CHARACTERIZATION OF ACID TREATED ALUM SLUDGE FOR ALUM RECOVERY IN WATER TREATMENT PLANTS

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By

James A. Susan

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Characteristics of acidified alum sludge were evaluated as they pertained to a process for the economical recovery of alum from water treatment plant sludge using liquid-ion exchange.

Five sludges were selected for evaluation with the help of a nationwide survey of alum users. These five sludges were tested to determine aluminum dissolution upon acidification, acid requirements, mixing time, concentration and settling characteristics of the residual solids, and requirements for ultimate disposal of the supernatant and solids.

Results showed that after settling the acidified sludges, the percentage of dissolved aluminum in the supernatant ranged from 65 to 95 percent. In order to obtain maximum aluminum dissolution, 1.5 moles of H_2SO_4 per mole of total aluminum in the sludge was required. Kinetics studies revealed that equilibrium was reached after 15 minutes of mixing. Solids concentration reductions in the sludge ranged from 35 to 90 percent upon acidification, depending on the sample. Final settled volume of the sludges was reduced by 80 percent at maximum aluminum dissolution. Due to the low pH of the supernatant and residual solids after acidification, 18.0 g/l and 24.9 g/l of lime as CaO was necessary to raise the pH to 6, respectively.

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A THESIS

Submitted to
Michigan State University
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MASTER OF SCIENCE

Department of Civil and Sanitary Engineering to my wife and parents

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CHAPTER 1

INTRODUCTION

Alum coagulation for water purification has received considerable attention due to problems associated with sludge disposal. Until recently the water utilities have dealt with the alum sludge disposal problem by returning the sludge back to the waterway. This disposal method is no longer acceptable. During the past several years there has been a growing awareness of the environmental crisis the nation faces. Partly as a result of this new awareness, several laws have been passed to begin cleaning up the environment. Much of the clean-up effort has been directed to the nations waterways. One of the goals set forth by these laws is to eliminate all discharges into the nation's waters. Because of this, the water utilities are being forced to look to different techniques to solve the alum sludge disposal problem.

1-1 Alum Usage and Associated Problems

Aluminum sulfate, or alum as it is commonly called in the water treatment field, is a coagulant used to remove colloidal particles and other soluble and insoluble matter from water. This organic and inorganic material causes a water to be turbid or colored. Removing colliodal suspensions from a water is difficult due to their small size and stability. Coagulants are used to alter the colloidal particles so that they will come together to form larger particle masses, thus allowing settling to take place. Ferric chloride, ferric sulfate, and lime are also used for coagulation. Of these, alum is used most often (1).

Because of its widespread use, alum sludge disposal is a major problem facing the water treatment industry. It has been estimated[1] that 14,000,000 tons (wet weight) of alum sludge is produced in the United States each year. Alum sludge has a very low solids concentration (usually between 0.5 and 2.0 percent) and is extremely difficult (costly) to dewater. Because of this, many treatment plants dispose of the sludge by dumping it back into the source waterway.

With the passage of the Water Pollution Control Act (PL 92-500) the water supply industry is required to meet certain deadlines for reducing and eventually eliminating all discharges. Under the act, the industry is mandated to achieve Best Practical Control Technology by July 1, 1977; Best Available Technology Economically Achievable by July 1, 1983; and elimination of all pollutant discharges by 1985. Since passage of this act, the industry has turned to lagoons, landfills and the local wastewater treatment plant to help solve the problem. While all these methods are currently being used for sludge disposal, they all have problems associated with them.

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[1] Estimated from alum usage notes provided by Allied Chemical Technical Services Division.

Disposing of the sludge in the sewer system increases the load on the wastewater treatment plant. Often times the plant does not have the capacity to handle the increased solids loading resulting from the alum sludge. Lagooning and landfilling are viable alternatives but also have problems associated with them. Lagoons require that a large tract of land be available near the treatment plant. In many locations, sizable quantities of open land are non-existent or very expensive. Lagoons eventually fill and must be cleaned of all the settled material. Landfills pose even larger and costlier problems. Generally, landfills require a solids concentration of between 20 and 40 percent. Since alum sludge does not dewater readily, obtaining the required solids concentration can be very expensive.

1-2 Rationale for Current Research

Because of the Water Pollution Control Act, alum coagulation plants are seeking acceptable and cost effective methods for alum sludge disposal to replace those currently in use. A solution to some of the disposal problems associated with alum sludges may now be possible as a result of an economical alum recovery system for water treatment plants currently under development. The proposed recovery process uses liquid-ion exchange (analogous to a resin ion-exchange process) to extract aluminum from acidified alum sludge.

1-3 Research Objectives

The research described in this thesis was designed to determine the sludge pretreatment required prior to the recovery process. Determining necessary pretreatment involved investigating initial sludge characteristics and characteristics of the acidified sludge. The work included conducting a nationwide survey of alum users as well as performing tests to determine basic alum sludge parameters prior to and after acidification. The tests were designed to evaluate aluminum dissolution, solids concentration and settling characteristics. It was anticipated that in addition to recovering the alum, the process would also reduce costs associated with sludge disposal by reducing sludge volume and improving dewatering characteristics.

In addition to discussing results of the tests that were made on the alum sludges, a summary of characteristics of alum coagulation, current alum sludge disposal techniques, and past alum recovery research will be included.

CHAPTER 2

CHARACTERISTICS OF ALUM SLUDGE

2-1 Alum as a Coagulant

Alum is used to remove turbidity, color, and other colloidal matter too small or stable to settle during the normal sedimentation process. Some dissolved substances, such as phosphates (in wastewater treatment) can also be removed by coagulating with alum.

Alum has been used as a coagulant throughout history. While the early Egyptians knew of alum as early as 2000 B.C., its use as a coagulant for water treatment was first noted by Plimy (ca. 77 AD) who described it as being useful for making bitter water potable. In 1767, common people in England treated muddy water by adding several grains of alum to a quart and allowed it to flocculate and settle. Alum was first used to treat municipal water supplies at Bolton, England in 1881. From that time to the present, alum has had widespread use as a coagulant throughout the water treatment industry (2).

Coagulants work by altering the surface characteristics of the colloid or solute so that the particles can approach each other within the range of attraction. Generally, there are four methods (or theories) by which a coagulant may destabilize colloidal material: 1) reduction of the charge layer on the colloid, 2) sorbtion of the coagulant onto the colloid, 3) formation of an insoluble mesh to trap colloidal material, or 4) chemical reaction. It is believed that all four of these mechanisms are taking place during coagulation.

2-2 Commercial Alum

Alum (aluminum sulfate) as used in water treatment plants is produced by grinding bauxite and bauxite clays and then reacting this ground material with sulfuric acid. The equation for this reaction is

$Al_2O_3(s) + 3H_2SO_4 + 11H_2O \rightarrow Al_2(SO_4)_3 \cdot 14H_2O.$

After the reaction is complete, the liquid is separated and adjusted to 8 to 8.3 percent Al_2O_3. Alum in this form has a molecular weight of 594 (including water of hydration). Alum may be purchased in either liquid or solid form but liquid is the preferred choice, except for small treatment systems. As delivered, liquid alum is 50% alum and 50% water. Table 2-1 gives some of the properties of commercial alum.

2-3 Alum Chemistry

When added to a water, aluminum sulfate reacts with alkalinity present according to the simplified reaction

$Al_2(SO_4)_3 \cdot 14H_2O + 6HCO_3^- \rightarrow 2Al(OH)_3(s) + 6CO_2 + 3SO_4^{-2} + 14H_2O.$

After all the alkalinity has reacted, the reaction proceeds as

$Al_2(SO_4)_3 \cdot 14H_2O \rightarrow 2Al(OH)_3(s) + 3H_2SO_4 + 8H_2O.$

TABLE 2-1

Properties of Commercial Alum

	Dry	Liquid
Chemical formula	$Al_2(SO_4)_3 \cdot 14H_2O$	$Al_2(SO_4)_3 \cdot 14H_2O$
Molecular weight	594	594
% Al_2O_3	17.1	8.3
Weight/gal, lbs/gal		11.13
Dry alum equivalent, lbs/gal		5.4
Bulk density, lbs/cu ft		
Ground	61-72	
Rice	56-63	
pH of 1% solution	3.5	
Solubility in water		
At 68°F	87 gms $Al_2(SO_4)_3 \cdot 14H_2O$/100 gms H_2O	
At 32°C	71 gms $Al_2(SO_4)_3 \cdot 14H_2O$/100 gms H_2O	
Crystallization point, °F		4

<u>Source</u>: American Cyanamid Co., Cyanamid Alum, p. 40, 1972.

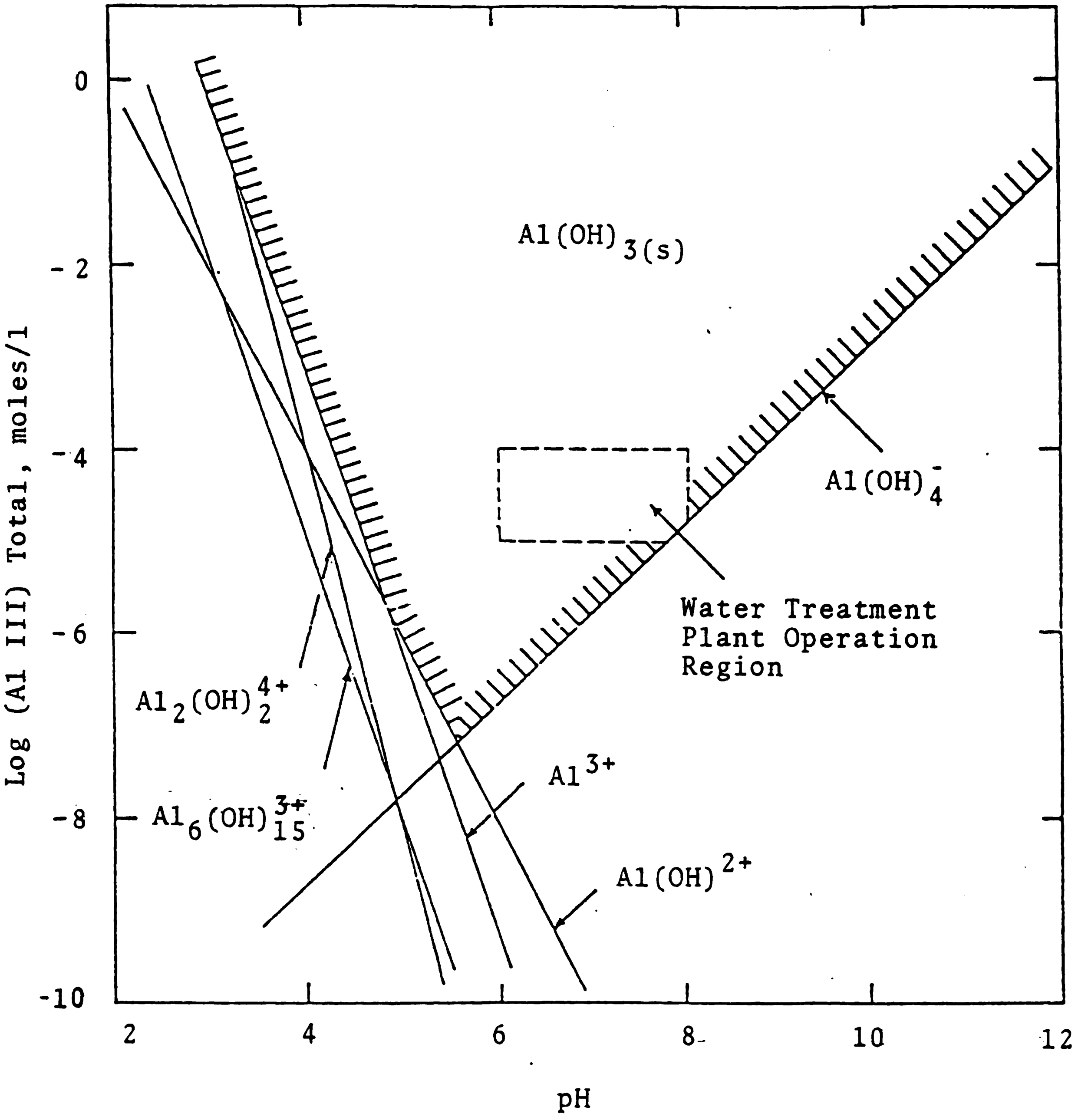
Two conclusions can be drawn from the previous two reactions. First, the amount of alum necessary to treat a water is not only dependent on the suspended matter present, but also on the alkalinity of the water since alkalinity reacts with alum. Second, as a result of adding alum to a water, the pH of that water will be lowered due to a change in the carbonate distribution and/or the formation of sulfuric acid.

2-4 Alum Sludge

Alum sludge has been described as, "bulky and gelatinous material with a relatively low solids content that is difficult to dewater" (3). The Environmental Protection Agency classified alum sludge as an industrial waste.

Under equilibrium conditions the aluminum contained in alum sludge would exist primarily as the insoluble aluminum hydroxide $Al(OH)_3(s)$ as shown in the two equations presented in the previous section. Singly and Sullivan (4) have shown that under the nonequilibrium conditions that exist in water treatment plants the predominant floc species is one of positive charge. The species formed is influenced by both the aluminum concentration and the pH of the solution. Figure 2-1 is a solubility diagram for aluminum hydroxide. The diagram shows the various species and the range of treatment plant operation. General forms of the polymerized molecules have been suggested by other authors. These include $Al_x(OH)_{2.5x}^{+0.5x}$ as suggested by Brossett (5), $Al_8(OH)_{20}^{+4}$ reported by Matyevic (6) and others such as $Al_7(OH)_{17}^{+3}$ and $Al_{13}(OH)_{34}^{+5}$.

