ALUMINUM HYDROLYSIS EFFECTS ON PHOSPHORUS REMOVAL FROM WASTEWATERS

By

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ABSTRACT

It is widely recognized that phosphorus removal from wastewaters by coagulation with aluminum salts is brought about not by the aluminum ion itself but by the hydrolysis products of the metal ion.

The present work investigated the effectiveness of the aluminum polymeric species in phosphorus removal. These species were formed by partially neutralizing an aluminum chloride solution with sodium hydroxide under controlled conditions and they were given the name PBAC for Polymerized Basic Aluminum Chloride. The results were compared with those obtained using Alum, the most commonly employed aluminum coagulant. Although the removal of phosphorus from wastewaters was the main objective, the work extended to other areas such as supernatant suspended solids removal, sludge filtrability and organics removal.

The factors that were found to influence the efficiency of the coagulants were:

(i) The aging time of the aluminum polymers,

(ii) The OH:Al molar ratio in the preparation of PBAC,

(iii) The Al:P molar ratio (Aluminum dosage),

(iv) The pH,

(v) The presence in the wastewater of other ionic species.

It was found that the removal of phosphorus could be adequately explained by a model involving complex formation and precipitation. It was shown, however, that the removal of organics cannot be attributed to a strictly chemical interaction and other mechanisms should be considered as well.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

PAGE

CHAPTER 3 EXPERIMENTAL (Cont'd)

TABLE OF CONTENTS (Cont'd)

LIST OF TABLES

LIST OF TABLES (Cont'd)

LIST OF TABLES (Cont'd)

LIST OF TABLES (Cont'd)

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

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CHAPTER 1

INTRODUCTION

Phosphorus plays a significant role in the aquatic environment. This was observed as early as the beginning of the century. Since then a lot of work has been focused on this element and a new term, Eutrophication, appeared in Environmental Sciences.

Eutrophication is the enrichment of surface waters with plant nutrients leading to increased plant productivity or "blooms". Phosphorus as well as other factors, such as light, temperature, mixing conditions, carbon dioxide, toxicant levels, concentration and the type of organisms present along with nutrients like nitrogen, iron, manganese and other trace elements are important in the development of blooms. Only a certain number of these appears to be controllable by man. Among them, phosphorus and nitrogen seem to be the most important in relation to algae and plant growth requirements. Since a certain type of algae, the blue-green algae, has the ability to utilize the atmospheric nitrogen, control of phosphorus input into the aquatic system will limit their growth.

The possible sources of phosphorus, as summarized by Porcela and Bishop (1975) are:

(i) Precipitation of the particulate atmospheric phosphorus,
(ii) Agricultural,
(iii) Runoff from urban and rural watersheds,
(iv) Domestic activities,
(v) Industrial and mining activities, and
(vi) Animal wastes.

Phosphorus from domestic activities is particularly important since it must be removed from wastewater. The total phosphorus concentration in domestic wastewaters ranges from 2 to 25 mg/l. Thirty to fifty percent originates from human wastes and fifty to seventy percent from detergents.

The removal of phosphorus from wastewaters has been extensively investigated in the last two decades. Precipitation by metal coagulants, such as Aluminum Sulfate, Ferric Chloride and Lime, has been found to be the most suitable method to accomplish phosphorus removal. Most investigators, even though they recognize the complexity of the reactions involved, consider that the solubility of simple compounds, such as $AlPO_4$ and $Al(OH)_3$, determines the removal of phosphorus. This leads to a misunderstanding of the role of the metal coagulant, since parameters like the pH, the hydrolysis of the metal ions, the effect of the presence of various ionic species and the principles of complex chemistry are either ignored or their role is misunderstood.

The main objective of this study is to investigate the removal of phosphorus considering the hydrolysis products of aluminum as the important species responsible for the precipitation. To achieve this objective aluminum polymeric species formed under controlled conditions were employed. These species are formed when an aluminum chloride solution is partially neutralized with sodium hydroxide. Solutions of these hydroxopolymers are denoted by PBAC which stands for Polymerized Basic Aluminum Chloride.

To evaluate the effectiveness of PBAC, the results are compared with the ones obtained with Aluminum Chloride (source of Al^{3+} ions) and Alum (Aluminum Sulfate, the most commonly used aluminum coagulant). Because of the anticipated complexity of the natural systems, both synthetic and domestic wastewaters were employed.

CHAPTER 2

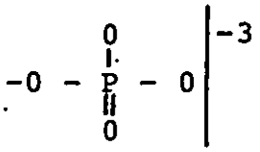
BACKGROUND

2.1 PHOSPHORUS IN WASTEWATERS

2.1.1 Forms of Phosphorus

Elemental phosphorus does not exist in nature. All phosphorus deposits are in the form of orthophosphate. In wastewaters, three categories of phosphorus forms exist: organic phosphorus, condensed inorganic phosphates and inorganic orthophosphates.

The orthophosphate structure consists of an atom of P surrounded by four oxygen atoms arranged at corners of a tetrahedron. The chemical configuration of the orthophosphate ion is shown below:

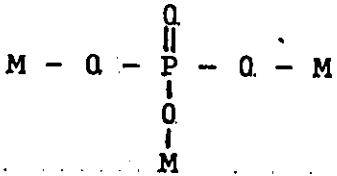
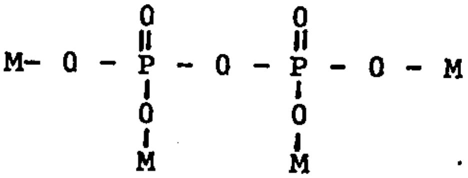
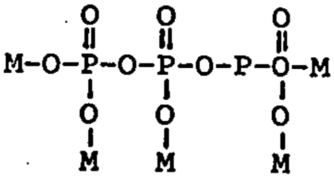
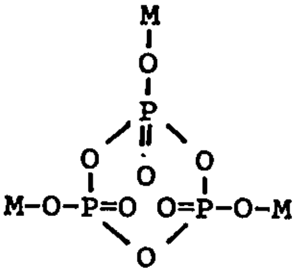


$$\left.\begin{array}{c} 0 \\ | \\ -0-P-0 \\ \| \\ 0 \end{array}\right|^{-3}$$

Condensed phosphates (or complex phosphates) are derived from orthophosphates by combination of one or more orthophosphate units. The chain products are called polyphosphates, the ring compounds metaphosphates and the cross-linked ones ultraphosphates.

Typical phosphate forms are shown in Table 2.1.

TABLE 2.1 Inorganic Phosphate Compounds

	Name	Formula	Structure
	Orthophosphate	M_3PO_4	 $M-O-\underset{\substack{\vert\\O\\\vert\\M}}{\overset{\substack{O\\\Vert}}{P}}-O-M$
Condensed Phosphates	Pyro-phosphate	$M_4P_2O_7$	 $M-O-\underset{\substack{\vert\\O\\\vert\\M}}{\overset{\substack{O\\\Vert}}{P}}-O-\underset{\substack{\vert\\O\\\vert\\M}}{\overset{\substack{O\\\Vert}}{P}}-O-M$
	Tripoly-phosphate	$M_5P_3O_{10}$	 $M-O-\underset{\substack{\vert\\O\\\vert\\M}}{\overset{\substack{O\\\Vert}}{P}}-O-\underset{\substack{\vert\\O\\\vert\\M}}{\overset{\substack{O\\\Vert}}{P}}-O-P-\underset{\substack{\vert\\O\\\vert\\M}}{\overset{\substack{O\\\Vert}}{O}}-M$
	Trimeta-phosphate	$(MPO_3)_3$	

M = Monovalent cation.

Table 2.2 lists the equilibrium constants and Figure 2.1 illustrates the distribution of ortho-, pyro- and tripoly-phosphate species with pH, based on typical concentrations occurring in wastewaters.

TABLE 2.2 Phosphate Equilibrium Constants

(From: Sillen and Martell, 1964)

Equilibrium	Log Equilibrium Constant at 298^{o}E
$H_3PO_4 = H^+ + H_2PO_4^-$	- 2.1
$H_2PO_4^- = H^+ + HPO_4^{2-}$	- 7.2
$HPO_4^{2-} = H^+ + PO_4^{3-}$	-12.3
$H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-}$	- 2.5
$H_2P_2O_7^{2-} = H^+ + HP_2O_7^{3-}$	- 6.7
$HP_2O_7^{3-} = H^+ + P_2O_7^{4-}$	- 9.4
$H_3P_3O_{10}^{-2} = H^+ + H_2P_3O_{10}^{-3}$	- 2.3
$H_2P_3O_{10}^{-3} = H^+ + HP_3O_{10}^{-4}$	- 6.5
$HP_3O_{10}^{-4} = H^+ + P_3O_{10}^{-5}$	- 9.2

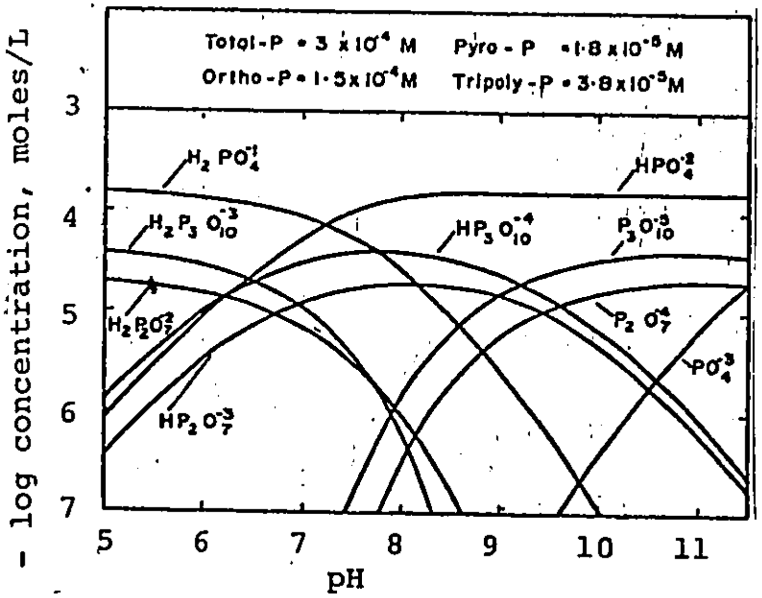


FIGURE 2.1 pH-Concentration Diagram for Phosphate Species (Jenkins, et al., 1971)

For most of the wastewaters met in practice, HPO_4^{2-} is the dominant phosphate species.

Not all forms of phosphorus can be assimilated by living organisms. Only soluble orthophosphate was found to be readily available to all forms of life, while some forms of life cannot utilize condensed phosphates (Katchman, 1961). During the treatment process, however, most of the organic and some of the condensed phosphates hydrolyse to orthophosphates. Finstein and Hunter (1967) studied three activated sludge and three trickling filter plants and they found that half of the condensed phosphorus was hydrolysed to orthophosphate during biological treatment. They reported that in the influent to the biological treatment units the condensed phosphorus constituted 15 to 70% of the total phosphorus while in the effluent, the percentages varied from 5 to 40%.

Factors that accomplish or influence the hydrolysis of condensed phosphates are the presence of micro-organisms, the pH, the temperature and the concentration of condensed phosphates (Heinke, 1969).

In a different way, phosphorus can be classified as soluble phosphorus and as insoluble. Insoluble forms are associated with organic phosphorus present in the form of cell protoplasm. In wastewater that has been treated by chemical precipitation, most of the effluent phosphorus will be in the insoluble form as calcium, aluminum on iron phosphates.

2.1.2 Treatment of Water for P Removal

The literature on phosphorus removal is extensive. The various processes have been reviewed by Eliassen and Tchobanoglous (1968), Nesbitt (1969), Nesbitt (1973), Jenkins, et al. (1971) and Long and Nesbitt (1975).

A summary of the methods used and the experiences gained is given below.

(i) Physical Treatment

These include sedimentation, flotation, filtration, land application-irrigation and reverse osmosis. The first three processes can remove only insoluble phosphorus either in the form of organic matter (bacteria) or in the form of insoluble inorganic salts. The phosphorus removal is low and averages about 10% (Jenkins and Menar, 1967). The removal with reverse osmosis is very high (99%), but the operational cost is considered very high too (EPA, 1970). Soil spreading resulted in 76 to 92% removal (Porçella and Bishop, 1975) but this method can be applied only when adequate land is available at low cost.

(ii) Biological Treatment

The biological removal of phosphorus in an activated sludge process is accomplished through assimilation into cell material. In a typically operating plant, the volatile mass of suspended solids normally contain between 2-3 percent phosphorus resulting in an average phosphorus removal of 20-30 percent (Jenkins and Menar, 1967). However, removals in the order of 90% have been reported (Vacker, et al., 1967; Carberry and Tenney, 1972). The phosphate uptake by the sludge in excess of that needed for cell synthesis is referred to by the name "luxury uptake". The "luxury uptake" theory was first introduced by Levin and Shapiro (1965). According to them the controlling factors were dissolved oxygen, rate of aeration, pH and the phosphate content of return sludge. This theory was supported by other investigators. Connell, et al. (1967) stated that "luxury uptake" occurs in the declining growth and bioflocculation phase and in the presence of 2 mg/l dissolved oxygen. However other investigators (Menar and Jenkins, 1969) reported that the enhanced phosphorus removal is due to chemical precipitation of calcium phosphate, which becomes physically entrapped into the activated sludge flocs and is removed with the waste activated sludge. Calcium phosphate precipitates when the pH rises due to decrease in CO_2 production at the last part of aeration basin and also due to stripping because of the aeration process.

Another biological process for P removal is the use of oxidation ponds. A successful operation requires a proper design for the removal of organic matter, operation in warm climate to ensure continuous biological activity and some method of harvesting the algae (Nesbitt, 1966).

(iii) Chemical Treatment

The chemical treatment includes processes such as Ion Exchange, Electrodialysis, Electrochemical Treatment, Sorption and Chemical Precipitation.

The Ion Exchange method is reported to give high phosphorus removal, 99% (Dryden, 1970) with a simultaneous reduction in total dissolved solids and organic matter. However, because of problems associated with the extensive pretreatment necessary to prevent the organic fouling of the resins, the disposal of used regenerant and the cost of regeneration, this method does not appear very promising. The recent development of macroporous resins that can absorb much more organic matter without fouling might bring this process into consideration again.

The results on phosphorus elimination by the means of electrodialysis are reported by Dryden (1970) to be very poor (removal around 23%).

Eliassen and Tchobanoglous (1968) reported about an electrochemical process developed in Norway, which is capable of removing orthophosphate by an average of 83 percent and ammonia nitrogen by 82 percent. In this process wastewater is mixed with seawater and enters a single cell with carbon electrodes. The current raises the pH and phosphorus and ammonia precipitate as $Ca_3(PO_4)_2$

and $MgNH_4PO_4$ along with $Mg(OH)_2$. The sludge is lifted to the top by the hydrogen bubbles and the chlorine developed at the anode acts as disinfectant of the effluent. Sea water is used to provide the magnesium required for precipitation.

Activated alumina has been used (Vee, 1966) as a sorption medium to remove phosphorus. The efficiency of the process was reported to be very high (99% reduction). This process does not require any salt addition and pH is not changed. The used activated alumina can be regenerated with small quantities of caustic and nitric acid. This method appears very promising and a lot of work has been directed towards it (Overman, et al, 1978; Smith and Hwang, 1978; Huang, 1977).

Chemical precipitation of phosphates is so far the most common and most economical method for phosphorus removal. There are two important factors which specify the process: The kind of coagulant and the point of addition of the coagulant. Aluminum and iron salts have been employed as well as calcium hydroxide (lime). Of the above mentioned salts Aluminum Sulphate (Alum) and Ferric Chloride are the ones used most. The application of the coagulant may be accomplished either as a tertiary treatment or as a combined biological-chemical or as primary one. The various characteristics and efficiencies of these types of operation are well described by Minton and Carlson (1972). Other factors that influence the elimination of phosphates are the pH, the coagulant dosage, the concentration and type of phosphates present, the presence of other ions, the age of the suspended solids, the temperature and the addition of polyelectrolytes that enhance flocculation. These factors not only affect the removal of phosphorus, but the removal of organics and suspended solids as well as the amount and characteristics of sludge produced. In Ontario it is common practice to add the coagulant in the aeration basin.

2.2 ALUMINUM CHEMISTRY

Aluminum ions exist in aqueous solution as hydrates coordinating six molecules of H_2O per metal ion. The products of hydrolysis are monomeric and polymeric species. The reaction of these complex species with water accounts for the acidic character of the aqueous aluminum ion (Matijevic, 1961; Stumm and Morgan, 1962).

2.2.1 Aqueous Aluminum Monomers

The monomers include the species $Al(H_2O)_6^{+3}$, $Al(OH)(H_2O)_5^{+2}$, $Al(OH)_2(H_2O)_4^{+1}$, $Al(OH)_{3(aq)}$, $Al(OH)_4(H_2O)_2^{-}$. Parks (1972) summarized the values of equilibrium constants and Gibbs free energies of formation of the mononuclear aluminum hydrolysis products. These values are given in Table 2.3. For simplicity, the water molecules associated are omitted.

TABLE 2.3 Formation Constants and Gibbs Free Energies of Formation of Mononuclear Hydroxoaluminum Complexes at 25°C (Parks, 1972).

Complex	$-\log \beta_n$	Free Energy Kcal/mole
Al^{3+}	-	-116 ± 1
$AlOH^{2+}$	8.99 ± 0.04	-165.84
$Al(OH)_2^+$	19.3 ± 0.1	-217.5
$Al(OH)_3(aq)$	26.8 ± 0.1	-265.3
$Al(OH)_4^-$	32.7 ± 0.1	-311.0 ± 0.1

The equilibrium constants correspond to the reactions:

$$Al^{3+} + OH^- = AlOH^{2+} \qquad \beta_1$$
$$Al^{3+} + 2OH^- = Al(OH)_2^+ \qquad \beta_2$$
$$Al^{3+} + 3OH^- = Al(OH)_3(aq) \qquad \beta_3$$
$$Al^{3+} + 4OH^- = Al(OH)_4^- \qquad \beta_4$$

Bersillon (1977) calculated the equilibrium composition of an aluminum solution based upon the following equations:

$$\log[Al(OH)_3(aq)] = -4.44$$
$$\log[Al(OH)_2^+] = 2.09 - pH$$

$$\log[\mathrm{AlOH}^{2+}] = 5.79 - 2\ \mathrm{pH}$$
$$\log[\mathrm{Al}^{3+}] = 10.82 - 3\ \mathrm{pH}$$
$$\log[\mathrm{Al(OH)}_4^-] = \mathrm{pH} - 12.42$$

The equilibrium composition of an aluminum solution as a function of pH is shown in Figure 2.2. According to this plot, the minimum solubility of $Al(OH)_3$ occurs at around pH 7. Similar solubility curves, appeared in the literature, show a minimum between pH 5.5 and 6 (Weber, 1972). These last curves were based upon the consideration by Stumm and Morgan (1962) that the species $Al(OH)_2^+$ does not exist. Their idea was a result of an earlier work by Brosset, et al. (1954). These investigators were able to explain experimental data by assuming that mononuclear complexes like $AlOH^{2+}$ and $Al(OH)_2^+$ were practically non-existant. Therefore, if one omitted the $Al(OH)_2^+$ curve, the minimum solubility would appear to occur at around pH 6.

There is strong evidence, however, that the maximum precipitation occurs at higher pH. In their solutions, Brosset and his co-workers used OH:Al molar ratios ranging from 0 to 2.5. Maximum precipitation occurs at higher ratios around 3. Thus it is only at lower ratios that the amount of $Al(OH)_2^+$ becomes insignificant and it can be neglected.

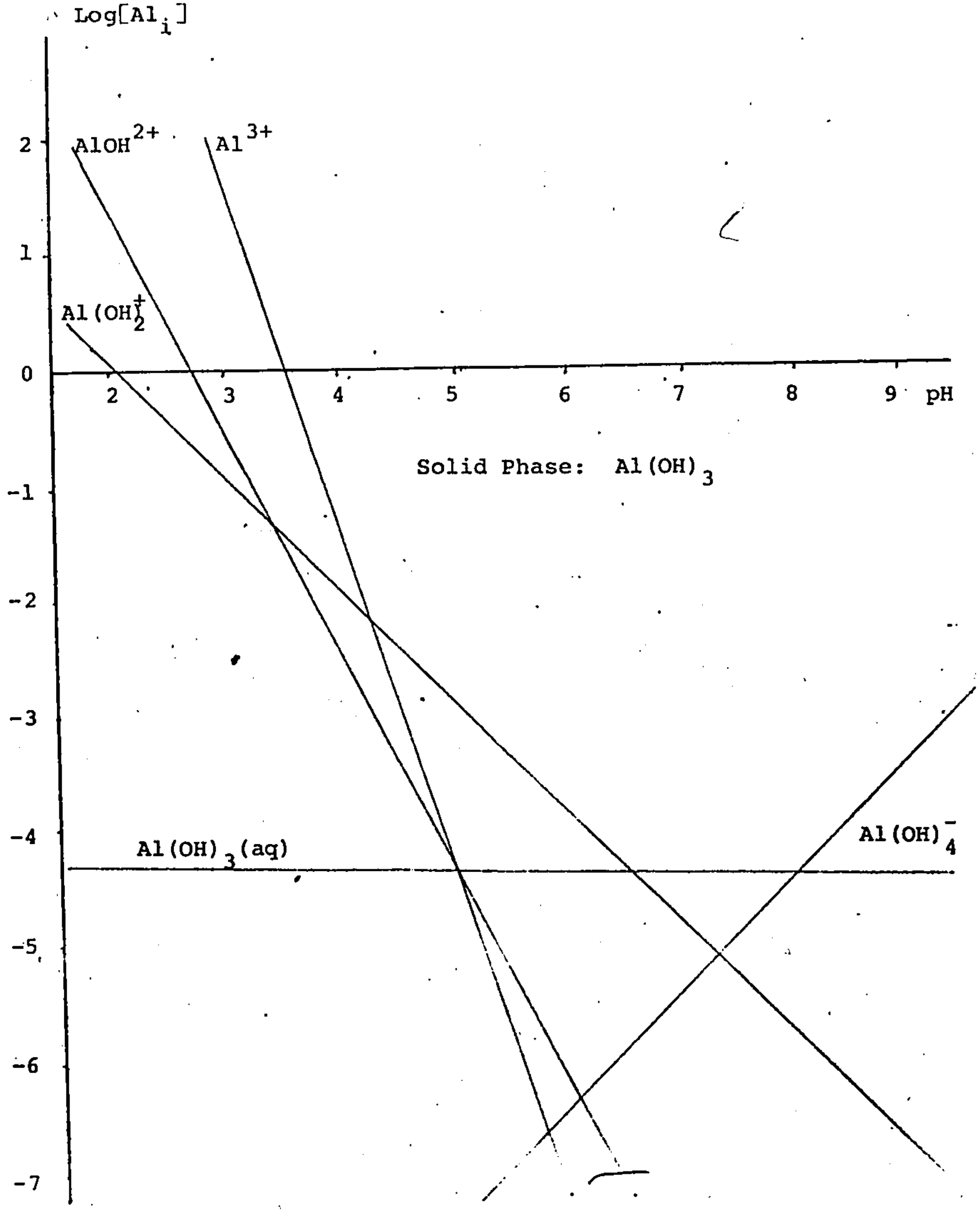


FIGURE 2.2 Equilibrium Composition of an Aluminum Solution (Bersillon,1977).

Hsu and Bates (1965) presented titration curves where it was shown that the maximum precipitation of $Al(OH)_3$ corresponding to an OH/Al molar ratio of 3 occurred at pH higher than 7. Similar data were presented by Sullivan and Singley (1968). The researchers were able to simulate titration data by considering a model requiring only mononuclear species. They showed that for a model like that, when the maximum precipitation of $Al(OH)_3$ occurs, the dominant species in solution is $Al(OH)_2^+$.

Although some investigators believe that the mononuclear species can explain adequately the behaviour of aluminum in aqueous solutions, it is generally accepted that the polynuclear species play the most important role.

2.2.2 Aqueous Aluminum Polymers

The importance of investigating the aluminum polymers in aqueous solutions arises from the fact that these species are the main hydrolysis products under the conditions used for the clarification of waters (Parks, 1972; Stumm and Morgan, 1962). In the literature we meet the names hydroxocomplexes (Stumm and Morgan, 1962), polycations (Van Cauwelaert, et al., 1969), hydroxopolymers (Hsu and Bates, 1964) which describe the various hydrolysis products.

The simplest aluminum polymer is the dimer $Al_2(OH)_2(H_2O)_8^{4+}$. Bersillon, et al.(1978) noticed that this species predominates over the monomer $AlOH^{2+}$ when the total aluminum concentration exceeds about 1 molar. The structure of the dimer can be described as two Al octaedra sharing an edge by hydroxide bridging. The dimer is represented in Figure 2.3.

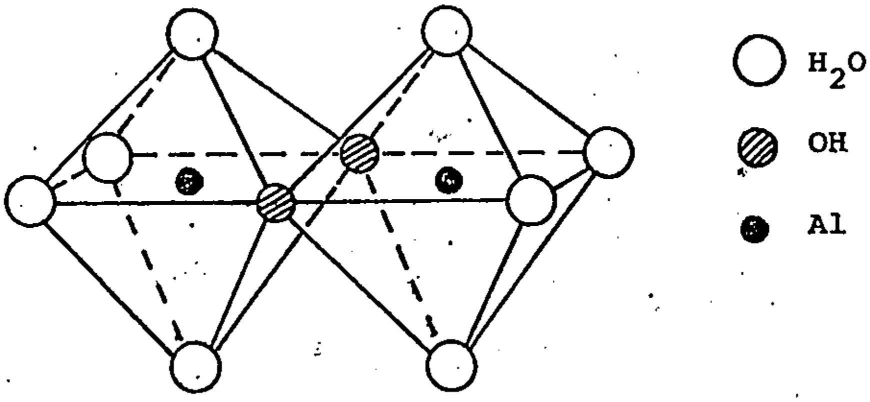


FIGURE 2.3 Structure of the Dimer $Al_2(OH)_2(H_2O)_8^{4+}$ (Hem and Roberson, 1967).

Further polymerization through hydroxide bridging can bring about either chainlike polymers of the general formula $Al_n(OH)_{2n-2}(H_2O)_{2n+2}^{+(n+2)}$ or sheetlike polymers as reported by Brosset, et al. (1954), Hsu (1968), Smith and Hem (1972), Brown and Hem (1975), Hsu and Bates (1962).

In the acidic range (for OH:Al ranging from 0 to 2.5). Brosset, et al. proposed either a single and rather large complex, such as $Al_6(OH)_{15}^{3+}$, or an infinite series of complexes $Al((OH)_5Al_2)_n^{3+n}$. They considered that such polynuclear complexes as $Al_2(OH)_2^{4+}$ and $Al_3(OH)_6^{3+}$ are by no means the main products. In the alkaline range, (OH:Al ranging from 3 to 4) they assumed the existence of a single complex $Al(OH)_4^-$ and solid $Al(OH)_3$. Brosset's. consideration about the hydrolysis products is in good agreement with Sillen's (1959) "Core links" theory.

Matijevic, et al. (1961) coagulated silver halide sols with aluminum salts. They found that at pH < 4 the simple hydrated Al^{3+} species predominates. In the pH range 4 to 7 the tetravalent hydrolysis product $Al_8(OH)_{20}^{4+}$ is proposed. At higher pH values they assumed the existence of $Al_8(OH)_{22}^{2+}$ and $Al_8(OH)_{24}$.

Stumm and Morgan (1962) suggested a stepwise conversion of the positive aluminum ion to the negative aluminate ion. The proposed conversion is illustrated in Figure 2.4.

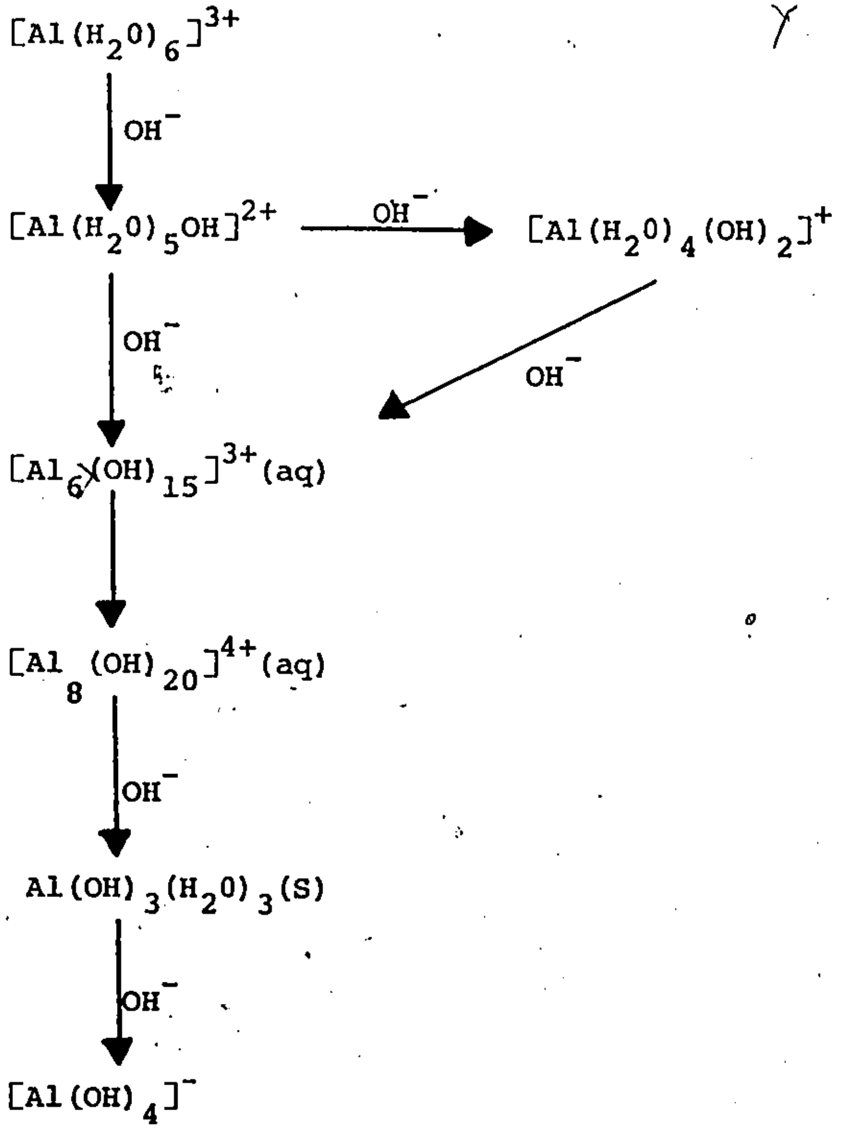


FIGURE 2.4 Stepwise Hydrolysis of the Tripositive Aluminum Ion to the Negative Aluminate Ion.

A comprehensive theory on the development of aluminum polymers was proposed by Hsu. In his attempt to understand why some aluminum hydroxopolymers are amorphous and others are crystalline, he considered two concepts: First, each aluminum ion in solution is coordinated with six molecules of H_2O and contributes half a positive charge to each. When a hydroxyl ion is attached on the coordination shell, half of its negative charge will neutralize half a positive charge of the aluminum ion, leaving the remaining half negative charge unsatisfied and so available to balance half a positive charge from another Al^{3+} ion. In this way, the OH^- functions as a bridge between two aluminum ions.

Secondly, it is considered that the hydroxo-aluminum ions tend to polymerize in a 6-membered ring unit or multiples of such units, structures similar to those found in gibbsite.

When NaOH is added to an aluminum salt solution, the aluminum ion is hydrolysed to $Al(OH)^{2+}$ and $Al(OH)_2^+$. According to the first concept, these two forms are not stable and therefore polymerization will occur immediately after the OH^- ion is attached to the aluminum ion. According to the second concept polymerization will lead to the formation of ring units composed of six $Al(OH)_2^+$ ions. The step of polymerization is given below:

$$\begin{array}{rcl}
\mathrm{Al}^{3+} + \mathrm{OH}^- & = & \mathrm{Al(OH)}^{2+} \\
\mathrm{Al(OH)}^{2+} + \mathrm{OH}^- & = & \mathrm{Al(OH)}_2^{+} \\
6\mathrm{Al(OH)}_2^{+} & = & \mathrm{Al}_6\mathrm{(OH)}_{12}^{6+} \\
\hline
6\mathrm{Al}^{3+} + 12\mathrm{OH}^- & = & \mathrm{Al}_6\mathrm{(OH)}_{12}^{6+}
\end{array}$$

The structure of the $\mathrm{Al}_6\mathrm{(OH)}_{12}^{6+}$ ring unit consisting of six aluminum octahedra is illustrated in Figure 2.5.

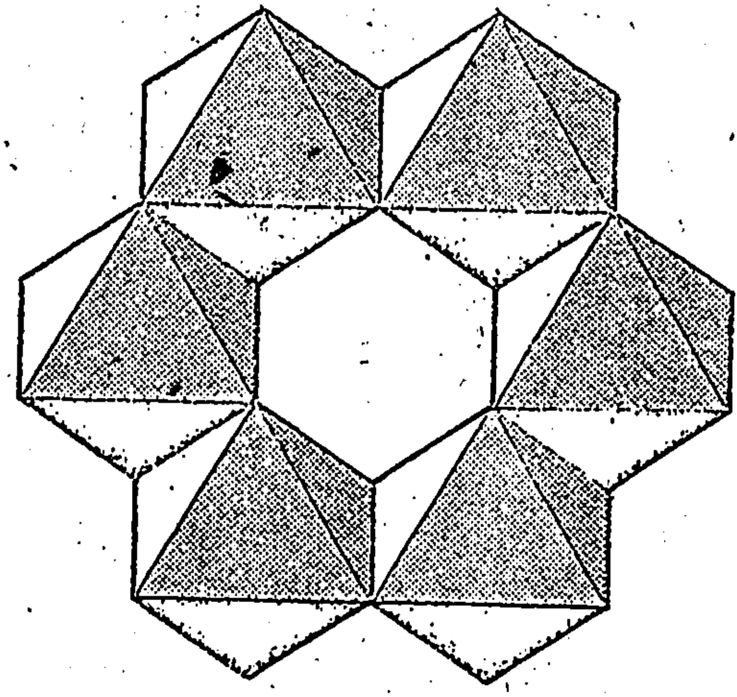


FIGURE 2.5 Structure of the $\mathrm{Al}_6\mathrm{(OH)}_{12}^{6+}$ ring unit (From Bersillon, 1977).

At NaOH/Al = 2 the above reaction will be complete and further OH^- addition will lead to the formation of double rings of the composition $\mathrm{Al}_{10}\mathrm{(OH)}_{22}^{8+}$ or triple rings consisting of $Al_{13}(OH)_{30}^{9+}$ rather than neutral $Al(OH)_3$ molecules. The net positive charge per aluminum will decrease with increasing OH/Al ratio, but all the hydroxopolymers will remain positively charged until the ratio reaches 3. At OH/Al = 2.75 and below, the positively charged polymers repel one another unless joined together by the counter-ions to form basic aluminum salts. The basic aluminum chloride is very soluble and precipitates only at high NaOH/Al ratios. On the contrary the basic aluminum sulphate precipitates even at NaOH/Al = 0.3. The precipitates will be amorphorus because of the diversity in the size and degree of hydration of the polymers and the counter-ions.

At NaOH/Al = 3.0 the net positive charge per aluminum disappears and all the polymers cluster together forming crystalline $Al(OH)_3$ in a matter of hours or days. The various steps in the formation of aluminum hydroxides are shown in Figure 2.6.

Johanson (1960) was the first to identify a polymeric structure with a formula $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. This is a tri-dimensional structure and includes twelve hexa-coordinated aluminum ions and one tetra-coordinated Al^{3+} ion. The existence of this polymer can not be explained by the Hsu's theory since this theory refers to

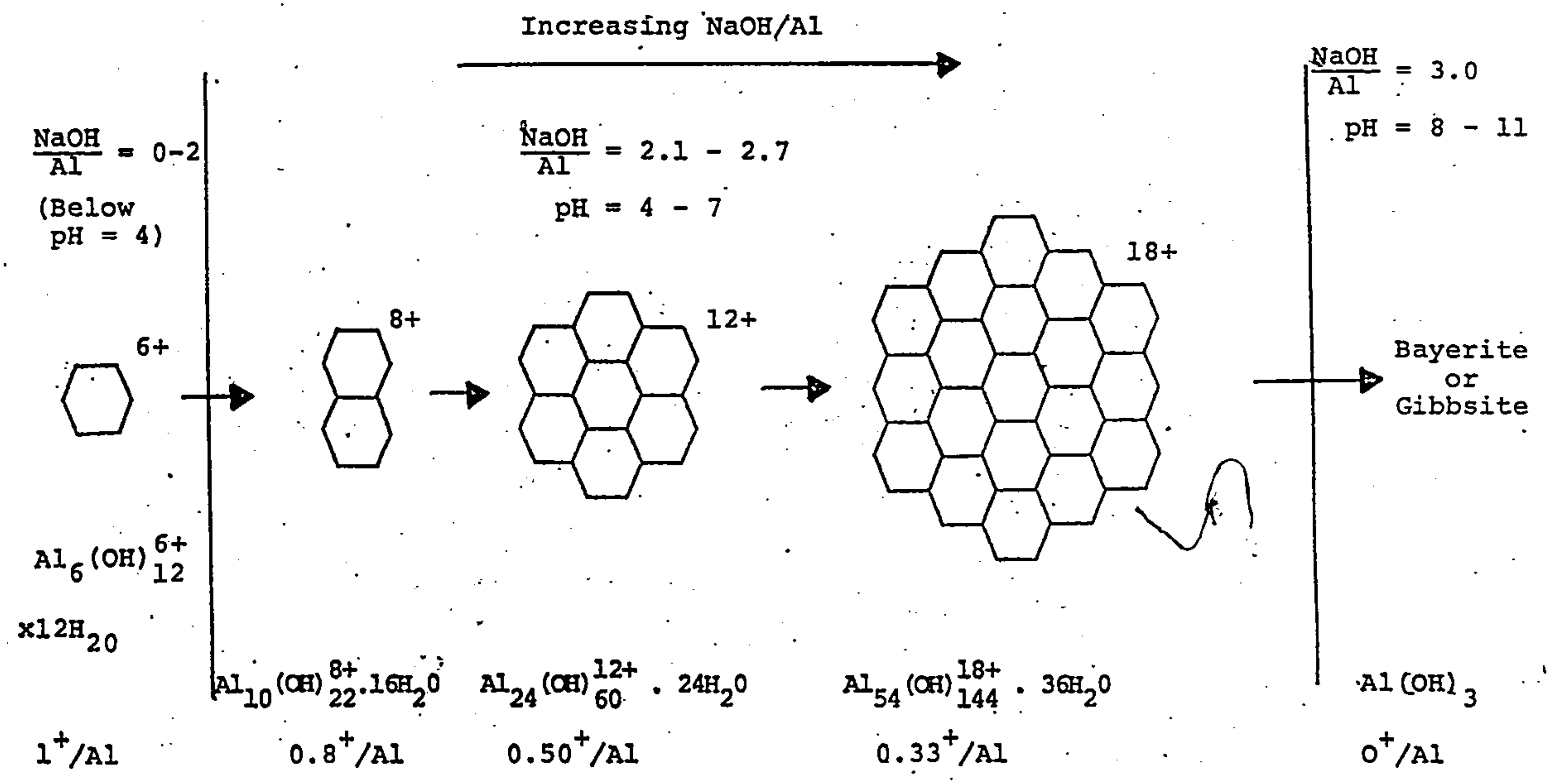


FIGURE 2.6 Development of Aluminum Hydroxides Proposed by Hsu.

the development of hydroxopolymers in two dimensions. The structure of this Al_{13} polymer is depicted in Figure 2.7.

