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Project Summary

Evaluation of Process Systems for Effective Management of Aluminum Finishing Wastewaters and Sludges

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Innovative processes for use in treatment of wastewaters and sludges produced in anodizing, etching and painting extruded aluminum were investigated. Due to the low quantities of wastewater aluminum from painting processes, emphasis was placed on those processes amenable to treatment of anodizing and etching wastewaters.

Segregated neutralization of spent caustic etch and spent anodize acids at temperatures of 60 to 90°C and pH values of 5.5 to 10 were examined. Major improvements in thickening and dewatering properties were achieved with increasing values of neutralization pH while neutralization temperature had minimal impact. Solids contents of dewatered sludge samples ranged from 33 to 54 percent while those of conventional aluminum-finishing sludges ranged from 9 to 17 percent, indicating the potential of segregated neutralization for major reductions in the mass of wet dewatered-sludge solids for disposal.

Recovery of spent caustic etch by precipitation of aluminum with calcium (i.e., lime) addition was studied. Stoichiometric precipitation of aluminum at temperatures of 25 to 60°C was achieved at calcium-aluminate (Ca/Al) ratios of 4 to 5.5 (mass basis). Calcium-aluminate sludges produced had excellent dewatering properties with dewatered-sludge solids contents of 45 to 53 percent. Recovery of spent etch for reuse would therefore be accompanied by a significant reduction in the mass of wet dewatered sludge solids for disposal.

Recovery of aluminum-finishing sludges using sulfuric-acid extraction to produce liquid alum (i.e., $Al_2(SO_4)_3 \cdot 14H_2O$) was examined with numerous types of sludges. Sludges produced by conventional neutralization, segregated neutralization, and those from proprietary etch-recovery processes were successfully extracted to produce commercial-strength (i.e., 8-8.3 percent as Al_2O_3) liquid alum. Sludge solids content was a critical variable with a minimum value of 20 percent required for production of a commercial-strength product.

Results of the research can be immediately implemented at many aluminum-finishing plants where sludge disposal restrictions and costs are increasing. Segregated neutralization and recovery of spent caustic etch can be used to increase the net solids content of dewatered sludge solids and thereby reduce the volume of dewatered-sludge available for disposal. Reclamation of dewatered-sludge solids using acid extraction for production of liquid alum has potential for virtual elimination of the need for sludge disposal while

producing a net income from this sludge-reclamation process.

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This Project Summary was developed by EPA's Industrial Environmental 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

Treatment of wastewaters from cleaning, milling, etching, anodizing and painting extruded aluminum results in the production of large quantities of residual suspended solids for disposal. These solids are composed primarily of aluminum hydroxides and are contained in suspensions that are highly gelatinous and difficult to thicken and dewater. The mass of wet dewatered sludge solids produced by an aluminum extrusion/anodizing plant, for example, may approach the mass rate of production of finished aluminum products. A major waste disposal problem for aluminum finishing plants is therefore disposal of large quantities of highly gelatinous sludge solids.

Characterization of wastewaters and sludges produced by aluminum-finishing plants has been examined earlier by the authors, as presented in a companion report. Wastewater suspensions from numerous eastern U.S. plants were examined with respect to conventional wastewater parameters, as well as priority-pollutant metals. Sludge thickening, dewatering, gravity-drainage and conditioning properties were examined in detail to establish optimal means of treating conventional aluminum-finishing wastewaters.

Thorough examination of properties of conventional wastewaters and sludges from aluminum-finishing plants resulted in the identification of numerous innovative treatment options which merited further consideration in the present study. Using wastewaters, sludges and spent finishing solutions and suspensions from aluminum-finishing plants, the following innovative treatment options were examined: (1) segregated neutralization of spent acids and bases, (2) reclamation of spent caustic etch by lime addition, and (3) reclamation of sludges as liquid alum. In addition, an extensive industrial-waste survey was conducted at an aluminum-finishing plant to establish sources and quantities of wastewater and waste aluminum. The overall impact of aluminum-finishing and waste-treatment practices on waste disposal economics and reclamation potential were presented.

