Philippine Engineering Journal (1992) XIII (1): 43 - 66

IMMOBILIZATION TECHNIQUE FOR TOXIC SLUDGE

Genandrialine L. Peralta, M.S.
Assistant Professor
Environmental Engineering
College of Engineering
University of the Philippines
Diliman, Quezon City

Feliciano C. Ballesteros, Jr.
University Research Assistant
National Engineering Center

Marivie L. Cepeda
University Research Assistant
National Engineering Center
University of the Philippines
Diliman, Quezon City

ABSTRACT

High concentrations of heavy metals such as Ag, As, Cd, Cr, Hg and Pb in a sludge generated from a cooling tower can not be directly disposed of in a sanitary landfill without risking groundwater contamination. Preliminary studies on the sludge show that the heavy metal concentrations are beyond the standards set by the USEPA. This necessitates the treatment of the sludge prior to final disposal.

The solidification technique was employed to immobilize the contaminants to a degree where it no longer poses an environmental hazard. The technique utilized silica-rich materials such as portland cement and rice hull ash as immobilizing agents.

Simulation studies of the behavior of the treated sludge during long-term storage showed significant reduction in heavy metal mobility to within the standards. X-ray diffraction (XRD) analysis of the cementitious product point to physical entrapment of the heavy metals within the ettringite/silicate matrix as the main immobilizing mechanism.

INTRODUCTION

The reduction of heavy metal mobility can be carried out using the following methods:

Sorption - involves the addition of solid to take up any free liquid in a waste. Examples are activated carbon, anhydrous sodium silicates, gypsum, clays, and smaller particulate materials. Most sorption processes merely remove the liquid on the surface of the solid and do not reduce contaminant leaching potential.

Lime-Fly Ash Pozzolan Reactions - employ a fine, non-crystalline silica in fly ash and the calcium in lime to produce low strength cementation. Physical trapping of the contaminant in the cured pozzolan concrete matrix is the primary containment mechanism.

Pozzolan Portland Cement Reaction - combines Portland cement and fly ash or other pozzolans to produce a relatively high strength waste/concrete matrix. Waste containment is primarily by entrapment of waste particles. Soluble silicates may be added to aid processing and to assist in metal containment through the formation of silica gels.

Thermoplastic Microencapsulation - blends waste particulates with melted asphalt or similar materials. Physical entrapment is the primary containment mechanism.

Macroencapsulation - isolates a large volume of waste by jacketing it with any acceptable material.

In pozzolan portland cement reactions, it is possible that chemical bonding may take place. The heavy metals may actually take part in the hydration of the silicates forming silicate-metal complexes. This paper describes the laboratory investigation of this phenomena as applied to the treatment of wastes contaminated with Ag, As, Cd, Cr, Hg, and Pb.

THEORETICAL CONSIDERATIONS

Cementitious Solidification

Chemical fixation using solidification is found to be the most common method of treatment of sludge containing toxic inorganics. There are four (4) processes of solidification that may handle toxic inorganics such as heavy metals. These are cement-based, lime-based, thermoplastic, and organic polymer techniques. The **cement-based** or **silica-based immobilization** is widely used due to its various advantages such as:

a. low cost;

b. low technology;

c. no specialized equipment needed;

d. no specialized labor once initial formulation has been established;

e. additives and equipment are readily available;

f. subsequent disposal may be to normal landfill; and,

g. the technique is tolerant of chemical variations in sludge.

Leaching Test Procedure

A fundamental measure of the potential hazard of a waste is its ability to generate leachate wherein its toxic constituents are present. There are over 60 worldwide test procedures (McFarland, 1988) which seeks to determine the likely concentration of contaminants in the leachate that may be generated. A comparison of the essential features of some of the procedures developed is shown in Table 1.

Table 1: Leachate Assessment Methods

Test Conditions	TCLP Test	ASTM	Japanese EPA	Harwell	IUCS
1. Sampling	Representative Sampling Procedure	Representative procedure as per ASTM Method	None	Representative sampling procedure	Use as anticipated field
2. Sample Mass	100 g	350 or 700 g or mass appropriate	10 g	100 g	125 g
3. Leaching media and modifier	Buffered acetic acid	Distilled water	HCl, NaOH or CO2 gas in water	Distilled water or buffered acetic acid	Deionized water
4. pH control	5.0 + 0.2 until 4 ml HAc per gram waste is consumed	None	5.8 to 6.3	None	None
5. Solid to Liquid	16:1	4:1	10:1	One bed volume	4:1
6. Time per elution	24 hours	48 hours	6 hours	hourly to equilibrium	2, 4, 8, 24, 48 hours
7. Temperature	20 + 0.5 C	18 - 27 C	Ambient	Ambient	Ambient
8. Agitation Technique	Rotational agitation at 40 rpm for 48 hours	Inverted at 25 times per min. for 3 mins. Then agitated for 48 hours	Not Addressed	Mechanical flask shaker 10 cycles per second	Reciprocating shaker
9. Surface area	Ground to pass 95mm sieve	Not Addressed	Not Addressed	Ground to Pea-Gravel size or smaller	Not Addressed
10. Separation Procedure	0.45 um vacuum filtration	5mm settling, then 0.45 um vacuum filtration	Centrifuging then filter type NR5	Watman No. 451	0.45 um vacuum filtration
11. Result reporting	mg/l of dissolved species	mass tested, final ph, mg/l of dissolved species	Not Specified	Plot of cone vs bed volume or as mg released per kg waste tested	Not Specified
12. Leachate standards	100 x drinking water	Not addressed	Not addressed	Not addressed	Not addressed

As can be inferred from the table, there is still no uniform test procedure which is adopted internationally. However, in a number of countries, there has been a general trend towards the adoption of the procedure developed in 1980 by the US Environmental Protection Agency's (USEPA) Office of Solid Waste which is known as Toxicity Characteristic Leaching Procedure (TCLP). This procedure consists of 28 days of curing, crushing of the solidified product to pass through a 9.5 mm standard sieve and leachate extraction. The concentration of heavy metals in the leachate is defined with an atomic absorption spectrophotometer (AAS).

Acetic acid is used as the extraction medium since organic acids are the type generated in a landfill where organic material is co-disposed with inorganics. Moreover, acetic acid is the strongest organic acid available.

Standards for Heavy Metals

Maximum permissible concentrations in leachate have been set at 100 times the drinking water standards (40 CFR Sec. 261.24). This factor is suggested, since there are attenuating processes such as dilution, and adsorption occurring underground that will affect the leachate concentration generated in a landfill. Some regulatory agencies are more conservative and have reduced the factor to a tenfold increase to the drinking water standards.

Instrumental Assessment

Microanalysis of the solidified product can help establish whether immobilization is due to chemical binding of the metals with the cement in the sludge or simply microencapsulation. This can be verified through the use of a scanning electron microscope (SEM) and X-ray diffractometer (XRD).

