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QUALITY OF PRODUCTS AND WASTE STREAMS PRODUCED
IN THE LIQUID-ION EXCHANGE ALUM RECOVERY PROCESS

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John Michael Przybyla

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David A Cornwell
Major professor

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QUALITY OF PRODUCTS AND WASTE STREAMS PRODUCED IN THE LIQUID-ION EXCHANGE ALUM RECOVERY PROCESS

By

John Michael Przybyla

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ABSTRACT

QUALITY OF PRODCUTS AND WASTE STREAMS PRODUCED IN THE LIQUID-ION EXCHANGE ALUM RECOVERY PROCESS

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The exit streams from the liquid-ion exchange alum recovery process were characterized, and treatment/disposal methods were analyzed.

Alum sludges from Tampa, Florida and Sharon, Pennsylvania were examined in the laboratory for suspended solids reduction upon acidification to pH 2.0, and were tested in the liquid-ion exchange alum recovery process. The results showed that the reduction of suspended solids in the alum recovery process was the same as that predicted by acidification of sludge.

A liquid-ion exchange alum recovery pilot plant was operated in Tampa. Results from the pilot plant showed that the neutralized settled raffinate contained less than 50 mg/l suspended solids. Results using the mixer/settler and rotating bucket extractors showed solvent losses to be 2.0 and 1.1 gallons per 1000 gallons of sludge feed, respectively. The recovered alum produced by the process was found to be equal in quality to commercial alum.

ACKNOWLEDGEMENTS

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INTRODUCTION

1.1 Alum Water Treatment

In the treatment of water supplies for drinking purposes, a number of chemicals are used. Aluminum sulfate, or alum, is used to treat surface waters for the coagulation and removal of colloidal suspensions that cause turbidity and color in water. Alum is the most widely used coagulant in the water treatment industry. The waste product of the coagulation process is alum sludge. Alum sludge is composed of water, organic solids, inorganic solids, and aluminum hydroxide.

1.2 Alum Sludge Disposal

Alum sludge leaving the sedimentation basin generally has a suspended solids concentration of 0.5 to 3.0%, the remainder being water. Because of the hydrous nature of the sludge, separating the water from the solids is extremely difficult and expensive. It has been estimated that 2.7 million tons (1) of dry solids are produced by the water treatment industry each year, a substantial portion of that being alum sludge.

In the past, much of the alum sludge was returned to the waterway. Since the passage of the Water Pollution Control Act Amendments of 1972, the emphasis on cleaning up the discharge of alum sludge has increased. Water treatment has been required to meet discharge control standards in the same manner as other industries, and to achieve zero discharge by 1985.

Treatment of alum sludge to meet the requirements of the Water Pollution Control Act has become a major concern of the water treatment industry. The goals of alum sludge treatment are: 1) to dewater the solids so they can be disposed of in a landfill, and 2) to produce a liquid fraction that can be returned to the waterway without violating discharge requirements.

A number of methods exist for treatment of alum sludge, including mechanical and non-mechanical forms of dewatering. The most popular non-mechinical treatment methods are lagooning, sand drying, and disposal to wastewater treatment plants. The first two methods require large tracts of land near the treatment plant. In many areas, these are not available. Disposal to a wastewater treatment plant requires the availability of a sewer system able to handle the sludge, and the willingness of the sewage treatment plant to accept the sludge. Mechanical dewatering methods can be used to treat the sludge on-site, but they are expensive to construct and operate.

1.3 Introduction To Research

Water treatment plants using alum that cannot use non-mechanical sludge disposal methods are, at present, forced to turn to more costly mechanical treatment methods. The liquid-ion exchange alum recovery process is a possible alternative to mechanical dewatering of sludge. The process recovers the aluminum from the sludge for reuse as a coagulant. Removal of the aluminum from the sludge aids in solids concentration and dewatering. Research on the process has been conducted on bench scale units, and on pilot scale units. The use of conventional mixer/settler equipment and the rotating bucket contactor unit were both investigated.

1.4 Research Objectives

Research on liquid-ion exchange alum recovery has been divided into two sections, 1) optimization of operational parameters, and 2) treatment and disposal (or use) of the exit streams from the process. This thesis will be concerned with the second area of study: process products and waste streams. The basic purpose of this research was to characterize the exit streams from the alum recovery process, and to investigate possible treatment/disposal options for the waste products.

CHAPTER 2

ALUM SLUDGE

2.1 Alum as a Coagulant

Coagulation is a process used in water treatment to remove color, turbidity and other colloidal matter from water. Colloidal particles are too small and stable to settle out in a normal settler. The addition of a coagulant to the water helps to destabilize the colloidal material to allow it to settle. The major mechanism of destabilization is the reduction of the charge layer on the colloid which allows colloids to flocculate together and settle out. A number of other destabilization mechanisms also take place during coagulation.

Commercial alum can be used in liquid or solid form, the liquid being preferred, because of its ease of use, except in small plants. Alum is produced by reacting sulfuric acid with ground bauxite or bauxite clay to produce a solution of about 10% as Al_2O_3. The reaction is;

$$Al_2O_3(s) + 3H_2SO_4 + 11H_2O \rightarrow Al_2(SO_4)_3 \cdot 14H_2O \qquad (2\text{-}1)$$

The solution is adjusted to 8.3% as Al_2O_3 for liquid alum, or evaporated to 17% as Al_2O_3 for the solid form. Commercial alum has a molecular weight of about 594, and contains about 60,000 mg/l as aluminum.

The reactions of alum with water are complex, leading to the formation of insoluble aluminum hydroxide species. The simplified reaction of alum with water with alkalinity present is:

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

After all the alkalinity has reacted, the reaction is:

$$Al_2(SO_4)_3 \cdot 14H_2O \rightarrow 2Al(OH)_3(s) + 3H_2SO_4 + 8H_2O \qquad (2\text{-}3)$$

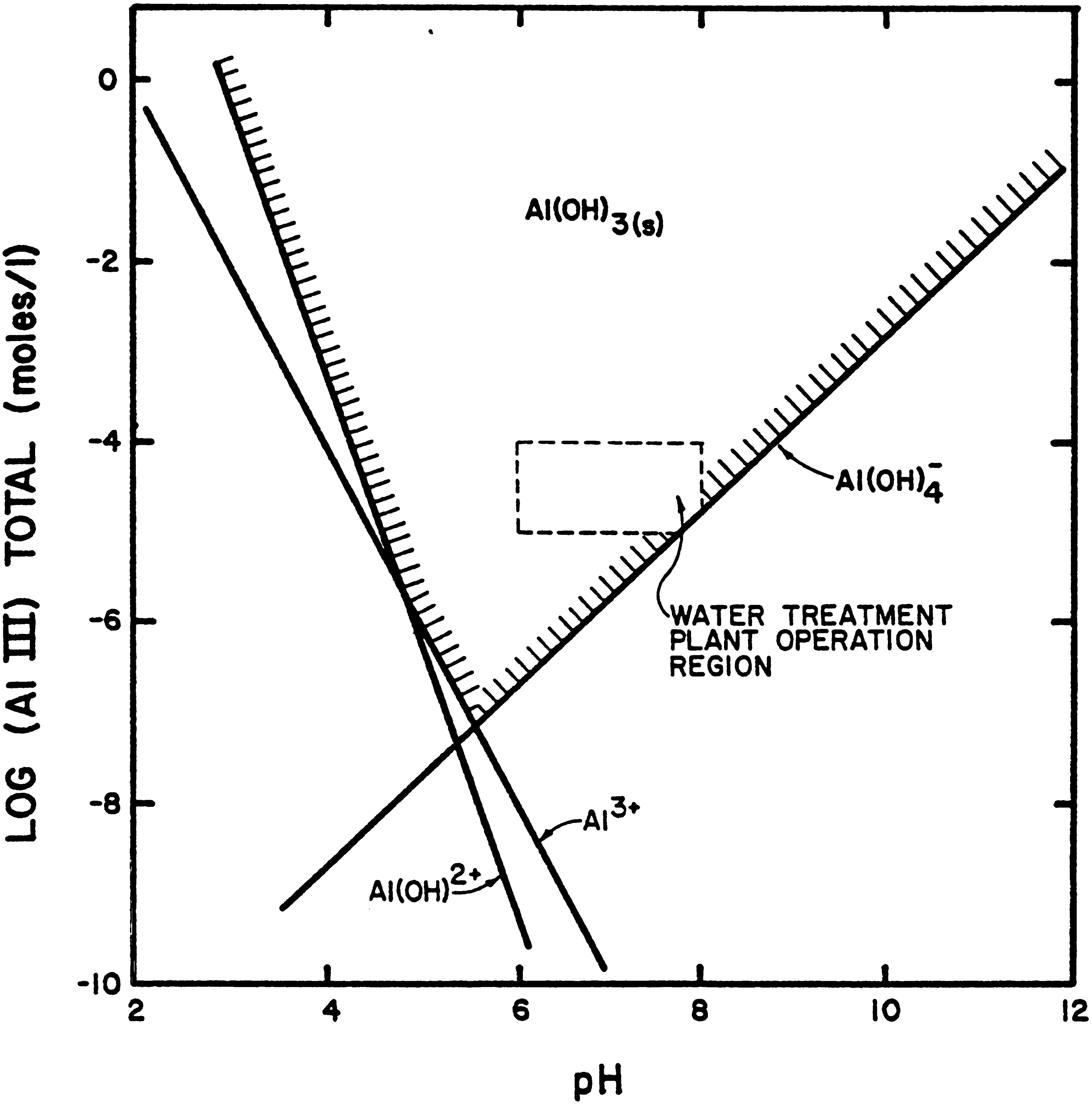
The addition of alum to water lowers the pH of the water, due to the change of the carbonate distribution and the formation of sulfuric acid.

2.2 Alum Sludge Chemistry

The reactions of alum with water are considerably more complex than those shown above, resulting in the formation of a number of insoluble forms of aluminum hydroxide. Figure 2-1 shows a solubility diagram for the precipitation of aluminum hydroxide. Aluminum hydroxide, $Al(OH)_3$, is the predominant species which would exist under equilibrium conditions. In the treatment process, however, equilibrium conditions do not exist, and a number of positively charged ions are formed, such as $Al_7(OH)_{17}^{+3}$. These large positively charged forms have 3 to 4 moles of water chemically bound to the aluminum hydroxide precipitate, which cannot be removed by typical dewatering methods (2). In addition to chemically bound water, there is also a significant amount of water which is absorbed onto the solids and is difficult to dewater. Because the water is so tightly bound with the aluminum and solids, alum sludge is the most difficult of the water treatment sludges to dewater.

2.3 Alum Sludge Characteristics

Alum is used to coagulate waters of varying quality, and the resulting alum sludges vary greatly. Some characteristics of alum sludges, as reported in the literature, are given in Table 2-1. Alum sludge generally has a suspended solids content of under 2%; often the solids content is much lower. Twenty to forty percent of the solids are organic in nature, the remainder are inorganic clays or silts. The BOD_5 (Biochemical Oxygen Demand, a measure of biodegradeability), of alum sludge is usually



Source: Chen, B.H.H., Ph.D. Dissertation, September, 1973, Blacksburg, Virginia.

FIGURE 2-1

SOLUBILITY DIAGRAM FOR ALUMINUM

TABLE 2-1

CHARACTERISTICS OF ALUM SLUDGE

Location	Water Source	Suspended Solids (percent)	BOD_5 (mg/l)	COD (mg/l)	Specific Resistance (m/kg)	Reference
General	-	0.3-1.5	30-100	500-10,000		3
General	-	0.2-2.0		30-5,000	$20x10^{12}$	4
Milwaukee	Lake	0.78			$5x10^{12}$	3
Auburn,Ala.		0.19			$5.5x10^{12}$	5
		0.59			$55x10^{12}$	
Rochester,NY	Lake	0.36	36-77	500-1000		6
San Fran Bay	Reservoir	1.0	100	2300		7
Erie County	Lake	0.16				8
Moberly,Mo.	Reservoir				$16x10^{12}$	9
Unknown	-	0.6-1.5			$3.0x10^{12}$	10
					$40x10^{12}$	
Radford,Va.	River	3.0			$1.6x10^{12}$	11
Timersville,Va.	River	1.4			$5.4x10^{12}$	11
Harrisonburg,Va.	River	2.1			$3.6x10^{12}$	11
Blacksburg,Va.	River	3.1			$4.1x10^{12}$	11

$s^2/g \ X \ 9.8 \ X \ 10^3 = m/kg$

under 100 mg/l. However, the COD (Chemical Oxygen Demand) of the sludge is considerably higher, which shows that the sludge can be chemically oxidized. The pH of alum sludge is generally in the 5.5 - 7.5 range. Alum sludge coming from sedimentation basins may include large numbers of microorganisms, but the sludge generally does not possess an unpleasant odor.

Table 2-1 also shows the results of specific resistance tests performed by other researchers. Specific resistance is used when making decisions about dewatering of sludge. Although the specific resistance results shown in Table 2-1 were taken under widely varying conditions, they all show that alum sludge does not dewater well. Calkins and Novak (9) have stated that sludges with a specific resistance greater than 1-10 X 10^{12} m/kg (1 to 10 X 10^9 s^2/g) filter poorly.

2.4 Sludge Treatment and Disposal Methods

Techniques for the treatment and disposal of alum sludge can be divided into two general categories, non-mechanical treatment, and mechanical dewatering. The non-mechanical methods generally require large tracts of land and, as a result, are not feasible for many plants. Mechanical methods are expensive, but they all produce a reasonably dry product which is suitable for ultimate disposal.

One disposal method which does not fit in either category above is disposal of the alum sludge to a wastewater treatment plant, often called co-disposal. The effect of alum sludge on the operation of an activated sludge treatment plant has been investigated by Salotto, Farrell and Dean (12). They concluded that disposal of alum sludge to a wastewater treatment plant would be preferable to dewatering at the treatment plant. However, problems with co-disposal make it unacceptable in many areas. Some sewage treatment plants refuse to accept alum sludge because of the high solids content of the sludge and the intermittent flow. Wastewater treatment plants that will treat alum sludges often charge high rates for accepting the sludge, and in some cases on-site treatment may be cheaper.

2.5 Non-Mechanical Methods

Many smaller plants use non-mechanical sludge dewatering techniques to treat alum sludge. The two major non-mechanical treatment methods are lagooning and sand drying. In northern locations, natural freezing of sludge is also an option.

The use of lagoons does not dewater sludge to any great extent. Sludge in lagoons will generally not thicken to over 10% suspended solids concentration (3), even over long periods of time. Many small plants with large tracts of land nearby use lagoons to hold the sludge, discharging the supernatant to the waterway. Eventually the lagoons fill up and other treatment methods must be found. Lagoons are also used along with other treatment methods to thicken sludge before further dewatering.

Sand drying beds can be used to dewater sludge in areas where the climate is favorable. Solids concentrations of up to 20% have been recorded by Neubauer (6) in bench scale tests. Chemical conditioning with polyelectrolytes is generally used to improve the dewatering of the sludge. Sand drying beds involve the use of large areas of land, and the collection and hauling of sludge is very labor intensive. Of course, in many areas of the country the weather conditions make alum sludge drying beds impractical.

2.6 Mechanical Methods

A number of mechanical dewatering devices have been tested for alum sludge treatment. Only three, centrifugation, vacuum filtration, and pressure filtration, have gained any degree of acceptance in the industry.

Two types of centrifuges have been used in water treatment for alum sludge dewatering, the basket centrifuge and the solid bowl centrifuge. Both types of centrifuges have the advantage of utilizing very little space. Centrifuges are, however, very sensitive to changes in feed flow rate or composition, and require considerable monitoring. Centrifuges are also very high maintenance items. Solid bowl centrifuges can produce solids concentrations of only 18% at most (3) (13), while concentrations of well over 30% (14) have been reported from basket centrifuges. Centrifuges, because of their high operating speeds, are probably the most difficult of the dewatering devices to operate and maintain, and as a result are not widely used in the water treatment industry.

Vacuum filters have been widely used for dewatering wastewater sludges for many years, but their application to water treatment is relatively recent. Rotary drum vacuum filters, used in conjunction with sludge conditioning, can dewater solids to concentrations of 20-35% (13). In many cases, however, vacuum filters are not practical for dewatering alum sludge because of its poor filterability. Extensive testing of conditioners to minimize the specific resistance of the sludge must be employed before choosing vacuum filtration for sludge dewatering. From the values presented in Table 2-1, it can be seen that many alum sludges are not suitable for vacuum filtration. As with the other mechanical dewatering devices, vacuum filters are very expensive items.

Filter presses have recently become important to the water treatment industry. By the end of 1976, five water treatment plants had pressure filters operating in this country, and four more facilities were planned (13). Filter presses can achieve total solids concentrations of 40-50% solids. To aid in filtration, a conditioner, usually lime, is added. This results in a high pH filtrate, which presents disposal problems. Filter presses also have the disadvantage that they are operated on a batch basis, necessitating sludge storage. They happen to be the most expensive of the mechanical devices to purchase, but generally require less maintenance than the others. For many plants, especially small ones, the high capital cost makes pressure filters undesirable.

2.7 Ultimate Disposal of Residues

With the exception of co-disposal to a wastewater treatment plant, none of the treatment methods mentioned above results in disposal of the sludge. Dewatering methods are employed only to put the sludge into a form where it can be easily disposed of. Attempts to use the sludge as a soil conditioner or soil stabilizer have met with little success (15). Currently, the only alternative for solids disposal is landfilling. In most cases, a solids content of 20-40% is required by landfill operators, although in some cases 15% (15) will be accepted. Because sanitary landfills are anaerobic systems operating in a pH range of 5.5 to 7.0, leaching of the aluminum may cause contamination of the groundwater. Because of this, some states have classified alum sludge as an industrial waste, limiting disposal to only a few secure landfills. In most states, sufficiently dewatered alum sludge is currently being disposed of in standard sanitary landfills without any apparent problems (15).

2.8 Government Legislation and Regulation

The Water Pollution Control Act Amendments of 1972 (PL 92-500) address alum sludge as an industrial discharge and required best practical control technology currently available by July 1, 1977, (BPCTCA), and best available technology economically achievable (BATEA), by July 1, 1983. A goal of zero discharge is set for 1985. The draft guidelines for the water treatment industry were published in 1975. The guidelines set discharge standards for pH and total suspended solids under BPCTCA, and recommended recycle of sludge supernatant (zero discharge) under BATEA. Because of delays associated with other projects, formal guidelines have not been promulgated. Effluent limitations are currently being set on a case by case basis by the states according to the National Pollutant Discharge Elimination System (NPDES).

NPDES regulations vary from state to state, and monitoring and enforcement programs are generally minimal or non-existent. The strictest guidelines generally used are a suspended solids concentration of 30 mg/l, and pH of 6.0 to 9.0. As a result of variation in regulations, there is a wide disparity in alum sludge disposal practices from state to state and even within states. Many plants still return sludge to the waterway. Other plants with inadequate lagoons or drying beds have no room for expansion. Disposal of alum sludge to sewage treatments is becoming increasingly expensive due to high surcharges assessed by the utility. For many water treatment facilities, the only alternative to meet BPCTCA requirements will be mechanical dewatering.

Disposal of the solids from alum sludge has also come under increasing federal requlation. Under the guidelines of the Solid Waste Disposal Act, PL 91-512, all landfills are recommended by the government to accept water plant sludges if the sludge contains no free moisture. The Resource Conservation and Recovery Act of 1976, PL 94-580, includes tough standards for landfilling of industrial wastes. Final regulations for hazardous waste criteria have not been proposed, but alum sludge, in light of the possibility of groundwater contamination, may be included as a hazardous waste. Regulations proposed in PL 94-580 will make disposal of hazardous wastes a difficult and extremely expensive undertaking.

CHAPTER 3

ALUM RECOVERY AND LIQUID-ION EXCHANGE

3.1 Previous Alum Recovery Research

The idea of recovering aluminum from alum sludge is not new. Alum recovery by lowering the pH level of sludges was first suggested early in this century. Insoluble aluminum hydroxide becomes soluble at both the low and high ends of the pH scale. Many other metals also dissolve at low and high pH levels. Roberts and Roddy (16) developed a sulfuric acid alum recovery system in Tampa, Florida in the late 1950's. They found that they had to depress the pH to 1.5 - 2.5, using approximately 1.5 moles sulfuric acid per mole of aluminum. (1.9 lb H_2SO_4 per lb $Al(OH)_3$). The reported reaction was:

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O \qquad (3\text{-}1)$$

In other research, Albrecht (3), Fulton (17), Chen, et al. (11), and Westerhoff (13), showed that carryover of impurities into the recovered alum was not a problem, and that the alum worked well as a coagulant. Researchers generally achieved aluminum recoveries of 75 to 95% at pH 2.0. In most cases, the settling and filtering characterists of the sludge improved after the aluminum was removed.

In practical applications in Tampa and Japan, problems have arisen with sulfuric acid alum recovery plants. Contamination of the recovered alum has proven to be the main problem. In Tampa, color built up in the recovered alum, negating its usefulness. In the plants in Japan heavy metals tended to build up in the recovered alum. In both cases, feeding the weak aluminum solution proved difficult and dosages were hard to control. In Tampa, the use of sulfuric acid to recover alum has been discontinued.

No new alum recovery plants can be built in Japan, although the existing facilities are still operational.

A different type of alum recovery for recovering aluminum from wastewater sludges was developed by Cornwell (18). In the process, sulfuric acid was added to the sludge to lower the pH to 2.0. The aluminum-rich supernatant was decanted from the residual solids, which were discarded. Aluminum was then extracted from the sludge supernatant by liquid-ion exchange. The liquid-ion exchange process selectively extracted aluminum without extracting appreciable metal contaminants. Cornwell found that about 90% of the aluminum present in the sludge could be recovered using this method. The process produced alum concentrated to as high as 54,000 mg/l as Al^{3+}.

3.2 The Alum Recovery Research Project

In 1976, a three year research project was begun at Michigan State University to investigate the application of the liquid-ion exchange technique for recovery of aluminum from water treatment plant sludges. The project was supported by Michigan State University and the American Water Works Association Research Foundation.

The results of the first year's work are summarized in Characterization of Acid Treated Alum Sludge, by Cornwell and Susan (19), and Feasibility Studies on Liquid-Ion Exchange Alum Recovery From Water Plant Sludges, by Cornwell and Lemunyon (20).

The initial work of the alum recovery project investigated existing alum sludge treatment and disposal methods. A survey of alum sludge treatment of over 50 water plants was conducted. Based on the results of the survey, four alum sludges were examined in the laboratory. The sludges were examined for aluminum content and dissolution, and settling behavior as related to aluminum dissolution.

Included in the first year of the project was investigation of the liquid-ion exchange process on a batch basis. The operation chemicals and optimum concentrations were first determined. Initial work was done with synthetic solutions of alum sludge. The results of synthetic test solutions were verified with alum sludge form Tampa, Florida. An alum recovery system was proposed for Tampa, Florida, using acidification to free the aluminum from the sludge. The proposed system called for a liquid-ion exchange process to purify and concentrate the aluminum. Based on the successful results of the first year, recommendation was made to continue the project onto continuous flow studies.

3.3 Introduction to Liquid-Ion Exchange

Liquid-ion exchange is a specific type of solvent extraction in which ions are exchanged. Solvent extraction is a process of extractive metallurgy where mixtures of two or more substances are used to isolate one or a number of components. One of the substances in the solvent extraction process must be immiscible with the treated solution, so that two separate phases exist. Liquid-ion exchange is not a new process. It was first developed to purify uranium during World War II. In recent years, liquid-ion exchange has been used successfully on a large scale in commercial application to recover metals from low grade ores. The terms pertaining to liquid-ion exchange used in this thesis are defined in the glossary.

3.4 The Chemistry of Liquid-Ion Exchange

The feed to the liquid-ion exchange process is raw alum sludge. Unlike the process described in the first year of research, the sludge is not acidified. The alum sludge, or the aqueous phase, is mixed in the extractor unit with the solvent, or organic phase. A diagram of the process is shown in Figure 3-1. The solvent is composed of the extractant, the diluent, and if necessary, the modifier. The extractant used in this case is a Stauffer Chemical Company product, MDEHPA (mono-di(2-ethylhexyl) phosphoric acid, 50-50 mixture), having an average formula weight of 266. A diagram of the mono and di-alkyl acids is shown in Figure 3-2. The diluent is a solvent for the extractant which is immiscible with water. The diluent used in this research was a Kerr McGee product, Kermac 627 (boiling point 389°F). Kermac 627 is refined kerosene (number 1 fuel oil). A high quality kerosene was successfully tested as a diluent in the first year's research. A small amount (about 2%) of tributyl phosphate was used as a modifier to help prevent the formation of a third phase. Generally, the solvent contained 80-90% diluent.

In the extractor, the hydrogen ions of the MDEHPA exchange with the aluminum ions in the sludge, lowering the pH of the sludge. In the extraction circuit, which will be described later, the two phases separate. The aluminum rich organic phase (the extract or loaded organic) goes next into the stripping circuit. Mixer/settlers, (usually two) are used in the stripping circuit. In the stripping circuit, the loaded organic is contacted with sulfuric acid. The hydrogen ions in the sulfuric acid exchange with the aluminum ions in the organic phase, producing alum, $Al_2(SO_4)_3$. The stripped organic phase has been regenerated to its original form, and can be returned to the extraction circuit to extract more aluminum. To facilitate use, the aluminum concentration in the recovered alum should be the same as that of commercial alum. By controlling acid feed rate to the strippers the desired aluminum concentration can be achieved.