Procedures

Laboratory-scale studies were conducted using wastes obtained from aluminum-finishing plants with production capacities ranging from 15 to 25 ton/d of finished architectural aluminum. Typical aluminum-finishing steps used by the participating plants included alkaline cleaner, caustic etch, acidic desmut, bright dip, conventional sulfuric-acid anodize, integral-color, sulfuric-acid anodize, dye, and seal. Waste treatment practices included neutralization, polymer conditioning, and gravity sedimentation followed by wastewater discharge to a sewer or stream. Gravity-thickened sludges were dewatered in lagoons and with pressure or vacuum filtration followed by land disposal.

Results and Discussion

The project was focused on four major topics which are presented below.

Industrial Waste Survey

A 24-hour survey was conducted at plant A-1 to determine the quantities of wastewater and waste aluminum discharged from individual finishing and rinsing tanks included in the anodize line and a parallel, paint line. During the survey, equal quantities of similar aluminum alloys were finished on each line, i.e., 18-19 tons of extruded aluminum with a total surface area of 7-8x10^3 m^2.

For the anodize line, 93 percent of the wastewater discharged was attributable to wastewater from rinse tanks following the various finishing steps in the line, as shown in Table 1. The majority (65 percent) of waste aluminum was contained in spent finishing solutions which accounted for only 6 percent of the total wastewater flow.

The paint line was a fully-automated system which had only one combined wastewater flow from the alkaline-rinse, chrome-conversion, and acidulating-rinse portions of the unit. The total wastewater flow from the paint line was 43 m^3/d and was only 8 percent of that from the anodize line. Waste aluminum was similarly low at 1.7 kg/d. Paint-line wastes, therefore, accounted for an extremely small portion of the total flow of wastewater and waste aluminum.

An examination of dragin rates from finishing tanks in the anodize line was made using mass flows of aluminum, as well as those for chromium and cadmium, in conjunction with wastewater flow data. Dragin rates ranged from 0.053 to 3.08 m^3/d (14 to 814 gal./d) with the higher rates attributable to the viscous solutions used in caustic etch, desmut, anodize and acid cleaner. Overall wastewater and waste aluminum discharge rates for the plant are presented in Table 2. The quantity of wastewater and waste aluminum from the paint line were marginal compared with those for an anodize line. Waste aluminum, which is central to the sludge disposal problem, was 2.95 percent (mass basis) of the aluminum finished on the anodize line but was only 0.01 percent (mass basis) of that finished on the paint line. In addition, wastewater flow was considerably higher from the anodize line. Therefore, major sludge disposal problems originate with the intensive surface treatments, such as caustic etch and sulfuric-acid anodize, which are required in anodizing extruded aluminum.

Segregated Neutralization

Major sources of waste aluminum in anodizing wastewaters were shown to be spent caustic etch and spent anodize acid. Neutralization of these concentrated wastes, apart from dilute rinsewaters and hence referred to as *segregated neutrali-*

Table 1. *Summary of Wastewater Flow and Waste Aluminum from Anodize Line at Plant A-1 During 24-h Survey*

Waste Source	*Flow m^3/d*	*Waste Aluminum kg/d*
Rinsewater	*495*	*195*
Spent Etch	*6*	*335*
Spent Anodize Acid	*26*	*36*
Other	*7*	--
Total	*534*	*566*

Table 2. *Wastewater and Waste Aluminum Flow Normalized to Finished-Metal Production*

Source	Unit Waste Discharge Rates: Surface Area Basis	Unit Waste Discharge Rates: Mass Basis
Flow		
Anodize Line	*73.4 m³/1000 m³*	*27.8 m³/ton*
Paint Line	*4.2 m³/1000 m³*	*2.5 m³/ton*
Waste Aluminum		
Anodize Line	*77.7 kg/1000 m²*	*29.5 kg/ton*
Paint Line	*0.2 kg/1000 m²*	*0.1 kg/ton*

(m^3/1000 m^3) x 24.5 gal./1000 ft^3.
(m^3/ton x 0.12 = gal./lb.

zation, was examined to determine the impact on sludge treatment, handling and disposal. Samples of spent caustic and spent anodize acid were collected from plant A-3 and used immediately for neutralization experiments in a completely-mixed flow reactor with a hydraulic retention time of approximately 10 minutes. Thickening and dewatering properties of suspensions which were neutralized at temperatures ranging from 60 to 90°C and pH values from 5.5 to 10 and stored for periods of 0 to 24 h were investigated. Neutralization temperature and storage for up to 24 h had minimal impacts on thickening and dewatering properties.

