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Chemical phosphate removal from wastewaters

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Chemical phosphate removal from wastewaters

by

Seung-Hyun Kim

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Civil and Construction Engineering
Major: Civil Engineering (Environmental Engineering)

Approved:

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In Charge of Major Work

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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa
1993

DEDICATION

To my parents, Ki-Young Kim and Ke-Sook You: without their help, I couldn't come this far.

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PAPER III. MODELING OF CHEMICAL PHOSPHATE REMOVAL

ACKNOWLEDGEMENTS

I would like to express my thanks to those who aided this work in various ways. They are:

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Thank you.

GENERAL INTRODUCTION

Chemical phosphate removal from domestic wastewaters has been a popular topic over the past three decades. Researchers have made extensive studies of chemical phosphate removal using iron and aluminum salts. Many areas of chemical phosphate removal have received attention. These areas include: pH-solubility relationships, metal to phosphate molar ratios, precipitant choices, chemical application points, etc.. Unlike these areas, already studied extensively, the roles of rapid mixing and modeling of chemical phosphate removal have not received much attention. Therefore, both rapid mixing and modeling of chemical phosphate removal were investigated in this dissertation.

This dissertation consists of two parts: rapid mixing and modeling of chemical phosphate removal. The first part consists of two papers prepared for publication and the second part consists of one paper. The two papers in the first part relate to rapid mixing in chemical phosphate removal. The first paper describes the evaluation of rapid-mixing parameters in chemical phosphate removal. The second paper, in which rapid-mixing parameters are further evaluated, is an extension of the first paper. Modeling of chemical phosphate removal is studied in the second part.

Environmental Engineering is not an isolated science and can benefit by interacting with other scientific areas. Borrowing a certain concept or technique from other scientific areas, which was already extensively studied in those areas, can help research works in Environmental Engineering.

In this dissertation, an attempt was made to couple research in Environmental Engineering with statistical techniques. Two important statistical concepts were used: experimental design and linear regression. Use of the experimental design can be found in the first part of this dissertation and use of the linear regression in the second part. Of various techniques available in the experimental design, two techniques, the analysis of variance (ANOVA) and the repeated measure ANOVA, were introduced. The ANOVA is well recognized, but the repeated measure ANOVA is relatively unexposed. Although it is relatively new, the repeated measure ANOVA can be very preciously utilized in research in Environmental Engineering because it can handle a situation where an interest is to repeatedly measure an experimental unit. The way things change with time is of universal interest in many research studies in Environmental Engineering as well as in other areas.

PAPER I.

RAPID MIXING IN CHEMICAL PHOSPHATE REMOVAL FROM WASTEWATERS (I)

ABSTRACT

Rapid mixing effects in chemical phosphate removal were investigated in this study. For this purpose, the effects of two rapid-mixing parameters (intensity and detention time) on chemical phosphate removal using aluminum salts were evaluated. In addition, the effect of aluminum solution strength on chemical phosphate removal was evaluated. Experiments, consisting of jar tests, were planned and carried out based on the following EPA recommendations for rapid-mixing parameters in chemical phosphate removal: G value of 300 sec^{-1} (intensity), 30 sec (detention time) and a minimum aluminum solution strength of 6 %. Results of this study indicated that chemical phosphate removal seemed unaffected by the mixing time, but was affected by the mixing intensity. The optimum mixing intensity for chemical phosphate removal was found to be a G value of 600 sec^{-1}. The study also indicated that the higher the aluminum solution strength, the better was the P removal efficiency.

1. INTRODUCTION

The importance of the rapid mixing influence on chemical phosphate removal has been pointed out by many researchers [2, 8, 4]. Unlike the above researchers, Kavanaugh et al. [11] expressed a different opinion about the role of rapid mixing in chemical phosphate removal. They investigated major physical-chemical process variables controlling the performance of post-precipitation phosphate removal with Fe(III) in a pilot plant. They found no statistically significant difference at the 90 % confidence level among three different rapid mixing devices employed in their study.

At present, very little is known about rapid mixing in chemical phosphate removal and no experimental data about rapid mixing in chemical phosphate removal are available in the literature. Therefore, it is not clear whether any rapid-mixing effects on chemical phosphate removal actually exist. Thus, this research was conducted to evaluate the effects of rapid mixing on chemical phosphate removal. More specifically, the study was designed to determine whether rapid mixing actually influences phosphate removal in any way. If so, what kind of rapid mixing condition favors phosphate removal was also studied. As far as rapid mixing is concerned, it can be described with two parameters: mixing intensity and detention time. Effects of each of these parameters on chemical phosphate removal were evaluated.

When alum or sodium aluminate is used as a coagulant to remove phosphates, EPA [6] recommends use of a minimum feed solution strength of 6 percent. EPA was not specific about the solution strength and it is unclear whether the solution strength is 6 % by weight as filter alum or sodium aluminate. This brings out the question: "On what basis, is this criterion set?". Unfortunately, EPA did not provide a specific reason for use of this solution strength.

Most metal ions such as aluminum and iron undergo hydrolysis in aqueous solution. The literature [2, 16] reported that hydrolysis impaired the phosphate removing capacity of these metal ions. Such hydrolysis progresses more favorably under high pH conditions than under low pH conditions. As the feed solution strengths of these metal ions decrease, pH values increase, creating more favorable conditions for hydrolysis. Therefore, the minimum feed solution strength (6 %) was probably set because of the hydrolysis limitation.

Although it establishes a minimum solution strength recommendation, the EPA design manual mentions nothing about a maximum solution strength. This implies, rightly or wrongly, that as long as the solution strength used is greater than 6 %, phosphate removal efficiencies are unimpaired. However, there may exist practical limitations in the solution strength. As the aluminum solution strength becomes greater, so does the viscosity of the solution. High viscosities should resist the dispersion of the stock solution into the wastewater to some extent, leading to the uneconomical usage of chemicals. Therefore, it is possible that there could exist an optimum solution strength in so far as phosphate removal is concerned. This optimum strength might vary, depending on the rapid-mix conditions. This relationship between rapid-mix conditions and an optimum solution strength was another topic evaluated in this research.

2. LITERATURE REVIEW

In order to predict experimental results, a literature review was conducted. Very little literature was available on this topic. This chapter is a summary of the few papers which discuss rapid-mixing kinetics for aluminum/iron hydrolysis and aging effects on chemical phosphate removal. Then, a summary of a paper which compared effects of different mixing devices on chemical phosphate removal is presented.

Since this study involves chemical phosphate removal using aluminum salts, a literature review was conducted to elucidate aluminum chemistry to help understand potential interactions of aluminum and phosphates.

2.1 Potential Effect of Rapid Mixing on Chemical Phosphate Removal

When metal ions such as Al(III) and Fe(III) are added to phosphate solutions, there will be competition between hydrolysis of the metal ions and reaction between PO_4^{3-} and the metal ions. There is a distinct possibility that the competition is related to rapid mixing. Two findings observed in previous research support the existence of a potential effect of rapid mixing on the competition. These involve both the rapid kinetics experienced in chemical phosphate removal and the reduced efficiency of hydrolyzed metal ions in removing phosphates.

2.1.1 Kinetics of chemical phosphate removal

Recht and Ghassemi [16] showed that the kinetics of chemical phosphate removal are very rapid. They conducted two kinetics studies: one with a batch apparatus and another with a kinetics apparatus.

In experiments with the batch apparatus, all variables such as solution pH, conductivity, and the residual phosphate concentration reached constant levels in less than 60 seconds after the addition of metal ions of Al(III) and Fe(III). To appreciate how fast this reaction is, they conducted a control experiment using HCl-NaOH neutralization. They observed a similar pattern of the change in pH and conductivity in the control experiment as in the reaction for chemical phosphate removal. Since an acid-base reaction is known to be instantaneous, they hypothesized that chemical phosphate removal might also be instantaneous and that the apparent time delay might have been due to the time required for complete mixing.

In experiments with the kinetics apparatus, only the pH of the solution leaving the reaction flask was monitored, which indicated a constant pH at all sampling ports. Since the travel time to reach the first sampling port was only 1.3 seconds, they reported that the reaction for chemical phosphate removal was complete within 1.3 seconds. They repeated the experiments after lowering the reaction temperature from 25^o C to 5^o C and did not find any measurable change in the rate and the extent of phosphate removal. These results indicate that the metal-phosphate reaction for phosphate removal may actually be much faster than 1.3 seconds, i.e., be instantaneous.

From their experiments, Recht and Ghassemi concluded that reactions between a metal ion of Al(III) or Fe(III) and phosphates are very rapid. They went on to say that the need for addition of metal ions in excess of stoichiometric requirements cannot be attributed to an inadequate mixing time which might be permitted for chemical phosphate removal, but can be explained in terms of occurence of competing reactions and dispersions of metal-phosphate precipitates into non-settleable and often extremely fine particles. However, they did not provide any specific reason why competing reactions cause the need for more than the stoichiometric amount of metal ions in chemical phosphate removal.

2.1.2 Hydrolysis and aging effects of metal ions on chemical phosphate removal

Recht and Ghassemi [16] also investigated an aging effect of metal ions of Al(III) and Fe(III) on chemical phosphate removal, using dilute aluminum and ferric nitrate solutions (7.72×10^{-4} M). Dilution of ferric nitrate resulted in rapid hydrolysis. The pH of the diluted ferric nitrate was 3.0. This was reflected in change in pH and conductivity with time. The solution pH dropped to 2.58 during the first 24-hour period. No such hydrolysis was observed in a diluted aluminum nitrate solution at pH 4.0 over a 2-month period.

The aged Fe(III) solution was then used to precipitate phosphates. Results of this experiment showed a steady decrease in phosphate removal capacity of the Fe(III) aged for different times. Under similar conditions, but at one unit higher pH (4.0 compared to 3.0), Al(III) exhibited no such tendency to hydrolysis.

These results indicate that hydrolysis resulting from aging decreased the effectiveness of the phosphate removal capacity of Fe(III). Although no hydrolysis occurred with Al(III) under their test conditions, Recht and Ghassemi said that Al(III) also undergoes hydrolysis at pH 6.0. Thus, there also exists a potential for reduced phosphate removal capacity for Al(III) at pH 6.0.

Diamadopoulos and Benedek [2] investigated the hydrolysis and aging effects of aluminum on chemical phosphate removal by using synthetic wastewaters. The synthetic wastewaters contained an initial orthophosphate concentration of 15 mg/l as P and bicarbonate alkalinity of 200 mg/l as $NaHCO_3$. They caused hydrolysis of aluminum by adding OH^- to an aluminum chloride solution, synthesizing polymerized basic aluminum chloride (PBAC).

They compared the phosphate removal capacities of unhydrolyzed aluminum salts (alum and aluminum chloride) and hydrolyzed aluminum salt (PBAC), using Al/P molar ratios of 1.0 and 2.75 in the pH range of 4 to 9. Their results indicate that unhydrolyzed aluminum salts possessed a higher phosphate removal capacity than hydrolyzed aluminum salts. The more OH^- that was added, the less was the phosphate removal capacity. Similar results were obtained with municipal wastewater. This indicates that aluminum salts with more polymers ,such as PBAC, are less effective in removing phosphates than aluminum salts with less polymers. The hydrolysis effect was more evident at a molar ratio of 1.0 than at the ratio of 2.75.

They also examined the aging effect using PBAC 2.2 at an Al/P molar ratio of 2.75. The PBAC 2.2 represents the polymerized basic aluminum chloride with a OH_{added}/Al_{total} molar ratio of 2.2. No measurable effect was observed in the experiments, which indicates that hydrolysis was complete before the PBAC 2.2 reacted with the phosphates.

Lijklema [4] also investigated the hydrolysis and aging effects of alum and ferric nitrate using synthetic wastewaters containing potassium phosphate alone with no bicarbonate alkalinity. Like the above researchers, he found that aging decreased the effectiveness of the phosphate removal capacity of Fe(III). According to his experiments, phosphate removal efficiency was more than 2 times greater for a given quantity of Al(III) when concentrated salts were added directly to a phosphate solution than when the phosphates were added to a solution containing a freshly precipitated aluminum hydroxide. What this indicates is that hydrolysis resulted in a decrease in the phosphate removal capacity of Al(III). Similar results were obtained with Fe(III).

Based on these results, Lijklema stated that the phosphate removal efficiency using Fe(III) or Al(III) depends largely on fast initial mixing.

2.2 Rapid Mixing Study

Only one study which evaluated effects of rapid mixing on chemical phosphate removal was found in the literature. Kavanaugh et al. [11] tried to identify the principal design parameters controlling the performance of a post-precipitation system using Fe(III) for removing phosphates in a pilot plant. During the experiments, they investigated the effects of the type of rapid-mixing device on the system performance. The rapid mixing devices compared included: a backmix reactor (CSTR) with a propeller mixer rotating at 400 rpm with a maximum mean hydraulic detention time of 30 seconds at a flow rate of 0.1 liter/second, an in-line mixing device containing two mixing elements with a hydraulic detention time of 0.05 second, and an in-line addition before a backmix reactor without in-line stirring.

The experimental results indicated that no statistically significant difference at the 90 % confidence level was found using these mixing devices, whereas solids/liquid separation in the sludge blanket clarifier was the critical process unit affecting system performance. They used actual wastewater which contained both components of phosphates (soluble and insoluble). Each component behaves differently in chemical phosphate removal. Phosphate precipitation will help remove soluble phosphates. On the other hand, the removal of particulate phosphates would largely depend on the clarifier performance, as Kavanaugh et al said. They did not provide any information about the composition of the phosphates (soluble and particulate phosphates). The particulate phosphate in the wastewaters used (secondary effluents) could be higher than that of the soluble phosphates. It is quite possible that rapid-mixing effects in their study have been reduced due to the level of particulate phosphate present in their wastewater.

2.3 Aluminum Chemistry

To understand chemical phosphate removal using aluminum salts, it is essential to have a sound background in aluminum chemistry. Thus, aluminum chemistry is briefly discussed here. Since aluminum chemistry is a very broad topic, only the area (aluminum hydrolysis) relevant to chemical phosphate removal is included. Thus, a discussion of Al(III) speciation and equilibrium aluminum hydrolysis products and their mechanism and kinetics are presented here.

It is well recognized that there are three different types of aluminum species: Al^a, Al^b, and Al^c. Smith [17] described these species as follows:

Al^a appears to be composed of monomeric species.

Al^b appears to be composed of polynuclear aluminum hydroxide species. It is very unstable and tends to convert to Al^c upon aging.

Al^c appears to be composed of clearly solid, colloidal particles. It may initially be all or partly amorphous, but rapidly becomes crystalline and takes on shapes of gibbsite. Its concentration increases as a function of aging time until equilibrium is achieved.

Aluminum hydrolysis involves two major steps: monomer formation and polymer formation. In monomer formation, we know that there are four hydroxoaluminum monomeric species. These are:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5OH^{2+} + H^+ \tag{2.1}$$

$$Al(H_2O)_5OH^{2+} \rightleftharpoons Al(H_2O)_4(OH)_2^+ + H^+ \tag{2.2}$$

$$Al(H_2O)_4(OH)_2^+ \rightleftharpoons Al(H_2O)_3(OH)_3^0 + H^+ \tag{2.3}$$

$$Al(H_2O)_3(OH)_3^0 \rightleftharpoons Al(H_2O)_2OH_4^- + H^+ \tag{2.4}$$

These reactions indicate that monomer formation is not a reaction between an aluminum ion and a hydroxide ion, as Ohashi and Morozumi [15] said. It is the deprotonation of a hydrated aluminum ion [9]. The first step in monomer formation is very similar to water deionization, which is also a deprotonation reaction. It is well known that the deprotonation is complete instantaneously. Therefore, it is reasonable to assume that monomer formation is an instantaneous reaction. It is actually a very fast reaction. The time scale for the first step ,2.1, in monomer formation is estimated to be on the order of 10^{-5} s [9].

Researchers generally agree that the monomers $Al(H_2O)_5OH^{2+}$ and $Al(H_2O)_2OH_4^-$ are present in aquatic solutions. The aluminate is present under high pH conditions. However, there is still controversy over whether the other two species are present. Kinetic information on the formation of the monomers other than $Al(H_2O)_5OH^{2+}$ are unavailable. More specifically, this information is available [15], however, the validity of the data are suspicious because the authors asserted incorrectly that the monomer formation is a reaction between an aluminum ion and a hydroxide ion.

Polymer formation is much more complicated. Researchers do not even agree on what polymeric species are available in aquatic solution. But, they do know that polymeric species will form under certain conditions and that aluminum hydrolysis cannot be explained with monomer formation alone. Nevertheless, there is strong evidence [1] that the following two polymers will exist in aquatic solution: $Al_2(OH)_2(H_2O)_8^{4+}$ or $Al_2(OH)_2(H_2O)_{10}^{4+}$ and $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$. The mechanism of polymer formation is quite different from that of monomer formation. Ravi Srivastava did a wonderful job of reviewing the literature about aluminum chemistry. Quoting from his Ph.D. dissertation proposal [18]:

> *It is a commonly held belief that the time scale for water exchange from the $Al(H_2O)_5OH^{2+}$ should be a factor of 10^1 or 10^2 faster than for the $Al(H_2O)_6^{3+}$ species. The increase in the water exchange rate of the monohydroxy species over the fully hydrated species is due to a decrease in the overall charge. The reduced charge decreases the hold of the central metal ion over the coordinated water molecules, resulting in an increased water exchange rate. Water exchange rate for the monohydroxy-aluminum species has not been measured and, therefore, is not known.*
>
> *The water exchange mechanism plays an important role in the polymer formation process. The mechanism for Al(III) polymer and complex formation are similar. In order for a hydrated metal ion to form a complex*

> *with a ligand, the following steps must take place;*
>
> - *Step 1. The ligand must diffuse to the outer-sphere of the hydrated metal ion and form an outer-sphere complex.*
> - *Step 2. There must be a swap such that the ligand gets into the inner-sphere while one coordinated water molecule leaves.*
>
> *Step 1 is a fast step. Step 2 is a slow step whose rate is critically dependent on the water exchange reaction which has (for $Al(H_2O)_6^{3+}$) a time scale of approx. 1 s.*

This suggests that kinetics of polymer formation is much slower than that of monomer formation (at least for the first step).

Recht and Ghassemi [16] tried to measure the speed of the reaction between aluminum and phosphate. They found that the reaction was complete in less than 1 second. Based on this, they said the reaction is instantaneous. But how fast is instantaneous? It seems that this reaction rate is similar to that for the aluminum complex formation. According to Srivastava [18], the mechanism of Al(III) polymer and complex formation are similar. Therefore, it is reasonable to assume that the rate of this reaction will also be slower than the monomer formation rate.

In summary, among the three possible reactions (monomer formation, polymer formation, and reaction between aluminum and phosphate), monomer formation (at least the first step) is the fastest reaction. It is complete instantaneously. Polymer formation and the reaction between aluminum and phosphate are probably on the same time scale. These reactions are complete in less than 1 s. But, these reactions are still much slower than the rate of monomer formation.

Now, let us apply this information to chemical phosphate removal. It is well known that aluminum hydrolysis is suppressed under low pH conditions. In most aluminum stock solutions, the pH is low enough to depress hydrolysis. Subsequently, aluminum is present as a hexaaquoaluminum ion, $Al(H_2O)_6^{3+}$. Upon addition to a PO_4^{3-}-bearing wastewater, the pH of the aluminum wastewater mixture increases because of base in the wastewater, like bicarbonate alkalinity. This will promote hydrolysis. As a result of the hydrolysis, a monomer (or monomers) will form. As said before, it is not clear whether only one monomer forms or two or more monomers form. Nevertheless, the first step in monomer formation will certainly be complete, resulting in the instantaneous formation of $Al(H_2O)_5OH^{2+}$.

The monomers so formed will be subject to competition between further hydroysis (polymer formation) and reaction with PO_4^{3-}. Some monomers react with themselves to form polymers. On the other hand, some monomers react with PO_4^{3-} to form precipitates of aluminum phosphate. After that, there is a competition again. Polymers so formed will keep growing in size, eventually transforming into precipitates of aluminum hydroxides. Some polymers will react with phosphates.

It is likely that the monomers and polymers will react with phosphates differently. The monomers will react with phosphate and form a solid aluminum phosphate. The reaction between the polymers and phosphates could lead to the formation of a solid aluminum hydroxyphosphate. Aluminum hydroxyphosphate is a very controversial product. This is indeed an imaginary product. There is no physical data for this compound because it is an imaginary compound. Since no physical data for this compound are available, it is very difficult to prove that this compound exists. And, by the same logic, it is also very difficult to say anything against the existence of this compound. Many researchers, like Ferguson [8], Hsu [10], etc., advocate the existence of this imaginary compound.

Why a solid of aluminum hydroxyhosphate might form if polymeric hydroxoaluminum species react with phosphate can be shown in Equations 2.5 and 2.6. Suppose that two polymers, which are present in solution, are ready to react with PO_4^{3-}. Then, the following reactions could result:

$$3Al_2(OH)_2^{4+} + 4PO_4^{3-} \rightleftharpoons Al_6(OH)_6(PO_4)_{4(s)} \tag{2.5}$$

$$3AlO_4Al_{12}(OH)_{24}^{7+} + 7PO_4^{3-} \rightleftharpoons Al_3O_{12}Al_{36}(OH)_{72}(PO_4)_{7(s)} \tag{2.6}$$

These equations show that more aluminum is necessary to remove phosphates on a molar basis. Again, it is not clear whether these imaginary compounds exist. But, if they do, this could be the way they form. Nonetheless, this indicates that more aluminum would be needed if polymers react with phosphates than if monomers react with phosphates. This is what researchers like Diamadopoulos and Benedek [2] and Lijklema [4] observed in their studies, as shown in the previous section.

3. EXPERIMENTS

Actual wastewater contains both soluble and particulate phosphates. The removal of particulate phosphates depends more on clarifier performance, whereas removal of soluble phosphates depends more on the process of phosphate precipitation. Since the effects of rapid mixing on the removal of soluble phosphates were to be evaluated in this investigation, experiments were conducted with a synthetic wastewater system containing $NaHCO_3$-NaH_2PO_4 without the presence of any particulate phosphates. Most previous laboratory experiments for phosphate removal were conducted by others using pure phosphate solutions without bicarbonate alkalinity. The systems without bicarbonate alkalinity do not represent wastewaters properly because most wastewaters contain considerable amount of bicarbonate alkalinity. In order to represent wastewaters more accurately, the system of $NaHCO_3$-NaH_2PO_4 was selected in this research. Both deionized and nanno pure waters were used to prepare the synthetic solutions used. Experimental results were not affected by the change to the use of either water.

Batch experiments, consisting of jar tests, were conducted using a jar test machine from Phipps and Bird. The solution volume used to represent the wastewater was 2.0 liters. A synthetic solution with an alkalinity of 100 mg/l as $CaCO_3$ and 5 mg/l of phosphates as P was prepared. These concentrations were selected because they represent typical medium-strength untreated domestic wastewater conditions.

To evaluate the effects of rapid mixing alone, no slow mixing and settling were provided in these experiments. Complete solids/liquid separation was assumed to result. Therefore, samples were collected and filtered through 0.45-μm filter papers immediately after rapid mixing. Filtrates were then analyzed for their residual phosphate concentrations using the Ascorbic Acid method (424.F) in Standard Methods [7]. These analyses were conducted using a Beckman model B spectrophotometer.

Table 3.1: Rapid mixing conditions evaluated

Intensity G, sec^{-1}	Detention time, seconds		
	Run 1	Run 2	Run 3
150	30	60	120
300	15	30	60
600	8	15	30
900	5	10	20
18800			1

The rapid mixing conditions evaluated are shown in Table 3.1. The intensity of rapid mixing is generally expressed by the average velocity gradient (shear rate), G. Camp and Stein [3] related the average velocity gradient to power dissipated per unit volume of liquid as follows;

$$G = \sqrt{\frac{P}{\mu V}} \tag{3.1}$$

G : average velocity gradient, sec^{-1}

P : power input, W

V : volume of liquid receiving power, m^3

μ : viscosity of liquid, Pa·sec

EPA [6] recommends the following rapid-mix conditions for chemical phosphate removal: G value of 300 sec^{-1} and a detention time of 30 sec. The rapid-mix conditions shown in Table 3.1 were selected based on this recommendation. Various intensities and detention times, greater and less than the EPA recommendation, were selected. A G value of 18800 sec^{-1} was selected in some experiments to see whether an extremely fast mixing helps chemical phosphate removal. This was done to determine whether the EPA recommendation of rapid mixing condition in chemical phosphate removal is reasonable. Jar tests were conducted at each combination of rapid mixing intensity and detention time shown in Table 3.1.

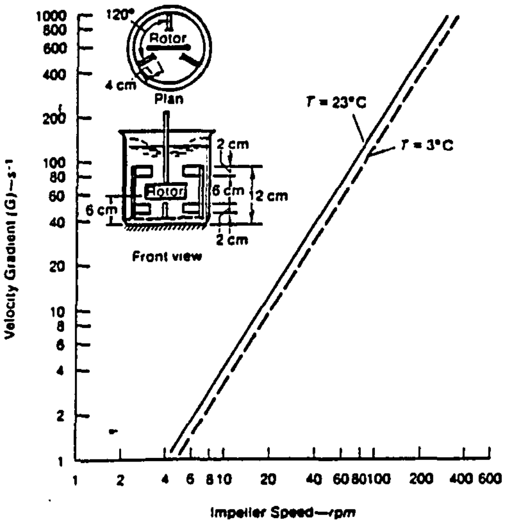

Figure 3.1: Laboratory G curve for flat paddle in the Hudson jar (Cornwell and Bishop, 1983)

Cornwell and Bishop [5] presented a relationship between G values and flat paddle impeller speed for use with Hudson jars and with gator jars. (Gator jars indicate use of square jars. Hudson jars indicate use of 2-liter beakers with stators, a siphon sampling port and a dosing tube.) In this study, Hudson jars were used. The Hudson jars used in this study did not have a dosing tube. Instead, chemicals were added using hypodermic syringes as near as possible to the impeller to obtain maximum mixing. The relationship of mixing speed to G values when using Hudson jars is shown in Figure 3.1. Various desired rapid mixing intensities (G values) were provided by adjusting the flat paddle impeller speed associated with the desired G value, according to the relationship in Figure 3.1. The maximum G value which can be produced in the jar test machine is 900 sec^{-1}. Therefore, a mixing intensity greater than this G value was provided using a blender. The blender used in this study was the HandyBlender II manufactured by Black & Decker. The blender has two speed modes: fast and slow. Only the fast mode was used. In order to calculate a G value for this blender, the electrical current was measured using a Tektronix CDM250 Digital Multimeter. Currents of 1.47 amperes and 1.23 amperes were recorded at fast and slow speed modes, respectively. A G value of 18800 sec^{-1} was calculated using equation 3.1. When this blender was operated with a solution volume of 1.0 liter, a very large vortex was formed. Therefore, a solution volume of 500 ml was used to avoid the formation of vortices.

EPA recommended that an aluminum solution of 6 % as a minimum strength be used for chemical phosphate removal. Based on this EPA recommendation and the solution strength of liquid alum (about 50 %), solution strengths of 1.0, 2.5, 5.0, 10, 25, and 50 % were prepared as needed. In this experiments, aluminum chloride was used as a coagulant. EPA was not specific whether the solution strength is 6 % as $Al_2(SO_4)_3 \cdot 14H_2O$ or $Al_2(SO_4)_3 \cdot 18H_2O$. If this solution strength is 6 % as $Al_2(SO_4)_3 \cdot 14H_2O$, this corresponds to about 5 % of aluminum chloride as $AlCl_3 \cdot 6H_2O$. All six solution strengths were used under each jar test condition to determine whether the EPA recommendation of a 6 % minimum solution strength is reasonable. All six jars were dosed to provide the same aluminum concentrations (50 mg/l as $AlCl_3 \cdot 6H_2O$). The molar ratio of Al to P was 1.28 at this concentration. All aluminum solutions were freshly prepared just before each jar test to avoid possible aging effects.

4. RESULTS AND DISCUSSION

4.1 Effects of Rapid Mixing Parameters on Chemical Phosphate Removal

Two rapid-mixing parameters (detention time and intensity) were evaluated to determine their effects on chemical phosphate removal. The study results are shown in Tables 4.1 through 4.5 and Figure 4.1, in which the main variable between tables is the G value (rapid mixing intensity). Within each table, the main variables are detention time of rapid mixing and aluminum solution strength.

Table 4.1: Residual phosphate concentration (mg/l as P) from jar tests at a G value of 150 sec^{-1} at a molar ratio (1.28) of $Al_{added}/P_{initial}$

Solution Strength	Detention time, seconds					Average
	30	30	60	60	120	
raw, 0 %	5.13	5.09	5.13	5.09	5.09	5.11
50 %	1.38	1.12	1.31	1.22	0.99	1.20
25 %	1.43	1.35	1.28	1.24	1.38	1.34
10 %	1.41	1.50	1.51	1.47	1.45	1.47
5.0 %	1.51	1.59	1.58	1.56	1.33	1.51
2.5 %	1.62	1.55	1.69	1.66	1.50	1.60
1.0 %	1.57	1.70	1.75	1.72	1.64	1.68

Table 4.2: Residual phosphate concentration (mg/l as P) from jar tests at a G value of 300 sec^{-1} at a molar ratio (1.28) of $Al_{added}/P_{initial}$

Solution Strength	Detention time, seconds					Average
	15	15	30	30	60	
raw, 0 %	5.09	5.09	5.09	5.09	5.09	5.09
50 %	1.30	0.87	1.18	1.09	1.13	1.11
25 %	1.29	1.15	1.22	1.20	1.24	1.22
10 %	1.36	1.50	1.46	1.32	1.35	1.40
5.0 %	1.41	1.50	1.46	1.29	1.28	1.39
2.5 %		1.45	1.57	1.37	1.32	1.43
1.0 %		1.58	1.62	1.50	1.54	1.56

Table 4.3: Residual phosphate concentration (mg/l as P) from jar tests at a G value of 600 sec^{-1} at a molar ratio (1.28) of $Al_{added}/P_{initial}$

Solution Strength	Detention time, seconds						Average
	8	8	15	15	30	30	
raw, 0 %	5.13	5.09	5.09	5.12	5.13	5.12	5.11
50 %	0.79	1.15	0.93	0.76	0.88	0.91	0.90
25 %	1.11	1.24	1.04	1.15	1.00	1.15	1.12
10 %	1.26	1.42	1.26	1.24	1.18	1.26	1.27
5.0 %	1.32	1.45	1.31	1.13	1.11	1.19	1.25
2.5 %	1.36	1.50	1.31	1.24	1.19	1.35	1.33
1.0 %	1.41	1.57	1.41	1.45	1.33	1.45	1.44

Table 4.4: Residual phosphate concentration (mg/l as P) from jar tests at a G value of 900 sec^{-1} at a molar ratio (1.28) of $Al_{added}/P_{initial}$

Solution Strength	Detention time, seconds						Average
	5	5	10	10	20	20	
raw, 0 %	5.09	5.12	5.09	5.12	5.09	5.12	5.11
50 %	0.84	1.17	0.88	0.98	0.93	0.78	0.93
25 %	1.21	1.03	1.29	1.00	1.05	1.13	1.12
10 %	1.18	1.29	1.28	1.18	1.16	1.35	1.24
5.0 %	1.23	1.31	1.26	1.29	1.03	1.35	1.25
2.5 %	1.36	1.35	1.33	1.31	1.20	1.31	1.31
1.0 %	1.41	1.53	1.45	1.55	1.38	1.50	1.47

Table 4.5: Residual phosphate concentration (mg/l as P) from jar tests at a G value of 18800 sec^{-1} at a molar ratio (1.28) of $Al_{added}/P_{initial}$

Solution Strength	Detention time, seconds			Average
	1	1	1	
raw, 0 %	5.12	5.12	5.12	5.12
50 %	1.01	0.99	1.03	1.01
25 %	1.36	1.38	1.20	1.31
10 %	1.51	1.49	1.43	1.48
5.0 %	1.65	1.52	1.56	1.58
2.5 %		1.68	1.67	1.68
1.0 %	1.61	1.65	1.70	1.65

4.1.1 Detention time

According to Tables 4.1–4.5, the removal of phosphate from synthetic wastewater using aluminum solutions of different strength seemed unaffected by the detention time of rapid mixing. This observation (conclusion) was not tested statistically because there were not enough data available to allow a statistical analysis.

4.1.2 Mixing intensity

Since it appeared that P removal efficiencies using aluminum solutions were relatively unaffected by the time of rapid mixing, all jar tests results under the same mixing intensity were treated equally. The means of residual phosphate concentrations under each G value were compared for every aluminum solution strength used. For comparison purposes, two statistical techniques were employed: the analysis of variance (ANOVA) and Duncan's multiple range test.

A t-test and the ANOVA are the most efficient and frequently used statistical techniques in comparing the equality of different means under normality assumptions. The main difference between a t-test and the ANOVA is the number of means to compare. When the number of means to compare is two, a t-test is used to test the equality of two means. However, when the number of means to compare is extended to more than two, a t-test is not a valid choice any more and instead, the ANOVA is used. The ANOVA is a more appropriate technique to test the equality of several means than a t-test [14]. A problem with the ANOVA is that it is not a proper choice in detecting where real differences lie. There are many techniques available for this purpose such as the least significant difference (LSD) method, Duncan's multiple range tests, Newman-Keuls test, and Tukey's test. The Duncan's multiple range test was selected for use because it is quite powerful [14]. According to Montgomery, the Duncan's method is very effective at detecting differences between means where real differences exist. The details of the ANOVA and the Duncan's test can be found in the "Design and Analysis of Experiments" [14].

The ANOVA was used to test the equality of the effects of different mixing intensities on chemical phosphate removal because more than two mixing intensities were compared. Once a difference was detected, the Duncan's test was used to establish which groups are statistically different and which groups are not. The Duncan's test was conducted at the 90 % confidence level.

The ANOVA test was conducted on the assumption that there is no rapid-mixing time effect on chemical phosphate removal. This brings out the following question: "What if this assumption does not hold?". The ANOVA test was performed as a completely randomized (CR) design at each level of a factor of interest. A model for this design is as follows:

$$y_{ij} = \mu + \tau_i + \epsilon_{ij} \tag{4.1}$$

y_{ij} : response

μ : general mean

τ_i : treatment effect

ϵ_{ij} : randon error

i : number of treatment

j : number of replication

A statistical analysis comparing treatment effects is based on the ratio of variability caused by treatment effects to variability caused by random errors. This ratio is called, F-value. The idea is that if the variability due to treatment effects is close to the variability due to random errors, then there is no difference between treatment effects. If the variability due to treatment effects is large compared to the one due to random errors, then there exists a difference between treatment effects.

In other words, the F-value is examined to see how big it is. It is expressed in terms of probability values. This probability value tells us a probability that an inference of the difference detected being significant is wrong. Therefore, if the F-value is large enough to support an evidence that a difference between treatments effects is significant, then the probability value should be low. A cut-line of the probability value is not explicitly defined, but generally a value of 0.05 is taken as the cut-line. If the probability value is less than 0.05, the difference can be interpreted as being significant.

To compare different mixing intensities, the ANOVA test was performed at each level of aluminum solution strength and to compare different aluminum solution strengths, the test was performed at each level of G value. If the above assumption does not hold, the variability caused by the time effect would be carried on to the random error term. This will increase the variability of an error. What it means is that the ANOVA test becomes insensitive. If there is a true difference between treatment effects, it will be more difficult for the ANOVA test to detect the difference. This experiment is not a well-designed experiment from statistical points of view because the experimental design makes statistical analysis more insensitive rather than more sensitive. Nonetheless, the experimental results still have significant meanings. If any difference is detected in this experiment, the difference will surely be found in a better designed experiment.

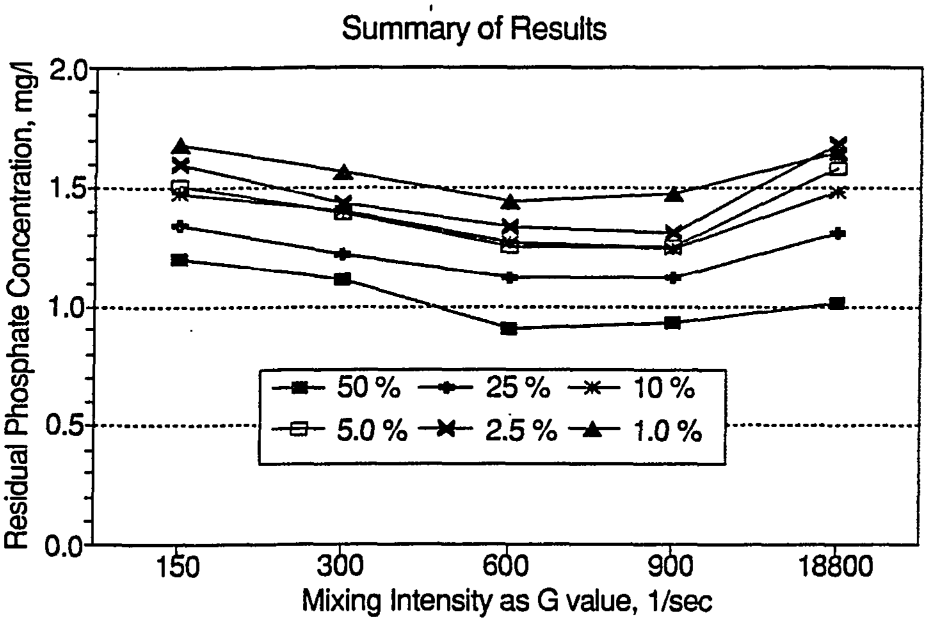

Figure 4.1: Residual phosphate concentration against the mixing intensity

Figure 4.1 is prepared based on the average value of residual phosphate concentration at each mixing intensity and aluminum solution strength. This figure together with Tables 4.1–4.5 show that P removal efficiency increased as the G value increased before it reached the value of 600 sec^{-1}. Further increase in G value deteriorated P removal efficiency. To see whether these results have significant meaning, the ANOVA test was carried out. Results of the ANOVA test are summarized in Table 4.6.

Table 4.6: Summary of the ANOVA test results for effects of different mixing intensities at each aluminum solution strength

Strength, %	1.0 %	2.5 %	5.0 %	10 %	25 %	50 %
F-value	12.40	14.13	8.41	12.55	6.97	4.47
Prob. value	0.0001	0.0001	0.0004	0.0001	0.0011	0.0096

Table 4.6 shows high F-values and low probability values under each aluminum solution strength. This indicates that there was.a statistically significant difference in the effects of different mixing intensities on chemical phosphate removal. The extent of the difference was weaker at the high aluminum solution strengths (25 % and 50 %) than at the low strengths (1.0 % through 10 %). Since the difference was found to exist, the Duncan's test followed to find where real diffrences lie.

Table 4.7 shows the results of Duncan's test for different mixing intensities. It shows that there was no statistically significant difference between the P removal efficiencies at G values of 600 sec^{-1} and 900 sec^{-1}. The observation holds for all the solution strengths used in this study. The P removal efficiencies at mixing intensity G values of 150 sec^{-1} and 18800 sec^{-1} were found to be not significantly different. However, a difference was detected between these G values of 150 sec^{-1} and 18800 sec^{-1} when a solution strength of 50 % was used.

Table 4.7: Results of Duncan's multiple range test for different mixing intensities at each aluminum solution strength at the 90 % confidence level.

Aluminum solution strength

1.0 %		2.5 %		5.0 %		10 %		25 %		50 %	
Duncan	G value	Duncan	G value	Duncan	G value	Duncan	G value	Duncan	G value	Duncan	G value
A	150	A	150	A	18800	A	18800	A	150	A	150
A	18800	A	18800	A	150	A	150	B A	18800	B A	300
B	300	B	300	B	300	A	300	B	300	B C	18800
C	900	B C	600	C	600	B	600	C	900	C	900
C	600	C	900	C	900	B	900	C	600	C	600

note : Duncan Indicates the Duncan grouping
Means with the same letter in the column of Duncan are not significantly different

A change in P removal efficiency was noticed when the G value increased from 300 sec^{-1} to 600 sec^{-1}. Better P removal efficiencies were obtained at the higher mixing intensity (600 sec^{-1}) than at the lower intensity (300 sec^{-1}). This observation was supported statistically for all solution strengths except 2.5 %. When a solution strength of 2.5 % was used, the improvement in the P removal efficiency due to the increase in the mixing intensity was not significant.

A similar change was observed when the G value decreased from 300 sec^{-1} to 150 sec^{-1}. Better P removal efficiencies were confirmed at the higher mixing intensity (300 sec^{-1}) than the lower intensity (150 sec^{-1}). When solution strengths were greater than the EPA recommendation (6 %), the improvement in the P removal efficiency was not significant. However, the improvement became significant when the solution strengths were less than 6 %. The only exception to the above observation occurred at the solution strength of 25 %. The improvement was statistically significant at a solution strength of 25 %.

These results confirm that rapid-mixing intensity affects chemical phosphate removal. The increase in the mixing intensity resulted in better P removal efficiency as long as the G value was kept lower than 600 sec^{-1}. Once the G value reached 600 sec^{-1}, the increase in the mixing intensity to 900 sec^{-1} did not improve the P removal efficiency. Instead, the P removal efficiency deteriorated at the highest G value (18800 sec^{-1}) used in this study. This suggests that a G value of 600 sec^{-1} rather than 300 sec^{-1} (the EPA recommendation) is more desirable and the optimum mixing intensity may be between 600 and 900 sec^{-1} in chemical phosphate removal processes.

When the G value was less than 600 sec^{-1}, the effects of the mixing intensity on chemical phosphate removal varied, depending on the aluminum solution strength. Chemical phosphate removal was affected by the change in the mixing intensity if the solution strength used was less than the EPA recommendation (6 %). In addition, the change in the mixing intensity affected chemical phosphate removal when the solution strength used was 25 %. However, the same change was not found to affect chemical phosphate removal when a solution strength of 10 % or 50 % was used.

In summary, P-removal efficiency improved as the mixing intensity increased. However, no more improvement was achieved after a certain intensity (G value of 600 sec^{-1}) was reached. When the intensity increased beyond this optimum intensity, no improvement in P-removal efficiency was observed. At an extremely high intensity, P-removal efficiency deteriorated.

Then, why did P-removal efficiency improve as the mixing intensity increased? This question can be addressed by the information in the literature review, together with the work of Clark [4] .

Clark and his collegues made extensive studies into the role of mixing in coagulation. They tried to simulate the effects of mixing conditions on Al(III) speciation for coagulation occurring in a mixed reactor. They found that rapid mixing affects Al(III) speciation. According to their work, slow mixing (low mixing intensity) promotes more production of polymers than does rapid mixing.

The review of aluminum chemistry in the literature showed that a reaction between phosphates and aluminum monomers will more likely lead to better P-removal efficiency, in terms of chemical usage, than a reaction between phosphates and aluminum polymers. Therefore, better P-removal efficiency should and will result at high mixing intensity, as shown in this study.

The reason why P-removal efficiency deteriorated at an extremely high mixing intensity is probably due to the different experimental conditions. All experiments, except at this high G value (18800 sec^{-1}), were conducted with a Hudson jar with a 2-liter solution volume. On the other hand, experiments at this high G value were conducted using a blender and a solution volume of 500 ml. It seemed that these different experimental conditions made comparison of results somewhat difficult.

4.2 Effects of Aluminum Solution Strength on Chemical Phosphate Removal

Figure 4.1 and Tables 4.1–4.5 show that P removal efficiency improved as the aluminum solution strength increased. The best P removal efficiency was always obtained at the highest solution strength used (50 %). These results were also analyzed by the ANOVA test and the results are summarized in Table 4.8.

Table 4.8: Summary of the ANOVA test results for effects of different aluminum solution strengths at each mixing intensity

G value, sec^{-1}	150	300	600	900	18800
F value	16.75	11.75	18.32	20.54	54.51
Prob. value	0.0001	0.0001	0.0001	0.0001	0.0001

Table 4.8 shows high F-values and low probability values under each mixing intensity. This indicates that there was a statistically significant difference in the effects of aluminum solution strength on chemical phosphate removal. The difference in P removal efficiencies at different aluminum solution strengths were more evident than the difference caused by different mixing intensities. The most evident effect was observed at a G value of 18800 sec^{-1}.

