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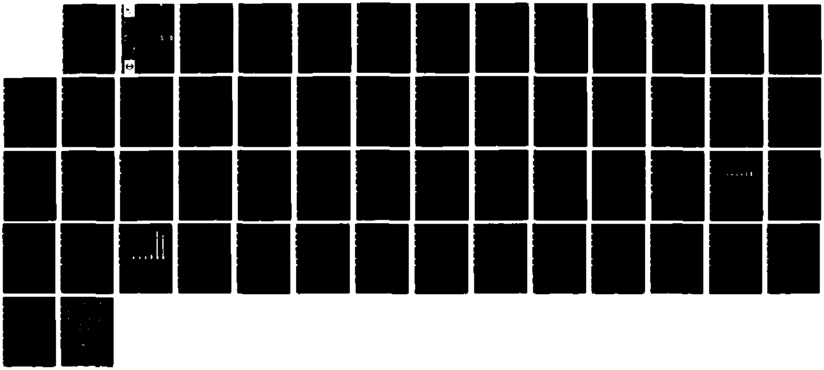

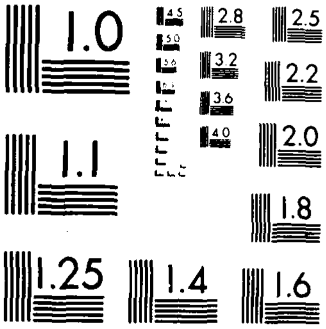
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US Army Corps
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TECHNICAL REPORT EL-88-5

INVESTIGATION AND EVALUATION OF THE PERFORMANCE OF SOLIDIFIED CELLULOSE AND STARCH XANTHATE HEAVY METAL SLUDGES

by

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Environmental Laboratory

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

This report presents the results of a laboratory investigation that evaluated the potential for metals to leach from cellulose and starch xanthate sludges and compares the results to the metal leaching characteristics of hydroxide precipitated sludge. Sludges were prepared using cellulose xanthate, starch xanthate, or calcium hydroxide to treat a synthetic waste solution containing four heavy metals (Cd, Cr, Ni, Hg) in a laboratory-scale study. Sludges were solidified with portland type I cement. Solidified and unsolidified sludges resulting from starch xanthate, cellulose xanthate, and hydroxide precipitation processes were tested for their physical and chemical characteristics. Physical tests performed on the solidified and unsolidified xanthate and hydroxide sludges included unconfined compressive strength and cone index tests. Chemical leaching characteristics of the unsolidified and solidified sludges were determined using the US Environmental Protection Agency's extraction procedure test and a serial graded batch extraction procedure. Physical test results from

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this study indicated that when compared to the unsolidified sludges, solidified sludges exhibited improved handling properties. The chemical leaching test results indicated that: (a) cellulose and starch xanthate sludges resulted in materials with a greater capacity to reduce the leaching of metals than the hydroxide sludges, (b) Hg was the only contaminant observed in the leachate of the solidified hydroxide sludge at significant concentrations, and (c) solidification of the sludges appeared to reduce the leaching of Cd, Ni, and Hg.

PREFACE

This report presents the results of a laboratory investigation that compared the heavy metal leachability of solidified and unsolidified sludges produced using cellulose and starch xanthate precipitation methods. The development of such innovative waste treatment and disposal methods is needed to allow Army facilities to meet current and future environmental regulations.

The study was conducted during the period January 1986 through September 1987. This report was written by Mr. R. Mark Bricka, Water Supply and Waste Treatment Group (WSWTG), Environmental Engineering Division (EED), Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES). The research was sponsored by the Department of Army In-House Laboratory Independent Research (ILIR) program under ILIR Project No. 4A161101A91D, Task Area 02, Work Unit 174. Chemical analyses were performed by the Analytical Laboratory Group, EL. Special assistance was given by Mr. M. John Cullinane, Jr. Direct supervision was provided by Mr. Norman R. Francingues, Jr., Chief, WSWTG. General supervision was provided by Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Chief, EL. Ms. Jessica S. Ruff of the WES Information Technology Laboratory edited the report.

The assistance of the International Paper Company located in Natchez, Miss., and Stout's Supply located in Ainsworth, Iowa, is gratefully acknowledged. These institutions supplied the cellulose and starch xanthate material used in this study free of charge.

COL Dwayne G. Lee, CE, was Commander and Director of WES. Dr. Robert W. Whalin was Technical Director.

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

CONVERSION FACTORS, NON-SI TO SI (METRIC) UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
gallons (US liquid)	3.785412	cubic decimetres
inches	2.54	centimetres
pounds (force) per square inch	6.894757	kilopascals
pounds (mass)	0.4535924	kilograms

INVESTIGATION AND EVALUATION OF THE PERFORMANCE OF SOLIDIFIED CELLULOSE AND STARCH XANTHATE HEAVY METAL SLUDGES

PART I: INTRODUCTION

Background

1. Metal plating is a process used to enhance the basic properties of a material by improving such characteristics as corrosion resistance, durability, electrical conductivity, and aesthetic appearance. These improvements provide low-cost materials that fill specific engineering requirements. For these reasons, there is a large demand for plated materials.

2. To support the demand for plated materials, over 13,000 plating facilities are operating in the United States (US Environmental Protection Agency (USEPA) 1980). The sizes of these plating operations vary from large-capacity processors that operate on a continual basis to small-capacity processors that plate materials using batch plating operations.

3. The military also has an extensive network of metal plating facilities. Plated metals are used in all types of military hardware, ranging from small items such as shell casings and electronic parts to large items such as gun barrels and engine parts. The continued operation of these metal plating facilities is vital in supporting the Nation's defense effort.

Plating operations

4. Typical plating operations usually take place in three steps: stripping, cleaning, and plating. A flow diagram of a typical metal plating process is shown in Figure 1.

5. The stripping process involves the removal of undesirable metal, metallic oxide, or other coatings that may be on the surface of the work piece. Stripping baths typically are made up of solutions of sulfuric, nitric, hydrochloric, and hydrofluoric acids.

6. The cleaning process is designed to remove soil, grease, and oil from the work piece. In order to plate a material, it must be free of unwanted surface deposits. Cleaning operations usually involve a series of steps that include: (a) precleaning with a solvent, (b) intermediate cleaning with alkaline cleaners, (c) electrocleaning to remove the last adhering traces of undesirable surface deposits, and (d) acid treatment to remove light oxide

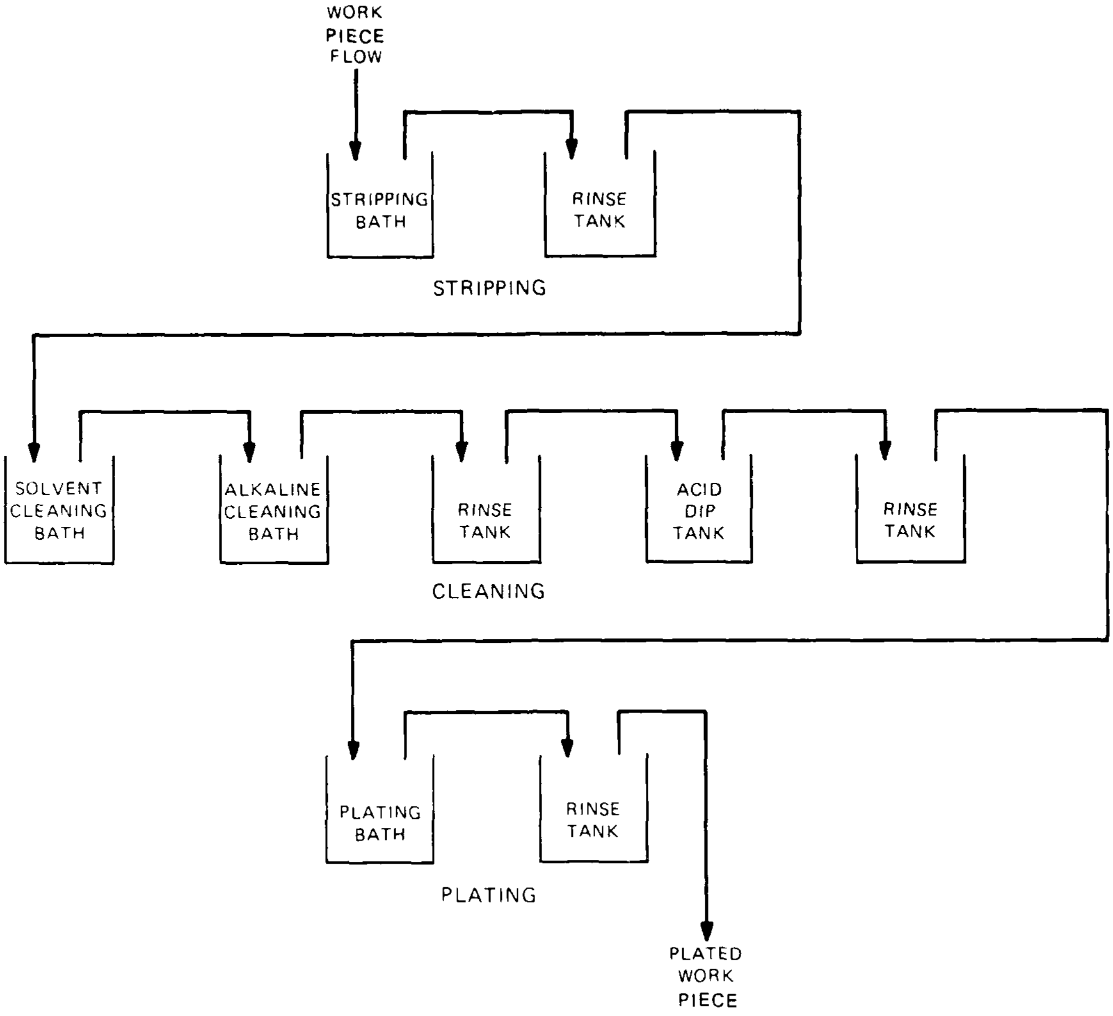

Figure 1. Typical metal plating process flow diagram

films. In general, the four types of cleaners used include organic solvents, acid solutions, alkaline electrocleaners, and alkaline cleaners (Lowenheim 1963).

7. The plating process is the step in which the actual deposition of the plating metal on the base metal occurs. The work piece is immersed in a solution containing dissolved metals, referred to as the plating bath. A current is passed through the work piece and solution. The current causes the metal in the plating bath to be deposited on the work piece.

Wastes produced by plating operations

8. Liquid wastes. Metals that are commonly plated include copper, nickel, silver, chromium, zinc, cadmium, lead, tin, gold, and iron (Sell 1981). Many of these metals are considered to be quite toxic. Plating

processes have several points at which waste generation can occur, as illustrated in Figure 2.

9. The three main sources of toxic metal wastes generated by plating operations are: (a) rinse water discharges, (b) spills, leaks, and drips of process solution into floor drains, and (c) periodic dumping of contaminated process solutions. Typically, these waste streams are combined, thus diluting

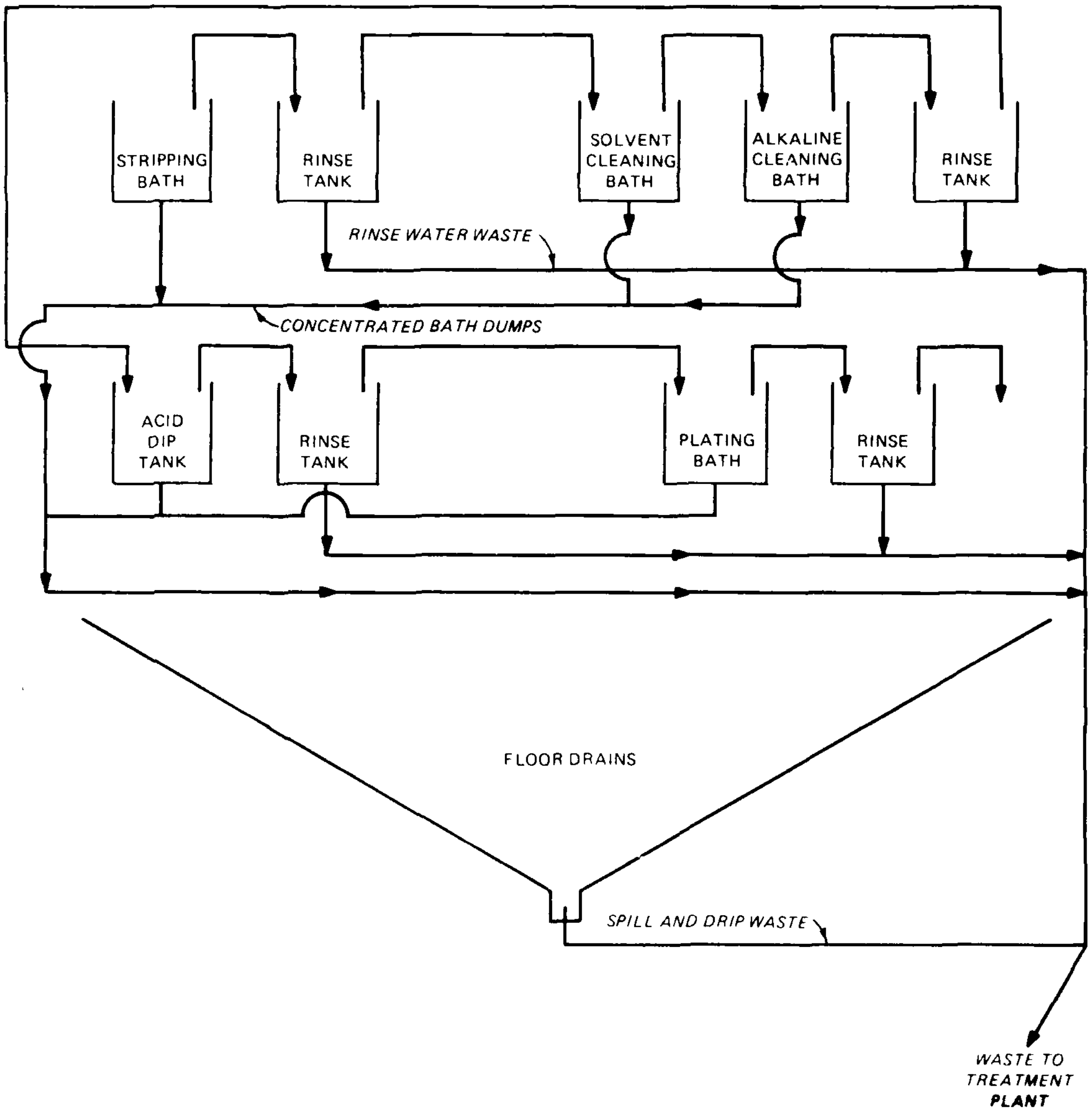

Figure 2. Plating operations waste flow diagram

the more concentrated process streams. Contaminant concentrations representative of metal plating wastewaters are given in Table 1.