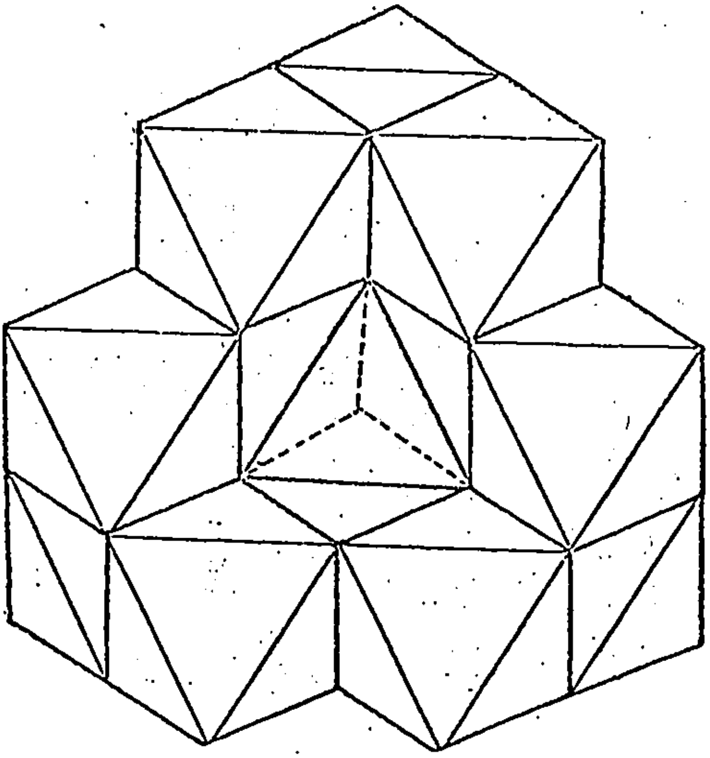


FIGURE 2.7 Structure of the $[Al^{VI}_{12}(OH)_{24}Al^{IV}O_4(H_2O)_{12}]^{7+}$ Polymer . (From Bersillon, 1977).

The existance of a tetra-coordinated aluminum is rare because this state is very unstable. In this case, however, the tetra-coordinated ion is very well protected in the centre of a tetrahedron formed by the twelve hexa-coordinated aluminum ions. The same polymer was identified by Rausch and Bale (1964) using small angle X-rays. Akitt, et al. (1972) using nuclear magnetic resonance suggested the following polymeric forms:

$[Al(H_2O)_6]^{3+}$, $[Al_2(OH)_2(H_2O)_8]^{4+}$,

$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]$ and probably

$[Al_8(OH)_{20}(H_2O)_{12}]^{4+}$.

Bottero, et al. (1979) and (1980), reported the identified species using NMR spectroscopy and titration data. The conditions under which the polymers were developed were:

- Aluminum concentration in the final solution 0.1 M.
- Degree of neutralization (NaOH/Al molar ratio) ranging from 0 to 2.5.
- Aging time up to 24 hours.
- Temperature 20°C.
- NaOH addition rate 125 ml per hour of 0.5N solution.

The identified species were:

$Al(H_2O)_6^{3+}$ $Al(OH)(H_2O)_5^{2+}$ $Al(OH)_2(H_2O)_4^{+}$

$Al_2(OH)_2(H_2O)_8^{4+}$ $Al_2(OH)_x(H_2O)^{(6-x)+}$

They also identified a polymer containing a tetra-coordinated aluminum. Analysing potentiometric data, they were able to identify this polymer having the formula $Al_{13}(OH)_{28}O_4(H_2O)_8^{3+}$. They also reported the existence of a non-settling gel for which they gave the formula $Al(OH)_3^{*}$. Their findings are illustrated in Figure 2.8, where the various aluminum polymeric species are represented as a percentage of the total aluminum in solution as a function of pH or the ratio B = OH/Al.

In Table 2.4 thermodynamic data is shown characterizing the various polymeric forms reported in the literature.

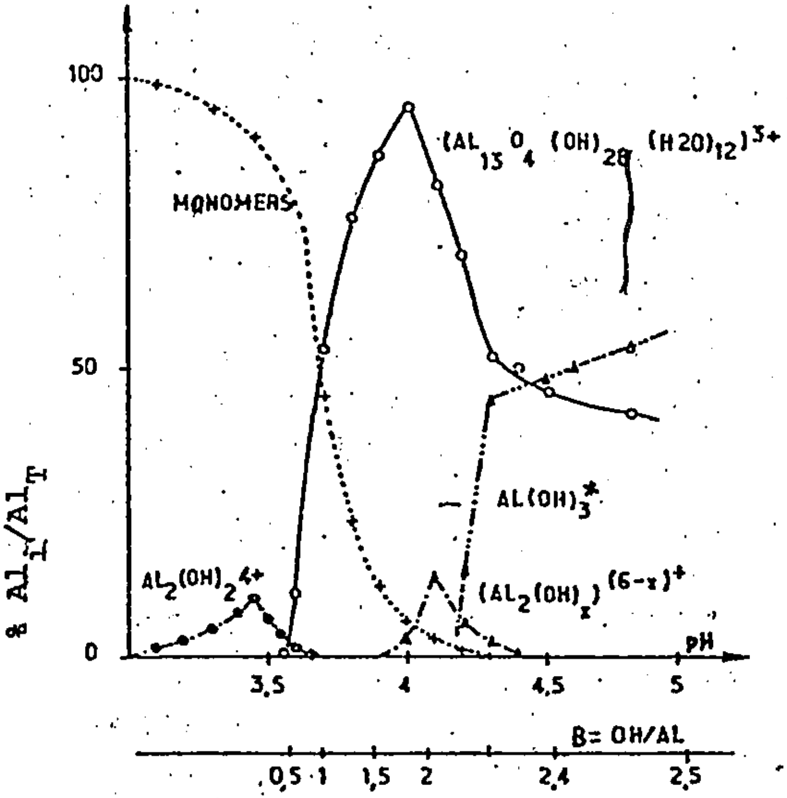


FIGURE 2.8 Aluminum Species as a Function of pH or the Ratio B = OH/Al (From Bottero, et al., 1980).

TABLE 2.4 Equilibrium Constants for Polymeric Hydroxoaluminum Complexes. (From Bottero, et al., 1980)

Complex	Log Kmn[1]
$Al_2(OH)_2^{4+}$	- 6.95
$Al_6(OH)_{15}^{3+}$	-47.0
$Al_7(OH)_{17}^{4+}$	-48.8
$Al_{13}(OH)_{34}^{5+}$	-97.6
$Al_{13}(OH)_{32}^{7+}$	-104.5
$Al_2(OH)_x^{(6-x)+}$	- 5.5
$Al(OH)_3^*$ gel	-10.1

[1] Kmn is the equilibrium constant for the reaction

$$mAl^{3+} + nH_2O = Al_m(OH)_n^{+3m-n} + nH^+$$

2.3 PHOSPHORUS REMOVAL WITH AL

2.3.1 Mechanism of Removal

The mechanism of phosphorus removal by means of aluminum salts was and still is, a matter of conflict among the investigators. Even though in some textbooks the phosphorus removal is attributed to the precipitation of insoluble aluminum phosphate, it is common knowledge that this is not fully correct, since under stoichiometric conditions (i.e., aluminum: phosphate molar ratio equal to one) only 60 to 70 percent of phosphorus can be removed (Benedek, et al., 1976).

Another model, presented by Lee, et al. (1959) and Henriksen (1962), was based on the idea that phosphates are removed by being adsorbed on aluminum hydroxide. Henriksen presented data showing that orthophosphates were removed following a Langmuir adsorption isotherm pattern. This theory is very questionable and has been highly criticized by a number of investigators. The weak points of this theory are:

- The optimum pH for phosphorus removal does not coincide with the optimum pH for $Al(OH)_3$ precipitation. Stumm and Morgan (1962) found that aluminum started to precipitate at a much lower pH in the presence of phosphate than in its absence. This is an indication that aluminum and phosphorus are involved in some kind of chemical interaction.
- Recht and Ghassemi (1970) reported that when the pH was kept constant, the removal of orthophosphate up to 1:1 metal to phosphate ratio was directly proportional to the

concentration of the added cation. This direct stoichiometric relationship indicates that a chemical reaction occurs between the metal cation and the phosphates.

- The theory of phosphate adsorption on aluminum hydroxide does not take into consideration the complex chemistry of aluminum and phosphorus.

Stumm and Morgan, in their previously mentioned work, recognized the complexity of an aluminum-orthophosphate system considering the hydrolysis of aluminum in aqueous solutions and the interference of hydroxyl ions parallel to phosphate activity. In their opinion, low metal to phosphate molar ratios lead to the formation of insoluble aluminum phosphate while at molar ratios higher than 1:1 a "mixed" aluminum hydroxophosphate is precipitated. Recht and Ghassemi suggested that the hydrolysis products of Al(III) and not the Al^{3+} ion alone are responsible for the precipitate formation. They found that for an initial orthophosphate concentration 12 mgP/l and pH equal to 6.0, 1.4 moles of Al(III) are required for precipitation of 1 mole of orthophosphate. This linear relationship was found to exist up to an 1:1 aluminum to phosphorus molar ratio.

Ferguson and King (1977) applied the above mentioned stoichiometric relationship (aluminum: phosphorus = 1.4:1 in the precipitate) to a model which enabled them to qualitatively reproduce the effects of alum dosage and pH observed in several experimental studies. The removal of phosphates was broken into three steps each one involving a different mechanism. In the first, insufficient aluminum is added. If the pH is in the proper range, the removal will be directly proportional to the coagulant dose. They considered that the stoichiometry leads to the formation of $Al_{1.4}PO_4(OH)_{1.2}$. At higher aluminum dosages (close to the stoichiometric requirement) removal can not be predicted from stoichiometry. In this zone the phosphate removal can be calculated from the equilibrium between the aluminum phosphate solid and the solution. Finally in zone three, the stoichiometric requirement is far exceeded and the excess aluminum precipitates as aluminum hydroxide.

Hsu approached the aluminum-phosphorus interaction from a different viewpoint. He suggested that the Al-OH-Al and $Al-PO_4-Al$ linkages tend to integrate into a whole unit. Thus, the precipitation of phosphate and aluminum are governed by the integrated particles rather than by $Al(OH)_3$ and $AlPO_4$ individually (Hsu, 1973; 1975; 1976). His model is based on the competitive action of

9

PO_4^- and OH^- on aluminum precipitation. He found that $AlPO_4$ was the precipitation product at high phosphate concentrations (phosphate/aluminum molar ratio 6 and above) and moderate acidity (pH = 3). Under such conditions, the activity of OH^- is too low to compete with PO_4^{3-} for Al^{3+}. However, in this case a large amount of phosphorus remained in solution. Generally, the sum of PO_4^{3-} and OH^- in the precipitation product was found to be equal to Al^{3+} in the precipitate, on an equivalent basis. Under optimum conditions all the aluminum was completely removed. In an earlier report (1968), Hsu presented data indicating that when aluminum hydroxopolymers were applied for phosphorus removal, the mechanism was a simple "neutralization" of the net positive charge of the polymeric species. Therefore, the precipitation was dependent on the concentrations of Al and P and the basicity of the polymers.

2.3.2 The Role of pH

It is always desirable in wastewater treatment to use optimum conditions for phosphorus removal. However, it is quite common to study the removal as a function of coagulant dosage. This principle does not consider the effect of pH on chemical precipitation and despite its simplicity is not always the best way to do so. On the other hand optimum pH conditions should not be considered by the means of the $AlPO_4$ equilibrium diagram, since, as it was shown, Aluminum Phosphate is not the precipitation product.

Very little agreement exists about the optimum pH range for phosphate precipitation. Henriksen (1962) was the first to show that the optimum basicity depends on the coagulant dosage. For a solution containing 17 mg/lP, the optimum pH ranged from 4.5-7.1 with 200 ppm of alum, but narrowed to 5.7-6.8 with 100 ppm of alum. Hsu was able to explain the discrepancies, met in the literature, considering the optimum pH range as a function of:

(1) the hydrolysis of aluminum in aqueous solutions,

(2) the competition of the various ions, present in solution, to react with Al^{3+},

(3) the concentration of aluminum and phosphorus in solution.

In samples with low P/Al molar ratio (Al in large excess) most of the aluminum will be as Al^{3+} in solution and the rest will form soluble complexes with phosphorus. When hydroxide is added to the solution, the hydroxyl ions will react preferentially with Al^{3+} (because of the higher charge per atom of Al) and form hydroxopolymers. After this stage, any additional OH^- can react with the aluminum-phosphate complexes and precipitation begins. When the phosphate content of the solution is high (phosphorus in excess) $Al-PO_4-Al$ linkages predominate over Al-OH-Al linkages in the reaction product. All the aluminum will be complexed with phosphates and any addition of OH^- will lead to the neutralization of these complexes and therefore to precipitation. For this reason, precipitation will occur at lower pH values. After passing the optimum pH range, the particles become negatively charged and restabilize. Depending on the dosage of the chemicals and in the absence of any other ions, Hsu showed that the optimum pH ranged from 2.5 to 7.5.

2.3.3 Effect of Foreign Components

The effect of foreign components on the coagulation of aluminum salts was reported as far back as 1925 by Miller. He considered the formation of a solid solution of aluminum salts in aluminum hydroxide in his attempt to explain the dependence of the pH of coagulation on the anions present. In 1946, Marion and Thomas suggested a theory of complex formation based on the ability of the various ions to co-ordinate with aluminum and the competitive action among them. According to Stumm and Morgan (1962) complex formation was responsible for the precipitation of aluminum hydroxide at lower pH in the presence of anions like ortho- and pyrophosphates. Hanna and Rubin (1970) studied the coagulation of Escherichia coli by aluminum salts in the presence of several diverse ions and they concluded that the effect of a particular anion depends on its ability to complex aluminum. They found that among the anions studied phosphate had a stronger affinity for aluminum than sulphate and nitrate.

A more detailed explanation on the effect of several ions on phosphorus removal by aluminum was given by Hsu (Yuan and Hsu, 1971; Hsu, 1973; Hsu, 1975). He considered two mechanisms of opposite effects.

- Foreign ions tend to neutralize the residual positive charge of a partially phosphated aluminum polymer leading to precipitation of both phosphate and aluminum together.
- These ions can also compete against phosphate in reacting with aluminum, therefore reducing the effectiveness of phosphate precipitation.

The beneficial or catastrophic effect of a particular ion will depend on the relative magnitude of these two mechanisms, which depends on the concentration of phosphorus, aluminum and ion in solution. For high P/Al molar ratios, all the aluminum will be complexed by phosphates. Any addition of anions (such as SO_4^{2-}) will lead to the competition of these with phosphates, therefore reducing the effectiveness of precipitation. At low P/Al ratios, any addition of anions up to the stoichiometric point, will lead to the precipitation of the aluminum-phosphate complexes at lower pH values since less hydroxide is required for the neutralization of the polymers. However, in excess of these anions, the competitive action becomes stronger and the effectiveness is lowered.

The order of magnitude of the affinity of the various anions to co-ordinate with aluminum is given below (from Fiessinger, 1976):

$$OH^- > F^- > PO_4^{3-} > SO_4^{2-} > Cl^- > NO_3^-$$

The effect of montmorillonite was similar to the one observed with sulfate and fluoride with its magnitude intermediate between them (Yuan and Hsu, 1971). Hsu (1975) also studied the effect of calcium. He concluded that calcium resulted in a great improvement in phosphate removal. This was due to the precipitation of a mixed phosphate of calcium and aluminum and especially for pH values above 6.8 to the formation of insoluble calcium phosphate.

In a recent paper (1980), Arvin and Petersen included the bicarbonate activity into an equilibrium model. They found that bicarbonate was complexed in the precipitate and showed that control of the bicarbonate activity can influence greatly the removal of phosphorus.

2.3.4 Effect of Temperature

Recht and Ghassemi (1970) conducted a series of experiments to study the possible effects of temperature on the kinetics and the efficiency of the removal of phosphorus by means of aluminum and ion(III) salts. They experimented with two temperature levels: The ambient temperature ($\sim 25^{\circ}C$) and $5^{\circ}C$. In both cases, they did not notice any measurable effect on the rate of removal of phosphates (the reaction was complete in less than 1 sec.) or on the extent of removal.

In the literature there is no indication on the effect of temperature on the phosphate removal when hydroxy-aluminum polymers are used to remove phosphorus.

2.3.5 Effect of Aging Time of the Aluminum Solution

In contrast to the behaviour of Fe(III) solutions, Recht and Ghassemi found that Al solutions were stable over a two month observation period. Using 0.772 mM solution of aluminum nitrate they did not observe any changes in pH, conductivity and the efficiency to precipitate phosphate.

However, the aging time affects the efficiency of the hydroxy-aluminum polymers to remove turbidity from water (Fiessinger and Bersillon, 1977).

2.3.6 The Nature of the Precipitates

Recht and Ghassemi reported that the precipitates obtained in the precipitation of phosphates with aluminum were found amorphorus after examination by X-ray diffraction analysis.

The same result was reached by Hsu (1968) in his work with hydroxy-aluminum polymers. The explanation given by Hsu is based on the concept that a phosphate ion tetrahedron tends to link two aluminum polymers together. Therefore, all the phosphate tetrahedra stay between polymers and twist them to different orientations. In the same work, Hsu noticed some degree of crystallization when he used $AlCl_3$ solution. However, the precipitation with $AlCl_3$ occurred at low pH (around 3) and high phosphorus to aluminum ratios (greater than 9). In this system, the product of precipitation is or it is very close to $AlPO_4$.

2.3.7 Condensed Phosphates Removal

Very little work has been done on the removal of condensed phosphates by aluminum. Sawyer (1952) reported that aluminum salts are very effective in removing all forms of phosphates. Stumm, however, showed (1964) that tripolyphosphates are not removed well. He suggested that this was due to the formation of soluble complexes such as $AlP_3O_{10}^{2-}$.

Ghassemi and Recht (1970) reported that orthophosphates, on an equivalent basis, is more efficiently precipitated by both aluminum and iron and over a broader pH range than are the polyphosphates. However they found that the optimum pH values for maximum removal were nearly the same. The discrepancies were explained as a different mechanism including both chemical reaction and physical adsorption. Benedek, et al. (1976) also observed a similar behaviour.

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

3.1.1 Sodium Phosphate

Sodium Phosphate ($Na_3PO_4.12H_20$) (ACS regent grade) was obtained from J.T. Baker Chemical Company, Phillipsburg, N.J. Stock solution of 4.5 g/l P was prepared and used for the preparation of synthetic wastewater.

3.1.2 Sodium Bicarbonate

Sodium Bicarbonate of ACS reagent grade was obtained from BDH Chemicals, Toronto. Stock solution of 60 g/l $NaHCO_3$ was prepared and used to provide buffering in the model wastewater.

3.1.3 Alum

Alum is the commercial name of Aluminum Sulfate. ACS reagent grade was obtained from the Fisher Scientific Company, Fair Lawn, N.J. 0.1 M as Al^{3+} Stock solution was prepared and used for the treatment of wastewater.

3.1.4 Aluminum Chloride

Aluminum Chloride was used in the preparation of PBAC. It was obtained in the form of $AlCl_3 \cdot 6H_2O$ (ACS reagent grade) from the J.T. Baker Chemical Company, Phillipsburg, N.J. Stock solution of 0.5 M as Al^{3+} was prepared and stored. Although there is no indication in the literature that such aluminum solutions hydrolyze, the stock solution was prepared every month.

3.1.5 Sodium Hydroxide

1 N Standard Solution was obtained from BDH Chemicals Co., Toronto, and diluted to total volume of 2ℓ. This gave a 0.5N solution which was used for both the preparation of PBAC and control of pH in the precipitation of phosphorus.

3.1.6 Hydrochloric Acid

0.5 N solution was prepared from 1 N Standard Solution obtained from the BDH Chemicals Co., Toronto, and was used in controlling the pH in the precipitation process.

3.2 WATER SOURCES

3.2.1 Synthetic Wastewater

The use of synthetic wastewater was considered necessary because the simplicity of this system could lead to a better understanding of the mechanisms involved. This wastewater was used for the study of phosphorus removal and settling rates.

Each batch of the wastewater was prepared by adding 10 ml of the phosphorus stock solution and 10 ml of the bicarbonate stock solution into a volume of approximately 3 ℓ of distilled water. A predetermined amount of 0.5 N hydrochloric acid or 0.5 N sodium hydroxide solution was also added to bring the pH to the desired level for the coagulation study. The phosphorus and bicarbonate concentrations were approximately 15 mg/l and 200 mg/l respectively.

3.2.2 Burlington Wastewater

This wastewater was taken from the aeration tank of an extended aeration pilot plant at Canadian Centre for Inland Waters located in Burlington, Ontario. The pilot plant influent was Burlington wastewater. The wastewater was used for the study of phosphorus removal, settling rates and supernatant suspended solids.

At the time of sampling, this wastewater had the following characteristics:

	Sample I	Sample II
Suspended Solids	2200	1800
TOC	4.9	6.0
P	1.9	1.6

All values are in mg/l. Sample I was used when the coagulant dosage was determined by the molar ratio Al:P equal to 1.0, while Sample II was used when a ratio of Al:P equal to 2.75 was employed. The samples were stored in a drum and aerated for five days until the experiments were over. Since the phosphorus concentration was low, the samples were spiked to a phosphorus level of approximately 5 mg/l.

3.2.3 Hamilton Wastewater

This wastewater was taken from the aeration basin of the Hamilton Sewage Treatment Plant. It was used to study phosphorus removal and the filtrability of the sludge. At the time of sampling the characteristics of the wastewater were:

Suspended Solids:	2800 mg/l
Filtered TOC:	5.9 mg/l
Phosphorus:	1.1 mg/l
Calcium:	20 mg/l
Iron:	5.35mg/l

No coagulant is added in the aeration tank of the plant because of the high iron concentration. The sample was spiked to approximately 7 mg/l P.

3.2.4 Domtar Wastewater

This is a treated wastewater from the Longford Mills Plant of Domtar Chemicals. The company manufactures a variety of chemicals. The effluent of the wastewater treatment unit has a low BOD level and a high COD which indicates a great deal of non-biodegradable materials. The average plant effluent characteristics for the year 1979 are given below (From Benedek, et al., 1980):

BOD = 9 mg/l
COD = 202 mg/l
P = 0.05 mg/l
S.S. = 11 mg/l
Flow Rate = 160 m^3/d

When the sample used was taken, it had the following characteristics:

Filtered TOC = 45.5 mg/l
pH = 5.45

The Domtar wastewater was used to study the efficiency of the coagulants to remove organics.

3.3 PBAC PREPARATION

A configuration of the system used for the preparation of PBAC is given in Figure 3.1. The procedure was as follows:

50 ml of the $AlCl_3$ stock solution were transferred into a 500 ml Erlenmeyer flask. Sodium hydroxide solution was mixed with distilled water to give a final volume of 200 ml and the solution was placed in a storage tank. The volume of the hydroxide solution was specified by the desired OH:Al molar ratio (Further on, this ratio will be referred as B, for basicity) and is given in Table 3.1.

TABLE 3.1 Amount of NaOH Solution Required to Give Desired Basicity

B = OH:Al	ml of NaOH Stock Solution
0.0	0
1.0	50
1.8	90
2.2	110
2.5	125

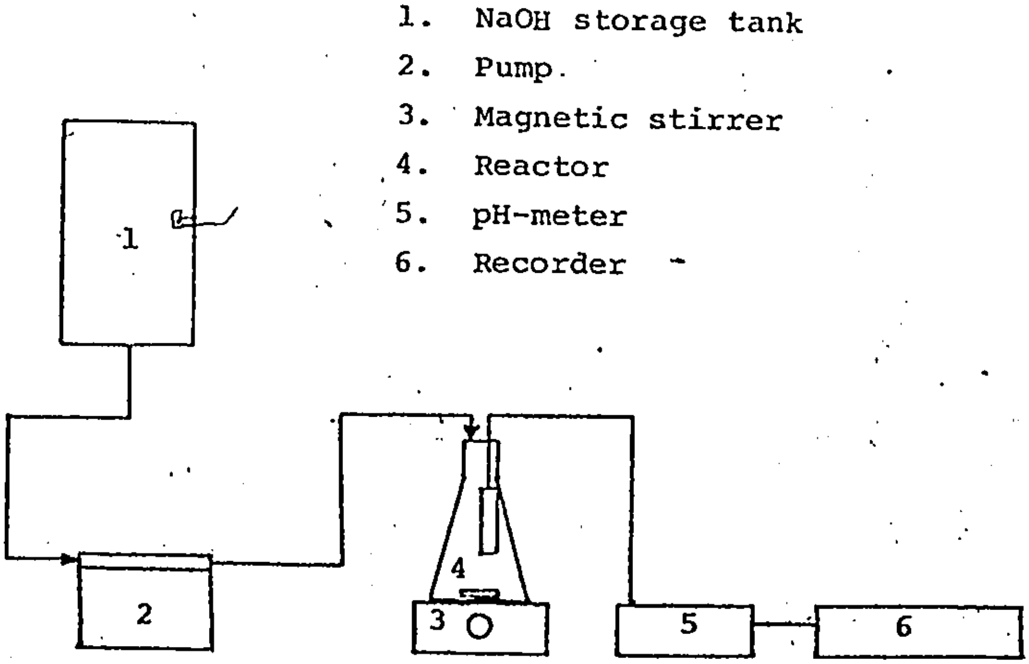


FIGURE 3.1 Configuration of the System Used for PBAC Preparation.

The OH:Al ratio in the preparation is indicated by a number following PBAC (for example, PBAC 1.8 means PBAC prepared when aluminum chloride was partially neutralized with sodium hydroxide to a molar ratio of OH:Al = 1.8).

The NaOH solution from the storage tank was added very slowly to the Erlenmeyer flask under vigorous mixing conditions. The rate of addition was 122 ml per hour and the temperature was 21 ± 1°C. Under these conditions the nature of the aluminum polymers is known (Bottero, et al., 1980). During the preparation, the pH was monitored continuously. The change of pH as a function of time for OH:Al ratios 2.2 and 2.5 is given in Figure 3.2.

When all the NaOH solution had been transferred into the flask, the operation was stopped and the PBAC solution (0.1 M as Al^{3+}) was left for aging.

3.4 COAGULATION STUDIES

3.4.1 Jar Test Apparatus

For the precipitation studies, a modified jar test apparatus was used. This modification was designed by Benedek, et al. (1976) and enabled the investigators to study overflow rates and consequently predict clarifier performance.

The jars had inside dimensions 0.10 m x 0.10 m base and 0.35 m height and were made from plexiglass. A horizontal sampling tube was inserted halfway across the jar at 76.2 mm from the bottom. The sampling probe had 3.2 mm holes drilled 10 mm apart, perpendicular to the axis. Sampling through the port was controlled by solenoid valves which in turn were controlled by a sample sequencer. The Phipps and Bird six place stirrer was modified to accept the new jars by doubling the length of its legs and by adding a second identical paddle

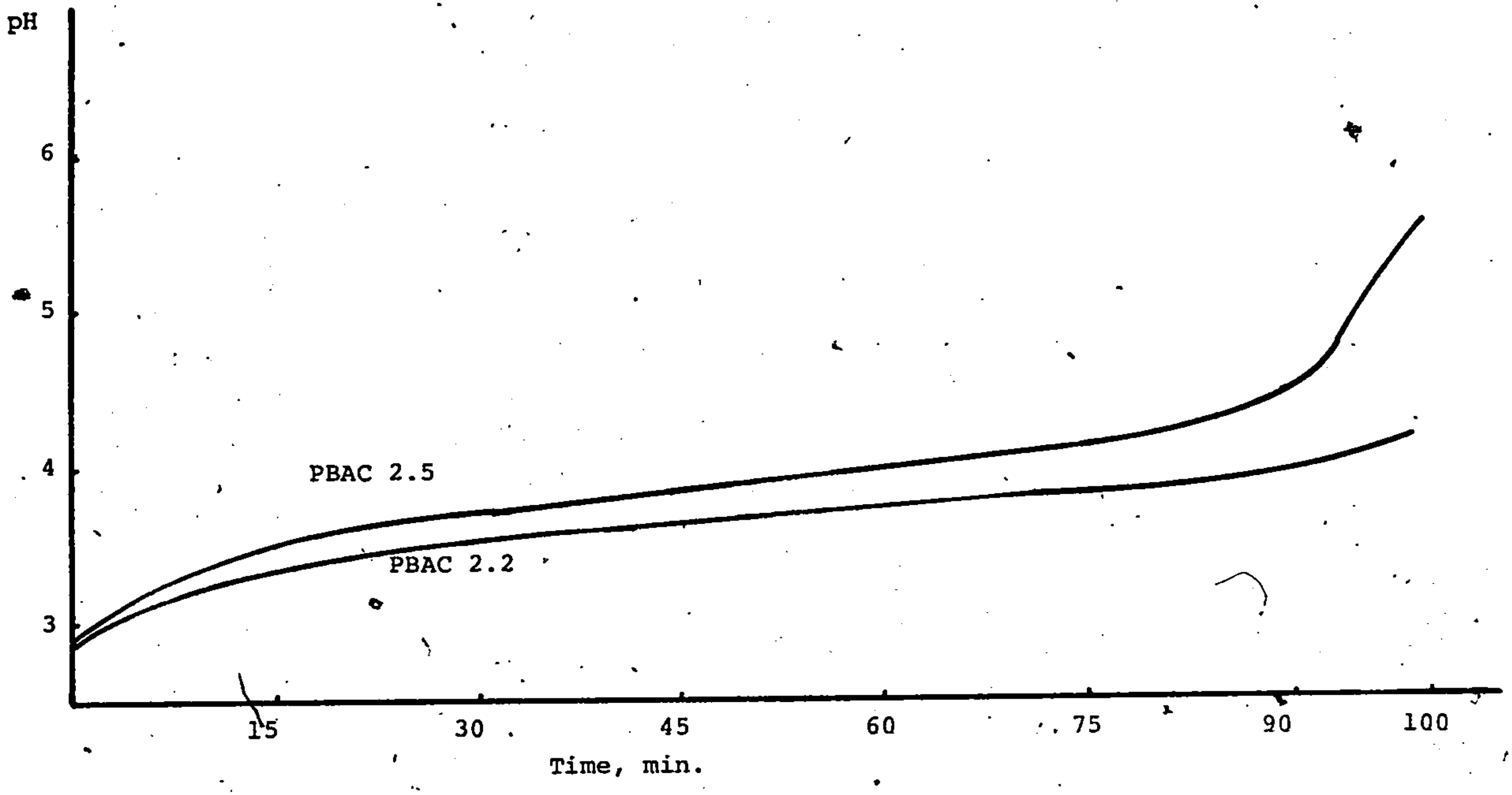


FIGURE 3.2 pH as a Function of Time During the Preparation of PBAC 2.2 and 2.5.

onto the lengthened shaft. A schematic representation of the batch settling apparatus is shown in Figure 3.3.

3.4.2 pH Control

The pH control was considered essential for better comparison of the efficiency of the various coagulants tested. The desired ultimate pH in each test was obtained by adding a predetermined amount of 0.5 N sodium hydroxide or hydrochloric acid solution to the wastewaters prior to coagulant addition. The exact amount of acid or base required was determined from sets of pH control curves. These curves were obtained from preliminary tests which were performed using model jars. Figure 3.4 shows such a set of curves obtained for the synthetic wastewater case and for Al:P ratio equal to 1.0. This kind of pH control was adequate since the pH values obtained at the end of the test were within ± 0.2 pH units of the desired value.

3.4.3 Experimental Procedure

For the synthetic wastewater case the start of each jar test was specified by the time the coagulant was added. Just before the addition of the coagulant, a predetermined amount of HCl or NaOH solution was added to control the pH. The various periods of the test were set according to the suggestions by Benedek, et al. (1976).

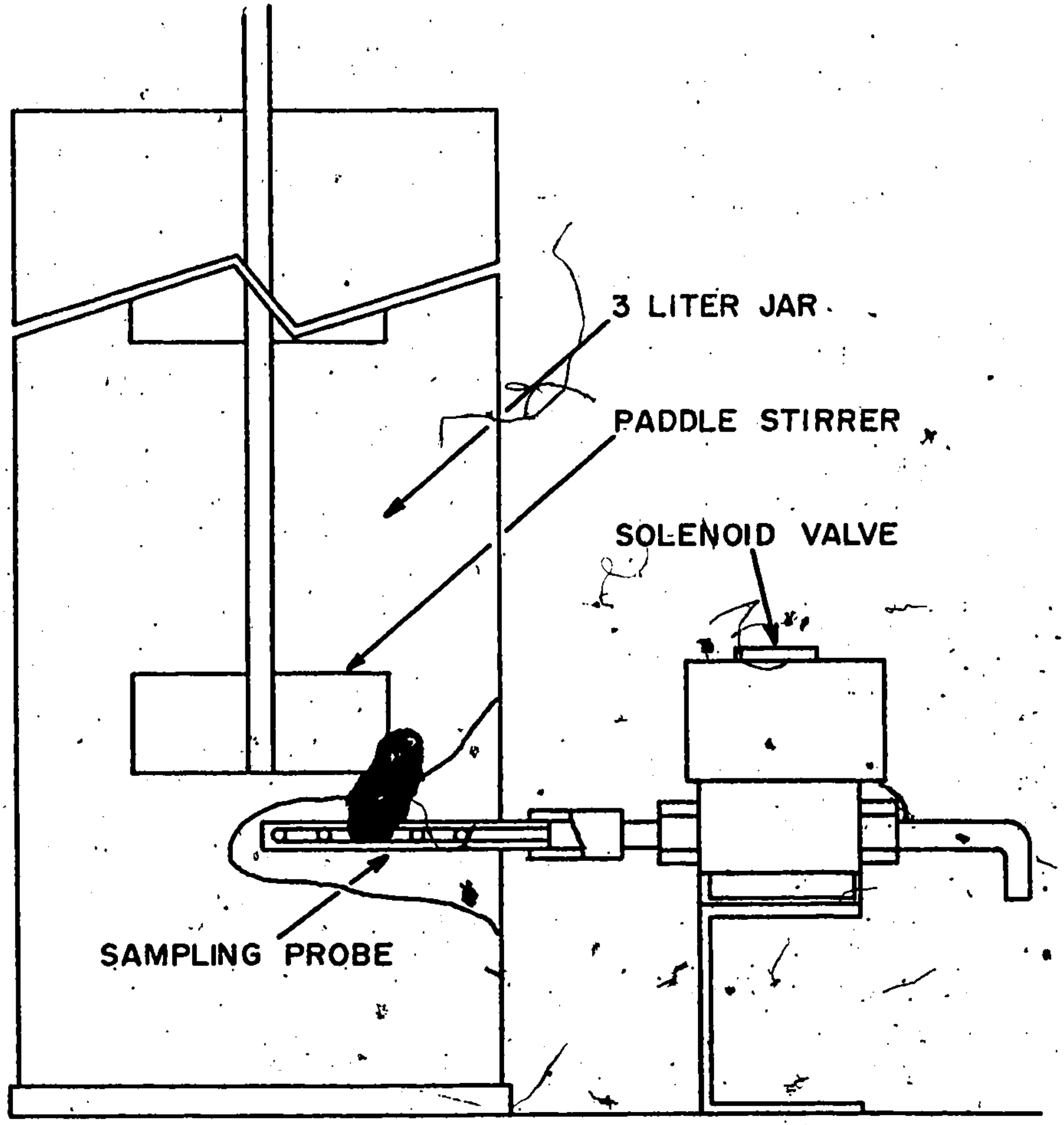


FIGURE 3.3 Schematic Representation of the Batch Settling Apparatus.

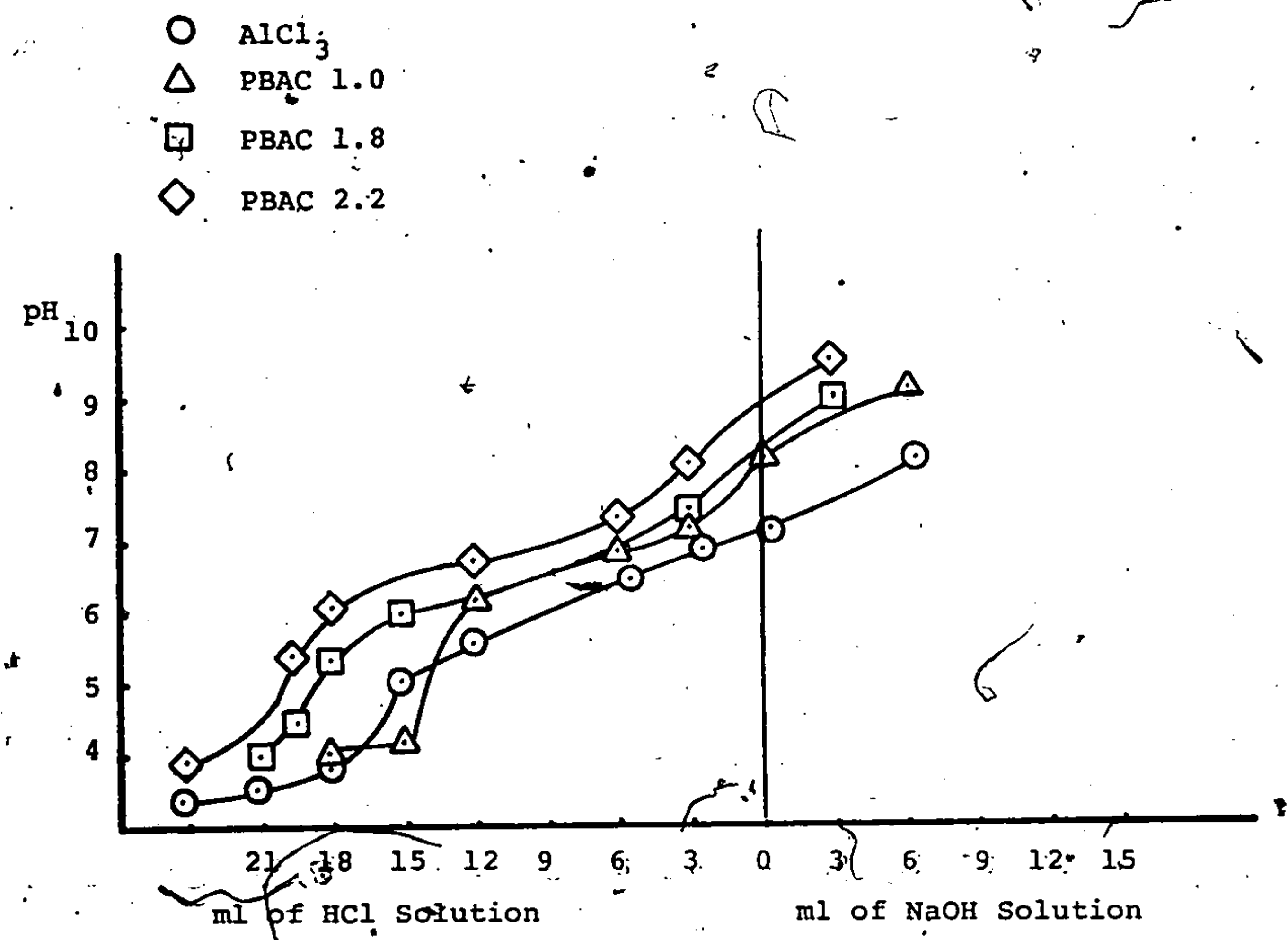


FIGURE 3.4 pH Control Curves for the Synthetic Wastewater Case and for Al:P = 1.0.

Rapid Mix: 6 min at 90 rpm
Slow Mix: 14 min at 30 rpm
Settling Period: 30 min.

During the rapid mix period one sample was taken from each jar. The phosphorus concentration in this determined the initial phosphorus level. During the settling period, samples were taken at 2.5, 5, 10, 15, 20 and 30 min. from the beginning of settling. When the settling operation was over, a last sample was taken from each jar. This was filtered through a 0.45 μ Sartorius membrane and used for the determination of the ultimate phosphorus concentration (i.e., phosphorus concentration at infinite time of settling). All sampling was made by the means of the sample sequencer and the volume of each sample was 30 ml.

One special set of experiments was conducted with aluminum chloride as coagulant and Al:P molar ratio equal to 1.0. The reason of conducting this particular set was to check the point in Hsu's theory that phosphates are complexed with aluminum at low pH and do not precipitate. Any addition of OH^- ions will neutralize the soluble complexes and precipitation will start at lower pH values. The difference in this test was in the order of mixing the chemicals. Instead of adding a predetermined amount of acid or base prior to coagulant addition, all samples were acidified to pH 3.4 and the coagulant was added. After that, sodium hydroxide solution was added to bring the pH to desired levels in the 4 to 9 range. The rest of the procedure was the same as before.

When domestic wastewater was used, a parallel activity of calcium was identified. In order to separate the effect of calcium from that of the aluminum coagulants, a different pattern of coagulation was followed:

A predetermined amount of acid or base solution was added at time zero under high stirring conditions (90 rpm). After three minutes of stirring a sample was taken and the pH was recorded. The soluble phosphorus content in this sample determined the initial phosphorus level and not the one measured after spiking the samples. After that, the coagulant was added and the procedure was the same as before. Two samples were taken: One from the supernatant after 10 min. of settling and the second when the procedure was over. The first one was analyzed for its suspended solids content and its total P concentration and the other for its filtered P concentration. The calcium content of all samples was also measured and in the Hamilton wastewater case the iron concentration as well. No other samples were taken during the settling period, the height of the solids interface, however, was recorded and used to calculate the settling rates.

When the industrial wastewater was used, no phosphorus was measured. The experimental procedure was similar to the one used for the synthetic wastewater case. Two samples were taken: One before the test started and the other after it was over. The first one specified the initial TOC concentration and the second one the final TOC level.

