	0.98
	0.25	400	1.13	1.00	1.13	1.00	1.13	1.00
	0.95	105	1.13	1.00	1.13	1.00	1.13	1.00

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(b) (mequiv metal/100 grams soil).

TABLE 36. EFFECT OF CHEMICAL DOSAGE ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOIL CONTAMINATED WITH MULTIPLE METALS (Cr, Cd, Ni, Cu, Zn) AND TREATED WITH VALFOR 200.

			Soils					
		Soil-	McClellan AFB		Robins AFB		Tinker AFB	
Metal	Dosage (a)	Chem (b)	Cap (c)	K	Cap (c)	K	Cap (c)	K
Cr	0.25	400	0.09	0.08	0.58	0.52	0.59	0.52
	0.95	105	0.00	0.00	0.42	0.37	0.32	0.28
	1.30	77	0.00	0.00	0.19	0.17	0.11	0.10
Cd	0.25	400	0.69	0.59	0.29	0.24	1.02	0.87
	0.95	105	1.11	0.95	0.95	0.81	1.14	0.98
	1.30	77	1.16	0.99	1.15	0.99	1.16	0.99
Ni	0.25	400	0.78	0.66	0.53	0.45	1.06	0.91
	0.95	105	1.06	0.90	1.05	0.90	1.14	0.98
	1.30	77	1.13	0.97	1.15	0.98	1.15	0.99
Cu	0.25	400	1.11	0.98	1.02	0.90	1.13	0.99
	0.95	105	1.13	0.99	1.13	0.99	1.13	0.99
	1.30	77	1.13	0.99	1.13	0.99	1.13	0.99
Zn	0.25	400	0.85	0.76	0.64	0.55	1.08	0.96
	0.95	105	1.09	0.96	1.08	0.96	1.11	0.98
	1.30	77	1.11	0.99	1.12	0.99	1.12	0.99

(a) (grams treatment chemical/100 grams soil).
(b) (grams soil/gram treatment chemical).
(b) (mequiv metal/100 grams soil).

The test results for the treatment of the soils with lime/ferrous sulfate and Valfor 200/ferrous sulfate are shown in Tables 37 and 38. Table 37 shows for soils contaminated with only Cr^{+6}, Valfor 200/ferrous sulfate is more effective than lime/ferrous sulfate at the highest dosage. Because the quantity of ferrous sulfate is approximately one-third of the stoichiometric amount required for Cr^{+6} reduction, the immobilization efficiency for Cr^{+6} is fairly low. As the lime dosage is increased, the soil pH increases and the conditions under which chromium hydroxide is formed are not favorable (29).

TABLE 37. EFFECT OF FERROUS SULFATE ADDITION ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOILS CONTAMINATED WITH CHROMIUM (+6).

Treatment Chemical	Dosage (a)	Soils: McClellan AFB Cap (b)	McClellan AFB K	Robins AFB Cap (b)	Robins AFB K	Tinker AFB Cap (b)	Tinker AFB K
Lime/$FeSO_4$	0.00/0.25	3.01	0.49	4.11	0.66	4.69	0.76
	0.13/0.25	3.47	0.56	4.69	0.76	3.88	0.63
	0.25/0.25	2.55	0.41	3.53	0.57	3.42	0.5[illegible]
	0.88/0.25	0.53	0.08	2.55	0.41	1.74	[illegible]
Valfor 200/ $FeSO_4$	0.88/0.25	2.20	0.36	3.70	0.60	3.94	0.63

(a) (grams treatment chemical/100 grams soil).
(b) (mequiv metal/100 grams soil).

In the multiple metal tests, where all five metals were combined, all of the five metals were virtually immobilized at the highest lime/ferrous sulfate dosage. Similar results also applied at the second highest dosage except for the immobilization of cadmium. A comparison between Tables 35 and 38 shows that increasing the dosage of ferrous sulfate at a given lime dosage generally reduces the immobilization efficiency of Cd, Ni, Cu and Zn, but increases the mobility of chromium (+6). Because the ferrous sulfate dosage is 50 percent higher than the stoichiometric requirement for Cr^{+6} reduction, almost all of the Cr^{+6} is immobilized independent of the lime dosage (or pH variation). This result is in contrast to the result for single metal (Cr^{+6}) soil contamination shown in Table 37, in which the ferrous sulfate dosage is one-third of the stoichiometric amount.

Cr, Ni and Cu were virtually immobilized at the Valfor 200/ferrous sulfate dosage used in the test program, but Cd and Zn were still not fully adsorbed on Valfor 200. This result cannot be explained by the selectivity characteristics of Valfor 200 shown in Section 3B.5 because Valfor 200 has a higher selectivity for Cd and Zn than for Ni and Cu and a much higher immobilization efficiency for Cd and Zn would be expected. However, selectivity is dependent upon pH and because the pH for the data

TABLE 38. EFFECT OF FERROUS SULFATE ADDITION ON TOTAL CAPACITY (MEQUIV/100 GRAMS) AND IMMOBILIZATION EFFICIENCY FOR SOILS CONTAMINATED WITH MULTIPLE METALS (Cr, Cd, Ni, Cu, Zn).

		Soils					
		McClellan AFB		Robins AFB		Tinker AFB	
Metal	Dosage (a)	Cap (b)	K	Cap (b)	K	Cap (b)	K
Lime-Ferrous Sulfate							
Cr	0.00/0.25	1.23	0.99	1.23	0.99	1.23	0.99
	0.13/0.25	1.23	0.99	1.23	0.99	1.23	0.99
	0.25/0.25	1.23	0.99	1.23	0.99	1.23	0.99
	0.88/0.25	1.23	0.99	1.23	0.99	1.23	0.99
Cd	0.00/0.25	0.24	0.20	0.20	0.16	0.03	0.02
	0.13/0.25	0.48	0.40	0.27	0.22	0.24	0.20
	0.25/0.25	0.42	0.35	0.45	0.37	0.93	0.78
	0.88/0.25	1.20	1.00	1.20	1.00	1.20	1.00
Ni	0.00/0.25	1.01	0.85	0.96	0.81	0.95	0.80
	0.13/0.25	1.05	0.88	0.99	0.82	1.05	0.88
	0.25/0.25	1.16	0.97	1.02	0.86	1.19	0.99
	0.88/0.25	1.19	0.99	1.19	0.99	1.19	0.99
Cu	0.00/0.25	1.05	0.93	0.97	0.85	1.12	0.98
	0.13/0.25	1.19	0.98	1.03	0.91	1.13	0.99
	0.25/0.25	1.13	0.99	1.13	0.99	1.13	0.99
	0.88/0.25	1.13	0.99	1.13	0.99	1.13	0.99
Zn	0.00/0.25	0.46	0.41	0.28	0.25	0.31	0.27
	0.13/0.25	0.73	0.66	0.46	0.41	0.87	0.78
	0.25/0.25	1.15	1.01	1.01	0.90	1.16	1.03
	0.88/0.25	1.16	1.04	1.16	1.04	1.16	1.04
Valfor 200-Ferrous Sulfate							
Cr	0.88/0.25	1.23	0.99	1.23	0.99	1.23	0.99
Cd	0.88/0.25	0.27	0.22	0.57	0.48	0.82	0.69
Ni	0.88/0.25	0.93	0.78	1.07	0.90	1.13	0.95
Cu	0.88/0.25	1.13	0.99	1.13	0.99	1.13	0.99
Zn	0.88/0.25	0.64	0.57	0.02	0.01	1.14	1.01

(a) (grams treatment chemical/100 grams soil).
(b) (mequiv metal/100 grams soil).

given in Section 3B.5 is not known a meaningful comparison between the laboratory and selectivity data cannot be made at this time. A comparison between Tables 36 and 38 again showed that ferrous sulfate addition decreases the immobilization efficiency of Cd, Ni, Cu and Zn, and increases the immobilization efficiency of Cr^{+6}. At the highest dosage, both lime/ferrous sulfate and Valfor 200/ferrous sulfate have the same capacity for chromium (see Table 38).

The total capacities and immobilization efficiencies of the soil/lime/ferrous sulfate system are generally higher than the soil/Valfor 200/ferrous sulfate system.

In summary, the addition of ferrous sulfate in combination with either lime or Valfor 200 (with lime or Valfor 200 dosage constant) tends to increase the mobility of Cd, Ni, Cu and Zn in the three soils tested, but increases the immobilization of Cr^{+6}. At the highest lime/ferrous sulfate dosages tested, all of the contaminant metals were virtually immobilized. Although Cd and Zn were relatively mobile at the Valfor 200/ferrous sulfate dosage [illegible], it would appear that by increasing the dosage further, all of the contaminant metals would also be completely immobilized.

The remainder of the test program focused on testing the effectiveness of lime and Valfor 200 treatment with and without ferrous sulfate addition in various soil column configurations.

C. DYNAMIC FLOW COLUMN TEST PROGRAM

As discussed in Section 4A.2, each column was packed to a height of 6 inches with soil at its native density. Before packing the columns, the requisite amount of treatment chemicals was added to the bulk soil and thoroughly mixed by the standard cone and quartering method. Once the columns were packed, each soil column was saturated under a vacuum with deionized water to remove entrained air. Metal salt solutions containing the contaminant metals were then passed through the columns. Preliminary tests indicated the Tinker AFB soil was incompatible with soil column testing because of its low permeability and was not used in the column test program.

At all times, the flow rates in the Robins AFB and McClellan AFB soils were maintained at realistic field conditions, at permeabilities corresponding to 10.6×10^{-4} to 11.4×10^{-4} cm/sec (3.8-4.1 cm/hr) (see Table 4). For the Robins AFB soil, each of the metal solutions was gravity-fed through the column at an average rate of 45 mL/hr. For the McClellan AFB soils, inconsistent flow rates through the columns, due to variations in soil packing, were rectified by regulating the flow rate at approximately 40 mL/hr with low volume peristaltic pumps.

Single and multiple metal solutions containing a total metal concentration of 30 mequiv/L and a natural pH of approximately 4.2 were passed through the columns and 10-20 mL aliquots of the effluent were gathered at periodic intervals and analyzed for the contaminant metals on a Perkin-Elmer Atomic Absorption Spectrophotometer. The composition and the salts used in the solutions are given in Table 13 and were the same as those used in the batch screening test program. In the case of multiple metal solutions all of the individual metal concentrations had the same mequiv/L concentration. The data collected showed the relationship between the pore volumes passed through the soil columns as a function of the effluent concentration expressed in terms of C/C_o. The tests were terminated when the effluent concentration, C, equaled the influent concentration, C_o, or when $C/C_o = 1.0$. The capacity of the soil-chemical additive system was equal to the absolute milliequivalent difference between the influent and effluent streams.

The pore volume, or the quantity of water within the pores of the saturated soil samples, was calculated using the following relationship:

$$V(p) = V(w) - V(s) \tag{6}$$

where:

V(p) = Pore volume (cc)

V(w) = Whole volume of soil in column (cc)

V(s) = Solid volume of soil (cc)

= Weight of soil added to column (cc)/specific gravity (g/cc)

The determination of specific gravity of the soil was calculated using the procedures outlined in ASTM Standard D-854-58 (Reference 35). The pore volumes in the packed McClellan AFB and Robins AFB soil columns were 95 and 75 cc, respectively.

An overview of the dynamic flow column test program is shown in Figure 11. Control tests were carried out by packing only the soil (without the treatment chemicals) in the columns, as described above, and passing single and multiple metal solutions through the columns. The capacity of the soil system was equal to the absolute milliequivalent difference between the influent and effluent streams. Table 39 summarizes the capacities of the two soils for various multiple metal combinations and compares the results for the column tests with the batch tests (see Table 20). The soil capacities for the column tests are much higher than for the batch tests.

The capacities and immobilization efficiencies of the Robins and McClellan soils were determined for the three multiple metal contaminant combinations, Cr-Ni-Cd, Cr-Ni and Cr-Cd. Each soil was treated with lime and Valfor 200/ferrous sulfate at three different dosages. Because precipitation is the mechanism of immobilization in lime-treated soil, pH was the basis for determining dosage for the lime experiments. The amount of lime added to the soil correlates to soil pHs 7.0, 8.5 and 10.0. For McClellan AFB soil, the lime dosage corresponds to 0.012, 0.042, and 0.12 grams lime/100 grams soil, respectively, while, for the Robins AFB soil the dosages are 0.044, 0.10, and 0.20 grams lime/100 grams soil, respectively. Valfor 200/ferrous sulfate was added at a weight ratio of 1:1 and at soil-to-Valfor 200 weight ratios of 200:1, 100:1 and 50:1; the soil-to-total chemical additive weight ratios were 100:1, 50:1 and 25:1. These dosages were consistent with the dosages applied in the batch equilibrium tests.

Table 40 summarizes the total capacity data for soils treated with lime and Valfor 200/ferrous sulfate at three different dosages. The data show that the total metal capacities and the individual metal capacities generally increase as the dosage is increased. Exceptions are found in the chromium capacity in the Cr-Cd and Cr-Ni systems with lime addition. In the Cr-Cd system, the chromium capacity is a maximum at pH 8.5 for the Robins AFB soil

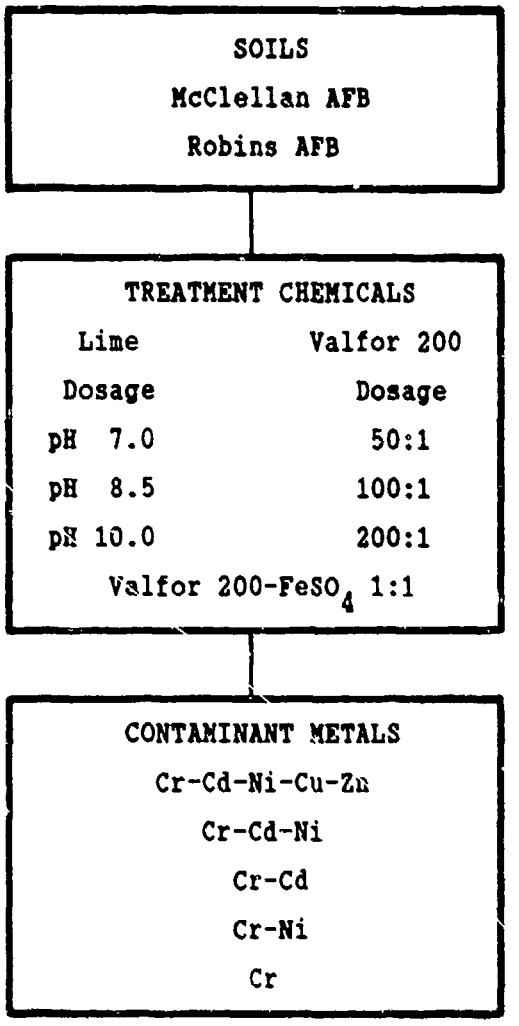


Figure 11. Overview of Dynamic Flow Column Test Program.

TABLE 39. SOIL CAPACITY (MEQUIV/100 GRAMS SOIL) FOR MULTIPLE METAL CONTAMINANTS.

