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Project Summary

Reclamation of Aluminum Finishing Sludges

F. Michael Saunders

The reclamation of aluminum-anodizing sludges produced as a result of finishing extruded architectural aluminum using etching and anodizing processes was studied by Georgia Tech Research Corporation. Two sequential phases focused on (1) enhanced dewatering of aluminum-anodizing sludges with recessed-chamber filter presses and (2) acidic extraction of dewatered aluminum-anodizing sludges to produce commercial-strength solutions of aluminum sulfate, i.e., liquid alum.

A high-pressure (14 to 15 bar) and a diaphragm filter press were effective in dewatering aluminum anodizing sludges to cake solids contents of 27% to 29% and 25% to 31%, respectively. These values were well above the 21% value required to justify pursuit of direct acidic extraction of aluminum. Commercial-strength solutions of aluminum sulfate with concentrations of 8% as Al_2O_3 were produced using conventional-neutralization, segregated-neutralization, etch-recovery sludge cakes. The trace metal contents of the alum products were, in general, typical of commercial products.

This Project Summary was developed by EPA's Water 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

Aluminum anodizing plants may produce up to 500 metric tons/month of finished architectural aluminum extrusions. In the finishing process, approximately 3% to 5% of the mass of the extrusions is discharged as soluble aluminum metal to plant wastewaters. These aluminum-bearing wastewaters are typically neutralized, resulting in the production of a highly gelatinous, aluminum-hydroxide suspension. When these suspensions are thickened and dewatered, the remaining wet residue can equal or exceed the mass of finished aluminum extrusions produced at a plant. This solid waste residue must then be disposed of in a landfill or by other acceptable methods. Solid waste reduction, therefore, has an extremely high priority in this industry and can be addressed through alterations in aluminum-finishing and waste-treatment procedures or by reclamation of the aluminum value in the dewatered solid waste residue.

A major deterrent to the reclamation of the aluminum value in aluminum-anodizing sludges is the high levels of moisture associated with dewatered sludge cakes. Moisture generally constitutes more than 80% of the total mass of dewatered sludges, thereby increasing sludge hauling and ultimate disposal costs and contributing to the dilution of the aluminum value. The high moisture content is attributable to the gelatinous, hydrophilic nature of the aluminum hydroxide precipitate formed during conventional neutralization of aluminum-anodizing wastewaters. To investigate the extent to which sludge moisture content could be reduced, recessed-chamber filter presses were selected for mechanical dewatering studies because of the high pressure differentials (e.g., 6 to 15 bar) typically achieved with these systems and their ability to produce dewatered sludge cakes with the lowest moisture content achievable by conventional mechanical dewatering systems.

The production of liquid alum from aluminum-anodizing sludges can be represented by the addition of sulfuric acid (H_2SO_4) to an aluminum-anodizing sludge containing dry fixed solids, represented by $Al(OH)_3$, and moisture. In an equation format, the acidic extraction of aluminum is represented by:

$$2Al(OH)_3 + xH_2O + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + (6 + x)\,H_2O \qquad (1)$$

To produce a commercial-strength solution of liquid alum containing 26.8% $Al_2(SO_4)_3$ (i.e., 8% as Al_2O_3), the aluminum-hydroxide content of a sludge would have to be equal to 16% on a fixed solids basis. This value is indicative of a total dry (103°C) solids content of approximately 21% for a dewatered sludge cake. This is an exceptionally high value that, when compared to current practice, is not routinely achieved. Therefore, effective dewatering of sludge solids was a critical step in establishing the potential for reclamation of aluminum-anodizing sludges. Without the ability to produce a dewatered sludge cake with a solids content of $\geq$ 21%, further consideration of direct reclamation of the aluminum value of aluminum-anodizing sludge was futile.

Previous studies have been conducted in the laboratory to establish the feasibility of producing liquid alum from aluminum-anodizing sludges. The purpose of this study was to conduct extractions with three types of aluminum-anodizing wastes, to establish the kinetics of the acidic extraction, and to evaluate the quality of the products produced.