Figure 2-1 Solubility of Aluminum Hydroxide as a Function of pH



<u>Source</u>: Chen, B. H. H., Ph.D. Dissertation, September, 1973, Blacksburg, Virginia.

All of the species mentioned above are associated with a high concentration of hydrated water molecules. It is for this reason that alum sludge is difficult and expensive to dewater. Many different sludges may be produced from a water treatment plant depending on the processes used. Of these many possible sludges, alum sludge causes the biggest problems with respect to dewatering and ultimate disposal. Table 2-2 and 2-3 rank dewatering characteristics of various water treatment sludges based on settled solids concentration and specific resistance.

TABLE 2-2

Ultimate Settled Solids for Various Chemical Sludges

Sludge	Location	Settled Solids, %
Excess lime and alum backwash	Boonville	3.96
Alum sludge	Moberly	4.05
Excess lime and iron backwash	Jefferson City	4.1
Iron backwash	St. Louis Co.	4.62
Excess lime and alum backwash	Boonville	7.4
High magnesium softening sludge	Kansas City	8.0
Lime and alum	Boonville	8.17
High magnesium softening sludge	Kansas City	8.6
Iron backwash	St. Louis	8.95
Lime and alum	Boonville	10.1
Cationic-flocculant backwash	St. Joseph	11.3
Iron (secondary basin)	St. Louis Co.	12.2
Lime and iron	Jefferson City	13.7
Lime and magnesium	Kansas City	15.2
Lime and alum	Boonville	16.5
Lime and iron	Jefferson City	19.1
Iron (secondary basin)	St. Louis	19.3
Iron (primary basin)	St. Louis Co.	21.1
Lime and iron	Jefferson City	22.9
Softening sludge	Kansas City	25.3
Lime and iron	Jefferson City	26.8
Lime and iron (primary basin)	St. Louis	35.6
Cationic flocculant	St. Joseph	35.8
Lime	St. Louis Co.	63.8

Source: D. J. Calkins and J. T. Novak, "Characterization of Chemical Sludges," Journal American Water Works Association, June, 1973.

TABLE 2-3

Specific Resistances for Various Chemical Sludges

Sludge	Location	Specific Resistance 10^6 (sec/g)
Lime and iron	Jefferson City	2.11
Lime and iron	Jefferson City	4.3
High magnesium softening sludge	Kansas City	5.49
Lime and alum	Boonville	5.83
Excess lime and alum backwash	Boonville	5.98
Lime and iron	Jefferson City	6.12
Lime and iron	Jefferson City	6.79
Lime and iron	Jefferson City	7.0
Softening	Kansas City	11.57
Excess lime and alum backwash	Boonville	13.2
Cationic flocculant	St. Joseph	14.1
Lime and iron	St. Louis	21.2
High magnesium softening sludge	Kansas City	25.1
Iron	St. Louis	40.8
Lime and alum	Boonville	53.4
Iron backwash	St. Louis Co.	76.8
Iron	St. Louis Co.	77.6
Cationic-flocculant backwash	St. Joseph	80.1
Iron backwash	St. Louis	121.8
Iron	St. Louis Co.	148.5
Alum	Moberly	164.3

<u>Source</u>: D. J. Calkins and J. T. Novak, "Characterization of Chemical Sludges," <u>Journal American Water Works Association</u>, June, 1973.

CHAPTER 3

ALUM SLUDGE DISPOSAL

3-1 Introduction

While many methods exist for treatment and disposal of alum sludge, only a few are in widespread use. Each treatment method has its own particular problems and drawbacks associated with it. Operating costs and inability to dewater the alum sludge to a required solids content are two of the big problems with current alum sludge dewatering and disposal techniques.

Ultimate disposal of alum sludge solids is usually accomplished by landfilling. If the sludge is to be landfilled with other material (e.g. solid waste), a solids content of between 20 and 40 percent is necessary. At a solids content of 20 percent, the sludge may be handled with normal earth moving equipment. At this solids concentration, alum sludge has the consistency of soft clay. In order to landfill the sludge by itself, a solids content above 40 percent is desirable. A solids content of between 40 and 50 percent gives alum sludge the consistency of stiff clay.

3-2 Non-Mechanical Dewatering

Many small water treatment plants use non-mechanical sludge dewatering techniques for handling alum sludge.

Lagoons and sand-drying beds are used alone or in combination to dewater alum sludge. Depending on the size of the treatment plant, these two methods require that a certain amount of land be available. Larger plants located in urban areas usually do not have the necessary amount of required land. Freeze or heat treatment may also be used in combination with either lagoons or sand-drying beds for sludge conditioning.

3-2-1 Freeze Treatment

Prior to ultimate disposal, alum sludge may be conditioned by either heating or freezing in order to break the floc structure thereby allowing the bound water to be released. Neither heating or freezing techniques have been used very often for sludge conditioning in the United States. Of the two, freezing has received the greatest attention. Freezing may be carried out in the out-of-doors using the natural climatic conditions or indoors using refrigeration units. Obviously natural freezing is limited to the cold winter months. This necessitates sludge storage during the warm months. Year round operation using refrigeration units can be very costly. While no cost figures are available, with the current energy situation one would expect that power costs would be prohibitively high.

Farrell, et al. (7), reported that after natural freezing, the solids content of an alum sludge increased from $0.32^{o}/_{o}$ to $18^{o}/_{o}$. In order to obtain a maximum solids concentration, freezing had to be complete. Partial freezing, even if repeated a number of times had little effect on improving the solids concentration of the sludge. Snow cover, even in extremely cold climates was also undesirable. The researchers suggested that sludge not be put out in snow and that if snow accumulated on freezing sludge it should be removed by either melting it with water or plowing it off. The depth to which the sludge could be applied depended on the climate, but could range from 1 inch to 22 inches. At the lower range it was reported that the system became harder to justify economically.

Sludge freezing using mechanical refrigeration removes the seasonal restrictions of natural freezing, but increases power costs for the treatment plant. Wilhelm and Silverblatt (8) believed that power costs can be competitive with costs of precoat or of pretreatment chemicals required for pressure or vacuum filtration in certain situations. Their study showed that freeze treated sludge readily settled to between 17% and 22% solids. This sludge was then further dewatered using vacuum filtration or lagoons where a solids content of 60% to 70% was possible. They noted that sludge must be frozen slowly and completely between 5°F and 25°F. Applied thickness varied from 1/2 inch to 2 inches depending on freezing time and temperature. Power costs were estimated to be 20% to 30% of the total cost for the system. Capital costs were put at 55% to 65% and other operating costs were 15%.

Advantages of the system were listed as: 1) no chemical conditioning was required, 2) a high solids content was obtainable, 3) it was unaffected by variations in the sludge, and 4) there was minimal operator attention. The disadvantage was the high power costs.

3-2-2 Lagoons

Many plants utilize lagoons as their only means of sludge disposal. Since lagoons eventually fill, they are usually used as storage prior to dewatering or other form of ultimate disposal. Lagoons do not change the characteristics of alum sludge and even after long periods of time, the sludge will thicken to less than 10% (9).

Neubaur (10) reported that after three years of operation, a 400′ x 320′ x 17′ lagoon with a 7′ sludge depth had an average solids concentration of only 4.3% at a loading rate of 0.37 gpd/ft^2. Solids concentration in the lagoon varied from 1.7% at the top of the sludge blanket to 14% at the bottom.

King, et al. (11) found that a 1,000,000 gallon lagoon used to hold filter backwash would remove 95% to 99% of the settleable solids and 62% to 90% of the suspended solids.

Storage in a lagoon will not improve sludge dewatering either. The principle advantage of lagoon storage is that it is free from control or maintenance. Disadvantages include the relatively large amount of land required, possibility of insect breeding and influences climate changes may have on its effectiveness. While operating costs are low, land acquisition and construction costs may be high, depending on the location.

3-2-3 Sand Drying Beds

Sand drying beds utilize two distinct mechanisms during the dewatering process: gravity drainage and air drying. Gravity drainage is controlled by the characteristics of the sludge itself while air drying is influenced by environmental factors such as wind velocity and temperature.

Chemical conditioning with application of polyelectrolytes has been shown to improve the dewatering qualities of alum sludge. Investigators have reported improved drainage rates of sludge applied to sand drying beds using polymers. Novak and Langford (12) reported that anionic polymer doses of between 10 mg/l and 35 mg/l improved sludge drainage based on specific resistance tests. The coefficient of compressability increased with the additon of 10 mg/l to 20 mg/l of polymer (non-ionic, cationic, or anionic).

Nuebaur (10) reported that solids concentrations of up to 20% were obtainable for alum sludge based on bench scale tests. Testing conditions varied with temperatures fluctuating between 69°F and 81°F. Relative humidity was between 72% and 93% and a constant 5 mile/hour wind was applied. Detention times varied from 70 to 100 hours.

Neubaur reports a loading rate for sand drying beds of 1000 ft^3 of alum sludge applied to 2000 square feet of beds per day or 3.74 gpd/ft^2. He estimated the cost of this type of system to be less than $5/million gallons of processed water. Sand drying beds usually consist of 6 to 9 inches of sand over an underdrain system composed of up to 12 inches of gravel and drain tiles, according to Neubaur. Sludge can be applied in up to 12 inch lifts.

Problems associated with sand drying beds include 1) land requirements, 2) long detention time, 3) rain and cold, 4) high labor costs for collection and hauling, and 5) penetration of the sludge into the bed causing clogging.

3-3 Mechanical Dewatering

Various mechanical dewatering systems have been tested for alum sludge disposal. Many have been tried, but only three have been accepted, although not widely used in the industry. These are centrifugation, vacuum filtration and pressure filtration.

3-3-1 Centrifugation

Two types of centrifuges are currently used for sludge dewatering: the solid-bowl centrifuge and the basket-bowl. For dewatering alum sludges the solid-bowl has proven to be more successful than the basket (1). In most cases polymers are added to condition the sludge prior to centrifugation. Centrifuges are very sensitive to changes in the concentration or composition of the sludge as well as the amount of polymer applied.

A cake dryness of 15% to 17% is considered good performance for a centrifuge. Albrecht (9) reported solids concentrations of 15% to 17% with feed solids between 0.4% and 6%. Loading rates varied depending on the size of the centriguge but Albrecht noted that the best performance was obtained when the feed rate was from 75% to 85% of the machines total solids or hydraulic capacity.

Solids concentrations of between 6% and 12% have been reported by Neubaur (10). These solids concentrations are too low to be handled by conventional earth moving equipment or to be landfilled. Disadvantages of centrifuges include: 1) low final solids concentration, 2) high power and maintenance costs, and 3) sensitivity to changes in feed solids content. Some advantages are: 1) small space requirements, 2) process automation, and 3) the ability to handle thickened or dilute sludge.

3-3-2 Vacuum Filtration

The rotary drum vacuum filter applies a vacuum to a porous medium to separate solids from sludge. Two basic types of rotary drum vacuum filters are used in water treatment; the traveling medium and the pre-coated medium filters. The traveling medium is continuously removed from the drum allowing it to be washed from both sides without diluting the sludge in the sludge vat. Because of the continuous washing the filter medium is always clean.

The precoat filter is coated with a filter medium and then shaved off as the drum moves. The filter is pre-coated with 2 to 3 inches of filter material which is then shaved off in 0.005 inch increments.

Under good conditions and with suitable pretreatment solids concentrations above 20% are possible with traveling belt filters. Pretreatment consists of polymers, lime, or both. Tests conducted by Gates and McDermott (13) suggested that minimum specific resistance was obtained using cationic polymers. Dosages ranged from 1.53% to 4.79% by weight. Anionic and non-ionic polymers also improved specific resistance at doses between 0.14 % and 0.26%, respectively. Bugg, King and Randall (14) on the other hand reported that while all three types improved filterability, the anionic polymer was by far superior to the cationic and slightly better than the non-ionic types at pH's above 5.0. Polymer dosages ranged up to 100 ppm. They noted that polymer doses should be based on a weight to weight basis as opposed to weight per volume of sludge. They found that cationic polymers were more effective than non-ionic and anionic at pH's below 5.0.

Pre-coating vacuum filters with diatomaceous earth has proven to be useful when filtering alum sludge. Pre-coating allows for successful operation under varying sludge conditions. Loading rates and other performance and operating data for a typical traveling belt vacuum filter and a pre-coat filter are given in Tables 3-1 and 3-2. Even with the improvements in sludge solids concentration using vacuum filters, they are costly to buy and install and have a high operating cost associated with them.

TABLE 3-1

Performance and Operating Data Obtained By the Travelling Belt Vacuum Filter On Alum Sludge Dewatering

Feed Concentration (%)	2 - 6
Flow Rate ($l/m^2/hr$)	0.7 - 1.4
(gal/sq ft/hr)	2 - 4
Dry Solids Yield ($kg/m^2/hr$)	0.15 - 0.25
lb/sq ft/hr)	0.75 - 1.25
Cake Concentration with Polymer (%)	15 - 17
Cake Concentration with Lime (%)	30 - 40
Filtrate Solids (mg/l)	100 - 200
Polymer Dosage (kg/t)	2.72 - 5.45
(lb/sq ft/hr)	6 - 12
Lime Dosage (%)	30 - 60
Drum Speed (rpm)	254 - 381
Operating Vacuum (mm Hg)	254 - 381
(in Hg)	10 - 15

Source: Westerhoff, G. P. and Daly, M. P., "Water Treatment Plant Waste Disposal", American Water Works Association, June, 1974.

