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OPTIMIZATION OF LIQUID-LIQUID EXTRACTION AND STRIPPING BATCH SYSTEMS FOR THE RECYCLING OF ALUMINUM COAGULANTS IN WATER TREATMENT PLANTS

By

Roger Mark Lemunyon

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ABSTRACT

OPTIMIZATION OF LIQUID-LIQUID EXTRACTION AND STRIPPING BATCH SYSTEMS FOR THE RECYCLING OF ALUMINUM COAGULANTS IN WATER TREATMENT PLANTS

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A procedure was developed for the recovery of aluminum when the aluminum was used as a coagulant in water treatment plants. A liquid-ion exchange process was developed to extract the aluminum from the sludge effluent and to regenerate liquid alum for reuse. The process was developed initially using synthetic solutions. This allowed large quantities of sludge to be readily available and solution characteristics to be easily changed. Water treatment plant sludge was then used to predict countercurrent, continuous flow operation. The alum sludge was collected from the Tampa, Florida water treatment plant.

The sludge was first reacted with sulfuric acid to dissolve the aluminum from the organic solids. The supernatant was then separated from the residual organic solids by sedimentation. When sedimentation was utilized, 85% of the available aluminum could be separated.

The acidified aluminum was separated from the supernatant by a liquid-ion exchange process. A kerosene solution containing a 0.84 M solution of extractant was contacted with the supernatant in a 1:1

volume ratio. The extractant was an equal molar solution of mono-di(2-ethylhexyl)phosphoric acid (MDEHPA). A minimum of 99% of the aluminum reacted with the MDEHPA and became kerosene soluble, resulting in separation from the supernatant. A two-stage, countercurrent extraction circuit was required for aluminum recovery.

The kerosene and water were very insoluble and readily separated in a settler. The aluminum rich organic phase was contacted with 6 N H_2SO_4 to force the aluminum into the acid. The organic:acid volume ratio was 15:1. The two-stage countercurrent circuit allowed 49000 mg/l of aluminum to enter the acid phase. The final alum concentration was 49%. The recovered alum was successfully reused for coagulation of a raw water. The organic solution was recycled back to the extraction circuit and successfully reused.

The overall aluminum recovery was greater than 84%.

ACKNOWLEDGMENT

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CHAPTER 1

INTRODUCTION

1.1. Description of the Problem

Water treatment management has undergone vast changes since the enactment of PL 92-500 in 1972. PL 92-500 has specified criteria of effluent quality, namely Best Practical Treatment Currently Available (BPTCA) by July 1, 1977, Best Practical Treatment Economically Available (BPTEA) by July 1, 1983, and a later zero discharge stipulation by the mid 1980s. BPTCA is generally defined as the equivalent sedimentation or filtration process presently being practiced in the water treatment field. BPTEA is generally defined as treatment technology that has been demonstrated on an advanced laboratory or pilot plant scale to be technically and economically feasible.

In order to meet BPTEA criteria, the water utility industry is being forced to abandon the practice of discharging sludge effluent back into the raw water source. At this time the most economical replacement for direct disposal of sludge to the source is dewatering the sludge followed by landfilling. It has been estimated that a 20 percent solids concentration is needed for landfilling the sludge in conjunction with other solid wastes, such as municipal refuse, and that a 40 percent solids concentration is needed for landfilling the sludge alone. Current technology has shown that vacuum filtration can result in a nearly 20 percent solids concentration when preceded by thickening. However, the process is very capital intensive and is generally shown

to be uneconomical. An alternative sludge disposal technique is required if sludges are to be economically and lawfully disposed.

Traditionally, surface water treatment is accomplished by the application of coagulants to the raw water. Aluminum coagulants in the form of aluminum sulfate or alum as it is more commonly named are prevalent in water treatment plants throughout the United States. It has been estimated that 14 million tons of wet weight alum sludge are produced nationally each year [1]. Since alum sludges are of such low density and contain large amounts of water of hydration, dewatering costs are high. In turn, final sludge disposal costs are high.

The zero discharge requirement of PL 92-500 makes alum recovery very attractive in two respects. First, alum recovery has the advantages of reducing coagulant costs and conserving the earth's resources. Secondly, the nature of the alum recovery process reduces sludge dewatering costs and the quantity of sludge requiring disposal.

1.2. Previous Alum Recovery Systems

Present alum recovery methods have not been able to compete economically with conventional alum disposal techniques.

Roberts and Roddy [2] examined the recovery of alum on both a pilot and full scale process. The recovery was reported to be based on the following reaction:

$$2Al(OH)_3(s) + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O$$

The pH range for complete dissolution was between 1.5 and 2.5 depending on the alkalinity of the water. It was estimated that the acid recovery method could reduce chemical costs by 70 percent.

Isaac and Vahidi [3] studied alum recovery as a method of sludge disposal. Isaac tested the alkaline and acid methods of aluminum recovery. He found that caustic soda was never very satisfactory in aluminum dissolution. He also found that the organic color in the sludge was much more soluble in alkali than in acid. Using the acidic method for aluminum recovery, tests were then run on fresh sludge and anaerobically digested sludge. At a pH of 2.5, corresponding to 70 percent aluminum recovery, a 74 percent volume reduction of sludge was obtained. The researchers concluded that the pH should be lowered to about 3.0 for a recovery of about 60 percent to 65 percent of the aluminum. This pH prevented organic color from dissolving to an excessive degree.

Webster [4] found that if sulfuric acid were added to alum sludge to reduce the pH to about 2.4, a clustering effect of the floc particles took place with extremely rapid settling of the insoluble matter. The supernatant liquor containing the alum represented about 80 percent recovery.

Tomono [5] reported that the Higoshimurayama, Tokyo, Japan water treatment plant utilizes alum recovery for the purpose of meeting national effluent regulations. The regulations prohibit water treatment plants from discharging sludge to nearby waterways. The 230-mgd plant utilizes sulfuric acid to reduce the pH of the alum sludge and to dissolve the aluminum from the solids. The recovered alum supernatant is then recycled to be used as a coagulant. The alum concentration ranges from 1.0-1.5 percent as $Al_2(SO_4)\cdot 18H_2O$. Manganese, also dissolved during pH reduction, contaminates the alum supernatant and

builds up after recycling. The alum then has to be disposed. This usually occurs after 3-4 recycles.

Streicher [6] conducted pilot tests to determine the usefulness of acid recovery of aluminum followed by filter pressing the remaining organic sludge. The pH was reduced to 1.5 to 2.5 by sulfuric acid. He found that when the ratio of $Al(OH)_3(s)$ to other suspended matter in the sludge was high, considerably less than stoichiometric amounts of sulfuric acid were required. If the ratio were low, more than stoichiometric amounts of acid were needed. Acid treatment resulted in reduction of sludge volume to less than 10% of the original volume and a concentration of the sludge to 20% solids. The alum recovery was 80% to 93%. The residual sludge was concentrated to 40% to 50% solids with the use of a filter press.

Westerhoff and Daly [7,8,9] conducted a complete study of various alum sludge dewatering facilities. They included pressure filtration with and without alum recovery, centrifugation, rotary vacuum filtration, horizontal vacuum filtration with and without alum recovery, coagulation, filter pressing, and freeze-thawing. The studies showed alum recovery followed by horizontal vacuum filtration to be a workable process warranting economic consideration. Alum recovery varied from 50% to 90%. Coagulation basin sludge was thickened from an initial 4% to 6% solids to a final 21% solids content by acid treatment. After filtration the solids content was 37%. However, because of the low alum dosage used for turbidity removal, the most economical method of alum sludge treatment was determined to be pressure filtration without alum recovery.

1.3. Rationale for Research

The review of alum recovery literature indicated that acid dissolution techniques for alum recovery may be applicable for plants with a raw water of high quality. These plants would have a low concentration of contaminants in the acidified sludge. However, those plants with poor water quality that use large quantities of alum cannot successfully apply simple acid dissolution for alum recovery methods. Simple acid dissolution techniques do not meet the major goals of an alum recovery process as outlined below:

1. The recovery system must have a procedure to prevent contamination of the recovered alum other than by decreasing aluminum dissolution. Presently by decreasing the overall recovery of aluminum, the make-up costs and costs for residual solids disposal are increased;

2. The recovery system must separate the residual solids from the acidified aluminum. Presently when sedimentation is used, a large amount of aluminum is lost in the wasted sludge. When filtration is used, the costs for sludge disposal remain high;

3. The recovered alum must be in a suitable concentration for ease of monitoring, pumping and dosage control.

1.4. Objectives of Research

Since this research is the first year study of a continuing research project, it is best to outline the purpose in two phases: overall and specific first year objectives.

The purpose of the overall research is to develop an economical aluminum recovery system in potable water treatment. A liquid -ion exchange procedure will be utilized. To become successful, the recovery system must meet the following objectives:

1. The recovered aluminum should be contaminate-free;

2. The recovery process should dissolve all the aluminum and recover as much as feasible for reuse;

3. The recovery system should result in residual solids which can be easily disposed;

4. The recovery alum concentration should be comparable to commercial alum to allow direct reuse.

The first year objective of this research was the static optimization of the extraction and stripping conditions in liquid -ion exchange laboratory batch systems. The purpose of this approach was to evaluate the future feasibility of using liquid -ion exchange for alum recovery and recycling. The end result of the first year research was to be a specific recommendation concerning continuation of the research on a continuous-flow basis in the laboratory.

The research was conducted in the following chronologic order. First, the liquid-ion exchange process was evaluated on synthetic aluminum solutions. The advantage of this approach was that control and variable parameters could be easily changed. Large quantities of synthetic solutions were also readily available. Secondly, the liquid-ion exchange process was applied to an alum sludge. The result was final optimization of parameters that need to be involved in the liquid-ion exchange operation.

CHAPTER 2

CHARACTERISTICS OF ALUMINUM COAGULANT SLUDGES

Alum sludges are characteristically different than other coagulant sludges found in water treatment processes. Water contained in the alum sludge is bound to the sludge itself through hydrogen bonding. The resultant sludge is of a high volume, low density aluminum-hydroxide water floc nature. Due to the hydrated nature of the sludge, conventional dewatering is difficult to apply and too expensive to justify.

Disposal of alum sludges can be more easily accomplished when the volume of sludge to be disposed can be reduced. Treatment of alum sludge has primarily been accomplished by vacuum filtration, filter pressing, sand drying beds, or centrifugation. The most effective means of sludge dewatering are vacuum filtration and filter pressing. The solids are separated from the water, leaving a higher concentration of solids. However, there is an economical obstacle faced by these conventional processes. The water contained in the alum sludge is bound to the sludge itself through hydrogen bonding, making the high volume reduction of sludge nearly impossible to achieve.

The following simplified reactions have been proposed to occur to account for the high volume, low density aluminum-hydroxide water floc formation:

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

or, in the absence of alkalinity

$$Al_2(SO_4)_3 \cdot 14H_2O = 2Al(OH)_3(S) + 2H_2SO_4 + 8H_2O$$

Under equilibrium conditions, aluminum would exist primarily as insoluble $Al(OH)_3$. However, researchers [10] have shown that under nonequilibrium conditions existing in water treatment plants the floc species is not $Al(OH)_3$ but a positively charged species. Two of the more accepted forms are $Al_x(OH)_2^{+0.5x}_{2.5x}$ by Brossett [11], and $Al_8(OH)^{+4.0}_{20}$ by Matijevic [12]. In all of the proposed species the aluminum is associated with a high concentration of hydrated water molecules.

Due to the hydrated nature of the sludge, the conventional dewatering processes are very expensive. An alternative to mechanically separating the hydrated water would be to dissolve the aluminum in solution, thereby releasing the hydrated water, and allowing the residual solids to settle.

The aluminum-hydroxide floc is amphoteric in that it will dissolve in acid or alkali. Recent studies [3] have indicated that acid dissolution is more effective in dissolving the aluminum.

If alum recovery is to compete favorably with existing sludge disposal processes, the cost savings must be large enough to offset the additional capital and operating costs required for recovery.

CHAPTER 3

LIQUID-ION EXCHANGE

3.1. Introduction

Solvent extraction is a unit process of extractive metallurgy. Mixtures of different substances are separated by treatment with a selective liquid solvent. At least one of the components of the mixture must be immiscible with the treated solvent so that at least two phases are formed over the entire range of operating conditions used. Liquid-ion exchange is a specific type of solvent extraction.

3.2. Terminology of Liquid-Ion Exchange

Terms used in liquid-ion exchange unit operations were defined in Appendix A. Additionally, the more important terms and operations essential to a working knowledge were discussed in the body of this research paper.

3.3. Historical Description of Liquid-Ion Exchange

Interest in liquid-ion exchange as a unit operation was intensified by its successful use in producing purified uranium compounds during the Second World War. From 1942 to 1953, the Mallinckrodt Chemical Works [13] operated a uranium refinery for the Atomic Energy Commission utilizing an ether extraction of uranium nitrate substantially as described by Peliot in 1842. A refinery placed into operation in 1953 by the National Lead Company [14] used tributylphosphate as the uranium

nitrate extractant in the same purification process. In this same period of time, the Bureau of Mines [15] started production to separate hafnium and zirconium under an Atomic Energy Commission project. The basic process used was developed by the Oak Ridge National Laboratory. Hafnium was extracted from hydrochloric acid as a thiocyanate complex by methyl isobutyl ketone.

Concurrent with these extraction developments, systematic searches for other extractants were conducted by a number of research laboratories, particularly those of the Dow Chemical Company [16] and the Oak Ridge National Laboratory [17]. These studies led to the commerical use of octyl pyrophosphone acid for recovering by-product uranium from phosphoric acid in 1955, and the use of alkylphosphoric acids and aliphatic amines for recovering uranium and vanadium from sulfuric acid solutions in 1956. Also in 1956, a Bureau of Mines [18] process enabling separation of columbium (present name, niobium) and tantalum was put into commercial use. The tantalum and columbium form complexes in a hydrofluric acid-sulfuric acid solution and then are extracted into hexone.

Liquid-ion exchange has been used since 1959 in processing tungsten ore for recovering thorium from uranium wastes. In 1963, General Mills [19] introduced their first extractant which would purify copper from leaching low-grade oxide ores. Copper purification by liquid-ion exchange has become so popular that today over 300,000 metric tons of cathode copper will be produced by liquid-ion exchange [20]. General Mills [21, 22, 23, 24] continues to research liquid-ion exchange and has become one of the leading authorities in this field.

In 1977, liquid-ion exchange is used in commercial plants for the recovery of uranium, molybdenum, vanadium, tungsten, thorium, copper, boron, tantalum, columbium, hafnium, aluminum, and zirconium. It has been shown in pilot plant work that liquid-ion exchange may be used for the recovery of nickel, cobalt, the rare earth metals, and iron. In principle, almost any metal and most of the non-metals can be separated and purified by a solvent extraction procedure. The question is often not how to do it technically, but how to do it economically.

3.4. Application of Liquid-Ion Exchange to Aluminum Purification

The research literature indicates that liquid-ion exchange has been applied in attempts to purify aluminum in two cases, one in waste dump leaching solutions and the other in wastewater sludges.

George [25] in 1968 reported that aluminum could be purified from iron acid leachings economically. The process description followed these essential steps:

1. Aluminum was extracted from an acidic sulfate solution essentially free of ferric iron, with a kerosene solution of an alkyl phosphoric acid, preferably a monoalkyl phosphoric acid. Extraction from acidic chloride or nitrate solutions was also possible.

2. Aluminum was stripped from the loaded organic extractant with 6-8 N HCl, to yield a solution of aluminum chloride rich in aluminum and depleted in H^+. Simultaneously, the organic extractant was regenerated to the acid form and was recycled to the extraction circuit.

3. The aluminum chloride strip solution was gassed with HCl to restore the concentration of free acid to 6-8 N. Simultaneously, most of the aluminum was selectively precipitated as crystalline $AlCl_3 \cdot 6H_2O$. The precipitate was filtered and washed with fresh HCl and the filtrate and washings were recycled to the stripping circuit. The principal impurity in the filtrate was ferric iron.

The buildup of ferric iron was controlled by extracting Fe^{+3}, as the chloride complex, from a small bleed stream, with a kerosene solution of tributyl phosphate or an alkyl amine.

4. The solid $AlCl_3 \cdot 6H_2O$ was thermally decomposed to produce alumina and recover HCl for reuse.

Although the extensive research indicated the process to be economically justified, no information could be found as to whether the process was ever put into commercial operation.

Cornwell, [26] in 1975, reported a procedure developed for the economical recovery of aluminum when the aluminum was used as a coagulant for phosphorus removal from domestic wastewater. After thickening of the sludge, the chemical-organic sludge was reacted with sulfuric acid to dissolve the aluminum and phosphorus. In order to separate the aluminum from the phosphorus, a liquid-ion exchange process was utilized. A kerosene solution of mixed mono- and di(2-ethylhexyl) phosphoric acid (MDEHPA) was contacted with the aluminum-phosphorus solution. The alkyl phosphates reacted with the aluminum causing the metal to become kerosene soluble. The aluminum rich kerosene phase was then contacted with sulfuric acid allowing the aluminum to transfer from the kerosene to the acid phase where it was recovered as alum. The work was not extended outside the laboratory.

3.5. Theoretical Description of Liquid-Ion Exchange

Liquid-ion exchange is the separation of cationic or anionic solutes from a liquid phase solution by contact with another immiscible liquid solution. The theory of operation is dependent on the differential solubilities of individual species in the two liquid phases.

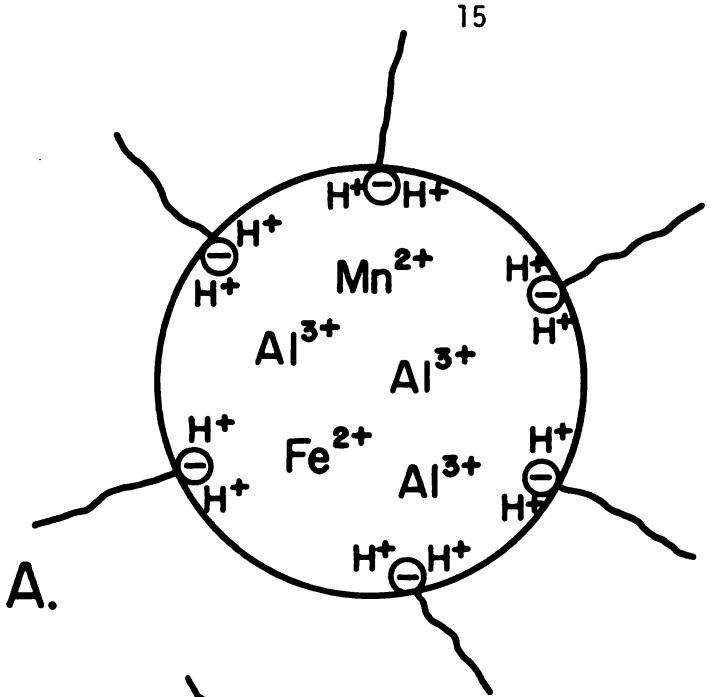
The process is very similar to resin-ion exchange. In liquid-ion

exchange, a small quantity of an organic soluble chemical called the extractant is dissolved in a second organic liquid called the diluent. The mixture is often referred to as the organic phase or solvent. The solution which is contacted with the organic phase during extraction is called the aqueous phase. For water treatment applications, the aqueous solution is the alum sludge.

The extractant can be one of two general types. The amines act by forming an organic soluble salt with anions while alkyl phosphates react with cations. The diluent is some inert hydrocarbon, such as kerosene, which serves as a carrier medium for the extractant. During the extraction operation the extractant reacts chemically with the desired metal in the aqueous phase forming a new compound which is soluble in the inert diluent.

A figurative representation of the process involved in the aluminum extraction is shown in Figure 3-1. The organic and aqueous phases are mixed such that small aqueous droplets are formed in the organic continuous phase. The extractant in the diluent contains a nonpolar part (the wavy lines in Figure 3-1A) causing the extractant to remain organic soluble, and a polar group (represented by the circle at the end of the wavy line in 3-1A) which sticks out into the aqueous phase and is the active site for aluminum complexation. The active site of the extractant ionizes. The aluminum-ion is exchanged for the H^+ ion such that the H^+ enters the aqueous phase and the Al^{3+} moves to the organic-aqueous interface (Figure 3-1B). When mixing is stopped and the dispersed phases are allowed to settle, rapid coalescence takes place. The result is a separation into an aluminum-rich organic phase an an aluminum-free aqueous phase (Figure 3-1C).

Figure 3-1. Schematic representation of aluminum extraction by liquid-ion exchange.


H+
H+
H+
H+
Mn2+
H+
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Al3+
Al3+
H+
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Fe2+
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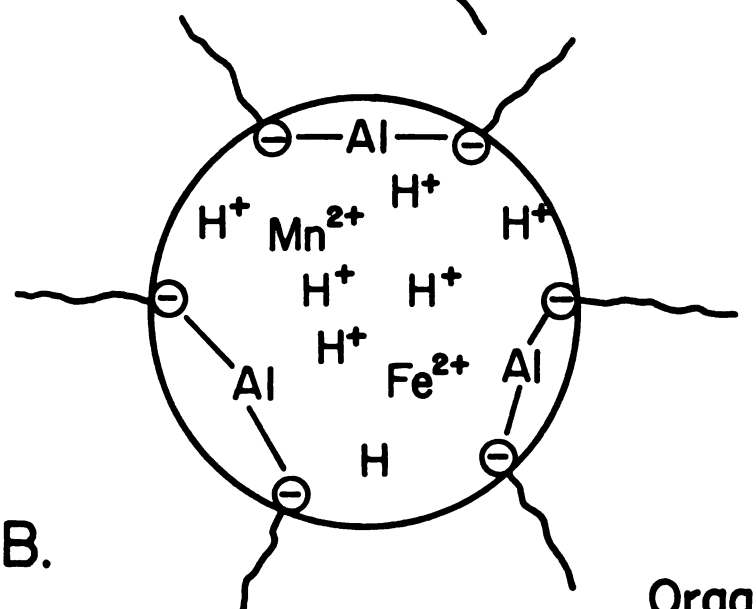
A.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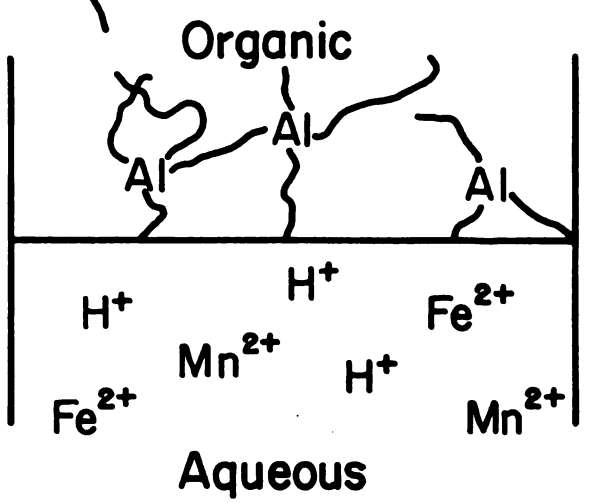

Organic
Al
Al
Al
H+
H+
Fe2+
Mn2+
H+
Fe2+
Mn2+
Aqueous

C.