Procedures

Two recessed-chamber, fixed-volume filter presses (i.e., 470 mm and 250 mm) were employed in the study to establish the extent to which aluminum-anodizing sludges could be dewatered. Low- and high-pressure filtration studies were conducted with the presses, and the larger press was operated with variable-volume diaphragm plates. Constant operational pressure ranges of 6 to 7 bar (87 to 102 psi) and 14 to 15 bar (203 to 218 psi) were employed throughout the studies and are typical, respectively, of low- and high-pressure systems marketed for waste treatment practice.

Pressure filtration studies were conducted at the site of an aluminum-anodizing facility producing architectural aluminum extrusions. Aluminum finishing processes included alkaline cleaning, caustic etching, acidic desmut, conventional and two-step sulfuric acid anodizing, and hot-water sealing. Wastewater treatment included neutralization with spent acid and virgin caustic; polymer flocculation; gravity sedimentation; rotary vacuum filtration of thickened sludge; and recycle of clarified water into finishing rinses. Samples of the underflow suspension from the clarifier were collected from the influent line to the rotary vacuum filter and were examined intensively on the filter presses. These sludge suspensions were identified as conventional neutralization (CN) suspensions. A CN suspension from a similar aluminum-anodizing plant was also examined.

One other type of suspension was examined during the pressure filtration studies. Suspensions formed by batch neutralization of spent caustic etch from the aluminum-finishing line with spent anodizing acid were identified as segregated neutralization (SN) suspensions. These suspensions were not produced in the plant treatment systems, but were produced experimentally in 0.2-m^3 (~50-gal) volumes for use in the filtration and acidic extraction portions of the study. These suspensions were formed by pumping anodizing acid into an intensively mixed, lined reactor containing spent caustic etch until a pH of 9 to 10 was achieved. These suspensions were then blended with CN suspensions or used directly in pressure filtration studies.

Acidic extraction of aluminum-anodizing sludges was conducted in a laboratory-scale reactor equipped with a mixer and temperature control system used to maintain post-acid-addition temperatures at 50°C to 90°C. Following addition of acid, samples were collected at 30- to 60-min intervals to monitor the progress of the reaction. A detailed material balance was conducted on total reaction mass and on the mass of aluminum in each reactor.

Three types of suspensions were examined. The CN and SN suspensions as included in filter-press dewatering studies were examined. In addition, an etch recovery (ER) sludge provided by an aluminum-anodizing plant was examined. This residue was produced from a patented system designed to remove aluminum from caustic etching suspensions allowing for the continuous recovery and reuse of the caustic etch suspension. The aluminum is crystallized as an aluminum hydrate (e.g., $Al_2O_3 \cdot x\,H_2O$) at temperatures of 55°C to 65°C, removed from the caustic etch, and water washed using, for example, a vacuum filtration system. The dewatered residue was provided as one sample in 0.2-m^3 volume and had a solids content of 91.6% and an aluminum content of 43.6 g/100 g fixed solids.

Filter Press Dewatering

Typical characteristics of the suspensions obtained from or experimentally produced at two aluminum-anodizing plants and examined during the filter press studies are included in Table 1. The two clarifier underflow suspensions, the primary focus of the dewatering studies, were slightly alkaline and relatively dilute. The specific resistance values for all suspensions were similar, although that for the SN suspension was the lowest, indicating slightly improved dewatering characteristics. Although not directly indicative of final cake solids content for a mechanical dewatering system, the dewatered cake solids concentration (C_k) determined as a part of the specific resistance test is effective in indicating the relative potential to which a suspension can be dewatered. The clarifier underflow from plant X had the lowest C_k value and was approximately 50% to 60% of that for the neutralization basin effluent and clarifier underflow from plant A. Furthermore, the solids content values for all CN suspensions ranged from 7% to 13%, well below the minimum desired value of 21%, indicating indirectly the nature of the problem with respect to aluminum recovery as liquid alum. SN suspensions produced experimentally had exceptionally high suspended solids concentrations and the lowest and highest values for specific resistance and specific-resistance cake solids (C_k), respectively. This indicated the high potential for use of SN suspensions in the production of liquid alum.

