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Phosphorus Removal From EBPR Sludge Dewatering Liquors Using Lanthanum Chloride, Aluminum Sulfate and Ferric Chloride

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PHOSPHORUS REMOVAL FROM EBPR SLUDGE DEWATERING LIQUORS

USING LANTHANUM CHLORIDE, ALUMINUM SULFATE

AND FERRIC CHLORIDE

by

Michael Strileski

Bachelor of Engineering in Chemical Engineering
McMaster University
2009

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science in Engineering - Civil and Environmental Engineering

Department of Civil and Environmental Engineering and Construction
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Michael Strileski

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ABSTRACT

by

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In wastewater treatment, enhanced biological phosphorus removal (EBPR) is becoming an increasingly popular alternative to chemical precipitation (CP) because of its lower costs and reduced sludge production. However, downstream solids handling processes such as digestion, sludge storage and dewatering promote an undesirable release (i.e. secondary release) of polyphosphate that was stored within EBPR sludge. Released phosphate is recycled to the head of the plant with the liquors of sludge dewatering processes. The concentration of phosphate in recycle streams from EBPR systems can be one to two orders of magnitude higher than the influent phosphorus concentration entering the EBPR system. Plants using EBPR often have to resort to chemical phosphorus removal from the recycle streams to reduce the P loading returning to the EBPR process. The present study addresses the potential of lanthanum chloride as an alternative coagulant for phosphate removal in EBPR sludge dewatering liquors as the use of lanthanum-based coagulants has shown a strong potential for phosphorus precipitation in wastewater applications. The hypothesis is that lanthanum chloride is capable of achieving greater orthophosphate removals than ferric chloride or aluminum sulfate (alum) because lanthanum salts have shown to have a wider effective pH range

and require lower doses than typical coagulants. Results indicate that on a molar basis, lanthanum is capable of removing >99% of orthophosphate from digested and non-digested EBPR sludge dewatering liquors at metal to phosphate ratios of 1:1 and 1.1:1, respectively. Similar removals using aluminum and ferric iron required molar ratios of 1.6:1 or greater. Additionally, in liquors with a high initial ortho-P concentration (>100 mg/L), lanthanum chloride achieved > 85% ortho-P removal at pHs as low as 2, whereas removal efficiency decreased with increasing ferric chloride dose due to pH depression. With alum, phosphate removal was essentially non-existent below pH 3. In liquors with low initial ortho-P concentrations (15 mg/L), ferric iron and lanthanum both achieved approximately 90% ortho-P removal at 2:1 molar doses. Thus, lanthanum chloride has shown to be an effective alternative coagulant in liquors with high initial ortho-P concentrations, but ferric chloride is more practical in liquors with low initial ortho-P concentrations because lanthanum and other rare earth salts are less commercially available and more costly than ferric chloride. However, for high phosphate concentrations, such as the ones present in return streams from EBPR systems, the use of lanthanum is promising. As more rare earth metal mines are open in the United States and abroad, fueled by the demand for these metals used in electronics (e.g. cell and smart phones), rare earth chlorides, which are a by-product of these mines, will become more commercially available at lower prices.

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CHAPTER 1

INTRODUCTION

The excess bioavailability of phosphorus can lead to eutrophication of water bodies and result in algal blooms. As effluent discharge limits become more stringent, there is continued interest in removing phosphorus from wastewater. The most common phosphorus removal treatment technologies are chemical precipitation (CP), enhanced biological phosphorus removal (EBPR), or a combination of the two (Caravelli et al., 2010). Chemical precipitation of phosphorus from wastewater is generally accomplished using metal salt coagulants, such as iron or aluminum, and can be performed at different stages within the treatment process. CP produces an insoluble metal phosphate that can be settled out and removed from water with sedimentation followed by sludge wasting or filtration. Iron (III) and aluminum (III) are often used as they produce good settling flocs within a short period of time (Thistleton et al., 2001). Alternative phosphate removal coagulants tested in the literature include organic polymers such as chitosan and *Moringa Oleifera*, lime, inorganic lanthanide and other rare earth salts and calcium salts (Niquette, 2004).

A critical parameter that determines the effectiveness of CP is pH. Metcalf and Eddy (2003) state that ferric chloride and alum yield good phosphorus removal in the pH range of 6.5 to 7 in practical applications. Other coagulants such as lanthanides have shown to have a wider effective pH range for CP. Phosphate precipitation by lanthanum has been proven effective over a pH range of 4.5 to 8.5 (Recht et al., 1970; Melnyk et al., 1974) and it has been reported that the lanthanum-phosphate complex can be formed in

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solutions with a pH as low as 4, with very low lanthanum and phosphate concentrations (0.695 and 0.15 mg/L, respectively) (Diatloff et al., 1993). Concerns with using lanthanum are that it can be toxic to some aquatic life depending on the concentration and application rate (Douglas et al., 2004).

In wastewater treatment, EBPR is becoming increasingly popular to CP because of its lower costs and reduced sludge production (Paul et al., 2001). During EBPR, volatile fatty acids (VFAs) such as acetate, propionate and butyrate are assimilated by polyphosphate accumulating organisms (PAOs) under anaerobic conditions and orthophosphate is released to the bulk liquid. Then, under aerobic conditions PAOs uptake and store excess phosphate as polyphosphate within the bacterial cells. During the subsequent clarification process, bacterial cells with a high polyphosphate content [2 to 5 times the amount of phosphorus of normal biomass (Rittmann and McCarty, 2001)] are wasted from the process, thereby removing phosphorus from the system.

In EBPR, downstream solids handling processes such as digestion, sludge storage and dewatering can promote an undesirable release (i.e. secondary release) of polyphosphate that was stored within EBPR wasted solids. The concentration of phosphate released from these processes is much greater than influent phosphorus concentrations. For instance, orthophosphate concentrations in dewatering centrate from EBPR digested sludge have been reported at 94.9 mg/L (Jaffer et al., 2002), 151 mg/L (Batista and Jeong, 2006; Marti et al., 2010), 167.1 mg/L (Pastor et al., 2008) and 170 mg/L (Pastor et al., 2010), while influent phosphorus concentrations are typically on the order of 4-12 mg/L (Metcalf and Eddy, 2003). Released phosphate is typically recycled to the head of the plant with the liquors of sludge dewatering processes. As a result,

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plants often have to resort back to chemical phosphorus removal from the recycle streams to reduce the P loading on the EBPR process. Another method used to remove phosphorus released from EBPR solids handling processes and prevent it from being recycled is to fix it in the form of struvite ($MgNH_4PO_4 \cdot 6H_2O$), which is a phosphate mineral that can be economically recovered from wastewaters (Münch and Barr, 2001; Parsons and Doyle, 2004; Marti et al., 2010).

1.1 Knowledge Gap and Hypothesis

The use of lanthanum-based coagulants has shown a strong potential for phosphorus precipitation in wastewater applications (Recht et al., 1970; Taouzi, 1995). However, the use of lanthanum for phosphorus precipitation from EBPR sludge dewatering recycle streams has not been sufficiently investigated. The goal of this research is to address this scientific knowledge gap. Recycle streams often have lower pH and high orthophosphate concentrations (i.e. >100 mg/L), but it has been shown that lanthanum salts have a wider effective pH range and require lower doses than typical coagulants (Recht et al., 1970). Therefore, it is hypothesized that lanthanum chloride will achieve greater orthophosphate removal in EBPR recycle streams than ferric chloride and aluminum sulfate.

1.2   Objectives

This research will focus on using lanthanum chloride as an alternative phosphate removal coagulant in EBPR recycle streams at low pH. The specific objectives of this research are as follows:

1) Perform batch tests to evaluate the effectiveness of lanthanum chloride for orthophosphate removal from low-pH EBPR recycle streams in comparison to ferric chloride and aluminum sulfate.

2) Compare experimental results for each coagulant with predictions of orthophosphate removal from chemical equilibrium models.

3) Communicate the potential benefits and/or limitations of lanthanum-based coagulants in terms of resource scarcity and cost.

CHAPTER 2

STATE OF KNOWLEDGE

2.1 Phosphorus in Wastewater

Phosphorus can be present in wastewater in the form of organic phosphate, orthophosphate or polyphosphate (Caravelli, 2010). In municipal wastewater, phosphorus is present in dissolved and particulate forms, but most occurs as dissolved phosphate and consists of about 50% orthophosphate, 35% condensed phosphates and 15% organic phosphates (Parsons and Smith, 2008). Human and kitchen wastes are the leading sources of phosphorus and account for 30% to 50% of the phosphorus in domestic wastewater (Cheremisinoff, 1994). Industrial wastes and agricultural runoff are other significant contributors of phosphorus in wastewater. As effluent discharge limits become more stringent, there is continued interest in removing phosphorus from wastewater. A typical municipal wastewater in the United States has a total phosphorus concentration of about 4 to 12 mg/L (Metcalf and Eddy, 2003) and needs to be adequately treated before being discharged to receiving waters. Otherwise, the excess bioavailability of phosphorus can lead to eutrophication of water bodies and result in algal blooms.

2.2 Phosphorus Removal Techniques

2.2.1 Chemical Precipitation Using Typical Coagulants

Chemical precipitation (CP) is a physico-chemical process in which di- or tri-valent metal salt coagulants are added to wastewater to precipitate insoluble metal phosphates (Morse et al., 1998). Effective CP processes have been reported to remove up to 90% of

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all influent phosphorus (Thistleton et al., 2002). In CP, the most important parameters to consider are pH and the concentration of metal ion added (Johnson and Amirtharajah, 1983).

Aluminum and iron salts are the most common coagulants used in CP as they produce good settling flocs within a short period of time (Thistleton et al., 2001). The addition of these coagulants to waters can remove phosphate by precipitation of metal phosphates as shown in equation 2.1:

$$Me^{3+} + H_nPO_4^{3-n} \leftrightarrow MePO_4 \text{ (s)} + nH^+ \qquad (2.1)$$

Furthermore, if particulate phosphate or other particulates are present, these coagulants destabilize colloidal materials and allow small particles to form larger, more settleable flocs that can be removed through sedimentation followed by solids wasting or filtration. Additionally, metal ions in excess of that required to form metal-phosphates can form precipitates with the hydroxyl (OH^-) ion to form metal-hydroxides [i.e. $Fe(OH)_3$ and $Al(OH)_3$] if the pH is favorable (Eqn 2.2 and 2.3). Dissolved phosphate can also be removed by adsorption onto the particulates of iron and aluminum hydroxides (Fettig et al., 1997; Smith et al., 2007).

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 \text{ (am)} \downarrow + 3H^+ \qquad (2.2)$$

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 \text{ (am)} \downarrow + 3H^+ \qquad (2.3)$$
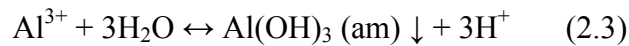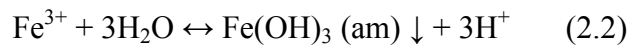
.   In practice, the precipitates that form are more complex and are a mixture from both the metal-hydroxide and metal-phosphate reactions (Parsons and Smith, 2008):

$$Me^{3+} \text{ (aq)} + yH_2O + xPO_4^{3-} \leftrightarrow Me(OH)_y(PO_4)_x \text{ (s)} + yH^+ \qquad (2.4)$$

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For phosphorus removal, $Al_{0.8}(H_2PO_4)(OH)_{1.4}$ and $Fe_{1.6}(H_2PO_4)(OH)_{3.8}$ are assumed to represent the precipitates formed after alum and ferric chloride addition, respectively (WEF and ASCE, 2009).

CP is a versatile phosphorus removal method as it can be applied at several different stages in the wastewater treatment process. Most commonly, metal-salts are dosed directly into the influent wastewater, added to the aeration basin, or applied to the mixed liquor prior to sedimentation. Also, ferric and ferrous chloride, alum, or organic polymers are commonly added to secondary wastewater effluent- before filtration- to aid in phosphorus removal. This practice is common in systems that remove phosphorus biologically (EBPR = enhanced biological phosphorus removal), but want to assure phosphate contained in biological solids is removed by coagulation/filtration.

Lime is also an effective phosphorus removal coagulant; however, sufficient amounts of lime must be added to raise the solution pH to at least 10. Due to the large sludge volumes produced and the operational and maintenance problems associated with the handling, storage, and feeding of lime, the use of lime for phosphorus removal is declining (EPA, 2000; Metcalf & Eddy, 2003).

2.2.1.1 The Effect of pH and Alkalinity

Scientists have known for a long time (Hudson and Wolfner, 1967) that coagulants hydrolize and polymerize very quickly once added to water, so pH decreases occur almost instantaneously. When a metal-salt is added to wastewater it acts as an acid and consumes alkalinity during phosphate precipitation. Fe^{3+} and Al^{3+} (as in ferric chloride

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and alum) consume three base equivalents per mole of metal added in the formation of metal-hydroxides:

$$Al_2(SO_4)_3 \cdot 14H_2O + 6HCO_3^- \rightarrow 2Al(OH)_3 \text{ (am) } \downarrow + 3SO_4^{2-} + 6CO_2 + 14H_2O \quad (2.5)$$

$$FeCl_3 \cdot 6H_2O + 3HCO_3^- \rightarrow Fe(OH)_3 \text{ (am) } \downarrow + 3Cl^- + 3CO_2 + 6H_2O \quad (2.6)$$
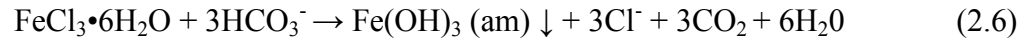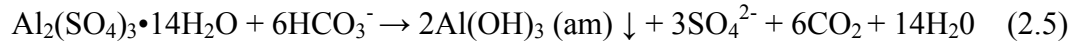
Particularly in low alkalinity waters, pH depression is an important consideration. Bases such as lime, sodium hydroxide or soda ash can be added to replenish alkalinity and increase the pH if necessary.

At alkaline pH values (pH 7-10) the surface of metal-hydroxides is more negatively charged, resulting in the formation of soluble metal-hydroxide complexes [i.e. $Me(OH)_4^-$] (Smith and Szabo, 2007). The adsorption of anionic phosphates on negatively charged metal-hydroxides is not favored, so with increasing pH, phosphorus removal efficiency decreases. At acidic pH, there is limited precipitation of metal hydroxides and soluble phosphate complexes form [i.e. $MeHPO_4^+$ and $MeH_2PO_4^{2+}$] (Smith and Szabo, 2007). In addition, phosphates that have precipitated can dissolve as the solution pH decreases. Thus, overdosing coagulants can lead to substantial pH decreases and reduced treatment efficacy

Metcalf and Eddy (2003) state that ferric chloride and alum yield good phosphorus removal in the pH range of 6.5 to 7 in practical applications. However, throughout the literature effective pH ranges for CP with these coagulants is quite variable. For instance, reported optimal pH values for removing phosphorus with ferric chloride range between 4 and 9 (Caravelli et al., 2010). The large range of effective pH can be attributed to the varying characteristics of wastewaters and different conditions used in phosphorus

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removal. More commonly, effective pH ranges for alum and ferric chloride are nearer 5.5 to 6.5 and 4.5 to 5.0, respectively (WEF and ASCE, 2009), which are closer to the pH of minimum solubility of their metal-phosphates (approximately pH 6.3 for $AlPO_4(s)$ and 5.3 for $FePO_4(s)$).