The aqueous phase which contains the aluminum to be extracted is called the feed. The aluminum-rich organic phase is called the extract and the aluminum-free aqueous phase is called the raffinate.

The stripping circuit is operated in much the same way as the extraction circuit except that a stripping agent is chosen which causes the aluminum to leave the organic and enter the strip phase. A sulfuric acid solution has been shown successful in this research as a stripping agent. As a result, aluminum in the organic phase exchanges for protons in the acid phase resulting in aluminum sulfate and regenerated solvent. It is usually operated in an organic:acid volume ratio of 3:1 or greater so that aluminum is correspondingly concentrated for reapplication as a coagulant.

3.6. Choice of Diluent, Extractant and Modifying Agents

3.6.1 Introduction

The purpose of the diluent is to serve as the carrier for the extractant. The purpose of the extractant is to selectively remove the desired metal from the aqueous phase. The purpose of the modifying agent is to enhance the effectiveness and efficiency of the diluent and extractant.

3.6.2 Choice of Diluent

The important parameters for diluents in liquid-ion exchange are:

1. Stability of diluent. There should be a minimum of evaporation losses and chemical interaction with other substances present;
2. Differential density of organic phase to aqueous phase. Allows for minimum settling area and time after mixing;

3. Low organic solubility in the aqueous phase. Minimizes losses of diluent which is an important economic consideration;

4. Minimum entrainment losses. Also an economic consideration.

Several diluents which are suitable for extraction systems are available. Specific diluents are usually chosen for each particular application. Kerosene is probably the most common diluent in extraction processes. Kerosene is used due to its availability, comparatively low cost, and relative safety in handling. Other fractionalized crude oil derivatives are now available commerically. Manufacturers closely control specifications so that uniformity of the product is maintained. The high, narrow boiling range and higher flash point in comparison with commercial kerosene have significantly reduced evaporation losses and fire hazards. An important property which exhibits more favorable results than kerosene is the faster rate of phase disengagement which results in minimum solvent entrainment losses and lower settling area requirements [27].

3.6.3. Choice of Extractant

The important parameters for extractants in liquid-ion exchange are:

1. Large number of active sites. Allows high concentration of extractant to be dissolved in the diluent;

2. Affinity of active site for the ion to be removed. Allows large number of desired ions to be complexed;

3. Selectivity of the active site. Allows the desired ion to be removed and other ions to remain in solution;

4. The degree of cross linking or polymerization of the extractant in the diluent. Allows high concentrations of the desired ion to be removed for a small concentration of extractant.

Extractants are not easily chosen. There is an almost unlimited number of choices facing the researcher. Some extractants can be eliminated because they are not commercially available. Of the extractants commercially available, two general groups emerge. The amines act by forming an organic soluble salt with anions while alkyl phosphates react with cations and, therefore, were chosen for study in aluminum extraction. Typical molecules of alkyl phosphoric acids are shown in Figure 3-2.

3.6.4. Modifying Agents

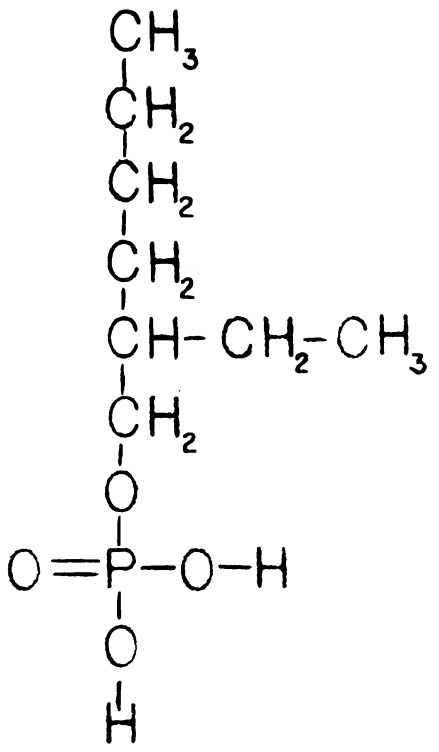
In addition to the diluent and the active extractant in liquid-ion exchange, there is often a third reagent called a modifier. The modifier may be added for one or more of three basic reasons. First is the synergistic effect that they may have on some extraction processes. Second, the modifier may improve phase separation. A third reason for the addition of modifiers is to prevent the formation of some insoluble compounds in the organic phase. For example, the addition of tributyl phosphate will prevent the formation of some insoluble sodium alkyl phosphate salts. Other modifying agents include isopropyl alcohol, phosphine oxides, and phosphonates.

3.7. Selectivity

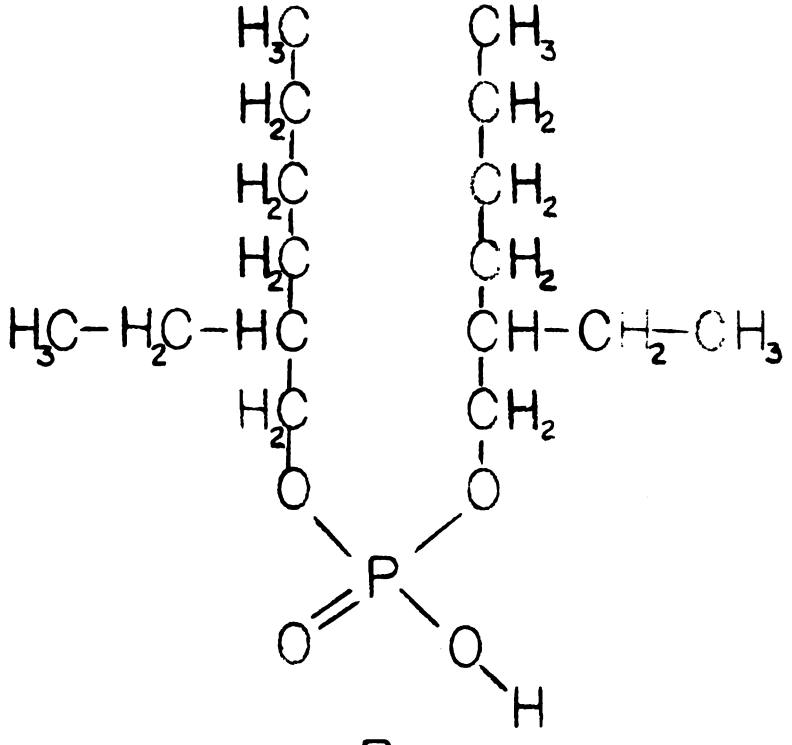
Whether or not liquid-ion exchange can be adopted for a specific application usually depends on the ability of the reagents to remove the desired ion and leave unwanted ions in solution. Selectivity in extraction is expressed by the selectivity ratio. The selectivity ratio is the extraction coefficient of the desired ion to be removed

Figure 3-2. Schematic diagram of alkyl phosphoric acids.

a) Mono(2-ethylhexyl) phosphoric acid
b) Di(2-ethylhexyl) phosphoric acid



A.



B.

in the circuit divided by the extraction coefficient of the unwanted ion. The greater the magnitude of the ratio, the more pronounced the separation of the desired and undesired ions.

Prognoses made from separation factors are trueonly if the extraction coefficients are nonvariant over the entire range of compositions. Careful analysis of initial concentrations and synergistic effects must be considered when utilizing selectivity ratios.

3.8. Solids Handlings During Extraction

The literature indicates mixed success in operating extraction circuits with solids. Although inert solids tend to decrease phase-disengagement rates and increase loss of solvent by entrainment, slurries containing a few percent solids are employed in refining uranium by tributyl phosphate and in recovering by-product uranium from phosphoric acid [16, 28]. Other laboratory investigations of uranium leach slurries have reported organic feed losses too high or recovery schemes too cumbersome for commercial adoption [29, 30]. No literature can be cited which attempted to incorporate organic solids into the extraction circuit as was attempted in this research.

3.9. Data Development in Liquid-Ion Exchange

Due to the high number of solvent-extractant-modifier combinations possible some preliminary exploratory work is often needed. The most common procedure for starting the study is to perform what are called "batch shake out tests." The organic phase mixture is shaken in a separatory funnel with some of the solution from which the extraction is to be made. After one or two minutes of shaking the phases are

allowed to separate and each phase is analyzed. This gives a guide as to what solvent combinations warrant further investigation. The visual observations made in this step regarding rate of phase disengagement, interfacial scum, insoluble compounds, etc., are very important.

After choosing some potential combinations, further extraction evaluation must be made and development of the fundamental design accomplished. This phase of the analysis can be divided into two steps. The first consists of development of distribution isotherms and the second consists of laboratory testing of the continuous flow process.

Data for distribution isotherms may be obtained in two ways: 1) single contacts of the aqueous feed with different volumes of organic feed, and 2) single contacts of an aqueous feed consecutively with fresh organic feed. Both procedures are used in the laboratory to design continuous flow processes. The first does have limitations.

The limitation of the first method is that the pH of the feed changes as it is contacted with different volumes of organic solvent. Since the extraction reaction is pH dependent (extraction increases with increasing pH) the resultant equilibrium data points are not representative of continuous flow operation.

As a result, the second method was chosen in developing distribution isotherms in this research. Slight modification was utilized by maintaining the same initial aqueous feed pH.

After the development of distribution isotherms, design of the continuous flow process must proceed. This can be accomplished by

utilizing McCabe-Thiele diagrams. These diagrams can be used to predict the number of countercurrent stages required to achieve any given percentage extraction of the desired metal.

3.10. Liquid-Ion Exchange Equipment

The extractive metallurgy industry has primarily adopted the mixer-settler concept for equipment design [31]. There are a number of important reasons for this. Differential contact extractors such as spray columns, plate columns, and packed columns are all characterized by incomplete separation of the two phases after mixing. Some of the dispersed phase will be carried along by movement of the continuous phase. The net effect is a loss in efficiency. Mixer-settlers achieve higher separation and approach ideal stages much better.

Another reason in favor of mixer-settlers is that the device is amenable to handling slight amounts of solids which sometimes occur in feed solutions. They also involve relatively small capital costs and are very simple to operate. With proper design all flows can be observed by the operator and sampled as required. They can be started up or shut down without any control problems.

The third and perhaps most compelling reason for using mixer-settler equipment is that a fast transition can be achieved from laboratory evaluation to operating the process in a continuous-flow system. Laboratory equipment is available which can allow direct scale-up to pilot plant studies. This equipment is specifically manufactured with this goal in mind. This allows final design parameters to be developed during the laboratory evaluation.

CHAPTER 4

EXPERIMENTAL APPARATUS AND PROCEDURES

4.1. General Description

The extraction and stripping experiments were divided into two categories: tests on synthetic feed solutions, and tests on treatment plant alum sludges. All of the extraction and stripping experiments were performed in batch mixer-settler units. Research as previously discussed has shown that batch mixer-settler data is reliable to predict and design continuous flow operations.

4.2. Aqueous Feed Solutions

4.2.1. Synthetic Feed Solutions

All synthetic feed solutions were prepared with reagent grade chemicals and distilled water. All glassware and operation materials were rinsed with tap water, cleaned with either dichromate acid or soap cleaning solution, rinsed three times with tap water, and three rinses with distilled water. Glassware that had contained organic matter was rinsed with acetone during the cleaning process.

Aluminum potassium sulfate (185.74 grams per liter) was used as the source of aluminum for preparation of 10,000 mg/l aluminum stock solution. Concentrated nitric acid (15 ml/l) was added to facilitate dissolution. All synthetic solutions were prepared from this stock. Sulfuric acid and/or potassium hydroxide were used for pH adjustments. The synthetic solutions allowed large quantities of feed solutions to

be made up at one time. Feed parameters could be easily varied.

4.2.2. Treatment Plant Alum Sludge Solutions

Due to the variability of alum sludges from all geographical locations in the United States, one sludge had to be chosen for the alum sludge studies. The Tampa, Florida sludge was selected. The reasons were that the sludge had a high organic solids percentage, was extremely colored, and contained a very high aluminum concentration (3000-3500 mg/l Al^{3+}).

The 65-mgd Tampa water treatment plant utilizes an average 100 mg/l liquid alum and 4-mg/l sodium silicate for coagulation and settling. The sludge contains 0.6% solids from the sedimentation tank, 1.7% solids from the lagoons, and nearly 20% solids after dewatering on sand drying beds. The sludge samples shipped to the laboratory were pumped from the bottom of a wet well immediately following the lagoons. A typical analysis of the sludge is presented in Table 4.1.

This sludge was felt to characterize the worst conditions that would be met in practical application. With the solids, organic losses could be quantitatively measured in the extraction circuit. Iron, manganese, and color contamination problems were expected to be encountered. The high aluminum concentration would test the efficiency of the liquid-ion exchange process.

Upon receiving sludge samples, immediate refrigeration was employed until the samples were utilized in the experiments. Samples were acidified with concentrated sulfuric acid to dissolve the aluminum from the solids where applicable.

TABLE 4.1

Tampa Sludge Characteristics

Parameter	
Dissolvable Inorganic Solids, %	61
Non-Dissolvable Inorganic Solids, %	6
Dissolvable Organic Solids, %	25
Non-Dissolvable Organic Solids, %	8
Suspended Solids, %	1.6
Total Aluminum Concentration, mg/l	3300
pH	6.58

4.3. Organic Feed Solutions

4.3.1. Alkyl Phosphoric Acids

Three alkyl phosphates were evaluated during this research. Two different alkyl phosphoric acids were supplied by Stauffer Chemicals, Eastern Research Center, Westport, Connecticut. One was di(2-ethylhexyl) phosphoric acid (DEHPA) and the other an equal molar mixture of mono- and di(2-ethylhexyl) phosphoric acid (MDEHPA). Octylphenol acid phosphate was supplied by Mobil Chemical Company, Phosphorus Division, Richmond, Virginia. Properties of the three acids are shown in Table 4.2 and Table 4.3. All of the chemicals were commercially available in large quantities at the time of this research. The acids were used as directly supplied by the manufacturers since the chemicals would not be further purified in full-scale operation. The alkyl phosphoric acid solutions were prepared by volumetrically measuring out the appropriate amount of solution and diluting in the proper diluent. All molar solutions of alkyl phosphates were reported as formal weights based on the average molecular weights in Table 4.2.

TABLE 4.2

Physical and Chemical Properties of Alkyl Acid Phosphates

Alkyl Phosphates	Average Mol. Weight	Percent P_2O_5	Specific Gravity	Physical State	Color APHA
Mono-Dialkyl (2-ethylhexyl) Phosphoric Acid*	266	26.0-27.5	1.020-1.030 (25°C)	Liquid	100
Dialkyl (2-ethylhexyl) Phosphoric Acid*	402	34.8-35.8	1.090-1.110 (25°C)	Liquid	3 NPA
Octylphenol Acid Phosphate**	276	-----	1.080 (65°C)	Semi-Solid	Light Tan

Source: *Stauffer Chemical Company, Alkyl Acid Phosphates, Westport, Connecticut, August 1972.

**Mobil Chemical Company, Phosphorus Chemicals, Richmond, Virginia, February 1977.

TABLE 4.3

Solubility Properties of Alkyl Acid Phosphates

Alkyl Phosphates	Water	Alcohol	Acetone	CCl_4	Hexane	Kerosene	Kermac 470 B	Kermac 627
Mono-Dialkyl (2-ethylhexyl) Phosphoric Acid*	I	S	S	S	---	S	S	S
Dialkyl (2-ethylhexyl) Phosphoric Acid*	R	S	S	S	---	S	S	S
Octylphenol Acid Phosphate**	I	S	S	---	I	I	I	I

Code: S = Soluble
I = Insoluble
R = Reacts

Source: *Stauffer Chemical Company, Alkyl Acid Phosphates, Westport, Connecticut, August, 1972.
**Mobil Chemical Company, Phosphorus Chemicals, Richmond, Virginia, February, 1977.

4.3.2. Diluents

Kerosene was supplied from the Michigan State University General Stores, East Lansing, Michigan. It is commercially identical to number one fuel oil. The Kermac 470B and 627 diluents were supplied by Kerr-McGee Refining Corporation, Oklahoma City, Oklahoma. Specific gravities and available specifications are shown in Table 4.4.

TABLE 4.4

Specific Gravities and Available Specifications of Diluents

Specifications	Kerosene	Diluents	
		Kermac 470B*	Kermac 627*
Specific Gravity	0.8344	0.8156	0.7892
API Gravity 60°F		42.0	47.8
Saybolt Color		23	28
Surface Tension @25°C		28.3	
Molecular Weight		175	
Pour Point			-25
Chemical Composition (%/Volume)			
Pariffin			65.9
Olefins			nil
Naphthenes			26.9
Aromatics			7.2
Distillation °F			
IBP		404	389
10%		421	416
20%		426	
50%		441	441
80%		459	
90%		470	470
95%		480	
dry point		485	492

Source: *Kerr-McGee Refining Corporation, Oklahoma City, Oklahoma, October 1974, October 1976.

4.4. Analytical Equipment and Techniques

4.4.1. Aluminum Determinations

The aluminum ion concentration was determined by atomic absorption spectophotometry. An "Instrument Laboratories Model 151" unit was utilized for all the determinations. A nitrous oxide flame was used as prescribed in the fourteenth edition of Standards Methods for the Examination of Water and Wastewater. All aqueous standards contained sufficient potassium ions which allowed the potassium to act as an ionization buffer for the aluminum. Samples analyzed in the recovered alum phase were compared to 2 N and 4 N sulfuric acid standards depending on the dilution used. Readings were made at 3092.7 Å. The range of optimum aluminum determinations was 10-100 ppm Al^{3+} in the aqueous phase.

Organic standards were prepared by utilizing the aluminum loaded organic phase after a single extraction stage. The aqueous sample was monitored and a mass balance completed to determine the aluminum concentration in the organic phase. Whenever possible samples were analyzed in the organic phase. The sensitivity of the readings is vastly improved over aqueous techniques. This advantage is due to the improvement of the flame condition which increased the signal to noise ratio. See Appendix B for a complete discussion.

4.4.2. pH Determinations

A "Corning Model 12" expanded scale pH meter was utilized for all pH readings. The meter was standardized at a pH of 2.00 for low pH determinations and a pH of 4.00 for mid-range measurements.

4.4.3. Extractant Loss Determinations

Loss of MDEHPA into the aqueous phase during the extraction process and into the recovered alum during the stripping process was measured by colorometric methods. A "Bausch-Lomb Spectronic 70 Spectrophotometer" was utilized for all determinations. An experimental procedure developed by Ashbrook [32] to measure di(2-ethylhexyl) phosphoric acid was utilized to measure MDEHPA in the extraction raffinate and recovered alum. Whatman No. 1 phase separating paper was employed to enhance the phase disengagement.

4.4.4. Organic Loss Determinations

Organic losses were measured by total organic carbon determinations on the aqueous raffinate after the extraction process and the recovered alum after the stripping process. An "Ionics Model 445 TOC analyser" was utilized for all determinations. Nitrogen gas was used as the fuel and coolant.

4.4.5. Heavy Metals Determinations

Chromium (VI), zinc (II), iron (II), iron (III), cadmium (II), manganese (II), and copper (II) were analyzed by atomic absorption spectrophotometry with the "Instrument Laboratories Model 151" atomic absorption unit. An acetylene flame was utilized. All standards were made in accordance to the fourteenth edition of Standards Methods for Examination of Water and Watewater. Readings were made at wavelengths suggested in the instrument manual.

4.4.6. Dispersion and Continuous Phase Determinations

An "Industrial Instruments Incorporated" conductivity bridge was

utilized to determine the mixing phase during extraction and stripping. Conductivity readings of zero mhos indicated that the mixing was operating organic continuous with the aqueous phase dispersed throughout the organic medium. Any conductivity reading greater than zero indicated that the aqueous phase was continuous and the organic phase was dispersed. Unless otherwise stated, all extraction and stripping circuits were operated organic continous.

4.4.7. Evaporation Loss Determinations

Diluent evaporation was quantitatively measured by exposing a known volume of each diluent to the free atmosphere. Evaporation dishes of identical surface area were employed. At 24-hour intervals the volume of diluent remaining in each dish was measured.

4.4.8. Specific Gravity Determinations

The specific gravity of commercial kerosene was measured in accordance to procedures outlined in the fourteenth edition of Standard Methods for the Examinaton of Water and Wastewater.

4.4.9. Polymer Optimization Determinations

Polymer evaluation was conducted by use of a "Phipps and Bird" jar stirrer. Rapid mix speed was 100 rpm for two minutes. Flocculation speed was 40 rpm for five minutes.

4.5. Experimental Procedures and Equipment

4.5.1. Procedures

The development of equilibrium curves is the major goal in designing an alum recovery process. As was stated previously there

are two procedures to obtain these curves. The first method entails single contacts of the aqueous feed with different volumes of organic feed. This method has limitations if the extraction and stripping reactions are pH dependent as was found to be the case in this research. The second method utilized single contacts of an aqueous feed consecutively with fresh organic feed. This procedure was utilized in the research to develop the extraction and stripping equilibrium curves.

Synthetic feed solutions could be easily made up with differing aluminum concentrations. This allowed initial operating parameters to be easily controlled and large volumes to be readily available.

When the continuous flow process was simulated in the laboratory, multiple contacts of aqueous feed were employed to simulate actual conditions as close as possible.

4.5.2. Equipment

Batch extraction experiments were conducted in 300-ml mixing reactors supplied by Bell Laboratories, Tucson, Arizona. Mixer motors, impellers, and rheostats were also supplied with each reactor. A "Herman H. Stict Company" tachometer-speed indicator was used to calibrate each rheostat with mixer unit. Calibration of rheostat settings with both impeller speed and revolutions per minute was accomplished. A "Precision Scientific Company Timer" was used to control mixing times. After mixing, the samples were immediately transferred to 250-ml separatory funnels where the organic and aqueous phases were allowed to separate.

CHAPTER 5

ALUMINUM RECOVERY FROM SYNTHETIC FEED SOLUTIONS

5.1. Introduction

Design of an aluminum recovery and recycling process required that the optimum operating conditions be established for the extraction stages and the stripping stages. While in application a continuous flow process would be employed, batch systems were studied in the laboratory. Scale-up of batch systems to continuous flow operation has been shown to be applicable.

In the extraction stages, the aluminum was removed from the synthetic aqueous solution by dissolution into the kerosene diluent. In the stripping stages the aluminum-rich kerosene phase was contacted with acid. The alum was recovered. The stripped kerosene was then recycled.

5.2. Extraction of Aluminum by an Equal Molar Mixture of Mono-Di(2-ethylhexyl) Phosphoric Acid

5.2.1. Introduction

Initial liquid-ion exchange studies of aluminum extraction utilized an alkyl phosphoric acid that had proven effectiveness in previous aluminum extraction studies. The extractant utilized by Cornwell [26] complexed aluminum when the aluminum was used as a coagulant for phosphorus removal in domestic wastewater treatment. The extractant was an equal molar solution of mono- and di(2-ethylhexyl)

phosphoric acid (MDEHPA). Kerosene, based on volume availability, was the diluent of choice. Synthetic aluminum solutions were prepared with aluminum potassium sulfate.

