Simultaneous Precipitation of Orthophosphate in Activated Sludge Systems with A1(III)

By

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Simultaneous Precipitation of Orthophosphate in Activated Sludge Systems with Al(III)

Dianne D. Gates

Abstract

This dissertation examines the simultaneous precipitation of soluble orthophosphate (SOP) when alum is dosed to an activated sludge aeration basin. The results of batch and continuous flow experimental studies were used to develop a model of this process.

This research identified three regions of chemical phosphorus removal, in each of which a different SOP removal mechanism appeared to apply:

Region 1 extends to SOP residual concentrations as low as 1.0 mg P/l. In this region the stoichiometric precipitation of $Al_{0.91}H_2PO_4(OH)_{1.73(s)}$ is the predominate phosphate removal mechanism.

Region 2 includes SOP residual concentrations in the range 0.1 -1.0 mg P/l. Phosphate removal in this region is described on the basis of the adsorption of SOP on to aluminum hydroxide solid surfaces.

Region 3 includes SOP residual concentrations as low as 0.02 mg P/l. The minimum SOP phosphate concentration that can be reached in this region is controlled by the presence of both aluminum-hydroxy-phosphate and aluminum hydroxide solids.

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Ph.D Candidate

Prof. Slawomir Hermanowicz
Co-Chair of Committee

Prof. David Jenkins
Co-Chair of Committee

Dedication

This dissertation is dedicated to my Ancestors,
(particularly my Grandmothers Icsia Gates and Vivian Petit)
all of whom had the ability, but not the opportunity
and to my children, Adrian Jerome and Ashley Nicole,
who have both.

Acknowledgement

I would like to begin by thanking my parents, Norman and Faye Gates for their immeasurable support during my graduate studies and for instilling in me an appreciation of education at a very early age. I would like to thank my sister, Donna and my brothers Norman Jr., Kevin and Derek for their encouragement and support.

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Special thanks to my Grandmother, Mrs. Icsia Gates and Miss Mary Ann Rezabek for playing such an important role in my life without even knowing it.

To Adrian and Ashley, I am glad you two are who you are and I am glad that you are mine. We made a <u>lot</u> of sacrifices to get where we are today. I appreciate your cooperation. And finally, to Tikisa Anderson thank you so much for being who you are and for giving me the guidance, encouragement, and support that I needed to get all this done. Thanks for not letting me quit the 10,000 times I was tempted to.

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1. INTRODUCTION

1.1 Problems Associated with Phosphates in Sewage

1.1.1 Eutrophication

Eutrophication is defined by the Organisation for Economic Co-operation and Development (OECD, 1970) as "the response in water to overenrichment by nutrients, particularly phosphorus and nitrogen." A typical response is an increase in the fertility of the water which can result in excessive algal blooms, heavy growth of certain rooted aquatic plants, algal mats, and deoxygenation. Drinking water sources can be impacted by unpleasant taste and odors from certain algal metabolic by-products and algal mass from blooms can clog municipal water treatment filters. Waters used for recreational purposes can be degraded by the build-up of unsightly slimes on shores that can contribute to vector problems. The eventual decay of algal mass can lead to dissolved oxygen depletion in the impacted water (OECD, 1970). This deoxygenation is extremely damaging and can lead to the elimination of fish species and seriously damage the existing ecological balance.

Cultural or "man made" eutrophication, is generally limited to fresh waters such as lakes and reservoirs, but has been experienced in estuaries and near shore ocean waters. The discharge of phosphorus (P)-containing wastewaters contributes significantly to eutrophication. Many methods of combating and controlling eutrophication focus on the reduction of P discharge (OECD, 1970).

1.1.2 Reclamation

The combination of population growth and increased industrialization have significantly increased water consumption with further increases expected to seriously impact the availability of usable water for domestic, agricultural and industrial purposes in the Western United States, England, and Western Europe (Olson and Pratte, 1978). Currently water treatment alternatives are being developed which would avoid or lessen the impact of water shortages. The primary focus of many of these efforts is wastewater reclamation, because the use of reclaimed wastewater would reduce the consumption of fresh water supplies. The principal objective of reclamation is to treat a wastewater to an extent that allows its safe and economical reuse (Englande, *et al.*, 1978). The primary end uses for reclaimed water are: supplementation of irrigation waters for agriculture, irrigation of recreational areas, ground water recharge and supplementation of industrial cooling and process waters (Olson and Pratte, 1978).

Most applications of reclaimed water, with the possible exception of agricultural irrigation, require the removal of some soluble phosphate. The extent of phosphate removal required depends on many things including the wastewater phosphate content and the discharge location or reuse application (Flook, 1978). Phosphorus removal is required for land applications of reclaimed wastewater to avoid the introduction of phosphates into surface waters through run-off and under ground leachates. Industrial uses of reclaimed water require the removal of phosphates to prevent the formation of scales which can deposit in equipment and piping.

1.2 Sources and Forms of Phosphorus in Sewage

A typical municipal wastewater contains between 3 to 7 mg/L of total phosphorus (P). The primary sources of P in sewage are fecal material, synthetic detergents and household cleaning products, fertilizers, and industrial discharges (Jenkins and Hermanowicz, 1989).

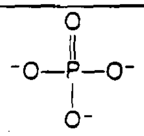
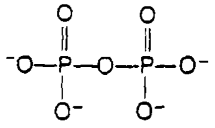
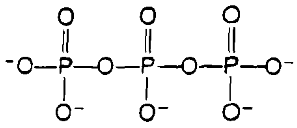
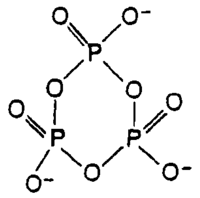
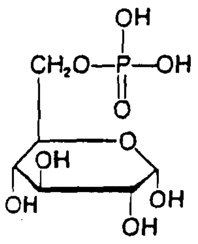
Phosphorus species can be grouped according to their chemical form ie: orthophosphate, condensed phosphate, and organic phosphate. Orthophosphates are salts of orthophosphoric acid (H_3PO_4) and condensed phosphates are two or more molecules of orthophosphate combined with the elimination of water (condensation) in chain or ring structure that contains phosphorus-oxygen-phosphorus bonds. Condensed phosphates can be hydrolysed to orthophosphates under appropriate conditions. Typical condensed phosphates found in municipal wastewater are tri-polyphosphates and pyrophosphates, which are detergent additives. Organic phosphates include any organically bound phosphorus species such as sugar phosphates and phospholipids (Jenkins and Hermanowicz, 1989). Phosphorus forms found in domestic wastewater and typical concentrations are summarized in Figure 1.1.

1.3 Current Regulations of Phosphorus Discharge

To minimize the impact of P discharge many regulatory bodies have imposed various P discharge limits. These limits vary considerably with location ranging from 0.01 mg P/l to 2.0 mg P/l (see Table 1.1) (Jenkins and Hermanowicz, 1989; EPA, 1987b).

Wastewater reclamation phosphate discharge limits are not as clearly defined as wastewater discharge limits and vary considerably depending on the particular reuse application (Englande, 1978).

Figure 1.1

Group	Structural Representation (Typical)	Species of Importance	Typical Conc. mg/l
Orthophosphate		H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, HPO_4^{2-} complexes	3-4
Polyphosphates	 pyrophosphate	$H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$, $HP_2O_7^{3-}$ complexes	
	 tripolyphosphate	$H_3P_3O_{10}^{2-}$, $H_2P_3O_{10}^{3-}$, $HP_3O_{10}^{4-}$, $P_3O_{10}^{5-}$, $HP_3O_{10}^{4-}$ complexes	2-3
Metaphosphates	 trimetaphosphate	$HP_3O_9^{2-}$, $P_3O_9^{3-}$	
Organic phosphates	 glucose 6-phosphate	Very many types, including phospholipids, sugar phosphates, nucleotides, phosphoamides, etc.	1

1.1 Phosphorus Forms in Raw Domestic Sewage and Typical Concentration Ranges

(adapted from Snoeyink and Jenkins, 1980)

Table 1.1
Phosphorus Effluent Discharge Standards

Location	mg P/l
USA	
Great Lakes	1.0
Florida	1.0
Chesapeake Bay Basin	
PA (lower Susquehanna)	2.0
MD	0.2, 1.0, 2.0
VA	0.2, 0.4, 0.5, 1.0
Washington DC	0.23
Reno Sparks, NV	0.5
Lake Tahoe, CA	1.0
Switzerland	1.0
Sweden	<1.0

1.4 Methods of Phosphorus Removal

A municipal wastewater treatment facility with primary sedimentation, conventional biological secondary treatment and anaerobic digestion of waste sludges can be expected to remove only 10 to 30 percent of the typical 3-7 mg P/l in the influent wastewater because P removal only takes place when solids containing P are wasted from the treatment facility (Jenkins and Hermanowicz, 1989). In conventional biological treatment facilities the P content of the waste sludge is approximately 2 percent (Jenkins and Hermanowicz, 1989; EPA, 1987b). Sludge wasting usually accounts for a phosphorus removal of approximately 2 mg/L (Jenkins and Hermanowicz, 1989). For a typical municipal wastewater with an influent P concentration of 6.0 mg/L, this would result in an effluent containing 4 mg P/l. Referring to Table 1.1 it is apparent that this concentration is in excess of all established P discharge limits. When such limits must be met, one of two types of P removal processes are employed to improve P removal. These are either physical-chemical methods or enhanced biological methods. The primary objective of both types of P removal processes is to convert soluble P into an insoluble form, either biomass in enhanced biological removal or a chemical precipitate in chemical/physical removal, so that improved

P removal can be achieved when solids are removed.

1.5 Research Objectives

The general objective of this research was to develop a method for predicting the performance of chemical P removal processes that employ the addition of aluminum salts to activated sludge aeration basins to form sparingly soluble aluminum phosphates. This process is known as simultaneous precipitation. The specific objectives were to develop a predictive model of simultaneous precipitation using controlled pH batch aluminum phosphate experiments and to verify the model with continuous flow activated sludge experiments.

2. CHEMICAL PHOSPHORUS REMOVAL

2.1 Overview of Chemical Phosphorus Removal

The specific objective of chemical P removal is to insolubilize influent P and physically remove the P-containing solids from the treated wastewater. This is typically achieved by dosing a metal salt to the wastewater and removing the P-containing solids by gravity. The P-containing solids formed during chemical P removal can be incorporated into primary or secondary sludge depending on the point of chemical addition within the process or generated separately if the metal cation is added after secondary clarification. P-containing solids are treated and disposed of together with other wastewater sludges (EPA, 1987a; Jenkins and Hermanowicz, 1989; Daigger, 1989). The addition of aluminum salts has been shown to have no adverse effect on the effectiveness of activated sludge processes (Lin and Carlson 1978). Chemical P removal is often selected over biological phosphorus removal because of its ease of implementation, its reliability and its ease of operation (EPA, 1987a).

Precipitation of P from wastewater with iron and aluminum salts was first employed approximately 30 years ago (Jenkins *et al.*, 1971). Early use of aluminum and iron salts for P removal had only one objective, that being the precipitation and removal of P. Later studies (Tenney and Stumm, 1965) investigated the use of aluminum and iron salts also as bioflocculation aids in addition to P precipitation.

Chemical P removal processes vary in the type of cation used for precipitation and the location of the chemical dosing point. The most commonly used chemicals for chemical P removal are aluminum, iron and calcium salts. The choice of dosing chemical is usually based on wastewater composition, desired P residual and costs.

2.1.1 Forms of Aluminum Used for Precipitation

The most common aluminum salt used for P precipitation from wastewater is aluminum sulfate ($Al_2SO_4.18H_2O$), commonly known as alum or filter alum. Alum can be purchased in either dry or liquid form. Dry alum is typically made into a liquid solution before dosing to wastewater. The choice between dry or liquid alum is based on cost. Liquid alum is much more expensive than dry alum because its increased weight results in higher transportation costs. The use of liquid alum becomes economically feasible only when its source is within approximately 160 km of the wastewater treatment facility (EPA, 1987a). Sodium aluminate ($Na_2Al_2O_3$) is sometimes used for P removal but is usually limited to low alkalinity wastewaters since it acts as a base and tends to increase pH and alkalinity. Sodium aluminate is available in either liquid or dry form (EPA, 1987a; Daigger, 1989). Comparative studies of alum and sodium aluminate indicated that alum is a more efficient P precipitant than sodium aluminate (Eberhardt and Nesbitt, 1968; Balmer, *et al.*, 1975)

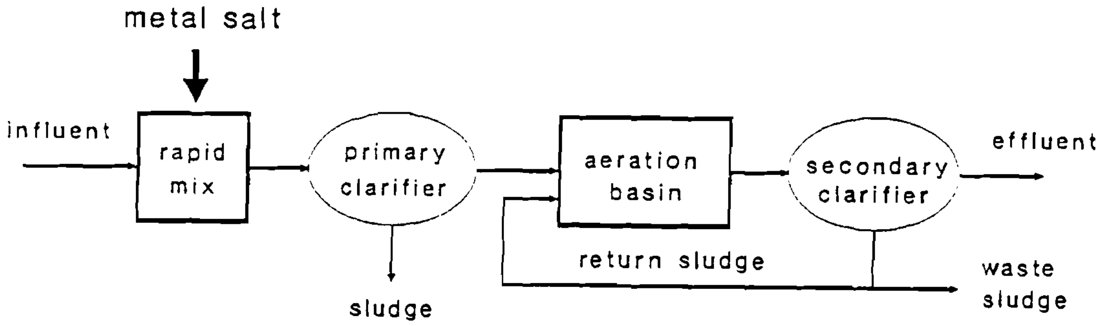
2.1.2 Selection of Dosing Point

Several points of metal cation addition have been investigated for chemical P removal. The most common points are shown in Figure 2.1.

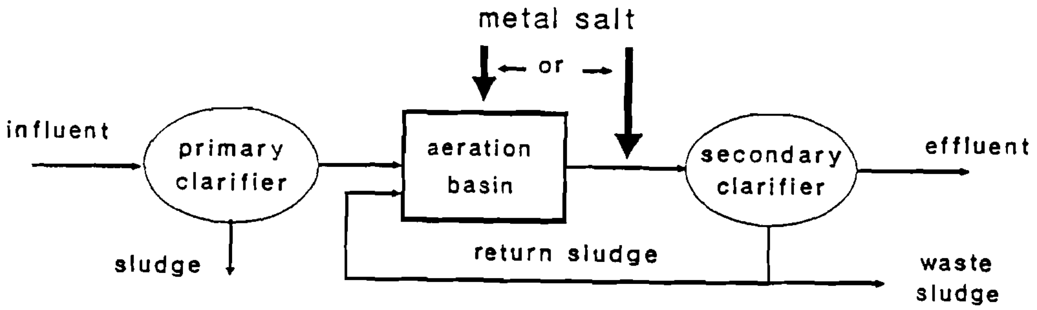
2.1.2.1 Pre-precipitation

Dosing prior to, or directly into the primary clarifier, (Figure 2.1a) is referred to as pre-precipitation. In pre-precipitation chemical precipitates are removed together with the primary sludge solids. Pre-precipitation cannot completely remove influent P because the bacterially mediated hydrolysis of condensed phosphate to orthophosphate, (which are more readily precipitated) is not always complete until after secondary treatment (Sawyer, 1962; Recht and Ghassemi, 1970). Pre-precipitation can reliably achieve total effluent P concentrations as low as 1 mg P/l. One of the principal advantages of pre-precipitation is the reduction of BOD and suspended solids

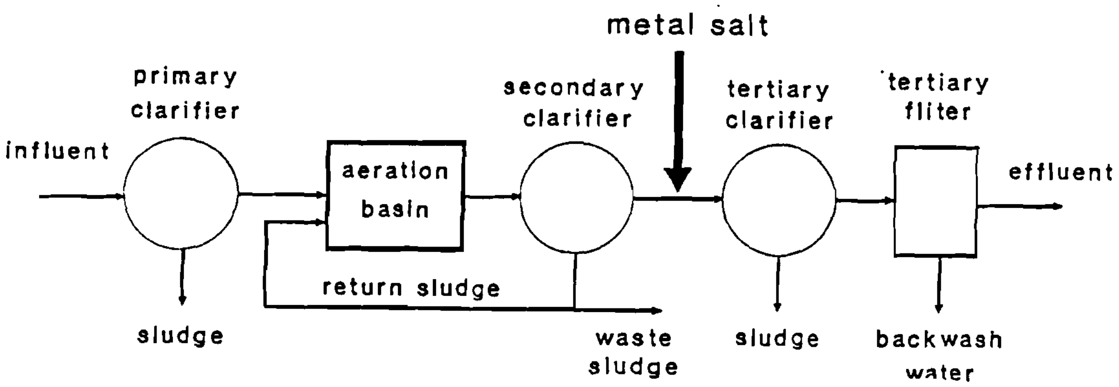
Figure 2.1
Dose Points for Chemical P-Removal



a. pre-precipitation



b. simultaneous precipitation



c. post-precipitation

loading to secondary treatment processes resulting from the enhanced suspended solids removal. Melkersson (1973) reported that 60-70 percent of influent organic matter can be removed with pre-precipitation. EPA (1987a) noted that metal addition increased BOD removal from 25-40% to 40-65% and increased suspended solids (SS) removal from 40-70% to 60-75%. Pre-precipitation also can protect biological processes from toxic materials such as heavy metals and dispersed oils which are removed with the chemical solids (Melkersson, 1973). Pre-precipitation typically requires a higher chemical dose than simultaneous precipitation because raw sewage has a more variable composition and higher strength than primary effluent.(EPA 1987a; Melkersson, 1973)

Pre-precipitation increases the volume and mass of primary solids produced. The increased sludge mass includes an inorganic fraction comprised of aluminum hydroxy phosphate and aluminum phosphate solids and an organic fraction contributed by the capture of suspended solids in the chemical flocs (EPA, 1987a; Bowker and Stensel, 1990). A survey of 22 wastewater treatment facilities showed that when pre-precipitation with alum was used to achieve total P residuals of 1 mg P/l the sludge mass increased by an average of 40% (EPA, 1987b). An EPA survey of 25 wastewater treatment facilities using pre-precipitation found that total plant sludge volume increased by approximately 60% from 3000 m^3 sludge/m^3 plant influent without alum addition to 4,750 m^3 sludge/m^3 plant influent with pre-precipitation and total sludge mass increased by 17% from 0.29 kg sludge/m^3 plant influent to 0.34 kg sludge/m^3 plant influent with pre-precipitation (EPA, 1987a; Bowker and Stensel, 1990). No clear trend in the character and treatability of the P-containing sludges is reported in the literature.

2.1.2.2 Simultaneous Precipitation

The addition of alum directly to secondary biological treatment units is commonly referred to as simultaneous precipitation (Figure 2.1b). With this dosing regime chemical precipitation occurs simultaneously with the biological degradation of wastewater organic matter, resulting in the formation of a mixed chemical/biological sludge. For many wastewater treatment facilities a minimum of retrofitting is needed to use simultaneous precipitation (EPA, 1987b).

Simultaneous precipitation increases the inert solids content of the mixed liquor suspended solids and increases overall solids production. The EPA (1987b) reports that simultaneous precipitation increases the sludge P content from approximately 1.5% on a dry solids basis without P removal to 4.5% with chemical P removal. The increase in inert solids requires that a higher level of total suspended solids (TSS) must be maintained in the aeration basin of activated sludge systems when simultaneous precipitation is used. SS removal is crucial for efficient P-removal when using simultaneous precipitation, because of the high P content of the SS in the effluent (EPA, 1987b). Melkersson (1973) studied the performance of 195 full scale treatment facilities employing P removal in Sweden, Finland, and Switzerland and found that the plants using simultaneous precipitation discharged an effluent with SS ranging from 20 to 40 mg/l and total P concentrations of 0.8 to 2.0 mg P/l. The effluent quality with simultaneous precipitation was inferior to that achieved by plants practicing pre-precipitation, which had effluent SS in the range 10-30 mg/l and effluent total P in the range 0.3-0.7 mg P/l. The EPA reported total P removal efficiencies with simultaneous precipitation similar to those reported for pre-precipitation with effluent total P concentrations of 1 mg P/l being reliably achieved (EPA, 1987a).

Simultaneous precipitation can have a positive effect on organic matter removal by biological treatment, due to improved bioflocculation (O'Melia, 1978). Roberts (1978) suggested that aluminum hydrolysis products, particularly aluminum hydroxide, can adsorb on to negatively charged colloidal organic particles in activated sludge and enhance their removal by neutralizing colloidal charge and promoting coagulation (floc formation).

Several studies have found that effluent turbidity increased when alum was dosed to the aeration basin of activated sludge systems under certain conditions (Minton and Carlson, 1972; Barth and Ettinger 1967; Eberhart and Nesbitt, 1968). The increased turbidity was attributed to the formation of difficult-to-settle colloidal aluminum-containing particles similar to those observed in laboratory distilled water studies (Recht and Ghassemi, 1970). Minton and Carlson suggested that the effluent turbidity level was determined by the relationship between type of chemical solid present (aluminum phosphate and/or aluminum hydroxide) and biological solids, and the detention time and degree of turbulence in the aeration basin. They suggested that the chemical precipitates, being positively charged, enhanced SS removal by neutralizing negatively charged biological solids. If the proportion of neutral aluminum hydroxide in the precipitate is too large, insufficient bioflocculation occurs. The effect of turbulence, which can destroy the chemical/biological flocs can be avoided by selecting a simultaneous precipitation dosing point where a minimum of high turbulence occurs (ie: inlet zone) and by minimizing the hydraulic detention time of the chemical solids formed in the activated sludge system (Minton and Carlson, 1972). Minton and Carlson minimized chemical solids detention time by dosing alum to the mixed liquor channel of activated sludge systems (Figure 2.1b).

The impact of simultaneous precipitation on the viability of activated sludge culture has been studied by several investigators (Minton and Carlson, 1972; Unz and Davis, 1975; Eberhart and Nesbitt, 1968; Barth and Ettinger 1967). Unz and Davis ran parallel full-scale studies comparing activated sludge samples from alum supplemented (AS) and alum unsupplemented (AUS) biological treatment systems. Over a period of 15 months, the microbial activity of grab samples from both treatment systems were monitored by counting viable microorganisms, protozoa, total and fecal coliforms, and streptococci. Unz and Davis found a greater density of viable bacteria in the alum supplemented samples and attributed this to an increase in microbial coalescence in the presence of aluminum hydrolysis products. Unz and Davis further postulated that the alum precipitates (aluminum hydroxide or aluminum phosphate not specified) concentrated wastewater organic matter, increasing the nutrient level in chemical/biological sludges which enhanced microbial growth. They concluded that alum addition to activated sludge systems had no adverse effect on the microbial population and possibly enhanced organic matter removal. Minton and Carlson (1972) observed that some loss of protozoa may have occurred as a results of alum addition, but that this did not appear to have any impact on process efficiency. They noted that caution must be exercised when dosing alum simultaneously to ensure that the alkalinity (and therefore pH) were not lowered to levels which would cause the destruction of the microbial culture. Eberhart and Nesbitt (1968) and Barth and Ettinger (1967) both conducted studies using continuous flow pilot system with alum dosed to the aeration basin and noted no change in biological activity, as measured by BOD removal, as a result of alum addition.

Simultaneous precipitation increased TSS volumes by 12%, from 5,110 m^3/m^3 plant influent without P removal to 5,710 m^3/m^3 plant influent with simultaneous precipitation. On a mass basis TSS increased by 24% from 0.17 kg sludge/m^3 plant influent to 0.21 kg sludge/m^3 plant influent in 22 plants practicing simultaneous precipitation (EPA, 1987a). Other studies (Soap and Detergent Association, 1989; Baillod *et al.*, 1977; and Mininni *et al.*, 1985) report similar increases in sludge production with simultaneous precipitation.

2.1.2.3 Post-Precipitation (Tertiary Treatment)

In some instances primary or simultaneous precipitation are insufficient to reduce phosphate concentrations to meet very low discharge standards ,< 0.5

mg P/l. In these cases post-precipitation is required (Figure 2.1c). With post-precipitation alum is added to wastewater in a separate stage after biological treatment. Chemical addition is followed by clarification and filtration. Melkersson (1973) found that wastewater treatment facilities using post-precipitation were able to remove over 90% of influent total P, discharging an effluent with a BOD of 5-15 mg/l; SS of 5-25 mg/l and total P of 0.1 to 0.5 mg P/l.

A significant increase in P-removal cost is incurred when tertiary treatment is used. The increase in cost can be attributed to higher chemical cost and the expense of improved SS removal. Chemical costs increase from $1.5/lb total P removed with pre- or simultaneous precipitation to $1.91/lb total P removed with post precipitation (EPA, 1987b). The increase in cost resulting from improved SS removal is difficult to account for and can have a considerable impact on P removal costs (EPA, 1987a).

2.1.2.4 Multiple Dosing Points

Addition of alum at several locations in the process stream increases operational flexibility and is an effective and economical method of chemical P removal. Multiple point dosing includes several dosing alternatives such as combining pre-precipitation with simultaneous precipitation, pre-precipitation and post precipitation, and simultaneous precipitation with post precipitation. Operating data from the Orilla, Ontario, Canada wastewater plant showed that multiple point dosing required less chemical and was less costly than single point dosing (EPA, 1987a). In a two stage full scale activated sludge system simultaneous precipitation with 64 mg/l alum was compared with multiple point dosing of 16 mg/l alum to the primary clarifier and 32 mg/l alum (48 mg/l total alum dosed) to the aeration basin. The multiple point alum dosing achieved the same P removal efficiency as simultaneous precipitation with a lower alum dose: 1.3 mg Al/mg P removed with simultaneous precipitation and 1.1 mg Al/mg P removed with multiple dose point P removal. Simultaneous precipitation removed 92% of influent total P and achieved effluent total P concentration of 0.65 mg P/l while multiple dose point precipitation removed 93% of influent total P and yielded an effluent with 0.36 mg P/l total P (Black, 1980; EPA, 1987a).

2.2 Mechanism of Aluminum Phosphate Precipitation

The mechanism of chemical P removal has been studied extensively (Ferguson and King, 1977; Jenkins *et al.*, 1984; Recht and Ghassemi, 1970; Stumm, 1964; Goldshmid and Rubin, 1978), however, the exact nature of the chemical processes involved is not fully understood. P removal can result from several interactions which occur when alum is dosed to the aeration basin of an activated sludge system:

1-- insolubilization of soluble phosphate species resulting in the formation a mixed biological/chemical solid

2-- uptake of soluble orthophosphate by microorganisms

3-- sweep flocculation of colloidal P-containing particles

2.2.1 Chemical Form of Phosphorus Removed by Precipitation

P is found in domestic sewage in a variety of forms: organically bound P, condensed phosphate and orthophosphate. Wastewater P can either be in solution (soluble) or particulate form. P species which can pass through a 0.45 µm pore-diameter membrane filter are classified as soluble species while those which do not are classified as particulate (or suspended). P that responds to colorimetric analysis without additional treatment are termed "reactive P" and consists primarily of orthophosphate. P that must be hydrolysed to orthophosphate with acid in order to be measured colorimetrically are typically condensed phosphates. Organic P must undergo extensive oxidative destruction before being converted to colorimetrically measurable orthophosphate. (Standard Methods, 1985)

Recht and Ghassemi (1970) conducted a series of experiments to determine how well several forms of P typically found in sewage were removed when aluminum salts were added to prepared P solutions and filtered secondary effluent. Aluminum nitrate ($Al(NO_3)_3.9H_2O$) was added to solutions of orthophosphate, pyrophosphate or tripolyphosphate at the three following mass ratios of applied aluminum to phosphate: ($Al^{3+}:PO_4^{3-}$) = 0.5:1, 1:1, and 2:1. Recht and Ghassemi were able to remove a significant fraction of orthophosphate within the pH range 4 to 8. The optimum pH for orthophosphate precipitation with aluminum was approximately 6.0, where an orthophosphate residual of 0.1 mg P/l was reached with a 2:1 ratio of aluminum to influent orthophosphate. Condensed phosphate could not be precipitated as effectively as orthophosphate. The optimum pH for condensed phosphate precipitation was close to 5.0 and at a 2:1 ratio of aluminum doses to influent P, pyrophosphate and tripolyphosphate residual concentrations of 0.9 and 3.8 mg P/l respectively were reached. Recht and Ghassemi found that pyrophosphate and tripolyphosphate precipitation occurred only in a narrow pH range ($4 < pH < 6$) with essentially no precipitation occurring outside this range. At a 1:1 ratio of aluminum to P, tripolyphosphate precipitation did not occur at any pH between 4 and 8.

Sawyer (1952) found that condensed phosphates were less readily precipitated than orthophosphate in experimental studies under controlled conditions. Sawyer conducted batch studies with tripolyphosphate and pyrophosphate enriched sewage dosed with alum and found that alum was effective in removing both condensed and ortho phosphate. Sawyer found that under identical conditions sodium aluminate was unable to remove tripolyphosphate and pyrophosphate at high pH ($pH > 8$) values. Sawyer's results with sodium aluminate have been interpreted by others (EPA, 1987a; Daigger, 1989; Heinke and Norman, 1970; Finstein and Hunter, 1967) to indicate that condensed phosphate is not as readily precipitated as orthophosphate.

Henriksen (1962) conducted laboratory batch precipitation studies using both prepared solutions and primary settled sewage. In sewage samples containing 11.5 mg/l orthophosphate and 5.65 mg/l polyphosphate, the polyphosphate appeared to be more effectively removed than orthophosphate. Henriksen's study did not consider whether the improved P removal resulted from the precipitation of polyphosphate or from the precipitation of orthophosphate produced by the hydrolysis of polyphosphate.

2.2.2 Protolysis of Phosphoric Acid

Phosphoric acid (H_3PO_4) is a triprotic acid which is successively deprotonated to PO_4^{3-} according to the following series of equilibria:

$$H_3PO_4 + H_2O <=> H_2PO_4^- + H_3O^+ \qquad pK_1 = -2.15 \tag{2.1}$$

$$H_2PO_4^- + H_2O <=> HPO_4^{2-} + H_3O^+ \qquad pK_2 = -7.20 \tag{2.2}$$

$$HPO_4^{2-} + H_2O <=> PO_4^{3-} + H_3O^+ \qquad pK_3 = -12.35 \tag{2.3}$$

The equilibrium constants shown above were taken from Smith and Martell (1976) and where obtained at 25°C and adjusted to 0 ionic strength.

Equations 2.1-2.3 can be used to determine the distribution of orthophosphate species in solution at equilibrium for a given pH and total soluble orthophosphate concentration. At pH 6.5 to 8.0, typical of domestic sewage (Snoeyink and Jenkins, 1980), orthophosphate is predominately present as $H_2PO_4^-$ and HPO_4^{2-}.

2.2.3 Hydrolysis of Condensed Phosphates

The role of condensed phosphate in P removal processes is unclear, although it seems likely that condensed phosphate is either precipitated in the condensed form or as orthophosphate following hydrolysis. The primary source of condensed phosphate in domestic wastewater is synthetic detergents. Pyrophosphate ($H_4P_2O_7$) and tripolyphosphate ($H_5P_3O_{10}$) constitute about 5-10% by weight of synthetic laundry detergents and their discharge accounts for approximately 50 to 60% of sewage condensed phosphate (Henderson-Sellers and Markland, 1987; Hortig and Horvath, 1982) in regions where detergent phosphate content is not regulated. The predominate forms of tripolyphosphate and pyrophosphate at typical wastewater pH (approx. 6.5 - 8.0) are $HP_3O_{10}^{4-}$ and $HP_2O_7^{3-}$. These hydrolyse to orthophosphate as follows (Odegaard, 1979):

$$HP_3O_{10}^{4-} + H_2O \Leftrightarrow HP_2O_7^{3-} + HPO_4^{2-} + 2H_3O^+ \quad (2.4)$$

$$HP_2O_7^{3-} + H_2O \Leftrightarrow 2\,HPO_4^{2-} + 2H_3O^+ \quad (2.5)$$

Finstein and Hunter (1967) analyzed influent and effluent samples from 3 full scale activated sludge plants and found that while aerobic biological treatment had little effect on the total P content of wastewater, the fraction of total P contributed by orthophosphate increased from 53% in the influent to 83% in the effluent. The increase in orthophosphate was attributed to condensed phosphate hydrolysis. Finstein and Hunter determined that the rapid hydrolysis of condensed phosphate to orthophosphate only occurred in the presence of activated sludge particles. They did not describe the role of activated sludge particles in condensed phosphate hydrolysis or investigate the role of pH on the rate of reaction.

The rate of tripolyphosphate and pyrophosphate hydrolysis is effected by many environmental factors. Heinke and Norman (1971) stated that the most predominant of these factors were temperature, pH and the presence of enzymes (organisms). They concluded that tripolyphosphate and pyrophosphate hydrolyse three times faster at 20°C than at 4°C and that the rate is at least one order of magnitude higher in the presence of microorganisms than in their absence. Heinke and Norman determined that the optimum pH for tripolyphosphate and pyrophosphate hydrolysis was 7.5. Snoeyink and Jenkins (1980) also discussed the effect of microorganisms on tripolyphosphate and pyrophosphate hydrolysis and attributed the increase in hydrolysis rate in their presence to enzymes that catalyze the hydrolysis reactions.

2.2.4 Protolysis of Aluminum Ions

Typically alum is added to wastewater for chemical P removal as an aqueous solution. The aqueous aluminum species that interact with soluble orthophosphate are unclear.

Several studies have been conducted on the nature of the aluminum species formed in pure water systems (Baes and Mesmer, 1976; Stumm and Morgan, 1962; Sullivan and Singley, 1968; O'Melia, 1978). When aqueous aluminum solutions are prepared a variety of mono and polynuclear aluminum hydrolysis products can be formed. The exact nature of these hydrolysis products depends on the total concentration of aluminum and the solution pH (Sullivan and Singley, 1968; Stumm and Morgan, 1962; Stumm and Morgan, 1970).

Sullivan and Singley (1968) challenged the postulate of Stumm and Morgan (1962) that polyhydroxy polynuclear aluminum complexes were responsible for traditional coagulation and flocculation. Sullivan and Singley titrated dilute solutions of Al(III) (10^{-5} to 10^{-3} M) with strong base (NaOH) in the pH range 4 to 10 and modeled their experimental results solely with mononuclear species. The authors concluded that at moderate aluminum concentrations (10^{-3} to 10^{-4} M) and low pH values <4.5, mononuclear protolysis products were formed with the Al^{3+}

cation being the most predominant. Sullivan and Singley reported that aluminum hydroxide ($Al(OH)_3(s)$) would be the predominant aluminum protolysis product at moderate concentrations (10^{-5} to 10^{-3} M) and pH values in the range 4.5 to 8. Above pH 8 the authors concluded $Al(OH)_4^-$ was the predominant species. Sullivan and Singley's findings are summarized in the following series of equations:

$$Al(H_2O)_6^{3+} + H_2O \Leftrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+ \qquad (2.6)$$

$$Al(H_2O)_5(OH)^{2+} + H_2O \Leftrightarrow Al(H_2O)_4(OH)_2^+ + H_3O^+ \qquad (2.7)$$

$$Al(H_2O)_4(OH)_2^+ + H_2O \Leftrightarrow Al(H_2O)_3(OH)_3^0{}_{(s)} + H_3O^+ \qquad (2.8)$$

$$Al(H_2O)_3(OH)_3^0{}_{(s)} + H_2O \Leftrightarrow Al(H_2O)_2(OH)_4^- + H_3O^+ \qquad (2.9)$$

Polynuclear aluminum protolysis products can be formed when aluminum, Al(III), solutions are prepared (Stumm and Morgan, 1962, 1970; O'Melia, 1978). Baes and Mesmers (1976) presented experimental results showing both the rapid and reversible formation of mononuclear species and the slower, transient formation of polynuclear hydrolysis products of aluminum and concluded that the most likely polynuclear aluminum protolysis product was $Al_{13}O_4(OH)_{24}^{7+}$.

Stumm and Morgan (1962, 1970) declared that the scheme of consecutive stepwise hydroxide binding proposed by

Bronsted (1938) and Sullivan and Singley (1968) was too simplistic and suggested that complex intermediate steps occurred during aluminum protolysis. Stumm and Morgan proposed that multinuclear species such as $Al_6(OH)_{15}^{3+}$ and $Al_8(OH)_{20}^{4+}$ are formed by hydrolytic and condensation reactions. Stumm and Morgan (1970) suggested that the mononuclear protolysis products suggested by equations 2.6 and 2.7 are negligible under conditions encountered in wastewater treatment and concluded that in solutions oversaturated with respect to the stable solid, aluminum hydroxide ($Al(OH)_{3(s)}$), or at pH values lower than the zero point charge of $Al(OH)_{3(s)}$, positively charged aluminum hydroxy polymers predominated. Stumm and Morgan's findings are summarized in Figure 2.2.

O'Melia (1978) discussed the speciation of solutions formed when alum is added to water to prepare stock solutions for coagulation and estimated the distribution of aluminum protolysis products using equilibrium calculations. O'Melia suggested that the hydroxo-aluminum polymers formed when alum stock solutions are added to wastewater could possibly be a function of the strength of the stock alum solution since the distribution of protolysis products depends on total concentration of aluminum. O'Melia's proposed distribution of aluminum protolysis products in stock alum solutions is shown in Figure 2.3.

Figure 2.2

Stepwise Conversion of Al(III) to the Aluminate Ion
(from Stumm and Morgan, 1962)

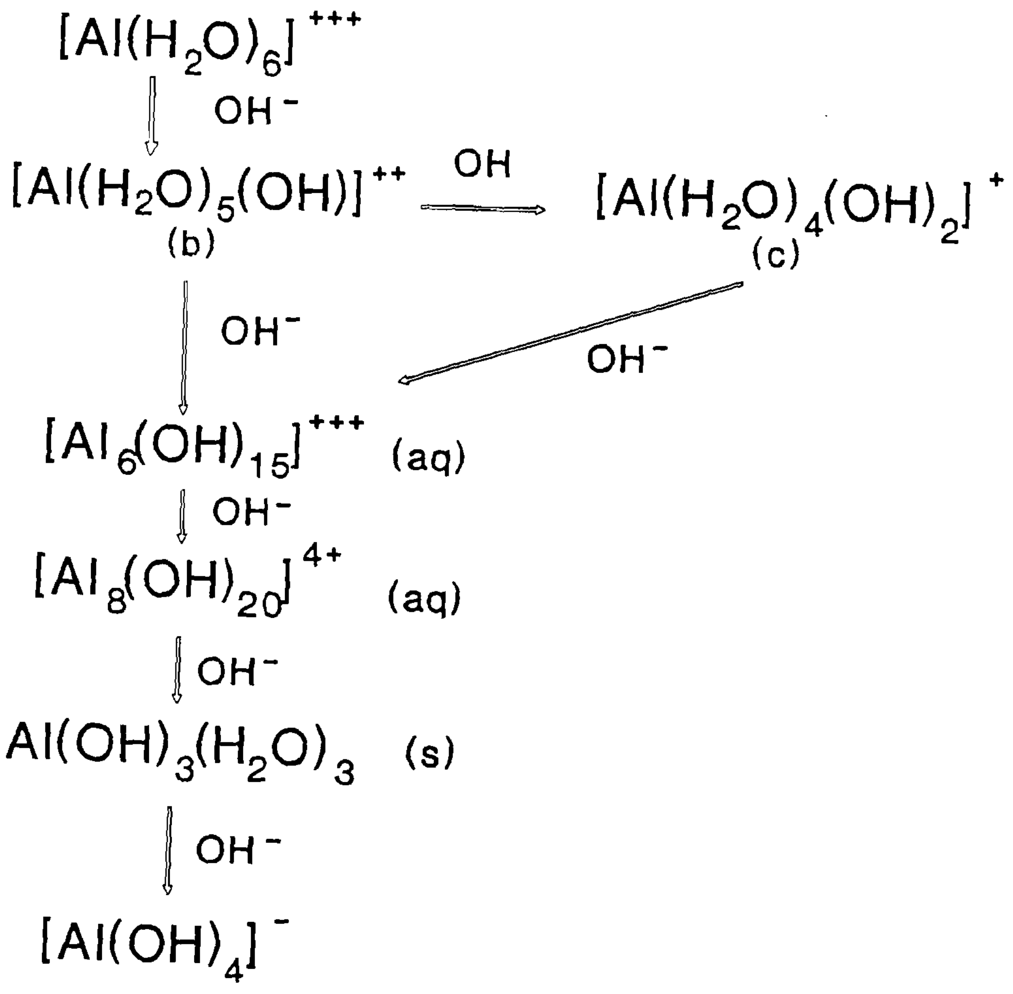
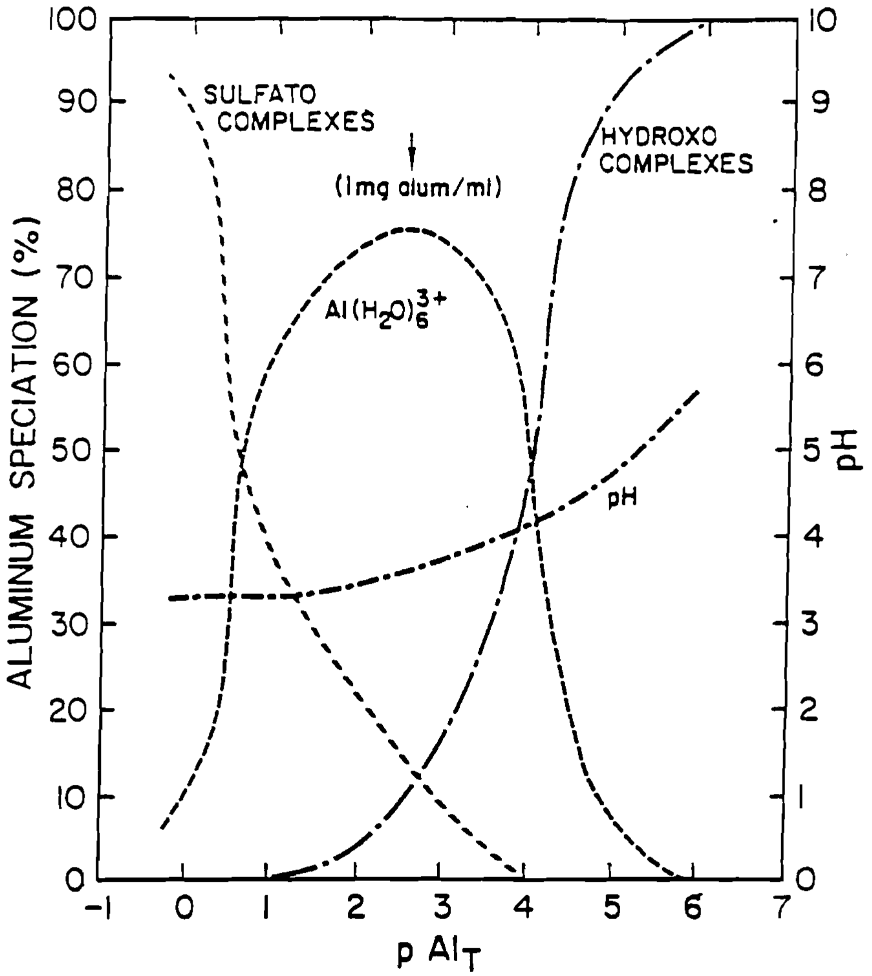


Figure 2.3

Distribution of Aluminum Protolysis Products



From O'Melia (1978)

2.2.5 Phosphate Insolubilization

The first stage of chemical P removal is the insolublization of soluble orthophosphate and aluminum hydrolysis products. Two possible insolublization mechanisms will be reviewed: (1) the precipitation of analuminum hydroxy phosphate solid and (2) the adsorption of phosphate onto a solid aluminum hydroxide surface. A third possible mechanism, colloidal P destabilization and coagulation will not be discussed in detail.

2.2.5.1 Aluminum Phosphate Precipitation

Precipitation occurs in three distinct steps: 1) nucleation, 2) crystal growth and 3) agglomeration and ripening. Nucleation involves the spontaneous formation of a solid phase on which solid precipitation can take place. Nucleation can be either homogeneous with the nucleus being formed from only component ions of the solid phase or heterogeneous with foreign particles (particles not included in the chemical composition of the solid phase) being included in the nucleus. Crystal growth occurs when ions associated with the solid phase diffuse to the solid surface and become incorporated into it. The final stage of precipitation is the agglomeration and ripening stage. In this stage the nature of the solid formed can undergo transformation to a more stable solid. (Snoeyink and Jenkins, 1980; Corey, 1981)

Whether or not ions in solutions will combine and form a particular solid phase depends on both thermodynamic and kinetic factors. Thermodynamics determine whether under a given set of conditions, a solid formation reaction will occur spontaneously ie. it will decreases the overall Gibbs Free energy of the system. Often a solid formation reaction is thermodynamically favored yet the solid product is not formed. This indicates that the rate of the reactions involved are extremely slow and prevent the formation of any product in the time frame of observation. This is kinetic control. (Snoeyink and Jenkins, 1980)

Recht and Ghassemi (1970), in a series of kinetic studies, determined the rate of aluminum phosphate precipitation to be very fast. They measured changes in pH and conductivity after aluminum nitrate was added to phosphate solution (Al:P = 1:1) and found both parameters decreased immediately after aluminum addition and then remained constant. Recht and Ghassemi concluded that aluminum phosphate precipitation reactions were complete within 1.3 seconds of aluminum addition.

Stumm and Morgan (1962) conducted laboratory studies which, they stated, offered substantial proof that chemical P removal with aluminum salts (aluminum perchlorate) resulted from the formation of an aluminum phosphate

($AlPO_{4(s)}$) precipitate. NaOH was used to titrate three separate solution: $10^{-2.6}$ M phosphoric acid (H_3PO_4); $10^{-2.6}$ M aluminum perchlorate ($Al(ClO_4)_3$); $10^{-2.6}$ M phosphoric acid + $10^{-2.6}$ M aluminum m perchlorate. They observed that three equivalent fractions of sodium hydroxide were needed to titrate the aluminum perchlorate solution to $Al(OH)_{3(s)}$ and proposed the reaction:

$$Al^{3+} + 3\ OH^- <=> Al(OH)_{3(s)} \qquad (2.10)$$

Stumm and Morgan postulated that if no chemical reactions occurred between aluminum and phosphate, a larger quantity of NaOH would be needed to titrate the solution containing both aluminum perchlorate and phosphoric acid because NaOH would be needed to titrate the orthophosphoric acid to PO_4^{3-} in addition to titrating the aluminum perchlorate to $Al(OH)_{3(s)}$. It was observed that the amount of NaOH required to titrate the aluminum perchlorate/phosphoric acid mixture was essentially the same as that required to titrate the aluminum perchlorate solution. This observation was interpreted as indicating that a chemical interaction occurred between Al^{3+} and H_3PO_4 as follows:

$$Al^{3+} + H_3PO_4 + 3\ OH^- <=> AlPO_{4(s)} + 3\ H_2O \qquad (2.11)$$

Stumm and Morgan worked with chemically defined distilled water solutions and did not attempt to determine the composition of the aluminum phosphate precipitate formed.

With chemical P removal from wastewater using alum, phosphate insolublization results from the formation of an aluminum phosphate solid of uncertain nature and stoichiometry. Several possible solids have been suggested. Stumm and Morgan (1962) suggested that $AlPO_{4(s)}$ is formed. Cole and Jackson (1950), in a series of distilled water studies identified variscite ($Al(OH)_2H_2PO_4(s)$) and sterrettite($[Al(OH)_2]_3HPO_4H_2PO_{4(s)}$) as the species formed when orthophosphate and aluminum protolysis products are combined. Arvin and Petersen (1980) presented a model in which the precipitation of a multi-component solid containing calcium and bicarbonate in addition to aluminum and phosphate ($Ca_kAl_u(H_2PO_4)_f(HCO_3)_c(OH)_h$) was proposed. Veith and Sposito (1977) added hydrous aluminum oxide to 10^{-3} M sodium phosphate solutions at a ratio of 1 mole applied aluminum to 1 mole phosphate and identified two amorphous aluminum hydroxy phosphate solids: $Al(OH)_2H_2PO_4$ and $Al(OH)NaPO_4$. Of the many solids proposed $AlPO_{4(s)}$ appears to be the most extensively cited and is often assumed to be representative of the aluminum phosphate precipitate formed when alum is added to wastewater (Stumm and Morgan, 1962).

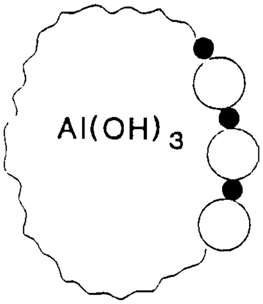
2.2.5.2 Adsorption

Adsorption is the adhesion of a layer of molecules on to the surface of a solid in contact with them. Adsorption of an aqueous molecule (the adsorbate) on to a solid surface (the adsorbent) takes place in four distinct steps. The first step is the transport of the adsorbate from the bulk liquid phase to the adsorbent/liquid interface. This is followed by the diffusion of the adsorbate across the adsorbent/liquid interface. Transport of the adsorbate within the pore space of the adsorbent is the third step. The final step is the adherence of the adsorbate to the adsorbent surface either by strong molecular interactive forces (chemical adsorption or chemisorption) or by weaker short range forces (physical adsorption). (Schindler, 1981; Montgomery, 1985)

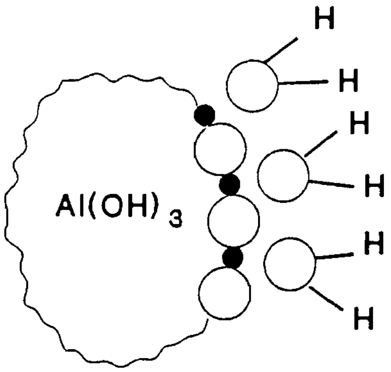
Metal hydroxide surfaces are ideal for adsorption because of their chemical characteristics. Adsorption of ions at metal hydroxide/water interfaces has been modeled as the formation of surface complexes by Haung and Stumm (1973), while the basis of other models is chemical co-ordination (Hingston *et al*, 1972; Parfitt *et al*., 1975) or simple and extended double layer mechanisms (Swenson, *et al*, 1948, Schindler 1981).