Scanning Electron Microscopy

In scanning electron microscopy (SEM), a beam of electrons is used to focus magnetically on the specimen. The electrons are scattered by solid objects, thus, casting a "shadow" on a fluorescent plate or photographic plate. The intensities of the signals emitted as a result of the interaction between the specimen and a finely focused electron probe are displayed as a scanning image on a display device called the cathode ray tube.

Scanning electron microscopy requires a "conductive" specimen. Hence, an ion sputtering device is used to perform rapid and efficient coating on the specimen.

A 200 angstrom units (A) film thickness is normally used, but it also varies with the conductivity of the sample. Because of the very short effective wavelength of the electrons of the order of 1 (A), high resolutions and magnifications are possible. Electron micrographs can be taken to show the visual structure of the treated and untreated samples.

X-Ray Diffraction Analysis

X-rays are a form of electromagnetic radiation produced when matter is bombarded by a stream of fast moving electrons. The application of X-rays to the study of crystals is the greatest single contribution ever given to crystallography, hence, to mineralogy.

The X-ray diffractometer is a powerful determinative tool which uses monochromatic X-radiation and a finely powdered sample. A narrow beam of X-rays of known wavelength produced by bombardment of copper (or other suitable target) is directed to the specimen. The crystalline particles in the specimen make the proper angle with the incident beam. When the beam strikes the sample, all possible diffraction takes place simultaneously. A Geiger tube rotates to pick up the reflected X-ray beams and records the information as peaks traced in ink on a strip chart (Henry, 1982).

Every crystalline substance produces its own pattern which, as it is dependent on the internal structure, is characteristic of that substance (Goldstein, 1981). A reference file of XRD data of all known minerals and crystalline compounds prepared by ASTM is used as a standard. Identification of the compounds present in the specimen is done by "comparison and search method."

Significance to Solidification Process

At the onset of solidification, when cement reacts with water, it forms a structure consisting of calcium sulpho-aluminates (ettringite) and its derivative monosulphate. It has been observed that the structures formed during the hydration of cement have the ability to either trap or bind the heavy metals present in the sludge such as mercury, lead, arsenic and chromium. Instrumental analysis of the treated sample could indicate whethe there is physical encapsulation of the metals within the cement matrix or chemical binding has indeed taken place. However, this evaluation is dependent on other factors such as concentration of the metals in the sample, the form in which they are present (ionic or in compound form) and the structure of the compound formed (amorphous or crystalline) (Bensted and Varna, 1971).

The significance of the ettringite formation in the reaction between tricalcium aluminate and gypsum of cement is still unclear. However, it is claimed by some investigators that in both ettringite ($Ca_6Al_2(SO_4.SiO_4.CO_3)\ 3(OH)_{12}.26H_2O$) and monosulphate ($3CaO.Al_2O_3.CaSO_4.12H_2O$), the Al^{+3} ions can be replaced by the heavy metals. Kujala, (1986) concluded that the metals in soil wastes bind themselves with the synthetically prepared minerals of calcium sulphoaluminates and monosulphates. Verification of this binding mechanism is done through scanning electron microscopy and X-ray diffraction analysis.

The same study stated that the shape of the ettringite formed can either be plate-like or needle-like. This ettringite microstructure may contain the metals in the sludge although it may not necessarily bind itself to the metals. The binding mechanism can only be defined by the X-ray diffractometer.

ASTM Standard Method for Compression Test

The solidified product must be able to withstand the normal pressures in an ordinary landfill. Available literature (Sell, 1988) suggests that a minimum pressure of 50 psi which is equivalent to that experienced at the bottom of a 100-foot landfill, should not cause destruction of the physical integrity of the solidified sample. This could hasten the travel of unbound metal ions to the unsaturated zone of the aquifer.

MATERIALS AND EQUIPMENT

Hazardous Wastes

Four samples of varying physical and chemical composition were collected for the study. The laboratory analysis of these samples are presented in Tables 2 and 3.

Cooling tower sludge characteristics in terms of heavy metals are shown in Table 3. Six heavy metals such as silver, arsenic, cadmium, chromium, mercury, and lead were compared with the standards. Almost all elements except cadmium and silver are way above the required standards. Arsenic and chromium have the highest amounts ranging from 100 - 500 times the standards.

Table 2. Physical Analyses of Cooling Tower Sludge Samples

I. Sample A

a) Bulk Specific Gravity = 1.67
b) pH = 3.8
c) Percent moisture* = 57.25 %

II. Sample B

a) Bulk Specific Gravity = 2.023
b) pH = 2.15
c) Percent moisture* = 45.42 %

III. Sample C

a) Bulk Specific Gravity = 1.2
b) pH = 2.7
c) Percent Moisture* = 66.62 %

IV. Sample D

a) Bulk Specific Gravity = 1.25
b) pH = 4.32
c) Percent free standing liquid = 35.00%
d) Percent moisture* = 89.44%

NOTE : Determined after air-drying of sample for 3 weeks.

Table 3. Typical Sludge Characteristics in Terms of Heavy Metal Concentration

		Element	Ag	As	Cd	Cr	Hg	Pb
METAL CONCENTRATION		Standard	5.0	5.0	1.0	5.0	0.2	5.0
	Sample A	Total Assay (mg/kg)	126	2200	1.05	1560	16	150
		100% Mobility (mg/kg)	6.30	110	0.053	78	0.80	7.50
		Remarks	F	F	F	F	F	F
	Sample B	Total Assay (mg/kg)	32	2600	0.28	2400	165	150
		100% Mobility (mg/kg)	1.60	130	0.014	120	8.25	7.50
		Remarks	F	F	P	F	F	F
	Sample C	Total Assay (mg/kg)	3	1270	-	720	40	170
		100% Mobility (mg/kg)	0.15	63.5	-	36	2.0	8.5
		Remarks	P	F	-	F	F	F
	Sample D	Total Assay (mg/kg)	90	2840	0.84	2400	108	89
		100% Mobility (mg/kg)	4.5	142	0.042	120	5.4	4.45
		Remarks	F	F	P	F	F	F

Legend: P - passed standards F - failed standards

Siliceous Sources

Two types of binders were used in the solidification process. One is pure portland cement and the other is 50% rice husk ash and 50% portland cement. A comparison of the composition of ordinary portland cement and rice husk ash reveals similar properties as shown in Tables 4 and 5.

RHA was prepared by open burning of rice husk continuously for 24 hours followed by pulverization to 325 microns to effect greater surface area for optimum contact.

Various formulations of the sludge to cement ratio were tried ranging from 1:1, 1:2, 1:3, 1:4, and 1:5. The mixtures were solidified in 5 cm x 5 cm x 5 cm steel cube molds. The inner surfaces of these molds were coated with motor oil to allow easy removal of the cemented material after setting. The sludge-binder-water mixtures were allowed to stay in the molds for 24 hours. Afterwards, the solidified samples were removed from the molds to undergo curing for 28 days at room temperature.