5.2.2. Kinetics Study

The first tests were conducted to determine the impeller speed and time needed to represent equilibrium conditions for the extraction process. The results are shown in Figure 5.1. This test was run at a feed pH of 2.0, 0.1 M MDEHPA solution, an initial aluminum concentration of 1000/mg/l, and a phase ratio of 1:1 (organic to aqueous). The minimum impeller tip speed to achieve 100% equilibrium during the extraction circuit was found to be 800 ft/min. The time to achieve this equilibrium was 10 minutes. At impeller speeds greater than 800 ft/min no further extraction took place although the time to equilibrize was lowered to 8 minutes. At impeller speeds equal to 1200 ft/min or higher, the reaction proceeded at the maximum rate as identical equilibrium curves were obtained.

The percentage equilibrium versus impeller speed in the extraction circuit can be seen in Figure 5.2. The extraction equilibrium is dependent on impeller speed up to 800 ft/min. Impeller speeds greater than this did not enhance equilibrium rates. All subsequent extraction tests were run at 800 ft/min with a mix time of 15 minutes to ensure completion of the reaction.

5.2.3. Initial Feed pH Considerations

The aqueous feed pH was varied between 1.0 and 7.0 to determine the effect on aluminum extraction. An aluminum solution containing 100 mg/l was contacted with a 0.1 M MDEHPA solution and the feed pH

Figure 5.1. Impeller speed versus time to reach extraction equilibrium. Feed pH = 2.0, 0.1 M MDEHPA, Al^{3+} = 1000 mg/l, 1:1 phase ratio.

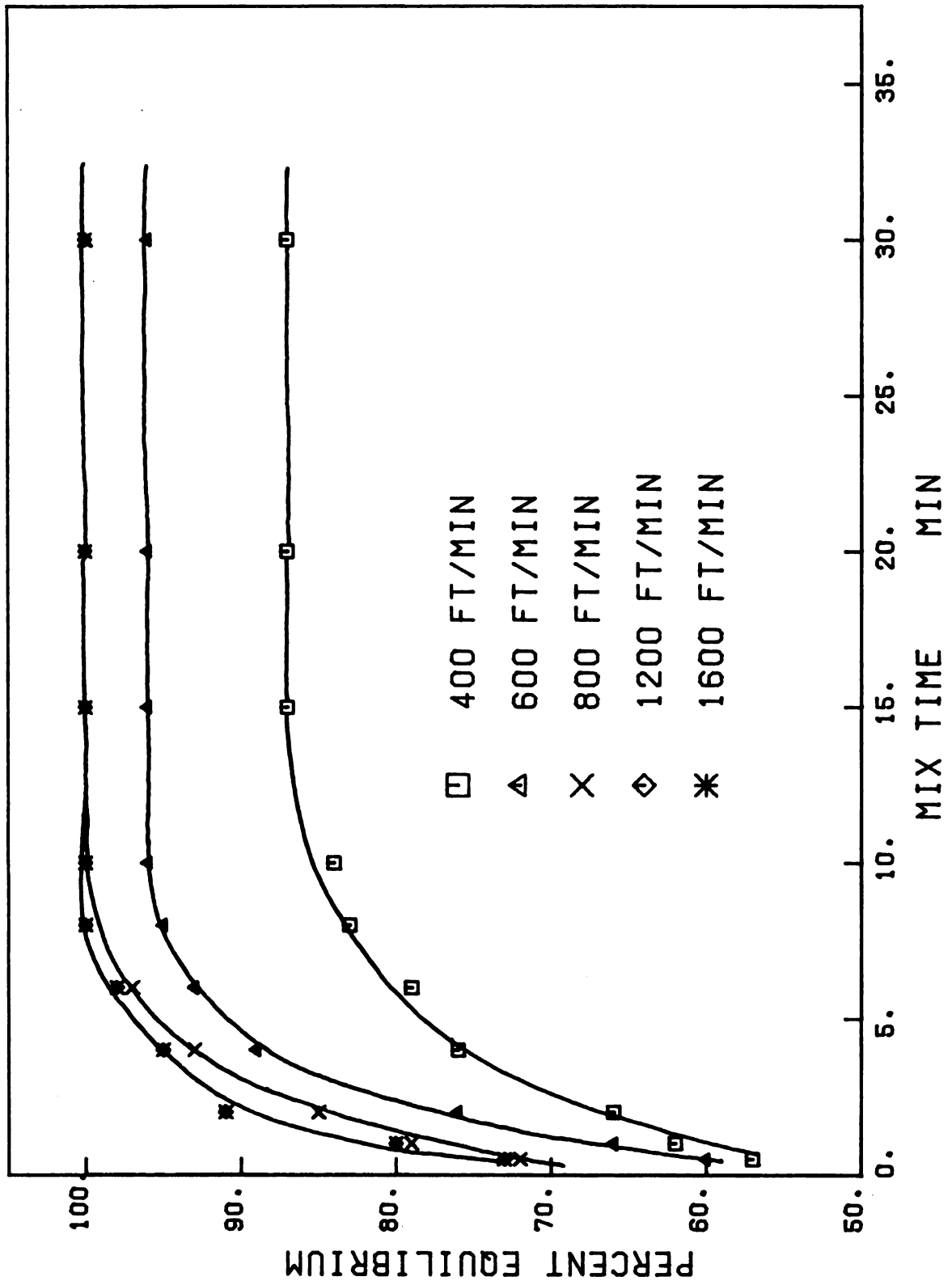
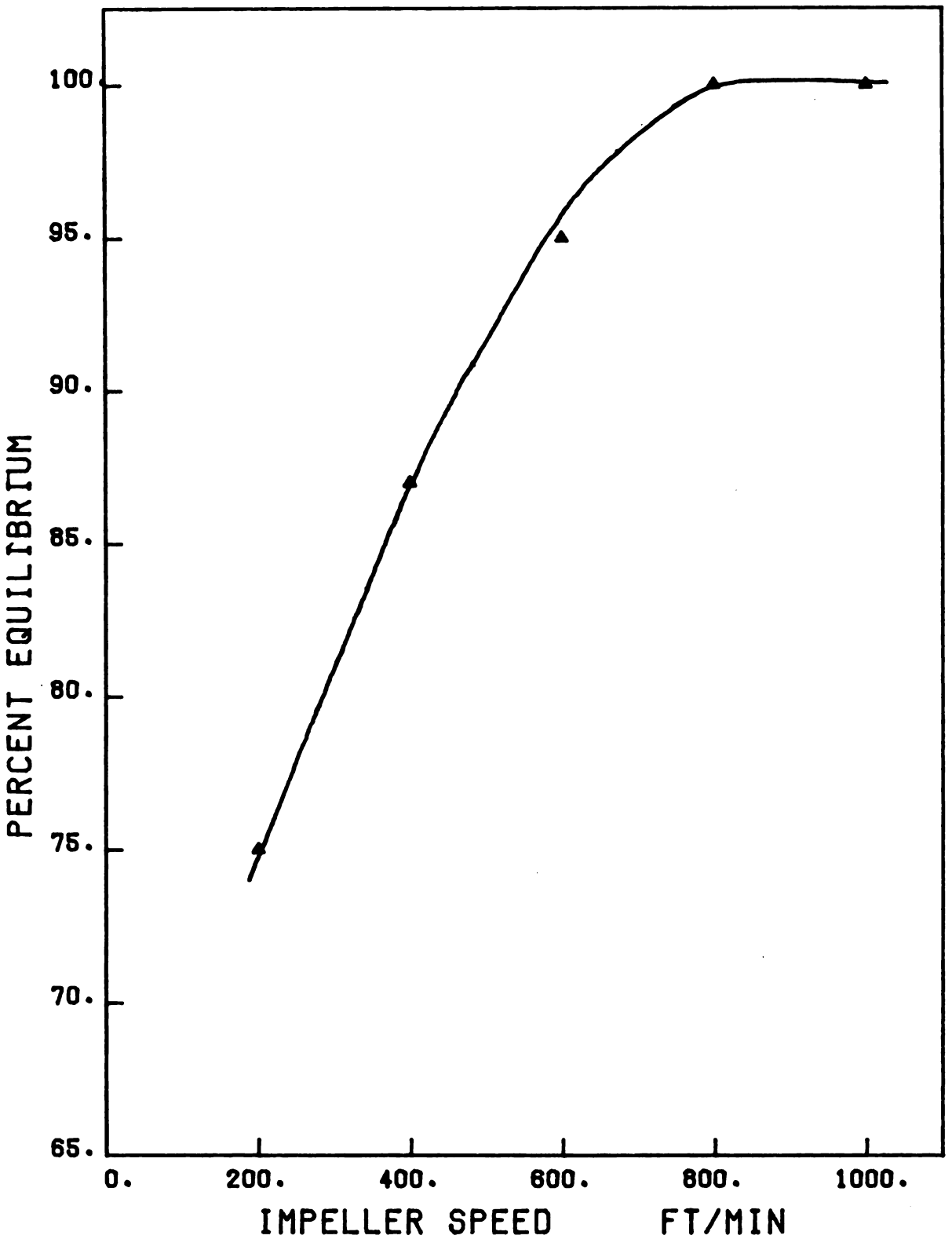

PERCENT EQUILIBRIUM
100.
90.
80.
70.
60.
50.
0.
5.
10.
15.
20.
25.
30.
35.
MIX TIME MIN
400 FT/MIN
600 FT/MIN
800 FT/MIN
1200 FT/MIN
1600 FT/MIN

Figure 5.2. Percent equilibrium versus impeller speed in the extraction circuit. Mix time = 15 minutes, feed pH = 2.0, 0.1 M MDEHPA, Al^{3+} = 1000 mg/l, 1:1 phase ratio.


100
95.
90.
85.
80.
75.
70.
65.
PERCENT EQUILIBRIUM
0.
200.
400.
600.
800.
1000.
IMPELLER SPEED FT/MIN

varied. The results are shown in Figure 5.3. The extraction efficiency increased sharply below a pH of 2.0 and increased almost linearly from a pH of 2.0 to 7.0. It was concluded that the extraction circuit proceeded more efficiently at the higher pH ranges and the reaction was indeed pH dependent.

The results of varying feed pH on extraction efficiency can be seen in Figure 5.4. A 0.1 M MDEHPA solution was contacted with various aluminum concentrations with two initial feed pH's of 2.0 and 4.0. The higher feed pH of 4.0 extracted more than twice the aluminum than the feed pH of 2.0 at the maximum loading of the extractant. This clearly shows the advantages of operating the extraction stages at the higher pH values.

5.2.4. Development of Extraction Equilibrium Curves

The extraction equilibrium curves for various concentrations of MDEHPA are shown in Figure 5.5. The extraction equilibrium curves were developed at a feed pH of 2.0 and a phase ratio of 1:1. All mix times were 15 minutes at impeller speeds of 800 ft/min. The first point at which the curves changed slope was the maximum amount of aluminum that could be extracted in a single contact with a given molarity of MDEHPA. By operating in this region, essentially all the aluminum that could be extracted in a single contact with a given molarity of MDEHPA. By operating in this region, essentially all the aluminum could be extracted in one stage. This indicated that the aluminum was initially extracted by a dimer of MDEHPA [26]. The linear portion of the curve represented aluminum being extracted as the MDEHPA reacted as a monomer. The leveling off portion of the

Figure 5.3. Initial feed pH versus aluminum extracted. Mix time = 15 minutes, 0.1 M MDEHPA, Al^{3+} = 1000 mg/l, 1:1 phase ratio.

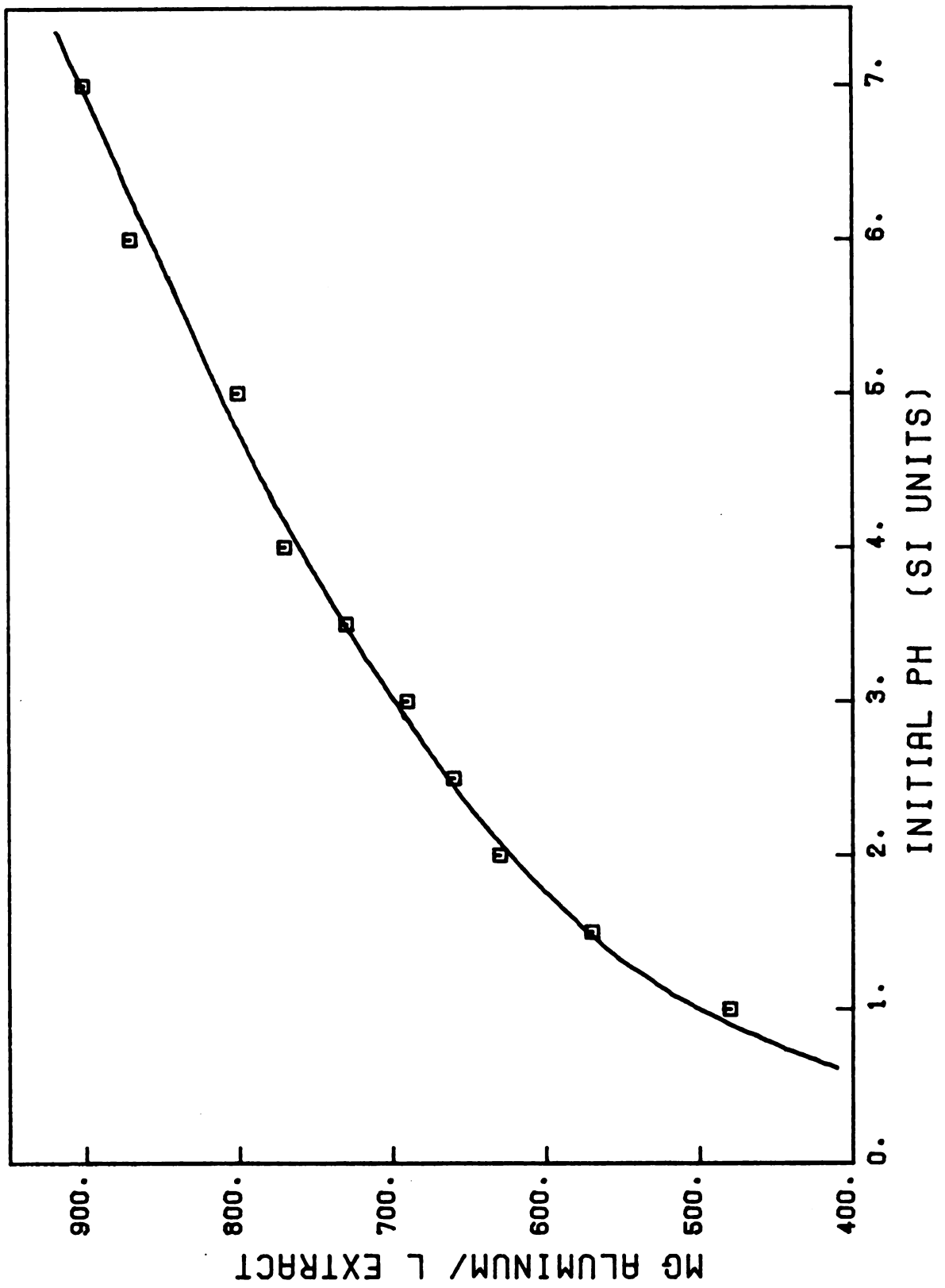

MG ALUMINUM/ L EXTRACT
900.
800.
700.
600.
500.
400.
0.
1.
2.
3.
4.
5.
6.
7.
INITIAL PH (SI UNITS)

Figure 5.4. Extraction equilibrium curves for various initial feed pH's. Mix time = 15 minutes, 0.1 M MDEHPA, Al^{3+} = 500-6000 mg/l, 1:1 phase ratio.

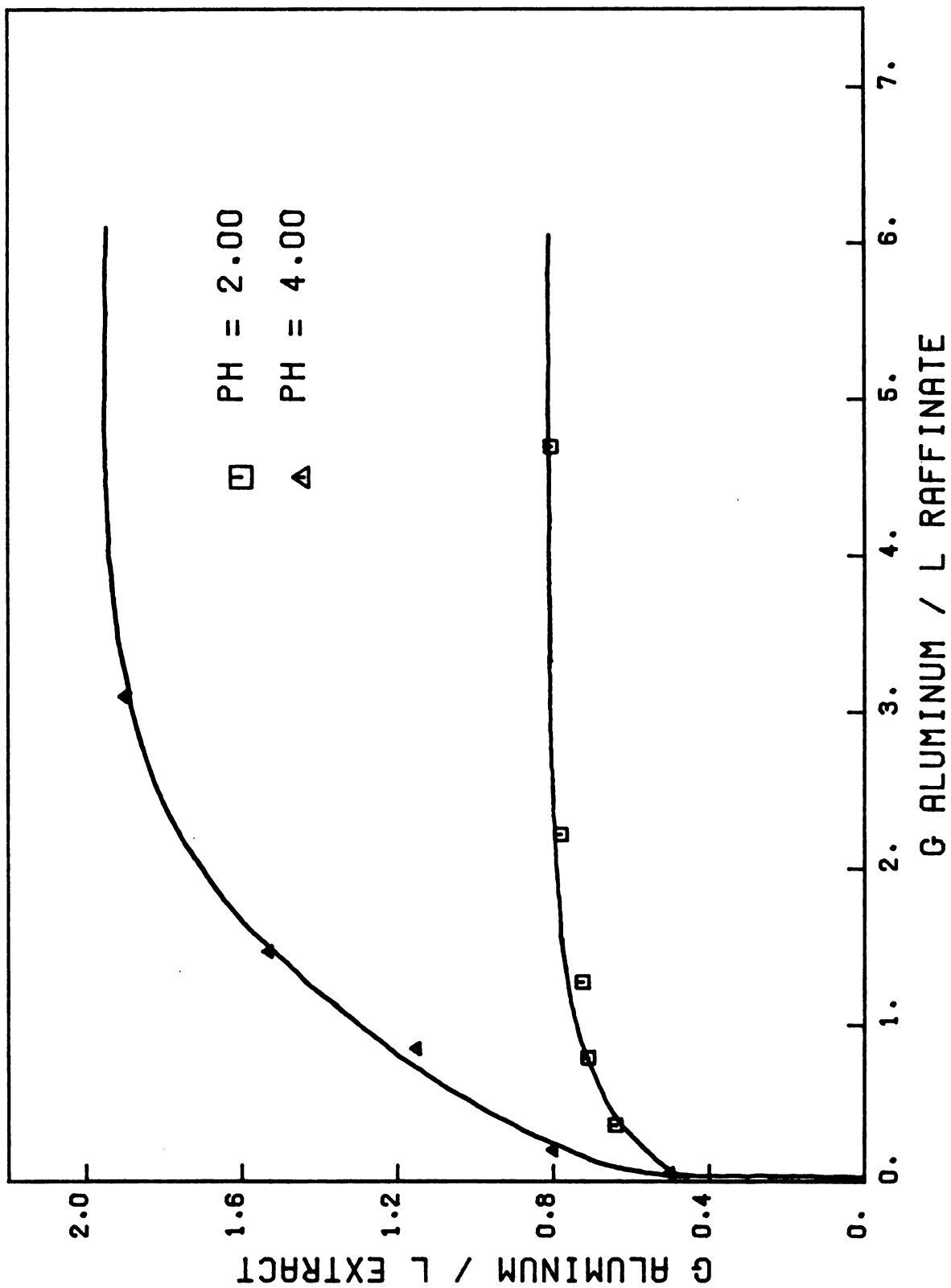
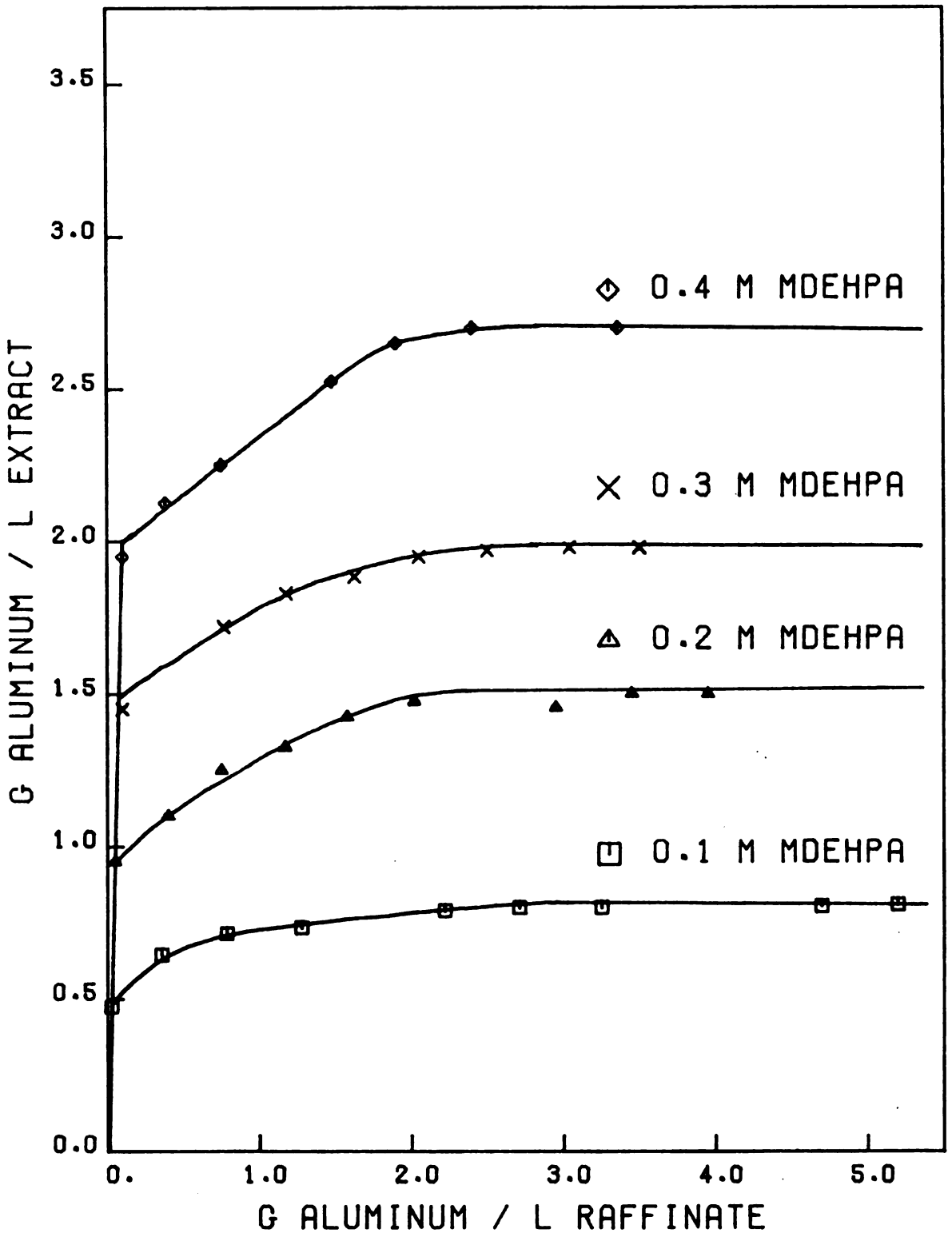

PH = 2.00
PH = 4.00
G ALUMINUM / L EXTRACT
G ALUMINUM / L RAFFINATE
0.
0.4
0.8
1.2
1.6
2.0
1.
2.
3.
4.
5.
6.
7.

Figure 5.5. Synthetic extraction equilibrium curves for various molarities MDEHPA. Feed pH = 2.0, Mix time = 15 minutes, Al^{3+} = 500-6000 mg/l, 1:1 phase ratio.


