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UNIVERSITY OF ALBERTA

**THE USE OF COAGULANTS AND COAGULANT SLUDGES IN WASTEWATER
PHOSPHORUS REDUCTION**

**BY
ANDREW BARR**



**A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Master of Science**

IN

ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA

FALL 1992



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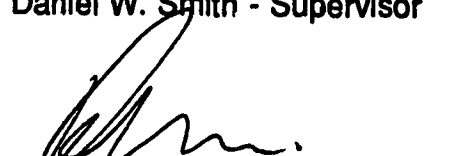
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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE USE OF COAGULANTS AND COAGULANT SLUDGES IN WASTEWATER PHOSPHORUS REDUCTION submitted by ANDREW J. BARR in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in ENVIRONMENTAL ENGINEERING.


Daniel W. Smith - Supervisor


Peter M. Huck


Jerry M. Whiting

Date 5 Oct 92

Dedication

To my wife, Janet, and my parents, Jim and Pat, who never pushed but always believed.

Abstract

A bench scale jar test study was undertaken at Edmonton's Gold Bar Wastewater Treatment Plant to determine the feasibility of using various coagulants for precipitation of phosphorus from municipal wastewater. Coagulants tested were alum, lime, and waste alum and lime sludge from the City's Rosedale Water Treatment Plant. This research was undertaken to evaluate the feasibility of chemical phosphorus removal as applied to Edmonton municipal wastewater. A secondary objective was to determine the feasibility (or impact) of disposal of waste sludges from water treatment plants to the municipal wastewater stream including the level of phosphorus removal.

Phosphorus removal efficiencies of the various coagulants were evaluated and compared in factorial design experiments which included polymer dosing as a factor. Further jar tests were run using alum and alum sludge to: 1) evaluate the effect of pH on precipitation; 2) characterize the nature and quantity of the precipitated solids; and 3) construct a dose-response surface for phosphorus removal. Other parameters measured in some or all of the tests were: suspended solids; turbidity; BOD; fecal coliforms; and nitrogen forms.

Alum was found to be the only coagulant that could, by itself, reduce effluent phosphorus levels to 1 mg/L or less. This level could also be reached using a combination of alum and alum sludge. Phosphorus removal with lime was less than expected while lime sludge exhibited no phosphorus removal capability.

It was found that pH played a significant role in phosphorus removal with alum and alum sludge, the lower the final pH, the better the removal. The phosphorus removal dose-response surface showed the alum to be 5 to 10 times more effective in removing phosphorus than alum sludge. Addition of

alum and alum sludge increased the precipitated solids by approximately 2 times compared to no coagulant addition, but increased the volume of solids by 3 to 4 times.

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List of Symbols and Abbreviations

Al	Aluminum
Al-Al₂(SO₄)₃	Aluminum expressed as Alum
BOD	Biochemical Oxygen Demand, mg/L
BOD₅	Five day BOD
Ca	Calcium
CaO	Quick Lime
Ca(OH)₂	Hydrated Lime
Ca-Ca(OH)₂	Calcium expressed as Hydrated Lime
F	F distribution (statistical)
G	Velocity Gradient, time⁻¹
Gt	Velocity Gradient * time, dimensionless
NTU	Nephelometric Turbidity Units
P	Phosphorus
PE	Primary Effluent
PO₄-P	Phosphate expressed as phosphorus
RI	Raw Influent
rpm	Revolutions per minute
SS	Suspended Solids
TKN	Total Kjeldahl Nitrogen

1.0 INTRODUCTION

1.1 The Problem

Eutrophication is the process of enrichment of a body of water with nutrients with a consequent deterioration of its quality. It causes problems ranging from flow retardation, especially in smaller rivers and streams, to algal blooms leading to consequent taste and odour problems in drinking waters. The increase in associated biological activity can also cause rapid depletion of dissolved oxygen in receiving waters, thus posing a threat to aquatic life. The two major nutrients of concern are nitrogen and phosphorus. Phosphorus is the limiting nutrient in most water bodies. Nitrogen is available in abundance for some forms of plant and microbial life, notably the blue-green algae, who fix gaseous atmospheric nitrogen and use it as a nutrient. Thus, the major concern has been eutrophication caused in receiving waters by phosphorus, as the growth-limiting plant nutrient (Doyle, 1987).

The sources of phosphorus are varied and include quantities leached from geologic formations, fertilized agricultural lands, and human waste. Phosphorus discharged from domestic wastewater treatment plants is considered to be one of the most significant and easy-to-control sources.

Methods of phosphorus removal in wastewater treatment plants (WWTPs) include chemical precipitation, biological uptake and ion exchange. The most common phosphorus removal mechanism is chemical precipitation, because of its relative simplicity, familiarity, and reliability. Common coagulants used in this process include aluminum sulphate (alum), ferric chloride, lime, and ferric sulphate.

1.2 Background

Increased levels of phosphorus in surface waters, public outcry over water pollution, and more economical and efficient methods of removal have prompted regulatory agencies to start enforcing stricter effluent pollutant levels on WWTPs discharging to open water bodies. The regulation of phosphorus discharge levels to the Great Lakes is a successful example of implementation of this strategy (Schmidtke, 1980).

It is anticipated that Alberta Environment will soon be imposing phosphorus discharge limits on the City of Edmonton's Gold Bar Wastewater Treatment Plant ("Gold Bar"). In light of this impending new discharge limit, the City and Alberta Environment are studying phosphorus removal options in order that a reliable and economic treatment system can be put in place. This study addresses chemical precipitation of phosphorus using standard chemical coagulants in pure form, as well as in the form of sludges, such as those from the City's Rossdale Water Treatment Plant ("Rossdale"). An additional review was made of the effects of chemical precipitation on the rating of WWTP clarifiers. A study of biological phosphorus removal at Gold Bar has already been undertaken (Doyle, 1987).

1.3 Objective

Bench-scale testing was done in order to determine the best coagulant, or combination of coagulants for Gold Bar wastewater. Coagulants tested were alum, lime, alum WTP sludge, lime WTP sludge, and a number of practical combinations of these. Testing included primary effluent and raw influent, though it was deemed that the only practical location to retrofit chemical addition at Gold Bar was somewhere between the grit chambers and the primary clarifiers. This would necessitate precipitation of the raw influent only.

Preliminary jar testing and a literature review were done in order to address whether biological clarifiers needed to be downrated after addition of chemical precipitants, i.e., would the additional solids generated by chemical precipitation of phosphorus reduce the overflow capacity of the clarifiers? Previous Alberta experience seemed to indicate that clarifiers had to be downrated because of this increase in influent suspended solids. For example, the City of Calgary downrated clarifier capacity at their Bonnybrook WWTP after the implementation of a chemical phosphorus removal process.

2.0 LITERATURE REVIEW

2.1 Introduction

Phosphorus is a naturally occurring nutrient known to be growth-rate limiting for certain aquatic organisms and fauna. If phosphorus from point sources such as wastewater treatment plants (a major source) is discharged to surface water bodies in sufficient quantity, it can cause increased eutrophication by accelerating the growth of biological organisms, such as blue-green algae, and can upset the natural balance of the ecosystem. For instance, during dark periods and after their death, these algae rob the water of much of its dissolved oxygen thus leading to disruption of certain species of fish. Experience has shown that limiting point source phosphorus discharges has aided in regeneration of the natural ecosystem in water bodies that previously suffered from accelerated eutrophication (Black, 1980). Of the various limiting strategies in WWTPs, chemical precipitation has proven to be one of the most effective and reliable methods of removing phosphorus from wastewater.

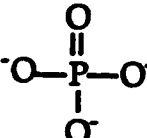
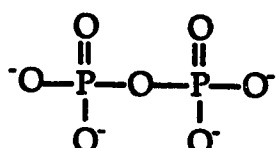
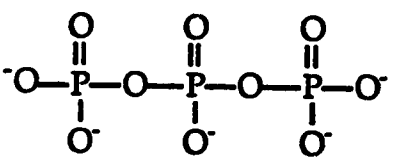
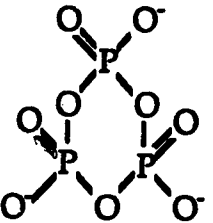
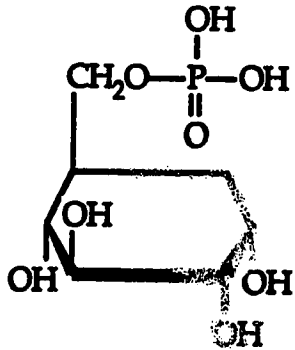
2.2 Chemical Characteristics of Phosphorus in Sewage

Phosphorus in sewage occurs in several forms, each of which has its own chemical properties. The major forms are particulate organic phosphates tied up in organic matter, orthophosphates, and the polyphosphates. The polyphosphates are also referred to as complex, or condensed phosphates. The orthophosphates occur in several different forms such as PO_4^{-3} , HPO_4^{-2} , H_2PO_4^- , H_3PO_4 , with the predominant form being dependent on pH (Metcalf and Eddy, 1991). In the past, orthophosphate was considered to be PO_4^{-3} , and was reported this way, but with the present practice of reporting phosphorus as P, one does not usually have to be concerned with the actual form. Orthophosphates are available for biological metabolism without further breakdown and are a natural byproduct of the decomposition of organic materials. In a well treated secondary effluent, a large fraction of the phosphorus present is in the form of orthophosphate. This is fortunate from the standpoint of precipitation because this is the easiest form to precipitate as will be discussed in later sections (Black and Veatch, 1976). The form of phosphate in a raw influent varies, dependent on site specific parameters such as travel time to the WWTP, and the amount of industrial wastewater being treated.

The bulk of the polyphosphates are made up of pyrophosphate, a two-phosphate chain, and tripolyphosphate, a three-phosphate chain. Another minor polyphosphate is hexametaphosphate with a chain length of about 15 phosphates. Intermediate chain length phosphates will be formed during hydrolysis of the long-chain phosphates (Schmid, 1969). The classes of phosphorus-containing compounds of importance in wastewater are shown in Table 2.1.

In general, orthophosphates and polyphosphates occur in sewage in equal quantities with organic particulate phosphate making up a small portion of the total phosphates. Municipal wastewaters generally contain 4 to 15 mg/L of phosphorus as P (Metcalf and Eddy, 1991). The polyphosphates in wastewater are hydrolyzed to orthophosphate,

Table 2.1 Classes of Phosphorus-Containing Compounds of Importance in Aquatic Systems (adapted from Snoeyink & Jenkins, 1980)

Group	Structural Representation (Typical)	Species of Importance	Acid Ionization Constants (25°C)
Orthophosphate		H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , HPO_4^{2-} complexes	$pK_{a,1} = 2.1$, $pK_{a,2} = 7.2$, $pK_{a,3} = 12.3$
Polyphosphates	<p>pyrophosphate</p>  <p>tripolyphosphate</p> 	$H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$, $HP_2O_7^{3-}$ complexes	$pK_{a,1} = 1.52$, $pK_{a,2} = 2.4$, $pK_{a,3} = 6.6$, $pK_{a,4} = 9.3$
Metaphosphates		$H_3P_3O_{10}^{2-}$, $H_2P_3O_{10}^{3-}$, $HP_3O_{10}^{4-}$, $P_3O_{10}^{5-}$, $HP_3O_{10}^{4-}$ complexes	$pK_{a,3} = 2.3$, $pK_{a,4} = 6.5$, $pK_{a,5} = 9.2$
Organic Phosphates	 <p>glucose 6-phosphate</p>	very many types, including phospholipids, sugar phosphates, nucleotides, phosphoamides, etc.	$pK_{a,3} = 2.1$

primarily by enzymatic action. The ratio of tripolyphosphate to pyrophosphate normally encountered in wastewater can be highly variable. As the wastewater is travelling to the wastewater treatment plant (WWTP) and being processed through the plant, tripolyphosphates may be hydrolyzed to pyrophosphates and orthophosphates, and the pyrophosphates further hydrolyzed to orthophosphates. The ratios of each of these phosphate forms to one another has a significant effect on precipitation and phosphorus removal (Schmid, 1969).

2.3 Chemical Phosphorus Removal

2.3.1 Chemical Precipitation

Chemical precipitation is a very complex process that is generally understood but that is difficult to explain fully. Reactions are often incomplete and numerous side reactions may occur, especially in a wastewater, which is heterogeneous by nature. The following discussion will provide a general overview of the nature of chemical precipitation, especially as it relates to phosphorus removal. A more complete discussion can be found in Snoeyink and Jenkins (1980).

The three main steps of chemical precipitation are: 1) nucleation, 2) crystal growth, and 3) agglomeration. Solutions that are supersaturated with respect to a certain solid may be stable indefinitely, but an increase in supersaturation or the addition of fine particles of a substance mixed into solution may trigger precipitation. Physically, precipitation is brought about by: 1) addition of a chemical, 2) rapid mixing, 3) flocculation, and 4) settlement.

2.3.1.1 Nucleation

A nucleus is a fine particle on which formation or precipitation of a solid phase can take place. Precipitates formed from homogeneous solution (i.e., a solution with no solid

phase in it) requires that the nucleus be formed from ions in solution. If the nuclei are formed from the component ions of the precipitate, the initial phase of precipitation is referred to as homogeneous nucleation; if foreign particles form the nuclei, the nucleation is said to be heterogeneous. Because virtually all aqueous solutions contain fine particles of various types, most nucleation is heterogeneous.

The creation of nuclei from precipitate ions is an energy consuming process with supersaturation being the source of energy for this organization of random constituents into structures with defined surfaces or nuclei. This energy requirement is less for heterogeneous nucleation than for homogeneous nucleation. For this reason, and because the rate of crystal growth is directly proportional to the surface area provided for crystallization, the recirculation of chemical sludge to a point ahead of the chemical addition point in the process is encouraged. In essence, the sludge contains precipitate and foreign particles for additional surface area on which nucleation can occur. The only requirement for the foreign particles is that they be similar in lattice structure and distance between adjacent ions (Snoeyink and Jenkins, 1980).

2.3.1.2 Crystal Growth

Crystals form by the deposition of the precipitate constituent ions onto nuclei. The rate of crystal growth is of critical importance because water and wastewater treatment processes often do not reach equilibrium. The rate of crystal growth can be expressed as

$$\frac{dC}{dt} = -kS(C - C^*)^n \quad (2.1)$$

- where:
- C* = saturation concentration, mole/litre
 - C = actual concentration of limiting ion, mole/litre
 - k = rate constant, litreⁿ time⁻¹ mg⁻¹, mole⁽¹⁻ⁿ⁾
 - S = surface area available for precipitation, mg/litre of a given particle size
 - n = constant (integer giving order of reaction)

The value of k depends on the nature of the solid being precipitated and the solution conditions. The value of the exponent n is unity when the rate of diffusion of ions from solution to the crystal surface controls the rate of crystal growth, if other processes such as the rate of reaction at the crystal surface are rate limiting then the value of n may be different than unity (Snoeyink and Jenkins, 1980; Wiechers, 1986).

From equation 2.1 a number of practical points become evident. Firstly, as previously mentioned, the rate of reaction is dependent on particle surface area thus recirculation of chemical sludges is encouraged. This is confirmed in a phosphate removal study of various reactor types by J.F. Ferguson et al (1973, as cited in Snoeyink and Jenkins, 1980). Secondly, the rate of reaction is dependent on solution concentration. Reactors that have regions of high concentration will have precipitation (or crystal growth) rates greater than equivalent reactors that are mixed throughout. Plug-flow reactors are therefore more efficient than CSTRs (completely stirred tank reactors); this was also confirmed in the Ferguson study.

2.3.1.3 Aging and Ripening

The initial solid formed by precipitation may not be the most stable solid (thermodynamically stable phase) for the reaction conditions. The crystal structure of solids that are not in the most stable phase will tend to change to the most stable phase over a period of time. This change in crystal structure is called "aging". An additional phenomena called "ripening" may also be noted where the crystal size of the precipitate increases. The selection of an equilibrium constant for precipitating solutions is extremely difficult. Besides aging and ripening, equilibrium constants are affected by such factors as agglomeration, complex formation, adsorption of impurities at the crystal interface, and formation of solid mixtures (Snoeyink and Jenkins, 1980). These factors are especially prevalent in wastewater chemistry.

2.3.1.4 Coagulation and Flocculation

Coagulation is the process whereby particles formed by precipitation/crystallization are destabilized. Precipitation of phosphate with alum or lime are examples of stable colloids or very small particle precipitates which do not settle readily from solution. These require destabilization by coagulation in order to allow flocculation and settlement to take place. Flocculation is the process whereby destabilized particles, or particles formed as a result of destabilization, are induced to come together, make contact and thereby form large(r) agglomerates (Wiechers, 1986). The flocculation process occurs in two stages. The first stage, perikinetic flocculation, is brought about by thermal agitation (Brownian movement) and is a naturally occurring random process that commences immediately after destabilization (coagulation). The second stage, orthokinetic flocculation, arises from induced velocity gradients in the liquid. Orthokinetic flocculation is the predominant flocculation process in most, if not all, wastewater treatment processes.

Velocity gradients in the liquid may be induced by setting the liquid in motion by passage around baffles, mechanical agitation, or by sedimentation within a settling basin if flocs are sufficiently formed. The principal parameter governing the rate of orthokinetic flocculation for a given flocculation system is the velocity gradient applied. The degree or extent of flocculation is determined by the velocity gradient and the time of flocculation whose product is referred to as the Gt (with units of sec^{-1}). These two parameters together influence the rate and extent of particle aggregation and/or breakup of these aggregates thus optimization of the flocculation process is essential.

2.3.1.5 Rapid Mixing

The purpose of rapid (flash) mixing is to disperse the coagulant chemical quickly and evenly in the raw water or wastewater. It is considered to be the most important part of the precipitation process because it is where the precipitation and destabilization reactions

occur, and where primary flocs are formed, the characteristics of which markedly influence subsequent flocculation kinetics (Wiechers, 1986). Proper rapid mixing is especially important when removing phosphate from wastewaters with metal salts which will predominantly form metal hydroxides rather than metal phosphates if not properly dispersed. The importance of the efficiency of a rapid mixing facility is evident if the time period required for destabilization is considered, i.e. of the order of 10^{-10} to 1.0 seconds (Bratby, 1980). This also implies that the traditional rapid mixing times of 30 to 60 seconds (at typical rapid mixing rpm, or energy input) may be unnecessary (Wiechers, 1986).

2.3.2 Precipitation of Phosphorus with Alum

Snoeyink and Jenkins (1980) state that when alum is added to water the aluminum ion interacts with the water to form hydroxo-complexes and solid $\text{Al}(\text{OH})_3(\text{s})$, and with orthophosphate present to form the solid aluminum phosphate, $\text{AlPO}_4(\text{s})$. The concentrations of PO_4^{3-} and OH^- , of course, are a function of pH. The relationship between aluminum hydroxide and aluminum phosphate at varying pH is indicated by the pC-pH diagram for pure water as shown in Figure 2.1. The figure indicates the optimum pH for phosphorus removal to be approximately 5.5 which is similar to the optimum pH for removal from municipal wastewater. Ferguson and King (1977) found that the optimum pH range for phosphorus removal from wastewater narrowed as the Al:P molar ratio increased but that its center was generally 5.5 to 6.0. Recht and Chassemi (1970) found the removal of orthophosphate to be affected by pH, and by the concentration of added aluminum salts. The optimum pH for phosphate precipitation was found to be close to 6.0 for Al(III).

As mentioned previously, when alum ($\text{Al}_2(\text{SO}_4)_3$) is added to wastewater, hydrolysis reactions occur leading to the formation of $\text{Al}(\text{OH})_3$ and the entrapment of suspended solids and clarification. Ionized aluminum also reacts directly with phosphorus

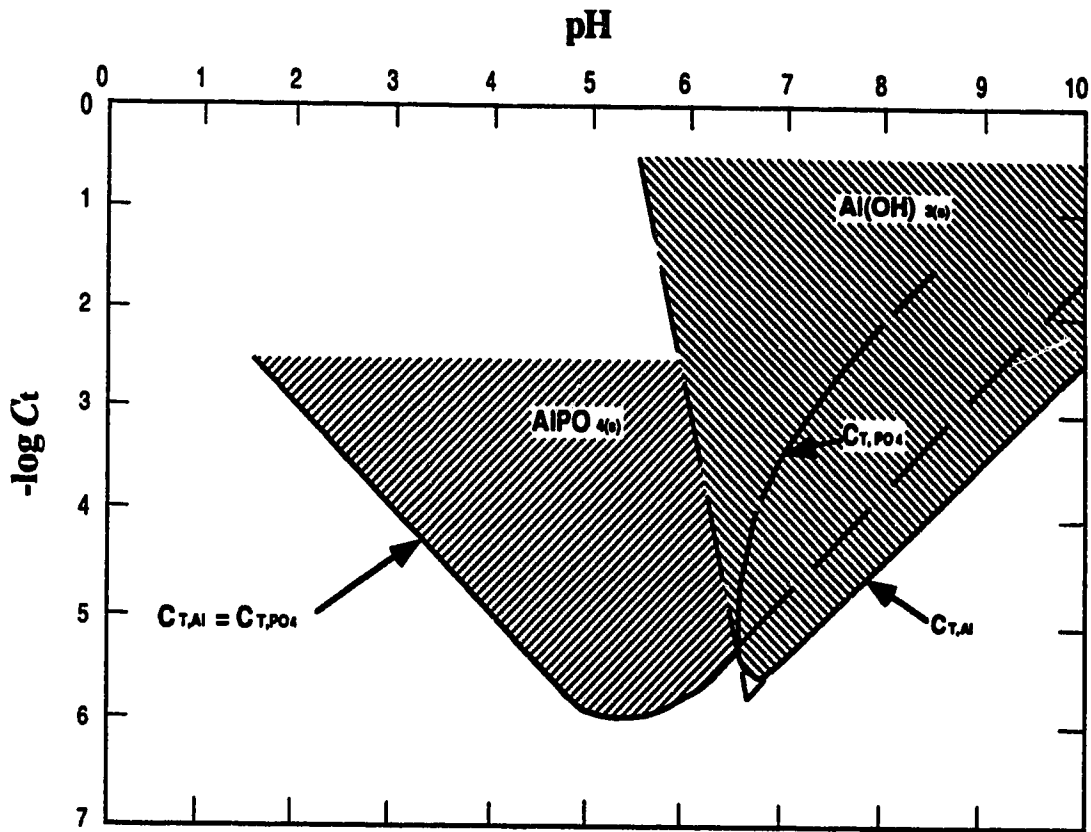


Figure 2.1 Concentration of phosphate and aluminum that can exist at various pH values when $\text{AlPO}_4(s)$ is precipitated from or dissolved in pure water. Concentrations of phosphate and aluminum are controlled by $\text{AlPO}_4(s)$ solubility below pH 5.4. Above pH 5.4 $C_{T,Al}$ is controlled by $\text{Al(OH)}_3(s)$ solubility, and thus C_{T,PO_4} concentrations in this range are greater than $C_{T,Al}$ (adapted from Snoeyink and Jenkins, 1980).

compounds. The following is a simplification of the complex reaction products formed, based on the phosphorus present existing in the orthophosphate form (represented as Na_3PO_4):



(Source: Ockershausen, 1980)

A report for the U.S. Federal Water Quality Administration (Recht and Chassemi, 1970) specifically addresses the kinetics and mechanism of precipitation as well as the nature of the precipitate formed in phosphate removal from wastewater using aluminum (III) salts. There has been conflicting literature as to the kinetics and chemistry of the reaction. For instance, Recht and Chassemi report that some authors presented results supporting the view that removal of phosphate involves its adsorption on precipitating aluminum hydroxides. But, according to others, the interaction of aluminum with orthophosphates resulted in the formation of insoluble aluminum phosphates.

Recht and Chassemi concluded, following extensive experimentation, that the reactions of the orthophosphate ion with Al(III) which result in the formation of precipitates were completed in less than 1 second. Further, for a constant pH, the removal of orthophosphate ion with aluminum salts up to about a 1:1 aluminum to phosphate molar ratio was found to be directly proportional to the concentration of the added aluminum. This relationship seemed to indicate that a chemical reaction was occurring between the aluminum and the phosphate and not an adsorption (physical or chemical) of phosphate on the precipitating aluminum hydroxide. This was confirmed by Ferguson and King (1977) who found that the removal of phosphate was approximately stoichiometric at an Al:P mole ratio of 1.4 until a residual of about 1 mg/L, if the final pH was between 5.2 and 6.9. Recht and Chassemi also found that when phosphate solutions with pH values of 5.0 and 6.0 were added to freshly precipitated colloidal suspensions formed by aluminum salt hydrolysis at the same pH, an immediate sharp rise in pH was observed which was

followed by a further small but gradual increase in pH. The rise in the pH was attributed to the replacement of the hydroxides by the phosphate ion in the colloidal particles. Another finding of the report was that for all precipitation scenarios tested, the removal of phosphate from solution was accompanied by complete precipitation of excess Al(III) by hydrolysis reactions; this was, of course, within the range of sensitivity of the analytical techniques used.