3.4.4 Settling Rates

The study of the settling rates for the synthetic wastewater case was based on the following theoretical considerations:

If C_o is the initial phosphorus concentration, C_u the residual and C_t the concentration at time of sampling t, then the fraction $\frac{C_t - C_u}{C_o - C_u}$ of the flocs will have a velocity less than u_t, where

$$u_t = \frac{h_t}{t} \quad \text{and} \quad h_t = h_o - \frac{V(N - 1)}{A} \qquad (1)$$

where h_t = liquid level above the sampling port at time t

h_o = initial liquid level above the sampling port, in this case 223.8 mm

A = horizontal cross sectional area of the jars, 100 cm^2

N = sample number

V = volume of individual samples, 30 ml.

According to the Hazen-Camp ideal sedimentation tank theory, the overall removal in a clarifier is defined as

$$R = (1 - X_o) + \frac{1}{V_o}\int_o^{X_o} u dx \qquad (2)$$

where: R = Total fraction of settleable solids removed,

V_o = Terminal velocity equal to the clarifier overflow rate, and

X_o = Fraction of settleable solids with terminal velocity less than V_o.

The integral term in the above equation is considered to correct for settling of particles entering the clarifier at levels lower than the water surface. In the present work, this term was neglected. Therefore, terminal velocities can be calculated to indicate the maximum allowable clarifier overflow rate for any required solids removal. Thus, terminal velocities can be converted to overflow rates by converting units of cm/min to $m^3/m^2.h$ (or m/h). Considering the times samples were taken and the liquid level in the jars a curve was drawn converting the sampling time to overflow rates (Figure 3.5). (Note that: 1 cm/min = 0.6 m/h).

When mixed liquor was used, the settling rates were studied by recording the height of the solids interface at various times.

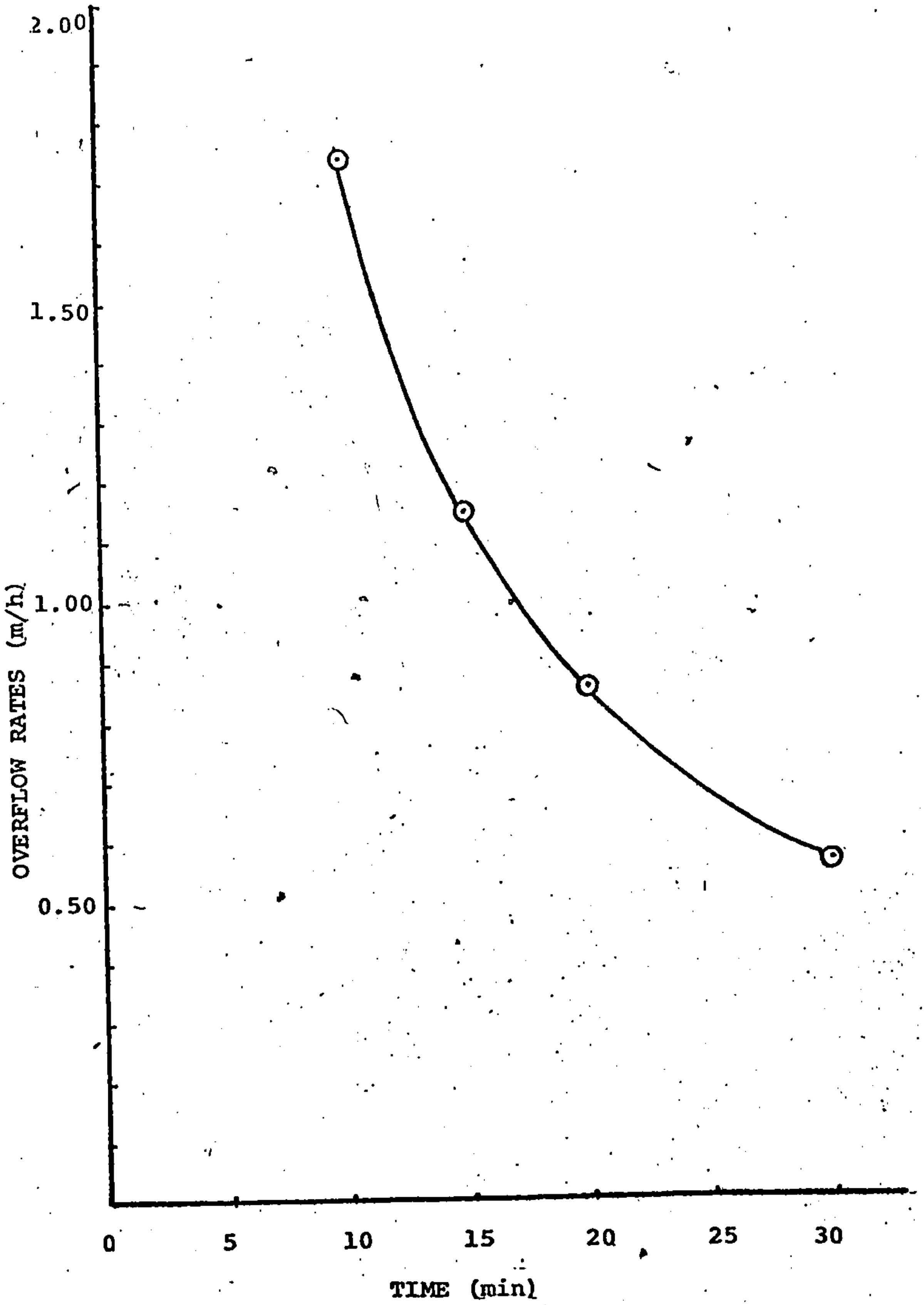


FIGURE 3.5 Overflow Rates as a Function of Sampling Time.

3.5 ANALYTICAL PROCEDURES

3.5.1 Phosphorus

Phosphorus was analyzed according to the 4-68 W and 3-68 W Technicon's Industrial Methods. The two methods are identical except for differences in sensitivity due to differences in colorimeter cell size. The 4-68 W Method used for P concentrations up to 20 mg/l and the 3-68 W for up to 7 mg/l.

According to these two automated procedures condensed phosphates present in the wastewater are converted to orthophosphate by means of hydrolysis with sulfuric acid and the total P concentration is then determined by the reduction of phosphomolybdic acid with aminonaphthol-sulfonic acid.

When synthetic wastewater was used, all samples were acidified with five drops of concentrated sulfuric acid and analyzed. In the case of the ultimate phosphorus concentration, the samples were first filtered through a 0.45 μ sartorious membrane and then acidified and analyzed. When mixed liquor was used all samples were first filtered and then acidified and analyzed unless the total phosphorus content was wanted. In this case, the samples first acidified and then filtered and analyzed.

3.5.2 Supernatant Suspended Solids

When the Burlington wastewater was used, a sample from the supernatant was taken from each jar and was analyzed for its suspended solids content. Since the concentration of solids was very low and the sample volume small, an indirect method of suspended solids analysis was employed. Using a Model DRT 1000 HF Intruments turbidimeter, the turbidity of the samples was determined and using a calibration curve the turbidity units were converted to suspended solids expressed as mg/l. As it can be seen in Figure 3.6, turbidity and suspended solids were very well correlated.

3.5.3 Metals

The analysis of calcium and iron was performed using a Varion Techron Atomic Absorption Spectrophotometer AA6, according to the manufacturers' operating manual.

3.5.4 pH

A Fisher Accumet Model 230 pH/Ion meter was used for pH measurements. This pH meter is accurate to ±0.05 units. The instrument was calibrated with standard buffer solutions.

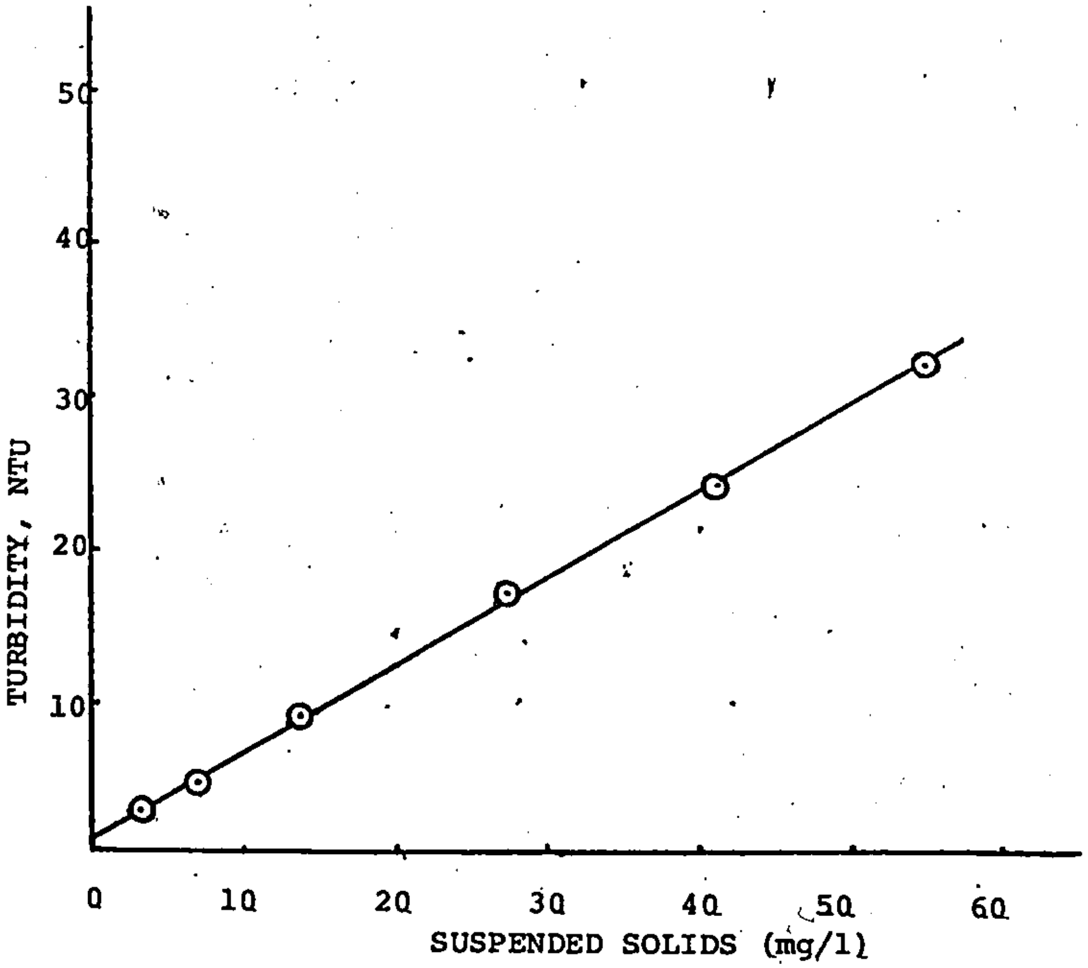


FIGURE 3.6 Calibration Curve for Correlation Between Turbidity and Suspended Solids

3.5.5 Specific Resistance

Studies on sludge filtrability were conducted according to the EPA Sludge Treatment and Disposal Manual (1973). For this purpose the Buchner funnel test was employed. The filtrability test was performed on the Hamilton wastewater. After the coagulation procedure was over, the treated solids were allowed to settle and 1.8 ℓ of supernatant were decanted from each jar. The remaining sludge had a concentration of suspended solids around 7000 mg/l. 100 ml of each sludge were used to perform a sludge filtrability test. The performance characteristics were:

Filter Paper: Two 7 cm in diameter Whatman No.4.

Pressure Drop: 20 in Hg.

Calculation of the specific resistance can be seen in the Appendix.

3.5.6. Organics

The organics content of the wastewater was analyzed using a Beckman 915 Total Organic Carbon Analyzer. The instrument is equipped with separate channels for the determination of Total Carbon and of Inorganic Carbon.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 THE EFFECT OF AGING TIME

The reasons for studying the effect of aging time were twofold: First, to investigate whether an optimal time exists with respect to maximum phosphorus removal and second to establish an operation aging time range.

PBAC with basicity of 2.2 was chosen to study aging time and its efficiency on phosphorus removal was tested. This basicity was chosen because PBAC 2.2 consists of large amounts of the highly hydrolyzed forms $[Al_{13}O_4(OH)_{28}(H_2O)_{12}]^{3+}$ and $Al(OH)_3^*$ gel. This PBAC was tested on synthetic wastewater. Maturation times studied were 0.5, 1, 3 and 24 hr. The Al:P molar employed was 2.75:1 and the pH ranged from 5 to 9.

4.1.1 Ultimate Phosphorus Removal

The effect of aging time on the efficiency of PBAC 2.2 to precipitate phosphorus is shown in Figure 4.1.1. The ultimate phorphorus removal (i.e., phosphorus removal at infinite time of settling) was plotted as a function to pH for the various aging times tested. For all examined

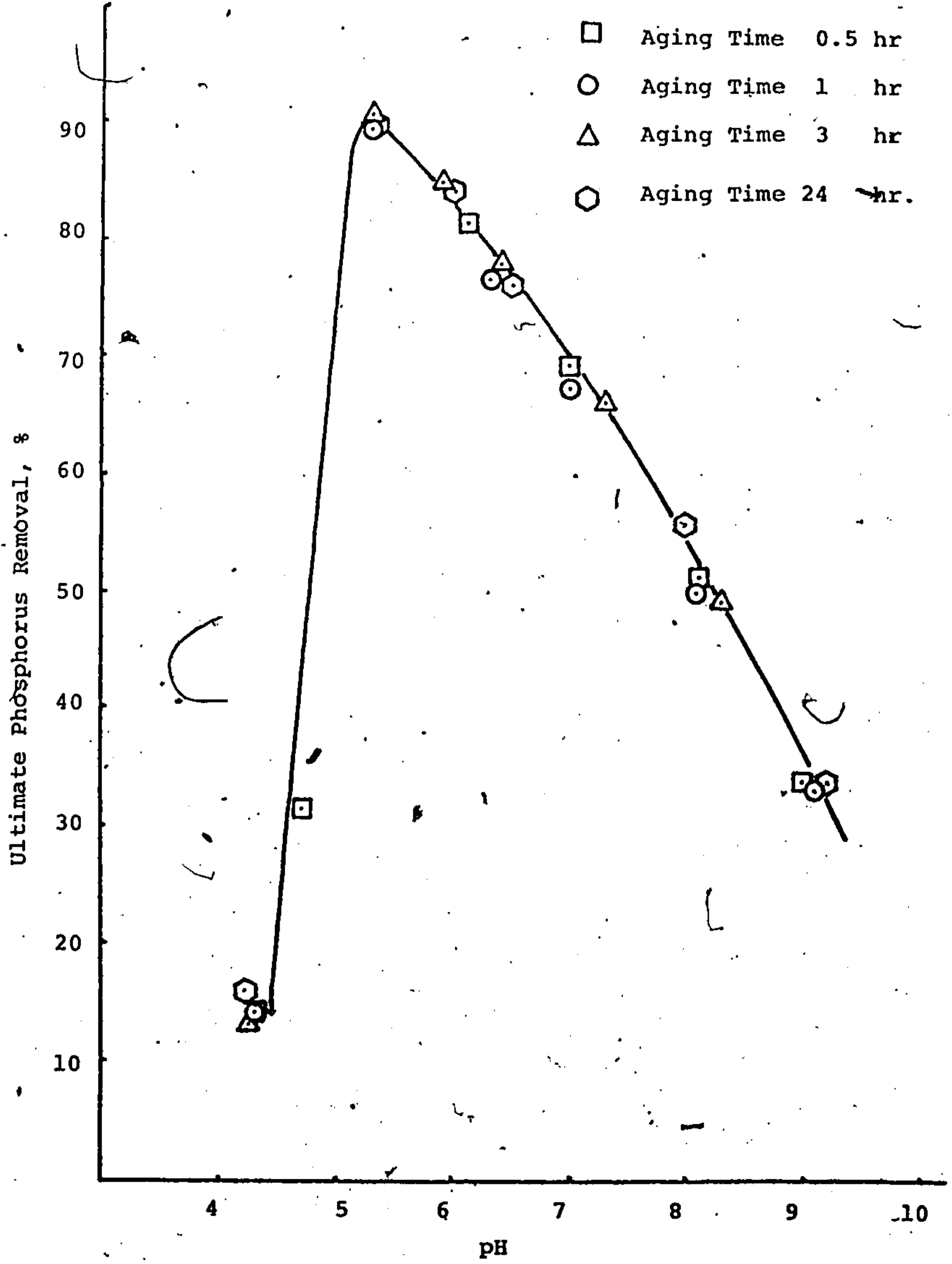


FIGURE 4.1.1 Effect of Aging Time on Ultimate Phosphorus Removal. (Coagulant: PBAC 2.2)

cases, phosphorus removal appeared to be maximum at pH 5.2. This maximum corresponds to 90% removal for all aging times. Generally aging time did not affect noticeably the observed removals. An aging time period of 2 hr. was, therefore, selected and it was assumed that minor variations in aging time would not influence the ultimate removal efficiency of the coagulants.

4.1.2 Settling Rates

During the first stages of settling, the phosphorus concentration in the withdrawn sample was higher than the initial concentration (Appendix A.2). This was due to the fact that the sampling port was well below the liquid surface. Therefore, withdrawal of the flocs deposited on the sampling tube resulted in the observed increase in concentration. Another reason which might have caused that was the fact that easily flocculated materials, such as aluminum flocs (Eckenfelder, 1980), may reach the hindered settling region even at low concentration, resulting in a slower settling at the lower part of the jar.

The percentage of flocs settled was calculated as:

$$\frac{C_o - C}{C_o - C_u} \times 100$$

where: C_o = Initial P concentration
C_u = Ultimate P concentration
C = P concentration at time of sampling t.

Figure 4.1.2 illustrates the percentage of flocs settled as a function of time for aging times 0.5 and 1 hr. The settling of the flocs depends on the pH of the solution. Very poor or no settling was observed below pH 5 or above pH 8. The settling curves are very steep up to 15 min of settling and then they reach a fairly constant level which at infinite time corresponds to the ultimate removal of the flocs.

The overflow rates required to achieve 90% removal of the flocs are depicted as a function of pH in Figure 4.1.3. The overflow rates were calculated by converting the time which corresponds to 90% removal of the flocs (Figure 4.1.2) to overflow rates by means of Figure 3.5. Ninety percent removal of the flocs was observed between the pH 5 and 8. Overflow rates corresponding to this removal ranged from 0.8 to 1.2 m/h. At pH 6.5 variation in aging time did not result in any difference in the overflow rates. However, at pH values below or above 6.5 significant differences were observed. These differences may be attributed to the fact that the extent of maturation time affects the size and charge of the aluminum polymeric species (Hsu and Bates, 1966) and, therefore, the settlability of the flocs.

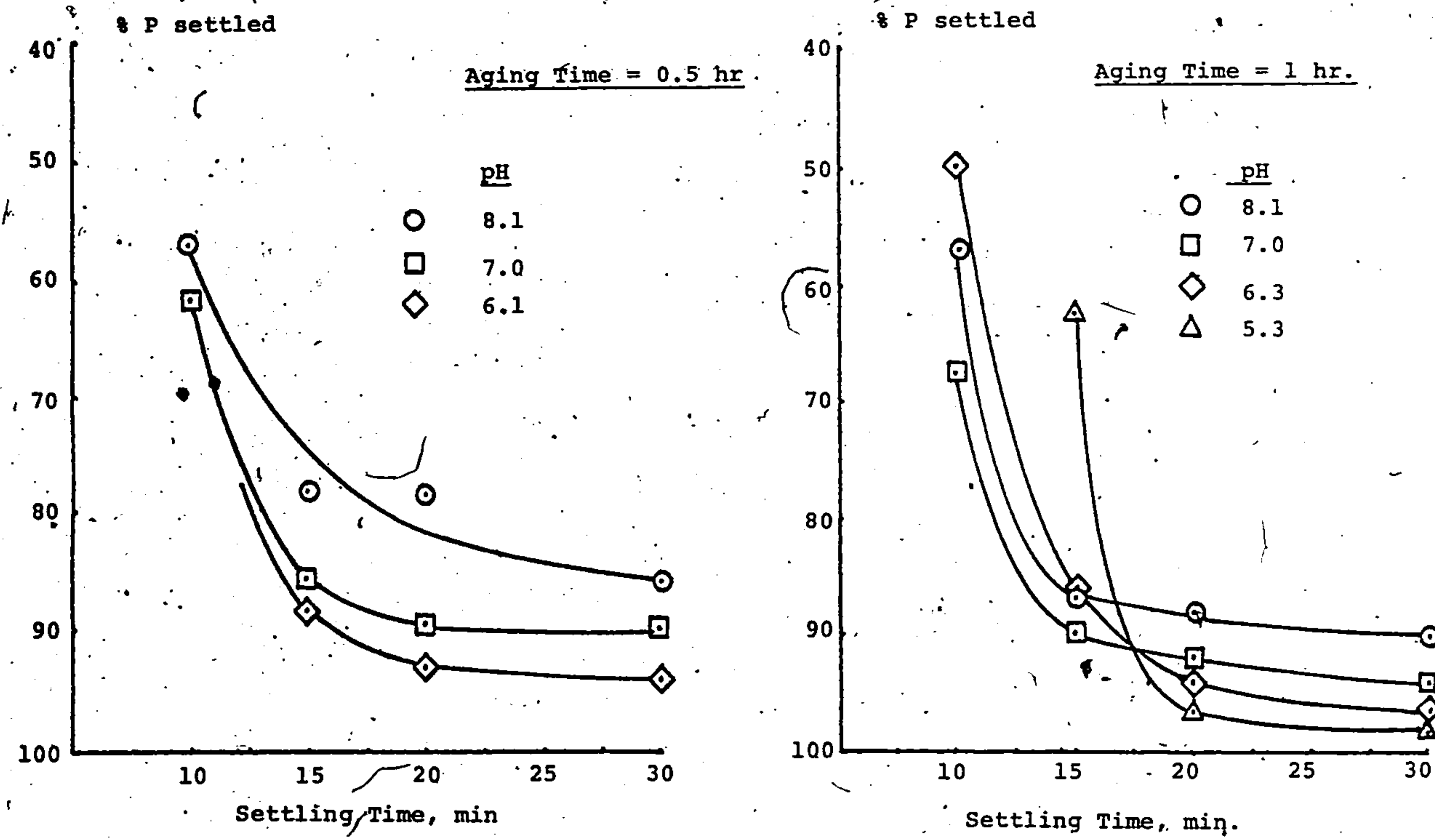


FIGURE 4.1.2 Effect of Floc Settleability as a Function of the Aging Time

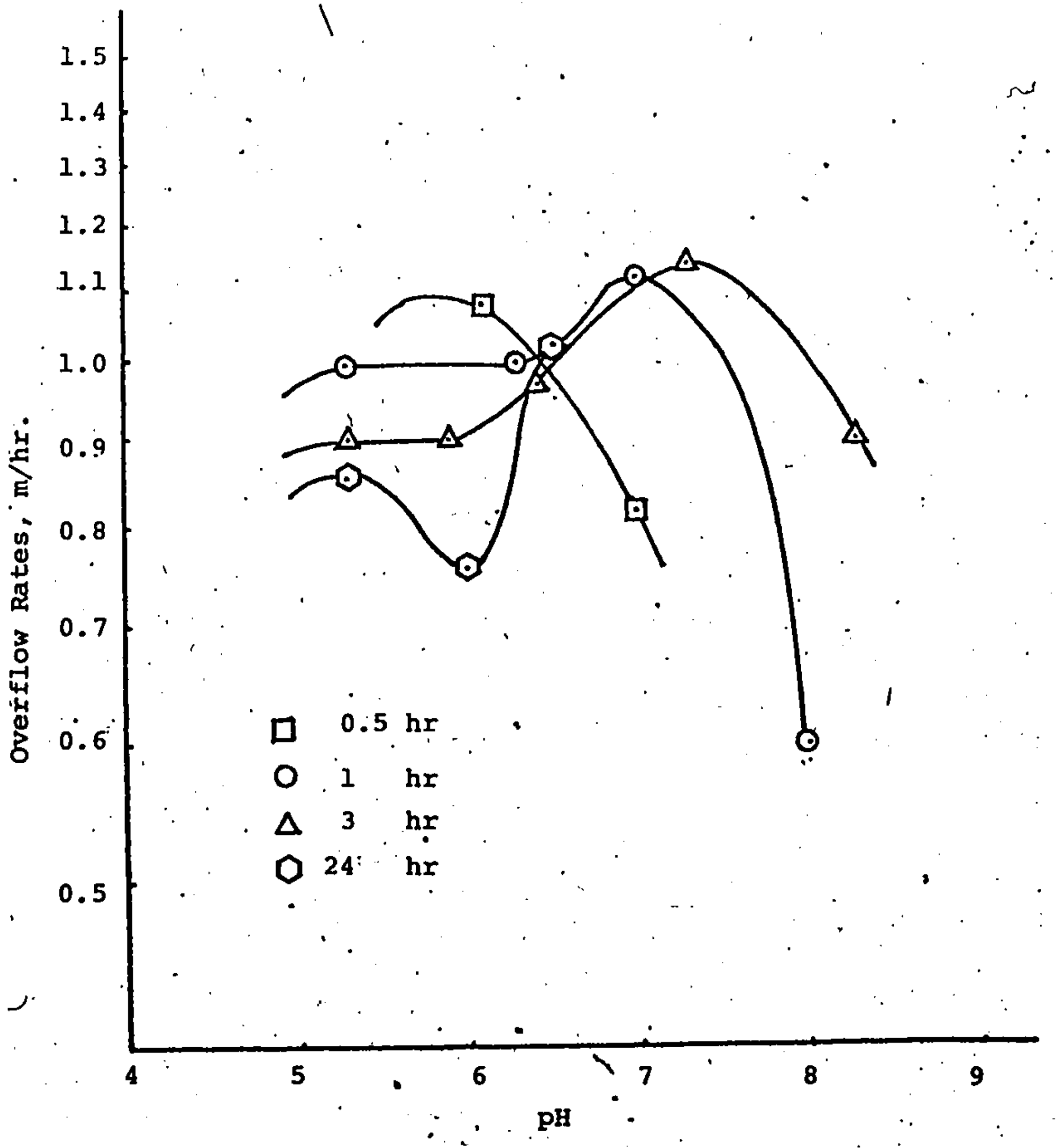


FIGURE 4.1.3 Effect of Aging Time on Overflow Rates for 90% Removal of Flocs

4.2 PHOSPHORUS REMOVAL - SYNTHETIC WASTEWATER

The study on the efficiency of the various coagulants to remove phosphorus was first carried out in synthetic wastewater. The coagulants used were Alum, Aluminum Chloride, and PBAC with basicities of 1.0, 1.8 and 2.2. Two aluminum dosages were investigated: one at an Al:P molar ratio of 1.0 and the second at 2.75. The pH ranged from 4 to 9.

For the low aluminum dosage, one additional run was performed. This run involved the addition of the coagulant at low pH and then the solution was brought to the 4 to 9 pH range by adding NaOH solution. This run is referred as alternative order of mixing.

4.2.1 Ultimate Phosphorus Removal

The ultimate phosphorus removal as a function of pH is illustrated in Figure 4.2.1 for Al:P = 1.0 and in Figure 4.2.2 for Al:P = 2.75. Phosphorus removal depends significantly on the pH. All curves shown exert maximum removals. For the low aluminum dosage, alum not only demonstrated the highest efficiency, but maximum precipitation started at lower pH. Ninety four percent of phosphorus was removed with a maximum at pH lower than 5. Aluminum cloride demonstrated a high removal efficiency (89%), but a little lower than the one of Alum.

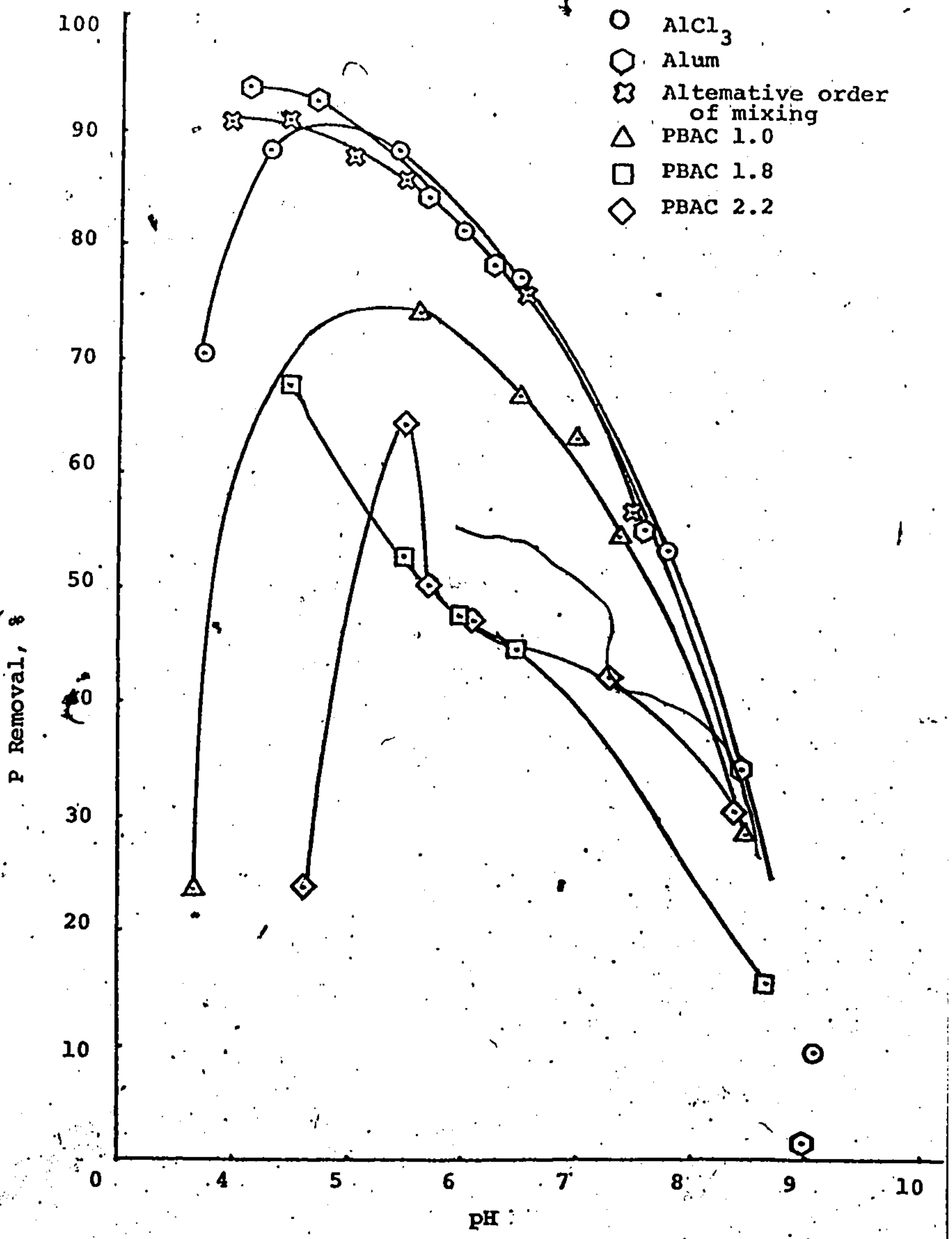


FIGURE 4.2.1 Ultimate Phosphorus Removal for Al:P = 1.0

The various PBAC's gave even lower removals with the highest one observed when PBAC 1.0 was used (75%). The results obtained when the alternative order of mixing was employed were identical to the ones obtained in the aluminum cloride case for pH higher than 5. Between pH 4 and 5, however, the alternative order of mixing resulted in a higher removal.

A similar trend appeared in the high aluminum dosage case (Figure 4.2.2). Alum, aluminum chloride and PBAC 1.0 gave removals in the vicinity of 100%. The pH range, however, within which alum showed this high efficiency, is broader than the one in the other two cases. Maximum phosphorus precipitation with alum ranged within pH 4 (this was the lowest pH employed) and 7, while in the aluminum chloride and PBAC 1.0 cases the pH for maximum removals was observed in the 5.5 to 6.5 region. PBAC 1.8 and PBAC 2.2 showed efficiencies lower than those observed with the other coagulants. As it can be seen from both Figures 4.2.1 and 4.2.2 the degree of pretreatment of the aluminum coagulants greatly affected their efficiency in precipitating phosphates. The higher the amount of sodium hydroxide added to the aluminum chloride solution in the preparation of PBAC, the lower its efficiency in phosphorus removal. This implies that in phosphate precipitation equilibrium between the various aluminum

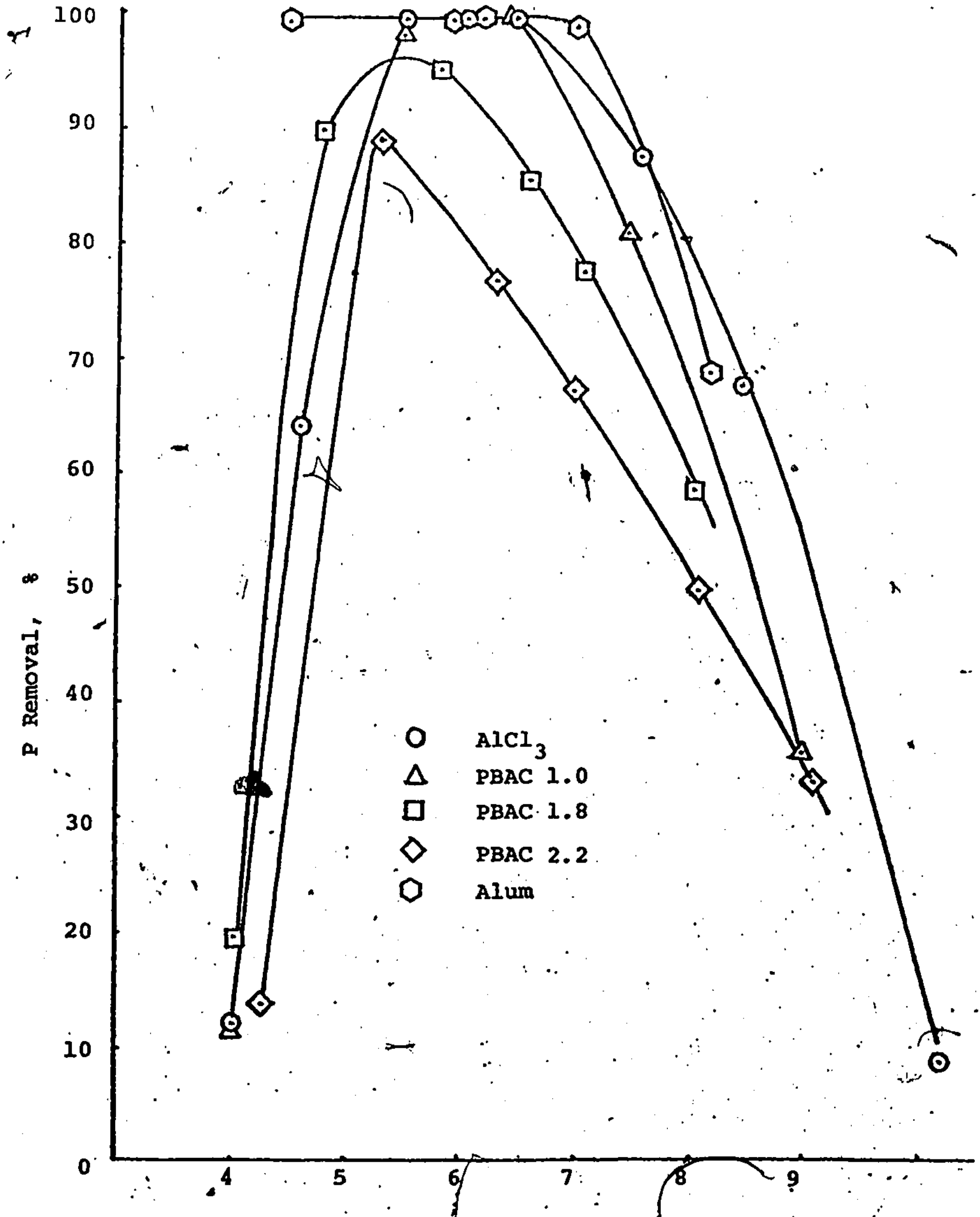


FIGURE 4.2.2 Ultimate Phosphorus Removal for Al:P = 2.75

species does not exist or, if it exists, it is extremely low. This can be realized by the fact that for different degrees of neutralization the coagulants gave different removals for the same pH. For this reason the precipitation of phosphates can not be explained by the equilibrium model of a single chemical compound, such as $AlPO_4$, neither as a co-precipitation of $AlPO_4$ and $Al(OH)_3$. On the contrary, a more sophisticated model involving complex formation could justify the observed results. The phosphorus precipitation can be seen as a result of the competitive action of phosphates, hydroxides and other ions present to react with aluminum species. Since hydroxyl ions are the strongest competitors, any addition of them to the coagulant will reduce its efficiency in phosphorus removal.

Precipitation occurs when the complex species formed from the competitive action of the various ions are neutral. For this reason the optimum pH range will depend on the type of species present. It can be seen from Figure 4.1.1 and 4.1.2 that when alum was employed, maximum precipitation started at lower pH values. This is due to the effect of sulfate ion, which, in relatively low concentrations, being a weaker competitor than the phosphates, helps the neutralization of the aluminum-phosphate-hydroxide complexes. These complexes in the absence of sulfates are positively charged at pH lower than the one for optimum precipitation. It should be noted that at high pH values the complexes are negatively charged due to the addition of hydroxyl ions to them and the particles are restabilized.

The complex formation model can also explain why in the alternative order of mixing maximum precipitation occurs at lower pH, as Figure 4.4.1 shows. At low pH aluminum is chemically bound with phosphates forming soluble complexes. Any small addition of hydroxide (slight increase in pH) will cause neutralization of these complexes before any competition begins. On the contrary, during the usual mixing the procedure goes from higher pH values to lower ones and the concentration of OH^- ions is higher promoting therefore the competition.

Another important observation discernible from both Figures 4.1.1 and 4.1.2 is that the optimum pH range is affected by the aluminum dosage. For the aluminum chloride case, where aluminum is present in the form of Al^{3+}, the optimum pH range for the highest dosage (pH range: 5.5-6.5) appeared to be 1 pH unit higher than the optimum pH range in the lower dosage (pH range: 4.3-5.5). In the high dosage coagulation the aluminum-phosphate complexes carry a higher positive charge and there still is some aluminum ions in the solution. Therefore, more hydroxyl ions are required to neutralize both the Al^{3+} and the complex species.

4.2.2 Settling Rates

The removal of phosphorus as a function of pH for an overflow rate of 1.15 m^3/m^2.h. for Al:P = 1.0 is illustrated in Figure 4.2.3. Aluminum chloride showed the highest efficiency removing up to 75% at pH 5.5. Alum gave high removals but this happened at pH below 5.5. The rest of the coagulants demonstrated lower efficiency, giving maximum removals lower than 55%.

Figure 4.2.4 illustrates phosphorus removal as a function of pH for Al:P = 2.75 and overflow rate of 1.15 m^3/m^2.h. Aluminum chloride, PBAC 1.0 and PBAC 1.8 showed removals between 90 and 95 percent at around pH 6. Alum showed the same high efficiency at pH 6, but high removals were observed at lower pH values, as well.

Comparing Figures 4.2.3 and 4.2.4 with Figures 4.2.1 and 4.2.2, where the ultimate phosphorus removal was plotted as a function of pH, one can see that even if phosphorus can be efficiently removed at pH values below the optimum pH range (Figures 4.2.1 and 4.2.2), the flocs do not settle, because they carry a positive charge. This trend is not followed when alum is used due to the presence of sulfate, which participates in the neutralization of the aluminum-phosphate-hydroxide polymers.

