108172

The Pennsylvania State University

The Graduate School

Environmental Pollution Control

Capital College

THE FIXATION OF HEAVY METALS IN A BALL MILL TAILINGS PILE AT THE JACK'S CREEK SUPERFUND SITE

A Paper in

Environmental Pollution Control

by

Roger D. Myers

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Environmental Pollution Control

June, 1995

I grant The Pennsylvania State University the nonexclusive right to use this work for the University's own purposes and to make single copies of the work available to the public on a not-for-profit basis if copies are not otherwise available.

Roger D. Myers

Roger D. Myers

ACKNOWLEDGMENTS

I would like to acknowledge the following individuals for their part in making this research paper possible:

- Mr. Garth Connor, EPA Remedial Project Manager, for permission to use the Jack's Creek Site for my research.
- Mr. Karl Yost, of Sevenson Environmental, Inc., for permission to use the MAECTITE reagents for my laboratory research and for supplying me with two scientific papers on the subject.

ABSTRACT

Lead, cadmium, and zinc can be chemically fixed using the MAECTITE treatment process on Ball Mill tailings pile material from the Jack's Creek Superfund Site. Leachable metal species within the pile are converted to geochemically stable and hardened mixed mineral forms using this patented process. The pile consists of 143,000 tons of brass dross fines that are hazardous by TCLP-characteristics for lead and cadmium. The MAECTITE treatment of the material results in a non-hazardous residual waste product. Sieve analysis of the pile shows a size-fraction above 4.75 mm diameter that contains very little leachable metals. The MAECTITE process has been shown to work best on a medium size-fraction sample of about 2-4 mm in diameter. A treatment rate of 3% has been shown to work best for the MAECTITE reagents on this tailings pile material. Chemical fixation can result in a 50% cost reduction for treatment additives over typical stabilization/solidification (S/S) techniques and will not be pH dependent. In addition, the MAECTITE process entails volume reductions achieved by reduced amounts of treatment additives and by increased densities by nucleation of the treated material, when compared to typical S/S techniques.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1

INTRODUCTION

This research paper deals with an innovative stabilization technique for remediation of heavy metals in waste media, called chemical fixation. Chemical fixation converts leachable heavy metals, such as lead, to insoluble minerals or salts within a waste matrix. This is an important contribution to the remediation of characteristic hazardous wastes, classified due to leaching of heavy metals above Toxicity Characteristic Leachate Procedure (TCLP) limits as defined by the United States Environmental Protection Agency (EPA). Chemical fixation has many advantages over more typical stabilization/solidification (S/S) techniques. The main advantages are reduced volumes of treatment reagents, reduced volume of treated material, reduced costs, faster curing times, and a manageable product that will maintain its integrity due to an irreversible chemical reaction. The particular chemical fixation additive considered in this paper is a proprietary process called MAECTITE.

A quantity of the MAECTITE fixation additive was obtained for the purpose of conducting bench-scale treatability tests at the Penn State-Harrisburg laboratory. Tests were conducted on a sample of Ball Mill tailings from the Jack's Creek Superfund site in Lewistown, Pennsylvania. The Ball Mill tailings pile consists of 143,000 tons of heavy metal-bearing hazardous waste. This is the largest single source of contamination at that site, however other sources of heavy metal waste existing at the site may also be treated by chemical fixation. The site has gone through the Remedial Investigation (RI) and Feasibility Study (FS) processes and will soon have a Record of Decision (ROD) published. The preferred alternative for remediation of the waste materials at the site includes onsite chemical fixation of waste piles and soils followed by onsite placement. Detailed information about the Jack's Creek site and the Ball Mill tailings pile material used in the laboratory research for this paper can be found in the Background section. This research may assist EPA in their evaluation towards selection of a remedy at the Jack's Creek site.

Since the chemical fixation process used in this research includes a proprietary agent that has been recently patented, little literature exists about the process. Two recent papers have been published on the MAECTITE process. These papers were written by the owners of the MAECTITE process, Sevenson Environmental. These papers have been obtained from Sevenson and are the basis of the Literature Review section. The chemical fixation process has been described in the literature without detailing the exact composition of the proprietary agents in order to protect the patent. The importance of this research is that it provides an unbiased evaluation of the effectiveness of fixation agents used in the MAECTITE process from the outside scientific community as tested under bench-scale laboratory conditions.

In addition to determining if the MAECTITE chemical fixation additives are effective for remediation of the Jack's Creek Ball Mill tailings pile material, this research will also determine if size fractionation of the tailings material is useful for remedial purposes. The research will show the size fraction(s) of the waste that the leachable metals are concentrated in, and if chemical fixation is able to treat one size fraction more effectively than another. This research will also provide some insights into the process chemistry of the chemical fixation technology.

Chapter 2

BACKGROUND

Several new stabilization techniques have recently emerged for the remediation of heavy metals in soils, sediments, sludges, waste waters, or dusts. These techniques can reduce the leachability of certain heavy metals. These new techniques use chemical fixation additives to convert leachable metals within a matrix to insoluble minerals or insoluble salts. They have several advantages over other commonly used fixation methods, such as Portland cement or Quicklime. First, the end product is not a solid monolith, but remains in the same basic form as the treated material. Next, the amount of additive needed to treat the contaminated matrix is usually very small compared to pozzolonic or lime additives typically used for stabilization. One of these new fixation techniques even reports some volume reduction following treatment. In addition, these techniques chemically bind leachable heavy metals in the matrix into new compounds. Most other solidification techniques result in the encapsulation of the material. These fixation techniques, therefore can prove to be less costly than other stabilization techniques due to the reduced amount of additives required and the simple mixing techniques utilized. Finally, the process reports a volume decrease in the treated material which can reduce material handling or storage/placement costs.

Jack's Creek Site History:

Two companies utilizing these chemical fixation techniques were screened for use as remedial options for a large tailings pile at a Superfund site in Pennsylvania. Several other sources of heavy metal contamination at the site may also be suitable for treatment with the chemical fixation additives. The Jack's Creek Site is located near the town of Maitland in a rural farming area of Mifflin County, Pennsylvania. The site was a former nonferrous metal smelting and precious metal reclamation facility, covering an area of approximately 100 acres next to Jack's Creek, a tributary of the Juniata River. The original owner of the site, Sitkin Smelting Company, operated at the site from 1958 until 1977. Two of Sitkin's main products from the smelting operation were several types of brass and bronze ingots. Brass is essentially an alloy of copper and zinc, while bronze is an alloy consisting mainly of copper and tin. The Sitkin Smelting Company also operated a nonferrous metals recycling operation which included aluminum, copper, and lead. Aluminum recycling activities included a smelter and an aluminum dross area. In addition to copper recycling, copper wire was recovered onsite by burning the insulation off of copper wire in an incinerator. Large quantities of car batteries and transformers were broken open to recover lead at the site.

Sitkin Smelting Company closed in 1977 when it declared bankruptcy. Part of the site is now owned by Mervin Krentzman as a ferrous scrap metal recycling business. Scrap aluminum is also recycled by the Krentzman operation. The site was proposed for inclusion on the National Priorities List (NPL) in June of 1988, with final listing in October of 1989 (Halliburton NUS, August, 1993).

Site Contaminants:

A variety of contamination sources exist at the site. A three-to four-acre area in the northeastern corner of the site was used for the storage of transformers. Transformers had been reportedly cracked open in this area, spilling Poly-Chlorinated Biphenyls (PCB)-laden oil onto the ground. An area of radioactive sources was discovered near the PCB spills. Radioactive switches were discovered in a pile of scrap telegraph machinery in 1991. In October of that year, the radioactive switches were removed.

The former Sitkin battery breaking operation at the site was the source of the battery casing piles observed on the surface and over the entire site. Used lead-acid batteries were brought to the site and cracked open at the battery breaking shed where the sulfuric acid was recovered and the lead plates inside were removed for recovery at the lead smelter. The remaining plastic or rubber casings were then crushed or stockpiled. The majority of the battery casings are currently found in one large pile directly behind the battery breaking shed. The casings have been mixed with soil as it appeared that soil was used to partially cover the pile. This battery casing pile is approximately 15,000 cubic yards in size. A second pile of battery casings and soil mixture is located southeast of the battery breaking shed and is approximately 3,500 cubic yards in size. Other smaller amounts of battery casing fragments are spread across the site. None of the battery casing piles are covered or lined.

Over 100 drums of soils and waste materials are scattered across the site. Several unlined lagoons are located at the site. These lagoons contain contaminated surface water and sediments. A large pile of aluminum dross, containing approximately 7,500 tons of material is located west of the old aluminum dross buildings. The dross pile was produced from the waste slag and other by-products of the former aluminum smelting operation. The uncovered and unlined aluminum dross pile contains high levels of heavy metals including aluminum, antimony, cadmium, chromium, copper, lead, nickel, silver, and zinc. TCLP tests on the aluminum dross material showed lead leaching above the regulatory limit of 5.0 mg/L.

Lead Extraction From Ores:

The main waste pile at the Jack's Creek site consists of 143,000 tons of tailings from past smelting operations, including lead smelting. There are three main steps in the extraction of lead ore. These are concentration of the sulfide ore by flotation, roasting to produce lead-oxide, then reduction to the metal. Roasting of the sulfide ore is done at about 600 degrees Celsius. The following reactions occur:

$2PbS + 3O_2 \dashrightarrow 2PbO + 2SO_2$ (main reaction)

$2SO_2 + O_2 \dashrightarrow 2SO_3$

$PbO + SO_3 \dashrightarrow PbSO_4$

$PbS + 2PbO \dashrightarrow 3Pb + SO_2$

$PbS + PbSO_4 \dashrightarrow 2Pb + 2SO_2$

$PbO + SiO_2 \dashrightarrow PbSiO_3$

The smelting of lead is then done at a temperature of about 400 degrees Celsius. The main reaction upon smelting is as follows:

$PbO + CO \dashrightarrow Pb + CO_2$

If any iron is present in the ore, two additional reactions will also occur:

$PbS + Fe \dashrightarrow Pb + FeS$

$PbO + Fe \dashrightarrow Pb + FeO$

Copper is then removed from the crude lead by flotation. The crude lead is liquefied and the copper floats to the top and is skimmed off. More impurities are then removed by oxidizing the crude lead with O_2 or a mixture of NaOH and $NaNO_3$. If the melt is cooled slowly, zinc and other impurities will crystallize out. (Fergusson 1990, p.22-23)

Ball Mill Tailing Pile:

The single largest waste pile at the site is the Ball Mill Tailings Pile, containing approximately 143,000 tons (about 44,000 cubic yards) of brass dross fines. The Ball Mill tailings consist of a dark gray, fine, soil-like material with white calcium carbonate crystals that was produced as a byproduct from crushing the slag of a nearby brass furnace. The slag from the brass furnace was drawn off as a liquid and then turned hard upon cooling. The hardened slag was then taken to a nearby grizzly in order to properly size it for the Ball Mill. The grizzly consisted of several railroad rails over which the slag was placed. Large bulldozers would drive over the grizzly and crush the slag. The crushed slag was then placed into the Ball Mill, which consisted of a large rotating drum with steel balls. Water would be added to the Ball Mill to control dust and dissipate heat. The Ball Mill was then rotated for several hours to pulverize the slag.

After crushing, the material was sent down a sloped vibrating table. This table was the major separating device in the process. The heavier metals would stay at the top of the table, while the lighter portions slid down. The heavy metals were recovered and sent back to the brass furnace. The lighter portion was sent to a second vibrating table where the process was repeated. After removing and recovering the heavier metals, the remaining material was pumped to a disc slurry.

The disc slurry had a large tank with about twelve rotating paddle wheels that were covered in a canvas-like material. Air and water would pass through the fine canvas-like material of the disc slurry, but not the tailings fines. As the paddle wheels rotated, the water flowing into the bags formed a filter cake on the outside. Further in the rotation, air was pulled through the bag to dry the filter cake. Finally, air was used to fill the bag and pop the filter cake off. A scraper bar was used to assist the process. The collected filter cake was stockpiled and is the material that makes up the current Ball Mill tailings pile. Bulldozers were used to push the filter cake to the top of the pile at the location where it currently sits. The intent was to eventually recover copper from this pile.

The remaining slurry that could not be recovered by the disc slurry process was pumped to a lagoon just east of the Ball Mill building to settle out. A small pile of this material is still present in that lagoon and has the same appearance and consistency as the tailings pile. Currently, the large tailings pile is covered by a single layer synthetic cap anchored with stakes and rubber tires. A silt fence surrounds the pile. The pile has been reshaped slightly in order to cover it. The pile is currently about 50 feet high and covers an area of about 1.5 acres or 62,500 square feet. This pile is the focus of the research for this paper.

Previous Remedial Activities:

In September of 1987, ERT consultants were contracted to perform a site characterization and conceptual site closure plan for the Ball Mill tailings pile on the Jack's Creek Site. This study included a surface and subsurface investigation of the Ball Mill tailings pile and the surrounding ground surface. Surface water and groundwater samples were also taken from Jack's Creek and newly installed groundwater wells. Both groundwater and surface water samples had positive results for barium, copper, lead, and zinc. However, none of the results exceeded the 1987 Safe Drinking Water Act levels or Clean Water Act criteria for those metals. Some lead values exceeded the 1987 proposed lead Maximum Contaminant Level (MCL) of 5 *u*g/L. In addition, soil samples from a boring through the center of the tailings pile had elevated levels of barium, copper, lead, and zinc with concentrations increasing with depth. Samples obtained from the pile's surface and shallow subsurface (up to two feet deep) had typically average concentrations of metals. These results indicate that the concentrations of metals may be relatively unevenly distributed throughout the shallow depths within the pile. Soil samples from borings around the base of the pile from the ground surface to two feet below ground surface contained considerably lower concentrations of metals. Analysis of soils from 5 to 10 feet below ground surface resulted in values that were even lower than those detected within the surface samples.

To further characterize the Ball Mill tailings pile contents and to verify the findings, ERT also completed an X-ray fluorescence spectrogram for a composite sample of tailings. The analysis indicated that the major components of the tailings were Zn declining concentration order) zinc, silica, copper, iron, calcium, and aluminum. Minor components were manganese and lead. In addition, ERT performed EP Toxicity analyses on seven samples of material from the Ball Mill tailings pile. The concentrations of lead in six of the seven extracts exceeded the EP Toxicity lead limit by more than an order of magnitude (Halliburton NUS August 1993, p.1-10).

EPA Remedial Investigation:

In 1991, EPA conducted a RI at the site performed by its Region III contractor, Halliburton NUS / Gannett Fleming, Inc. In addition to an extensive site sampling investigation, several types of samples were collected from the Ball Mill tailings pile in order to better characterize it. Samples of the pile were obtained from the surface and subsurface to determine the chemical composition and hazardous characteristics. Seven individual samples were collected from various locations over the surface of the pile. Two borings were drilled down through the top of the pile to collect samples from the interior and beneath the pile. Two leachate samples were collected from the bottom of the pile during installation of the borings.

Surface and subsurface samples from the pile revealed that the pile contains high levels of heavy metals including barium, beryllium, antimony, cadmium, cobalt, copper, lead, nickel, silver, sodium, and zinc. A summary of the inorganic contaminants found in the pile is presented in Table 1. Lead concentrations in the pile ranged from 3,130 mg/kg to 15,100 mg/kg, cadmium concentrations ranged from 9.4 mg/kg to 77.1 mg/kg, while zinc concentrations ranged from 17,800 mg/kg to 196,000 mg/kg. TCLP extracts from the tailings pile show that cadmium and lead are leaching at concentrations that exceed regulatory levels. TCLP inorganic data for samples taken at various depths within the pile are presented in Table 2. TCLP lead results from the pile ranged from 1.26 mg/L to 43.6 mg/L. TCLP cadmium results from the pile ranged from 0.1 mg/L to 1.32 mg/L. TCLP zinc results from the pile ranged from 248 mg/L to 1,950 mg/L. The tailings pile is typified by a high soil pH ranging from 9.0 to 9.8.

The leachate in the perched aquifer beneath the pile has a high pH (above 9.0) and buffering capacity with a very high turbidity content and a coffee-like color. High concentrations of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium,

TABLE 1

SUMMARY OF INORGANIC CONCENTRATIONS IN BALL MILL TAILINGS PILE

JACK'S CREEK SITE

Chemical	CRDL (mg/kg)	Ball Mill Tailings Pile			Soil Under Pile
		Concentraion Range (mg/kg)	Average Concentration (mg/kg)	Frequency of Detection	Concentration Range (mg/kg)
Aluminum	40	12800-26200	20538	16/16	9260-9380
Antimony	12	178-330	268	16/16	ND
Arsenic	2	3.5-13.4	7.8	16/16	4.5-5.0
Barium	40	270-542	378	16/16	46.4-72.7
Beryllium	1	41.4-155.0	73.8	16/16	1.6-1.7
Cadmium	1	9.4-77.1	31.8	16/16	ND
Calcium	1000	7150.00	12358	16/16	1040-1490
Chromium	2	40.3-107.0	67.6	16/16	13.6-16.5
Cobalt	10	19-35	27	16/16	9.1-12.2
Copper	5	10900.0-36700.0	23868.8	16/16	171-291
Iron	20	19500-31100	26031	16/16	18000-27300
Lead	1	3130.0-15100.0	6688.8	16/16	93.8-226
Magnesium	1000	2950-7950	4027	16/16	1850-2540
Manganese	3	3020.0-13300.0	5335.6	16/16	242-801
Mercury	0.2	0.13-0.44	0.17	8/16	ND
Nickel	8	203-1260	457	16/16	19.8-33.1
Potassium	1000	687-1510	1027	16/16	914-1700
Selenium	1	2.0-16.5	7.4	16/16	ND
Silver	2	7.0-30.0	16.6	16/16	ND
Sodium	1000	11500-43100	23188	16/16	1510-2290
Thallium	2	ND	ND	0/16	ND-0.21
Vanadium	10	12-23	16	16/16	14.6-18.4
Zinc	4	17800.0-196000.0	142612.5	16/16	1360-1640
Cyanide	2	0.5-0.5	0.2	1/16	ND

CRDL = Contract Required Detection Limit

Reference: Halliburton NUS. August 1993, p. 4-91.

TABLE 2

SUMMARY OF INORGANIC TCLP DATA FOR BALL MILL PILE SAMPLES

JACK'S CREEK SITE

Analyte	CRDL (ug/L)	TCLP Regulatory Levels (ug/L)	Sample Location				
			GBH-112-00 (ug/L)	GBH-112-20 (ug/L)	GBH-112-40 (ug/L)	GBH-112-40A* (ug/L)	GBH-113-10 (ug/L)
Aluminum	40		ND	ND	ND	ND	ND
Antimony	12		293	ND	ND	ND	ND
Arsenic	2	5,000	ND	ND	ND	ND	ND
Barium	40	100,000	4,540	4,960	1,290	1,210	5,520
Beryllium	1		ND	38.4	5.2	5	27.8
Cadmium	1	1,000	1,320	375	101	98	1,000
Calcium	1000		184,000	303,000	256,000	268,000	217,000
Chromium	2	5,000	ND	ND	ND	ND	ND
Cobalt	10		78.1	63.9	29.9	30.7	130
Copper	5		57,400	81,700	9,050	8,600	116,000
Iron	20		ND	ND	ND	ND	ND
Lead	1	5,000	27,100	22,100	1,280	1,260	43,600
Magnesium	1000		33,100	14,900	11,700	12,000	33,100
Manganese	3		31,100	39,000	34,900	34,600	37,800
Mercury	0.2	200	ND	ND	ND	ND	ND
Nickel	8		2,290	959	377	380	2,820
Potassium	1000		13,900	24,400	37,900	38,300	15,900
Selenium	1	1,000	ND	ND	51.2	86.6	ND
Silver	2	5,000	ND	ND	ND	ND	ND
Sodium	1000		30,500	760,000	1,590,000	1,540,000	254,000
Thallium	2		ND	ND	ND	ND	ND
Vanadium	10		ND	ND	ND	ND	ND
Zinc	4		1,950,000	589,000	255,000	248,000	1,730,000

CRDL = Contract Required Detection Limit

Note: GBH-112 and GBH-113 are boreholes through the top of the BallMill tailings pile.
The last two numbers (ie - 00, -20, -40) indicate the depth of the sample in feet.
The -40 and -50 foot samples are getting under the pile to the native soils.

A* = duplicate sample.

▨ exceeds reguatory limts

Reference: Halliburton NUS. August 1993, p. 4-92.

TABLE 2 Continued

SUMMARY OF INORGANIC TCLP DATA FOR BALL MILL PILE SAMPLES

JACK'S CREEK SITE

Analyte	CRDL (ug/L)	TCLP Regulatory Levels (ug/L)	Sample Location GBH-113-30 (ug/L)	JC-WA-001-00 (ug/L)	JC-WA-002-00 (ug/L)	JC-WA-003-00 (ug/L)	GBH-113-50 (ug/L)
Aluminum	200		ND	ND	ND	ND	ND
Antimony	60		244	ND	ND	ND	ND
Arsenic	10	5,000	ND	ND	ND	ND	ND
Barium	200	100,000	4,450	4,350	2,900	4,010	824
Beryllium	5		119	ND	2.3	11	27.9
Cadmium	5	1,000	133	1,240	111	1,380	19.6
Calcium	5000		352,000	195,000	171,000	164,000	70,900
Chromium	10	5,000	ND	ND	ND	ND	ND
Cobalt	50		72	71.2	36.3	86.5	95
Copper	25		61,000	43,600	3,310	21,400	8,320
Iron	100		ND	ND	ND	ND	ND
Lead	3	5,000	5,840	28,100	1,260	17,800	1,700
Magnesium	5000		18,000	28,700	24,700	27,200	13,100
Manganese	15		60,200	23,400	20,300	17,600	8,040
Mercury	0.2	200	ND	ND	ND	ND	ND
Nickel	40		749	1,850	325	1,450	102
Potassium	5000		30,900	15,500	12,100	16,200	2,240
Selenium	5	1,000	22	ND	ND	ND	ND
Silver	10	5,000	ND	ND	ND	ND	ND
Sodium	5000		488,000	414,000	1,570,000	484,000	1,410,000
Thallium	10		ND	ND	ND	ND	ND
Vanadium	50		ND	ND	ND	ND	ND
Zinc	20		1,030,000	1,800,000	402,000	1,790,000	95,200

CRDL = Contract Required Detection Limit.