		Soil Capacity (mequiv/100 grams)		
Soil	Test	Cr-Cd-Ni	Cr-Cd	Cr-Ni
McClellan AFB	Column	0.75-1.86-1.62(4.23)[a]	0.88-2.16(3.04)	0.97-2.13(3.10)
	Batch	0.29-0.95-1.30(2.54)	0.51-0.94(1.45)	0.17-1.89(2.06)
Robins AFB	Column	1.98-1.23-0.59(3.80)	2.56-1.60(4.16)	2.34-1.23(3.57)
	Batch	1.19-0.50-0.85(2.44)	1.31-0.94(2.25)	1.23-1.87(3.10)

[a] Numbers in parenthesis indicate totals.

TABLE 40. EFFECT OF DOSAGE ON TOTAL SOIL COLUMN CAPACITY (MEQUIV/100 GRAMS SOIL) FOR MULTIPLE METAL CONTAMINANTS.

Chemical Additive	Dosage	Capacity (mequiv/100 grams soil) Cr-Cd-Ni	Cr-Cd	Cr-Ni
McClellan AFB				
Soil Only		0.75-1.86-1.62 (4.2)[a]	0.88-2.16 (3.0)	0.97-2.13 (3.1)
Lime	pH 7.0	1.97-1.23-2.45 (5.7)	2.59-3.65 (6.2)	1.26-3.68 (4.9)
Lime	pH 8.5	1.41-1.72-3.47 (6.6)	2.45-4.99 (7.4)	2.03-4.62 (6.7)
Lime	pH 10.0	2.50-3.89-4.77(11.2)	1.78-6.14 (7.9)	1.81-6.00 (7.8)
Val 200/$FeSO_4$	200:1[b]	3.26-1.37-2.97 (7.6)	4.36-4.13 (8.5)	3.34-2.56 (5.9)
Val 200/$FeSO_4$	100:1[b]	5.25-2.02-3.33(10.6)	6.70-4.82(11.5)	7.40-4.59(12.0)
Val 200/$FeSO_4$	50:1[b]	16.11-7.61-7.01(30.7)	13.66-5.88(19.5)	11.38-5.71(17.1)
Robins AFB				
Soil Only		1.98-1.23-0.59 (3.8)	2.56-1.60 (4.2)	2.34-1.23 (3.6)
Lime	pH 7.0	2.42-0.82-1.87 (5.1)	2.56-1.60 (4.2)	3.24-2.15 (5.4)
Lime	pH 8.5	3.25-1.46-2.58 (7.3)	4.23-2.71 (6.9)	4.28-3.61 (7.8)
Lime	pH 10.0	4.10-2.74-4.32(11.2)	3.12-4.88 (8.0)	4.91-5.73(10.6)
Val 200/$FeSO_4$	200:1[b]	3.40-0.66-1.41 (5.5)	5.39-0.59 (6.0)	3.96-1.90 (5.9)
Val 200/$FeSO_4$	100:1[b]	8.44-4.62-5.08(18.1)	7.48-1.56 (9.0)	13.73-9.28(23.0)
Val 200/$FeSO_4$	50:1[b]	11.75-3.04-3.70(18.5)	15.27-4.10(19.4)	14.22-3.96(18.2)

[a] Numbers in parenthesis indicate totals.
[b] (grams soil/gram Valfor 200); Valfor 200:$FeSO_4$ = 1:1.

and at pH 7.0 for the McClellan AFB soil. In the Cr-Ni system, the chromium capacity is a maximum at pH 8.5 for the McClellan AFB soil. Although the exact mechanism is not understood, these results may be attributed to the pH-dependent amphoteric nature of Cd and Cr hydroxides. Another exception is Robins AFB soil contaminated with Cr-Ni-Cd and Cr-Ni and treated with Valfor 200/ferrous sulfate, where the Ni and Cd capacities are maximum at a dosage of 100:1. This result may be attributed to a high selectivity for the hexavalent chromium, which is reduced to the trivalent chromium cation form, Cr^{+3}, and a finite total metal capacity. It may be possible to increase the Cd and Ni capacities by adding excess Valfor 200 relative to ferrous sulfate. Additional adsorption sites would be available for contaminant divalent metal removal in the event that iron is selectively adsorbed relative to both Ni and Cd. The data also show that at dosages of 100:1 and 50:1, the immobilizing action of Valfor 200/ferrous sulfate exceeds that of lime and has an exceptional affinity for chromium relative to both Ni and Cd.

Table 41 shows the differential chemical additive capacities for the McClellan and Robins AFB soils. The differential capacity is the difference in the capacity of the soil with the treatment chemicals added (Table 40) and capacity of the soil without the chemical additive (Table 39). It is expressed in terms of mequiv/gram chemical additive and is obtained by dividing the differential capacity in terms of mequiv/100 grams of soil by the dosage in grams chemical additive/100 grams soil. In general, the values of the differential capacities for the column tests are consistent with and fall within the range of the values for the batch tests reported earlier. Because the soil columns were run to exhaustion (breakthrough), the total and differential capacities obtained will be higher than the two other column tests that will be run during the remainder of the test program.

Additional tests were performed to determine the capacities and immobilization efficiencies of the Robins AFB and McClellan AFB soils for the single Cr^{+6} and the five multiple metal combination, Cr-Ni-Cd-Zn-Cu. The single metal Cr^{+6} concentration was 30 mequiv/L and was 6 mequiv/L for each of the five contaminant metals (for a total of 30 mequiv/L) in the multiple metal solution. Table 42 summarizes the capacity data for both soils treated with lime and Valfor 200/ferrous sulfate. The numbers in parenthesis are the

TABLE 41. EFFECT OF DOSAGE ON DIFFERENTIAL COLUMN CAPACITY (MEQUIV/GRAM CHEMICAL ADDITIVE) FOR MULTIPLE METAL CONTAMINANTS.

Chemical Additive	Dosage	Capacity (mequiv/gram chemical additive) Cr-Cd-Ni	Cr-Cd	Cr-Ni
McClellan AFB				
Lime	pH 7.0	101.7- [a] -46.7(148)[b]	142.5-124.2(267)	24.2-129.2(153)
Lime	pH 8.5	15.7- 2.4-38.3(56)	25.4- 67.4(93)	25.2- 59.3(85)
Lime	pH 10.0	14.6-18.9-24.2(58)	7.5- 33.2(41)	7.0- 32.2(39)
Val 200/$FeSO_4$	200:1[c]	2.51- [a] -1.11(3.6)	3.48-1.97(5.5)	2.37-0.43(2.8)
Val 200/$FeSO_4$	100:1	2.25-0.20-0.73(3.2)	2.91-1.33(4.2)	3.22-1.23(4.5)
Val 200/$FeSO_4$	50:1	3.84-1.50-1.29(6.6)	3.20-0.93(4.1)	2.60-0.90(3.5)
Robins AFB				
Lime	pH 7.0	10.0- 5.2-14.6(30)	0.0- 0.0(0)	20.5- 20.9(41)
Lime	pH 8.5	12.7- 8.7-13.5(35)	16.7- 11.1(28)	19.4- 23.8(43)
Lime	pH 10.0	10.6-10.8-15.5(37)	2.8- 16.4(19)	12.9- 22.5(35)
Val 200/$FeSO_4$	200:1	1.42-0.07-0.18(1.7)	2.83- [a] (2.8)	1.62-0.67(2.3)
Val 200/$FeSO_4$	100:1	3.23-2.02-1.93(7.2)	2.46- [a] (2.5)	5.70-4.03(9.7)
Val 200/$FeSO_4$	50:1	2.44-0.61-0.62(3.7)	3.18-0.63 (3.8)	2.97-0.68(3.7)

[a] Differential capacity is negative; the total capacity with chemical addition was less than the soil capacity without chemical addition.
[b] Numbers in parenthesis indicate totals.
[c] Dosage indicates soil/Valfor 200 ratio by weight; Valfor 200/$FeSO_4$ = 1:1.

total capacity for all five heavy metals. As with the data presented above, the total metal capacity for treated McClellan AFB soil increases with increasing dosage rates. The maximum total metal capacity for the McClellan AFB soil is realized at a lime-adjusted pH of 10 and at a 100:1 Valfor 200/ferrous sulfate dosage for the treated Robins AFB soil. Soils contaminated with only chromium and treated with the Valfor 200/ferrous

TABLE 42. EFFECT OF DOSAGE ON TOTAL CAPACITY (MEQUIV/100 GRAMS SOIL) FOR HEXAVALENT CHROMIUM AND FIVE METAL CONTAMINANTS

Chemical Additive	Dosage	Capacity (mequiv/100 grams soil) Cr	Cr-Cd-Ni-Cu-Zn
McClellan AFB			
Lime	pH 7.0	4.84	1.20-0.73-1.68-0.78-2.58 (6.97)
Lime	pH 8.5	4.40	1.09-0.75-1.51-1.82-3.33 (8.50)
Lime	pH 10.0	1.77	1.26-1.49-1.47-4.16-1.60 (9.98)
Valfor 200/$FeSO_4$	200:1	6.49	2.39-0.29-1.18-0.57-2.13 (6.56)
Valfor 200/$FeSO_4$	100:1	12.25	3.12-0.62-2.01-0.45-3.39 (9.59)
Valfor 200/$FeSO_4$	50:1	17.58	10.32-4.49-1.51-2.20-3.53(22.05)
Robins AFB			
Lime	pH 7.0	8.33	2.50-2.14-1.31-0.95-0.66 (7.56)
Lime	pH 8.5	11.52	2.83-0.77-1.26-0.92-0.83 (6.61)
Lime	pH 10.0	9.99	2.31-1.44-1.43-1.53-2.08 (8.79)
Valfor 200	100:1		4.59-3.22-3.19-3.05-4.00(18.05)
Valfor 200/$FeSO_4$	200:1	6.92	3.71-0.18-0.79-0.18-1.34 (6.20)
Valfor 200/$FeSO_4$	100:1	14.14	6.67-1.97-2.02-1.59-5.63(17.88)
Valfor 200/$FeSO_4$	50:1	8.70	9.45-1.49-1.46-2.49-0.05(14.94)

sulfate additive exhibit a high capacity for chromium. The multiple-metal test data with Valfor 200/ferrous sulfate addition generally shows chromium and zinc are selectively adsorbed relative to cadmium, nickel and copper.

D. LONG-TERM STABILITY COLUMN TEST PROGRAM

The objective of this portion of the test program was to determine the microbial degradation, if any, of the best treatment additives in soil, and the leachability, if any, of test soils contaminated with hexavalent chromium and treated with the best chemical additives, as determined from the batch screening and dynamic flow column tests.

Twelve soil columns were used in this test program. Six soil columns were prepared for each one of the two soils (Robins AFB and McClellan AFB). Each column contained soil contaminated with hexavalent chromium (Cr^{+6}). Two soil columns were treated with the appropriate dosage of lime to bring the soil pH to a value of 10, while three other columns were treated with equal doses of Valfor 200/ferrous sulfate. Equal parts by weight (1:1) of Valfor 200 and ferrous sulfate were mixed together and a 100:1 dosage (by weight) of soil/Valfor 200 was applied. For each soil type, one column was packed with soil and the hexavalent chromium, without a treatment chemical, and used as a control. No treatment additive was applied to these two columns, but they did receive a deionized water leachate rinse.

Each column contained 600 grams of soil which was contaminated with 0.6 liters of a metal salt solution (CrO_3) containing 30 mequiv/L of hexavalent chromium. This was the same total metal concentration used in the sorption equilibrium batch tests and the dynamic flow column tests and is equivalent to 3 mequiv/100 grams soil. For each column, the soil was mixed with the metal solution and reacted to equilibrium in an Erlenmeyer flask on the reciprocal shaker. The contaminated soils were air-dried for 48 hours and oven-dried for an additional 24 hours at 65 ^{o}C to insure complete drying and simulate the drying of a spill which might occur in the field. For the columns containing Valfor 200/ferrous sulfate, six grams of Valfor 200 and six grams of ferrous sulfate were mixed into the contaminated soils using the cone and quartering method. Similarly, 0.75 grams of lime were mixed into the McClellan AFB soil and 1.17 grams mixed into the Robins AFB soil to raise the pH of the remainder of the soil columns to 10.

An overview of the long-term stability column test program is given in Figure 12. The contaminated soils with and without the treatment chemicals were packed to the in situ density of each soil. The columns were filled with deaerated, deionized water and allowed to saturate the soils for 2 days. Following this saturation period, the stopcocks at the base of the soil columns were opened while the leachate solutions were gravity-fed through each soil column.

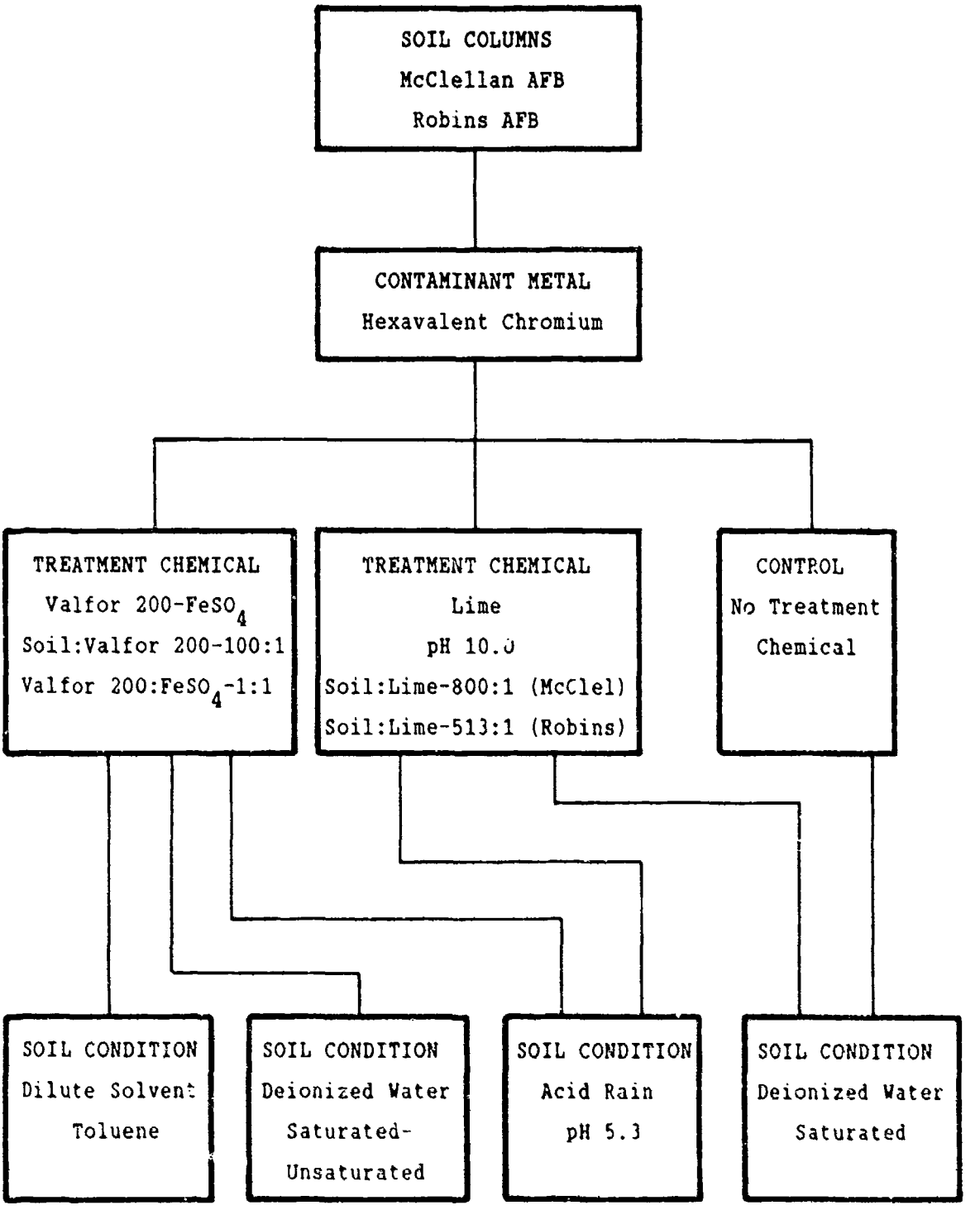


Figure 12. Overview of Long-Term Stability Column Test Program.