High-pressure and low-pressure filtration studies were conducted at constant feed pressures of 6 to 7 bar (87 to 102 psi) and 14 to 15 bar (203 to 218 psi) using two pilot-scale filter presses. Replicate runs were usually performed for an individual suspension at each feed pressure with each replicate run being conducted for a variable time of filtration. For example, a CN suspension from plant A was examined in one series of runs at two concentrations and three filtration time intervals for each operational pressure, as indicated in Table 2. Filtrate volume data were also collected as a function of time, as presented in Figure 1 for runs 24 through 29. The runs were highly reproducible with respect to filtrate volume. This allowed for evaluation of the effect of filtration time on dewatered cake solids, evaluation of the ultimate filtrate volume that could be produced at infinite filtration time, and, thereby, the ultimate dewatered-cake solids concentration, $(C_k)_{ULT}$. Using a procedure developed in conjunction with this study, the ultimate filtrate volume was established using a procedure illustrated in Figure 2. With the projected ultimate filtrate volume (i.e., filtrate volume at a projected filtration rate of zero), both the ultimate cake solids concentration, $(C_k)_{ULT}$, and the cake solids concentration at the point of collection of 90% of the ultimate filtrate volume, $(C_k)_{0.9}$, were calculated. This is illustrated in Table 3 for all low-pressure and high-pressure runs with CN suspensions from plant A. The ultimate cake solids concentrations, $(C_k)_{ULT}$, for both low- and high-pressure filtration were at or above the desired value of 21%, as were all $(C_k)_{0.9}$ values, indicating that it was feasible to explore the acidic extraction of sludge aluminum. Data collected for a similar CN sludge from plant X indicated that high- and low-pressure filtration produced $(C_k)_{ULT}$ values of 24.5% and 17.6%, respectively, indicating that only high-pressure filtration would be acceptable. Therefore, in general, CN sludges can be dewatered to solids concentrations ranging from 18% to 29% using filter-press systems. Furthermore, high-pressure systems appear most suitable for production of dewatered sludge cakes that are suitable for direct production of liquid alum.

SN suspensions, produced by direct neutralization of spent caustic etch suspensions (containing elevated concentrations of aluminum, e.g., 50 to 150 g/L) with spent desmut or anodizing acids, have better dewatering properties than CN suspensions, as shown in Table 1. Samples of these experimentally produced suspensions were blended with CN suspensions, since both would be produced at a plant employing SN, to determine the impact on dewatering. Data in Table 4 indicate a dramatic impact of SN solids on ultimate solids concentration, as well as the high level of cake solids concentration, i.e., 51%, that can be achieved with SN suspensions alone.

The use of variable-volume, or diaphragm, plates was examined on the 470-mm press using a low-pressure (6 to 7 bar) addition of a suspension to the press followed by a high-pressure (15.5 bar) squeeze cycle, in which the contents of each chamber were compressed until no filtrate was released. Examples of the filtrate volume collected with time during the fill (or filter) and squeeze portions of several replicate runs are presented in Figure 3. Following filtration with the diaphragm plates, the CN suspensions from plant A had final cake solids concentrations that ranged from 25% to 31% and averaged 29%. These values were equivalent to or slightly higher than the analogous $(C_k)_{ULT}$ values obtained for high pressure filtration (see Table 3). The limited increase in cake solids concentration would not appear to warrant the use of diaphragm plates, although a comparison of capital and operating costs may dictate otherwise.