Extraction Assembly

To evaluate the leaching behavior of the solid product during storage, the conditions peculiar to the disposal site should be duplicated. Continuous acid extraction of the pulverized samples for 18 hours in a rotary extractor will simulate water seepage. An ASTM specified extractor assembly rotating on its axis at 30 + 2 rpm was fabricated for this purpose.

Microanalysis

A scanning electron microscope with a capability of 10000x magnification was used to study the morphology of the cement products. In addition, an X-ray diffractometer was used to supplement the work of the scanning electron microscope.

Compressive Strength

ASTM Standard Designation # C684-89 outlines the procedure for evaluating compressive strength at the end of the 7th, 14th, 21st, and 28th days of curing concrete in water. This test was carried out for the 1:2 sludge to cement ratio for all four samples. Triplicate specimens from each sample type were withdrawn from the curing vessel after 7, 14, 21, and 28 days of curing and tested for structural integrity. The compression tests were performed using the Universal Testing Machine with 60,000 lbs capacity at the UP College of Engineering's Material Testing Laboratory.

Table 4 - Chemical and Physical Properties of Ordinary Portland Cement (OPC)

1.	Chemical Composition	Percent
	Silicon dioxide,SiO_2	20.81
	Aluminum oxide, Al_2O_3	5.57
	Ferric oxide,Fe_2O_3	3.04
	Calcium oxide, CaO	65.60
	Magnesium oxide, MgO	0.77
	Sulphur trioxide, SO_3	2.52
	Free lime, $Ca(OH)_2$	0.97
	Tricalcium silicate	59.90
	Tricalcium aluminate	9.60
	Dicalcium silicate	14.50
	Tetracalcium aluminoferrite	9.25
	Loss of ignition	1.10
	Insoluble residue	0.40
2.	Specific Surface Area*	
	(Blaine's)sq. cm. per gram	3315

Source: MUJIB (1987)

Table 5 - Chemical and Physical Properties of Rice Husk Ash (RHA)

1.	Chemical Composition	Percent
	Silicon Dioxide, SiO_2	91.16
	Aluminum Oxide, Al_2O_3	0.51
	Ferric Oxide, Fe_2O_3	0.86
	Calcium Oxide, CaO	0.57
	Magnesium Oxide, MgO	0.24
	Sulfur Trioxide, SO_3	trace
	Sodium Oxide, Na_2O	0.07
	Potassium Oxide, K_2O	2.88
	Carbon, C	0.54
	Loss of ignition	0.28
2.	Specific Surface Area* (Blaine's) sq. cm. per gram	12450
3.	Specific Gravity	2.13
4.	Porosity	0.65

* 95% passing Sieve ASTM No. 325

Source: MUJIB (1987)

DISCUSSION OF FINDINGS AND RESULTS

The results of this study indicate successful immobilization by cement of the heavy metals in the sludge. The instrumental assessment of the immobilization mechanism confirmed physical entrapment of the heavy metals within the silica matrix of the solidified cement and sludge.

Characteristics of Solidified Product

Physical properties of the fixated sludge such as density, compressive strength and permeability were studied as tools in the evaluation of its behavior during temporary storage.

Density

The density data as tabulated below (Table 6) reveal that generally the sludge is less dense when treated. This is mainly due to the evaporation of water in the raw sludge prior to cement solidification. The density of the fixated sludge will be used to calculate the approximate size of the concrete mold that could be easily and manually carried to a disposal site.

Table 6 - Comparative Densities
(in g/ml)

Sample	Raw	Treated
A	1.67	1.62
B	2.02	1.85
C	1.20	1.15
D	1.25	1.56

Compressive Strength

The results of this test shown in Table 7 and Figure 1 reveal that all four samples (1:2 sludge to cement ratio) pass the minimum requirement of 50 psi compressive strength for disposal in a sanitary landfill. This requirement is met as early as the 7th day of curing as in the case of sample C. Thus, the possibility that free liquids containing unbound heavy metals being released as landfill leachate is remote.

Table 7 - Compressive Strength (psi) Binder : Portland Cement
Sludge to Cement Ratio 1:2

Curing Time (days)	Compressive Strength, psi*			
	Sample A	Sample B	Sample C	Sample D
7	82	820	94	304
14	162	960	333	379
21	245	1181	360	392
28'	413	1132	358	412

* Minimum Requirement : 50 psi (Sell, 1988)

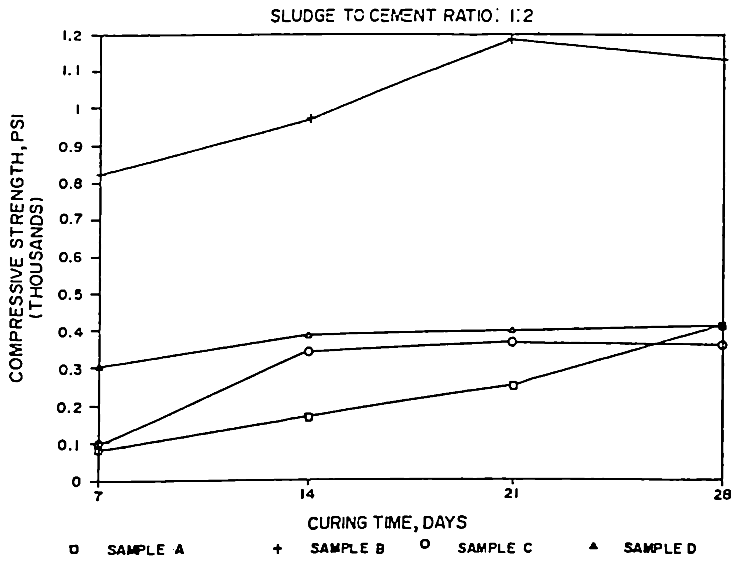

Figure 1. Compressive Strength

Permeability

Permeability is a property of a solid material to allow liquids to flow through it. A material with a high permeability allows liquids to pass through it at a rapid rate.

Permeability of a material is expressed as permeability coefficient (K) with units of cm/sec. The smaller the value of K the less permeable the material. It is usually measured using the Falling Head Permeameter or the Constant Head Permeameter. Another method is the test for solid porous substances conducted for ceramic research.

In the case of fixated sludge, if the permeability is high, more water will be permitted to pass through the mass, with corresponding increase in leaching of toxic materials.

A typical concrete has a permeability of 10^{-6} while a typical fixated sludge has a K of 10^{-7} cm/sec (Barnes, et al., 1981).

The time it will take for the water to permeate through a layer of material can be calculated from the formula:

$$t = 2.3 (L/K) \log (h_o/h_1)$$

where

K = permeability coefficient, cm/sec
L = thickness of the material, cm
h_o = the initial depth of the water
h_1 = the final depth of the water

Supposing, a 100 cm thick fixated sludge is covered by water 10 cm deep, which slowly permeates through until the final depth of the water is 1 cm if its K is 10^{-7} cm/sec, then the time for the water to permeate through to reach 1 cm is:

$$t = [\,2.3\,(100/10^{-7}) \log (10/1)\,]\ \text{sec}$$

$$= 73\ \text{years}$$

Toxicity Characteristic Leaching Procedure

The results of the leaching test performed on the fixated sludges are presented in Tables 8 to 11. These results are also depicted graphically in Figures 2 to 5.

