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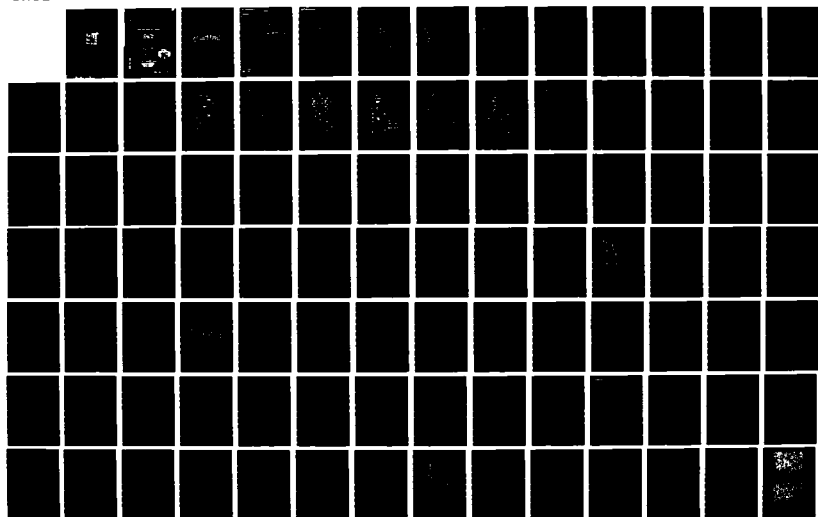
PLATING WASTE SLUDGE METAL RECOVERY(U) AMAX EXTRACTIVE
RESEARCH AND DEVELOPMENT INC GOLDEN CO H T HEPWORTH
30 MAY 85 AMAX-6921 AMXTH-TE-TR-85015 DRAK11-84-C-0045

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution Unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) AMXTH-TE-TR-85015		
6a. NAME OF PERFORMING ORGANIZATION AMAX Extractive Research & Development, Inc.		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION U. S. Army Toxic and Hazardous Materials Agency	
6c. ADDRESS (City, State, and ZIP Code) 5950 McIntyre Street Golden, CO 80403		7b. ADDRESS (City, State, and ZIP Code) Attn: AMXTH-TE-D Aberdeen Proving Ground, MD 21010-5401			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. DAAK11-84-C-0045	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO. 61102	PROJECT NO. AH68	TASK NO. P-14	WORK UNIT ACCESSION NO. B-13
11. TITLE (Include Security Classification) PLATING WASTE SLUDGE METAL RECOVERY (U)					
12. PERSONAL AUTHOR(S) Hepworth, Malcolm T.					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM May 84 TO May 85		14. DATE OF REPORT (Year, Month, Day) 1985 May 30	
15. PAGE COUNT 92					
16. SUPPLEMENTARY NOTATION <i>From OVER</i>					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Plating Sludge, Metals, Recovery.		
			Acid Leach, Separation.		
			EP Toxicity, Extraction.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
The U. S. Army Toxic and Hazardous Materials Agency has requested that AMAX Extractive Research & Development, Inc. conduct a five-phase program to review the literature on the current state-of-the-art in metal recovery from plating wastes, to propose a typical plating sludge composition and aging treatment (in lieu of actual U. S. Army plating wastes), to develop a research and design test plan for treating this typical plating sludge, to conduct the test program, and to summarize the results in a final report. The final report proposes a sulfuric acid leach of hydroxide plating sludges, containing copper, cadmium, zinc, nickel, iron, and chromium, to extract greater than 99 percent of the heavy metal values, followed by lime treatment of the resulting filter cake to render it nonhazardous to EP testing. The sulfuric acid leach extract may be treated by selective sulfide precipitation at a controlled pH regime in order to produce					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL David E. Renard			22b. TELEPHONE (Include Area Code) 301-671-2054		22c. OFFICE SYMBOL AMXTH-TE-D

Block 19

a mixed sulfide of copper and cadmium with most of the zinc present in the original extract separate from a leach liquor containing more than 98 percent of the chromium, which does not form a sulfide precipitate. Nickel and iron are not selectively separated under the sulfide precipitation conditions. However, a solvent extraction process using di(2-ethyl-hexyl) phosphoric acid can be used for recovering nickel, iron, and chromium from the resulting filtrate. *Originator-supplied keywords:*

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ABSTRACT

The U. S. Army Toxic and Hazardous Materials Agency has requested that AMAX Extractive Research & Development, Inc. conduct a five-phase program to review the literature on the current state-of-the-art in metal recovery from plating wastes, to propose a typical plating sludge composition and aging treatment (in lieu of actual U. S. Army plating wastes), to develop a research and design test plan for treating this typical plating sludge, to conduct the test program, and to summarize the results in a final report.

This final report proposes a sulfuric acid leach of hydroxide plating sludges, containing copper, cadmium, zinc, nickel, iron, and chromium, to extract greater than 99 percent of the heavy metal values, followed by lime treatment of the resulting filter cake to render it nonhazardous to EP testing. The sulfuric acid leach extract may be treated by selective sulfide precipitation at a controlled pH regime in order to produce a mixed sulfide of copper and cadmium with most of the zinc present in the original extract separate from a leach liquor containing more than 98 percent of the chromium, which does not form a sulfide precipitate. Nickel and iron are not selectively separated under the sulfide precipitation conditions. However, a solvent extraction process using di(2-ethylhexyl) phosphoric acid can be used for recovering nickel, iron, and chromium from the resulting filtrate.

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INTRODUCTION

The U. S. Army Toxic and Hazardous Materials Agency has requested that AMAX Extractive Research & Development review the current state-of-the-art in metal recovery from existing plating waste sludges. The Army has stated in their solicitation for this contract that separation and recovery will become advantageous in the future, with the present time being the appropriate period to consider technology development. We believe that the Army will set the pace regarding what can be done to recycle potentially valuable and strategic metals, such as chromium, for which there is essentially no commercially viable domestic source. Plating wastes represent a significant stockpile of metal values which may be of strategic significance. Furthermore, by developing the requisite technology for utilization and detoxification of plating wastes, the Army will be developing the technology which will enable smaller plating businesses to recover and process potentially valuable sludges.

The program, as originally outlined (Solicitation DAAK11-84-0015, December 5, 1983), divided the effort into five phases:

- Phase I - Literature Review
- Phase II - Army Survey Review
- Phase III - Research and Design Test Plan
- Phase IV - Experimental Procedure and Analysis
- Phase V - Technical Report

It was the intention in Phase II to examine typical Army plating sludges; however, this was not possible. In lieu of this, a typical estimated aggregate of electroplating sludge compositions was agreed upon by discussion of the sponsor as part of Phase III - Research and Design Test Plan. This technical report (Phase V) summarizes the program as described in the original solicitation.

PHASE I - LITERATURE REVIEW

Phase I of the project "Plating Waste Sludge Metal Recovery Mechanisms" (DAAK11-84-R-0015) requires a search of the literature to build a base of knowledge on the current status of generation and treatment of waste sludges from plating operations. Initially, a computer search of several data bases (chemical abstracts, Dialog, etc.) was done to locate publications covering the subject within the past 15 years. Key words used in the search were sludge, hydroxide, plating, and recovery. Initially, only hydroxide sludges were considered, since 22 of the 23 installations described in the report "Plating Wastes Survey" produce this type of sludge, while the other installation produces a sulfide sludge.¹ In the initial search, approximately 100 citations were found relating to recovery of metals from hydroxide sludges from plating installations. In addition to this initial search, a published search from the National Technical Information Service (NTIS) was obtained which listed 304 citations covering the years 1970 to 1983 with regard to "Metal-Containing Liquid Wastes".² Due to the number of citations found in these initial searches dating back to only 1970, it was decided not to intentionally search the literature prior to this date. Instead, appropriate publications, books, and conference proceedings from this 15-year period were ordered, collected, and categorized for use as the technical information base for the project. Once these articles were received, they were reviewed for pertinent information, and the references contained within them were used to order additional articles, if warranted. At the time of this writing, numerous publications from journals and conference proceedings, as well as government reports and reference books, have been collected and categorized.

Many hundreds of studies relating to treatment of waste streams have been conducted. However, studies on pretreatment or treatment of the resulting sludges, especially plating sludges, have not been so numerous. Indeed, treatment methods involving sludge dissolution with resultant metal recovery appear to have received less emphasis in the past because of unfavorable economic considerations. Relatively inexpensive disposal costs have precluded development and installation of methods or processes aimed at metal recovery from sludges. However, as disposal costs continue to rise and as concern for solid waste pollution of the environment grows, the incentive to recover and recycle metal values from solid wastes will increase. As a result, dissolution and recovery processes may become viable when all factors are considered.

After searching the available literature, a convenient method of classifying the articles became apparent. Many publications or books dealt with solid waste disposal in relatively general terms and could readily be classified as reviews of current technology in this area. Other studies were aimed at characterizing sludges in order to understand variables effecting sludge generation so that improvements to the sludge-producing process could be made with a resultant decrease in sludge generation. In some instances, sludge was recycled. Finally, the studies of greatest interest with regard to the current project dealt with methods for dissolving and recovering metal values from sludges, although many interesting processes are applied to sludges that are not plating wastes. It should also be understood that although most studies or reviews can conveniently fit into one of these three classifications, some of the studies could easily

fit into all three categories, or two of the three categories. A summary of the more important articles collected, as they fit into one of the three categories, follows.

REVIEW ARTICLES

Review articles appeared in journals or government reports,³⁻¹² conference proceedings,¹³⁻¹⁴ and books.¹⁵⁻²⁰ A very thorough review of waste management on a worldwide basis is published as a committee report.²¹ This study, which was conducted by a NATO committee, surveys the Federal Republic of Germany, France, the United States of America, Canada, The Netherlands, and the United Kingdom with respect to the production and treatment of plating wastes. It tends to treat individual metals separately, rather than as mixed sludges from several plating operations. Although the information contained in any of the publications may vary due to completeness of technology description and with regard to publishing date, the articles follow a general pattern of presentation. The publications, government reports, or conference proceedings generally begin with an introduction to the problem of waste management with reference made to generation of hazardous waste as defined by the government. For publications since 1980, the Federal Register of May 19, 1980, is most often used.²² Guidelines for disposal of waste are usually set forth, and estimates of either the number of plants in the United States producing plating sludge or of the weight of sludge produced are usually stated to give the reader an idea of the extent of this problem. The article or publication then proceeds to review the current methods for sludge treatment or disposal divided into categories. These categories may often include: 1) physical treatment, such as filtration, to reduce sludge volume, 2) thermal treatment, such as incineration or calcination, to reduce sludge volume and possibly transform the sludge from hazardous to nonhazardous, 3) chemical treatment, such as digestion with acid, to recover and recycle metals or to render the sludge nonhazardous, 4) encapsulation or fixation in order to immobilize toxic metal ions with regard to leachability by groundwater, and 5) landfilling applications which may be the primary method of disposal or may follow any of the above pretreatment methods. Reference is then made to particular industrial applications employing any of these processes or to laboratory or pilot-scale studies that may warrant development of a new process. The primary difference between journal articles and books is the depth of discussion. Obviously, in books, whole chapters can be devoted to a single process or treatment of a specific sludge; whereas in journal articles, the descriptions are significantly condensed.

ARTICLES ON PROPERTIES OF SLUDGES

Studies have been done to investigate the effects of mixed metal hydroxides compared to single metal hydroxides with regard to sludge stability.²³ The effects of sludge aging on metal extraction and proposed mechanisms for aging have also been enumerated.²³⁻²⁵ Several studies have correlated plant operations with physical properties of sludges in order to decrease production of sludges.²⁶⁻²⁹ Variables such as pH of precipitation, effect of rinsing, type of precipitant, as well as other parameters, have been investigated in order to reduce generation of sludges. In one study, use of a proprietary filter decreased sludge volume due to better dewatering not attainable with other filters;³⁰ while in another study, sludge was recycled in filtering operations for

several days prior to discharge in order to increase percent solids of the final sludge.³¹ Another study investigated optimum dewatering techniques;³² while in another study, chemical additives were used to improve sludge dewatering.³³ All of the studies' goals were aimed at decreasing sludge volume through characterization of the sludge and by using better physical means of dewatering or sludge compaction.

ARTICLES ON PROCESSING SLUDGES

The final category for many of the articles collected is the one of greatest interest to the current project. This category lists articles dealing with dissolution of sludges and resultant metal recovery. Two excellent books are available from the Noyes Data Corporation that deal with waste processing.^{35,36} The first of these is an encyclopedia arranged alphabetically according to inorganic compound or metal recovery from wastes.³⁵ Processes are described for recovery of chromium, zinc, cadmium, nickel, copper, tin, and other metals from various process wastes. This work is a compilation of many known processes and provides excellent references. The second book is divided into specific processes for treatment of waste effluents (both solid and liquid).³⁶ Chapters are written that cover processes such as adsorption, calcination, and dissolution. Also included are economic comparisons of the various processes. This publication is a valuable comparative reference source.

Publications are available that describe sludge dissolution by acids³⁷⁻⁴³ and bases.⁴⁴ Emphasis in these studies is placed primarily on factors affecting dissolution, such as pH, temperature, acid type (or base type), and percent solids. Once the metal is solubilized, metal recovery can be accomplished by many standard processes now in use, such as activated carbon⁴⁵ and membranes.^{46,47} However, solvent extraction as a means of metal recovery from dissolved wastes is receiving the greatest attention.⁴⁸⁻⁵³ In one study, an organic acid solvent was used to dissolve the sludge instead of an inorganic acid.⁵³ In a new handbook of solvent extraction, two chapters are devoted entirely to solvent extraction applications in waste metal recovery.⁴⁸ This book is also a valuable reference source.

Finally, several studies have been devoted to not only investigating metal dissolution from sludges but also investigating metal recovery from these solutions by solvent extraction, cementation, precipitation, etc.^{48,54-58} In some of these studies, integrated processes are proposed for specific waste solids.^{48,56,57} Of particular interest is a report to the Environmental Protection Agency by a team at Montana College of Mineral Science and Technology.⁵⁴ In this report, a metal hydroxide sludge containing iron, copper, chromium, nickel, zinc, and cadmium was readily leached with sulfuric acid in the pH range of 0.5 to 1.5 with greater than 95 percent extraction of the metallic constituents within 30 minutes at 25°C. The subsequent recovery steps for each of the valuable metallic constituents by solvent extraction follows a jarosite precipitation of iron.

PHASE IV - EXPERIMENTAL PROCEDURE AND ANALYSIS

The experimental procedure and analysis follows the outline presented in the previous section of this report.

PREPARATION, AGING, AND CHARACTERIZATION OF METAL HYDROXIDE SLUDGES

Objective

Prepare a plating sludge which will, insofar as possible, simulate United States Army hydroxide plating wastes for subsequent use in the following sections of this program.

Experimental Procedure

A sludge similar in composition to an EPA estimated aggregate plating sludge⁶ was produced by lime addition at pH 9.0 to a sulfate solution of the analysis shown in Table 1. A quantity of stock solution (120 liters) was prepared by dissolution of reagent grade chemicals. The hydrated chromium sulfate salt was prepared separately by grinding to a powder, dissolution in a small quantity of hot water (90°C), and adding that solution to the stock solution. This procedure was necessary because of the extremely slow rate of dissolution of trivalent chromium sulfate salts.

Table 1. Estimated Aggregate of
Electroplating Sludge Compositions⁶

<u>Compound</u>	<u>Dry Weight, %</u>	<u>Metal</u>	<u>Dry Weight, %</u>
Cu(OH) ₂	12.3	Cu	8.0
Cr(OH) ₃	14.8	Cr	7.5
Ni(OH) ₃ *	39.1	Ni	21.0
Zn(OH) ₂	17.1	Zn	11.0
Cd(OH) ₂	1.7	Cd	1.0
Impurities**	<u>15.0</u>	"Non-Metals"***	<u>51.5</u>
Total	100.0	Total	100.0

* Although nickel is reported as trivalent by this reference, this species is not stable in equilibrium with trivalent chromium.

** Primarily as calcium as mixed hydroxide and sulfate.

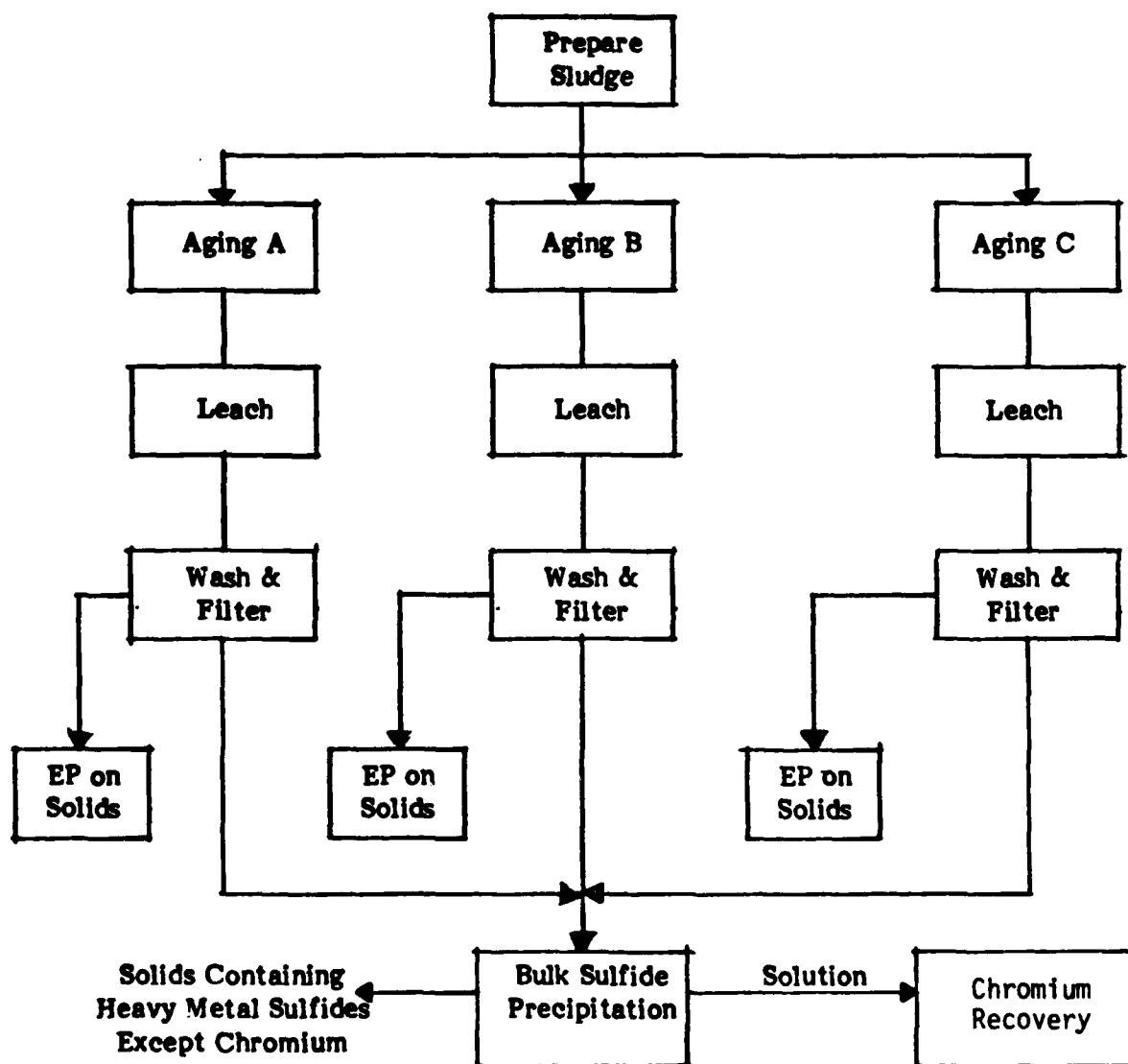


Figure 4. Flow diagram of plating sludge metal recovery test program (sulfide precipitation route).

OUTLINE OF TEST PROGRAM

The test program is divided into several steps as shown in the process flow diagram shown in Figure 4. These major steps are:

1. Preparation, Aging, and Characterization of Metal Hydroxide Sludges
2. Leaching of Sludges and Characterization of Leach Residues (Filter Cakes)
3. Extraction Testing on Filter Cakes from Sulfuric Acid Leaching of Metal Hydroxide Sludges
4. Separation of Metals by Sulfide Precipitation

The emphasis in this Research and Design Test Plan covers as many of the process steps as possible in order to answer basic questions as follows:

- For an aggressive sulfuric acid leach, does a prior aging history significantly affect the leach kinetics and recovery?
- Upon leaching, can a residual gypsum cake be made sufficiently inert by washing and pH adjustment to yield a waste which can be readily discarded?
- Can a bulk sulfide separation of heavy metals from chromium be effected or is a more complex scheme of separation by solvent extraction required?

Once these basic questions are answered, then more specific and intensive attention can be given to the individual steps in order to optimize them with respect to efficiency and scale-up. These details would require more effort and time than is available in the present study.

PHASE III - RESEARCH AND DESIGN TEST PLAN

In the prior two phases, several alternative approaches to extraction and recovery have been described in the flowsheets in figures 1a, 1b, 2 and 3. These included ammonia and caustic leaching which were selective for certain species. However, the prior history of the sludge with respect to its aging or syneresis has a pronounced effect upon the selectivity of leach and leach kinetics. Since we will of necessity be working with synthetic sludges and eventually with sludges from a variety of installations, a preferred type of leach would be an aggressive leach which does not depend, to a significant extent, on prior sludge history. A sulfuric acid leach has the following potential advantages:

1. Sulfuric acid is, on an equivalent basis, the least expensive reagent as compared with caustic or ammonia. The latter can be recovered by a distillation process, but the distillation stage represents an additional unit operation to the total process.
2. The starting plating solutions from which the sludges were originally formed were sulfates. The sludges, therefore, are made up of metal hydroxides and gypsum. A sulfuric acid leach has no effect on gypsum, which tends to be the major constituent and returns the heavy metals to a mixed-metal leach liquor, having sulfide as the common anion.
3. The heat effect of both dilution of concentrated sulfuric acid and the heat of reaction between the acid and basic hydroxides can serve to accelerate the leach kinetics without additional heating requirements.
4. The two recovery schemes which follow (bulk sulfide precipitation and solvent extraction) require an acid pH.
5. Stagewise leaching with countercurrent flow of solids and acid can be employed to minimize acid addition and maximize washing of the gypsum cake. Caustic or ammonia leaching tends to be incomplete, and the gelatinous nature of ferrous or ferric hydroxides tends to be a "sponge" for heavy metals. Therefore, in these later leach schemes, an inert residue devoid of the potential for further environmental leaching is probably not possible.

GOALS OF EXPERIMENTAL PROGRAM

Effort is directed towards a generally applicable leach process which is inexpensive and which produces an inert leach residue which will pass the EPA Extraction Procedure (Appendix A). Furthermore the leach liquor should be processed in such a manner so as to separate chromium, nickel, and iron from copper, cadmium, and zinc. The former three elements (Cr, Ni, and Fe) are basic constituent metals of stainless steels and may be reprocessed as such or reused in plating applications after further separations. The latter three elements (Cu, Cd, and Zn) are separable in copper refining operations and are readily precipitated as sulfides.

In each of the above schemes, a secondary sludge is generated. Presumably this sludge will be much more compact and will be in the nonhazardous category. Unless the secondary sludge is highly crystalline, it will inevitably contain some heavy metals. The presence of excess lime and/or calcium carbonate may be sufficient for it to pass the EPA leach test. Particular attention will be devoted to an examination of this secondary waste.