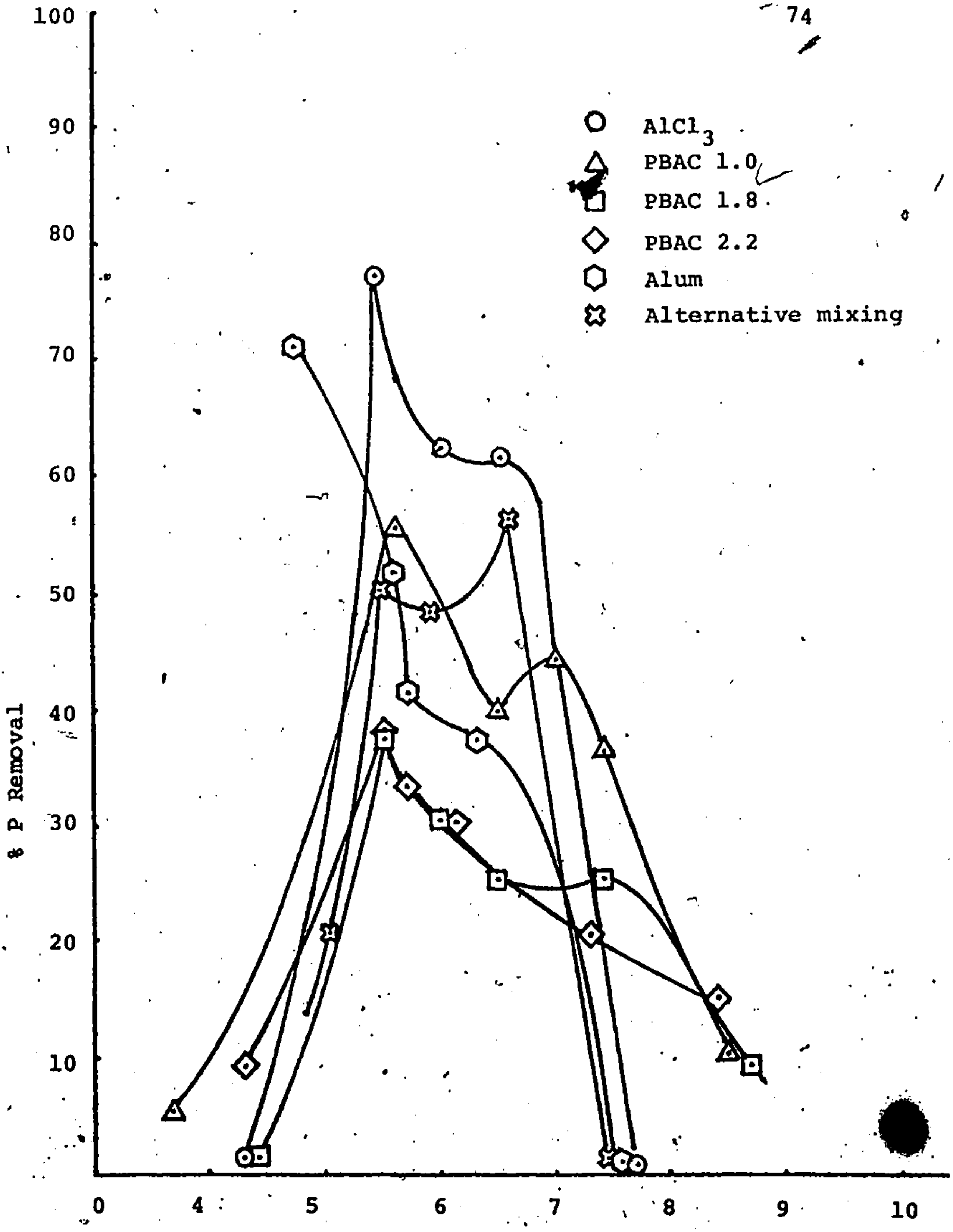


FIGURE 4.2.3 Phosphorus Removal for Al:P = 1.0

Overflow Rate = 1.15 m/hr.

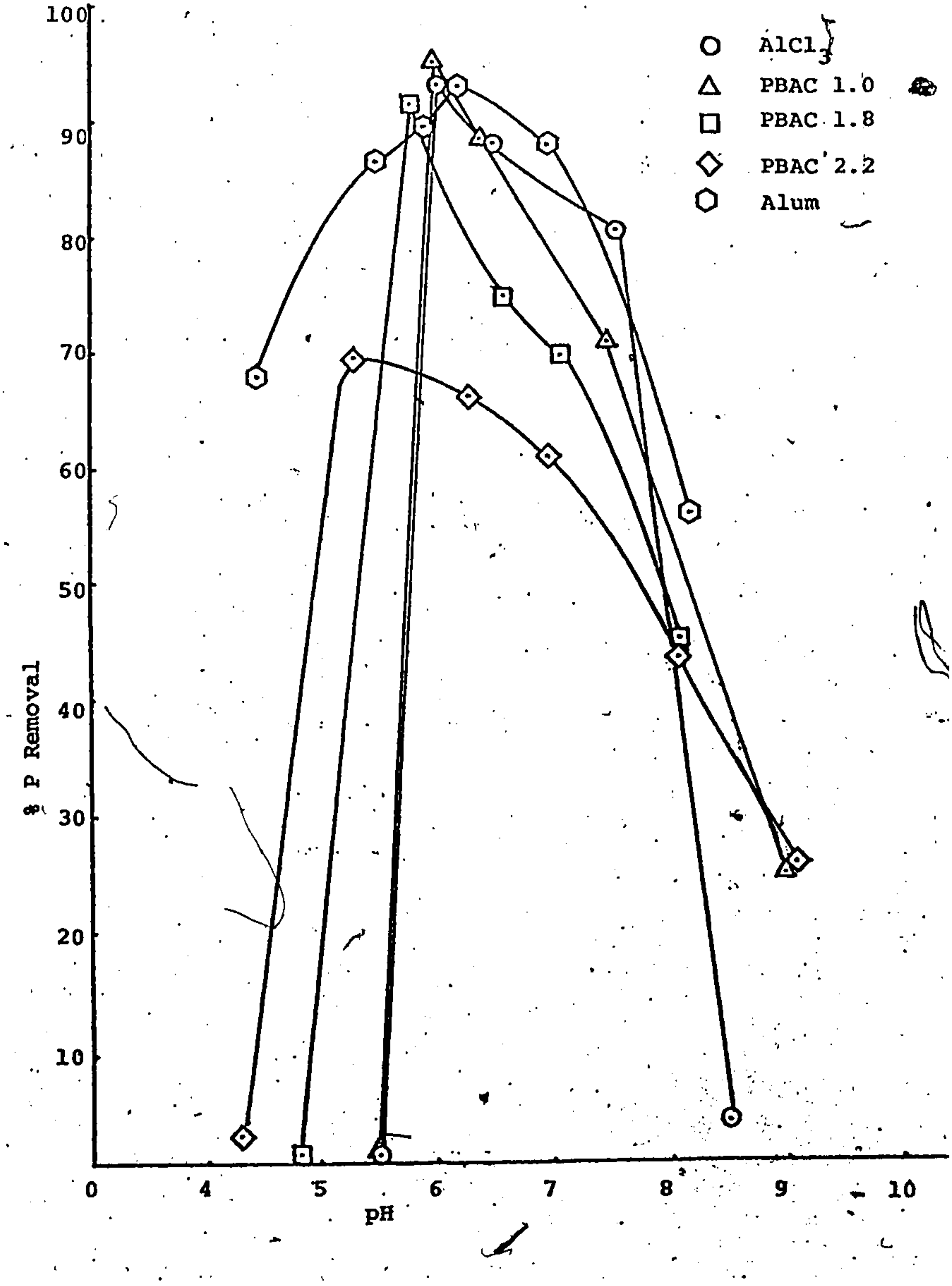


FIGURE 4.2.4 Phorphorus Removal for Al:P = 2.75

Overflow Rate = 1.15 m/hr.

The overflow rates for 90% removal of the flocs as a function of pH are depicted in Figures 4.2.5 and 4.2.6. For the low aluminum dosage (Figure 4.2.5) only aluminum chloride gave flocs, 90 percent of which settled in the time period of 30 min. In this case, however, the overflow rates for 90% removal of the flocs were lower than 0.8 $m^3/m^2.h$. When the rest of the coagulants were used, 90% removal of the flocs was not achieved even at overflow rates as low as 0.55 $m^3/m^2.h$. (30 min of settling). For the high aluminum dosage (Figure 4.2.6) 90% removal of the flocs was achieved at overflow rates as high as 1.6 $m^3/m^2.h$ for the PBAC 1.0 case and 1.4 $m^3/m^2.h$ for alum, aluminum chloride and PBAC 1.0 at pH around 6.

Another important point, discernible from the settlability curves (Figures 4.2.3 to 4.2.6) was that the settling of the flocs exerted two local maxima, one at around pH 6 and the other at around pH 7. The first maximum appeared at the pH value where maximum ultimate removal was observed. At this point the hydroxy-polymers are neutralized and settling is fast. For the second maximum two possible mechanisms may be considered responsible. The first one involves the formation of some aluminum hydroxide at pH around 7 where the lowest solubility of $Al(OH)_3$ exists. The hydroxide particles then

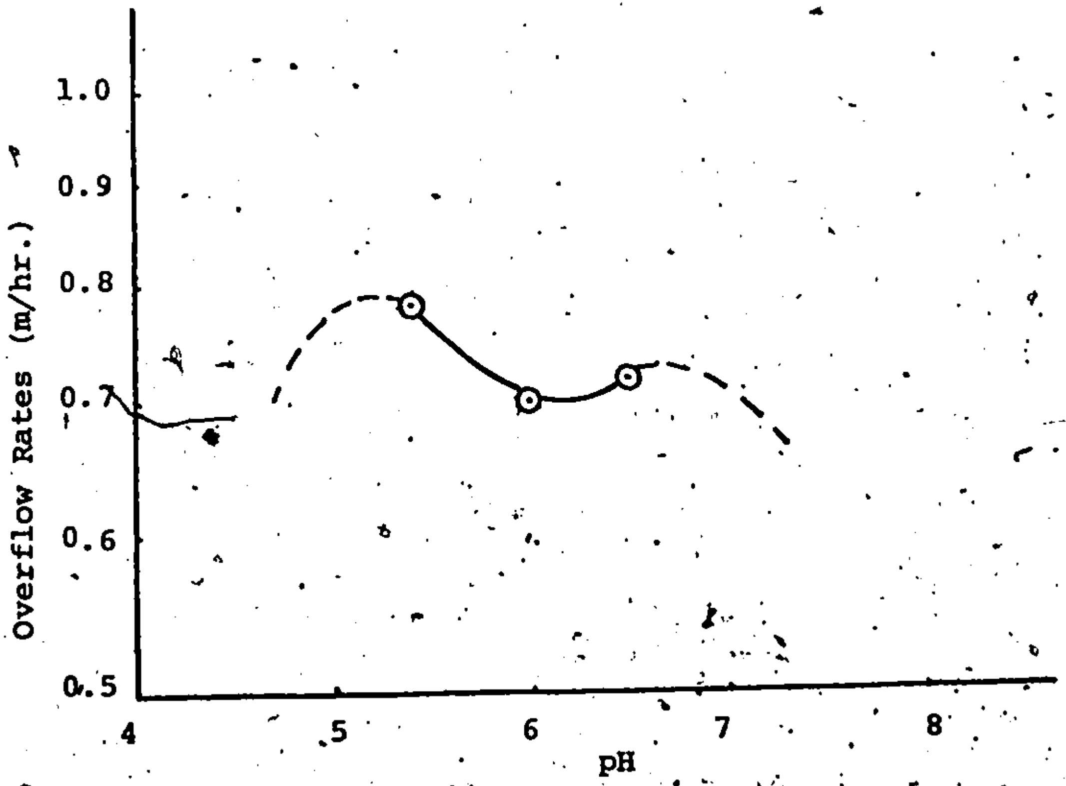


FIGURE 4.2.5 Overflow Rates for 90% Removal of Flocs
Coagulant: $AlCl_3$
Dosage: Al:P = 1.0

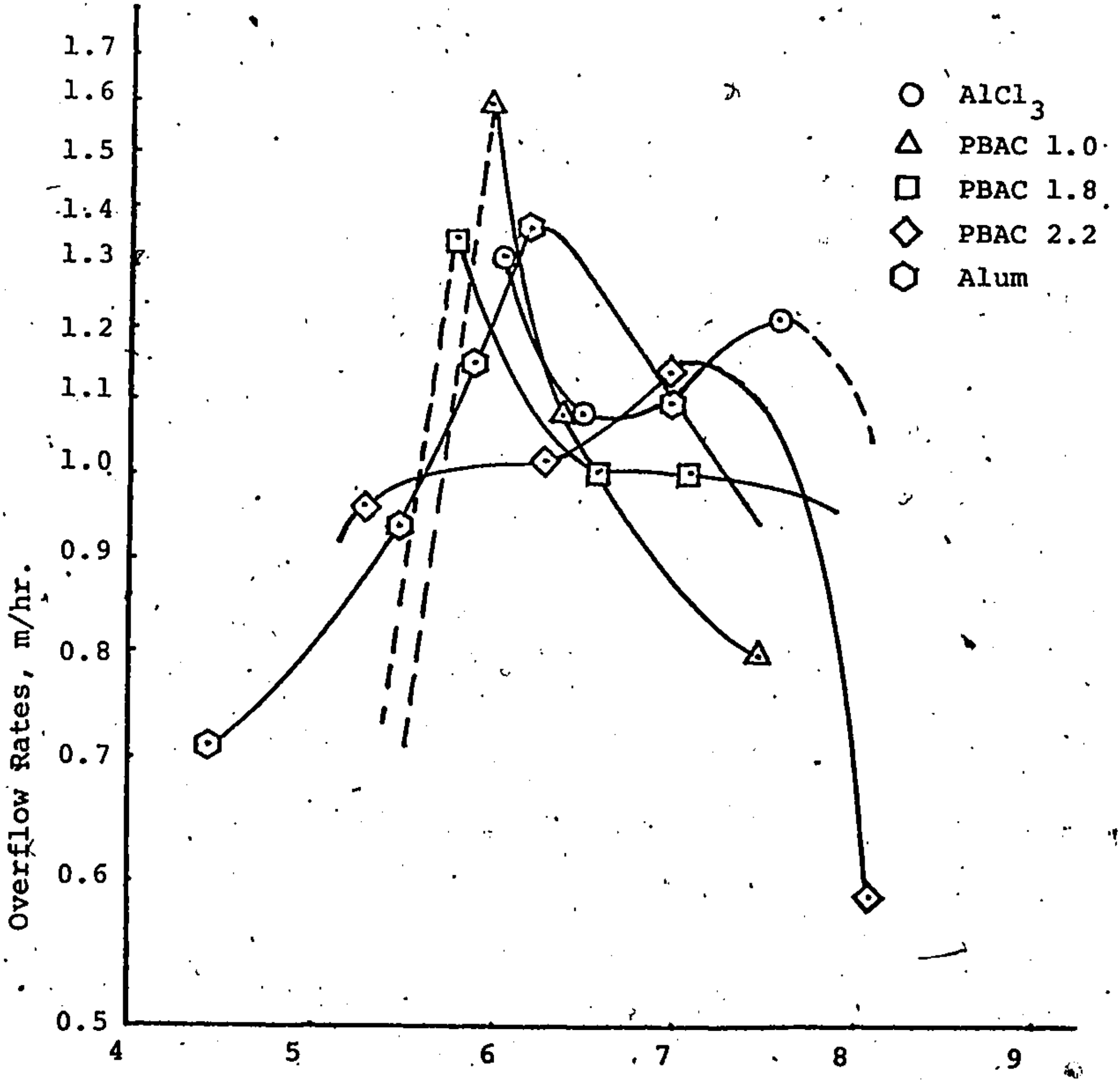


FIGURE 4.2.6 Overflow Rates for 90% Removal of the Flocs

Al:P = 2.75

become nucleation sites for the aggregation of the polymeric species and therefore they enhance the settling of the flocs. The second mechanism considers the change of one phosphate form ($H_2PO_4^-$) to another (HPO_4^{2-}) which occurs at around pH 6.5. If these two forms show slightly different competitive activity with respect to complex formation with aluminum, this might affect the charge and the size of the flocs formed.

This trend was not observed when alum was employed and that may be attributed to the direct involvement of SO_4^{2-} ions in the formation of the polymers.

It should be noted that a similar behaviour was observed when ferric chloride was used for phosphates removal (Benedek, et al., 1976). The authors explained the trend as a result of the maximum precipitation of $FePO_4$ at pH 5.5 and $Fe(OH)_3$ at pH 8.0.

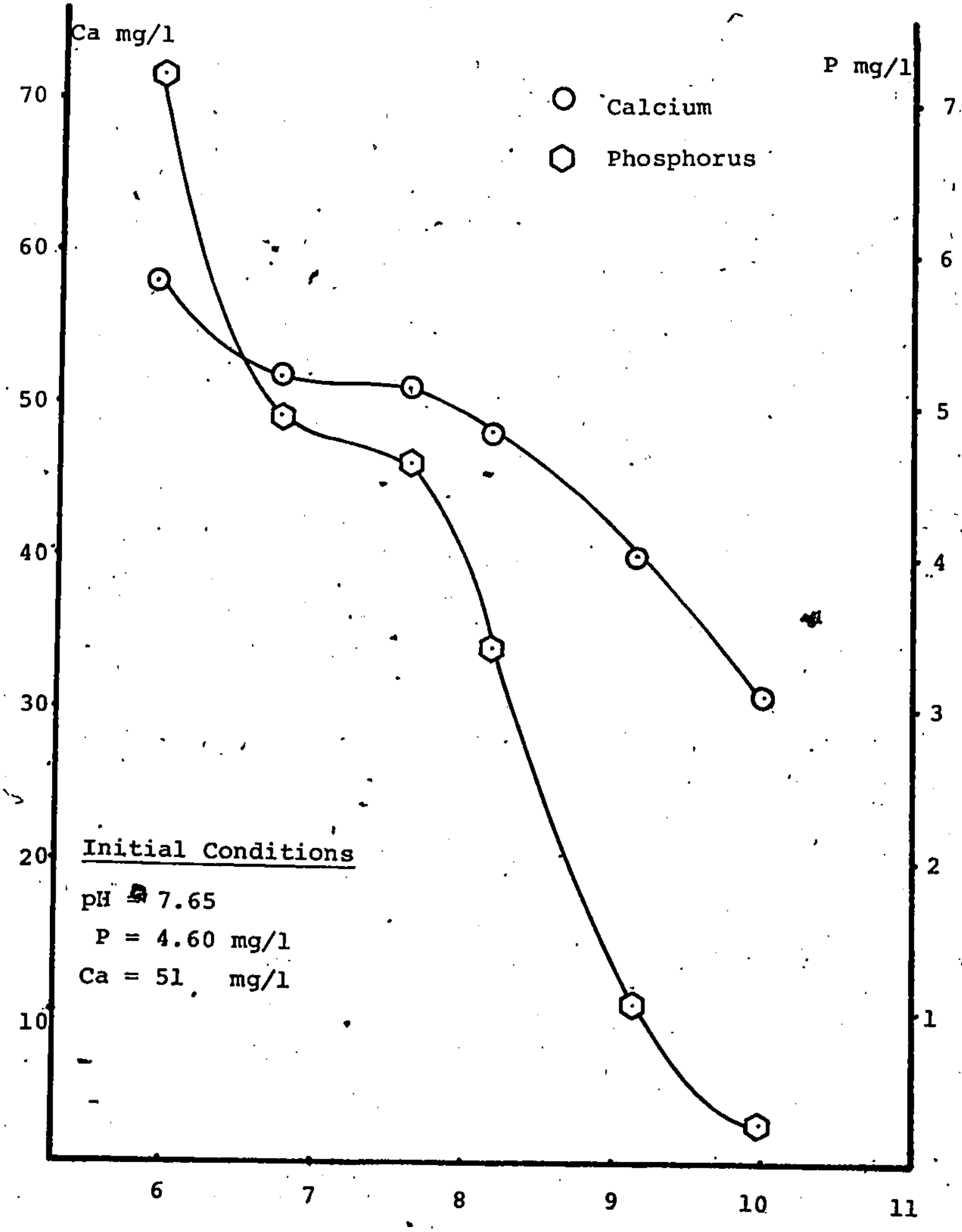
4.3 STUDIES ON MUNICIPAL WASTEWATERS

The study of phosphorus removal was performed on both Burlington and Hamilton wastewaters taken from the aeration tank of the sewage treatment systems. In addition to these studies, the effect of coagulants on parameters such as sludge settleability, supernatant suspended solids and sludge dewaterability was examined. These parameters were examined with respect to aluminum dosages employed for phosphorus removal.

4.3.1 Phosphorus Removal

The removal of phosphorus from wastewaters is not only affected by the coagulant added, but by the presence of soluble calcium, as well. Calcium, naturally present in all domestic wastewaters, can remove phosphorus at pH levels above 8 (Kronin, 1973). Therefore, in the study of the efficiency of aluminum coagulants, care should be taken to eliminate the effect of calcium at high pH.

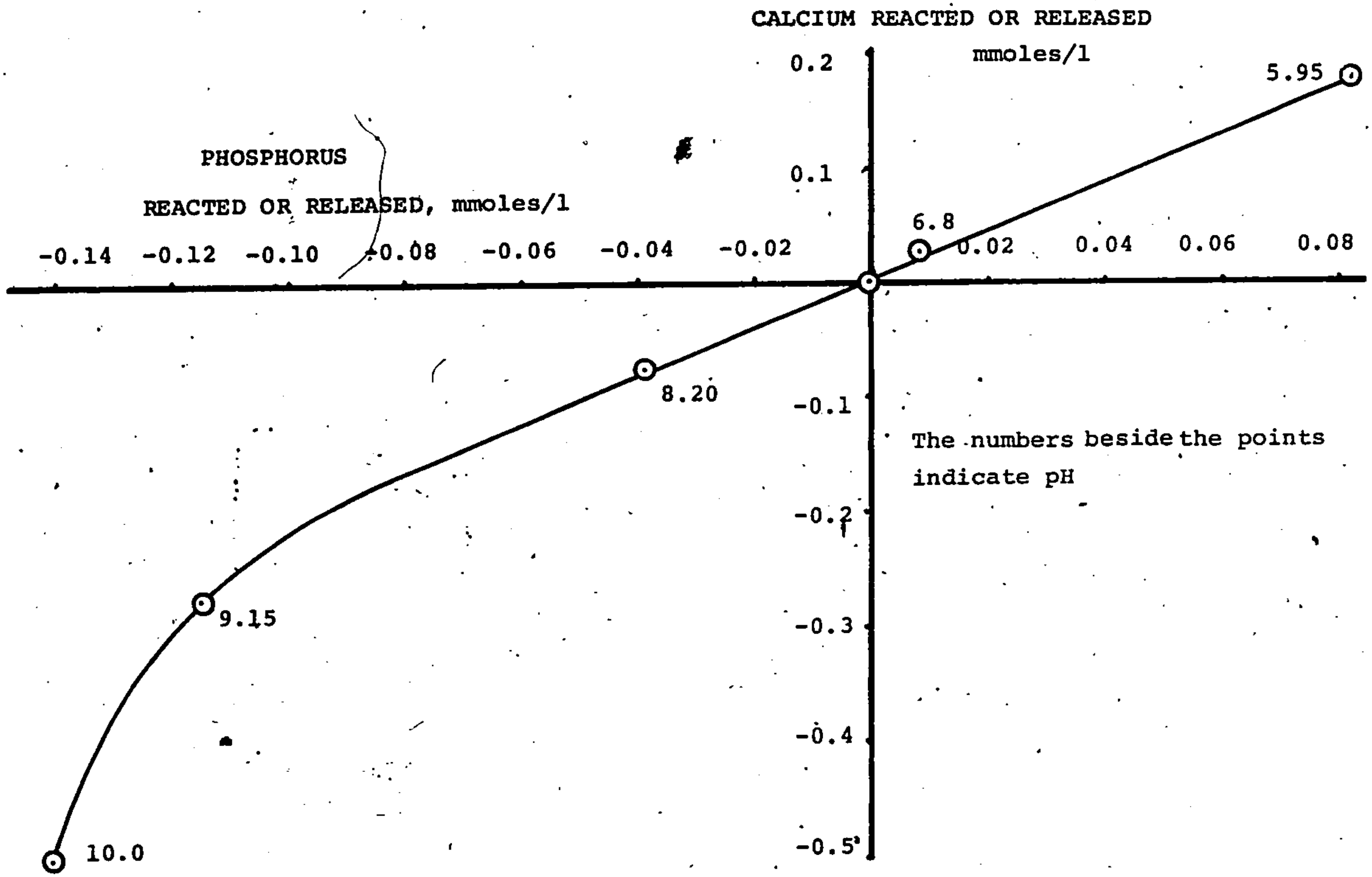
Figure 4.3.1 presents the soluble phosphorus and calcium concentrations in Burlington wastewater as a function of pH. The initial P level was 4.60 mg/l at pH = 7.65. When the pH was increased to 10, the phosphorus concentration dropped to 0.3 mg/l 10, the calcium level decreased to 31 mg/l from 51 mg/l at pH 7.65. Quite surprisingly, however, the concentrations of both calcium and phosphorus increased at low pH, reaching values of 58 mg/l and 7.1 mg/l respectively at pH 6. It appeared that some phosphorus was chemically bound with calcium in some form of insoluble calcium phosphate and was released into the solution at low pH. Figure 4.3.2 provides evidence for this reasoning. Here, the mmoles of Ca^{2+}, released into the solution at low pH or precipitated at high pH, were



Initial Conditions

pH = 7.65
P = 4.60 mg/l
Ca = 51 mg/l

FIGURE 4.3.1 Calcium and Phosphorus Concentration in Burlington Wastewater as a Function of pH. (Coagulant: None)

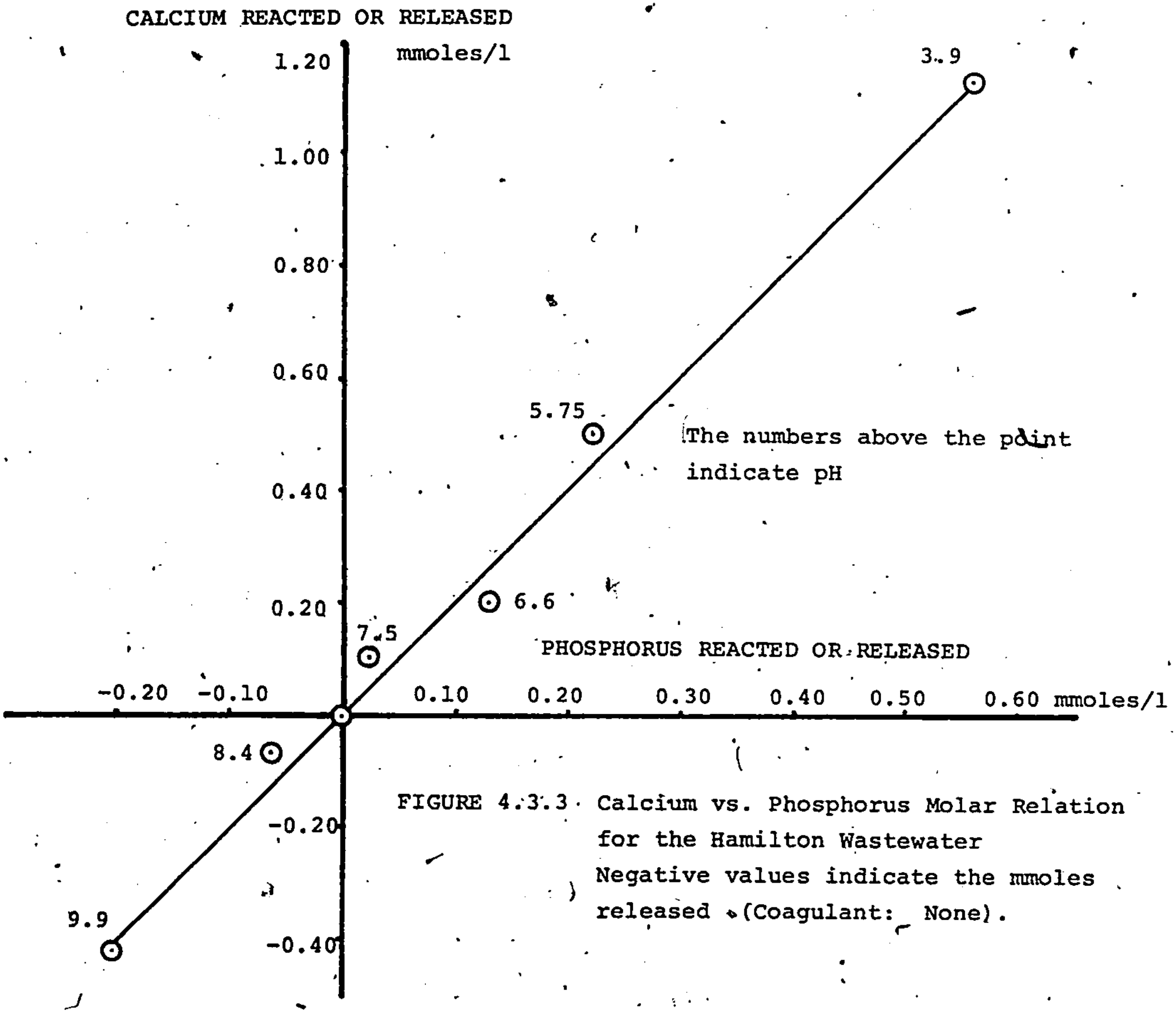


The numbers beside the points indicate pH

FIGURE 4.3.2. Calcium vs. Phosphorus Molar Relation for the Burlington w/w Negative values indicate the mmoles precipitated, while positive over the mmoles released. (No coagulant was used).

plotted versus the mmoles of phosphorus released or precipitated. There is a linear relationship between these two variables up to pH 8.5. This linearity indicates that a certain stoichiometry exists between the insoluble Ca^{2+} and PO_4^{3-}. The stoichiometric molar ratio between these two species is given by the slope of the staight line. The slope was found to be around 2. The calcium phosphate form which is generally accepted to be most common is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). The Ca:(PO_4) molar ratio in this substance is 10:6, which lies close to the molar ratio found in the calcium phosphate of the wastewater. It should be noted that the slope of the line presented in Figure 4.3.2 increases at high pH, a fact that indicates that at high pH calcium precipitates in some other form, as well, probably as calcium carbonate.

A similar study was performed on the Hamilton wastewater. In this case, as in the case before, no coagulant was added into the solution. Once again, a linear relationship seemed to hold between the calcium released or precipitated and the phosphorus released or precipitated, as it can be seen in Figure 4.3.3. The stoichiometric molar ratio in this case was found again to be 2. These two systems show in good agreement that insoluble calcium phosphate, probably in the form of



The numbers above the point indicate pH

FIGURE 4.3.3 Calcium vs. Phosphorus Molar Relation for the Hamilton Wastewater Negative values indicate the mmoles released (Coagulant: None).

hydroxyapatite, exists in the aeration tank of wastewater treatment plants, and it seems likely that the inorganic flocs are entrapped into the biological flocs.

To separate the effect of calcium from that of the aluminum coagulants, when they applied to Burlington wastewater, the phosphorus concentration was measured after adjusting the pH prior to coagulant addition. Figure 4.3.4 illustrates the phosphorus level after the addition of acid or base as a function of pH. The curve is similar to the one observed in the blank solution case (Figure 4.3.1). Figure 4.3.4 also shows the phosphorus concentration after the addition of the coagulant. The coagulant used was aluminum chloride at a dosage of Al:P = 2.75. The difference in P concentration in these two curves characterizes the removal due to coagulant, which is shown in Figure 4.3.5. In the same figure the overall removal is illustrated, as well. The term overall removal is referred to the removal with respect to the phosphorus concentration at its natural pH. There are two distinct parts in the overall removal curve. The first one, below pH 8, is due to the effect of the aluminum coagulant and the second one, above pH 8, due to calcium phosphate precipitation. The calcium removal, also shown in Figure 4.3.5, proceeds parallel to phosphorus removal at pH values above 8.

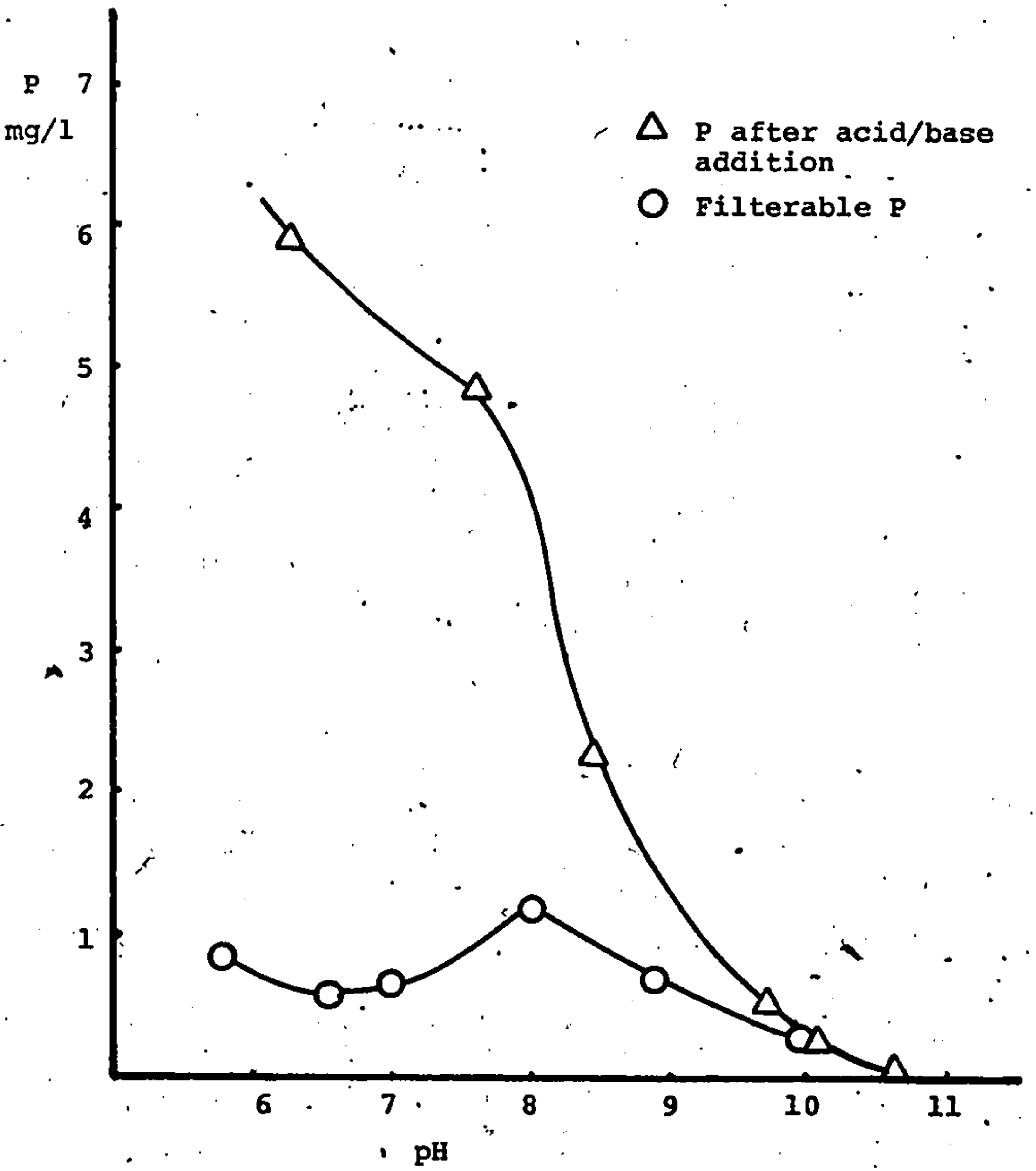


FIGURE 4.3.4. Phosphorus Level for Al:P = 2.75
Coagulant: $AlCl_3$
Burlington Wastewater

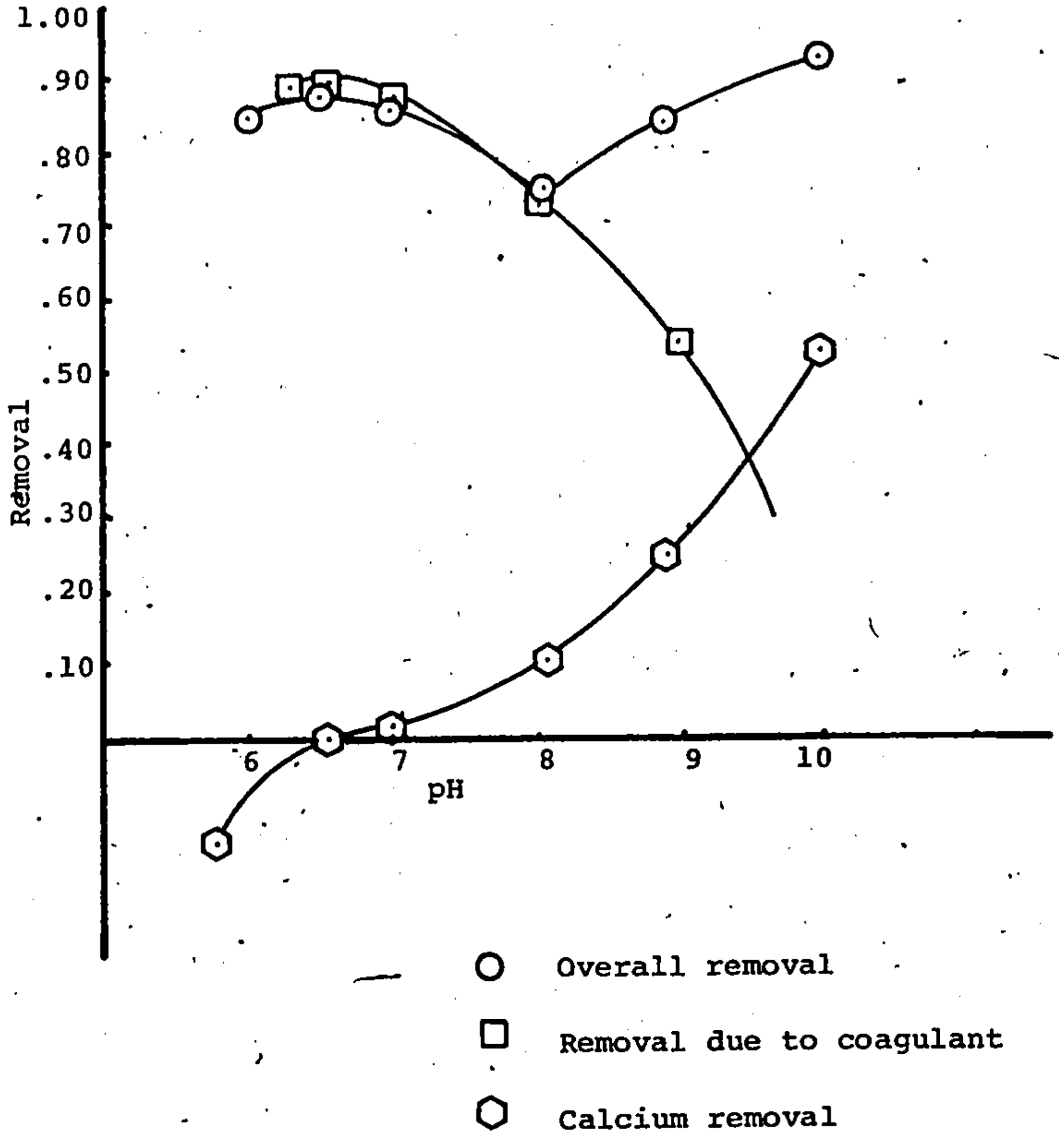


FIGURE 4.3.5 Phosphorus Removal for Al:P = 2.75
Coagulant: $AlCl_3$
Burlington Wastewater

The effect of the other aluminum coagulants was similar to that of aluminum chloride. Figure 4.3.6 shows the effect of alum. Once again, the overall removal curve consists of two parts: Below pH 8, any removal of the initially present dissolved phosphorus and phosphorus released from calcium phosphate is due to aluminum, while at pH higher than 8 the removal of phosphates is due to calcium. Similar trends, shown by PBAC 1.0, 1.8 and 2.2, are presented in the Appendix.

Figure 4.3.7 summarizes the efficiency of the various coagulants to remove phosphorus from the Burlington wastewater at an Al:P molar ratio of 2.75. Comparison of Figure 4.3.7 with Figure 4.2.2, where phosphorus removal from synthetic wastewater was depicted as a function of pH, shows that the behaviour of the coagulants in both systems was similar. Aluminum chloride and alum gave the highest removals while PBAC demonstrated lower efficiencies. Once again, the higher the basicity of PBAC, the lower the observed removals were.

The removals observed in the Burlington wastewater case were lower than those obtained in the synthetic wastewater case for all coagulants employed. This can be attributed to the presence of condensed phosphates and a variety of other species in the natural system, which interfere with the removal of phosphorus.