Table 1

Effluent Characteristics of 22 Electroplating Shops (USEPA 1980)

Contaminant	Effluent Concentration, mg/ℓ	
	Maximum	Average
Cyanide, total	95.9	14.4
Copper	47.2	4.7
Nickel	52.2	5.7
Chromium, total	178.0	20.2
Zinc	101.4	14.3
Lead	3.0	0.4
Cadmium	24.3	4.3

10. Solid wastes. Regulations under the Clean Water Act (Government Institutes 1984) limit the heavy metal concentrations that can be discharged to surface waters. Thus, it is usually necessary for the operators of metal plating facilities to treat all wastewaters prior to discharge. Treatment of metal plating wastewaters usually results in the generation of additional waste sludges. Typically, the removal of heavy metals from wastewater results in the production of large amounts of sludges containing high concentrations of heavy metals. These sludges are listed by the USEPA under the Resource Conservation and Recovery Act (RCRA) as a hazardous waste, and therefore must be stored, treated, and/or disposed in an approved manner.

11. The disposal of metal-contaminated sludges generated by wastewater treatment poses one of the largest waste disposal problems facing the Department of the Army (DA). At least 23 Army Materiel Command installations currently perform metal plating operations that generate wastewaters contaminated with heavy metals. Treatment of these wastewaters produces over 27 million gallons* of metal-contaminated sludges per year, resulting in DA disposal costs of over $20 million annually (Bradbury and Thompson 1986).

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* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 4.

Wastewater treatment technologies

12. *Hydroxide precipitation.* Approximately 75 percent of electroplating facilities use precipitation methods to treat their wastewaters (Ku and Peters 1987). Conventional hydroxide precipitation of heavy metals is by far the most widely used treatment technology to remove heavy metals (Dean, Bosqui, and Laouette 1972; Patterson, Allen, and Scala 1977). Metals are removed by adding lime or sodium hydroxide to adjust the pH of the wastewater to the point at which metals exhibit minimum solubility. The metals precipitate as metal hydroxides and can be removed from the wastewater by flocculation and sedimentation. The typical hydroxide reaction is shown in Equation 1.

$$X(OH)_2 + M^{++} \longrightarrow M(OH)_2 \downarrow + X^{++} \quad \text{(hydroxide reaction)} \qquad (1)$$

where

$X(OH)_2$ = hydroxide (typically calcium or sodium)
M^{++} = metal ion
$M(OH)_2$ = metal hydroxide
X^{++} = cation

13. Some common limitations of the hydroxide process include the following:

a. Hydroxide precipitated metals tend to resolubilize if the pH is changed.

b. The removal of metals, by hydroxide precipitation of mixed metal wastes solutions, may not be effective because the minimum solubilities for various metal hydroxides occur at different pH values (Figure 3).

c. The presence of complexing ions has an adverse effect on metal removal.

d. Chromium VI is not removed by this technique and requires pretreatment prior to the precipitation step.

e. Cyanide interferes with heavy metal removal by hydroxide precipitation.

f. Hydroxide precipitation produces large volumes of sludge.

g. The amorphous particle structure of hydroxide sludges makes these sludges difficult to dewater and increases the sludge volume and disposal costs (Cushnie 1984, USEPA 1982a).

14. *Other heavy metal precipitation methods.* Several precipitation methods offer alternatives to conventional hydroxide precipitation treatment

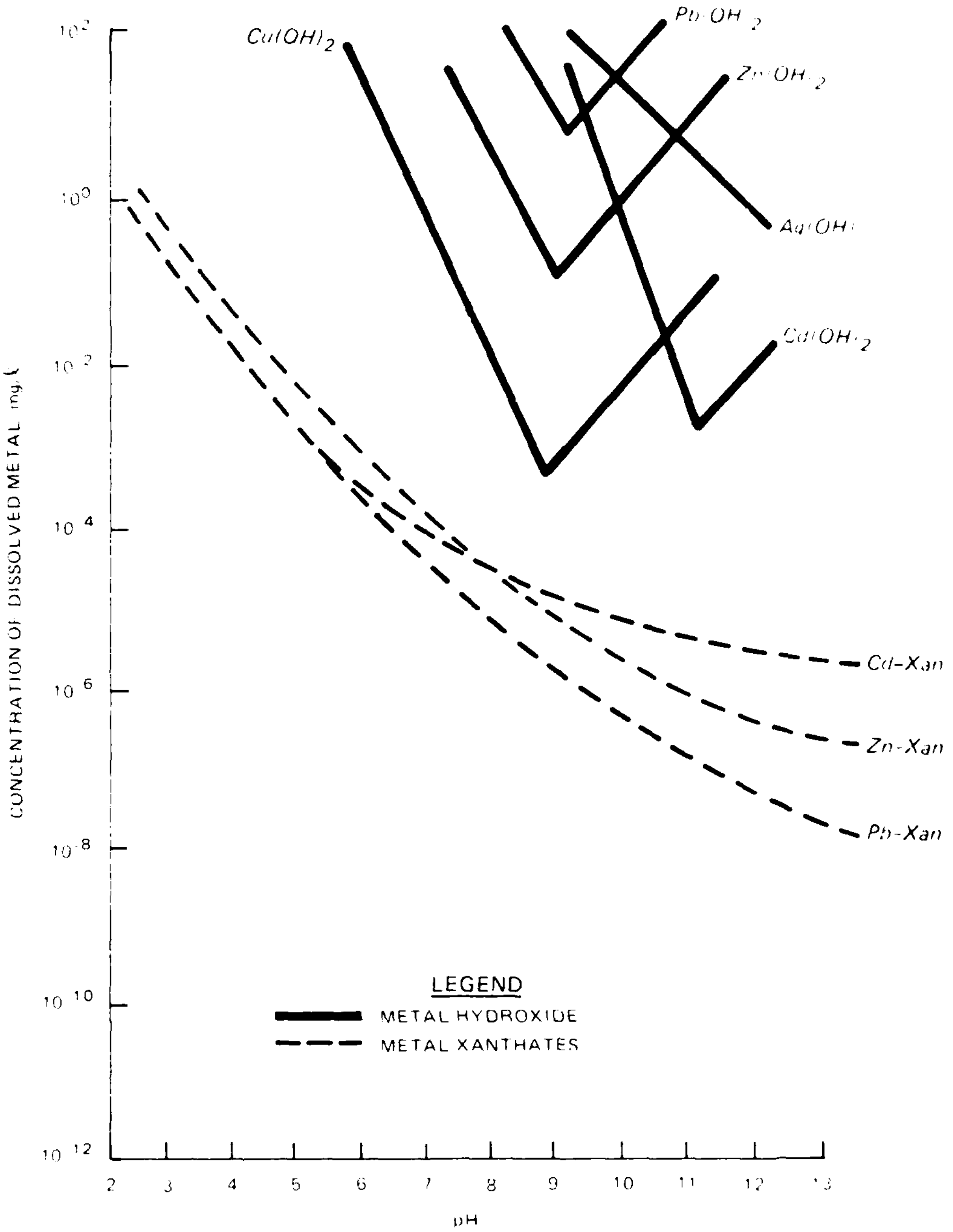

Figure 3. pH versus metal concentrations for xanthates and hydroxide compounds

methods. These include sulfide, sodium borohydride, and xanthate precipitation techniques (Cushnie 1985).

15. Extensive work has been performed on sulfide precipitation (USEPA 1980). Results of this work indicate that sulfide precipitation is an effective alternative to the more conventional hydroxide precipitation methods. The high reactivity of sulfides (S^{--}, HS^-) with heavy metals and the insolubility of heavy metal sulfide sludges are attractive features of this process. Unfortunately, some sulfide precipitation processes have the potential to produce nauseous and toxic hydrogen sulfide gas. Due to safety concerns, sulfide precipitation is not widely used as a wastewater treatment method.

16. Sodium borohydride precipitation is a newly developed wastewater treatment process. This precipitation process offers advantages similar to those of sulfide precipitation. Unfortunately, this process may produce hydrogen, an extremely flammable and explosive gas, as a by-product in the precipitation reaction. This tends to discourage wide application of sodium borohydride technology.

17. Another newly developed precipitation process involves the use of xanthates. Xanthates have been shown to be an effective method of heavy metal removal (Holland 1975; Wing, Doane, and Russell 1975; Wing et al. 1978; Flynn, Carnahan, and Lindstrom 1980). The results of preliminary research indicate that xanthate precipitation offers metal removal efficiencies similar to the sulfide and sodium borohydride precipitation methods. Xanthate precipitation methods also appear to pose less potential for the release of toxic and dangerous gases than the previously discussed precipitation methods.

18. The removal of heavy metals using xanthate precipitation was developed by the US Department of Agriculture (Wing, Doane, and Russell 1975; Wing et al. 1978). Wing et al. (1978) used an insoluble starch xanthate to remove heavy metals from industrial wastewater. Xanthate precipitation, however, is not limited to starch xanthates. An entire family of xanthates, including starch xanthates, cellulose xanthates, and alcohol xanthates, can potentially be used for wastewater treatment (Holland 1975).

19. Xanthates are aliphatic sulfur compounds formed by reacting carbon disulfide with an organic substrate under caustic conditions, as shown in Equation 2.

$$\mathrm{R + SCS \xrightarrow[(NaOH)]{} R\text{-}OCSSNa} \qquad (2)$$

where

R = organic substrate (i.e., starch, cellulose, etc.)
SCS = carbon disulfide
NaOH = sodium hydroxide
R-OCSSNa = xanthate

20. Xanthates remove metals from solution utilizing a simple substitution reaction that is similar to hydroxide precipitation (Wing 1974, Marani et al. 1980). Equations 3 and 4 show typical xanthate reactions.

$$\mathrm{R\text{-}OCSSNa + M^{+} \xrightarrow[NaOH]{} R\text{-}OCSSM\downarrow + Na^{+}} \qquad (3)$$

or

$$\mathrm{2(R\text{-}OCSSNa) + M^{++} \xrightarrow[NaOH]{} R\text{-}OCSS\text{-}M\text{-}SSCO\text{-}R\downarrow + 2Na^{+}} \qquad (4)$$

21. Xanthate precipitation offers several advantages over hydroxide precipitation, including the following:

a. A higher degree of metal removal.
b. Less sensitivity to pH fluctuations (Figure 3).
c. Less sensitivity to the presence of complexing agents.
d. Improved sludge dewatering properties.
e. Capability for the selective removal of metals according to the following hierarchy (Flynn, Carnahan, and Lindstrom 1980):

$$\mathrm{Na \ll Ca - Mg - Mn < Zn < Ni < Cd < Pb - Cu - Hg}$$

Based on the above facts, xanthate precipitation methods appear to be an attractive alternative to hydroxide precipitation.

22. Although xanthate precipitation offers several advantages over hydroxide precipitation, xanthate precipitation also produces a heavy metal-contaminated, residual sludge. Xanthate sludges, like hydroxide sludges, must be handled in accordance with RCRA waste disposal requirements.

23. Sludge treatment and disposal. Shallow land burial is the current accepted disposal method for solid or semisolid heavy metal wastes. Due to

the nature of this disposal technique, the wastes have a high probability of coming in contact with water that provides a media for leaching and transporting contaminants into the surrounding environment.

24. Chemical stabilization/solidification (S/S) using cement or pozzolan-based technologies is the current method of choice for reducing the mobility of heavy metals in liquid or semisolid waste. In this process, the heavy metal contaminants are immobilized by encapsulation in the cemented matrix and by conversion of the metals to a less soluble form. The S/S involves the mixing of the waste with a binder material to enhance the physical properties of the waste and to chemically bind the free liquid. Under the RCRA, all hazardous wastes disposed of in landfills must exhibit properties of a solid by passing the bulk liquid testing procedure, USEPA method 9095 (USEPA 1982b), which is flowcharted in Figure 4.