Schindler (1981) presented a unified co-ordination model of anion adsorption on metal hydroxide surfaces that included a description of the formation of hydroxy surfaces on aqueous metal oxides (Figure 2.4). In the presence of water the surface metal ions coordinate water molecules (Figure 2.4b). Next the coordinated water molecules dissociate and hydrogen ions chemically adsorb

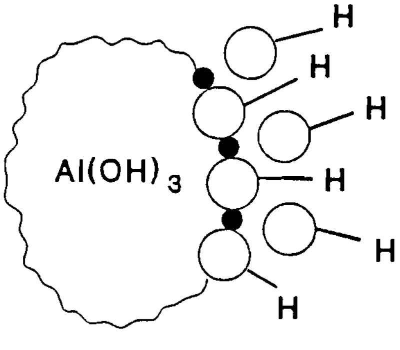
Figure 2.4
Formation of Hydroxylated Surfaces



a) aluminum hydroxide solid



b) coordination of water molecules at surface Al

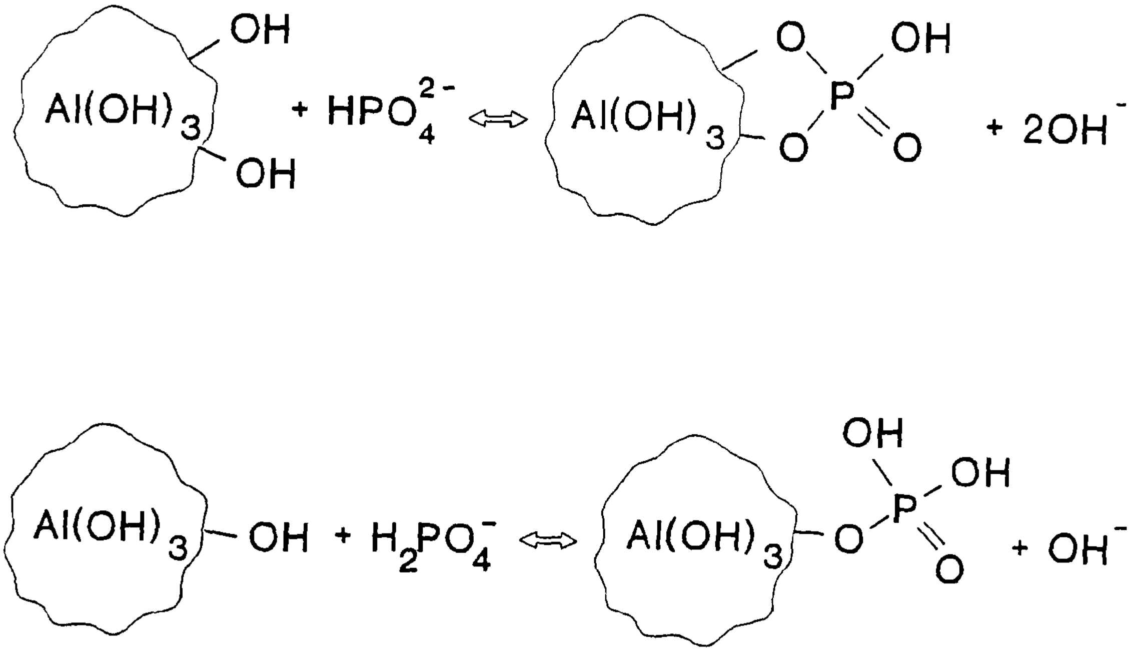


c) water molecules dissociate and hydrogen atom chemisorbs to surface oxygen resulting in hydroxylated surface (chemisorption) to surface oxygens. This results in the formation of surface hydroxyl groups on the metal oxide water interface. Studies of the kinetics of the hydroxylation of aluminum oxide indicate this process is very rapid (Schindler, 1981). Hydroxylated surfaces can participate in coordination reactions. An example of this type of reaction is the replacement of a surface hydroxide group by a dissolved ligand such as orthophosphate (Figure 2.5).

Corey (1981) in discussing anion adsorption on aluminum protolysis products stated that the surface of aluminum protolysis products carried a net positive charge. Both the composition and the surface charge of the aluminum protolysis product depended on pH and total aluminum concentration. Corey proposed the polynuclear species $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, as a possible charged species and suggested that it would precipitate when the charge was neutralized by the adsorption of an anion such as phosphate, fluoride, selenate, or arsenate. Hsu (1976) showed that aluminum protolysis products were precipitated when sufficient phosphate (as NaH_2PO_4) was added to neutralize the net positive charge of prepared $AlCl_3$/distilled water solutions in the pH range 3-8.

Corey (1981) attempted to distinguish between precipitation and adsorption and noted that precipitation is a three dimensional process while adsorption is a two

Figure 2.5
Adsorption of Orthophosphate on to Hydroxylated Surfaces



dimensional process occurring primarily on the surface of a solid. Corey further suggested that at high adsorbate concentration, adsorption can eventually lead to the nucleation and precipitation of an additional solid phase. Corey stated:

> "The fact than an ion is specifically adsorbed on the surface of a substrate suggests that it has a tendency to form an insoluble compound or stable complex with the ion of opposite charge in the substrate... As more and more adsorbate ion is added, nucleation of a new solid phase will occur at some point, and the solubility of the adsorbate ion would then be controlled by the solubility of the new solid phase, rather that by the adsorption reaction."

If enough adsorbate is in solution and no other ions in solution form precipitates with the adsorbate, then the adsorbate will eventually nucleate a second solid phase made up of adsorbate ions and ions derived from the dissolution of the adsorbent. Robarge and Carey (1979) conducted a series of experiments with polynuclear aluminum protolysis products and phosphate which confirmed this hypothesis. When the Al:P dose ratio was < 2 their results indicated phosphate adsorption and a minimum H_2PO_4 concentration of 5×10^{-6} M could be reached. When the Al:P ratio was > 2:1 the experimental results (particularly pH decline) suggested that a second solid phase

($Al(OH)_2(H_2PO_4)_3$) was being formed. Robarge and Corey were unable to define the boundary between adsorption and adsorption/precipitation, but presented conditions in which the adsorption/precipitation process would not be expected ie. in solutions which were undersaturated with respect to the expected new solid phase. For aluminum phosphate precipitation, nucleation of a new phase would not be expected if the aqueous concentration of aluminum and phosphate did not exceed the solubility product of the aluminum-hydroxy-phosphate solid.

2.2.6 Effect of System Composition on Chemical P-Removal

2.2.6.1 Age of Alum Dosing Solution

Diamadopoulos and Benedek (1984a) studied the effect of the degree of aluminum hydrolysis on phosphorus removal. They concluded that the nature of the hydrolysis products, most significantly the degree of polymerization, had a marked effect on phosphorus removal. This was attributed to a relative affinity effect. They suggested that phosphorus removal resulted from a competitive complex formation reactions occurring at the aluminum coordination shell and concluded that polymeric aluminum hydrolysis products were less likely to form complexes with (and remove) phosphate from solution due to the greater affinity of hydroxides for the aluminum ion than for the phosphate. Since the degree of polymerization of aluminum protolysis products increases with time, this study suggested that the use of fresh alum solutions would be desired over aged aluminum solutions.

Stumm (1964) stated that aluminum solutions ($Al(ClO_4)_3$) would hydrolyze and polymerize with ageing and become less effective precipitants because the coordination sites of the aluminum ions would be partially occupied with OH^- ions and become unavailable for phosphate precipitation.

Recht and Ghassemi (1970) studied the impact of precipitant aging by monitoring the pH, conductivity and removal capacity of aluminum nitrate solutions (7.72×10^{-4} mole P/l) aged for periods up to 2 months. In these experiments aging of the aluminum solution did not appear to have any impact on phosphate removal capacity (mole P removed/mole Al dosed). Recht and Ghassemi concluded that aluminum solutions do not undergo significant hydrolysis after preparation.

2.2.6.2 Effects of pH

Many studies of chemical P removal have addressed the effect of system pH on phosphate removal (Ferguson and King, 1977; Lea *et al.*, 1954; Henriksen, 1962; Hsu, 1975,1976; Recht and Ghassemi, 1970; Stumm, 1964; Long and Nesbitt, 1975; Arvin and Petersen, 1980; Lin and Carlson, 1978; Minton and Carlson, 1972; Eberhardt and Nesbitt, 1968; Diamadopoulos and Benedek, 1984b) usually with the goal of determining the optimum pH range for precipitation. The pH at which the minimum phosphate residual is observed or at which the maximum amount of phosphate can be removed per unit dose of aluminum is usually considered the optimum pH. Optimum pH values for aluminum phosphate precipitation reported in the literature range from 4.0 to 8.8. Some variation in optimum pH values can be attributed to the fact that some studies (Stumm, 1964; Snoeyink and Jenkins, 1980) predicted optimum pH using chemical equilibrium models, while others (Hsu, 1975,1976; Recht and Ghassemi, 1970; Henriksen, 1962) measured optimum pH in distilled water solutions, and still others (Eberhardt and Nesbitt, 1968; Minton and Carlson, 1972; Lin and Carlson, 1978; Arvin and Petersen, 1980) observed optimum pH values in pilot and full scale simultaneous precipitation systems. Both the determination of the optimum pH and the impact of pH values outside the optimum range on P removal will be discussed.

2.2.6.2.1 Predicting Optimum pH Using Chemical Equilibria

Stumm (1964), Stumm and Morgan (1962), and Snoeyink and Jenkins (1980) estimated the optimum pH for aluminum phosphate precipitation using chemical equilibrium relationships. With this method, the equilibrium concentration of soluble orthophosphate in solutions saturated with aluminum phosphate and/or aluminum hydroxide solid is determined as a function of pH. Stumm and Snoeyink and Jenkins used similar equilibrium relationships (Table 2.1). Both studies considered aluminum phosphate ($AlPO_{4(s)}$) as the aluminum phosphate precipitate, although Snoeyink and Jenkins noted that other authors (Recht and Ghassemi, 1970) observed the formation of an aluminum-hydroxy-phosphate solid during chemical P removal with aluminum nitrate. Both investigators assumed that aluminum-phosphate soluble complexes would not appreciably affect $AlPO_{4(s)}$ solubility. Snoeyink and Jenkins further assumed that polymeric aluminum protolysis products were not formed.

Snoeyink and Jenkins estimated the optimum pH by first determining the equilibrium concentration of Al^{3} and PO_4^{3-} through rearranging equations 2.12 through 2.19 with the following results:

Table 2.1

2.1 Chemical Equilibria used by Stumm (1962), and Snoeyink and Jenkins (1980)

I. Solubility of Phosphates

$Al^{3+} + PO_4^{3-} \Leftrightarrow AlPO_4(s)$	log K_{so}	23 [21]
		(2.12)

II. Hydrolysis of Al^{3+}

$6Al^{3+} + 15OH^- \Leftrightarrow Al_6OH_{13}^{3+}$	log K	163 [--]
		(2.13)
$Al^{3+} + 2H_2O \Leftrightarrow AlOH^{2+} + H_3O^+$	log K_1	-- [-5.0]
		(2.14)
$Al^{3+} + 4H_2O \Leftrightarrow Al(OH)_4^- + 4H_3O^+$	log K_4	-- [-21.7]
		(2.15)
$Al_{3+} + 3OH^- \Leftrightarrow Al(OH)_3(s)$	log K_{so}	32 [33]
		(2.16)

Table 2.1 (cont.)

III. Hydrolysis of Phosphoric Acid

$H_3PO_4 \iff H_2PO_4^{-} + H^{+}$ log $K_{a,1}$ -1.9 [-2.1] (2.17)

$H_2PO_4^{-} \iff HPO_4^{2-} + H^{+}$ log $K_{a,2}$ -6.6 [-7.2] (2.18)

$HPO_4^{2-} \iff PO_4^{3-} + H^{+}$ log $K_{a,3}$ -11.8 [-12.3] (2.19)

equilibrium constants in brackets are values used by Snoeyink and Jenkins

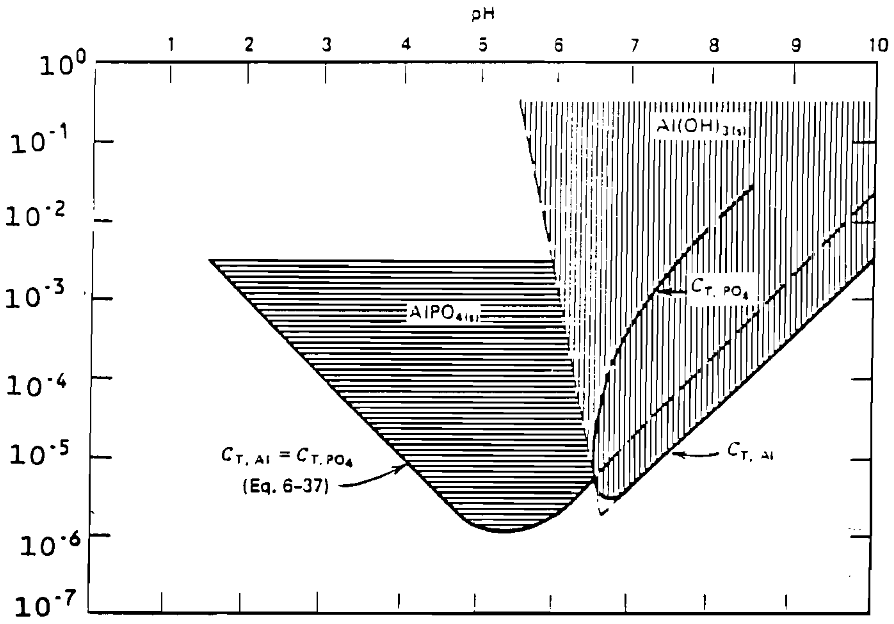
$$[Al^{3+}] = C_{T,Al}(1 + K_1/[H^+] + K_4/[H^+]^4)^{-1} \qquad (2.20)$$

$$[PO_4^{3-}] = C_{T,PO4}([H^+]^3/K_{a,1}K_{a,2}K_{a,3} + [H^+]^2/K_{a,2}K_{a,3} + [H^+]/K_{a,3} + 1)^{-1} \qquad (2.21)$$

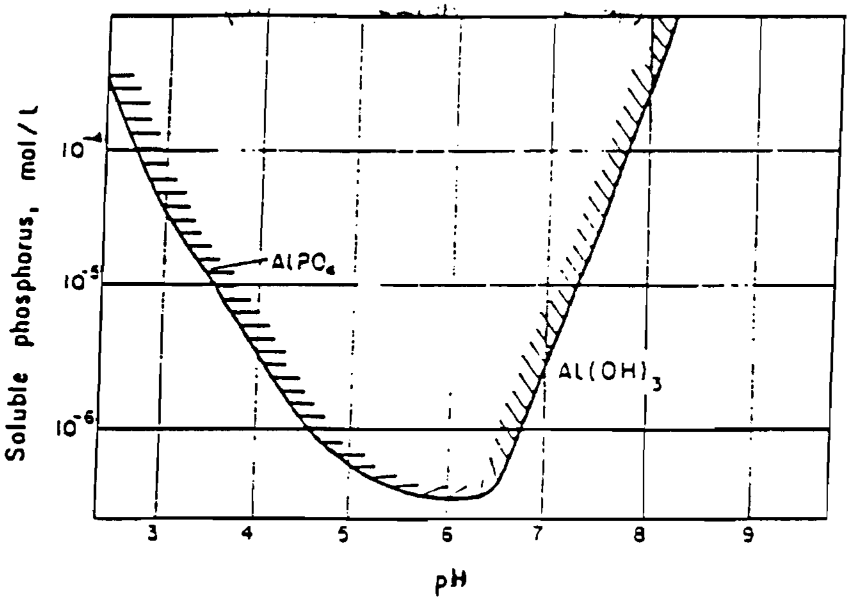
Combination of equations 2.20 and 2.21 with the solubility relationship for $AlPO_{4(s)}$ (2.12) gave an expression which was then solved to determine the equilibrium orthophosphate concentration as a function of pH (see Figure 2.6a). Using a similar approach Stumm developed the solubility curve shown in Figure 2.6b. Both investigators selected the pH of minimum phosphate concentration as the optimum pH. Stumm predicted an optimum pH for aluminum phosphate precipitation of 6.3 while Snoeyink and Jenkins suggested that the optimum pH for aluminum phosphate precipitation in solutions in equilibrium with $AlPO_{4(s)}$ was pH 5.5. Snoeyink and Jenkins stated that, at pH values greater than 5.4, fresh $Al(OH)_{3(s)}$ would begin to form in addition to $AlPO_{4(s)}$ and calculated the equilibrium soluble orthophosphate concentration in solutions containing both $AlPO_{4(s)}$ and fresh $Al(OH)_{3(s)}$. Higher orthophosphate equilibrium concentrations were predicted by Snoeyink and Jenkins in solutions containing $AlPO_{4(s)}$ and $Al(OH)_{3(s)}$ than in solutions containing only $AlPO_{4(s)}$. This suggested that chemical P-removal under conditions that allowed the formation of $Al(OH)_{3(s)}$ ie. pH > 5.4 and Al^{3+} dose:P ratios > 1, additional aluminum would have to be added to remove soluble orthophosphate.

Figure 2.6

Minimum Phosphate Solubility Predicted by Stumm and Snoeyink and Jenkins



a. Snoeyink and Jenkins (1980)



b. Stumm (1962)

Ferguson and King (1977) estimated the optimum pH for phosphate precipitation using their model of aluminum phosphate precipitation by solving equilibrium relationships and using a solubility product for the aluminum phosphate precipitate ($K_{so} = 10^{-34}$) determined from the operating results of full scale chemical P removal systems. The lowest phosphate residual concentration ($10^{-6.3}$ M) was predicted for the condition when soluble phosphate was in equilibrium with $AlPO_{4(s)}$ and $Al(OH)_{3(s)}$ at a pH between 5.5 and 6.

2.2.6.2.2 Determination of Optimum pH for P-Removal Using Laboratory and Field Studies

Recht and Ghassemi (1970), in batch experiments, adjusted the pH of secondary effluent and distilled water orthophosphate solutions to values in the range 4.0 to 9.0 by adding acid (HCl) or base (NaOH) prior to dosing aluminum at an Al:P ratio of 2:1. Only a small drop in pH was reported after aluminum addition and no attempt was made to adjust pH. Under these conditions, aluminum addition to secondary effluent produced a minimum orthophosphate residual (0.04 mg P/l) at pH 6.0, and orthophosphate residuals of < 0.3 mg/l in the pH range 4.6 to 6.8. An optimum pH of 6.0 was reported for the distilled water orthophosphate solutions.

Hsu (1975, 1976) concluded that the optimum pH range was a function of the mole ratio (R) of initial phosphate concentration in solution to the applied aluminum dose. The optimum pH range was 6-8 for R=0.2 and pH 4-5.7 for R>4.

Henriksen (1962) studied the effect of pH on P removal in a series of jar tests using distilled water phosphate solutions and domestic sewage. Aluminum was added to prepared orthophosphate solutions (17.0 mg P/l) using aluminum sulfate (70,100,150, and 200 mg/l) solutions. Various amounts of acetic acid were added concurrently with the aluminum sulfate to ensure that the total quantity of acid added to each jar test was constant. The pH of the solutions was neither measured before aluminum addition nor controlled during the experiments. The pH of the jar test filtrate was measured 1 hr after aluminum addition. The removal capacity (C),(the amount P removed (mg) per unit of aluminum (mg) dosed) for each jar test was determined. Experimental findings were presented as a function of removal capacity, with no mention of the phosphate residuals achieved. Henriksen observed that for all aluminum sulfate doses, the maximum removal capacity was found in the pH range 5.6 to 6.5. The decrease in removal capacity above pH 7 was attributed to the formation of aluminate (AlO_2^-) which did not remove phosphate efficiently. Settled sewage samples, with 11.45 mg P/l orthophosphate and 5.75 mg P/l condensed phosphate and initial pH of 7.8, were investigated using the same jar test procedure. The optimum pH for P removal with aluminum sulfate in the sewage samples was 6.0 to 7.1. Henriksen (1962) was unable to explain the upward shift of the optimum pH range in the settled sewage study compared to the experimentation on distilled water phosphate solutions.

Diamadopoulos and Benedek (1984), citing the work of Hsu (1975), suggested that phosphate precipitation resulted from competitive interactions between phosphate, hydroxyl and other ions for coordination sites on aluminum protolysis products and that the optimum pH range depended on the aluminum dose and the concentration and types of ions present in solution. Diamadopoulos and Benedek (1984) conducted a series of experiments using procedures similar to those of Henriksen (1962). In synthetic sewage studies (5 mg P/l) with alum addition, the pH of maximum precipitation was 4.7 at an Al:P dose ratio of 1 and pH 4.2 to 5.5 at Al:P of 2.75. Studies with domestic sewage showed maximum P removal in the pH range 6.0 to 7.5. They concluded that the lower optimum pH range observed at higher alum doses was due to the effect of sulfate ion which helped to neutralize the charge of the aluminum-phosphate-hydroxide complexes formed resulting in enhanced coagulation and phosphate precipitation.

Minton and Carlson (1972) noted that most previous laboratory and full scale studies (Henriksen, 1962; Stumm, 1964; Recht and Ghassemi, 1970;) only reported the final effluent pH and not the pH at the point of aluminum addition; further they did not take into consideration the pH drop that will result from aluminum addition. The work of Lin (1972) indicated that a pH drop as large as 0.65 units occurred between the pH of mixed liquor at the dose point of simultaneous precipitation and the effluent. Lin and Carlson (1975) compared the results of batch experiments and field studies on a continuous flow wastewater plant practicing aluminum phosphate precipitation. In batch studies the addition of 10 mg/l Al (Al:P = 1.7) reduced the pH from an initial value of approximately 7 to 6.1. Lin and Carlson (1975) found in field studies that the orthophosphate residual appeared to depend more on the alum dose than on the Al:P ratio and attributed this to the pH reduction that occurred when alum was added. Lin and Carlson expected the optimum pH for aluminum phosphate precipitation to coincide with the pH minimum solubility of $AlPO_{4(s)}$ reported by Stumm (1964) (pH 6.3) and suggested that the maximum phosphate removals found at high alum doses resulted from alum induced pH reduction to the optimum pH range.

Arvin and Petersen (1980) noted a significant difference in the optimum pH determined in batch experiments where alum was added to activated sludge mixed liquor (pH = 7.1-8.0) and those reported in the literature (pH= 5.5-6.5) (Stumm, 1964; Henriksen, 1962; Recht and Ghassemi,1970; Ferguson and King, 1977). Arvin and Petersen concluded that the optimum pH was a function of operational conditions, particularly the initial pH, alkalinity and system composition. Arvin and Petersen referred to the optimum pH described by equilibrium relationships as the "empirical pH" optimum and that observed in batch studies at fixed alkalinity as the "system pH" optimum.

2.2.6.2.3 Impact of pH on P-Removal

Stumm (1964) postulated that hydroxide ions were more strongly attracted to aluminum than phosphate ions and that the extent of $AlPO_{4(s)}$ precipitation depended on the ratio of $PO_{43-}/(OH^-)^3$. Thus aluminum phosphate precipitation was enhanced at lower pH values where the (OH^-) concentration would be lower.

Ferguson and King (1977) suggested that P removal increased as the pH decreased for a constant Al:P ratio and constant influent phosphate concentration until the solubility limit of the aluminum hydroxide/aluminum phosphate two precipitate system was reached. For systems at equilibrium with aluminum hydroxide and aluminum phosphate solids, residual phosphate concentrations greater than the minimum values would be expected if the pH were reduced to values beyond the optimum range. Ferguson and King stated that under certain conditions (high alkalinity, low alum dose) it would be advisable to add acid to a wastewater to lower the pH within the optimum range. Lin and Carlson (1975) postulated that a greater than minimum phosphate residual would be obtained at higher alum doses if alum addition resulted in a pH reduction to values lower than 6.0.

Hsu (1975) proposed that the pH dependency of aluminum phosphate precipitation was related to the surface charge of the precipitate formed and believed that hydroxide ions played a significant role in neutralizing the charge of aluminum phosphate colloidal particles. Hsu (1975), in experiments on chemically defined distilled water systems, suggested that as the pH was increased towards its optimum value the positive surface charge of colloidal aluminum phosphate was neutralized and the particles destabilized and settled. Beyond the optimum pH range the colloidal particles became negatively charged and restabilized.

Recht and Ghassemi (1970) observed that at the optimum pH, large settleable flocs were formed, but outside of this range ($pH<5$ or $pH>7$) colloidal suspensions were formed that were difficult to remove. The authors suggested that the formation of difficult-to-settle precipitates outside the optimum range could have resulted from the adsorption of ions onto the aluminum phosphate precipitate surface which created charged colloidal particles. Recht and Ghassemi (1970) observed a strong pH dependence in studies of tripolyphosphate and pyrophosphate precipitation, with the optimum pH being 5.0 and very little removal observed beyond the optimum pH.

2.2.6.3 Effect of Alkalinity

The role of alkalinity in chemical P removal is addressed in some previous studies of chemical phosphorus removal (Ferguson and King, 1977; Lin and Carlson, 1975; Arvin and Petersen, 1980). Lin and Carlson (1975) and Ferguson and King (1977) considered the impact of alkalinity to be limited to its effect on equilibrium pH due to its buffering capacity. Ferguson and King gave a series of equations that can be solved to determine the pH reduction that will occur when alum is added to a water with known alkalinity and phosphate concentration. Ferguson and King predicted the effect of alkalinity using their equilibrium model and found that at high alkalinity (8 meq/l) and low alum doses, phosphate removal was limited because pH reduction was insufficient to reach the optimum pH range for P removal (5.2 to 6.9). The model also predicted that, with low initial alkalinity (1.5 meq/l) and high alum doses, residual phosphate in excess of the minimum phosphate concentration could be reached because the pH would be reduced to a value lower than the optimum pH.

Arvin and Petersen (1980) suggest that the role of alkalinity in chemical P removal goes beyond its role as a buffer and that bicarbonate can be incorporated in the aluminum-phosphate containing precipitate. They used the solid $(Ca_kAl_u(H_2PO_4)_f(HCO_3)_c(OH)_{h(s)})$ in their equilibrium model of chemical P removal. Results of batch experiments revealed that a low alkalinity was necessary to obtain low soluble phosphate concentration.

2.2.6.4 Role of Other Ions

Studies addressing the impact of other ions have usually focused on the impact of Ca^{2+} and/or SO_4^{2-} on chemical P removal (Hsu, 1975,1976; Diamodopoulos and Benedek, 1984b; Arvin and Petersen, 1980). Hsu (1975,1976) proposed that the addition of sulfate enhanced phosphorus removal processes in acidic systems because its negative charge reduced the positive charge on the surface of aluminum hydroxide and phosphate colloids.

The role of calcium in chemical P removal can either be as a component of mixed aluminum-phosphate-calcium-hydroxide or calcium phosphate solid or as an adsorbed species contributing to the net charge of colloidal aluminum and phosphate containing solids. Diamodopoulos and Benedek (1984b) investigated chemical P removal using the mixed liquor of two batch activated sludge systems to which alum (11 mg Al/l , Al:P = 2.75) was added. The authors suggested that a calcium phosphate solid, unidentified, but indicated to have a Ca:PO_4 stoichiometry of 2, was present in the mixed liquor. At pH values below 7.5, in the absence of alum dosing, the dissolved calcium and phosphate concentration increased and the dissolution of the calcium phosphate solid was suggested. At pH values greater than 7.5 dissolved calcium and phosphate concentrations decreased and calcium phosphate precipitation was proposed. These investigators concluded that calcium phosphate precipitation and dissolution reactions occurred in parallel with the aluminum phosphate precipitation reactions and that both types of precipitation mechanisms must be considered when evaluating chemical P removal by alum addition.

2.3 Selected Models of Chemical Phosphorus Removal

Chemical P removal by simultaneous precipitation has been extensively studied on a laboratory and field scale. The primary focus of some studies was to gather operational data sufficient to make generalizations regarding the importance of pH, and the selection of effective dosages and points of application (Eberhardt and Nesbitt, 1968; Lin and Carlson, 1975; Barth and Ettinger, 1967). Others have attempted to develop models which describe the mechanism of simultaneous precipitation and predict either the phosphate residuals that could be reached with a given aluminum dose and/or the aluminum dose required to achieve a desired degree of P removal (Ferguson and King, 1977; Jenkins *et al.*, 1984; Luedecke *et al.*, 1988; Goldshmid and Rubin, 1978). Several models have been developed which described chemical phosphorus removal using the precipitation of aluminum-hydroxy-phosphate and aluminum hydroxide solid as the predominant phosphate removal mechanism (Ferguson and King, 1977; Jenkins *et al.*, 1984) while others developed models which included adsorption of phosphate onto aluminum hydroxide solid surfaces as a removal mechanism (Goldshmid and Rubin, 1978; Lea *et al.*, 1954).

2.3.1 Precipitation Based Models

Ferguson and King's (1977) conceptual and numerical model for aluminum phosphate precipitation defines three zones of phosphorus removal in each of which a unique relationship was developed to describe orthophosphate removal. The model is applicable to the removal of soluble orthophosphate from wastewater and does not address either the physical removal of the precipitates formed or the precipitation of condensed phosphates. An important assumption in Ferguson and King's model is that precipitation was the only phosphate removal mechanism. The authors acknowledged that evidence could be found in the literature supporting an adsorption mechanism but chose to exclude it from the model. The model is based on the precipitation of an aluminum hydroxide and/or an aluminum phosphate solid, the latter being the least soluble and the first to precipitate. Ferguson and King used simple chemical equilibria and mass balances to describe phosphorus removal in each of the three zones.

The first zone occurs when insufficient aluminum is added to precipitate all of the influent orthophosphate as an aluminum-hydroxy-phosphate solid. In this zone the authors suggest that phosphate removal is directly proportional (stoichiometric) to the aluminum dose. They concluded that phosphate removal in this zone can be predicted if the stoichiometric ratio (on a molar basis) of aluminum to phosphate in the precipitate at a given pH is known. On the basis of a literature review they assumed that the mole ratio of 1.4 would be applicable to aluminum phosphate precipitation in wastewater, suggesting a precipitate with the formula: $(Al_{1.4}PO_4(OH)_{1.2})$. The stoichiometric ratio (r=1.4) was determined by Recht and Ghassemi (1970) using experiments in which aluminum salts were added to orthophosphate-distilled water solutions in the absence of biological solids and at pH 6. Ferguson and King believed that constant (stoichiometric) removal ratios larger than 1.5 reported by Lea *et al.* (R=2.95, 1954), Dryden and Stern (1968) (R=1.75) reflected the precipitation of aluminum hydroxide solid in addition to aluminum-hydroxy-phosphate and were larger than the removal ratio of the aluminum-hydroxy-phosphate solid.

The second zone is encountered when aluminum doses are close to the stoichiometric requirement for complete orthophosphate precipitation. In this zone, phosphate removal is no longer stoichiometric but must be predicted by considering the equilibrium relationship established between the aluminum-hydroxy-phosphate solid and the aqueous solution because residual phosphate concentration is governed by the solubility of the aluminum-hydroxy-phosphate solid.

At high aluminum doses, well beyond stoichiometric requirements, the third phosphate removal zone is reached. In this zone, the authors proposed that aluminum-hydroxy-phosphate and aluminum hydroxide solids are both present. The phosphate residual was determined by equilibria between both aluminum-containing solids and the aqueous aluminum and phosphate concentrations.

Phosphate removal in zones 2 and 3 can be modeled numerically using equilibrium relationships between solid and soluble aluminum and phosphate-containing species. The authors used stability constants from several accepted sources including Sillen and Martel (1964) and Baes and Mesmer (1976). In addition, an equilibrium constant was estimated for the soluble aluminum phosphate complex ($AlH_2PO_4^{2+}$) which allowed a fit of the model with experimental data. The authors used a solubility constant of 10^{-34} for the aluminum phosphate solid which provided reasonable agreement between experimental data and model prediction. The equilibria used by Ferguson and King (1977) as the basis of their model are summarized in Table 2.2. Ferguson and King omitted polymeric aluminum protolysis products from the model because the constants reported for these species in the literature were inconsistent. For zone 2 calculations, mass balances on phosphate and aluminum were combined with equilibrium relationships to produce an equation that could be solved for phosphate residual (Figure 2.7). The calculation of the orthophosphate residual in zone 2 depends on both the final pH and the dose parameter, ($PO_{4\,initial} - 1/1.4\ Al_{dose}$). In the stoichiometric removal zone the dose parameter describes the phosphate residual obtained for a given aluminum dose. The authors defined the boundary between the first and second removal zone as being where the total ortho P residual ($H_2PO_{4^-}$ + HPO_4^- + $AlH_2PO_4^{2+}$) predicted by the equilibrium model was 25% greater than the total

Table 2.2

Chemical Equilibria used by Ferguson and King

Reaction	Stability constant	log K
$H_2PO_4^- \Leftrightarrow HPO_4^{2-} + H^+$	K_2	-7.2 (2.23)
$HPO_4^{2-} \Leftrightarrow PO_4^{3-} + H^+$	K_3	-12.2 (2.24)
$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$	K_1	-6.3 (2.25)
$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$	K_2	-10.3 (2.26)
$H_2O \Leftrightarrow H^+ + OH^-$	K_w	-14.0 (2.27)
$Al^{3+} + H_2O \Leftrightarrow AlOH^{2+} + H^+$	$^*K_1$	5.0 (2.28)
$AlOH^{2+} + H_2O \Leftrightarrow Al(OH)_2^+ + H^+$	$^*K_2$	3.7 (2.29)
$Al(OH)_2^+ + H_2O \Leftrightarrow Al(OH)_3^0(aq) + H^+$	$^*K_3$	6.5 (2.30)
$Al(OH)_3^0(aq) + H_2O \Leftrightarrow Al(OH)_4^- + H^+$	$^*K_4$	8.1 (2.31)
$Al^{3+} + H_2PO_4^- \Leftrightarrow AlH_2PO_4^{2+}$	K	6.0 (2.32)

Table 2.2 (cont.)

Chemical Equilibria used by Ferguson and King

$Al_{1.4}PO_4(OH)_{1.2}(s)$ <=>			
	$1.4Al^{3+} + PO_4^{3-} + 1.2\ OH^-$	K_{so}	-34.0 (2.33)
$Al(OH)_3(s) + 3H^+$ <=> $Al^{3+} + 3\ H_2O$		$^*K_{so}$	+10.3 (2.34)

Figure 2.7

Ferguson and King (1977) zone II relationship describing phosphate residual concentration

$$
\begin{aligned}
&(PO_4^{3-})\left[\frac{(H^+)^2}{K_2K_3}+\frac{(H^+)}{K_3}\right]+(PO_4^{3-})^{0.4/1.4}\times(0.4/1.4)\left[\frac{KK_{so}^{1/1.4}\,(H^+)^{2.2/1.4}}{K_w^{1.2/1.4}\,K_2K_3}\right]\\
&-\;(PO_4^{3-})^{-1/1.4}\,(1/1.4)\left[\frac{K_{so}^{1/1.4}(H^+)^{1.2/1.4}}{K}\right]\\
&\times\left[1+\frac{{}^{*}K_1}{(H^+)}+\frac{{}^{*}K_1\,{}^{*}K_2}{(H^+)^2}+\frac{{}^{*}K_1\,{}^{*}K_2\,{}^{*}K_3}{(H^+)^3}+\frac{{}^{*}K_1\,{}^{*}K_2\,{}^{*}K_3\,{}^{*}K_4}{(H^+)^4}\right]\\
&-\left[PO^{3-}_{4\ \mathrm{initial}}-(1/1.4)Al_{\mathrm{dose}}\right]=0
\end{aligned}
\tag{2.35}
$$

orthophosphate residual predicted by stoichiometric removal (dose parameter). With the model, Ferguson and King concluded that the minimum phosphate residual that can be achieved in the first zone is pH dependent and predicted the minimum stoichiometric phosphate residual obtainable at pH from 6.8-7.5 was 3 mg P/l and 1 mg P/l for pH 5.2-6.8.

Beyond the stoichiometric removal zone, phosphate residual concentration was determined by aluminum-hydroxy-phosphate solubility until excess aluminum was added resulting in the formation of solid aluminum hydroxide. In an aqueous system with two solids present and a fixed temperature and pressure, the concentrations of all species are fixed (Phase Rule). From this Ferguson and King concluded that the orthophosphate residual in the third zone would be that phosphate concentration that would exist in equilibrium with aluminum-hydroxy-phosphate and aluminum hydroxide solids. This equilibrium orthophosphate concentration was predicted by first calculating the soluble Al^{3+} concentration at the final pH using equation 2.34 and then calculating the phosphate concentration based on the solubility of aluminum-hydroxy-phosphate using equation 2.33. These calculation gave what the authors believed to be the unique soluble orthophosphate residual the could be reached at any given pH, with a minimum phosphate residual of $10^{-6.3}$ M (0.02 mg P/l) being reached at pH between 5.5 and 6.0. Ferguson and King suggested that the minimum phosphate concentration was that at the boundary between zones 2 and 3, and that dosing aluminum beyond that needed to reach the boundary would not result in any further phosphate removal. The authors stated that if aluminum was dosed in excess of the amount required to reach the optimum pH, higher phosphate residuals would result because the pH would be reduced to a value outside the optimum range. The excess aluminum required to reach the boundary between zones 2 and 3 was estimated using equation 2.35 and the expected phosphate residual at the boundary. Ferguson and King predicted an excess of aluminum of approx. 30 mg/l as alum beyond the stoichiometric requirement would be required to reach the minimum phosphate concentration.

With this model the final phosphate residuals in zones 2 and 3 could be computed if the initial phosphate concentration, initial pH and aluminum dose were known. The Ferguson and King model predicted that phosphate residuals as low as 0.02 mg P/l ($10^{-6.3}$ M) could be reached at the boundary between zones 2 and 3.

Ferguson and King (1977) used limited published data for the calibration of their model (including studies by Lea, *et al.*, 1954; Sawyer, 1972; and Lancaster, CA, 1967). Model predictions were also compared with jar test results on chemically defined distilled water, orthophosphate solutions. The authors were able to reasonably fit model predictions with experimental results. The removal zones described by Ferguson and King are shown in Figure 2.8 where phosphate residual is shown as a function of pH.

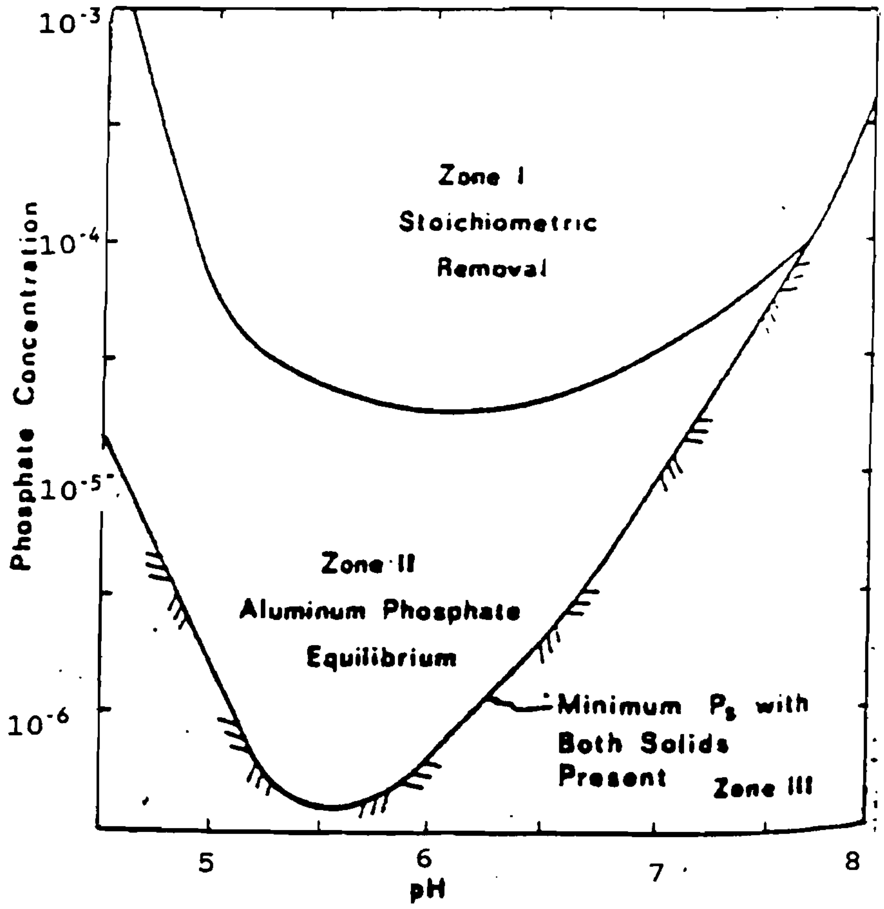
Jenkins, *et al.* (1984) presented a computer model of phosphate precipitation that included several modifications of the Ferguson and King (1977) model. The model was developed to describe P-removal using either alum or ferric chloride and like the Ferguson and King (1977) model assumed that precipitation of an metal-hydroxy-phosphate solid was the primary soluble orthophosphate removal mechanism. The model of Jenkins, *et al.* did not include adsorption mechanisms and the Al:P ratio of the metal-hydroxy-phosphate precipitate was adjustable with the value of 1.4 used by Ferguson and King (1977) selected as a default value.

The model of Jenkins, *et al.* was developed to predict the final phosphate residual as a function of the metal cation dose. Three metal dose schemes were included in the model:

1. Insufficient metal dosed to precipitate any phosphate (zero ppt zone)
2. Metal dose less than or equal to stoichiometric amount needed to precipitate influent phosphate (one ppt zone)
3. Metal dose sufficiently greater than stoichiometric dose to result in precipitation of metal hydroxide solid in addition to metal-hydroxy-phosphate precipitate (two ppt zone)

Figure 2.8

Three Zones of Orthophosphate Removal Described by Ferguson and King



(adapted from Ferguson and King, 1977)

Jenkins *et al.* predicted orthophosphate residual concentrations in the one and two precipitate zones using equilibrium relationships derived in a similar manner to those in the Ferguson and King (1977) model. The model of Jenkins *et al.* included several general relationships that were used to predict which precipitation zone would be encountered with a particular metal dose concentration. They proposed that the zero precipitate zone would be encountered if the aluminum and phosphate concentrations were insufficient to exceed to solubility limit of aluminum-hydroxy-phosphate precipitate:

$$Al_rPO_4(OH)_{(3r-3)(s)} \Leftrightarrow rAl^{3+} + PO_4^{3-} + (3r-3)OH^- \qquad (2.35)$$

with:

$$K_{so} = [Al^{3+}]^r[PO_4^{3-}][OH^-]^{3r-3} \qquad (2.36)$$

The authors stated that if the condition described by equation 2.37 existed no aluminum-hydroxy-phosphate precipitate would form and the addition of aluminum would result only in the reduction of pH.

$$K_{so} > [Al^{3+}]^r[PO_4^{3-}][OH^-]^{3r-3} \qquad (2.37)$$

Jenkins *et al.* assumed that when aluminum was dosed in sufficient quantities to form solids, aluminum-hydroxy-phosphate precipitated first. Jenkins *et al.* further assumed that aluminum hydroxide would precipitate only when sufficient Al^{3+} remained after aluminum-hydroxy-phosphate precipitation to exceed its soluubility limit:

$$Al(OH)_{3(s)} + 3H^{+} <=> Al^{3+} + H_2O \tag{2.38}$$

with

$$K_{so} = [Al^{3+}]/[H^{+}]^{3} \tag{2.39}$$

The minimum Al^{3+} concentration, ($[Al^{3+}]_{limit}$), needed for aluminum hydroxide precipitation was:

$$[Al^{3+}]_{limit} = K_{so}[H^{+}]^{3} \tag{2.40}$$

Jenkins *et al.*, (1984) estimated the amount of aluminum available following aluminum-hydroxy-phosphate precipitation using equations 2.35 and 2.36 as:

$$[Al^{3+}]_{available} = K_{so}{}^{1/r}/[PO_4{}^{3-}]^{1/r}[OH^{-}]^{(3r-3)/r} \tag{2.41}$$

When the ratio of available aluminum to the limiting aluminum concentration exceeded 1.2 (equation 2.42) and the total amount of aluminum dosed exceed the amount of aluminum required for complete precipitation of influent soluble orthophosphate (equation 2.43) the model predicts that two precipitates would be formed.

$$[Al^{3+}]_{avail}/[Al^{3+}]_{limit} > 1.2 \tag{2.42}$$

$$Al_{dose} > rPO_{4(initial)} \tag{2.43}$$

The model of Jenkins, *et al.* indicated that the boundary between one and two precipitates zones depended on the initial PO_4 concentration and equilibrium aluminum concentration. The limiting aluminum concentration was determined on the basis of $Al(OH)_{3(s)}$ solubility and the available aluminum concentration was determined on the basis of aluminum-hydroxy-phosphate solubility.

Jenkins, *et al.* noted a discontinuity occurred at the boundary between zones 1 and 2 which was addressed by manual extrapolation across the boundary. The discontinuity occurred because, in the one precipitate zone the aluminum concentration was assumed to be controlled by the solubility of the aluminum-hydroxy-phosphate solid, but in the two precipitate zone the aluminum concentration was assumed to be controlled by aluminum hydroxide solubility. Two methods of extrapolation were suggested which allowed the prediction of results comparable to those presented by Ferguson and King (1977). Jenkins, *et al.* noted that extrapolation was most often required for cases where soluble orthophosphate residual concentration was between 0.8 and 1.5 mg P/l. Since uncertainty is inherent with extrapolation, they suggested further experimental work should be conducted to describe phosphate removal when orthophosphate residual concentrations in the range requiring extrapolation were reached.

2.3.2 Models Including Adsorption

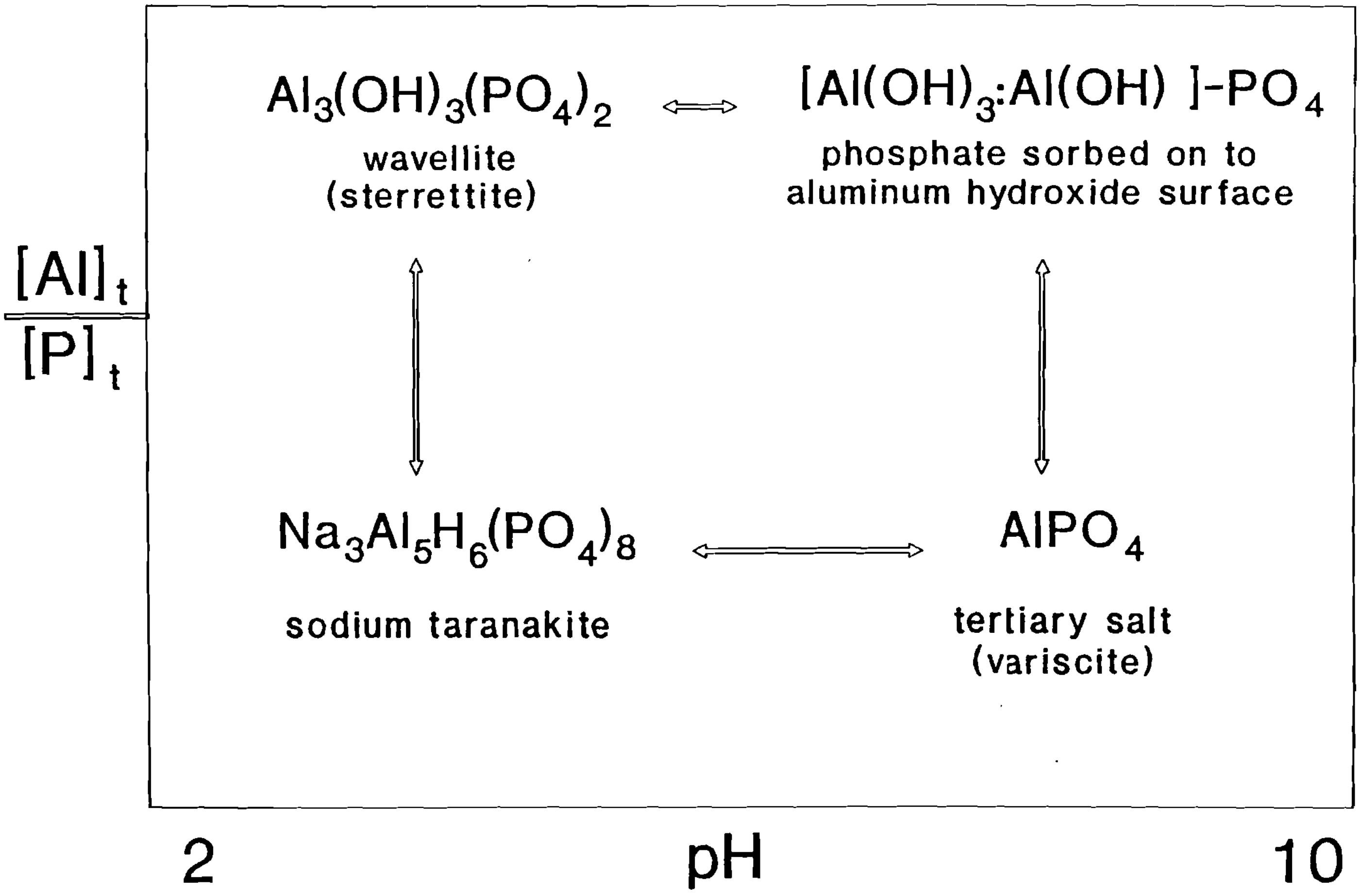
Goldshmid and Rubin (1978) presented a model of chemical phosphorus removal with aluminum (added as $Al(NO_3)_3$) that included both precipitation and adsorption mechanisms. These authors proposed that a variety of aluminum phosphate solids could be precipitated, the exact nature of which depended on pH, and the initial phosphate and aluminum concentrations. The precipitates formed in the jar test were separated, dried and analyzed. These results and the results of phosphometric titrations were used to identify probable solids in aluminum phosphate precipitates (Figure 2.9). On the basis of experiments measuring the soluble aluminum concentration in the pH range 2 through 11 in phosphate solutions (0.1, 0.2, 0.5, and 1.0 M) they concluded that the pH of maximum insolubility for aluminum-and-phosphate-containing precipitates was 6.5 and at this pH transformations were occurring from one solid phase to another. Further, it was proposed that in systems where aluminum was in excess of phosphate and at pH values greater than 6.5, aluminum phosphate solid ($AlPO_4$) hydrolyzed to an aluminum hydroxide solid and soluble phosphate then adsorbed on to the aluminum hydroxide surface.