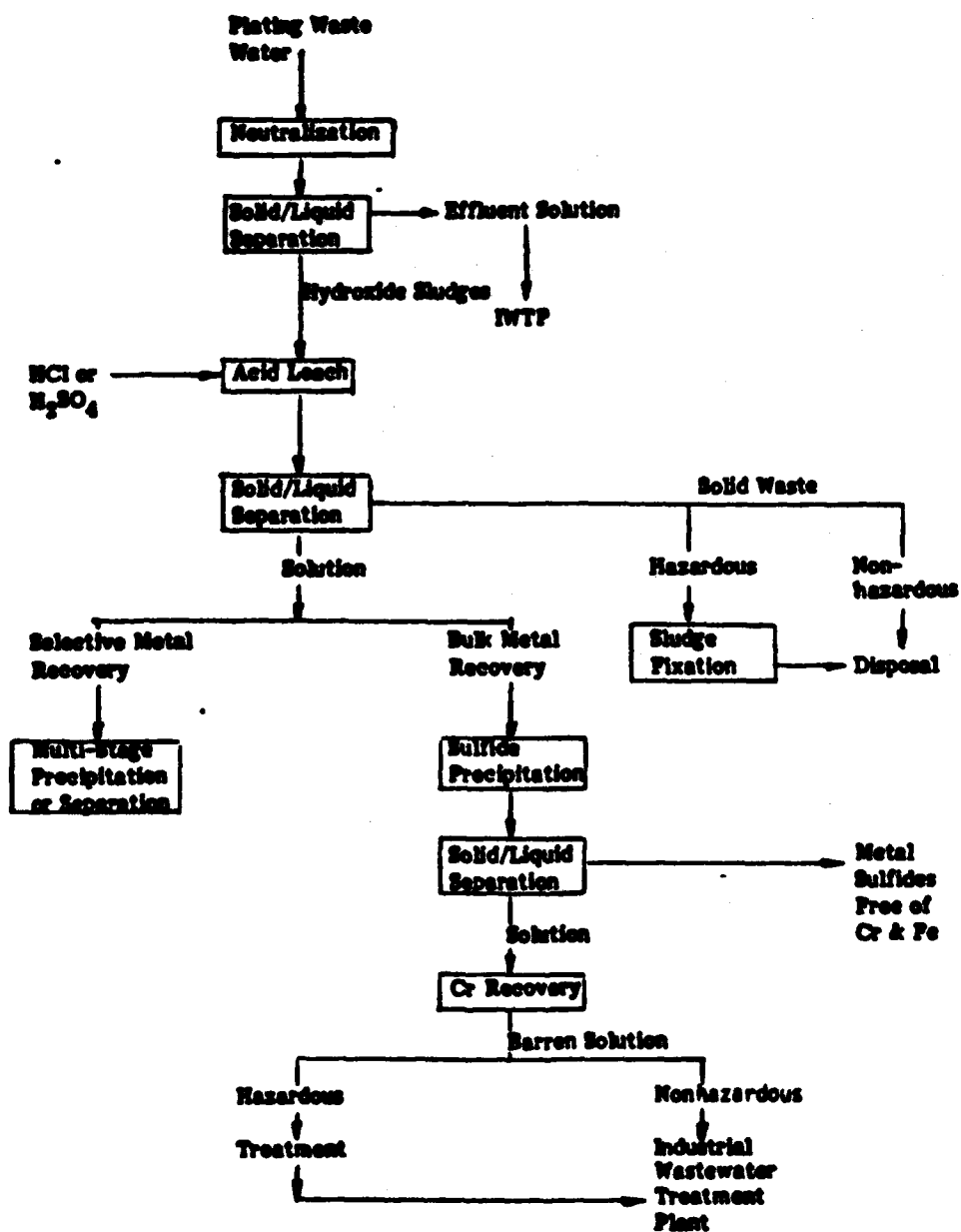


Figure 3. A conceptual flowsheet for acid leach of hydroxide sludge.

properly controlled, it may be possible to leach the amphoteric element, zinc, selectively. This prior history may require calcination under neutral or slightly reductive conditions to convert soluble hydroxides to more inert oxides. If this calcination step is necessary, then the overall process economics may eliminate this process, as compared with other approaches. Following the extraction of zinc, aqueous air oxidation or more expensive peroxides can be used to promote the formation of dichromate, which is then readily soluble in caustic. These steps would be studied. Following the caustic dissolution, acidic dissolution of the solids would be conducted in a manner similar to that described under the sub-heading "Acid Leach" below. If a chrome/zinc separation by control of oxidation potential is not feasible, then the flow diagram outlines two alternative approaches for treating the leach liquor containing zinc and chromium. Since the initial starting sludge contains chromium and zinc not far from the atomic ratio of 1 to 1, production of zinc chromate (ZnCrO_4) may be a possibility.

Acid Leaching

This approach, as illustrated in Figure 3, is the most straightforward and generally applicable approach, as it provides an aggressive solvent (sulfuric acid preferred) which solubilizes most of the species except calcium (and lead, if present). It avoids formation of gelatinous precipitates which may be associated with recently precipitated plating solutions, especially those containing iron. Such precipitates are, of course, hard to wash and filter. Sulfuric acid is a preferred reagent because of its lower cost to hydrochloric acid, its compatibility with equipment, its low volatility because it forms, sparingly, soluble calcium sulfate and also because it is not consumed by the gypsum present. For plating wastes containing lead, however, hydrochloric acid may be preferred. If an iron rejection step is desired, countercurrent leaching under controlled conditions of pH with added sodium sulfate can be used to reject iron in the form of jarosite. For the purposes of this proposal, however, an aggressive single-stage leach may be desirable in order to minimize retention time of leaching and assure complete solubilization of all species but calcium. Since the remaining solids have already been subjected to a highly aggressive leach, they should be sufficiently inert upon further liming to pass the EPA leach test. This point will be verified.

Following the acid leach step, two schemes for treatment of the solution are shown, namely, selective metal recovery and bulk metal recovery. The former uses multistage sulfide precipitation of copper, cadmium, zinc, and nickel from iron and chromium by control of the solution pH. Alternatively, solvent extraction using pH control or several extractants yields a selective separation. The former treatment scheme yields a bulk sulfide precipitate of copper, cadmium, zinc, and nickel, while iron and chromium are left in solution again by proper control of solution pH. Chromium is then recovered from the solution. The bulk sulfide precipitates may be an acceptable feed to a metallurgical refinery; however, a determination would have to be made regarding their solubility.

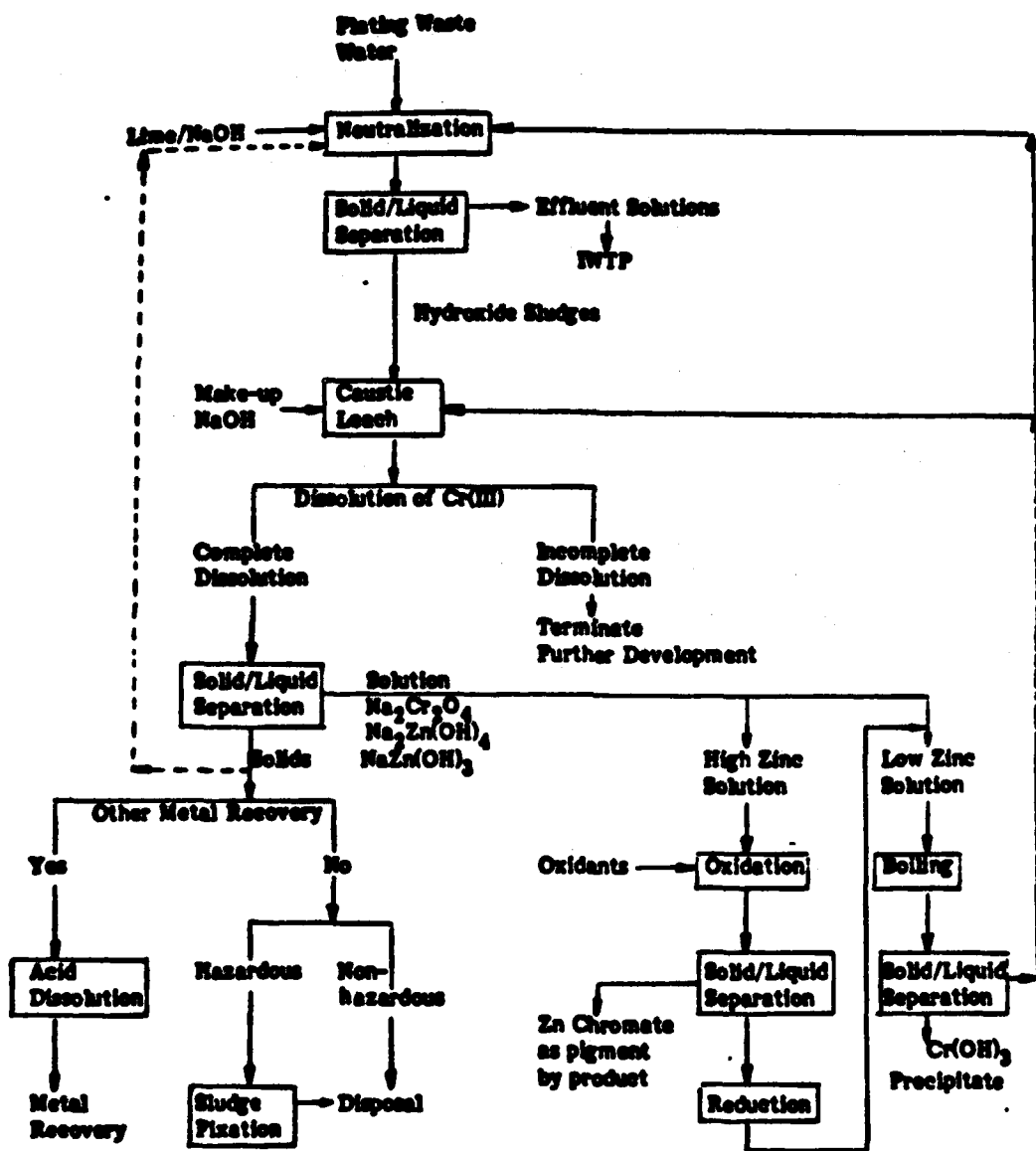


Figure 2. A conceptual flowsheet for caustic leaching of hydroxide sludge.



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solutions, but it is readily oxidized by such benign oxidants as air to the soluble dichromate species in the presence of added caustic. This step would require testing. The leach solution of sodium dichromate would then be crystallized for recovery of chromium. The washed sludge would require stabilization by a trace reductant, such as sulfur dioxide, to reduce any chromium present to the trivalent state. The pH of this secondary sludge would be adjusted to the range of 7 to 8 to minimize residual chromium solubility.

4. As an alternative to caustic leaching of the chromium from the sludge from Step 3 is an acid leach with sulfuric acid to produce the hydrated trivalent form $\text{Cr}(\text{H}_2\text{O})_6^{+++}$. This species can then be oxidized by hydrogen peroxide or other oxidant to the dichromate form, followed by ion exchange² with tertiary amines dissolved in aromatic kerosene.
5. A variation of the acid leach described in Step 4 is electrooxidation of trivalent chromium solutions in a cationic membrane cell¹³ to separate the dichromate cation ($\text{Cr}_2\text{O}_7^{=}$) from other cations. By recycle of the acidic anolyte from the electrooxidation process to the acid leach, it may be possible to solubilize the sludge without added acid.
6. Sludge products would be produced from either steps 4 or 5. They would be an alkaline sludge consisting primarily of a mixture of calcium carbonate and calcium sulfate (Step 4) or an acidic sludge consisting primarily of calcium sulfate. They would require testing by the EPA prescribed leach procedure to determine whether they are nonhazardous, especially with respect to chromium and cadmium. Low temperature calcination and blending with added lime are remedies which may retard solubilization of heavy-metal oxides so that groundwater leaching (simulated by dilute acetic acid in the EPA test procedure) does not attack these oxides in preference to calcium carbonate and lime. Emphasis in our study will include the examination of mechanisms of groundwater leaching as simulated by the EPA leach procedure and techniques for rendering secondary sludges immune to attack.

A variation of the MAR process is shown in Figure 1b. This flowsheet is taken from a study by Battelle Laboratories⁶⁰ undertaken for the U.S. Environmental Protection Agency. A stage-wise leach with ammonium carbonate of dried sludges attempts a separation of an initial leach liquor which is copper rich and a secondary leach liquor which is nickel rich. This staged-leach process is sensitive to the prior history of the sludge and is dependent upon relative leach kinetics of copper and nickel.

Caustic Leaching

Figure 2 shows a conceptual flowsheet for caustic leaching of a hydroxide sludge. As was discussed earlier in the ammonia dissolution scheme, chromium in its trivalent state is not highly soluble in caustic and may exhibit slow dissolution kinetics under anaerobic conditions if its hydroxide or oxide is sufficiently crystalline because of aging. Accordingly, if the prior history of the sample and the leach conditions are

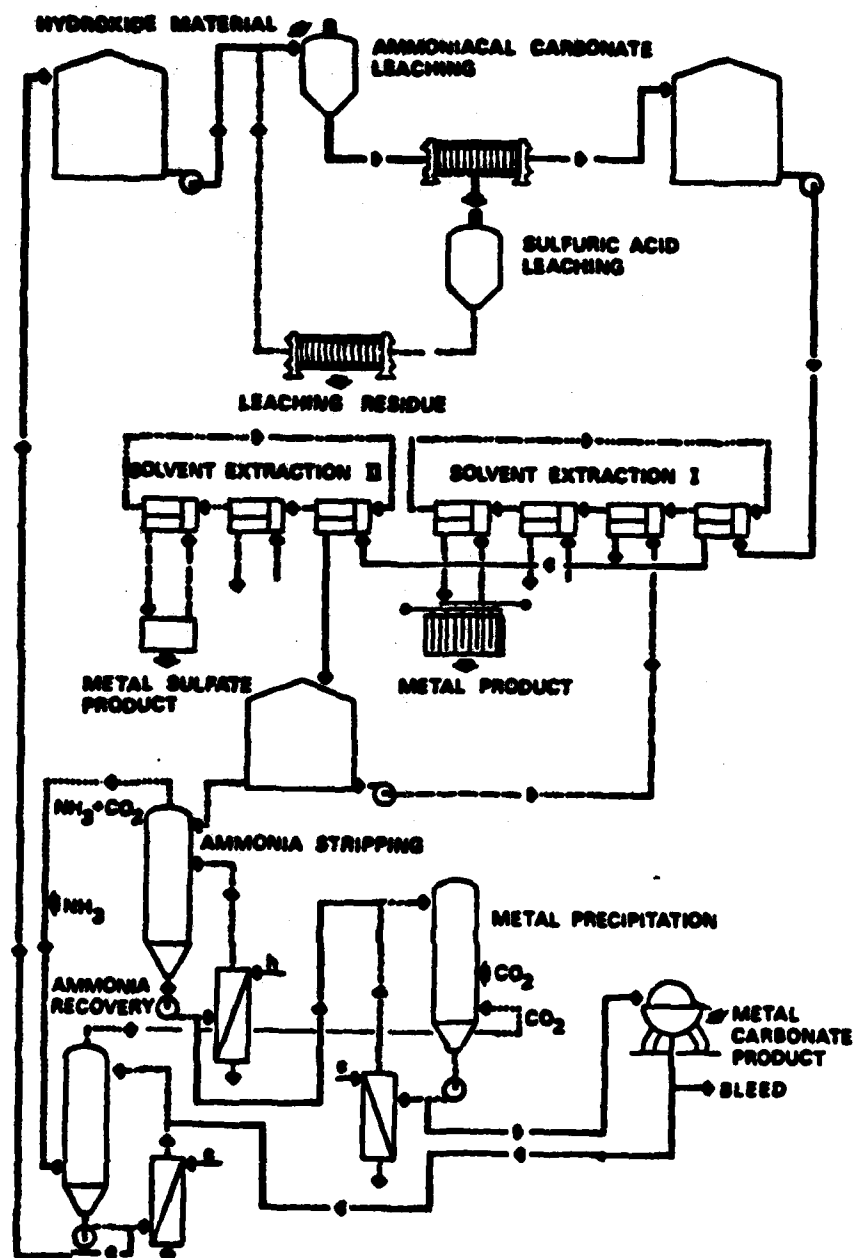


Figure 1a. Ammonia leach MAR⁴⁸ process.

this aging treatment, the sludge will be examined for moisture content, density, crystal structure, and morphology by optical and electron microscopy and by X-ray diffraction. The sludge would also be chemically analyzed.

POTENTIAL PROCESSES

This synthetic sludge would be the starting point for a test program aimed at determining critical steps in detoxification and recovery processes. The objective of such processes is to minimize the volume of secondary discard products (secondary sludges) and to render them inert to the EPA leach test for hazardous substances. Although three leaching operations are listed below (ammonia leach followed by acid or caustic leaching, caustic leaching, and acid leaching), it is not the recommendation of this program to pursue all three. Twidwell⁵⁴ indicates that sulfuric acid leaching yields high extractions of the heavy metal species. Since the residual solids from a sulfuric acid leach are, upon liming, apt to be relatively inert to the more benign conditions associated with the EPA leach test, we recommend that sulfuric acid leaching be the leach of choice for metal recovery. For the purpose of comparison, however, three leach methods are given below, namely ammonia leaching, caustic leaching, and sulfuric acid leaching.

Ammonia Leaching

This scheme effects separation of nickel, copper, zinc, and cadmium (metals which form strong amine complexes) from chromium and iron by selective leaching of these amine-forming elements with an ammonium carbonate/ammonia solution. This approach is a modified version of a process developed by the Swedish Company, MX-Processor, called the MAR Process.⁴⁸

The first two steps below are associated with the MAR Process; however, steps 3 and 4 are specific to the chromium-containing sludges which we expect to encounter.

1. Leach with an ammoniacal carbonate solution which leaves iron, chromium, and calcium as insoluble hydroxides. Nickel, copper, cadmium, and zinc are converted to soluble amine complexes (see attached Figure 1a).
2. The ammoniacal solution is then treated by solvent extraction to separate copper and nickel from zinc and cadmium. Copper may be reclaimed as the metal from the strip solution by electrowinning. The process of electrowinning consists of depositing copper from solution at the cathode in an electrolytic cell having an inert anode. Nickel could be recovered from its strip solution by crystallization as nickel sulfate. Zinc and cadmium can then be recovered by precipitation of the raffinate (i.e., the original leach liquor from which copper and nickel were removed by solvent extraction) as carbonates. This second step is relatively straightforward and may not require extensive study.
3. Additional steps are those associated with treatment of the remaining chromium-rich sludge. The chromite species $\text{Cr}(\text{OH})_3$ is only sparingly soluble in alkaline

remaining from a metal recovery operation must pass the EPA leach test (see Appendix A) for the hazardous elements of cadmium and chromium. Emphasis in our studies will be on chromium as the metallic element which is the most difficult to remove and recover of the listed species. Since electroplating wastes originate primarily from rinse solutions rather than disposal of plating bath solutions, we propose to produce a sludge by liming dilute solutions formulated to produce a sludge similar to that described above. However, since rinse baths generally contain sulfates, liming of these solutions will necessarily form a significant amount of gypsum as a coprecipitated compound, along with the metal hydroxides. Furthermore, iron should be included in any sludge to be treated, as its occurrence has been reported by Procko²⁶ in his studies on Air Force electroplating wastewater samples. Therefore, after recovery of the valuable constituents from sludges, one can expect that the secondary sludge will consist primarily of gypsum and iron hydroxide compounds.

We propose, therefore, based upon these considerations, to formulate a hydroxide sludge by lime treatment to pH 9 of an aqueous sulfate solution to produce a sludge of the approximate composition below:

<u>Compound</u>	<u>Dry Weight, %</u>
Cu(OH) ₂	7
Cr(OH) ₃	10
Ni(OH) ₂	7
Fe(OH) ₂	7
Cd(OH) ₂	1
Zn(OH) ₂	7
CaSO ₄	<u>61</u>
Total	100

Although chromium would normally be predominantly in the hexavalent state, for the purposes of simplicity the starting solution would be made up from chromium in its trivalent state. Also, Procko aged his sludges at room temperature for six weeks. A portion of the sludges produced could be so aged; however, an acceleration of the aging process is recommended as follows: upon filtering, the sludge would be stored in loosely-sealed containers for one week at 150°F to attempt simulation of storage in a landfill. This temperature and time is based upon an activation energy of about 13,000 calories per gram mole for the dehydroxylation of clays,⁵⁹ which represents a doubling of rate for every 10 degrees centigrade of temperature. Consequently, a one-week holding time at 150°F represents about a half-year of storage at ambient temperatures. This choice of temperature and time is only a starting point, which could be modified if preliminary tests indicated temperature and time were significant factors in the properties of the sludge. The goal of the aging treatment is to attempt to produce a sludge which is similar to one which has undergone ambient storage. After

PHASE II - ARMY SURVEY REVIEW

The U. S. Army Mobility Equipment Research and Development Command, Fort Belvoir, Virginia, has published a report, "Plating Wastes Survey", reviewing 23 Army operations involved in plating of various metals.¹ An examination of this report has indicated that the Army operations vary in size from about 100 gallons/day to about 200,000 gallons/day in terms of wastewater production, which upon neutralization generates sludge. The report does not give information on the metal assays of the waste streams, the tonnage of sludge produced, or the chemical composition of the sludge; however, it does establish a basis for selecting a sludge composition which is more or less typical. For example, 22 of the 23 sludges which are generated are hydroxides rather than sulfides. Also, cyanide is essentially absent because of prior oxidation to harmless cyanates, and furthermore, chromium generally has been reduced to the trivalent state and precipitated. Since the sponsor has indicated that it is not possible to execute Phase II (Army Survey Review) as originally planned, we intend to use the Plating Wastes Survey as the basis for establishing general parameters of sludge makeup.

The study by Procko²³ establishes some of the parameters associated with the mechanism of syneresis in the aging of plating sludges. He made up a synthetic wastewater according to an analysis of an Air Force electroplating wastewater sample which was considered typical of wastewaters from other DoD plating shops. This wastewater contained, in the order of decreasing concentrations, chromium, calcium, magnesium, iron, copper, cadmium, and nickel. This synthetic wastewater was then reacted with a reductant to reduce hexavalent chromium to the trivalent state, followed by precipitation with lime or caustic soda to a pH of 9. The sludge resulting from this precipitation process was then subjected to several aging treatments, including a six-week storage process at room temperature. The aging reduced the solubility of heavy metals to the EPA Extraction Test and to some degree simulates field conditions.

The approach of Procko in preparing a sludge from a synthetic solution and aging of the sludge will be the basis of our studies. The composition of the synthetic solution will be based on a sludge described by the EPA as "An Estimated Aggregate of Electroplating Sludge Composition". This sludge offers a broad spectrum of hydroxyl species as listed in the table below.

In the following section on "Potential Processes", we suggest a formulation based generally upon the above "Estimated Aggregate" to include iron in a mix of elements which should yield a sludge having properties similar to that generated in DoD plating practice.

DEVELOPMENT OF SYNTHETIC SLUDGE

Any detoxification and recovery process should be sufficiently flexible to treat a mix of elements at various stages of aging. At a minimum, any secondary sludge

In order to avoid formation of large inhomogenous masses of precipitate, the procedure for preparation of the sludge was as follows:

1. A lime slurry containing 10 percent by weight Ca(OH)_2 was maintained in suspension in a stirred feed vessel equipped with a peristaltic pump. The rate of delivery of the lime slurry was variable and controlled by an automatic titrator connected to a pH probe located in a 20-liter mixing chamber.
2. Twenty liters of deionized water were added initially to the mixing chamber, which was equipped with a 6.5 cm single-bladed impeller operated at 750 RPM. The mixing chamber was covered with a sealed lid to exclude air and equipped with an overflow to a 55-gallon tank to serve as a receiving vessel for the sludge.
3. The stock solution was then pumped at a constant rate of 10 ml/min into the vortex of the mixing vessel where it was combined with the lime slurry added at a variable rate to maintain pH control at 9.0. In practice, this rate was 2.5 ml/min.
4. The agitation rate was sufficient to maintain the solids in suspension so that a slurry of uniform concentration was discharged via the overflow to the 55-gallon settling chamber.
5. The system was operated continuously at 22°C for several days until an equivalent dry weight of nearly 24 kg of sludge was produced. The sludge was allowed to settle over a weekend without the need for addition of flocculants, since it formed large flocs naturally. The clear solution was then decanted, filtered to remove any trace solids, and submitted for analysis.
6. The sludge was then mixed, filtered, and weighed to determine the gross moist-cake weight.
7. A sample of sludge was then oven-dried at 110°C overnight to determine the moisture content and then submitted for analysis.
8. The remaining moist sludge was divided into three portions (A, B, and C) (see Figure 4) for subsequent aging. Portion A was stored in a tightly-sealed container for subsequent acid leaching (to occur within 1 to 2 days of preparation). Portion B was stored in a loosely-sealed container and placed in an oven held at 65°C for one week. Portion C was placed in an open container, covered with porous fabric, and aged at room temperature (22°C) for six weeks.

Experimental Results and Discussion

Table 2 shows the assays of starting solution, filtrate, and sludge filter cake. The predominant compound is calcium sulfate, as is expected. A discussion of the mineralogical properties of the starting sludge A and the two aged sludges B and C is given in Appendix B. The results can be summarized as follows:

Table 2. Preparation of Plating Sludge

	Assay							
	Cu	Cr	Ni	Fe	Cd	Zn	Ca	SO ₄ ⁻
Stock Solution	3.52 g/l	5.08 g/l	3.54 g/l	3.41 g/l	0.440 g/l	3.88 g/l	—	—
Filtrate	0.10 ppm	0.055 ppm	<0.014 ppm	0.03 ppm	0.06 ppm	0.042 ppm	665 ppm	—
Filter Cake ¹ (Dry Basis)	3.55%	5.09%	3.42%	3.28%	0.460%	3.92%	15.8%	29.5%

¹ 43.8% solids as produced. Assays on dry basis.

X-ray diffraction analysis shows the metal hydroxides to be amorphous. Two crystalline phases, isomorphs, of calcium sulfate were identified: bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum converts to the hemi-hydrated bassanite at elevated temperatures; whereas at lower temperatures, gypsum is the stable phase. The three leach residues can be categorized as follows:

Type A (No Aging)

This sludge contains amorphous metal hydroxides and coarser-grained, needle-like crystals of bassanite. The moisture content was 56.2% by weight.

Type B (Seven Days Aging at 65°C)

This sludge contains amorphous metal hydroxides and a trace of gypsum. The moisture content was 6.6 percent by weight.

Type C (Six-Weeks Aging at 22°C)

This sludge contains amorphous metal hydroxides and gypsum crystals. The moisture content was 12.4 percent by weight.

Type C sludge is probably more characteristic of actual plating sludges which have been aged in a natural environment. The free moisture is slowly incorporated into the calcium sulfate as water of crystallization converting the hemi-hydrated form bassanite into the stable form of gypsum with two waters of hydration. The reduced free moisture content of Type C over Type A is partly due to this conversion and partly due to evaporation in dry laboratory conditions. Conversion to gypsum may even be accelerated when moist conditions are present (exposure to rain).