Note: GBH-112 and GBH-113 are boreholes through the top of the BallMill tailings pile.
The last two numbers (ie - 00, -20, -40) indicate the depth of the sample in feet.
The -40 and -50 foot samples are getting under the pile to the native soils.

A* = duplicate sample.

▨ exceeds regulatory limits

Reference: Halliburton NUS. August 1993, p. 4-92.

copper, iron, lead, manganese, mercury, nickel, and zinc were found in total samples of this liquid, while high concentrations of antimony, arsenic, beryllium, lead, and manganese were found in the dissolved state as shown in Table 3.

Two samples taken from the pile, at 20- and 30-feet deep respectively, were submitted for mineralogical determination by X-ray diffraction and size determination by sieve analysis. The grain size distribution results are presented in Table 4.

In X-ray diffraction, samples are irradiated with a monochromatic X-ray beam of short wavelength. The X-rays interact with the atoms in crystalline structures and are scattered in a unique diffraction pattern which produces a fingerprint of the atomic or molecular structure. The two samples from the Ball Mill tailings pile were each scanned twice. One scan was completed on a random powder mount and a second scan was completed on an oriented mount to identify specific clay mineralogy. The amount of each of the major minerals present was semiquantitatively determined using the internal standard, corundum. Diffraction patterns were identified by computer matching with standards of the Joint Committee on Powder Diffraction Standards. The mineralogical characteristics the two samples is presented in Table 5.

The two samples differ significantly in their mineralogical composition and relative abundance of their components. Common to both samples are quartz, calcite, albite, biotite, montmorillonite, and iron oxides, of which montmorillonite has the highest cation exchange capacity. The most abundant mineral in one sample was zeolite, while the most abundant mineral in the second sample was chlorite. Lacking from both samples were minerals that contain significant amounts of lead, copper, or zinc such as the metallic sulfides or carbonates.

<u>Other Contaminated Media</u>:

The post smelting and recycling activities have contributed in part or in whole to the general contamination of other solid media at the site. Surface soils across the site are characteristically devoid of vegetation. Soils, fill material, and waste pile materials have eroded and moved around the site extensively over the years, making virgin soil indistinguishable. Generally the surface soils consisted of brown, red and gray silts with grades of sand and some clay. Fill material, tailings pile fines, and battery casing

TABLE 3

SUMMARY OF TOTAL AND DISSOLVED INORGANIC CONCENTRATIONS IN BALL MILL TAILINGS LEACHATE

JACK'S CREEK SITE

Chemical	CRDL (ug/l)	Total Leachate		Dissolved Leachate Concentrations (ug/l)
		Concentraion Range (ug/l)	Average Concentration (ug/l)	
Aluminum	200	34600-78300	306320	ND
Antimony	60	220-6850	1523	172
Arsenic	10	70-186	96.0	56.7
Barium	200	806-4760	2335	147
Beryllium	5	74.8-2600.0	781.3	7.7
Cadmium	5	25.7-452.0	205.0	ND
Calcium	5,000	34600-501000	161980	ND
Chromium	10	55-2150	691	ND
Cobalt	50	49-609	212	ND
Copper	25	18300-258000	124120	956
Iron	100	41800-725000	255980	139
Lead	3	4620.0-91500.0	41052.0	630
Magnesium	5,000	7630-96700	37446	957
Manganese	15	2840-150000	45292	121
Mercury	0.2	0.32-4.50	1.84	0.38
Nickel	40	344-4240	2169	39.6
Potassium	5,000	20100-167000	94900	143000
Selenium	5	44.1-178.0	45.9	13
Silver	10	11-249	81	ND
Sodium	5,000	6260000-8150000	7250000.	6100000
Thallium	10	ND	ND	ND
Vanadium	50	208-418	316	71.9
Zinc	20	43400-4260000	1310780.0	712
Cyanide	10	28-28	10.0	NA

NA	Not Analyzed
ND	Not Detected

Reference: Halliburton NUS. August 1993, p. 4-47.

TABLE 4

SUMMARY OF GRAIN SIZE DATA FOR TAILINGS PILE SOIL SAMPLE

JACK'S CREEK SITE

Sieve Size		Particle Size Percent Passing	
English	Metric (millimeters)	Sample GBH-112-30	Sample GBH-113-20
3.0 in	76.20	100	100
1.5 in	38.10	100	100
0.75 in	19.00	100	92.1
0.375 in	9.50	100	86.6
No. 4	4.75	100	82.5
No. 8	2.36	100	78.7
No. 10	1.95	99.4	78.2
No. 16	1.18	97.48	69.32
No. 30	0.60	85.46	57.26
No. 50	0.30	70.78	46.56
No. 100	0.15	53.10	33.56
No. 200	0.075	40.09	23.15

Notes: JC-WA-112-30 Specific Gravity = 4.126
JC-WA-113-20 Specific Gravity = 3.201

Time (minutes)		Hydrometer Particle Size	
		GBH-112-30 (mm)	GBH-113-20 (mm)
2		0.028	0.030
5		0.018	0.019
15		0.011	0.011
30		0.008	0.008
60		0.006	0.006
250		0.003	0.003
1,440		0.001	0.001

Reference: Halliburton NUS. August 1993, p. 4-94.

TABLE 5

MINERALOGY OF BALL MILL TAILINGS

JACK'S CREEK SITE

Mineral	Percent
Location GBH-112-30	
Quartz	15
Calcite	5
Zeolite (1)	47
Microcline	11
Albite	6
Mica (2)	16
Corrensite	Not quantified
Montomorillonite	Not quantified
Iron Oxides	Trace
Gypsum	Trace
Location GBH-113-20	
Quartz	29.00
Calcite	6.00
Albite	15.0
Illite	10.0
Biotite	5.0
Chlorite	35.0
Montomorillonite	Not quantified
Iron Oxides	Trace

Notes:

(1) May be Laumontite, Thompsonite, or Mordenite

(2) Biotite/Muscovite

Reference: Halliburton NUS. August 1993, p. 4-95.

fragments were frequently seen in the surface soils. Surface soils at the site were shown to be contaminated with mainly heavy metals. The highest metal concentrations in surface soils were from antimony, cadmium, copper, lead, selenium, silver, and zinc. PCB's were also detected in surface soils. The heavy metal contamination in surface soils is fairly widespread. The average lead concentrations in surface soils is presented in Figure 1, where most of the site surface soils exceed 1,000 mg/kg of lead with a sizable portion of the surface soils exceeding 10,000 mg/kg of lead. Surface soils have also been shown to be leaching lead as evidenced by elevated TCLP results, some exceeding regulatory levels. Shallow subsurface soil samples taken from two-feet depths across the site showed similar types of heavy metal contaminants. Concentrations of cadmium, copper, selenium, silver, and zinc tended to decrease in the shallow subsurface soils, while concentrations of antimony and lead seemed to increase in the shallow subsurface soils. Deeper subsurface soil samples taken across the site showed dramatically reduced heavy metal concentrations.

Several tributaries that flow across the site into Jacks Creek, contain heavy metals. Twenty-four acres of the site lie within the 100-year floodplain of Jacks Creek. Sediments collected from Jacks Creek, tributaries, and floodplains next to the creek, contained heavy metals, PCB's and Base Neutrals/Acid Extractables (BNA's). Heavy metals such as calcium, copper, lead, and zinc are elevated in sediments of Jacks Creek adjacent to the site and decrease in concentration farther downstream. These same heavy metals were also elevated in onsite tributary sediments. Cadmium, copper, lead, and zinc were elevated in the floodplain sediment samples (Halliburton NUS August 1993).

Site Removal Actions:

In August of 1991, the Emergency Response Section of EPA completed several removal actions at the site. To limit the contaminants reaching Jack's Creek, the EPA installed a temporary synthetic cap over the Ball Mill tailings pile. The cap was designed for a useful lifespan of five years and served to reduce dispersion of contaminated dusts by wind transport and reduced rainfall infiltration along with surface erosion. The cap was later secured with stakes, tires, and rope due to the effects of wind on the pile. A silt fence and rip-rap were also placed around the base of the pile to reduce erosion. In

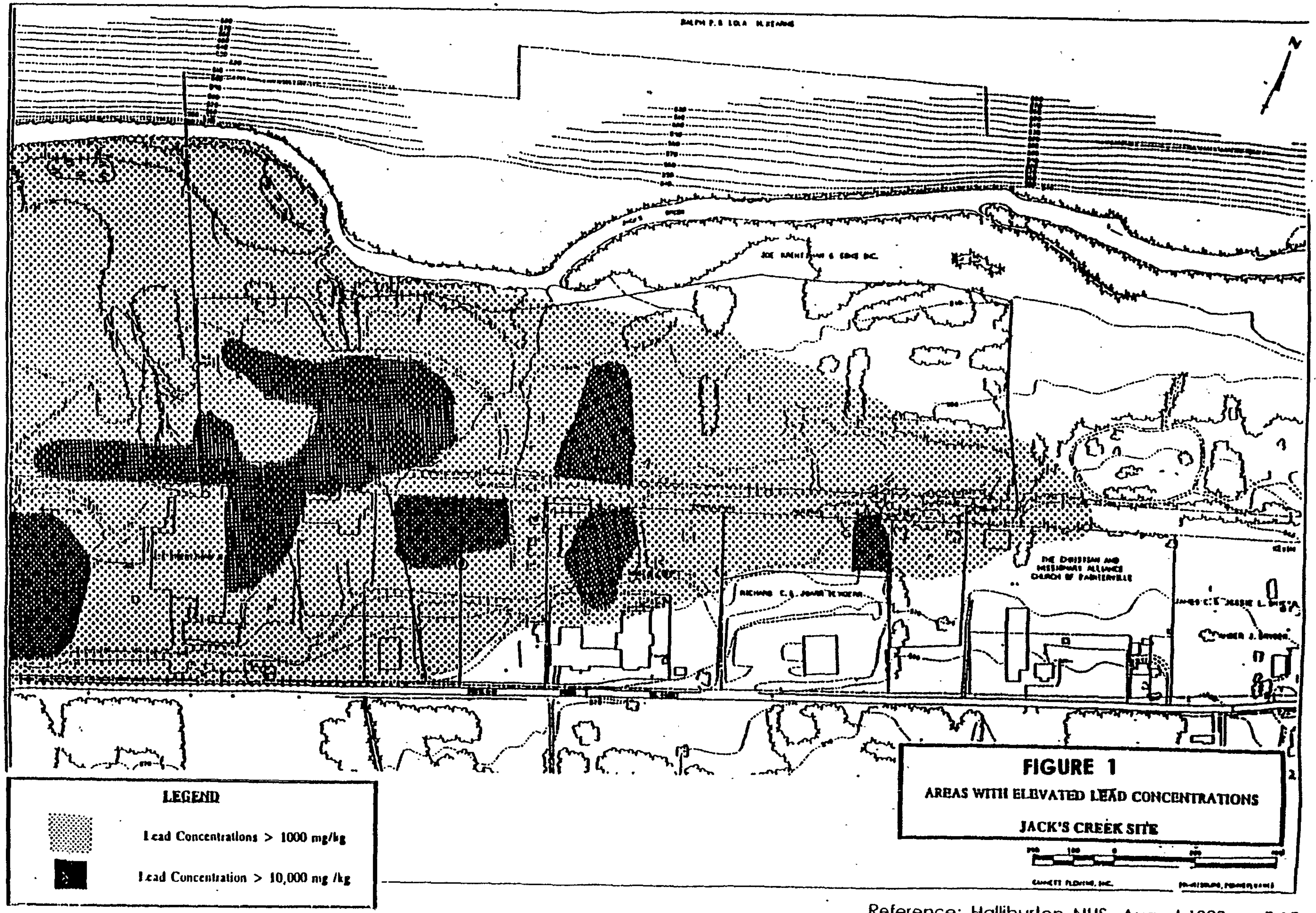


FIGURE 1

AREAS WITH ELEVATED LEAD CONCENTRATIONS

JACK'S CREEK SITE

Reference: Halliburton, NUS. August 1993. p. 7-17 addition, an eight-foot high chainlink fence was installed around the site to limit access to the site and the waste pile. Other removal activities completed by EPA included measures to limit erosion of surficial materials. These involved construction of diking, rip-rapping runoff channels, and an attempt to revegetate floodplain areas with soil-stabilizing vegetation.

Contaminant Fate and Transport:

In August of 1993, Gannett Fleming completed the Final RI Report. The report detailed the physical characteristics of the site, the nature and extent of contamination, the environmental fate and transport of the contaminants, and a baseline risk assessment. The migration and transport of contaminants within and through the Ball Mill tailings pile was modeled through an evaluation of contaminant data and site characteristics. The migration of contaminants into the groundwater can occur through infiltration of water down through the waste pile containing soluble metal species. Leaching was evidenced by the high inorganic concentrations detected in the perched aquifer beneath the tailings pile. Contaminated surface materials were potentially transported away from the pile by surface water transport, wind erosion, or by flooding of Jack's Creek prior to the installation of the cap. The pile is located within the 100-year floodplain. Track-out of wastes by vehicles represents another mechanism of contaminant migration. The contaminant migration routes from the pile can also impact ecological receptors. Heavy metals in surface soils can directly be uptaken into vegetation. Lead and other metals have been shown in the RI to be directly uptaken into plants (Brown, 1983). Very high concentrations of some metals can result in mortality of vegetation, seeds, rhizomes, tubers and other plant propagules. This may be the case at the Jack's Creek site since most of the site is devoid of vegetation.

The fate of heavy metals in the pile is largely controlled by weathering and the absorptive capacity of the material. The process of absorption will control the amount of heavy metals that can be retained within the soil. Since lead is a primary contaminant at this site, the mobility of lead is of particular importance. Soils have a relatively large capacity for the absorption of ionic lead. The capacity of the soil to absorb lead can be reasonably predicted based on a correlation equation involving pH and cation exchange capacity. Precipitation of lead as a carbonate, fixation by organic matter, or sorption by hydrous oxides may be individually or collectively responsible for the absorptive capacity. The total capacity of a soil to attenuate lead can be predicted based on a linear relationship (Zimdahl and Skogerboe, 1977).

$$N = 2.8 \text{ x } 10EE\text{-}6\ (A) + 1.1 \text{ x } 10EE\text{-}5\ (B) - 4.9 \text{ x } 10EE\text{-}5$$

Where:

N = saturation capacity of a soil (mol lead/gram soil)
A = cation exchange capacity, CEC (meq/100 grams soil)
B = pH of soil

CEC values and pH values for samples collected during the RI were used for various soil samples taken at different depths across the site. These values are shown in Table 6 along with the calculated saturation capacity of lead and the total lead concentration in each soil sample. The CEC values represent the quantity of ions held in exchangeable form in the soil. It also represents the total number of negative charges per unit quantity of soil neutralized by easily replaceable cations. The calculated saturation capacities for lead are specific to each location, however an average saturation capacity for lead of 12,458 mg/kg was calculated for evaluation purposes. Total lead concentrations in soils across the site that exceed this value would be expected to leach lead to the soils below them and subsequently into the aquifer. This is likely the same scenario that occurs in the Ball Mill tailings pile since heavy metals were already observed leaching into the perched aquifer beneath the pile, however no CEC information was collected there.

Another method that can be used to determine if heavy metals are leaching into solution utilizes the average soil concentration of the elements and the limiting molar concentration for each element in the soil solution (Lindsay, 1979). Table 7 shows the average soil concentrations for selected elements and the maximum concentration of each element in the soil solution if all that element at its average reference level were to dissolve in the water present at 10% of the dry weight of the soil. This parameter is expressed as

TABLE 6

SOIL SATURATION CAPACITY FOR LEAD

JACK'S CREEK SITE

SOIL SAMPLE	SOIL LEAD CONCENTRATION (mg/kg)	CATION EXCHANGE CAPACITY (A) (meq/100g)	pH (B)	SOIL SATURATION CAPACITY (N)	
				(mol lead/g soil)	(mg/kg)
GBH-101-06	23.1	11.6	5.8	47.28 EE-6	9,796
GBH-103-06	543	14	9.0	89.2 EE-6	18,482
GBH-104-11	23.1	13.6	6.7	62.78 EE-6	13,008
GBH-105-25	18.9	14.4	6.2	59.52 EE-6	12,333
GBH-106-11	10.2	17.3	5.3	57.74 EE-6	11,964
GBH-108-11	10.4	7.9	6.8	47.92 EE-6	9,929
GBH-111-00	42400	13.3	5.3	46.54 EE-6	9,643
GBH-201-00	23.8	6.8	5.6	31.64 EE-6	6,556
GBH-202-00	91.4	15	5.9	57.9 EE-6	11,997
GBH-203-06	27.9	12.2	5.6	46.76 EE-6	9,689
GBH-203-06A	27.9	11.9	5.8	48.12 EE-6	9,970
GBH-206-00	106	17.7	8.5	94.06 EE-6	19,489
GBH-207-11	ND	12	6.5	56.1 EE-6	11,624
GBH-208-06	5.5	16.3	5.3	54.95 EE-6	11,384
GBH-210-11	8.6	16.7	9.2	98.96 EE-6	20,505
GBH-212-06	15.9	13.9	6.6	62.52 EE-6	12,954

ND = Not detected

Notes: Molecular weight of lead = 207.2 grams/mol
Average saturation capacity = 12,458 mg/kg

Reference: Halliburton NUS. August 1993, p. 5-18.

TABLE 7

MOLAR CONCENTRATIONS OF VARIOUS ELEMENTS IN SOILS

JACK'S CREEK SITE

Element	Atomic Weight (g)	Selected Average for Soils	
		ppm	Molar Concentration at 10% Moisture log M
Ag	107.87	0.05	-5.33
Al	26.98	71000	1.42
As	74.92	5	-3.18
B	10.81	10	-2.03
Ba	137.34	430	-1.50
Be	9.01	6	-2.18
Br	79.91	5	-3.20
C	12.01	20000	1.22
Ca	40.08	13700	0.53
Cd	112.40	0.06	-5.27
Cl	35.45	100	-1.55
Co	58.93	8	-2.87
Cr	52.00	100	-1.72
Cs	132.91	6	-3.35
Cu	63.54	30	-2.33
F	19.00	200	-0.98
Fe	55.85	38000	0.83
Ga	69.72	14	-2.70
Ge	72.59	1	-3.86
Hg	200.59	0.03	-5.83
I	126.90	5	-3.40
K	39.10	8300	0.33
La	138.91	30	-2.67
Li	6.94	20	-1.54
Mg	24.31	5000	0.31
Mn	54.94	600	-0.96
Mo	95.94	2	-3.68
N	14.01	1400	0.00
Na	22.99	6300	0.44
Ni	58.71	40	-2.17
O	16.00	490000	2.49
P	30.97	600	-0.71
Pb	207.19	10	-3.32
Rb	85.47	10	-2.93
S	32.06	700	-0.66
Sc	44.96	7	-2.81
Se	78.96	0.3	-4.42
Si	28.09	320000	2.06
Sn	118.69	10	-3.07
Sr	87.62	200	-1.64
Ti	47.90	4000	-0.08
V	50.94	100	-1.71
Y	88.91	50	-2.25
Zn	65.37	50	-2.12
Zr	91.22	300	-1.48

Source: Lindsay, 1979

log M (moles per liter) and provides the limiting molar concentration for each element in the soil solution. The average molar concentrations of elements in soils (log M) can be adjusted to correspond to actual elemental compositions and moisture contents for a site. For example, if soil at the site contains 500 ppm of zinc rather than 50 ppm as shown in the table, the log ratio (500/50) = 1.00 can be added to -2.12 (log M value) to give -1.12 M for the maximum concentration of zinc possible in this soil at 10% moisture. Furthermore, if the moisture content of this soil was 40% instead of 10%, the ratio (log 10/40) = -0.60 can be added to -1.21 to give -1.71 M for the maximum concentration of zinc in this soil. Likewise, the maximum concentration of zinc in an aqueous suspension of soil consisting of 1 gram of soil per 100 ml of water (log 0.1/100) = -3.00, would yield a maximum concentration of 10EE-4.12 M or about 750 *ug*/L Using the site data, maximum concentrations of various elements can be calculated for the soil and for the groundwater in the vadose zone. Table 8 shows maximum calculated concentrations of lead, zinc, and cadmium for several groundwater samples using this method along with inorganic data from the surface soils collected at these locations. The calculated concentrations should represent the amount of heavy metals that could be in the groundwater from the natural dissolution of metals in the soil. These calculated maximum concentrations are then compared to the actual concentrations of heavy metals found in the groundwater. Groundwater concentrations that greatly exceed the calculated maximums cannot be attributed solely to natural dissolution. Other chemical or physical factors (such as pH or mineral species) must be responsible for the additional leaching at these locations. The samples denoted GBH-112 and GBH-113 were from the perched aquifer beneath the Ball Mill tailings pile.