For an initial phosphate concentration of 12 mg/L P, Recht and Chassemi found the minimum residual phosphate concentration was 3.5 mg/L P when a 1:1 aluminum-to-orthophosphate molar ratio was used. With a 2:1 molar ratio, the minimum residual phosphate concentration was lowered to 0.10 mg/L P. At and very near the pH of optimum precipitation, the aluminum-phosphate reaction resulted in large, easily settleable flocs. Immediately outside this range colloidal suspensions were formed that could be effectively removed by filtration through 100 micron membranes. At pH levels higher or lower than this pH region no turbidity was observed.

Recht and Chassemi (1970) also experimented with the removal of condensed phosphates by precipitation with aluminum salts. They found the removal to be very dependent on pH and the reactant concentration ratio. When a 2:1 aluminum-to-phosphate equivalence ratio was used with pyrophosphate (initial concentration = 18 mg/L P) and tripolyphosphate (initial concentration = 21.6 mg/L P), maximum removal of phosphate was observed at a pH level close to 5.0. At this ratio of reactants, a minimum pyrophosphate residual concentration of 0.9 mg/L P and minimum tripolyphosphate concentration of 3.80 mg/L P was observed. Practically no phosphate was removed at pH levels +/- 1 unit from that of maximum removal. It was thought that pH affected the degree of fineness (dispersion) of the colloidal precipitates, i.e., the floc size. Outside of the narrow pH range stated, precipitate particles were too fine to remove by settling. This was evidenced by increases in turbidity outside of this range. The same effect was noted for orthophosphate though its ability to "disperse" the precipitates was not as pronounced as

the polyphosphates, i.e., its optimum pH range was not as narrow. This is thought to be one of the reasons that orthophosphate is easier to precipitate than condensed phosphates. At a 1:1 aluminum-to-phosphate reactant ratio Al(III) could affect no removal of tripolyphosphate at several pH levels examined. As with orthophosphate precipitation, good correlations were found between the formation and settleability of the precipitates and the extent of phosphate removal.

2.3.3 Precipitation of Phosphorus with Alum Sludge

There have been a number of studies done on the upgrading of sewage treatment using alum sludge or, conversely, the disposal of alum sludge to sewage treatment plants and its effect on biological treatment processes. However, though all of these articles or studies note increased levels of phosphorus removal with increased alum sludge dose (usually dosing on the basis of aluminum concentration), there has been little attempt to determine the mechanism of phosphorus removal.

Recht and Chassemi (1970) noted that it was originally thought that adsorption onto aluminum hydroxide flocs (which make up the bulk of waste alum sludges from water treatment plants) was the prevalent mechanism of phosphorus removal when alum was added to wastewaters. They subsequently showed that it was likely that phosphorus removal using alum was predominantly a stoichiometric chemical reaction rather than an adsorptive process, especially under certain conditions. The phosphorus removal noted with the addition of waste alum sludge may be an adsorptive process though it has been noted to be not nearly as effective or efficient as the addition of alum. O'Brien and Warriner (1972) conclude that the mechanism responsible for reduction of phosphates by waste water treatment plant sludge is the same as that for aluminum hydroxide, namely, an adsorption phenomenon.

A study of the effect of solution chemistry on coagulation with hydrolyzed Al(III) in a kaolonite solution by Letterman and Vanderbrook (1983) noted the following.

Aluminum hydrolysis products adsorb on kaolin particles, eventually forming a complete coating of aluminum hydroxide precipitate as the aluminum concentration is increased. When the precipitate had a high positive charge it tended to stabilize the negatively charged kaolin particles thus allowing for more effective flocculation. This phenomenon was generally noted at lower pH conditions and in dilute solutions. The removal of phosphorus generally correlates well with suspended solids removal thus this is likely another explanation of the mechanism of phosphorus removal.

Morgan et al (1977) noted that the removal of phosphorus (in addition to other wastewater components that are capable of being physically coagulated by aluminum hydroxide) with respect to alum sludge dosage followed a first order relationship. That is, the coagulation ability of the alum sludge in wastewater increased at a decreasing rate.

2.3.4 Precipitation of Phosphorus with Lime

Phosphorus removal with lime is a non-stoichiometric process in that the chemical dosing rate is not dependent on the level of phosphorus to be removed from the waste stream. Rather, it is a pH dependent process that relies on the solubility product of calcium hydroxy apatite being increasingly exceeded as pH increases with the bulk of phosphate being precipitated at pH values above 10. Thus, it is ideal for removing high concentrations of phosphates from small quantities of effluent such as phosphorus rich side streams typical of some biological phosphorus removal processes. The application of lime treatment to main streams of sewage works is not usually favoured because: 1) the high pH requirements have a deleterious effect on organisms in the secondary treatment process and lowering the pH would cause the calcium hydroxy apatite to redissolve; and, 2) the high dosages of lime required to raise the pH to desired levels and the large quantities of sludge produced (Wiechers, 1986).

At ion concentrations normally occurring in wastewater, orthophosphate precipitates as a crystal of variable composition exhibiting the pattern of an apatite. Usually

referred to as tricalcium phosphate, this apatite precipitate is in reality a hydroxylapatite (hydroxyapatite) for which the base formula is $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. The variable composition or amount of hydration are not taken into account in this formula. The Ca/P mole ratios have been noted in the literature as varying from 1.33 to 2.0 though the formula suggests a Ca/P ratio of 1.67 (Schmid and McKinney, 1969). There have been a number of theories put forward to explain the reason for the variable composition of the apatite crystal. Van Wazer (1958; as cited in Schmid and McKinney, 1969) concluded that isomorphic substitution both at the surface and within the crystal is the principal reason. Corbridge (1978) states that the non-stoichiometry can in many cases only be accounted for by vacancies or substitution in the crystal lattice or at the surface. For instance, hydrogen ions may be substituted for calcium ions within the structural positions (Schmid and McKinney, 1969).

Calcium orthophosphates are generally very insoluble compounds and reactions involving them are often slow to go to completion. Hydroxylapatite is the least soluble of the calcium orthophosphates (Corbridge, 1978). Schmid and McKinney state that, "Solubility products reported in the literature for this precipitate show variations over the range of 10^{11} ." Under very controlled conditions Clark (1955; as cited in Schmid and McKinney, 1969) arrived at a solubility product given by

$$K_{25^{\circ}} = [\text{Ca}]^{10}[\text{PO}_4]^6[\text{OH}]^2 = 10^{-115}$$

A typical curve indicating phosphorus removal from wastewater with the use of lime is shown in Figure 2.2. Schmid and McKinney (1969) did a number of experiments to determine phosphate removal vs. pH for orthophosphate and polyphosphate from distilled water at ion concentrations normally encountered after lime treatment. Curves were derived for each so that they could be compared with one another and with a curve illustrating typical total phosphate removal from domestic wastewater (see Figures 2.3, 2.4, and 2.5, respectively). It was determined that the two curves (Figure 2.3 - orthophosphate

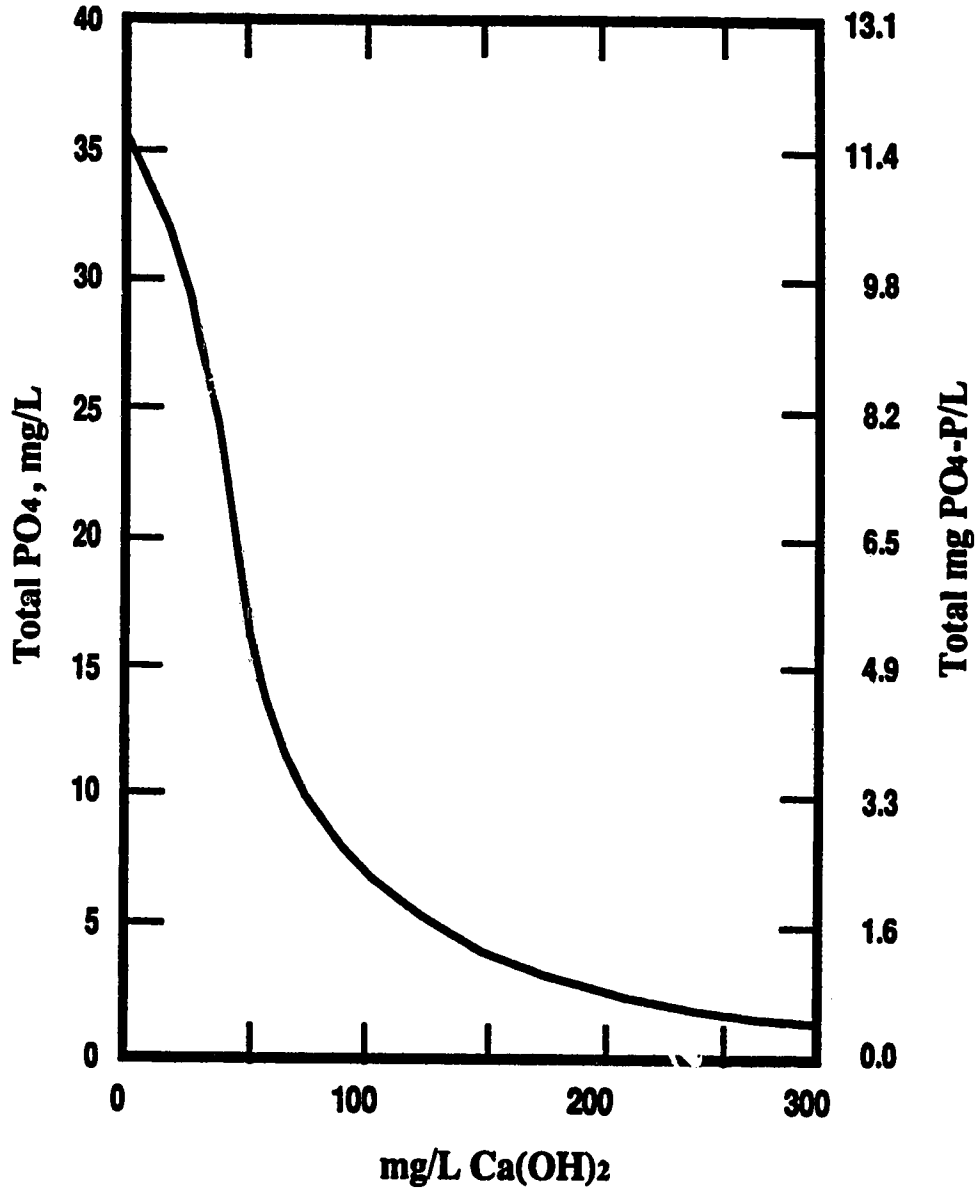


Figure 2.2 Typical Curve Indicating Phosphorus Removal from Wastewater (adapted from Schmid and McKinney, 1969).

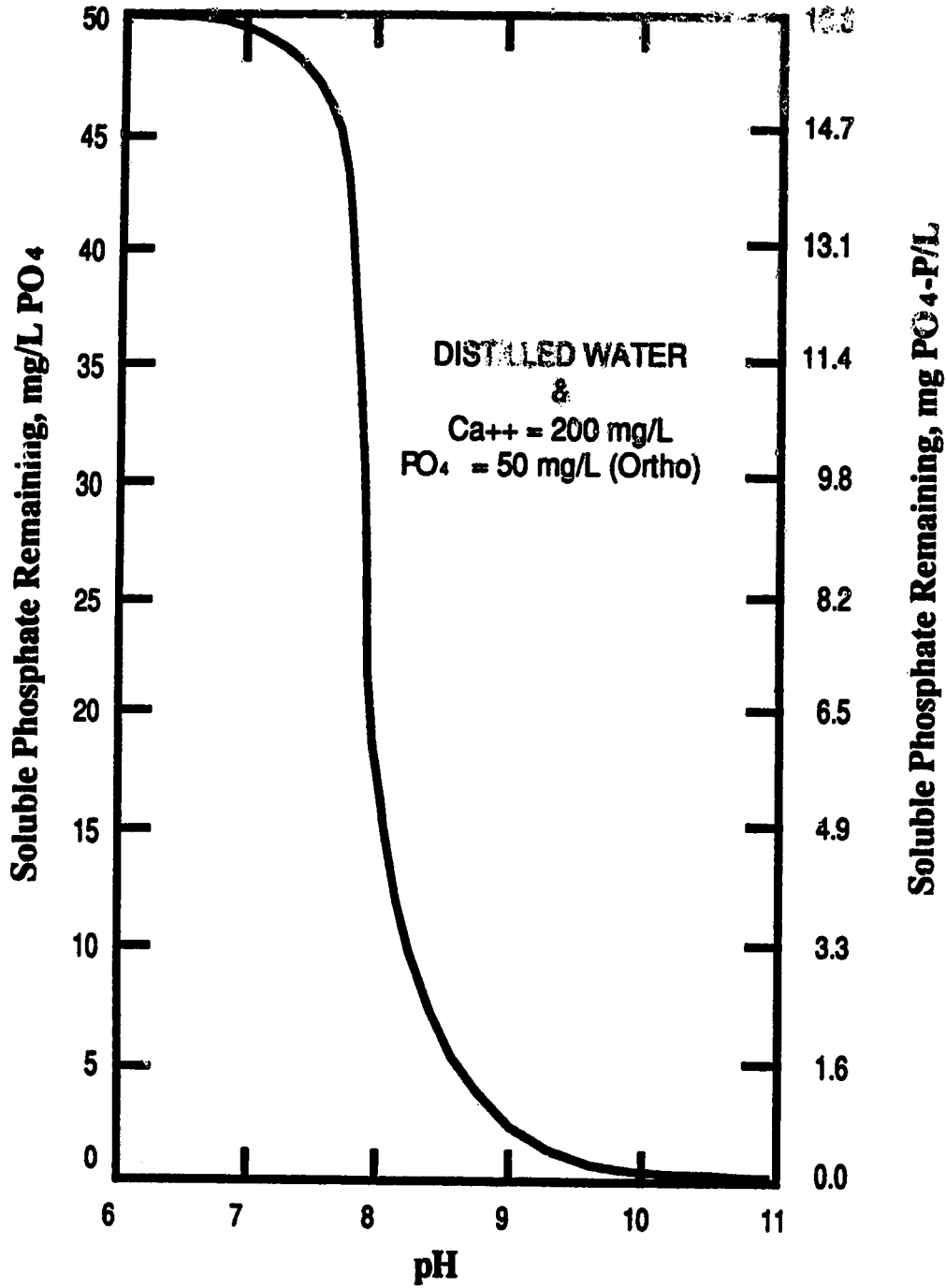


Figure 2.3 Orthophosphate Remaining vs. pH (adapted from Schmid and McKinney, 1969).

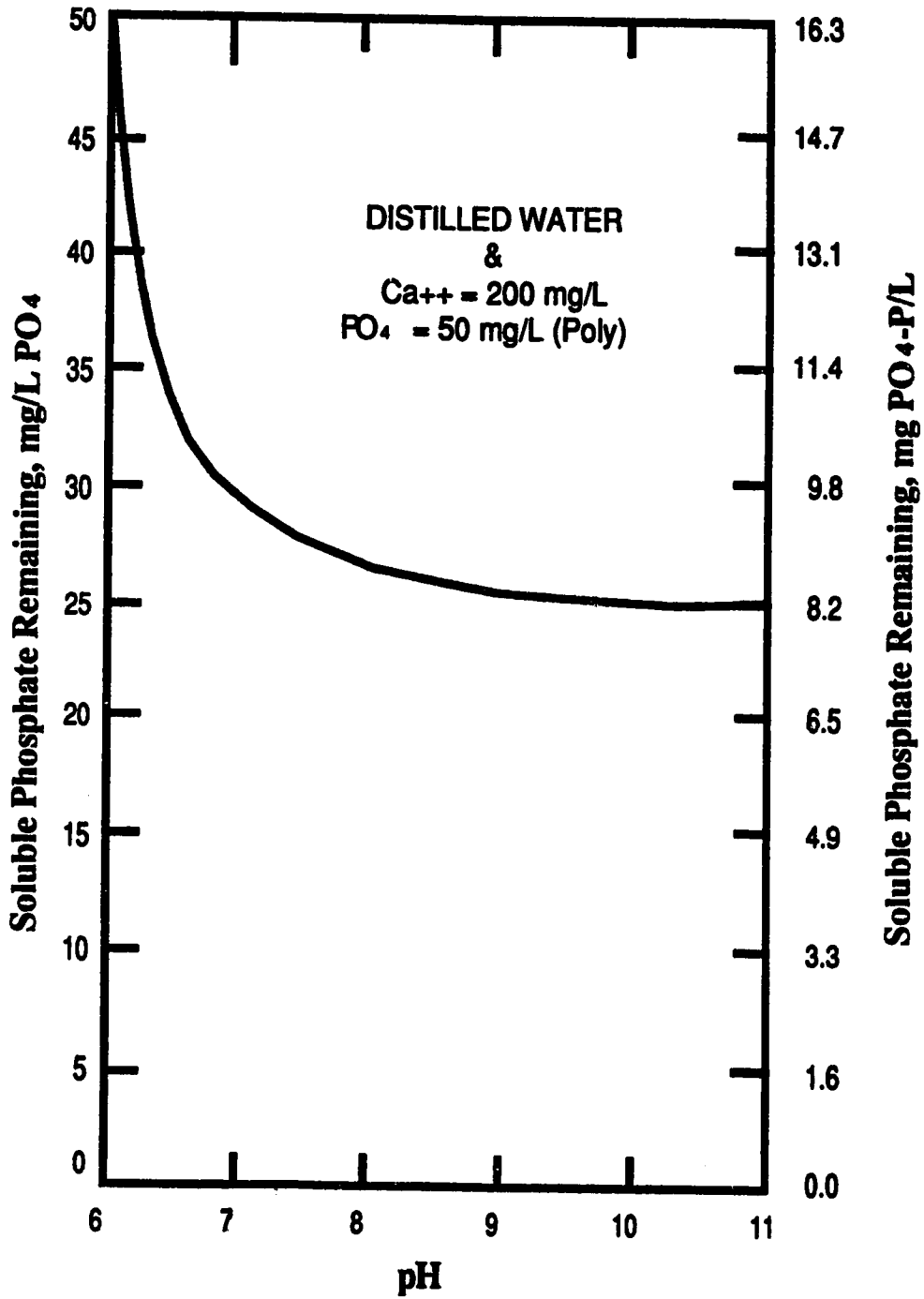


Figure 2.4 Polyphosphate Remaining vs. pH (adapted from Schmid and McKinney, 1969).

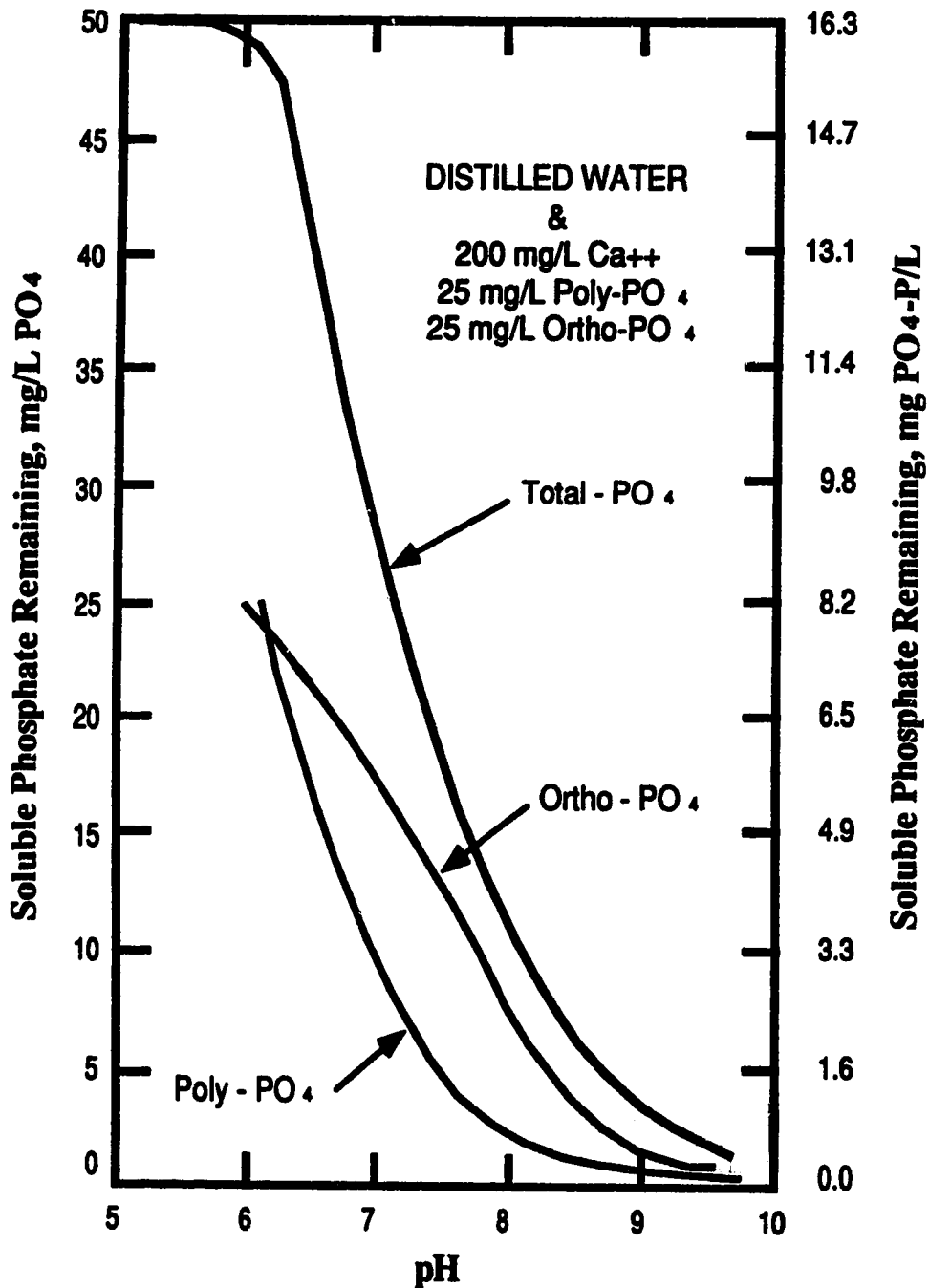


Figure 2.5 Poly- and Orthophosphate Remaining vs. pH (adapted from Schmid and McKinney, 1969).

and Figure 2.4 - polyphosphate) were different from one another and from the typical total phosphate removal curve (Figure 2.2). But, when the orthophosphate and polyphosphate removal curves were combined they appeared to be the same as that for a typical phosphate removal curve for wastewater (Figure 2.5).

The difference between the two phosphate curves was attributed, in part, to adsorption. Adsorption studies were conducted on the various phosphate forms to resolve what happens when those forms are combined. It was found that orthophosphate will adsorb onto the polyphosphate floc at a pH near 7.0 which explains why orthophosphate will precipitate in the presence of polyphosphate at this pH but not by itself as shown in Figure 2.3. As the pH was raised and orthophosphate began to form a precipitate, the polyphosphate was found to be adsorbed readily to the orthophosphate floc. Additionally, the polyphosphate mixture was found to adsorb readily to the calcium carbonate precipitate. If the pH was raised sufficiently high to precipitate calcium carbonate then the pinpoint floc of calcium carbonate would adsorb polyphosphates resulting in phosphate carry over. This was not considered to be significant because under normal conditions the phosphate precipitation reaction will proceed much faster than the calcium carbonate precipitation reaction. Thus, most of the phosphate will have been precipitated or adsorbed before it can be adsorbed to the calcium carbonate precipitate.

Of the polyphosphate forms, pyrophosphate produces a heavy fast settling precipitate with calcium, tripolyphosphate will form a precipitate that is a fine floc and will neither flocculate nor settle well (Schmid and McKinney, 1969).

Based on the above discussion, the precipitation, settling, and adsorption characteristics have wide ranging implications as to the removal of phosphorus from wastewaters. This is especially true for industrial wastewaters that may contain only tripolyphosphates that would have to be hydrolyzed to the pyro and/or ortho forms in order to obtain a low residual phosphate concentration. Fortunately, for normal domestic

wastewaters this relationship is not critical and a good balance of ortho and polyphosphates naturally exists which aids in good overall removal.

2.3.5 Precipitation of Phosphorus with Lime Sludge

A review of the available literature found that very little, if any, research work had been done in this area. This is likely because the mechanism of phosphorus removal using lime (i.e. raising pH) would not be prevalent due to the sludges' relatively inert nature thus rendering it ineffective as a precipitant. Calcium carbonate and magnesium hydroxide, the primary constituents of lime-soda ash softening, are reasonably stable at the pHs typical of municipal sewage (6 to 8) (Hammer, 1977). Schmid and McKinney (1969) stated that there was some adsorption of polyphosphates to calcium carbonate precipitate but this was observed at a higher pH.

2.3.5 Polymer Addition

Polymers are generally used as coagulant aids for cases where slow-settling precipitates, or fragile flocs easily fragmented under hydraulic forces in basins, are causing difficulties in flocculation. These long-chain, high-molecular-mass, organic chemicals serve to benefit flocculation by improving settling and toughness of flocs. They can be classified according to the type of charge on the polymer chain. Those possessing negative charges are called anionic, those positively charged are called cationic, and those carrying no electrical charge are nonionic.