TABLE 3-2

Typical Precoat Performance Data
On Alum Sludge Dewatering

Feed Concentration (%)	2 - 6
Feed Rate ($l/m^2/hr$)	0.7 - 2.1
(gal/sq ft/hr)	2 - 6
Dry Solids Yield ($kg/m^2/hr$)	0.2 - 0.3
(lb/sq ft/hr)	1.0 - 1.5
Cake Concentration (%)	30 - 35
Filtrate Suspended Solids (mg/l)	10 - 20
Solids Recovery (%)	99+
Precoat Recovery (%)	30 - 35
Precoat Rate ($kg/m^2/hr$)	0.02 - 0.04
(lb/sq ft/hr)	0.1 - 0.2
Precoat Thickness (mm)	38.1 - 63.5
(in)	1.5 - 2.5
Drum Speed (rpm)	0.2 - 0.3
Operating Vacuum (mm Hg)	127 - 508
(in Hg)	5 - 20

Source: Westerhoff, G. P. and Daly, M. P., "Water Treatment Plant Waste Disposal", Journal American Water Works Association, June, 1974.

3-3-3 Pressure Filtration

Filter presses are a relatively new method of sludge dewatering in the United States. At the end of 1976, five plants were using pressure filters for sludge dewatering and four others were planned (1). As with most of the other sludge dewatering systems, the use of conditioners is necessary in order to obtain a high cake solids. Lime, fly ash and polymers are all used as conditioning agents, with lime being preferred. When lime is used, enough is added to the sludge to raise the pH to around 11. The lime and sludge must be mixed for at least 30 minutes to prevent the lime from plating out on the filter media and inside of pipes. Sometimes both lime and polymers are added for conditioning.

Thomas (15) reported that with feed solids between 0.5% and 1.5%, alum sludge cake solids were as high as 35% to 40%. Conditioning consisted of 1 mg/l of polyelectrolyte or 10% lime. Westerhoff and Gruninger (16) reported solids concentrations of up to 50% after pressure filtration. Problems with pressure filters are that 1) they are a batch system necessitating sludge storage, 2) they have a high labor cost associated with them, and 3) if lime is used as a conditioner, filtrate disposal causes problems due to its high (around 11) pH and significant amounts of soluble aluminum present do to the high pH.

Neilsen, et al. (17) in 1973 tested a centrifuge, pressure filter and vacuum filter for their effectiveness for dewatering a particular alum sludge from a 40 mgd water treatment plant. A summary of the results of his study are presented in Table 3-3.

TABLE 3-3

Economic and Performance Summary for Alum Sludge Dewatering

Parameters	Scroll Centrifuge	Pressure Filter	Basket Centrifuge	Vacuum Filter
Solids loading (dry basis)*				
Nominal-per unit	9,500	34,000	9,500	10,000
Total	19,000	19,000	19,000	19,000
Overload-per unit	34,000	68,000	22,000	20,000
(Overload conditions = 60,000 lb/day)				
Total	68,000	68,000	66,000	60,000
Machine requirement				
Machine size	28 gpm	64x81-in.	120 gal bowl	416 ft^2
Assumed equipment life-years	20	30	20	25
Number for nominal load	2	1/2	2	2
Number for overload	2	1	3	3
Solids output				
Nominal-solids by wt., %	16	30	15	15
-gal/day of wet cake	12,700	10,600	13,500	13,500
Overload-solids by wt., %	16	20	10	10
-gal/day of wet cake	45,400	35,300	73,700	73,700
Polyelectrolyte dose (lb/T)				
Nominal load	3.0	4.0	4.5	1.5
Overload	8.0	4.0	5.0	2.0
Initial machine costs				
Machine cost-each	$40,000	$400,000	$ 45,000	$ 38,000
Total for overload	80,000	400,000	135,000	104,000

*All solids loading units are lb/day

T = Ton of dry solids

TABLE 3-3 (con't)

Parameters	Scroll Centrifuge	Pressure Filter	Basket Centrifuge	Vacuum Filter
Annual cost for 1,700 T/yr				
Machine capital recovery @ 5%	$ 6,420	$ 26,020	$ 10,830	$ 7,380
Operation and maint-nominal	4,800	4,000	1,500	3,000
Power-nominal	3,850	1,190	3,210	10,900
Polyelectrolyte cost-nom (1,200 T/yr)	6,840	9,100	10,300	3,420
-overload (500 T/yr)	7,600	3,800	4,750	1,900
Disposal @ $5/cu yd†	56,100	34,400	68,700	68,700
Labor-1/2 man day/day (incl. benefits and overhead)	9,450	9,450	9,450	9,450
Total Annual Cost	$95,060	$ 87,960	$108,740	$104,750
Unit Cost $/T	56	52	64	62

†Uncompacted unit weight in truck haul assumed = 70 lbs/ft^2

T = Ton of dry solids

Source: R. L. Nielsen, et al., "Alum Sludge Thickening and Disposal", *Journal American Water Works Association*, *65*, 385 (June, 1973).

Table 3-4 presents a review of the treatment methods discussed to this point.

3-3-4 Extractive Treatment

Olson (18) described a sludge drying process which made use of aliphalic amine solvents which mix with water when cooled below 65°F (18°C). The system was called B.E.S.T. for basic extractive sludge treatment. After the solvent and water were mixed together the solids were easily removed using a centrifuge. The solvent-water mixture was then separated by raising the temperature of the mixture to above 140°F (55°C). The solvent was then recycled and the water (which was clear, sterile and pathogen free) was disposed of. The solids were then vacuum filtered without pretreatment to 48% solids. Tests indicated that 72 ft^2 of filter would be able to handle 50 tons of dry weight solids per day. Costs of this system may be very high due to large solvent losses and power costs for heating the solvent and water.

3-4 Ultimate Disposal

Since alum sludge can no longer be returned to the waterways, it is usually landfilled as a means of ultimate disposal. As mentioned previously, landfilling alum sludge requires a solids content of between 20% and 40%, depending on the landfill. In most cases the sludge is simply spread and compacted either alone or with other wastes. Since alum sludge is classified as an industrial

TABLE 3-4

Summary of Alum Sludge Treatment Methods

Method	Pre-conditioning	Loading Rate	Final Solids	Cost	Space Required	Industry Application	Reference
1. Freeze Treatment							
Farrell (natural	none		18%	low	large	limited	7
Silverblatt and Wilhelm (refrigeration)	none		17-22%	high	moderate	limited	8
2. Lagoons							
Neubaur	none	0.37 gpd/ft^2	4.3%	low	large	widespread	10
King	none			low	large	widespread	11
3. Sand-Drying Beds							
Neubaur	polymers	3.7 gpd/ft^2	20%	moderate	large	limited	10
4. Centrifugation							
Albrecht	polymers	75-85% of machine capacity	15-17%	high	small	limited	9
Neubaur	polymers		6-12%	high	small	limited	10
Neilsen	polymers		15%	high	small	limited	17

TABLE 3-4 (con't)

Method	Pre-conditioning	Loading Rate	Final Solids	Cost	Space Required	Industry Application	Reference
5. Vacuum Filtration							
Westerhoff (Traveling Belt)	polymer or lime	2-4 gal/ft^2/hr	15-17% w/polymer 30-40% w/lime	high	small	limited	1
Westerhoff (Precoat)	none	2-6 gal/ft^2/hr	30-35%	high	small	limited	1
Neilsen	polymer		15%	high	small	limited	17
6. Pressure Filtration							
Thomas	polymer or lime		35-40%	moderate	small	expanding	15
Westerhoff and Gruninger	lime		50%	moderate	small	expanding	16
Neilsen	polymer		30%	moderate	small	expanding	17

waste some states will not allow the sludge to be landfilled or require that it only be handled by those landfills licensed to accept such wastes.

The biggest question concerning landfilling of alum sludge is that of the leachate. Between pH 5.0 and pH 8.5 the aluminum hydroxide is quite stable. Above or below these values, aluminum in the sludge becomes soluble. While the aluminum does leach out, the quantities are usually small and after being diluted in the groundwater, the aluminum concentration would be very low, often comparable to the concentration in finished water from a water treatment plant (1).

CHAPTER 4

LITERATURE REVIEW OF ALUM RECOVERY RESEARCH

4-1 Acid Treatment of Alum Sludge

As reported by Roberts and Roddy (19), alum recovery is not a new concept. In 1903, W. M. Jewell developed an alum recovery process using sulfuric acid. W. R. Mathis patented a similar process in 1923.

Some of the earliest reported work with alum recovery was by Palin (20) in 1954. Filter washwater was treated with concentrated sulfuric acid in amounts ranging from 0.5 to 1 percent by volume. Chlorine in dosages from 10 to 100 mg/l was also added to bleach color. This treated washwater was then used, along with fresh alum for coagulation. Despite a 60% reduction in alum, the cost of sulfuric acid proved to be more expensive than the cost of alum saved. In a second experiment, oven charred sludge was mixed with sulfuric acid. Four tons of air-dryed sludge would yield about 0.6 tons of charred sludge containing approximately 0.3 tons of aluminum as Al_2O_3. When 0.9 tons of sulfuric acid were added, the yield of aluminum sulfate cake was approximately 2 tons (14% Al_2O_3). Palin noted that in addition to recovering usable alum, the recovery process also helped to ease sludge disposal problems.

In 1960, Roberts and Roddy (19) described an alum recovery system for the city of Tampa. Sulfuric acid was used to recover aluminum from alum sludge based on the reported reaction

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

Approximately 1.9 lb. of sulfuric acid was required to react with each pound of aluminum hydroxide (or 1.5 moles per mole of Al). The pH for complete aluminum dissolution ranged between 1.5 and 2.5 for highly alkaline and less alkaline waters respectively. After repeated alum recycle in the pilot system no reduction of treated water quality was observed. A savings of 70% in chemical costs was realized.

Isaac and Vahidi (21) found that while aluminum hydroxide may be dissolved by either acid or alkali, acid was the superior choice. At a pH of 2.7, 60% of the aluminum was recovered from sludge samples. A pH of 11 resulted in a recovery of only 10%. In addition they observed that organic color was much more soluble in the alkali than in the acid. When working with fresh sludge they found that reducing the pH below 3 did not increase the degree of recovery, but did increase the amount of dissolved color present. At pH 3, the volume of the settled sludge was reduced by two-thirds. While the recovered alum was effective for removing color, it was not as efficient as fresh alum.

In laboratory experiments Webster (22) found that when the pH of alum sludge was depressed to about 2.4 with sulfuric acid, a clustering effect of the floc particles took place and the insoluble matter settled very rapidly. The supernatant contained 80% of the alum. During pilot plant studies, good coagulation was not obtained with recycled alum recovered below pH 3.0. Webster concluded that the alum reduced the pH of the raw water below the range for acceptable color removal. Consequently, the pH of the sludge was reduced to 3.5 for alum recovery and reuse. No adverse effects resulted from continued recycling of the recovered alum at pH 3.5.

Fulton (23) described a recovery system using alum sludge. Alum sludge with a solids content between 0.2% and 2% was mixed with sulfuric acid for 10 minutes in a high energy mixer. By reacting 1.9 lb of acid with 1.0 lb of aluminum hydroxide, 2.2 lb of alum was produced (all dry weights). This demand increased depending on organic and inorganic matter in the sludge. After mixing, the acidified sludge was settled. An overflow rate of 250 gpd/ft^2 was recommended for sludge at a pH of 2. He reported that this system would be feasible for plants in the 200 to 500 mgd range. For plants of this size, estimated costs would be between 3 and 5 dollars per million gallons. Skilled operators would be necessary to properly operate the system. Fulton noted that there may be potential problems with contamination of the recovered alum by iron and/or manganese since the two metals dissolve with the aluminum upon acidification. Iron dissolution was based on

$$Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O.$$

Westerhoff (24) conducted a 14 week pilot plant study to determine the suitability of using recovered alum as a primary raw water coagulant and to determine the build up of water contaminants through the recovery and recycle of alum in a closed system. He described three categories of potential impurities: 1) inert material removed during settling, 2) impurities capable of being reconverted to soluble form during acidification, such as iron and manganese, and 3) impurities from sulfuric acid. The sludge pH was reduced to 2.0 during the study. Measurements were made on total microscopic count, coliform, hardness alkalinity, cyanide, fluoride, phenol, dissolved solids, nitrates, sulfates, chlorides and several metals such as copper, lead, and zinc. The study showed that buildup of impurities was not a problem and that the recovered alum worked well as a coagulant. Recently Westerhoff (1) noted that construction of recovery systems in Japan has been halted due to concern over the possible recycling and accumulation of heavy metals.

In another experiment Fulton (25) described an alum recovery system using sulfuric acid to reduce the pH of alum sludge to 2.0. After acidification, the sludge would go to a filter press for dewatering. The filter would be treated with diatomaceous earth or fly ash so that the pH of the sludge would not rise, as would be the case if lime were used. An estimated 40% to 50% solids would be attainable. Fulton estimated that for a 100 mgd plant, a savings of 67% could be realized with alum recovery over other conventional dewatering and disposal techniques. The system would be advantageous for plants over 40 mgd. There would be no advantage for plants under 10 mgd and anything in between would be dependent on the particular plant. Table 4-1 gives the effects of various raw water constituents on sludge dewatering, acidification and alum filtration.

A pilot plant study by Gruninger (3) showed that with a long detention time in the acidulator and careful maintenance of a pH of 2 a recovery of 75% could result. The acidified sludge was allowed to settle for up to 14 hours. Detention times in excess of this had little effect on improving the level of alum recovery. Tests showed that after 18 cycles there was no significant build up of contaminants and no significant diference in the product water when using recovered alum or virgin alum. Tests also indicated that the residual solids dewatered better than untreated sludge and produced a dryer cake.