Another important factor that assists in predicting the mobility of inorganic species is pH. pH is defined as a measure of the hydrogen ion concentration (Masterton and Slowinski, 1973). This value is given by the formula pH = -log [H+]. pH is important with respect to the ability of a metal to remain soluble or to precipitate as a particular salt. Several metals, however, are soluble at both basic and acidic conditions. These metals are considered amphoteric. The most important amphoteric metal at the site is lead. Other amphoteric metals include antimony, aluminum, chromium, tin, and zinc. The Ball Mill

TABLE 8

COMPARISON OF CALCULATED MAXIMUM CONCENTRATIONS TO ACTUAL CONTAMINANTS IN GROUNDWATER

JACK'S CREEK SITE

Sample Location	Surface Soil Concentrations				Groundwater					
					Lead		Zinc		Copper	
	Lead (mg/kg)	Zinc (mg/kg)	Copper (mg/kg)	% Moisture	Calculated Maximum (ug/L)	Actual Average (ug/L)	Calculated Maximum (ug/L)	Actual Average (ug/L)	Calculated Maximum (ug/L)	Actual Average (ug/L)
GMW-200S	972	899	541	11.5	475	34.1	1350	84.8	843	19.7
GMW-201S	23 8	233	30	9.7	11.5	▨ 320	355	1120	47	51.6
GMW-202	91 4	340	177	12.9	43.6	24.1	513	92.7	276	38.4
GMW-203	20.5	225	57.2	20	10	14.3	339	10	89	40.7
GMW-204	22500	9380	4580	10.5	10700	118	14100	451	7140	17.0
GMW-205	11.7	57.4	22	18.4	5.6	▨ 56	87	239	34	15.2
GMW-206	106	1910	277	18.2	51.3	89.1	2880	1193	436	276
GMW-207	6700	11900	14600	22.5	3240	35.8	18200	150	22800	19.2
GMW-208	232	404	320	13.1	110	142	616	1078	499	28.8
GMW-209	6.8	<2	<2.5	9.9	3.2	12.6	<3.0	26.9	<3.8	15.1
GBH-112	8730	133000	30400	24.1	4170	5180	204000	45450	47400	23800
GBH-113	8120	147000	30700	22.9	3890	▨ 66000	233000	▨ 2150000	47900	▨ 491000

Notes: ▨ Average concentrations that exceed calculated maximums by an order of magnitude or more

Reference: Halliburton NUS, August 1993, p. 5-27.

tailings pile had high pH values ranging from 8.8 to 9.8. The leachate under the pile also had high liquid pH values, ranging from 9.5 to 10.0. It is widely known that metals will become mobile in an acidic environment, yet the amphoteric metals will also become mobile in basic environments. It is likely that the metals in the Ball Mill tailings pile and the leachate beneath it have become mobile and have migrated into the groundwater or have been transported by overland flow into the surface water.

Mineralogy of the Pile:

A mineralogical analysis of the Ball Mill tailings pile was conducted by Hazen Research in 1991 (START, March 1993). The analysis utilized XRF scanning, optical microscopy, x-ray diffraction, and inorganic analysis to determine the composition of the pile. In addition, wet screenings were conducted to analyze metal content on various size fractions. All of the elements were found in the tailings material that would be expected in a milled secondary-bronze dross generated from a firebrick-lined rotary furnace. These included Cu, Zn, Pb, Sn, SiO2, B2O3, Al2O3, Na2O, MnO, Fe2O3, and C. These 11 components account for greater than 80% of the tailings pile composition. The remainder is likely the dilution material following discharge, water of hydration, or miscellaneous tramp materials from the scrap-metal feedstock to the furnace.

The major component of the tailings pile is a family of amorphous zinc-aluminum-iron-calcium silicates, of which the calcium zinc silicate portion contains lead. Mineralization products from natural sources were present in lower quantities and were not a major contributor. A likely source of the TCLP lead and TCLP cadmium in the pile is zincite (ZnO) and willemite (Zn2SiO4) containing PbO inclusions. Nearly half of the Ball Mill tailings zinc content is accounted for by the ZnO and Zn2SiO4 minerals. Most of the balance of the zinc is tied up in the glassy aluminum-iron-calcium silicates. Screening analysis indicated that the heavy metals zinc, copper, lead, or iron were not substantially enriched in any of the size fractions.

A summary of major potential minerals within the tailings pile includes eleven minerals listed in increasing order of their solubility equilibrium constants. These are quartz (SiO2), microcline (KAlSi3O8), albite (NaAlSi3O8), cerussite (PbCO3), calcite

($CaCO_3$), illite, zincite (ZnO), lead oxide (PbO), willemite (Zn_2SiO_4), muscovite , and chlorite.

Quartz is the most stable SiO_2 mineral. The amorphous silica found in the pile is the least stable silica form and would be slightly soluble. The Ball Mill tailings pile contains more silicates than anything else. The reason for this is that sand was added into the smelter to effect the flux of the smelting reactions. The sand did not end up in the products, and therefore became part of the Ball Mill tailings. Microcline has one of the lowest solubilties of the potassium aluminosilicates. In alkaline soils, microcline is sufficiently stable to prevent potassium weathering or leaching above normal levels. Albite minerals are too soluble to persist or precipitate in natural soils, therefore this mineral would be expected to dissolve. In poorly drained arid soils, the rate of sodium weathering often exceeds the rate of natural sodium leaching from the soil and sodium salts accumulate to become phytotoxic. Cerussite is a lead-bearing mineral that is naturally stable in soils and especially at higher pH values. An increase in carbon dioxide levels will also cause cerussite to become more stable. Calcite is also known as calcium carbonate. When present, it has a dominating influence on soil properties. Calcareous soils have pH ranges of 7.3 to 8.5. Only in sodium affected soils does the pH rise above 8.5. The amount of carbon dioxide gas in the soil will also have a positive affect on the solubility of calcite. Illite is a secondary clay mineral that is fairly stable in soils and is among those most often found. Illite is commonly more stable than chlorite as one of the aluminosilicates. Acidic environments will cause illite to become more soluble, while basic environments of pH 8 to 10 will cause it to be more stable. The solubility of illite appears to be too high to permit its formation in natural soils. Zincite is more soluble than zinc in soil or willemite. Its solubility decreases 100-fold for each unit increase in pH. Zincite is also too soluble to persist in natural soils. This mineral makes good zinc fertilizer in soil because it dissolves sufficiently to maintain levels of ionic zinc that are adequate for plants. Lead oxide is found in two forms; red and yellow. These oxides of lead are the most soluble of the lead minerals, even at high pH conditions. Willemite is a zinc mineral of intermediate solubility between zinc in soil and zincite. Since it is very soluble, it is difficult to account for the zinc found in most natural soils. Muscovite is the least soluble mineral of the potassium aluminosilicates. It is slightly pH-dependent and is most stable at higher pH values. Muscovite disappears when soils become acidic and potassium is leached. Chlorite is highly pH dependent. It is most stable in alkaline environments and may be expected as a stable mineral above a pH of 7.5.

Many of these minerals are stable only at high pH ranges. Since the tailings pile is highly basic (pH above 9), it promotes the stability of many of the minerals found during the mineralogical analysis. Past disposal practices of battery acid may be the cause of some of the heavy metals found in the perched water directly beneath the pile.

Risk Assessment:

A human health risk assessment was conducted on the site for the Remedial Investigation (Halliburton NUS August 1993, p.6-1). A portion of the risk assessment concentrated on the Ball Mill tailings pile. Exposure to the tailings pile was difficult to evaluate since this source is not contacted on a daily basis. Occasional exposure is possible, however. Chemicals in the Ball Mill tailings pile that pose a concern can be identified by comparing detected levels to EPA's risk-based screening values as presented in Table 9. This comparison was only performed to identify those contaminants that posed the greatest risk. Chemicals exceeding the risk-based screening levels included antimony, arsenic, beryllium, cadmium, copper, lead, manganese, zinc, and PCBs. Risk was calculated for ingestion of soils from the tailings pile as well as dermal contact with the pile for trespassers and for workers at the scrapyard nearby. Table 10 shows the exposure variables that were used to calculate the intake of contaminants from the pile. Table 10 also outlines the toxicity values for the chemicals of concern that were used to calculate the risk numbers. Carcinogenic risks can then be estimated by combining information in the dose-response assessment with an estimate of the individual intake of a contaminant by a receptor. Risks are then calculated. The calculated carcinogenic risk for inadvertent ingestion of Ball Mill tailings pile by adult scrapyard workers was 8.5 x 10EE-5 for exposure to beryllium and PCBs. Lead was present, but a slope factor was not available to calculate additional risk. The calculated carcinogenic risk for dermal exposure of the Ball Mill tailings pile by adult scrapyard workers was 1.0 x 10EE -6 for exposure to PCBs. Media with risks above 1.0 x 10EE-6 may be considered for remediation. This

TABLE 9

TOXICITY VALUES FOR CHEMICALS OF POTENTIAL CONCERN

JACK'S CREEK SITE

Parameter	Reference Dose (mg/kg/day)		Slope Factors (mg/kg/day)		EPA Cancer Classification	Type of Cancer
	Oral	Inhalation	Oral	Inhalation		
Cadmium	5.0E-4 *	NA	NA	6.1 **	B1	Lung, respiratory tract
Lead	NA	NA	NA	NA	B2	Intestinal tract, respiratory tract, kidney
Zinc	3.0E-1 *	NA	NA	NA	D	NA

* IRIS, March, 1993
** HEAST, FY, 1992
NA = Not Available
B = Probable Human Carcinogen
D = Not Classifiable

Reference: Halliburton NUS, August 1993, p. 6-122.

TABLE 10

EXPOSURE VARIABLES USED TO CALCULATE INTAKE OF CONTAMINANATS VIA INGESTION OF SURFACE SOILS

JACK'S CREEK SITE

Variable	Receptor	Value	Rationale
Intake rate (R)	Adult Employee	250 milligrams/day	Assumes outdoor exposure, based on professional judgment
	Adult Trespasser	250 milligrams/day	Assumes same exposure as an employee
	Child Trespasser (age 7-12)	250 milligrams/day	Assumes same exposure as an employee
	Adult	100 milligrams/day	EPA suggested value
	Child (age 7-12)	100 milligrams/day	EPA suggested value
Fraction ingested from contaminated source (FI)	Adult Employee	1.0	Assumes all material is from contaminated source
	Adult Trespasser	1.0	Assumes all material is from contaminated source
	Child Trespasser (age 7-12)	1.0	Assumes all material is from contaminated source
	Adult	1.0	Assumes all material is from contaminated source
	Child (age 7-12)	1.0	Assumes all material is from contaminated source
Exposure Frequency (EF)	Adult Employee	250 days/year (for soils in scrap yard)	EPA suggested value for worker exposure
		30 days/year (for confined area and waste piles)	Assumes worker handles waste pile material on average 2.5 days per month
	Adult Trespasser	12 days/year	Assumes trespasser visits site one per month
	Child Trespasser (ages 7-12)	12 days/year	Assumes trespasser visits site one per month
	Adult	50 days/year	Assumes adult hunts or hikes in area approximately one per week
	Child (age 7-12)	200 days/year	Assumes older children play outside on a regular basis
Exposure duration (ED)	Adult Employee	30 years	EPA suggested value
	Adult Trespasser	30 years	Assumes person lives in area for 30 years

TABLE 10

EXPOSURE VARIABLES USED TO CALCULATE INTAKE OF CONTAMINANATS VIA INGESTION OF SURFACE SOILS

JACK'S CREEK SITE

Variable	Receptor	Value	Rationale
Exposure duration (ED)	Child Trespasser (age 7-12)	6 years	Time period between the ages of 7 and 12
	Adult	30 years	EPA suggested value
	Child (age 7-12)	6 years	EPA suggested value
Body Weight (BW)	Adult Employee	70 kilograms	EPA suggested value
	Adult Trespasser	70 kilograms	EPA suggested value
	Child Trespasser (age 7-12)	30 kilograms	Identifies approximate average weight for children between 7 and 12 years old
	Adult	70 kilograms	EPA suggested value
	Child (age 7-12)	30 kilograms	Identifies approximate average weight for children between 7 and 12 years old

Reference: Halliburton NUS. August 1993, p. 6-108.

equates to one additional case of cancer in 1,000,000 persons.

Noncarcinogenic risks are calculated by comparing a time-weighted daily intake to an acceptable level such as a chemical-specific and time-specific reference dose. The calculated noncarcinogenic hazard indices for ingestion of Ball Mill tailings material by adult workers was 1.4 for exposure to manganese and copper. The calculated hazard indices for dermal contact of tailings material by adult workers was <0.01. If the hazard quotient exceeds 1.0, there is a potential health risk associated with exposure to that particular chemical. Lead was also not evaluated in the noncarcinogenic risk assessment because of the unavailability of a toxic value, or reference dose. Toxicity for noncarcinogens is based on the organ affected by exposure (i.e., lungs, liver, kidney). Different chemicals affect different organs. The target organs for the heavy metal present in the Ball Mill tailings pile are presented in Table 11.

Feasibility Study:

A Final Feasibility Study (FS) for the Jacks Creek Site was completed in 1993 (Halliburton NUS November 1993). The FS was prepared to evaluate a range of remedial alternatives that will protect human health and the environment from the risks associated with the site. The primary objectives that are emphasized include:

- Protect human health and the environment
- Meet Applicable or Relevant and Appropriate Requirements (ARARs)
- Provide permanent solutions to contamination problems and long-term effectiveness
- Permanently reduce the toxicity, mobility, and volume of contaminants
- Provide cost-effective solutions

Remedial action objectives were developed for the various media described in the RI. In general, the remedial action objectives are to mitigate or reduce unacceptable risks and to prevent the ingestion, inhalation, or direct contact with contaminated materials that would result in a combined carcinogenic risk that exceeds 1 x 10EE-4 to 1 x 10EE-6, a combined hazard index that exceeds 1.0, concentrations greater than published regulatory levels, or the potential to be acutely hazardous when handled. Specific remedial action

TABLE 11

LIST OF TARGET ORGANS AND POTENTIAL EFFECTS FOR CHEMICALS OF CONCERN

JACK'S CREEK SITE

Chemical	Target Organ	Toxic Effect in Humans
Cadmium	Respiratory system, kidneys, prostate, blood	A human poison by inhalation and possibly other routes. Posion experimentally by ingestion, inhalation, intraperitoneal, subcutaneious, intramuscular, and intravenous routes. In humans inhalation causes an increase of protein in the urine. An experimental carcinogen, tumorigen, neoplastigen, and teratogen. Experimental reproductive effects. Mutagenic data exists. Cadmium compounds cause cancer when inhaled. Cadmium compounds are poisonous when ingested and reaction is violent. As such, little cadmium is absorbed, vomiting removes compounds from stomach.
Lead	Intestinal tract, central nervous system, kidneys, blood, gingival tissue	Poison by ingestion. Moderately toxic by intraperitoneal route. A suspected carcinogen of the lungs and kidneys. Human systemic effects by ingestion and inhalation: loss of appetite, anemia, malaise, insomnia, headache, irritability, muscle and joint pains, tremors, flaccid paralysis without anesthesia, hallucinations and distorted perceptions, muscle weakness, gastritis and liver changes. Major organ systems effected include nervous system, blood system, and kidneys. Young children especially susceptible to neurological effects.
Zinc	Skin, respiratory system, intestinal tract	Human systemic effects by ingestion: cough, dyspnea, and sweating. A human skin irritant. Pure zinc powder, dust, fumes, are relatively non-toxic to humans by inhalation. The oxidation of zinc fumes immediately prior to inhalation of the presence of impurities such as cadmium, antimony, aresenic, or lead may cause zinc to be more toxic. Inhalation may cause sweat taste, throat dryness, cough, weakness, generalized aches, chills, fever, nausea, vomiting. Zinc compounds have variable toxicity, but generally low toxicity. Some zinc salts, such as chromates and aresenates, are experimental carcinogens.

Reference: Halliburton NUS. August 1993, p. 6-134.

objectives developed for the Ball Mill tailings pile were to minimize exposure to materials from the pile that were contaminated with unacceptable concentrations of PCBs, lead, and other heavy metals; and to minimize migration of contaminants from the pile that would result in unacceptable concentrations in the soils, groundwater, surface water, or sediments.

Remediation cleanup goals were established for the carcinogenic contaminants found in the Ball Mill tailings pile. The maximum concentration of beryllium in the pile was 155 mg/kg, which had a carcinogenic risk value of 8.4 x 10EE-5. A cleanup goal that would reduce risk to 1 x 10EE-6 for a worker would be approximately 2 mg/kg. The maximum concentration of lead detected in the pile was 15,100 mg/kg. According to EPA guidance, a lead cleanup goal of 1,000 mg/kg for an industrial setting will result in significant risk reduction. The maximum detected concentration of PCBs in the Ball Mill tailings pile was 1.4 mg/kg, with an associated carcinogenic risk of 1.4 x 10EE-6. This risk level is probably acceptable based on the exposure assumptions, therefore no cleanup for PCBs is needed for the Ball Mill tailings pile. In the event that a solidification / stabilization (S/S) remediation technology were used to immobilize the heavy metals in the pile, these cleanup goals would not be applicable; instead a leaching test (such as TCLP) would be used for that determination. The TCLP regulatory level for lead is 5.0 mg/L, while the TCLP regulatory level for cadmium is 1.0 mg/L.

Potential remedial technologies were initially identified and screened according to their overall applicability to the primary contaminants and conditions present at the site. The screened technologies were then evaluated based on effectiveness and implementability considerations. The screened technologies that were considered for the Ball Mill tailings pile were as follows:

- No action
- Institutional actions (access restrictions, medical monitoring, additional investigations)
- Containment (multimedia cap, clay and soil)
- Removal
- Solidification/Stabilization (cement-based, silicate-based, chemical fixation)

- Fluid Extraction (soil washing)
- Offsite disposal
- Onsite disposal
- Resource recovery (smelting)

Based on the results of the preliminary screening, several alternatives were carried through for evaluation against the nine criteria described below.

- Overall Protection of Human Health and the Environment
- Compliance with ARARs
- Long-term Effectiveness and Permanence
- Reduction of Toxicity, Mobility, or Volume through Treatment
- Short-term Effectiveness
- Implementability
- Cost
- State Acceptance
- Community Acceptance

Some important cost considerations were discussed in the November, 1993 FS. The following cost estimates, excluding transportation costs, were provided as criteria for evaluation:

--Resource Recovery by Horsehead Resources ($180/ton)
--Hazardous Waste Disposal ($260/ton)
--Soil Washing ($50/ton)
--Chemical Fixation ($35-$50/ton)

The alternatives retained for evaluation against these criteria for the Ball Mill tailings pile are summarized as follows:

Alternative 1 -- No Action
Alternative 2 -- Limited Actions

Alternative 3 -- Limited Actions / Multimedia Cap over the pile
Alternative 4 -- Limited Actions / Chemical Fixation of the pile / Onsite placement of the treated material
Alternative 5 -- Limited Actions / Chemical Fixation / Offsite disposal in a nonhazardous landfill
Alternative 6 -- Limited Actions / Multimedia Cap / Groundwater pump and treat
Alternative 7 -- Limited Actions / Chemical Fixation / Onsite placement / Groundwater pump and treat

Based on an evaluation of the nine criteria, Alternative 4 was chosen as the best alternative for the site. The EPA, state and community concurred with this evaluation.

Several limited treatability studies were conducted on the Ball Mill tailings material during the course of the FS. Conventional solidification/stabilization techniques were evaluated through EPA's research engineering lab in Cincinnati, Ohio. Chemical fixation techniques were evaluated through two companies, RMT, Inc. of Madison, Wisconsin, and Sevenson Environmental of Chicago, Illinois. These companies conducted treatability screening tests on samples of the Ball Mill tailings material. The results are presented in Tables 12 and 13, respectively. The treatability screening tests were modified TCLP leaching tests that are not suitable for regulatory submittals. Both companies showed that their chemical fixation technology was capable of reducing the TCLP levels to below regulatory levels for characteristic hazardous wastes for lead and cadmium.

Sevenson Environmental later sent me samples of their proprietary chemical fixation powder and liquid with which I was able to use for the original research presented in this paper. Permission to use the Jack's Creek site for this research was granted by the EPA Remedial Project Manager, Mr. Garth Connor. Collection of samples for the research was accomplished by myself, since I was the Field Operations Leader for the Remedial Investigation of the Jack's Creek site, under Gannett Fleming, Inc.

TABLE 12

RMT, INC. SCREENING TEST RESULTS

JACK'S CREEK SITE

SCREENING TCLP TEST RESULTS				
SAMPLE	Final pH	Cadmium mg/L	Lead mg/L	Zinc mg/L
Untreated	5.80	1.53	48	2580
+ 10% Additive (5%A + 5%B)	5.74	0.36	<0.6	420
+ 20% Additive (10%A + 10%B)	9.19	<0.15	<0.6	1.05

Note: The screening TCLP test is a modified, scaled-down TCLP leaching test that gives results that are similar to those of a standard TCLP test on the waste material. The screening test is not suitable for regulatory submittals.

Reference: RMT, Inc. January 1993.