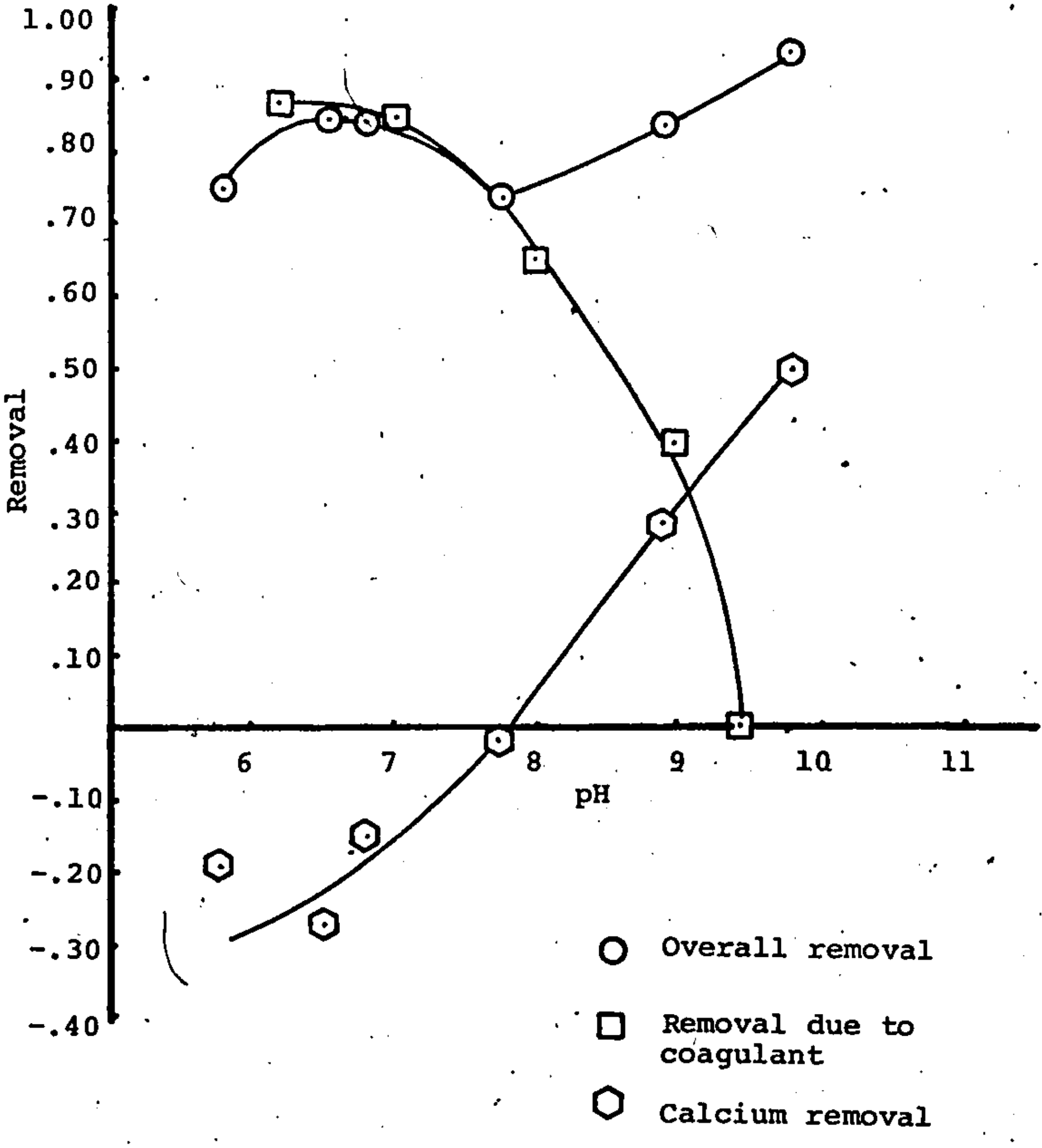


FIGURE 4.3.6 Phosphorus Removal for Al:P = 2.75
Coagulant: Alum
Burlington Wastewater

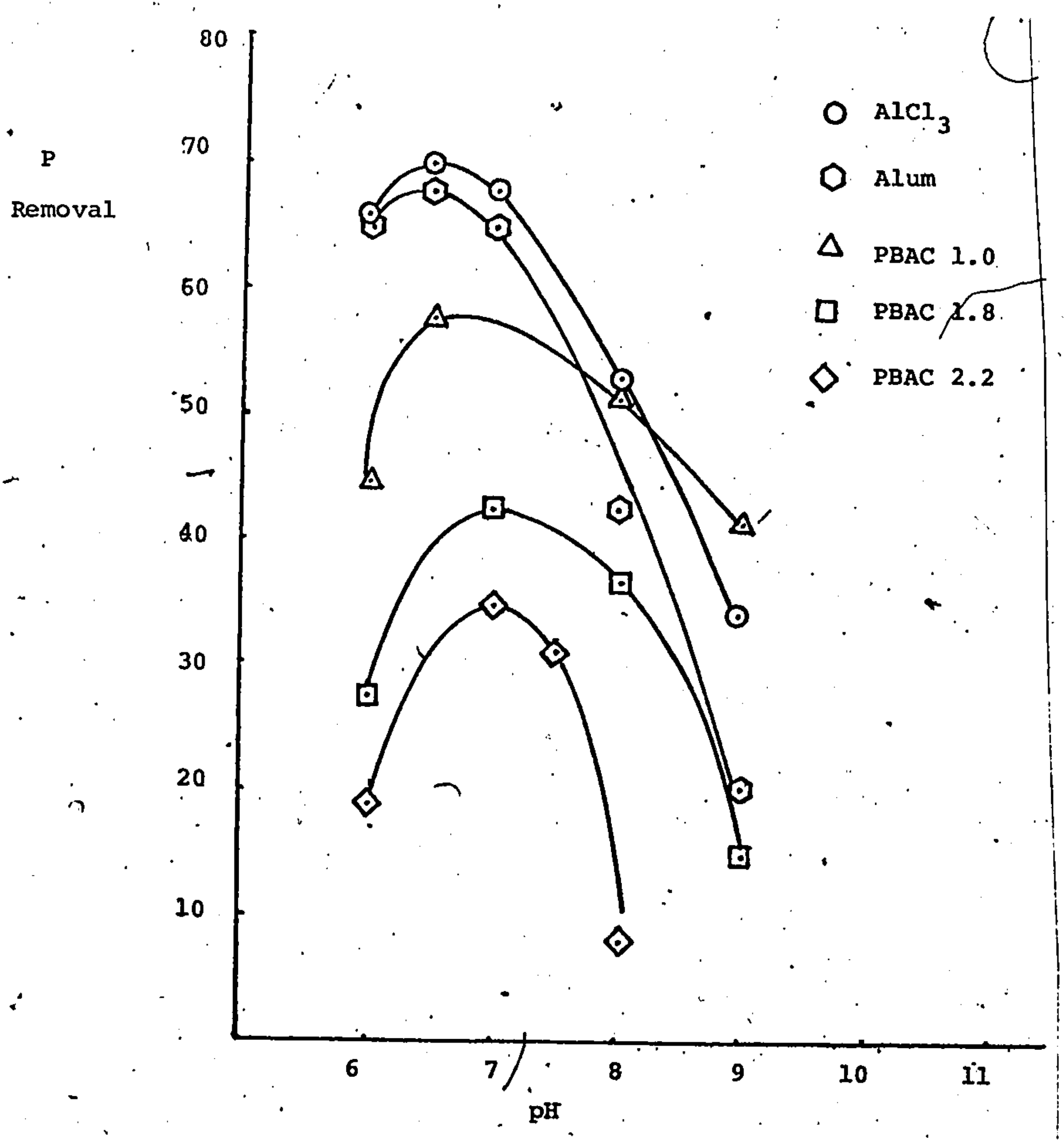


FIGURE 4.3.7 Efficiency of the Various Coagulants to Remove P from Burlington Wastewater

Al:P = 2.75

The calcium-aluminum interaction was verified on the Hamilton wastewater. Figure 4.3.8 illustrates the overall phosphorus removal as a function of pH when alum was used at an Al:P ratio of 2.0. Phosphorus was effectively removed at pH 10 due to calcium phosphate precipitation. At lower pH values, however, even if alum removes up to 70% of phosphorus, the amount of phosphorus released was high enough to keep the overall removal lower than a 60% level. Figure 4.3.8 also illustrates the removal of phosphorus due to alum and the removal of calcium. These two curves show a behaviour similar to that observed in the Burlington wastewater case.

When the Hamilton wastewater was used, the iron, present in the wastewater, was measured as well. The iron concentration was plotted as a function of pH in Figure 4.3.9 for both the blank case and when alum was used (Al:P = 2.0). At around pH 8, which was the natural pH of the wastewater, the iron concentration was found to be high (approximately 5.3 mg/l). This can not be justified by the solubility of $Fe(OH)_3$ at this pH (10^{-11} gmoles/l). It seems most likely that iron forms soluble chelates with organics. When the pH increased or decreased, the iron concentration dropped significantly. This may be attributed to precipitation of iron hydroxide at lower pH or to precipitation of insoluble chelates at higher pH.

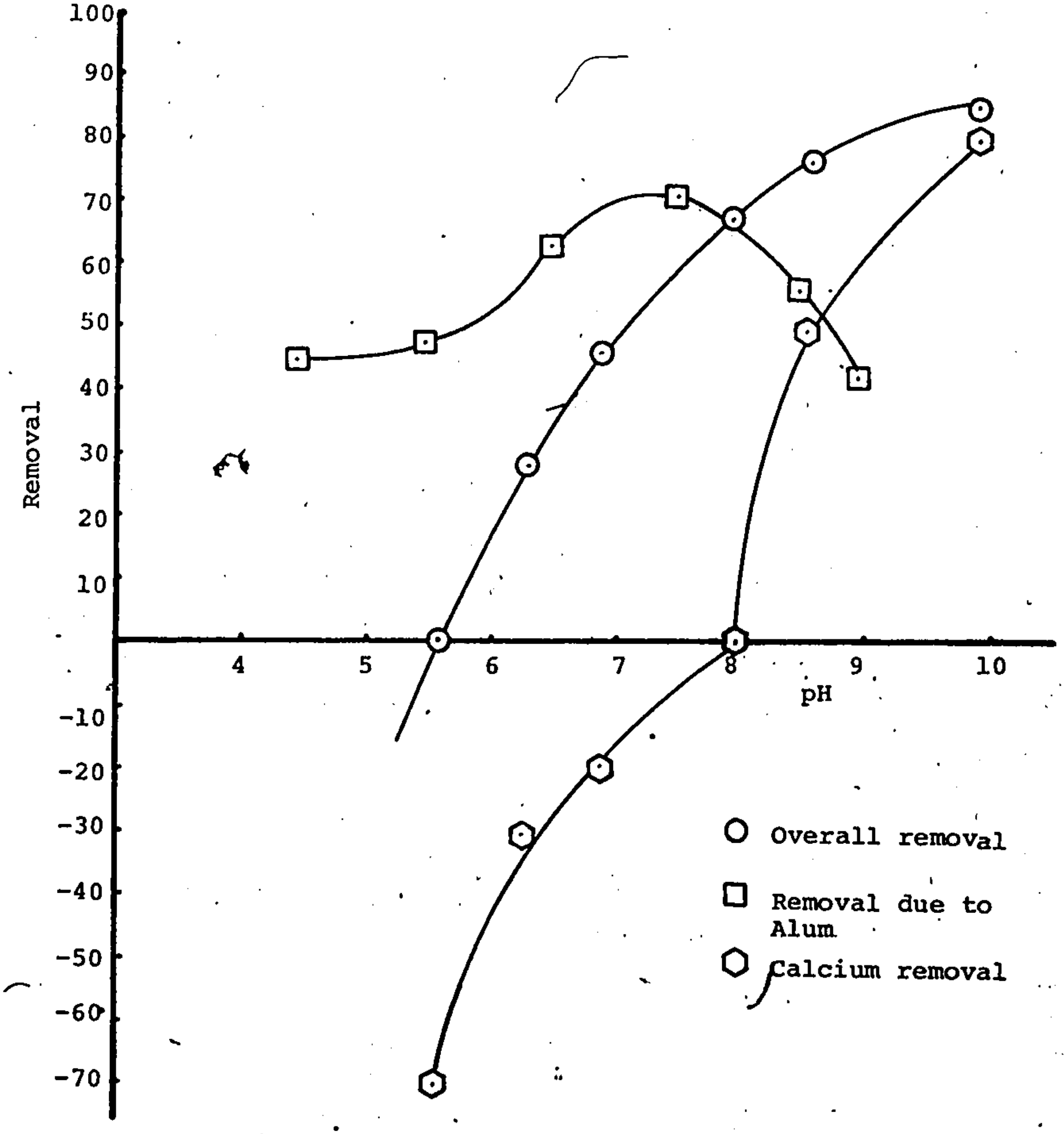


FIGURE 4.3.8 Phosphorus Removal for Hamilton Wastewater

Coagulant: Alum Al:P = 2.0

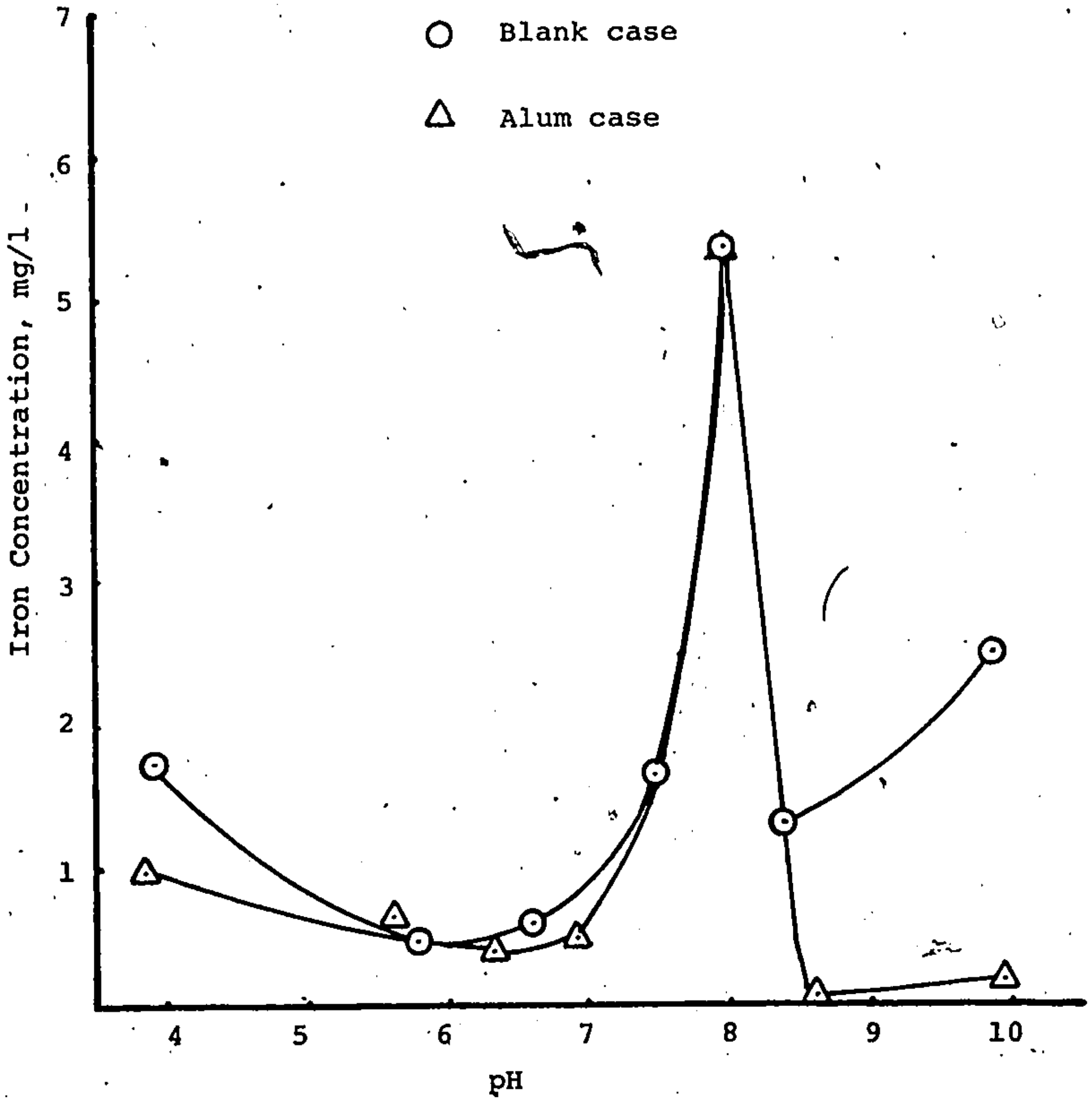


FIGURE 4.3.9 Iron Concentration for the Hamilton Wastewater

4.3.2 Supernatant Suspended Solids

When the Burlington wastewater was used for the study of phosphorus removal, samples from the supernatant liquid were taken after 10 min of settling and analyzed for suspended solids. Figure 4.3.10 illustrates the supernatant suspended solids concentration as a function of pH for Al:P = 2.75. For the blank solution case, the supernatant solids concentration did not appear to be affected by the pH, fluctuating around 8 mg/l. When aluminum coagulants were used, the supernatant suspended solids concentration followed an inverse U-shape curve with a maximum between pH 8 and 9. This pH range, where the maximum concentration occurs, coincides with the pH range where the precipitation efficiency of both aluminum and calcium is low. This indicates that the nature of the flocs is inorganic phosphate precipitates and therefore its settleability is highly affected by the pH. In the case of the blank solution, the flocs are mostly biological and the effect of pH is not very strong.

The inorganic phosphate nature of the supernatant solids, when coagulants were used, is also demonstrated in Figure 4.3.12. It can be seen that in the aluminum chloride case, the insoluble phosphorus curve denoted by P_{total}-$P_{filterable}$, proceeds parallel to the supernatant solids concentration curve, showing a maximum at the same pH,

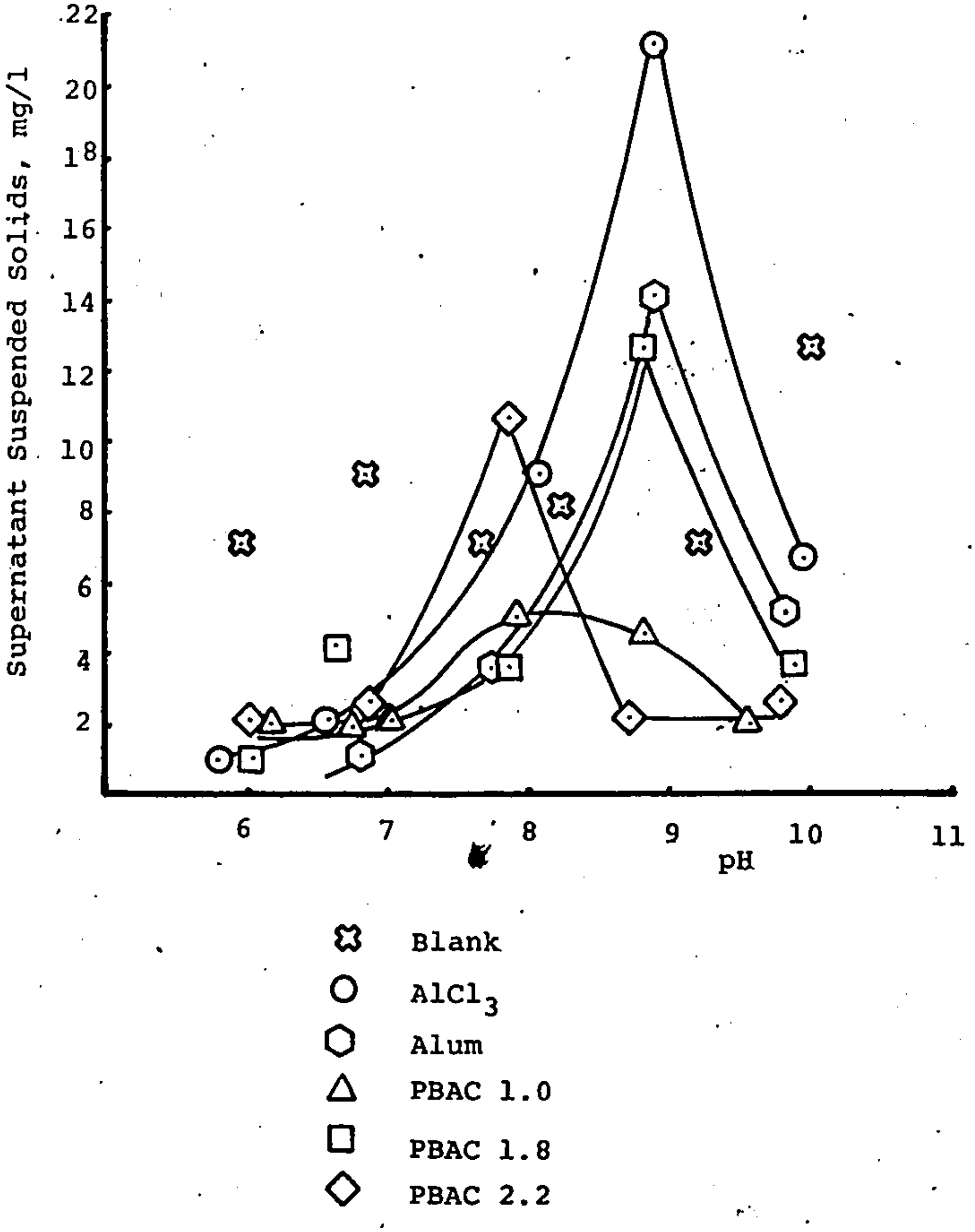


FIGURE 4.3.10 Supernatant Suspended Solids for the Burlington Wastewater
Al:P = 2.75

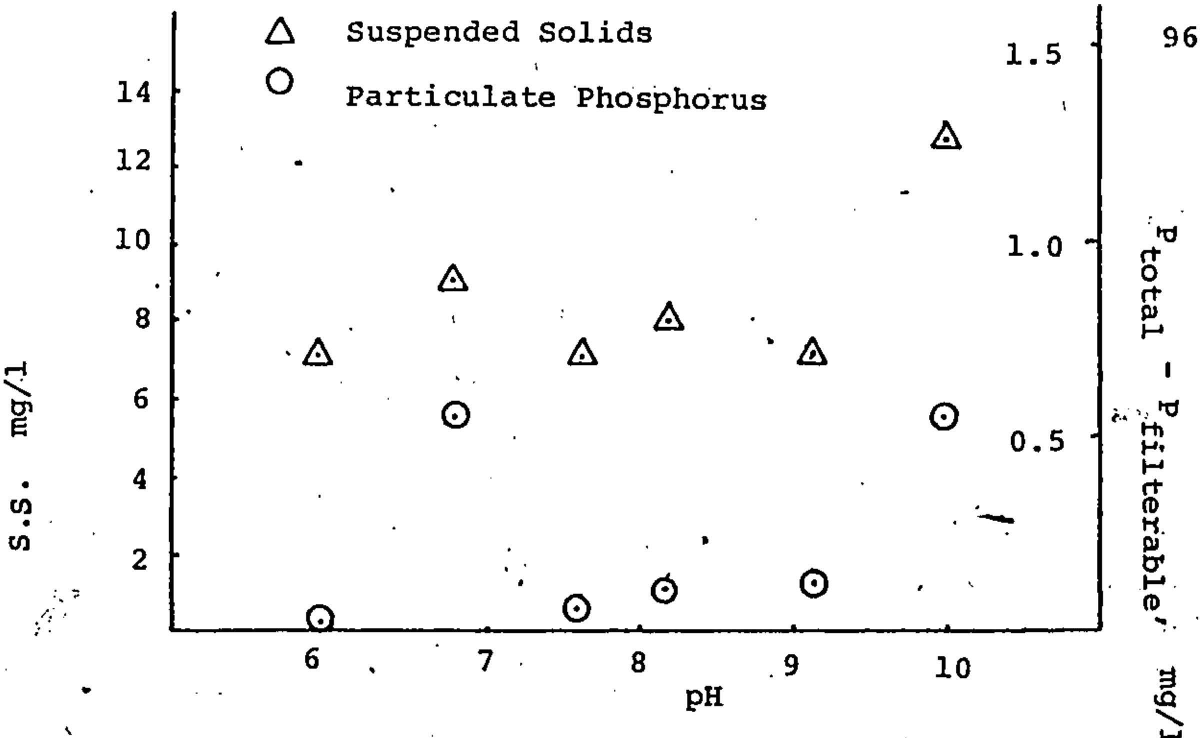


FIGURE 4.3.11 Supernatant S.S. Concentration for Blank Burlington Wastewater

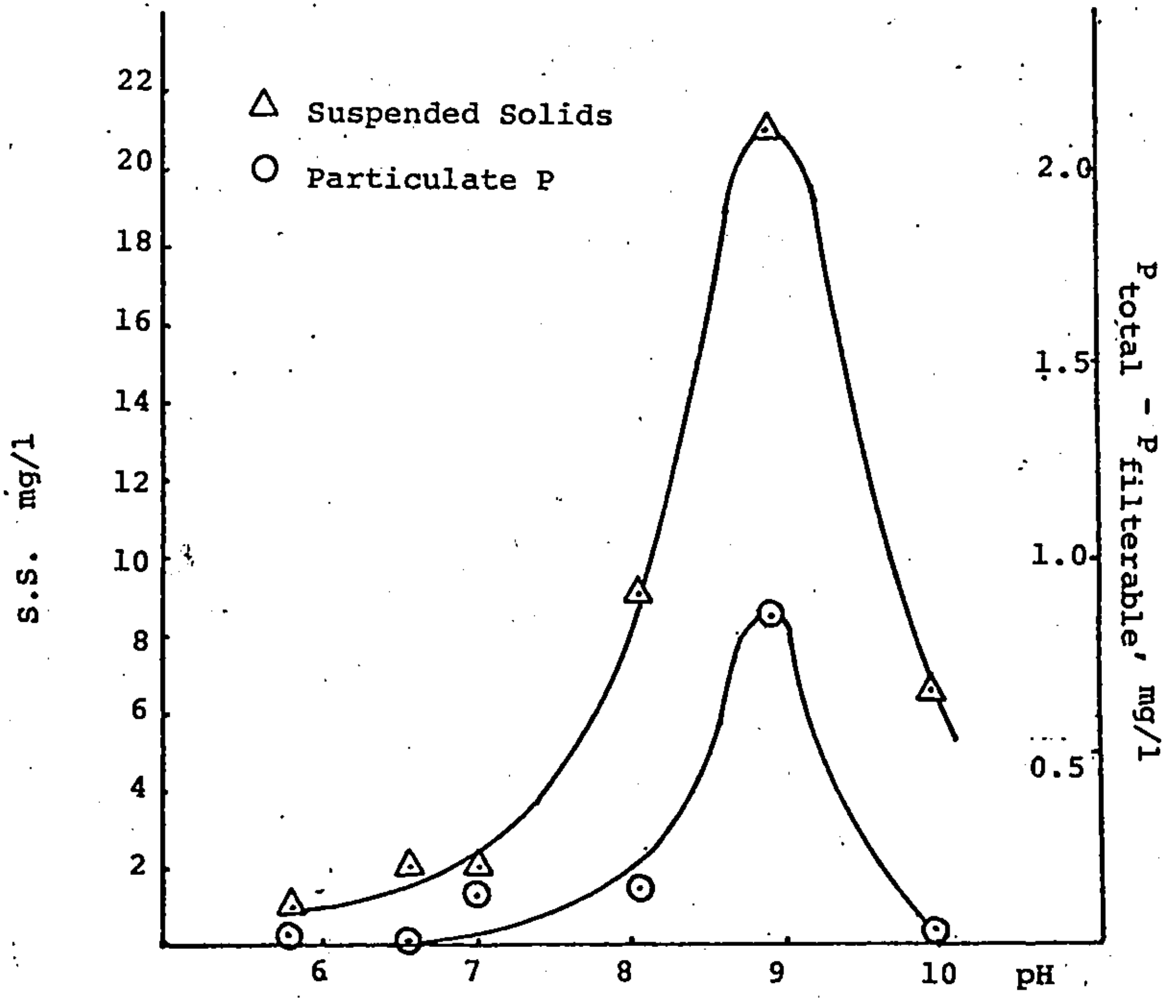


FIGURE 4.3.12 Supernatant S.S. Concentration for $AlCl_3$ Burlington Wastewater

where maximum solids concentration exists. In the blank case, Figure 4.3.11, the particulate P concentration appeared random and not affected by the pH.

Among the various coagulants used, PBAC 1.0 gave the lowest solids concentration (less than 6 mg/l), while aluminum chloride demonstrated the poorest efficiency giving supernatant solids concentrations up to 25 mg/l.

4.3.3 Settling Rates

When the Burlington wastewater was used for the study of phosphorus removal, the effect of the aluminum coagulant on the settling of the flocs was examined. The settling rates were calculated from the rate of change with time of the height of the solids interface.

Table 4.1.13 illustrates the settling rates as a function of pH for Al:P = 1.0. For the case of the blank, the settling rates were almost constant within the pH range studied, ranging between 1.4 and 1.5 m/h. The addition of the coagulants enhanced settling with the exception of alum. Aluminum chloride showed the highest efficiency followed by PBAC 1.0. The settling rates observed when aluminum chloride was used were up to 90% higher than those observed in the blank case.

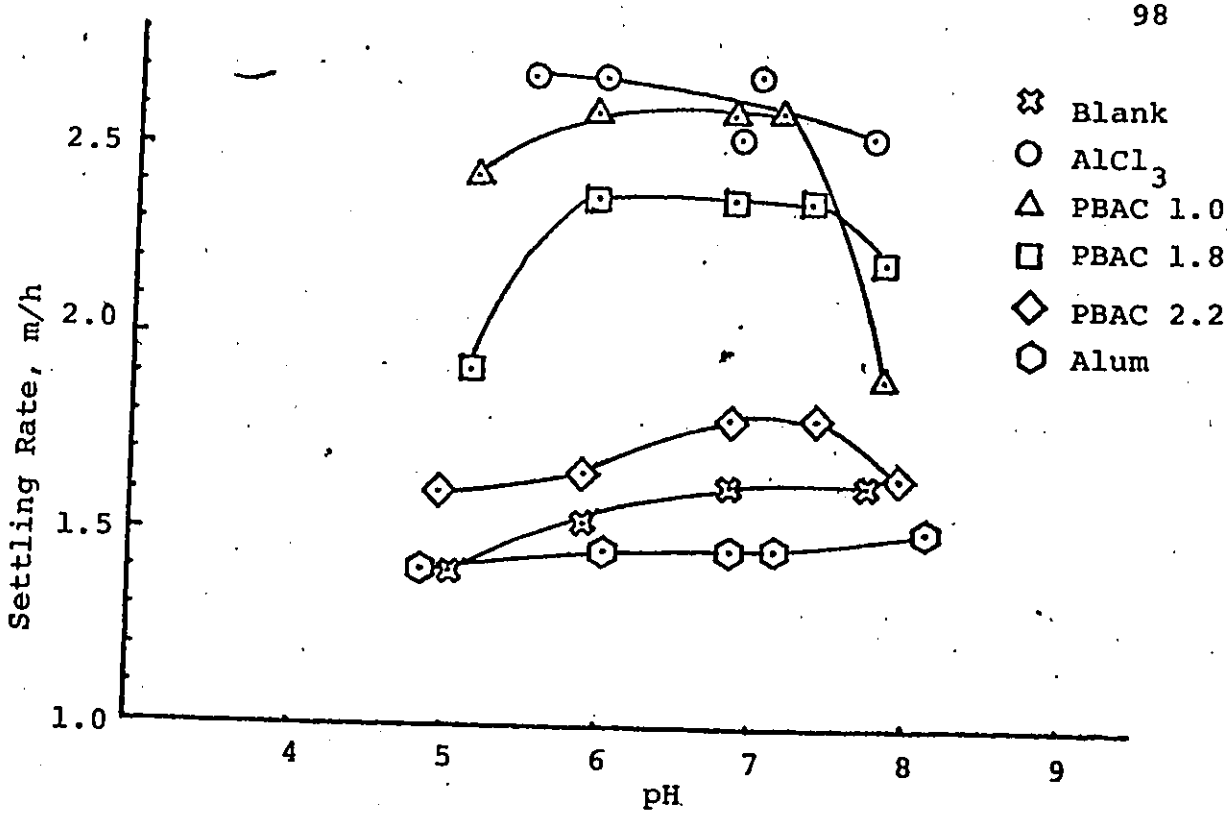


FIGURE 4.3.13 Settling Rates as a Function of pH for Al:P = 1.0
Suspended Solids Concentration: 2200mg/l

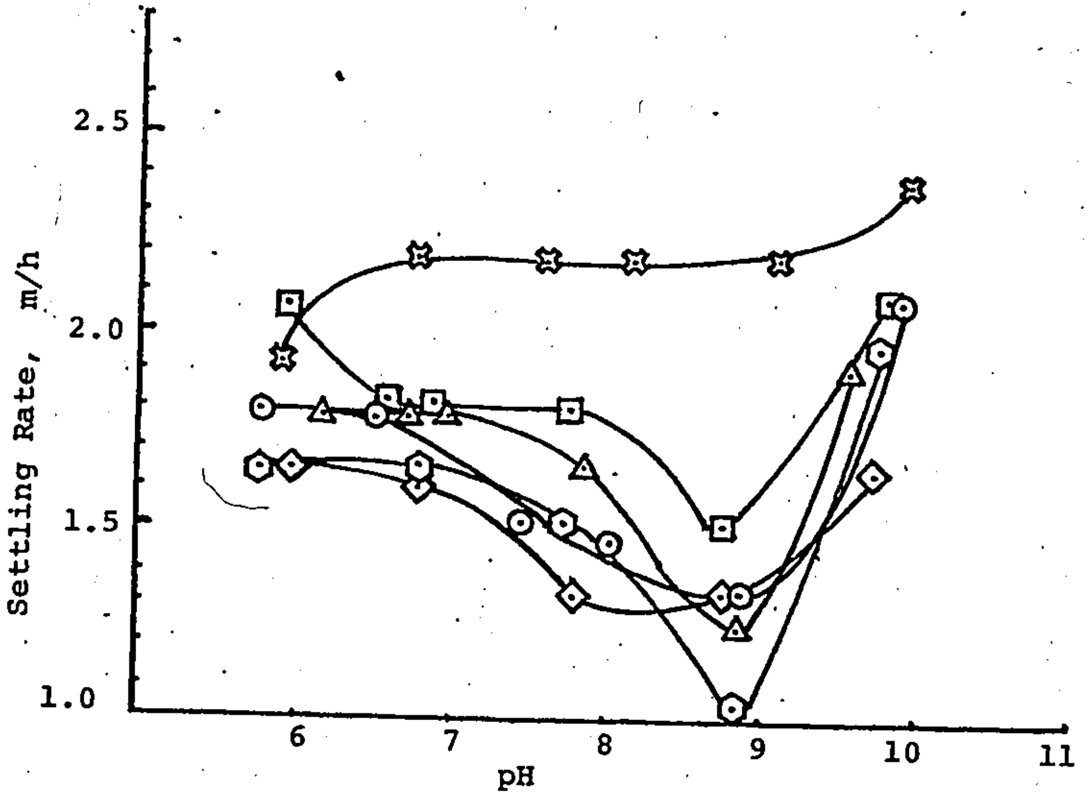


FIGURE 4.3.14 Settling Rates as a Function of pH for Al:P = 2.75 Suspended Solids Concentration: 1800 mg/l

The results for the high aluminum dosage (Al:P = 2.75) are shown in Figure 4.3.14. The settling rates observed in the blank solution case were higher than those observed in the blank solution employed for the low aluminum dosage. This was expected because the mixed liquor used for the high aluminum dosage sludy had a lower solids content (1800 mg/l vs. 2200 mg/l). Since activated sludge follows the hindered type of settling, the sludge with the higher solids concentration exhibited a lower settling rate. The addition of the coagulants reduced the settling rates to a considerable extent. The settling rates appeared to have a minimum at around pH 9. The somewhat surprising reduction in settling rates after the addition of the coagulants may be attributed to two facts: either the aluminum dosage and the solids concentration were such that some restabilization of the organic colloids occurred or to the slow-settling highly hydrated inorganic precipitates (EPA, 1975).

4.3.4 Studies on Sludge Filtrability

The study on sludge filtrability was performed on the Hamilton wastewater. After treating the wastewater for phosphorus removal with a dosage of 12 mg/l Al^{3+} (Al:P molar ratio equal to 2.0) the sludge was concentrated to around 7000 mg/l suspended solids and the Buchner funnel test was performed. The coagulants used were alum, aluminum chloride and PBAC with basicities of 1.0, 1.8 and 2.5. One additional test was performed without any coagulant.

The results of the test are shown in Figure 4.3.15 where the specific resistance has been plotted as a function of pH. It can be seen that pH has a marked effect on the specific resistance for the blank solution case. The lower the pH, the lower the specific resistance. At pH 4, for instance, the specific resistance corresponds to a value of 2 x 10^{-8} S^2/g but at pH 10 it was found to be more than six times as much. The same trend was found when coagulants were used. This was expected since the sludge particles under ordinary conditions are negatively charged and, at low pH, the negative charges located at the surface of the particles will tend to be neutralized by the abundance of the H^+ ions in solution.

When coagulants were used the specific resistance was greatly influenced by the pH and the type of coagulant. $AlCl_3$ and PBAC 1.8 showed a local maximum between pH 5 and 5.5, then a local minimum at pH 8 and at higher pH values the specific resistance increased. PBAC 1.0 showed a fairly constant behaviour throughout the studied range with higher values at pH between 4.5 and 5.5 and a lower one around 5. PBAC 2.5 showed a local maximum

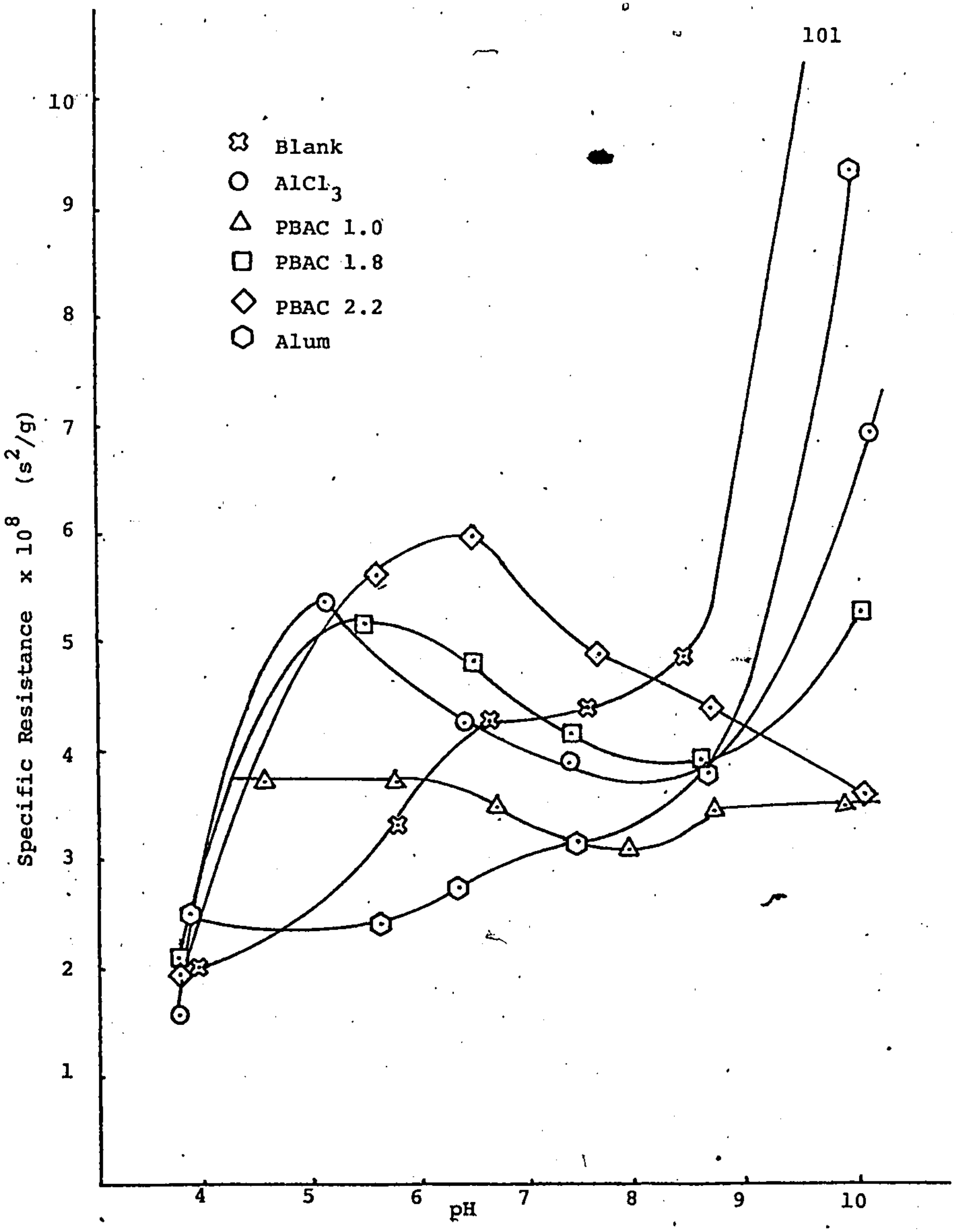


FIGURE 4.3.15 Specific Resistance as a Function of pH

at pH 6.5 and the specific resistance continued to lower even at pH levels as high as 10. Generally, all the above coagulants did not improve the sludge dewaterability at low pH values. Alum, however, was the only one which appeared to lower the specific resistance throughout the pH range.