Though polymers are generally much more expensive than coagulation chemicals on a unit cost basis, low dosage requirements and other benefits can usually offset this increased cost. The polymer dosage required as a flocculant aid is generally in the order of 0.1 to 1.0 mg/L. In coagulation of some waters (and wastewaters) anionic or nonionic polymers can significantly reduce metal coagulant dose, especially alum, required for satisfactory flocculation thus helping to offset the increased cost. A further benefit is the

reduction in the quantity of waste sludge produced compared to a coagulant without polymer addition. Sludge handling is a major operating cost so the improved dewaterability of sludge with polymer addition further helps to offset polymer costs (Hammer, 1977).

There is no single mechanism of destabilization by polyelectrolytes which may be considered applicable in all instances. However, the two principal mechanisms are: 1) a bridging model, where polyelectrolyte segments are adsorbed on the surface of adjacent colloids thereby binding them together, and 2) an electrostatic patch model whereby ionic polyelectrolytes, bearing a charge of opposite sign to the suspended material, are adsorbed and thereby reduce the potential energy of repulsion between adjacent colloids. These two models or mechanisms may operate concurrently or one may predominate in which case the particular mechanism is usually fairly simple to identify. A full discussion of polyelectrolytes and mechanisms of destabilization is contained in "Coagulation and Flocculation" by John Bratby (1980).

2.4 Biological Phosphorus Removal

Biological phosphorus removal in the activated sludge process has become a known technology over the last 20 to 30 years. Phosphorus removals of 70 to 90% can be achieved compared to removals of 30 to 40% in the normal activated sludge process treating domestic wastewater (Yeoman et al., 1986). There are a number of modifications to the activated sludge process that have been developed in order to facilitate phosphorus removal (see Metcalf and Eddy, 1991) but the fundamentals of each are the same. The process basically involves stressing of microorganisms, chiefly bacteria, in an anaerobic zone followed by "luxury uptake" of phosphorus in an aerobic zone. The phosphorus is thus incorporated into cell tissue that is removed in the sludge during clarification. Phosphorus can then be removed by conventional chemical precipitation, wasting the sludge, or by further biological methods.

The key to the process is the alternating of anaerobic and aerobic zones. The anaerobic conditions stress the microorganisms forcing them to release stored polyphosphates as orthophosphate but subsequently increasing their phosphorus uptake ability when exposed to aerobic conditions. The phosphorus taken up in the aerobic zone includes that released in the anaerobic zone as well as phosphorus in the influent wastewater stream. The total phosphorus uptake by the microorganisms is in excess of the phosphorus requirement for normal metabolism (Yeoman, 1986). It is also believed that the anaerobic zone provides an environmental advantage to the phosphorus removing bacteria in that it selectively promotes their growth over the other aerobic bacteria in the system (Marais et al., 1983). Thus, additional phosphorus consuming bacteria result from reproduction further increasing the phosphorus uptake capacity.

2.5 Chemical Phosphorus Removal in Biological Plants

Many existing municipal wastewater treatment plants are looking at having to retrofit phosphorus removal capability due to new limits being put on effluent phosphorus discharge. The addition of coagulants in primary or secondary treatment is often a viable alternative because of the reliability of this method and the relatively small capital costs involved. In many cases the necessary rapid mixing can be provided in existing grit chambers or aeration tanks while flocculation and precipitation can occur in existing clarification facilities. This is an alternative to biological phosphorus removal that may have lower operating costs, but usually requires a major capital expenditure for new facilities, or refurbishing of existing facilities.

A major consequence of the addition of coagulants to existing biological treatment facilities, especially upstream in the process, is the change in regime of the wastewater, i.e., operating parameters will likely change in the aeration tanks with the addition of chemicals before primary treatment. Sludge production also increases as will be discussed in a later section.

Chemicals can be added at various points in the process but many of the effects on the process are similar despite the change in application point. The relative merits of each application point will be discussed in a later section but the benefits and effects of chemical addition will be discussed in general terms with the application point only being discussed where required.

2.5.1 Effects and Benefits of Chemical Phosphorus Removal

Associated with chemical phosphorus removal are other benefits which may make it a viable alternative for many WWTPs. These could include reductions in:

- suspended solids;
- turbidity;
- biochemical oxygen demand;
- fecal coliforms; and
- chemical oxygen demand.

Lin and Carlson (1975) found that addition of alum to the activated sludge process resulted in an effluent containing more nonbiodegradable organic matter and inorganic compounds, because alum is more likely to flocculate the biodegradable portion of organic matter. The addition of aluminum hydroxide to pilot plant mixed liquor has been found to shift the suspended solids remaining in the supernatant from organic substances to inorganic substances (Hsu and Pipes, 1973). This results in somewhat of a reduction in COD but the benefits are offset by toxic effects to microorganisms if the aluminum hydroxide concentration is too high. Thus, the increase in phosphorus removal with increasing dose and improved flocculation of the sludge mass must be balanced against the deleterious effect on the microorganisms which is usually manifested by a deflocculation of the sludge mass produced. Salotto et al (1973) found that the addition of alum sludge decreased volatile-solids content of the primary sludge produced. In addition, process efficiency improved as did settleability of the waste activated sludge. The effects and

benefits of disposing of waste alum sludge to domestic wastewater treatment plants rather than addition for phosphorus removal will be discussed more fully in a later section.

A study by Davis and Unz (1973) of the microbiology of an activated sludge process chemically treated with alum for phosphorus removal determined that the combined effluent was of higher quality than the biological effluent alone. The settled effluent from the chemical-biological treatment contained fewer total coliforms, fecal coliforms, and fecal streptococci than did the counterpart biological effluents (used as a control).

A full-scale study of phosphorus removal by lime addition in an activated sludge plant was undertaken by Black and Mills (1970). Lime was added to the influent channel of the primary clarifier; primary treatment performance improved dramatically as was indicated by the increases in BOD, SS, and P removal. The secondary treatment performance was affected by the reduced organic loading at the initiation of the lime treatment. The mixed liquor suspended solids dropped considerably from its normal level of 2200¹ ppm and there was considerable difficulty in reaching a stable level for about three weeks. At this time the suspended solids level returned to about 1600 ppm where it remained until the conclusion of the study. Various process modifications had to be made to achieve this equilibrium but the resulting sludge developed a very deep brown colour indicating a healthy and active medium. Overall, the lime addition increased organic capacity of the entire process; increased hydraulic capacity of the primary clarifiers and aeration process; increased overall efficiencies of BOD and SS removals; and improved oil, grease and scum removal in the primary clarifier.

2.5.2 Disposal of Water Treatment Plant Waste Alum Sludge

Many water utilities are looking at alternatives for disposal of waste alum sludge due to stricter permitting requirements that do not allow the dumping of these wastes to a

¹ Generally, at the suspended solids concentrations being discussed here, 1 ppm (part per million) is equivalent to 1 mg/L.

receiving water body. At the same time, many wastewater treatment utilities are looking at having to more strictly control effluent pollutant levels including new or stricter controls on nutrient levels being discharged to receiving water bodies. Often, these two utilities have found it to be of mutual benefit to study the option of disposing of waste alum sludges to the municipal sewer system. The alum sludge can be disposed of like conventional sewage sludges (solving the water utility's problem) but may also enhance treatment at the wastewater facility by aiding in the precipitation of phosphorus (thus helping to solve the wastewater utility's problem). Many of the papers written to date on disposal of water treatment waste alum sludges to sewage treatment plants deal with the problem generally. Rather than dealing specifically with nutrient removal (though phosphorus removal is one of the primary benefits), other benefits such as BOD and SS reduction are also discussed extensively.

Extensive work has been done by Hsu and Pipes (1972 and 1973)², on the effects aluminum hydroxide has on wastewater treatment processes. They studied the effects of aluminum hydroxide floc on several important wastewater treatment processes including aeration and secondary settling of activated sludge, anaerobic sludge digestion, and sludge dewatering before and after digestion (1973). The purpose of the study was to determine feasibility of disposal of water treatment plant sludge to a wastewater treatment plant. It was determined that the most important effect on secondary processes was the increase in sludge production. Other effects found were as follows:

- treatment efficiency, as measured by COD and phosphate removal, improved;
- compactability of bulking sludge was improved dramatically with the addition of aluminum hydroxide to the mixed liquor;

² The work most often cited is actually a conference presentation at the 27th Industrial Waste Conference at Purdue University in West Lafayette, Indiana (1972). The presentation was entitled, "The Effects of Aluminum Hydroxide on Primary Wastewater Treatment Processes." This work was continued with a further study of the effects of aluminum hydroxide on other wastewater treatment processes (Hsu & Pipes, 1973).

- no effect was found on nitrification;
- total gas production was decreased by addition of aluminum hydroxide during anaerobic sludge digestion; and
- sludge dewatering, either before or after digestion, was improved.

Salotto et al (1973) determined that the bulk of alum sludge from WTPs disposed of to domestic sewer systems settled out with the primary sludge in the WWTP. Carryover of some of the slower settling solids from the alum sludge occurred but these solids improved settling of the waste activated sludge and improved process efficiency. Reductions in COD or phosphates were not noted with sludge addition, it was thought that the water treatment plant sludge being added was too dilute to generate any appreciable effects. Hsu and Pipes (1972) determined that at lower doses, the aluminum hydroxide disposed of to primary clarifiers would actually contribute to an increase in suspended solids. As this dose increased the settling phenomenon changed from "flocculant settling" to "zone settling" hence the sludge settled as a mass and the suspended solids were actually reduced below levels typical of normal primary clarification (i.e. when no aluminum hydroxide was added). Of course, the amount of sludge that would have to be added to change the principal settling mechanism would be significant. Other parameters such as COD, volatile suspended solids, and phosphate decreased continuously with the addition of aluminum hydroxide. The aluminum content of the settled wastewater was 10 mg/L and this concentration did not cause any adverse effect on the biological processes that followed primary clarification.

Culp and Wilson (1979) found no adverse effects on overall WWTP performance with the addition of alum sludge. Primary settling efficiency increased slightly, COD removals were unaffected, and phosphorus removal increased marginally. O'Brien and Warriner (1972) concluded that water treatment plant sludges do not impair the performance of a pilot primary sewage treatment plant at dosages up to about 10 percent of hydraulic flow. They determined that the amount of sludge required to remove 75 to 98

percent of phosphorus from sewage was 7 to 9 times greater than the required dosage using alum (as aluminum). Reductions in COD were improved with sludge addition. A further finding was that the alum and alum sludge together enhanced the phosphate removal performance of each, with combined removals greater than the cumulative effects of each if used separately. Monteith and Baldwin (1974) found that alum dosages could be reduced by 50 percent with the addition of 15 mg/L of alum sludge and that a small quantity of alum can reduce alum sludge requirements for phosphate removal to a great extent.

Nelson et al (1978) found the following changes due to addition of alum sludge to an activated sludge wastewater treatment plant:

- efficiency of primary settling decreased about 10%;
- efficiencies of COD and BOD removals were not changed;
- phosphorus removal improved by 12%; and
- scum removal and sludge settling were improved in secondary clarification.

As in all previous studies mentioned, no adverse effects on overall wastewater treatment plant performance were observed.

2.5.3 Process Configurations for Chemical Phosphorus Removal

The general locations that phosphorus can be removed from the municipal wastewater treatment process are classified as: 1) pre-precipitation, 2) co-precipitation, and 3) post-precipitation (Metcalf and Eddy, 1991). There are other configurations such as primary or secondary precipitation (Melkersson, 1973) but these methods are much less commonly used and will not be discussed here. The following discussion generally relates to conventional activated sludge plants, i.e., those with aeration tanks. Most of the processes discussed are applicable to treatment plants with trickling filters though some configurations cannot be applied to the co-precipitation stage because of pH control or mixing limitations.

When determining the best process configuration for chemical P removal consideration must be given to alkalinity of the influent wastewater. Proper choice of a chemical addition point may remove the necessity of pH adjustment at some point later in the process. Alum addition tends to depress pH thus the greater the alkalinity (or buffering capacity) the less process upset will occur, especially during aeration. For low alkalinity wastewater, alum addition immediately prior to or in the aeration basin may cause the pH to decrease to the point that microbial life is adversely affected. Lime addition is pH dependent thus the greater the alkalinity of the wastewater, the greater the lime demand to raise the pH. For this reason, lime addition is suitable in primary and tertiary treatment processes only, where pH adjustments can be made if necessary.

2.5.3.1 Pre-precipitation

Removal of phosphorus from wastewater can be accomplished by chemical addition to the conventional primary treatment process and precipitation of phosphorus rich sludge in the primary sedimentation basins. This process is illustrated in Figure 2.6.

Advantages of this particular process design include flexibility in chemical feeding; adequate reaction times and mixing conditions; flocculation and removal of more suspended solids and suspended BOD in the primary settler; and reduced loading of suspended solids and BOD to secondary treatment processes (Black and Veatch, 1976). According to Melkersson (1973), the pre-precipitation process can usually be applied quickly and with low additional costs to an existing treatment plant having mechanical and biological treatment steps. Reduced loading to secondary treatment processes is especially significant to plants that may already be overloaded, i.e., process flows to secondary treatment can be increased because solids loading has been decreased. In a new plant, a smaller biological section and less air is required in comparison with a conventional activated sludge plant having the same amount of incoming raw sewage (Melkersson, 1973).

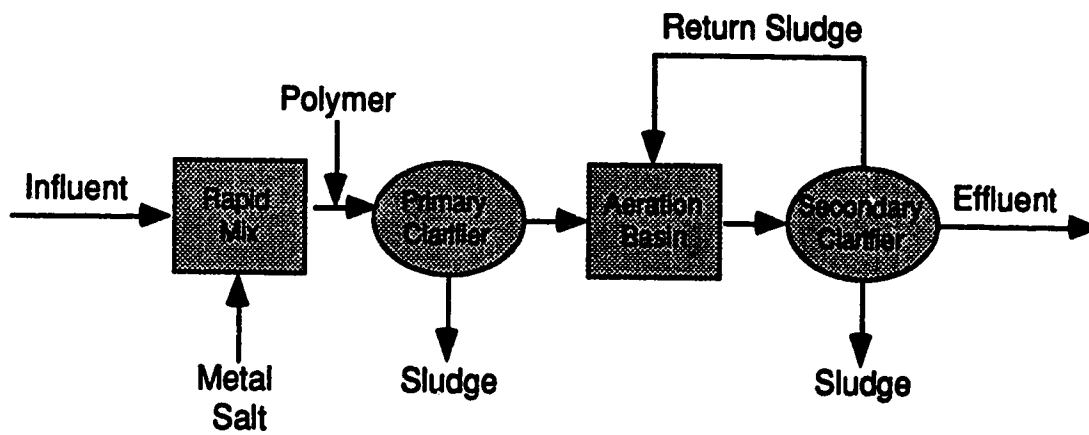


Figure 2.6 Pre-precipitation process (adapted from Melkersson, 1973)

Pre-precipitation protects the biological step from toxic material such as heavy metals and dispersed oils, which are removed in the primary sedimentation basins. Additionally, the pre-precipitation step can substantially improve treatment in plants connected to combined sewers following heavy rainfalls because it can tolerate considerable hydraulic overload. The chemical addition still removes organic and suspended matter and phosphorus from the wastewater before it has to overflow from primary treatment directly into the receiving water, i.e., bypassing the biological step (or secondary treatment) due to system overload (Melkersson, 1973).

The main disadvantage of addition of precipitants prior to primary sedimentation is that all the phosphate may not be in the ortho form thus reducing precipitation efficiency (see previous discussion). Higher phosphorus removals can be obtained with chemical addition at later points in the process (Black and Veatch, 1976). A second disadvantage is that existing treatment facilities that are making a chemical P removal addition may experience problems with too much P, BOD, and SS removal in the primary treatment process thus hindering secondary treatment. For instance, the MLSS or BOD/P ratio may be too low to provide adequate treatment because the aeration basin(s) had originally been designed for higher loadings. Also, the carbon-phosphorus relationship might be too unfavourable in the biological steps (Melkersson, 1973).

2.5.3.2 Co-precipitation

Co-precipitation is defined as the addition of chemicals to form precipitates that are removed along with waste biological sludge. Chemicals can be added to: 1) the effluent from primary sedimentation facilities, 2) the mixed liquor (in the activated-sludge process), or 3) the effluent from a biological treatment process before secondary sedimentation. (Metcalf and Eddy, 1991). The process is illustrated in Figure 2.7. As previously mentioned, the addition of lime in this step would cause process upset due to the effect of a pH change on microbial life in the aeration process, for this reason, lime addition in this

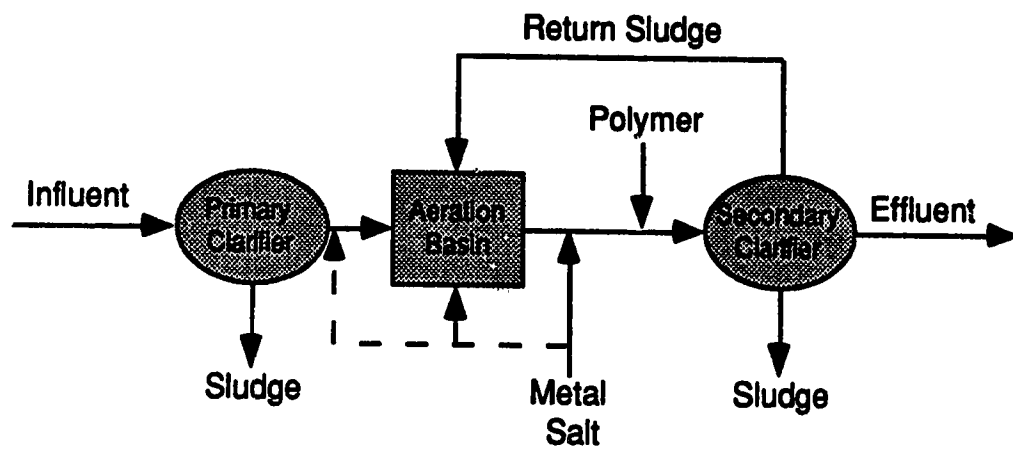


Figure 2.7 Co-precipitation process (adapted from Melkersson, 1973)

phase will not be discussed. Further, it should be remembered that alkalinity must be sufficient to buffer pH changes due to the addition of metal salts such as alum. The mechanism of phosphorus removal by alum addition in the biological process is one of precipitation, adsorption, exchange, and agglomeration as influenced by the pH and ionic composition of the wastewater (Black and Veatch, 1976).

At this point in the process most of the polyphosphates and organic phosphorus are in the orthophosphate form hence they can be more easily precipitated. Chemical addition ahead of or in the aeration tanks negates the requirement of rapid mixing or flocculation facilities hence the process can be easily retro-fitted to existing plants. Addition following aeration but before final sedimentation requires a turbulent area, such as a weir, for proper mixing and adequate time for reaction/flocculation. Most existing treatment facilities can meet this requirement but some preliminary work may have to be done to ensure facilities are adequate. It has been reported (Wahbeh and Hamann, 1971) that Al:P mole ratios of 1.5 to 2 have essentially completely removed soluble phosphorus in this stage. Apparently, the biological performance of the activated sludge process as measured by BOD removal is not affected adversely by additions of up to 335 mg/L of alum, dependent on alkalinity of course (Wahbeh and Hamann, 1971). Generally, the later the chemical addition in the secondary treatment process the better the removal because more time is allowed for all the phosphorus to convert to orthophosphate.

According to Wahbeh and Hamann (1971), the velocity gradient in aeration tanks is higher than required for chemical flocculation thus it is expected that some chemical floc as well as biological floc will disintegrate. This will also occur with solids recycled. This may account for some of the suspended solids in the effluent unless reflocculation occurs in the final clarifier. In new design situations, it may be advantageous to provide a brief period of gentle solids agitation prior to solids separation to promote reflocculation of the chemical-biological solids.

Unlike pre-precipitation, the co-precipitation process is subject to microbial kills from toxic industrial wastes such as heavy metals or dispersed oils. They are more sensitive to hydraulic overload and do not cope with storm water, for the case of combined sewers, in heavy rainfall as well as pre-precipitation. The suspended solids are considerably higher than for pre- and post-precipitation, due to increased biological solids, hence hydraulic overloading is more likely to cause suspended phosphorus to enter the receiving waters (Melkersson, 1973).

Sludges resulting from aluminum addition are amenable to anaerobic or aerobic digestion. In conjunction with laboratory scale aluminum addition to activated sludge units at the University of Missouri at Rolla, laboratory scale anaerobic digesters were studied to determine the fate of the aluminum and phosphorus. The digesters were fed 70 percent activated sludge and 30 percent primary sludge. Detention time in the digesters was 15 days. The phosphorus which had been precipitated with aluminum was concentrated in the digester sludge and was not released to the supernatant. Tests confirmed that the aluminum was retained in the digester sludge. Comparing the digesters which were fed aluminum sludge with a control digester, using the parameters of volatile acids and gas production, the digester performance was similar. Mulbarger indicates that it would be reasonably conservative to design solids handling equipment for the organic solids loading on the basis of conventionally used criteria, assuming that the additional chemical solids that must be handled will be compensated for by the increase in sludge dewaterability. (Wahbeh and Hamann, 1971).

2.5.3.3 Post-precipitation

Post-precipitation is defined as the addition of chemicals to effluent from the secondary sedimentation facilities and subsequent removal of the chemical precipitates. These precipitates are usually removed in separate sedimentation facilities or in effluent filters (Metcalf and Eddy, 1991). Additional treatment of secondary effluent is generally

referred to as tertiary treatment. Post-precipitation processes give the best quality of effluent, which should be particularly considered when high removal of phosphorus, highest hygienic performance, and lowest content of organic material are wanted (Melkersson, 1973). The process is illustrated in Figure 2.8.

Both lime and alum can be used for precipitation though there is usually a requirement for pH adjustment if lime is the chemical of choice. If available, excess CO₂ from the anaerobic digesters can be used to adjust the pH if required.

The post-precipitation sludge is low in organic matter. These "chemical" sludges are usually stabilized together with the excess biological sludge in the anaerobic digesters, at least for the larger plants. Phosphorus is usually not released by anaerobic digestion from sludges obtained with aluminum precipitation. Sometimes the sludges are stabilized by the addition of quick lime (Melkersson, 1973).

2.6 Phosphorus Sludge Characteristics

Sludge production in the chemical-biological process is significantly greater than in biological treatment alone. This is to be expected because of the sludge produced by mineral addition. The waste sludge resulting from the chemical-biological process has been estimated to be about double the weight of the sludge produced by the biological process alone (Wahbeh and Hamann, 1971).

Generally, it can be expected that the lime sludges will dewater much better than the alum sludges due to the alum sludges' gelatinous nature. Though lime sludges are higher in volume they generally do not require chemical conditioning by the likes of an anionic polymer as long as calcium carbonate is the prevalent precipitate (King et al, 1979).

When disposing of chemically precipitated sewage sludges it must be kept in mind that if heavy metals are prevalent in the raw sewage flow, then significant amounts will likely precipitate out of solution and be present in the sludge. Heavy metals tend to accumulate in soils when disposed of to land and this should be taken into consideration

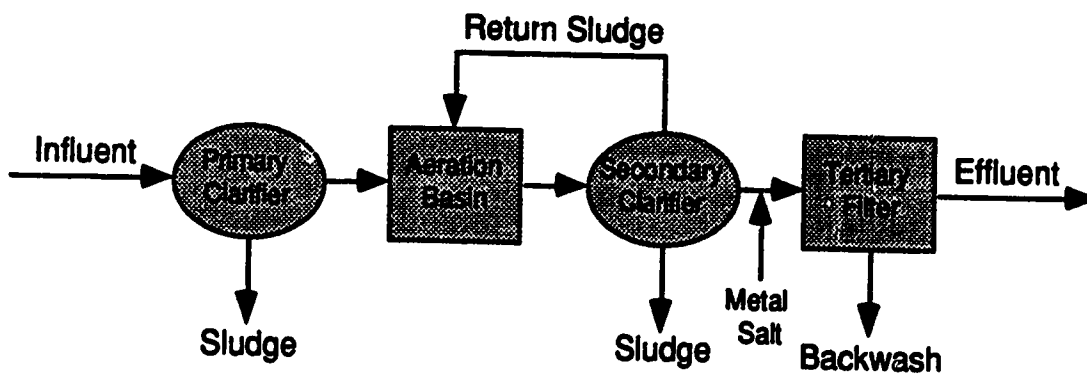


Figure 2.8 Post-precipitation process (adapted from Melkersson, 1973)

when making sludge disposal decisions. Generally, national and provincial guidelines stipulate that levels of cadmium, zinc, copper, lead, chromium and mercury must be limited due to toxicity concerns (Environment Canada, 1984). These guidelines usually stipulate maximum cumulative loadings of these elements to agricultural type lands hence limiting some sludge disposal options.

An item of further concern is disposal of aluminum rich sludges. There is some circumstantial evidence that an association between presence of aluminum compounds and development of neurological disorders and impaired bone mineralization exists in humans and other mammals³. A study by the Alberta Environmental Centre (1987) found waste alum sludges from the water treatment plants they tested to exhibit no toxic effects to rats or rainbow trout. These sludges were also found to be non-toxic using a microbial toxicity test system (Microtox). Aluminum was found to be effectively bound to sludges within the pH range 4.5 - 10.0, releasing less than 0.02 percent of its total aluminum content. The bioconcentration factor of aluminum in rainbow trout exposed to alum sludge ranged from 0.4 to 12.3. It was felt that despite these apparently favourable short term results more study should be given to long term exposure and the disposal of these sludges in areas of high exposure to humans or other mammals.