Neutralization pH had a dramatic impact on sludge thickening and dewatering properties. Sludge thickening properties, as measured by interfacial settling velocity, were improved for unconditioned suspensions as pH was increased. Similarly, specific resistance measurements indicated dewatering properties improved with increasing values of neutralization pH. In addition to improved dewatering rates, significant reductions in the wet mass of dewatered sludge solids were achieved. Cake solids concentrations ranged from 33 to 54 percent (mass basis) following standard laboratory dewatering tests and, as indicated in Figure 1, improved with increasing values of neutralization pH. When compared with cake solids concentrations of 9 to 17 percent obtained in a similar manner with conventional aluminum-finishing sludges, the values presented in Figure 1 indicate the potential of segregated neutralization for significant reductions in the quantity of sludges produced for disposal. As an example, it is assumed that 65 percent of waste aluminum at a plant is treated by segregated neutralization to achieve a dewatered sludge with a solids content of 40 percent, and the remainder of the

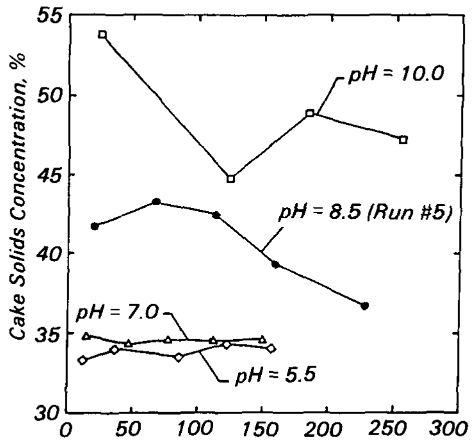

Figure 1. *Solids content of laboratory-dewatered sludge following segregated neutralization at 80°C.*

waste aluminum is dewatered to a solids content of 15 percent. In comparison to a plant producing one combined dewatered sludge by conventional neutralization with a solids content of 15 percent, use of segregated neutralization to treat a small portion of the total wastewater flow would result in a 40 percent reduction in the wet mass of sludge to be disposed.

Improved thickening and dewatering properties following segregated neutralization were attributed to the formation of crystalline aluminum hydroxides as opposed to amorphous precipitates. Decreased sludge compressibility, as well as improved thickening and dewatering properties, were indicative of the apparent formation of hydroxides such as gibbsite, boehmite, pseudo-boehmite and nordstrandite.

Caustic Etch Recovery

Spent caustic etch is a major source of waste aluminum with aluminum concentrations as high as 70 g/L. Removal of aluminum from this concentrated source of waste aluminum has potential for recovery of spent etch for reuse in finishing extruded aluminum, as well as reduction in handling of waste sludge solids. Addition of calcium to spent caustic etch was examined to establish the extent to which aluminum was precipitated in the form of calcium aluminates; the ease with which the precipitate could be removed from suspension; and, to a lesser extent, the potential for recovery of the remaining caustic etch solution. All experimental studies were conducted in batch reactors maintained at constant temperature. Lime ($Ca(OH)_2$) was added to fresh samples of spent caustic etch, mixed and examined with respect to removal of aluminum and calcium, as well as dewatering properties of precipitated solids.

Removal of aluminum from spent etch was a function of reaction time, temperature, and calcium addition. For a reaction time of 6h, the Ca/Al ratio for stoichiometric removal of aluminum ranged from 2.7 to 3.7 on a molar basis (4.0 to 5.5 on a mass basis) at temperatures of 60°C and 25°C, respectively. Production of aluminum-free etch from spent etch was therefore feasible and could be controlled by the level of lime addition used.

Since aluminum concentrations in spent etch frequently range from 20 to 70 g/L, precipitation of aluminum by calcium addition produced a suspension of sufficient concentration (e.g., suspended solids of 80 to 300 g/L) to warrant direct filtration to remove precipitated aluminates. Specific resistance data, collected at temperatures of 25 to 60°C, indicate good dewatering properties for the suspensions produced. In addition, solids concentrations for dewatered cakes ranged from 45 to 53 percent. Therefore, precipitation of aluminum from spent caustic etch with lime produced a suspension which was easily dewatered to high solids contents. Controlled lime addition would, furthermore, allow for regulation of aluminum concentrations in reclaimed etch, depending on aluminum-finishing requirements.