Table 43 lists the test conditions and results for the long-term stability column tests for both the McClellan AFB and Robins AFB soils. The total throughput in liters, average flow rate in pore volumes per day, and test duration in days are given for each treatment chemical and leachate solution.

1. McClellan AFB Soil

Deionized water was passed through and saturated a column of chromium-contaminated McClellan AFB soil. The soil was allowed to dry out at least three times during the test duration (27 days) to determine the effects of immobilization in an unsaturated condition. A total of 1.45 liters of deionized water was passed through the McClellan AFB soil treated with Valfor 200/ferrous sulfate in 27 days. The McClellan AFB soil column treated with lime exhibited higher flow rates and resulted in a total throughput of 2.85 liters of deionized water.

In another column, a total throughput of 2.23 liters of water saturated with toluene was applied to soil treated with Valfor 200/ferrous sulfate. Similarly, 1.80 liters of simulated acid rain (deionized water adjusted to a pH 5.3 with sulfuric acid) was applied to soil treated with Valfor 200/ferrous sulfate and 3.08 liters to the column treated with lime. A total throughput of 29.35 liters of deionized water was applied to the control soil column. The McClellan AFB long-term stability columns were tested for 22-28 days at average flow rates of 0.6 to 1.2 pore volumes per day.

2. Robins AFB Soil

Similar tests were run for the Robins AFB soil and the results are summarized in Table 43.

3. Test Results and Discussion of Results

Figures 13 and 14 show the effluent concentration of hexavalent chromium in the various leachates from the McClellan AFB and Robins AFB

TABLE 43. LONG-TERM STABILITY COLUMN TEST CONDITIONS.

Treatment Chemicals	Leachate Solution	Total Throughput (Liters)	Average Flow Rate[a]	Duration (Days)
McClellan AFB				
Control	Deionized Water Saturated	2.44	1.07	24.0
Valfor 200-$FeSO_4$	Deionized Water Saturated-Unsaturated	1.45	0.56	27.4
Valfor 200-$FeSO_4$	Solvent-Toluene	2.23	0.89	26.4
Valfor 200-$FeSO_4$	Simulated Acid Rain pH 5.3	1.80	0.87	21.8
Lime	Deionized Water Saturated-Unsatuated	2.85	1.09	27.4
Lime	Simulated Acid Rain pH 5.3	3.08	1.17	27.7
Robins AFB				
Control	Deionized Water Saturated	2.53	0.72	46.9
Valfor 200-$FeSO_4$	Deionized Water Saturated-Unsaturated	3.78	1.05	48.0
Valfor 200-$FeSO_4$	Solvent-Toluene	3.66	0.92	53.0
Valfor 200-$FeSO_4$	Simul Acid Rain pH 5.3	2.38	0.76	41.5
Lime	Deionized Water Saturated	1.25	0.68	24.7
Lime	Simulated Acid Rain pH 5.3	3.31	1.10	40.0

[a] Pore volumes per day.

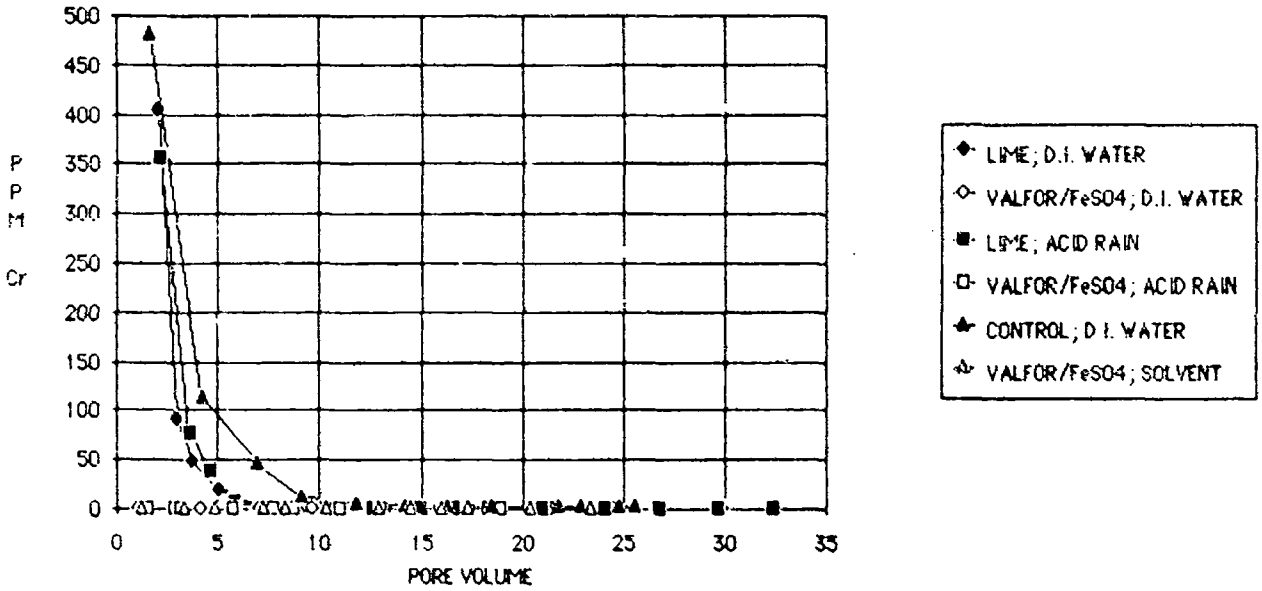


Figure 13. Effluent Leachate Concentration from Long-Term Stability Soil Columns. McClellan AFB Soil.

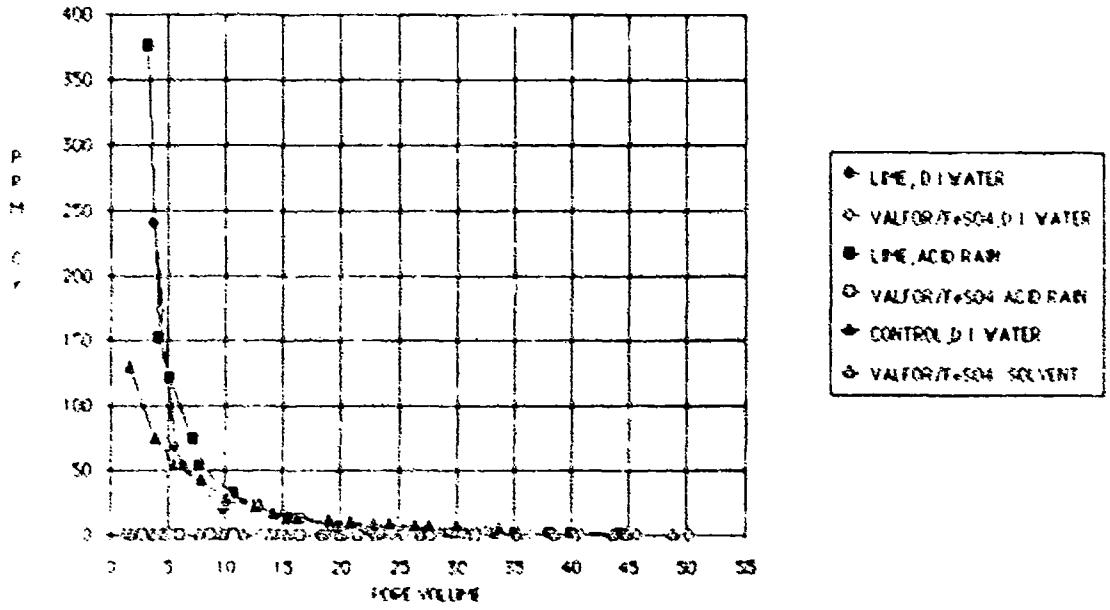
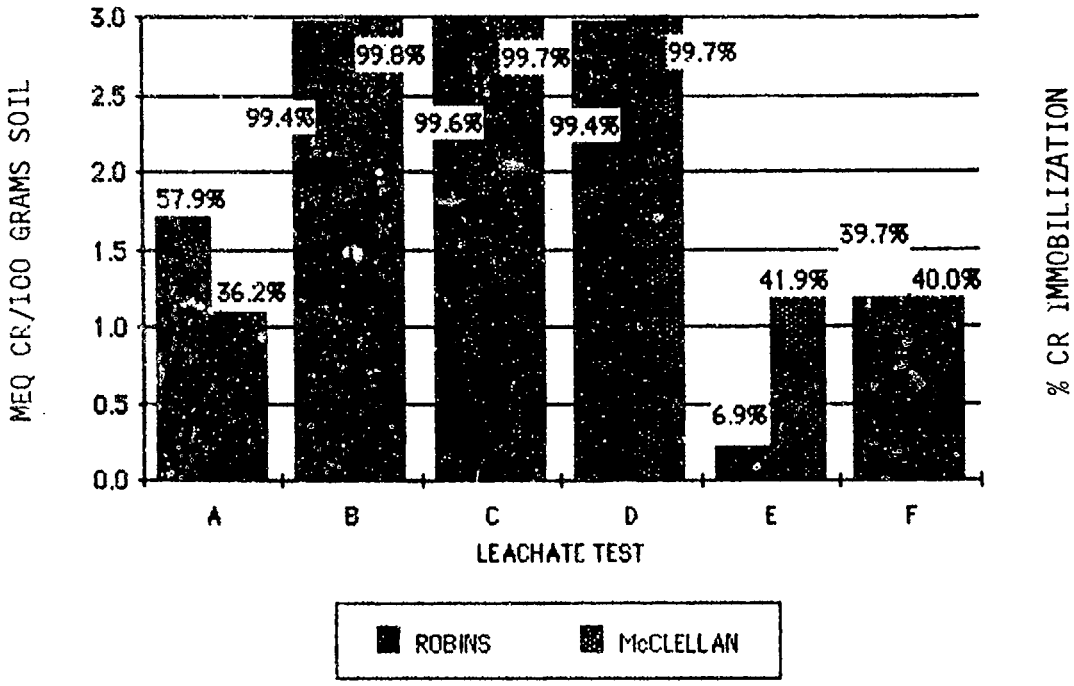


Figure 14. Effl ent Leachate Concentration fros Long-Term Stability Soil Columns. Robins AFB Soil.

soils. The leachate effluent concentrations are listed in Appendix B. The figures show that Valfor 200/ferrous sulfate is responsible for the complete immobilization of chromium in the soil. Most of the chromium concentrations in the various leachates of the Valfor 200/ferrous sulfate treated soils are less than the analytical detection limit (0.25 ppm). The metal concentrations in these leachates are considerably less than the concentrations in the deionized water leachate from the corresponding control columns. This indicates that acid rain, dilute solvent, and saturated-unsaturated conditions are ineffective in desorbing hexavalent chromium from contaminated soils treated with a combination of the Valfor 200/ferrous sulfate treatment chemicals.

Lime addition, to adjust the soil pH to a value of 10, was ineffective in immobilizing hexavalent chromium in the soil. The metal concentrations in the acid rain and deionized water leachates are equivalent to or greater than the metal concentrations in the deionized water leachate of the corresponding control columns. An increase of the hexavalent chromium concentration in the leachate from the lime-treated Robins AFB soil following the application of an acid rain solution indicates that the acid rain (low pH conditions) is responsible for the increased chromium removal in this column (see Figure 14). The shape of the removal curves indicates the majority of the metal is removed in the first two to five leachate pore volumes.

The total capacities and immobilization efficiencies of the soil-treatment chemical systems for various leachates are shown in Figure 15. The amount of immobilized chromium (+6) was determined by measuring the total quantity of chromium (+6) found in the leachate effluent from the effluent concentration profiles shown in Figures 14 and 15 and subtracting it from the total chromium initially placed in the soil column. The effectiveness of Valfor 200/ferrous sulfate is reflected in its high total capacity and immobilization efficiency. The chemical additives use only part of their capacity in the leachate tests (Table 44). Therefore, the differential capacities of the chemical additives for the leachate tests (as shown in Table 44) are lower than the results of the dynamic flow column tests, which were run to breakthrough or complete exhaustion (see Table 41). In the latter case, the full capacity of the additives are utilized.



Test	Treatment Chemicals	Leachate Solution	Cap (a) McClellan	Cap (a) Robins	K McClellan	K Robins
A	Control	Deionized Water Saturated	1.09	1.74	0.362	0.579
B	Valfor 200- $FeSO_4$	Deionized Water Sat-Unsat	2.99	2.98	0.998	0.994
C		Solvent-Toluene	2.99	2.99	0.997	0.996
D		Simulated Acid Rain	2.99	2.98	0.997	0.994
E	Lime	Simulated Acid Rain	1.26	0.21	0.419	0.069
F		Deionized Water Sat-Unsat	1.20	1.19	0.400	0.397

(a) (mequiv/100 grams soil).

Figure 15. Total Capacity and Immobilization Efficiency for Long-Term Stability Soil Columns.

TABLE 44. DIFFERENTIAL CAPACITY OF TREATMENT CHEMICALS IN LONG-TERM STABILITY SOIL COLUMNS.

Test	Treatment Chemicals	Leachate Solution	Differential Capacity (mequiv/gram chemical additive) McClellan	Robins
B	Valfor 200-$FeSO_4$	Deionized Water Sat-Unsat	0.95	0.62
C		Solvent-Toluene	0.95	0.62
D		Simulated Acid Rain	0.95	0.62
E	Lime	Simulated Acid Rain	1.36	a
F		Deionized Water Sat-Unsat	0.88	a

[a] The differential capacity is negative; the total capacity for the control case exceeded the total capacity with lime addition.