2.6.1 Alum Sewage Sludge

For the purposes of this discussion the sewage sludge produced with the addition of alum and with the addition of alum sludge will be discussed together. Where necessary, any differences in properties between the resultant sewage sludges will be pointed out.

Hsu and Pipes (1973) found that aluminum hydroxide improved flocculation of the sludge mass and improved dewatering properties. Another study determined that the addition of alum did not greatly change the handling and dewatering characteristics of waste

³ This statement by Geraldine et al (1984) is cited in an Alberta Environmental Centre study (1987) but no further information on the reference could be found in the body of the report.

sewage sludge except that: 1) the combined sludge was easier to mix, and 2) the centrifuge yield increased by about 25 percent (Culp and Wilson, 1979). Wilson et al (1975) found that high concentrations of alum or water works sludge tended to produce a sludge that was difficult to handle. Dosage of less than 100 mg/L of fresh alum or 40 mg/L of water works sludge were handled successfully. The ability to handle this sludge set the upper limit of phosphorus removals that could be obtained consistently by using this system. The addition of anionic polymer has been found to significantly improve the dewatering characteristics of alum sewage sludge hence reducing the sludge handling capacity required (King et al, 1979).

Kirk et al (1988) found that with the addition of alum before primary clarification the volume of unconsolidated raw sludge increased 71 percent over the untreated control sludge and that after consolidation the volume was 57 percent greater. With the addition of polymer the volume increases reduced to 46 and 15 percent, respectively⁴.

A study of phosphorus removal within existing wastewater treatment facilities by Boyko and Rupke (1976) determined the effects of chemical addition for phosphorus removal on primary treatment and secondary treatment plants. In the secondary treatment plants with alum addition they found:

- a 5 to 25 percent increase in solids on a dry weight basis (or 1.05 to 1.25 times original);
- a decrease in solids concentration in the raw sludge, dropping total solids content from the normal 4.0 - 5.5 percent to 3.5 - 5.0 percent; and that
- the combination of these two effects increased the overall wet sludge volume by approximately 35 percent (or 1.35 times original).

⁴ Results of this work should be treated with some circumspection due to difficulty in removing sludges from the consolidation tanks. It was thought that consolidation would have actually been greater.

In the primary treatment plants with alum addition they found:

- sludge production increased by 100 percent on a dry weight basis due to increased solids capture (or 2 times original);
- sludge solids concentration decreased by 20 percent; and that
- the net effect on sludge volume was a 150 percent increase (or 2.5 times original).

When using vacuum filters for the dewatering of raw undigested chemical sludges a significant increase in conditioning costs was experienced with alum addition (it is assumed that these conditioning costs were polymer addition). A decrease in cake solids content and filter yield was also noted.

The increase in wet sludge volume (in a secondary treatment plant) of 35 percent determined by Boyko and Rupke is consistent with other literature. Ericsson (1973) estimated a 30 percent increase in mixed primary and excess sludge with the addition of alum. Another study found that the addition of waste alum sludge to a full-scale secondary treatment plant increased the solids that went to sludge dewatering and disposal facilities by 30 percent (Nelson et al, 1978; Culp and Wilson, 1979).

Wilson et al (1975) found, as did Boyko and Rupke, that raw sludge resulting from chemical additions was slightly lower in solids content.

2.6.2 Lime Sewage Sludge

As with its water treatment plant counterpart, lime sewage sludge is generally found to dewater more satisfactorily than alum type sludges while not requiring polymer conditioning. Kirk et al (1988) found that with the addition of lime before primary clarification the volume of unconsolidated, treated sludge was 48% greater than the

untreated control, after consolidation the volume was 39% greater⁵. Though polymers aided in dewatering they were not deemed necessary.

A note of interest is that Schmid and McKinney (1969) determined that calcium phosphate precipitate forms in a matter of seconds and that the sludge produced is a gelatinous type precipitate that does not de-water well by itself but can be conditioned fairly well with anionic polymers. The addition of lime to domestic sewage usually forms an abundance of calcium carbonate⁶ as the lime softens the waste stream which likely inundates the calcium phosphate precipitate; this calcium carbonate sludge is easily dewatered though volumes are high. There was a time in the mid 1800's when several patents were issued for the *addition* of phosphates to raw wastewater prior to lime addition to increase BOD and SS removal efficiencies; this process required lower lime dosages because clarification occurred by the precipitation of phosphates rather than calcium carbonate. Eventually, in spite of increased removal efficiencies and lower lime requirement, the process was abandoned due to the cost of the additional phosphates.

A study of phosphorus removal within existing wastewater treatment facilities by Boyko and Rupke (1976) determined the effects of chemical addition for phosphorus removal on primary treatment and secondary treatment plants. In the secondary treatment plants with lime addition they found:

- sludge production increased 150 percent on a dry weight basis (or 2.5 times original);
- solids content of the sludge increased from 4.5 to 9 percent; and that
- the net effect was a 25 percent increase in sludge volume to be handled (or 1.25 times original).

⁵ As previously mentioned, results of this work should be treated with some circumspection due to difficulty in removing sludges from the consolidation tanks. It was thought that consolidation would have actually been greater.

⁶ There was evidence in the Schmid and McKinney study that suggested even low levels of soluble phosphate seriously inhibit the precipitation of calcium carbonate under laboratory control conditions.

A reduction in conditioning costs and an increase in filter yield and sludge cake solids was noted with lime addition to the secondary plant (vacuum filters were used for the dewatering of raw undigested chemical sludges). In the primary plants with lime addition they found:

- sludge production increased 200 percent on a dry weight basis (or 3 times original);
- solids concentration increased from 7 percent to 15 percent; and that
- the net effect was a 50 percent increase in sludge volume (or 1.5 times original).

These findings were more or less consistent with Schmid and McKinney (1969) who found that sludge produced in the primary unit, by weight, can be expected to be twice that obtained by conventional settling (as compared with 2.5 times for a secondary treatment plant as determined by Boyko and Rupke).

2.6.3 Effect on Existing Clarification Facilities

Due to the positive correlation found between effluent phosphorus levels and suspended solids (Schmidtke, 1980; Monteith and Baldwin, 1974), the necessity of determining the effects of chemical addition to biological clarifiers has become of concern. In the past 20 to 30 years there have been relatively few articles published on sedimentation in dilute suspensions (Heinke et al, 1986), and articles dealing specifically with settling characteristics of chemically treated wastewater, especially raw wastewater, appear to be even less prevalent.

Heinke et al (1986) concludes that the addition of chemicals, such as alum or ferric chloride, increases the settling rate of physical-chemical flocs significantly and that addition of polymer further increases settling rates thereby improving effluent quality. With the addition of chemicals to the wastewater, for the likes of phosphorus removal, significantly smaller settling tanks are required to achieve the same removals (P, BOD, SS), or existing tank capacities can be increased. As a result of studies done on primary WWTPs in Sarnia

and Windsor, Ontario, existing settling tank capacities were nearly doubled with the addition of chemicals.

Boyko and Rupke (1976) found that for metal salt addition, hydraulic loads above $36\text{-}39\text{ m}^3/\text{m}^2/\text{day}$ (750-800 igpd/sq. ft.) in the final clarifiers of the plants studied caused a steady deterioration in effluent quality. Constantine et al (1974) recommend not exceeding $59\text{ m}^3/\text{m}^2/\text{day}$ (1200 igpd/sq. ft.) with ferric chloride addition but are not clear on whether this is for all clarifiers or for final clarifiers only. A further finding of this study was that this loading should be halved for lime because of excessive floc carryover. Lime generally produces a denser, faster settling floc than metal salts so they found this result to be somewhat surprising.

As mentioned in a previous section, Nelson et al (1978) found the efficiency of primary settling decreased about 10% with the addition of waste alum sludge. O'Brien and Warriner (1972) concluded that suspended solids performance of primary clarifiers may be enhanced by sludge addition providing solids overload does not occur. A study by Hsu and Pipes (1973) found that the flocculation effect of aluminum hydroxide increased the settling velocity of bulking sludge in the secondary clarifiers when added to the mixed liquor from the aeration tanks.

A study by Black and Mills (1970) found that the addition of lime greatly improved the performance of a primary clarifier that was giving poor treatment. The BOD and SS removals were only 21 and 37% respectively, these improved to 72 and 78% respectively with the addition of lime. The total phosphorus reduction was increased to 82%. No mention was made of having to reduce clarifier capacity to obtain these removal levels.

2.6.4 Effect on Anaerobic Digestion

There have been a number of studies done on the digestability of chemically precipitated alum sludges. Boyko and Rupke (1976) state that problems associated with digestion of sludges resulting from metallic salt precipitation relate more to capacity rather

than operation. Inadequate heat exchanger capacity, caused by increased digester hydraulic loading and high gas production rates, resulted in inadequate gas-liquid separation and foaming in the primary digester of the full-scale plant they were studying. These problems did not arise as a direct result of chemical addition but rather were compounded by the increased volatile solids load on the digestion system. No inhibitive effects of the accumulated metal salts were observed, nor was a significant portion of the phosphorus resolubilized during the digestion process. The difficulty encountered with many existing plants is that the sludge handling facilities such as clarifier (settling tank) underflow pumps and anaerobic digesters may not be able to handle the increase in sludge volume characteristic of chemical addition to wastewater (Wiechers, 1986).

Hsu and Pipes (1973) determined concentrations of aluminum hydroxide greater than 100 mg/L (as aluminum) would affect anaerobic digestion. They hypothesized that the effect of retardation was on the acid-forming bacteria and not the methane-forming bacteria. It should be noted that this dosage is rather high and would generally not be typical of the aluminum concentration in waste alum sludge being used to precipitate phosphorus, unless it was added to the wastewater stream as a slug dose.

A study on the addition of waste alum sludge to the municipal wastewater stream (Salotto et al, 1973) found that the inert nature of the chemical solids dramatically decreased the percentage of volatile solids in the primary sludge. In this case, the sewage was quite weak but the inference was that a slug dosage of alum sludge may have an adverse effect on the sewage sludge digestability. Hsu and Pipes (1972) noted the same phenomenon and concluded that the digestability, in terms of gas production per unit weight of solids, of the sludge would decrease with increasing alum sludge addition. Nelson et al (1978; see also Culp and Wilson, 1979) noted that 23% more solids, on a dry basis, went to the digesters and that the total volatile solids load increased. It was found that digester gas production increased beyond that attributable to this greater volatile solids loading; it was presumed that this was due to improved mixing of digester contents.

Wilson et al (1975) found that digested solids concentrations resulting from the addition of alum and waste alum sludge to a Tampa, Florida plant were much lower than normal, being only 4.9 percent instead of the normal 9.2 percent when discharged to the drying beds.

The effect of lime addition on anaerobic digestion was addressed by Boyko and Rupke (1976). A digester treating sludge encountered some operational problems due to erratic lime dosing producing massive slugs of high pH sludge that raised the digester pH dramatically. Eventually, gas production ceased and the digester had to be emptied manually. Subsequent studies determined that extended retention time in the primary clarifier allowed the sludge to partially neutralize itself allowing for proper digester operation. The only significant change was the high solids content of the digested sludge.

2.7 Literature Review Summary

The previous discussion of the literature raised some points that were of particular relevance to this jar test study. These points are listed below:

- 1) It was not known if the phosphate in the Gold Bar raw influent was sufficiently hydrolyzed (to orthophosphate) for easy precipitation. This was one of the reasons that precipitation was carried out with wastewater from two different locations, i.e., before and after the primary clarifiers. Essentially, precipitating raw influent and primary effluent simulated the pre-precipitation and co-precipitation processes, respectively.
- 2) The effect of pH on chemical precipitation was duly noted for both alum and lime. Particular attention was paid to the pH effects on alum precipitation of phosphorus because it was a known secondary parameter that may have had a significant effect on the precipitation mechanism.

- 3) Though precipitation kinetics play a key role in phosphorus removal, no attempt was made to quantify these kinetics other than to set rapid mix and flocculation times and energies.
- 4) There was little specific information available on phosphorus precipitation mechanisms for either of the water treatment plant sludges. An attempt was made to confirm that it was not just a physical removal of suspended phosphorus being noted in the jar tests.
- 5) Polymers were included as a jar test parameter because of their ability to condition sludges, particularly alum sludges, and their solids removal capability.
- 6) Parameters such as BOD, suspended solids, turbidity, and coliforms were measured in some jar tests to confirm the removals noted in the literature.
- 7) Preliminary characterization of some of the chemically precipitated sewage sludges was carried out to confirm changes in volume and solids.
- 8) It would likely not be feasible to try and determine the effect of chemical precipitation on existing clarification facilities. Jar test observations would not likely account for enough of the process variables, i.e., upflow velocity.
- 9) No attempt would be made to characterize the chemical sludges effect on anaerobic digesters.

3.0 DESIGN OF JAR TEST STUDY

3.1 Factorial Design

Biological and chemical process yields are determined by the influence of process variables or factors. The factorial design procedure is one of the best and most efficient methods of estimating the effects of any controllable factor on a process. In addition,

modification of any individual factor due to variation in other factors may be measured, i.e., the interaction effect of two or more factors can be estimated.

A full factorial design experiment designed to test n factors will test all factor combinations at each of m levels. This is termed an m^n factorial and will require m^n independent random trials or runs. The average effect on the process of varying any single factor, over the range studied, can be determined from these trials. A change in effect of a particular variable brought about by a change in a second variable can also be measured. This is termed a two (or 1×2) level interaction. Consideration of interaction levels is important. It is often found that the simultaneous modification of two factors, the independent modifications of which have been found advantageous to the process, does not always cause an additive improvement and may in fact be of no advantage at all. The effect on the two level interaction of variation in a third variable may also be calculated. This is a three or $1 \times 2 \times 3$ level interaction. In general, $1 \times 2 \times \dots \times n$ interaction effects can be measured but it is usually found that interactions greater than the two level are not statistically significant, i.e., physically meaningful to the process.

A rapid increase in the necessary number of trials as the number of factors increases is one consideration that limits the application of full factorial design experiments. For example, consider three factors at two levels, this would require 2^3 or 8 trials. Adding three more factors brings the total number of trials to 2^6 or 64. Therefore, it is important to establish as much information as possible about the processes involved so that the number of factors and levels studied can be minimized with confidence. The use of fractional factorial design is one method of establishing this information with a minimum of resources, this is discussed in further detail in Box, Hunter, and Hunter (1978).

In order to determine the experimental error in this study a series of three center point replicate jars were run for each factorial design jar test. Each parameter for the replicates was set at the median of the upper and lower level being tested in the factorial portion of the test. A comparison of variance was then made by comparing the center point

replicate mean square and the mean square for each parameter included in the factorial design to determine if the parameter was significant at the levels being tested. Assuming that these variances were computed from independent random samples drawn from normally distributed populations the random variable

$$F_{(v_1, v_2)} = \frac{s_1^2/v_1}{s_2^2/v_2} \quad (3.1)$$

where: s_1^2 = sample 1 variance (factorial parameter)
 s_2^2 = sample 2 variance (center point replicates)
 s_1^2/v_1 = sample 1 mean square
 s_2^2/v_2 = sample 2 mean square

follows the F distribution, with $v_1 = (n_1 - 1)$ and $v_2 = (n_2 - 1)$ degrees of freedom associated with the numerator and denominator, respectively. The null hypothesis was that the two population variances were the same. If the calculated F - ratio was greater than the tabulated F - ratio for a given confidence interval (usually 95%) then the null hypothesis was found to be false and the parameter was considered to be significant (Kennedy and Neville, 1986).

The choice of experimental factors and the coagulant combinations will be discussed in a later section.

3.2 Choice of Factors in the Jar Test Study

Many factors, both known and unknown may affect the efficiency of chemical precipitation of phosphorus from wastewater. These factors and the heterogeneous nature of wastewater are what make jar testing and experimental design necessary. As previously mentioned, it is necessary to establish as much information about the process as possible in order to limit the number of factors tested hence the number of trials required, yet to generate representative data that allows valid conclusions and recommendations to be made. For the case of chemical precipitation of phosphorus from wastewater, enough literature

exists to make this exercise fairly simple, at least in relation to some of the newer and less studied processes.

Among the factors affecting the coagulation of phosphorus from wastewater are the following:

- chemical addition point,
- chemical,
- chemical dose,
- rapid mix time and energy,
- flocculation mix time and energy,
- settling time,
- pH,
- phosphate form, and
- addition of polyelectrolyte.

Two 2^3 factorial design screening tests were run in order to determine optimum rapid mix and flocculation times and energies. Both tests used alum as a coagulant, the first test was run using primary effluent, the second using raw influent. This also provided some preliminary information as to coagulant dose, addition point, pH, and settling time. The mixing times and energies were optimized to get best experimental results. Also, there would be little control over these parameters in a plant retrofit situation that would likely be dependent on channel mixing and clarification for rapid mix and flocculation, respectively. The change in wastewater (primary and raw) between the two tests provided some information as to removal efficiency with chemical addition at different points in the plant. These and other runs eventually led to the use of only raw influent for the experiments. The pH was closely monitored and its effect noted. Enough time was allowed for essentially all gravity settling to occur. This was another parameter that there would be difficulty in controlling in a retrofit situation.

Factorial design is usually implemented to maximize results for a given set of experimental parameters thus saving limited resources and labour. The screening tests provided valuable information that allowed the remainder of the jar testing for this phosphorus removal study to investigate two controllable factors at two levels thus yielding a 2² design. The two factors were:

- coagulant dose, and
- polyelectrolyte addition.

Of all the known factors, these were the easiest to control in an existing plant such as Gold Bar that would have to be retrofitted. This is also the case for many other existing plants that are looking to begin phosphorus removal from their wastewater stream; factors such as rapid mixing, flocculation and settling are usually constrained or set by existing process parameters unless new facilities are constructed (which is usually not economically feasible).

As there were a number of chemical (or coagulant) combinations to be tested (> 2 levels) this factor could not be included directly into the two level factorial design so a separate factorial experiment was performed for each chemical combination. Initially, six chemical combinations were tried: 1) alum only, 2) lime only, 3) alum WTP sludge only, 4) lime WTP sludge only, 5) alum + alum sludge, and 6) lime + lime sludge. Each of these chemical combinations was to be added to the raw influent (RI) and primary effluent (PE) (for a total of 12 jar tests) of the plant to simulate different chemical addition points to the process. It was soon realized that other than a difference in initial phosphorus levels, the two wastewaters essentially demonstrated the same phosphorus removal characteristics for a given molar ratio of coagulant to total phosphorus and all remaining jar tests were carried out on the raw influent only. This aspect will be covered more specifically in a later section.

3.3 Setting Variable Parameters

As explained previously, it is not practical or economically feasible to test all the parameters affecting phosphorus removal from domestic wastewater because of the large number of experimental runs required and limited control over these parameters in existing plants. However, it is necessary to set reasonable levels for most parameters in order that the jar tests yield results that can be easily interpreted and that they are somewhat representative of conditions that may be found in the plant process stream. It was necessary to set these parameters at fixed levels in order that their fluctuation didn't interfere with results for the parameters of interest. For the purposes of this study, the variable parameters were generally set at optimal levels with the understanding that these conditions may or may not exist in the plant.

It was decided to run two screening jar tests in order to determine the effect of varying the mixing and flocculation Gt's along with coagulant dose (in this case, alum). A 2³ factorial jar test (Screening Test #1) was run with mixing Gt, flocculation Gt, and alum dose as the independent parameters. Results of this screening test are summarized in Tables 1 through 3 of Appendix I. Alum dose was included in both screening tests in order to get a feel for dosing levels to be used in the formal jar testing to follow. The measured dependent parameters for the screening tests were turbidity and total phosphorus. It was determined from Screening Test #1 that rapid mixing Gt had little effect on the degree of phosphorus removal within the levels specified. A rapid mixing Gt of 3300 sec.⁻¹ (30 seconds @ 100 rpm) was set for the remainder of the jar tests. This time was later increased to 45 seconds to facilitate addition and proper mixing of the polymer.

The second screening jar test was used to distinguish whether the flocculation Gt effect noted in the first screening test was due to contact time or mixing energy. Results of this test are summarized in Tables 4 through 6 of Appendix I. The three independent parameters were flocculation rpm, flocculation Gt, and alum dose. Flocculation time

should have actually been the parameter tested rather than flocculation Gt but flocculation rpm was found to have little effect within the levels tested which meant that flocculation time was likely the critical parameter⁷. Thus, a two-dimensional plot of alum dose vs. flocculation time, determined by dividing flocculation Gt by G for the given rpm, yielded a response surface for which the optimal flocculation time could be determined. Any time over 15 minutes was deemed to produce optimal phosphorus removal. Flocculation time for the remaining jar tests was set at 20 minutes, at 30 rpm this yielded a flocculation Gt of 28800 sec⁻¹.

It was decided that the only other factor (or parameter) to be set would be settling time. From observations made during the screening tests it was decided that 30 minutes was more than an adequate amount of time for the coagulated solids to precipitate out of the wastewater. The initial pH of the wastewater was not standardized for any of the jar tests though in the later stages of the jar testing it did appear to be a fairly relevant factor, especially when attempting to remove phosphorus using alum. This observation will be discussed in a later section.

3.4 Chemical Dosing

In order to aid the determination of proper chemical (or coagulant) dosing preliminary experimental work mainly involved characterizing the wastewater at various points in the plant to establish benchmark phosphorus levels. Other wastewater parameters such as suspended solids, nitrogen forms, biochemical oxygen demand, and fecal coliforms were also determined. This preliminary work also aided in the familiarization with experimental and analytical techniques.

⁷ Flocculation Gt is the product of time and mixing energy (or G for a specific type of mixing device at a given rpm). As flocculation rpm yielded little effect as an independent parameter it was assumed that the Gt effect noted could be totally attributed to the difference in mixing time.

As mentioned previously, the screening jar tests were used to help establish suitable alum dosing levels for the jar tests to follow. The literature indicated that a 1:1 to 2:1 molar ratio of aluminum to phosphorus would be required to reduce the effluent orthophosphate (PO_4^{3-}) to one mg/L or less (as phosphorus) (Recht and Ghassemi, 1970). The screening tests confirmed this and the remainder of the jar tests were used to better define the relationship between alum dose and the degree of phosphorus removal.

The lime dosing was more difficult to establish as it was necessary to soften the wastewater before significant levels of phosphorus could be removed. The first approach was to establish an approximation of total hardness and alkalinity of the wastewater and to estimate the lime requirement for complete lime softening. To this was added an additional 1.25 milliequivalents of lime for pH adjustment as well as the stoichiometric requirement for precipitation of the orthophosphate as $\text{Ca}_3(\text{PO}_4)_2$. The upper and lower lime dosing levels of the factorial design then bracketed this dose of lime. A second method used to establish lime dosing was a phosphorus removal graph published by Parsons (1965). Knowing only the initial and target phosphorus levels the figure yielded an approximate lime dosage. The first lime requirement method (softening + phosphorus) was found to be the most effective.

3.5 Polymer Dosing

Polymers can significantly enhance solids removal by increasing the size of very small particles thus increasing settling velocity. The question to be answered in this study was would the projected increase in solids removal significantly reduce the effluent phosphorus levels?

A review of the literature determined that an anionic polymer would likely yield the best solids removal in chemically dosed wastewater. The polymer of choice, due to its availability from the Rosedale Water Treatment Plant, was Percol LT27A manufactured by Allied Colloids. It is a high molecular weight, anionic polyelectrolyte supplied as a free-

flowing granular powder that is completely soluble in water, thus high viscosity stock solutions could be made from it.

Inexperience with polymers led to initial dosing being too high and incorrect addition to the jars. A discussion with a technical representative from Allied Colloids established suitable dosing levels and the proper method of polymer addition.

3.6 Effect on Precipitated Solids (or Sludge)

The secondary objective of the study was to establish whether the increase in precipitated solids initiated by the chemical phosphorus removal process warranted downrating of existing biological clarifiers. A series of jar tests was carried out with alum, alum sludge, and polymer in order to characterize the solids produced with and without chemical precipitation. This testing was very preliminary but it helped to give a feel for the characteristic changes in the sludge once chemical precipitation was initiated.

3.7 Equipment and Materials

All of the jar testing was done in a mobile lab established at the Gold Bar plant by the Environmental Engineering group at the University of Alberta (Figure 3.1). The dimensions of the lab are approximately 12 m long by 4 m wide. There is a small office area that doubles as an analytical area and a large open room with benches suitable for the establishment of pilot plant scale projects.

The apparatus used for jar testing consisted of two 6-place jar stirrers, 12 clear plexi-glass jars with siphoning spigots and clamps, and 2 fluorescent lighting stands (Figure 3.2). Analytical equipment included a spectrophotometer, turbidimeter, digital pH meter, drying oven, hot plates, vacuum filtration apparatus and pump, electronic balance, and a dessicator.

A cargo van was rented from the University to transport samples and equipment between the University and the Gold Bar plant.