25. Regulatory requirements. As environmental regulations become more stringent, the allowable concentration of contaminants that can be discharged into streams and lakes is expected to be reduced. Eventually, the limits for the metal concentration that can be discharged may be so low that conventional precipitation methods, hydroxide precipitation, etc., may no longer be effective methods of treatment. Xanthate and other innovative treatment methods may offer the only practical alternatives.

26. In addition to the stricter discharge regulations, the regulations regarding land disposal of hazardous waste are currently undergoing radical changes. In the near future, sludges that leach even small amounts of metals into the environment may be banned from land disposal. Xanthate sludges (solidified or unsolidified) may possess physical/chemical characteristics that make it possible to avoid such restrictions.

Purpose and Scope

27. The purposes of this research were to investigate the heavy metal leachability of sludges produced using cellulose and starch xanthate precipitation methods and to evaluate the effects of a typical S/S technique on the sludges. Physical and chemical properties of solidified and unsolidified xanthate sludges are compared to sludge prepared using typical hydroxide precipitation.

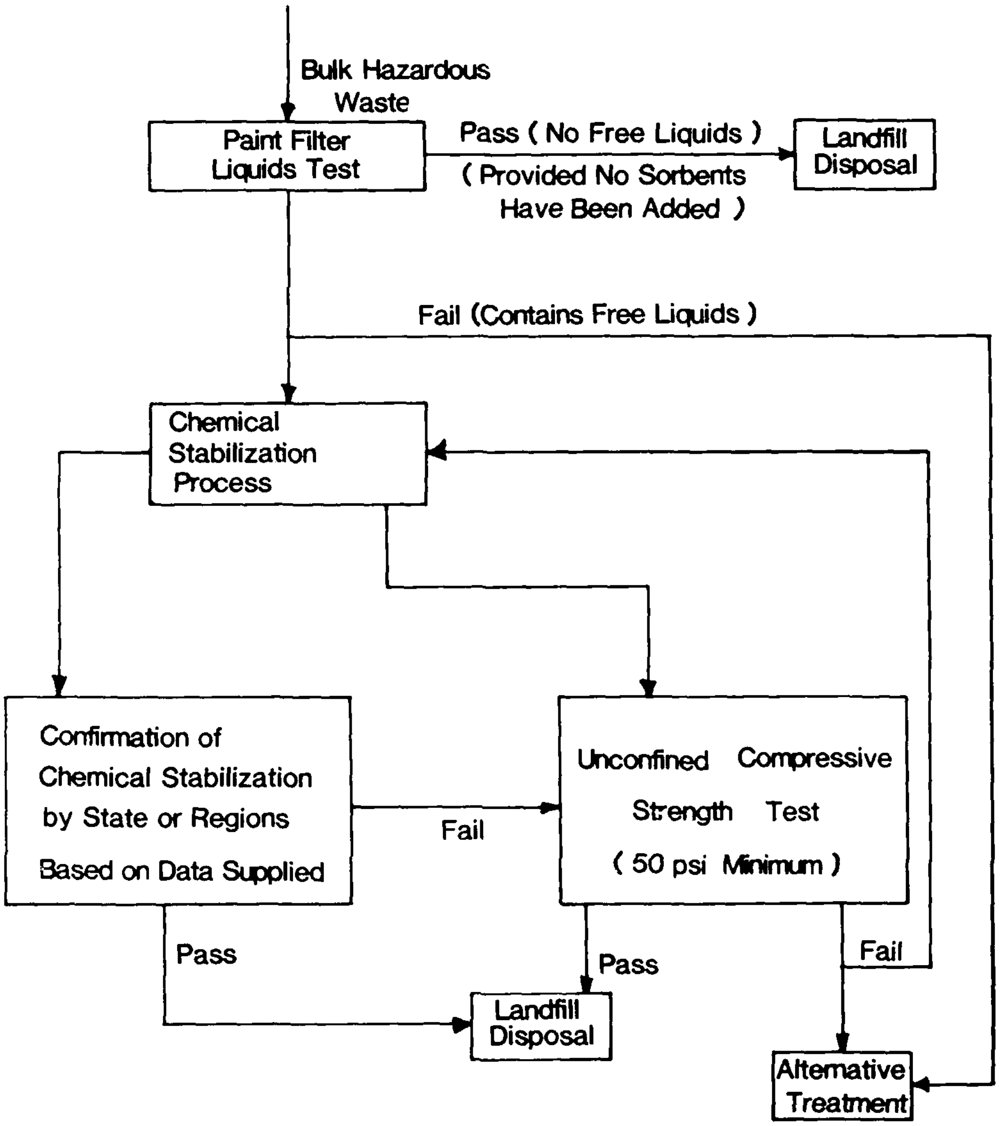

Figure 4. USEPA testing scheme for solidified/stabilized materials (after USEPA 1986)

28. Sludges were prepared using cellulose xanthate, starch xanthate, or calcium hydroxide to treat a synthetic waste solution containing four heavy metals (Cd, Cr, Ni, and Hg). The sludges were solidified with portland type I cement, and the solidified and unsolidified sludges were evaluated using the unconfined compressive strength (UCS) test, the cone index (CI) test, the USEPA extraction procedure (EP) test, and a serial graded batch extraction procedure (SGBEP).

Organization of Report

29. This report is presented in four parts. Plating methodologies and waste treatment techniques were introduced in Part I. In Part II the materials and methods used in this study are described. Sample preparation and the various testing methods used to evaluate the test specimens are also discussed. The data generated by testing the specimens and a discussion of the test results are presented in Part III. Finally, conclusions and recommendations resulting from this study are discussed in Part IV.

PART II: MATERIALS AND METHODS

General Approach to the Investigation

30. This study was conducted in five phases as summarized below.

- a. Phase I. An investigation was conducted to determine the most promising types of xanthate materials to be used in the study.
- b. Phase II. Screening tests were performed to determine the calcium hydroxide and xanthate dosages required to effectively treat a synthetic metal plating waste.
- c. Phase III. Cellulose xanthate, starch xanthate, and calcium hydroxide were used to precipitate four heavy metals (Cd, Cr, Ni, and Hg) from a synthetic metal plating wastewater. Three sludges were produced: (1) a starch xanthate/metal sludge, (2) a cellulose xanthate/metal sludge, and (3) a metal hydroxide sludge.
- d. Phase IV. The cellulose xanthate, starch xanthate, and hydroxide sludges were each divided into two subsamples. One subsample of each was solidified using portland cement. The other subsample was not solidified and served as a control.
- e. Phase V. The physical and contaminant release properties of the solidified and unsolidified sludges were evaluated.

A project flowchart including material processing, sample organization, and sample testing is shown in Figure 5.

Selection of Xanthate Materials

31. As discussed previously, several compounds can provide acceptable substrates for xanthation. Thus, the first step in this study was to narrow the range of xanthate materials selected for use and evaluation.

32. A literature review was conducted to determine if previous studies had been performed using xanthates. This review revealed several laboratory studies that used xanthates as a waste treatment method. The majority of the studies evaluated the effectiveness of starch xanthate in removing heavy metals from wastewaters (Michelsen et al. 1975; Wing, Doane, and Russell 1975; Hanway, Mumford, and Barth 1976; Wing et al. 1978; USEPA 1979; Marani, Macchi, and Coretti 1985). The use of cellulose xanthate and alcohol xanthate as waste treatment methods have also been investigated but to a lesser extent

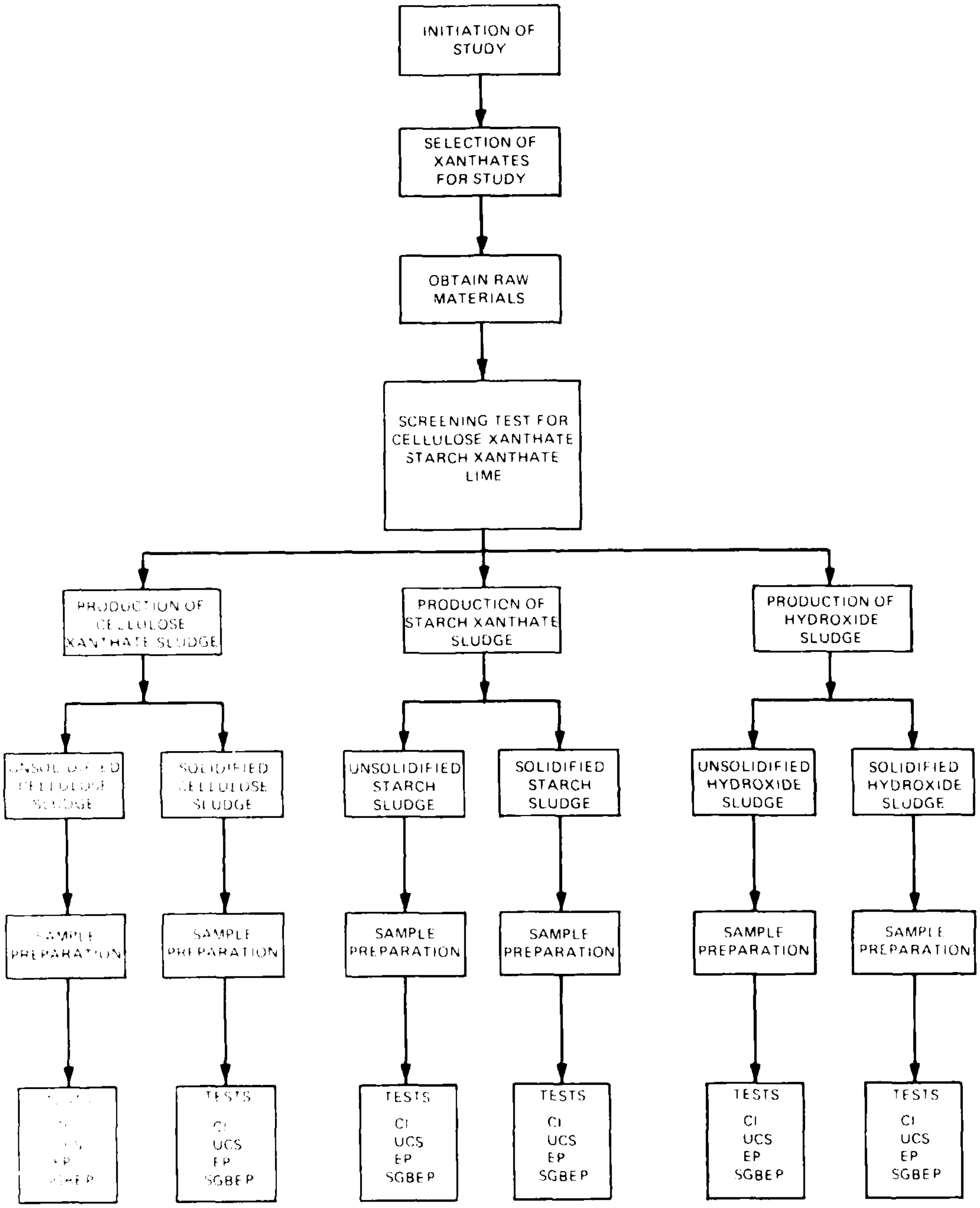

Figure 5. Project flow diagram

(Holland 1975; Hanway, Mumford, and Barth 1976; Flynn, Carnahan, and Lindstrom 1980; Ali, Cooper, and Neufeld 1987).

33. Based on the literature review, starch and cellulose xanthates were selected as the materials for evaluation in this study. The rationale for selecting the materials is summarized below.

a. Cellulose provides a durable substrate and is thought to be less susceptible to biological attack than other substrates.

b. Cellulose xanthate is expected to react with heavy metals to produce an easily settleable and filterable sludge.

c. Since cellulose xanthate is produced as an intermediate in the production of rayon, the rayon industry provides both a base for technical information on cellulose xanthate production and a potential source for cellulose xanthate.

d. Extensive laboratory-scale studies have been performed that demonstrate the effectiveness of starch xanthate to remove heavy metals from wastewaters.

e. Starches are easily cross-linked to produce insoluble starch xanthates.

f. There is a commercial supplier of insoluble starch xanthate to provide a source for this material.

34. The starch xanthate used in this study was produced by reacting a cross-linked starch with carbon disulfide. The starch xanthate material used in this study met the following criteria:

Compound	Percent
Total sulfur	18
Sodium and magnesium	18
Caustic	14
Water	35

35. The cellulose xanthate material was produced by steeping 4- by 5-in. squares of dissolving paper pulp in a solution of 18.5-percent sodium hydroxide. The sheets were soaked for 30 min. After soaking, the excess caustic was drained, and the sheets were dewatered with a hydraulic press. The caustic-soaked sheets were shredded and aged for 24 hr at 20° C. The cellulose xanthate was produced by reacting the caustic-soaked paper pulp, alkali cellulose, with 34-percent carbon disulfide for 3 hr. The temperature was held constant at 22° C during the reaction. An analysis of this material was not performed.