E. HAZARDOUS WASTE SITE SIMULATION TEST PROGRAM

Soil can pick up specific metal ions from waste solutions and later give them up because of intervening conditions in the soil acting on the passage of liquid containing the metallic waste. Soil columns simulating conditions in actual hazardous waste sites were constructed to determine the immobilization efficiency of treated soil in a dynamically changing soil environment. An overview of the hazardous waste site simulation test program is given in Figure 16.

Eighteen-hundred grams of each soil (McClellan AFB, Robins AFB) were contaminated with 1.8 liters of a 30 mequiv/L total metal solution containing equal milliequivalent concentrations (10 mequiv/L) of Cr, Cd and Ni. The soil contamination rate of 3 mequiv (total metal contamination) per 100 grams of soil was the same as in the long-term stability tests. Each contaminated soil was treated with 18 grams of Valfor 200 and 18 grams of ferrous sulfate; the soil-to-Valfor 200 dosage was 100:1, the same as for the long-term stability tests. The treatment chemicals were added to the soil and mixed prior to column packing. Eighteen-hundred grams of contaminated soil without the treatment chemicals were used as a control.

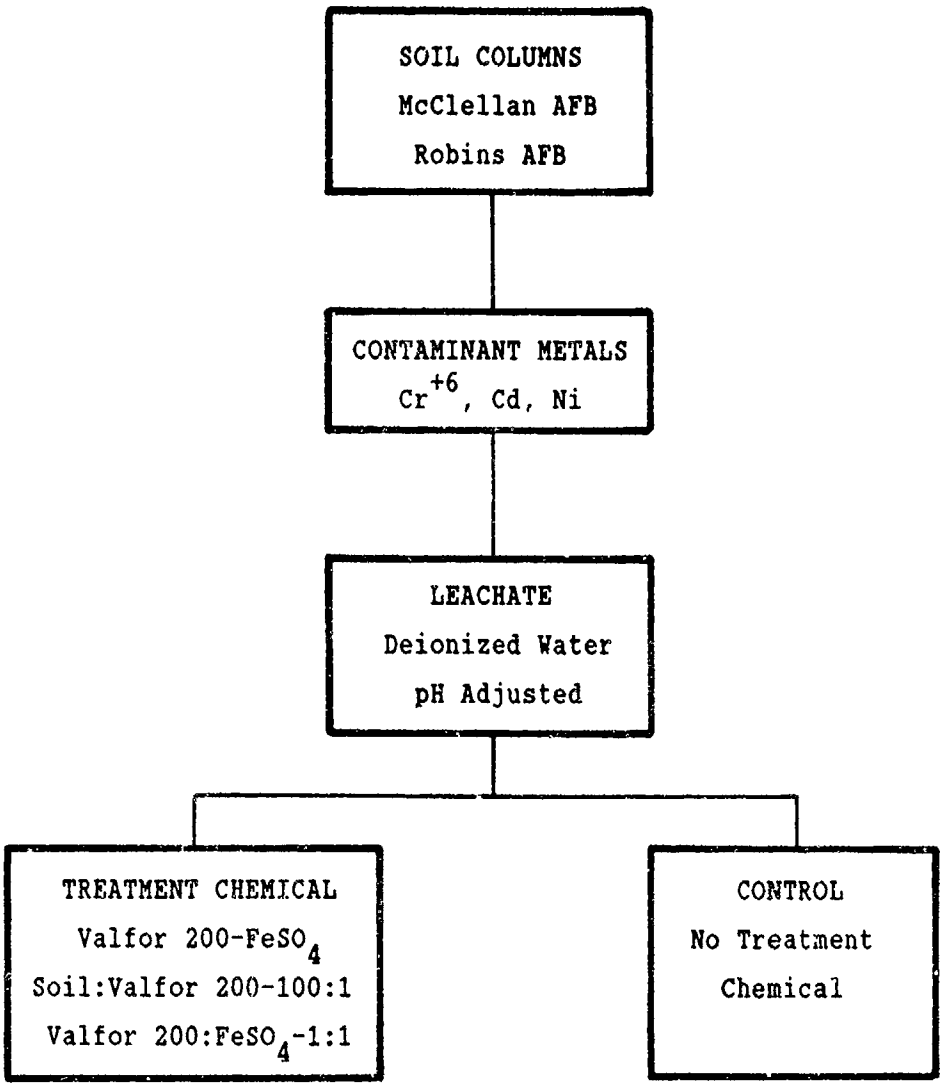


Figure 16. Overview of Hazardous Waste Site Simulation Test Program.

Four hazardous waste site simulator columns were assembled; each column consisted of a top 2-foot long section (Section A), followed by three bottom 1-foot long sections (Sections B, C, D) (see Figure 17). The top 2-foot sections of two of the columns were packed with the contaminated soil from each AFB and treated with Valfor 200/ferrous sulfate. The top two 2-foot sections of the other two columns were filled with contaminated soil (without the treatment chemicals) and used, as discussed above, as controls. All of the bottom three 1-foot sections in each column were filled with uncontaminated, untreated soil and represent the virgin soil below the contaminated soil on a hazardous waste site.

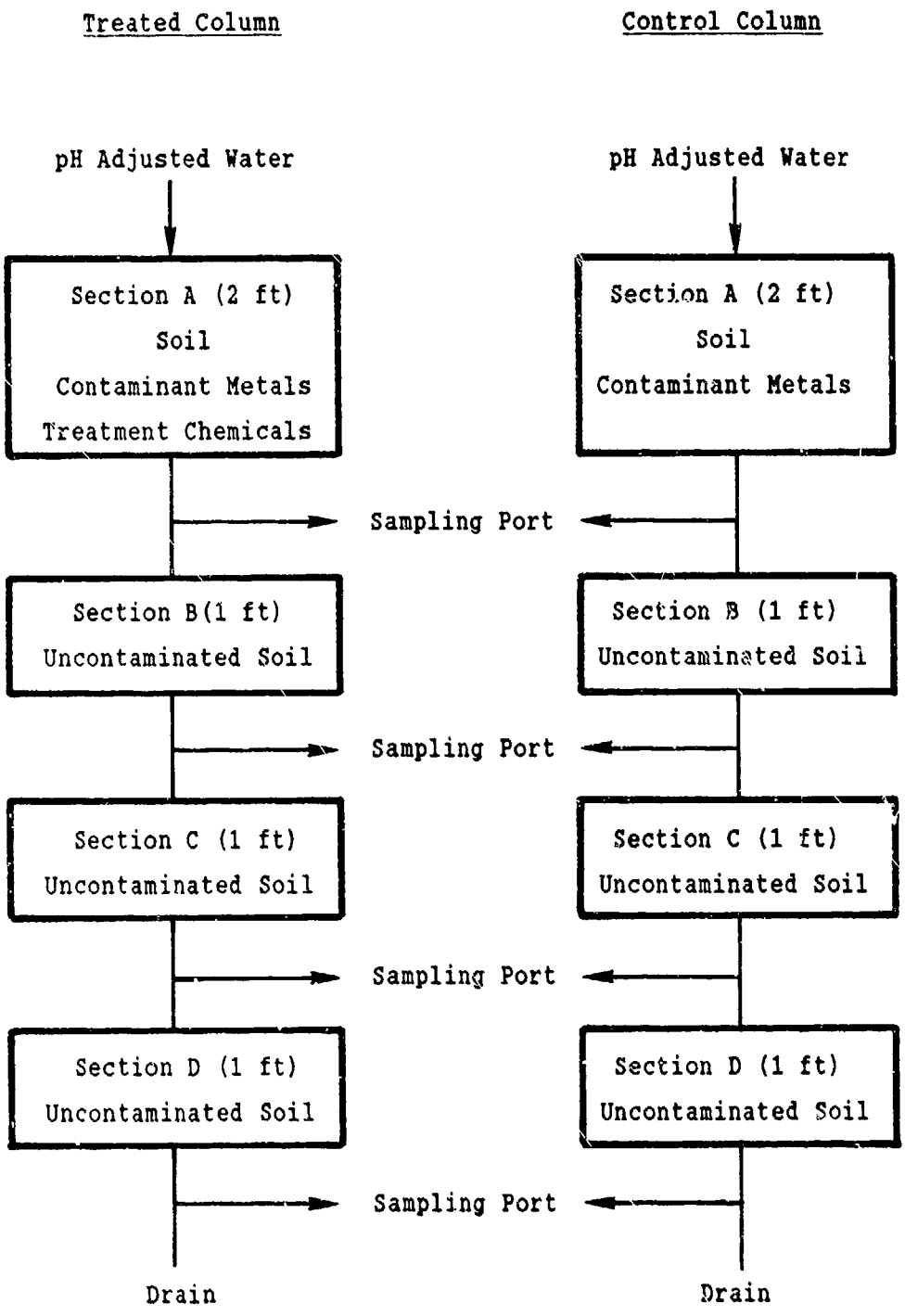


Figure 17. Schematic of Hazardous Waste Site Simulator.

The soil in each section was compacted to its native density by the procedures previously described. All the soil columns were saturated with deionized water prior to testing. Water was used as the leachate fluid and was gravity-fed through the columns. The hazardous waste site columns were continuously leached with deionized water at a flow rate equal to their "as-packed" permeability. Table 45 shows the total leachate throughput and flow rates through the control and soil-treated columns.

TABLE 45. HAZARDOUS WASTE SITE SIMULATOR TEST CONDITIONS.

Soil	Column	Test Duration (Days)	Total Through-put (L)	Total Pore Vol	Flow Rate[a]	Perm-eability[b]
McClellan AFB	Control	114	3.822	4.96	0.044	19.1
	Treated	114	0.858	1.11	0.01	4.3
Robins AFB	Control	114	27.897	493.6	4.33	140
	Treated	114	0.991	1.76	0.015	5.0

a (pore volumes per day).
b ($cm\text{-}sec^{-1} \times 10^{-8}$).

In the control columns, the hydraulic capacity of the McClellan AFB soil was reduced by the gradual deposit of a sediment clay layer on top of the soil columns, resulting in a substantially less throughput. The soil columns receiving the Valfor 200/ferrous sulfate treatment additive experienced a marked decrease in permeability. This permeability change indicates that the addition of the Valfor 200/ferrous sulfate mixture causes metal precipitation, presumably as sulfides and/or complexation with Valfor 200.

Originally, extract leachate samples for analysis were taken from sampling ports (three-way valves) placed between each section of the column to monitor the passage of Cr, Cd and Ni from one section of the column to the next section. Inadequate amounts of the samples were obtained from the ports because of reduced soil permeability. Instead, the total distribution of

metal retained by each soil column after leaching was determined by analyzing the soil in each column.

The hazardous waste site testing program was terminated after the columns were continuously leached with deionized water for 114 days. All effluents were analyzed for Cr, Cd and Ni by the digestion method described in Section II.D.2. Columns treated with Valfor 200/ferrous sulfate were also analyzed for iron.

The distributions of Cr, Cd and Ni retained by the soil columns were determined after the leachate test was concluded by analyzing the soil columns. Initially, the metal content in the soils was measured by determining the concentration of readily extractable metals (Section II.D.2). In the McClellan and Robins AFB hazardous waste site simulator treated and control columns, all of the Cd was accounted for using this method. This was also the case for Ni in the McClellan and Robins AFB control columns. However, in the other columns, specifically the McClellan and Robins AFB treated soil columns for Ni and Cr^{+6}, and to some extent, in the control columns for Cr^{+6}, only a fraction of the original doped metal values were observed. It was concluded that Ni and to some extent Cr^{+6} are bound tightly to the soil as a result of treatment with Valfor 200/ferrous sulfate. A mass balance for Ni and Cr^{+6} was determined only after a column soil sample was entirely digested (see Section II.D.2). The quantity of metal retained by the soil (mg metal/100 grams soil) was calculated by multiplying the concentration (mg/L) determined in the soil extract by the volume of the extraction solution used (liters), divided by the weight of the soil being extracted (grams); the data was normalized for 100 grams of soil.

The results of continuously leaching deionized water through the hazardous waste site simulator columns are shown as the histograms of Figures 18 and 19. The height of the histogram bar labeled A (initial) represents the quantity of the individual metal species initially added to Section A, in mg/100 g soil, prior to leachate testing. The height of the histogram bars labeled A, B, C, and D (treated, control) corresponds to the quantity of the individual metal species in the 1st (A) section and each successive [2nd (B),

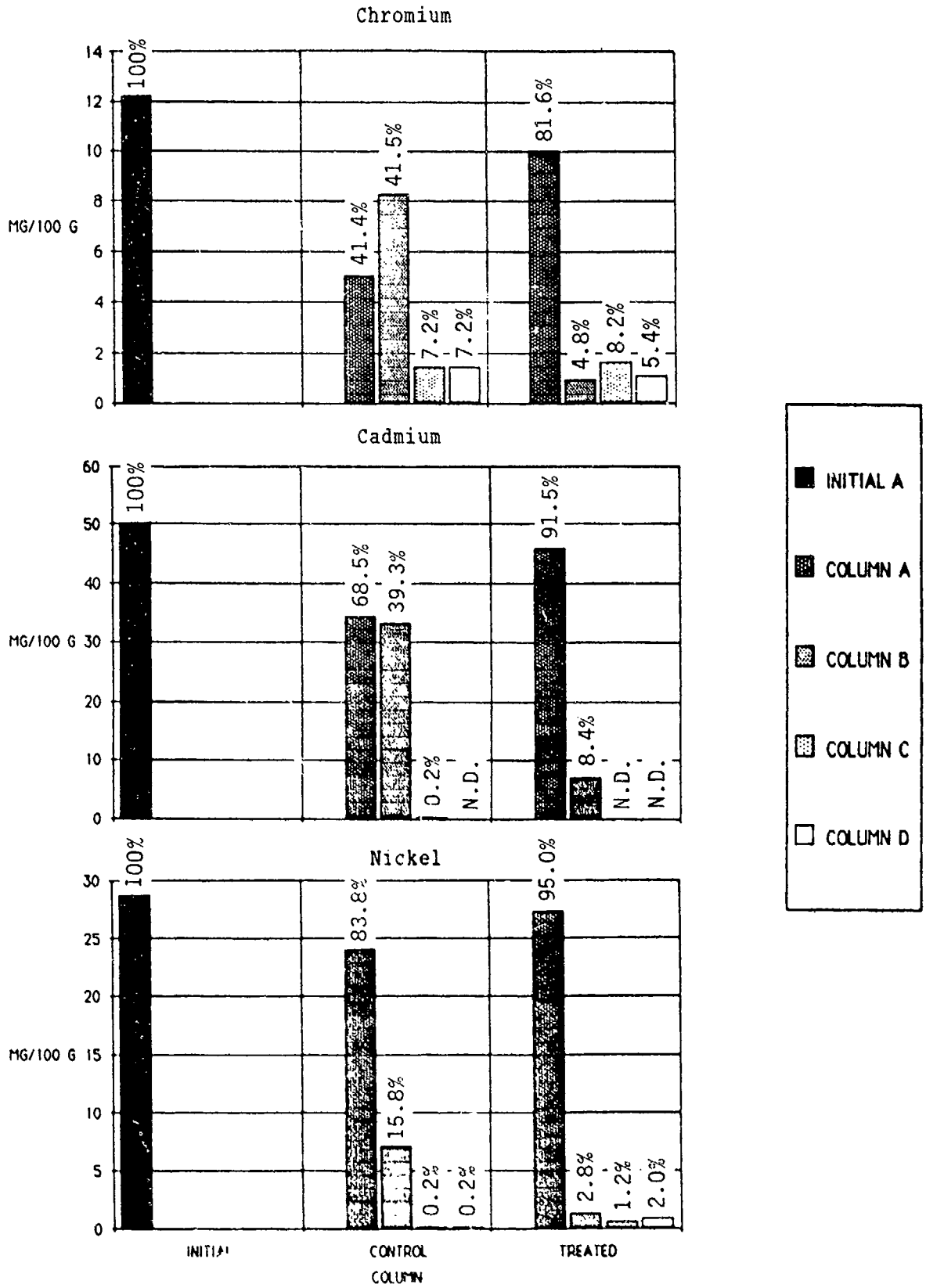


Figure 18. Concentration Profiles of Hazardous Waste Site Simulator for McClellan AFB Soil.

