TREATMENT OF ALUMINUM-FINISHING WASTEWATERS AND SLUDGES

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A comprehensive study of wastewaters and sludges produced in the aluminum finishing industry was conducted. Emphasis was placed on those wastes containing major quantities of aqueous aluminum from painting, etching and anodizing processes at major aluminum finishing plants. Chemical characterization of neutralized wastewaters included measurement of solids, aluminum, organic carbon, alkalinity and priority-pollutant metals.

Wastewaters were examined with respect to thickening, dewatering, gravity draining and polyelectrolyte conditioning treatment processes. Polyelectrolyte-conditioning was shown to be required for settling and thickening of aluminum-finishing sludges. Improvements in dewatering and gravity draining properties with polyelectrolyte conditioning are presented. The impact of high-temperature neutralization on sludge properties is discussed.

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Introduction

The use of aluminum in the building and construction, transportation, electrical, and container and packaging industries continues to expand as the demand for durable light-weight metal components increases. Over 6.5 x 10^6 Mg (metric ton) of aluminum are currently produced as mill products for domestic consumption in the United States with 23% produced as extruded parts, 42% as sheet, plate and foil, 7% as rod, bar and wire, and 28% as castings, impacts and powder products (1). These mill products are produced in over 600 production facilities using a wide variety of surface treatment and finishing processes.

Aluminum finishing processes include numerous physical and chemical treatments used to improve surface appearance, durability, and adhesion properties. Physical surface treatments, such as buffing, brushing or milling, produce solid wastes and oil-bound suspensions which can be effectively reclaimed or treated. Chemical surface treatments however result in the production of large volumes of wastewaters which are more difficult to treat. Chemical finishing processes conventionally utilized by the aluminum industry include chemical etching, electrochemical etching, painting, chemical milling, dyeing and anodizing. The wastewaters associated with these processes generally consist of large volumes of rinse waters and smaller volumes of chemical spills and spent or contaminated finishing solutions and suspensions. Dissolved aluminum is the primary contaminant in these wastewaters and generally dictates subsequent wastewater treatment systems. These treatment systems conventionally include wastewater neutralization, clarification and sludge dewatering processes.

The objective of the research presented in this study was to examine wastewaters and sludges produced by extrusion/anodizing plants. The wastewaters were specifically to be characterized with respect to chemical characteristics properties and thickening and dewatering properties.

Perspective of Extrusion/Anodizing Industry

Aluminum Finishing

Anodizing is used as a finishing process for extruded architectural and structural aluminum because of the durable, decorative, and corrosion-resistance finish applied. Numerous alloys of aluminum are anodized, depending on surface and structural properties desired. The 6000 series alloys, however, are most typically employed (1). These alloys contain Cr, Cu, Fe, Mg, Mn, Si, Ti and Zn at levels ranging from 0.05 to 2% and may also contain B, Bi and Pb (2). Regardless of specific alloy used within the 6000 series, aluminum content is typically greater than 94% (2).

The use of anodizing to finish aluminum extrusions requires that numerous preliminary finishing steps be employed. These steps are performed in a series of batch tanks into which racks of extruded aluminum materials are sequentially immersed. An initial step is a cleaning step to remove surface grease and oil, as indicated in Table I. A continuous-flow, counter-current rinse typically follows the cleaning step, as well as all other subsequent finishing steps, to remove residual cleaning solution from the aluminum material.

A chemical etch typically follows the cleaning step and is used to remove residual surface oxides prior to anodizing. The chemical etching step is an agressive surface treatment using hot caustic soda and results in a higher removal of aluminum and aluminum-alloy components than all other finishing steps combined. Following immersion in the etch tank, the extruded aluminum surface is covered with a thin film (i.e. a "smut" film) of numerous precipitated alloy metals which are removed in a desmut step. The desmut solution is typically HNO_3 (see Table 1) which dissolves the smut film leaving a bare aluminum surface for anodizing.

Table I. Aluminum Finishing Steps Used In Anodizing (1,3)

Finishing Step	Purpose of Finishing Step	Typical Finishing Tank
Clean	Remove Surface Contaminants	Alkaline Detergents Temp = 40-60°C
Etch	Remove Surface Oxides	Caustic Soda = 2-10% Sequestrant = 0.5-5% Temp = 40-60°C
Desmut	Remove Smudge Film	Nitric Acid = 5-30%
Bright Dip	Enhance Luster (Optional)	Phosphoric Acid = 70-80% Nitric Acid = 3% Copper = 0.1% Ammonia = 0.1%
Anodize	Provide Protective and Decorative Surface Coat	Clear Coat -H_2SO_4: Sulfuric Acid = 15-20% Temp = 20-30°C Hard Coat -H_2SO_4: Sulfuric Acid = 0.3-0.5% Organic Acids = 0.5-15% Temp = 15-25°C
Dye	Apply Surface Color (Optional)	Proprietary Dyes
Seal	Form Aluminum-Oxide-Mono-Hydrate to Seal Surface Oxide	Nickel Acetate = 0.1-0.5% pH = 5-6.5 Temp = 40-60°C

Numerous anodizing processes are available for use depending upon the surface quality, durability and appearance desired (3). Two anodizing finishes are, however, typically utilized in the anodizing of architectural and structural aluminum materials. These are clear-coat sulfuric acid anodizing and hard-coat sulfuric acid anodizing. Clear-coat finishes are clear, durable, matte finishes which do not change the color of aluminum. Clear-coat anodizing is performed in 15 to 20% H_2SO_4 with the extruded aluminum material serving as the anode during the passage of current through the tank. A hard-coat finish is bronze to black in color and is applied in a manner similar to clear-coat anodizing using lower concentrations of H_2SO_4 and in the presence of one or more of organic acids (e.g. oxalic acid, sulfophthallic acid, sulfanilic acid). Acid dissolution of aluminum occurs during clear-coat anodizing to levels of 10-20 g/l (3). However, aluminum levels greater than 0.6 to 1 g/l have a negative impact on hard-coat finishes and aluminum must be continuously removed from the anodizing solution with an in-line cation exchange resin.

Following rinsing, anodized aluminum is sealed using a hot-water solution or with a dilute solution of nickel acetate. As indicated in Table I, two optional finishing steps may also be used in the process of anodizing aluminum materials. A bright-dip process is used to improve metal luster while a dyeing step is used to color the anodized aluminum surface.

Treatment of Aluminum Finishing Wastewaters

Wastewaters from aluminum finishing processes contain a variety of inorganic and organic contaminants originating in finishing chemicals and contaminants from the aluminum alloys being treated. These contaminants are discharged to a wastewater collection system in rinse water discharges and dragout and spills of finishing solutions. Spent finishing solutions and blowdown from finishing processes constitute a major source of the total mass of discharged wastewater contaminants, especially aluminum.