Goldshmid and Rubin (1978) proposed a mathematical treatment of phosphate adsorption on aluminum hydroxide surfaces based on a model presented by Kurbatov et al. (1951). Adsorption was described by applying mass action laws to the following idealized adsorption reaction:

$$\begin{gathered} v[Al(OH)_3{:}Al(OH)_2]\text{-}OH_{(surf)} \quad + \quad PO_4^{3-} \quad \Leftrightarrow \\ [Al(OH)_3{:}Al(OH)_2]_v\text{-}PO_{4(surf)}^{(3-v)-} \quad + \quad v\ OH^- \qquad (2.44) \end{gathered}$$

Figure 2.9

Transformation Between Phosphate Species
(from Goldshmid and Rubin, 1978)



The following equilibrium expression was derived:

$$K_{ad} = \frac{\{[Al(OH)_3{:}Al(OH)_2]_v\text{-}PO_{4(surf)(3\text{-}v)\text{-}}\}\ [OH^-]^v}{\{[Al(OH)_3{:}Al(OH)_2]\text{-}OH_{(surf)}\}^v[PO_{43\text{-}}]} \quad (2.45)$$

where:

K_{ad} = equilibrium adsorption constant

$\{[Al(OH)_3{:}Al(OH)_2]_v\text{-}PO_{4(surf)}{}^{(3\text{-}V)\text{-}}\}$ = concentration aluminum hydroxide with phosphate adsorbed on to surface

$\{[Al(OH)_3{:}Al(OH)_2]\text{-}OH_{(surf)}\}$ = concentration of aluminum hydroxide available for adsorption

Equation (2.45) was simplified by assuming that the concentration of phosphate sorbed surfaces was equal to the amount of phosphate sorbed and that the total concentration of free surface available for adsorption was a linear function of the applied aluminum concentration:

$$\{[Al(OH)_3{:}Al(OH)_2]_v\text{-}PO_{4(surf)}{}^{(3\text{-}v)\text{-}}\} = [P_i] - [P_f] \quad (2.46)$$

$[P_i]$ = initial phosphate concentration

$[P_f]$ = final phosphate concentration

and

$$\{[Al(OH)_3{:}Al(OH)_2]\text{-}OH_{(surf)}\} = Q[Al_t] \quad (2.47)$$

Q = coefficient of linearity

$[Al_t]$ = applied aluminum concentration

Goldshmid and Rubin combined equations 2.45-2.46 with dissociation relationships for orthophosphate and water and derived the following:

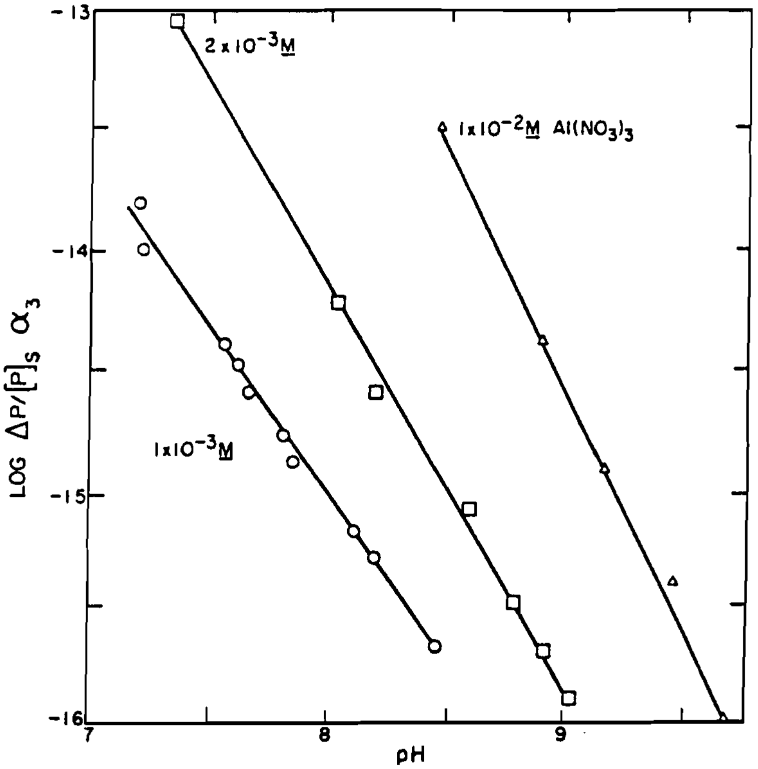
$$\log \frac{P}{[P_f]a_3} = -v(pH) + \log \frac{K_{ad}(Q[Al_t])^v}{K_w^v} \qquad (2.48)$$

Equation 2.48 was plotted using the results of laboratory studies and fitted the experimental results quite well (Figure 2.10). The slope of the isotherms (v) indicated the amount of hydroxide displaced per equivalent of phosphate sorbed. Goldshmid and Rubin observed that the slope (v) increased with increases in the applied aluminum concentration and suggested that this indicated that the activity of the adsorbent ($Al(OH)_3$) depended on the amount of phosphate adsorbed.

The aluminum and phosphate concentration ranges studied by Goldshmid and Rubin (1978) were limited (1×10^{-3} to 3×10^{-4} M phosphate; 1×10^{-3} to 2×10^{-2} M aluminum) and did not encompass the entire range of concentrations encountered in wastewaters. It remains to be determined whether the adsorption model presented by Goldshmidt and Rubin applies to chemical phosphorus removal in activated sludge systems.

Figure 2.10

Phosphate Adsorption Isotherms Described by Goldshmid and Rubin



Plots showing the pH-dependent sorption of phosphate on aluminum hydroxide at three applied aluminum nitrate concentrations. Initial phosphate concentration was 0.001 *M*.

(from Goldshmid and Rubin, 1978)

Luedecke *et al.* (1988) presented a model of ferric phosphate precipitation that included both precipitation and adsorption mechanisms, and defined the conditions required for the formation of one or two precipitates during chemical P-removal. Ferric phosphate precipitation appeared to result from similar mechanisms as aluminum phosphate precipitation and is often modeled in an analogous fashion (Stumm, 1962; Minton and Carlson, 1972; Recht and Ghassemi, 1970; Hsu, 1976). Luedecke *et al.* described four possible precipitation schemes:

- no precipitates
- only metal hydroxy phosphate precipitate
- only metal hydroxide precipitate
- both metal-hydroxy-phosphate and metal hydroxide precipitates

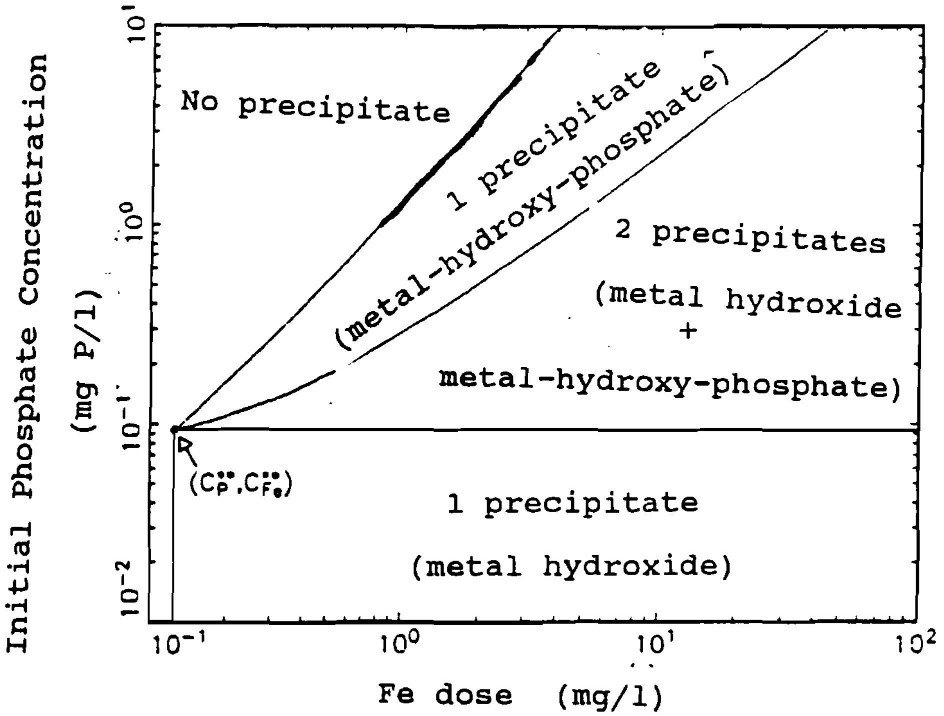
They postulated that the actual zone encountered during chemical P-removal depended on initial phosphate concentration and metal dose. The solubility of ferric phosphate was used together with orthophosphoric acid dissociation equilibria and Fe(III) protolysis equilibria to determine the minimum metal dose required to precipitate ferric phosphate. Luedecke *et al.* suggested that metal doses below the limiting value would not result in the formation of any precipitate, but in the formation of soluble metal phosphate complexes. When the initial concentration of soluble phosphate was lower than the concentration of phosphate in equilibrium with metal phosphate and metal hydroxide, the authors proposed that only aluminum hydroxide precipitate would be formed. Luedecke *et al.* suggested boundaries between metal phosphate precipitation and the two precipitate region similar to those proposed by Jenkins *et al.* (1984). The four precipitation regions suggested by Luedecke *et al.* are shown in Figure 2.11.

Luedecke *et al.* developed equilibrium relationships to describe chemical P-removal similar to those used by Ferguson and King (1977) and Jenkins *et al.* (1984). The model predicted that the ratio of metal dosed to phosphate removed (Me:P) would remain constant as the phosphate residual decreased due to stoichiometric precipitation of metal phosphate. Once the two precipitate region was reached no further decline in phosphate residual would occur and the Me:P ratio would increase dramatically as metal hydroxide precipitated in addition to metal-hydroxy-phosphate. A comparison of batch and continuous flow experimental results with equilibrium based precipitation model predictions (Figure 2.12) indicated that the model did not adequately describe phosphate removal.

Luedecke *et al* (1984) modified their model to include adsorption of orthophosphate on to the chemical precipitates. The amount of adsorbent available for precipitation was determined using material balances, and

Figure 2.11

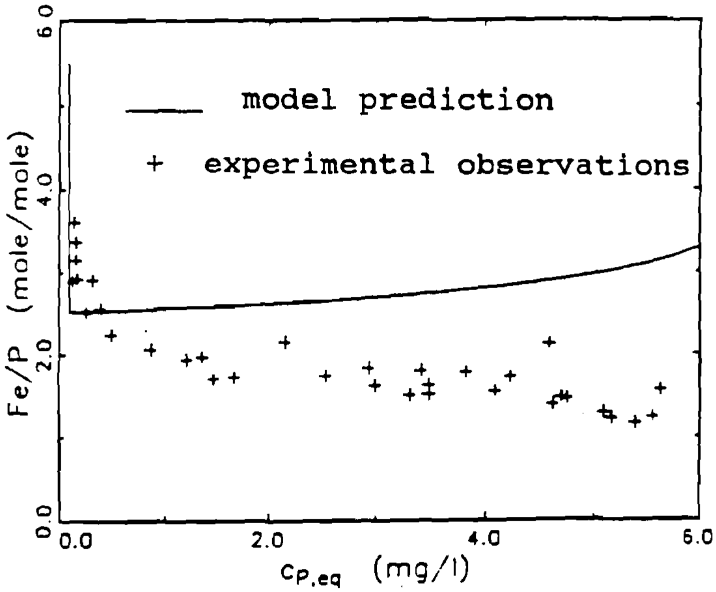
Four Precipitation Regions Defined by Luedecke *et al.*



(adapted with permission from Luedecke *et al.*, 1988)

Figure 2.12

Comparison of Precipitation Based Model Predictions and Experimental Observations of Luedecke *et al.*



(from Luedecke *et al.*)

assuming it was equal to the sum of the metal phosphate and metal hydroxide precipitate concentrations. The equilibrium expression for adsorption used in the model was:

$$Cp_{ads} = K_a * X_a * [PO_4^{3-}]_{res} / [OH^-]^3 \qquad (2.49)$$

where:

Cp_{ads} = concentration of adsorbed phosphate

K_a = adsorption coefficient

X_a = amount of adsorbent

with:

$$X_a = (3r-3) * C_{p,ppt} + C_{Me,ppt} \qquad (2.50)$$

where:

$C_{p,ppt}$ = amount of metal phosphate precipitate

$C_{Me,ppt}$ = amount of metal hydroxide precipitate

When these relatioships were included in the chemical P-removal model, Luedecke *et al.* were able to fit ferric phosphate precipitation significantly better than with the model based solely on precipitation (Figure 2.13).

Figure 2.13

Agreement Between Model of Luedecke *et al.* Including Adsorption and Experimental Observations

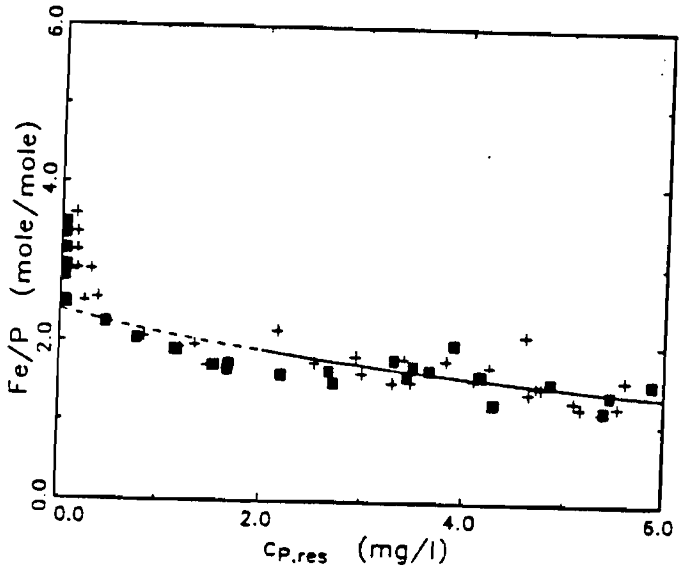


Fig. 5. Observed and calculated values of Fe/P ratios for pH=6.8 (+ observed, • calculated, solid and broken lines: estimation of r)

(From Luedecke *et al.*, reprinted with permission)

3 RESEARCH RATIONALE

3.1 Research Rationale

Existing models of aluminum phosphate precipitation are largely conceptual and theoretical. They are not readily useable for predicting the performance of P removal in a wastewater treatment facility nor are they expressed in terms of readily measurable field parameters. Of the existing models of aluminum phosphate precipitation that of Ferguson and King (1977) is the most often cited although it is subject to limitations, many of which are also found in other models of aluminum phosphate precipitation. For example the Ferguson and King (1977) model of aluminum phosphate precipitation allows the prediction of orthophosphate residual concentration while most phosphate discharge standards are in terms of total phosphate concentration.

Laboratory and field scale studies (Recht and Ghassemi, 1970; Eberhardt and Nesbitt, 1968) have revealed that, at low alum doses, the amount of soluble orthophosphate removed was directly proportional (stoichiometric) to the amount of aluminum ion dosed to the wastewater. This behavior is consistent with the hypothesis that a constant composition aluminum phosphate solid is formed (Ferguson and King, 1977; Stumm and Morgan, 1962). The nature and stoichiometry of this solid is unclear although, as a simplification, $AlPO_4$ with a stoichiometric ratio (Al:P) of 1 is sometimes used (Stumm and Morgan, 1962; Snoeyink and Jenkins, 1980; Goldshmid and Rubin, 1978). Stoichiometric ratio values ranging from 1.0 to 2.75 can be found in the literature (Recht and Ghassemi, 1970; Lea, *et al*. 1954; Sawyer, 1972; Goldshmid and Rubin, 1978). A better understanding of the stoichiometry of the aluminum phosphate solid would help in determining the appropriate aluminum dose needed to obtain a given phosphate residual in the stoichiometric region.

The point of transition between stoichiometric and non-stoichiometric phosphorus removal is poorly defined. The location of this point is of considerable importance because, in the non-stoichiometric region, higher Al:P dose ratios are required, resulting in increased chemical and sludge disposal costs. Since many of the effluent phosphate standards set will require phosphate residuals in this region, clarification of this issue is important.

The mechanism of non-stoichiometric P removal requires further study to understand role of aluminum in P removal at high dose ratios (Al:P > 1.0). If the primary role of aluminum is to reduce pH once aluminum phosphate solubility is exceeded (Stumm, 1964; Ferguson and King, 1977; Snoeyink and Jenkins, 1980), this could perhaps be more economically achieved using other acids. If aluminum forms a solid phase subject to adsorption (Goldshmid and Rubin, 1978; Henriksen, 1962; Corey, 1981) its role in chemical P removal is more significant than pH reduction and may be better described on the basis of adsorption.

There is some disagreement in the literature concerning the nature of the phosphorus removal mechanism in the non-stoichiometric region. Compelling arguments exist for both an adsorption and a precipitation-based mechanism of non-stoichiometric phosphate removal (Stumm, 1964; Hsu, 1975; Lea *et al.*, 1954; Henriksen, 1962; Goldshmid and Rubin, 1978; Ferguson and King, 1977; Luedecke *et al.*, 1988). Stumm (1962) was able to describe chemical P removal strictly on the basis of precipitation and stated that even though phosphate removal could be described using adsorption isotherms, the use of isotherms did not conclusively demonstrate that adsorption occurred during chemical P removal. Goldshmid and Rubin (1978) felt that observations of chemical P removal were best described by a combination of mechanisms including adsorption, depending on the initial concentration of phosphate and aluminum.

Many of the models of aluminum phosphate precipitation were calibrated using the results of experiments conducted in distilled water solutions. These type of experiments do not take into consideration the effects of other components found in wastewaters and the presence of biomass when simultaneous aluminum phosphate precipitation is practiced in activated sludge systems. This is particularly important with respect to the removal of condensed phosphates.

The extent of condensed phosphate hydrolysis and its impact on chemical P removal has been addressed but is not included in most models of aluminum phosphate precipitation. Stumm (1964) proposed that condensed phosphate has a strong tendency to form soluble complexes with aluminum, and that tripolyphosphate could not be removed by aluminum. Others (Sawyer, 1962; Lin and Carlson, 1975) found that aluminum phosphate precipitation resulted in a reduction in both condensed and ortho phosphate concentration. These studies did not determine whether the condensed phosphate reduction resulted from the precipitation of a solid containing condensed phosphate or of orthophosphate solids formed from condensed phosphate hydrolysis. If, as might reasonably be expected, condensed phosphate hydrolysis is significant, this could result in lower stoichiometric ratio values because more soluble orthophosphate is being removed from solution than predicted by measurement of only the influent and effluent orthophosphate concentrations.

The effect of pH on aluminum phosphate precipitation is not well defined. A wide range of optimum pH values can be found in the literature (Stumm, 1964; Snoeyink and

Jenkins, 1980; Recht and Ghassemi, 1970). Many optimum pH values were determined using distilled water solutions or using estimates of the solubility product of aluminum phosphate and aluminum hydroxide solids. Studies on pilot or full scale activated sludge systems typically report the pH of the influent and effluent but do not report or control the pH at the point of mixing or in the aeration basin. This is not appropriate because of the rapid rate of aluminum phosphate precipitation reactions.

3.2 Research Objectives

The primary goal of this study is to develop a model of orthophosphate removal from wastewater by the addition of aluminum salts directly to the aeration basin of activated sludge systems. The objective was to develop a model with as general a form as possible, with applicability to full scale processes, and with significant calibration using controlled laboratory experimental data. Specific goals were:

1. To clarify or define the boundary between the stoichiometric and non-stoichiometric P removal regions.
2. To estimate relevant stoichiometric coefficients and stability constants for the chemical precipitates formed.

3. To determine whether precipitation or adsorption, better describes orthophosphate removal in the non-stoichiometric removal region.
4. To investigate the impact of condensed phosphate hydrolysis on aluminum phosphate precipitation.
5. To investigate the effect of pH on aluminum phosphate precipitation.

4 EXPERIMENTAL METHODS, MATERIALS, AND SCOPE

The general objective of this research was to develop a model for predicting the performance of chemical P removal processes using alum as a precipitant added to the aeration basin of activated sludge systems. This general objective was reached by the fulfillment of the following specific objectives:

(1) Development of a predictive model based on aluminum phosphate precipitation in controlled pH batch aluminum phosphate experiments.

(2) Calibration of the predictive model using a bench-scale continuous-flow activated sludge system.

(3) Application of the results of the calibrated model to predict P-removal by alum addition in practice.

4.1 Continuous Flow Experiments

4.1.1 Materials

Continuous flow experiments were carried out in a 37-l bench scale activated sludge system consisting of a feed reservoir, aeration basin, secondary clarifier and an effluent reservoir. The aeration basin was constructed from a 30 cm x 46 cm x 62 cm rotationally molded 0.65 cm thick polyethylene tank. Mixed liquor flowed by gravity from the aeration basin to a 10-l secondary clarifier constructed from a 4-l Erhlemeyer flask with its bottom removed and attached to a 20-cm diameter x 24 cm plexiglass cylinder. Treated effluent flowed by gravity from the clarifier into a 160 l effluent reservoir. A schematic of the bench scale activated sludge system is shown in Figures 4.1 and 4.2.

4.1.1.1 Mixing and Aeration

Mixing in the aeration basin was provided by four flat blade impellers attached to a sprocket and pulley system driven by a Bodine 0.05 Hp motor coupled with a Minarik variable speed controller. Compressed air was provided to the aeration basin through 6 submerged air stones. The air stones were secured using 1/4 in Swagelock fittings permanently attached to holes drilled around the lower perimeter of the aeration basin.

4.1.1.2 pH Control

The pH of the mixed liquor in the aeration basin was held constant at 7.2 for the duration of the continuous flow experiments using a Chemtrix Type 45A pH/MV Controller-Recorder. An Orion model 91-05 combination pH

Figure 4.1
Continuous Flow Activated Sludge System

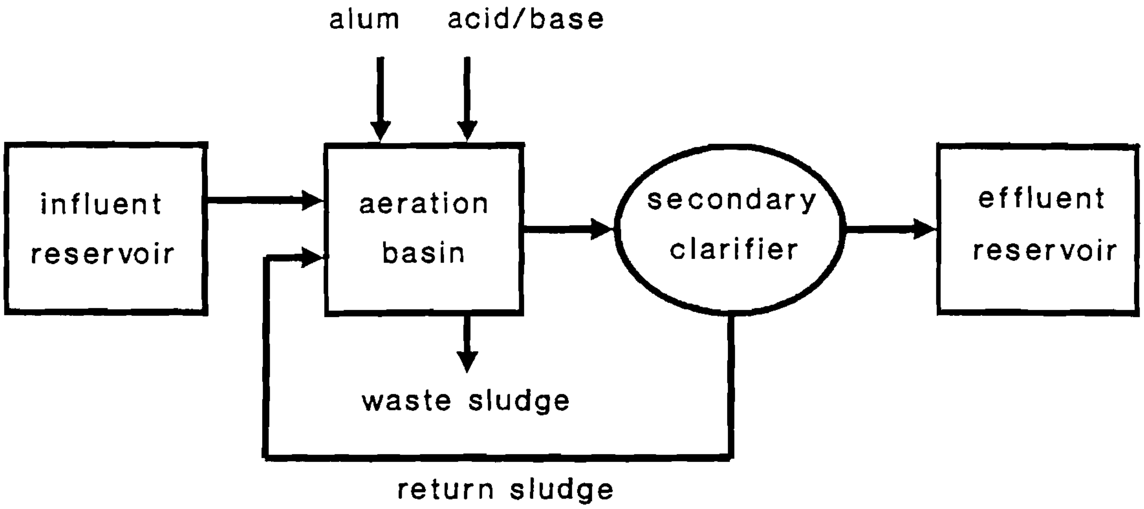
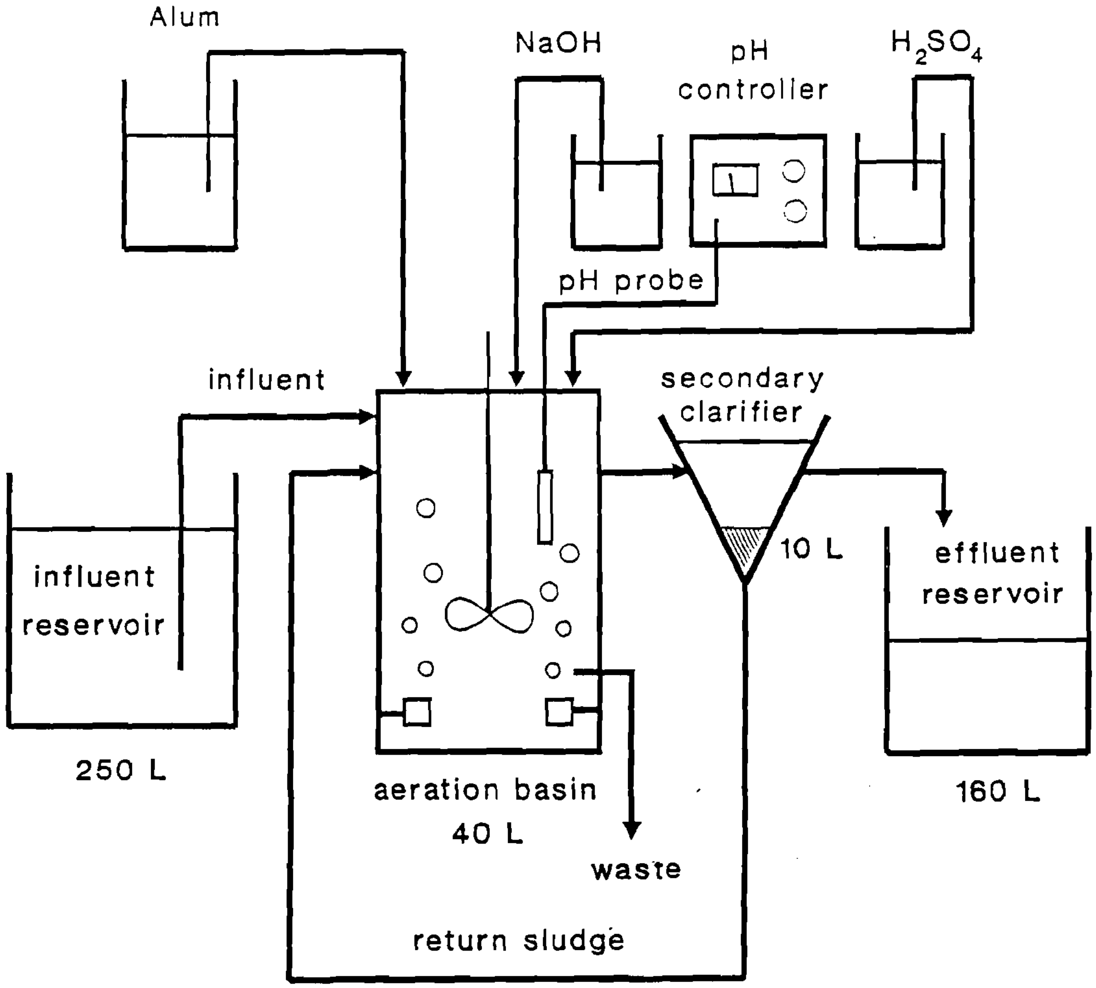


Figure 4.2
Continuous Flow Activated Sludge System



electrode was submerged in the aeration basin near the mixed liquor overflow. The low and high set points for the pH controller were set at 7.1 and 7.3 respectively. When the aeration basin pH was lower than pH 7.1, 0.25 N sodium hydroxide (NaOH) was added to the aeration basin, at the rate of 1 ml/min, using a Sage Instruments Model 375A peristaltic tubing pump. Base addition continued until the aeration basin pH returned to the allowable range. When the aeration basin pH exceeded 7.3, 0.1 N sulfuric acid (H_2SO_4)was added to the aeration basin at the rate of 1 ml/min using a Sage Instruments Model 375A peristaltic tubing pump.

4.1.1.3 Alum Addition

An aluminum sulfate solution was prepared daily for dosing to the aeration basin using 'Baker Analyzed' Reagent grade aluminum sulfate ($Al_2(SO_4)_3.18H_2O$). The fresh alum solution was placed in a 1-l graduate cylinder and fed directly to the aeration basin at the rate of 1 l/day using a Sage Model 375A peristaltic tubing pump at a point approx. 10 cm below the liquid surface and midway between the influent and recycle feed points.

4.1.1.4 Feed

The continuous flow activated sludge system was fed with City of Richmond, CA settled domestic sewage obtained from the SEERHL wastewater treatment plant. Fresh settled sewage was pumped to the feed reservoir daily and from this vessel the activated sludge system was fed at the rate of 60 ml/min using a Cole-Parmer Masterflex pump and controller.

4.1.1.5 Operation and Maintenance

The bench scale activated sludge system was started up using East Bay Municipal District (EBMUD) Oakland, CA return activated sludge (RAS). The continuous flow activated sludge system was operated at a constant mixed liquor volatile suspended solids (MLVSS) concentration of 1500 mg/L and a mean cell residence time (MCRT) of 8 days.

A regular maintenance schedule was followed to prevent unwanted wall growths and/or septic conditions from developing. The feed reservoir was drained and washed out daily. The inside walls of the aeration basin and clarifier were brushed daily. Influent tubing was squeezed to remove wall growth build-up when necessary.

4.1.2 Scope of Continuous Flow Experiments

4.1.2.1 Control Study

First a series of bench scale activated sludge experiments were conducted without alum addition to determine the extent of condensed phosphate hydrolysis in the feed reservoir and aeration basin and to determine COD removal efficiency. Additionally, the results of these experiments allowed a phosphate mass balance to be determined. Experiments without alum addition were conducted over two separate 6-week periods. Influent samples were taken at the feed tube inlet to the aeration basin immediately upon filling the feed reservoir with fresh settled sewage and then again after 24 hr. Effluent samples were taken 24 hr after filling the feed reservoir. A 24-hr composite effluent sample was obtained by thoroughly mixing the effluent reservoir contents with a mixing rod and then withdrawing a sample from well below the surface. Mixed liquor grab samples were also taken during this series of experiments. A portion of every sample was filtered through a combination of a Whatman Glass Microfibre (GFC) and an 0.45 μm Millipore membrane filter. Filtered and unfiltered samples were placed in separate 100 ml acid-washed glass storage bottles and stored at 4°C. No chemical preservatives were added to any of the stored samples. Every effort was made to analyze all samples within 48 hr of sampling. All control study samples were analyzed for total, total soluble and ortho phosphate, TSS and VSS, soluble calcium and soluble COD. The alkalinity of the mixed liquor samples was measured.

4.1.2.2 Precipitation Study

The aluminum phosphate precipitation study consisted of 9 series of continuous flow experiments. Alum doses to the aeration basin ranged between 2 and 25 mg Al/l of sewage. Each series of experiments consisted of a 3-week equilibration period followed by 4-8 weeks of sampling and analysis. Influent samples were taken immediately after the feed reservoir was filled and then 24 hr later as described in the control study (4.1.2.1). Effluent composite samples were taken from the effluent reservoir 24 hr after initial feeding. Influent and effluent samples were analyzed for total, total soluble and ortho phosphate.

4.2 Batch Experiments

4.2.1 Materials

Batch experiments were run in 3 parallel systems each consisting of a 2-l glass graduate cylinder (Figure 4.3).

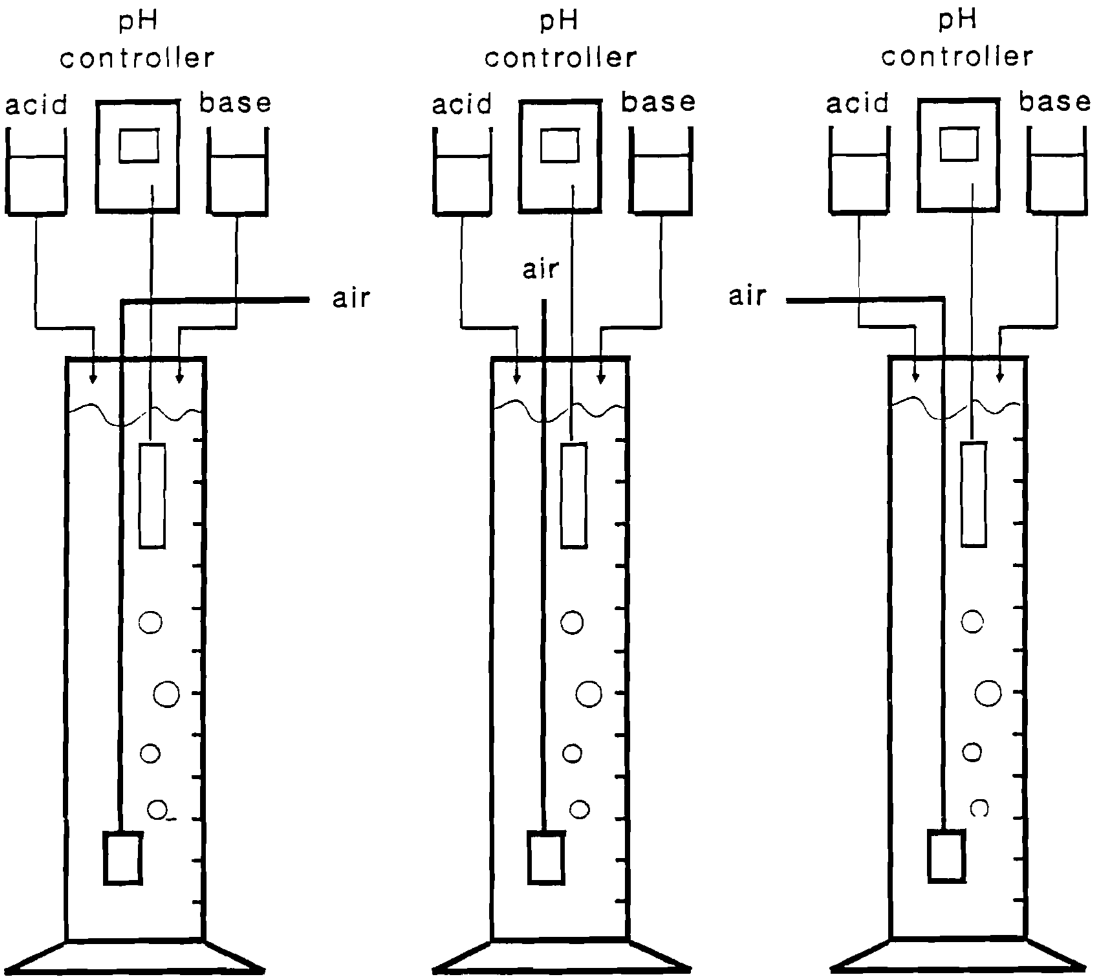
4.2.1.1 Mixing and Aeration

The contents of the batch systems were mixed with compressed air fed to each batch reactor through a 1 cm x 2.5 cm cylindrical air stone. The air flow rate was regulated using a Brooks-Mite gas flow meter adjusted to maintain a constant air flow rate of 3.5 SCFH.

4.2.1.2 Feed

Each batch reactor was filled with a mixture of 1-l of mixed liquor from the continuous flow activated sludge system and 1-l of primary settled sewage taken either from the laboratory sewage feed line or from the feed reservoir of the continuous flow activated sludge system. In the event that the amount of mixed liquor to be wasted from the activated sludge reactor was insufficient to provide mixed liquor for a series of batch experiments, additional

Figure 4.3
Batch Experiment Setup



quantities of mixed liquor were obtained from a fill-and-draw activated sludge system (Section 4.3).

4.2.1.3 pH Control

The contents of the batch reactors were maintained at a constant pH using Cole-Parmer model 5652-00 pH meter-controllers. Cole-Parmer model 60648 combination pH electrodes were used for pH measurement. Additions of either 0.025 M NaOH or 0.025 M H_2SO_4 were used to maintain the desired pH value using Masterflex tubing pumps.

4.2.2 Methods

All batch experiments were conducted as follows:

(i) The batch reactors were filled with the sewage/mixed liquor feed described in Section 4.2.1.2.

(ii) Aeration was initiated and the pH of the systems was adjusted to the desired value.

(iii) Aeration was continued and the pH controlled at the desired value for a period of 2 hr.

(iv) Following this initial 2 hr period, a sample was withdrawn and a measured dose of alum solution was added to each batch system.

(v) After alum addition, aeration and pH control continued for each batch reactor for 1 hr.

(vi) A final batch sample was withdrawn for analysis.
All sample were filtered through a combination of Whatman Glass Microfibre (GFC) and 0.45 µm Millipore membrane filters immediately upon withdrawal. The batch procedure is summarized in Figure 4.4.

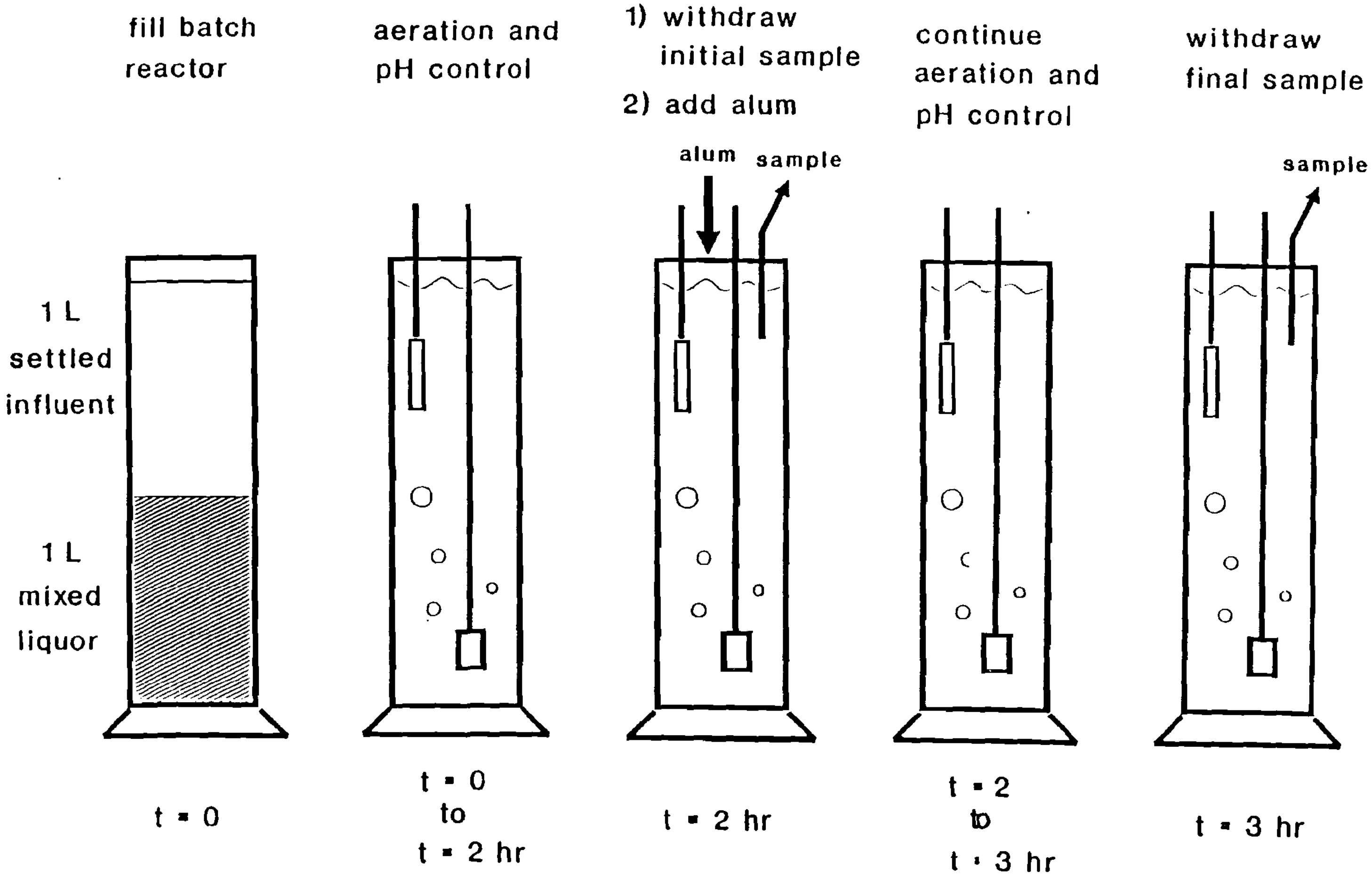
4.2.2.1 Equilibration Studies

For the equilibration studies pre-alum and post-alum addition periods of 8 hr were investigated during which samples were withdrawn every 10 min for the first 2 hr and then hourly for a further 8 hr. The equilibration study samples were analyzed for total, total soluble and ortho phosphates and soluble calcium. Alkalinity measurements were made for selected pre-alum addition experiments. Based on the results of these studies a pre-alum addition mixing time of 2 hr and a post-alum addition time of 1 hr were selected for the batch precipitation studies.

4.2.2.2 Batch Precipitation Studies

Batch precipitation studies were conducted at pH values of 6.0, 6.5, 6.8, 7.0, 7.2,and 7.5. Twenty four alum doses of between 0.5 and 100 mg Al/l of sewage were investigated at each pH. In runs with high alum doses, concentrated NaOH (10 M) was added to the batch reactor immediately

Figure 4.4
Batch Experimental Procedures

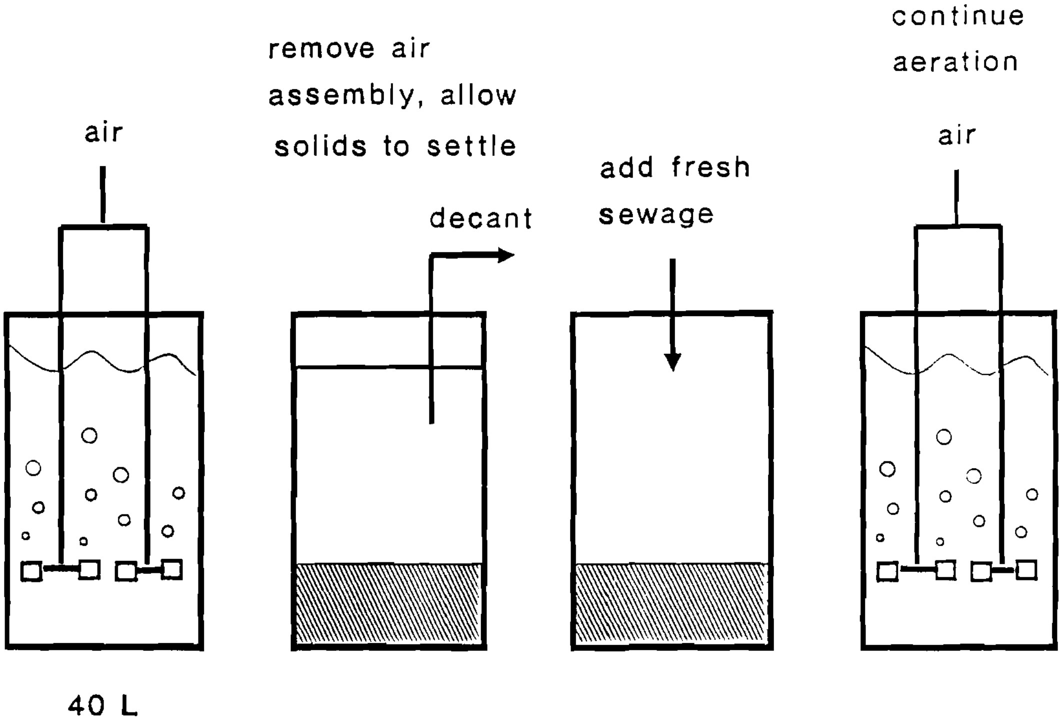


after alum addition to prevent foaming problems associated with sustained low pH. The liquid volume contained in the batch reactors was recorded prior to sample withdrawal. Samples were stored at 4°C up to a maximum of 5 days before analysis. All samples were analyzed for soluble orthophosphate. Soluble calcium concentration was measured in the precipitation studies at pH values of 6.0, 6.5, 7.2, and 7.5.

4.3 Fill-and-Draw Reactor

A fill-and-draw batch activated sludge system consisting of a 40-l plexiglass aeration basin was operated to supply mixed liquor for the batch studies. Feed for the fill-and-draw activated sludge system was waste mixed liquor from the continuous flow activated sludge system. Air to the fill-and-draw system was provided through a removable airstone assembly and was sufficient to keep the contents well mixed (see Figure 4.5). On a regular basis (daily during batch studies, bi-weekly at other times) aeration was stopped and the sludge allowed to settle, after which the supernatant was withdrawn and discarded. Fresh settled sewage was then added to the fill-and-draw reactor to a volume of 40-l. Since mixed liquor was withdrawn from the fill-and-draw reactor on a regular basis for batch studies, no additional wasting of solids was practiced.

Figure 4.5
Fill and Draw Reactor Operation



4.4 Analytical Methods

The following analytical methods were used:

(i) Influent and effluent samples were analyzed for COD using the Open Reflux Method (Standard Methods(1985)# 508A).

(ii) Influent, effluent and mixed liquor total, total soluble and soluble orthophosphate concentrations were determined using the ascorbic acid method (Standard Methods (1985) #424-F) and the persulfate digestion method (Standard Method (1985) # 424C-III). A 1.0 cm light path was used for spectrophotometric analysis.

The detection limit of the spectrophotometer used to measure orthophosphate concentration was determined after running a series of phosphate standards. The detection limit of the Coleman spec 55 was found to be 0.0108 mg P/L. This value is significant because Standard Methods indicates that with 1 cm curvettes the detectable phosphate range lies between 0.15 and 1.3 mg P/L. Experimental results indicate that linearity is followed in the range well below that given in Standard Methods.

(iii) Mixed liquor samples were analyzed for total suspended solids (TSS) and volatile suspended solids (VSS) using Standard Methods (1985) #209 A-D.

(iv) The alkalinity of the mixed liquor samples was determined using sulfuric acid titration (Standard Methods (1985) #403).

(v) Soluble calcium and aluminum were measured by atomic adsorption spectrophotometry (Standard Methods 311 A and 306 A) using at least three standards with each series of samples analyzed.

5 EXPERIMENTAL RESULTS

5.1 Continuous Flow Experiments

5.1.1 Control Study

Two series of mass balance experiments were conducted with the objective of evaluating the accuracy of analytical methods and determining the extent of condensed phosphate hydrolysis in the continuous flow activated sludge system. The forms of phosphorus measured are summarized in Table 5.1. Mass balances on total, particulate, total soluble, and soluble ortho phosphate were determined using the following mass balance relationship:

$$\begin{array}{l}\text{rate of change}\\ \text{of P mass}\\ \text{with time}\end{array} = \text{mass in} - \text{mass out} \pm \text{net accumulation} \qquad (5.1)$$

All mass balances were calculated assuming steady state conditions existed. Therefore, the rate of change of the phosphate mass with time was equal to zero. A sample mass balance calculation is given in Figure 5.1. The results of the control study mass balances are presented in Tables 5.2 - 5.3, and indicate that a material balance can be closed for total and particulate phosphate fractions.