Table 8 shows the leachate analysis of sample A. For the leachate to pass standards, the sludge has to be mixed with cement with a sludge to cement ratio of at least 1:2. From Table 9, the heavy metal contaminants in sample B were successfully immobilized using a fivefold cement component. In the case of sample C, immobilization to within standards started with a 1:3 sludge to cement ratio. In contrast, this formulation is insufficient to successfully immobilize the Chromium in Sample D which requires a higher formulation. This is due to its relatively higher chromium concentration compared to Samples A and C.

The immobilization potential of the alternative binder, i.e., use of rice husk ash as 50% cement substitute was also evaluated using samples A and C. It is noted in Tables 12 and 13 that rice husk ash if used in combination with portland cement can be a better binder for the target contaminants from the technical as well as economic standpoint. This can be attributed to the higher silica content of the rice husk ash binder and its greater surface area.

Instrumental Assessment

The results of the examination of the stabilized sludge using scanning electron microscopy (SEM) showed the formation of needle-like structures known as ettringites resulting from the hydration of cement. The micrograph structures are shown in Figures 6 to 9. For purposes of comparison, photos of the untreated samples were also taken. Figures 6 & 8 show the micrograph structures of raw samples A and B while Figures 7 & 9 show their structures after treatment.

The change in structure is observed from a cloud-like to needle-like formation. The needle-like structures indicate that the metals are entrapped within the ettringite structures though not necessarily chemically bound within the ettringite matrix. This could be the actual phenomenon for the immobilization process.

The XRD analysis confirms the findings in the SEM analysis. The upper chart in Figure 10 shows the XRD analysis of sample A, raw versus the treated sample (lower chart) with a sludge to cement ratio of 1:2. This shows that the ettringite, calcium aluminate sulfate silicate carbonate hydroxide hydrate ($Ca_6Al_2(SO_4.SiO_4.CO_3)_3(OH)_{12}\ .26H_2O$) was formed during the

Table 8: Leachate Analysis of Treated Sample
Binder: Pure Portland Cement

Element	Standard (ppm)	Metal concentration in leachate, ppm					
		Formulations (Sludge : Binder)					
		1:2	Remarks	1:3	Remarks	1:4	Remarks
Ag	5.0	0.060	P	0.050	P	0.050	P
As	5.0	0.002	P	0.009	P	<0.001	P
Cd	1.0	< 0.01	P	< 0.01	P	<0.01	P
Cr	5.0	0.012	P	0.11	P	0.017	P
Hg	0.2	0.058	P	0.0595	P	0.0275	P
Pb	5.0	<0.2	P	<0.2	P	<0.2	P

Table 9: Leachate Analysis of Treated Sample B
Binder: Pure Portland Cement

Element	Standard* (ppm)	Metal concentration in leachate, ppm					
		Formulations (Sludge : Binder)					
		1:1	Remarks	1:3	Remarks	1:5	Remarks
Ag	5.0	0.450	P	0.060	P	0.030	P
As	5.0	0.015	P	0.025	P	0.046	P
Cd	1.0	<0.01	P	<0.01	P	<0.01	P
Cr	5.0	0.094	P	0.056	P	0.015	P
Hg	0.2	1.485	F	0.315	F	0.047	P
Pb	5.0	<0.2	P	<0.2	P	<0.2	P

Legend: P - Passed F - Failed

* Standard is based on the 1989 USEPA Code of Federal Regulations, Title 40 : Protection of the Environment Sec. 261.24

Table 10: Leachate Analysis of Treated Sample C
Binder: Pure Portland Cement

Element	Standard (ppm)	Metal concentration in leachate, ppm					
		Formulations (Sludge : Binder)					
		1:2	Remarks	1:3	Remarks	1:4	Remarks
Ag	5.0	0.050	P	0.120	P	0.190	P
As	5.0	0.008	P	0.003	P	0.001	P
Cd	1.0	0.019	P	0.020	P	0.022	P
Cr	5.0	6.840	F	4.720	P	3.950	P
Hg	0.2	0.001	P	0.001	P	0.001	P
Pb	5.0	0.178	P	0.130	P	0.149	P

Table 11: Leachate Analysis of Treated Sample D
Binder: Pure Portland Cement

Element	Standard* (ppm)	Metal concentration in leachate, ppm					
		Formulations (Sludge : Binder)					
		1:2	Remarks	1:3	Remarks	1:4	Remarks
Ag	5.0	0.610	P	0.540	P	0.510	P
As	5.0	0.010	P	0.013	P	0.027	P
Cd	1.0	0.020	P	0.029	P	0.028	P
Cr	5.0	10.060	F	7.280	F	9.270	F
Hg	0.2	0.060	P	0.062	P	0.064	P
Pb	5.0	0.120	P	0.061	P	0.056	P

Legend: P - Passed F - Failed

* Standard is based on the 1989 USEPA Code of Federal Regulations, Title 40 : Protection of the Environment Sec. 261.24