Wastewater Characteristics. Water consumption rates for aluminum extrusion/anodizing plants are high for metal finishing industries, e.g. 25-70 m^3/kg aluminum finished (4). High water use rates are, in part due to heavy liquid films dragged out of viscous process tanks, such as alkaline etch tanks, and the resulting need for large volumes of water to remove these films. Racking techniques for aluminum products being finished, in addition, add to increased water use. Extruded aluminum parts are frequently long, thin sections which are densely racked. Sagging of thin aluminum strips is minimized with supports but is not eliminated. Aluminum parts must also be placed on racks to minimize gas pocketing. Both of these racking procedures result in increased dragout of finishing solutions, increasing rinse water requirements.

High dragout rates result in high levels of waste aluminum and other contaminants in rinse water effluents. The high levels of aluminum (1-75 g/l) contained in spent etch and anodize wastes, which are frequently used to neutralize combined plant wastewaters, contribute significantly to wastewater aluminum content. A survey of aluminum finishing plants indicated that 0.9 to 2.4% of the mass of aluminum extruded and finished in extrusion/anodizing plants was dissolved and discharged to waste (1).

Wastewater Treatment Systems. In conjunction with the research presented herein, The Aluminum Association, Inc. conducted a survey of 37 industrial aluminum finishing plants, of which 22 were extrusion/anodizing plants (1). The results of the survey indicated that the conventional flow scheme for treatment of combined rinsewaters, concentrated spills and spent process solutions and suspensions typically included (i) pH neutralization and precipitation of aluminum, (ii) coagulant (polyelectrolyte) addition and (iii) gravity clarification. Clarified effluents are typically discharged to a receiving stream or domestic sewerage system.

Regarding sludge treatment and disposal systems, the average sludge (dry solids) production rate for the 22 plants was 1.6 Mg/d, with a range of values of 1.4×10^{-2} to 5.8 Mg/d. Half of the plants disposed of suspended solids collected during gravity sedimentation without further treatment. Gravity clarifier underflow suspensions had an average suspended solids concentration of 22 g/l with a range of 0.1 to 50 g/l.

Of the plants using sludge dewatering systems, vacuum and pressure filtration and sand drying beds were used predominantly, although a belt filter and a centrifuge were used at two plants. Solids content for mechanically dewatered sludge solids ranged from 1-20% (dry solids) and averaged 16.5%. Disposal of thickened and dewatered sludges included (i) placement in domestic and segregated landfill sites, (ii) discharge to lagoons, (iii) blending with soil and, (iv) stockpiling on plant site for subsequent recovery.

A primary concern of the majority of the industries was the increasing difficulty associated with disposal of the typically gelatinous aluminum hydroxide sludges with low solids content. To bring aluminum sludge disposal into proper perspective, if aluminum is assumed to be the primary metallic component of an anodizing wastewater sludge and it is precipitated as $Al(OH)_3$, a dewatered sludge at 16.5% dry solids content (i.e., the average survey value (1)) represents 16.9 kg of wet sludge for each kg of aluminum precipitated. Furthermore, if 0.9 to 2.4% of the aluminum finished is dissolved during finishing (1), a typical extruxion/anodizing plant will generate 0.15 to 0.4 kg of wet dewatered sludge for each kg of aluminum finished. If dewatered solids content is less than 16.5%, the quantity of dewatered sludge available for disposal will approach anodizing production levels. The extrusion/anodize industry is therefore faced with the disposal of a waste sludge which may equal 40% of the mass of its finished extruded product.

The research reported herein is initial research focused on this sludge disposal problem. The primary objective of the initial work was to chemically characterize extrusion-anodizing wastewaters and to establish baseline data with regard to sludge thickening and dewatering properties.

Experimental Methods and Materials

Participating Plants

To examine actual anodizing wastewater suspensions and sludges, three extrusion/anodizing plants were identified for participation in the project in conjunction with The Aluminum Association, Inc. The three plants were designated A1, A2 and A3 and are all located in the southern region of the United States. As indicated in Table II, a variety of finishing processes were employed at the plants. At plant A1, slightly more than half of the total aluminum production is anodized using clear- and hard-coat finishes and the associated finishing processes of dyeing and bright dipping. The remaining portion of the aluminum production is painted. Painting wastewaters are treated for chromate reduction and combined with anodizing wastewaters for subsequent neutralization, gravity sedimentation and discharge. Plants A2 and A3 do not paint aluminum but use anodizing as the primary surface finishing process. Both plant A2 and A3 use clear-coat anodizing while plant A3 also uses a hard-coat anodizing process.

Wastewater Sampling Procedures

Grab samples of wastewater were collected in volumes of 0.4-1.2 m^3 at plant sites during periods of typical plant operation by plant personnel and shipped directly to the laboratory for analysis. The wastewaters were collected following neutralization, immediately prior to the addition of polyelectrolyte conditioners, and placed in lined 0.2-m^3 barrels for direct shipment. Shipments from the individual plants were staggered to allow for immediate analysis of each wastewater upon receipt. Control testing procedures were utilized to assure that wastewater characteristics remained constant during the period of laboratory analysis (1).

Table II. Participating Extrusion/Anodize Plants

Plant	Al Production Rate	Finishing Processes	Waste Treatment Processes
A1	9×10^5 kg/mo	Anodize: Hard Clear Dyeing Bright Dip Painting: Conversion-Coating	Wastewater Chromate Reduction Lime Precipitation Neutralization Sedimentation Sludge: Lagoon
A2	3.6×10^5 kg/mo	Anodize: Clear Dyeing Bright Dip	Wastewater: Neutralization Sedimentation Sludge: Vacuum Filtration Landfill
A3	6.8×10^5 kg/mo	Anodize: Clear Hard	Wastewater: Neutralization Sedimentation Sludge Pressure Filtration Land

Chemical Characterization

Immediately upon receipt of a wastewater, representative samples were collected and immediately analyzed for pH, temperature, total, dissolved and suspended solids, filtrable and total alkalinity, filtrable and non-filtrable aluminum and filtrable inorganic (SIC) and organic (SOC) carbon. Samples, in addition, were collected and prepared for detailed metal analysis for major and trace metals. Procedures for sample preservation, metal analysis, as well as for the above conventional analyses were as presented in Standard Methods (5).

Thickening and Dewatering Procedures

Thickening data were collected in 6-cm stirred cylinders at an initial sludge depth of 36 cm (1). A stirrer rotational speed of 1 rpm was used in all experiments. Data were also collected in 9- and 15-cm stirred cylinders at initial sludge depths of 36 and 100 cm. Sludge dewatering characteristics were determined using specific resistance measurements. Standard procedures using a vacuum-assisted Buchner funnel apparatus were followed (6).