Table 5.1
Phosphate Forms Used in Control Study

Measured:

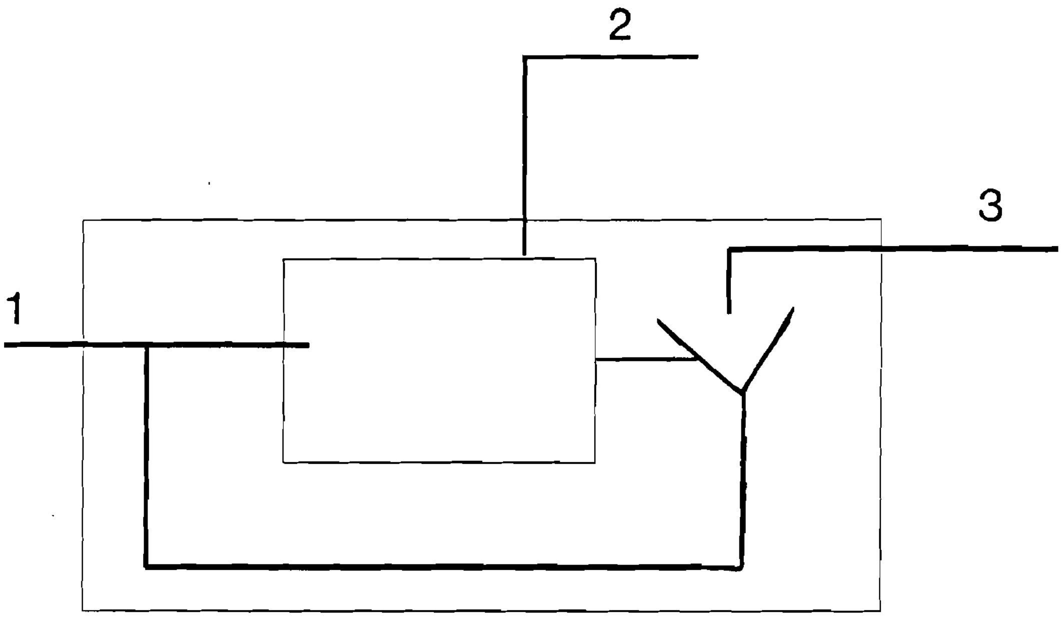
- Total Phosphate (TP)
- Total Soluble Phosphate (TSP)
- Ortho Phosphate (soluble) (SOP)

Calculated:

- Particulate Phosphate (PP)
  PP = TP - TSP

- Soluble Non-Ortho Phosphate (SNOP)
  SNOP = TSP - SOP

Figure 5.1
Phosphate Mass Balance Sample Calculation



Total Phosphate Mass Balance

Total P in (1) = 5760 mg

Total P out = Waste + Effluent (2 + 3)
= 5180 mg + 636 mg = 5816

net accumulation = -(mass in - mass out)
= 56 mg

Table 5.2
Phosphate Mass Balance Results

Expt #1	mass in (mg)	mass out (mg)	net accum *	% change
TP	5760	5820	+60	1.0
PP	790	780	-10	1.2
SNOP	680	140	-540	79
SOP	4280	4980	+700	16

* net accumulation

+ = generation
− = depletion

Table 5.3
Phosphate Mass Balance Results

Expt #2	mass in (mg)	mass out (mg)	net accum *	% change
TP	3910	3970	+60	1.5
PP	800	770	-30	3.8
SNOP	360	90	-270	75
SOP	2760	3110	+350	13

* net accumulation

\+ = generation
\- = depletion

There is an average 15% increase in the ortho phosphate fraction and an average decrease of 77% in the soluble non-ortho phosphate fraction.

5.1.2 Aluminum Mass Balance

An attempt was made to conduct a mass balance on aluminum but the effluent dissolved Al level was below the limit of detectability of the most sensitive atomic absorption spectrophotometer used (Perkins Elmer model 308A; Al^{3+} detection limit 1.0 μg/ml). It was concluded that all of the aluminum dosed to the continuous flow reactor was incorporated into a chemical precipitate or adsorbed on solids.

5.1.3 Continuous Flow Controlled pH Study

Continuous flow experiments were conducted at a constant pH of 7.2 using 9 alum doses yielding between 1.8 and 27.5 mg Al^{3+}/l. The results of these continuous flow experiments are shown in Figures 5.2 through 5.10. Figure 5.11 shows the soluble orthophosphate (SOP) residual (mg P/l) plotted as a function of the removal ratio, defined as the ratio of the amount of aluminum dosed per mole of SOP removed:

$$R = \text{Al dose (mole)} / \text{PO}_4 \text{ removed (mole)} \qquad (5.2)$$

where:

R = removal ratio

PO_4 removed = PO_4 influent (mole) - PO_4 effluent (mole)

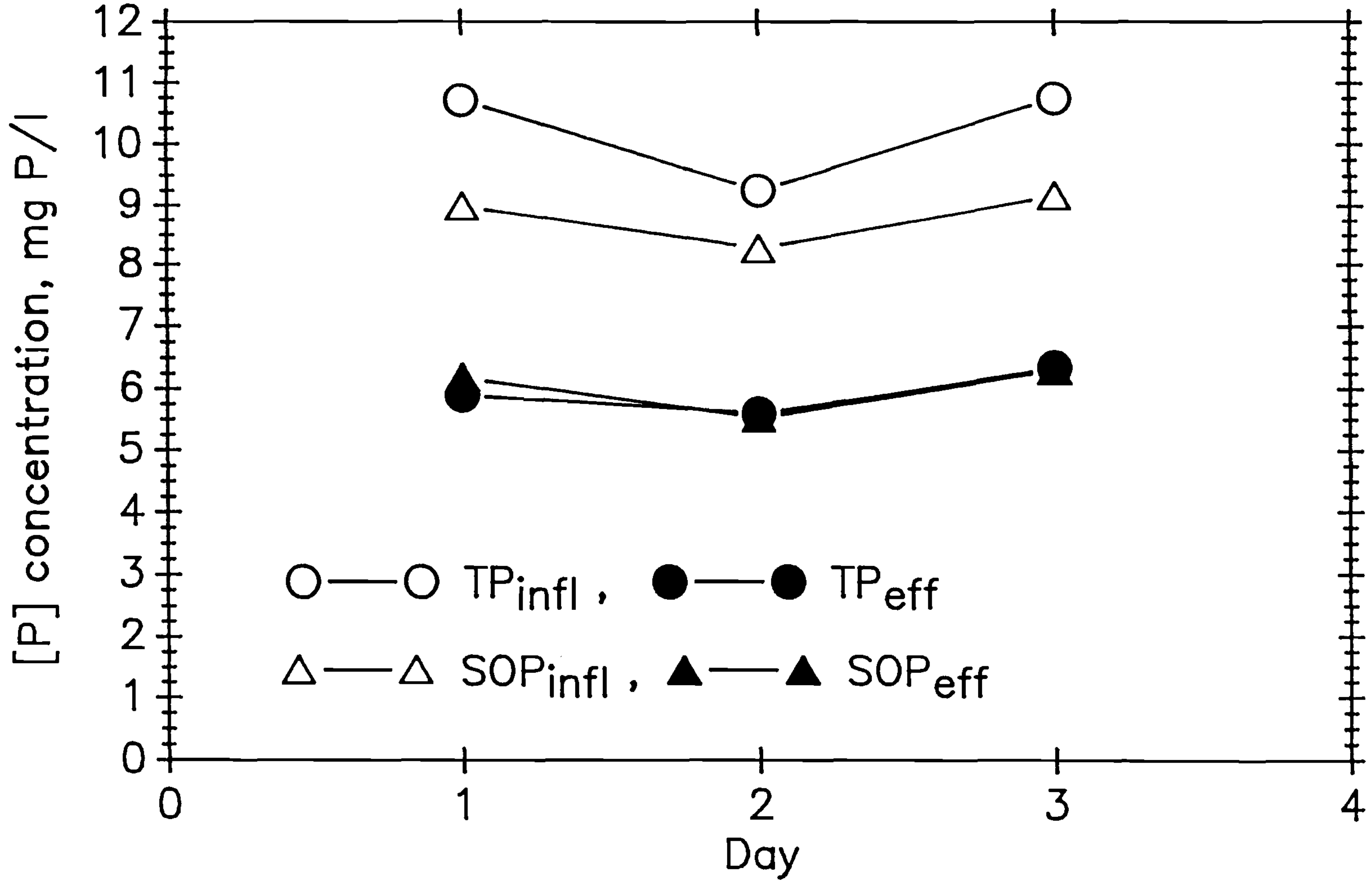


Figure 5.2 Continuous flow experimental results with Alum dose #1 (1.8 mg Al$^{(III)}$ /l).

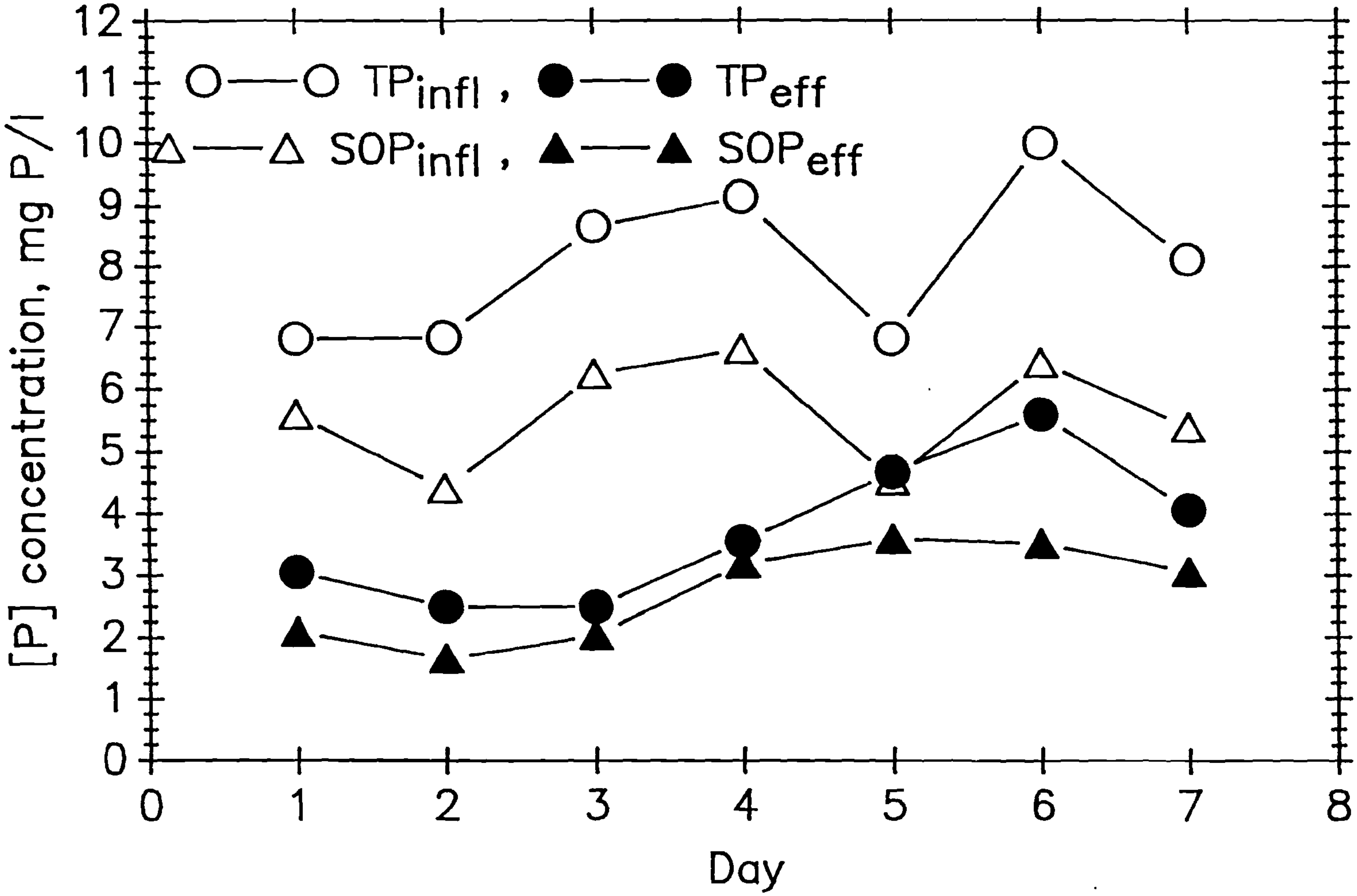


Figure 5.3 Continuous flow experimental results with alum dose #2 (3.5 mg Al(III) /l).

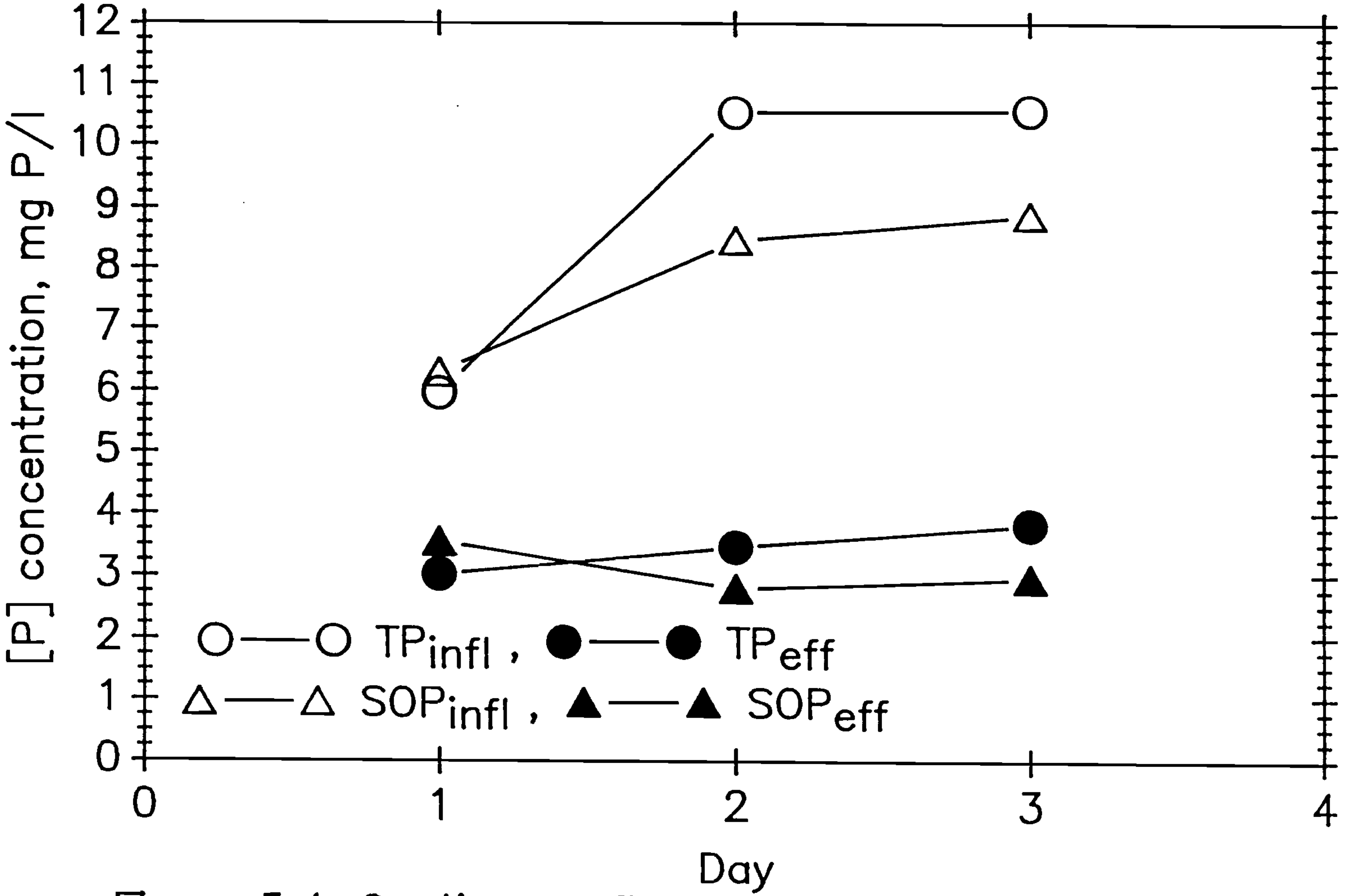


Figure 5.4 Continuous flow experimental results with alum dose #3 (6.8 mg Al(III) /l).

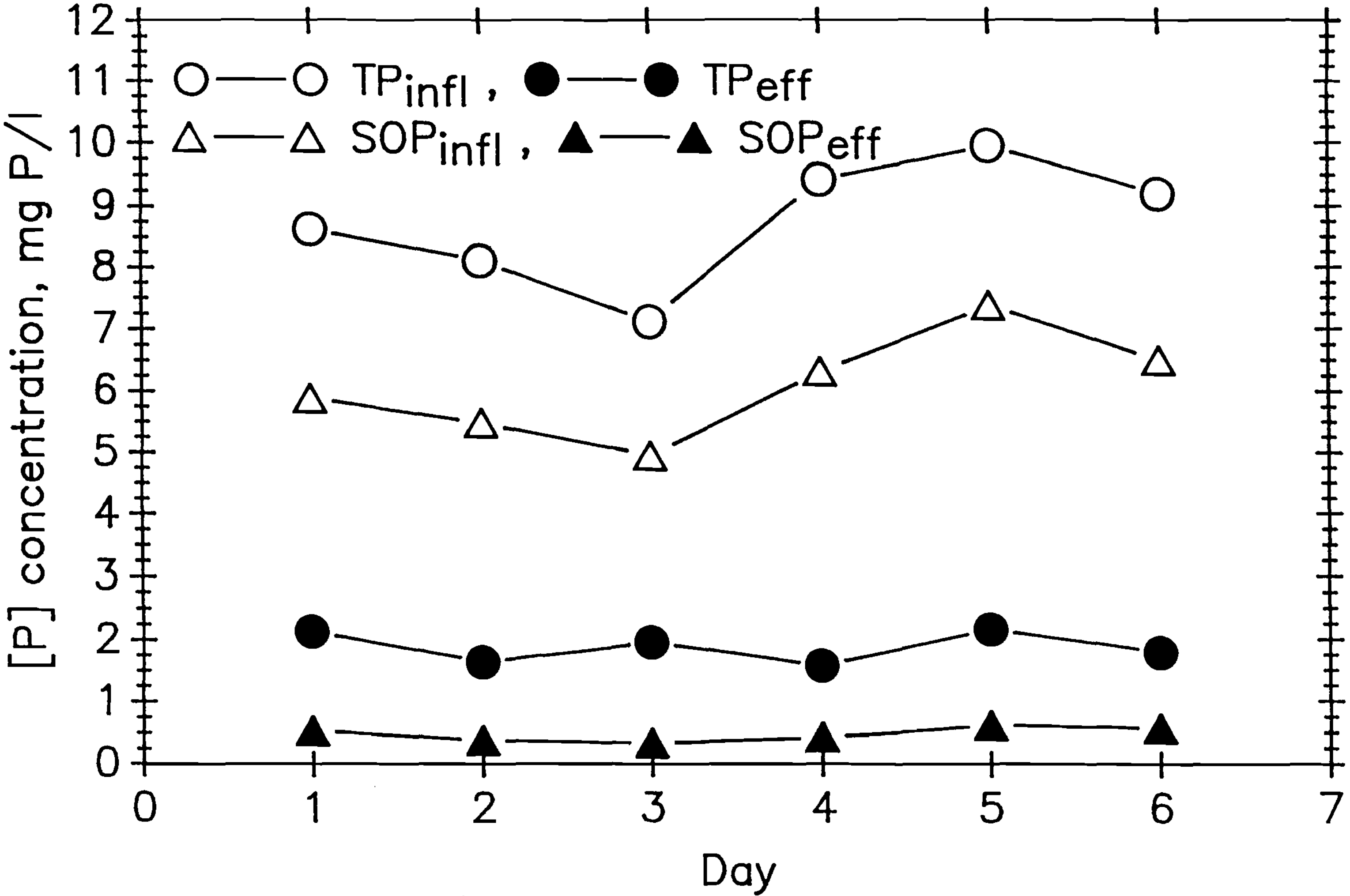


Figure 5.5 Continuous flow experimental results with alum dose #4 (8.5mg Al$^{(III)}$ /l).

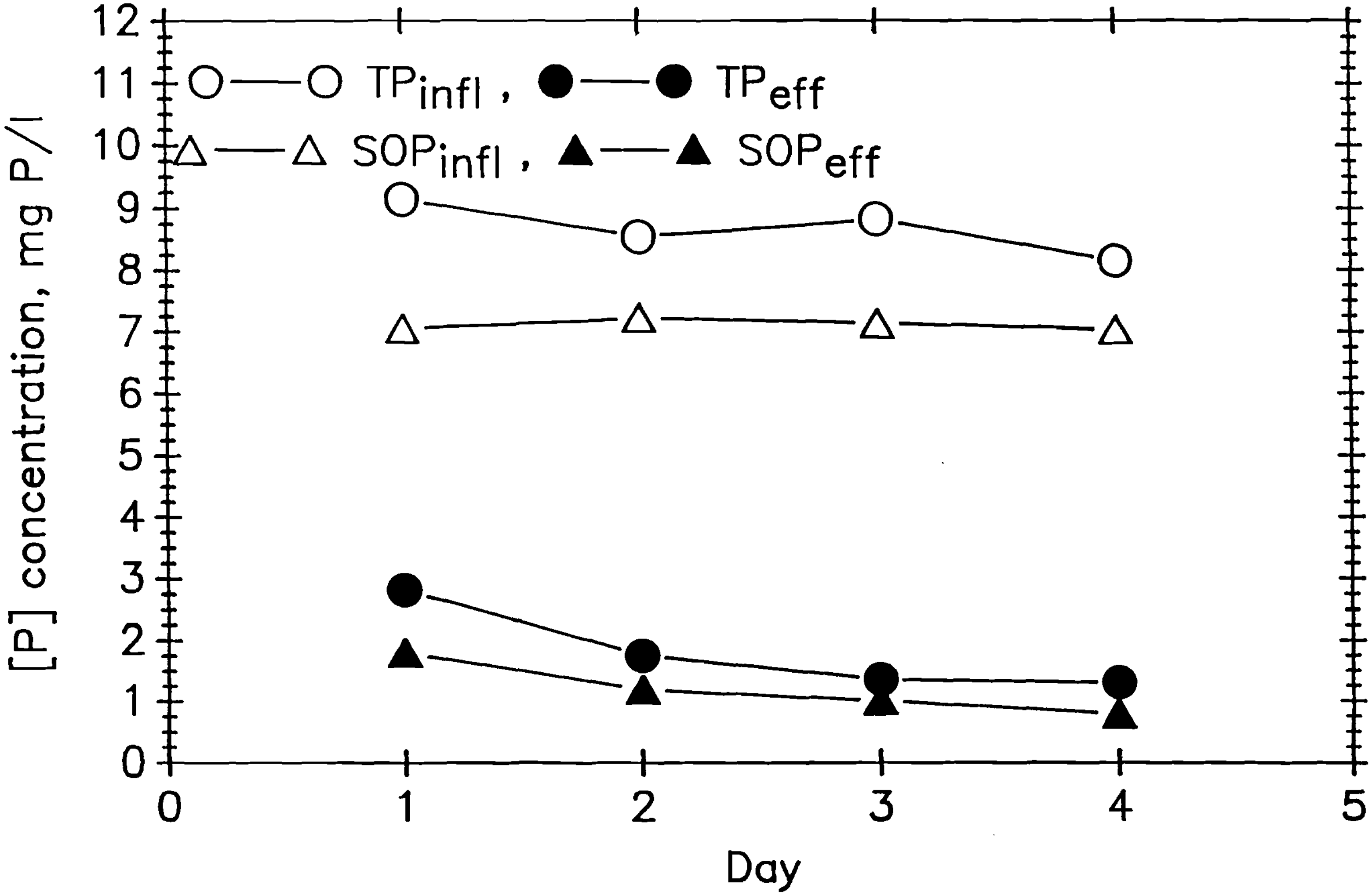


Figure 5.6 Continuous flow experimental results with alum dose #5 (10 mg Al$^{(III)}$ /l).

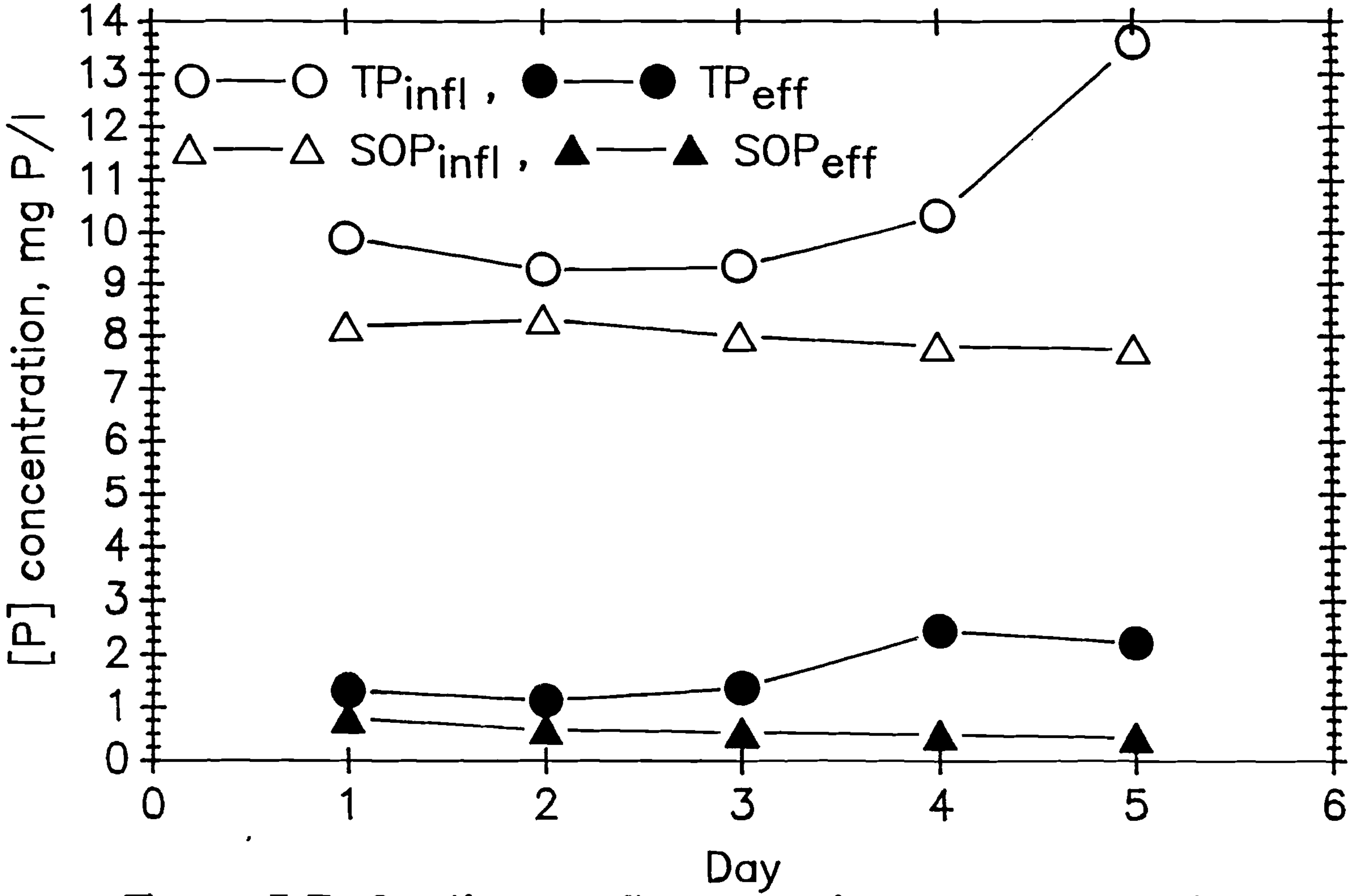


Figure 5.7 Continuous flow experimental results with alum dose #6 (13 mg Al(III) /l).

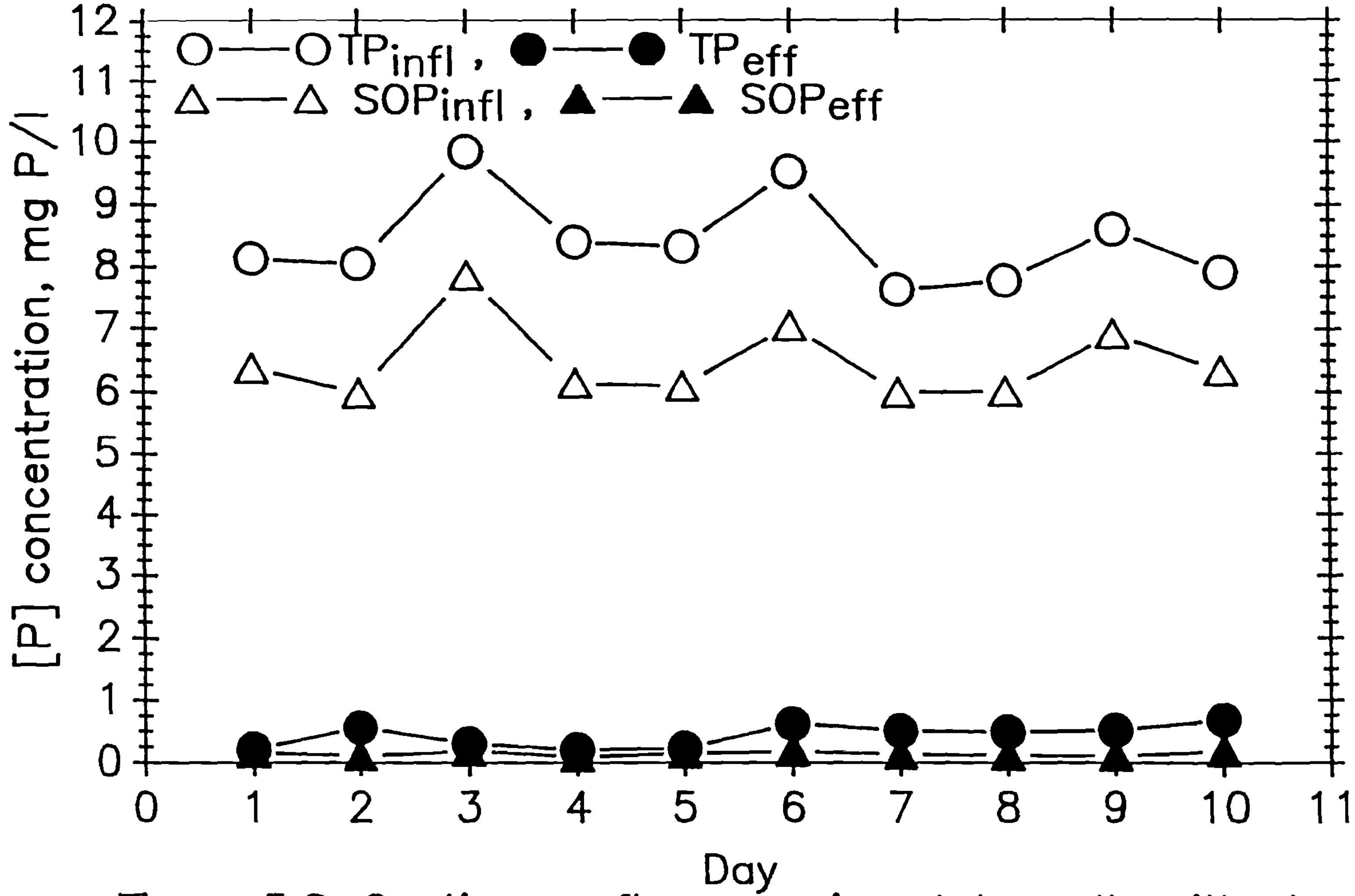


Figure 5.8 Continuous flow experimental results with alum dose #7 (17 mg Al(III) /l).

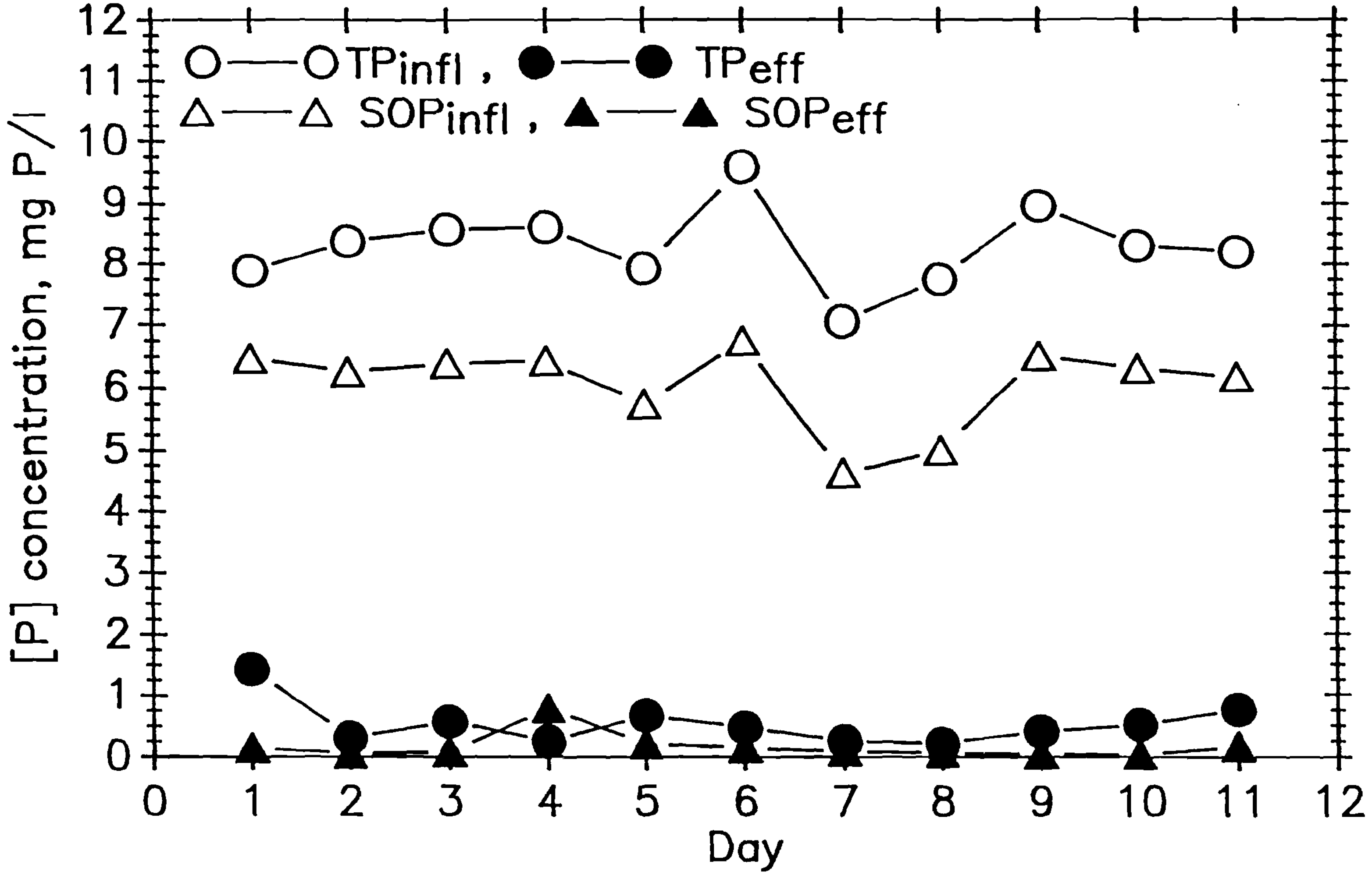


Figure 5.9 Continuous flow experimental results with alum dose #8 (20 mg $Al^{(III)}$ /l).

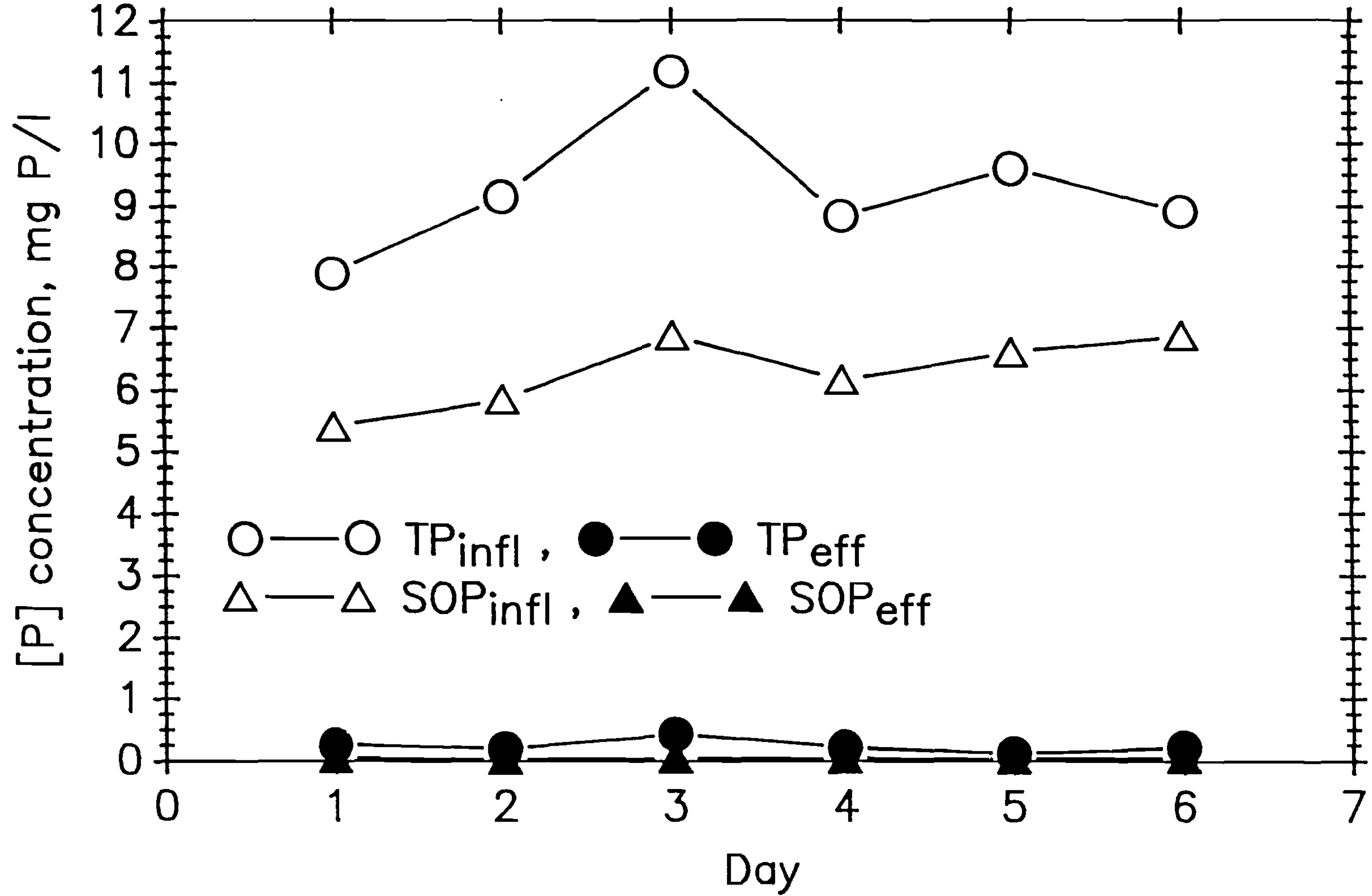


Figure 5.10 Continuous flow experimental results with alum dose #9 (27 mg $Al^{(III)}$ /l).

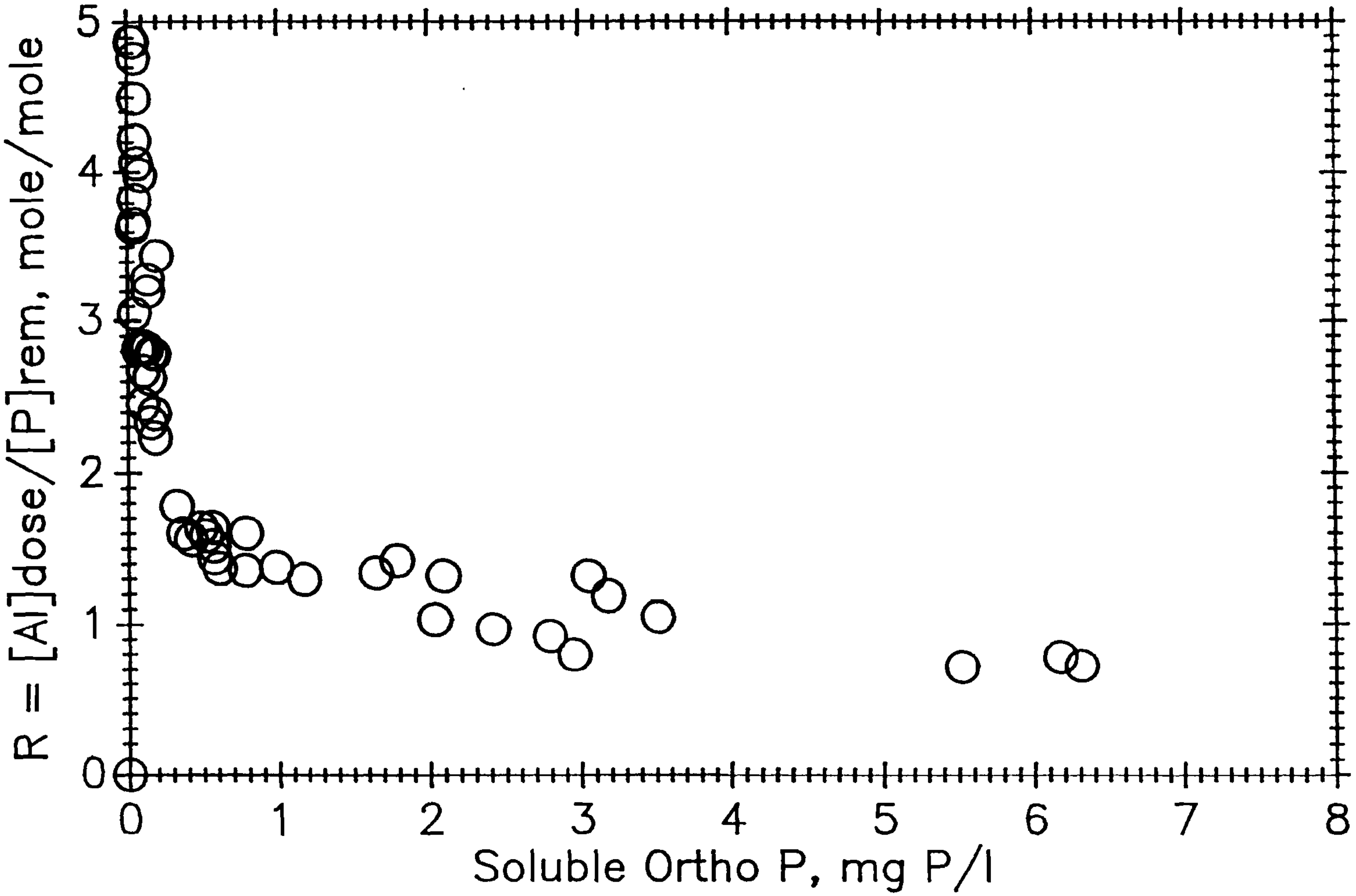


Figure 5.11 Continuous flow experimental results (pH =7.2, Al dose = 1.8 to 27 mg Al(III) /l).

5.2 Batch Experiment Results

5.2.1 Equilibration Time Study

Experiments were conducted to determine the optimum aeration time required between mixing sewage and mixed liquor and adding alum. It was felt that some time may be needed to allow any biological phosphorus removal and hydrolysis of condensed phosphates to take place and to allow a reasonably constant SOP concentration to be achieved in the batch reactors. The equilibration studies were conducted at three pH values: 6.5, 7.2, and 8.0. The parameters monitored were the SOP and soluble calcium concentrations both before and after alum addition. The results (Figures 5.12 and 5.13) indicate that there was little change in the SOP or soluble calcium concentration over an 8 hr period. The average change in SOP was between 3-8% of the initial SOP concentration over the 8 hr period.

A similar equilibration study was conducted to determine the amount of time required to produce a steady value of SOP concentration following alum addition. The change in SOP concentration after alum addition is shown in Figure 5.14.

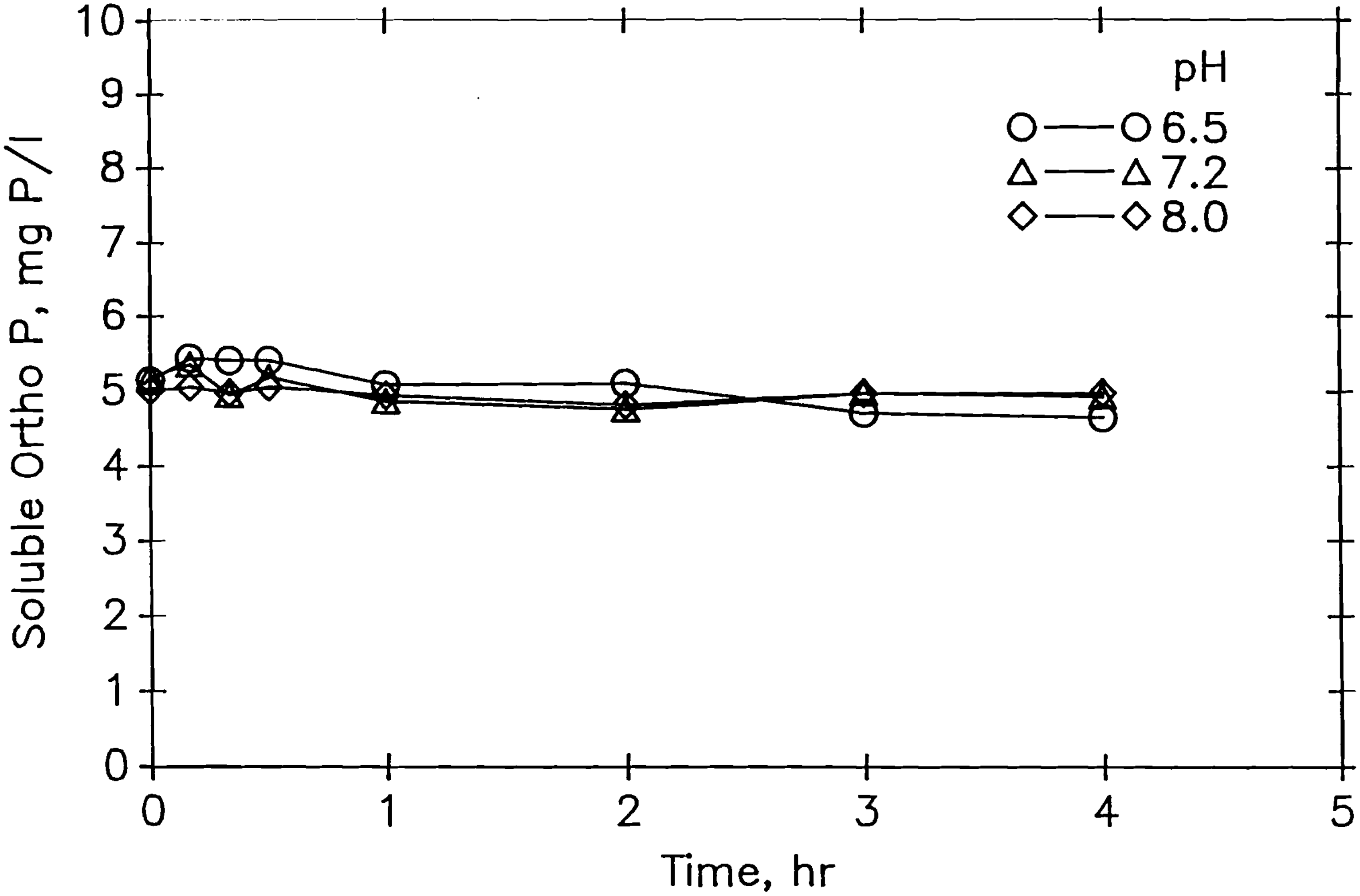


Figure 5.12 Change in SOP concentration before alum addition

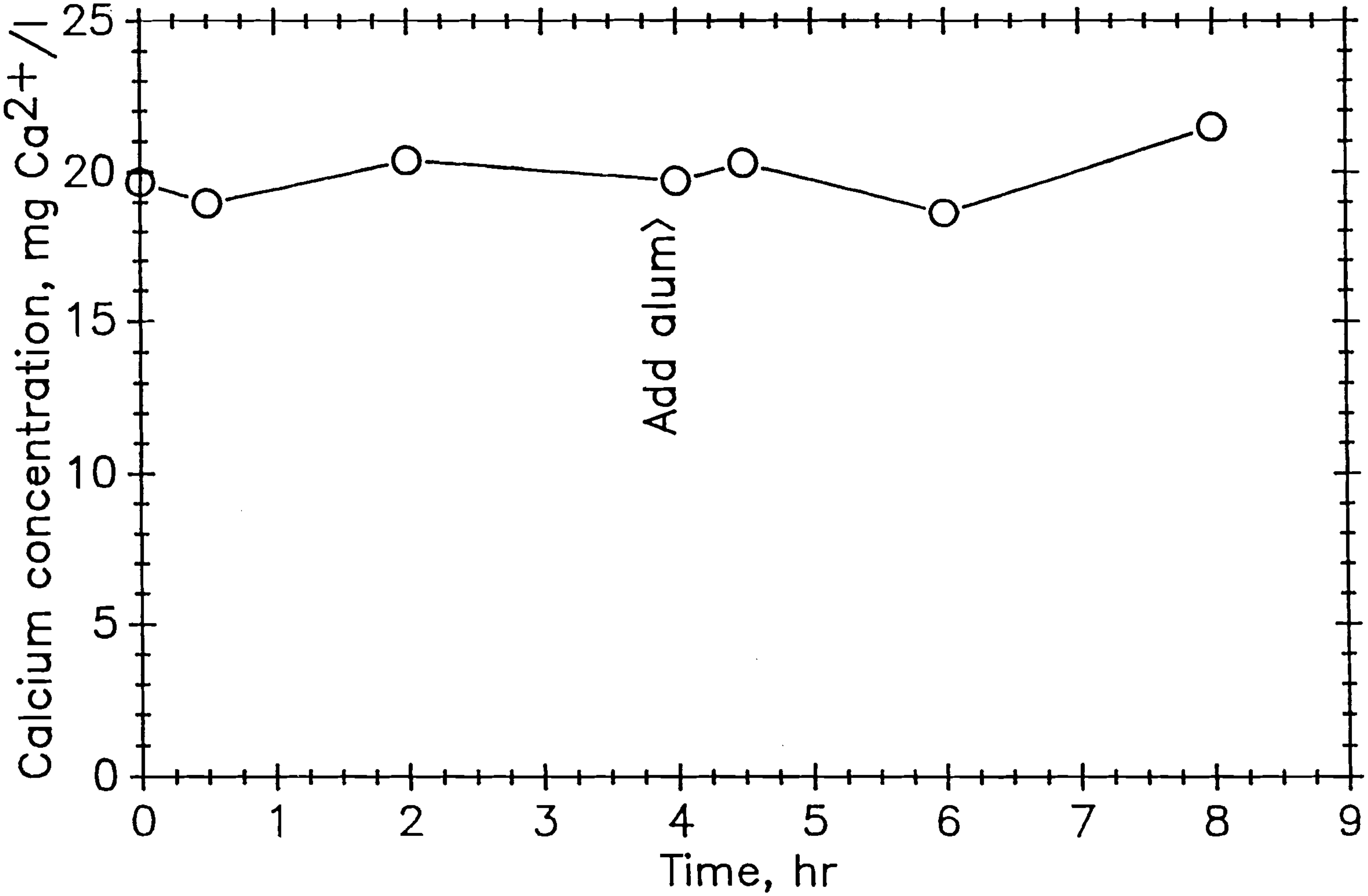


Figure 5.13 Change in calcium concentration before and and after the addition of 4.5 mg Al(III) /l at pH 7.2 .