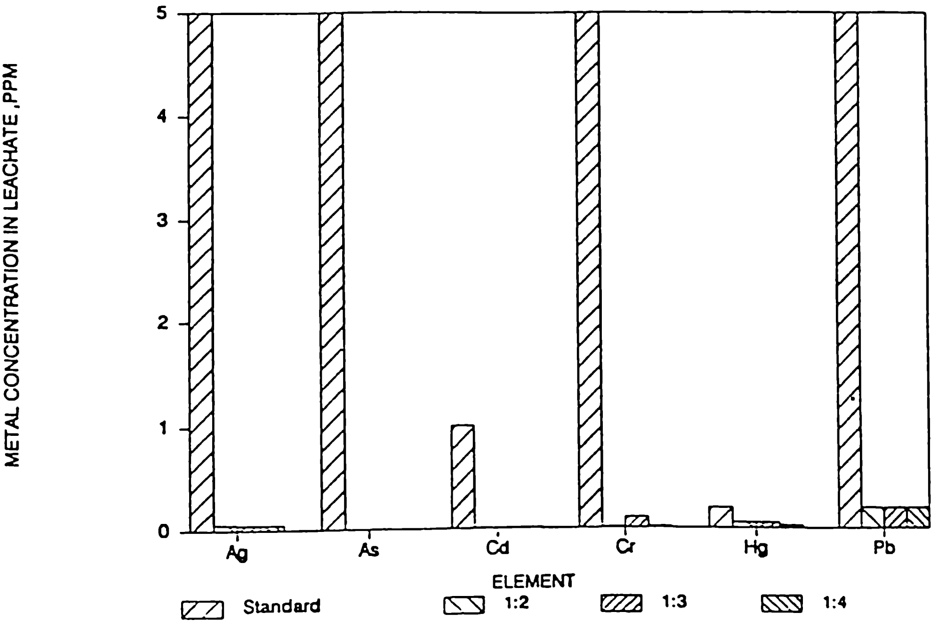

Figure 2. Leachate Analysis Sample A
Binder: Portland Cement

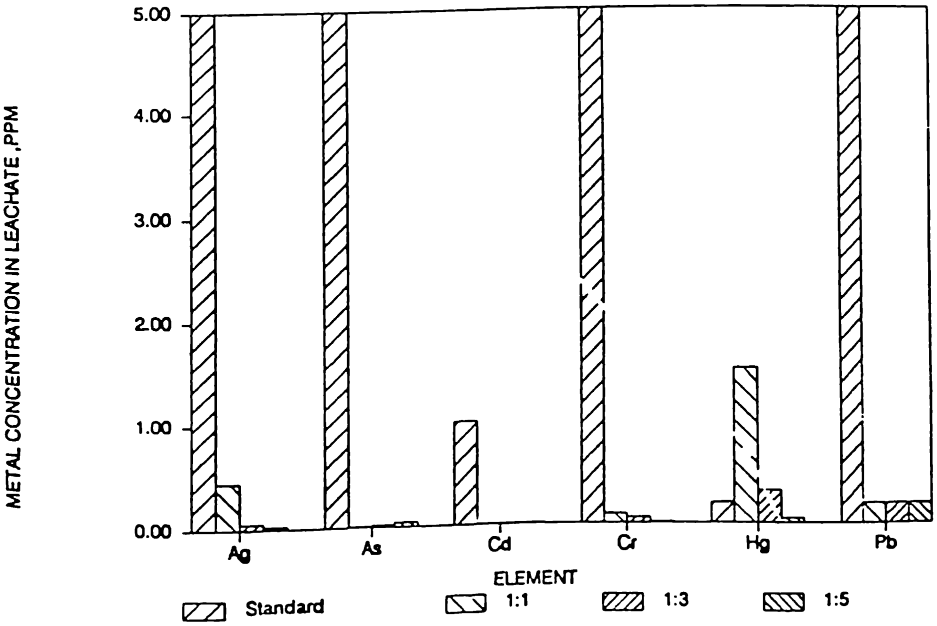

Figure 3. Leachate Analysis Sample B
Binder: Portland Cement

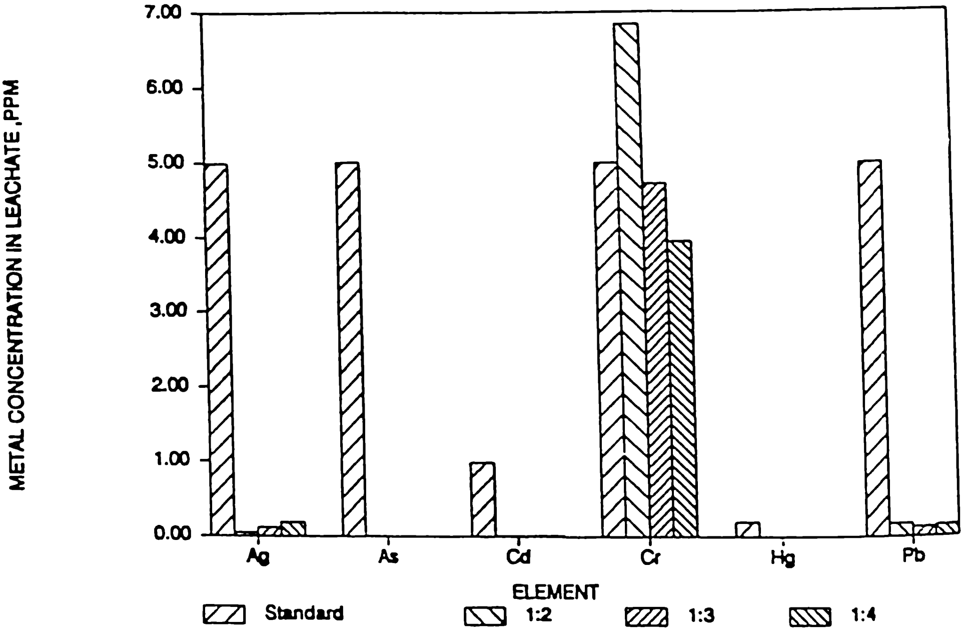

Figure 4: Leachate Analysis Sample C
Binder: Portland Cement

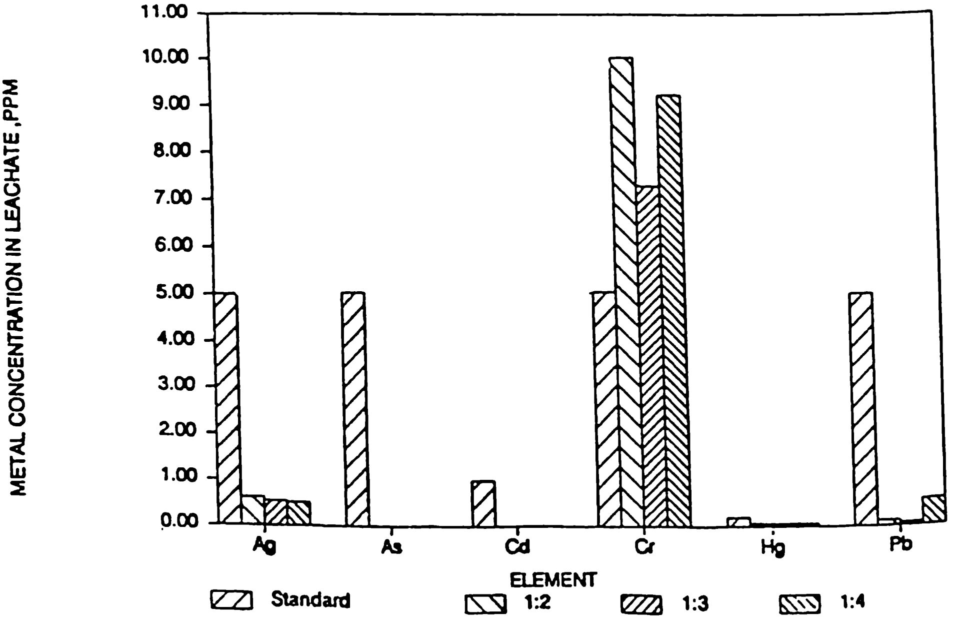

Figure 5. Leachate Analysis Sample D
Binder: Portland Cement

Table 12: Comparison of Various Immobilization Potentials for Sample A

Element	Standard* (ppm)	Metal concentration in leachate, ppm					
		1:2		1:4		1:5	
		PC	PR	PC	PR	PC	PR
Ag	5.0	0.060	0.020	0.050	<0.02	<0.02	<0.02
As	5.0	0.002	0.008	0.001	0.008	<0.001	0.004
Cd	1.0	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	5.0	0.120	0.055	0.017	0.018	0.016	0.011
Hg	0.2	0.058	0.003	0.028	0.037	0.029	0.021
Pb	5.0	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table 13: Comparison of Various Immobilization Potentials for Sample C

