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Characterization, Reclamation and Final Disposal of Aluminum Bearing Sludges

By

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CHARACTERIZATION, RECLAMATION AND FINAL DISPOSAL OF ALUMINUM BEARING SLUDGES

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ABSTRACT

This research project was focused on an investigation of wastewaters and sludge suspensions produced in surface finishing of aluminum mill products. Emphasis was placed on wastewaters containing major quantities of waste aluminum from painting, etching and anodizing processes at major aluminum finishing plants. The overall objective was to document the chemical characteristics of aluminum-finishing wastewaters and develop an extensive data base on conventional wastewater treatment processes for use in design and optimization of these treatment systems by the industry.

An extensive literature review on wastewater and sludge treatment processes was conducted as well as a survey of 35 major aluminumfinishing facilities in the United States. Survey data were used to identify four industrial plants for extensive participation in the experimental phases of the project.

Detailed chemical analyses were used to establish concentrations of conventional wastewater constituents and priority-pollutant metals. The majority of sludge metal-content was attributable to aluminum while trace levels of most of the priority-pollutant metals were detected.

The results of the experimental investigation of sludge thickening, dewatering and drainage characteristics indicated that polyelectrolyte conditioning was required to effectively treat conventional sludges. Sludges containing solids precipitated at high temperatures had improved thickening and dewatering characteristics. Leaching properties of dewatered sludges were examined and indicated that the sludges were amenable to co-disposal with domestic refuse.

This report was submitted in fulfillment of a contract with The Aluminum Association Inc., Washington D.C. Continuation of the research project has been made possible by funding from the U.S. Environmental Protection Agency and the Aluminum Extruders Council.

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SECTION 1

INTRODUCTION

Concern with the disposal of metal-finishing sludges has stimulated research and development of more effective ways for sludge handling and treatment. Considerable effort in this regard has been expended by the aluminum-finishing industry. However, using conventional treatment techniques, some aluminum-anodizing facilities may have to dispose of a mass of wet dewatered sludge equal to the mass of aluminum finished. Therefore, investigation of conventional technology is required to determine the extent to which it can be improved or altered to more effectively dispose of residual sludge solids.

Only limited data were available on sludge chemical characteristics and properties and how these varied from plant to plant. Furthermore very limited data were available on trace metal content, especially toxic metals included in current drinking water standards and on the priority pollutant list. Information to be used in the rational design of sedimentation and dewatering equipment is generally lacking in the industry. Therefore, design, in general, must proceed on the basis of extrapolation of past practices. The focus of the research reported herein was, therefore, to address these issues.

SECTION 2

SUMMARY

Considerable data are available in the published literature on "alum" sludges produced in the treatment of drinking water using surface water sources. These data provide considerable insight into the effects of sludge properties and process variables on the performance of processes used in the treatment of aluminumfinishing wastewaters and sludges. However, only limited published data relating directly to aluminum-finishing sludges are available.

An aluminum-finishing sludge survey of 35 plants using anodizing, etching, painting and coil-coating processes was conducted. The plants produced sludge at an average rate of 300-2000 kg/d with minimum and maximum rates of 17-8800 kg/d, respectively. The majority of the facilities employed neutralization and gravitysedimentation for treatment of plant wastewaters. Techniques for treatment of thickened sludges included pressure and vacuum filtration, sand drying beds and certrifugation, while ultimate disposal was typically to land systems, a municipal sewer or licensed industrial disposal facility. Using survey results, four plants were selected for participation in the study of sludge characteristics, treatment and disposal. Three anodize facilities with finished-aluminum production rates of 3.6x10⁵ to 9x10⁵ kg/mo were selected for study. The three plants collectively used the following processes: chrome-conversion coating and painting, caustic etching, clear-coat and integral-color sulfuric-acid anodizing, bright-dipping and dyeing. Wastewater treatment at each plant included neutralization followed by gravity-sedimentation. Other treatment processes included: chrome reduction, vacuum filtration, pressure filtration and lagoon dewatering. The fourth plant studied in detail was an etching-facility at a major aluminum-alloy producer. Wastewater treatment at the etch plant included in-place neutralization of etchdesmut rinse water followed by pressure filtration and recycle of filtrate for reuse as rinse water.

Investigation of the chemical and physical characteristics of aluminum-finishing wastewaters and sludges from the four plants was achieved by collection of numerous wastewater samples at the industrial sites and shipment to the Environmental Engineering laboratories at the Georgia Institute of Technology. Chemical characterization included examination of numerous conventional wastewater parameters as well as examination of priority pollutant metals. The pH of the neutralized wastewaters varied from 7.0 to 10.5. Suspended solids concentrations of neutralized wastewaters varied from 0.41 to 4.35 g/l and averaged 2.4 g/l. The bulk of the suspended solids was attributable to precipitated aluminum. Aluminum content of the sludges averaged 0.31g Al/g SS and 0.41g Al/g NVSS. When expressed as Al(OH)₃, sludge aluminum was shown to account for virtually all of the suspended solids

contained in the sludge suspensions. Instrumental neutron activation analysis (INAA) indicated major additional metals included sodium (Na), potassium (K), calcium (Ca) and iron (Fe) with lesser quantities of copper (Cu) and zinc (Zn). Examination of trace metal composition of neutralized aluminum-finishing wastewaters indicated the presence of the following metals in one or more of the wastewaters: Arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), silver (Ag) and zinc (Zn). The majority of these trace metals were contained in the suspended form and were, therefore, not typically discharged with the neutralized wastewater but were contained in the thickened sludge suspensions.

A wastewater survey conducted at an extrusion/anodize plant indicated that the bulk of the wastewater originated in rinse tanks while the majority (73.3 percent) of waste aluminum was contained in concentrated etch used to neutralize plant wastewaters. It was estimated that 3.4 - 5.1 percent of extruded aluminum that was finished was discharged to waste treatment.

Thickening characteristics of aluminum-finishing sludges were effectively established with measurements of zone settling velocities over a range of suspended solids concentrations. Thickening properties of conventional, unconditioned sludges produced at ambient temperatures at anodizing, etching and painting plants were very similar. Unconditioned sludges thickened very poorly and can not be treated economically. Unconditioned sludges containing suspended solids produced at high-temperatures (generated by neutralization of concentrated basic and acidic wastes) thickened more effectively than ambient-temperature sludges, however, their thickening properties were also poor.

Anionic polyelectrolytes used at participating plants and one selected as a control were effectively used to significantly improve sludge thickening properties, as measured by zone settling velocities. Polyelectrolytes doses of 0.5 to 10 mg/l for most neutralized wastewater effluents were effective in improving sludge thickening properties by several orders of magnitude. Variations in the improvement in thickening properties resulted in a broader range of zone settling velocities for conditioned sludges. The suspension generated, in-part, at high temperature however continued to have the best thickening properties.

Dewatering properties of aluminum-finishing sludges were measured effectively using specific resistance, filter leaf and capillary suction time measurements. Conventional, unconditioned sludges at suspended solids concentrations of 1.3 to 36.1 g/l had specific resistance values of 2.8 x 10^{11} to 5.1 x 10^{12} m/kg, indicative of poor dewatering characteristics. Filter leaf data were consistent with specific resistance data ranging from 0.27 to 20.54 kg/m²-h. Dewateredsludge solids content ranged from 8.5 to 14 percent for anodize sludges and from 18.8 to 20.1 percent for etch sludges.

Unconditioned, sludge suspensions containing solids generated at high temperatures had specific resistance values of $1.8 - 4.1 \times 10^{11}$ m/kg, indicative of improved dewatering characteristics over other sludge suspensions. Filter yields for the sludge generated at high temperature were 2.43 - 41.5 kg/m²-h and dewatered-sludge solids were 18.5 - 19.5 percent. The unconditioned sludges were, therefore, difficult to dewater and high-temperature precipitation of sludge solids resulted in definite improvements in dewatering characteristics.

The use of anionic-polyelectrolyte conditioning immediately prior to dewatering generally improved the rate with which water could be removed from feed suspensions. However, polyelectrolyte-conditioning resulted in significant deterioration in the ability with which solids could be collected on a vacuumfilter leaf. Polyelectrolyte-conditioning had no significant impact on solids content of the dewatered sludge, in fact, solids content tended to decrease slightly upon conditioning with polyelectrolytes.

Sludge drainage characteristics were effectively evaluated using smallscale, simulated, sand-drying beds. Sludge drainage rates decreased with increases in suspended solids concentration and were significantly improved with polyelectrolyte-conditioning.

Regarding ultimate disposal of aluminum-finishing sludges, a primary concern was the heavy-metal composition of the sludges and the extent to which these metals can be leached. The bulk of the sludges was composed of aluminum while no detectable levels of antimony (Sb) or thallium (Tl) were observed in any sludges. The levels of mercury (Hg) silver (Ag), and beryllium (Be) were at low negligable levels. Major trace metals were arsenic (As), cadmium (Cd), chrome (Cr), nickel (Ni), lead (Pb) and zinc (Zn). These metals were contained in the suspended form and were not generally available for direct removal by displacement.

The EPA Extraction Procedure (EPA-EP) was used to evaluate the extent to which sludge metals were extractable and the amenability of the sludges to co-disposal with domestic refuse. Initial studies indicated that storage of sludge samples for a 2-month period had negligible impact on the results of the EPA-EP. Results of EPA-EP tests indicated that none of the sludges would be classified as a hazardous material when considering leachable metals. All sludge extracts contained arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb) and selenium (Se) with silver (Ag) and mercury (Hg) detected in several sludge extracts. All concentrations were less than 30 μ g/l and well below the EP limits for hazardous waste classification of 0.2 - 5 mg/l. Other metals detected in all EP tests included copper (Cu), nickel (Ni), and zinc (Zn). Beryllium (Be) was detected in several extracts while antimony (Sb) and thallium (T1) were not detected in any extracts. Of all of the trace metals detected, the concentrations of zinc (Zn), copper (Cu) and nickel (Ni) were commonly the highest, i.e. 50-6800 mg/1,8.5 - 6250 mg/1 and 8 - 1855 mg/1, respectively. An analysis of dissolved and suspended metals in sludge samples indicated that the majority, typically greater than 90 percent, of the extracted metals were leached from suspended metals and were not attributable to metals dissolved in interstitial water.

SECTION 3

RECOMMENDATIONS

The results of the research on conventional treatment systems should be compared to and used to improve performance levels of treatment systems at existing facilities in the industry. Research should continue to expand into innovative processes to be employed in conjunction with, or separate from, existing conventional treatment systems. Results on improved thickening and dewatering characteristics of sludge suspensions containing solids generated under high-temperature donditions indicate that this process alternative should especially be pursued.

SECTION 4

LITERATURE REVIEW

ALUMINUM FINISHING INDUSTRY

The uses of aluminum products for architectural and structural purposes in the building and construction industry; automotive applications in the transportation industry; consumer durable goods; electrical equipment, fixtures and wire in the electrical industry; beverage cans; and household and institutional foil and packaging materials are continuing to expand as the demand for the durable, light-weight metal increases. For example, in the Unites States in 1979, approximately 6 million metric tons (i.e., 6.33 x 10⁹ kg) of aluminum were used for domestic consumption (Amer. Bureau Metal Statistics, 1979). 0f the total consumption, approximately 1.1 million metric tons were used for extruded products which were anodized or otherwise finished in approximately 220 integrated and non-integrated plants (ABMS, 1979; Aluminum Association, 1978). These plants vary in size from plants with 1 to 3 extrusion presses to large plants employing as many as 18 extrusion presses. An additional 3.6 million metric tons of aluminum were converted to sheet, plate and foil forms which are typically etched, painted, or finished in numerous other manners in over 75 plants (ABMS, 1979; Aluminum Association, 1978). Approximately 0.6 million metric tons of aluminum were produced as aluminum rod, bar, wire and cable mill products and finished in approximately 300 plant production lines (Aluminum Association, 1978). The remaining aluminum was shipped as castings, powders, flake, pastes, forgings and impacts. Therefore, aluminum mill products were produced in well over 600 production facilities in numerous forms using a wide variety of surface treatment and finishing processes. The continuing emphasis on energy conservation in this country as well as a continuing demand for durable light-weight metals indicates the demand for finished aluminum products will remain strong and continue to expand.

With the emphasis of this study on water quality control, it is appropriate to consider the nature of the finishing processes used in the industry. Aluminum finishing processes include numerous physical and chemical treatments used to improve surface appearance, durability and adhesion properties. Physical surface treatments produce solid wastes and oil-bound suspensions which can be effectively recycled or treated and disposed. Chemical surface treatments, however, result in the production of large volumes of wastewaters containing considerable quantities of aluminum and other metals. Chemical finishing processes conventionally utilized by the aluminum industry include chemical and electrochemical etching and polishing, chemical milling, painting and anodizing. The wastewaters associated with these finishing processes consist of large volumes of rinse waters, and smaller volumes of chemical spills and spent or contaminated finishing solutions and suspensions. Conventional treatment of these wastewaters includes neutralization of the combined wastewaters and gravity clarification followed by discharge to a receiving stream or sanitary sewer. The precipitated solids formed upon neutralization and concentrated by gravity sedimentation are discharged to sludge lagoons, dewatered and disposed of in landfills and lagoons or blended with soil or stockpiled. Consideration of chemical finishing processes is therefore essential to the investigation of water quality and sludge treatment issues associated with the aluminum finishing industry.

Aluminum Finishing Processes

Aluminum surfaces are easily finished and nearly all of the finishes that can be applied to heavier metals can be utilized as easily on aluminum. The finishing of aluminum is a complex process with numerable variables, depending on the aluminum alloy being finished, the desired surface finish, and the specific finishing process employed. Aluminum finishing processes typically used include those summarized in Table 1.

Finishing Process	Process Description	
Mechanical Finishing	Metal is polished, buffed, scratch- brushed or colored.	
Cleaning	Dirt, oil and grease are removed with alkaline detergents or weak acids.	
Deoxidizing	Electrochemical formation of surface oxides to enhance metal hardness, cor- rosion and wear resistance and elec- trical insulation.	
Chemical Finishing	Formation of chemical conversion finish to strengthen natural surface oxide, prepare surface for paint treatments, brighten the surface and enhance metal luster.	
Surface Coatings	Surface coatings applied by electro- plating, painting and porcelain enameling.	

TABLE 1. PROCESSES USED TO FINISH ALUMINUM SURFACES

Aluminum finishing processes typically utilize many common steps but vary widely in the configuration of the finishing process system and chemicals utilized as a result of the alloys processed; type, size and configuration of aluminum products; and the nature of the desired finish. The emphasis of the research project was placed on those finishing processes which produce wastewaters from which large quantities of voluminous aluminum hydroxide sludges were produced. Therefore chemical finishing processes, including etching, electrolytic and chemical polishing, painting and anodizing processes used in extrusion/anodize, etch and paint plants, were examined.

Anodizing--

Numerous alloys of aluminum are anodized following extrusion, depending on structural and surface properties desired but 6000 series alloys, however, are most typically utilized. These alloys contain silicon, iron, copper, manganese, and magnesium and many contain chrome, zinc, titanium, lead, bismuth, and boron (Aluminum Association, 1979). The chemical composition limits of 6000-series alloys frequently anodized are presented in Table 2. Magnesium, silicon, iron, copper and magnesium are major alloy constituents. The alloy composition of each constituent metal may range from zero to 2.0 percent with aluminum typically constituting more than 95 percent of alloy metal. In addition to variations in alloys anodized, aluminum extrusion plants may employ numerous types of anodizing systems to finish extruded materials.

Chemical	<u>Composition</u>	of Alloy, % Tot	al Metal	
	6061	6063	<u>6463</u>	
Si	0.4-0.8	0.2-0.6	0.2-0.6	
Fe	0.7	0.35	0.15	•
Cu	0.15-0.4	0.1	0.2	
Mn ·	0.15	0.1	0.05	
Mg	0.8-1.2	0.45-0.9	0.45-0.9	
Cr	0.04-0.35	0.1		
Zn	0.25	0.1		
Ti	0.15	0.1		

TABLE 2. CHEMICAL COMPOSITION LIMITS OF WROUGHT ALUMINUM ALLOYS*

*The Aluminum Association, Inc. (1975)

Individual steps in anodizing are typically performed in a series of batch tanks into which racks of extruded aluminum materials are sequentially immersed. The steps involved in anodizing of extruded aluminum are summarized in Table 3. A general anodizing sequence may not typically include bright dip or dye steps, which may be utilized in conjunction with an anodizing step to achieve a bright metallic luster or a colored aluminum surface, respectively. Each finishing step on an anodize line is typically followed by one or more rinse steps.

The bulk of the volume of wastewater associated with anodizing processes originates in the continuous-flow rinse baths while the bulk of wastewater aluminum is contained in spent etch and anodizing wastes. Soluble aluminum levels in anodizing tanks are monitored continuously and must be maintained below specified levels to assure a proper surface finish. The contents of integral-color anodize tanks, for example, are usually regenerated using continuous, on-line, ion-exchange systems to maintain aluminum concentrations below 0.5 g Al⁺³/1. Spent ion-exchange resins are regenerated using virgin acid or acid from a conventional sulfuric-acid anodize system. Regenerant acid is typically discharged as wastewater and neutralized with spent caustic from an etch tank by semicontinuous addition of both to a wastewater neutralization basin or, less frequently, through direct mixing of spent etch and anodize wastes on a batch basis.

There is typically no wastewater discharge from a bright dip process. Dragout from this process tank is collected and concentrated in a subsequent rinse tank which is reclaimed for agricultural purposes.

Etching--

Plants producing aluminum rod, bar, wire and cable products and some foil products typically etch aluminum for milling or subsequent finishing purposes, but do not apply a finish. Such plants utilize chemical processes similar to the initial surface preparation steps utilized by anodizing plants. For example, an initial cleaning step is followed by etch and desmut steps, as described in Table 3. An alkaline etch rinse and acidic desmut rinse may be achieved in separate or combined tanks. For combined rinse tank systems, the pH of the rinse water is maintained at near-neutral values and aluminum is precipitated directly in the rinse tank. The contents of separate rinse tanks are combined following discharge to achieve wastewater neutralization and precipitation of aluminum. Neutralized etch and desmut rinse wastes constitute the major sources of wastewater and sludge solids in etch plants.

Painting--

The painting of aluminum is typically preceded by formation of a surface conversion coat. Conversion coatings are surface films formed through chemical reactions in which a portion of the base metal is converted to one of the components of the film, thereby making the film an integral part of the metal surface. Excellent adhesion properties of the films, or conversion coatings, improve the stability and durability of painted surfaces. Formation of conversion coatings is achieved through chemical reaction, in the absence of an externallyapplied potential, and an initial chemical cleaning of the aluminum surface is required.

Conversion coatings are formed with several types of chemical additives including an active compound, which attacks the aluminum surface and provides

PURPOSE OF FINISHING	TYPICAL FINISHING SOLUTION CHEMICAL	CHARACTERISTICS PHYSICAL	CONTRIBUTION TO OR EFFECTS ON WASTEWATER QUALITY
Removal of surface con- taminants such as grease and soil	Alkaline Detergents	T ^o = 40-60 ^o C	Degradable detergents and accumulated grease add to waste organic strength
Removal of surface oxides	Caustic soda = 2-10% Sequestrant ≈ 0.5-5%	T ⁰ = 40-60 ⁰ C Air Mixing	Aluminum removed from sur- face accumulates as sodium aluminate to levels of 10- 70 g Al ⁺³ /1. The major single source $(50-70\%)$ of waste aluminum in extrusion prodise plants
			anouise plants.
Removal of smudge film formed during etching	Nitric acid = 5-30%		Nitrates are primary source of effluent nitrogen.
Optional step used to enhance luster of aluminum surface	Phosphoric acid = 70-80% Nitric acid = 3% Copper = 0.1% Ammonia = 0.1%		Recovery of drag-out achieved with multiple rinses. Contribution to wastewater is typically minor.
Application of a uniform	Sulfunic Acid Anodiza		
aluminum oxide to provide	Sulturic Actu Anouize		
decorative and protective film on surface. Numerous processes used including clear-coat and integrated- color sulfuric acid anodizing	Sulfuric acid = 15-20%	T ⁰ = 20-30 ⁰ C Air Mixing	Aluminum levels of 5 to 20 g Al ⁺³ /l may be contained in anodize solutions. Re- covery is not typically practiced and drag-out of metal keeps aluminum levels in balance.
	Integral-Color Sulfuric Act		
	Sulfuric acid = 0.3-0.5% Numerous organic acids, for example, Oxalic acid = Sulfosalicylic acid = 7-15% Sulfophtahllic acid = 0.5-0 Sulfanilic acid = 5-7%.	T ⁰ = 15-25 ⁰ C Air Mixing 0.5-5%; ; ; 8%;	Aluminum level of <0.5 g/l are maintained with io exchange resins to remove dissolved Al from anodizing solution.
	PURPOSE OF FINISHING STEP Removal of surface con- taminants such as grease and soil Removal of surface oxides Removal of surface oxides Optional step used to enhance luster of aluminum surface Application of a uniform aluminum oxide to provide decorative and protective film on surface. Numerous processes used including clear-coat and integrated- color sulfuric acid anodizing	PURPOSE OF FINISHING STEPTYPICAL FINISHING SOLUTION CHEMICALRemoval of surface con- taminants such as grease and soilAlkaline DetergentsRemoval of surface oxidesCaustic soda = 2-10% Sequestrant = 0.5-5%Removal of smudge film formed during etchingNitric acid = 5-30% Phosphoric acid = 70-80% Nitric acid = 3% Copper = 0.1% Ammonia = 0.1%Application of a uniform aluminum oxide to provide decorative and protective film on surface. Numerous processes used including clear-coat and integrated- color sulfuric acid anodizingSulfuric Acid Anodize Sulfuric acid = 15-20%Integral-Color Sulfuric Acid sulfuric acid = 0.3-0.5% Numerous organic acids, for example, Oxalic acid = 7-15%	PURPOSE OF FINISHING STEPTYPICAL FINISHING SOLUTION CHARACTERISTICS CHEMICALRemoval of surface con- taminants such as grease and soilAlkaline Detergents $T^0 = 40-60^{\circ}C$ Air MixingRemoval of surface oxidesCaustic soda = 2-10% Sequestrant = 0.5-5% $T^0 = 40-60^{\circ}C$ Air MixingRemoval of smudge film formed during etchingNitric acid = 5-30% Phosphoric acid = 70-80% Nitric acid = 3% Copper = 0.1% Ammonia = 0.1%Nitric acid = 70-80% Air MixingApplication of a uniform aluminum oxide to provide decorative and protective film on surface. Numerous processes used including clear-coat and integrated- color sulfuric acid anodizingSulfuric Acid Anodize Sulfuric acid = 15-20% Air MixingIntegral-Color Sulfuric Acid Anodize Sulforia acids, for example, Oxalic acids, Sulfosalicylic acid = 7-15%; Sulfophtahlic acid = 70-50%; Sulfophtahlic acid = 0.5-08%; Sulfophtahlic acid = 0.5-08%;

INDER D. ACOMINGIA TRISHING STEPS USED IN ANUDIZING

+

aluminum ions for the conversion product; a film former, such as an oxidizing agent assisting in the formation of an aluminum oxide or an anion which forms an insoluble compound with aluminum ions; and an inhibitor, which regulates aluminum attack, or an accelerator to facilitate reduction reactions. Numerous conversion coating processes are used, including alkaline oxide coatings, crystalline and amorphous-phosphate coatings, amorphous-chromate coatings and boehmite coatings. The chemical composition of typical process solutions are indicated in Table 4. The treatment of wastewaters from amorphous-chromate coating processes, i.e., the one most extensively used, typically includes pretreatment processes to oxidize hexavalent chromium and remove cyanide. Subsequent treatment is focused on aluminum precipitation, followed by sludge treatment and disposal.

Coating	Solution Composition	Treatment Conditions
Alkaline Oxide	NaCO ₃ = 3%	$T = 100^{\circ}C$
	Na ₂ Cr0 ₄ = 1%	$\Theta \star = 5 \min$
Amorphous	$H_{3}PO_{4} = 7\%$	$T = 40-55^{\circ}C$
Phosphate	$KHF_{2} = 0.2\%$	⊖* = 0.5-5 min
	$Cr0_3 = 0.4\%$	
Chrystalline Phosphate	$Zn^{+2} = 0.7\%$	$T = 55-60^{\circ}C$
	$PO_4 = 1\%$	⊖* = 2-5 min -
	$NO_3 = 2\%$	
	$BF_4 = 1\%$	
Amorphous Chromate	$Na_2Cr_2O_7 = 0.8\%$	T = 20-35 ⁰ C
orn ond ce	$K_{3}Fe(CN)_{6} = 0.5\%$	⊙* = 0.5-5 min
	NaF = 0.1%	
	$HNO_{3} = 0.3\%$	
	(pH = 1.5)	

TABLE 4. CHEMICAL CONVERSION COATING PROCESSES (VAN HORN, 1967)

*0 = typical time allowed for chemical reaction

Wastewater Characteristics

Wastewaters from aluminum finishing processes contain a variety of inorganic and organic contaminants originating in finishing chemicals and solutions and the aluminum alloys finished. These contaminants are discharged to wastewater collection systems in rinse-water discharges and drag-out and spills of finishing solutions. Spent finishing solutions and blowdown from finishing processes also constitute a major source of the total mass of discharged wastewater contaminants, especially aluminum.

Water consumption rates for aluminum finishing plants, especially anodizing and etching plants, are high for metal finishing industries and range from 25 to 67 m³/Mg of aluminum finished (Steward and McDonald, 1979). High water use rates are due to heavy liquid films which are dragged out of viscous process solutions (e.g., alkaline etch) and the resulting need for large volumes of water to remove these liquid films. Racking techniques for aluminum products being finished also 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 products, in addition, must be placed on racks to minimize gas pocketing since H₂ gas is produced during anodizing and since compressed air is frequently used to mix process solutions. Both of these racking procedures, i.e. sagging and minimizing gas pocketing, result in increased drag-out of finishing solutions which increases rinse water requirements.

High drag-out levels, in conjunction with the need to effectively remove the associated finishing solutions to minimize surface contamination, result in high levels of waste aluminum and other process contaminants in rinse water effluents. High levels of aluminum (10-75 g Al⁺³/1) contained in spent etch and anodize wastes, frequently used to neutralize combined plant wastewaters, contribute significantly to wastewater aluminum content. High levels of dissolved aluminum in wastewaters result in production of extremely high quantities of solids which are collected as highly gelatinous and voluminous sludges that are difficult to thicken and dewater.

Heavy metals contained in aluminum finishing wastewaters include both hexavalent and trivalent chromium, which may be present in conversion-coating, anodizing, sealing and rack-cleaning solutions. Alloy metals such as copper and zinc are dissolved, much like aluminum, in many of the aluminum finishing steps. Nickel is a common component of anodize-seal solutions and sealing rinse waters and must be treated. Due to the presence of these metals, wastewater effluents must be monitored and controlled from aluminum finishing wastewaters. Furthermore, as a result of the removal and concentration of heavy metals in finishing sludges, heavy metal contamination of soil, groundwater and surface runoff resulting from sludge disposal techniques must be closely monitored.

While not routinely of concern with regard to current wastewater treatment practice, aluminum finishing wastewaters contain high levels of dissolved solids (e.g., 1.5 to 6.0 g/l for anodizing and painting wastes and up to 315 g/l

for etch plant wastes) which limit the reuse potential for these wastewaters. Dissolved species in addition to those above may include the following: sodium, potassium, iron, manganese, magnesium, silicate, nitrate, sulfate, and acetate. Depending on the levels of cleaning detergents, etch sequestrants, spent dye, organic acids and acetate discharged to waste through drag-out and spills, wastewater organic matter may be high (e.g. 30-100 mg/1 TOC) and require further treatment. This additional treatment is not typically achieved on site, but by discharge to a domestic wastewater treatment plant employing secondary treatment. Aluminum finishing wastewaters therefore contain high levels of dissolved aluminum and a wide diversity of metals, including numerous toxic heavy metals, which require treatment to limit the discharge of suspended matter and reduce wastewater toxicity.

Wastewater Treatment

Treatment of aluminum anodizing, etching and painting wastewaters is frequently accomplished with similar treatment systems. Plants employing two separate finishing lines (e.g., an anodize line and a paint line) may treat all wastewaters in a single, integrated, wastewater treatment system. Pretreatment of large volumes of segregated wastewaters is not typically practiced due generally to the highly acidic or alkaline characteristics of these wastewater fractions. Wastewaters from painting processes utilizing chromate solutions to develop surface conversion coatings are, however, typically pretreated for chromate reduction. Reduction of hexavalent chromium is achieved under acidic conditions using, for example, ferrous iron, sulfur dioxide or sulfite as reducing agents (Nemerow, 1979). Trivalent chromium ions are then precipitated as chromium hydroxide under alkaline conditions with the addition of lime. This suspension of chromium hydroxide may then be clarified separately or combined with other aluminum-bearing wastewaters for further treatment.

Conventional treatment of aluminum finishing wastewaters is achieved through mixing all influent rinse waters, spent process solutions and suspensions and process spills in a multi-stage neutralization system. Highly-concentrated spent etch and anodize solutions are usually collected and stored for use in controlling wastewater pH in the neutralization system. Therefore, rinse waters and spills with relatively low levels of dissolved aluminum are typically neutralized with highly-concentrated acidic and alkaline suspensions containing high levels of waste aluminum. Upon neutralization of combined wastewaters to pH values ranging from pH = 6-8, aluminum is precipitated as an aluminum hydroxide (Stumm and Morgan, 1970).

Neutralized aluminum hydroxide suspensions are typically clarified using gravity sedimentation with clarified wastewater being discharged to a receiving stream or sewerage system for additional treatment. Reuse of clarified process wastewaters if not routinely practiced due to the high mineral content of treated wastewater and availability of low-cost water from domestic systems or industrial wells. Thickened sludge is (1) discharged to sludge lagoons for further thickening and consolidation or (2) dewatered and disposed of on the land.

An alternative treatment scheme (Lancy, Ltd, 1971; Wernick and Pinner, 1972) is utilized in some limited instances and may be used to provide for extensive

savings on water make-up and sludge treatment costs through reduction of sludge volumes. This "integrated or closed-loop treatment" approach employs segregation of major alkaline and acidic wastewaters from dilute rinse waters. Highly contaminated alkaline and acidic rinse waters, e.g., initial rinses following etching and anodizing processes, are neutralized and the resulting aluminum sludge suspension is clarified. Clarified effluent is then used as an "aluminumtreatment" rinse in rinse tanks immediately following etching and anodizing processes and settled sludge is dewatered and disposed to land. Secondary and tertiary rinse waters in countercurrent systems are neutralized, clarified and reused in all but terminal rinse baths, e.g., those following dyeing and sealing where makeup water is added (Wernick and Pinner, 1972).

Settled sludges formed during the treatment of wastewaters from anodizing, etching and painting processes typically have a low suspended solids concentration, e.g., 0.5 to 2.0 percent dry solids and occupy a large volume. Sludge dewatering processes are utilized to reduce sludge volume through increases in sludge solids concentration to values ranging from 8-20 percent dry solids. Settled and dewatered sludge, however, remain highly gelatinous and voluminous. Steward and McDonald (1979) and Wernick and Pinner (1972) indicated that settled sludge production rates may vary from 20 to 60 kg wet solids/kg aluminum finished, further indicating the voluminous characteristics of these sludges.

Components contained in clarified wastewaters following separation of settleable solids will depend on the finishing processes utilized, the extent of water reuse and the aluminum alloy being finished. Wastewater contaminants which may appear in treated effluents include the following metals: aluminum, arsenic, barium, bismuth, cadmium, calcium, chromium, copper, iron, lead, manganese, magnesium, mercury, nickel, selenium, silver, silica and zinc; as well as chromate, chloride, fluoride, nitrate, acetate, sulfate, bicarbonate, carbonate and phosphate ions and detergents and complexing agents used in cleaning (Wernick and Pinner, 1972; Fukuyana et al, 1974).

SLUDGE TREATMENT AND DISPOSAL

Sludges are produced as by-products in the course of treatment of wastewaters using physical-chemical and biological processes. Methods for the treatment and disposal of sludges vary with the type of sludge. The review herein is focused on the treatment and disposal of chemical sludges typical of those resulting from the finishing of aluminum mill products.

Aluminum finishing wastewaters from cleaning, etching, anodizing and other finishing processes contain high levels of soluble aluminum. Soluble aluminum species are precipitated as hydroxide forms upon neutralization of combined rinse, etch and anodize wastewaters at or near ambient temperature and neutral pH. Aluminum hydroxide sludges are subjected to a number of treatment processes prior to final disposal. A schematic diagram of potential sludge handling techniques for such a chemical sludge is illustrated in Figure 1. Typically, sludge is first thickened to reduce the volume handled by subsequent operations. The most widely used unit for thickening purposes for chemical sludges is a gravity thickener. A subsequent dewatering operation transforms the sludge from a liquid to a semi-solid state by removing water. Typical dewatering processes include vacuum filtration, centrifugation, sludge drying beds and other mechanical





systems. Prior to the dewatering and/or thickening process, sludges may be subject to conditioning processes to improve dewatering and thickening characteristics. The conditioning processes include, for example, chemical conditioning, heat treatment, freezing and irradiation. The last step in a sludge handling system is ultimate disposal of the sludge which is generally a form of disposal to land.

Gravity Thickening

Thickening is the process of removing water from sludge by concentration of suspended matter in a smaller volume. Thickening provides reduced sludge volumes which can be handled at lower treatment costs due to savings in the physical size of a plant, labor, chemical conditioners and power. For the design of a thickener, it is required that settling characteristics of a sludge be known. Very limited information is available on settling characteristics of aluminum hydroxide sludges. Much of the available data are for sludges produced in the treatment of drinking waters using aluminum sulfate as a coagulant. These sludges contain aluminum hydroxide, clay, silt and colloidal organic compounds removed from water and are typically referred to as "alum sludges".

In the early 1960s there were some studies on settleability of alum sludges from water treatment plants. However, these studies were typically focused on other problems and settling experiments were conducted as supplementary studies. Roberts and Roddy (1960) found that the practicality of alum recovery from alum sludges using acidification was limited by the thickening characteristics of a sludge, and reported on the settling characteristics of alum sludges from laboratory and pilot-plant investigations. Doe <u>et al</u>. (1965) indicated that thickening of alum sludge was necessary to improve upon the economic performance of a sludge-freezing process. Alum sludge was concentrated from 0.5 to 1.9 percent in a thickener. These studies did not, however, present basic information on settling characteristics of alum sludges which could be used for design purposes or for characterizing sludges.

Extensive data regarding settling characteristics of alum sludge were presented by Gates and McDermott (1968), Neubauer (1968) and Reid (1978). Gates and McDermott (1968) conducted settling tests in 1-1 graduated cylinders and observed that zone settling velocities of alum sludge varied from 2 to 0.01 cm/ min for a suspended solids concentration range of 1310 to 22,880 mg/l. However, because of the use of a small settling column the results were likely influenced by laboratory artifacts associated with small column diameters and heights. Neubauer (1968) performed settling tests in 100-ml graduated cylinders and a 2.44-m octagonal settling column and observed that the settling rate was influenced by the type of container. Initial studies indicated that alum sludges from two treatment plants could be readily concentrated to 0.84 percent solids from an initial suspended solids concentration of 0.36 percent solids. Reid (1978) eliminated the influence of column height and diameter by using a relatively large settling column (2.44 m high and 15 cm in diameter) and by stirring the contents of the settling column at 1 rpm. Settling velocity data for alum sludges from Hemphill Water Treatment Plant (Reid, 1978) are shown with the data presented by Gates and McDermott (1968) in Figure 2. In the following sections, the use of zone settling data in thickener design will be illustrated as well as factors influencing zone settling velocity in laboratory studies.




Thickener Design--

In the design and operation of a thickener, settling properties of a sludge being thickened should be known. Settling characteristics of sludges are easily determined by placement of a sludge in a settling column and observation of the position of the liquid-solids interface with time. A typical plot of interface · height with time is shown in Figure 3. An initial lag period in interface subsidence may be considered as time required for the attenuation of turbulence, the flocculation of solids and the formation of channels through sludge solids in a settling column. The linear portion of the curve corresponds to the settling of a sludge at a uniform rate. The zone settling velocity of a sludge at an initial suspended solids concentration is determined from this slope. After constant settling, sludge solids settle at an ever-decreasing rate which is caused by the appearance of layers of higher concentration at the interface (Kynch, 1952) and by compression of the underlying bed of solids (Roberts, 1949). Similarly, settling tests can and should be conducted at other initial suspended solids concentrations. Once settling velocity data as a function of suspended solids concentration are collected, a thickener can be designed with the use of these settling data.

The concept in the design of a thickener is based on the work of Coe and Clevenger (1917). In a gravity thickener, sludge concentration may vary from feed to underflow concentration and each sludge concentration layer has a fixed capacity of transmitting solids to the next lowest layer. Rational design of a thickener requires the determination of the solids concentration of the layer with the lowest capacity to transmit solids. This requirement establishes the minimum area for the thickener to assure a fixed level of performance. The layer of lowest capacity for transmitting solids can be determined from a solidsflux curve which is constructed using settling data.