Since the coagulant dosage was not varied in these experiments, it is difficult to explain this strange behaviour. However, it seems possible that in the pH range between 4 and 7, where most of the coagulants have had a negative effect on sludge filtrability and the coagulation efficiency is higher, the dosage employed resulted in charge reversal since the process is sensitive to excessive dosages (Eckenfelder, 1980). Under these experimental conditions the presence of sulfate ion (SO_4^{2-}) was beneficial.

4.4 ORGANICS REMOVAL

The study on the efficiency of the various aluminum coagulants to remove organics was performed on the Domtar wastewater. This industrial wastewater had a TOC of 45.5 mg/l. The coagulants employed were alum aluminum chloride and PBAC with basicities of 1.0, 1.8 and 2.5.

Figure 4.4.1 illustrates the effect of aluminum dosage on the removal. It can be seen that the three forms of PBAC exhibited a constant behaviour in the studied

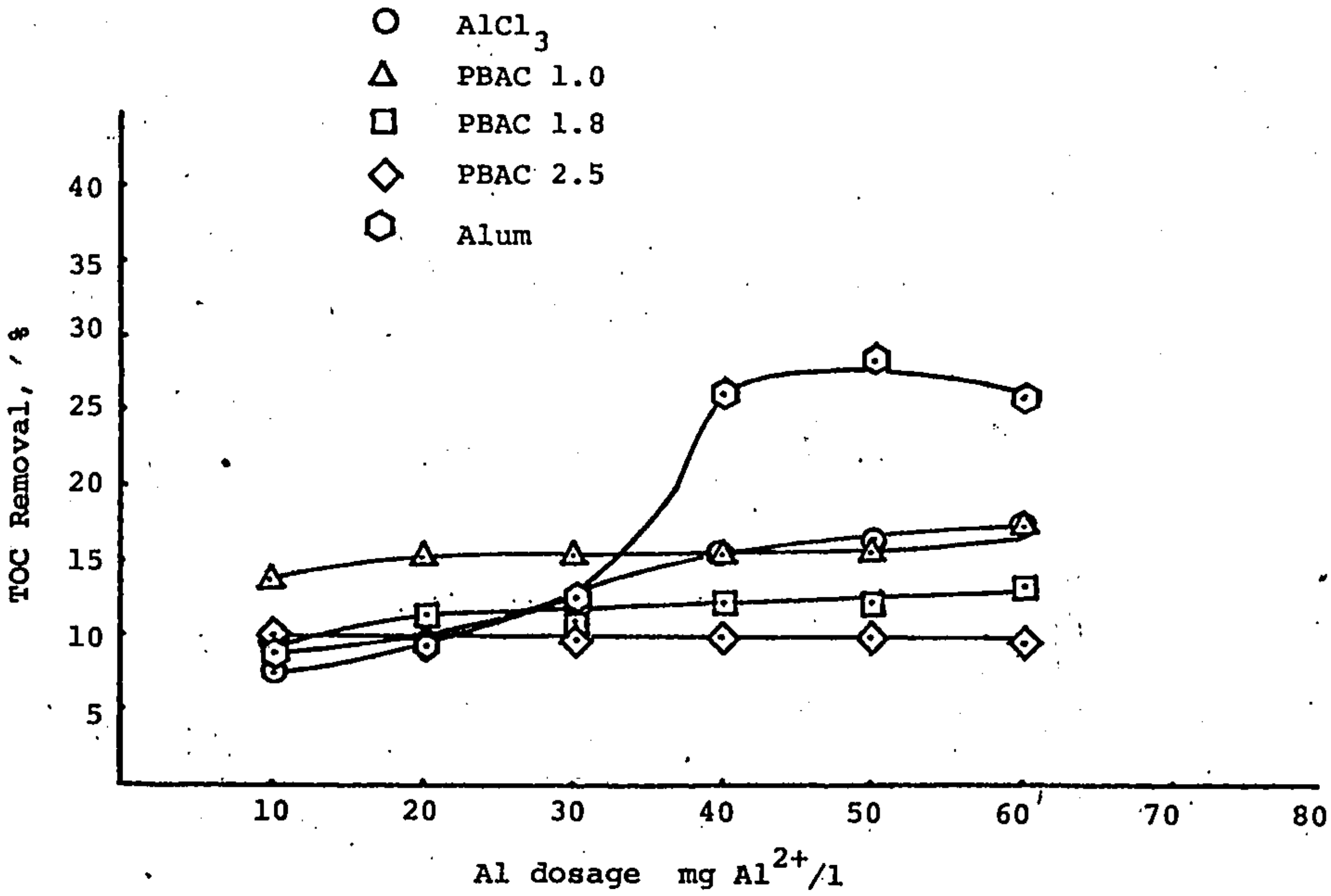


FIGURE 4.4.1 TOC Removal as a Function of Alum Dosage

range, i.e. 15% removal for PBAC 1.0, 12% for PBAC 1.8 and 10% for PBAC 2.5. Aluminum chloride and alum showed low efficiencies at low dosages, but their ability to remove organics increased as the dose increased. Up to 30 mg/l Al^{3+} their behaviour was identical, but at higher dosages alum reached the highest removals observed (around 38%) while $AlCl_3$ removed up to 17%.

In this set of experiments aluminum dosage was the operating variable and no concern was taken about control of pH. Therefore alum being more acidic than the others, lowered the pH to a greater extent. This led to higher removal especially at higher dosages. It has been found that alum is more efficient in removing organics at pH between 5 and 6 (AWWA Committee Report, 1979). Therefore, high alum dosages will remove more organics not only due to the higher metal ion concentration, but due to a decrease in pH as well.

To study the effect of pH on the removal of TOC, a low aluminum dosage of 13 mg/l was employed. The pH ranged from 4 to 9. The TOC removal as a function of pH for the various coagulants is shown in Figure 4.4.2. All the coagulants appeared to have a fairly constant behaviour giving a little higher removals at low pH. PBAC's with high basicity are more efficient

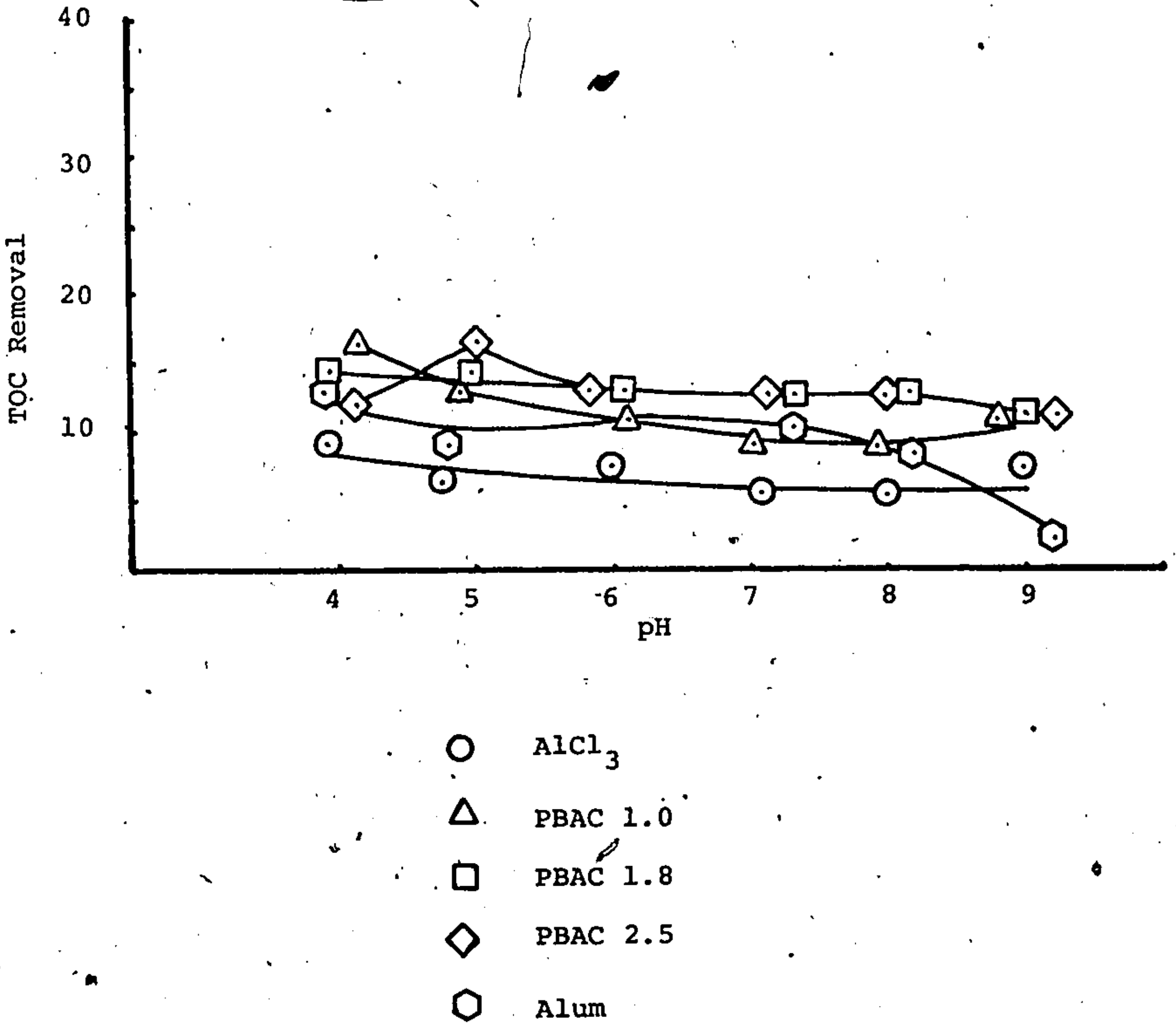


FIGURE 4.4.2 TOC Removal as a Function of pH

Aluminum dosage = 13 mg/l

but even these are able to remove only about 15% of the TOC. $AlCl_3$ gave the poorest results with alum and PBAC 1.0 lying in between.

These results, presented in Figure 4.4.2, are somehow surprising. There is a strong belief by people in the field that organics removal by means of coagulation is carried out through two mechanisms - charge neutralization and precipitation. Hall and Packham (1965) attributed the removal of humic and fulvic materials strictly to chemical precipitation, while Stumm and Morgan (1962) considered the destabilization of organics as being caused by electrostatic or chemical interactions, reducing the charge of the compounds and altering their solubility. Any removal involved a solid phase was considered to occur at high aluminum dosages where aluminum hydroxide precipitates. These concepts, however, are unable to explain the observed trend. If chemical precipitation or charge neutralization were the only mechanisms, it is difficult to explain the fact that PBAC 2.5 shows high efficiency in removing organics, because of the large amount of hydroxyl ions associated with the Al^{3+} ions. It is most likely that an adsorption mechanism plays an important role, too. The presence of $Al(OH)_3^*$ gel in the PBAC 2.5 solution strengthens this reasoning. There is not enough evidence in the literature how this occurs. Greenland (1971) after studying the interactions between organics and clays suggests an ion exchange mode of adsorption which is reversible and influenced greatly by the electrolyte concentration. He emphasized the importance of the polyhydroxy-complexes of aluminum which provide positive sites on the clay surface and facilitate the exchange adsorption. Another work by Schnitzer and Kahn (1972) provides some evidence about an irreversible sorption of the organic matter and its incorporation into the surface hydroxyl layer.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Based on the previous results the following conclusions can be drawn:

1. The removal of phosphates from water cannot be adequately described on the basis of equilibrium conditions of single compounds such as $AlPO_4$ and $Al(OH)_3$. On the contrary it was found that chemical precipitation is brought about through complex formation. The degree of phosphorus removal depends on the degree of hydrolysis of the coagulant and its concentration, the presence and the concentration of other ions and the pH. The model proposed by Hsu (1975) was found to explain the results. According to this model the interaction of an ion (in this case phosphate) with the aluminum ion depends upon the chemical affinity between these two ionic species and the competitive action from a

third one which also wants to occupy a site on the coordination shell.

2. For the conditions of these experiments, which are close to the ones usually met in practice, the higher the basicity (or the degree of hydrolysis of aluminum) the smaller the ability of the coagulant to precipitate the phosphates. This is caused by the higher affinity of OH^- ions to interact with Al^{3+}.
3. The most important factors affecting the optimum pH range for maximum P removal are the Al:P ratio, the OH:Al ratio and the presence and concentration of other ions. For higher aluminum dosages the optimum range moves to the higher pH values, because more hydroxyl ions are required to neutralize the $Al\text{-}PO_4$ positively charged complexes.
4. The presence of SO_4^{2-} has a beneficial effect on the removal, especially at lower pH values. Sulfate ions being a less strong competitor to phosphates help the neutralization of the complexes when the OH^- concentration is low.
5. When domestic wastewaters were used, the various coagulants gave results similar to

those observed in the synthetic wastewater case. The efficiencies, however, were smaller due to the presence of polyphosphates and other ionic species. Higher removals were observed at high pH (around 10) than at any other pH and this was attributed to calcium phosphate precipitation.

6. Calcium phosphate is entrapped in the biological flocs and phosphorus is released into the water when the pH decreases. Since the addition of alum will lower the pH, the efficiency of the coagulant will appear to be less than it actually is. This parallel activity, i.e. the release of phosphorus and the effect of the coagulant, leads to an optimum pH range which is not necessarily the pH at which the precipitation is performed in practice.

7. The study on the removal of supernatant suspended solids showed that this process proceeds parallel to phosphorus removal. In the pH range between 8 and 9, where neither aluminum nor calcium are effective in removing P, the supernatant suspended solids concentration

was found to be high. The nature of the solids was inorganic phosphates.

8. The pH and the nature and dosage of the coagulants greatly affected the removal of organics. It was shown, however that the removal of organics cannot be attributed to a strictly chemical interaction, but another mechanism, such as adsorption, should be taken into consideration as well.

5.2 RECOMMENDATIONS

Considering the previously presented conclusions, the following recommendations are suggested:

1. Since the coagulant dosage itself should not be the only operating variable in processes used for the removal of suspended solids and turbidity or for dewatering sludges, new investigations should focus on parameters such as pH and the hydrolysis products of metal ions.
2. A complete mechanism of the organics removal by means of coagulation should be examined, with respect to both lumped parameters, like TOC, and specific compounds.

3. An investigation of optimum conditions for operation of a water treatment plant should be performed. This analysis will investigate the feasibility of low pH treatment both from an economical point of view and for a better quality water perspective.

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APPENDIX 1

pH CONTROL CURVES

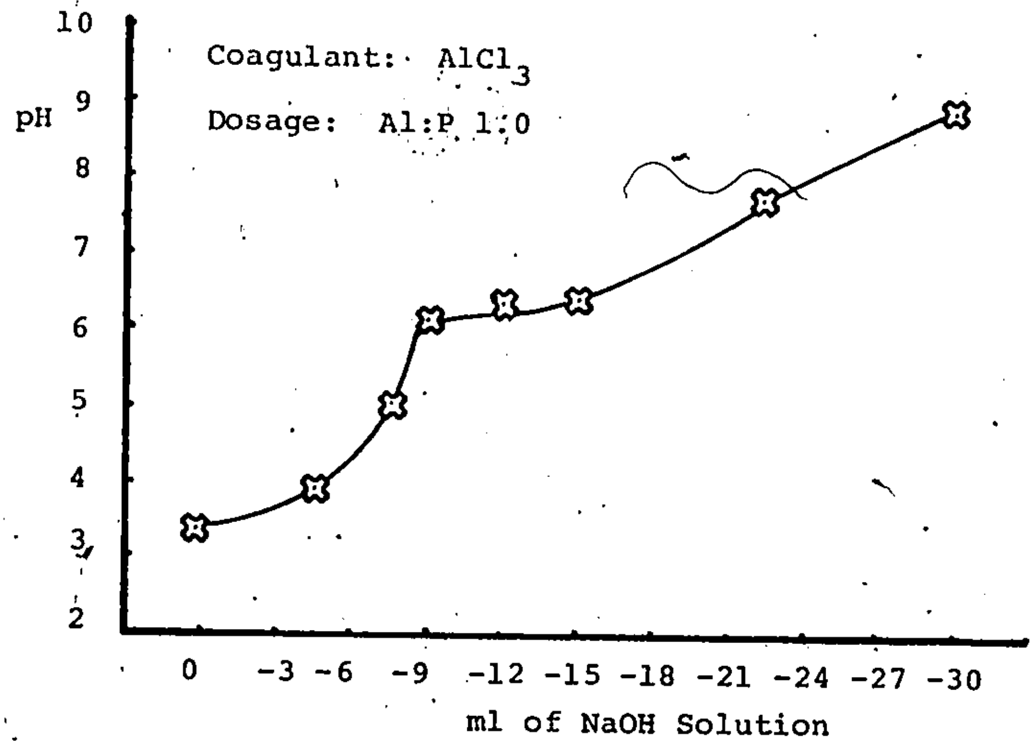

FIGURE A1.1 pH Control for Alternative Order of Mixing in Synthetic Wastewater

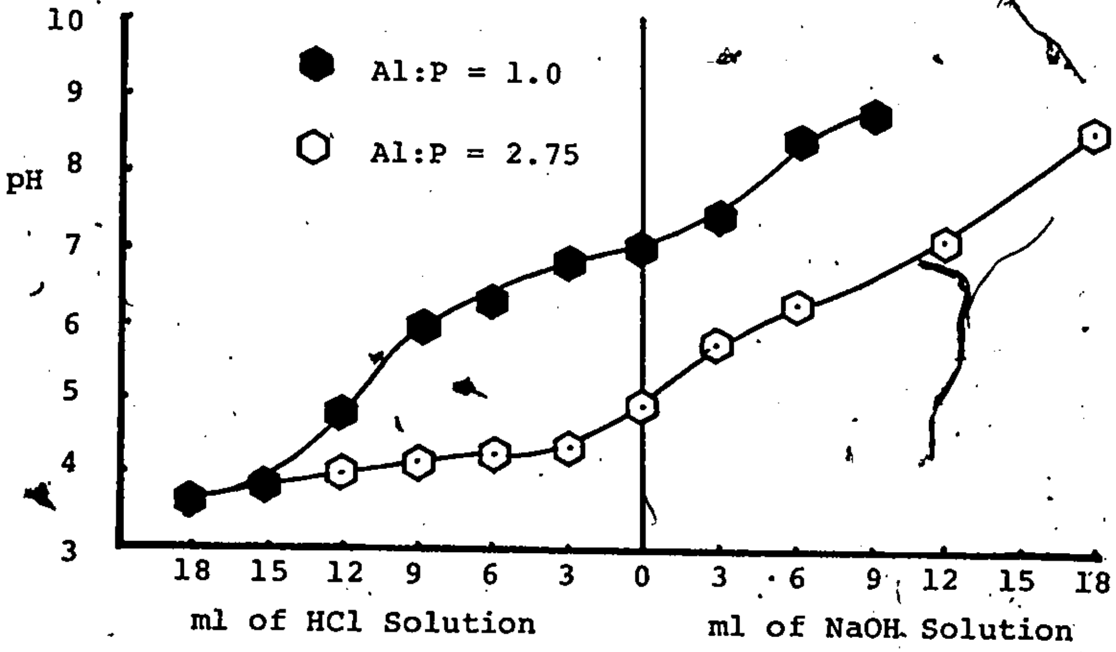

FIGURE A1.2 pH Control for Synthetic Wastewater Coagulant: Alum

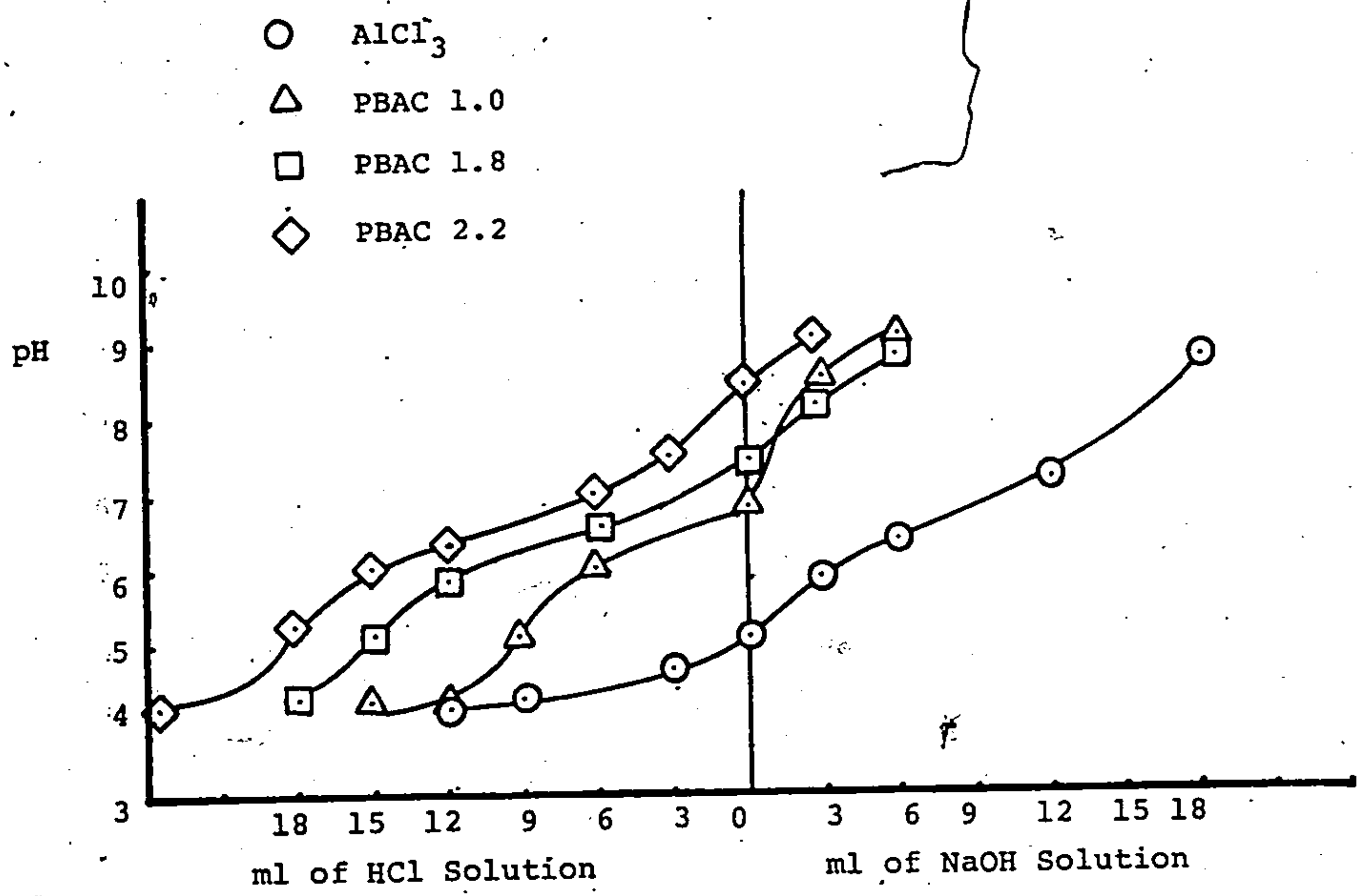

FIGURE A1.3 pH Control Curves for Synthetic Wastewater
Al:P = 2.75

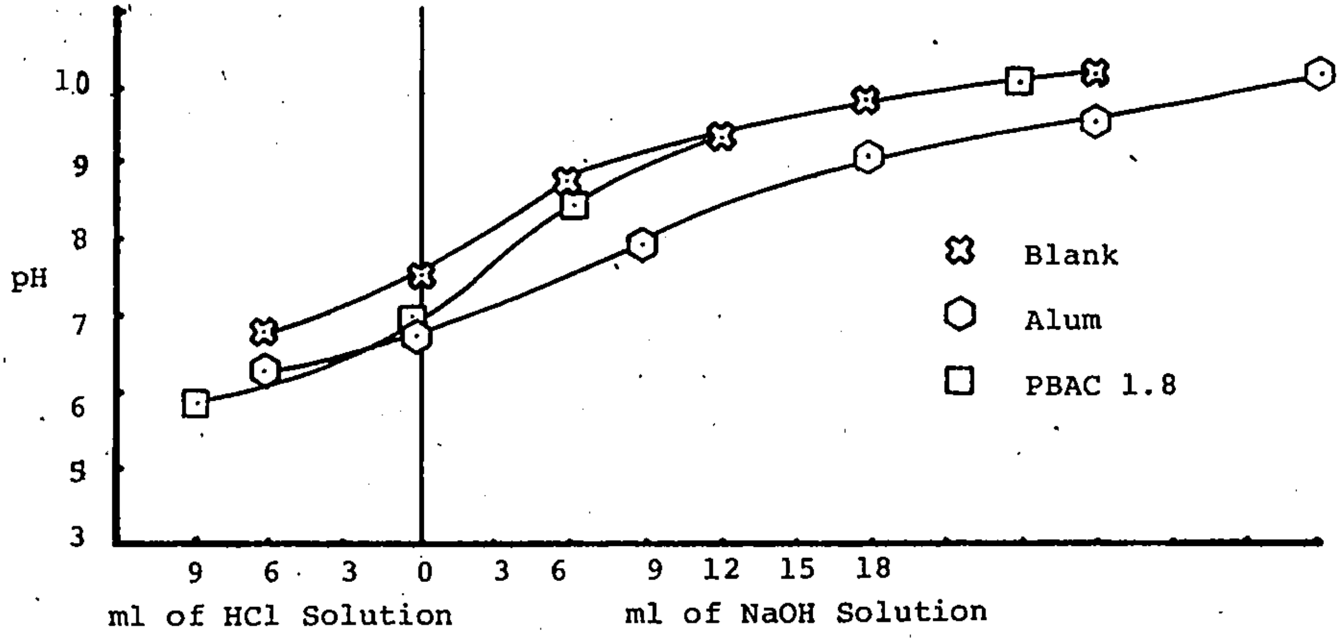

FIGURE A1.4 pH Control Curves for Burlington Wastewater
Al:P = 2.75

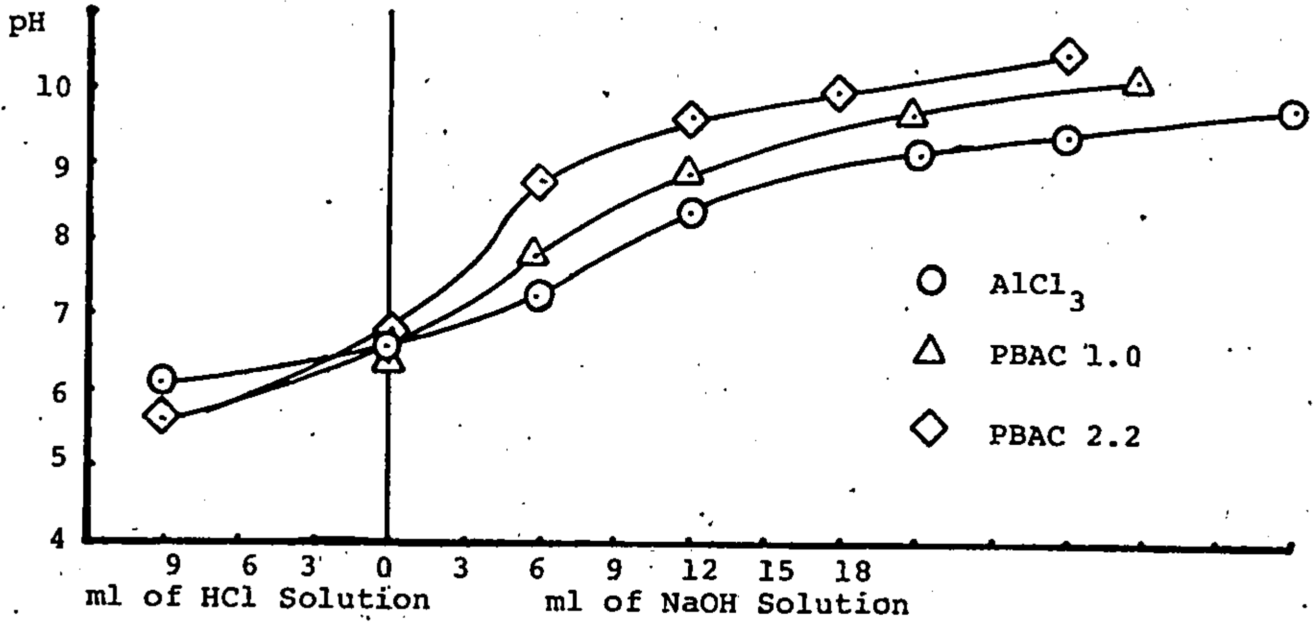

FIGURE A1.5 pH Control Curves for Burlington Wastewater
Al:P = 2.75

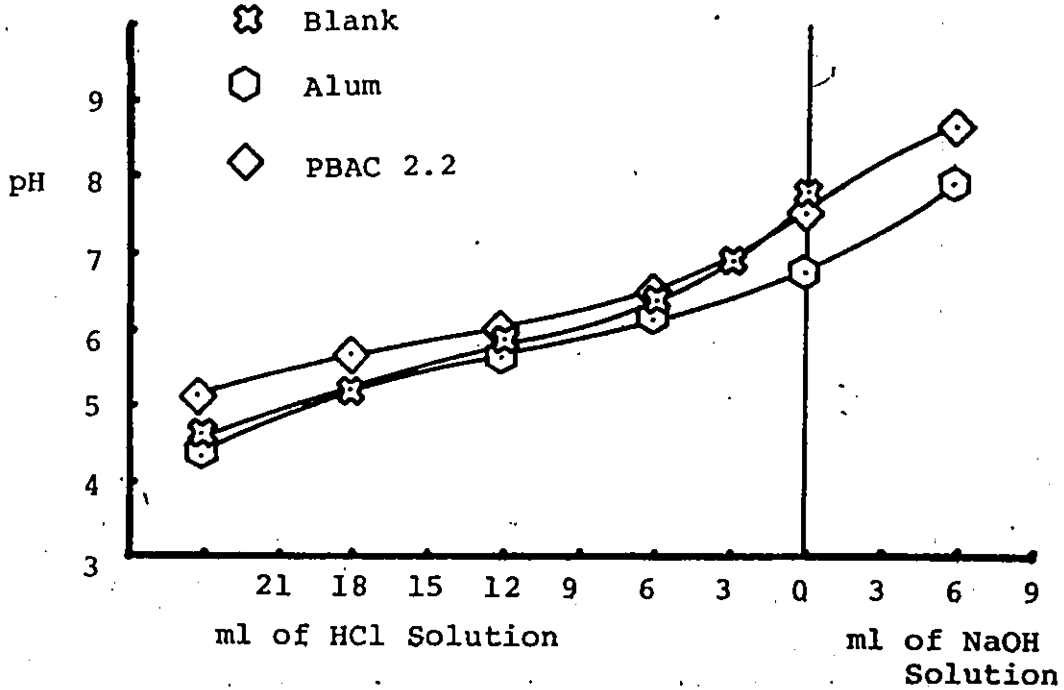

FIGURE A1.6 pH Control Curves for Burlington Wastewater Al:P = 1.0

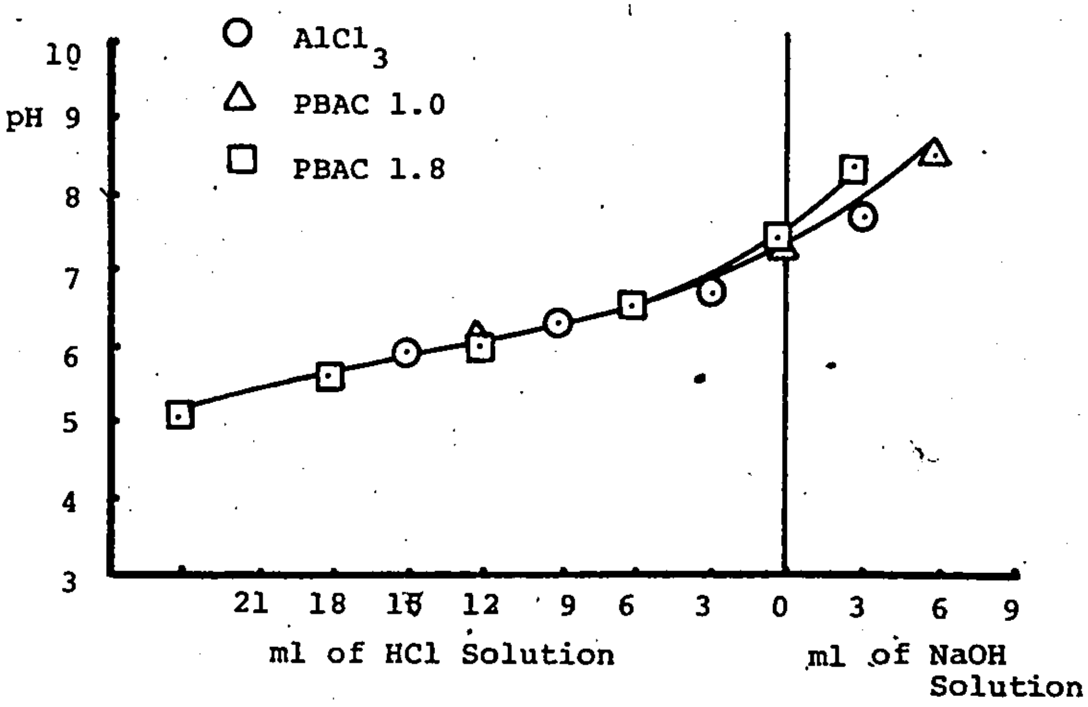

FIGURE A1.7 pH Control Curves for Burlington Wastewater Al:P = 1.0

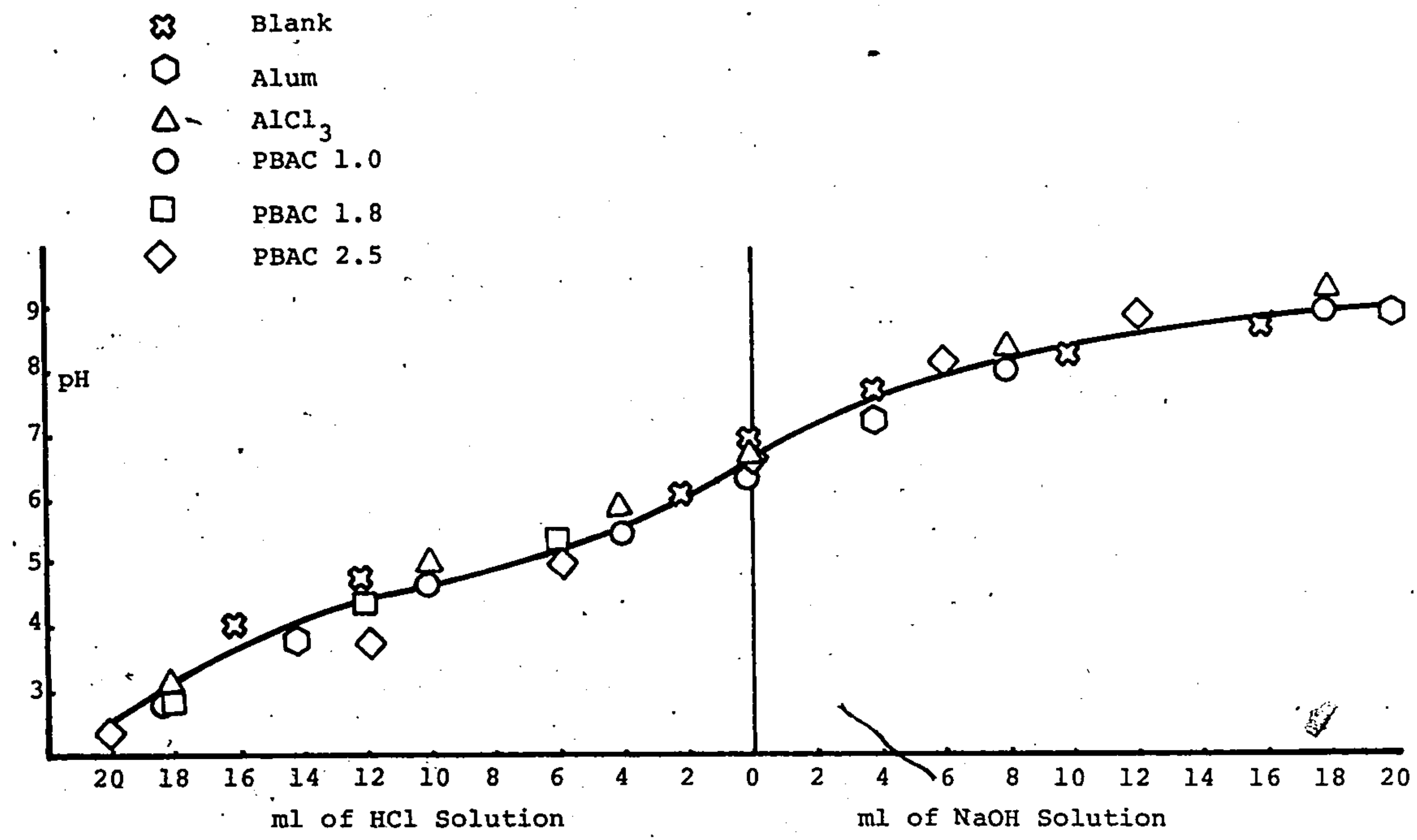

FIGURE A1.8 pH Control Curves for Al:P = 2.0 Hamilton Wastewater

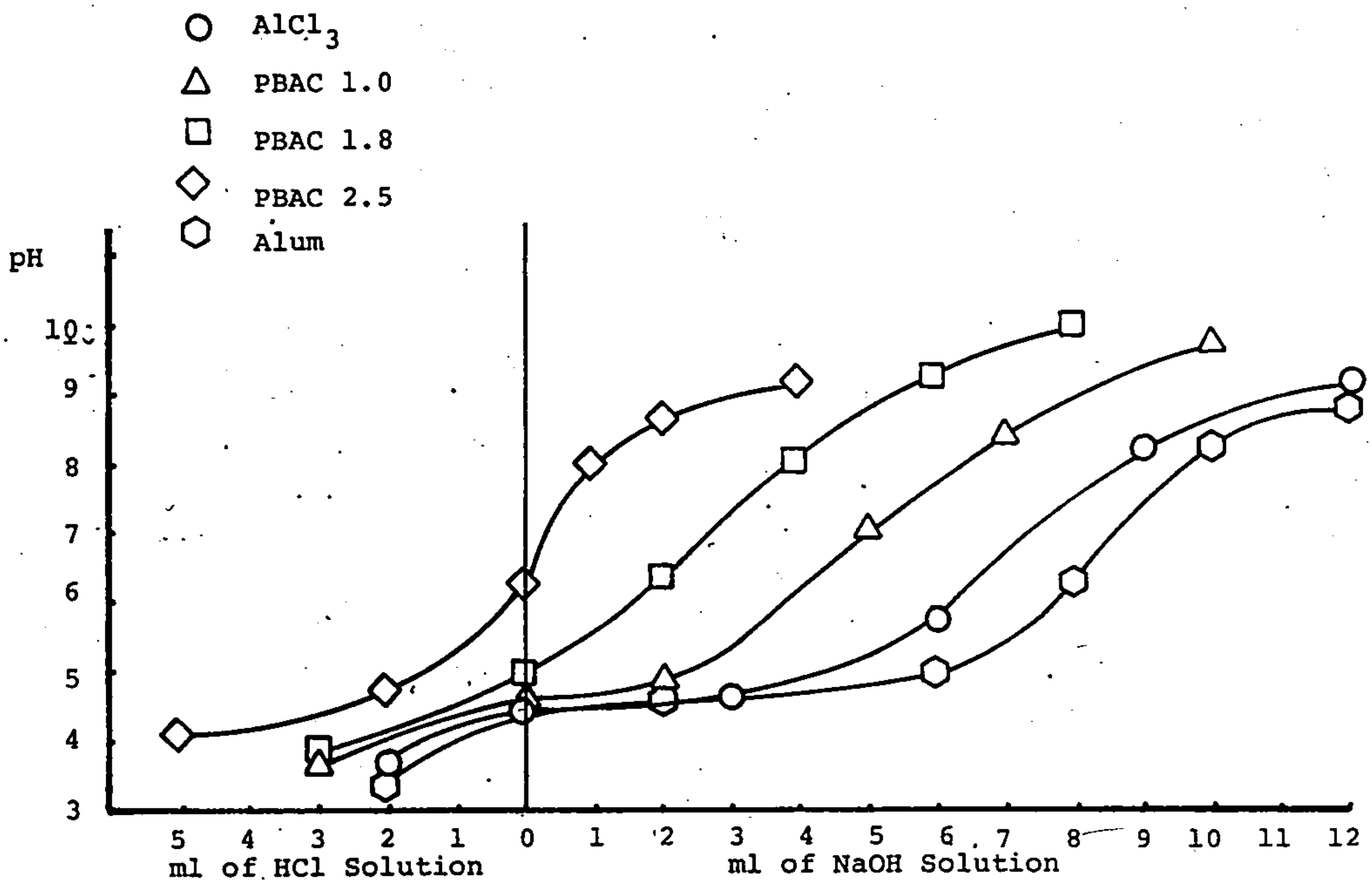

FIGURE A1.9 pH Control Curves for Domtar Wastewater

APPENDIX 2

EFFECT OF AGING TIME

A2.1 Raw Data

TABLE A2.1 Phosphorus Remaining in Solution After Treatment With PBAC 2.2 (mg/l)
Aging Time = 0.5 hr.