Table 1. *Typical Characteristics of Aluminum-Anodizing Suspensions from Participating Plants*

		Suspended Solids	Specific Resistance		Capillary Suction Time
	pH	SS, g/L	r, Tm/kg+	C_k, %	Seconds
Plant A					
Neutralization basin effluent	8.2	2.4	3	12	60
Clarifier underflow	8.2	41	4	13	150
*Segregated neutralization**	9.6	143	1.4	47	530
Plant C					
Clarifier underflow	7.6	21	3	7	66

**Suspension produced experimentally at plant A but not a typical part of plant waste flow.*
+TM/kg = 10^{12} meters/kg

Table 2. *Results for Filter Press Dewatering of CN Suspensions (Plant A, Runs 24-29)*

	Influent Suspension					
	Suspended Solids	Specific Resistance		Filtration Pressure	Time of Filtration	Cake Solids
Runs	g/L	r, Tm/kg*	C_k, %	bar	min	%
24,25,26	73	3.6	15.4	14-15	75,50,35	28.1,26.4,25.3
27,28,29	37	2.6	14.7	14-15	156,90,68	28.9,25.1,23.6

**Tm/kg = 10^{12} meters/kg*

Acidic Extraction of Sludges

Extractions were conducted on numerous aluminum anodizing sludges, following dewatering by pressure filtration, and on blends of dewatered sludges. Each extraction was initiated by addition of a fixed mass of sulfuric acid to a known mass of dewatered sludge. A temperature control system was used to maintain a prescribed control temperature. The temperature, however, was not controlled during the initial acid addition phase but was controlled at temperatures of 50°C to 90°C following dissipation of heat associated with the initial exothermic reaction.

The characteristics of the sludges extracted are summarized in Table 5. The aluminum content of the sludges, expressed on a mass basis in terms of the fixed (550°C) solids, varied from 31% to 43.6%, comparing favorably with the $Al(OH)_3$ form, with a theoretical aluminum content of 34.6%, used in Equation 1 to describe the chemistry of the acidic extraction. Sulfuric acid was added to dewatered cakes, in accordance with Equation 1, at the rate of 1.89 g H_2SO_4/g fixed solids or 5.44 g H_2SO_4/g Al. Acid doses were also expressed as a percentage of the stoichiometric acid dose based on sludge aluminum content (e.g., the addition of 5.44 g H_2SO_4/g Al to a sludge cake would represent a stoichiometric dose of 100%).

Filtrate aluminum data in Figure 4 indicate the results of a typical acidic extraction. In general, with an initial 1-hr period, the aluminum contained in the sludge cakes was extracted to near completion and approached the concentration of commercial-strength liquid alum (i.e., 8% as Al_2O_3). Because of the robust exothermic nature of the reaction during the initial period, the controlled reaction temperature had only a minimal effect on the rate of the reaction, as measured after a 0.5-hr extraction period.