Table 4.9: Results of Duncan's multiple range test for different aluminum solution strengths at each G value at the 90 % confidence level.

Rapid mixing intensity, sec-1

150		300		600		900		18800	
Duncan	Strength	Duncan	Strength	Duncan	Strength	Duncan	Strength	Duncan	Strength
A	1	A	1	A	1	A	1	A	2.5
B A	2.5	B	2.5	B	2.5	B	2.5	B A	1
B C	5	B	5	B	5	B	5	B	5
C	10	B	10	B	10	B	10	C	10
D	25	C	25	C	25	C	25	D	25
E	50	C	50	D	50	D	50	E	50

note : Duncan indicates the Duncan grouping
Means with the same letter are not significantly different

The Duncan's test was also performed to find where real differences exist. Table 4.9 shows results of a Duncan's test for different aluminum solution strengths. At a G value of 600 sec^{-1}, which was found to be a better intensity than the EPA recommendation (300 sec^{-1}), there was no significant difference in the effects of solution strength (2.5 %, 5.0 %, and 10 %) on chemical phosphate removal. Poorer P removal efficiency was obtained when the solution strength was lower (1.0 %) than at the above strengths and the better efficiencies were obtained when the solution strengths were higher (25 % and 50 %). The use of a solution strength of 50 % resulted in better P removal efficiency than the use of a strength of 25 %. The conclusion that there was improvement in P removal efficiency due to the increase in the solution strength from 25 % to 50 % was justified by the Duncan's test. The same observations were made at a G value of 900 sec^{-1}. Similar observations were made at a G value of 300 sec^{-1}, however, the difference between the P removal efficiencies for solution strengths of 25 % and 50 % was found to be insignificant by the Duncan's test.

At other mixing intensities (150 sec^{-1} and 18800 sec^{-1}), better P removal efficiencies were obtained with solution strengths greater than 6 %. When aluminum solution strengths less than 6 % were used, there was not much difference in the effects of the solution strengths. Once the solution strength became greater than 6 %, the P removal efficiency improved as solution strength increased. The difference in P removal efficiency for solution strengths of 10, 25 and 50 % was found to be significant by the Duncan's test.

These results indicate that aluminum solution strength affects chemical phosphate removal. The higher the solution strength, the better the P removal efficiency.

However, the use of the minimum solution strength of 6 % (the EPA recommendation) was not justified statistically at the most commonly used mixing intensities (300 sec^{-1}, 600 sec^{-1}, and 900 sec^{-1}). At these intensities, there were no significant differences in the P removal efficiencies from solution strengths of 2.5 % to 10 %.

Then, why was P removal efficiency affected by use of different aluminum solution strengths? An answer to this question might be obtained with help of Al(III) speciation.

It is likely that three different types of Al(III) will react with phosphate differently. The solid part of Al(III), Al^c, will not react with phosphate, at least chemically. On the other hand, monomers and polymers will react with phosphate chemically.

Assuming that Al^c will not react with phosphate, better P removal efficiency could be obtained if more monomers plus polymers and less Al^c form when aluminum salts are added to wastewater.

The author believes that Al(III) speciation is the reason why P removal efficiency was affected by use of different aluminum solution strength. There are many factors influencing Al(III) speciation such as a ratio of OH/Al, neutralization rate, mixing conditions, and initial Al concentration [1]. Besides these factors, Al(III) speciation can be influenced by use of different aluminum solution strength. Since better P removal efficiency was obtained at higher solution strength, more monomers plus polymers and less Al^c should be obtained at higher alumium solution strength than at the lower strength. Preliminary experiments supported this hypothesis [12].

5. CONCLUSIONS

This study demonstrates that rapid mixing affects chemical phosphate removal. It is affected by the intensity of rapid mixing. This has to be due to the existence of different Al(III) speciation under different mixing conditions. More polymers form under low mixing intensity [4]. Since reactions between polymers and phosphates lead to poor P removal efficiency than reactions between monomers and phosphates, better P removal efficiency resulted at high mixing intensity.

The difference in the effects of different mixing intensities on chemical phosphate removal (150, 300, 600, 900, and 18800 sec^{-1}) was proved to exist by the ANOVA test.

According to the Duncan's test at the 90 % confidence level, an optimum mixing intensity for chemical phosphate removal exists. The optimum mixing intensity was a G value of 600 sec^{-1}. This G value is twice the G value recommended by EPA (300 sec^{-1}). An increase in the mixing intensity from a G value of 600 to 900 sec^{-1} did not improve P removal efficiency. The actual optimum value may be somewhere between mixing intensities of 600 and 900 sec^{-1}. An increase in the mixing intensity up to the G value of 600 sec^{-1} from a G value of 300 sec^{-1} resulted in improvement in P removal efficiency. A split decision was made for results when the G value was increased from 150 to 300 sec^{-1} where an improvement in the P removal efficiency could be justified when aluminum solution strengths of 1.0, 2.5, 5.0, and 25 % as $AlCl_3 \cdot 6H_2O$ were used; whereas, it was not justified when the solution strength was 10 or 50 % as $AlCl_3 \cdot 6H_2O$.

This study also revealed that use of different solution strengths can result in different P removal efficiency. The higher the solution strength used, the better the P removal efficiency at essentially all mixing intensities used. This suggests the use of the highest possible solution strength in chemical phosphate removal. However, it should be noted that the use of such high solution strengths in chemical phosphate removal can pose problems because a solution with high strength has a very low pH. The low pH value can induce corrosion problems. For example, the pH of the solution at a strength of 50 % was well below 1.0.

The EPA recommendation of a minimum 6 % solution strength could not be justified in this study. Apparently, the selection of such a minimum solution strength is somewhat arbitrary. At the optimum mixing intensity (G value of 600 sec^{-1}), there was no statistically significant difference in the P removal efficiencies over the range of the solution strengths from 2.5 % to 10 % as $AlCl_3 \cdot 6H_2O$. However, solution strengths of 25 and 50 % as $AlCl_3 \cdot 6H_2O$ produced significantly improved performance.

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PAPER II.

RAPID MIXING IN CHEMICAL PHOSPHATE REMOVAL FROM WASTEWATERS (II)

ABSTRACT

Rapid mixing effects in chemical phosphate removal were investigated in this study. Extensive studies of the effects of the time of rapid mixing and optimum mixing intensity on chemical phosphate removal were made. Experiments were conducted using a synthetic wastewater, containing $NaHCO_3$ and NaH_2PO_4. Effects of mixing times of 10, 30, 60, 90, 120, 180 seconds and G values of 500, 600, 700, 800, 900, 1000 sec^{-1} were compared. Results of this study indicated that there was a statistically significant difference in performance among the mixing times compared. Further analysis indicated that P-removal efficiency deteriorated over time after a mixing time of 60 seconds. The time trend was found to be the same for different G values and to be a linear fashion. No statistically significant difference was detected in the effects of the G values compared in this study.

It was found that chemical phosphate removal could be affected by using a different chemical injection method. Better P-removal efficiency was obtained when chemicals (aluminum chloride) were injected using a hypodermic syringe without a needle than when the same chemicals were injected using a hypodermic syringe through a needle. This effect has to be due to the relative ease in mixing when chemicals were injected without a needle.

1. INTRODUCTION

Previous study [3] showed that chemical phosphate removal appeared to be unaffected by the time of rapid mixing, but affected by the intensity of rapid mixing. The study also showed that the optimum mixing intensity for chemical phosphate removal appeared to be a G value of 600 sec^{-1} and an increase in the mixing intensity from a G value of 600 to 900 sec^{-1} did not help in improving P-removal efficiency. This suggested that the actual optimum G value for chemical phosphate removal might exist somewhere between mixing intensities (G value) of 600 and 900 sec^{-1}.

This study was conducted in continuation of the previous study. Objectives of this study were as follows:

- to determine whether the time of rapid mixing affects chemical phosphate removal,
- to determine whether an optimum mixing intensity for chemical phosphate removal lies between G values of 600 sec^{-1} and 900 sec^{-1}.

2. EXPERIMENTS

Table 2.1 shows experimental parameters used in this study. To find out whether the time of rapid mixing affects chemical phosphate removal, six different detention times in rapid mixing were compared. Also, six different G values were used to find out whether there exists an optimum mixing intensity for chemical phosphate removal between G values of 500 and 1,000 sec^{-1}. At each G value, five replicate runs were conducted. The order of these runs were chosen randomly to ensure that other factors, which can potentially affect experimental results, are not correlated with the factors of interest in this study.

Table 2.1: Experimental parameters involved in this study

Time, seconds	10	30	60	90	120	180
G, sec^{-1}	500	600	700	800	900	1000

Experimental conditions used in this study were almost the same as those in the previous study [3]. A synthetic wastewater containing $NaHCO_3$-NaH_2PO_4 was also used in this study with the same alkalinity and phosphate levels: alkalinity of 100 mg/l as $CaCO_3$ and phosphate of 5 mg/l as P. Aluminum chloride was also used as the precipitant at a dosage of 50 mg/l as $AlCl_3 \cdot 6H_2O$. This corresponds to a molar ratio of 1.28 for $Al_{added}/P_{initial}$.

The only differences are that a different reactor and a fixed aluminum solution strength were used. Aluminum chloride was prepared at a solution strength of 25 % by weight as $AlCl_3 \cdot 6H_2O$.

The electric motor attached to the Phipps-Bird jar test machine used previously [3] became unstable when it was operating at relatively high speed (around G value of 600 sec^{-1}). This made it difficult to distinguish between G values at intervals of 100 sec^{-1} when the jar test G value reached about 600 sec^{-1}. Therefore, a different electric motor, which operated under stable conditions at the G values used in this study, was employed. The motor formed a part of a Cole-Parmer Master Servodyne. Attached to the electric motor was an Ametek Model 1736 tachometer from Cole-Parmer. The tachometer was used to measure the speed of the motor. Both the Master Servodyne and the tachometer were connected to the reactor, shown in Figure 2.1. The reactor was similar to the reactor used by Argaman and Kaufman [1]. The solution volume of 18 liters was also used in this study as was used by Argaman and Kaufman. They presented a relationship between velocity gradient (G, sec^{-1}) and paddle speed. Since the same reactor with the same solution volume was used as were used by Argaman and Kaufman, G values used in this study were obtained by selecting a proper paddle speed based on their paddle speed vs. G value relationship, shown in Figure 2.2. A turbine paddle was used to mix the solution. The K value of 0.12 was used for calculation of G values.

During the experiments, the wastewater pH was measured using a Fisher Accumet pH Meter Model 610. Phosphate concentrations in the filtrate were measured using a Beckman model B spectrometer after filtration of the wastewater through 0.45 μm filter membranes using the Ascorbic Acid method (424.F) in the Standards Methods [7].

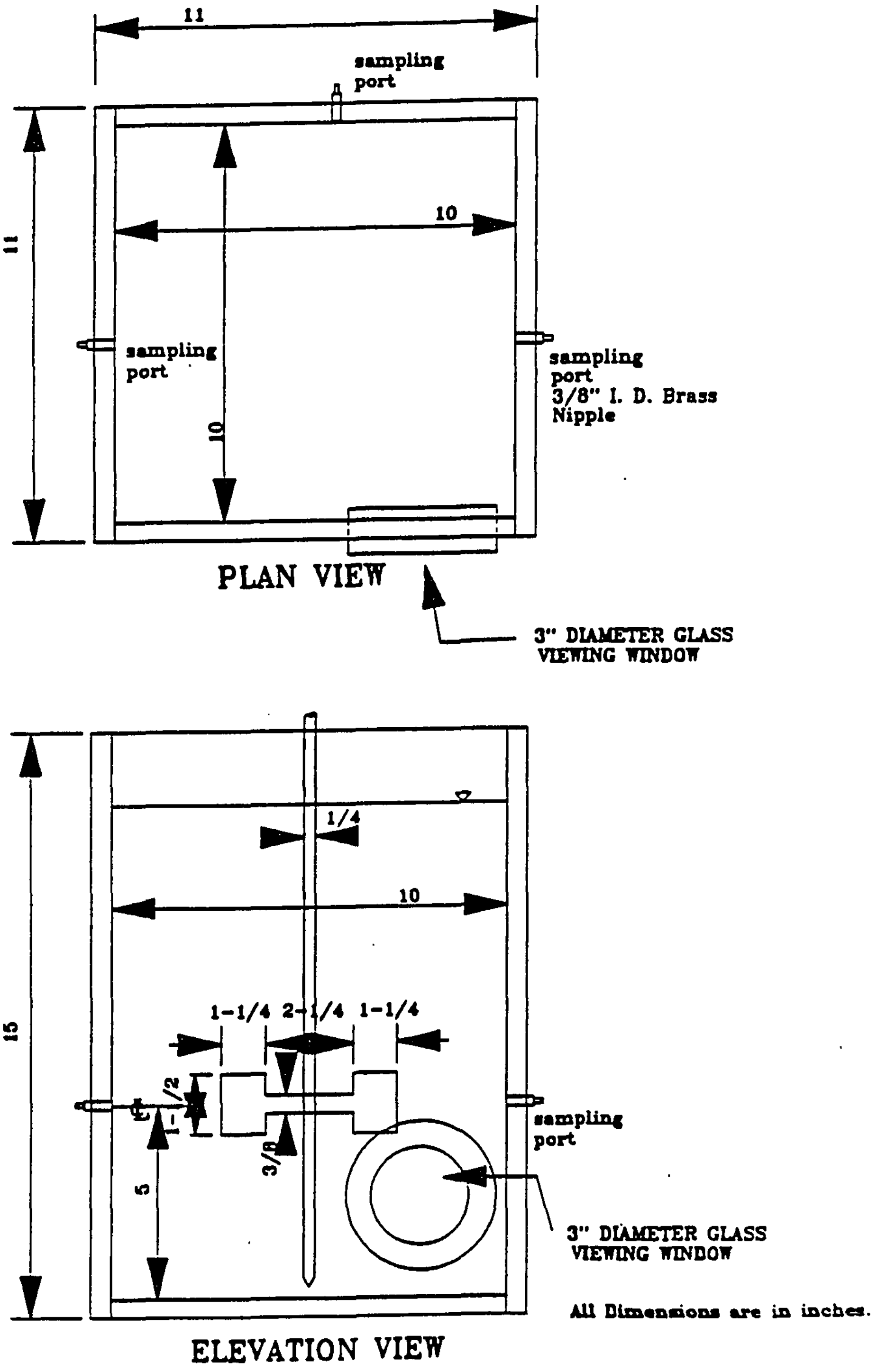

Figure 2.1: Schematic diagram of the reactor used in this study

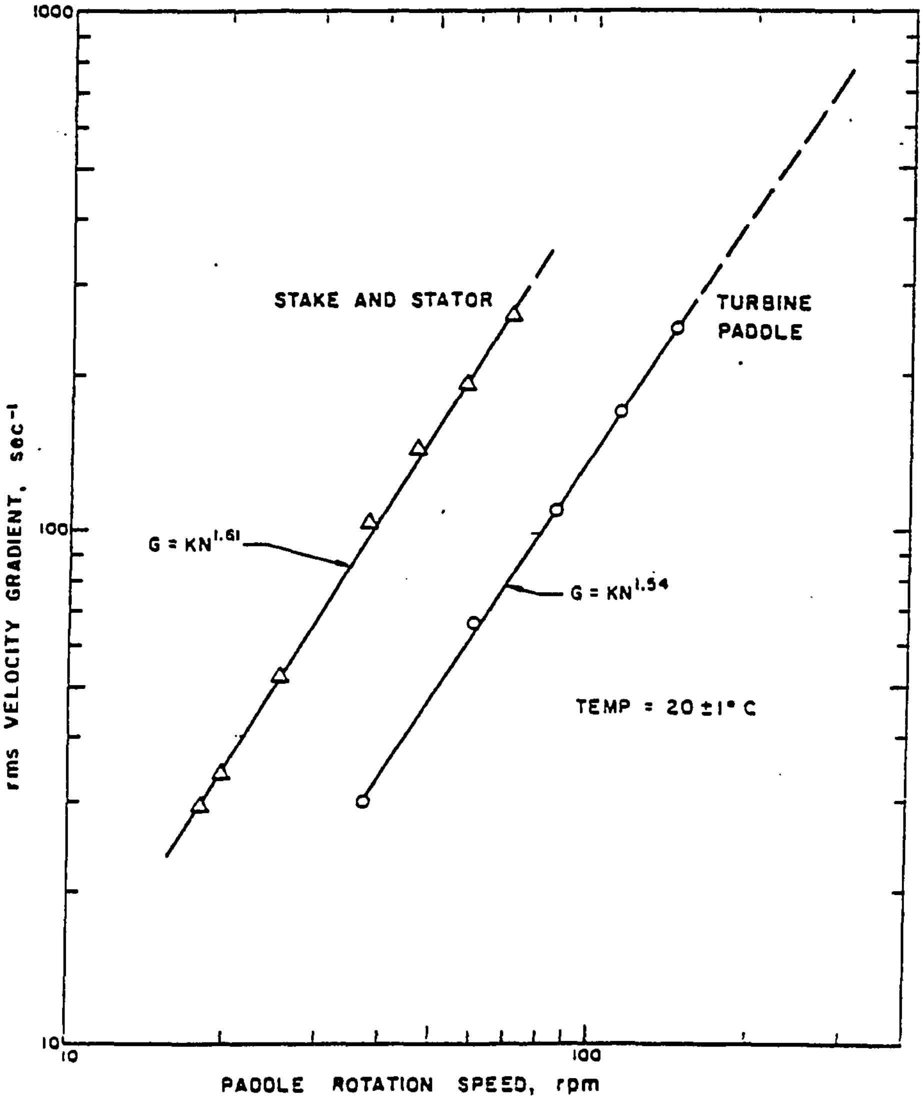

Figure 2.2: Relationship between velocity gradients and paddle speed (Argaman and Kaufman, 1968)

3. RESULTS AND DISCUSSION

Experimental results are shown in Tables 3.1 through 3.6, in which the main variable between tables is a G value (rapid-mixing intensity). Within each table, the main variable is the time of rapid mixing. Figure 3.1 was prepared based on Tables 3.1 – 3.6. In the figure, average residual phosphate values were plotted against the mixing time.

The synthetic solution showed a pH value of 8.08. This value dropped to 6.93 after chemical (50 mg/l of aluminum chloride as $AlCl_3 \cdot 6H_2O$) was injected into the solution.

Table 3.1: Residual phosphate concentrations (mg/l as P) at a G value of 500 sec^{-1}

Time seconds	Test number					Average
	1	2	3	4	5	
10	1.56	1.61	1.55	1.50	1.50	1.54
30	1.61	1.62	1.56	1.55	1.54	1.57
60	1.58	1.61	1.56	1.56	1.55	1.57
90	1.57	1.61	1.56	1.56	1.53	1.56
120	1.67	1.63	1.56	1.60	1.56	1.60
180	1.61	1.63	1.56	1.57	1.56	1.59
Average	1.60	1.62	1.56	1.56	1.54	1.57

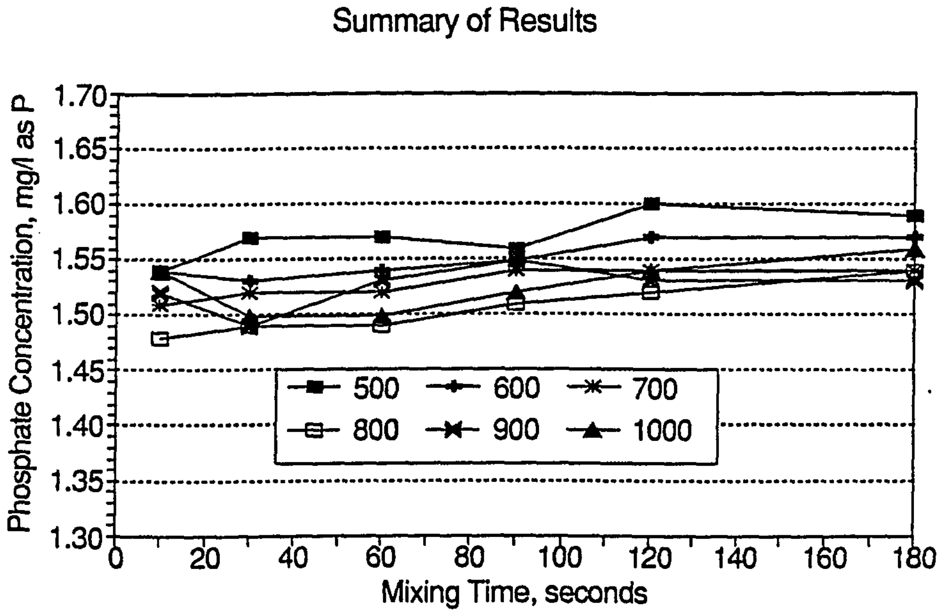

Figure 3.1: Residual phosphate concentration against the mixing time at G values of 500 - 1000 sec^{-1}

Table 3.2: Residual phosphate concentrations (mg/l as P)at a G value of 600 sec^{-1}

Time seconds	Test number					Average
	1	2	3	4	5	
10	1.48	1.68	1.56	1.45	1.54	1.54
30	1.47		1.56	1.55	1.53	1.53
60	1.48	1.62	1.56	1.53	1.50	1.54
90	1.50	1.61	1.56	1.56	1.52	1.55
120	1.52	1.66	1.58	1.56	1.51	1.57
180	1.53	1.66	1.58	1.56	1.52	1.57
Average	1.50	1.56	1.57	1.53	1.52	1.54

Table 3.3: Residual phosphate concentrations (mg/l as P) at a G value of 700 sec^{-1}

Time seconds	Test number					Average
	1	2	3	4	5	
10	1.56	1.57	1.45	1.48	1.48	1.51
30	1.56	1.50	1.50	1.56	1.50	1.52
60	1.56	1.54	1.50	1.56	1.46	1.52
90	1.56	1.56	1.50	1.56	1.50	1.54
120	1.56	1.58	1.52	1.56	1.50	1.54
180	1.56	1.57	1.54	1.55	1.50	1.54
Average	1.56	1.55	1.50	1.54	1.49	1.53

Table 3.4: Residual phosphate concentrations (mg/l as P) at a G value of 800 sec^{-1}

Time seconds	Test number					Average
	1	2	3	4	5	
10	1.50	1.45	1.50		1.45	1.48
30	1.53	1.50	1.53	1.45	1.45	1.49
60	1.45	1.53	1.54	1.50	1.45	1.49
90	1.50	1.54	1.56	1.50	1.45	1.51
120	1.50	1.56	1.56	1.51	1.47	1.52
180	1.56	1.56	1.56	1.56	1.49	1.54
Average	1.51	1.52	1.54	1.50	1.46	1.51

Table 3.5: Residual phosphate concentrations (mg/l as P) at a G value of 900 sec^{-1}

Time seconds	Test number					Average
	1	2	3	4	5	
10		1.48	1.56	1.63	1.40	1.52
30		1.50	1.40	1.65	1.42	1.49
60	1.56	1.50	1.56	1.61	1.41	1.53
90	1.53	1.52	1.61	1.62	1.45	1.55
120		1.48	1.58	1.63	1.45	1.53
180	1.47	1.51	1.60	1.67	1.40	1.53
Average	1.52	1.50	1.55	1.64	1.42	1.52

Table 3.6: Residual phosphate concentrations (mg/l as P) at a G value of 1000 sec^{-1}

Time seconds	Test number					Average
	1	2	3	4	5	
10	1.72	1.50	1.50	1.45	1.53	1.54
30	1.58	1.56	1.47	1.47	1.40	1.50
60	1.58	1.56	1.48	1.45	1.45	1.50
90	1.58	1.55	1.50	1.49	1.47	1.52
120	1.68	1.56	1.59	1.49	1.47	1.54
180	1.61	1.61	1.56	1.50	1.50	1.56
Average	1.61	1.56	1.52	1.48	1.46	1.52

3.1 Optimum Mixing Intensity in Chemical Phosphate Removal

Tables 3.1 through 3.6 showed that there was not much difference in the residual phosphate concentrations when the intensity of rapid mixing in chemical phosphate removal varied from a G value of 500 to 1,000 sec^{-1}. The best P-removal efficiency (the lowest residual phosphate concentration) was obtained at a G value of 800 sec^{-1}. G values above and below this value (800 sec^{-1}) resulted in higher residual phosphate concentrations.

These results were evaluated statistically. Two factors were evaluated in this experiment: the mixing intensity and the mixing time. This experiment has 30 experimental units: six different G values and five replicates for each G value. A completely randomized (CR) design was used to randomize these experimental units and to evaluate a main-effect of the mixing intensity. Each experimental unit has six sub-units based on the mixing time: 10, 30, 60, 90, 120, and 180 seconds. A "repeated measure scheme" was used to evaluate a main effect of the mixing time and an interaction between the mixing time and the intensity.

A repeated measure scheme is a modification of a split-plot design. In most experimental designs, only one observation is made for each experimental unit. However, more than one measurement is sometimes taken from one experimental unit. Each primary experimental unit has several measures associated with it. This is called a "repeated measure scheme". In a repeated measure scheme, these values arise from measuring the entire primary unit at several times. The primary unit is not subdivided into smaller units, no treatment is randomized, but a number of measures are taken sequentially on each primary unit. This is a difference between a repeated measure scheme and a split-plot design. In a split-plot design, the primary unit is subdivided into smaller units and these smaller units can be randomized. However, this can not be done in a repeated measure scheme. Suppose repeated measurements are made over time. The order of treatment applied on the smaller units could not be randomized due to its nature. Because of this nature, a more conservative method should be adopted in the analysis of a repeated measure scheme. This scheme can be analyzed by both an univariate and a multivariate analysis. More detailed information about a repeated measure scheme can be found in *The design of experiments* [5].

In this experiment, six different measurements of residual phosphate concentration over a period of the mixing time are the repeated measurements. Both univariate and multivariate analyses were used in this study. When these two analyses gave conflicting results, more conservative results were taken. Table 3.7 shows an ANOVA (analysis of variance) table corresponding to a univariate analysis.

Table 3.7: Summary of the repeated measure ANOVA test among six different mixing intensities

Source	df	F-value	Pr.> F
G	5	0.93	0.4805
Error a	21		
Time	5	8.36	0.0001
G·Time	25	0.73	0.8179
Error b	105		

Table 3.7 summarizes results of the repeated measure ANOVA test among different G values. In the table, F-value is a ratio of variability due to treatment effects to variabilibty due to random errors. This ratio indicates a measure of how treatment effects are significant. In order for the treatment effects to become significant, this ratio should be greater than the unity. In other words, the variability due to the treatment effects should exceed the variability due to random errors. This is an F-test, testing a null hypothesis that no treatment effect exists against an alternative hypothesis that a treatment effect exists. Results of this F-test is indicated in the fourth column of the table. This column shows probability that the null hypothesis is right. If the probability is less than a predetermined significance level, we can negate the null hypothesis and accept the alternative hypothesis. If the probability

is greater than the significance level, there is not enough evidence to negate the null hypothesis. The significance level of 0.05 is ususally taken.

Table 3.7 shows low F-value (0.93) and high probability (0.4805) for the effects of the mixing intensity (G). This indicates that the difference in residual phosphate concentrations caused by the change in the mixing intensity from a G value of 500 to 1,000 sec^{-1} is insignificant statistically. Although the lowest residual phosphate concentration was obtained when a G value of 800 sec^{-1} was used for the mixing intensity, this was not supported statistically. In other words, there is not enough evidence available that the optimum mixing intensity is a G value of 800 sec^{-1} in chemical phosphate removal. Once the mixing intensity reached a G value of 500 sec^{-1}, P-removal efficiency was practically the same within the range of the experiments up to a G value of 1,000 sec^{-1}.

3.2 Effects of the Time of Rapid Mixing on Chemical Phosphate Removal

Examination of Table 3.7 shows high F-value (8.36) and low probability (0.0001) for the effects of the mixing time and low F-value (0.73) and high probability (0.8179) for the effects of the interaction between the mixing time and the intensity.

High F-value together with low probability indicates that the effects of the mixing time are significant. However, this ANOVA table does not tell the whole story. The probability (0.0001) shown in the Table 3.7 is obtained with 5 and 105 degrees of freedom (df). In a repeated measure scheme, we should use a more conservative analysis because randomization could not be obtained in this experiment. The probability should be obtained with 1 and 21 df instead of 5 and 105 df. The F-value at these df is 4.32 with the significance level of 0.05 and 8.02 with the significance level of 0.01. Since the F-value 8.36 is greater than these numbers, we can say that the probability is less than 0.01. This indicates that the effects of the mixing time are indeed significant.

Low F-value together with high probability indicates that the effects of the interaction between the mixing time and the intensity are insignificant. This means that a change in residual phosphate concentration according to mixing time is the same regardless of the mixing intensity.

Table 3.8: Summary of the repeated measure ANOVA test among six different detention times of rapid mixing

Statistic	No Time Effect		no G·Time effect	
	F	Pr. > F	F	Pr. > F
Wilk's Lambda	9.8063	0.0002	0.9696	0.5170
Pillai's Trace	9.8063	0.0002	0.9706	0.5117
Hotelling-Lawley Trace	9.8063	0.0002	0.9490	0.5413
Roy's Greatest Root	9.8063	0.0002	3.8909	0.0119

Results of a multivariate analysis are summarized in Table 3.8, in which the second and the third columns show the result of the analysis of the time effect and the fourth and the fifth columns show the result of the analysis of the interaction effect (G·time). Table 3.8 indicates that there is a significant change in residual phosphate concentrations over time. This is confirmed by all four tests used in this analysis. Three of the four tests suggest that the G·Time interaction is not significant. As shown above, the univariate test confirmed that differences due to time are significant and the G·Time interaction is not a significant factor.

What these results indicate is that P-removal efficiency was indeed affected by the time of rapid mixing in this experiment. There is insufficient evidence to indicate that the time trend is different for different levels of G.

Since it was found that the time trend might be the same for different levels of G, further analysis was performed to study the time trend. For this purpose, the factor of the mixing time is partitioned into a polynomial component (linear, quadratic, cubic, etc.). A summary of this test is shown in Table 3.9. This table indicates that only the linear component is significant. This means that the only way in which the mixing time affects P-removal efficiency is through its linear component. In other words, the residual phosphate concentration increased with increasing rapid mixing durations.

Table 3.9: Summary of further repeated measure ANOVA test studying the polynomial components

Source	df	F-value	Pr.> F
Linear component	1	28.97	0.0001
Quadratic component	1	0.47	0.5010
Cubic component	1	1.24	0.2781
Fourth order component	1	0.26	0.6151
Fifth order component	1	0.92	0.3487

More careful examination of data shown in Tables 3.1 through 3.6 together with Figure 3.1 indicates that the residual phosphate concentrations started to increase after a certain mixing time was reached. This indicates that P-removal efficiency might not be affected by the mixing time until a critical time is reached. To study this hypothesis, the multivariate analysis was conducted with modification. Less than six repeated measurements were used in the analysis, i.e., five, four and three levels of the mixing time were used successively in the multivariate analysis to determine when the mixing time effect was insignificant. Results of this analysis indicated that a critical mixing time was 60 seconds. When the mixing time used was less than 60 seconds, there is insufficient evidence that P-removal efficiency was affected by the rapid mixing time. Both an univariate and a multivariate analyses confirmed this. Once the time exceeded the critical time, P-removal efficiency was affected by the time. P-removal efficiency deteriorated with increased rapid mixing durations above the critical mixing time.

3.3 Effects of the Chemical Injection Method on Chemical Phosphate Removal

While the role of rapid mixing in chemical phospate removal was being studied, it was found that the chemical injection method affected P-removal efficiency. In this study, aluminum solution was injected into the reactor using a hypodermic syringe through a needle. The needle was sometimes detached from the syringe and dropped into the reactor by accident. Subsequently, chemicals were injected without a needle. When this happened, better P-removal efficiency was always obtained.

This effect was shown most dramatically when aged aluminum chloride was used as a precipitant to remove phosphates. Although detailed experimental results are not reported, it was found during the study that P-removal efficiency deteriorated when aged aluminum solutions were used, compared to when fresh aluminum solutions were used. When aluminum chloride with a 50 % solution strength as $AlCl_3 \cdot 6H_2O$ (5 days old) was injected by syringe without a needle into a synthetic wastewater, the residual phosphate concentration dropped to 0.35 mg/l as P. On the other hand, the residual phosphate concentration was 1.97 mg/l as P when the same chemicals were injected through a needle. The synthetic wastewater had an initial phosphate level of 5.58 mg/l as P and an initial alkalinity level of 100 mg/l as $CaCO_3$. The mixing intensity had a G value of 300 sec^{-1} and the mixing time was 60 seconds. The molar ratio of $Al_{added}/P_{removed}$ was 1.2 for an injection without a needle and 1.8 for an injection with a needle. When fresh aluminum chloride was used, the gap narrowed. In terms of the molar ratio, the molar ratio for an injection without a needle stayed the same (1.2), but for an injection with a needle the molar ratio decreased to 1.6. This suggests that the deterioration in P-removal efficiency resulting from the use of aged aluminum salts in chemical phosphate removal can be eliminated by injecting the chemical without a needle.

Since examination of this effect was not an objective of this study, it was not followed-up systematically. However, a needle was inadvertantly dropped many times during this study and another study in which modeling of chemical phosphate removal was studied. A consistently better P-removal efficiency was obtained when chemicals were injected without a needle than with a needle.

Thus, the question surfaces, “Why does this happen?”. To address this question, the physical differences arising from injecting chemicals without a needle and with a needle should be examined. Srivastava et al. [6] said,

> *When substance A is introduced into a reactor full of substance B while mixing is going on, the droplets of A increase their volume because of cloud growth as well as vortex stretching. Thus, there will be an increasingly large cloud being transported around the reactor.*

Importance of cloud growth is shown in the above statements. Physical differences in injection of chemicals without a needle and with a needle can be explained, in terms of the cloud volume. When chemicals were injected without a needle, the initial cloud volume gets bigger than when chemicals were injected through a needle.

Big initial cloud volume requires less energy in obtaining rapid mixing. This leads to more efficient rapid mixing in an injection of chemicals without the needle.

Also, it took longer to add required aluminum solution with the needle than without the needle. Therefore, there was more time available for polymer formation when aluminum solution was injected with the needle. Since polymer was found ineffective in removing phosphates [2, 4], this could result in the deterioration in P-removal efficiency.

4. CONCLUSIONS

According to this study, there is strong evidence that chemical phosphate removal was deteriorated by increased mixing time, provided that the mixing time exceeded 60 seconds. However, when the mixing time employed was in the range of 10–60 seconds, there was insufficient evidence that the mixing time was a significant factor. Once more than 60 seconds of the mixing time was used, the mixing time affected (decreased) P-removal efficiency. When the mixing time affected P-removal efficiency, the time trend was a linear fashion and the same trend was observed regardless of the mixing intensity. This means that whether the mixing intensity was a G value of 500 or 1000 sec^{-1}, the time trend was a linear fashion and P-removal efficiency deteriorated in a linear fashion over a time period of 90–180 seconds.

There was insufficient evidence that an optimum mixing intensity lies between G values of 500 and 1,000 sec^{-1}. Practically, no difference was detected among the different G levels compared in this study.

During this study, it was observed that better P-removal efficiency could result when chemicals were injected without a needle. This has to be due to the relative easiness in rapid mixing when chemicals were injected without a needle than when chemicals were injected with a needle. This observation was not tested statistically.

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PAPER III.

MODELING OF CHEMICAL PHOSPHATE REMOVAL FROM WASTEWATERS

ABSTRACT

This study showed that phosphates were removed stoichiometrically by forming aluminum hydroxyphosphate, $Al_{1.2}H_2PO_4(OH)_{2.6}$, rather than aluminum phosphate in chemical phosphate removal. It was also shown that calcium-phosphate precipitation could occur at an initial stage of chemical phosphate removal when calcium was present in the wastewater. The precipitates could be tricalcium phosphate. Aluminum chloride and alum were compared in their effects on chemical phosphate removal. There was no difference between use of these two chemicals.

Equilibrium models for chemical phosphate removal, the Ferguson model and the Luedecke et al. model, were evaluated in this study. Comparison between simulation and the experimental results using the synthetic wastewater showed that the Ferguson model predicted residual parameters well, especially residual phosphate values. However, the equilibrium models were found to have some problems and are, therefore, unable to explain what is happening in chemical phosphate removal. Chemical phosphate removal is much more complicated than expected. Since a regression approach is believed better in data fitting, regression models predicting residual parameters such as alkalinity, pH, and phosphate in chemical phosphate removal were developed. These models predicted residual parameters well.

1. INTRODUCTION

A model for chemical phosphate removal from wastewaters using alum or aluminum chloride as the precipitant, if properly prepared, should provide an insight into the mechanism of chemical phosphate removal. Besides that, it should be able to predict such important parameters as the residual phosphate concentration, alkalinity, and pH.

There are two approaches available in developing models for chemical phosphate removal: a chemical equilibrium approach and a regression approach. A chemical equilibrium approach is very instructive if it builds on a sound foundation, because it provides a way of understanding potential chemical interactions. Restrictions encountered in using this approach come from limitations in thermodynamic data and interferences from rate dependent reactions. On the other hand, a regression approach does not provide a conceptual basis for understanding chemical phosphate removal. A model developed by implementing this approach simply predicts residual parameters like phosphate concentration, alkalinity, and pH. An advantage of this approach, however, is that it allows us to evaluate independent variables involved in chemical phosphate removal so that we can figure out which parameters are important.

Currently, there are two phosphate precipitation models available in the literature: the Ferguson model [6, 7] and the Luedecke et al. model [17]. Both models are based on a chemical equilibrium approach. A major difference between these two models is the foundation on which the model is built, i.e., the mechanism of chemical phosphate removal. The Ferguson model assumes that precipitation is the only mechanism responsible for removing phosphates in chemical phosphate removal. The model then simulates the precipitation of aluminum hydroxyphosphate. The Luedecke et al. model assumes that both precipitation and adsorption are responsible for removing phosphates in chemical phosphate removal. The model simulates adsorption of phosphates on solids of ferric hydroxides and ferric hydroxyphosphates as well as precipitation of ferric hydroxyphosphates. These equilibrium models were evaluated in this study.

Originally, it was planned to develop a new model based on a chemical equilibrium approach (more specifically, using the Ferguson approach). However, modeling of chemical phosphate removal was attempted by using a different approach (regression approach) in this study because of reasons explained below.

Two parameters are essential in the Ferguson model: the stoichiometric molar ratio (Al/P) in the phosphate solid and solubility data for the solid formed. Information concerning these parameters was expected to be obtained from experiments. It was soon found experimentally that the stoichiometric ratio is not constant and is influenced by such parameters as the initial phosphate and alkalinity levels as well as the chemical mixing intensity. This made selection of a proper value of the stoichiometric ratio very difficult.

Careful examination of the Ferguson model also revealed that the model simplified equilibrium calculations so that the model would be workable using available numerical methods. That is possible when models are simple and involve a small number of species like the Ferguson model. However, when modeling of chemical phosphate removal became more comprehensive and included more species (like calcium) than those in the Ferguson model, it became very difficult to solve the equilibrium system by numerical methods. The model for chemical phosphate removal with no calcium interaction considered can be described with four unknowns: Al-H-PO_4-CO_3. This could be solved by setting up four equations. These four equations can be obtained from mass balances, equilibrium relations, and a proton condition or a charge balance equation.

To develop the equilibrium model, four equations were obtained from mass balances of Al, PO_4, and CO_3, their equilibrium relations and a proton condition. As in the Ferguson model, two solids were assumed to precipitate: aluminum hydroxyphosphate and aluminum hydroxide solids. When the aluminum molar concentration is less than the phosphate molar concentration, a solid of aluminum hydroxyphosphate will form; when it is greater than the phosphate concentration, both solids will form. In the single precipitate case, those four equations could be reduced to two nonlinear equations after some algebraic manipulation. In the double precipitate case, these equations could be reduced to a single nonlinear equation. In order to solve the two nonlinear equations simultaneously, a computer subroutine called SNSQE was used. A subroutine of FZERO was used to solve a single nonlinear equation. Both subroutines are stored in the software library of the Mathematics Department at Iowa State University. These subroutines were accessed through the Project Vincent. The SNSQE is a modification of Newton's method and the FZERO is a combination of the bisection method and the secant method.

The subroutine of FZERO worked fine, enabling one to solve a double precipitate case. However, the subroutine of SNSQE could not give an answer. Apparently, the numbers involved in equilibrium calculations were too small so that the Jacobian matrix becomes nearly singular, resulting in no answer. This made the equilibrium model developed unable to solve a single precipitate case. In other words, the model cannot give an answer when the molar concentration of aluminum added is less than that of the phosphate, i.e., a single precipitate case. When it was assumed that both solids always precipitate, the model could predict the residual phosphate well only when the initial alkalinity and phosphate levels were low, like 50 mg/l as $CaCO_3$ and 3.10 mg/l as P, respectively. Simulation results from use of the model under these conditions are shown in the chapter on evaluation of equilibrium models. This model was not discussed in this study because it is not complete.

As this study progressed, it was realized that chemical phosphate removal is a much more complicated process than what was first thought. There are many things that the equilibrium model cannot explain about chemical phosphate removal. Modeling of chemical phosphate removal cannot be described with a chemical equilibrium approach alone. The equilibrium model cannot give an insight into the mechanism of chemical phosphate removal. All the equilibrium model can do is predict the residual parameters such as residual phosphate concentration, pH, alkalinity. Even this became possible only after manipulation of the thermodynamic data to increase the accuracy of the prediction. This is more like a job of data fitting.

As far as data fitting is concerned, a regression approach could give better results than a chemical equilibrium approach. Therefore, regression modeling of chemical phosphate removal was attempted in this study.

In addition, a difference between use of aluminum chloride and alum as the precipitant and their effects on chemical phosphate removal was investigated. Alum is the most popular choice of aluminum salt in water and wastewater treatment. Although aluminum chloride has been quite often used in laboratory-scale experiments when aluminum chemistry and/or chemical phosphate removal was studied, it is very rarely used in actual field situations. Examination of the equilibrium model indicated that aluminum chloride might be more effective in removing phosphates than alum. The reason why a chemical equilibrium approach favors aluminum chloride over alum is explained later. Therefore, both aluminum salts were used to compare their differences.

Most wastewaters contain a considerable amount of calcium. However, both of the equilibrium models mentioned above fail to incorporate any calcium effect on chemical phosphate removal. Incorporating the calcium effect makes the equilibrium system very complex and that probably is the reason why these two models did not touch the calcium effect. Unlike a chemical equilibrium approach, a regression approach does not become so complex with the calcium addition. Therefore, regression models which incorporate the calcium effect were also developed and the calcium effect was investigated.

In summary, this study has the following objectives:

- to compare aluminum chloride and alum in their effects on chemical phosphate removal,
- to investigate any calcium effect on chemical phosphate removal,
- to evaluate currently available equilibrium models, and
- to develop regression models for chemical phosphate removal.

2. LITERATURE REVIEW

2.1 Models Currently Available in the Literature

2.1.1 Ferguson model

Ferguson envisioned chemical phosphate removal as precipitation of metal (aluminum in his model) and phosphate [6]. He then developed his model of chemical phosphate removal based on several assumptions. These assumptions are:

1. The model was to describe orthophosphate precipitation. This means other forms of phosphates such as condensed and organic phosphates are not considered in the model. Therefore, this model is more applicable to precipitation of phosphates in secondary effluent rather than in raw wastewater. Biological activities occurring in secondary treatment help hydrolyze condensed and organic phosphates into orthophosphates. As a result, most phosphates in secondary effluent usually consist of orthophosphates.
2. Solids separation is not described. Complete solid/liquid separation is assumed. This indicates that the removal of particulate phosphate is not described by the model because removal of particulate phosphate largely depends on clarifier performance. The model describes removal of soluble phosphates only.
3. Precipitation is the sole mechanism that results in phosphate removal.

4. Of the possible precipitates (aluminum phosphate and aluminum hydroxide), the phosphate solid precipitates first. When the aluminum molar concentration is less than the phosphate molar concentration, a phosphate solid exists alone. When the aluminum concentration exceeds the phosphate concentration, both phosphate and hydroxide solids form in the process of chemical phosphate removal.

5. The molar ratio of aluminum to phosphate in the precipitated phosphate solid is constant at all pH values.

6. The system is presumed closed to transfer of CO_2 from the solution to the atmosphere. The carbonate system in the solution is not in equilibrium with CO_2 in the atmosphere.