In a gravity thickener, settling of sludge solids occurs because of gravity settling of the solids and the removal of solids from the bottom of the thickener. The solids transmitted through a layer in the thickener can be expressed as

$$G = (C_{i} V_{i}) + (C_{i} U)$$

where: G = total solids flux through ith layer, ML⁻²T⁻¹

 C_i = solids concentration of ith layer, ML⁻³

 V_i = solids settling rate in ith layer, LT⁻¹

U = solids removal rate from the bottom of the thickener, LT^{-1}

(1)

The first term on the right side of Equation 1 corresponds to the solid flux due to settling of solids and the second term corresponds to solids removal from the bottom of a thickener. When total flux is plotted versus suspended solids concentration, a curve as illustrated in Figure 4 is developed. It is apparent that a layer with a suspended solids concentration of C_1 can transmit solids at



Figure 3. A Typical Settling Curve



Figure 4. Total Flux Curve

a lower capacity than the other layers having solids concentrations in the range of influent solids concentration (C_e) to underflow solids concentration (C_U). Then the area of the thickener can be found by setting the influent solids application rate (assuming complete removal of influent solids) equal to the limiting flux, or

(2)

$$A = \frac{Q_e \cdot C_e}{G_l}$$

where: A = Surface area of the thickener, L^2

 $Q_e = Influent flow rate, L^3T^{-1}$

 C_{p} = Influent solids concentration, ML^{-3}

 G_{L} = Limiting solids flux, $ML^{-2}T^{-1}$

In determining the volume of a thickener, in addition to the volume required to retain a defined sludge zone, some additional volume should be provided to store solids accumulated during periods of peak solids loadings. It should be also remembered that the factors which influence the magnitude of zone settling velocity of sludge may lead to over- or under-design of thickeners. Therefore, care should be taken to avoid any artificial conditions associated with determining zone settling velocities from laboratory settling units (Dick, 1972; Vesilind, 1979). The effect of laboratory conditions on settling rates of sludges may vary from sludge to sludge. Therefore, each laboratory condition, e.g., column height, column diameter, stirring rate and filling procedure, should be evaluated before using settling data to characterize sludges or for design purposes. In the following sections, the effects of some of the laboratory conditions on settling rates of sludges are discussed.

Measurement of Sludge Thickening Characteristics--

The effect of column diameter on the settling rate of the activated sludge has been investigated by Vesilind (1971). Two mechanisms are proposed for the behavior of sludges in small-diameter columns. At high suspended solids concentrations, flocs form bridges between each other and across a column resulting in slower settling rates than obtained in larger columns. At dilute suspended solids concentrations, displaced water takes a path of least resistance to replace subsiding sludge solids. Water flows along the smooth wall of the column rather than by a more tortuous route through the pores of the sludge mass. This, so-called "wall-effect" results in a higher settling velocity than obtained in larger diameter columns. At very high suspended solids concentrations and with small-diameter columns, agglomeration may not occur at all and compression, rather than settling, may occur.

Dick and Ewing (1967) have shown that settling velocities are increased by increasing initial sludge depths. Lower settling rates in short columns are caused by increased structural support (i.e., higher interparticle forces) of underlying layers to overlying layers. This support diminishes with decreasing suspended solids concentration and increasing initial depth.

Vesilind (1971) reported on the effect of gentle stirring on the settleability of activated sludge. While at relatively dilute suspended solids concentrations, stirring is indicated to have no beneficial effect, at higher concentrations, however, stirring increases settleability in small-diameter cylinders. This is caused by a) enhancing the agglomeration of sludge, b) eliminating bridging within sludge bed solids and c) minimizing the effects of structural support between layers. Laboratory settling tests should therefore be conducted in relatively large-diameter columns and in tall-cylinders with stirring mechanisms to minimize the artificial conditions created in the laboratory.

Sludge Conditioning

Sludges are conditioned by chemical and physical means to alter their properties so that water can be removed more readily. With the conditioning process, sludge is transformed from an amorphous gel-like structure to a porous material. Basically there are two methods for conditioning: chemical methods and physical methods. The efficacy of alternate conditioning methods can be evaluated by use of parameters such as specific resistance, filter yield, CST, settling velocity in case of gravity thickening and drainage rate for sand drainage of sludges.

Chemical Conditioning--

Chemical conditioning refers to conditioning methods in which inorganic chemicals and organic polyelectrolytes are used. Information as to the type of chemicals used for dewatering of aluminum sludges is very limited. In aluminum finishing industries, polymers, mainly anionic polymers, are used and lime and polymers are utilized for conditioning alum sludges.

Depending upon the type of ionizable groups on monomeric units, polymers can be cationic, anionic or ampholytic (i.e., containing both positive and negative groups). If the polymer does not contain any ionizable groups it is termed nonionic. Destabilization of particles by polymers is accomplished by bridge formation and charge neutralization depending upon the charge of the particles and the polymer.

Chemical bridging theory developed by LaMer and coworkers (Healy and LaMer, 1962; LaMer and Healy, 1963) provides a rational explanation of destabilization of suspensions. The reactions which occur between particles and polymers with the same charge, as presented by O'Melia (1972), are presented below. When a polymer is mixed with a suspension, polymer chains attach to surfaces of particles at one or more adsorption sites with the remainder of the molecule extending into the bulk solution (Figure 5a). The extended segments attach to vacant adsorption sites on other destabilized particle forming a "chemical bridge" between the particles (Figure 5b). If destabilized particles do not attach to other particles, the extended segment may attach to the same particle giving raise to a potential restabilization of the particle (Figure 5c). If a polymer is added in excess, surfaces of suspension particles can be covered and no sites will remain for the formation of bridges (Figure 5d).



Figure 5. Reactions Which can Occur Between the Colloidal Particles and Polyelectrolytes in the Bridging Model (After O'Melia 1972) When strong mixing is imposed on the system, rupture of destabilized particles may occur (Figure 5e) and the resulting floc fragments may be subject to restabilization (Figure 5f).

Destabilization of particles with polymers of opposite charge may be explained on the basis of charge neutralization and chemical bridging theory. When a polymer having a charge different from that of suspension particles is mixed with the suspension, destabilization of particles occurs as a result of the attachment of polymer through coulombic interactions (O'Melia, 1972). However, if the polymer is added in excess, restabilization of particles occur due to charge reversal of the particles. That is, the net charge on the particle is reversed from its original charge to the opposite charge.

The process of conditioning with polyelectrolytes is complicated because of the involvement of many variables, including (1) experimental variables such as, degree and time of mixing of polymer with suspension, temperature of the experiment, dilution of conditioning chemical, (2) sludge characteristics such as, type of the suspension (aluminum hydroxide, lime, iron or other metal hydroxides), pH of the suspension, particle size, liquid viscosity and solids content, (3) polyelectrolyte characteristics such as charge type (cationic, anionic or nonionic), molecular weight and age of polymer solution. In the following section some of these factors will be discussed in detail.

<u>Mixing</u>-- In conditioning suspensions with polymers, mixing is applied to provide transport of polymer to surfaces of suspension particles. In the case of poor mixing, this initial step of adsorption or attachment may be the ratelimiting step and the other steps of pore diffusion and surface attachment may not proceed to completion. Akers (1972) and Gale (1971) reported that adsorption of polyelectrolytes on particle surfaces was an irreversible phenomenon so that for adsorption to occur evenly it is essential that a polymer be distributed effectively throughout the suspension. Turner (1976) found that specific resistance of polymer-conditioned alum sludge suspensions decreased as the mixing speed increased from 100 to 370 rpm. Subsequent deterioration occurred as the mixing time of 1 min and polymer dose of 6.04×10^{-4} g /g solids were used. Decreasing specific resistance may be attributed to the formation of porous sludge structure while increasing specific resistance was considered to be due to floc and aggregate breakup, i.e., breakup of polymer-solids bonds.

Time of mixing is also critical for effective conditioning. Prolonged mixing was observed to result in lower filtration rates of slimes conditioned with flocculant carboxy-methyl-dextron (LaMer and Healy, 1963). Gale <u>et al</u>. (1967) reported similar results indicating that the specific resistance of 4 percent (dry solids) sewage sludge conditioned with 1.8 percent Al₂0₃ increased upon prolonged stirring up to 7 h.

Temperature and Dilution-- The temperature of dilution water for preparation a polymer solution has a pronounced effect on the conditioning with polymers. Experience has shown that increased temperatures lowers the effectiveness of polymer as a conditioner. LaMer et al. (1957a) reported that NOPCO-A polymer prepared with cold water gave double the filtration rates of NOPCO-A polymer prepared with hot water in conditioning a slime. Also, dilution of the polymer at high speeds (or blending) has an adverse effect on polymer conditioning due apparently to excessive polymer shear.

Type of Suspension-- In the process of coagulation and flocculation destabilization of particles is brought about by adsorption and charge neutralization. Although adsorption and charge neutralization may occur between positively-charged surfaces and anionic polymers and vice versa, adsorption can take place between surfaces and polymers charged with the same charge. In these cases both electrostatic and chemical forces play an important role in particle destabilization. French et al. (1954) observed that flocculation of kaolinite particles occurred due to formation of bonds between hydrogen groups of polymer Lytron 886 and hydroxyl groups on clay surfaces. Perkel and Ullman (1961) reported that the adsorption of polydimethyl siloxane (PDS) from benzene on dried glass was apparently due to (Si-O-Si)-groups on the polymer orientating with the (-O-Si-O-Si-O-)- structure of the heat-treated silica. LaMer and Smellie (1956) suggested that R-OH and COO⁻ groups on potato starch were absorbed onto various minerals. Since surface properties of each suspension may be unique in its characteristics, the degree of interaction between particle surfaces and polymer varies with the type of suspension and polymer.

Hydroxides of metals in aqueous suspension are generally electrically charged. The charge on metal hydroxide surfaces is developed by one of the following mechanisms: a) amphoteric dissociation of surface MOH groups; b) adsorption of metal-hydroxo-complexes derived from the hydrolysis products of material dissolved from the solid, i.e., from amphoteric dissociation of $M^{+2}(OH)_{2(aq)}(Parks, 1965)$. Surface charges of metal hydroxides are influenced by factors such as solution pH, charge and concentration of ionic impurities, temperature and age of the hydroxide suspension.

Aluminum hydroxide has a positive charge at low pH values because of greater dissociation of OH⁻ ions from the hydrated aluminum ion. As pH increases dissociation of H⁺ ions approaches to that of OH⁻ ions; and at a pH where dissociation are equal, aluminum hydroxide carries no charge. This point is called zero point of charge (ZPC). Furthermore, an increase in pH results in more dissociation of H⁺ ions so that the surface charge becomes negative. ZPC values for aluminum hydroxides are presented in Table 5. It is apparent that even for the same type of hydroxides there are some variations in ZPC. The variations in ZPC have been attributed to the hydration state of aluminum hydroxide, presence of impurities, cationic size and charge, temperature, and aging.

The change in ZPC of hydroxide surfaces with changes in hydration states has been interpreted in terms of the dependence of the acid strength of surface MOH groups on the $(0^{-2})/(0H^{-})$ ratio by Robinson et al. (1964). An increase in this ratio was reported to result in an increase in acid strength. The higher the acid strength of surface MOH groups the lower the ZPC of surface

TADLE 3. ZERO FUTNI OF CHARGE FOR ALOHINON INTITUDROVIE	TABLE	5.	ZERO	POINT	OF	CHARGE	FOR	ALUMINUM	TRIHYDROXID
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Aluminum Tr	ihydroxide	629 BOARS	
<u>Description</u>	Preparation	Zero Point of Charge	Reference
Gibbsite;	Aging of Na ₃ AIO ₃ (aq)	4.9	Schuylenborgh (1951)
Gibbsite;	Natural (two samples)	5.0, 5.2	Schuylenbörgh and Sanger (1949)
Gibbsite:	Synthetic aged for 72 days in 0.1M KC1	3.8 -	Kozmina <u>et al</u> . (1963)
	Same sample as above, ignited at 200 ⁰ C and aged for >2days in 0.1M KCl	5.0	Kozmina (1963)
Bayerite;	Hydrolysis of purified Al(OC ₂ H _c) ₂	9.3 7 0.2	Korpi and Holmes (Parks, 1965)
Bayerite;	Synthesfzed ³ from AlCl ₃ and NH ₂ OH(ag)	7.5	Schuylenborgh (1951)
Bayerite;	Synthesized from Na ₃ AlO ₃ (ag) + CO ₂ (g)	5.4	Schuylenborgh (1951)
Bayerite;	Hydrolysis of purified Al(OC ₂ H ₅) ₃	9.2	Fricke and keefer (1949)
Amorphous		1.12	
A1(OH) ₃ ;	Thermal treatment and aging of the hydrolysis products of aluminum ethylate	8.0	Fricke and Keefer (1949)

Specific adsorption of anions would be expected to produce a negative surface charge. In such a case, the pH at which zero surface charge was observed would be lowered because increased H⁺ adsorption would be necessary to neutralize the negative charge of the anion (Parks, 1965). Adsorption of cations by negatively charged surfaces produce a shift in pH to higher values (Modi and Fuerstenau, 1957). In general, counter ions charged oppositely to the surface play the determining role in the electrokinetic behavior of the surface. Also the higher the valence of ions, the more effective they are in charging electrokinetic properties of surfaces (0'Melia, 1972).

Heat treatment of suspensions would be expected to result in superficial loss of surface oxygens and, consequently, a shift in the ZPC (Parks, 1965). Presumably, aging results in loss of excess molecular water which is subsequently lost resulting in a shift in ZPC to acidic pH values (Robinson <u>et al.</u>, 1964). There is a linear relationship between ZPC and the ratio of cationic charge to radius, i.e. Z/r. As the Z/r ratio increases the acid strength of surface MOH groups increases and ZPC decreases (Parks, 1965). Particle Size and Concentration-- Polymer requirements for a suspension increase with decreasing particle size, even at a constant solids content. Since particle destabilization by organic polyelectrolytes is a surface attachment process, it is obvious that as suspension surface area increases, or as particle size decreases, the concentration of polymer required to produce optimum filtration rates, subsidence velocity and drainage rates would increase. LaMer et al. (1957b) found that optimum concentration of the polymer, Lytron 886, increased in a parabolic fashion with an increase in specific surface area of $Ca_3(PO_4)_2$ particles at constant $Ca_3(PO_4)_2$ content. Similar results were observed when PAM-M was used as a flocculent for $Ca_3(PO_4)_2$

LaMer et al. (1957b) also investigated the effect of solids content of $Ca_3(PO_4)_2$ slimes on coagulant requirements with two polymeric flocculants. The relationship between optimum flocculent dosage and solids content of $Ca_3(PO_4)_2$ slimes was parabolic. Novak and O'Brien (1975) observed a linear relationship between optimum polymer dose dictated by a minimum specific resistance (at a single specified solids concentration) and solids concentration for two chemical sludges. Bugg et al. (1970) found that specific resistance of an alum sludge decreased and then increased with increasing solids content, ranging from 0.86 to 3.35 percent when conditioned with polymer (Nalco 675) at a dosage of 90 mg/l. From the foregoing discussion it is apparent that there may not be a consistent relationship between particle size, solids content and polymer dose and that the relationship may vary with surface and polymer characteristics.

<u>pH</u>-- The effects of pH on conditioning of a suspension have been shown to be important (Gale and Baskerville, 1970; Knocke <u>et al.</u>, 1980). Variation in pH can produce simultaneous changes in the nature of a polymer as well as particle surface characteristics such as zeta potential, degree of hydrolysis and solubility of chemical species involved in flocculation. Gale and Baskerville (1970) observed that CST of a digested sludge conditioned with a polymer was lowest at pH 5.5 while it increased both at acidic and alkaline pH values. Knocke <u>et al</u>. (1980) reported that the pH of a nickel hydroxide suspension had a considerable effect on particle size. As the pH of suspension increased, the size of the nickel hydroxide particles increased. As will be discussed later, an increase in particle size decreases the polymer requirement of the suspension. Novak and O'Brien (1975) found that cationic polymers performed best at neutral and slightly acidic pH values for chemical sludges. Non-ionic and anionic polymers of low charge density functioned well between pH values of 6 and 8.5.

<u>Type of Polymer</u>-- Several authors have investigated the behavior of cationic, anionic and non-ionic polyelectrolytes in colloidal suspensions. If particles in a suspension are negatively charged, cationic polymers act as a coagulant by reducing zeta potential and by bridging particles with extended segments of adsorbed polymer molecules (O'Melia, 1972). A practical consequence of such behavior is that for a suspension of negatively-charged particles, cationic polymers may provide better conditioning relative to that of anionic and nonionic polymers when they are tested at the same molecular weight. For this reason, cationic polymers used in practice are generally of a lower molecular weight than anionic polymers (O'Melia, 1972; Bugg <u>et al.</u>, 1970).

In a suspension of negatively-charged particles, anionic polymers cannot reduce particle zeta potential because of the similar charges. Ruehrwein and Ware (1952) demonstrated that anionic polyelectrolytes cannot be absorbed into interplanar spacing of montmorillonite and assumed therefore that polyanions were not effective flocculating agents. However, anionic polymers can be adsorbed on kaolinite by a process of anion exchange, where the carboxylate ions replace adsorbed anions on kaolinite surfaces. The ability of anionic polymers to aggregate negative particles can be enhanced with the use of cations such as Ca^{++} . Cations aid in aggregation of particles through reduction in zeta potential so that adsorption of polymer chains by particle surfaces can take place more readily. A more detailed coverage of cation effects in conjunction with anionic polymers is presented by O'Melia (1972) and Sommerauer et al. (1968).

The flocculation of particles by nonionic polymers is achieved through formation of bridges between particles by polymer chains. In order for these polymers to bridge the potential energy barriers between two negatively-charged particles, a minimum molecular weight is necessary. This minimum molecular weight is reported to be approximately 10^{6} (O'Melia, 1972).

Studies with chemical sludges (Novak and O'Brien, 1975; King et al., 1971) and alum sludges (Bugg et al., 1970) indicated that cationic polymers are effective coagulants at slightly acidic and neutral pH values. Anionic and nonionic polymers function well at neutral and alkaline pH values. The observations by Bugg et al. (1970) and King et al. (1971) confirmed the theory of coagulation by polymers. Bugg et al. (1970) reported that when an anionic polymer was added to a suspension of alum sludge, suspension zeta potential increased at neutral and alkaline pH values and considerable improvement (about 20-60 times) in specific resistance was observed. The increase in zeta potential was due to the fact that anionic polymer units were first absorbed at the surfaces of suspension particles. Since the particles and the adsorbed polymer were negatively charged, zeta potential of the surfaces increased. Cationic polymers showed a decrease in zeta potential of ferric sulfate sludges together with an improvement in specific resistance as polymer dose increased. This observation confirmed that suspension destabilization with cationic polymers was brought about by charge neutralization and formation of chemical bridges between suspension particles.

Polymer Molecular Weight-- An increase in polymer molecular weight increases the fraction of particle surfaces covered with polymer. Linke and Booth (1960) showed that as the molecular weight of a polyacrylamide polymer was increased, more polymer was adsorbed onto the particles, resulting in a smaller dose of polymer to achieve optimum flocculation. The results also indicated that a high degree of flocculation cannot be achieved by using low molecular weight polyelectrolytes. Novak and O'Brein (1975) observed that optimum polymer doses for alum suspensions decreased with increasing polymer molecular weight for both anionic or cationic polymers and the relationship was curvilinear. Lime Addition-- When lime is used as a conditioner agent for alum sludge, various types of reactions may occur, depending upon the Ca⁺⁺ dosage and pH of the solution. Lime reacts in the liquid phase to convert bicarbonate ions to carbonate ions which combine with Ca⁺⁺ to form a CaCO₃ precipitate which is readily filtrable (Dick, 1972). With the addition of lime, pH of a suspension may be raised to a range as high as 12-12.4. Aluminum hydroxide (Al(OH)₃(s)), which is in the form of a precipitate at near-neutral pH forms a number of anionic complexes (e.g., (Al(OH)₃) OH⁻) at elevated pH valued (Hayden and Ruben, 1974). Upon reaction of these anionic complexes with Ca⁺⁺, numerous anhydrous and hydrous calcium aluminates are formed (Gale, 1971). Among the hydrous forms of calcium aluminates, there is a general agreement that the cubic 3CaOAl₁O₃GH₂O is the only stable aluminate between room temperature and 215° (Kelly, 1960). It is also possible that depending upon the quantity and reactivity of impurities a number of other aluminates involving impurities may form such as calcium sulfoaluminates (Jones, 1939). Experience has shown that calcium aluminates have better filtrability characteristics than that of alum sludge alone (Pisani, 1980). Turner (1977) observed that filtrability of alum sludge, as measured by specific resistance, was improved by about 300-fold with lime addition of 30 percent (mass basis). Webster (1966) reported that filter press performance was increased by the addition of lime to alum sludge.

Other Variables--The performance of a polymer may be affected by other factors such as degree of hydrolysis and polymer age. Novak and O'Brein (1975) reported that at a near-neutral pH range, anionic polymers with a range of 15 to 30 percent hydrolysis resulted in the lowest polymer doses to reduce the specific resistance of chemical sludges substantially below initial levels. Experience has also shown that aging of polymers reduces their coagulating ability.

Physical Conditioning --

A number of physical conditioning methods are available for altering sludge properties so that water can be removed more readily. However, these methods have not found common application in this country. These methods include freezing, heat and pressure conditioning, use of ultrasonic vibrations and electrical potentials and solvent extraction (Dick, 1972).

<u>Freezing</u>--Slow, complete freezing followed by thawing has been observed to improve thickening and dewatering characteristics of aluminum hydroxide sludges (Palin, 1954; Doe <u>et al.</u>, 1965; Bishop and Fulton, 1968; Farrell et al., 1970). Palin (1954) reported that after freezing and thawing a 2 percent alum sludge settled by gravity to 20.2 percent and could be filtered to a concentration of 33.9 percent solids by weight. Doe <u>et al.</u> (1965) reported conditioning by freezing could be economical if a period of 90 min for freezing and 45 min for thawing was applied using a batch process. Bishop and Fulton (1968) suggested that freezing and thawing might be economical for northern regions where weather conditions allowed for freezing. Farrell <u>et al.</u>, (1970) examined the effects of complete freezing and partial freezing on dewatering characteristics of aluminum hydroxide sludges. It was observed that partial freezing was not as effective as complete freezing. At the end of a thrid freeze-thaw cycle using partial freezing, sludge specific resistance was reduced to one-third of its priginal value. However, when a complete-freeze and thaw cycle was used, specific resistance was reduced by more than three orders of magnitude.

<u>Heat Treatment</u>--Thickening and dewatering characteristics of aluminum hydroxide sludges are improved by application of heat. It was reported (<u>AWWA</u> <u>Res. Foundation</u>, 1969) that heat treatment or "boiling the sludge under pressure" would result in destruction of the gelatinous nature of alum sludge. Palin (1954) found that alum sludge subjected to heat and pressure well below those of the Porteous process (i.e., 140^o-200^oC and 150-200 psi) had substantially lower sludge volumes than untreated alum sludge. However, he did not report the temperature to which sludge was subjected prior to settling tests. Very little additional data are available on the heat treatment of aluminum sludge and further research is needed.

Sludge Dewatering

Dewatering is a physical process used to reduce mositure content of sludge for the purpose of reducing the cost of sludge handling and disposal, reduction in surface runoff and leachate production at a disposal site and removal of odor-causing and putrescible material. Dewatered sludge solids concentrations for organic sludges are in the range of 20-30 percent and range up to 60 percent for inorganic sludges (Dick, 1972).

Dewatering is carried out either by mechanical devices such as vacuum filters, centrifuges, press filters, or sand drying beds. In the former case, dewatering is accomplished by physical means which include filtration, squeezing, vacuum withdrawal, and centrifugal compaction. In the latter case, dewatering occurs through natural evaporation and gravity drainage. The selection of a specific process is based on many factors including the type of sludge, the cost of a dewatering process and the cost of ultimate disposal. For plants where the quantity of sludge is small and space is available, lagoons and sand drying beds are frequently selected.

Measurement of Sludge Dewatering Characterisitcs--

A number of parameters are used to evaluate sludge dewaterability. These include specific resistance, filter yield and Capillary Suction Time (CST) which are discussed below.

Specific Resistance-- Specific resistance is the resistance of a sludge cake to the passage of water. The higher specific resistance is, the more difficult it is to dewater a sludge. Theoretical development of specific resistance is based on Darcy's or Poiseville's laws. Using Poiseville's laws, Carman (1938) derived an expression for flow through a filter-cake.

$$\frac{\mathrm{d}\mathbf{V}}{\mathrm{d}\theta} = \frac{P}{\mu} \quad \frac{A}{\mathrm{LR}_{c}} \tag{3}$$

where: $dV/d\theta$ = rate of filtrate flow, $L^{3}T^{-1}$

- P = pressure drop across filter-cake, $ML^{-1}T^{-2}$
 - A = area of filter-cake, L^2
 - μ = absolute viscosity of filtrate, ML⁻¹T⁻¹

L = thickness of filter-cake, L R_c = resistance of filter cake, L^{-2}

If the rate of flow through the filter cake and supporting medium is constant, total resistance is the arithmetic sum of filter cake resistance and supporting medium resistance, i.e.

$$\frac{\mathrm{d}\mathbf{V}}{\mathrm{d}\theta} = \frac{P}{\mu} \frac{A}{(\mathrm{LR}_{\mathrm{C}} + \mathrm{R}_{\mathrm{m}})} \tag{4}$$

where: $R_m = resistance of filter, L^{-1}$

Although the thickness of the filter cake can be easily expressed as

$$L = \frac{cake \ volume}{cake \ area}$$
(5)

the cake volume cannot be easily determined. Therefore, it can be expressed as a product of the mass of dry solids deposited per unit volume of filtrate, w, (ML⁻³); the density of dry solids, ρ_s (ML⁻³); moisture content, ϕ and the volume of filtrate, V, or (L⁻³)

cake volume =
$$\frac{W.V}{\rho_{s}(1-\phi)}$$
 (6)

combining equations 4, 5 and 6

$$\frac{dV}{d\theta} = \frac{P}{\mu} \frac{A^2}{[(R_c/\rho_s(1-\phi)).wV+R_mA]}$$
(7)

Since cake resistance, R , (i.e., resistance by unit volume) can be replaced by resistance by unit dry weight the equation is then

$$\frac{dV}{d\theta} = \frac{P}{\mu} \frac{A^2}{(r \cdot wV + R_m A)}$$
(8)

where: $r = specific resistance, LM^{-1}$.

Jpon integration of Equation 8 the following equation is developed,

$$\frac{\theta}{V} = \frac{\mu r w}{2 P A^2} V + \frac{\mu R_m}{P A}$$
(9)

The expression in Equation 8 indicates that if a plot of θ/V vs. V produced a straight line, Darcy's law can be applied to compressible sludge cake solids. From the slope, m, of such a straight line, specific resistance of sludge can be determined.

$$r = \frac{2PA^2m}{\mu W}$$
(10)

Equation 9 and 10 are valid only if P, r, w and R_m are constant throughout the filtration process.

During the process of filtration of compressible cakes under constant pressure, the force transmitted by the particles within the cake increases curvilinearly along the thickness of the cake. Therefore, solids in the stratum adjacent to the filter medium are more deformed and consolidated than the upper stratas. This observation indicates that specific resistance of each layer within the cake varies according to the variations in pressure. The highest resistance is encountered from the layer next to the filter medium and the least from the layer at the top of the cake. Similar observations can be found with regard to the variation in solids content of the cake. Gale (1967) found that at the upper levels of a cake, moisture content is higher and decreases along the thickness of the cake. The higher force encountered on the particles in lower strata squeeze out liquid from voids of the cake and increase sludge solids content. In equation 10, specific resistance, r, and solids content of the cake per unit volume of filtrate, w, correspond to the average specific resistance and average solids content of the cake. If a plot of θ/V vs. V does not yield a straight line relationship, variations in specific resistance and solids content within the cake do not offset each other or resistance of the filter medium, R_m , is affected by fine particles in the filtrate or both.

Specific resistance of compressible sludges are influenced by applied pressure differential, P. A number of investigators have proposed numerous types of relationships between specific resistance and pressure drop through the cake (Gilse, et al., 1930, 1931; Walker et al. 1937). Perhaps the most widely used relationship is the one suggested by Walker et al. (1937), that is,

$$r = r^{2}P^{3}$$
(11)

where: r' = cake constant

s = compressibility constant

Experiments by Coackley and Jones (1956) and Novak and O'Brien (1975) have shown that Equation 11 is applicable to a variety of sludges including biological and chemical sludges such as activated, raw, digested-humus and alum sludges. The compressibility coefficient, s, indicates the relative extent to which a sludge is compressible. When s is zero the sludge is in-compressible and increasing values of s indicate increasing compressibility of a sludge.

Considerable confusion has been associated with the exact meaning of the term w. Glen <u>et al.</u> (1973) defined w as the sludge suspended solids concentration; Coakley and Jones (1956) as the ratio of mass of dry cake solids per mass of liquid in a sludge prior to filtration; Tebbutt (1970) as solids concentration of sludge; and Swanwick and Davidson (1961) as mass of sludge solids per unit volume of filtrate.

In the derivation of the specific resistance expression by Carmen (1938), w was expressed as mass of dry cake solids per unit volume of filtrate. Gale (1967) has shown using a mass balance that if w is expressed as sludge suspended solids rather than mass of dry cake solids per unit volume of filtrate, there will be variations in specific resistance with sludge solids concentration. Vesilind (1979), used a material balance on solids and liquids and presented an expression for calculation of w,

$$w = \frac{C_{\rm K} C_{\rm o}}{100(C_{\rm K} - C_{\rm o})}$$
(12)

where: C_{K} = cake solids concentration, percent dry solids C_{o} = feed solids concentration, percent dry solids

It is apparent from Equation 12 and from definition of w that as feed solids concentration approaches cake solids concentration, w, r approaches infinity. Therefore, the filtration expression derived above cannot be used at high suspended solids concentrations since the physical processes controlling the removal of water under a pressure difference are quite different from those assumed.

Specific resistance is influenced by a number of sludge properties and cake properties which include particle size (Knocke <u>et al.</u>, 1980; Karr and Keinath, 1976), cake porosity (Gale, 1967), pH (Knocke <u>et al.</u>, 1980; Karr and Keinath, 1976), temperature (Karr and Keinath, 1976), organic and nitrogen content (Karr and Keinath, 1976) and bound water content (Heukelekian and Weisburg, 1956).

To relate specific resistance to sludge physical properties, it is useful to examine it with respect to the Carmen-Kozeny Equation for flow through porous media, i.e.,

$$r = \frac{36K}{d_{\rho}^2} \frac{(1-\epsilon)}{\epsilon^3} \frac{1}{P_{P}}$$
(13)

where: K = parameter related to the particle shape d_e = effective particle diameter, L ϵ = porosity of the cake P_p = density of cake particles, ML⁻³

According to Equation 13, a decrease in cake particle size results in an increase in specific resistance proportional to the square of the particle diameter. Since specific resistance is defined as the resistance by unit weight, if the density of particles was doubled there would be only half as nany particles and the resistance would be halved.

The effect of porosity on specific resistance is apparent from Equation 13, i.e., as porosity increases specific resistance decreases. A rather

significant increase in porosity from 0.35 to 0.63 therefore would result in a ten-fold decrease in specific resistance. The effect of bound water content on specific resistance can be considered in conjunction with porosity and particle effects. If bound water is defined as the water which cannot be filtered under a pressure applied in practice and is bound to the particles, its effect may be explained as follows. Higher bound water contents decrease the porosity of the cake, increase the mass of dry cake per unit volume of filtrate and thereby specific resistance is increased.

Particle size distribution also has a pronounced effect on specific resistance. A sludge with a narrow particle size distribution would tend to have a lower specific resistance than would be observed with a broad particle size distribution. This is caused by decreased porosity due to presence of fine particles.

The effect of pH on specific resistance was examined by Knocke <u>et al</u>. (1980) with nickel hydroxide sludges. An increase in pH from 8.1 to 12.4 brought about an increase in particle size from 10 to 20µm. According to Equation 13, if the floc size is doubled specific resistance is reduced by a factor of 4, assuming that all other parameters such as porosity, particle density and particle shape do not change. Knocke <u>et al</u>. (1980) observed experimentally that a 3-fold decrease in specific resistance occurred when particle size was increased by a factor of two. Hatfield (1969) reported the effect of pH on particle size was realized through the effect of pH on the surface charge of colloidal particles.

Temperature may affect dewatering characteristics of sludges through filtrate viscosity and changes in the characteristics of sludges. An increase in temperature results in lower filtrate viscosity. According to Equation 10, as long as there is no change in sludge characteristics, a decrease in filtrate viscosity causes an increase in specific resistance. However, it is reported that increased temperatures may alter sludge characteristics. Brooks (1970) indicated that heat treatment of sewage sludges improved dewatering characteristics, in part, by destroying colloidal material. Doe (1965) reported similar observations indicating that heat treatment resulted in destruction of the gelatinous nature of alum sludge. Turner (1976) observed that an increase in sludge temperature from 10° C to 55° C had negligible effects on the specific resistance of an alum sludge.

Specific resistance data may be used for predicting performance and design of vacuum filters. Using Equation 9 and assuming that the resistance of the medium (R_m) is negligible, i.e., $R_m = 0$, then

$$\frac{V}{A} = \left[\frac{2P\theta}{\mu w rP}\right]^{\frac{1}{2}}$$
(14)

If θ is taken as the form time for a drum filter

 $\theta = k\theta_{c}$

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(15)

where: k = fraction of the cycle time attributable to cake formation $\theta_{c} = \text{cycle time, T}$

The yield for a vacuum filter is expressed as dry weight of solids filtered per unit time and unit area, i.e.,

$$Y = \frac{V_W}{A_{\theta_c}}$$
(16)

Combining Equations 14, 15 and 16 yield a relationship for vacuum filter yield, Y, $ML^{-2}T^{-1}$,

$$Y = \left[\frac{2Pwk}{\mu r\theta}\right]^{\frac{1}{2}}$$
(17)

At variable pressures, Equation 17 yields

$$Y = \left[\frac{2p^{1-s}kw}{\mu r^{2}\theta_{c}}\right]^{\frac{1}{2}}$$
(18)

During the operation of a vacuum filter, yield can be maximized by proper selection of operating variables. According to Equation 16, to obtain maximum yield the fraction of cycle time devoted to the cake formation, i.e., k, should be maximized and the cycle time, θ , should be minimized. In other words, cake drying time should be minimized. However, these goals should be weighted against the necessity of having sufficient drying time to produce a cake with a desired moisture content. Although increasing pressure yields a higher filter yield, its effect diminishes with increasing sludge compressibility. According to Equation 13, w can be increased by applying higher feed solids concentration. Feed solids concentration, however, cannot be increased indefinitely because at very high solids concentrations, filtration will not occur at all. Finally, both specific resistance and filtrate viscosity should be minimized in order to optimize the yield. Specific resistance can be decreased with the use of conditioner and viscosity may be lowered by increasing temperature. However, this goal should be weighted against higher specific resistances associated with increasing temperatures.

<u>Filter Leaf Tests</u> -- A convenient and reliable procedure for developing design and operational information about rotary vacuum filters is available with the use of filter leaf apparatus. The apparatus consists of a round disc over which filter media is placed. The disc is connected to a vacuum source through a graduated cylinder in which filtrate is collected after the disc is submerged into a sludge suspension. The use of a filter leaf apparatus provides a better approximation of rotary vacuum filters than specific resistance apparatus because (1) the filter leaf apparatus allows the use of the same filtering media as that of a vacuum filter and (2) the same cycle time as encountered with the /acuum filter can be applied. The usual form, drying and discharge times are 30 s, 60 s, and 30 s, respectively (Vesilind, 1979).

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The yield of a filter leaf apparatus may be calculated by the following expression

$$Y = \frac{W}{A\theta_{c}}$$

(19)

where: W = dry weight of cake on the filter leaf, M A = area of the filter leaf, L^{-2}

With the use of a filter leaf test, it is possible to evaluate the effect of numerous variables on filter yield. These variables include pressure (or vacuum), from time and cycle time, feed solids concentration and drum submergence. Utilizing these results, predictions as to the performance of vacuum filters can be made.

Schepman and Cornell (1956) observed an inverse relationship between filter yield and cycle time for a combined primary-activated sludge. Filter yield varied by a power of -0.75 with cycle time, contrary to a power of -0.5 expected from Equation 17. It was observed that it was possible to predict the performance of pilot-scale plants from filter leaf tests.

<u>CST</u> -- Another parameter which has been used for measuring dewaterability characteristics of sludges is capillary suction time (CST). In a CST test, a sludge suspension is placed in a metal reservoir which is placed on the center of a filter paper. The liquid in the sludge is removed by the capillary action of the absorbent paper. The time required for the liquid front to travel between two points is termed CST. CST is influenced by the factors such as the properties of the paper, surface tension, suspension and ambient temperature, suspended solids content and other sludge properties. Baskerville and Gale (1968) reported that two basic properties of the filter paper were of fundamental importance; i.e., the capillary suction pressure and the filtrateabsorbing capacity per unit area. The first property should be much higher than the hydrostatic head of the sludge in the reservoir so that CST becomes independent of hydrostatic head. Filtrate-absorbing capacity should also be high so that CST only represents cake resistance and not the combination of resistances of cake and the paper.

In addition to affecting sludge properties, temperature may influence filtrate viscosity. Baskerville and Gale (1968) observed that CST of two sludges decreased with an increase in temperature from about 10°C to 32°C. The change in viscosity followed the same pattern as did CST indicating that the temperature effect on CST was through the effect on viscosity. CST also varied with suspended solids concentration. However, the effect of solids content on CST was not as pronounced with rapidly-filtering sludges as it is with slowlyfiltering sludges (Baskerville and Gale, 1968).

A low CST value is an indication of a well-dewatering sludges and vice versa. Since the CST method required a very short period for analysis, development of a relationship between CST and specific resistance for a given sludge may be extremely useful in sludge characterization and in process evaluation. Gale (1971) developed a relationship between (rC_1) and CST for sewage sludge

in which r corresponded to the specific resistance calculated with the use of w as cake suspended solids concentration and C_1 was the feed suspended solids concentration.

Mechanical Sludge Dewatering--

A number of mechanical dewatering devices are available which include vacuum filters, filter presses, gravity filters, belt filters and centrifuges. In addition to the following descriptions, detailed discussions are presented by Dick (1972), Metcalf and Eddy (1979), Vesilind (1979) and Perry and Chilton (1973).