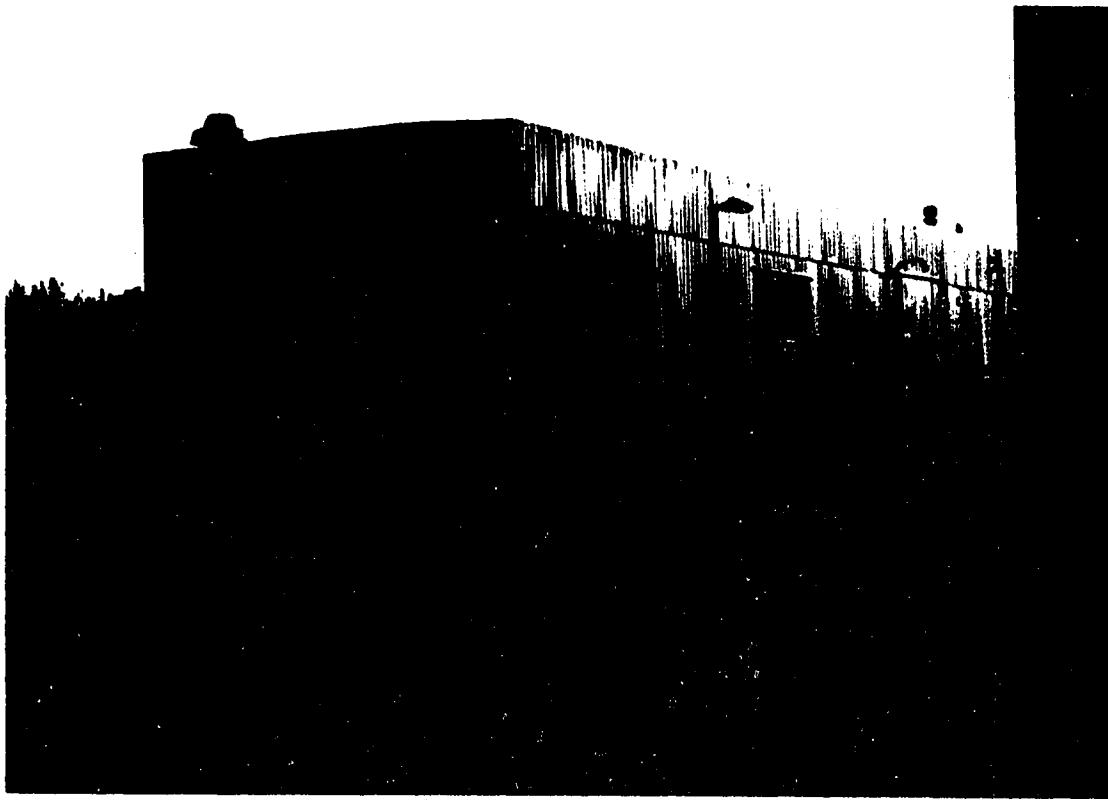


Figure 3.1 Mobile Laboratory at the Gold Bar Wastewater Treatment Plant.

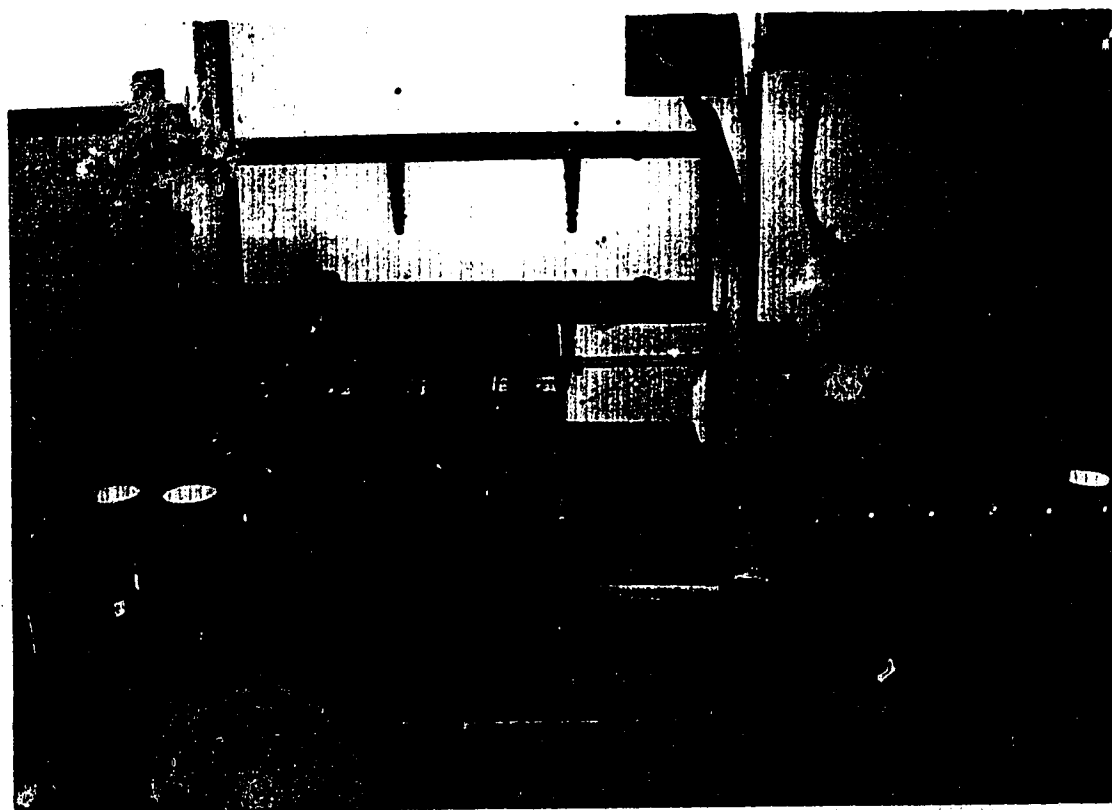


Figure 3.2 Jar Testing Apparatus (in use) and Digital pH Meter.

The alum, alum sludge, and lime sludge were obtained from the Rosedale Water Treatment Plant. Unslaked lime was also provided by Rosedale but it was found that hydrated lime was easier to work with at the jar test scale because it dissolved in the stock lime solution better.

4.0 METHODS AND PROCEDURES

4.1 Biochemical Oxygen Demand (BOD)

Unfiltered and some filtered BOD₅ determinations were made for a number of jar tests in order to determine the decrease in oxygen demand brought about by chemical precipitation. The 5-day BOD test and the oxygen determination (Winkler titration) were done according to Standard Methods (5210 Biochemical Oxygen Demand and 4500-O Dissolved Oxygen respectively - Standard Methods, 1989). Nitrification was inhibited in order to determine carbonaceous substrate removal only. Determinations were carried out in the Newton Research Building at the University, samples were transported and tested soon after jar testing.

4.2 Fecal Coliforms

Fecal coliforms were determined by the membrane filtration technique (9222 Membrane Filter Technique - Standard Methods, 1989). Periodic counts were taken before and after precipitation of phosphorus in order to determine bacterial removal by coagulation. All determinations were done in the membrane filtration lab of the Newton Research Building.

4.3 Nitrogen Forms

Total kjeldahl nitrogen, ammonia nitrogen, nitrites, and nitrates were determined by the City of Edmonton Gold Bar lab. Total kjeldahl and ammonia were analyzed using an Autoanalyzer II, nitrites and nitrates were analyzed using a TRAACS 800 Autoanalyser.

4.4 pH

The pH was monitored before and after jar testing to determine the effect of reaction and precipitation. A Fisher Accumet digital pH meter, Model 805 MP was used for all monitoring.

4.5 Suspended Solids (SS)

Suspended solids determinations were carried out before and after jar testing. All determinations were carried out in the U of A laboratory trailer located at Gold Bar. The Standard Methods solids determination procedure was used (2540 Solids - Standard Methods, 1989).

4.6 Total Phosphorus (TP)

A total phosphorus determination was carried out on each sample before and after jar testing. All testing was carried out in the U of A laboratory trailer located at Gold Bar. The persulphate digestion method and ascorbic acid colourimetric method were used for digestion and analysis, respectively (4500P - Standard Methods, 1989). Some of the initial analysis was done using the stannous chloride colourimetric method. The Bausch and Lomb Spectronic 20 spectrophotometer was used for colourimetric determination.

4.7 Turbidity

Turbidity determinations were carried out at the Gold Bar trailer lab before and after all jar testing. A Hach Model 2100A turbidimeter was used for all testing.

5.0 DISCUSSION OF OBSERVATIONS AND RESULTS

5.1 Jar Testing Experimental Approach

Initially, it was decided to test each one of the coagulants (alum, lime, alum sludge, and lime sludge) for phosphorus removal in both primary effluent and raw influent. This would have made for 8 preliminary jar tests from which further testing efforts could be planned. After jar testing the alum and lime on each of the two wastewaters it was realized that the results produced for each particular coagulant were very similar for both the primary and the raw. It was decided in the interests of time to forego further testing of the primary effluent and concentrate on testing of the raw influent as the most likely chemical addition point at the Gold Bar plant would be before the primary clarifiers.

After jar testing the pure chemicals in the first four jar tests, jar tests 5 and 6 dealt with the alum and lime sludges respectively. The alum sludge originally sampled from the Rosedale plant was found to have too low an aluminum concentration to make it viable for addition to the jars as a coagulant. Low turbidity in the North Saskatchewan river during the winter yielded low concentration alum sludges which made it necessary to concentrate them before using them as a coagulant. The assay of the concentrated alum sludge yielded a much higher aluminum concentration hence the sludge could be used in the jar testing. The aluminum concentration in the sludge was expressed as alum with 14 waters of hydration ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) for easy comparison with the pure alum dosing.

The lime sludge obtained from the Rosedale plant was already concentrated in a centrifuge. Lab analysis determined total calcium, which was the controlling parameter for

dosing the wastewater. The calcium concentration of the sludge was expressed as hydrated lime ($\text{Ca}(\text{OH})_2$) to make it compatible with the pure lime dosing.

The alum sludge yielded significant phosphorus removal results while the lime sludge results were less favourable. The decision was made to repeat the raw influent pure chemical jar tests on the alum (Jar test 2) and on the lime (Jar test 3) substituting 50 percent of the pure chemical with 50 percent sludge expressed as the respective pure chemical (as indicated previously). It was hoped that the sludges would be viable pure chemical substitutes. Jar test 7 was run using the alum and alum sludge, Jar test 8 was run using the lime and lime sludge. An evaluation of these two jar tests determined that the alum and alum sludge combination warranted more testing but that the lime and lime sludge combination did not appear to be feasible. The pure lime jar tests had not yielded adequate phosphorus removal capabilities, the phosphorus removal using lime sludge was next to nil⁸, and the combination of the two appeared to yield no net benefit. Consequently, it was decided to eliminate further testing of lime or lime sludge and to concentrate efforts on the alum and alum sludge.

Jar test 9 was used to determine the actual contribution that the alum sludge made to phosphorus removal in Jar test 7. Jar test 7 was essentially repeated but with only the alum added, it was hoped that the alum sludge contribution could be determined by taking the difference between phosphorus levels in the corresponding jars between the two jar tests. The difficulty encountered was that the raw wastewater differed in nature between the two jar tests therefore one had to be careful making inferences from the data gathered. Though the two tests yielded good results the effects of varying pH and initial phosphorus levels had to be taken into account when drawing conclusions. Inclusion of alum versus alum

⁸ As will be discussed in a later section, there was a net phosphorus removal using lime sludge but this was attributed to settlement of suspended solids laced with phosphorus. The phosphorus levels achieved were similar to those achieved during primary clarification.

sludge as another factorial parameter may have been a better way to determine their respective effects.

Now that the significance of the alum, alum sludge, and polymer doses was established, it was decided that the remainder of the jar tests would be used to gather more information on dosing levels, nature of the sludge produced, the response surface model for dosing with alum and alum sludge, and any other data that might be relevant. The remainder of the jar tests were not factorial design experiments but rather experiments focusing on specific areas to be studied.

Jar test 10 was used to better characterize the nature of the phosphorus removal mechanism by precipitating filtered and unfiltered samples to determine the degree to which dissolved versus suspended phosphorus was being removed from the wastewater. This was done for alum, alum sludge, and a 1:1 combination of the two. Raw influent samples were filtered through Whatman 934 AH filters (the standard filter used for suspended solids determinations). The doses used on the unfiltered samples were replicates of doses used in previous jar tests in order to provide a check on the reproducibility of phosphorus removal results. It was arbitrarily decided to halve the chemical doses for the filtered samples; it was later realized that the same dosing levels should have been used for both the filtered and unfiltered (this will be discussed in a later section). This necessitated the filtered samples being re-run in Jar test 11 at the same dose as the unfiltered samples had been run in Jar test 10. The remainder of the runs in Jar test 11 were used to test phosphorus removal on filtered samples at other dosing levels so a quasi dose - response curve might be established. Jar test 10 provided the first clear indication that pH was a relevant parameter and that its control may have been warranted for the duration of the testing. This will also be discussed in a later section.

Jar test 12 was used to better define a response surface for alum and alum sludge dosing of unfiltered samples. Alum to sludge ratios other than 1:1 were tried to aid in the defining of this surface.

As noted previously, it was felt that pH was playing a major role in the degree of phosphorus removal for a given set of conditions; in order to test this hypothesis Jar test 13 was run with a standard alum dose but varying the initial pH by 0.2 for each jar. Unfortunately, though the initial pH's were different, the final pH's of each of the jars ended up about the same hence the phosphorus removal was more or less the same. Despite this problem there was enough data from this and previous jar tests to clearly indicate that pH was a major factor in the degree of phosphorus removal for a given alum and/or alum sludge dose.

A number of other jars were run in Jar test 13 with standard doses of alum, alum sludge, and polymer at the same initial pH so that the precipitated sludge could be characterized. The volume of sludge produced in a 2 litre jar was recorded and the phosphorus levels and suspended solids analyzed.

5.2 Effects of Various Coagulants on Phosphorus Removal

All jar test results are tabulated in Appendix I. Reference to these results can be made by consulting Table 5.1 which summarizes the relevant points for each jar test. All coagulants tried exhibited some degree of phosphorus removal. Alum was found to be the most efficient followed by lime and alum sludge which demonstrated similar phosphorus removal capabilities. The lime sludge did demonstrate some phosphorus removal ability but most of this was attributed to removal of phosphorus laden solids.

5.2.1 Alum

Pure alum was used as the coagulant for some or all of the runs in Jar tests 1, 2, 9, 10, 11, 12, and 13 as well as in the two initial screening tests used to set variable parameters. Phosphorus levels as low as 0.22 mg/L were achieved in Jar test 2. The target level was 1 mg/L so dosing was cut back for the remainder of the jar tests in order that the optimum dose for this level could be approximated.

Table 5.1 Jar Test Summary

Jar Test	Wastewater	Coagulant(s)	Factorial Design	Appendix I Table(s)	Remarks
S.T. 1	primary	alum	yes	1 - 3	
S.T. 2	raw	alum	yes	4 - 6	
1	primary	alum	yes	7 - 9	
2	raw	alum	yes	10 - 12	
3	raw	lime	yes	13 - 15	
4	primary	lime	yes	16 - 18	
5	raw	alum sldg	yes	19 - 21	
6	raw	lime sldg	yes	22 - 24	
7	raw	alum/alum sldg	yes	25 - 27	
8	raw	lime/lime sldg	yes	28 - 30	
9	raw	alum	yes	31 - 33	
10	raw	alum/alum sldg	no	34	filtered and unfiltered
11	raw	alum/alum sldg	no	35	filtered and unfiltered
12	raw	alum/alum sldg	no	36	response surface
13	raw	alum/alum sldg	no	37 - 38	pH effect and sldg prop

The alum demonstrated superior phosphorus removal capabilities to all other coagulants tested in this study and was the only chemical tested that could by itself achieve the target phosphate - phosphorus level. In combination with alum sludge the target removal level could also be achieved. All factorial jar tests using alum yielded significant phosphorus removal effects at the 95 percent confidence level.

The alum was provided by the Rosedale plant in a 48.5% solution (as $Al_2(SO_4)_3 \cdot 14H_2O$) which was diluted down to a suitable stock solution for addition to the jars used. All alum concentrations stated are as aluminum sulphate with 14 waters of hydration as indicated above.

5.2.2 Alum Sludge

Testing of alum sludge in Jar test 5 produced significant results though the lowest phosphorus level achieved was 2.64 mg/L ($PO_4^{3-} - P$), well above the target of 1 mg/L. It was felt that doses higher than that used in this jar test were impractical and that other

detrimental effects such as increases in suspended solids concentrations would undermine the benefits of decreased phosphorus levels. All concentrations of alum sludge are actually aluminum stated as aluminum sulphate with 14 waters of hydration ($\text{Al}^{3+} - \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$).

Practicality was a consideration because, as previously mentioned, it was necessary to concentrate the alum sludge to reduce dosing volumes to the jars to a practical level⁹. The initial alum sludge sample aluminum concentration was so low that it would have taken a 1.2 litre addition of sludge to a 2 litre jar of wastewater to achieve the dosing level desired. Hence, the alum sludge had to be concentrated by a factor of approximately 40 by settling and decanting the supernatant to achieve reasonable dosing volumes. It was considered to be highly unlikely that the necessary volumes of concentrated alum sludge could be produced by the water treatment plants year round for the purposes of phosphorus removal at the sewage treatment plant. Thus, it was felt that the pursuit of alum sludge as a coagulation supplement rather than as the primary coagulant was more feasible.

Jar test 7 was used to determine the effectiveness of alum sludge as a phosphorus precipitation supplement to alum. It was thought that the alum sludge might provide increased surface area for nucleation thus enhancing precipitation with alum (see section on chemical precipitation). This test was essentially a repeat of Jar test 2 but with alum sludge being substituted for 50 percent of the alum (a 1:1 alum to alum sludge ratio), and the lower dosing level being raised from 100 to 150 mg/L. Results were encouraging, especially at the lower dose level where the phosphorus levels achieved with the alum sludge substitution were essentially the same as with alum in Jar test 2. The removal levels at the upper dose level were much better with alum alone than in combination with the sludge. The phosphorus removal effect of the coagulant combination in Jar test 7 was found to be

⁹ Alum sludge samples were taken during the winter when turbidities and suspended solids of the raw river water were low thus the sludge was very dilute. During the summer when higher amounts of suspended solids are being removed the sludge concentrations are much higher.

statistically significant. The results of the factorial portion of these two jar tests as well as Jar test 9 are summarized in Table 5.2.

Table 5.2 Summary of Factorial Portion of Jar Tests 2, 7, and 9

Jar Test	Jar	Alum (mg/L*)	Alum Sludge (mg/L**)	Polymer (mg/L)	pH	Turb. (NTU)	P (mg PO ₄ -P/L)	SS (mg/L)
2	Raw	-	-	-	7.73	74.0	14.11	570.0
	1	100	-	0	7.15	39.0	4.27	78.2
	2	300	-	0	6.58	4.4	0.45	7.7
	3	100	-	1	7.15	22.0	2.79	37.8
	4	300	-	1	6.56	2.5	0.22	5.1
7	Raw	-	-	-	8.37	95.0	13.68	585.0
	1	75	75	0	7.52	41.0	3.97	66.6
	2	150	150	0	7.17	22.0	1.61	31.6
	3	75	75	1	7.54	33.0	3.47	50.2
	4	150	150	1	7.17	16.0	1.31	23.8
9	Raw	-	-	-	8.01	95.0	11.75	500.0
	1	75	-	0	7.39	56.0	6.15	102.0
	2	150	-	0	7.09	17.0	1.62	30.0
	3	75	-	1	7.40	44.0	5.13	66.0
	4	150	-	1	7.09	13.0	1.09	20.4

* Al₂(SO₄)₃ • 14H₂O

** Al - Al₂(SO₄)₃ • 14H₂O

The effectiveness of alum sludge as a phosphorus removal supplement to alum was further tested in Jar test 9 where the same doses of alum as in Jar test 7 were added to each jar but without any alum sludge. Essentially the same levels of phosphorus and solids reduction were achieved at the upper dose levels as in Jar test 7. The telling difference was at the lower dose level, where the effluent phosphorus concentrations were approximately 50 percent higher than in Jar test 7 as were the suspended solids concentrations. The data implied that, at lower dosing levels, the alum sludge enhanced suspended solids settling thus reducing phosphorus levels because small colloidal phosphorus particles were being removed. As alum dose increased, it was likely this effect became less prevalent because

the alum was available in sufficient quantity to coagulate phosphorus and remove solids alone, and its stronger coagulation characteristics overshadowed the sludges effect.

Runs 5 and 6 in Jar test 10 and run 3 in Jar test 11 (shown in Table 5.3) determined that dissolved phosphorus was being precipitated out of solution by the alum sludge. The basis for this argument is that the final phosphorus concentrations were lower than that of the raw influent after it was passed through a filter (assuming the remaining phosphorus in the filtrate is in solution). This meant that there was likely some chemical reaction or adsorption taking place and the phosphorus removal effect noted could not just be attributed to enhanced solids removal as was thought after the completion of Jar test 5.

Table 5.3 The Effect of Alum Sludge on Dissolved Phosphorus

Jar Test	Jar	Alum Sludge (mg/L*)	Raw P (mg PO ₄ -P/L)	Final P (mg PO ₄ -P/L)	Remarks
10	5	750	11.86	3.13	unfiltered raw
	6	375	6.20	4.48	filtered raw
11	3	750	5.65	2.24	filtered raw

* Al - Al₂(SO₄)₃ • 14H₂O

5.2.3 Lime

Phosphorus removal capability of the lime was less than anticipated based on the literature review. It was thought that perhaps the phosphorus form may have had some effect. Reference can be made to Schmid and McKinney (1969) for more discussion of this aspect. Lime was tested in Jar tests 3 and 4, and a 1:1 lime to lime sludge combination was tested in Jar test 8. Some difficulty was encountered using the unslaked lime (CaO, often called quicklime) from the Rossdale plant because it did not appear to be dissolving properly in the stock solution. Hydrated lime (Ca(OH)₂) was substituted for the remainder of the jar tests.

Though the results of Jar tests 3, 4, and 8 were statistically significant, the best phosphorus level achieved was 1.75 mg PO₄³⁻ - P/L using a dose of 350 mg/L of lime (as Ca(OH)₂) on primary effluent (Jar test 4). The target phosphorus removal level of 1 mg/L could not be met with reasonable doses of lime thus it was abandoned as a suitable coagulant for use at Gold Bar. Other factors in this decision included: 1) the difficulty that lime handling at the plant would represent in comparison with alum, and 2) lime precipitation of phosphorus was a pH dependent process which would likely require a second process refurbishment for pH adjustment following precipitation thus representing an additional expense. More testing would have been completed if the lime or combination of lime and lime sludge had shown more phosphorus removal promise than that indicated by these jar tests.

5.2.4 Lime Sludge

Jar test 6 clearly shows a net phosphorus removal when compared with the influent phosphorus level but the statistical analysis (F-ratio) indicated that the effect of increasing lime sludge concentration was insignificant. Results of Jar tests 6 and 8 are shown in Table 5.4. The phosphorus levels achieved were approximately the same as typical phosphorus levels for primary effluent at the plant (6 to 8 mg PO₄³⁻ - P/L) which indicated that removal could likely be attributed to settlement of phosphorus entrained solids with little or no effect on dissolved phosphorus.

The lime sludge was combined with lime in Jar test 8 in the hope of providing more surface area for nucleation thus enhancing precipitation with lime (see discussion of chemical precipitation). The sludge appeared to have little or no effect as in Jar test 6. As precipitation of phosphorus with lime is a pH dependent process and the lime sludge had little or no effect on pH it was concluded that it was essentially inert and would be of no benefit in phosphorus removal. As can be seen in Jar test 6 the suspended solids level actually increased with increasing lime sludge dose. This observation supported the

Table 5.4 Summary of Factorial Portion of Jar Tests 6 and 8

Jar Test	Jar	Lime		Polymer (mg/L)	pH	Turb. (NTU)	P (mg PO ₄ -P/L)	SS (mg/L)
		Lime (mg/L*)	Sludge (mg/L**)					
6	Raw	-	-	-	7.96	87.0	11.64	380.0
	1	-	200	0	7.90	78.0	7.13	83.9
	2	-	800	0	7.98	110.0	6.36	140.2
	3	-	200	1	7.92	75.0	7.44	75.0
	4	-	800	1	7.98	100.0	6.59	156.7
8	Raw	-	-	-	7.91	89.0	12.60	447.0
	1	100	100	0	9.36	86.0	6.18	124.0
	2	200	200	0	9.84	53.0	4.78	70.8
	3	100	100	1	9.38	61.0	5.81	102.0
	4	200	200	1	9.84	48.0	3.93	58.3

* Ca(OH)₂/L

** Ca - Ca(OH)₂/L

conclusion that the lime sludge was inert and did not dissolve readily when added to the wastewater. The phosphorus levels achieved for the amount of lime/sludge being added were unacceptable thus it was abandoned.

5.3 Polymer Addition

Polymer was added to enhance removal of very small suspended colloidal particles of phosphorus brought on by addition of coagulants to the wastewater, hence aiding the phosphorus removal process. For instance, it was thought that if the polymer's suspended solids removal characteristics were statistically significant then it would likely yield significant phosphorus removal effects as well. Conversely, if the suspended solids removal was not significant then the phosphorus removal would not likely be significant. This relationship held true for most jar tests but there were some exceptions.