7. Rapid equilibrium is reached. The rates of preciptation and dissolution are not considered in the model. Assuming equilibrium is always reached, the model calculates equilibrium concentrations.

8. Equilibrium constants are defined at 25^o C with no activity corrections. Considering the error contained in the equilibrium constants, an error caused by different temperature and ionic strength is assumed to be negligible.

Table 2.1 shows the equilibrium stability constants used in the calculation of the Ferguson model and the reactions involved.

The Ferguson model calculates the equilibrium pH, satisfying the charge balance equation. All calculations were made in molar concentrations. Figure 2.1 illustrates the procedures used for computation with the model. These procedures are explained step by step below. The step number matches the number shown in Figure 2.1.

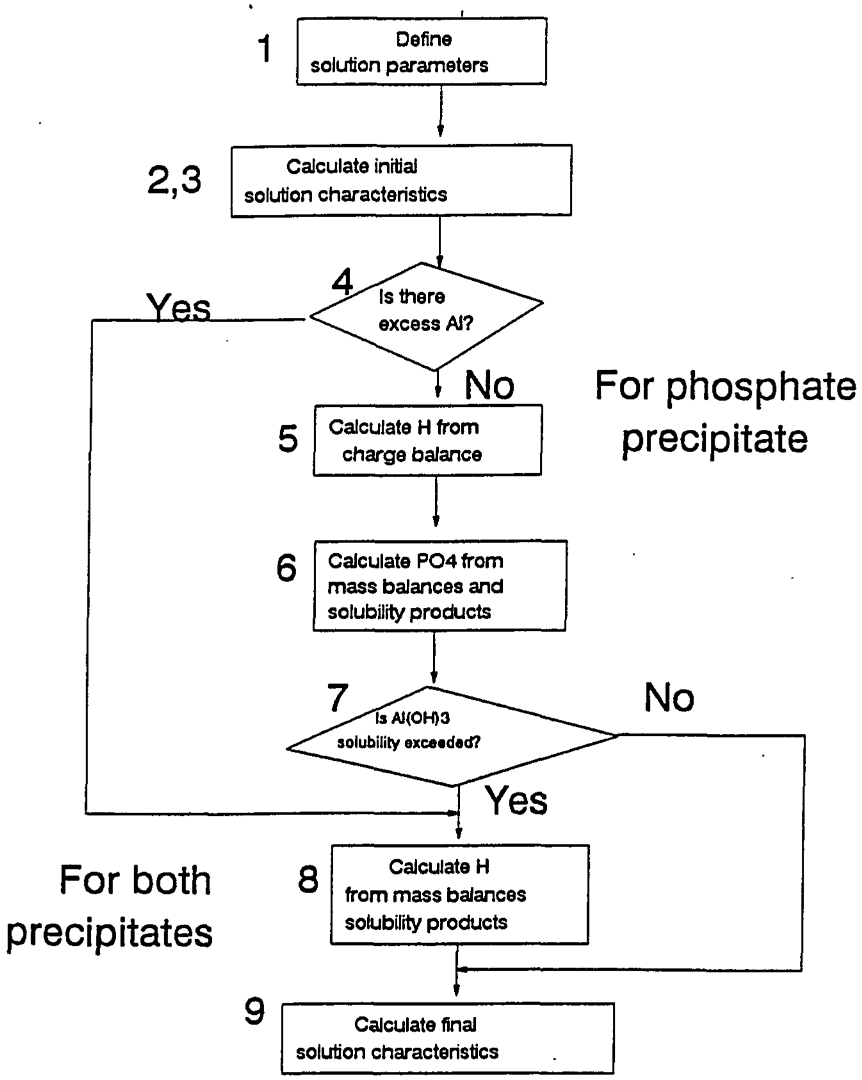


Figure 2.1: Schematic diagram of the Ferguson model

Table 2.1: Equilibrium stability constants used in the Ferguson model at 25^oC (Ferguson, 1972)

Reactions	pK values
$H_2O = H^+ + OH^-$	14
$H_2CO_3 = H^+ + HCO_3^-$	6.2
$HCO_3^- = H^+ + CO_3^{2-}$	10.2
$H_3PO_4 = H^+ + H_2PO_4^-$	2.2
$H_2PO_4^- = H^+ + HPO_4^{2-}$	7.2
$HPO_4^{2-} = H^+ + PO_4^{3-}$	12.2
$NH_4OH + H^+ + NH_4 + H_2O$	-9.2
$Al^{3+} + OH^- = Al(OH)^{2+}$	-9.0
$Al^{3+} + 4OH^- = Al(OH)_4^-$	-32.5
$Al(OH)_{3(s)} = Al^{3+} + 3OH^-$	30.4
$Al_{1.4}PO_4(OH)_{1.2(s)} = 1.4Al^{3+} + PO_4^{3-} + 1.2OH^-$	32.2

1. The initial analytical description of wastewater quality parameters such as orthophosphate, ammonia nitrogen, total alkalinity, and pH are given.

2. The initial species distributions for phosphate, ammonia, and carbonate are calculated, based on the initial analytical information given. To compute the carbonate concentration from the initial alkalinity, Ferguson made corrections for the influence of phosphate and ammonia on the alkalinity. For pH values between 6 and 9, the following relationships are believed valid and can be solved for the bicarbonate concentration.

$$Alkalinity = [HCO_3^-] + [HPO_4^{2-}] + [NH_4OH] \tag{2.1}$$

3. The initial concentration of cations associated with anions, Mi^+ in eq/l, is calculated from the electroneutrality (charge balance) equation.

$$\begin{aligned} Mi^+ &= [H_2PO_4^-] + 2[HPO_4^{2-}] + [HCO_3^-] + 2[CO_3^{2-}] + \\ &\quad [OH^-] - [H^+] - [NH_4^+] \end{aligned} \tag{2.2}$$

4. Decide whether a single precipitate or double precipitates is formed. If the molar concentration of aluminum is less than that of phosphate (P_T[1] > 1.4 Al_T[2]), a solid of aluminum phosphate alone precipitates. If otherwise, both precipitates (aluminum phosphate and hydroxide) form. Ferguson noted that a molar ratio of aluminum to phosphorus (Al/P) in a phosphate solid was always reported to be higher than 1.0 in almost all literature data. Recht and Ghassemi [21] determined the ratio of Al/P in a phosphate solid to be 1.4, with excess aluminum precipitated as an amorphous $Al(OH)_{3(s)}$. Based on this study, Ferguson took the ratio of 1.4 and then, calculated a solubility product of $10^{-32.2}$ for an imaginary solid of $Al_{1.4}PO_4(OH)_{1.2(s)}$. Ferguson selected this value specifically to bring the model results in line with experimental results.

5. In the case of a single precipitate, the final pH is calculated from the charge balance equation, using a successive search method.

$$\begin{aligned} [H^+] + [NH_4^+] + Mi^+ &= C_A + [HCO_3^-] + [H_2PO_4^-] + \\ &\quad 2[HPO_4^{2-}] + [OH^-] \end{aligned} \tag{2.3}$$

---

[1] total phosphate concentration

[2] total aluminum concentration

Ferguson calculated the acidity, C_A in eq/l, resulting from the aluminum addition, based on the assumed precipitation reaction.

$$1.4[Al^{3+}] + [H_2PO_4^-] + 1.2H_2O = Al_{1.4}PO_4(OH)_{1.2(s)} + 3.2H^+ \quad (2.4)$$

$$C_A = \frac{3.2Al_T}{1.4} \quad (2.5)$$

Assuming the soluble phosphate concentration is nearly equal to P_T - $1.4Al_T$, the charge balance can be directly solved for the H^+ concentration.

6. The concentration of phosphate is calculated from mass balances of aluminum and phosphate and the solubility product of aluminum phosphate, using the Newton-Raphson method.

$$\begin{aligned} Al_T &= 1.4Al_{1.4}PO_4(OH)_{1.2(s)} + [Al^{3+}] + \\ &\quad [AlOH^{2+}] + [Al(OH)_4^-] \quad (2.6) \\ P_T &= Al_{1.4}PO_4(OH)_{1.2(s)} + [H_2PO_4^-] + [HPO_4^{2-}] \quad (2.7) \end{aligned}$$

$$[Al^{3+}]^{1.4}[PO_4^{3-}][OH^-]^{1.2} = 10^{-32.2} \quad (2.8)$$

7. Check whether the solubility of aluminum hydroxide is exceeded.

8. In the case of double precipitates, the final pH of the solution is calculated from mass balances of aluminum and phosphate and solubility products of aluminum phosphate and hydroxide, by using a successive search method.

$$\begin{aligned} Al_T &= Al(OH)_{3(s)} + 1.4Al_{1.4}PO_4(OH)_{1.2(s)} + \\ &\quad [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_4^-] \quad (2.9) \\ P_T &= Al_{1.4}PO_4(OH)_{1.2(s)} + [H_2PO_4^-] + [HPO_4^{2-}] \quad (2.10) \end{aligned}$$

$$[Al^{3+}]^{1.4}[PO_4^{3-}][OH^-]^{1.2} = 10^{-32.2} \tag{2.11}$$

$$[Al^{3+}][OH^-]^3 = 10^{-30.4} \tag{2.12}$$

9. The final distributions of species are calculated, based on the final pH.

Ferguson and King [7] refined the Ferguson model. They described the precipitation of phosphate for three possible conditions. In the first (zone I), insufficient aluminum is added to precipitate all the phosphates. If the pH is in the proper range, stoichiometric removal of phosphate would result. Zone II is reached as the aluminum dose nears the stoichiometric requirement. In zone II, the removal is less than predicted from stoichiometry. The extent of removal is determined from the equilibria between aluminum phosphate and the solution. Finally, in zone III, the aluminum dose exceeds the stoichiometric requirement by 0.1 to 0.2 mM (about 25 %). Excess aluminum is used in co-precipitation of aluminum phosphate and hydroxide. The extent of removal is determined from the equilibria between these two precipitates and the solution.

Ferguson and King set the boundary between the zones I and II, where the phosphate residual is 25 % greater than the stoichiometric residual. It is unclear why they took the value of 25 % to divide the boundary. The use of the excess dose of aluminum (0.1 to 0.2 mM) over the stoichiometric requirement for the condition of zone III was also not explained. This approach is basically the same as that used for the development of the initial Ferguson model. Zone II is equivalent to the case of a single precipitate, aluminum phosphate. Zone III is equivalent to the case of double precipitates.

Ferguson and King also incorporated an aluminum phosphate complex, $AlH_2PO_4^{2+}$ in their model. The earlier version of this model predicted steadily decreasing phosphate residuals as the pH dropped below 6. However, the pH-solubility relationship indicates an increasing phosphate residual after a certain metal dosage. Ferguson postulated that this deficiency could be corrected or explained by either formation of polymeric hydroxoaluminum species or by soluble aluminum phosphate complexes. Ferguson and King found evidence for the presence of both kinds of complexes in the literature. However, they did not include the aluminum polymers.

It is generally recognized that two aluminum phosphate complexes are present: $AlH_2PO_4^{2+}$ and $AlHPO_4^{+}$. Stumm and Leckie [23] reported equilibrium stability constants of 10^3 and 10^8 for $AlH_2PO_4^{2+}$ and $AlHPO_4^{+}$, respectively. However, Ferguson and King used only one complex, $AlH_2PO_4^{2+}$ with the arbitrarily chosen equilibrium stability constant of 10^6. This was done to keep model results in good agreement with experimental results.

2.1.2 Luedecke et al. model

The model of Luedecke et al. uses ferric salts (ferric chloride) as the phosphate precipitant. Like Ferguson, Luedecke et al. [17] assumed that only two precipitates were possible in chemical phosphate removal as follows:

$$rFe^{3+} + PO_4^{3-} + (3r-3)OH^- = Fe_rPO_4(OH)_{3r-3(s)} \tag{2.13}$$

$$Fe^{3+} + 2H_2O = am - FeOOH_{(s)} + 3H^+ \tag{2.14}$$

The precipitate of ferric hydroxyphosphate is expressed in a general form. These ferric and phosphate ions form an integrated aquatic solution and they undergo acid/base equilibria, hydrolysis, and complexation. Table 2.2 shows these reactions with the pK values of their stability constants. These constants were defined at 25^o C with zero ionic strength.

Table 2.2: Equilibrium stability constants used in the Luedecke et al. model at 25^o C and zero ionic strength (Luedecke et al., 1989)

Reactions	pK values
$H_3PO_4 = H^+ + H_2PO_4^-$	2.1
$H_2PO_4^- = H^+ + HPO_4^{2-}$	7.2
$HPO_4^{2-} = H^+ + PO_4^{3-}$	12.2
$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$	2.2
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	5.7
$Fe^{3+} + 3H_2O = Fe(OH)_3^0 + 3H^+$	12.0
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	21.6
$Fe^{3+} + HPO_4^{2-} = FeHPO_4^+$	-9.0
$Fe^{3+} + H_2PO_4^- = FeH_2PO_4^{2+}$	pK_{FP}
$Fe^{3+} + 2H_2O = am - FeOOH_{(s)} + 3H^+$	-0.5
$rFe^{3+} + PO_4^{3-} + (3r\text{-}3)OH^- = Fe_rPO_4(OH)_{3r-3(s)}$	pK_S

The stability constants of $FeH_2PO_4^{2+}$ and $Fe_rPO_4(OH)_{3r-3(s)}$ were not given in Table 2.2. Thermodynamic data of ferric phosphate, $Fe_rPO_4(OH)_{3r-3(s)}$, are available in literature only at r = 1. Even these data often led to a result indicating higher phosphate residuals than expected [17]. The literature also reported a wide range of values of the stability constant for $FeH_2PO_4^{2+}$. Therefore, they decided these constants should be left blank for estimation from experiments.

With two possible precipitates, four precipitation regions could exist in chemical phosphate removal.

- no precipitation

- $Fe_rPO_4(OH)_{3r-3(s)}$ precipitation
- $am-FeOOH_{(s)}$ precipitation
- co-precipitation of $Fe_rPO_4(OH)_{3r-3(s)}$ and $am-FeOOH_{(s)}$

Conditions for each region can be determined from mass balances of Fe(III) and phosphate. The mass balances for Fe(III) and phosphate in a general form are as follows:

$$\begin{aligned} C_{P,in} &= C_{P,eq} + C_{P,pre} && (2.15) \\ C_{Fe,dose} &= C_{Fe,eq} + rC_{P,pre} + C_{Fe,pre} && (2.16) \end{aligned}$$

$C_{P,in}$: initial phosphate molar concentration
$C_{Fe,dose}$: molar dose of Fe(III) salt
$C_{P,eq}$: equilibrium phosphate molar concentration
$C_{Fe,eq}$: equilibrium Fe(III) molar concentration
$C_{P,pre}$: molar concentration of $Fe_rPO_4(OH)_{3r-3(s)}$
$C_{Fe,pre}$: molar concentration of $am-FeOOH_{(s)}$

First, the regions of co-precipitation and $am-FeOOH_{(s)}$ precipitation are determined. To do this, it is assumed that co-precipitation occurs. This allows transformation of concentrations of Fe^{3+} and PO_4^{3-} in terms of the H^+ concentration. Substitution of these expressions into a set of equilibrium equations in Table 2.2 allows calculation of equilibrium molar concentrations of soluble species of Fe(III) and phosphate as follows:

$$C_P^{**} = [H_3PO_4]^{**} + [H_2PO_4^-]^{**} + [HPO_4^{2-}]^{**} +$$

$$
\begin{aligned}
& [PO_4^{3-}]^{**} + [FeH_2PO_4^{2+}]^{**} + [FeHPO_4^{+}]^{**} && (2.17) \\
C_{Fe}^{**} = \; & [Fe^{3+}]^{**} + [FeOH^{2+}]^{**} + [Fe(OH)_2^{+}]^{**} + \\
& [Fe(OH)_3^{0}]^{**} + [Fe(OH)_4^{-}]^{**} + [FeH_2PO_4^{2+}]^{**} + \\
& [FeHPO_4^{+}]^{**} && (2.18)
\end{aligned}
$$

$**$: conditions of co-precipitation

Thus far, all calculations are made in terms of the H^+ concentration. Once the value of the solution pH is given, the calculation is finished. The C_P^{**} and C_{Fe}^{**} represent maximum molar concentrations of Fe(III) and phosphate that can co-exist with $Fe_rPO_4(OH)_{3r-3(s)}$ and $am - FeOOH_{(s)}$ precipitates. The amount of each precipitate can be calculated from the mass balance equations (equations 2.15 and 2.16).

$$
\begin{aligned}
C_{P,pre} &= C_{P,in} - C_P^{**} && (2.19) \\
C_{Fe,pre} &= C_{Fe,dose} - C_{Fe}^{**} - r(C_{P,in} - C_P^{**}) && (2.20)
\end{aligned}
$$

From these equations, it becomes clear that the conditions of co-precipitation are:

$$
\begin{aligned}
C_{Fe,dose} - C_{Fe}^{**} &> r(C_{P,in} - C_P^{**}) && (2.21) \\
C_{P,in} &> C_P^{**} && (2.22)
\end{aligned}
$$

If $C_{P,in} < C_P^{**}$, then $Fe_rPO_4(OH)_{3r-3(s)}$ will not precipitate. This, with the condition of $C_{Fe,dose} > C_{Fe}^{**}$, constitutes the condition for am-FeOOH precipitation. Conditions for the regions of $Fe_rPO_4(OH)_{3r-3}$ precipitation and no precipitation are determined by renewing the mass balances as follows:

$$C_{P,in} = C_{P,eq} + C_{P,pre} \tag{2.23}$$

$$C_{Fe,dose} = C_{Fe,eq} + rC_{P,pre} \tag{2.24}$$

This case is more complex than the case of co-precipitation. Concentrations of Fe^{3+} and PO_4^{3-} are related through the solubility product of $Fe_rPO_4(OH)_{3r-3(s)}$ alone, and subsequently, they can not be expressed in terms of the H^+ concentration. After the mass balances (equations of 2.23 and 2.24) are expressed in terms of the Fe^{3+} and the PO_4^{3-} concentrations, the term of the Fe^{3+} concentration can be eliminated from the solubility product of $Fe_rPO_4(OH)_{3r-3(s)}$. Then, the equilibrium concentrations of phosphate (C_P^*) and Fe(III) (C_{Fe}^*) become functions of the H^+ and the PO_4^{3-} concentrations. Here, the single asterisk superscript denotes conditions of $Fe_rPO_4(OH)_{3r-3(s)}$ precipitation. At constant pH, C_{Fe}^* and C_P^* can be calculated for a range of values of the PO_4^{3-} concentrations. No precipitate will form if $C_{Fe,dose} < C_{Fe}^*$. If the reverse is true, the condition for $Fe_rPO_4(OH)_{3r-3(s)}$ precipitation is satisfied.

Luedecke et al. performed calculations for a solution pH of 6.8 and assumed values of r= 2.5, pK_S = 96.7, and pK_{FP} = - 21.5. These values were estimated from their experiments. Figure 2.2 shows the model simulation result. This figure indicates that the model predicted that the Fe/P molar ratio increased as $C_{P,eq}$ increased, whereas experimental values followed an opposite trend.

Luedecke et al. postulated that the discrepancy was caused by adsorption of phosphates on the formed precipitates. To explain the adsorption, they proposed that the phosphate equilibrium concentration, $C_{P,eq}$, consists of two fractions: an

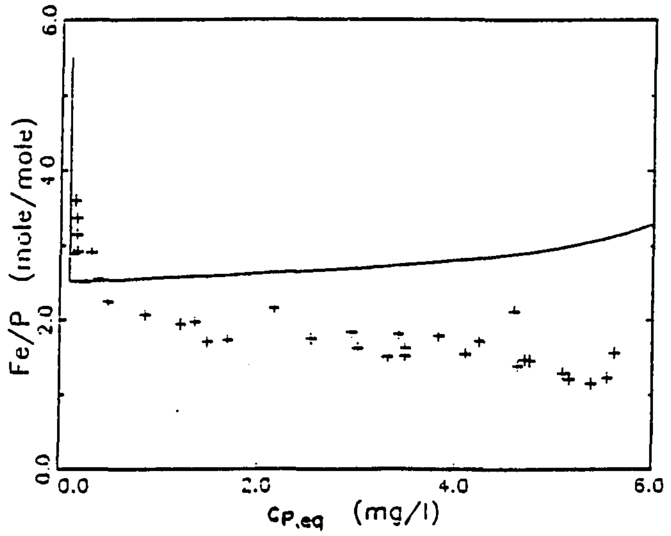


Figure 2.2: Calculated and experimentally observed Fe/P ratios for the Luedecke et al. model (Luedecke et al., 1989)

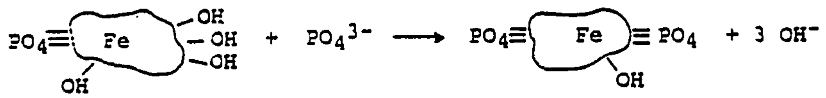


Figure 2.3: Adsorption mechanism of phosphate ions for the Luedecke et al. model (Luedecke et al., 1989)

adsorbed fraction, $C_{P,ads}$ and a fraction remaining in solution, $C_{P,res}$. They postulated that phosphates can adsorb on both precipitates, if both are present in solution, in competition with hydroxide ions, as shown in Figure 2.3.

The concentration of adsorbed phosphate, $C_{P,ads}$, is proportional to the amount of adsorbing precipitates, Xa, and remains in equilibrium with $C_{P,res}$ and hydroxide ion concentration as follows:

$$C_{P,ads} = \frac{Ka Xa C_{P,res}}{[OH^-]^3} \tag{2.25}$$

Ka : adsorption coefficient

The Xa is adjusted based on the number of available OH^- groups as follows:

$$Xa = (3r - 3)C_{P,pre} + C_{Fe,pre} \tag{2.26}$$

Figure 2.4 shows the results of the model calculation (after adsorption correction) made for pH 6.8 and $C_{P,in}$ = 8 mg/l, Ka in the range of 0 to 2 X 10^{-12} mol^2 / l^2

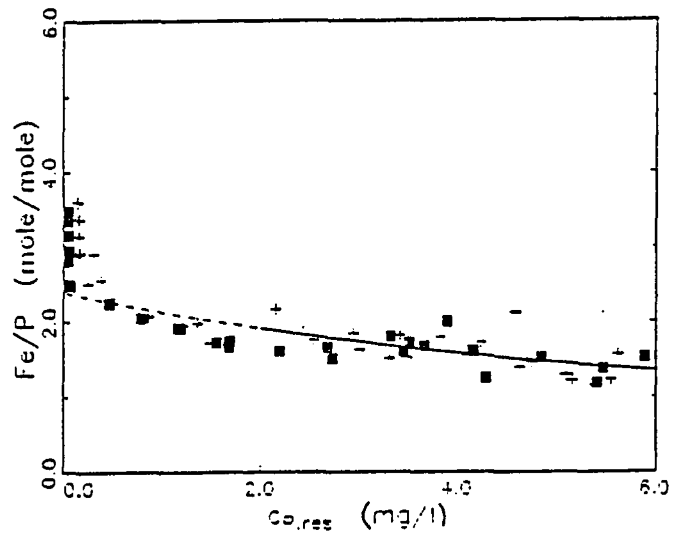


Figure 2.4: Calculated Fe/P ratios with adsorption considered for the Luedecke et al. model (Luedecke et al., 1989)

and assumed values of r = 2.5, pK_S = 96.7, and pK_{FP} = - 21.5. The Fe/P ratios were lower than those in the absence of adsorption.

All of these calculations become possible only after proper values of r, pK_S, pK_{FP}, K_a are assigned at constant pH. Luedecke et al. estimated these values from laboratory experiments. They conducted batch and continuous flow experiments using settled domestic sewage from the city of Richmond, CA. Equation 2.25 indicates that the adsorbed phosphate concentration, $C_{P,ads}$, reaches 0 as the equilibrium residual phosphate concentration, $C_{P,res}$, approaches 0. Therefore, they took the stoichiometric coefficient, r (2.5), at the zero value of $C_{P,res}$. Other parameters such as pK_S, pK_{FP}, and Ka were estimated, using the Gauss-Newton method of minimization of residual sum of squares, i.e., least squares estimate.

2.2 Linear Regression

Smoothing of data is very frequently used in data analysis. Smoothing allows us to approximate the data by a simple function so that we can study any trend involved in the data. Smoothing, data-fitting, can be expressed in words as follows:

$$observation = model + residuals \tag{2.27}$$

Suppose that we have the following data set.

$$(x_i, y_i)\; i = 1, 2, \cdots, n$$

Often, we are interested in relating the dependent variable, here y, to the independent variables, here x. This is called "regression analysis". An objective of regression anaysis is to build a regression model so that we can predict values of the dependent variable based on information of the independent variables.

The regression model has the following general form:

$$y_i = \beta_0\phi_0(x_i) + \beta_1\phi_1(x_i) + \cdots + \beta_p\phi_p(x_i) + \epsilon_i \tag{2.28}$$

$$y_i = b_0\phi_0(x_i) + b_1\phi_1(x_i) + \cdots + b_p\phi_p(x_i) \tag{2.29}$$

Equation 2.28 shows a population regression model. We do not know this population model and therefore we try to estimate this population model as closely as possible with an estimated model. An estimated model is shown in equation 2.29. The function $\phi(x)$ are the model functions. The coefficients of b_i are called "parameters" of a model. These are the estimates of β_i in the population model. The ϵ_i in the population model represents residuals. Comparing equation 2.28 to equation 2.27, it becomes obvious that a model correponds to a portion except residuals in equation 2.28. In regression analysis, we often try to find a proper model with minimum residuals.

Whether a model is linear or nonlinear depends on how the parameters are combined in the model. If the model parameters are combined linearly, a model is called a "linear regression model". In other words, if a model consists of a linear function of parameters, it becomes a linear model. On the other hand, a model becomes a nonlinear model when the parameters are combined nonlinearly. A model would still be linear even though the model functions are nonlinear, like quadratic, or cubic, etc. A model of a linear combination of polynomial functions (like quadratic, or cubic) is still linear. In this study, no nonlinear models were used. All models used are linear models.

A linear model is more concisely expressed using vector/matrix notation, as shown in equation 2.30.

$$Y = Xb \tag{2.30}$$

$$\begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix} = \begin{bmatrix} 1 & x_{11} & \cdots & x_{p1} \\ 1 & x_{12} & \cdots & x_{p2} \\ \vdots & \vdots & \ddots & \vdots \\ 1 & x_{1n} & \cdots & x_{pn} \end{bmatrix} \begin{bmatrix} b_0 \\ b_1 \\ \vdots \\ b_p \end{bmatrix}$$

This equation shows that Y is the observation vector with a size of n by 1, the X is the model matrix with a size of n by (p+1), and b is the parameter vector with a size of (p+1) by 1. Perhaps the understanding this vector/matrix notation can be better achieved by using an example. Suppose that we have the following quadratic linear regression model and four data values of the independent variable, x :

$$y = b_0 + b_1 x + b_2 x^2 \tag{2.31}$$

Then, Y, X, and b can have the following components:

$$\begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix} = \begin{bmatrix} 1 & x_1 & x_1^2 \\ 1 & x_2 & x_2^2 \\ 1 & x_3 & x_3^2 \\ 1 & x_4 & x_4^2 \end{bmatrix} \begin{bmatrix} b_0 \\ b_1 \\ b_2 \end{bmatrix} \tag{2.32}$$

Regression analysis consists of two stages: determining a model and computing the parameters. The parameters will be estimated by minimizing the residuals as small as possible. A numerical technique used for this purpose is "least squares estimate". If we use the same quadratic linear regression model (equation 2.31), a principle of this numerical technique can be described as follows:

$$minimize \sum_{i=1}^{n} (y_i - b_0 - b_1 x_i - b_2 x_i^2)^2 \tag{2.33}$$

Minimizing residuals allows us to maximize the portion which can be accounted for by a model. The parameter vector, b, which is calculated by the least squares estimate, will be in a vector notation as follows:

$$b = (X'X)^{-1}(X'Y) \tag{2.34}$$

Here, the X' indicates the transpose of the matrix X and the $(X'X)^{-1}$ indicates the inverse of the matrix of $X'X$. A job of computing parameters is usually done by SAS[3].

---

[3] statistical software

Determining a proper model is time-consuming. It needs a background of experience and sometimes a bit of luck. However, once experience is acquired, determining a model can be performed very efficiently. There are certainly some guidelines to follow in model building. These guidelines are explained, based on a review of *Linear Statistical Models* [2].

2.2.1 Statistical tests performed for a regression model

The most important and frequently used tests for a regression model are an overall F-test and the t-test for an individual independent variable. An overall F-test is used to test whether the dependent variable is significantly related to the independent variables. Suppose that we have the following population regression model:

$$y = \beta_0 + \beta_1 x_1 + \cdots + \beta_p x_p + \epsilon \tag{2.35}$$

An overall F-test tests the null hypothesis:

$$H_0 : \beta_1 = \beta_2 = \cdots = \beta_p = 0$$

versus the alternative hypothesis:

$$H_1 : \mathit{At\ least\ one\ of}\ \beta_1, \beta_2, \cdots, \beta_p\ \mathit{is\ not\ equal\ to\ zero.}$$

If we can reject the H_0 in favor of the H_1 with a small probability of Type I error (i.e, ≤ 0.05), then it is reasonable to say that at least one of the independent variables affects the dependent variable.

Once an overall F-test indicates that there are significant relationships between the dependent variable and the independent variables, then a t-test is performed to test significance of each independent variable in a model. In the t-test, the null hypothesis ($H_0 : \beta_j = 0$) is tested against the alternative hypothesis ($H_1 : \beta_j \neq 0$). If we can reject the H_0 in favor of the H_1 with a probability of Type I error of $\leq$ 0.05, then it is reasonable to say that the independent variable x_j is significantly related to the dependent variable, y.

2.2.2 Assumptions

Statistical tests such as an overall F-test and t-test, which are discussed in the previous section, are performed to help determine a proper model. In other words, inferences made from these statistical tests are used to determine a proper regression model. Those inferences are valid only after the following assumptions are satisfied:

1. **Constant Variance.** The different populations of potential values of the dependent variable corresponding to different values of the independent variable have *equal variances.*

2. **Independence.** Any one value of the dependent variable is *statistically independent* of any other value of the dependent variable.

3. **Normality.** For any value of the independent variable, the corresponding population of potential values of the dependent variable has a *normal distribution.*

Then, a question arises: how can we check these assumptions? and if these assumptions are violated, what action should we take to correct the violation?. The validity of these assumptions can be determined by examining *residual plots.* Residual plots are usually constructed against

- Values of the independent variables.

- Values of the predicted values (by the model) of the dependent variable.
- The time order in which the historical data have been observed.

In most cases, assumptions are correct provided that residual plots show no definite pattern.

Besides giving information about the assumptions, residual plots tell us whether the functional form of a model is incorrect or correct. If residual plots show a certain pattern, like a straight line, or curvature, when they are plotted against the independent variable, this indicates that the model developed is inadequate. Incorporating a linear or quadratic relationship of the independent variable will make a model better. If little or no pattern exists in the appropriate residual plots, the relationship between the dependent variable and the independent variables is probably properly accounted for.

When the first assumption is violated, residual plots usually show "fan out" or "funnel in" patterns. A residual plot that fans out indicates that residuals increase with increasing values of the criterion used in the residual plot. This would suggest that the constant variance assumption is violated. Similarly, a residual plot that funnels in indicates that the residuals decrease with increasing values of the criterion. This also suggest that the constant assumption is violated. Figure 2.5 shows cases in which the constant variable assumption is violated as well as a case in which this assumption holds.

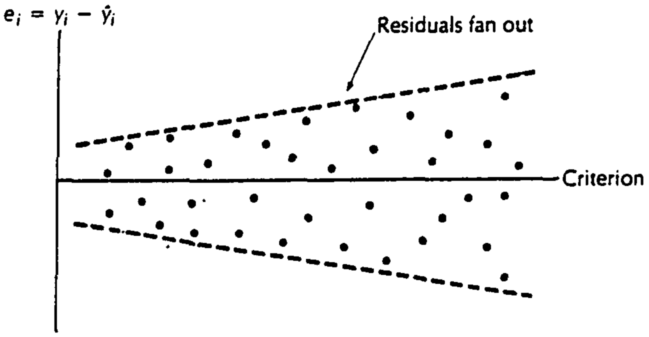
The second assumption of independence is most likely to be violated when the data being analyzed are *time series data.* This means that the data have been collected in a time sequence. In this case, the time-ordered data can be autocorrelated. There are two kinds of autocorrelations: positive and negative. When positive autocorrelation exists, a residual plot shows cyclical pattern. On the other hand, an alternate pattern shows in a residual plot when negative autocorrelation is present. Autocorrelation can be also tested be a statistical test, called the "Durbin-Watson test". Figure 2.6 shows positive and negative autocorrelation.

The third assumption of normality can be checked by examining a normal plot. If the normality assumption holds and if a model has the correct function form, this plot should have a straight-line appearance. Substantial departure from a straight-line appearance indicates a violation of the normality assumption.

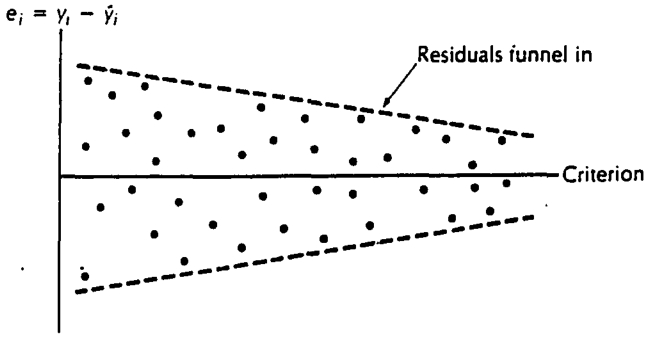
Before we discuss remedial actions needed to correct violation of the assumptions, it is important to note the comment made by the authors of Linear Statistical Models. Followings are quotes from them [2]:

> *It is important to reiterate that although the formulas for the confidence intervals, prediction intervals, and hypothesis test in this book are strictly valid only when the inference assumptions hold, these formulas are still approximately correct even when mild departures from the inference assumptions can be detected. In fact, these assumptions very seldom, if ever, exactly hold in any practical regression problem. Therefore, in practice, only pronounced departures from the inference assumptions are considered to be serious enough to need remedial actions.*

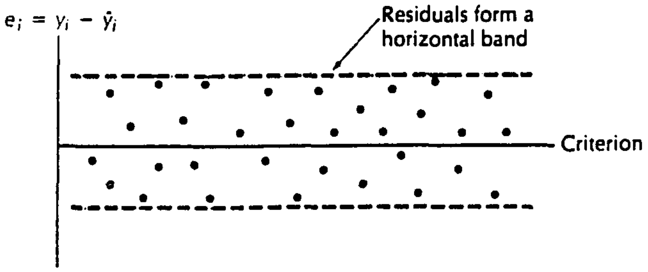
When an increasing or decreasing error variance exists, we must equalize the variances of the population of potential error terms. Most frequently, the error variance is a function of one of the independent variables. This leads to a fan-out or funnel-in pattern in a residual plot against the independent variable. In this case, the problem can be corrected by using a transformed model. A transformed model can usually



(a) Nonconstant error variance: Error variance increases with increasing values of the criterion

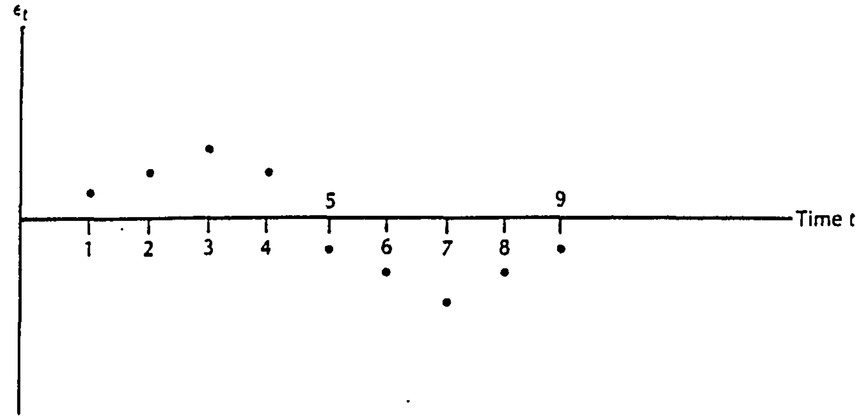


(b) Nonconstant error variance: Error variance decreases with increasing values of the criterion

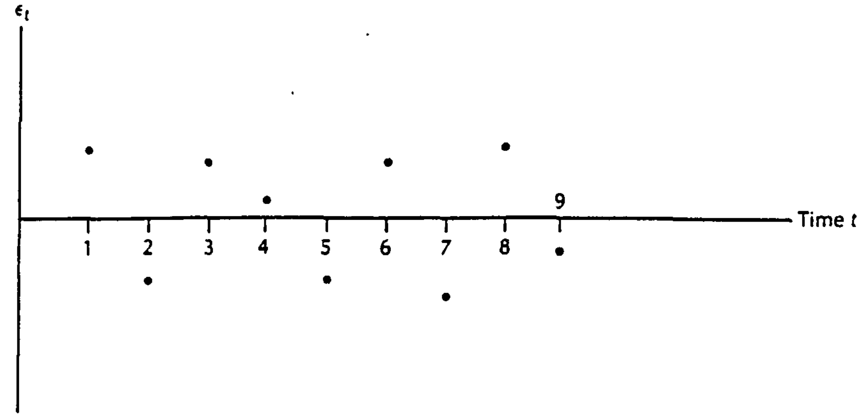


(c) Constant error variance with increasing values of the criterion

Figure 2.5: Residual plots and the constant variance assumption (Bowerman and O'Connell, 1990)



(a) Positive autocorrelation in the error terms: Cyclical pattern



(b) Negative autocorrelation in the error terms: Alternating pattern

Figure 2.6: Residual plots and the independence assumption (Bowerman and O'Connell, 1990)

be obtained by dividing a model with a square root or just the independent variable itself.

Similary, transformation can be performed to correct violation of other inference assumptions. However, often, transformation itself is not enough to remedy the violations.

2.2.3 Interaction

A linear regression model often contains an interaction term. An interaction term measures the extent to which the relationship between the dependent variable and the independent variable depends on the other independent variable. Suppose that we have the following linear regression model:

$$y = b_0 + b_1 x_1 + b_2 x_2.$$

Existence of interaction can be illustrated best by examining a graph. The dependent variable, y, is plotted against the independent variable, x_1 on different values of the another independent variable of x_2, as shown in Figure 2.7. We examine the graph to see whether the slope relating y to x_1 is different for different values of x_2. If these two lines cross, this indicates a sure sign of interaction. If these two lines run parallel, it implies that no interaction exists in a model. An interaction term is mesured by the cross-product term in a regression model. In our example, interaction can be represented by a cross-product term of $x_1 x_2$.

2.2.4 Criteria used for model building

In order to select an appropriate model, we have to consider all reasonable models and compare them on the basis of some criteria. These criteria include multiple

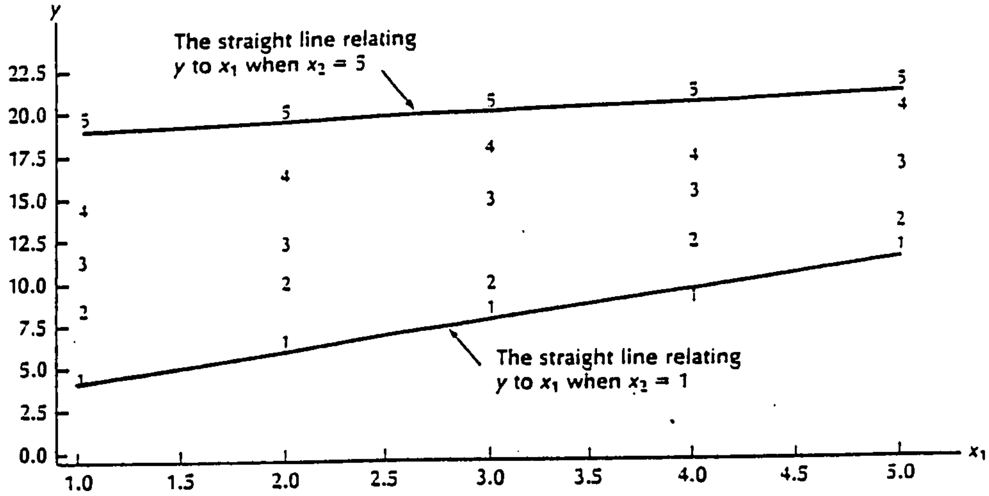


Figure 2.7: Illustrated example of interaction (Bowerman and O'Connell, 1990)

coefficient of determination (R^2), standard error (s), and C(p) statistic. R^2 is the most popularly used criterion.

$$R^2 = \frac{explained\,variation}{total\,variation} \tag{2.36}$$

The above equation indicates that the larger R^2 is, the larger the proportion of the total variation that is explained by a regression model. One trick hidden in this criterion is that this value increases as the number of independent variables increases. Adding any independent variable to a regression model will increase the value of R^2 regardless of the importance of the independent variable added. Therefore, care should be taken using this criterion, especially when models compared have different numbers of independent variables.

The second criterion is the standard error of s. The smaller the s is, the better a model is.

The third criterion is the C(p) statistic. The smaller the C(p) is, the better a model is. Followings are quotes from *Linear Statistical Models* [2]:

> *While we want C to be small, in addition it can be shown from the theory behind the C statistic that we also wish to find a model for which the C statistic roughly equals k (k equals the number of parameters in the model). If a model has a C statistic substantially greater than k, it can be shown that this model has substantial bias and is undesirable. Thus although we want to find a model for which C is as small as possible, if C for such a model is substantially greater than k, we may prefer to choose a different model for which C is slightly larger and more nearly equal to the number of parameters in that (different) model. If a particular model has a small*

> *value of C and C for this model is less than k, then the model should be considered desirable.*

The k in the quotes is equal to (p+1).

3. EXPERIMENTS

Experiments, conducted in this study, were conducted in two stages. In the first stage, no calcium interaction was considered and two different aluminum salts, aluminum chloride and alum, were used as coagulants to remove phosphates. A difference between the effects of these two coagulants on chemical phosphate removal was investigated in the first stage. In the second stage, calcium interaction was considered and only one aluminum salt (alum) was used as a coagulant. Alum was chosen because aluminum chloride is rarely used as a precipitant in chemical phosphate removal. An effect of calcium on chemical phosphate removal was investigated at this stage.

Since removal of soluble phosphates from wastewaters was our main interest in this study, a synthetic wastewater was prepared without including any particulate phosphate. A system of $NaHCO_3$-NaH_2PO_4 was used as the synthetic wastewater in the first stage and that of $Ca(NO_3)_2$-$NaHCO_3$-NaH_2PO_4 was used in the second stage. These systems was selected to incorporate two important components of wastewater: bicarbonate alkalinity and calcium. Concentrations of calcium, alkalinity and phosphates used for the synthetic wastewater were selected so as to cover typical ranges of concentrations of these three components found in domestic wastewaters. Table 3.1 shows the three different levels of calcium, alkalinity, and phosphate

Table 3.1: Three levels of calcium, alkalinity, and phosphate used for the synthetic wastewaters

Components	Low	Medium	High
Calcium, mg/l as Ca	0	100	200
Inorganic Phosphates, mg/l as P	3.0	5.0	10
Alkalinity, mg/l as $CaCO_3$	50	100	200

used in the synthetic wastewater. Every combination of these components was used to prepare the synthetic wastewaters.

Batch experiments, consisting of jar tests using a Phipps and Bird machine, were conducted with each synthetic wastewater. Rapid mixing only was provided at a G value of 600 sec^{-1}. This G value was selected because the previous study [11] found that optimum chemical phosphate removal was obtained at this mixing intensity.

While rapid mixing was underway, aluminum salts were injected through a hypodermic syringe (with a needle) into the synthetic wastewater. Rapid mixing continued for 15 seconds after chemical injection. The mixing time of 15 seconds was selected because the previous study [12] found that there was not much difference in the time effects on chemical phosphate removal as long as the mixing time was in the range of 10–60 seconds. Then, rapid mixing was terminated and the supernatant was taken and filtered through a filter paper with a pore size of 0.45 μm. The filtrate was analyzed to determine its phosphate concentration using a Beckman model B spectrophotometer. Phosphate was measured in accordance with the Ascorbic Acid method in Standard Methods [8]. Another aliquot of supernatant was taken and used to determine its alkalinity and pH. The pH was measured using a Cole-Parmer model 05669-20 pH meter.