As will be discussed subsequently in the section on leaching, Type B sludge, which was heated and artificially aged, exhibited poor filtration characteristics after sulfuric acid leaching. This is probably a result of the many nuclei of gypsum which were present. These nuclei of gypsum form many fine crystallites, a situation not experienced in Type C sludge, where sufficient time has elapsed for large crystals of the stable gypsum phase are allowed to form.

2. LEACHING OF SLUDGES AND CHARACTERIZATION OF LEACH RESIDUES (FILTER CAKES)

Objective

The objective of the leach procedure is to maximize the recovery of the valuable metal species and produce a secondary leached filter-cake which has a low solubility of heavy metals, especially cadmium and chromium.

Experimental Procedure

Plating sludges of uniform composition but different aging histories, as described in the previous section, were used as solid feeds to the sulfuric acid leaching tests. Five leach tests were performed as follows:

<u>Test No.</u>	<u>Cake Type</u>
1	A (No Aging)
2	A (No Aging), duplicate of Test 1
3	B (7-Days Aging at 65°C)
4	C (6-Weeks Aging at 22°C)
5	C (6-Weeks Aging at 22°C), more aggressive washing than Test 4

Samples of each plating sludge were dried at 110°C overnight to determine the moisture content. In a given test, the moist sludge, as-received, was pulped with deionized water to a pulp density ranging between 20 to 30 percent solids by weight after correction for the interstitial water was made. A measured volume (somewhat less than 1 liter) of the slurried pulp was transferred to a stirred 2-liter reactor (kettle equipped with baffles and a 6.5 cm long, single-bladed impeller-agitator, operated at 750 RPM). An initial sample of slurry was taken to verify the pulp density by weight measurement before and after drying. The dry solids were assayed for Cu, Cr, Ni, Fe, Cd, Zn, Ca, and $\text{SO}_4^{=}$ (see Appendix C for assay procedure).

Timing of the actual leach commenced upon addition of sufficient concentrated (96.5 percent) sulfuric acid in order to bring the solution pH (corrected for the temperature elevation) to 1.5. The sulfuric acid was added from a graduated pipette to maintain this pH during the test. In practice, it was found that the acid requirement for cake dissolution was essentially satisfied in 10 minutes for all tests. After 30 minutes of contact, the volume of acid which was added was noted, and an additional 10 percent acid was added. The pH drop was noted. Ten-milliliter samples of slurry were withdrawn at intervals of 15 minutes after withdrawing a 30-minute sample. These samples were filtered and submitted for assay. After 90 minutes from the initial acid addition, the test was terminated and the kettle contents transferred to a Buchner funnel filtration apparatus.

During the test, the temperature was noted, rising during sulfuric acid addition and essentially being maintained constant within a few degrees centigrade by kettle insulation. At the end of the test, two 250-ml portions of 0.1 normal sulfuric acid solutions were heated to the slurry temperature and used as separate washes on the filter cake. The leach liquor and wash liquor volumes were measured but not combined. Each solution was submitted for analysis. A portion of the moist filter cake

was set aside for subsequent EP extraction testing, while another sample was dried and the moisture content determined. This dried cake was assayed. Upon correcting for samples taken, the percent of each element extracted was recorded, as based upon the solids assay. The "accountability" for the mass balance was calculated by adding the mass of a particular element in solution samples and final filter cake, dividing that summation by the mass originally present in the initial sludge addition, and multiplying the quotient by 100 to yield a percent accountability figure.

In one test (Test Number 5), a more vigorous leach procedure was used in which a Waring-type blender was used to repulp the solids between washes. Furthermore, in addition to the two washes with 0.1N H_2SO_4 , two washes with deionized water, for a total of four washes, were performed on the leached filter cake.

Experimental Results and Discussion

Test procedures and test results are presented in Tables 3 through 8. The leach temperature was not controlled, reaching a maximum value just after acid addition as a result of the enthalpy of dilution and reaction between the acid and basic hydroxides. An inspection of the solution assays shows that leaching was essentially complete within the first 30 minutes. Also, the final metal concentrations in the leach liquors show that they are a function of the original pulp density which varied from 28.5 percent by weight (Test 1) to 18.4 percent by weight (Test 4).

In comparing the final leach liquors with the original stock solution from which the original synthetic plating sludges were prepared, a 2.5 to 3.5-fold concentration ratio of the metallic species is noted. The exact concentration ratio is, of course, a function of the pulp density of the starting slurry. If it were desirable to attempt to achieve a high concentration ratio associated with a typical plating solution, then multistage contact would be required. In our experimental leach studies, such high concentrations as might be achieved through multistage contact was avoided partly to keep the test program within a limited scope and also to avoid reaching saturation limits associated with potential "double salt" formation.

Table 3 summarizes the five leach tests which were performed. In all five tests, metal recovery was close to 100 percent with the exception of cadmium which was nearer to 98 percent. This lower recovery of cadmium may be a result of its low starting level initially or a result of precision in analysis which tends to be lower for low concentrations. Since the recoveries of metals are all uniformly high in all five tests, it is more instructive to compare the terminal filter cake assays. For example, in Test 3 on sludge Type B in which accelerated aging was performed as a prior sludge treatment, the terminal leached filter cake assays were the highest for the five tests. The accelerated aging is seen to make the sludge more refractory to leaching.

Table 3. Summary of Acid Leach of Plating Sludges

Test Conditions: 90-minute leach at pH of 1.25. Final cake washed twice on cake with 250 ml 0.1N H_2SO_4 except C (Run 2). For C (Run 2) cake was repulped in Waring-type blender, washed twice with 250 ml 0.1N H_2SO_4 at 70°C, once with 250 ml deionized water at 70°C, and once with 250 ml of deionized water at 25°C for a total of 4 washes with pulping by blender each wash.

Test No.	Sludge Type	Percent Solids Sludge	Mass Acid Per Mass Dry Sludge	Pulp Density %	Final Assay of Filter Cake (%) and Percent Extracted (Parentheses)					
					Cu	Cr	Ni	Fe	Cd	Zn
1	A (No Aging)	62.5	0.614	28.5	0.034 (99.4)	0.048 (99.4)	0.021 (99.7)	0.037 (99.3)	0.017 (97.5)	0.034 (99.5)
2	A (No Aging)	62.5	0.601	28.5	0.032 (99.4)	0.047 (99.4)	0.018 (99.7)	0.015 (99.7)	0.021 (97.0)	0.021 (99.6)
3	B (7-Days Aging at 65°C)	93.3	0.697	20.3	0.050 (99.2)	0.075 (99.1)	0.035 (99.4)	0.036 (99.3)	0.020 (97.3)	0.042 (99.4)
4	C (6-Weeks Aging at 22°C)	87.0	0.687	18.4	0.032 (99.5)	0.030 (99.7)	0.022 (99.6)	0.024 (99.6)	0.012 (98.7)	0.023 (99.6)
5 ¹	C (6-Weeks Aging at 22°C)	88.9	0.687	18.4	0.026 (99.6)	0.034 (99.6)	0.016 (99.7)	0.018 (99.7)	0.014 (98.2)	0.017 (99.7)

¹ More aggressive washing procedure.

Table 6. Sulfuric Acid Leach of Sludge Type A, Test No. 1, Notebook Page 1124-14

Test Conditions:	
Mass Moist Sludge Added	570.52 g
Mass Sludge Dry (Calculated)	356.74 g
Mass Sludge (Dry) Not Leached	4.92 g ¹
Net Sludge Added (Dry)	351.82 g ²
Volume Deionized Water Added	680 ml
Volume of Water Associated with Moist Sludge	214 ml
Total Water Content of Leach (Before Acid Addition)	894 ml
Initial Percent Solids (Before Acid Addition)	28.5%
Mass Leached and Washed Cake (Dry)	205.82 g
Average Temperature of Slurry	60°C
Total Acid Added to Leach	119 ml ³
Ratio of Grams Acid Added Per Gram Dry Sludge (Acid Specific Gravity 1.84 g/ml)	0.614
Final pH of Slurry After 90 Minutes	1.35
Wash Temperature	45°C

Time (min)	Sample	Volume (ml)	Assays and Masses of Elements in Samples									
			Cu	Cr	Bi	Fe	Cd	Zn	Ca	SO ₄		
			g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %
Sludge A ² (Dry Basis)		(Solids)	3.55%	12.49	17.91	3.42%	12.03	3.28%	11.54	0.446%	1.62	3.92%
0 Time Sample Filtrate		7.4	12.0 g/l	0.09	16.9 g/l	0.13	11.6 g/l	0.09	11.2 g/l	0.08	1.46 g/l	0.01
30 Time Sample Filtrate		7.6	11.6 g/l	0.09	16.1 g/l	0.12	11.2 g/l	0.09	10.8 g/l	0.08	1.47 g/l	0.01
45 Time Sample Filtrate		7.8	12.5 g/l	0.10	17.6 g/l	0.14	12.1 g/l	0.09	11.7 g/l	0.09	1.58 g/l	0.01
60 Time Sample Filtrate		8.2	12.1 g/l	0.10	16.9 g/l	0.14	11.7 g/l	0.10	11.3 g/l	0.09	1.53 g/l	0.01
75 Time Sample Filtrate		7.6	12.6 g/l	0.10	17.6 g/l	0.13	12.2 g/l	0.09	11.8 g/l	0.09	1.62 g/l	0.01
90 Time Sample Filtrate		850	13.2 g/l	11.22	18.6 g/l	15.81	12.7 g/l	10.80	12.3 g/l	10.46	1.68 g/l	1.43
First Wash Filtrate		220	1.91 g/l	0.42	2.63 g/l	0.58	1.90 g/l	0.42	1.76 g/l	0.39	0.25 g/l	0.06
Second Wash Filtrate		260	0.19 g/l	0.05	0.27 g/l	0.07	0.183 g/l	0.05	0.177 g/l	0.046	0.027 g/l	0.01
Splash Residue Filtrate		140	0.45 g/l	0.09	0.91 g/l	0.13	0.627 g/l	0.09	0.609 g/l	0.09	0.083 g/l	0.01
Filtrate Cake		(Solids)	0.039%	0.07	0.048%	0.10	0.028%	0.04	0.038%	0.08	0.017%	0.04
Percent Extracted ⁴			99.4	99.4	99.7	99.3	97.5	99.5	99.5	99.5	99.5	99.5
Accountability, %			98.6	96.9	98.5	99.6	98.8	102.0	101.4	100.3	104.14	100.3

¹ Splash residue collected from reactor lid.

² See first sample entry.

³ 106 ml at 30 minutes.

⁴ Calculated on basis of solids input and solids output.

Table 5. Sulfuric Acid Leach of Sludge Type A, Test No. 2, Notebook Page 1124-16
(Duplicate of 1124-14)

Test Conditions:
 Mass Moist Sludge Added 570.52 g
 Mass Sludge Dry (Calculated) 356.74 g
 Mass Sludge (Dry) Not Leached 2.16 g¹
 Mass Sludge Added (Dry) 354.59 g²
 Volume Releasized Water Added 680 ml
 Volume of Water Associated with Moist Sludge 214 ml
 Total Water Content of Leach (Before Acid Addition) 894 ml
 Initial Percent Solids (Before Acid Addition) 28.5%
 Mass Leached and Washed Cake (Dry) 229.97 g
 Average Temperature of Slurry 60°C
 Total Acid Added to Leach 116.6 ml³
 Ratio of Gross Acid Added Per Gram Dry Sludge 0.601
 Acid Specific Gravity 1.84 g/ml
 Final pH of Slurry After 90 Minutes 1.25
 Wash Temperature 42°C

Time (min)	Sample	Volume (ml)	Assays and Masses of Elements in Samples									
			Cu	Cr	Mn	Fe	Cd	Zn	Ca	NO ₃		
			g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %
0	Sludge A ² (Dry Basis)	(Solids)	3.55%	12.59	16.05	3.42%	12.13	3.28%	11.63	0.460%	1.63	3.92%
30	Time Sample Filtrate	8.8	9.82 g/l	0.09	14.3 g/l	0.13	9.34 g/l	0.08	1.18 g/l	0.01	11.3 g/l	0.10
45	Time Sample Filtrate	7.2	12.6 g/l	0.09	17.7 g/l	0.13	11.8 g/l	0.08	1.54 g/l	0.01	13.8 g/l	0.10
60	Time Sample Filtrate	7.6	12.8 g/l	0.09	17.4 g/l	0.13	12.1 g/l	0.08	1.57 g/l	0.01	14.0 g/l	0.10
75	Time Sample Filtrate	7.5	12.5 g/l	0.10	17.2 g/l	0.13	11.7 g/l	0.09	1.52 g/l	0.01	13.6 g/l	0.10
90	Leach Filtrate	825	13.2 g/l	10.89	17.9 g/l	0.13	11.9 g/l	0.09	1.56 g/l	0.01	14.1 g/l	0.11
	First Wash Filtrate	260	2.09 g/l	0.54	2.83 g/l	0.76	1.96 g/l	0.51	0.26 g/l	0.07	2.26 g/l	0.59
	Second Wash Filtrate	250	0.101 g/l	0.03	0.14 g/l	0.03	0.094 g/l	0.02	0.02 g/l	0.01	0.11 g/l	0.03
	Splash Residue Filtrate	190	0.44 g/l	0.08	0.62 g/l	0.12	0.41 g/l	0.08	0.05 g/l	0.01	0.48 g/l	0.09
	Filter Cake	(Solids)	0.032%	0.074	0.047%	0.115	0.018%	0.04	0.021%	0.05	0.021%	0.05
	Percent Extracted ⁴		99.4	99.4	99.7	99.7	99.7	99.6	97.0	99.6	99.6	99.6
	Accountability, %		96.0	94.7	93.4	96.6	96.6	96.4	101.7	82.1	101.7	82.1

¹ Splash residue collected from reactor lid.

² See first sample entry.

³ 106 ml at 30 minutes.

⁴ Calculated on basis of solids input and solids output.

Table 6. Sulfuric Acid Leach of Sludge Type B, Test No. 3, Notebook Page 1124-20

Test Conditions:

Mass Moist Sludge Added	271.41 g
Mass Sludge Dry (Calculated)	253.47 g
Mass Sludge (Dry) Not Leached	2.41 g ¹
Net Sludge Added (Dry)	251.06 g ²
Volume Deionized Water Added	979 ml
Volume of Water Associated with Moist Sludge	18 ml
Total Water Content of Leach (Before Acid Addition)	997 ml
Initial Percent Solids (Before Acid Addition)	20.3%
Mass Leached and Washed Cake (Dry)	149.76 g
Average Temperature of Slurry	55°C
Total Acid Added to Leach	96 ml ³
Ratio of Grams Acid Added Per Gram Dry Sludge	0.697
(Acid Specific Gravity 1.84 g/ml)	1.30
Final pH of Slurry After 90 Minutes	41°C
Wash Temperature	

Time (min)	Samples	Volume (ml)	Assays and Masses of Elements in Samples															
			Cu		Cr		Mn		Fe		Cd		Zn		Ca		SO ₄	
			g/l or %	g	g/l or %	g	g/l or %	g	g/l or %	g	g/l or %	g	g/l or %	g	g/l or %	g	g/l or %	g
	Sludge #2 (Dry Basis)	(Solids)	3.55%	8.91	5.09%	12.78	3.42%	8.59	3.28%	8.23	0.460%	1.15	3.92%	9.84	15.8%	39.67	29.5%	74.06
0	Time Sample Filtrate	3.8	8.40 g/l	0.03	12.4 g/l	0.05	7.97 g/l	0.03	7.84 g/l	0.03	0.87 g/l	0.003	9.67 g/l	0.04	0.13 g/l	0.0005		
30	Time Sample Filtrate	6.4	9.38 g/l	0.06	13.4 g/l	0.09	8.86 g/l	0.06	8.58 g/l	0.05	1.19 g/l	0.01	10.6 g/l	0.07	0.59 g/l	0.004		
45	Time Sample Filtrate	6.6	9.30 g/l	0.06	13.4 g/l	0.09	8.72 g/l	0.06	8.55 g/l	0.06	1.17 g/l	0.01	10.5 g/l	0.07	0.57 g/l	0.004		
60	Time Sample Filtrate	7.0	8.67 g/l	0.06	12.5 g/l	0.09	8.17 g/l	0.06	8.00 g/l	0.06	1.09 g/l	0.01	9.81 g/l	0.07	0.52 g/l	0.004		
75	Time Sample Filtrate	6.6	9.37 g/l	0.06	13.6 g/l	0.09	8.80 g/l	0.06	8.65 g/l	0.06	1.18 g/l	0.01	10.7 g/l	0.07	0.55 g/l	0.004		
90	Leach Filtrate	765	9.82 g/l	7.51	13.9 g/l	10.63	9.27 g/l	7.09	8.99 g/l	6.88	1.24 g/l	0.947	11.1 g/l	8.49	0.55 g/l	0.421		
	First Wash Filtrate	400	3.54 g/l	1.42	5.05 g/l	2.02	3.32 g/l	1.33	3.28 g/l	1.31	0.44 g/l	0.176	3.95 g/l	1.58	0.55 g/l	0.22		
	Second Wash Filtrate	260	0.57 g/l	0.15	0.79 g/l	0.21	0.53 g/l	0.14	0.51 g/l	0.13	0.07 g/l	0.018	0.63 g/l	0.16	0.67 g/l	0.17		
	Slurry Residue Filtrate	216																
	Filter Cake	(Solids)	0.050%	0.07	0.07%	0.11	0.035%	0.05	0.036%	0.054	0.020%	0.03	0.04%	0.05	25.6%	36.34	43.2%	64.70
	Percent Extracted ⁴		99.2		99.12		99.4		99.3		97.3		99.4		98.7		87.4	
	Accountability, %		105.7		104.6		102.6		104.9		103.0		107.8					

¹ Splash residue collected from reactor lid.

² See first sample entry.

³ 87 ml at 30 minutes.

⁴ Calculated on basis of solids input and solids output.

Table 7. Sulfuric Acid Leach of Sludge Type C, Test No. 4, Notebook Page 1126-40

Test Conditions:
 Mass Moist Sludge Added 263.16 g
 Mass Sludge Dry (Calculated) 230.40 g
 Mass Sludge (Dry) Not Leached 1.42 g¹
 Mass Sludge Added (Dry) 228.98 g²
 Volume Deionized Water Added 987 ml
 Volume of Water Associated with Moist Sludge 33 ml
 Total Water Content of Leach (Before Acid Addition) 1020 ml
 Initial Percent Solids (Before Acid Addition) 18.4%
 Mass Leached and Washed Cake (Dry) 137.3 g
 Average Temperature of Slurry 45°C
 Total Acid Added to Leach 86 ml³
 Ratio of Grams Acid Added Per Gram Dry Sludge (Acid Specific Gravity 1.04 g/ml) 0.687
 Final pH of Slurry After 90 Minutes 1.20
 Wash Temperature 40°C

Time (min)	Sample	Volume (ml)	Analysis and Masses of Elements in Samples									
			Cu	Cr	Mn	Fe	Cd	Zn	Ca	SO ₄		
			g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %	g/l or %
0	Sludge C ² (Dry Basis)	(Solids)	3.55%	8.12%	11.65%	3.42%	7.83%	3.28%	7.51%	0.460%	1.05	3.92%
30	Time Sample Filtrate	8.2	7.95 g/l	0.065	11.6 g/l	0.095	8.05 g/l	0.066	7.10 g/l	0.056	0.91 g/l	0.008
45	Time Sample Filtrate	7.6	9.00 g/l	0.068	12.7 g/l	0.097	8.95 g/l	0.068	7.70 g/l	0.059	1.05 g/l	0.008
60	Time Sample Filtrate	7.5	8.30 g/l	0.062	12.0 g/l	0.090	8.55 g/l	0.064	7.15 g/l	0.054	0.97 g/l	0.007
75	Time Sample Filtrate	8.4	8.25 g/l	0.069	11.9 g/l	0.100	8.55 g/l	0.072	7.25 g/l	0.061	0.99 g/l	0.008
90	Leach Filtrate	1000	8.15 g/l	0.067	11.7 g/l	0.096	8.40 g/l	0.069	6.95 g/l	0.057	0.95 g/l	0.008
	First Wash Filtrate	280	1.15 g/l	0.322	1.65 g/l	0.462	1.19 g/l	0.333	1.05 g/l	0.294	0.97 g/l	0.97
	Second Wash Filtrate	240	0.075 g/l	0.018	0.103 g/l	0.025	0.073 g/l	0.018	0.071 g/l	0.017	0.010 g/l	0.002
	Splash Residue Filtrate	75	0.334 g/l	0.025	0.471 g/l	0.035	0.321 g/l	0.024	0.285 g/l	0.021	0.036 g/l	0.003
	Filter Cake	(Solids)	0.032%	0.044	0.030%	0.041	0.022%	0.030	0.024%	0.033	0.012%	0.017
	Percent Extracted ⁴		99.5	99.7	99.6	99.6	98.7	99.6	98.6	98.7	99.6	99.6
	Accountability, %		111.8	110.2	119.3	102.1	101.8	106.7	120.00	134.8	66.3%	91.02

¹ Splash residue collected from reactor lid.

² See first sample entry.

³ 78 ml at 30 minutes.

⁴ Calculated on basis of solids input and solids output.

Table 8. Sulfuric Acid Leach of Sludge Type C, Test No. 5, Notebook Page 1124-44

Test Conditions:		Analysis and Names of Elements in Samples																	Mass Solids g After Each Filtration		
Sample	Volume (ml)	Cu g/l or %	Cr g/l or %	Ni g/l or %	Fe g/l or %	Cd g/l or %	Zn g/l or %	Ca g/l or %	SO ₄ ²⁻ g/l or %											g	
Sludge C ² (Dry Basis)		3.53%	8.12%	5.09%	11.65%	3.42%	7.83%	3.28%	7.51%	0.460%	1.053	3.92%	8.930	15.8%	36.17%	29.3%	67.59%	227.17			
Leach Filtrate	1100																	228.06			
First Wash Filtrate	294																	223.39			
Second Wash Filtrate	282																	214.8			
Third Wash Filtrate	296																	207.55			
Fourth Wash Filtrate	280																	137.21 ⁴			
Final Cake (Moist)		0.026%	0.036	0.034%	0.047	0.016%	0.022	0.018%	0.025	0.014%	0.019	0.017%	0.023	30.7%	42.12	64.8%	88.91				
Percent Extracted ⁵		99.6	99.6	99.7	99.7	99.7	99.7	99.7	98.2	99.7		99.7									

Test Conditions:
 Mass Moist Sludge Added 263.16 g
 Mass Sludge Dry (Calculated) 230.40 g
 Mass Sludge (Dry) Not Leached 1.42 g¹
 Net Sludge Added (Dry) 228.98 g²
 Volume Deionized Water Added 987 ml
 Volume of Water Associated with Moist Sludge 33 ml
 Total Water Content of Leach (Before Acid Addition) 1020 ml
 Initial Percent Solids (Before Acid Addition) 18.4%
 Mass Leached and Washed Cake (Dry) 137.21 g
 Total Acid Added to Leach 86 ml
 Ratio of Grams Acid Added Per Gram Dry Sludge (Acid Specific Gravity 1.84 g/ml) 0.691
 Temperature of First 2 Washes (0.1M H₂SO₄)³ 70°C
 Temperature of Third Wash (D.I. H₂O)³ 70°C
 Temperature of Fourth Wash (D.I. H₂O)³ 25°C
 Duration of Leach 90 min.

- 1 Splash residue collected from reactor lid.
- 2 See first sample entry.
- 3 Waring blender used to repulp.
- 4 Dry basis.
- 5 Calculated on basis of solids input and solids output.

A comparison of the morphology of the solids before and after leaching is given in tabular form below. (For microstructures and further details, consult Appendix B).

	Solids Type (Treatment)		
	A (No Aging)	B (Accelerated Aging, 1 Week at 65°C)	C (Six-Weeks Aging at 22°C)
Sludge (Before Leach)	Bassanite	Bassanite with fine nuclei of gypsum	Gypsum
Cake (After Leach)	Bassanite	Bassanite with approximately equal quantities of gypsum in a felted mass.	Bassanite on needles which were formerly gypsum.

Both filter cakes A and C exhibited slow filtration rates* because of their interwoven crystalline structure, but sludge B filtered very slowly because of the dense felted-mass of fine crystallites present. The leach temperature of approximately 50 to 60°C is high enough to convert the calcium sulfate to the hemi-hydrated form (bassanite). In Type C sludge, the bassanite formed as long needles on gypsum as pseudomorphs. This crystalline form enabled somewhat more rapid filtration rates to be achieved. These morphological differences account for the higher metal content of filter cake from leach Type B sludge than the other two sludges.

In Test 5, effort was directed towards a more aggressive wash procedure. Comparison between Tests 4 and 5 for the same feed material, the same leach procedure, but different wash procedure shows that the filter cake from Test 5 was lower in metallic constituents, generally.

3. EXTRACTION TESTING ON FILTER CAKES FROM SULFURIC ACID LEACHING OF METAL HYDROXIDE SLUDGES

Objective

The objective of the extraction tests on the filter cakes produced from sulfuric acid leaching of metal hydroxide sludges is to determine the effect of leaching, washing, and added lime on the solubility of the filter cakes in a simulated environmental exposure.

* Approximately 0.7 milliliter of filtrate per sq cm of surface per hour in a 2 cm thick bed under "house vacuum". A Whatman #42 filter (slow) was used.