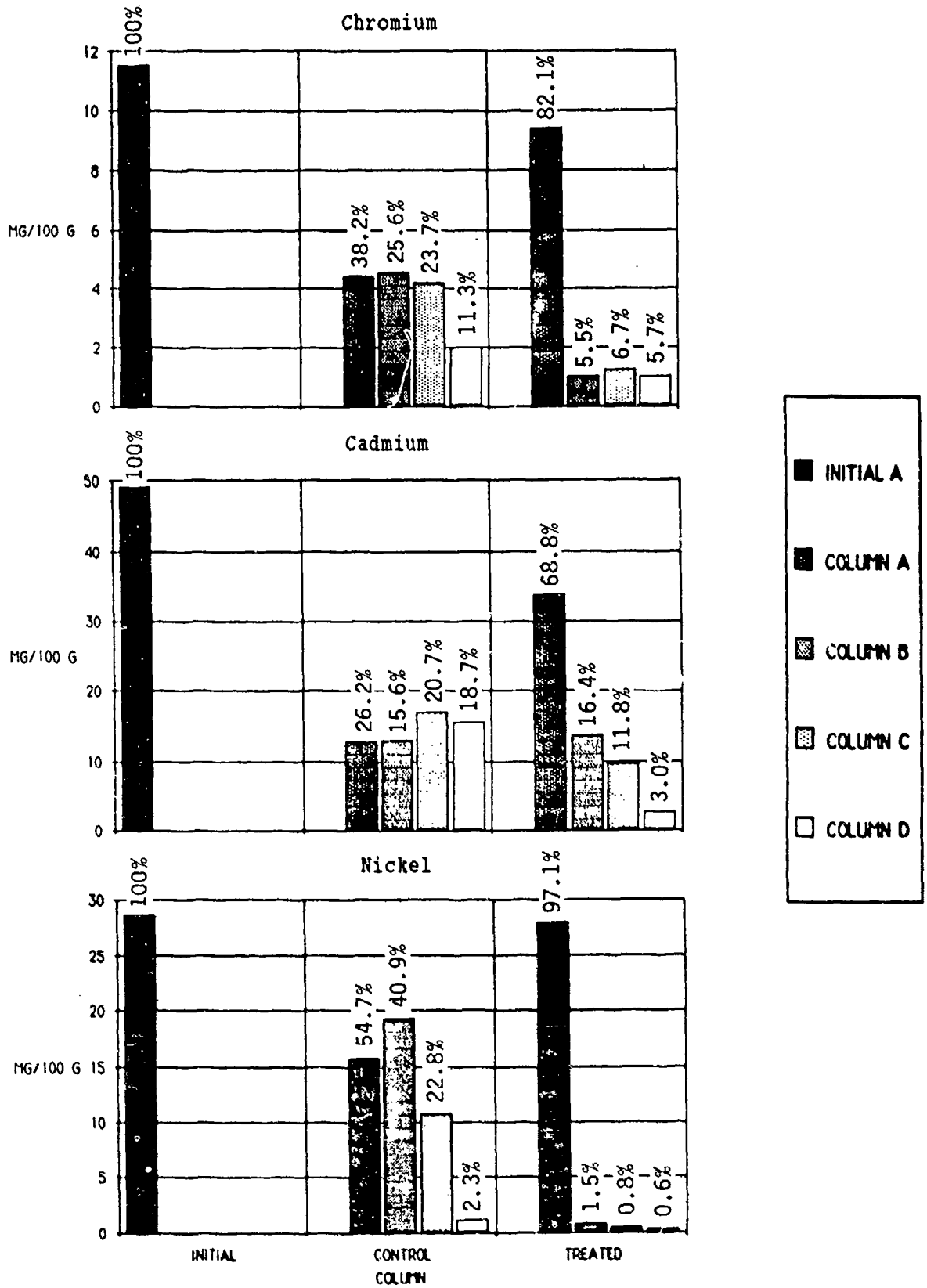


Figure 19. Concentration Profiles of Hazardous Waste Site Simulator for Robins AFB Soil.

3rd (C), and 4th (D)] section of the treated and control soils at the conclusion of the leachate tests.

The quantity of metal retained by the soil in the top section (A) changes as the metals are leached from the section. The quantities of metals found in the succeeding virgin soils (B, C, D) generally are different. Although the soils in the top soil segment (Section A) start out the same, in effect they become different soils because of the passage of continuously leached water. The amount of metal in Sections B, C, and D depends on the amount of metal leached from the treated section (A) and the succeeding soil section (B, C).

The soil can also displace its naturally occuring ions for the contaminant metal ions. In addition, the soil in the columns can pick up certain metal ions from the leachate solution and give them up again, changing the composition of the leachate entering successive soil columns.

The difference in the metal quantity for a given species (mg/100 grams soil) or height of the histogram bar between A (initial) and A (treated) multipled by the amount of soil in the section of column is the total amount of metal (species) that challenges the next layer of soil (Section B), i.e., is the amount of metal that the next layer of soil initally sees. The same situation applies for the control column. The quantity of a metal species found in a particular soil section after leaching divided by the amount of that metal species that challenges that section is the fraction immobilized (immobilization efficiency) in that soil section.

The difference between the initial amount of contaminant metal added to the top section (A) and the cumulative sum of a metal species found in each section (Sections A, B, C, D) after leachate testing should be equal to the amount of metal found in the leachate from the last section (D). This represents the mass balance for that particular metal species in the hazardous waste site simulator (see Table 46). The quantity of a particular metal species did not always balance. For example, the amount of cadmium immobilized in the Robins control hazardous waste simulator was equal to 0.812, i.e., 81.2 percent of the amount of cadmium initially added to the

TABLE 46. HAZARDOUS WASTE SITE SIMULATOR CONTAMINANT METAL MASS BALANCE (AS PERCENT OF INDIVIDUAL CONTAMINANT METAL SPECIES INITIALLY ADDED TO SECTION A)

	Cr (percent)		Cd (percent)		Ni (percent)	
	McClellan	Robins	McClellan	Robins	McClellan	Robins
Section A						
Treated	81.6	82.1	91.5	68.8	95.0	97.1
Control	41.4	38.2	68.5	26.2	83.8	54.7
Section B						
Treated	4.8	5.5	8.4	15.6	2.8	1.5
Control	41.5	25.6	39.3	16.4	15.8	40.9
Section C						
Treated	8.2	6.7	ND	11.8	1.7	0.8
Control	7.2	23.7	0.2	20.7	0.2	22.8
Section D						
Treated	5.4	5.7	ND	3.0	2.0	0.6
Control	7.2	11.3	ND	18.7	0.2	2.3
Subtotal A,B,C,D						
Treated	100.0	100.0	99.9	99.2	101.5	100.0
Control	97.3	98.8	108.0	82.0	100.0	120.7
Effluent						
Treated	ND	ND	ND	ND	ND	ND
Control	ND	ND	ND	21.2	ND	ND
Total						
Treated	100.0	100.0	99.9	99.2	101.5	100.0
Control	97.3	98.8	108.0	103.2	100.0	120.7

ND Not detected.

column (Section A) was retained in the soil column. Analysis showed that an additional 0.212 (21.2 percent) of cadmium was found in the effluent, giving a total mass of 1.024, i.e., an additional 2.4 percent of cadmium was not accounted for. Mass balances different than 1.0 are indicative of metal distribution inhomogeneity within the soil sampled for analysis. All of the column leachate effluents were analyzed for Cr, Cd and Ni. Only cadmium was detected in the Robins AFB hazardous waste site simulator columns; the concentrations of Cr^{+6} and Ni were below the sensitivity of the analysis.

The difference in the heights of the histograms indicated that Cr, Cd and Ni are not complexing in the soil to the same degree. Varying metal ion mobilities, as indicated by the amount of metal retained in each section, implies that either the free metal ion or the metal complex is immobilized to the soil with nonuniform bonding strength. Whether the contaminant metal in Sections B, C and D is in the form of a free metal ion or complexed metal is unclear. Digestion of the soils for analysis dissolves naturally occuring aluminum (found in the soil) making it difficult to distinguish it from the aluminum found in Valfor 200.

Immobilization of Cr, Cd and Ni in contaminated soils treated with Valfor 200/ferrous sulfate was undoubtedly enhanced relative to the untreated control columns. The immobilization effects of the treatment chemical are more pronounced in the lower metal capacity Robins AFB soil when compared to the higher metal capacity McClellan AFB soil (see Figures 18, 19 and Table 46). Most of the chromium (82.1 percent), cadmium (68.8 percent) and nickel (97.1 percent) in the Robins AFB soil was immobilized in the treated top section (A), compared to the untreated or control column [chromium (38.2 percent, cadmium (26.0) and nickel (54.7)]. With the exception of cadmium in the Robins AFB soil, excellent immobilization of these metals in the top section resulted in less metal available to challenge the lower soil sections (B, C, D).

Cadmium appears to be very mobile, as characterized by finding 21.2 percent of the total cadmium in the the Robins AFB control column leachate effluent. The mobility of cadmium is further corroborated by the results of the dynamic flow and long-term stability column tests. Cadmium was

immobilized by the Valfor 200/ferrous sulfate treatment additive to the extent that none was detected in the effluent of either treated soil column. No other metals in either soil column effluent exceeded the detection levels of the AA.

The average pH of the McClellan and Robins AFB control soil column effluents were 7.96 and 6.62, respectively. The average pH of the McClellan and Robins AFB treated soil column effluents were 7.40 and 7.08, respectively. However, the treated column effluents taken on the last day of testing were recorded at 5.74 for the McClellan AFB soil and 4.08 for the Robins AFB soil indicating that ferrous sulfate may be responsible for the change in the effluent pH.

On a qualitative basis, a distinct difference was observed in the quality of the effluent streams. Treatment of the soils with Valfor 200/ferrous sulfate produced a light brown effluent. In contrast, the effluent from the untreated control columns was relatively clear. Analysis of the leachate showed that iron was not detected and the brown color cannot be attributed to the ferrous sulfate treatment additive. The decrease in pH of the soil column effluent, attributed to the ferrous sulfate, may be responsible for extracting higher levels of humic and/or fulvic acids in the effluent, resulting in the colored effluent.

Valfor 200 is a sodium aluminosilicate that has a high sorption capacity for divalent and trivalent heavy metals. The high distribution of exchangeable sodium cations in Valfor 200 accounts for its high sorptive capacity for Cd and Ni. Valfor 200 is not selective for chromium in the hexavalent state. The addition of ferrous sulfate reduces Cr^{+6} to the less toxic, less mobile trivalent species, Cr^{+3}, which is readily sorbed onto the Valfor 200 surface or precipitated as insoluble chromium hydroxide. Co-precipitation of iron and the contaminant metal sulfides also occurs in Section A of the treated soils.

Qualitative observation shows that precipitation occurs and becomes more pronounced in Section A with time. The use of ferrous sulfate instead of ferrous sulfide virtually eliminates the problem of hydrogen sulfide

evolution. Since sulfide itself is toxic, this process uses freshly prepared ferrous sulfate with soils (which have intrinsic reducing characteristics) as the source of the sulfide ions. FeS dissociates into ferrous and sulfide ions to the degree predicted by its solubility product. The sulfide ions are consumed as the dissolved contaminant metal ion is precipitated as a metal sulfide. Analysis of the column effluents by polaragraphy did not detect the presence of sulfides.

Results of the hazardous waste simulator study indicate that in situ treatment is a viable solution for the immobilization of Cr, Cd and Ni in contaminated soil. The use of Valfor 200/ferrous sulfate mixtures as a treatment additive for the immobilization of heavy metals proved effective in the McClellan and Robins AFB soils. The treatment additives provided immobilization efficiencies superior to the leached control columns that contained no chemical additives. Contaminant metal immobilization is derived not only from simple ion exchange considerations, but also strong covalent bonding responsible for precipitation and chemisorption of metal contaminants.

SECTION VI

IN SITU TREATMENT COSTS

The costs of treating soil contaminated with heavy metals by in situ immobilization will be compared to the costs of contaminated soil removal and offsite treatment. The costs of in situ immobilization consist of the chemical additive costs and the costs of soil preparation and chemical additive application.

The chemical additive costs are given by the following equation:

$$\text{Chemical Costs (\$)} = W\ M\ C/1000\ Cap \qquad (7)$$

where:

W = Soil weight (kgr)
M = Metal loading (mequiv/kgram soil)
C = Unit chemical cost ($/kgr)
Cap = Differential capacity (mequiv/gram chemical additive)

The costs will be based on the treatment of 1 acre-foot of contaminated soil, which is equivalent to 4.4×10^4 ft^3 (1.6×10^3 cu yd, 1.2×10^3 m^3).

The dry densities of the contaminated soils tested in the program were in the range 99.7 to 118.0 lbs/ft^3 (Table 4). For calculational purposes, the dry density is 110 lb/ft^3 (specific gravity = 1.76). The weight of one acre-foot of soil, W, is equal to 4.8×10^6 lbs (2.4×10^3 tons, 2.2×10^6 kgr).

The total metal loading, M, for the long-term stability and Hazardous Waste Site Simulator test programs was 3 mequiv/100 grams soil or 30 mequiv/kgram. The soil was loaded with equal milliequivalent concentrations of the contaminant metals. Table 47 lists the concentration of each metal in the soil in terms of mg/kgr.

TABLE 47. METAL LOADING IN SOILS.

Metal Contamination	Contaminant Metal	Metal Loading (mequiv/kgram)	(mgram/kgram)
Cr	Cr^{+6}	30	260
Cr, Cd	Cr^{+6}	15	130
	Cd^{+2}	15	843
Cr, Ni	Cr^{+6}	15	130
	Ni^{+2}	15	440
Cr, Cd, Ni	Cr^{+6}	10	87
	Cd^{+2}	10	562
	Ni^{+2}	10	294

The differential column capacities were obtained under varying conditions. Table 48 sumarizes the total differential capacities for the Valfor 200/ferrous sulfate chemical additive system for the column test program (see Tables 41 and 44). The total differential capacity is the sum of the differential capacities for each individual metal. The differential capacities for the dynamic flow column tests are the maximum because they correspond to full saturation of the soil and Valfor 200/ferrous sulfate with the heavy metals. They are a factor of 3.2 to 11.4 times higher than those obtained with the hazardous waste simulator column tests.