36. The lime used in this study was a technical grade calcium hydroxide. An analysis of the lime indicated that it contained the following:

Compound	Percent
Calcium hydroxide	95.0
Insoluble HCl	0.10
Sulfur compounds (as SO_4)	0.2
Heavy metals (as Pb)	0.003
Iron (as Fe)	0.02
MgO	0.75

Metal Removal Capacity of Xanthates

Xanthate titration

37. To determine an estimate of the required xanthate-to-waste ratio, it was necessary to develop a method that could quantify the metal removal capacity of the xanthate. A potentiometric titration method similar to the method used by Herrent and Jnoff (1948) was chosen. A Brinkman model E536 automatic titrator was used to carry out these titrations. A silver sulfide/silver electrode was used as the indication electrode, and a glass potassium electrode was used as the reference electrode. Xanthate slurries were titrated using a silver nitrate solution as the titrant.

38. The titration of xanthates with a silver nitrate solution theoretically produces a curve having the shape shown in Figure 6. The end point is indicated by the steep rise in the electromotive force (e.m.f.). The end point is indicative of the silver assimilation capacity of the xanthate. In other words, the end point is where the equivalence of the silver and xanthate are equal.

39. The general shape of an experimental xanthate titration curve is shown in Figure 7. The plateaus at -700 mv, -100 mv, and +200 mv indicate titration end points. The first plateau corresponds to silver precipitation by the sulfide ions, the second plateau corresponds to thiocarbonate precipitation, and the third plateau corresponds to silver xanthate precipitation (Marani et al. 1981, Herrent and Jnoff 1948). Sulfides and thiocarbonates are intermediates formed during xanthate production which contaminate the xanthate. In addition to contamination by thiocarbonates and sulfide, xanthates are also contaminated by hydroxides (due to the fact they are produced in excess caustic conditions). These contaminants will coprecipitate

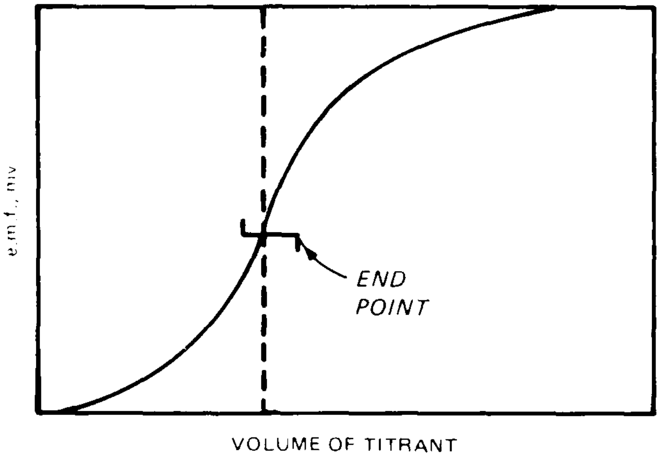

Figure 6. Theoretical xanthate titration curve

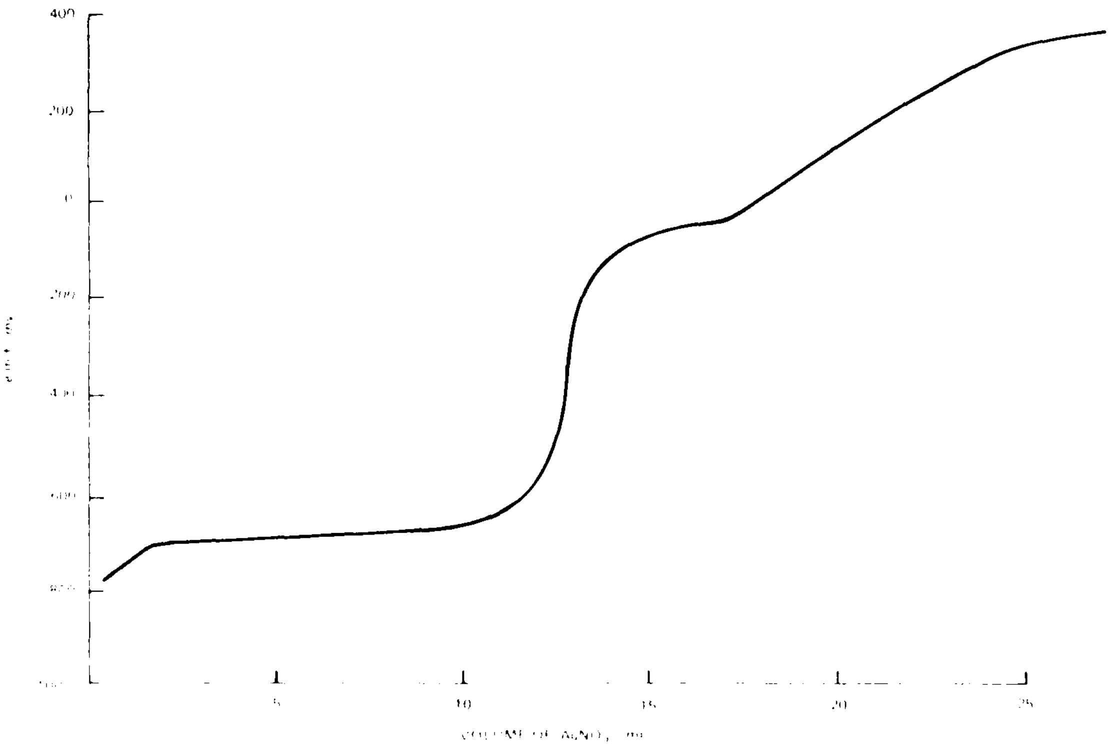

Figure 7. Experimental xanthate titration curve

metals. Under normal circumstances this would aid in the xanthate's ability to extract metals from wastewaters, but the object of this study was to quantitate the ability of the xanthates to immobilize heavy metals. It was therefore necessary to neutralize the caustic and, if possible, wash the other contaminants from the xanthates prior to treating the metal waste solution.

40. To neutralize excess hydroxide ions and remove the intermediates, xanthates were slurried with a 0.5 N acetic acid (HOAc) solution. This weak organic acid was selected because a strong mineral acid could break the xanthate chemical bonds. The slurry was filtered, and the dewatered cake was reslurried with distilled water to wash excess acid from the xanthate cake. Figure 8 presents a titration curve of silver nitrate versus starch xanthate after the pH of the starch xanthate was lowered from 12.0 to 7.0 using an acetic acid wash. It is evident that the silver removal capacity of the xanthate has been reduced, and the plateaus that indicate contamination by the intermediates have been eliminated. In fact, all the plateaus have been eliminated.

Silver back-titration

41. When xanthates were acid washed, the equivalence point was not evident, as illustrated in Figure 8. To determine where the equivalence point occurred, potassium thiocyanate (KSCN) was used to back-titrate the excess silver ions in the xanthate titrate.

42. Several KSCN back-titrations were performed using aliquots of supernatant removed from the silver/xanthate titrant. The KSCN back-titrations indicated the equivalence point occurs at approximately +300 mv. Using this information and employing stoichiometric relationships, the xanthates' ability to remove any metal ions or combination of metal ions can be calculated. Thus, the theoretical xanthate-to-waste dosage can be determined.

Synthetic Waste Formulation

43. The synthetic metal plating waste was prepared by dissolving four metal nitrate salts, cadmium nitrate ($Cd(NO_3)2.4H_2O$), chromium nitrate ($Cr(NO_3)3.9H_2O$), nickelous nitrate ($Ni(NO_3)2.6H_2O$), and mercury nitrate ($Hg(NO_3)_2$) in American Society for Testing and Materials type III water (ASTM 1986). A series of jar tests were conducted to determine the optimal synthetic waste concentration for starch and cellulose xanthate sludge

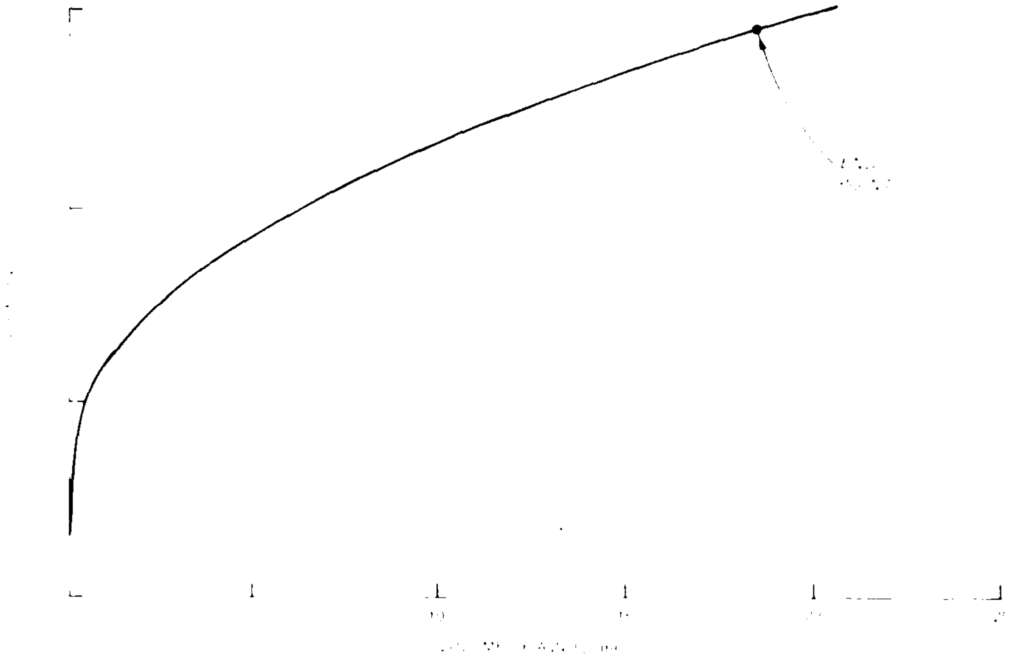

Figure 8. Experimental xanthate titration curve after acid washing

production. The jar tests were performed using a Phipps and Bird six-paddle stirring apparatus and six 1-ℓ mixing vessels. Synthetic waste concentrations ranging from 600 times the limits set for the EP (Cd = 600, Cr = 3,000, Ni = 3,000, and Hg = 120 ppm) to 100 times the EP limits (Cd = 10, Cr = 50, Ni = 50, and Hg = 2 ppm) were evaluated using the theoretical xanthate dosages.

44. The jar tests indicated that waste mixtures prepared at contaminant concentrations 300 times above the EP limits produced sludges that are difficult to dewater. Synthetic waste mixtures at concentrations between 50 and 250 times the EP limits produced sludges that could be more easily dewatered. The sludge that offered optimal dewatering characteristics was produced using a synthetic waste concentration slightly greater than 100 times the EP limit. Thus, a synthetic waste concentration slightly above 100 times the EP limit was selected for use in this study.

45. Jar tests were also performed on calcium hydroxide precipitation. These jar tests indicated that varying the synthetic metal concentration while using a constant calcium hydroxide dosage had no effect on the dewaterability of the sludges produced. Based on these results, the same synthetic metal

waste concentration used for xanthates precipitation was also used for calcium hydroxide precipitation.

46. A synthetic waste with Ni, Cr, and Hg concentrations approximately 100 times the EP limit was used for this study. Due to a calculation error as the synthetic waste was prepared, a Cd concentration of 454 times the EP was used throughout this study. The synthetic waste formulation is shown in Table 2.

47. The hydroxide and xanthate sludges used in the study were produced by treating this waste with the calcium hydroxide and xanthate dosages listed in Table 3. The dosages for the xanthate materials were slightly less than the theoretical dosage rates, which ensured that the metal xanthate sludge would not be diluted by excess insoluble xanthate material.

Table 2

Synthetic Waste Formulation

Compound as Nitrate Salts	Metal Compound Concentration g/ℓ	Metal Ionic Concentration ppm	100 × EP Limit Metal Ion Concentration ppm
$Cd(NO_3)_2 \cdot 4H_2O$	1.250	454	100
$Cr(No_3)_3 \cdot 9H_2O$	4.518	587	500
$Ni(NO_3)_2 \cdot 6H_2O$	2.906	587	No limit
$Hg(NO_3)_2 \cdot H_2O$	0.040	23.4	20

Table 3

Hydroxide and Xanthate Dosage Rates

Material	Dosage Rate per Volume of Synthetic Waste, g/ℓ (Wet Weight)
Cellulose xanthate	32.2
Starch xanthate	32.4
Calcium hydroxide	3.60

Production of Test Sludges

Cellulose xanthate

48. A slurry was formed by mixing 13.43 lb of cellulose xanthate and 25 gal of ASTM type III water in a 55-gal tank. This slurry was mixed for 30 min, and the cellulose material dissolved. The mixture had a pH of 12.5. The alkalinity of the slurry was neutralized with 0.5 N HOAc to a pH of 7.0. Since the cellulose xanthate material dissolved, it was not washed. A 25-gal aliquot of the synthetic metal wastewater was added to the cellulose slurry solution and mixed. This mixture was allowed to settle for 15 hr. Since the mixture did not separate well, the entire 50 gal of material was dewatered. The sludge was separated from the supernatant using a Sparkler "VR" horizontal plate filter press. The supernatant was passed through Sparkler cellulose filter paper with a pore size of 12 μ. The maximum solids concentration obtained by dewatering the sludge was 11.3 percent (by weight). Approximately 5 gal of cellulose xanthate sludge was produced with a density of 3 lb/gal. This material was stored at 4° C until needed for testing.