Experimental Procedure

The Extraction Procedure (EP test) is fully described in Appendix A. The EP test is an attempt to accelerate leaching conditions which may occur under conditions of environmental exposure in order to compare one residue with another with respect to release of toxic constituents. In brief, the test is performed as follows:

One hundred grams (equivalent dry weight) of as-received (moist) filter cake is slurried with 1.6 liters deionized water (includes correction for water present in cake). The pH of the slurry is adjusted to 5.0 at 25°C with 0.5 normal acetic acid (but not to exceed 4 ml of acetic acid per gram of dry equivalent solids). The slurry is agitated for 24 hours at a temperature in the range of 20 to 40°C (in practice ~ 25°C). Acetic acid is added to maintain a pH of 5.0 provided the above limit is not exceeded. The final volume of extract is noted, and the extract is routinely analyzed for the following elements: As, Cd, Cu, Fe, Mn, Mo, Pb, Zn, Al, Ba, Be, Ca, Co, Cr, Mg, Ni, V, Hg, Se, and Ag. The maximum levels of heavy metals which are allowed in order for a sludge to be classified nonhazardous is given as:

	<u>EPA Permitted Level, mg/l</u>
Arsenic	0.50
Barium	10.0
Cadmium	0.10
Chromium (Total)	0.50
Lead	0.50
Mercury	0.02
Selenium	0.10
Silver	0.50

Six leach cakes were examined by the EP procedure. The prior history of the cakes is given in Table 9. In the first three tests, cakes A (no aging), B (accelerated aging at 65°C), and C (6-weeks aging) are compared. The prior leach history of these cakes was identical, namely two dilute sulfuric acid washes followed by two deionized water washes. When the filter cakes were pulped with deionized water for the extraction test, sufficient lime was added to bring the pH to 9.0 prior to the addition of acetic acid. The last column shows the acetic acid requirement to react with the added lime and bring the pH to 5.0.

In Test 4, which was performed on cake type C, a more vigorous washing procedure was used in that a Waring type blender was employed to produce a smooth paste during each pulping operation. The blender was operated for 5 minutes, as solution was added for each of 4 washes. No lime was added to the liquid for the extraction tests.

Table 9. Extraction Procedure Tests on Filter Cakes from Sulfuric Acid Leaching of Sludges

Procedure EP Test: Slurry 100 grams of cake (dry weight) with 1.6 liters D.I. H_2O . Adjust pH to 5.0 with 0.5N acetic acid, but not to exceed 4 ml of acetic acid per gram of solids. Mix 24 hours at a temperature between 20 and 40°C.

Cake Originating from Sludge Type	Prior Cake Preparation	Parts Per Million (Mass Basis) of Elements						Acetic Acid Required gms/gm Cake
		Cu	Cr	Ni	Fe	Cd	Zn	
A (No Aging)	Two 0.1N H_2SO_4 (250 ml) washes at 70°C, plus two (250 ml) D.I. water washes at 60°C using stirred reactor. Add sufficient lime to pulped solids in extraction test to bring starting pH to 9.0.	0.88	0.53	0.53	0.075	1.24	0.98	0.50
B (7 Days at 65°C)	As above.	7.19	4.10	9.39	0.19	2.29	12.4	0.80
C (6 Weeks at 22°C)	As above.	1.21	1.16	1.13	0.053	1.09	1.67	0.76
C (6 Weeks at 22°C)	Two 0.1N H_2SO_4 (250 ml) washes at 70°C, one 250 ml D.I. water wash at 70°C, one 250 ml D.I. water wash at 25°C, repulp and treat with Waring-type blender between each wash.	0.30	0.22	0.13	0.092	0.67	0.38	0.07
C (6 Weeks at 22°C)	As above plus add 1 part by weight $Ca(OH)_2$ to 10 parts by weight dry cake.	0.011	0.11	0.12	0.016	0.036	0.058	1.22
C	Two 0.1N H_2SO_4 (250 ml) washes at 70°C followed by two deionized water washes (250 ml) at 60°C in stirred reactor. Add sufficient lime (one part $Ca(OH)_2$ per 2.4 parts cake) to maintain pH at 10.0 in acetic acid leach.	0.007	0.13	<0.014	0.015	0.009	0.026	2.83

try is test number, second entry is notebook number and page number for cross-reference with B.

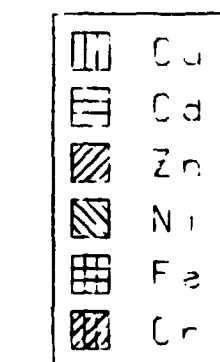
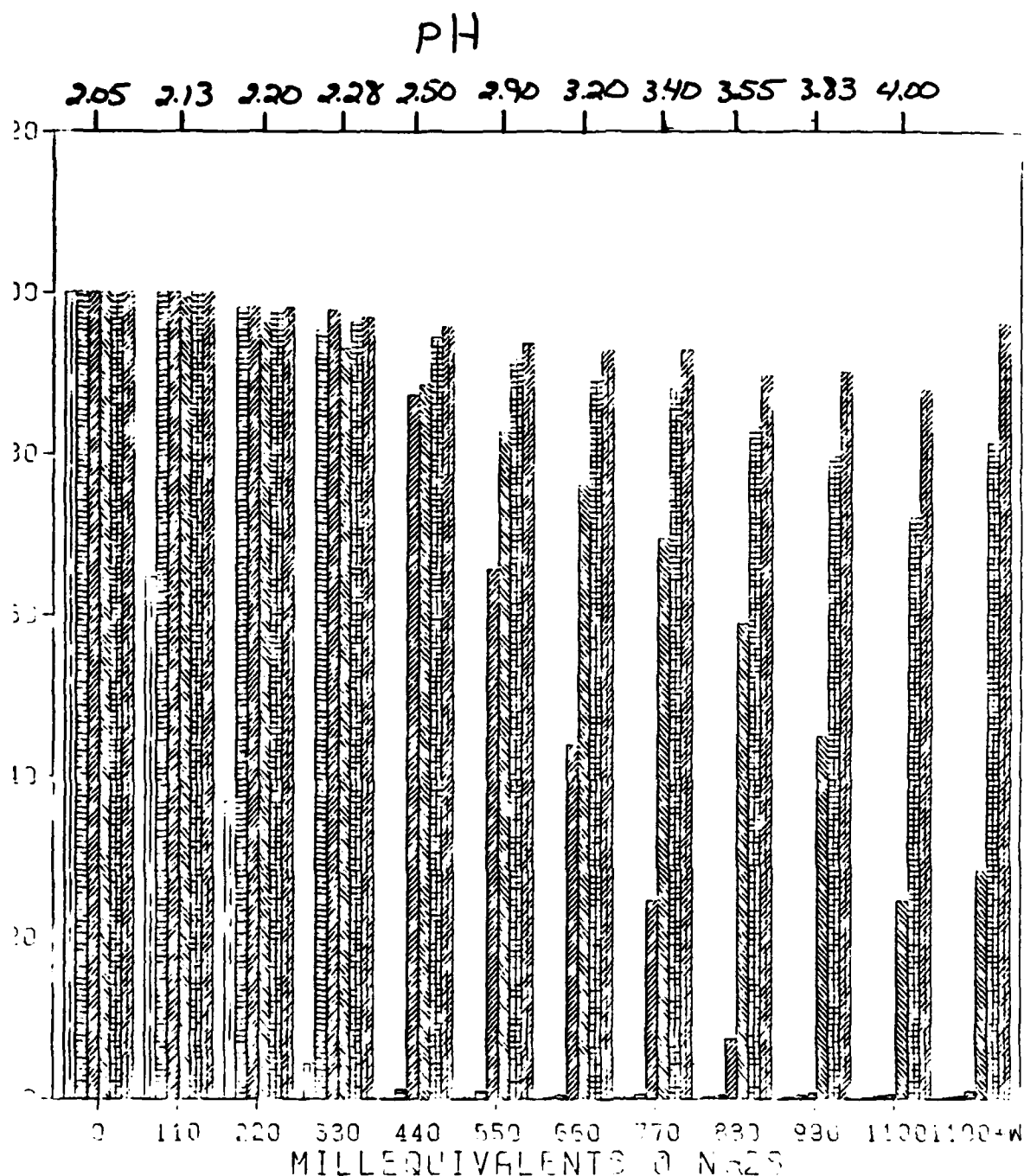


Figure 7. Sulfide Precipitation Test 2 (1124-28) (22°C). Distribution of elements as weight percent in solution versus sodium sulfide addition and solution pH, weight percent element remaining in solution (test conditions in tables 11 and 15).

Table 15. Sulfide Precipitation Test -
Calculations on Percent Element Remaining in Solution
Test Number 2, Notebook Page Number 1124-28

Test Conditions:

Starting solution 1 liter of sulfate
solution of the following assay (all g/l)

<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>
12.3	1.16	15.6	11.0	11.3	17.2

Add 29.5 g/l $S^{=}$ as Na_2S at a rate of
2 ml/minute

Temperature: 25°C

Duration: 300 minutes

Wash: 2 liters deionized water

Milliequivalents Sulfide Added	Weight % Remaining in Solution						
	pH	Cu	Cd	Zn	Ni	Fe	Cr
0		100	100	100	100	100	100
110	2.13	64.72	100	100	99.25	100	100
220	2.20	36.84	98.12	98.22	96.21	97.82	98.10
330	2.28	4.35	95.24	97.84	92.98	96.36	96.80
440	2.50	0.10	1.12	87.25	88.55	94.37	95.76
550	2.90	0.12	0.85	65.51	82.64	91.75	93.67
660	3.20	0.05	0.33	43.83	76.06	89.36	92.65
770	3.40	0.10	0.45	24.51	69.39	87.96	92.85
880	3.55	0.08	0.35	7.34	58.86	83.23	89.65
990	3.83	0.09	0.36	0.61	44.92	79.60	90.13
1100	4.00	0.11	0.25	0.42	24.43	72.11	87.92
1100 + Wash		0.11	0.25	0.81	28.18	81.32	96.21

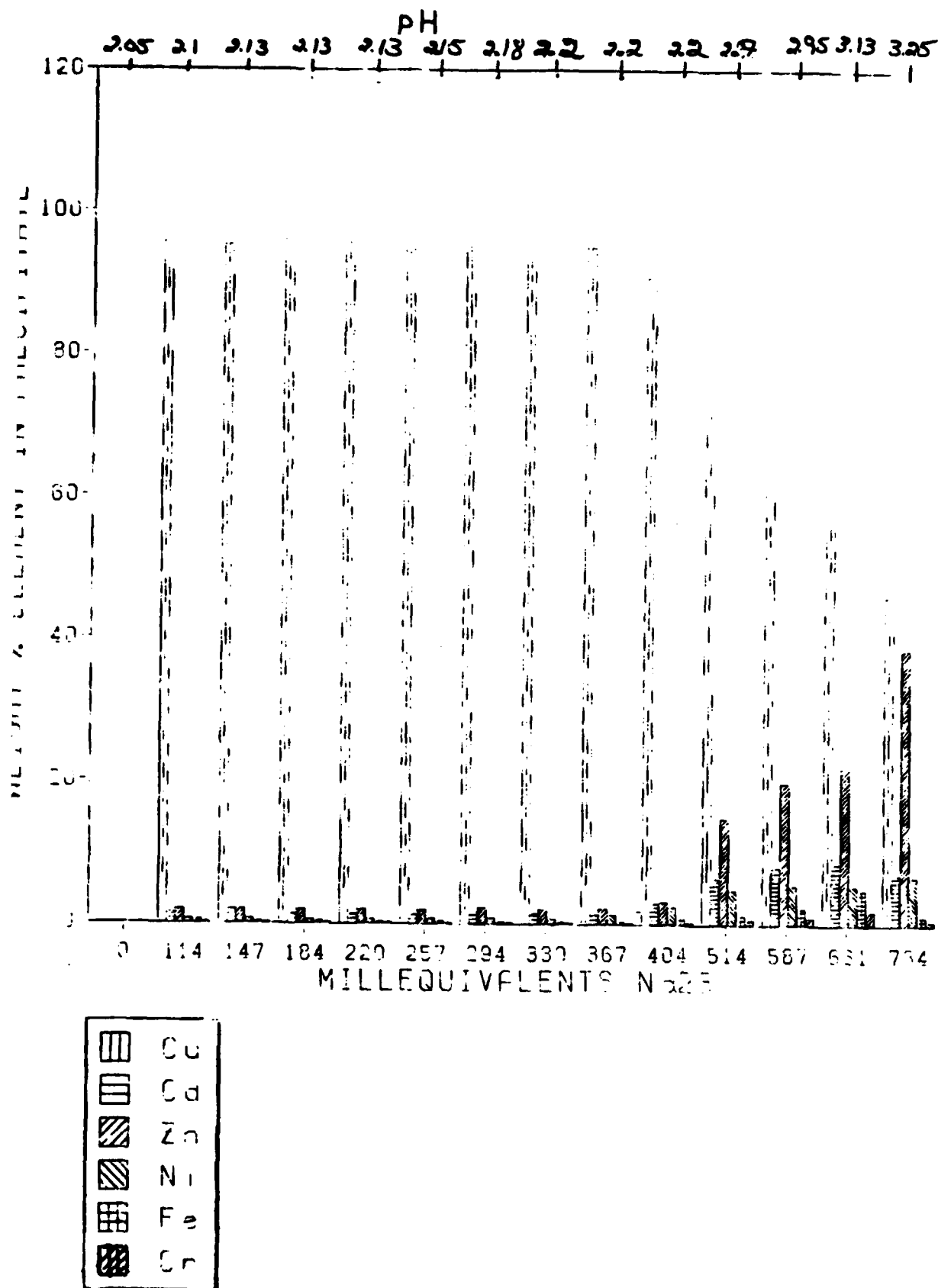


Figure 6. Sulfide Precipitation Test 1 (1124-26) (22°C). Distribution of elements as weight percent in solution versus sodium sulfide addition and solution pH, weight percent element reporting to precipitate (test conditions in tables 10 and 14).

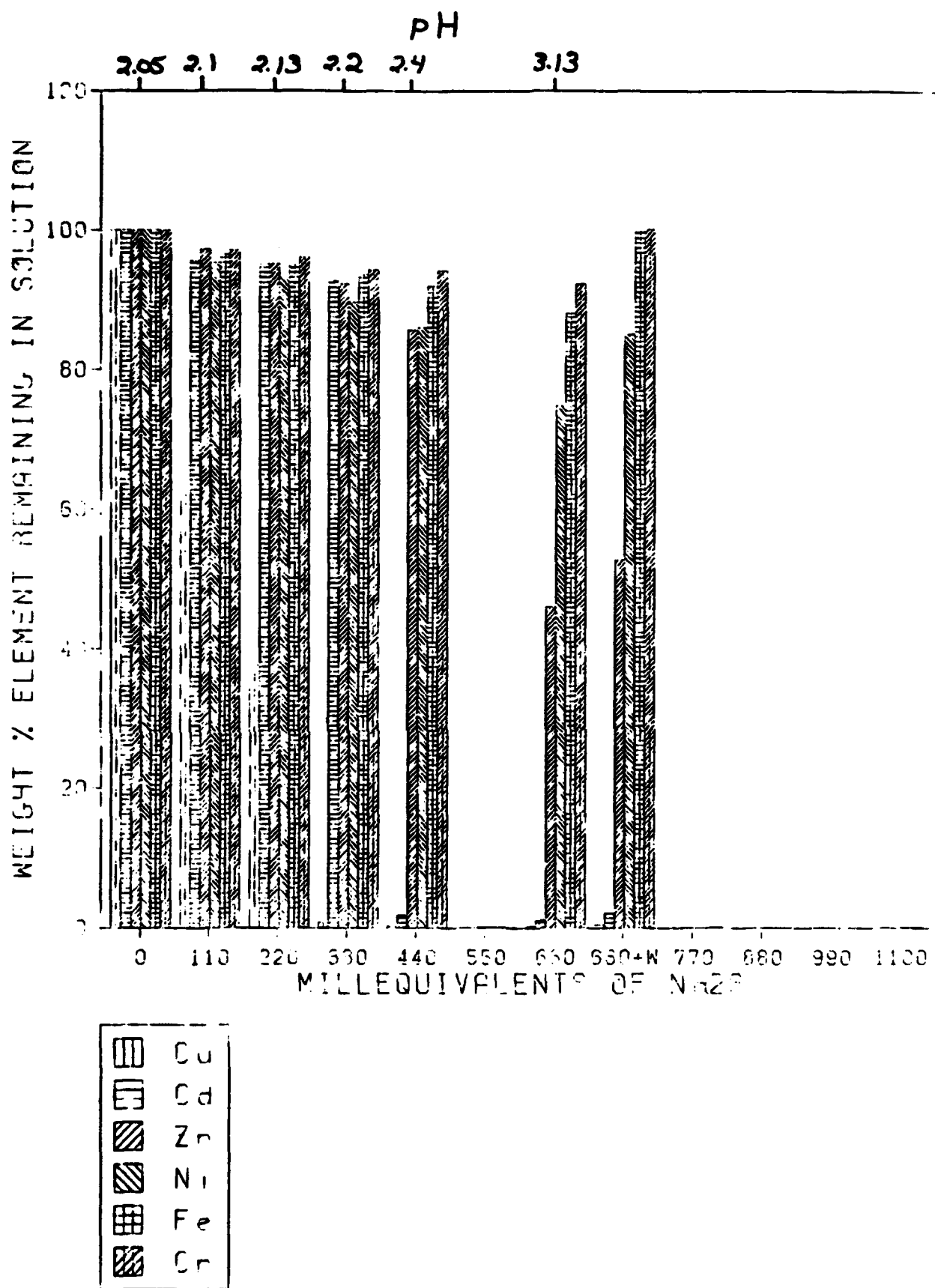


Figure 5. Sulfide Precipitation Test 1 (1124-26) (22°C). Distribution of elements as weight percent in solution versus sodium sulfide addition and solution pH, weight percent element remaining in solution (test conditions in tables 10 and 14).

Figures 5 and 6 show the test results as a histogram as weight percent element remaining in solution versus milliequivalents of added sodium sulfide and pH (Figure 5) and weight percent element in precipitate (Figure 6).

Test 2

The results of Test 2 are summarized in Tables 11 and 15 and Figure 7. Essentially the same starting solution as was used in Test 1 was subject to a higher cumulative sulfide addition (1,100 milliequivalents added as compared with 734 in Test 1). The terminal solution pH in Test 2 was also higher (4.0 compared with 3.25 for Test 1). The test results, as summarized in Table 15, show that in Test 2, copper, cadmium, and zinc are removed to low levels (less than 1 percent remaining in solution) at the terminal condition of pH 4.0. Nickel and iron remain in solution at 24 and 72 percent, respectively, and chromium is seen to be precipitated to some extent. However, upon washing the precipitate, chromium remaining in the combined solutions is 96 percent.

Test 3

The results of Test 3 are summarized in Tables 12 and 16 and Figure 8. This test, which was conducted at 60°C, shows a shift in solution pH to lower values by virtue of the higher degree of dissociation of bisulfate ion at elevated temperature. Copper, cadmium, and zinc are removed to low terminal levels. If dilution and sampling had not occurred, chromium at a starting concentration of 17.7 g/l is calculated to be approximately 16.1 g/l for less than 9 percent removal from solution. Upon washing the precipitate, negligible amounts of copper and cadmium are returned to solution; however, better than 99 percent of the chromium is solubilized.

Test 4

The results of Test 4 are summarized in Tables 13 and 17 and Figure 9. This test differed from the prior three tests in that a portion of the solids which had been precipitated in the first three tests was combined with the leach liquor prior to addition of aqueous sodium sulfide. An examination of Table 13 at a time of zero minutes after addition of the precipitated (seed) shows a decline in copper concentration from 12.5 g/l to 0.003 g/l and an increase in zinc concentration from 15.0 g/l to 23.8 g/l. Clearly an exchange between copper and zinc as sulfides occurs. An examination of Table 13 shows that 614 milliequivalents of added sodium sulfide was insufficient to precipitate zinc to low levels. Also, chromium losses to the precipitate have occurred. Recycling of seed served to improve the filtration rates which were originally about 1.5 ml per hour per sq cm of filter cake to 5 ml per hour per sq cm.

**Table 14. Sulfide Precipitation Test -
Calculations on Percent Element Remaining in Solution
Test Number 1, Notebook Page Number 1124-26**

Test Conditions:

Starting solution 1 liter of sulfate
solution of the following assay (all g/l)

<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>
12.5	1.12	15.0	10.7	11.1	15.0

Add 58.9 g/l $S^{=}$ as Na_2S at a rate of
1 ml/minute

Temperature: 25°C

Duration: 200 minutes

Wash: 2 liters deionized water

Milliequivalents Sulfide Added	Weight % Remaining in Solution						
	pH	Cu	Cd	Zn	Ni	Fe	Cr
0	2.05	100	100	100	100	100	100
110	2.10	66.32	95.60	97.21	95.30	96.46	97.11
220	2.13	37.67	95.12	95.16	93.18	95.04	96.04
330	2.20	0.75	92.65	92.24	89.64	93.58	94.21
440	2.40	0.14	1.71	85.67	86.05	91.94	94.15
660	3.13	0.16	0.99	45.96	74.78	88.04	92.23
660 + Wash		0.38	2.06	52.68	85.02	99.71	100

Experimental Results

Test 1 (see Table 10)

In this test, a total of 734 milliequivalents of sulfide was added to the stock solution whose assay is shown under the heading of zero time. The solution assays are shown to decrease with increasing sulfide addition as a result of four factors. 1) Metal ions are being removed from solution by precipitation, 2) metal ions are being removed by sampling, 3) a dilution occurs by virtue of adding sulfide in aqueous solution, and 4) although a reflux condenser was used to recover evaporated water, some losses due to evaporation occurred. The actual data as measured are reported in this table; however, by utilization of the reported information on sample volume and final leach liquor volume, it is possible to correct for the various sampling effects in order to calculate the weight percent of each element remaining in solution. This correction was applied in Table 14, Calculation on Percent Element Remaining in Solution. An examination of this latter table indicates the order in which sulfide combines with the metallic species for their precipitation. For this solution by the addition of 330 milliequivalents of sulfide ion and a solution pH of 2.20, less than 1 percent (0.75 percent) of the original copper remains in solution. Upon increasing the quantity of sulfide added to 440 milliequivalents and a pH of 2.40, not only does the copper level drop further but also the cadmium level in solution is seen to have dropped to about 2 percent (1.71 percent) of its original value. At the sulfide addition to 660 milliequivalents, the percent zinc remaining in solution is seen to drop, but only to about 46 percent of the starting level. This test indicated that insufficient sulfide had been added to remove zinc from solution. The level of chromium was seen to drop but then return to its original level (100 percent in solution) upon washing.

Test Conditions:

Concentration of Na₂S solution added.
 Test terminated at 614 milliequivalents of
 sulfide added.
 Test Temperature = 22°C
 16.4 g/l S²⁻ or 1.023 milliequivalents S²⁻/ml
 and pH of 3.35
 Solids from previous tests added (132.29
 grams wet weight or 103.83 grams dry weight).