The only jar test that apparently directly refuted this hypothesis was Jar test 1 (alum in primary effluent) where the polymer's suspended solids removal capability was not found to be significant though the phosphorus removal was. The likely reason for this

anomaly is that polymer was added to this jar test too early and at too high a dose. Jar test 5 with alum sludge yielded a significant suspended solids effect but it was positive indicating an increase in suspended solids with increasing polymer dose. This increase in suspended solids was likely the reason that polymer addition did not significantly effect phosphorus removal. Suspended solids removal was significant in Jar test 8 with lime sludge but phosphorus removal was not (see Table 5.4). This was likely a reflection on the fact that lime sludge was an ineffective coagulant hence the solids being removed were not phosphorus laden colloids. The remainder of the jar tests indicated a positive correlation between phosphorus and suspended solids removal.

5.4 Other Effects of Coagulant Addition to Wastewater

The following parameters were monitored in some or all of the jar tests in order to assess the effect that chemical precipitation of phosphorus had on them. The data were ~~also used~~ aid in assessing the effect of chemical precipitation of phosphorus on other areas of the biological wastewater treatment process. The majority of the discussion focuses on the factorial portion of the experimentation (Jar tests 1 - 9). Exceptions will be noted.

5.4.1 Suspended Solids

All jar tests other than initial screening measured suspended solids concentrations as a dependent parameter, the statistical significance of the results was determined for all factorially designed experiments (Jar tests 1 - 9). Suspended solids were considered to be an important parameter because: 1) they would likely be reduced enough to require adjustments be made in the aeration portion of the activated sludge process, and ; 2) as discussed in the Literature Review section, suspended solids removal and phosphorus removal are closely correlated. Analysis also aided in the determination of effects on the clarifiers themselves such as in making an estimation on the increase in precipitated solids being handled.

The effect of coagulants on suspended solids concentrations was found to be statistically significant in all but one of the factorial jar tests. Jar test 4 (using lime on primary effluent) indicated the lime's effect to be insignificant. The number 4 jar in this test formed a very large colloidal mass early in the flocculation portion which was not noted in any of the other jars or jar tests. This was thought to be an anomaly and served to seriously skew the statistical analysis relating to suspended solids. The turbidity results indicated the lime dose to be significant which served to further call the solids results into question (see discussion below).

Of the remaining jar tests, only Jar test 6 (lime sludge in raw influent) indicated a positive effect or an increase in suspended solids with increasing coagulant dose. This was likely due to the fact that the material was basically inert as was evidenced by the phosphorus removal effects noted in the same test. The lime sludge neither dissolved nor reacted hence it only served to increase the amount of suspended solids to be settled which increased effluent solids concentrations.

5.4.2 Turbidity

Turbidity was included as a dependent parameter in all jar tests because of the ease of measurement and that it acted as a quasi-check on the suspended solids concentrations. It followed the same statistical pattern as the suspended solids for every jar test other than number 4. Jar test 4 indicated lime dose to be a statistically significant parameter for turbidity but not for suspended solids. As per the suspended solids discussion it was thought that the turbidity was more indicative of the actual lime effect and the suspended solids statistics were disregarded.

5.4.3 Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) testing was carried out in Jar tests 5, 7, 8, 9, 10, and 12; it was included as a complete factorial design dependent parameter in tests 5

and 7 (see Table 5.5). Both the alum sludge and the 1:1 combination of alum and alum sludge in Jar tests 5 and 7, respectively, yielded significant BOD reduction effects. The polymer effect was significant in Jar test 5 but not in 7, the effect was positive for both cases meaning the BOD reduction was actually lessened by polymer addition. There was no apparent explanation for this phenomenon. This same trend is illustrated in Jar test 8 with a 1:1 ratio of lime to lime sludge and Jar test 9 with alum. Though BOD is not included as a full parameter in these tests, the results at the upper dose level with and without polymer were measured and indicate the same results.

Table 5.5 Summary of Jar Tests 5 and 7, Biochemical Oxygen Demand and Fecal Coliform Results

Jar Test	Jar	Alum (mg/L*)	Alum Sludge (mg/L**)	Polymer (mg/L)	BOD (mg/L)	Fecal Coliform
5	Raw	-	-	-	304	-
	1	-	150	0	115	-
	2	-	750	0	87	-
	3	-	150	1	128	-
	4	-	750	1	111	-
7	Raw	-	-	-	331	3.51E+06
	1	75	75	0	108	1.12E+05
	2	150	150	0	74	1.28E+05
	3	75	75	1	120	9.36E+05
	4	150	150	1	91	4.63E+04

* $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$

** $\text{Al} - \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$

Filtering raw influent as in Jar test 10 reduced BOD from 303 to 76 mg/L, a 75 percent reduction. All chemically precipitated unfiltered samples yielded BODs lower than the filtered samples indicating some dissolved BOD was being removed. The coagulants being used were alum, alum sludge, and a 1:1 combination of the two.

5.4.4 Fecal Coliforms

Fecal coliforms (FCs) were included as a full parameter in only one of the factorial design experiments, Jar test 7 (see Table 5.5). The results appeared quite erratic and did not follow the pattern of any of the other measured parameters (the analyses for each jar were completed in triplicate with acceptable variations). An increase in alum without polymer had little effect; a high dose of alum with polymer reduced the count by 20 times over the low alum dose with polymer; the addition of polymer increased the count at the low alum dose by 8 times over low dose with no polymer but reduced it by 3 times at the high alum dose. Alum, polymer, and the interaction of the two were all statistically significant with the interaction effect having the highest F - ratio. All statistics were calculated using logs as the fecal coliforms follow a log-normal distribution.

Jar test 8 with a 1:1 ratio of lime and lime sludge, and Jar test 9 with alum, tested FCs at high coagulant doses with and without polymer but did not exhibit as much effect as indicated in Jar test 7. The lower effectiveness of the lime and lime sludge combination, and the lower overall coagulant dose in Jar test 9 as opposed to Jar test 7 may explain this observation.

Filtering of raw influent reduced FCs by 2.5 times over the unfiltered raw influent in Jar test 10, chemical precipitation of the unfiltered raw influent with alum or a 1:1 combination of alum and alum sludge reduced FC counts by more than 300 times. The addition of an alum sludge only to the raw influent reduced the FC count by 7.5 times.

5.4.5 Nitrogen Forms

Total kjeldahl nitrogen (TKN) and ammonia were included as full parameters in factorial design Jar tests 7 and 9. The effects of any factor or interaction on either were insignificant for both alum and a 1:1 alum to alum sludge combination. The F - ratios in Jar test 7 indicate TKN to be significant for all factors and interactions but this is due to the

very low variance in the center point replicates which, based on other nitrogen results collected, was likely an anomaly.

The low level of oxidation of the raw influent made the nitrite and nitrate results next to nil therefore these analyses will not be discussed further. The nitrogen form findings and effects were consistent with those of Hsu and Pipes (1973).

5.5 The Effect of pH

The precipitation of phosphorus with lime is a pH dependent process as previously mentioned but as its use was abandoned after preliminary jar testing it will not be discussed further. Though pH was known to be an independent parameter that affected phosphorus removal with alum it was not included in the study because: 1) it was not thought to be as significant as other factors; 2) the use of pH adjustment in the full plant was not considered likely; and, 3) time and budget considerations for the study had to be taken into account. After completion of jar testing and comparison of results, especially replicates of the same alum dose, it was felt that pH had played more of a role in phosphorus precipitation than initially thought. As noted in the literature review, the effect of pH was discussed in various articles (Hsu, 1975; Letterman and Vanderbrook, 1983; Francisco et al, 1976).

One of the main reasons pH affects the precipitation of phosphorus is that the key phosphorus precipitate, aluminum phosphate (AlPO_4), is in competition with the precipitation of aluminum hydroxides ($\text{Al}(\text{OH})_3$). Based on the solubility product of these two compounds, aluminum hydroxide is 23 times more soluble than aluminum phosphate in distilled water (pH 7.0 at 25° C) thus the aluminum phosphate should be the most likely to precipitate (Snoeyink and Jenkins, 1980). But, as can be seen from Figure 2.1, above pH 5.4 the precipitation of AlPO_4 in distilled water is affected by pH, the greater the pH the greater the preference of precipitation of $\text{Al}(\text{OH})_3$ over AlPO_4 . The heterogeneous nature of wastewater makes it difficult to compare solubility relationships between it and distilled

water but the same basic trends should apply, ie., the lower the pH the better the precipitation of phosphorus as $AlPO_4$.

One difficulty in attempting to control pH is that though the initial level may be set at a specific value by the addition of acid or base, the amount the pH changes with addition of a certain amount of a particular coagulant is still dependent on the buffering capacity of the wastewater. Such was the case in Jar test 13 where the initial pH was varied from 8.2 to 7.6 in jars 1 through 4 but the final pH in all jars ended up within 0.12 of one another. As a result of this effect, phosphorus removal levels did not demonstrate the effect of pH as was originally intended. The variation in initial phosphorus levels caused further difficulties when comparing replicate coagulant doses where the final pH was different. For some cases, the differences in final phosphorus levels for identical coagulant dose could not only be attributed to pH effects, but also to different stoichiometric requirements for phosphorus removal based on influent phosphorus levels.

The jar tests and runs where pH effects were noted are illustrated in the following table. Only replicates that had approximately the same influent phosphorus level are shown.

Table 5.6 Replicate Alum Doses Exhibiting a pH Effect on P - Removal

Jar Test	Init. pH	Init. P (mg PO_4 -P/L)	Alum (mg/L*)	Alum Sludge (mg/L**)	Final pH	Final P (mg PO_4 -P/L)
12	8.04	11.59	100	200	7.30	3.70
12	8.04	11.59	100	300	7.31	3.41
11	7.77	12.08	100	100	7.07	2.95
9	8.01	11.75	150	0	7.09	1.62
12	8.04	11.59	150	0	7.10	1.71
10	7.80	11.86	150	0	6.95	0.96
7	8.37	13.68	150	150	7.17	1.61
10	7.80	11.86	150	150	6.99	0.82

* $Al_2(SO_4)_3 \cdot 14H_2O$

** Al - $Al_2(SO_4)_3 \cdot 14H_2O$

The first set of analyses in Table 5.6 were included because the pH effect is exhibited despite the increase in alum sludge dose. The analyses shown in bold type are those that exhibited lower effluent phosphorus levels with lower pH.

5.6 The Response Surface (Alum and Alum Sludge)

Jar tests 10 through 12 as well as selected runs from previous jar tests were used to try and determine a phosphorus removal dose response surface for alum and alum sludge. This is similar to a dose response curve except that the surface is in three dimensions rather than two and can be illustrated as contours on a two-dimensional plot. Special attention was paid to trying to characterize the response surface between the 1 and 2 mg/L phosphorus levels which was thought to be a suitable removal prior to aeration. The aeration of the sewage would likely remove at least a further 1 mg/L of phosphorus¹⁰ thus yielding a final effluent concentration less than 1 mg/L. Care must be taken not to remove too much phosphorus before aeration or the microbial population may be starved (nutrient limited) and aeration process efficiency reduced.

The heterogeneity of the wastewater, including varying influent phosphorus and pH levels, made it difficult to plot a response surface from which meaningful conclusions could be drawn (see Figure 5.1). Molar ratios of alum and alum sludge to influent phosphorus levels were used on the surface axes rather than dosage concentrations to try and filter out the influent phosphorus variations. This helped the surface definition but there were still some significant anomalies and gaps that made interpretation difficult. The most obvious trend was that the surface sloped in the direction of alum dose much more steeply than in the direction of alum sludge dose. The difference in slopes illustrated the

¹⁰ According to Viessman & Hammer (1985) the approximate BOD/nitrogen/phosphorus (BOD:N:P) weight ratio required for biological treatment is 100:5:1. The aeration tanks at Gold Bar are removing approximately 150 mg/L BOD hence the statement that a minimum of 1 mg/L of phosphorus is likely being removed during aeration.

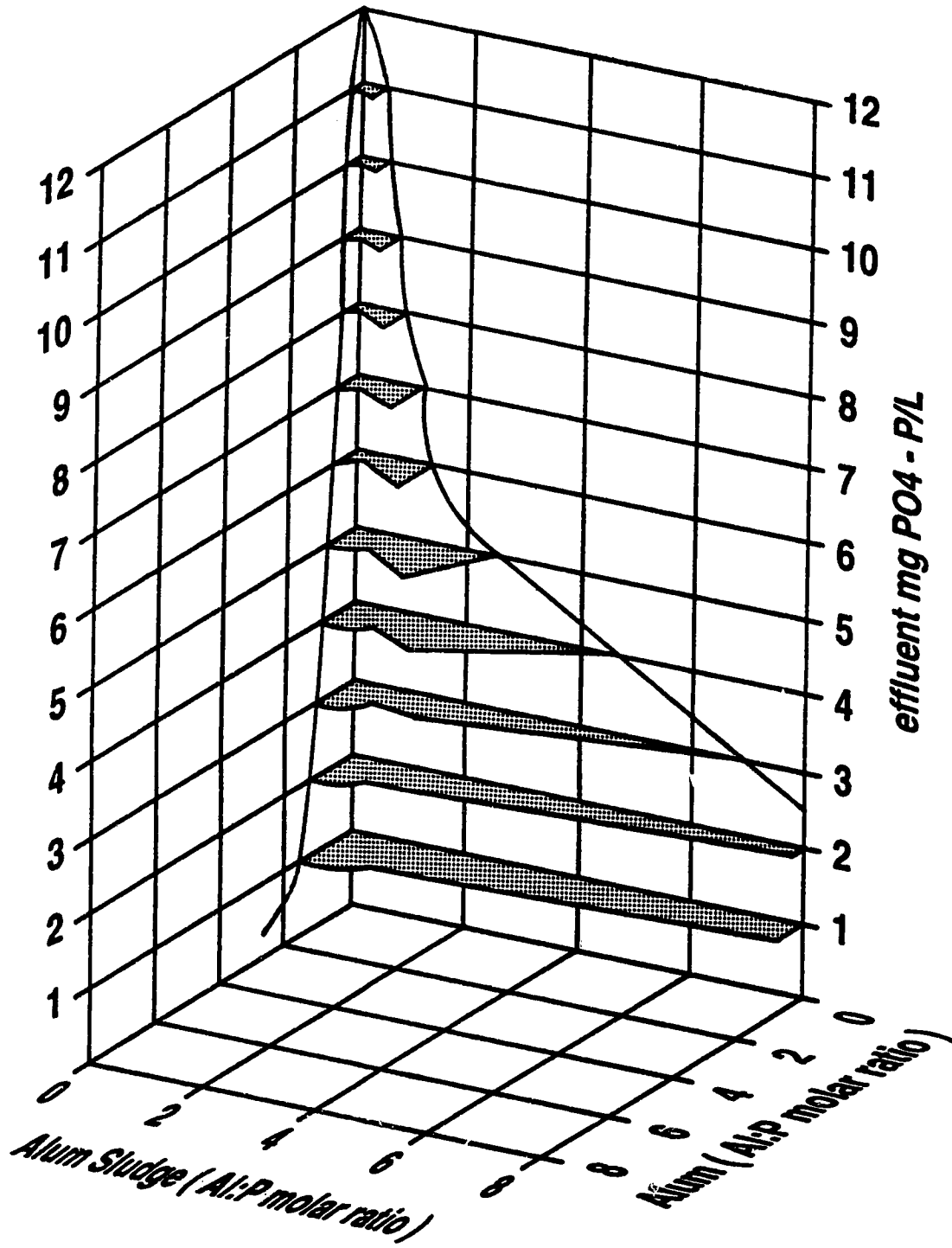


Figure 5.1 Response Surface for Phosphorus Removal with Alum and Alum Sludge.

superior efficiency of alum in precipitating phosphorus from the wastewater. The slope of the alum was 5 to 10 times that of alum sludge dependent on the phosphorus level being examined. This is consistent with the findings of Narasiah (1985), and O'Blenis and Warriner (1972).

5.7 Sludge Production

The precipitated, phosphorus rich, sludge was characterized in Jar test 13 in order that the effect on settling tank, or clarifier, capacity could be hypothesized. The results are summarized in Table 38 of Appendix I but Table 5.7 normalizes results to one cubic meter of wastewater.

Table 5.7 Normalized Results of Sludge Characterization from Jar Test 13.

Alum (mg/L)	Alum Sdg. (mg/L)	Polymer (mg/L)	P (mg/L)	SS (mg/L)	Sludge Vol. (L*)	Dry Susp. Sol. (Kg*)
150	0	0	124	6517	53	0.342
150	0	0.5	155	8367	40	0.335
150	150	0	117	7500	55	0.413
150	150	0.5	135	9567	48	0.454
0	0	0	149	13017	15	0.195

* these quantities are for the sludge precipitated from one cubic meter of raw influent

The addition of a coagulant reduced the suspended solids concentration of the sludges by 50 to 100 percent dependent on if a polymer was used or not but the volume of sludge increased anywhere from 3 to 4 times. Due to difficulty in separating all the supernatant from the sludge, the sludge volumes were checked by doing a phosphorus mass balance for each jar. All calculated volumes were within 15 percent of measured indicating reasonably good supernatant separation.

From Table 5.7 it can be seen that the total amount of precipitated solids essentially doubles with the addition of a coagulant. This combined with the increase in volume imply that the clarifier capacity may have to be downrated based on sludge handling capability

after the addition of chemical precipitation to the process. The scope of this study did not allow for settling tests to be done that could have determined settling velocities and reduction in overflow capacity. The fluffiness (increased volume) of the chemically precipitated sludge when compared with the primary settled sludge (no coagulant or polymer) and the increase in solids seemed to imply settling velocities would be reduced. Conversely, visual observations of the settling chemical flocs determined that they generally settled more quickly than the biological flocs and that the addition of polymer brought on even faster settling. No conclusions as to the downrating of clarifiers after chemical addition can be substantiated from the data gathered in this study. A pilot scale study should be undertaken to determine settling velocities of chemically precipitated flocs in wastewater and the associated overflow capacity of wastewater clarifiers.

The addition of polymers with the alum and alum sludge served to concentrate the precipitated sludge more than coagulant alone. Polymer reduced the sludge volume but the total amount of precipitated solids essentially remained the same. Note the 20 to 25 percent increase in total precipitated solids for the alum sludge addition when compared with the alum alone.

6.0 CONCLUSIONS

The evaluation of coagulants and sludges from water treatment coagulation and softening efforts for wastewater phosphate reduction resulted in the following conclusions:

- Alum was the only coagulant tested that reduced phosphorus concentrations to target levels.
- Alum sludge exhibited some phosphorus removal capabilities but appeared to be 5 to 10 times less effective than pure alum.
- Alum sludge combined with alum supplemented the alum's suspended solids removal capability, therefore marginally increasing phosphorus removal capabilities.
- Lime exhibited phosphorus removal capabilities, but the quantities required to meet target levels were relatively large.
- Lime sludge exhibited no phosphorus removal capabilities; all phosphorus reduction was attributed to settlement of phosphorus-entrained suspended solids. Also, the effluent suspended solids concentrations increased with increasing sludge dose thus addition of lime sludge was of negative benefit.
- pH is a significant factor in phosphorus removal with alum. The lower the pH, the better the phosphorus removal for a given dose of alum.
- Polymers yielded some significant phosphorus removal effects, but the greatest benefit may be the reduced settling time (increased settling velocity) required to achieve the same phosphorus removal as using chemicals without polymer addition. The addition of an anionic polymer may increase settling velocities to a level that would eliminate any need to reduce clarifier capacity because of increased solids.
- Disposal of alum sludge at sewage treatment plants may be a viable option, considering the benefit derived from marginal increases in solids and

phosphorus removal, but before this is done, the impact of aluminum-rich sludge on farm land will have to be evaluated.

- Addition of coagulants to the wastewater increased the total settled solids in the jar tests by 1.7 to 2.3 times compared to no coagulant addition, but increased the volume of the settled solids by as much as 3.7 times. Chemical addition reduced the suspended solids concentration of the sludge by as much as 50 percent.
- The data gathered in this study is not sufficient to make any recommendations about whether existing clarifier capacities need to be downrated with the addition of chemical coagulants.
- The variable nature of the wastewater made it difficult to compare results between jar tests for some cases.

7.0 RECOMMENDATIONS

- pH should be included as a factor in experimentation, or at least the initial pH should be standardized at a certain level.
- Before attempting chemical phosphorus removal in the primary treatment process area of a plant, a study should be undertaken to quantify the effect of reduced influent solids and phosphorus levels to the aeration tanks.
- Research should define the regulatory implications of disposing of alum in sewage sludges that may be land farmed, or have some other secondary use.
- Investigations should consider whether alum could be added to the aeration tanks in say, the last pass, for phosphorus precipitation in the secondary, rather than the primary clarifiers. The reduced phosphorus levels would lessen the total alum requirement, but would likely necessitate a radical change to aeration parameters, in light of the change in recycle sludge composition.

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- A pilot-scale study should be undertaken to determine if the increased solids due to chemical precipitation of phosphorus actually reduce the overflow capacity of existing biological clarifiers.

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APPENDIX I. DATA TABLES

Table I.1 Results Summary Table for Screening Test #1, Alum and Primary Effluent, Factorial Design.

Initial Analyses:

pH = 7.92

Turbidity = 53 NTU

6.60 mg PO₄-P/L

Jar	Alum Dose (mg/L)	Rapid Mixing Gt	Flocculation Gt	pH	Turbidity (NTU)	Phosphorus (mg PO ₄ -P/L)
1	100	1100	7200	7.07	15.0	2.15
2	250	1100	7200	6.59	3.4	0.39
3	100	6600	7200	7.14	12.0	1.80
4	250	6600	7200	6.63	3.0	0.45
5	100	1100	28800	7.18	6.2	1.20
6	250	1100	28800	6.66	1.5	0.25
7	100	6600	28800	7.18	5.8	1.11
8	250	6600	28800	6.64	2.1	0.44
9	175	3850	18000	6.87	2.3	0.42
10	175	3850	18000	6.89	2.8	0.52
11	175	3850	18000	6.88	2.8	0.39
12	175	3850	18000	6.88	2.5	0.24

Center Point Replicates ----->

MEAN	6.88	2.6	0.39
SDEV	0.008	0.245	0.116
M.S.	0.0001	0.0600	0.0134

Rapid Mixing @ 100 rpm
 Flocculation Mixing @ 30 rpm
 Settling Time = 30 minutes
 Primary Effluent

Table I.2 Table of Signs and Effects for Screening Test #1, Alum and Primary Effluent.

Table of Signs

JAR	MEAN	A	B	C	AB	AC	BC	ABC	pH	TURB.	P
1	1	-1	-1	-1	1	1	1	-1	7.07	15.0	2.15
2	1	1	-1	-1	-1	-1	1	1	6.59	3.4	0.39
3	1	-1	1	-1	-1	1	-1	1	7.14	12.0	1.80
4	1	1	1	-1	1	-1	-1	-1	6.63	9.0	0.45
5	1	-1	-1	1	1	-1	-1	1	7.18	6.2	1.20
6	1	1	-1	1	-1	1	-1	-1	6.66	1.5	0.25
	1	-1	1	1	-1	-1	1	-1	7.18	5.8	1.11
	1	1	1	1	1	1	1	1	6.64	2.1	0.44

A - Alum Dose
 B - Rapid Mix Gt
 C - Flocculation Gt

Effect	pH	Turbidity	P
Mean	6.89	6.1	0.97
<u>Main Effects</u>			
Alum Dose, A	-0.51	-7.3	-1.18
Rapid Mix Gt, B	0.02	-0.8	-0.05
Flocculation Gt, C	0.06	-4.5	-0.45
<u>Two-Factor Interactions</u>			
A x B	-0.01	0.9	0.17
A x C	-0.02	3.1	0.37
B x C	-0.03	0.9	0.10
<u>Three-Factor Interactions</u>			
A x B x C	0.00	-0.4	-0.03

Table I.3 Analysis of Variance Tables for Main Effects and Interactions of Screening Test #1, Alum and Primary Effluent.

Analysis of Variance For pH

**95% Confidence
F(0.05,1,3) = 18.51**

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	0.5253125	0.5253125	7879.7	Yes
B	1	0.0010125	0.0010125	15.2	No
C	1	0.0066125	0.0066125	99.2	Yes
AB	1	0.0003125	0.0003125	4.7	No
AC	1	0.0006125	0.0006125	9.2	No
BC	1	0.0021125	0.0021125	31.7	Yes
ABC	1	1.25E-05	1.25E-05	0.2	No
Total	7	0.5359875			
Error	3	0.0002	0.0001		

Analysis of Variance For Turbidity

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	105.125	105.125	1752.1	Yes
B	1	1.28	1.28	21.3	Yes
C	1	39.605	39.605	660.1	Yes
AB	1	1.62	1.62	27.0	Yes
AC	1	18.605	18.605	310.1	Yes
BC	1	1.62	1.62	27.0	Yes
ABC	1	0.32	0.32	5.3	No
Total	7	168.175			
Error	3	0.1800	0.0600		

Analysis of Variance For Phosphorus

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	2.7966125	2.7966125	208.3	Yes
B	1	0.0045125	0.0045125	0.3	No
C	1	0.4005125	0.4005125	29.8	Yes
AB	1	0.0595125	0.0595125	4.4	No
AC	1	0.2775125	0.2775125	20.7	Yes
BC	1	0.0190125	0.0190125	1.4	No
ABC	1	0.0021125	0.0021125	0.2	No
Total	7	3.5597875			
Error	3	0.0403	0.0134		

Table I.4 Results Summary Table for Screening Test #2, Alum and Raw Influent, Factorial Design.