2.2.1.2 Coagulant Dose

Based on reaction stoichiometry (Eqn 2.1), an iron-to-phosphate or aluminum-to-phosphate mole ratio of 1:1 should be required to form metal-phosphate precipitates. However, to achieve 80 to 98% soluble phosphate removal from wastewater containing a typical initial soluble phosphate concentration, metal-to-phosphate molar doses greater than 1.5 to 2 are usually required (Szabo et al., 2008). To obtain very low residual orthophosphate concentrations (<0.1 mg/L), metal doses much greater than 1:1 are required (Szabo et al., 2008). This is due to the many competing reactions occurring alongside the production of insoluble metal phosphates during CP. Hydrolysis products of iron and aluminum react with other ligands such as SO_4^{2-} or natural organic matter (NOM) to form soluble or insoluble products (MWH, 2005). These competing reactions reduce the availability of metal ions available for phosphate precipitation, which affects the dose of coagulant required. Thus, the dose of metal salt cannot be calculated based on the phosphate concentration of the solution, rather it is best if it is determined in the laboratory for each individual case (Metcalf and Eddy, 2003).

2.2.1.3 Solids Considerations

The formation of precipitates from CP means that there will be an increase in the mass and volume of sludge produced. When CP is performed, up to 95% more sludge is generated (Yeoman et al., 1988). The sludge that is generated from CP contains more

inert materials (i.e. ferric phosphate) and less soluble phosphates. The difference in sludge composition produced from CP can impact downstream treatment process such as anaerobic digestion.

As shown in equations 2.5 and 2.6, each mole of alum and ferric chloride will form 2 moles and 1 mole of metal-hydroxide, respectively. Thus, 1 mg of alum will produce 0.26 mg of insoluble aluminum hydroxide and 1 mg of ferric chloride will produce about 0.4 mg of ferric hydroxide (MWH, 2005).

2.2.1.4 Rare-Earth Elements and Lanthanum as a Coagulant

Lanthanum belongs to the rare-earth element group (sometimes called lanthanides), which consists of the elements lanthanum to lutetium (atomic numbers 57 through 71) and Yttrium (atomic number 39). Rare-earth metals have been historically known for their use in petroleum cracking catalysts, iron and steel alloying agents, glass polishing compounds and glass additives, permanent magnets, and phosphors for television and lighting (Hedrick, 1985). Some of the rare-earth metals are abundant in the earth's crust, whereas others are rare. Lanthanum, cerium and neodymium are the three most abundant rare-earth metals and collectively they are more abundant than nickel or copper (Hedrick, 1985). China has the largest reserves of rare-earth metals, comprising of approximately 80% of the world's total (Brown et al., 1990). At present, lanthanum is not widely available commercially in the United States. However, the opening of new rare-earth mines in the U.S. and expansion of these mines overseas are likely to expand the supply of rare-earth metals in the market that can be used for water and wastewater treatment.

Rare-earth metals have a strong potential to be used as coagulants for chemical phosphorus removal as rare-earth phosphates are very insoluble in water (Firsching and Brune, 1991). The solubility product, log K_{sp}, of lanthanum-phosphate in water has been reported at -26.15 (Firsching and Brune, 1991) and -25.75 (Liu and Byrne, 1997). In addition, the molar ratio of lanthanum to phosphate is 1:1 as seen in equation 2.7:

$$LaPO_4 \text{ (s)} \leftrightarrow La^{3+} \text{ (aq)} + PO_4^{3-} \text{ (aq)} \qquad (2.7)$$
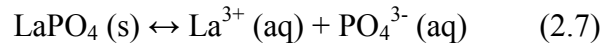
Phosphate precipitation using lanthanum was shown to be more effective at a wider pH range than iron(III) or aluminum salts as early as the 1970s (Recht et al., 1970; Melnyk et al., 1974). Recht et al. (1970) demonstrated effective phosphate precipitation with lanthanum in the pH range of 4.5 – 8.5. Furthering this, Diatloff et al. (1993) showed that the lanthanum-phosphate complex can be formed in solutions with a pH as low as 4, with phosphate and lanthanum concentrations as low as 0.695 and 0.15 mg/L, respectively.

In addition to coagulation, lanthanum-based adsorbents have also been widely investigated due to their high phosphate adsorption capacity. Some adsorbents tested in the literature include lanthanum-impregnated silica gels (Wasay et al., 1996), lanthanum-doped vesuvianite (Li et al., 2009), La(III)-modified zeolites (Li et al., 2005; Ning et al., 2008), lanthanum-loaded orange waste gels (Biswas et al., 2007), La(III)-chelex resin (Wu et al, 2007) and lanthanum-doped mesoporous silicates (Ou et al, 2007; Zhang et al., 2010).

Rare-earth metals are considered only slightly toxic (Hedrick, 1985), although concerns with using lanthanum are that it can be toxic to some aquatic life depending on

the concentration and application rate (Douglas et al., 2004). Oral et al. (2010) showed that developmental defects occurred in sea urchin embryos when exposed to lanthanum at a concentration of 10^{-5}M (1.4 mg/L). In a study by Burkes and McCleskey (1947), 39 species of bacteria were prevented from growth in lanthanum chloride concentrations varying from 0.0002 to 0.0008 M (48.8 mg/L to 195.2 mg/L). Kangguo et al. (2006) found that the mycelia growth of pathogenic fungi was significantly restrained when treated with lanthanum and stated that the toxicity of lanthanum is similar to some common organic fungicides. The effect of rare-earth metals on plants is not fully understood. On one hand they have shown to increase crop yields and improve the quality of crops (Hu et al., 2004; Liu et al., 2006), yet contrasting studies have shown that rare-earth metals were toxic to plants (Diatloff and Smith, 1995; Huang et al., 1996). These contrasting observations are most likely ascribed to the various application rates of rare-earth metals. From this, it can be inferred that the benefits and toxic effects of rare-earth metals are similar to those of other trace metals until a more solid understanding of their effects are determined.

2.2.2 Enhanced Biological Phosphorus Removal

EBPR is becoming an increasingly popular alternative wastewater treatment technology to CP because of its lower costs and reduced sludge production (Paul et al., 2001; Oehmen, 2007). A successful EBPR process is capable of removing 80 to 90% of influent phosphorus without chemical addition and can produce effluents with orthophosphate concentrations below 1 mg P/L (Morse et al., 1998; Greaves et al., 1999).

Only a select number of bacteria have been identified as being able to perform EBPR (Crocetti et al., 2000; Crocetti et al., 2002; Kong et al., 2005) and have been

referred to as Polyphosphate Accumulating Organisms (PAOs). While PAOs are critical for phosphorus removal in EBPR systems, in full-scale plants PAOs typically account for only 15-25% of the total bacteria population (Nielsen et al., 2011). During EBPR (Figure 2.1), volatile fatty acids (VFAs) such as acetate, propionate and butyrate are assimilated by PAOs under anaerobic conditions and are converted to polyhydroxyalkanoates (PHAs) (Stratful et al., 1999). Degradation of intracellular polyphosphate (PP) provides energy for PHA storage and cell maintenance, while orthophosphate is released to the bulk liquid. Then, under aerobic conditions, PAOs uptake and store phosphate in excess of their metabolic needs in a process referred to as "luxury uptake" (Levin and Shapiro, 1965). Phosphorus is removed from the system as a result of wasting biosolids rich in accumulated polyphosphate after secondary clarification. Hence, the phosphorus content of the sludge and its wasting is of utmost importance in EBPR systems as this is the method by which P is effectively removed from the system (Mulkerrins et al., 1994).
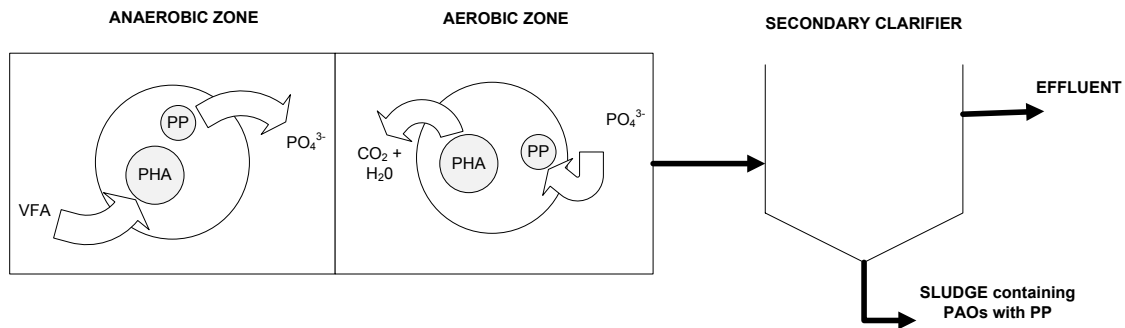
Figure 2.1   Enhanced Biological Phosphorus Removal process

Secondary clarifier performance also dictates the efficiency of phosphorus removal in EBPR. A high concentration of suspended solids in the secondary clarifier effluent will

increase effluent total phosphorus levels if downstream filtration is not performed because the suspended solids are rich in accumulated polyphosphate. Furthermore, secondary phosphorus release (release in the absence of exogenous carbon input) can occur if the sludge retention time in a secondary clarifier is too long, resulting in increased effluent soluble phosphorus concentrations (Csiti, 1991). Schönberger (1990) suggested that retention times in secondary clarifiers should not exceed 1 hour to prevent secondary phosphorus release.

2.3   Classification of Wastewater Sludges

Sludge produced in municipal wastewater treatment plants can be classified as primary or secondary sludge depending on the treatment method used in their production. Primary sludge is produced through the sedimentation of raw sewage that has not undergone biological treatment. Coagulants are often added to primary settling tanks to aid in solids settling and to precipitate phosphates, thereby producing sludge containing phosphorus as metal-phosphates. Secondary sludge is generated via biological treatment and is comprised largely of microorganisms. The phosphorus content of secondary sludge is typically much greater than in primary sludge, especially sludge generated from EBPR processes. Successful EBPR processes produce biomass that contains 2 to 5 times the P content of normal biomass (Rittmann & McCarty, 2001) and the phosphorus content of EBPR activated sludge has been reported in the range of 4.1 to 15.6% P on a dry weight basis (Mino et al., 1998). In contrast, primary sludge that has been chemically treated has been shown to contain only 1 to 2% P on a dry weight basis (Ghyoot and Verstraete, 1997).

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2.4 Secondary Phosphorus Release During Sludge Handling

Sludge handling is one of the major problems associated with biological phosphorus removal (Fujimoto et al., 1991) as secondary phosphorus release (P-release) can occur during sludge dewatering, storage and digestion. Under anaerobic conditions, stored polyphosphate can be released into the liquors produced from these solids handling processes and recycled back to the plant inlet. These return streams, which are typically 1 to 5% of the influent wastewater flow, can result in increased effluent phosphorus concentrations, potentially exceeding effluent limits (Pöpel and Jardin, 1993). In order to prevent overloading the EBPR process with phosphorus, return liquors should be pre-treated prior to being recycled (Murakami et al., 1987; Pitman et al., 1991). Figure 2.2 was prepared to demonstrate possible return liquors that can be produced from various sludge handling processes.

Phosphate release during solids dewatering can promote the formation of precipitates such as vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), when iron is used as a coagulant, and struvite ($MgNH_4PO_4 \cdot 6H_2O$), in processes that use anaerobic digestion. Unintentional precipitation of these minerals in wastewater treatment plants is undesirable as crystalline solids can build up and clog pipes and equipment leading to operational problems and increased maintenance costs.
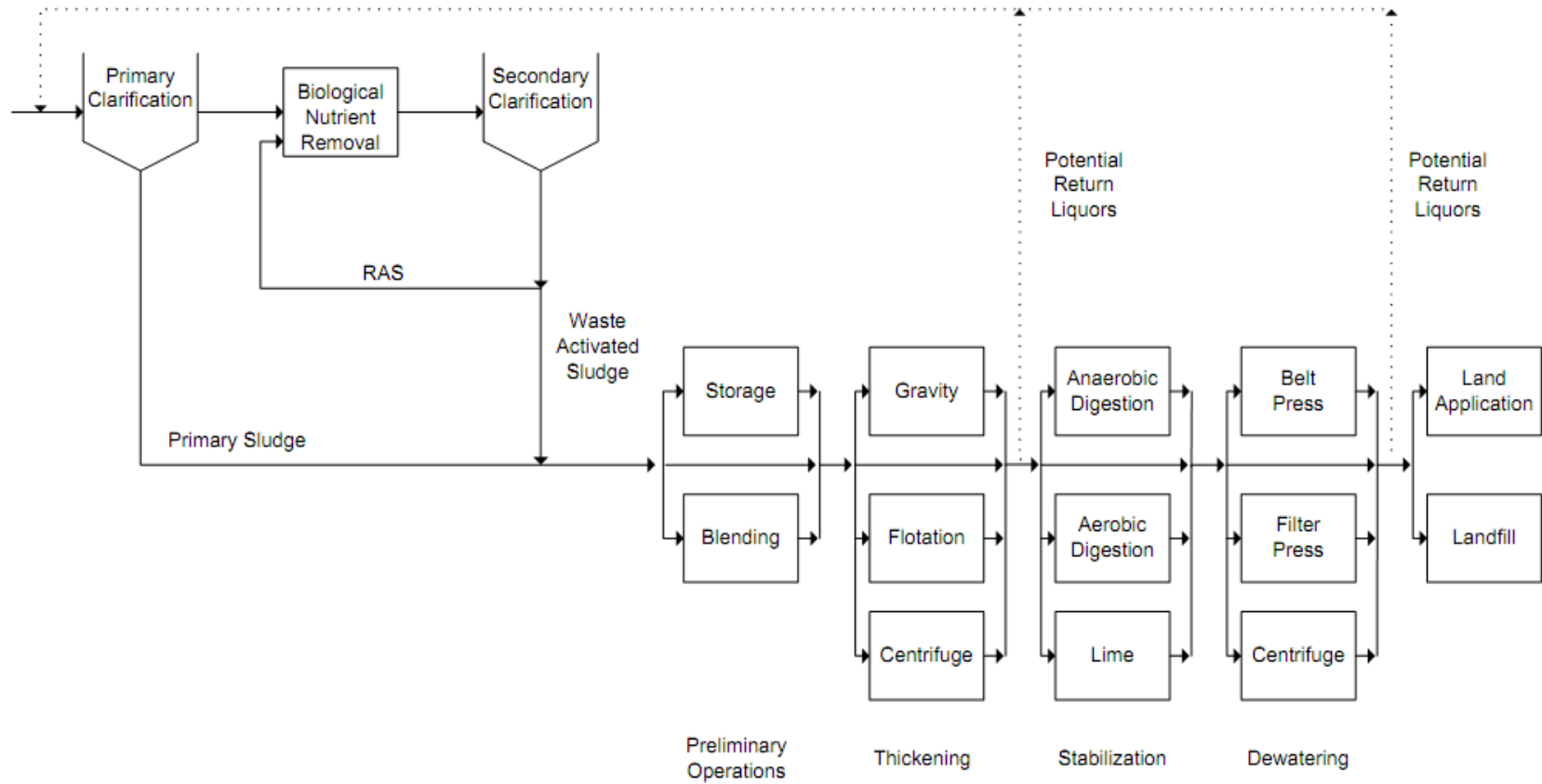
Figure 2.2   Potential return liquors that can be produced during solids processing

Aeration of waste activated sludge can inhibit and delay secondary P-release by increasing phosphate binding to the solid phase. Co-aeration of raw primary sludge with EBPR activated sludge causes the virtual complete removal of phosphate from the liquid phase, providing a simple method of removing phosphates without chemical addition (Pitman et al., 1991). However, sludge aeration may not always be an economically viable option for plants or may not be operationally possible.

2.4.1 Anaerobic Digestion of Sludge

Anaerobic digestion, also called methanogenesis, is the biological process in which bacteria convert organic matter to methane gas in the absence of oxygen. Anaerobic digestion is one of the most widely used processes for the stabilization of solids and biosolids due to its high performance in volume reduction and the production of biogas that makes the process profitable (Metcalf & Eddy, 2003; Vindis et al., 2009). The major application of anaerobic digestion is to stabilize industrial and municipal sludges produced in wastewater treatment. A general range of alkalinity for a well-functioning anaerobic digester is about 2000 to 5000 mg/L (Metcalf and Eddy, 2003).