Two different aluminum salts, aluminum chloride and alum, were prepared freshly before each experiment to avoid any possible aging effect. They were prepared at a solution strength of 25 % by weight as $AlCl_3 \cdot 6H_2O$ or $Al_2(SO_4)_3 \cdot 18H_2O$, depending on the chemical used. This strength was chosen because the previous study [11] showed that better P-removal efficiency was obtained at higher solution strength. According to that study, better P-removal efficiency was obtained at a strength of 50 % than 25 %. A solution strength of 50 % was not chosen for use here because it was difficult to dissolve chemicals, especially alum, at this high strength. Aluminum chloride was added to the synthetic wastewater at a concentration range of 12.5–250 mg/l as $AlCl_3 \cdot 6H_2O$ and alum at the range of 12.5–350 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$.

In each jar test, a control experiment was conducted to check the accuracy of the analytical methods and experiments. In a control experiment, no chemical was added to the synthetic wastewater and its alkalinity and phosphate levels were measured. The measured concentrations were used to represent the actual alkalinity and phosphate concentrations in the synthetic wastewater.

4. EXPERIMENTAL RESULTS

Experiments were performed to develop regression models which can predict the residual alkalinity, pH, and phosphate concentrations after chemical phosphate removal. Since the experiments were designed to cover typical ranges of concentrations of three important components (calcium, alkalinity, and phosphate) in wastewaters, some general trends in chemical phosphate removal were observed during the experiments. The experimental results are presented in terms of residual concentrations of alkalinity, pH, and phosphate in this chapter.. This chapter is divided into three sections. Each section covers one parameter. Raw data characterizing the individual experiments are found in Appendices A and B, which show the residual alkalinity, pH, and phosphate concentrations at each aluminum chloride and at each alum dosage, respectively.

In order to show the experimental results graphically, Figures 4.1 through 4.12 were prepared. In these figures, the dependent variables (residual alkalinity concentration, pH, or phosphate concentration) were plotted against the associated dosages of aluminum salts (either aluminum chloride or alum) used for phosphate removal from the synthetic wastewater. The phosphate concentrations were expressed in mg/l as P, the alkalinity concentrations in mg/l as $CaCO_3$, and the pH values in pH units. Concentrations of aluminum salts were expressed in mg/l of aluminum chloride as

$AlCl_3 \cdot 6H_2O$ or of alum as $Al_2(SO_4)_3 \cdot 18H_2O$, depending on the chemical used.

The actual initial concentrations of alkalinity and phosphate, and the pH in the synthetic wastewater were determined by averaging values obtained from the control experiments. In the control experiments, the average values of low, medium, and high levels of the alkalinity expressed as $CaCO_3$ were 50, 101, and 198 mg/l, respectively and the corresponding initial values of the low, medium, and high levels of phosphate expressed as P were 3.10, 5.16, and 10.25 mg/l, respectively. The corresponding pH values are summarized in Table 4.1.

Table 4.1: Average pH values for the synthetic wastewaters

Calcium Levels, as Ca	Alkalinity Levels	Phosphate Level Low	 Medium	 High
0	Low	7.40	7.24	7.03
0	Medium	8.26	7.82	7.53
0	High	8.78	8.14	7.70
100	Low	7.49	7.27	7.04
100	Medium	7.90	7.68	7.49
100	High		7.92	7.73
200	Low	7.13	7.05	6.82
200	Medium	7.52	7.36	7.19
200	High	7.70	7.53	7.39

Table 4.1 shows that the pH of the synthetic wastewaters decreased as the initial phosphate level increased and as the initial alkalinity level decreased. As calcium was added to the wastewater, the extent of these effects were reduced. The pH values were always lower at a calcium concentration of 200 mg/l as Ca than at calcium concentrations of 0 and 100 mg/l.

4.1 Alkalinity

Alkalinity decreased linearly with increasing dosages of aluminum salts regardless of whether aluminum chloride or alum was used as the precipitant, as shown in Figures 4.1 and 4.2. Figures 4.1 and 4.2 show the residual alkalinity (RALK) as a function of aluminum chloride and alum dosages, respectively. The symbols of 5, 1, and 2 in Figure 4.1 represent the wastewater's initial alkalinity levels (5 for the low alkalinity, 1 for the medium alkalinity and 2 for the high alkalinity) and the symbols of 0, 1, and 2 in Figure 4.2 represent the initial calcium concentrations of 0, 100, and 200 mg/l as Ca. In these figures, data for all three phosphate levels were included. Examination of these figures shows that the decreasing pattern of the residual alkalinity was not affected by use of different aluminum salts nor the presence of calcium in the wastewater.

The linear lines in these figures indicate that alkalinity was destroyed stoichiometrically in chemical phosphate removal. The stoichiometric information can be obtained from the slope of these lines. By examining these figures and performing regression analysis, it was found that 1 mole of Al(III) destroyed 2.4 eq of alkalinity. Ferguson [6] presented the following stoichiometric equation to describe the relationship between alkalinity destruction and alum addition in chemical phosphate removal.

$$1.4Al^{3+} + H_2PO_4^- + 1.2H_2O \rightleftharpoons Al_{1.4}PO_4(OH)_{1.2} \downarrow +3.2H^+ \qquad (4.1)$$

According to this equation, 1 mole of Al(III) destroys 2.3 eq of alkalinity which is close to the value (2.4 eq) obtained in the experiments.

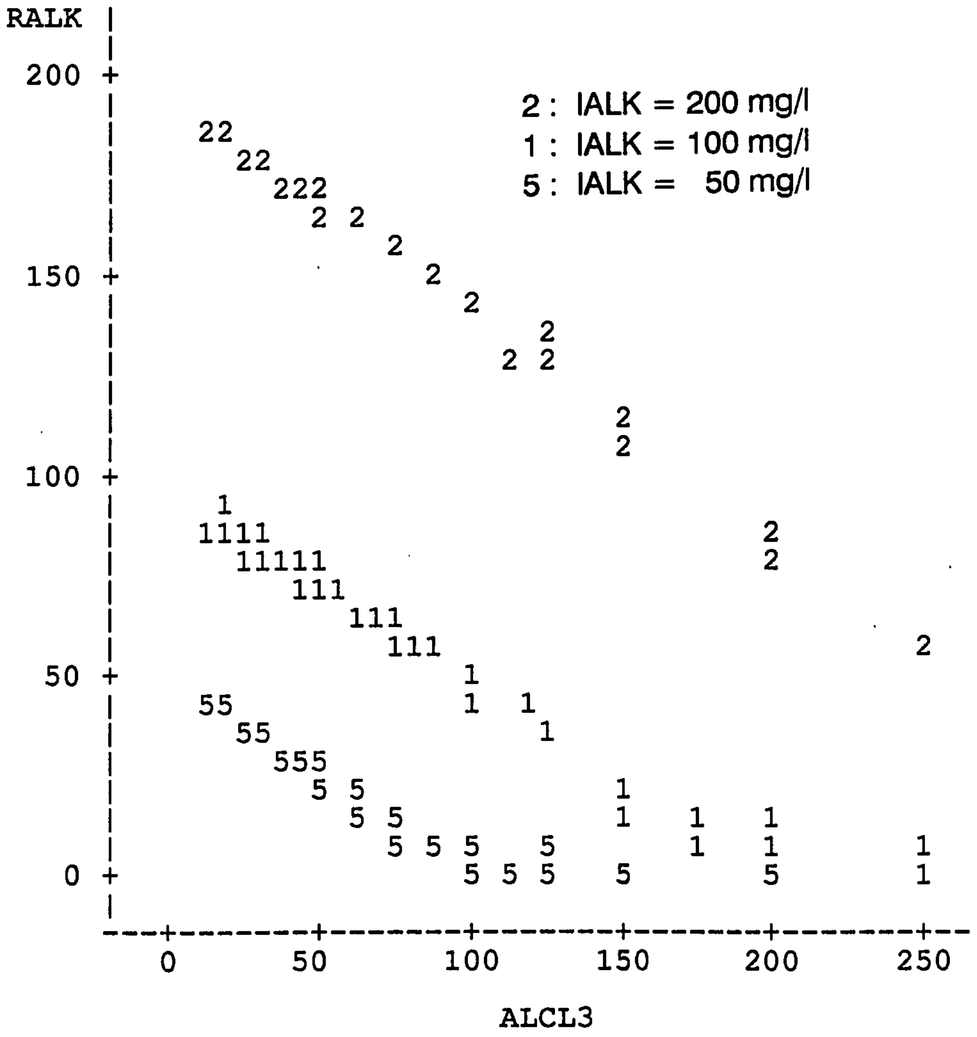


Figure 4.1: Residual alkalinity (mg/l as $CaCO_3$) as a function of aluminum chloride dosage (mg/l as $AlCl_3 \cdot 6H_2O$)

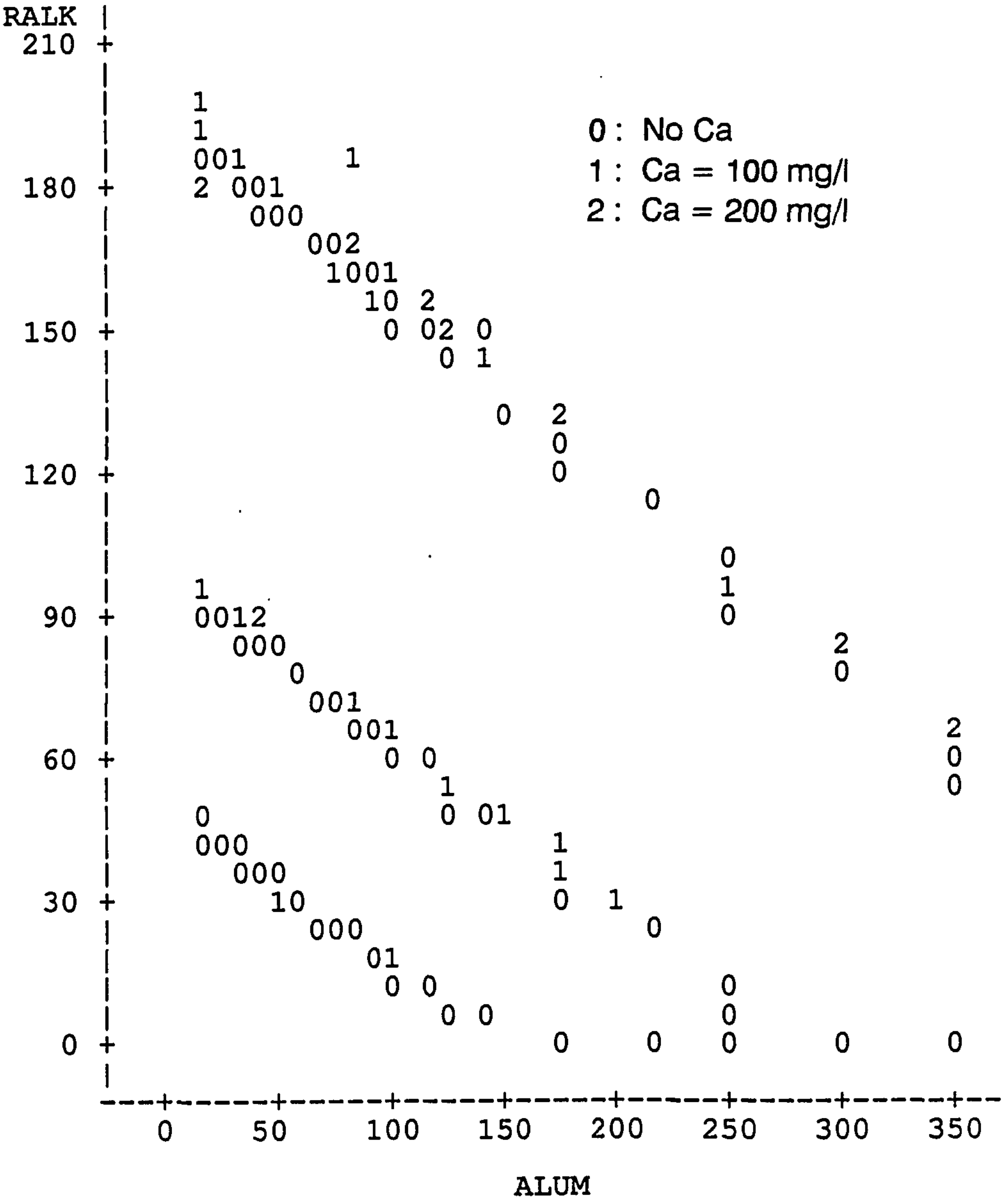


Figure 4.2: Residual alkalinity (mg/l as $CaCO_3$) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$)

4.2 pH

Figure 4.3 shows the residual pH (RPH) as a function of the aluminum chloride dosage. There are three curves in the figure. These curves are differentiated by their initial alkalinity levels. The top curve shows the pH variation as a function of aluminum chloride dosage at the high initial alkalinity level. The middle and bottom curves show the pH variations as a function of the aluminum chloride dosages at the medium and low initial alkalinity levels, respectively. Figures 4.4 through 4.6 show residual pH as a function of alum dosage. The variable between the figures is the initial alkalinity level: Figure 4.4 at the low level, Figure 4.5 at the medium level, and Figure 4.6 at the high level. In these figures, the symbols 0, 1, and 2 represent the wastewater calcium concentrations of 0, 100, and 200 mg/l as Ca, respectively.

The variation in the pH of the wastewater can be explained in terms of its buffer intensity. The following equation shows a buffer intensity:

$$\beta = -\frac{dC_A}{dpH} \tag{4.2}$$

where β represents a buffer intensity and C_A represents acid added. According to this equation, an inverse of the wastewater's buffer intensity indicates the negative slope of the pH with increasing aluminum dosage. Therefore, the curvature of the pH versus alum dosage relationship shown in the figures indicates that the buffer intensity was not constant and varied over the range of aluminum dosages used in this study from 0–250 mg/l using aluminum chloride and 0–350 mg/l using alum. The buffer intensity of the wastewater depends on the initial alkalinity level: the higher the wastewater alkalinity, the higher the buffer intensity. That explains why the pH decrease was less at the high alkalinity level than at other levels, and why the

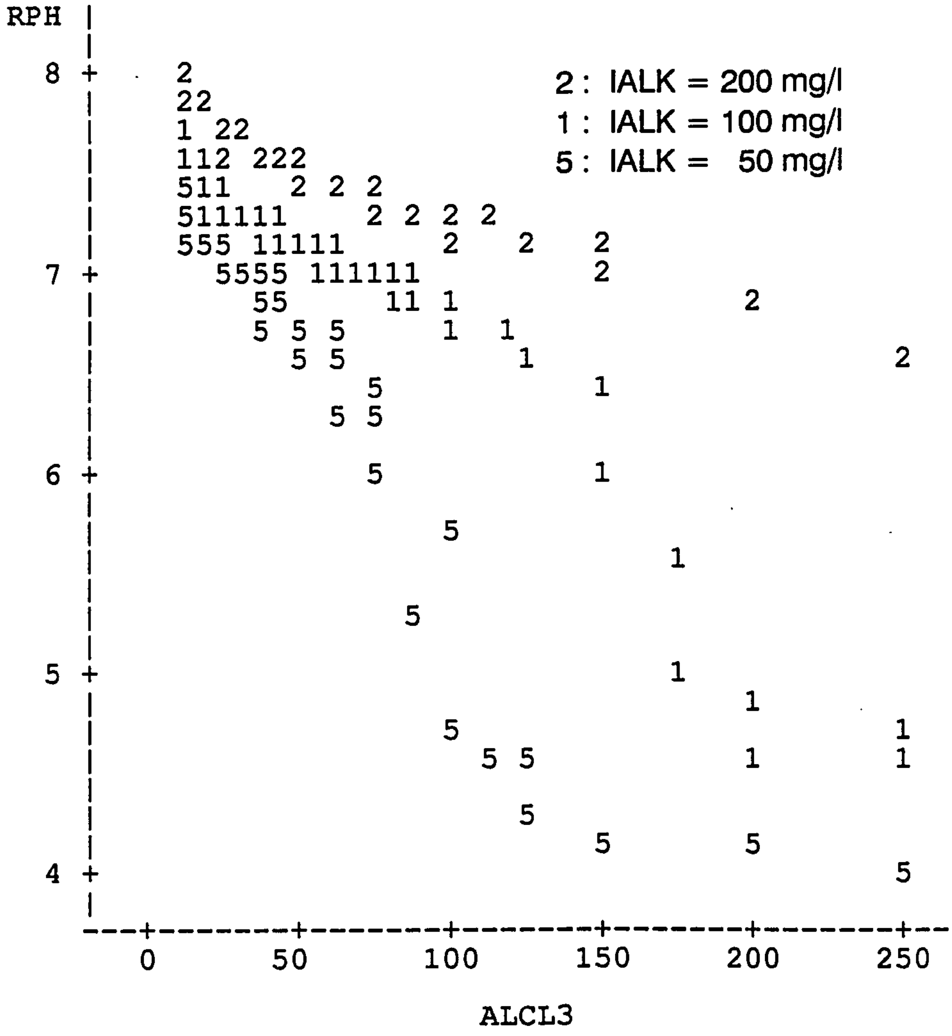


Figure 4.3: Residual pH as a function of aluminum chloride dosage (mg/l as $AlCl_3 \cdot 6H_2O$)

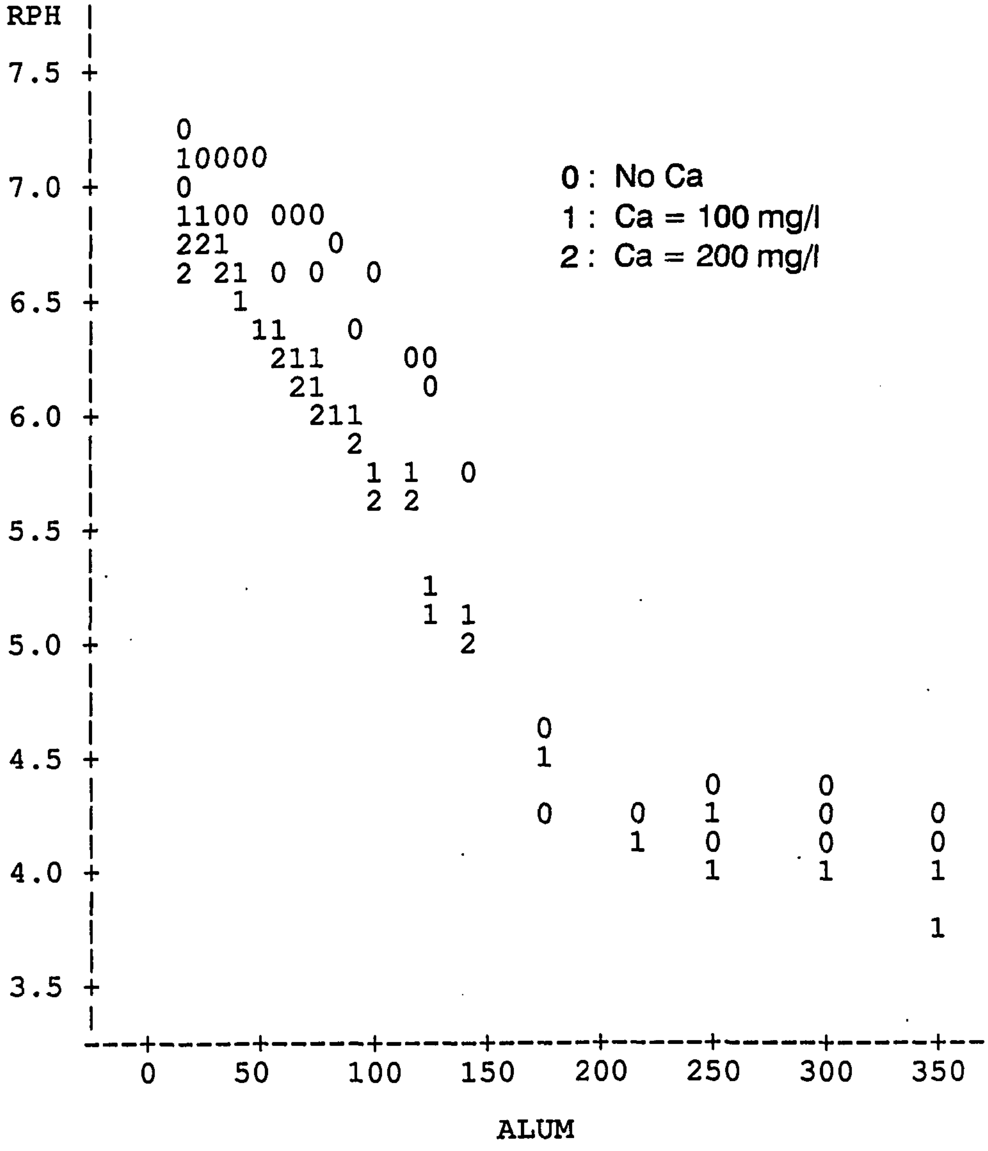


Figure 4.4: Residual pH as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) at the low initial alkalinity level

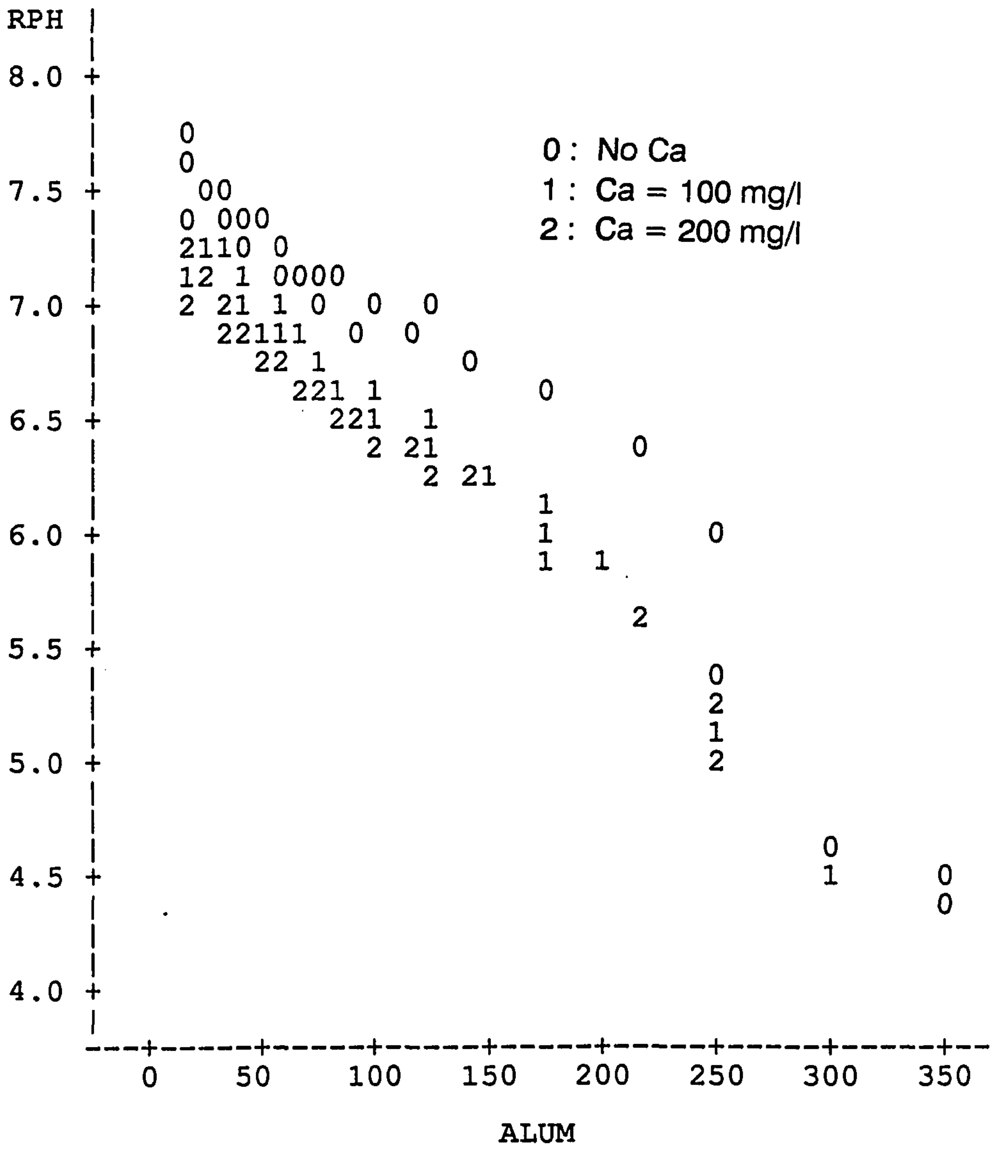


Figure 4.5: Residual pH as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) at the medium initial alkalinity level

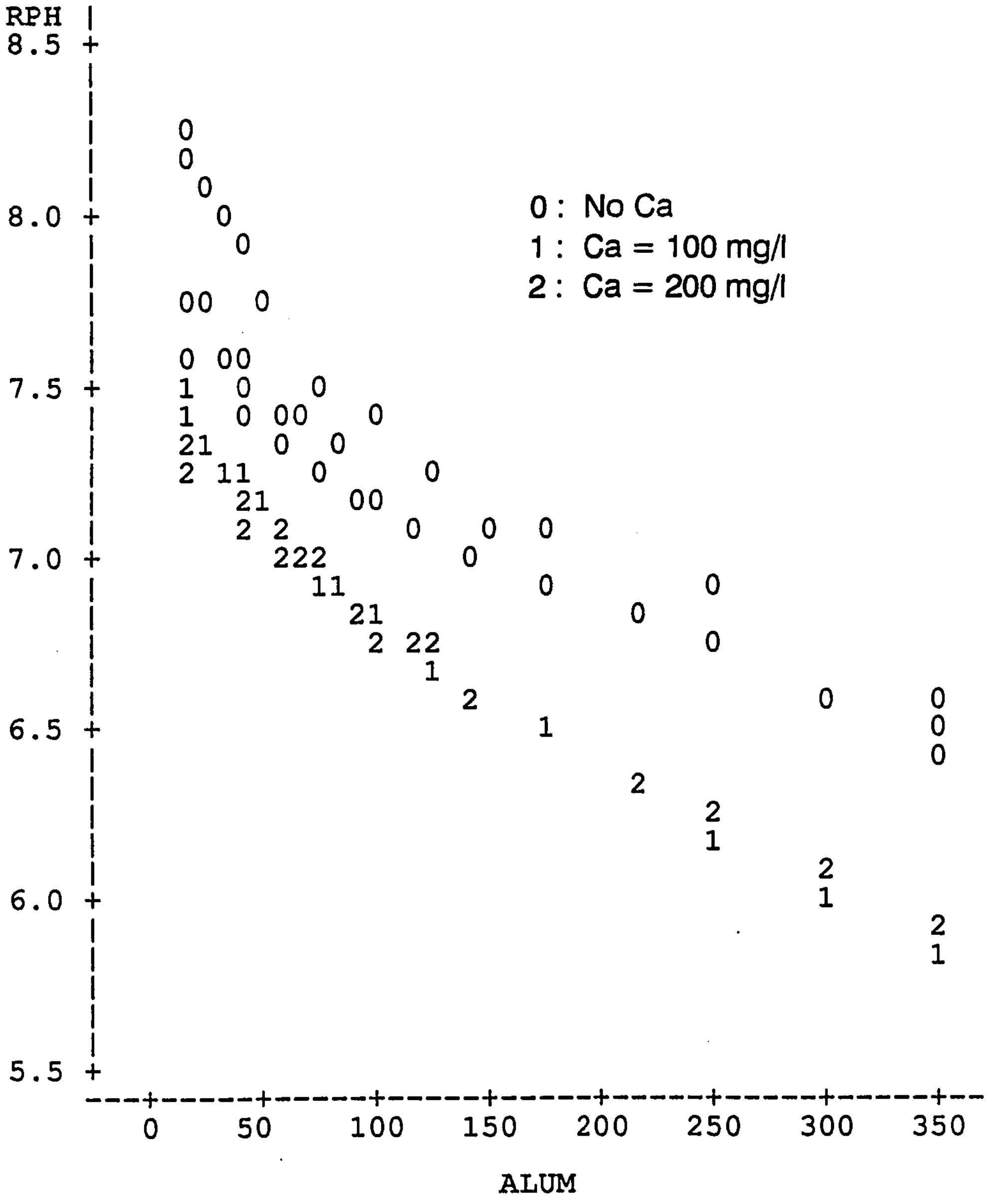


Figure 4.6: Residual pH as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) at the high initial alkalinity level

pH decrease at the medium alkalinity level was less than at the low alkalinity level.

Since bicarbonate is a major source of alkalinity in the wastewater, the maximum buffer intensity occurs at the pK value for the first dissociation constant of carbonic acid (6.3) and the minimum buffer intensity occurs at the equivalence point of carbonic acid (4.3–4.5). Figures 4.3–4.6 show that the pH varied less with addition of aluminum salts around a pH of 6.3. As the wastewater pH approached the equivalence point of carbonic acid, however, a more rapid pH drop occurred because of the lower buffer intensity. Once the wastewater pH reaches the equivalence point of carbonic acid, the wastewater loses its alkalinity. Figures 4.3–4.6 indicate that rapid pH drop existed when the initial alkalinity level was low or medium. A rapid pH drop occurred over aluminum chloride dosages of 75–150 mg/l and 150–250 mg/l for the low and the medium alkalinity levels, respectively. The corresponding alkalinity values were 16 to 0 mg/l and 24 to 0 mg/l, respectively. With use of alum, the pH drop occurred over alum dosages of 125–212.5 mg/l and 250–350 mg/l for the low and the medium initial alkalinity levels, respectively. The corresponding alkalinity values for these alum dosages were 6 to 0 mg/l and 10 to 0 mg/l, respectively. This indicates that the wastewater lost its alkalinity when 150 mg/l of aluminum chloride or 212.5 mg/l of alum was added to the wastewater with the low initial alkalinity level and when 250 mg/l of aluminum chloride or 350 mg/l of alum was added to the wastewater with the medium alkalinity level. These aluminum dosages are close in terms of their molar concentrations. When the wastewater's alkalinity level was high, the wastewater did not lose all of its alkalinity up to the highest aluminum dosages (250 mg/l for aluminum chloride and 350 mg/l for alum) used in this study because of its high buffer intensity. Overall, the decreasing pH pattern was similar, regardless of which aluminum salt was used when no calcium was present in the wastewater.

After the rapid pH drop, the pH varied little with aluminum addition. This indicates that a buffer intensity of the wastewater increases again due to the presence of protons and phosphate, $H_2PO_4^-$.

When calcium was present in the wastewater, the decreasing pattern in pH was not different from the pattern observed when no calcium was present in the wastewater. According to Table 4.1, the initial pH value of the wastewater with calcium present was always lower than that of the wastewater without any calcium. Because of this low initial pH value, the residual pH value observed when calcium was present in the wastewater was lower than the residual pH value observed when no calcium was present in the wastewater. Therefore, the pH variation curves were compressed when calcium was present in the wastewater, compared to the curves obtained when no calcium was present in the wastewater. This made the extent of rapid pH drop less serious with calcium as compared to the extent observed without calcium.

4.3 Phosphate

Figures 4.7–4.9 show the residual phosphate concentration (ROP) as a function of aluminum chloride dosage. These figures are differentiated by the phosphate levels in the initial synthetic wastewater: Figure 4.7 for the low phosphate level, Figure 4.8 for the medium phosphate level, and Figure 4.9 for the high phosphate level. In these figures, the numerical symbols represent the initial alkalinity levels. The symbols of 5, 1, and 2 in these figures represent the wastewater's initial alkalinity levels: 5 for the low alkalinity, 1 for the medium alkalinity, and 2 for the high alkalinity.

Figures 4.10 through 4.12 show the residual phosphate concentration as a function of alum dosage. The variable between these figures is the alkalinity value in the initial synthetic wastewater: Figure 4.10 for the low level, Figure 4.11 for the medium level, and Figure 4.12 for the high level. The symbols 0, 1, and 2 in these figures represent the initial calcium concentrations, 0, 100, 200 mg/l as Ca, respectively.

The results shown in the figures indicate that the residual phosphate concentration in the synthetic wastewater steadily decreased with increase in aluminum dosages until it reached its minimum level and then leveled off or increased with higher aluminum dosages. When the initial alkalinity level was high, the ROP leveled off. When the initial alkalinity level was medium or low, the ROP increased. The extent of the increase was more significant with use of aluminum chloride than with use of alum.

The phosphate concentration began to increase when the alkalinity of the wastewater was almost depleted. Tables 4.2 and 4.3 show the residual alkalinity values when the increase in the phosphate concentration started with use of aluminum chloride or of alum, respectively. These alkalinity values indicate that the phosphate concentration in the wastewater increased as the alkalinity ran out. Depletion of alkalinity in the wastewater also caused a random behavior in the phosphate concentration observed when the wastewater had a calcium level of 200 mg/l and the low alkalinity level. This random behavior is shown in Figure 4.10.

The extent of the increase in the residual phosphate concentration was more significant when using aluminum chloride than when using alum. This could be caused by differences in the anion effects of a chloride ion versus a sulfate ion. Apparently, the sulfate ion was more effective in suppressing the increase in the residual phos-

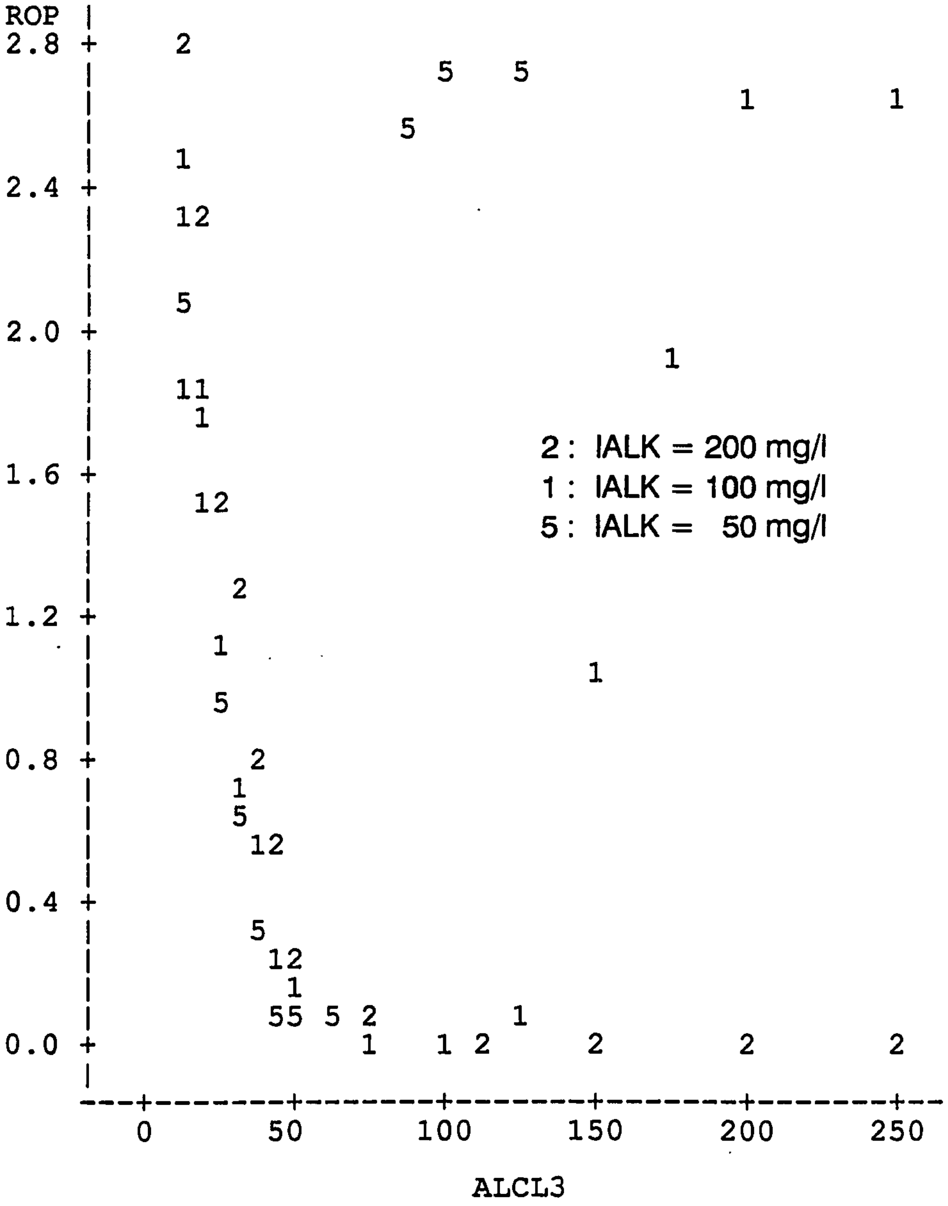


Figure 4.7: Residual phosphate (mg/l as P) as a function of aluminum chloride dosage (mg/l as $AlCl_3 \cdot 6H_2O$) at the low initial phosphate level

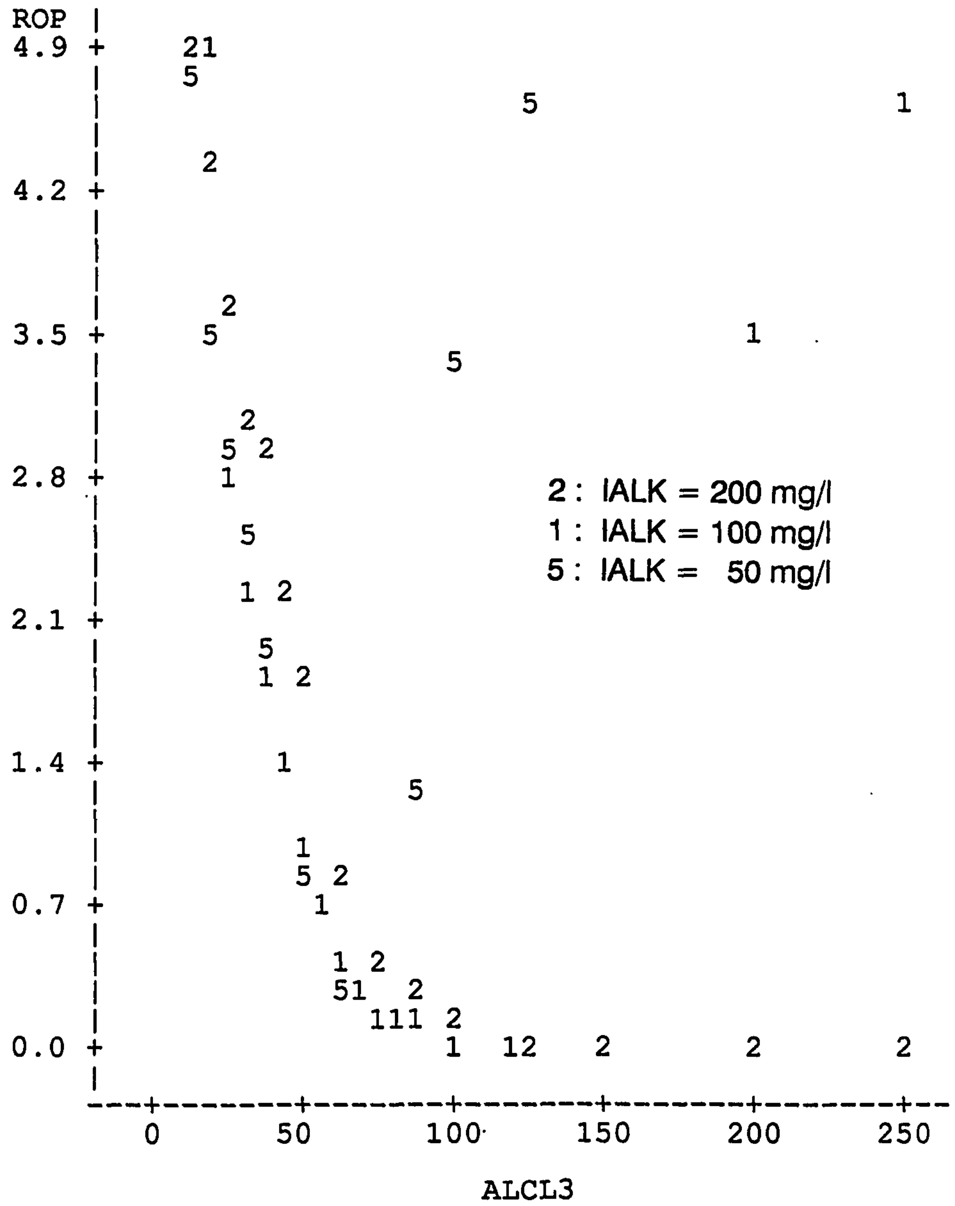


Figure 4.8: Residual phosphate (mg/l as P) as a function of aluminum chloride dosage (mg/l as $AlCl_3 \cdot 6H_2O$) at the medium initial phosphate level

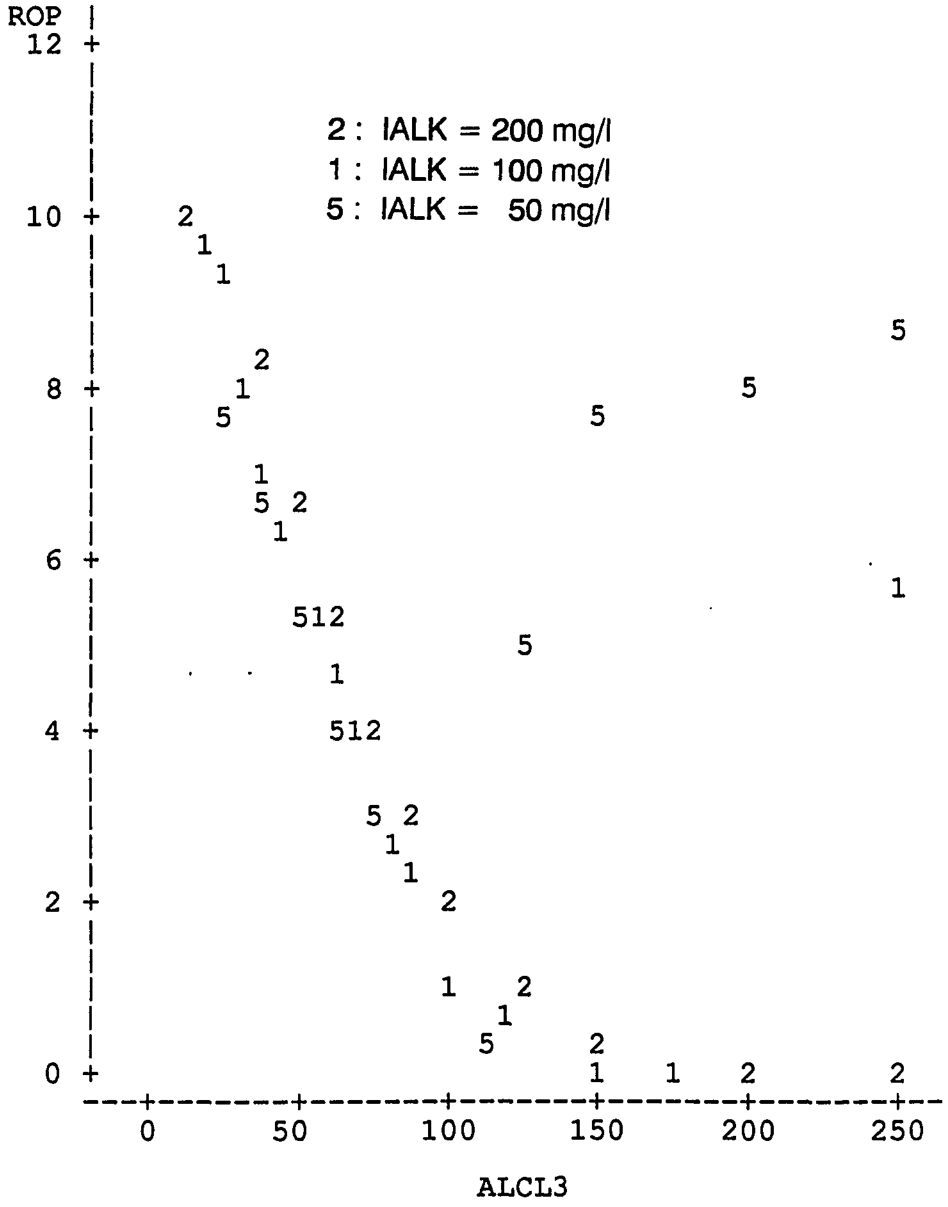


Figure 4.9: Residual phosphate (mg/l as P) as a function of aluminum chloride dosage (mg/l as $AlCl_3 \cdot 6H_2O$) at the high initial phosphate level