Time, Min	Volume of Na ₂ S Solution Added, ml	S ²⁻ Added Milli- equivalents	pH	Volume Solution or Sample, ml	Mass Residue, g	Assays of Solutions, g/l					Chromium Mass Balance (Solutions), g	
						Cu	Cr	Ni	Fe	Cd	Zn	
Prior to Seed Addition	--	--	2.05	1,000		12.5	16.8	10.7	11.1	1.12	15.0	16.8
0	0	0	2.93	0	132.39	0.003	13.7	9.65	9.29	0.73	23.8	
10	20	20.46	2.70									
20	40	40.92	2.85									
30	60	61.38	3.00									
40	80	81.84	3.03	5.1		0.014	12.8	9.06	8.75	0.010	21.3	
50	100	102.30	3.03	5.0		0.017	12.7	8.85	8.54	0.008	20.1	
60	120	122.76	3.05	5.0		0.017	12.6	8.68	8.43	0.007	19.4	
70	140	143.22	3.08	5.1		0.012	12.3	8.51	8.33	0.006	18.6	
80	160	163.68	3.10	5.2		0.020	12.1	8.35	8.17	0.007	17.9	
90	180	184.14	3.10	5.3		0.016	12.1	8.26	8.11	0.006	17.3	
100	200	204.60	3.10	5.2		0.008	11.5	7.88	7.80	0.004	16.0	
110	220	225.06	3.10	5.0		0.016	11.8	8.00	7.93	0.006	15.8	
120	240	245.52	3.13	5.0		0.011	11.6	7.72	7.68	0.005	14.8	
130	260	265.98	3.15	5.1		0.015	11.6	7.71	7.72	0.005	14.5	
140	280	286.44	3.18	5.0		0.012	10.7	7.28	7.33	0.005	13.2	
150	300	306.90	3.20	5.1		0.017	10.6	7.09	7.19	0.005	12.5	
160	320	327.36	3.20	5.2		0.014	10.8	6.99	7.16	0.005	11.6	
170	340	347.82	3.20	5.2		0.007	10.4	6.78	7.03	0.003	10.9	
180	360	368.28	3.20	5.0		0.009	10.3	6.55	6.82	0.004	9.85	
190	380	388.74	3.13	5.1		0.009	10.5	6.67	6.91	0.004	9.94	
200	400	409.20	3.23	5.0		0.008	10.3	6.52	6.83	0.003	9.26	
210	420	429.66	3.25	5.0		0.014	9.73	6.17	6.54	0.004	8.42	
220	440	450.12	3.25	5.3								
230	460					0.010	9.90	6.12	6.54	0.003	7.97	
240	480	491.04	3.30	5.0		0.008	9.82	6.04	6.53	0.003	7.56	
250	500	511.50	3.30	5.1		0.013	9.92	6.03	6.56	0.003	7.81	
260	520	531.96	3.30	5.0		0.011	8.97	5.43	6.01	0.003	5.82	
270	540	552.40	3.30	5.2		0.013	9.11	5.32	6.01	0.004	5.61	
280	560	572.88	3.33	5.1		0.008	8.80	5.19	5.95	0.003	5.13	
290	580	593.34	3.35	5.0		0.009	8.88	5.20	5.92	0.003	4.83	
300	600	613.8	3.35	5.0		0.013	8.96	5.09	5.87	0.004	4.41	1.547
Final Liquor				1,380	367.72							12.365
Solids (Wet)					103.73							
Solids (Dry)				1,650		<0.2	1.12	1.16	1.02	0.7	1.86	1.848
Wash												15.76

Table 12. Sulfide Precipitation Test, Test No. 3, Notebook Page 1124-32

Test Conditions: Concentration of Na ₂ S solution added. Test terminated at 1,101 milliequivalents of sulfide added. Test Temperature = 60°C 29.5 g/l S ⁻² or 1.84 milliequivalents S ⁻² /ml and pH of 2.65												
Time, Min	Volume of Na ₂ S Solution Added, ml	S ⁻² Added Mill-equivalents	pH	Volume Solution or Sample, ml	Mass Residue, g	Assays of Solutions, g/l					Chromium Mass Balance (Solutions), g	
						Cu	Cr	Ni	Fe	Cd		Zn
Start	--	--	--	1,000	--	12.7	17.7	11.3	11.6	1.19	16.2	17.1
0	0	0	1.50	5.0	--							
10	20	36.7	1.35									
20	40	73.4	1.40									
30	60	110.1	1.30	5.2		8.16	16.6	10.4	10.8	1.11	15.1	
40	80	146.8	1.30	5.0		6.79	16.6	10.5	10.9	1.12	15.2	
50	100	183.5	1.40	5.0		5.44	16.2	10.2	10.6	1.08	14.8	
60	120	220.2	1.40	5.1		4.06	16.0	9.96	10.4	1.08	14.5	
70	140	256.9	1.48	5.2		2.81	15.7	9.76	10.2	1.05	14.5	
80	160	293.6	1.50	5.1		1.59	15.3	9.47	9.96	1.03	13.9	
90	180	330.3	1.50	5.0		0.34	14.8	9.11	9.62	0.99	13.6	
100	200	367.0	1.53	5.1		0.010	14.6	8.88	9.50	0.192	13.2	
110	220	403.7	1.60	5.1		0.016	15.0	8.98	9.72	0.015	12.8	
120	240	440.4	1.65	5.1		0.023	14.3	8.37	9.26	0.011	11.6	
130	260	477.1	1.70	5.0		0.024	14.1	8.07	9.10	0.010	10.7	
140	280	513.8	1.80	5.3		0.009	14.0	7.88	9.04	0.004	9.94	
150	300	550.5	1.85	5.2		0.019	13.6	7.29	8.75	0.006	8.43	
160	320	587.2	1.90	5.1		0.016	13.6	7.24	8.77	0.006	8.24	
170	340	623.9	1.95	5.1		0.023	13.3	6.90	8.57	0.007	7.39	
180	360	660.6	2.00	5.1		0.022	13.2	6.56	8.45	0.007	6.48	
190	380	697.3	2.05	5.1		0.018	12.9	6.25	8.27	0.006	5.80	
200	400	734.0	2.10	5.1		0.019	13.0	6.04	8.27	0.005	5.11	
210	420	770.7	2.10	5.2		0.003	12.5	5.53	7.95	0.002	4.15	
220	440	807.4	2.15	5.0		0.012	12.4	5.33	7.92	0.004	3.61	
230	460	844.1	2.23	5.0		0.004	12.1	4.98	7.74	0.002	2.82	
240	480	880.8	2.25	5.0		0.016	12.0	4.63	7.61	0.004	2.27	
250	500	917.5	2.30	5.0		0.019	11.9	4.33	7.50	0.005	1.67	
260	520	954.2	2.35	5.1		0.018	11.6	3.94	7.30	0.004	1.11	
270	540	990.9	2.40	5.1		0.027	11.6	3.64	7.30	0.005	0.670	
280	560	1,027.6	2.45	5.1		0.013	11.2	3.19	7.02	0.003	0.331	
290	580	1,064.3	2.55	5.1		0.021	11.1	2.74	6.91	0.004	0.177	
300	600	1,101	2.65	5.0		0.018	11.1	2.30	6.90	0.004	0.108	1.902
Final Liquor				1,260								13.986
Solids (Wet)				48.41								
Solids (Dry)				14.51								
Wash				1,780		0.002	0.790	0.327	0.555	0.001	0.148	1.406

Table 11. Sulfide Precipitation Test, Test No. 2, Notebook Page 1124-28

Test Conditions: Concentration of Na ₂ S solution added. Test terminated at 1,101 milliequivalents of sulfide added. Test Temperature = 22°C 29.5 g/l S ²⁻ or 1.84 milliequivalents S ²⁻ /ml and pH of 4.00												
Time, Min	Volume of Na ₂ S Solution Added, ml	S ²⁻ Added Milliequivalents	pH	Volume Solution or Sample, ml	Mass Residue, g	Assays of Solutions, g/l					Chromium Mass Balance (Solutions), g	
						Cu	Cr	Ni	Fe	Cd	Zn	
Start	--	0	2.05	1,000	--	12.3	17.18	11.0	11.3	1.16	15.6	17.18
0	0	0	2.05	5.0	1.5							
5	6	22.0	2.05	--	--							
10	20	36.7	2.08	--	--							
20	40	73.4	2.10	--	--							
30	60	110.1	2.13	5.2		8.31	16.5	10.4	10.8	1.11	15.3	
40	80	146.8	2.15	5.0		6.85	16.0	10.1	10.6	1.08	14.6	
50	100	183.5	2.20	5.3		5.43	15.8	9.96	10.3	1.05	14.5	
60	120	220.2	2.20	5.1		4.14	15.4	9.67	10.1	1.04	14.0	
70	140	256.9	2.20	5.1		2.69	14.9	9.27	9.77	0.99	13.6	
80	160	293.6	2.23	5.1		1.63	14.9	9.26	9.80	1.00	13.5	
90	180	330.3	2.28	5.2		0.47	14.6	8.98	9.56	0.97	13.4	
100	200	367.0	2.30	5.1		0.008	14.3	8.68	9.34	0.463	12.9	
110	220	403.7	2.38	5.1		0.009	14.2	8.54	9.27	0.014	12.3	
120	240	440.4	2.50	5.2		0.010	13.9	8.23	9.01	0.011	11.5	
130	260	477.1	2.65	5.1		0.012	13.6	7.95	8.79	0.011	10.4	
140	280	513.8	2.80	5.1		0.011	13.3	7.62	8.55	0.010	9.34	
150	300	550.5	2.90	5.0		0.012	13.1	7.40	8.44	0.008	8.32	
160	320	587.2	3.00	5.0		0.012	13.1	7.18	8.36	0.008	7.40	
170	340	623.9	3.08	5.0		0.007	12.9	6.95	8.22	0.004	6.44	
180	360	660.6	3.20	5.0		0.005	12.5	6.57	7.93	0.003	5.37	
190	380	697.3	3.20	5.1		0.007	12.2	6.25	7.72	0.004	4.49	
200	400	734.0	3.30	5.0		0.009	12.3	6.12	7.73	0.005	3.73	
210	420	770.7	3.40	5.0		0.009	12.1	5.79	7.54	0.004	2.90	
220	440	807.4	3.45	5.1		0.008	11.8	5.42	7.34	0.004	2.00	
230	460	844.1	3.50	5.1		0.004	11.7	5.19	7.23	0.002	1.43	
240	480	880.8	3.55	5.1		0.007	11.3	4.75	6.90	0.003	0.84	
250	500	917.5	3.65	5.2		0.006	11.3	4.45	6.87	0.004	0.331	
260	520	954.2	3.0	5.1		0.004	11.0	3.98	6.57	0.002	0.121	
270	540	990.9	3.83	5.0		0.008	11.0	3.51	6.39	0.003	0.068	
280	560	1,027.6	3.90	5.0		0.010	10.8	2.89	6.13	0.003	0.057	
290	580	1,064.3	3.90	5.0		0.005	10.6	2.35	5.90	0.002	0.034	
300	600	1,101.0	4.00	5.3		0.009	10.4	1.85	5.61	0.002	0.045	1.246
Final Liquor				1,340		0.009	10.4	1.85	5.61	0.002	0.045	13.936
Solids (Wet)				58.51								
Solids (Dry)				15.11								
Wash				1,780		<0.2	0.800	0.232	0.585	<0.2	0.034	1.424
												96.72

Table 10. Sulfide Precipitation Test, Test No. 1, Notebook Page 1124-26

Test Conditions: Concentration of Na ₂ S solution added. Test terminated at 134 milliequivalents of sulfide added. Test Temperature = 22°C 58.9 g/l S ²⁻ or 3.67 milliequivalents S ²⁻ /ml and pH of 3.25												
Time, Min	Volume of Na ₂ S Solution Added, ml	S ²⁻ Added Milliequivalents	pH	Volume Solution or Sample, ml	Mass Residue, g	Assays of Solutions, g/l					Chromium Mass Balance (Solutions), g	
						Cu	Cr	Ni	Fe	Cd		Zn
Start	--	--	2.05	1,000	--	12.5	16.8	10.7	11.1	1.12	15.0	16.80 ¹
0	0	0	2.05	5.0	0							
5	6	22.0	2.05	--								
10	10	36.7	2.08	--								
20	20	73.4	2.10	--								
30	30	113.8	2.10	5.3	0.62	8.13	16.0	10.0	10.5	1.05	14.3	-0.0752
40	40	146.8	2.13	5.3	0.66	7.15	16.1	10.0	10.5	1.07	14.3	-0.0752
50	50	183.5	2.13	5.0	0.43	5.92	16.1	10.0	10.6	1.07	14.5	-0.0742
60	60	220.2	2.13	5.1	0.77	4.48	15.6	9.64	10.2	1.03	13.8	-0.0682
70	70	256.9	2.15	5.3	0.84	3.13	15.5	9.47	10.2	1.02	13.6	-0.0692
80	80	293.6	2.18	5.4	1.03	1.95	15.4	9.35	10.1	1.01	13.5	-0.0672
90	90	330.3	2.20	5.4	0.92	0.090	15.1	9.15	9.91	0.99	13.2	-0.0682
100	100	367.0	2.20	5.1	1.12	0.031	15.5	9.29	10.1	0.77	13.6	-0.0622
110	110	403.7	2.28	5.6	1.24	0.016	15.0	8.84	9.75	0.033	12.7	-0.0652
120	120	440.4	2.40	5.5	1.20	0.017	14.9	8.67	9.61	0.018	12.1	-0.0642
140	140	513.8	2.70	5.0	1.34	0.022	14.7	8.27	9.43	0.014	10.2	-0.0542
160	160	587.2	2.95	5.3	1.37	0.017	15.0	8.17	9.53	0.011	8.61	-0.0592
180	180	660.6	3.13	5.0	1.78	0.018	14.0	7.23	8.83	0.010	6.23	-0.0512
200	200	734.0	3.25	5.2	1.55	0.011	14.2	6.99	8.87	0.006	4.52	-0.0522
Final Liquor				1,040	1.55	0.011	14.2	6.99	8.87	0.006	4.52	-14.7682
Solids (Wet)				--	38.66							
Solids (Dry)				--	10.04							
Wash				4,000		0.007	0.487	0.274	0.324	0.003	0.252	-1.9482
												17.6192

1 Input.
2 Output.

atomic number and the approximate concentration on a cathode-ray tube by means of a computer program interface developed by the manufacturer of the equipment, namely Kevex, Inc.) This procedure was not repeated for tests 2 to 4.

During the sulfide addition, the solution pH was monitored. After a predetermined quantity of sulfide had been added, the test was stopped by transferring the slurry contents to a Buchner filtration apparatus and separating the filtrate from the filter cake. Filtration continued until the cake was nearly dry but not "cracked" (i.e., split by shrinkage). The volume of the filtrate was then determined. The filter cake was subsequently washed with deionized water, and the volume of wash solution was measured. The filtrate and wash solutions were submitted for analysis. The filter cake was weighed moist, and a portion was sampled and dried to determine the percent solids. The moist filter cake was then stored under water in an air-tight container to be incorporated in Test 4.

Four tests were performed. Test conditions are summarized below.

Test 1 (see Table 10)

To 1 liter of metal stock solution was added a sodium sulfide solution assaying 58.9 grams sulfide per liter at a test temperature of 22°C. Samples were taken at the time intervals indicated and centrifuged, and the filtrate was analyzed by atomic absorption. The solids from these samples were analyzed by EDFs. Table 10 presents the results on solution assays.

Test 2 (see Table 11)

This test was similar to Test 1 with the following exceptions. The sodium sulfide solution was one-half the concentration as that used in Test 1. The test was continued to a higher level of sulfide addition. EDFs was not used on the centrifuged solids.

Test 3 (see Table 12)

This test was similar to Test 2 with the exception that it was conducted at 60°C. The shift in solution pH to lower values was a result of the elevated temperature.

Test 4 (see Table 13)

Test conditions were similar to Test 2 with the exception that sulfide precipitates from the prior 3 tests were combined and added to the metal stock solution prior to the addition of the aqueous sulfide solution. One solution assay was taken after the addition of the precipitate but before addition of the aqueous sulfide solution.

to the cake as it was being slurried for the extraction test. The EP test specifies that a terminal pH of 5.0 (but not more than 4 ml of 0.5N) acetic acid be added per gram of solids. If sufficient lime in excess of the amount required for neutralization of the maximum specified acetic acid chemical equivalent is added, then the terminal pH of the extract can be held at 8.0. At this pH (Test 5), cadmium levels of 0.036 ppm were present in the extract. The level of acetic acid added was 1.22 grams per gram of cake.

Test 6 used a higher level of lime addition, namely 1 part Ca(OH)_2 per 2.4 parts of cake. A final pH of 10.0 was achieved. At this level, somewhat lower levels of heavy metal content were noted, except for chromium which increased slightly. Some air oxidation of chromium probably occurred, and in its hexavalent state, its amphoteric behavior would contribute to some increase in its solubility.

4. SEPARATION OF METALS BY SULFIDE PRECIPITATION

Objective

The objective of the sulfide precipitation tests is to effect a separation between the metallic species of the sulfuric acid leach liquors by controlled additions of sodium sulfide. Sodium sulfide is a basic constituent, and therefore, its addition to acidic solutions has the effect of raising the solution pH.

Experimental Procedure

A stock solution consisting of heavy metal sulfates similar in composition to that produced in prior leach tests on plating sludges was prepared. This stock solution was analyzed prior to testing. One liter of this liquor was placed in a 2-liter glass kettle equipped with baffles and a 6.5 cm, single-bladed impeller-agitator operated at 750 RPM. The kettle was provided with a pH probe, a sampling tube, a reflux column to condense vapors, and a heating mantel.

A second aqueous stock solution of sodium sulfide was prepared and analyzed for sulfide concentration. This stock solution was placed in a measuring burette for monitored and controlled addition to the kettle at a rate of 1 ml/minute. Samples of slurry were withdrawn at 10-minute intervals and centrifuged. The samples of filtrate were submitted for analysis of the metallic constituents, namely copper, cadmium, zinc, nickel, iron, and chromium. Analysis was by the standard addition method using atomic absorption techniques against a known standard (see Appendix B for further details). In addition to solution assays, energy-dispersive X-ray fluorescence-spectrometry (EDXFS) was performed on the solids taken from the 10-minute samples in precipitation test Number 1. (The sample was bombarded with broad-band X-rays having sufficient energy to displace inner-shell electrons from their orbits. As other electrons from the outer orbits collapse to fill the created vacancies, secondary X-ray photons are generated. These photons are of specific energies according to the elements emitting them. An energy-dispersive detector then displays the element

Tests 5 and 6 show the effect of increasing lime additions upon extract concentrations. In Test 5, 1 part of Ca(OH)_2 was added to 10 parts by weight of filter cake (on a dry basis). In Test 6, the quantity of lime was increased to 1 part Ca(OH)_2 to 2.4 parts by weight of filter cake (on a dry basis).

Experimental Results and Discussion

Effect of Prior Sludge History

Attention is directed to Table 9, tests 1, 2, and 3, in which the prior sludge history is compared. In Appendix B, the sulfuric acid leach residues are characterized by mineralogical analysis. In that appendix, photomicrographs in Figures 2, 4, and 6 were taken of the filter cake feed to EP tests 1, 2, and 3, respectively. Figure 4 shows why EP Test 2 on Type B filter cake yielded the highest extract levels of heavy metals. The photomicrograph consists of a felted-mass of fine-grained gypsum which has formed at 66°C as a decomposition product of the metastable coarser-grained bassanite. This felted-mass has poor filtration characteristics, and therefore, some occluded solution phase is trapped in the interstitial volume between each washing. This accounts for the poorer results in the final EP leach.

EP Test 1 on Type A cake (freshly precipitated and leached) is now compared with EP Test 3 on Type C cake (aged 6 weeks at 22°C). In Appendix B, the two cakes are compared in Figures 2 and 6. The difference between these cakes is that Type A cake is made up of bassanite, whereas Type C cake is undergoing transformation to gypsum in the pseudomorphic shape of the original bassanite crystals. During this transformation, some trapping of heavy metals (either by chemisorption, by mechanical occlusion, or by lattice substitution) may occur. As a result, the sulfuric acid leaches are not as effective in removing trace heavy metal constituents. During the long-time (24-hour) acetic acid leaches associated with the extraction procedure, the trapped heavy metal constituents are solubilized.

Effect of More Vigorous Washing Procedure

A comparison between tests 3 and 4 in Table 9 shows that the latter yields lower heavy-metal extract assays by about one-third. This difference is a result of breaking down the bassanite pseudomorphs by the action of the blender to reduce the aspect ratio of the needle-like crystals. The chopped-crystals are easier to wash, and as a result, the starting solids contain a lower heavy metal assay (see Table 3).

Effect of Lime Addition

Tests 4, 5, and 6 (Table 9) compare the effect of lime addition on fixing heavy metal ions. In Test 4, no free lime was present, since the prior cake had been thoroughly leached with acid washes and water. Although the levels of heavy metals in the extract are low, cadmium at 0.67 ppm is still above the EPA standard of 0.1 ppm. In Test 5, 10 percent (by dry weight equivalent) of hydrated lime (Ca(OH)_2) was added

Table 16. Sulfide Precipitation Test -
Calculations on Percent Element Remaining in Solution
Test Number 3, Notebook Page Number 1124-32

Test Conditions:

Starting solution 1 liter of sulfate
solution of the following assay (all g/l)

<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>
12.7	1.19	16.2	11.3	11.6	17.7

Add 29.5 g/l $S^{=}$ as Na_2S at a rate of
2 ml/minute

Temperature: 60°C

Duration: 300 minutes

Wash: 2 liters deionized water

<u>Milliequivalents</u> <u>Sulfide Added</u>	<u>Weight % Remaining in Solution</u>						
	<u>pH</u>	<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>
0	1.50	100	100	100	100	100	100
110	1.30	67.45	97.92	97.85	96.62	97.74	98.29
220	1.40	35.00	99.35	97.98	96.49	98.15	98.96
330	1.50	3.05	94.80	95.66	97.01	94.50	95.28
440	1.65	0.21	0.17	84.79	87.71	94.53	95.67
550	1.85	0.18	0.62	63.94	79.27	92.68	94.41
660	2.00	0.22	0.75	50.94	73.92	92.76	94.97
770	2.10	0.03	0.22	19.03	64.50	90.33	92.07
880	2.25	0.17	0.46	8.14	55.64	89.09	92.07
990	2.40	0.30	0.59	5.82	45.35	88.59	92.26
1100	2.65	0.11	0.49	0.97	29.56	86.40	91.09
1100 + Wash		0.23	0.64	2.59	34.72	94.92	99.03

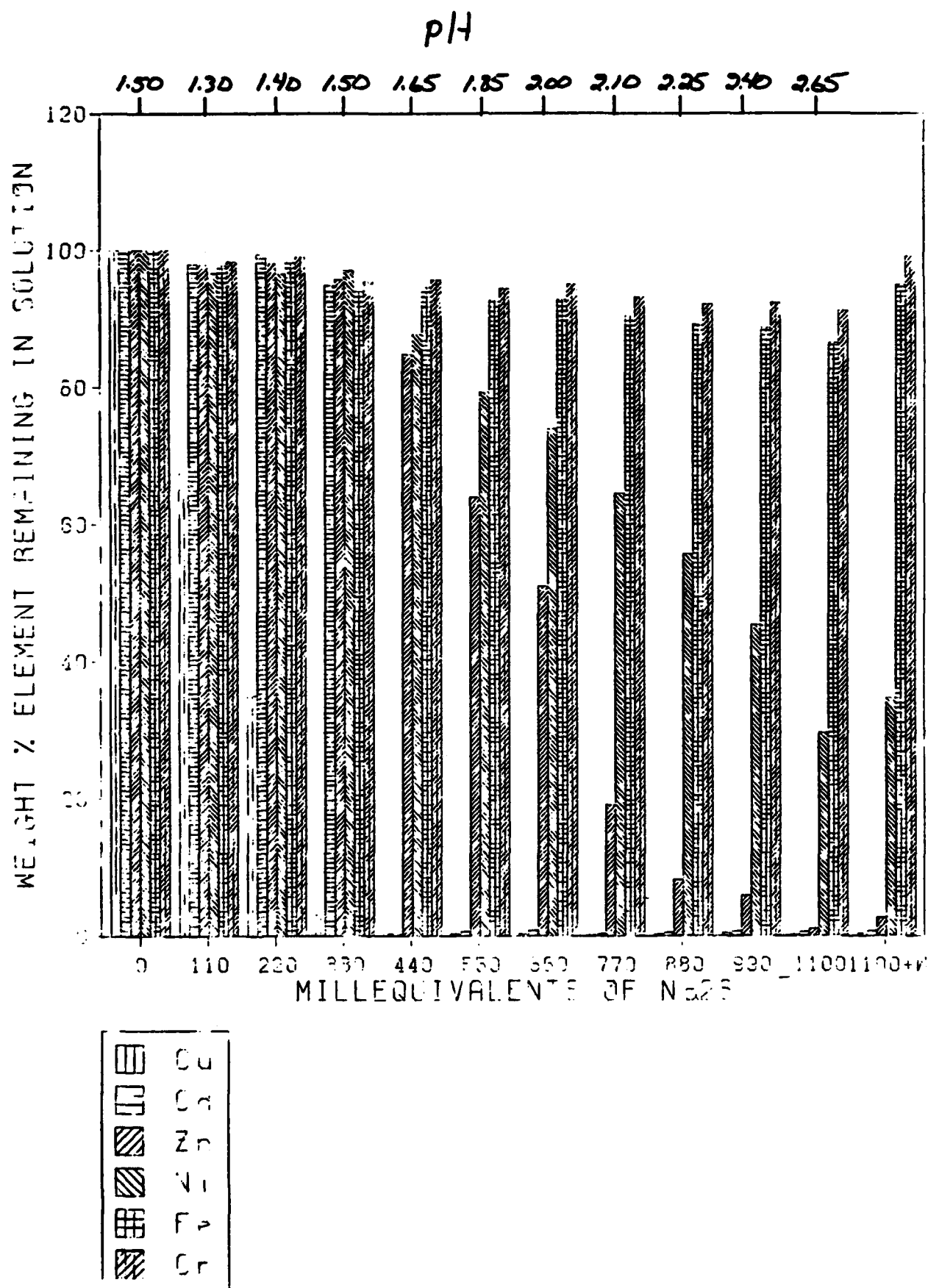


Figure 8. Sulfide Precipitation Test 3 (1124-32) (60°C). Distribution of elements as weight percent in solution versus sodium sulfide addition and solution pH, weight percent element remaining in solution (test conditions in tables 12 and 16).

Table 17. Sulfide Precipitation Test -
Calculations on Percent Element Remaining in Solution
Test Number 4, Notebook Page Number 1124-36

Test Conditions:

Starting solution 1 liter of sulfate
solution of the following assay (all g/l)

<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>
12.5	1.12	15.0	10.7	11.1	16.8

Add 16.4 g/l $S^{=}$ as Na_2S at a rate of
2 ml/minute

Temperature: 22°C

Duration: 300 minutes

Add 100 grams of equivalent dry weight
moist sulfide solids from previous tests.