Time \ pH	4.3	4.7	6.1	7.0	8.1	9.0
0	14.8	15.3	15.7	15.0	15.0	15.0
2.5	14.8	15.0	15.7	15.3	17.7	15.3
5	14.8	15.7	15.3	15.7	16.6	16.6
10	15.7	15.9	12.6	8.6	10.5	12.8
15	15.0	15.0	4.4	6.1	9.0	11.6
20	14.8	15.3	3.8	5.7	9.0	11.6
30	14.0	15.7	3.7	5.7	8.4	11.1
Infinite	12.7	10.5	2.9	4.6	7.3	9.9

TABLE A2.2 Phosphorus Remaining in Solution After Treatment with PBAC 2.2 (mg/l). Aging Time = 1 hr

Time \ pH	4.3	5.3	6.3	7.0	8.1	9.1
0	15.0	15.3	15.1	15.1	15.0	15.0
2.5	14.8	16.3	15.7	15.7	15.4	15.9
5	14.4	16.7	15.9	15.9	15.6	14.6
10	14.4	15.3	9.3	8.2	10.7	12.0
15	14.6	4.7	5.1	5.9	8.5	11.1
20	14.4	2.1	4.2	5.7	8.4	11.1
30	14.4	1.9	3.9	5.5	8.2	10.9
Infinite	12.9	1.6	3.5	4.9	7.5	10.0

TABLE A2.3 Phosphorus Remaining in Solution After Treatment with PBAC 2.2 (mg/l). Aging Time = 3hr

Time \ pH	4.5	5.3	5.9	6.4	7.3	8.3
0	14.4	15.0	15.2	14.6	15.0	15.2
2.5	14.4	15.5	15.5	15.2	15.2	15.2
5	15.0	16.7	16.3	15.2	16.3	15.2
10	14.0	>20	12.8	9.6	8.7	10.25
15	14.3	7.55	5.5	4.8	6.0	8.8
20	14.6	2.35	3.35	3.85	5.8	8.35
30	14.0	2.15	2.95	3.6	5.55	8.15
Infinite	12.5	1.3	2.25	3.1	5.05	7.65

TABLE A2.4 Phosphorus Remaining in Solution After Treatment with PBAC 2.2 (mg/l) Aging Time = 24 hr.

pH / Time	4.5	5.3	6.0	6.5	8.0	9.2
0	14.5	15.0	14.8	14.5	14.5	14.8
2.5	14.8	15.75	15.5	15.25	14.8	14.8
5	14.5	15.6	15.75	15.25	15.0	15.0
10	14.8	>20	10.8	9.0	10.2	12.3
15	14.8	6.55	5.1	4.7	8.2	11.2
20	14.3	2.65	3.6	<1.95	7.85	11.1
30	14.3	2.1	3.45	<1.2	7.7	10.95
∞	12.2	1.4	2.3	3.4	6.4	9.75

A2.2 Percentage of Phosphorus Settled

TABLE A2.5 Percentage of Phosphorus Settled as a Function of pH and Aging Time

pH / Time	Aging Time = 0.5hr.				Aging Time = 1 hr.				
	6.1	7.0	8.1	9.0	5.3	6.3	7.0	8.1	9.1
10	24	61.5	58.5	43	-	50	67.5	57	60
15	88.2	85.5	78	66.5	77.5	86	90	87	78
20	93	89.5	78	66.5	96.5	94	92	88	78
30	94	89.5	85.7	76.5	98	96.5	94	90.5	82

pH / Time	Aging Time = 3 hr.				Aging Time = 24 hr.				
	5.3	5.9	6.4	7.3	8.3	5.3	6.0	6.5	8.0
10	-	18.5	43.5	63	65.5	-	32	49.5	53
15	54	75	85	90.5	85	62	78	88	78
20	92	91.5	93.5	92.5	91	91	89.5	92	82
30	94	94.5	95.5	95	93.5	95	91	93	84

APPENDIX 3

PHOSPHORUS REMOVAL FROM SYNTHETIC WASTEWATER

A3.1 Raw Data

TABLE A3.1 Phosphorus Concentration for Al:P = 1.0
Coagulant: $AlCl_3$

pH Time	3.75	4.3	5.4	6.0	6.5	7.8	9.1
0	14.5	13.9	14.1	14.75	14.0	13.9	14.0
2.5		13.4	14.3	15.0	14.4	13.75	14.0
5		14.0	13.65	14.1	14.65	13.9	14.0
10		13.45	5.8	9.35	7.45	13.9	14.2
15		13.7	3.2	5.5	5.35	14.2	14.3
20		13.7	2.9	4.25	4.5	14.2	14.5
30		13.8	2.4	3.7	3.95	14.2	14.8
Infinite	4.3	1.6	1.6	2.7	3.1	6.45	12.7

TABLE A3.2 Phosphorus Concentration for Al:P = 0
Coagulant: PBAC 1.0

pH Time	3.7	5.6	6.5	7.0	7.4	8.5
0	15.0	15.3	15.3	15.7	15.3	15.3
2.5	14.2	15.3	15.3	15.3	15.7	14.7
5	14.2	15.3	15.0	14.2	14.7	15.3
10	14.2	11.6	11.8	11.9	12.1	13.9
15	14.2	6.8	9.2	8.7	9.7	13.7
20	14.2	5.6	7.2	7.6	9.0	13.4
30	14.2	5.3	6.8	7.5	8.7	12.4
Infinite	11.4	3.9	5.1	5.7	6.9	10.9

TABLE A3.3 Phosphorus Concentration for Al:P = 1.0
Coagulant: PBAC 1.8

pH Time	4.4	5.5	6.0	6.5	7.4	8.7
0	14.1	13.7	13.7	14.1	14.2	14.45
2.5	13.9	14.2	14.2	14.45	14.3	14.2
5	13.9	14.45	14.65	15.1	14.8	15.1
10	14.1	11.35	11.55	13.6	12.1	13.1
15	13.9	8.55	9.55	10.5	10.6	13.1
20	13.9	7.85	8.55	9.4	10.25	12.85
30	13.75	7.25	8.1	9.0	10.2	12.85
Infinite	4.5	6.45	7.1	7.75	9.35	12.2

TABLE A3.4 Phosphorus Concentration for Al:P = 1.0
Coagulant: PBAC 2.2

pH Time	4.6	5.5	5.7	6.1	7.3	8.4
0	15.9	15.9	15.6	15.1	15.0	14.7
2.5	14.6	14.7	14.7	14.7	15.15	14.8
5	14.8	13.7	14.7	15.25	15.25	15.0
10	14.7	11.0	13.15	12.15	12.85	12.9
15	14.4	9.8	10.35	10.55	11.8	12.5
20	14.7	9.15	9.35	10.0	11.1	12.3
30	14.4	7.3	8.75	9.1	9.8	10.95
Infinite	12.1	5.65	7.7	7.9	8.6	10.2

TABLE A3.5 Phosphorus Concentration for Al:P = 1.0
Coagulant: Alum

pH Time	4.1	4.7	5.55	5.7	6.3	7.6	8.45
0	14.6	13.2	13.0	13.9	13.9	14.2	14.2
2.5		15.3	14.8	14.8	14.4	14.15	14.4
5		10.15	15.7	14.4	15.35	14.8	14.4
10		10.0	9.8	11.75	11.95	14.4	14.4
15		5.8	6.25	8.1	8.7	14.4	14.1
20		4.6	4.1	5.65	6.0	13.6	14.15
30		3.75	3.6	4.55	4.7	13.3	14.4
Infinite	0.9	0.9	1.8	2.15	3.0	6.4	9.4

TABLE A3.6 Phosphorus Concentration for Alternative Mixing, Coagulant: $AlCl_3$, Al:P = 1.0

PH / Time	4.0	4.5	5.05	5.45	5.9	6.55	7.45	8.45
0	14.6	14.6	14.3	15.0	15.0	15.0	13.9	13.9
2.5		14.4	14.3	14.6	14.6	15.35	14.6	14.3
5		14.6	14.6	15.35	15.0	16.7	14.6	14.3
10		14.6	14.0	11.85	11.45	9.45	13.7	14.3
15		13.7	11.25	7.4	7.75	6.5	13.7	15.0
20		13.7	9.25	5.4	5.4	5.55	12.7	14.3
30		14.0	8.45	4.7	4.7	5.0	11.65	15.0
Infinite	1.15	1.25	1.7	2.0	2.65	3.5	6.0	13.7

TABLE A3.7 Phosphorus Concentration for Al:P = 2.75
Coagulant: $AlCl_3$

pH / Time	4.0	4.6	5.5	6.05	6.5	7.6	8.5	10.2
0	14.7	15.0	15.0	15.0	15.0	14.75	15.0	15.0
2.5	13.7	14.7	15.3	15.0	15.3	14.75	15.0	15.3
5	14.7	15.7	15.3	15.35	16.0	14.75	14.7	15.0
10	14.2	14.7	15.0	4.0	5.5	5.45	14.7	15.0
15	14.2	15.0	15.0	1.0	1.8	2.9	14.5	15.3
20	14.5	15.0	15.0	0.6	0.8	2.7	14.2	15.3
30	13.9	14.7	15.3	0.5	0.7	2.55	13.4	15.3
Infinite	12.9	5.4	0.1	0.1	0.1	1.85	4.9	13.7

TABLE A3.8 Phosphorus Concentration for Al:P = 2.75
Coagulant: PBAC 1.0

pH Time	4.0	5.5	6.0	6.4	7.5	9.0
0	14.0	14.5	14.8	14.8	14.8	14.4
2.5	13.5	14.7	17.5	15.4	15.4	15.0
5	14.1	15.0	8.4	15.0	15.4	14.4
10	13.8	15.0	1.8	5.3	6.9	11.7
15	13.6	14.7	0.7	1.7	5.3	10.8
20	13.8	15.0	0.5	1.1	4.1	10.9
30	14.6	14.8	0.4	0.8	3.7	10.3
Infinite	12.4	0.2	0.1	0.1	2.8	9.3

TABLE A3.9 Phosphorus Concentration for Al:P=2.75
Coagulant: PBAC 1.8

pH Time	4.1	4.8	5.8	6.6	7.1	8.1
0	14.7	14.8	15.4	15.1	15.4	15.7
2.5	14.5	14.8	15.7	15.1	15.7	15.7
5	14.4	14.4	17.4	16.2	15.7	15.4
10	14.6	14.6	5.6	7.8	7.9	11.1
15	14.9	14.8	1.3	3.8	4.7	8.6
20	15.3	15.0	1.2	3.1	4.5	8.2
30	15.3	15.8	1.0	3.0	4.4	7.9
Infinite	11.8	1.5	0.7	2.1	3.35	6.4

TABLE A3.10 Phosphorus Concentration for Al:P = 2.75
Coagulant: PBAC 2.2

pH Time	4.3	5.3	6.3	7.0	8.1	9.1
0	15.0	15.3	15.1	15.1	15.0	15.0
2.5	14.8	16.3	15.7	15.7	15.4	15.9
5	14.4	16.7	15.9	15.9	15.6	14.6
10	14.4	15.3	9.3	8.2	10.7	12.0
15	14.6	4.7	5.1	5.9	8.5	11.1
20	14.4	2.1	4.2	5.7	8.4	11.1
30	14.4	1.9	3.9	5.5	8.2	10.9
Infinite	12.9	1.6	3.5	4.9	7.5	10.0

TABLE A3.11 Phosphorus Concentration for Al:P = 2.75
Coagulant: Alum

pH Time	4.45	5.5	5.9	6.2	7.0	8.2
0	14.3	14.7	15.6	14.3	14.3	14.7
2.5	14.0	15.7	15.7	15.6	14.7	13.7
5	13.25	16.3	16.7	16.3	16.3	14.0
10	11.75	6.15	4.95	4.45	5.2	9.05
15	4.55	2.0	1.6	1.0	1.75	6.5
20	2.5	1.3	1.2	0.8	1.0	6.4
30	0.25	0.15	0.15	0.2	0.2	6.0
Infinite	0.1	0.1	0.1	0.1	0.15	0.15

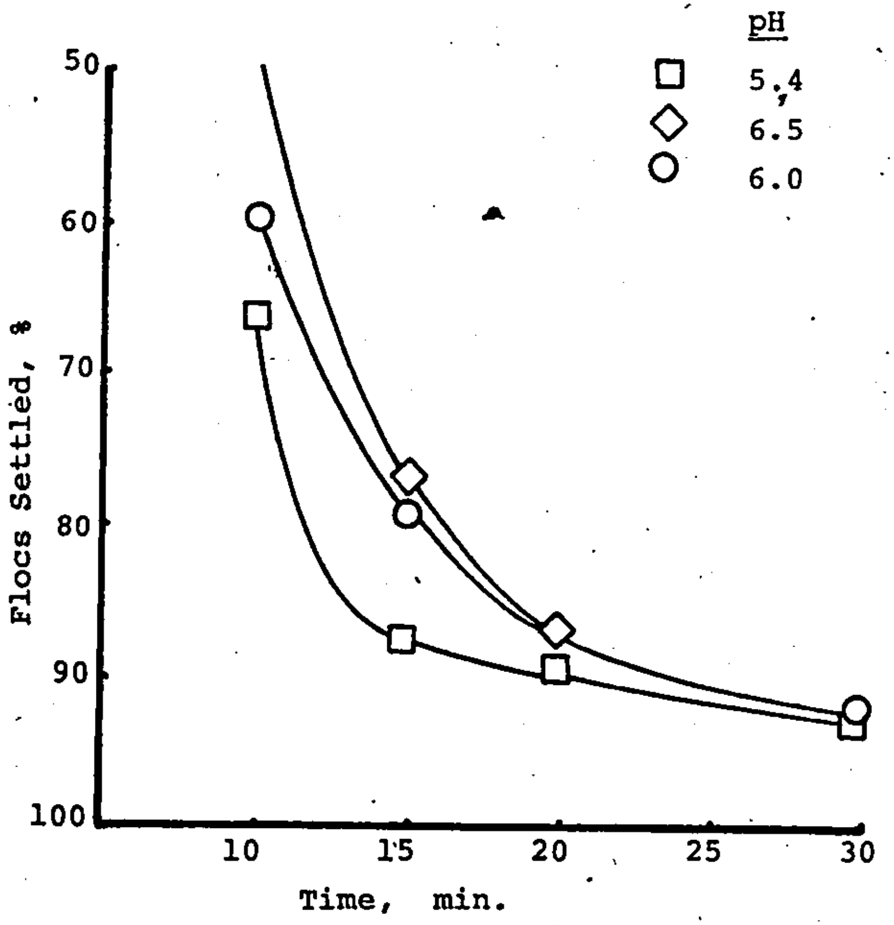

FIGURE A3.1 Percentage of Flocs Settled for Al:P = 1.0 Coagulant: $AlCl_3$

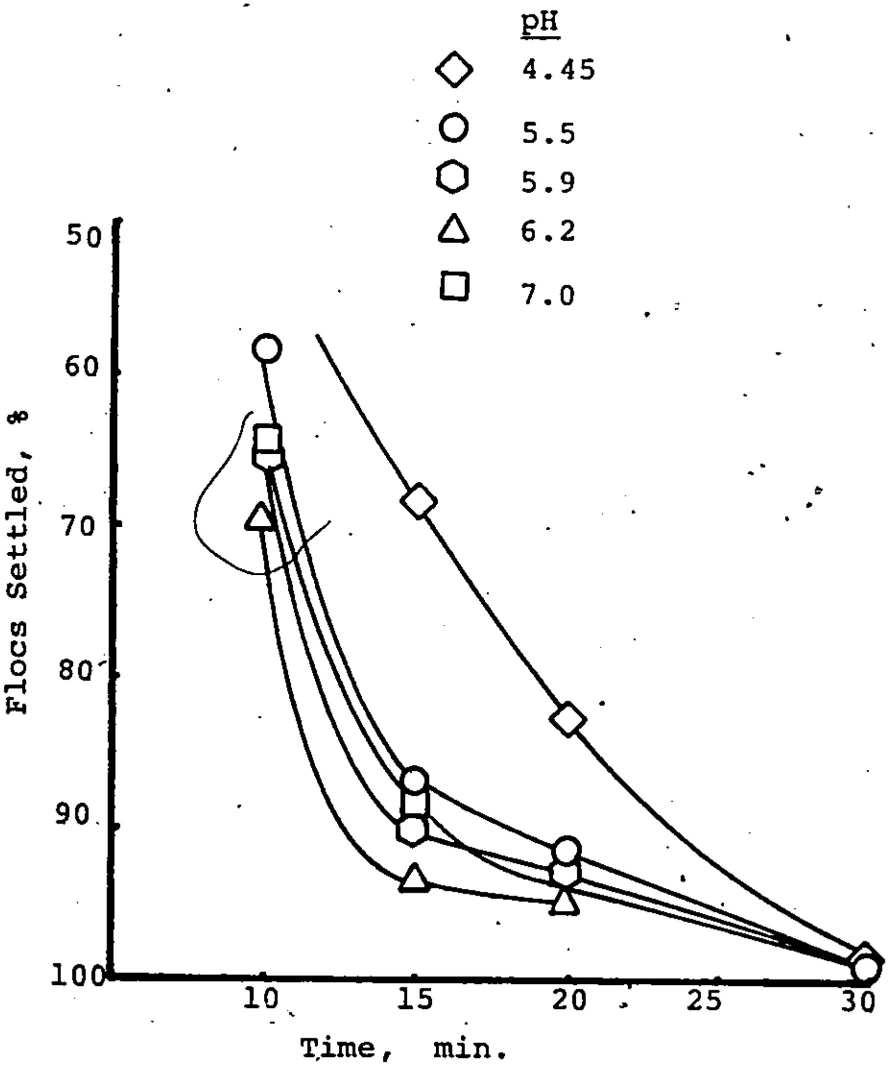

Figure A3.2 Percentage of Flocs Settled for Al:P = 2.75 Coagulant: Alum

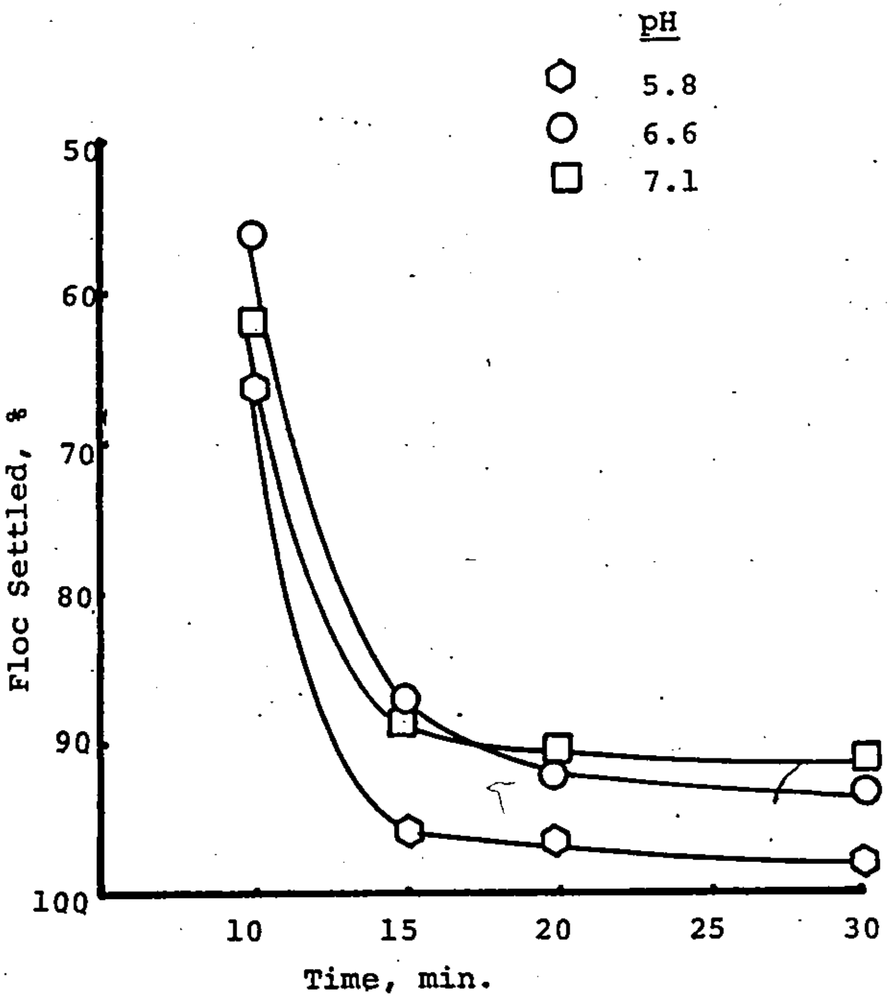

FIGURE A3.3 Percentage of Flocs Settled for Al:P = 2.75 Coagulant: PBAC 1.8

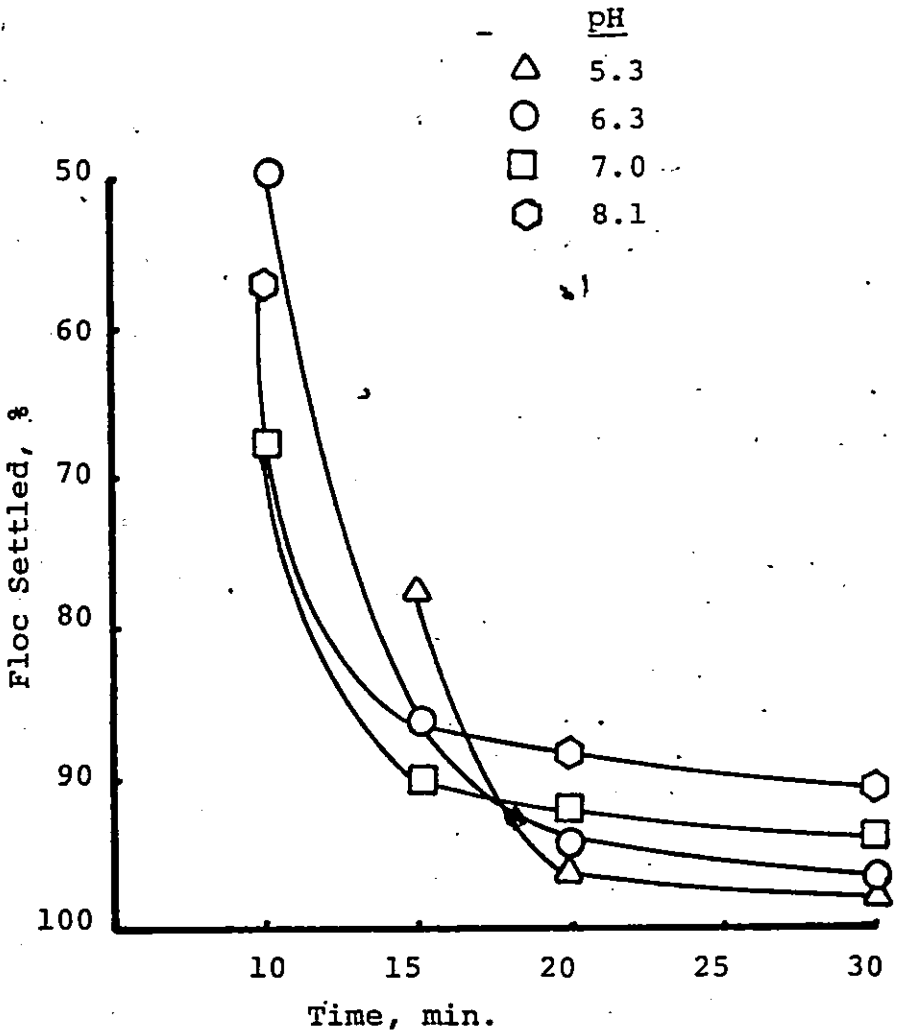

FIGURE A3.4 Percentage of Flocs Settled for Al:P = 2.75 Coagulant: PBAC 2.2

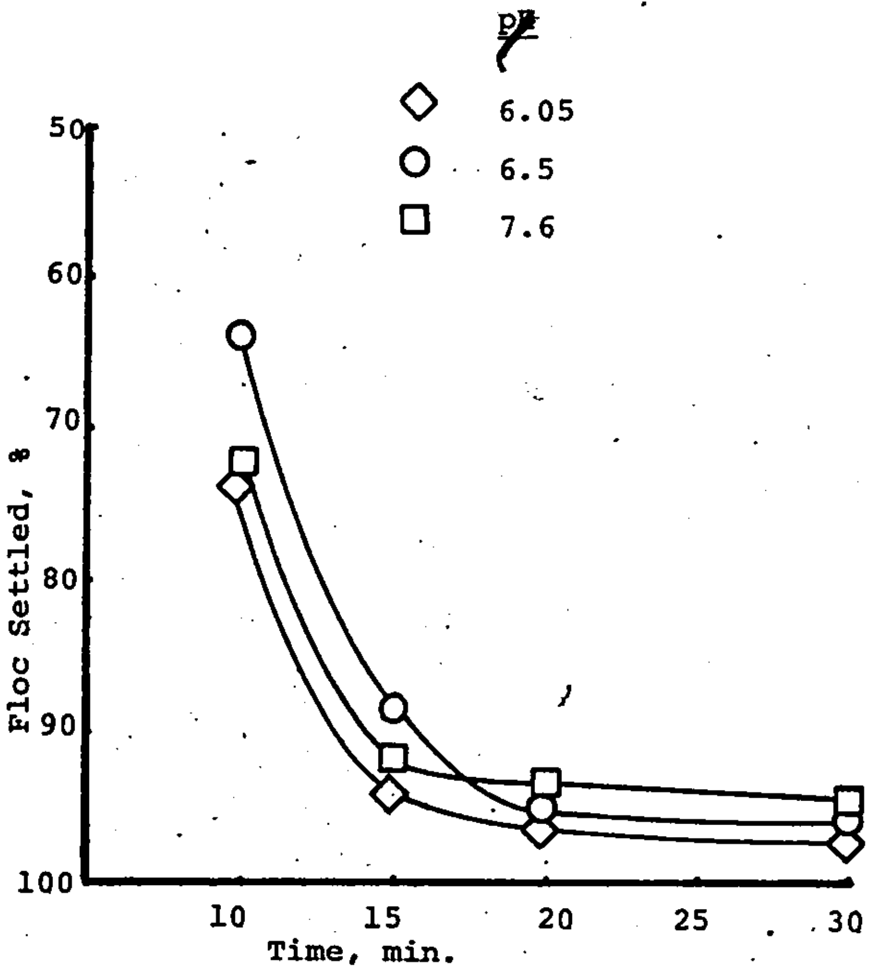

FIGURE A3.5 Percentage of Flocs Settled for Al:P = 2.75 Coagulant: $AlCl_3$

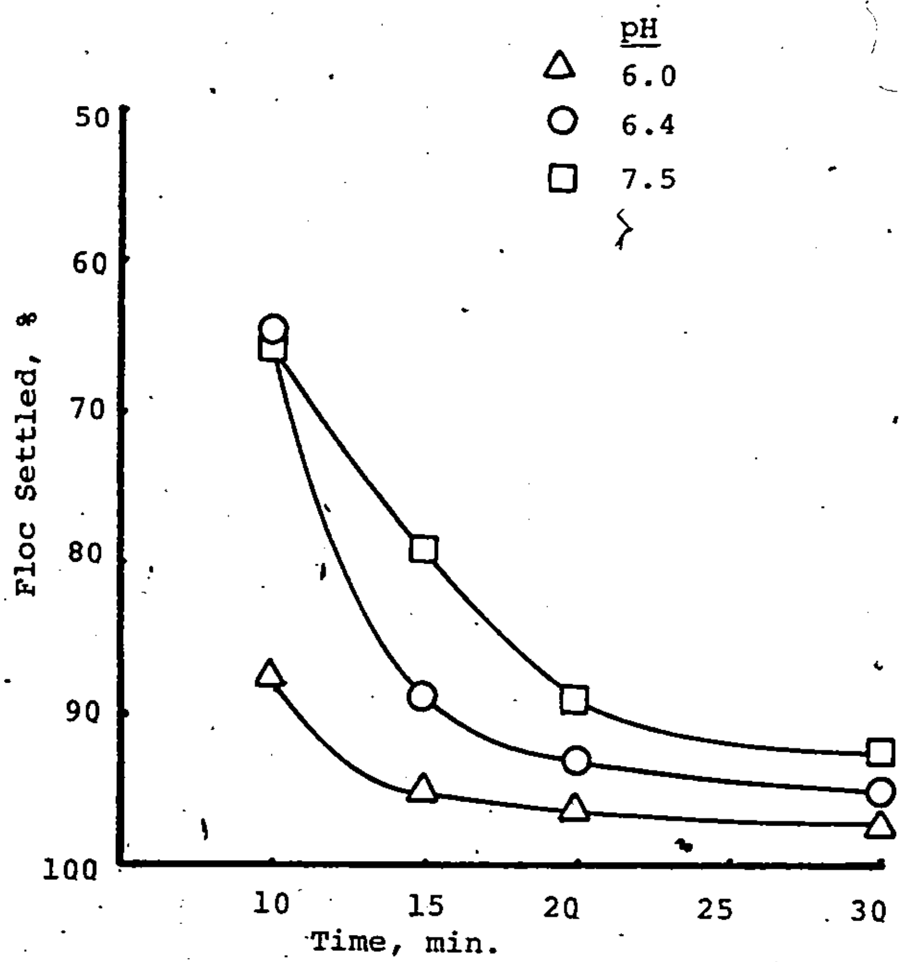

FIGURE A3.6 Percentage of Flocs Settled for Al:P = 2.75 Coagulant: PBAC 1.0

APPENDIX 4

PHOSPHORUS REMOVAL FROM DOMESTIC WASTEWATERS

A4.1 Raw Data

TABLE A4.1 Phosphorus Concentration for Al:P = 1.0
Burlington Wastewater

Coagulant		Initial	Final				
$AlCl_3$	pH	7.9	5.6	6.05	6.95	7.05	7.8
	P	5.4	3.45	2.3	1.35	1.50	1.35
PBAC 1.0	pH	7.85	5.25	6.0	6.9	7.2	7.9
	P	5.7	6.5	3.95	2.4	2.25	1.9
PBAC 1.8	pH	7.9	5.2	6.0	6.9	7.4	7.9
	P	5.8	7.75	4.8	3.3	3.1	2.75
PBAC 2.2	pH	7.8	5.0	5.95	6.9	7.45	8.0
	P	6.1	10.5	7.4	4.5	4.3	3.1
Alum	pH	7.85	4.9	6.1	6.9	7.2	8.2
	P	6.3	10.15	4.85	2.9	2.8	1.75
Blank	pH	7.85	5.1	5.95	6.9	7.8	7.95
	P	6.4	14.2	10.0	7.5	6.5	5.0

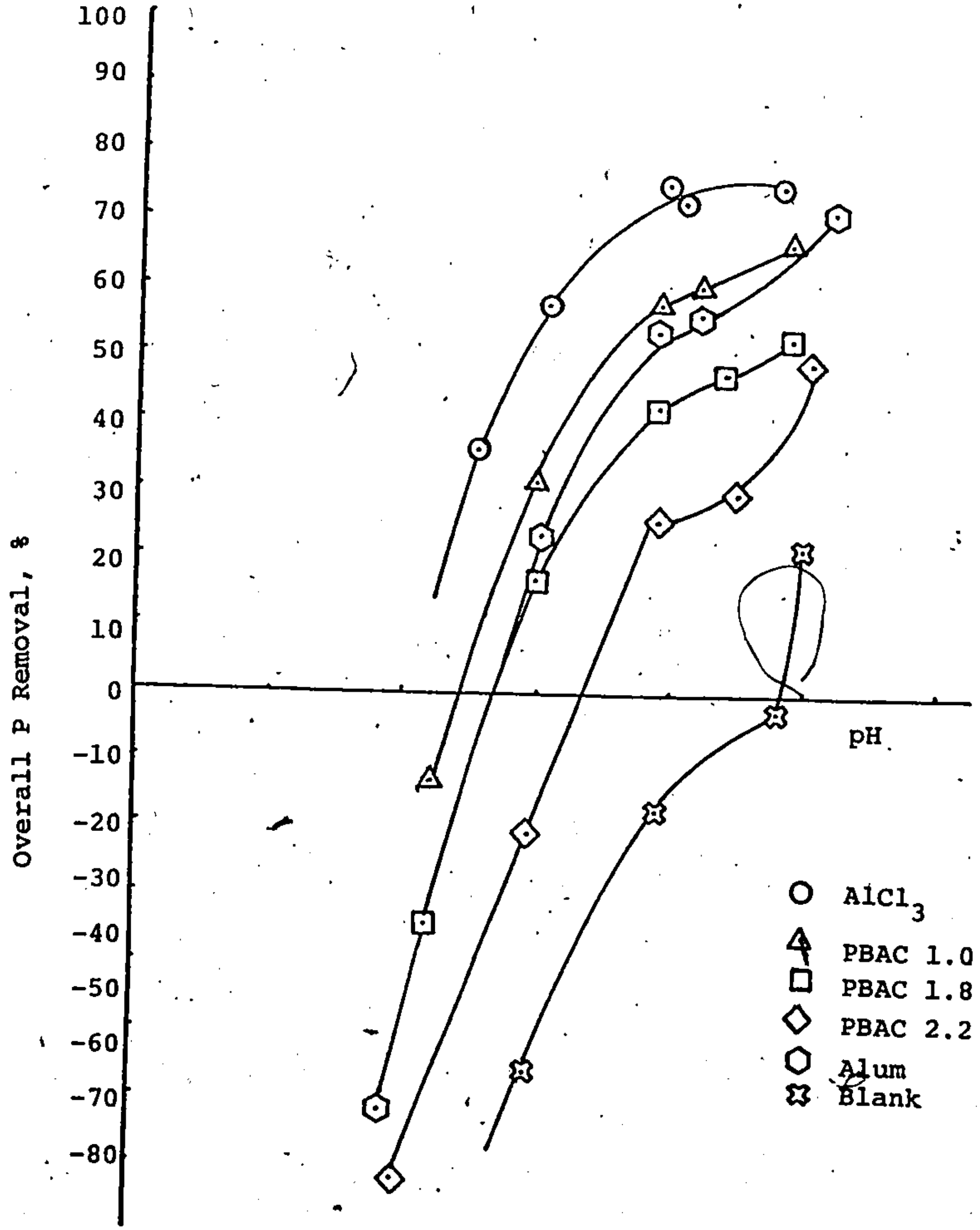

FIGURE A4.1 Overall Phosphorus Removal for Al:P = 1.0
Burlington Wastewater

TABLE A4.2 Phosphorus Concentration for Burlington Wastewater Blank
Initial Filtered P = 4.60
Initial Dissolved Ca = 51 mg/l

pH after a/b addition	5.95	6.8	7.65	8.2	9.05	10.0
P " "	7.15	4.87	4.6	3.4	1.05	0.25
P Total	7.17	5.42	4.65	3.5	1.17	0.8
Ca Dissolved	58	52	51	48	40	31

(Notice that since no coagulant was used, P after acid or base addition is the final P level).