A recovery system using ultrafiltration (UF) to separate solids from recovered alum was investigated by Lindsey and Tongkasame (26). The UF membranes as used by the researchers were non-cellulosic organic polymers having an extremely thin surface layer (5μ) and a porous structure of the same material. Using sulfuric acid to depress the pH to 2 resulted in a recovery of 98%. The ratio of acid required to sludge fixed solids was 2.20 by weight at a pH of 2. The recovered alum was effective through all cycles but

TABLE 4-1

Waste Influences on Disposal Process

Grouping	Influences on Sludge Dewatering	Acidulation	Alum Filtration
Aluminum hydroxide	inhibits	complete reaction	*
Organic additives	inhibits	hydrolyzed	*
Inert additives			
Clay	enhances	*	enhances
Carbon	*	*	*
Inert raw-water solids	enhances	*	enhances
Convertible raw-water mineral matter	*†	complete reaction	*
Organic raw-water solids	inhibits	hydrolyzed	*

*No significant influence
†Would inhibit after accumulation in alum recovery

Source: G. P. Fulton, "Recover Alum to Reduce Waste-Disposal Costs", *Journal American Water Works Association*, 66, 312, May, 1974.

there was a build-up of color after several cycles. They proposed that the higher the solids content in the raw sludge, the more economical the system would be.

Chen, et al. (27), evaluated several water and wastewater alum sludges for alum recovery. The reported recovery was based on the formula

$2Al_x(OH)_y^{(3x-y)+} + 3xH_2SO_4 \rightarrow xAl(SO_4)_3 + 2yH_2O + (6x - 2y)H^+$.

The researchers noted that pH was not a good control parameter for a recovery system since the pH level at which maximum aluminum recovery was achieved varied from 3.0 to 1.0. After acidification and settling, Chen, et al. found that the acidified alum sludge volume was reduced by 80%. Good settling occured when aluminum recovery exceeded 60% to 80%. The remaining solids filtered better than that of raw sludge. Specific resistance reached a minimum when aluminum recovery was in the range of 60% to 80%. The recovered alum was found to be better than fresh alum for low turbidity waters. At higher turbidity levels, fresh alum was more efficient. Chen, et al. concluded that this phenomena was a result of impurities and foreign particulates in the recovered alum solution. These impurities provided some nucleation to aid in the coagulation of the low turbidity waters.

Tomono (28) of the Tokyo Water Works reporting on Tokyo's alum recovery system noted that economic feasibility depended on the raw water condition; eg., alum reclamation would be advantageous where raw water alkalinity (and turbidity) was high and large doses of alum were required. Tokyo selected sulfuric acid alum recovery to reduce sludge volume and to lower capital and operating costs when compared to lime conditioning and dewatering. Manganese contamination was of some concern but studies showed that only 0.01 ppm would be added to the product water by using the recovered alum. Tomono points out that actual plant operation has revealed the following facts: 1) concentration of reclaimed alum will usually be 1.0% to 1.5% as $Al_2(SO_4)_3 \cdot 18H_2O$, 2) dissolution of aluminum is not complete through the mixing tank and the thickening tank, some dissolution still takes place in the second thickening tank, 3) solids concentrations of up to 20% may be achieved in these tanks, 4) filterability of the acidified sludge is good, and 5) another tank provided between the sludge retaining basin and acid mixing tank would serve to balance out any fluctuating sludge conditions from the sludge basin.

CHAPTER 5

SLUDGE SURVEY

5-1 Sludge Survey Results

Before laboratory testing began a survey of alum users was made. The survey was designed to aid in evaluating the magnitude of the alum sludge disposal problem, to select representative sludges for evaluation and to determine how the industry was treating and disposing of its sludge. Approximately 300 questionaires were sent to AWWA member consulting firms and project sponsors. The firms were requested to complete the questionaires based on alum coagulation plants they had designed or were associated with. A summary of the responses is presented in Table 5-1.

Alum users were classified by raw water source (lake, reservoir, or river) in Table 5-2. Average values of turbidity, color, suspended solids and alum dose were then computed for each of the classifications. The data for lakes was potentially biased due to a large percentage of responses from plants taking water from the Great Lakes, specifically Lake Michigan. In Table 5-3, Lake Michigan data was separated from other lakes. A review of the data showed that, as expected, turbidity and color levels were higher from the river sources than either lakes or reservoirs. Correspondingly, the river sources required higher alum doses

TABLE 5-1

Responses to Sludge Survey

	Consultants	Sponsors	Total
Forms sent	284	32	316
Number of replys	52	22	74
Number of completed forms	52	23	75

TABLE 5-2

Raw Water Quality as a Function of Water Source

Source	Percent of Responses	Average Turbidity, FTU	Average Color, Pt-Co Units	Average SS, mg/l	Average Alum Dose, mg/l, 17% Al_2O_3
Lakes	46	10	17	48	13
Rivers	32	26	45	48	29
Reservoirs	22	11	18	21	16

TABLE 5-3

Raw Water Quality of Lake Sources

Source	Average Turbidity, FTU	Average Color, Pt-Co Units	Average SS, mg/l	Average Alum Dose, mg/l, 17% Al_2O_3
Lake Michigan	6	3	45	7
All other lakes	16	28	61	23

than the other two source classifications. Forty-six percent of those responding utilized a lake as the raw water source. Rivers were used by 32% while 22% obtained their raw water from reservoirs.

Using data obtained from the survey, an attempt was made to develop a relationship between raw water parameters and alum dose. All data were computerized and regression equations were developed to relate various combinations of raw water data to alum usage. The equation

$X = 8.790 - 0.223Y + 0.767Z$

where: X = alum dose, mg/l

Y = turbidity, JTU

Z = Color, Pt-Co

had a correlation coefficient of 0.89. A correlation coefficient of 1 indicates a perfect fit. The equation presented is not a perfect fit, but could be used as a rough estimate for determining alum dose, given certain raw water parameters. This equation was applicable for turbidity ranges from 2 JTU to 75 JTU and for color values between 5 and 144 Pt-Co units.

Reported costs for alum varied widely depending on location, quantity of alum used, and type of alum used. Transportation costs undoubtably contributed a large amount to variations in costs from one location to another. The average cost for liquid alum (17.1% Al_2O_3) was found to be $85.62/ton. Solid alum was much more expensive at $142.94/ton. The reported ranges were from $53.00 to $193.00 per ton for liquid alum and $109.50 to $240.00 per ton for the solid type.

Disposal methods currently being used were also inventoried (Table 5-4). Of those responding, lagoons were found to be the largest and most common disposal method. Lagoons were used by 43% of the plants surveyed to dispose of 70% of the total sludge flow. While only one percent of the total sludge flow was being returned to the rivers and lakes, 20% of the plants indicated that they were returning sludge to the raw water source. On some forms (18%) this question was left unanswered.

The survey also revealed that the sludge flow averaged 0.6 percent of the treated water flow and the solids concentration from sedimentation was under 1 percent.

TABLE 5-4

Methods of Sludge Disposal

Method	Percent of Total Flow	Percent of Responses
Lagoon	70	43
WWTP	27	27
Rivers & Lakes	1	20
Other	2	10

CHAPTER 6

LABORATORY METHODS AND MATERIALS

6-1 Introduction

Experiments were designed to evaluate five sludge parameters: aluminum dissolution; acid requirements; suspended solids concentration; settling characteristics; and mixing requirements. In addition to tests on the acidified sludge, each sample was evaluated for initial characteristics. These included suspended solids concentration, pH, settling characteristics and total aluminum.

6-2 Sludge Evaluation

6-2-1 Sludge Selection

From the survey, four sludges were selected for laboratory testing. The samples were taken from treatment plants located in Tampa, Florida; Indianapolis, Indiana; Concord, California; and Moline, Illinois. Selected raw water parameters for the four plants are given in Table 6-1. The average color of Tampa's raw water was about 100 Pt-Co units, requiring an average alum dose of 100 mg/l, the highest of any sludge tested. Concord used about 41 mg/l of alum to remove primarily turbidity. The Indianapolis source contained significant

TABLE 6-1

Raw Water Quality of Sample Sludges

Parameter	Indianapolis	Concord	Tampa	Moline
Turbidity, JTU	45	42	0.63	71
Suspended Solids, mg/l	36	--	252	--
Color, Pt-Co Units	30	7	100	26
Average Alum Dose, mg/l	24	41	100	43

Note: average values as reported from questionaires.

amounts of turbidity and color. An average alum dose of 24 mg/l was used. Moline added 43 mg/l of alum to remove 71 JTU of turbidity and 26 Pt-Co units of color. Moline also added 141 mg/l of lime. In addition to the four sludges discussed above, a sample from Washington D. C. was also analyzed. Raw water data for this sample was not available.

For classification purposes, the sludge solids were analyzed for dissolvable and non-dissolvable solids at pH 1 (Table 6-2). The Tampa sludge was high in dissolvable solids, both organic and inorganic, indicating that a large reduction in suspended solids would be expected by utilizing alum recovery. A high amount of dissolvable organic solids indicated that the dissolved sludge would be highly colored, and probably unsuitable for direct recycle. The Washington, Indianapolis, and Concord samples contained a smaller proportion of dissolvable solids. As a result, acidifying the sludge would not give as large a suspended solids reduction. Dissolvable solids for these sludges ranged from 35% to 54%, respectively. The Moline sludge contained 9% of total dissolvable solids. Little solids reduction would be expected upon acidification of this sample.

6-2-2 Sludge Preparation

Each sludge was tested as follows: a representative, one-liter sample was mixed on a magnetic stirrer while concentrated sulfuric acid was added. Enough acid was added

TABLE 6-2

Sludge Characteristics

Parameter	Washington	Indianapolis	Concord	Tampa	Moline
Dissolvable inorganic solids, %	9	26	36	61	7
Non-dissolvable inorganic solids, %	49	52	18	6	79
Dissolvable organic solids, %	26	12	18	25	2
Non-dissolvable organic solids, %	16	9	28	8	13
Solids Concentration, %	12.1	1.7	1.7	1.6	1.7

to lower the pH of the sludge to the desired level. The pH was determined with a Corning Model 12 research pH meter. During equilibrium studies the acidified sample was mixed for about one hour to ensure completion of the reaction. Once mixing was complete, a 10 ml sample was withdrawn for suspended solids analysis. The remaining volume was transfered to a one-liter graduate cylinder for settling tests. After settling the supernatant was decanted and analyzed for aluminum.

6-3 Total aluminum Analysis

Total aluminum determinations for the alum sludges were made by digesting the sludge with concentrated acid. Three acids and two methods were tested to determine which gave the most consistant and accurate results with minimal preparation.

The first method tested was to mix and heat acid and sludge for 30 minutes. Two concentrated acids were evaluated. Forty milliliters of sludge was mixed with various quantities of H_2SO_4 or HCl. The sample was then diluted and analyzed for aluminum using atomic absorbtion methods. Results of these tests are given in Table 6-3.

A procedure given in Standard Methods (29) for total metal analysis was also evaluated. The method given is more difficult and time consuming than those previously mentioned. A 50 ml sludge sample was placed in a beaker and 5 ml of concentrated HNO_3 was added. The mixture was evaporated to near dryness. An additional 5 ml of HNO_3 was then added

TABLE 6-3

Results of Methods for Total Aluminum Analysis

Acid	Quantity, ml	Al, mg/l	Average Al, mg/l	Standard deviation
HCl	40	280 250 230	253	25
HCl	20	248 240 218	235	16
HCl	10	225 269 213	236	30
H_2SO_4	40	280 260 270	270	10
H_2SO_4	20	255 233 233	240	13
H_2SO_4	10	238 219 269	242	25
HNO_3		245 265	255	14

and heated until a gentle refluxing action occured. The beaker was then allowed to cool and the volume was adjusted to 50 ml with distilled water. The sample was then diluted and analyzed for aluminum. The results for this test are also given in Table 6-3.

The optimum method (based on time required and precision) for aluminum determination in alum sludges was found to be:

1. Combine 40 ml of sludge with 40 ml of concentrated H_2SO_4.
2. Mix and heat with a Corning hot plate set at low for about 30 minutes.
3. After cooling, transfer mixture to a small graduate cylinder and make up the volume to 80 ml with distilled water.
4. Dilute and analyze for aluminum using atomic absorbtion techniques.

As can be seen in Table 6-3, this method gave consistant results, taking into account small errors associated with atomic absorbtion analysis. The HNO_3 method took from 2 to 3 hours to complete. In addition to the long time required, variances could occur due to solids adhering to the sides of the beaker as may have been the case during these tests, or in certain cases because it is a much more complete digestion, a higher aluminum concentration may result from non-alum aluminum compounds which are dissolved.

6-4 Aluminum Dissolution

Aluminum dissolution is a function of the pH to which the sludge sample is lowered. Tests were made at various pH's to determine how much aluminum was dissolved. After settling, a small quantity of supernatant was removed and analyzed for aluminum. Results were reported as percent aluminum dissolved based on the total aluminum in the sludge, as found by the method outlined in the previous section.

6-5 Aluminum Analysis

Aluminum determinations were made on a Scientific Instruments Model 151 atomic absorbtion spectropotometer. The instrument is accurate for aluminum concentrations between 1 mg/l and 100 mg/l. Concentrations in all the sludge samples were well above 100 mg/l. As a result, all samples were diluted prior to analysis. Acid normality affected the aluminum determination by changing the standard curve for the instrument. As the acid normality of the sample increased, the standard curve was lowered slightly. Diluting the samples prior to analysis not only brought the aluminum concentration into the instruments range but also adjusted the acid normality of the sample to that of the standards used to develop a standard curve. Aluminum standards were made with aluminum potassium sulfate.

Instrument precision was reported in literature to be ±10% when analyzing for aluminum. Once analysis began, errors were held to about 1 or 2 percent.

6-6 Solids Concentration and Settling Characteristics

Prior to settling, each sample was analyzed for both total and volatile suspended solids. Procedures were as described in <u>Standard Methods</u> (29) for determination of filterable residue. Glass fiber filters were used for the tests.