Wash: 2 liters deionized water

Milliequivalents $S^{=}$ Added as Na_2S	Weight % Remaining in Solution						
	pH	Cu	Cd	Zn	Ni	Fe	Cr
Without Seed	2.05	100	100	100	100	100	100
With Seed	2.93	0.02	62.60	151.77	87.27	83.03	79.10
61	3.00	0.12	0.90	143.32	86.46	82.52	77.98
123	3.05	0.11	0.57	130.52	84.69	81.93	78.15
184	3.10	0.07	0.39	116.83	81.60	79.83	75.72
246	3.13	0.14	0.51	110.04	82.98	82.12	79.71
307	3.20	0.11	0.42	96.09	79.53	80.15	77.73
368	3.20	0.09	0.44	80.40	75.82	78.02	76.12
430	3.25	0.15	0.45	71.15	73.94	77.46	74.44
491	3.30	0.09	0.35	66.29	75.11	80.26	77.96
552	3.30	0.15	0.49	50.80	68.96	76.28	74.69
614	3.35	0.15	0.50	41.20	67.44	76.87	75.79
614 + Wash		0.15	0.53	60.88	84.84	91.99	86.52

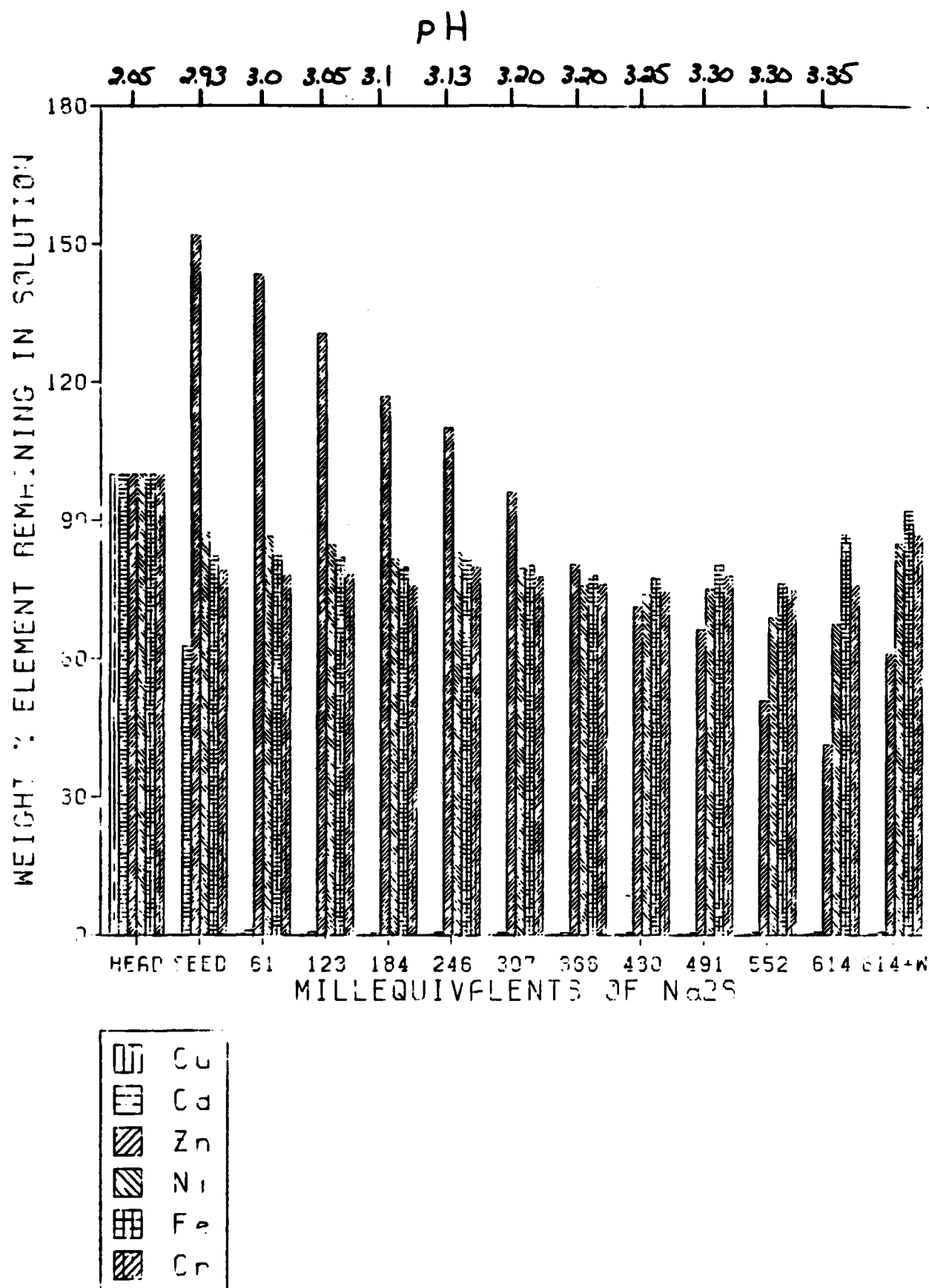


Figure 9. Sulfide Precipitation Test 4 (1124-48) (22°C) (recycled seed from prior test added). Distribution of elements as weight percent in solution versus sodium sulfide addition and solution pH, weight percent element remaining in solution (test conditions in tables 13 and 17).

Discussion of Sulfide Precipitation Tests

Background for Use of Selective Sulfide Precipitation

The method of selective sulfide precipitation with adjustment of pH as a technique in chemical separations is well established. Simons⁶¹ has recalculated and tabulated the solubility products of common metal sulfides. The table below lists these values for copper, lead, cadmium, zinc, nickel, and iron, the common electroplating species.

<u>Metal Sulfide</u>	<u>Solubility Product (Expressed as Log₁₀)</u>
Cu ₂ S	-47.70
PbS	-27.03
CdS	-26.15
ZnS	-24.05
NiS	-20.55
FeS	-17.31

The above data represent a wide range of possible concentrations of metal ions in solution for a given sulfide ion concentration and have been the basis for metal separations, both in the chemical laboratory and on a commercial scale. In order to estimate the metal ion concentration from the solubility product, a knowledge of the sulfide ion concentration is required. This sulfide ion concentration can be calculated from the ionization constants of hydrogen sulfide gas.

From the data compilation of Garrels and Christ⁶², the solubility and ionization constants of hydrogen sulfide can be found as follows:

$$H_2S(g) = H_2S(aq) K_{(1)} = \frac{[H_2S]_{aq}}{p H_2S(g)} = 0.103 \quad (1)$$

where $p H_2S(g)$ is the pressure of H_2S over the aqueous phase in atmospheres, and $[H_2S]_{aq}$ is the molality of H_2S in aqueous solution.



$$K_2 = \frac{[H^+][HS^-]}{[H_2S]_{aq}} = 9.89 \times 10^{-8}$$



$$K_3 = \frac{[\text{H}^+][\text{S}^{=2}]}{[\text{HS}]} = 1.47 \times 10^{-14}$$

From the above equilibria by summing equations (1), (2), and (3) and taking products of the equilibria constants, the following relationship may be derived:



$$K_4 = \frac{[\text{H}^+]^2[\text{S}^{=2}]}{p \text{H}_2\text{S (g)}} = 1.50 \times 10^{-22}$$

The bracketed terms represent chemical activities of the ionic species, which can be approximated by their molalities for dilute solutions.

By rearrangement of the equilibrium expression for Equation (4) and substituting $p \text{H}_2\text{S}$ as 1 atmosphere in the expression, one can express the equilibrium sulfide level as a function of solution pH as follows:

$$[\text{S}^{=2}] = \frac{K_4}{[\text{H}^+]^2} \quad (5)$$

Taking logarithms of both sides of the above equation and substituting the expression $\text{pH} = -\log [\text{H}^+]$, the following relationship emerges:

$$\log [\text{S}^{=2}] = \log K_4 + 2 \text{ pH} = -21.8 + 2 \text{ pH} \quad (6)$$

From the tabular listing of metal sulfide solubility products, it is possible to express the concentration of the metal ion as a function of solution pH as follows:

<u>Metal Sulfide Solubility Product Expression</u>	<u>Expression for Metal Ion Concentration</u>
$\log [\text{Cu}^{+2}]^2 [\text{S}^{=2}]$	$\log [\text{Cu}^{+2}] = -12.95 - \text{pH}$
$\log [\text{Pb}^{++}] [\text{S}^{=2}]$	$\log [\text{Pb}^{++}] = -5.24 - 2 \text{ pH}$
$\log [\text{Cd}^{++}] [\text{S}^{=2}]$	$\log [\text{Cd}^{++}] = -4.35 - 2 \text{ pH}$
$\log [\text{Zn}^{++}] [\text{S}^{=2}]$	$\log [\text{Zn}^{++}] = -2.25 - 2 \text{ pH}$
$\log [\text{Ni}^{++}] [\text{S}^{=2}]$	$\log [\text{Ni}^{++}] = -1.25 - 2 \text{ pH}$
$\log [\text{Fe}^{++}] [\text{S}^{=2}]$	$\log [\text{Fe}^{++}] = 4.49 - 2 \text{ pH}$
$\log [\text{Cr}^{+++}] [\text{OH}^-]^3$	$\log [\text{Cr}^{+++}] = 11.83 - 3 \text{ pH}$

In the table above, we have included in the last line an expression for the ionization of trivalent chromium hydroxide from the data tabulated by Latimer.⁶³ Lingane⁶⁴ states of chromium, "If one were following the systematic hydrogen sulfide scheme of analysis, he would find chromium in the ammonium sulfide group, but it occurs there as hydrous Cr_2O_3 because this compound is more insoluble (and thus more stable) than Cr_2S_3 ".

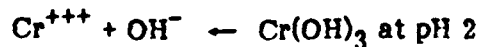
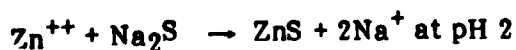
As will be shown below, it is theoretically possible to maintain chromium in solution while quantitatively precipitating the other heavy metal constituents by stagewise additions of sodium sulfide to the leach liquor using solution pH as a control. The following discussion does not take into account coprecipitation effects which most assuredly will occur in a mixed metal system. If one uses 1,000 and 1 mg/liter as a threshold, it is possible to calculate the pH at which each metal species should theoretically reach these thresholds as tabulated below.

Table 18. Calculated Solubilities of Metal Ion Species in Sulfide Solutions in Equilibrium with H_2S Gas at One Atmosphere Pressure

<u>Metal Ion Species</u>	<u>pH Value at 25°C</u>	
	<u>1,000 mg/liter</u>	<u>1 mg/liter</u>
Cu^+	<0*	0*
Pb^{++}	<0*	0.04
Cd^{++}	<0*	0.35
Zn^{++}	<0*	1.28
Ni^{++}	0.26	1.76
Fe^{++}	3.12	4.62
Cr^{+++} (Value for hydroxide)	4.52	5.52

* pH values less than zero indicate that this species is highly insoluble even in highly acidic sulfide solutions.

An examination of the above table indicates that from theoretical considerations, it is possible to make a quantitative separation of chromium from copper, lead, cadmium, zinc, and possibly nickel by stagewise addition of sulfide, e.g.



The assumption that chromium is an unassociated cation is somewhat simplistic, as Finholt, et al.,⁶⁵ have reported the formation of a dimeric species in sulfate solution at pH 2 of stoichiometry $(\text{H}_2\text{O})_4\text{Cr}(\text{OH})\text{SO}_4 \cdot \text{Cr}(\text{H}_2\text{O})_4^{+3}$. This polymerization of chromium may have some significance with respect to its stability.

Comparison of Predicted Results with Experimental Results

The theoretical predictions given in Table 18 are for sulfide ion with a hydrogen sulfide overpressure of one atmosphere pressure; therefore, they are not strictly applicable to our test situation in which sodium sulfide in an alkaline solution was added to an acidic leach liquor. The hydrogen sulfide gas overpressure under our experimental conditions is orders of magnitude smaller than one atmosphere (in fact, not detectable by odor at a threshold of detection limit of about 1 ppm in the vapor phase). Furthermore, pH and sulfide addition were interdependent. Therefore, the predictions are only a guide to indicate that at pH values less than 4.0, chromium should be relatively unaffected by precipitation, whereas copper, cadmium, and zinc should be quantitatively precipitated.

Of the four tests, numbers 2 and 3 show the best results with respects to maintaining chromium in solution and precipitation of copper, cadmium, and zinc. In Test Number 2, a terminal pH of 4.0 was reached. At this value of pH, trivalent chromium should have a solubility of more than 30 g/l in equilibrium with its hydroxide; however, Table 15 indicates that only 87.9 percent of the original chromium remained in solution. Upon washing with deionized water (which would tend to raise the pH slightly), chromium was solubilized so that 96.2 percent of the chromium reported to the combined initial filtrate and wash solutions.

A balance of equivalents of metal ions participating in the sulfide precipitation (excluding chromium which does form stable sulfides) can be conducted as shown in Table 19. This table shows that within a limit of experimental error (9.8 percent for Test 2 and 6.0 percent for Test 3), added sulfide precipitates an equivalent quantity of heavy metals. The increase in chromium occurring upon washing is most dramatic in Test 3 (Table 16), which shows 99 percent of the original chromium recovered to the original solution. This recovery of chromium is confirmed by an assay on the precipitate, which indicates about 0.2 percent chromium in the solids.

These tests show that a separation between a solid sulfide containing copper and cadmium is readily made from chromium and that by careful control of pH, zinc will follow copper and cadmium. As is expected, nickel and iron tend to be divided between the solution and the precipitate. By washing the solids, chromium recovery to the combined filtrates is nearly quantitative.

**Table 19. Balance of Equivalents
of Metal and Sulfide Reacted**

<u>Sulfide Precipitation Test</u>	<u>Species</u>	<u>Starting Solution, Gram-Milli- equivalents</u>		<u>Weight Fraction Precipitated at End of Test (Prior to Washing)</u>		<u>Milli- equivalents Precipitated</u>
Test No. 2	Cu	387	x	0.9989	=	387
	Cd	21	x	0.9975	=	21
	Zn	477	x	0.9958	=	475
	Ni	281	x	0.7557	=	212
	Fe	405	x	0.2789	=	<u>113</u>
Total						1,208
Sulfide Added						1,100
Variance (%)						9.8%
Test No. 3	Cu	400	x	0.9989	=	400
	Cd	21	x	0.9951	=	21
	Zn	496	x	0.9903	=	491
	Ni	289	x	0.7044	=	198
	Fe	415	x	0.1360	=	<u>56</u>
Total						1,166
Sulfide Added						1,100
Variance (%)						6.0%

5. RECOVERY OF CHROMIUM BY SOLVENT EXTRACTION

Objective

After sulfide precipitation to remove cadmium, copper, zinc, and some nickel, the treated solution will primarily contain chromium (III), iron (II), and some nickel. Chromium can be recovered by oxidizing the solution to oxidize iron (II) to iron (III) and by raising the solution pH to precipitate a chromium-iron sludge. Nickel would primarily remain in solution. However, the ultimate disposal of such a sludge may not be straightforward, and the sludge may require further treatment. An alternative to hydroxide precipitation at this stage in the process is solvent extraction. Solvent extraction may result in separation of iron from chromium, and concentration of each specie would then be possible. In order to investigate this possibility, a few solvent extraction tests were performed to determine iron (II) and chromium (III) loading as a function of solution pH.

Experimental Procedure

Batch shakeout tests were conducted to study iron (II) and chromium (III) loading as a function of solution pH. The shakeout tests were conducted in a baffled 400-ml beaker of 2-3/8-inch inside diameter with a drain valve at the bottom to allow for withdrawal of separated phases. A standard test was conducted at 22°C, using 150 ml of organic phase and 75 ml of aqueous phase and a contact time of 15 minutes. Agitation was supplied by a slotted disk impeller (1-1/2-inch diameter), rotating at 1,000 RPM. The solution pH was adjusted to the desired value using sulfuric acid or sodium hydroxide solution. After the 15-minute contact time, the phases were allowed to separate. After complete phase separation was obtained, samples of each phase were taken, filtered, and submitted for assay. The aqueous phase pH was recorded, the organic and aqueous phases were recontacted, and the solution pH was adjusted to the desired value. This procedure was repeated several times to determine iron (II) and chromium (III) loading at several pH values.

In each shakeout test conducted, samples of both the organic and aqueous phases were submitted for assay. The aqueous sample required no further preparation, while the organics were prepared by a wet-ash technique. The aqueous phases were then assayed by induction coupled plasma (ICP) spectroscopy. Good agreement was obtained between assays of the loaded organic and raffinate in comparison to the feed aqueous assay.

Experimental Results

Results of three sets of experiments are shown in Table 20. Feed to all three experiments was solution that had undergone sulfide precipitation to remove copper, cadmium, and zinc. The feed solution which was obtained by combining filtrates from several sulfide precipitation tests contained 11.4 g/l Cr (III), 6.8 g/l Fe (II), 3.6 g/l Ni, and 1.6 g/l Zn. A complete description of each test is given below.

**Table 20. Results of Solvent Extraction^a
of Plating Waste Solution^b**

Test No.	Organic Composition	pH	Metal Extracted, %				Metal Loaded g/l
			Zn	Fe (II)	Cr (III)	Ni	
1	20 v/o DEHPA Escaid 200	1.16	42.2	13.9	0.03	0.0	0.8
		1.95	95.6	46.8	2.2	0.2	2.2
		2.85	98.9	82.3	21.2	0.8	5.6
		3.85	99.9	99.8	54.0	6.3	8.8
		4.55	99.9	99.9	79.5	42.8	11.3
2	20 v/o DEHPA 10 v/o DMOO Escaid 200	1.25	32.4	60.0	0.1	78.1	4.4
		2.04	92.9	97.2	2.8	98.7	7.5
		2.86	98.9	99.2	27.8	99.9	9.8
		3.79	99.7	99.9	61.8	99.9	12.6
		4.50	99.8	99.9	79.7	99.9	13.0
3	10 v/o DEHPA 20 v/o DMOO Escaid 200	1.25	30.8	49.1	0.03	81.0	3.3
		2.05	46.1	86.9	0.4	98.4	5.7
		2.85	90.8	98.7	1.9	99.8	6.5
		3.74	97.9	99.8	19.8	99.9	7.9
		4.50	98.7	99.9	38.3	99.9	8.9

^a All tests were conducted at 22°C using an organic-to-aqueous phase ratio of 2-to-1.

^b The feed solution contained: 11.4 g/l Cr⁺³, 6.84 g/l Fe⁺², 3.64 g/l Ni, and 1.57 g/l Zn.

Test 1 (Table 20)

In the first test, the organic consisted of 20 volume percent di-2-ethylhexyl phosphoric acid (DEHPA) diluted in Escaid 200 (an aliphatic diluent). The test results show that with this organic composition, the order of metal loading was Zn > Fe (II) > Cr (III) > Ni.

Test 2 (Table 20)

In the second test, the organic consisted of 20 volume percent DEHPA plus 10 volume percent 3,7 dimethyloctanal oxime (DMOO) diluted in Escaid 200. The non-chelating oxime (DMOO) acts as a synergist and can affect the order of metal extraction. This effect was pronounced since the order of metal extraction was Ni > Fe (II) > Zn > Cr (III).

Test 3 (Table 20)

In the third test, the organic consisted of 10 volume percent DEHPA plus 20 volume percent DMOO diluted in Escaid 200. The order of metal extraction in this test is $\text{Ni} > \text{Fe (II)} > \text{Zn} \gg \text{Cr (III)}$.

Discussion of Solvent Extraction Results

In the optimized process, zinc will be removed from the solution during sulfide precipitation. Therefore, the solution to be used in solvent extraction (or hydroxide precipitation) would primarily consist of iron (II), chromium (III), and some nickel. Based on the results shown in Table 20, it appears that separation of iron from chromium is possible using DEHPA (Test 1). The test results shown for Test 1 in Table 20 indicate that at pH 1.95, iron (II) extraction was 51.5 percent, chromium (III) extraction was 2.2 percent, and nickel extraction was 0.1 percent. The iron (II)-to-chromium (III) separation factor (the ratio of the concentration of iron in the organic divided by the iron in the aqueous divided by the ratio of the concentration of chromium in the organic divided by the chromium in the aqueous) at pH 1.95 is 39.4. The separation factors at pH 2.84 and 3.85 are 17.3 and 102, respectively. These high separation factors indicate that in a multiple-stage countercurrent, continuous solvent extraction circuit, a high degree of iron and chromium separation can be obtained. The approach to separating iron from chromium could be done using either one of two methods: 1) the iron could be extracted prior to chromium by controlling the pH or 2) both iron and chromium could be extracted, followed by selective stripping. In either case, concentrated and purified iron (II) and chromium (III) strip solutions would be obtained.

SUMMARY AND CONCLUSIONS

A "typical" electroplating sludge, consisting of a high proportion of calcium hydroxide and also containing heavy metal hydroxides of copper, cadmium, zinc, iron, nickel, and chromium, was prepared and aged. The aging treatment had little effect upon the recovery of the heavy metals upon subsequent sulfuric acid leaching. Metal recoveries of greater than 99 percent (with the exception of cadmium which was closer to 98 percent) in the leach liquor were observed upon leaching at 65°C at pulp densities ranging from 20 to 30 percent at a solution pH of 1.5. Time samples on the leach liquor indicated that the extraction was essentially complete in 30 minutes of leaching. The filter cakes from the leaching tests were found to be innocuous, as determined by the Extraction Procedure Test when 10 percent by weight lime was added to the filter cake.

The leach liquors were then subject to controlled additions of sodium sulfide in order to effect a separation between elements which readily form sulfides from solution. In one test conducted at 60°C with sodium sulfide added to a solution pH of 1.5, copper and cadmium were removed quantitatively from solution; however, zinc concentrations of 100 mg/liter were still present under these conditions. Chromium was unaffected by the precipitation process at this pH, with 99 percent soluble after filtering the filter cake. Under these conditions, nickel reports principally to the sulfide precipitate and iron to the chromium-rich solution.

Finally, a series of solvent extraction tests were performed on combined filtrates from several of the sulfide precipitation tests. High separation factors between chromium and iron, and between chromium and nickel, were observed. This indicates that concentrated and purified iron, nickel, and chromium strip solutions can be obtained with the appropriate countercurrent continuous solvent extraction circuit operating with DEHPA as the organic extractant.

The following conclusions were reached for the sludges that were prepared:

Aging of metal plating sludges has little effect upon recovery of heavy metals by sulfuric acid leaching, except that accelerated aging at elevated temperature tends to increase, slightly, the terminal heavy metal assays of the leached filter cakes.

Sulfuric acid leaching of the prepared plating sludges is effective in short contact times (~ 30 minutes) in effecting greater than 99 percent recovery of copper, chromium, nickel, zinc, and iron and greater than 97 percent recovery of cadmium in the leach liquor. Under the leaching conditions employed (pH of 1.5, initial pulp density of ~ 20 percent), it was not possible to render the residual filter cake into compliance as nonhazardous as specified by the Extraction Procedure Test. More rigorous conditions of leaching (countercurrent, with stronger acid) may be required.

However, the residual filter cake after leaching can be rendered innocuous to the Extraction Procedure Test by blending 10 percent by weight of lime to the solids which are primarily calcium sulfate.

Sulfide precipitation under controlled pH on the sulfuric acid leach liquors is effective in separating copper and cadmium quantitatively as sulfides from chromium which remains in solution. Zinc is nearly quantitatively precipitated, whereas nickel and iron report both to the sulfide precipitate and the leach liquor.

Separation between divalent iron and chromium and between nickel and chromium was undertaken in shakeout tests. An organic consisting of 20 volume percent di-2-ethylhexyl phosphoric acid (DEHPA) diluted in Escaid 200 (an aliphatic diluent) was shown to effect a separation between chromium, iron, and nickel.

Filtration rates of both the sulfuric acid leached sludge residues and of the sulfide precipitates without added filter aid tend to be quite slow.

Analytical Procedures

When atomic absorption is used, the following EPA method will be used:

	<u>Flame Atomic Absorption</u>	<u>Furnace Atomic Absorption</u>
Cd	213-1	213-2
Cr	218-1	218-2
As		206-2
Cu	220-1	220-2
Pb	239-1	242-1
Zn	289-1	289-2
Fe	236-1	236-2
Ca	215-1	
Mg	242-1	

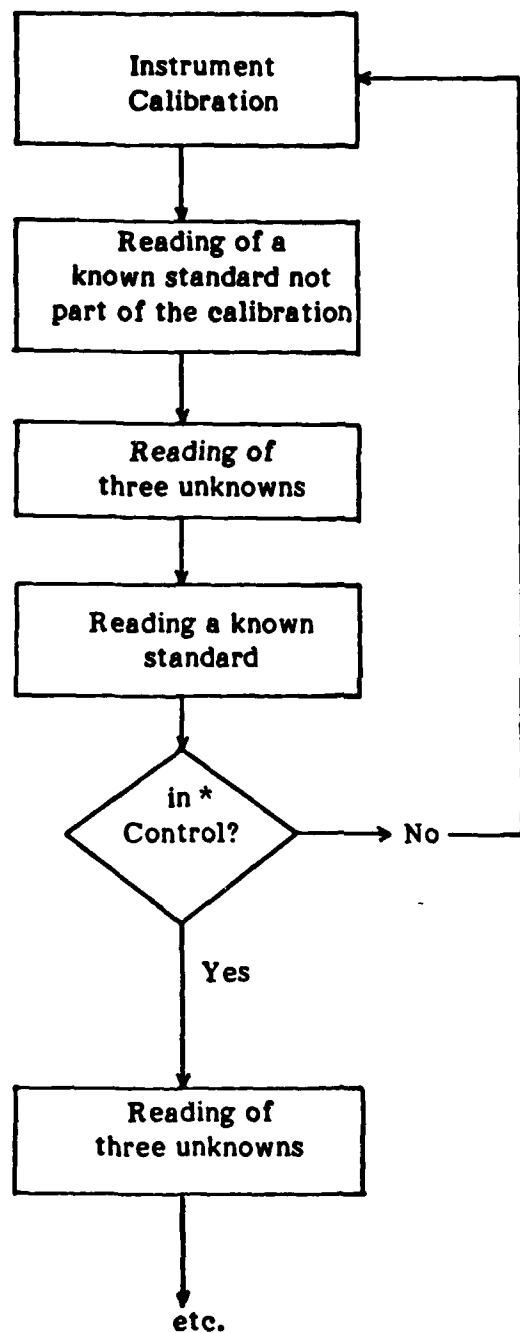
Analysis of organic compounds in the effluents (e.g. DEHPA, Adogen 283, Alamine 336, elating oximes, alcohol, diluent, etc.) will be done in-house, with quality control provided by a certified laboratory (Rocky Mountain Analytical). This laboratory maintains its certification through an ongoing round robin program with EPA.