Starch xanthate

49. Starch xanthate (42 lb) was placed in a 55-gal tank and slurried with 40 gal of ASTM type III water. This solution had a pH of 12.6. The pH was lowered to 7.0 with 0.5 N HOAc to remove the excess alkalinity. This slurry settled quickly and was filtered using the Sparkler filter as previously described. The resulting starch xanthate cake was reslurried with 17 gal of ASTM type III water to remove the intermediates from the starch xanthate. The slurry was filtered with the Sparkler filter, and the washing step was repeated. The washed starch xanthate was divided into two 18.8-lb portions, and each portion was slurried in 35 gal of the synthetic metal waste solution. Each of the metal waste/xanthate slurries was left undisturbed for 15 hr to allow the solids to settle. The supernatant was decanted from each tank. The sludges from the separate batches were homogenized and dewatered using the Sparkler filter. Approximately 4.5 gal of starch xanthate sludge was produced with a density of 5.3 lb/gal and a solids content of 32.6 percent (by weight). This material was stored at 4° C until needed for testing.

Hydroxide

50. The process used to produce the sludge for this study is described briefly as follows: 500 gal of the synthetic metal wastewater was prepared in

a 600-gal stainless steel tank. Then, 15 lb of calcium hydroxide was added to the synthetic metal wastewater and mixed for 30 min. After 15 hr of settling, the supernatant was decanted. The sludge was filtered with an Eimco Model 3613 vacuum drum filter. The dewatered sludge produced had a density of 11.7 lb/gal and a solids content of 32.44 percent (by weight). This material was stored at 4° C until needed for testing.

Preparation of Test Specimens

51. Supernatant water was added to the starch xanthate and hydroxide sludges until a 25-percent (by weight) solids content was obtained. Because of the previously discussed problems with dewatering, the cellulose xanthate sludge was evaluated at the 11.3-percent solids content.

52. The three metal sludges (cellulose xanthate, starch xanthate, and hydroxide) were divided into two subsamples. Aliquots of the unsolidified subsamples of the cellulose xanthate, starch xanthate, and hydroxide sludges were placed in twenty-one 2- by 2-in. brass cube molds and four standard proctor cylindrical molds 4.5 in. in height and 4.0 in. in diameter. The other subsamples were solidified using Type I portland cement. A 0.3:1 cement to sludge ratio (weight/weight) was used for the starch xanthate and hydroxide sludges. A 0.355:1 cement-to-sludge ratio (weight/weight) was used for the cellulose xanthate sludge to maintain the same water-to-cement ratio. A Hobart C-100 mixer was used to mix each sludge with the cement. Aliquots of each of the solidified sludges (starch xanthate, cellulose xanthate, and hydroxide) were poured into twenty-one 2- by 2-in brass molds and four standard proctor cylindrical molds and vibrated on a Sentron model VP61D1 vibrating table to remove air voids.

53. The solidified and unsolidified samples were cured in the molds at 23° C and 98-percent relative humidity for a minimum of 24 hr. Specimens were removed from the molds when they developed sufficient strength to be free-standing. After removal from the molds, the specimens were cured under the same conditions until tested.

Test Protocols

54. The solidified and unsolidified sludges were subjected to chemical and physical testing to evaluate their physical strength and metal leachability characteristics. The test methods are described individually below.

Unconfined compressive strength

55. Unconfined compressive strength was determined using ASTM method C109-86, Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens) (ASTM 1986). ASTM C109-86 was modified slightly because the material was fluid and could not be tamped. The molded specimens were vibrated, to eliminate voids. The UCS test was performed on four sets of five cubes that had cured for time periods of 7, 14, 21, and 28 days. The surface area of each cube was determined using a Flower Max-Cal caliper, and each cube was crushed using a Tinius Olsen Super L compression apparatus. The UCS was reported as the force per unit surface area (pounds per square inch) required to fracture the cube.

Cone index test

56. The cone index measures the resistance of a material to the penetration of a 30-deg right circular cone. The method specified in TM 5-530 was followed (US Army 1971). The CI value is reported as force per unit area of the cone base required to push the cone through a test material at a rate of 72 in./min. Two cones are available for this test. The standard WES (US Army Engineer Waterways Experiment Station) cone has an area of 0.5 in.; the airfield penetrometer has a base area of 0.2 in. It was convenient to use the standard WES cone on material with a CI less than 100 psi and to use the airfield penetrometer on materials with a CI greater then 100 psi. Each of the four specimens (cylindrical molds) for the solidified and unsolidified sludges was tested each time the CI readings were determined. Cone index readings were periodically taken as the specimens cured until they exceeded 750 psi, the maximum reading of the airfield penetrometer, or after 28 days of curing, whichever occurred first.

USEPA extraction procedure (EP) test

57. Each sludge (solidified and unsolidified) was subjected to the EP test. Four replicate extractions were performed on each material, resulting in a total of 24 extractions.

58. USEPA Method 1310 (USEPA 1982b) was the method followed with the exception that all materials leached were ground to pass a No. 16 standard soil sieve. The solid material used in the extraction was composited from several of the 2- by 2-in. cubes and the 4-in. cylinders. This material was composited and ground. The ground solids were divided into four aliquots, and the EP extraction was performed on each sample. This extraction consisted of contacting dilute acetic acid with approximately 100 g of solid waste using a 20-to-1 liquid-to-solid (L/S) ratio. The duration of the test varied from 24 to 28 hr, depending upon the waste alkalinity. After the samples were extracted, the liquids were separated from the solids using a Millipore (HAWP 142-50) membrane and pressure filter. The EP extract was then analyzed for Cd, Cr, Hg, and Ni according to the analytical methods prescribed by the USEPA and outlined in Table 4.

Serial graded batch extraction procedure

59. Several batch leaching procedures have been developed that generate test results more easily extrapolated to field leaching conditions than the EP test. Sequential batch leaching procedures (SBLP) have been proposed by several authors (Roy, Hassett, and Griffin 1986; Lowenbach 1978; Perket and Webster 1981). In general, these SBLP procedures consist of contacting a solid with a liquid until steady-state conditions are achieved, separating the solid phase from the liquid, and recontacting the extracted solid with fresh liquid.

60. The serial graded batch extraction procedure is similar to the SBLP; however, the SGBEP involves contacting the solid with a leaching fluid at varying ratios (Houle and Long 1980, Betteker 1986). Like the SBLP, the SGBEP simulates varying pore volumes of water contacting the solid. The SGBEP uses several simplifying assumptions and provides a method that is much easier to perform than the SBLP.

61. The SGBEP used to investigate contaminant release in this study is described as follows. Waste samples used in the extraction step were prepared in the same manner as described for the EP test. The SGBEP was conducted by contacting the wastes samples (solidified and unsolidified) with ASTM type I water on an Eberbach mechanical shaker for 24 hr at approximate L/S ratios of 2 ml:1 g, 5 ml:1 g, 10 ml:1 g, and 50 ml:1 g. The extractions were run in triplicate in 250-ml polyethylene bottles laid in the horizontal position.

Table 4

Chemical Analysis Methods

Parameter of Interest	USEPA* Digestion Method	USEPA* Analytical Method	High Level Analyses (>50 ppm)	Low Level Analyses (<50 ppm)
Cadmium	3020	7131	Bechman Spectrospan III B DC (direct current) Argan plasma emission spectrophotometer	Perkin-Elmer 500 atomic adsorption spectrophotometer with HGA 500 graphite flame
Chromium	3020	7191	Bechman Spectrospan III B DC (direct current) Agan plasma emission spectrophotometer	Perkin-Elmer 500 atomic adsorption spectrophotometer with HGA 500 graphite glame
Nickel	3020	7521	Bechman Spectrospan III B DC (direct current) Agan plasma emission spectrophotometer	Perkin-Elmer 500 atomic adsorption spectrophotometer with HGA 500 graphite flame
Mercury	NA**	7471	NA	Perkin-Elmer 503 atomic adsorption spectrophotometer with cold vapor technique

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* See USEPA 1982b.

** NA = not applicable.

The extract was filtered through Gelman Metricel GN-6 (pore size, 0.45 μ) cellulose fiber filters after shaking for the prescribed time. Method blanks were prepared by carrying ASTM type I water through the same shaking and filtration procedures. The filtered extracts were analyzed for Cd, Cr, Hg, and Ni using the methods outlined in Table 4.

62. In addition to leaching tests, three representative samples of each of the solidified and unsolidified wastes were digested according to USEPA digestion method 3050 (USEPA 1982b). The digestate was analyzed for Cd, Cr, and Ni using the methods outlined in Table 4. Waste samples analyzed for Hg were digested and analyzed according to USEPA method 7470 (USEPA 1982b). Table 5 lists the bulk metal concentrations found in the unsolidified and solidified cellulose xanthate, starch xanthate, and hydroxide sludges.

Table 5

Unsolidified and Solidified Sludge Metal Concentrations

	Contaminant mg/g, Dry Weight			
Sludge	Cr	Cd	Hg	Ni
Unsolidified cellulose	19.7	19.89	0.637	19.8
Unsolidified starch	17.6	33.23	1.15	13.1
Unsolidified hydroxide	74.9	16.34	0.975	80.0
Solidified cellulose	3.88	3.76	0.153	4.22
Solidified starch	7.46	14.1	0.563	5.49
Solidified hydroxide	29.5	6.73	0.363	31.25

63. Using the preleached solid phase concentration and the postleached aqueous phase concentration, the total postleach contaminant concentration in the solid phase was determined using Equation 5.

$$q = qo - C\left(\frac{V}{M}\right) \qquad (5)$$

where

q = total contaminant concentration in the solid phase after leaching mg/kg

q_o = initial contaminant concentration in the solid phase, mg/kg

C = contaminant concentration in the aqueous phase, mg/ℓ

V = volume of the aqueous phase (leachate), ℓ

M = mass of solidified waste, kg

All calculations performed on the sludges were based on the sludge's dry weight. Desorption isotherms for each waste were developed by plotting q versus C at constant temperature.

PART III: DISCUSSION OF RESULTS

64. Physical and chemical tests were used to evaluate the physical strength and the metal leachability characteristics for the solidified and unsolidified starch xanthate, cellulose xanthate, and hydroxide sludge materials. The physical test results for the cone index and the unconfined compressive strength test and the chemical test results for the USEPA extraction procedure and the serial graded batch extraction procedure are presented in this part.

Physical Test Results

65. Results of the CI and UCS tests are presented in Figures 9 and 10, respectively. As expected, the solidified sludges developed higher strengths than the unsolidified sludges.

Cone index test

66. Cone index values were obtained by taking several penetration readings during the sample curing period. The penetration readings were plotted against time, and a curve was drawn through the data points. These curves are presented in Figure 9.

67. The unsolidified starch and cellulose xanthate materials indicated only a slight resistance to penetration. The unsolidified hydroxide sludges did not develop resistance to penetration. The largest CI value measured for the unsolidified material was 40 psi, indicating that it is unlikely that the unsolidified materials will produce sludges that will develop large 28-day UCS.

68. The solidification of these sludges produced materials with substantial CI values. The solidified starch and cellulose xanthate sludges reached the maximum cone reading of 750 psi in less than 10 days of curing. The solidified hydroxide sludge produced a material that gained strength quickly during the first 4 days of curing; however, the rate of strength development decreased as curing time increased. Unlike the solidified xanthate sludges, the solidified hydroxide sludges did not reach the 750 psi maximum CI value, but achieved a CI value of only 280 after 28 days of curing.

69. Myers (1986) reports that the CI test is indicative of the strength development of materials, which is reflected in the results of this study.