TABLE 13

SEVENSON ENVIRONMENTAL INC

TREATABILITY TEST RESULTS

JACK'S CREEK SITE

Test Run	Sample Description Dose of MAECTITE	Total Lead %	TCLP Lead (mg/l)	
			Before Treatment	After Treatment
I	Heavily Spiked Waste Soils Heavy	2.05	33	0.7
II	Moderately Spike Waste Soil Moderate	0.95	2.2	BDL * (<0.5)
III	Unspiked Waste Soil Minimal	0.85	2.2	1.6

BDL = Below Detection Limit at <0.5 mg/l

Parameter (Units)	Measured Value (MAECORP's Lab)
pH (S.U.)	9.2
ORP (mV)	142
Total Lead (%)	0.85
TCLP Lead (mg/l)	2
Predominant Minerals	—
Texture	—
Bulk Density (g/ml)	1.06
Specific Gravity (g/ml)	—

Reference: MAECORP, Inc. April, 1993

Chapter 3

OBJECTIVE

The objectives of this research are two-fold. First, to determine if the MAECTITE chemical fixation technique is useful to treat the hazardous Ball Mill tailings pile at the Jack's Creek Superfund Site. This will show how effective the treatment additives are at stabilizing heavy metals such as lead, cadmium, and zinc. In addition, the most cost effective treatment ratios can be determined. Secondly, this research will show whether size classification would be useful to more effectively remediate the pile, or whether the fixation technique may be more effective on certain size fractions of a waste material. The research will show whether the TCLP metals are concentrated in a certain size fraction and which size fraction the chemical fixation technique can best treat. Waste volume to be treated may be reduced if certain size fractions are found to be non-hazardous. In addition, the research will show if the particle size of the material is a relevant factor in treatment using this chemical fixation technique.

Chapter 4

LITERATURE REVIEW

The MAECTITE chemical fixation treatment process is a unique patented process owned by Sevenson Environmental Services, Inc. (Sevenson) of Niagara Falls, New York. Few scientific papers are available about the process, with the exception of several papers presented by Sevenson about their proprietary treatment process. This literature review covers two of the latest scientific papers presented by Sevenson at different conferences during 1994. These papers were obtained by permission, directly from Sevenson (Yost January, 1995), (Yost, Pal, Chisick, and Jesernig May 10, 1994), (Yost, Elia, and Chisick December 1, 1994).

Lead and other heavy metals are chemically fixed using the MAECTITE treatment process. In general terms, treatment reactions convert leachable metal species to geochemically stable and hardened mixed mineral forms within the waste matrix that are resistant to EPTOX, TCLP, Multiple Extraction Procedure (MEP), acid-leach and other test methods utilized to define RCRA toxic waste. This allows treated waste to be disposed of as a non-hazardous waste instead of as a hazardous waste. The MAECTITE chemical treatment process forms non-leachable minerals through isomorphic reaction-series induced nucleation. The process often reduces waste volume by over 20% with limited or no mass increase partially due to increased particle density, eliminated interstitial space, dehydration of the waste matrix, and destruction of semi-stable carbonates. The MAECTITE process creates new chemical bonds and crystal nucleation from the disassociated metal species and yields new metal-substituted crystal compounds. The metal-substituted crystal precipitates are in the hexagonal and orthorhombic crystallographic systems that are stable in acidic, alkaline, and other harsh environmental settings.

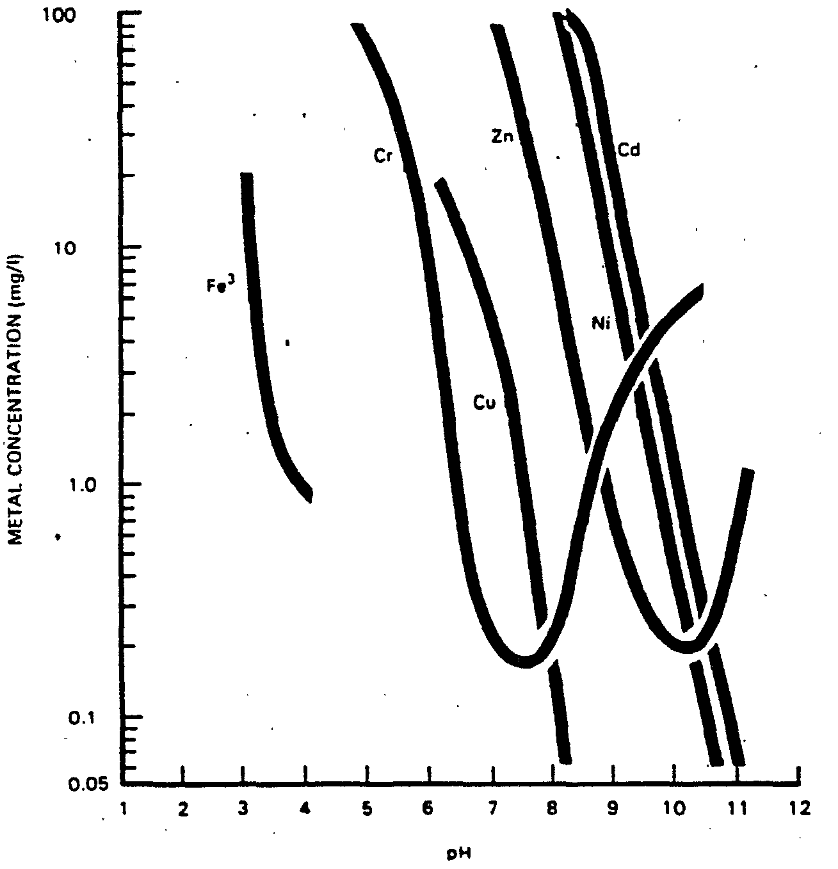
Chemical fixation techniques are contrasted with other more typical waste stabilization / solidification (S/S) methods. S/S methods utilize the engineered concept of physical binding mechanisms to encapsulate, entrap, absorb, contain, coat, or seal target analytes within a waste matrix. These methods physically immobilize heavy metals by surface effects, plate polarity, hydration and / or adhesion principles. Materials such as cement, silica, and pozzolons are mixed with waste materials and water in typical S/S methods at large mass and volume ratios to achieve effective treatment. The effectiveness may also be due to the increased bulk of the material or from the dilution factor (large percentages of reagents will dilute the waste material). Another important mechanism that S/S techniques use is a reduction in solubility of the metals into solution by adjusting the system pH. The buffering effect of most typical S/S methods is well known. Figure 2 shows the effect that pH adjustment has on various metal species (EPA July, 1973). This figure shows the minimum solubility for Cadmium to be greater than pH 11.0. While cadmium is amphoteric, its minimum solubility is higher than the others and is not shown on the figure. Zinc solubility is shown to be amphoteric with the minimum solubility at about pH 10.0. Lead is not shown on this figure, but is amphoteric with a minimum solubility between pH 8.0 to 9.0. If the pH of the waste material is buffered to the point of minimum solubility, the metals will not leach out, but will remain as metal hydroxides. The problem is that if the waste pH is ever altered, the hydroxide precipitates will resolubilize, leaching the heavy metals.

Following extended periods of curing time, S/S treated wastes are subjected to leaching tests (currently TCLP) as well as costly and lengthy geotechnical test methods, such as unconfined compressive strength and permeability, to demonstrate that the physical binding mechanisms of the end-product mixtures could withstand the rigorous physical conditions that may be encountered in the final waste placement areas. S/S failure is determined by the presence of fractures in the treated material and other defects such as permeability or strength problems. In addition, weakly absorbed metals may be dissociated and diffuse when exposed to highly acidic or basic environments. Site remediation costs are elevated due to the increased mass and volume of the treated waste from transportation and final disposal costs if taken offsite, and due to prolonged project duration's(Yost, Elia, and Chisick December 1, 1994).

The MAECTITE chemical fixation treatment method has several advantages over the typical S/S techniques. Most importantly, chemical fixation creates new compounds, while S/S methods may leave the contaminants in their present form, or create mixtures.

FIGURE 2

METAL SOLUBILITY AS A FUNCTION OF pH



SOURCE: U.S. Environmental Protection Agency. *Waste Treatment: Upgrading Metal-Finishing Facilities To Reduce Pollution*. EPA 625/3-73-002. July 1973.

Mixtures can be readily degraded or separated by physical and chemical forces; compounds cannot. This has been proven by heavy metal concentration data obtained from extraction fluids after treated materials were exposed to intense ultrasonic energy for extended periods of time. The S/S methods utilizing physical binding mechanisms could not withstand the ultrasonic energy as the endstructures were weakened or disintegrated, allowing the exposed analytes to disperse into the extraction fluids. Next, the MAECTITE chemical fixation method does not require large volumes of treatment chemicals to be effective. Treatment additives typically range from 1 to 5% by weight of the waste material, while S/S methods may require up to 50%. In addition, the MAECTITE method reports 20% to 55% volume reduction at various sites following treatment. Also, the MAECTITE chemical fixation method requires simple mixing techniques and only 3-5 hours of curing time. Some S/S methods require from several hours to days of curing time. Although a minimal amount of water is required as a mixing lubricant and dust inhibitor in the MAECTITE method, the treated material complies with the paint filter test for disposal requirements. Last, since the MAECTITE method incorporates the heavy metal species into new complexed molecular structures as compounds and since the treated material remains unsolidified in its same basic form, prolonged exposure to acidic conditions becomes the critical component to long-term waste integrity, not geotechnical methods. The Multiple Extraction Procedure (MEP) test was designed to simulate 1000 year exposure to acid rain and leachate. This test overcomes the buffering capacity of a treated material. This is of great importance, since cement and hydroxide S/S methods rely on their buffering capacities to prevent heavy metal leaching. S/S methods create metal hydroxides which are insoluble at various alkaline pH ranges. Once the buffering capacity of the waste is exceeded with acidity, the hydroxides will dissipate, the physical binding mechanisms will weaken, and the metals will leach. The old EPTOX and current TCLP extraction methods cannot overcome these S/S buffering capacities during the limited extraction duration's. MAECTITE formed mineral crystal compounds are not susceptible to acidic, neutral, or basic degradation conditions and will remain geologically stable, preventing heavy metal leaching. Finally, the MAECTITE chemical treatment process is universal in the sense that a wide variety of solid waste and debris can be treated for leachable lead primarily, but also for barium, chromium, cadmium, selenium, and nickel (See Table 14). Materials such as battery casings, lead projectiles, sludges, filter cake, slag, abrasives with paint, wire-fluff and chop, rubble, lead-dross on carbon, and all kinds of clay, soil, gravel, concrete, sand, and boulders have been successfully treated to below regulatory levels (See Table 15).

The MAECTITE chemical treatment process utilizes two categories of treatment chemicals in variable amounts to effectively treat a waste material. The first group of treatment chemicals are calcium and/or magnesium based buffers, salts and/or bases. The particular type depends on the waste type and is determined with a treatability study. These treatment additives form insoluble and hard mineral species of the Barite Group (metal-substituted sulfates) in the treated waste material. The second group of treatment chemicals can be either a liquid or a solid and are capable of supplying anions that preferentially form insoluble metal compounds at normal temperatures and pressures. This group of chemicals form mixed mineral species of the Apatite (metal-substituted phosphates), Anglesite ($PbSO4$), and Pyromorphite ($PbPO4$) families. When components of both treatment chemical groups are present in the correct amounts, thermodynamically efficient chemical reactions proceed yielding the synthetic mineral species listed in Table 16.

Physical chemists know much about the mineral solubility for pure-phase solids. Pure-phase solids are not natural, nor are they what is encountered in hazardous waste remediation projects at industries, landfills and uncontained spills. The real world is composed of non-pure and coprecipitated intertwinned mineral solids. The MAECTITE chemical process is a classical mineralogical and geochemical approach to address this precept of nature. It is a true low-temperature mineral dissolution-precipitation reaction of a suite of isomorphic mineral-solids resulting in the control of various inorganic ions. Mineral solids which have analogous compositions and closely related in their crystalline geometric forms, but in the same crystallographic system, are said to be isomorphic. Reaction precipitates will tend to carry out of solution other constituents that are normally soluble, causing a coprecipitate and effectively removing the particular ions.

TABLE 14

CHEMICAL TREATMENT OF VARIOUS IONS

BY MAECTITE PROCESS

Metal Type	Application (level)	Untreated Conc. Range	Treated Conc. Range	Regulatory Limit
Lead	Commercial (full-scale)	> 5 to 3720	< 1	5
Cadmium	Commercial (full-scale)	> 1 to 1596	< 0.1 to 0.7	1
Selenium	Commercial (bench-scale)	> 1 to 300	< 0.0025	1
Chromium*	Commercial (bench-scale)	> 5 to 660	< 0.3	5
Nickel	Laboratory (bench-scale)	> 5 to 250	< 0.5	N.R.
Barium	Laboratory (bench-scale)	> 400	< 10	100

N.R. = Not Regulated under RCRA "Land Ban" criteria

* Chromium (VI) was treated by the patent-pending, proprietary Chromtite treatment technology that is applicable to multivalent species. Chromtite is a sister technology to MAECTITE.

\- All analytical units in mg/l in TCLP extract

Reference: Yost, Pal, Chisick, and Jesernig. May 10, 1994.

TABLE 15

APPLICATION OF MAECTITE CHEMICAL TREATMENT PROCESS TO A DIVERSE VARIETY OF WASTE MEDIA

WASTE TYPE (MATRIX)	TOTAL LEAD %	LEACHABLE LEAD (mg/l)	
		Before Treatment	After Treatment
Sandy loam	2.2	163.7	1.5
Lead birdshot	16.1	3,720	ND
Lead buckshot	11.4	1,705	ND
Clayey slag	14.6	91.8	ND
Slag-lead smelter	6.6	21.3	2.0
Topsoil	15.8	44.5	1.4
	14.6	91.8	ND
	0.344	83.5	0.5
Silt sand/debris	0.56	34.6	ND
Battery casings	0.6 - 12	288	0.6
	2.0	160	0.3
Organic humus soil	0.31 - 1.9	23.2	ND
Silty sand	4 - 5	687	0.7
Solid waste	1.1	9.7	0.01
	0.4	72.4	3.4
Sludge-industrial waste	2.2	59.3	1.6
Filter cake	2.9	245.3	1.1
Gravel	0.16	7.5	0.5
Road gravel	0.34	46	ND
Gray clay	2.2	495	0.2
Grayish brown ash	9.5	520	0.3
Brown soil-gravel clay (till)	1.37	263	2.1
Brown soil-gravel sand (till)	3.97	303	1.6
Soil with PbO	29.9	3,659	ND
Clarifier sludge	0.85	57.1	0.3
RCRA organic sludge	9.4	580	ND
Carbon with lead dross	12.6	105.6	0.5
Foundry sand with bentonite	1.96	461.2	ND
Wire fluff	0.33 - 0.134	15.9 - 130	0.7
Wire chip	0.3 - 0.7	28	1.9

NOTE: **ND = Not Detected** (i.e., <0.5 mg/l) BDL = Below Detection Limit (i.e. <0.1
Listed results from bench-, engineering-, and full-scale application
All anayltical procedures performed in accordance with SW-846 (USEPA)

TABLE 16

Synthetic Mineral Species of Lead Detected in a

Treated Sample (Listed in Decreasing Order of Abundance)

Abundance	Crystal System	Isomorphic Groups	Mineral Species
31-41%	Hexagonal	(A)	Calcium Substituted Hydroxy Lead Apatite
28-29%	Hexagonal + Orthorhombic	(A) + (B)	Mixed Calcium Lead Phosphate Sulfates
21-22%	Orthorhombic	(B)	Calcium Anglesite
3-6%	Orthorhombic	(B)	Anglesite
2-7%	Hexagonal	(A)	Lead Hydroxuy/Chlor Apatite
1-3%	Hexagonal	(A)	Pyromorphite
1-2%	Hexagonal (R)	(A) *	Organo-Lead Phosphate Sulfate

(A) = Apatite Group

(B) = Barite Group

* = Complexation by Organic is dictated by the Crystal System, a Pseudo-rhombohedral of the Hexagonal System

R = Pseudo-Rhombohedral of the Hexagonal System

Note - Mineralogic assay conducted by x-ray fluorescence spectrometry, polarized light microscopy (PLM) and scanning electron microscopy (SEM) methods on batttery reclamation site soils and waste after one year from treatment by the MAECTITE chemical process

Reference: Yost, Pal, Chisick, and Jesernig. May 10, 1994.

The calcium ions are key to the MAECTITE chemical treatment process. An example of an isomorphous coprecipitation reaction between calcium and lead can be explained as follows. A Pb ion commonly coprecipitates with a Ca ion where Pb+2 substitutes for Ca+2 within a defined crystal lattice to form a common mineral solid. The Pb+2 substitution for Ca+2 usually occurs based on availability of the closest ion to a vacant crystal-lattice site when Ca+2 has been naturally depleted or if the available Ca+2 can be manipulated out of the system. This isomorphous coprecipitation event can be explained by the fact that two ions with similar radii and the same charge will preferentially concentrate the ion of smaller radii into the early forming species of a crystallizing mineral species.

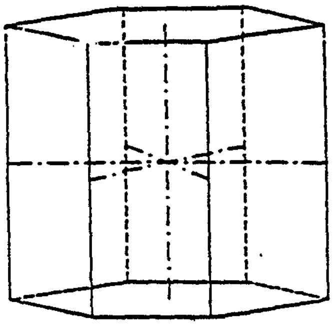
Sometimes ionic substitution occurs even when two ions have distinctly different chemical character and valence charges, without changing the crystallographic system. This can occur if two stable mineral formulas possess an equal number of atoms and valence charges, and their crystallographic forms are composed of geometrically similar basic crystal-units, arranged in a similar geometric arrangement. When the relative size of the atoms and several physical properties are nearly the same, an isomorphous condition exists that will sustain the substitution / coprecipitation reaction.

Sometimes a different type of ionic substitution (called twinning) can occur within minerals of different crystallographic systems. Twinning is when the lesser of two mineral coprecipitates, which are not in the same crystallographic system, form in a compatable crystallographic system or mimic the major crystallographic system. This will only occur with compatible crystallographic systems that are prone to twinning such as the orthorhombic-crystallographic system which mimics the hexagonal-crystallographic system. The prismatic angles of about 60 and 120 degrees of the orthorhombic-crystallographic system will simulate the simple hexagonal-crystallographic system as a result of successive intertwinng (See Figure 3). This explains why the Barite Group (orthorhombic-crystallographic system) will crystallize from the mother solution and with the Apatite Group (hexagonal-crystallographic system).

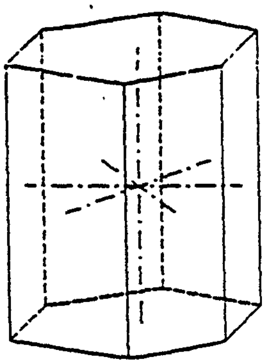
The MAECTITE process uses the two isomorphous mineral groups, Apatite and Barite, along with the manipulation of the Ca+2 ions as described above to remove the

FIGURE 3

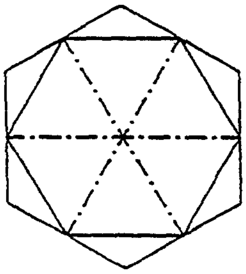
CRYSTALLOGRAPHIC TWINNING MAECTITE® CHEMICAL PROCESS



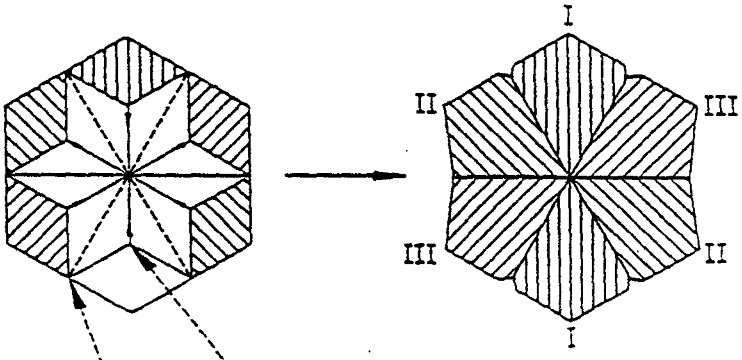
HEXAGONAL SYSTEM
FIRST ORDER PRISM



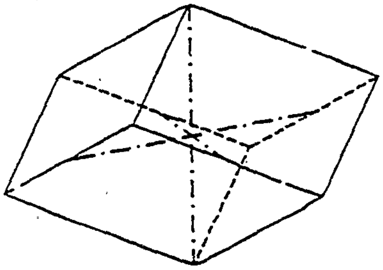
HEXAGONAL SYSTEM
SECOND ORDER PRISM



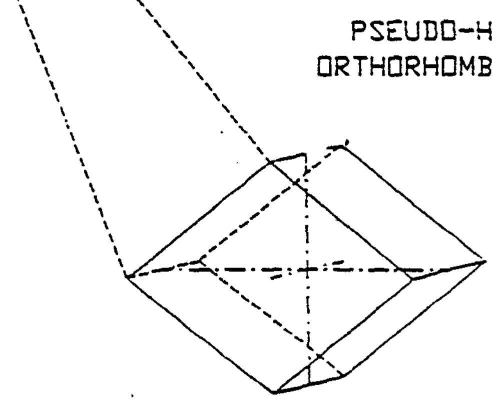
HEXAGONAL SYSTEM
(Top View)



PSEUDO-HEXAGONAL
ORTHORHOMBIC TWINNING



RHOMBOHEDRAL DIVISION OF
HEXAGONAL SYSTEM



ORTHORHOMBIC SYSTEM

Reference: Yost, Pal, Chisick, and Jesernig. May 10, 1994.

heavy metal ions from the solution. The Apatite Group includes the hexagonal-crystallographic compounds such as Apatite (Calcium phosphate) consisting of Ca-rich Pb-poor then Pb-rich Ca-poor substituted Hydroxyapatite and Pyromorphite (Lead phosphate). The Barite Group includes the orthorhombic-crystallographic compounds consisting of Ca-rich Pb-poor then Pb-rich Ca-poor Anglesites and Anglesite (Lead sulfate) intertwinned. Once the sulfate ions are consumed from the solution, the reaction shifts to a post-coprecipitation stage reverting to the Apatite Group and scavenging the remaining heavy metal ions to form Plumbohydroxyapatite and Pyromorphite.