Element	Standard* (ppm)	Metal concentration in leachate, ppm					
		1:2		1:3		1:4	
		PC	PR	PC	PR	PC	PR
Ag	5.0	0.050	0.000	0.120	0.030	0.190	0.060
As	5.0	0.008	0.082	0.003	0.020	0.001	0.028
Cd	1.0	0.019	0.006	0.020	0.010	0.022	0.009
Cr	5.0	6.840	4.330	4.720	2.620	3.950	2.210
Hg	0.2	0.001	0.002	0.001	0.006	0.001	0.006
Pb	5.0	0.178	0.144	0.130	0.070	0.149	0.138

Legend: PC -Binder is pure Portland Cement
PR -Binder is 50% Portland Cement & 50% RHA

* - Standard is based on the 1989 USEPA Code of Federal Regulations, Title 40 : Protection of the Environment Sec. 261.24

Figure 6. Microstructure of Raw Sample A
Magnification: 25 KV x 3000

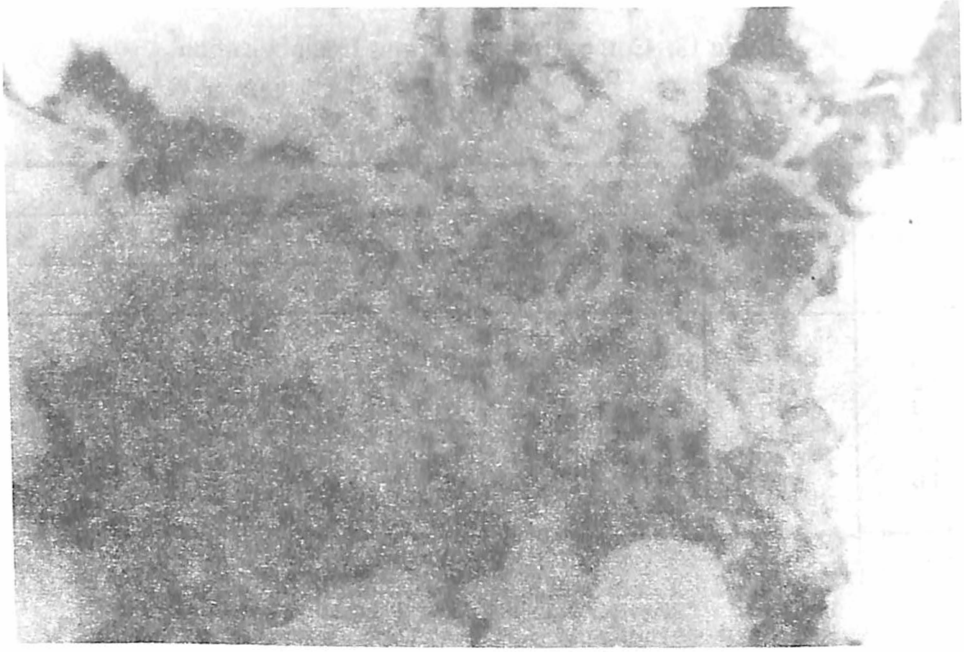

Figure 7. Microstructure of Treated Sample A
Binder: Portland Cement
Magnification: 25 KV x 6000

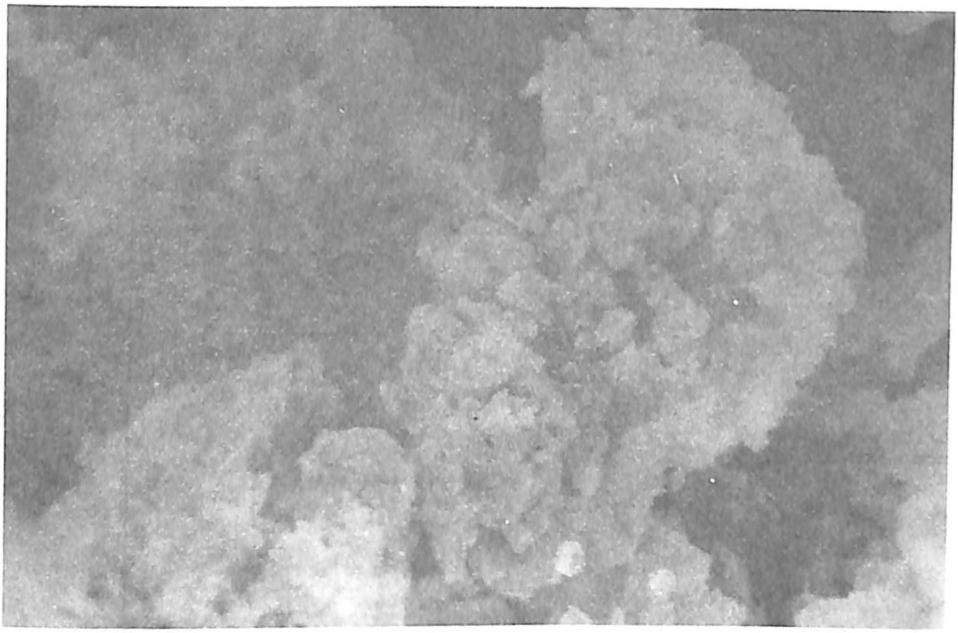

Figure 8. Microstructure of Raw Sample B
Magnification: 25 KV x 3000

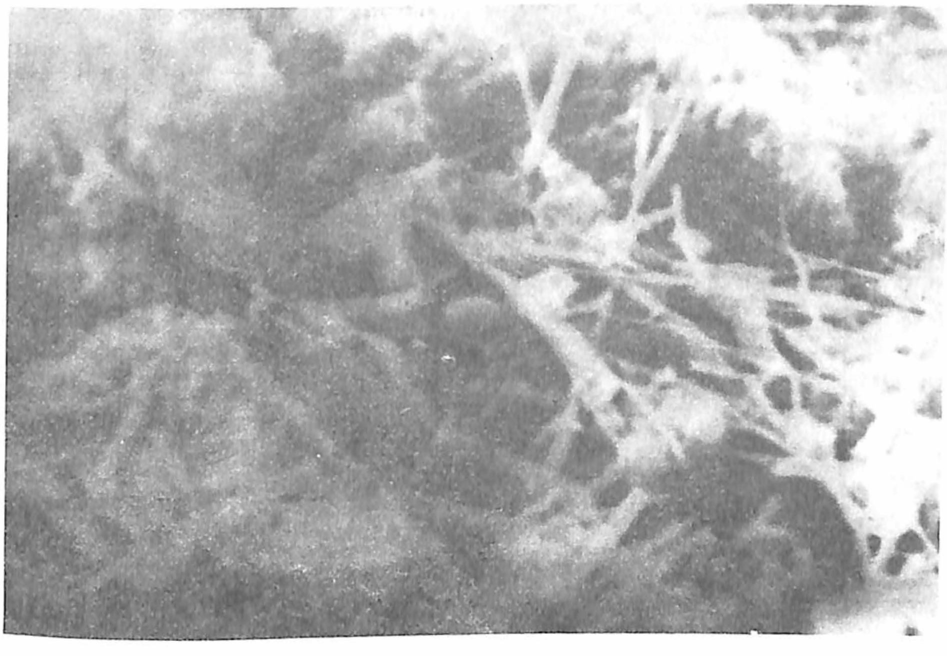

Figure 9. Microstructure of Treated Sample B
Binder: Portland Cement
Magnification: 15 KV x 10,000