In many applications, primary and secondary sludges are digested simultaneously. Stored phosphate in secondary sludge is biologically bound and can be easily released under anaerobic conditions, whereas primary sludge often consists of chemically precipitated phosphorus that remains with the solids (Seyfried et al., 1988). After digestion, process waters can contain up to 1000 mg/L ammonia nitrogen as well as a considerable amounts of COD and phosphate (Arnold et al, 2000). Murakami et al. (1987) and Mavinic et al. (1998) showed that up to 60% and 80% of phosphorus removed in the EBPR process can be released during anaerobic digestion, respectively. Jardin and

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Popel (1994) estimated a P-feedback of 40% the influent phosphorus in EBPR digested sludge with a very high phosphorus content of 6 to 7%. Tables 2.1 and 2.2 show orthophosphate concentrations presented in the literature for EBPR digested sludge dewatering liquors and digested sludge dewatering liquors mixed with thickener supernatant, respectively.

Table 2.1   Orthophosphate Concentrations of EBPR Anaerobically Digested Dewatering Liquors Presented in the Literature

Plant Type	Ortho-P [mg/L]	Reference
Full-Scale	60-130	Pitman et al., 1991
Pilot	95	Jaffer et al., 2002
Full-Scale	44	Abe, 1995
Full-Scale	80	Williams, 1998
Full-Scale	70 ± 8	Munch and Barr, 2001
Full-Scale	202	Fujimoto et al., 1991
Full-Scale	293	Webb et al., 1995

Table 2.2   Orthophosphate Concentrations of EBPR Anaerobically Digested Sludge Dewatering Liquors Mixed with Thickener Supernatant Presented in the Literature

Plant Type	Ortho-P [mg/L]	Reference
Pilot	43-151	Marti et al., 2010
Pilot	43.6-167.1	Pastor et al., 2008
Pilot	50-170	Pastor et al., 2010
Full-Scale	160	Williams, 2012

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2.4.2 Sludge Thickening and Dewatering

Dewatering units with optimal solids capturing capabilities minimize the carry-over of phosphate-rich solids into the liquid recycle stream. Lötter (1989) reported that the efficiency of solids capture in dissolved air flotation (DAF) units and dewatering equipment was important, as phosphorus-rich activated sludge solids readily released phosphate under anaerobic conditions. Pitman et al. (1991) found that up to 20 mg/L of orthophosphate could be released from WAS thickening using belt presses. Mota-Filho and Batista (2003) observed orthophosphate concentrations as high as 125 mg/L in the filtrate of filter presses in a full-scale EBPR plant. The dewatering of undigested BNR sludge should occur as quickly as possible to minimize the release of orthophosphate into the liquid phase (Pitman, 1999).

2.4.3 Sludge Storage

Sludge is often stored prior to further processing depending on the capacity of downstream treatment equipment. Sludge that is stored under anaerobic conditions can promote secondary P-release, the degree of which is dependent on the storage time. Mota-Filho and Batista (2003) reported orthophosphate releases of 153 and 277 mg/L during sludge holding and suggested that the high phosphorus release was brought forth by the high soluble organic matter content of the primary sludge. The authors also suggested that almost 40% of the phosphorus removed in the EBPR process can be released if primary and secondary sludges are combined and stored under anaerobic conditions for 12 hours.

2.4.4 Example Impact of EBPR Sludge Dewatering Recycle Liquors on Phosphorus Loading

Figure 2.3 demonstrates the potential impact of sludge dewatering recycle liquors on phosphorus loading to the EBPR process. A 100 MGD influent wastewater flow with 2-4 mg P/L and a 1 MGD recycle liquor with 150 mg P/L was considered. These values are within the range reported for recycle streams, 1-5% of the treated flow. The concentrations of phosphorus in both streams are also within reported levels (Metcalf and Eddy, 2003; Pastor et al., 2010). The phosphorus loading on the process is 1668-3336 lbs P/day and 1251 lbs P/day for the influent and recycle liquor, respectively. Thus, the recycle liquor can increase influent phosphorus loadings by 38-75%. It can be seen from this example that recycle liquors can substantially increase phosphorus loadings if not adequately treated, which can have adverse effects on the EBPR process. For example, higher influent phosphorus concentrations would require higher levels of volatile fatty acids (VFAs) in the influent wastewater if the removal efficiency is to be maintained. Having sufficient VFAs is paramount to the successful performance of EBPR systems.

Influent

Process

Flow = 100 MGD
P = 2-4 mg/L
Loading = 1668-3336 lbs
                              P/day

Recycle Liquor

Flow = 1 MGD
P = 150 mg/L
Loading = 1251 lbs P/day
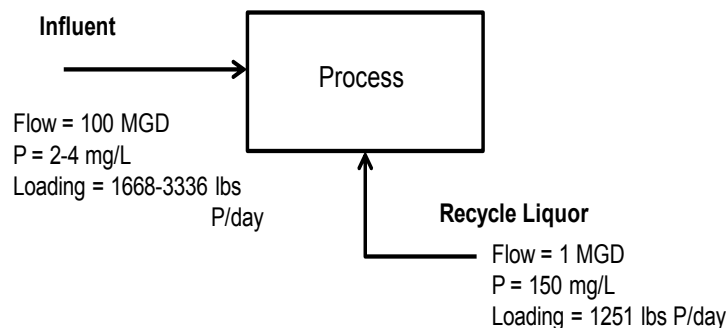
Figure 2.3 Example impact of a 1 MGD EBPR sludge dewatering recycle liquor on a 100 MGD process where phosphorus removal is performed biologically

2.5 Phosphorus Removal from Return Liquors

2.5.1 Chemical Precipitation

Chemical precipitation can be performed to re-precipitate released phosphorus from return liquors in the same manner as it can be used in primary or secondary treatment. In a study by Fujimoto et al. (1991), ferric chloride and lime were tested as coagulants to remove phosphorus from return streams. Ferric chloride achieved greater than 85% orthophosphate removal at a Fe:P molar ratio of approximately 3:1 whereas lime had similar removal efficiencies at Fe:P molar ratios greater than 6:1. A combination of lime and ferric chloride yielded the best results as similar orthophosphate removals were seen at a 1:1 molar ratio, along with greater than 90% removal of total phosphorus (Fujimoto et al., 1991).

2.5.2 Struvite Formation

Controlled struvite crystallization (Figure 2.2) is a process that can be used to remove and recover phosphorus from return liquors, especially in EBPR plants that use anaerobic digestion (Münch and Barr, 2001; Parsons and Doyle, 2004; Marti et al., 2010). Struvite has shown strong potential in the fertilizer industry and it has been found to be as good a fertilizer as commercial mono calcium phosphates in plant-growth trials (Johnston and Richards, 2003).
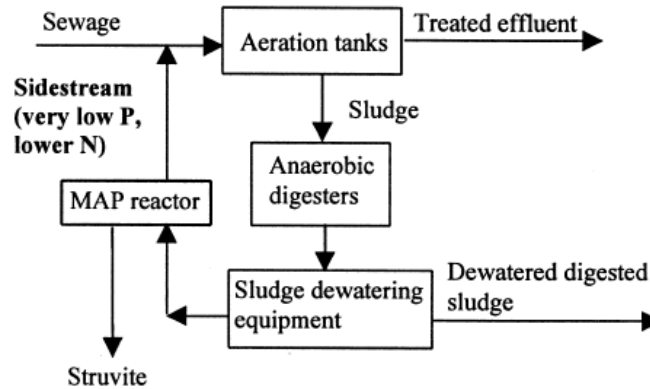
Figure 2.4   Process flow diagram of EBPR wastewater treatment plant with sidestream treatment by MAP process (Source: Munch and Barr, 2001)

Struvite (magnesium ammonium phosphate hexahydrate, or MAP) is composed of equimolar amounts of magnesium, ammonia and phosphate with the chemical formula $MgNH_4PO_4 \cdot 6H_2O$. Orthophosphate (PO_4^{3-}) released during anaerobic digestion provides phosphorus for the formation of struvite. Nitrogenous material in primary sludge that is degraded provides ammonia and magnesium comes from degradation of organic material and poly-P hydrolysis (Wild et al., 1997; Jardin and Pöpel, 1996). Typically, magnesium to phosphate molar ratios greater than 1.05:1 are required to guarantee phosphorus removal as struvite (Fujimoto et al., 1991; Jaffer 2002).

Many authors have studied the effects of pH on struvite precipitation and the optimal pH range for struvite formation has been reported at 8.5 to 9 (Le Corre et al., 2009). The solubility of struvite decreases with pH, so to effectively form struvite the pH should be raised to at least 8, which can be accomplished by the addition of sodium hydroxide, lime, or through aeration (Fujimoto et al., 1991).

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CHAPTER 3

MATERIALS AND METHODS

3.1   Description of Wastewater Treatment Plants

Samples used in this study were collected from two full-scale wastewater treatment plants (herein referred to as Plant A and Plant B) in the southwestern United States.

Plant A (Figure 3.1) treats approximately 95 million gallons of wastewater daily (MGD) using physical, chemical and biological processes. Raw wastewater initially flows through bar screens and grit chambers for removal of coarse materials and is then sent to primary clarifiers where ferric chloride is added to aid settling and partially remove phosphorus. Then, the wastewater is pumped from the primary clarifiers to the Enhanced Biological Phosphorus Removal (EBPR) process, followed by sedimentation of the aerated mixed liquor in the secondary clarifiers. A portion of the secondary sludge, or returned activated sludge (RAS), is returned to the anoxic zone of the EBPR process and the remaining waste activated sludge (WAS) is sent to the dissolved air flotation thickeners (DAFT) for dewatering. Secondary clarifier effluent is then processed through dual media filters and disinfected with ultraviolet light (UV) prior to discharge. In the solids processing, settled sludge from the primary clarifiers is dewatered in the dewatering centrifuges along with thickened EBPR sludge from the top of the DAFT. The liquor from the bottom of the DAFT with low solids content is returned to the EBPR process. Centrate from the dewatering centrifuges (where samples were collected for this study) is recycled to the head of the primary clarifiers after ferric chloride addition to precipitate soluble phosphates.
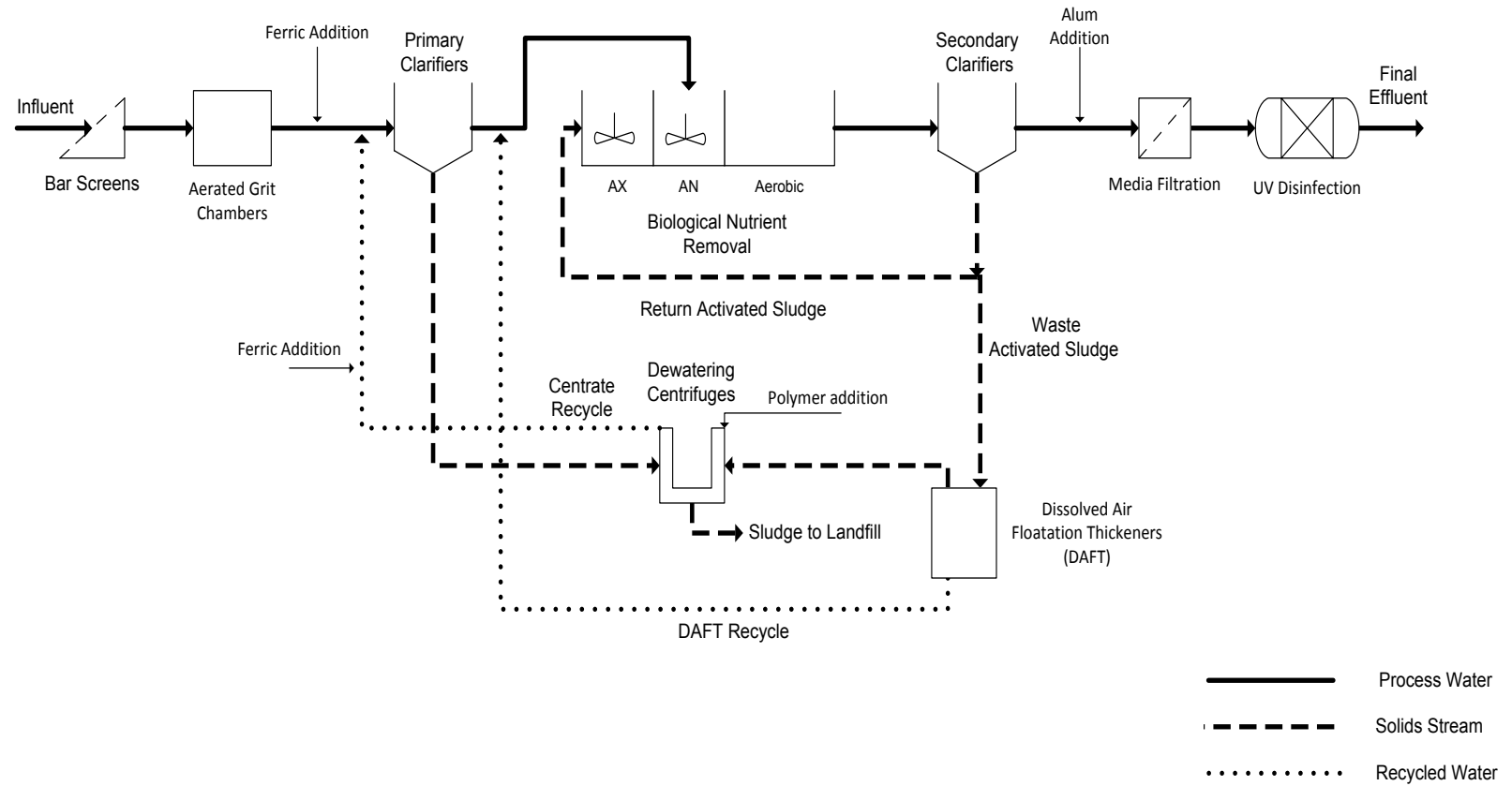
Figure 3.1   Wastewater treatment Plant A schematic

Plant B (Figure 3.2) currently treats approximately 40 MGD of wastewater. After screening, influent is split into two streams based on the phosphorus removal process. About 30 MGD undergoes primary sedimentation and biological nutrient removal (BNR) followed by final clarification. The remaining 10 MGD is treated with ferric chloride for chemical phosphorus removal (CP) and to aid solids settling in the primary sedimentation basins. Effluent from the primary sedimentation basins is sent to the trickling filters for BOD removal, followed by secondary sedimentation, ammonia oxidation in the nitrification basins and final clarification. Final clarifier effluent from each process is filtered, chlorinated and dechlorinated before discharge. In the solids processing, thickened primary sludge and thickened waste activated sludge (TWAS) from both the BNR and nitrification basins are anaerobically digested. Ferric chloride is added to the digesters to minimize the potential for struvite scale formation. Polymer is added to the digested sludge before it is dewatered in the dewatering centrifuges. The resulting sludge cake is sent to the landfill and the centrate (where samples were collected for this study) is recycled to the head of the primary clarifiers.