If two or more strippers are used in the stripping circuit, the flow of the two phases is countercurrent to take advantage of the driving force

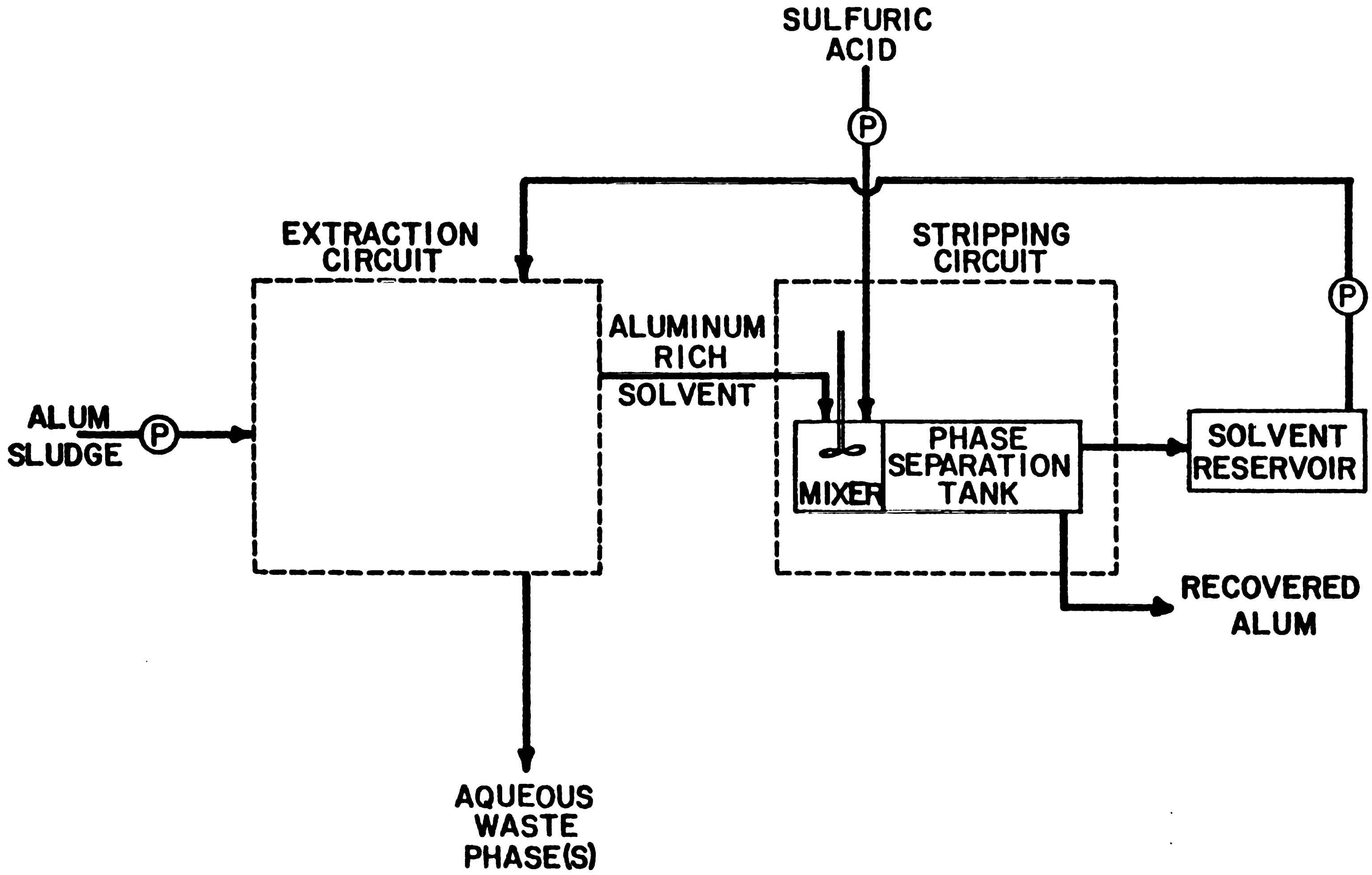
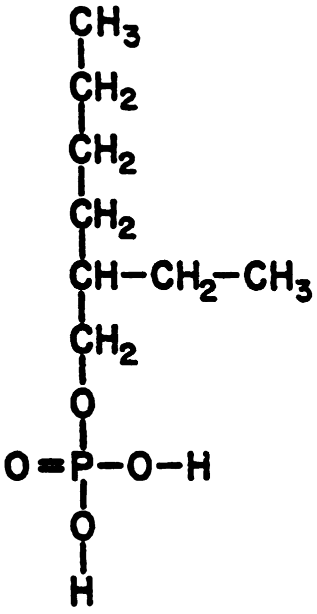
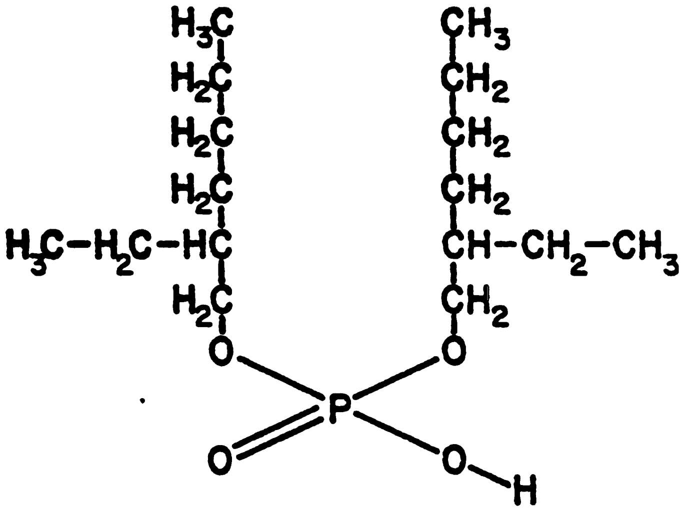


FIGURE 3-1

SCHEMATIC FLOW DIAGRAM OF THE LIQUID ION-EXCHANGE ALUM RECOVERY PROCESS



A.



B.

FIGURE 3-2
EXTRACTANT ACIDS

LEGEND:

A = MONO (2-ETHYLHEXYL) PHOSPHORIC ACID
B = DI (2-ETHYLHEXYL) PHOSPHORIC ACID

differential. That is, the fresh acid contacts the partially stripped organic phase, and the acid partially loaded with aluminum contacts the loaded organic phase. A stripping circuit operated in this manner generally has a very high efficiency.

3.5 Goals of Alum Recovery Research

The purpose of the alum recovery research project was to develop an economical alum recovery system that could be used in the water treatment industry. The alum recovery process must meet the following objectives:

1. The process should recover as much of the aluminum as possible.
2. The recovered alum should be of equal or better quality (in terms of contamination) than commercial alum.
3. The recovered alum aluminum concentration should be equal to the aluminum concentration of commercial alum to facilitate reuse.
4. Dewatering of the waste stream(s) and disposal of the residuals should be less expensive than dewatering the original sludge.

The process was tested during the first year of this research on a bench scale laboratory unit. The second year was devoted to the operation of a pilot scale unit.

CHAPTER 4

DESCRIPTION OF RESEARCH

4.1 The Mixer/Settler Extractor

The mixer/settler liquid-ion exchange unit used in the laboratory was supplied by Bell Engineering. The pilot scale units were also supplied by Bell Engineering. A diagram of a mixer/settler unit is shown in Figure 4-1.

In both the laboratory and pilot scale units, the organic and aqueous phases were pumped into the bottom of the mixer. The relative flow rates of the phases determined the feed phase ratio. The feed phase ratio is defined as the volume of organic solution being fed to the system divided by the volume of aqueous solution being fed. The mixed solution flowed over a weir into the phase separation tank. The solvent flowed over a weir and out of the tank, and in the bench scale unit, the aqueous phase flowed out the bottom of the settler. In the pilot scale unit, the aqueous phase flowed under the solvent weir over another weir, and out of the tank. Due to the pumping action of the mixer impellers, the solvent flowed from tank to tank without having to be pumped. In the extractor, a portion of the solvent was recycled back to the mixer to keep a high operating phase ratio. In the strippers, a portion of the acid was recycled to keep the operating phase ratio lower than the feed phase ratio. The operating phase ratio (O.P.R.) is defined as:

$$\text{O.P.R.} = \frac{\text{solvent being fed} + \text{solvent being recycled}}{\text{aqueous being fed} + \text{aqueous being recycled}} \qquad (4\text{-}1)$$

A high O.P.R. results in high entrainment of organic into the aqueous phase. All mixers were normally operated with the organic phase continuous, the aqueous phase being dispersed in the organic. A low O.P.R.

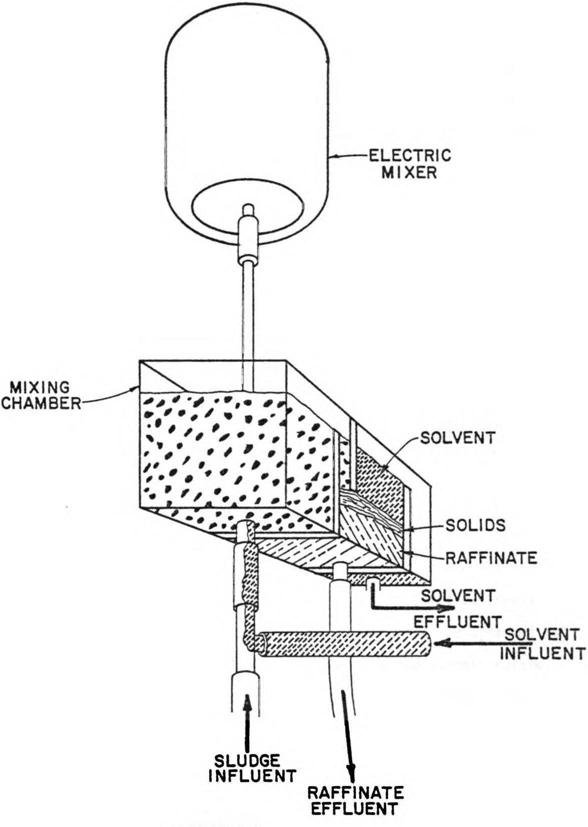


FIGURE 4-1

DIAGRAM OF THE MIXER/SETTLER EXTRACTOR

results in a change of phase continuity.

The mixer impeller rotates at a high speed (800 f.p.m. tip speed as found to be optimal from previous work (20)), and as a result, in the extractor, the aqueous phase consists of two components. The major component was the bulk of the original alum sludge, without the solids. This component is the raffinate. The other component is the bleed solids, which were produced at 10-35% of the original sludge flow rate. The bleed solids were usually lighter than the raffinate, and were drawn off with a siphon device in both the lab and the pilot plant.

4.2 The Rotating Contactor Extractor

The rotating contactors, also called the RTL contactors or rotating bucket contactors were supplied by RTL, Ltd. The rotating contactor served the purpose of a mixer/settler in a single unit, using gentle mixing to allow for easy phase separation. A diagram of the rotating contactor is presented in Figure 4-2.

As with the mixer/settlers, the sludge and the stripped organic must be pumped into the contactor. In the case of the rotating contactor, however, the solvent is pumped into the top half of the contactor, and the sludge into the bottom half. The contactor is a simple cylinder with a series of small buckets around the perimeter. The buckets are separated by and attached to a series of circular plates. The plates are attached to a central shaft which rotates inside the cylinder. As the buckets rotate, they bring the heavy phase up into the light phase and vice versa. The gentle mixing (the buckets rotate at 2-8 rpm) allows extraction of aluminum to occur without the formation of a separate solids layer. The solvent is pumped out the far end of the contactor, and the aqueous phase flows out by gravity. Originally, the contactor was run countercurrent, but it was

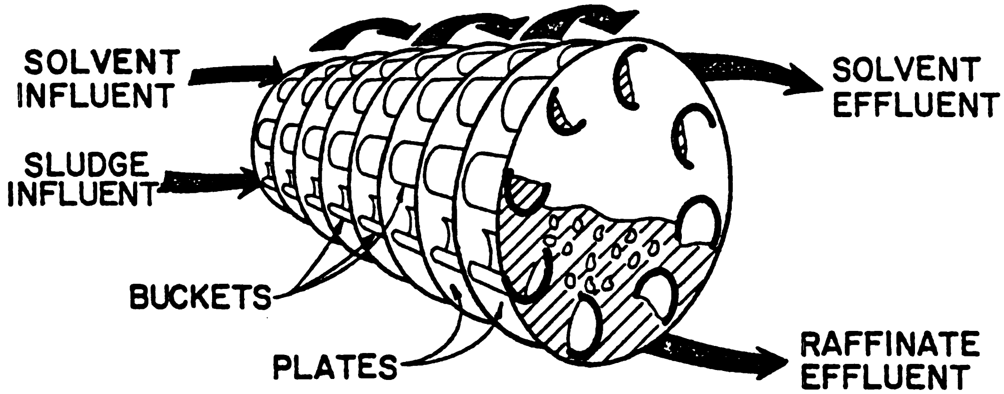


FIGURE 4-2

CUTAWAY VIEW OF THE ROTATING CONTACTOR EXTRACTOR found that cocurrent flow gave better results. The RTL contactor was also tested for stripping, but it failed to perform as well as the mixer/settlers.

Using the RTL contactor with alum sludge as the feed resulted in only one aqueous waste stream: the raffinate. In both the lab and the pilot plant, the RTL raffinate flow rate was the same as the alum sludge flow rate, and was drawn off by gravity.

4.3 Research Chronology

In the fall of 1977, research was begun with the bench scale continuous flow mixer/settler unit, using synthetic aluminum feed solutions. Equipment and operational problems plagued the initial work, and it was not until the summer of 1978 that serious work was begun with alum sludge as the feed. In the fall of 1978 research with the RTL contactor was begun in the lab. In late 1978 and early 1979, the mixer/settler pilot plant was built and installed in Tampa. At the same time, more data was being gathered in the lab using alum sludge form Sharon, Pennsylvania and the mixer/settler equipment. In February of 1979, the Tampa pilot plant was put into operation, and alum sludge was being used in the laboratory in the RTL contactor. The pilot scale RTL contactor was tested for only a short time in Tampa during the late summer and early fall of 1979. In October of 1979, the testing in Tampa was concluded. A chronology chart of the research is presented in Figure 4-3.

4.4 Specific Objectives of This Research

As discussed in Chapter 1, the research described in this thesis was concerned with the exit streams from the liquid-ion exchange process. For the process using the mixer/settler extractor, there are three exit streams,

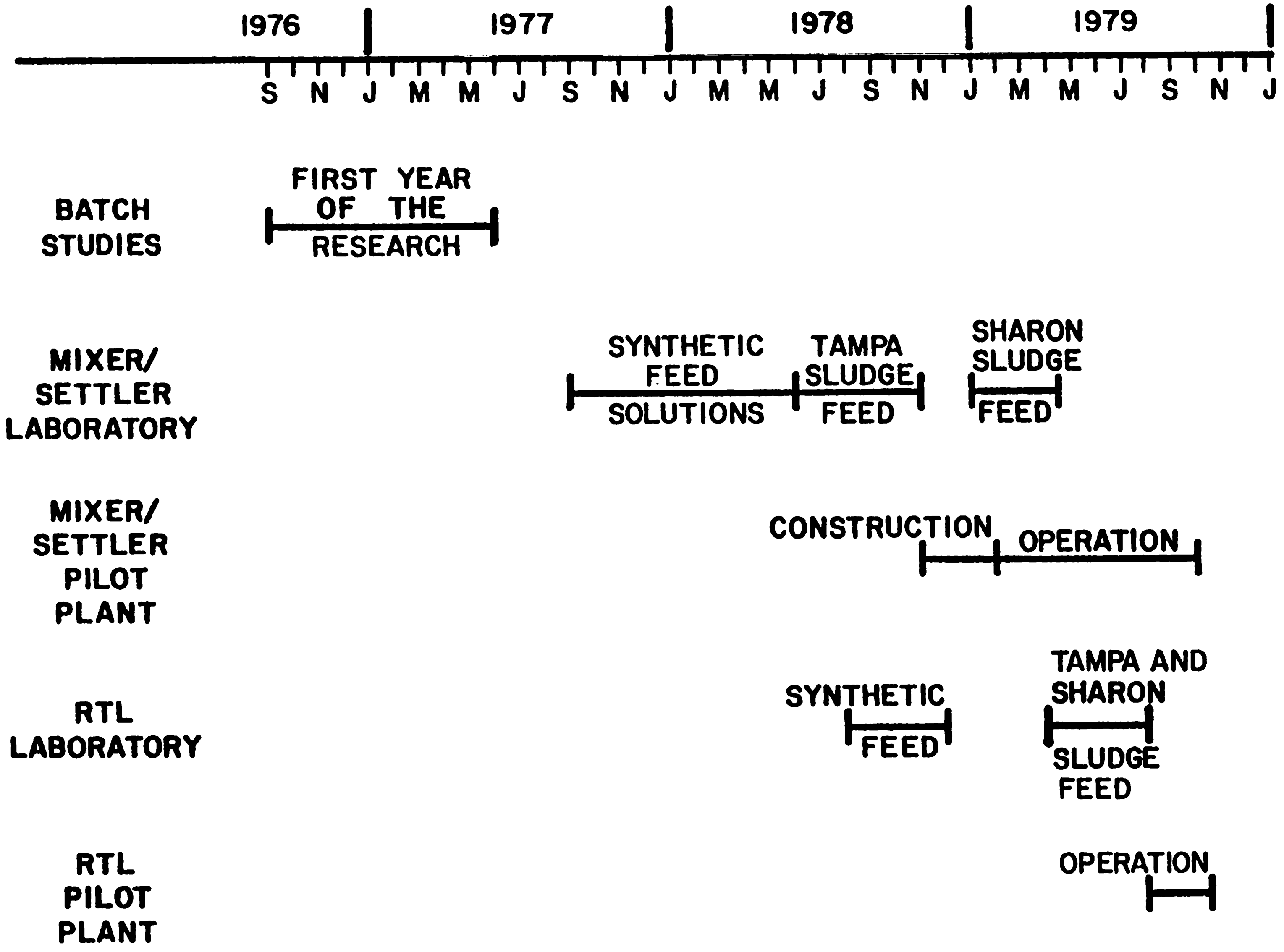


FIGURE 4-3

RESEARCH CHRONOLOGY

the solids, the raffinate, and the alum. The alum recovery process using the rotating contactor extractor produces two exit streams, the raffinate and the alum. The specific goals of the research are as outlined below:

For the mixer/settler solids:

1. Characterization of the exit stream.
2. Treatment of the solids to recover solvent.
3. Investigation of dewatering and disposal of the solids.
4. Design values of important parameters for full scale system in Tampa.

For the mixer/settler and RTL raffinate:

1. Characterization of the exit stream.
2. Investigation of solvent losses and recovery.
3. Treatment alternatives to allow disposal to the waterway.
4. Design values of important parameters for full scale system in Tampa.

For the recovered alum:

1. Comparison of quality with commercial alum.
2. Treatment to reduce Total Organic Carbon contamination.
3. Testing of the recovered alum in coagulation of raw water.
4. Design values of important parameters for full scale system in Tampa.

CHAPTER 5

CHARACTERIZATION OF SLUDGES

5.1 Selection of Sludges

Using the results of the first year of the alum recovery research, alum sludge from Tampa was selected for continuous flow studies on the bench scale mixer/settler unit. Tampa has a 65 million gallon per day (mgd) water plant which treats a highly colored water from the Hillsborough River. Tampa uses approximately 100 mg/l liquid alum for coagulation, producing about 600,000 gallons of 0.6% solids sludge per day. The sludge is thickened in lagoons to about 1.2% suspended solids. The sludge supernatant is used for watering a nearby golf course. The solids are dewatered on sand drying beds and trucked to a landfill. During the summer rainy season, the drying beds become overloaded and cannot keep up with the sludge production.

The Tampa sludge was thought to be an extraordinarily difficult sludge to use in the alum recovery system. Because of the nature of the sludge, contamination with metals and color seemed likely. More important, the organic nature of the solids would tend to make them behave poorly in the extraction system. Solvent loss into the solids was expected to be more of a problem with Tampa sludge than with most alum sludges.

The second sludge studied in the lab was a more typical sludge. The sludge came from the Shenango Valley Water Company's water plant in Sharon, Pennsylvania. The plant treats about 11 mgd of surface water from a reservoir, using about 40 mg/l alum. Approximately 20,000 gallons of 2% solids sludge are produced per day. More data on the two water treatment plants is presented in Table 5-1.

TABLE 5-1

WATER TREATMENT PLANT PARAMETERS

	Tampa	Sharon
Raw Water (yearly averages)		
Turbidity (FTU)	0.6	8
Color (Pt-Co units)	100	26
Alkalinity (mg/l $CaCO_3$)	84	50
Hardness (mg/l $CaCO_3$)	118	89
Alum Dose (mg/l)	100	40
Alum Sludge		
Flow (gpd)	600,000	20,000
Concentration (% solids)	0.6	2.0

It was hoped that the results from the Sharon sludge would be indicative of the results from a more typical alum sludge. It was originally expected that a second pilot plant could be built and operated in Sharon, but this proved to be impossible due to time constraints.

Characterization of the sludge is used to predict the behavior of the alum recovery system. Aluminum content and dissolution are vital parameters in the operation of the liquid-ion exchange process. Suspended solids reduction upon acidification should be related to the amount of solids produced by the process. Other sludge parameters may prove to be useful in predicting the behavior of the alum recovery system.

5.2 Previous Research

Characterization of sludges similar to that described above has been used by researchers to predict the behavior of acid treatment alum recovery systems. Research by Chen, et al. (11) showed that for most sludges, 90% of the aluminum could be recovered from sludges by lowering the pH to 2.0. They also found that the initial settling velocity of the sludge increased from 2 to 4 times after acidification.

Research conducted during the first year of the alum recovery research project investigated alum sludge characteristics in detail. Tests were run on four sludges, including sludge from Tampa. The results from the tests on the sludges were as follows: (references (19) and (20).)

1. 95% of the aluminum in Tampa sludge could be dissolved at pH 2 (The other sludges averaged 90% dissolution at pH 1).
2. Tampa sludge showed 85% suspended solids reduction upon aluminum dissolution by acidification. (The other sludges showed an average of 40% S.S. weight reduction.)
3. With all sludges, the solids settled faster after acidification than before.

4. All sludges exhibited about 80% settled volume reduction upon acidification.
5. The characteristics of the Tampa sludge are as presented in Table 5-2.

5.3 Experimental Methods

Sludge samples were tested for aluminum and suspended solids reduction upon acidification using the following procedure. A 250 ml or larger sample of sludge was mixed in a beaker using a magnetic stirrer. If the sludge was noticeably anaerobic, a small amount of hydrogen peroxide (2-5 drops) was added before any samples were taken. Using a Corning model 12 pH meter, pH readings were taken. Suspended solids samples of 5 - 10 ml were taken using transfer pipettes. Glass fiber filters were used for suspended solids determinations. All weights were determined using a Mettler H analytic balance. Sulfuric acid was added to the sludge to lower the pH. Samples were taken only after 15 minutes of constant pH readings. Suspended solids measurements were taken according to the procedure outlined in Standard Methods (21) for determination of filterable residue. Aluminum values were determined in the laboratory with a Varian Model 375 Atomic Absorption Spectrophotometer. Aluminum determinations were conducted according to the procedure outlined in the manual for the Spectrophotometer. Concentrations of aluminum could be best detected in the range of 10 - 100 mg/l. Samples above 100 mg/l Al^{3+} were diluted prior to analysis. All aluminum values run in Tampa were determined by the laboratory staff of the water treatment plant. Determinations were made on an Instrumentation Laboratory Model 151 Atomic Absorption Spectrophotometer.

TABLE 5-2

TAMPA SLUDGE CHARACTERISTICS

Parameter	Value
Dissolvable Inorganic Solids (%)	61
Non-Dissolvable Inorganic Solids (%)	6
Dissolvable Volatile Solids (%)	25
Non-Dissolvable Volatile Solids (%)	8
Average Suspended Solids Concentration (%)	1.6
Total Aluminum Concentration (mg/l)	3300
pH	7.4

5.4 Laboratory Results of Tampa Sludge

A characterization of Tampa sludge has already been presented in Table 5-2. The large amount of dissolvable organic solids shows that color carryover into the recovered alum may be a problem with Tampa sludge. The Tampa sludge also showed a high amount of dissolvable solids as noted previously in section 5.2. The sludge used in the lab from Tampa was thickened sludge, obtained from the lagoons. The sludge was shipped to the lab in 55 gallon drums. Two drums were received, each exhibiting the same characteristics. The Tampa sludge was about 2% solids. Almost 50% of the solids were organic in nature. Approximately 1740 mg/l Al^{3+} was dissolved at pH 3.0, 1870 mg/l Al^{3+} was available at pH 2.0. The Tampa sludge exhibited a maximum solids reduction of 73.5% at pH 1.0 as shown in Figure 5-1.

5.5 Laboratory Results of Sharon Sludge

Two 55 gallon drums of sludge were received from Sharon. The first drum contained sludge with 2% suspended solids. The sludge in the second drum was about twice as thick. Because of the differences in the sludges, results have been reported for Sharon sludge no. 1 and Sharon sludge no. 2.

The Sharon sludges are characterized in Table 5-3. The dissolvable organic solids in the Sharon sludge are very low, especially when compared to the values in Tampa sludge. A high amount of non-dissolvable inorganic solids shows that the solids are composed mostly of inert clays and silts.

The results of Table 5-3 show that the Sharon sludge does not exhibit a high degree of solids reduction as the pH is lowered. This is further shown in Figure 5-2. Sharon sludge shows an average maximum solids reduction of only 35%. This would indicate that the bleed solids production in the alum recovery system from Sharon sludge would be much greater than that from the Tampa sludge.