<u>Vacuum Filters</u> -- These are the most commonly used dewatering devices in wastewater treatment. Vacuum filtration is accomplished on cylindrical drum filters with a filtration septum of a cloth of natural or synthetic fibers, coil springs or a wire-mesh fabric. Typical cake solids achieved with vacuum filters are 20-30%.

During the operation of the unit, a portion of filter drum is submerged into a vat containing sludge. As the drum is slowly rotated, a portion of the drum in the sludge suspension is subjected to an internal vacuum by which sludge is drawn onto the drum surface. Liquid is drawn into the drum through the cake. After the formation of a cake, it is subjected to air drying and cake moisture is reduced by vacuum removal of port water and by the passage of air through the cake. Sludge cake solids are released from the drum by a slight air pressure and removed with a knife edge or by gravity discharge. The filter cloth is then washed and enters the vat for a return cycle. Therefore, total cycle consists of 3 phases of cake formation (form time), air drying of the cake (drying time) and cake discharge (discharge time). Specific resistance and filter leaf measurements are used for design and operational purposes.

<u>Filter Presses</u> -- A filter press consists of parallel plates covered on both sides with a filter medium. In operation, sludge is introduced between the plates under pressure (40 to 150 N/cm²) and the liquid in the sludge is forced through a filter cloth. After a period of pressing time, the press is opened and sludge is removed. Typical values of filter cake solids range from 50 to 60 percent (Dick, 1972). Advantages of the system include high cake solids, low chemical consumption and excellent filtrate quality, while disadvantages include high labor costs, short cloth life and cyclic operation.

<u>Horizontal Belt Filters</u> -- Several new sludge dewatering devices were developed in the past few years. Some of them are moving-screen filters, belt pressure filters, capillary dewatering systems and rotary gravity filters. The basic mechanism associated with these systems is that water is removed in two sequential steps, i.e., gravity drainage and forced drainage. In the forced drainage step, sludge is subject to pressure, or capillary force followed by pressure. The operating complexity, energy requirements and the performance (solids capture and moisture content) of these systems are similar to that of vacuum filters.

<u>Centrifuges</u> -- Centrifugation processes have recently found common use in dewatering sludges. The two types used are solid bowl and basket centrifuges. The operation of the solid-bowl centrifuge is continuous. It has a long

horizontally-mounted bowl with a helical scroll mounted on the shaft. Feedsludge is introduced through a hollow shaft. Because of the high speed of the bowl, sludge is separated from centrate and concentrated on the periphery. Solids are moved to a discharge point by an inner slower-spinning, helical scroll. The level of liquid in the bowl is controlled by adjustable ports or weirs.

A basket centrifuge is operated on a batch basis. Sludge is initially introduced into the basket. Solids concentrate on the walls of basket during a run and centrate is accumulated in the interial area. When the solids holding capacity of the basket is reached it is stopped and solids are removed. A detailed analysis of the performance and design procedure for centrifuges has been presented by Vesilind (1979).

Gravity Sludge Dewatering --

Gravity dewatering of sludges is accomplished on sludge drying beds. Sludge drying beds generally consist of 15cm of sand overlying 30cm of gravel in which open-jointed tiles are placed for removal of filtrate (Dick, 1972). Sludge is spread on the sand surface at a depth ranging from 15 to 30 cm. Removal of water from sludge is achieved by simultaneous occurrance of drainage and evaporation of water. In the initial few days, drainage is the dominant mechanism for dewatering with evaporative drying then becoming predominant.

The rate of drainage is influenced by factors such as sludge characteristics, sludge depth and solids content with particle size and particle-size distribution being the basic sludge properties influencing sludge drainage rate. With different types of sludges, variation of drainage rate with time may vary considerably. In some cases, initially the drainage rate is high and decreases sharply after a certain period (Randall et al., 1971) and in other cases, it may decrease gradually (Hamlin and El-Hattab, 1967). A varying drainage rate may also be encountered (Quon and Johnson, 1966). An initial high drainage rate followed by an abrupt decrease in drainage rate occurs with sludges possessing a rather uniform particle size distribution. Gradual decreasing drainage rates may be encountered with sludges having a broad particle size distribution. Hamlin and El-Hattab (1967) suggested that as filtration progresses, more and more fine particles are entrained within the water passing through the cake. These particles clog the pores of the sand bed and form an impermeable layer between the cake and the sand bed. Therefore, the drainage rate decreases as the filtration continues with time. Variable drainage rate is encountered in cases where air or fine particles plug pores of a sand bed. Quon and Johnson (1966) observed a high initial drainage rate which decreased with time. After a period it increased and then decreased again. It was hypothesized that the initial decrease in the drainage rate may be due to two factors, i.e., air in the voids of the sand bed and clogging of sand bed by fine particles and subsequent purging of fine particles.

Voids in a sand bed contain air which is not completely free to move. As water percolates through a bed, the drainage rate is low because of low effective porosity. As filtration continues, air is absorbed by the liquid phase and the drainage rate increases. Subsequent decreases in the drainage rate are due to the increased solids content of the cake accumulated at the surface. Therefore, a decrease in the drainage rate is due to the movement of fine particles down into the sand bed and a subsequent decrease in the porosity of the sand bed. However, upon formation of a permeable layer at the bed-cake interface, fine particles cannot penetrate further into the sand bed. Thereafter, accumulated fine particles are purged and the drainage rate is due to the increased resistance of the cake to the passage of liquid through it.

Some investigators have attempted to correlate sludge filtration properties (e.g., specific resistance) to gravity sludge dewatering (Swanwick <u>et al.</u>, 1964; Logsdon and Jeffrey, 1966). Swanwick <u>et al.</u>, (1964) established a well-defined relationship between drainage rate and solids content ranging from 0.75 to about 4.0 percent solids. Similar observations were reported by Hamlin and El-Hattab (1967).

The rate of sludge drying is determined by the temperature, relative humidity and velocity of air. The general pattern of drying a sludge for a given set of conditions can be described as follows. After the sludge is subjected to a fixed radiant intensity, the surface temperature of the sludge is adjusted to the temperature set by the radiant intensity. During this period the drying rate increases. A steady state is reached when the sludge surface temperature is equivalent to the ambient temperature. At steady state, drying occurs at a constant rate which is referred to as the constant rate period (Quon and Tamblyn, 1965; Nebiker, 1967). After a low moisture content is reached the drying rate decreases sharply. This period is called fallingrate drying period. During this period the radiant energy is utilized for increasing surface temperature and sludge bulk temperature. The mositure content existing between the constant and falling rate periods is referred to as the critical moisture content.

The effect of temperature, relative humidity and velocity of air was investigated by Quon and Ward (1965). These workers found that for a given air velocity, the sludge drying rate varied linearly with humidity difference, i.e., (H_s-H) , and with a temperature difference parameter, i.e., $((t_d-t_w)\lambda)$. The parameters, H, H, t, t, and λ corresponded to ambient air humidity, saturation humidity of air, dry and wet bulb temperatures and latent heat of vaporization of water, respectively. Drying rate was also found to increase with increasing air velocity.

Variations in the constant drying rate with sludge type, solids content, sludge depth was investigated by Nebiker (1967) and Quon and Ward (1965). Vebiker (1967) found that constant drying rate was independent of sludge depths ranging from 10-40cm but was dependent upon sludge type. The types of sludges investigated were digested, activated and trickling-filter sludge. Quon and Vard (1965) observed no difference between constant drying rates of a sludge for depths of 1.25, 3.75 and 6.25cm. Novak and Montgomery (1975) reported that drying rates varied for alum, lime and iron and lime softening sludges. It was indicated that sludge drying rate varied with solids content between 20 to 40 percent and applied sludge depths of 20 to 80cm. However, it was not clear whether the reported sludge drying rates corresponded to constant or falling drying rate or the average of these two. Porter <u>et al</u>. (1973) stated that the internal mechanism of liquid flow does not affect the constant drying rate. The falling drying rate was governed by the rate of internal moisture movement which was influenced by diffusion, capillary action and pressure gradients caused by shrinkage. Therefore, sludge depth and solids content, as well as sludge characteristics such as particle size, are important in determining the falling rate in the drying process.

Some variations in conventional sludge drying bed particles include the use of covered beds and paved beds. Covered beds with greenhouse-like envelopes are used where sludges are dewatered continuously throughout the year. Because of the protection from snow and air, 20-to 40 percent reduction in area of drying beds is achieved when covered beds are used (Dick, 1972). Paved beds of concrete and bituminous material have been constructed. They have limited provisions for drainage but are easy to clean and free of clogging problems. However, drying beds with sand bottoms perform better than those with impervious bottoms (Randall, 1969). Open beds are used where land is abundant and isolated so not to create complaints due to odor production associated with biological sludges. The major disadvantages of drying beds include large area requirement, the need for digestion of biological sludges, dependence on climatic conditions and great amount of labor required to lift the sludge from the beds. The advantages are ease of operation, and low operational costs relative to mechanical systems.

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LEACHING OF DISPOSED SLUDGES

Removal of metals from aluminum-finishing and other wastewaters results in generation of concentrated sludges which may contain high levels of extractable heavy metals. Since commonly used methods of disposing of sludges is placement in a municipal sanitary landfill, such disposal practices may lead to solubilization of metals, with potential groundwater and surface water contamination. Development of a test procedure to evaluate a sludge for co-disposal in a municipal sanitary landfill must therefore account for conditions which influence leaching in a landfill.

Leachate Generation and Testing

Water infiltrating a solid waste landfill percolates downward, contacting deposited solids, leaching soluble materials, and producing leachate. Leaching is the preferential solution of constituents from a solid mixture by contact with a liquid solvent (Boyle <u>et al.</u>, 1979). Phenomena occurring in leaching are simple washing of the surface of a solid, dissolving of a solute from the matrix of an insoluble solid, osmosis, ion exchange, and sorption-desorption making it difficult to apply a single theory to explain leaching action.

According to Ham <u>et al</u>. (1979a), the ideal leach test would be useful in determining four characteristics regarding the release of a contaminant: the highest concentration of a contaminant found in the leachate; the factors controlling this concentration; the total amount available from a given amount of waste; and the release pattern with time. Such an ideal test to study kinetics of release and physical-chemical changes occurring in a waste as it is leached is often not feasible due to lengthly time requirements. A quick, standard leach test should be useful in predicting peak contaminant concentrations expected from actual landfills. A solvent that would extract only leachable waste components in the same release pattern as in the landfill would also be desirable (Ham et al., 1979a).

Batch and Column Tests

The leaching potential of a waste to be landfilled can be determined by using batch or column tests. With a batch test, solid waste is placed in a container with a specified amount of liquid and agitated. After a specified time, liquid and solid are separated with liquid being analyzed for various contaminants leached from the waste.

Column tests more closely approximate the physical conditions of a landfill, as the waste is packed in a column and the liquid is passed through it. While a column test may result in data that closely represent the release pattern of the waste constituents during continuous leaching, the time required to adequately study leaching is a drawback. In addition, there are problems with channelling, clogging, edge effects, and reproducibility of data (Boyle, et al, 1979).

The best practical model of a landfill for solid waste leachate analysis s the lysimeter. Normally constructed to simulate field conditions as closely as possible, a lysimeter is expensive to construct and requires substantial land area. Unless the rainfall rate is accelerated, lysimeter studies may take 2 to 3 years before adequate data are collected. Therefore, the need for reproducibility of data and a quick, practical standard test of leaching potential has dictated that such a test be a batch test.

Leach Test Variables

Results obtained from any leach test are dependent on several physicalchemical parameters: leaching solution composition, pH, liquid to solid ratio, time, agitation, and surface area of the sludge. Proper selection of leach test variables can result in a valid prediction of the release of some contaminants, e.g., heavy metals, from a landfill.

Leaching Solution --

The composition of a standard leaching solution should duplicate liquid contacting waste in a landfill. Boyle et al. (1979) described three types of landfills; segregated, mixed industrial, and municipal. While each landfill generates a unique leachate due to the actual waste composition, a leaching solution to simulate liquid composition prior to contact with a waste can be developed for each landfill type. In a segregated landfill where a waste is landfilled by itself, the leaching solution can be simulated with distilled water or synthetic rainwater. The leaching solution can be contacted with the actual waste to simulate uncontaminated rain passing through a thick layer of landfilled waste. For an industrial landfill where there are mixed wastes, a leaching solution can be developed in a similar manner if the types of wastes in the landfill are known. Distilled water can be passed through a composite of wastes known to already be in the landfill, resulting in a leaching solution unique to a particular landfill. The use of this leaching solution or actual leachate from the landfill on a sludge to be disposed would indicate wastes incompatible for co-disposal. For example, a sludge that releases large amounts of heavy metals under acid leaching conditions should not be landfilled with an acid waste.

Municipal landfills may have differing characteristics depending on refuse composition and compaction, state of decomposition, dimensions of the landfill, age, channelling of moisture, and climatic effects (Ham <u>et al.</u> 1979). While rainwater does percolate through a municipal landfill, actively-decomposing organic material produces organic acids which tend to control the pH of the waste environment. In addition to initial flushing of contaminants, the relatively low pH (4.5-5.5) in a biologically-active landfill can increase leaching of metals. Use of a weak organic acid for a leaching solution can be used to simulate the pH conditions in an active landfill.

pH --

The pH of a leaching solution is an important controlling factor in the release of contaminants from a sludge. Heavy metal solubilities generally decrease above pH 7 for hydroxide precipitates (EPA, 1973). Metal sulfide solubilities are on the order of 10⁵-10⁷ times lower than metal hydroxide solubilities (Freedman and Shannon, 1973). Therefore, with sulfides present in a landfill, metal leaching will be controlled by metal sulfide solubilities. Since distilled water has no buffer capacity, a sludge will control the pH of a leaching solution of distilled water. In a municipal landfill, first-stage

products of anaerobic bacterial decomposition are volatile fatty acids which can result in solubilization of metal hydroxide, carbonate, and oxide sludges. Bacteria which perform the second-stage conversion of organic acids to methane gas are very sensitive to heavy metals. As the heavy metals inhibit methaneformers, the acid-formers continue to produce acid and lower the pH, causing more metal dissolution, and resulting in less methane bacteria activity. The use of acetic acid to lower pH for a batch leaching test has been used to simulate acid conditions in a municipal landfill (Lancy, 1978).

The principal source of sulfates in aluminum finishing sludge is sulfuric acid anodizing solutions. In the anaerobic environment of a landfill, sulfurreducing bacteria can biologically reduce sulfates to sulfides. Dissolved metal ions can precipitate as a metal sulfide when the metal ion contacts a sulfide ion. If sufficient sulfides are present, solubilized metal ions will be tied up as insoluble metal sulfides, resulting in lower metal concentrations in leachate. Therefore, the presence of sulfides in a landfill tends to reduce leaching of heavy metals to levels below 10 μ g/l at pH = 5 (Freedman and Shannon, 1973).

McCarthy (1979) performed batch extractions showing the effect of pH on various metal finishing sludges. Metal concentrations followed typical metal solubilities; most metals were highly soluble at low pH and decreased in solubility as pH increased. Some metal sludges reached a minimum solubility near pH 8.5 (i.e. the initial pH) and increased in concentration as pH increased.

The pH of a leaching solution can affect concentrations of metal extracted when a metal vessel, e.g., a stainless steel container, is used. Epler <u>et al</u>. (1980) performed blank extractions without sludge and reported significantly higher inorganic priority pollutant concentrations on extracts performed at pH 3.5, as opposed to extractions performed at pH 10. The principal metals extracted were Ni, Cu, Zn and Cn. Extracted concentrations at pH 3.5 for the 4 metals wer 107, 52, 45 and 37 μ g/l, respectively, while at pH 10 the respective concentrations were 6.4, 4.0, 0.57 and 6.1 μ g/l.

Solid to Liquid Factors --

<u>Solid-Liquid Ratio</u> -- High or low solid-liquid ratios could result in a leach test giving low estimates of extractable contaminants from a sludge sample. For high solid-liquid ratios- the release of contaminants from a sludge may be limited by saturation concentrations. If a particular pollutant reaches the saturation level in a leachate, a higher solid-liquid ratio would not produce a proportionate concentration increase in the extract liquid. For low solidliquid ratios, the mass of pollutants released into solution may not produce a concentration above the minimum detection limit of the analytical method. Each pollutant has an optimum dissolution rate corresponding to some particular solid-liquid ratio due to the concentration of the contaminant in the sludge (Thompson, 1979). The concentration of a very soluble parameter will be directly dependent on the solid-liquid ratio.

In a given waste, several chemical constituents may be of interest. These may have different factors controlling their concentrations, and so may show

different dependencies on the solid-liquid ratio. Several currently available leaching tests start with a high solid-liquid ratio and saturated conditions. The ratio of a percolating drop of leachate is higher than used in many tests. If the results of a leaching test are to be directly related to landfill conditions, a correlation between the annual rainfall, the waste density, and the solid-liquid ratio of the test must be made to determine how much leachate a unit area of waste will contact with time, and thus the time span to which the ratio corresponds (Ham <u>et al.</u>, 1979a).

Interstitial Water -- The properties of metal finishing sludges impose special demands on the design of a test procedure in order to account for sludge moisture content (Steward, 1980). The majority of the weight of these sludges is water which is around or bound within a relatively smaller quantity of solid material. This water may contain high concentrations of dissolved salts, detergents, peptizing materials, and compounds which can complex or chelate heavy metals. These include compounds resulting from batch dumps of alkaline cleaners, acid dips, and plating baths from metal finishing. The quality of the interstitial water should be similar to the wastewater effluent being discharged from dewatering equipment of the plant generating the sludge. Residual traces of soluble heavy metals are found in metal finishing wastes in the range of 0.1 to 10 mg/l (Steward, 1980). These residual traces affect leach test results by a dilution factor determined by the solid-liquid ratio of the test. A more important impact comes from the combined effect of organic and inorganic materials in interstitial water. These compounds may significantly lower the pH of the leaching solution and cause the leaching solution to dissolve more metal than it ordinarily would if flushed out of the landfilled waste with the first rain.

Minor <u>et al.</u>, (1980) reported the interstitial water of some metal finishing sludges to be so high in metal content that a 20-fold dilution with a leaching solution resulted in metal concentrations above EPA limits, without even allowing for any leaching to occur. A typical example was a plating sludge at 6 percent solids with 4 mg/l of Cr in the filtrate. With 75 ml of water removed prior to extraction and a 1:20 solid (wet) to liquid ratio, the required leaching solution produced a Cr level of 0.53 mg/l which was above the then proposed 1978 hazardous waste limit of 0.5 mg/l. Since Minor <u>et al.(1980)</u> reported on the study, the limit was raised by a factor of 10. Now such a waste might not necessarily be hazardous unless significant leaching occurred, but the effect of interstitial water is still significant. The inclusion of soluble netal species in interstitial water is not representative of long-term sludge leaching.

McCarthy (1979) proposed that interstitial water effects on leach tests be overcome by more effective dewatering of a sludge prior to a leach test. The sludge should be tested at the same moisture content at which it will be placed in a landfill.

<u>Solid-Liquid Separation</u> -- Solid-liquid separation in a leach test is required both before and after testing. Before testing, the sludge may need to be in a dewatered form as it would go to a landfill. After testing, the liquid portion of the mixture must be removed for analysis. Solids removal can be achieved by centrifugation and filtration. When small solid particles tend to clog a filter, separation by centrifugation may prove to be a more efficient method, providing the centrate or the filtrate from a coarse prefilter is ultimately filtered through a 0.45 μ m membrane filter. Membrane filters can pass particulate matter in the lower colloidal size range which will be measured as soluble species. Although particles larger than colloidal size are often found in leachate from sludge disposal sites, the leachate is usually filtered before analysis.

Time of Contact --

<u>Release Pattern</u> -- The time of contact between a leaching solution and a sludge is a significant variable in batch or column leach tests because the release and migration of contaminants is not an instantaneous process. Sludge constituents may equilibrate at different rates. Lee and Plumb (1974) reported four release patterns in a leaching study with taconite tailings as shown in Figure 6. Their experiment was 500 d in duration and used a very low solidliquid ratio, i.e., 1:1000, with distilled water as the leaching solution. The variety of release patterns reported indicated no single optimum sampling time for all constituents; nor could a short leaching time assure equilibrium to have been reached for all contaminants. A test should be long enough to allow rapidly equilibrating species to reach equilibrium and to release an analytically measurable amount of most species present. The test should not be so long that biological growth or saturation of chemical species occurs.

Minor <u>et al</u>. (1980) studies release patterns for heavy metals in metal finishing sludges and reported a rapidly decreasing rate of release of Cd and Cr with time during a column leach test as depicted in Figure 7. The initially high reading was indicated as being due to soluble Cr in interstitial water.

<u>Successive Extractions</u> -- Using successive extractions in a batch test is an approach that can be used to develop kinetic information similar to that for a column test. Not only can a release pattern be determined, but also the factors affecting that release can be discovered. If a waste contains an acidsoluble metal carbonate and an acid-soluble trace metal, the acid in the leachate could be neutralized by dissolution of the metal carbonate. Following complete dissolution of the metal carbonate, the acid will dictate leaching conditions and metal will be leached from the sludge. Had only one elution been used, the netal carbonate might still have been present and little of the acid-soluble netal would have been leached (Ham et al., 1979a).

Instead of using fresh leaching solution on one sludge, the same leachate can be used on replicate volumes of the same type sludge to find the maximum concentration that contaminants can reach in the leachate, instead of finding release characteristics. More information can be found by using both leachate and sludge sample replacement in successive elutions than by using either method along (Ham et al., 1979a).

Agitation Technique --

<u>Concentration Gradient</u> -- Mixing of solvent and solids is desirable to avoid build-up of concentration gradients between leaching solution and sludge solids; too much mixing will produce turbulence which may result in attrition



Figure 6. Conceptual Leaching Release Patterns with Time (From Lee and Plumb, 1974)





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of solids, exposing new surfaces for reaction. Boyle <u>et al</u>. (1979) reported that vigorous agitation caused particle abrasion of iron foundry waste and gave unusually high results.

Shaking -- One agitation technique reported by Thompson (1979) was shaking for a short time followed by settling. Ham <u>et al</u>. (1979a) reported shaking and settling yielded significant concentration gradients between the settled waste and the leaching solution, so the method was not satisfactory for a leach test. Other methods, such as reciprocal shaking, wrist action shaking or circular shaking are more suitable provided they produce well-mixed systems and do not promote excessive abrasion.

<u>Stirring</u> -- In initial regulations (Federal Register, 1978), the EPA specified stirring as the only acceptable method of agitation for a leach test. The waste was to be agitated by two blades spinning at 40 rpm. Epler <u>et al</u>. (1980) reported problems with sample grinding for particles of 6.35 mm diameter for extractor designs having a fixed blade near the vessel bottom, and recommended replacing the secured stainless steel blade with a Telfon stirrer shaft with two moveable blades that swing out when rotated.

The EPA subsequently specified an acceptable extractor as one which would prevent stratification of a waste sample and leaching solution, and insure that all sample surfaces continuously contact well mixed leaching solution. There are two types of acceptable extractors: stirrers and tumblers (EPA, 1980).

Particle Size --

The particle size distribution of a sludge influences leach test results because solution of sludge contaminants is dependent on surface area. Small particles have a higher surface area per unit weight than do larger particles, so more pollutants may be released from smaller particles. Ham <u>et al</u>. (1979a) advocated initial control of particle size by grinding, cutting, or agitation to simulate any expected physical breakdown of the waste in the landfill. A waste that was brittle or had low shear strength could be broken into smaller pieces by compaction in a landfill. For sludges that were treated to increase particle size by fixation, Thompson (1979) stated that any attempt at particle size modification such as grinding or sizing was not only an additional timeconsuming step in the conduct of a leach test, but was unrepresentative of conditions in a disposal site.

Sludge Age --

In conducting batch leach tests, Minor <u>et al</u>. (1980) allowed some dewatered metal plating sludge to be exposed to the atmosphere for three months prior to extraction. During the three month storage period, a significant but unspecified decrease in moisture content was apparent. Leach tests resulted in a 50-90 percent decrease in Cd, Pb, and Cr concentrations in leachate. It was indicated that an unspecified form of curing took place during the drying process which fixed the toxic metals, making them unavailable for dissolution. Such a significant reduction in sludge leaching might be possible with dewatering using sanddrying beds as a treatment method to permit long-term drying. No studies were reported on the effects of aging of dilute suspensions of these sludges prior to dewatering.

Batch Leach Tests: EPA Extraction Procedure

1. -

There are numerous batch leaching tests that have been developed. Listed in Table 6 are leach test variables according to type of leaching solution, solid-liquid ratio, contact time, and agitation. These leach test variables are the result of a survey by Abelson and Lowenbach (1977), who reported categories of test variables rather than naming specific tests.

TABLE 6. SUMMARY OF VARIABLES ASSOCIATED WITH EXISTING LEACH TESTS (ABELSON AND LOWENBACH, 1977)

Variable	Description Usin	Number of Tests g Indicated Variable
Leaching Solution	H ₂ O (distilled, deionized) H ₂ O with pH adjustment Sfte specific Acetate buffer Synthetic municipal landfill leachate Synthetic natural rainwater Bacterial nutrient media Tests with more than one leachate	17 5 1 1 1 1 1 5
Solid/Liquid Ratio	<1:4 1:4 1:5 1:10 >1:10 variable	4 4 3 5 2 - 2
Time/elution	<1 h 1-24 h 24 h 48 h 72 h >72 h	1 3 7 3 2 3
Number of Elutions	1 3 5 7 10	15 1 1 2
Agitation	Shaker Stirring Gas agitation Shaking w/ settling	9 7 1 2

Batch leach tests developed for use with sludges include an Elutriate test (Thompson, 1979), test developed by Kunes (1975), Minnesota and IUCS tests (Ham <u>et al.</u>, 1979b), SLT test developed by Ham <u>et al.</u> (1979b), the ASTM test (Malloy, 1979) and the Extraction Procedure (EP) test developed by EPA (1980). These tests have been summarized in detail by Kutz (1980). Only the EP test which has become a standard test for examining sludges for consideration for co-disposal with domestic refuse, is examined in detail herein.

The EP is a laboratory test in which a representative sample of waste is extracted with distilled water at pH 5, maintained with acetic acid. Extract liquid obtained from the EP is analyzed for the 8 elements, 4 pesticides, and 2 herbicides listed on Table 7 to determine if the respective threshold concentrations are met or exceeded.

Hazardous Waste Number	Contaminant	Maximum Concentration (mg/1)
D004	Arsenic (As)	5.0
D005	Barium (Ba)	100.0
D006	Cadmium (Cd)	1.0
D007	Chromium (Cr)	5.0
D008	Lead (Pb)	5.0
D009	Mercury (Hg)	0.2
D010	Selenium (Sc)	1.0
D011	Silver (Ag)	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2, 4-D	10.0
D017	2,3, 5-TP (Silvex)	1.0

TABLE 7. EP EXTRACT MAXIMUM CONTAMINANT CONCENTRATIONS FOR HAZARDOUS WASTE

Sample Separation Procedure --

A representative sample of 100 g minimum size is placed in a 0.45 μ m nembrane filter holder under 517 kN/m² pressure. For samples with solids that to not absorb on the filter or clog it, vacuum filters using the same membrane can be used. This procedure is intended to result in separation of the free liquid portion from any solid matter having a particle size greater than 0.45 m. Epler <u>et al.</u> (1980) reported vacuum filtration adequate for a wide 'ariety of sludges analyzed. If the sample will not filter, a centrifuge can be used to dewater the solids provided the centrate is filtered and the filcrate is stored at 4°C. If the solids are less than 0.5 percent of the waste, the filtrate is analyzed directly. Solids analysis is determined by drying the sample for 24 h at 80° C.

Structural Integrity/Particle Size Reduction --

Solid material must pass a 9.5 mm U. S. standard sieve prior to extraction. If not, the sample is placed in a compaction tester with a 0.33 kg hammer and free fall of 15.2 cm. After 15 blows of the hammer, the material is removed and ready to be extracted. This procedure may be used with wastes that have been treated by a fixation process to bond particles together and reduce leaching, as it simulates the compactive effort a landfilled waste may experience. Fixated wastes may be cast in cylinders 3.3 cm in diameter by 7.1 cm long and allowed to cure for 30 d prior to testing.

Extraction of Solid Material --

Solids obtained from the separation procedure or the particle reduction step are immediately weighed to prevent drying of the sample. These wet solids are placed in an extractor with 16 times their weight of deionized water. An acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and leaching solution, but also insure that all sample surfaces are continuously brought into contact with well mixed leaching solution.

Two acceptable extractors include a stirred device and a tumbler. The stirred device has 2 blades which spin at \geq 40 rpm and can use either automatic or manual pH adjustment. A Telfon stirrer should be used to prevent background leaching and reduce particle abrasion. Epler et al. (1980) reported the type-316 stainless steel extractor contaminated blank extract solutions with metals dissolving from the vessel wall and stirring blade. To avoid contamination, a glass or Telfon vessel should be used. Plexiglas is unacceptable as a vessel due to poor resistance to particle abrasion. A high-torque, low-rpm stirring motor and its accompanying solid-state controller are adequate to provide positive, variable-speed propulsion of the stirring rod. A conical bearing surface for the stirring rod on the bottom of the vessel is an important improvement because it assures positive centering of the stirring rod in the vessel and minimizes grinding action and clogging between the stirring rod end and the vessel bottom.

A tumbler is a rotary extractor consisting of a rack-or box-type device holding a number of plastic or glass bottles which are rotated at about 29 rpm. Manual pH adjustment is used. Glass or fluorocarbon bottles must be used for wastes containing organic compounds.

After the solid material and deionized water are placed in an extractor, agitation is initiated and solution pH is measured in situ. If pH is greater than 5.0, the pH of the solution must be decreased to 5.0 ± 0.2 by the addition of 0.5 N acetic acid. If the pH is equal to 5.0 or less, no acetic acid is added. pH may be controlled either manually at increasing intervals of 15, 30, and 60 min up to 6 h or a pH controller connected to a pump can be used to maintain pH for the 24 h extraction period. The amount of acid added cannot exceed 4 ml acid/g solid or the solid-liquid ratio will exceed 1:20. If, for a 100-g sample, the volume of acid added reaches 400 ml, the extraction continues up to 24 h but no more acid is added. An example of the inability of 400 ml of 0.5 N acetic acid to control the pH of a sludge with very high alkalinity was illustrated by Epler <u>et al</u>. (1980), who conducted the EP on textile wastes. The addition of the maximum acetic acid only lowered pH from 8.7 to 7.3. At the end of the 24-h extraction period, deionized water is added to the extractor to bring the solid-liquid ratio to 1:20. For example, with 100 g of solids using 250 ml of acetic acid, 150 ml of water must be added.

Following the adjustment of the solid-liquid ratio to 1:20, the mixture of solids and leaching solution is separated by filtration. The solids are discarded and the liquid is combined with any filtrate originally obtained. This mixture constitutes the EP extract and is subjected to analysis.

Column Leach Tests

Column leach tests more closely approximate landfill performance kinetically than do batch leach tests. Column tests, however, often require more time to perform than batch tests. No bench-scale column test procedure for predicting waste performance when co-disposed in a sanitary landfill has been published as an acceptable leach test.

Chemfix developed a column percolation test in 1974 to characterize the rate of leaching on small samples of solid waste (Federal Register, 1978). This was a steady state procedure with distilled water entering and leaving the column at 1 ml/min to simulate leaching by rain or groundwater. A 100-g sample was placed in a 4 x 60 cm chromatography column containing 2.5 cm of cotton or glass wool at the bottom interface (Boyle <u>et al.</u>, 1979). Leachate was collected in 100 ml increments for analysis. Passing 800 ml of distilled water through the column simulated 63.5 cm of rainfall passing through a land-fill.

Minor <u>et al</u>. (1980) reported on the development of a dynamic test to simulate the environment of a segregated landfill and to test the leaching tendencies of electroplating sludges in such an environment. The test was simple to minimize test variables. Sludges were subjected to a constant head of 7.6 cm of deionized water to simulate percolation of rainwater through a landfill at a constant rate. Leaching rates, while relatively constant for each sludge, varied from 60 to 2200 ml/d or 1.0 to 35.6 cm of rainfall. The samples were not allowed to run dry to prevent cracking and short-circuiting of leaching solution. Leachate was measured for pH, conductance, and metals on Days 1, 2, 3, 5, 7 and every seventh day thereafter.

SLUDGE RECLAMATION AND WASTE ULTIMATE DISPOSAL

Wastes solids generated in a plant are usually subjected to processes involving volume reduction such as thickening and dewatering before ultimate disposal. Reduction in waste handling and disposal can also be achieved through recovery of useful by-products. In this regard, sludges from aluminum finishing industries have potential for recovery of alum from waste suspensions.

Reclamation of Aluminum from Sludges

Aluminum sludges from aluminum finishing industries contain mainly aluminum hydroxide with varying degrees of impurities, such as heavy metals and organic substances. Aluminum sludges may be reclaimed by conversion of aluminum hydroxide to aluminum sulfate. This conversion may be carried out in two steps; aluminum dissolution or acid extraction and impurity removal which may be achieved with several processes, e.g., ion exchange and ultrafiltration.

In practice, water treatment plant sludges, referred to as "alum sludges", have been used for the recovery of aluminum for reuse as a coagulant (i.e., as "alum" or aluminum sulfate). Since aluminum sludges from aluminum finishing industries and alum sludges contain the same primary constituent, i.e., aluminum hydroxide, it is possible that aluminum recovery technology used with alum sludges may also be applied to aluminum finishing sludges. Aluminum recovery practices used in conjunction with alum sludges are described below.

Acid Extraction --

Recovery of aluminum from alum sludges with the use of an acid, usually sulfuric acid, is a well known process. As early as 1903, aluminum recovery was practiced in the United States (Roberts and Roddy, 1960). Later, the process found wide-spread application in countries such as Japan, Great Britian and Poland (Chen et al., 1976).

Although some variations of the acid extraction process may be encountered in practice, the process generally consists of a rapid-mix unit followed by a separator as indicated in Figure 8. Alum sludge is thichened in a gravity thickener and sludge from the underflow is pumped into a rapid-mix tank where it is mixed with sulfuric acid. The acidified sludge is transferred to a separator with the supernatant from the separator being liquid alum which can be reused as a coagulant in the water treatment process. Sludge from the underflow of the separator is neutralized with lime in a neutralization tank and transferred to a dewatering unit. Solids from the dewatering unit are disposed to a water body or a sanitary landfill for final disposal. The liquid may be returned to the treatment plant or disposed to a water body. An alternate process used by Webster (1966) included the use of a separator equipped with a slow-speed stirrer as a replacement for the rapid-mix unit.

The strength of recovered alum should be greater than 2.0 percent since at lower solution strengths the rate of coagulation is greatly reduced. Solutions with an alum content lower than 1.0 percent alum may not be suitable for coagulation (Fulton, 1974). For this reason concentrated sludge from a gravity thickener should contain at least 2 percent solids before the acid extraction is to be initiated.

In the rapid-mix tank, reaction between sulfuric acid and aluminum hydroxide may be written as follows

$$2A1(OH)_3 + 3H_2SO_4 \Longrightarrow A1_2(SO_4)_3 + 6H_2O$$
(19)




As is apparent from the stoichiometric relationship, the amount of aluminum recovered varies with the quantity of acid added. Chen et al. (1976) observed that most sludge samples exhibited an acid demand which could be predicted from stoichiometric considerations for up to about 80 percent aluminum recovery. Beyond this level, acid demand could not be determined from stoichiometric relationships. It was also indicated that one of the sludge samples appeared to have an immediate acid demand which was unrelated to the aluminum recovery process. When aluminum recovery was 80 percent effective, suspension pH was 3.0 for most of the sludge samples. Cornwell and Susan (1979) reported that aluminum recovery varied between 50 to 90 percent at pH 3 with five alum sludges . In addition, the optimal acid dose occurred at a sulfuric acid to total aluminum molar ratio of].5:1 which was approximately equal to the stoichiometric ratio. However, further increases in acid addition did not appear to increase aluminum recovery significantly. Experience at full-scale aluminum recovery plants in Japan indicated that 50 to 70 percent aluminum recovery at pH 2-2.5 is observed with alum sludges (Gruninger, 1975). Gruninger (1975) observed in pilot plant studies that about 75 percent of influent aluminum hydroxide was recovered as alum at pH 2. However, Lindsey and Tongkasame (1975) reported 98 percent aluminum extraction at pH 2. Webster (1966) found that aluminum recovery was about 80 percent complete at pH 3.

With most alum sludges, complete (100 percent) aluminum recovery is possible. However, unwanted usbstances, such as toxic metals, are also dissolved and may accumulate to undesirable levels upon recycling of alum sludge. Webster (1966) and Isaac and Vahidi (1961) reported that supernatant coloration increased significantly at pH levels below pH 3. Isaac and Vahidi (1961) observed that the amount of color extracted from sludge had an adverse affect on the efficiency of the recovered alum as a coagulant.

Wide variations observed in aluminum recovery may be due to different sludge characteristics and experimental conditions employed. For example, Webster (1966) employed a slow-stirred settling unit with a detention time of 24 h in place of a rapid-mix unit. Chen <u>et al.</u> (1976) used a mixing unit with a 30 min detention time and stirring rate of 30 rpm. Cornwell and Susan (1979) applied a detention period of 15 min while Westerhoff and Daly (1974) reported the use of a 25 min detention time for the acidulator in a pilot-plant study and 10 min in full-size plants in Japan. Goldman and Watson (1975) used a detention time of 10 min in the acidulator and Gruninger (1975) found that longer detention that recovered alum concentration increased linearly with increasing solids concentration.