TABLE A4.3 Phosphorus Concentration for Burlington Wastewater
Coagulant: $AlCl_3$ Al:P = 2.75
Initial Dissolved Ca = 51 mg/l
Initial Filtered P = 4.90 mg/l

pH after a/b addition	6.3	7.6	8.5	9.7	10.05	10.6
P " "	5.95	4.9	2.3	0.52	0.25	0.10
pH Final	5.8	6.55	7.0	8.05	8.9	9.95
P "	0.87	0.6	0.67	1.20	0.75	0.32
P Total	0.87	0.6	0.80	1.35	1.60	0.35
Ca Dissolved	58	51	50	46	38	24

TABLE A4.4 Phosphorus Concentration for Burlington Wastewater

Coagulant: Alum Al:P = 2.75

Initial Dissolved Ca = 50 mg/l

Initial Filtered P = 4.95

pH after a/b addition	6.2	7.5	8.2	9.2	9.8	10.8
P " "	7.0	4.95	2.92	0.90	0.15	0.10
pH Final	5.8	6.55	6.8	7.75	8.9	9.8
P "	1.20	0.70	0.75	1.30	0.77	0.32
P Total	1.20	0.75	0.80	1.30	1.05	0.50
Ca Dissolved	60	64	58	51	36	25

TABLE A4.5 Phosphorus Concentration for Burlington Wastewater

Coagulant: PBAC 1.0 Al:P = 2.75

Initial Dissolved Ca = 51 mg/l

Initial Filtered P = 5.35 mg/l

pH after a/b addition	6.45	7.4	8.2	9.05	9.65	10.35
P " "	6.05	5.35	3.5	2.0	0.2	0.1
pH Final	6.2	6.75	7.0	7.9	8.8	9.6
P Final	1.85	1.30	1.30	1.57	0.90	0.42
P Total	1.87	1.30	1.35	1.70	1.00	0.40
Ca Dissolved	51	50	48	44	38	27

TABLE A4.6 Phosphorus Concentration for Burlington Wastewater

Coagulant: PBAC 1.8 Al:P = 2.75

Initial Dissolved Ca = 47 mg/l

Initial Filtered P = 5.35

pH after a/b addition	6.2	7.55	7.9	8.8	9.6	10.4
P " "	7.30	5.40	4.7	4.0	3.4	2.8
pH Final	6.0	6.6	6.9	7.8	8.8	9.85
P Final	4.05	2.35	2.2	2.15	1.0	0.25
P Total	3.85	2.35	2.2	2.15	1.15	0.30
Ca Dissolved	55	50	46	46	39	28

TABLE A4.7 Phosphorus Concentration for Burlington Wastewater

Coagulant: PBAC 2.2 Al:P = 2.75

Initial Dissolved Ca = 47 mg/l

Initial Filtered p = 6.55

pH after a/b addition	6.0	7.05	7.3	8.5	9.4	10.3
P " "	8.65	6.60	6.32	1.90	0.42	0.10
pH Final	6.0	6.80	6.85	7.85	8.7	9.75
P "	5.30	3.65	3.15	2.60	1.35	0.25
P Total	5.25	3.80	3.15	2.77	1.37	0.37
Ca Dissolved	55	47	47	44	40	28

TABLE A4.8 Phosphorus Concentration for Hamilton Wastewater

Coagulant: None, Initial pH = 8

Initial Filtered P = 7.3 mg/l

Initial Dissolved Fe = 5.35 mg/l

Initial Dissolved Ca = 20 mg/l

pH Final	3.9	5.75	6.6	7.5	8.4	9.9
P Final	24.6	14.1	11.3	7.95	5.3	0.85
Ca	65	40	28	24	17	3
Fe	1.7	0.45	0.6	1.65	1.3	2.5

TABLE A4.9 Phosphorus Concentration for Hamilton Wastewater

Coagulant: Alum Al:P = 2.0

Initial Filtered P = 6.8 mg/l

Initial Dissolved Fe = 5.3 mg/l

Initial Dissolved Ca = 20 mg/l

pH after acid/base addition	4.1	5.85	6.5	7.1	9.1	10.5
P " "	24.9	14.7	12.3	10.2	2.15	0.55
pH Final	3.85	5.6	6.3	6.9	8.6	9.95
P Final	16.1	6.8	4.9	3.7	1.6	10.5
Ca Dissolved	54	34	26	24	10	4
Fe Dissolved	0.95	0.65	0.4	0.5	0.1	0.2

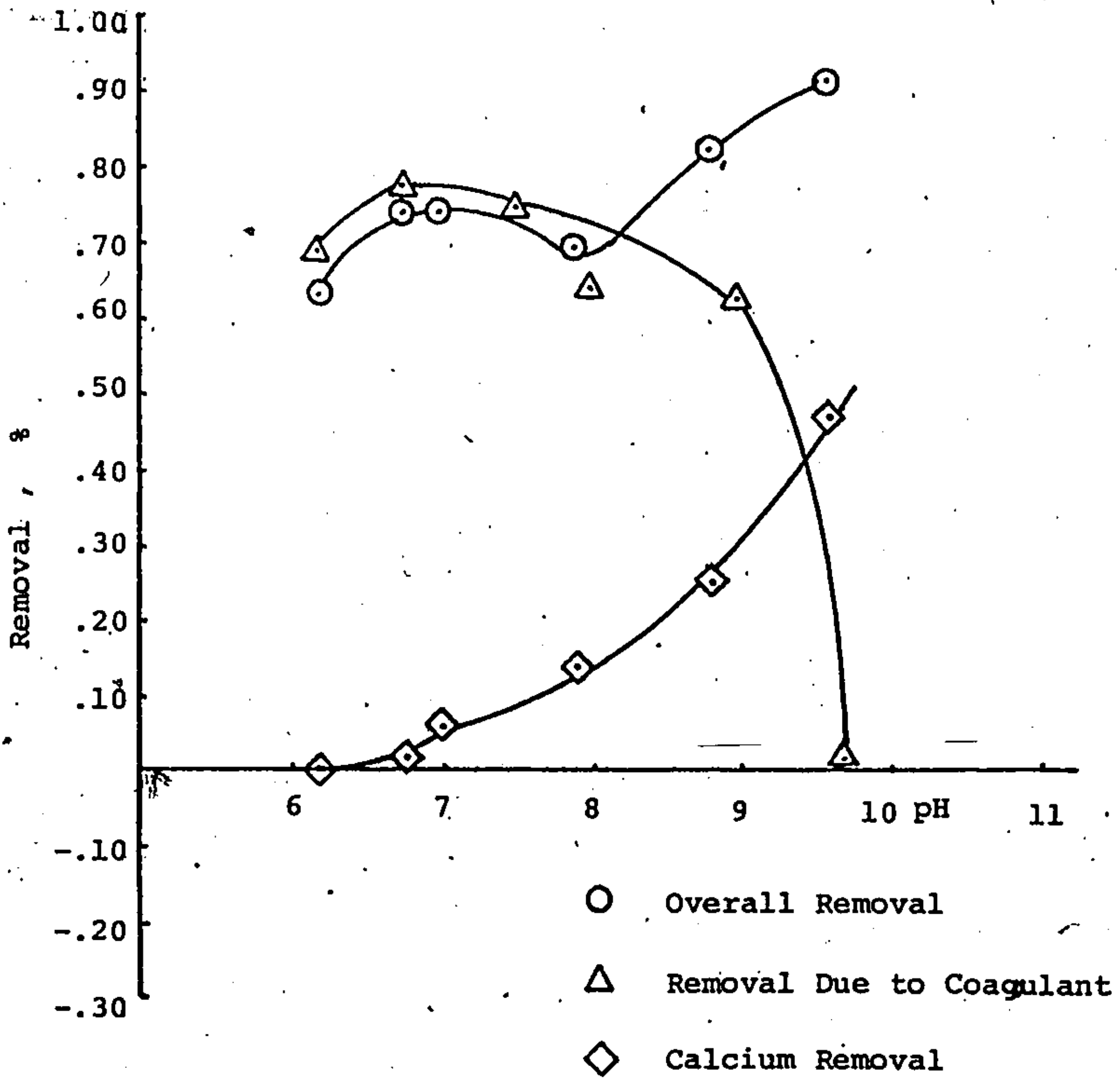

FIGURE A4.2 Phosphorus Removal for Al:P = 2.75
Coagulant: PBAC 1.0
Burlington Wastewater

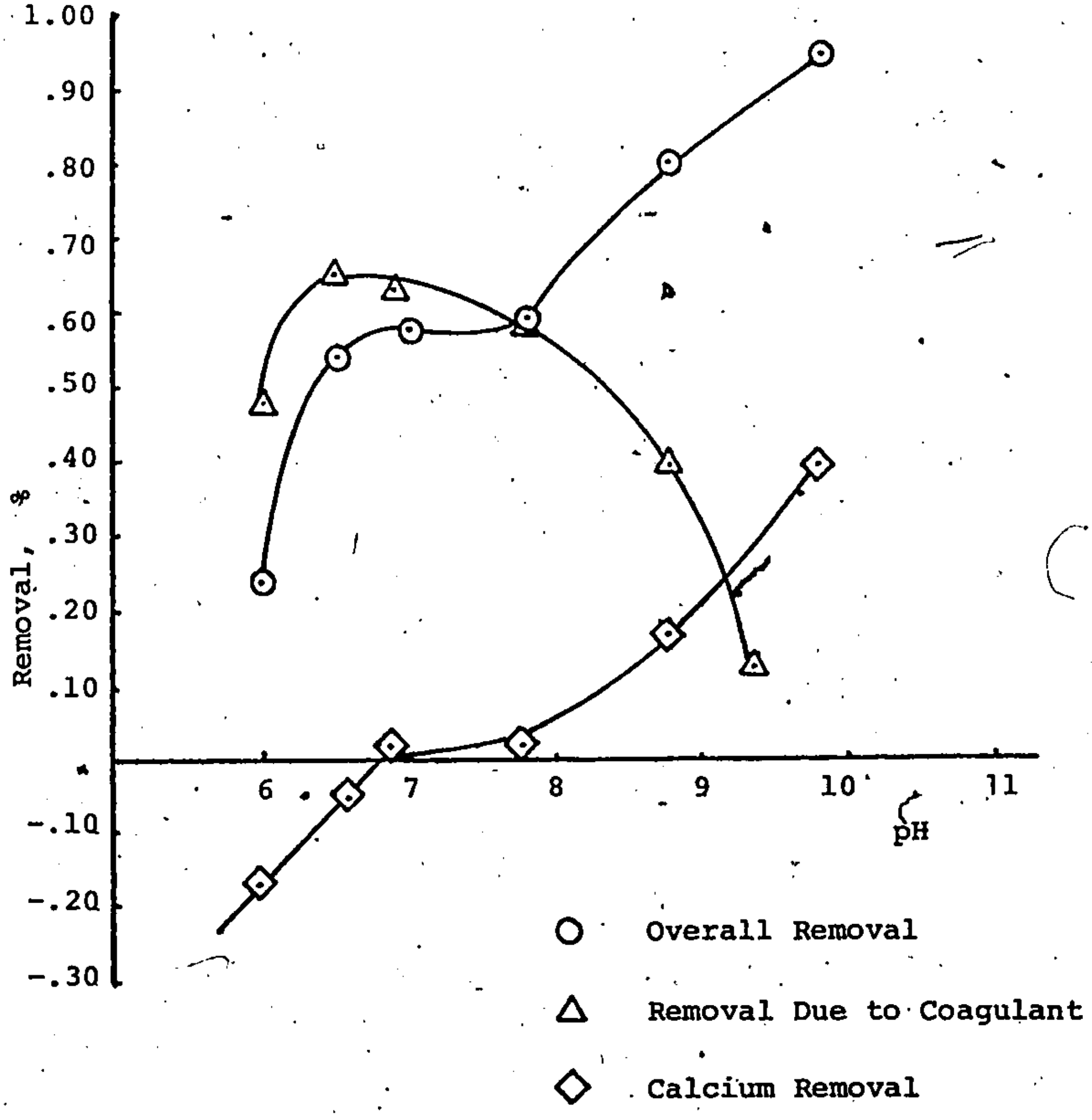

FIGURE A4.3 Phosphorus Removal for Al:P = 2.75
Coagulant: PBAC 1.8
Burlington Wastewater

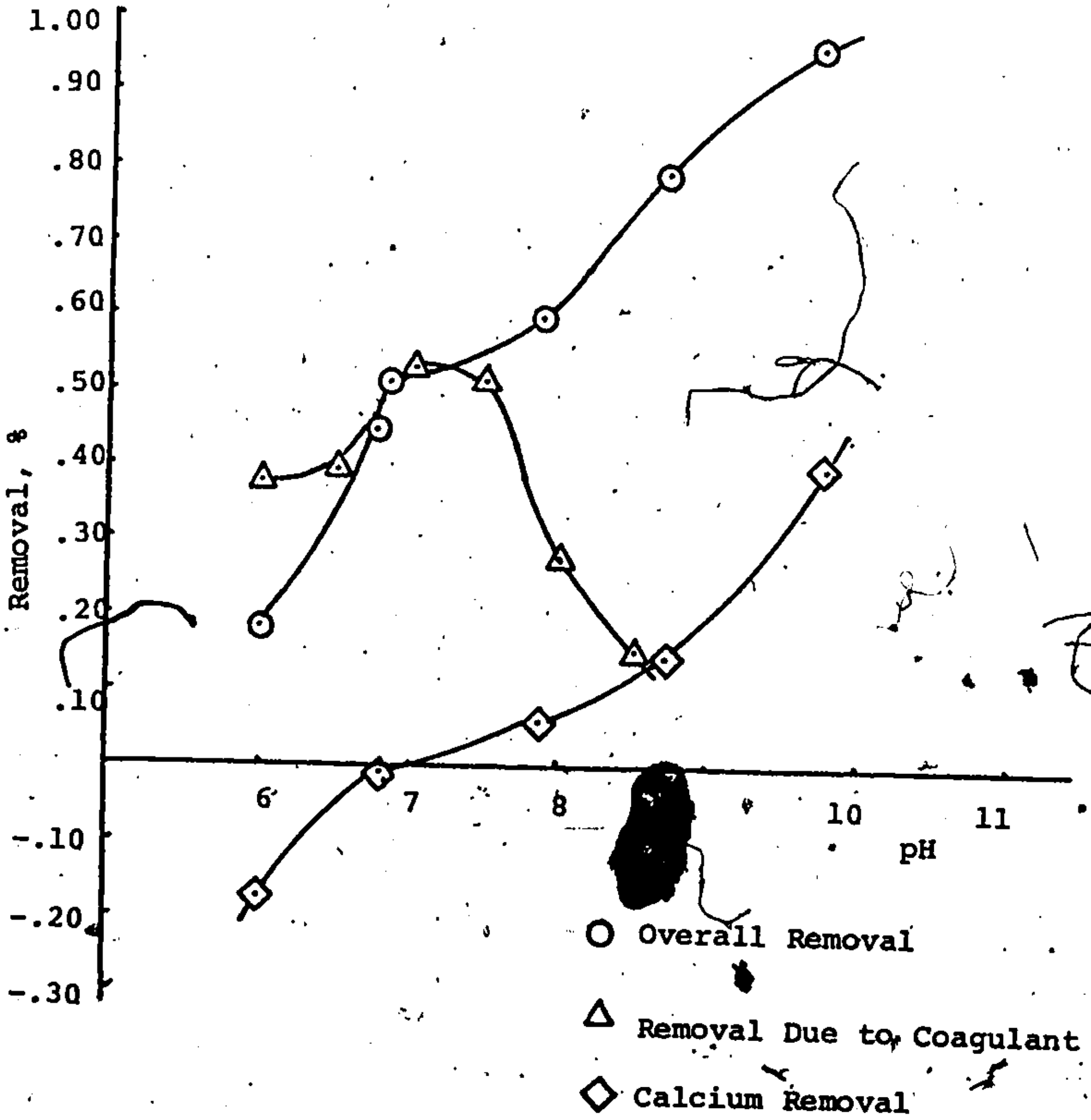

FIGURE A4.4 Phosphorus Removal for Al:P = 2.75
Coagulant: PBAC 2.2
Burlington Wastewater

APPENDIX 5

SUPERNATANT SUSPENDED SOLIDS REMOVAL

TABLE A5.1 Supernatant Suspended Solids Concentration. Burlington Wastewater, Al:P = 2.75

Blank	pH	5.95	6.8	7.65	8.2	9.15	10.0
	SS	7	9	7	8	7	12.5
$AlCl_3$	pH	5.8	6.55	7.0	8.05	8.9	9.95
	SS	1	2	2	9	21	6.5
Alum	pH	5.9	6.55	6.8	7.75	8.9	9.8
	SS	0	2	1	3.5	14	5
PBAC 1.0	pH	6.2	6.75	7.0	7.9	8.8	9.6
	SS	2	2	2	5	4.5	2
PBAC 1.8	pH	6.0	6.6	6.9	7.8	8.8	9.95
	SS	1	4	2	3.5	12.5	3.5
PBAC 2.2	pH	6.0	6.8	6.85	7.85	8.7	9.75
	SS	2	2.5	2.5	10.5	2	2.5

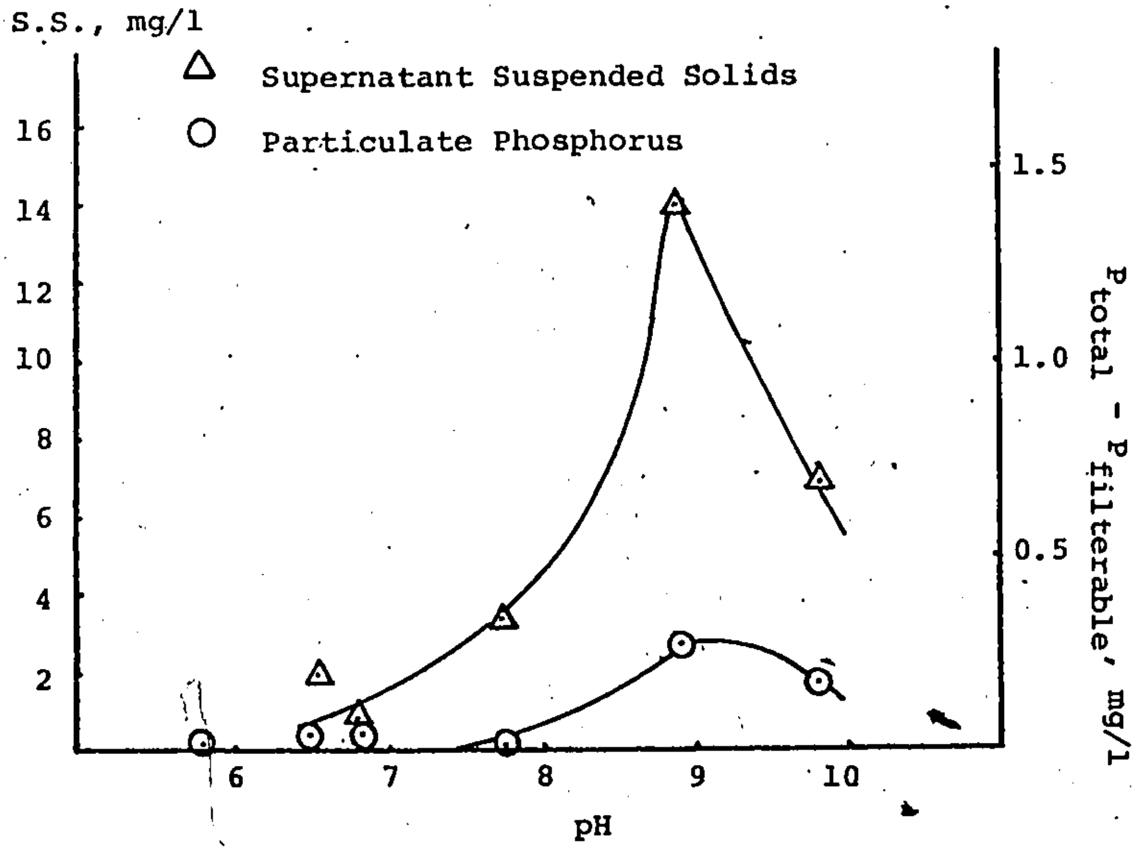

FIGURE A5.1 Supernatant Suspended Solids for Alum Burlington Wastewater

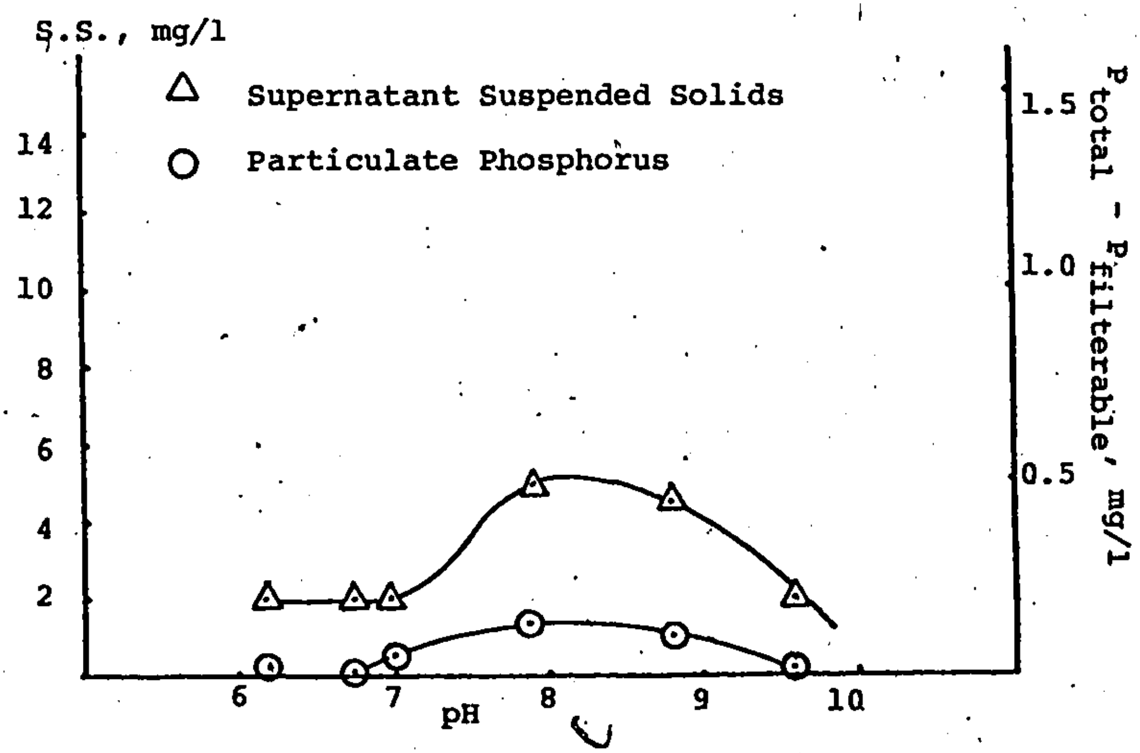

FIGURE A5.2 Supernatant Suspended Solids for PBAC 1.0 Burlington Wastewater

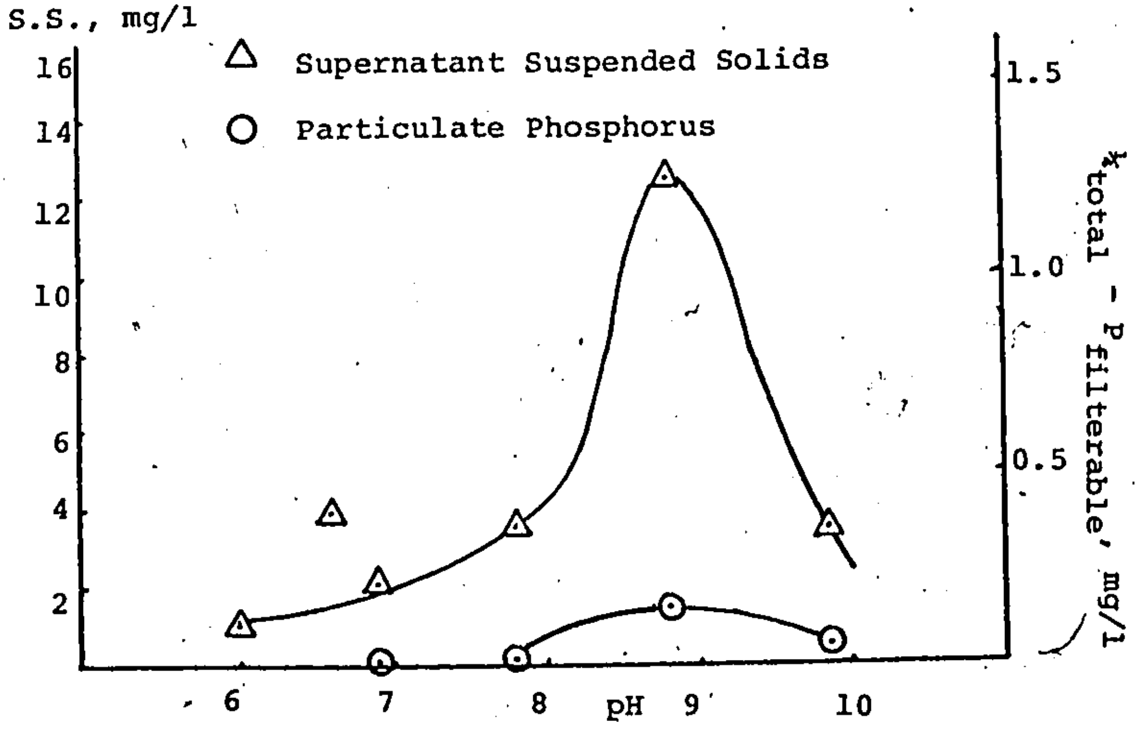

FIGURE A5.3 Supernatant Suspended Solids for PBAC 1.8 Burlington Wastewater

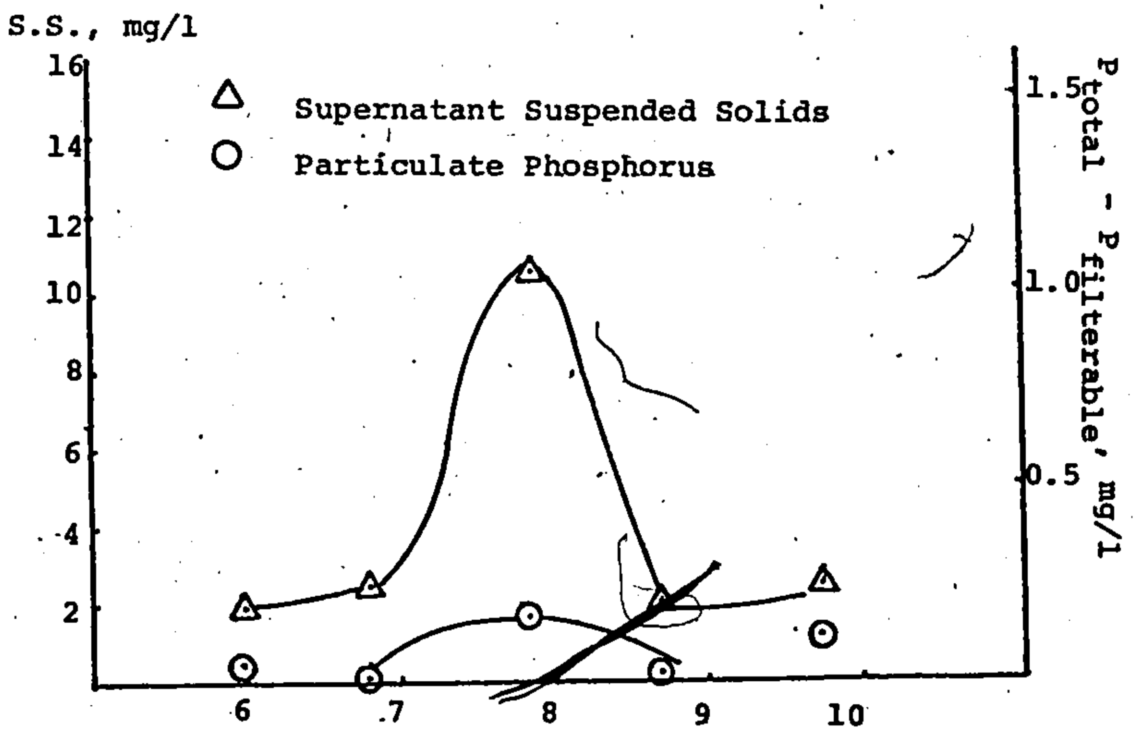

FIGURE A5.4 Supernatant Suspended Solids for PBAC 2.2 Burlington Wastewater

APPENDIX 6

SETTLING OF ACTIVATED SLUDGES FROM BURLINGTON WASTEWATER - RAW DATA

TABLE A6.1 Settling of Solids for Al:P = 1.0

Coagulant: None

Time	Height				
0	0	0	0	0	0
1	1	1	1	1.5	1
2	2.5	3	3.5	3.5	3.5
3	5	5.5	6	6.5	6
4	7	8.5	9	9	9
5	9.5	10.5	11.5	11	11
7	13	14	14.5	14.5	14
10	15	16	16.5	16.5	16.5
15	17.5	18	18.5	18.5	18.5
20	19	19.5	19.5	20	18.5
pH	5.1	5.95	6.9	7.8	7.95

TABLE A6.2 Settling of Solids for Al:P = 1.0
Coagulant: $AlCl_3$

Time	Height				
0	0.0	0.0	0.0	0.0	0.0
1	2.5	2.5	2.5	2.5	2.5
2	7.0	7.0	6.5	7.0	6.5
3	11.5	11	11	11.5	11
4	14	14	14	14.5	14
5	16	16	16	16	16
6	17	17	17	17	17
8	19	19	18.5	19	18.5
10	20	20	19.5	19	18.5
12	21	20.5	20.5	21	20.5
15	21.5	21.5	21.5	21.5	21.5
20	22.5	22.5	22.5	22.5	22.5
pH	5.6	6.05	6.95	7.05	7.8

TABLE A6.3 Settling of Solids for Al:P = 1.0
Coagulant: PBAC 1.0

Time	Height				
0	0	0	0	0	0
1	1.5	2.5	2.5	2	1.5
2	5	6.5	6.5	6	4.5
3	9.5	11	11	11	8
4	13	14	14	14	11
5	15	15.5	16	16	13.5
7	17	18	18	18	16.5
10	19	19.5	19.5	19.5	18
15	21	21.5	21.5	21.5	20
20	22	22.5	22.5	22.5	21.5
pH	5.25	6.0	6.9	7.2	7.9

TABLE A6.4 Settling of Solids for Al:P = 1.0
Coagulant: PBAC 1.8

Time	Height				
0	0	0	0	0	0
1	1.5	2	2	2	1.5
2	4.5	6	6	6	5
3	8	10	10.5	10	9
4	11	13	13	13	12
5	13.5	15	15	15	14
7	16	17.5	17.5	17	16.5
10	18	19	19	19	18.5
15	20	21	21	21	20
20	21	22	22	22	21.5
pH	5.2	6.0	6.9	7.4	7.9

TABLE A6.5 Settling of Solids for Al:P = 1.0
Coagulant: PBAC 2.2

Time	Height				
0	0	0	0	0	0
1	1	1.5	2	2	1.5
2	3.5	4	5	4.5	4
3	7	7	8	8	7
4	9	9.5	10.5	10.5	9.5
5	11.5	12	13	12.5	11.5
7	14.5	14.5	15	15	14
10	16.5	17	17.5	17	16.5
15	19	19	19.5	19.5	19.5
20	20.5	20.5	21	21	20.5
pH	5.0	5.95	6.9	7.45	8.0

TABLE A6.6 Settling of Solids for Al:P = 1.0
Coagulant: Alum

Time	Height				
0	0	0	0	0	0
1	1	2	1.5	2	1.5
2	3	4	4	4	3.5
3	5	7	6.5	7	6
4	8	9	9	9	8.5
5	10	11	11	11	10
7	15.5	16	16	16	15.5
15	17.5	18	18	18	17.5
20	19	19.5	19.5	19.5	19
pH	4.9	6.1	6.9	7.2	8.2

TABLE A6.7 Settling of Solids for Al:P = 2.75
Coagulant: Blank

Time	Height					
0	0	0	0	0	0	0
1	2	2	2	2	2	2
2	4.5	5	5	5.5	5	6
3	8	9	9	9	9	10
4	11	12	12	11	12	12.5
5	13	14	14.5	13	14	14
7	16	16	17	16	16	17
10	18	18.5	19	18	17.5	18.5
20	21	21.5	21.5	21	21.5	21.5
pH	5.95	6.8	7.65	8.2	9.15	10.0

TABLE A6.8 Settling of Solids for Al:P = 2.75
Coagulant: $AlCl_3$

Time	Height					
0	0	0	0	0	0	0
1	2	2	1	1	1	3
2	5	5	3.5	3	2.5	7
3	8	8	6	5.5	5	10.5
4	10	10	9	8	7	13
5	12	12	11	10	9	15
7	15	15	14	13	11.5	18
10	17	17	16.5	14	14	19
20	20.5	20	20	19	18	22
pH	5.8	6.55	7.0	8.05	8.9	9.95

TABLE A6.9 Settling of Solids for Al:P = 2.75
Coagulant: Alum

Time	Height					
0	0	0	0	0	0	0
1	2.5	2	2	1.5	1.5	3
2	5	5	4	4	3	6
3	8	8	7	6	4.5	9.5
4	10.5	10.5	9.5	9	7	12
5	12	12	11	11	8	14
7	15	15	14	14	11	16.5
10	17	17	16.5	16	14	18.5
20	20.5	20.5	20	19.5	8	21.5
pH	5.8	6.55	6.8	7.55	8.9	9.8

TABLE A6.10 Settling of Solids for Al:P = 2.75
Coagulant: PBAC 1.0

Time	Height					
0	0	0	0	0	0	0
1	1	1	1	0.5	0.5	1.5
2	3	4	3	2.5	2	5
3	6	7	6	4.5	3.5	8
4	9	10	8	7	6	11
5	11.5	12	10.5	10	8	13
7	14.5	15	13.5	12.5	11	16
10	17	17	16	15	14	18
20	20	20.5	20	19	18	22
pH	6.2	6.75	7.0	7.9	8.8	9.6

TABLE A6.11 Settling of Solids for Al:P = 2.75
Coagulant: PBAC 1.8

Time	Height					
0	0	0	0	0	0	0
1	2	2	2	1.5	1	3
2	6	5	5	4	3	6.5
3	9.5	8.5	8	7	5.5	10
4	12	10	10	10	8	12.5
5	14	13.5	13	12	10	14.5
7	17	16	16	15	13	17
10	18.5	18	17.5	16	15.5	19
20	22	21	21	20.5	19	22
pH	6.0	6.6	6.9	7.8	8.8	9.85

TABLE A6.12 Settling of Solids for Al:P = 2.75
Coagulant: PBAC 2.2

Time	Height					
0	0	0	0	0	0	0
1	1	1	1	0.5	1	1.5
2	3.5	3	3	2.5	2.5	4
3	6.5	5.5	5	4.5	4.5	7
4	9	8.5	8	7	7	9.5
5	11	10.5	10	9	9	11
7	14	14	13	12.5	12.5	14
10	16.5	16.5	16	15	15	16.5
20	20	20	20	20	19.5	20.5
pH	6.0	6.8	6.85	7.85	8.7	9.75

APPENDIX 7

SLUDGE FILTRABILITY STUDY

A7.1 Calculation of the Specific Resistance

The specific resistance is given by:

$$r = \frac{2PA^2b}{\mu w}$$

where:

r = Average specific cake resistance, sec^2/g

P = Pressure drop through filter medium and sludge cake, in cm of water

: $20 \text{ in Hg} \times 2.54 \frac{cm}{in} \times 13.6$

$= 690.88 \text{ cm } H_2O$

A = Area of filtering surface, cm^2

: $\pi(7)^2 = 153.94 \text{ cm}^2$

b = Slope of t/V vs. V plot in sec/ml^2

: The values found multiplied by 60.

μ = Viscosity of filtrate in poise

: Assumed 0.01 p

w = Weight of dry cake solids per unit volume of filtrate.

: Amount of solids on the filter = 0.7 g

Assumed: Density of solids = Density of filtrate

= 1.0 g/ml

$$w = \frac{0.7}{99.3} = 0.00705 \ \text{g/ml}$$

Therefore: $$r = \frac{2 \times 690.88 \times 153.94 \times 60b}{0.01 \times 0.00705}$$

or $$r = 1.81043 \times 10\text{"}b \ \text{sec}^2/\text{g.}$$

A7.2 Results of the Buchner Funnel Test

TABLE A7.1 Volume of Water Filtered as a Function of Time. Coagulant: None

Time	Volume, ml					
0	2.5	0	0	0	0	0
0.5	28	22	22	22	20	17
1	38	31	30	29.5	27	21
1.5	45	37	35.5	35	32	23
2	50	41	39.5	39	36	25
2.5	55.5	45	44	43	40	27
3	60	49	47	45.5	42	29
3.5	64	52	50	48.5	45	30.5
4	68	55	52.5	51	48	32
4.5	60	57.5	55	53.5	51	33
5	73	60	57	56	52.5	34.5
6	76	64.5	61	60	56	36.5
7	84	69	65	64	60	39
8	89	73	69	67	63	41
9	93	76.5	72	70	66	42.5
10	95	80	75	73	68.5	44
12	98	86	80	74	74.5	48.5
15	99	91.5	87	84	81	52
pH	3.9	5.75	6.6	7.5	8.4	9.9

TABLE A7.2 Volume of Water Filtered as a Function of Time. Coagulant: Alum

Time	Volume, ml					
0	0	0	0	0	0	0
0.5	27	26	24	23	19.5	14
1	36.5	34	32.5	31	27	18
1.5	42.5	40.5	39	37	32	21
2	47.5	46	43	41.5	37	24
2.5	52	50.5	48	46	41	26
3	56	54.5	52	50	44	28
3.5	60	59	55.5	53	47	30
4	63	62	59	56.5	50	31.5
4.5	66	65.5	62	59	53	33.5
5	69	69	65	62	55	35
6	74	74.5	70	67	59.5	38
7	79	79	74.5	71.5	64	40
8	83	83	78.5	76	67.5	42.5
9	87	87	82.5	79.5	71	45
10	90.5	89	86.5	83	74	47
12	94	92.5	92	88	80	51
15	96.5	95	94	92	87	57
pH	3.85	5.6	6.3	6.9	8.6	9.95

TABLE A7.3 Volume of Water Filtered as a Function Time
Coagulant: $AlCl_3$

Time	Volume, ml					
0	0	0	0	0	0	0
0.5	32	22	22	24	24	19
1	42	28	29	32	31.5	24
1.5	50	33	34.5	37.5	37	28
2	56	37	38.5	41.5	41	31
2.5	61	40	42	45	45	34
3	66	42.5	45	48.5	48.5	36
3.5	70	45	48	51.5	51.5	38
4	74	47.5	50.5	54	54	40
4.5	77.5	49.5	53	56.5	56.5	42.5
5	81	51.5	55	59	59	44
6	87	55.5	59.5	63	63	47.5
7	92	59	63	67.5	67.5	50.5
8	94	62	66.5	71	71	53.5
9	95.5	65	69.5	74.5	74.5	56
10	97	68	72.5	78	78	58.5
12	98	73	78	83.5	84	63
15	98.5	79	85	89	91.5	68
pH	3.75	5.1	6.4	7.35	8.6	10.1

TABLE A7.4 Volume of Water Filtered as a Function of Time

Coagulant: PBAC 1.0

Time	Volume, ml					
0	0	0	0	0	0	0
0.5	22	23	29	25	27	21
1	30	30	36	33	34.5	29
1.5	35	36	41.5	39	40	34
2	40	40.5	46	44	44	38.5
2.5	43.5	44	49.5	48	48	42
3	47	47	53	52	51.5	45.5
3.5	50	50	56.5	56	54	48.5
4	53	53	59	58.5	57	52
4.5	55.5	55.5	61.5	61.5	60	54.5
5	58	58	64	64	62.5	57
6	62.5	62.5	69	69	67.5	62
7	66.5	66	72.5	73.5	71.5	66
8	70	70	76.5	78	76	70
9	73.5	73.5	80	82	80	73.5
10	77	76.5	83.5	85	83	77
12	82.5	82	89	91	88.5	83
15	89.5	89	93	97	93	89
pH	4.55	5.75	6.7	7.9	8.7	9.9

TABLE A7.5 Volume of Water Filtered as a Function of Time

Coagulant: PBAC 1.8

Time	Volume, ml					
0	0	0	0	0	0	0
0.5	28	22	22	22	21	20
1	37	27.5	29	29	28	26.5
1.5	43	32.5	34	34	34	30.5
2	47.5	36.5	38	38.5	38	34
2.5	52.5	39	41.5	42	42	37
3	56	42	45	45	45	40
3.5	59.5	44.5	47.5	48	48.5	42.5
4	62.5	47	50	50.5	51.5	45
4.5	65.5	49.5	52	53	54	47
5	68	51.5	54	55	56.5	49
6	73.5	55	58.5	60	61	53
7	78	59	63	63.5	65	57
8	82	62	65.5	67	68.5	60
9	86	65	68.5	70	72	62.5
10	89.5	68	71.5	73	75	65.5
12	93.5	72.5	77	79	81	70.5
15	96.5	79	84	86	88	77.5
pH	3.8	5.45	6.45	7.35	8.6	10.0

TABLE A7.6 Volume of Water Filtered as a Function of Time

Coagulant: PBAC 2.5

Time	Volume, ml					
0	0	0	0	0	0	0
0.5	32	20	19	23	22	23
1	42	27	25	28.5	29	30
1.5	49	31.5	29	33	33.5	35.5
2	55	35	33	37	38	40
2.5	60	38	36	40.5	41	43.5
3	64.5	41	38.5	43	44	47
3.5	68.5	43.5	41	46	47	50
4	72	45.5	43.5	48.5	50	53
4.5	75.5	48	45.5	51	52	56
5	79	50	47.5	53	54,5	58.5
6	85	53.5	51	57	59	63
7	90	57	54.5	60.5	62.5	67.5
8	93	60	57	64	66	71.5
9	95	6.25	60	67	69	75
10	96	65	63	70	72	79
12	97.5	70	68	75.5	78	85
15	98	76	74	82.5	85	91
pH	3.80	5.55	6.45	7.6	8.65	10.0

TABLE A7.7 Estimated Values of the Slope b and Specific Resistance for the Various Cases

Coagulant							
None	Slope x 10^3	1.125	1.84	2.36	2.42	2.66	6.925
	Specific Resistance x 10^8	2.037	3.33	4.27	4.38	4.82	12.54
	pH	3.9	5.75	6.6	7.5	8.4	9.9
$AlCl_3$	Slope x 10^3	1.012	2.98	2.35	2.18	2.116	3.8
	Specific Resistance x 10^8	1.83	5.40	4.25	3.95	3.83	6.88
	pH	3.75	5.1	6.4	7.35	8.6	10.1
PBAC 1.0	Slope x 10^3	2.06	2.06	1.925	1.71	1.90	1.94
	Specific Resistance x 10^8	3.73	3.73	3.49	3.10	3.44	3.51
	pH	4.55	5.75	6.7	7.9	8.7	9.9
PBAC 1.8	Slope x 10^3	1.137	2.857	2.667	2.30	2.133	2.917
	Specific Resistance x 10^8	2.06	5.17	4.83	4.16	3.86	5.28
	pH	3.8	5.45	6.45	7.35	8.6	10.0
PBAC 2.5	Slope x 10^3	1.113	3.10	3.30	2.70	2.417	1.963
	Specific Resistance x 10^8	2.01	5.61	5.97	4.89	4.38	3.55
	pH	3.80	5.55	6.45	7.6	8.65	10.0
Alum	Slope x 10^3	1.38	1.35	1.525	1.725	2.075	5.15
	Specific Resistance x 10^8	2.50	2.44	2.76	3.12	3.76	9.32
	pH	3.85	5.6	6.3	6.7	8.6	9.95

APPENDIX 8

RESULTS FROM THE STUDY ON ORGANICS REMOVAL

TABLE A8.1 Effect of Different Al^{3+} Dosages on Organics Removal.

Initial TOC = 45.5 mg/l

Coagulant	Remaining TOC					
$AlCl_3$	42.0	41.2	39.5	38.5	38.0	37.7
PBAC 1.0	39.2	38.5	38.5	38.5	38.7	37.7
PBAC 1.8	41.5	40.5	40.7	40.0	40.7	39.5
PBAC 2.5	41.0	41.0	41.2	41.2	41.0	41.2
Alum	41.5	41.0	39.5	33.7	32.5	33.7
Al^{2+} dose, (mg/l)	10	20	30	40	50	60

TABLE A8.2 Effect of pH on Organics Removal

Initial TOC = 45.5 mg/l

Al^{3+} dosage = 13 mg/l

Coagulant	Remaining TOC					
$AlCl_3$	41.5	42.5	42.0	43.0	43.0	42.0
pH	3.9	4.75	6.0	7.1	8.0	9.0
PBAC 1.0	38.0	39.7	40.0	41.5	41.2	40.0
pH	4.15	4.9	6.1	7.0	7.95	8.85
PBAC 1.8	38.5	39.0	39.7	39.5	39.5	40.2
pH	3.95	4.95	6.05	7.3	8.1	9.0
PBAC 2.5	40.0	38.0	39.7	39.5	39.5	40.5
pH	4.1	5.0	5.85	7.15	8.0	9.2
Alum	39.5	41.5	40.5	41.0	41.7	44.5
pH	3.9	4.8	6.1	7.3	8.15	9.2