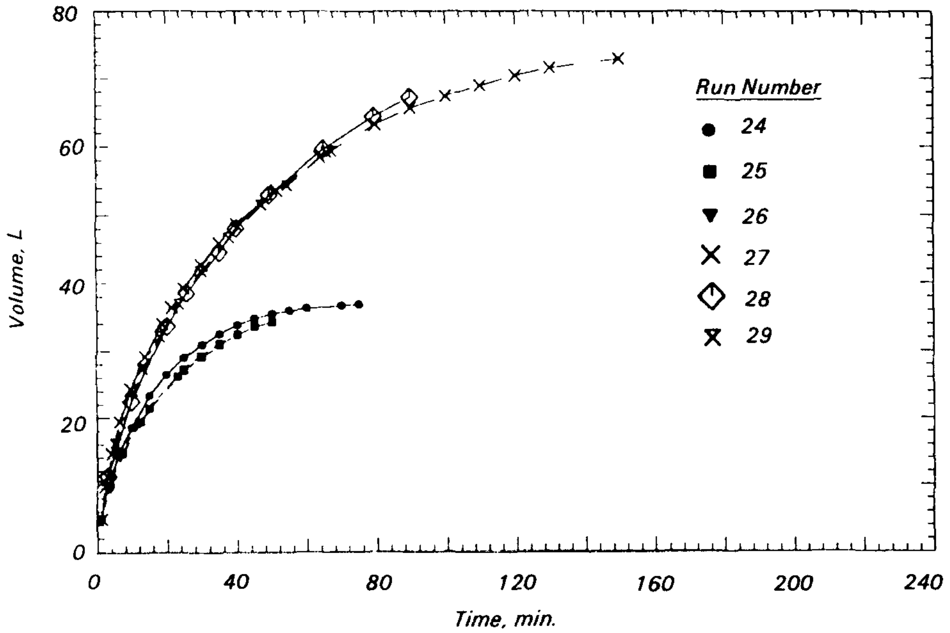

Figure 1. *Cumulative filtrate volume for high-pressure (14 to 15 bar) dewatering of CN sludges.*

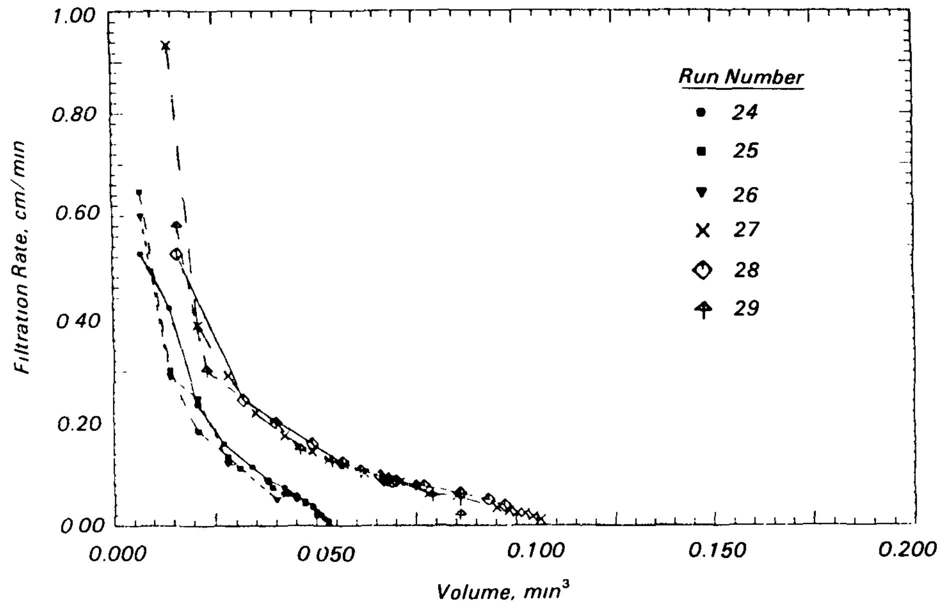

Figure 2. *Filtration rate for high pressure dewatering of CN sludges and projection of ultimate filtrate volume produced.*

Data in Table 6 indicate that 89% to 109% of the aluminum placed in the reactors was accounted for in the studies conducted. In addition, the data indicate that, for all but the ER cakes, 93% to 100% of the aluminum was extracted and appeared in the soluble form as aluminum sulfate. Those instances in which the percentage extracted was low (i.e., 93%) were attributable to extractions in which acid addition was less than the stoichiometric amount.

For ER cakes, the level of aluminum extracted ranged from 69% to 85%. In some extractions of these cakes, dilution water (required because of the high solids content of these sludges) was withheld until later portions of the extraction. This produced an elevated acid strength in the initial extraction phase, and a higher level of aluminum extraction (i.e., 81% to 85%), as compared to those in which the additional water was added prior to acid addition and lower portions were extracted (i.e., 68% to 69%).

The trace metal content of liquid alum produced with CN-2, SN-1, and ER-1, sludge cakes compared favorably with commercial products. Data in Table 7 indicated that concentrations of cadmium, chromium, iron, silver, and zinc in alum produced from aluminum-anodizing cakes compared favorably with those contained in commercial alum products obtained from, and used at, two large municipal water treatment plants. The concentrations of lead were moderately higher than those in the commercial products.