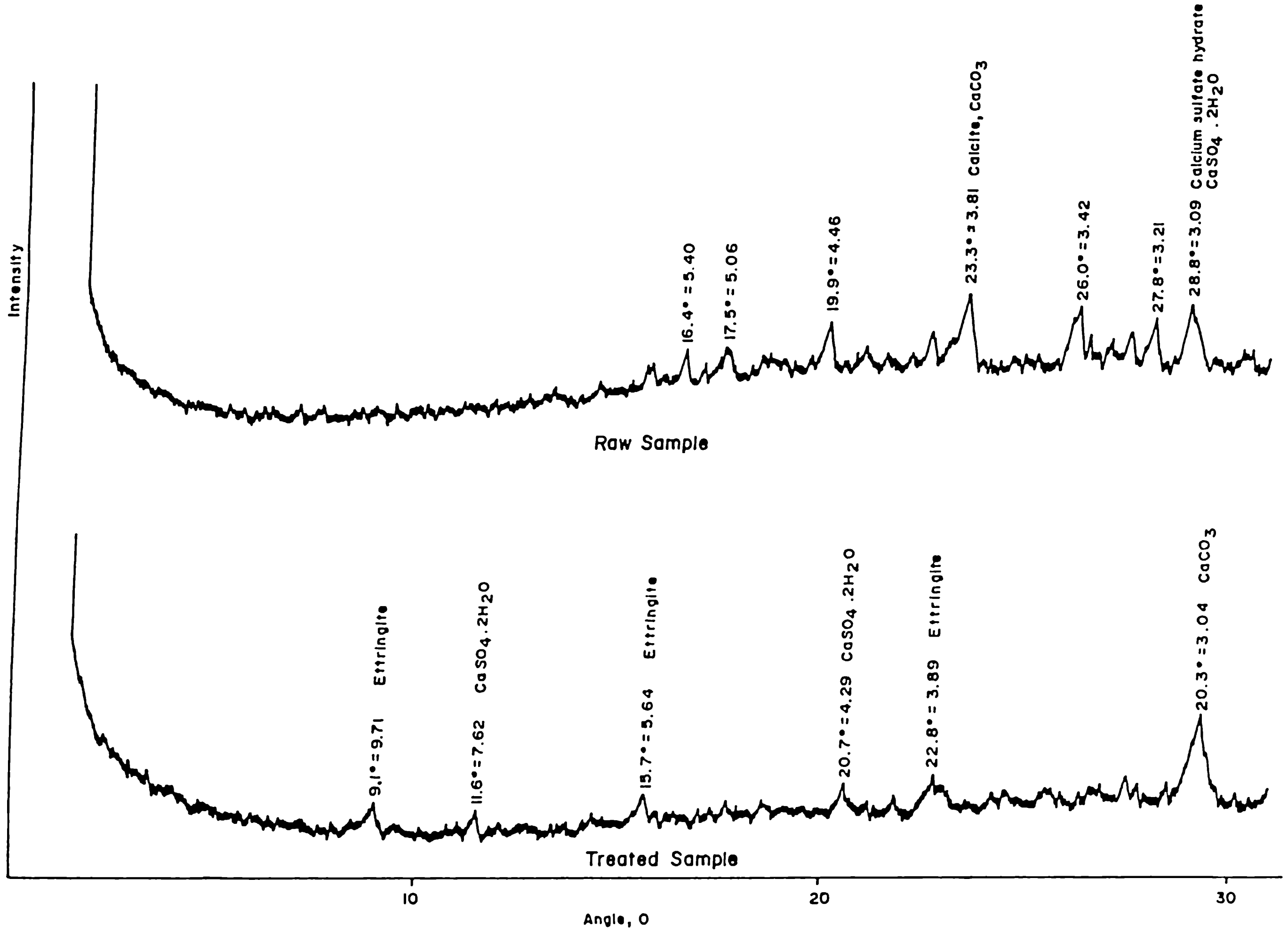

Figure 10. XRD Chart of Sample A

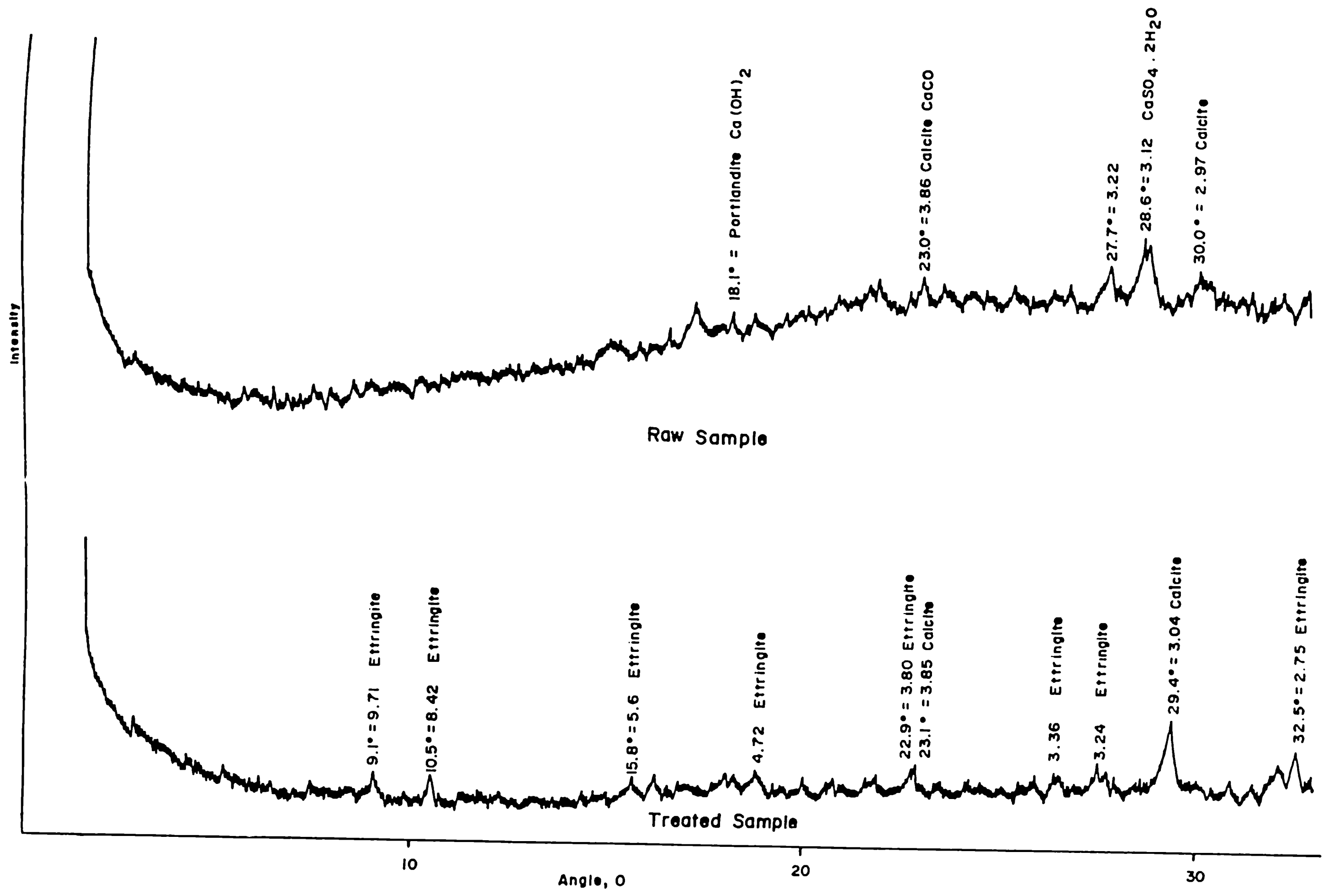

Figure 11. XRD Chart of Sample B

hydration process of cement. Calcite ($CaCO_3$) and calcium sulfate hydrate ($CaSO_4.2H_2O$) were found in both treated and untreated samples.

The XRD analysis of sample B in Figure 11 is almost the same with sample A except that there was the presence of portlandite, $Ca(OH)_2$, in the untreated sample. This is due to the use of lime in the corrosion control system in the cooling towers. The XRD chart of raw sample B showed the presence of calcium sulfate hydrate, calcite and portlandite in the XRD analysis. Calcium hydroxide was the most dominant among them as shown by the peak of the strip chart. The higher the intensity, the greater is the amount of the compound present in the sample being analyzed.

The compounds that were defined with XRD analysis, however, were only those minerals formed in the hydration of cement, i.e., ettringite and calcium sulfate hydrate. The absence of metals attached to the ettringite means that the binding was physical in nature. The metals were entrapped within the ettringite matrix and no chemical reaction took place. Moreover, in order for the metals to bind with the cement hydration products, they must be in ionic form to combine easily. The amorphous structure of the stabilized sludge also contributed to the low intensities obtained.

A material with a higher permeability coefficient will allow water to pass through it in less time than a material with a lower permeability coefficient.

Treatment Procedures Under Field Conditions

A suggested procedure for solidification on a wider scale is presented below:

1. Dry the slurry/sludge to approximate a wet or moist state. Do not decant or discard the liquid phase. Dewatering should be carried out through solar evaporation only. Provisions for wind protection should be made in the drying area preferably under a shed.
2. Grind the dried sludge to pass through a 9.5 mm standard sieve.
3. Mix cement, sludge, and water in the correct amounts. Mixing should be sufficient to ensure uniform consistency. Transfer to molds (30.5 cm x 21.5 cm x 21.5 cm) for setting.
4. Remove the solid product from the molds and cure for 28 days by covering with wet sacks at room temperature. Using a water hose, spray the sack cover with water daily ensuring that the sacks are kept moist at all times.
5. After 28 days, perform the leaching test on the fixated sludge and compare the results to the leaching standards.
6. If the leachate data passes the standards, haul the fixated sludge to final disposal site.
7. If it fails the leaching test, crush and pulverize the sample to pass through a 9.5 mm standard sieve and resolidify until it passes the test.

8. Since it may be necessary to retrieve the fixated waste in the future, it should be properly labeled (source, solidification date, formulation used) prior to disposal. It is possible that a new technology to detoxify the waste may become available or the waste may become a resource, hence, this precaution on labeling.