Sludge drainability studies were conducted on conditioned and unconditioned sludges using eight acrylic sand beds. The diameter of the cylindrical beds was 8.9 cm and each bed contained layers of gravel and sand (1). Drainable water was collected and measured in cylindrical columns connected to the beds by vinyl tubing. A 1-liter volume of sludge was routinely applied to the sand beds and filtrate volume was recorded with time. The beds and filtrate collection cylinders were covered and interconnected with vinyl tubing to minimize evaporational losses.

Sludge Conditioning. Polyelectrolyte conditioners were investigated to determine their effects on sludge thickening, dewatering and draining characteristics. Four polyelectrolytes were used, including three polyelectrolytes used at the participating plants and a control polyelectrolyte, as indicated in Table III. All polymers were anionic polyacrylamide polyelectrolytes. Sludge conditioning was routinely performed in a 3.2 liter baffled cylindrical mixing chamber which had a diameter of 12.7 cm (1). A standard sludge volume of 1 liter was mixed in the chamber with a single-blade (2.6 cm x 7.8 cm) stirrer operated at 200 rpm for 60 s. When examining the effects of polymer conditioning on sludge characteristics, both unconditioned and conditioner sludge samples were treated in the above manner, without and with polymer addition, respectively.

Table III. Polyelectrolyte Conditioners

Polyelectrolyte	Charge	Mol. Wt.	Plant
Caraflok 91AP[a]	Anionic	9×10^6	Control
HF-190[b]	Anionic	(Medium)	A1
Purifloc A23[c]	Anionic	$> 10^6$	A3
Separan AP 273[c]	Anionic	3×10^6	A2

a. Carus Chemical Co.; LaSalle IL
b. Amchem Products Inc.; Ambler PA
c. Dow Chemical Co.; Midland MI

Results

Wastewater Chemical Characteristics

General. The characteristics of wastewater samples collected following neutralization at the plant sites are presented in Table IV. Two samples were collected at plants A2 and A3. The two samples from plant A2 were taken during a period of routine week-day plant operation when only rinse waters and spills were being treated (i.e. sample 242-79) and during a weekend period when finishing operations were not in use (i.e. sample 319-79). During this latter period, only spent finishing solutions and suspensions (e.g. spent etch and spent anodize solutions) were being discharged to the treatment system. All other samples were taken during week-day periods when routine finishing operations were in use since neither plant A1 or A3 used a segregated treatment scheme similar to that at plant A2.

Table IV. Characteristics of Anodizing Aluminum Wastewaters from Neutralization Basin Effluents

Plant	A1	A2		A3	
Sample Identification	21-80	242-79	319-79	161-79	201-79
Solids					
Total, g/l	9.04	1.72	108.6	9.78	7.23
Volatility, %	15.6	14.5	12.4	-	10.9
Suspended, g/l	3.21	0.41	57.26	4.35	1.84
Volatility, %	25.5	28.9	16.1	-	21.7
Dissolved, g/l	6.04	1.34	52.43	5.43	5.39
Volatility, %	10.3	12.7	8.0	-	7.2
pH	7.0	8.0	7.0	7.2	10.5
Alkalinity, mg $CaCO_3$/l					
Total	311	159	2800	535	1134
Filtrable	75	74	120	54	78
Aluminum					
Filtrable, mg/l	0.4	3.9	2.5		118
Non-Filtrable, mg/l	950	116.1	15,600		862
Non-Filtrable, g/kgISS*	397	398	324		598
Carbon					
SOC, mg/l	15.7	4	81.5		93
SIC, mg/l	11.8	19	0		

*ISS = Inert Suspended Solids

As indicated in Table IV, the wastewater samples were neutral or slightly alkaline in pH except sample A3-201-79 which had a pH of 10.5. Filtrable alkalinity values were typically low indicating that most of the suspension alkalinity was due to the precipitated aluminum solids. Suspended solids ranged from 1.84 to 4.35 g/l for plants A1 and A3. While the dilute rinse wastewater at plant A2 (i.e., A2-242-79) contained a low level of suspended solids, the wastewater resulting from treatment of concentrated finishing solutions (i.e., A2-319-79) contained an extremely high level of suspended solids due to the treatment of high levels of aluminum contained in spent finishing solution. Total dissolved solids varied from 1.34 to 6.04 g/l for all samples, except sample A2-319-79 which contained 52.43 g/l.

Filtrable aluminum concentrations were low for suspensions at or near neutral pH and the majority of wastewater aluminum was in suspension as expected from aluminum solubility data (7). The inert suspended solids in the wastewater suspensions at or near neutral pH contained 32-40% aluminum. These values were in agreement with the theoretical composition of precipitated aluminum hydroxide ($Al(OH)_3$), i.e., 34.6% aluminum. The sludge sample at an elevated pH value, i.e., A3-201-79, contained 59.8% aluminum based on inert suspended solids and the chemical form was apparently altered from that of $Al(OH)_3$.

Trace Metal Composition. The neutralized wastewater samples were examined with respect to toxic metals. Thirteen priority-pollutant metals, as identified by the U. S. Environmental Protection Agency, were chosen as the metals of concern and were silver, Ag; arsenic, As; beryllium, Be; cadmium, Cd; chromium, Cr; copper, Cu; mercury, Hg; nickel, Ni; lead, Pb; antimony, Sb; selenium, Se; thallium, Ti; and zinc, Zn. Metals examined included those used to examine the toxicity of sludges in the EPA Extraction Procedure (8), i.e. Ag, As, Cd, Cr, Hg, Pb and Se.

Metal distribution in dewatered sludges was examined by analysis of total and dissolved metals following acid digestion (1) and are presented in Table V as dissolved and suspended metal concentrations. The metal antimony (Sb) and thallium (Ti) were not detected in any sludge samples and were not included in the table.

Table V. Trace Metal Composition of Neutralized Wastewaters at Plants A1, A2 and A3.

Plant	A1		A2		A3	
	Dissolved µg/l	Suspended mg/kg	Dissolved µg/l	Suspended mg/kg	Dissolved µg/l	Suspended mg/kg
Metals						
Ag, Silver	-	-	49	1.6	-	-
As, Arsenic	18	<3	160	<3	54	3
Be, Beryllium	-	-	1.7	0.2	-	-
Cd, Cadmium	5.6	15	1.2	0.9	0.8	1.2
Cr, Chromium	1500	2600	180	21	9	89
Cu, Copper	25	140	130	35	48	23
Hg, Mercury	-	-	28	<0.1	-	-
Ni, Nickel	78	115	74	64	260	2200
Pb, Lead	1.4	19	24	24	1	10
Se, Selenium	130	<1	1700	1	38	<1
Zn, Zinc	1500	3000	1400	<26	70	120

For plant A1, chromium (1500 µg/l) and zinc (1500 µg/l) were the major dissolved metals detected. The source of the chromium was attributed to dichromates contained in paint-line wastewaters which were discharged with anodizing wastes to a common neutralization facility at plant A1. Although dissolved chromium and zinc levels were relatively high, 99.4% of each was contained in the suspended form in a dewatered sludge with a solids content of 8.3%, indicating a high degree of metal precipitation. In addition, with the exception of selenium (42%), more than approximately 96% of all metals were contained in the suspended form of the sludge.