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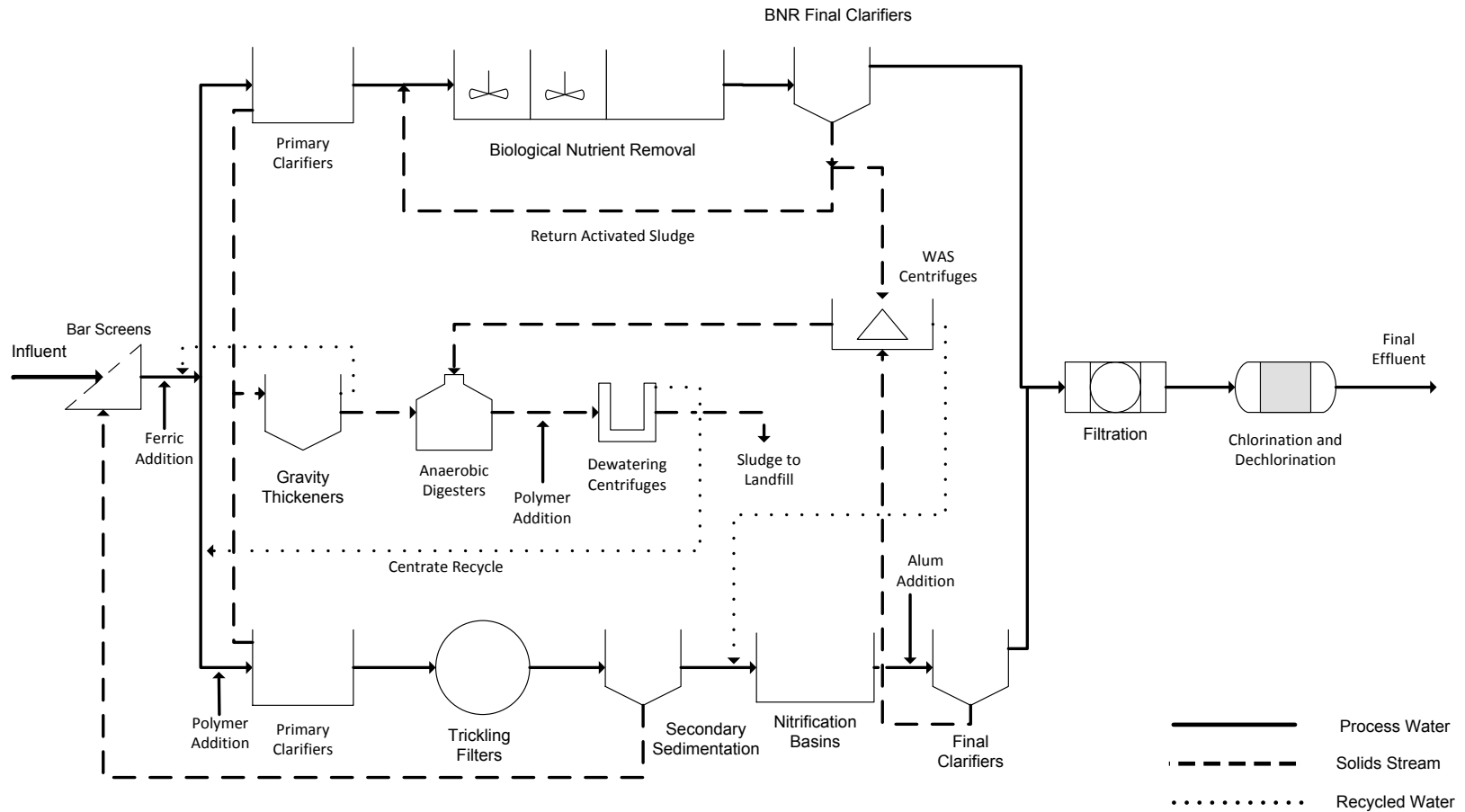
Figure 3.2   Wastewater treatment Plant B schematic

3.2 Waters Used in This Study

3.2.1 EBPR Sludge Dewatering Centrate Liquors

Sludge dewatering centrate liquors from Plant A and Plant B were used in batch testing. Centrate 1 (non-digested EBPR dewatering centrate) was collected from Plant A and Centrate 2 to 6 (anaerobically digested dewatering centrate) was collected from Plant B. The initial pH of Centrate 4 through 6 was decreased by the addition of 1M HCl. Table 3.1 outlines a summary of the centrate samples used in this study and their characteristics.

Table 3.1   Summary Characteristics of Centrate Samples Used in This Study

NAME	TYPE	INITIAL pH	INITIAL ORTHO-P [mg/L]	NH$_3$-N [mg/L]	ALKALINITY [mg/L as CaCO$_3$]
Centrate 1	Non-Digested EBPR	6.5	102	52	483
Centrate 2	Anaerobically Digested	7.85	112	544	2633
Centrate 3	Anaerobically Digested	7.75	115	720	3833
Centrate 4	Anaerobically Digested	5.5	123	754	433
Centrate 5	Anaerobically Digested	4.5	116-127	776	<1
Centrate 6	Anaerobically Digested	4.5	15	636	<1

3.2.1.1 Sample Collection and Preservation

Approximately 20L of centrate was collected from each plant per sample. Samples were placed on ice and brought to UNLV's Environmental Engineering laboratory for analysis. Ten mL of sample was filtered immediately (0.45 micron) for initial orthophosphate analysis. Samples were stored at 4°C and used within 72 hours of collection.

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3.2.2 Synthetic Phosphate Solutions

Synthetic solutions were prepared by dissolving reagent grade sodium phosphate monobasic (NaH_2PO_4, Sigma-Aldrich) in deionized water (DI). The pH of the synthetic phosphate solutions was adjusted by the addition of sodium bicarbonate ($NaHCO_3$, 1000 meq/L).

3.3 Batch Tests

3.3.1 Batch Test Procedures

Precipitation tests were conducted at room temperature using a Phipps and Bird six-place stirrer. Five hundred mL of sample was placed in a 1-L glass beaker, and the desired coagulant concentration was added while being stirred at 100 rpm. After 2 minutes of rapidly mixing the coagulant at 100 rpm, the stirring rate was reduced to a slow mix (33 rpm) for 20 minutes to allow flocs to grow so they can settle more easily. Mixing was then stopped and the sample was quickly transferred to a graduated cylinder and the solids were permitted to settle for 30 minutes. Following the 30 minute settling period, the volume of settled solids was recorded in mL and 10 mL of supernatant was collected for turbidity determination. Next, a portion of the sample was filtered through 0.45 micron filter paper for orthophosphate analysis.

3.3.2 Analytical Methods

3.3.2.1 pH

The initial and final pH of the batch test solutions was measured using an AR 10 Fisher Scientific pH meter. The pH meter was calibrated using a two-point calibration with pH 7 and pH 4 buffers.

3.3.2.2 Orthophosphate and Ammonia

Orthophosphate and ammonia concentrations in filtered samples were determined spectrophotometrically using a Hach DR 5000 spectrophotometer. The USEPA PhosVer® 3 Method was used to determine reactive phosphorus (orthophosphate) and ammonia-nitrogen was determined using the salicylate method.

3.3.2.3 Alkalinity

Alkalinity was determined by titration using *Standard Methods for the Examination of Water & Wastewater* with pH 4.5 as the titration endpoint. The following equation was used to calculate total alkalinity in mg $CaCO_3$/L:

$$\text{Alkalinity,} \frac{\text{mg } CaCO_3}{\text{L}} = \frac{A \text{ x } N \text{ x } 50\,000}{\text{mL sample}} \qquad (3.1)$$

where:

A = mL standard acid used   N = normality of standard acid

3.3.2.4 Turbidity

Turbidity was measured using a HACH 2100N turbidimeter in accordance with the Nephelometric Method (Standard Methods 2130 B). The turbidity meter was

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calibrated using five formazin polymer standard reference solutions of <0.1, 20, 200, 1000, and 4000 NTU.

3.3.3 Quality Assurance and Quality Control Measures (QA/QC)

3.3.3.1 Quality Assurance

The follow measures were taken in order to minimize experimental error and maintain accuracy in obtaining results:

1. Samples were adequately labeled and stored at 4˚C when not in use.

2. Stock solutions (100 mg/mL) of alum, ferric chloride and lanthanum chloride were prepared fresh for each set of batch tests. The stock solutions were mixed for 30 minutes to ensure uniform concentrations. When not in use, the stock solutions were covered to prevent contamination and stored at 4˚C.

3. The accuracy of micropipettes was checked by weighing known volumes of dispensed DI water on an analytical balance.

4. Due to the sensitivity of the phosphate analysis, all glassware was soaked in a phosphate-free weak acid solution for at least 24 hours. The glassware was then cleaned and rinsed 3 times with tap water, followed by at least 3 rinses with DI water.

3.3.3.2 Quality Control

For batch testing, duplicate samples were run for every 2 to 3 samples tested to reduce uncertainties in analysis. Analytical measurements such as turbidity and phosphate concentration were replicated and statistical analysis was performed to control the quality of measurements.

3.4   Chemical Equilibrium Modeling

MINEQL+ (Version 4.6), a commercial chemical equilibrium modeling system, was used to predict orthophosphate removal at various pHs using equimolar concentrations of metal cation (Fe^{3+}, Al^{3+} or La^{3+}) and orthophosphate. The chemical components and conditions used in the modeling are presented in Table 3.2. In addition, the major reactions and equilibrium constants considered in the phosphate precipitation models are summarized in Table 3.3.

Table 3.2   Parameters Used in MINEQL+ Modeling

Component*	Value
pH	1~8
Al^{3+}	6.63 x 10^{-5} M
Ca^{2+}	1.88 x 10^{-3} M
Fe^{3+}, La^{3+} or Al^{3+}	3.61 x 10^{-3} M
K^{+}	3.53 x 10^{-3} M
Mg^{2+}	2.23 x 10^{-3} M
NH_4^{+} - N	4.20 x 10^{-2} M
PO_4^{3-}	3.61 x 10^{-3} M
CO_2 Partial Pressure	$10^{-3.5}$ atm
Ionic Strength**, μ	2.06 x 10^{-2} ~ 5.21 x 10^{-2}

* Concentrations of Al^{3+}, Ca^{2+}, K^{+} and Mg^{2+} were used from a similar centrate sample in Batista and Jeong (2006) as they were not quantified in this study.

**Please refer to Appendix A for ionic strength calculation. It was not possible to determine the concentration of all components in the centrate and only major components were used in calculating ionic strength. Additionally, a charge balance was not performed.

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Table 3.3   Reactions and Equilibrium Constants Used in MINEQL+ Modeling

Reaction	log K	Source
$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$	-2.1	Snoeyink and Jenkins, 1980
$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$	-7.2	
$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$	-12.3	
Fe(III) Addition		
$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+$	-2.2	Stumm and Morgan, 1970
$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+$	-5.7	
$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	-2.9	
$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3\ (aq)}^0 + 3H^+$	-12	
$Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_4^- + 4H^+$	-22	
$3Fe^{3+} + 4H_2O \leftrightarrow Fe_3(OH)_4^{5+} + 4H^+$	-6.3	Amirtharajah and O'Melia, 1990
$Fe^{3+} + HPO_4^{2-} \leftrightarrow FeHPO_4^+$	9	Luedecke et al., 1989
$Fe^{3+} + H_2PO_4^- \leftrightarrow FeH_2PO_4^{2+}$	21.5	
$FePO_{4\ (s)} \leftrightarrow Fe^{3+} + PO_4^{3-}$	-26	Stumm and Morgan, 1970
$Fe(OH)_{3\ (s)} + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	3.19	MINEQL+
Al(III) Addition		
$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+$	-5	Stumm and Morgan, 1970
$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+$	-10.1	
$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_{3\ (aq)}^0 + 3H^+$	-16.9	
$Al^{3+} + 4H_2O \leftrightarrow Al(OH)_4^- + 4H^+$	-22.7	
$AlPO_{4\ (s)} \leftrightarrow Al^{3+} + PO_4^{3-}$	-21	
$Al(OH)_{3\ (am)} + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	10.8	
La(III) Addition		
$La^{3+} + H_2O \leftrightarrow La(OH)^{2+} + H^+$	-9.04	Stumm and Morgan, 1970
$La^{3+} + 2H_2O \leftrightarrow La(OH)_2^+ + 2H^+$	-18.23	
$La^{3+} + 3H_2O \leftrightarrow La(OH)_{3\ (aq)}^0 + 3H^+$	-26.56	Yakubovich and Alekseev, 2012
$LaPO_{4\ (s)} \leftrightarrow La^{3+} + PO_4^{3-}$	-25.75	Liu and Byrne, 1997
$La(OH)_{3\ (s)} + 3H^+ \leftrightarrow La^{3+} + 3H_2O$	21.29	MINEQL+

The ionic strength of the centrate was calculated using the following equation devised by Lewis and Randall (Snoeyink and Jenkins, 1980) (Equation 3.2).

$$\mu = \frac{1}{2}\sum_i (C_i Z_i^2) \qquad (3.2)$$

where:

μ = ionic strength C_i = concentration of species, i Z_i = charge of species, i

To determine variations of the modeling results with respect to ionic strength, sensitivity analyses were performed by varying the ionic strength from 0.002 to 0.100. No major differences were seen in the amount of orthophosphate removal or amount of precipitate formed at different ionic strengths.

3.4.1 Precipitation Modeling and Comparison with Experimental Results

Modeling results showed the residual orthophosphate concentration at each tested pH value from pH 1 to 8. Orthophosphate percent removal (%R) was determined by subtracting residual orthophosphate from the initial concentration. The results of the model were plotted against experimental data for a qualitative comparison of phosphate removal.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 The Effect of pH on Orthophosphate Removal

4.1.2 Titration Curves

In chemical precipitation of phosphorus from wastewater, pH is one of the most important considerations. Because metal salts act as an acid and consume alkalinity when added to water, it is important to determine the amount of pH depression that will occur. If the pH drops too low, bases such as lime, soda ash or sodium hydroxide have to be added which can increase operating costs. Additionally, the desired pH for biological treatment is around neutral, so pH adjustments may have to be performed if the waters are recycled to the head of the biological treatment process.

Titration curves were prepared to determine the extent of pH depression when adding similar amounts of the trivalent cations Fe^{3+}, Al^{3+} and La^{3+} (as in ferric chloride, aluminum sulfate and lanthanum chloride, respectively) to EBPR digested sludge dewatering liquors with high orthophosphate concentrations (Figure 4.1). It is evident from Figure 4.1 that the addition of iron (Fe^{3+}) results in a more substantial pH decrease than either Al^{3+} or La^{3+}. There is a distinct inflection point in the Fe^{3+} curve at approximately 0.03 mol Fe^{3+}/L (~167.5 mg Fe^{3+}/L) where bicarbonate alkalinity is consumed. Additionally, the final pH with ferric iron addition reaches approximately 2, which is almost 2 pH units lower than Al(III) and 2.5 pH units lower than La(III) at the same molar addition. Thus, careful consideration of pH depression must be made when using metal salt coagulants in EBPR digested sludge dewatering liquors, especially with

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iron(III) based coagulants. Of the three coagulants used in this study, lanthanum addition results in the least pH depression.
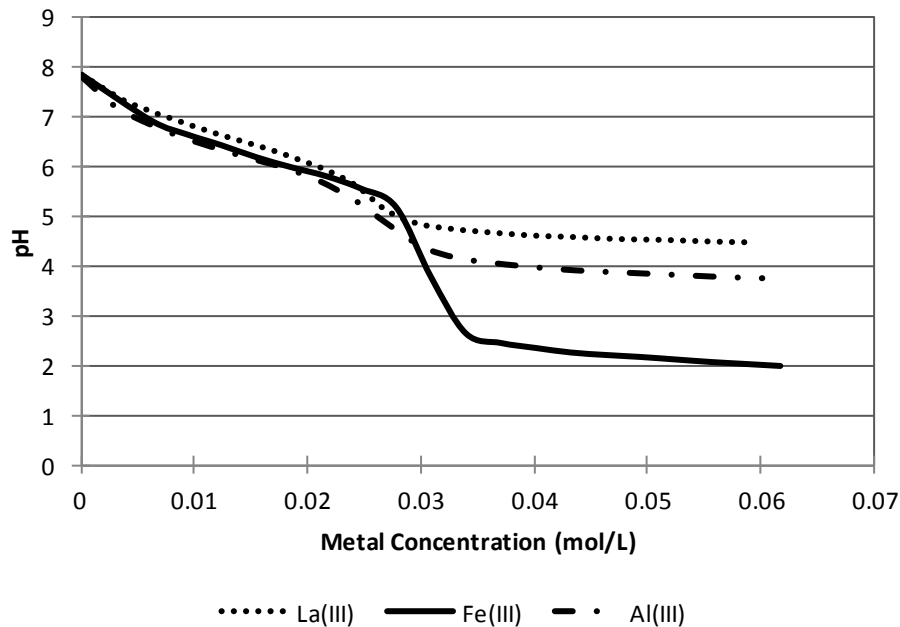
Figure 4.1   Titration curves of an actual sludge dewatering liquor from Plant B
containing 115 mg/L ortho-P with salts of lanthanum, iron and aluminum

4.1.3   Orthophosphate Removal versus Final pH

Coagulants such as lanthanum chloride, ferric chloride, and alum reduce the concentration of phosphorus in water by precipitating insoluble metal-phosphates. At the same time, however, the pH of the water decreases because the coagulation process consumes alkalinity. This fact has been known for a long time, and Hudson and Wolfner (1967) observed that coagulants hydrolyze rapidly once added to water, so pH decreases occur almost instantaneously. Therefore, the final pH, after addition of the coagulant, is

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more representative of the actual pH under which the reactions occur. Figures 4.2 to 4.4 show % orthophosphate removal versus final pH as a function of molar ratios of orthophosphate to lanthanum [La(III)], aluminum [Al(III)] and iron(III), respectively. Each sample used in batch testing had a high initial orthophosphate concentration ranging from 102 to 127 mg/L.