Precipitation reactions tend to carry other ions from the initial solution. Precipitation / crystallization during chemical fixation occurs in a succession of steps as the chemical process attempts to reach equilibrium. The driving force of the reaction is coincidental crystal nucleation and heat loss. During nucleation, there are increased chances of dislocations of ions in the crystal's lattice space which promotes the substitution of other ions into the crystallographic structure. The dislocation mechanism leads to the desired formation of coprecipitated isomorphous minerals in a reaction-series. As coprecipitation continues, the larger crystals grow at the expense of the smaller crystals with the smaller crystals dissolving and reciprocating on the surfaces of the larger crystals. If the coprecipitates are not within the same crystallographic-system, the lesser mineral will form in a compatible crystallographic-system or mimic the major mineral crystallographic-system through twinning. The process continues until equilibrium is reached with the initial solution depleted by nucleation, coprecipitation and post-coprecipitation forming new distinct minerals with the initial leachable heavy metal ions (Yost, Pal, Chisick, and Jesernig May 10, 1994).

Many barriers to precipitation occur naturally due to factors such as the pH, oxidation potentials, or ionic concentrations of the precipitating salts. The desired precipitation of mineral-solids occurs if they are isomorphic, that is having the same type of formula and if they crystallize in similar geometric forms. The fixation of leachable ions and introduction into the solid phase is controlled by the following :

- Unsatisfied valence produced by broken bonds at surfaces and edges of mineral-solids
- Unbalanced charges caused by isomorphic substitution
- Dissociation of OH- radicals, when the H+ may be readily exchanged
- Accessibility of atoms in crystallographic positions when brought to the exchange site as a result of a change in the environment
- Availability of exchangeable constituents in the solute
- Eh-pH relationships
- General chemistry of the environmental setting
- Pressure and temperature conditions

The Eh-pH relationships are the most definitive element in surface soil conditions. The availability and solubility of various ions is strongly controlled by this relationship. Eh-pH diagrams are constructed for pure mineral solids to show solubility relationships. In the real world of mixed mineral forms, Eh-pH are effects of H+ ion activity which is a major control of the MAECTITE chemical treatment process. Eh shows the available electrons in the environment. A large number of electrons (high Eh) equates to a reducing environment, while the absence of electrons (low Eh) equates to an oxidizing environment. On the other hand, pH shows the available protons in the environment. A large number of protons (low pH) represents an acidic environment, while a scarcity of protons (high pH) represents a basic environment. Eh-pH diagrams are useful for plotting the interactions of dissolved minerals, dissolved minerals and other natural solids, and reactions between two or more solids.

The MAECTITE chemical treatment process has been successful on various full-scale applications of hazardous materials and wastes. A summary of various types of successfully treated materials, showing pre- and post-treatment analytical data was shown in Table 15. Several full-scale case studies are presented below to demonstrate the size and types of projects completed to date.

Site A: (unnamed)

Remedial Type: Emergency Response Action/State Superfund
Location: Indiana
Contaminant: Leachable lead (EPTOX)/lead oxide
Source: Battery Reclamation
Quantity of Waste: 5390 tons
Production Capacity: 200 tons/day
Type of Waste: sand, sandy-silt, gravel, rock, and clay
Range of Total Lead: 0.1 to 29.9%
Range of EPTOX Lead: 20 to 3659 mg/L
Treated Material: < 5.0 mg/L lead (EPTOX)
Volume Reduction: 36.4%

Site B: (unnamed)
Remedial Type: Emergency Response Action/Federal Superfund
Location: Wisconsin
Contaminant: Leachable lead (TCLP)/crushed batteries
Source: Battery Reclamation
Quantity of Waste: 11,000 tons
Production Capacity: 400 tons/day
Type of Waste: silty-sand, gravel, clay, rock, casing ash
Range of Total Lead: 2.03 to 3.55%
Range of TCLP Lead: 5.0 to 422.4 mg/L
Treated Material: < 5.0 mg/L lead (TCLP)
Volume Reduction: 22.4%

Site C: Traub Battery and Autobody Site
Remedial Type: Federal Superfund
Location: Sioux Falls, South Dakota

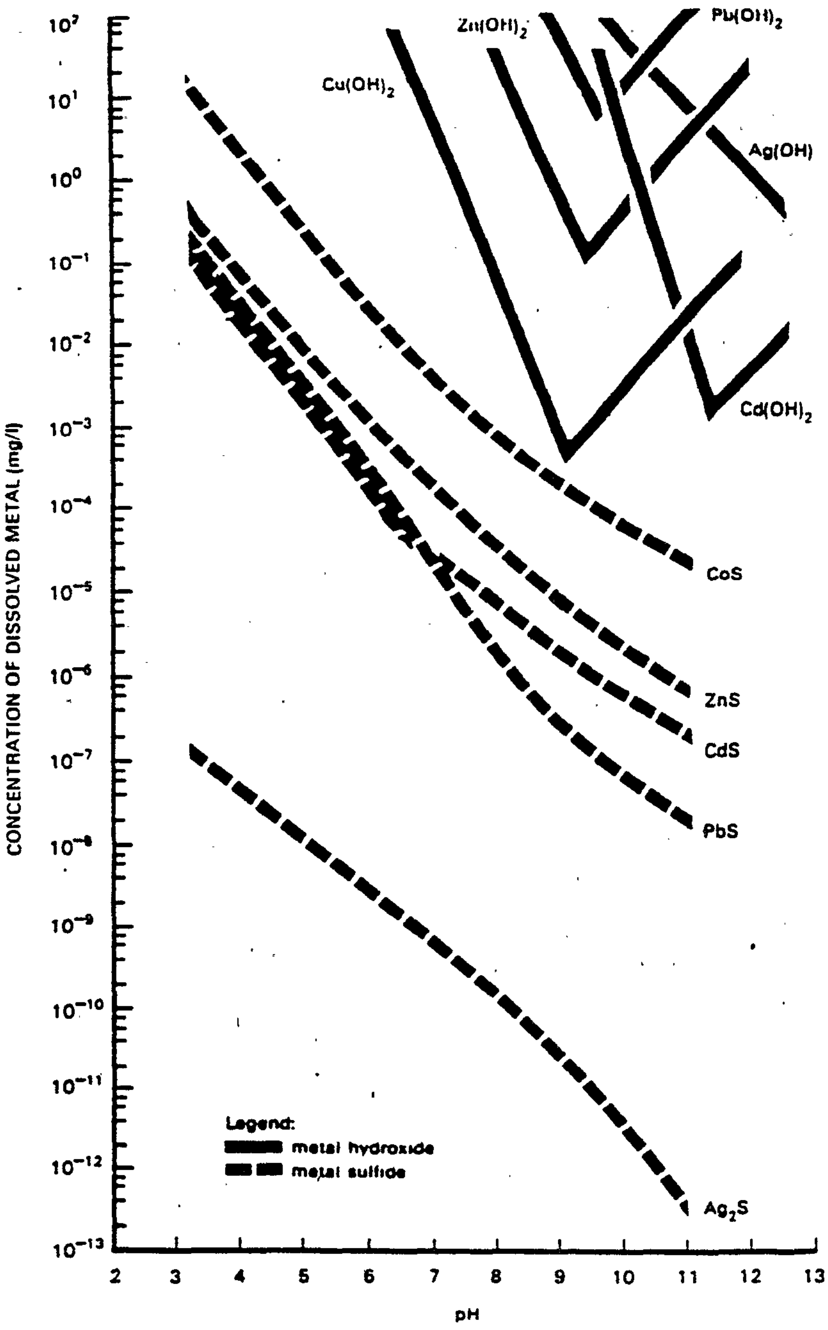
Contaminant:	Leachable lead (TCLP)/crushed batteries
Source:	Battery Reclamation
Quantity of Waste:	4,000 tons
Production Capacity:	> 400 tons/day
Type of Waste:	sod, silty-sand, loess, clay
Range of Total Lead:	up to 2.0%
Range of TCLP Lead:	5.0 to 85 mg/L
Treated Material:	< 0.1 mg/L lead (TCLP), < 1.0 mg/L (MEP)
Volume Reduction:	not reported

Site D:	Marathon Battery Site
Remedial Type:	Federal Superfund
Location:	Cold Spring, New York
Contaminant:	Leachable cadmium and lead (TCLP)
Source:	Battery Manufacturing Plant
Quantity of Waste:	115,000 to 125,000 cubic yards
Production Capacity:	2000 tons/day
Type of Waste:	peats, marsh sediments, surface soils
Range of Total Cadmium:	up to 1.36%
Range of TCLP Cadmium:	up to 200 mg/L
Treated Material:	< 1.0 mg/L cadmium (TCLP)
Volume Reduction:	not reported

Absent from the Sevenson literature is any discussion about sulfide precipitation. The precipitation of metal-sulfides from the treatment of the waste material should not be overlooked as a potential reaction. The high reactivity of sulfides with heavy metal ions and the insolubility of heavy-metal sulfides over a broad pH range make these precipitates a potential end product. Figure 4 shows the solubility's of various metal-hydroxides compared to various metal-sulfides as a function of pH (Freedman and Shannon Jan.-Feb.

FIGURE 4

SOLUBILITIES OF METAL HYDROXIDES AND SULFIDES AS A FUNCTION OF pH



Note.—Plotted data for metal sulfides based on experimental data listed in Seidell's solubilities.

SOURCE: Solubilities for metal hydroxides are taken from curves by Freedman and Shannon, "Modem Alkaline Cooling Water Treatment," in *Industrial Water Engineering* (p. 31), Jan.-Feb. 1973.

1973). This figure shows the sulfide solubility for galena (PbS) to be 8 orders of magnitude less soluble than lead-hydroxide at a pH of about 9.0. In addition, the solubility's of zinc-sulfide and cadmium-sulfide are shown to be extremely low. Another observation from this figure is that the solubility effects at low pH are much more pronounced than at higher pH values.

The MAECTITE process is not described as a sulfide precipitation process. In fact the only sulfur-containing compounds described in the process are the sulfates (-SO4) of the Barite group. While the production of metal-sulfides from metal ions and sulfides (S-2 and HS-) are the preferred reactions, other more energy consumptive reactions with sulfates are possible. This is illustrated for PbS (galena) below: (Lindsay, 1979 p.336)

Reaction	Log K
Pb(+2) + S(-2) -----> PbS (galena)	27.51
soil-Pb + SO4(-2) + 8e + 8H --------> PbS (galena) + 4H2O	39.75
PbCO3 (cerussite) + SO4(-2) +8e +10H -----> PbS + CO2 + 5H2O	52.90

Chapter 5

METHODOLOGY

The research conducted on the Ball Mill tailings pile material involved various sampling methods and types of chemical and physical analytical techniques. These methods can be described as follows:

- Composite Sampling
- Sample Preparation
- Moisture Content
- pH Measurement
- Grain Size Distribution
- TCLP Extractions
- Atomic Absorption Analysis
- Instrument Sensitivity
- Instrument Detection Limit

Composite Sampling

A composite Ball Mill tailings pile sample was collected from the 143,000 ton waste pile at the Jack's Creek Superfund Site. The pile was completely covered with a synthetic material and anchored with stakes and tires on a random grid pattern over the entire surface area. Access to the waste material could only be gained where the stakes penetrated the pile. Approximately equal portions of pile material were obtained from 20 to 30 staked locations from various sides and elevations of the pile. A total volume of approximately 15 gallons of sample was placed into two-ten gallon Rubbermaid containers. Each container was blended separately for approximately thirty minutes using a trowel by hand. Appropriate personal protective equipment including gloves and tyvek coveralls were used. The material was somewhat moist and produced little if any dust. Following blending, a lid was placed on each container and sealed shut with duct tape.

Sample Preparation

A total of sixteen samples was prepared from the Ball Mill tailings material for this research. Table 17 shows the approximate amounts of waste material and treatment reagents for each of the samples. For sample numbers 1 through 4, a representative sample of approximately 40.0 grams was placed into each of four, one-liter polyethylene containers. Approximately 2.0 grams of MAECTITE powder and 2.0 ml of MAECTITE liquid were placed into container number 2 (5% treatment). Approximately 1.2 grams of MAECTITE powder and 1.2 ml of MAECTITE liquid were placed into container number 3 (3% treatment). Approximately 0.4 grams of MAECTITE powder and 0.4 ml of MAECTITE liquid were placed into container number 4 (1% treatment). Each of the four containers were shaken vigorously for 10 minutes to mix the contents; once when the powder was added and again when the liquid was added. The samples were kept in the sealed polyethylene containers at room temperature for 12 days until extraction. Sevenson recommends curing times of 3 to 5 hours minimum.

Sample numbers 5 through 8 were prepared after a sieve analysis and size fractionating were completed on a portion of Ball Mill tailings material. Large (4.75-9.5 mm), medium (2.36-4.75 mm) and small (0.6-1.18 mm) size fractions of the Ball Mill tailings material were selected from the sieve analysis. Approximately 40.0 grams of each size fraction were placed into each of three one-liter polyethylene containers. In addition, approximately 40.0 grams of the small tailings fraction were placed into sample container number 8 as a duplicate. No treatment materials were placed into these containers. Each container was sealed, shaken and then kept at room temperature for 15 days until extraction.

Sample numbers 9 through 12 were also prepared after a sieve analysis and size fractionating were completed. A 3.0% treatment dosage was chosen for these samples. Approximately 40.0 grams each of the large, medium, and small size fractions were placed into one-liter polyethylene containers. In addition, approximately 40.0 grams of the small size fraction tailings material was placed into sample container number 12 as a duplicate. Approximately 1.20 grams of MAECTITE powder was placed into each of the four

TABLE 17

SAMPLE PREPARATION

NO.	SAMPLE DESCRIPTION	Amount of Ball Mill Material (grams)	Amount of MAECTITE Powder (grams)	Amount of MAECTITE liquid (ml)	Amount of Reagent Water (ml)
1	Tailings pile sample, untreated	40.0	--	--	--
2	Tailings treated with 5% Maectite	40.0	2.0	2.0	--
3	Tailings treated with 3% Maectite	40.0	1.2	1.2	--
4	Tailings treated with 1% Maectite	40.0	0.4	0.4	--
5	Large tailings fraction, untreated	40.0	--	--	--
6	Medium tailings fraction, untreated	40.0	--	--	--
7	Small tailings fraction, untreated	40.0	--	--	--
8	Duplicate of No. 7	40.0	--	--	--
9	Large fraction, treated with 3% Maectite	40.0	1.2	1.2	--
10	Medium fraction, treated with 3% Maectite	40.0	1.2	1.2	--
11	Small fraction, treated with 3% Maectite	40.0	1.2	1.2	--
12	Duplicate of No. 11	40.0	1.2	1.2	--
13	Tailings, treated with 20% Quicklime	50.0	10.0 (a)	--	10.0
14	Tailings, treated with 20% Portland Cement	50.0	10.0 (b)	--	10.0
15	Water blank	--	--	--	50.0
16	Water blank, treated with 3% Maectite	--	1.5	1.5	50.0

<	less than the detection limit
--	not applicable
(a)	Quicklime
(b)	Portland Cement

containers. The containers were sealed and shaken vigorously for ten minutes. Each container was then opened and approximately 1.2 ml of the MAECTITE liquid was added. Again the containers were closed and shaken vigorously for ten minutes. These samples were kept in the sealed polyethylene containers at room temperature for 13 days until extraction.

Sample numbers 13 and 14 were prepared as comparative treatment samples. Approximately 50.0 grams each of tailings pile material were placed into polyethylene containers number 13 and 14. Approximately 10.0 grams of Corson's Miracle Lime, Type S (Quicklime) were placed into container number 13, while 10.0 grams of Portland Cement, Type I were placed into container number 14. Each container was shaken vigorously for ten minutes. Approximately 10.0 ml of reagent water was then added to each of these two containers, sealed, and again shaken for ten minutes. These samples were stored at room temperature for one day until extraction.

Sample numbers 15 and 16 were prepared as blanks for quality control. Approximately 50.0 milliliters (ml) of reagent water were placed into each polyethylene sample container. Approximately 1.5 ml of MAECTITE liquid and 1.5 grams of MAECTITE powder were then added to sample container number 16, as a "treated" blank. Both containers were stirred for ten minutes and then sealed and stored at room temperature for one day until extraction.

Moisture Content

The moisture content of the prepared samples was determined by the ASTM D2216-80 Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures. The drying oven used was maintained at 100 degrees Celsius +/- 5 degrees. The same analytical balance was used for all weight measurements, having a repeatable precision of better than 0.01 grams. Representative sample sizes of approximately 10.0 grams were measured precisely into individual specimen containers. The containers were then placed into the drying oven for a time period of two to six days. Upon removal from the oven, specimens were reweighed on the same analytical balance and the moisture content was calculated using the following equation:

$$w = [(W1-W2)/(W2-Wc)] \times 100$$

$$= Ww/Ws \times 100$$

where:

w = water content, %,
W1 = mass of container and moist specimen, g,
W2 = mass of container and oven-dried specimen, g,
Wc = mass of container, g,
Ww = mass of water, g, and
Ws = mass of solid particles, g.

pH Measurement

All pH measurements were conducted with the same Omega pH meter, model number PHB-56. An Orion combination electrode and a temperature compensation probe were utilized. New pH standards were made up initially in 100 ml volumetric flasks with reagent water. A pH standard 7.00+/- 0.02 was made from certified Metrepak pHydrion Buffer capsules. A pH standard 4.00+/- 0.02 was also made from certified Metrepak pHydrion Buffer capsules. The calibration of the pH meter followed the two-point calibration procedure outlined in the Omega instruction manual. Calibration of the instrument was conducted daily prior to usage and a calibration verification followed at the end of each day. The pH probe and the temperature probe were always rinsed with distilled water and blotted dry between every measurement.

Grain-size Distribution

A particle size analysis, or grainsize distribution, was conducted on a representative sample of the Ball Mill tailings material using a standard sieve analysis. A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of ASTM Specification E 11, were used. These included the following sieves:

3-in. (75-mm)
1.5-in. (37.5-mm)
3/4-in. (19.0-mm)
3/8-in. (9.5-mm)
No. 4 (4.75-mm)
No. 8 (2.36-mm)
No. 16 (1.18-mm)
No. 30 (600-um)
No. 50 (300-um)
No. 100 (150-um)
No. 200 (75-um)

The sieve analysis was conducted on an initial sample size of approximately 190 grams. This is about the maximum amount of material that would fit onto the seives. The sample was weighed on a Mettler balance, sensitive to 0.01 grams. The representative sample was obtained from the previously composited Ball Mill Tailings Pile sample. The sample was placed into the top sieve and the set of sieves was then clamped into place on a Gilson sieve shaker. The Gilson shaker speed was set at 5 on a scale of 1 to 6. The timer on the Gilson shaker was set for 15 minutes and the sieving proceeded for the full period. Once completed, the sample fractions retained on each sieve were weighed on the Mettler balance and recorded in the logbook. The individual size fractions retained on the sieves were kept separate for further testing. Immediately following this sieve analysis, a second sample of similar size was placed onto the Gilson sieve shaker for particle size separation. The fractions retained on these individual sieves were added to the previous fractions to produce enough volume for subsequent testing purposes.

Three size fractions were chosen from the sieve analysis of the Ball Mill Tailings Pile material for subsequent testing. The particle size analysis showed a distribution of sample material on seven sieves, ranging from 3/8 inch (9.5-mm) to No. 100 (150-um). From these sieves, a large, medium, and small particle size fraction was chosen while giving consideration to the cumulative amounts available. The material retained on the No. 4 sieve was chosen as the large size fraction. The material retained on the No. 8 sieve was chosen as the medium size fraction. The material retained on the No. 30 sieve was chosen as the small size fraction.

TCLP Extractions

The Toxicity Characteristic Leaching Procedure (TCLP) used in this research, followed Method 1311 (40 CFR 261 Appendix II). The method was applied for extraction of solid samples for metals analysis. The TCLP method entailed a step by step process as outlined below:

- Preliminary determination of percent solids.
- Determine whether the waste requires particle size reduction.
- Determine the appropriate extraction fluid to use.
- Weigh out a subsample of the waste.
- Determine the amount of extraction fluid to use.
- Extraction of the waste.
- Filtration of the extract.
- Record final pH and preserve the sample.

The percent solids for TCLP is defined as that fraction of a waste sample from which no liquid may be forced out by an applied pressure. The samples used for this research were defined as 100% solids because no liquid could be forced out of them.

Particle size reduction is required for TCLP samples if their surface area per gram of material is less than 3.1 square centimeters. This equates to a particle size of less than 1.0 centimeter at its narrowest dimension (i.e., it is capable of passing through a 9.5 mm or 0.375 inch standard sieve). Only 14% of the Ball Mill Tailings Pile material would not pass through the 9.5 mm sieve. None of the size fractionated samples were larger than the 9.5 mm sieve. No particle size reductions were required for any of the TCLP extractions.

In order to determine the appropriate extraction fluid to use, the pH of the sample, as a slurry, needed to be measured. A 5.0 gram subsample of the solid material was added to 96.5 ml of reagent water, covered and stirred vigorously for 5 minutes. The slurry pH was then measured. If the pH was less than 5.0, then extraction fluid No. 1 was used. If the pH was greater than 5.0, then 3.5 ml of 1 Normal hydrochloric acid was added, the slurry was heated to 50 degrees Celsius for ten minutes, and the pH was measured after cooling. If the second pH was less than 5.0, then extraction fluid No. 1 was used. If the second pH was greater than 5.0, then extraction fluid No. 2 was used.

Extraction fluid No. 1 was prepared by adding 5.7 ml glacial acetic acid to 500 ml of reagent water. To this was added 64.3 ml of 1 Normal sodium hydroxide and diluted to 1.0 liter. The pH of this extraction fluid was then measured to assure it was 4.93 +/- 0.05.