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
G ALUMINUM / L EXTRACT
0.4 M MDEHPA
0.3 M MDEHPA
0.2 M MDEHPA
0.1 M MDEHPA
0.
1.0
2.0
3.0
4.0
5.0
G ALUMINUM / L RAFFINATE

curve represented the maximum amount of aluminum that could be extracted by the given molarity of MDEHPA.

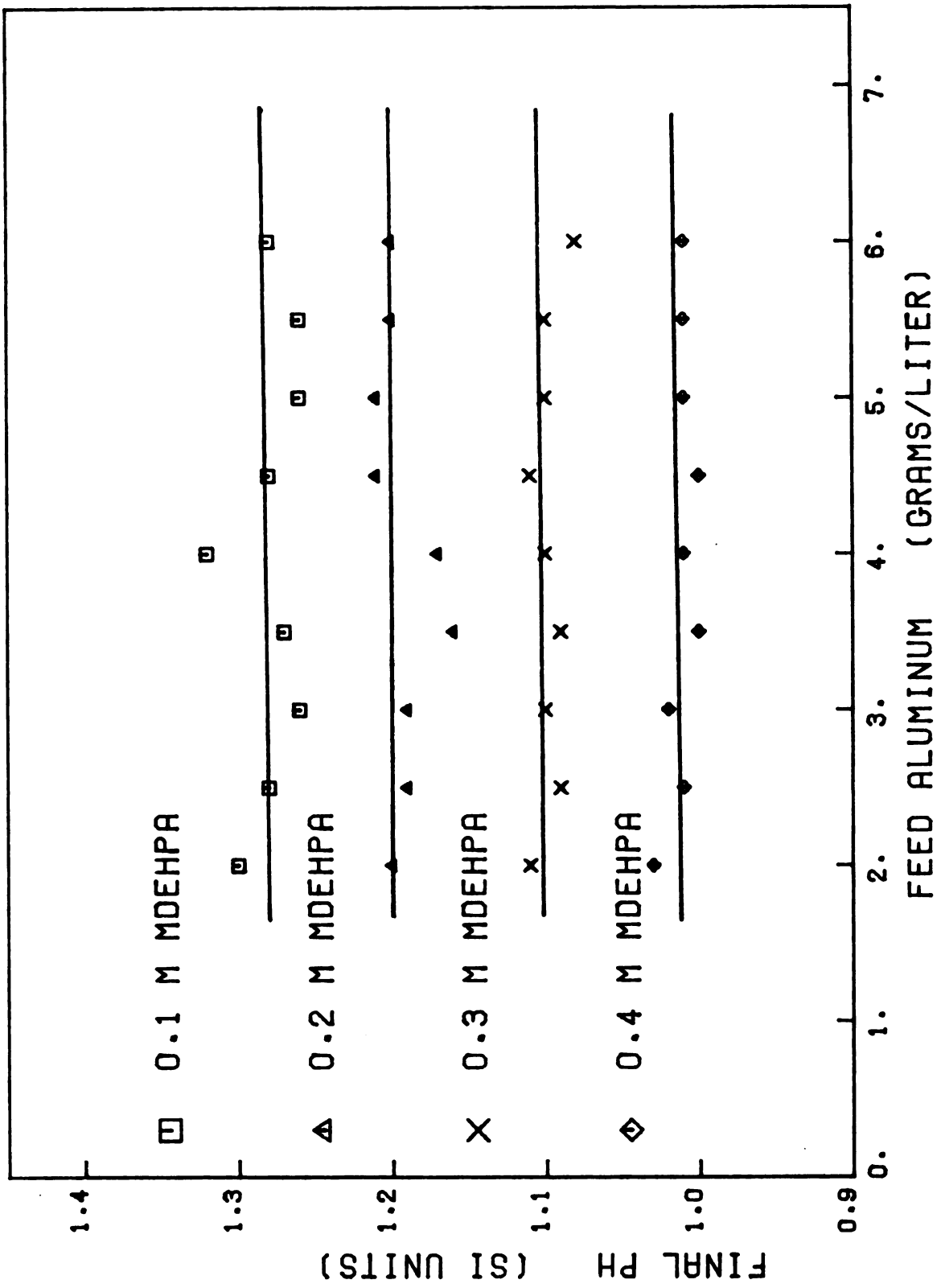
Raffinate pH's were measured after each extraction circuit. The results are shown in Figure 5.6. For all the aluminum concentrations contacted with any given molarity of MDEHPA the raffinate pH remained constant. From the theoretical exchange reaction [26] the pH would be expected to vary inversely with the aluminum concentration extracted. Since the raffinate pH remained constant (Figure 5.6) as various concentrations of aluminum were extracted (Figure 5.5), this proposition was not supported. One possible explanation is that entrained MDEHPA in the aqueous phase during extraction causes the lowering in pH. Another possible explanation is that potassium ions present in the synthetic solutions are extracted after all the aluminum is complexed. The additional exchange of hydrogen ions would result in a lower pH. This reaction would occur until all the extractant is complexed.

The raffinate solutions, when extraction was operated in the dimer range, were cloudy after settling. The monomer raffinate solutions were extremely clear. This would help explain MDEHPA entrainment in the aqueous phase during these tests. The cloudiness may have represented excess MDEHPA which was not complexed with aluminum. Only after several days did the solutions clear up. It was qualitatively concluded that in order to minimize extractant losses, the ion exchange reaction should be operated in the monomer extraction range.

5.2.5 Modifying Agents

During all the extraction tests on the synthetic solutions, the two phases separated very quickly and distinctly. Phase separation was always complete in five minutes or less. No modifier solutions

Figure 5.6. Final raffinate pH versus initial aluminum concentration. Mix time = 15 minutes, Feed pH = 2.0, 1:1 phase ratio.


FINAL PH (SI UNITS)
1.4
1.3
1.2
1.1
1.0
0.9
0.
1.
2.
3.
4.
5.
6.
7.
FEED ALUMINUM (GRAMS/LITER)
0.1 M MDEHPA
0.2 M MDEHPA
0.3 M MDEHPA
0.4 M MDEHPA

necessary to prevent third phase build-up as is reported in some liquid-ion exchange processes [33].

5.2.6. Selectivity of MDEHPA

The selectivity of the extraction reaction for various heavy metals often found in water treatment facilities was next investigated. The metals chosen for study were copper (II), cadmium (II), manganese (II), zinc (II), iron (II), iron (III), and chromium (VI). Two separate experiments on selectivity were conducted. In one experiment aluminum and the metal in question were combined and contacted with MDEHPA solutions. The aluminum concentration was sufficiently high to be present in excess for complexing with the extractant. A solution of 500 mg/l aluminum and 25 mg/l of the selective metal was contacted with a 0.1 M MDEHPA solution in a 1:1 phase ratio. In the other experiment, 1000 mg/l of the selective metal was contacted alone with a 0.1 M MDEHPA solution and compared with 1000 mg/l aluminum contacted alone with the same concentration of extractant.

The results are shown in Table 5.1. The selectivity ratio is defined as the ratio of the extraction coefficient of aluminum to the extraction coefficient of the selective element in question. Extraction coefficient is defined as the ratio of the metal concentration in the organic phase to the metal concentration in the aqueous phase.

The results indicate that MDEHPA is an excellent selective extractant for aluminum. In the presence of excess aluminum, the selectivity ratio for other heavy metals ranged from 30 to greater than 1800. Even in the absence of aluminum, the heavy metals were not appreciably extracted; selectivity ratios ranged from 2 to 180. In commercial

TABLE 5.1

Selectivity of MDEHPA: Aluminum versus Heavy Metals

Experiment One	100 ml 500 mg/l Aluminum 25 mg/l Selective Metal 100 ml 0.1 M MDEHPA
Experiment Two	100 ml 1000 mg/l Selective Metal 100 ml 0.1 M MDEHPA

Experiment Number	Element (Charge)	Aluminum Extracted mg/l	Selective Metal Extracted mg/l	Selectivity Ratio
One	Cu (II)	475	4.5	190
	Cd (II)	475	3.0	300
	Mn (II)	475	2.5	360
	Zn (II)	475	0.5	(>1800)
	Fe (II)	475	5.0	170
	Fe (III)	475	19.0	30
	Cr (VI)	475	10.0	75
Two	Cu (II)	640	140	11
	Cd (II)	640	70	22
	Mn (II)	640	80	20
	Zn (II)	640	10	178
	Fe (II)	640	85	19
	Fe (III)	640	320	2
	Cr (VI)	640	210	7

application, selectivities are usually much higher than in the laboratory [22]. As a result, no contamination of heavy metals would be expected in operation of the aluminum recovery system.

5.3. Stripping of Aluminum - Mono-Di(2-ethylhexyl) Phosphoric Acid

5.3.1. Introduction

Stripping of aluminum can be accomplished by either acid or alkali. The alkali has had mixed success in the literature and was not attempted in this research. Acid solutions studied were hydrochloric and sulfuric acids.

5.3.2. Kinetics Study

The first tests conducted in the stripping circuit were kinetic tests. These were carried out in the same manner as the extraction kinetic tests. The results of varying impeller speeds to achieve equilibrium can be seen in Figure 5.7. A 6 N H_2SO_4 acid solution was contacted with loaded organic containing 640 mg/l aluminum at a 3:1 phase ratio (organic:aqueous). Complete stripping equilibrium was achieved at an impeller speed of 800 ft/min with a mix time of 12 minutes. Impeller speeds greater than 800 ft/min gave no higher stripping efficiencies, but did achieve equilibrium in a shorter time of 8 minutes. The reaction initially proceeded more quickly than the extraction process; approximately 90% equilibrium at the end of 2 minutes as compared with the extraction process being 75% complete in 2 minutes.

Figure 5.8 shows the percent equilibrium versus impeller speed in the stripping circuit. The stripping process equilibriated at 800 ft/min and increasing of the impeller speed did not enhance the reaction. Higher equilibrium percentages were achieved with the stripping reactions than could be achieved with the extraction reaction at the lower impeller speeds. At 200 ft/min, the stripping equilibrium

Figure 5.7. Impeller speed versus time to reach stripping equilibrium. Organic = 640 mg/l Al^{3+}, Acid = 6 N H_2SO_4, 3:1 phase ratio.

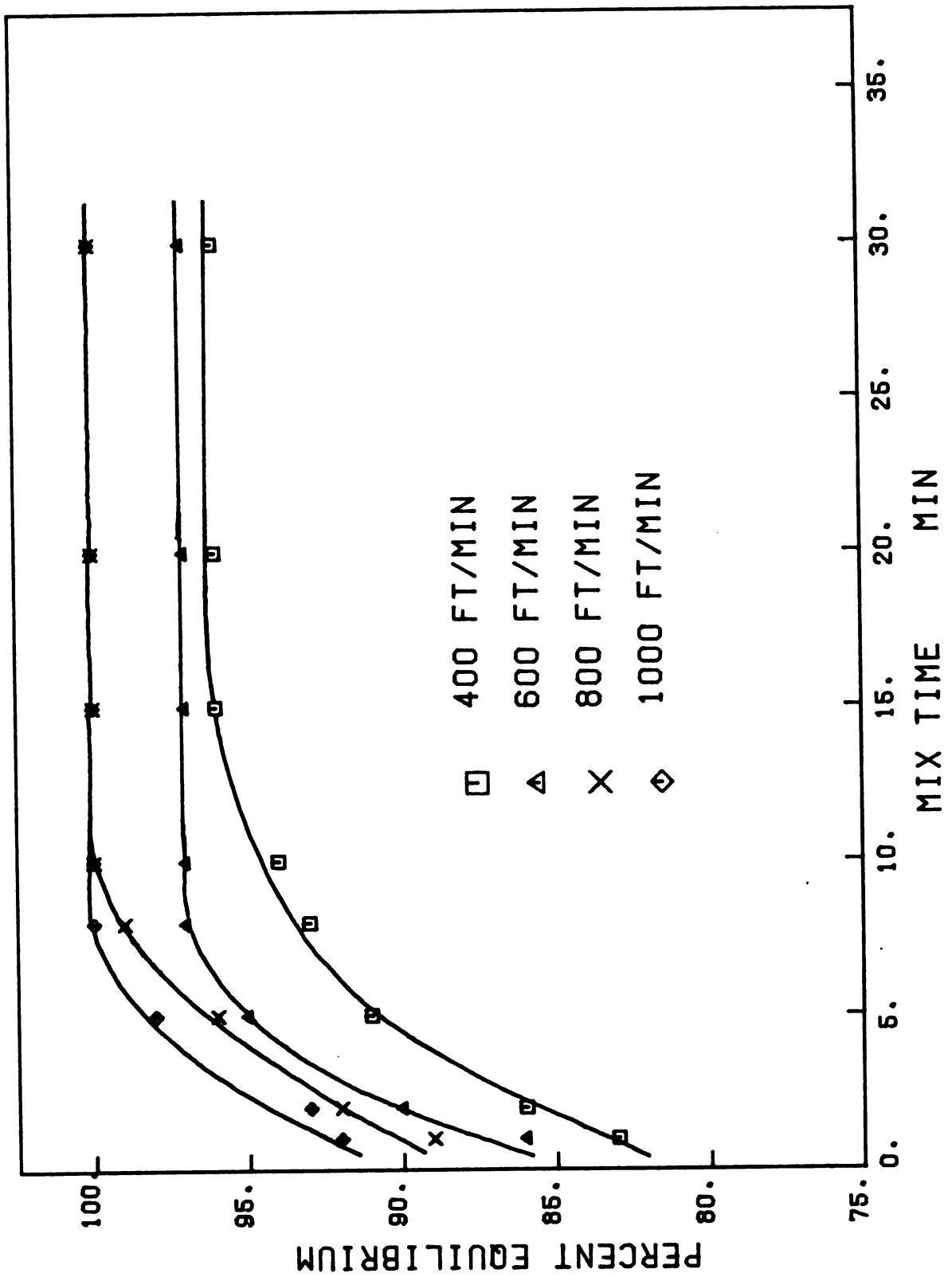
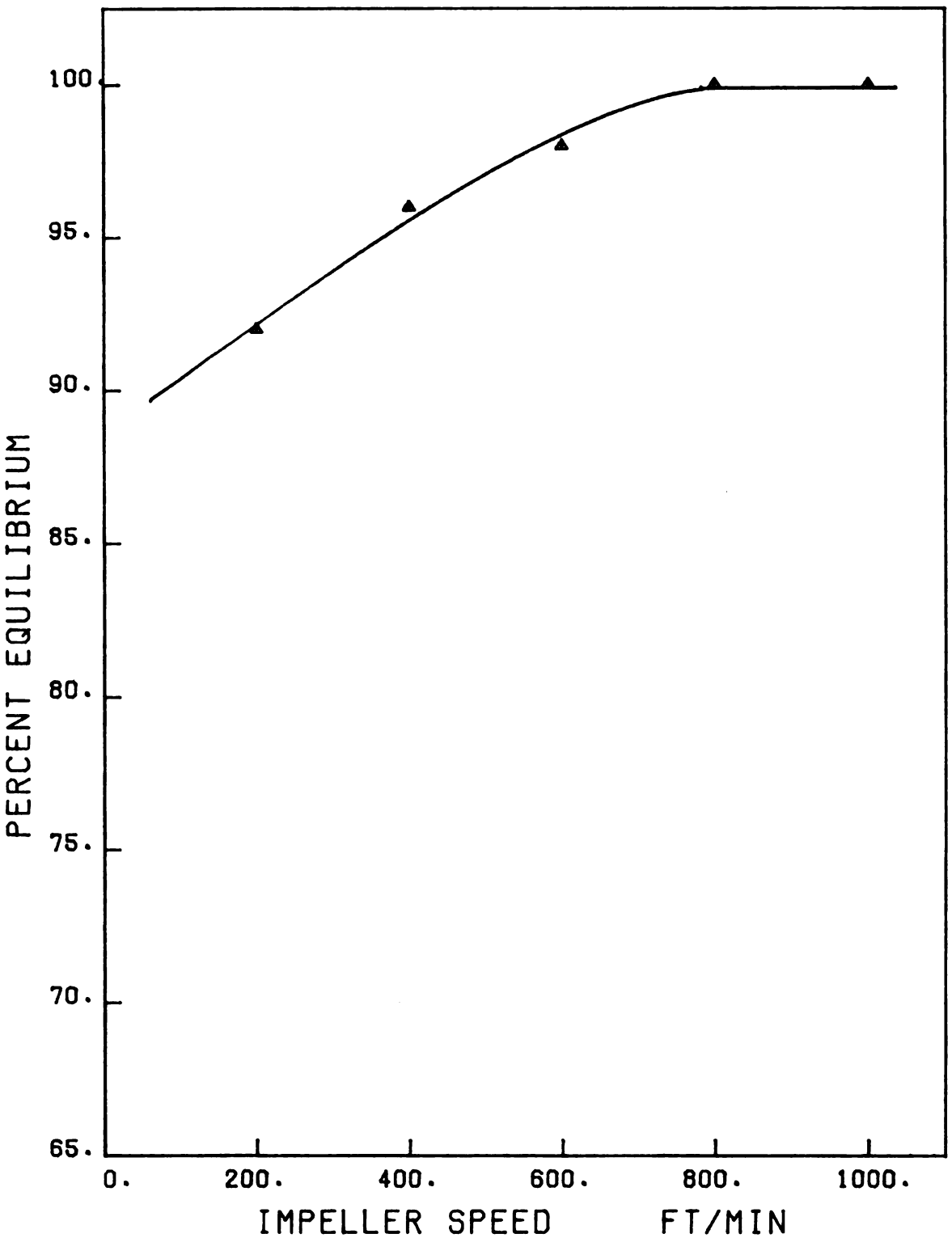

PERCENT EQUILIBRIUM
100
95.
90.
85.
80.
75.
0.
5.
10.
15.
20.
25.
30.
35.
MIX TIME MIN
400 FT/MIN
600 FT/MIN
800 FT/MIN
1000 FT/MIN

Figure 5.8. Percent equilibrium versus impeller speed in the stripping circuit. Mix time = 15 minutes, Organic = 640 mg/l Al^{3+}, Acid = 6 N H_2SO_4, 3:1 phase ratio.


100.
95.
90.
85.
80.
75.
70.
65.
PERCENT EQUILIBRIUM
0.
200.
400.
600.
800.
1000.
IMPELLER SPEED FT/MIN

had reached 92% while the extraction equilibrium was only 75%. All further tests were evaluated at 800 ft/min with a mix time of 15 minutes to ensure equilibrium conditions had been reached.

5.3.3. Acid Evaluation

The next tests evaluated the performance of different acids in the stripping circuit. Figure 5.9 shows the results using hydrochloric and sulfuric acid. Loaded organic containing 640 mg/l aluminum was contacted for 20 minutes at a 3:1 phase ratio. The results indicate that 6 N HCl and 9 N H_2SO_4 are equally effective in stripping the aluminum loaded organic phase. Based on the cost of each acid, sulfuric acid was chosen as the stripping acid of choice in all further experiments. Sulfuric acid also supplies the sulfur for regenerated aluminum sulfate, the alum coagulant used in water treatment facilities. The hydrochloric strip solutions were yellowish to orange while the sulfuric strip solutions were crystal clear.

The next experiments were conducted to evaluate acid stripping as a function of acid normality and phase ratio. The results are shown in Figure 5.10. Loaded extract containing 640 mg/l aluminum was contacted with sulfuric acid normalities ranging from 3 N to 12 N and with phase ratios of 3:1, 5:1, 10:1, 15:1, and 20:1. The 9 N H_2SO_4 acid at a phase ratio of 3:1 was shown to have the highest stripping efficiency. It would be expected that lower phase ratios (i.e., 1:1) would give even better stripping efficiencies.

5.3.4. Development of Stripping Equilibrium Curves

The final tests on the synthetic solutions involved establishing stripping distribution curves. Varying concentrations of organically

Figure 5.9. Comparison of acid type and normality on stripping efficiency. Mix time = 20 minutes, Organic = 640 mg/l Al^{3+}, 3:1 phase ratio.

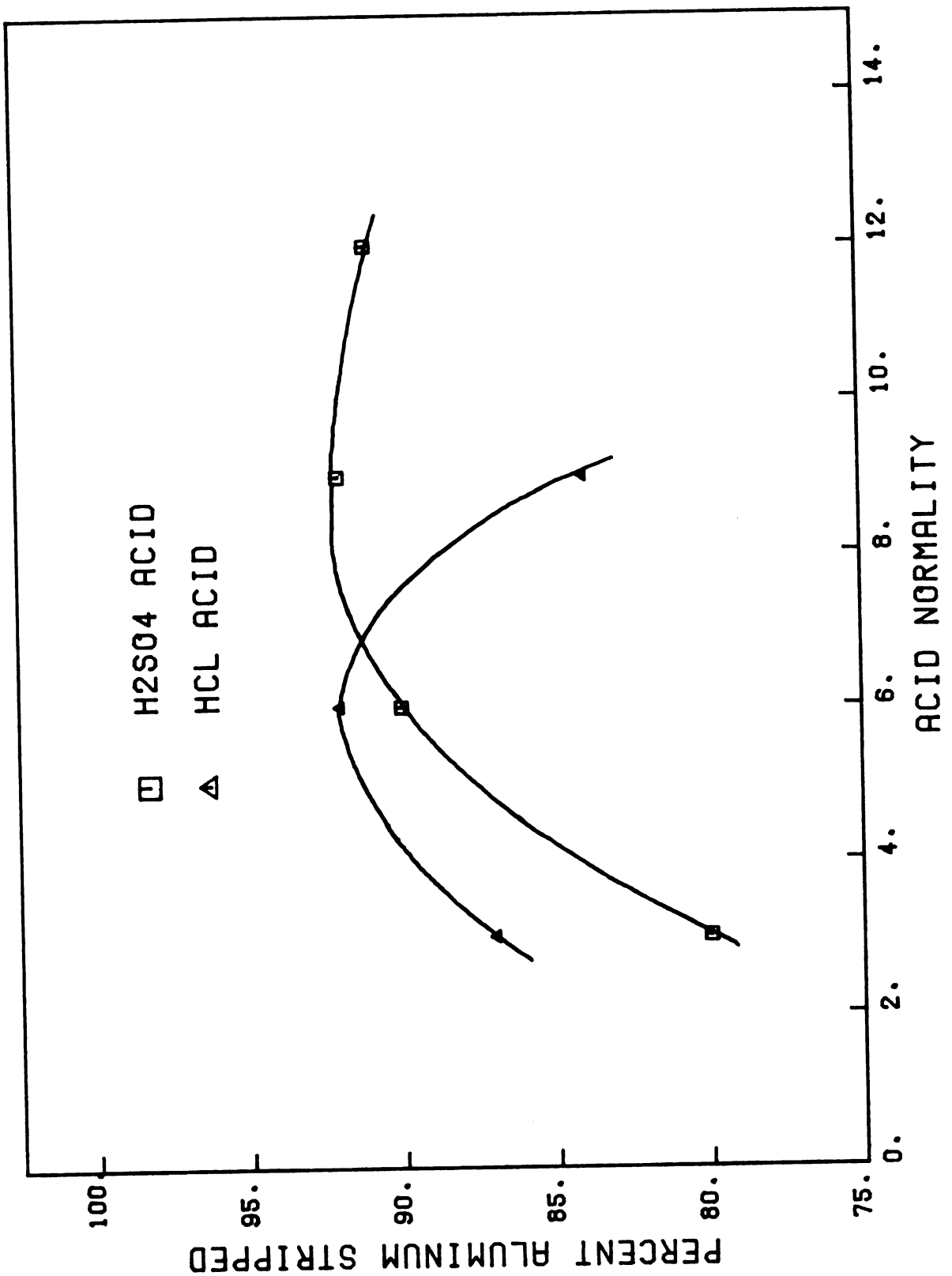
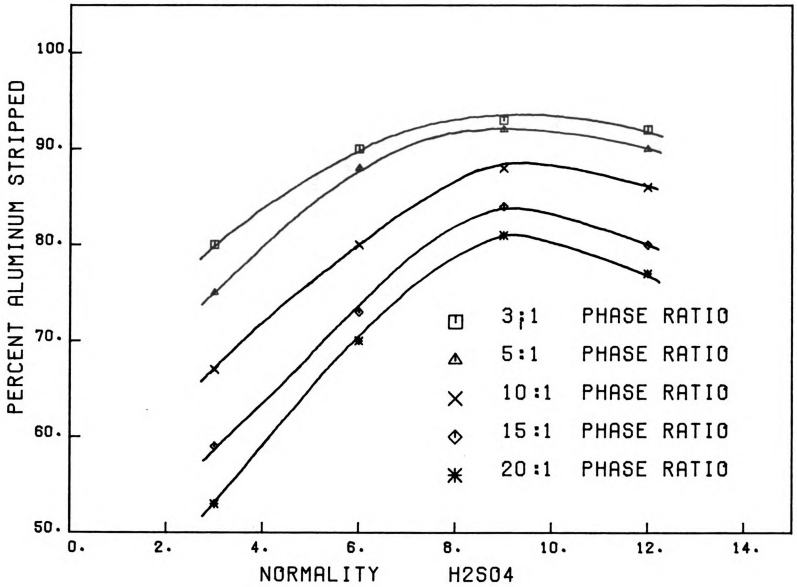

H2SO4 ACID
HCL ACID
PERCENT ALUMINUM STRIPPED
ACID NORMALITY
100
95.
90.
85.
80.
75.
0.
2.
4.
6.
8.
10.
12.
14.