Significant quantities of dissolved selenium (1700 μg/l) were detected in plant A2 sludge and the selenium may have been attributable to a dyeing line at the plant. The majority of the selenium was contained in the dissolved form (i.e. 87.3%) and was therefore ineffectively removed with the thickened sludge following neutralization and precipitation. With the exception of mercury (49.5%), from 82% to 99% of the metals detected were contained in the suspended form in the wet sludge containing 19.8% solids.

Dissolved metals in plant A3 sludge were relatively low with nickel being the major trace metal and other metals being at or below 70 μg/l. With the exception of selenium (78%), the majority (89% to 99.9%) of the metals were in the suspended form.

In summary, most of the heavy metals in the aliminum-finishing sludges examined were present in the suspended solids and not dissolved in interstital water. The major trace metals contained in the suspended form of all sludges were Cr, Cu, Ni, Pb, and Zn. Only sludge from plant A2 contained Hg, which was mostly in the dissolved form. In addition to Sb and Ti which were not detected in any samples, Ag, Be, and Hg could virtually be neglected because they were only detected in sludge from plant A2 in very low concentrations. While As, Cd, and Se were in all sludge samples, the amounts present were also low. Sludges from plants A2 and A3 had 20-fold less Cr than sludge from plant A1 while plant A3 sludge contained approximately 20 to 35-fold more Ni than other sludges. Finally an overall assessment of sludge metal content indicated that all trace metals constituted a very small portion of the total sludge suspensions.

Sludge Thickening

Control settling tests were conducted to determine the effects of settling column diameter (6-15 cm) and sludge height (36-100 cm) on zone settling velocity data. As indicated in Figure 1, variations in zone settling velocity data for a single sludge at various column diameters and initial sludge heights were minimal. All subsequent zone settling data were therefore collected in 6-cm diameter cylinders with an initial sludge height of 35 cm.

Unconditioned Wastewaters. Zone settling data for anodizing wastewaters with neutral or near-neutral pH values are presented in Figure 2. The data for all suspensions, except A2-319-79, were very similar. Data for the wastewater from plant A1 and the dilute rinse wastewater from A2 (i.e., A2-21-80) were virtually identical while those for plant A3 were slightly higher.

A major difference in settling characteristics was apparent for the two wastewaters collected at plant A2. At similar suspended solids concentrations, the wastewater suspension resulting from neutralization of concentrated spent finishing solutions and suspensions (i.e., A2-319-79) settled more effectively than did that collected following routine neutralization of dilute plant rinse waters (i.e., A2-242-79). The differences in settling velocities for plant A2 sludges were between one and three orders of magnitude, over the range of similar suspended solids concentrations. Neutralization of concentrated finishing solutions containing strong acids and bases as done at plant A2, would appear to result in the production of a suspension with greatly improved thickening properties.

Conditioned Wastewaters. Anionic polyelectrolytes typically used at plants A1, A2 and A3 were used to determine the effects of polyelectrolyte

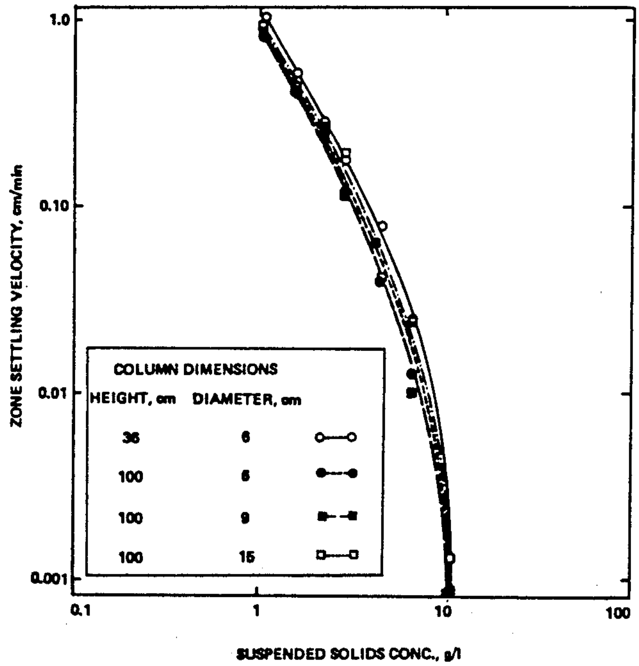

Figure 1. Effects of Column Height and Diameter on Zone Settling Velocity

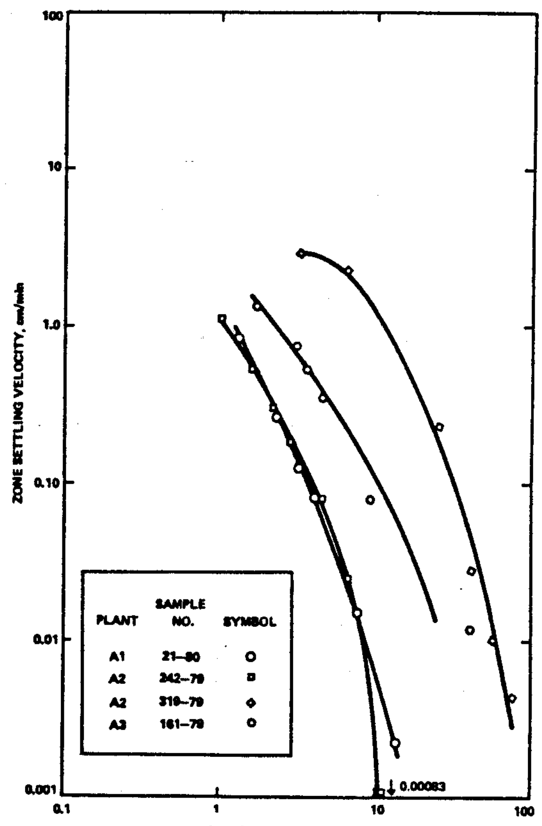

Figure 2. Settling Properties of Unconditioned Aluminum-Finishing Sludges

conditioning on suspension thickening characteristics. To determine an appropriate polyelectrolyte dose, a series of suspension samples was dosed with increasing levels of the selected polyelectrolyte and examined to determine sludge settling velocity. As indicated in Figure 3, increasing levels of polyelectrolyte initially resulted in a significant increase in sludge settling velocity followed by a decrease. Increased polyelectrolyte addition and resulting agglomeration of sludge particles, in addition to improvement in sludge settling characteristics, frequently resulted in a transition from true zone settling to hindered flocculent settling behavior. Since the prime objective was to monitor effects of polyelectrolyte addition on wastewater thickening and not clarification characteristics, a polyelectrolyte dose resulting in the highest zone settling velocity for a suspension was selected for further testing. Therefore, from the data in Figure 4, it is apparent that a polyelectrolyte of 10 mg/l resulted in the most improved settling characteristics, for the sludge examined. This dose was then normalized using the suspended solids concentration of the suspension being tested to a polyelectrolyte dose rate for use in subsequent testing with a broad range of suspended solids concentrations. Similar data were collected for each wastewater.