Sludge Reclamation as Liquid Alum

Extensive examination of the metal composition of aluminum-finishing sludges indicated that aluminum was the major metal present. Based on inert suspended solids (ISS), aluminum content ranged from 0.27 to 0.6 kg Al/kg ISS, averaged 0.35 kg Al/kg ISS, and was typical of that for aluminum hydroxide, i.e., 0.346 kg Al/kg $Al(OH)_3$. Other metals commonly contained in sludge solids included arsenic, cadmium, chromium, copper, lead, nickel and zinc. These latter metals were however, only minor constituents with concentrations ranging from 10 to 2000 mg/kg. Therefore aluminum-finishing sludges were established to be excellent sources of aluminum, presumably as a collection of numerous aluminum hydroxides, which contained low levels of other metals but contained high levels of moisture, e.g., 83 to 91 percent moisture. These characteristics indicated the potential for use of aluminum-finishing sludges in production of aluminum sulfate, i.e., "alum."

A laboratory-scale investigation of the production of alum from aluminum-finishing sludges was conducted with a heated batch reactor. Various types of sludges were examined including: (1) sludge from two conventional anodizing plants (samples A-2 and A-3); (2) sludge produced by segregated neutralization of spent caustic etch and anodize acid (sample SN); and (3) sludge solids from two proprietary etch-recovery systems (samples ER-1 and ER-2). All sludge samples were collected from field or laboratory dewatering systems and examined without pretreatment, except sample A-3-2 which was air dried to a solids content similar to that of sample A-2. Sludge sample A-3-1 was typical of the majority of the aluminum-finishing sludges examined during a previous study, while sample A-2 was a mixture of a suspension produced by segregated neutralization and a suspension produced by conventional neutralization of dilute rinse-waters.

Characteristics of the sludges examined are presented in Table 3. The solids content of the sludges varied considerably while aluminum content (based on dry inert solids) was consistent, between 32 and 38 percent, and was, in general, typical of aluminum hydroxide precipitates. Based on aluminum content of each sludge sample, sulfuric acid requirements were calculated according to the following equation:

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$$

and were based on stoichiometric extraction of sludge-aluminum and the goal to produce a commercial-strength product. Commercial grade alum has an aluminum content of 8.0 to 8.3 percent as Al_2O_3.

Solubilization of aluminum in sludge samples A-2, A-3-1, A-3-2, and SN was rapid and was complete within 60 minutes. Aluminum solubilization for samples ER-1 and ER-2 was complete after 120 minutes, when conducted at an elevated acid strength during extraction. The quality of the alum products produced from sludge samples is indicated in Table 4. "Predicted" values of Al_2O_3 content in Table 4 were target values used to establish sulfuric acid requirements. Data for conventional sludges from two aluminum-finishing plants (A-2; A-3) indicated the potential for production of commercial-grade alum from these sludges. Extraction of samples A-2 and A-3-2 produced commercial-strength alum while that for A-3-1 did not. The solids content of sample A-3-1 was the lowest of sludges examined and the moisture contained in the dewatered sludge resulted in the production of a diluted product. However, when air-dried to a solids content of 21.1 percent, the sludge (A-3-2) was effectively used to produce a commercial-strength product. Using Equation 1, the theoretical minimum value for sludge solids content required to produce a commercial-strength alum (i.e., 8.0 percent Al_2O_3) was estimated to be 20 percent. Data for samples A-2 and A-3 experimentally confirmed this theoretical value.

Table 4. *Composition of Alum Produced by Acid Extraction of Aluminum-Finishing Sludges*

Sample	*Al_2O_3 percent Predicted*	*Al_2O_3 percent Measured*
A-2	*8.3*	*8.9*
A-3-1	*5.3*	*5.9*
A-3-2	*8.3*	*8.4*
SN	*8.3*	*8.5*
ER-1	*8.3*	*8.7*
ER-2	*8.3*	*8.5*

In addition to aluminum content, free-acid and free-aluminum concentrations and concentrations of iron, calcium, potassium, magnesium and priority pollutant metals were investigated. All parameters were within acceptable limits for product quality and no restrictions on the commercial use of alum produced from aluminum-finishing sludge was anticipated.