As observed in Figure 4.2, orthophosphate removal increased with increasing pH at lanthanum to phosphate molar ratios of 0.8:1, 1:1 and 1.2:1. At neutral pH, approximately 95% ortho-P removal occurred at a 0.8:1 molar ratio and greater than 99% removal was achieved at 1:1 and 1.2:1 molar ratios. Recht et al. (1970) reported that effectiveness of lanthanum for phosphate removal extends well above pH 7 and into the alkaline range, including pH levels of typical domestic wastewater (7 to 8). This makes lanthanum-based coagulants attractive for wastewater applications as there would not be a need for costly pH adjustments. However, lanthanum chloride also proved to be an effective coagulant at low pH. At very low pH values of approximately 2 to 3, about 70% removal was observed at a 0.8:1 molar ratio and high 70% to low 90% removals were seen at ratios of 1:1 and 1.2:1. It is important to note that ortho-P removal increased with increasing lanthanum chloride dosages at low pH. At a 2:1 molar dose, ortho-P removal increased to 88% at the lowest pH of 2. Thus, higher molar doses of lanthanum can be applied at very low pH without fear of decreasing ortho-P removal as is the case with ferric iron and aluminum.
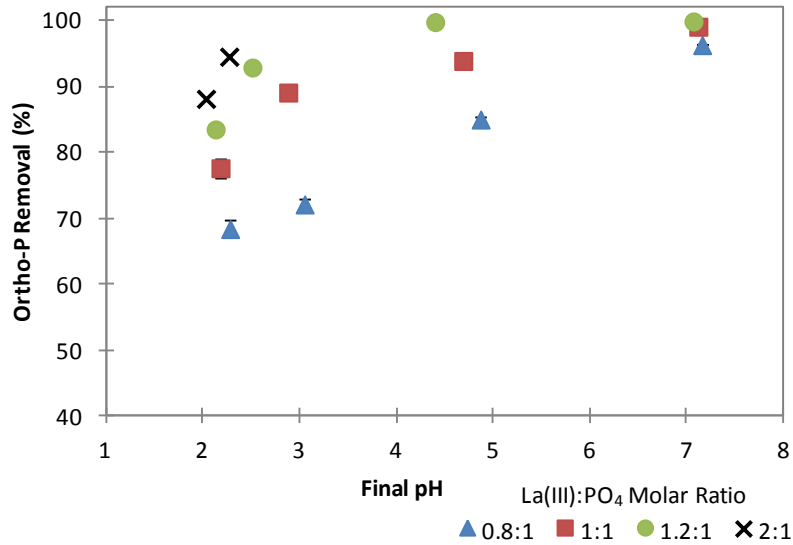
Figure 4.2   Ortho-P removal versus final pH in sludge dewatering liquors with high
initial ortho-P concentrations at La(III):PO$_4$ molar ratios of 0.8:1, 1:1, 1.2:1 and 2:1
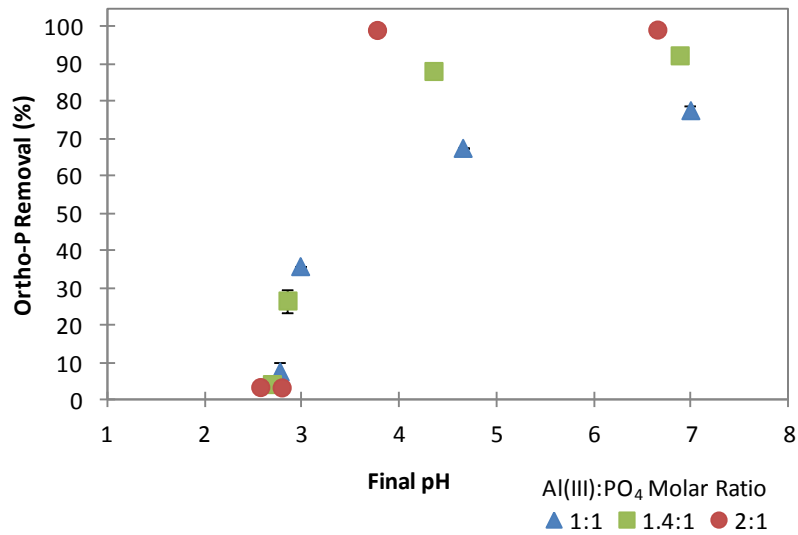
Figure 4.3   Ortho-P removal versus final pH in sludge dewatering liquors with high
initial ortho-P concentrations at Al(III):PO$_4$ molar ratios of 1:1, 1.4:1 and 2:1
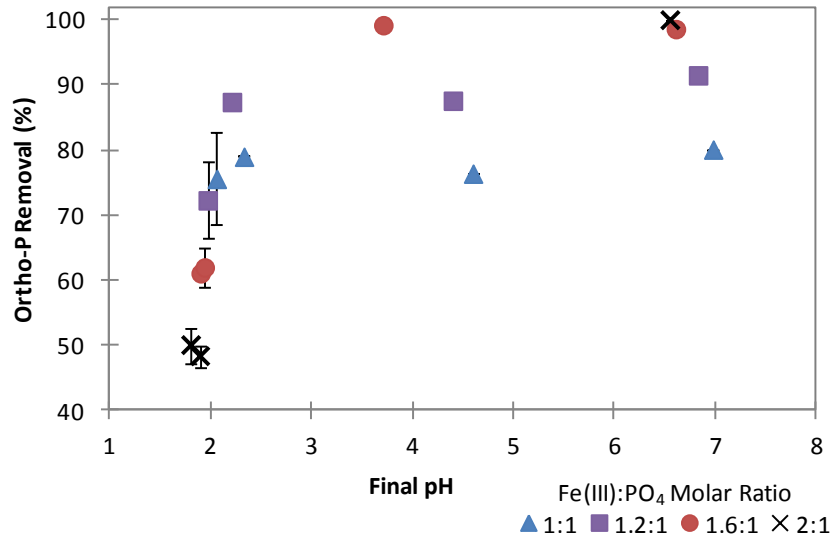
Figure 4.4   Ortho-P removal versus final pH in sludge dewatering liquors with high initial ortho-P concentrations at Fe(III):PO$_4$ molar ratios of 1:1, 1.2:1, 1.6:1 and 2:1

Figure 4.4 shows that at a 1:1 Fe(III):P molar ratio, percent removals were in the mid to high 70s for very low pHs just greater than 2, as well as at pH 4.5 and 7. At a 1.2:1 molar ratio, 90% removal was achieved near neutral pH and high 80% removals were seen at pH 2.2 and 4.4. However, the percent removal decreased to the low 70s when the final pH was 2. This effect was more substantial as the molar dose increased to 1.6:1, then 2:1. At a 1.6:1 dose the final pH was just below 2 and low 60% removals were observed. Then, as the dose increased to 2:1 only 50% removals were observed at pHs just below 2. In contrast, near complete removals were achieved with 1.6:1 and 2:1 molar doses at final pHs of approximately 6.5. The decrease in P removal as pH decreases suggests that the solubility of ferric iron increases at low pH. This is because ferric (oxy-)hydroxide phases have small solubility products. For example, the log Ksp of Fe(OH)$_3$ is

-38.6, so the theoretical maximum concentrations of non-complexed ferric iron at pH 2 is 140 mg/L compared to 140 ng/L at pH 4 (Johnson et al., 2012).

4.2 The Effect of Initial Orthophosphate Concentration on Orthophosphate Removal in Low Alkalinity Wastewater

As previously discussed, the addition of metal salt coagulants to wastewater consumes alkalinity and lowers pH. In EBPR sludge dewatering liquors with high ortho-P concentrations (i.e. >100 mg/L PO_4-P) greater amounts of coagulant is required than in liquors with low ortho-P concentrations. Thus, larger additions of coagulant will consume more alkalinity and result in greater pH depression. This is especially important in the case of ferric chloride use because lower pH will result in the destruction of oxyhydroxides that negatively affect phosphorus removal. Therefore, treating high phosphorus concentration streams, such as sludge dewatering return streams, with ferric chloride becomes less effective because of the depression in pH. In low alkalinity waters this effect is more substantial as pH depression will occur more rapidly. Using coagulants that do not depress the pH as much may be a viable solution to treating these streams.

To test the effect of initial ortho-P concentration on P removal in low alkalinity waters, batch tests were performed with liquors containing a high initial ortho-P concentration of 116-127 mg/L, as well as liquors with a low ortho-P concentration of 15 mg/L. The initial pH of each sample was 4.5 and alkalinity was less than 1 mg/L as $CaCO_3$. Ortho-P removal versus coagulant dose for both high and low initial ortho-P concentrations was plotted (Figure 4.5) for ferric chloride (4.5a), alum (4.5b) and

lanthanum chloride (4.5c). In addition, the final solution pH was plotted on the secondary axis.

At low ortho-P concentrations using ferric chloride, P removal increased from approximately 50% at a 1:1 molar ratio to nearly 90% removal at a 2:1 molar ratio (Figure 4.5a). The final solution pH dropped from about 3.5 to just below 3 while increasing from a 1:1 to 2:1 molar dose. On the other hand, at high ortho-P concentrations P removals decreased with increasing ferric chloride addition. A 75% removal was observed at a 1:1 molar ratio and steadily decreased to approximately 50% at a 2:1 molar ratio. This was not expected as the addition of more coagulant, in theory, should remove more phosphate. The decrease in removal is attributed to the decrease in final pH, which lowered to just below 2 after a 2:1 ferric dose.

P removals using alum were the least effective as seen in Figure 4.5b. At low initial ortho-P concentrations, removals increased from only 28% at a 1:1 molar dose to around 40% at a 2:1 dose. Similar to ferric chloride, at high initial ortho-P concentrations removals decreased with increasing dose. Only a 10% removal was observed at a 1:1 alum dose and decreased to below 5% at a 2:1 dose. Thus, alum is not an effective coagulant in liquors below pH 4.5.
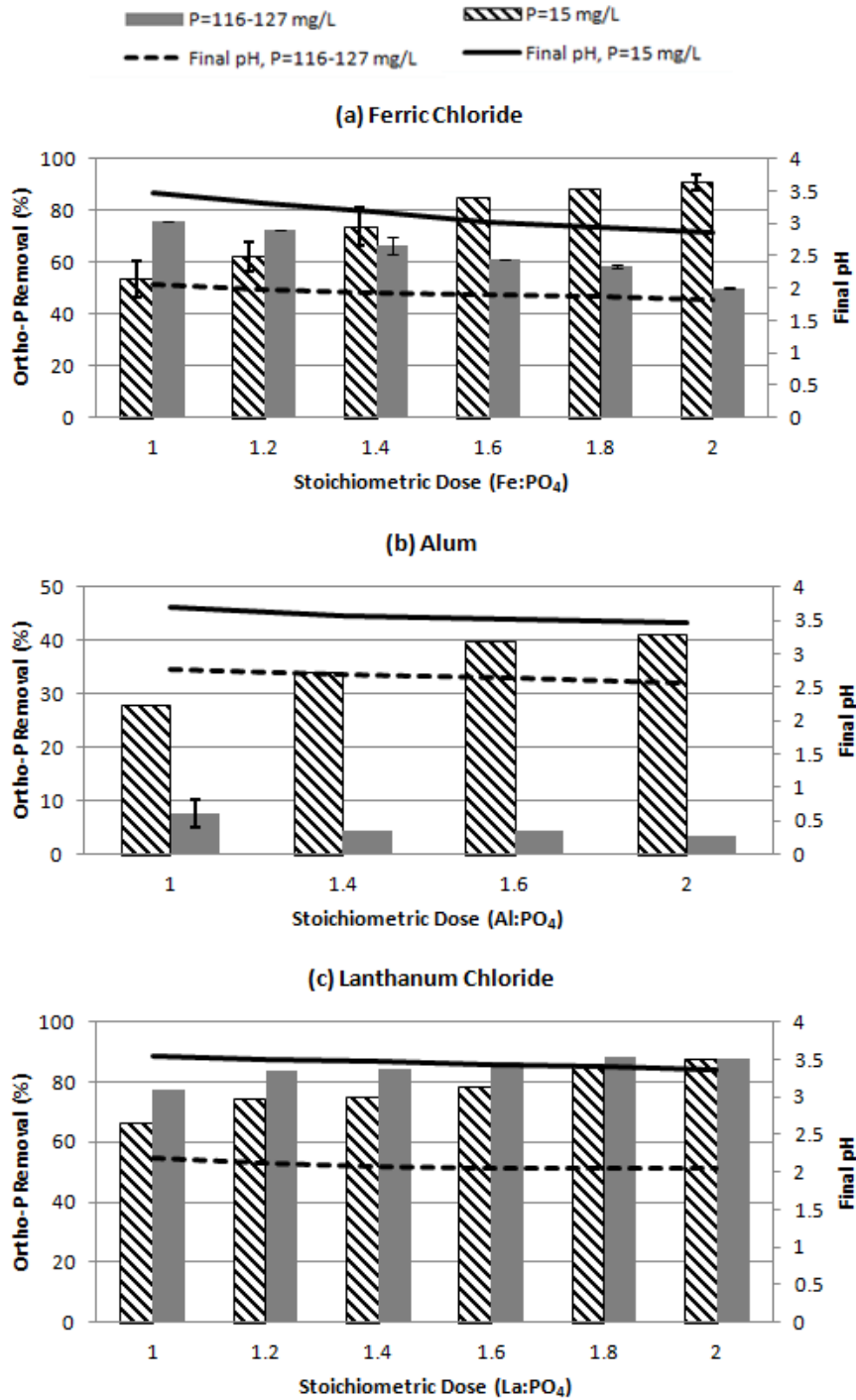
Figure 4.5   Ortho-P removal with respect to coagulant dose in low alkalinity EBPR sludge dewatering liquors with high and low initial ortho-P concentrations. Initial solution pH = 4.5. Final solution pH is plotted on the secondary axis

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With high initial ortho-P concentrations (116-127 mg/L) using lanthanum as a coagulant, the final solution pH dropped to approximately 2 at a 2:1 dose as it did with ferric iron (Figure 4.5c). However, in contrast, P removals increased with increasing lanthanum dose. At a 1:1 molar dose approximately 65% P removal was observed and it increased to about 85% with a 2:1 dose. This suggests that the resolubilization of lanthanum complexes does not occur at pH 2 to the extent of ferric complexes. At a low ortho-P concentration of 15 mg/L, P removals using lanthanum increased from approximately 65% at a 1:1 molar ratio to about 88% at a 2:1 ratio. These removals were very similar to ferric chloride at low initial ortho-P concentrations because less coagulant is required and pH depression is not as extensive as in waters with high initial ortho-P concentrations. It is important to note that with lanthanum, greater % removals were seen with high initial ortho-P concentrations compared to low concentrations at the same molar dose. For example, at a 1:1 molar dose, 77% removal was achieved when initial ortho-P was high, whereas only 67% removal was seen with low initial ortho-P. This is also typical with alum and ferric chloride as it has been shown that higher initial ortho-P concentrations require lower molar doses (Smith et al., 2007).