Analysis is performed by cold flame atomic emission using lithium as an internal standard.

Following are examples of detection limits in liquid samples obtained by our graphite furnace techniques:

As : 1 ppb	Fe : 1 ppb
Cd : 0.1 ppb	Pb : 1 ppb
Cr : 1 ppb	Zn : 0.05 ppb
Cu : 1 ppb	

Calibration curve is also used; the following diagram describes the procedure:

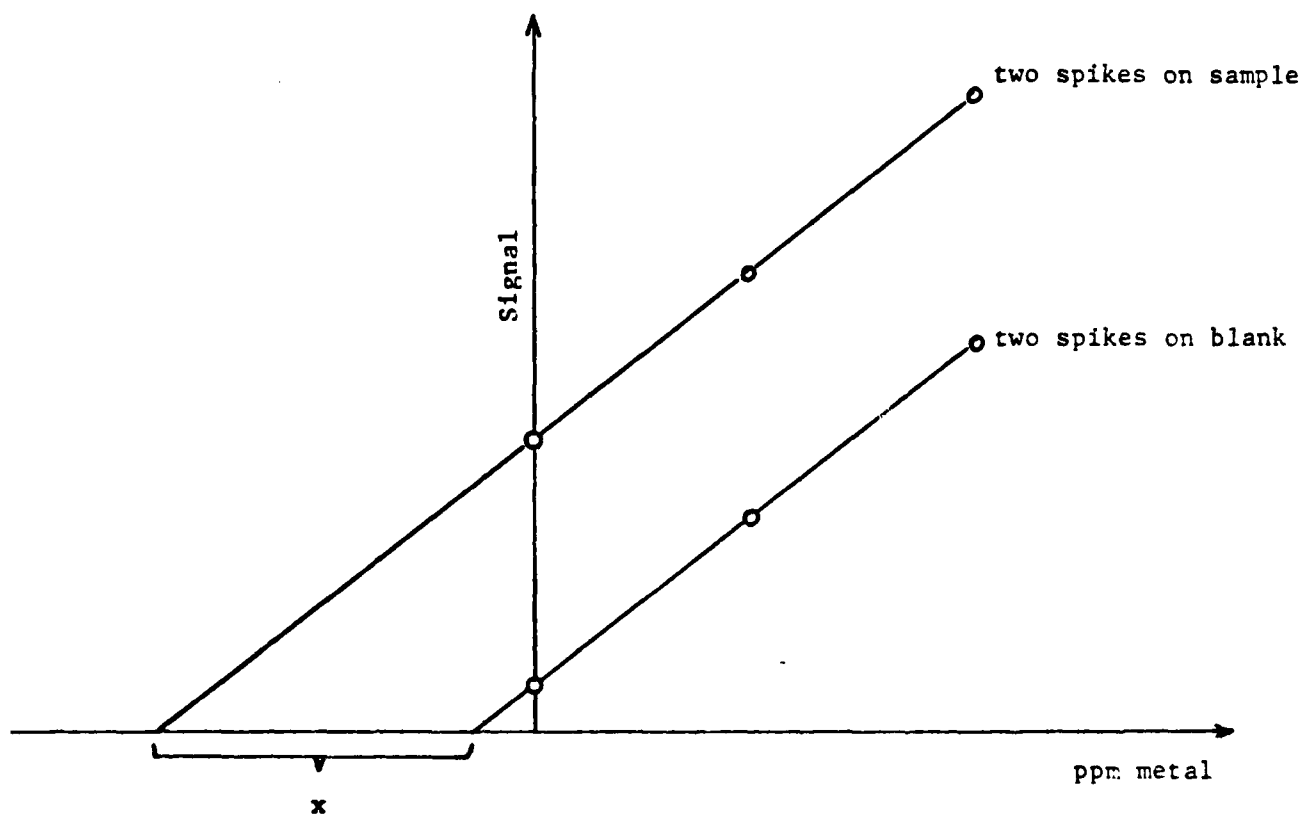


* A reading on standards within twice the standard deviation of the accepted value of standard.

Calibration Procedures and Frequency

Standard addition techniques are used systematically on all samples, all blanks and all EPA or Internal control samples.

Results are plotted as follows:



MAX

RESEARCH & DEVELOPMENT, INC.
THEFT, GOLDEN, COLORADO 80401
303-279-7636

ANALYTICAL REPORT

JOB NUMBER

79711

DATE SUBMITTED: _____

SUBMITTED BY: _____ EXT _____

DATE COMPLETED: _____

COPIES TO: _____

WORKING
PLACE NUMBER _____

DEPT NO _____

SAMPLE PREP

YES ☐NO ☐EXPEDITE ☐

AUTHORIZED BY _____

SAMPLE MATRIX/COMPOSITION
e.g. pH MAJOR IONS
ELEMENTS ETC.

ION

EST

EST

EST

EST

EST

EST

TURNS

CODE

DATE

DETER

METHOD

COMMENTS

4. Sampling Procedure

- o Analyzed samples should have only one phase
- o If any sample presents two phases, they will be separated and analyzed separately (0.45 - micron membrane filter)
- o Composite sampling is recommended
- o All samples analyzed for metals will be collected in polyethylene disposable flasks with a polypropylene cap, preserved with HNO_3 until pH 2, kept cool (4°C) until analysis, and analyzed within 24 hours for metals.

5. Sample Custody

- Process Sampling Operations

The following figure shows a recommended sample label containing all information necessary for effective sample tracking.

Sample description:	
Test Reference:	
Location:	
Time:	
Media:	
Preservative:	
Sample ID No.:	
Remarks:	

Laboratory tracking of samples is performed by systematic use of standard analytical reports as shown in the attached example.

CHEMICAL ANALYTICAL TECHNIQUES EMPLOYED

Element To Be Determined	Available Technique *			
	Limit of Detection in Solids, ppm (Based Upon 100-Fold Dilution of Solid)		Limit of Detection in Liquids, ppm	
	ICP	Flame AA	ICP	Flame AA
Cu	0.3	0.3	0.003	0.003
Cr	0.4	0.5	0.004	0.005
Ni	0.8	0.8	0.008	0.008
Fe	0.3	0.5	0.003	0.005
Cd	2.0	0.6	0.002	0.0006
Zn	0.2	0.2	0.002	0.002
Ca	0.005	0.05	0.00005	0.0005
SO ₄ ⁼	3.0	—	0.03	—

2. Quality control is performed in the following methods:

- Cross checking of results using different available methods of dissolution and instrumentation.
- Comparison with known standards.
- Use of electrothermal atomization (flameless AA) on selected samples and LECO on sulfur.

3. Interference phenomena are overcome by:

- Use of standard additions on samples and blanks.
- Use of internal standards.

On critical samples, assays will be performed in triplicate.

When anomalous assay values appear, they will be repeated in duplicate.

* The detection limit is the concentration of an analyte that will give a signal equal to twice the standard deviation of the background emission at that wavelength (noise). Values less than twice the detection limit are not reported.

APPENDIX A

CHEMICAL ANALYTICAL TECHNIQUES EMPLOYED

Aqueous solution samples were subjected to inductively coupled plasma analysis (ICP) or flame atomic absorption (Flame AA).

Solid samples were subjected to sodium peroxide fusion by standard methods to render them soluble.

The table following gives the limit of detection of the two methods for each element. The text which follows gives sampling procedure, sample custody, a typical analytical report, calibration procedures and frequency, a flow diagram for instrument calibration, EPA analytical procedures (used on EP extraction tests), a flow diagram for data reduction, a flow diagram for internal quality control checks, performance and system audits, preventive maintenance, a flow diagram showing routine procedures used to assess data precision, etc., and finally an excerpt from the Code of Federal Regulations on the extraction procedure (EP) used. The section in this excerpt on "Structural Integrity Procedure" was not required for our filter cakes.

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some further treatment. This matter would require some discussion with several copper refineries. Accordingly:

- It is recommended that some typical copper or zinc refineries be approached in a discussion regarding the acceptability of mixed sulfides as a feedstock. Questions of composition and tonnages which might become available would be the subject of discussion. A result of these discussions may be that a bulk mixed sulfide is not an acceptable feed in that tolling charges would be unacceptably high. Such a conclusion would require the study of an alternate method of effecting a separation of the metallic constituents from aqueous sulfate leach liquors.
- It is recommended that the limited solvent extraction shakeout tests which were conducted on the filtrates from the sulfide precipitation tests be extended to include bench-scale countercurrent continuous testing. Effort should be directed towards obtaining high purity strip solutions of chromium.

RECOMMENDATIONS FOR FUTURE WORK

Since it was not possible for this program to obtain actual plating sludges, a decision was made to choose a method of recovery (sulfuric acid leaching) which would be minimally effected by the prior history of the sludge. This expectation was realized for the three synthetically prepared and aged sludges that were studied; however, it would be desirable to test actual field sludges to ascertain that they are universally amenable to high recoveries of heavy metals by sulfuric acid leaching. Accordingly:

- It is recommended that the studies on sulfuric acid leaching be extended to a variety of field sludges to determine recovery levels.

No filter aid or other means of accelerating filtration rates were employed in the present study. Filtration rates were, as a result, extremely slow. Accordingly:

- It is recommended that the use of filter aid and other aids to filtration be studied upon sulfuric acid leaching to improve filtration rates, and that these rates be measured on equipment capable of more precise determination of filtration rates than was used in the present study.

Effort was directed upon multiple washing of the filter cakes in order to produce a cake which would contain minimal quantities of heavy metals in an effort to pass the EP test without the addition of lime. This was done by batch processes. Accordingly:

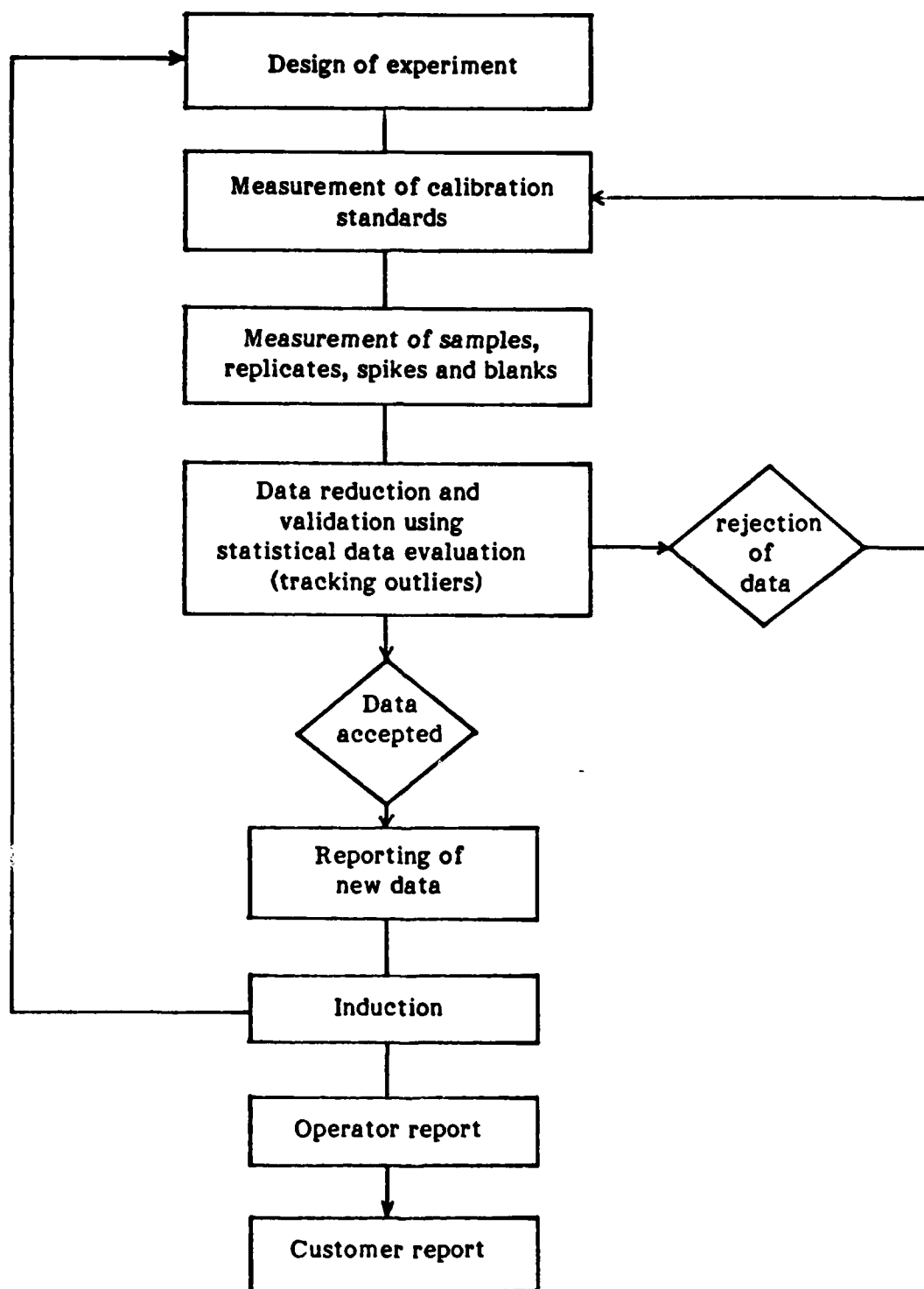
- It is recommended that countercurrent leach and washing procedures be examined to determine optimum contact conditions to maximize recovery consistent with the best use of equipment. Effort should also be directed in determining whether more rigorous leaching conditions can enable the leached filter cakes to pass the Extraction Procedure Test for hazardous materials without further lime blending. This should be done initially on a bench scale.

The sulfuric acid-leached filter cakes may still contain on the order of 0.1 percent heavy metals by weight. Lime additions enable them to pass the EP leach procedure. It is desirable that these filter cakes be examined by the EPA or other government authority to determine whether or not they represent a suitable material for nonhazardous disposal. Accordingly:

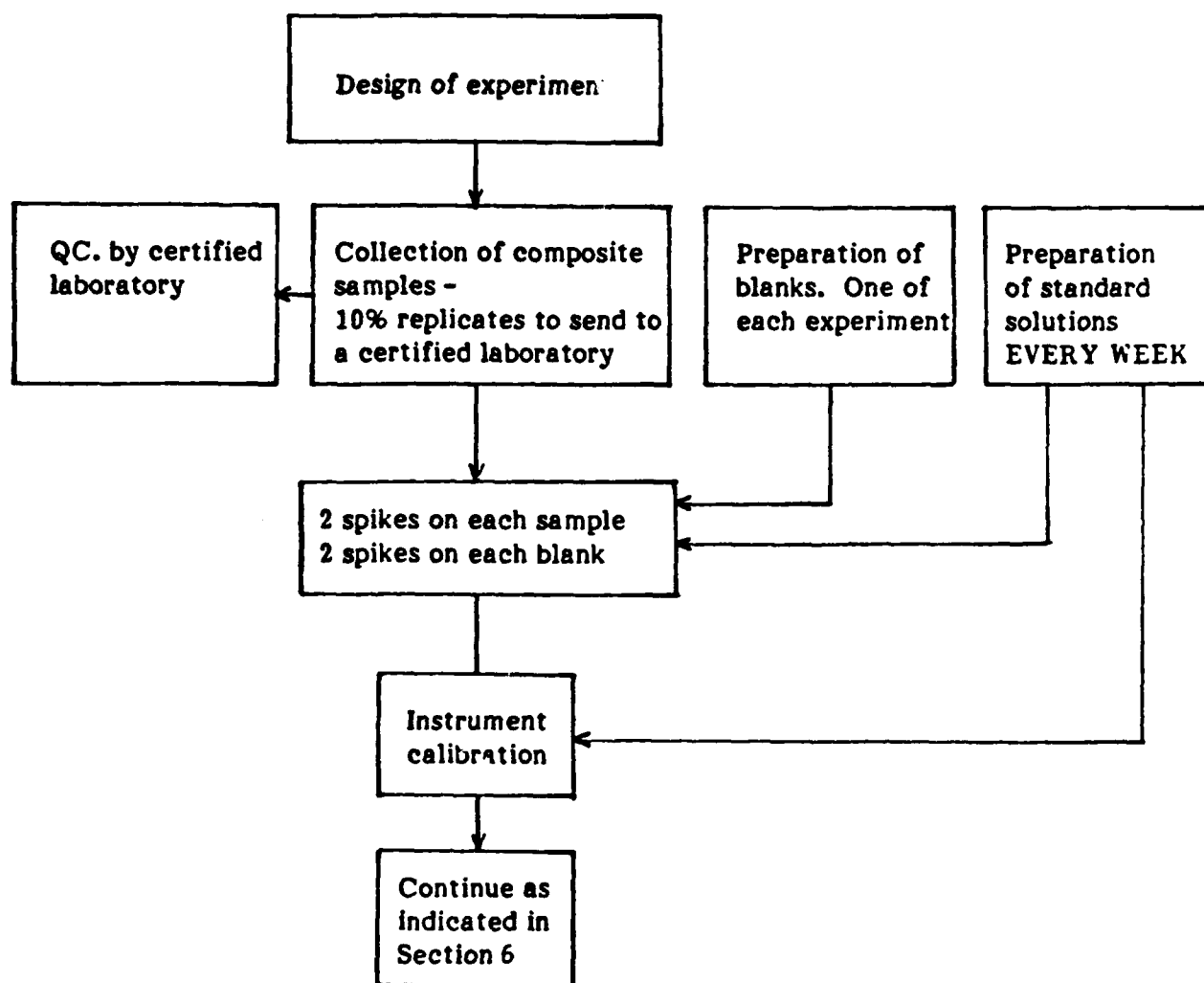
- It is recommended that sulfuric acid-leached filter cakes be prepared (with or without lime-blending as required) from actual metal plating sludges and that they be submitted to the EPA for their examination to determine if they can be disposed of as a nonhazardous waste.

Sulfide precipitation was chosen as a means of effecting a simple separation between copper, cadmium, and zinc as sulfides which may be a treatable feed to a copper or zinc refinery and chromium which can be reused in a plating circuit after

8. Data Reduction, Validation and Reporting



9. Internal Quality Control Checks



10. Performance and System Audits

To evaluate with customer, shortly before and during operation of experiments.

11. Preventive Maintenance

Our equipment is maintained on a regular basis. Key equipment is protected by service contracts.

o **ICP - ARL 34000**

Service performed by internal expert (G. Mears). ARL service available upon request. Log of maintenance available.
One unit.

o **Flame atomic absorption**

Three units: IL-951; IL-751; IL-551.
Service performed by internal expert (A. Johnson).
IL service available upon request. Log of maintenance available.

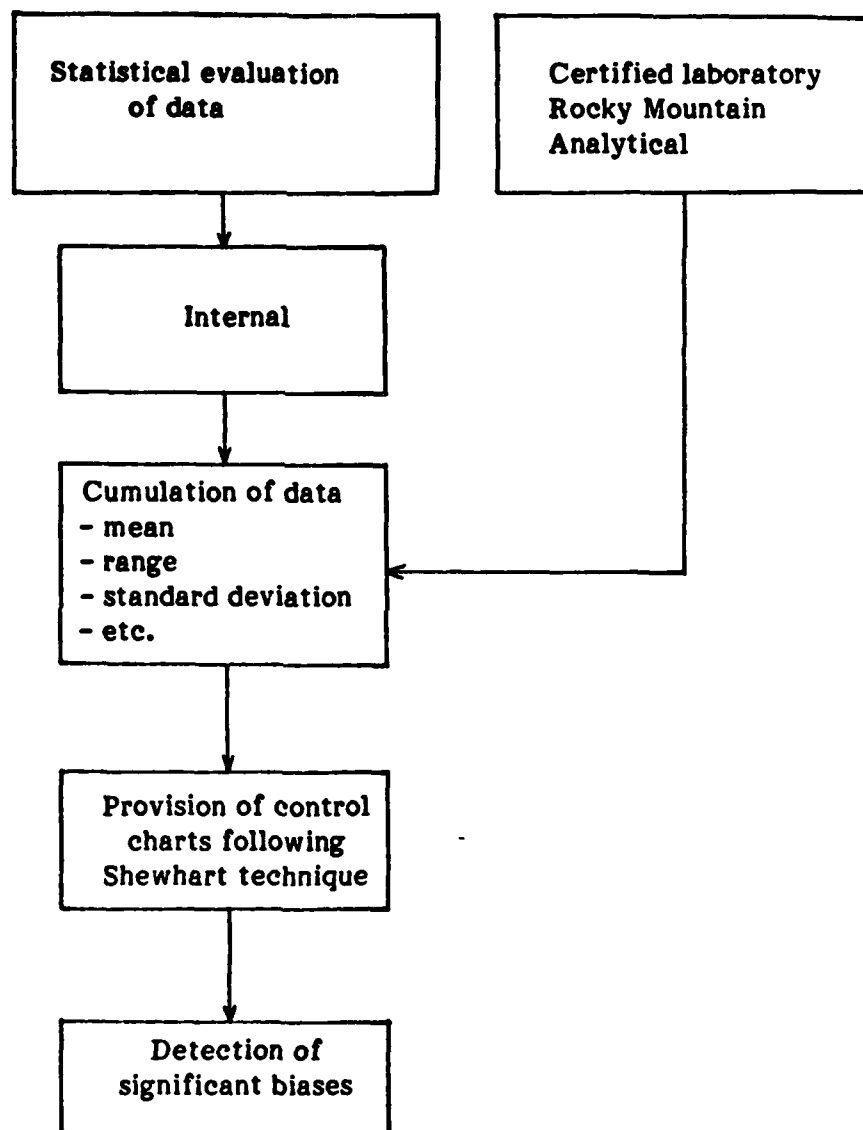
o **Furnace atomic absorption**

Two units: each unit composed of one IL-551, one IL-655, one IL-254, and one Versagraph 800 series strip chart recorder.

Note: All furnace work is recorded on strip chart recorder.

Service performed by internal expert (A. Johnson).
IL service available upon request.

12. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness



13. Corrective Action

This should be defined as the need arises.

14. Quality Assurance Reports to Management

A complete report concerning QA and QC activities is provided with each Project Progress Report, with emphasis on problems encountered and corrective actions taken.

EP TOXICITY TEST PROCEDURE

Code of Federal Regulations (FR) 261.33 Appendix II, Volume 40, Parts 199-399, pp 380-382

Part 261, App. II

Title 40—Protection of Environment

This manual also contains additional information on application of these protocols.

APPENDIX II—EP TOXICITY TEST PROCEDURES

A. Extraction Procedure (EP)

1. A representative sample of the waste to be tested (minimum size 100 grams) shall be obtained using the methods specified in Appendix I or any other method capable of yielding a representative sample within the meaning of Part 260. [For detailed guidance on conducting the various aspects of the EP see "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods" (incorporated by reference, see § 260.11).]

2. The sample shall be separated into its component liquid and solid phases using the method described in "Separation Procedure" below. If the solid residue^a obtained using this method totals less than 0.5% of the original weight of the waste, the residue can be discarded and the operator shall treat the liquid phase as the extract and proceed immediately to Step 8.

3. The solid material obtained from the Separation Procedure shall be evaluated for its particle size. If the solid material has a surface area, per gram of material equal to, or greater than, 3.1 cm² or passes through a 9.5 mm (0.375 inch) standard sieve, the operator shall proceed to Step 4. If the surface area is smaller or the particle size larger than specified above, the solid material shall be prepared for extraction by crushing, cutting or grinding the material so that it passes through a 9.5 mm (0.375 inch) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described below.

4. The solid material obtained in Step 3 shall be weighed and placed in an extractor with 16 times its weight of deionized water. Do not allow the material to dry prior to weighing. For purposes of this test, an acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also insure that all sample surfaces are continuously brought into contact with well mixed extraction fluid.

^aThe percent solids is determined by drying the filter pad at 80°C until it reaches constant weight and then calculating the percent solids using the following equation:
Percent solids =

$$\frac{(\text{weight of pad + solids}) - (\text{tare weight of pad})}{\text{initial weight of sample}} \times 100$$

5. After the solid material and deionized water are placed in the extractor, the operator shall begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution shall be decreased to 5.0 ± 0.2 by adding 0.5 N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution shall be monitored, as described below, during the course of the extraction and if the pH rises above 5.2, 0.5N acetic acid shall be added to bring the pH down to 5.0 ± 0.2 . However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture shall be agitated for 24 hours and maintained at 20°-40°C (68°-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed:

(a) A pH meter shall be calibrated in accordance with the manufacturer's specifications.

