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Project Summary

Recovery of Metals Using Aluminum Displacement

Steven C. Meyers

Metal finishing operations generate waste streams containing heavy metals such as copper, lead, tin, and nickel. Standard pretreatment practice has involved removing these metals from the effluent before discharge using a variety of techniques, primarily precipitation as a sludge that must be disposed of as a hazardous waste. This project investigated aluminum displacement as a pretreatment process for selected waste streams. The process has the potential of producing not only effluent suitable for discharge but also nonhazardous pure metal suitable for recovery.

Testing of copper sulfate solutions at various flow rates showed copper removal in a range of 85% to 97%. The pH was determined to have an insignificant effect on copper removal when held in a range of pH 2 to 3.5. Recirculation testing of copper sulfate solutions reduced copper concentrations from 200 to 1.5 ppm. Recirculation testing of tin/lead fluoborate solutions reduced lead concentrations from 104 to 0.65 ppm. Eight other waste streams were evaluated to determine metal removal efficiency.

This Project Summary was developed by EPA's Risk Reduction Engineering 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

Waste streams containing copper and lead are common in the printed circuit industry. Printed circuit fabrication processes such as cleaning, microetching, etching, electroless plating, and electroplating all generate rinsewater containing low concentrations of these and other regulated heavy metals. Standard pretreatment practice often generates a sludge that must be handled and disposed of as a hazardous waste.

Removal of copper from etching solutions using displacement with aluminum was reported in the mid-1960's. Because of aluminum's position in the electromotive series, metal ions with lower oxidation potentials such as copper and lead will be reduced to their metallic state if brought into contact with aluminum metal under certain conditions. The aluminum is consumed stoichiometrically based on the input of more noble metal ions. The process holds the promise of yielding a nonhazardous product suitable for metal recovery.

The project objective was to study the variables that affect the recovery of copper and lead metal from printed circuit and metal finishing waste streams using displacement with aluminum metal. The variables include aluminum configuration, waste stream composition, flow rates, contact times, solution pH, and aluminum surface activity.

Procedure

Reactor Design

Test equipment for this project included a 15-gal aluminum exchange reactor, input holding tank, metering pump, and output holding tank (Figure 1).

Air agitation produces mechanical motion in the reactor to assist in removing metal particles from the surface of the aluminum as displacement occurs. Metal particles, which are displaced from solution, settle to the bottom of the tank and are collected by pumping the solution through a cartridge filter. Strips of aluminum are supported above this screen. Solution flow in the reactor is from a bottom distribution

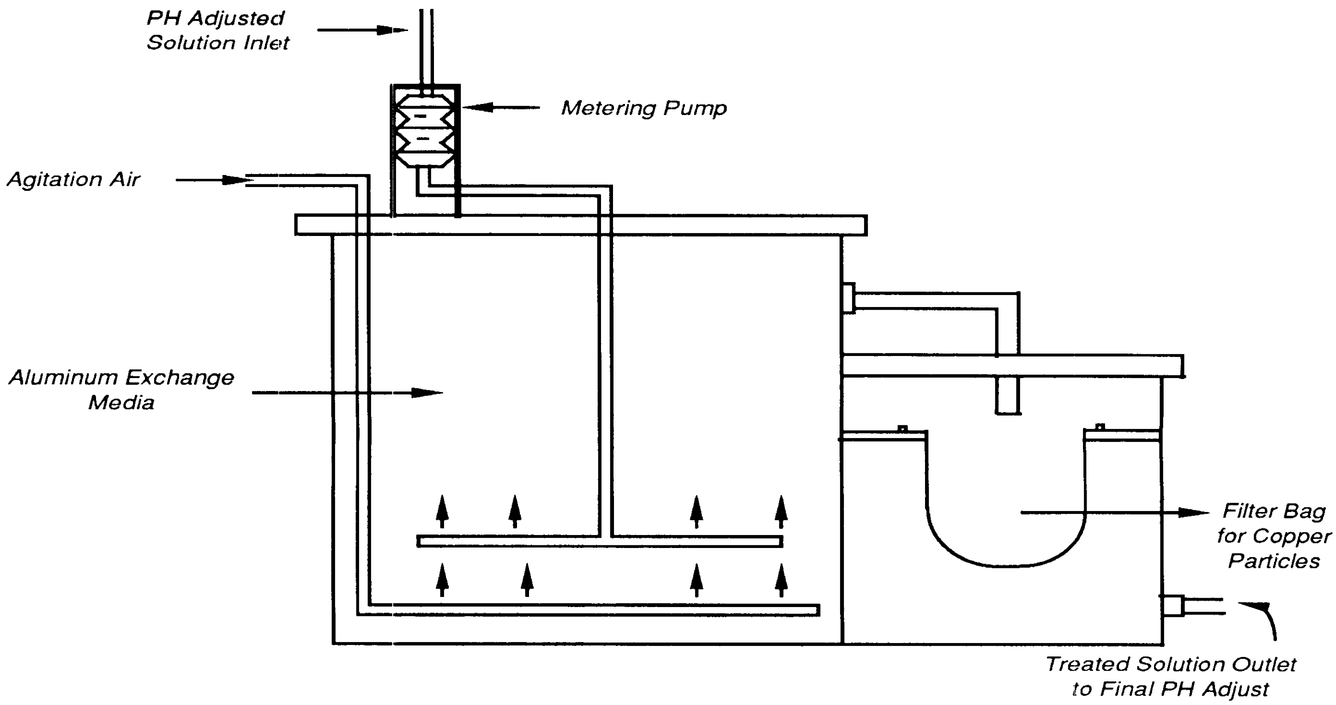

Figure I. Aluminum exchange reactor for metal recovery.

sparger up through the aluminum and out through a fitting near the top of the reactor.

