



Project Summary

Metal Value Recovery from Metal Hydroxide Sludges

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A two-year study of the potential for metal values from metal finishing hydroxide sludges was completed. The objectives of the study were to:

- Develop flowsheets to separate and recover metal values from metal finishing hydroxide sludge materials and operate the flowsheets on a laboratory scale (Phase I),
- Develop a test assembly of unit operations to accomplish the separation of metal values on a pilot scale of 75-100 pounds of sludge per day,
- Verify that the pilot-scale unit operations accomplish appropriate separations, and
- Delineate potential operational problems.

The Phase I research successfully accomplished the stated objectives. Flowsheets were designed and tested on a laboratory scale prior to pilot-scale testing. The flowsheets consist of: sulfuric acid leaching, iron removal by jarosite precipitation (high iron bearing solutions) or iron solvent extraction (low iron bearing solutions); copper removal by solvent extraction and copper recovery by either electrowinning or copper sulfate crystallization; zinc removal by solvent extraction and zinc recovery as zinc sulfate by crystallization; chromium oxidation and subsequent recovery by lead chromate precipitation; nickel removal by sulfide precipitation or nickel sulfate crystallization, and final solution cleanup of low concentration residual ions by ion exchange.

Full-scale tests were performed to ascertain the applicability of each unit operation. Continuous tests were per-

formed to investigate solvent reagent degradation; develop mass balances, and delineate operational problems. The successful application of metallurgical unit operations to multicomponent complex mixed metal sludges demonstrated that treatment of such material is possible and economical.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In recent years, increased emphasis has been placed on preventing the introduction of heavy metal containing industrial wastewaters into publicly owned treatment works and the environment. Legislation has established regulatory authority for controlling the discharge of heavy metals into the environment and also has mandated resource recovery whenever economically feasible. Many of the newer treatment and control technologies can remove metals from wastewater, i.e., a sludge, concentrate, or regenerate form is created and is, in most cases, disposed of in a landfill. Metals are recoverable, but are not recovered significantly because of a lack of proven technologies.

Process wastewaters from the metal finishing and electroplating industry contain cyanides and heavy metals. These wastewaters have a detrimental effect on the environment if discharged directly. Such discharges are regulated by Federal, state, county, or city ordinances, and require installation of treatment facilities. One of the treatment technologies pres-



ently in use is oxidation (or reduction), neutralization and precipitation, which destroys cyanide and removes heavy metals as a hydroxide sludge. Traditionally, hydroxide sludge has been disposed of in hazardous landfill sites.

Disposal in landfills has certain inherent disadvantages:

1. Perpetual maintenance of the disposal site is required,
2. Dilution of metal content by mixing with other types of waste materials, thus making recovery at a later date more difficult, and
3. Permanent loss of nonrenewable metals.

Recovery of heavy metals from metal finishing sludges will alleviate or reduce the disposal problem and provide for conservation of energy and metal resources. In the full report, the present study outlines a technical methodology to treat metal bearing sludges by hydrometallurgical techniques.

The treatment of hydroxide sludges for metal value recovery will produce several beneficial results, i.e., economic benefits from the metal values recovered will help offset the cost of recovery/treatment; nonrenewable resource metals will be recycled for use by society; and significantly less hazardous material will be disposed of in landfills.

Purpose and Objectives

The purpose of the present study was to investigate at an advanced laboratory scale the potential for application of well-established hydrometallurgical techniques to a mixed metal sludge. The design, development, fabrication, acquisition, assembly, and testwork for such a treatment system was conducted at the Montana Tech Foundation Mineral Research Center in Butte, Montana (Phase I). Further testwork (Phase II) was conducted at the Montana College of Mineral Science and Technology, Butte, Montana, and at a waste generating site in Camarillo, California.

The objectives of the study were to:

- Develop flowsheets to separate and recover metal values from metal finishing hydroxide sludge materials,
- Develop a test assembly of unit operations to accomplish the separation of metal values on a scale of 75-100 pounds of sludge per day, and
- Confirm that the large scale unit operations can accomplish appropriate

separations and establish the metal recovery efficiency for each unit operation; delineate process and materials handling problems when treating complex mixed metal sludge materials.

Study Methodology

The experimental study was conducted in two phases. The first-phase study objectives were to develop preliminary flowsheets for the separation and recovery of metal values from mixed metal sludge materials; to perform laboratory studies to test the applicability of the preliminary flowsheets; to develop a test assembly of unit operations capable of treating 75-100 pounds of sludge per day; and to conduct preliminary testwork in the test assembly to delineate conditions for successful operation and/or to note potential operational problems.

Phase I was conducted by the Montana Tech Foundation at its Minerals Research Center in Butte, Montana. The technical supervision of the project was performed by Dr. L. G. Twidwell, Montana Enviromet.

A team of extractive metallurgists was assembled as an advisory and review group to propose, discuss, and select potential flowsheets for laboratory testing and development. The team included: Dr. L. G. Twidwell, Director of Montana Enviromet and Professor of Metallurgical Engineering at the Montana College of Mineral Science and Technology, whose expertise is pyrometallurgy and hydrometallurgy; Dr. D. Robinson, consultant for DRESCO Corporation, whose expertise is electrometallurgy and solvent extraction processes; Dr. T. J. O'Keefe, Professor of Metallurgical Engineering at the University of Missouri at Rolla, whose expertise is electrometallurgy; Dr. W. Opie, President for Research and Development, AMAX Corporation, whose expertise is extractive metallurgical techniques applied to secondary materials; Mr. A. Mehta, a consultant for Phoenix Metals, whose expertise is environmental concerns and waste processing technology as related to the electroplating industry; and Mr. J. Downey, a private consultant whose expertise is development of pilot-scale studies.