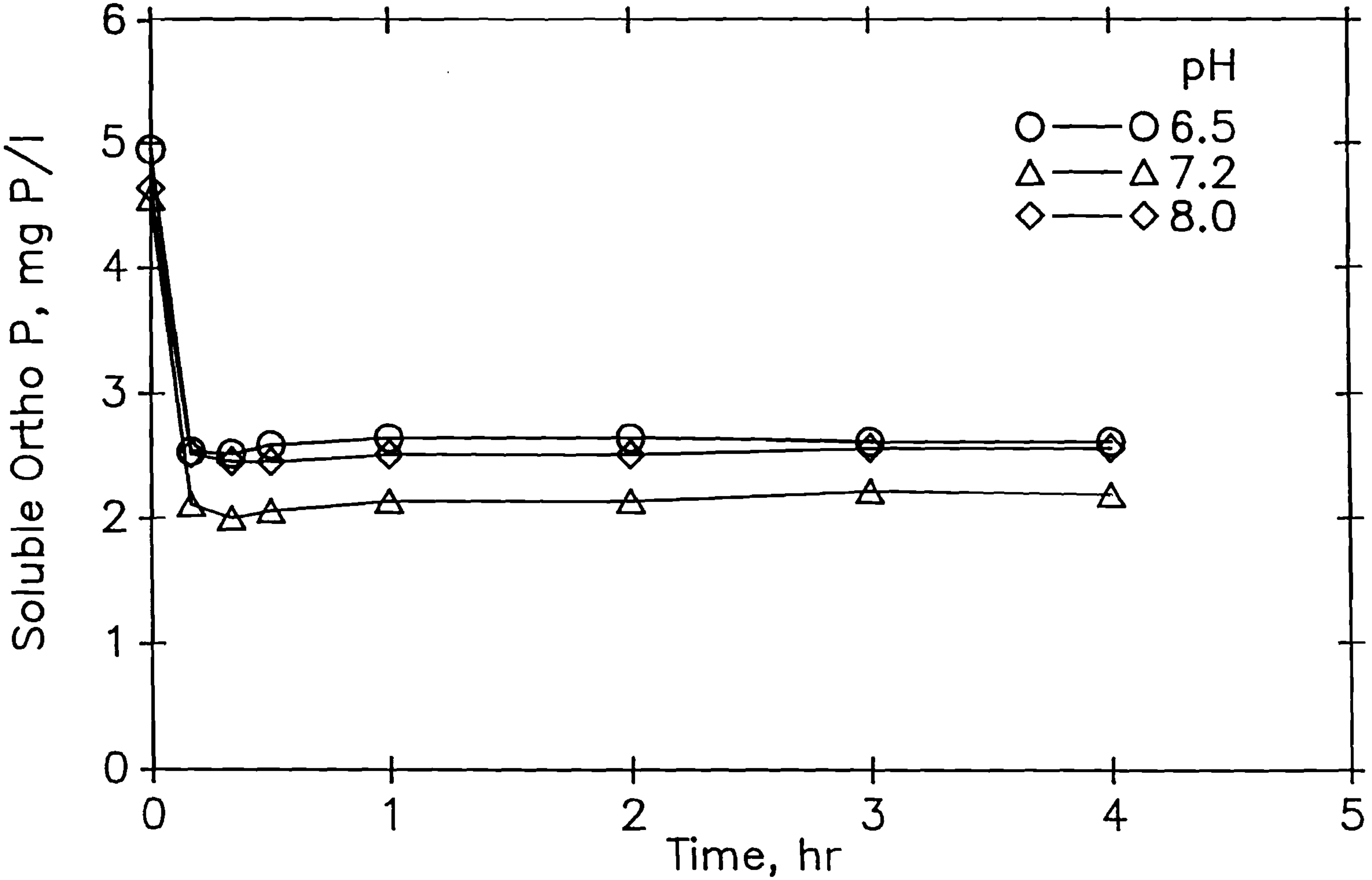


Figure 5.14 Change in SOP concentration after the addition of 4.5 mg Al(III) /l.

At all three pH values studied, following the addition of a low dose of alum (4.5 mg Al^{3+}/l) there was a rapid decrease in SOP concentration within 10 min and no further significant decrease over a period of 4 hr. A second post alum-addition study was conducted at a constant pH (7.2) to determine whether the magnitude of the alum dose had any influence on these results. Figure 5.15 shows that the results of this experiment were the same as at low alum doses.

Equilibration times of 2 hrs before alum addition and one hr following alum addition were selected for the batch phosphate removal studies. These times were chosen so that more than one series of batch experiments could be conducted during an 8 hr work period. The selected equilibration times should be sufficient to allow any changes in SOP concentration to occur before sampling and analysis.

5.2.2 Sludge Composition Study

A series of batch experiments was conducted to determine whether the use of mixed liquor containing aluminum hydroxy phosphate precipitate would effect the outcome of the batch experiments. Possible effects were an increase in soluble orthophosphate concentration resulting from the dissolution of the aluminum hydroxy phosphate

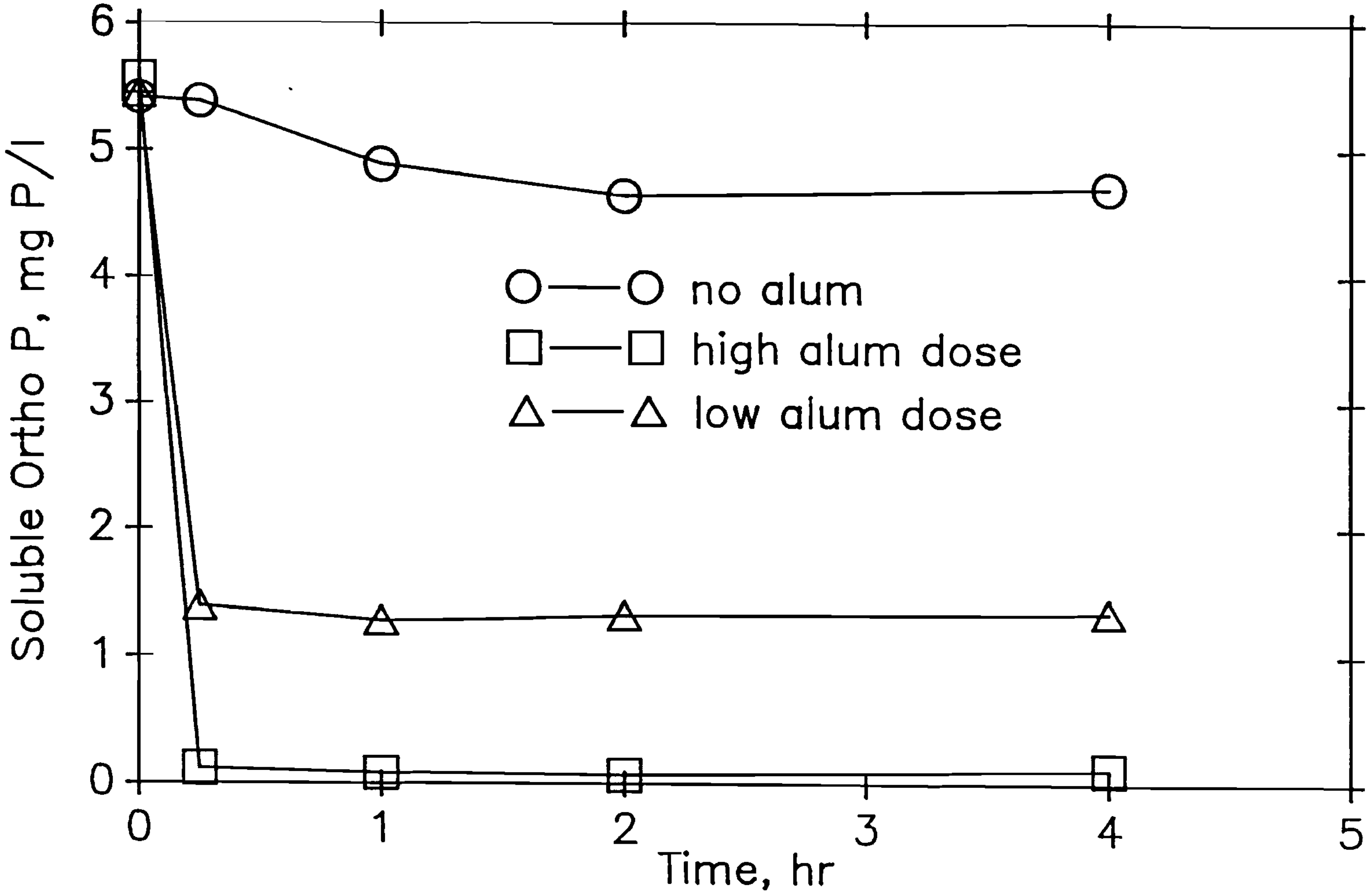


Figure 5.15 Change in SOP concentration after the addition of high (20 mg Al$^{(III)}$ /l) and low (5 mg Al$^{(III)}$ /l) doses of alum.

precipitate or an increase in soluble orthophosphate removal resulting from adsorption onto the aluminum hydroxy phosphate precipitate. For this series of experiments 3 batch test were run in parallel at pH 7.2 using mixed liquor from 3 different sources. Mixed liquor A, (which was used for the duration of the batch studies), was waste mixed liquor from the laboratory scale continuous flow activated sludge system dosed with between 5 and 8 mg Al^{3+}/l. Mixed liquor B was from a laboratory fill-and-draw reactor and mixed liquor C was the waste sludge from a pilot scale trickling filter plant. Sludges B and C contained no aluminum-hydroxy-phosphate precipitates. Alum was dosed to each batch reactor at a concentration of 4.5 mg Al^{3+}/l. The results of these experiments are summarized in Figure 5.16 and Table 5.3. There was insufficient data to determine if the differences observed in the sludge composition study were significant. Since the magnitude of the differences was not that large they were assumed to have resulted from experimental and sampling errors. It was therefore concluded that the presence of chemical precipitates at the level found in the mixed liquor used in the batch experiments would have no effect on phosphate removal in these experiments.

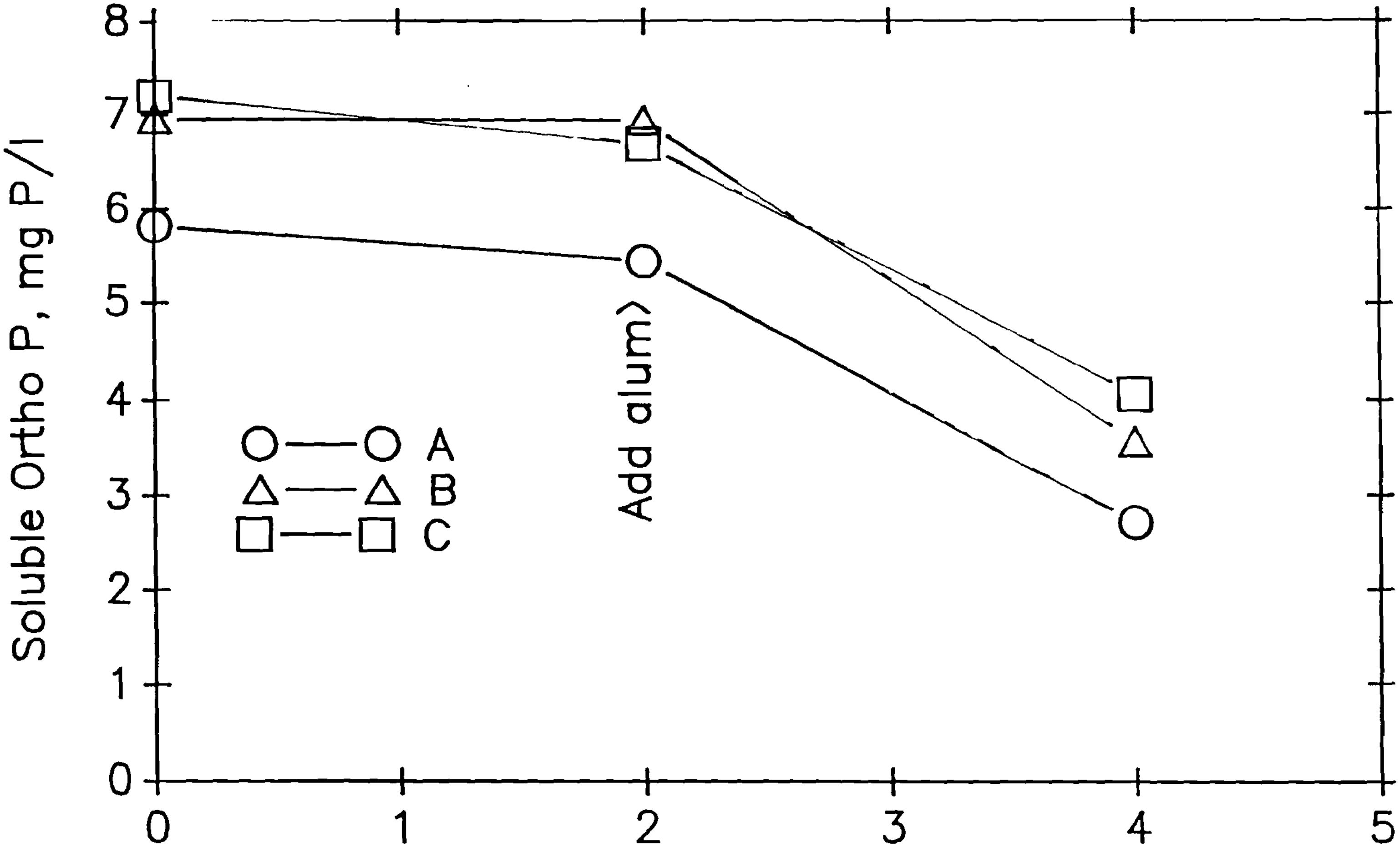


Figure 5.16 Sludge composition study, pH = 7.2, alum dose 4.5 mg Al^{3+}/l (A= cont. flow, B= fill–and–draw, C=trickling filter)

Table 5.4
Summary of sludge composition study results

	Sludge A	Sludge B	Sludge C
% remove SOP	46	51	56
Removal ratio(R)	1.5	1.2	1.6

5.2.3 Phosphate Removal Study

The objective of this series of experiments was to determine phosphate removal achieved when various amounts of alum were added to settled sewage and mixed liquor under controlled pH conditions. Batch phosphate removal studies were conducted at the following 6 pH levels: 6.0, 6.5, 6.8, 7.0, 7.2, 7.5, to cover the pH range of generally encountered in operating activated sludge facilities. The results of the controlled pH batch studies are shown in Figures 5.17 the form of the percentage of influent SOP removed versus aluminum dose ratio. The aluminum dose ratio is defined as:

$$D = Al^{3+} \text{ dose (mole)}/\ PO_4 \text{ influent (mole)} \qquad (5.4)$$

The same general trend is apparent at all pH values studied. At lower dose ratios a steady increase in % SOP removal is observed as D increases. All plots level off as high % SOP removal is approached ($D>1.5$). SOP removals as high as 99.5% were observed in experiments using high dose ratios (approx. 20 mole of Al^{3+} per mole of influent SOP).

Figures 5.18 shows the SOP residual plotted as a function of the removal ratio, (R) (defined in section 5.1.3, equation 5.2). The same general trend in removal ratios appears to be followed at all pH values investigated. At SOP residual concentrations greater than

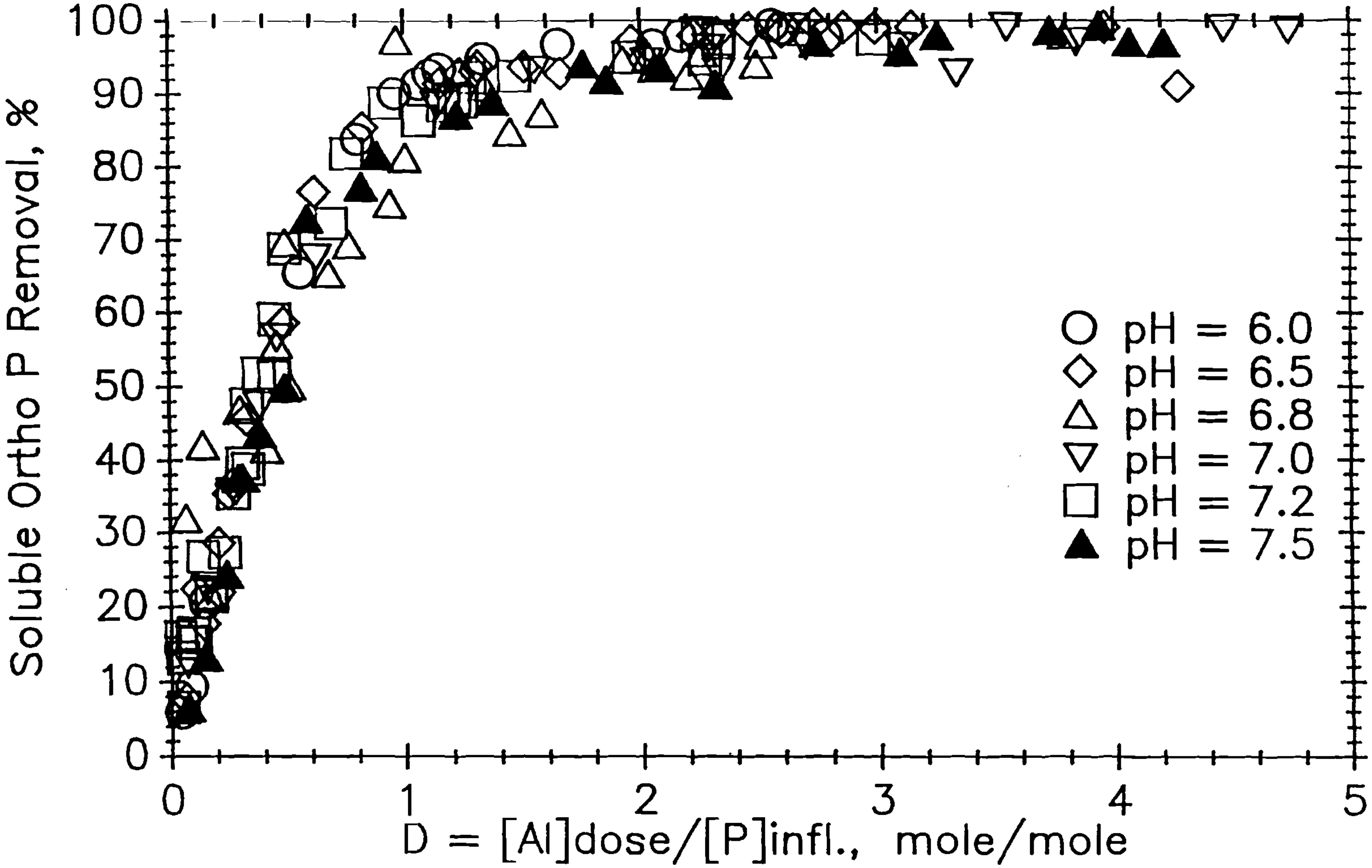


Figure 5.17 Batch experimental results (pH = 6.0 to 7.5, Al dose = 0.3 to 100 mg Al(III) /l).

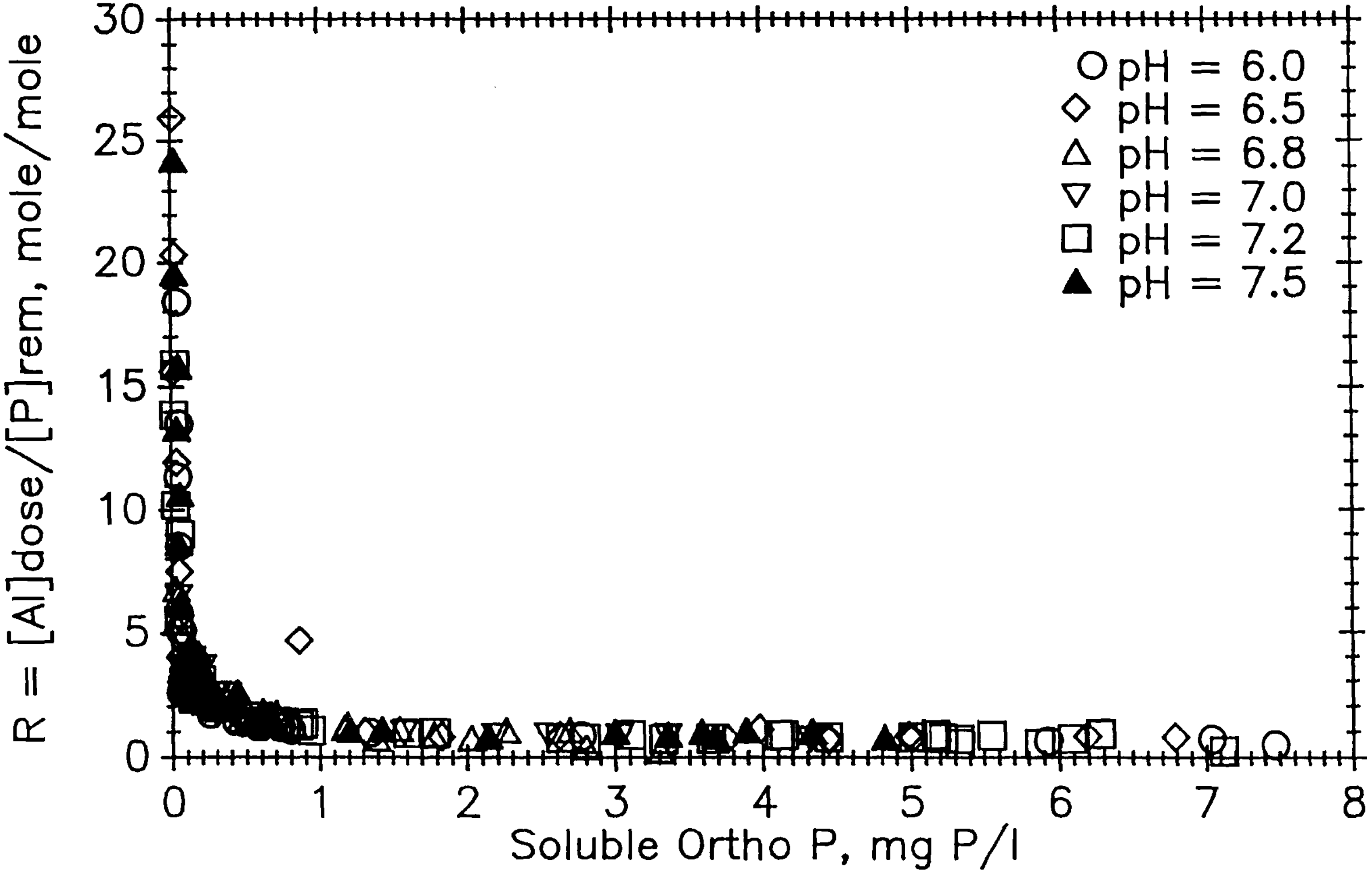


Figure 5.18 Batch experimental results for phosphate removal study.

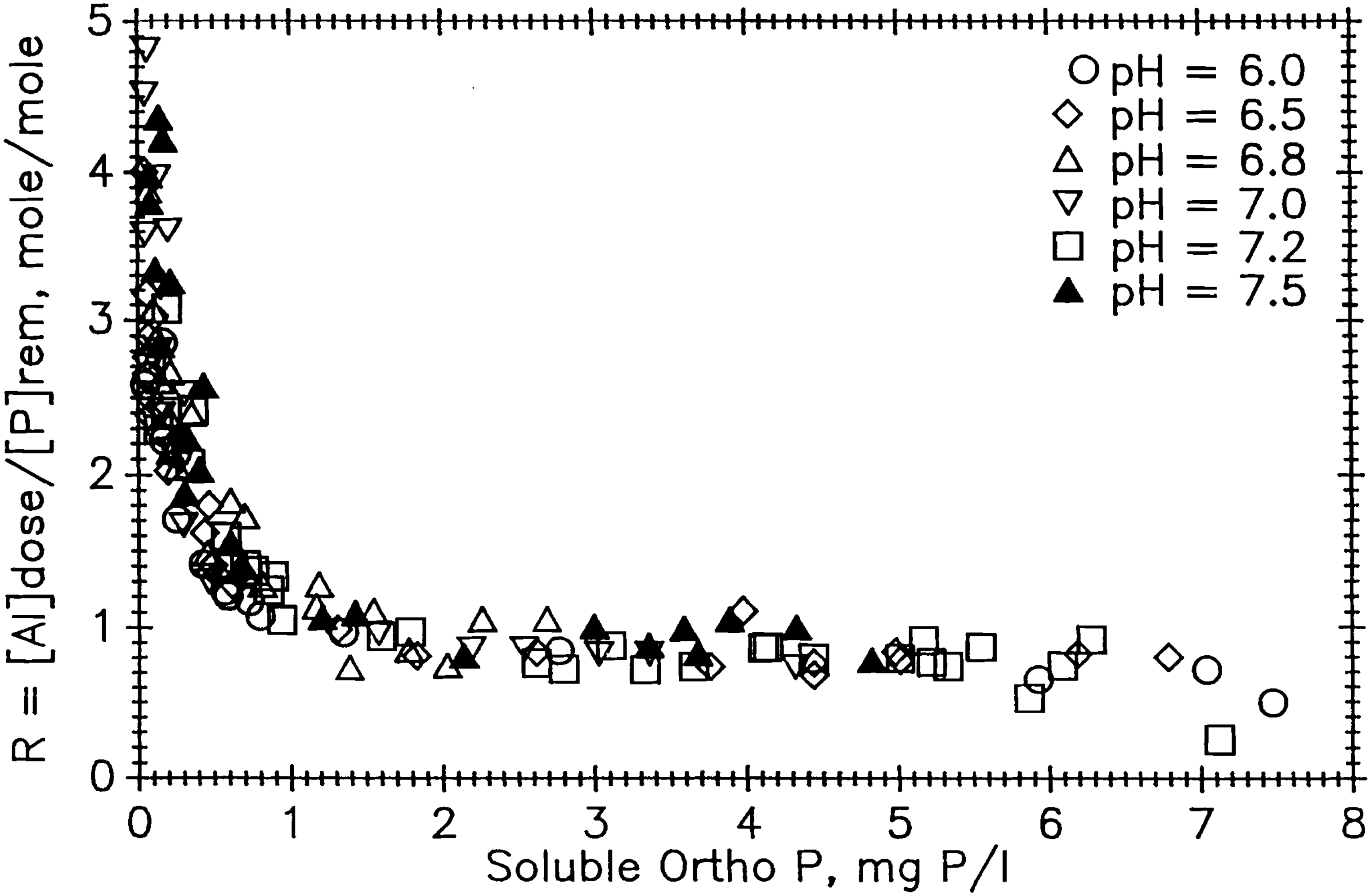


Figure 5.19 Batch experimental results for phosphate removal study (R < 5.0).

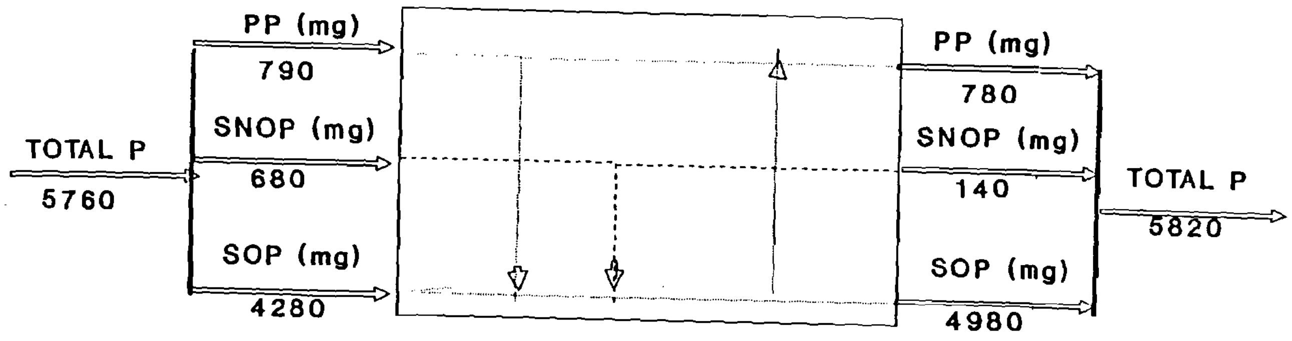
approx. 1.0 mg P/l the removal ratio is constant at values ranging from 0.86 to 1.12. At moderate to low SOP residual concentrations (approx. 0.1 to 1.0 mg P/l) the removal ratio varies between 1.5 and 3.0 and increases with decreasing SOP concentration in this range. At very low SOP residuals, where the soluble orthophosphate residual reaches a seemingly irreducible residual of 0.05 to 0.07 mg P/l, the removal ratio increases from 5 to greater than 25.

6 DISCUSSION

6.1 Control Study

Continuous flow experiments without alum addition were conducted to investigate phosphate transformations during biological treatment and to assess the need for including background phosphate removal in the model of simultaneous precipitation of phosphate with alum. Phosphate species measured in the control study were influent, effluent and mixed liquor total, particulate, soluble non-ortho and soluble orthophosphate. In Figures 6.1 and 6.2 material balances on several phosphate species are shown. The material balances revealed significant changes in soluble non-orthophosphate (SNOP) and soluble orthophosphate (SOP) concentration and small changes in particulate (PP) and total phosphate (TP), but did not differentiate between the several transformations undergone by phosphate species in activated sludge aeration basins. These transformations and their possible impact on phosphate species distribution are summarized in Table 6.1. Also illustrated in Figures 6.1 and 6.2 are lines which represent the phosphate transformation most likely to occur in the activated sludge aeration basin without alum addition.

Figure 6.1
Control Study Material Balance
Expt #1

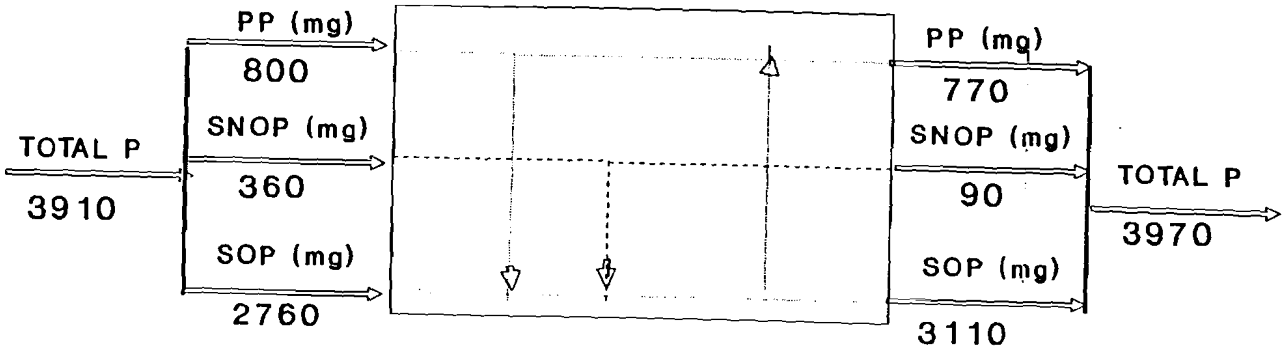


PP = Particulate P

SNOP = Soluble Non-Ortho P

SOP = Soluble Ortho P

Figure 6.2
Control Study Material Balance
Expt #2



PP = Particulate P

SNOP = Soluble Non-Ortho P

SOP = Soluble Ortho P

Table 6.1

Phosphate Transformations in Activated Sludge Aeration Basins without Alum Addition

	Transformation	Impact
1.	Hydrolysis of condensed phosphates	decrease SNOP increase SOP
2.	Uptake of soluble orthophosphate by microorganisms	decrease SOP increase PP
3.	Solubilization of particulate phosphate	decrease PP increase SNOP and SOP

Minton and Carlson (1972) suggested that background removal of 5 to 95% of total P occurred during simultaneous precipitation. In this study the total P mass remained essentially constant suggesting that the background removal of total P was not large enough to require inclusion in the chemical P removal model.

A significant decrease in SNOP (avg net decrease = 405 mg) and an increase in SOP (avg net increase = 525 mg) were observed in the control study. A small decrease in PP mass was observed during the control study (avg net decrease = 20 mg). The control study results indicated that the average net increase in SOP was equal to 40% of the sum of influent SNOP and PP. This finding suggests that hydrolysis of SNOP and PP to SOP should very likely be included in the development of the aluminum phosphate simultaneous precipitation model.

The impact of SNOP and PP hydrolysis on aluminum phosphate precipitation was investigated by developing a removal ratio relationship that included the hydrolysis of these P fractions:

$$R^{*} = (\text{Al dose(mg)}/\text{SOP}^{*}\text{ removed(mg)}) \times 1.15 \text{ (mole/mole)} \quad (6.1)$$

where:

R^{*} = adjusted removal ratio

$$SOP^{*} \text{ removed} = SOP_{inf}(mg) - SOP_{eff}(mg) + 0.4 \times (SNOP_{inf}(mg) + PP_{inf}(mg) \quad (6.2)$$

The term $0.4 \times (SNOP_{inf}(mg) + PP_{inf}(mg))$ in equation 6.2 represents the increase in SOP expected from the hydrolysis of SNOP and PP. A comparison of the standard removal ratio "R" (see section 5.1.3) and the adjusted removal ratio "R^{*}" (equation 6.1) is shown in Figure 6.3 for the continuous flow alum addition study. The average adjusted removal ratio (R^{*}) was 14% lower than the average standard removal ratio (R). A one way analysis of variance (F-ratio) was used to determine whether the decrease in R^{*} was statistically significant by comparing R and R^{*} for SOP_{res} greater than 1.0 mg P/l. The statistical analysis was limited to this range of data because at SOP_{res} greater than 1.0 mg P/l the R and R^{*} values were no longer constant. Statistical analysis (Appendix 1) indicated that there was no significant difference between the value of R (avg=1.08, σ=0.25) and R^{*} (avg=0.90, σ=0.22) for SOP_{res} greater than 1.0 mg P/l at the 99% confidence level. On this basis, the hydrolysis of SNOP and PP to SOP was not included in the development of the aluminum phosphate precipitation model.

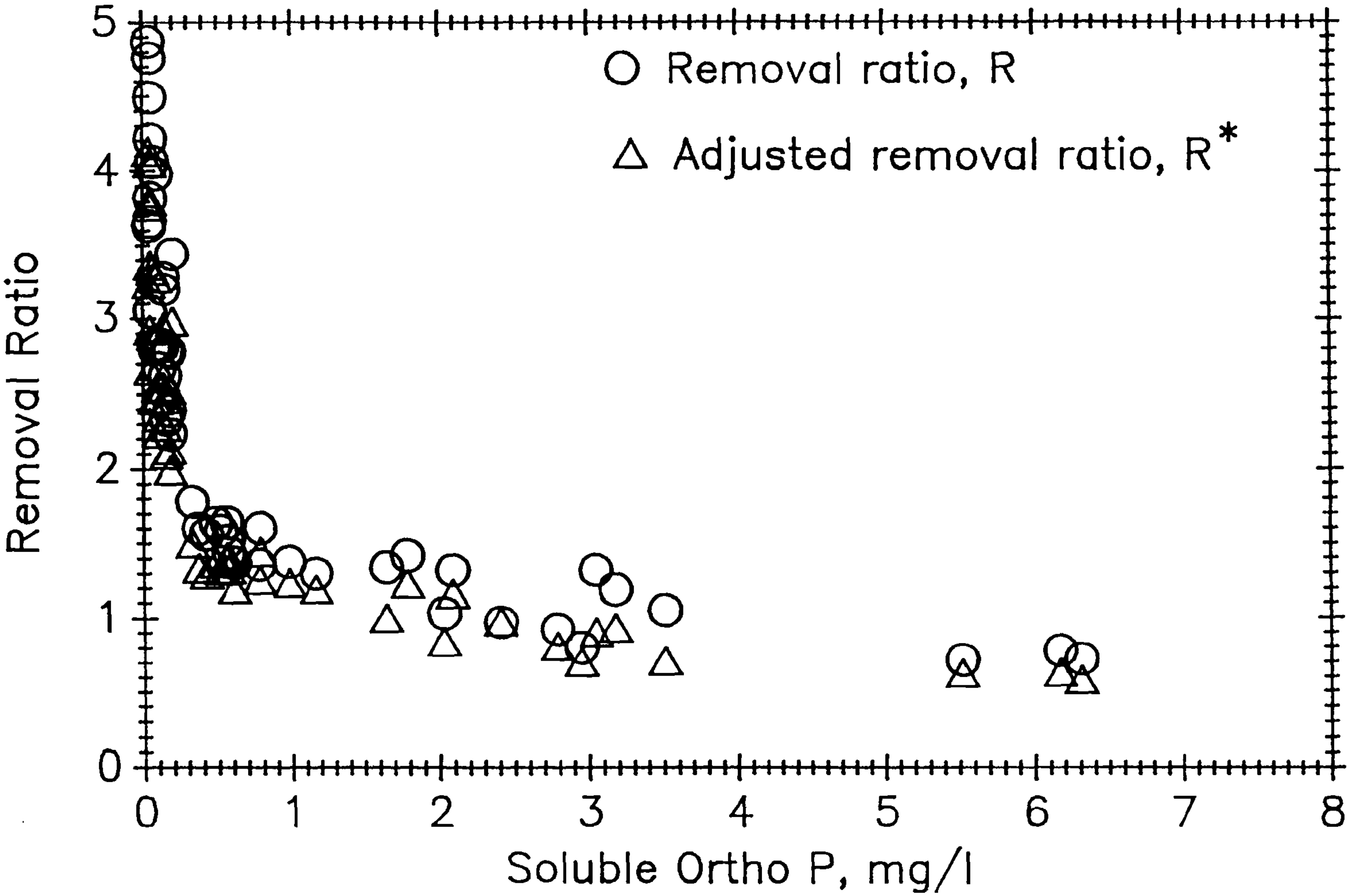


Figure 6.3 Effect of SNOP and PP hydrolysis on P removal in continuous flow experiments

6.2 Comparison of Continuous Flow and Batch Experiments

Two types of experiments were used to generate data for the development of the aluminum phosphate precipitation model: 1) continuous flow experiments and 2) batch experiments, which allowed the data collection over a shorter period of time (3 hr) than the continuous flow experiments (24 hr). A comparison of the batch and continuous flow experimental conditions and protocols is given in Table 6.2.

Results obtained from the continuous flow experiment at pH 7.2 are compared with those of the batch study at the same pH in Figures 6.4 and 6.5. The same trends in data were observed in both types of experiments. Statistical analysis of the removal ratio (R) for SOP_{res} of > 1.0 mg P/l using the Student's t-test indicated that there was no significant difference between the continuous flow and batch experimental results at the 99% confidence level (Appendix 2). On this basis, it was concluded that both the batch and continuous flow experimental results could be used together in the development of the aluminum phosphate precipitation model.

Table 6.2
Comparison of Continuous Flow and Batch Experiments

	Continuous	Batch
biomass present	yes	yes
aeration	yes	yes
pH control	yes	yes
hydraulic res. time	8 hr	3 hr
solids retention time	approx 8 days	3 hr
alum addition	continuous at 1 ml/min	spike dose

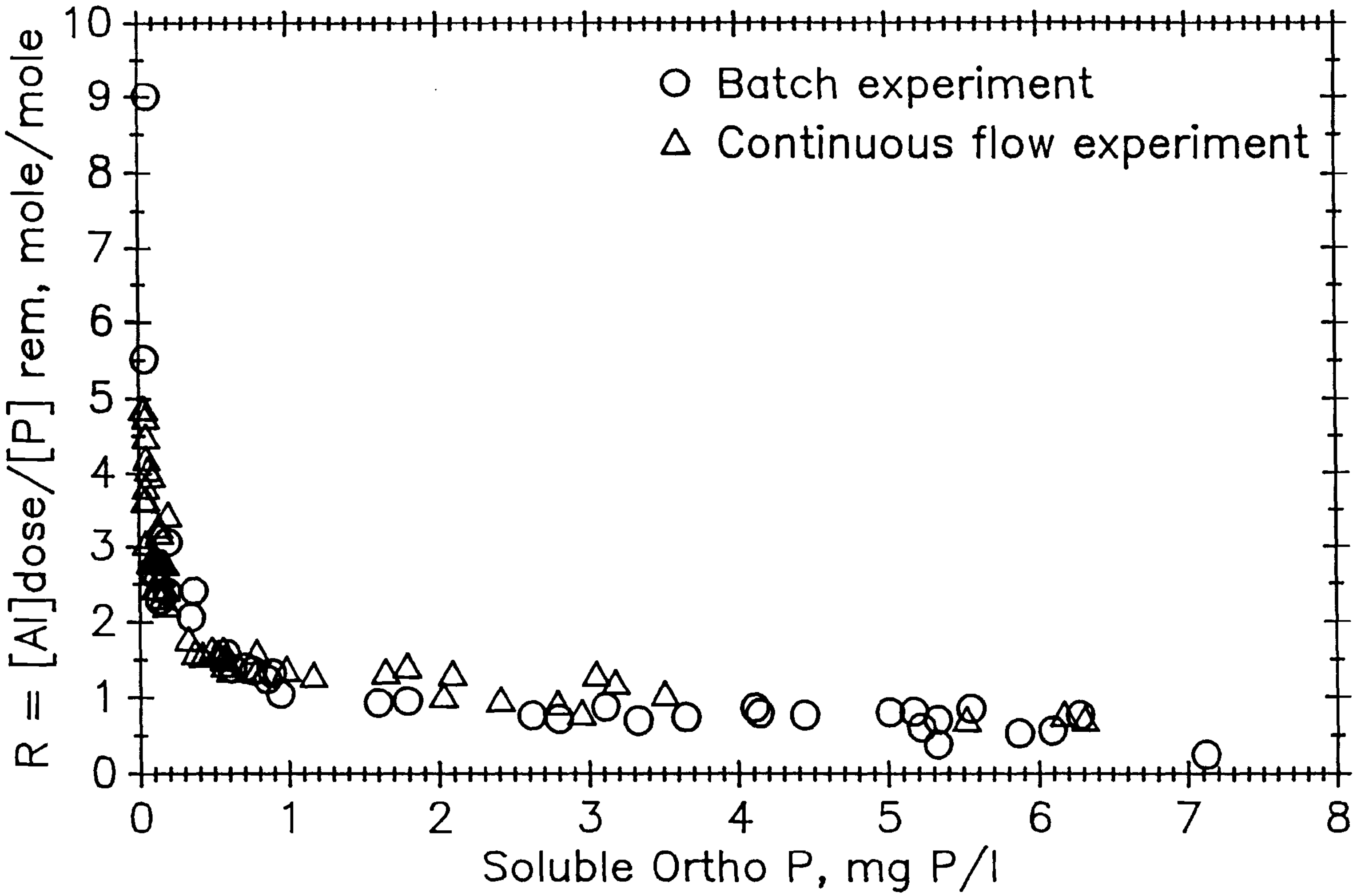


Figure 6.4 Comparison of batch and continuous flow experiments at pH 7.2.

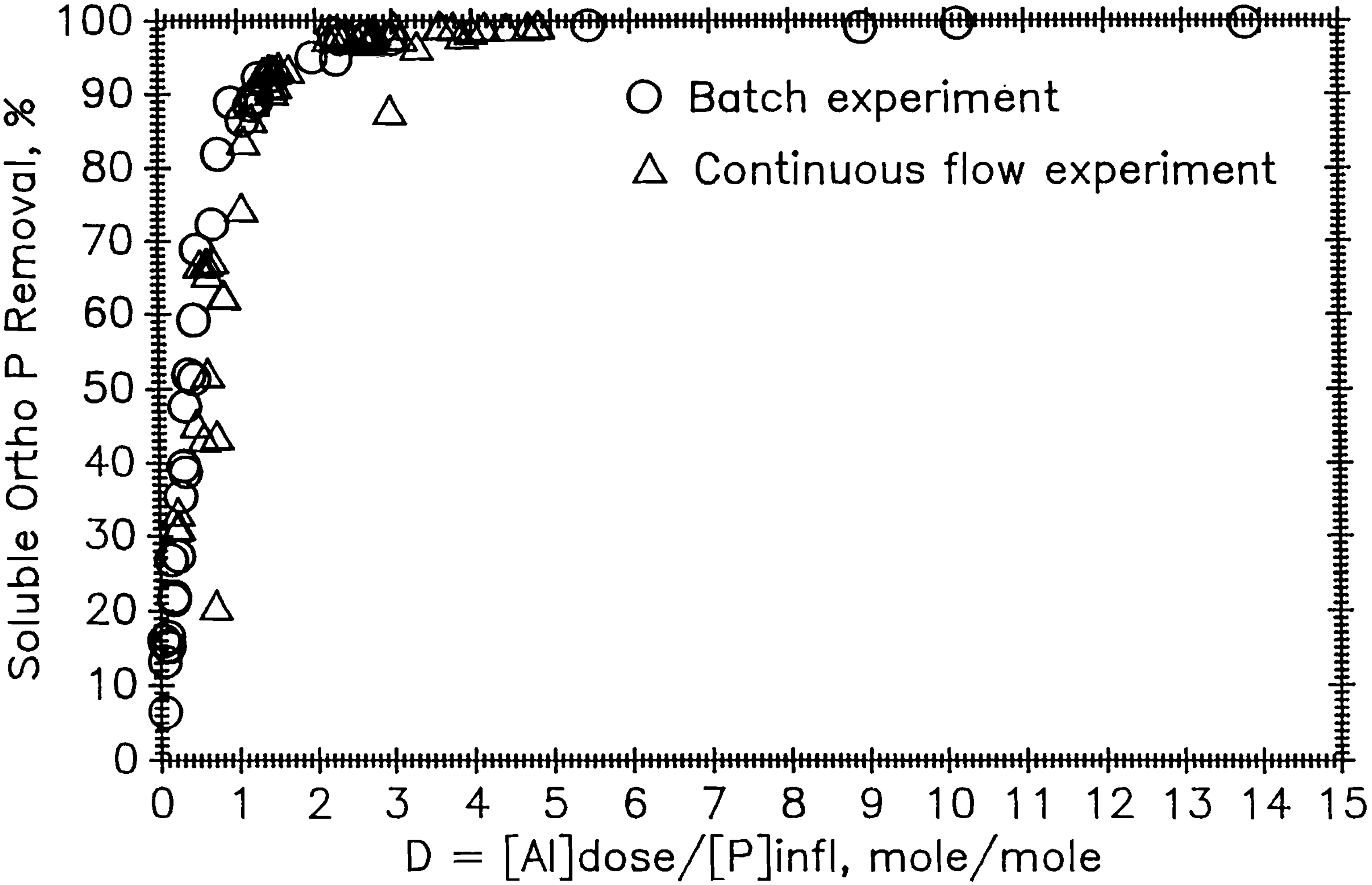


Figure 6.5 Comparison of batch and continuous flow experiments at pH 7.2.

6.3 Model Development

The residual SOP concentration plotted as a function of the removal ratio R appears to fall within three distinct regions (Figure 6.6). The first region is characterized by moderate to high SOP residuals (between 1 to 8 mg P/l or $10^{-4.5}$ to $10^{-3.6}$ M) and a nearly constant R. SOP residuals in this region were reached using aluminum doses between 0.3 to 7.0 mg Al^{3+}/l (10^{-5} to $10^{-3.6}$ M). In the second region R increases as the SOP residual concentration decreases. This region is reached with aluminum doses of between 7.0 and 24.0 mg Al^{3+}/l ($10^{-3.6}$ to $10^{-3.1}$ M) and includes SOP residuals from approx. 1.0 to 0.1 mg P/l ($10^{-4.5}$ to $10^{-5.5}$ M). The third region includes very low SOP residuals (between 0.1 and 0.02 mg P/l; $10^{-5.5}$ to $10^{-6.2}$ M) and is reached with aluminum doses from 25 to 100 mg Al^{3+}/l ($10^{-3.0}$ to $10^{-2.4}$ M). It is characterized by a rapid increase in R as aluminum dose increases. This increase in R is not accompanied by a substantial decrease in SOP residual.