Extraction fluid No. 2 was prepared by adding 5.7 ml glacial acetic acid into 1.0 liter of reagent water. The pH of this extraction fluid was then measured to assure it was 2.88 +/- 0.05.

The TCLP extraction method calls for a minimum sample size of 100 grams. Due to a minimal requirement for extract volume and a limited volume capacity in the extractor vessels, a sample size of 20.0 grams was selected for all TCLP extractions. The same laboratory balance was used for all weight measurements throughout the research. This balance had a precision of +/- 0.01 grams.

The amount of extraction fluid No. 1 or No. 2 to use was calculated by the following equation:

Weight of extraction fluid = [20 x percent solids x weight of waste filtered]/ 100

The extraction fluid was slowly added to the 1 liter polyethylene extraction bottle which contained the solid sample. The bottle was capped and placed onto the agitation apparatus. The agitation apparatus was a Millipore Rotary Agitator, catalogue No. YT30 ORA HW, capable of rotating four extraction vessels in an end-over-end fashion at 30 rpm +/- 2. The agitator was allowed to rotate for 18 hours +/- 2 and at a room temperature of 23 degrees Celsius +/- 2, before the extraction vessels were removed.

Following extraction, the solution was separated into its liquid and solid phases by filtering through a new borosilicate glass fiber filter with an effective pore size of 0.6 to

0.8 microns using gradual vacuum pressure. This filtered liquid material is defined as the TCLP extract.

The pH of the TCLP extract was measured immediately following extraction. After pH measurement, the extract was preserved for later analysis with nitric acid to a pH of less than 2.0. Upon acidification, all extracts were observed for signs of precipitation. None of the extracts precipitated upon acidification. All extracts were then placed in the laboratory refrigerator at a temperature of less than 4 degrees Celsius.

Atomic Absorption Analysis

All TCLP extracts were analyzed for lead, cadmium, and zinc on the model 360 Perkin-Elmer atomic absorption (AA)spectrophotometer at the Penn State-Harrisburg laboratory. Analysis was by the direct aspiration (flame) technique, following the 7000 series Methods of SW-846 for lead, cadmium, and zinc. Metal concentrations were determined from calibration curves for standards created for each metal. Some samples were diluted in order to analyze them on the linear range of the instrument. If dilution of the sample was required, the concentration of the sample was calculated as follows:

$$\text{ug/L metal in sample} = A[(C+B)/C]$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = amount of blank matrix used for dilution, ml.
C = sample aliquot, ml.

The Perkin-Elmer AA was set up in the same fashion for every analysis. The following steps outline the set-up sequence:

- The ventilation fan was turned on.
- The LAMP CURRENT knob was turned fully counterclockwise.
- The SIGNAL control was set to TC1.

- The POWER button was turned on.
- The LAMP button was depressed while the LAMP CURRENT knob was turned to read the value on the hollow cathode lamp being used.
- The ENERGY button was depressed.
- The SLIT width control was set to NORMAL 0.7 nm.
- The COARSE ADJUST wavelength was set to the appropriate value for that metal.
- The air supply was turned on.
- The acetylene tank was opened to a pressure of 12 psig.
- The Oxidant Selector Valve was turned to AIR.
- The IGNITE button was depressed until a flame was seen, and the FUEL valve was flipped up.
- The FUEL FLOW control was adjusted to 32.
- The OXIDANT FLOW control was adjusted to 55.
- The FINE ADJUST knob and the GAIN control were used to obtain maximum needle deflection on the meter scale.
- The ABS(Absorbance) MODE button was depressed.
- The SIGNAL control was set to INT 10.

The instrument was then ready to aspirate samples for analysis. A blank solution was intermittently aspirated between samples. The Auto Zero button was used to initialize the blank solution.

Lead analysis on the AA was performed in accordance with Method 7420 of SW-846. A lead hollow cathode lamp and a wavelength of 217.6 nm were used for all lead analysis. Lead calibration standards were prepared from certified standards from two suppliers. Certified stock solutions of lead from EM Science and Fisher at 1,000 mg/L Pb were used to prepare dilute standards for calibration purposes. Stock solutions from two suppliers were used for comparison and to verify the standards. Lead calibration standards of 15.0 mg/L, 10.0 mg/L, 5.0 mg/L, 2.5 mg/L, and 1.0 mg/L were prepared using volumetric flasks, volumetric pipettes, and Type II water for both EM Science and

Fisher stock solutions. The prepared standards were used to construct calibration curves, following Beer's Law, prior to each set of lead analyses on the AA and they were used to perform periodic calibration checks. In addition, the standards were used to establish the sensitivity and the detection limit of the instrument. Beer's Law describes the linear relationship between absorbance and concentration.

Cadmium analysis on the AA was performed in accordance with Method 7130 of SW-846. A cadmium hollow cathode lamp and a wavelength of 229.4 nm were used for all cadmium analysis. Cadmium calibration standards were prepared from a Fisher certified stock solution of 1,000 mg/L cadmium. Cadmium calibration standards of 1.0 mg/L, 2.0 mg/L, 5.0 mg/L, and 10.0 mg/L were prepared with volumetric flasks, volumetric pipettes, and Type II water from the Fisher standard. These cadmium prepared standards were used to construct initial calibration curves following Beer's Law, perform intermittent calibration checks, calculate instrument sensitivity, and calculate the detection limit for cadmium.

Zinc analysis on the AA was performed in accordance with Method 7950 of SW-846. A zinc hollow cathode lamp and a wavelength of 214.2 nm were used for all zinc analysis. Zinc calibration standards were prepared from a Fisher certified stock solution of 1,000 mg/L zinc. Zinc calibration standards of 0.5 mg/L, 1.0 mg/L, and 2.0 mg/L were prepared with volumetric flasks, volumetric pipettes, and Type II water. These zinc prepared standards were then used to construct initial calibration curves following Beer's Law, and perform intermittent calibration checks. In addition, these zinc standards were also used to calculate the sensitivity and the detection limit of the instrument for this element.

Instrument Sensitivity

Sensitivity in atomic absorption is defined as the concentration of an element (in mg/L) required to produce a signal of 1% absorption (0.0044 absorbance units). When working in the linear range of the instrument for a particular metal, the sensitivity can be calculated as follows:

Sensitivity = (Conc. of Std. x 0.0044) / Measured Abs.

The Sensitivity of the instrument is therefore calculated by reading the absorbance produced by a known concentration of the element, and solving the equation above. The sensitivity can be used to determine if the instrument is performing up to specifications.

Instrument Detection Limit

The Detection Limit is defined as the concentration of the element which will produce a signal-to- noise ratio of 2.0. The Detection Limit considers both the signal amplitude and the baseline noise. It is the lowest concentration which can be differentiated from zero. The procedure used to calculate the Detection Limit for a particular element was done as follows:

- Two concentrations of the element were prepared.
- The lower concentration standard was made at approximately 5 times the expected Detection Limit.
- The second standard was made at twice the concentration of the lower standard.
- A reading was taken for each standard alternately, twenty times, with blank readings taken between each standard.
- The blank readings taken before and after each standard were subtracted from each standard.
- The mean and the standard deviation was calculated for the corrected high standard readings and the corrected low standard readings.
- If the ratio of the means did not correspond to the ratio of the concentrations, the data was rejected.
- The detection limits for the two standards were calculated as follows:

Detection Limit = (Standard Conc. x 2 x standard deviation) / mean

- The calculation was made for each standard and the Detection Limit was the average of the two results.

Chapter 6

RESULTS and DISCUSSION

The most significant results of this research are the TCLP results of lead, cadmium, and zinc on the treated and untreated samples. These results are summarized in Table 18. Several important observations can be made on these results. The TCLP sample results from the untreated sample of Ball Mill tailings material (sample No. 1) indicated that lead and cadmium have exceeded the regulatory limit with the zinc concentrations being elevated. TCLP results above the regulatory limits define this material as a characteristic hazardous waste. The TCLP sample results from treated samples of the Ball Mill tailings material using MAECTITE treatment dosages of 5% and 3%, respectively (sample Nos. 2 and 3) indicated that lead and cadmium have been reduced to below regulatory levels with zinc concentrations being reduced dramatically. These treatment dosages will produce a material that is not considered a hazardous waste. The TCLP sample results from treatment using a dosage of 1% MAECTITE on the Ball Mill tailings material (sample No. 4) indicated that this dosage was not enough to reduce lead and cadmium to below regulatory levels. From these set of results, a treatment dosage of 3% was chosen for subsequent analyses. All treatment reactions were slightly exothermic.

Sample numbers 5 through 8 were samples of Ball Mill tailings material that had been separated by size classification. The large size fraction consisted of particles between 4.75 and 9.5 mm; the medium size fraction consisted of particles between 2.36 and 4.75 mm; and the small size fraction consisted of particles between 0.6 and 1.18 mm. TCLP results from the size fractionated samples indicated that the majority of the TCLP lead, cadmium, and zinc in the Ball Mill tailings material is distributed in the medium and small size fractions (sample Nos. 6, 7, and 8). The TCLP results from the large size fraction (sample No. 5) had greatly reduced concentrations of lead, cadmium, and zinc with lead just above the regulatory limit. These results may not be totally surprising or unexpected.

TABLE 18

FINAL TCLP-LEACHATE RESULTS

SAMPLE NO.	SAMPLE DESCRIPTION	TCLP RESULTS (mg/l)		
		LEAD	CADMIUM	ZINC
1	Tailings pile sample, untreated	34.4	1.14	2090
2	Tailings treated with 5% Maectite	1.3	0.44	520
3	Tailings treated with 3% Maectite	2.5	0.44	586
4	Tailings treated with 1% Maectite	11.1	1.14	1886
5	Large tailings fraction, untreated	8.3	0.49	341
6	Medium tailings fraction, untreated	43.3	1.18	1886
7	Small tailings fraction, untreated	37.8	1.43	2081
8	Duplicate of No. 7	37.2	1.26	1805
9	Large fraction, treated with 3% Maectite	5.7	0.86	1968
10	Medium fraction, treated with 3% Maectite	1.3	0.34	536
11	Small fraction, treated with 3% Maectite	3.7	0.95	2194
12	Duplicate of No. 11	2.5	0.91	2081
13	Tailings, treated with 20% Quicklime	<0.60	<0.10	0.72
14	Tailings, treated with 20% Portland Cement	<0.60	<0.10	0.26
15	Water blank	<0.60	<0.10	1.53
16	Water blank, treated with 3% Maectite	<0.60	<0.10	3.50
Calculated Detection Limits of PSU-Hbg AA		0.60	0.10	0.08
TCLP Regulatory Limits		5.0	1.0	N.E.

<	less than the detection limit
N.E.	none established
▨	exceeds TCLP Regulatory Limits

The differences in surface area alone between the three size fractions may be enough to account for these results. The smaller size fractions will have more surface area available and hence have more surface sites available for adsorption of lead. It is interesting to note, however, that the TCLP test does not differentiate between size fractions below 9.75 mm. This makes size differentiation below 9.75 mm valid for purposes of determining a characteristic hazardous waste under current regulations..

Sample numbers 9 through 12 were samples of the same size-separated Ball Mill tailings material from samples 5 through 8 discussed above, following treatment at a dosage of 3% MAECTITE material. This was done to determine which size fraction was best suited for treatment using the MAECTITE reagents. The TCLP results indicated that the treatment additives could reduce the lead and cadmium concentrations to below regulatory levels in the medium and small size fraction samples (sample Nos. 10, 11, and 12). The medium size fraction had slightly lower TCLP lead and cadmium results than the small size fraction, but much lower zinc concentrations. TCLP zinc concentrations were barely affected by treatment on the small size fraction. The large size fraction showed little to no reduction in TCLP metals following treatment.

A comparison of TCLP leachate results before and after treatment for each size fraction is a useful tool for identifying treatment capabilities between the size fractions. TCLP results are compared for the same size fractions before and after treatment. Again, if surface area is considered, it may be expected that treatment of the smaller size fraction tailings materials would be more effective than treatment of the large tailings materials. This seems to be the case for lead. Here, the largest size fraction had the worst treatment results, while the medium and small fractions had much better treatment results, with the medium fraction slightly better. Cadmium and zinc results did not show any reductions after treatment for the large size fraction. Cadmium and zinc had much more dramatic differences between the medium and the small fraction treatment results. These two metals show a definite preference to the medium size fraction for treatment with the MAECTITE technology. The small fraction samples showed minimal treatment for cadmium and no treatment for zinc. It may have been useful to analyze the particle size of the filtered residues following the TCLP 18-hour extractions. A comparison of initial particle sizes and particle sizes following extractions may give insight into the treatment differences between size fractions.

Sample numbers 13 and 14 were the same Ball Mill tailings material as described for samples 1 through 4, but were treated with quicklime and Portland cement respectively as comparative S/S methods. A typical treatment dosage of 20% was chosen for each of these samples. The TCLP results for these two samples indicated that these reagents could reduce leachable lead and cadmium to below detectable levels and reduce leachable zinc to less than 1 mg/l. With such good results, it would be prudent to next try lower treatment dosages (such as 10%, 5%, or 3%) to obtain an optimum or more cost effective dosage.

Sample numbers 15 and 16 of Table 18 were treated and untreated water blanks used for QA/QC purposes. Both sets of TCLP results for these water blanks showed lead and cadmium below detectable levels and zinc below 4 mg/l.

Table 19 shows the percent reduction in TCLP-metals results for all treated samples. Lead concentrations showed greater than 90% reduction in all treated samples with the exception of the treated large fraction of tailings material (10% reduction in lead) and for the tailings material treated with only 1% MAECTITE reagent (67% reduction). Cadmium results showed varied treatment results. The two traditional stabilization methods showed approximately 90% reduction in TCLP-cadmium, the 5% and 3% MAECTITE treatments of the tailings material showed about 61% reduction in TCLP-cadmium, the small-fraction tailings materials showed about 35% reduction in TCLP-cadmium, and the medium-fraction tailings material showed about 71% reduction. The 1% treated tailings material had no reduction in TCLP-cadmium, while the large-fraction treated tailings material actually had an increase in TCLP-cadmium. The results for zinc were similar to those observed for cadmium. The traditional stabilization methods showed greater than 99% reduction in TCLP-zinc. The 5% and 3% MAECTITE treated tailings material showed 72 to 75% reduction in TCLP-zinc, while the 1% treated material showed only 10% reduction. The medium-fraction treated tailings material showed a 72% reduction in TCLP-zinc, the small-fraction material exhibited no reduction, and the large-fraction treated sample showed an increase in TCLP-zinc. It appears that the traditional

TABLE 19

FINAL TCLP-LEACHATE PERCENT REDUCTIONS

NO.	SAMPLE DESCRIPTION	TCLP RESULTS (mg/l)			PERCENT REDUCTION		
		LEAD	CADMIUM	ZINC	LEAD	CADMIIUM	ZINC
1	Tailings pile sample, untreated	34.4	1.14	2090	--	--	--
2	Tailings treated with 5% Maectite	1.3	0.44	520	96.25	61.40	75.12
3	Tailings treated with 3% Maectite	2.5	0.44	586	92.85	61.40	71.96
4	Tailings treated with 1% Maectite	11.1	1.14	1886	67.85	0.00	9.76
5	Large tailings fraction, untreated	6.3	0.49	341	--	--	--
6	Medium tailings fraction, untreated	43.3	1.18	1886	--	--	--
7	Small tailings fraction, untreated	37.8	1.43	2081	--	--	--
8	Duplicate of No. 7	37.2	1.26	1805	--	--	--
9	Large fraction, treated with 3% Maectite	5.7	0.86	1968	10.25	-75.51	-477.13
10	Medium fraction, treated with 3% Maectite	1.3	0.34	536	97.02	71.19	71.58
11	Small fraction, treated with 3% Maectite	3.7	0.95	2194	90.25	33.57	-5.43
12	Duplicate of No. 11	2.5	0.91	2081	93.50	36.36	0.00
13	Tailings, treated with 20% Quicklime	<0.60	<0.10	0.72	98.26	91.23	99.97
14	Tailings, treated with 20% Portland Cement	<0.60	<0.10	0.26	98.26	91.23	99.99
15	Water blank	<0.60	<0.10	1.53	--	--	--
16	Water blank, treated with 3% Maectite	<0.60	<0.10	3.50	--	--	--

< less than the detection limit

-- not applicable

S/S techniques worked better than the MAECTITE process in this case.

Atomic Absorption raw data including standards, linear best-fit and formula, linear correlation, and absorbance and concentration data for all 16 samples are shown in Figures 5 through 9 for lead, cadmium. and zinc analyses. Correlation factors for all data shown were greater than 0.999. All data found in Table 18 comes from the raw data in Figures 5 through 9. Atomic Absorption detection limits for lead, cadmium, and zinc were calculated for the AA at PSU-Harrisburg by the procedure outlined in the methodology section. These are reported as 0.60, 0.10, and 0.08 mg/l on Table 18 for lead, cadmium, and zinc, respectively. The raw data used to calculate the detection limits as well as the instrument sensitivity levels are shown in Table 20.

A major contributing factor for leachability of heavy metals within a matrix is the sample pH. A comparison of initial sample pH values to the final extract pH values following TCLP extractions for all sixteen samples, is shown in Table 21. The initial pH results indicate that untreated Ball Mill tailings pile materials have a pH ranging from 9.06 to 9.17. Ball Mill tailings pile materials that were treated with 3% MAECTITE reagents had an initial pH (following treatment, but prior to extraction) ranging from 7.90 to 8.45. Ball Mill tailings pile materials that were treated with 5% MAECTITE reagents had an initial pH of 7.48, while those treated with 1% MAECTITE reagents had an initial pH of 8.61. The Ball Mill tailings pile material that was treated with 20% quicklime had an initial soil pH of 12.00, while the sample treated with 20% Portland cement had an initial soil pH of 11.35.

The type of leaching solution used for each sample (solution 1 or 2 as described in Chapter 5) is shown in Table 21. The final extract pH values for untreated Ball Mill tailings materials, using leaching solution number 2, ranged from 5.76 to 6.05. The final extract pH values for 3% MAECTITE treated Ball Mill tailings materials, using leaching solution number 1, ranged from 6.31 to 6.50. Final extract pH values for 3% treated materials, using leaching solution number 2, ranged from 5.36 to 5.43. All untreated Ball Mill tailings materials and MAECTITE treated samples had final extract pH values between 5.36 and 6.50, regardless of which extraction fluid was used. These pH values

FIGURE 5

Lead First Run
Atomic Absorption Results

Sample No.	Absorbence (y-value)	Concentration (x-value)
1	26.6	34.40
2	1	1.29
3	1.9	2.46
4	8.55	11.06
5	4.9	6.34
6	33.5	43.32
7	29.3	37.89
8	28.75	37.18
9	4.4	5.69
10	1	1.29
11	2.85	3.69
12	1.9	2.46
13	0.33	0.43
14	0.23	0.30
15	0	0.00
16	0	0.00