Polyelectrolyte conditioning data are presented in Figure 4 for all plants. When compared with data presented in Figure 2, it is readily apparent that conditioning resulted in significant improvements in all wastewater samples examined. This is more graphically apparent in Figures 5 and 6 where data for samples A1-21-80 and A3-161-79 are presented, respectively.

To determine if significant variations occurred in the conditioning response of the polyelectrolytes, wastewater suspensions were conditioned with each polyelectrolyte to determine the most effective application rate. Settling data were then collected using each polyelectrolyte with samples of a single wastewater suspension. Data for the A2-242-79 wastewater sample from plant A2 are presented in Figure 7. As previously indicated in Figures 2 and 4 and also shown in Figure 7, polyelectrolyte conditioning of the wastewater from plant A2 resulted in significant improvements in wastewater thickening characteristics. Secondly, it is apparent from Figure 7 that there were no significant differences in the extent of improvement provided by the three polyelectrolytes examined.

Dewatering Properties

Anodizing wastewater samples from plants A1, A2 and A3 were examined to determine their dewatering properties with and without polyelectrolyte conditioning.

Unconditioned Suspensions. The dewatering characteristics of anodizing wastewaters were determined using specific resistance values, as indicated in Table VI. To compare dewatering characteristics, specific resistance data for a suspended solids concentration of 10 g/l, a commonly achieved concentration for gravity thickened sludges, are presented. Significant variations occurred with specific resistance values ranging from 3.6×10^{11} to 4.1×10^{12} m/kg at a suspended solids concentration of 10 g/l. The sludges from plant A2 were both the most difficult (i.e., A2-283-79) and the easiest (i.e. A2-319-79) sludges to dewater, based on specific resistance values. The sludge produced by neutralization of concentrated finishing solutions and suspensions (i.e. A2-319-79), in addition to having improved thickening characteristics over all other anodizing wastewaters, was apparently one of the easiest sludges to dewater. It should be noted, however, that the unconditioned sludge from plant A3 (i.e. 161-79) had specific resistance values which

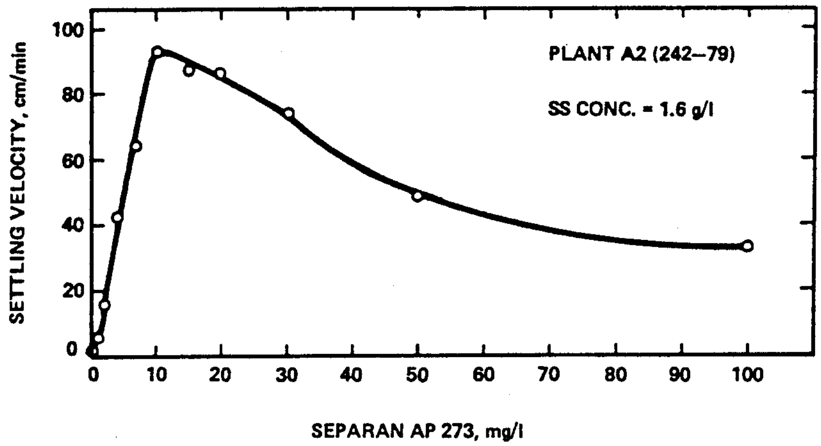

Figure 3. Optimum Polyelectrolyte Dose Determination for Settling of Sludge Sample A2-242-79