CONCLUSION

The results of the study clearly show that the mobility of heavy metals can be effectively reduced by the S/S process using cement and RHA as silicate sources. Although the immobilization mechanism was mainly physical and not chemical, the substantial reduction in mobility qualifies the S/S process as a feasible treatment technology for the immobilization of hazardous wastes particularly heavy metal wastes. The specific conclusions drawn are the following:

1. Leaching of heavy metals can be minimized or retarded to meet standards by blending the waste using a minimum of twice the weight of sludge as in the case of sample A. Sample B and C require four and three times the weight of the sludge respectively for effective immobilization. For Sample D, owing to the irregular behavior of chromium leachate, no definite formulation can be specified. However, effective immobilization of the rest of the metals was achieved at a sludge to cement ratio of 1:2. These findings show that immobilization is more effective when the silica is available at higher amounts as in higher formulations.

2. In the investigation of the bonding mechanism of cement on heavy metals, the results of the leachate analysis supplements the findings of the instrumental investigation. Crystal capture or physical entrapment of the metal contaminant in the ettringite/silicate matrix is the main mechanism responsible for the immobilization process: Chemical bonding is thus ruled out. The heavy metals leached out into the extraction fluid came from the destruction of the entrapping silicate structures which is verified by the XRD analysis.

REFERENCES

1. Barnes, D.; D. J. Cook and R. Soothill (1981). Report on the Immobilization Techniques for Hazardous Wastes. Unisearch Ltd. Victoria: Environmental Protection Authority of Victoria.

2. Bensted, J., and S. Varna (1971). Studies of Ettringite and Its Derivatives. Pollution Engineering Journal 2: 73-76.

3 Goldstein, J. (1981). Scanning Electron Microscopy and X-ray Analysis: Plenum Press.

4. Henry, N.F.M.; H. Lipson and W. Wooster (1982). The Interpretation of X-ray Diffraction Photographs. New York: Van Nostrand.

5. Kujala, K. (1986). Stabilization of Hazardous Wastes and Muds. Proceedings of the International Symposium on Environmental Geotechnology. (Allentown, Pennsylvania). p. 540.

6. McFarland, R. (1988). Report on a Study on the Immobilization of Hazardous Waste. Prepared for the Advisory Committee on Chemicals in the Environment, Australian Environment Council.

7. Mujib, F. (1987). An Alternative Mix Design Using Rice Husk Ash. Masteral Thesis. Asian Institute of Technology.

8. Sell, N. J. (1988). Solidifiers for Hazardous Waste Disposal. Pollution Engineering Journal. August. p. 147.

9. U.S. (1989). Office of the Federal Register, National Archives and Records Administration. Code of Federal Regulations, 1989. Title 40, Protection of Environment. Washington, D.C.: Government Printing Office.