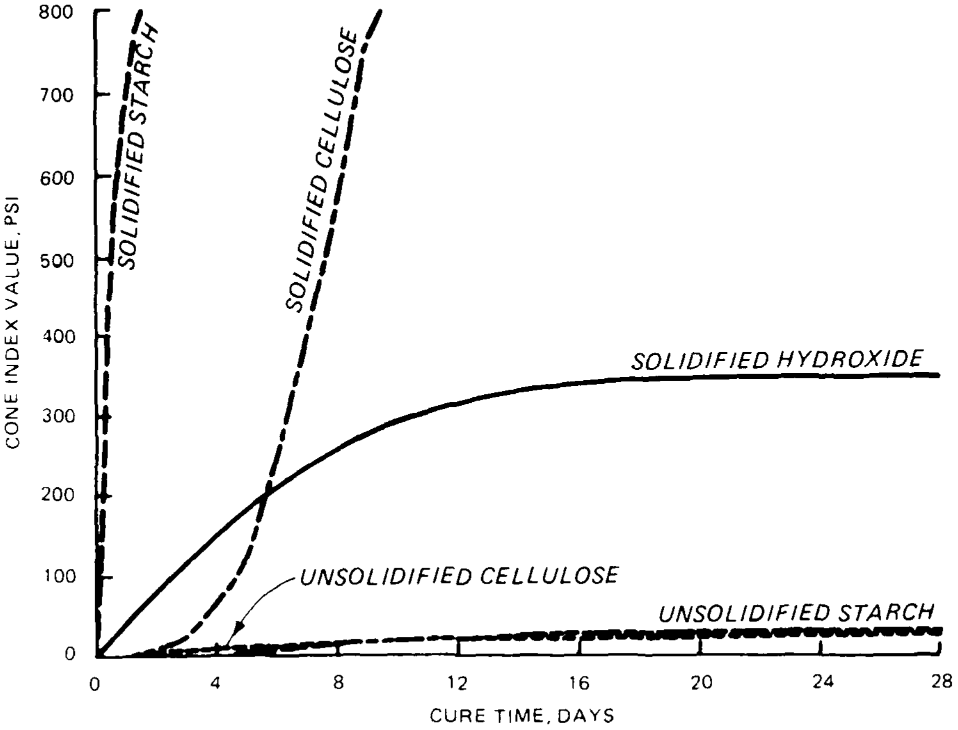

Figure 9. Cone index versus curing time for all sludges

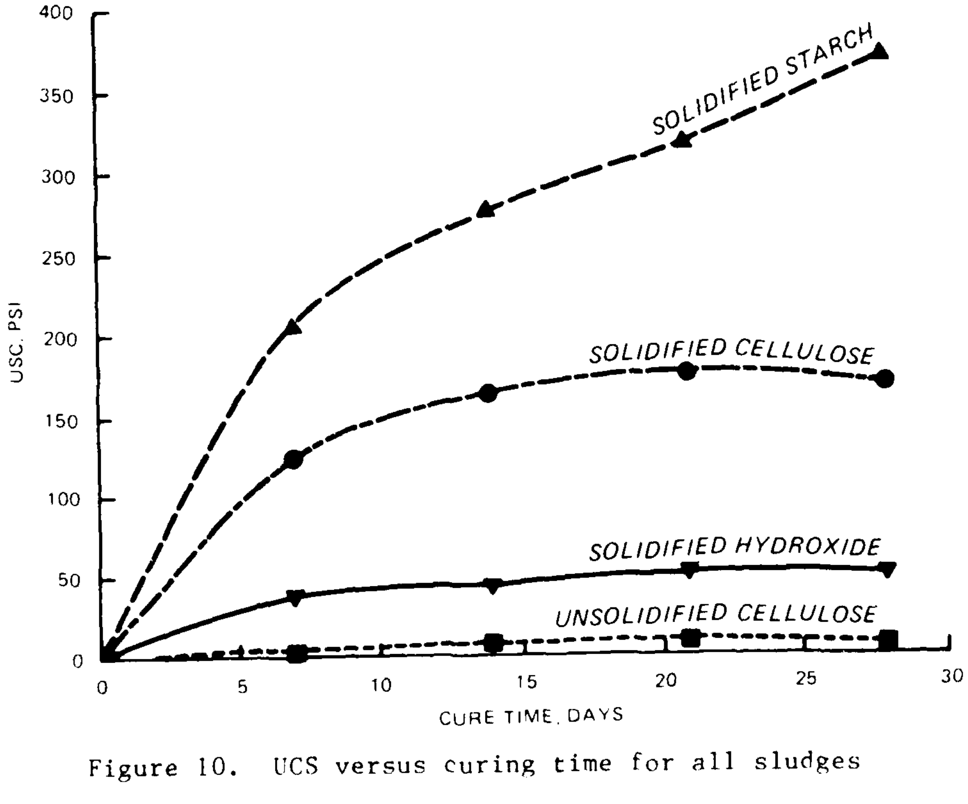

Figure 10. UCS versus curing time for all sludges

The materials that developed the highest CI readings by 7 days of curing developed the highest strengths at 28 days of curing.

70. Cone index information is also useful to indicate the trafficability of materials. Although application of the cone penetration test to accessing the trafficability of solidified waste has never been verified, CI information has been used as an indicator of vehicular mobility for a wide variety of environments (Meyer 1966, Hammitt 1970, Mitchell and Houston 1974). Cone index values required to support one pass for construction equipment range between 15 and 30 psi. Unsolidified xanthate sludges must cure more than a week to develop this strength, while the solidified sludges developed this strength in less than 48 hr. From a operations standpoint, this could be advantageous in speeding the placement of waste in a landfill.

Unconfined compressive strength test

71. Figure 10 presents the UCS versus curing time for the solidified and unsolidified sludges. No curves are presented for the unsolidified hydroxide or unsolidified starch xanthate sludges because these materials did not develop a measurable UCS.

72. Solidified starch and cellulose xanthate sludges developed 28-day UCS of 337 and 154 psi, respectively. The solidified hydroxide sludge developed a 28-day UCS of 46 psi, and the unsolidified cellulose sludge developed a 28-day UCS of 7 psi. These data confirm the results of the CI test, which indicated that solidified starch and cellulose xanthate sludges would develop much greater strengths than the hydroxide sludge.

73. The shape of the UCS curves also yields information on the ultimate strength development characteristics of the waste materials. The UCS curves for the hydroxide and cellulose xanthate sludges indicate that these materials achieve most of their strength by 28 days. The UCS curve for the solidified starch xanthate sludge indicates that a gain in UCS will probably be observed well beyond the 28-day curing period.

74. It is interesting to note that, while all the solidified materials had a constant water-to-binder ratio, the xanthate sludges developed a 28-day UCS 3.5 times greater than the hydroxide sludge. The lower strength of the solidified hydroxide sludge could present a potential problem since the USEPA uses the UCS as an indirect method for determining the chemical stability of treated waste products. The minimum strength recommended, to measure adequate

chemical bonding, is 50 psi (USEPA 1986). The solidified hydroxide sludge could probably met this criterion if a larger binder-to-sludge ratio is used.

Contaminant Release Results

EP test

75. The results of the EP tests are presented in Figure 11 and Tables 6 and 7. Data in Table 6 for the four replicate samples indicate that all but the Cr data for the unsolidified starch and the Cd, Cr, and Ni data for the unsolidified hydroxide had a high degree of reproducibility. This variability cannot be accounted for except by the inherent variability in the EP testing procedure (American Resource Corporation and Environmental Engineering and Management 1984).

76. The EP results presented in Table 7 indicate that all solidified sludges, with the exception of Hg for the solidified hydroxide sludge, passed the EP test. The unsolidified cellulose and starch xanthate sludges, on the other hand, failed the EP for Ni, and the unsolidified hydroxide sludges failed the EP for each of the metals tested (Cd, Cr, Hg, and Ni).

77. The data presented in Table 6 indicate that solidification is effective in reducing the leachability of the heavy metals for the xanthate and hydroxide sludges. The metal concentrations found in the leachate generated from the solidified xanthate and hydroxide sludges were two to three orders of magnitude lower than those found in the leachate from the unsolidified sludges. Only the Hg data for the hydroxide sludges indicated that solidification was not an effective treatment method.

78. Metals from the hydroxide sludges are susceptible to leaching due to the fact that under the acetic condition of the EP test, metal hydroxide can become soluble. Solidification of these sludges using hydrating agents produces materials with high acid neutralization capacity resulting from the addition of a high alkaline binder. Thus, when the EP test is performed, the acid is neutralized and the pH of the leaching fluid remains elevated. This produces conditions under which many metals remain insoluble. Hg was leached from the solidified sludge because Hg(II) does not form an insoluble hydroxide or oxide like the Ni, Cd, and Cr(III). Hg(II) is suspected of producing an oxide that is semisoluble, thus offering an explanation why mercury was found in the EP leachate of the hydroxide sludges.

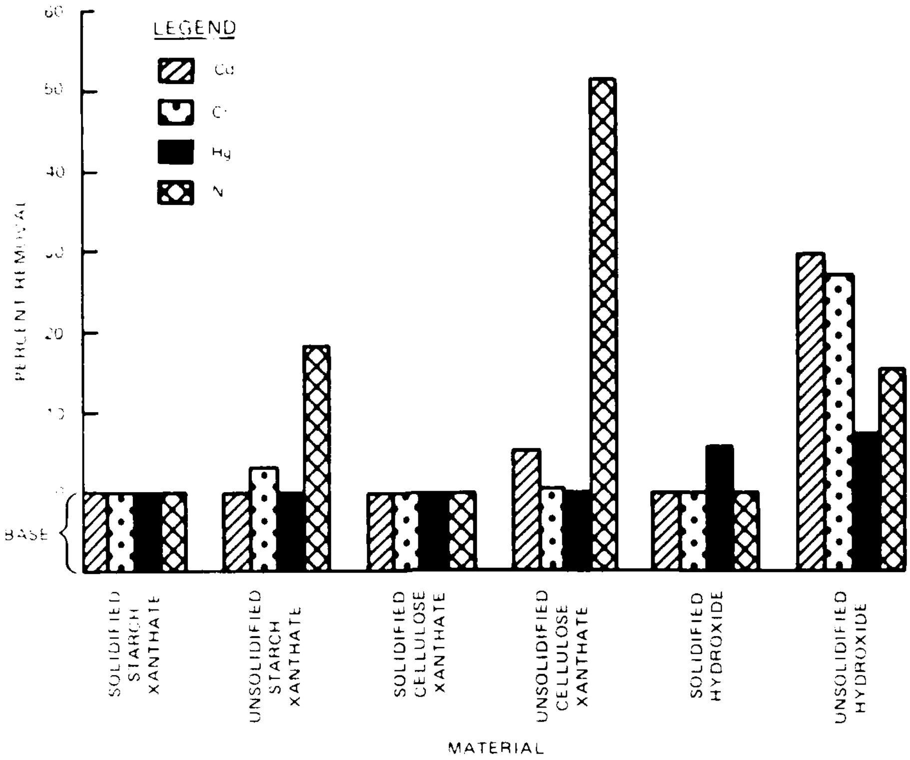

Figure 11. Results from EP tests presented as the percent of contaminant removal from the solid phase

79. Figure 11 presents the EP results as a percentage of the metal removed from the waste on a dry weight basis. This figure illustrates that the metals were more immobile in the solidified sludges than in the untreated sludges and that xanthate precipitation more effectively immobilized the Cd, Cr, and Hg than did hydroxide precipitation. This figure also indicates the extractability of Ni from the unsolidified xanthate sludges. Flynn, Carnahan, and Lindstrom (1980) report that Ni is more loosely bound to the xanthate than the Cd, Cr, and Hg, thus offering a possible explanation why Cd, Cr, and Hg are more immobile in the xanthate sludges than the Ni.

80. Comparison of the EP results for the unsolidified xanthate and hydroxide sludges indicates that, generally, the unsolidified cellulose and starch xanthates/metal complexes were more effective in reducing the leaching of metals than the unsolidified hydroxides. The solidified starch and cellulose xanthate sludges were equally effective as the solidified hydroxide sludge in reducing the leaching of metals, except for Hg. Solidified

Table 6

EP Leachate Concentrations

Sample Description	Sample No.*	Metal Concentration, ppm			
		Cd	Cr	Hg	Ni
Solidified starch	1	<0.0001	0.064	<0.0008	0.13
	2	<0.0001	0.062	<0.0008	0.104
	3	<0.0001	0.064	<0.0008	0.13
	4	<0.0001	0.067	<0.0008	0.103
	M	<0.0001	0.0643	<0.0008	0.1168
	SD	--	0.0021	--	0.0153
Unsolidified starch	5	0.182	4.18	<0.0008	32.9
	6	0.171	4.25	<0.0008	32.8
	7	0.386	17.4	<0.0008	62.9
	8	0.473	24.8	<0.0008	75.2
	M	0.3030	12.66	<0.0008	50.95
	SD	0.1504	10.21	--	21.49
Solidified cellulose	9	<0.0001	0.075	0.002	0.003
	10	<0.0001	0.074	0.002	0.003
	11	<0.0001	0.071	<0.002	0.004
	12	<0.0001	0.08	<0.002	0.005
	M	<0.0001	0.0750	0.002	0.0038
	SD	--	0.0037	--	0.0010
Unsolidified cellulose	13	25.3	3.07	0.0105	244
	14	26.8	3.11	0.0141	252
	15	24.8	2.29	0.0135	224
	16	27.3	5.07	0.015	271
	M	26.05	3.385	0.0133	248.3
	SD	1.190	1.185	0.0020	19.64
Solidified hydroxide	17	<0.0001	0.011	0.843	0.002
	18	<0.0001	0.011	0.60	0.004
	19	<0.0001	0.016	0.349	0.003
	20	<0.0001	0.017	0.378	<0.001
	M	<0.0001	0.0138	0.565	0.0025
	SD	--	0.0032	0.2412	0.0013
Unsolidified hydroxide	21	25.9	106	0.493	50.8
	22	48.4	198	0.558	70.4
	23	90.8	383	1.54	355
	24	66.6	281	0.766	119
	M	57.93	242.0	0.8392	148.8
	SD	27.52	118.1	0.4814	140.4

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* M = mean; SD = standard deviation.

Table 7

Pass-Fail Results for the EP Test

			Waste Contaminant Concentration Below the EP Limit* (Yes/No)			
Sludge	Type	Sample No.	Cd	Cr	Hg	Ni
Starch	Solidified	1	Y	Y	Y	Y
		2	Y	Y	Y	Y
		3	Y	Y	Y	Y
		4	Y	Y	Y	Y
Starch	Unsolidified	5	Y	Y	Y	N
		6	Y	Y	Y	N
		7	Y	N	Y	N
		8	Y	N	Y	N
Cellulose	Solidified	9	Y	Y	Y	Y
		10	Y	Y	Y	Y
		11	Y	Y	Y	Y
		12	Y	Y	Y	Y
Cellulose	Unsolidified	13	N	Y	Y	N
		14	N	Y	Y	N
		15	N	Y	Y	N
		16	N	Y	Y	N
Hydroxide	Solidified	17	Y	Y	N	Y
		18	Y	Y	N	Y
		19	Y	Y	N	Y
		20	Y	Y	N	Y
Hydroxide	Unsolidified	21	N	N	N	N
		22	N	N	N	N
		23	N	N	N	N
		24	N	N	N	N

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* EP limits are as follows: Cd = 1.0 mg/ℓ, Cr = 5.0 mg/ℓ, Ni = 5.0 mg/ℓ (based on the "California list" for metals); Ng = 0.2 mg/ℓ.

cellulose and starch xanthate sludges were more effective in reducing Hg leaching than the solidified hydroxide sludge.