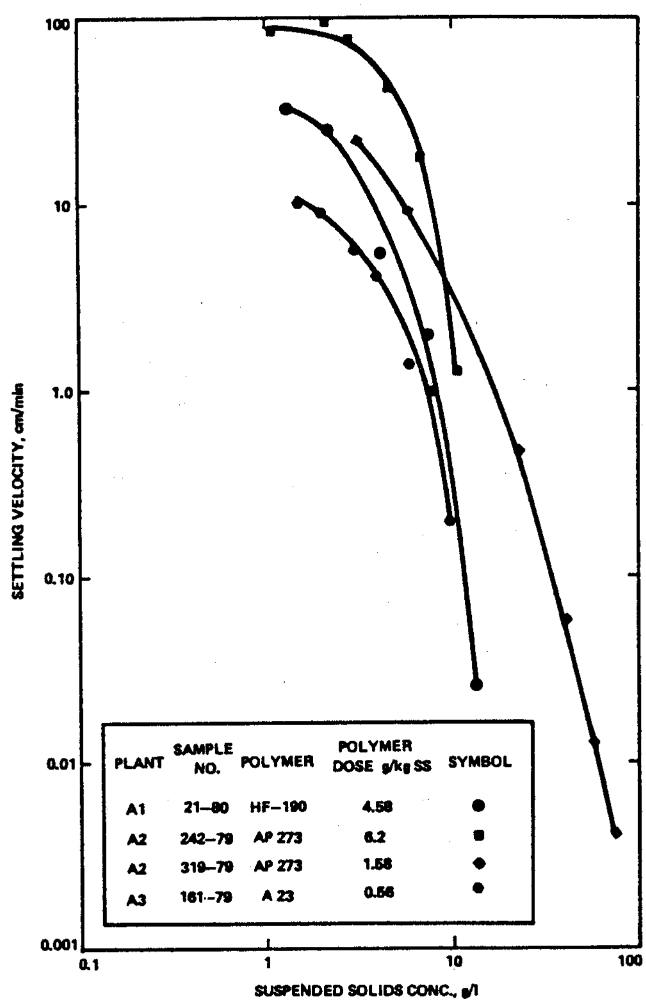

Figure 4. Settling Properties of Conditioned Aluminum-Finishing Sludges

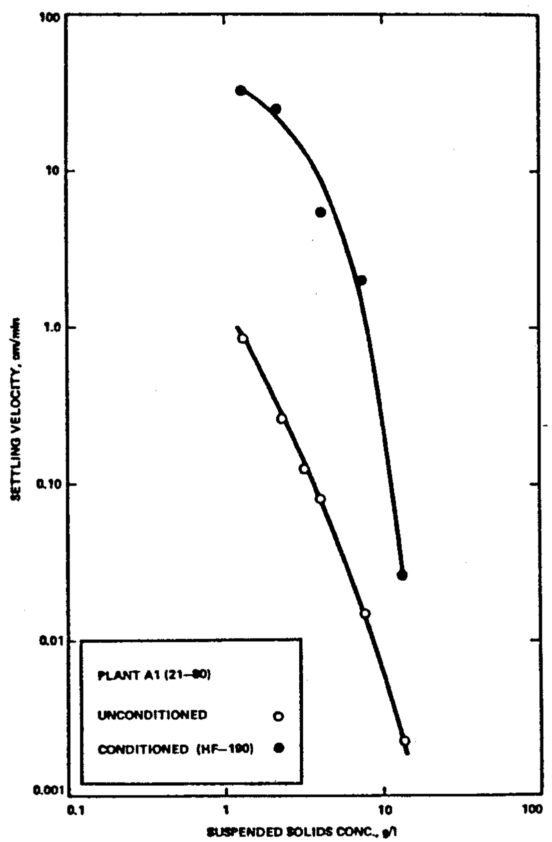

Figure 5. Effect of Polyelectrolyte Conditioning on Settling Properties (A1-21-80)

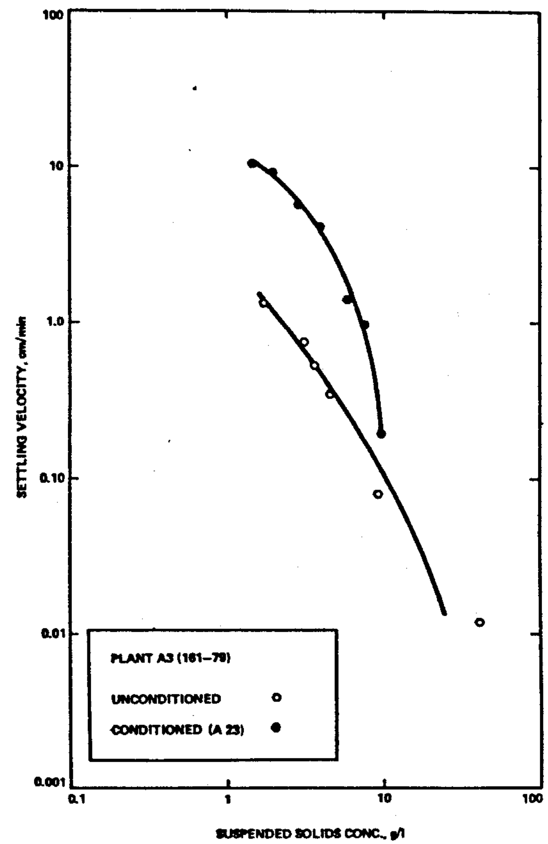

Figure 6. Effect of Polyelectrolyte Conditioning on Settling Properties (A3-161-79)

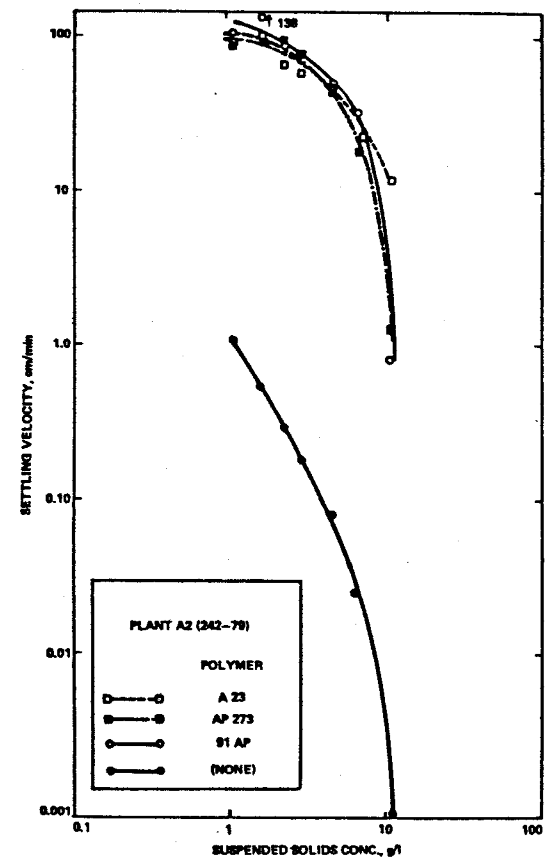

Figure 7. Effect of Polyelectrolytes on Settling Properties (A2-242-79)

were similar to those for the concentrated A2 wastewater sample (i.e. A2-319-79).

Table VI. Specific Resistance, r, of Unconditioned Aluminum Sludges

Plant	r Specific Resist. (at SS = 10 g/l) 10^{11} m/kg	SS Range g/l	r Specific Resist. Range 10^{11} m/kg
A1	19.2	1.3-13.3	20.7-26.9
A2 (283)	41.0	1.3-16.4	41. -52.
A2 (319)	3.6	3.3-79.7	1.8- 4.1
A3	3.8	3.4-36.1	2.8-3.5

Conditioned Suspensions. To determine the effects of conditioning on sludge dewatering characteristics, a series of sludge samples was dosed with increasing levels of polyelectrolyte and specific resistance values were determined. Typical results presented in Figure 8 indicate an effective polyelectrolyte (Separan AP 273) dose of 4.8 g/kg SS. Specific resistance values were then determined for a range of suspended solids concentrations using the predetermined effective polyelectrolyte dose. Data presented in Table VII indicate the effective polyelectrolyte doses and the associated specific resistance values for the suspended solids concentrations of the three anodizing sludges.

Table VII. Polymer Conditioning of Aluminum-Finishing Sludges: Specific Resistance and Dewatered Cake Solids

Plant	Polymer		Sludge	Specific Resist.		Cake Solids	
	Type	Dose g/kgSS	Conc. g/l	Uncond. 10^{11} m/kg	Cond. 10^{11} m/kg	Uncond. %	Cond. %
A1	HF-190	4.58	3.3	22.2	3.1	9.4	9.0
A1	91-AP	4.58	3.3	22.2	1.7	9.4	9.1
A2 (283)	AP-273	4.8	6.3	42.0	0.9	7.6	8.1
A2 (319)	AP-273	1.05	9.5	3.0	1.2	19.1	17.2
A3	A 23	0.76	10.5	3.6	2.6	8.2	6.9

Polyelectrolyte conditioning resulted in improved sludge dewatering characteristics for all sludges. The improvement, however, varied with