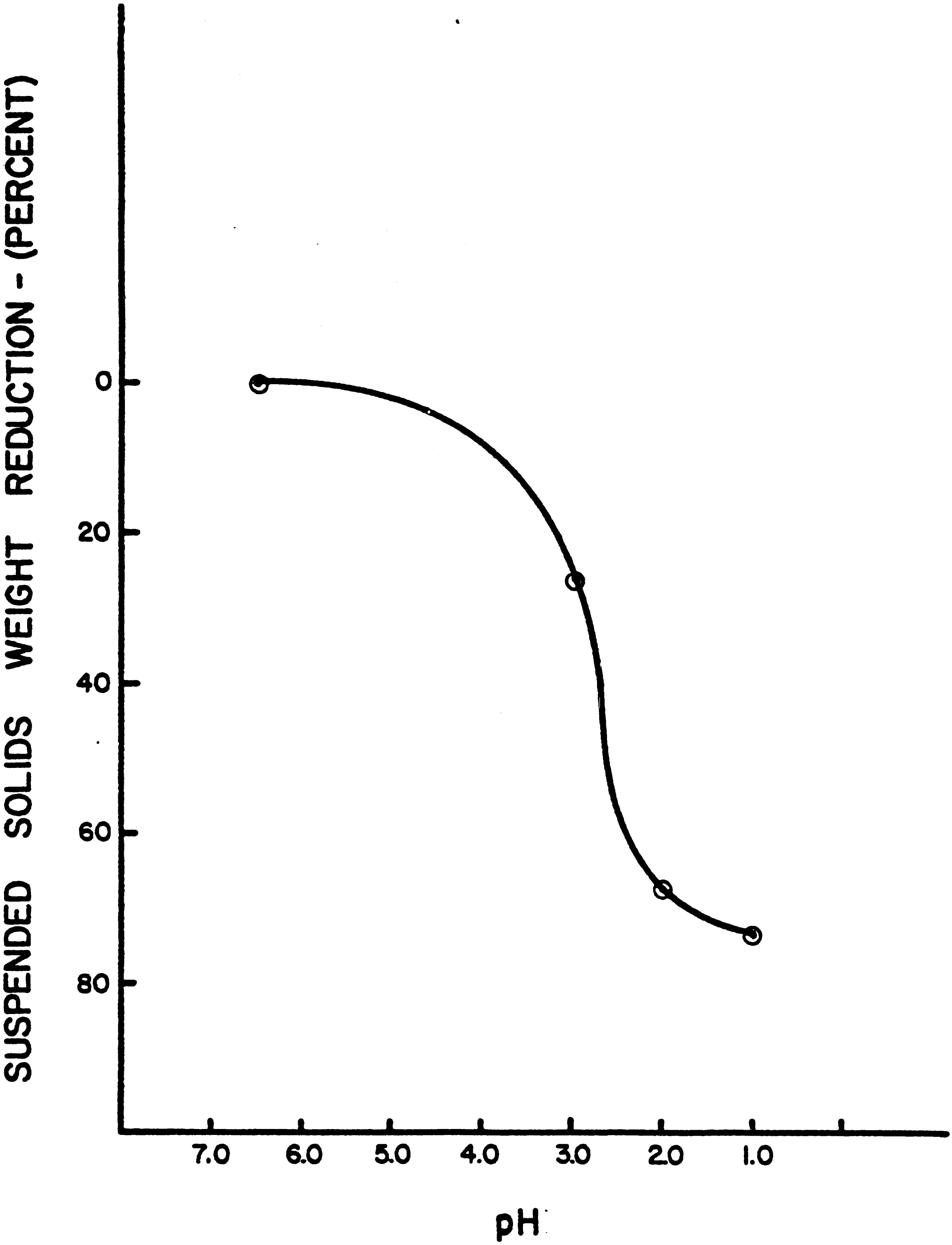


FIGURE 5-1

SUSPENDED SOLIDS REDUCTION OF TAMPA SLUDGE IN THE LAB VS. pH

TABLE 5-3

SHARON SLUDGE CHARACTERISTICS

Parameter	Sludge #1	Sludge #2
Dissolvable Inorganic Solids (%)	32.7	19.4
Non-Dissolvable Inorganic Solids (%)	55	56.6
Dissolvable Volatile Solids (%)	2.3	5.6
Non-Dissolvable Volatile Solids (%)	10	18
Average Suspended Solids (%)	1.9	3.6
Total Aluminum Concentration (mg/l)	1700	2200
pH	7.3	7.7

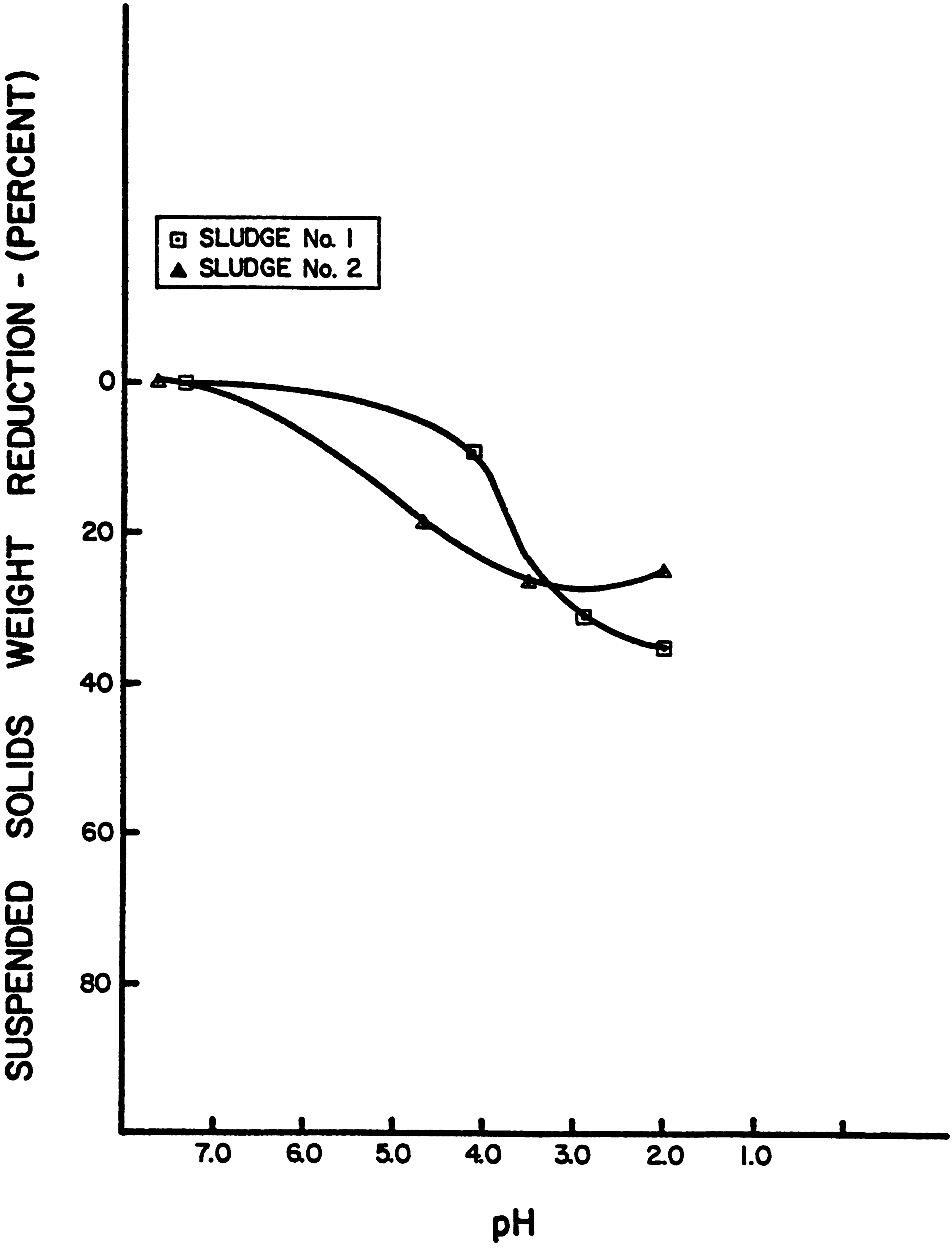


FIGURE 5-2

SUSPENDED SOLIDS REDUCTION OF SHARON SLUDGE VS. pH

Figure 5-3 shows the available aluminum dissolution as a function of pH. Available aluminum is defined as the amount of aluminum dissolved at pH 1.0. Sharon sludge, like most sludges, shows very little dissolution at pH 4, but dissolution increases rapidly as the pH is lowered to 3. As with Tampa sludge, the large majority of the available aluminum is dissolved by the time the pH reaches 2.0.

5.6 Tampa Pilot Sludge Results

In Tampa, alum sludge directly form the sedimentation basins was used in the alum recovery process. The sludge was much thinner than the sludges tested in the lab, averaging about 0.4 percent solids and about 600 mg/l dissolvable aluminum. Because of the changes in raw water and problems associated with plant operation, wide fluctuations in sludge strength were common. Solids concentrations ranged from less than 0.10 percent solids to almost 1 percent solids. Respective aluminum concentrations were from 80 to over 1200 mg/l as Al^{3+}.

A definite correlation was noted between aluminum concentration and solids content. When raw water color was constant a plot of aluminum concentration at pH 2 vs. solids concentration showed a linear relationship. When the raw water color changed, a new line could be drawn through the data points. Figure 5-4 shows the relationship between aluminum content at pH 2.0 and the suspended solids concentration of the sludge for selected dates in the summer and fall of 1979. The raw water color increased from 95 Pt-Co units on August 14th to 240 Pt-Co units by August 29th. The change in color caused the alum to be more efficient in promoting solids settling. As the color increased, less alum was needed to coagulate a constant amount of solids. This resulted in a decrease in the aluminum

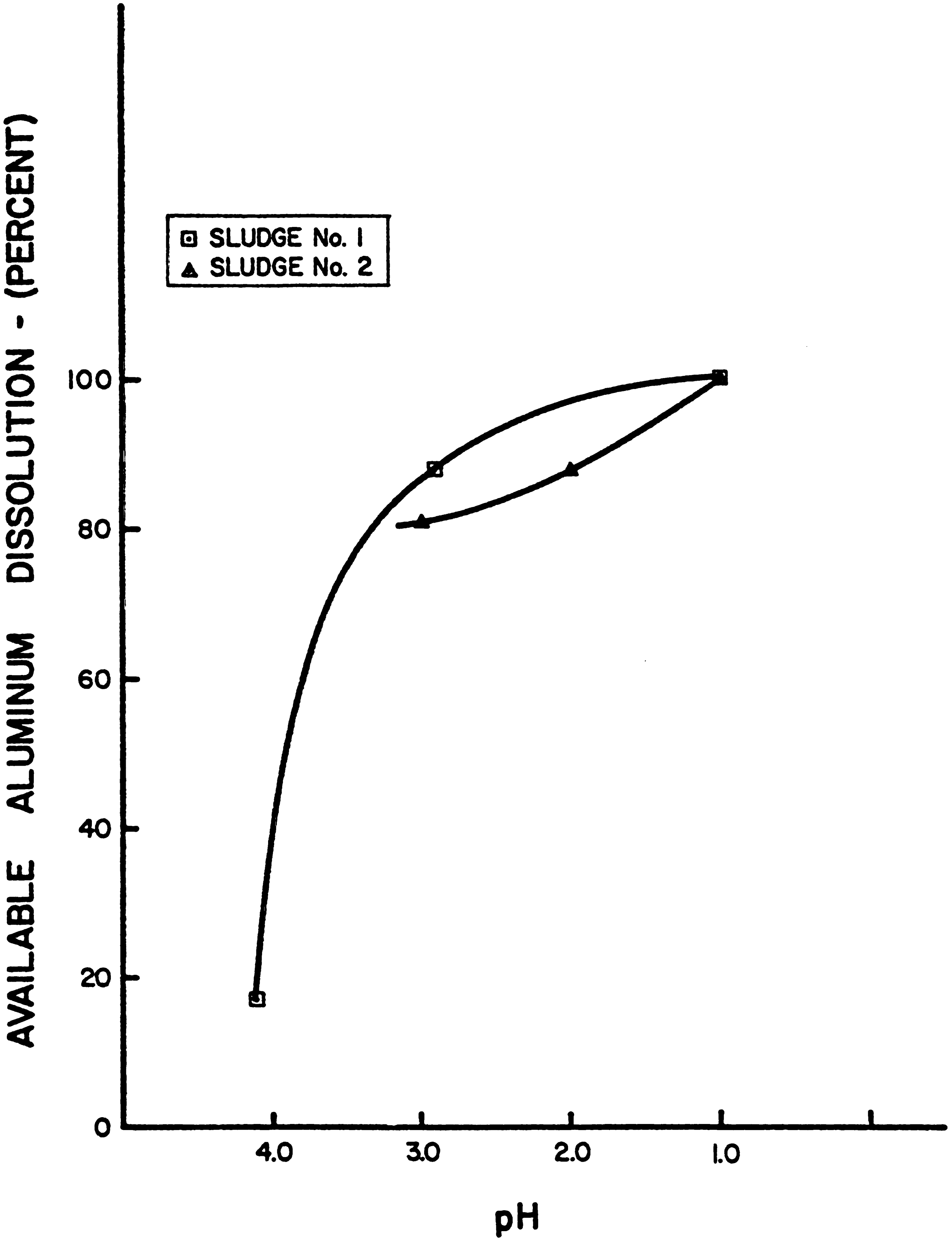


FIGURE 5-3

ALUMINUM DISSOLUTION OF SHARON SLUDGE VS. pH

FIGURE 5-4

ALUMINUM CONCENTRATION AT pH 2 VS. SUSPENDED SOLIDS CONTENT FOR TAMPA SLUDGE

LEGEND:

————————	$y = 1734x + 111.5$ $r = 0.949$ Average color = 104 Pt-Co units (some samples thickened)
....	$y = 1148x + 130.7$ $r = 0.869$ Average color = 213 Pt-Co units
----------	$y = 1769x - 303.9$ $r = 0.872$ Average color = 228 Pt-Co units

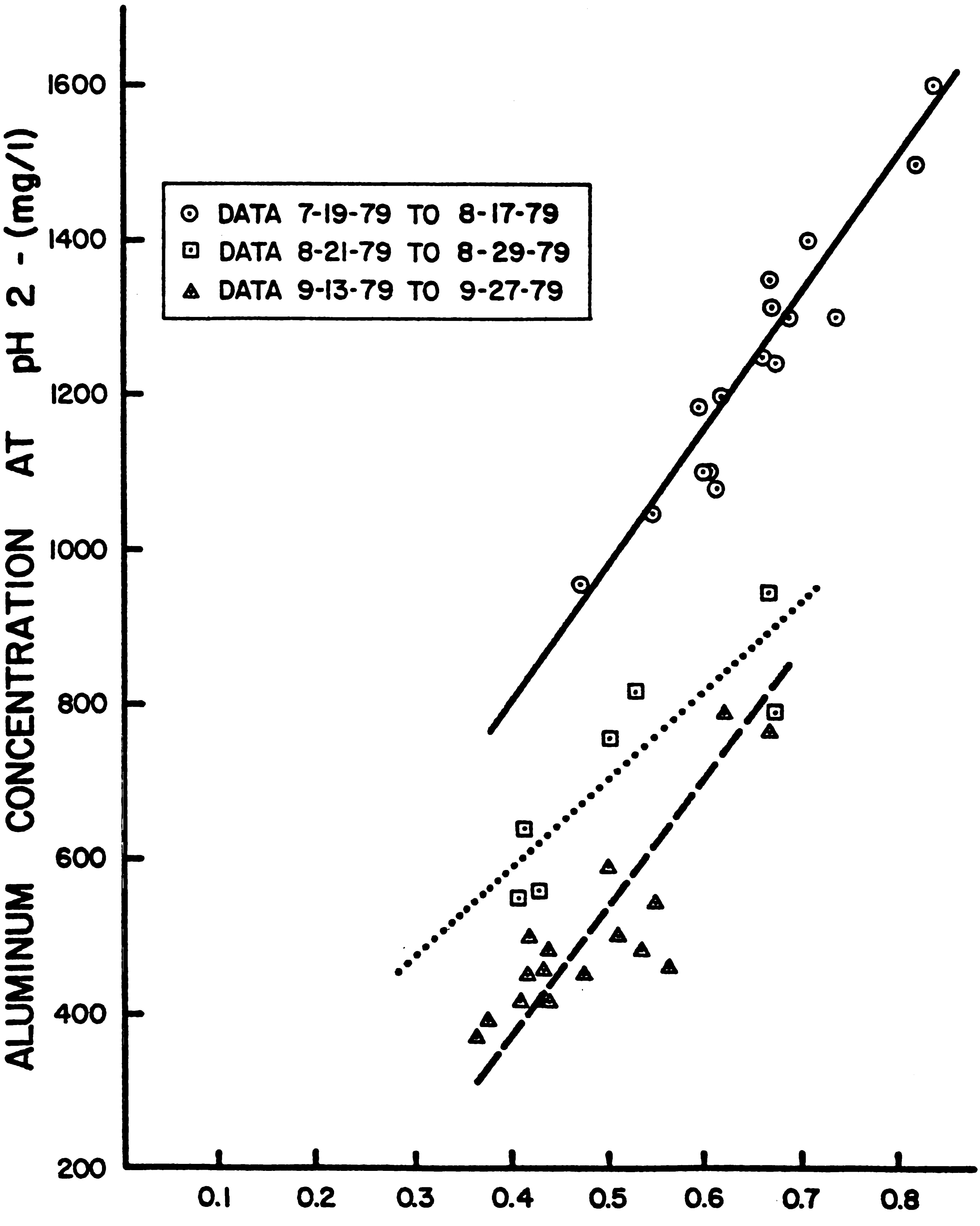

DATA 7-19-79 TO 8-17-79
DATA 8-21-79 TO 8-29-79
DATA 9-13-79 TO 9-27-79
ALUMINUM CONCENTRATION AT pH 2 - (mg/l)
SUSPENDED SOLIDS CONTENT - (%)
1600
1400
1200
1000
800
600
400
200
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

FIGURE 5-4

concentration in the sludge. However, the solids concentration also decreased during this time, lowering the influent aluminum concentrations still further.

Successful operation of the alum recovery process required knowledge of the aluminum content of the sludge in order to set the sulfuric acid flow rate. The changing nature of the sludge made daily aluminum determinations an operational necessity. However, atomic absorption analysis by the Tampa laboratory staff often took two to three days, resulting in operational problems. Suspended solids concentrations were more easily determined, and results were available on a daily basis. Suspended solids values and a plot such as Figure 5-4 were used to determine approximate aluminum values for operational purposes.

Changes in the raw water also influenced the reduction in suspended solids experienced by the sludge upon acidification. During the time from July 19th to August 17th when the raw water color was low, the sludge exhibited an average of 91% suspended solids weight reduction upon acidification to pH 2.0. During most of the spring and early summer, the raw water color was low and the sludge showed suspended solids reduction values in the range of 90%. Sludge produced during late August (high raw water color) showed an average of 78% weight reduction at pH 2.0, and only 66% weight reduction at pH 2.5. The sludge from September when the color was well over 200 Pt-Co units showed only 71% weight reduction at pH 2.0. The use of sludge from highly colored water would be expected to give much higher bleed solids production in the alum recovery system than sludge from lower colored water. Under normal conditions, the raw water color is about 100 Pt-Co units or below. Only during the summer rainy season does the color increase to 200 units or above.

The drastic change in sludge strength from the laboratory to the pilot plant underscores the need for proper sampling technique. The Tampa pilot scale system was designed based on the sludge tested in the lab. As a result, numerous changes had to be made in pilot plant equipment and procedures due to the weak sludge. Good sludge samples are vitally important to the successful design of a large scale system from laboratory data.

CHAPTER 6

THE BLEED SOLIDS

6.1 Introduction and Background

When the alum sludge and the solvent are mixed together at high speed, a third phase, called the bleed solids, is formed. The bleed solids waste stream is produced only from the mixer/settler extractor unit. The bleed solids stream is not produced in the rotating contactor extractor.

Literature from the solvent extraction industry mentions problems with solids in solvent extraction systems. The general practice is to minimize the amount of solids entering the system by employing sedimentation or filtering devices. Suspended solids (S.S.) concentrations in aqueous feed streams are generally kept below 10 mg/l (22). Data on large solids production rates, and the problems associated with them, does not exist. However, even when feeding filtered waste streams, some solids buildup does occur in extractor settlers. In the industry, bleed solids are periodically drawn off and centrifuged to recover the lost solvent. Because solids are withdrawn at long intervals, small centrifuges can be used to process the solids.

The expected rate of bleed solids production can be estimated from the amount of suspended solids reduction upon acidification of sludge. Past research (18) has shown that acidification of alum sludge reduces the amount of suspended solids present. Results from the first year of the alum recovery research show that a 90% reduction of suspended solids from Tampa sludge can be achieved at pH 2. Most other sludges were found to exhibit only 30-40% suspended solids reduction (19).

Results from tests with batch mixers indicate that when the extractor was operated aqueous phase continuous, a very stable emulsion was formed.

This emulsion, formed by the aluminum hydroxide floc bonds, is light enough to exist in the organic phase, which indicates that it is made up mostly of solvent. When the batch tests were operated with the organic phase continuous (O.P.R. greater than 2:1), no stable emulsion formed. Only a thin layer of solids was noticed at the aqueous-organic interface, and these solids were all in the aqueous phase. Research on the nature of these solids was not pursued further with the batch apparatus.

The objectives in studying the bleed solids stream were to characterize the solids and to recover the solvent from the solids. The specific objectives in determining bleed solids characteristics were:

1) to determine if the bleed solids production rate would be predicted by sludge characteristics,
2) to determine the suspended solids concentration of the bleed solids stream,
3) to determine the solvent content of the bleed solids, and
4) to identify operational parameters that influence bleed solids characteristics.

The specific objectives in studying solvent recovery were:

1) to minimize the loss of solvent by processing the bleed solids, and
2) to determine what the solvent loss was in order to assess its impact on the process.

High solvent losses make the process economically unattractive due to the high costs associated with replacing the diluent and extractant.

6.2 Methods and Materials

The solids were drawn off with the use of a pipette in the laboratory set-up. In Tampa, a section of PVC pipe with a valve was used to siphon the solids. Suspended solids samples were dried at 103°C for one hour, then cooled for at least three hours before weighing. The procedure outlined in Standard Methods (21) was followed in measuring suspended solids. Glass fiber filters were used throughout. Unless otherwise indicated, all tests were performed on completely mixed samples. The bleed solids production rate was computed by measuring the volume of solids drawn off over a specified time period, and dividing by the total volume of sludge fed during that time. Bleed solids production rates were generally computed every 20-50 hours of operation. Inaccuracies in suction technique and measurement resulted in errors in individual readings, but overall results are valid.

A number of techniques were used to measure solvent loss. In the lab, the processed bleed solids were distilled to measure solvent loss. A drawing of the distillation apparatus is shown in Figure 6-1. Using the volume of solvent collected, the weight of solids digested, and the solids production rate, solvent losses could be computed in terms of gallons per 1000 gallons of sludge fed. By also measuring the volume of water collected by distillation, the solids content of the bleed solids could be determined. Problems were encountered in measurement of solvent content of the solids using this apparatus. Cleaning of the distillation flask after each digestion proved to be especially difficult. This resulted in the carryover of solvent from one digestion to the next. The use of a sonic cleaning chamber alleviated the problem somewhat, but the process was never completely accurate.

In Tampa, a similar set-up was employed to determine solvent losses. However, the lack of a sonic cleaning chamber resulted in problems with solvent carryover. Useful results were obtained only by boiling the water in the distillation flask a number of times after each digestion. This process was very time consuming, and proved to be a great handicap to successful operation.

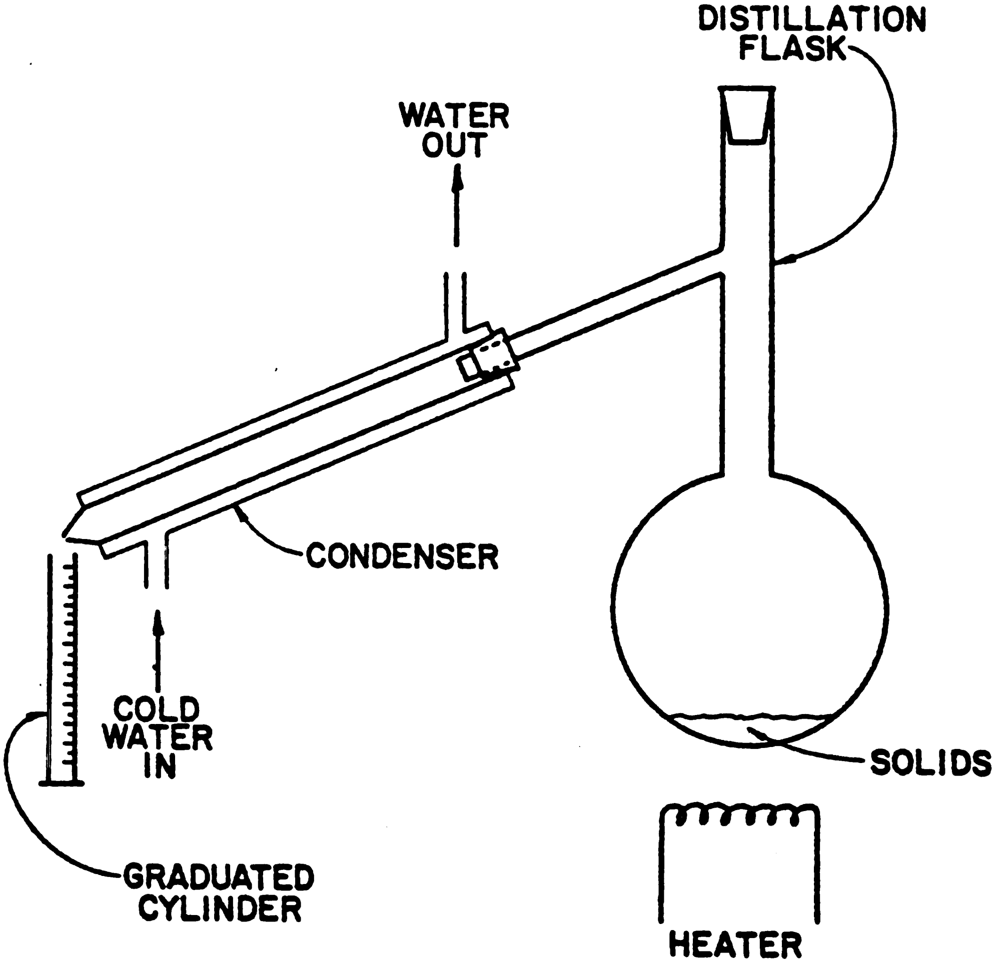


FIGURE 6-1

SOLVENT DISTILLATION APPARATUS

A second method was used in Tampa to determine solvent loss. It gave quick, consistent results, although probably not 100 percent recovery of solvent. The second method involved the use of Soda Ash (Na_2CO_3) to free up the solvent from the solids, and a small laboratory centrifuge to facilitate separation. A small amount (1 ml per 14 ml sample) of Soda Ash slurry was added to the sample, which was mixed, then centrifuged. The result was a separation of the solvent from the aqueous phase, leaving a small layer of residual solids behind. Digestion of these residual solids produced no detectable organic solvent. The centrifuge method could give consistent results in about 1/10 of the time of the distillation method.

At no time was any attempt made to determine the constituents of the solvent lost to the residual solids. It would be expected that the lost solvent would have the same extractant/diluent concentration as the solvent in the system, But no tests were undertaken to prove this.

All pH determinations in the laboratory were done on a Corning Model 12 pH meter. The meter was standardized at pH 4.00 and 7.00 before use. In Tampa, a Beckman Zeromatic SS-3 pH meter was used. It was also standardized at pH 4.00 and 7.00.

Vacuum filtration tests were run to determine the filter yields with bleed solids. The tests were run with a Buchner funnel vacuum filtration apparatus as shown in Figure 6-2. The tests were run according to the procedure outlined by Coackley and Jones (23).