A model of aluminum phosphate precipitation was developed which described SOP removal in each of these three P removal regions. The model addresses only the removal of SOP in activated sludge system aeration basins.

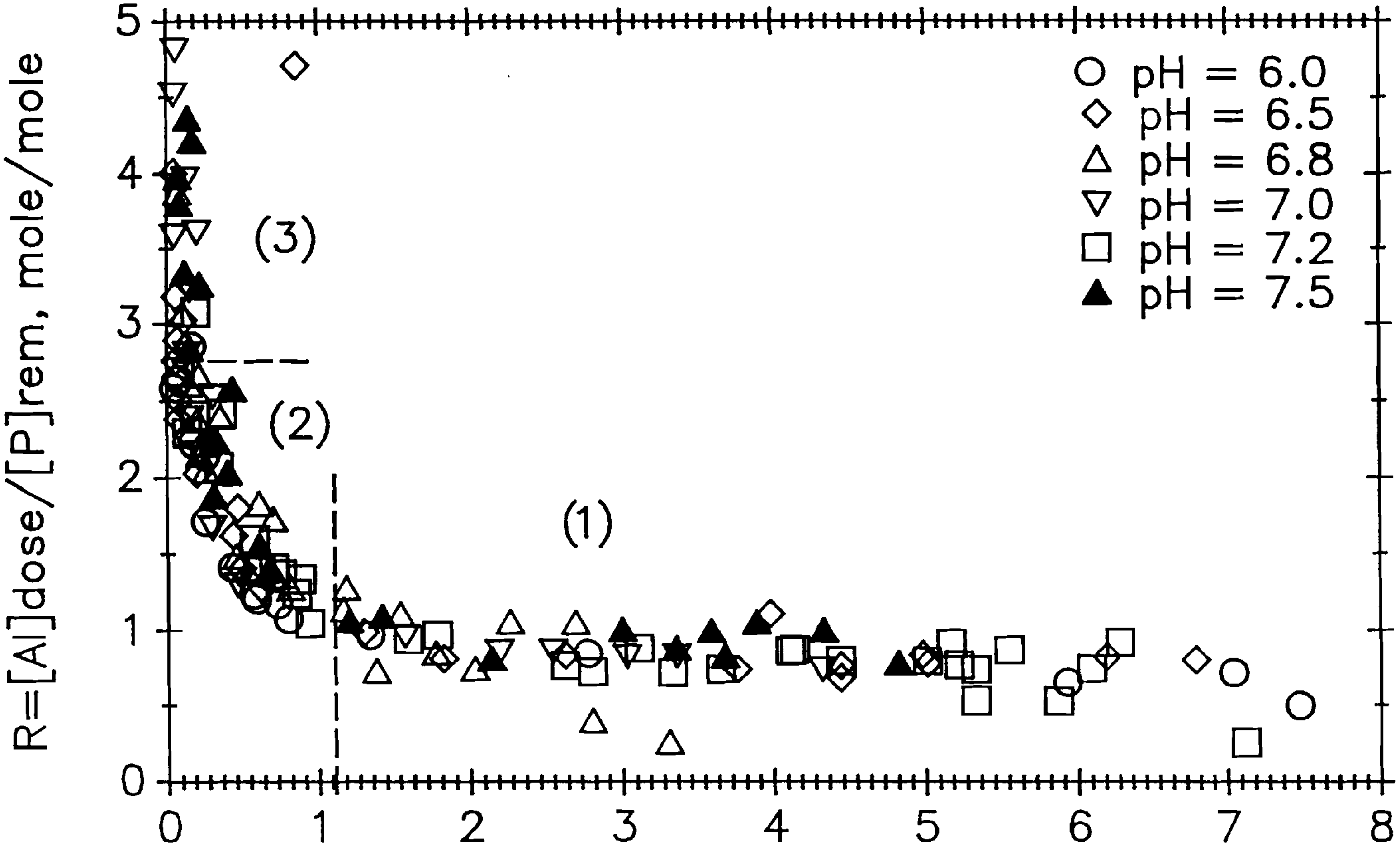


Figure 6.6 Three apparent soluble ortho P removal regions obtained by simultaneous aluminum phosphate precipitation

6.3.1 Region One

At low alum doses (0.3 to 6.8 mg Al^{3+}/l) the linear relationship between the alum dose and SOP removed, (constant R value), suggests the stoichiometric formation and precipitation of an aluminum-hydroxy-phosphate solid as follows:

$$r\ Al^{3+} + H_2PO_4^- + (3r-1)\ OH^- \Longleftrightarrow \Longleftrightarrow Al_rH_2PO_4(OH)_{(3r-1)}\ (s) \qquad (6.3)$$

This finding agrees with the models of Ferguson and King (1977), Jenkins *et al.* (1984), Goldshmid and Rubin (1978), Stumm (1962) and Luedecke *et al.* (1988). The identity and crystallinity (if any) of the specific aluminum-hydroxy-phosphate precipitate was not investigated. It was assumed that an amorphous solid was formed as suggested by Hsu (1975), Diamodopolous and Benedek (1984) and Robarge (1979). The results of this research were used to determine the value of the stoichiometric ratio (r) of aluminum to phosphate in the aluminum-hydroxy-phosphate precipitate, since this information can be used to estimate alum doses required to achieve a desired SOP residual in the stoichiometric precipitation region.

6.3.1.2 Estimation of the Stoichiometric Coefficient (r)

Three assumptions were made in estimating r: 1) all of the aluminum dosed to the activated sludge aeration basin precipitated as an aluminum-hydroxy-phosphate or as an aluminum hydroxide solid and 2) the formation of aluminum hydroxide solid in the stoichiometric removal region was negligible and 3) P removal in the stoichiometric removal region is due solely to the precipitation of an aluminum-hydroxy-phosphate solid. The inability to detect any soluble aluminum in the effluent supports the validity of the first assumption. If these assumptions are valid, then all of the aluminum dosed and SOP removed is incorporated into the aluminum-hydroxy-phosphate solid. Under these conditions the stoichiometric ratio of aluminum to phosphate in the aluminum-hydroxy-phosphate precipitate is equal to R.

As a first approximation, based on visual inspection of the experimental results, it was assumed that the stoichiometric precipitation region extended down to SOP residuals of 1.0 mg P/l. The average R was then calculated independently at each pH value for all batch and continuous flow experiments resulting in SOP residual concentrations of ≥ 1.0 mg P/l (Figure 6.7). The absence of any significant trend in the average R values with pH led to the conclusion that the observed variation in R with pH was

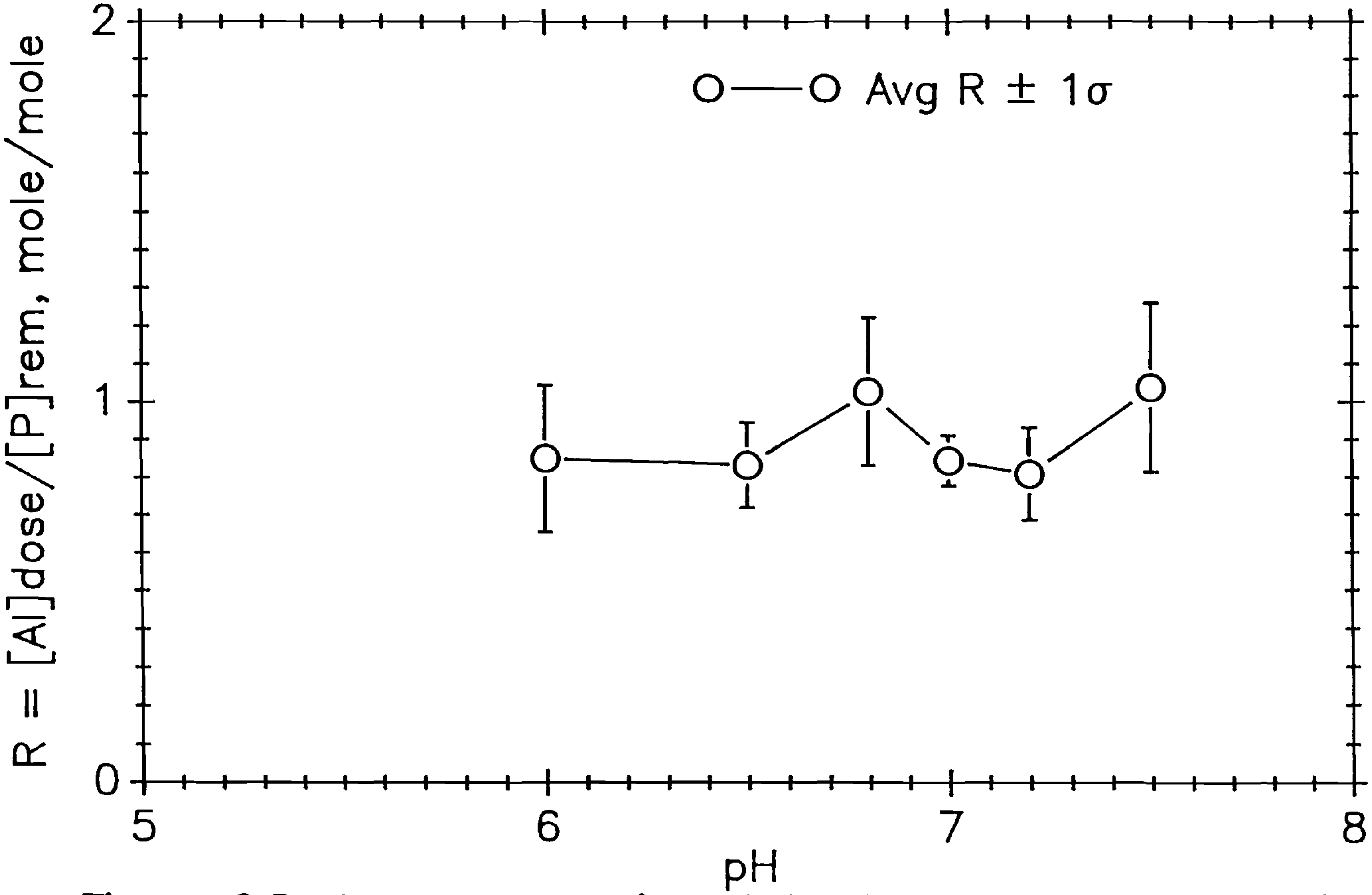


Figure 6.7 Average experimental values of R for SOP residual concentrations > 1.0 mg P/l at a range of pH values.

due experimental error and that r was independent of pH.

The batch experimental results were used to determine the lower SOP residual concentration limit of the stoichiometric P removal region. First the R at selected SOP residual concentrations, ranging from 6.0 to 0.5 mg P/l, were averaged for all pH values (see Figure 6.8). The average R values were then compared statistically using a one way analysis of variance (F-ratio) to determine the residual SOP concentration at which the R was no longer a constant. It was found that for SOP residuals of 6.1, 4.2, 3.2, and 1.1 mg P/l (data points #1-4) there was no significant difference in the average R at the 99% confidence level (Appendix 3). Further analysis revealed that when the R at an SOP residual of 0.85 mg P/l (data point #5) was included in the analysis of variance, a significant difference was found between the R values at the 99% confidence level. These findings were interpreted to mean that the transition from the stoichiometric region to the second removal region occurred at a SOP residual concentration between 0.85 and 1.1 mg P/l. Since there was insufficient data to further define the boundary between the first and second removal region, the lower limit for the stoichiometric precipitation of SOP with alum was set at an SOP residual concentration of 1.0 mg P/l.

R values at all pH values and SOP residual concentrations of ≥ 1.0 mg P/l were combined and averaged.

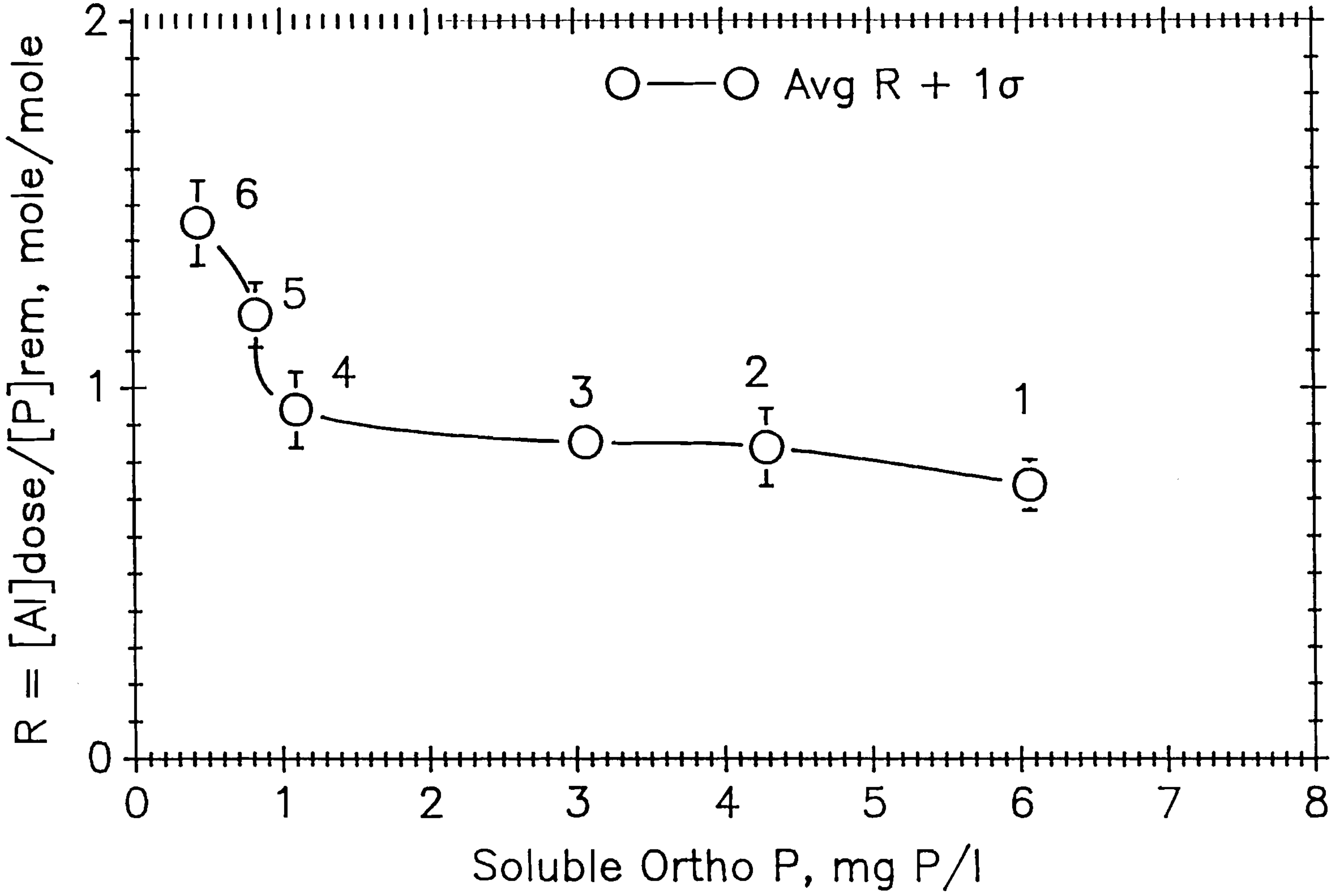


Figure 6.8 Average experimental values of R for selected SOP residual concentration for batch experiments at pH 6.0–7.5.

The r value in the aluminum-hydroxy-phosphate precipitate was determined to be 0.91 ± 0.11 (avg r ± 1σ), suggesting the precipitation of a solid with the stoichiometry $Al_{0.91}H_2PO_4(OH)_{1.73}$.

This r value is significantly less than that used by Ferguson and King (1977) (r = 1.4) and Jenkins *et al.* (1984) (r = 1.5) in the development of previous phosphorus removal models, suggesting that more SOP is removed by a given dose of alum in the stoichiometric region than previously predicted. Ferguson and King selected r = 1.4 based on the work of Recht and Ghassemi (1970). A significant difference between this study and the work of Recht and Ghassemi is the presence of biological solids during aluminum phosphate precipitation. This suggests that, with simultaneous precipitation, the stoichiometric removal of SOP is enhanced by other, as yet unaccounted for, phosphorus removal mechanisms or by the formation of a different precipitate in the presence of activated sludge. Adsorption of SOP on to the chemical/biological solids is possible, although if this occurred the R would not be constant in the stoichiometric region.

6.3.1.3 Estimation of Alum Dose

The stoichiometric ratio ($r = 0.91 \pm 0.11$) can be used to determine the aluminum dose required to achieve an SOP residual of ≥ 1.0 mg P/l (3.2×10^{-5} M/l). R, the aluminum requirement, and SOP residual are related as follows for SOP ≥ 1 mg P/l:

$$r = Al^{(III)}_{reqd}(\text{mole})/SOP_{remv}(\text{mole}) \qquad (6.4)$$

where:

r = stoichiometric ratio of aluminum to phosphate in precipitate = 0.91 ± 0.11

$Al^{(III)}_{reqd}$ = aluminum required for desired SOP removal (mole)

SOP_{remv} = SOP removal required to reach a desired SOP residual (SOP_{res}) (mole)

$$SOP_{remv} = SOP_{infl} - SOP_{res} \qquad (6.5)$$

Substituting equation 6.6 into 6.5 and rearranging yields:

$$SOP_{res} = SOP_{infl.} - Al^{(III)}_{reqd}/r \qquad (6.6)$$

Figure 6.9 compares the experimental results at all pH values and model predictions made using equation 6.6.

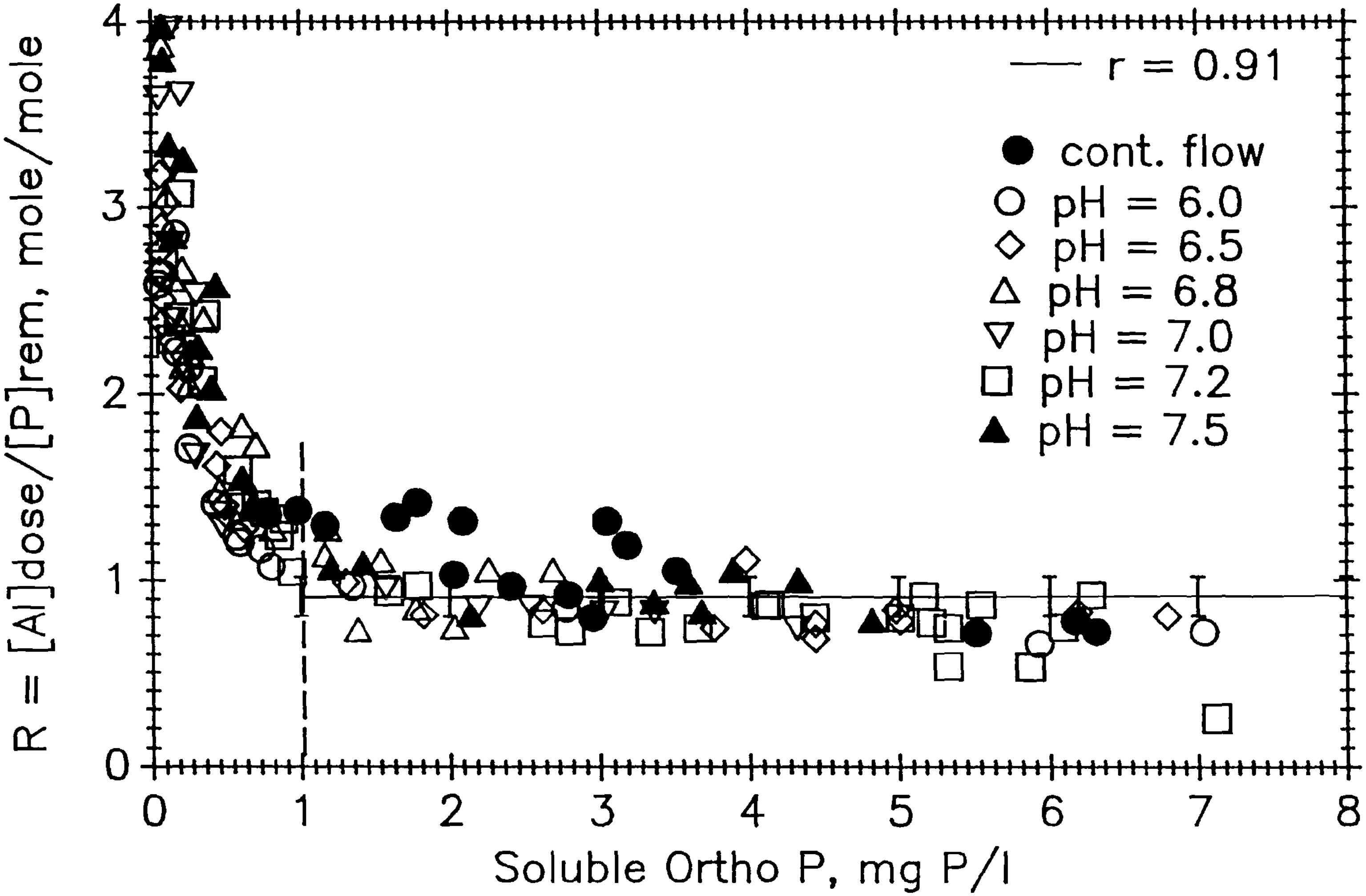


Figure 6.9 Agreement between model predictions and experimental observations in stoichiometric removal region

6.3.2 Region Two

Previous models of simultaneous chemical P removal with alum, based solely on the precipitation of aluminum-hydroxy-phosphate and aluminum hydroxide solids have not been verified with extensive experimental data. Such models predict that, at a constant pH and initial SOP conc., the SOP residual would decrease linearly with alum dose due to stoichiometric precipitation of aluminum-hydroxy-phosphate solid until an SOP residual concentration in equilibrium with the aluminum-hydroxy-phosphate solid was reached. Beyond the solubility limit for aluminum-hydroxy-phosphate solid, in the presence of aluminum, previous precipitation models have assumed that aluminum hydroxide precipitates in addition to the aluminum-hydroxy-phosphate precipitate. The Phase Rule dictates that in the presence of two solids unique SOP and aluminum residual concentrations exist at equilibrium. Under these conditions, the soluble aluminum and SOP residual concentrations would be controlled by the solubility of both the aluminum hydroxide and aluminum-hydroxy-phosphate precipitates. Precipitation based models of SOP removal would predict the trends shown in Figures 6.10 and 6.11 when alum is added to phosphate containing wastewater at a constant pH. A comparison of the experimental observations and Figure 6.11 indicate that they deviate from the idealized precipitation based models (see Figure 6.12).

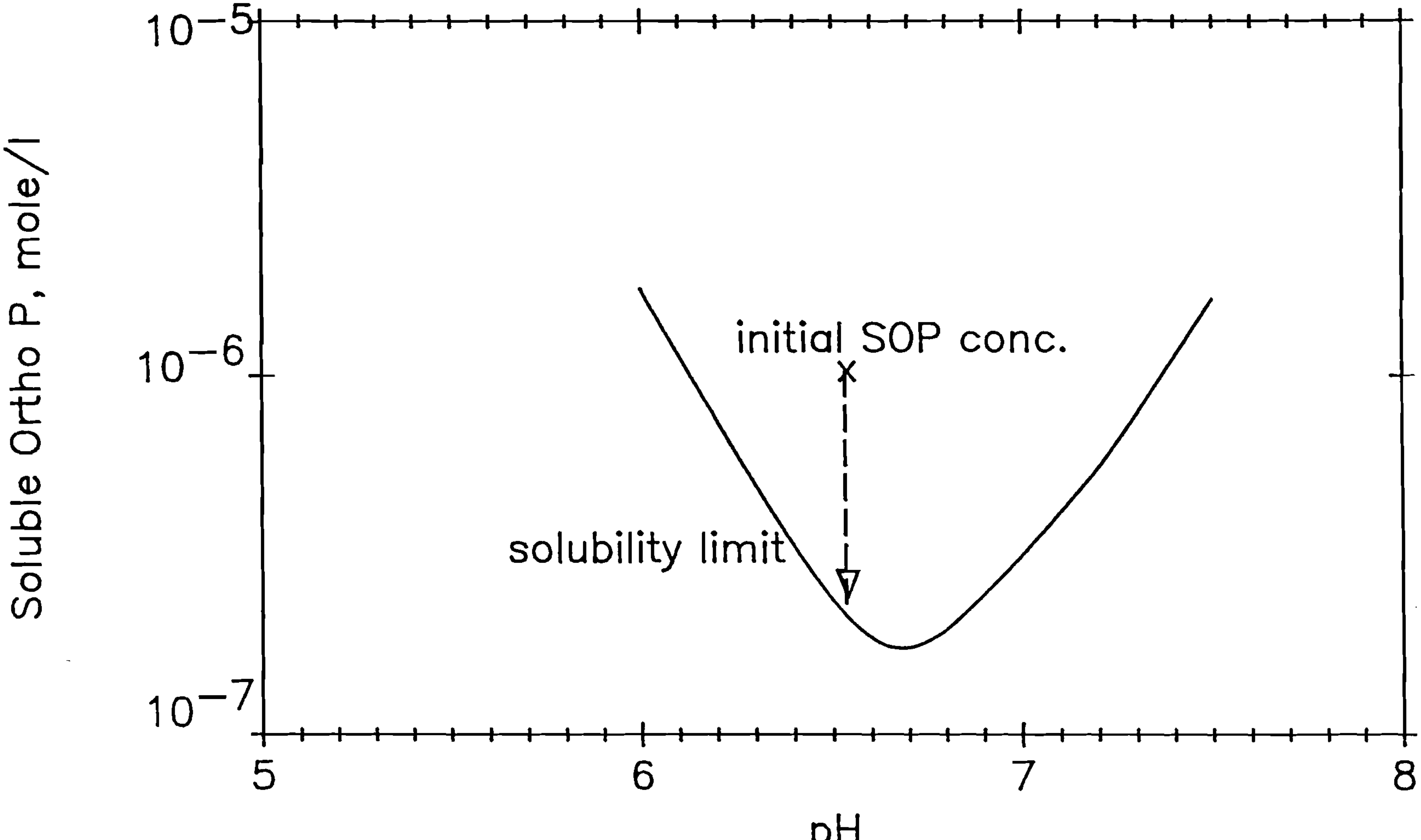


Figure 6.10 Precipitation based model predictions of change in [SOP] at constant pH with increasing alum addition

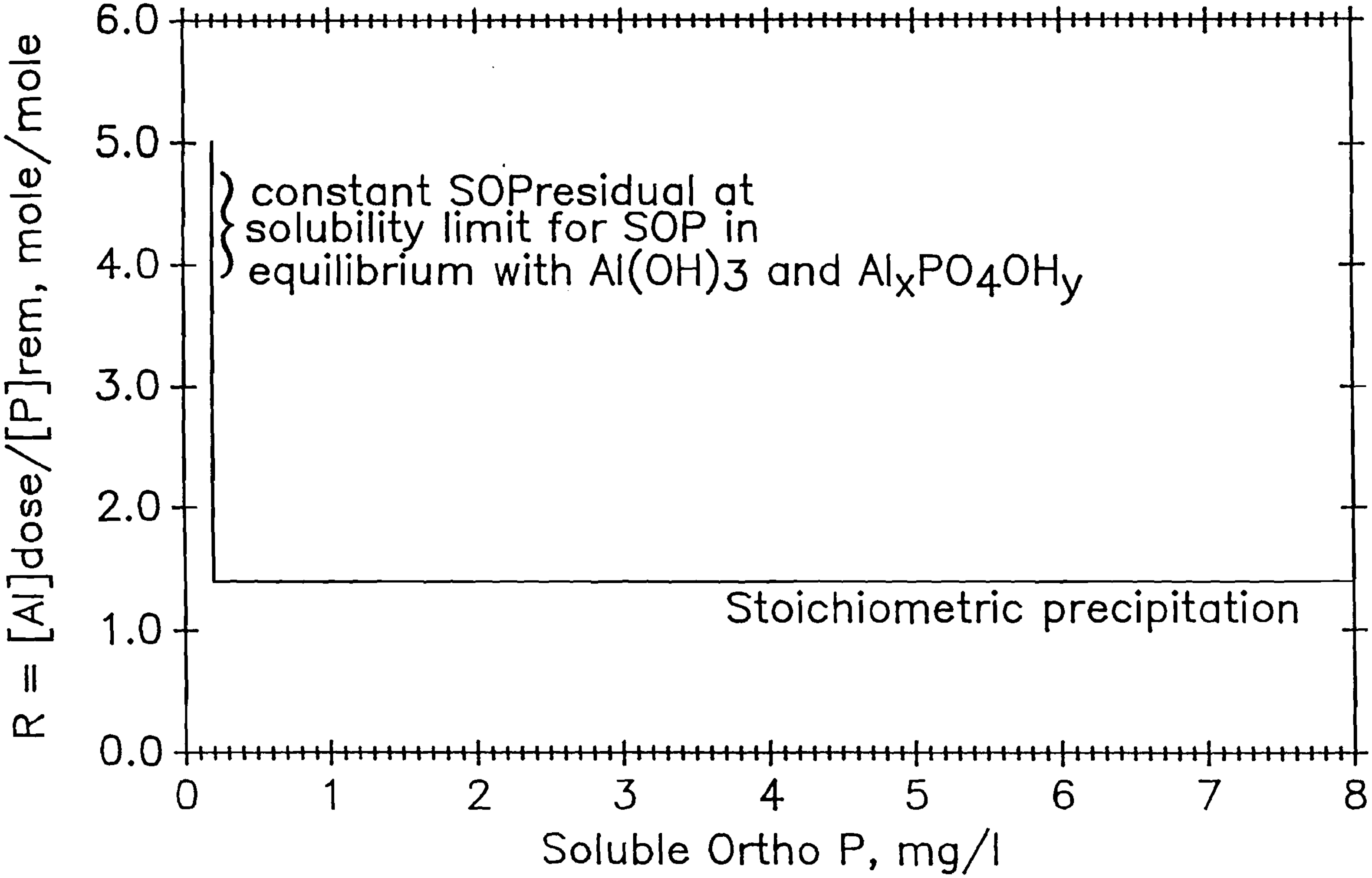


Figure 6.11 Relationship between R and SOP residual at constant pH predicted by precipitation based models of P−removal

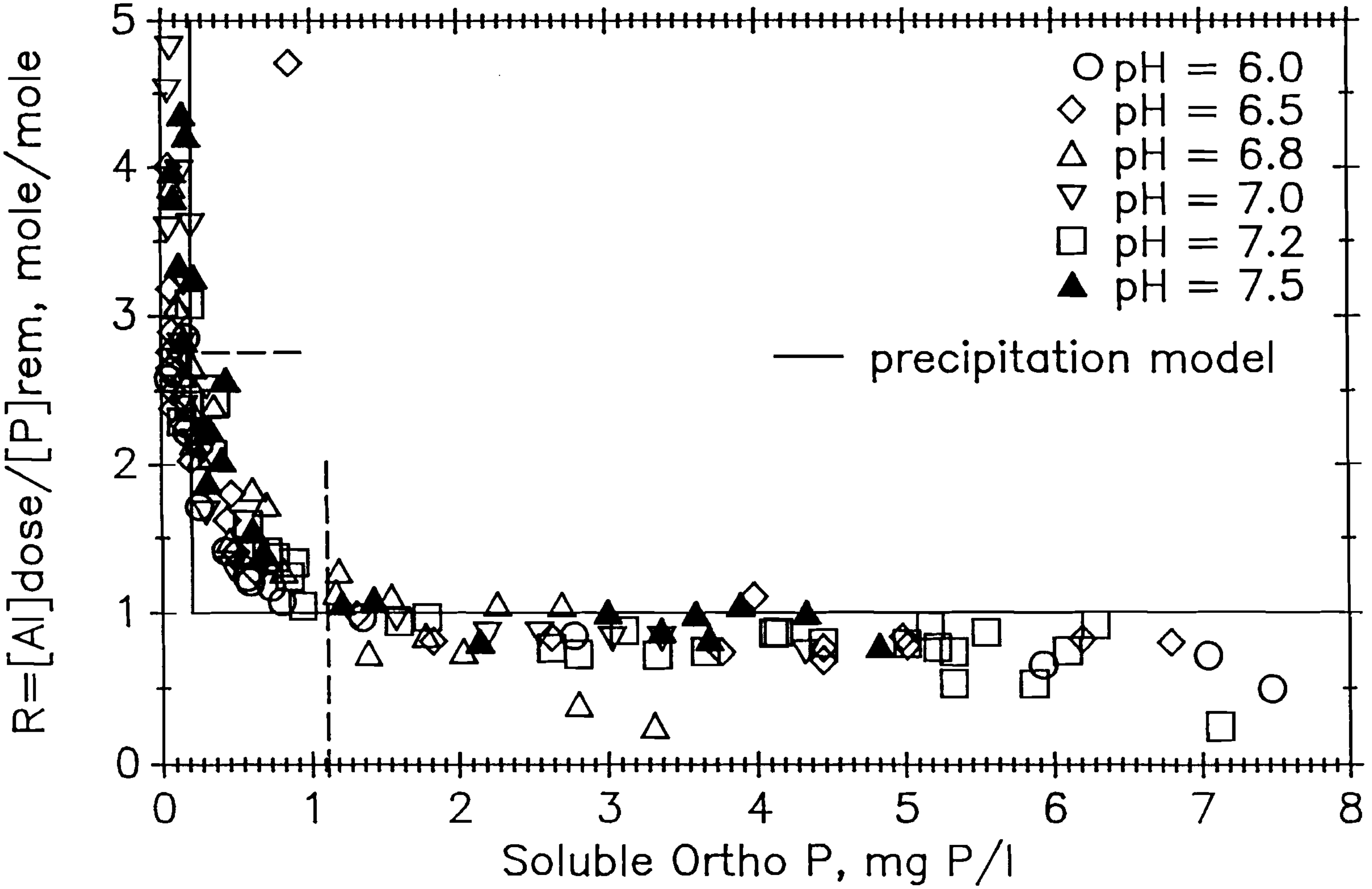


Figure 6.12 Comparison of batch experimental results and precipitation based model prediction.

Ferguson and King (1977) suggested that the SOP concentration reached when alum is dosed in excess of stoichiometric requirements but not sufficient to precipitate two solids, is determined by the equilibrium between the aluminum-hydroxy-phosphate precipitate and aqueous aluminum and phosphate concentrations. The alum dose region where this occurred was from 5.0 to 6.5 mg $Al^{(III)}$/1 and was considered narrow and unimportant.

Goldshmid and Rubin (1978) suggested that with aluminum doses in excess of stoichiometry and at pH values of < 6.0, the hydrolysis of aluminum-hydroxy-phosphate solids to aluminum hydroxide was followed by the adsorption of SOP on to the aluminum hydroxide solid surface. Goldshmid and Rubin described the adsorption of SOP on to aluminum hydroxide solid surfaces using equilibrium relationships.

6.3.2.1 Second Removal Region Model Development

This model assumes that when aluminum is dosed in excess of stoichiometric requirements for aluminum-hydroxy-phosphate precipitation, an aluminum hydroxide solid is formed and the second removal region is encountered. This model further assumes that in the second removal region any aluminum-hydroxy-phosphate precipitate formed hydrolyses to aluminum hydroxide and that phosphate removal results from the adsorption of SOP onto aluminum hydroxide solid surfaces as proposed by Goldshmid and Rubin (1978). The second phosphorus removal region described by this model includes SOP residual concentrations between approx. 1.0 and 0.1 mg P/l ($10^{-4.9}$ to $10^{-5.5}$ M), and alum doses between 5.5 and 25 mg $Al^{(III)}$/l. The second removal region described by this model covers a wider range of alum dose and SOP residual concentrations than the model of Ferguson and King (1978).

No attempt was made to identify the chemical precipitates formed to verify if the aluminum phosphate hydrolysis proposed by Goldshmid and Rubin occurred. It is reasonable to expect at alum doses used in the second removal region an aluminum hydroxide solid could be formed, with the most likely precipitate being an amorphous form of the stable hydroxide ($Al(OH)_{3(s)}$), gibbsite.

SOP residuals as a function of alum dose in this region were predicted by modifying the adsorption model of Goldshmid and Rubin (1978). Goldshmid and Rubin constructed adsorption isotherms for SOP adsorption on to aluminum hydroxide surfaces using the following equilibrium adsorption relationship:

$$v[Al(OH)_3{:}Al(OH)_2]\text{-}OH_{(surf)} + PO_4^{3-} <=>$$
$$[Al(OH)_3{:}Al(OH)_2]\text{-}PO_{4(surf)}^{(3-v)-} + vOH^- \qquad (6.7)$$

It was assumed that using equilibrium relationships would be acceptable because of the expected rapid rate of the reactions between aluminum ions and SOP. From equation 6.7, the following can be derived:

$$SOP_{(remv)}/\alpha_3 \times SOP_{(res)} = K_a\ [Al]^v/[OH]^v \qquad (6.8)$$

with

$SOP_{(remv)}$ = SOP removed , mole/l

$SOP_{(res)}$ = SOP residual, mole/l

K_a = equilibrium adsorption coefficient

v = stoichiometric coefficient

α_3 = distribution coefficient of PO_4^{3-}

[Al] = aluminum dose, mole Al^{3+}/l

[OH] = hydroxide concentration, mole/l

The term making up the left hand side of equation 6.8 will be referred to as the phosphate removal quotient (Q). A linear relationship between Q and [Al] will be observed if adsorption describes SOP removal in this region. Figure 6.13 shows that the relationship between Q and [Al] is indeed linear and therefore descriptive of SOP removal for the range of aluminum doses from 0.0001M to 0.001M Al^{3+}/l. Values of K_a and v were estimated at each pH value for the range of aluminum doses where the adsorption isotherms showed the best fit to the experimental data. K_a and v were found to depend on pH as follows:

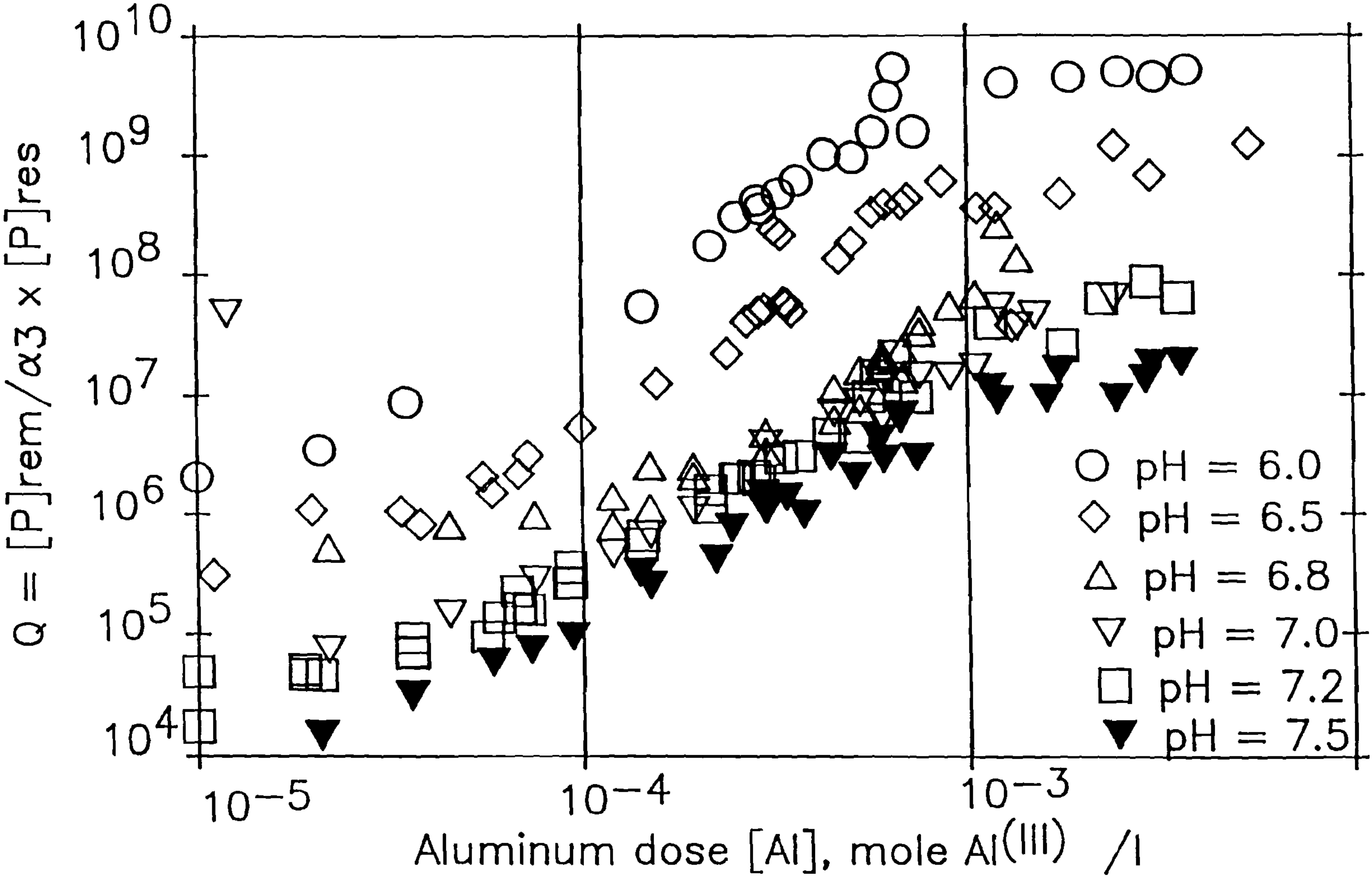


Figure 6.13 Adsorption isotherms of batch experimental results using equation 6.8

$$v = -0.46\text{pH} + 5.14 \qquad (6.9)$$

$$\log(K_a) = 1.98\text{pH} - 14.0 \qquad (6.10)$$

Lines showing model predictions at constant pH (using equations 6.8 through 6.10) in the second SOP removal region are shown with the experimental observations in Figure 6.14. The agreement between model predictions and experimental observations is good.

The equilibrium relationship used as the basis of the Goldshmid and Rubin model (equation 6.7) only describes the removal of PO_4^{3-}. Inspection of the distribution constants for orthophosphoric acid in the pH range of interest (Table 6.3) shows that the PO_4^{3-} concentration is extremely small and the use of this species in the development of the adsorption model may be inappropriate. At the pH range used in this study, it is reasonable to expect that the SOP species available for adsorption are primarily $H_2PO_4^-$ and. HPO_4^{2-} rather than PO_4^{3-}. The model of Goldshmid and Rubin was modified to reflect the removal of all SOP species by eliminating α_3 in the calculation of the phosphate removal quotient (Q) as follows:

$$SOP_{(remv)}/SOP_{res} = K_a^* \; [Al]^{v^*}/[OH]^{v^*} \qquad (6.11)$$

The terms Q^*, v^* and K_a^* in equation 6.11 relate to the adsorption of all SOP species. Comparing Figures 6.15 and 6.13 reveals that the adsorption model proposed by

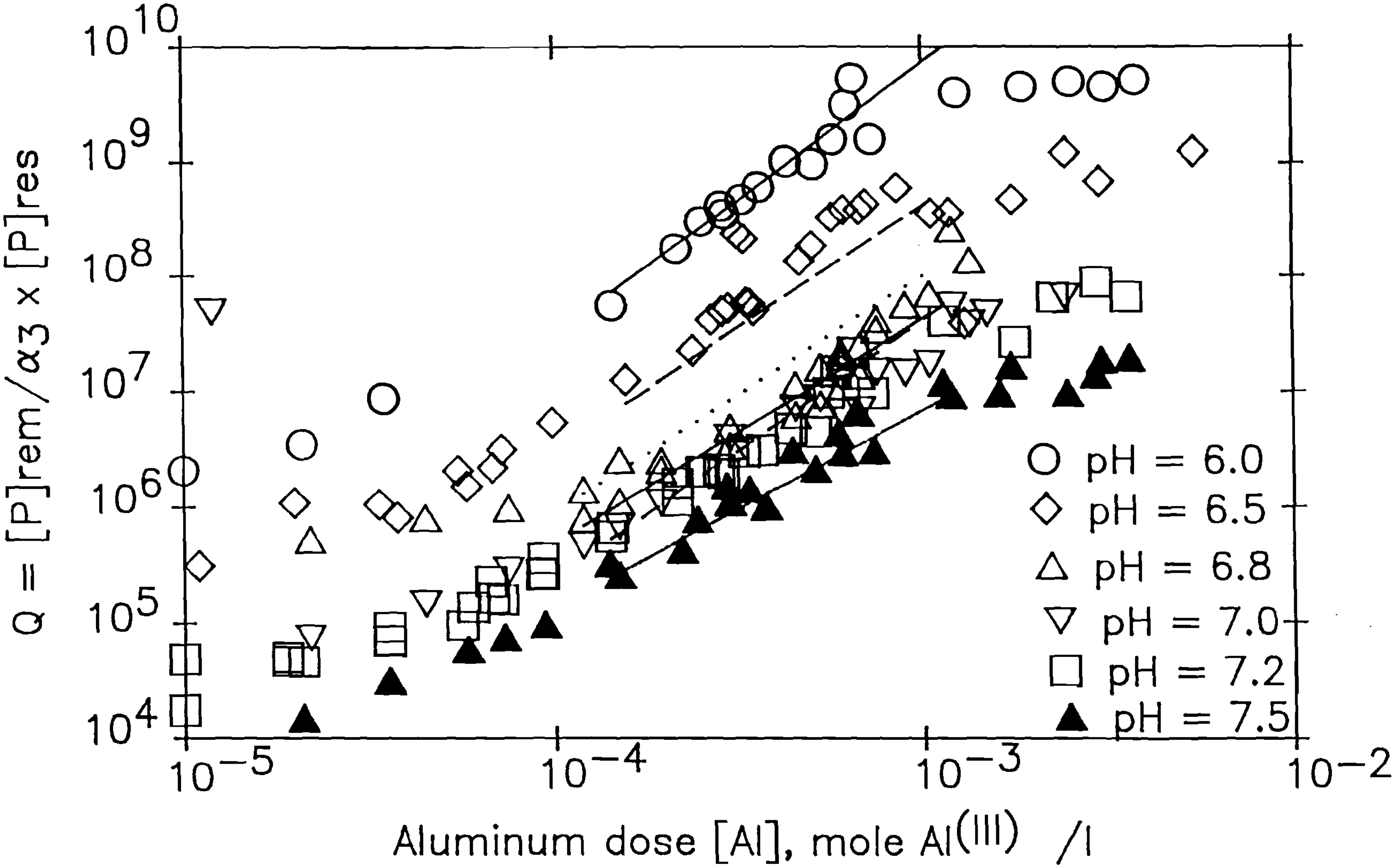


Figure 6.14 Agreement between Goldshmid and Rubin model and

Table 6.3
Acid distribution constants

pH	a1	a2	a3
6.0	0.941	0.059	$2.98x10^{-8}$
6.5	0.833	0.166	$2.64x10^{-7}$
6.8	0.715	0.285	$8.96x10^{-7}$
7.0	0.613	0.387	$1.93x10^{-6}$
7.2	0.499	0.500	$3.98x10^{-6}$
7.5	0.334	0.666	$1.04e-5^{-6}$

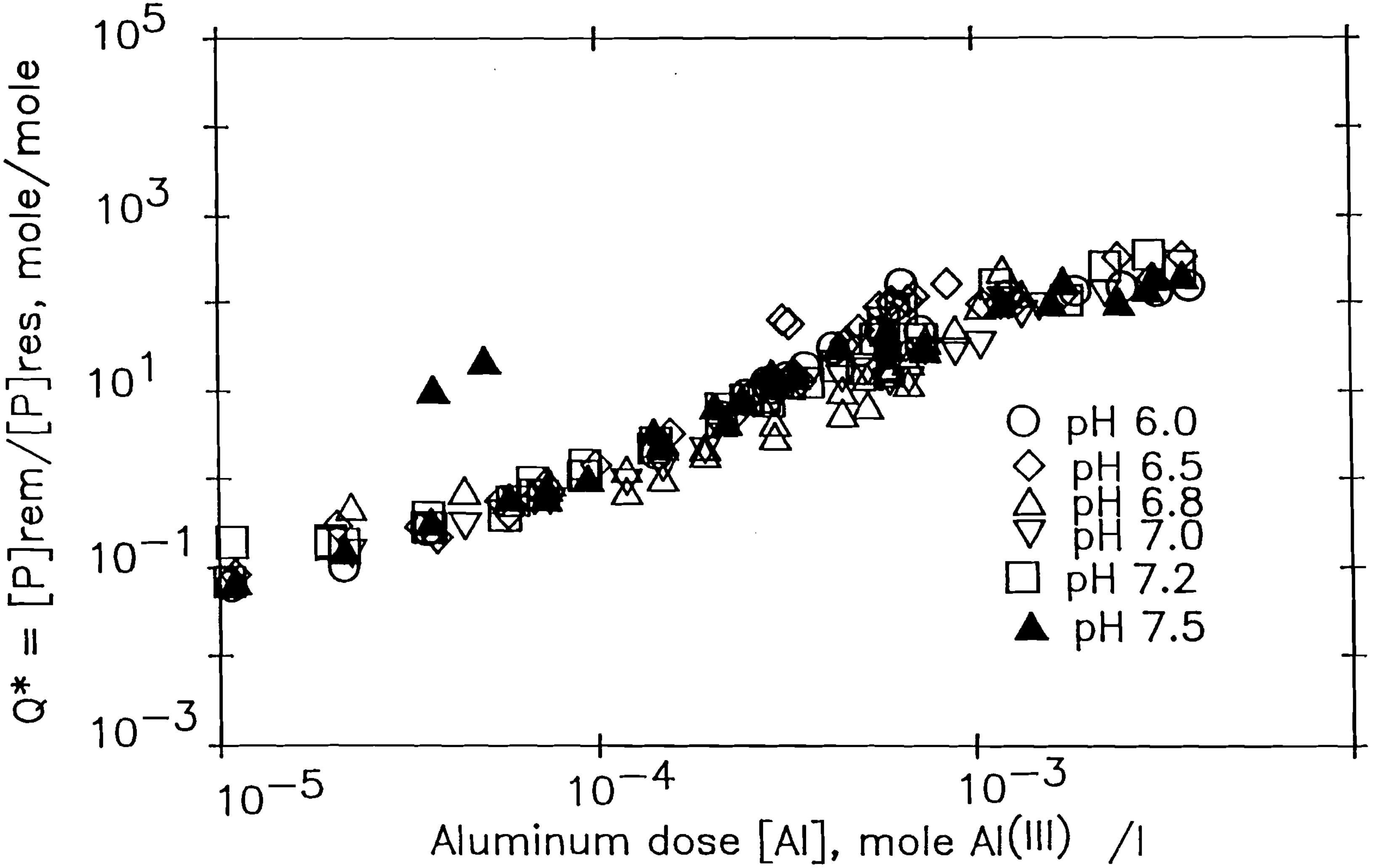


Figure 6.15 Adsorption isotherms using modified model (eq. 6.11)

Goldshmid and Rubin differs from adsorption described using equation 6.11. The adsorption isotherms in Figure 6.15 indicate that Q^* is linear with [Al] for the same range of [Al] as Q, but that the range of Q^* values is not as wide as the range of Q values. The Goldshmid and Rubin model (equation 6.8) predicted Q values that varied widely as a result of the range of α_3 values in the pH range 6.0 to 7.5, suggesting a more significant effect of pH on SOP adsorption than equation 6.11. The relationships between v^*, K_a^* and pH based on the adsorption of all SOP species (using equation 6.11) are:

$$v^* = -0.46\text{pH} + 5.14 \qquad (6.12)$$

$$\log(K_a^*) = 3.69\text{pH} - 31.7 \qquad (6.13)$$

6.3.2.2 Estimation of Alum Dose Requirements

The aluminum dose required to achieve an SOP residuals of between 1 and 0.1 mg P/l under controlled pH conditions can be estimated using equations 6.11 through 6.13 and the following procedure:

1. determine required SOP removal

$$SOP_{remv} = SOP_{infl} - SOP_{res} \qquad (6.14)$$

where:

SOP_{remv} = required SOP removal, M

SOP_{infl} = influent SOP, M

SOP_{res} = desired SOP residual, M

2. determine v and K_a' at the pH of interest using equations 6.12 and 6.13

3. calculate aluminum dose using:

$$Al^{(III)}_{reqd} = \{(SOP_{remv}/SOP_{res}) \times ([OH]^{v}/K_a')\}^{1/v} \qquad (6.15)$$

where:

$Al^{(III)}_{reqd}$ = aluminum dose needed to reach desired SOP residual, mole/l

The agreement between model predictions and experimental observations is shown in Figures 6.16 through 6.21. For each of the pH values investigated the adsorption model describes SOP removal quite well. The lowest SOP residual reached in this region appeared to depend on pH, with the lowest SOP residual being reached at pH 6.0. Goldshmid and Rubin suggested that the value of v was representative of the number of hydroxyl exchanged during adsorption. The currently proposed model found that v decreased as the pH increased. This would suggest that SOP adsorption would be enhanced at lower pH values.