Initial Analyses:

pH = 8.05

Turbidity = 93 NTU

11.25 mg PO₄-P/L

Jar	Alum Dose (mg/L)	Flocculation rpm	Flocculation Gt	pH	Turbidity (NTU)	Phosphorus (mg PO ₄ -P/L)
1	150	20	7200	7.03	16.0	1.69
2	350	20	7200	6.41	3.9	0.31
3	150	40	7200	6.94	16.0	1.62
4	350	40	7200	6.34	4.8	0.36
5	150	20	28800	7.01	13.0	1.15
6	350	20	28800	6.44	3.0	0.21
7	150	40	28800	6.96	9.6	1.07
8	350	40	28800	6.39	3.0	0.22
9	250	30	18000	6.69	4.4	0.35
10	250	30	18000	6.69	4.3	0.37
11	250	30	18000	6.69	4.2	0.41
12	250	30	18000	6.67	4.3	0.38

Center Point Replicates ----->

MEAN	6.69	4.3	0.38
SDEV	0.010	0.082	0.025
M.S.	0.0001	0.0067	0.0006

Rapid Mix 30 sec. @ 100 rpm

Settling Time = 30 minutes

Raw Influent

Table I.5 Table of Signs and Effects for Screening Test #2, Alum and Raw Influent.

Table of Signs

JAR	MEAN	A	B	C	AB	AC	BC	ABC	pH	TURB.	P
1	1	-1	-1	-1	1	1	1	-1	7.03	16.0	1.69
2	1	1	-1	-1	-1	-1	1	1	6.41	3.9	0.31
3	1	-1	1	-1	-1	1	-1	1	6.94	16.0	1.62
4	1	1	1	-1	1	-1	-1	-1	6.34	4.8	0.36
5	1	-1	-1	1	1	-1	-1	1	7.01	13.0	1.15
6	1	1	-1	1	-1	1	-1	-1	6.44	3.0	0.21
7	1	-1	1	1	-1	-1	1	-1	6.96	9.6	1.07
8	1	1	1	1	1	1	1	1	6.39	3.0	0.22

A - Alum Dose
 B - Flocculation rpm
 C - Flocculation Gt

Effect	pH	Turbidity	P
Mean	6.69	8.7	0.83
<u>Main Effects</u>			
Alum Dose, A	-0.59	-10.0	-1.11
Flocculation rpm, B	-0.07	-0.6	-0.02
Flocculation Gt, C	0.02	-3.0	-0.33
<u>Two-Factor Interactions</u>			
A x B	0.00	1.1	0.05
A x C	0.02	1.7	0.21
B x C	0.02	-1.1	-0.01
<u>Three-Factor Interactions</u>			
A x B x C	-0.01	0.6	-0.01

Table I.6 Analysis of Variance Tables for Main Effects and Interactions of Screening Test #2, Alum and Raw Influent.

Analysis of Variance For pH

95% Confidence F(0.05,1,3) = 18.51

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	0.6962	0.6962	6962.0	Yes
B	1	0.00845	0.00845	84.5	Yes
C	1	0.0008	0.0008	8.0	No
AB	1	5E-05	5E-05	0.5	No
AC	1	0.0008	0.0008	8.0	No
BC	1	0.00045	0.00045	4.5	No
ABC	1	5E-05	5E-05	0.5	No
Total	7	0.7068			
Error	3	0.0003	0.0001		

Analysis of Variance For Turbidity

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	199.00125	199.00125	29850.2	Yes
B	1	0.78125	0.78125	117.2	Yes
C	1	18.30125	18.30125	2745.2	Yes
AB	1	2.31125	2.31125	346.7	Yes
AC	1	5.61125	5.61125	841.7	Yes
BC	1	2.31125	2.31125	346.7	Yes
ABC	1	0.78125	0.78125	117.2	Yes
Total	7	229.09875			
Error	3	0.0200	0.0067		

Analysis of Variance For Phosphorus

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	2.4531125	2.4531125	3925.0	Yes
B	1	0.0010125	0.0010125	1.6	No
C	1	0.2211125	0.2211125	353.8	Yes
AB	1	0.0055125	0.0055125	8.8	No
AC	1	0.0903125	0.0903125	144.5	Yes
BC	1	0.0003125	0.0003125	0.5	No
ABC	1	0.0001125	0.0001125	0.2	No
Total	7	2.7714875			
Error	3	0.0019	0.0006		

Table I.7 Results Summary Table for Jar Test #1, Alum and Primary Effluent, Factorial Design.

Initial Analyses:

pH = 7.98

Turbidity = 64 NTU

8.01 mg PO₄-P/L

Suspended Solids = 85 mg/L

Jar	Alum Dose (mg/L*)	Polymer Dose (mg/L)	pH	Turbidity (NTU)	Phosphorus (mg PO ₄ -P/L)	Suspended Solids (mg/L)
1	75	0	7.32	28.0	4.41	53.3
2	225	0	6.73	3.0	0.38	7.0
3	75	10	7.32	25.0	3.01	70.0
4	225	10	6.72	3.4	0.40	6.7
5	150	5	6.98	15.0	1.53	22.5
6	150	5	7.00	14.0	1.45	26.7
7	150	5	6.98	14.0	1.37	28.3

Center Point Replicates ---->

MEAN	14.3	1.45	25.8
SDEV	0.577	0.080	2.996
M.S.	0.3333	0.0064	8.9733

Rapid Mixing Alum 30 seconds @ 100 rpm

Flocculation Mixing 20 minutes @ 20 rpm

Settling Time = 30 minutes

Rapid Mixing Polymer for 5 minutes @ 100 rpm prior to adding Alum

Primary Effluent

* - mg Al₂(SO₄)₃ • 14H₂O /L

Table I.8 Table of Signs and Effects for Jar Test #1, Alum and Primary Effluent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS
1	1	-1	-1	1	7.32	28.0	4.41	53.3
2	1	1	-1	-1	6.73	3.0	0.38	7.0
3	1	-1	1	-1	7.32	25.0	3.01	70.0
4	1	1	1	1	6.72	3.4	0.40	6.7

A - Alum Dose
B - Polymer Dose

Effect	pH	Turbidity	P	SS
Mean	7.02	14.9	2.05	34.3
Main Effects				
Alum Dose, A	-0.60	-23.3	-3.32	-54.8
Polymer Dose, B	-0.01	-1.3	-0.69	8.2
Two-Factor Interaction				
A x B	-0.01	1.7	0.71	-8.5

Table I.9 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #1, Alum and Primary Effluent.

95% Confidence
F(0.05,1,2) = 18.51

Analysis of Variance For Turbidity

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	542.89	542.89	1628.7	Yes
B	1	1.69	1.69	5.1	No
AB	1	2.89	2.89	8.7	No
Total	3	547.47			
Error	2	0.67	0.33		

Analysis of Variance For Phosphorus

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	11.0224	11.0224	1722.2	Yes
B	1	0.4761	0.4761	74.4	Yes
AB	1	0.5041	0.5041	78.8	Yes
Total	3	12.0026			
Error	2	0.0128	0.0064		

Analysis of Variance For Suspended Solids

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	3003.04	3003.04	334.7	Yes
B	1	67.24	67.24	7.5	No
AB	1	72.25	72.25	8.1	No
Total	3	3142.53			
Error	2	17.95	8.97		

Table I.10 Results Summary Table for Jar Test #2, Alum and Raw Influent, Factorial Design.

Initial Analyses:

pH = 7.73
 Turbidity = 74 NTU
 14.11 mg PO4-P/L
 Suspended Solids = 570 mg/L

Jar	Alum Dose (mg/L*)	Polymer Dose (mg/L)	pH	Turbidity (NTU)	Phosphorus (mg PO4-P/L)	Suspended Solids (mg/L)
1	100	0	7.15	39.0	4.27	78.2
2	300	0	6.58	4.4	0.45	7.7
3	100	1	7.15	22.0	2.79	37.8
4	300	1	6.56	2.5	0.22	5.1
5	200	0.5	6.83	3.4	0.40	9.0
6	200	0.5	6.83	2.7	0.30	10.0
7	200	0.5	6.83	2.6	0.35	8.6

Center Point Replicates ---->	MEAN	2.9	0.35	9.2
	SDEV	0.436	0.050	0.721
	M.S.	0.1900	0.0025	0.5200

Rapid Mixing Alum 60 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Rapid Mixed Polymer for 30 seconds @ 100 rpm following 30 seconds of Rapid Mixing Alum
 Raw Influent
 * - mg Al₂(SO₄)₃ • 14H₂O /L

Table I.11 Table of Signs and Effects for Jar Test #2, Alum and Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS
1	1	-1	-1	1	7.15	39.0	4.27	78.2
2	1	1	-1	-1	6.58	4.4	0.45	7.7
3	1	-1	1	-1	7.15	22.0	2.79	37.8
4	1	1	1	1	6.56	2.5	0.22	5.1

A - Alum Dose
B - Polymer Dose

Effect	pH	Turbidity	P	SS
Mean	6.86	17.0	1.93	32.2
<u>Main Effects</u>				
Alum Dose, A	-0.58	-27.1	-3.20	-51.6
Polymer Dose, B	-0.01	-9.5	-0.86	-21.5
<u>Two-Factor Interaction</u>				
A x B	-0.01	7.6	0.63	18.9

Table I.12 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #2, Alum and Raw Influent.

95% Confidence
F(0.05,1,2) = 18.51

Analysis of Variance For Turbidity

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	731.7025	731.7025	3851.1	Yes
B	1	89.3025	89.3025	470.0	Yes
AB	1	57.0025	57.0025	300.0	Yes
Total	3	878.0075			
Error	2	0.38		0.19	

Analysis of Variance For Phosphorus

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	10.208025	10.208025	4083.2	Yes
B	1	0.731025	0.731025	292.4	Yes
AB	1	0.390625	0.390625	156.2	Yes
Total	3	11.329675			
Error	2	0.005		0.0025	

Analysis of Variance For Suspended Solids

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	2662.56	2662.56	5120.3	Yes
B	1	462.25	462.25	888.9	Yes
AB	1	357.21	357.21	686.9	Yes
Total	3	3482.02			
Error	2	1.04		0.52	

Table I.13 Results Summary Table for Jar Test #3, Lime and Raw Influent, Factorial Design.

Initial Analyses:

pH = 7.55

Turbidity = 95 NTU

13.11 mg PO₄-P/L

Suspended Solids = 497 mg/L

Total Hardness = 194 mg/L (as CaCO₃)

Total Alkalinity = 245 mg/L (as CaCO₃)

Jar	Lime Dose (mg/L*)	Polymer Dose (mg/L)	pH	Turbidity (NTU)	Phosphorus (mg PO ₄ -P/L)	Suspended Solids (mg/L)
1	198	0	9.87	62.0	3.89	73.1
2	264	0	10.09	51.0	3.60	65.7
3	198	1	9.84	57.0	3.40	58.9
4	264	1	10.25	46.0	3.08	47.9
5	231	0.5	9.95	53.0	3.51	51.1
6	231	0.5	10.00	50.0	3.60	52.9
7	231	0.5	9.93	50.0	3.44	50.0

Center Point Replicates ---->

MEAN	51.0	3.52	51.3
SDEV	1.732	0.080	1.464
M.S.	3.0000	0.0064	2.1433

Rapid Mixing Lime 60 seconds @ 100 rpm

Flocculation Mixing 20 minutes @ 30 rpm

Settling Time = 30 minutes

Rapid Mixed Polymer for 30 seconds @ 100 rpm following 30 seconds of Rapid Mixing Lime

Raw Influent

Quick Lime (CaO) did not mix well in stock solution, majority of solids were suspended rather than dissolved.

* - mg CaO as Ca(OH)₂ /L

Table I.14 Table of Signs and Effects for Jar Test #3, Lime and Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS
1	1	-1	-1	1	9.87	62.0	3.89	73.1
2	1	1	-1	-1	10.09	51.0	3.60	65.7
3	1	-1	1	-1	9.84	57.0	3.40	58.9
4	1	1	1	1	10.25	46.0	3.08	47.9

A - Lime Dose
 B - Polymer Dose

Effect	pH	Turbidity	P	SS
Mean	10.01	54.0	3.49	61.4
<u>Main Effects</u>				
Lime Dose, A	0.32	-11.0	-0.31	-9.2
Polymer Dose, B	0.07	-5.0	-0.51	-16.0
<u>Two-Factor Interaction</u>				
A x B	0.10	0.0	-0.02	-1.8

Table I.15 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #3, Lime and Raw Influent.

**95% Confidence
F(0.05,1,2) = 18.51**

Analysis of Variance For Turbidity

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	121	121	40.3	Yes
B	1	25	25	8.3	No
AB	1	0	0	0.0	No
Total	3	146			
Error	2	6		3	

Analysis of Variance For Phosphorus

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	0.093025	0.093025	14.5	No
B	1	0.255025	0.255025	39.6	Yes
AB	1	0.000225	0.000225	0.0	No
Total	3	0.348275			
Error	2	0.0129		0.0064	

Analysis of Variance For Suspended Solids

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	84.64	84.64	39.5	Yes
B	1	256	256	119.4	Yes
AB	1	3.24	3.24	1.5	No
Total	3	343.88			
Error	2	4.2867		2.1433	

Table I.16 Results Summary Table for Jar Test #4, Lime and Primary Effluent, Factorial Design.

Initial Analyses:

pH = 7.70

Turbidity = 64 NTU

9.51 mg PO₄-P/L

Suspended Solids = 88 mg/L

Total Hardness = 221 mg/L (as CaCO₃)

Total Alkalinity = 238 mg/L (as CaCO₃)

Jar	Lime Dose (mg/L*)	Polymer Dose (mg/L)	pH	Turbidity (NTU)	Phosphorus (mg PO ₄ -P/L)	Suspended Solids (mg/L)
1	200	0	9.71	46.0	4.36	67.1
2	350	0	10.27	28.0	2.47	41.1
3	200	1	9.68	43.0	3.94	66.4
4	350	1	10.16	42.0	1.75	106.4
5	275	0.5	10.00	33.0	2.86	51.0
6	275	0.5	9.98	30.0	2.44	50.0
7	275	0.5	9.96	30.0	2.66	67.1

Center Point Replicates ---->

MEAN	31.0	2.65	56.0
SDEV	1.732	0.210	9.597
M.S.	3.0000	0.0441	92.1033

Rapid Mixing Lime 45 seconds @ 100 rpm

Flocculation Mixing 20 minutes @ 30 rpm

Settling Time = 30 minutes

Rapid Mixed Polymer for 15 seconds @ 100 rpm following 30 seconds of Rapid Mixing Lime

Primary Effluent

Hydrated Lime (Ca(OH)₂) did not mix well in stock solution, majority of solids were suspended rather than dissolved (even after heating)

* - mg Ca(OH)₂ /L

Table I.17 Table of Signs and Effects for Jar Test #4, Lime and Primary Effluent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS
1	1	-1	-1	1	9.71	46.0	4.36	67.1
2	1	1	-1	-1	10.27	28.0	2.47	41.1
3	1	-1	1	-1	9.68	43.0	3.94	66.4
4	1	1	1	1	10.16	42.0	1.75	106.4

A - Lime Dose
B - Polymer Dose

Effect	pH	Turbidity	P	SS
Mean	9.96	39.8	3.13	70.3
<u>Main Effects</u>				
Lime Dose, A	0.52	-9.5	-2.04	7.0
Polymer Dose, B	-0.07	5.5	-0.57	32.3
<u>Two-Factor Interaction</u>				
A x B	-0.04	8.5	-0.15	33.0

Table I.18 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #4, Lime and Primary Effluent.

95% Confidence
F(0.05,1,2) = 18.51

Analysis of Variance For Turbidity

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	90.25	90.25	30.1	Yes
B	1	30.25	30.25	10.1	No
AB	1	72.25	72.25	24.1	Yes
Total	3	192.75			
Error	2	6		3	

Analysis of Variance For Phosphorus

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	4.1616	4.1616	94.3	Yes
B	1	0.3249	0.3249	7.4	No
AB	1	0.0225	0.0225	0.5	No
Total	3	4.509			
Error	2	0.0883		0.0441	

Analysis of Variance For Suspended Solids

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	49	49	0.5	No
B	1	1043.29	1043.29	11.3	No
AB	1	1089	1089	11.8	No
Total	3	2181.29			
Error	2	184.2067		92.1033	

Table I.19 Results Summary Table for Jar Test #5, Alum Sludge and Raw Influent, Factorial Design.

Initial Analyses:

pH = 8.08
 Turbidity = 100 NTU
 10.47 mg PO₄-P/L
 Suspended Solids = 390 mg/L
 BOD = 304 mg/L

Jar	Alum Dose (mg/L*)	Sludge Dose (mg/L)	Polymer Dose (mg/L)	pH	Turb. (NTU)	Phosphorus (mg PO ₄ -P/L)	S.S. (mg/L)	BOD (mg/L)
1	150		0	8.03	48.0	5.28	53.2	115.0
2	750		0	8.01	30.0	2.64	37.1	87.0
3	150		1	8.06	49.0	5.13	83.5	128.0
4	750		1	8.03	35.0	2.96	63.3	111.0
5	450		0.5	8.03	40.0	4.02	65.0	110.0
6	450		0.5	8.05	38.0	3.77	61.8	105.0
7	450		0.5	8.03	39.0	3.84	62.3	110.0

Center Point Replicates ----->	MEAN	39.0	3.88	63.0	108.3
	SDEV	1.000	0.129	1.721	2.887
	M.S.	1.0000	0.0166	2.9633	8.3333

Rapid Mixing Alum Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Rapid Mixed Polymer for 15 seconds @ 100 rpm following 30 seconds of Rapid Mixing Alum
 Raw Influent

* - mg Al-Al₂(SO₄)₃ • 14H₂O /L

Table I.20 Table of Signs and Effects for Jar Test #5, Alum Sludge and Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS	BOD
1	1	-1	-1	1	8.03	48.0	5.28	53.2	115.0
2	1	1	-1	-1	8.01	30.0	2.64	37.1	87.0
3	1	-1	1	-1	8.06	49.0	5.13	83.5	128.0
4	1	1	1	1	8.03	35.0	2.96	63.3	111.0

A - Alum Sludge Dose

B - Polymer Dose

Effect	pH	Turbidity	P	SS	BOD
Mean	8.03	40.5	4.00	59.3	110.3
Main Effects					
Alum Sludge Dose, A	-0.03	-16.0	-2.41	-18.2	-22.5
Polymer Dose, B	0.03	3.0	0.09	28.2	18.5
Two-Factor Interaction					
A x B	-0.01	2.0	0.24	-2.1	5.5

Table I.21 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #5, Alum Sludge and Raw Influent.

Analysis of Variance For Turbidity

**95% Confidence
F(0.05,1,2) = 18.51**

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	256	256	256.0	Yes
B	1	9	9	9.0	No
AB	1	4	4	4.0	No
Total	3	269			
Error	2	2		1	

Analysis of Variance For Phosphorus

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	5.784025	5.784025	347.7	Yes
B	1	0.007225	0.007225	0.4	No
AB	1	0.055225	0.055225	3.3	No
Total	3	5.846475			
Error	2	0.0333		0.0166	

Analysis of Variance For Suspended Solids

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	329.4225	329.4225	111.2	Yes
B	1	798.0625	798.0625	269.3	Yes
AB	1	4.2025	4.2025	1.4	No
Total	3	1131.6875			
Error	2	5.9267		2.9633	

Analysis of Variance For Biochemical Oxygen Demand

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	506.25	506.25	60.8	Yes
B	1	342.25	342.25	41.1	Yes
AB	1	30.25	30.25	3.6	No
Total	3	878.75			
Error	2	16.6667		8.3333	

Table I.22 Results Summary Table for Jar Test #6, Lime Sludge and Raw Influent, Factorial Design.

Initial Analyses:

pH = 7.96
 Turbidity = 87 NTU
 11.64 mg PO₄-P/L
 Suspended Solids = 380 mg/L

Total Hardness = 191 mg/L (as CaCO₃)
 Total Alkalinity = 298 mg/L (as CaCO₃)

Jar	Lime Sludge Dose (mg/L*)	Polymer Dose (mg/L)	pH	Turb. (NTU)	Phosphorus (mg PO ₄ -P/L)	S.S. (mg/L)
1	200	0	7.90	78.0	7.13	83.9
2	800	0	7.98	110.0	6.36	140.2
3	200	1	7.92	75.0	7.44	75.0
4	800	1	7.98	100.0	6.59	156.7
5	500	0.5	7.94	92.0	6.59	115.0
6	500	0.5	7.96	94.0	6.51	110.0
7	500	0.5	8.01	97.0	6.92	127.5

Center Point Replicates ----->	MEAN	94.3	6.67	117.5
	SDEV	2.517	0.217	9.014
	M.S.	6.3333	0.0472	81.2500

Rapid Mixing Lime Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Rapid Mixed Polymer for 15 seconds @ 100 rpm following 30 seconds of Rapid Mixing Lime
 Raw Influent
 Lime Sludge did not mix well in stock solution, majority of solids were suspended rather than dissolved
 * - mg Ca-Ca(OH)₂ /L

Table I.23 Table of Signs and Effects for Jar Test #6, Lime Sludge and Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS
1	1	-1	-1	1	7.90	78.0	7.13	83.9
2	1	1	-1	-1	7.98	110.0	6.36	140.2
3	1	-1	1	-1	7.92	75.0	7.44	75.0
4	1	1	1	1	7.98	100.0	6.59	156.7

A - Lime Sludge Dose

B - Polymer Dose

Effect	pH	Turbidity	P	SS
Mean	7.95	90.8	6.88	114.0
<u>Main Effects</u>				
Lime Sludge Dose, A	0.07	28.5	-0.81	69.0
Polymer Dose, B	0.01	-6.5	0.27	3.8
<u>Two-Factor Interaction</u>				
A x B	-0.01	-3.5	-0.04	12.7

Table I.24 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #6, Lime Sludge and Raw Influent.

Analysis of Variance For Turbidity					
<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	812.25	812.25	128.2	Yes
B	1	42.25	42.25	6.7	No
AB	1	12.25	12.25	1.9	No
Total	3	866.75			
Error	2	12.6667	6.3333		

95% Confidence
F(0.05,1,2) = 18.51

Analysis of Variance For Phosphorus					
<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	0.6561	0.6561	13.9	No
B	1	0.0729	0.0729	1.5	No
AB	1	0.0016	0.0016	0.0	No
Total	3	0.7306			
Error	2	0.0945	0.0472		

Analysis of Variance For Suspended Solids					
<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	4761	4761	58.6	Yes
B	1	14.44	14.44	0.2	No
AB	1	161.29	161.29	2.0	No
Total	3	4936.73			
Error	2	162.5000	81.2500		

Table I.25 Results Summary Table for Jar Test #7, Alum and Alum Sludge in Raw Influent, Factorial Design.

Initial Analyses:

pH = 8.37
 Turbidity = 95 NTU
 13.68 mg PO4-P/L
 Suspended Solids = 585 mg/L

BOD = 331 mg/L
 F.C.'s = 3.51E+06
 NH3 = 39.093 mg/L
 TKN = 45.267 mg/L

Jar	Alum/Sludge Polymer (mg/L*)	(mg/L)	pH	Turb. (NTU)	PO4-P (mg/L)	S.S. (mg/L)	BOD (mg/L)	Fecal Coliform	NH3 (mg/L)	TKN (mg/L)
1	150	0	7.52	41.0	3.97	66.6	108.0	1.12E+05	35.544	49.280
2	300	0	7.17	22.0	1.61	31.6	74.0	1.28E+05	37.572	45.267
3	150	1	7.54	33.0	3.47	50.2	120.0	9.36E+05	37.268	49.074
4	300	1	7.17	16.0	1.31	23.8	91.0	4.63E+04	38.028	48.045
5	225	0.5	7.34	30.0	2.87	49.9	98.0	5.29E+05	38.079	47.222
6	225	0.5	7.32	30.0	2.69	50.0	94.0	4.45E+05	36.862	47.222
7	225	0.5	7.32	28.0	2.75	50.1	90.0	4.59E+05	39.093	47.531

Center Point Replicates ---	MEAN	29.3	2.77	50.0	94.0	5.677876	38.011	47.325
	SDEV	1.155	0.092	0.100	4.000	0.040042	1.117	0.178
	M.S.	1.3333	0.0084	0.0100	16.0000	0.001603	1.248	0.032

Note: fecal coliform statistics are calculated from the logs of the counts.