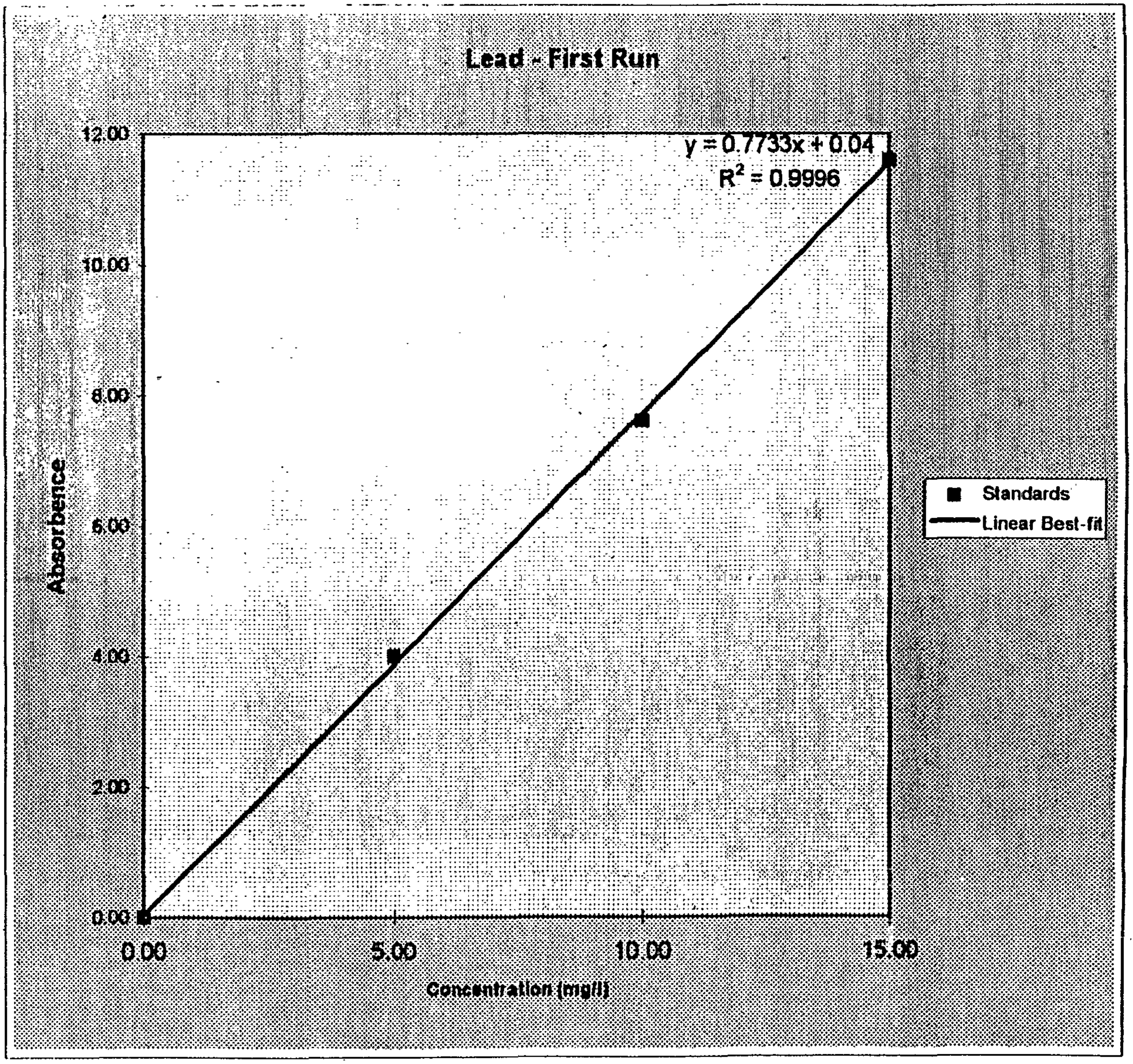
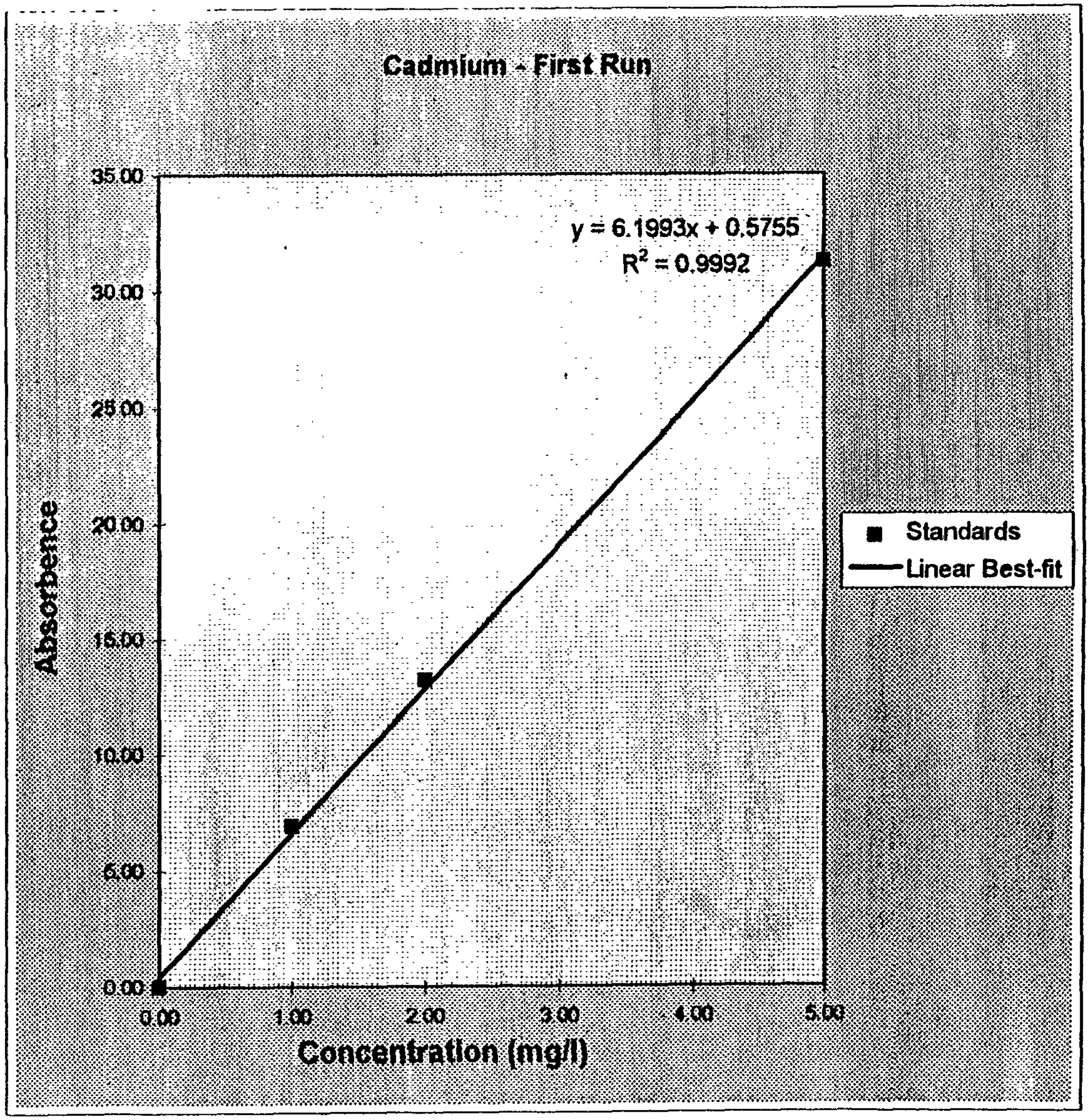


FIGURE 6

Cadmium First Run
Atomic Absorption Results

Sample No.	Absorbence (y-value)	Concentration (x-value)
1	7.06	1.14
2	2.74	0.44
3	2.74	0.44
4	7.06	1.14
5	3.01	0.49
6	7.32	1.18
7	8.89	1.43
8	7.84	1.26
9	5.36	0.86
10	2.09	0.34
11	5.88	0.95
12	5.62	0.91
13	0.26	0.04
14	0.13	0.02
15	0	0.00
16	0.26	0.04



Cadmium Second Run
Atomic Absorption Results

Sample No.	Absorbence (y-value)	Concentration (x-value)
1	7.06	1.31
2	2.74	0.51
3	2.74	0.51
4	7 06	1.31
5	3.01	0 56
6	7.32	1.36
7	8 89	1 65
8	7 84	1 46
9	5 36	1 00
10	2 09	0 39
11	5.88	1 09
12	5 62	1 04
13	0.26	0.05
14	0.13	0.02
15	0	0.00
16	0.26	0.05

FIGURE 7

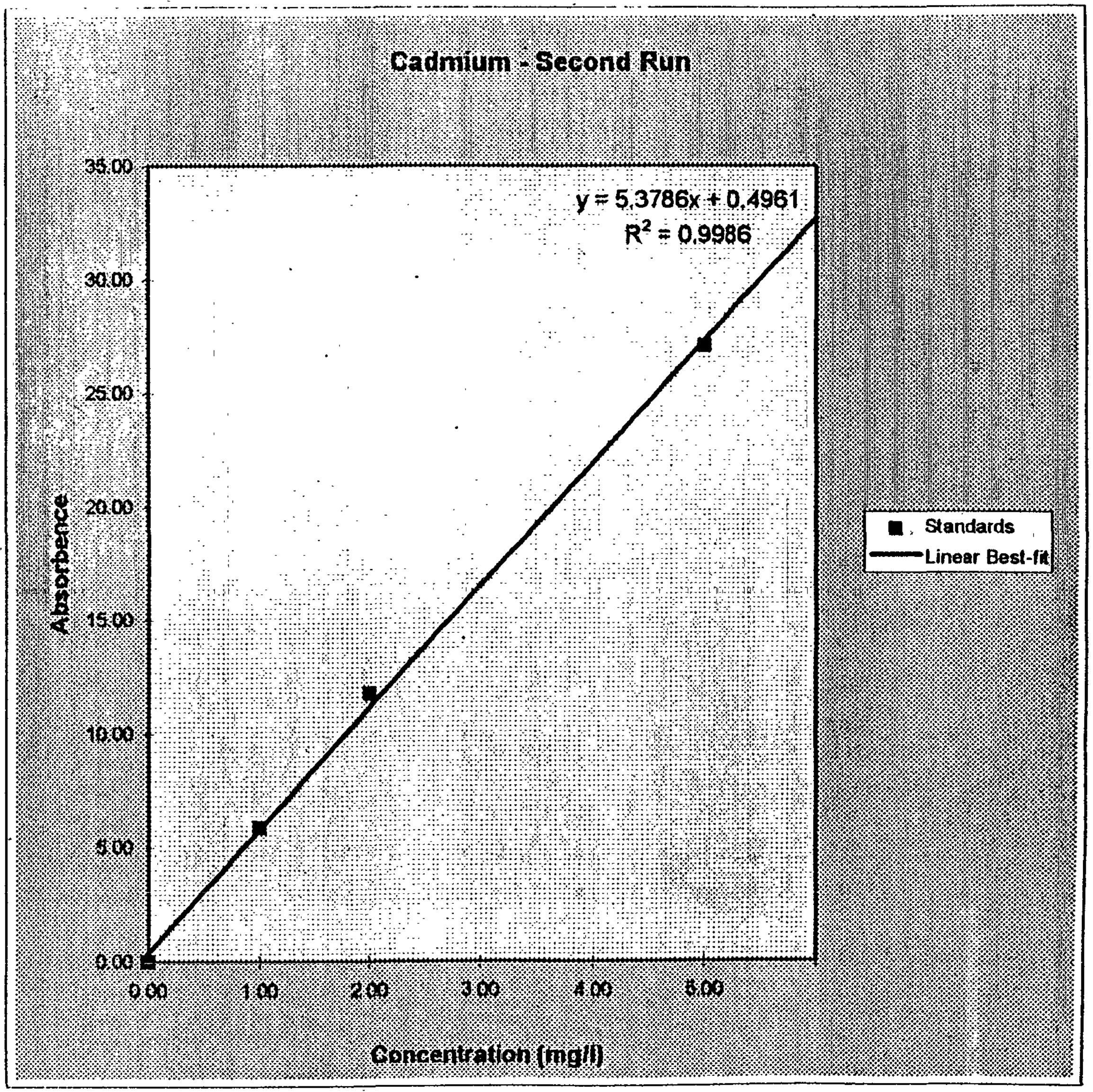


FIGURE 8

Zinc First Run
Atomic Absorption Results

Sample No.	Absorbence (y-value	Concentration (x-value)
1	16800	1648.03
2	4180	410.05
3	4710	462.04
4	15160	1487.15
5	2740	268.79
6	15160	1487.15
7	16730	1641.16
8	14510	1423.39
9	15820	1551.89
10	4310	422.80
11	17640	1730.43
12	16730	1641.16
13	5.75	0.56
14	2.09	0.21
15	12.28	1.20
16	28.1	2.76

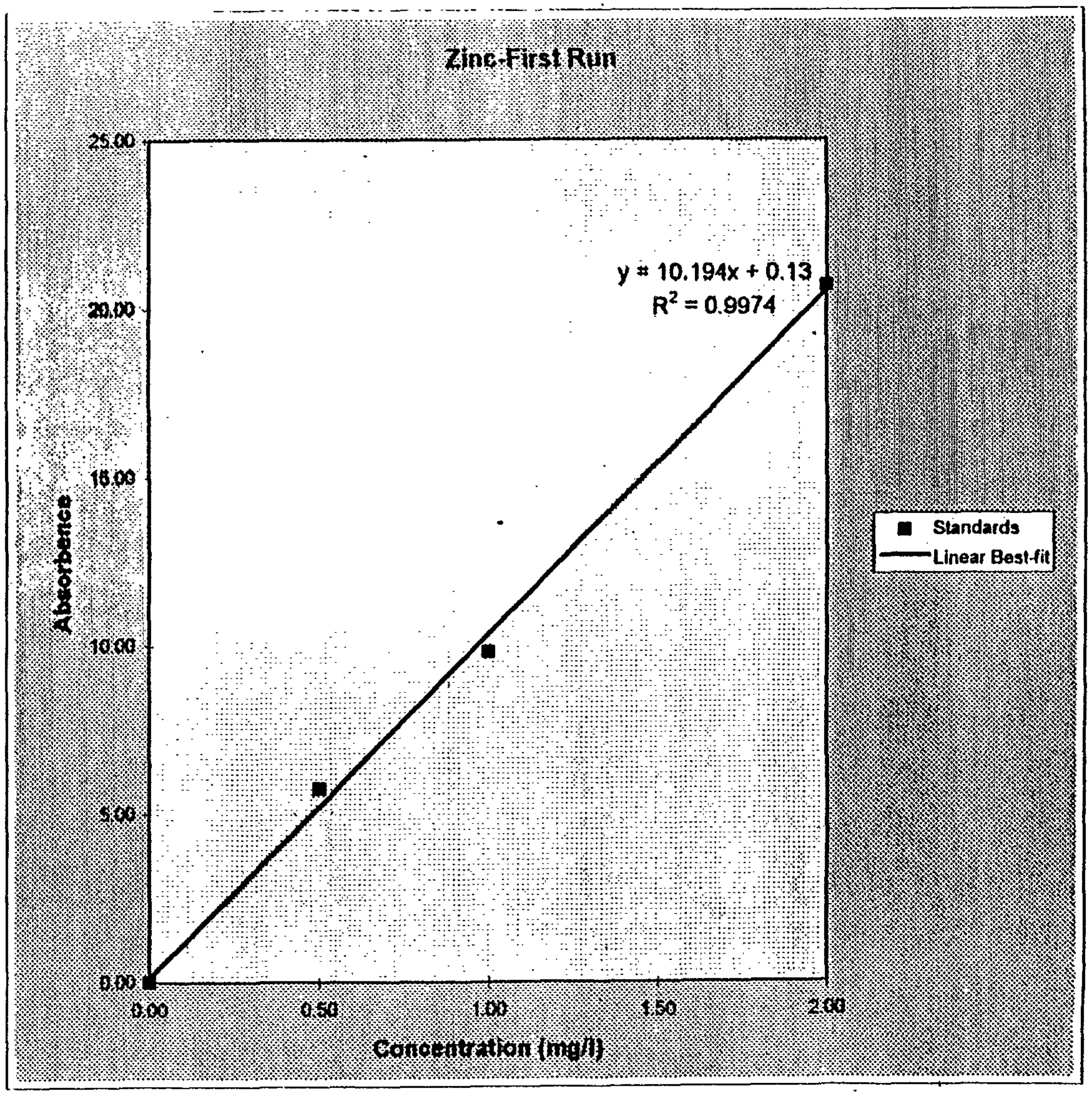


FIGURE 9

Zinc Second Run
Atomic Absorption Results

Sample No.	Absorbence (y-value)	Concentration (x-values)
1	16800	2089.55
2	4180	519.90
3	4710	585.82
4	15160	1885 57
5	2740	340 80
6	15160	1885 57
7	16730	2080 85
8	14510	1804 73
9	15820	1967 66
10	4310	536 07
11	17640	2194 03
12	16730	2080 85
13	5 75	0 72
14	2 09	0 26
15	12.28	1.53
16	28.1	3.50

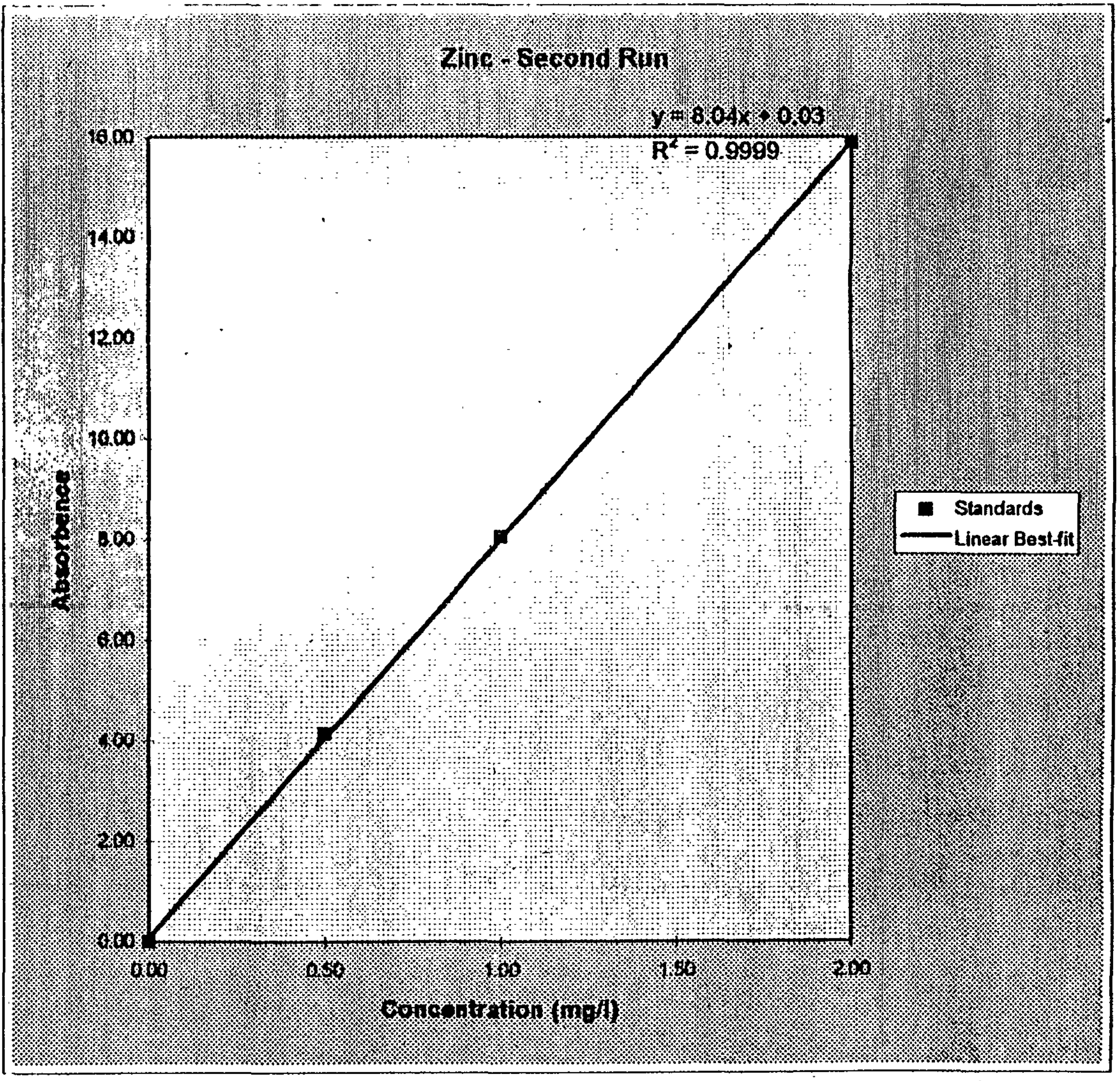


TABLE 20

CALCULATION OF INSTRUMENT DETECTION LIMITS
AND
INSTRUMENT SENSITIVITY

AA-run number	AA - Absorbance Values					
	LEAD		CADMIUM		ZINC	
	5.0 mg/l	10.0 mg/l	1.0 mg/l	2.0 mg/l	0.5 mg/l	1.0 mg/l
1	3.22	6.72	7.06	12.94	6.27	18.43
2	2.72	6.72	6.86	13.33	5.10	18.43
3	3.22	6.72	7.06	13.53	6.67	19.61
4	3.22	6.72	7.06	14.12	5.88	19.61
5	2.72	6.72	6.67	13.73	5.88	19.61
6	3.22	6.72	7.06	13.33	5.49	18.43
7	3.22	6.72	6.67	13.73	5.88	18.43
8	3.22	6.72	7.25	12.94	5.88	20.00
9	3.22	6.72	6.67	13.33	5.49	20.00
10	2.92	6.72	7.06	14.51	6.28	18.43
11	3.72	6.72	6.67	14.31	5.88	18.82
12	3.22	6.72	7.06	13.73	5.10	19.21
13	3.22	6.92	7.06	14.12	5.10	19.21
14	2.92	6.72	6.67	13.73	5.10	18.82
15	3.22	6.72	6.67	13.33	6.67	19.22
16	3.72	7.22	6.67	13.33	5.49	18.43
17	3.22	6.72	7.06	13.33	5.49	18.43
18	3.22	6.72	6.67	13.73	6.67	18.04
19	2.92	6.72	6.67	14.51	5.88	19.61
20	3.22	6.72	6.67	14.12	6.27	20.00
Mean	3.18	6.76	6.86	13.69	5.82	19.04
Std. Dev.	0.25	0.12	0.21	0.47	0.53	0.64
Ratio of Means	0.47		0.50		0.31	
Ratio of Std. Devs.	0.47		0.44		0.82	
Detection Limits *	0.80	0.35	0.06	0.14	0.09	0.07
Avg. Detection Limit	0.6 mg/l		0.1 mg/l		0.08 mg/l	
Sensitivity **	0.0069	0.0065	0.00064	0.00064	0.00038	0.0002
Avg. Sensitivity	0.0067		0.00064		0.0003	

AA = Atomic Absorption
* = (Conc.of standard x 2 x Std.Dev.) / Mean of Absorbances
** =(Conc. of standard x 0.0044) / Measured Absorbance

TABLE 21

EXTRACTION
pH RESULTS

SAMPLE NO.	SAMPLE DESCRIPTION	Initial Sample pH	Intermediate pH (3.5ml HCl added)	Extraction Fluid used *	Final Extract pH
1	Tailings pile sample, untreated	9.17	5.23	2	5.76
2	Tailings treated with 5% Maectite	7.48	4.62	1	6.03
3	Tailings treated with 3% Maectite	7.97	4.82	1	6.31
4	Tailings treated with 1% Maectite	8.61	5.36	2	5.58
5	Large tailings fraction, untreated	9.09	4.78	1	6.75
6	Medium tailings fraction, untreated	9.06	5.47	2	5.93
7	Small tailings fraction, untreated	9.10	6.05	2	6.02
8	Duplicate of No. 7	9.12	5.89	2	6.05
9	Large fraction, treated with 3% Maectite	8.45	5.34	2	5.43
10	Medium fraction, treated with 3% Maectite	8.21	4.70	1	6.50
11	Small fraction, treated with 3% Maectite	7.99	5.16	2	5.36
12	Duplicate of No. 11	7.90	5.04	2	5.38
13	Tailings, treated with 20% Quicklime	12.00	11.48	2	9.23
14	Tailings, treated with 20% Portland Cement	11.35	10.05	2	9.37
15	Water blank	6.15	1.79	1	4.96
16	Water blank, treated with 3% Maectite	2.30	-	1	4.57

* 1 = glacial acetic acid + 1 N sodium hydroxide solution @ pH 4.93 (+/- 0.05)
2 = glacial acetic acid solution @ pH 2.88 (+/- 0.05)

are in sharp contrast to the final extract pH values of the samples treated with conventional S/S reagents (samples 13 and 14). The quicklime treated sample had a final extract pH of 9.23, while the Portland cement treated sample had a final extract pH of 9.37. This is important with repect to solubility of various metals as a function of pH. The final pH range shown for the S/S treated materials would be expected to promote minimal solubility in the metals tested, while the final pH range for the untreated and the MAECTITE treated materials would be expected to solublize these metals.