Model predictions using equations 6.11 through 6.14 were compared with the continuous flow experimental results (Figure 6.22). The model agreement between model predictions and the continuous flow results is good, although at aluminum doses greater than approx. 0.0006 M the model predicted lower values of Q^* (avg. difference = 12%) than observed experimentally. The difference in

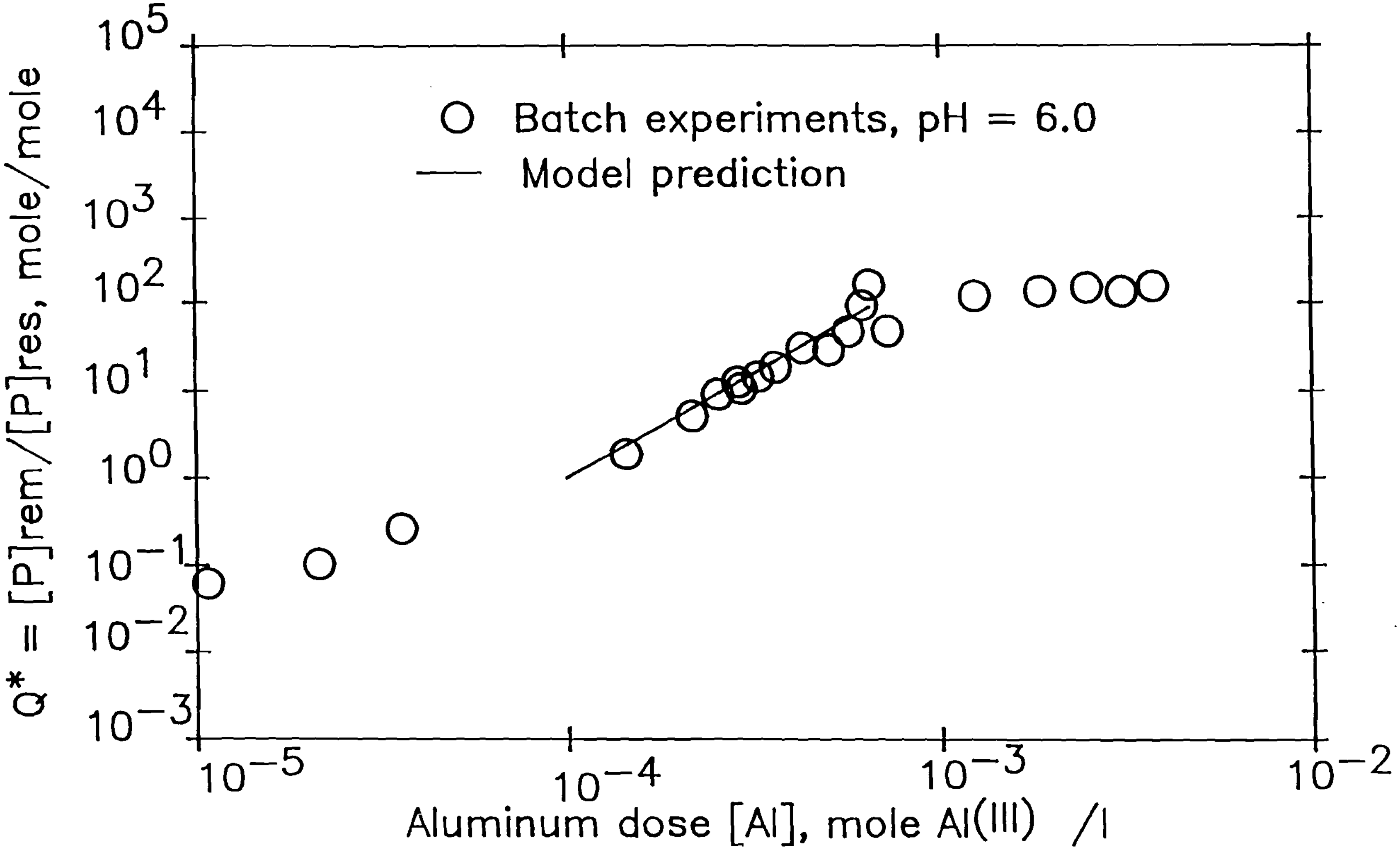


Figure 6.16 Comparison of experimental results and SOP adsorption model in second SOP removal region.

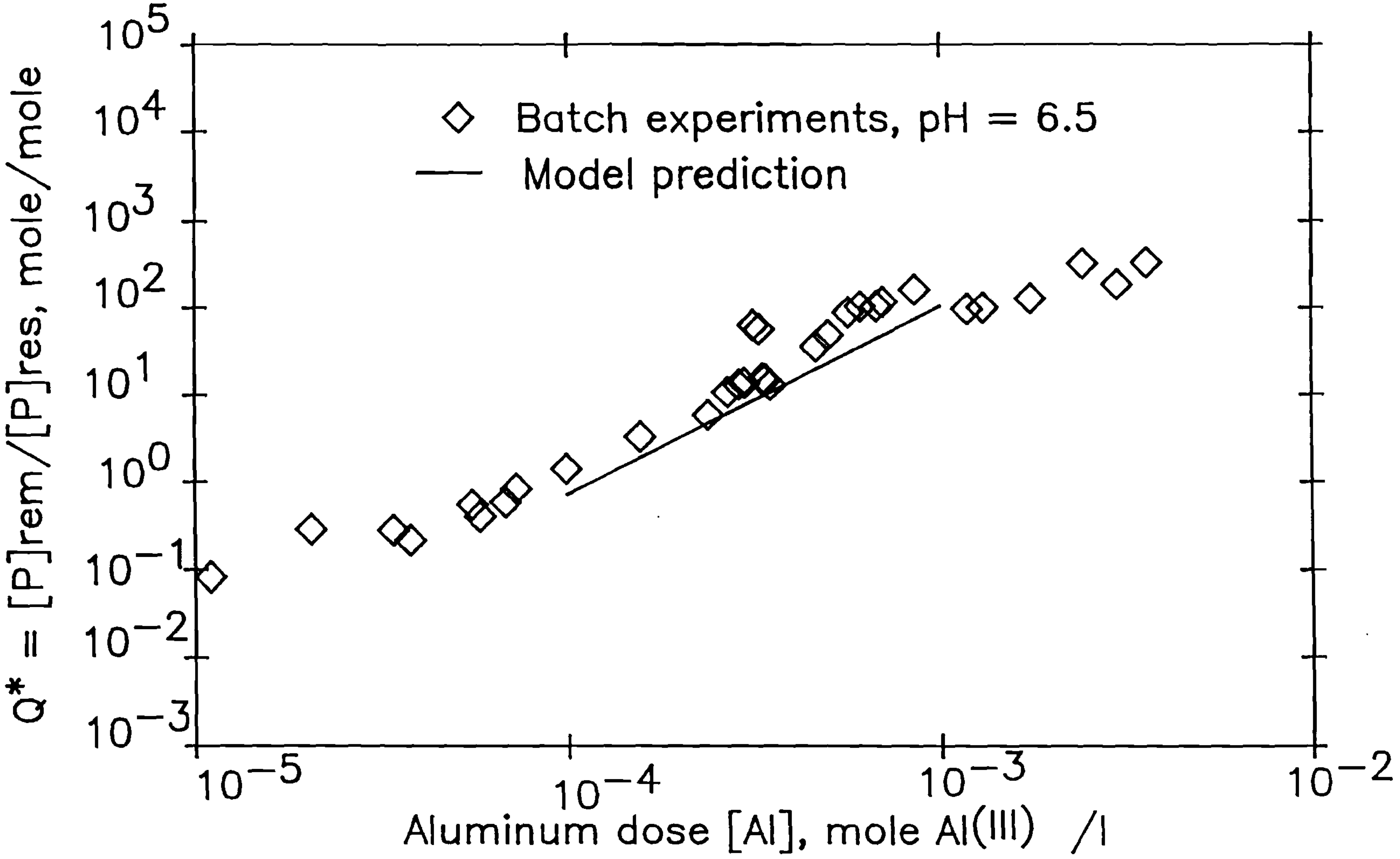


Figure 6.17 Comparison of experimental results and SOP adsorption model in second SOP removal region.

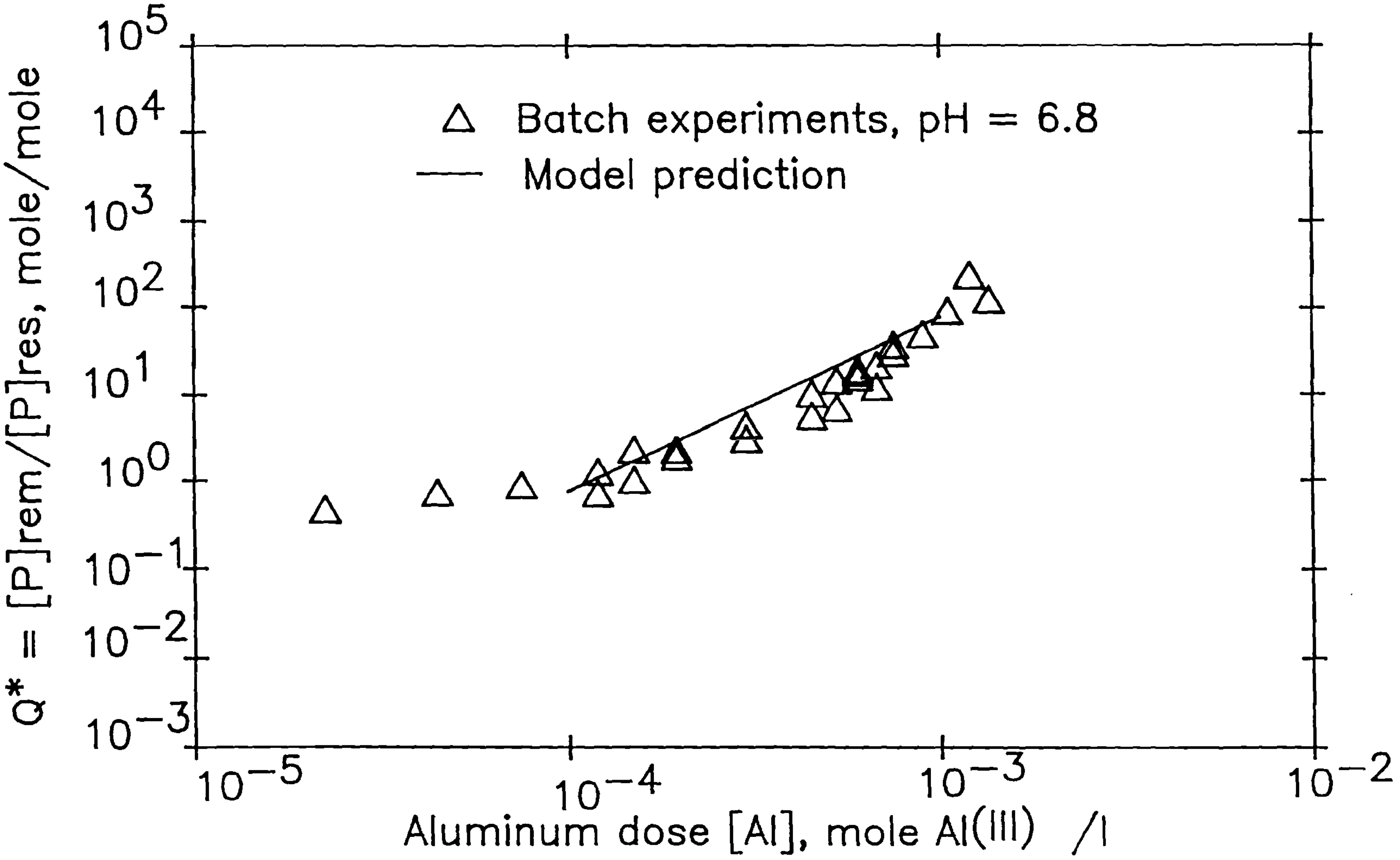


Figure 6.18 Comparison of experimental results and SOP adsorption model in second SOP removal region.

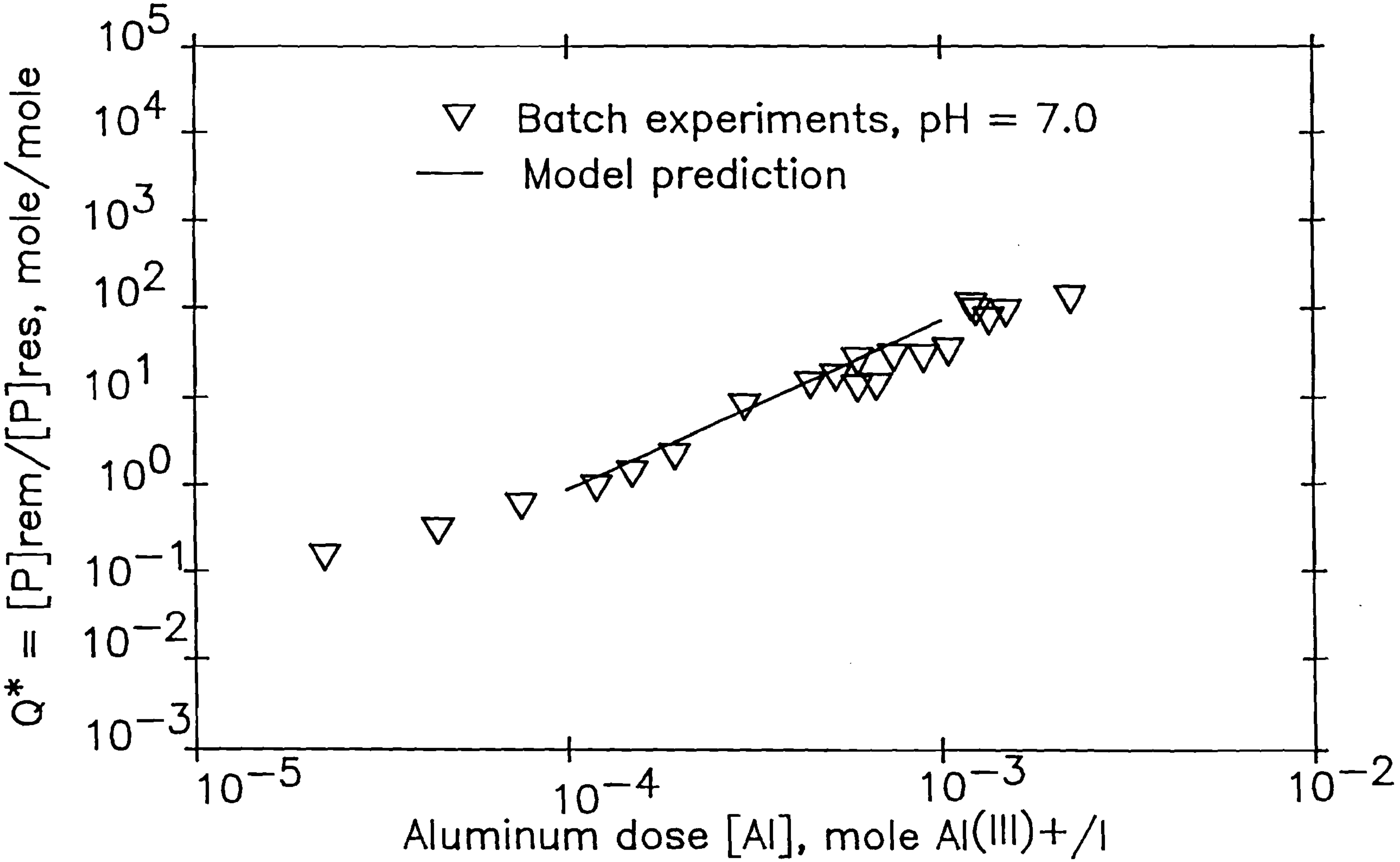


Figure 6.19 Comparison of experimental results and SOP adsorption model in second SOP removal region.

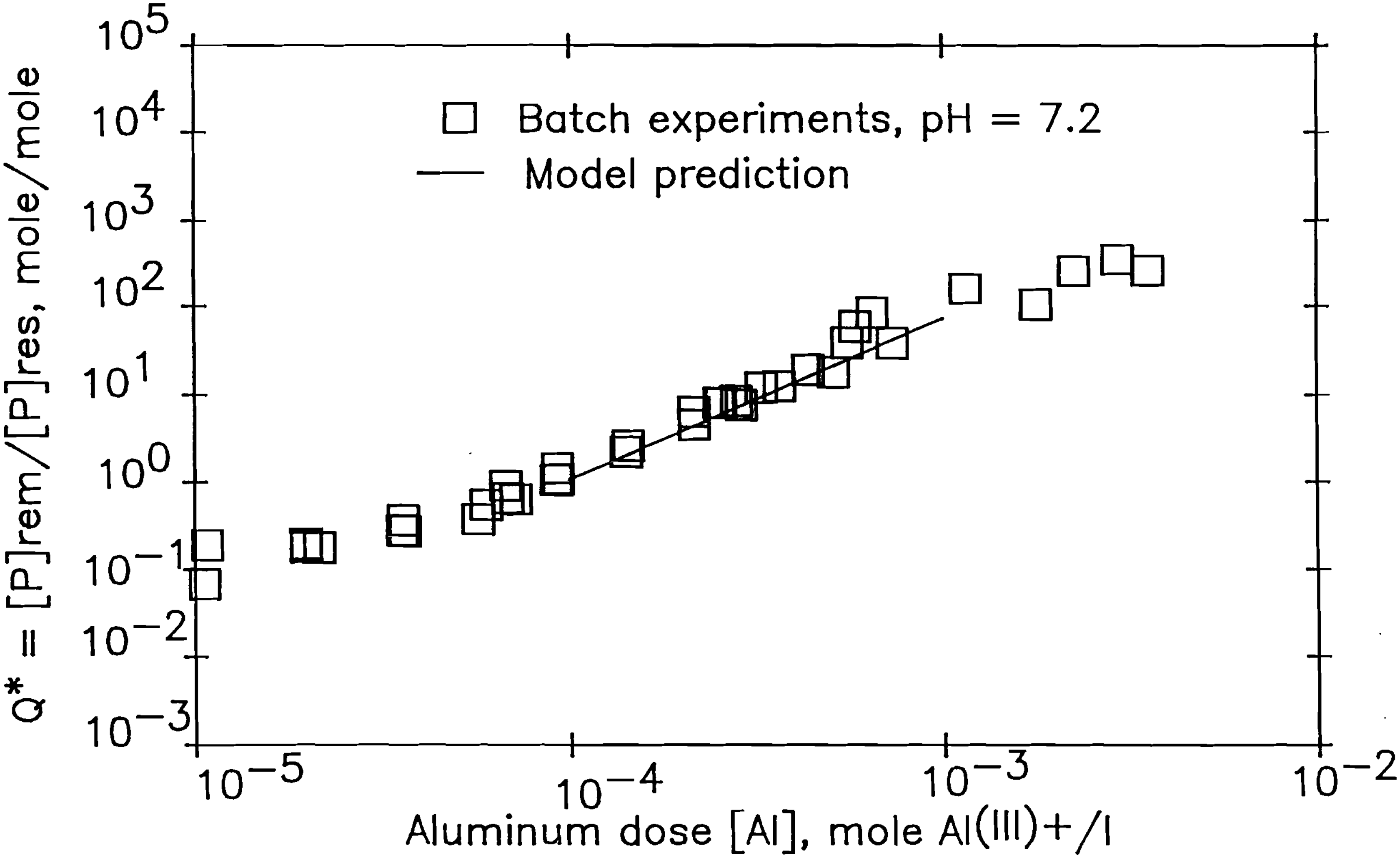


Figure 6.20 Comparison of experimental results and SOP adsorption model in second SOP removal region.

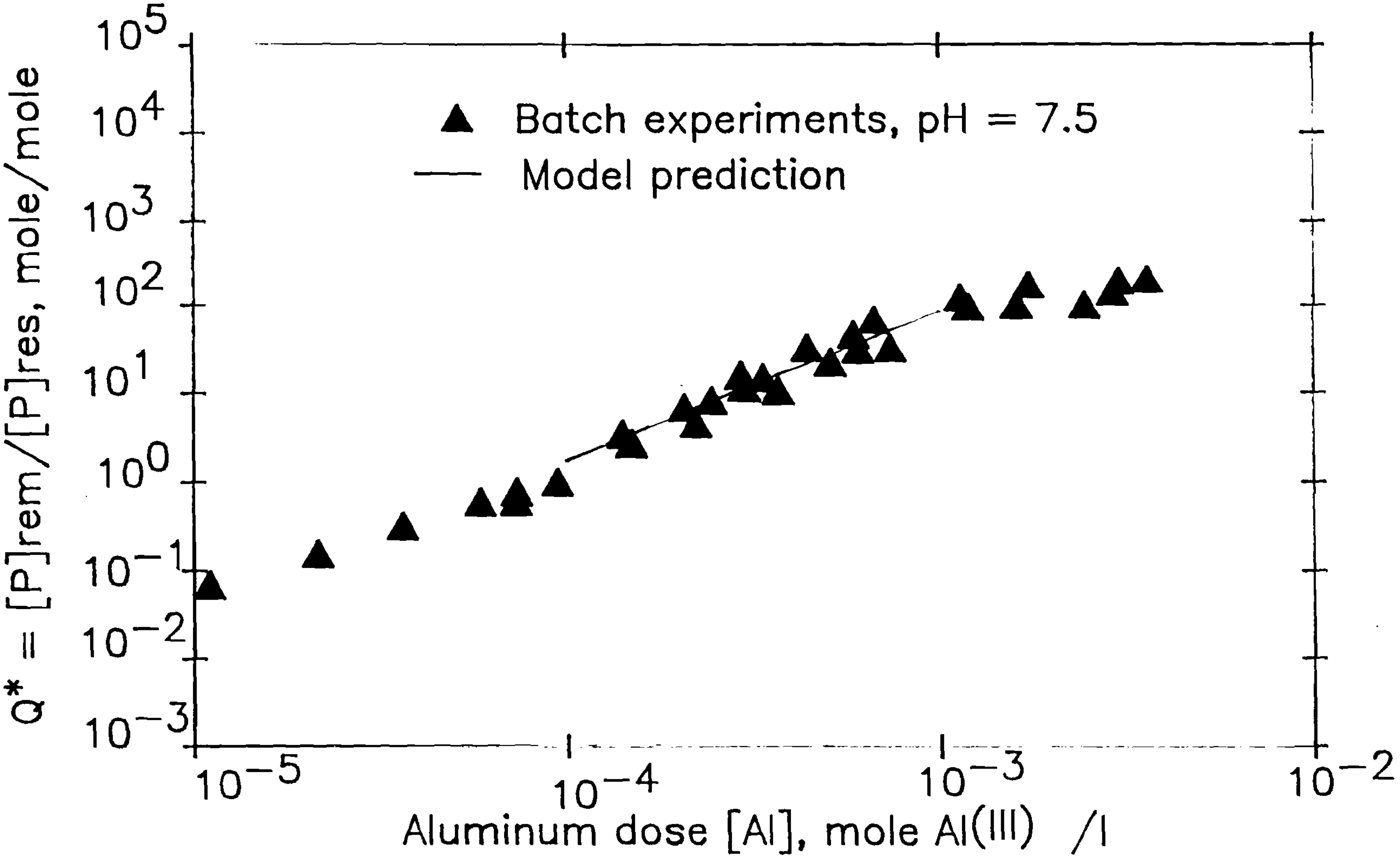


Figure 6.21 Comparison of experimental results and SOP adsorption model in second SOP removal region.

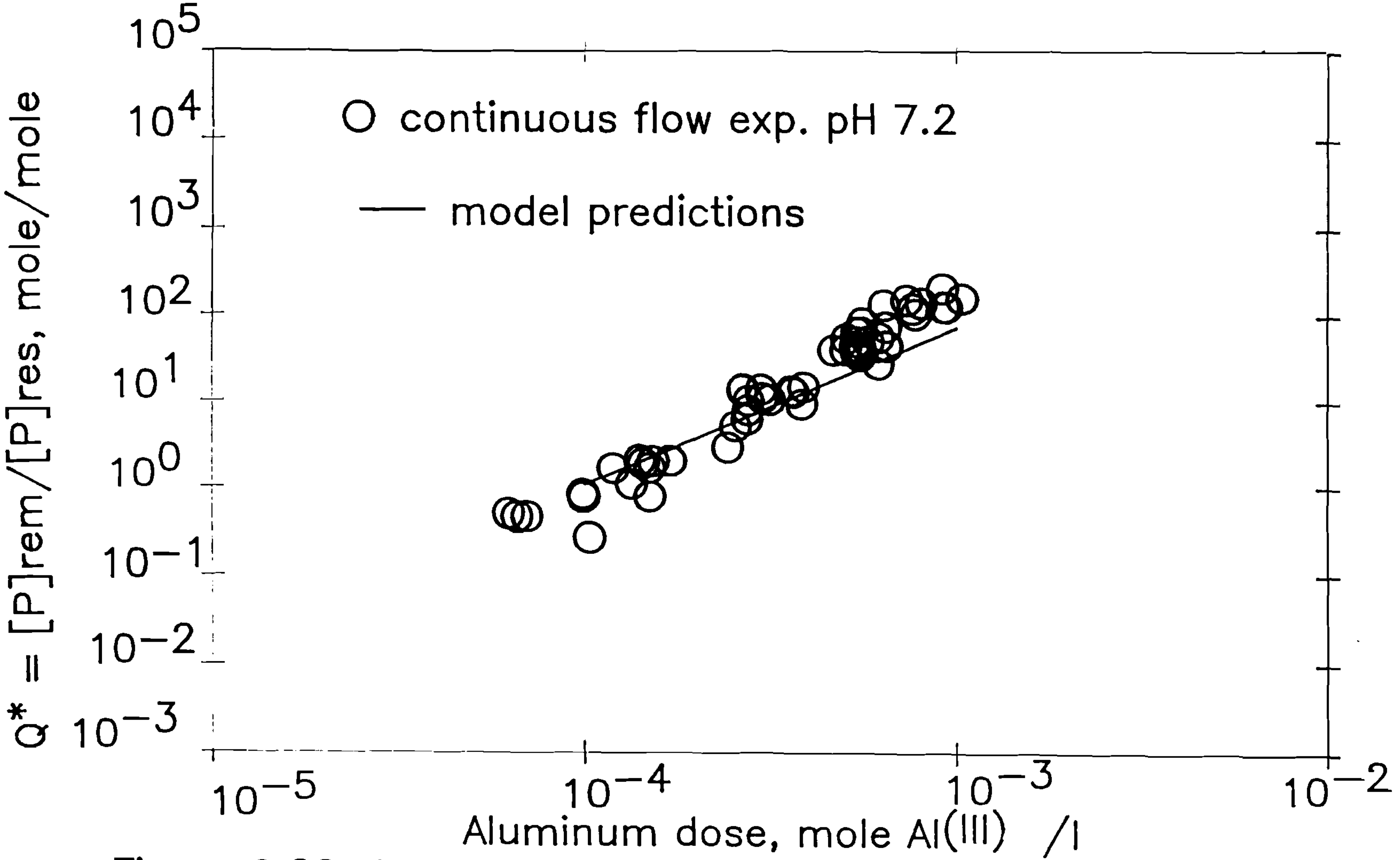


Figure 6.22 Agreement between model prediction and continuous flow experimental results in the second P−removal region.

predicted and observed Q^* values suggests that less SOP is removed (higher SOP residual reached) with a given aluminum dose in the continuous flow system than predicted by the model. This finding was interpreted as reflecting the experimental error included in the relationships describing K_a^* and v^*. New values of K_a^* and v^* were calculated using the continuous flow data giving:

$$\log K_a^{**} = -7.3$$

$$v^{**} = 2.52$$

Figure 6.23 shows the continuous flow results and model predictions using equation 6.15 and K_a^{**} and v^{**}. The average difference between model predictions and experimental observations is less than 1% when the recalculated values of K_a^{**} and v^{**} are used. It was concluded that the adsorption relationships, based on the model of Goldshmid and Rubin (1978), could be used to describe SOP removal in the second SOP removal region. The relationships describing K_a^* and v^* (equations 6.12 and 6.13) could be used to estimate aluminum doses, although more accurate predictions can be obtained using continuous flow data at the pH of interest.

At low aluminum doses (<0.0001 mole/l) and high SOP residuals, SOP removal is controlled by the precipitation of the aluminum-hydroxy-phosphate solid and the adsorption model is inapplicable. The adsorption model also does not adequately describe SOP removal at very high $Al^{(III)}$ doses.

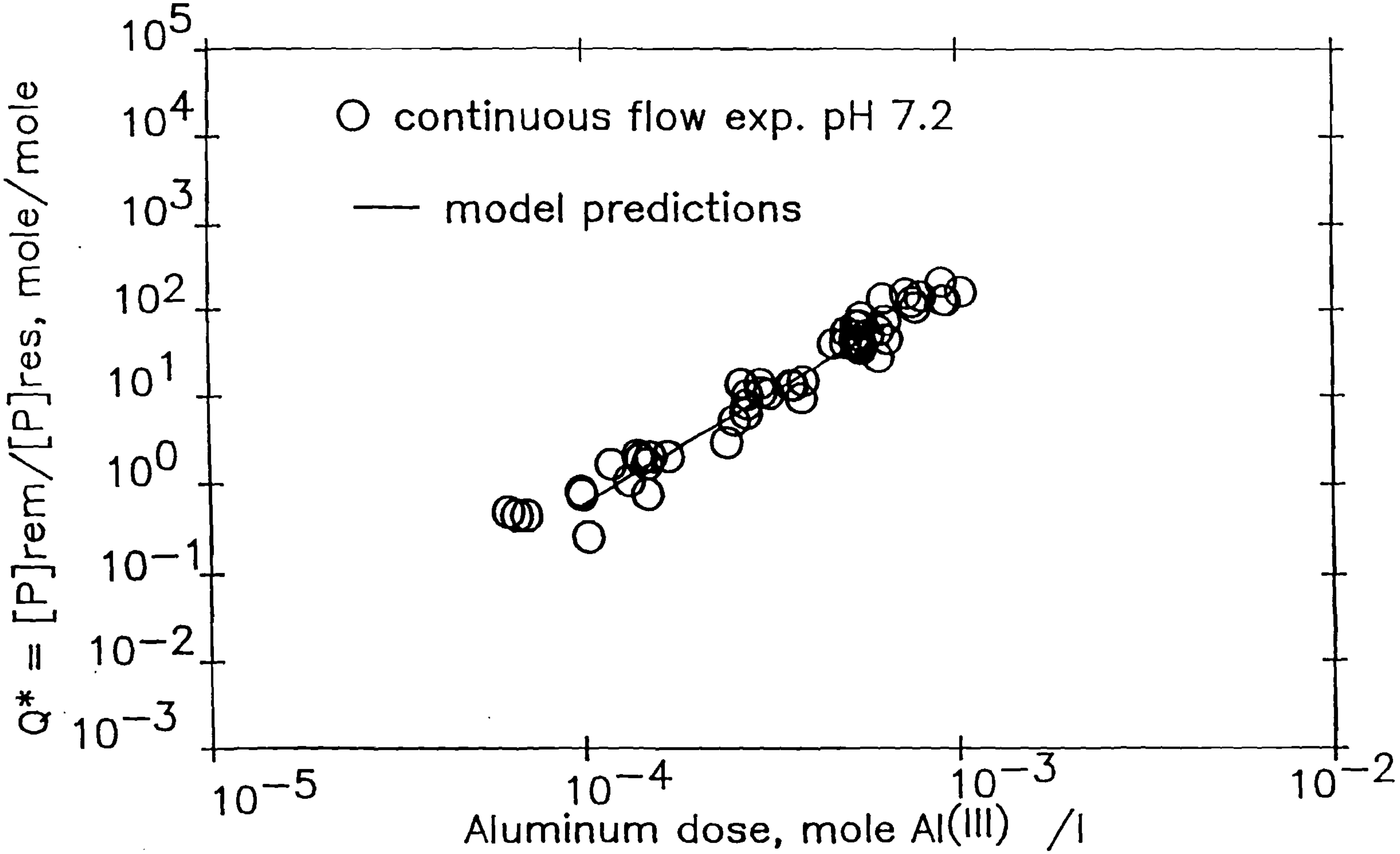


Figure 6.23 Agreement between model prediction and continuous experimental results using constants derived wtih continuous flow data.

6.3.3 Removal Region 3

At alum doses of greater than approx. 25 mg Al^{3+}/l the adsorption model no longer describes SOP removal adequately. In this third SOP removal region it appears that a constant SOP residual concentration is reached that appears to be the minimum SOP level possible using simultaneous aluminum phosphate precipitation.

This model proposes, that at high alum doses (>25 mg/l) both aluminum-hydroxy-phosphate and aluminum hydroxide solids are present. Since alum doses required to reach the third region are in considerable excess of the amount needed to stoichiometrically precipitate all the influent SOP as aluminum-hydroxy-phosphate, it is reasonable to expect that aluminum hydroxide solid is formed. Both Ferguson and King (1977) and Jenkins *et al.* (1984) suggested that the co-precipitation of aluminum-hydroxy-phosphate and aluminum hydroxide occurred at high aluminum doses, but proposed that this occurred at lower aluminum doses than suggested by the currently proposed model.

The transition point between the second region, where SOP adsorption on to aluminum hydroxide solids predominates to the third region is uncertain. The aluminum-hydroxy-phosphate solid phase in the third removal region could possibly result from the nucleation of a second solid (aluminum-hydroxy-phosphate) phase on the metal hydroxide surface after sufficient SOP has adsorbed, as suggested by Robarge and Corey (1979) and Corey (1975). Extensive analysis of the precipitates formed would be required to determine whether this was occurring during the simultaneous precipitation of SOP with alum.

The minimum SOP concentration at each pH was determined by averaging the values of all SOP concentrations reached with alum doses greater than 25 mg $Al^{(III)}$/l. Data collected at pH 7.0 were not adequate to estimate the minimum SOP concentration and were excluded from the model development. The experimental observations show that, at all pH values studied, very low SOP residual concentrations could be reached ($10^{-5.5}$ M to $10^{-6.2}$ M; 0.09 to 0.02 mg P/l) and that the minimum SOP concentration was a function of pH (Figure 6.24).

A model was developed which predicted the minimum SOP concentration as a function of pH. The model included the simultaneous solution of mass balance and chemical equilibria describing aluminum and phosphate concentration. The chemical equilibrium relationships used in the development of this model are listed in Table 6.4. Equilibrium constants were selected after a review of the literature (Smith and Martel, 1976; Baes and Mesmer, 1976) and were adjusted to zero ionic strength using the DeBye-Huckel limiting law.

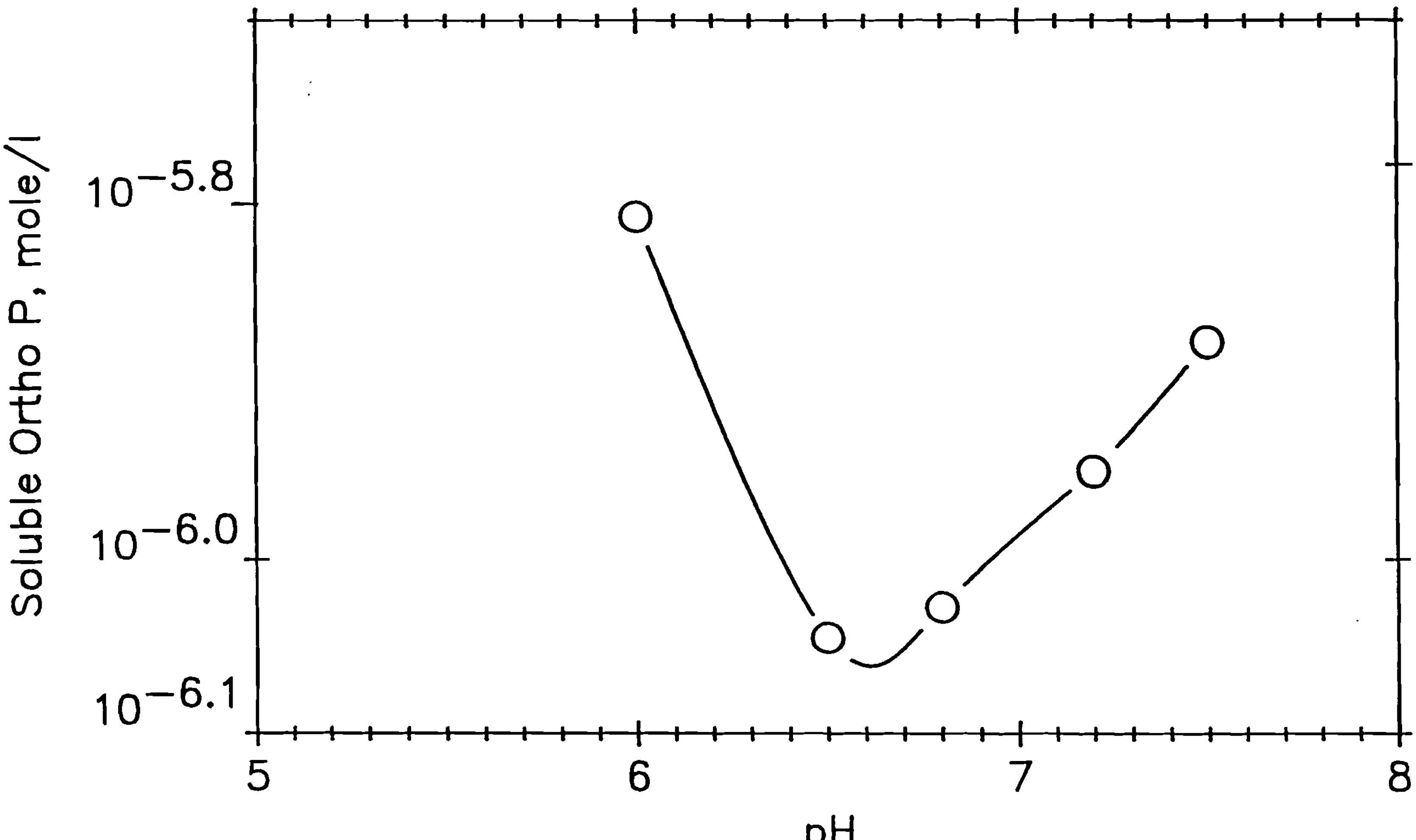


Figure 6.24 Observed minimum SOP residual as a function of pH

Table 6.4

Chemical Equilibria

1.0 Dissociation of phosphoric acid

$H_3PO_4 + H_2O \Leftrightarrow H_2PO_4^- + H_3O^+$ $\quad pk_1 = -2.15$ (6.16)

$H_2PO_4^- + H_2O \Leftrightarrow HPO_4^{2-} + H_3O^+$ $\quad pk_2 = -7.20$ (6.17)

$HPO_4^{2-} + H_2O \Leftrightarrow PO_4^{3-} + H_3O^+$ $\quad pk_3 = -12.35$ (6.18)

2.0 Protolysis of aluminum

$Al^{3+} + H_2O \Leftrightarrow Al(OH)^{2+} + H_3O^+$ $\quad pk_1' = 5.0$ (6.19)

$Al^{3+} + 4H_2O \Leftrightarrow Al(OH)_4^- + 4H_3O^+$ $\quad pk_4 = 21.7$ (6.20)

3.0 Complex formation

$Al^{3+} + H_2PO_4^- \Leftrightarrow Al(H_2PO_4)^{2+}$ $\quad pK_c = ??$ (6.21)

4.0 Solid formation

$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_{3(s)} + 3H_3O^+$ $\quad pK_{so} = 9.1$ (6.22)

$0.91Al^{3+} + H_2PO_4^- + 1.73(OH^-) \Leftrightarrow Al_{0.91}(H_2PO_4)(OH)_{1.73(s)}$ $\quad pK_{so}^* = ??$ (6.23)

Before estimating the minimum SOP residual as a function of pH, it was first necessary to estimate the solubility product of the aluminum-hydroxy-phosphate solid and the stability constant of the aluminum phosphate soluble complex. Mass balances on aluminum and soluble orthophosphate were reduced to equation 6.24 (see Figure 6.25) using the chemical equilibria listed in Table 6.4. The derivation of equation 6.24 is detailed in Appendix 4. The solubility product (K_{so}) of the aluminum-hydroxy-phosphate solid (equation 6.23) and the equilibrium constant (K_c) of the aluminum phosphate complex (equation 6.21) were then estimated using the batch experimental results. The equilibrium constants (± 1σ) were estimated using a nonlinear least square procedure with the following results:

$pK_{so} = 29.7 \pm 0.17$

$pK_c = -10.9 \pm 0.24$

The estimated equilibrium constants were used to develop a curve describing the equilibrium between SOP and aluminum-hydroxy-phosphate and aluminum hydroxide precipitates. Determination of the minimum SOP concentration is summarized in the following series of calculations:

Figure 6.25
Equilibrium constant relationship (eqn 6.24)

$$K_{so} = \left(10^{9.1}[H^+]^3\right)^{0.91}$$

$$\times \left[\frac{C_{T,SOP}}{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + \frac{K_3K_2}{[H^+]^2} + K_c(10^{9.1})[H^+]^3} \right] \times \left[OH^-\right]^{1.73}$$

1. Calculate $[H^+]$ at the pH of interest
2. Calculate equilibrium Al^{3+} concentration assuming $Al(OH)_{3(s)}$ controls Al^{3+} concentration. Rearranging equation 6.22 gives:

$$[Al^{3+}] = (10^{-9.1})[H^+]^3 \qquad (6.25)$$

3. Using $[Al^{3+}]$ from step 2 and estimated K_{so} for $Al_{0.91}H_2PO_4(OH)_{1.73(s)}$ calculate $H_2PO_4^-$ concentration. Rearranging equation 6.23 gives:

$$[H_2PO_4^-] = K_{so}/[Al^{3+}]^{0.91}[OH^-]^{1.73} \qquad (6.26)$$

4. Calculate H_3PO_4, HPO_4^{2-}, PO_4^{3-} using equations 6.16 through 6.18.

$$[H_3PO_4] = [H_2PO_4^-][OH]/K_1 \qquad (6.27)$$

$$[HPO_4^{2-}] = K_2[H_2PO_4^-]/[H^+] \qquad (6.28)$$

$$[PO_4^{3-}] = K_3K_2[H_2PO_4^-]/[H^+]^2 \qquad (6.29)$$

5. Calculate $[Al(H_2PO_4)^-]$ using equation 6.21 and estimated K_c, $[Al^{3+}]$, and $[H_2PO_4^-]$ values

$$[Al(H_2PO_4)^{2+}] = K_c[Al^{3+}][H_2PO_4^-] \qquad (6.30)$$

6. Calculate SOP_{mres} using:

$$SOP_{mres} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [Al(H_2PO_4)^{2+}] \qquad (6.31)$$

were:

SOP_{mres} = minimum SOP residual concentration in equilibrium with $Al(OH)_{3(s)}$ and $Al_{0.91}(H_2PO_4)(OH)_{1.73(s)}$

In Figure 6.26 the predicted solubility curve and the experimental observations in the third removal region are compared. The model predicted lower minimum SOP residuals and a greater changes in SOP_{mres} with pH than the experimental observations indicated. The value of the aluminum-hydroxy-phosphate solubility product was adjusted to allow a better fit the experimental data. The following equilibrium constants were used to develop a solubility curve that fit the experimental observations better (see Figure 6.27):

$pK_{so} = 29.3$

$pK_c = -10.9$

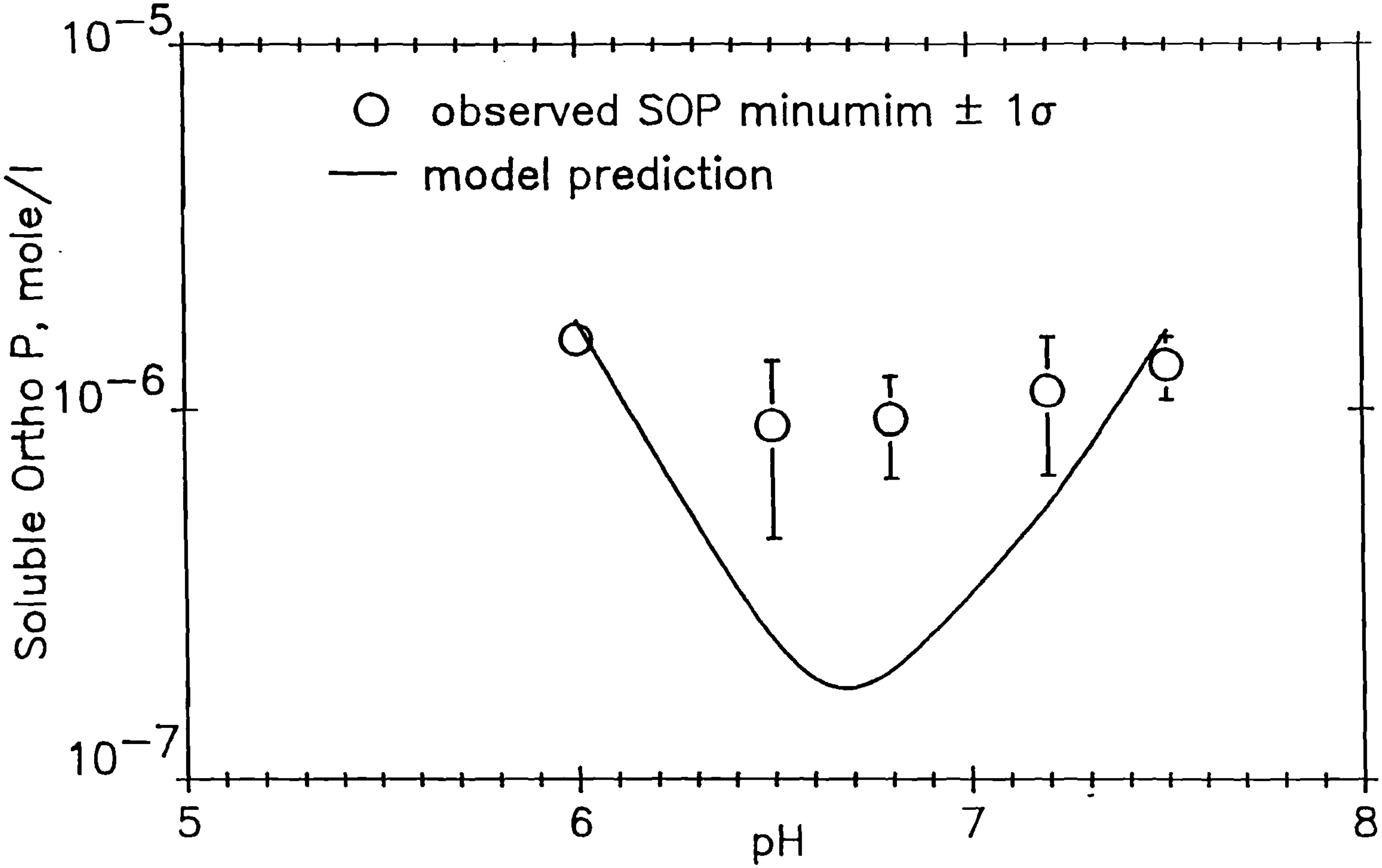


Figure 6.26 Comparison of observed [SOP] minimum and predicted SOP concentration in equilibrium with $Al(OH)_3$ and $Al_{.91}PO_4(OH)_{1.73}$.