6.3 Laboratory Results

6.3.1 Characteristics of Solids

During the laboratory run with Tampa sludge, the research was concentrated on optimization of the system, and few suspended solids numbers were

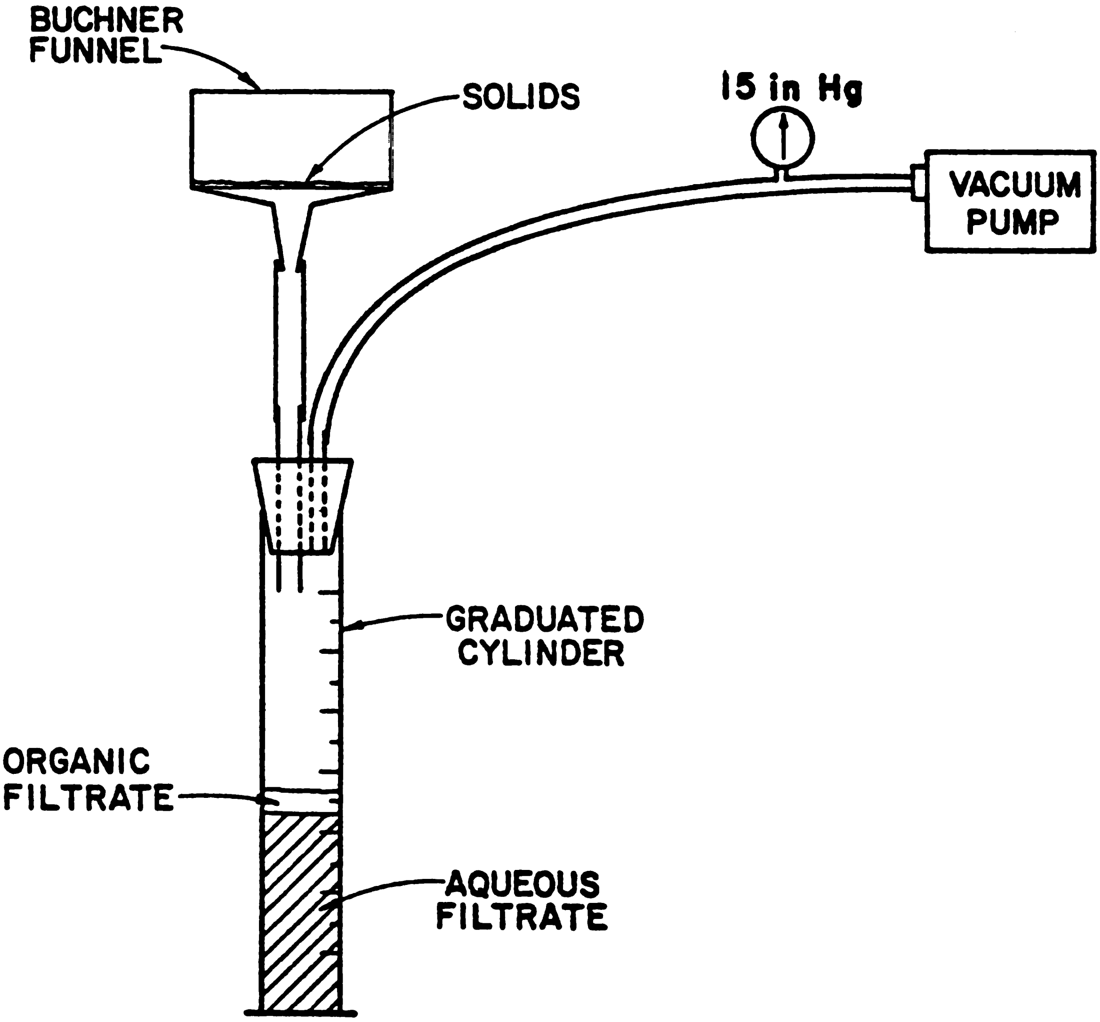


FIGURE 6-2

VACUUM FILTRATION APPARATUS

taken. The few solids numbers were all taken near the end of the Tampa sludge run, when the system was operating well. The data shows that the bleed solids were about 5 percent suspended solids, and contained an average of 19 percent solvent by volume. The bleed solids flow rate was 22% of the original sludge flow. Because the solids samples were dried at only 103°C, these values also include the weight of the organic solvent. Values can be corrected by subtracting the solvent content from the suspended solids concentration. The corrected suspended solids value can be computed by:

$$\text{Corrected S.S.} = \text{S.S.} - (\text{percent solvent}) \times \begin{pmatrix}\text{spec. grav.} \\ \text{of solvent}\end{pmatrix} \qquad (6\text{-}1)$$

For the Tampa bleed solids, the corrected suspended solids average concentration would be 4.2 percent. With this value, the weight reduction in suspended solids can be computed by:

$$\text{W.R.} = 1 - \frac{(\text{C.S.})\left(\frac{\text{S.D.R.}}{100}\right)}{\text{F.S.S.}} \times 100 \qquad (6\text{-}2)$$

Where:

W.R. = suspended solids weight reduction, percent

C.S. = corrected bleed suspended solids con., percent

S.D.R. = bleed solids drawoff rate, percent of feed flow

F.S.S. = feed suspended solids con., percent

For Tampa sludge,

$$\text{Weight reduction} = 1 - \frac{(4.2)\left(\frac{22}{100}\right)}{2.2} \times 100 = 58\% \qquad (6\text{-}3)$$

This number is less than the 73 percent weight reduction experienced by Tampa sludge upon acidification to pH 2.0. However, the system was operating such that the raffinate (and solids) pH at this time was 2.2 - 2.4. At this pH level, the acidified sludge exhibits only about 60 percent suspended solids weight reduction, as shown in figure 5-1.

The results from Sharon sludge number 1 show reasonably good agreement with the suspended solids weight reduction vs. pH relationship portrayed in Figure 5-2. The results from all sludges are presented in Table 6-1. Sharon sludge no. 1 was used for the bulk of the testing, but its concentration increased markedly as the solids settled in the 55 gallon drum. For that reason, the results from March first through March third with Sharon sludge no. 2 from March 19th through March 22nd. Sharon sludge no. 2 was diluted for all subsequent tests and this is reflected in the results presented in Table 6-1. The results show that Sharon sludge number 1 had a bleed solids flow rate of 27 percent of the sludge feed rate. The sludge exhibited a 37 percent weight reduction in suspended solids content (correcting for solvent in bleed solids. This agrees approximately with the maximum of 35 percent weight reduction shown by Sharon sludge number 1 at pH 2 as discussed in section 5.5. The raffinate pH during this period (1.5 to 2.28) was generally quite low, generally averaging about 2.2.

The results using thickened sludge (data from 3-1 to 3-22, table 6-1) should seem to indicate that the thickened sludge had a very poor effect on the behavior of the system. The bleed solids flow rate from March first through March 22nd averaged 45 percent of the sludge feed rate. The corrected weight reduction in suspended solids was only 8.5 percent. Three possible explanations for the poor solids reduction exist: 1) the thicker sludge causes very high solids production, 2) Sharon sludge number 2 does not exhibit appreciable solids reduction, or 3) the system was not working as well as it should. The results from dilute Sharon sludge number 2 (data from 3-23 to 4-12, table 6-1) show that the thinner sludge had a higher solids production rate than the thick sludge. This means that the thick

TABLE 6-1

CHARACTERISTICS OF LABORATORY BLEED SOLIDS

Location of Sludge	Dates of Data	Suspended Solids Concentration Percent FEED (Mean)	BLEED (Mean)	BLEED (Corr. Mean)	Volume of Organic in Solids, (Percent, Mean)	Bleed Solids Flow, (Percent of Feed)	Suspended Solids (Weight Reduction Percent)	Hours of Operation (Fig. 6-3)
Tampa	9-18 to 9-23	2.2	5.0	4.2	18.8	22	59	-
Sharon No.1	1-5 to 2-28	1.9	5.7	4.5	20.9	27	37	0-430
Sharon No.1 and No.2	3-1 to 3-22	3.6	9.3	7.4	} 20.0	45	8.5	430-515
Sharon No.2	3-23 to 4-12	2.1	4.8	3.8		48	11.9	515-640

sludge did not cause the poor solids behavior. Implication of Sharon sludge number 2 as the cause of the problem is a logical choice. Sharon sludge number 2 shows less than 30 percent solids reduction upon acidification. In order to adequately assess the effect of the changes in sludge, a plot of the operating characteristics of the alum recovery system is presented in Figure 6-3. Figure 6-3 presents values of raffinate pH and bleed solids production rates vs. the hours of operation of the alum recovery system. The bleed solids production rates shown are averages, taken over varied intervals of consistent system behavior. The arrows are identified in the key as times at which changes in the system were made. Figure 6-3 shows that not all of the high solids production rates occurred with the use of Sharon sludge number 2. The bleed solids production rate was very high during the period of the 430th to 478th hours of operation, when thick sludge number 1 was being fed. The plot does show that the performance of the system, as measured by raffinate pH, did decline over time. As the extractant depressed the raffinate pH, and usually caused much lower solids production rates over the next few days. In figure 6-3, the arrows labeled B,C,E,F, and J indicate times when fresh extractant was added to the system. Compared to the total amount of extractant presumably present, only small amounts of extractant were added at any one time. The deterioration of the extractant was manifested by a polymerization of extractant and the extracted aluminum when excess aluminum was present in the system. This problem occurred at varying intensities throughout the data run presented in Figure 6-3.

Another factor which may have influenced the poor behavior of the system is biological growth in the sludge. Over time, Sharon sludge number 1 became anaerobic due to biological growth. Sharon sludge number 2 was anaerobic when received in the laboratory. It should also be noted that

FIGURE 6-3

RAFFINATE pH AND BLEED SOLIDS PRODUCTION RATE
DURING LABORATORY RUN WITH SHARON SLUDGE

LEGEND:

A = Startup - sludge no. 1
B = Added extractant (5% of inventory)
C = Added extractant (5% of inventory)
D = Feed pH lowered
E = Added extractant (1% of inventory)
F = Added extractant (9% of inventory)
G = Thick sludge no. 1
H = Start - sludge no. 2
I = Dilute sludge no. 2
J = Added extractant (5% of inventory)

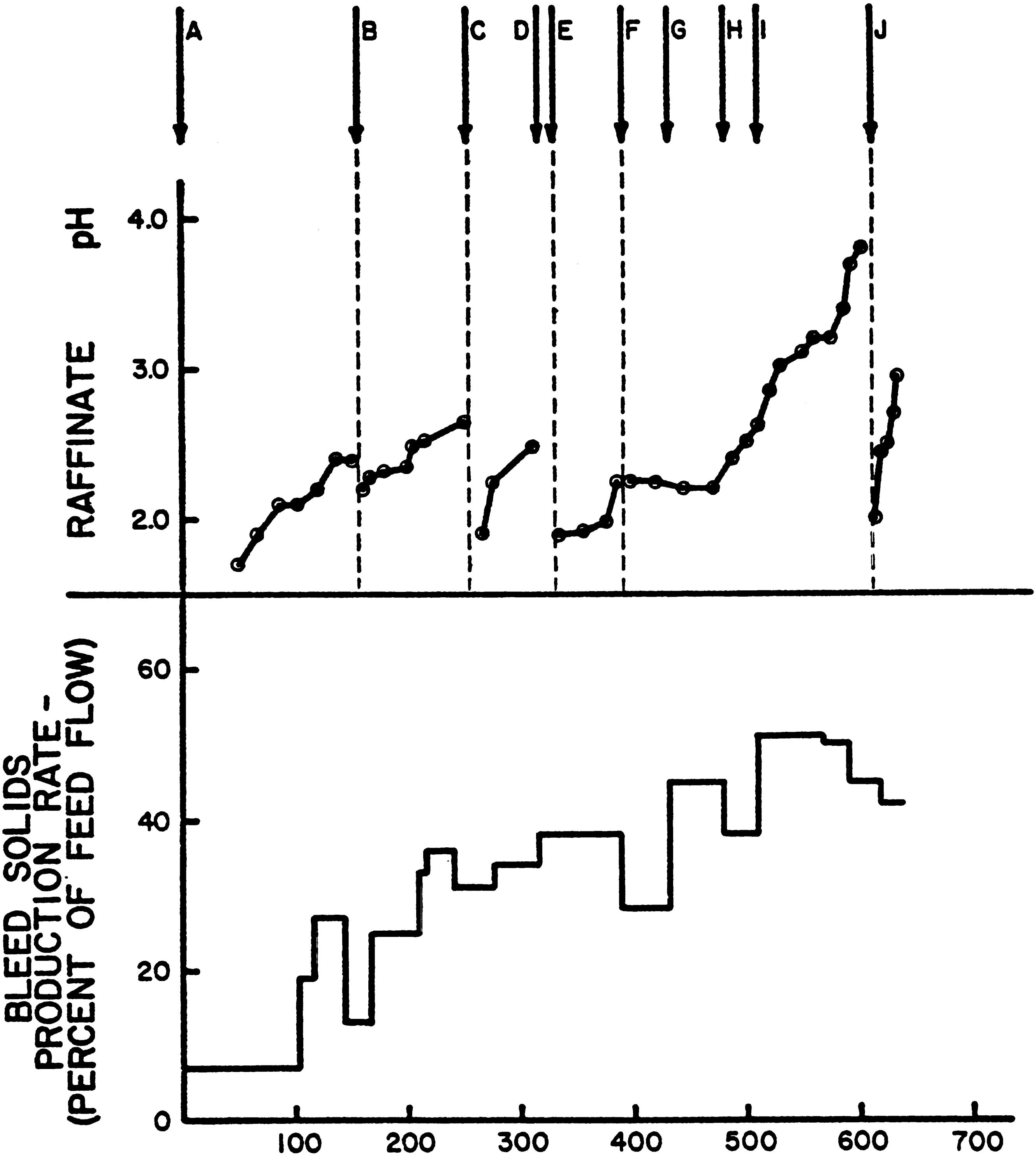

A
B
C
D
E
F
G
H
I
J
RAFFINATE pH
4.0
3.0
2.0
BLEED SOLIDS PRODUCTION RATE - (PERCENT OF FEED FLOW)
60
40
20
0
100
200
300
400
500
600
700
HOURS OF OPERATION

FIGURE 6-3

after about the 315th hour of operation, the pH of the feed sludge was lowered to 4.0 before use. It was hoped that this would lead to better extraction but it did not. Later tests proved that lowering of the feed pH made extraction more difficult because the driving force was decreased. The combination of the deterioration of extractant, change in sludge and lowering of the feed pH all combined to have a detrimental effect on the performance of the alum recovery system.

Figure 6-4 shows the relationship between solids production rate and average raffinate pH for the Sharon sludges. Except for a few stray points, the figure shows both sludges behaved basically the same. From the plot it can be seen to keep the solids production rate at less than 30 percent of the feed flow rate, the raffinate pH must be kept below 2.4.

6.3.2 Recovery of Solvent

It was hoped that a number of small solids dewatering devices could be tested in the laboratory, but this proved to be impossible due to the unavailability of equipment. A small Sharples liquid-liquid Laboratory Super centrifuge was used in the lab for solids processing throughout the Tampa and Sharon sludge runs. The centrifuge developed 3500 g of separation force rotating at 12,000 rpm. The centrifuge had a solids capacity of about 50 ml. Two separate liquid streams were discharged, and the discharge could be controlled by the use of various sized ring dams. When operating correctly, the centrifuge produced a clean solvent stream and a slightly turbid aqueous stream, with the solids remaining in the bowl. The centrifuge was fed by gravity from a separatory funnel, where feed flow rate could be controlled. Operation of the centrifuge was on a batch basis only. The centrifuge had to be shut down and cleaned manually when the solids layer on the outer wall built up to the point where solids were discharged

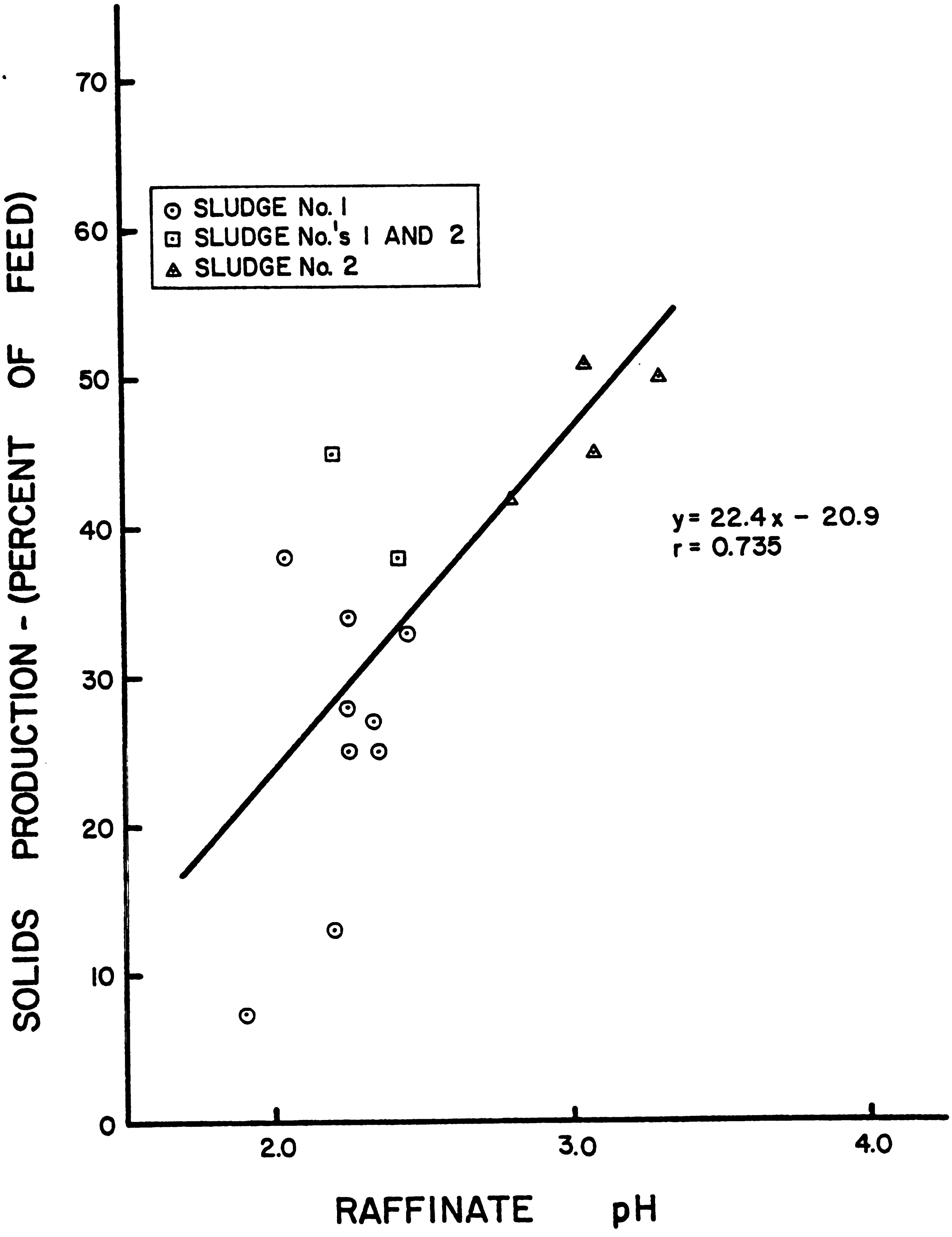


FIGURE 6-4

PERCENT BLEED SOLIDS PRODUCTION VS. AVERAGE RAFFINATE pH FOR SHARON SLUDGE with the recovered solvent.

The results from centrifugation of the solvent are presented in Table 6-2. The results from Tampa sludge show that the loss of solvent into the centrifuged solids when the raffinate pH was less than 2.0 averaged about 1 gallon per 1000 gallons of sludge feed. Neutralization of Tampa bleed solids before centrifugation led to an increase in the amount of organic lost into the dewatered solids and, as a result, a much higher solvent loss.

The results from Sharon sludge number 1 indicate that losses are low (below 2.0 gallons per 1000 gallons of sludge feed) only if the raffinate pH is below 2.20. Losses with Sharon sludge number 1 increase dramatically with a small increase in raffinate pH above 2.2. Results from Sharon sludge number 2 were all at high pH levels, and solvent losses are also high. The high solids production rate associated with this data also helps to contribute to high solvent losses. Results from all three sludges show that the centrifuge can dewater the sludge to 35 to 40 percent suspended solids concentration. Solvent loss was also determined as a volume of solvent per dry weight of solids. The average solvent loss was 0.20 liters per kilogram (0.12 gallons per pound) of dry solids.

Figure 6-5 shows the relationship between organic loss to the dewatered solids and the raffinate pH. From the plot, it can be readily seen that if the raffinate pH is kept below 2.2, solvent losses will be less than 2 gallons per 1000 gallons of sludge feed.

An attempt was made to dewater the solids using a Buchner funnel vacuum filtration apparatus. Bleed solids could be dewatered to 22 to 28 percent suspended solids concentration without neutralization, 20 to 24 percent S. S. concentration after neutralization. The measured solvent loss to the dewatered solids was about 0.9 gallons per 100 gallons of sludge

TABLE 6-2

RESULTS FROM LABORATORY CENTRIFUGATION OF BLEED SOLIDS

Sample	pH	Cent. Solids (% S.S.)	Lost Organic (% of Bleed) Solids	Bleed Solids (% of Sludge)	SOLVENT LOSS	
					(gal/1000 gal sludge feed)	(liter solvent/ kg solids)
Tampa	1.8	39			1.5	0.40
"	1.7				0.34	
"	6.0		6.0			0.24
"	2.3		0.63			
"	1.8		0.67	24	1.6	
"	6.1		3.3	24	8.0	
"	1.9		0.20	23	0.44	
"	2.1	35				
"	5.0		3.0			0.19
"	2.1	30				
Sharon #1	1.83	47	0.50	7	0.35	0.19
"	2.21	47	0.64	27	1.7	0.21
"	2.35	41	1.7	33	5.6	0.23
"	2.25	49	1.6	34	5.3	0.17
"	1.97	49	0.35	38	1.3	0.09
Sharon #2	5.4	44	3.4	52	17	0.26
"	4.2	39	0.8	45	3.6	0.12
"	5.9	41	1.2	45	5.4	0.14

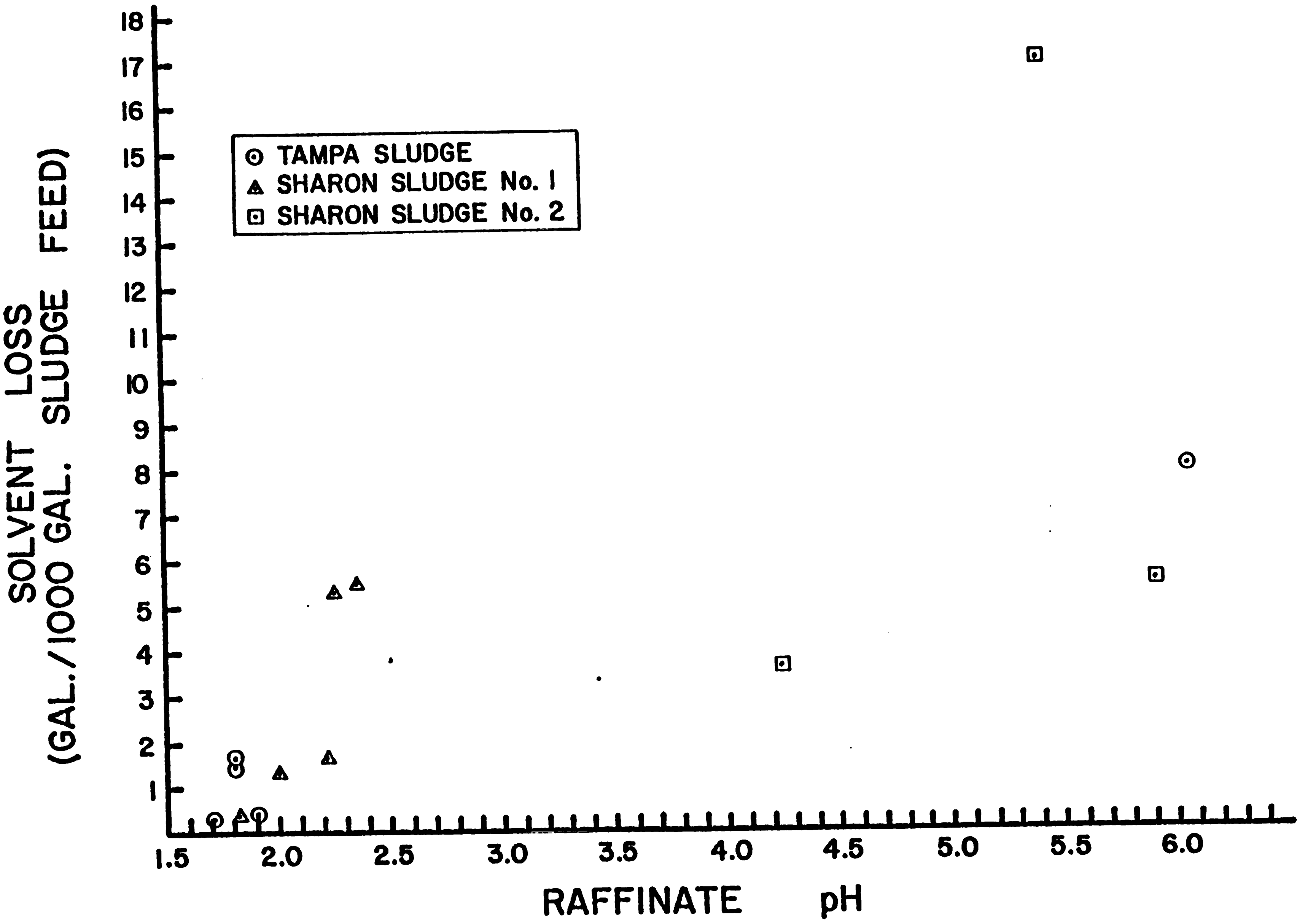


FIGURE 6-5

SOLVENT LOSS TO DEWATERED SOLIDS VS. RAFFINATE pH feed. However, vacuum filtration to recover solvent was a slow process, as the water was removed from the solids before the solvent. Recovery of the solvent resulted in very low filter yields as shown in Table 6-3. The results show that neutralization of bleed solids resulted in lower yields than the already poor values of the pH bleed solids. The filter yields of the Sharon sludges are included for comparison.

The use of soda ash to aid in solvent recovery was not attempted in the laboratory.

6.4 Pilot Plant Results

6.4.1 Characteristics of Solids

In Chapter 5, the wide variations in the raw sludge at Tampa were discussed. These variations produced bleed solids that were unlike those encountered in the lab. When Tampa sludge was fed to the pilot plant system, the solids produced were thin and bulky compared to the solids in the lab. When the very dilute sludge was used as a system feed, the bleed solids were much thinner than at other times. Often under these conditions, "bubbles" of trapped air were formed which caused the solids to float in the solvent. When a thicker sludge was fed, the solids became more concentrated, but they never did approach the concentrations achieved in the lab. The thickness of the bleed solids, and the amount of solids drawn off, were both highly dependent on the draw-off technique and the position of the solids-solvent interface. Only with practice did it become possible to draw-off thick solids with a minimum amount of solvent.

As in the early part of the laboratory operation, the research in Tampa concentrated mainly on the operational aspects of the system, and data taking was somewhat neglected. So, most of the results are based on less data than would be preferred.

TABLE 6-3

FILTER YIELDS OF LABORATORY SOLIDS SAMPLES

Sample	pH	Loading Rate ($lb/ft^2/hr$)	Cake (% S.S.)	Solvent Recovery(%)
Bleed Solids	3.2	.114	22.0	100
		.227	19.9	60
		.454	16.4	20
Bleed Solids	6.3	.031	19.8	100
		.068	16.5	50
		.226	12.3	20
Bleed Solids	5.6	.026	23.5	100
		.074	19.6	50
		.172	16.8	25
Bleed Solids	3.1	.092	27.9	100
		.264	22.9	50
		.410	21.1	25
Sharon Sludge #1		2.21	17.6	-
Sharon Sludge #2		1.22	13.9	-

In pilot plant operation, the bleed solids concentration ranged from 0.3 to 1.3 percent suspended solids concentration. An average value should be about 0.8 percent S.S. The solids draw-off rate averaged 10 to 20 percent of the sludge flow rate. During operation of the DeLaval centrifuge, the solids drawoff rate was intentionally increased to provide bleed solids high in solvent. This will be discussed further in the next section.

An average suspended solids weight reduction can be computed using equation 6-2 and the average data described above. Assuming a feed solids concentration of 0.4 percent suspended solids, and a bleed solids concentration of 0.8 percent S.S. at 15 percent of the sludge flow rate, the reduction in suspended solids is 70 percent by weight.

The pilot plant bleed solids contained much larger amounts of solvent than in the lab. The bleed solids as drawn off generally contained 40 to 60 percent solvent by volume. On occasion, the solvent content was much higher, this was due to the drawoff technique.

In Section 6.3.1 it was noted that no relationship between feed solids concentration and bleed solids draw-off rate seemed to exist. In the pilot plant, a relationship was noted. A plot of feed solids concentration vs. solids draw-off rate is shown in Figure 6-6. An increase in the suspended solids content of the sludge causes an increase in bleed solids draw-off rate. An equation for the relationship was computed using linear regression techniques. Because of high solvent losses (which will be discussed in the next section), fresh solvent frequently had to be added to the system. As a result, raffinate pH levels stayed in the pH 1.8 to 2.2 range at all times when operating the mixer/settler extractors. As expected, no changes in bleed solids characteristics over time were noticed.