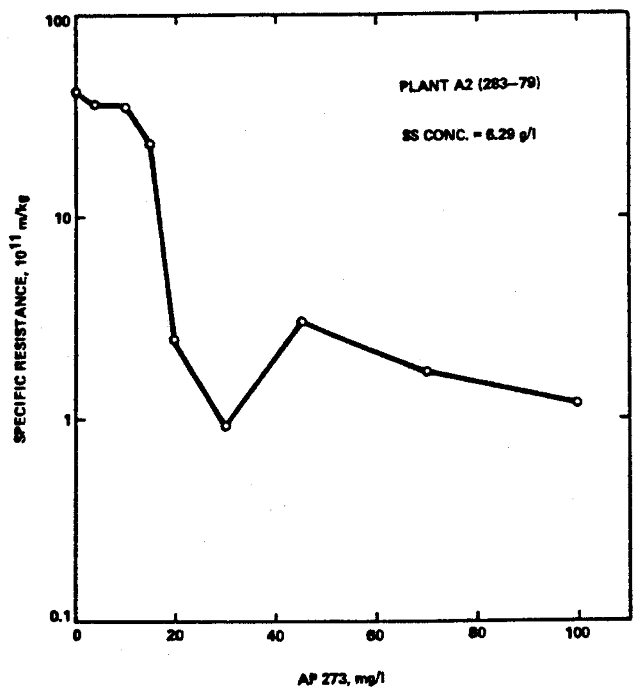

Figure 8. Optimum Polyelectrolyte Determination for Dewatering of Sample A2-283-79

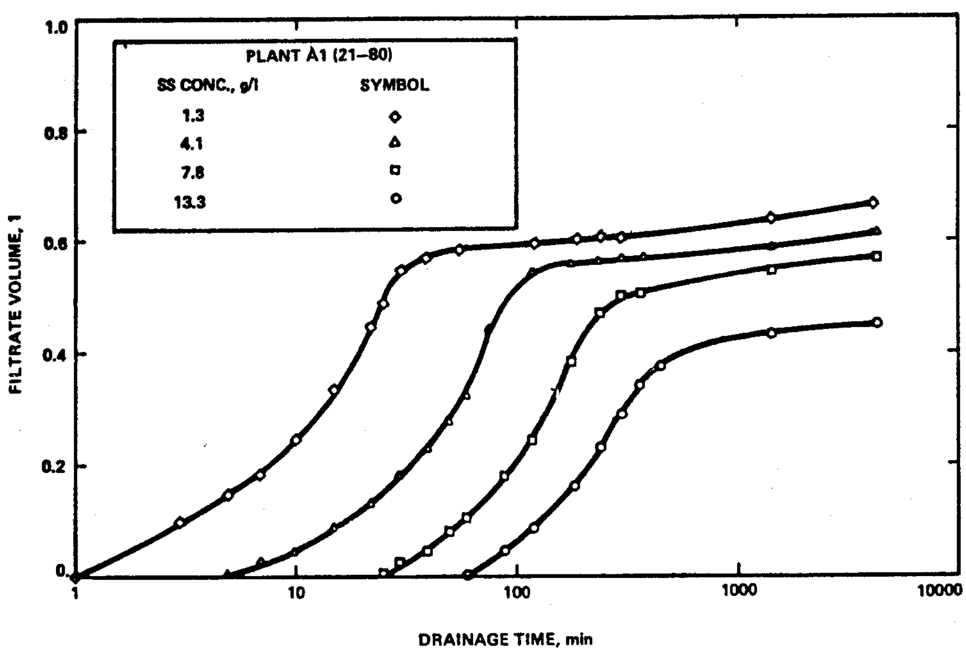

Figure 9. Gravity Drainage Properties for Sample A1-21-80

sludges. Specific resistance values for sludges which had the better dewatering properties prior to conditioning (i.e., A2-319-79 and A3-161-79) were reduced by factors of 2.5 and 1.4, respectively. However, the remaining sludges which did not dewater well prior to conditioning, had significantly improved dewatering properties following conditioning. Specific resistance values for these sludges were reduced by factors of 7 to 47 indicating major improvement in dewatering potential when using polyelectrolyte conditioners.

Polyelectrolyte conditioning did, however, not result in any significant improvement in the solids content of the final dewatered cake collected during the specific resistance tests. In all cases but one (i.e., A2-283-79) cake solids content decreased following polyelectrolyte conditioning. This resulted from a slight increase in water retention by the hydrophilic polyelectrolyte or was an anomolous result due to the increased rate of water removal and resulting increased potential for the cake to crack prior to the removal of all free and pore water.

Gravity Drainage Properties

Sludge gravity drainage properties were examined to determine the rate of removal of water on sand drying beds. Small simulated beds were used to examine both unconditioned and conditioned sludges.

Unconditioned Suspensions. Data presented in Figure 9 for sludge from plant A1 indicate typical drainage patterns for the aluminum-finishing sludges examined. An initial slow rate of drainage preceeded a period of rapidly increasing drainage which was followed by an abrupt decrease in drainage rate. As suspended solids concentration increased, less drainage volume was collected for any fixed period of time. However, gravity drainage was typically complete in less than 1000 min (0.7 d). Further drying by solar evaporation, although not evaluated in the studies reported here, would result in the removal of additional quantities of water.

Conditioned Suspensions. To determine the effects of polyelectrolytes on gravity drainage properties, suspensions were conditioned with varying levels of polyelectrolyte and allowed to gravity drain on clean sand drying beds. The time to achieve 50% of total drainage was used to normalize drainage data for evaluation purposes. Data presented in Figure 10 for a plant A1 suspension were typical of those collected. Although not indicated in Figure 10, the total volume of gravity drainage did not vary with polyelectrolyte dose, however, the rate of drainage was significantly affected. The optimum dose of polyelectrolyte was selected as the lowest dose resulting in the most rapid drainage, e.g. 20 mg/l of HF-190 (Figure 10) at a suspended solids (SS) concentration of 3.3 g/l or 6.06 g/kg SS. This and other similar polyelectrolyte doses were used to examine suspension drainage properties over ranges of suspended solids concentration.

Data presented in Figure 11 indicate the effects of two polyelectrolytes on the drainage properties of the suspension from plant A1. It is apparent that polyelectrolyte addition resulted in significant improvements in the rate of drainage. It is also apparent that the extent of improvement varied with suspended solids concentration. Generally the greatest improvement was achieved at or near the suspended solids concentration at which the optimum polyelectrolyte dose rate was evaluated. It was therefore apparent that polyelectrolyte dose varied with suspended solids concentration and should be determined at or near the suspended solids concentration to be applied to a drying bed.