Concentrations of nickel and tin in alum produced from a conventional sludge (CN-2) were significantly higher than those in the commercial products. This was attributed to the nickel and tin used in the two-step anodizing process at the plant. Nickel and tin concentrations in the alum produced from SN and ER cakes were well below the concentrations contained in the commercial products. Therefore, with the exception of nickel and tin originating from a two-step anodizing system, the levels of trace metals contained in the alum produced from aluminum-anodizing sludges were similar to those contained in commercial

Table 3. *Predicted Cake Solids Concentrations for Filter-Press Dewatering of CN Suspensions from Plant A*

Range of Suspended Solids	*Predicated Cake Solids Concentration*	
g/L	$(C_k)_{ULT}$, %	$(C_k)_{09}$, %
High pressure (14 to 15 bar)		
21-73*	27-29	25-26
Low pressure (6 to 7 bar)		
17-61+	22-25	21-23

**Results for a total of 15 runs.*
+Results for a total of 13 runs.

Table 4. *Predicted Cake Solids Concentration for High-Pressure Filter-Press Dewatering of Blends of SN and CN Suspension*

SN Suspension in Blend of SN-1 and CN-2 Suspensions	*Suspended Solids*	*Predicted Cake Solids Concentration*	
% (by volume)	*g/L*	$(C_k)_{ULT}$, %	$(C_k)_{09}$, %
0	38	29	27
5	47	33	31
15	60	37	34
30	78	39	37
100	180	51	49

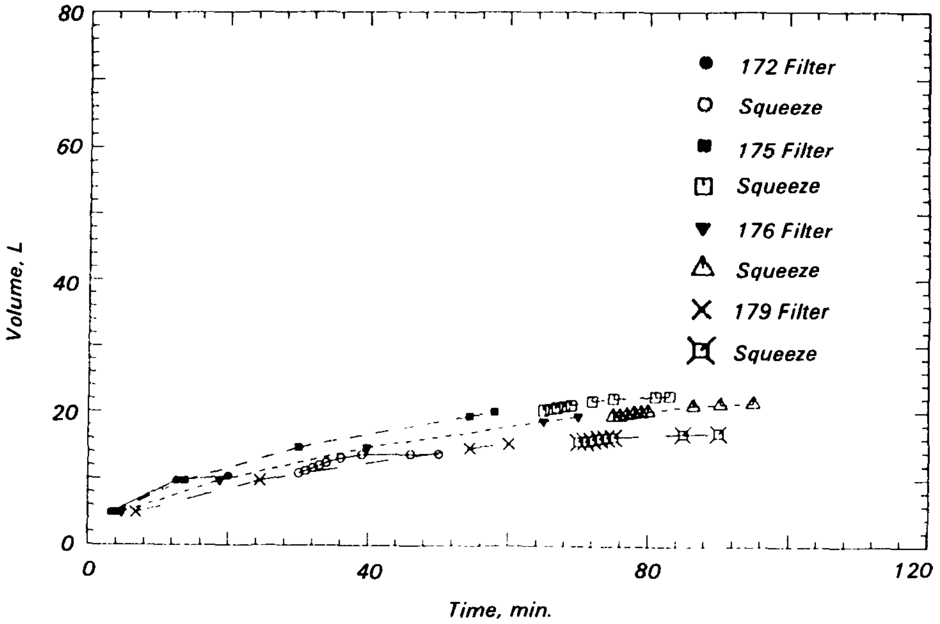

Figure 3. *Cumulative filtrate volume for filter and squeeze portions of diaphragm filter press dewatering of CN sludges.*

alum, indicating the potential utility of the alum for use in coagulation of drinking waters. However, since less than 10% of commercial alum is actually used in the treatment of drinking water, it is apparent that the alum products produced from aluminum-anodizing sludges can be marketed for non-potable-water uses in industry.