Settling characteristics were determined by settling a sample for two hours in a one-liter graduate cylinder. Interfacial height was recorded at various time intervals between 5 minutes and 15 minutes. After the test had been completed, the final sludge volume was recorded. Settling tests were also used to determine the effect of various polymers and activated silica on settling the acidified sludge.

6-7 Kinetics Studies

In order to determine detention times required during acidification, kinetics tests were made. These tests involved adding enough acid to lower the pH to 2.0. After adding the acid, samples were withdrawn from the mixing acidified sludge at various time intervals. The samples were immediately filtered to remove the solids, thereby stopping the reaction. Each sample was analyzed to determine how much aluminum dissolved at the various sampling times.

CHAPTER 7

EXPERIMENTAL RESULTS

7-1 Introduction

Tests were performed and results analyzed to determine the applicability of the various sludges examined to the recovery process, to aid in evaluating system design, to estimate essential items for capital and operating costs, to determine tank sizing, and to investigate ultimate disposal.

7-2 Results of Sludge Testing

7-2-1 Aluminum Dissolution

Any alum recovery system is based on the fact that aluminum in alum sludge will dissolve upon acidification. The amount of aluminum dissolved is a function of the pH to which the sludge is lowered. As noted previously, aluminum dissolution percentages were based on total aluminum found in the sludge. Table 7-1 gives values of total aluminum for each sludge tested. Total aluminum ranged from 295 mg/l in the Moline sludge to 3750 mg/l in the Washington sample. The results for aluminum dissolution are shown in Figure 7-1. At pH 1, dissolved aluminum ranged from a high of 99% for Tampa to a low of about 70% for the Concord sample. About 90% of the total aluminum in the Moline and Washington sludges dissolved at a pH of 1.0.

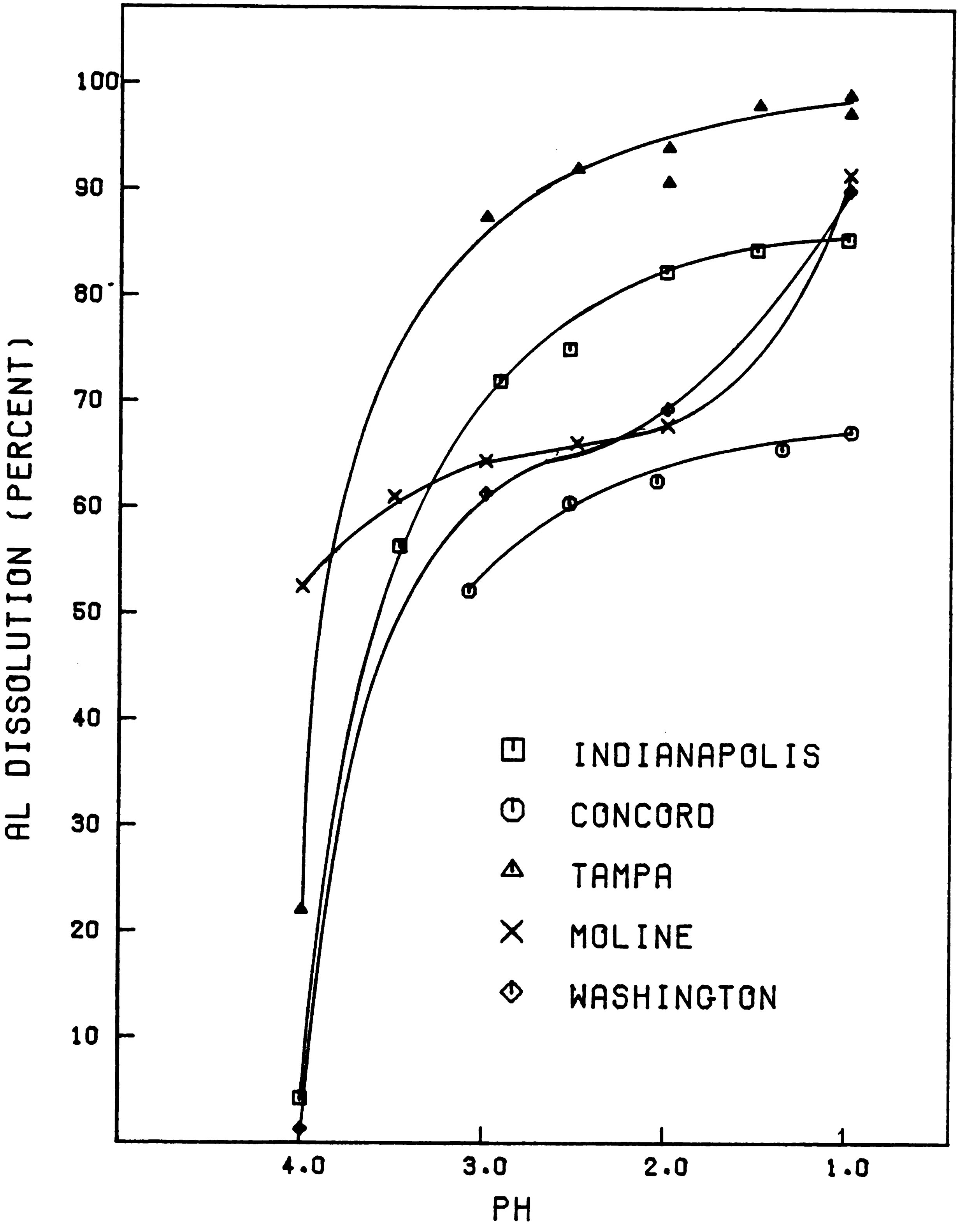
TABLE 7-1

Total Aluminum Concentration of Sample Sludges

Sample	Total Al, mg/l*
Tampa	3500
Indianapolis	2400
Concord	2400
Washington	3750
Moline	295

*Note: expressed based on sludge solids concentrations in Table 6-2.

Figure 7-1 Aluminum Dissolution as a Function of pH


AL DISSOLUTION (PERCENT)
100
90
80
70
60
50
40
30
20
10
4.0
3.0
2.0
1.0
PH
INDIANAPOLIS
CONCORD
TAMPA
MOLINE
WASHINGTON

Regression analysis indicated that for the particular sludges tested, a relationship existed between the percentage of aluminum dissolved and raw water color. Based on these two parameters the following equation was developed:

$$X = 73.049 + 0.287Y$$

where: X = percent aluminum dissolved

Y = raw water color, Pt-Co units

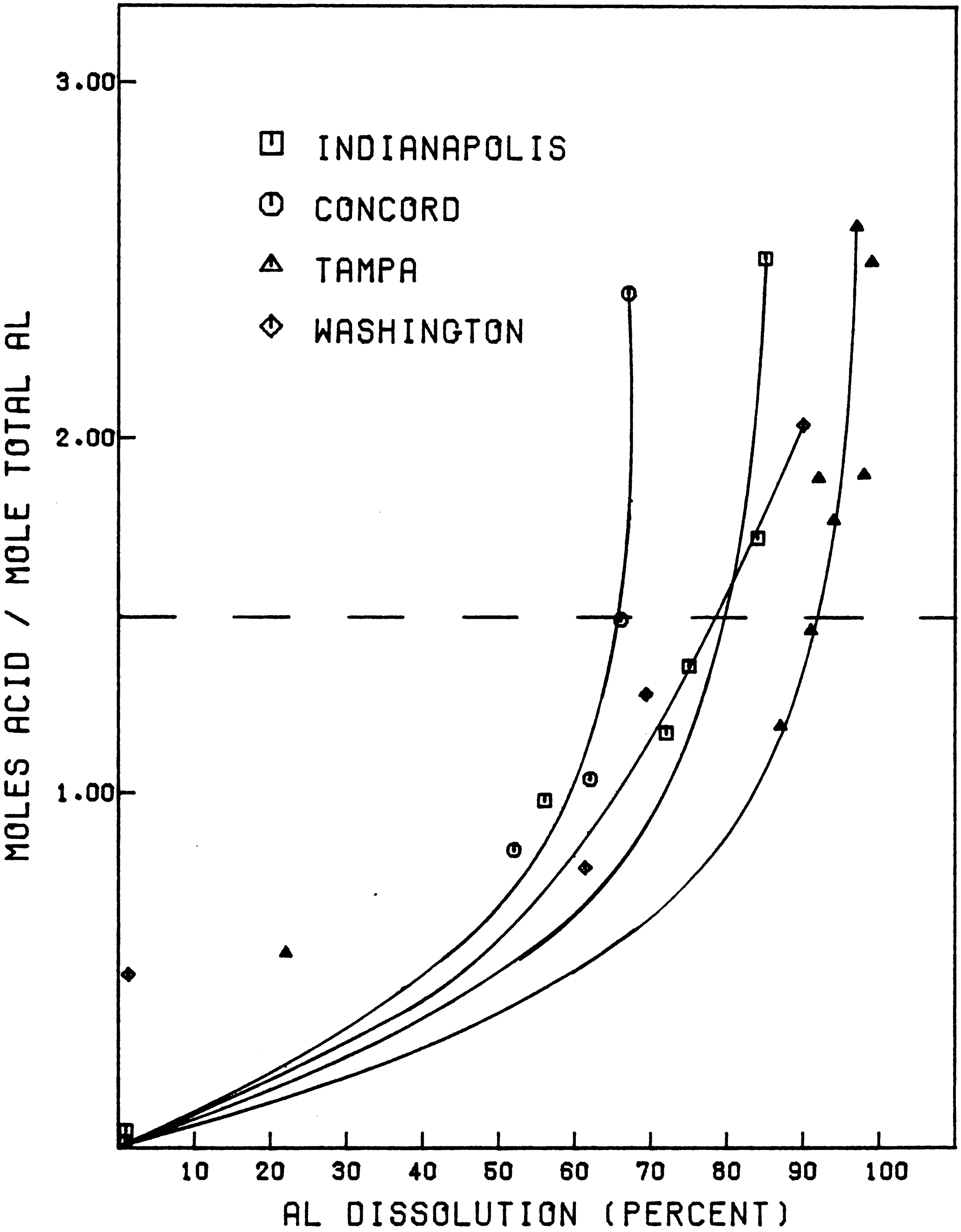
This equation had a correlation coefficient of 0.81.

7-2-2 Acid Demand

Sulfuric acid costs will be one of the largest expenses for this portion of the recovery system. Acid requirements for a particular plant can be estimated by first determining the total aluminum in the sludge. In Figure 7-2, the molar ratio of sulfuric acid to total aluminum in the sludge is plotted. After an H_2SO_4 : total Al^{3+} molar ratio of 1.5:1 (or 3 equivalents of acid) is reached, there is little improvement in aluminum dissolution. For these sludges it would not appear to be economical to operate above the 1.5:1 ratio. The acid demand corresponds to approximately 0.5 pounds of sulfuric acid per pound of alum.

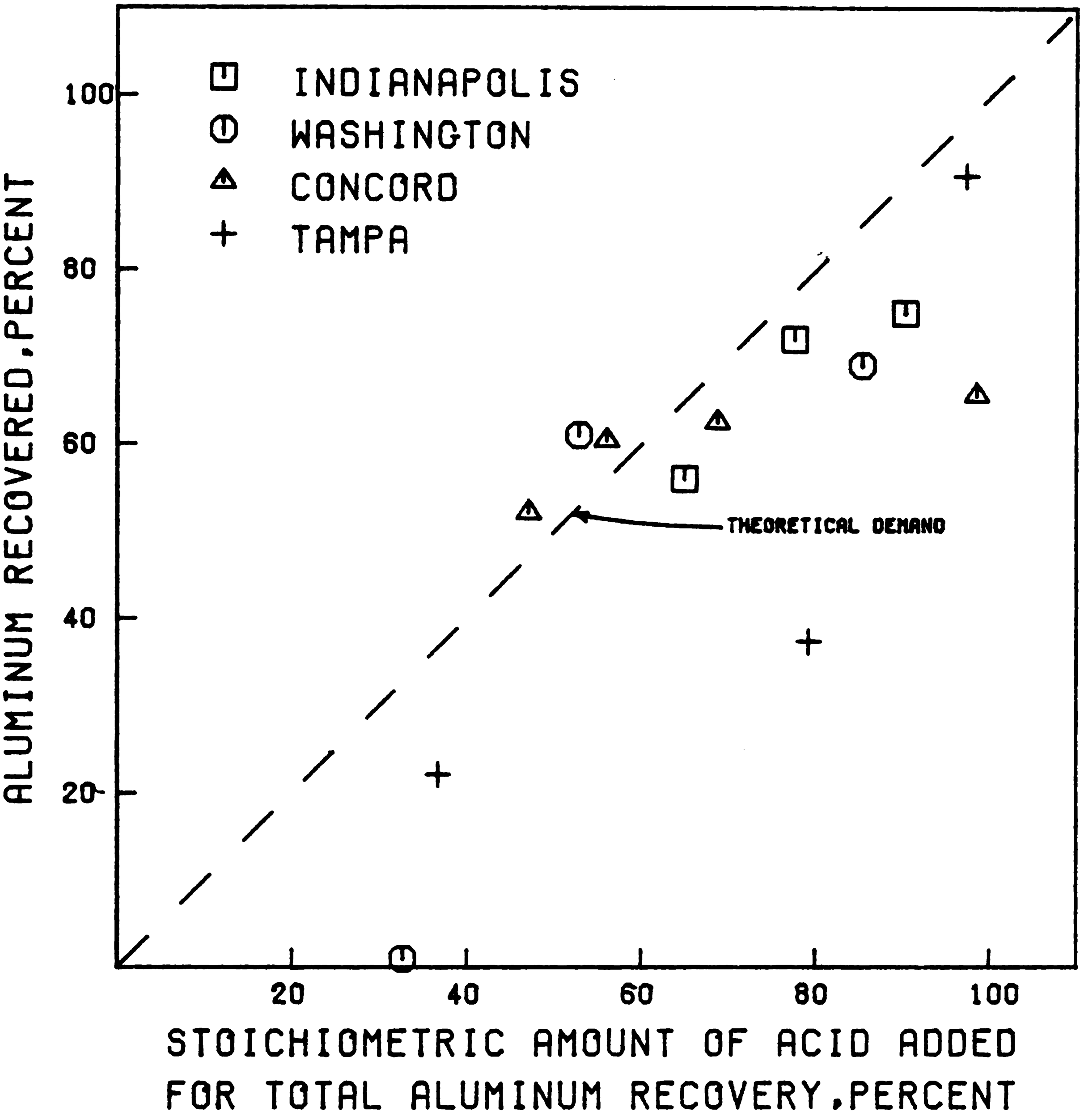
The 1.5:1 molar ratio of acid to total aluminum also corresponds to the theoretical requirements based on the stoichiometry of alum recovery. In Figure 7-3, data collected during this study are plotted with the theoretical acid requirements. The data reported represent those values for pH 2 or above. Below pH 2 (i.e. pH 1) acid demand ranged from 72% (Tampa) to 35% (Washington) above theoretical.