Alum sludge is typically difficult to thicken and dewater because the gelationous aluminum hydroxide matrix binds large amounts of water. Acidification of the sludge first releases some of the bound-and free-water from the matrix. Continued acidification releases water further and aluminum dissolution starts. After acidification, the remaining sludge suspension settles and thickens well. The volume of sludge settled varies with the degree of acidification (pH) and detention time in the separator. Although very low pH (less than 2) values can be applied to obtain complete aluminum recovery this is generally not suggested because of dissolution of color and other impurities. Therefore, process conditions must be established to achieve the desired aluminum recovery, minimize solution color and impurities and maximize conditioning and dewatering characteristics of the residual sludge. Once an effective pH value is chosen, the effect of variable such as detention time can be examined.

Detention times employed in practice for separators vary widely. The detention time employed by Chen et al. (1976) was 1 hour for settling tests conducted in a *i*=1 graduated cylinder. Cornwell and Susan (1979) used a 1-1 graduated cylinder as a settling column and a 2-hour settling time. A volume reduction of approximately 80 percent was observed with three sludges (Cornwell and Susan, 1979). However, prior to acidification, sludge volume reductions of only 7 percent were achieved. In addition to sludge volume reduction, a reduction is achieved in the dry weight of residual solids. Isaac and Vahidi (1961) observed that the sludge volume could be reduced by 67 percent at pH 3 after 24 h settling in a 250 ml graduated cylinder, and higher volume reductions were possible at lower pH values. However, in this case, coloration of supernatant occurred very rapidly. Goldman and Watson (1975) found that sludge volume could be reduced from 890 ml to 435 ml by lowering pH from 7.1 to 3.0 and employing a settling period of 1 hour in a 1-1 graduated cylinder. Westerhoff and Daly (1974) reported on the use of 14 to 20 h detention times for the separator in pilot-plant studies. Detention times ranging from 14 h to 60 h did not influence the concentration of recovered-alum. Finally, Webster (1966) used a detention period of 5 days in a separator.

Sludge from a separator is typically neutralized by lime addition and is then subjected to one of many commonly employed dewatering processes, such as vacuum filtration, centrifugation, and filter-press filtration. Chen et al. (1976) reported that the filtrability characteristics of acidified sludge (i.e., sludge remaining after acidification) varied with the extent of aluminum recovered or the extent to which pH was lowered. Specific resistance of all sludges generally decreased initially and then increased with increasing percent aluminum recovered. The minimum specific resistance corresponded to 60-80 percent aluminum recovery. Minimum specific resistances obtained with acidified sludges were 2 to 7-fold less than the specific resistance of original sludges. Similar observations were reported by Goldman and Watson (1975) and Gruninger (1975). Isaac and Vahidi (1961) reported that when the pH of alum sludge was reduced from about 7 to 5 with the addition of sulfuric acid, in addition to the reduction in the volume of sludge, the specific resistance of the acidified sludge was reduced more than 2-fold. After dewatering waste sludge solids are transferred to a disposal site which could be either a landfill or a body of vater.

Supernatant from a separator and dewatering equipment should be tested for impurity concentration and for effectiveness as a coagulant. Complete recovery of aluminum and elimination of the use of virgin acid may not be effectively ichieved. Therefore a mixture of recovered alum and virgin alum is typically ised. Alum impurities must be considered in this regard. Impurities in recovered alum may include:

- (1) impurities converted to the soluble form in the acidulation process such as iron, manganese, chromium and other metals,
- (2) impurities present in sulfuric acid added, and
- (3) inert additives (such as clay and carbon for water treatment plant sludges) that may not be completely removed after the acidulation process.

The concentration of impurities vary with the type of sludge and amount of sulfuric acid added.

Characteristics of an alum sludge from a water treatment plant and the supernatant collected from the acidified sludge are presented in Table 8.

TABLE 8.	CHARACTERISTICS	OF AN AI	LUM SLUDGE	AND	SUPERNATANT
	FROM AN A	ACIDIFIE) SLUDGE*		

	Parameter	r <u>Concentration</u> or Value
	Alum	Supernatant from
Parameter	Sludge	Acidified Sludge
рН	6.5	3.0
Alkalinity, mg/l as CaCO ₂	297	-
Acidity, mg/l as CaCO ₂	197	-
Total Solids (TS), mg/l	5740	9630
Suspended Solids (SS), mg/1	5630	_
Volatile Solids, % of TS	60.3	63.5
COD, mg/1	2740	2740
TOC, mg/1	1050	1050
Color	Brown	Brown
Turbidity_JTU	7500	-
A1 $mq/1$	795	740
Fe mg/1	29	29
Ca mg/1	nil	nil
Mg mg/1	nil	nil
PO ₄ -P, mg/1	nil	nil

* Lindsey and Tongkasame, 1975

The aluminum concentration of 740 mg/l presented in the table is equivalent to 1400 mg/l of Al₂O₃ or 0.14 percent. All of the iron present in sludge was dissolved at pH 3 and the iron concentration of 29 mg/l corresponded to fl mg/l of Fe₂O₃ or 0.0041 percent. For purposes of comparison, a typical analysis of liquid aluminum slufate (Manufacturer Allied Chemicals, N. J.) is presented in Table 9. In the commercial grade alum, the total Al₂O₃ was 8.3 percent and total iron as Fe₂O₃ was 0.2 percent. While the iron content of acidified sludge was very low, the aluminum content was also very low. That is, the ratio of (Al₂O₃) in commercial alum to that in the acidified sludge was 60. Since it is suggested that alum solutions lower than 1.0 percent might not be suitable for coagulation (Fulton 1974), the strength of a solution from an acidified sludge sludge can be increased by increasing suspended solids concentration. Westerhoff and Daly (1974) reported that recovered-alum concentration increased from 0.25 percent to 0.75 percent linearly with the increase in sludge solids concentration from 1.0 percent to 6.5 percent.

	Grade of Aluminum Sulfate					
Constituent	Commercial**	Iron-Free				
Total Al $_{0}$ (%)	8.3	8.3				
Free Alog $(\%)$	0.1	0.1				
Total Iron as Fe ₀ 0 ₂ (%)	0.2	0.004				
Actual Fe $_0(\%)$ 2 3	0.03					
Insoluble in water (%)	0.01	0.004				
Lead, mg/l	4					
Cadmium, mg/1	0.5					
Copper, mg/1	2					
Silver, ma	0.1					
Chromium, mg/l	30	•				
Arsenic, ma/1	0.1					
Zinc. mg/l	1					
Nickel, mg/l	1					
Titanium, mg/l	130					
Strontium, mg/1	1					
Calcium, mg/1	1					
Magnesium, mg/1	6					
Sodium, mg/l	80					
Potassium as K ₂ O ₂ , mg/1	7					
Manganese, mg/f 3	I					
Cobolt, mg/l	3					

TABLE 9. COMPOSITION OF LIQUID ALUMINUM SULFATE*

* Allied Chemicals, Inc.

** Aluminum sulfate manufactured from bauxite

The effect of repeated use of recovered alum solution on water quality was studied by Webster (1966). Over the 10-month test period the quality of water treated with recovered alum was considerably better than raw water as indicated in Table 10.

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TABLE 10. COMPARISON OF RAW WATER QUALITY WITH TREATED WATER QUALITY

Parameter	Raw	Treated Water	
	05 50		
Color, Hazen units	25-50		
pH	6.8-7.4	5.5*	
Iron, mg/l	0.08-0.19	0-0.05	
Manganese, mg/1	0-0.05	ni1-0.04	
Silica, mgSi/1	3-5	1-4	
Zinc, mg/1	0		
Copper, mg/l	0	-	
Lead, mg/1	0	100 C	
A1, mg/1		<0.1	

* pH when raw water pH = 6.8

Similar observations were reported by Westerhoff and Daly (1975). They reported that, according to the results of bacteriological, physical and chemical analysis including 10 heavy metals, there was no indication of a buildup of any constituents in the effluent from a pilot plant when compared to the effluent of a full-scale plant using commercial alum after eighteen alum cycles. However, there was an indication that aluminum concentration was higher in treated effluent. Although some studies indicated that there were no buildup of heavy metals in plant filtered water with the repeated use of recovered alum, it was suggested that in those studies, the lack of contaminant accumulation appeared to result from the relatively high quality of the raw water (Westenhoff and Cornwell 1978). Recent concern over the danger from a possible accumulation of heavy metals and consequently a degredation of plant filtered water has halted the use of recovered alum in plants constructed after 1972 (Committee Report, 1978). Several methods to remove metals are in the development stage such as solvent extraction and ultrafiltration.

Solvent Extraction--

A schematic diagram of the liquid-ion exchange process for recovering alum is presented in Figure 9. Aluminum hydroxide sludge is concentrated in a gravity thickening unit and then mixed with sulfuric acid in an acidulator. Acidified supernatant containing aluminum is separated from the remaining sludge. Sludge is neutralized with lime and dewatered for ultimate disposal. Supernatant is transferred to a liquid-ion exchange unit for removal of heavy metals.



Figure 9. Schematic Diagram of Alum-Recovery Process

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In a liquid-ion exchange system an organically-soluble substance the extractant, is dissolved in an organic solvent, the diluent. This mixture of extractant in diluent may be referred to as the organic or solvent phase. The system can be operated either diluent-continuous or water-continuous. In the former case, the diluent and water are mixed in such a way that water droplets are formed and in the latter case, organic droplets are formed. In the extraction process, the extractant reacts chemically with aluminum ions present in water droplets to form a metal-extractant complex that is soluble in the diluent. The extractant contains nonpolar and polar portions as indicated in Figure 10. The nonpolar portion contributes to extractant solubility and the polar portion is the reactive site. Active sites of the extractant ionize (Figure 10a) and aluminum ions are exchanged for H⁺ ions with H^+ ions being transferred to the aqueous phase and A1³⁺ ions forming complexes with the extractant (Figure 10b). When the mixture (water solvents) is transferred to a separator the two phases, i.e. aluminum-rich organic phase and aluminum-free aqueous phase, are separated (Figure 10c). In the second step of the extraction process $A1^{3+}$ ions are stripped from the extractant using sulfuric acid. In this cycle, H ⁺ ions exchange for $A1^{3+}$ ions at the active sites on the extractant resulting in production of a regenerated extractant and an acidified solution of aluminum sulfate.

Extractants should have certain properties to be used in aluminum extraction. These include high reactivity with aluminum, stability, low toxicity and low water solubility. Cornwell (1979) used acidic organophosphorus (i.e., Mono and Di(2-ethylhexyl) Phosphoric Acid) extractants for aluminum extraction. In addition to the diluent and the active extractant in liquid-ion exchange, there may be a third reagent called a modifier. The primary functions of modifiers are to exert a synergistic effect on extraction processes, improve phase separation (i.e., water-solvent phase) and prevent the formation of some insoluble compounds in the organic phase.

Since there are many candidate organic solvents, it is necessary to exaluate the effectiveness of some of them. In addition, it is necessary to evaluate the effect of experimental variables on the extraction procedure. These include feed pH and Al³⁺ concentration mixing intensity and duration, and sulfuric acid strength.

Cornwell and Lemunyon (1980) working with a synthetic aluminum solution found that impeller tip velocity of 4 m/s with an equilibrium time of 7 min was optimum to achieve 100 percent extraction equilibrium for an experimental run in which the following conditions were used: 0.1M mono and di(2-ethylhexyl) phosphoric acid (MDEHPA) as extractant; kerosene as diluent; a feed pH of 2.0; an initial aluminum concentration of 1000 mg/l and a phase ratio of 1:1 on a volumetric basis. It was observed that aluminum concentration extracted from the feed increased with increasing feed pH and feed aluminum concentraiton. Cornwell and Lemunyon (1980) studied the relative selectivity of MDEHPA for aluminum over various metals, such as copper (II), cadmium (II), manganese (II), zinc (II), iron (II), iron (III) and chromium (VI). A solution of 500 mg/l aluminum and 25 mg/l of the selected metal was contacted with 0.1M MDEHPA. For each metal the selectivity ratio was determined. The selectivity ratio is the ratio of the extraction coefficient of aluminum to the extraction





coefficient of the metal in question. The extraction coefficient is defined as the ratio of the metal concentration in the organic phase to that in aqueous phase at equilibrium. A high value of the selectivity ratio indicates that MDEHPA is highly selective for aluminum over the selected metal. The results indicated that the selectivity ratio varied from 6 for Fe(III) to 930 for Zn(II).

Similar results were observed in extractant stripping studies. Impeller speed, equilibrium time, acid strength and type were found to influence the efficiency of stripping (Cornwell and Lemunyon, 1975). The experiments using aluminum solutions were repeated with alum sludge suspensions. It was reported that while the rate of alum recovery was slower with alum sludge, stripping rate was the same as obtained with synthetic solutions.

Ultrafiltration --

In the alum recovery process, pressure-driven membrane processes such as reverse osmosis (RO) and ultrafiltration (UF) can be used for removal of color. Ultrafiltration membranes are noncellulosic, organic polymers having a thin $(5\mu m)$ surface layer and a porous structure. Separations take place at the membrane surface and in the supportive, porous structure. Openings at the surface are larger than water molecules but smaller than molecules, such as color bodies, enzymes and proteins of higher molecular weight. Ultrafiltration processes were examined by Lindsey and Tongkasome (1975) for removal of color and high molecular weight organic compounds. It was found that with PMIO membranes, TOC removal ranged between 50 to 66 percent. Permeate (solution passed through membrane) and aluminum recovery were over 90 and 80 percent, respectively.

Ultimate Disposal of Sludge

Examination of ultimate disposal of aluminum-finishing sludges is facilitated through examination of similar sludge suspensions generated in the treatment of surface waters for drinking purposes. Such alum sludges are subjected to a number of operations for volume reduction and reclamation. The resulting sludge solids are ultimately disposed to the environment, i.e., to land, water or air. A number of disposal sites for alum sludges (Committee Report, 1972) are listed in Table 11. Although lakes and streams constituted the main body of disposal sites by 1969, their use as an ultimate discharge location decreased considerably from 1953 to 1969 because of the concern over possible damage of alum sludges on marine life. While 92 percent of water treatment plants discharged alum sludges into lakes and streams by 1969. Contrary to the policy on marine discharge, the land application of alum sludges increased from 4 percent in 1953 to 30 percent by 1969. Similarly,there was a large increase in disposal of alum sludge to sewer systems for the same period.

Disposal to Land --

A number of sludge disposal alternatives are available for inland communities, such as disposal in a lagoon, landfilling or into a sewer system.

	Percentag Indicated	e of Plant Using Disposal Methods	
Point of Disposal	1953	<u>1969</u>	
Stream or Lake	92	49	-
Sewer or Drain	4	21	
Dry Creek	1	6	
Landfill	0	- 6	24.5
Lagoons	3	18	
Recycled	-		

TABLE 11. METHODS FOR DISPOSAL OF ALUM SLUDGES

<u>Lagooning</u> -- Lagooning of alum sludges may be preferable for rural areas where land is available and inexpensive. There are basically four factors that must be considered in the design of lagoons; 1) the volume of sludge to be handled, 2) the quantity of dry solids, 3) the rate of evaporation from a lagoon and the frequency of cleaning desired.

Lagoons are usually constructed by excavation or by enclosing a lowlying area with dikes and care must be taken not to create any health or other hazards. They must be built as at least two basins so that while sludge is drying in one of the basins the other one can be used for disposal. In cases, when a lagoon is not the ultimate disposal site, a third lagoon may be required for cleaning and preparation for sludge discharge. Lagoons can be operated in several ways: (1) lagoons can be filled at one time and left for drying. (2) sludge can be applied as shallow layers followed by drying. (3) a single shallow sludge layer can be applied. In the latter case, sludge lagoon a sludge drying bed. Other design information for lagoons are given by Bishop and Fulton (1968).

Landfilling -- Disposal of alum sludges to landfill has shown considerable increases in the past 10-15 years. Alum sludge can either be disposed to a sanitary landfill or to a segregated landfill. The disposal of alum sludge to a sanitary landfill has become a point of concern for regulatory agencies because sanitary landfills are anaerobic systems in which pH is in the range of 5.5 to 7.0. In this acidic pH range heavy metals may be dissolved in leachate and pollute groundwater supplies. To determine the extent of groundwater contamination by land disposal of lime-conditioned alum sludge, a lysimeter study was conducted by Monroe County Water Authority in New York State (Committee Report, 1978). The lysimeter was operated for 79 days with a total of 12m³ leachate passing through the lysimeter which was equivalent to 35 years of rainfall. If it is assumed that 50 percent of rainfall infiltrates the ground, the equivalent testing period of the lysimeter was about 70 years. The results of this study were: (1) pH ranged between 9 and 10; (2) aluminum concentration in the leachate first increased to 11 mg/l during the first seven days and decrease to 3 mg/l for the remainder of the period; (3) the concentration of chlorides increased to 16.1 mg/l by the end of the experiment. Based on these observations it was reported that a sanitary landfill containing alum sludge and refuse with a pH 9 might have an aluminum concentration of 6 mg/l. Assuming a dilution of 100/l with groundwater, it was estimated that aluminum concentration in the groundwater would be about 0.06 mg/l which is a level comparable to the concentration in finished water from a water treatment plant. The study concluded that landfilling of alum sludge was feasible in a special landfill where only dewatered sludge was deposited or at a sanitary landfill site in combination with other waste. In another study on disposal of alum sludge on land, it was found that the toxicity of the runoff from dried sludge was negligible (Nielsen et al.1973).

Very few studies have evaluated the effect of leachate from alum sludge on groundwater, surface runoff and land pollution. Therefore, additional studies are needed to determine the concentration of heavy metals in leachate and their subsequent effects on groundwater, surface runoff and land.

There are a number of examples of alum sludge disposal practices to landfills (Committee Report, 1978). In Atlanta, dewatered alum sludge from the Chattahoochee and Hemphill Water Treatment Plants are transported to a sanitary landfill site. It is mixed with the garbage and spread and compacted by a bulldozer or landfill compacter. In Houston, alum sludge cake is mixed with soil and spread and compacted by a bulldozer at the disposal site next to the water treatment plant. In Oakland, Sobrante filter plant of East Bay Municipal Utility District was initially required to dispose to only Class 1 landfills. However, after economic impacts of such limitation were investigated sludges from this plant is now accepted to Class 2 landfills. New York classifies alum sludge as an industrial sludge which is not permitted to a sanitary landfill.

Discharge to Sewerage System -- Disposal of alum sludge to sewerage systems has also increased considerably in the past 10-15 years. There are diverse reactions as to the effect of alum sludges on sewage treatment plant operations. In some plants, alum was reported as helpful in assisting coagulation of sewage solids. In others, poor dewatering characteristics of alum sludge led to higher sludge volumes and an increase in digestion capacity (Committee Report, 1972). AWWA Research Foundation on Disposal of Water Treatment Wastes (1969) recommended that the following considerations should be evaluated before discharging a coagulant sludge (e.g., alum sludge) into a sewer system: (1) Damage by sludge to sewer system, (2) Amenability of sludge to existing wastewater treatment processes, (3) Hydraulic capacity of sewage treatment facilities and (4) The effect of sludge on the efficiency of sewage treatment systems.

Disposal to Water --

The discharge of alum sludges into a water body is the most economical method of disposal. However, growing concern of regulatory agencies on the toxic effect of heavy metals on marine life have eliminated this method of disposal. Two types of ocean disposal have been practiced - pipeline transport with discharge through diffusers and transport by barges or tankers (Dick, 1972). With the ocean outfall systems, sludge is introduced at the ocean bottom through a diffuser designed to provide a high initial dilution and subsequent dispersion for a given location and to mix sludge and seawater in proportion which prevent sludge rising through the density gradient of the ocean to the surface. Ocean outfall systems are most common on the West Coast of the United States where deep-water bodies are encountered at short distances. Two major criteria in designing ocean disposal systems for domestic wastewater sludges have been bacteriological quality in nearby beaches and the magnitude of initial dilution. With alum (and aluminum-finishing) sludges the primary concern is initial dilution, since bacteriological quality is not of concern.

Sludge disposal by barges and tankers has been more common on the East Coast of the United States where the ocean is relatively shallow. Committee Report (1972) indicated that some water-treatment plants have barged their sludge as far as 200 miles. A disadvantage of this method of disposal is that sludge is released to the surface layer of the ocean. However, the advantage is that sludge is not discharged to a fixed location continuously.

Disposal to Air --

Biological and thermal decomposition of organic matter releases carbon dioxide and water into air. However, alum sludges contain very small amounts of organic material and it is not practical to decompose it biologically and thermally. The athmosphere is furthermore not suitable for disposal of particulate materials of alum sludge.

SECTION 5

METHODS OF ANALYSIS AND EXPERIMENTAL APPARATUS

To accomplish the objectives of the project, samples from various aluminum finishing industries were subjected to physical and chemical characterization which included settling, specific resistance, filter leaf, CST and sludge drainage bed tests as well as routine chemical analyses. The sampling locations used at each plant are described in conjunction with the presentation of sludge characteristics. In most cases, samples were taken from locations permitting a mass balance on conservative substituents. Samples were also coded to indicate day (Julian calendar) and year of collection, plant type and identity of sampling location. For example, code A3-201-79-1 indicated that sample number 1 was collected from anodizing plant (A) designated Number 3 (i.e., A3) on day 201 (June 12) in year 1979.

SAMPLE COLLECTION

Extensive research was conducted using sludges collected from three extrusion/anodizing plants located in Georgia (2) and Arkansas and one etch plant in Ohio. To conduct a detailed examination of the physical and chemical properties of wastewaters produced at these facilities, large volumes of wastewater were required. Since a number of the plants applied polymeric-conditioning agents to neutralized wastewaters, wastewater samples were collected from neutralization basin effluents prior to polymer addition. Since extensive testing of sludge physical properties required a minimum of 2 kg of suspended solids and effluent suspended solids concentrations were as low as 1-2 g/l, wastewater samples of $0.4-1\text{m}^3$ (100-250 gal) were commonly collected. Except at plant A3 (see Section 7) where project personnel collected wastewater samples, plant personnel were responsible for collection of wastewater samples. Washed, plastic-lined carboys $(0.2m^3)$ were used for collection and transport of wastewater suspensions. Carboys of wastewater were shipped directly to the laboratory over a 2-3d period. Upon receipt, all carboys were emptied into a large epoxy-lined container and mixed extensively to eliminate minor variations between the several wastewater samples. A volume (e.g., 1-51) of this mixed wastewater was collected immediately for detailed chemical analysis. The remaining suspension was immediately examined extensively over a 7 to 10d period.

ANALYTICAL METHODS

Routine Chemical Analyses

Samples in suspension and solution form were routinely subjected to initial characterization for pH, alkalinity or acidity, total solids (TS), total volatile solids (TVS), suspended solids (SS), volatile suspended solids (VSS) and aluminum concentration. Total carbon and inorganic carbon analyses were carried out using a Beckman Model 915 Total Organic Carbon Analyzer for filtered samples. Analyses for pH, alkalinity, acidity, TS, TVS, SS and VSS analyses were performed in accordance with methods presented in Standard Methods (1976).

Samples for aluminum determination were pretreated prior to analysis. Suspensions were acid-digested in accord with the method given by EPA (1979). For solutions, pH was lowered to less than 2 with the addition of concentrated nitric acid, HNO₃. Aluminum determinations were made by use of a Perkin-Elmer Atomic Absorption Spectrophotometer (Model 303). Suspensions were further subjected to pretreatment for Instrumental Neutron Activation Analysis (INAA) to determine the type of elements present in the solid and solution phases of the sample. A sketch of the pretreatment steps are given in Figure 11.

Trace Metal Analysis

Preservation and Storage--

In analyzing for trace amounts of metals, special attention was paid to storage and treatment of samples. Sample containers were chosen to avoid metalbinding sites or release of contaminating metals into sample solutions and inert linear polyethylene containers were used throughout the study. An initial detergent cleaning was followed by soaking polyethylene containers in 1:1 HCl for 7 d followed by soaking in 1:1 HNO3 for 7 d (EPA, 1980a). The containers were then rinsed twice with distilled water and soaked in double-distilled water at least 7 d or until needed.

Preservation of samples for trace metal analysis was by the addition of 2 ml of concentrated HNO₃/l of sample, resulting in a 0.2% HNO₃ matrix recommended for most atomic absorption spectrophotometry. Most acidifed solutions are stable for several months, although the maximum storage time before deterioration is highly dependent on sample composition. Methods of preservation of hazardous waste recommend acidification without refrigeration for dissolved metal analysis and samples for this project were stored up to one month prior to analysis, although 6 months was acceptable (EPA, 1980b).

Digestion Procedure--

For determination of total metals in dewatered sludge samples, a digestion procedure was performed as specified by EPA (1979). A 1-g sample of dewatered sludge was weighted to ± 0.1 mg in a tared 250-ml glass beaker and the sludge was suspended in 50 ml of double distilled water and 3 ml of Ultrex ultrapure HNO₃. After covering with a watch glass, the beaker was placed on a hot plate and evaporated to near dryness without boiling. After



Figure 11: Treatment of Aluminum Sludge Samples for Routine Chemical Analysis and Neutron Activation Analysis (INAA) cooling, another 3 ml of HNO₃ was added and the beaker was returned to the hot plate at a slightly higher temperature so that refluxing occurred. After another cooling and third addition of 3 ml of HNO₃, refluxing completed the digestion, as the liquid was light yellow in color with no suspended colored particles. After cooling, 0.5 ml of HNO₃ was added and the beaker walls were washed down with double distilled water. The contents were diluted to 100 ml and filtered with a 0.45 μ m membrane filter to remove silicates and insoluble material that could clog the atomizer of the flame atomic absorption spectrophotometer.

Metal Analysis--

Three methods were used for metal analysis: flame atomic absorption, graphite furnace atomic absorption, and cold vapor method of mercury determination. Flame atomic absorption was used for all Zn determinations and for Cu and Ni determinations above 2 mg/l to insure more accurate results than would be possible due to an excessive number of dilutions, i.e., 10^{-3} , required if the graphite furnace were used. The graphite furnace was used to determine all 13 inorganic priority pollutants, except Hg and Zn, present in concentrations below 2 mg/l.

<u>Graphite Furnace Atomic Absorption</u> - Analytical Methods -- Determination of eleven metals (i.e., Ag, As, Be, Cd, Cr, Cu, Ni, Pb, Sb, Se, Tl) was by flameless atomic absorption using a graphite furnace due to its high sensitivity. The instrument utilized was a Perkin-Elmer Model 703 atomic absorption spectrophotometer equipped with a Deuterium Background Corrector, a Perkin-Elmer Model HGA-220 Graphite Furnace, a Perkin-Elmer HGA-2200 Controller, and a Perkin-Elmer Model 56 strip chart recorder. The atomic absorption spectrophotometer provided integrated readings in absorbance, concentration, and emission intensity. Background correction was used with all metals. Integration times were different for each metal and were equal to about 75% of atomization time.

The graphite furnace, approximately 28 mm long and 8 mm in diameter, was installed in the sample compartment of the spectrophotometer. The tube was positioned so that the spectrophotometer sample beam passed through the tube center. Samples were pipetted using fixed volume (5, 10, 20 or 50 μ l) pipettes through the center hole of the tube. Disposable pipette tips were used to reduce the risk of contamination. If there had been any question of contamination between samples, pipette tips would have been pretreated as described for polyethylene bottles.

The operational variables for the graphite furnace system are summarized in Table 12. Purge gas for the graphite furnace was argon, supplied at a flow of 35 ml/min. A gas-interrupt mode was used for Ag, Cd, Cr, Cu, Ni and Pb to increase sensitivity. As and Se analyses were performed using special treatment with Ni(NO₃)₂, due to their high volatility. After addition of Ni(NO₃)₂, the sample could be charred at a higher temperature without loss of metal and still give complete ashing and removal of matrix constituents that caused interference during atomization. The Se matrix was prepared by adding 2 ml 1:1 HNO₃, 2 ml 30 percent H₂O₂, and 2 ml 5 percent Ni(NO₃)₂ solution to both the standard and sample volumes of 100 ml and for

Meta]	Matrix	Wavelength	Tem	perature &	Time	Integration	Detection
		(nm)	(^o C, s)	Ash (^o C, s)	Atomize (^O C, s)	Time (s)	Limit* (µg/l)
Silver, Ag	0.2% HNO ₃	328.1	125 ,6 0	400, 35	2700,10	7	1
Arsenic, As	1% HNO ₃ + 1% Ni(NO ₃) ₂	193.7	150, 70	1000, 20	2700,10	. 4	4
Beryllium, Be	1% HC1	234.9	125,60	1000,40	2800,10	7	0.2
Cadmium, Cd	0.2% HNO3	229.4	125,60	250,35	2100,10	7	0.1
Chromium, Cr	0.2% HNO3	358.0	125,65	1000,20	2700, 10	7	1
Copper, Cu	0.2% HNO3	325.1	125,60	900,20	2700, 10	7	1
Nickel, Ni	0.2% HNO3	232.3	105,60	600, 30	2800, 5	3.5	I
Lead, Pb	0.2% HNO3	218.4	125, 50	500, 30	2350, 10	· 7	1
Antimony, Sb	0.2% HNO3	217.9	105, 70	205, 20	2500, 3	2.5	3
Selenium, Se	1% HNO ₃ + 2% H ₂ O ₂ + 2% Ni(NO ₂) ₂	196.4	125, 50	1200, 30	2700, 4	2.5	2
Thallium	0.2% HNO ₃	276.8	100,60	100,10	2800, 3	2 '	1

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TABLE 12. GRAPHITE FURNACE OPERATING CONDITIONS

*EPA, 1980a

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As, a 1 percent $Ni(NO_3)_2$ solution was pipetted directly into the graphite furnace. The volume of $Ni(NO_3)_2$ added was equal to the combined volumes of the sample and the added standard solution.

Method of Standard Addition -- Matrix effects can be caused by substances that absorb at the same wavelength as an element. Standard addition methods incorporate matrix effects into the determination of metal concentrations. Known amounts of a standard solution of the metal being analyzed were added to a sample. The sample and the standard were then in the same matrix, so interferences were taken into account (Willard et al., 1974).

To establish the precision of analyses for trace metals, ten identical samples were analyzed for Ag, As, Be, Cd, Cr, Cu, Ni, Pb, and Se. The results of these analyses are presented in Table 13. The lowest coefficient of variation was 11 percent $(27 \mu g/1)$ for Cd and the highest was 89 percent for As (54 μ q/l). Considering the relatively low levels of metal being analyzed, these results compare favorably with those reported by Williamson (1979), who reported coefficients of variation of 4-61 percent for As and 6-80% for Cd from analysis of sewage sludges. Epler et al. (1980) analyzed EP extracts from sewage sludge at Oak Ridge National Laboratory (ORNL) and reported coefficients of variation on the order of ten times lower for quadruplicate samples (e.g., As = 4 percent, Be = 5 percent, Cd = 0 percent, Cr = 6 percent, Cu = 2 percent, Ni = 6 percent, Pb = 10 percent). In another analysis of the identical sewage sludge sample, similar coefficients of variation were reported by a second investigator, but there was a significant difference in accuracy for many metals. Compared to results of ORNL for As, Cr, Cu, Ni, and Pb, the data were 12 percent, 52 percent, 19 percent, 15 percent, and 34 percent higher, respectively, for the second investigation. This comparison would indicate that realistic data could be expected to vary by as much as 60 percent for trace levels of metal.

Cold Vapor Method for Mercury Determination -- The cold vapor method of Standard Methods (1976) was used for Hg analyses. A sample was placed in a reaction vessel (250-ml Erlyenmeyer flask) where 5 ml of conc H2SO4 and 2.5 ml of conc HNO3 were added. After addition of 15 ml of KMnO4 solution (50g/1), there was a 15 min waiting period to insure adequate oxidation of the sample by KMnO4. After 15 min, 8 ml of K₂S₂O₈ solution (50g/l) was added, followed by addition of a solution containing 120g NaCl/l and 120g $(HN_2OH)_2 \cdot H_2SO_4/1$ in sufficient quantity to reduce the excess KMnO₄. The addition was halted as soon as excess KMnO4 was reduced. A 5-ml volume of SnCl₂ solution (100 g/l) was immediately (within 3 s) added and mercury vapor was formed by reduction of mercuric ions in solution. The reaction vessel was inserted into the apparatus rubber fitting as quickly as possible to trap all the mercury vapor. The Hg vapor was swept by compressed air through a drying tube and into an absorption cell where the absorbance was recorded continuously. Standards and samples were run in duplicate with good agreement. The absorbance curve was plotted using relative numerical values of absorbance area which were obtained by weighing cut-out striprecorder paper outlines of Hq absorbance data.

		μg/Ι	<u>μg/1</u>	%%
Ag	A2	7.2	1.7	24
As	A3	54.	48.	89
Ве	A2	0.34	0.16	47
Cd	E1	27.	3.	11
Cr	A1	30.	6.6-	22
Cu	A3	9.1	1.07	12
Ni	A3	1890	400	21
Pb	A2	5.6	1.2	21
Se	A2	130	50	38

TABLE 13. COEFFICIENTS OF VARIATION FOR METALS ANALYZED BY GRAPHITE FURNACE

Mercury standards of 0, 1, 3, and 4 μ g/l were used to develop calibration curves for Hg determination. Absorbance data for standards fit a straight line with absorptivity = 0.0133 1/ μ g-cm and correlation coefficient of 0.9998. Ten samples of filtrate from dewatered A2 sludge were analyzed for Hg with the following results: a mean concentration of 27.0 μ g/l with a coefficient of variation of 34 percent. Williamson (1979) reported similar coefficients of variation.

Flame Atomic Absorption -- When analyzing for Zn, there were high absorbances for blank double-distilled water being used for trace metal analysis by graphite furnace. Therefore, less-sensitive flame atomic absorption was used for Zn determination. A Model 303 Perkin-Elmer Spectrophotometer was used with a range of Zn standards from 0.5 to 3.0 mg/l. Additionally, flame atomic absorption was used for Cu and Ni-concentrations in excess of 2 mg/l. Analyses followed conventional standardcurve procedures. No precision data were obtained for Cu, Ni and Zn analyses; however, analysis of duplicate samples consistently gave identical peak heights when analyzing for these metals.

EXPERIMENTAL APPARATUS AND PROCEDURES

Sludge Settling

Sludge settling equipment consisted of two storage tanks, a centrifugal pump and mainfold system and three circular settling columns with diameters of 6, 9 and 15 cm. The steel storage tanks had volumes of 200% (plastic-lines) and 600% (epoxy-lined) and were used for storage and mixing during the settling tests. A centrifugal pump and manifold system were used to fill and empty settling columns from the bottom at constant rates. Initial sludge depth in columns was 1.0 m. During the settling tests, contents were stirred at column walls with stainless-steel wire mixers rotated at a tip velocity of 0.31 cm/s to minimize wall effects. The tip velocity corresponded to 60, 40 and 24 rph for column diameters of 6, 9 and 15 cm, respectively. Settling tests were conducted by recording the height of the sludge-liquid interface for a least 60 min. To examine sludge thickening properties, settling tests were performed at numerous initial suspended-solids concentrations with dilutions being made in one of the storage tanks using sludge supernatant. To provide a well-mixed sludge sample prior to a settling test, the contents of the storage tank were mixed for approximately 5 min.

In addition to tall settling columns with a sludge depth of 1.0 m, several small columns were used. These columns were standard 1-1, graduated cylinders with a column depth of 44 cm and a diameter of 6 cm. Settling analyses were run at initial sludge depths of 36 cm with a tip speed of 0.31 cm/s and experiments were conducted for a period of at least 60 min.

Sludge Conditioning

Sludge conditioning experiments were performed to determine the effectiveness of selected polyelectrolytes on sludge thickening and dewatering characteristics. A mixing chamber with a diameter of 12.7 cm, a volume of 3.2 and four 1.3-cm wide, 90° vertical baffles was used. Mixing was provided with a variable speed controller and motor using a single steel paddle (2.6 cm x 7.8 cm). A standard 1-1 volume of sludge was added to the mixing chamber, flash-mixed for 1 min at a specified rate and a known amount of polyelectrolyte was added. The rate of mixing was varied from 80 to 730 rpm and the results indicated that the rate of mixing between this range had no significang effect on sludges conditioned at polyelectrolytes doses of up to 4 mg/l (Figure 12). However, later studies indicated that it was impossible to perform accurate settling tests with sludges conditioned at doses greater than 15 mg/l and mixed at higher speeds (i.e., 730 rpm). Air bubbles created during flash mixing accumulated in the upper layer of a sludge in a settling column and the sludge structure was broken into two layers. The upper layer was stagnant throughout the test while the lower layer settled. To prevent these problems, flash mixing was conducted at 200 rpm for 1 min in subsequent tests.

In selection of polymers, the initial criterion were to select types which were being used by aluminum finishing industries from which sludge samples were collected. In addition, another polymer, Caraflok 91AP, was also used for comparison purposes since earlier studies with alum sludges had indicated it to be an excellent conditioning agent. The type and characteristics of the polyelectrolytes used by each plant are presented in Table 14. Since manufacturers use different methods for molecular weight determination, the molecular weight values given in Table 14 should be compared only on a broad relative basis.



Figure 12. Effect of Mixing Speed at Time of Polymer Addition on Zone Settling Velocity

TABLE 14. POLYELECTROLYTE CONDITIONING AGENTS

Polymer	Charge	Mol. Wt.	Composition	Plant
Caraflok 91AP ^a	Slightly Anionic	9 x 10 ⁶	Polyacrylamide	
HF - 190 ^b	Anionic	(Medium)	Polyacrylamide	A1
Separan AP 273 ^C	Anionic	3 x 10 ⁶	Polyacrylamide	Ť A2
Purifloc A23 ^C	Anionic	> 10 ⁶	- Polyacrylamide	A3

a. Carus Chemical Co., LaSalle, IL

b. Amchem Products Inc., Ambler, PA

c. Dow Chemical Co., Midland, MI

Sludge Dewatering

Dewatering characteristics of aluminum sludges were examined using three tests; Buchner funnel test, filter leaf test and Capillary Suction Time (CST) test. In the Buchner funnel test (O'Connor, 1975) specific resistance (resistance exerted by sludge to the passage of liquid under a specified vacuum) of sludges was measured. For this purpose, a 300 ml volume of sludge was filtered under a vacuum of 38 cm Hg (50 kN/m^2) using No. 1 Whatman filter paper placed in a 9-cm diameter Buchner funnel with an effective filtering diameter of 7.5 cm. The volume of filtered liquid was recorded with time and the test was terminated when a major crack in the sludge surface caused a sudden drop in vacuum.