The chemical costs to treat 1 acre-foot of soil contaminated with 30 mequiv total metal/kgram soil (or 0.94 milligram metal/gram soil, or 940 ppm) with Valfor 200/ferrous sulfate are given in Table 49, and are calculated from Equation (7). The chemical dosage was taken to be 100:1. Depending upon the value of the differential capacity used in the estimate, the chemical treatment costs ranged from $33,300/acre-ft to $81,200/acre-ft, or $13.9/ton to $33.8/ton. More precise estimates can only be made if the distribution of metals in the soil is measured at a given site and the chemical dosage is known as a function of the total metal loading.

TABLE 48. SUMMARY OF DIFFERENTIAL CAPACITY DATA FOR VALFOR 200/FERROUS SULFATE ADDITION.

Metal Contamination[a]	Dosage[b]	Differential Capacity (mequiv/gram chem add) Dynamic Flow Column	Long-Term Stability	Hazardous Waste Simulator
McClellan AFB				
Cr	100:1		0.95	
Cr, Cd	200:1	5.5		
	100:1	4.2		
	50:1	4.1		
Cr, Ni	200:1	2.8		
	100:1	4.5		
	50:1	3.5		
Cr, Cd, Ni	200:1	3.6		
	100:1	3.2		0.39
	50:1	6.6		
Robins AFB				
Cr	100:1		0.62	
Cr, Cd	200:1	2.8		
	100:1	2.5		
	50:1	3.8		
Cr, Ni	200:1	2.3		
	100:1	9.7		
	50:1	3.7		
Cr, Cd, Ni	200:1	1.7		
	100:1	7.2		0.63
	50:1	3.7		

[a] Total metal contamination is 30 mequiv/kgram soil.
[b] (grams soil/gram Valfor 200); Valfor 200/ferrous sulfate = 1:1 by weight.

TABLE 49. CHEMICAL COSTS.

Soil	Differential Capacity (mequiv/gram chem add)	Cost ($/acre-ft)	Cost ($/ton)
McClellan AFB	0.39	81,200	33.8
	0.95	33,300	13.9
Robins AFB	0.62	50,300	20.9

Tilling is the most common method of introducing dry chemicals into the soil. Routine tilling can mix dry chemical additives into the soil to a depth of 1 to 2 feet. Special deep tilling equipment is available which can reach as deep as 5 feet into the ground. The costs of tilling in dry chemicals to the soil to a depth of 5 feet has been estimated at $1,000/acre-foot or $0.42/ton and is based on the rental of tilling equipment and labor costs for 1 day, the time it would take to treat 1 acre-ft. These costs are negligble relative to the chemical treatment costs for the illustrative example given in this section.

As a basis of comparison, the costs of transporting the contaminated soil to, and disposing the contaminated soil in a secured landfill has been estimated at $357,000/acre-ft to $595,000/acre-ft, or $150/ton to $250/ton, depending upon the location of and distance to the secured landfill and the disposal and/or treatment costs. For the particular example given in this section, the chemical treatment costs for the in situ immobilization of heavy metals in soil are much lower than offsite treatment.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The overall aim of this program was to evaluate the effect of cost-effective, innovative, in situ immobilization technologies on the leaching behavior of five heavy metals common to many contaminated soils and groundwater (hexavalent chromium, Cr^{+6}; cadmium, Cd^{+2}; nickel, Ni^{+2}; copper, Cu^{+2}; and zinc, Zn^{+2}). The high level of soil contamination used in this study, consistent with actual contaminated waste sites, possess environmental and health hazards. In addition, the amount of soil requiring treatment is difficult and expensive to dispose of by conventional shallow land burial.

The conclusions of this study are based on the test results of an experimental program consisting of two phases: batch equilibirum testing and column testing. The batch equilibrium tests were used to screen a large number of chemical additives while the column testing was used to determine the immobilization efficiency of the best treatment additives.

The results of this study indicate that in situ treatment is a viable solution for the immobilzation of the heavy metals, Cr, Cd, Ni, Cu and Zn from contaminated soils. The use of Valfor 200/ferrous sulfate combination treatment for the immobilization of hexavalent chromium, cadmium and nickel proved very effective in the hazardous waste site simulator containing soils excavated from McClellan AFB and Robins AFB. In the control columns, the use of a deionized water leach appears to flush the metal from the contaminated soil as observed from the high metal content found in adjoining soil columns, in comparison to the treated columns.

Consideration of in situ immobilization treatment involves the fate of the heavy metals, as well as the treatment additive itself, over long periods of time. In situ immobilization implies that the heavy metals are strongly bound, involving complex synergistic mechanisms that include natural soil chelation and complex formation with the treatment additive. The mechanism

for chromium (+6) immobilization involved reduction to Cr^{+3} with ferrous sulfate and selective adsorption onto the surfaces of Valfor 200. For the other metals, the major mechanisms involved adsorption onto the Valfor 200 by ion exchange and coprecipitation with iron as metal sulfides.

If the treatment is to be effective, the heavy metals cannot be desorbed from the soil-chemical additive system over long periods, given a dynamically changing environment, particularly with respect to acid rain leaching. Leachate (hazardous waste site simulator) tests were run over approximately a 4-month period in control columns and in columns to which the treatment chemicals were added to the first 2 feet of the column. The heavy metals were also added to the first 2 feet of the column. The test results demonstrated that the heavy metals migrated down through the control soil column at different rates, but that with chemical treatment, the heavy metals mobility was drastically reduced and between 82 to 95 percent of the metals (the exception being 69 percent for cadmium in the Robins AFB soil) was confined to the part of the column containing the chemical additives. Furthermore, Cr^{+6} and in particular Ni, were so tightly bound to the treated soil that a total digestion of the soil (using concentrated acids) was required to determine the total metal distribution within the soil columns.

Long-term stability tests with soils contaminated with only hexavalent chromium showed that very little leaching occured, indicating that the treatment chemicals and the metal complexes they formed were stable over a period of 25 days after being subjected to various leach solutions.

B. RECOMMENDATIONS

The laboratory testing procedures used in this study were designed to approach actual field conditions so that more reliable predictions of pollutant fate and immobilization effectiveness could be made. Even with the best designs, the magnitude of the observed effect is attributed only to those factors purposely varied in the experiment. For example, the specific conditions and procedures used in any leaching evaluation will play a major role in the apparent immobilization efficiency of a particular treatment. The test procedures used in the reported study required that most of the

tests be run in a saturated soil environment. Constant submersion can cause reactions of the treatment chemicals, such as hydration of Valfor 200, which may affect their immobilization properties. In addition, these conditions may support biological activity which affect the sequestering of heavy metals.

While the results of small-scale column testing can be used in confidence when comparing results between similarly performed tests, extrapolation to field conditions should be made with caution. The reported study begins to define the comparative effectiveness of different in situ treatment additives as appplied to several common problem industrial heavy metals. The difficulties and considerations necessary in designing satisfactory leaching test protocols are apparent. Laboratory tank studies should be carried out to begin to understand the interactions between the soil dynamics and metal immobilization. Projects on a "pilot" field scale, reproducing actual soil and environmental conditions are needed to give a complete evaluation of immobilization/stabilization processes applied to hazardous waste sites.

SECTION VIII

REFERENCES

1. Pickering, W.F., "Selective Chemical Extraction of Soil Components and Bound Metal Species," Critical Reviews in Analytical Chemistry, vol. 12, no. 4, pp. 233-267, CRC Press, Boca Raton, Florida, November, 1981.

2. Farrah, H. and Pickering, W.F., "Influence of Clay-Solute Interactions on Aqueous Heavy Metal Ion Levels," Water, Air and Soil Pollution, vol. 8, pp. 189-197, 1977.

3. Hatton, D. and Pickering, W.F., "The Effect of pH on the Retention of Cu, Pb, Zn and Cd by Clay-Humic Acid Mixtures," Water, Air and Soil Pollution, vol. 14, pp. 13-21, 1980.

4. In-Place Density by the Drive Cylinder Method, ASTM Standard D-2937, American Society of Testing and Materials, Philadelphia, PA.

5. Grain Size Analysis- Hydrometer Method, ASTM Standard D-422, American Society of Testing and Materials, Philadelphia, PA.

6. Calmon, C. and Simon, G.P., "The Ion Exchangers," in Ion Exchange for Pollution Control (C. Calmon and H. Gold, eds.), vol. 1, chapter 23, pp. 23-39, CRC Press, Boca Raton, FL, 1979.

7. Amberlite Ion Exchange Resins - Amberlite IR-124, Rohm and Haas Company, Philadelphia, PA, 1975.

8. Helfferich, F., Ion Exchange, pp. 156-159, McGraw-Hill, New York, 1962.

9. Calmon, C., "Specific and Chelate Exchangers: New Functional Polymers for Water and Wastewater Treatment," J. AWWA., vol. 73, no. 12, pp. 652-656, December 1981.

10. Calmon, C., "Specific Ion Exchangers," in Ion Exchange for Pollution Control (C. Calmon and H. Gold, eds.), vol. 2, chapter 15, pp. 151-154, CRC Press, Boca Raton, Florida, 1979.

11. Gold, H., Czupryna, G., Calmon, C.C., Robinson, J.M., and Levy, R.D., Purifying Air Force Plating Baths by Chelate Ion Exchange, U.S. Air Force Report No. ESL-TR-85-48, Engineering and Services Laboratory, Headquarters, Air Force Engineering and Services Center, Tyndall AFB, FL, July 1985.

12. Assche, C.V. and Uyttebroeck, P., "Heavy Metals in Soils and Their Neutralization," Agricultural Wastes, vol. 2, pp. 279-291, Applied Science Publishers, Ltd, England, 1980.

13. Waitz, W.H. Jr., Ion Exchange in Heavy Metals Removal and Recovery, Amber-Hi-Lites, No. 162, Rohm and Haas Co., Philadelphia, PA, 1979.

14. Duolite CS-346 Technical Sheet, Diamond Shamrock, Cleveland, OH.

15. Jones, K.C. and Grinstead, R.R., "Properties and Hydrometallurgical Applications of Two New Chelating Ion Exchange Resins," Chem. Ind., pp. 637-641, 6 August 1977.

16. Grinstead, R.R., "New Developments in the Chemistry of XFS 4195 and XFS 43084 Chelating Ion Exchange Resin," in Ion Exchange Technology (D. Naden and M. Streat, eds.), pp. 509-518, Society of Chemical Industry, London, 1984.

17. Chemical Engineering, p. 11, 6 February 1984.

18. Holbein, B.E., DeVoe, I.W., Neirinck, L.G., Nathan, M.F. and Arzibettu, P.E., "DeVoe-Holbein Technology: New Technology for Closed-Loop Source Reduction of Toxic heavy Metal Wastes in the Nuclear and Metal Finishing Industries," in Proceedings Massachusetts Hazardous Waste Source Reduction, Bureau of Solid Waste Disposal, pp. 66-88, Boston, MA, 1984.

19. DeVoe, I.W. and Holbein, B.E., Insoluble Chelating Compositions, U.S. Patent No. 4,530,963, 23 July 1985.

20. Farrah, H. and Pickering, W.F., "The Sorption of Copper Species by Clays - I. Kaolinite," Aust. J. Chem., vol 29, pp. 1167-1176, 1976.

21. Farrah, H. and Pickering, W.F., "The Sorption of Copper Species by Clays - II. Illite and Montmorillonite," Aust. J. Chem., vol 29, pp. 1177-1184, 1976.

22. Farrah, H. and Pickering, W.F., "The Sorption of Zinc Species by Clay Minerals," Aust. J. Chem., vol 29, pp. 1649-1156, 1976.

23. Farrah, H. and Pickering, W.F., "The Sorption of Lead and Cadmium Species by Clay Minerals," Aust. J. Chem., vol. 30, pp.1417-1422, 1977.

24. Industrial Chemical Specifications Sheet, American Colloid Company, Environmental Products Division, Skokie, IL, 1979.

25. Atlapulgus Clay Products, Engelhard Industries, Minerals and Chemical Division, Menlo Park, CA.

26. Aluminum Silicate Pigments for Industrial Applications, Engelhard Industries, Minerals and Chemical Division, Menlo Park, CA.

27. Adsorption and Ion Exchange with Synthetic Zeolites (F.H. Flank, ed.), ACS Symposium Series No. 135, American Chemical Society, Washington, D.C., 1980.

28. Valfor Aluminosilicates Bulletin ZG100-1, The PQ Corporation, Valley Forge, PA.

29. Patterson, J.W., Wastewater Treatment Technology, Ann Arbor Science, Ann Arbor, MI, 1975.

30. Malone, P.G. and Karn, R.A., "Toxic Metal Removal from Electroplating Wastewater using Silylated Silica Gel," Paper No. EL-82-3 (AD A-120030), U.S. Army Engineers Waterways Experiment Station, Vicksburg, MS, September 1962.

31. Wing, R.E., et al., "Removal of Heavy Metals from Industrial Wastewaters Using Insoluble Starch Xanthate," U.S. Environmental Protection Agency Report No. EPA-600/2-78-085, Industrial Environmental Research Laboratory, Cincinnati, Ohio, May 1978.

32. Wing, R.E., "Starch-Based Products in Heavy Metal Removal," in Ion Exchange for Pollution Control (C. Calmon and H. Gold, eds.), vol. 2, chapter 20, pp. 177-193, CRC Press, Boca Raton, Florida, 1979.

33. Wing, R.E., "Dissolved Heavy-Metal Removal by Insoluble Starch Xanthate (ISX)," Environmental Progress, vol 2., no. 4, pp. 269-272, November 1983.

34. Standard Methods for the Examination of Water and Wastewater, Fifteenth Edition, American Public Health Association, Washington, D.C., 1980.

35. Specific Gravity of Soil Solids, ASTM Standard D-854-58, American Society of Testing and Materials, Philadelphia, PA.

APPENDIX A

BATCH SCREENING TEST DATA AND ANALYSIS

The total capacity (mequiv/100 grams soil) for the batch screening test data is repeated again (see Tables 21 through 26) for each test soil and for each chemical dosage (100 percent, 100:1 dosage). The differential capacities (mequiv/gram chemical additive) and chemical treatment costs ($/equiv metal)) are then calculated for each chemical additive.

TABLE A-1. TEST DATA AND ANALYSIS FOR MCCLELLAN AFB SOIL, 100 PERCENT DOSAGE.