7-2 Acid Demand as a Function of Aluminum Dissolution



3.00
2.00
1.00
□ INDIANAPOLIS
○ CONCORD
△ TAMPA
◇ WASHINGTON
MOLES ACID / MOLE TOTAL AL
10
20
30
40
50
60
70
80
90
100
AL DISSOLUTION (PERCENT)

Figure 7-3 Percent Aluminum Recovered as a Function of Amount of Sulfuric Acid Added


INDIANAPOLIS
WASHINGTON
CONCORD
TAMPA
THEORETICAL DEMAND
ALUMINUM RECOVERED, PERCENT
100
80
60
40
20
20
40
60
80
100
STOICHIOMETRIC AMOUNT OF ACID ADDED FOR TOTAL ALUMINUM RECOVERY, PERCENT

Because of the large quantity of lime ($CaCO_3$) present in the Moline sludge, acid requirements were much higher than theoretical predictions. Acid requirements for the Moline sludge are given in Table 7-2.

7-2-3 Kinetic Studies

The previous data presented were based on equilibrium studies. Kinetics studies indicated that equilibrium was obtained after about 20 minutes of mixing. Results of the mixing tests conducted on the Tampa and Indianapolis sludges (which behaved essentially the same) are shown in Figure 7-4.

7-2-4 Solids Concentration Reduction

Reduction in solids concentration varied depending on the sludge. As shown in Figure 7-5, acidification reduced the Tampa solids concentration by 90%. Reducing the pH of the other sludges shown gave solids reductions of between 30% and 40%. The Moline sludge, due to its high lime content, showed little reduction in solids concentration (less than 1% at maximum aluminum dissolution). Except for Indianapolis, no further solids reduction occured by lowering the pH beyond the point of maximum aluminum dissolution.

7-2-5 Settling Characteristics

Prior to acidification, little settling occured in any of the sludge samples. After acidifying the samples,

TABLE 7-2

Acid Demand of the Moline Sludge

pH	Al dissolution, %	Moles acid/mole total Al
1	91.5	25.93
2	67.8	18.48
2.5	66.1	16.29
3	64.4	15.10
3.5	61.0	14.46
4	52.5	13.50

Figure 7-4 Kinetic Test Results for Aluminum Dissolution

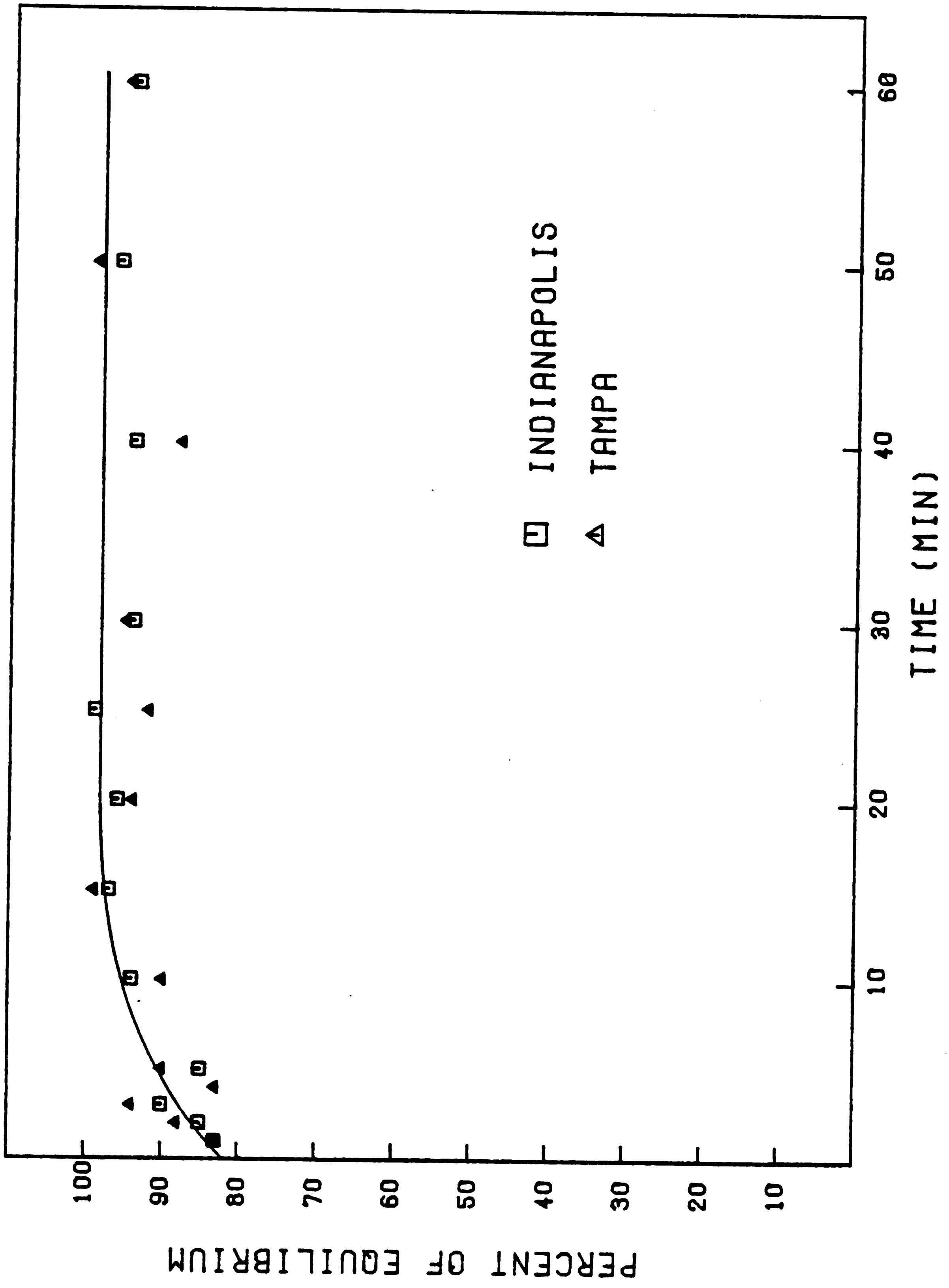
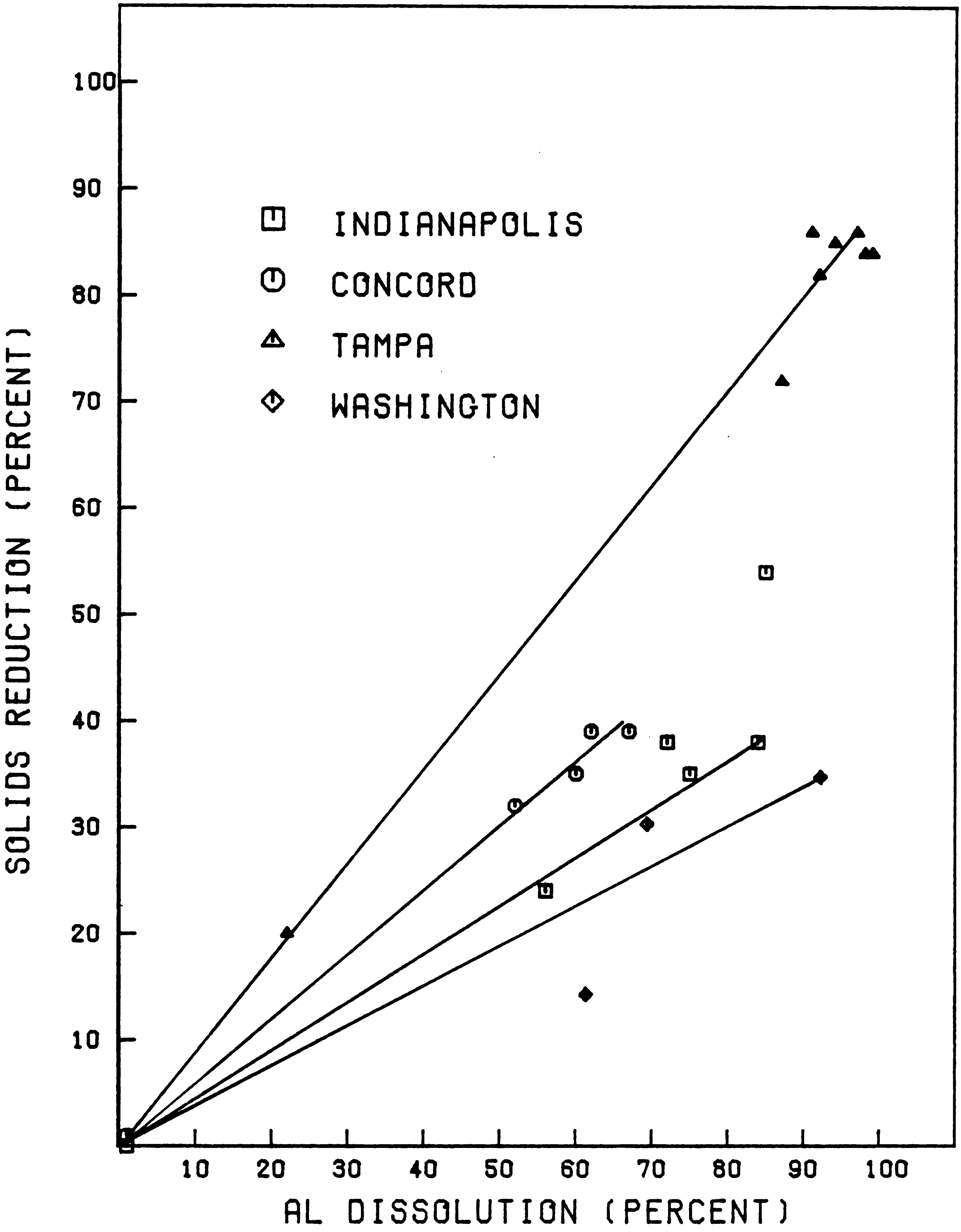

PERCENT OF EQUILIBRIUM
100
90
80
70
60
50
40
30
20
10
TIME (MIN)
10
20
30
40
50
60
□ INDIANAPOLIS
△ TAMPA

Figure 7-5 Relationship Between Solids Concentration Reduction and Aluminum Dissolution



INDIANAPOLIS
CONCORD
TAMPA
WASHINGTON
SOLIDS REDUCTION (PERCENT)
AL DISSOLUTION (PERCENT)
10
20
30
40
50
60
70
80
90
100

dramatic improvements in settling were made. This was true in all cases except for the Moline and Washington samples. Because of its high lime content, the Moline sludge settled essentially the same both prior to acidification and at all pH′s. The Washington sample was thickened to near the maximum amount possible prior to acidification. Lowering the pH of this sample did little to improve its settling characteristics

Zone settling curves for the Concord sludge, at various pH′s are shown in Figure 7-6. Similar improvements were realized for the Tampa and Indianapolis samples, however the latter two sludges did not exhibit zone settling characteristics due to their lower solids concentration. Therefore, sludge zone interfacial height after 2 hours of settling was plotted against pH in Figures 7-7 and 7-8.

As shown in Figure 7-9, the ultimate settled volume reduction was not proportional to aluminum dissolution. Unlike suspended solids reductions, all these samples exhibited approximately the same volume reduction at their maximum aluminum dissolution. Approximately 80°/₀ sludge volume reduction could be expected for each of these sludges with alum recovery. To obtain maximum settling, what appeared to be important was that all of the readily dissolvable aluminum be dissolved.