Figure 5.10. Acid stripping as a function of H_2SO_4 normality and phase ratio. Mix time = 15 minutes, Organic = 640 mg/l Al^{3+}, Acid = 3 N - 12 N H_2SO_4, Phase Ratio = 3:1 - 20:1.


PERCENT ALUMINUM STRIPPED
100.
90.
80.
70.
60.
50.
0.
2.
4.
6.
8.
10.
12.
14.
NORMALITY H2SO4
3:1 PHASE RATIO
5:1 PHASE RATIO
10:1 PHASE RATIO
15:1 PHASE RATIO
20:1 PHASE RATIO

loaded aluminum, contacted in the monomer extraction range, were contacted with 6 N sulfuric acid. Six isotherms were developed by varying the organic to aqueous phase ratio. High phase ratios were desirable in order to concentrate the aluminum to the concentration of commercial liquid alum (49000 mg/l Al^{3+}). The results can be seen in Figure 5.11.

Each curve illustrates an initial segment where essentially all the aluminum was stripped. A fairly linear portion was next exhibited. The curves were not seen to level off. This is due to the high aluminum concentration required initially in the organic phase and difficulties in achieving this in the laboratory. A concentration of stripped aluminum equal to 64000 mg/l was achieved with a 40:1 phase ratio.

5.4. Selection of Support Extractants

While the research of Cornwell [26] and this study fully support MDEHPA as being an effective extractant, a need was felt to have a second extractant that would have applicability in aluminum complexing. Two other extractants were evaluated for use in the alum recovery process.

Octylphenol acid phosphate was analyzed for use as an extractant. Problems were encountered in dissolving the octylphenol acid in the diluent. The manufacturer, Mobil Chemical Company, was notified by the researcher and currently is undertaking research to enhance their product's solubility. Experiments on this extractant were discontinued at that time. When and if Mobil can resolve this problem, octylphenol acid phosphate may show applicability in aluminum extraction.

Di(2-ethylhexyl) phosphoric acid (DEHPA) was evaluated for use

Figure 5.11. Synthetic stripping equilibrium curves for various phase ratios of H_2SO_4 acid. Mix time = 15 minutes, Organic = 500-6000 mg/l Al^{3+}, Phase Ratios - 3:1 - 40:1.

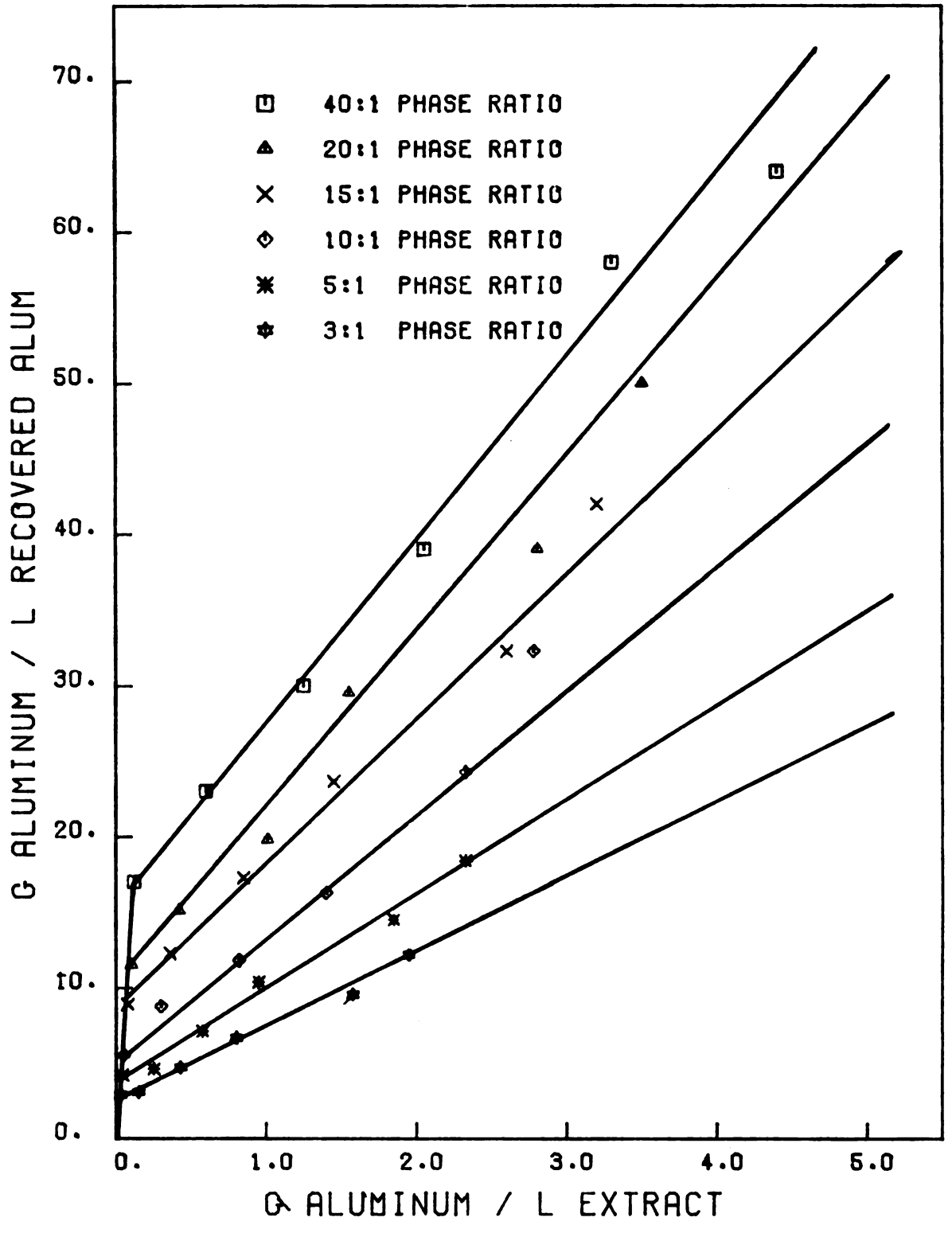
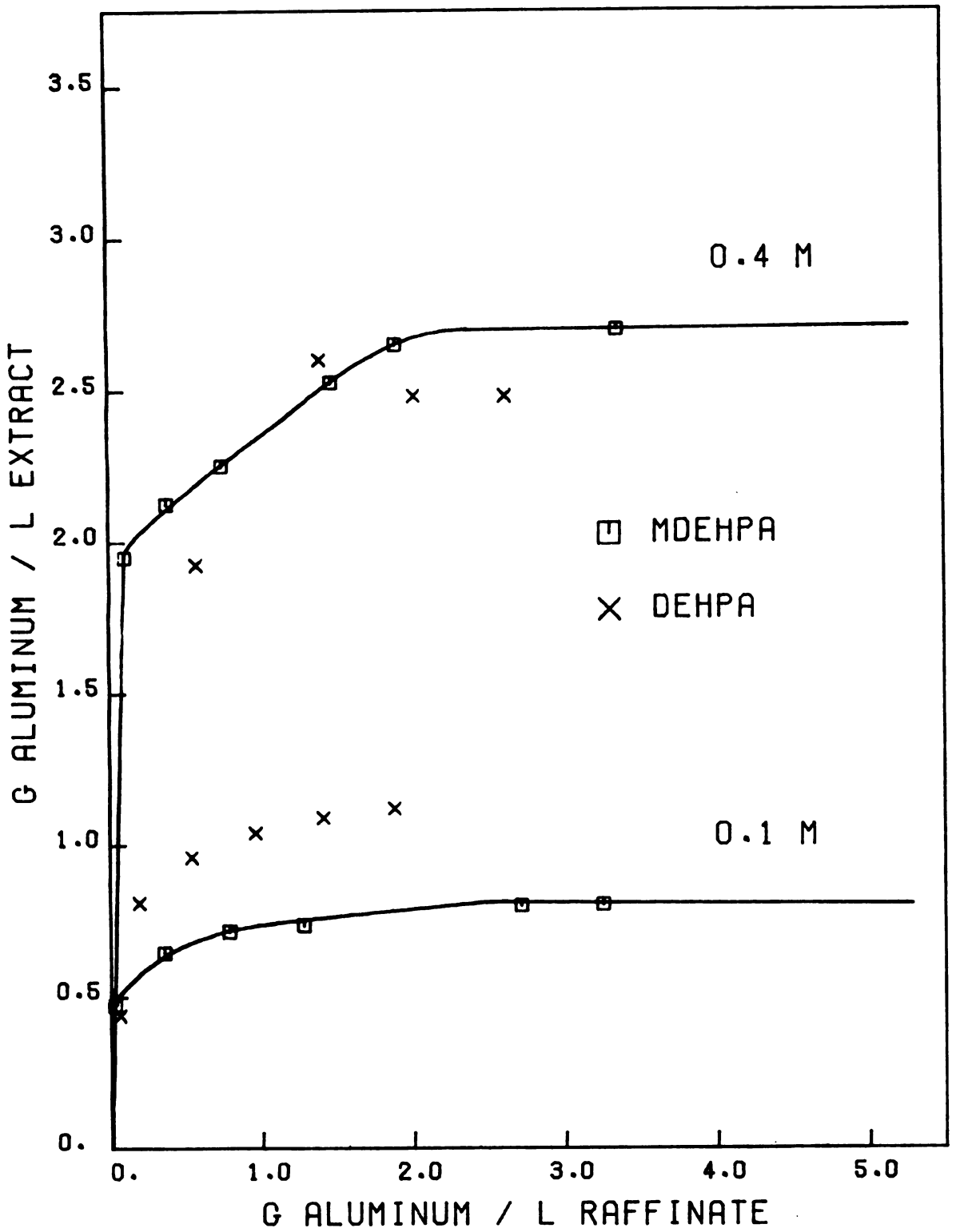

40:1 PHASE RATIO
20:1 PHASE RATIO
15:1 PHASE RATIO
10:1 PHASE RATIO
5:1 PHASE RATIO
3:1 PHASE RATIO
G ALUMINUM / L RECOVERED ALUM
G ALUMINUM / L EXTRACT
0.
10.
20.
30.
40.
50.
60.
70.
0.
1.0
2.0
3.0
4.0
5.0

Figure 5.12. Comparison of synthetic extraction equilibrium curves utilizing MDEHPA and DEHPA as extractants. Mix time = 15 minutes, Al^{3+} = 500-600 mg/l, 1:1 phase ratio.


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
G ALUMINUM / L EXTRACT
0.4 M
MDEHPA
DEHPA
0.1 M
0.
1.0
2.0
3.0
4.0
5.0
G ALUMINUM / L RAFFINATE

as an extractant. Equilibrium isotherms were established and compared to the MDEHPA isotherms already established. The results are shown in Figure 5.12. The results indicate that DEHPA is at least equal and probably better in extraction effectiveness than MDEHPA. However, addition of a neutral compound, tributyl phosphate, was needed to help prevent a third phase formation during settling. The third phase contained both aqueous and organic droplets that had a tendency not to disengage. The phase disengagement time was also longer.

As a result, DEHPA was concluded to be an extractant worthy of consideration as a backup to MDEHPA. The extractant would require more control during operation in order to prevent third phase formation. No further studies were undertaken during this research.

5.5. Selection of Support Diluents

This and other liquid-ion exchange research has successfully used kerosene as the diluent for the organic phase. Recent research has developed other fractionalized crude oil deriviatives for use as diluents. Specifications are closely controlled so that uniformity of the product can be maintained. This is not done with kerosene. Evaporation and fire hazards have been minimized with these diluents. Manufacturers also claim faster rates of phase disengagement which result in minimum solvent entrainment losses and lower settling area requirements.

Two of these diluents, Kermac 470B and 627, were evaluated for use as organic solvents. Both Kermac 470B and Kermac 627 were manufactured by Kerr-McGee Refining Corporation. Extraction isotherms were established in exactly the same manner as previously outlined

for the MDEHPA, but the new diluents were substituted for kerosene. The results of these diluents on extraction efficiency can be seen in Figure 5.13. The results indicate that these two diluents were equally as effective as kerosene in aluminum extraction.

Phase disengagement rates were next evaluated. This is an important parameter for determining settler area and detention time. Observations revealed that all three of the diluents exhibit rapid phase disengagement. Secondary break was complete in 3-8 minutes for the Kerr-McGee products and in approximately 10 minutes for kerosene.

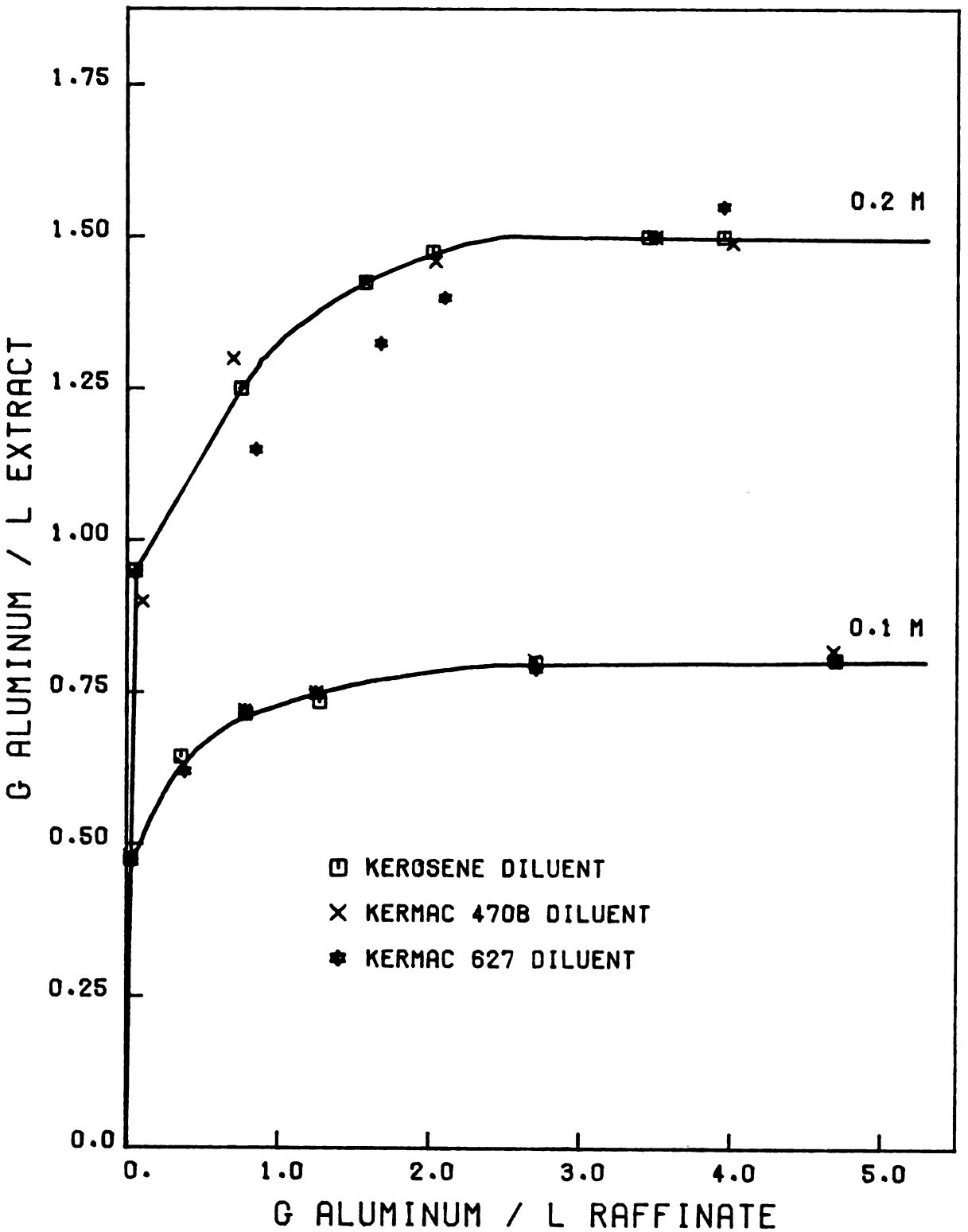
Evaporation losses were evaluated for four days for the three diluents. The tests were not run under controlled conditions so the results are only relative. Both Kerr-McGee diluents had losses of 160 ml/day/m^2 compared to 460 ml/day/m^2 for kerosene.

The physical and chemical characteristics reported by the manufacturer in conjunction with the demonstrated effectiveness in operation indicates that either Kerr-McGee diluent could and should be used as a replacement for kerosene in future research. The costs for the Kerr-McGee products were very comparable to kerosene at the time of this research. The only reason these diluents were not utilized further was their reduced availability in the time restraints imposed.

5.6. Solvent Loss Considerations

Loss of the diluent or extractant into the aqueous phase during extraction is an important economic consideration. Losses within the circuit can occur by evaporation, by chemical attack, or by entrainment of the organic phase into the aqueous phase during mixing. The first two sources of loss are minimal especially where commercial

Figure 5.13. Comparison of diluents on extraction efficiency. Mix time = 15 minutes, Al^{3+} = 500-6000 mg/l, 1:1 phase ratio.


1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.0
G ALUMINUM / L EXTRACT
0.2 M
0.1 M
KEROSENE DILUENT
KERMAC 470B DILUENT
KERMAC 627 DILUENT
0.
1.0
2.0
3.0
4.0
5.0
G ALUMINUM / L RAFFINATE

diluents are used that specifically try to eliminate these factors. The loss of solvent by entrainment in the raffinate constitutes the largest source of losses within the circuit. Entrainment losses are in turn related to the dispersion phase during mixing. Research has shown that when the extraction circuit is operated organic continuous, aqueous dispersed, organic losses can be minimized.

In order to monitor organic losses, two analytical methods were employed. One utilized total organic carbon analysis to determine the combined diluent and extractant losses. The second method analyzed extractant losses only by a spectrophotometric method. In this way both diluent and extractant losses could be quantitatively measured.

Synthetic solutions of different aluminum concentrations, diluents, and molarities of MDEHPA were contacted at a 1:1 phase ratio. All extraction circuits were operated organic continuous. The raffinate solutions were analyzed for total organic carbon and MDEHPA concentrations. Table 5.2 shows the results.

The results indicated that most of the organic losses were associated with the diluent (83% as mg/l C). Aluminum concentration, the type of diluent, or the molarity of extractant did not have any effect on organic losses. Another important result was that the MDEHPA extractant entrainment was 180 mg/l as extractant.

It was felt that much of the organic losses were unavoidable due to the nature of the settling apparatus. The organic solution adhered to the sides of the separatory funnel and were flushed out with the recovered raffinate solutions. Also it was believed that organic losses would taper off after repeated contacts with feed and acid solutions due to impurities in the diluents initially. Another

TABLE 5.2

Organic Loss Determinations

Sample Constituents	Total Organic Carbon Losses mg/l C	Extractant Losses		Diluent Losses mg/l C	Extractant Losses Per Extractant Contact Percent
		mg/l MDEHPA	mg/l C		
300 Al 0.4 M MDEHPA Diluent - Kerosene	2000	210	110	1890	0.20
5000 Al 0.7 M MDEHPA Kerosene	2200	110	60	2140	0.06
3000 Al 0.4 M MDEHPA Kermac 470B	2000	100	60	1940	0.09
5000 Al 0.7 M MDEHPA Kermac 470B	2100	110	60	2040	0.06
3000 Al 0.4 M MDEHPA Kermac 627	2100	400	210	1890	0.38
5000 Al 0.7 M MDEHPA Kermac 627	2000	160	85	1915	0.09

experiment was employed where the organic phase was repeatingly contacted with feed and acid solutions alternatingly. The phases were allowed to settle in long Teflon burets for periods of at least six hours to minimize entrainment losses. A 0.4 M MDEHPA solution in both kerosene and 470B was contacted with 3000 mg/l aluminum and 3 N H_2SO_4 in alternating circuits. Eight separate contacts were made, four in the extraction circuit and four in the stripping circuit.

The results indicated two findings. First, longer settling times lowered entrainment losses. Total organic carbon losses in the extraction stages were lowered to 1200 mg/l as C and extractant losses to 80 mg/l as MDEHPA. Total organic losses in the stripping stages were 800 mg/l as C. Extractant losses averaged 0.08% per extractant contact. Secondly, repeated contacts had no effect on lowering organic losses. Losses remained constant through each contact. Both diluents reported equal results.

CHAPTER 6

ALUMINUM RECOVERY FROM ALUM SLUDGE SOLUTIONS

6.1. Introduction

The extraction and stripping of aluminum from sludge samples attempted to optimize the particular parameters studied with synthetic solutions. The introduction of solids into the recovery process was the most complicated of these parameters to optimize. The sludge slurry contained solid particles bound up with the aluminum ions. The aluminum could not be extracted until it was dissolved into solution. The dissolution of aluminum necessitated a reduction in pH. The solids introduced contamination problems and critical economic considerations. Solid particles lodged at the organic-water interface and may inhibit draw-off rates in the settler. Solid particles also tended to cohese organic droplets to their surface. Substantial organic losses may result.