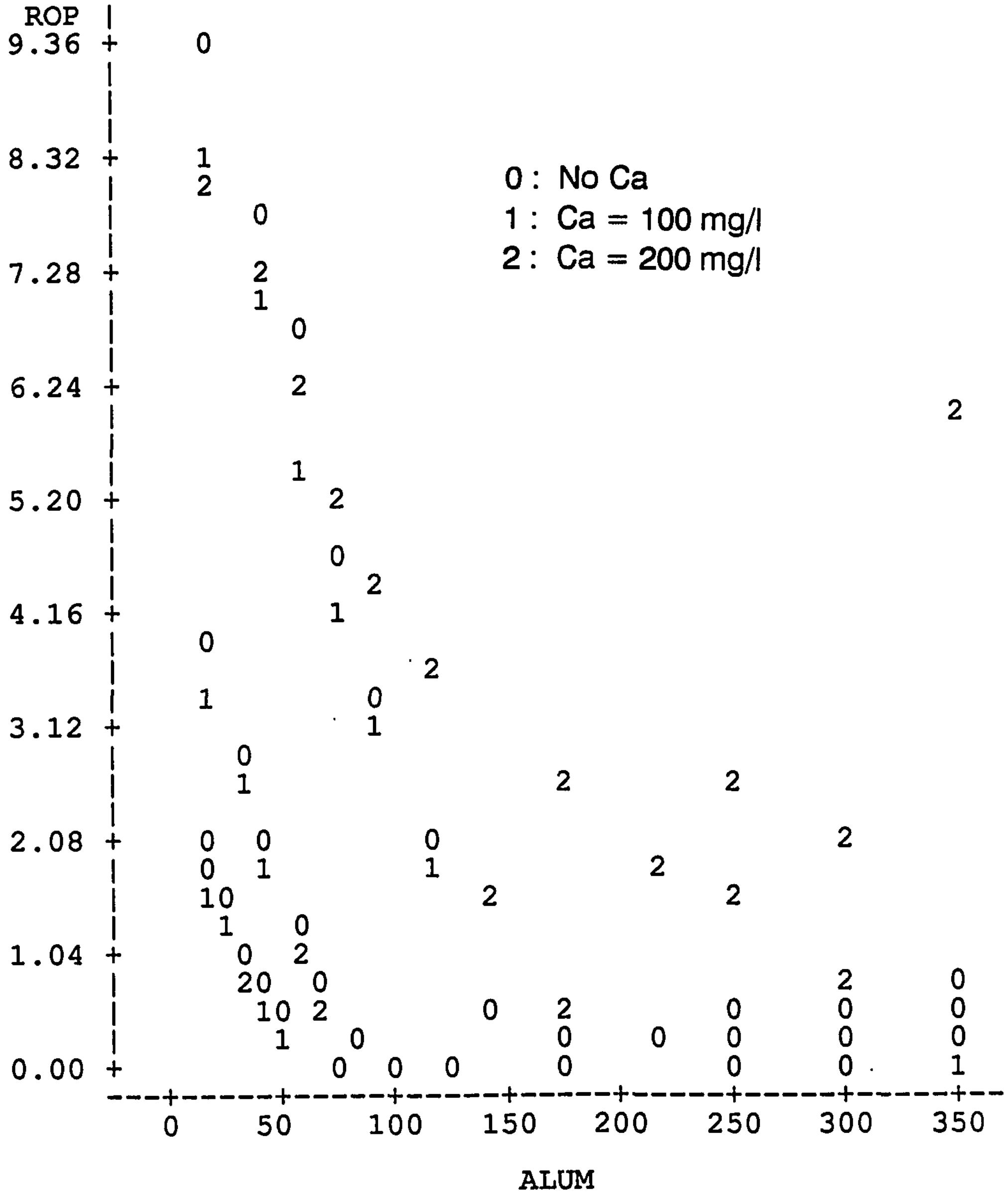


Figure 4.10: Residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) at the low initial alkalinity level

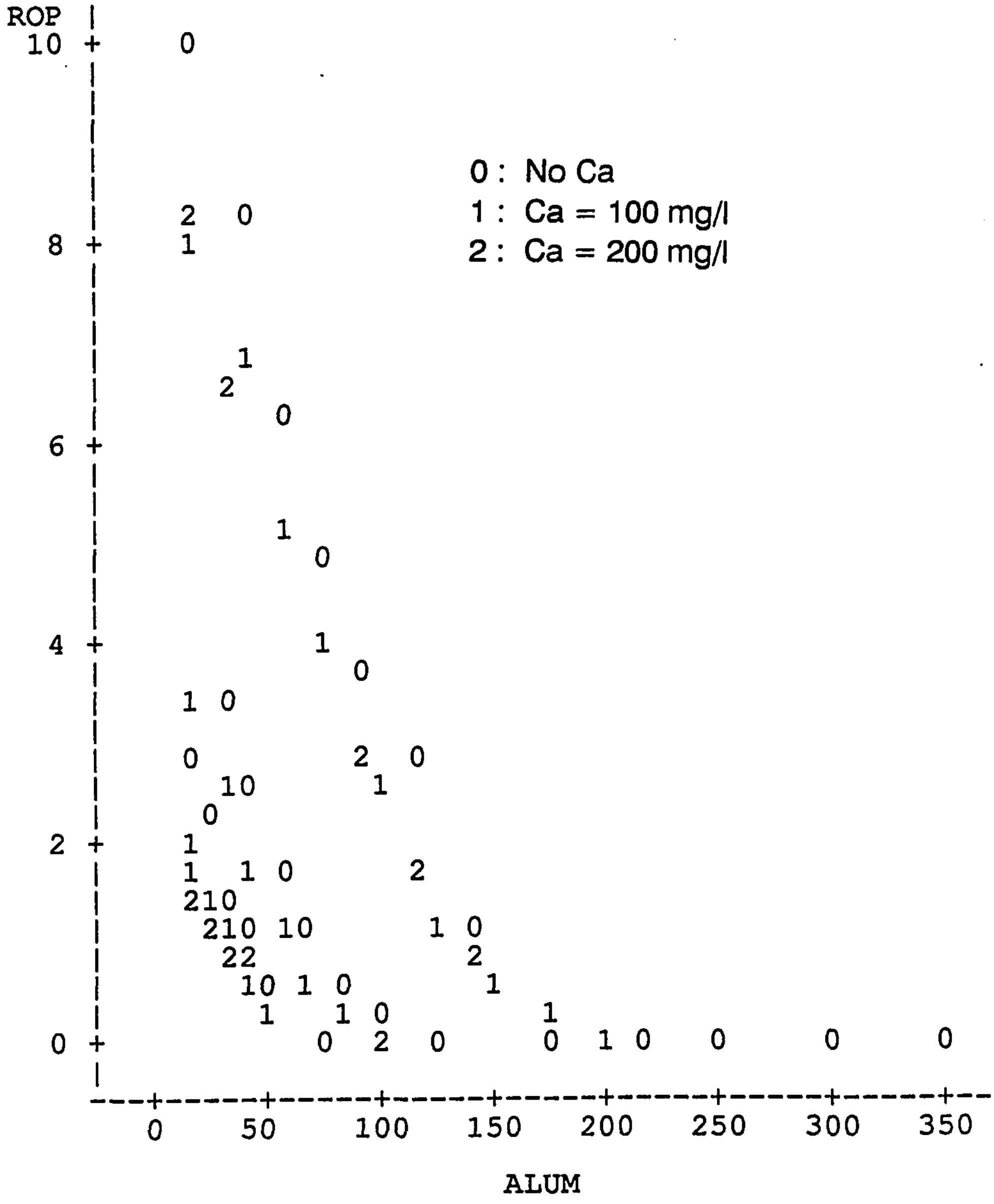


Figure 4.11: Residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) at the medium initial alkalinity level

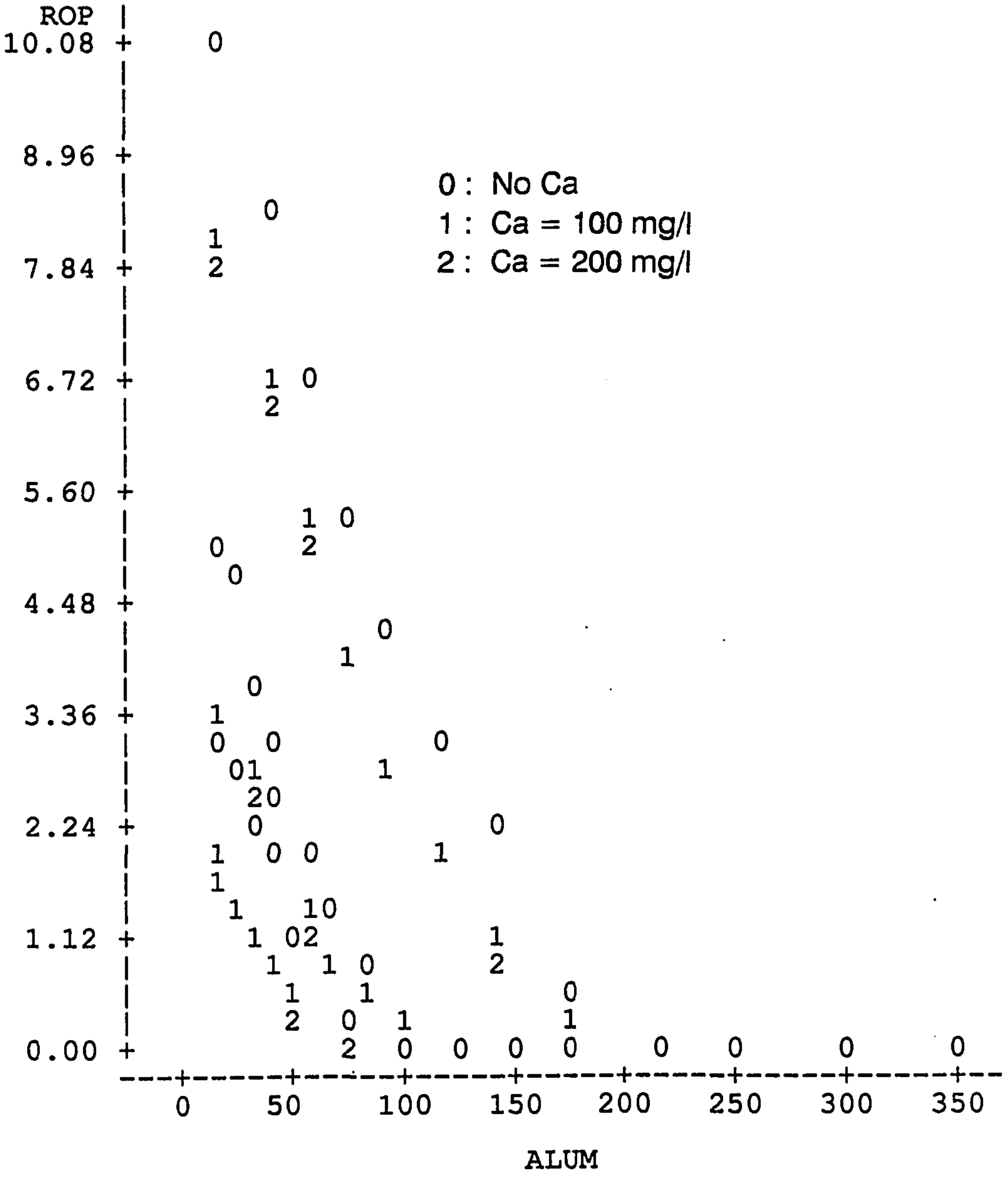


Figure 4.12: Residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) at the high initial alkalinity level

Table 4.2: Residual alkalinity in mg/l as $CaCO_3$ when an increase in the residual phosphate concentration started when using aluminum chloride

Initial Alkalinity Levels	Phosphate Levels Low	Medium	High
Low	5	4	0
Medium	20	9	3

Table 4.3: Residual alkalinity in mg/l as $CaCO_3$ when an increase in the residual phosphate concentration started when using alum

Calcium Levels, as Ca	Alkalinity Levels	Phosphate Levels Low	Medium	High
0	Low	1	1	0
0	Medium	2	2	2
100	Low	0	0	0
100	Medium	0	1	2
200	Low	0	0	0
200	Medium	0	0	2

phate concentration than was the chloride ion. Fortunately, this anion effect was minimal while the wastewater still had some of its alkalinity. It became evident only after the wastewater lost its alkalinity.

Tables 4.4 and 4.5 show the minimum residual phosphate concentrations obtained and the corresponding aluminum dosages when using aluminum chloride and when using alum, respectively. Aluminum dosages are expressed in mg/l as well as mmol/l as Al so that the comparison between aluminum chloride and alum can be made. According to these tables, the minimum residual phosphate concentrations obtained with use of aluminum chloride were close to those obtained with use of alum. Also, the corresponding aluminum dosages were close in terms of their molar concentrations. This suggests that there was no difference in the residual phosphate

Table 4.4: The minimum residual phosphate concentration (mg/l as P) and the corresponding aluminum chloride dosage (mg/l as $AlCl_3 \cdot 6H_2O$) under each experimental condition

Alkalinity	Low IOP[a]		Medium IOP		High IOP	
Levels	ROP[b]	$AlCl_3$[c]	ROP	$AlCl_3$	ROP	$AlCl_3$
Low	0.04	62.5 (0.26)[d]	0.07	75 (0.31)	0.29	112.5 (0.46)
Medium	0.02	100 (0.41)	0.03	118.75 (0.49)	0.11	175 (0.72)
High	0.01	112.5 (0.46)	0.01	200 (0.83)	0.05	200 (0.83)

[a] initial phosphate level
[b] the minimum residual phosphate concentration in mg/l as P
[c] the corresponding aluminum chloride dosage in mg/l as $AlCl_3 \cdot 6H_2O$
[d] aluminum dosage in mmol/l as Al

concentration whether aluminum chloride or alum was used as a precipitant as long as the residual phosphate concentration was decreasing. These tables also show that a low residual phosphate concentration could be obtained easily whether alum or aluminum chloride was used as the precipitant.

4.3.1 Stoichiometric phosphate removal

Many researchers [10, 4, 6, 7] have advocated the existence of aluminum hydroxyphosphate. Of these researchers, Ferguson [6, 7] proposed a stoichiometric formula of $Al_{1.4}PO_4(OH)_{1.2}$ for aluminum hydroxyphosphate, based on the work of Recht and Ghassemi. In order to see whether aluminum hydroxyphosphate forms, a molar ratio of Al(III) added to P removed, $[Al]_a/[P]_r$ was examined using the experimental data in which alum was used as the precipitant. According to Ferguson, phosphate residuals are controlled by the solubility of aluminum hydroxyphosphate when a molar aluminum dosage, Al_T, is less than an initial molar phosphate concentration,

Table 4.5: The minimum residual phosphate concentration (mg/l as P) and the corresponding alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) under each experimental condition

	Low IOP[a]		Medium IOP		High IOP	
	ROP[b]	ALUM[c]	ROP	ALUM	ROP	ALUM
Ca = 0 mg/l						
Low IALK[d]	0.02	125 (0.38)[e]	0.04	125 (0.38)	0.28	175 (0.53)
Med IALK	0.02	125 (0.38)	0.02	175 (0.53)	0.04	250 (0.75)
High IALK	0.01	175 (0.53)	0.04	250 (0.75)	0.07	250 (0.75)
Ca = 100 mg/l						
Low IALK	0.01	125 (0.38)	0.04	125 (0.38)	0.24	175 (0.53)
Med IALK	0.01	125 (0.38)	0.01	250 (0.75)	0.04	250 (0.75)
High IALK	0.01	250 (0.75)	0.02	175 (0.53)	0.06	250 (0.75)
Ca = 200 mg/l						
Low IALK	0.01	125 (0.38)	0.04	125 (0.38)	0.48	175 (0.53)
Med IALK	0.01	100 (0.30)	0.01	250 (0.75)	0.03	250 (0.75)
High IALK	0.02	250 (0.75)	0.04	175 (0.53)	0.02	350 (1.05)

[a] initial phosphate level
[b] the minimum residual phosphate concentration in mg/l as P
[c] the corresponding alum concentration in mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$
[d] initial alkalinity level
[e] aluminum dosage in mmol/l as Al

P_T. Using this approach, data in which $Al_T < P_T$ were selected. The relationship between Al(III) added and P removed was calculated for these data and is shown in Figure 4.13. In the calculation, data in which the molar ratio of $[Al]_a/[P]_r$ is less than 1 was excluded because aluminum-phosphate precipitation cannot account for a molar ratio less than 1.

Figure 4.13 clearly shows that a linear relationship exists between Al(III) added and P removed. Therefore, a simple linear regression was performed to estimate the ratio of $[Al]_a/[P]_r$. The regression analysis showed that the ratio is 1.2 with an R^2 value of 0.97. When regression analysis was performed for data in which calcium was not present in the wastewater, the ratio was still the same (1.2) regardless of whether aluminum chloride or alum was used as the precipitant. The only difference in the regression result was that the regression line obtained without calcium had a higher Y-intercept than the line obtained with calcium, as shown in Figure 4.13. This indicates that stoichiometric phosphate removal occurred in chemical phosphate removal regardless of whether aluminum chloride or alum was used as the precipitant and regardless of whether or not calcium was present in the wastewater. When calcium was present in the wastewater, the stoichiometric removal was obtained immediately with the addition of the aluminum salts. When no calcium was present in the wastewater, a threshold aluminum dosage was needed to initiate the stoichiometric removal. This indicates that the presence of calcium in the wastewater helped in phosphate removal. This benefit of calcium is discussed in the next section.

A regression analysis of the data in Figure 4.13 when no calcium was present in the wastewater resulted in a ratio of 1.4 when the regression line was forced to pass through the origin. This ratio is the same as that obtained by Ferguson, who per-

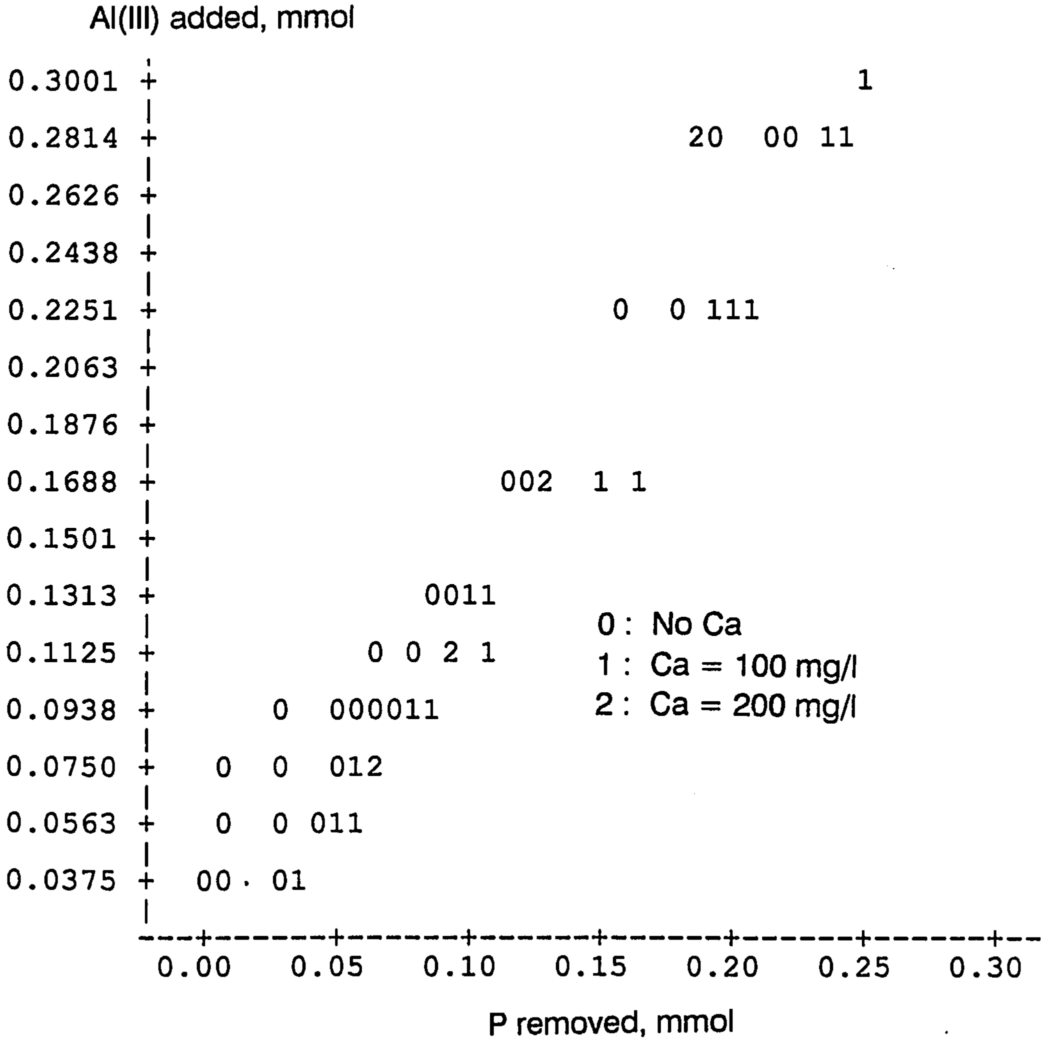


Figure 4.13: The relationship between Al_{added} and $P_{removed}$ when a molar dosage of Al(III) is less than an initial molar phosphate concentration when alum was used as a precipitant

formed experiments without calcium in the wastewater. This suggests that Ferguson might have obtained a stoichiometric ratio of 1.2, but reported the ratio of 1.4 by forcing his regression line to pass through the origin.

In chemical phosphate removal in field practice, the wastewater pH will be generally less than 7. This favors the presence of phosphate species of $H_2PO_4^-$. Using this phosphate species with an $[Al]_a/[P]_r$ ratio of 1.2, a stoichiometric formula of $Al_{1.2}H_2PO_4(OH)_{2.6}$ is hypothesized for aluminum hydroxyphosphate. Based on this hypothesis, the following equation can be used to describe the formation of aluminum hydroxyphosphate:

$$1.2Al^{3+} + H_2PO_4^{-1} + 2.6HCO_3^{-1} \rightleftharpoons Al_{1.2}H_2PO_4(OH)_{2.6} \downarrow + 2.6CO_2 \uparrow \quad (4.3)$$

As described in the previous section, it was observed that 2.4 eq of alkalinity were destroyed by addition of aluminum salts in chemical phosphate removal. This alkalinity destruction is related to the formation of a phosphate solid, as shown in Equation 4.3. Suppose that a solid of aluminum hydroxyphosphate does form in chemical phosphate removal and then think about how it forms in chemical phosphate removal. If all Al(III) added into the wastewater undergo complete hydrolysis, then all of the Al(III) turn into aluminum hydroxides. Phosphates can be adsorbed onto these aluminum hydroxides and the precipitate develops into a solid of aluminum hydroxyphosphate. To maintain electroneutrality of the solid, hydroxide ions will have to be released into the solution. According to this scenario, 3 eq of alkalinity will be destroyed when Al(III) hydrolysis is complete and after the hydrolysis, 0.6 eq of alkalinity will be released into the solution so that 2.4 eq of alkalinity is destroyed for each mole of Al(III) used. According to Equation 4.3, 2.6 eq of alkalinity is destroyed for 1.2 eq of Al(III). This corresponds to 2.2 eq of alkalinity for each mole of Al(III).

This leaves 0.2 eq of alkalinity unaccounted for. This portion of the alkalinity could be consumed in other reactions.

According to this adsorption hypothesis, there should be no difference in removal of phosphate regardless of whether the phosphates are added into a solution in equilibrium with aluminum hydroxide or concentrated aluminum salts are added into a phosphate solution. This is because aluminum hydrolysis is complete in both cases. This is not what researchers have found. Lijklema [16] found that better P removal was obtained when the aluminum salts were added into a phosphate solution than when phosphates were added into a diluted aluminum solution. This adsorption hypothesis cannot explain why the P removal efficiency varied with these two experimental conditions.

In another scenario, what if not all of the Al(III) added into the wastewater undergoes complete hydrolysis? Some of the Al(III) added will complete hydrolysis forming aluminum hydroxide. Phosphates can then be adsorbed onto these aluminum hydroxides and the precipitates eventually can develop into aluminum hydroxyphosphate. On the other hand, some of the Al(III) added does not experience hydrolysis and forms aluminum hydroxy complexes. These aluminum hydroxy complexes ,whether they are monomers or polymers, react with phosphates forming aluminum hydroxyphosphate. According to this scenario, there are two pathways by which aluminum hydroxyphosphate can form in chemical phosphate removal. Under certain experimental conditions, more of the Al(III) used undergoes complete hydrolysis and under different experimental conditions, less Al(III) undergoes complete hydrolysis. This scenario becomes more flexible. Depending on the experimental conditions, the stoichiometric ratio can change. The stoichiometric ratios obtained under different experimental conditions represent the average $[Al]_a/[P]_r$ molar ratios resulting from two pathways. This suggests that although stoichiometric phosphate removal occurs in chemical phosphate removal, the $[Al]_a/[P]_r$ molar ratio in a phosphate solid can be different, depending on the experimental conditions. Better P removal efficiency can be obtained when the portion of Al(III) which completes the hydrolysis becomes less. This scenario seems more plausible than the adsorption hypothesis.

4.3.2 Calcium effects

Calcium effects on the residual phosphate concentration were noted, as shown in Figures 4.10–4.12. The presence of calcium in the wastewater aided phosphate removal. The benefit of calcium was evident only at low alum dosages. At high alum dosages, this benefit diminished.

As shown in the previous section, the residual pH was always lower when calcium was present in the wastewater than when no calcium was present. This suggests that the benefit of calcium could be related to the low pH values: the solubility of aluminum hydroxyphosphate is lower at low pH values than at high pH values while the pH is in the range of 6 to 9.

This hypothesis was tested using the data in which $Al_T < P_T$. The Al_T represents a molar dosage of Al(III) and P_T represents an initial molar phosphate concentration. Based on the stoichiometric formula of $Al_{1.2}H_2PO_4(OH)_{2.6}$, the following equation describes the equilibrium solubility product (K_S) for aluminum hydroxyphosphate:

$$K_S = [Al^{3+}]^{1.2}[H_2PO_4^-][OH^-]^{2.6} \tag{4.4}$$

where $[Al^{3+}]$ and $[H_2PO_4^-]$ are a function of the wastewater pH. They can be expressed as follows:

$$[Al^{3+}] = \frac{Al_S}{1+\frac{K_{A1}}{[H^+]}+\frac{K_{A2}}{[H^+]^2}+\frac{K_{A3}}{[H^+]^3}+\frac{K_{A4}}{[H^+]^4}} = \frac{Al_S}{\alpha_{Al}} \tag{4.5}$$

$$[H_2PO_4^-] = \frac{P_S}{\frac{[H^+]}{K_{P1}}+1+\frac{K_{P2}}{[H^+]}+\frac{K_{P2}K_{P3}}{[H^+]^2}} = \frac{P_S}{\alpha_P} \tag{4.6}$$

where Al_S and P_S represent soluble aluminum and phosphate molar concentrations. In these equations, the following equilibrium constants were used: 10^{-5} for K_{A1}, $10^{-10.1}$ for K_{A2}, $10^{-16.8}$ for K_{A3}, $10^{-22.7}$ for K_{A4}, $10^{-2.2}$ for K_{P1}, $10^{-7.2}$ for K_{P2}, and $10^{-12.3}$ for K_{P3}. Equation 4.4 can then be rearranged by using Equations 4.5 and 4.6 as follows:

$$K_S = \frac{Al_S^{1.2}P_S K_W^{2.6}}{\alpha_{Al}^{1.2}\alpha_P[H^+]^{2.6}} \tag{4.7}$$

where K_W is an equilibrium dissociation constant of water. If we assume $Al_S = P_S$ for simplicity of calculation, Equation 4.7 can be solved for P_S as follows:

$$P_S^{2.2} = \frac{K_S[H^+]^{2.6}\alpha_{Al}^{1.2}\alpha_P}{K_W^{2.6}} \tag{4.8}$$

By taking logarithm on both sides of Equation 4.8,the following equation can be obtained:

$$\log P_S = \frac{\log K_S + 1.2\log\alpha_{Al} + \log\alpha_P + 36.4 - 2.6pH}{2.2} \tag{4.9}$$

In order to solve the above equation, we need to know K_S, α_{Al}, α_P, and the wastewater pH. As shown in Equations 4.5 and 4.6, α_{Al} and α_P are a function of the wastewater pH. Therefore, we can solve P_S once the wastewater pH and K_S are known. The equilibrium solubility product, K_S which can be obtained from Equation 4.7 was calculated using the data in which $Al_T < P_T$. Since Al_S was not measured, it was estimated by assuming that all Al(III) removed were incorporated into aluminum hydroxyphosphate. Then, Al_S can be described as follows:

$$Al_S = Al_T - 1.2(P_T - P_S) \tag{4.10}$$

where Al_T represents a molar dosage of Al(III) and P_T represents an initial molar phosphate concentration. The calculation showed that the negative logarithm of the equilibrium solubility product, pK_S for $Al_{1.2}H_2PO_4(OH)_{2.6}$ is 35.3. Using this solubility product, $\log P_S$ was calculated in the pH range of 5 to 9 and the result is shown in Figure 4.14.

Figure 4.14 indicates that soluble molar phosphate concentration increases with increasing pH in the pH range of 6 to 9. This confirms the above hypothesis: the solubility of aluminum hydroxyphosphate favors low pH conditions over high pH conditions in maintaining low phosphate residuals at least in the pH range of 6 to 9. This shows that the benefit of calcium was caused by low pH values resulting from dissolving calcium nitrate.

Table 4.6 shows the residual phosphate concentration and the corresponding alum dosage needed to satisfy an assumed phosphate discharge limit of 0.5 mg/l as P. Some residual phosphate concentrations were much less than 0.5 mg/l. These values were the closest experimental values to 0.5 mg/l. This table shows that the alum dosage required to satisfy the discharge limit was not affected by the presence

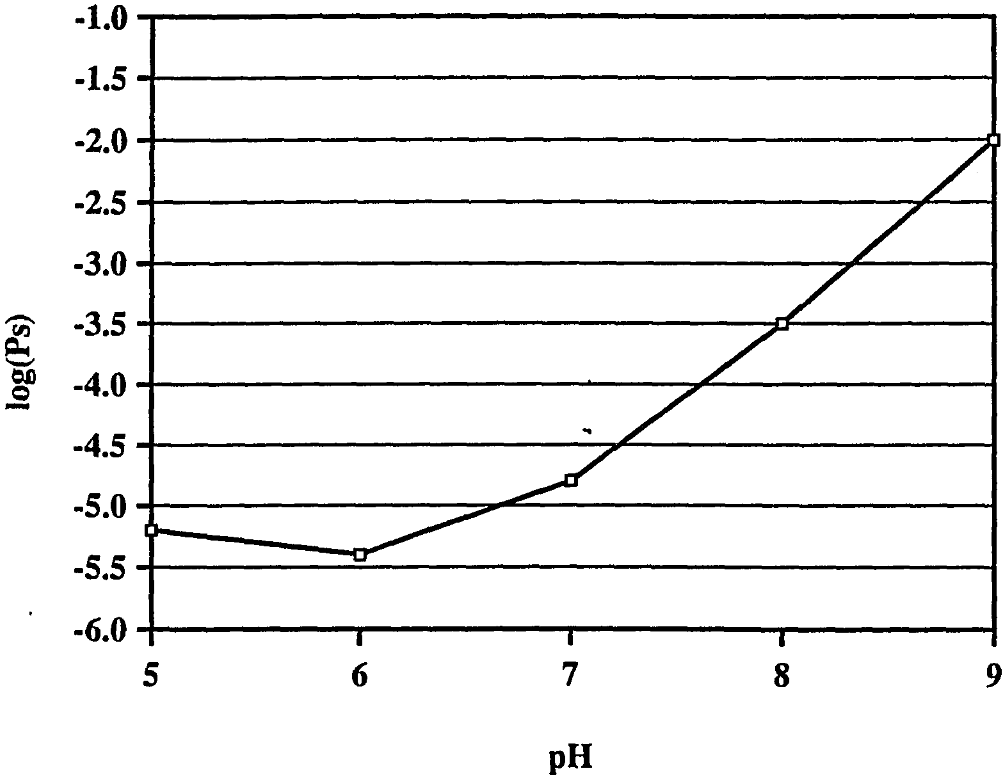


Figure 4.14: Variation of soluble molar phosphate concentration with the pH

Table 4.6: The phosphate concentration (mg/l as P) and the corresponding alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) which exceed the assumed discharge limit of 0.5 mg/l under each experimental condition

Alkalinity	Low IOP[a]		Medium IOP		High IOP	
Levels	ROP[b]	ALUM[c]	ROP	ALUM	ROP	ALUM
Ca = 0 mg/l						
Low	0.42	50	0.30	81.25	0.28	175
Medium	0.07	75	0.15	100	0.06	212.5
High	0.26	75	0.05	100	0.45	175
Ca = 100 mg/l						
Low	0.26	50	0.34	81.25	0.24	175
Medium	0.31	50	0.30	81.25	0.22	175
High	0.45	50	0.43	81.25	0.34	175
Ca = 200 mg/l						
Low	0.21	50	0.24	81.25	0.48	175
Medium	0.27	50	0.31	81.25	0.15	175
High	0.40	50	0.42	81.25	0.29	175

[a] initial phosphate level

[b] the minimum phosphate concentration in mg/l as P

[c] the corresponding alum concentration in mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$

of calcium in the wastewater. Whether calcium was present or not, the same alum dosage was needed to meet the discharge limit. Therefore, the benefit of calcium was no longer evident. Under these conditions, alum dosages were high ($Al_T > 1.2P_T$) such that the residual phosphate concentration was not controlled by the solubility of aluminum hydroxyphosphate and the benefit of calcium was not noted. Although the alum dosage required to meet a 0.5 mg/l as P residual limit increased with the initial phosphate level, an $[Al]_a/[P]_r$ molar ratio to satisfy the discharge limit was 1.6, regardless of the different initial conditions. This high stoichiometric ratio of $[Al]_a/[P]_r$ also showed that the residual phosphate concentration was no longer controlled by the solubility of aluminum hydroxyphosphate once $Al_T > P_T$.

4.3.3 Calcium-phosphate precipitation

There was one interesting observation made when calcium was in the synthetic wastewater. The $[Al]_a/[P]_r$ molar ratio obtained at low alum dosage was sometimes less than 1 when calcium was present in the wastewater. This could not be explained by aluminum-phosphate precipitation. Another mechanism must be brought in. Table 4.7 shows the $[Al]_a/[P]_r$ molar ratios obtained at an alum dosage of 18.75 mg/l. This table also shows the negative logarithm of the prevailing solubility product, pQ_S, calculated based on a solid of tricalcium phosphate. According to this table, the molar ratio was less than 1 when the initial phosphate level was medium to high and when there was medium to high alkalinity level. This suggests that calcium-phosphate precipitation might take place under these conditions.

There are a variety of calcium-phosphate solids which could be formed. Of these solids, hydroxyapatite, $Ca_5(PO_4)_3(OH)$, is the most stable one thermodynamically. However, phosphate levels in wastewater treated with calcium salts far exceed the calculated equilibrium phosphate levels based on hydroxyapatite. This suggests that the dissolved phosphate levels are controlled by some other more soluble calcium-phosphate solids. Menar and Jenkins [18] studied calcium-phosphate precipitation in wastewater treatment and found that dissolved phosphate residuals were controlled by an amorphous tricalcium phosphate, $Ca_3(PO_4)_2$. They presented the negative logarithm of the equilibrium solubility product for this solid form as 23.56, which is lower than values (25–29) reported in the literature [18].

Based on the work of Menar and Jenkins, it was assumed that the tricalcium phosphate phase controlled the residual phosphate concentration at a low alum dosage of 18.75 mg/l. Then, the solubility product was calculated under each experimental

Table 4.7: The molar ratios of $Al_{added}/P_{removed}$ at an alum dosage of 18.75 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$ and the pQ_S values for tricalcium phosphate under each experimental condition

Alkalinity	Low IOP[a]		Medium IOP		High IOP	
Levels	Al/P	pQ_S	Al/P	pQ_S	Al/P	pQ_S
Ca = 0 mg/l						
Low	1.36 (7.22)[b]		1.40 (7.04)		2.13 (6.98)	
Medium	7.26 (7.65)				6.01 (7.39)	
High	14.5 (8.15)		8.71 (7.77)		6.01 (7.55)	
Ca = 100 mg/l						
Low	1.20 (6.95)	28.6	1.05 (6.91)	28.1	0.85 (6.87)	27.5
Medium	1.26 (7.39)	27.8	1.09 (7.66)		0.76 (7.10)	27.3
High	1.28 (7.43)	28.3	0.98 (7.30)	28.0	0.80 (7.25)	27.1
Ca = 200 mg/l						
Low	1.12 (6.84)	28.1	1.00 (6.77)	27.6	0.84 (6.65)	27.3
Medium	1.10 (7.17)	27.6	0.99 (7.11)	27.0	0.83 (7.00)	26.6
High	1.26 (7.41)	27.4	0.95 (7.30)	27.1	0.76 (7.25)	26.5

[a] initial phosphate level

[b] values in parenthesis are the residual pH

condition by using the following equation:

$$Ca_3(PO_4)_2 \downarrow \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-} \tag{4.11}$$

The solubility product for the above equation is:

$$Q_S = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{4.12}$$

According to Menar and Jenkins, the most significant calcium complex is $CaCO_{3(aq)}$. Then, $[Ca^{2+}]$ can be expressed as follows:

$$[Ca^{2+}] = \frac{Ca_S}{1 + K_{CaCO_3}[CO_3^{2-}]} \tag{4.13}$$

where Ca_S represents the soluble molar calcium concentration and K_{CaCO_3} represents the equilibrium stability constant for $CaCO_{3(aq)}$. The value of 1590, which was used by Menar and Jenkins, was used for this constant in the calculation. By assuming that all calcium removed is incorporated into tricalcium phosphate, the Ca_S can be obtained as follows:

$$Ca_S = Ca_T - 1.5(P_T - P_S) \tag{4.14}$$

where Ca_T and P_T represent total molar calcium and phosphate concentrations, respectively and P_S represents the soluble molar phosphate concentration. The $[CO_3^{2-}]$ can be obtained from the residual alkalinity. If the contribution from phosphates is neglected together with $[OH^-]$ and $[H^+]$, alkalinity can be expressed as follows:

$$\begin{aligned} Alkalinity, eq/l &= [HCO_3^-] + 2[CO_3^{2-}] \\ &= [CO_3^{2-}](\frac{[H^+]}{K_{C1}} + 2) \end{aligned} \tag{4.15}$$

where K_{C1} ($10^{-6.3}$) represents the first dissociation constant for carbonic acid at 25°C. The $[PO_4^{3-}]$ can be obtained as follows:

$$[PO_4^{3-}] = \frac{P_S}{1 + \frac{[H^+]}{K_{P3}} + \frac{[H^+]^2}{K_{P2}K_{P3}} + \frac{[H^+]^3}{K_{P1}K_{P2}K_{P3}}} \tag{4.16}$$

where K_{P1} ($10^{-2.2}$), K_{P2} ($10^{-7.2}$), and K_{P3} ($10^{-12.3}$) represent the dissociation constants for H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-}, respectively.

The solubility product can be calculated using the following procedures:

1. Equation 4.15 is solved for $[CO_3^{2-}]$.
2. Equation 4.14 is solved to obtain Ca_S.
3. Then, $[CO_3^{2-}]$ and Ca_S are used in Equation 4.13 to obtain $[Ca^{2+}]$.
4. $[PO_4^{3-}]$ is obtained from Equation 4.16.
5. $[Ca^{2+}]$ and $[PO_4^{3-}]$ are then used to obtain the solubility product from Equation 4.12.

The calculated negative logrithm of the solubility product, pQ_S for tricalcium phosphate is shown in Table 4.7. When the wastewater had a calcium level of 100 mg/l and a high alkalinity level, the measured residual pH values were not available for the medium and the high phosphate levels. The pQ_S was calculated using the residual pH values (7.30 and 7.25) when the calcium level is 200 mg/l. As the calcium level increased, lower pH values were obtained. Therefore, use of the pH values at the higher calcium level could underestimate the residual pH. This could result in a more conservative calculation of pQ_S. The pQ_S was not calculated when the wastewater had the calcium level of 100 mg/l and the medium alkalinity and phosphate levels because of an apparent error in the residual pH. The residual pH normally decreased as the phosphate level increased. Under all the experimental conditions, lower pH values were obtained at the higher phosphate level if all other conditions were the same. When the calcium level was 100 mg/l and the initial alkalinity level was medium, the residual pH values were recorded as 7.39, 7.66, and 7.10 for the low, medium, and the high phosphate levels, respectively. This indicates an error in the pH value of 7.66 for the medium phosphate level. This value should be less than 7.39 and higher than 7.10.

According to this table, the $[Al]_a/[P]_r$ molar ratio was less than 1 when the pQ_S was less than 27.5. There were two exceptions. When the wastewater had a calcium level of 200 mg/l, the low phosphate level and the high alkalilnity level. The $[Al]_a/[P]_r$ ratio was 1.26 and the pQ_S was 27.4. When the wastewater had a calcium level of 100 mg/l, the medium phosphate and the high alkalinity level, the $[Al]_a/[P]_r$ ratio was 0.98 and the pQ_S was 28. These could be caused by an error in measurement of the residual phosphate.

Table 4.7 shows that a low Al/P molar ratio could be caused by calcium-phosphate precipitation, $Ca_3(PO_4)_2$. This table also suggests that the equilibrium solubility product for this solid was 27.5 provided that the residual phosphate concentration was controlled by tricalcium phosphate. This value is higher than the value (23.56) proposed by Menar and Jenkins, but is in agreement with values (25–29) reported in the literature.

5. EVALUATION OF EQUILIBRIUM MODELS

5.1 Evaluation of the Ferguson Model

Ferguson developed two phosphate preciptation models: the first version, Ferguson model (I), and the second version, Ferguson model (II). After Ferguson developed the first version of his model, he realized the deficiency of his model in predicting an increase in the residual phosphate concentration at high alum dosages. To correct this problem, he included formation of an aluminum phosphate complex in the second version of his model. Therefore, the main difference between the two models is whether an aluminum phosphate complex is or is not included. The Ferguson model (I) was able to be recopied in BASIC language, and its simulation results were compared to the experimental results obtained in this study as well as to simulation results using a regression model, which is developed in the next chapter. However, the Ferguson model (II) could not be recopied because Ferguson was not specific in the details of how they incorporated an aluminum phosphate complex into the model.

The Ferguson model (I) takes easily measured wastewater parameters (such as pH, alkalinity, and orthophosphates, etc.), and predicts final wastewater characteristics after the addition of alum. The Ferguson model is based on formation of two aluminum solids, aluminum phosphates and hydroxides. As discussed previously, some researchers [10, 4] proposed the presence of aluminum hydroxyphosphate, which is an imaginary precipitate for which no physical data are available. Ferguson agreed with them and used the formation of a hydroxyphosphate solid in his models [6, 7].

The Ferguson models were evaluated by considering two objectives of the model for chemical phosphate removal. The Ferguson model (I) predicted well such important parameters as the residual phosphate concentration, pH, and alkalinity. Raw data for simulation results using the Ferguson model are attached in Appendices C and D. Appendix C included the raw data for simulation results of the residual phosphate concentration by the Ferguson model (I). It also shows model simulation results for the residual phosphate concentration obtained using the Kim regression model. Appendix D shows raw data for simulation results of the residual pH and residual alkalinity values obtained using the Ferguson model (I) and the Kim regression model.