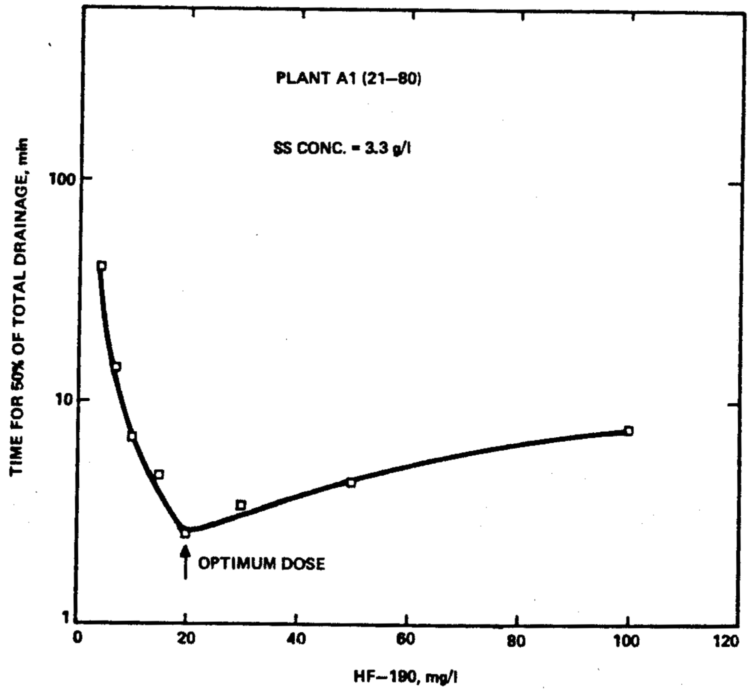

Figure 10. Optimum Polyelectrolyte Dose Determination for Gravity Drainage of Sample A1-21-80

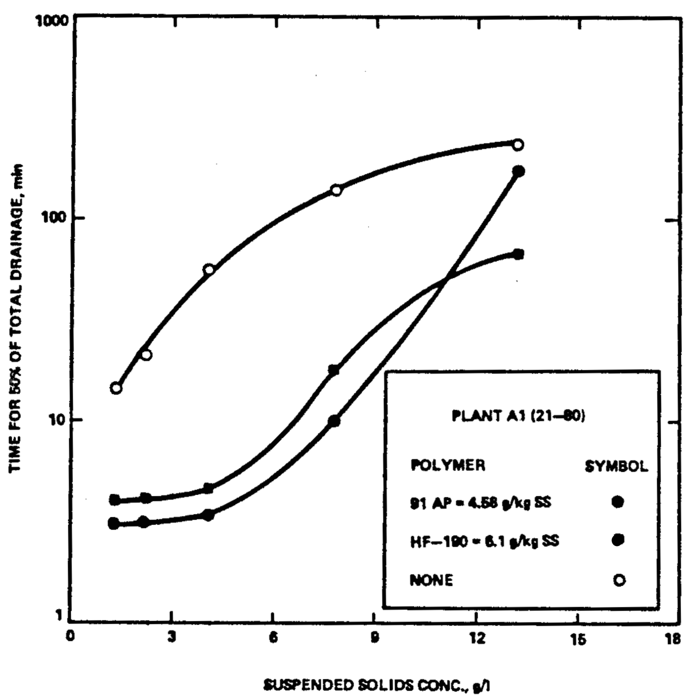

Figure 11. Effect of Polyelectrolyte Conditioning on Gravity Drainage of Sample A1-21-80

Conclusions

Wastewaters generated in the aluminum extrusion/anodizing industry are generated in numerous rinsing and finishing processes which may vary from industry to industry. However, in virtually all cases examined in this research (1), variations in the properties of the conventionally-generated wastewater suspensions were not extensive enough to result in separate classifications for the suspensions.

The sludge suspensions contained aluminum as the primary metallic constituent. Suspended solids data indicated 32 to 60% of the inert suspended solids were aluminum which was generally consistent with a therotical formulation for the sludge of aluminum hydroxide, $Al(OH)_3$. Dissolved solids for conventional suspensions varied from 1.34 to 6.04 g/l indicating a relatively high level of salt addition through use. The majority of the dissolved solids were inorganic constituents since organic carbon levels were typically low, i.e. 4 to 93 mg/l. Of the toxic metals examined, Cr, Se and Zn were the only metals detected in mg/l levels, i.e. 1.4 to 1.7 mg/l. Concentrations of these metals were not, however, consistently high and were detected at much lower concentrations in several samples. The remaining metals (Ag, As, Be, Cd, Cu, Hg, Ni and Pb) were detected in the dissolved form at concentrations less than or equal to 260 μg/l indicating a low composition of toxic metals. Furthermore, the majority of all toxic metals except Se were contained in the suspended form and were effectively fixed in the sludge suspensions following treatment by neutralization at the individual plants.

With respect to sludge treatment, thickening properties of unconditioned suspensions were unacceptable and polyelectrolyte conditioning is a necessary requirement. Polyelectrolyte selection must be performed with consideration of the effect of varying suspended solids concentration on the optimum range of application. Proper application can, however, result in major improvements in sludge thickening properties although thickened sludge concentrations of 1 to 2% solids may be all that can be achieved.

Sludge dewatering properties of aluminum-finishing sludges were generally poor but were typical of other metal-hydroxide sludges (1). Polyelectrolyte-conditioning resulted in improved dewatering properties but the improvements were not as dramatic as those noted for thickening properties. While water was more rapidly removed from the sludge suspensions following polyelectrolyte-conditioning, the extent to which dewatering was achieved was not improved. That is, the solids content of dewatered cakes did not increase following polyelectrolyte conditioning, but in fact decreased slightly. Therefore, polyelectrolyte-conditioning resulted in improved rates of water removal but did not improve the extent to which water was removed.

Dewatering of sludge suspensions by gravity drainage was shown to be an effective treatment alternative. Prediction and control of solar evaporation however are major drawbacks to this mode of dewatering. Polyelectrolyte-conditioning resulted in improved drainage rates but did not increase the extent to which water was removed from the dewatered cake. Optimum polyelectrolyte dose was shown to vary with suspended solids concentration.

With respect to overall characteristics of aluminum-finishing suspensions, the suspension composed of solids generated from neutralization of concentrated spent finishing solutions (i.e. sample A2-319-79) consistently had the best properties with respect to sludge treatment.

Thickening properties of the suspension were superior to the conventional suspensions and specific resistance values were among the lowest for the suspensions examined. Furthermore, cake solids content of unconditioned and conditioned samples of A2-319-79 were as much as 2.5 times those of conventional sludges. These improvements in treatment properties were attributed to the conditions under which the suspension was generated. Discharge of concentrated etch and acid wastewaters at plant A2 to a neutralization basin without the discharge of rinse waters resulted in the production of elevated temperatures. At elevated temperatures the form of the aluminum hydroxide precipitated is much more crystalline-like than the gelatinous precipitates produced at lower temperatures as illustrated in detail by Saunders *et al.* (9) and Medero (10). Therefore, the high-temperature neutralization achieved for convenience of operation at plant A2 resulted in the production of a sludge which could be more effectively treated for disposal.

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