6.2. Extraction of Aluminum from the Tampa Sludge

6.2.1. Introduction

The extraction of aluminum from the Tampa sludge was undertaken in two phases: extraction after sludge acidification and extraction before sludge acidification. The reason for this approach was to evaluate the need of the acidification stage prior to entering the extraction circuit. Solids were not removed after acidification and prior to extraction. Extraction after sludge acidification would

follow closely the situation studied on synthetic solutions. If extraction before sludge acidification could be shown successful, the acidification stage and its associated cost could be eliminated.

6.2.2. Extraction After Sludge Acidification

6.2.2.1. Kinetics Study.--The first test involved establishing kinetic curves to determine optimum mix speeds and times for extraction to achieve equilibrium. This test was run in exactly the same manner as were the synthetic kinetic tests. The results are shown in Figure 6.1. The data indicated that the sludge solids slightly slowed the extraction equilibrium as compared with the synthetic solutions. At an impeller speed of 800 ft/min equilibrium was reached in 15 minutes as compared to 10 minutes for the synthetic solutions. If the impeller speed was increased to 1000 ft/min, the equilibrium time was reduced to 12 minutes. All further extraction tests were run at 800 ft/min for 20 minutes to ensure reaction completion.

6.2.2.2. Development of Extraction Equilibrium Curves.--Extraction equilibrium curves for the Tampa sludge were next evaluated. The equilibrium points shown in Table 6.1 were developed with an initial feed pH = 2.0, a 1:1 phase ratio, an impeller speed of 800 ft/min, and a 20 minute mix time. The equilibrium points corresponded to the curves developed on synthetic feed solutions (Figure 5.5). The total aluminum concentration of the Tampa sludge was found to be 3300 mg/l. From these data it was concluded that the synthetic extraction equilibrium curves could be used to predict the number of contact stages and extraction efficiencies of each stage for the Tampa sludge.

Figure 6.1. Impeller speed versus time to reach equilibrium in the Tampa sludge. Feed pH = 2.0, 0.1 M MDEHPA, Al^{3+} = 3300 mg/l, 1:1 phase ratio.

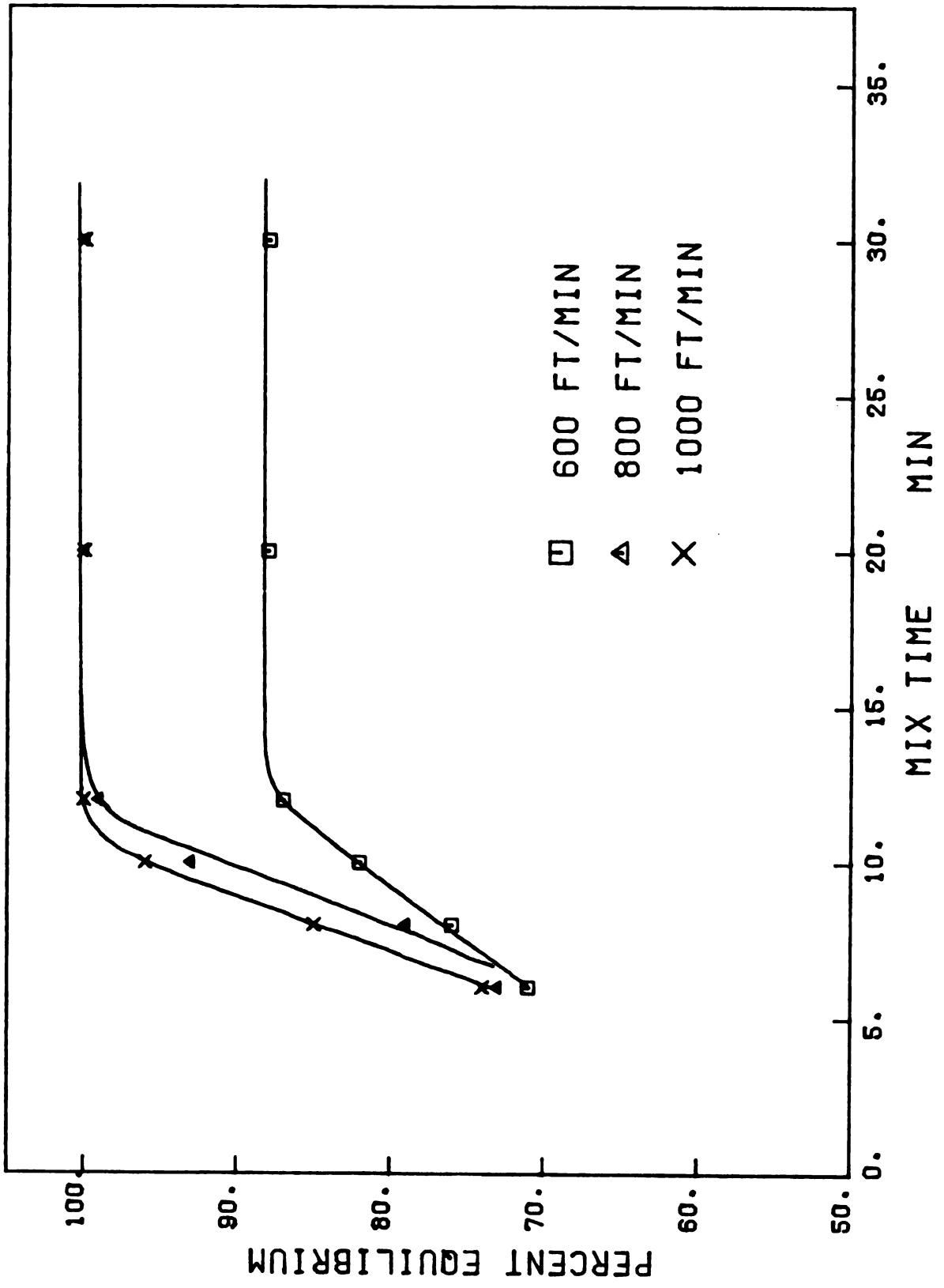

PERCENT EQUILIBRIUM
100
90.
80.
70.
60.
50.
0.
5.
10.
15.
20.
25.
30.
35.
MIX TIME MIN
600 FT/MIN
800 FT/MIN
1000 FT/MIN

TABLE 6.1

Extraction of Tampa Sludge with MDEHPA

Initial Feed Aluminum mg/l	Molarity MDEHPA	Organic Aluminum mg/l	Aqueous Aluminum mg/l
3300	0.1	750	2550
3300	0.1	785	2515
3300	0.2	1560	1640
3300	0.2	1520	1680
3300	0.3	1850	1350
3300	0.3	1800	1490
3300	0.4	2250	950
3300	0.4	2225	975

Tests were next undertaken to evaluate extraction when the initial feed pH was 1.0. The results indicated that the overall extraction efficiency decreased. Therefore an attempt was made to calculate the scale factor for the feed pH = 1.0 equilibrium curve. It was found that if the molarity of the MDEHPA concentration was multiplied by 1.3 that the synthetic equilibrium curves based on a feed pH of 2.0 could be utilized for design purposes. The scale-up factor of 1.3 was felt to be accurate for any design on the Tampa sludge. New factors should be evaluated for each different feed pH used.

6.2.3. Extraction Before Sludge Acidification

The equilibrium curves produced thus far were made by contacting the sludge with sulfuric acid to achieve the desired feed solution pH. Since the sulfuric acid represented a major cost in the recovery process, tests were undertaken to evaluate if higher feed pH's could result in complete aluminum recovery. The basis of the theory is the

extractant's ability to release hydrogen ions as aluminum was extracted. The release of hydrogen ions would lower the pH and dissolve more aluminum into solution for extraction.

Experiments were conducted to evaluate initial sludge pH versus final raffinate pH and aluminum extracted. Tampa sludge at varying initial feed pH's was contacted with a 0.52 M solution of MDEHPA at a 1:1 phase ratio. At the feed pH's from 7.0 to 3.0 the extraction operated aqueous continuous, organic dispersed. This was opposite to all extraction tests up to now. With the extraction circuit operating aqueous continuous the solids would remain in the organic phase throughout the settling stage. The organic phase was very thick and appeared to be emulsified. The problem with operating aqueous continuous was that solids carry-over would be evident in the stripping circuit. Also, organic losses would be high. All attempts to vary impeller speed and mix time did not change this characteristic. When the pH of the feed sludge was lowered to 2.5 the extraction circuit could be operated kerosene continuous and the solids would remain in the raffinate during settling. The explanation for this phenomenon can be attributed to the nature of the aluminum hydroxide-solids floc formed during coagulation. Stable emulsions are formed at the high pH due to the strength of the floc particle bonds. The strong floc particle bonds trap the organic and do not allow the two phases to separate. As the pH of the sludge is lowered, the strength of the aluminum hydroxide-solids bond weakens and the floc is unable to trap the organic.

The phase ratio was changed to 2:1 and the experiment repeated. At all the different feed pH values the extraction circuit operated

organic continuous. The results of contacting 0.23 and 0.52 M solutions of MDEHPA with the varied Tampa sludge pH readings can be seen in Figure 6.2. All of the solids remained in the aqueous phase. The extractant in the organic phase acted to reduce the pH as aluminum was complexed.

The result of initial sludge pH versus aluminum extracted for the 0.23 and 0.52 M solutions of MDEHPA is shown in Figure 6.3. The figure indicates that there existed an optimum feed pH where essentially all of the aluminum was extracted in one contact. For the 0.23 M solution of MDEHPA, a feed pH of 4.0 gave 99% extraction. For a 0.52 M solution of MDEHPA, a feed pH = 5.0 gave essentially complete extraction in one contact. It was concluded that a higher molarity of extractant would complex all of the aluminum at a high feed pH. This is in turn would lower acid requirements before extraction.

At a higher feed pH the extraction effectiveness declined. This was due because either, 1) not enough aluminum was in solution for the extraction to start, or 2) there was not sufficient quantities of acidic extractant to first lower the pH and release hydrogen ions into solution.

The next experiment was to determine the molarity of extractant needed to obtain complete extraction at the raw sludge pH. Figure 6.4 shows the results. A MDEHPA molarity of 0.6 extracted 99% of the aluminum in the sludge in one contact. The raffinate pH was equal to 1.78.

Figure 6.2. Initial pH versus final pH for varying molarities of MDEHPA. Mix time = 20 minutes, 2:1 phase ratio.

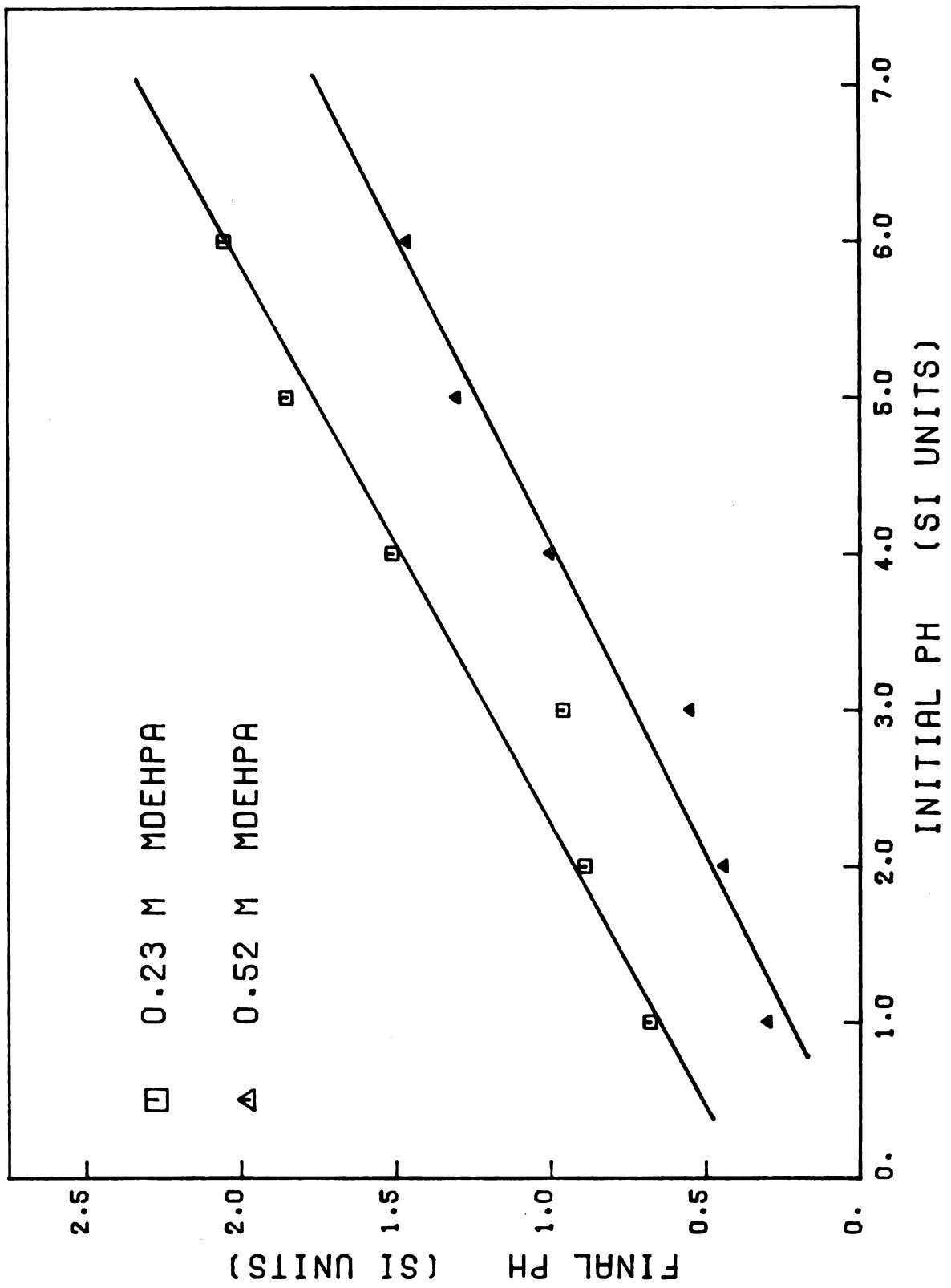

FINAL PH (SI UNITS)
INITIAL PH (SI UNITS)
0.23 M MDEHPA
0.52 M MDEHPA
0.
0.5
1.0
1.5
2.0
2.5
1.0
2.0
3.0
4.0
5.0
6.0
7.0

Figure 6.3. Initial sludge pH versus extraction efficiency. Initial Al^{3+} = 3300 mg/l, mix time = 15 minutes, phase ratio 2:1.

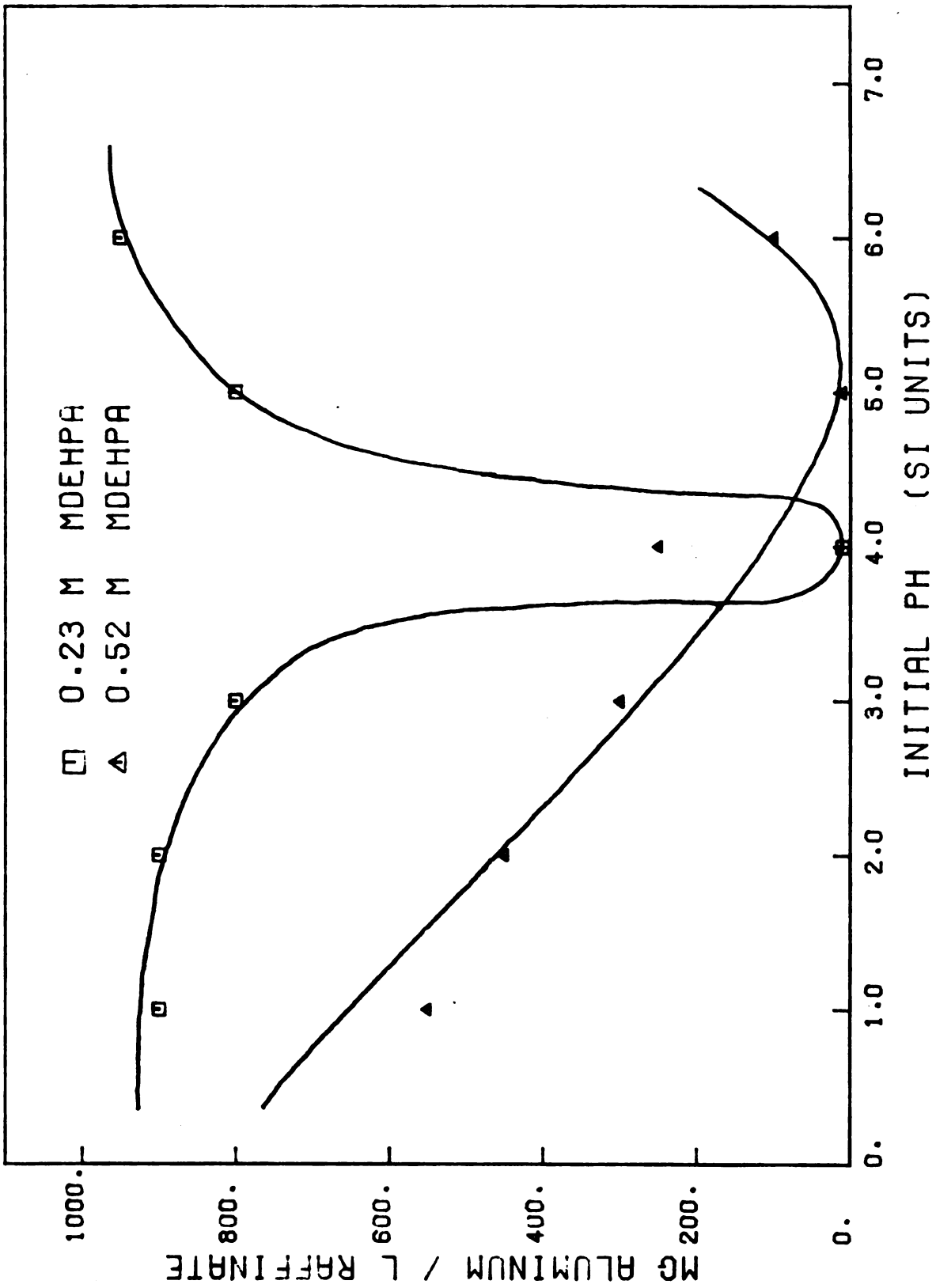
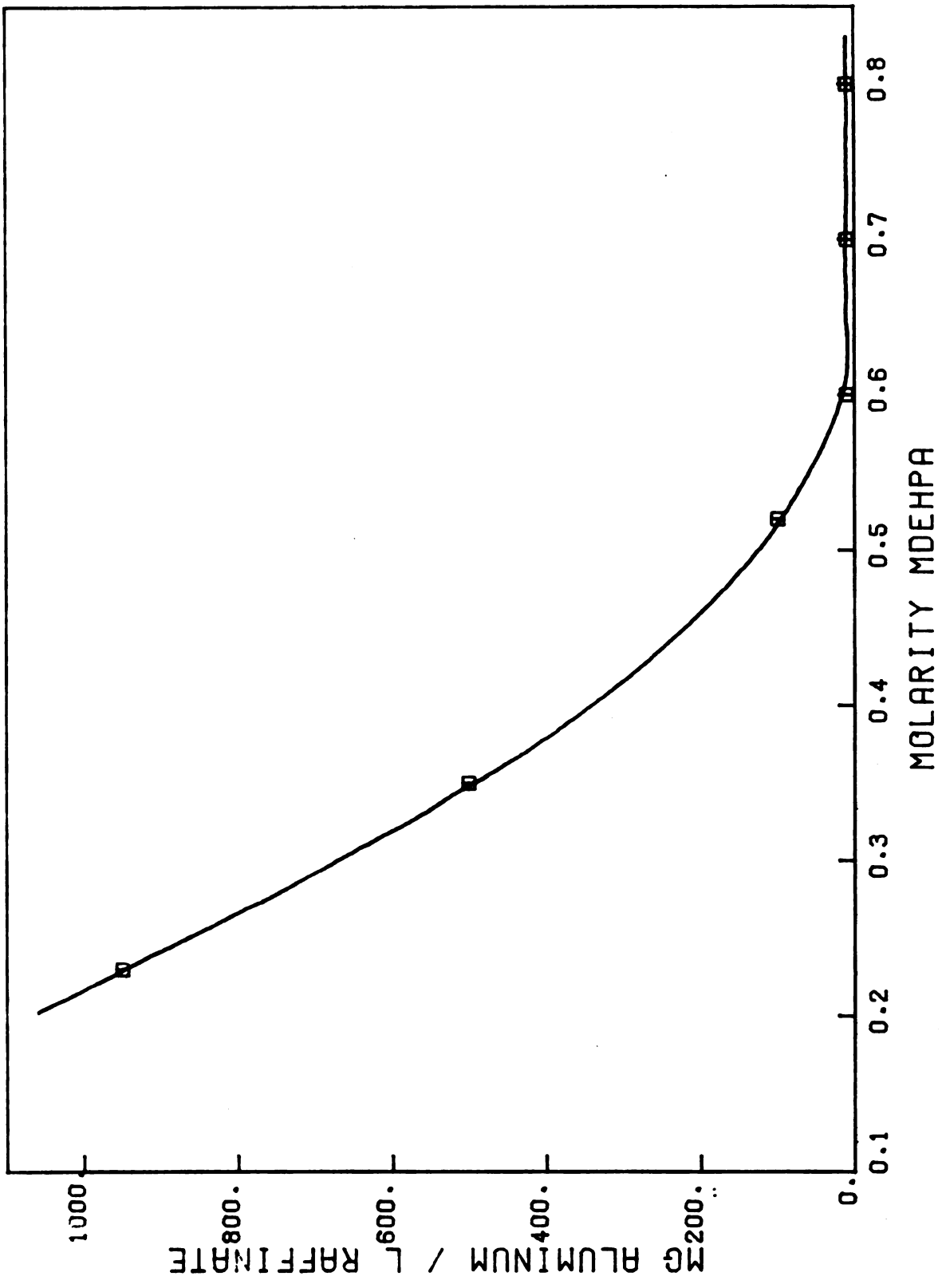

0.23 M MDEHPA
0.52 M MDEHPA
MG ALUMINUM / L RAFFINATE
INITIAL PH (SI UNITS)
0.
200.
400.
600.
800.
1000.
1.0
2.0
3.0
4.0
5.0
6.0
7.0

Figure 6.4. Molarity of MDEHPA to extract all the aluminum from the Tampa sludge at the raw sludge pH. Initial Al^{3+} = 3300 mg/l, mix time = 15 minutes, 2:1 phase ratio.


MG ALUMINUM / L RAFFINATE
1000
800.
600.
400.
200.
0.
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
MOLARITY MDEHPA

6.2.4. Summary

The major problem associated with the introduction of solids into the extraction circuit was the scum layer formed at the organic-aqueous interface. This problem was anticipated since other extractive metallurgic processes had reported similar problems in operation [29, 30]. These solids accumulated at the interface and did not seem to interfere with the extraction operation.

A possible problem associated with this scum build up may result if the layer keeps increasing in thickness. Research with slurry operations of this kind have shown that the thickness of the layer reaches a certain level and then increases only slowly with extended operation [34]. A continuous flow study is necessary to fully evaluate this possible complication.