Treatment Chemical	Dosage (a)	Soil/ Chem (b)	Para-meter	Total Capacity (mequiv/100 grams) Cr	Cd	Ni	Cu	Zn	Unit Cost (c)
Lime	0.26	392	Cap	0.00	5.29	5.83	5.71	6.25	0.20
			K	0.00	0.95	0.98	1.00	0.99	
Valfor Z84-326	0.81	123	Cap	0.40	4.43	4.12	5.46	5.23	2.20
			K	0.07	0.79	0.70	0.96	0.83	
ISX	0.85	118	Cap	0.36	3.45	4.21	5.12	5.00	3.74
			K	0.06	0.62	0.71	0.90	0.80	
Duolite CS-346	0.88	114	Cap	3.81	2.34	3.03	4.08	3.93	11.00
			K	0.69	0.42	0.51	0.71	0.62	
Dow XFS-4195C	0.89	113	Cap	3.82	3.54	3.16	4.77	4.63	11.00
			K	0.69	0.63	0.53	0.83	0.74	
Valfor 200	0.95	106	Cap	0.06	4.83	5.13	5.71	6.02	0.55
			K	0.01	0.86	0.87	1.00	0.96	
Metal Scrb-7	1.61	62	Cap	0.70	2.96	3.60	4.39	4.01	2.32
			K	0.13	0.53	0.61	0.77	0.64	
Amberlite IR-124	3.45	29	Cap	0.69	5.38	5.85	5.63	5.17	6.61
			K	0.13	0.96	0.99	0.98	0.82	
Amberlite IR-718C	3.92	26	Cap	2.61	3.27	4.11	5.47	4.39	11.00
			K	0.48	0.58	0.69	0.96	0.70	
Ben 125 Bentonite	4.17	24	Cap	0.58	3.27	4.17	4.60	4.70	0.30
			K	0.11	0.58	0.70	0.80	0.75	
Raw Greensand	6.39	16	Cap	0.42	1.81	2.73	3.45	3.32	0.62
			K	0.08	0.32	0.46	0.60	0.53	
HMP 20 Bentonite	7.15	14	Cap	0.06	4.03	4.84	5.23	5.54	0.71
			K	0.01	0.72	0.82	0.92	0.88	
Soil Only	0.00		Cap	0.21	2.41	2.77	3.40	2.61	
			K	0.04	0.40	0.48	0.58	0.44	

(a) Grams chemical additive/100 grams soil
(b) Grams soil/gram chemical additive
(c) $/kg

TABLE A-1. TEST DATA AND ANALYSIS FOR MCCLELLAN AFB SOIL, 100 PERCENT DOSAGE (CONCLUDED).

Treatment Chemical	Differential Capacity (mequiv/gram)					Treatment Cost ($/equiv)				
	Cr	Cd	Ni	Cu	Zn	Cr	Cd	Ni	Cu	Zn
Lime	-0.82	11.29	12.00	9.06	14.27	-0.24	0.02	0.02	0.02	0.01
Valfor Z84-326	0.23	2.49	1.67	2.54	3.23	9.38	0.88	1.32	0.87	0.68
ISX	0.18	1.22	1.69	2.02	2.81	21.19	3.06	2.21	1.85	1.33
Duolite CS-346	4.11	-0.08	0.30	0.78	1.51	2.67	-137.50	37.02	14.15	7.29
Dow XFS-4195C	4.08	1.28	0.44	1.55	2.28	2.70	8.62	24.96	7.11	4.82
Valfor 200	-0.16	2.56	2.50	2.44	3.61	-3.47	0.22	0.22	0.23	0.15
Metal Sorb-7	0.31	0.34	0.52	0.62	0.87	7.60	6.77	4.49	3.76	2.66
Amberlite IR-124	0.14	0.86	0.89	0.65	0.74	47.51	7.68	7.40	10.23	8.91
Amberlite IR-718C	0.61	0.22	0.34	0.53	0.45	17.97	50.14	32.18	20.83	24.22
Ben 125 Bentonite	0.09	0.21	0.34	0.29	0.50	3.34	1.44	0.88	1.03	0.59
Raw Greensand	0.03	-0.09	-0.01	0.01	0.11	10.76	-6.57	-98.49	78.79	5.55
HMP 20 Bentonite	-0.02	0.23	0.29	0.26	0.41	-33.50	3.11	2.43	2.75	1.72

TABLE A-2. TEST DATA AND ANALYSIS FOR ROBINS AFB SOIL, 100 PERCENT DOSAGE.

Treatment Chemical	Dosage (a)	Soil/ Chem (b)	Para-meter	Total Capacity (mequiv/100 grams) Cr	Cd	Ni	Cu	Zn	Unit Cost (c)
Lime	0.26	392	Cap	1.56	5.01	5.74	4.79	6.22	0.20
			K	0.26	0.90	0.97	0.86	0.99	
Valfor Z84-326	0.81	123	Cap	1.79	3.67	2.20	4.89	5.08	2.20
			K	0.30	0.66	0.37	0.88	0.81	
ISX	0.85	118	Cap	3.06	2.21	2.84	2.72	3.78	3.74
			K	0.51	0.40	0.48	0.49	0.60	
Duolite CS-346	0.88	114	Cap	5.19	1.58	1.56	2.65	2.48	11.00
			K	0.87	0.28	0.26	0.48	0.39	
Dow XFS-4195C	0.89	113	Cap	4.95	2.38	2.22	3.61	3.85	11.00
			K	0.83	0.43	0.38	0.65	0.61	
Valfor 200	0.95	106	Cap	0.98	4.25	4.22	4.99	5.54	0.55
			K	0.16	0.76	0.71	0.90	0.88	
Metal Sorb-7	1.61	62	Cap	2.31	2.12	2.27	3.16	3.47	2.32
			K	0.39	0.38	0.38	0.57	0.55	
Amberlite IR-124	3.45	29	Cap	2.02	5.39	5.03	4.97	6.19	6.61
			K	0.34	0.96	0.85	0.89	0.98	
Amberlite IR-718C	3.92	26	Cap	3.70	2.30	3.12	4.90	3.10	11.00
			K	0.62	0.41	0.53	0.88	0.49	
Ben 125 Bentonite	4.17	24	Cap	1.44	2.38	2.60	3.46	4.31	0.30
			K	0.24	0.43	0.44	0.62	0.69	
Raw Greensand	6.39	16	Cap	1.90	1.54	1.68	1.95	2.63	0.62
			K	0.32	0.28	0.28	0.35	0.42	
HMP 20 Bentonite	7.15	14	Cap	1.79	3.41	4.52	4.71	5.15	0.71
			K	0.30	0.61	0.76	0.85	0.82	
Soil Only	0.00		Cap	1.79	1.23	1.46	1.67	1.31	
			K	0.32	0.20	0.26	0.32	0.22	

(a) Grams chemical additive/100 grams soil
(b) Grams soil/gram chemical additive
(c) $/kg

TABLE A-2. TEST DATA AND ANALYSIS FOR ROBINS AFB SOIL, 100 PERCENT DOSAGE (CONCLUDED).

Treatment Chemical	Differential Capacity (mequiv/gram)					Treatment Cost ($/equiv)				
	Cr	Cd	Ni	Cu	Zn	Cr	Cd	Ni	Cu	Zn
Lime	-0.90	14.82	16.78	11.45	19.25	-0.22	0.01	0.01	0.02	0.01
Valfor Z84-326	0.00	3.01	0.91	3.73	4.65	ERR	0.73	2.41	0.59	0.47
ISX	1.49	1.15	1.62	1.00	2.91	2.50	3.24	2.30	3.74	1.29
Duolite CS-346	3.89	0.40	0.11	0.89	1.34	2.83	27.50	96.25	12.34	8.23
Dow XFS-4195C	3.57	1.30	0.86	1.97	2.87	3.08	8.47	12.81	5.59	3.83
Valfor 200	-0.86	3.20	2.92	3.30	4.48	-0.64	0.17	0.19	0.17	0.12
Metal Sorb-7	0.32	0.55	0.50	0.80	1.35	7.16	4.18	4.60	2.89	1.72
Amberlite IR-124	0.07	1.21	1.03	0.90	1.41	99.15	5.48	6.39	7.36	4.67
Amberlite IR-718C	0.49	0.27	0.42	0.77	0.46	22.58	40.30	25.98	14.23	24.09
Ben 125 Bentonite	-0.08	0.28	0.27	0.38	0.72	-3.53	1.08	1.09	0.78	0.41
Raw Greensand	0.02	0.05	0.03	0.01	0.21	35.81	12.71	17.91	49.24	2.98
HMP 20 Bentonite	0.00	0.31	0.43	0.40	0.54	ERR	2.31	1.65	1.77	1.31

TABLE A-3. TEST DATA AND ANALYSIS FOR TINKER AFB SOIL, 100 PERCENT DOSAGE.

Treatment Chemical	Dosage (a)	Soil/ Chem (b)	Para-meter	Total Capacity (mequiv/100 grams) Cr	Cd	Ni	Cu	Zn	Unit Cost (c)
Lime	0.26	392	Cap	0.98	6.29	5.87	5.72	6.24	0.20
			K	0.17	0.97	0.99	1.00	0.99	
Valfor Z84-326	0.81	123	Cap	0.33	6.01	5.42	5.71	5.90	2.20
			K	0.07	0.93	0.92	1.00	0.94	
ISX	0.85	118	Cap	1.64	5.27	5.33	5.64	6.03	3.74
			K	0.29	0.81	0.91	0.99	0.96	
Duolite CS-346	0.88	114	Cap	3.56	5.04	5.08	5.42	5.44	11.00
			K	0.62	0.78	0.86	0.95	0.86	
Dow XFS-4195C	0.89	113	Cap	2.41	5.76	5.04	5.75	5.76	11.00
			K	0.42	0.89	0.86	1.00	0.92	
Valfor 200	0.95	106	Cap	0.00	6.11	5.59	5.72	6.16	0.55
			K	-	0.94	0.95	1.00	0.98	
Metal Sorb-7	1.61	62	Cap	2.07	5.46	5.06	5.47	5.68	2.32
			K	0.36	0.84	0.86	0.96	0.90	
Amberlite IR-124	3.45	29	Cap	1.16	6.24	5.89	5.71	6.15	6.61
			K	0.20	0.96	1.00	1.00	0.98	
Amberlite IR-718C	3.92	26	Cap	3.61	5.89	5.59	5.80	5.85	11.00
			K	0.63	0.91	0.95	1.00	0.93	
Ben 125 Bentonite	4.17	24	Cap	0.56	5.50	5.33	5.49	5.76	0.30
			K	0.10	0.85	0.91	0.96	0.92	
Raw Greensand	6.39	16	Cap	1.53	4.58	4.67	5.24	5.45	0.62
			K	0.27	0.70	0.79	0.92	0.87	
HMP 20 Bentonite	7.15	14	Cap	1.04	5.78	5.58	5.70	6.06	0.71
			K	0.18	0.89	0.95	1.00	0.96	
Soil Only	0.00		Cap	1.40	4.62	4.64	5.68	4.62	
			K	0.26	0.76	0.82	0.92	0.80	

(a) Grams chemical additive/100 grams soil
(b) Grams soil/gram chemical additive
(c) $/kg

TABLE A-3. TEST DATA AND ANALYSIS FOR TINKER AFB SOIL, 100 PERCENT DOSAGE (CONCLUDED).

Treatment Chemical	Differential Capacity (mequiv/gram)					Treatment Cost ($/equiv)				
	Cr	Cd	Ni	Cu	Zn	Cr	Cd	Ni	Cu	Zn
Lime	-1.65	6.55	4.82	0.15	6.35	-0.12	0.03	0.04	1.26	0.03
Valfor Z64-326	-1.32	1.72	0.96	0.04	1.58	-1.67	1.28	2.28	59.40	1.39
ISX	0.28	0.76	0.81	-0.05	1.66	13.25	4.89	4.61	-79.48	2.25
Duolite CS-346	2.47	0.48	0.50	-0.30	0.94	4.46	22.92	21.88	-37.02	11.74
Dow XFS-4195C	1.14	1.29	0.45	0.08	1.29	9.64	8.54	24.34	139.07	8.54
Valfor 200	-1.48	1.58	1.01	0.04	1.63	-0.37	0.35	0.55	13.02	0.34
Metal Sorb-7	0.42	0.52	0.26	-0.13	0.66	5.56	4.43	8.87	-17.73	3.51
Amberlite IR-124	-0.07	0.47	0.36	0.01	0.44	-95.02	14.08	18.24	760.15	14.90
Amberlite IR-718C	0.56	0.32	0.24	0.03	0.31	19.51	33.95	45.39	359.33	35.06
Ben 125 Bentonite	-0.20	0.21	0.17	-0.05	0.27	-1.47	1.41	1.79	-6.51	1.09
Raw Greensand	0.02	-0.01	0.00	-0.07	0.13	30.30	-98.49	131.32	-8.95	4.75
HMP 20 Bentonite	-0.05	0.16	0.13	0.00	0.10	-13.99	4.34	5.36	251.86	3.50

TABLE A-4. TEST DATA AND ANALYSIS FOR MCCLELLAN AFB SOIL, 100:1 DOSAGE.

Treatment Chemical	Dosage (a)	Soil/ Chem (b)	Para-meter	Total Capacity (mequiv/100 grams) Cr	Cd	Ni	Cu	Zn	Unit Cost (c)
Lime	0.88	114	Cap	1.54	5.80	6.18	5.62	5.70	0.20
			K	0.29	1.00	1.06	1.00	1.00	
Valfor Z84-326	0.81	123	Cap	0.40	4.43	4.12	5.46	5.23	2.20
			K	0.07	0.79	0.70	0.96	0.83	
ISX	0.85	118	Cap	0.36	3.45	4.21	5.12	5.00	3.74
			K	0.06	0.62	0.71	0.90	0.80	
Duolite CS-346	0.88	114	Cap	3.81	2.34	3.03	4.08	3.93	11.00
			K	0.69	0.42	0.51	0.71	0.62	
Dow XFS-4195C	0.89	113	Cap	3.82	3.54	3.16	4.77	4.63	11.00
			K	0.69	0.63	0.53	0.83	0.74	
Valfor 200	0.95	106	Cap	0.06	4.83	5.13	5.71	6.02	0.55
			K	0.01	0.86	0.87	1.00	0.96	
Metal Sorb-7	0.88	114	Cap	1.13	3.00	3.56	3.90	3.09	2.32
			K	0.21	0.52	0.61	0.69	0.54	
Amberlite IR-124	0.88	114	Cap	0.38	3.84	4.21	4.31	4.01	6.61
			K	0.07	0.66	0.72	0.77	0.70	
Amberlite IR-718C	0.88	114	Cap	1.54	3.04	3.58	3.68	3.24	11.00
			K	0.29	0.52	0.62	0.65	0.57	
Ben 125 Bentonite	0.88	114	Cap	0.52	2.24	3.50	3.46	3.09	0.30
			K	0.10	0.39	0.60	0.61	0.54	
Raw Greensand	0.88	114	Cap	0.50	2.38	3.16	3.30	2.63	0.62
			K	0.09	0.41	0.54	0.59	0.46	
HMP 20 Bentonite	0.88	114	Cap	0.20	2.88	2.64	3.77	3.31	0.71
			K	0.04	0.50	0.45	0.67	0.58	
Soil Only	0.00		Cap	0.21	2.41	2.77	3.40	2.61	
			K	0.04	0.40	0.48	0.58	0.44	

(a) Grams chemical additive/100 grams soil
(b) Grams soil/gram chemical additive
(c) $/kg

TABLE A-4. TEST DATA AND ANALYSIS FOR MCCLELLAN AFB SOIL, 100:1 DOSAGE (CONCLUDED).