Because lanthanum-based coagulants are not commercially available in North America and rare earth extraction is costly, ferric chloride would be a more cost effective coagulant in sludge dewatering liquors with low ortho-P concentrations where pH depression is not as great of a concern.

4.3 The Effect of Coagulant Dose

The effect of coagulant dose was determined by adding increasing metal to orthophosphate molar doses ranging from 0.6:1 to 2:1. Four EBPR sludge dewatering liquors with high orthophosphate concentrations (102 to 127 mg/L) were used which had initial pHs of 7.85, 6.5, 5.5 and 4.5. Figure 4.5 shows orthophosphate removal versus metal salt (as La^{3+}, Al^{3+} and Fe^{3+}) molar dosage for each of the four solutions of different initial pHs.
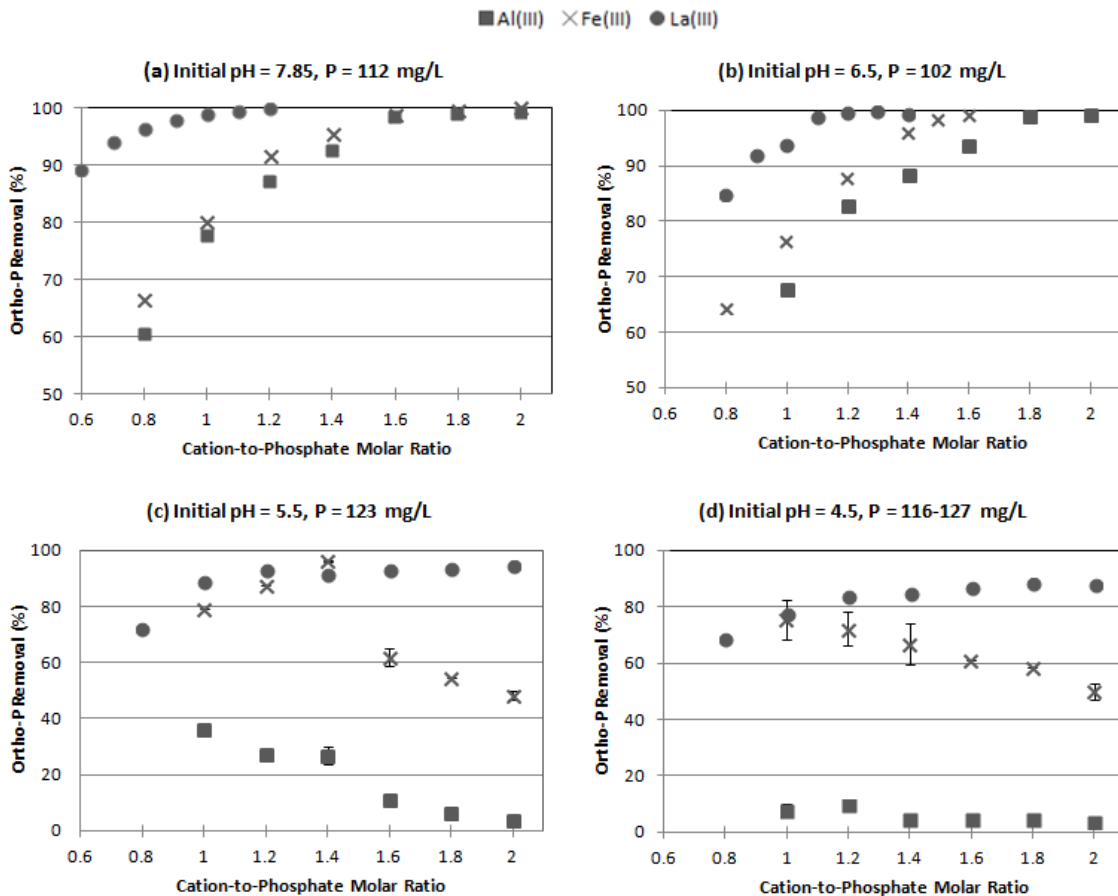
Figure 4.6 Orthophosphate removal with respect to metal dose at initial pH of (a) 7.85 (b) 6.5 (c) 5.5 (d) 4.5 and high orthophosphate concentrations (102-127 mg/L)

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At initial pH values of 7.85 (Figure 4.5a) and 6.5 (Figure 4.5b), an increase in removal with increasing coagulant dose was observed for all three coagulants, and as removals approached 100%, they began to level off. Lanthanum achieved a higher ortho-P removal at lower molar doses than either ferric iron or aluminum. Greater than 99% removals were achieved with lanthanum at molar ratios of 1:1 and 1.1:1 for initial pHs of 7.85 and 6.5, respectively. In comparison, molar doses of 1.6:1 to 2:1 were required for aluminum and ferric iron to obtain 99% removals, which was expected because to achieve 80 to 98% soluble phosphate removal from wastewater containing a typical initial soluble phosphate concentration, metal-to-phosphate molar doses greater than 1.5 to 2 are usually required (Szabo et al., 2008). Recht et al. (1970) observed complete phosphate removal with lanthanum at molar ratios as low as 0.9:1 and suggested that the mono- and dihydrogen orthophosphate ions in addition to the trivalent orthophosphate ion are involved in precipitate formation. The authors also suggested that a chemical reaction occurs between phosphate and lanthanum and that physical processes such as adsorption are not likely involved in P removal.

As shown in Figure 4.6c, at an initial pH of 5.5 P removal with lanthanum is fairly consistent at molar ratios of 1:1 up to 2:1, as indicated by the slight increase from approximately 88% removal at 1:1 to 94% at 2:1. P removal with ferric chloride at a 1:1 molar ratio was about 80%, increased to 85% at a 1.2:1 ratio and further increased to 98% at a 1.4:1 ratio. Then, at a 1.6:1 ratio P removal drastically dropped to approximately 60% and continued to decrease to below 50% at a 2:1 dose. At a 1.6:1 molar ratio with ferric chloride the final solution pH dropped below 2 causing the removal efficiency to decrease. P removal with alum followed a similar decreasing trend as removal below

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40% at a 1:1 ratio continued to drop to less than 5% at a 2:1 removal. This is because the final solution pH was below 3 and continued to decrease.

At an initial pH of 4.5 (Figure 4.6d), lanthanum is the only coagulant in which an increasing trend in P removal is observed with increasing coagulant dose. At a 1:1 molar ratio, both lanthanum and ferric iron achieve a similar removal of about 78%. However, removal with lanthanum gradually increases to 88% while removal with ferric iron gradually decreases to 50% at 2:1 molar ratios. At an initial pH of 4.5 and in the absence of alkalinity, a 1.2:1 molar dose of ferric iron dropped the pH below 2 causing removal efficiencies to decrease and continue to decrease with increasing dose. Alum did not show any significant P removal at an initial pH of 4.5 as removals were less than 10% at molar doses of 1:1 to 2:1.

4.4   Sludge Consideration

The wet solids volume (mL) settled after 30 minutes was used to quantify the total amount of sludge generated per 500 mL of batch solution with a high initial ortho-P concentration (102 to 123 mg/L). Figure 4.7 shows ortho-P removal as a function of settled solids volume for initial pHs of (a) 7.85 (b) 6.5 (c) 5.5 and (d) 4.5.

At an initial pH of 7.85 (Figure 4.7a), the amount of settled solids increases with increasing ortho-P removal for ferric chloride, lanthanum chloride and alum. Ferric chloride produced the highest amount of solids, followed by lanthanum chloride, then alum.

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At an initial pH of 6.5 (Figure 4.7b), ferric chloride and lanthanum chloride produced similar volumes of solids at over 80% removals, which is approximately 20 to 25% of the total sample volume. Alum produced less than 3% solids at 80 to 100% removals. It would appear that a smaller amount of solids production at high P removals would be ideal as this would produce less sludge to be handled by the primary clarifiers when the dewatering liquors are recycled. However, in the case of alum, the small amount of settled solids and high removal is deceiving and the turbidity of the sample above the settled solids needs to be considered. In fact, the turbidity was as high as 521 NTU meaning that even though high P removals were achieved, there was very poor floc formation and settling.
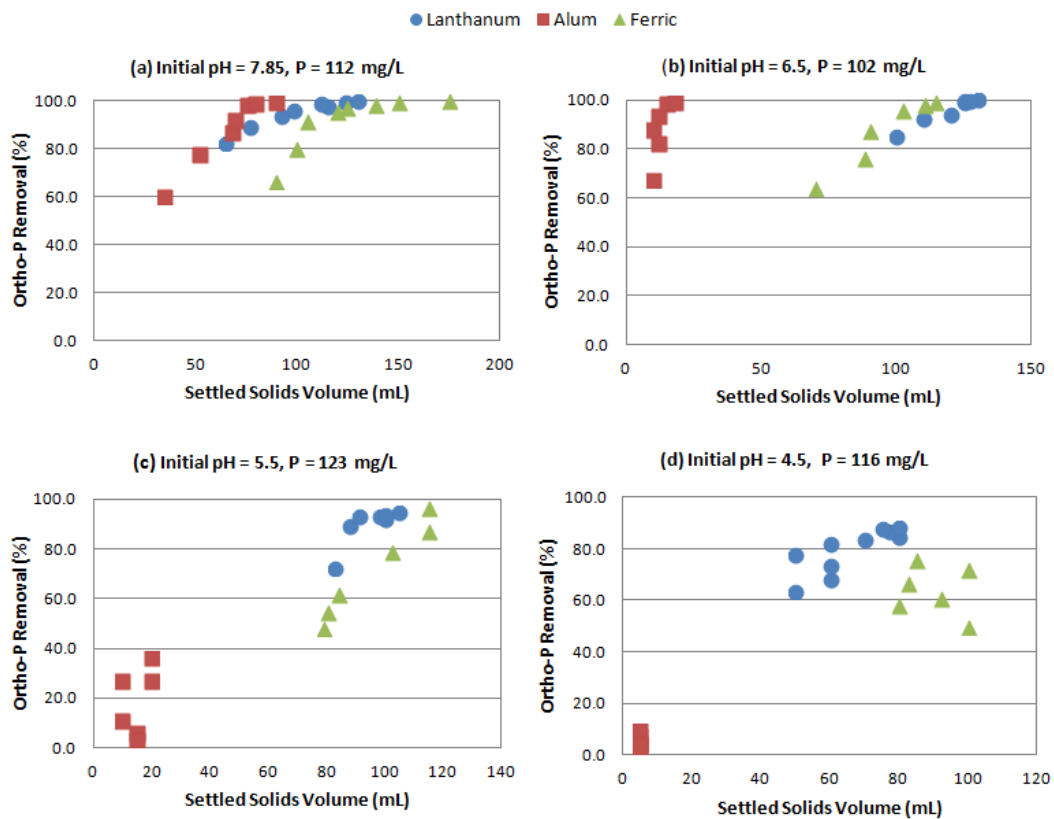
Figure 4.7   Ortho-P removal versus settled solids volume (mL) at initial pH of (a) 7.85 (b) 6.5 (c) 5.5 and (d) 4.5. Intial sample volume = 500 mL

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At an initial pH of 5.5 (Figure 4.7c), similar solids volumes were produced for lanthanum chloride and ferric chloride, totalling 15 to 25% the total sample volume. In addition, the settled solids volume increased with increasing P removal. Alum produced less than 4% solids with P removals below 40%.

At an initial pH of 4.5 (Figure 4.7d), lanthanum chloride produced settled solids volumes 10 to 15% of the total sample volume at ortho-P removals of 60 to 88%. Ferric chloride produced 15 to 20% settled solids at P removals from 45 to 75%. There is no clear relationship between settled solids volume and P removal. Settled solids are essentially non-existent with alum as P removals were less than 10%.

The turbidity of each batch test sample's supernatant was measured after 30 minutes of solids settling. Figure 4.8 shows ortho-P removal versus turbidity for each coagulant. With lanthanum, there appears to be a relationship between turbidity and ortho-P removal wherein turbidity increases with decreasing removal. At >99% percent removal with lanthanum, the turbidity was below 50 NTU and turbidity increased to approximately 175 NTU as ortho-P removals decreased just below 70%. Ferric chloride did not follow a similar trend as turbidity values less than 50 NTU were seen for removals ranging from 50 to >99% removal. The turbidity measurements in Figure 4.8 are for all pH values ranging from 2 to 7 and the wide range of ortho-P removals with turbidity less than 50 NTU shows the complexity of the reactions that occur with iron. Alum produced the most turbid waters of the three coagulants. At 99% ortho-P removal, the turbidity was approximately 140 NTU, which is almost 3 times the turbidity of lanthanum or ferric chloride at similar removals. A highly turbid liquor is less desirable as it will increase the solids content in the recycled liquor or require filtration.

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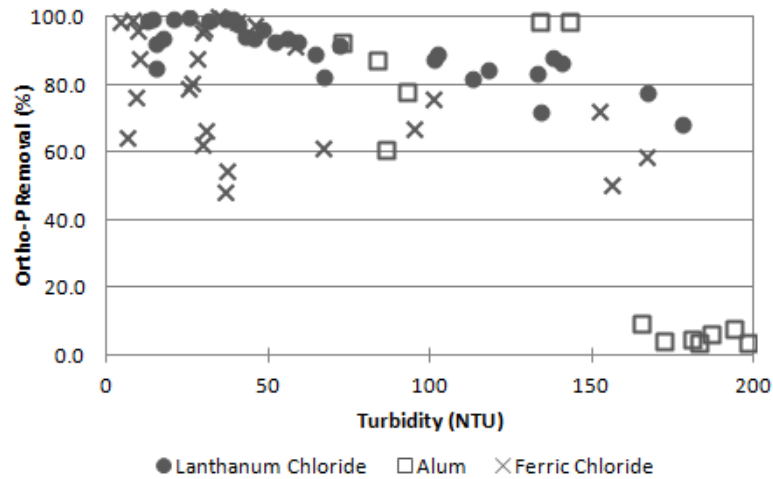
Figure 4.8 Turbidity of batch test supernatant after 30 minutes of solids settling using lanthanum chloride, alum and ferric chloride

4.5 Equilibrium Modeling with MINEQL+

Orthophosphate removals were predicted using the chemical equilibrium modeling software MINEQL+ (Version 4.6). An initial ortho-P concentration of 112 mg/L and an equimolar amount of trivalent metal (Fe^{3+}, Al^{3+} or La^{3+}) was used in each of the models and ortho-P removal was determined at pHs from 1 to 8. Figure 4.9 shows the results of the equilibrium modeling predictions in comparison to experimental and theoretical results (from synthetic solutions) for ferric chloride (4.9a), lanthanum chloride (4.9b) and alum (4.9c).