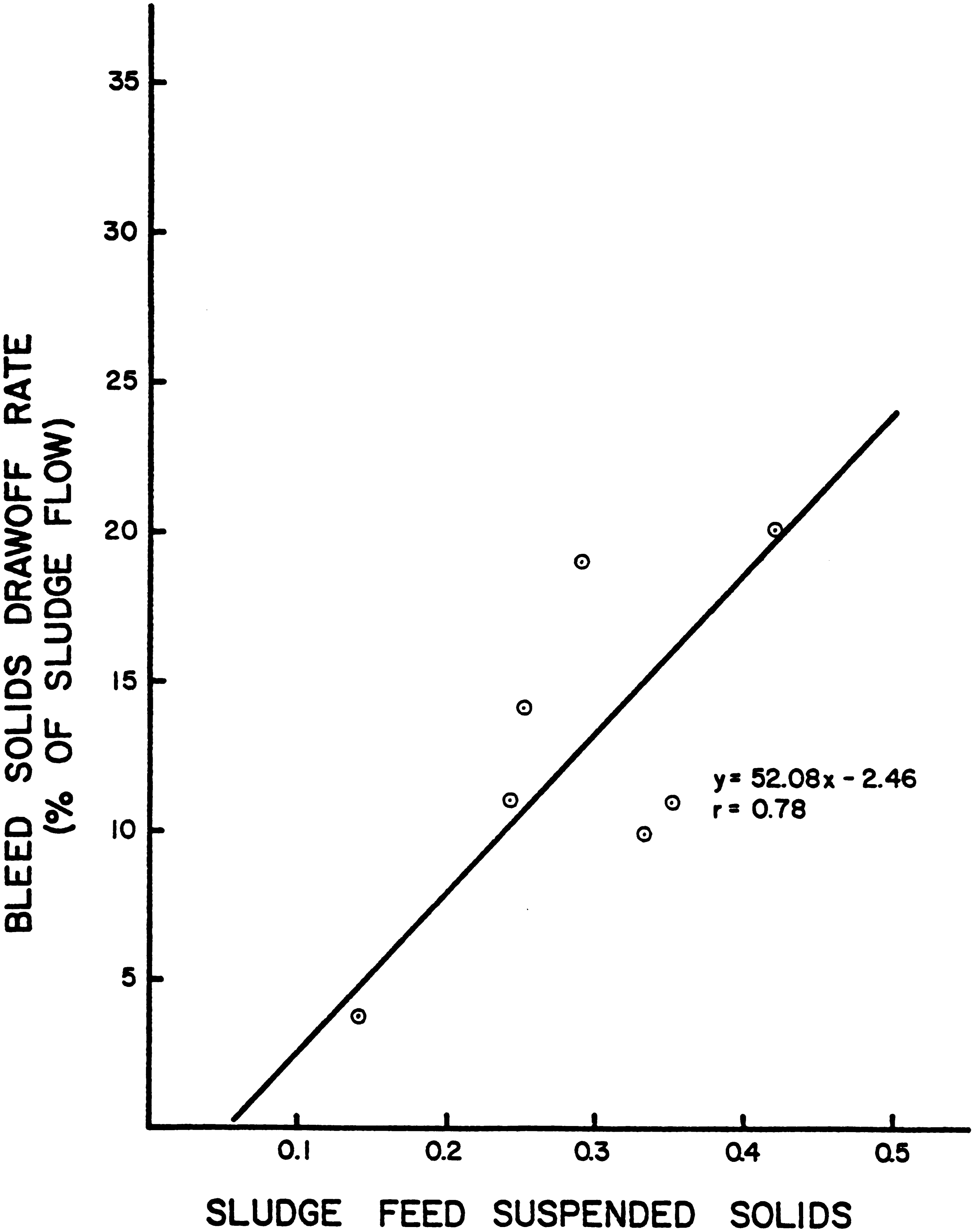


FIGURE 6-6

TAMPA SLUDGE FEED SUSPENDED SOLIDS CONCENTRATION VS. SOLIDS DRAWOFF RATE

6.4.2 Recovery of Solvent

Three methods of solvent recovery were investigated in Tampa. The first method involved the use of a Sharples Model P-600 Super Decanter Scroll Centrifuge. The centrifuge was rated at 2 gpm but could be operated at a maximum of 0.3 gpm for successful solvent recovery. The centrifuge developed 3000 g rotating at 6000 rpm. The scroll was adjusted to minimize the differential speed between scroll and bowl. The centrifuge was fed by a variable speed Moyno pump, discharges were all gravity flow.

Initially, the centrifuge was intended to dewater the solids and produce a solvent-aqueous centrate. In operation, the machine did not dewater the solids, but instead mixed them back into the solvent, producing a messy emulsion. As a result, the machine was modified to produce two liquid streams. The intention was to produce a clean solvent stream and a solids-aqueous waste stream. The basic goal was achieved, but the separation of the streams was incomplete. The centrifuged solids (called the waste stream) contained far more solvent than expected. Results from the use of the laboratory centrifuge to determine solvent loss indicated that the centrifuged solids contained 5-20 percent solvent. Furthermore, the solvent which was discharged by the centrifuge was not highly clarified. At high flow rates (above 0.35 gpm), the solvent stream was very high in suspended solids. Under the worst conditions, the solvent stream had to be re-centrifuged.

Because of the length of the data-taking period and the size of the solvent losses, these losses could be measured directly by keeping track of solvent inventory. The overall solvent losses using the Sharples centrifuge were 12 gallons of solvent per 1000 gallons of sludge feed. This was clearly unsatisfactory, and other solvent recovery methods were investigated starting in July.

The addition of a salt to neutralize the emulsion layer double charge would be expected to aid in the break up of the solvent-solids emulsion. Soda Ash (Na_2CO_3) was tested as a salt to recovery solvent. Addition of the Soda Ash to the bleed solids produced separation of the bleed solids into clean solvent and a dark, cloudy, aqueous waste slurry. The procedure used to recover the solvent was as follows: 1) add 5-8 g/l Na_2CO_3 to bleed solids while mixing vigorously, 2) let settle 2-8 hours without agitation, 3) draw off solvent and solids separately.

Separation of the solvent from the solids was almost complete, leaving a very thin band of solids at the aqueous-organic interface. The bulk of the solids were dispersed into the aqueous phase, free from solvent. Because of the set-up employed in Tampa, recovery of solvent was by manual methods. This made for higher solvent losses than would be possible using good equipment. Loss of solvent using Soda Ash was confined to the narrow band of solids which gathered at the interface. These solids constituted about 5 percent of the original sludge volume and did not.appear to build up over time. Solvent losses using Soda Ash were measured to be 4 gallons of solvent per 1000 gallons of sludge feed. The bulk of these losses were due to the manual transfer of solvent to the organic reservoir. No solvent was detected in the aqueous waste slurry stream. Using proper technique and equipment, the solvent losses would be expected to be significantly lower.

Other potential problems arose with the Soda Ash solvent recovery method. The first potential problem is the effect of the Soda Ash on the extractant. Any extractant which is not completely loaded with aluminum when contacted with Soda Ash will probably extract sodium. This sodium will be stripped out and will end up in the recovered alum. Research by Blake, et al., (24) indicates that Soda Ash does not affect the extractant in any permanent manner, but the problem of sodium carryover does exist. The second problem is that of sodium introduced into the waste stream. In Tampa, the supernatant from the sludge lagoons and drying beds is sprayed onto a nearby golf course. A high sodium concentration in this stream would make it unacceptable for watering grass. Problems would be encountered in full scale operation with the batch process which proved to be necessary. A large amount of bleed solids storage space would be required for operation of a Soda Ash solvent recovery system as described above. The use of a floatation device to aid in mixing and separation may allow a continuous process to be employed.

The third solvent recovery method which was investigated also involved the use of a centrifuge. A BRPX-207 solids Ejecting Centrifuge was rented from the DeLaval Separator Company and tested for two weeks. The amount of time available limited data taking, but a preliminary assessment of the machine can be made.

Because of the way the centrifuge was set up, the best results were obtained with a bleed solids stream high in solvent content. This resulted in a very high bleed solids draw-off rate, which averaged 35 percent of the feed flow rate during operation of the DeLaval centrifuge. The BRPX-207 developed 6500 g rotating at 1800 rpm, and was designed to operate at 5-10 gpm. The centrifuge produces three exit streams: the clean solvent, which is discharged under pressure, the aqueous phase, which is discharged by gravity, and solids, which come out in a timed "shot" under high pressure. The length of time between shots, shot size, and the solvent backpressure could all be controlled by the operator. Before each shot, the bowl was purged with water to minimize the solvent lost in the shot. The purge process does result in some solids being forced into the recovered solvent stream. The shot cycle was generally adjusted to run between 1½ and 4 minutes, with the shot volume set at about 1 gallon, which would be half the total bowl volume. As the feed flow rate to the centrifuge was increased, the shot cycle time had to be lowered in order to keep the solvent clean. At most times, the maximum flow rate to the machine was about 2 gpm, but higher values could be achieved. Initial tests were conducted to gain a basic knowledge of the characteristics of the centrifuge. Numerous tests were run while adjusting the parameters of the centrifuge and varying flow rates in order to determine optimum performance. Only at the very end of the testing cycle was meaningful solvent loss data generated. Results presented below are based on a minimum of 100 gallons of bleed solids per test.

The characteristics of the aqueous waste streams from the centrifuge are presented in Table 6-4. The slurry is the combination of the water waste stream and shot from the centrifuge. The shot averaged 4.1 percent suspended solids concentration, while the water waste phase contained 0.27 percent (2700 mg/l) S.S. concentration. Combining the water waste and the shot produced a slurry which averaged 1.2 percent S.S. concentration. Data from September 20th to September 23rd (the end of the testing) show that the average slurry flow rate was about 1/3 of the bleed solids flow rate. This means that the bleed solids were very high in solvent content. The high solvent content accounts for the high solids drawoff rates necessary with this centrifuge. The average bleed solids concentration was measured to be 0.5 percent suspended solids. Using the slurry data, the suspended solids weight reduction in the alum recovery system is computed to be 66 percent. At the time this data was being taken (September), the raw water color was quite high. As a result, the average suspended solids

TABLE 6-4

CHARACTERISTICS OF DELAVAL CENTRIFUGE AQUEOUS WASTE STREAMS

Date	Run No.	Bleed Solids Prod. (% of Feed)	Shot (% S.S.)	Water Waste (% S.S.)	Slurry (% S.S.)	Slurry Flow Rate (% of Bleed Solids)	S.S. Reduction From Feed (%)
9-12	11	45	6.8	0.22			
	14		4.2				
9-13	16	29	6.9	0.16			
	18		2.7				
9-14	20	36	3.1	0.38			
9-18	27	28	4.2				
9-19		39					
9-20		30					
9-22	37	34	1.9	0.40	1.4	41	56
9-23	40	42		0.11			
	42				1.1	29	72
	43	—	3.5	0.31	1.2	29	71
Average		35	4.1	0.27	1.2		66
Std. Dev.		6.3	1.8	0.11	0.2		9

weight reduction was only 67 percent upon acidification of sludge. So the alum recovery system achieved over 98 percent of the suspended solids reduction predicted by tests of the sludge.

Overall, the DeLaval Centrifuge did a good job of recovering the solvent. Solvent losses were measured in the slurry using the laboratory centrifuge Soda Ash method described in Section 6.2. Losses could only be kept low when the bleed solids were consistent in nature and high in solvent. With the ring dam (105 mm diameter) employed during the tests, most of the solvent loss was into the shot. Losses could be decreased if the feed were automatically cut off during the purge-shot portion of the cycle, as designed. However, equipment incompatability required disconnection of the automatic shut-off valve. Tests with manual feed shut off showed that much lower losses could be achieved. The results from the centrifuge solvent loss tests are presented in Table 6-5. The results show that as feed flow rate is increased, the cycle time decreases. The results also show that solvent losses increase with increasing flow rate. A plot of the relationship between flow rate and solvent loss is shown in Figure 6-7. The Figure also shows the improved solvent loss value achieved by shutting off the feed flow during the purge-shot part of the cycle.

Although more tests must be performed before a final analysis can be made, the results show that the centrifuge can be used to cut solvent losses to 2 gallons per 1000 gallons of sludge feed. Flow rates through the BRPX-207 of 2 gpm are feasible even without feed cut-off during the purge-shot. With the feed cut-off, as designed, flow rates of 4 gpm or above are probably possible with solvent losses at 2 gallons per 1000 or below.

Centrifuge aqueous streams from September 22nd and September 23rd were neutralized using reagent lime. The neutralization results are presented

TABLE 6-5

DELAVAL CENTRIFUGE SOLVENT LOSS DATA

Date	Run No.	Flow (gpm)	Cycle Time (min.)	Feed off during shot ?	Percent Solvent in Slurry	Solvent Loss (gal/1000 gal. Sludge Feed)
9-20	36	3.5	2	no	4	4
9-22	37	1.7	2½	no	1	1.5
	39	3.1	1½	no	3	2.7
9-23	40	1.7	7½	no	1.3	2.3
	42	4.5	1½	yes	2.0	2.4
	43	2.4	3½	no	2.7	3.2
	44	3.2	1½	no	3.3	3.1

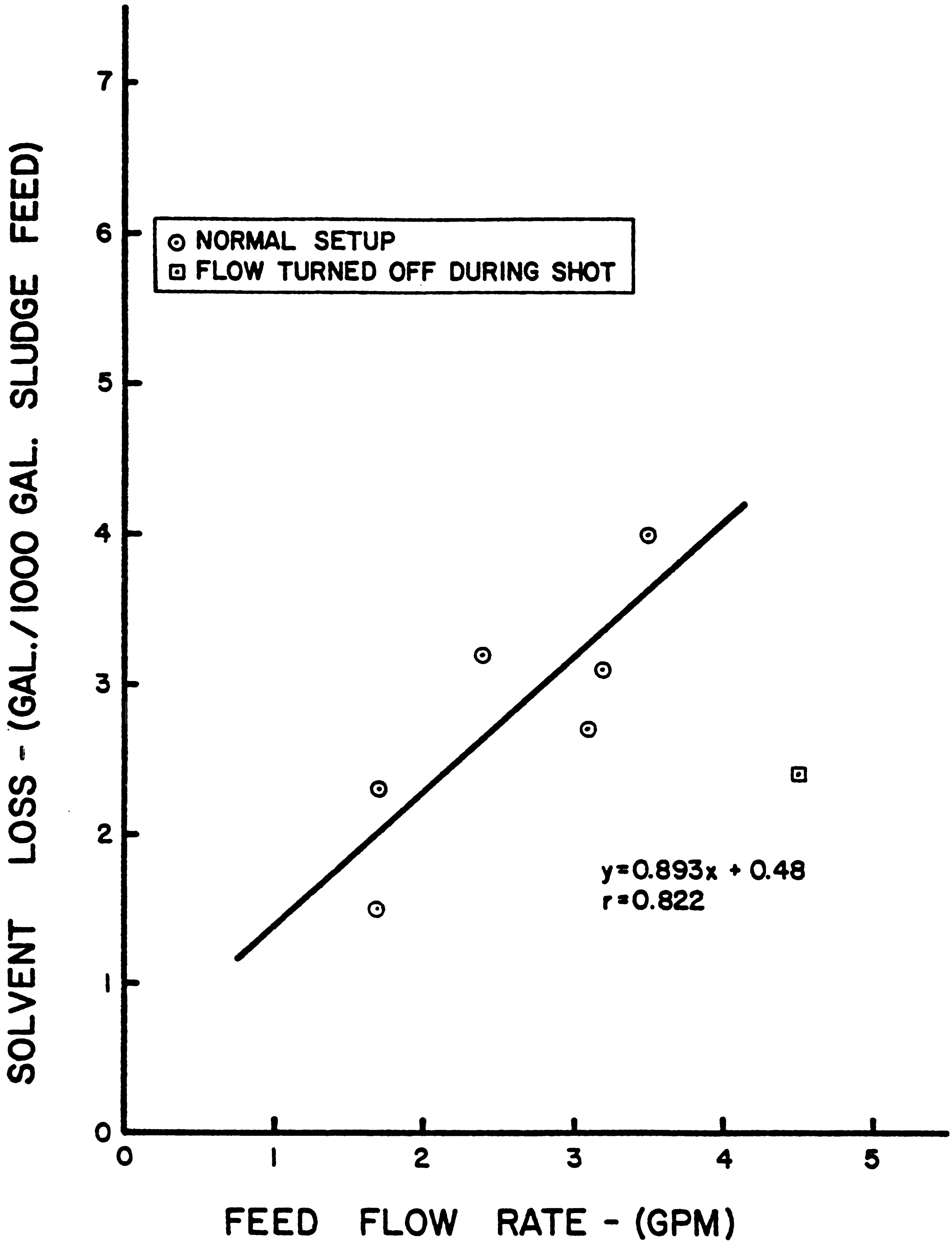


FIGURE 6-7

SOLVENT LOSS VS. FLOW RATE FOR THE DELAVAL CENTRIFUGE in Table 6-6. After 1 hour of settling, the average suspended solids concentration in the slurry was reduced from 1.2 percent to 0.30 percent (3000 mg/l). The average lime dose to neutralize the slurry was 2.9 g/l as 100 percent CaO.

6.5 Discussion of Results

6.5.1 Prediction of Performance from Sludge Characteristics

The use of sludge characteristics to predict the behavior of the mixer/settler extractor was mentioned in Chapter 5. The results from both the lab and the pilot plant show that alum sludge acidification tests can be used to predict the amount of solids produced in the alum recovery process. Results from Tampa sludge show that the weight reduction in suspended solids shown in the alum recovery process is 80 to 100 percent weight reduction experienced by the sludges upon acidification. When the system was operating properly, Sharon sludge showed 100 percent of the suspended solids weight reduction prediction from acidification of sludge.

The sludges from Sharon and Tampa varied greatly in terms of the nature of solids in the sludges. The Tampa sludge was made up of predominantly dissolvable organic and inorganic solids, while the Sharon sludges had a high degree of inorganic solids. The organic solids were expected to dewater poorly when compared to the inorganic solids. Although the Tampa bleed solids did not dewater quite as well as the Sharon bleed solids in the lab, both sludges could be easily dewatered using the small Sharples centrifuge. Solvent recovery appeared to be roughly the same with both sludges, although wide variations in recovery rates were reported. Neutralization of the solids prior to centrifugation resulted in high solvent losses to the solids and would not be acceptable.

TABLE 6-6

NEUTRALIZATION RESULTS OF DELAVAL CENTRIFUGE AQUEOUS STREAMS

Date	Sample	Run No.	% Suspended Solids before	% Suspended Solids settled(after)	lime demand (g/l CaO)
9-22	Water Waste	37	0.40	0.140	2.3
	Slurry	37	1.4	0.312	3.4
9-23	Water Waste	40	0.11	0.018	6.1
	Slurry	42	1.1	0.157	3.4
	Slurry	43	1.2	0.337	1.8
Slurry Ave: =				0.269	2.9

6.5.2 Prediction of Pilot Plant Performance from Laboratory Data

The ability of the laboratory alum recovery unit to predict the behavior of a large scale system is of great importance. In future applications, the design of a full scale system would be based on laboratory results. One of the aims of this research is to establish the relationships between laboratory data and pilot plant results. In Tampa, this was extremely difficult due to the difference in sludges from the lab to the plant.

Reduction in suspended solids, both in volume and weight, is one of the major advantages of the alum recovery process. The Tampa pilot plant sludge did not exhibit consistent suspended solids reduction quantities over the length of the study, making comparisons with the laboratory apparatus difficult. Other factors may have influenced the solids performance. The sludge used in Tampa was fresh while that in the lab was anaerobic and old. From the results with Sharon sludge, the anaerobic sludge probably gave poorer results than fresh sludge would have.

The thickening of bleed solids which occurred in the lab was not noticed in Tampa. In all cases in the lab, the bleed solids were about twice as thick as the feed solids. In Tampa, the bleed solids were about the same thickness as the feed sludge. The feeding of a thin sludge, such as that at Tampa, may not allow the solids layer to thicken properly, resulting in a dilute bleed solids stream. These dilute solids contained a much higher solvent than the bleed solids produced in the lab. It did appear that when the feed sludge to the Tampa system was relatively thick the Tampa bleed solids were much thicker. This would indicate that the relationships noted in the lab would hold true in a larger scale facility, given the same feed strength used in the lab.

The major problem encountered in Tampa that was not predicted from laboratory data was the failure of the Sharples centrifuge. The small centrifuge operating at 3500 g dewatered the bleed solids and recovered a high proportion of solvent in the solids. The large centrifuge developed 3000 g, but it did not dewater the solids to any appreciable extent. Solvent recovery with the large centrifuge was also very poor. The main reason for the poor performance was probably the rotating scroll. The action of the scroll probably tended to partially mix layers after they had been centrifuged which resulted in poor separation.

The DeLaval Ejector centrifuge performed much better. Although solids were again not highly dewatered, solvent recovery was reasonably high. This is in part due to the separation force available, and in part due to the characteristics of this type of machine. Unlike the Sharples centrifuge, the DeLaval is designed to handle two liquid phases and solids. With further research into the operating parameters of the DeLaval centrifuge, losses probably could be lowered furthur.

The Soda Ash solvent recovery method appeared to be a feasible method for solvent recovery. However, problems due to sodium contamination make the method unacceptable at Tampa.

6.6 Disposal of the Aqueous Wastes

Neutralization of the waste stream required a high dose of lime. However, the flow rate of the aqueous waste stream from the DeLaval centrifuge is only 10 to 15 percent of the original sludge flow. After neutralization of the aqueous waste stream, a number of possible disposal alternatives exist. In many plants, the waste stream could be mixed with the filter backwash water and disposed of with the backwash water. Disposal to a wastewater treatment plant may be feasible, since the waste stream has only

10 to 30 percent of the suspended solids of the original alum sludge. Another potential disposal alternative is land spraying after settling. Also, the waste slurry could be settled and the supernatant could be returned to the watercourse. Of course, the aqueous waste stream could be combined with the raffinate, either before or after settling, and disposed of with the raffinate. In Tampa, the aqueous waste stream will probably be mixed with the raffinate before settling or neutralization.

6.7 Conclusions

The primary goal of solids treatment is to recover the solvent as inexpensively as possible. Optimization of the parameters of the system in order to achieve that goal can be accomplished by: operating the mixer/settler system at a pH level of 2.2 or below, using a solids ejector type of centrifuge (such as the DeLaval) to recover the solvent, and by operating the centrifuge so that the amount of solvent lost to the solids is minimized.

Design of a large scale system for Tampa will be based on results of the pilot scale system. The operating characteristics pertaining to the solids for a full scale system are given below.

Given a thickened sludge of 1.2 percent suspended solids at 200 gpm:

1) The solids draw-off rate would be 30 to 50 gpm.
2) Two 50 gpm DeLaval Ejector type centrifuges would be used to recover the solvent.
3) The centrifuges would be operated so that a bleed solids stream containing 50 percent or less solvent could be used as the feed. The operating parameters would be adjusted to expel all solvent from the bowl before the solids shot.
4) The recovered solvent flow would be 10 to 30 gpm.
5) The waste slurry flow would be 10 to 30 gpm. The waste slurry would contain 1.2 percent S.S.

6) The solvent content of the waste slurry would be about 2 percent by volume. The solvent loss into the waste slurry would be 2 gallons per 1000 gallons of sludge feed.

7) The waste slurry would be neutralized using 3.0 g/l CaO, or 2.5 lbs. of CaO per 1000 gallons of sludge feed, or 500 lbs. of CaO per day.

8) Approximately 3000 lbs. of dry solids would be produced each day.

9) 20,000 to 40,000 gallons of waste slurry will be settled and disposed of each day.

CHAPTER 7

THE RAFFINATE

7.1 Introduction

The raffinate is a waste stream produced in both extractor units. It is basically the original alum sludge with most of the aluminum removed. The raffinate is dark in color, and it may possess settleable solids. The raffinate will need to be neutralized before discharging to the waterway.

The major objective of this chapter is to identify the important parameters that will be used to design the full scale alum recovery system. The specific objectives to be examined for the mixer/settler raffinate are:

1) the suspended solids content,
2) the lime dose required for neutralization,
3) the settling time of the raffinate,
4) the metals concentrations in the, raffinate, and if possible,
5) the solvent loss into the raffinate.

The objectives to be examined for the RTL raffinate include those above and also include:

1) the reduction in suspended solids from raw sludge samples and comparison with results from acidification of sludge, and
2) attempts to recover solvent lost to the raffinate.

In addition, a comprehensive testing schedule using the small RTL unit in Tampa allowed a detailed examination of solvent stability to be conducted, and those results are presented in this chapter.

7.2 Background and Previous Research

The solvent extraction industry generally pays very little attention to the raffinate, except to ensure that they have extracted as much of the target metal as possible. Solvent extraction raffinates are generally neutralized and discharged to the nearest body of water, or recycled to leach more metal. As a result, little research has been conducted on treatment of raffinates. Data on raffinate effects on receiving water is non-existent.

Solvent extraction processes generally use prescreening or sedimentation to remove all possible solids from the aqueous feed stream. Raffinates produced from such processes will naturally be low in solids content. Neutralization of such raffinates with lime would result in a solution with a large amount of easily settled solids.

Because the raffinate flow rate is roughly the same as the flow rate of the alum sludge, it probably would be required to meet the same discharge standards as alum sludge. As discussed in Section 2.8, NPDES standards of 30 mg/l suspended solids and a pH of 6.0 to 9.0 are common for alum sludge. It is expected that raffinate streams meeting these standards could be discharged into receiving waters. In some cases, some or all of the raffinate may be used for land spraying instead of being discharged.

Two major problems could be encountered with disposal of the raffinate. The major potential problems are metals uptake by plants and toxicity of organics that are present in the raffinate. Both of these subjects have not been adequately researched. The information that is available on raffinate disposal problems is presented below.

Neutralization of the raffinate and settling of solids should minimize the possible problems with metals, as most metals are not highly soluble at pH 6 to 9. Soluble metals are subject to uptake by plants. Disposal of raffinates into effluent streams which provide irrigation for grazing may prove to be hazardous to animals. Studies investigated by Ritcey, et al.

(25) show that complexed metals are generally less toxic to fish than the ion alone. However, studies indicate that metal-organic complexes can cross cell membranes more easily than metal salts, so they may concentrate more highly in plants. In the stomachs of many fish and animals, the acid environment would cause degradation of the metal-organic complex (stripping), which may lead to increased toxicity. This is an area of study where very little research has been done, and the true hazards to plant and animal life are unknown.

The problems associated with loss of organics into the raffinate may be of greater environmental importance. Further tests discussed by Ritcey (25) show the effects of various petrochemicals on minnows, blue gills, goldfish, and guppies. The results show that 96 hour Median Tollerance Limits (TL_{m96}) for most petrochemicals ranged from 10 to 100 mg/l. As an example, benzene showed TL_m's from 22 to 37 mg/l depending on the type of fish. Two solvent extraction organic solutions were tested for toxicity on coho salmon. The result for Alamine 336 in Kerosene was 110 ppm TL_{m96}, while LIX 64N in Kerosene produced a TL_{m96} of 240 ppm (25). No data on toxicity of the chemicals used in this process exists. This is another area where new research would be helpful.