Conclusions

Research was conducted on filter-press dewatering followed by reclamation of three types of aluminum-anodizing sludges as commercial-strength liquid alum. Numerous conclusions were drawn from the study.

Pressure filtration studies were conducted with two pilot-scale, fixed-volume, recessed-chamber filter presses at low (6 to 7 bar) and high (14 to 15 bar) pressures. The solids content of dewatered sludge cakes at the ultimate completion of a filter press run were projected from filtration rate data. CN suspensions had ultimate cake solids contents of 22% to 25% and 27% to 29%, respectively, at low (6 to 7 bar) and high (14 to 15 bar) pressures for suspensions with suspended solids concentrations of 17 to 73 g/L.

SN suspensions could be effectively dewatered separately and resulted in major improvements in the dewatering of CN suspensions when blended with them. At low and high pressures, ultimate cake solids contents of 49% and 51%, respectively, were achieved with SN suspensions. Blends of SN suspensions at 5% to 30% volumetric ratios with CN suspensions resulted in ultimate solids contents of 33% to 39% with high-pressure filtration and 31% to 37% with low-pressure filtration.

A diaphragm press was used effectively to dewater aluminum anodizing suspensions. CN suspensions had final cake solids contents of 25% to 31%, while 5% to 30% volumetric blends of SN suspensions with CN suspensions had solids contents of 31% to 43%.

Commercial-strength solutions of liquid alum can be effectively and rapidly produced with the addition of sulfuric acid. Addition of stoichiometric quantities of acid, based on sludge aluminum content, resulted in virtually complete extraction within 30 to 60 min.

CN sludge cakes with solids contents of 17% to 18% were extracted to produce liquid alum with concentrations of 7.4% to 8.8% as Al_2O_3. A total of 93% to 97% of the aluminum was extracted.

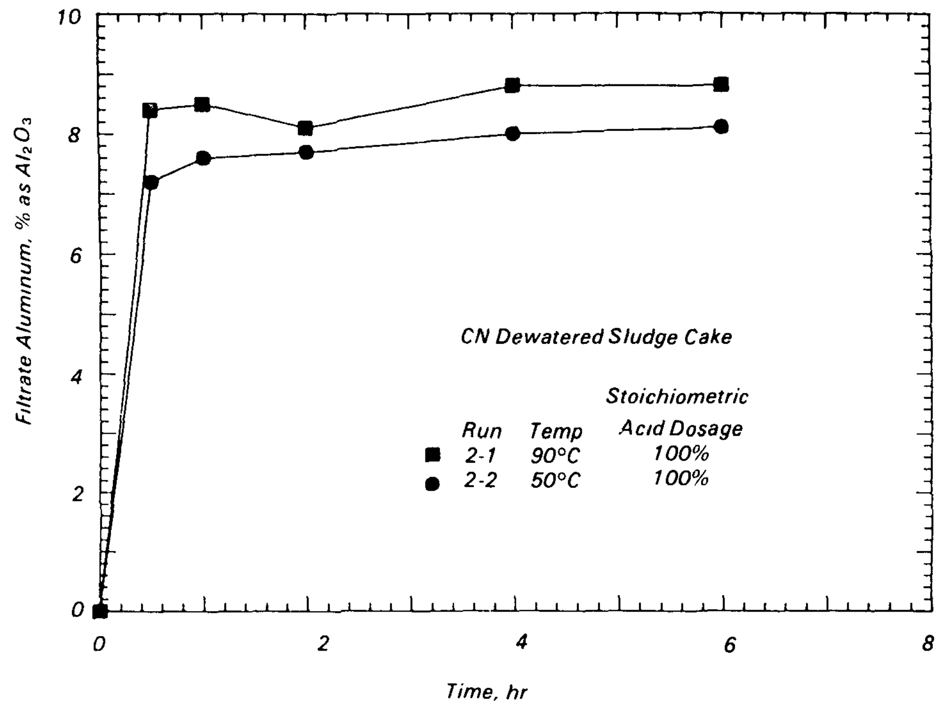

Figure 4. *Filtrate aluminum concentration for sulfuric acid extraction of sludge cake CN-2.*

