



Project Summary

Metal Value Recovery from Metal Hydroxide Sludges: Removal of Iron and Recovery of Chromium

L. G. Twidwell and D. R. Dahnke

This experimental study was conducted in three phases. The third phase results are summarized in this report. 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.

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

The results of the Phase I and Phase II studies are reported in EPA 600/ 2-85/128 "Metal Value Recovery from Metal Hydroxide Sludges," March 1985 (PB86 157294/AS).

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

The objectives of this Phase III investigation were: to develop flowsheets to separate and recover metal values from electroplating sludge materials; to collect bench scale experimental data to verify the feasibility of the proposed flowsheets; to demonstrate the effectiveness of the separation techniques on a large-scale (75-100 pounds of sludge per day); and to develop a first order economic evaluation of the proposed flowsheets for an exemplary centralized treatment facility. The emphasis of the project was directed toward investigating the application of phosphate precipitation as a means of selectively separating iron and chromium from divalent cation species.

These objectives have been accomplished. Flowsheets and alternatives are discussed in the body of the main report. The developed flowsheets have been verified to be feasible by laboratory test work and selective metal value separations have been shown to be possible, e.g., iron and chromium can be separated from divalent metals such as zinc, nickel, and cadmium. Large-scale test work has also verified that effective separations are feasible and practical, and an economic evaluation has been performed showing that an excellent return on investment is possible.

Background

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. It also has mandated resource recovery whenever economically feasible. Many treatment and control technologies have come into existence to remove metals from these wastewaters, but a sludge, concentrate, or regenerate form is created and, in most cases, disposed in a landfill. Metals are recoverable, but are not recovered significantly because of a lack of proven, cost-effective 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 directly discharged. Such discharges are regulated by Federal, State, County and/or City ordinances, which may require installation of pretreatment works. Some of the treatment technologies presently in use involve chemical oxidation (or reduction), neutralization, and precipitation to destroy cyanide and remove heavy metals as hydroxide sludges. These sludges have traditionally been disposed in hazardous landfill sites. Should heavy metals be recovered from metal finishing sludges, the alleviation of disposal problems can provide for conservation of energy and metal resources. This study outlines a technical method that offers a procedure for treating metal bearing sludges via hydrometallurgical techniques. The treatment of hydroxide sludges for metal value recovery will produce several beneficial results: economic benefits from the metal recovered will help offset the cost of recovery/treatment; non-renewable resources will be recycled for use by society; and there will be significantly less hazardous material to be disposed.

Iron and Chromium Removal

It has been demonstrated that conventional hydrometallurgical unit operations can be applied to mixed metal hydroxide sludge materials. Effective and selective separations of metal values from complex mixed metal solutions have been accomplished, e.g., separation of Fe, Cu, Zn, Cr, and Ni. However, two unit operations are high

cost energy processes, i.e., removal of iron and oxidation with subsequent recovery of chromium.

The present study was initiated to investigate an alternative and potentially more cost-effective way for removing iron and recovering chromium from mixed metal solutions. Bench-scale test work by Dahnke has shown that trivalent cations can very effectively be stripped from solutions in preference to divalent cations under conditions of low pH and room temperature by phosphate precipitation. The successful application of simple precipitation of iron and chromium from mixed solutions could mean elimination of the two high cost unit operations:

1. Iron removal by jarosite precipitation;
2. Chromium recovery by oxidation to chromate.

The substitution of relatively simple precipitation processes for the above more complex processes should significantly increase the cost-effectiveness of the overall metal value recovery sequence.

Results and Conclusions

An extremely large data base has been generated during the course of the present study for both the bench-scale and the large-scale test work. The bench-scale study results support the following conclusions:

1. Trivalent cations can be effectively and selectively separated from divalent and monovalent solution species.
2. Ferric iron concentrations can be lowered to a few mg/liter in acidic solutions.
3. Ferric phosphate precipitation is rapid and selective over trivalent chromium and divalent cations under room temperature conditions.
4. Ferric phosphate precipitates as small spherites showing excellent filtering characteristics.
5. Ferric phosphate precipitates in a similar manner from acidic solution under essentially the same experimental conditions regardless of the solvent matrix, e.g., from sulfate, chloride, nitrate or ammonium solutions.
6. Ferric phosphate can be converted to ferric hydroxide with the regeneration of the phosphate reagent by a caustic leach.
7. Chromium phosphate requires a precipitation incubation time of several hours at room temperature but is very rapid at elevated temperatures, therefore, the

difference in the room temperature precipitation kinetics for iron and chromium provides a means for separating these two trivalent cations.

8. Filterability of chromium phosphate (small spherites) precipitated from an elevated temperature solution about the same as the filter ability of ferric phosphate.
9. Chromium phosphate can be converted to marketable products by a soda ash roast process producing high market value metal chromate or chromic acid.

The objective of the large-scale test work was to demonstrate on a significant quantity of actual sludge material that selective separations could be accomplished. The large-scale test work confirmed the bench scale results. Important conclusions that have resulted include:

1. Sulfuric acid leaching was very effective in redissolving the metals from electroplating sludge. In the case of the electromachining sludge, however, the leach residue contained most of the niobium and titanium and therefore provided a valuable recoverable residue.
2. The weight of solids that must be disposed, including the leach residue and converted ferric phosphate (ferric hydroxide), was less than the weight of the starting sludge. Both the leach residue and ferric phosphate solids pass the EPA TCLP test can normally be disposed in non-hazardous disposal sites.
3. The metal products that are recovered are of sufficient purity to serve as feedstock for commercial uses or for conversion to other marketable products.

L. G. Twidwell and D. R. Dahnke are with Montana College of Mineral Science and Technology, Butte, MT 59701.

John F. Martin is the EPA Project Officer (see below)

The complete report, entitled "Metal Value Recovery from Metal Hydroxide Sludges: Removal of Iron and Recovery of Chromium," (Order No. PB 88-176 078/AS; Cost: \$25.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
Environmental Protection
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