As shown in Figure 4.9a, modeling predicts 100% removal for ferric chloride at pH 1.5 to 6.5, followed by a rapid decrease in removal to pH 7. Experimental results,

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however, show a high 70% to 80% removal for all final solution pHs of 2-2.5, 4.6-4.8 and 7.
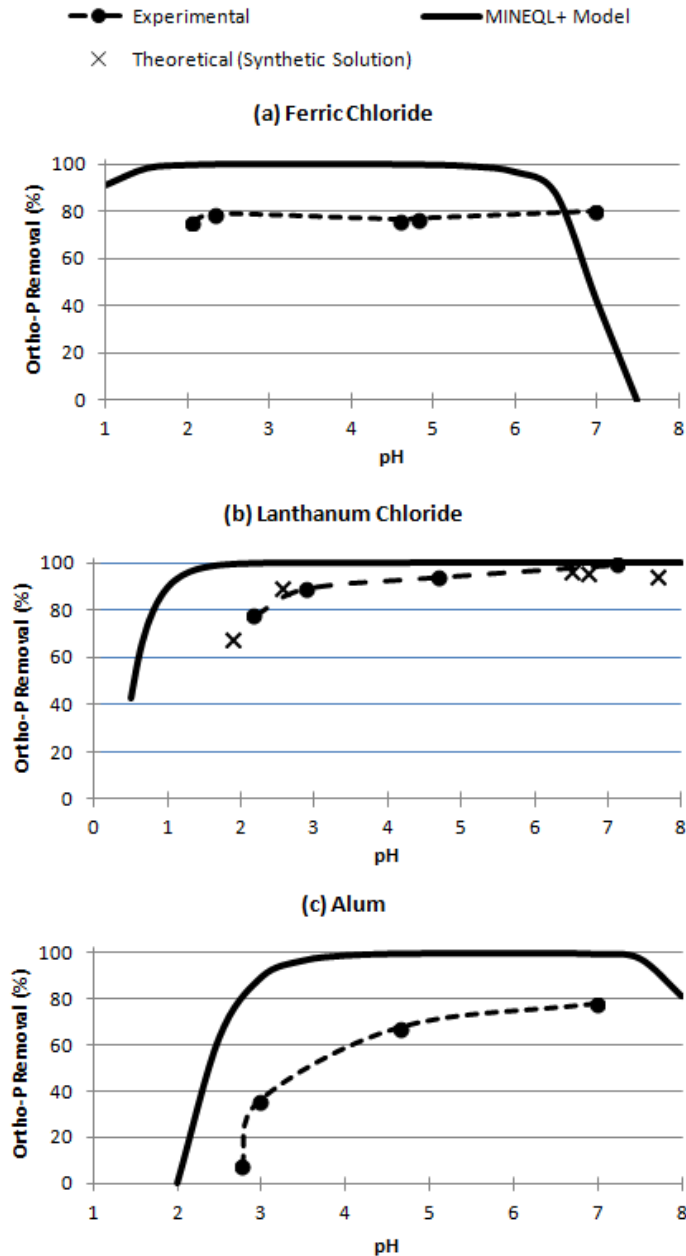
Figure 4.9   MINEQL+ model results in comparison to experimental and theoretical results for (a) ferric chloride (b) lanthanum chloride and (c) alum

In Figure 4.9b, modeling predicts 100% removal for lanthanum at pH 1.5 to 8. Experimental results show a 99% percent removal at neutral pH, a 94% removal at pH 4.7 and a steady decrease to 89% and 78% at pH 2.9 and 2.2, respectively. It may be seen, comparing experimental results with theoretical results, that phosphate removal from EBPR sludge dewatering liquors has a similar dependence on pH as phosphate removal from pure, synthetic solutions.

As seen in Figure 4.9c, modeling predicts greater than 90% removals for alum at pH 3 to 6. Experimental results show a 36% removal at pH 3, 68% removal at pH 4.7 and 78% removal at pH 7.

It was expected that greater ortho-P removals would be predicted in equilibrium modeling than would be determined experimentally because there are many compounds present in the EBPR sludge dewatering liquors that were not accounted for in the model. Hydrolysis products of the metal salts can react with other ligands to form soluble or insoluble products (MWH, 2005). These competing reactions may reduce the amount of metal ions available for phosphate precipitation. Additionally, some phosphate could be adsorbing on mixed liquor suspended solids, which is not considered in the model. The limitations of these models are that only single stage precipitations were considered and other mechanisms such as adsorption and co-precipitation may be taking place.

CHAPTER 5

CONCLUSIONS AND IMPLICATIONS

The objective of this research was to evaluate the effectiveness of lanthanum chloride for phosphate removal from EBPR recycle streams in comparison to ferric chloride and aluminum sulfate. To determine this, batch tests were performed on actual EBPR sludge dewatering liquors of varying pH and initial orthophosphate concentrations.

The following conclusions can be drawn from this research:

- The addition of La(III) to wastewater results in less pH depression than Fe(III) or Al(III). Thus, lanthanum chloride is an attractive coagulant as costly pH adjustments are minimized.

- On a molar ratio basis, lanthanum is more effective than aluminum and ferric iron for the precipitation of orthophosphates. Greater than 99% ortho-P removal was achieved using lanthanum to phosphate molar ratios of 1:1 and 1.1:1 in digested EBPR sludge dewatering liquor (Initial pH = 7.85) and non-digested sludge dewatering liquor (Initial pH = 6.5) with high initial orthophosphate concentrations (>100 mg/L), respectively. Metal to phosphate molar ratios from 1.6:1 to 2:1 were required to achieve 99% removals with aluminum and ferric.

- In liquors with a high initial ortho-P concentration (>100 mg/L), lanthanum chloride achieved greater than 85% ortho-P removal at pHs as low as 2, whereas removal efficiency decreased with increasing ferric chloride dose due to pH depression.

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- In low alkalinity liquors with low initial ortho-P concentrations (15 mg/L), ferric iron and lanthanum both achieved similar removals of 88 to 90% at 2:1 molar doses. Because of the lower cost and commercial availability of ferric chloride, it is the more practicable coagulant for liquors with low initial ortho-P concentrations.

- Aluminum sulfate is not an effective coagulant for phosphate removal in low pH sludge dewatering liquors. Below pH 3, less than 40% ortho-P removal was achieved, and removals decreased to below 5% with increasing alum dose and pH decrease.

5.1 Implications of Research Findings to the Application of Lanthanum for the Treatment of Recycle Streams in EBPR Systems

The results of this study show that lanthanum salts have a good potential to be a viable coagulant in real-world EBPR sludge dewatering liquors. It was shown that lanthanum achieves high ortho-P removals at lower molar ratios than either aluminum or ferric iron. This means that there will be less chemical demand when using lanthanum-based coagulants, which will reduce on-site chemical volumes and handling. Additionally, as less chemicals will be used, chemical storage containers will not have to be refilled as often, thus having a positive environmental impact by keeping more trucks off the road for deliveries.

The use of lanthanum can reduce the potential of operational problems arising due to scaling from the formation of vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitates. Vivianite will not be able to form since there will not be

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sufficient iron available, and by decreasing the amount of phosphate in the sludge dewatering liquor by precipitation with lanthanum, it will decrease the potential for struvite formation. There may also be use for lanthanum in digesters to prevent struvite formation. Substantially decreasing the potential for scaling in pipes and equipment is valuable in avoiding costly maintenance.

Sludge production is an important consideration in wastewater treatment plant operations as larger sludge volumes increase dewatering equipment usage and sludge disposal. In this study there was only approximately a 5% difference in sludge production (by volume) observed between ferric chloride and lanthanum chloride at similar ortho-P removals. At present, ferric chloride is the most commonly used coagulant for phosphorus removal in sludge dewatering liquors. Because lanthanum chloride produces very similar sludge volumes, the use of lanthanum-based coagulants should not have a significant positive or negative impact on sludge generation. However, the dewatering properties of sludge containing lanthanum need to be evaluated. It may be the case that sludge resulting from lanthanum precipitation is more easily dewaterable, which can decrease shipping costs associated with sludge disposal. In addition, it needs to be determined whether lanthanum-based sludge from wastewater treatment applications has potential agricultural uses, or if it meets the metal requirements for landfill disposal. Potential toxicity of lanthanum-containing sludge has to be evaluated as well.

A major concern in using lanthanum-based coagulants is that lanthanum has been proven to be toxic to some strains of bacteria and therefore has disinfectant properties. This is important because if lanthanum is used in recycle streams there is potential for excess lanthanum to return to the biological system and have adverse effects on the

microbial population. Although residual lanthanum was not measured in this study, Recht et al. (1970) reported that no lanthanum was detected after phosphorus precipitation with the use of excess lanthanum (2:1 La/PO$_4$ molar ratio). The fact that the excess lanthanum precipitated is promising as it suggests that residual lanthanum in recycle streams may not be an issue. However, further research into this and the disinfectant properties of lanthanum on wastewater microbes- especially those present in EBPR systems- is critical in determining if lanthanum is a feasible coagulant in wastewater applications.

Not only does lanthanum show potential for phosphate removal in EBPR sludge dewatering liquors, but with its wide effective pH range and strong affinity with phosphate, there is the possibility for lanthanum usage in many other water treatment applications.

5.2 The Significance of Cost to the Feasibility of Lanthanum Chloride Use in Wastewater Treatment

EBPR is an inexpensive and practical phosphorus removal technology in warm regions of the United States. In the cold regions of the country, sufficient volatile fatty acids cannot be generated for EBPR, thus chemical phosphorus removal is predominant. Ferric and ferrous chloride and alum are widely used for this purpose. The concentrations of phosphorus in influent waters are small and according to the results of this research, ferric chloride and lanthanum chloride would perform very similarly with no major depression in pH. Thus, the use of lanthanum as the primary coagulant for phosphorus removal in a plant is less likely, unless its cost is lowered.

Cost is a major factor in determining whether lanthanum-based coagulants will be used in wastewater applications. Currently there are a few companies that supply lanthanum chloride and although quotations for lanthanum pricing are hard to obtain, vendors indicate that lanthanum chloride is 5-10 times more expensive than ferric chloride. To evaluate the potential costs associated with phosphate removal in EBPR return streams using lanthanum chloride, in comparison to ferric chloride and alum, yearly chemical costs with respect to ortho-P removal were determined (Figure 5.1). A 1.0 MGD recycle stream with an initial pH of 7.85 and 112 mg/L ortho-P was used in the cost estimation, which is based on actual data from Centrate 2 used in this study. Ortho-P removals with respect to molar dosage were considered from data obtained in batch tests (Figure 4.6a). Bulk prices for ferric chloride ($0.3842 per lb) and aluminum sulfate ($0.289 per lb) were based on an actual quotation received from Brenntag Pacific, Inc. (Las Vegas, NV). A quotation for lanthanum chloride was not possible, so the cost of lanthanum chloride was estimated at 5 times the cost of ferric chloride. The specifications of each chemical are presented in Table 5.1. Some wastewaters do not have a strong buffering capacity and the addition of coagulant will depress the pH, necessitating pH adjustment. The cost of pH adjustment chemicals was not considered in the cost computation, and this cost can be significant. If pH adjustment is needed, using ferric chloride will require more chemicals to adjust the pH due to its greater pH depression. This will increase the overall cost of ferric chloride in comparison to lanthanum chloride.
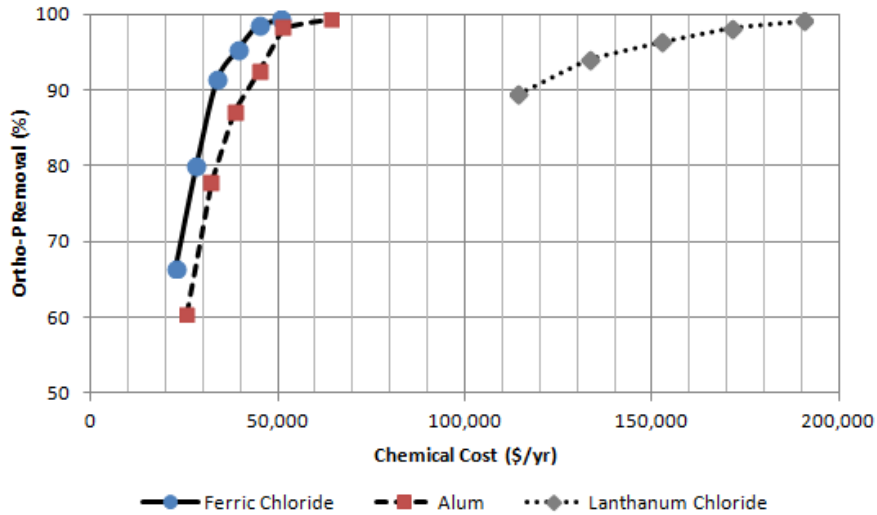
Figure 5.1   Chemical cost estimation with respect to ortho-P removal for lanthanum chloride, ferric chloride and alum usage in a 1.0 MGD recycle stream at initial pH 7.85 with 112 mg/L initial ortho-P

Table 5.1   Specifications of Chemicals Used in Cost Estimation

	Ferric Chloride	**Aluminum Sulfate**	**Lanthanum Chloride**
Chemical Formula	$FeCl_3$	$Al_2(SO_4)_3 \cdot 14H_2O$	$LaCl_3$
Concentration	39% as $FeCl_3$	8.1% as Al_2O_3	42% as $LaCl_3$
Specific Gravity	1.400	1.327	1.460
Chemical Supplier	Brenntag Pacific, Inc.	Brenntag Pacific, Inc.	Blue Line Co.

It can be seen that the yearly chemical cost of alum and ferric chloride is similar, but ferric chloride is slightly cheaper than alum. To achieve approximately 99% ortho-P removal, the yearly chemical costs for alum and ferric chloride is about $50,000 and $65,000, respectively. However, despite the lower doses required with lanthanum

chloride to achieve 99% ortho-P removal, the yearly chemical cost is close to $190,000. This is over 3.5 times the cost of ferric chloride even though lanthanum achieved 99% ortho-P removal at a 1:1 molar dose compared to ferric iron requiring a 1.8:1 molar dose to achieve 99% ortho-P removal. If the market price of lanthanum chloride is up to 10 times that of ferric chloride, this cost would double. To be competitive with ferric chloride economically, the price of lanthanum chloride would have to be as low as 1.3 times the cost of ferric chloride, even considering the lower molar ratios required for lanthanum to achieve similar ortho-P removals.

This cost estimation clearly shows that lanthanum chloride is currently not an economical coagulant for phosphate removal in EBPR recycle steams. However, the use of lanthanum-based coagulants is promising and lanthanum may find a very suitable application in the treatment of return streams to supplement EBPR. This is specifically the case for streams with high phosphorus concentrations and lower pH values, where ferric chloride is not effective because it becomes less effective with increasing dosages due to pH depression. As more rare earth metal mines are open in the United States and abroad, fueled by the demand for these metals used in electronics (e.g. cell and smart phones), rare earth chlorides, which are a by-product of these mines, will become more commercially available at lower prices.