6.3. Stripping of Aluminum-MDEHPA

6.3.1. Kinetics Study

The initial stripping tests on the Tampa sludge was a kinetic study. The results indicated that the sludge stripping circuit operated in exactly the same manner as the synthetic feed solutions. A mix time of 12 minutes at 800 ft/min resulted in equilibrium being reached. This agreement was expected since no solids were present in the stripping circuit.

6.3.2. Comparison of Stripping when Extraction Occurs in the Monomer and Dimer Ranges

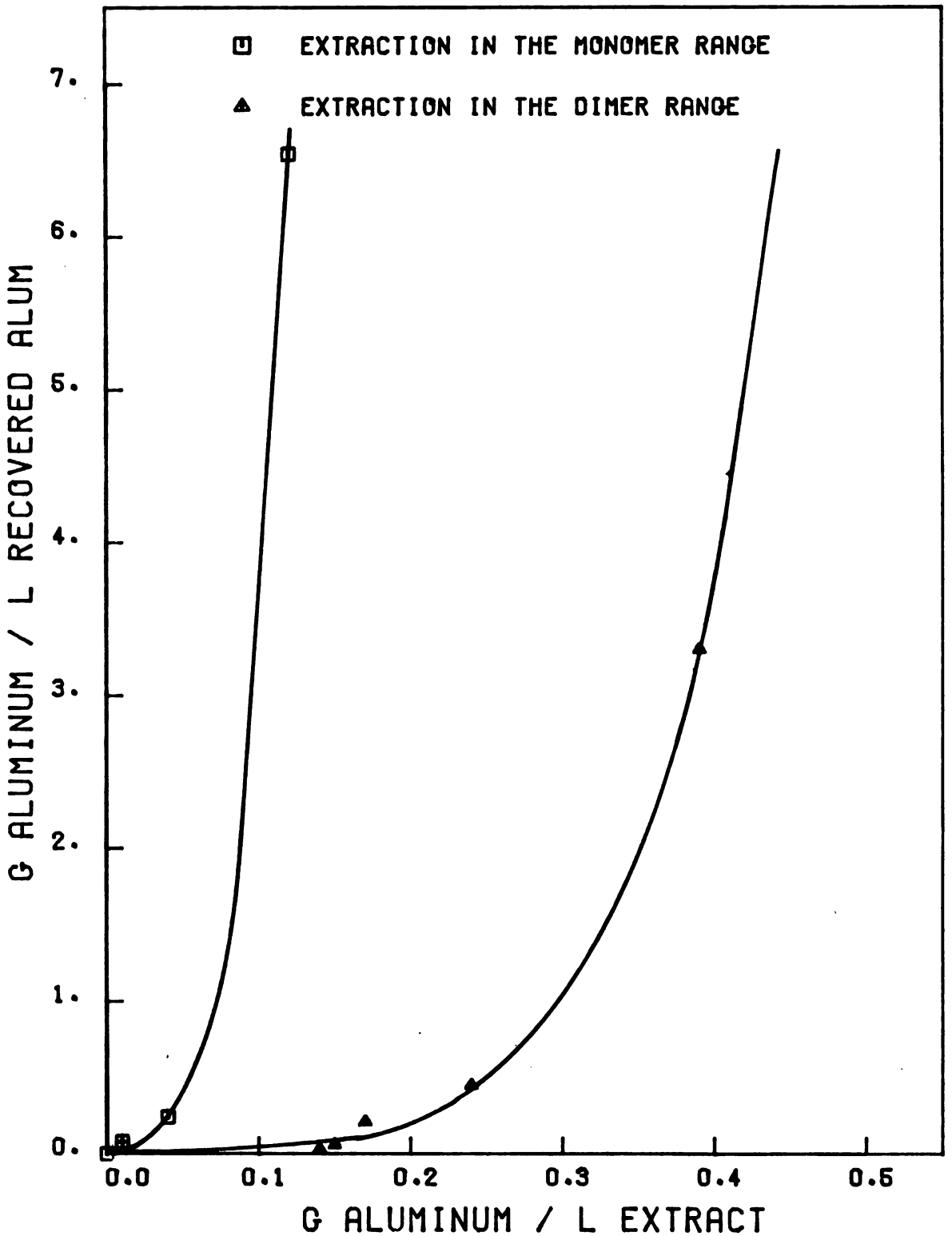
As was stated earlier the stripping circuit was greatly dependent on whether the extraction was operated in the monomeric or dimeric ranges during extraction. Figure 6.5 exhibits the stripping as

Figure 6.5. Aluminum stripping as a function of extraction in the monomer and dimer ranges.

1) Monomer extraction range - 0.35 M MDEHPA contacted in two stages with the Tampa sludge (pH = 2.0) in a 1:1 phase ratio. Final Al^{3+} concentration in the organic phase = 2300 mg/l.

2) Dimer extraction range - 0.52 M MDEHPA contacted in one stage with the Tampa sludge (pH = 2.0) in a 2:1 phase ratio. Final Al^{3+} concentration in the organic phase = 1500 mg/l.

3) Stripping conditions - 3 N H_2SO_4, 3:1 phase ratio.


EXTRACTION IN THE MONOMER RANGE
EXTRACTION IN THE DIMER RANGE
G ALUMINUM / L RECOVERED ALUM
G ALUMINUM / L EXTRACT
0.
1.
2.
3.
4.
5.
6.
7.
0.0
0.1
0.2
0.3
0.4
0.5

functions of extraction in the monomeric or dimeric ranges. One aluminum loaded organic sample contained 0.52 M MDEHPA contacted in one stage with the Tampa sludge at a phase ratio of 2:1. This represented the extration circuit in the dimer range. The loaded organic phase contained 1500 mg/l aluminum. The other organic sample contained 0.35 M MDEHPA contacted in two stages with the Tampa sludge at a phase ratio of 1:1. This represented the monomeric extraction circuit. This organic phase contained 2300 mg/l aluminum. All of the organic was recycled to the next contact stage during the stripping circuits. Both organic phases were then contacted with 3 N H_2SO_4 at a 3:1 phase ratio. Table 6.2 summarizes the equilibrium concentrations, stripping coefficients, and the cumulative percents of aluminum stripped for the two extraction ranges. The figure clearly shows the higher stripping efficiencies achieved when the extraction circuit was operated in the monomeric range.

With a phase ratio of 3:1, 3 N H_2SO_4 could strip 100% of the aluminum in the loaded Tampa organic (2300 mg/l Al) in four contacts when the extraction circuit was operated in the monomeric range. The same acid, operating under the exact conditions, could only strip 91% of the aluminum loaded organic phase (1500 mg/l Al^{3+}) in five contacts when the extraction was operated in the dimer range. This clearly shows the advantages of operating the extraction circuit in the monomer ranges.

6.3.3. Development of Stripping Equilibrium Curves

All stripping equilibrium curves utilized Tampa sludge which had been extracted in the monomer range. Molarities of extractant

TABLE 6.2

Stripping of MDEHPA in the Monomer and Dimer Extraction Ranges

Contact Number	Acid Type and Strength	Phase Ratio (Organic:Acid)	Extract Aluminum (mg/l)	Stripped Aluminum (mg/l)	Stripping Coefficient	Cumulative Aluminum Stripped, Percent
			Dimer Range			
1	3N H_2SO_4	3:1	390	3300	8.5	74
2			240	450	1.9	84
3			170	210	1.2	89
4			150	60	0.4	90
5			140	30	0.2	91
			Monomer Range			
1	3N H_2SO_4	3:1	120	6540	54.5	95
2			40	240	6.0	98
3			15	75	5.0	99
4			0	45	---	100
5			0	0	---	---

were varied to result in organic solutions containing 500 to 3000 mg/l Al^{3+}. Each of these organic solutions were contacted with 6 N H_2SO_4 in various phase ratios ranging from 3:1 to 40:1. The high phase ratios were desirable to concentrate the recovered alum to commercial strength and also minimize acid costs. The results in Table 6.3 indicate that the sludge solutions behave in the same manner as the synthetic solutions. Prediction of number of contact stages and phase ratios could be determined from any of the stripping equilibrium curves.

TABLE 6.3

Stripping of Tampa Sludge - MDEHPA

Initial Organic Aluminum mg/l	Sulfuric Strip Acid	Phase Ratio Organic: Aqueous	Final Organic Aluminum mg/l	Recovered Alum Concentration mg/l Al^{3+}
3300	6 N	3:1	950	7050
3300	6 N	5:1	1070	11150
4150	6 N	10:1	1975	21750
4150	6 N	15:1	2150	30000
4150	6 N	20:1	2200	39000

6.4. Phase Dispersion Considerations

There are two types of dispersions: one is a dispersion of aqueous droplets in the organic phase and is called organic continuous. The other dispersion has organic droplets in the aqueous phase and is called aqueous continuous. The type of dispersion in which the organic droplets are dispersed in the aqueous phase are very prone to

have stable emulsions. The raffinate, when leaving the extraction circuit, may still have in it entrained organic droplets which represent solvent losses. When solids are present in the system, emulsions become tight non-breaking flocs which trap the organic and do not allow the two phases to separate. When aqueous droplets are dispersed in the organic phase during mixing, emulsions are less likely to form and solvent losses can be minimized.

Solids, present in any appreciable amounts, contribute to the emulsion formation. It is therefore very important to operate the extraction circuit organic continuous with the aqueous droplets dispersed.

This research tried to determine the methods that extraction circuits could be operated organic continous. The literature indicated that operating in a certain phase is dependent on many factors and cannot be generally defined. Ordinarily the continuous phase will be the one which is present in the greatest volume although this is not always true. The type of extractant, surfactants, or solubility agents present, and the way in which mixing is started are also listed as factors in determining the continuous phase during mixing.

Phase volume was the controlling factor on dispersion phases for the mixing of synthetic aluminum solutions. Whichever phase was present in the greatest volume was the continuous phase. Adding the aqueous phase to the already mixing organic phase and conversely, and adding modifiers did not change the dispersion phase.

When solids were introduced into the system during the extraction of the Tampa sludge, three factors determined the continuous phase. The method of mixing, the relative volumes of each phase, and

the feed pH were the important factors in determining the continuous phase. When the organic phase was added to the already mixing aqueous phase, the extraction circuit always operated aqueous continuous. This occurred even when the organic to aqueous phase ratio was 8:1. When the aqueous phase was added to the already mixing organic phase, the circuit operated in the phase which was present in the greatest volume. At a phase ratio of 1:1, the extraction circuit operated organic continuous when the pH was approximately 2.5 or less and aqueous continuous when the pH was greater than 2.5.

The solids had a great influence on the dispersion phase. Emulsion formation was an evident problem in working with the sludge samples. At the 1:1 phase ratio the critical pH represented the point when the aluminum floc particles were dissolved from the sludge solids and the aluminum was put into solution. It appeared evident that once the aluminum hydroxide solids floc was broken, the solids did not contribute to emulsion formation.

To conclude, the synthetic aluminum solutions could be operated at a 1:1 phase ratio, be organic continuous, and minimize organic losses. The Tampa sludge must be operated at a minimum of 1.1:1.0 phase ratio if the pH is greater than 2.5 or at a 1:1 phase ratio as long as the sludge pH was depressed to 2.5 before entering the extraction circuit. The aqueous phase should be added to a mixing organic phase. This ensures minimum organic losses.

6.5. Color Contamination Considerations

It was observed that during the extraction circuit color did not transfer into the kerosene phase. The organic phase was somewhat

cloudy but appeared to clear after a time in the settler. After the organic phase was contacted with the sulfuric acid in the strip circuit, no color change could be visually detected in the strip solutions.

6.6. Interfacial Phase Disengagement with Polymers

A variety of polymers were evaluated to test the polymer's ability to settle the solids built-up at the organic-aqueous interface. All of the polymers were commercially available. The polymers tested included cationic, anionic, and nonanionic charged types along with absorbant clay.

Polymer addition took place at three different points during the extraction circuit. First, polymers were added during the extraction mixing to the combined organic and aqueous phases. Secondly, polymers were added to the combined phases after extraction, were rapid mixed, flocculated, and allowed to coagulate in the settlers. Finally, polymers were added to the raffinate in the settlers. The raffinate phase was rapid mixed, flocculated, and allowed to settle. Care was taken not to disturb the organic phase in the settler.

The tests indicated that polymers and absorbant clay did not enhance the settling characteristics of the solids at the interface layer. This can probably be attributed to the nature of the solids in the Tampa sludge. The solids are predominately organic and have a very low specific gravity. The organic solids also have a tendency to absorb organic droplets to their surface. The inert solids do not have this characteristic. The inorganic solids did not accumulate at the interface.

Different alum sludges need to be evaluated separately. The type of solids, whether organic or inorganic in nature, play a large role in interfacial solid settling characteristics.

CHAPTER 7

PROCESS DESIGN FOR ALUMINUM RECOVERY BY LIQUID-ION EXCHANGE

7.1. Introduction

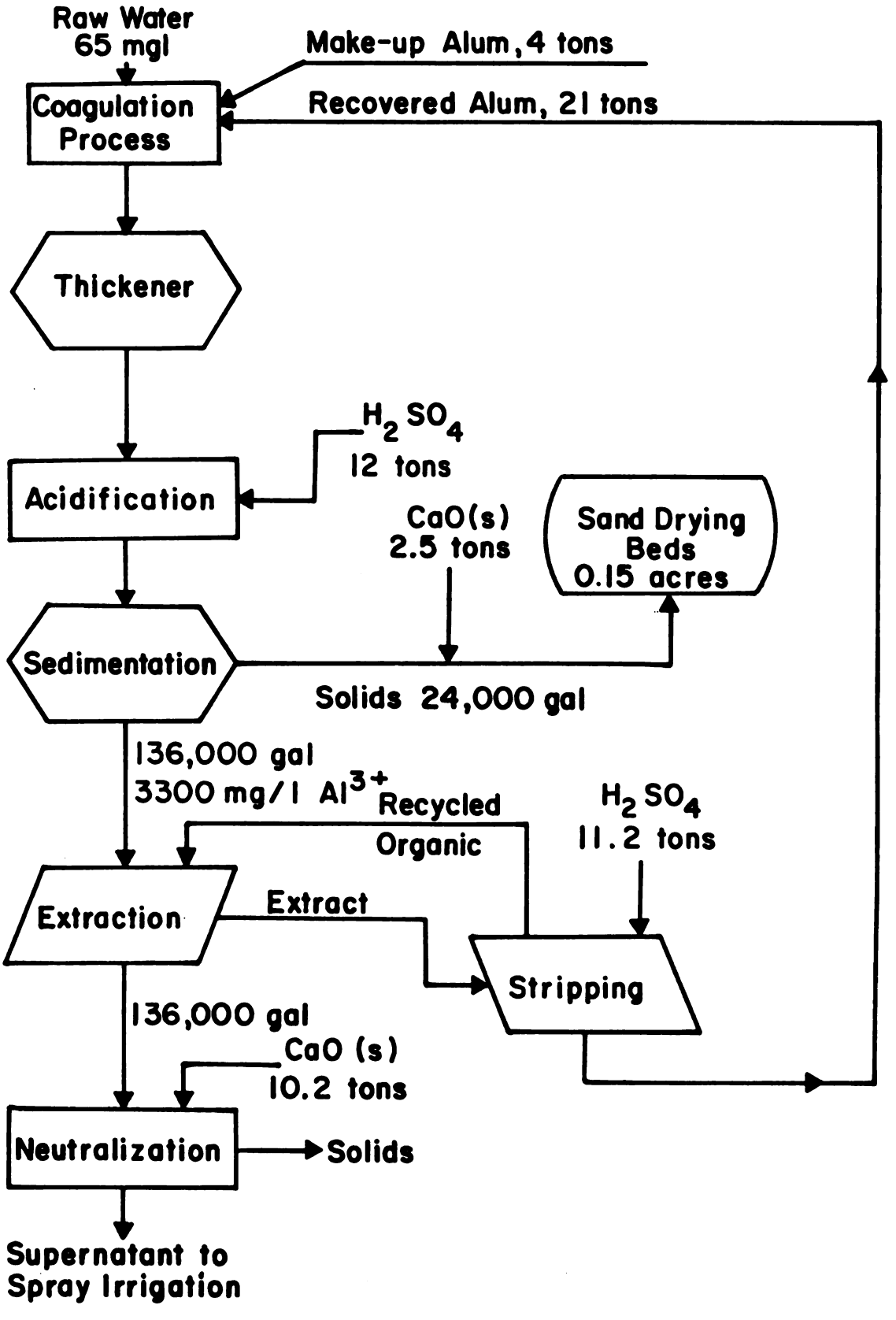
This chapter is designed to show how the data of Chapter 6 can be applied to the Tampa, Florida process. Sludge flows and chemical demands were calculated based on the Tampa plant flow of 65 mgd. The process has been assumed to operate 24 hours per day.

A general flow diagram of the recovery process is shown in Figure 7.1. It should be emphasized that the operating data have been collected only in the laboratory on a small scale. While full-scale processes generally perform better than laboratory scale [35], problems may be encountered which were not anticipated in the laboratory. Of major importance in the process design was the optimization of the extraction and stripping stages. They will be particularly detailed here. All of the experiments attempted here simulated a countercurrent continuous flow operation by use of multiple batch systems as outlined by Cornwell [26].

7.2. Sludge Pre-Treatment

The 65 mgd Tampa water plant utilizes an average 100 ppm liquid alum for water purification. From the sludge lagoons the volume averages 160000 gpd. The sludge would then be acidified with concentrated sulfuric acid. The acid requirement would be 1.5 moles of

Figure 7.1. Flow diagram of alum recovery by liquid-ion exchange for the Tampa, Florida water plant.


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

acid per mole of aluminum [1] or 12 tons per day of H_2SO_4. The acidified sludge would then be sent to the sedimentation tank. After a two hour detention time, 15% (24000 gpd) of the volume would be solids and could be directed to neutralization and then sand drying beds. The supernatant would make up the rest of the sludge volume (136000 gpd) and would contain 3300 mg/l aluminum. The aluminum recovery would be 85%.

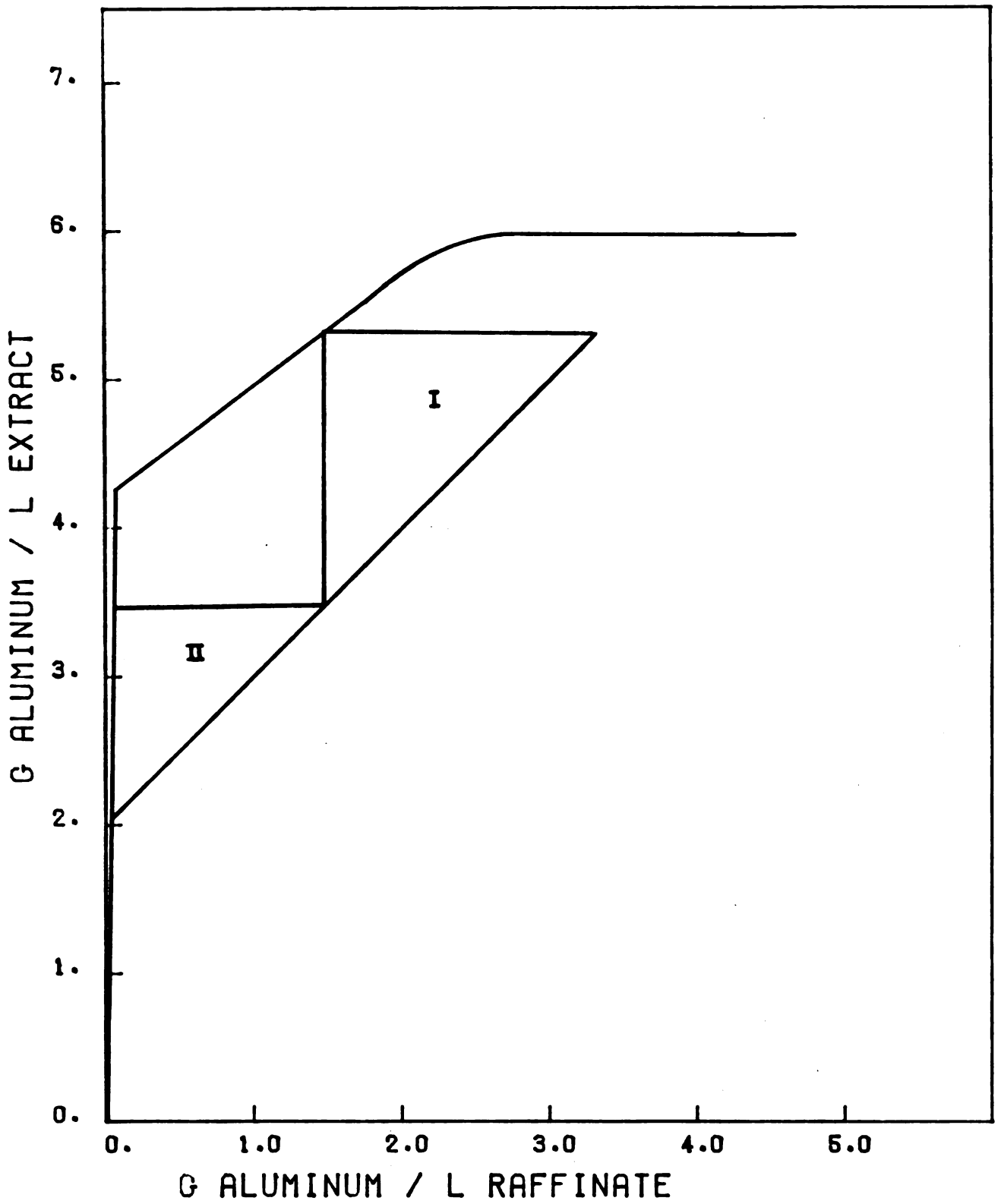
7.3. Aluminum Extraction

An aluminum concentration in the sludge feed of 3300 mg/l was extracted in two countercurrent stages as shown in Figure 7.2. The equilibrium curve was extrapolated from the equilibrium curves in Figure 5.5. A MDEHPA concentration of 0.84 M was determined to be needed. Figure 7.2 was constructed by the McCabe-Thiele procedure.

In order to concentrate the aluminum in the stripping stages to that of commercial liquid alum, 2050 mg/l aluminum was recycled in the organic phase to the extraction circuit from the stripping circuit (see Section 7.5). The operating line was drawn to extract 99% of the 3300 mg/l aluminum in the sludge feed. The phase ratio was 1:1. The organic phase was loaded to 5317 mg/l aluminum.

The feed rate for both the organic and the aqueous flow was 136000 gpd. With a 15 min mixing and settling time, the mixer and settler volumes must each be 2830 gal. Mixing vessels are usually circular rather than rectangular and are fitted with four vertical baffles. Each baffle has a length equal to the liquid depth and width equal to one-tenth the tank diameter. The impeller diameter is usually one-third to one-half the vessel diameter with the shaft

Figure 7.2. Graphical determination of number of stages necessary for 99% aluminum extraction. Sludge feed concentration = 3300 mg/l, recycled organic concentration = 2050 mg/l, feed pH = 2.0, phase ratio = 1:1, mix time = 15 minutes, MDEHPA = 0.84 M.