(b) The pH of the solution shall be checked and, if necessary, 0.5N acetic acid shall be manually added to the extractor until the pH reaches 5.0 ± 0.2 . The pH of the solution shall be adjusted at 15, 30 and 60 minute intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5N pH units.

(c) The adjustment procedure shall be continued for at least 6 hours.

(d) If at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH shall be adjusted to 5.0 ± 0.2 and the extraction continued for an additional four hours, during which the pH shall be adjusted at one hour intervals.

6. At the end of the 24 hour extraction period, deionized water shall be added to the extractor in an amount determined by the following equation:

$$V = (20(W) - 16(W)) - A$$

V = ml deionized water to be added

W = weight in grams of solid charged to extractor

A = ml of 0.5N acetic acid added during extraction

7. The material in the extractor shall be separated into its component liquid and solid phases as described under "Separation Procedure."

8. The liquids resulting from Steps 2 and 7 shall be combined. This combined liquid (or the waste itself if it has less than ¼ percent solids, as noted in step 2) is the extract and

shall be analyzed for the presence of any of the contaminants specified in Table I of § 261.24 using the Analytical Procedures designated below.

Separation Procedure

Equipment: A filter holder, designed for filtration media having a nominal pore size of 0.45 micrometers and capable of applying a 5.3 kg/cm² (75 psi) hydrostatic pressure to the solution being filtered, shall be used. For mixtures containing nonabsorptive solids, where separation can be effected without imposing a 5.3 kg/cm² pressure differential, vacuum filters employing a 0.45 micrometers filter media can be used. (For further guidance on filtration equipment or procedures see "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" incorporated by reference, see § 260.11). Procedure:

(i) Following manufacturer's directions, the filter unit shall be assembled with a filter bed consisting of a 0.45 micrometer filter membrane. For difficult or slow to filter mixtures a prefilter bed consisting of the following prefilters in increasing pore size (0.65 micrometer membrane, fine glass fiber prefilter, and coarse glass fiber prefilter) can be used.

(ii) The waste shall be poured into the filtration unit.

(iii) The reservoir shall be slowly pressurized until liquid begins to flow from the filtrate outlet at which point the pressure in the filter shall be immediately lowered to 10-15 psig. Filtration shall be continued until liquid flow ceases.

(iv) The pressure shall be increased stepwise in 10 psi increments to 75 psig and filtration continued until flow ceases or the

pressurizing gas begins to exit from the filtrate outlet.

(v) The filter unit shall be depressurized, the solid material removed and weighed and then transferred to the extraction apparatus, or, in the case of final filtration prior to analysis, discarded. Do not allow the material retained on the filter pad to dry prior to weighing.

(vi) The liquid phase shall be stored at 4°C for subsequent use in Step 2.

B. Structural Integrity Procedure

Equipment: A Structural Integrity Tester having a 3.18 cm (1.25 in.) diameter hammer weighing 0.33 kg (0.73 lbs.) and having a free fall of 15.24 cm (6 in.) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet the specifications shown in Figure 1.

Procedure

1. The sample holder shall be filled with the material to be tested. If the sample of waste is a large monolithic block, a portion shall be cut from the block having the dimensions of a 3.3 cm (1.3 in.) diameter x 7.1 cm (2.8 in.) cylinder. For a fixated waste, samples may be cast in the form of a 3.3 cm (1.3 in.) diameter x 7.1 cm (2.8 in.) cylinder for purposes of conducting this test. In such cases, the waste may be allowed to cure for 30 days prior to further testing.

2. The sample holder shall be placed into the Structural Integrity Tester, then the hammer shall be raised to its maximum height and dropped. This shall be repeated fifteen times.

3. The material shall be removed from the sample holder, weighed, and transferred to the extraction apparatus for extraction.

Analytical Procedures for Analyzing Extract Contaminants

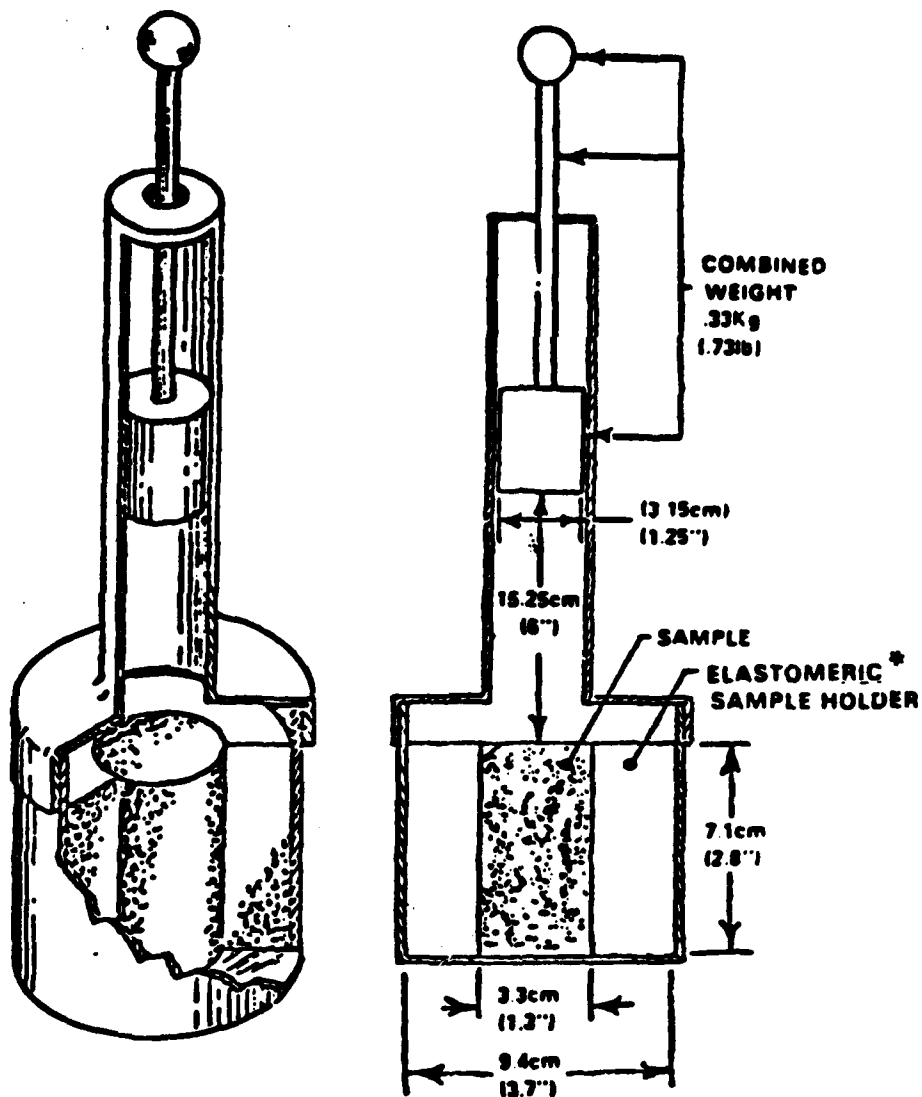
The test methods for analyzing the extract are as follows:

1. For arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, lindane, methoxychlor, toxaphene, 2,4-D[2,4-dichlorophenoxyacetic acid] or 2,4,5-TP [2,4,5-trichlorophenoxypropionic acid]: "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods" (incorporated by reference, see § 260.11).

2. [Reserved]

For all analyses, the methods of standard addition shall be used for quantification of species concentration.

*This procedure is intended to result in separation of the "free" liquid portion of the waste from any solid matter having a particle size >0.45 µm. If the sample will not filter, various other separation techniques can be used to aid in the filtration. As described above, pressure filtration is employed to speed up the filtration process. This does not alter the nature of the separation. If liquid does not separate during filtration, the waste can be centrifuged. If separation occurs during centrifugation, the liquid portion (centrifugate) is filtered through the 0.45 µm filter prior to becoming mixed with the liquid portion of the waste obtained from the initial filtration. Any material that will not pass through the filter after centrifugation is considered a solid and is extracted.



*ELASTOMERIC SAMPLE HOLDER FABRICATED OF MATERIAL FIRM ENOUGH TO SUPPORT THE SAMPLE

Figure 1
COMPACTION TESTER

[45 FR 33119, May 19, 1980, as amended at 46 FR 35247, July 7, 1981]

Excerpt from U.S. Department of Commerce NTIS PB-297-453:
"Proceedings of Conference on Advanced Pollution Control
for the Metal Finishing Industry (2nd), Held at
Kissimmee, Florida, on February 5-7, 1979

of lime. A solution containing 20 mg/l of each metal was used for the test. Equal portions of this solution were treated, one by SulfexTM and the other by lime. The sludge produced by each procedure was then subjected to the leaching test recommended by the EPA. The pH of the Sulfex mixture was 5.7. The pH of the hydroxide mixture was 5.8.

The Sulfex mixture gave no odor of H₂S nor was there any evidence of H₂S detectable by lead acetate paper.

EXTRACT LEVEL mg l			
	<i>EPA Proposed Regulation</i>	<i>Sulfex</i>	<i>Hydroxide</i>
Arsenic	0.50	-	-
Barium	10.0	-	-
Cadmium	0.10	0.02	1000
Chromium (Total)	0.50	< 0.05	1.5
Lead	0.50	0.20	55
Mercury	0.02	-	-
Selenium	0.10	-	-
Silver	0.50	0.02	0.21
MAY BE CONSIDERED IN FUTURE			
Ni	-	35	> 33
Fe	3	820	< 1
Zn	50	0.36	1475
Cu	10	0.03	259

These data would suggest that disposal of sulfide sludges will present no more of a problem than disposal of hydroxide sludges. Both appear to be material that should be disposed in a secure landfill.

APPENDIX B

MINERALOGY OF SLUDGES AND FILTER CAKES

AMAX EXTRACTIVE RESEARCH & DEVELOPMENT, INC.
Inter-Office Memorandum

SUBJECT: Mineralogical Analysis of Synthetic Plating Sludge
and Leach Residue Cake (6921)

March 20, 1985

M. Hepworth

TO: J.R. Odekirk

INTRODUCTION

Three synthetic, selectively aged, plating sludges and their leach residues were investigated mineralogically to characterize and identify the phases present. The sludges were produced by reacting metal sulfates with CaO to yield metal hydroxides and calcium sulfate hydrates. The leach residues consist of residual phases after an acid (HNO_3) leach and subsequent wash.

SUMMARY

Aging of synthetic plating sludges at room temperature for 6 weeks resulted in transformation of gypsum at the expense of previously formed bassanite. Sludges for which there was no aging period contained bassanite and amorphous metal hydroxides. Sludge aged at 66°C for 7 days contained bassanite, metal hydroxides and a trace amount of gypsum.

Leach residues of synthetic sludges, which had been aged under normal, low temperature conditions, contained bassanite. The leach residue from a 7-day period of accelerated aging at 66°C contained both bassanite and gypsum.

Results

Microscopic and X-ray diffraction analyses were made on three aged, synthetic sludges and their leach residues to characterize and identify the phases present. Results of these analyses are as follows:

No. 1124-16; No Aging

The sludge consists of fine-grained, amorphous metal hydroxides and coarser grained bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$), Figure 1. Bassanite is one of four phases reported in the system $\text{CaSO}_4 - \text{H}_2\text{O}$, and is referred to as a "soluble-anhydrite" or "hemihydrate". Gypsum, which is the most common phase in the system, converts to the

able hemihydrate form (bassanite) in water at elevated temperatures.¹ With time, because of differences in solubility, lower temperatures and poor crystal stability, bassanite will convert to gypsum. In this case, sludge which has not aged contains bassanite and metal hydroxides.

The leach residue from this sludge contains mostly bassanite and a trace amount of gypsum, Figure 2. Bassanite appears to occur as remnants of crystals which had formed earlier. The acid leach appears to have dissolved the metal hydroxides.

o. 1124-20; 7 day aging at 66°C

The sludge from this test was treated at an elevated temperature (66°C) for 7 days to accelerate the aging process. X-ray diffraction analysis shows that the sludge consists of bassanite, metal hydroxides (?) and a trace amount of gypsum. The fine-grained metal hydroxides observed microscopically are amorphous and could not be identified by X-ray diffraction analyses, Figure 3.

The leach residue of this accelerated aged sludge consists of both bassanite and a small amount of gypsum, Figure 4. The gypsum is present as fine-grained, needle-shaped crystals which make up a felted groundmass. The presence of the fine-grained gypsum may cause some problems in filtering of leach residues. It is indicated that accelerated aging could result in handling problems.

o. 1124-40; 42 days aging

Sludge from this test had been allowed to age for 42 days (6 weeks) at room temperature before being leached. In addition to containing metal hydroxides, the sludge also contains gypsum. No bassanite was detected. The presence of gypsum is attributed to the long aging period. The gypsum has formed at the expense of bassanite, Figure 5.

Treatment of the sludge produced two residues which had different wash characteristics. One wash was made using a total of 500 ml of deionized water at 60°C; the other wash used a total of 1000 ml of 0.1 normal H₂SO₄ at 70°C and a blender to help break up the solids. The mineral constituent in both leach residues is bassanite. Apparently, the crystals formed during the 42 day aging period were altered to bassanite during the acid leach. The crystals shown in Figure 6 are bassanite pseudomorphs after gypsum.

Comparison of the leach residues, Figures 6 and 7, shows that the bassanite crystals are of a smaller size in the acid-washed-leach residue. These small crystals are attributed to breakage of larger crystals by the blender blades during agitation.

In summary, the following conditions were noted during the mineralogical investigation.

Malacke, C., et. al., "Dana's System of Mineralogy", Vol II, 7th Ed., John Wiley & Sons, New York, 1963.

uced aging of synthetic sludge by heating results in the formation of fine-grained sum crystals. Such fine-grained crystals will result in filtering problems.

ig term, low-temperature aging of synthetic sludge yields gypsum rather than sanite crystals.

ld leaching of low temperature, aged sludge results in conversion of gypsum stals to bassanite pseudomorphs.

ring of leach residues in a blender tends to grind crystals to a smaller size.

ld leaching of synthetic plating sludge has resulted in dissolution of fine-grained tal hydroxides.

JROdekirk

J.R. Odekirk

S. Chou
C. Jha

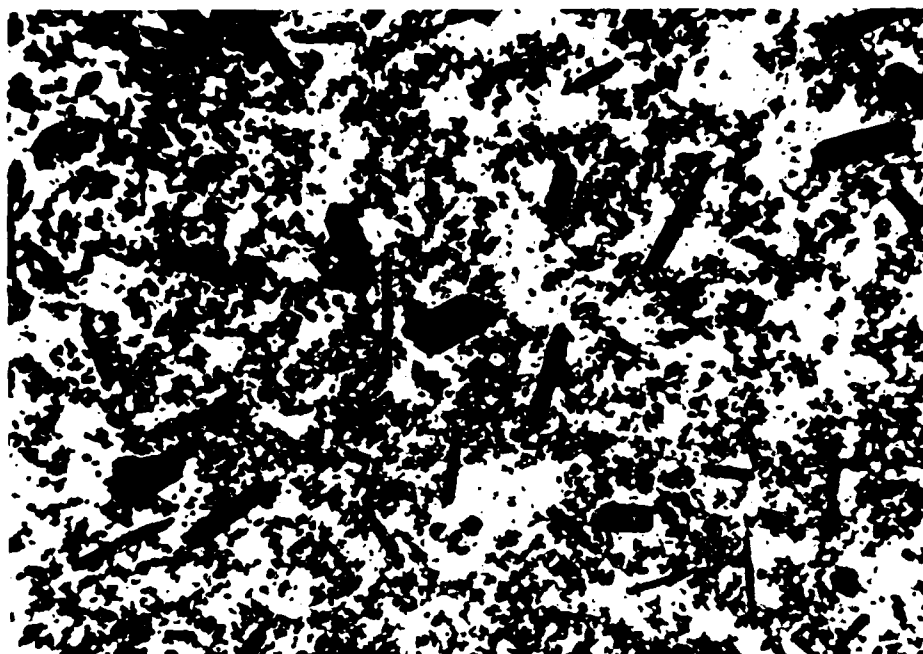


Figure 1. Test No. 1124-16; sludge.

tomicrograph showing fine-grained metal hydroxides and crystals of bassanite.



Figure 2. Test No. 1124-16; leach cake.

tomicrograph showing residual crystals of bassanite. The metal hydroxides leached away. 75X.

AD-A157 098

PLATING WASTE SLUDGE METAL RECOVERY(U) AMAX EXTRACTIVE
RESEARCH AND DEVELOPMENT INC GOLDEN CO M T HEPWORTH
30 MAY 85 AMAX-6921 AMXTH-TE-TR-85015 DAK11-84-C-0045

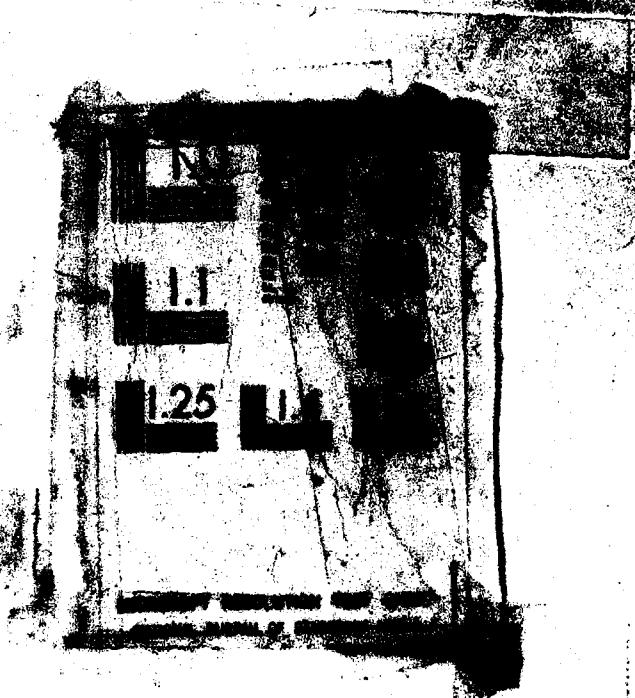
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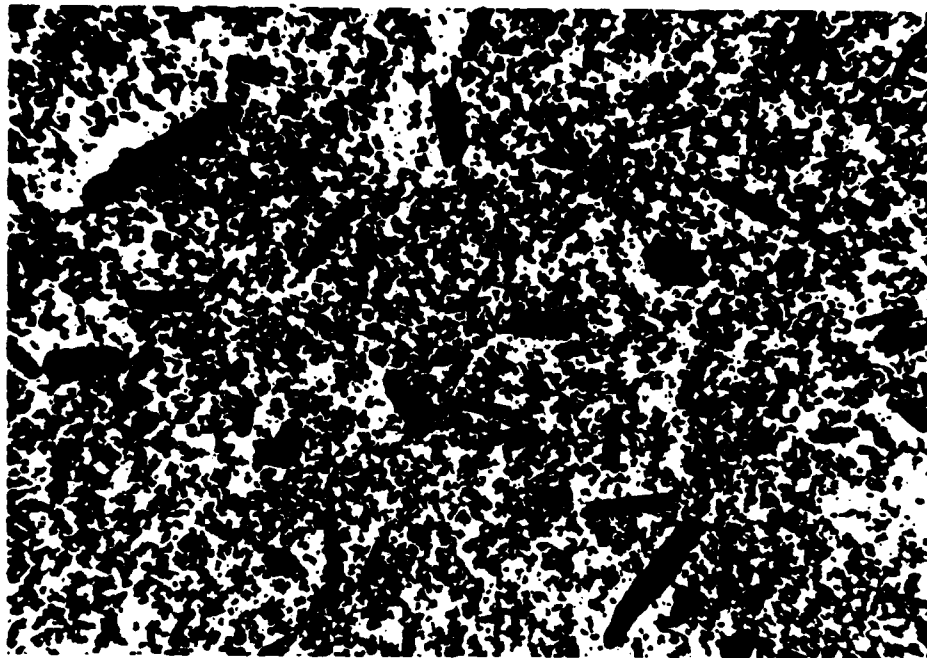


Figure 3. Test No. 1124-20; sludge.

Photomicrograph showing fine-grained metal hydroxides and crystals of bassanite. Gypsum in trace amounts occurs as very small needle-like crystals. 75X.

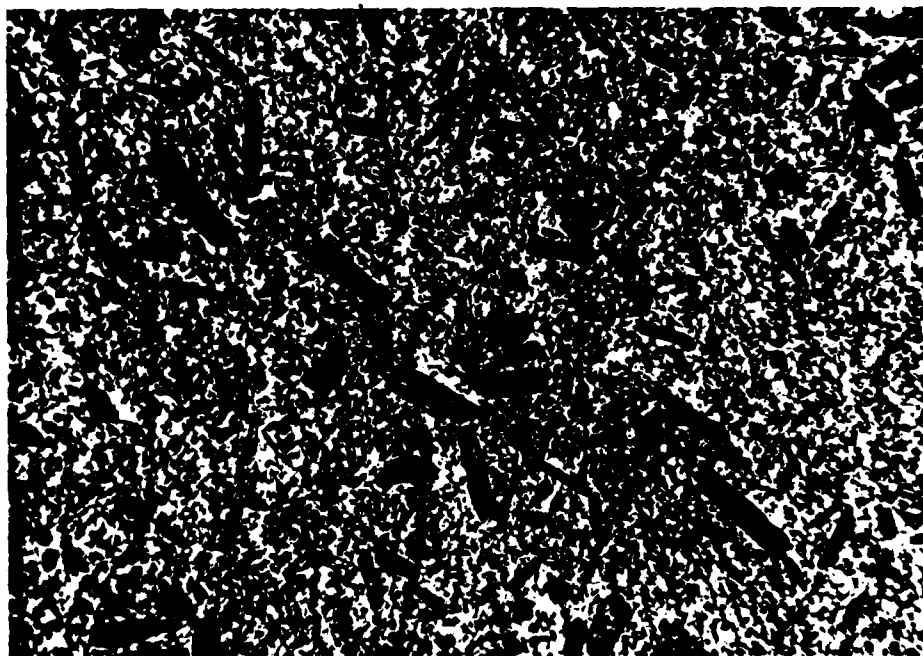


Figure 4. Test No. 1124-20; leach cake.

Photomicrograph showing fine-grained needles of gypsum and coarser grained crystals of bassanite. 75X.



Figure 5. Test No. 1124-40; sludge.

Photomicrograph of aged sludge (42 days) showing fine-grained metal hydroxides and gypsum crystals. 75X.



Figure 6. Test No. 1124-40; leach cake, H₂O wash.

Photomicrograph showing bassanite pseudomorphs after gypsum. Metal hydroxides have been leached away. 75X.

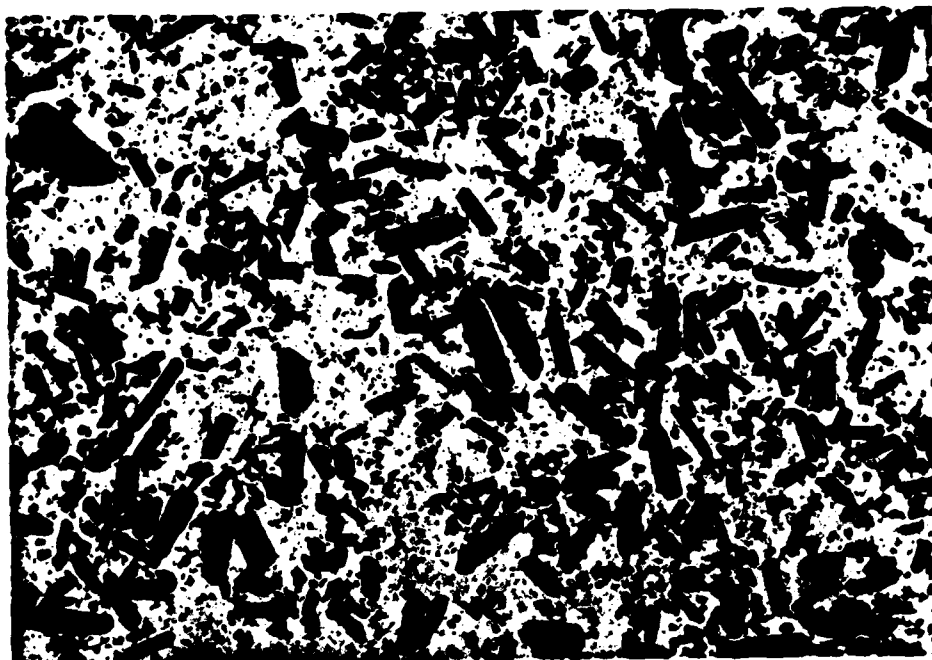


Figure 7. Test No. 1124-40; leach cake, acid wash.

Photomicrograph showing bassanite pseudomorphs after gypsum. The smaller grain size is attributed to grinding by the blender blades. 75X.

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Commander U. S. Army Toxic and Hazardous Materials Agency Attention: AMXTH-TE-D Aberdeen Proving Ground, MD 21010-5401	5
Commander U. S. Army Toxic and Hazardous Materials Agency Attention: AMXTH-ES Aberdeen Proving Ground, MD 21010-5401	2
Defense Logistics Studies Information Exchange U. S. Army Logistics Management Center Fort Lee, VA 23801	2

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