A summary of percent moisture results is shown for some of the sixteen samples in Table 22. Not all samples were tested. The results indicate that untreated Ball Mill tailings materials contained between 20.86 and 22.42% moisture. All size fractions had roughly the same moisture content. Samples treated with MAECTITE had slightly higher moisture contents, ranging from 21.25 to 25.00% moisture. According to literature, there is a minimum moisture content required for effective MAECTITE treatment. This has not been evaluated.

A dry sieve analysis was conducted on a representative sample of the Ball Mill tailings material. The results of that sieve analysis are shown in Table 23. The largest fraction of sample (26.69%) was retained on the No. 30 (600-um) sieve. This was the portion chosen for the small size fraction during the initial testing. Sieve No. 16 (1.18-mm) retained the second highest percentage of material at 19.76%. Sieve No. 8 (2.36-mm) followed by retaining 19.06% of the sample material. The material retained on this sieve was chosen as the medium size fraction of Ball Mill tailings material in the initial testing. The 3/8-inch sieve (9.5-mm) retained 14.62% of the sample, while the No. 4 sieve (4.75-mm) retained 12.94%. The material retained on the No. 4 sieve (4.75-mm) was chosen as the large size fraction material in the initial testing. The overall sieve analysis indicates that the Ball Mill tailings sample is in the range of coarse to fine sand.

An analysis of quality assurance data is shown in Table 24 for the duplicate samples run during the research. Two sets of duplicate samples were run. The first set of duplicate samples were conducted on untreated samples of small size fraction tailings material. The relative percent difference (RPD) for TCLP results on these samples were 0.4%, 3.2%, and 3.6% for lead, cadmium, and zinc respectively. The second set of

TABLE 22

MOISTURE CONTENT

SAMPLE NO.	SAMPLE DESCRIPTION	% Moisture	% Solids
1	Tailings pile sample, untreated	22.42	77.58
2	Tailings treated with 5% Maectite	21.25	78.75
3	Tailings treated with 3% Maectite	23.88	76.12
4	Tailings treated with 1% Maectite	25.00	75.00
5	Large tailings fraction, untreated	20.90	79.10
6	Medium tailings fraction, untreated	21.70	78.30
7	Small tailings fraction, untreated	20.86	79.14
8	Duplicate of No. 7	21.32	78.68
9	Large fraction, treated with 3% Maectite	–	–
10	Medium fraction, treated with 3% Maectite	–	–
11	Small fraction, treated with 3% Maectite	–	–
12	Duplicate of No. 11	–	–
13	Tailings, treated with 20% Quicklime	–	–
14	Tailings, treated with 20% Portland Cement	–	–
15	Water blank	100.00	0.00
16	Water blank, treated with 3% Maectite	97.00	3.00

-- not analyzed

TABLE 23

SIEVE ANALYSIS

Sieve Size		Weight Retained (grams)	Percent Retained	Cumulative % Passing
English	Metric (mm)			
3/4"	19.00	0.0	0.00	100
3/8"	9.50	27.0	14.62	85.38
	4.75	23.9	12.94	72.44
No. 8	2.36	35.2	19.06	53.38
No 16	1.18	36.5	19.76	33.62
No. 30	0.60	49.3	26.69	6.93
No. 50	0.30	12.7	6.88	0.05
No. 100	0.15	0.1	0.05	0.00
No. 200	0.075	0.0	0.00	0.00

Total Sample Size = 189.3 grams

TABLE 24

DUPLICATE RESULTS - RELATIVE PERCENT DIFFERENCES

NO.	SAMPLE DESCRIPTION	TCLP RESULTS (mg/l)			RELATIVE % DIFFERENCE		
		LEAD	CADMIUM	ZINC	LEAD	CADMIUM	ZINC
1	Tailings pile sample, untreated	34.4	1.14	2090	--	--	--
2	Tailings treated with 5% Maectite	1.3	0.44	520	--	--	--
3	Tailings treated with 3% Maectite	2.5	0.44	586	--	--	--
4	Tailings treated with 1% Maectite	11.1	1.14	1886	--	--	--
5	Large tailings fraction, untreated	6.3	0.49	341	--	--	--
6	Medium tailings fraction, untreated	43.3	1.18	1886	--	--	--
7	Small tailings fraction, untreated	37.8	1.43	2081	0.44	3.16	3.55
8	Duplicate of No. 7	37.2	1.26	1805	0.44	3.16	3.55
9	Large fraction, treated with 3% Maectite	5.7	0.86	1968	--	--	--
10	Medium fraction, treated with 3% Maectite	1.3	0.34	536	--	--	--
11	Small fraction, treated with 3% Maectite	3.7	0.95	2194	10.00	1.08	1.32
12	Duplicate of No. 11	2.5	0.91	2081	10.00	1.08	1.32
13	Tailings, treated with 20% Quicklime	<0.60	<0.10	0.72	--	--	--
14	Tailings, treated with 20% Portland Cement	<0.60	<0.10	0.26	--	--	--
15	Water blank	<0.60	<0.10	1.53	--	--	--
16	Water blank, treated with 3% Maectite	<0.60	<0.10	3.50	--	--	--

< less than

-- not applicable

duplicate samples were conducted on MAECTITE treated samples of small size fraction tailings material. The RPD for TCLP data on these samples were 10%, 1.1%, and 1.3% for lead, cadmium, and zinc respectively.

Chapter 7

SUMMARY

The MAECTITE treatment has been shown to be effective at reducing TCLP-lead and TCLP-cadmium to below regulatory levels, using a minimum treatment rate of 3%. This treatment can effectively change the waste classification from a characteristic hazardous waste to a residual waste. In addition, the MAECTITE treatment can also reduce the levels of TCLP-zinc significantly. Since there are currently no regulatory levels established for TCLP-zinc, the effectiveness would be dependent upon the attainment of site specific remediation goals.

Central to this paper is the issue of waste size classification. The data has shown that the TCLP-lead, -cadmium, and -zinc have been released from the medium and small size fractions. This may be due to the surface area differences. Weathering rates may also differ between the particle sizes, having an effect on leaching rates. Very little TCLP-lead, -cadmium, or -zinc were found in the large size fraction. In fact, this fraction of the waste was right around the TCLP regulatory level for lead (based on one sample). If the large size fraction is classified as non-hazardous, it would be beneficial to screen it out. This would eliminate about 28% of the waste from treatment. For a pile of 143,000 tons, this amounts to about 40,000 tons of material. This would greatly reduce the remediation costs.

Several interesting conclusions can be made about the three size fractions that were treated with 3% MAECTITE material. First, very little if any treatment was seen in the large size fraction sample. In fact, TCLP levels for cadmium and zinc were higher in the treated sample than in the untreated sample. The ineffectiveness of the treatment on the large size fraction may be attributed to the reduced surface area of the large fraction when compared to the surface area available for treatment on the medium size fraction sample. The MAECTITE materials can only react with the TCLP metals that it contacts. Since the TCLP method required no further size reduction for this fraction (<3/8 inch), the treatment materials may not have been exposed to the TCLP metals that were physically bound within the matrix. This discovery may also lend credence to the crushing of large-sized wastes to less than 5 mm prior to treatment (for large fraction wastes with high levels of TCLP metals). The 3% MAECTITE treatment worked well on both the medium- and small-size fractions for lead, however it worked slightly better on the medium-size fraction. For TCLP-lead, a 97% reduction was realized for the medium fraction and only a 90% reduction in the small fraction. For TCLP-cadmium, a 71% reduction was realized for the medium fraction and only a 34% reduction for the small fraction. For TCLP-zinc, a 72% reduction was realized for the medium fraction, while no reduction was seen in the small fraction. There doesn't seem to be an explanation for why the treatment additives can treat TCLP lead for both the medium and small size fractions, yet is ineffective for treatment of TCLP-cadmium and TCLP-zinc in the small size fraction. If more information was known about the chemistry behind the patented MAECTITE process, an understanding of this phenomenon may be more apparent. The results, however, do point to the fact that the MAECTITE treatment process has a preference for certain size fractions. The medium size fraction consistently had the best reduction in TCLP metals following treatment. This would not be expected to be the case if one considered the surface area of the material to be the limiting factor.

The results of the testing using typical S/S treatment techniques showed excellent reduction in TCLP lead, cadmium and zinc. Quicklime and Portland Cement treatments (using a 20% dosage) reduced TCLP lead by greater than 98%, TCLP cadmium by greater than 91%, and TCLP zinc by greater than 99%. Additional testing using lower rates of treatment reagents may show an optimal dosage less than 20%. These treatment results may however be influenced by the pH factor.

Table 21 showed the initial sample pH values, intermediate pH values, and final TCLP-extract pH values for each sample, according to the TCLP extraction procedure discussed in Chapter 5. An interesting observation is that the initial sample pH values for untreated samples range from 9.06 to 9.17. Initial pH values for MAECTITE treated samples range from 7.48 to 8.61. This shows that the MAECTITE additives do acidify the sample matrix upon treatment. All of these samples are in the pH range of 7.0 to 9.0. For the amphoteric metals discussed in this paper, this is the pH range of lowest solubility, with the exception of cadmium. Water percolating through materials in these pH ranges would not tend to leach the metals into solution. In sharp contrast are the initial pH ranges of the Quicklime and Portland Cement treated samples. These samples have initial pH values of 12.00 and 11.35, respectively. For amphoteric metals, extremely basic pH values will have somewhat the same effect as acidic pH ranges, that is to leach metals into solution. The minimum solubility for cadmium is closer to this pH range so it will make it less soluble.

The initial pH results in Table 21 were compared with the final TCLP extract pH values. It was noted all that the TCLP extraction fluids have reduced the solution pH values of untreated samples and samples treated with MAECTITE additives to a similar range of 5.36 to 6.75. This is a slightly acidic range that would tend to leach amphoteric metal species into solution. This was compared to the final TCLP extract pH values of Quicklime and Portland Cement treated samples (pH 9.23 and pH 9.37). The buffering capacities of these two stabilization additives have neutralized the acidic extraction fluids to end up with a solution pH value in the stable range for amphoteric metals (see Figure 5). When comparing the relative concentrations of amphoteric metals leaching into solution, it is shown that the samples with final extract pH values of around 9.0 (Quicklime and Cement stabilized samples) have the lowest concentrations of metals. The other samples with final extract pH values in the range of 5.0 to 6.0 have considerably higher concentrations of heavy metals.

In general, the pH values of the final extract seemed to have some effect on the concentration of leached metals in solution. Samples with final extract pH values above 6.0 tended to have lower concentrations of leachable metals than samples with final extract pH values below 6.0. From a comparison of initial sample pH values with intermediate pH values and final extract pH values, it appears that the addition of the MAECTITE additives have a slight buffering effect on the tailings pile samples. This may help to account for the reduced concentrations of leachable metals in treated samples.

The mineralogy analysis of the Ball Mill tailings pile has been shown to be consistent with the lead smelting process. These show lead to be found as PbCO3 (cerussite) or PbO (lead oxide), cadmium as CdCO3 (otavite), and zinc as ZnO (zincite).

Lead and zinc are also shown to be concentrated in the Zincite and Willemite (Zn2SiO4) minerals found in the pile. The high pH of the pile retains many of these minerals as insoluble species. The mineralogical composition of the treated Ball Mill tailings material is yet unknown, but according to the literature review, it primarily contains phosphate- and sulfate-substituted species.

At first glance, the results of the TCLP testing for the 16 samples may not appear significant due to the limited number of replicate samples analyzed. This was understood at the onset of the experiment, but was done to prevent an excessive amount of time in the laboratory. The number of data points shown are considered a minimal amount to draw conclusions along with a few QA/QC samples to confirm accuracy. An analysis of duplicate samples shows the data to have low relative percent difference results. The duplicate untreated small size fraction sample had a relative percent difference of 0.44%, 3.16%, and 3.55% for lead, cadmium, and zinc respectively. The duplicate treated small size fraction sample had a relative percent difference of 10%, 1.08%, and 1.32% for lead, cadmium, and zinc respectively. The water blanks did not show the potential for contamination of the deionized dilution water used or contamination of bottleware. TCLP results for lead and cadmium aqueous blanks were less than the detection limits, while TCLP zinc results for blanks were extremely low, as to be insignificant.

An economic analysis of the remediation of the Ball Mill tailings pile was evaluated for several options during the FS phase of the Jack's Creek Site investigation (see Chapter 2). Chemical fixation with MAECTITE was shown to be the most feasible cost option at $35-50/ton for treatment alone. This was in comparison to resource recovery, hazardous waste disposal, and soil washing options. The difference between S/S technologies and chemical fixation is mainly the cost of the additives and the rate of application. The cost of treatment additives for chemical fixation is about $350/ton of reagent. The cost of Portland Cement is about $100-150/ton of dry cement. At a rate of 3%, the cost for additives to treat the 143,000 ton Ball Mill tailings pile with the chemical fixation process would be about $1.5 Million. Assuming a rate of 20%, the cost for additives to treat the tailings pile with Portland Cement would be about $2.9 Million, assuming the low-end cost range. The result is that chemical fixation is about half the cost of S/S treatment for additives alone for the assumed treatment levels. The cost differences would be minimized if lower treatment dosages of Portland Cement were proven effective.

The MAECTITE reagents used for this research consisted of a powder and a liquid mixed at a 1:1 ratio by weight. According to the manufacturer, this particular liquid and powder was formulated for the fixation of lead in particular. There are, according to the manufacturer, other formulations of the liquid and powder that will be more effective for the fixation of cadmium and possibly zinc.

Analysis of several additional parameters would have been useful during the research of the treatment of the Ball Mill tailings material. Of primary importance would be to rerun the experiments, including the S/S techniques, using other leaching techniques such as the multiple extraction technique or water leaching using deionized water, rain water, or site groundwater. Based on these results, it may be necessary to vary the treatment rates of the MAECTITE treatment or the S/S methods to find the optimal treatment rates of both. An analysis of cation exchange capacity (CEC) would have been useful for predicting the absorptive capacities of the waste material and for gaining an understanding of the fate and transport mechanisms within the pile. A total metals analysis of the material prior to and after treatment would have been useful for looking at surface area effects and for mass balance. An analysis of volume reduction following treatment using the MAECTITE reagents would also have been useful for verifying volume reduction capabilities stated in the literature review. An analysis of particle size conducted on the filtered residue following each TCLP extraction would be useful to evaluate if particle sizes have been reduced in the tumbler. It may prove useful to retest the small fraction samples to include all of the fines below the No. 16 seive to better evaluate metal interaction within the pile. Finally, an analysis of the untreated and treated samples for various mineral species, especially sulfides, would be useful to better understand the treatment process.

The positive results of this research, using the MAECTITE treatment for the fixation of lead, cadmium, and zinc in the Ball Mill tailings pile, may have additional implications for the rest of the waste sources at the Jack's Creek Site. This pile and the industrial operations that formed this pile, have contributed to the contamination of the other media at the site. Thousands of tons of sediments and soils across the site are contaminated with heavy metals, lead in particular. It is likely that the same reagents that fixate lead in the Ball Mill tailings pile could be used to treat the other contaminated solid media across the site. Additional treatability studies would be required to determine the effectiveness of this technology for specific waste streams.

Chapter 8

CONCLUSIONS and RECOMMENDATIONS

There are several conclusions that can be made about the data derived from this paper. In addition, there are several unanswered questions created by this paper and the need for subsequent work to better understand the process of chemical fixation. One overarching conclusion that can be made from the data is that the MAECTITE treatment has been shown to be effective at reducing TCLP-lead and TCLP-cadmium to below regulatory levels, using a minimum treatment rate of 3%. This treatment will effectively change the waste classification from a characteristic hazardous waste to a residual waste. In addition, the MAECTITE treatment can also reduce the levels of TCLP-zinc significantly.

Central to this paper is the issue of waste size classification. The data has shown that the TCLP-lead, -cadmium, and -zinc have been released from the medium and small size fractions, but not from the large size fraction. This may be due to the surface area differences. Weathering rates may also differ between the particle sizes, having an effect on leaching rates. The results, however, do point to the fact that the MAECTITE treatment process has a preference for certain size fractions. The medium size fraction consistently had the best reduction in TCLP metals following treatment. This would not be expected to be the case if one considered only the surface area of the material to be the limiting factor.

Of particular interest to this experiment, were the pH results. The buffering capacities of Portland Cement and Quicklime additives have neutralized the acidic extraction fluids to end up with a solution pH value in the stable range for the amphoteric metals discussed. Other samples had final extract pH values in the range of 5.0 to 6.0 with considerably higher concentrations of heavy metals. In general, the pH values of the final extract had an effect on the concentration of leached metals in solution. Samples with final extract pH values above 6.0 tended to have lower concentrations of leachable metals than samples with final extract pH values below 6.0.

These observations and conclusions about pH effects on the concentrations of leachable metals point to the need for additional leachability tests using other leaching solutions. Acid-rain water, distilled water, or site groundwater leaching tests may be useful for evaluating the high pH effects of cement and quicklime, while the Multiple Extraction Procedure may be useful for evaluating the neutral pH effects of the raw tailings material and the treated material.

Chemical fixation with MAECTITE was also shown to be the most feasible cost option. The difference between S/S technologies and chemical fixation is mainly the cost of the additives and the rate of application. The result is that chemical fixation is about half the cost of S/S treatment for additives alone for the assumed treatment levels. The cost differences would be minimized if lower treatment dosages of Portland Cement were proven effective.

The MAECTITE reagents used for this research consisted of a powder and a liquid mixed at a 1:1 ratio by weight. According to the manufacturer, this particular liquid and powder was formulated for the fixation of lead in particular. There are, according to the manufacturer, other formulations of the liquid and powder that will be more effective for the fixation of cadmium and possibly zinc. Additional research on selection of an optimum fixation agent for specific contaminants should be conducted. In addition, the ratio of liquid to powder treatment reagents used during this research was determined from the initial treatability screening results done by Sevenson Environmental. Additional research should also be conducted on a variety of liquid to powder ratios to determine the most effective ratio for treatment of specific contaminants.

Other recommendations for additional work on this subject include the calculation of optimal treatment rates for the S/S technologies, analysis of partical size on the filtered residue following TCLP extractions, analysis of smaller size fractions, and analysis of treated and untreated samples for mineral species.

REFERENCES

Brown, K. W., *Hazardous Waste Land Treatment.* Prepared for USEPA Municipal Environmental Research Lab., Cincinnati, Ohio. NTIS PB89-179014. 1983.

40 Code of Federal Regulations, Part 261, Appendix II, Method 1311. *Toxicity Characteristics Leachate Procedure*. Federal Register. Vol. 55 No. 61, March 29, 1990.

Fergusson, J. E., *The Heavy Elements: Chemistry, Environmental Impact and Health Effects.* Pergamon Press. 1990.

Freedman and Shannon. *Modern Alkaline Cooling Water Treatment*. Industrial Water Engineering. January - February 1973. p.31.

Halliburton NUS Corp./Gannett Fleming, Inc. *Final Remedial Investigation Report - Volume I - Jack's Creek Site*. August, 1993.

Halliburton NUS Corp./Gannett Fleming, Inc. *Final Feasibility Study Report - Jack's Creek Site.* November, 1993.

Lindsay, W. L. *Chemical Equilibria in Soils*. John Wiley and Sons, New York. 1979.

MAECORP, Inc. Treatability Study of Jack's Creek Site. April 1, 1993.

Masterton, W. L. and E. J. Slowinski. *Chemical Principles*. W. B. Saunders Company. 1973.

RMT, Inc. Screening Test Results of Jack's Creek Site. January 14, 1993.

START. Superfund Technical Assistance Response Team. *Recycling Options for Jack's Creek Ball Mill Tailings Waste*. March 1993.

USEPA. *Waste Treatment: Upgrading Metal Finishing Facilities To Reduce Pollution*. EPA 625/3-73-002. July, 1973.

Yost, K. W., A. Elia, and S. A. Chisick. *MAECTITE Chemical Treatment Technology: Selected Case Histories for Lead and Cadmium*. Superfund XV Conference. December 1, 1994.

Yost, K. W., D. Pal, S. A. Chisick, and W. V. Jesernig. *Lead and Other Heavy Metal Fixation in Soils and Solid Waste by the MAECTITE Chemical Treatment Process.* Purdue Industrial Waste Conference. May 10, 1994.

Yost, K. W., Sevenson Environmental, Chicago Illinois. Teleconference with R. D. Myers. January, 1995.

Zimdahl R. L. and R. K. Skogerboe. *Behavior of Lead in Soil.* Environmental Science and Technology, Volume II, No. 13. 1977.