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APPENDIX A

CALCULATION OF IONIC STRENGTH

The ionic strength of the sludge dewatering liquors can be calculated using the following equation devised by Lewis and Randall (Snoeyink and Jenkins, 1980):

$$\mu = \frac{1}{2}\sum_i(C_i Z_i^2) \qquad (A.1)$$

where:

μ = ionic strength C_i = concentration of species, i Z_i = charge of species, i

From this, the ionic strength can be calculated:

Table A.1   Calculation of Ionic Strength, Initial pH = 6.5 and P = 102 mg/L

SPECIES	C_i [mol/L]	Z_i	$C_i Z_i^2$
Al^{3+}	6.63E-05	3	5.97E-04
Ca^{2+}	1.88E-03	2	7.54E-03
Fe^{3+}	2.29E-05	3	2.06E-04
K^+	3.53E-03	1	3.53E-03
Mg^{2+}	2.23E-03	2	8.94E-03
NH_4^+-N	2.89E-03	1	2.89E-03
PO_4^{3-}	1.07E-03	3	9.67E-03
HCO_3^-	7.92E-03	1	7.92E-03
Ionic Strength, μ = 2.06E-02			

APPENDIX B

BATCH TEST RAW DATA

Table B.1   Initial pH = 4.5, P = 15 mg/L

LANTHANUM CHLORIDE							
Inital Ortho-P Concentration	Stoichiometric Dose	LaCl$_3$ Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
15	1.0	118.5	5	398	3.54	5.03	66.5
15	1.2	142.2	5	571	3.49	3.71	75.3
15	1.2	142.2	5	783	3.50	4.02	73.2
15	1.4	165.9	5	773	3.47	3.77	74.9
15	1.6	189.6	5	669	3.42	3.38	77.5
15	1.6	189.6	5	616	3.43	3.01	79.9
15	1.8	213.3	5	390	3.40	2.16	85.6
15	2.0	237.0	5	387	3.36	2.06	86.3
15	2.0	237.0	5	336	3.36	1.68	88.8
ALUMINUM SULFATE							
Inital Ortho-P Concentration	Stoichiometric Dose	Alum Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
15	1	144.0	5	208	3.69	10.8	28.0
15	1.4	201.6	10	337	3.56	9.78	34.8
15	1.4	201.6	10	241	3.57	9.98	33.5
15	1.6	230.4	10	329	3.52	9.01	39.9
15	2	288.0	10	520	3.47	8.93	40.5
15	2	288.0	10	464	3.48	8.78	41.5
FERRIC CHLORIDE							
Inital Ortho-P Concentration	Stoichiometric Dose	Ferric Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
15	1.0	78.0	5	311	3.48	6.95	53.7
15	1.2	93.6	8	286	3.31	5.68	62.1
15	1.4	109.2	15	370	3.18	4.32	71.2
15	1.4	109.2	15	319	3.17	3.62	75.9
15	1.6	124.8	25	414	3.02	2.29	84.7
15	1.8	140.4	45	402	2.94	1.73	88.5
15	1.8	140.4	45	285	2.92	1.85	87.7
15	2.0	156.0	50	322	2.86	1.38	90.8
15	2.0	156.0	46	228	2.85	1.36	90.9

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Table B.2   Initial pH = 5.5, P = 123 mg/L

LANTHANUM CHLORIDE							
Inital Ortho-P Concentration	Stoichiometric Dose	LaCl$_3$ Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
123	0.8	777	83	134	3.05	34.33	72.1
123	1.0	972	85	113	2.89	14.11	88.5
123	1.0	972	90	91.6	2.87	12.74	89.6
123	1.2	1166	90	51	2.51	8.02	93.5
123	1.2	1166	92	54	2.52	9.55	92.2
123	1.4	1360	100	72	2.33	10.12	91.8
123	1.6	1555	95	59	2.32	8.18	93.3
123	1.6	1555	100	59	2.32	8.95	92.7
123	1.8	1749	100	45	2.31	7.58	93.8
123	2.0	1943	105	43	2.28	6.89	94.4
ALUMINUM SULFATE							
Inital Ortho-P Concentration	Stoichiometric Dose	Alum Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
123	1.0	1181	20	314	2.98	78.79	35.9
123	1.2	1417	20	273	2.87	89.79	27.0
123	1.4	1653	10	292	2.85	92.82	24.5
123	1.4	1653	10	383	2.85	87.47	28.9
123	1.6	1889	10	365	2.81	109.54	10.9
123	1.8	2125	15	179	2.80	116.69	5.1
123	1.8	2125	15	195	2.80	114.81	6.7
123	2.0	2362	15	183	2.79	118.81	3.4
FERRIC CHLORIDE							
Inital Ortho-P Concentration	Stoichiometric Dose	Ferric Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
123	1.0	640	102	25	2.33	25.80	79.0
123	1.2	768	115	28	2.21	15.55	87.4
123	1.4	895	115	29	2.12	4.65	96.2
123	1.4	895	115	32	2.13	4.35	96.5
123	1.6	1023	78	32	1.94	49.31	59.9
123	1.6	1023	80	27	1.94	44.25	64.0
123	1.8	1151	80	37	1.92	55.92	54.5
123	2.0	1279	83	37	1.90	62.27	49.4
123	2.0	1279	85	36	1.89	64.98	47.2

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Table B.3   Initial pH = 6.5, P = 102 mg/L

				LANTHANUM CHLORIDE			
Inital Ortho-P Concentration	Stoichiometric Dose	LaCl$_3$ Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
102	0.8	645	100	15	4.87	15.31	85.0
102	0.9	725	110	12	4.76	8.17	92.0
102	0.9	725	110	18	4.76	7.88	92.3
102	1.0	806	120	17	4.69	6.52	93.6
102	1.0	806	120	18	4.67	5.91	94.2
102	1.1	886	125	15	4.47	0.88	99.1
102	1.1	886	125	11	4.47	1.02	99.0
102	1.2	967	125	20	4.40	0.16	99.8
102	1.3	1048	130	25	4.39	0.09	99.9
102	1.4	1128	125	13	4.36	0.20	99.8
102	1.4	1128	130	15	4.36	0.64	99.4
				ALUMINUM SULFATE			
Inital Ortho-P Concentration	Stoichiometric Dose	Alum Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
102	1.0	979	10	202	4.65	33.09	67.6
102	1.2	1175	12	345	4.45	17.60	82.7
102	1.4	1371	10	512	4.35	12.25	88.0
102	1.4	1371	10	521	4.36	11.81	88.4
102	1.6	1567	12	419	4.11	6.42	93.7
102	1.8	1763	15	482	3.85	1.07	99.0
102	1.8	1763	15	504	3.85	0.91	99.1
102	2.0	1958	18	448	3.77	0.85	99.2
				FERRIC CHLORIDE			
Inital Ortho-P Concentration	Stoichiometric Dose	Ferric Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
102	0.8	424	70	6.62	4.77	36.41	64.3
102	1.0	530	85	9.24	4.61	23.71	76.8
102	1.0	530	92	9.37	4.59	24.43	76.0
102	1.2	636	90	10.4	4.40	12.60	87.6
102	1.4	743	105	12.3	4.13	3.95	96.1
102	1.4	743	100	7.51	4.13	4.05	96.0
102	1.5	796	110	4.41	4.11	1.68	98.4
102	1.6	849	118	9.12	3.71	0.83	99.2
102	1.6	849	110	7.09	3.71	0.74	99.3

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Table B.4   Initial pH = 7.85, P = 112 mg/L

Inital Ortho-P Concentration	Stoichiometric Dose	LaCl₃ Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
LANTHANUM CHLORIDE							
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
112	0.5	442	65	67	7.18	19.40	82.7
112	0.6	531	75	66	7.17	12.63	88.7
112	0.6	531	78	62	7.17	11.12	90.1
112	0.7	619	92	56	7.17	6.61	94.1
112	0.8	708	95	47	7.16	4.24	96.2
112	0.8	708	100	49	7.16	3.97	96.5
112	0.9	796	115	40	7.14	2.12	98.1
112	1.0	885	112	31	7.12	1.04	99.1
112	1.1	973	120	38	7.09	0.50	99.6
112	1.1	973	128	38	7.09	0.71	99.4
112	1.2	1062	130	36	7.07	0.10	99.9

Inital Ortho-P Concentration	Stoichiometric Dose	Alum Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
ALUMINUM SULFATE							
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
112	0.8	860	35	86	7.13	44.33	60.4
112	1.0	1075	50	94	6.99	25.89	76.9
112	1.0	1075	55	91	6.98	23.98	78.6
112	1.2	1290	68	84	6.91	14.33	87.2
112	1.4	1505	70	72	6.88	8.48	92.4
112	1.6	1720	73	152	6.75	1.91	98.3
112	1.8	1935	80	134	6.67	1.33	98.8
112	1.8	1935	84	147	6.67	1.47	98.7
112	2.0	2150	90	203	6.65	0.79	99.3

Inital Ortho-P Concentration	Stoichiometric Dose	Ferric Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
FERRIC CHLORIDE							
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
112	0.8	466	90	31	7.04	37.46	66.6
112	1.0	582	100	26	6.98	22.30	80.1
112	1.2	699	105	59	6.83	9.53	91.5
112	1.4	815	120	30	6.82	5.10	95.4
112	1.5	874	125	46	6.67	3.01	97.3
112	1.6	932	138	43	6.61	1.64	98.5
112	1.6	932	140	38	6.61	1.46	98.7
112	1.8	1048	150	35	6.57	0.70	99.4
112	2.0	1165	175	35	6.56	0.06	99.9

Table B.5   Initial pH = 4.5, P = 116-127 mg/L

| LANTHANUM CHLORIDE							
Inital Ortho-P Concentration	Stoichiometric Dose	LaCl$_3$ Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
116	0.8	733	60	178	2.28	35.03	69.8
116	0.8	733	50	176	2.28	38.36	66.9
116	0.9	825	80	222	2.23	30.96	73.3
116	1.0	916	50	218	2.17	27.11	76.6
116	1.0	916	60	116	2.19	24.85	78.6
116	1.1	1008	60	113	2.15	21.06	81.8
116	1.2	1100	90	110	2.13	18.85	83.8
116	1.2	1100	70	156	2.13	19.5	83.2
127	1.4	1405	80	118	2.07	19.77	84.4
127	1.6	1605	80	108	2.06	18.4	85.5
127	1.6	1605	75	173	2.06	15.69	87.6
127	1.8	1806	80	138	2.05	15.18	88.0
123	2.0	1943	75	101	2.04	14.85	87.9
ALUMINUM SULFATE							
Inital Ortho-P Concentration	Stoichiometric Dose	Alum Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
116	1.0	1114	5	222	2.77	109.18	5.9
116	1.0	1114	5	166	2.77	105.03	9.5
116	1.2	1336	5	165	2.73	105.09	9.4
116	1.4	1559	5	178	2.69	110.09	5.1
116	1.4	1559	3	166	2.70	112.00	3.4
116	1.6	1782	5	181	2.65	110.87	4.4
116	1.8	2004	5	247	2.61	111.40	4.0
116	1.8	2004	5	182	2.60	110.00	5.2
116	2.0	2227	5	198	2.57	111.90	3.5
FERRIC CHLORIDE							
Inital Ortho-P Concentration	Stoichiometric Dose	Ferric Dose	Settled Solids Volume	Final Turbidity	Final pH	Final Ortho-P Concentration	Percent Removal
[mg/L]	--	[mg/L]	[mL]	[NTU]	--	[mg/L]	%
116	1.0	603	70	48	2.08	33.10	71.5
127	1.0	660	85	154	2.03	23.56	81.4
116	1.2	724	90	131	1.98	35.70	69.2
127	1.2	792	90	174	1.96	28.62	77.5
116	1.4	844	90	55	1.93	30.61	73.6
127	1.4	925	65	95	1.91	46.63	63.3
116	1.6	965	85	62	1.90	44.76	61.4
116	1.6	965	85	73	1.89	45.44	60.8
116	1.8	1086	85	167	1.86	48.07	58.6
127	2.0	1321	60	220	1.81	58.58	53.9
127	2.0	1321	90	156	1.81	63.49	50.0

APPENDIX C

MINEQL+ MODELING OUTPUT
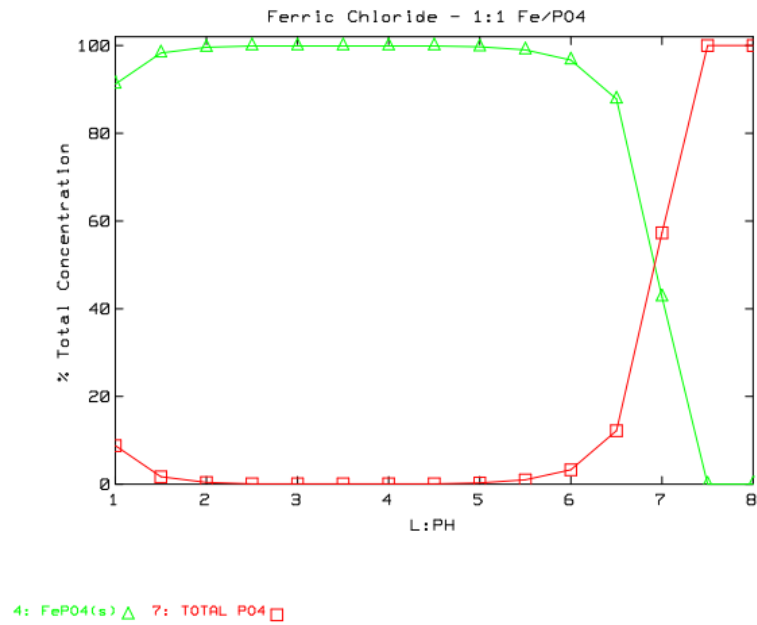
Figure C.1   Percent ortho-P and FePO$_4$ (s) remaining after a 1:1 Fe:PO$_4$ molar dose as
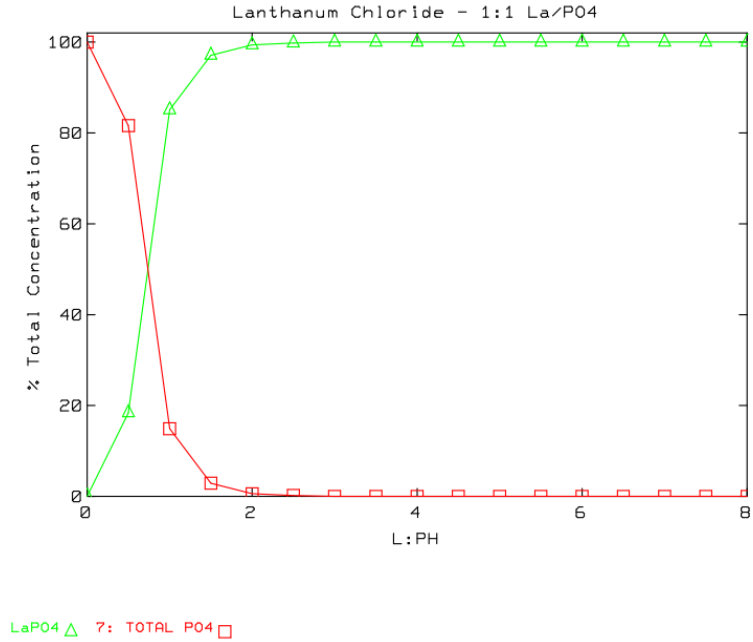predicted with MINEQL+

Figure C.2   Percent ortho-P and LaPO$_4$ (s) after a 1:1 La:PO$_4$ molar dose as predicted with MINEQL+
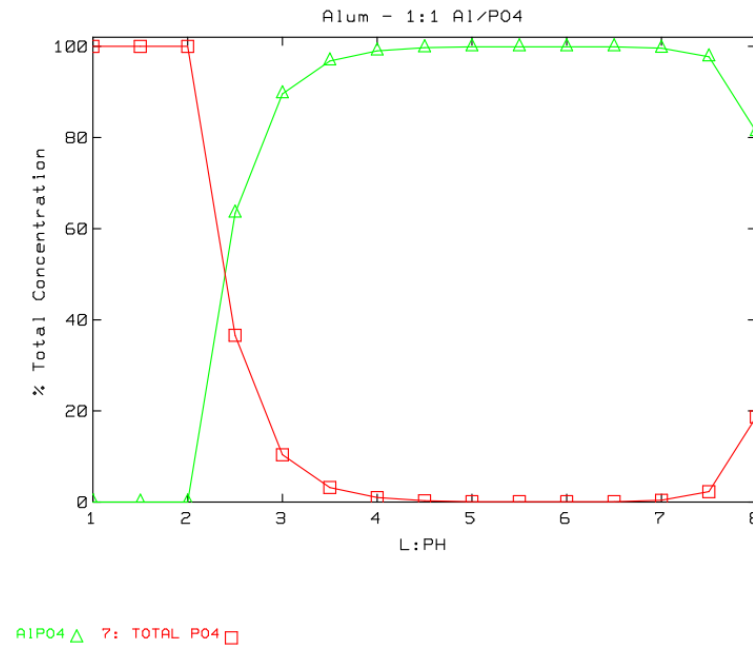

Figure C.3   Percent ortho-P and AlPO$_4$ (s) after a 1:1 Al:PO$_4$ molar dose as predicted with MINEQL+

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