The loss of solvent into the raffinate is a subject which has been studied because of the cost of replacing the solvent. Studies by Rowden, et al. (26), using LIX 64N in Napoleum 470 to extract copper show that the loss of solvent into the raffinate (organic entrainment) using mixer/settler equipment was quite low. Solvent losses were reported to be less than 20 ppm as the extractor operating phase ratio was varied from 1:1 to 4:1. Research using DEHPA to extract cobalt as reported by Ritcey et. al. (25) and (27) gives solvent losses of 30-56 ppm into the raffinate. Because of the differences in equipment, operating parameters, and chemicals, direct application of this data to the liquid-ion exchange alum recovery process sould not be valid. Data on the loss of solvent using rotating contactors does not appear to be available.

7.3 Methods and Materials

The raffinates from both the mixer/settler and the RTL unit were assessed for suspended solids. In the laboratory, the suspended solids values were measured at infrequent intervals on composite samples of raffinate. Unless otherwise noted, all samples were completely mixed. The bench scale RTL unit was also tested in Tampa for approximately one month. A rigorous solids testing schedule was followed with most values being measured daily. At this time, solvent degradation and solvent loss values were also measured. During the pilot scale studies for both units, frequent measurements of suspended solids were conducted. Solvent losses with the RTL unit were also assessed during the pilot scale operation.

All suspended solids values were tested according to the procedures outlined in Standard Methods (21). Neutralization of raffinate was conducted using reagent grade lime ($Ca(OH)_2$), unless otherwise noted. pH measurements were conducted on a Corning Model 12 pH meter in the laboratory. In Tampa, a Beckman Zeromatic SS-3 pH meter was used. Both meters were standardized at pH 4.0 and 7.0 before use.

All analysis of meters in the laboratory was performed on a Varian Model 375 Atomic Absorption Spectrophotometer. In Tampa, an Instrumentation Laboratory Model 151 Atomic Absorption Spectrophotometer was used for metals analysis. All tests were performed in accordance with procedures outlined in equipment instruction manuals and Standard Methods (21). In Tampa, all metals analysis was performed by the laboratory staff.

Measurement of solvent losses into the raffinate proved to be especially difficult. The digestion method used to determine solvent losses in the bleed solids is impractical with the raffinate. At the expected loss levels, gallons of raffinate would have to be digested to produce one milliliter of solvent. In commercial applications, measurements of Total Organic Carbon (T.O.C.) are used to determine solvent content. This is not possible in this situation because the color in the raffinate would also be measured in any T.O.C. readings. A colorimetric method for determining the concentration of the extractant exists, but interference from the color in the raffinate also makes this unworkable. As a result, solvent losses in the RTL unit were measured only in the solids. In most cases, the small number of floating solids that accumulated in the settled RTL raffinate were the only part of the raffinate which was analyzed for solvent losses. In cases where no floating solids occurred, the bottom solids were examined for solvent. All solvent loss values were measured by the digestion technique presented in section 6.2. This method gave the best results with the type of solids produced by the RTL unit.

7.4 Experimental Results

7.4.1 Laboratory Mixer/Settler

Due to the equipment and techniques being used in the lab, the suspended solids values of the raffinate from the mixer/settler unit were expected to be high. Withdrawal of solids tended to stir up the solids that had collected at the aqueous-organic interface, and these solids went into the raffinate. The suspended solids values of the raffinate were at times very high due to the problems associated with bleed solids withdrawal.

The raffinate suspended solids results from the laboratory mixer/settler unit are presented in Table 7-1. The results show a high suspended solids content in the completely mixed samples. Neutralization leads to a large increase in suspended solids content. The solids settle well, with the average suspended solids value being 227 mg/l after one hour of settling. Unfortunately, neutralized, settled suspended solids values were not measured. Raffinate from Sharon sludge showed lower suspended solids values than Tampa raffinate in every category. This was probably due to the inorganic nature of the Sharon solids which caused fewer solids to be dispersed into the raffinate.

Neutralization results from the raffinates are also shown in Table 7-1. A plot of lime dose vs. the pH of raffinate from Tampa sludge is shown in Figure 7-1. The plot shows a high lime dose is required to raise the pH level to about 4. Above this point, the plot becomes virtually a straight line. The lime dose to reach pH 6 is about 1.1 g/l as CaO. The results from neutralization of raffinate from Sharon sludge were similar, although the lime dose was much lower.

Past results and research have shown that the raffinate does contain some solvent. Because of the problems associated with measurement of solvent in the raffinate, no determination of solvent content in the raffinate was attempted. Raffinate was collected in 5 gallon carboys and allowed to settle to allow any entrained solvent to float to the surface. Visual inspection failed to detect any solvent.

The aluminum content of the raffinate varied according to the operational conditions of the system. Under normal operating circumstances, the raffinate contained 5-50 mg/l aluminum (measured as Al^{3+}) at pH 2. Feed sludges to the laboratory system ranged from 1100 to 2200 mg/l as Al^{3+} at pH 2.

TABLE 7-1

RAFFINATE RESULTS FROM LABORATORY MIXER/SETTLERS

SAMPLE	Suspended Solids(mg/l)	Settled Suspended Solids(mg/l)	Neutralized Suspended Solids(mg/l)	Lime Demand to pH 6 (g/l CaO)
Tampa	615	351		
Tampa	2300	224	4330	1.1
Sharon	590			
Sharon	350			
Sharon	500			
Sharon		105	2400	0.4

FIGURE 7-1

LIME DOSE VS. RAFFINATE pH FOR LABORATORY MIXER/SETTLER
(TAMPA SLUDGE FEED)

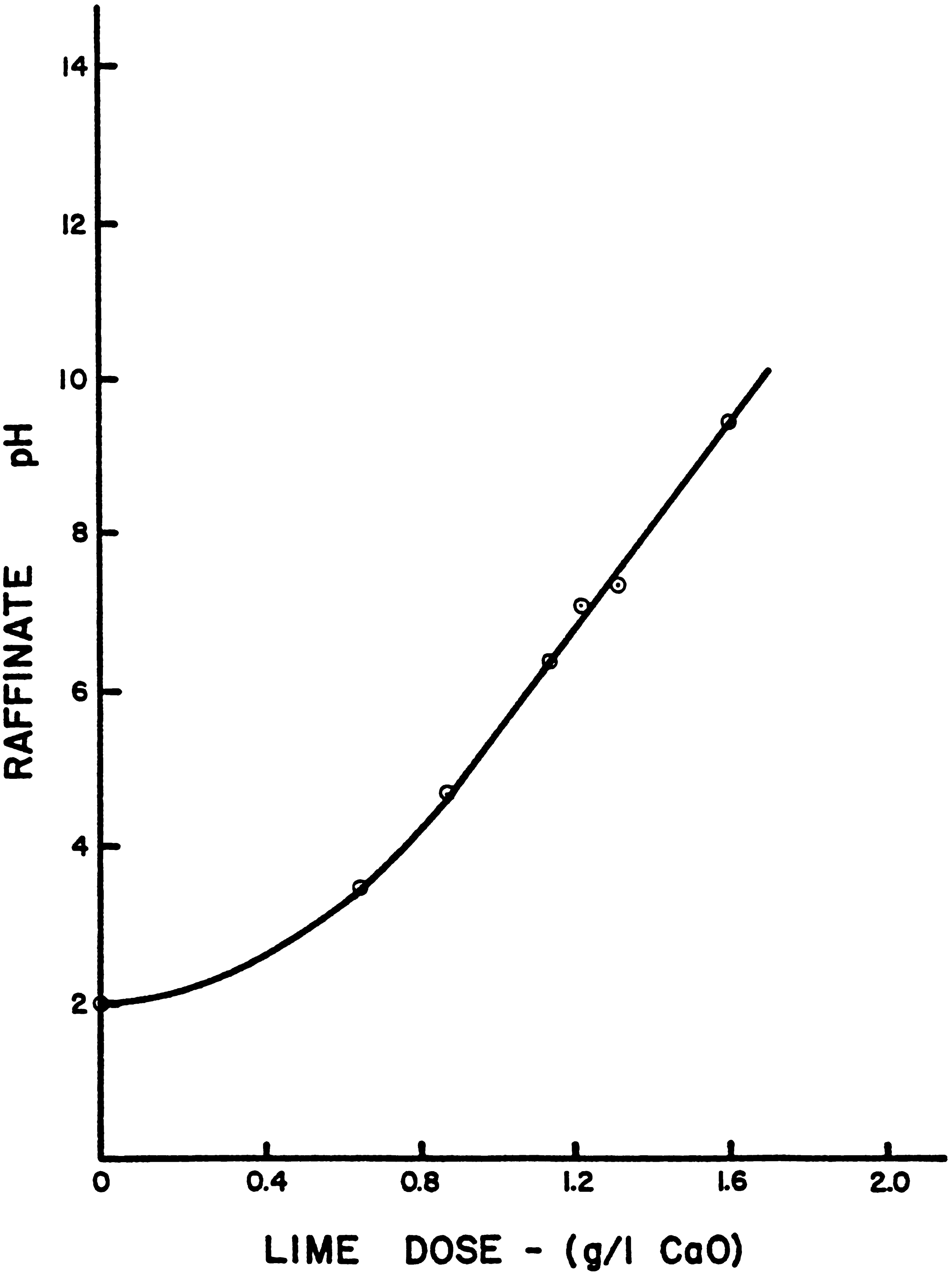


FIGURE 7-1

7.4.2 Tampa Mixer/Settler

The raffinate produced by the pilot plant mixer/settler was similar in nature to the laboratory raffinate. The raffinate flow rate was measured to be approximately 90 percent of the sludge flow rate. The raffinate was highly colored, but contained few suspended solids. Those that were present settled rapidly. All samples tested during the pilot plant operation were grab samples, and were taken while the alum recovery system was operating. Samples of raw sludge and raffinate were analyzed for aluminum at frequent (usually daily) intervals. Samples were analyzed for suspended solids at less frequent intervals during the spring and early summer. Only during the last part of the summer when the DeLaval Centrifuge was operational were suspended solids analyzed daily. A summary of the results of the Tampa mixer/settler data is given in Table 7-2.

The aluminum recovery rate was over 90 percent. The suspended solids content of the raffinate was quite low when compared with laboratory results; some raffinate samples had less than 30 mg/l S.S. The variations in raffinate suspended solids values appeared to be based on the operation of the system rather than on raw sludge characteristics. No relationship between sludge suspended solids concentration and raffinate suspended solids was noted.

A small number of raffinate samples were neutralized with reagent grade lime. The neutralized raffinate samples averaged 2484 mg/l suspended solids when mixed. However, the added solids settle rapidly. After settling for one hour, the neutralized raffinate showed the same suspended solids content as the settled raffinate before neutralization. The suspended solids content in settled raffinate samples averaged less than 50 mg/l. The average lime dose required to raise the raffinate pH to 7

TABLE 7-2

SUMMARY OF TAMPA MIXER/SETTLER RESULTS

Characteristic	Mean	Std. Dev.	No. of samples	Range of Values Minimum	Maximum
Al^{3+} in pH2 sludge (mg/l)	589	308	42	80	1240
Al^{3+} in pH2 raffinate (mg/l)	53.7	50.4	39	4	200
Daily percent Al^{3+} recovery	91.4%	4.7%	37	75.9%	97.1%
Raw sludge suspended solids (mg/l)	3800	1800	17	80	6600
Raffinate suspended solids (mg/l)	131	100	9	27	340

was 1.3 g/l CaO.

Aluminum determinations on neutralized raffinates showed that most of the aluminum becomes insoluble at pH 7. The aluminum content of the neutralized raffinate samples ranged from 1 to 10 mg/l as Al^{3+}. Acidified raw sludge, raffinate, and neutralized raffinate samples were also analyzed for heavy metals. The results are presented in Table 7-3. The pH 2 raffinate shows roughly the same concentrations of most metals as the original sludge. The fact that some of the metals concentrations are higher in the neutralized raffinate than in the pH 2 raffinate is a sign that some of the measurements are not accurate, as all metals tested are more soluble at the lower pH.

7.4.3 Laboratory RTL Unit

The raffinate is the only waste stream from the rotating contactor unit. As a result, considerations of solvent loss and suspended solids reduction, along with raffinate suspended solids, are relevant to this section. These topics, along with aluminum recovery and metals results, will be discussed below. Along with its use in the laboratory, the laboratory RTL unit was also tested in Tampa. The results from the two test locations will be discussed separately. Because the large RTL unit was only tested for three weeks, some of the areas of interest were not adequately studied. This will be further discussed in the section covering the pilot RTL unit.

The laboratory testing of the small RTL unit was conducted under restrictive time constraints and very few suspended solids values were analyzed. Feed solutions from both Tampa and Sharon were tested on the unit. For these tests, a small clarifier was used to settle the solids out of the raffinate. A number of parameters which were later found to be significant were not recorded in the lab tests. The results from the laboratory

TABLE 7-3

MIXER/SETTLER RAFFINATE METALS ANALYSIS

	pH 2 Sludge	pH 2 Raffinate	Neutralized Raffinate
Aluminum (Al)	850	29	3.0
Barium (Ba)	<1.0	<1.0	<1.0
Cadmium (Cd)	<0.01	<0.01	<0.01
Chromium (Cr)	0.35	0.57	0.12
Cobalt (Co)	0.08	0.03	0.08
Copper (Cu)	0.45	0.36	0.21
Iron (Fe)	33	312	0.47
Lead (Pb)	0.50	0.13	0.15
Magnesium (Mg)	12	11.8	18
Manganese (Mn)	0.34	0.30	0.13
Silver (Ag)	<0.01	<0.01	<0.01
Zinc (Zn)	0.11	0.08	0.05
Sodium (Na)	12	8.5	11
Potassium (K)	2.2	2.0	1.9

operation of the small RTL unit are presented in Table 7-4. The results show that an average of 97 percent of the aluminum was recovered. The reduction in suspended solids from Tampa sludge was only 14 percent at a raffinate pH of 2.3. The results from Sharon sludge show a solids reduction of 35 percent with a raffinate pH of 2.2. As no floating solids were noticed in the raffinate, solvent losses were measured by distillation of the settled solids from the clarifier. These solids produced losses of less than 1 gallon of solvent per 1000 gallons of sludge feed. The effluent from the clarifier was not examined for solvent losses or suspended solids content. The lime demand to neutralize the raffinate to pH 6 was 0.9 g/l as CaO. The clarifier produced about 10 percent suspended solids concentration in the settled solids.

During the testing of the small RTL unit in Tampa, samples were analyzed for suspended solids and aluminum on a daily basis. A summary of the results from the six weeks of analysis are presented in Table 7-5. The average aluminum recovery rate was 94.5 percent. The mean daily suspended solids reduction was about 45 percent. Because of the large number of suspended solids samples, a detailed analysis of solids behavior in the RTL system can be undertaken.

During the first two weeks of tests, fresh extractant was contacted with sludge in the extractor at high flow rates in order to determine the capacity of the system. Phase ratios of 1:1 were used throughout the tests. The results from the first two weeks of testing showed that the reduction of suspended solids in the extractor decreased with increasing pH. Some samples at pH levels above 3.0 showed more suspended solids in the raffinate than in the raw sludge. The low temperature employed for drying the solids does not drive off the solvent in the solids which account for some

TABLE 7-4

LABORATORY RTL RESULTS

	Raw Sludge		Raffinate			Clarifier Solids	
SLUDGE	Al^{3+}(mg/l)	Suspended Solids(%)	Al^{3+}(mg/l)	pH	Suspended Solids(%)	Solvent Loss (gal/1000 gal)	Suspended Solids(%)
Tampa	1000	0.35	30	2.3	0.30	0.95	10.1
Sharon	650	1.0	20	2.2	0.65	0.8	9.8

TABLE 7-5

SUMMARY OF SMALL RTL UNIT AT TAMPA

Characteristic	Mean	Std. Dev.	No. of Samples	Range of Values Minimum	Maximum
Al^{3+} in pH2 sludge (mg/l)	1154	374	27	550	2280
Al^{3+} in pH2 raffinate (mg/l)	49	34	29	8	103
Daily percent Al^{3+} recovery	94.5	4.2	29	87.5	99.5
Raw sludge suspended solids (%)	0.61	0.11	24	0.41	0.84
Raffinate suspended solids (%)	0.30	0.15	24	0.14	0.74
Neutralized Raffinate suspended solids (%)	0.42	0.13	22	0.25	0.83

of the error in the suspended solids results.

Approximately four weeks of data was collected while using the RTL contactor to examine solvent degradation. Over this time, the same sample of solvent was contacted with sludge 25 times. The solvent was loaded in the RTL unit and stripped using a conventional mixer. After settling, the stripped solvent was returned to the solvent reservoir for re-use in the system. Raffinate pH and suspended solids of the raffinate, raw sludge and acidified sludge were measured with each loading of the solvent.

A plot of pH and raffinate suspended solids reduction from raw sludge vs. the number of extractant loadings is shown in Figure 7-2. The results show that during the times when the extractant was being loaded for the first time (far left of figure), the values of raffinate pH and suspended solids reduction varied greatly. This was due to the high flow rates employed, resulting in overloading of the system and poor extraction, which resulted in high raffinate pH and low suspended solids reduction values. When the flow rates were decreased, the raffinate pH lowered to 2.0, and the suspended solids reduction from raw sludge increased to almost 80 percent.

The results from the 25 loadings of the extractant are also presented in Figure 7-2. Included are the suspended solids reduction values of raw sludge samples which were acidified. The sludge samples were acidified to the same pH level as the raffinate. The alum recovery system, when operating properly, should achieve roughly the same suspended solids reduction (measured in the raffinate) as the acidified sludge. The results show a rapid decrease in solvent quality within the first 12 loadings, as manifested in the poor suspended solids reduction and rising raffinate pH. A similar occurance was noted with Sharon sludge in the laboratory mixer/settler units (section 6.3.1). During the first twelve loadings, the

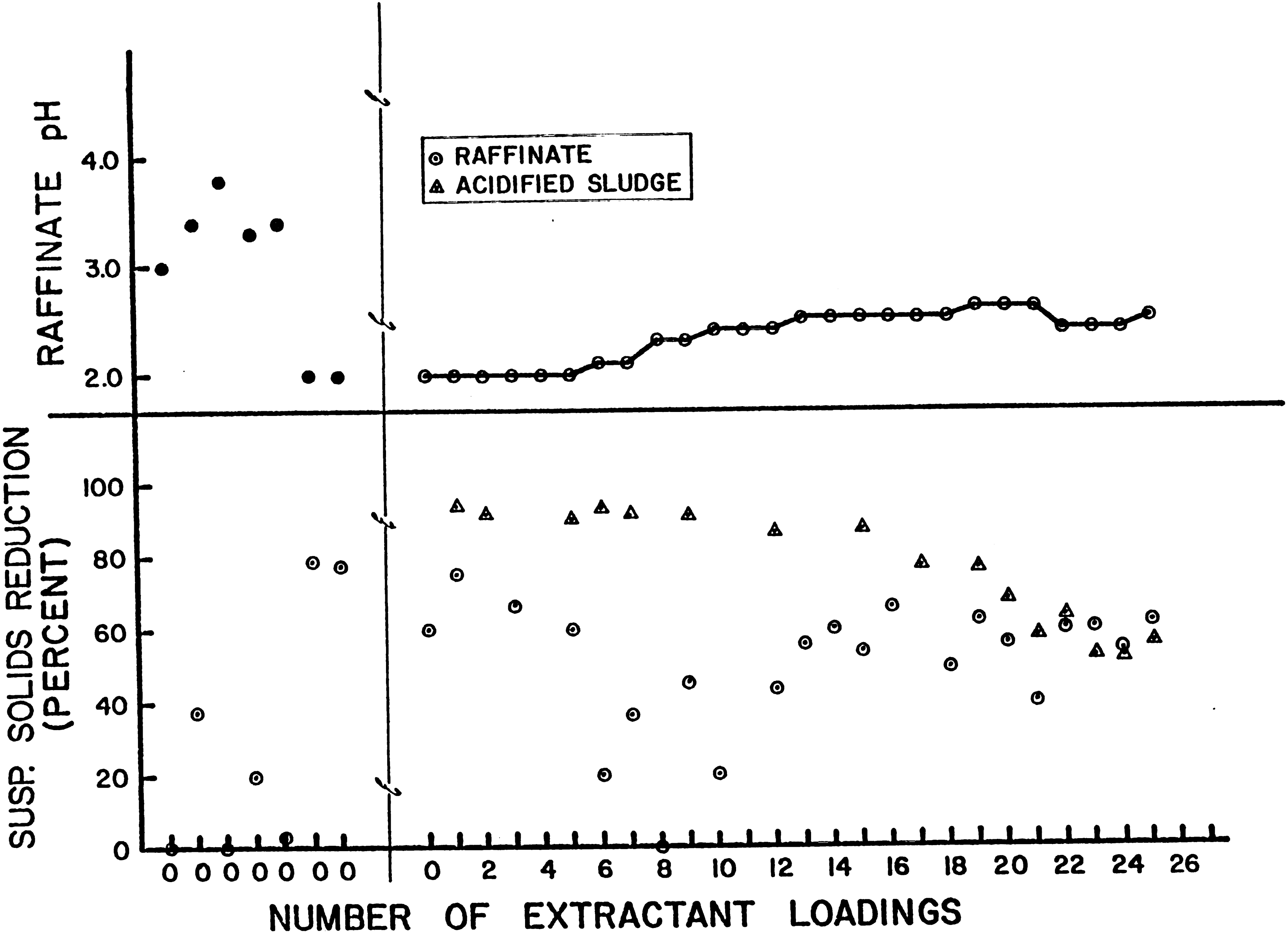


FIGURE 7-2

RAFFINATE pH AND SUSPENDED SOLIDS REDUCTION VS. NUMBER OF EXTRACTANT LOADINGS raffinate pH rose from 2.0 to 2.5, and the suspended solids reduction decreased from about 60 percent to about 40 percent. In some cases, values of less than 25 percent suspended solids reduction were noted. During the first twelve loadings, the sludge exhibited 90 percent or better suspended solids reduction when the pH was lowered to the same pH level as the raffinate.

The system appeared to improve after the thirteenth loading. The raffinate pH fluctuated in the pH 2.4 to 2.6 range for the remainder of the test. The raffinate exhibited better solids reduction qualities as the test proceeded, averaging 60 percent reduction over the second half of the test. During this time, the sludge change which was discussed in Section 5.6 occurred, as the raw water color increased from about 100 Pt-Co units to over 200 Pt-Co units. This resulted in a much lower suspended solids reduction of the acidified sludge as shown during the last week of the test in Figure 7-2. In some cases, suspended solids reductions of less than 60 percent were noted. During the last four days of the test, the suspended solids reduction of the raffinate was as high or higher than the reduction of the acidified sludge.

During these tests, no measurements of solvent quality were conducted. Subsequent tests on the solvent which had been loaded 25 times showed that only the Di(2-ethylhexyl) phosphoric acid remained. The mono form was shown to be slightly soluble in the raffinate, and it had washed out over time.

Solvent losses in the raffinate were measured on only two occasions during this test period. No losses were found in the settled raffinate solids, but losses were detected in the floating solids. As the raffinate pH increased, so did the amount of floating solids present. At pH levels below 2.4, floating solids layers were thin or non-existent. As the raffinate pH increased to 3.0, 5 to 20 percent of the solids in the raffinate were floating. Above pH 3.2, virtually all the solids in the raffinate were floating. These floating solids contained a large amount of solvent, and at high pH levels, losses would be very high. Solvent loss values were measured at raffinate pH levels of 2.6 and 2.3. The losses were measured to be 3 to 4 gallons per 1000 gallons of sludge feed.

Raffinate samples were neutralized using slaked lime form the limehouse at the plant. Neutralization resulted in an increase in suspended solids concentration of about 40 percent as shown in Table 7-5. After one hour of settling, the raffinate suspended solids values averaged 445 mg/l (0.045 percent). Aluminum concentrations in the neutralized raffinate samples were below 10 mg/l as Al^{3+} in all cases.

7.4.4 Tampa RTL Unit

The large RTL unit arrived in Tampa in August of 1979. Only two weeks were available for testing, so less data was collected than was desired. Due to the short time available, the testing program concentrated on determining the extraction efficiency of the extractor at various flow rates. The data reflects the fact that the contactor was not always operating at optimal conditions. As a result, raffinate pH levels were often high, and performance in other areas was also poor. All results and conclusions of this section are based on the data that exists, and in some cases better results might be expected under normal operating conditions.

At the time of the tests with the large RTL unit, the raw water color was over 200 Pt-Co units. As a result, the raw sludge was relatively weak, and exhibited an average suspended solids reduction upon acidification of only 71 percent.

A summary of the results from the pilot RTL unit are presented in Table 7-6. The results show that even including the times of poor operation, the RTL unit recovers over 90 percent of the aluminum in the sludge. Suspended solids values in the raffinate were in most cases measured inaccurately and few accurate values were available. The existing data were taken during times of high raffinate pH and shows poor suspended solids reduction. The average daily suspended solids reduction was measured to be 37.6 percent, which is about half the reduction shown by acidified sludge. Raffinate pH levels ranged from 2.4 to 2.7 during this time. No correlation was noted between raffinate pH and solids reduction.

Solvent loss data is also presented in Table 7-6. A definite correlation was noted between raffinate pH and solvent loss. As the raffinate pH rose due to the operating conditions, the number of floating solids increased. These floating solids contained 60 to 80 percent solvent by volume. A plot of solvent loss vs. raffinate pH is shown in Figure 7-3. The plot shows that at raffinate pH levels below 2.4, the solvent loss was 2 gallons per 1000 gallons of sludge feed or less.

Figure 7-4 shows how solvent loss was related to the percent of aluminum extracted by the system. Although only a few points are available , the plot does show that as the percentage of aluminum extracted by the system decreased, the loss of solvent increased. This plot shows that if the extraction efficiency can be maintained above 90 percent, solvent losses will be about 1.5 gallons per 1000 gallons of sludge feed or less.

Neutralization results on the raffinate show that 2.6 g/l of CaO are needed to raise the pH to 7.0. A metals analysis was run on the raffinate from the pilot RTL unit. The results are presented in Table 7-7.