Rapid Mixing Alum/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Rapid Mixed Polymer for 15 seconds @ 100 rpm following 30 seconds of Rapid Mixing Alum
 Raw Influent
 Alum and Alum Sludge were added to jars separately

* - 50% mg Al-Al2(SO4)3 • 14H2O /L (alum sludge)
 - 50% mg Al2(SO4)3 • 14H2O /L (alum)

Table I.26 Table of Signs and Effects for Jar Test #7, Alum and Alum Sludge in Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS	BOD	log FC	NH3	TKN
1	1	-1	-1	1	7.52	41.0	3.97	66.6	108.0	5.05	35.54	49.28
2	1	1	-1	-1	7.17	22.0	1.61	31.6	74.0	5.11	37.57	45.27
3	1	-1	1	-1	7.54	33.0	3.47	50.2	120.0	5.97	37.27	49.07
4	1	1	1	1	7.17	16.0	1.31	23.8	91.0	4.67	38.03	48.05

A - Alum/Sludge Dose
 B - Polymer Dose

Effect	pH	Turbidity	P	SS	BOD
Mean	7.35	28.0	2.59	43.1	98.3
<u>Main Effects</u>					
Alum/Sludge Dose, A	-0.36	-18.0	-2.26	-30.7	-31.5
Polymer Dose, B	0.01	-7.0	-0.40	-12.1	14.5
<u>Two-Factor Interaction</u>					
A x B	-0.01	1.0	0.10	4.3	2.5

Effect	log FC	NH3	TKN
Mean	5.20	37.1	47.92
<u>Main Effects</u>			
Alum/Sludge Dose, A	-0.62	1.4	-2.52
Polymer Dose, B	0.24	1.1	1.29
<u>Two-Factor Interaction</u>			
A x B	-0.68	-0.6	1.49

Table I.27 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #7, Alum and Alum Sludge in Raw Influent.

Analysis of Variance For Turbidity

95% Confidence
F(0.05,1,2) = 18.51

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	324	324	243.0	Yes
B	1	49	49	36.8	Yes
AB	1	1	1	0.8	No
Total	3	374			
Error	2	2.6667	1.3333		

Analysis of Variance For Phosphorus

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	5.1076	5.1076	608.0	Yes
B	1	0.16	0.16	19.0	Yes
AB	1	0.01	0.01	1.2	No
Total	3	5.2776			
Error	2	0.0168	0.0084		

Analysis of Variance For Suspended Solids

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	942.49	942.49	94249.0	Yes
B	1	146.41	146.41	14641.0	Yes
AB	1	18.49	18.49	1849.0	Yes
Total	3	1107.39			
Error	2	0.0200	0.0100		

Analysis of Variance For Biochemical Oxygen Demand

Source	D.F.	Sum of Squares	Mean Square	F-Ratio	Significant
A	1	992.25	992.25	62.0	Yes
B	1	210.25	210.25	13.1	No
AB	1	6.25	6.25	0.4	No
Total	3	1208.75			
Error	2	32.0000	16.0000		

Table I.27 (continued)

Analysis of Variance For Log Fecal Coliforms

95% Confidence F(0.05,1,2) = 18.51

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	0.389190638	0.389190638	242.7	Yes
B	1	0.057702969	0.057702969	36.0	Yes
AB	1	0.464910425	0.464910425	290.0	Yes
Total	3	0.911804033			
Error	2	0.0032	0.0016		

Analysis of Variance For Ammonia

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	1.943236	1.943236	1.6	No
B	1	1.1881	1.1881	1.0	No
AB	1	0.401956	0.401956	0.3	No
Total	3	3.533292			
Error	2	2.496	1.248		

Analysis of Variance For Total Kjeldahl Nitrogen

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	6.355441	6.355441	199.7	Yes
B	1	1.653796	1.653796	52.0	Yes
AB	1	2.226064	2.226064	69.9	Yes
Total	3	10.235301			
Error	2	0.064	0.032		

Table I.28 Results Summary Table for Jar Test #8, Lime and Lime Sludge in Raw Influent, Factorial Design.

Initial Analyses:

pH = 7.91 BOD = 370 mg/L
 Turbidity = 89 NTU F.C.'s = 1.95E+06
 12.60 mg PO₄-P/L
 Suspended Solids = 447 mg/L

Jar	Lime/Sludge (mg/L*)	Polymer (mg/L)	pH	Turb. (NTU)	Phosphorus (mg PO ₄ -P/L)	S.S. (mg/L)	BOD (mg/L)	Fecal Coliform
1	200	0	9.36	86.0	6.18	124.0	n/a	n/a
2	400	0	9.84	53.0	4.78	70.8	127.0	1.18E+06
3	200	1	9.38	61.0	5.81	102.0	n/a	n/a
4	400	1	9.84	48.0	3.93	58.3	132.0	9.32E+05
5	300	0.5	9.63	58.0	4.95	70.0	n/a	n/a
6	300	0.5	9.62	59.0	4.95	68.0	n/a	n/a
7	300	0.5	9.60	59.0	5.21	70.0	n/a	n/a

Center Point Replicates -----	MEAN	58.7	5.04	69.3
	SDEV	0.577	0.150	1.155
	M.S.	0.3333	0.0225	1.3333

Rapid Mixing Lime/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Rapid Mixed Polymer for 15 seconds @ 100 rpm following 30 seconds of Rapid Mixing Lime
 Raw Influent
 Lime and Lime Sludge were added to jars separately

* - 50% mg Ca-Ca(OH)₂ /L (lime sludge)
 - 50% mg Ca(OH)₂ /L (lime)

Table I.29 Table of Signs and Effects for Jar Test #8, Lime and Lime Sludge in Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS
1	1	-1	-1	1	9.36	86.0	6.18	124.0
2	1	1	-1	-1	9.84	53.0	4.78	70.8
3	1	-1	1	-1	9.38	61.0	5.81	102.0
4	1	1	1	1	9.84	48.0	3.93	58.3

A - Lime/Sludge Dose

B - Polymer Dose

Effect	pH	Turbidity	P	SS
Mean	9.61	62.0	5.18	88.8
Main Effects				
Lime/Sludge Dose, A	0.47	-23.0	-1.64	-48.5
Polymer Dose, B	0.01	-15.0	-0.61	-17.3
Two-Factor Interaction				
A x B	-0.01	10.0	-0.24	4.8

Table I.30 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #8, Lime and Lime Sludge in Raw Influent.

**95% Confidence
F(0.05,1,2) = 18.51**

Analysis of Variance For Turbidity

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	529	529	1587.0	Yes
B	1	225	225	675.0	Yes
AB	1	100	100	300.0	Yes
Total	3	854			
Error	2	0.6667	0.3333		

Analysis of Variance For Phosphorus

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	2.6896	2.6896	119.4	Yes
B	1	0.3721	0.3721	16.5	No
AB	1	0.0576	0.0576	2.6	No
Total	3	3.1193			
Error	2	0.0451	0.0225		

Analysis of Variance For Suspended Solids

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	2347.4025	2347.4025	1760.6	Yes
B	1	297.5625	297.5625	223.2	Yes
AB	1	22.5625	22.5625	16.9	No
Total	3	2667.5275			
Error	2	2.6667	1.3333		

Table I.31 Results Summary Table for Jar Test #9, Alum and Raw Influent, Factorial Design.

Initial Analyses:

pH = 8.01
 Turbidity = 95 NTU
 11.75 mg PO₄-P/L
 Suspended Solids = 500 mg/L

BOD = 408 mg/L
 F.C.'s = 2.46E+06
 NH₃ = 41.627 mg/L
 TKN = 71.811 mg/L

Jar	Alum (mg/L*)	Polymer (mg/L)	pH	Turb. (NTU)	PO ₄ -P (mg/L)	S.S. (mg/L)	BOD (mg/L)	Fecal Coliform	NH ₃ (mg/L)	TKN (mg/L)
1	75	0	7.39	56.0	6.15	102.0	n/a	n/a	40.917	55.556
2	150	0	7.09	17.0	1.62	30.0	100.0	8.60E+04	41.729	51.029
3	75	1	7.40	44.0	5.13	66.0	n/a	n/a	42.641	51.235
4	150	1	7.09	13.0	1.09	20.4	111.0	5.36E+04	40.208	47.119
5	112.5	0.5	7.22	34.0	3.43	44.7	n/a	n/a	42.641	55.556
6	112.5	0.5	7.24	29.0	3.40	38.0	n/a	n/a	42.134	56.790
7	112.5	0.5	7.22	31.0	3.47	42.0	n/a	n/a	43.756	53.292

Center Point Replicates	MEAN	31.3	3.43	41.6		42.844	55.213
	SDEV	2.517	0.035	3.371		0.830	1.774
	M.S.	6.3333	0.0012	11.3633		0.689	3.147

Rapid Mixing Alum 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Rapid Mixed Polymer for 15 seconds @ 100 rpm following 30 seconds of Rapid Mixing Alum
 Raw Influent

* - mg Al₂(SO₄)₃ • 14H₂O /L (alum)

Table I.32 Table of Signs and Effects for Jar Test #9, Alum and Raw Influent.

Table of Signs

JAR	MEAN	A	B	AB	pH	TURB.	P	SS	BOD	FC	NH3	TKN
1	1	-1	-1	1	7.39	56.0	6.15	102.0	n/a	n/a	40.92	55.56
2	1	1	-1	-1	7.09	17.0	1.62	30.0	100.0	8.60E+04	41.73	51.03
3	1	-1	1	-1	7.40	44.0	5.13	66.0	n/a	n/a	42.64	51.24
4	1	1	1	1	7.09	13.0	1.09	20.4	111.0	5.36E+04	40.21	47.12

A - Alum Dose
B - Polymer Dose

Effect	pH	Turbidity	P	SS	BOD
Mean	7.24	32.5	3.50	54.6	105.5
<u>Main Effects</u>					
Alum Dose, A	-0.31	-35.0	-4.29	-58.8	n/a
Polymer Dose, B	0.00	-8.0	-0.78	-22.8	n/a
<u>Two-Factor Interaction</u>					
A x B	-0.01	4.0	0.25	13.2	n/a

Effect	F.C.	NH3	TKN
Mean	6.98E+04	41.4	51.23
<u>Main Effects</u>			
Alum Dose, A	n/a	-0.8	-4.32
Polymer Dose, B	n/a	0.1	-4.12
<u>Two-Factor Interaction</u>			
A x B	n/a	-1.6	0.21

Table I.33 Analysis of Variance Tables for Main Effects and Interactions of Jar Test #9, Alum and Raw Influent.

Analysis of Variance For Turbidity **95% Confidence
F(0.05,1,2) = 18.51**

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	1225	1225	193.4	Yes
B	1	64	64	10.1	No
AB	1	16	16	2.5	No
Total	3	1305			
Error	2	12.6667	6.3333		

Analysis of Variance For Phosphorus

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	18.361225	18.361225	14887.5	Yes
B	1	0.600625	0.600625	487.0	Yes
AB	1	0.060025	0.060025	48.7	Yes
Total	3	19.021875			
Error	2	0.0025	0.0012		

Analysis of Variance For Suspended Solids

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	3457.44	3457.44	304.3	Yes
B	1	519.84	519.84	45.7	Yes
AB	1	174.24	174.24	15.3	No
Total	3	4151.52			
Error	2	22.7267	11.3633		

Table I.33 (continued)

Analysis of Variance For Ammonia

95% Confidence
F(0.05,1,2) = 18.51

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	0.65691025	0.65691025	1.0	No
B	1	0.01030225	0.01030225	0.0	No
AB	1	2.63250625	2.63250625	3.8	No
Total	3	3.29971875			
Error	2	1.377	0.689		

Analysis of Variance For Total Kjeldahl Nitrogen

<u>Source</u>	<u>D.F.</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F-Ratio</u>	<u>Significant</u>
A	1	18.67536225	18.67536225	5.9	No
B	1	16.93734025	16.93734025	5.4	No
AB	1	0.04223025	0.04223025	0.0	No
Total	3	35.65493275			
Error	2	6.295	3.147		

Table I.34 Results Summary Table for Jar Test #10, Alum and Alum Sludge, Filtered and Unfiltered Raw Influent.

Initial Analyses:											
Unfiltered						Filtered					
pH = 7.80			F.C.'s = 7.42E+06			pH = 7.98			F.C.'s = 3.08E+06		
Turbidity = 99 NTU			NH3 = 34.632 mg/L			Turb.= 21 NTU			NH3 = 36.254 mg/L		
11.86 mg PO4-P/L			TKN = 67.490 mg/L			6.20 mg PO4-P/L					
Suspended Solids = 537 mg/L						BOD = 76 mg/L			TKN = 48.971 mg/L		
BOD = 303 mg/L											

Jar	Alum (mg/L*)	Alum Slg. (mg/L**)	Sldg.	pH	Turb. (NTU)	PO4-P (mg/L)	S.S. (mg/L)	BOD (mg/L)	Fecal Coliform	NH3 (mg/L)	TKN (mg/L)
1	150	0	unfil.	6.95	8.0	0.96	19.1	53.0	2.32E+04	36.051	51.029
2	75	0	fil.	7.39	26.5	5.19	49.3	63.0	6.29E+05	33.618	47.737
3	150	150	unfil.	6.99	7.5	0.82	18.3	16.0	1.69E+04	32.706	38.724
4	75	75	fil.	7.39	22.0	4.20	39.2	58.0	5.49E+05	33.213	45.267
5	0	750	unfil.	7.72	28.0	3.13	35.5	67.0	9.81E+05	32.706	47.942
6	0	375	fil.	7.96	19.0	4.48	21.0	53.0	1.22E+06	33.618	47.119

Rapid Mixing Alum/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Alum and Alum Sludge added to jars 3 & 4 separately
 Raw Influent

* - mg Al₂(SO₄)₃ • 14H₂O /L
 ** - mg Al - Al₂(SO₄)₃ • 14H₂O /L

Table I.35 Results Summary Table for Jar Test #11, Alum and Alum Sludge, Filtered and Unfiltered Raw Influent.

Initial Analyses:

<p>Unfiltered pH = 7.77 Turbidity = 105 NTU 12.08 mg PO4-P/L Suspended Solids = 350 mg/L</p>	<p>Filtered pH = 7.99 Turbidity = 22 NTU 5.65 mg PO4-P/L</p>
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Jar	Alum Dose (mg/L*)	Alum Sludge Dose (mg/L**)	pH	Turb. (NTU)	Phosphorus (mg PO4-P/L)	SS (mg/L)
1	150	0	fil. 6.89	5.1	0.72	6.2
2	150	150	fil. 6.93	4.5	0.57	5.8
3	0	750	fil. 7.88	15.0	2.24	10.3
4	100	0	fil. 7.18	23.0	3.56	31.5
5	100	100	fil. 7.18	21.0	3.05	29.1
6	100	100	unfil. 7.07	27.0	2.95	45.0

Rapid Mixing Alum/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Alum and Alum Sludge added to jars 2, 5, & 6 separately
 Raw Influent

* - mg Al₂(SO₄)₃ • 14H₂O /L
 ** - mg Al - Al₂(SO₄)₃ • 14H₂O /L

Table I.36 Results Summary Table for Jar Test #12, Alum and Alum Sludge in Raw Influent.

Initial Analyses:

pH = 8.04
 Turbidity = 105 NTU
 11.59 mg PO₄-P/L
 Suspended Solids = 523 mg/L
 BOD = 402 mg/L
 F.C.'s = 2.79E+06

Jar	Alum (mg/L*)	Alum Sludge (mg/L**)	pH	Turb. (NTU)	Phosphorus (mg PO ₄ -P/L)	SS (mg/L)	BOD (mg/L)	Fecal Coliform
1	125	0	7.16	30.0	3.30	56.3	124.0	3.92E+05
2	125	125	7.18	27.0	2.97	43.0	112.0	3.77E+04
3	100	200	7.30	36.0	3.70	53.8	n/a	n/a
4	125	250	7.21	26.0	2.52	37.3	n/a	n/a
5	100	300	7.31	35.0	3.41	53.3	126.0	8.08E+05
6	75	400	7.43	36.0	3.55	54.2	n/a	n/a
7	150	0	7.10	17.0	1.71	24.7	115.0	1.15E+05

Rapid Mixing Alum/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Alum and Alum Sludge added to jars separately
 Raw Influent

* - mg Al₂(SO₄)₃ • 14H₂O /L
 ** - mg Al - Al₂(SO₄)₃ • 14H₂O /L

Table I.37 Results Summary Table for Jar Test #13, Alum and Alum Sludge in Raw Influent.

Initial Analyses:

pH = 7.75
 Turbidity = 82 NTU
 7.66 mg PO₄-P/L
 Suspended Solids = 300 mg/L

Jar	Alum Dose (mg/L*)	Alum Sludge Dose (mg/L**)	Initial pH	Polymer (mg/L)	Final pH	Turb. (NTU)	Phosphorus (mg PO ₄ -P/L)	SS (mg/L)
1	150	0	8.22	0	6.74	5.6	0.60	10.0
2	150	0	8.06	0	6.73	5.7	0.54	10.8
3	150	0	7.82	0	6.69	5.0	0.52	8.8
4	150	0	7.58	0	6.62	4.9	0.62	8.6
5	150	0	7.82	0.5	6.67	4.8	0.44	8.7
6	150	150	7.81	0	6.69	4.5	0.35	8.3
7	150	150	7.82	0.5	6.71	5.1	0.44	9.7
8	0	0	7.86	0	7.75	46.0	5.53	66.0

Rapid Mixing Alum/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Alum and Alum Sludge added to jars separately
 Raw Influent

* - mg Al₂(SO₄)₃ • 14H₂O /L

** - mg Al - Al₂(SO₄)₃ • 14H₂O /L

Table I.38 Results Summary Table for Jar Test #13 Sludge Properties.

Initial Analyses:

pH = 7.75
 Turbidity = 82 NTU
 7.66 mg PO₄-P/L
 Suspended Solids = 300 mg/L

Jar	Alum Dose (mg/L*)	Alum Sludge Dose (mg/L**)	Polymer Dose (mg/L)	Phosphorus (mg PO ₄ -P/L)	SS (mg/L)	Approx. Sludge Volume (mL***)	Calc. Sludge Volume (mL***)
3	150	0	0	124	6517	105	116
5	150	0	0.5	155	8367	80	93
6	150	150	0	117	7500	110	125
7	150	150	0.5	135	9567	95	107
8	0	0	0	149	13017	30	30

Rapid Mixing Alum/Sludge 45 seconds @ 100 rpm
 Flocculation Mixing 20 minutes @ 30 rpm
 Settling Time = 30 minutes
 Alum and Alum Sludge added to jars separately
 Raw Influent

* - mg Al₂(SO₄)₃ • 14H₂O /L
 ** - mg Al - Al₂(SO₄)₃ • 14H₂O /L
 *** - 2 litre jar volume

APPENDIX II - ANALYTICAL TESTING METHODS

Most of the analytical procedures followed throughout the experimental program were as outlined in *Standard Methods for the Examination of Water and Wastewater*, 17th Ed., 1989. These procedures are listed and referenced in Table II.1.

Total phosphorus concentrations were determined in the University of Alberta Mobile Laboratory at the Gold Bar Wastewater Treatment Plant with some testing being replicated by the City's Gold Bar Laboratory. A persulphate digestion followed by the ascorbic acid colourimetric method was used for all jar test samples, some of the preliminary testing was done using the stannous chloride colourimetric method. Turbidity, suspended solids, and pH were all determined in the University Lab at Gold Bar. BODs and fecal coliforms were determined in the Newton Research Building on the U of A campus. All nitrogen forms were determined by an autoanalyser in the City's Gold Bar Laboratory. Total hardness and alkalinity determinations were done either at private labs or at the City's Rossdale Water Treatment Plant Laboratory.

Instrumented analyses carried out are listed in Table II.2

Wastewater Phosphorus Reduction by Coagulant Addition

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Table II.1 Standard Methods used in Chemical Phosphorus Removal Study.

<u>Parameter</u>	<u>Test Method</u>	<u>Standard Methods Test #</u>
BOD	Biochemical Oxygen Demand	5210
	Dissolved Oxygen (Azide Modification, i.e. Winkler T.)	4500-O C
Fecal Coliform	Fecal Coliform Membrane Filter Procedure	9222 D
Total Phosphorus	Sample Preparation, Persulphate Digestion	4500-P B
	Ascorbic Acid Method	4500-P E
Suspended Solids	Total Suspended Solids Dried at 103-105° C	2540 D
Turbidity	Nephelometric Method	2130 B

Table II.2 Instrumented Analysis used in the Chemical Phosphorus Removal Study.

<u>Parameter</u>	<u>Instrument</u>
Ammonia (NH ₃)	Technicon Automatic Analyser II
Nitrite (NO ₂ -N)	TRAACS 800 Autoanalyser
Nitrate (NO ₃ -N)	TRAACS 800 Autoanalyser
Orthophosphate (PO ₄ -P)	Bausch & Lomb Spectronic 20 spectrophotometer
pH	Fisher Accumet, Model 805 MP pH meter
Total Kjeldahl Nitrogen	Technicon Automatic Analyser II
Turbidity	Hach Model 2100A turbidimeter

APPENDIX III - EXAMPLE OF FACTORIAL ANALYSIS

The phosphorus removal results from Jar Test #2 will be used to demonstrate the statistical analysis of a 2² factorial design experiment. This will include calculation of the main effects and interactions, and the analysis of variance. The variables investigated were:

- alum dose; and
- polymer dose.

Two-level factorial design requires that each variable be set at a high and low level in order that its effect may be quantified. The high and low levels chosen for Jar Test #2 are shown in Table III.1.

Table III.1 Levels of Variables for Phosphorus Removal in Factorial Design Jar Test #2.

	<u>Low Level</u>	<u>High Level</u>
Alum Dose (mg/L)	100	300
Polymer Dose (mg/L)	0	1

The results of the four runs (2²) are contained in Table III.2 along with three center point replicates, note that the dosing levels of these replicates is the mean of the high and low levels for each parameter.

Table III.2 Phosphorus Removal Results for Factorial Design Jar Test #2.

Jar	Alum Dose (mg/L)	Poly Dose (mg/L)	Phosphorus (mg/L)
1	100	0	4.27
2	300	0	0.45
3	100	1	2.79
4	300	1	0.22
5	200	0.5	0.40
6	200	0.5	0.30
7	200	0.5	0.35

From Table III.2 it can be seen that the only difference between jar number 1 and jar number 2 is the alum dose used. It is therefore assumed that the difference in phosphorus between the two jars is due to this difference in alum dose. Hence, it appears that increasing the alum dose from 100 mg/L to 300 mg/L caused a decrease in effluent phosphorus from 4.27 mg/L to 0.45 mg/L, a difference of -3.82 mg/L.

Similarly, the change in removal between jars 3 and 4 can be calculated as -2.57 mg/L. The minus signs indicate an increase in phosphorus removal. Thus, the average effect of changing the alum dose from 100 mg/L to 300 mg/L can be calculated. This quantity is termed the main effect of the alum dose and is calculated below:

$$1/2(-3.82 - 2.57) = -3.20 \text{ mg/L} \tag{III.1}$$

On average, increasing the alum dose from 100 mg/L to 300 mg/L produces a decrease in effluent phosphorus of 3.20 mg/L. The relative magnitude of this number is high indicating that alum dosing is likely significant in removing phosphorus. Considering jars 1 and 3, and 2 and 4 the main effect of polymer dosing can be calculated in a similar way yielding a result of -0.86 mg/L.

Calculation of the alum dose main effect showed that the same change in alum dose did not always produce the same change in effluent phosphorus concentration. The difference was more than could be explained by experimental error alone (as indicated by the center point replicates). The only other change in the system was the polymer dose. The variables are said to have interacted and this interaction can be quantified in the same manner as the main effects were.

Consider the influence changing the polymer dose has on increasing the alum dose. Firstly, the effect of changing polymer while the alum is at its low setting is checked, this is the difference between jars 1 and 3 which is 1.48 mg/L. Next, the effect of changing polymer while the alum is at its high setting is checked, this is the difference between jars 2 and 4 which is 0.23 mg/L. It can be seen that a difference of 1.25 mg/L exists (1.48 - 0.23) in alum dose effect as a result of increasing polymer dose. Half this number (0.63 mg/L) is by convention termed the alum dose x polymer dose interaction.

For larger factorial designs there exists more than one two level interaction and higher interactions such as three or more. The number of main effects and interactions total the same as the number of degrees of freedom in the system with the degree of the highest level interaction being the same as the number of parameters being tested. For instance, a 2^4 factorial experiment would have a total of 16 runs with 15 degrees of freedom. There would be 4 main effects, 6 two factor interactions, 4 three factor interactions, and 1 four factor interaction for a total of 15.

It can easily be shown that a two level interaction (or any other level for that matter) is the same in either direction, i.e. the alum dose x polymer dose interaction has the same value as the polymer dose x alum dose interaction. Three level interactions and higher are generally small and usually considered to be insignificant. In fact, they are often used as a measure of the experimental error when other means are unavailable.

Table III.3 lists the main effects and interactions for phosphorus removal in Jar Test #2.

Table III.3 Main Effects and Interactions for Phosphorus Removal from Factorial Design Jar Test #2.

<u>Main Effects</u>	<u>mg P/L</u>
Alum Dose, A	-3.20
Polymer Dose, B	-0.86
Interaction	
A x B	0.63