Figure 7-6 Zone Settling Curves for Concord Sludge

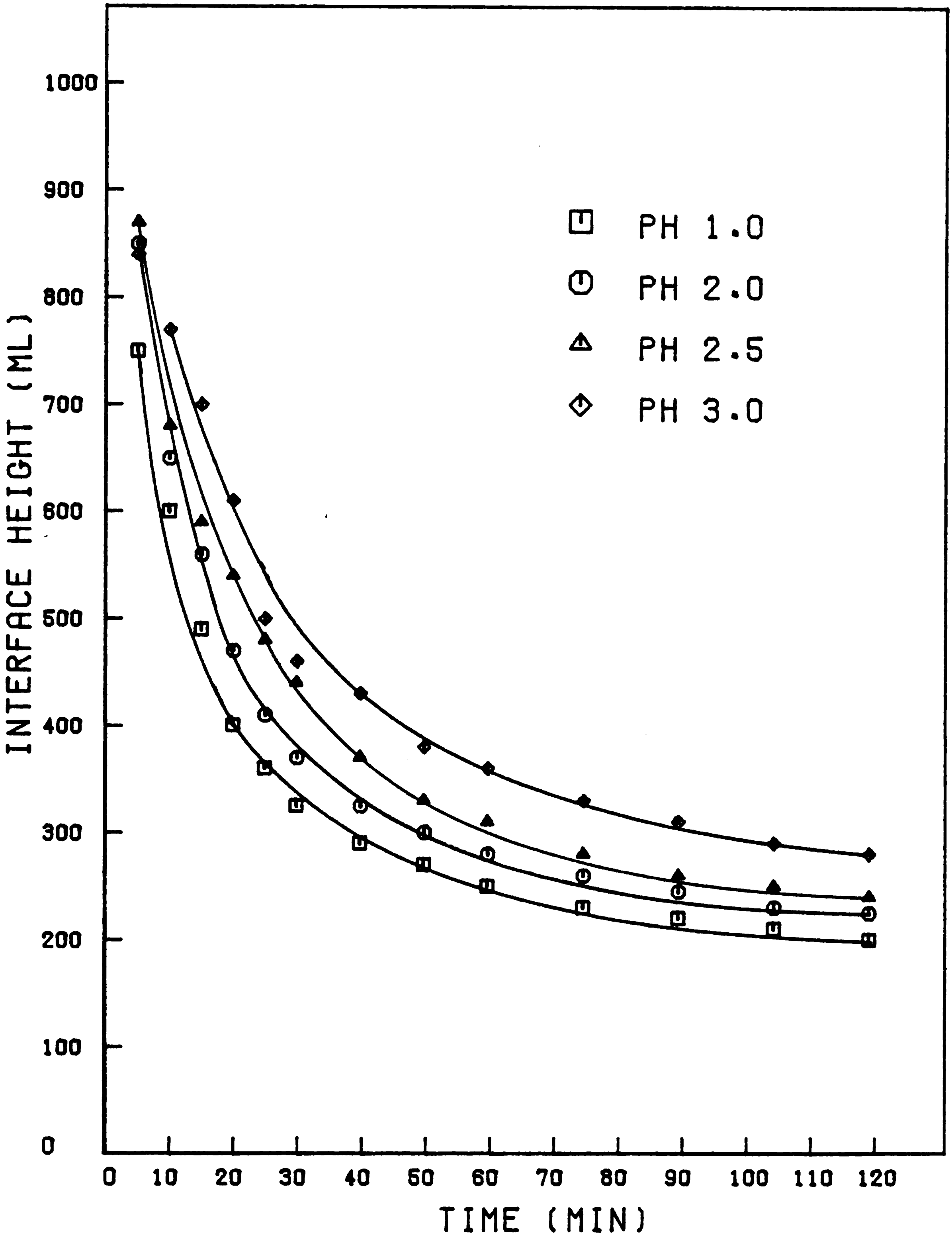

□ PH 1.0
○ PH 2.0
△ PH 2.5
◇ PH 3.0
INTERFACE HEIGHT (ML)
0
100
200
300
400
500
600
700
800
900
1000
TIME (MIN)
0
10
20
30
40
50
60
70
80
90
100
110
120

Figure 7-7 Settled Height as a Function of pH for Indianapolis Sludge

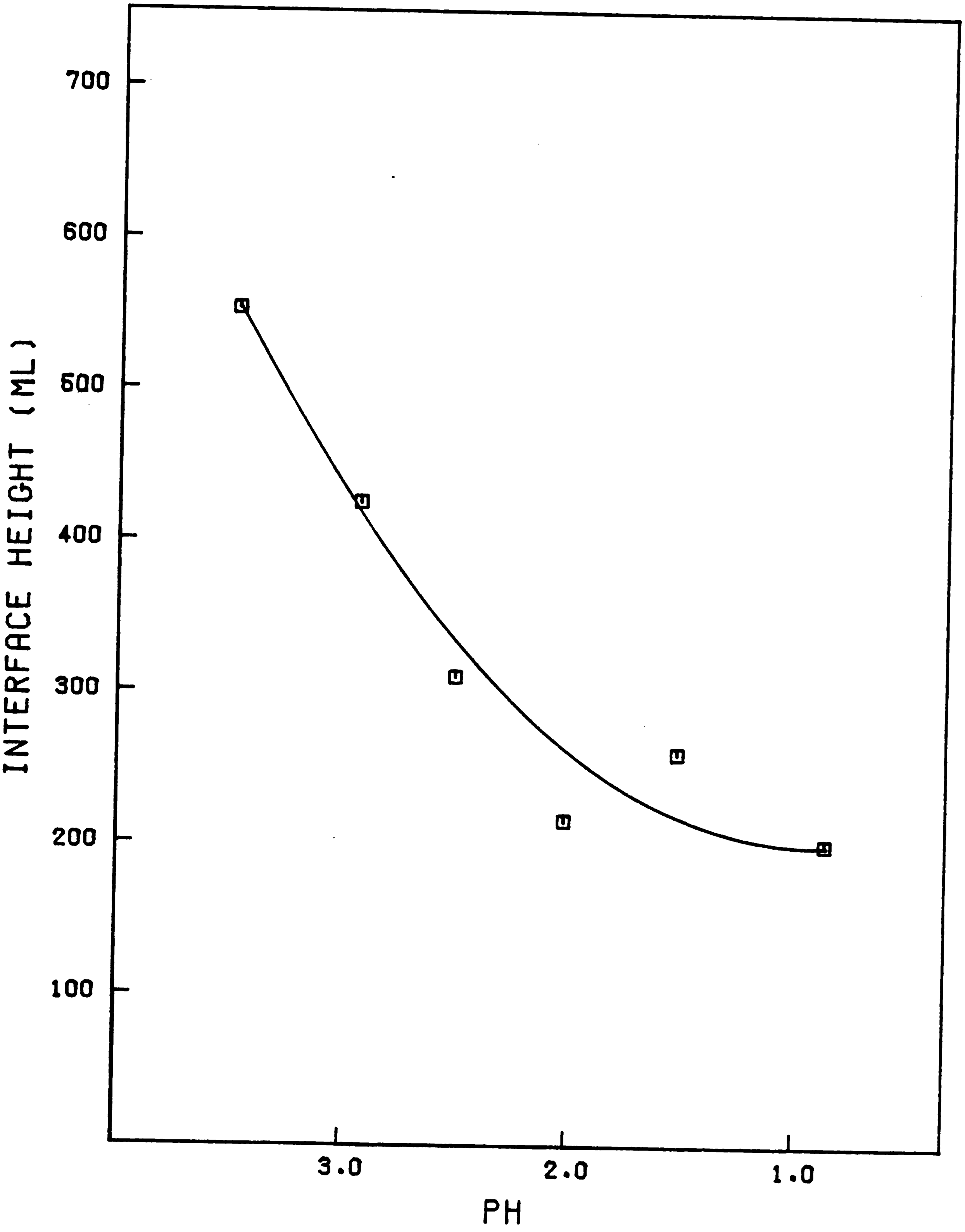

INTERFACE HEIGHT (ML)
700
600
500
400
300
200
100
3.0
2.0
1.0
PH

Figure 7-8 Settled Height as a Function of pH for Tampa Sludge

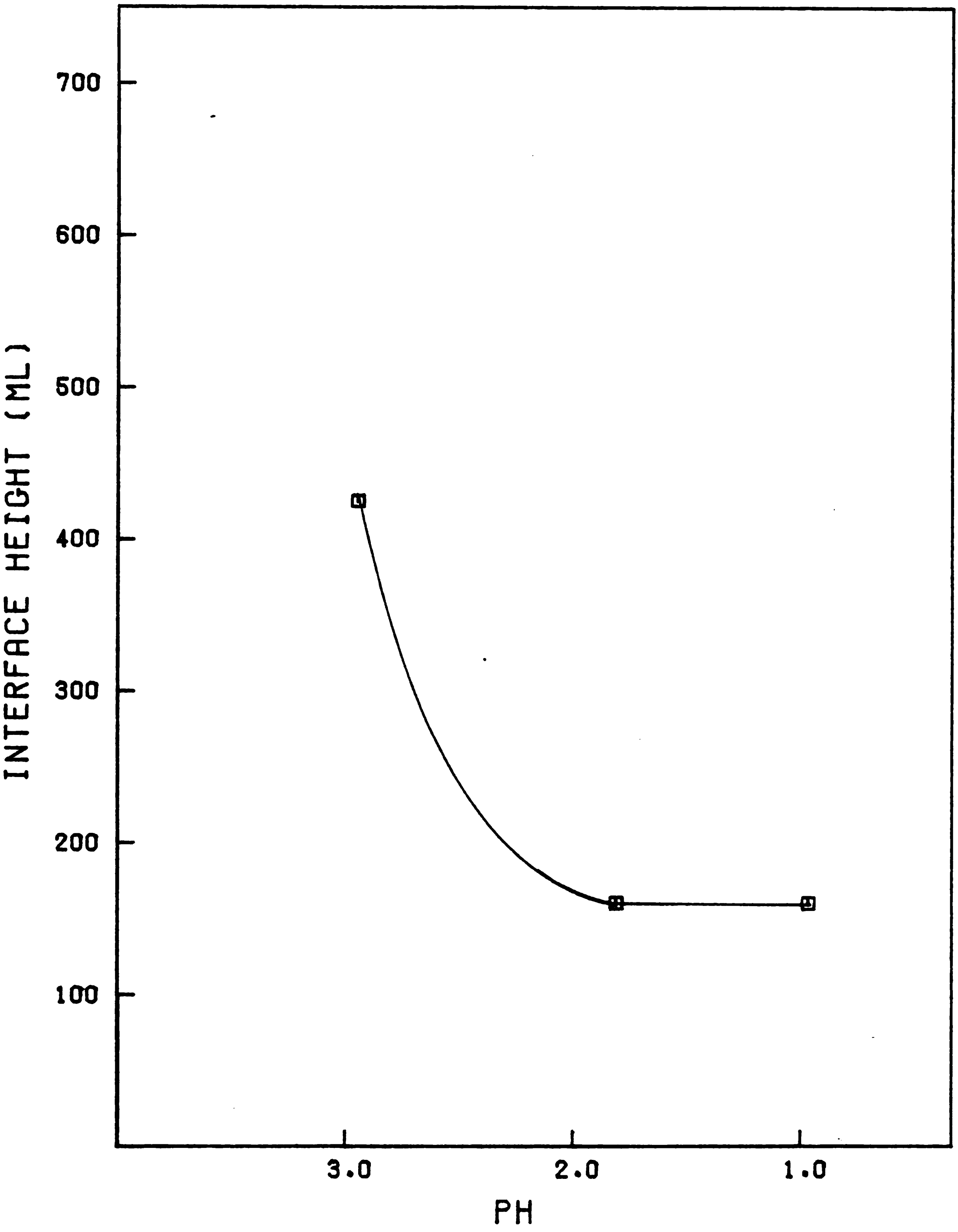
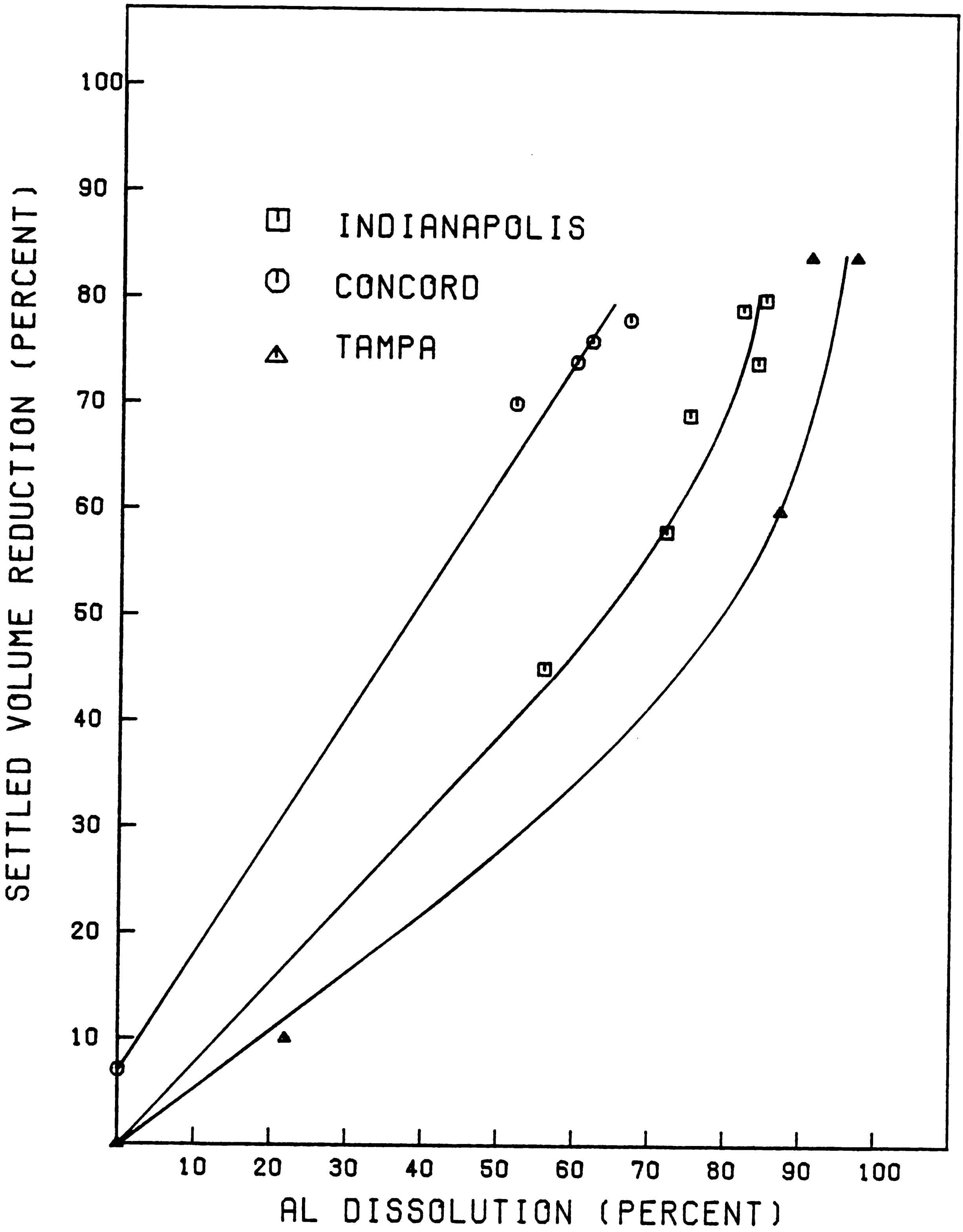

INTERFACE HEIGHT (ML)
700
600
500
400
300
200
100
3.0
2.0
1.0
PH

Figure 7-9 Relationship Between Settled Volume Reduction and Aluminum Dissolution


INDIANAPOLIS
CONCORD
TAMPA
SETTLED VOLUME REDUCTION (PERCENT)
AL DISSOLUTION (PERCENT)
10
20
30
40
50
60
70
80
90
100
10
20
30
40
50
60
70
80
90
100

7-2-6 Polymers

Though acidification improved settling characteristics of the sludges studied, further improvements were attempted through the use of polymers and activated silica. In general, neither polymers nor activated silica produced any marked improvements in settling the acidified sludge. Results of several polymers tested on pH 2 Indianapolis sludge are given in Table 7-3. These results were based on polymer doses of 0.7 mg/l. Nonionic and anionic polymers produced better results on the acidified sludge than did cationic polymers. Larger doses of nonionic polymer up to 30 mg/l showed an improvement of only 9$^{o}/_{o}$ over untreated pH 2 Tampa sludge. Activated silica had no effect on settling.