Process economics were investigated for an aluminum extrusion/anodizing plant finishing approximately 25 ton/d of extruded aluminum. A capital investment of $80,000 was estimated for a plant producing a dewatered sludge with a solids content of 20 percent or greater. The estimated payback period for the capital investment was 14 to 21 months, exclusive of any economic benefits realized as a result of elimination of the need to dispose of sludge solids and using a price for the sale of alum equal to 60 percent of the current market value. The production of liquid alum from aluminum-finishing sludges therefore has the potential to profitably reclaim waste aluminum and eliminate a major sludge disposal problem.

Table 3. *Characteristics of Aluminum-Finishing Sludges Used in Alum Production Studies*

Sample	*Solids Content percent*	*Aluminum Content percent**
A-2	*21.3*	*35*
A-3-1	*13.5*	*34*
*A-3-2***	*21.1*	*34*
SN	*32.9*	*32*
ER-1	*95.1*	*37*
ER-2	*90.4*	*38*

**Percent as dry inert solids.*
***Air dried to increase solids content.*

Conclusions

The results of the research on innovative treatment processes indicate that they have excellent potential for achieving major reductions in wet mass of sludges available for disposal; recovery of spent caustic etching solutions; and economical reclamation of waste aluminum as a marketable product.

The results of an initial industrial plant survey provided the justification for pursuit of the three innovative processes investigated. From the survey it was concluded that:

1. The majority of waste metal from an anodize line was aluminum removed from alloy surfaces during etching and anodizing with finishing-solution additives providing minor metal loadings. Rinsewaters contributed the bulk of the wastewater discharged while spent caustic etch, spent anodize acids and dragout from etching tanks were the sources of more than 90 percent of waste aluminum.
2. Waste-metal quantities in paint line wastes were significantly lower than those in anodize lines and were equally attributable to aluminum removed from alloy surfaces and chromium discharged from finishing solutions.

Segregated neutralization of concentrated finishing solutions was investigated as a means of reducing the volume of sludge solids produced. It was concluded that:

1. Segregated neutralization of concentrated spent etch and acid solutions could be achieved at temperatures of 60 to 90°C in 9 to 10 minutes.
2. Thickening properties of sludges produced by segregated neutralization were improved significantly by alkaline neutralization over neutral or acidic neutralization.
3. Batch flux analysis indicated that thickened sludge concentrations of 4 to 5 percent solids could be routinely achieved in sedimentation basins conventionally used in the industry as compared to conventional-neutralization sludge concentrations of 1 to 2 percent.
4. Dewatering properties of sludges produced by segregated neutralization were improved by use of alkaline pH values. Cake solids concentrations from 35 to 54 percent solids were achieved at alkaline pH values indicating a major reduction in final sludge volume.
5. Evaluation of implementation of segregated neutralization to treat spent finishing solutions at plant A-3 indicated that predicted reductions in wet sludge mass ranged from 73 to 80 percent, resulting in a major reduction in sludge disposal costs.

Recovery of spent caustic etch by precipitation of aluminum with lime was investigated. It was concluded that:

1. Removal of aluminum from caustic etch solutions was achieved by precipitation of calcium aluminate using lime addition at reaction temperatures of 25 to 60°C.
2. Reaction kinetics were affected by reaction temperature, reaction time and the Ca/Al ratio.
3. Sludge solids produced at Ca/Al mass ratios of 1.5 to 4.5 and temperatures of 25 to 60°C had excellent dewatering characteristics.
4. Analysis of the impact of implementation of etch recovery with lime addition at a full-scale anodizing plant indicated a 24-percent reduction in wet sludge mass was achieved as well as a potential chemical saving of $500/day through recovery of spent etching solution.

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***Alfred B. Craig, Jr.** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of Process Systems for Effective Management of Aluminum Finishing Wastewaters and Sludges," (Order No. PB 84-170 661; Cost: $16.00, subject to change) will be available only from:
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