Solutions were evaluated both on "flow through" and on a recirculation basis, although not every solution was evaluated under recirculation. Recirculation has potential for use with low-volume waste streams where a holding tank could be used to accumulate waste for treatment. Flow-through operation is more appropriate for the majority of metal finishing shops because of a lack of holding-tank capacity.

Solutions

Common metal finishing waste streams were fabricated for testing aluminum displacement. These solutions and their function in printed circuit fabrication are listed in Table 1.

All analyses for metal concentrations employed atomic absorption spectrophotometry; accepted procedures for accurate analysis at the application concentrations were, of course, used. Solutions fabricated for testing were at metal concentrations of approximately 200 ppm and pH of 2.5.

Table 1. *Aluminum Displacement Solutions and Their Function*

Metal Solution	Function
Copper sulfate	Most common electroplating solution
Copper ammonia chloride	Alkaline etchant used to remove copper from bare or copper-plated printed circuit boards
Copper/ EDTA complex	Very common electroless plating solution
Hydrogen peroxide/ sulfuric acid	Etchant used to clean copper surfaces
Copper nitrate	Solution resulting from use of nitric acid to strip racks used to hold work during processing
Tin/lead fluoborate	Common electroplating solution
Solder brightener	Solution used to remove small amounts of tin and lead from printed circuit boards as part of post-processing cleaning
Nickel sulfate	Electroplating solution

Results and Discussion

Flow-through Testing

The flow rate for all flow-through testing was 0.15 gpm using 25 gal of solution. Samples were taken at half-hour intervals after reactor outflow began. Contact time was 75 min. Results of this testing are given in Table 2.

The flow-through system did not efficiently remove copper complexed with EDTA. Recirculation might improve these results. Copper nitrate and nickel sulfate showed no displacement activity under these conditions. The nitric acid component of the copper nitrate solution may interfere with the reaction, reversing it as quickly as it proceeds. Due to its position in the electromotive series, nickel may not be effectively removed using a system of this type.

Recirculation Testing

Tin-lead fluoborate solution was reduced from 104 to 0.65 ppm with a contact time of 3-1/2 hr. Copper sulfate solution was reduced from a concentration of 200 to 1.5 ppm with a contact time of 24 hr. All recirculation testing was done at 0.15 gpm using 25 gal of solution.

Aluminum Exchange Material

The best configuration for the aluminum is shredded foil produced with a heavy-duty shredder using 5/8 x 12 x 0.012-in. aluminum entry foil, twisted to eliminate parallel surfaces. The aluminum was a 3003 alloy containing 1.5% maganese and .05% to 0.2% copper.

Table 2. Test Results for Metal Removal

Waste Streams	Metal Removed	Percent Removed
Copper sulfate	Copper	96
Copper ammonia chloride	Copper	90
Copper EDTA	Copper	51
Peroxide sulfuric etchant	Copper	89
Copper nitrate	Copper	0
Lead fluoborate	Lead	90
Tin chloride	Tin	85
Nickel sulfate	Nickel	0

Other Results

- A regeneration process was developed to cleanse aluminum exchange material. This involved lowering the pH of the input solution to 0.5 for approximately 1 hr to create an accelerated mild etch.
- The chloride ion present during the displacement process was of no importance.
- Thorough air agitation is critical to displacement efficiency but will vary by input flow and waste stream characteristics.

Conclusions and Recommendations

Results of this project indicate that the aluminum displacement process holds promise as a pretreatment and recovery technology for certain applications. Copper, lead, and tin were removed at efficiencies of 85+% with a single pass through the aluminum exchange reactors. Recirculation shows even higher removal efficiencies.

The low equipment cost and simplicity of operation make this an attractive technology for many smaller metal finishing operations. Aluminum exchange material is readily available. Metal is recovered in a form amenable to management as a resource rather than as a waste.

Efficient use of this technology requires segregation of metal-bearing, non-metal-bearing, and complexed metal streams. Care should also be taken to reduce rinsewater flow to the minimum with the use of dragout rinses and countercurrent flow rinses. The resulting low volume waste streams should be suitable up to a metal concentration of 200 ppm.

Further research is needed on the application of recirculation to complexed waste streams and to those with lower metal removal efficiencies. The pH and concentration optimization of these streams may also yield further expansion of the application of this technology.

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Steven C. Meyers is with Circuit Chemistry Corporation, Maple Plain, MN 55359.
James. S. Bridges is the EPA Project Officer (see below).
The complete report, entitled "Recovery of Metals Using Aluminum Displacement," (Order No. PB 89-222 590/AS; Cost: $15.00, 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:

Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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