Filter leaf test measurements are used to obtain design and performance data for vacuum filters and were utilized to measure filter yields. An Eimco filter leaf test apparatus, equipped with NY-319F 3/1 Br Twill Multifilament cloth and a filtration area of 92 cm², was operated under a vacuum of 50 cm Hg (66 kN/m²) with a drying time of 1 min and a form time of 2 min. The test was performed in accordance with the method described by O'Connor (1975).

CST is the time required for the liquid fraction of a sludge to travel 1 cm between two concentric circles on filter paper by capillary action (Baskerville and Gale, 1968). CST measurements were used for the comparison of dewaterability of sludges. A type 92/1 CST Apparatus (Triton Electronics Limited) and two hollow, cylindrical, metal reservoirs of 10 mm and 18 mm in diameter were used. The CST filter paper (7cm x 9cm) was Whatman 17 Chromatography-grade paper. These tests were utilized to characterize dewaterability of sludges as well as to determine the effect of polyelectrolyte conditioning on dewaterability. The polyelectrolytes and mixing unit described previously were used for conditioning sludges.

Sludge Drainage

Sludge drainability studies were conducted on conditioned and unconditioned sludges. Eight acrylic and sand-drying beds with an internal diameter of 8.9 cm, height of 50 cm and a flange at the top end were used. The beds consisted of 4 layers; gravel $(0.6 \times 1.3 \text{ cm}; 7.5 \text{ cm depth})$, fine gravel (0.3 x 0.6 cm; 7.5 cm depth), sand (effective size = 0.58 mm, uniformity coefficient = 1.33, 5 cm depth) and fine sand (effective size = 0.21 mm, uniformity coefficient = 2.2, 10 cm depth). Sludge filtrate was collected in acrylic columns (internal diameter = 7.5 cm, height = 40 cm) connected to nozzles at the bottom of sand drying beds. The beds and filtrate collectors were connected with vinyl tubing to form a closed system so that evaporation during gravity drainage could be eliminated. Conditioned or unconditioned sludges of 1-1 volume were applied and filtrate volume was recorded with time. The dewatering effectiveness of polymers was evaluated at optimum doses, i.e., the dose at which the highest settling rate, the minimum specific resistance, the maximum filter yield, the minimum capillary suction time, or maximum sludge drainage rate was observed. For this reason, sludges at a fixed concentration were dosed with incremental doses of a polymer and the optimum dose was determined using a mass ratio (g polymer/g suspended solids). Polymer doses for all other solids concentrations of a sludge were then determined with this ratio.

Extraction Procedures for Dewatered Sludge Samples

The standard EPA Extraction Procedure (EP) was routinely used to examine the leaching characteristics of dewatered sludge samples (EPA, 1980a). An ASTM test, however, was also investigated briefly to determine the effect of using an unbuffered extraction solution on leaching characteristics.

EPA Extraction Procedure --

Apparatus -- The apparatus used for conducting the standard EPA Extraction Procedure (EP) consisted of a 2-1 Pyrex beaker with a Telfon stirrer, a variable-speed electric motor, a pH controller (Fisher Accumet pH Controller Model 650), a plunger pump (Gorman-Rupp 100 ml/min), and a 100-ml graduated cylinder. The plunger pump was the lowest flow rate pump available for use in the laboratory, so that minimal excess acid would be pumped into the 2-1 beaker during the 1-s time lag between pH probe and pump controller. Tygon tubing was used to transfer acetic acid from a graduated cylinder to the 2-1 beaker using the plunger pump. A modification to the 2-1 beaker was a 1-cm high conical tip projecting upward from the center of the vessel bottom as applied by a glassblower. The conical tip functioned as a support to center a stirrer. A Telfon stirrer was fabricated with a 24-cm long shaft which was 1-cm in diameter. Two flat blades, 4.6-cm long and 2.0-cm wide, were attached to the bottom of the shaft using epoxy cement. The blades were at 180° to each other and at 30° to the vertical

Extraction Procedure -- A stirring extraction was performed as specified by EPA (1980a). Dewatered sludge was weighted to 100 ± 1 g and placed in a 2-1 beaker with 1.6 1 double-distilled water. The pH meter was standardized

at pH 4 and 6 and the pH controller was set at pH 5.1. The plunger pump was operated by the pH controller so that 0.5 N acetic acid could be supplied to the 2-1 beaker. With a pH probe supported in the EP liquid, the pump was automatically activated to add acid whenever pH was above 5.1 during a 24-h extraction. After 24 h, the volume of acetic acid used was recorded and the solid-liquid ratio was adjusted to 1:20 by adding 400 ml double-distilled water, less the volume of acid added.

Following the 24-h EP, the contents of the extraction vessel were filtered through a Buchner funnel containing a prefilter of Whatman #1 paper. Dewatered solids were discarded and the filtrate was filtered through a 0.45 µm membrane filter (Gelman 60173). Filtrate was stored in two 1-1 polyethylene bottles at room temperature following preservation with 0.2% HNO₃.

ASTM Procedure --

In this test, dewatered sludge, $350\pm lg$, was placed in a 2-1 wide-mouth polyethylene bottle and 1.4 l of double-distilled water was added. The initial pH value of this suspension was determined. The polyethylene bottle was placed on a reciprocating platform shaker with a 2.5-cm diameter orbit and operated at 70 rpm. After 48 h, the vessel was removed, pH was measured, and the liquid was separated as for the EPA EP test, in accord with the procedures presented by Malloy (1979).

SECTION 6

ALUMINUM-FINISHING SLUDGE SURVEY

SLUDGE SURVEY

An aluminum finishing sludge survey was initiated by The Aluminum Association, Inc. using a questionnaire presented in Appendix A. Thirtyseven industrial plants were surveyed with thirty five of the plants involved in anodizing, etching and painting operations. Twenty-two anodizing plants, including two with anodizing and painting lines, seven painting/ coil coating plants and eleven etching plants responded to the survey. Data provided by the plants on sludge production and characteristics are presented in Table 15. Although extensive data were provided throughout the survey, the data were not always comprehensive.

At the plants surveyed, wastewater treatment practices conventionally included collection of all rinse waters, spills and spent finishing solutions in a staged neutualization basin. Following pH adjustment to nearneutral values, aluminum-hydroxide-laden suspensions were clarified by gravity sedimentation, although one facility employed direct centrifugation of neutralized wastewater. Techniques employed in treatment of gravity thickened sludges are summarized in Table 16.

Filtration systems were used by the majority of the reporting plant (i.e., 13 of 16 plants) for sludge dewatering, while sand drying bends and centrifugation systems were used by the remaining plants. The disposal techniques used for thickened and dewatered sludge solids are also presented in Table 16. A large number of reporting plants place gravity-thickened sludge directly into lagoon systems as a means of ultimate disposal. Landfill systems, land spreading and stockpiling on land were collectively used most extensively for sludge disposal. Finally sludge disposal at several facilities was achieved through a licensed disposal facility or through discharge to an industrial sewer.

Sludge characteristics were presented in numerous responses to the survey and are summarized in Table 17. With the exception of one plant (XXVII) reporting a concentration of 50 percent, the concentration of gravity thickened sludge suspensions ranged from 0.01 to 5 percent solids (i.e. 0.1-50g/1). Dewatered sludge concentrations, furthermore, ranged from 1 to 30 percent solids. While sludge production rates averaged between 300-200 kg/d the total quantity of sludge reported for all 35 plants was 57,000 kg/d (62.8 tons/d) or an overall average of 1600 kg/d (1.8 ton/d).

					Sludg	e Quanti	ties & Char	acteristics		
					Production					
		Type of	Wastewater	Wastewater & Sludge	Rate	Solids	Content	Indicated	Quantity	
Number	Location	Plant	Characteristics	Treatment System	(dry solids)	Settled	Dewatered	Composition	On Site	Comments
ANODIZI	NG_PLANTS									
I	Florida	Anodizinş	3 -	Wastewater: Bisulfide reduction of Cr(VI), neutralization of etch and anodizing acid Sludge: Centrifugation followed by vacuum filtration	0.25T/d	3.5%	-	A1 (OH) 3	0.25-0.5T	-
II	Florida	Anodizing	g [·] –	Wastewater: Neutrali- zation, cascade sedi- mentation Sludge: Underflow transported by tanker to landfill	1.25-2.1T/c (10,000gal, @ 3-5% sol	1 3-5% /d Lids)	-	al (OH) 3	-	Recovery of sodium aluminate by manu- facturers has not been well received.
III	Florida	Anodizinş	g – ,	Wastewater: Neutrali- zation, batch sedi- mentation, sand bed filtration Sludge: Underflow transported by tanker to landfill	0.21T/d (1,000 gal, @ 5% solid:	3-5% /d s)	-	A1(OH) ₃	-	Recovery of sodium aluminate by manu- facturers has not been well received.
IV	Mississipp	pi Anodiz:	ing – .	Wastewater: Neutrali- zation to pH = 6-8, sedimentation. Sludge: Underflow dewatered on filter belt	3T/d		20%	A1(OH) ₃ '	7-8T	Recovery of sodium aluminate by manufac- turers has not been well received.
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TABLE 15. SUMMARY OF ALUMINUM FINISHING SLUDGE SURVEY TAKEN BY THE ALUMINUM ASSOCIATION, INC. (FEBRUARY-APRIL 1979)

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				•		S1u	dge Quant	ities & Cha	aracteristics		
	Number	Location	Type of Plant	Wastewater Characteristics	Wastewater & Sludge Treatment System	Production Rate (dry solids)	Solids Settled	Content Dewatered	Indicated Composition	Quantity On Site	Comments
	V	Georgia	Anodizing	-	Wastewater: pH neutralization, flocculation, sedimentation Sludge: Underflow dewatered in filter press (2); disposed	6.4T/d	1.5%	12%	A1(OH) ₃ A1 ₂ (SO ₄) ₃	500T	Byproduct recovery potential of sludge is good in dry form.
	VI	Indiana	Anodizing	-	Wastewater: Flow mixing, pH neutrali- zation (H ₂ SO ₄), discharge to sanitary sewer	0.1T A1/d	-		A1 ₂ 0 ₃ A1(OH) ₃ A1 ₂ (S0 ₄) ₃	-	
2	VII	Southeast	Anodizing & Etching	-	Wastewater: (pH neutralization), sedimentation Sludge: rotary vacuum filter	0.66T/d	3%	13%	Al (OH) ₃ (@ 742# Al/d)	-	
	VIII	Southeast	Anodizing & Etching		Sludge: Sand bed dewatering, sludge mixed with soil	0.44T/d	0.5%	-	A1 (OH) 3	783T	`
	IX	Texas	Anodizing	Sludge.Analysis (Conc = mg/l) As <0.05 B <0.5 Cd <0.02 Cr = 2.52 Co = 104 Cu = 7.9 Pb = 0.5 Mn = 2.1 Hg = 0.005 N1 = 0.97	Wastewater: pH neutralization, polymer flocculation, sedimentation in parallel plate separator Sludge: Underflow to holding pond; Permuit DCG dewatering unit available, but not used.	2.6T/d (0.171b/ ft ^{2.} d for surface ar anodized)	1.3% ea	3-4%	A1(OH) ₃ , A1 ₂ O ₃ ,	60,000 ft	 I. Parallel plate separator is unsatis- factory; conventional sedimentation being examined. Investigated use in alumina process but water content presented problems Briefly investigated use of sludge and spent caustic in cement manu- facturing - no results to report.

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						S1	udge Quant	tities & (characteristics		
•	Number	Location	Type of Plant	Wastewater Characteristics	H Wastewater & Sludge Treatment System	Production Rate (dry solids)	Solids Settled D	Content ewatered	Indicated Composition	Quantity On Site	Comments
	IX .	Texas (con	tinued)	Se <0.05 Ag <0.05 Zn = 1.53 Fe = 71 F = <.1 Cl = 94.7 SO ₄ = 255 pH = 10.4 % solids = 1.36% Sp gray = 1.0091			5	1 •			
	v	Wach-	Anodizina	5p. grav. 1.0071	Masteriatori Tue bolding	2 ST/4	1 5_2%		A1 (OU) _05%	8 000T	
	A .	ington (SW)	Andrizing		lagoons without pre- treatment	(0.07 1b/ 1b product)	1.5-2%	-	NaAl0 ₂	0,0001	
82	XI	Arkansas	Anodizing	, - ,	Wastewater: pH neutralization, polyelectrolyte flocculation, sedimentation Sludge: Underflow to rotary vacuum filter, cake to city landfill	2.5T/d	4%	20%	-	-	Alum manufacture is favorable except for high water content.
(6	XII plants)	Ind., VA., Ca, PA, GA, TX	Anodizing & Etching	-	Wastewater: pH neutralization, flocculation, sedi- mentation, overflow water used for rinsing Sludge: Underflow dewatered on pressure or vacuum filter, cake hauled to landfills	2.5T/d (each plant)	-	14.8%	· · · ·	-	·

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								Sludge C	uantities A	Characterist	cs	
	Number	Location	Type of Plant	Wastev Charac	water steristics	Wastewater & Sludge Treatment System	Production Rate (dry solids)	Solid Settled	s Content Dewatered	Composition	Quantity On Site	Comments
	XIII	Michigan	Anodizing and Die Etching			Wastewater: Equali- zation of rinse water and ion exchange rinse, pH neutrali- zation, sedimentation in lagoons. (Batch treatment of etch and anodize wastes does occur) Sludge: Lagoon solids are dewatered and placed in plant landfill.	0.18T/d	-	1 ⁻ -20 ⁺ %	A1(OH) ₃	300,000 ft ³ at 15% solids	Contacts have been made (1) to use etch baths as coagulant in water treatment, (2) use etch or sludge as a source of alumimum in alum production (3) for use of waste etch by an acid-rich anodizing plant.
00	XIV	California	Anodizing			Collection and disposal on local landfill.	0.015T/d	0.01%	10%	A1(OH) ₃ A1 ₂ 0 ₂	1.7T(dry)	
ω	xv	California	Anodizing		<u> </u>	Collection and disposal on local landfill.	0.11T/d	0.02%	10%	A1 (OH) ₃ A1 ₂ O ₃	22 T (dry)	
	Combine	d Anodizing	Painting H	Plants								
	XVI	Georgia	 Anodi (Bright D (2) Conve coating 	zing ip) rsion		Wastewater: (1) pH neutralization lagoon settling. (2) Reduction of Cr(VI) lime neutralization, lagoon settling.	0.2T A1/d	- ·	<1%	A1 (OH) 3	-	

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					5	Sludge Qua	ntities & (Characteristics			
Number	Location	Type of Plant	Wastewater Characteristics	Wastewater & Sludge Treatment System	Production Rate (dry solids)	Solids Settled	Content Dewatered	Indicated Composition	Quantity <u>On Site</u>	Comments	_
XVII	Georgia	Anodizing & Painting	- 3	Wastewater: Chrome(VI) reduction of paint line followed by lime neutralization; neutralization of anodize and paint line wastes, sedimen- tation, discharge to series of lagoons and then a stream.	2.5T/d	2%	-	A1(OH) ₃	80,000 yd ³ (wet)		
				sludge lagoons.				•			
PAINTIN	G/COIL COA	TING PLANTS									
xvIII .84	Alabama	Coil Coating	-	Wastewater: Sulfite reduction of Cr(VI); 2-stage pH adjustment; sedimentation. Sludge: Vacuum filtration, city landfill.	0.36T/d	1.4%	7.4%	A1 (OH) $_{3}$ (.88g/1) A1PO ₄ A1 ₂ (SO ₄) $_{3}$ Cr (OH) $_{3}$ CaSO ₄ Zn (CN) $_{2}$			
XIX	Ohio	Coil Coating	Treated <u>Effluent:</u> Q = 60-80gpm Cr(VI)=0.05mg/1 Cr(Total) = 0.25 mg/1 F = 12 mg/1 Susp. Sol. = 30 mg/1 pH = 7-9	Wastewater: Acidic SO reduction of Cr(VI), lime neutralization, sedimentation. Sludge: Underflow dewatered in filter press; solids dumped on plant site	0.5T/d	-	- - -	A1 (0H) $_{3}$ -70.4 Cr (0H) $_{3}$ -16.7 CaF ₂ 10.6 Metal Ferro- cyanide1.5 CaPO ₄ <u>0.8</u> 100	75T 7 2 2 2 2 7	· · · · · · · · · · · · · · · · · ·	
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						ge Quanti	ties & Char	acteristics			
Number	Location	Type of Plant	Wastewater Characteristics	Wastewater & Sludge Treatment System	Production Rate (dry solids)	Solids Settled	Content Dewatered	Indicated Composition	Quantity On Site	Comments	·
XX	Michigan	Paint Line	Wastewater is from regeneration of resin used to treat chromate treatment bath and recircu- lating rinse water.	Wastewater in holding tank is periodically acidified for chrome reduction, pH neutrali zation, batch sedimen- tation Sludge: Hauled away by sludge handler	0.038T/d (0.5 1b/1000 1b of produc	2% t)	-	A1 (OH) 3	-		
XXI	Kentucky	Paint Line	-	Wastewater: Chrome(VI) reduction with bisulfi lime neutralization, chrome reduction waste combined with caustic cleaner waste and neutralized, sedimenta Sludge: Underflow haul to lagoon	0.063T/d te, (1.5 1b/10 1b produc tion ed	2% 00 t)	(10%)	A1(OH) ₃ A1 ₂ (PO ₄) ₃	1500 yd ³ (wet)		
XXII	Alabama	Coil Coating (Chrome conversion coating)	n	Wastewater: pH reducti (pH = 2-3) & SO ₂ additi lime neutralization, p flocculation, sediment Sludge: Underflow dewa on vacuum filter	on 0.06T/d on, olymer ation tered	5%	30%	A1 (OH) ₃ A1 ₂ 0 ₃			
XXIII	Alabama	Coil Coating (Chrome conver- sion coating)	Sludge Analysis (% by <u>weight)</u> Ca = 9.5% P-PO ₂ =16.8% SO ₃ =12% A1=2% Cr ⁺³ = 3.6% F = 4.9% Si & C=23.2% Moisture=28%	Wastewater: pH reducti (pH = $2-3$) & SO ₂ additi lime neutralization, p mer flocculation, sedi tation. Sludge: Underflow dewa on vacuum filter with coat.	on 0.47T/d on, oly- men- tered pre-	2-3%	28%	A12 ⁰ 3 A12(S04)3	40-80yd ³		

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						SI	ludge Ouar	ntities & C)	naracteristics			
	5000 Core		Type of	Wastewater	Wastewater & Sludge	Production Rate	Solids	Content	Indicated	Quantity	Commonta	
	Number	Location	Plant	Characteristics	freatment System	(dry solids)	Settled	Dewatered	Composition	<u>on site</u>	Comments	
	XXIV	Ohio	Coil Coating	-	Wastewater: pH reduc- tion $(pH=2-3) \& SO_2$	0.437T/d	5%	30%	A1 (OH) 3 A1 ₂ 03	-		2
			Coating	•	neutralization, polymer flocculation,				A1 ₂ (S0 ₄) ₃			
					sedimentation. Sludge: Underflow dewatered with vacuum filter.				•			
	ETCHING	PLANTS		•								
	xxv	Ohio	Rod and	e e	Wastewater: pH	0.4-0.5T/c	1 -	۱ -	- A1 (OH) 3	-		
86			Wire Etching		etch rinse. Sludge: Pressure filtration with diatomaceous earth	(wet)		2° -	Pb; Cu			
5,				<i>,</i>	media; sludge is recycled offsite.				i.			
	XXVI	Texas	Extrusion Die and Tooling	$\frac{\text{Caustic Dip Vat}}{\text{COD} = 15.2 \text{ mg/l}}$ BOD = 55 mg/l TDS = 315 c/l	(234 gal. of effluent and small amount of solids are drained at a rate of 1 gpm	- 1	-	-	-	-	,	
	`		Eccling	Susp.Sol.=785mg/1 pH = 13 F = 6.5 mg/1	once every 3 months)				1			.21
				Al = 26 g/l B = 5.3 mg/l Cd = 0.04	7.				1 I		í	
				Cr(Tot) = 0.2 Cu <0.1 mg/1 Fe = 1.4 mg/1			1					
				Pb = 0.5 mg/1 Ni = 0.1 mg/1 Na = 125 g/1					x			i,
		•		Sn = 20 mg/l Zn = 1.7 mg/l Oil & Grease = 46	mg/l					ł		

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					c	ludge Ous	ntitiee & (haracteristics		,	
Number	Location	Type of Plant	Wastewater Characteristics	Wastewater & Sludge Treatment System	Production Rate (dry solids)	Solids Settled	Content Dewatered	Indicated Composition	Quantity On Site	Comments	
XXVII	Illinois	Die Etching	-	Wastewater: Two 100 gal etch tanks are flushed each week. Once each month accumulator tank is hauled by licensed contractor	0.06T/d (200gal/wk)	50%	-	Hydrated Alum (25% Al)	ina —	. 	
XXVIII	California	Etching		Wastewater: 5,000 gal of etch tank shipped off site for disposal every 3 wks	0.5T/d	33%	-	Aluminates	5,000 gal	-	
XXIX	Maryland	Die Etching	-	Wastewater: Hauled away once/month	y (5000gal/ 30d)	-	-	A1(OH) ₃	-		•
XXX	Pennsyl- vania	Etching of Forgings	Sludge Analysis (conc=mg/1) Alkalinity=113,000 Total Solids= 697,000 Susp.Solids=10,970 Al = 145,000 Cr = 28.3 Cu = 13.8 Fe = 28.5 Ni = 11.0 Zn = 3.7 Pb = 2.0 (pH = 14)	Wastewater: Tanks vacuumed into portage tank, waste is dumped in open pit and subse- quently covered with soil.	-	-	-	- 	-		
XXXI	Cali- fornia	Die Etching (6000 series alloys)	-	Wastewater: Liquid is weekly drained to industrial sewer.	.01T/d	20% `	-		 A		
					,			·		•	

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				-	Sludge	Quantit	ies & Chara	cteristics		
Number	Location	Type of Plant	Wastewater Characteristics	Wastewater & Sludge Treatment System	Production Rate (dry_solids)	Solids Settled	Content Dewatered	Indicated Composition	Quantity <u>On Site</u>	Comments
XXXII	North _. Carolina	Electro- lytic Etching of Foil		Wastewater: Pumped to settling lagoon	2.5T/d (0.6 1b/1b product)	10%	40%	A1 ₂ 0 ₃ A1 ₂ 0 ₃ •H ₂ 0 A1 ₂ 0 ₃ •3H ₂ 0	1000T	Filter dewatering and reclamation has been explored.
XXXIII	Tennessee	Caustic Etch of Aluminum Sheet	-	Wastewater: Discharged to lagoon	8T/d	-	 \	-	· _	Caustic recovery system to recovery sludge as Al(OH) ₃ (dry).
XXXIV	New York	Die Etching	-	Wastewater: Trans- ported to county- operated liquid waste disposal facility	0.013T/d	5%	-	A1 (OH) 3	1500 gal	
XXXV	Pennsyl- vania	Die Etching	-	Wastewater: Batches of 1800-2000 gal of caustic waste are hauled away without treatment for disposal	(400 gal/d)	-	-	-'	-	
OTHER P	LANTS									
XXXVI	Wash- ington	Foundry	-	Aluminum dross traded for metal. Reclaimed in a rotary type furnace for reuse 80% of metal is lost in process.	0.12T/d	-		_ ' i	5000 lb	. .
XXXVII	Arkansas	-	_	Sludge Solids: Landfill	1.3T/d (2.6 lb/ lb product)	99.5%	-	Mill Oil (50% of volume) Diatomaceous Fullers earth Aluminum fine Aluminum oxid from rolling from filter	earth s e & media	

	Plant Description				
	Anodize and . Anodize/Paint	Etch	Paint and Coil Coating	A11	
SLUDGE TREATMENT					
Vacuum Filtration	4	-	4	8	
Pressure Filtration	2	1	1	4	
Sand Beds	2	-	-	2	
Belt Filtration	1			1	
Centrifugation	1			1	
SLUDGE DISPOSAL					
Lagoon	5	3	1	9	
Landfill	4	1	2	7	
Haul to licensed disposal					
facility	-	4	1	5	
Industrial Sewer	-	2	-	2	
Blend with Soil	1	-	-	1	
Stockpile (for future			×		
reclamation)	1	-	-	1	

TABLE 16. ALUMINUM-FINISHING TREATMENT AND DISPOSAL TECHNIQUES

TABLE 17. CHARACTERISTICS OF ALUMINUM-FINISHING SLUDGES IN SURVEY

		<u>Plant Descri</u>	ption
SLUDGE CHARACTERISTICS	Anodize Anodize/Pa	Etch	Paint and <u>Coil Coating</u>
Settled Solids Concentration Average (%) Range (%)	2.2 0.01-5	25 5-50	2.6 1.4-5
Dewatered Solids Concentratio Average (%) Range (%)	<u>on</u> 16 1-20	2	24 7.4-30
<u>Sludge Production Rate</u> Individual Plants Average (10 ³ kg/d) Range (10 ³ kg/d)	2 0.017-7	2 0.014-8.8	0.3 0.04-0.6
All Plants Number of Plants Cumulative Sludge Pro- duction Rate (10 ³ kg/o	22 1) 42.7	6 12.2	7 2.12

Note: $(10^3 \text{ kg/d}) \times 0.908 = \text{Short ton/d}$
PLANT SELECTION

In conjunction with the Environmental Task Group and data from the Aluminum-finishing sludge survey, five finishing plants were initially selected and are described in Tables 18 and 19. The three anodizing plants presented in Table 18 finish similar quantities of aluminum using dissimilar process lines. Plant Al uses both painting and anodizing, including integral-color and clear-coat sulfuric acid anodizing. Plants A2 and A3 only anodize aluminum with Plant A2 using a clear-coat process while Plant A3 uses both integralcolor and clear-coat processes. Wastewater treatment practices are similar at the three anodizing plants, except for sludge dewatering, which is accomplished using three different techniques, i.e., lagoon dewatering (A1), vacuum filtration (A2), and pressure filtration (A3).

As presented in Table 19, two etch plants were selected initially. Plant El used a chemical etch to clean and mill aluminum stock and wire. The primary source of wastewater was tanks used for rinsing aluminum from both the etch and desmut tanks. These rinse tanks were continuously adjusted with acid and base to a neutral pH and precipitated aluminum hydroxide was allowed to accumulate. A pre-coat pressure filter was available for use in regenerating the rinse tank and dewatering sludge solids.

Plant E2 used an electrochemical etch of foil for use in the electrical capacitor industry. An aluminum-oxide sludge was produced in a saline solution during electrochemical etching. The sludge, unlike gelatinous aluminum hydroxide sludges from chemical etching and anodizing processes, was composed of high density, granular particulates. No treatment was provided for the electrochemical etch sludge except lagoon disposal for dewatering.

Plant Designation	Finishing Lines and Production Rates	Wastewater and Sludge Treatment Systems	Sludge Production Rate Wet Basis Dry Basis'
Al	<u>Paint Line</u> : 3.6-4.5x10 ⁵ kg/mo	Paint Line: Two-stage chrome reduction followed by lime neutralization	1.3x10 ⁻³ m3/s 6.8x10 ⁴ kg/mo. At 20% Solids
	<u>Anodize Line</u> (clear-coat and integral-color anodize with bright dip and gold dyeing lines): 4.0 - 4.5x10 ⁵ kg/mo	Anodize Line: Wastewater mixed with lime-neutralized paint- line wastewater; 3-stage pH neturalization, sedimentation, series of lagoons and stream -discharge; sludge: stored in lagoons.	
		Total anodize/paint-line waste- water flow = 1.5x10 ⁻² m3/s (0.35 mgd). (Anodize-flow to paint-line flow = 7.3)	
A2	Anodize Line (clear coat anodize w/bright dip and dye lines): 3.6x10 ⁵ kg/mo or 1.24x10 ⁵ m ² /mo.	pH neutralization; polyelectrolyt flocculation; sedimentation with effluent discharge to surface stream and sludge dewatered on a vacuum filter and landfilled.	e 1.8 x 10 ⁵ kg/mo.3.6x10 ⁴ kg/mo '(20% solids)
A3	Anodize Line (incl. integral-color and clear- coat anodize): 6.8x10 ⁵ kg/mo	3-stage pH neutralization; polyelectrolyte flocculation; sedimentation with effluent dis- charge to stream, sludge dewater- ing on 2 filter presses and cake disposal to land on plant site.	1.45x10 ⁶ kg/mo. 1.7x10 ⁵ kg/mo

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TABLE 18. DESCRIPTION OF ANODIZING PLANTS SELECTED FOR RESEARCH PROJECT

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TABLE 19. DESCRIPTION OF ETCHING PLANTS SELECTED FOR RESEARCH PROJECT

Plant Designation	Finishing Lines	Wastewater and Sludge Treatment Systems		<u>Sludge Produ</u> Wet Basis	ction Rates Dry Basis
E1	Caustic etch of stock and wire	One rinse tank is used as the rinse follow- ing etch and desmut; pH of rinse is continuously adjusted to neutral pH with H_2SO_4 . Rinse tank effluent is filtered with pre- coat diatomite pressure filter. Sludge cake is disposed to landfill and filtrate is discharged to sewer or reused.		- -	-
E2	Electrochemical etching of foil	Sludge collected during process is de- watered in sludge lagoons.	, 	1-1.4x10 ⁵ kg/ mo	4.5 -6.8 x104 kg/mo or 2.5-3.6 x104 kg- A1/mo.
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SECTION 7

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PLANT INSPECTIONS AND WASTEWATER CHARACTERISTICS

PLANT INSPECTIONS

Following plant selection, site visits were made to each of the five plants. During each site visit, detailed information was obtained on the aluminum finishing processes and wastewater and sludge treatment processes. Sufficient information was collected during each visit to develop (1) a detailed flow sheet for plant finishing processes indicating the flow of aluminum through the processes and the sources of wastewaters, (2) a detailed description of the chemical contents of each finishing tank and the chemical replacement and wastewater disposal frequency for each, (3) a schematic diagram of the wastewater treatment and sludge disposal system, and (4) a detailed description of the physical and chemical characteristics and operational techniques for the wastewater and sludge disposal processes. This information was then used in establishing wastewater collection points. Descriptions of wastewater treatment systems are presented in the following subsection in conjunction with wastewater characterization data.

WASTEWATER COLLECTION SCHEDULE

Wastewaters from three anodizing and one etch plant were examined. Scheduling problems associated with a labor strike did not allow for examination of wastewater suspensions from plant E2. A chronological listing of the wastewater samples received from plants A1, A2, A3, and E1 are presented in Table 20. Due to regional proximity of plant A3 and the ease with which samples could be collected by project personnel, it was selected for analysis initially. Suspensions collected from A3 were used to evaluate testing procedures and establish standard operating ranges for many of the tests used with all sludge samples.

Wastewater samples from plant A2 were next examined. Two types of samples were collected due to variations in wastewater treatment practices on weekday (A2-218-79; A2-242-79; A2-293-79) and weekend periods (A2-319-79). The weekday samples had low suspended solids concentrations and two shipments of large volumes of this wastewater were required. Extensive evaluation of wastewaters from plants A1 and E1 were next conducted to complete the conventional wastewater examination phase of the project. Results of the study are presented in essentially the chronological order of receipt of samples.

<u>Plant</u>	Date*	Sample Volume	Sample Description	Type of Analyses
A3	161-79	0.2m ³	Neutralization Basin Effluent	Chemical; Settle, Dewater,Condition
A3	201-79	0.26m ³	Neutralization Basin Effluent	Chemical
A2	218-79	22	Neutralization Basin Effluent (weekday sample)	Chemical
A2	242-79	0.4m ³	Neutralization Basin Effluent (weekday sample)	Chemical; Settle, Condition
E1	263-79	8l	Etch/Desmut Rinse	Chemical
A2	283-79	0.4m ³	 Neutralization Basin Effluent (weekday sample) 	Settle, Dewater, Sand dry
A2	319-79	0.2m ³	Neutralization Basin Effluent (weekend sample during etch dump)	Chemical; Settle, Condition, Dewater Sand dry, EP
Al	21-80	0.8m ³	Neutralization Basin Effluent	Chemical; Settle, Condition, Dewater Sand dry, EP
El	80-80	0.4m ³	Etch/Desmut Rinse	Chemical; Settle, Condition, Dewater Sand dry, EP
A3	147-80		Neutralization Basin Effluent	Chemical; EP

TABLE 20. CHRONOLOGICAL LISTING OF SLUDGE SAMPLES EXAMINED

*Date is expressed using Julian calendar date and last two digits of year.

CHEMICAL CHARACTERISTICS OF WASTEWATERS

Wastewaters received from industrial plants were immediately sampled for routine chemical characterization. Samples were also collected for analysis of complete metal composition using INAA and analysis of trace concentrations of priority pollutant metals. The results of the routine chemical characterization are presented below for each plant. Trace metal and INAA results are presented in a subsequent subsection.

Plant A3

A 3-stage neutralization basin and a clarifier are included in the wastewater treatment system at Plant A3. A schematic diagram of the wastewater treatment system and sampling points are presented in Figure 13. The chemical characteristics of samples A3-161-79 and A3-201-79 are shown in Table 21.

	NEUTRALIZATION BASIN		CLAR	IFIER	
	STAGE 1 201-79-1	STA 161-79-2	GE 3 201-79-2	EFFLUENT 201-79-3	UNDERFLOW 201-79-4
рH	10.3	. 7.2	10.5	9.7	9.6
Temperature, ^O C	21	25	21	21	21
Total Solids, g/% Total Volatile Solids, %	6.51 12.4	9.78 -	7.23 10.9	-	25.8 11.8
Suspended Solids, g/% Volatile Susp. Solids, %	2.19 28.3	4.35 -	1.84 21.7	1	23.98 23.0
Dissolved Solids, g/% Volatile Diss. Solids, %	-	5.43	2	6.81 44.9	2
Alkalinity Total, mg/2 as CaCO ₃ Dissolved, mg/2 as CaCO ₃	942 509	535 54	1134 781	- 310	2268
Aluminum Total, mg-Al/& as CaCO ₃ Dissolved, mg-Al/& Suspended, gAl/g SS	980 71. 0.415	-	980 118 0.468	- 34 -	6250 - 0.26
Dissolved Organic Carbon, mg/L Dissolved Incorports Carbon	96	-	93	76	-
mg/2	0	-	0	0	-

TABLE 21. PLANT A3 WASTEWATER CHARACTERISTICS (Samples A3-161-79 and A3-201-79)

Samples collected on day 201-79 were grab samples and fluctuations in plant wastewater characteristics are reflected in the data presented. The pH for sample A3-201-79 was slightly above conventional levels but aluminum levels were still reduced by as much as 90 percent in the neutralization basin. Suspended solids concentrations in the neutralization basin ranged from 1.84 to 4.35 g/l and dissolved solids ranged from 4.32 to 5.39 g/l indicating the addition of high levels of dissolved and suspended solids to the water. The suspended solids concentration of the underflow was 2.4 percent solids indicating good thickening properties for the clarifier system.





The high alkalinity values for A3-201-79 samples was due to high pH values of 9.6 - 10.5 and to the presence of suspended aluminum hydroxide. Since aluminum hydroxide is dissolved at pH values below 5, the aluminum hydroxide solids were titrated during alkalinity measurements. Aluminum concentrations indicated that it constituted 26 to 47 percent of the suspended solids in the wastewater samples and was in general agreement with the theoretical value of 34.6 percent for A1(OH), precipitates. Finally, the dissolved organic carbon (DOC) levels indicated a high level of organic matter i.e. at the level of a low-strength domestic wastewater (Metcalf and Eddy, 1979).

Plant A2

As indicated in Figure 14, wastewater samples from Plant A2 were collected from the neutralization tank prior to the point of polymer (Separan AP273) addition. Concentrated finishing solutions and wastewaters from caustic etch and sulfuric anodize tanks were only discharged to the wastewater treatment system when aluminum finishing processes are not in use, i.e. on weekends. Consequently, the level of aluminum routinely discharged to the treatment system during the work week was relatively low. Since wastewater samples were initially collected on a week day when only rinse waters were being discharged to the neutralization basin, two types of samples were then collected. One was a composite of the total wastewater on the day of operation (Sample 1), while the second was concentrated using a sequential filland-draw technique in which sludge solids were concentrated by repeated settling of numerous suspension samples (Sample 2). These two samples were then used to examine "normal" sludge characteristics at Plant A2.

In comparison with Plant A3 (Table 21), Plant A2 Wastewater (Table 22) discharged during weekday operation was more dilute with respect to both dissolved and suspended solids. In addition, aluminum and alkalinity concentration were much lower. Dissolved organic carbon (DOC) was at trace levels indicative of surface water concentrations. Suspended aluminum was 0.264 to 0.283gA1/gSS which was below the theoretical value of 0.345gA1/gSS. However, normalization of aluminum data to inert (i.e. non-volatile) suspended solids resulted in values of 0.342 to 0.386gA1/gSS, which were agreement with the theoretical value.