The simulation results for residual alkalinity and pH using the Ferguson model (I) are summarized in two figures (Figures 5.1 and 5.2). Figure 5.1 shows the comparison of residual alkalinity values from the experimental results obtained in this study and simulation results predicted by the Ferguson model (I). The comparison of pH is shown in Figure 5.2. In these figures, the symbol "F" represents simulation results using the Ferguson model and that of "*" represents the experimental results.

Examination of Figure 5.1 and Appendix D indicates that simulation results for the residual alkalinity values predicted by the Ferguson model (I) were consistently higher than the experimental results. A better fit was obtained under the condition of a low initial alkalinity level than under medium and high initial alkalinity conditions. Overall, the residual alkalinity values predicted by the Ferguson model were in good agreement with those obtained from the experiments conducted in this study.

The results shown in Figure 5.2 and Appendix D show that the Ferguson model

(I) was unable to predict the rapid pH drop which was observed at the low and the medium initial alkalinity levels. The Ferguson model (I) predicted that the residual pH values would decrease somewhat linearly with increasing alum dosages.

A main objective of the Ferguson model (I) was to be able to predict the residual phosphate concentration. Being able to predict the residual pH and alkalinity values was supposed to be a by-product of this model. In order to illustrate how well the Ferguson model (I) predicted the residual phosphate concentration, a comparison between the simulation results using the Ferguson model (I) and the experimental results in this study are shown in Figures 5.3–5.11. These figures also show simulation results using the Kim regression model. Each figure compares the experimental results to simulation results under each experimental condition.

These figures show that the Ferguson model (I) was better at predicting the residual phosphate concentration than in predicting the residual pH or alkalinity. The worse fit was obtained under the condition of high alkalinity and low phosphate levels.

Even though the Ferguson model predicts these parameters well, his model seems to be more like a data-fitting. Why their model is more like a data-fitting is explained below, with some problems noted in the use of the Ferguson model.

5.1.1 Complexes

According to the first version of the Ferguson model [6], the residual phosphate concentration steadily decreases as the alum dosage increases. After some experiments, Ferguson realized that the residual phosphate concentration actually increases at high alum dosages. He postulated [7] that incorporation of aluminum polymers

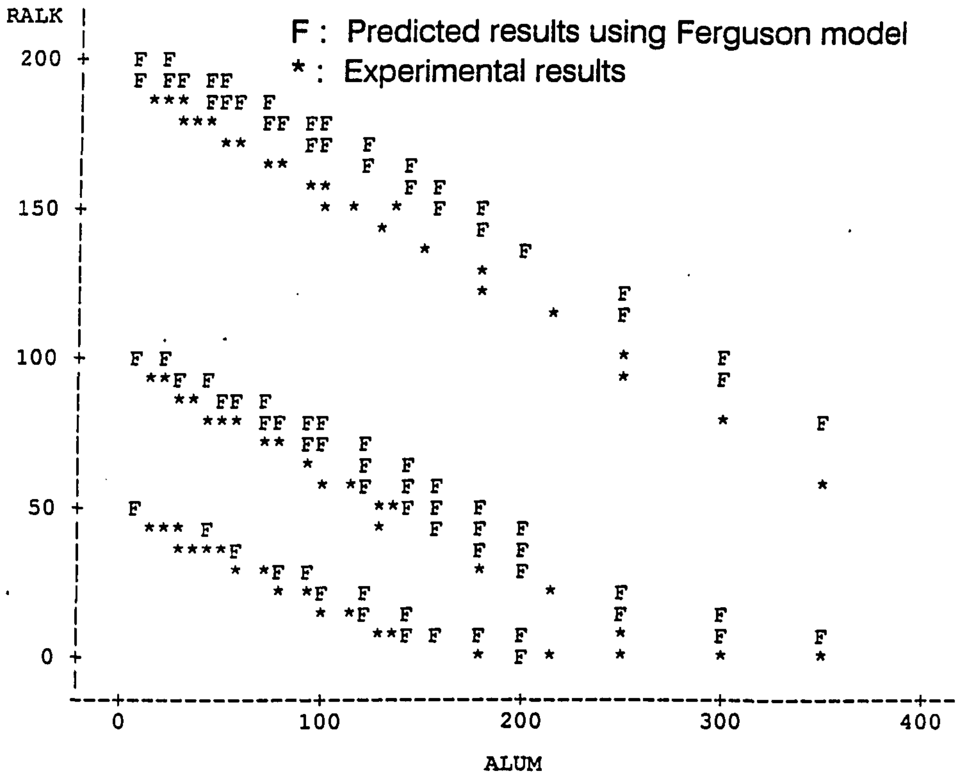


Figure 5.1: Comparison of residual alkalinity (mg/l as $CaCO_3$) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental and simulation results using the Ferguson model

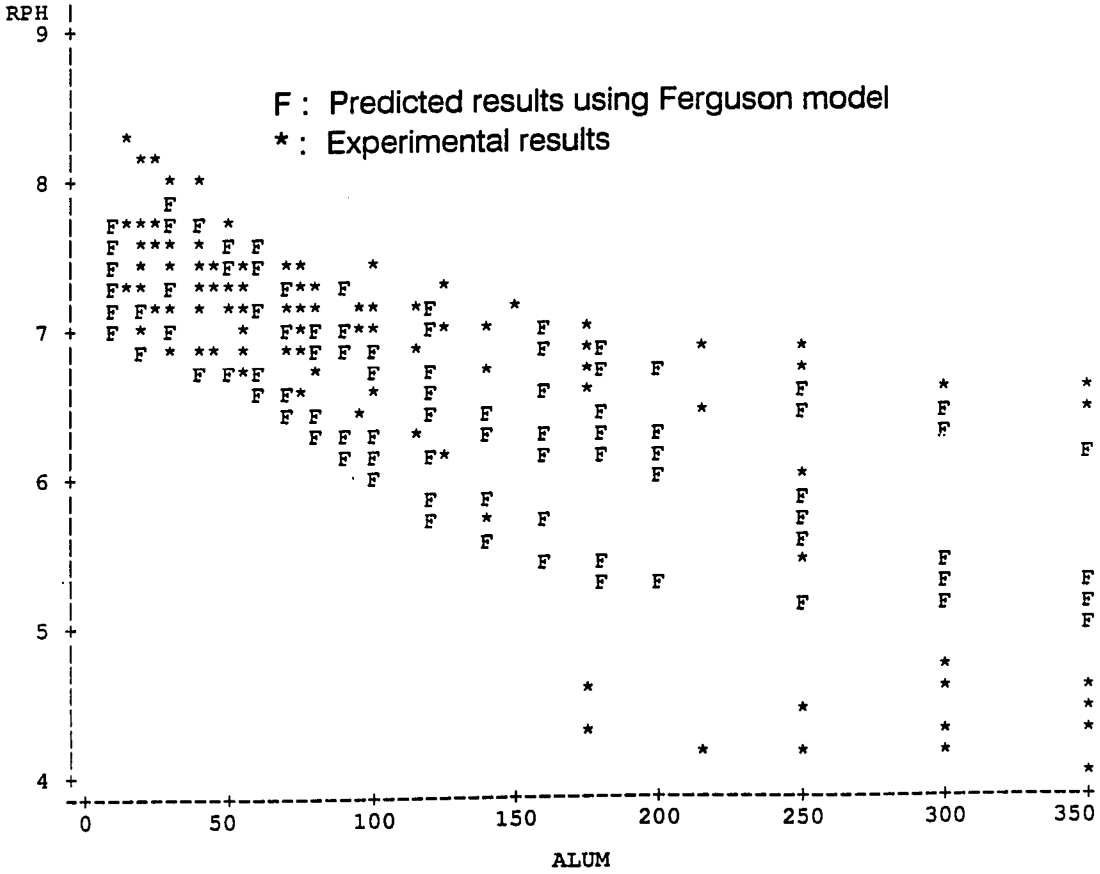


Figure 5.2: Comparison of residual pH as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model.

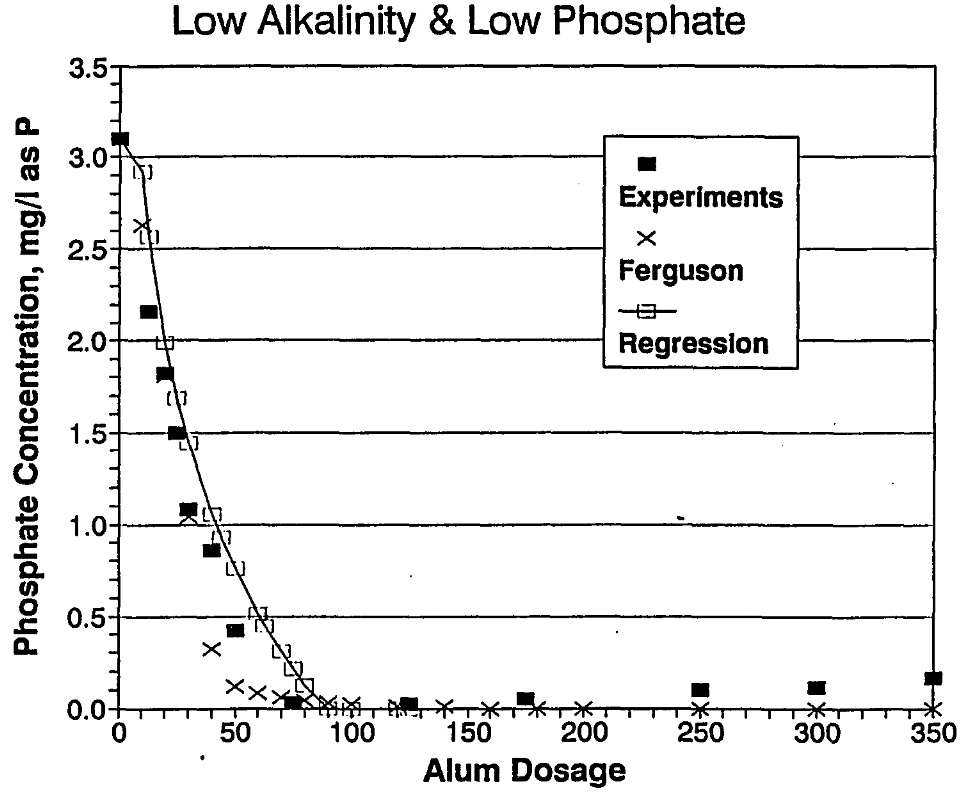


Figure 5.3: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the low initial alkalinity and low initial phosphate levels

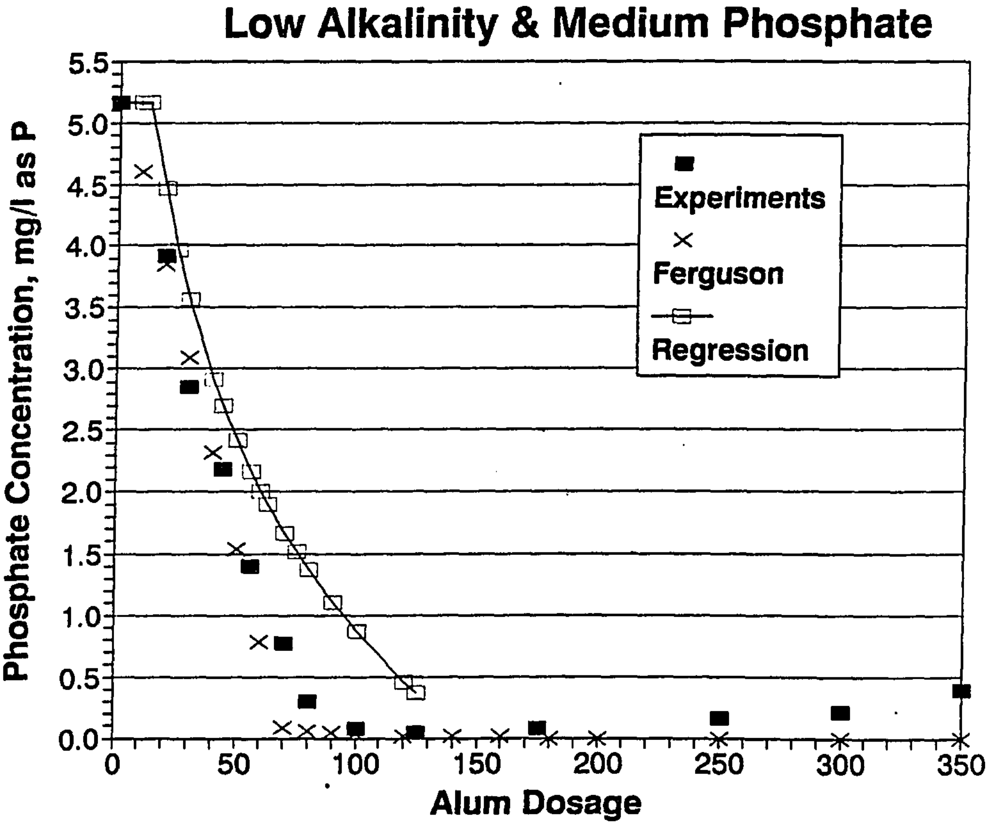


Figure 5.4: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the low initial alkalinity and medium initial phosphate levels

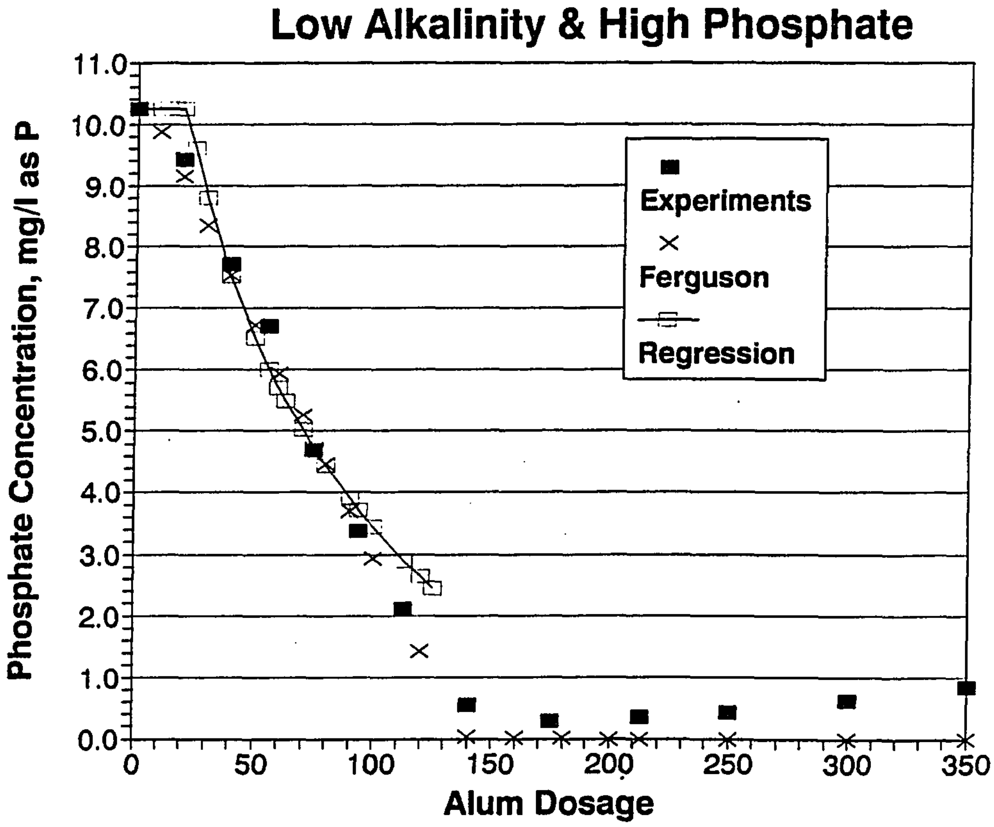


Figure 5.5: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the low initial alkalinity and high initial phosphate levels

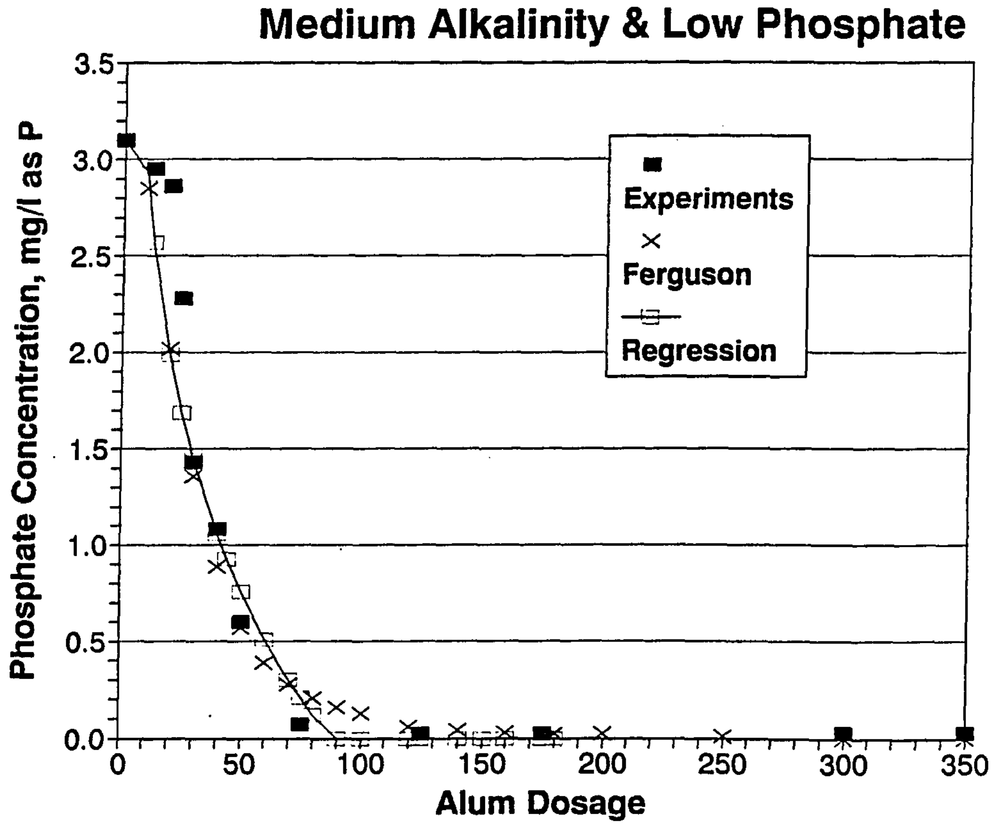


Figure 5.6: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the medium initial alkalinity and low initial phosphate levels

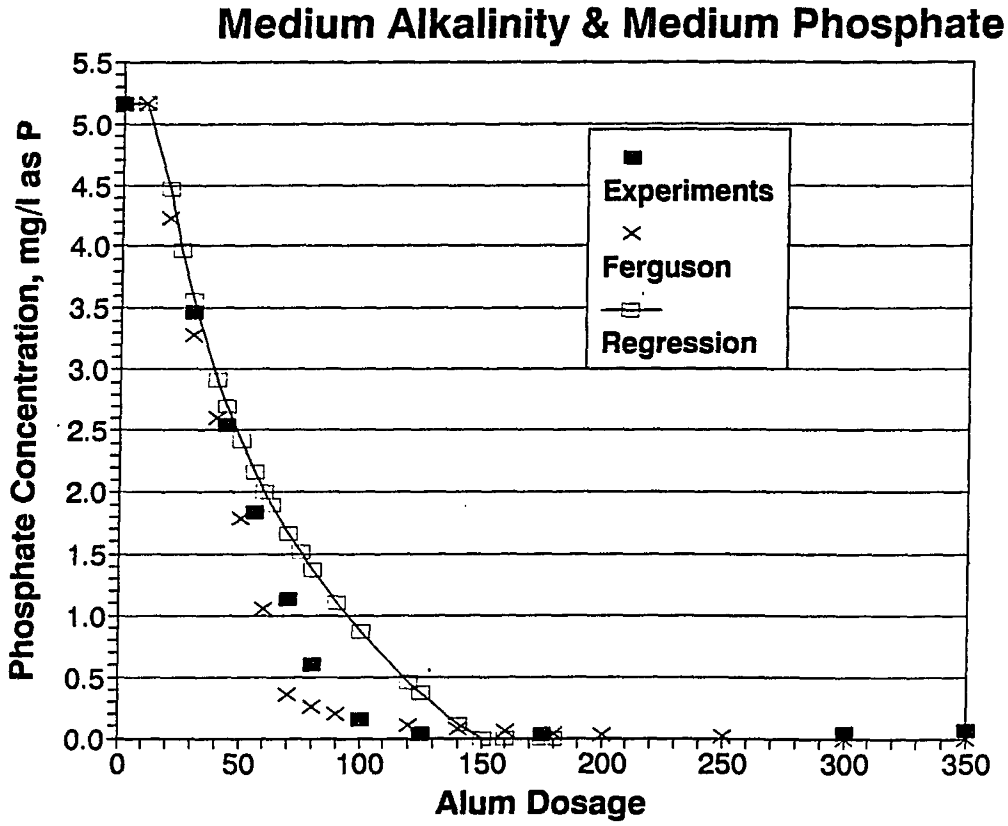


Figure 5.7: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the medium initial alkalinity and medium initial phosphate levels

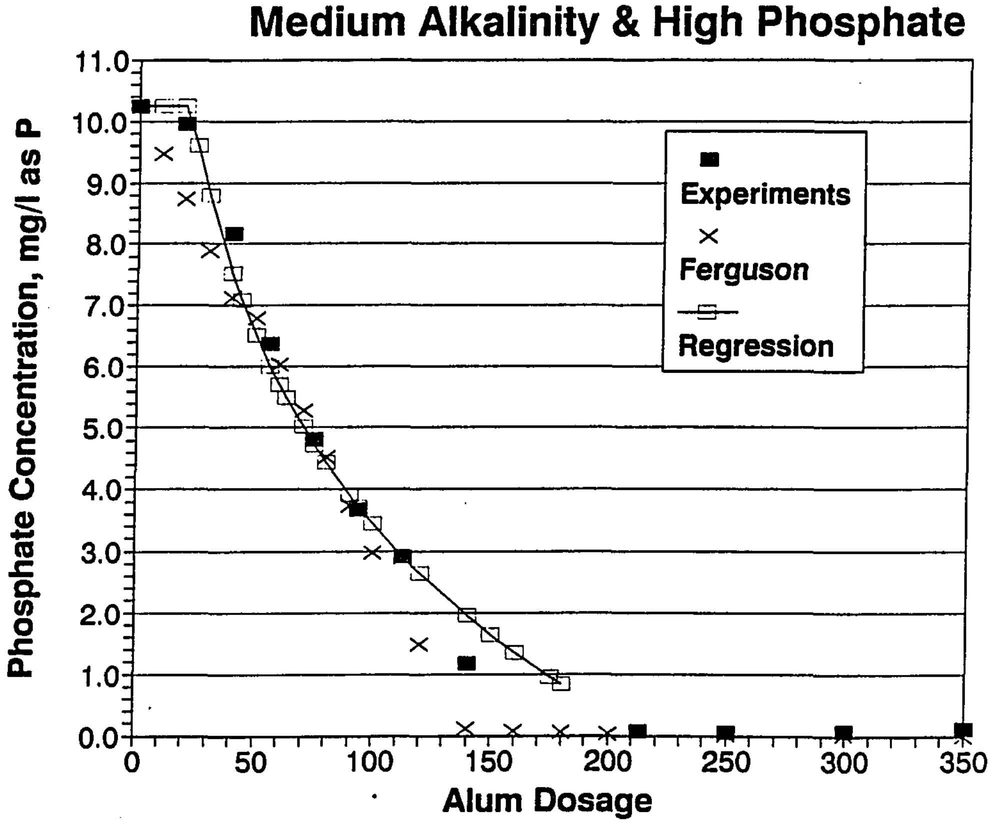


Figure 5.8: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the medium initial alkalinity and high initial phosphate levels

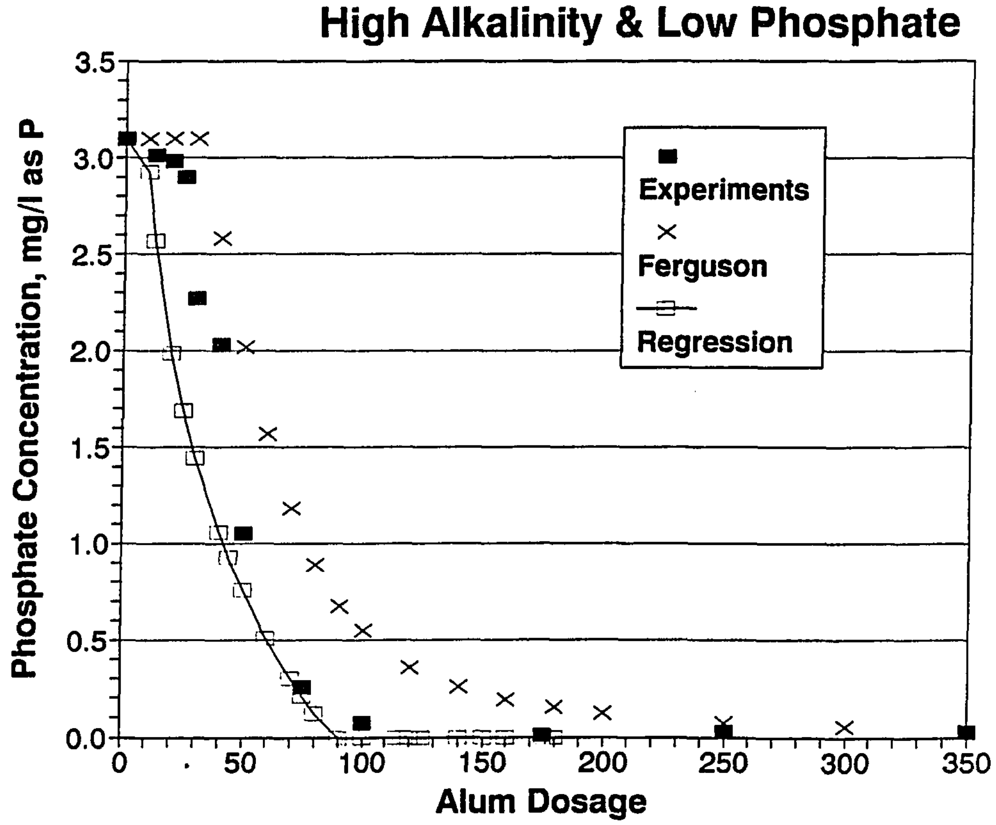


Figure 5.9: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the high initial alkalinity and low initial phosphate levels

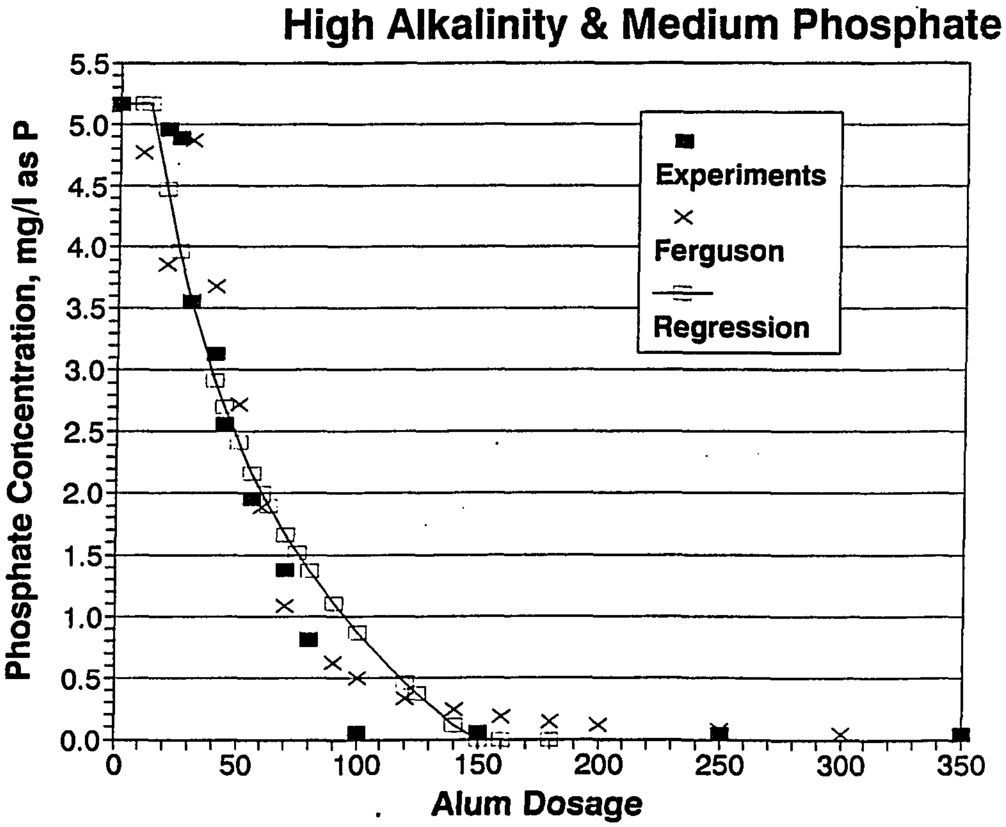


Figure 5.10: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the high initial alkalinity and medium initial phosphate levels

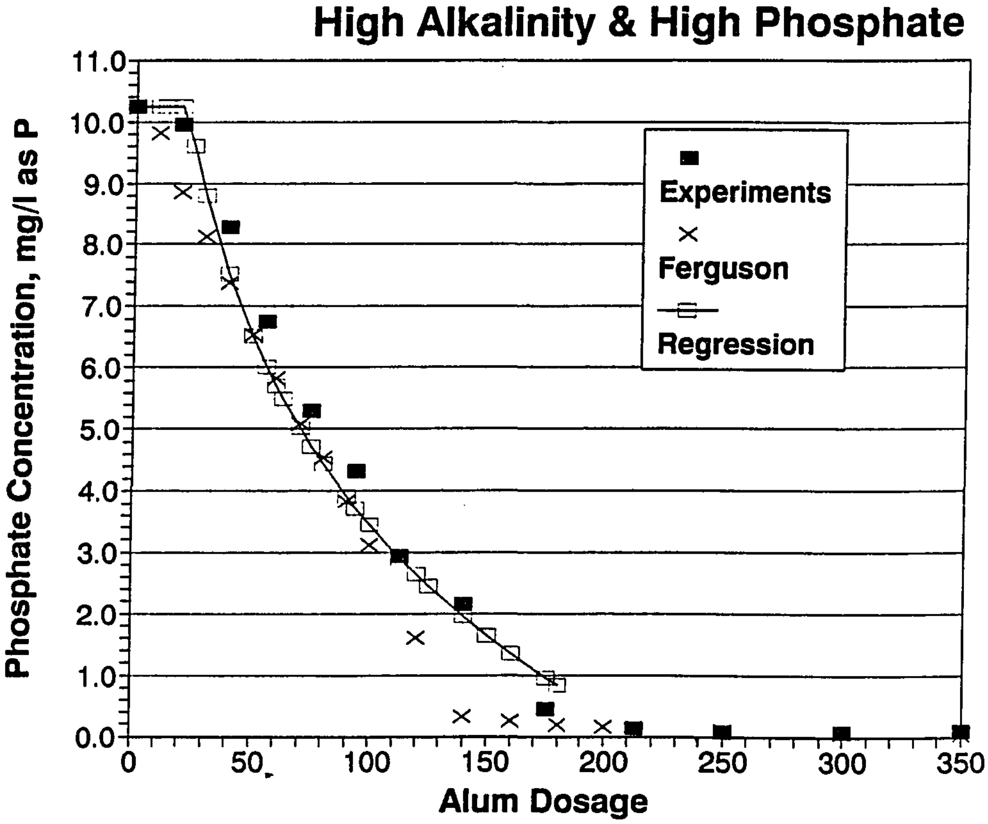


Figure 5.11: Comparison of residual phosphate (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) between the experimental results and simulation results using the Ferguson model and the Kim regression model at the high initial alkalinity and high initial phosphate levels

and aluminum phosphate complexes would correct the problem. Therefore, he incorporated an aluminum phosphate complex, $AlH_2PO_4^{2+}$ in the second version of his model. However, he did not include aluminum polymers in the model partly for the following reasons [7]:

- because Parks found it unnecessary to include polymeric species to model aluminum hydroxide soubility, and
- because there is no general agreement on the value of the stability constants for polymeric species in equilibrium, let alone in solutions in which rapid precipitation is taking place.

The second reason implies that equilibrium is not reached in a rapid precipitation process like chemcial phosphate removal. This is quite possible. A problem with this reason is that the Ferguson models are based on a chemical equilibrium approach. His model therefore becomes invalid if an equilibrium assumption does not hold. Ferguson explicitly mentioned this when he made assumptions for his models. He assumed that rapid equilibrium is reached and the model calculates equilibrium concentrations.

It is correct that there is much controversy concerning the equilibrium constants for aluminum polymeric species. However, the existence of polymeric species is well-established [1]. The author also found that aluminum polymeric species could exist in chemical phosphate removal [13]. Ferguson did not include polymeric species in his models due to a numerical problem. Inclusion of polymeric species in an equilibrium model makes numerical computation very complicated. Because of this numerical difficulty, there is no equilibrium model available which can incorporate the existence of aluminum hydroxypolymers. Consequently, no information is available to estimate how the polymers would influence chemical phosphate removal.

It should be pointed out that inclusion of an aluminum phosphate complex in a model makes the residual phosphate concentration increase with high dosage of aluminum salts according to a chemical equilibrium approach. As aluminum dosage increases, concentrations of soluble phosphate species associated with a proton (H_3PO_4, $H_2PO_4^-$, $HPO4^{2-}$, and PO_4^{3-}) decrease, but concentrations of the aluminum phosphate complexes ($AlH_2PO_4^{2+}$ and $AlHPO_4^+$) increase. This is illustrated in Figure 5.12.

This figure was prepared based on the equilibrium model. The equilibrium model was made using the Ferguson approach. For simplicity of equilibrium calculations, both solids (aluminum hydroxyphosphate and aluminum hydroxide) were assumed to precipitate. In the figure, the H-PO4 represents soluble phosphate species associated with a proton, and the C-PO4 represents aluminum phosphate complexes, and the S-PO4 represents soluble phosphate concentrations. The equilibrium model so prepared predicted the residual phosphate concentration well only when the initial alkalinity and phosphate levels were low. According to this figure, the model predicts that concentrations of phosphate species associated with a proton decrease and those of aluminum phosphate complexes increase with increasing alum concentration. The model predicted too large an increase in the aluminum phosphate complexes.

The Ferguson model (II) was also able to track this path of variation of soluble phosphate species, as shown in Figure 5.13. This figure tells us that the residual phosphate concentration jumps back to its initial level quickly after reaching the minimum concentration. This simulation result was not observed in the experiments with alum, but was observed in the experiments with aluminum chloride.

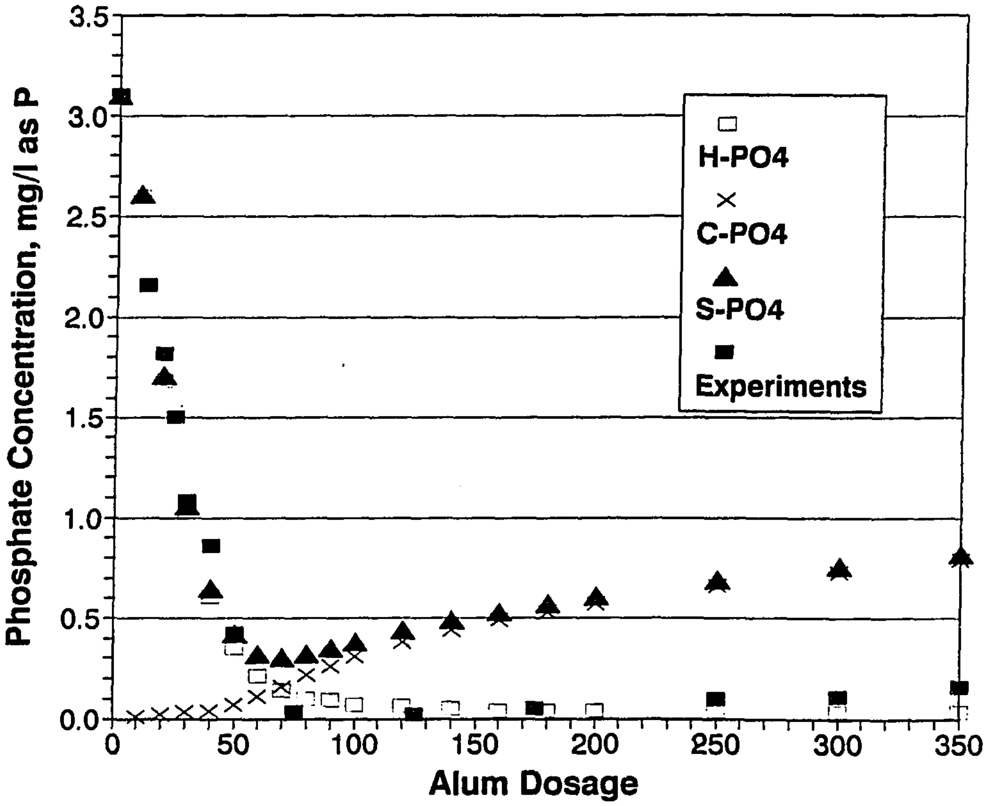


Figure 5.12: Variation of soluble phosphate species with increasing alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$)

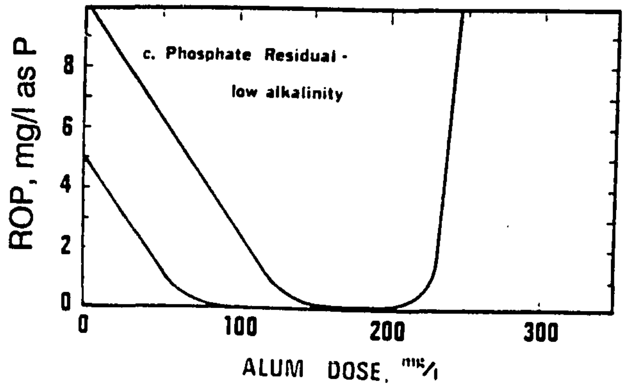


Figure 5.13: Simulation of the residual phosphate concentrations against alum dosage at an initial alkalinity concentration of 1.5 meq/l by the Ferguson model (II) (Ferguson and King, 1977)

5.1.2 Chemical effects

The more significant defect of the Ferguson models is its incapability of incorporating chemical effects. The Ferguson model does not provide any means to differentiate different aluminum salts, like aluminum chloride and alum.

Based on an equilibrium approach, a difference between aluminum chloride and alum develops when aluminum sulfato complexes of $AlSO_4^+$ and $Al(SO_4)_2^-$ are present in the final system of wastewater after chemical addition. This is shown in Table 5.1.

Table 5.1 describes an equilibrium system after aluminum salts of aluminum chloride or alum are added to the synthetic wastewater containing $NaHCO_3$-NaH_2PO_4. After addition of aluminum salts, aluminum will certainly react with ligands of phos-

Table 5.1: Equilibrium system of synthetic wastewater ($NaHCO_3$-NaH_2PO_4) after addition of aluminum salts

	CO_3^{2-}	$PO_4 3-$	Cl^-/SO_4^{2-}	OH^-
Al^{3+}		$AlH_2PO_4^+$ $AlHPO_4 2+$ solid	$AlSO_4^+$ $Al(SO_4)_2^-$	$AlOH^{2+}$ $Al(OH)_2^+$ $Al(OH)_3^o$ $Al(OH)_4^-$ solid
Na^+				
H^+	HCO_3^- H_2CO_3	HPO_4^{2-} $H_2PO_4^-$ H_3PO_4		water

phate and hydroxide, resuting in formation of aluminum phosphate complexes and aluminum hydroxide complexes (monomers alone). Formation of any polymers is neglected in this table. Since chloride is very reluctant in forming a complex, we can assume that there will be no complex formation between aluminum and chloride. However, there will be complex formation between aluminum and sulfate [1]. Forming aluminum sulfato complexes means that less aluminum will be available for a reaction with phosphates, leading to less efficient P-removal with alum than with aluminum chloride.

However, experimental results did not support this hypothesis. There seems to be no difference in P-removal efficiency when aluminum chloride was used as the precipitant and when alum was used as the precipitant prior to the time that the minimum phosphate concentration is reached, as shown in Figures 4.3–4.6 and 4.11–4.13. After the minimum phosphate level is reached, the residual phosphate concentration bounced back to its initial value at the low and the medium initial alkalinity level when aluminum chloride was used as a coagulant. When alum was used, the extent of the increase was minimal and the residual phosphate concentration was less than 1.0 mg/l. This cannot be explained by a chemical equilibrium approach. The phosphate concentration increased when the wastewater lost all of its alkalinity. After all of alkalinity were depleted, an anion effect became evident. It appears that a sulfate ion is more effective in suppressing the increase in the phosphate concentration than a chloride ion. This cannot be explained by a chemical equilibrium approach. The only way a chemical equilibrium approach incorporates an anion effect is by including a complex. Apparently, anions does more than that and influences chemical phosphate removal somewhat differently from what is predicted by an equilibrium approach. This is another example of how complex chemical phosphate removal is.

According to a chemical equilibrium approach, the Ferguson model (II) simulates chemical phosphate removal when aluminum chloride is used rather than when alum is used as a precipitant. This model did not include aluminum sulfato complexes, leading to a case of aluminum chloride as a precipitant. The simulation results showed that the residual phosphate concentration bounced back to its original value quickly, as shown in Figure 5.13. This is exactly what was observed in experiments when aluminum chloride was used as a precipitant, as shown in Figure 4.3–4.6.

5.2 Evaluation of the Luedecke et al. model

Like the Ferguson model, the Luedecke et al. model is based on formation of two solids, ferric hydroxyphosphate, $Fe_rPO_4(OH)_{3r-3(s)}$ and ferric hydroxide, $am - FeOOH_{(s)}$. However, the Luedecke et al. model is unable to predict the final wastewater pH. Once a solution pH is given, the model computes equilibrium concentrations of species present in solution at that pH.

When Luedecke et al. plotted Fe/P ratios against equilibrium concentrations of phosphate ($C_{P,eq}$), they found their model made a wrong prediction, as shown in Figure 2.2. The model predicted increasing Fe/P ratios as $C_{P,eq}$ increased, which was opposite to their experimental data. They then introduced adsorption into their model to keep the model predictions in line with experimental observations. Based on the adsorption mechanism, they assumed a stoichiometric ratio of 2.5 at the zero value of residual phosphate, $C_{P,res}$. The approach for selecting the stoichiometric ratio used in the Luedecke et al. model is opposite to that used in the Ferguson model.

Ferguson and King [7] proposed three possible precipitation regions. They contended that the stoichiometric precipitation of phosphate would occur in zone I. In zone I, where insufficient aluminum is added to precipitate all of the phosphates, phosphate residuals are high compared to those in other zones. As the zone moves from I to III, phosphate residuals will decrease and the amount of aluminum needed to precipitate a given amount of the phosphates will increase. This will result in increasing Al/P ratios as phosphate residuals decrease. Assuming that the behavior of aluminum is the same as Fe(III) in phosphate precipitation, this was what Luedecke et al. observed in their experiments, as shown in Figure 2.2. The experimental observations made by Luedecke et al. may be explained by phosphate precipitation alone (Ferguson approach) rather than by phosphate precipitation and adsorption (Luedecke et al. approach).

The Ferguson model seems more practical than the Luedecke et al. model because the Ferguson model predicts the final wastewater pH, whereas the Luedecke et al. model does not. In addition, the application of the Luedecke et al. model should be preceded by a determination of an adsorption coefficient. This renders the application of the Luedecke et al. model more difficult.

6. REGRESSION MODELING

Regression modeling was used to determine a model which can predict a dependent variable based on the information about the independent variables. In this chapter, regression models were developed for the dependent variables of RALK[1], RPH[2], and ROP[3]. For each dependent variable, two regression models were developed: one without calcium in the wastewater and the other with calcium in the wastewater.

When regression models were developed using data in which no calcium is present in the wastewater, the data using aluminum chloride and alum as the precipitant were combined. The regression model developed in that way was used to compare use of aluminum chloride and alum in their effects on chemical phosphate removal. In order to differentiate between aluminum chloride and alum usage, a dummy variable (DCHEM) was introduced. This dummy variable was the only qualitative variable used in this study; all other variables were quantitative variables. The DCHEM was given a value of 1 or 0, depending on whether alum or aluminum chloride was used, respectively. When alum was used, the value of 1 was assigned to DCHEM. The value of 0 was assigned to DCHEM when aluminum chloride was used.