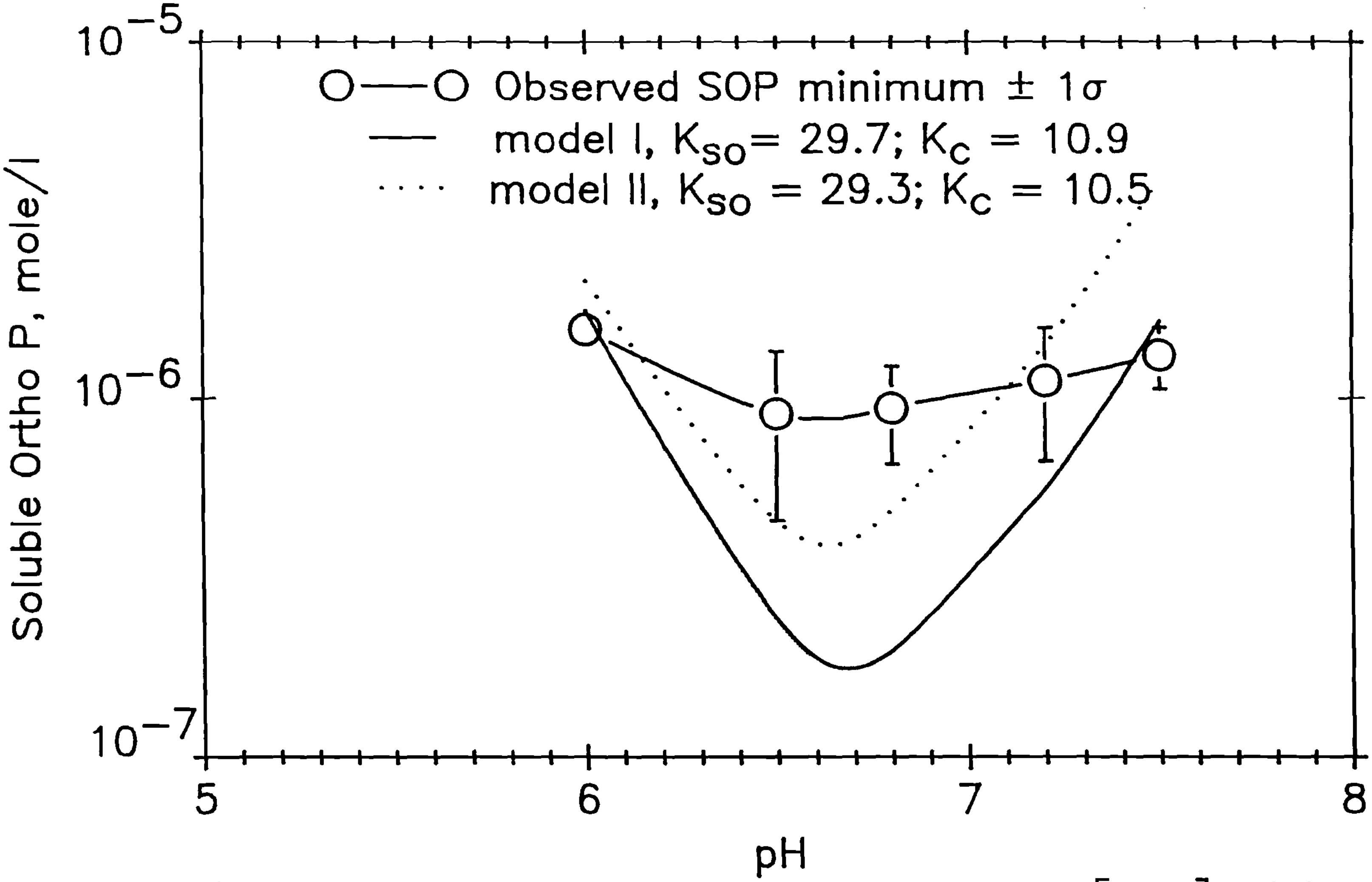


Figure 6.27 Agreement between observed [SOP] minimum and prediction of equilibrium based models.

Comparing the model predictions using $K_{so} = 10^{-29.7}$ with predictions using $K_{so} = 10^{-29.3}$ revealed that adjusting the solubility product shifted the solubility curve upwards and improved the agreement between model predictions and experimental observations at all pH values except 7.5. It is possible that at pH 7.5 the equilibrium SOP concentration could be controlled by the presence of hydroxyapatite ($Ca_5(PO_4)_3OH_{(s)}$) or calcium phosphate and $Al(OH)_{3(s)}$ instead of $Al_{0.91}H_2PO_4(OH)_{1.73(s)}$ and $Al(OH)_{3(s)}$. Diamodopolous and Benedek (1984) reported that calcium phosphate interactions were possible at pH values greater than 7.5 and Snoeyink and Jenkins (1980) stated that under certain conditions ß-calcium phosphate (β-$Ca_3(PO_4)_2$) controlled residual SOP concentration in wastewater during chemical P-removal. The average calcium concentration during the batch studies (25 mg Ca/l; 0.63mM) was sufficient to suggest the formation of calcium phosphate precipitates at higher pH values (> 7.2).

For the sake of simplicity it was necessary to limit the number of aluminum and phosphate containing soluble species included in the model. Species which may have facilitated the development of a model able to fit the experimental observations better may have been excluded from this model (particularly hydroxyapatite or ß-calcium phosphate at pH > 7.2). In the third removal region very low SOP residual concentration are predicted and observed and that these concentrations approach the detection limit of the analytical methods used in this study. The nature of the precipitated formed is uncertain. If the SOP containing precipitates are colloidal in nature, they may not be removed by filtration through 0.45 µM filters and contribute to inaccurate measurement of the SOP residual concentration. It was concluded that the modified equilibrium constants, $K_{so} = 10^{-29.3}$ and $K_c = 10^{10.9}$ were able to model the experimental observations better than the equilibrium constants previously estimated in this study and provided an acceptable fit of the experimental observations.

The proposed model predicted an optimum pH value (pH = 6.65) that agreed with the findings previous investigators (Henriksen, 1962; Diamodopolous and Benedek, 1984) who worked with sewage, but was consistently higher than the optimum pH predicted using chemically defined distilled water solutions (Stumm, 1962; Ferguson and King, 1977; Recht and Ghassemi, 1970). Comparison of the estimated K_{so} and previously published values reveals that the values found in this study differ from those of previous investigators. An aluminum-hydroxy-phosphate solid that is less soluble than that suggested by Stumm (1962) and more soluble than the solid described by Ferguson and King (1977) predicted.

In Figure 6.28 the minimum SOP concentrations predicted by the currently proposed model and the model of Ferguson and King (1977) are compared with the experimental observations. The pH of optimum co-precipitation predicted by the currently proposed model (pH = 6.65) agrees with the observed optimum pH between pH 6.5 and 6.8. The optimum pH predicted by Ferguson and King (pH 5.5 to 6.0) is significantly less than the observed optimum pH. At pH values greater than 6.2, the model of Ferguson and King predicted SOP residuals significantly greater than observed. Both models predict a greater change with pH in the minimum SOP residual than the experimental observations indicated. The currently proposed model was prepared using a different stoichiometry for the aluminum-hydroxy-phosphate solid and different equilibrium constants for this solid and the aluminum phosphate soluble complex than the model of Ferguson and King, which was developed to fit the experimental observations of Recht and Ghassemi (1970). Ferguson and King estimated equilibrium constants for the aluminum-hydroxy-phosphate solid and aluminum phosphate complex of 10^{-34} and 10^{6} respectively. A significant difference between the data used in this study and that used by Ferguson and King, is the presence of biological solids during aluminum phosphate precipitation.

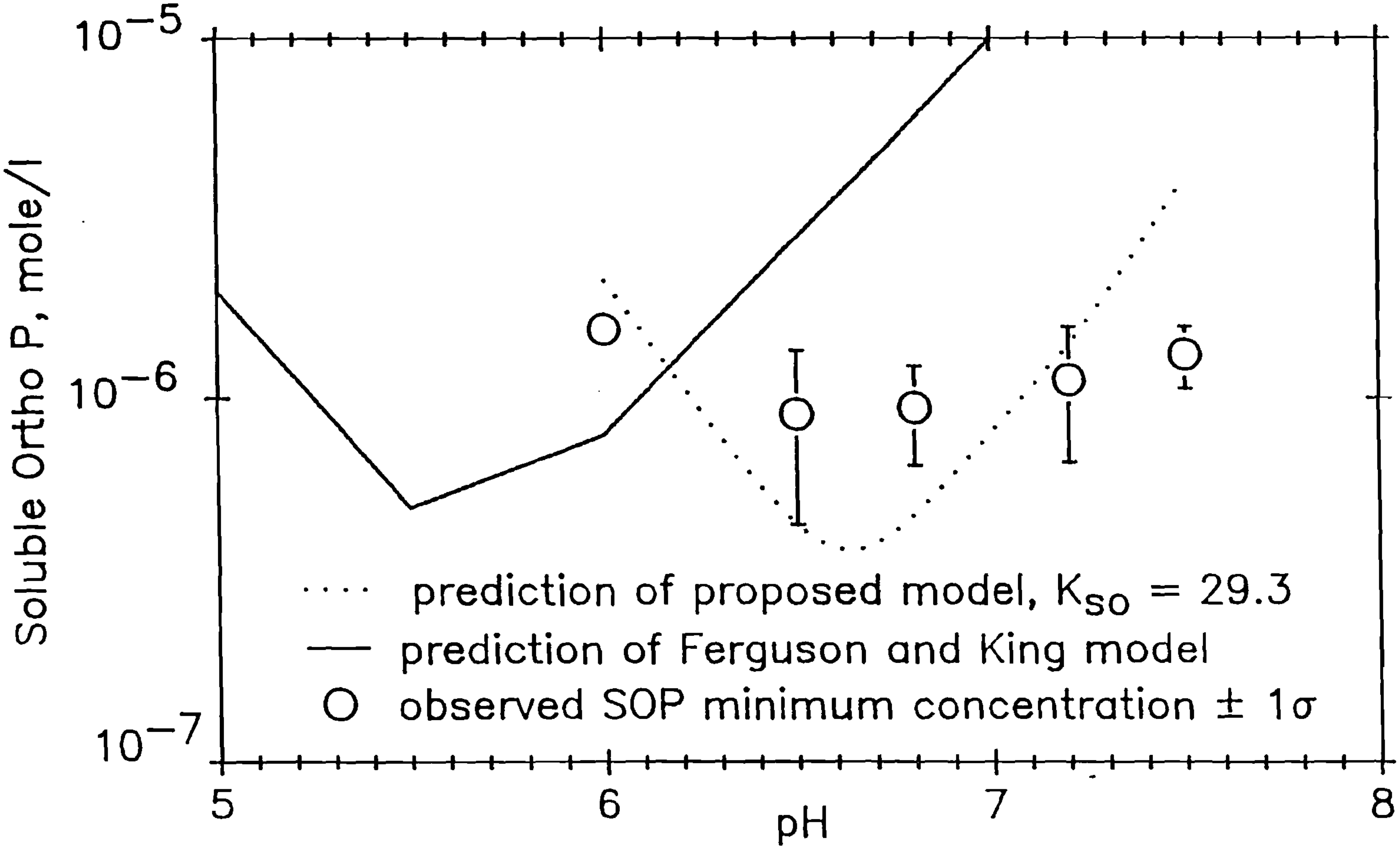


Figure 6.28 Comparison of observed SOP minimum and predicted SOP conc. in equilibrium with $Al(OH)_3$ and $Al_xPO_4(OH)_y$

7 CONCLUSIONS

Soluble orthophosphate (SOP) residuals as low as 0.02 mg P/l can be achieved with chemical phosphorus removal when alum is dosed to the aeration basin of activated sludge systems (simultaneous precipitation). This research identified three regions of phosphorus removal, in each of which a different phosphorus removal mechanism applied. The following conclusions have been reached concerning simultaneous aluminum phosphate precipitation:

1.0 In the first phosphate removal region, P removal resulted from the stoichiometric precipitation of an aluminum-hydroxy-phosphate solid. SOP residual concentrations as low as 1.0 mg P/l ($10^{-4.5}$ M) could be reached by stoichiometric precipitation. The composition of the solid formed could be empirically described as $Al_{0.91}H_2PO4(OH)_{1.73(s)}$ and appeared to be independent of pH. The solubility product (K_{so}) of the solid was estimated to be $10^{-29.3}$.

2.0 In the second phosphate removal region, SOP removal could be adequately modeled by assuming adsorption of SOP on an aluminum hydroxide precipitate:

$$\mathrm{v[Al(OH)_3{:}Al(OH)_2]\text{-}OH_{(surf)} + SOP \Longleftrightarrow}$$
$$\mathrm{[Al(OH)_3{:}Al(OH)_2]_v\text{-}SOP_{(surf)} + v(OH^-)} \qquad (7.1)$$

The second phosphate removal region extends over the range of SOP residuals from 1.0 to 0.1 mg P/l and is typically reached when using alum doses between 7.0 and 24 mg Al^{3+}/l.

3.0 Co-precipitation of $Al(OH)_{3(s)}$ and $Al_{0.91}H_2PO_4(OH)_{1.73(s)}$ occurred in the third phosphate removal region. Alum doses of greater than 25 mg $Al_{(III)+}$/l were needed to reach the third removal region. In this region minimum SOP residual concentrations were reached. The observed minimum SOP concentration varied slightly with pH. The absolute minimum SOP concentration was observed between pH 6.5 and 6.8. Chemical equilibria and mass balances were used to model SOP removal in the third region. The model predicted the absolute minimum SOP concentration at a pH of 6.65. On either side of this pH value the residual SOP concentrations increased due to the postulated formation of the soluble complex, $AlH_2PO_4^{2+}$. The stability constant of this complex was estimated at $10^{10.9}$.

4. The hydrolysis of SNOP and PP to SOP was evaluated using 2 series of control studies. An increase in SOP mass

equal to 40% of the influent SNOP and PP mass was observed. R^* values including the hydrolysis of SNOP and PP were statistically compared with standard R values for the continuous flow study. The increase in SOP mass was found to not have a significant effect on simultaneous aluminum phosphate precipitation.

8 APPLICATION TO PRACTICE

8.1 Summary of Model

This research has shown that simultaneous precipitation of phosphate using alum can achieve SOP residuals of as low as 0.02 mg P/l in municipal wastewaters. A model of simultaneous aluminum phosphate precipitation was developed which described phosphate removal on the basis of mass balances and equilibrium equations of precipitation and adsorption processes.

Stoichiometric alum doses can be used to obtain SOP residuals as low as 1.0 mg P/l. Stoichiometric precipitation was found to be independent of pH. SOP residual concentrations below 1.0 mg P/l and greater than 0.1 mg P/l require greater than stoichiometric alum doses. Non-stoichiometric P-removal to reach SOP residuals in the range 1.0 to 0.1 mg P/l appears to involve an adsorption mechanism. The extent of SOP removal by adsorption depended on the amount of adsorbent ($Al(OH)_{3(s)}$) available for adsorption. This was assumed to be directly proportional to the alum dose. This would suggest that simultaneous precipitation with alum to achieve SOP residual concentrations in the range 1.0 to 0.1 mg P/l could not be achieved more economically by reducing the alum dose and using less expensive acids, such as sulfuric acid, for pH control as suggested by Ferguson and King (1977).

Co-precipitation of $Al_{0.91}H_2PO_4(OH)_{1.73(s)}$ and $Al(OH)_{3(s)}$ occurred in the third P-removal region where a minimum SOP residual concentration was reached. The pH for minimum SOP concentration was predicted to be approx. 6.65, although low SOP residuals (0.02 to 0.04 mg P/l) could be achieved at all pH values within the range 6.0 to 7.5.

8.2 Role of pH

This research showed that very low SOP residual concentrations could be achieved using alum doses of similar magnitude at all pH levels in the range of pH (pH 6.0 -7.5) which includes the pH values typically found in the aeration basin of activated sludge systems. These observations suggest that pH control is not necessary to achieve very low SOP residuals (0.02 to 0.04 mg P/l) by simultaneous aluminum phosphate precipitation. This is not to imply that pH is without a role in simultaneous aluminum phosphate precipitation, but the need for pH control in the process would seem to depend more on maintaining a pH satisfactory for biological activity than for producing a low SOP residual.

8.3 Use of Model in Practice

Several adjustments are required before the aluminum phosphate precipitation model developed during this study can be applied in practice for several reasons including:

- The pH was controlled during experiments so that the pH after alum addition was known while in operating activated sludge plants the pH typically is not controlled.
- The model was developed on the basis of SOP removal and phosphate discharge standards are usually written in terms of total phosphate concentration.

8.3.1 Determination of final pH

Since pH control is usually not employed in practice, the final pH in the aeration basin after alum addition must be either measured using full or pilot scale systems or estimated using equilibrium relationships. The equations needed to calculate the pH after alum addition are given in the literature (Ferguson and King, 1977 and Jenkins *et al.*, 1984).

8.3.2 Relating TP and SOP concentration

TP is often the only phosphate concentration measured in practice and many phosphate discharge limits are written in terms of effluent TP. This model predicts alum doses required to reach a desired SOP concentration. The SOP concentration that must be reached in order to ensure that effluent TP concentration limits are not exceeded must be determined before the proposed model can be used in practice.

TP concentrations can be significantly greater than the SOP concentration due to primarily the contribution of PP to TP. The effluent suspended solids of simultaneous aluminum phosphate precipitation processes includes two P-containing fractions; activated sludge particles and chemical precipitates. The contribution of these two fractions to TP can be calculated by adding phosphate concentrations in the activated sludge particles and chemical precipitates. In Table 8.1 the SOP residual concentration required to meet effluent TP discharge limits is shown for several effluent SS levels.

Table 8.1

8.1 SOP Concentrations Required to Meet Various Effluent TP Requirements at various Effluent SS

	Required SOP (mg P/l)			
Total Phosphate (mg P/l)	SS 5 (mg/l)	SS 10 (mg/l)	SS 15 (mg/l)	SS 20 (mg/l)
0.01	**	**	**	**
0.1	**	**	**	**
0.25	0.03	**	**	**
0.3	0.08	**	**	**
0.4	0.18	**	**	**
0.5	0.28	0.05	**	**
0.6	0.38	0.15	**	**
0.7	0.48	0.25	0.03	**
0.8	0.58	0.35	0.13	**
0.9	0.68	0.45	0.23	**
1.0	0.78	0.55	0.33	0.1
1.5	1.28	1.05	0.83	0.6
2.0	1.78	1.55	1.33	1.1
2.5	2.28	2.05	1.83	1.6

(Effluent SS = 4.5% P)
** TP requirement can not be met using chemical P-removal at indicated SS level

8.4 Sample Calculations of Aluminum Doses

The alum dose required to treat a typical domestic wastewater to meet the following effluent TP discharge limits will be calculated:

		Case #1	Case #2	Case#3
	Influent	Effluent	Effluent	Effluent
BOD	200 mg/l	15 mg/l	15 mg/l	15 mg/l
SS	210 mg/l	10 mg/l	10 mg/l	5 mg/l
TP	8.0 mg P/l	2.0 mg P/l	1.0 mg P/l	0.25 mgP/l
SOP	6.0 mg P/l			
pH	7.0	7.0	7.0	7.0

Assume that the design average daily wastewater flow is 11,350 m^3/day (3.0 mgd) and that a 49% liquid alum solution with 4.37% aluminum by weight and a density of 1330 kg/m^3 (11.1 lb/gal) is available to treat the wastewater.

Case #1

Use Table 8.1 to determine the SOP residual required to reach effluent TP concentration of 2.0 mg P/l:

SOP_{res} = 1.55 mg P/l

Since SOP_{res} is > 1.0 mg P/l stoichiometric removal region 1 model relationships are applicable to case #1.

The aluminum dose is calculated using equation 6.4:

$$r = Al^{(III)}_{reqd}(\text{mole})/SOP_{remv}(\text{mole}) \qquad (6.4)$$

where:

r = stoichiometric ratio of aluminum to phosphate in precipitate = 0.91 ± 0.11

$Al^{(III)}_{reqd}$ = aluminum required for desired SOP removal (mole)

SOP_{remv} = SOP removal required to reach a desired SOP residual (mole)

for case #1:

$$SOP_{remv} = (6.0 \text{ mg P/l} - 1.55 \text{ mg P/l}) \times (31{,}000 \text{ mg P/mole})^{-1}$$
$$= 1.44 \times 10^{-4} \text{ mole P removed/l}$$

from equation 6.4:

$$Al^{(III)}_{reqd} = 0.91 \ \frac{\text{mole } Al^{(III)}}{\text{mole P remv}} \times 1.44 \times 10^{-4} \text{ mole P remv/l}$$
$$= \underline{1.31 \times 10^{-4} \text{ mole } Al^{(III)}/\text{l wastewater}}$$
$$\underline{(4.1 \text{ mg Al/l})}$$

The mass of aluminum required to treat the wastewater is calculated as follows:

$$1.31 \times 10^{-4} \frac{\text{mole Al}^{(III)}}{\text{l wastewater}} \times 11{,}350 \frac{\text{m}^3}{\text{day}} \times 0.027 \frac{\text{Kg Al}^{(III)}}{\text{mole}}$$

$$\times 1000 \frac{\text{l}}{\text{m}^3} = \underline{\text{40.1 Kg Al/day (88.4 lb/day)}}$$

The volume of 49% alum solution required to treat the wastewater is calculated in the following manner:

the weight of aluminum in the alum solutions is calculated first:

$$1330 \frac{\text{Kg}}{\text{m}^3\text{alum soln}} \times 0.044 \text{ aluminum} = 58 \frac{\text{Kg Al}}{\text{m}^3\text{ alum soln}}$$

the volume of alum solution needed is calculated next:

$$40.1 \frac{\text{Kg Al}}{\text{day}} \times 1 \frac{\text{m}^3}{\text{58 Kg}} \text{ alum soln} = \underline{\text{0.69 m}^3\text{/day (182 gal/day)}}$$

$$= \frac{\text{61 gal Al solution}}{\text{MG wastewater}}$$

Case #2

The required SOP_{res} for case #2 of 0.55 mg P/l (from Table 8.1) is within the range of SOP residual concentrations found in the second P-removal region. The alum dose can be calculated using equations 6.12 through 6.15 as follows:

calculate SOP_{remv} in the same manner as Case #1:

$$SOP_{remv} = (6.0 \text{ mg P/l} - 0.55 \text{ mg P/l}) \times (31{,}000 \text{ mg P/mole})^{-1}$$
$$= 1.76 \times 10^{-4} \text{ mole/l}$$

calculate v^* and K_a^* using equations 6.12 and 6.13 for pH = 7.0

$$v^* = -0.46\text{pH} + 5.14 = 1.92$$
$$\log(K_a^*) = 3.69\text{pH} - 31.7 = -5.87$$
$$K_a^* = 1.35 \times 10^{-6}$$

The aluminum dose is calculated using equation 6.15:

$$Al^{(III)}_{reqd} = \{(SOP_{remv}/SOP_{res}) \times ([OH]^{v}/K_a^*)\}^{1/v}$$

$$= \left[\frac{1.76 \times 10^{-4}}{1.77 \times 10^{-5}} \times \frac{(1 \times 10^{-7})^{1.92}}{1.35 \times 10^{-6}} \right]^{1/1.92}$$

= <u>3.77×10^{-4} mole $Al^{(III)}$/l wastewater (11.7 mg Al/l)</u>

Using the same calculations as given for Case #1 the following alum dose requirements were calculated:

mass of Aluminum needed:

116 Kg $Al^{(III)}$/day (255 lb/day)

volume of 49% alum solution required:

2 m^3/day (528 gal/day)

or

$\frac{\text{176 gal soln}}{\text{MG wastewater}}$

Case #3

The required SOP residual from Table 8.1 is 0.03 mg P/l and falls within the third P removal region. Within the the third P removal region, the minimum SOP residual concentration obtainable by simultaneous precipitation would be reached (approx. 1 x 10^{-6} M or 0.031 mg Al/l). In order to reach the third P removal region it is necessary to use alum doses that are sufficient to insure that both aluminum-hydroxy-phosphate and aluminum hydroxide precipitates are formed. A review of the experimental observations revealed that the minimum ratio of Al:P required to reach the third removal region varied between 3.6 and 5.0. It is suggested than an Al:P ratio of 5.0 be used to insure that minimum SOP residual concentrations are reached when very low SOP residual concentrations are required. The alum dose required for Case #3 can is calculated as follows:

1. calculate SOP_{remv} using SOP_{mres} as the SOP_{res} concentration

$$
\begin{aligned}
SOP_{remv} &= SOP_{infl} - SOP_{mres} \\
&= (6.0 - 0.031)(31{,}000)^{-1} \\
&= 1.93 \times 10^{-4} \text{ mole P removed/l}
\end{aligned}
$$

2. calculate Al dose with Al:P = 5.0

$$
\begin{aligned}
Al^{(III)}_{reqd} &= SOP_{remv} \times 5 \\
&= (1.93 \times 10^{-4}) \times 5 \\
&= \underline{9.65 \times 10^{-4} \text{mole } Al^{(III)}/\text{l wastewater (26 mg/l)}}
\end{aligned}
$$

3. calculate volume of 49% alum solution required in same manner as case #1

<u>5.1 m³/day (1345 gal/day) alum solution</u>

or

$$\frac{\text{448 gal soln}}{\text{MG wastewater}}$$

9 RECOMMENDATIONS FOR FUTURE RESEARCH

This research provided data on the simultaneous precipitation of SOP with alum. Sufficient data were collected to develop a model of aluminum phosphate precipitation. Several areas exists which should be further investigated to better understand this process such as:

1. The simultaneous aluminum phosphate precipitation model developed should be calibrated and verified with full scale operating data. This data should include, at a minimum, the pH in the aeration basin after alum addition, and influent and effluent SOP concentration and ideally TP, TSP, PP, SNOP, alkalinity, $Al^{(III)}$ residual concentration, and influent, effluent and mixed liquor TSS and VSS.

2. The nature of the precipitates formed in the three proposed removal regions should be further examined in detailed studies where the chemical solids are separated from the biological solids and identified using analytical methods such as x-ray diffraction.

3. The adsorption mechanism proposed for the second removal region should be further investigated to verify

whether adsorption is the actual SOP removal mechanism in this region. This could be achieved by adding chemically defined aluminum hydroxide solutions to phosphate containing wastewaters and observing the degree of phosphate removal. The SOP level in the wastewater should be adjusted such that $Al^{(III)}$ is dosed in excess of stoichiometric requirements. The proposed adsorption mechanism should be further investigated to determine the effect of recirculated precipitates on P-removal.

4. This study revealed that low SOP residual concentrations can be achieved in the pH range 6.0 to 7.5, but did not address the effect of the pH drop experienced after alum addition on chemical P-removal. Uncontrolled pH experiments should be conducted to further investigate the effect of pH on SOP removal, particularly the effect of the low pH levels reached when high alum doses are used.

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Appendix 1

Removal ratio (R) and Adjusted removal ratio (R^*)

Null Hypothesis

H_0: $X_1 = X_2$

H_1: X_1 < or > X_2

where X_1 and X_2 are the average values of the R^* and R for continuous flow experiments for SOP residual > 1.0 mg P/l

Test used

One way analysis of variance (ANOVA) using F-ratio (F)

F = mean square between/mean square within

where:

mean square between = sum of squares between/(k-1)

mean square within = sum of squares within/(N-k)

Sum of squares

Between: $n_i(X_i - X)^2$

Within: $(X_{ij} - X_i)^2$

Degrees of freedom

Between: k - 1

Within: N - k

where:

n_i = sample size

X_i = sample mean

X = overall estimated mean

X_{ij} = observation

k = number in population

N = total number of observations

<u>calculation of test statistics</u>

variance table

Source	Sum of Squares	Degrees of freedom	Mean Square
Between	0.24	1	0.24
Within	1.7	28	0.06

$F = 0.24/0.06 = 4.0$

From a table of F values

$F_{1,28(.95)} = 4.20$

therefore

$F = 4.0 < F_{1,28(.95)}$

<u>Conclusion</u>

Do not reject the null hypothesis. There is no significant difference between the average R and R^* for continuous flow experiments with SOP residuals > 1.0 mg P/l.

Appendix 2

Batch pH =7.2 and continuous flow experiments

Null Hypothesis

H_0: $X_1 = X_2$

H_1: X_1 < or > X_2

where X_1 and X_2 are the average values of the R in cases for SOP residuals > 1.0 mg P/l

Test used

Student's T-test of probability distribution (need reference)

calculation of test statistics

$X_1 = 0.92$	$X_2 = 0.81$
$S_1 = 0.24$	$S_2 = 0.12$
$n_1 = 34$	$n_2 = 19$

where:

X_1 = average R for batch experiments at pH 7.2 with SOP residual > 1.0 mg P/l

X_2 = average removal ratio for continuous flow alum addition experiments with SOP residual greater than 1.0 mg P/l

S_1 and S_2 = standard deviation in the calculation of X_1 and X_2

n_1 and n_2 = sample size relevant to the calculation of X_1 and X_2

The T value for the test was determined using:

$$T = \frac{(X_1 - X_2)}{S_p(1/n_1 + 1/n_2)^{0.5}}$$

where

$$S_p = \{((n_1-1)S_1^2 + (n_2-1)S_2^2)/((n_1-1)\ (n_2-1))\}^{0.5}$$

giving:

$$T = 1.9$$

The degrees of freedom for the test:

$$df = (n_1 + n_2) - 2 = 51$$

From table of T values for two tailed Student's T-test

$$t_{0.01,51} = 2.7$$

therefore:

$$T < t_{0.01,51}$$

<u>Conclusion</u>

Do not reject the null hypothesis H_0. There is no significant difference between the average R for the continuous flow experiments and the batch experiments at pH 7.2, for SOP residuals > 1.0 mg P/l.

Appendix 3

Estimation of first removal region boundary

Null Hypothesis

H_0: $X_1 = X_2 = X_3 = X_4$

H_1: at least one average is different

where X_1, X_2, X_3, and X_4 are the average values of R for SOP residual concentrations of 6.1, 4.2, 3.2, and 1.1 mg P/l respectively at all batch experiment pH values.

Test used

One way analysis of variance (ANOVA) using F-ratio (F)

F = mean square between/mean square within

where:

mean square between = sum of squares between/(k-1)

mean square within = sum of squares within/(N-k)

Sum of squares

Between: $n_i(X_i - X)^2$

Within: $(X_{ij} - X_i)^2$

Degrees of freedom

Between: k - 1

Within: N - k

where:

n_i = sample size

X_i = sample mean

X = overall estimated mean

X_{ij} = observation

k = number in population

N = total number of observations

calculation of test statistics

variance table

Source	Sum of Squares	Degrees of freedom	Mean Square
Between	0.1	3	0.033
Within	0.123	12	0.01

$F = 0.033/0.01 = 3.22$

From a table of F values

$F_{3,12(.95)} = 3.49$

therefore

$F = 3.22 < F_{3,12(.95)}$

conclusion

Do not reject the null hypothesis. There is no significant difference between the average R for the batch experiments for SOP residuals of 6.1, 4.2, 3.2, and 1.1 mg P/l.

Null Hypothesis

H_0: $X_1 = X_2 = X_3 = X_4 = X_5$

H_1: at least one average is different

where X_1, X_2, X_3, X_4, and X_5 are the average values of the R for SOP residual concentrations of 6.1, 4.2, 3.2, 1.1 and 0.85 mg P/l respectively at all batch experiment pH values.

Test used

One way analysis of variance (ANOVA) using F-ratio (F)

F = mean square between/mean square within

where:

mean square between = sum of squares between/(k-1)

mean square within = sum of squares within/(N-k)

Sum of squares

Between: $n_i(X_i - X)^2$

Within: $(X_{ij} - X_i)^2$

Degrees of freedom

Between: $k - 1$

Within: $N - k$

where:

n_i = sample size

X_i = sample mean

X = overall estimated mean

X_{ij} = observation

k = number in population

N = total number of observations

calculation of test statistics

variance table

Source	Sum of Squares	Degrees of freedom	Mean Square
Between	0.38	4	0.095
Within	0.15	15	0.01

$F = 0.095/0.01 = 9.2$

From a table of F values

$F_{4,15(.99)} = 4.89$

therefore

$F = 9.2 > F_{4,15(.99)}$

Conclusion

Reject the null hypothesis. It can be stated with at least a 99% level of confidence that a significant difference exist between the average R for batch experiments giving SOP residual concentrations of 6.1, 4.2, 3.2, 1.1, and 0.85 mg P/l.

Appendix 4

Derivation of region 3 equilibrium relationship

1. Define $C_{T,SOP}$ as total concentration of soluble orthophosphate at equilibrium:

$$C_{T,SOP} = H_3PO_4 + H_2PO_4^- + HPO_4^{2-} + PO_4^{3-} + AlH_2PO_4^{2+} \quad (1)$$

2. get all quantities in $C_{T,SOP}$ in terms of H_2PO_4

$$H_3PO_4 = \frac{[H_2PO_4^-][H]}{K_1} \quad (2)$$

$$HPO_4^{2-} = \frac{K_2[H_2PO_4^-]}{[H^+]} \quad (3)$$

$$PO_4^{3-} = \frac{K_3K_2[H_2PO_4^-]}{[H^+]^2} \quad (4)$$

$$AlH_2PO_4^{2+} = K_c[Al][H_2PO_4] \quad (5)$$

3. Substitute equations 2, 3, 4, and 5 into equation 1

$$C_{T,SOP} = \frac{[H_2PO_4^-][H^+]}{K_1} + [H_2PO_4^-] + \frac{K_2[H_2PO_4^-]}{[H^+]} + \frac{K_3K_2[H_2PO_4^-]}{[H^+]^2}$$

$$+ K_c[Al][H_2PO_4^-] \qquad (6)$$

4. Solve equation 6 for $H_2PO_4^-$ concentration at equilibrium

$$[H_2PO_4^-] = \frac{C_{T,SOP}}{\left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + \frac{K_3K_2}{[H^+]^2} + K_c[Al]\right)} \qquad (7)$$

5. Assume $Al(OH)_3$ (S) controls Al^{3+} concentration at equilibrium

$$[Al] = 10^{9.1}[H^+]^3 \qquad (8)$$

6. Define equilibrium constant for the aluminum–hydroxy–phosphate precipitate, $Al_{0.91}H_2PO_4(OH)_{1.73}(S)$:

$$K_{so} = [Al]^{0.91}[H_2PO_4^-]\,[OH^-]^{1.73} \qquad (9)$$

7. Substitute equations 7 and 8 into equation 9

$$K_{so} = (10^{9.1}[H^+]^3)^{0.91}$$

$$\times \left[\frac{C_{T,SOP}}{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + \frac{K_3K_2}{[H^+]^2} + K_c(10^{9.1})[H^+]^3} \right] \times \left[OH^-\right]^{1.73}$$

Appendix 5

Raw Data

Raw data Batch Experiment pH = 6.0

date	V1 liters	V2 liters	P1 mg/l	P2 mg/l	Al Dose moles
Aug 16	2.1	2.04	7.93	7.47	2.25E-05
Aug 16	2.1	2.04	7.77	7.04	4.5E-05
Aug 16	2.1	2.04	7.47	5.93	7.51E-05
Aug 17	2.08	2.06	8.04	2.77	0.0003
Aug 17	2.08	2.14	8.33	1.35	0.00045
Aug 17	2.08	2.14	8.12	0.8	0.000526
Aug 17	2.06	2.16	8.49	0.73	0.000601
Aug 17	2.08	2.2	8.74	0.57	0.000676
Aug 17	2.08	2.22	8.39	0.43	0.000751
Aug 19	2.1	2.13	7.96	0.59	0.000601
Aug 19	2.11	2.22	8.01	0.254	0.000901
Aug 19	2.08	2.3	7.6	0.254	0.00105
Aug 19	2.1	2.26	8.15	0.17	0.0012
Aug 19	2.08	2.28	7.85	0.049	0.00135
Aug 19	2.06	2.24	8.09	0.168	0.0015
Dec 18	1.95	2	7.38	0.079	0.00121
Dec 18	1.95	2.03	7.61	0.064	0.00242
Dec 18	1.95	2.15	6.84	0.051	0.00364
Dec 18	1.94	2	6.87	0.046	0.00485
Dec 18	1.96	2.06	7.15	0.053	0.00606
Dec 18	1.94	2.02	6.36	0.041	0.00727

V1 = volume before initial sample is withdrawn
v2 = volume before final sample is withdrawn
P1 = initial soluble orthophosphate, mg P/l
P2 = final soluble orthophosphate, mg P/l
Al dose = total moles of Al^{3+} added to the batch system

Raw data Batch Experiment pH = 6.5

date	V1 liters	V2 liters	P1 mg/l	P2 mg/l	Al Dose moles
July 13	2.04	2.04	5.39	4.98	2.25E-05
July 13	2.18	2.34	5.71	4.44	4.5E-05
July 13	2.18	2.26	5.09	3.98	7.51E-05
July 13	2.16	2.24	6.87	4.44	0.00012
July 13	2.06	2.1	6.9	3.76	0.00015
July 13	1.96	1.97	6.33	2.62	0.000195
July 14	1.97	1.965	8.25	6.79	7.51E-05
July 14	2.06	2.15	8.66	6.19	0.00012
July 14	2.2	2.28	7.92	5.01	0.00015
July 18	1.91	1.92	7.85	1.83	0.0003
July 18	1.88	2.08	8.96	1.31	0.00045
July 18	1.95	2.18	7.25	0.62	0.000526
July 18	2.01	2.06	7.12	0.49	0.000601
July 18	1.98	2.1	7.01	0.44	0.000676
July 18	2.14	2.28	6.55	0.47	0.000751
July 20	2.08	2.26	7.25	0.52	0.000601
July 20	1.94	2.22	7.33	0.2	0.000901
July 20	2.1	2.24	6.95	0.14	0.00105
July 20	2.12	2.28	7.12	0.08	0.0012
July 20	2	2.22	7.31	0.07	0.00135
July 20	2.14	2.2	6.9	0.059	0.0015
July 22	2.14	2.4	3.76	0.059	0.000676
July 22	2.06	2.26	4.36	0.076	0.000676
July 22	2.02	2.14	7.9	0.49	0.000676
July 25	2.12	2.24	9.71	0.06	0.00182
July 25	2.28	2.16	10.99	0.114	0.00242
July 25	2.32	2.36	9.47	0.86	0.00303
Dec 22	1.98	2.04	4.78	0.046	0.00121
Dec 22	2.04	2.12	4.96	0.051	0.00242
Dec 22	2.08	2.14	4.58	0.036	0.00364
Jan 3	2	2.06	4.83	0.015	0.00485
Jan 3	2.02	2.1	4.6	0.025	0.00606
Jan 3	2.02	2.16	4.32	0.013	0.00727

V1 = volume before initial sample is withdrawn
v2 = volume before final sample is withdrawn
P1 = initial soluble orthophosphate, mg P/l
P2 = final soluble orthophosphate, mg P/l
Al dose = total moles of Al^{3+} added to the batch system

Raw data Batch Experiment pH = 6.8

date	V1 liters	V2 liters	P1 mg/l	P2 mg/l	Al Dose moles
Jan 10	2.06	2.2	4.86	3.31	2.25E-05
Jan 10	2.04	2.26	4.83	2.8	4.5E-05
Jan 10	2.02	2.26	3.82	2.03	7.51E-05
Jan 10	2.02	2.1	4.02	1.78	0.00012
Jan 10	2.06	2.2	4.58	1.39	0.00015
Jan 10	2.06	2.18	3.82	1.17	0.000195
Jan 12	2.06	2.16	4.78	1.19	0.0003
Jan 12	2.08	2.22	4.63	0.702	0.00045
Jan 12	1.94	2.04	4.07	0.265	0.000526
Jan 12	2	2.1	4.83	0.259	0.000601
Jan 12	2.02	2.14	4.71	0.356	0.000676
Jan 12	1.925	2.18	4.07	0.107	0.000751
Jan 17	2.08	2.16	3.59	0.216	0.000601
Jan 17	2.08	2.19	3.54	0.071	0.000901
Jan 17	2.02	2.32	2.54	0.041	0.00105
Jan 17	2.02	2.12	3.43	0.02	0.0012
Jan 17	2.02	2.13	3.08	0.025	0.00135
Jan 31	2.12	2.38	4.35	0.814	0.0003
Jan 31	2.04	2.12	5.09	0.458	0.00045
Jan 31	2.14	2.26	4.81	0.61	0.000526
Feb 6	2.1	2.18	4.35	0.216	0.000601
Feb 6	2.02	2.1	4.58	0.203	0.000676
Feb 6	2.02	2.16	4.58	0.148	0.000751
Feb 6	1.96	2.04	4.6	2.69	0.00012
Feb 6	2	2.06	4.53	2.26	0.00015
Feb 6	1.98	2.2	4.48	1.55	0.000195

V1 = volume before initial sample is withdrawn
v2 = volume before final sample is withdrawn
P1 = initial soluble orthophosphate, mg P/l
P2 = final soluble orthophosphate, mg P/l
Al dose = total moles of Al^{3+} added to the batch system

Raw data Batch Experiment pH = 7.0

date	V1 liters	V2 liters	P1 mg/l	P2 mg/l	Al Dose moles
Jan 23	1.98	2.04	4.93	4.32	2.25E-05
Jan 23	2.04	2.12	4.32	3.36	4.5E-05
Jan 23	1.77	1.82	4.71	3.03	7.51E-05
Jan 23	2	2.1	4.83	2.54	0.00012
Jan 23	2	2.14	5.06	2.19	0.00015
Jan 23	1.98	2.14	4.88	1.58	0.000195
Jan 24	2	2.08	4.07	0.468	0.0003
Jan 24	2.02	2.1	4.45	0.3	0.00045
Jan 24	2.1	2.2	3.82	0.214	0.000526
Jan 24	1.98	2.06	4.1	0.153	0.000601
Jan 24	2.06	2.18	4.35	0.305	0.000676
Jan 24	2.14	2.2	4.02	0.137	0.000751
Jan 25	2	2.06	2.79	0.203	0.000601
Jan 25	2.01	2.1	4.48	0.155	0.000901
Jan 25	1.96	2.04	4.32	0.127	0.00105
Jan 25	1.95	2.06	4.27	0.046	0.0012
Jan 25	1.97	2.14	4.48	0.061	0.00135
Jan 25	2	2.1	4.32	0.048	0.0015
Jan 30	1.96	2	5.39	0.051	0.00121
Jan 30	2.24	2.2	5.21	0.041	0.00242

V1 = volume before initial sample is withdrawn
v2 = volume before final sample is withdrawn
P1 = initial soluble orthophosphate, mg P/l
P2 = final soluble orthophosphate, mg P/l
Al dose = total moles of Al^{3+} added to the batch system

Raw data Batch Experiment pH = 7.2

date	V1 liters	V2 liters	P1 mg/l	P2 mg/l	Al Dose moles
June 14	2.264	2.36	6.14	5.33	2.25E-05
June 14	2.092	2.11	6.28	5.33	4.5E-05
June 14	2.084	2.08	6.41	5.01	7.51E-05
June 14	2.082	2.084	6.71	4.11	0.00015
June 14	2.114	2.134	6.39	3.11	0.000195
June 16	2.122	2.146	6.71	6.28	2.25E-05
June 16	2.268	2.366	6.25	5.22	4.5E-05
June 16	2.051	2.116	6.58	5.17	7.51E-05
June 16	2.107	2.122	7.63	5.55	0.00012
June 16	2.189	2.33	6.85	4.14	0.00015
June 16	2.088	2.09	7.58	3.65	0.000195
June 20	2.085	2.09	8.47	7.12	2.25E-05
June 20	2.269	2.37	7.19	6.09	4.5E-05
June 20	2.073	2.07	8.01	5.87	7.51E-05
June 20	2	2.04	6.87	4.44	0.00012
June 20	2.22	2.29	6.36	3.33	0.00015
June 20	2.096	2.106	6.41	2.62	0.000195
July 5	2.08	2.17	6.47	1.79	0.0003
July 5	2.08	2.14	6.28	0.855	0.00045
July 5	2.06	2.14	6.36	0.704	0.000526
July 5	2.08	2.18	7.66	0.888	0.000601
July 5	2.06	2.2	7.96	0.617	0.000676
July 5	2.05	2.16	7.74	0.579	0.000751
July 6	2.11	2.16	8.98	2.8	0.0003
July 6	2.08	2.19	8.82	1.6	0.00045
July 6	2.09	2.18	8.44	0.942	0.000526
July 7	2.14	2.26	7.17	0.758	0.000601
July 7	2.06	2.24	6.93	0.346	0.000901
July 7	2.06	2.19	6.93	0.368	0.00105
July 7	2.06	2.24	8.04	0.135	0.0012
July 7	2.08	2.3	7.58	0.089	0.00135
July 7	2.04	2.3	7.63	0.195	0.0015
July 11	2.18	2.3	7.36	0.187	0.00121
July 11	2.1	2.28	6.52	0.041	0.00242
July 11	2.05	2.3	6.17	0.059	0.00364
July 11	2.16	2.38	6.85	0.027	0.00485
July 11	2.06	2.28	6.6	0.019	0.00606
July 11	2.05	2.25	6.95	0.027	0.00727

V1 = volume before initial sample is withdrawn
v2 = volume before final sample is withdrawn
P1 = initial soluble orthophosphate, mg P/l
P2 = final soluble orthophosphate, mg P/l
Al dose = total moles of Al^{3+} added to the batch system

Raw data Batch Experiment pH = 7.5

date	V1 liters	V2 liters	P1 mg/l	P2 mg/l	Al Dose moles
Aug 8	2.04	2.02	4.63	4.33	2.25E-05
Aug 8	2.08	2.06	4.49	3.89	4.5E-05
Aug 8	2.04	2.04	4.74	3.59	7.51E-05
Aug 8	2.04	2.04	5.89	3.68	0.00012
Aug 8	2.04	2.04	5.95	3.36	0.00015
Aug 8	2.06	2.1	5.98	3	0.000195
Aug 10	2.12	2.12	5.33	1.21	0.0003
Aug 10	2.16	2.2	5.28	0.68	0.00045
Aug 10	2.14	2.2	5.55	0.61	0.000526
Aug 10	2	2.1	5.01	0.406	0.000601
Aug 10	2	2.2	5.01	0.319	0.000676
Aug 10	2	2.22	5.01	0.438	0.000751
Aug 11	2.04	2.14	5.19	0.31	0.000601
Aug 11	2.04	2.16	4.98	0.15	0.000901
Aug 11	2.06	2.24	5.09	0.22	0.00105
Aug 11	2.04	2.26	5.6	0.12	0.0012
Aug 11	2.02	2.3	5.55	0.081	0.00135
Aug 11	2.03	2.32	5.63	0.17	0.0015
Aug 15	2.12	2.32	8.98	0.073	0.00242
Aug 15	2.1	2.2	8.77	0.051	0.00364
Aug 15	2.08	2.22	8.55	0.059	0.00606
Aug 15	2.05	2.04	7.71	4.82	0.00015
Aug 15	2	2.02	7.9	2.14	0.0003
Aug 15	2.02	2.04	7.77	1.43	0.00045
Jan 4	2	2.1	4.45	0.14	0.00121
Jan 4	2.02	2.21	4.35	0.045	0.00242
Jan 4	2.26	2.08	3.79	0.038	0.00364
Jan 5	1.98	2.1	4.86	0.048	0.00485
Jan 5	2	2.15	4.83	0.025	0.00606
Jan 5	2.02	2.28	4.63	0.023	0.00727

V1 = volume before initial sample is withdrawn
v2 = volume before final sample is withdrawn
PI = initial soluble orthophosphate, mg P/l
P2 = final soluble orthophosphate, mg P/l
Al dose = total moles of Al^{3+} added to the batch system