At Plant A2, waste etch and anodize solutions were discharged to wastewater treatment systems during periods when aluminum finishing processes were inactive. Neutralization of these concentrated acids and bases resulted in significant elevation of wastewater temperature and in the production of the bulk of waste aluminum precipitated on a weekly basis. The characteristics of sample A2-319-79, collected during a weekend discharge of concentrated solutions and suspensions, are presented in Table 23. As expected, both dissolved and suspended solids concentrations were extremely high resulting in a total solids concentration of 108.59g/l. Aluminum levels were also high, accounting for 27.2 percent of suspended solids (32.4 percent based on inert suspended solids). DOC concentration was relatively high, compared with weekday samples, but was not exceptionally high considering the nature of the concentrated wastes being treated.





Sample Description Sample Date and Number	\$ <i>7</i>	Neutralizat	<u>Lion Basin</u> A2-242-79-2
		<u>AL LIL 75 I</u>	
рН		8.0	6.3
Temperature, ^O C		21	21 _
Total Solids, g/l Total Volatile Solids, %		1.72	8.0 22.9
Suspended Solids, g/l Volatile Susp. Solids, %	-	0.41 31.7	6.43 26.9
Dissolved Solids, g/l Volatile Diss. Solids, %		1.34 12.7	1.66 7.8
Alkalinity Total, mg/l as CaCO ₃ Dissolved, mg/l as CaCO ₃		159 74	233 116
Aluminum Total, mg-Al/l Dissolved, mg-Al/l Suspended, g-Al/g-SS		120 3.9 0.283	1700 - 0.264
Dissolved Carbon Organic, mg/l Inorganic, mg/l		4 19	7 29

TABLE 22. PLANT A2 (A2-242-79) WASTEWATER CHARACTERISTICS

	1. T	Neutralization Basin (A2-319-79)	
рН		7.0	
Total Solids, g/l Total Volatile Solids %		108.59 12.4	~
Suspended Solids, g/l Volatile Susp. Solids, %	5	57.26 16.1	
Dissolved Solids, g/l Volatile Diss. Solids,%		52.43 8.1	
Alkalinity Total, mg/l as CaCO ₃ Dissolved, mg/l as CaCO ₃		2800 120	
Aluminum Total, mg-Al/l Dissolved, mg-Al/l Suspended, g-Al/g-SS	9	15,600 2.5 0.272	
Dissolved Carbon Organic, mg/l Inorganic, mg/l	÷	81.5 0	

TABLE 23. PLANT A2 (A2-319-79) WASTEWATER CHARACTERISTICS

Plant Al

Wastewater samples were collected at Plant Al following neutralization of combined anodize and paint-line wastewaters as indicated in Figure 15. Nearly equal quantities of aluminum extrusions were finished in the two lines. However, the flow of wastewater from the paint-line included only about 10 to 15 percent of the total plant wastewater flow.

Paint-line wastewater was pre-treated for chrome reduction and limeneutralized prior to discharge to the neutralization basin. During the time of wastewater collection, no sludge was recycled to the neutralization basin and wastewater was collected prior to polymer addition. The chemical characteristics of the sample collected, i.e. Al-21-80, are presented in Table 24.

Solids content of the wastewater sample was similar to plant A3 with suspended solids at 3.21 g/l and a dissolved solids of 6.04 g/l. Aluminum content was similar to previous suspensions with values of 0.296 and



0.397g-Al/g-SS, based on total and inert (non-volatile) suspended solids, respectively. A DOC concentration of 16 mg/l indicated a low organic content for the wastewater.

	Neutralization Basin (A1-21-80)	*
рН	7.0	.
Temperature	20	
Total Solids, g/l Total Volatile Solids, %	9.04 15.6	
Suspended Solids, g/l Volatile Susp. Solids, % -	3.21 25.5	
Dissolved Solids, g/l Volatile Diss. Solids, %	6.04 10.3	
Alkalinity Total, mg/l as CaCO ₃ Dissolved, mg/l as CaCO ₃	311 75	
Aluminum Total, mg-Al/l Dissolved, mg-Al/l Suspended, g-Al/g-SS	950 0.4 0.296	
Dissolved Carbon Organic, mg/l Inorganic, mg/l	16 12	

TABLE 24. PLANT A1 WASTEWATER CHARACTERISTICS

15

Plant El

Aluminum extrusions, wire, and stock are etched for chemical milling purposes and in preparation for shipment, as indicated in Figure 16, and aluminum finishing and wastewater treatment systems are closely integrated at this facility. The rinse tank was used to rinse aluminum products following immersion in caustic etch and the subsequent desmut solution. Sequential rinsing of caustic and acidic solutions from aluminum products in one tank minimized chemical requirements for maintaining pH near neutral values and reduced water requirements. Rinse waters, furthermore, were treated using a pressure filter to remove suspended matter with the filtrate



Figure 16. Schematic Diagram of Plant El Wastewater Treatment System

being regarded for use as a rinse water.

With the assistance of plant personnel, an intensive sampling program was completed at Plant E-1 with the hot-rinse tanks. The two-tank rinse system was operated as two independent single-stage rinses and was the only source of wastewater sludge at the plant. The sampling program consisted of five days of sampling with three samples collected each day, i.e. one sample during each 8-h shift. The collected samples were immediately analyzed for temperature and pH, as indicated in Table 25, and then split into two 150-ml aliquots. One aliquot was utilized to prepare composite sample while the second aliquot was filtered with a glass-fiber filter (Gelman A/E) and then utilized to prepare a "filtered" composite sample.

In addition, data were provided by plant personnel indicating the quantity of the specific aluminum alloys which were etched during the study and the portions which were actually processed through the rinse tank sampled. Samples were collected for approximately 59 percent of the total mass of aluminum etched and for approximately 54 percent of the total surface area etched. Initial chemical characterization data for the wastewater sample are presented in Table 26. A considerable quantity of suspended material passed through the glass-fiber filters used at the plant site. From analysis of the tabulated data and production data, the rate at which aluminum was etched from the surface of aluminum stock and wire was 0.13 g Al⁺³/kg aluminum wire and stock that was finished $0.029m^2/kg$.

Day	<u>Shift</u>	Time	Temperature,°C	pH
Monday	1	0715	19	8.5
	2	1545	29.5	11.1
	3	2330	18	10.9
Tuesday	1	0715	18	10.6
ý	2	1530	30	12.2
	3	2330	18	11.5
Wednesday	1	0715	15.5	8.7
	2	1530	29.5	10.7
	3	2330	28	9.9
Thursday	1	0730	15.5	8.7
	2	1530	30.5	6.2
	3	2330	17	3.1
Friday	1	0715	17	5.8
	2	1530	30	5.5
	3	2330	17	4.4
			Avg. = $\overline{22.2^{\circ}C}$	

TABLE 25. CHARACTERISTICS OF INDIVIDUAL SAMPLES USED TO MAKE 5-DAY COMPOSITE SAMPLE (E1-263-79)

	·/ -	Hot Rinse (E1-2 Unfiltered Composite	63-79) Filtered Composite
рН		10.5	10.6
Total Solids, g/l Total Volatile Solids, %		11.3 28.2 -	6.05 32.2
Suspended Solids, g/l Volatile Susp. Solids, %		2.65 23.8	0.84 33.3
Dissolved Solids, g/l Volatile Diss. Solids, %		2.90 20.7	5.21 32.1
Alkalinity Total, mg/l as CaCO ₃ Dissolved, mg/l as CaCO ₃		698 391	434 -
Aluminum Total, mg/l Dissolved, mg/l Suspended, g Al/g SS	·	562 14.8 0.206	161 - 0.192
Dissolved Carbon Organic, mg/l Inorganic, mg/l		15 31	20 31

TABLE 26. CHEMICAL CHARACTERISTICS OF WASTEWATER COMPOSITE FROM PLANT E1

METAL COMPOSITION OF WASTEWATERS

INAA Analysis

Wastewaters received from finishing plants were sampled and prepared for Instrumental Neutron Activation Analysis (INAA). These samples were prepared as indicated in Figure 11 and forwarded immediately to the Environmental Chemistry Research Laboratory at the University of Illinois (Urbana, IL 61801). Under the direction of Dr. P. K. Hopke, the samples were irradiated and examined over approximately a 6-week period for constituent metals. The INAA results for plants A3, A2, A1 and E1 are presented in Tables 27-34.

Data are presented for dissolved metals contained in membrane filtrates (pore size of 0.45μ m), suspended metals and total metal concentration in the suspensions. INAA analysis was excellent for detection of overall metal composition and identification of major metallic components. The major dissolved metallic components of the aluminum finishing wastewaters were Na, K, Ca, and Fe with potentially high concentrations (i.e., mg/l levels) of Cu and Zn. Suspended metals were similar in composition to the dissolved species. Aluminum levels were not examined with INAA, but it was obviously the major metal in all suspensions, as indicated previously.

Trace Metal Analysis

Initial chemical characterization of wastewater samples indicated that the aluminum content of sludge suspended solids varied from 0.2 to 0.38gAl/gSS on a total suspended solids basis. Wastewater suspended solids samples contained from 16 to 32 percent volatile solids due to bound and hydrated water in the gelatinous sludges, residual organic surfactants and sequestrants removed as a result of aluminum precipitation, and formation of metal oxides upon drying at 103°C for 6-12h. To eliminate this volatile solids fraction from the above calculation, sludge aluminum content was expressed as a function of non-volatile suspended solids (NVSS). Aluminum content values presented in Table 35 ranged from 0.270 to 0.505gAl/gNVSS, based on inert or non-volatile solids fractions.

Examination of wastewater aluminum content is best done by consideration of the compound being precipitated. At near-neutral pH values and ambient temberature, aluminum is precipitated as an amorphous aluminum hydroxide, A1(OH)₃ (Hanna and Ruben, 1970, and Stumm and Morgan, 1972). Theoretical aluminum content of aluminum hydroxide sludges should then be 0.346gA1/gA1(OH)₃, i.e., 27/78. If the majority of the solids precipitated upon neutralization of alumnum finishing wastewaters were A1(OH)₃, the theoretical value for wastewater iluminum content is 0.346gA1/gNVSS. The range of 0.270-0.505gA1/gNVSS was therefore consistent with this ratio. For sludge samples from plants A2, A1, and 11, sludge aluminum averaged 0.342gA1/gNVSS, a value in direct accord with the theoretical value. Aluminum content values for plant A3 neutralization samples is precipitated at the high pH values reported for the sample. The aluminum concent for clarifier underflow at plant A3 was consistent with the theoretical value, possibly attributable to the lower pH value for this suspension. Therefore, the aluminum content for all sludge samples (except the A3 neutralization).

		NEUTRALIZATION BA	SIN INFLUENT	
L	DISSOLVED	SUSPEN	NDED	TOTAL 49/1
-	$(10176) \times 10^4$	$(5.45+0.05)\times10^4)$	$(2.4970.02) \times 10^4$	(106.45 + 6.05)×10 ⁴
	<5x10 ⁴	0,23x10 ⁴	0.10	5.23x10 ⁴
	<2.7x10 ³	(2.39∓0.25)×10 ³	(1.1 1 0.11)x10 ³	(5.09 1 0.25)x10 ³
	0.95∓0.15	0.1770.01	0.08∓0.005	1.12∓0.16
	< 31	146∓3	66.7 - 0.4	<177-13
	< 360	170∓5	77.6+2.3	<53075
	<3700	222207540	10146∓246	<25920 - 540
	<7	3.6∓ 0.4	1.64∓0.18	<10.6∓0.4
	<740	740∓90	338741	<1480
	<140000	< 6510	<2972	<146510
	1440∓90	340∓10	155∓5	17807100
	<1100 -	93∓24	42.5+11	<1193∓24
	<1100	<60	<27.4	<1160
	<28	< 6	<2.7	<34
	<1700	<91	<41.6	<1791
	<1700	<210	<95.9	<1910
	< 42	9.171.5	4.2=0.7	<51.1∓1.5
	<13	<2.3	<1.04	<15.3
	<250	< 35	<16	<285
	<1.1	0.17∓0.03	0.08∓0.01	<1.27+0.03
	<5.1	<0.7	<0.32	5.8
	<400	<24	<11.0	<424
	<21	< 3	<1.37	<24
	<3.5	<1.5	<0.68	<36.5
	<1300	<220	<100	<1520
1	<2	<0.10	<0.05	<2.1
	<2.3	1.3∓0.2	0.6∓0.1	<3.9∓0.2
	<2.6	<0,42	0.2	<3.02
	<5.8	<1.0	<0.46	<6.8
1	<140	<18	<8.22	<168

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BLE 27. METAL COMPOSITION BY INAA OF NEUTRALIZATION BASIN INFLUENT AT PLANT A3 (Sample A3-201-79-1)

	NEUTRALIZATION BAS	IN EFFLUENT	
DISSOLVED	SUSPE	TOTAL	
µg/l	μg/1	mg/kg	μ <u>g/1</u>
$(108+7) \times 10^4$	(4.37 + 0.04)×10 ⁴	(2.38 - 0.02)x10 ⁴	(112.37 - 7.04)×10 ⁴
<5x10 ⁴	<0.19x10 ⁴	<0.1x10 ⁴	<5.19x10 ⁴
<2.7x10 ³	(4.14∓0.41)×10 ³	<2.25+0.22)×10 ³	<(6,84+0:41)x10 ³
0.8∓0.11	0.13∓0.01	0.07+0.005	0.93+0.12
64711	11072.3	59.871.2	174713.3
<320	130∓3.9	70.6+2.1	<(450∓3.9)
<4400	16560∓390	9000 7 212	<(20960 - 390)
<10	26∓0.4	14.170.2	<(36∓0.4)
<80	500762	272∓34	<(580∓62)
<140000	<5420	<2946	<145420
<340	310712	16877	<750+12
<1000	<39	<21	<1039
<1100	<45	<24	<1145
<30	<4.3	<2.3	<34.3
<1800	<72	<39	<1872
<1800	<163	· <89	<1963
<41	<5.6	<3.0	<46.6
<18	<1.8	<1.0	<19.8
<260	<33	<18	<293
<1.4	0.2870.05	0.15+0.03	<(1.68∓0.05)
<5.6	<0.5	<0.3	<6.1
<430	<19	<10	<449
<22	<3	<1.6	<25
<33	<1.2	<0.7	<34.3
<1400	<190	<103	<1590
<2.2	<0.09	<0.05	<2.29
<2.2	2370.6	12.5+0.3	<(25.2+0.6)
<2.7	<0.35	<0.2	<3.05
<6.0	<1.4	<0.8	<7.4
<160	<14	<8.0	<174

E 28. METAL COMPOSITION BY INAA OF NEUTRALIZATION BASIN EFFLUENT AT PLANT A3 (Sample A3-201-79-2)

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	CLARIFIER		CLARIFIER UNDERFLOW					
-AL	EFFLUENT (FILTRATE) µg/1_	DISSOLVED µg/l	SUSPEND	EDmg/kg	TOTAL			
	$(10877) \times 10^4$	$(10176) \times 10^4$	$(35.770.3) \times 10^4$	$(1.58\pm0.01)\times10^4$	$(136.7 + 6.3) 10^4$			
	<2.7x10 ³	<2.6x10 ³	92.8711.1.)x10 ³	$(4.1 \pm 0.5) \times 10^3$	<(95.4 - 11.1)x10 ³			
	0.48∓0.09 58∓9	1.3 1 0.2 37 1 9	5 - 0.4 1953-783	0.22 1 0.02 86.2 1 3.7	6.3 - 0.6 1990 - 92			
	<400	<320	2493∓111	110∓5	<28137111			
	<3800	<3700	364255∓9695	16082∓428	<(367955∓9695)			
	<7	<7	63071.0	27.8∓0.04	<(637+1.0)			
	<730	<730	12050∓1801	532780	<(1278071801)			
	<150000	<140000	<124650	<5503	<264650			
	268781	1060∓80	5900 7 332	260∓15	6960∓412			
	<1100	<1000	11087360	48.9715.9	2108∓360			
	<1100	<1100	<1108	<48.9	<2208			
	32∓10	<28	<249	<11	<277			
	<1700	<1700	<1801	<80	<3501			
	<1600	<1000	<7479	<330	<8479			
	<43	<41	<332	<14.7	<373			
1	<17	<17	<8.3	<0.4	<25.3			
1	<220	<280	<1662	<73.4	<1942			
	<1.4	3.570 4	<6.4	<0.3	<(9.9+0.4)			
	<5.1	<4.9	<24.9	<1.01	<29.8			
	<410	<400	<416	<18.4	<816			
	<21	<21	<180	<7.9	<201			
	<38	<33	<32	<1.4	<65			
	1370∓40	<1400	<11218	<495	<12618			
	<2	<2	4.370.7	0.1970.03	<(6.3+0.7)			
	2.4+0.7	2.4	7077.1	3.170.3	<72.4+7.1			
	<2.6	<2.6	<19.4	<0.9	<22			
	<6.1	<5.9	163.716.6	7.270.7	<(168.9716.6)			
1	<140	<140	<540	<23.8	<680			

3LE 29. METAL COMPOSITION BY INAA OF CLARIFIER EFFLUENT AND UNDERFLOW AT PLANT A3 (Samples A3-201-79-3 & 4)

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		NEUTRALIZATION BAS	IN EFFLUENT	
TAL	DISSOLVED	SUSPE	NDED	TOTAL
	<u>μg/1</u>	μg/1	mg/kg	μ g/1
	$(381\bar{+}4) \times 10^3$	3510∓37	$(8.57+0.9)\times10^3$	$(381.5+4.04) \times 10^3$
	<27x10 ³	<156	<0.38x10 ³	$<27.2 \times 10^3$
	<63x10 ³	<2990	_<7.31x10 ³	<66x10 ³
	.655+.06	0.123∓0.002	-0.30170.01	0.778+0.062
	69.5+8.8	32.670.6	79.75+1.46	102.179.4
	130 <u>+</u> 13	74.5∓0.9	182.272.2	204.5713.9
	<2.9x10 ³	2544∓64	$< 6.22 \times 10^3$	<5444∓64
	5.5 <u>+</u> 1.4	2.170.1	5,13∓0.16	7.6+1.5
	<510	1371∓41	<3352	<1881∓41
	<5200	<313	<765	<5513
	567∓52	373712	<911∓28	<940∓64
	<370	13.270.3	<32.270.8	<383.2∓0.3
	15∓3	1.67	3.970.3	16.673.1
	<30	<2.1	<5.1	<32.1
	19175	2.0+0.1	4.970.1	19374.1
	<87	<3.3	<8.0	<90.3
	<1400	<108	<264	<1508
	<890	<48.3	<118	<938.3
	<41	<2.04	<5.0	<43.04
	<1.1	<0.69	<1.7	<1.79
	<46	<2.42	<5.93	<48.42
	<11	<0.09	<0.21	<11.09
	10.1∓0.5	0.5470.01	1.33∓0.03	10.64∓0.51
	<3.8	<0.21	<0.52	<4.01
	<550	32.2+6.9	78.7+16.9	<582.2∓6.9
	<4.0	1.67∓0.03	4.0970.08	<5.67∓0.03
	<20	2.81 +0.46	6.8671.12	<22.81∓0.46
	<4.6	0.46∓0.09	1.12∓0.22	<5.06∓0.09
	0.5	0.04570.009	0.1170.02	0.545∓0.008
	<2.0	<0.046	<0.11	<2.046
1 · · ·	<18	0.198∓0.044	0.48∓0.11	<18.2+0.04
	<2.1	<0.11	<0.27	<2.22
	<3.3	<0.06	<0.15	<3.36
	<2.2	0.11∓0.03	0.27+0.07	<2.31 1 0.03
	<3.0	<0.10	<0.25	<3.1
	<26	<1.7	<4.16	<27.7
	3.170.1	0.109∓0.004	0.27∓0.01	3.2170.1
	<3.2	0.819∓0.051	2.0∓0.12	<4.02∓0.05
	<2.4	0.6970.05	1.66∓0.11	<3.09∓0.05
	<6.3	<0.64	<1.57	<6.94

BLE 30. METAL COMPOSITION BY INAA OF NEUTRALIZATION BASIN EFFLUENT AT PLANT A2 (Sample A2-242-79).

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		NEUTRALIZATION BAS	IN EFFLUENT	
METAL	DISSOLVED	SUSPEI	NDED	TOTAL
	μg/1	μg/1	mg/kg	µg/1
Na	$(1.37 + 0.02) \times 10^7$	(4.33∓0.04)×10 ⁶	(75.5∓0.73)x10 ³	(18.03+0.24)×10 ⁶
K	<8.0x10 ⁵	<1.67x10 ⁵	<2.92x10 ³	9.67x10 ⁵
Ca	<3.0x10 ⁵	<6.27	<10.95x10 ³	9.27x10 ⁵
Sc	1.13∓0.13	<10.03	<0.18	11.16∓0.13
Cr	<86	<836	<14.6	<92 ⁻ 2
Mn	<930	1820∓140	31.7972.45	<2750+140
Fe	<0.6x10 ⁴	<8.36x10 ⁴	<1.46x10 ³	<8.96x10 ⁴
Co	<10	66.88∓18.81	1.17∓0.33	<76.88718.81
Ni	<980	<18809	<328.5	<19789
Cu	<1400000	<271686	<4745	<1671686
Zn	410∓80	<5016	<87.6	<5426∓80
Ga	<7500 -	<2299	<40.1	<9799
As	<140	<230	<4.01	<370
Se	91∓16	1787∓192	31.2+3.36	1878 - 208
Br	1940∓40	738∓41.8	12.8870.73	2678-81.8
Rb	<110	<2926	<51.1	<3036
Sr	< 31 00	<68966	<1204	<72066
Mo	<450	<899	<15.69	<1349
Ag	<27	<648	<11.31	<675
Cd	<720	<1275	<22.26	<1995
In	<320	<81.5	<1.42	<401.5
Sb	<20	196710.2	3.42-0.18	<216-10.2
Cs	<7	<150.5	<2.63	<157.5
Ba	<15000	<25079	<438	<40079 -
La	<20	<77.3	<1.35	<97.3
Ce	<740	<606.1	<10.58	<1346.1
Sm	<40	<75.2	<1.31	<115.2
Eu	<10	<25.1	<0.44	<35.1
Tb	<20	<33.4	<0.58	<53.4
Dv	<2000	<205	<3.58	<2205
Yb	<40	<71.1	<1.24	<111.1
Lu .	<30	<48.1	<0.84	<78.1
Hf	<5	<64.8	<1.13	<69.8
Ta	<12	1563	27.3+0.62	<1575+35.5
W	<29	<502	<8.76	<531
Au	<3	21.172.3	0.3770.04	<24.172.3
Нд	10∓2	<58.5	<1.02	<68.5+2
Th	<7	<73.1	<1.28	<80.1
и.	<80	<140	<2.45	<220

TABLE 31. METAL COMPOSITION BY INAA OF NEUTRALIZATION BASIN EFFLUENT AT PLANT A2 (Sample A2-319-79)

		NEUTRALIZATION BASIN	N EFFLUENT	
	DISSOLVED	SUSPENI	DED	TOTAL
	µg/1	ug/1	mg/kg	µq/1
	(0.159∓0.002)×10 ⁷	(11.49 - 0.147)x10 ⁴	(3.58∓0.046)x10 ⁴	(170.49+2.147)x10 ⁴
	<1.0x10 ⁵	<0.735x10 ⁴	<0.23x10 ⁴	<10.74x10 ⁴
	<1.0×10 ⁵	<4.90x10 ⁴	<1.53x10 ⁴	<14.90x10 ⁴
	0.8670.18	<1.03	<0.32	<1.89+0.18
	<68	4680798.02	1458730.5	<4748∓98.02
	<80	129.978.09	40.4672.52	<209.978.09
	<6x10 ³	<0.98x10 ⁴	<0.30x10 ⁴	<1.58x10 ⁴
	<7	23.77-2.94	7.4+0.92	<30.77+2.94
	<870	<1568	<488.55	<2438
	<120000	<12497	< 3893	<132497
	<280	914-112.7	284.7735.11	<11947112.7
	<820	139.67∓29.40	43,51∓9,16	<959.67+29.40
	<40	<13.0	<4.05	< 53
	<38	183.53716.42	57.1775.11	<191.53+16.42
	275∓9	24.0172.70	7.48∓0.84	299.01711.70
	<180	<31.85	<9.92	<211.85
	<2900	<3431	<1069	<6331
	<170	<68.61	<21.37	<238.61
	<23	<46.56	<14.50	<69.56
	<260	<83.31	<25.95	<343.31
•	<10	<3.43	<1.07	<13.43
	<9 7 2	<1.72	<0.53	<10.72+2
	<7	<14.95	<4.66	<21.95
	<5500	<1568	<489	<7068
	<20	<4.66	<1.45	<24.66
	<50	<71.06	<22.14	<121.06
	<10	<5.88	<1,83	<15.88
	<5	<1.47	<0.46	<6.47
	<7	<2.21	<0.69	<9.21
	<40	<11.76	<3.66	<51.76
	<10	<4.41	<1.37	<14.41
	<10	<3.43	<1.07	<13.43
	< 4	<6.62	<2.06	<10.62
	<4	162.273.68	50.5371.14	<166.273.68
	<100	<29.4	<9.16	<129.4
	<1	0.78+0.1	0.2470.03	<1.78∓0.1
	<4.5	< 6.37	<1.98	<10.87
	< 5	<7.84	<2.44	<12.84
	< 30	< 9.06	< 2.82	<39.06

E 32. METAL COMPOSITION BY INAA OF NEUTRALIZATION BASIN ÉFFLUENT AT PLANT AI (Sample A1-21-80) _____

5-DA	Y COMPOSITE			FILTERED 5-DAY COMPOSIT
DISSOLVED	SUSPE	NDED	TOTAL	- (1
<u> </u>	<u> </u>	Mg/Kg4	<u> </u>	<u> </u>
(60.97+0.53)x10*	(7.93+0.47)×10 ⁺	(3+0.18)×10	(68.9 +)x10 ⁻	(91.56 + 0.67)×10 ⁻⁴
<3.37x10 ⁺	7.63X10'	2.88x10	<11x10'	<4.11x10 ⁺
<6.95x10	73.05x10'	27.62x10'	<80x10'	<9.78x10'
0.31+0.06	7.31+0.54	2.75x10	_ 7.62+0.6	0.70+0.18
82+9	1168-91	441.6+34.4	12507100	170714
72+14	4618796	1746∓36.3	46907110	841719
0.33×104	(2.87+0.4)104	(1.09∓0.15)x10 ⁴	(3.2∓0,4)×10 ⁴	<0.5x10 ⁴
<8.6	69.7∓8.1	26.473.1	78.348.1	<8.7
<580	1820	688	<2400	<860
<67000	523000	197732	<590000	<82000
<230	17470∓7 <u>2</u> 0	6605 - 272	177007720	990 - 120
<470	1030	389	<1500	<580
<15	165∓20	62.4∓7.6	180720	23 <u>+</u> 4
<32	198	74.9	<230	<42
153∓5	537∓5	203∓2	690∓10	169∓4
<100	520	196.6	<620	<161
<1700	5700 - 2400	2155∓907	7400∓2300	<2400
<1000	6340	2397	<7340	<1400
<37	213	80.5	<250	<42
<13	86	32.5	<99	<17
<64	216	81.7	<280	<91
<12	20	7.6	<32	<9.3
4.3+0.5	43.7+1.5	16.570.6	48-72	5 570 4
<4.4	27.6	10.4	<32	<6.4
<610	7690	2907	<8300	<800
<9.2	17.8	6.7	<27	<4.9
<21	179	67.7	<200	<25
<4	46	17.4	<50	5.171.4
<1.8	10.273	3.9+1.1	1273	<0.7
<2.6	6.4	2.4	< 9	<3
<21	72	27 2	<93	<23
<2.2	15.8	6.0	<18	· <2 7
<3.6	6.4	2 4	<10	<4
<2 4	17.6	6.7	<20	13
< 3.7	18.3	6.9	<22	<5 A
<28	222	83.9	~250	<30
1 670 1	22 410 9	8 5IN 3	24-1	1 820 1
~3.5	1355150	512110	1360-50	1.070.1
-2.5	17 5	515713	-20	4.071.2
12.5	17.5	0.0	<20	< 3

LE 33. METAL COMPOSITION BY INAA OF ETCH/DESMUT RINSE WATER COMPOSITE AT PLANT E1 (Sample E1-263-79)

		NEUTRALIZATION BASI	NEFFLUENT	
AL	DISSOLVED	SUSPEN	DED	TOTAL
	ug/1	ug/1	mg/kg	μg/1
-	(0.203+0.002)×10 ⁷	(7.89∓0.12)×10 ⁴	(1.9270.03)×10 ⁴	(210.89 ⁺ 2.12)×10 ⁴
	<8.7x10 ⁴	<0.55x10 ⁴	<0.13x10 ⁴	<9.25x10 ⁴
	<50x10 ⁴	<9.73x10 ⁴	<2.37x10 ⁴	<59.73x10 ⁴
	<2.6	1.19∓0.16	0.2970.04	<3.79+0.16
	<200	1277-36,5	310.778.9	<1477∓36.5
	2860∓80	913.2718.2	222.2+4.4	3773.2+98.2
	<2.8x10 ⁴	(5.90∓0.16)×10 ⁴	(1.43∓0.04)x10 ⁴	<(8.7 7 0.16)x10 ⁴
	<51	14.6+1.2	3.55+0.30	<65.5+1.2
	<4100	<620.2	<150.8	<4720.2
	<170000	47546+3648	11568∓888	<217546+3648
	34007600 -	12160∓365	2959788.8	15560∓965
	<1200	262.7+26.8	63.9∓6.5	<1462.7+26.8
	<45	<37.7	<9.17	<82.7
	<200	<30.4	<7.4	<230.4
	<613∓12	<37.7	<9.17	<650.7+12
	<1000	<92.4	<22.5	<1092.4
	<25000	<1702	<414.2	<26702
1.	<14000	<170.2	<41.4	<14170.2
	<120	<76.6	<18.6	<196.6
	<120	<17.02	<4.14	<137.02
	<200	<133.8	< 32.5	< 333.8
	<36	<2.07	<0.50	<38.07
	<85	4.970.9	1.1870.21	<89.9 1 0.9
	<36	<5.23	<1.27	<41.23
	<3400	<1216	<295.9	<4616
	1372	6.69∓1.09	1.63+0.27	19.69+3.09
	<120	<25.5	<6.21	<145.5
	<14	<13.4	<3.25	<27.4
	<20	<1.58	<0.38	<21.58
1	<4.2	<0.67	<0.16	<4.87
	<78	<46.2	<11.24	<1 24 .2
	<10	<2.92	<0.71	<12.92
	<2.1	<0.35	<0.09	<2.45
1	<16	<2.43	<0.59	<18.43
	<30	<255.4	<62.1	<285.4
	<110	<340.5	<82.8	<450.5
1	<160	0.74∓0.13	0.18∓0.03	<160.74∓0.13
	<170	<2.80	< 0.68	<172.80
1	<16	<2.92	<0.71	<18.92
	<21	<11.67	<2.84	<32.67

LE 34. METAL COMPOSITION BY INAA OF ETCH/DESMUT RINSE WATER COMPOSITE AT PLANT EI (Sample E1-80-80)

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basin) averaged 0.348gAl/gNVSS, indicating that the vast majority of the sludge solids were composed of aluminum precipitated apparently as amorphous Al(OH)₃. The values for A3 neutralization basins were higher than the theoretical value, further indicating that the major sludge metal was aluminum.

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DESCRIPTION	gA1/gSS	gA1/gNVSS*
Neutralization Basin-1 Neutralization Basin-3 Clarifier Underflow	0.415 0.468 <u>0.26</u> (0.381)**	0.579 0.598 <u>0.338</u> (0.505)
Neutralization Basin Weekday Weekday Weekend	0.283 0.264 <u>0.272</u> (0.273)	$\begin{array}{r} 0.395 \\ 0.361 \\ \underline{0.324} \\ (0.360) \end{array}$
Neutralization Basin	0.296	0.397
Rinse Tank	0.206	0.270
	Neutralization Basin-1 Neutralization Basin-3 Clarifier Underflow Neutralization Basin Weekday Weekday Weekend Neutralization Basin Rinse Tank	DESCRIPTIONGAT/G33Neutralization Basin-10.415Neutralization Basin-30.468Clarifier Underflow0.26(0.381)**Neutralization Basin0.283Weekday0.264Weekday0.272Weekend0.272(0.273)0.296Rinse Tank0.206

TABLE 35. ALUMINUM CONTENT OF SLUDGE SOLIDS

*NVSS = Non-volatile suspended solids.

'Bracketed () terms are average values for plant samples.

Detection of aluminum by INAA was impossible due to the presence of numerous netals with similar activation half-life values. However, the major metals decected by INAA, e.g., Ca, Fe, and Cu, were present at approximately 1-200mg/kgSS evels which were at least three orders of magnitude below the 0.2-0.38g/gSS values for Al.

Further concern for the metal composition of aluminum sludge samples was ocused on those metals which are indicated as being potentially toxic. The priority pollutant metals, i.e., Ag, As, Cd, Cr, Hg, Pb, Se, Be, Cu, Ni, Sb, 1, and Zn, were chosen as the major metals of concern. This list of metals ncluded those cited in EPA Drinking Water Standards, i.e., Ag, As, Cd, Cr, Hg, 'b, and Se (EPA, 1980a), and used to evaluate hazardous waste characteristics in he EPA-EP leach test.

Trace metal composition data were collected for sludge samples from each acility. The data were collected immediately after measurement of the compostion of filtered leachates developed with the EPA-EP test. Those metals unetected in EP leachates at $\mu q/l$ -levels were not analysed and are not reported. As indicated in Section 5 (Analytical Methods), trace metal analyses were performed to determine both dissolved and suspended metal concentrations. Results were therefore presented for dissolved and suspended metal concentrations, and total metal composition was reported on a wet solids basis for a dewatered sludge sample. Dewatered sludge moisture content values used in these latter calculations were obtained using the procedure established for specific resistance tests for uniformity and to simulate results obtained at plants using vacuum and pressure filtration systems. Results for dissolved and suspended metals and the solids content of a dewatered sludge were used to calculate the (1) mass of metal in a wet sludge and (2) the portion of total sludge metal in the suspended form. Results for the samples examined are presented in the following tables.

Metal distribution in sludge from plant A3 with 11.8 percent solids (dry) is presented in Table 36. The major metal in the dry solids was Ni, which was the major metal in the filtrate at 260 μ g/ ℓ . Except for As and Se, over 98 percent of most metals were present in the solid phase. In reference to Ni content, plant A3 used a Ni-Acetate in the seal bath following anodizing, which could account for the high amount of Ni in plant wastewater.

			DEWATERED SLUDGE	
METAL	DISSOLVED	SUSPENDED mg/kg(dry)	mg/kg(wet)	FRACTION IN SUSPENDED FORM
As	54	3	0.40	0.885
Cd	0.8	1.2	0.14	0.995
Cr	9	89	10.51	0.999
Cu	48	23	2.76	0.985
Ni	260	2200	259.83	0.999
Pb	1	10	1.18	0.999
Se	38	<1	<0.15	<0.779
Zn	70	120	14.22	0.996

TABLE 36. TRACE METAL COMPOSITION OF WASTEWATER AT PLANT A3.

Sludge solids content = 11.8 percent.

Metal distribution in sludge from plant A2 with 19.8 percent solids is preented in Table 37. No significant quantities of trace metals were found in the uspended fraction, but the dissolved fraction contained 1.7 mg/ ℓ of Se and 1.4 g/ℓ of Zn. The operation of a dye line at the plant may account for the presence of Se. With the exception of Se and Hg, over 82 percent of most metals were preent in the suspended fraction of the dewatered sludge.

			DEWATER	ED SLUDGE
METAL	DISSOLVED	SUSPENDED mg/kg(dry)	mg/kg(wet)	FRACTION IN SUSPENDED FORM
Ag	49	1.6	0.36	0.88
As	160	<3	<0.72	<0.825
Ве	1.7	0.2	0.04	0.968
Cd	1.2	0.9	0.18	0.99
Cr	180	21	4.30	0,967
Cu	130	35 -	7.03	0.986
Hg	28	<0.1	<0.04	<0.495
Ni	74	64	12.73	0.995
Pb	24	24	4.77	0.996
Se	1700	1	1.56	0.127
Zn	1400	<26	<6.27	<0.821

TABLE 37. TRACE METAL COMPOSITION OF WASTEWATER AT PLANT A2.

Metal distribution in sludge from plant Al with 8.3 percent dry solids is presented in Table 38. The highest dissolved and suspended metal concentrations were for Cr and Zn. With the exception of Se, which was contained at low levels in precipitated sludge solids, more than 99 percent of most metals were contained in the suspended phase of a dewatered sludge sample (8.3 percent). The source of Cr, the only significant hazardous component of the sludge, was probably not the alloys finished at plant Al, as they contained no significant quantity of Cr. A paint line was used at plant Al in which a dichromate derivative was used to prepare aluminum extrusions for painting and could be the source of Cr in the sludge.

TABLE 38. TRACE METAL COMPOSITION OF WASTEWATER AT PLANT A1.

			DEWATERED SLUDGE	
IETAL	DISSOLVED µg/l	SUSPENDED mg/kg(dry)	mg/kg(wet)	FRACTION IN SUSPENDED FORM
As	18	<3	<0.26	<0.957
Cd	5.6	15	1.25	0.996
Cr	1500	2600	217.18	0.994
Cu	25	140	11.64	0.998
Ni	78	115	9.62	0.992
Pb	1.4	19	11.58	0.998
Se	130	<1	<0.20	<0.415
Zn	1500	3000	250.38	0.994

Metal distribution in sludge from plant El with 17.3 percent solids is listed in Table 39. The dry solids were 0.9 percent Cu and 0.36 percent Zn; however, there was almost no dissolved Cu while Zn was at 3.5 mg/ ℓ . Two additional significant suspended metals were Cr and Pb, which were, however, at low concentrations in the dissolved phase. -In addition to dissolved Zn, Ni was also present at 140 µg/ ℓ . Most of the metals in a dewatered sludge were in the suspended form.