The recommended flowsheets formulated by the advisory and review team were investigated at a bench-scale level to ascertain applicability or nonapplicability of potential unit operations. A flowsheet was developed that had several feasible alternative unit operations. Laboratory demonstrations were performed for each unit operation and each alternate

unit operation. A test assembly was then developed to treat 75-100 pounds of sludge material per day. Preliminary testwork was conducted on a pilot scale during Phase I of the project.

The second-phase objectives of the study were to investigate potential alternate unit operations identified in Phase I; further test the assembly developed in Phase I; develop long-term continuous test data for the unit operations; and delineate potential process and materials handling problems.

Conclusions—Large-Scale Test Program

- A sulfuric acid leach operation is effective and efficient in redissolving metal values. The dissolution is rapid and without control problems. Conditions can be specified to achieve greater than ninety percent extraction of all contained metals; between eighty and ninety percent of the starting sludge mass is taken into solution.
- Iron is removed from solution by a jarosite precipitation process. This process allows iron to be removed from an acidic, pH 1.5-2.5, solution as a crystalline compound that is a readily filterable solid product. Elevated temperatures, 88°-92°C, and chemical pH control are required for the precipitation to be accomplished in a relatively short period of time, six to eight hours. Mechanical control of the system is not a problem. Over two hundred liters of solution can be treated in an eight-hour shift. Solid—liquid separation is readily accomplished by simple settling; pumping most of the cleared solution from the settling vessel, and filtering the remaining slurry using a filter press for cake consolidation and washing.
- An alternate iron removal process applicable to low iron bearing solutions (<a few grams per liter) involves the use of solvent extraction at low pH with subsequent removal of iron from the organic phase by hydrochloric acid stripping. Iron content in the aqueous leach solution can be effectively lowered to less than 50 ppm. Minimal crud formation results by controlling leach solution pH and by selection of the proper kerosene diluent.
- Copper is effectively and selectively removed from a mixed metal bearing solution by solvent extraction. The copper content can be decreased to low concentrations, <30 mg/l, without

appreciable extraction of any other metal specie. The recovery of copper by solvent extraction requires only three stages of extraction and two stages of strip. Five cells will accommodate the treatment of over 200 liters of leach solution per day (eight hours). Large-scale continuous test-work has been performed for periods up to seven hours. Mechanical control of the solution flowrate and interface levels is easily achieved and does not require constant attention.

- Zinc is effectively and selectively removed from a zinc-chromium-nickel bearing solution by solvent extraction. Iron, aluminum, and calcium are partially coextracted with zinc. The iron concentration is normally relatively low because of the previous jarosite precipitation process. The solvent extraction process provides a means of removing the residual iron from the leach solution. Subsequently, the iron can be separated from the zinc by a selective stripping process.
- Chromium removal is accomplished by first oxidizing the chromium with chlorine gas; electrochemically or potentially with $\text{SO}_2\text{-O}_2$ gas mixtures, then precipitating the dichromate ion as lead chromate. Oxidation was shown to be effective in laboratory-scale test reactors. Large-scale oxidation test-work using chlorine and an electrochemical reactor has been performed successfully. A recycle system for stripping the oxidized chromium from the leach solution has been operated successfully: the solution is exposed to lead sulfate in an agitated reactor; lead chromate precipitates; the lead chromate product is crystalline and dense and settles rapidly; the solution, essentially free of lead chromate solid, is pumped from the solids for further treatment for nickel removal; the lead chromate is redissolved in sulfuric acid to form a concentrated chromic acid solution and lead sulfate; the lead sulfate solid is separated from the chromic acid and is recycled to the lead chromate precipitation reactor.
- Nickel can be removed by sulfide precipitation. The reaction is rapid and near quantitative. The pH is maintained in the range 4-5 so hydrogen sulfide is not released. The solid product is readily filterable. Quantitative removal of nickel is not necessary because practically all the final solution can be recycled to the leach-jarosite precipi-

tation unit operation. Therefore, the addition of a deficiency of sulfide (less than the stoichiometric requirement for complete nickel removal) is desirable so that all of the added sulfide ions are consumed. Then, when the solution is recycled to the acid leach step, hydrogen sulfide gas will not be formed.

Economics of Recovery

First-order cost estimates indicate that a 50-ton-per-day recovery plant with a more or less typical plating plant sludge would yield a return on investment of $41\% \pm 12\%$. This estimate is based on the very preliminary equipment costs developed by the investigators. Table 1 illustrates the method used to calculate ROI, taking an overall tax rate of 50%.

Table 1. Process Cost: First Order Estimate

Factored Capital Cost Estimate	Annualized Capital Cost	Cost (\$)		
		Operation Cost Per Year	Total Cost Per Year	Product Value
3,868,800	1,071,900	1,362,200	2,434,100	5,643,400

$$ROI = \left(\frac{5,643,400 - 2,434,100}{3,868,800} \right) (.5) (100) = 41\% \pm 12\%$$

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S. Garry Howell is the EPA Project Officer (see below).

The complete report, entitled "Metal Value Recovery from Metal Hydroxide Sludges," (Order No. PB 86-157 294/AS; Cost: \$40.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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