TABLE 7-6

SUMMARY OF LARGE RTL RESULTS

Characteristic	Mean	Std. Dev.	No. of Samples	Range of Values Minimum	Range of Values Maximum
Al^{3+} in pH2 sludge (mg/l)	484	98	16	370	790
Al^{3+} in pH2 raffinate (mg/l)	47	18	17	22	83
Daily percent Al^{3+} recovery	90.1	3.7	13	83	95
Raw sludge suspended solids (mg/l)	0.48	0.07	17	0.36	0.62
Raffinate suspended solids (mg/l)	0.25	0.03	5	0.23	0.31
Solvent Losses (gal/1000 gal)	1.6	0.86	9	1.1	3.5

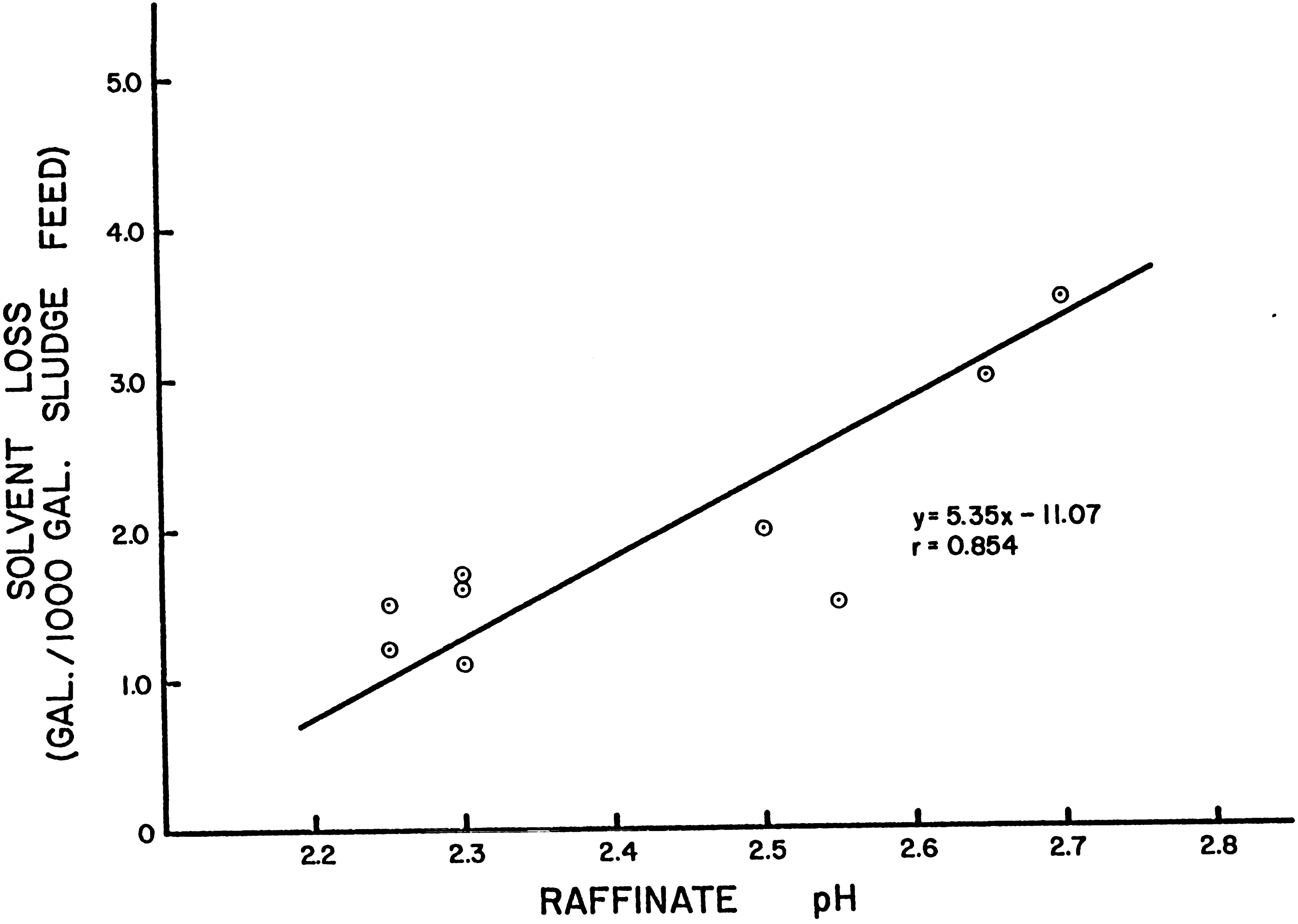


FIGURE 7-3

SOLVENT LOSS VS. LARGE RTL RAFFINATE pH

FIGURE 7-4

SOLVENT LOSS VS. PERCENT ALUMINUM EXTRACTED FOR THE LARGE RTL UNIT

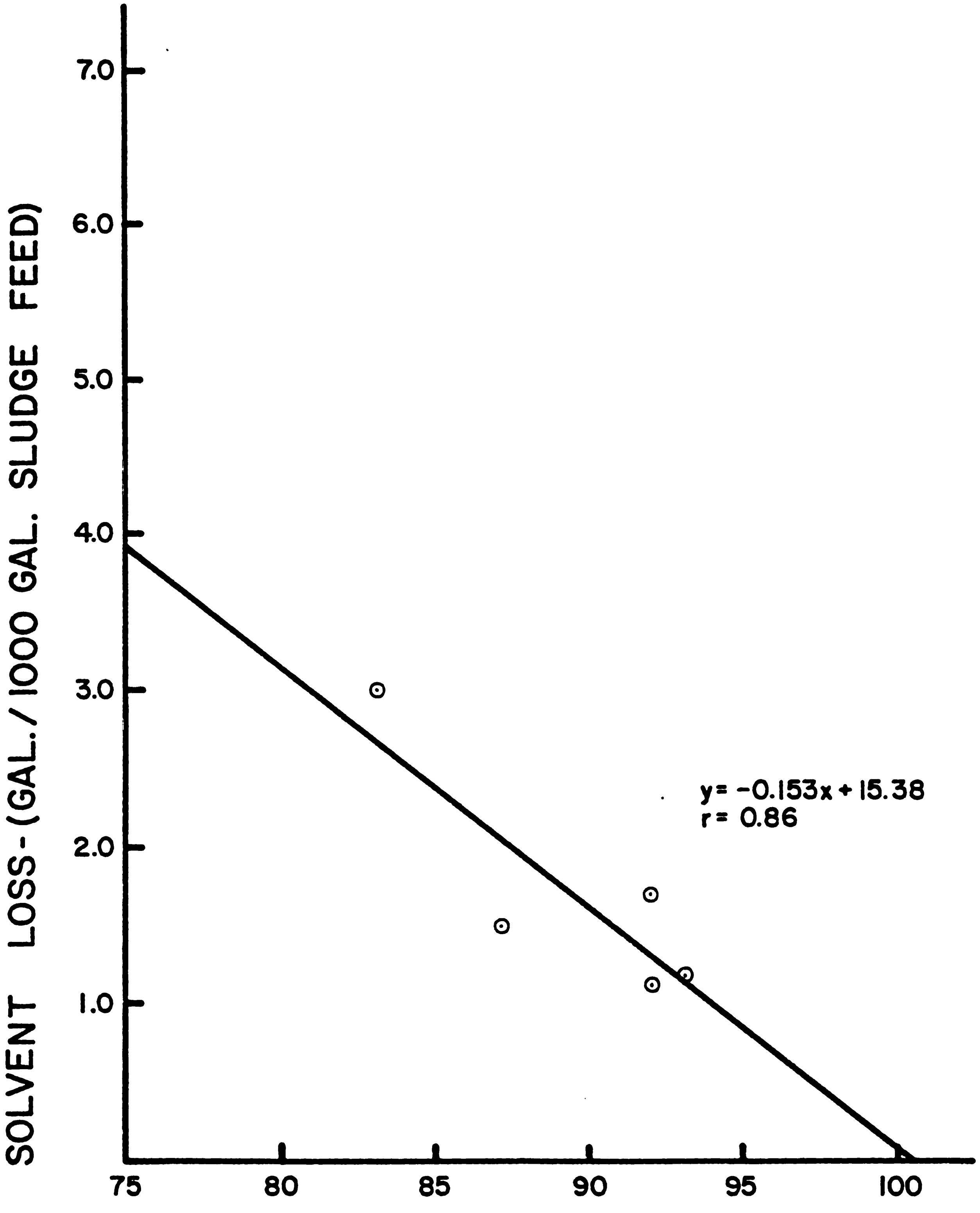

SOLVENT LOSS-(GAL./1000 GAL. SLUDGE FEED)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
75
80
85
90
95
100
PERCENT ALUMINUM EXTRACTED
y= -0.153x + 15.38
r= 0.86

FIGURE 7-4

TABLE 7-7

RTL RAFFINATE METALS ANALYSIS

(All Values mg/l)

	pH 2 Sludge	pH 2 Raffinate	Neutralized Raffinate
Aluminum (Al)	320	48	3.3
Barium (Ba)	<0.1	<0.1	<0.1
Cadmium (Cd)	0.02	0.01	0.02
Chromium (Cr)	0.13	0.13	0.15
Cobalt (Co)	0.002	<0.001	<0.001
Copper (Cu)	0.11	0.12	0.12
Iron (Fe)	17	8.1	7.8
Lead (Pb)	0.25	0.15	0.09
Magnesium (Mg)	6.5	6.5	4.7
Manganese (Mn)	0.24	0.27	0.15
Silver (Ag)	0.02	0.01	0.01
Zinc (Zn)	0.15	0.10	0.12

The results show that the raffinate is of roughly the same quality as the acidified alum sludge. Again the readings of neutralized raffinate that are higher than pH 2 raffinate indicate laboratory error.

7.5 Summary and Discussion

7.5.1 Mixer/Settler Results

The laboratory mixer/settler accurately predicted the qualities of the pilot plant raffinate. In fact, the suspended solids concentrations from the pilot scale unit were much lower than those encountered in the lab. Both systems recovered over 90 percent of the available aluminum in the sludge. In terms of aluminum extraction, the results from a bench scale alum recovery unit can be used in predicting the behavior of a large alum recovery system. The low values of suspended solids in the Sharon raffinate show that a sludge of this nature would probably produce a neutralized raffinate that would meet NPDES discharge requirements (less than 30 mg/l S.S.) with minimal settling. The neutralized raffinate from the pilot scale unit in Tampa must be settled for 1 to 2 hours. NPDES standards could probably be met after settling. The amount of soluble metals measured in the neutralized raffinate would not present a problem in the receiving water. The effects of any entrained solvent are unknown. Neutralization of the raffinate could, in many plants, be accomplished simply by mixing the raffinate with filter backwash water. The combined waste stream could then be settled and discharged to the waterway. If sewers are available, the raffinate could be dishcarged to a wastewater treatment plant. The absence of solids and metals should make the raffinate acceptable to the wastewater treatment plant. In some areas, the neutralized raffinate could be land sprayed, possibly without settling.

7.5.2 RTL Results

The results from both the laboratory and pilot plant operation show that the RTL unit can extract aluminum as efficiently as the mixer/settler extractor. In addition, the RTL unit has distinct advantages over the mixer/settler in other operational areas.

The small RTL extractor adequately predicted the results of the pilot scale unit. Both systems recovered over 90 percent of the available aluminum.

Although the large and small RTL units did show some agreement in suspended solids reduction results, neither achieved the reduction expected from acidification results. The laboratory RTL unit achieved only 14 percent reduction with Tampa sludge, but it showed a 35 percent reduction of Sharon sludge. The Sharon sludge showed only 37 percent reduction upon acidification, much less than the sludge from Tampa. The results with the small RTL unit in Tampa are equally confusing. The Tampa sludges showed only about half of the solids reduction experienced by the sludges upon acidification. The large unit, although hampered by the operating conditions, did not achieve even 50 percent of the suspended solids reduction predicted by acidification.

The explanation for the apparent poor performance of the solids lies in the loss of the mono-form of the extractant into the RTL raffinate. The fact that no MEHPA was detected in the solvent from the small RTL unit after 25 loadings means that the MEHPA was slowly dissolving into the raffinate. The extractant would not be driven off upon drying at 103°C and would show up with the suspended solids. Calculations show that if the MEHPA was lost over the first 20 loadings in the small RTL test at Tampa in equal increments, the weight of extractant lost each day would be larger than the total weight of suspended solids that would be predicted to be in the raffinate. This would mean that the suspended solids values would be more than twice as large as they would be if the extractant was insoluble. It could be postulated that very little extractant was lost during the first few loadings in the lab, and that by the twentieth loading, all the MEHPA was gone. This would explain the very high raffinate suspended solids levels during the major portion of the RTL test. This means that only those values taken during the last few days of the test are representative of the performance of the system with a stable extractant. The extractant solubility also explains the results with the small RTL unit in the lab. Fresh extractant was used for the test with Tampa sludge, and its deterioration resulted in the high suspended solids results of the test. The results from the run with Sharon sludge involved the use of solvent which had been used for the Tampa sludge run. The mono form of the extractant had probably all been dissolved by this time, so the Sharon results were not affected. The raffinate from Sharon sludge achieved over 90 percent of the suspended solids reduction predicted of it by acidification of sludge. The results with the pilot RTL unit are also tainted with the loss of MEHPA. Large batches of fresh extractant were made up not long before the RTL unit arrived in Tampa, and again just after testing started. With the large inventory employed, the MEHPA would not have had time to fully decay before the tests were finished. As a result, all S.S. results with the pilot scale RTL unit are in error. The overall results show that more research must be conducted with a stable extractant before the suspended solids characteristics of the RTL raffinate can be completely understood. Results to date show that the RTL unit can achieve 90 percent or more of the suspended solids reduction predicted by acidification of sludge when the extractant is stable.

The suspended solids from the RTL unit settle rapidly. In the lab, these solids compressed to a suspended solids concentration of 10 percent. The suspended solids content of the neutralized raffinate from the small unit in Tampa that had been settled for one hour was under 500 mg/l. Although no results were analyzed for the large RTL unit, its performance would likely be as good or better than the results from the small units. In a large scale plant, the neutralized raffinate from the RTL extractor would have to be settled before disposal. A sedimentation basin with a four hour detention time would be adequate for settling. A skimming apparatus would be necessary to remove floating solids for further processing. Further settling, filtering, or diluting of the raffinate may be necessary to reach the discharge goal of 30 mg/l. After settling, the neutralized RTL raffinate could be disposed of in any of the ways mentioned in Section 7.4.1.

The most important advantage of the RTL unit over the mixer/settler extractor is the absence of a separate solids phase which must be centrifuged. Solvent losses into the solids from all tests with the RTL units are below 4 gallons per 1000 gallons of sludge feed. These losses are before any type of treatment for solvent recovery. The solvent loss with the pilot RTL unit averaged only 1.6 gallons per 1000 gallons of sludge feed. These losses were concentrated in the thin layer of top solids which formed quickly on the settled raffinate. In full scale operation, these floating solids could be recovered for further processing to recover solvent. The use of a centrifuge rated to handle two percent of the sludge flow rate would be adequate to process the floating solids. Tests with a small laboratory centrifuge that does not develop a high g force show that about 30 percent of the solvent in the floating solids could be recovered. This would reduce solvent loss to about 1 gallon per 1000 gallons of sludge feed.

No tests were conducted with a large centrifuge, but it would be expected that a large centrifuge could reduce losses further.

The tests on RTL raffinate show that it possesses roughly the same concentrations of metals as the alum sludge. With the use of a stable extractant, the problem of solvent in the raffinate should be minimized. As with the mixer/settler raffinate, the metals concentrations present in the waste stream would not be expected to damage the aquatic environment.

7.6 Conclusions

7.6.1 Mixer/Settler Design

The characteristics of the mixer/settler raffinate for a full scale Tampa alum recovery facility are given below.

Assumptions: Sludge Flow of 300,000 gallons per day to the process, 24 hour operation (at 200 gpm) of the process.

1. The raffinate flow rate would be 210,000 to 270,000 gallons per day.
2. A settling basin of approximately 17,000 gallons (2300 cubic feet) would be required for the raffinate.
3. Approximately 3000 pounds of 100 percent CaO would be required each day for raffinate neutralization.
4. Approximately 6000 pounds of dry solids would be produced each day.
5. The raffinate will be discharged into the Hillsborough River, except for that needed for watering the golf course.

7.6.2 RTL Design

The characteristics of the RTL raffinate for a full scale alum recovery facility in Tampa are described below:

Assume: a sludge flow of 300,000 gallons per day at 1.2 percent S.S., 24 hour operation (at 200 gpm).

1. The RTL raffinate flow rate will be 300,000 gallons per day.
2. A 3000 gallon floatation/skimming tank will be used to recover the floating solids from the raffinate.
3. Approximately 75,000 gallons (10,000 cubic feet) of lagoon space will be required to settle the neutralized RTL raffinate.
4. Approximately 6500 pounds of 100 percent CaO will be required each day for raffinate neutralization.
5. Approximately 10,000 to 14,000 pounds of dry solids will be produced each day, depending on the solids reduction qualities of the sludge.
6. Solvent losses will be 1 gallon per 1000 gallons of sludge feed or less.
7. A DeLaval solids ejecting centrifuge rated at 10 gpm will be used to recover solvent from the floating solids.
8. The raffinate will be discharged to the Hillsborough River, except for that needed to water the golf course.

CHAPTER 8

THE RECOVERED ALUM

8.1 Introduction

The analysis of the recovered alum also includes an analysis of the stripping circuits. Mixer/settler strippers were used in conjunction with both types of extraction units. The aqueous stream entering the stripping circuit is sulfuric acid. Results from the first year of research showed that 6 Normal acid produced the best results (20). The acid flow rate to the system is based on the theoretical amount of aluminum available in the sludge. The acid flow rate was controlled to give a recovered alum concentration of 45,000 mg/l as Al^{3+} according to:

$$\text{Acid flow} = \frac{0.9(\text{Al concentration in sludge (mg/l)})}{45{,}000 \text{ mg/l}} \times (\text{Sludge Flow}) \qquad (8\text{-}1)$$

The acid is recycled to keep phase ratios as low as possible, while keeping the organic phase continuous, and to achieve the maximum number of acid contacts with the organic phase.

8.2 Background

During the first year of the alum recovery research project, the selectivity of the extractant was investigated. The results indicate that MDEHPA has a high selectivity for aluminum over potential metal contaminants under conditions encountered in alum sludge. The saturation value of the metals was also evaluated. Saturation value is the maximum amount of metal which could be added to the raw water (ignoring the natural losses of the organic phase and the preferential aluminum extraction). For chromium, this value was 0.006 mg/l, the highest for any of the metals.

The carryover of metals and color into the recovered alum has been a problem with acid treatment alum recovery systems. Color carryover was investigated during the first year of the alum recovery research project. No color contamination was detected in the recovered alum by qualitative measurements. Contamination of the recovered alum with solvent was not assessed. Contamination of the recovered alum can come from four sources, 1) the extraction and stripping of contaminants, 2) entrainment of the organic phase into the alum, 3) entrainment of the raffinate into the loaded extractant which is transferred to the alum, and 4) contamination of the acid. At the phase ratios under which the stripping circuit was normally operated, (4:1 to 3:1) research conducted by Rowden, et. al. (26), shows that entrainment of organic into the aqueous phase is quite low. Their research indicates that organic entrainment is generally less than 50 ppm. However, their research also indicates potential problems with aqueous entrainment into the organic phase. Reported aqueous entrainment values increase dramatically with increases in the operating phase ratio in mixer/settler extractors. Aqueous entrainment values increase from 4000 ppm at an O.P.R. of 2:1 to 15,000 ppm at an O.P.R. of 4:1. These tests were conducted with a copper extraction apparatus using different types of mixers and different chemicals than employed in the alum recovery system, so the results cannot be directly transferred to the alum recovery set-up. However, the high entrainment values of aqueous and the trend of the entrainment values to increase as the operating phase ratio increases are of interest. Carryover of raffinate into the recovered alum would lead to a decrease of aluminum concentration of the recovered alum, as well as contamination with color and metals. Contamination of alum by color or entrained solvent can be measured as total organic carbon (T.O.C.). Tests by Ritcey, et. al. (27), have shown that T.O.C. can be removed from solvent extraction raffinates with the use of activated carbon. Activated carbon would also be expected to remove T.O.C. from the recovered alum.

Commercial alum is manufactured by leaching the aluminum out of bauxite clays with sulfuric acid. Iron present in the clay is also leached out into the acid and this is a major quality control problem with some clays. The leach liquor contains approximately 10 percent Al_2O_3(28). This liquor is diluted to give the 8.3 percent Al_2O_3 found in commercial alum. The American Water Works Association standard for aluminum sulfate (29) requires a minimum of 8.0 percent available water soluble alumina (Al_2O_3) in liquid alum. The standard also calls for a 0.3 percent excess of Al_2O_3 over that theoretically required to combine with the SO_3 present, a maximum iron (Fe_2O_3) content of 0.75 percent, and a maximum suspended solids content of 0.2 percent. Section 5A (Impurities) states that:

> The aluminum sulfate supplied under this standard shall contain no soluble material or organic substances in quantities capable of producing deleterious or injurious effects on public health or water quality.

No quantitative standards for contamination with heavy metals are provided in the standard.

The major objective of this chapter is to characterize the recovered alum stream in terms of contamination. Contamination of the recovered alum in terms of metals concentrations will be presented. These values will be compared with respective contamination results on samples of commercial alum. Jar tests were run with samples of recovered and commercial alum to check the effectiveness of recovered alum in coagulation. When possible, an attempt was made to determine the source of metals contamination in the recovered alum. Finally, samples of water from Tampa which had been treated with recovered and commercial alum were examined for formation of trihalomethanes in order to assess the impact of the recovered alum on organic contamination of finished water.

8.3 Methods and Materials

In the laboratory, the recovered alum was analyzed for metal and organic-color contamination. In addition, the recovered alum was used for jar tests to check its effectiveness against commercial alum. The analysis of metals in the lab was conducted on a Varian Model 375 Atomic Absorption Spectrophotometer. Procedures outlined in Standard Methods (21) and in the operational manual were followed throughout. Contamination with color and organic constituents was measured as T.O.C. on an Ionics Model 445 T.O.C. analyzer. The procedure outlined in the instruction manual was followed when measuring T.O.C.

The jar tests in the laboratory were conducted in 2 liter beakers. A Phipps and Byrd stirrer was used for rapid mix and flocculation of the test water. After dosing with alum, the water was mixed for one minute at 100 rpm. The water was then flocculated for 20 minutes at 30 rpm. The water was allowed to settle for 30 minutes before samples were taken. Turbidity measurements were taken on a Hach Turbidity meter. All other measurements were taken according to the procedures in Standard Methods (21).

All analyses performed at Tampa were by the laboratory staff at the Tampa water plant. Atomic Absorption analysis was performed on an Instrumentation Laboratory Model 151 Atomic Absorption Spectrophotometer. A Varian Aerograph Series 3400 Gas Cromatograph was used to measure total trihalomethanes (TTHM) in the treated water. pH measurements were on a Beckman Zeromatic SS-3 pH meter. The jar test performed in Tampa utilized one liter samples of raw water. After dosing with alum and 5 mg/l SiO_2, the samples were mixed for one minute at 100 rpm. A rapid mix at 22 rpm followed for 15 minutes. Slow mix (flocculation) at 12 rpm continued for 12 minutes. The samples were settled for one hour before testing. Procedures outlined in Standard Methods (21) were followed for analysis of color and alkalinity in the samples.

8.4 Experimental Results

8.4.1 Laboratory Recovered Alum

Problems were encountered at times in the lab in achieving high aluminum concentrations in the recovered alum. The problems were mainly due to the equipment, particularly the acid feed pump. Accurate measurement of flow rates at the low volumes used proved to be the biggest obstacle to successful operation. With frequent, careful adjustment of acid flow rate, aluminum concentrations as high as 60,000 mg/l as Al^{3+} were achieved. Generally, aluminum concentrations were kept in the range of 40,000 mg/l as Al^{3+}. Above 50,000 mg/l, precipitation of aluminum sulfate often occured in the lines.

Carryover of the raffinate into the alum was noticeable in the laboratory apparatus. This resulted in color contamination in the recovered alum and a slight solids buildup in the settler unit of the first stripper. The color contamination in the alum produced from Tampa sludge was much more pronounced than the contamination in the alum produced from Sharon sludge.

The concentrations of selected metals in samples of recovered and commercial alum are presented in Table 8-1. The sample of recovered alum from Sharon sludge was a composite sample taken over a long period of operation. The sample of recovered alum from Tampa sludge shows a high concentration of aluminum. The commercial alum sample is from the East

TABLE 8-1

METALS CONCENTRATIONS IN LABORATORY ALUM

	(All Values mg/l) Sharon-Recovered Alum	Tampa-Recovered Alum	Commercial Alum
Aluminum (Al)	37,500	57,400	61,800
Cadmium (Cd)	1.0	0.5	1.1
Chromium (Cr)	2.6	2.0	3.8
Copper (Cu)	5.1	4	1
Iron (Fe)	1090	71	1800
Zinc (Zn)	65	90	40

Lansing-Meridian Township Water Treatment Plant in East Lansing, Michigan. The results presented in Table 8-1 show that the recovered alum samples are of roughly the same quality as the samples of commercial alum. Most important, the concentrations of Cadmium and Chromium are lower in the recovered alum than in commercial alum.

Total organic carbon tests on recovered alum show that the T.O.C. of the alum was higher than that of commercial alum. Laboratory samples of recovered alum from Tampa sludge showed a T.O.C. concentration of 220 mg/l. In contrast, commercial alum from Meridian Township showed only 26 mg/l T.O.C. Preliminary tests were conducted with activated carbon to assess its ability to remove the T.O.C. from the recovered alum. Tests showed that a dose of 10 g/l of HD3000 Darco Activated Carbon reduced the T.O.C. from 220 to 90 mg/l. No tests were conducted on alum from Sharon, as it contained less color.

The recovered alum was used in the lab to perform a jar test. The sample of recovered alum from Tampa that has already been described in Table 8-1 was used for the test. Commercial alum was used to coagulate the same water in order to compare results. The raw water had the following characteristics: alkalinity = 310 mg/l as $CaCO_3$, color = 250 Pt-Co units, turbidity = 50 T.U., and a temperature of 22°C. The results from the jar test are given in Table 8-2. The results show that the recovered alum performed virtually the same as commercial alum in reducing color and turbidity in the water. Because the recovered alum had more free acid than the commercial alum, it lowered the pH and alkalinity levels more than commercial alum.

TABLE 8-2

JAR TEST WITH RECOVERED AND COMMERCIAL ALUM

Alum Dose(mg/l)	TURBIDITY (T.U.)		COLOR (Pt-Co Units)		pH		ALKALINITY (mg/l $CaCO_3$)	
	Recovered	Commercial	Recovered	Commercial	Recovered	Commercial	Recovered	Commercial
20	3.0	5.7	50	60	7.1	6.8	220	256
40	0.7	2.7	27	33	6.5	6.3	162	213
60	1.7	2.2	27	25	6.0	6.1	106	148
80	2.3	2.5	25	22	5.3	5.7	46	137
100	4.8	2.6	25	20	4.5	5.4	10	78

8.4.2 Tampa Recovered Alum

In Tampa, maintaining a high recovered alum strength proved to be a problem. The weak sludge made the buildup of aluminum a much slower process than was anticipated. This problem was compounded by the fact that the acid feed pump was sized on the basis of the alum sludge used in the lab. With the dilute sludge, the acid feed rate had to be lowered according to equation 8-1 in order to maintain a high aluminum concentration. This meant that the acid pump was operating at the very low end of its pumping curve, where consistent flow rates were not easy to achieve.

A larger problem with the alum was due to the carryover of raffinate into the loaded organic and consequently to the recovered alum. Solvent from the extractor goes into the second stripper where it is contacted with acid which has already been partially loaded with aluminum in the first stripper. Any raffinate which is in the loaded organic transfers directly to the acid in the mixer. This results in dilution and contamination of the recovered alum.

Due to the problems described above, the recovered alum strength averaged about 35,000 mg/l as Al^{3+}. Tests showed that at an operating phase ratio of 5:1 or above in the mixer extractor, the aqueous entrainment in the loaded organic was about 2000 ppm.