			DEWATERED SLUDGE	
METAL	DISSOLVED	SUSPENDED mg/kg(wet)	mg/kg(wet)	FRACTION IN SUSPENDED FORM
As	61	49	8.53	0.994
Cd	58	٦٦	1.95	0.974
Cr	7	1200	207.61	0.999
Cu	29	9000	1557.02	0.999
Ni	140	150	26.07	0.995
Pb	1.2	610	105.53	0.999
Se	72	<1	0.23	<0.752
Zn	3500	3600	625.69	0.995

TABLE 39. TRACE METAL COMPOSITION OF WASTEWATER AT PLANT E1.

In summary, most of heavy metals in aluminum-finishing sludges from plants A1, A2, A3, and El were present in the suspended solids and not dissolved in interstitial water. The major trace metals contained in the suspended form of all four sludges were As, Cd, 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 vere not detected in any samples, Ag, Be, and Hg should be neglected because they vere only detected in sludge from plant A2 in very low concentrations. While As, Cd, and Se were in all four sludge samples, the amounts present were also low. Sludge from plant El contained 100- to 500-fold more Cu and Pb than other sludges, vhile sludge from plant A3 contained about ten-fold more Ni than other sludges. Sludges from plants A2 and A3 had 20-fold less Cr than sludges from plants A1 and Cl, while sludge from plant El had 3- to 100-fold more Zn than sludges from plants A1, A2, and A3.

SECTION 8

INDUSTRIAL PLANT WASTEWATER SURVEY

To establish the mass flow of wastewater and aluminum in an industrial plant an intensive industrial waste survey was conducted at Plant A3. This plant was chosen due its proximity to the laboratory facility and was dictated by economic factors associated with the labor-intensive nature of the study. The plant was, however, similar to the anodizing portions of Plant A1 and A3 and was considered to be typical of extrusion/anodize plants finishing architectural aluminum.

PLANT DESCRIPTION

Plant A3 has conventional clear-coat and integrated-color sulfuric acid anodizing capabilities. A schematic flow diagram of the anodizing line is presented in Figure 17. The plant has cleaning, alkaline etching and desmut steps prior to anodizing. Integral-color anodizing solutions are continuously circulated through an ion-exchange system to control aluminum build-up in the finishing solution. Rinse tanks and seal tanks are used to remove dragout from metal surfaces and to seal the anodized metal surface. A description of process operations and chemicals used in these operations are presented in Table 40.

The major sources of wastewater include rinse waters, ion-exchange regeneration acid and caustic etch wastes. All rinse wastewaters and cooling waters are discharged to a pit below the anodizing area. These pit wastewaters flow by gravity to an equalization tank into which the acid regenerant waste is also discharged, as indicated schematically in Figure 18. Wastewaters discharged to the equalization pit are pumped into a three-stage neutralization basin in which pH values are adjusted to near-neutral values. Spent etch wastes are stored in two tanks and metered into the neutrization basin for pH adjustment. In the three-stage neutralization system, wastes are neutralized in the pH range of 6 to 9 and aluminum hydroxide is precipitated. After addition of a polymer following neutralization, the wastewater is discharged to clarifier and the clarifier effluent is discharged to an industrial sewer. The thickened sludge is dewatered onto filter presses and dewatered sludge solids are disposed on land at the plant site.

SURVEY PROCEDURES AND TECHNIQUES

The industrial wastewater survey was conducted to determine the total and individual wastewater flows throughout the plant; the mass flow of aluminum



FIGURE 17. Schematic Diagram of Anodizing Line and Sampling Locations at Plant A3.

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Tank Number	Tank Description	Tank Contents and Characteristics	Comments
1	Caustic	Caustic decant @ 0.5-0.75 ₃ g/1 V = 20.44m ³ T = 55°C Al+3 = 60 g/1	To strip spacers and work racks; contains decanted flow from #5 and #7. Waste pumped to caustic storage tanks and used in waste- water neutralization.
2	Rinse	Continuous-overflow water rinse V = 20.44m ³ T = ambient	To rinse spacers and work racks only. Continuous discharge to waste.
3	Cleaner	SC-77 low-foam soak @ 0.4 g/l V = 47.58m ³ T = 60-71 °C	Higher temperatures cause etching action. Lower temperatures cause foaming.
5,7	Etch	Caustic @ 0.75 g/l; Sodium Tetrasulfide & Glucoheptanate both @ 3%; Sodium Nitrate @ 2 g/l of Caustic; Zinc.	To etch material and to reduce gloss. Quick transfer to rinse tanks is necessary to prevent drain marks or caustic burns. Decanted flow discharged to tank #1.
		V = 37.85m ³ T = 57-60 °C A1 ⁺³ = 35 to 55 g/1	
6,8	Rinse	Continuous-overflow water rinse	To prevent neutralization of the desmut tank. Con-
		$V = 37.85m^3$ T = ambient	tinuous discharge to waste.
9	Desmut	SC 582 & SC 593 Sulfuric Acid Nitric Acid V = 37.85m ³ T = ambient	To remove smut. Total chemical concentration @ 12% or above

TABLE 40. DESCRIPTION OF ANODIZING PROCESSLINE AT PLANT A3

TABLE 40. (continued)

Tank Number	Tank Description	Tank Contents and Characteristics	Comments
10,11	Rinse	Continuous overflow Water rinse V = 20,44m ³ T = ambient	Overflow from #11 goes to #10. To rinse desmut acid. Spray mist system on both. Continuous discharge to waste.
-	Holding (2)	Continuous overflow water rinse V_= 34.1 & 20.44m ³ T_= ambient	Overflow to desmut rinse tank #11.
12,13 14,16 22,23 & 24	Integral- Color Anodize	Sulfophthalic Acid @ 70 to 75 g/l Sulfuric Acid @ 3.5-4.0 g/l V = 23.85m ³ T = 15 °C	To develop bronze and black finishes. Tank contents are regenerated continuously with ion- exchange resins.
15,25	Clear-Coat Anodize	A1 ⁺³ = 0.6-1.1 g/1 Sulfuric Acid @ 18-20% by wt V = 23.85m ³ T = 17-20 °C A1 ⁺³ = 20 g/1	When aluminum content exceeds 20 g/l the tank is dumped.
18A, 28A & 28B	Rinse	Continuous overflow water rinse V = 20.44m ³ T = ambient	Rinse after clear-coat anodizing only. Over- flow from # 28B to @ 28A Continuous discharge to waste.
18B,20 21, 30 &31	Seal	SC 576 @ 0.003 g/1 V = 37.85m ³ T = 80 °C pH = 5.0 to 6.0	Seal metal after anodiz- ing. High pH causes powder, low pH causes poor seal. pH adjusted with flake caustic and acetic acid.

TABLE 40. (continued)

Tank Number	Tank Description	Tank Contents and Characteristics	Comments
19,29	Warm Rinse	Continuous overflow Water rinse V = 20.44m ³ T = 60 °C pH = 5.0 to 6.0	Prevent crazing of coat- ing and to rinse seal chemicals. Overflow from # 29 to # 40. Continuous discharge to waste from # 19.
40	Rinse	Continuous overflow warm tap water rinse	To rinse work rods. Continuous discharge to waste

All tanks, except the cleaner tank #3 and rinse tank #40, are provided with air agitation.



Figure 18. Sampling Locations at Plant A3.

through the plant, and the sources and quantities of wastes generated within the plant. In determination of total wastewater flow within the plant, flow rates of the waste components making up the total wastewater flow, e.g., rinse waters, etch wastes and acid-regenerant wastes, were determined individually. In addition to the flow rate measurements within the finishing areas, the wastewater flow rate through the wastewater treatment plant and total anodizearea influent were measured so that a mass balance on water can be performed. Wastewater flows for continuous-flow rinse tanks were determined through measurement of all influent water flows to each tank. These influent flows were measured at the beginning of the survey using calibrated containers and a stopwatch. The flows were not adjusted throughout the survey and remained constant during the period of investigation. Wastewater flow through the treatment plant was determined using a rectangular weir at the the discharge of the second stage of the neutralization tank. Water flow rates from domestic and industrial supplies were determined using the permanent flow meters in the plant.

For determination of mass flow of aluminum through the plant, rinse waters, etch wastewater, acid-regenerant wastewater and process suspensions i.e., anodizing, caustic etch, desmut, seal tank suspensions, were analyzed with respect to aluminum concentration. They were also analyzed for alkalinity or acidity, temperature and pH.

The location of sampling points are shown in Figures 17 and 18. Samples were collected at 1-h intervals for a period of 8-h on the first shift. The samples were then included into a single composite sample for each location. Discrete samples were taken from acid-regenerant and spent-etch wastes. Aluminum, alkalinity, acidity, temperature and pH were determined in accordance with the procedures described in <u>Standard Methods</u> (1976) as indicated in Section 5.

WASTEWATER FLOWS AND CHARACTERISTICS

Rinse Wastewater

The results of the analysis conducted on rinse wastewaters are presented in Table 41. Water flow rate into the rinse tanks varied considerably from $1.3m^3/h$ for warm rinse to $105m^3/h$ for desmut rinse. Alkalinity of rinse wastewaters from spacer caustic, caustic and warm rinse tanks were determined and phenolphthalein and methyl orange alkalinity ranges were 240-2420 mg/l as CaCO₃ and 30-3380 mg/l as CaCO₃, respectively. Acidity for desmut rinse and integrated-color and clear-coat anodize rinses was determined. The ranges of methylorange and phenolphthalein acidity were 190-1710 mg/l as CaCO₃ and 500-2590 mg/l as CaCO₃, respectively. Temperatures of the samples were calculated on an hourly basis and ranged from 19°C to 54°C. The pH values of the composite samples varied between 1.9 to 12.0. The aluminum content of the rinse water samples varied between 5 to 1216 mg/l being maximum for caustic rinse wastewater.
Sample Location* #	Description of Tank	pН	Temp.	Alkal phenolphthale (mg/l	<u>linity</u> in <u>total</u> CaCO ₃)	Ac methyl oran (mg/l	<u>idity</u> <u>ige total</u> CaCO ₃)	Flow <u>Rate</u> (m ³ /h)	Aluminum <u>Content</u> mg/l
AN-2	Spacers Caustic Rinse	10.1	22.0	240	550	-	-	2.2	105.4
AN-6	Caustic Rinse	12.0	20.5	2,420	3,380	-	-	6.8	1216.0
AN-8	Caustic Rinse	11.8	20.5	1,990	3,050	-	· · · · · · · ·	7.3	704.0
AN-10	Desmut Rinse	2,6	19.0	-	-	190	500	10.5	24.7
AN-15	Hard-Coat An. Rinse	2.6	20.0	-	-	450 ,	710	3.4	13.2
AN-18a	Clear-Coat An. Rinse	2.4	19.0	-	-	470	580	3.4	10.8
AN-19	Warm Rinse	6.9	54.0	-	60	-		1.3	5.0
AN-25	Hard-Coat An. Rinse	2.4	19.0	-	-	430	740	2.7	24.0
AN-28a	Clear-Coat An. Rinse	1.9	21.0	-	-	1,710	2,590	2.5	135.0
AN-29	Warm & Work Rod Rinse	6.6	54.0	-	30	-	-	1.9	5.0
-	Transfer Tank	-	-	-	-	-	-'	1.3	-

TABLE 41. SURVEY RESULTS FOR RINSE WASTEWATERS AT PLANT A3.

*AN-#; Samples taken from a numbered tank (#) in the anodize (AN) line.

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Treatment Plant Wastewater

Analyses were conducted on the influent to the wastewater neutralization basin, claifier influent and clarifier effluent. The flow rate of the neutralization basin influent was not measured directly but was calculated from flow rate data for all rinse waters and averaged 43.3m³/h. The flow rate through the treatment plant (i.e., 3rd neutralization basin influent) was 43.7m³/h, indicating excellent agreement with the flow rate calculated from rinse tank flow rates. Temperature for all three suspension was 21°C and pH values were 5.1, 7.6 and 7.1 for pit wastewater effluent, clarifier influent and effluent, respectively.

Clarifier influent and effluent alkalinities were 290 and 60 mg/l as $CaCO_3$, respectively. The pit wastewater acidity was determined as 270 mg/l as $CaCO_3$. Aluminum content was 310 mg/l for pit wastewater, 1110 mg/l for clarifier influent and 30 mg/l for clarifier effluent.

Ion-Exchange Acid-Regenerant Wastewater

Wastewater from ion-exchange resins used to remove aluminum from integralcolor anodizing tanks (No. 12, 14-16, and 23-24) were analyzed. The average aluminum concentration in the acid-regenerant waste from the ion-exchange unit was found to be 0.896 g/l and the average acid-regenerant flow rate was 3,928 l/h.

Regeneration of three ion exchange systems was conducted on the day of the survey in the following steps: (1) pneumatic discharge of anodize solution in ion exchange tank to a holding tank; (2) backwash of resin with water and an initial air agitation; (3) resin regeneration with 15 percent sulfuric acid; (4) water backwash; and (5) addition of anodize from holding tank to resin. The initial (1) and final (5) steps did not result in a wastewater discharge. Therefore, the wastewater produced during regeneration was composed of an initial flow of water followed by a highly-acidic flow of sulfuric and a final water flow. The total regeneration cycle covered about 2h, for each resin system, while wastewater discharges occurred over a 1h period. The average flow over the lh discharge period for the three ion exchange systems ranged from 8.8-13.9 1/h. Since resin regeneration occurred only during the acid addition step, aluminum was only detected during this portion of the cycle as indicated in Figure 19. Aluminum levels as high as 6.2 g/l were detected during the regeneration cycle. This high level of aluminum was, however, much lower than required for consideration of recovery as aluminum sulfate, where aluminum concentrations of 40-45 g/l are necessary.

The total wastewater flow from regeneration of ion-exchange systems was discharged to a holding tank, from which the wastewater was slowly metered into the wastewater equalization basin (see Figure 18).

Spent Etch Wastewater

The average flow rate of spent etch used in neutralization of plant wastewaters was determined to be $0.77m^3/h$. Determination of the aluminum content in the spent etch wastewater was achieved with samples taken at the beginning





and end of the survey from spent etch storage tanks. Aluminum concentration was 55 g/l at the beginning and 49 g/l at the end of the survey. No change in alkalinity and pH was observed during the survey with alkalinity and pH values of 280 g/l as CaCO₃ and 12.1, respectively.

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Finishing Suspensions and Solutions

All anodizing process tanks were sampled during the survey. Individual samples were taken from the cleaner and desmut tanks, and composite-grab samples were taken from integral-color and clear-coat anodizing, sealing and etching tanks to determine the aluminum concentration of these suspensions. The results are presented in Table 42. Aluminum concentration ranged from 0.02 g/l for integrated-color seal to 28 g/l for etching tanks.

TABLE 42. ALUMINUM CONTENT OF ANODIZING PROCESS SUSPENSIONS.

TANK DESCRIPTION	TANK #	ALUMINUM CONTENT (g/l)
Cleaner	3	0.14
Etching	5,7	28.0
Desmut	9	1.2
Integrated-Color Anodizir	ig 12	0.37
Integrated-Color Anodizir	g (22,23,24,12,13,14,16)	0.3
Clear-Coat Anodizing	(17,26,27)	6.0
Integrated-Color Seal	(20,21,31)	0.02
Clear-Coat Seal	(30,18b)	0.03

WASTEWATER MATERIAL BALANCES

Water-Wastewater

Water-use data were collected for water withdrawn from on-site industrial wells and from the domestic water supply for use in the anodize finishing area. Wastewater flow data were also collected for all identified point-sources in the plant finishing area as well as flow data in the wastewater neutralization facility. An evaluation of the water budget for the plant is presented in Table 43.

Description			Flow (m ³ /d)	
WATER 1. Domestic Supply			51.8	
2. Industrial Supply		TOTAL	<u>293.8</u> 345.6	~
WASTEWATER				
 Individual Wastewater flows a. Rinse Waters b. Acidic Ion-Exchange Regenerant c. Spent-Etch 	τοτάι	WASTEWATER	1039.2 92.3 17.8	
2. Wastewater Flow (Neutralization Basin)		WAJILWAILK	1048.8	

TABLE 43. WASTEWATER MATERIAL BALANCE AT PLANT A3

Initially, comparison of the measured water use of $345.6m^3/d$ with measured wastewater flows of 1048.8 and 1149.3 m^3/d indicate that water flow measurements were grossly underestimated. The flow meters used to measure the two water flows were not calibrated and were obviously in error.

Wastewater flow was estimated by summation of all direct measurements of wastewaters discharged from finishing tanks, i.e., $1149.3m^3/d$, and by measurement of the combined wastewater discharged to the neutralization basin, i.e., $1048.8m^3/d$. In comparison of these two flows, the ion-exchange regeneration flow, i.e. $92.3m^3/d$, must be subtracted from the estimated flow of $1149.3m^3/d$ since this wastewater was not discharged to the neutralization basin during the survey. This was done to allow for the accurate measurement of this waste flow. Therefore the flow measured at the neutralization basin, $1048.8m^3/d$, and the flow estimated by summation of finishing solution flows, $1149.3 - 92.3 = 1057m^3/d$, were different by 0.8 percent. This agreement was excellent and confirmed the errors associated with measurement of influent water.

Due to the limited availability of aluminum production data at the plant during the survey, wastewater flows could not be related directly to production rates. However plant production was estimated to be 6.8 x 10^5 kg/mo. Using 20 and 30 days for the period of plant operation, the average wastewater flow, and hence water use, for the plant would be $3.4x10^{-2}$ m³/kg (4 gal/lb.) and $5.1x10^{-2}$ m³/kg (6 gal/lb.), respectively. These values are within the range of 2.5 - $6.7x10^{-2}$ m³/kg (3-8 gal/lb.) for the aluminum finishing industry (Steward and McDonald, 1979).

Aluminum

The mass flow of aluminum associated with individual process wastewaters are presented in Table 44. Analysis of the data are facilitated first by comparison of the aluminum mass flow in rinse wastewaters (i.e. 346.3 kg/d) and that in the influent to the neutralization basin, i.e., 322.2 kg/d. The difference of approximately 7 percent between these values was an excellent agreement considering the semi-batch nature of the finishing operation and the hourly-sampling period used in the survey.

Since spent etch was used to neutralize combined wastewaters, the impact of this addition on aluminum mass flow is of importance. The neutralization basin effluent contained an aluminum mass flow of 1164.2 kg/d, a value much higher than that from the rinse water flows. The aluminum in the spent etch flow was 853.6 kg/d. When added to the aluminum mass flow in the neutralization basin influent, the total influent aluminum was 1175.8 kg/d (853.6 + 322.2). This aluminum flow was then within 1 percent of the measured value of 1164.2 kg/d, again confirming the precision in both aluminum and wastewater flow measurements. Finally, it was apparent that 66.4 percent of the measured aluminum mass flow was attributable to spent etch used to neutralize combined plant wastewaters. The portion of extruded aluminum lost to the wastewater treatment system was of interest. Using a 20 and 30d plant operation period and a production rate of 6.8 x 10⁵ kg/mo, the percent of finished aluminum discharged to the wastewater treatment was 3.4 to 5.1 percent. These values are high, indicate a significant loss of aluminum during finishing and are indicative of a significant sludge disposal problem.

SAMPLE NUMBER	DESCRIPTION OF SAMPLE		FLOW RATE	ALUMINUM CONTENT	MASS FLOW ALUMINUM (kg/d)
			(m ³ /h)	(g/l)	
FINISHI	NG SOLUTIONS				
AN-2	Spacers Caustic Rinse		2.20	0.105	5.6
AN-6	Caustic Rinse		6.79	1.216	198.2
AN-8	Caustic Rinse		7.35	0.704	124.2
AN-10	Desmut Rinse	5 a - 10	10.54	0.025	6.3
AN-15	Hard-Coat Anodizing Rinse		3.38	0.013	1.1
AN-18a	Clear-Coat Anodizing Rinse		3.38	0.011	0.9
AN-19	Warm Rinse		1.33	0.005	0.2
AN-25	Hard-Coat Anodizing Rinse		2.65	0.024	1.5
AN-28a	Clear-Coat Anodizing Rinse		2.48	0.135	8.1
AN-29	Warm & Work Rod Rinse		1.89	0.005	0.2
SE-1	Spent Etch Waste		0.74	48.000	853.6
AR-1	Acid Regenerant Waste		3.93	0.896	84.5
WASTEWA	TER FLOWS			·	
Neutral	ization Basin Influent		43.30	0.310	322.2
Neutral	ization Basin Effluent		43.7	1.110	1,164.2

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SECTION 9-

SLUDGE TREATMENT AND DISPOSAL

SETTLING PROPERTIES

Settling Test Variables - -

Characterization of sludge thickening properties must be done using zone settling data for a sludge suspension at various suspended solids concentrations. Batch settling tests are performed in stirred columns to determine interfacial or zone settling velocities as illustrated in Figure 20. Zone settling velocity and sludge concentration data can then be utilized to evaluate the effect of sedimentation basin size or thickening performance and the effects of sludge conditioning on thickening properties.

Settling characteristics of sludge are influenced by test conditions such as column diameter and column height. An evaluation of influence of column diameter was performed using settling columns with diameters of 6, 9, and 15 cm and a 1.0-m-sludge depth. In Figures 20-25, variations of zone settling velocity with suspended solids concentration are indicated for plants A1, A2, A3 and E1. Comparison of zone settling velocities for columns with varying diameters indicated that the effect of column diameter was minimal and could be neglected within the column diameter range of 6 to 15 cm.

The influence of column height on zone settling velocity is illustrated in Figures 26-29 for settling tests conducted at initial sludge depths of 36 and 100 cm with a column diameter of 6 cm. It is apparent that zone settling velocities of the sludges tested were not significantly influenced by column height. To minimize the effect of column diameter and height, the contents of the settling columns were stirred at a tip velocity of 0.31 cm/s. It is known that slow stirring of settling columns aids in formation of large aggregates and decreases the extent of channeling and bridging which alters the settling behavior of sludge in small-diameter settling column (Vesilind, 1979). Since no effect of column diameter and depth on zone settling velocity of sludges was observed, and to minimize the amount of sludge required for study in all subsequent studies of sedimentation, small columns with a 6-cm diameter and 36-cm sludgeheight and equipped with small stirring units (1 rpm or tip velocity of 0.31 cm/s) were used.

Time of storage in transit and in the laboratory was examined using a sludge sample from Plant A3. As indicated in Figure 30, storage for a period of 6 d had minimal effects on zone settling velocities. Effects at higher concentrations were not examined due to the minimal effects indicated at concentrations up to 7 g/l.



Figure 20. Typical Batch Settling Curves Showing Zone Settling Velocity, v, at Sludge Concentration, c, for an Aluminum Finishing Sludge



Figure 21. Settling Properties of Aluminum Finishing Sludge Sample A1-21-80

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Figure 22. Settling Properties of Aluminum Finishing Sludge Sample A2-242-79.



Figure 23. Settling Properties of Aluminum Finishing Sludge Sample A2-283-79.















Figure 27. Influence of Column Height on Settling Properties of Aluminum Finishing Sludge Sample A2-242-79



Suspended Solids Concentration, g/l

Figure 28. Influence of Column Height on Settling Properties of Aluminum Finishing Sludge Sample A3-161-79



Suspended Solids Concentration, g/l





Figure 30. Effect of Storage on Settling Properties of Aluminum Finishing Sludge Sample A3-161-79. (Column Height = 100 cm, Column Diameter = 6 cm).

Unconditioned Sludges - -

Curves of zone settling velocity and suspended solids concentration are shown for all the sludges examined in Figure 31. The settling velocities for sample A2-319-79 were much higher than those for other sludges. This sludge sample was generated at temperature and alkaline pH values resulting from the mixing of concentrated etch and anodize samples during a weekend period when rinse waters were not being discharged to waste treatment. The 2 to 10 fold variation in settling velocities of the sludges can also be attributed to numerous factors, including generation temperature , pH and variations in waste composition. The sludge generated from an etch waste (Plant El) had better settling characteristics than Plants Al and A2. However, there is not an indication that this will always occur.

Differences in settling characteristics of sludges can best be indicated with solids flux relationships. Batch solid flux curves for sludges from 3 anodize plants are presented in Figure 32 . It should be indicated that batch solids flux is equal to the product of zone settling velocity, V;, and an associated suspended solids concentration, C_i , or solids flux = $V_i C_i^1$. The use of examples is an effective way to indicate differences in sludge thickening characteristics. For a wastewater flow of 50m /h(220gpm) with a suspended solids concentration of 2g/1 applied to a clarifier with a diameter of 11.3m (37 ft), the sludge mass application rate to the clarifier would be $lkg/m^2 \cdot h$ (0.2 lb/ft².h). Assuming complete removal of influent solids in the clarifier. the maximum obtainable underflow suspended solids concentration can be predicted using a batch flux curve, such as those presented in Figure 32. For the unconditioned sludge samples from plants Al, A2 and A3, the maximum under flow suspended solids concentrations developed under continuous operation for identical sludge mass application rates of lkg/m²·h would be 3.1 g/l, 3.2 g/l and 16.7 g/l, respectively, as indicated by the three tangent lines in Figure 32. The performance for plants Al and A2 would be totally unacceptable while performance for Plant A3 would result in a sludge volume reduction of 91 percent. These results, however, are not typical of conventional systems since polymer conditioning is commonly used with these sludge suspensions.

Polyelectrolyte-Conditioned Sludges - -

Polyelectrolytes used by several aluminum finishing plants were used to evaluate their effect on sludge settling characterisitcs. The polyelectrolytes used for evaluation were previously presented in Table 14. As with unconditioned sludges $1-\ell$ graduated cylinders were used to examine settling characteristics of polyelectrolyte-conditioned sludges. Furthermore, use of small sludge volumes (i.e.l ℓ) was required to be able to extensively and effectivety evaluate necessary polyelectrolyte conditioning.

Optimum dose, i.e. dose at which settling velocity was at a maximum value for one suspended solids concentration, was determined by application of incremental doses of polymer to previously unconditioned samples. In preliminary studies the dose which resulted in the highest sludge settling velocity was selected as the optimum dose. At this dose, the sludge exhibited discrete settling rather than zone settling and in such cases it was not possible to plot conventional batch flux curves encountered for sludges exhibiting zone settling



Suspended Solids Concentration, g/l

Figure 31. Settling Properties of Aluminum Finishing Sludges (Column Height = 36 cm, Column Diameter = 6 cm)



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characteristics. Therefore, in the subsequent studies, optimum dose was selected as the dose at which 'true' zone settling velocity values were maximized but always at dose levels below which zone settling characteristics started to deteriorate.

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A typical example of variations in settling velocity with polyelectrolyte dose is presented in Figure 33 for polyelectrolytes HF-190, used by Plant A1, and Caraflock 91AP, used for comparison purposes. It was observed that large aggregates were formed as the polyelectrolyte dose increased initially. Continued increases in polyelectrolyte dose resulted in formation of very large aggregates that no longer exhibited zone settling characteristics, but, exhibited discrete settling characteristics. Furthermore, increases in polyelectrolyte dose produced rice-like aggregates which settled slower than those observed at lower doses, due apparently to increase viscosity of the liquid at higher polyelectrolyte doses. The highest dose at which sludge continued to exhibit a zone settling was 15 mg/l for both HF-190 and Caraflok 91AP. However, the associated zone settling velocities for HF-190 and Caraflok 91AP were 8 cm/min and 20 cm/min, respectively, resulting in 60- and 150- fold increases in zone settling velocities, respectively, as compared to unconditioned suspensions.

Variations in settling velocities with polyelectrolyte doses for samples collected from Plant A2 on day 242 are presented in Figure 34 for three polyelectrolytes, Purifloc A23, Separan AP273 and Caraflok 91 AP. As indicated previously, the "optimum dose" corresponded to the dose at which the highest zone settling velocity was observed. At the optimum doses, settling velocities of sludges dosed with Purifloc A23, Separan AP273 and Caraflok 91 AP were 102, 93 and 138 cm/min, respectively and corresponded to 204-, 186- and 276-fold increases, respectively.

Optimum polyelectrolyte dose determination for sludge sample A2-319-79 is presented in Figure 35. There was an initial gradual increase in settling velocity with Separan AP273 doses up to 15 mg/l. Above 15 mg/l of Separan AP273, settling velocity was essentially constant up to a dose of about 80 mg/l. Also, sludge zone settling behavior deteriorated above doses of 15 mg/l and, when a dose of 150 mg/l was reached, the sludge showed discrete settling characteristics. Therefore, an optimum dose of 15 mg/l was selected. The zone settling velocity at the optimum dose was about 9 cm/min and the resulting increase in zone settling velocity was about 15-fold.

Optimum polyelectrolyte dose was determined for Plant A3 as shown in Figure 36. At a suspended solids concentration of 5.3 g/l, a Purifloc A23 dose of approximately 3 mg/l was effective in increasing sludge zone settling velocity. The zone settling velocity was increased from approximately 0.33 cm/min to 2.6 cm/min, a 7.8-fold increase.

For Plant El, optimum dose at a suspended solids concentration of 3.2 g/l was 4 mg/l, as presented in Figure 37. Beyond this dose the sludge did not show zone settling characteristics. The zone settling velocities of unconditioned and conditioned with the optimum polymer dose were 1.16 and 14 cm/min, respectively, corresponding to a 12-fold increase in zone settling velocity.



Polyelectrolyte Dose, mg/l

Figure 33. Optimum Dose Determination for Settling of Sludge Sample Al-21-80. (Column Height = 36 cm, Column Diameter = 6 cm)













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ure 37. Optimum Dose Determination for Settling of Sludge Sample E1-80-80. (Column Height = 36 cm, Column Diameter = 6 cm) To determine the extent of effectiveness of polyelectrolyte conditioning, zone settling tests were conducted on a series of suspension samples dosed with polyelectrolytes at numerous suspended solids concentrations. The polyelectrolyte dose used for these additional suspended solids concentrations was determined by multiplying suspended solids concentration by the mass polyelectrolyte-sludge mass ratio (g polyelectrolyte/g SS) determined at the above "optimum dose". These polyelectrolyte application doses are presented in Table 45.

Sludge Sample	Polyelectrolyte Dose (g/kg SS)					
	Caraflok 91AP	<u>HF-190</u>	Separan AP273	Purtfloc A23		
A1-21-80	4.58	4.58	-	-		
A2-242-79	4.34	-	6.2	9.3		
A2-319-79		÷	1,58	-		
A3-161-79	0.0		-	0.56		
E1-80-80	1.25	-	-	-		

TABLE 45. POLYELECTROLYTE DOSE RATE FOR SETTLING ANALYSIS OF CONDITIONED SLUDGE

Zone settling velocities for conditioned, as well as unconditioned, sludges are presented in Figures 38-43. It is readily apparent that sludge setteability improved in all cases with conditioning. As observed with each sludge sample except A2-242-79, the increase in zone settling velocity was higher at low suspended solids concentrations than at higher suspended solids concentrations. This observation was attributed to the fact that at higher suspended solids concentrations, sludge particles were smaller in size and, therefore, suspensions specific surface area was higher and required a higher polyelectrolyte dose to achieve "optimal" results. Conditioning by polyelectrolytes is attributed to formation of "chemical bridges" between particles and subsequent formation of larger particles. Although the "optimum dose" determined at a low suspended solids concentration was enough to effectively cover the surface of particles at low concentration, a higher dose was required for a higher unit suspension surface area. The result was poorer flocculation of particles as suspended solids concentration increased and consequently lower zone settling velocities. As indicated previously for Plant A2 (sample A2-242-79), "optimum dose" was determined differently that is, the dose which resulted in the highest settling velocity which was admittedly not a zone settling velocity, however. This polyelectrolyte dose was considerably higher than the dose determined



Figure 38. Influence of Polymer Conditioning on Settling Properties of Sludge Sample Al-21-80. (Column Height = 36 cm, Column Diameter = 6 cm)



Figure 39. Influence of Polymer Conditioning on Settling Properties of Sludge Sample Al-21-80 (Column Height = 36 cm, Column Diameter = 6 cm)



Figure 40. Influence of Polymer Conditioning on Settling Properties of Sludge Sample A2-242-79. (Column Height = 36 cm, Column Diameter = 6 cm)





Figure 41. Influence of Polymer Conditioning on Settling Properties of Sludge Sample A2-319-79. (Column Height = 36 cm, Column Diameter = 6 cm)



ire 42. Influence of Polymer Conditioning on
 Settling Properties of Sludge Sample
 A3-161-79.
 (Column Height = 36 cm, Column Diameter
 = 6 cm)



Figure 43. Influence of Polymer Conditioning on Settling Properties of Sludge Sample El-80-80. (Column Height = 36 cm, Column Diameter = 6 cm) on the basis that sludge would still exhibit zone settling characteristics. Therefore, throughout the suspended solids concentrations used in experiments with sample A2-242-79, the polyelectrolyte dose might have been sufficiently high for effective flocculation. The results confirm that "optimum polyelectrolyte dose" should be determined not only at a single suspended solids concentration but at numerous levels of suspended solids concentrations over the range to be examined.

For the sludge sample A2-319-79 (Figure 41), the insignificant differences between zone settling velocities for conditioned and unconditioned samples at higher suspended solids concentrations may be attributed to an increasing polyelectrolyte demand with increasing suspended solids concentration. Also, this sludge suspension exhibited the best settling characteristics of the sludges examined, indicating that the conditions under which the suspension was generated may affect sludge settling characteristics.

Zone settling velocity data for all conditioned sludge samples are presented in Figure 44. By comparison with similar data for unconditioned sludges in Figure 31, it is apparent that polyelectrolyte conditioning significantly increased zone settling values. For a detailed examination of this improvement, settling data for unconditioned and conditioned portions of sample A2-319-80 are presented as batch flux curves in Figure 45. In a previous example with Figure 32, a solids flux of 1 kg/m².h was examined. Use of such a low value in this instance, however, would be of little value due to the significantly improved thickening characteristics of the suspensions presented in Figure 45. A solids flux of 12 kg/m².h was chosen for examination purposes. From the data for the unconditioned sludge, it is apparent that a thickened sludge of 31 g/l, or 3.1 percent solids, could be generated at this flux. Upon conditioning the sludge, an underflow of 45 q/1, or 4.5 percent solids, could be achieved at the flux loading of 12 kg/m².h. This improvement in thickening characteristics would therefore result in a 31 percent reduction in the volume of sludge available for subsequent dewatering or disposal. Similar results are apparent from the analysis of flux curves for other conditioned sludges as presented in Figure 46.

A summary of results for unconditioned sludges in Figure 31 and for conditioned sludges in Figure 46 is presented in Table 46. Flux values indicated for polymer-conditioned sludges were set arbitrarly at 2.7 and 50 kg/m².h. The flux and underflow data for unconditioned sludges were those presented previously in Figure 32. For sludge samples A1-21-80 and A2-242-79, polymer conditioning allowed for a 40-fold increase in the solids loading rate (i.e. flux) while simultaneously increasing the underflow concentration by factors of 1.88 and 3.8, respectively. The results for sample A3-161-79 were not as dramatic. However, solids loading rate necessary to achieve an underflow concentration sludge was increased by a factor of 2.7 allowing for a 63% reduction in surface area of the sedimentation basin. Therefore polymer conditioning of aluminum-finishing wastewaters resulted in significant improvement in thickening properties of resulting sludge suspensions.


Figure 44. Influence of Polymer Conditioning on Settling Properties of Aluminum Finishing Sludges.







Figure 46. Batch Solids Flux Curves for Conditioned Sludges.

Sludge Sample	Conditioning Polymer	/ - Selected Flux kg/m ² .h	Maximum Underflow Concentration g/l
A1-21-80		1	3.2
A1-21-80	HF-190	40	6.0
A2-242-79		1	3.1
A2-242-79	SEPARAN AP 273	40	11.8
A3-161-79		1	17.0
A3-161-79	PURIFLOC A23	2.7	17.0

TABLE 46. SUMMARY COMPARISON OF THICKENING CHARACTERISTICS OF CONDITIONED AND UNCONDITIONED SLUDGES.

SLUDGE DEWATERING

Evaluation of sludge dewatering characteristics of aluminum-finishing sludges was made with specific resistance, filter yield and CST measurements. Specific resistance values for aluminum sludges ranged from 1.8 x 10^{11} to 51 x 10^{11} m/kg, as indicated in Table 47. These values are consistent with specific resistance values of most inorganic sludges and are well below the values for organic sludges presented in Table 48.

Filter yield and associated cake solids concentrations for aluminum sludge samples are presented in Table 49. Filter yield varied between 0.37 and 41.15 kg/m²-h and cake solids concentration between 8.5 - 20.1 percent (dry basis). From an examination of the filter yield values and cake solids concentrations, it is apparent that there is no well-defined relationship between these two parameters. The values of filter yield and cake solids concentration for various types of sludges are given in Table 50. The values of filter yield and cake solids concentration obtained for aluminum-finishing sludges are comparable to those reported in Table 50 for similar sludges. CST values for aluminumfinishing sludges are reported in Table 51 and varied from 10.5 to 129.8 s.

Since specific resistance, filter yield and CST were the parameters used to evaluate the dewatering characteristics of sludges, the data were examined to determine if any valuable relationships between these parameters could be developed for a given sludge. In Figure 47 the relationship between the product of specific resistance (r) and dry weight of solids per unit volume of filtrate collected (w) and filter yield is presented. For each type of sludge the value of rw was linearly related to filter yield. Specific resistance (based on filtrate volume) or rw increased in proportion to the increase in filter yield. The linear relationship indicated that specific resistance (based on filtrate volume), or rw, for each sludge layer was constant and the total specific resistance was the arithmetic sum of the specific resistances (based on filtrate volume) of each layer. However, the values of (rw) for indicidual layers varied with the characteristics of the sludges.