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[1] residual alkalinity in the wastewater in mg/l as $CaCO_3$

[2] residual pH of the wastewater in pH units

[3] residual phosphate in the wastewater in mg/l as P

After the regression model was developed using data in which no calcium was present in the wastewater, another model was developed using data in which calcium is present in the wastewater. Since most wastewaters contain considerable amount of calcium, this model can be used in field situations to predict residual parameters of alkalinity, pH, and phosphate.

These models were developed using SAS based on the following guidelines:

- Plots of a dependent variable against all independent variables (IALK[4], IPH[5], IOP[6], CA[7]and AL[8]) were examined to see which independent variable was important in relating to a dependent variable and to see whether there was any interaction between any independent variables. Once important independent variables, including possible interaction terms, were detected, a function form of those important independent variables was determined in relating to a dependent variable. This procedure allowed one to select all possibly important independent variables in predicting a dependent variable.

- All of these independent variables were checked by using a SAS procedure called RSQUARE. This procedure gives R^2 values and C(p) statistics for each combination of independent variables. Candidates for a model were selected based on these R^2 values and C(p) statistics.

- These candidates were then tested to see whether all independent variables

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[4] initial alkalinity in the wastewater in mg/l as $CaCO_3$

[5] initial pH of the wastewater

[6] initial phosphate in the wastewater in mg/l as P

[7] initial calcium in the wastewater in mg/l as $CaCO_3$

[8] dosage of aluminum salts in mole/l as Al

involved were significant. A model was selected if all independent variables were found significant by a t-test. When more than two candidates satisfied all criteria, then a candidate with fewer independent variables was chosen as a model.

- Once a model was chosen, its regression assumption was checked. If necessary, transformation was performed to correct any assumption violation.

In developing a model, only the constant variance assumption was checked to verify a model. While developing a regression model, it was learned that satisfying all regression assumptions simultanteously was sometimes difficult. This may be the reason why Bowerman and O'Connell [2] emphasized that only major departures from the assumptions should receive remedial actions. The independence assumption is assumed to hold because violation of this assumption occurs mostly for time series data. Data used in this study were not time series data. This leaves two assumptions: the constant variance and the normality assumptions. In this study, the normality assumption was assumed to hold and only the constant variance assumption was checked because the constant variance assumption is most likely to be violated.

6.1 Model for Residual Alkalinity

6.1.1 Without calcium

Based on the data in which no calcium was present in the wastewater, the following model was found to be the best to relate the residual alkalinity with the independent variables:

$$RALK = -0.06893 + 0.9692(IALK) - 117807(AL) \tag{6.1}$$

This model has a R^2 value of 0.9990 and a C(p) statistic of 4.

This model indicates that there is practically no difference in the residual alkalinity regardless of whether aluminum chloride or alum is used as a precipitant. This is shown by the absence of the DCHEM term in the model. If the difference was significant, the DCHEM term should appear in the model. This agrees well with the experimental observations. Figures 4.1 and 4.2 show that the decreasing pattern of the residual alkalinity was not affected by any other factor except aluminum dosage, as long as some alkalinity remained in the wastewater.

6.1.2 With calcium

Based on the data in which calcium is present in the wastewater, the following model was found to be the best to predict the residual alkalinity:

$$RALK = 3.852 + 0.9517(IALK) - 122283(AL) \tag{6.2}$$

This model has a R^2 value of 0.9958 and a C(p) statistic of 8.

This model predicted the residual alkalinity values well, as shown in Figure 6.1. This figure includes data at all initial phosphate levels. The symbol of "P" in the figure represents the predicted values. Careful examination of Figures 5.1 and 6.1 shows that the regression model predicted the residual alkalinity values better than did the Ferguson model (I).

This model indicates that the residual alkalinity linearly decreases with increasing alum dosage. This model also indicates that adding 1 mole of alum will destroy 2.4 eq of alkalinity in chemical phosphate removal.

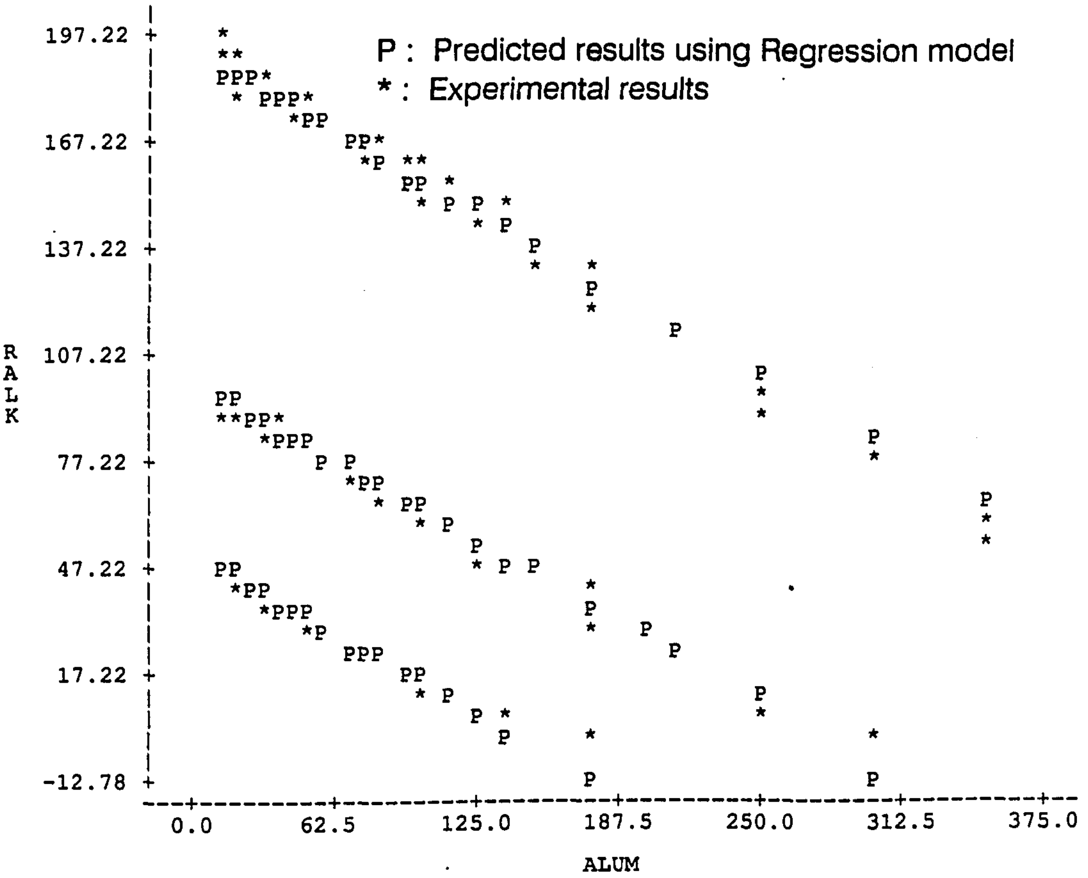

Figure 6.1: Comparison between the simulation and the experimental results of residual alkalinity (mg/l as $CaCO_3$) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) when calcium is present in the wastewater

6.2 Model for Residual pH

6.2.1 Without calcium

Based on the data in which no calcium is present in the wastewater, several candidates were selected for "best regression model" to predict the residual pH values. These candidates are shown in Table 6.1.

Table 6.1: Possible regression models for predicting residual pH when no calcium is present in the wastewater

No	Parameters	C(p)	R^2
1	IPH, AL · IALK, AL · IPH	9	0.9119
2	AL^2, IPH, AL · IALK, AL · IPH	3	0.9153
3	AL^2, IPH, AL · IALK, AL · IPH, AL · DCHEM	4	0.9155
4	AL, IPH, AL · IALK, AL · IPH	11	0.9119

Candidates 3 and 4 were discarded because the parameters of AL · DCHEM and AL were found insignificant in predicting RPH by a t-test. Since the DCHEM was found to be insignificant, there is practically no difference in the predicted residual pH between use of aluminum chloride and use of alum. Of the candidates 1 and 2, either one can be selected as the best regression model to relate the residual pH to the independent variables. Candidate model 2 shows the best R^2 value with low C(p) statistic. Candidate model 1 also has a high R^2 value, but its C(p) statistic is high. Therefore, candidate model 2 was selected as the best regression model to predict the residual pH when no calcium is present in the wastewater.

$$\begin{aligned} RPH &= 3.544 + 732443(AL^2) + 0.5397(IPH) + \\ &\quad 21.04(AL \cdot IALK) - 757.7(AL \cdot IPH) \end{aligned} \tag{6.3}$$

This regression model indicates that initial wastewater pH and alkalinity together with the aluminum dosage are important in predicting the residual pH. This is reasonable. The residual pH is determined by the wastewater's buffer intensity. The buffer intensity is a function of both pH and alkalinity. Therefore, the effects of the aluminum dosage become different depending on both the alkalinity and pH of the wastewater. This is reflected by two interaction terms in the regression model. As the wastewater's initial alkalinity increases, the extent of the decrease in the residual pH decreases, as indicated by the interaction between AL · IALK.

6.2.2 With calcium

Based on the data in which calcium is present in the wastewater, several candidates were also selected for the best regression model to predict the residual pH. These candidates are shown in Table 6.2.

Table 6.2: Possible regression models for predicting residual pH when calcium is present in the wastewater

No	Parameters	C(p)	R^2
1	IPH, AL · IALK, AL · IPH	52	0.9386
2	AL^2, IPH, AL · IALK, AL · IPH	4	0.9520
3	AL, IPH, AL · IALK, AL · IPH	11	0.9394

Candidate 3 was discarded because the parameter AL was found insignificant in predicting RPH by a t-test. This left two candidates: Candidate 2 was selected as the best regression model to predict the residual pH when calcium is present in the wastewater because Candidate 1 has too high a C(p) statistic. The resulting regression model is:

$$\begin{aligned} RPH &= 1.393 + 1365216(AL^2) + 0.8042(IPH) + \\ &\quad 15.45(AL \cdot IALK) - 767.6(AL \cdot IPH) \end{aligned} \qquad (6.4)$$

Comparison of the simulation results using this model to the experimental results is shown in Figure 6.2. This figure includes data at all initial alkalinity and phosphate levels. The symbol of "P" in the figure represents the predicted value. As indicated by the lower R^2 value, the prediction accuracy of the regression model for RPH was poorer than that of the model for predicting RALK. However, this model predicted the residual pH well. Compared to the Ferguson model (I), it is difficult to say which one provides the better prediction of the residual pH.

6.3 Model for Residual Phosphate

The regression model for predicting residual alkalinity indicates that all of the alkalinity will be destroyed by adding about 135 mg/l of alum as $Al_2(SO_4)_3 \cdot 18H_2O$ when the wastewater's alkalinity level is low (50 mg/l as $CaCO_3$). In the experiments, it was found that the residual phosphate concentration increased when all of the alkalinity in the wastewater had been destroyed. In practical situations, alum will not be added to such an extent that all of the alkalinities in wastewaters are consumed. Also, it is not likely that an alum dosage of more than 200 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$ will be used in chemical phosphate removal. Therefore, regression models for predicting residual phosphate concentration were developed using selected data. When alum was used as a precipitant, data in which the residual alkalinity value is greater than 0 and the alum dosage is less than 200 mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$

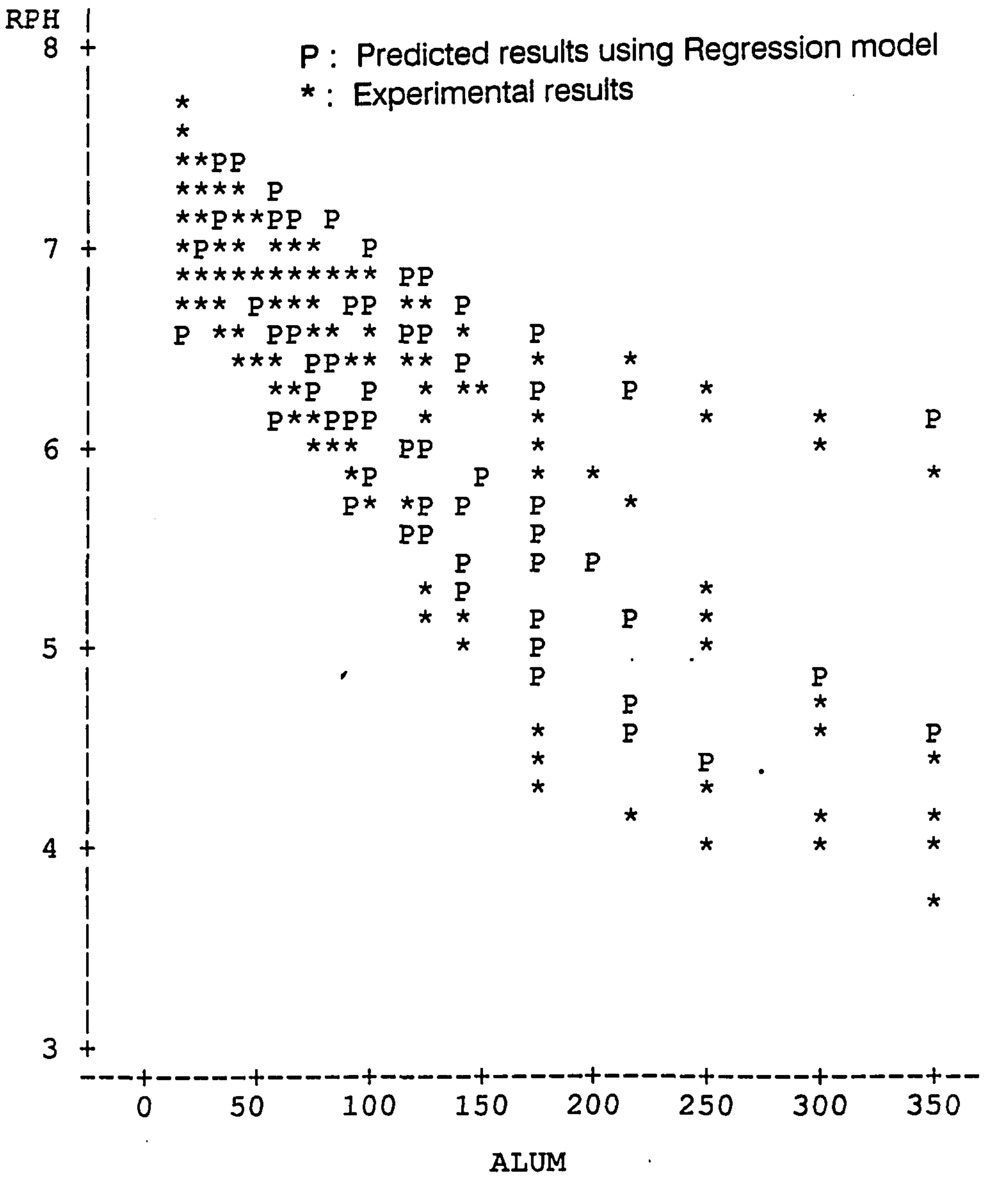

Figure 6.2: Comparison between regression model simulation results and the experimental results of residual pH as a function of aluminum dosage (mole/l as Al) when calcium is present in the wastewater

were used. When aluminum chloride was used, data in which the residual alkalinity value is greater than 20 mg/l as $CaCO_3$ and aluminum chloride dosage is less than 145 mg/l as $AlCl_3 \cdot 6H_2O$ were used. The reason why only residual alkalinity values greater than 20 mg/l were used is because an increase in the phosphate concentration occurred when the residual alkalinity was less than this value, as shown in Table 4.2.

Figures 4.7 through 4.12 demonstrate that the decreasing pattern of residual phosphate with increasing aluminum dosage was in a complex function form. To simplify the function form, the natural logarithm of the aluminum dosage was used for expressing the aluminum dosage. Figure 6.3 shows the residual phosphate concentration as a function of the natural logarithm of the aluminum dosage, $\ln(AL)$. According to this figure, the residual phosphate concentration decreased linearly with the $\ln(AL)$. Slopes of these lines were different as a function of the wastewater's initial phosphate level. As shown in Figures 4.7–4.12, there is not much difference in the residual phosphate concentration using high aluminum dosages. This difference becomes even smaller on the logarithm scale. Therefore, the residual phosphate concentrations converge at high aluminum dosages using the logarithm scale to represent aluminum dosage.

6.3.1 Without calcium

Based on the information in Figure 6.3, several candidate models were selected for the best regression model to predict the residual phosphate concentration when no calcium is present in the wastewater. These candidates are shown in Table 6.3.

Candidate models 2 and 3 were discarded because the parameters of DCHEM and $\ln(AL)$ were found to be insignificant parameters by a t-test. Candidate model 1 was

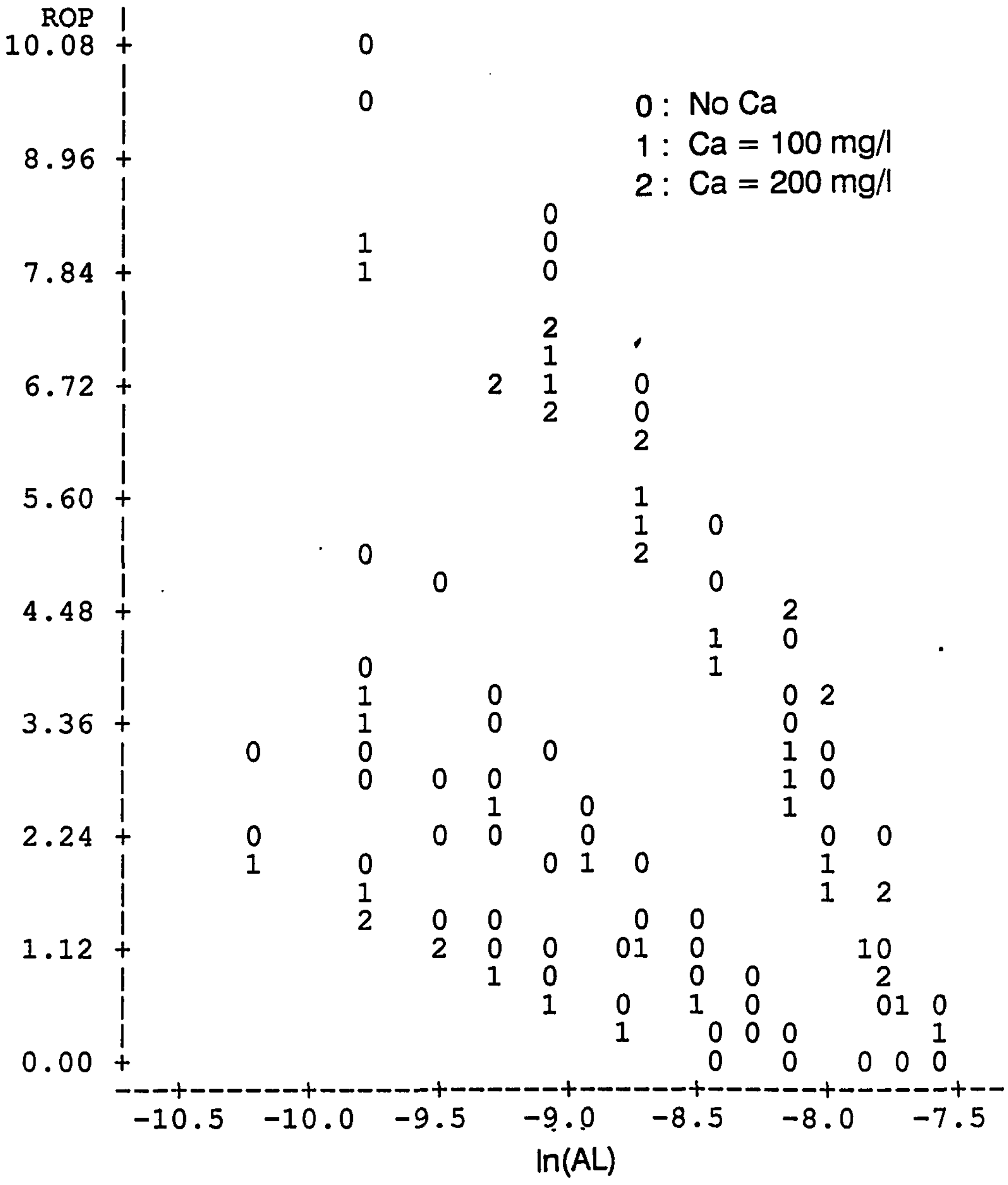

Figure 6.3: Residual phosphate concentration (mg/l as P) as a the function of natural logarithm of aluminum dosage (mole/l)

Table 6.3: Possible regression models for predicting residual phosphate when no calcium is present in the wastewater

No	Parameters	C(p)	R^2
1	IOP, $\ln(AL)\cdot$ IOP	1	0.9485
2	IOP, $\ln(AL)\cdot$ IOP, DCHEM	2	0.9487
3	$\ln(AL)$, IOP, $\ln(AL)\cdot$ IOP, DCHEM	4	0.9488

selected as the best regression model to predict the residual phosphate concentration when no calcium is present in the wastewater.

$$ROP = -1.744 - 3.012(IOP) - 0.4337(\ln(AL)\cdot IOP) \tag{6.5}$$

This regression model indicates that there is practically no difference in the residual phosphate concentration based on the use of aluminum chloride or alum as the precipitant as evidenced by the absence of the DCHEM term in the model. According to this model, only the initial phosphate concentration and aluminum dosage are important in predicting the residual phosphate concentration.

Comparison of simulation results using this model to the experimental results is shown in the previous chapter (Figures 5.3–5.11). The regression model predicted a negative residual phosphate concentration at high aluminum dosages. Since negative concentrations cannot exist, these negative values were considered as zero in preparing those figures. Those figures show that the model predicted the residual phosphate concentration well. It is difficult to say which one (regression model or Ferguson model) provides the better fit in predicting the residual phosphate concentration.

6.3.2 With calcium

Based on the data in which calcium is present in the wastewater, two possible candidate models were selected for evaluation as the best regression model to predict the residual phosphate concentration. These candidates are shown in Table 6.4.

Table 6.4: Possible regression models for predicting residual phosphate concentration when calcium is present in the wastewater

No	Parameters	C(p)	R^2
1	IOP, $\ln(AL) \cdot$ IOP	5	0.9524
2	$\ln(AL)$, IOP, $\ln(AL) \cdot$ IOP	4	0.9535

Candidate model 1 was selected as the best regression model to predict the residual phosphate concentration when calcium is present in the wastewater because the parameter $\ln(AL)$ was found to be insignificant by a t-test.

$$ROP = -1.567 - 2.415(IOP) - 0.3484(\ln(AL) \cdot IOP) \tag{6.6}$$

The simulation results using this model are compared in Figure 6.4 to the experimental results obtained when calcium is present in the wastewater. The data shown in this figure include all initial alkalinity and phosphate levels. This figure shows that the regression model predicts the residual phosphate concentration well when calcium is present in the wastewater.

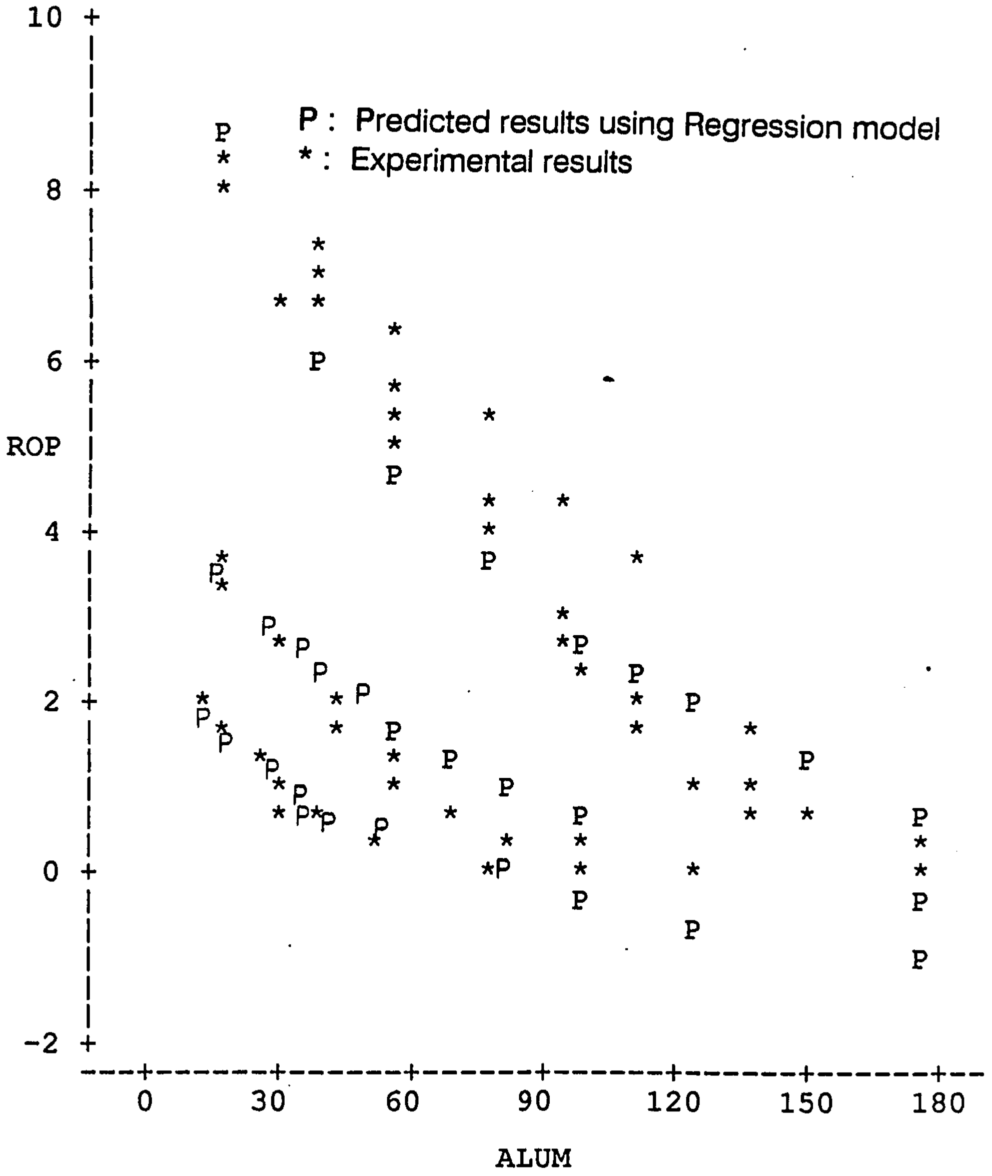

Figure 6.4: Comparison between regression model simulation results and the experimental results of the residual phosphate concentration (mg/l as P) as a function of alum dosage (mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$) when calcium is present in the wastewater

7. CONCLUSIONS

7.1 Comparison Between Use of Aluminum Chloride and Alum

There was no difference between use of aluminum chloride and alum as a phosphate precipitant in their effects on chemical phosphate removal. Their effects were evaluated in terms of three residual parameters of alkalinity, pH, and phosphate.

Experimental results showed no difference in the residual alkalinity and pH, but showed a difference in the residual phosphate concentration. Whether aluminum chloride or alum was used as a precipitant, the phosphate concentration decreased at low aluminum dosages. There was no difference in the decreasing pattern between use of aluminum chloride and use of alum. The phosphate concentration increased at high aluminum dosages because the wastewater lost its alkalinity. Since the wastewater still had enough alkalinity even at high aluminum dosages, no such an increase was observed at high alkalinity level. The increase occurred at the low and medium alkalinity levels. A difference between use of aluminum chloride and use of alum was the extent of the increase in the phosphate concentration at high aluminum dosages. The extent of the increase was minimal with use of alum, compared to that observed with use of aluminum chloride. This increase in the phosphate concentration seemed to be caused by the anions in the aluminum salt. The anion effects, which were not noticed when the wastewater still contained its alkalinity, became conspicuous after all of the alkalinity was consumed. Comparing two anions, the sulfate ion from use of alum suppressed the increase in the phosphate concentration more effectively than the chloride ion in the aluminum chloride.

Since the increase in the phosphate concentration was caused by lack of its alkalinity, comparison between aluminum chloride and alum using regression analysis was made using the data in which the phosphate concentration decreased with addition of aluminum salts. The comparison result using linear regression showed that the difference was practically insignificant.

7.2 Stoichiometric Phosphate Removal

Phosphates were found to be removed stoichiometrically in chemical phosphate removal while the molar dosage of Al(III) was less than the initial molar phosphate concentration. The stoichiometric ratio (1.2) between $Al(III)_{added}$ and $P_{removed}$ suggested that phosphates were removed by forming a solid of aluminum hydroxyphosphate as follows:

$$1.2Al^{3+} + H_2PO_4^- + 2.6HCO_3^- \rightleftharpoons Al_{1.2}H_2PO_4(OH)_{2.6} \downarrow + 2.6CO_2 \uparrow \qquad (7.1)$$

The equilibrium solubility product for aluminum hydroxyphosphate was calculated and its negative logarithm was found to be 35.3. Examination of the solubility of aluminum hydroxyphosphate indicates that soluble phosphate residual reaches its minimum around a pH of 6.0 and increases as the pH moves away from pH 6.0.

7.3 Calcium Effects

A calcium effect was not observed on the residual alkalinity and pH, but there was an effect on the residual phosphate.

The decreasing pattern of the residual pH was the same whether calcium was present in the wastewater or not. Since the initial pH of the wastewater with calcium was lower than that of the wastewater without calcium, the residual pH was always lower when calcium was present in the wastewater than when no calcium was present. This made the pH variation curves with increasing aluminum dosage obtained with calcium more compressed than the curves obtained without calcium.

Calcium was found to be beneficial to chemical phosphate removal at low aluminum dosage. A stoichiometric phosphate removal occurred immediately with addition of aluminum salts when calcium was present in the wastewater. A threshold dosage was needed to initiate the stoichiometric removal when no calcium was present in the wastewater. This was caused by low pH values. While phosphates were removed stoichiometrically, phosphate residuals were controlled by the solubility of aluminum hydroxyphosphate. The solubility of aluminum hydroxyphosphate favored low pH conditions over high pH conditions for low phosphate residuals while the pH stayed in the range of 6 to 9. The benefit of calcium diminished at high aluminum dosages because phosphate residuals were no longer controlled by the solubility of aluminum hydroxyphosphate alone. At high aluminum dosages, phosphate residuals were controlled by the solubility of aluminum hydroxyphosphate as well as by the solubility of aluminum hydroxide.

When calcium was present in the wastewater, a ratio of $[Al]_a/[P]_r$ was sometimes less than 1. This could be caused by calcium-phosphate precipitation. The calculation of solubility product suggested that tricalcium phosphate could precipitate at the low alum dosage (18.75 mg/l). The calculation also indicated that the negative logarithm of the equilibrium solubility product is 27.5 rather than 23.56 suggested by Menar and Jenkins. With further addition of aluminum salts, the residual pH decreased and this tricalcium phosphate dissolved.

7.4 Evaluation of Equilibrium Models

Currently available models which describe chemical phosphate removal based on a chemical equilibrium approach were evaluated. Of the two models described in the literature, the Ferguson model seems more practical for convenient use than the Luedecke et al. model for two reasons. These are:

- The Ferguson model predicts the final wastewater pH, whereas the Luedecke et al. model does not. Once the pH is given, the Luedecke et al. model starts working.
- The Luedecke et al. model was originally based on phosphate precipitation to describe chemical phosphate removal. After the model results were found not to agree with experimental results, adsorption was brought in to keep the model results in agreement with experimental results. This necessitates that an adsorption coefficient be determined before the model starts working.

For these reasons, use of the Ferguson model was mainly evaluated in this study. Once developed, a model for chemical phosphate removal should be able to describe what is happening in chemical phosphate removal and be able to predict residual parameters. In terms of predicting residual parameters, the Ferguson model worked very well. The model was able to predict the residual alkalinity, pH, and phosphate values with considerable accuracy. Of these parameters, the Ferguson model predicted the residual phosphate concentration best. Despite its accuracy in predicting the residual parameters, the Ferguson model was unable to give a real picture of what was going on during chemical phosphate removal. The reason was explained by some problems noted in use of the Ferguson model. These problems are:

- The Ferguson model did not incorporate the use of aluminum polymers even though these polymers are predominant aluminum species present in chemical phosphate removal. Apparently, the Ferguson model excluded the polymers and used the monomers as sole aluminum hydroxo complexes due to difficulty in making numerical solutions of the model.
- According to a chemical equilibrium approach, use of aluminum chloride should make the residual phosphate concentration less than does use of alum. This conclusion was found to be wrong in the experiments. This adds to the list of reasons why chemical phosphate removal cannot be explained using a chemical equilibrium approach alone.

7.5 Regression Modeling

Regression models to predict the residual parameters were developed based on jar tests with synthetic wastewaters containing $NaHCO_3$-NaH_2PO_4 and $Ca(NO_3)_2$-$NaHCO_3$-NaH_2PO_4. Regression models developed with the synthetic wastewater without calcium were used to compare aluminum chloride and alum in their effects on chemical phosphate removal. Regression analysis so performed indicates that there is practically no difference between aluminum chloride and alum in their effects on chemical phosphate removal. Regression models developed with the synthetic wastewater with calcium are presented so that they can be used to predict residual parameters.

7.5.1 Alkalinity

The regression model to predict the residual alkalinity is shown in equation 7.2.

$$RALK = 3.852 + 0.9517(IALK) - 122283(AL) \tag{7.2}$$

In this regression model, RALK and IALK represent the residual and initial alkalinity values in mg/l as $CaCO_3$ and AL represent aluminum dosage in mole/l. This model has a R^2 value of 0.9958 and a C(p) statistic of 8.

7.5.2 pH

The regression model to predict the residual pH is shown in equation 7.3.

$$\begin{aligned} RPH &= 1.393 + 1365126(AL^2) + 0.8042(IPH) + \\ & \quad 15.45(AL \cdot IALK) - 767.6(AL \cdot IPH) \end{aligned} \tag{7.3}$$

In this regression model, RPH and IPH represent the residual and initial pH and IALK and AL are the same as defined in the alkalinity model. This model has a R^2 value of 0.9520 and a C(p) statistic of 4.

7.5.3 Phosphate

The regression model to predict the residual phosphate is shown in equation 7.4.

$$ROP = -1.567 - 2.415(IOP) - 0.3484(\ln(AL) \cdot IOP) \tag{7.4}$$

In this regression model, IOP represents the initial phosphate value in mg/l as P and $\ln(AL)$ represents the natural logarithm of aluminum dosage. This model has a R^2 value of 0.9524 and a C(p) statistic of 5.

7.5.4 Comparison between the regression model and the Ferguson model

The Ferguson model predicted the residual phosphate concentration better than it did the residual alkalinity and pH values. On the other hand, the regression model was at its best when used to predict the residual alkalinity values. The regression model still predicted the residual phosphate concentration well. The accuracy of predicting the residual phosphate concentration using the regression model was not less than the accuracy using the Ferguson model.

The Ferguson model predicted the residual phosphate concentration well and is valuable for this purpose. The Ferguson model can be used for design purposes if post-precipitation is desired to remove phosphates because it can give a fairly good prediction of the residual alkalinity, pH, and phosphate concentrations. However, when wastewater has a large amount of condensed and organic phosphates as well as particulate phosphates, the Ferguson model cannot be considered as a reliable model.

The regression models developed in this study can be also used for design purposes if post-precipitation is desired. However, these models cannot be used when major components of the phosphates to be removed are condensed and organic phosphates as well as particulate phosphates. A major advantage of a regression model is that it can be custom-developed for a specific wastewater condition. If wastewater has more condensed and organic phosphates, jar tests can be conducted to cover all possible plant conditions. Those experimental conditions can then be used to develop a new plant-specific regression model.

Chemical phosphate removal was found to be more complicated than expected. There are still many things to learn about chemical phosphate removal. For example, a model based on a chemical equilibrium approach cannot explain the chemical effect. This does not mean that developing a better equilibrium model should be discouraged. Instead, efforts should be made to develop a better equilibrium model. A better equilibrium model should include the presence and effects of aluminum polymer as well as anion effects, or other unknown effects. Sometimes, a regression model can be more valuable than an equilibrium model because of the many uncertainties in chemical phosphate removal. In this study, regression modeling for chemical phosphate removal has been conducted to demonstrate that it can be developed easily and can be used successfully in predicting residual parameters such as alkalinity, pH, and phosphate.

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APPENDIX A. RAW DATA FROM EXPERIMENTS WITH ALUMINUM CHLORIDE

Raw data from experiments using aluminum chloride as a precipitant are shown in this appendix. Below are nomenclature used:

IALK initial alkalinity in mg/l as $CaCO_3$

IOP initial phosphate in mg/l as P

ALCL3 aluminum chloride dosage in mg/l as $AlCl_3 \cdot 6H_2O$

RALK residual alkalinity in mg/l as $CaCO_3$

RPH residual pH

ROP residual phosphate in mg/l as P

```
                         NO CALCIUM

-------------- IALK=50 IOP=3.1 -------------

OBS        ALCL3       RALK        RPH        ROP

  1        12.50        43        7.36       2.08
  2        18.75        40        7.26       1.51
  3        25.00        36        7.13       0.93
  4        31.25        34        7.06       0.61
  5        37.50        31        7.04       0.34
  6        43.75        27        7.00       0.11
  7        50.00        23        6.67       0.11
  8        62.50        17        6.33       0.04
  9        75.00        10        5.93       0.04
 10        87.50         5        5.27       2.53
 11       100.00         5        4.69       2.71
 12       125.00         5        4.54       2.71

-------------- IALK=50 IOP=5.16 ------------

OBS        ALCL3       RALK        RPH        ROP

 13        12.50        43        7.28       4.70
 14        18.75        40        7.17       3.53
 15        25.00        37        7.07       2.90
 16        31.25        35        6.98       2.49
 17        37.50        32        6.92       1.96
 18        43.75        28        6.84       1.38
 19        50.00        25        6.77       0.80
 20        62.50        19        6.73       0.23
 21        75.00        12        6.48       0.07
 22        87.50         4        5.27       1.29
 23       100.00         3        4.73       3.39
 24       125.00         3        4.61       4.57
```

```
                         NO CALCIUM

----------- IALK=50 IOP=10.25 -------------

  OBS     ALCL3      RALK      RPH      ROP

   25      12.5       44      7.12     9.96
   26      25.0       37      6.93     7.74
   27      37.5       32      6.74     6.57
   28      50.0       26      6.64     5.42
   29      62.5       21      6.50     4.12
   30      75.0       16      6.34     3.09
   31     100.0        4      5.67     0.95
   32     112.5        0      4.63     0.29
   33     125.0        0      4.32     4.95
   34     150.0        0      4.20     7.53
   35     200.0        0      4.11     7.97
   36     250.0        0      4.05     8.64

----------- IALK=101 IOP=3.1 ------------

 OBS      ALCL3      RALK      RPH      ROP

  37      12.50       86      7.53     2.30
  38      13.75       89      7.70     2.49
  39      15.00       87      7.60     1.84
  40      16.25       88      7.61     1.86
  41      17.50       87      7.59     1.72
  42      18.75       85      7.47     1.55
  43      25.00       82      7.38     1.15
  44      31.25       79      7.35     0.73
  45      37.50       77      7.32     0.53
  46      43.75       74      7.26     0.27
  47      50.00       69      7.20     0.14
  48      75.00       56      6.95     0.03
  49     100.00       41      6.80     0.02
  50     125.00       33      6.60     0.04
  51     150.00       20      5.93     1.05
  52     175.00       15      4.97     1.90
  53     200.00       11      4.63     2.63
  54     250.00        0      4.50     2.66
```

```
                      NO CALCIUM

----------- IALK=101 IOP=5.16 ------------

 OBS        ALCL3      RALK       RPH       ROP

  55        18.75       90       7.50      4.84
  56        25.00       88       7.42      2.86
  57        31.25       83       7.33      2.28
  58        37.50       80       7.25      1.79
  59        43.75       79       7.21      1.45
  60        50.00       76       7.14      1.02
  61        56.25       71       7.12      0.69
  62        62.50       67       7.12      0.39
  63        68.75       65       7.03      0.26
  64        75.00       61       6.99      0.13
  65        81.25       59       7.00      0.09
  66        87.50       59       6.95      0.09
  67       100.00        .        .        0.05
  68       118.75        .        .        0.03
  69       150.00       24       6.46      0.04
  70       200.00        9       4.80      3.56
  71       250.00        9       4.68      4.65

----------- IALK=101 IOP=10.25 -----------

 OBS        ALCL3      RALK       RPH       ROP

  72        18.75       87       7.33      9.79
  73        25.00       84       7.30      9.40
  74        31.25       82       7.25      7.95
  75        37.50       77       7.19      7.13
  76        43.75       76       7.14      6.46
  77        56.25       71       7.06      5.20
  78        62.50       67       7.00      4.66
  79        68.75       64       6.96      3.98
  80        75.00       63       6.93       .
  81        81.25       56       6.92      2.63
  82        87.50       54       6.81      2.18
  83       100.00       47       6.74      1.15
  84       118.75       41       6.75      0.62
  85       150.00       16       5.98      0.14
  86       175.00        9       5.62      0.11
  87       250.00        3       4.65      5.53
```

```
                         NO CALCIUM

------------- IALK=198 IOP=3.1 -------------

    OBS       ALCL3       RALK        RPH        ROP

     88       12.50        186       7.94       2.82
     89       18.75        184       7.88       2.29
     90       25.00        181       7.75       1.50
     91       31.25        177       7.69       1.28
     92       37.50        172       7.56       0.78
     93       43.75          .          .       0.57
     94       50.00        166       7.56       0.27
     95       75.00        155       7.40       0.05
     96      112.50        132       7.24       0.01
     97      150.00        109       7.08       0.01
     98      200.00         78       6.90       0.01
     99      250.00         54       6.55       0.01

------------ IALK=198 IOP=5.16 ------------

    OBS       ALCL3       RALK        RPH        ROP

    100       12.50        186       7.88       4.84
    101       18.75        184       7.82       4.30
    102       25.00        180       7.74       3.62
    103       31.25        179       7.67       3.11
    104       37.50        174       7.60       2.95
    105       43.75        173       7.57       2.21
    106       50.00        171       7.62       1.76
    107       62.50        162       7.46       0.84
    108       75.00        156       7.41       0.37
    109       87.50        148       7.31       0.30
    110      100.00        140       7.30       0.07
    111      125.00        126       7.19       0.04
    112      150.00        111       7.02       0.04
    113      200.00         81       6.82       0.01
    114      250.00         57       6.58       0.02
```

```
                         NO CALCIUM

   ------------ IALK=198 IOP=10.25 ---------

      OBS      ALCL3      RALK       RPH       ROP

      115       12.5       187      7.81     10.14
      116       25.0       180      7.60      9.48
      117       37.5       174      7.54      8.35
      118       50.0       167      7.46      6.57
      119       62.5       163      7.39      5.27
      120       75.0       154      7.32      4.06
      121       87.5       150      7.25      2.90
      122      100.0       145      7.18      2.09
      123      125.0       133      7.10      0.91
      124      150.0       116      7.04      0.18
      125      200.0        89      6.84      0.05
      126      250.0        59      6.62      0.06
```

APPENDIX B. RAW DATA FROM EXPERIMENTS WITH ALUM

Raw data from experiments using alum as a precipitant are shown in this appendix. Below are nomenclature used:

CA initial calcium in mg/l as Ca

IALK initial alkalinity values mg/l as $CaCO_3$

IOP initial phosphate in mg/l as P

ALUM alum dosage in mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$

RALK residual alkalinity in mg/l as $CaCO_3$

RPH residual pH

ROP residual phosphate in mg/l as P

```
                        WITH CALCIUM

------------ CA=0 IALK=50 IOP=3.1 -----------

    OBS       ALUM       RALK       RPH       ROP

      1      12.50        45       7.30      2.16
      2      18.75        43       7.22      1.82
      3      25.00        41       7.17      1.50
      4      31.25        39       7.15      1.08
      5      37.50        37       7.14      0.86
      6      50.00        33       7.10      0.42
      7      75.00        21       6.90      0.03
      8     125.00         6       6.17      0.02
      9     175.00         1       4.59      0.05
     10     250.00         0       4.40      0.10
     11     300.00         0       4.31      0.11
     12     350.00         0       4.24      0.16

----------- CA=0 IALK=50 IOP=5.16 ------------

    OBS       ALUM       RALK       RPH       ROP

     13      18.75        43       7.04      3.92
     14      31.25        38       6.92      2.86
     15      43.75        34       6.88      2.18
     16      56.25        30       6.83      1.40
     17      68.75        26       6.84      0.77
     18      81.25        21       6.78      0.30
     19     100.00        14       6.62      0.07
     20     125.00         5       6.21      0.04
     21     175.00         1       4.57      0.07
     22     250.00         0       4.39      0.16
     23     300.00         0       4.32      0.21
     24     350.00         0       4.22      0.39
```

```
                   WITH CALCIUM

----------- CA=0 IALK=50 IOP=10.25 -----------

   OBS       ALUM       RALK       RPH       ROP

    25      18.75       42        6.98      9.43
    26      37.50       37        6.83      7.72
    27      56.25       30        6.67      6.72
    28      75.00       24        6.60      4.70
    29      93.75       18        6.42      3.39
    30     112.50       13        6.30      2.10
    31     137.50        4        5.78      0.54
    32     175.00        0        4.31      0.28
    33     212.50        0        4.20      0.34
    34     250.00        0        4.13      0.42
    35     300.00        0        4.09      0.61
    36     350.00        0        4.07      0.84

----------- CA=0 IALK=101 IOP=3.1 ------------

   OBS       ALUM       RALK       RPH       ROP

    37      12.50       92        7.75      2.95
    38      18.75       91        7.65      2.86
    39      25.00       89        7.51      2.28
    40      31.25       86        7.47      1.43
    41      37.50       83        7.41      1.08
    42      50.00       81        7.33      0.60
    43      75.00       69        7.13      0.07
    44     125.00       48        6.99      0.02
    45     175.00       31        6.57      0.02
    46     250.00        6        5.43      0.02
    47     300.00        2        4.63      0.03
    48     350.00        0        4.48      0.03
```

```
                         WITH CALCIUM

----------- CA=0 IALK=101 IOP=5.16 -----------

    OBS       ALUM       RALK       RPH       ROP

     49       31.25       86        7.36      3.47
     50       43.75       82        7.29      2.54
     51       56.25       77        7.20      1.84
     52       68.75       73        7.15      1.13
     53       81.25       68        7.12      0.60
     54      100.00       60        7.00      0.15
     55      125.00       46        6.94      0.03
     56      175.00       27        6.65      0.02
     57      300.00        2        4.68      0.04
     58      350.00        0        4.51      0.06

---------- CA=0 IALK=101 IOP=10.25 -----------

    OBS       ALUM       RALK       RPH       ROP

     59       18.75       90        7.39      9.96
     60       37.50       84        7.25      8.17
     61       56.25       77        7.07      6.39
     62       75.00       70        7.00      4.82
     63       93.75       64        6.93      3.67
     64      112.50       60        6.87      2.91
     65      137.50       50        6.70      1.17
     66      212.50       21        6.40      0.06
     67      250.00       10        5.95      0.04
     68      300.00        2        4.64      0.07
     69      350.00        0        4.40      0.10
```

WITH CALCIUM

```
----------- CA=0 IALK=198 IOP=3.1 -----------

 OBS       ALUM        RALK        RPH        ROP

  70       12.50        188       8.27       3.01
  71       18.75        186       8.15       2.98
  72       25.00        184       8.08       2.90
  73       31.25        182       8.01       2.27
  74       37.50        181       7.95       2.03
  75       50.00        174       7.78       1.05
  76       75.00        165       7.49       0.26
  77      100.00        156       7.38       0.07
  78      125.00        143       7.28       0.03
  79      175.00        120       7.06       0.01
  80      250.00         91       6.90       0.03
  81      350.00         56       6.60       0.03

----------- CA=0 IALK=198 IOP=5.16 -----------

 OBS       ALUM        RALK        RPH        ROP

  82       18.75        186       7.77       4.96
  83       25.00        184       7.73       4.89
  84       31.25        181       7.56       3.55
  85       37.50        179       7.57       3.13
  86       43.75        176       7.49       2.56
  87       56.25        171       7.42       1.96
  88       68.75        167       7.39       1.38
  89       81.25        162       7.35       0.81
  90      100.00        149       7.20       0.05
  91      150.00        134       7.09       0.05
  92      250.00         91       6.73       0.04
  93      350.00         56       6.50       0.04
```

```
                      WITH CALCIUM

---------- CA=0 IALK=198 IOP=10.25 -----------

   OBS       ALUM       RALK       RPH        ROP

    94       18.75       185       7.55       9.96
    95       37.50       179       7.44       8.29
    96       56.25       172       7.34       6.75
    97       75.00       166       7.27       5.30
    98       93.75       160       7.18       4.33
    99      112.50       152       7.10       2.94
   100      137.50       148       7.04       2.15
   101      175.00       128       6.90       0.45
   102      212.50       113       6.83       0.13
   103      250.00       103       6.71       0.07
   104      300.00        75       6.62       0.07
   105      350.00        60       6.44       0.09

----------- CA=100 IALK=50 IOP=3.1 -----------

   OBS       ALUM       RALK       RPH        ROP

   106       12.50       47        7.11       2.02
   107       18.75       44        6.95       1.65
   108       25.00       42        6.85       1.28
   109       31.25       39        6.72       0.91
   110       37.50       37        6.63       0.63
   111       50.00       31        6.42       0.26
   112       75.00       24        6.08       0.09
   113      125.00        3        5.13       0.01
   114      175.00        0        4.47       0.01
   115      250.00        0        4.24       0.02
   116      300.00        0        4.17       0.05
   117      350.00        0        4.05       0.07
```

WITH CALCIUM

```
---------- CA=100 IALK=50 IOP=5.16 -----------

   OBS       ALUM       RALK        RPH        ROP

   118       18.75       43         6.91       3.50
   119       31.25       39         6.73       2.72
   120       43.75       34         6.55       1.89
   121       56.25        .          .          .
   122       68.75       26         6.26       0.69
   123       81.25       21         6.06       0.34
   124      100.00       15         5.73       0.05
   125      125.00        6         5.25       0.04
   126      175.00        0         4.47       0.08
   127      250.00        0         4.27       0.12
   128      300.00        0         4.19       0.16
   129      350.00        0         4.11       0.26

---------- CA=100 IALK=50 IOP=10.25 ----------

   OBS       ALUM       RALK        RPH        ROP

   130       18.75       45         6.87       8.20
   131       37.50       37         6.61       6.92
   132       56.25       31         6.40       5.57
   133       75.00       23         6.20       4.17
   134       93.75       18         6.02       3.02
   135      112.50       12         5.72       1.78
   136      137.50        5         5.13       0.56
   137      175.00        0         4.30       0.24
   138      212.50        0         4.13       0.34
   139      250.00        0         4.06       0.40
   140      300.00        0         3.94       0.54
   141      350.00        0         3.73       0.65
```

```
                   WITH CALCIUM

--------- CA=100 IALK=101 IOP=3.1 ------------

   OBS      ALUM      RALK      RPH      ROP

   142      12.50      97      7.58     2.02
   143      18.75      94      7.39     1.72
   144      25.00      92      7.27     1.35
   145      31.25      89      7.22     1.00
   146      37.50      86      7.04     0.66
   147      50.00      82      6.88     0.31
   148      75.00      72      6.75     0.07
   149     125.00      51      6.36     0.01
   150     175.00      32      5.88     0.02
   151     250.00       8      5.10     0.01
   152     300.00       2      4.58     0.01
   153     350.00       0      4.40     0.02

---------- CA=100 IALK=101 IOP=5.16 ----------

   OBS      ALUM      RALK      RPH      ROP

   154      18.75      94      7.66     3.56
   155      31.25      88      7.31     2.56
   156      43.75      84      7.16     1.84
   157      56.25      79      7.03     1.18
   158      68.75      74      6.89     0.63
   159      81.25      69      6.60     0.30
   160     100.00      64      6.48     0.15
   161     125.00      53      6.47     0.06
   162     175.00      34      5.99     0.02
   163     250.00       8      5.17     0.01
   164     300.00       1      4.56     0.02
   165     350.00       0      4.45     0.04
```

```
                    WITH CALCIUM

-------- CA=100 IALK=101 IOP=10.25 -----------

   OBS       ALUM       RALK       RPH       ROP

   166       18.75       94       7.10      7.95
   167       37.50       86       7.00      6.75
   168       56.25       79       6.84      5.25
   169       75.00       72       6.73      3.98
   170      100.00       63       6.58      2.44
   171      125.00       53       6.41      1.13
   172      150.00       48       6.29      0.66
   173      175.00       39       6.13      0.22
   174      200.00       28       5.91      0.07
   175      250.00       11       5.35      0.04
   176      300.00        2       4.61      0.06
   177      350.00        0       4.46      0.13

---------- CA=100 IALK=198 IOP=3.1 -----------

   OBS       ALUM       RALK       RPH       ROP

   178       12.50      195       7.49      2.09
   179       18.75      190       7.43      1.74
   180       25.00      186       7.36      1.39
   181       31.25      184       7.29      1.12
   182       37.50      181       7.23      0.81
   183       50.00      178       7.13      0.45
   184       75.00      168       6.94       .
   185      100.00      159       6.82      0.04
   186      125.00        .       6.70      0.02
   187      175.00      128       6.47      0.02
   188      250.00       95       6.20      0.01
   189      350.00       60       5.82      0.01
```

```
                         WITH CALCIUM

--------- CA=100 IALK=198 IOP=5.16 -----------

   OBS      ALUM       RALK      RPH      ROP

   190      18.75      186        .       3.39
   191      31.25      180        .       2.73
   192      43.75      175        .       1.96
   193      56.25      172        .       1.32
   194      68.75      167        .       0.83
   195      81.25      187      6.90      0.43
   196     100.00      155        .       0.24
   197     125.00      143      6.70      0.08
   198     175.00      125      6.48      0.02
   199     250.00       93      6.20      0.02
   200     300.00       76      6.02      0.02
   201     350.00       56      5.82      0.04

--------- CA=100 IALK=198 IOP=10.25 ----------

    OBS      ALUM       RALK     RPH      ROP

    202      18.75      185       .       8.06
    203      37.50      177       .       6.66
    204      56.25      171       .       5.27
    205      75.00      163       .       3.92
    206      93.75      156       .       2.75
    207     112.50      150       .       1.92
    208     137.50      142       .       1.15
    209     175.00      128       .       0.34
    210     212.50      112       .       0.12
    211     250.00       98       .       0.06
    212     300.00        .       .        .
    213     350.00       60       .       0.07
```

```
                    WITH CALCIUM

---------- CA=200 IALK=50 IOP=3.1 ------------

   OBS       ALUM      RALK      RPH      ROP

   214      12.50       45      6.96     1.84
   215      18.75       43      6.84     1.55
   216      25.00       40      6.76     1.21
   217      31.25       39      6.67     0.88
   218      37.50       37      6.60     0.64
   219      50.00       32      6.41     0.21
   220      75.00       23      6.06     0.03
   221     100.00       13      5.66     0.02
   222     125.00        5      5.18     0.01
   223     175.00        0      4.56     0.04
   224     250.00        0      4.32     0.08
   225     350.00        0      4.21     0.14

---------- CA=200 IALK=50 IOP=5.16 -----------

   OBS       ALUM      RALK      RPH      ROP

   226      18.75       43      6.77     3.42
   227      31.25       39      6.62     2.63
   228      43.75       33      6.47     1.83
   229      56.25       29      6.29     1.15
   230      68.75       25      6.17     0.59
   231      81.25       21      6.00     0.24
   232     100.00       14      5.70     0.05
   233     125.00        7      5.19     0.04
   234     175.00        0      4.47     2.69
   235     250.00        0      4.28     2.56
   236     300.00        0      4.20     0.86
   237     350.00        0      4.14     0.51
```

```
                    WITH CALCIUM

--------- CA=200 IALK=50 IOP=10.25 ------------

   OBS     ALUM      RALK     RPH     ROP

   238     18.75      43      6.65    8.17
   239     37.50      36      6.46    7.33
   240     56.25      29      6.28    6.26
   241     75.00      24      6.11    5.30
   242     93.75      18      5.91    4.43
   243    112.50      12      5.65    3.68
   244    137.50       5      4.99    1.62
   245    175.00       0      4.27    0.48
   246    212.50       0      4.14    1.87
   247    250.00       0      4.07    1.68
   248    300.00       0      4.00    2.16
   249    350.00       0      3.95    5.89

---------- CA=200 IALK=101 IOP=3.1 ------------

   OBS     ALUM      RALK     RPH     ROP

   250     12.50      96      7.28    1.96
   251     18.75      94      7.17    1.51
   252     25.00      92      7.10    1.26
   253     31.25      88      7.00    0.81
   254     37.50      88      6.98    0.75
   255     50.00      82      6.81    0.27
   256     75.00      71      6.60    0.04
   257    100.00      61      6.41    0.02
   258    125.00      50      6.21    0.01
   259    175.00      31      5.85    0.01
   260    250.00       9      5.06    0.01
   261    350.00       0      4.45    0.03
```

```
                    WITH CALCIUM

--------- CA=200 IALK=101 IOP=5.16 ------------

   OBS       ALUM        RALK       RPH       ROP

   262       18.75        93        7.11      3.40
   263       31.25        89        6.98      2.59
   264       43.75        84        6.86      1.82
   265       56.25        79        6.75      1.18
   266       68.75        74        6.65      0.68
   267       81.25        70        6.53      0.31
   268      100.00        61        6.41      0.08
   269      125.00        53        6.27      0.04
   270      175.00        32        5.87      0.02
   271      250.00         8        5.10      0.01
   272      300.00         2        4.65      0.02
   273      350.00         0        4.45      0.04

--------- CA=200 IALK=101 IOP=10.25 -----------

   OBS       ALUM        RALK       RPH       ROP

   274       18.75        94        7.00      8.15
   275       31.25        86        6.83      6.62
   276       56.25        79        6.70      5.25
   277       75.00        72        6.60      4.05
   278       93.75        65        6.48      2.79
   279      112.50        59        6.36      1.82
   280      137.50        50        6.23      0.86
   281      175.00        36        5.98      0.15
   282      212.50        22        5.68      0.06
   283      250.00        12        5.27      0.03
   284      300.00         2        4.65      0.06
   285      350.00         0        4.42      0.11
```

```
                        WITH CALCIUM

--------- CA=200 IALK=198 IOP=3.1 -------------

   OBS        ALUM        RALK        RPH       ROP

   286       12.50         194       7.43      2.02
   287       18.75         188       7.41      1.72
   288       25.00         186       7.33      1.32
   289       31.25         184       7.28      1.10
   290       37.50         182       7.23      0.78
   291       50.00         177       7.14      0.40
   292       75.00         170       6.99      0.13
   293      100.00         160       6.84      0.05
   294      125.00         150       6.71      0.04
   295      175.00         127       6.47      0.03
   296      250.00          95       6.18      0.02
   297      350.00          60       5.82      0.03

---------- CA=200 IALK=198 IOP=5.16 -----------

   OBS        ALUM        RALK        RPH       ROP

   298       18.75         185       7.30      3.33
   299       31.25         184       7.22      2.56
   300       43.75         177       7.14      1.83
   301       56.25         174       7.05      1.25
   302       68.75         170       6.98      0.75
   303       81.25         166       6.89      0.42
   304      100.00         160       6.79      0.15
   305      125.00         149       6.69      0.06
   306      175.00         128       6.47      0.01
   307      250.00          97       6.22      0.01
   308      300.00          75       6.06      0.01
   309      350.00          61       5.82      0.02
```

WITH CALCIUM

```
--------- CA=200 IALK=198 IOP=10.25 ------------

   OBS        ALUM       RALK       RPH       ROP

   310        18.75       182       7.25      7.95
   311        37.50       178       7.11      6.57
   312        56.25       172       7.00      5.09
   313        75.00       166       6.90      3.86
   314        93.75       161       6.82      2.69
   315       112.50       155       6.76      1.82
   316       137.50       143       6.62      0.91
   317       175.00       130       6.49      0.29
   318       212.50       116       6.37      0.11
   319       250.00       103       6.25      0.05
   320       300.00        82       6.08      0.05
   321       350.00        66       5.89      0.02
```

APPENDIX C. RAW DATA FOR COMPARISON OF RESIDUAL PHOSPHATE CONCENTRATIONS BETWEEN EXPERIMENTAL AND SIMULATION RESULTS

Simulation results of the residual phosphate concentrations using the Ferguson model and the regression model together with experimental results are shown in this appendix. These results, shown in nine pages, correspond to a situation where no calcium is present in the wastewater. The first three pages contain the results for the low initial alkalinity level, the next three pages for the medium level, and the last three pages for the high level. Under each alkalinity level, the first page includes the results for the low initial phosphate level, the second page for the medium level, and the third page for the high level.

Below are nomenclature used:

CHEM alum dosage in mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$

ROP residual phosphate measured in mg/l as P

R-OP residual phosphate predicted using the regression model in mg/l as P

F-PO4 residual phosphate predicted using the Ferguson model in mg/l as P

Low Alkalinity and Low Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	3.10	3.10	3.10
50	3.10	7.40	10		2.63	2.92
50	3.10	7.40	13	2.16		2.57
50	3.10	7.40	20	1.82	1.81	1.99
50	3.10	7.40	25	1.50		1.69
50	3.10	7.40	30	1.08	1.04	1.44
50	3.10	7.40	40	0.86	0.32	1.06
50	3.10	7.40	44			0.93
50	3.10	7.40	50	0.42	0.12	0.76
50	3.10	7.40	60		0.08	0.51
50	3.10	7.40	63			0.45
50	3.10	7.40	70		0.06	0.30
50	3.10	7.40	75	0.03		0.21
50	3.10	7.40	80		0.04	0.12
50	3.10	7.40	90		0.03	0.00
50	3.10	7.40	100		0.02	0.00
50	3.10	7.40	120		0.01	0.00
50	3.10	7.40	125	0.02		0.00
50	3.10	7.40	140		0.01	
50	3.10	7.40	160		0.00	
50	3.10	7.40	175	0.05		
50	3.10	7.40	180		0.00	
50	3.10	7.40	200		0.00	
50	3.10	7.40	250	0.10	0.00	
50	3.10	7.40	300	0.11	0.00	
50	3.10	7.40	350	0.16	0.00	

Low Alkalinity and Medium Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	5.16	5.16	5.16
50	5.16	7.24	10		4.60	5.16
50	5.16	7.24	13			5.16
50	5.16	7.24	20	3.92	3.85	4.47
50	5.16	7.24	25			3.97
50	5.16	7.24	30	2.86	3.09	3.56
50	5.16	7.24	40		2.32	2.92
50	5.16	7.24	44	2.18		2.70
50	5.16	7.24	50		1.53	2.42
50	5.16	7.24	56	1.40		2.16
50	5.16	7.24	60		0.78	2.01
50	5.16	7.24	63			1.90
50	5.16	7.24	70	0.77	0.08	1.66
50	5.16	7.24	75			1.51
50	5.16	7.24	80	0.30	0.05	1.37
50	5.16	7.24	90		0.04	1.10
50	5.16	7.24	100	0.07	0.03	0.87
50	5.16	7.24	120		0.01	0.46
50	5.16	7.24	125	0.04		0.37
50	5.16	7.24	140		0.01	
50	5.16	7.24	160		0.01	
50	5.16	7.24	175	0.07		
50	5.16	7.24	180		0.00	
50	5.16	7.24	200		0.00	
50	5.16	7.24	250	0.16	0.00	
50	5.16	7.24	300	0.21	0.00	
50	5.16	7.24	350	0.39	0.00	

Low Alkalinity and High Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	10.25	10.25	10.25
50	10.25	7.03	10		9.88	10.25
50	10.25	7.03	13			10.25
50	10.25	7.03	20	9.43	9.14	10.25
50	10.25	7.03	25			9.60
50	10.25	7.03	30		8.34	8.79
50	10.25	7.03	40	7.72	7.53	7.51
50	10.25	7.03	50		6.73	6.52
50	10.25	7.03	56	6.72		6.02
50	10.25	7.03	60		5.95	5.71
50	10.25	7.03	63			5.50
50	10.25	7.03	70		5.26	5.03
50	10.25	7.03	75	4.70		4.72
50	10.25	7.03	80		4.47	4.43
50	10.25	7.03	90		3.70	3.91
50	10.25	7.03	94	3.39		3.72
50	10.25	7.03	100		2.93	3.44
50	10.25	7.03	113	2.10		2.90
50	10.25	7.03	120		1.43	2.63
50	10.25	7.03	125			2.45
50	10.25	7.03	140	0.54	0.02	
50	10.25	7.03	150			
50	10.25	7.03	160		0.01	
50	10.25	7.03	175	0.28		
50	10.25	7.03	180		0.01	
50	10.25	7.03	200		0.00	
50	10.25	7.03	213	0.34	0.00	
50	10.25	7.03	250	0.42	0.00	
50	10.25	7.03	300	0.61	0.00	
50	10.25	7.03	350	0.84	0.00	

Medium Alkalinity and Low Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	3.10	3.10	3.10
101	3.10	8.26	10		2.85	2.92
101	3.10	8.26	13	2.95		2.57
101	3.10	8.26	20	2.86	2.02	1.99
101	3.10	8.26	25	2.28		1.69
101	3.10	8.26	30	1.43	1.36	1.44
101	3.10	8.26	40	1.08	0.89	1.06
101	3.10	8.26	44			0.93
101	3.10	8.26	50	0.60	0.57	0.76
101	3.10	8.26	60		0.39	0.51
101	3.10	8.26	70		0.28	0.30
101	3.10	8.26	75	0.07		0.21
101	3.10	8.26	80		0.21	0.12
101	3.10	8.26	90		0.16	0.00
101	3.10	8.26	100		0.13	0.00
101	3.10	8.26	120		0.06	0.00
101	3.10	8.26	125	0.02		0.00
101	3.10	8.26	140		0.04	0.00
101	3.10	8.26	150			0.00
101	3.10	8.26	160		0.03	0.00
101	3.10	8.26	175	0.02		0.00
101	3.10	8.26	180		0.02	0.00
101	3.10	8.26	200		0.02	
101	3.10	8.26	250		0.01	
101	3.10	8.26	300	0.03	0.00	
101	3.10	8.26	350	0.03	0.00	

Medium Alkalinity and Medium Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	5.16	5.16	5.16
101	5.16	7.82	10		5.16	5.16
101	5.16	7.82	20		4.23	4.47
101	5.16	7.82	25			3.97
101	5.16	7.82	30	3.47	3.28	3.56
101	5.16	7.82	40		2.60	2.92
101	5.16	7.82	44	2.54		2.70
101	5.16	7.82	50		1.79	2.42
101	5.16	7.82	56	1.84		2.16
101	5.16	7.82	60		1.05	2.01
101	5.16	7.82	63			1.90
101	5.16	7.82	70	1.13	0.36	1.66
101	5.16	7.82	75			1.51
101	5.16	7.82	80	0.60	0.26	1.37
101	5.16	7.82	90		0.20	1.10
101	5.16	7.82	100	0.15	0.15	0.87
101	5.16	7.82	120		0.10	0.46
101	5.16	7.82	125	0.03		0.37
101	5.16	7.82	140		0.07	0.11
101	5.16	7.82	150			0.00
101	5.16	7.82	160		0.05	0.00
101	5.16	7.82	175	0.02		0.00
101	5.16	7.82	180		0.03	0.00
101	5.16	7.82	200		0.02	
101	5.16	7.82	250		0.01	
101	5.16	7.82	300	0.04	0.00	
101	5.16	7.82	350	0.06	0.00	

Medium Alkalinity and High Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	10.25	10.25	10.25
101	10.25	7.53	10		9.46	10.25
101	10.25	7.53	20	9.96	8.73	10.25
101	10.25	7.53	25			9.60
101	10.25	7.53	30		7.90	8.79
101	10.25	7.53	40	8.17	7.13	7.51
101	10.25	7.53	44			7.09
101	10.25	7.53	50		6.80	6.52
101	10.25	7.53	56	6.39		6.02
101	10.25	7.53	60		6.05	5.71
101	10.25	7.53	63			5.50
101	10.25	7.53	70		5.29	5.03
101	10.25	7.53	75	4.82		4.72
101	10.25	7.53	80		4.52	4.43
101	10.25	7.53	90		3.74	3.91
101	10.25	7.53	94	3.67		3.72
101	10.25	7.53	100		2.97	3.44
101	10.25	7.53	113	2.91		2.90
101	10.25	7.53	120		1.48	2.63
101	10.25	7.53	140	1.17	0.10	1.95
101	10.25	7.53	150			1.64
101	10.25	7.53	160		0.07	1.35
101	10.25	7.53	175			0.95
101	10.25	7.53	180		0.05	0.83
101	10.25	7.53	200		0.03	
101	10.25	7.53	213	0.06		
101	10.25	7.53	250	0.04	0.01	
101	10.25	7.53	300	0.07	0.01	
101	10.25	7.53	350	0.10	0.00	

High Alkalinity and Low Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	3.10	3.10	3.10
198	3.10	8.78	10		3.10	2.92
198	3.10	8.78	13	3.01		2.57
198	3.10	8.78	20	2.98	3.10	1.99
198	3.10	8.78	25	2.90		1.69
198	3.10	8.78	30	2.27	3.10	1.44
198	3.10	8.78	40	2.03	2.58	1.06
198	3.10	8.78	44			0.93
198	3.10	8.78	50	1.05	2.02	0.76
198	3.10	8.78	60		1.57	0.51
198	3.10	8.78	70		1.18	0.30
198	3.10	8.78	75	0.26		0.21
198	3.10	8.78	80		0.89	0.12
198	3.10	8.78	90		0.68	0.00
198	3.10	8.78	100	0.07	0.55	0.00
198	3.10	8.78	113			0.00
198	3.10	8.78	120		0.36	0.00
198	3.10	8.78	125			0.00
198	3.10	8.78	140		0.26	0.00
198	3.10	8.78	150			0.00
198	3.10	8.78	160		0.19	0.00
198	3.10	8.78	175	0.01		0.00
198	3.10	8.78	180		0.15	0.00
198	3.10	8.78	200		0.12	
198	3.10	8.78	250	0.03	0.07	
198	3.10	8.78	300		0.05	
198	3.10	8.78	350	0.03	0.03	

High Alkalinity and Medium Phosphate Levels

IALK	IOP	IPH	CHEM	ALUM ROP	F-PO4	R-OP
			0	5.16	5.16	5.16
198	5.16	8.14	10		4.77	5.16
198	5.16	8.14	13			5.16
198	5.16	8.14	20	4.96	3.86	4.47
198	5.16	8.14	25	4.89		3.97
198	5.16	8.14	30	3.55	4.87	3.56
198	5.16	8.14	40	3.13	3.68	2.92
198	5.16	8.14	44	2.56		2.70
198	5.16	8.14	50		2.72	2.42
198	5.16	8.14	56	1.96		2.16
198	5.16	8.14	60		1.89	2.01
198	5.16	8.14	63			1.90
198	5.16	8.14	70	1.38	1.08	1.66
198	5.16	8.14	75			1.51
198	5.16	8.14	80	0.81	0.82	1.37
198	5.16	8.14	90		0.62	1.10
198	5.16	8.14	100	0.05	0.50	0.87
198	5.16	8.14	120		0.33	0.46
198	5.16	8.14	125			0.37
198	5.16	8.14	140		0.24	0.11
198	5.16	8.14	150	0.05		0.00
198	5.16	8.14	160		0.18	0.00
198	5.16	8.14	180		0.14	0.00
198	5.16	8.14	200		0.11	
198	5.16	8.14	250	0.04	0.07	
198	5.16	8.14	300		0.04	
198	5.16	8.14	350	0.04	0.03	

High Alkalinity and High Phosphate Levels

				ALUM		
IALK	IOP	IPH	CHEM	ROP	F-PO4	R-OP
			0	10.25	10.25	10.25
198	10.25	7.70	10		9.82	10.25
198	10.25	7.70	13			10.25
198	10.25	7.70	20	9.96	8.86	10.25
198	10.25	7.70	25			9.60
198	10.25	7.70	30		8.13	8.79
198	10.25	7.70	40	8.29	7.39	7.51
198	10.25	7.70	50		6.53	6.52
198	10.25	7.70	56	6.75		6.02
198	10.25	7.70	60		5.84	5.71
198	10.25	7.70	63			5.50
198	10.25	7.70	70		5.09	5.03
198	10.25	7.70	75	5.30		4.72
198	10.25	7.70	80		4.53	4.43
198	10.25	7.70	90		3.84	3.91
198	10.25	7.70	94	4.33		3.72
198	10.25	7.70	100		3.10	3.44
198	10.25	7.70	113	2.94		2.90
198	10.25	7.70	120		1.59	2.63
198	10.25	7.70	125			2.45
198	10.25	7.70	140	2.15	0.33	1.95
198	10.25	7.70	150			1.64
198	10.25	7.70	160		0.24	1.35
198	10.25	7.70	175	0.45		0.95
198	10.25	7.70	180		0.18	0.83
198	10.25	7.70	200		0.14	
198	10.25	7.70	213	0.13		
198	10.25	7.70	250	0.07	0.08	
198	10.25	7.70	300	0.07	0.05	
198	10.25	7.70	350	0.09	0.03	

APPENDIX D. RAW DATA FOR COMPARISON OF RESIDUAL ALKALINITY AND PH BETWEEN EXPERIMENTAL AND SIMULATION RESULTS

Simulation results of the residual alkalinity and pH values determined using the regression model and the Ferguson model together with experimental results are shown in this appendix. These results correspond to a situation where no calcium is present in the wastewater. The first three pages contain the results for the low initial alkalinity level, the next three pages for the medium level, and the last three pages for the high level. Under each alkalinity level, the first page includes the results for the low initial phosphate level, the second page for the medium level, and the third page for the high level.

Below are nomenclature used:

CHEM alum dosage in mg/l as $Al_2(SO_4)_3 \cdot 18H_2O$

RPH residual pH measured

RAL residual alkalinity measured in mg/l as $CaCO_3$

F-PH residual pH predicted using the Ferguson model

F-ALK residual alkalinity predicted using the Ferguson model in mg/l as $CaCO_3$

R-PH residual pH predicted using the regression model

R-ALK residual alkalinity predicted using the regression model in mg/l as $CaCO_3$

Low Alkalinity and Low Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.25	48	7.20	45
13	7.30	45			7.15	44
20	7.22	43	7.13	45	7.05	41
25	7.17	41			6.98	40
30	7.15	39	7.00	43	6.91	38
40	7.14	37	6.89	40	6.77	34
44					6.72	33
50	7.10	33	6.71	36	6.64	31
60			6.57	32	6.50	27
63					6.46	26
70			6.44	28	6.37	24
75	6.90	21			6.31	22
80			6.32	25	6.24	20
90			6.19	21	6.12	17
100			6.06	17	5.99	13
120			5.78	11	5.75	6
125	6.17	6			5.70	4
140			5.54	7	5.52	0
160			5.39	5	5.30	0
175	4.59	1			5.14	0
180			5.30	4	5.09	0
200			5.24	3	4.89	0
250	4.40	0	5.15	3	4.43	0
300	4.31	0	5.09	2	4.03	0
350	4.24	0	5.04	2	3.70	0

Low Alkalinity and Medium Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.13	48	7.07	45
13					7.03	44
20	7.04	43	7.02	45	6.93	41
25					6.86	40
30	6.92	38	6.92	42	6.80	38
40			6.82	40	6.66	34
44	6.88	34			6.61	33
50			6.73	37	6.53	31
56	6.83	30			6.45	29
60			6.65	35	6.40	27
63					6.36	26
70	6.84	26	6.54	32	6.27	24
75					6.21	22
80	6.78	21	6.42	28	6.15	20
90			6.29	24	6.02	17
100	6.62	14	6.18	21	5.90	13
120			5.90	13	5.67	6
125	6.21	5			5.61	4
140			5.63	8	5.45	0
160			5.44	6	5.23	0
175	4.57	1			5.08	0
180			5.34	4	5.03	0
200			5.27	4	4.84	0
250	4.39	0	5.16	3	4.39	0
300	4.32	0	5.10	2	4.01	0
350	4.22	0	5.05	2	3.70	0

Low Alkalinity and High Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			6.95	48	6.91	45
13					6.87	44
20	6.98	42	6.87	45	6.77	41
25					6.71	40
30			6.80	42	6.64	38
40	6.83	37	6.72	40	6.51	34
50			6.65	37	6.38	31
56	6.67	30			6.31	29
60			6.57	35	6.26	27
63					6.22	26
70			6.49	32	6.14	24
75	6.60	24			6.07	22
80			6.42	29	6.02	20
90			6.34	27	5.90	17
94	6.42	18			5.85	15
100			6.27	24	5.78	13
113	6.30	13			5.64	8
120			6.09	19	5.56	6
125					5.50	4
140	5.78	4	5.91	14	5.34	0
150					5.24	0
160			5.65	9	5.14	0
175	4.31	0			4.99	0
180			5.45	6	4.95	0
200			5.34	4	4.76	0
213	4.20	0			4.65	0
250	4.13	0	5.20	3	4.35	0
300	4.09	0	5.12	3	3.99	0
350	4.07	0	5.06	2	3.70	0

Medium Alkalinity and Low Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.63	97	7.89	94
13	7.75	92			7.85	93
20	7.65	91	7.54	94	7.75	91
25	7.51	89			7.68	89
30	7.47	86	7.44	93	7.62	87
40	7.41	83	7.33	90	7.48	84
44					7.43	82
50	7.33	81	7.20	87	7.35	80
60			7.09	84	7.22	77
70			6.99	80	7.09	73
75	7.13	69			7.03	71
80			6.90	77	6.97	70
90			6.81	73	6.84	66
100			6.72	69	6.72	62
120			6.43	60	6.49	55
125	6.99	48			6.43	54
140			6.32	53	6.27	48
150					6.16	45
160			6.20	46	6.06	41
175	6.57	31			5.90	36
180			6.08	38	5.85	34
200			5.94	31	5.66	27
250	5.43	6	5.57	16	5.22	9
300	4.63	2	5.32	9	4.84	0
350	4.48	0	5.19	7	4.52	0

Medium Alkalinity and Medium Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.68	100	7.55	94
20			7.57	97	7.42	91
25					7.36	89
30	7.36	86	7.45	94	7.29	87
40			7.35	92	7.17	84
44	7.29	82			7.12	82
50			7.27	89	7.05	80
56	7.20	77			6.97	78
60			7.19	86	6.93	77
63					6.89	76
70	7.15	73	7.06	82	6.81	73
75					6.75	71
80	7.12	68	6.96	79	6.69	70
90			6.87	75	6.58	66
100	7.00	60	6.78	72	6.47	62
120			6.63	64	6.26	55
125	6.94	46			6.21	54
140			6.49	57	6.06	48
150					5.96	45
160			6.35	49	5.86	41
175	6.65	27			5.73	36
180			6.23	42	5.68	34
200			6.08	34	5.51	27
250			5.68	17	5.12	9
300	4.68	2	5.35	9	4.79	0
350	4.51	0	5.21	6	4.52	0

Medium Alkalinity and High Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.45	99	7.32	94
20	7.39	90	7.38	96	7.20	91
25					7.14	89
30			7.30	93	7.08	87
40	7.25	84	7.24	91	6.96	84
44					6.92	82
50			7.16	88	6.85	80
56	7.07	77			6.78	78
60			7.10	86	6.73	77
63					6.70	76
70			7.05	84	6.62	73
75	7.00	70			6.57	71
80			6.99	81	6.51	70
90			6.94	78	6.41	66
94	6.93	64			6.37	65
100			6.87	75	6.31	62
113	6.87	60			6.17	58
120			6.77	70	6.11	55
140	6.70	50	6.66	64	5.92	48
150					5.83	45
160			6.52	57	5.74	41
175					5.61	36
180			6.38	50	5.57	34
200			6.24	42	5.41	27
213	6.40	21			5.31	23
250	5.95	10	5.86	23	5.05	9
300	4.64	2	5.47	11	4.76	0
350	4.40	0	5.27	7	4.52	0

High Alkalinity and Low Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.77	199	8.34	188
13	8.27	188			8.31	187
20	8.15	186	7.72	197	8.24	185
25	8.08	184			8.19	183
30	8.01	182	7.67	195	8.13	181
40	7.95	181	7.61	192	8.03	178
50	7.78	174	7.54	190	7.93	174
60			7.48	188	7.84	171
70			7.40	185	7.74	167
75	7.49	165			7.69	165
80			7.33	181	7.65	164
90			7.25	178	7.56	160
100	7.38	156	7.19	175	7.47	156
113					7.36	152
120			7.06	167	7.31	149
125	7.28	143			7.27	148
140			6.96	160	7.15	142
150					7.07	139
160			6.86	153	7.00	135
175	7.06	120			6.90	130
180			6.78	146	6.86	128
200			6.71	139	6.74	121
250	6.90	91	6.52	119	6.46	103
300			6.35	100	6.25	86
350	6.60	56	6.19	82	6.09	68

High Alkalinity and Medium Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.76	194	7.84	188
13					7.82	187
20	7.77	186	7.71	192	7.75	185
25	7.73	184			7.71	183
30	7.56	181	7.81	195	7.66	181
40	7.57	179	7.72	192	7.58	178
44	7.49	176			7.54	176
50			7.65	189	7.49	174
56	7.42	171			7.44	172
60			7.57	186	7.41	171
63					7.39	170
70	7.39	167	7.38	180	7.33	167
75					7.29	165
80	7.35	162	7.30	176	7.25	164
90			7.23	173	7.18	160
100	7.20	149	7.16	170	7.11	156
120			7.04	162	6.97	149
125					6.93	148
140			6.94	155	6.84	142
150	7.09	134			6.78	139
160			6.85	148	6.72	135
180			6.76	140	6.61	128
200			6.68	133	6.52	121
250	6.73	91	6.49	114	6.31	103
300			6.33	95	6.17	86
350	6.50	56	6.15	76	6.10	68

High Alkalinity and High Phosphate Levels

		ALUM				
CHEM	RPH	RALK	F-PH	F-ALK	R-PH	R-ALK
10			7.65	197	7.50	188
13					7.48	187
20	7.55	185	7.58	194	7.42	185
25					7.38	183
30			7.53	191	7.34	181
40	7.44	179	7.48	189	7.26	178
50			7.43	186	7.19	174
56	7.34	172			7.14	172
60			7.38	184	7.12	171
63					7.10	170
70			7.33	181	7.05	167
75	7.27	166			7.01	165
80			7.29	178	6.98	164
90			7.25	176	6.91	160
94	7.18	160			6.89	159
100			7.20	173	6.85	156
113	7.10	152			6.78	152
120			7.13	168	6.74	149
125					6.71	148
140	7.04	148	7.04	161	6.63	142
150					6.58	139
160			6.94	154	6.53	135
175	6.90	128			6.46	130
180			6.84	147	6.44	128
200			6.75	139	6.37	121
213	6.83	113			6.32	117
250	6.71	103	6.57	121	6.21	103
300	6.62	75	6.39	102	6.12	86
350	6.44	60	6.21	82	6.10	68

GENERAL CONCLUSIONS

This study covers two subjects of chemical phosphate removal: rapid mixing and modeling.

In order to study rapid mixing of chemical phosphate removal, two rapid-mixing parameters (intensity and time) and aluminum solution strength were evaluated. The study demonstrates that all three parameters affect chemical phosphate removal.

Five G values were evaluated: 150, 300, 600, 900, and 18800 sec^{-1}. The study revealed that P-removal efficiency improved as the mixing intensity increased from a G value of 150 to 600 sec^{-1}, but did not by further increase in G value. Instead of improvement, P-removal efficiency deteriorated at extremely fast mixing intensity (G value of 18800 sec^{-1}). This indicates that an optimum mixing intensity for chemical phosphate removal is a G value of 600 sec^{-1}.

The effect of the mixing time was not significant while the time was in the range of 10–60 seconds. The effect became significant once more than 60 seconds of mixing time was used. The time trend was found to be a linear fashion and constant over G values of 500–1000 sec^{-1}, indicating no interaction. This means that P-removal efficiency deteriorated with time once the mixing time exceeded 60 seconds and this trend was the same at all mixing intensities.

It may be confusing because the first paper concluded that chemical phosphate removal is relatively unaffected by mixing time, whereas the second paper concluded that it is affected by mixing time. As mentioned in the first paper, no statistical test was performed to confirm that the mixing time is not an important factor in chemical phosphate removal. Therefore, only two parameters were evaluated in the first paper: the mixing intensity and aluminum solution strength. The mixing time was evaluated in the second paper. As concluded in the second paper, the mixing time affects chemical phosphate removal, but not until the time becomes greater than 60 seconds.

Besides the rapid-mixing parameters, aluminum solution strength was found to influence chemical phosphate removal. The higher the solution strength used, the better was P-removal efficiency at all mixing intensities. Of six different aluminum solution strengths (1, 2.5, 5, 10, 25, and 50 %) evaluated, there was no statistically significant difference in P-removal efficiencies over the range of the solution strengths from 2.5–10 % as $AlCl_3 \cdot 6H_2O$.

While trying to model chemical phosphate removal using linear regression, effects of use of different aluminum salts and a calcium effect were investigated. Also, the currently available equilibrium models for chemical phosphate removal were evaluated.

Comparison between aluminum chloride and alum revealed that their effects on chemical phosphate removal were negligible. A difference between use of these two aluminum salts was shown in the residual phosphate concentration at high aluminum dosages. The phosphate concentration increased once the wastewater's alkalinity was depleted. The extent of the increase was more serious with use of aluminum chloride than with use of alum. The difference in the extent should be caused by anion effects. Apparently, a sulfate ion was more effective in suppressing the increase in the phosphate concentration than a chloride ion. This anion effect was minimal when the wastewater had alkalinity, but was evident after the wastewater lost its alkalinity. Since chemicals are not added to wastewaters in such an extent that all alkalnities of wastewaters are consumed, this effect was ignored.

This study found that phosphates were removed stoichiometrically at low aluminum dosages. The stoichiometric information suggested the formation of aluminum hydroxyphosphate, $Al_{1.2}H_2PO_4(OH)_{2.6}$, rather than aluminum phosphate, $AlPO_4$ in chemical phosphate removal. This indicated that phosphate residuals were controlled by the solubility of aluminum hydroxyphosphate. The solubility of aluminum hydroxyphosphate was found to favor low pH conditions over high pH conditions for low phosphate residuals while the wastewater's pH was in the range of 6–9.

The presence of calcium helped chemical phosphate removal. The synthetic wastewater with calcium had lower pH than the wastewater without calcium. These low pH conditions shifted the solubility of aluminum hydroxyphosphate into low phosphate residuals. Therefore, a lower phosphate concentration was obtained when calcium was present in the wastewater than when no calcium was present in the wastewater. This benefit of calcium disappeared at high aluminum dosages because phosphate residuals were no longer controlled by the solubility of aluminum hydroxyphosphate at high aluminum dosages.

When calcium was present in the wastewater, calcium-phosphate precipitation occurred at the very low alum dosage (18.75 mg/l) under certain conditions such as high initial phosphate concentration. This was shown by a less than 1 molar ratio of Al/P. At this low alum dosage, the wastewater's pH was still high enough to encourage precipitation of tricalcium phosphate. With further addition of alum, these precipitates were dissolved and aluminum hydroxyphosphate formed.

Evaluation of the Ferguson model revealed that the model predicted the residual phosphate values well. Nonetheless, the Ferguson model is more like data fitting because of some problems described earlier. A chemical equilibrium approach predicts that use of aluminum chloride produces lower residual phosphate concentrations than use of alum. This was not supported experimentally nor statistically. This indicates that chemical phosphate removal cannot be explained by a chemical equilibrium approach alone.

Regression models developed by linear regression predicted the residual alkalinity, pH, and phosphate well. Compared to the Ferguson model, the regression models predicted the residual alkalinity better. Both models were good in predicting the residual phosphate, but the prediction accuracy was not so good for the residual pH.

Since both the Ferguson model and the regression model predicted the residual phosphate values well, these two models could be used for design purposes. When post-precipitation is planned to removal phosphates, either model can be used to predict the residual parameters. Limitation for using these models come when wastewaters contain more condensed, organic, and particulate phosphates than orthophosphates. Under these conditions, regression modeling might be better than the Ferguson model because it can be customized to any specific situation.