7.
6.
5.
4.
3.
2.
1.
0.
G ALUMINUM / L EXTRACT
I
II
0.
1.0
2.0
3.0
4.0
5.0
G ALUMINUM / L RAFFINATE

placed along the vessel axis. Agitation power varies greatly from mixer to mixer, but 0.2 Hp per cubic foot seems to be a representative value. Using a value of 0.2 Hp per cubic foot, approximately 76 Hp is needed per mixing vessel, or a total of 152 Hp for the complete extraction circuit. Flow of the organic and aqueous phases from the mixers to the settlers is usually accomplished by impeller action. Baffles may be supplied to minimize the settler volume required.

The aluminum concentration in the feed, extract, and raffinate were, respectively, 3300 mg/l, 5317 mg/l, and 33 mg/l. This resulted in an aluminum recovery of 99% in the extraction circuit. There would be 136000 gpd of organic and 136000 gpd of aqueous raffinate leaving this process.

7.4. Disposal of Aqueous Raffinate Solution

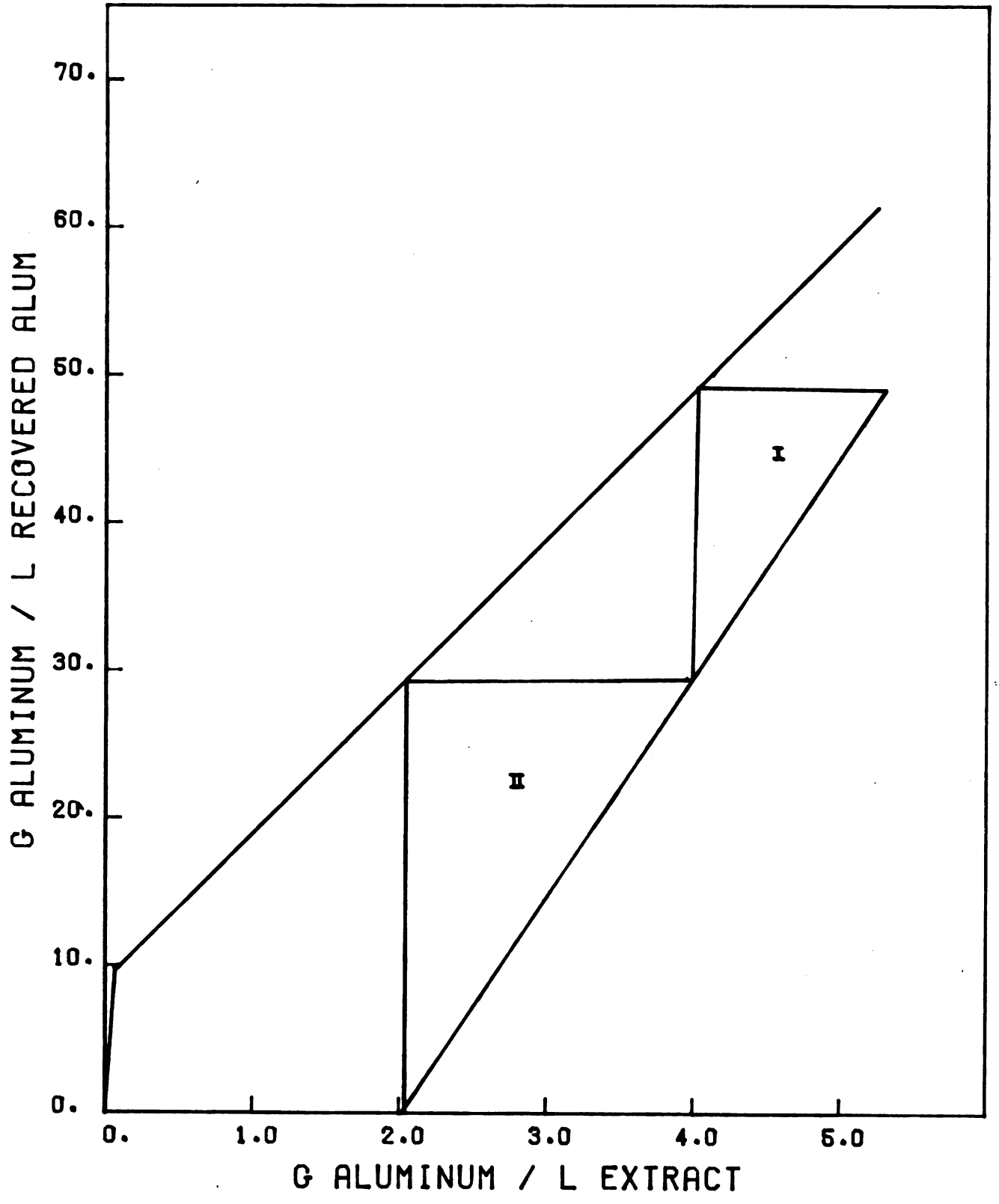
The aqueous raffinate from the extraction circuit had a pH of 0.7 and would require lime neutralization before disposal. Lime requirements were found to be 8364 lbs/day $Ca(OH)_2(s)$ for the 136000 gpd of raffinate [1]. Any solids precipitating out would be sent to the sand drying beds. The neutralized aqueous raffinate would be used for spray irrigation.

7.5. Stripping of the Extract

The organic flow into the stripping circuit was 13600 gpd. The aluminum concentration was 5317 mg/l. The stripping circuit was carried out in two countercurrent stages as shown in Figure 7.3. The organic: 6 N H_2SO_4 phase ratio was 15:1. The organic, acid, and returned solvent aluminum concentrations were respectively 5317 mg/l, 49000 mg/l, and 2050 mg/l. The 2050 mg/l aluminum in the organic

Figure 7.3. Graphical determination of number of stages necessary for Aluminum stripping.

Incoming organic aluminum = 5317 mg/l.
Outgoing organic aluminum = 2050 mg/l.
Final acid concentration - 49000 mg/l Al^{3+}.
Acid = 6 N H_2SO_4, organic:acid phase ratio = 15:1, mix time = 15 minutes.


70.
60.
50.
40.
30.
20.
10.
0.
G ALUMINUM / L RECOVERED ALUM
I
II
0.
1.0
2.0
3.0
4.0
5.0
G ALUMINUM / L EXTRACT

phase was recycled to obtain higher feed aluminum concentrations in the extraction circuit. The final alum concentration was 49% as alum. At the organic:acid flow rate of 15:1, there would be 9070 gpd of recovered alum and 136000 gpd organic solvent. Mix times of 15 minutes would be required in each mixer and settler. Each tank would have a volume of 1510 gallons.

The total acid requirement would be 1515 gpd of concentrated sulfuric acid (11.24 tons per day).

7.6. Organic Recycle

The stripped organic phase was recirculated to the extraction circuit. The extractant successfully reproduced the initial extraction efficiencies. Since the solvent contains excess acidity, an additional stage may be beneficial. The solvent could be washed with water at a 1:1 phase ratio before recirculation. A portion of the aqueous stream could be continually bled off and directed to the acidifer to help lower the pH of the sludge solution.

Overall, 11315 gal or organic solution are needed in the process system at one time. The solvent would cycle through the system 12 times per day.

7.7. Recovered Alum Solution

The total volume of recirculated alum was 9070 gpd. The concentration was 4.9% Al^{3+}, the same as that of commercial liquid alum. The recovered alum was successfully reused for coagulation of a raw water. It was calculated that 6.3 gpm pump would be required for alum recirculation.

7.8. Summary

The percentages of aluminum recovered in the acidification, extraction, and stripping stages were 85%, 99%, and 100% respectively. This resulted in an overall recovery of 84%.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The stated objective of this research was to evaluate the future feasibility of using liquid-ion exchange for alum recovery and recycling in water treatment plants. A process was developed whereby contaminate free alum could be recovered from water effluent and reused as a coagulant. In this chapter a summary of the process design for alum recovery is presented. This is followed by recommendations for future research.

8.1. Summary of Alum Recovery by Liquid-Ion Exchange

At a pH of 2, essentially all the aluminum present in the sludge was dissolved. During pH reduction, the organic solids would flocculate and settle. The dissolved aluminum could be separated from the solids by sedimentation. Sedimentation resulted in 85% aluminum separation.

The acidified aluminum was separated from the supernatant by a liquid-ion exchange process. The supernatant was contacted with kerosene containing a 0.84 M solution of extractant in a 1:1 volume ratio. The extractant was an equal molar mixture of mono- and di(2-ethylhexyl) phosphoric acid (MDEHPA). A minimum of 99% of the aluminum reacted with the MDEHPA and became kerosene soluble, resulting in separation from the supernatant. A two stage, countercurrent extraction circuit would be required for aluminum recovery.

Additionally, several findings pertaining to the extraction

circuit were reported. Iron (II), manganese (II), and color did not contaminate the kerosene-aluminum solution. Organic losses were minimized by operating the circuit organic continuous. When the extraction circuit operated in the monomer range of the extractant, stripping efficiencies were greatly enhanced. Commercial diluents, especially manufactured for liquid-ion exchange processes, lowered organic losses of evaporation and entrainment when compared with kerosene. No modifying agents were required for the aluminum-MDEHPA complexing. Di(2-ethylhexyl) phosphoric acid (DEHPA) was concluded to be an extractant of practical utility in the extraction process.

The aluminum rich organic phase was contacted with 6 N H_2SO_4 to force the aluminum into the acid phase. The organic:acid volume ratio was 15:1. Essentially 100% of the aluminum entering the stripping circuit went into the acid phase when operated in a two-stage countercurrent circuit. The final alum concentration was 49% as alum. The organic solution was recycled and reused in the extraction circuit. The recovered alum was successfully reused as a coagulant in the water treatment plant.

The overall aluminum recovery was 84%.

8.2. Suggested Future Research

It is the recommendation of this research that the alum recovery process be continued during the second year of the research grant period. Application should be extended to a laboratory, continuous flow process.

APPENDIX

APPENDIX A

APPENDIX A

GLOSSARY FOR LIQUID-ION EXCHANGE

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

Antisynergism. - Suppression of extraction caused by using a combination of extractants or diluents; antonym of synergism.

Aqueous Phase. - Aqueous solution containing the solute to be extracted.

Carrier. - Inert organic solvent in which an active organic extractant is dissolved; also referred to as the diluent, or solvent.

Coalescence. - Growth or combination of small dispersed droplets into larger drops.

Cocurrent multistage contact. - See Crosscurrent extraction.

Combination extractant. - Organic solution of two or more extractants.

Compartment-type mixer-settler. - Multiple-stage contactor featuring adjacent compartments sharing common interior walls.

Contactor. - Device for dispersing and disengaging immiscible solutions; extractor. May be single stage, as in a mixer-settler, or multiple stage, as in columns and certain centrifuges.

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

Countercurrent extraction. - Multistage extraction in which the aqueous and organic solutions flow in opposite directions.

Crosscurrent extraction. - Treatment of a batch of aqueous solution by repeated contacts with fresh organic extractant; also called simple multiple contact, cocurrent multistage contact, and multistage cocurrent extraction.

Differential extraction. - Procedure for extracting a batch of aqueous solution by continuously feeding and simultaneously withdrawing organic feed from a contractor; differs from crosscurrent extraction in that organic feed is introduced continuously instead of batchwise.

Diluent. - See Carrier.

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

Dispersion. - Mixture of immiscible phases in which one phase is diffused throughout the other (continuous phase).

Distribution coefficient. - See extraction coefficient, E_a^o, or stripping coefficient, S_o^a.

Distribution isotherm. - Graphical representation of isothermal equilibrium concentrations of a metal solute in aqueous and organic solutions over an ordered range of conditions in extraction (extraction isotherm) or stripping (stripping isotherm). Also equilibrum curve or distribution curve.

Emulsion. - A mixture consisting of small droplets of one liquid dispersed in a continuum of another immiscible liquid.

Equilibrate. - To disperse and disengage aqueous and organic solutions for the purpose of determining the equilibrium concentrations of metal solute in the respective phases.

Equilibrium curve - See distribution isotherm.

Extract. - Organic phase after extraction (loaded solvent). The solution into which transfer of a metal solute is effected; used as a verb to describe transfer of a metal solute between two immiscible liquids.

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

Extraction coefficient, E_a^o. - Ratio of the metal concentration in the organic extract to the metal concentration in the aqueous raffinate.

Extraction isotherm. - See Distribution isotherm.

Extractor. - Synonym for contactor, or mixer.

Feed. - Aqueous solution containing the metal solute to be extracted.

Flooding. - Discharge of mixed phases from one or both exit ports of a contactor. Flooding may occur in a single-stage contactor and in any or all stages of a series of contactors.

Fractional (double) solvent extraction. - Process in which two immiscible organic liquids (double solvents) are passed countercurrently through a multistage contactor to separately extract metal solutes from an aqueous feed introduced at an intermediate stage (usually the middle stage).

Internal mixer-settler. - Contacting device in which the mixer (usually shrouded) or mixer compartment is within the settler.

Internal recycle. - Circulation of aqueous or organic solutions from a settler to the mixer in the same stage for control of the phase ratio during mixing independently of the feed ratios.

Inversion. - Change in continuous phase from organic to aqueous or vice versa; breaking an emulsion by treatment with an excess of the dispersed phase.

Liquid-Ion Exchange. - Solvent extraction when 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.

Loading capacity. - Saturation limit of metal solute in organic or strip liquor.

McCabe-Thiele diagram. - A composite plot of the distribution isotherm and the operating line. It is used for estimating the theoretical extraction stages required to obtain specific results in a solvent extraction system. The diagram can be prepared for either extracting or stripping operations.

Mixer-settler. - Device for liquid-liquid extraction comprising separate mixing and settling compartments.

Modifying agent. - Substance added to an organic solution to increase the solubility of the extractant or of salts of the extractant that form during extraction or stripping.

Operating line. - Curve depicting the relationship between the metal solute content of organic and aqueous solutions in a countercurrent system. In a McCabe-Thiele diagram (Cartesian coordinates) of solute distribution between two immiscible phases, the operating line is linear with a slope equal to the ratio of feed to solvent. The line contains points representing the solute concentration in the influent and effluent streams throughout the system.

Organic phase. - Organic solvent.

Phase inversion. - Reversal of the continuous and dispersed phases, See Inversion.

Phase ratio. - Volume ratio of the organic solvent to the aqueous feed.

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

Primary break. - Separation of a dispersion into two layers with a distinct common boundary.

Raffinate. - The liquid phase from which solute has been removed by single- or multiple-stage contacting with an immiscible solvent.

Reextraction. - See stripping.

Scrub. - Removal of impurities from the solvent prior to recirculation of the solvent into the extraction stage. The scrub stage usually follows the stripping operation.

Secondary break. - Coalescence and separation of a fine dispersion present in either or both phases after the primary break.

Sedimentation. - See Phase separation.

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

Selectivity. - Ability to extract one solute from a mixture of solutes.

Selectivity coefficient. - Ratio of the extraction coefficients of two substances, used to express selectivity. Designated by or S_B^A.

Settling. - Separation of dispersed immiscible liquids by coalescence and sedimentation.

Solvent. - In liquid-liquid extraction, the liquid phase that preferentially dissolves the extractable solute from the feed. Often the term is 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 organic liquid.

Stage. - Single contact (dispersion and disengagement); sometimes refers to a theoretical stage which is a contact that attains equilibrium conditions. Involves one mixer and settler.

Stage efficiency. - Ratio of actual mass transfer in a specific stage to theoretical transfer in that stage under equilibrium conditions.

Stripping. - Removal of extracted metal solute from loaded organic extract; reextraction; back extraction. Selective stripping refers to separate removal of specific metal solutes from an extract containing more than one metal solute. Also called back extraction or reextraction.

Stripping coefficient, S_o^a. - Ratio of the metal concentration in the aqueous extract to the metal concentration in the organic raffinate.

Stripping isotherm. - See Distribution isotherm.

Synergism. - Cooperative effect of two or more extractants that exceeds the sum of the individual effects.

Wash. - Removal of contaminationg solutes from organic solution; scrub.

APPENDIX B

APPENDIX B

DETERMINATION OF ALUMINUM IN AN ORGANIC SOLVENT BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

I. Introduction

A method was developed for determination of aluminum^{3+} by atomic absorption spectrophotometry. Liquid-ion exchange was utilized to complex aluminum in the aqueous solution into an organic phase. Kerosene was used as the organic solvent for extraction. An equal molar mixture of mono-di(2-ethylhexyl)phosphoric acid (MDEHPA) was the extractant of choice.

II. Experimental

A. Equipment - An Instrument Laboratories Model 151 atomic absorption spectrophotometer with a premixed burner was used. A hollow cathode lamp served as the light source and the wavelength used was 3092.7 Å. Samples were aspirated by a nitrous oxide - acetylene flame and nitrous oxide burner head system.

B. Reagents - Commercial kerosene (number one fuel oil) and aluminum potassium sulfate were used for standard solutions. Deionized water was used for preparing standard solutions. MDEHPA, as supplied by Stauffer Chemical Company, was utilized.

C. Standard Aluminum Solutions - 9.287 grams aluminum potassium sulfate was dissolved in deionized water to 1 liter and the pH adjusted to 2.0 with sulfuric acid. The aluminum concentration was 500 ppm Al^{3+}.

D. Extraction Solution - 266 ml of MDEHPA was dissolved in kerosene to 1 liter (1.0 M solution of MDEHPA).

E. Standard Organic Solution - Equal volumes of standard aluminum solution and extraction solution were mixed in batch reactors for 15 minutes at 800 ft/min. The solution was allowed to settle in a separatory funnel for 30 minutes. The organic solution was drawn off and used as the 500 ppm Al^{3+} in the organic solution. Appropriate dilutions were made from this stock. The solution is stable for up to 3 months if tightly sealed.

F. Operating Conditions - The operational parameters were so adjusted that optimum sensitivity could be obtained. These parameters were:

current in the hollow cathode lamp - 13mA

burner height - 10 (scale unit of the instrument)

nitrous oxide flow rate - 11 SCFH

oxygen-acetylene flow rate - so adjusted that the red feather of the flame was 3/4 - 1 inch in height

rate of aspiration - 2-3 ml/min

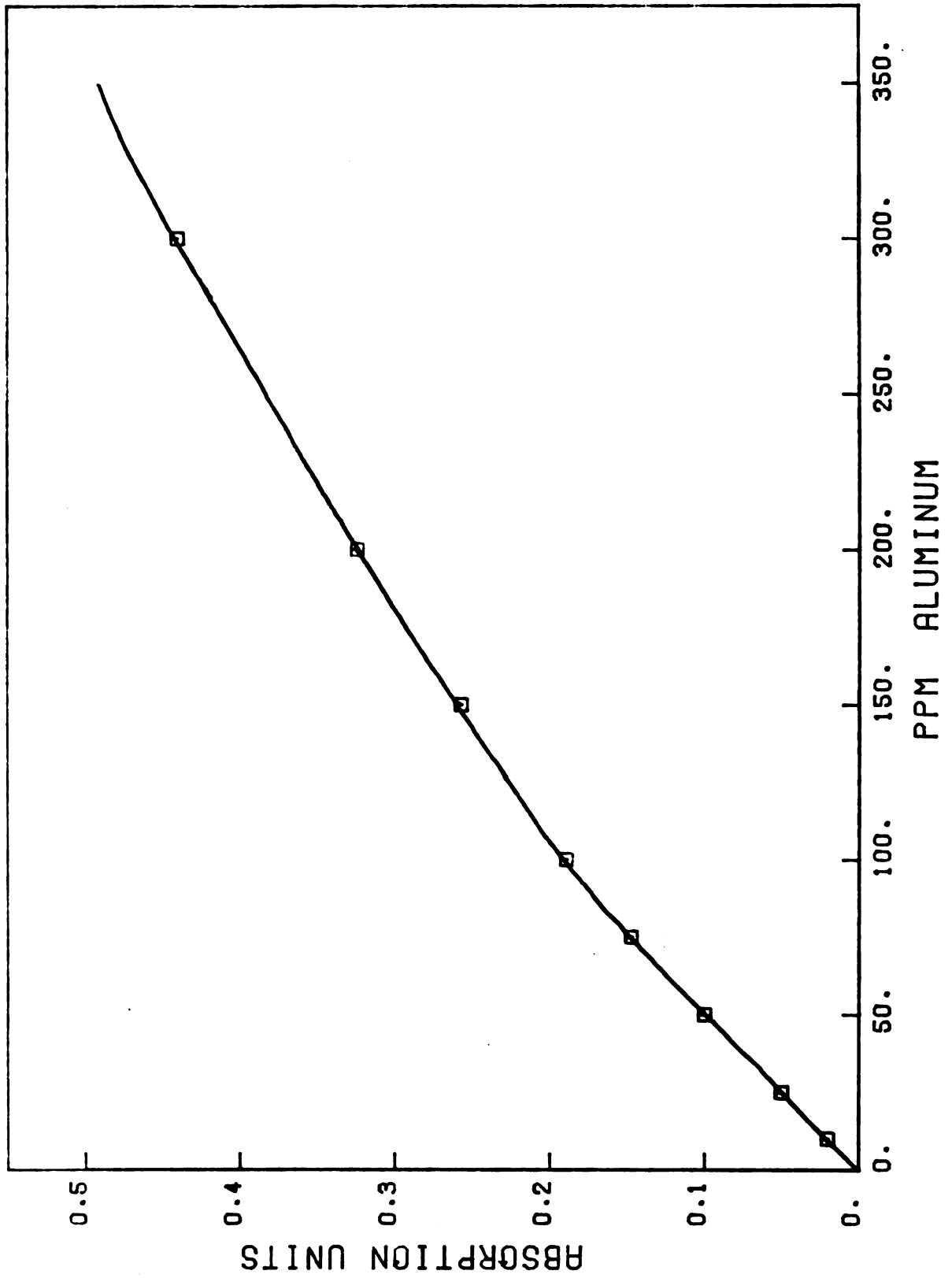
slit width - 320

G. Typical Absorption Curve for Aluminum Determination - See Figure 1.

III. Procedure

Unknown aqueous samples containing up to 5000 ppm Al^{3+} were contacted with the 1.0 M extraction solution in a 1:1 phase ratio. Samples were mixed for 15 minutes at 800 ft/min and allowed to separate. The organic phase was measured by atomic absorption spectrophotometry

Figure 1. Standard curve for aluminum determinations in the organic phase.


ABSORPTION UNITS
0.
0.1
0.2
0.3
0.4
0.5
0.
50.
100.
150.
200.
250.
300.
350.
PPM ALUMINUM

and compared to known standards.

IV. Interferences

Other metal ions are not extracted by this procedure. Selectivity ratios were reported:

Metal	Selectivity Ratio
Cu^{2+}	190
Cd^{2+}	300
Mn^{2+}	360
Zn^{2+}	>1800
Fe^{2+}	170
Fe^{3+}	30
Cr^{6+}	75

V. Effects of Solids in Unknown Solution

Aqueous solutions containing up to 3% solids had no effect on aluminum determinations.

VI. Aluminum determinations were conducted on the Tampa, Florida water treatment alum sludge. Alum was utilized as a coagulant in water purification. The aluminum concentration was found to be 3000 ppm Al^{3+}:

Test	Aluminum Concentration, ppm
1	3300
2	3300
3	3250
4	3300
5	3300
6	3350

This compared very well with other techniques for aluminum determinations attempted.

VII. Discussion

Liquid ion exchange is a very useful technique for aluminum determinations. The sensitivity in an organic solvent is vastly improved over aqueous techniques. This advantage is due to the improvement of the flame condition which increases the noise to signal ratio.

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