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PROJECT SUMMARY

Recovery of Metals from Metal Finishing Waste Streams Using Aluminum Displacement

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Metal finishing operations generate wastestreams containing heavy metals such as copper, lead, tin and nickel. Standard pretreatment practice has involved removal of these metals from the effluent prior to discharge using a variety of techniques, primarily precipitation in a sludge which must be disposed as a hazardous waste. This project investigates aluminum displacement as a pretreatment process for selected wastestreams. The process has the potential of producing not only effluent suitable for discharge, but also non-hazardous metal particles suitable for recovery.

Testing of copper sulfate solutions at various flow rates showed copper removal in a range from 85-973. pH was determined to have an insignificant effect on copper removal when held in a range of pH 2-3.5. Recirculation testing of copper sulfate solutions showed a reduction in copper concentration from 200 ppm to 1.5 ppm. Recicrculation testing of tin/lead fluoborate solutions showed a reduction in lead concentrations from 104 ppm to 0.65 ppm. Bight other wastestreams were evaluated to determine metal removal efficiency.

Introduction

Wastestreams 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 concentration of these and other regulated heavy metals. Standard pretreatment practice often generates a sludge which must be handled and disposed as hazardous waste.

Removal of copper from etching solutions using displacement with aluminum was reported in the mid-1960's. Due to the position of aluminum 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 non-hazardous product suitable for recovery of metal values.

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

Procedures

Reactor design

Test equipment for this project included a 15-gallon aluminum exchange reactor, input holding tank, metering pump, and output holding tank.

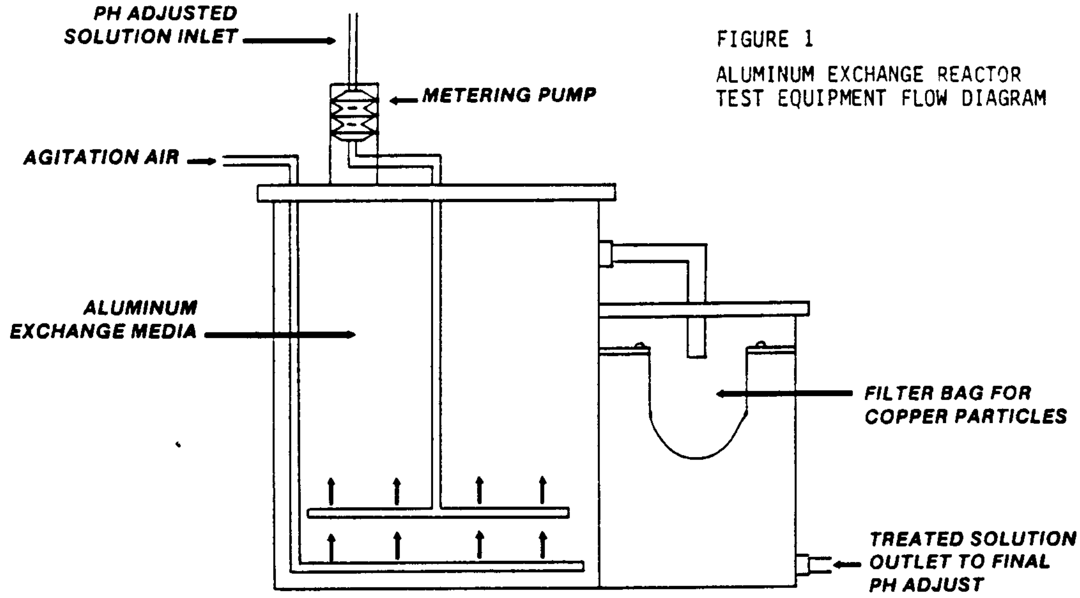

FIGURE 1

ALUMINUM EXCHANGE REACTOR TEST EQUIPMENT FLOW DIAGRAM

Air agitation is used to produce 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 reactor through a screen raised above 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 sparger up through the aluminum and out through a fitting near the top of the reactor.

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

Solutions

Common metal finishing wastestreams were fabricated for testing using aluminum displacement. These solutions and their function in printed circuit fabrication are as follows.

Copper sulfate	- Most common electroplating solution used for printed circuit manufacturing
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	- Removes small amounts of tin and lead from printed circuit boards as part of post-processing cleaning.
Nickel sulfate -	Electroplating solution

All analysis for metal concentrations was performed using atomic absorption spectrophotometry using accepted procedures for accurate analysis at the applicable concentrations.

Solutions fabricated for testing were at metal concentrations of approximately 200 ppm and a pH of 2.5.

Results and Discussion

Flow through testing

The flow rate for all flow through testing was 0.15 gpm using 25 gallons of solution. Samples were taken at half-hour intervals after reactor outflow began. Contact time was 75 minutes. Results of this testing are as follows.

Waste Stream	Metal	Percent Removed
1. Copper Sulfate	Copper	96
2. Copper Ammonia Chloride	Copper	90
3. Copper EDTA	Copper	51
4. Peroxide Sulfuric Etchant	Copper	89
5. Copper Nitrate	Copper	0
6. Lead Fluoborate	Lead	90
7. Tin Chloride	Tin	85
8. Nickel Sulfate	Nickel	0

Copper complexed with EDTA was not efficiently removed using the flow through system. 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 ppm to 0.65 ppm with a contact time of 3 l/2 hours. Copper sulfate solution was reduced from a concentration of 200 ppm to 1.5 ppm with a contact time of 24 hours. All recirculation testing was done at 0.15 gpn using 25 gallons of solution.

These data indicate promise for use of the aluminum displacement process with low-volume wastestreams.

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" aluminum entry foil and twisted to eliminate parallel surfaces. The aluminum used is a 3003 alloy containing 1.5% manganese and .05 -

Other results

- A regeneration process was developed to cleanse the aluminum exchange material. This involves lowering the pH of the input solution to 0.5 for approximately one hour to create an accelerated mild etch.
- Presence of the chloride ion during the displacement process was found to be of no importance.
- Thorough air agitation is critical to displacement efficiency, but will vary by input flow and 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+% using 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 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 possible using dragout rinses and countercurrent flow rinses. The resulting low volume wastestreams should be suitable up to a metal concentration of 200 ppm.

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