Serial graded batch extraction procedure

81. The results of the SGBEP were evaluated by using desorption isotherms and by comparing the percent of contaminant leached at a L/S ratio of 20:1, the L/S ratio used for the EP test. Outliers were discarded from the data set utilizing the Q test (Skoog and West 1979).

82. EP-SGBEP comparison. As indicated by comparing Figures 11 and 12, the SGBEP at a L/S ratio of 20:1 generated leachates with contaminant concentrations two to three orders of magnitude lower than those observed for the EP leachate. This can be attributed to the fact that most metal ions pose a higher degree of solubility in acid solutions.

83. Although the amount of contaminants observed in the SGBEP leachate differs greatly from that of the EP leachate, general trends observed in the EP data are also observed in the SGBEP data at the L/S ratio of 20:1. The Hg concentration in the leachate from the hydroxide sludges was 10 times higher than that observed in the leachate from the other sludges. The Ni concentration in the leachate from the unsolidified cellulose xanthate sludges was much higher than that observed in the leachates from the other sludges. In general, unsolidified xanthate reduced the leachability of the metals more effectively than the unsolidified hydroxide sludges, and the solidified xanthate sludges reduced the leachability of the metals more effectively than the solidified hydroxide sludges. The results of both the EP and SGBEP, at a L/S ratio of 20:1, indicate that, in general, xanthate precipitation produces sludges with less potential for leaching.

84. Desorption isotherms. Desorption isotherms were prepared for each treatment process and for each of the metal contaminants investigated, yielding a total of 24 desorption isotherms. To compare the effectiveness of the various treatment processes in reducing the leachability of the metals, all SGBEP data were normalized to the initial contaminant concentration of the sludge by dividing q by q_o. Desorption isotherms were generated by plotting the average q/q_o versus the average C at a constant temperature of 23°C.

85. Three sorption isotherm models have been used extensively to model desorption phenomena: the linear model, the Langmuir model, and the Freundlich model (Weber 1972, Reynolds 1982). A fourth model, the no-release

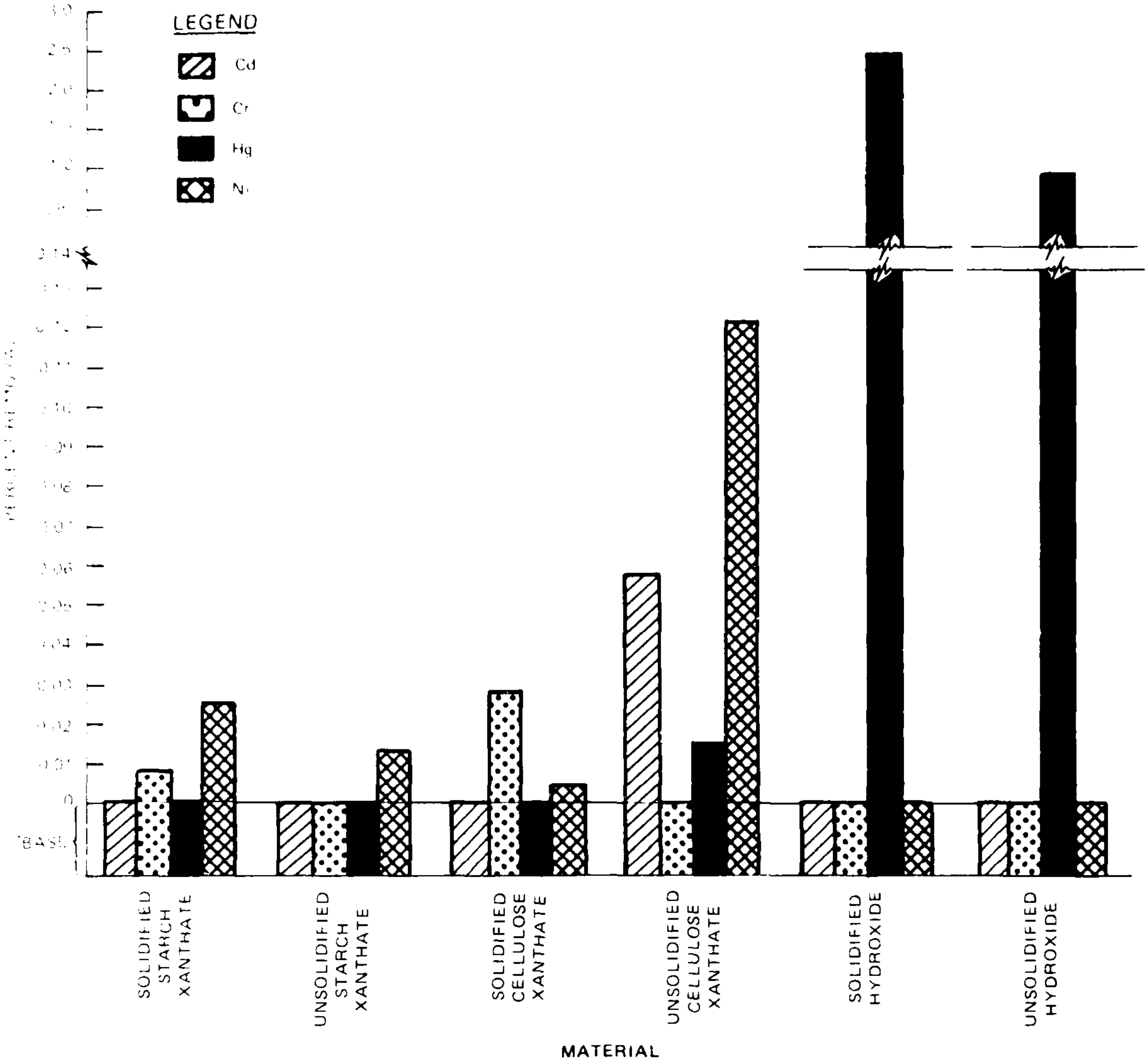

Figure 12. Results of the SGBEP at a L/S ratio of 20:1, presented as the percent of contaminant removed from the solid phase

isotherm model, was also necessary to fully characterize the data generated in this study. The no-release isotherm model is used to describe the situation in which the contaminant has been effectively immobilized and, thus, very little contaminant is detected in the leachate. Because the leachate concentration is near the analytical detection limits, along with the combined variability of the batch leaching and analytical procedures, the data for the no-release isotherm are generally scattered. Figure 13 illustrates examples of each of these types of desorption isotherms.

86. The equations for each of the isotherm models, except the no-release isotherm, are given in Equations 6 through 8.

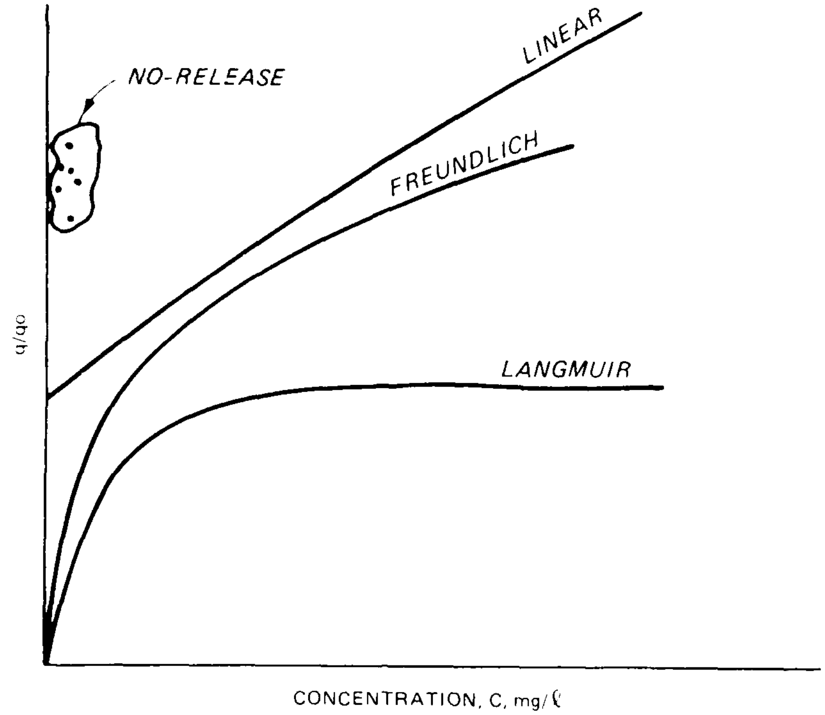

Figure 13. Graphical representation of isotherm models

$$\text{Linear:} \quad q = (Kd)C + qr \tag{6}$$

$$\text{Langmuir:} \quad q = \frac{abC}{(1 + bC)} \tag{7}$$

$$\text{Freundlich:} \quad q = Kc^{1/n} \tag{8}$$

where

q = solid phase concentration, mg/kg

Kd = distribution coefficient, ℓ/kg

C = aqueous phase concentration, mg/ℓ

qr = solid phase contaminant concentration resistant to leaching, mg/kg

a = Langmuir sorption capacity, mg/kg

b = Langmuir coefficient related to entropy, ℓ/mg

K = Freundlich coefficient, ℓ/kg

n = dimensionless coefficient

These models were fit to the experimental desorption isotherm data using linear regression. The model that resulted in the largest regression coefficient, r^2, was selected as the model that most closely fit the experimental data. Generally, the isotherm model of best fit was dependent on the metal of interest, as indicated in Table 8.

Table 8

Desorption Isotherm Model Results

Metal Leached	Sludge Type	Binder	Isotherm Type	Contaminant Release Coefficients	
				a/qo	b/qo
Cadmium	Cellulose xanthate	--	Langmuir	1.00024	77.2735
	Cellulose xanthate	Cement	No-release	--	--
	Starch xanthate	--	No-release	--	--
	Starch xanthate	Cement	No-release	--	--
	Hydroxide	--	No-release	--	--
	Hydroxide	Cement	No-release	--	--
Chromium	Cellulose xanthate	--	Langmuir	1.0000	488,827
	Cellulose xanthate	Cement	Langmuir	1.0007	2,085
	Starch xanthate	--	Langmuir	1.0001	58,842
	Starch xanthate	Cement	Langmuir	1.0003	4,543
	Hydroxide	--	Langmuir	1.0000	-1,581,820
	Hydroxide	Cement	Langmuir	1.0001	27,933
				qr/qo	k/qo
Mercury	Cellulose xanthate	--	No-release	--	--
	Cellulose xanthate	Cement	No-release	--	--
	Starch xanthate	--	No-release	--	--
	Starch xanthate	Cement	No-release	--	--
	Hydroxide	--	Linear	0.14936	2.6862
	Hydroxide	Cement	Linear	0.8654	0.7264
				k/qo	n
Nickel	Cellulose xanthate	--	Freundlich	0.9910	139.8
	Cellulose xanthate	Cement	No-release	--	--
	Starch xanthate	--	Freundlich	1.0000	5,762.3
	Starch xanthate	Cement	Freundlich	1.0000	10,223.2
	Hydroxide	--	No-release	--	--
	Hydroxide	Cement	No-release	--	--

87. The desorption modeling effort resulted in the generation of the various constants (presented in Table 8). The constants also offer a useful tool when evaluating desorption data. By comparing these constants and the shapes of the desorption isotherms, the effectiveness of the various waste treatment processes can be evaluated. Results of the desorption isotherms and their respective models are discussed below.

88. Cadmium. As indicated by Table 8, all sludges, except the unsolidified cellulose xanthate, were modeled with the no-release isotherm. Thus, all the treatment processes evaluated, except for the unsolidified cellulose xanthate, were effective in the immobilization of cadmium. The unsolidified cellulose xanthate sludge was modeled with the Langmuir isotherm, indicating slight cadmium mobility.

89. Chromium. Desorption isotherms for chromium are shown in Figure 14. Small amounts of Cr were measured in the leachate for each treatment process evaluated. These data were modeled using the Langmuir isotherm. As indicated in Table 8, the Langmuir coefficient a/qo is approximately 1.0 for all treatment processes evaluated and, thus, has little effect on the model's shape. The Langmuir coefficient b/qo , therefore, controls the model's shape and indicates the effectiveness of the various treatment processes.

90. The larger b/qo , the more effective the treatment process is in immobilizing Cr. For example, in Figure 14, the solidified hydroxide is more effective in reducing the leaching of Cr than the solidified starch xanthate, and the solidified starch xanthate has less leaching potential for Cr than the solidified cellulose xanthate. Chromium mobility in the sludges is ranked from the least leachable to the most leachable as follows:

Unsolidified cellulose xanthate > Unsolidified starch xanthate
> Solidified hydroxide > Solidified starch xanthate > Solidified
cellulose xanthate > Unsolidified hydroxide

It is interesting to note that the solidified xanthate sludges leached more Cr than the unsolidified xanthate sludges, indicating that, for Cr, solidification of the xanthate materials offers no metal immobilization advantages.