With easily-dewatered sludges, filter yield is much higher when compared with the sludges difficult to dewater. Variation of specific resistance with filter yield for a suspended solids concentration of 10 g/l is presented in Figure 48. Below a specific resistance of 5×10^{11} m/kg, increases in filter yield were relatively independent of sludge dewatering characteristics. This observation may not, however, apply to a larger variety of sludges. Figure 49, a linear relationship is presented between specific resistance i.e., (rw), and CST for all of the sludges tested. Since specific resistance and CST are both influenced by suspended solids concentration the effects were essentially eliminated by plotting specific resistance and CST at a fixed suspended solids concentration (i.e. 10 g/l) in Figure 50. Based on the limited data available, it may be stated that a single linear relationship was obtained for all the sludges tested. The reasons for use of CST were that the measurement time is much shorter than that for specific resistance, only small sample volumes are required and the test is easier to conduct. If a universal relationship similar to the one presented in Figure 50 could be developed for all aluminum sludges specific resistance and filter yield values for these sludges could be determined from CST measurements. As indicated in Figures 47-50, a linear relationship existed between filter yield and CST which is presented in Figure 51.

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	SS Conc	Specific Resistance ~					
Plant	Range g/1	At Susp. Solids = 10 g/1 10^{11} m/kg	At SS Range 10 ¹¹ m/kg				
A1-21-80	1.3-13.3	19.2	18.7-26.9				
A2-283-79	1.3-16.4	41.0	40.0-51.0				
A2-319-79	3.3-79.7	3.6	1.8-4.1				
A3-161-79	3.4-36.1	3.8	2.8-3.8				
E1-80-80	1.3-18.7	7.5	7.2-10.1				

TABLE 47. SPECIFIC RESISTANCE OF UNCONDITIONED ALUMINUM SLUDGES

LESSTINGE OF SELECTED INVIGANTE AND URGANIE SEUDGES

Тур	e of Sludg <u>e</u>	Specific Resistance 10 ¹¹ m/kg	Pressure 10 ¹¹ N/m ²	Reference
Α.	Inorganic Sludges	<u> </u>		
	Nickel Hydroxide (pH 9-11.3)	1-200		Knocke <u>et al</u> ., 1980
	Cupric Hydroxide (pH 9.5-11)	5-30	_	Knocke <u>et</u> <u>a</u> l., 1980
	Chromium Hydroxide (pH 7-9.5)	5-50	-	Knocke <u>et</u> <u>al</u> ., 1989
	Synthetic mixed-metal Sludge	15-60	-	Knocke <u>et</u> <u>al</u> ., 1980
	Electroplating Sludges	130-145	-	Knocke <u>et</u> <u>al</u> ., 1980
	Water Treatment Plant Sludge	52	5.08	Glenn <u>et</u> <u>al</u> ., 1973
	Bentonite	31	5.08	Glenn <u>et al</u> ., 1973
	Alum Sludge	130-440	5.08	Gates and McDermott, 1968
	Alum Sludge (pH 4-8)	140-170	-	Bugg <u>et</u> <u>al</u> ., 1970
	Gelatinous Fe(OH) ₃	150	17.3	Gale, 1971
	Gelatinous Al(OH)3	220	17.3	Gale, 1971
	Gelatinous $Mg(OH)_2$	30	17.3	Gale, 1971
	Colloidal Clay	50	17.3	Gale, 1971
	Precipitated CaCO ₃	2	17.3	Gale, 1971
	Alum Sludge	18	7.6	Turner, 1976
	Alum Sludge	180	7.6	Turner, 1976
	Lime Softening	1.45	5.08	Novak and Montgomery, 1975
	Lime Softening .	3.40	5.08	Novak and Montgomery, 1975
	Iron and Lime	3.26	5.08	Novak and Montgomery, 1975
	Alum Sludge	41.1	5.08	Novak and Montgomery, 1975
	Alum Sludge	252	5.08	Novak and Montgomery, 1975

TADLE 40. (CONCINUED...)

Type of Sludge	Specific Resistance	Pressure	Reference
A. Inorganic Sludges (continued)	<u>10 III/ Kg</u>	<u>10 10 10 11</u>	
Alum Sludge	38.6	-	Novak and Langford, 1977
Alum Sludge	82	-	Novak and Langford, 1977
Iron-Lime	4.6	-	Novak and O'Brien, 1975
Alum Sludge	165	-	Novak and O'Brien, 1975
Ferric Sulfate Sludge	340-572	-	King <u>et</u> <u>al</u> ., 1971
Thixotropic Mud	1500	156	Gale, 1971
B. Organic_Sludges_			
Raw Sludge	2180	5 .0 8	Karr & Keinath, 1978
Activated Sludge	480	5.08	Karr & Keinath, 1978
Anaerobic Sludge	9320	5.08	Karr & Keineth, 1978
Raw Sludge	1500-5000	_	Metcalf & Eddy, Inc., 1979
Activated Sludge	100-1000	_	Metcalf & Eddy, Inc., 1979
Digested Sludge	1000-6000	_	Metcalf & Eddy, Inc., 1979
Raw Sludge	900	1.0	Gale <u>et</u> <u>al</u> ., 1967

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Plant	SS Concentration Range g/1	Filter Yield at SS= 10 g/1 kg/m ² -h	Cake Solids at SS= 10 g/1 %	Filter Yield at SS= 10 g/1 %	Cake Solids Range %
A1-21 -80	1.3-13.3	2.27	12.7	0.37-2.76	12.6-13.8
A2-283-79	1.3-16.4	2.05	11.9	0.39-3.06	11.6-14.0
A2-319-79	3.3-79.7	3.69	19.3	2.43-41.15	18.5-19.5
A3-161-79	3.4-36.1	7.38	8.5	2.53-20.54	8.5-9.2
E1-80 -80	1.3-18.7	3.03	18.9	0.52-5.47	18.8-20.1

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TADLE 49. FILTER TIELDS AND CAKE SULIDS CONCENTRATIONS FOR UNCONDITIONED ALUMINUM SLUDGES

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		Solids Concer	itration		
Туре	of Sludge		Lake 	kg/m ² -h	Reference
Α.	Inorganic Sludges				
	Alum Sludge	-	9	24.4	Nielsen <u>et al</u> ., 1973
	Alum Sludge	-	15	4.9	Nielsen et al., 1973
	Carbon Processing	1.4	19	4.4	Ford, 1970
Β.	Organic Sludges				
	Pulp and Paper	5	18	77.9	Ford, 1970
	Primary	5.5-16	30-46	39-63.3	Schepman and Cornell, 1956
	Digested-Primary	5.6-9.5	23-28.5	53.6-70.6	Schepman and Cornell, 1956
	Digested-Primary and Activated Sludge	4.5	21	14.6	Schepman and Cornell, 1956
	Digested Domestic Sludge	7	29	48.7	Dahlstrom and Cornell, 1958
	Activated Sludge	1.6	13	2.4	Gale, 1968
	Activated Sludge	3.5	16	19.5	Dahlstrom and Cornell, 1958
	Trickling Filter Humus	4.9	20	10.7	Gale, 1968

TABLE 50. FILTER YIELD AND CAKE SOLIDS CONCENTRATION OF VARIOUS UNCONDITIONED AND CHEMICALLY-CONDITIONED SLUDGES

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Sample	Susp. Solids Conc. Range	! / !	CST (10 mm reservoir) At SS= 10 g/1	Range
·	(g/1)		<u>S</u>	<u>S</u>
Al-21 -79	1.3-13.3		50.3	19.6-66
A2-283-79	1.3-16.4		86	20.5-129.8
A2-319-79	3.3-79.7	-	29	19.4-99.8
A3-161-79	3.4-36.1		26.0	18.1-53.7
E1-80 -80	1.3-18.7		25.3	10.5-37.6

TABLE 51. CST VALUES FOR UNCONDITIONED ALUMINUM-FINISHING SLUDGE SAMPLES



Figure 47. Relationship between the Product of Specific Resistance, r, and Cake Solids per Unit Volume of Filtrate, w, and Filter Yield for Aluminum-Finishing Sludges.



Figure 48. Relationship between Specific Resistance and Filter Yield for Aluminum Finishing Sludges.



Figure 49. Relationship between the Product of Specific Resistance and Cake Solids per Unit Volume of Filtrate and CST for Aluminum-Finishing Sludges.



Figure 50. Relationship between Specific Resistance and CST for Aluminum-finishing Sludges.



Figure 51. Relationship between Filter Yield and CST for Aluminum-Finishing Sludges.

Effect of Polyelectrolyte-Conditioning on Sludge Dewaterability

Evaluation of the effectiveness of polyelectrolytes in conditioning of aluminum sludges was made with the use of the polyelectrolytes previously described (Table 14). Polyelectrolytes were added to sludges in incremental doses over a range of concentrations from 0 to 100 mg/l (in some cases to 30 mg/l and 200 mg/l) at a mixing speed of 200 rpm for 60s in the mixing chamber used for sludge conditioning. Variations in specific resistance, filter yield and CST are plotted as function of polyelectrolyte dose in Figures 52 to 57.

Specific resistance was observed to drop sharply with increasing polyelectrolyte doses and then either continue to decrease gradually or increase slightly with increasing polyelectrolyte addition. CST, in most cases, decreased initially and then increased with increasing polyelectrolyte doses. Filter yield did not increase with the addition of polyelectrolytes but decreased with increasing addition of polyelectrolyte. For this reason, the selection of an "optimum" polymer dose was based on variations in specific resistance and CST. When minimum specific resistance and CST values were attained, the polyelectrolyte dose at those minimum values was designated an "optimal" dose. If the minimum value obtained from specific resistance was different from that for a minimum CST value, the dose corresponding to the minimum specific resistance was chosen as the "optimum" dose since CST was often an insensitive measure of dewatering characteristics, especially at low CST values. When well-defined minimum specific resistance and CST values were not attained, but rather they were reduced to low levels initially and slowly declined as further polymer was added, the "optimal" dose was taken as the concentration above which additional polyelectrolyte had little effect.

Variations in specific resistance and CST may be best explained by plotting (filtration time + filtrate volume) vs (filtrate volume), i.e., Θ/V and V, respectively, at various polyelectrolyte doses. For example, as presented in Figure 58, as polyelectrolyte dose increased from 0 to 10 mg/l, the slope of the θ/V vs V line decreased because larger particles were formed which exerted a lower resistance to the passage of water as compared to that exerted by smaller particles. As polyelectrolyte dose was increased further (i.e., an overdosed sludge), most of the applied polyelectrolyte was adsorbed onto suspended particles while some was remained in solution. In this case, two responses may be predicted for dewaterability measurements using the Buchner funnel test for specific resistance. When polyelectrolyte dose is high, large aggregates are produced which present a low resistance to the passage of water, such as shown by the flat portion of curve c in Figure 58. As the filtration process continued, a portion of the water was removed rapidly while another portion was held tightly by the solids, due to the hydrophilic nature of the polymer-solid structure. This latter process is indicated by the steep portion of curve c in Figure 58.

Specific resistance of sludges for the flat and steep portions of the plots in Figure 58 at various polyelectrolyte doses are presented in Table 52. It is apparent that there was an increase in specific resistance calculated from the steep portion of the θ/V vs V curves as polyelectrolyte dose increased. There was also a slight increase in specific resistance calculated from the flat portion of the θ/V vs V curves represented specific resistance due to both solid and liquid phases or due to only the liquid phase, CST measurements were carried out on the supernatant of the samples dosed at 70 mg/l and 100 mg/l of Separan AP273.



Figure 52. Effect of Polyelectrolyte (HF-190) Conditioning on Specific Resistance, Filter Yield and CST for Sludge Sample A1-21-80.



Figure 53.

Effect of Polyelectrolyte (Caraflok 91AP) Conditioning on Specific Resistance, Filter Yield and CST for Sludge Sample AL-21-80.



Figure 54. Effect of Polyelectrolyte Conditioning on Specific Resistance, Filter Yield and CST for Sludge Sample A2-283-79.



Polyelectrolyte Dose, mg/l

Figure 55. Effect of Polyelectrolyte Conditioning on Specific Resistance, Filter Yield and CST for Sludge Sample A2-319-79.



Figure 56. Effect of Polyelectrolyte Conditioning on Specific Resistance, Filter Yield and CST for sludge Sample A3-161-79.







Volume of Filtrate, ml

Figure 58. Effect of Polyelectrolyte Dose on Experimental Data Obtained for Specific Resistance Measurement for Sludge Sample A2-283-79.

		Specific Re	esistance, m/kg
Polyelectrolyte dos	e, mg/1	r _l , flat portion of curve	r ₂ , steep portion of curve
0		4.21 x 10^{12}	
4		3.66 x 10 ¹²	-
10		3.69×10^{12}	
15		2.33 x 10^{12}	-
20		2.49 x 10^{11}	4.75 x 10 ¹²
30		0.92 x 10 ¹¹	3.72×10^{12}
45		3.01 x 10 ¹¹	9.06 x 10^{12}
70	-	1.75×10^{11}	13.54×10^{12}
100		1.21 x 10 ¹¹	10.25 x 10 ¹²
TABLE 53.	COMPARISON O	F SLUDGE AND SUPERNATA	ANT CST VALUES
		CST (10 mm	n reservoir)
		Sludge Sample	Cupainsteat
Polyelectrolyte dos	e, mg/1	S	Supernatinat
Polyelectrolyte dos 70	e, mg/1	S52.6	63.1

TABLE 52. SPECIFIC RESISTANCE VALUES FOR POLYELECTROLYTE-CONDITIONED SLUDGE (SAMPLE A2-283-79)

As indicated in Table 53, at higher polyelectrolyte doses specific resistance exerted by the supernatant. However, this observation did not establish if specific resistance was due to polyelectrolyte or due to fine particles. Therefore, solutions of distilled water containing polyelectrolyte concentrations of 0 to 20 mg/l were prepared and used for CST and Buchner funnel experiments. As presented in Table 54, the results clearly indicated that polyelectrolyte decreased the drainability of the liquid phase. Therefore, the slight increase in specific resistance calculated from the flat portion of θ/V vs V curves may be attributed to the increase in polyelectrolyte dose in the liquid phase.

Polyoletrolyte doce	Volume filtered per Unit time, ml/s	CST (10 mm reservoir)
Polyelctrolyte dose		
0	39.6	9.4
10	1.70	23.8
20	0.14	33.0

TABLE 54. EFFECT OF POLYELECTROLYTE CONCENTRATION ON CST VALUES OF DISTILLED WATER

In Figures 59 through 70 the variations of specific resistance, filter yield and CST with suspended solids concentration are presented for both unconditioned and conditioned sludges from Plants Al, A2, A3, and El. Polyelectrolyte-conditioning of sludges at suspended solids concentrations other than those indicated in Figures 53-57 was carried out by adding a quantity of polyelectrolyte calculated by multiplying the concentration of suspended solids with the mass ratio of polyelectrolyte dose to suspended solids concentration determined at an optimum polyelectrolyte dose. Both filter yield and CST increased with solids concentration while specific resistance of unconditioned sludge was fairly constant. This occurred because specific resistance measurements are normalized to solids concentration and the other measurements are not. Although specific resistance of unconditioned sludge did not change considerably, specific resistance of conditioned sludges generally increased with solids concentration to the point where, in some instances, the specific resistance of conditioned and unconditioned sludges were equal. This observation may be explained by the hypothesis that optimum polyelectrolyte dose determined at a relatively low suspended solids concentration may not be an optimum value at higher solids concentrations because specific surface area of particles per unit weight of solids is expected to be lower at lower solids concentrations than encountered at higher solids concentrations. Similar results were observed with CST. Although CST increased with suspended solids concentration, the rate of increase for conditioned sludges was higher than for unconditioned sludges indicating similar response as that for specific resistance. In some cases, (i.e., sample A2-283-79) an initial decrease in CST was observed. The higher CST values encountered at lower solids concentrations than the solids concentration at which optimum dose was determined may be attributed to the presence of more polyelectrolyte than would be determined from surface area considerations. Filter yield was not increased with polyelectrolyte conditioning for all the sludges tested. Polyelectrolyte-conditioned sludge samples therefore could be more easily dewatered with respect to the rate of water removal but not necessarily to a lower moisture content.



Figure 59. Variation of Specific Resistance and CST with Suspended Solids Concentration for Sludge Sample A1-21-80.



Figure 60. Variation of Specific Resistance and CST with Suspended Solids Concentration for Sludge Sample A1-21-80.



Figure 61. Variation of Filter Yield with Suspended Solids Concentration for Sludge Sample A1-21-80

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Figure 62. Variation of Filter Yield with Suspended Solids Concentration for Sludge Sample Al-21-80.

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Figure 63. Variation of Specific Resistance and CST with Suspended Solids Concentration for Sludge Sample A2-283-79.



Figure 64. Variation of Filter Yield with Suspended Solids Concentration for Sludge Sample A2-283-79



Figure 65. Variation of Specific Resistance and CST with Suspended Solids Concentration for Sludge Sample A2-319-79

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Figure 66. Variation of Filter Yield with Suspended Solids Concentration for Sludge Sample A2-319-79



Figure 67. Variation of Specific Resistance and CST with Total Solids Concentration for Sludge Sample A3-161-79

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Figure 68. Variation of Filter Yield with Total Solids Concentration for Sludge Sample A3-161-79

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Figure 69. Variation of Specific Resistance and CST with Suspended Solids Concentration for Sludge Sample E1-80-80



Suspended Solids Concentration, g/l

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Figure 70. Variation of Filter Yield with Suspended Solids Concentration for Sludge Sample E1-80-80.

SLUDGE DRAINABILITY

Drainability characteristics of aluminum-finishing sludges from Plants Al, A2 and El were examined using gravity drainage sand beds. Variations in sludge drainage with time at various suspended solids concentrations are shown in Figures 71 through 74. At a fixed solids concentration, a typical drainage volume vs drainage time curve include three fairly distinct phases. An initial high rate of drainage was followed by a declining rate of drainage. The drainage phase was much slower than the second phase and very little drainage occurred. Initial high rates of drainage occurred during the formation of sludge cake. Once a cake was formed, the rate of drainage was lowered due to the resistance offerred by the cake to the passage of liquid. The time required to achieve a given volume of drainage increased with suspended solids concentration.

Effect of Polyelectrolyte-Conditioning on Sludge Drainability

Evaluation of the effectiveness of polyelectrolytes in improving drainage characteristics of aluminum-finishing sludges was carried out with the use of polyelectrolytes previously described (Table 14). Polyelectrolytes were added to sludges in incremental amounts on a range of 0 to 100 and 200 mg/l. Variations in filtrate volume with drainage time were observed at various polyelectrolyte doses at fixed suspended solids concentrations. From these data, drainage times for a fixed drainage volume (i.e., 50% of total filtrate volume drained) at a fixed suspended solids concentration were then obtained. The data for Plant A1, A2 and E1 are presented in Figures 75 through 84. Optimum dose was determined in a similar fashion as described for sludge dewaterability studies. Either the dose which resulted in minimum drainage time for 50 percent of total drained water at a specified solids concentration (Figure 76) or the dose beyond which additional polyelectrolyte dose had little improvement in drainage time (Figure 82) was selected as the optimum polyelectrolyte dose.

Improvements in sludge drainage characteristics with increasing polyelectrolyte doses were observed initially. Further continued increases in polyelectrolyte dose resulted ultimately in deterioration of drainage characteristics of the sludges. This deterioration was attributed to increasing concentrations of polyelectrolytes in the liquid phase as observed in specific resistance measurements.

Using an optimum polyelectrolyte dose per unit weight of solids, polyelectrolyte doses for other suspended solids concentrations were computed on a simple ratio basis. Drainage curves for sludge samples dosed at optimum polymer doses are presented in Figures 85 through 93. It is interesting to observe that, while the drainage time for 50 percent of total drained volume increased curvilinearly with increasing solids concentration, optimally-conditioned sludges revealed different behaviour with increasing solids concentration. In some cases, drainage time was relatively constant (i.e. Figures 87 and 93) at low solids concentrations and increased sharply with further increases in solids concentration. In some instances drainage time increased with increasing solids concentration as shown in Figure 91. In other cases, drainage time first dropped and then increased with solids concentration as shown in Figure 89. These observations indicated that polyelectrolyte dose determined as the optimum dose at a fixed solids concentration may not be the optimum for other solids concentrations. Similar or higher drainage times at solids concentrations lower than those observed at higher concentrations, for which optimum dosages were determined, may be attributed to excess polymer not utilized by solids surfaces and remaining in the liquid phase. Also, the increasing deterioration in drainage characteristics with increasing solids concentration may be due to the fact that the increased mass of polyelectrolyte was insufficient for the increased surface area (per unit weight of solids) as solids concentration increased. Additional studies are needed to ascertain the validity of this hypothesis however it is obvious that optimum polyelectrolyte dose is a function of suspended solids concentration and should be determined separately.



Figure 71. Drainage Characteristics of Aluminum Finishing Sludge Sample A1-21-80.

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Figure 73. Drainage Characteristics of Aluminum Finishing Sludge Sample A2-319-79.

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Figure 74. Drainage Characteristics of Aluminum Finishing Sludge Sample E1-80-80



Figure 75. Effect of Polyelectrolyte Conditioning on Drainage Characteristics of Aluminum Finishing Sludge Sample A1-21-80.

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Figure 76. Variation of Drainage Characteristics of Aluminum-Finishing Sludge Sample A1-21-80

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Figure 77. Effect of Polyelectrolyte Conditioning (HF-190) on Drainage Characteristics of Aluminum-Finishing Sludge Sample A1-21-80



Figure 78. Variation of Drainage Characteristics of Polyelectrolyte-Conditioned Sludge Sample A1-21-80



Time of Drainage, min

Figure 79. Effect of Polyelectrolyte-Conditioning (Separan'AP273) on Drainage Characteristics of Aluminum-Finishing Sludge Sample A2-283-79.



Figure 80. Variation of Drainage Characteristics of Aluminum-Finishing Sludge Sample A2-283-79 with Polyelectrolyte (Separan AP273) Dose.



Figure 81. Effect of Polyelectrolyte-Conditioning on Drainage Characteristics of Aluminum-Finishing Sludge Sample A2-319-79.

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Figure 82. Variation of Drainage Characteristics of Aluminum-Finishing Sludge Sample A2-319-79 with Polyelectrolyte (Separan AP273) Dose.

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Figure 83. Effect of Polyelectrolyte-Conditioning on Drainage Characteristics of Aluminum-Finishing Sludge Sample El-80-80

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Figure 84. Variation of Drainage Characteristics of Aluminum-Finishing Sludge Sample El-80-80 with Polyelectrolyte (Caraflok 91AP) Dose.



Figure 85. Effect of Suspended Solids Concentration on Drainage Characteristics of Optimally-Conditioned (HF-190) Sludge Sample A1-21-80.

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Figure 86. Effect of Suspended Solids Concentration on Drainage Characteristics of Optimally-Conditioned (Caraflok 91AP) Sludge Sample A1-21-80.

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Figure 87. Effect of Suspended Solids Concentration on Time to Drain 50% of Total Drainable Water for Optimally-Conditioned Sludge Sample Al-21-80.



Figure 88. Effect of Suspended Solids Concentration on Drainage Characteristics of Optimally-Conditioned Sludge Sample A2-283-79.

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Figure 89.

 Effect of Suspended Solids Concentration on Time to Drain 50% of Total Drainable Water for Optimally-Conditioned Sludge Sample A2-283-79.



Figure 90. Effect of Suspended Solids Concentration on Drainage Characteristics of Optimally-Conditioned Sludge Sample A2-319-79.

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Figure 91. Effect of Suspended Solids Concentration on Time to Drain 50% of Total Drainable Water for Optimally-Conditioned Sludge Sample A2-319-79.



Figure 92. Effect of Suspended Solids Concentration on Drainage Characteristics of Optimally-Conditioned Sludge Sample E1-80-80.

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SLUDGE LEACHING

The majority of the trace metals contained in the sludge samples were in the suspended form and leaching of sludge metals would therefore result from solubilization of suspended metals and not by physical displacement of interstitial water. To confirm this and to determine the extent to which metals were leached from the sludges, the EPA-EP was conducted with each of the sludges.

The physical and chemical characteristics of the sludge samples subjected to the EP are listed in Table 55. Since all sludges were in the pH range of 6-7, only 20-30ml of 0.5N acetic acid was required to maintain pH 5 during the 24-h extraction.

Sludge Sample	<u>A1-21-80</u>	A2-319-79	<u>A3-147-80</u>	<u>A3-147-80</u>	E1-80-80
Total Solids, %	8.3	19.8	11.8	11.8	17.3
Initial pH	6.7	6.5	6.9	6.9	6.3
Final pH	5.1	5.1	5.1	5.1	5.1
Volume 0.5 N Acetic Acid Added, ml	24	20	30	30	23
Sludge Age, d	154	115	3	63	96

TABLE 55. PHYSICAL AND CHEMICAL CHARACTERISTICS OF DEWATERED ALUMINUM-FINISHING SLUDGES SUBJECTED TO EP.

Effect of Sludge Age on EP Results

Whereas Minor et al. (1980) reported reductions of 50-90 percent in extractable Cd, Pb, and Cr from a dewatered, metal-finishing sludge which was aged 3 months while open to the atmosphere, sludge aged in a closed container for 63 d did not result in any significant reduction in extractable Cd, Pb, or Cr, as shown in Table 56. In addition, there was no significant reduction in Cu or Se. Metals not detected were Ag, Be, Hg, Sb, and Tl. Although As showed almost a three-fold increase in concentration, this increase was not considered significant due to the low level of As present. In addition, the variation could be attributed to the high coefficient of variation for measurement of As. Additionally, the apparent 45 percent decrease in Zn was not apparently significant either, as spectrophotometer sensitivity was low at concentrations below 0.2 mg/l. For the same reason, the 44 percent decrease in Cr was considered insignificant.

Aging did result in a 28 percent reduction in extractable Ni, which was present in large quantities (0.22 percent of total dry solids). With the exception of Ni, the effect of aging did not significantly change the results of the EP. Therefore, storing sludge samples in closed containers for 2-3 months prior to performing the EP should not have affected the results significantly. As indicated in Table 55, the aging of sludge samples for Plants Al, A2 and El was between three to five months.

	EP Metal Conc	entration, µg/l	
<u>Metal</u>	Unaged Sludge (3d)	Aged Sludge (63d)	Percent Change with Aging
Ag	0	0	0 ~
As	4	15	+275
Ве	0	0	0
Cd	1.2	1.3	+8
Cr	4.5	2.5	- 44
Cu	13	13.5	+4
Hg	0	0	0
Ni	1855	1330	-28
РЬ	1.5	1.5	0
Sb	0	0	0
Se	<2	<2 .	0
Т1	0	0	0
Zn	200	110	-45

TABLE 56. EFFECT OF SLUDGE AGE ON EP FOR SLUDGE SAMPLE A3-147-80

Metal Concentrations in EP Extracts.

The analysis of EP extracts provided metal concentrations for 13 inorganic priority pollutants in sludge samples from Plants A1, A2, A3 and E1. The results of duplicate EP tests are listed in Tables 57 and 58. In Table 57, EP results are compared with EP-extract maximum contaminant concentrations for the EPA primary drinking water standards (multiplied by 100). In Table 58, EP results are presented for other metals for which there are no such standards.

Based on present criteria for the EPA-EP test, none of the aluminum-finishing sludges could be classified as an EP toxic waste and could therefore be codisposed with municipal refuse in a sanitary landfill. Of the metals listed for EP toxicity limits, the limit that came closest to being exceeded was Se for sludge sample A2-319-79, which was 7 percent of the limit. For the metals Cd and Cr, which are of greatest concern to EPA for electroplating sludges, EP extract levels were less than 3.6 percent of the limit. The remaining metals on the list, i.e., Ag, As, Hg, and Pb, were either absent or barely detectable with few exceptions. Sludge E1-80-80 had the highest levels of As and Pb with Pb (54 μ g/l) being ten times more than that for any other sludge. Sludge sample A1-21-80 had the highest Cd and Cr levels, each of which was 28 μ g/l, and were higher than any other metals in that sludge.

	(Sludge Me	EP Limit			
<u>Metal</u>	<u>A1-21-80</u>	<u>A2-319-79</u>	<u>A3-147-80</u>	<u>E1-80-80</u>	(µg/1)
Ag	<1	4.1	0	0	5,000
As	6	9	4	11.5	5,000
Cd	28	1.55	1.2	25.5	1,000 -
Cr	28	18	4.5	1.65	5,000
Hg	0.85	1.45	0	- 0 -	200
Pb	2.5	6.5	1.5	54	5,000
Se	<2	69.5	<2	<2	1,000

TABLE 57. RESULTS OF EP TESTS FOR Ag, Cd, Cr, Hg, Pb, and Se

None of the metals in Table 58 are listed in EPA drinking water standards and are currently of no major concern with respect to hazardous waste assessment, with the exception of Ni. While Ni is not listed in primary drinking water standards, and therefore not limited in the EP extract, it is listed in Appendix VIII of Section 3001 of RCRA as a hazardous constituent. The only sludge containing significantly high Ni levels in the EP extract was A3-147-80, where Ni was 1,855 μ g/l. The other metals leached in significant quantities were Cu and Zn. No Sb or Tl were detected in any sludge EP extract, and very little Be was detected.

TABLE 58. RE	ESULTS OF	EΡ	TESTS	FOR	Be,	Cu,	Ni,	Sb,	Τ1,	and	Zn
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	Sludge Me	tal Concentratio	on in EP Extract	(µg/l)	
Metal	<u>A1-21-80</u>	<u>A2-319-79</u>	<u>A3-147-80</u>	E1-80-80	
Be	0	0.25	0	<0.2	
Cu	11	8.5	13	6250	
Ni	14.5	109	1855	8	
Sb	0	0	0	0	
Т1	0	0	0	0	
Zn	2950	<50	200	6800	

Comparison of ASTM Leach Test with EP.

Presented in Table 59 are the results of duplicate EP and ASTM leach tests of sludge A2-319-79. The results for As, Be, and Hg were higher for the ASTM test than for the EP, but considering the indicated coefficients of variation for metal analysis, the difference was not significant. The ASTM test resulted in significantly higher concentrations of Ag, Cr, Cu, Ni, Se, and Zn. Especially higher in the ASTM test were Cu and Zn, which were 694 percent and 1500 percent higher, respectively. The 1500 percent figure for Zn may be misleading because the spectrophotometer sensitivity below 100 μ g was poor, so the reading could have been 0-100 μ g/l, in which case the difference could have been as low as 650 percent.

The reason for higher concentrations of most metals may have been the higher solid-liquid ratio (1:5) of the ASTM test compared to the solid-liquid ratio (1:20) of the EP. Neglecting other factors, the effect of solid-liquid ratio alone should have been to increase ASTM test metal concentrations by a factor of 4 over EP results. Since results for Cu and Zn showed more than a 6-fold increase, the effect of pH was negligible, since decreasing pH would have increased concentration, cancelling the effect of increased dilution. The 6-fold increase for Cu and Zn might have been due to the longer agitation time (48 h vs. 24 h) of the ASTM test compared to the EP.

The ASTM test resulted in a 61 percent lower concentration of Cd over the EP. The effect of increased metal solubility of Cd at pH 5 in the EP compared to pH 7 in the ASTM test was apparently greater than the dilution effect resulting from a difference in the solid-liquid ratio between the two tests. The Pb concentration was insignificantly lower for the ASTM test.

The ASTM test resulted in about a 100 percent increase in Cr and Ni over the EP. Apparently the anticipated 4-fold increase from dilution alone was reduced by the increased solubilities of Cr and Ni at pH 5 over pH 7.

Impact of Pore Water on EP Results

As discussed previously, the presence of significant amounts of soluble metals in interstitial water in a sludge could influence EP results by increasing metals concentrations beyond the levels due to leaching alone. Considering that Cd, Cr, and Ni are the metals for which electroplating sludges, and therefore anodizing sludges, were initially declared hazardous, the metal concentrations for the EP extract were predicted for the case of dilution of interstitial water only, in order to determine the amount of metal apparently leached from the sludge solids. To compute these "predicted" EP concentrations, sludge filtrate concentrations were multiplied by the volume of water in a 100 g sludge sample to yield a mass of soluble metal. This value was divided by the 2-1 EP liquid volume to predict EP concentration. The predicted EP concentration was subtracted from the actual EP concentration to determine the predicted percentage of metal in the liquid due to leaching. Finally, the percentage of total dry solids that leached into the liquid was determined by dividing the difference between actual and predicted EP concentrations by dry solids available for leaching. The predicted concentrations are listed in Table 60 and are compared to actual EP results.

Metal	<u>ΕΡ (μg/1</u>)	ASTM (µg/l)	lŗ	<u>CV*(%</u>)		Present <u>Results</u>	Change .over E	in ASTM P Results
Ag	4.1	9.2		24			+124	
As	9	17.5		89			94	
Be	0.25	0.4		47			+60	-
Cd	1.55	0.6		11		-	-61	
Cr	18	34		22	71	-	+89	
Cu	8.5	67.5		12			+694	
Hg	1.45	2.05		34			+41	
Ni	109	220		21			+102	
Pb	6.5	3.8		21			-42	
Sb	0	- 0		-			0	
Se	69.5	135		38			+94	
ΤI	. 0	0		-			0	
Zn	<50	850				:	>1600	

TABLE 59. COMPARISON OF ASTM LEACH TEST WITH EP

*Coefficient of Variation (CV) for analytical technique used for each metal

TABLE 60. COMPARISON OF PREDICTED AND ACTUAL EP METAL DATA

Sludge Sample	Metal	EP Metal Actual µg/l	Cor	<u>Predicted</u> µg/1	Percent of EP Metal due to leaching %	Total Percent of Suspended- Metal leached %
A1-21-80	Cd Cr	28 28		0.3 69	99	44 *
	N٦	14.5		3.6	/5	2.3
A2-319-79	Cd Cr	1.55 18		0.05	97 60	16 5.2
	Νï	109	6	3.0	97	17
A3-147-80	Cd Cr Ni	1.2 4.5 1855	÷	0.04 0.4 11	97 91 99	17 0.78 14
		1000			55	17
E1-80-80	Cd	25.5		2.4	91	24 2
	Cr	1.65		0.3	82	1.7×10^{-3}
	Ni	8		5.8	27	0.17
*No appare	nt leach	ing of sus	penc	led metal		

The influence of pore water on EP results was most pronounced for Cr, the least soluble of the three metals. With sludge Sample Al-2l-80, apparently no leaching of Cr occurred, even though the dry solids contained 2.6 percent Cr. Cadmium was the most soluble metal with no less than 16 percent of available Cd leaching out of the solids, compared to 0-5.2 percent for Cr. Since Cd is much more mobile at pH 5 than Cr, if acid conditions exist in a municipal landfill, Cd could be expected to leach from the sludge quickly relative to Cr, assuming the presence of metal hydroxide complexes in the liquid phase.

Impact of Alloy Impurities on EP Results

The potential impact of alloy impurities on EP results were analyzed only with sludge samples from Plants El and A2, since data obtained for aluminum alloys finished at plants Al and A3 indicated that no significant impurities were contained in the alloys finished. Based on the alloy impurities reported for plants El and A2, data in Table 6l were developed to estimate the contribution of alloy impurity metals to sludge solids. For sludge sample A2-319-79, the apparent impact of Cr and Cu alloy impurities was minor. That is, when based on metal content expressed as percent of alloy and sludge aluminum, the Cr and Cu content of the sludge (0.0065 percent and 0.0113 percent, respectively) was well below that of the alloys used, i.e. 0.1 percent for both Cr and Cu.

For sludge sample E1-80-80, the Zn content of the sludge and alloy were identical, indicating that all of the Zn could have resulted from stripping of Zn from the alloys finished. A similar correlation was possible for Cu since the Cu content of the sludge was equal to 80 percent of the Cu content of the alloy. However, Cr levels in the sludge were 3.3 times higher than that in the alloy, indicating that Cr may be added to the etch wastes during processing.

		Metal Co	mposition	Ratio of
Sludge <u>Sample</u>	<u>Metal</u>	Alloy (% of Alloy Aluminum)	Sludge (% of Sludge Aluminum)	Sludge Metal to Alloy Metal
A2-319-	79 Cr	0.1	0.0065	0.065
A2-319-	79 Cu	0.1	0.0113	0.113
E1-80-8	0 Cr	0.1	0.33	3.3
E1-80-8	0 Cu	3.1	2.5	0.8
E1-80-8	0 Zn	1.0	1.0	1.0

TABLE 61. COMPARISON OF ALLOY IMPURITIES WITH SLUDGE COMPOSITION

When evaluating the data in Table 61, it must be emphasized that correlations (or the lack of correlation) between alloy impurities and sludge composition could be attributable to variations in the metals being finished at the time of sampling. A significant portion of the material finished results from specific requests for special alloys. Therefore, average alloy composition may not be indicative of the alloys processed during a fixed time interval when sludge samples were collected.

SECTION 10

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ALUMINUM-BEARING SLUDGE QUESTIONAIRE

The Aluminum Association, Inc. developed a questionaire to survey the industry regarding sludge management issues. The questionaire included requests for the following information:

- 1. Georgraphic location of facility (preferably state, but regional location is acceptable).
- 2. Brief description of process which generates sludge including raw materials utilized.
- 3. Volume of sludge produced (tons of dry solids per day and, if possible, tons of dry solids per unit of product.
- 4. Sludge characteristics:
 - a. Water content as generated (before any dewatering efforts).
 - b. Aluminum content and predominant form, i.e., aluminum hydroxide, aluminum oxide, aluminum sulfate.
 - c. Aluminum compounds present.
 - d. Water content in present storage system (after any dewatering efforts).
 - e. Amount of material on hand.
 - f. Provide any information on constituents present which you feel might reduce the reusability of this material.
- 5. Do you anticipate any significant changes in the rate of sludge generation or the character of the sludge in the next five years?
- 6. Briefly describe present treatment and disposal systems.
- Briefly describe any efforts you have undertaken to determine a use for this material.