Table 5. *Characteristics of Aluminum-Anodizing Sludge Cakes Used in Acidic Extraction Studies*

Sludge Cake	*Cake Solids* *Total, %*	 *Fixed, %*	*Aluminum Content g/100g fixed solids*
Conventional Neutralization			
CN-1	*18.1*	*13.3*	*35.6*
CN-2	*17.4*	*13.9*	*39.2*
Segregated Neutralization			
SN-1	*36.8*	*29.9*	*31.0*
Etch Recovery			
ER-1	*91.6*	*66.4*	*43.6*
Blended Cakes			
CN-2 & SN-1	*25.2*	*21.4*	*34.6*
CN-2 & ER-1	*30.2*	*22.5*	*41.3*

SN sludge cakes with solids contents of 36.8% were extracted to produce liquid alum with concentrations of 8.1% to 9.0% as Al_2O_3. An ER sludge with a solids content of 91.6% produced a liquid alum with a concentration of 8.3% to 9.2% Al_2O_3. Acid addition resulted in extraction of 69% to 85% of the aluminum. Addition of SN or ER solids to CN solids increased the aluminum content of the blended sludge and could be effectively extracted to easily produce commercial-strength liquid alum.

The cadmium, chromium, and iron concentrations of liquid alum produced from CN sludges were less than those of commercial alum products, while lead, silver, and zinc concentrations were slightly above those for commercial alum products. The concentrations of nickel and tin were sixfold to seventeenfold higher than those in commercial alum. The high nickel and tin concentrations were attributed to dragout from the two-step anodizing process and to the use of nickel in seal tanks. Segregation of these wastes from plant wastewaters may be needed to eliminate them from the sludges produced for extraction and reclamation.

The full report was submitted in fulfillment of CR110290-01-0 by Georgia Institute of Technology under the sponsorship of the U.S. Environmental Protection Agency.

Table 6. *Material Balance on Aluminum and Alum Product Quality for Acidic Extraction of Sludge Cakes*

Sludge Cake	Reactor Material Balance-Aluminum % Al recovered	Alum Product: Al extracted into soluble form % of total Al	Alum Product: Concentration % as Al_2O_3
Conventional Neutralization			
CN-1	104	93-97	7.4-8.0
CN-2	99	97	8.1-8.8
Segregated Neutralization			
SN-1	100-105	99-100	8.1-9.0
Etch Recovery			
ER-1	89-109	69-85	8.3-9.2
Blends			
CN-2 & SN-1	99	99	8.2
CN-2 & ER-1	102	82	8.8

Table 7. *Metal Content of Liquid-Alum Samples, Produced from CN-2, SN-1, and ER-1 Sludge Cakes, and Two Commercial Alum Products*

	Concentration, mg/L				
	Sludge-Cake Alum			Commercial Alum	
Metal	CN-2	SN-1	ER-1	Plant 1	Plant 2
Cadmium, Cd	0.4	0.3	0.3	0.03	0.3
Chromium, Cr	30.0	4.4	3.7	78	0.9
Iron, Fe	60.0	18.3	21.0	1845	2080
Lead, Pb	20	19	26	6.6	4.1
Nickel, Ni	752	8	7	44	44
Silver, Ag	0.7	0.2	0.08	0.25	0.2
Tin, Sn	914	28	17	155	—
Zinc, An	12	6	7	8.5	8.5

F. Michael Saunders is with Georgia Institute of Technology, Atlanta, GA 30332.
***Thomas J. Powers** is the EPA Project Officer (see below).*

The complete report, entitled "Reclamation of Aluminum Finishing Sludges," (Order No. PB 88-133 566/AS; Cost: $19.95, 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:

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