Treatment Chemical	Differential Capacity (mequiv/gram)					Treatment Cost ($/equiv)				
	Cr	Cd	Ni	Cu	Zn	Cr	Cd	Ni	Cu	Zn
Lime	1.52	3.87	3.90	2.54	3.53	0.13	0.05	0.05	0.08	0.06
Valfor Z84-326	0.23	2.49	1.67	2.54	3.23	9.38	0.88	1.32	0.87	0.68
ISX	0.18	1.22	1.69	2.02	2.81	21.19	3.06	2.21	1.85	1.33
Duolite CS-346	4.11	-0.08	0.30	0.78	1.51	2.67	-137.50	37.02	14.15	7.29
Dow XFS-4195C	4.08	1.28	0.44	1.55	2.28	2.70	8.62	24.96	7.11	4.82
Valfor 200	-0.16	2.56	2.50	2.44	3.61	-3.47	0.22	0.22	0.23	0.15
Metal Sorb-7	1.05	0.67	0.90	0.57	0.55	2.21	3.44	2.57	4.06	4.23
Amberlite IR-124	0.19	1.63	1.65	1.04	1.60	34.02	4.04	4.02	6.36	4.13
Amberlite IR-718C	1.52	0.72	0.93	0.32	0.72	7.24	15.28	11.88	34.38	15.28
Ben 125 Bentonite	0.35	-0.19	0.83	0.07	0.55	0.84	-1.53	0.36	4.33	0.54
Raw Greensand	0.33	-0.03	0.45	-0.11	0.02	1.86	-18.00	1.38	-5.40	26.99
HMP 20 Bentonite	-0.01	0.54	-0.15	0.42	0.80	-61.69	1.31	-4.75	1.67	0.88

TABLE A-5. TEST DATA AND ANALYSIS FOR ROBINS AFB SOIL, 100:1 DOSAGE.

Treatment Chemical	Dosage (a)	Soil/ Chem (b)	Para-meter	Total Capacity (mequiv/100 grams) Cr	Cd	Ni	Cu	Zn	Unit Cost (c)
Lime	0.88	114	Cap	3.84	5.80	6.19	5.63	5.69	0.20
			K	0.71	1.00	1.06	1.00	1.00	
Valfor Z84-326	0.81	123	Cap	1.79	3.67	2.20	4.89	5.08	2.20
			K	0.30	0.66	0.37	0.88	0.81	
ISX	0.85	118	Cap	3.06	2.21	2.84	2.72	3.78	3.74
			K	0.51	0.40	0.48	0.49	0.60	
Duolite CS-346	0.88	114	Cap	5.19	1.58	1.56	2.65	2.48	11.00
			K	0.87	0.28	0.26	0.48	0.39	
Dow XFS-4195C	0.89	113	Cap	4.95	2.38	2.22	3.61	3.85	11.00
			K	0.83	0.43	0.38	0.65	0.61	
Valfor 200	0.95	106	Cap	0.98	4.25	4.22	4.99	5.54	0.55
			K	0.16	0.76	0.71	0.90	0.88	
Metal Sorb-7	0.88	114	Cap	1.88	1.88	2.42	2.70	2.55	2.32
			K	0.35	0.32	0.42	0.48	0.45	
Amberlite IR-124	0.88	114	Cap	1.54	3.18	3.55	3.71	3.70	6.61
			K	0.29	0.55	0.61	0.66	0.65	
Amberlite IR-718C	0.88	114	Cap	2.89	1.80	2.10	2.65	2.17	11.00
			K	0.54	0.31	0.36	0.47	0.38	
Ben 125 Bentonite	0.88	114	Cap	1.59	1.71	2.30	2.37	2.33	0.30
			K	0.29	0.29	0.40	0.42	0.41	
Raw Greensand	0.88	114	Cap	1.88	1.62	1.90	2.02	2.02	0.62
			K	0.35	0.28	0.33	0.36	0.36	
HMP 20 Bentonite	0.88	114	Cap	1.81	1.88	2.64	2.73	2.82	0.71
			K	0.34	0.32	0.49	0.48	0.50	
Soil Only	0.00		Cap	1.79	1.23	1.46	1.87	1.31	
			K	0.32	0.20	0.26	0.32	0.22	

(a) Grams chemical additive/100 grams soil
(b) Grams soil/gram chemical additive
(c) $/kg

TABLE A-5. TEST DATA AND ANALYSIS FOR ROBINS AFB SOIL, 100:1 DOSAGE (CONCLUDED).

Treatment Chemical	Differential Capacity (mequiv/gram)					Treatment Cost ($/equiv)				
	Cr	Cd	Ni	Cu	Zn	Cr	Cd	Ni	Cu	Zn
Lime	2.34	5.22	5.41	4.30	5.01	0.08	0.04	0.04	0.05	0.04
Valfor Z84-326	0.00	3.01	0.91	3.73	4.65	ERR	0.73	2.41	0.59	0.47
ISX	1.49	1.15	1.62	1.00	2.91	2.50	3.24	2.30	3.74	1.29
Duolite CS-346	3.89	0.40	0.11	0.89	1.34	2.83	27.50	96.25	12.34	8.23
Dow XFS-4195C	3.57	1.30	0.86	1.97	2.87	3.08	8.47	12.81	5.59	3.83
Valfor 200	-0.86	3.20	2.92	3.30	4.48	-0.64	0.17	0.19	0.17	0.12
Metal Sorb-7	0.10	0.74	1.10	0.95	1.42	22.56	3.12	2.11	2.45	1.64
Amberlite IR-124	-0.29	2.23	2.39	2.10	2.73	-23.14	2.97	2.77	3.14	2.42
Amberlite IR-718C	1.26	0.65	0.73	0.89	0.98	8.75	16.89	15.04	12.34	11.19
Ben 125 Bentonite	-0.23	0.55	0.96	0.57	1.17	-1.30	0.54	0.31	0.52	0.25
Raw Greensand	0.10	0.45	0.50	0.17	0.81	6.00	1.38	1.23	3.60	0.76
HMP 20 Bentonite	0.02	0.74	1.35	0.98	1.73	30.84	0.95	0.52	0.72	0.41

TABLE A-6. TEST DATA AND ANALYSIS FOR TINKER AFB SOIL, 100:1 DOSAGE.

Treatment Chemical	Dosage (a)	Soil/ Chem (b)	Para-meter	Total Capacity (mequiv/100 grams) Cr	Cd	Ni	Cu	Zn	Unit Cost (c)
Lime	0.88	114	Cap	0.90	5.80	5.86	5.63	5.69	0.20
			K	0.17	1.00	1.01	1.00	1.00	
Valfor Z84-326	0.81	123	Cap	0.33	6.01	5.42	5.71	5.90	2.20
			K	0.07	0.93	0.92	1.00	0.94	
ISX	0.85	118	Cap	1.64	5.27	5.33	5.64	6.03	3.74
			K	0.29	0.81	0.91	0.99	0.96	
Duolite CS-346	0.88	114	Cap	3.56	5.04	5.08	5.42	5.44	11.00
			K	0.62	0.78	0.86	0.95	0.86	
Dow XFS-4195C	0.89	113	Cap	2.41	5.76	5.04	5.75	5.76	11.00
			K	0.42	0.89	0.86	1.00	0.92	
Valfor 200	0.95	106	Cap	0.00	6.11	5.59	5.72	6.16	0.55
			K	-	0.94	0.95	1.00	0.98	
Metal Sorb-7	0.88	114	Cap	1.74	4.74	5.06	5.35	4.97	2.32
			K	0.32	0.82	0.86	0.95	0.87	
Amberlite IR-124	0.88	114	Cap	0.30	5.01	5.26	5.42	5.13	6.61
			K	0.06	0.86	0.91	0.96	0.90	
Amberlite IR-718C	0.88	114	Cap	2.10	4.69	5.24	5.27	4.97	11.00
			K	0.39	0.81	0.90	0.94	0.87	
Ben 125 Bentonite	0.88	114	Cap	0.98	4.55	5.06	5.30	4.90	0.30
			K	0.18	0.78	0.87	0.94	0.86	
Raw Greensand	0.88	114	Cap	1.32	4.41	4.99	5.33	4.82	0.62
			K	0.24	0.76	0.86	0.95	0.85	
HMP 20 Bentonite	0.88	114	Cap	0.95	4.67	5.43	5.52	5.08	0.71
			K	0.17	0.81	0.93	0.98	0.89	
Soil Only	0.00		Cap	1.40	4.62	4.64	5.68	4.62	
			K	0.26	0.76	0.82	0.92	0.80	

(a) Grams chemical additive/100 grams soil
(b) Grams soil/gram chemical additive
(c) $/kg

TABLE A-6. TEST DATA AND ANALYSIS FOR TINKER AFB SOIL, 100:1 DOSAGE (CONCLUDED).

Treatment Chemical	Differential Capacity (mequiv/gram)					Treatment Cost ($/equiv)				
	Cr	Cd	Ni	Cu	Zn	Cr	Cd	Ni	Cu	Zn
Lime	-0.57	1.35	1.39	-0.06	1.22	-0.35	0.15	0.14	-3.47	0.16
Valfor Z84-326	-1.32	1.72	0.96	0.04	1.58	-1.67	1.28	2.28	59.40	1.39
ISX	0.28	0.76	0.81	-0.05	1.66	13.25	4.89	4.61	-79.48	2.25
Duolite CS-346	2.47	0.48	0.50	-0.30	0.94	4.46	22.92	21.88	-37.02	11.74
Dow XFS-4195C	1.14	1.29	0.45	0.08	1.29	9.64	8.54	24.34	139.07	8.54
Valfor 200	-1.48	1.58	1.01	0.04	1.63	-0.37	0.35	0.55	13.02	0.34
Metal Sorb-7	0.39	0.14	0.48	-0.38	0.40	5.97	16.92	4.83	-6.15	5.80
Amberlite IR-124	-1.26	0.45	0.71	-0.30	0.58	-5.26	14.83	9.33	-22.25	11.34
Amberlite IR-718C	0.80	0.08	0.69	-0.47	0.40	13.75	137.50	16.04	-23.48	27.50
Ben 125 Bentonite	-0.48	-0.08	0.48	-0.43	0.32	-0.62	-3.71	0.62	-0.68	0.93
Raw Greensand	-0.09	-0.24	0.40	-0.40	0.23	-6.75	-2.57	1.54	-1.54	2.70
HMP 20 Bentonite	-0.51	0.06	0.90	-0.18	0.53	-1.37	12.34	0.78	-3.86	1.34

APPENDIX B

LONG-TERM STABILITY COLUMN TEST DATA

The effluent concentration of hexavalent chromium in the various leachates from the McClellan AFB and Robins AFB soils are listed in this section. These data are presented in graphical form as Figures 13 and 14.

TABLE B-1. EFFLUENT CONCENTRATIONS FROM MCCLELLAN AFB, LONG-TERM STABILITY TEST COLUMNS.

Control, Deionized Water

PORE VOLUME	PPM Cr
1.71	480
4.23	114
6.95	46
9.16	12
11.81	5.2
14.29	3.1
16.33	3.4
18.59	2.5
21.81	1.65
22.97	2.4
24.84	2.9
25.64	2.8

Lime, Deionized Water

PORE VOLUME	PPM Cr
2.03	404
2.98	92
3.79	48
5.07	19
7.28	2.2
9.38	1.6
10.83	0.4
13.38	0
15.88	0
17.44	0
21.56	0
24.62	0
26.74	0
29.96	0

Lime, Acid Rain

PORE VOLUME	PPM Cr
2.21	356
3.68	77
4.67	38.5
5.9	7.8
8.46	0
10.39	0
12.66	0
15.08	0
16.62	0
18.38	0
21.05	0
24.13	0
26.85	0
29.72	0
32.4	0

Valfor 200/$FeSO_4$, Solvent

PORE VOLUME	PPM Cr
1.26	0
3.31	0
4.81	0
7.25	0
8.39	0
10.33	0
12.91	0
14.51	0
16.07	0
17.33	0
20.42	0
23.44	0

Valfor 200/$FeSO_4$, Deionized Water

PORE VOLUME	PPM Cr
1.1	0
2.89	0
4.16	0
5.78	0
6.96	0
7.09	0
8.36	0
9.68	0
10.72	0
12.42	0
15.24	0

Valfor 200/$FeSO_4$, Acid Rain

PORE VOLUME	PPM Cr
1.58	0
2.84	0
3.12	0
5.75	0
7.75	0
8.8	0
11.06	0
13.04	0
14.34	0
16.16	0
18.9	0

TABLE B-2. EFFLUENT CONCENTRATIONS FROM ROBINS AFB, LONG-TERM STABILITY TEST COLUMNS.

Control, Deionized Water

PORE VOLUME	PPM Cr
1.79	130
3.96	74
5.6	53
7.95	41.5
10.19	27
12.71	20.6
14.15	16.3
16.38	13.6
18.97	11.1
20.94	10.4
22.91	8.3
24.27	7.6
26.42	7.1
27.73	6.7
30.05	6.3
33.76	5

Valfor 200/$FeSO_4$, Solvent

PORE VOLUME	PPM Cr
1.84	0
3.71	0
4.63	0
7.88	0
9.76	0
11.67	0
13.87	0
15.4	0
18.35	0
19.91	0
23.11	0
26.87	0
30.98	0
35.33	0
38.58	0
40.42	0
43.75	0
44.82	0
48.82	0

Lime, Deionized Water

PORE VOLUME	PPM Cr
3.72	240
5.69	68
6.38	54
9.87	19
10.19	23
10.83	27
12.62	24
13.03	18.8
16.68	13.4

Valfor 200/$FeSO_4$, Deionized Water

PORE VOLUME	PPM Cr
1.95	0.33
3.66	0
5.5	0
8.25	0
9.98	0
13.11	0
14.34	0
18.22	0
19.55	0
20.74	0
24.45	0
27.33	0
30.21	0
33.05	0
36.54	0
40.2	0
40.93	0
45.74	0
50.27	0

Lime, Acid Rain

PORE VOLUME	PPM Cr
3.20	376
4.27	152
5.18	121
7.19	74
7.80	54
10.69	33
12.84	23
15.68	12.5
19.65	6.4
22.62	3.7
25.74	3.0
29.39	2.5
29.92	2.1
33.53	1.9
35.18	2.06
38.07	1.66
40.03	1.35
44.07	1.13

Valfor 200/$FeSO_4$, Acid Rain

PORE VOLUME	PPM Cr
1.59	0.31
2.86	0.27
4.46	0
6.09	0
8.74	0
10.85	0
14.96	0
16.55	0
18.76	0
20.25	0
21.48	0
23.4	0
25.61	0
27.93	0
31.77	0

*U.S. GOVERNMENT PRINTING OFFICE: [illegible]