Metals tests were conducted on the recovered alum twice in Tampa. The results of the first test (in May) are presented in Table 8-3. The results of the second test (in October) are presented in Table 8-4. At the time of the second test, the pilot scale RTL unit was the extractor for the system. The results show that both recovered alum samples are considerably lower in aluminum than commercial alum. However, in terms of metal contamination, the recovered alum matches up well with commercial alum. The recovered alum is consistently higher than the commercial alum only in Magnesium,

TABLE 8-3

METALS CONTAMINATION IN ALUM
(MAY, 1979)

		(All Values mg/l)	
	Recovered Alum	6N H_2SO_4 Acid	Commercial (Allied) Alum
Aluminum (Al)	32,000	9	57,000
Barium (Ba)	<1.0	<1.0	<1.0
Cadmium (Cd)	0.4	0.4	0.7
Chromium (Cr^{+3})	2.3	<0.1	2.6
Cobalt (Co)	1.8	1.2	3.0
Copper (Cu)	1.5	0.6	1.5
Iron (Fe)	30	35	850
Lead (Pb)	16	4.3	10
Magnesium (Mg)	40	7	33
Manganese (Mn)	7	0.7	7
Potassium (K)	3.3	1.8	2.3
Silver (Ag)	0.6	<0.1	0.6
Sodium (Na)	37	44	37
Zinc (Zn)	13	0.6	0.2

TABLE 8-4

METALS CONTAMINATION IN ALUM
(OCTOBER, 1979)

	(All Values mg/l) Recovered Alum	6$\underline{N}$ H_2SO_4 Acid	Commercial (Allied) Alum
Aluminum (Al)	30,000	2.2	54,000
Barium (Ba)	<0.2	<0.2	<0.2
Cadmium (Cd)	0.20	0.39	0.39
Chromium (Cr^{3+})	1.12	0.05	22
Cobalt (Co)	1.92	1.3	1.70
Copper (Cu)	5.0	0.30	0.80
Iron (Fe)	700	81	1400
Lead (Pb)	3.2	7.2	8.9
Magnesium (Mg)	28	-	5.5
Manganese (Mn)	2.72	0.61	1.80
Potassium (K)	17	-	57
Silver (Ag)	0.36	1.6	0.10
Sodium (Na)	47	-	19
Zinc (Zn)	0.15	7.6	1.7

while the recovered alum is consistently lower in Cadmium, Chromium, and Iron. An attempt was made to determine the sources of the contaminants in the recovered alum. The results are presented in Table 8-5 for the first sample of recovered alum. The results show that the computed values are rarely even close to the measured concentrations. This is another indication that the analysis was not performed accurately. However, the results do show that in many cases, such as Cadium, Magnesium, and Silver, a large portion of the metal detected in the recovered alum was contributed by the acid. The results also show that in many cases the metals concentrations present in the recovered alum cannot be accounted for in any of the sources. Because of the effect of the dilution of the alum by entrained raffinate, attempts were made to lower the phase ratio in the extractor. At operating phase ratios of 4:1 or below, aqueous entrainment was greatly reduced, and the alum strength could be increased easily. However, the extractor tended to "flip" or change phase continuity from organic phase continuous to aqueous phase continuous when the O.P.R. was below 3:1. Under aqueous phase continuous conditions, a very stable emulsion was formed in the mixer as described in Section 6.1. Therefore, great care was required to operate the system successfully at low phase ratios.

A metals balance was also computed on the results from the tests taken in October. The results are presented in Table 8-6. Because the RTL unit was being used to extract aluminum during this time, aqueous entrainment was assumed to be zero. The results indicate that the acid was a major contributor to the contamination with Chromium, Cobalt, Copper, Manganese, Silver, and Zinc. Again, the results show poor agreement between computed and measured values in most cases.

TABLE 8-5

METALS MASS BALANCE IN RECOVERED ALUM (MAY, 1979)

(All Values mg/l)

Metal	(A) Concen. in Sludge	(B) Concentration in Raffinate	(C) Amount Extracted into Alum	(D) Concen. in 6N Acid	(E) Computed Concentrat. in Alum	(F) Measured Concen. in Alum
Al	850	29	48,300	9	30,400	32,000
Ba	<1.0	<1.0	-	<1.0	<1.0	<1.0
Cd	<0.01	<0.01	-	0.4	0.25	0.4
Cr	0.35	0.57	0	<0.1	<0.1	2.3
Co	0.08	0.03	2.9	1.2	2.6	1.8
Cu	0.45	0.36	5.3	0.6	3.8	1.5
Fe	33	3.2	1752	35	1126	30
Pb	0.50	0.13	21.8	4.3	16.5	16
Mg	12	11.8	11.8	7.0	16.2	40
Mn	0.34	0.30	2.4	0.7	2.1	7.0
K	2.2	2.0	11.8	1.8	9.3	3.3
Ag	<0.21	<0.01	-	<0.1	<0.1	0.6
Na	12	8.5	206	44	161	37
Zn	0.11	0.08	1.8	0.6	1.5	13

Assume the system is recovering 90 % of the 850 mg/l Al^{3+} in the sludge and that the acid dose is set to concentrate the recovered alum to 45,000 mg/l Al^{3+}.

$$C = A\text{-}B \times \frac{45{,}000}{0.9(850)}$$

$$C = A\text{-}B \times 58.8$$

Assume: Ext. P.R. = 5:1 → 2000 ppm entrained aqueous sludge flow = 1 gpm

Entrained raffinate flow = 0.002(5 gpm) = 0.01 gpm

$$\text{Acid flow} = \frac{(0.9)(850)}{45{,}000}(1) = 0.017$$

$$E = \frac{(C + D)\ 1.7 + (B)\ 1}{2.7}$$

TABLE 8-6

METALS MASS BALANCE IN RECOVERED ALUM (OCTOVER, 1979)

(All Values mg/l)

Metal	(A) Conc. in Sludge	(B) Conc. in Raffinate	(C) Amount Extracted into Alum	(D) Conc. in 6N Acid	(E) Computed Conc. Alum	(F) Measured Conc. Alum
Al	320	48	42,400	2.2	42,400	30,000
Ba	<0.1	<0.1	-	<0.2	<0.2	<0.2
Cd	0.02	0.01	1.6	0.39	1.99	0.20
Cr	0.13	0.13	0	0.05	0.05	1.12
Co	0.002	<0.001	0.31	1.3	1.61	1.90
Cu	0.11	0.12	0	0.30	0.30	5.0
Fe	17	8.1	1390	81	1470	700
Pb	0.25	0.15	15.6	7.2	22.8	3.2
Mg	6.5	6.5	0	-	-	28
Mn	0.24	0.27	0	0.61	0.61	2.72
K	-	-	-	-	-	17
Ag	0.02	0.01	1.6	1.6	3.2	0.36
Na	-	-	-	-	-	47
Zn	0.15	0.10	7.8	7.6	15.4	0.15

Assume that 90% of the 320 mg/l Al^{3+} in the sludge is recovered and that the acid flow rate is set to concentrate the recovered alum to 45,000 mg/l Al^{3+}.

$$C = A - B \times \frac{(45{,}000)}{320(.9)}$$

$$C = A - B \times 156$$

Assume no aqueous entrainment

$$E = C + D$$

The total organic carbon in the recovered alum was measured and compared with the T.O.C. of commercial alum from Allied Chemical Company. The recovered alum was found to contain 206 mg/l T.O.C., while the commercial alum contained 100 mg/l T.O.C. The recovered alum did possess a darker color than commercial alum, so it is expected that the bulk of the T.O.C. in the recovered alum is color from the raffinate. The recovered alum was tested for T.O.C. removal with three different activated carbons. A dose of 7.5 g/l of Calgon Filtrasorb 400 reduced the T.O.C. to 23 mg/l, the best performance. Carbon from Husky Industries reduced the T.O.C. to 80 mg/l with a 10 g/l dose. A sample of alum dosed with 10 g/l of carbon from both the Calgon and Westvaco tests was colorless. Further activated carbon tests necessary for the design of an activated carbon filter for the alum recovery process are proceding, but are outside the scope of this thesis.

A jar test was performed in Tampa with samples of the recovered alum and commercial alum from Allied Chemical Company. The raw water from the Hillsborough River exhibited the following characteristics: color = 170 Pt-Co units, alkalinity = 70 mg/l $CaCO_3$, total hardness = 92 mg/l $CaCO_3$, and pH = 7.01. The results of the jar test are presented in Table 8-7. Because the recovered alum was so dilute, larger amounts were used to give equal aluminum doses with both alums. As a result, the recovered alum possessed more free acid than the commercial alum and this is reflected in the results.

Samples of the coagulated water from the jar tests were chlorinated and tested for both residual chlorine and total trihalomethanes (TTHM) after one hour and after 24 hours. The results are presented in Table 8-8. The results show that the amount of TTHM's formed are virtually the same with both samples of water, even though the sample coagulated with

TABLE 8-7

JAR TEST WITH RECOVERED AND COMMERCIAL ALUM IN TAMPA

Alum Dose(mg/l)	COLOR (Pt Co Units) Recovered	COLOR (Pt Co Units) Commercial	ALKALINITY (mg/l $CaCO_3$) Recovered	ALKALINITY (mg/l $CaCO_3$) Commercial	pH Recovered	pH Commercial
103	18	18	13	24	5.70	6.05
137	15	12	1	11	4.85	5.70
171	20	13	0	4	4.55	5.01

TABLE 8-8

RESULTS OF TTHM ANALYSIS OF RAW WATER TREATED WITH RECOVERED AND COMMERCIAL ALUM

Sample	Alum Dose(mg/l)	Chlorine Dose(ppm)	Chlorine Residual 1 hr.(ppm)	Chlorine Residual 24 hrs.(ppm)	TTHM 1 hr. (ppb)	TTHM 24 hr. (ppb)
Commercial	6	3.9	3.1	1.2	88	206
	8	5.3	4.9	2.8	47	135
	10	3.1	2.8	5.5	34	113
Recovered	6	9.4	7.8	5.3	78	192
	8	10.5	7.4	5.6	52	136
	10	8.5	2.1	0.3	36	127

recovered alum had been subjected to a much higher chlorine dose. The recovered alum used in these tests had been dosed with activated carbon to remove color.

8.5 Conclusions

The results from all tests show that the recovered alum is basically equal in quality to commercial alum. Only in color contamination (expressed as T.O.C.) is the recovered alum of poorer quality than commercial. This problem can be adequately solved with the use of a granular activated carbon filter on the recovered alum stream. Tests show that the use of the recovered alum does not result in the production of any more trihalomethanes than the use of commercial alum.

In a full scale alum recovery system, it is expected that alum strength could be maintained. In a system with mixer/settler extractors, the operating phase ratio must be kept in the 4:1 range to minimize entrainment. In a system using RTL extractors, the entrainment problems did not occur.

A full scale alum recovery system in Tampa would produce approximately 2700 gallons of contaminant free commercial strength alum each day. Approximately 300 gallons of commercial alum would be required each day for make-up.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Summary of Major Results

The basic objectives of the research were to: 1) recover as much aluminum as possible, 2) produce recovered alum of the same quality and strength as commercial alum, and 3) to dewater and dispose of the waste streams less expensively than with alum sludge.

Over 90 percent of the available aluminum in the sludge was recovered, meaning that alum savings would be quite substantial. The recovered alum was of the same quality as commercial alum and performs equally as well. No cost values were computed on disposing of the wastes from the alum recovery process, but based on the reduction in suspended solids, the savings should be substantial.

9.2 Summary of Specific Results

The specific conclusions of the research described in this thesis are described below.

1. Tampa alum sludge exhibits 70 to 90 percent suspended solids reduction upon acidification, depending on raw water color. Sharon alum sludge exhibits 35 to 40 percent suspended solids reduction upon acidification.

2. 80 percent or more of the aluminum in the sludges from both Sharon and Tampa was dissolved at pH 3.0.

3. The mixer/settler could achieve 80 to 100 percent of the suspended solids reduction predicted by sludge acidification.

4. The bleed solids stream from the mixer/settler units constituted 20 percent of the sludge flow rate.

5. The mixer/settler system requires a solids-ejector centrifuge able to treat 20 percent of the sludge flow rate. The minimum solvent loss was 2 gallons per 1000 gallons of sludge fed to the system.

6. The mono form of MDEHPA is partially soluble in the raffinate and was lost from the system over time.

7. The mixer/settler raffinate after neutralization and settling, contained less that 100 mg/l suspended solids.

8. A lime dose of 1.3 g/l of 100 percent quicklime (CaO) was required to neutralize the mixer/settler raffinate.

9. A mass balance for a full scale mixer/settler alum recovery system in Tampa is presented in Figure 9-1.

10. The solvent loss from the RTL extractor system was 1 gallon per 1000 gallons of sludge fed to the system.

11. The RTL system gave 50 to 100 percent of the suspended solids reduction predicted by acidification of sludge.

12. The RTL system requires a solids ejector type centrifuge able to treat one percent of the alum sludge flow rate.

13. Neutralization of the RTL raffinate required approximately 2.6 g/l of 100 percent quicklime (CaO).

14. A mass balance for a full scale alum recovery system with an RTL extractor is shown in Figure 9-2.

15. Both systems recovered over 90 percent of the available aluminum in the sludge.

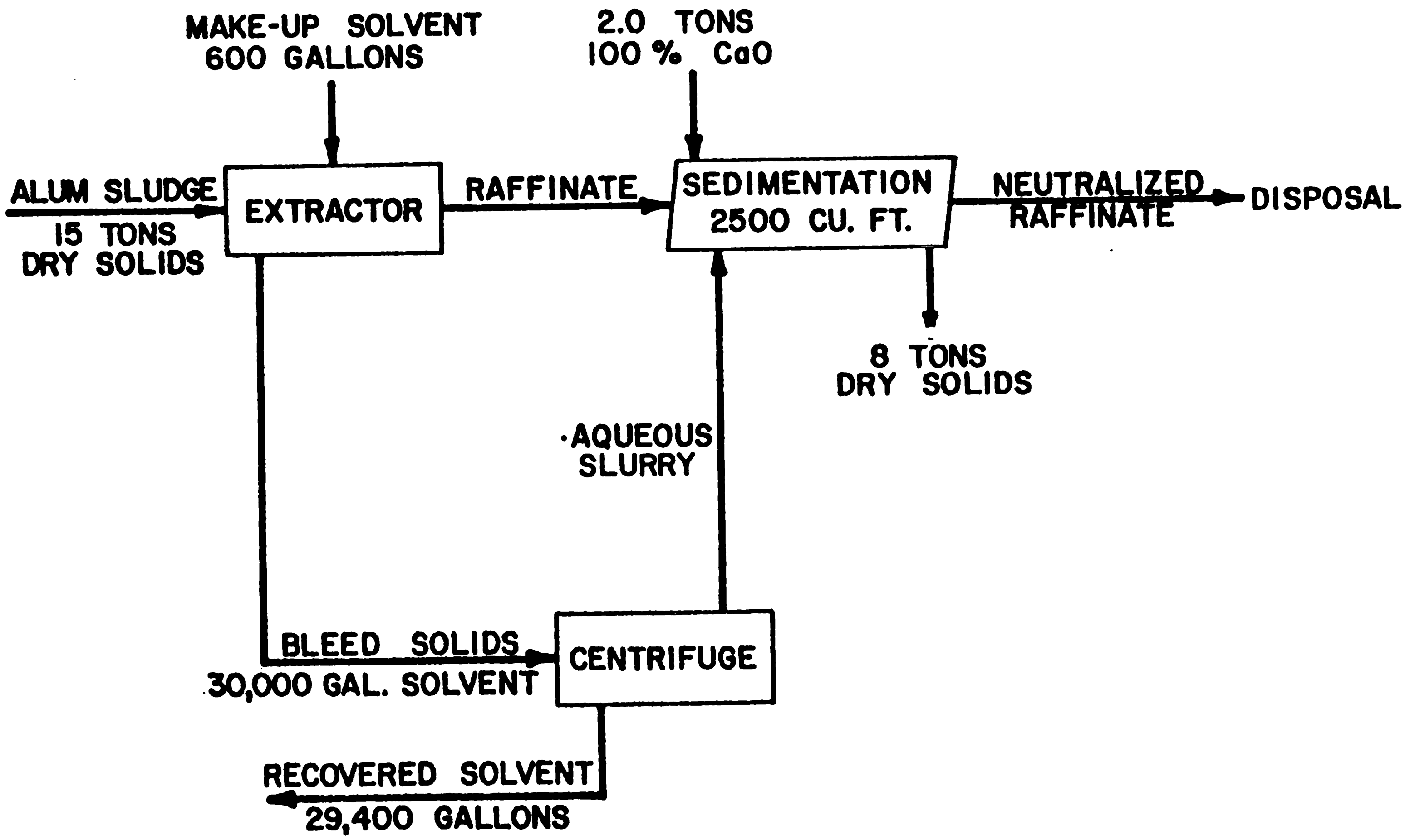


FIGURE 9-1

MATERIALS BALANCE WITH THE MIXER/SETTLER FULL SCALE SYSTEM IN TAMPA

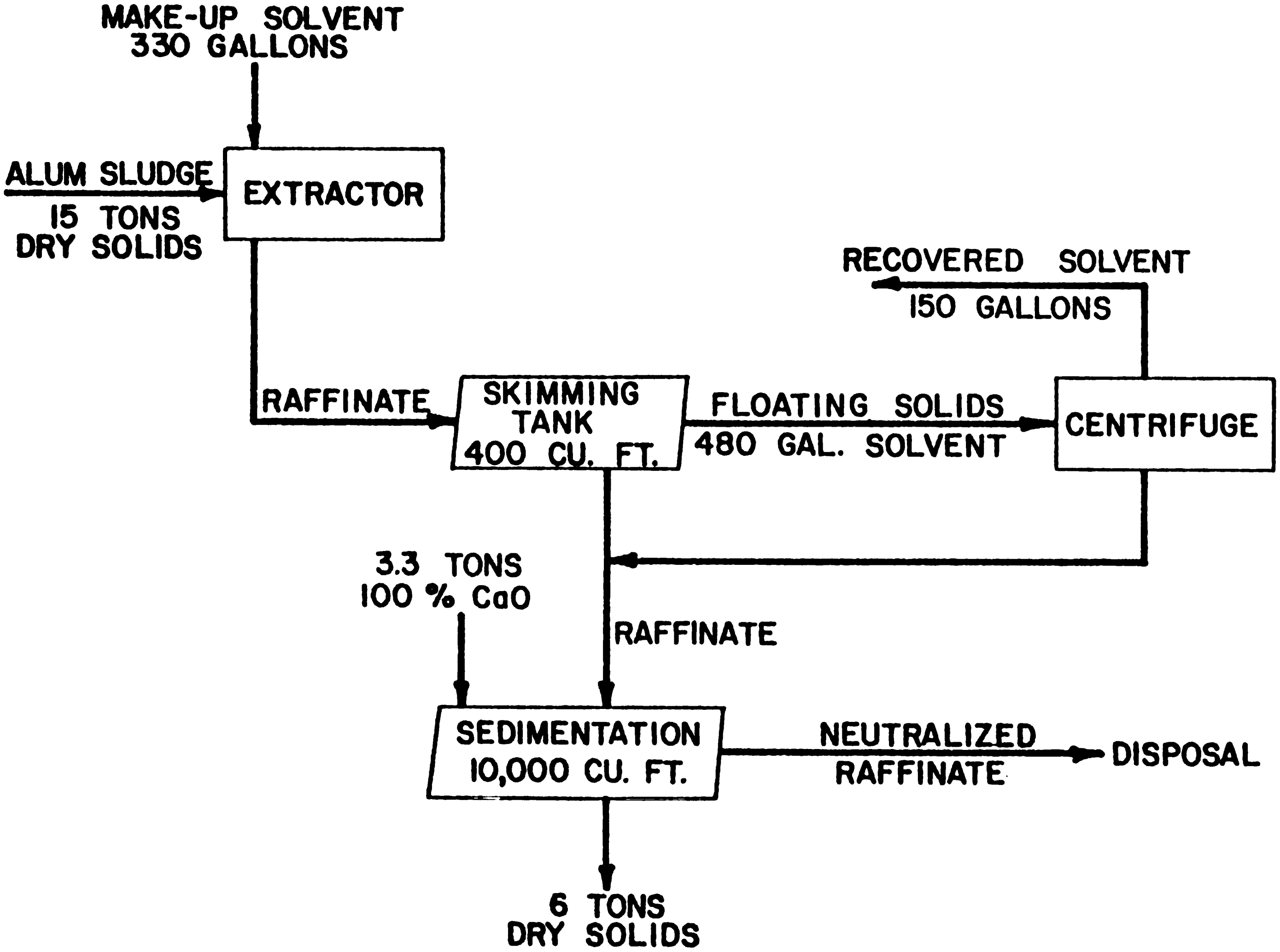


FIGURE 9-2

MATERIALS BALANCE WITH THE RTL FULL SCALE SYSTEM IN TAMPA

16. The recovered alum produced in the alum recovery system was of the same quality as commercial alum in terms of metals contamination, and of somewhat poorer quality in terms of organic contamination.

17. The use of a small granular activated carbon (G.A.C.) filter on the recovered alum reduced the organic contamination value to less than commercial levels.

18. Recovered alum treated with G.A.C. added no more trihalomethanes to the treated water than commercial alum.

9.3 Selection of Full Scale System

One of the extractor systems must be selected for full scale design in Tampa. Each system has its advantages and these are defined below. The advantages of the mixer/settler extractor are as follows:

1. The mixer/settler raffinate has lower suspended solids and requires a smaller lime dose. This would allow for shorter settling times and lower lime cost.

2. The mixer/settler system extracts slightly more aluminum than the RTL extractor.

3. More and better operational data exists on the mixer/settler extractor.

The advantages of the RTL extractor are as presented below:

1. The RTL unit is much easier to operate, and requires less operator attention.

2. Recovery of solvent requires a much smaller centrifuge than with the mixer/settlers.

3. A higher amount of solvent can be recovered with the RTL unit than with the mixer/settlers.

4. Contamination of the recovered alum with raffinate carryover is much less with the RTL unit than with the mixer/settlers.

Based on the information available, the RTL unit was selected for the full scale system in Tampa. The ease of operation of the unit was a very important consideration in selecting the RTL system over the mixer/settler extractor. Other considerations, such as the low solvent loss and requirement for a small centrifuge (as opposed to a large centrifuge with the mixer/settlers) were more important than the advantages of the mixer/settlers. Results of this work will be used as part of the design basis for the full scale system in Tampa.

9.4 Future Research

In previous chapters, many areas of future research were noted. Many other subjects that should be investigated have not been mentioned yet. Major areas in which future research would be helpful are presented below. They are presented with the most important topics (in terms of design for Tampa) listed first. Some of the subjects described below have been examined previously; others have never been investigated.

1) Check the stability of a new extractant (probably Di (2-ethylhexyl) phosphoric acid, DEHPA) in long term operation.

2) For the RTL raffinate:
   a) Determine the suspended solids reduction in the RTL system with a stable extractant.
   b) Determine solvent losses in the RTL system with a stable extractant.
   c) Test a centrifuge for recovery of solvent from floating solids in the RTL raffinate.

   d) Determine lime demand to neutralize raffinate.
   e) Find the maximum S.S. concentration to which the raffinate solids will settle.
   f) Determine the effluent S.S. concentration from the settling basin.
   g) Test the ability of the settled solids to dry on sand drying beds (or other dewatering mechanism).
   h) Test neutralized, settled raffinate for watering golf courses.
   i) Find an ultimate disposal method for the raffinate (probably back to the river).

3) For the mixer/settler bleed solids:
   a) Test solids-ejector centrifuge further to find lowest solvent losses.
   b) Attempt solvent recovery from bleed solids with other mechanical methods, such as belt filter or pressure filter.
   c) Test neutralization and settling characteristics of aqueous waste streams.

4) For the mixer/settler raffinate:
   a) Determine the neutralized, settled suspended solids concentration of the raffinate.
   b) Find an ultimate disposal method for the raffinate and aqueous waste from bleed solids.
   c) Test solids from raffinate and bleed solids for sand drying or other dewatering methods.
   d) Test neutralized, settled raffinate for spraying onto golf course.

5) For the recovered alum:
    a) Determine design parameters for granular activated carbon treatment of recovered alum.
    b) Test recovered alum further for contamination of treated water.

APPENDIX

APPENDIX

GLOSSARY FOR LIQUID-ION EXCHANGE

Alkyl Phosphate - A long chained phosphoric acid of the general form $R_2 = P(O)OH$. Each R group may be an 8-12 carbon chain or one R may be an additional Oh group.

Aqueous Phase - Water based solution.

Bleed Solids - Combination of solids, solvent and water which builds up at the aqueous-organic interface with the mixer/settler extractor.

Cocurrent Contact - Single or multiple contact in which the aqueous and organic solutions flow in the same direction.

Contactor - Device for dispersing and disengaging immiscible solutions; extractor or stripper. May be single stage, as in a mixer/settler or multiple stage, as a rotating bucket contactor.

Continuous Phase - Bulk component that contains droplets of the dispersed component in a mixture of two immiscible solutions.

Countercurrent Contact - Multistage contact in which the aqueous and organic phases flow in opposite directions between stages.

Dewatered Solids - Solids from the extractor which have been processed in order to remove water and solvent.

Diluent - Inert organic solvent in which an active organic extractant is dissolved; also referred to as the solvent.

Dispersed Phase - Component that is diffused as droplets throughout the continuous component in a mixture of two immiscible solutions.

Emulsion - A stable mixture consisting of small droplets of one liquid dispersed in a continuum of another immiscible liquid. The stability is dependent on the strength of the double layer charge of the emulsion.

Extract - Organic phase after extraction (loaded solvent).

Extractant - Organic soluble compound which causes distribution of the metal solute to favor the solvent phase. See alkyl phosphate.

Extractor - Contactor or mixer in which the extraction process takes place.

Feed - Aqueous solution containing the metal to be extracted.

Feed Phase Ratio - Ratio of organic feed flow to aqueous feed flow.

Floating Solids - Combination of solids, solvent, and water which floats in the settled RTL raffinate.

Liquid-Ion Exchange - Solvent extraction where solute transfer involves the exchange of cations or anions between phases.

Loaded Organic - Organic solvent containing metal solute after contacting the aqueous feed liquor; the extract.

Mixer/Settler - Device for liquid-liquid extraction comprising separate mixing and settling compartments. Depicted in Figure 4-1.

Modifying Agent - Substance added to an organic solution to increase the solubility of the extractant (or salts of the extractant) in the solvent.

Operating Phase Ratio - Ratio of total organic flow to mixer to total aqueous flow to the mixer.

Organic Phase - Combination of organic diluent and extractant; often called solvent.

Phase Separation - Separation of immiscible solutions into separate layers due to differences in specific gravity.

Raffinate - The liquid phase from which solute has been removed by extraction.

Rotating Bucket Extractor - See RTL extractor

Rotating Contactor Extractor - See RTL extractor.

RTL Extractor - Device for liquid-liquid extraction comprising a series of slowly rotating buckets separated by baffles. The baffles form a series of compartments in which extraction occurs by gentle mixing. Depicted in Figure 4-2.

Selective Extraction - The specific removal of a desired solute from a feed solution containing two or more solutes.

Solvent - Strictly the diluent. However, often used to describe the organic phase.

Solvent Extraction - Separation of one or more metallic solutes from a mixture by mass transfer between immiscible phases in which at least one phase is an organic liquid.

Stripping - Removal of extracted metal from loaded organic extract.

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