91. Mercury. Desorption isotherms for mercury are shown in Figure 15. Xanthate appears to be effective in immobilizing Hg. As shown in Table 8, all the xanthate desorption data for Hg were fit by the no-release desorption

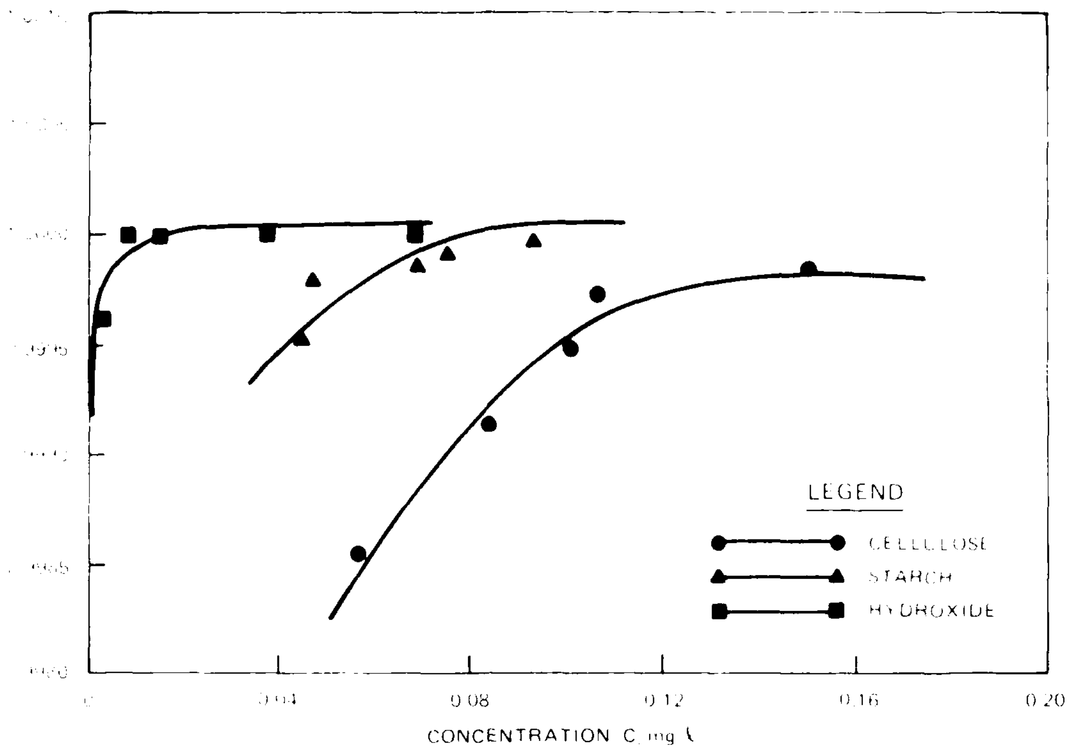

Figure 14. Chromium desorption isotherm for solidified starch, cellulose, and hydroxide sludge

model. The hydroxide sludge is the only material that had release of Hg, and these data were fit by the linear isotherm model.

92. The linear model generates two coefficients, qr/qo and k/qo . The linear coefficient qr/qo indicates the portion of contaminant that is resistant to leaching. Thus, the larger qr/qo , the larger the reduction in contaminant release. The coefficient k/qo controls the slope of the line; the steeper the slope, the less the potential for leaching. Thus, larger values for k/qo are indicative of lower contaminant releases.

93. The value for qr/qo for the solidified hydroxide sludge is 5.8 times larger than the qr/qo for the unsolidified hydroxide sludge. This indicates that the fraction of leachable Hg in the unsolidified hydroxide sludge is 5.8 times that in the solidified hydroxide sludge. While generally large values for k/qo indicate lower Hg releases, this is not true for these desorption data. Figure 15 indicates when large Hg concentrations are observed in the solid phase, $q/qo > 0.90$, the unsolidified hydroxide sludge will produce leachate with lower Hg concentration than the solidified hydroxide sludge. For $0.85 \leq q/qo \leq 0.90$, the solidified hydroxide sludge

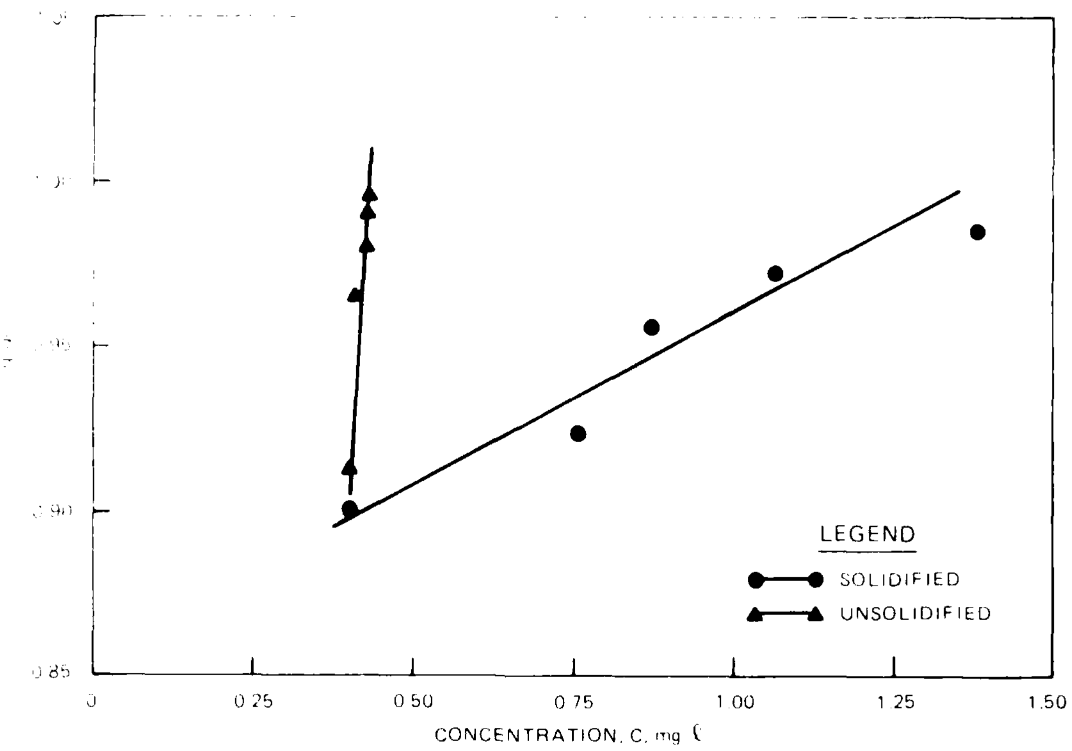

Figure 15. Mercury desorption isotherms for solidified and unsolidified hydroxide sludges

generates less contaminated leachates, and for q/qo < 0.85 the solidified material does not leach Hg while the unsolidified material does. Thus, when many pore-volumes of water pass through the sludges, the solidified hydroxide sludge will leach less Hg than the unsolidified hydroxide sludge, although the solidified hydroxide sludge will produce leachate with higher initial Hg concentrations.

94. Nickel. Desorption isotherms for nickel are shown in Figure 16. As indicated in Table 8, nickel release from the solidified cellulose xanthate, solidified hydroxide, and unsolidified hydroxide sludges was modeled by the no-release isotherm, indicating effective immobilization of Ni. The unsolidified cellulose xanthate, unsolidified starch xanthate, and solidified starch xanthate did not completely reduce the leaching potential for Ni; thus, contaminant release was modeled using the Freundlich model.

95. For the treatment processes studied, the Freundlich coefficient, k/qo, is approximately equal to 1.0 and thus has little effect on the model's shape. The Freundlich coefficient, n, is the controlling coefficient and is used to indicate Ni leaching for this system. As indicated by Figure 16,

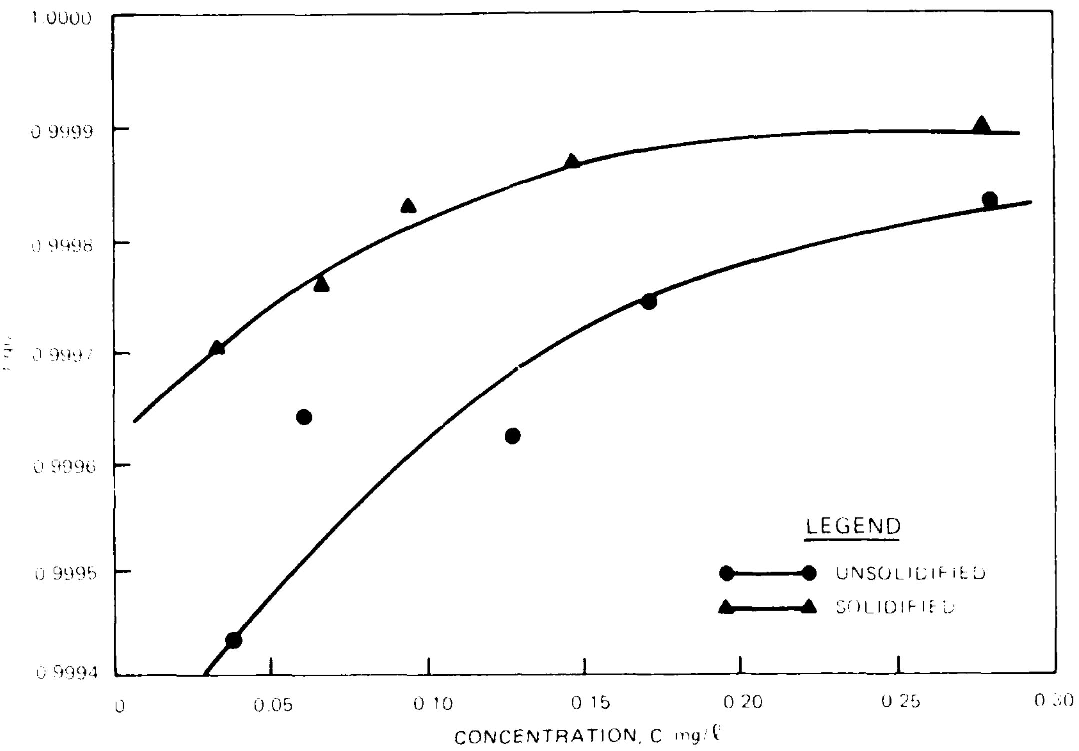

Figure 16. Nickel desorption isotherms for solidified and unsolidified starch sludge

larger values for n are indicative of the more effective treatment processes. Thus, solidified starch xanthate, with n = 10,223 , is approximately 1.8 times as effective in immobilizing Ni than the unsolidified starch xanthate with n = 5,762 . Unsolidified starch is approximately 41 times more effective than the unsolidified cellulose sludge in reducing the leaching of Ni.

96. As shown in Figure 16 (the nickel data for the solidified and unsolidified starch xanthate), at a q/qo of 0.99975, the concentration of Ni in the leachate is 0.06 mg/ℓ for the solidified sludge and 0.18 mg/ℓ for the unsolidified sludge. Thus, for a q/qo of 0.99975, the solidified starch xanthate sludge is three times more effective in reducing the potential for leaching than the unsolidified starch xanthate.

97. <u>SGBEP summary.</u> In summarizing the results of the SGBEP, it appears as though only small amounts of the contaminants leached from any of the sludges. Mercury was the only contaminant for which cellulose and starch xanthates reduce leaching more effectively than the hydroxide sludges.

Generally, the hydroxide sludges were as effective in reducing the leaching of Cd, Cr, and Ni as the cellulose and starch xanthate sludges.

98. Solidification of the cellulose xanthate, starch xanthate, and hydroxide sludges generally reduced the potential for metals to leach from the sludges. Chromium is the only contaminant where mobility increased after the sludges were solidified.

PART IV: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

99. A laboratory study was conducted to investigate the heavy metal leachability of sludges produced using cellulose and starch xanthate precipitation methods and to evaluate the effects of solidification on these sludges. Results from physical and chemical tests conducted on the solidified and unsolidified xanthates were compared to results from tests conducted on the solidified and unsolidified hydroxide sludges. Based on the results of these tests, the following conclusions can be drawn.

- a. Solidification, in most cases, appeared to reduce the leachability of the heavy metals. Starch and cellulose xanthate sludges passed the EP test after being solidified.
- b. Under neutral leaching conditions, solidification of the xanthate and hydroxide sludges increased the mobility of chromium.
- c. Starch and cellulose xanthates/metal complexes appear to be more effective in reducing the leaching of metals than metal hydroxides.
- d. Starch xanthate was more effective than cellulose xanthate in reducing the leaching of metals.
- e. Less cement would be required to solidify a starch or cellulose xanthate metal sludge than would be required to solidify an equal weight of a hydroxide metal sludge.

Recommendations

100. Starch and cellulose precipitation methods appear to be effective methods of removing and immobilizing heavy metals. Because this study addressed only the metal immobilization potential of xanthates, additional research should be conducted to address the following topics:

- a. The long-term physical and chemical stability of xanthates and their potential for biodegradation.
- b. The compatibility of xanthates with other solidification agents (e.g., lime/fly ash).
- c. The effectiveness of xanthates in immobilizing other heavy metals not studied in this investigation.
- d. The potential for the delisting of xanthate sludges as a hazardous waste.

e. The economics of full-scale application of xanthate precipitation techniques.

f. The potential for selectively removing and recovering metals from wastewaters by using xanthates.

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