7-2-7 Contamination

As noted in the literature review presented earlier, one problem with reported alum recovery systems is the buildup of contaminants in the recovered alum (supernatant of the acidified sludge). Many researchers have reported that color, manganese, and other substances dissolve along with aluminum upon acidification. Visual inspection of all samples after acidification showed that large quantities of color dissolved at all pH's. Tests performed on the Tampa sludge verified that at pH 2, all of the manganese (6.2 mg/l) present in the alum sludge was dissolved and present in the supernatant. Tests for iron were not performed but similar results as those for manganese would be expected.

TABLE 7-3

Effects of Polymers on Indianapolis Sludge, pH 2.0

Sample	Volume Reduction, %	Solids Concentration, %
Untreated	66	2.13
Nonionic	72	2.58
Low anionic	69	2.33
Medium anionic	68	2.26
Medium high anionic	67	2.19
Medium cationic	66	2.13

Note: based on polymer dose of 0.7 mg/l.

7-2-8 Neutralization

In order to properly dispose of the settled solids after acidification and the supernatant after aluminum recovery, a final pH of about 6.0 is required. Landfills will not usually accept low pH wastes. In order to make these wastes acceptable for ultimate disposal, lime in the form of calcium hydroxide [$Ca(OH)_2(s)$] was added. The supernatant, after aluminum recovery, required 23.1 g/l of calcium hydroxide or 18.0 g/l of CaO for neutralization. Settled solids after acidification had a lime demand of 24.9 g/l as CaO (Table 7-4). As a result of the lime addition to the supernatant, the solids concentration increased from a negligible amount to 6.3% due to the formation of calcium sulfate ($CaSO_4 \cdot 2H_2O$).

Neutralization may also be accomplished using lime softening sludge. Thickened softening sludge with a solids content of 56.1% from the East Lansing Water Treatment Plant was used for neutralization. Approximately 89.5 g/l (wet weight) was required to raise the pH of the supernatant from 0.7 to 6.0. After neutralization, the solids concentration of the sample increased to about 4.8%.

TABLE 7-4

Waste Neutralization

Sample	Initial pH	Final pH	Lime Added g/l as CaO
Setttled Solids	2.0	6.5	24.9
Supernatant	0.7	6.0	18.0

CHAPTER 8

PROPOSED RECOVERY SYSTEM

8-1 Introduction

A summary of results obtained from sludge testing will be presented along with a flow diagram of the proposed recovery system based on results obtained from evaluation of the Tampa sludge. Included is a brief explanation of aluminum recovery with liquid-ion exchange.

8-2 Summary of the Results

1. Based on the survey, the following equation was developed using regression analysis to relate raw water parameters to alum dose:

   $X = 8.970 - 0.233Y + 0.767Z$

   where: X = alum dose, mg/l

   Y = turbidity, JTU

   Z = color, Pt-Co units

2. Average cost for liquid alum was found to be \$85.62/ton. On the average, solid alum cost \$142.94/ton.

3. Twenty percent of the plants responding to the survey were still returning alum sludge to a waterway.

4. At a pH of 1, aluminum dissolution in the alum sludges tested ranged from 65°/o for Concord to 99°/o for Tampa.

5. Aluminum dissolution was found to be related to raw water color by the following regression equation:

   $X = 73.049 + 0.287Y$

   where: X = aluminum dissolution, %

   Y = raw water color, Pt-Co units

6. Acid costs may be estimated for a particular plant by knowing the total aluminum in the sludge. To obtain close to maximum dissolution, a 1.5:1 molar ratio of slufuric acid to Al^{3+} is required (approximately 0.5 lb H_2SO_4/lb Alum).

7. Kinetics studies indicated that acidified sludge required between 10 and 20 minutes of mixing to obtain maximum aluminum dissolution.

8. At a pH of 1, suspended solids reductions ranged from 35% to 90%.

9. After acidification, sludge settling improved dramatically. Independent of the maximum amount of aluminum dissolution, ultimate settled sludge volume was reduced by 80% after maximum aluminum dissolution was achieved.

10. Polymers and activated silica had little or no effect on improving settling characteristics of the acidified sludge.

11. Upon acidification, large amounts of color and manganese in the sludge are dissolved along with aluminum.

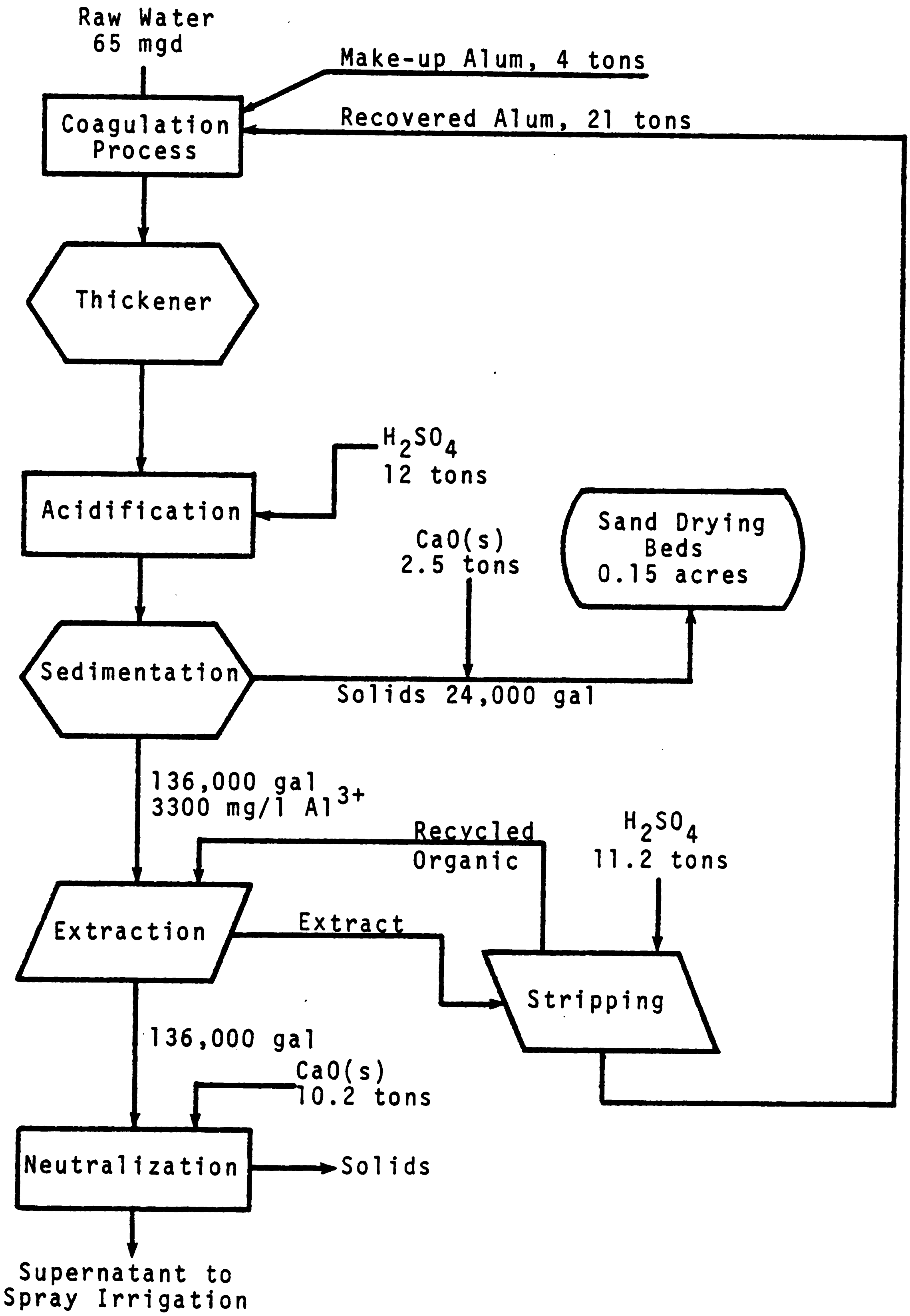
12. To be acceptable for ultimate disposal, 24.9 g/l and 18.0 g/l of lime as CaO are required to raise the pH of the settled solids and supernatant respectively, to a pH of about 6.0

8-3 Alum Recovery with Liquid-Ion Exchange

As noted previously during the literature review (Chapter 4) the problem in alum recovery is potential contamination of the recovered alum from color, manganese, iron and heavy metals. Tests (Chapter 7) showed that color and manganese do indeed dissolve during acidification. The proposed alum recovery system for which the research discussed in this thesis was done, utilizes a liquid-ion exchange procedure to recover aluminum from acidified sludge. The objective of using liquid-ion exchange is to purify and concentrate the recovered alum.

The basic flow diagram under which the process may be operated for a 65 mgd plant along with flow volumes and chemical requirements is shown in Figure 8-1. All values are based on results of tests performed on the Tampa sludge sample. The first step in the process is to dissolve the settled or thickened (in this case thickened) alum sludge by acidifying with concentrated H_2SO_4. The sludge flow of 160,000 gpd (11.35 tons dry solids/day) which results would require about 12 tons of acid per day. The supernatant would then be separated from the residual solids by either sedimentation, filtration or centrifugation. Though sedimentation would be the most economical method for separation, filtration or centrifugation would allow for more aluminum recovery and a greater residual solids concentration. For the system being discussed, a 15% loss of aluminum would occur during sedimentation. The low pH solids would then be neutralized with lime (or otherwise conditioned) for ultimate disposal, in this case via

Figure 8-1 Flow Diagram for Proposed Alum Recovery System


Raw Water
65 mgd
Make-up Alum, 4 tons
Recovered Alum, 21 tons
Coagulation Process
Thickener
H_2SO_4
12 tons
Acidification
CaO(s)
2.5 tons
Sand Drying Beds
0.15 acres
Sedimentation
Solids 24,000 gal
136,000 gal
3300 mg/l Al^{3+}
Recycled Organic
H_2SO_4
11.2 tons
Extraction
Extract
Stripping
136,000 gal
CaO(s)
10.2 tons
Neutralization
Solids
Supernatant to Spray Irrigation

sand-drying beds (at a loading rate of 3.7 gpd/ft^2). Approximately 2.5 tons/day of CaO would be necessasy for neutralization. The supernatant, containing aluminum and potential impurities, flows to the extraction stage.

The extraction process uses a liquid extraction procedure for separating the aluminum from any contaminants in the dissolved sludge. The procedure is often referred to as liquid-ion exchange in that it is analogous to resin-ion exchange processes. Rather than the aqueous aluminum being exchanged for Na^+ of H^+ onto a solid resin, the aqueous aluminum is exchanged for a cation in another liquid, the second liquid being organic. In such operations the solution which contains the solute to be extracted is called the solvent. The solvent employed has the properties of being completely immiscible in water so that there are two distinct liquid phases, similar to the solid-liquid phases in resin-ion exchange. The process of transferring the solute, in this case aluminum, from the feed into the solvent is called extraction. The solute-rich solvent product is called the extract, and the residual feed from which the solute has been removed is called the raffinate. It is often desired to extract one substance from the feed while leaving the others behind, hence the term selective extraction. Extraction is performed in two countercurrent stages. After extraction, the aqueous, low pH, aluminum free supernatant is mixed with lime to raise the pH for ultimate disposal. Approximately 10.2 tons/day of CaO would be required to raise the pH to about 6.0. As a result of the lime addition, solids increased to approximately $6.3^{9}/_{9}$. Settled solids from this neutralization step would then go to sand-drying beds while the supernatant would be used for spray irragation.

After the aluminum is removed from the aqueous phase, the extract is "regenerated" by contact with sulfuric acid. During "regeneration" (referred to as stripping) the aluminum leaves the extract and exchanges for the protons in the acid, resulting in recovered aluminum sulfate and regenerated solvent. About 11.2 tons/day of H_2SO_4 is required during the two stage stripping operation. After stripping the organic solvent is recycled back for further extraction and the recovered alum is sent back to the beginning of the plant for further coagulation.

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