Characteristics and Conditioning of Anaerobically Digested Sludge from A Biological Phosphorus Removal Plant

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CHARACTERISTICS AND CONDITIONING OF ANAEROBICALLY DIGESTED SLUDGE FROM A BIOLOGICAL PHOSPHORUS REMOVAL PLANT

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(Abstract)

A study of the anaerobically digested sludge form a full-scale biological phosphorus removal (BPR) plant (York River Wastewater Treatment Plant, York River, Va.) was conducted to determine the effects of BPR on sludge characteristics and conditioning requirements. Data collected from the plant indicated that both the total and soluble phosphorus (P) concentrations in the anaerobically digested sludge increased dramatically with the initiation of BPR. Accompanying this increase in total P was an increase in the total concentrations of magnesium and potassium content of the sludge, supporting the observations

that these ions are co-transported with P during the accumulation and release of P by P accumulating organisms.

The majority of the phosphate present in the pre- and post-BPR anaerobically digested sludges was bound by calcium, magnesium, and iron phosphorus precipitates including hydroxyapatite, struvite, and vivianite. Calcium phosphorus precipitates were the most prevalent in both sludges, but the percentage of magnesium phosphorus precipitates increased with the onset of BPR.

Cationic organic polymer conditioning dosages needed to achieve acceptable sludge dewatering rates for the post-BPR sludge were similar to those required by the pre-BPR sludge. The cationic organic polymer used to condition these sludges was ineffective in removing excess phosphate; therefore, the addition of either one or both of the inorganic chemicals ferric chloride and calcium hydroxide was required to remove soluble phosphorus. Conditioning with either ferric chloride or calcium hydroxide alone was not effective in achieving acceptable dewatering rates; however, when used together the chemicals produced acceptable dewatering rates and soluble P removal from the post-BPR sludge.

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CHAPTER I

INTRODUCTION

Under the proper conditions, certain microorganisms have the ability to store phosphorus in excess of stoichiometric growth requirements. When these organisms are exposed first to anaerobic and then to aerobic conditions in the presence of organic substrate, they can achieve high degrees of soluble phosphorus removal from phosphorus-rich waters. This phenomenon, called biological phosphorus removal (BPR), is beginning to receive much attention as a method of removing soluble phosphorus from municipal wastewater.

Whereas the conventional activated sludge process may remove 20-30 percent of the influent soluble phosphorus and yield a waste sludge containing 1.5-2.0 percent phosphorus by weight, BPR treatment plants typically produce influent phosphorus removals between 80-95 percent and a sludge containing 5.0-6.0 percent phosphorus by weight. Several wastewater treatment plants have recently modified their conventional activated sludge process to include BPR.

Most of the research studies conducted to date have focused on the removal mechanism and efficiency of the BPR process. Less work has been done on the ultimate fate of the excess phosphorus in the waste sludge during subsequent sludge processing. For example, anaerobic conditions favor the release of phosphorus from phosphorus- accumulating organisms. Consequently, if anaerobic digestion is used as a method of sludge stabilization and solids reduction, a significant fraction of the stored phosphorus may be released into solution once the waste BPR sludge enters the anaerobic digester. Since many plants recycle anaerobic digester supernatant and sludge dewatering filtrate to the headworks of the plant, the recycling of large amounts of phosphorus into the BPR system is a major operational concern. Given this possibility, the fate of the excess phosphorus introduced into the digester must be determined. Further, methods of conditioning anaerobic sludge for the concurrent improvement of dewatering rates and the control of soluble phosphorus concentration must also be investigated.

This research project was designed to address the following objectives:

1. Compare the dewatering characteristics and conditioning requirements of anaerobically digested sludge obtained before BPR conversion with those of sludge obtained after plant conversion to BPR;

2. Determine the optimum dosages of ferric chloride, lime, and polymer required to condition the post-BPR anaerobically digested sludge for phosphorus removal and improved dewatering rates; and

3. Attempt to identify the metal precipitates responsible for controlling soluble levels of phosphorus in the anaerobic digester.

CHAPTER II

LITERATURE REVIEW

MECHANISM OF BIOLOGICAL PHOSPHORUS REMOVAL

In 1965, Levin and Shapiro (1) reported that wastewater microorganisms exposed to anaerobic/aerobic conditions in sequence take up phosphorus in greater amounts than they normally assimilate. The microorganisms present in wastewater most associated with the phenomenon of excess phosphorus uptake have been identified by Fuhs and Chen (2) to be *Acinetobacter*. When exposed to anaerobic conditions in the presence of substrate, acclimated *Acinetobacter* generate energy from the ATP - ADP + P reaction using polyphosphate stored in the cell. This energy is used to synthesize fatty acids for storage as poly-B-hydroxybutarate (PHB). During subsequent aerobic conditions, the *Acinetobacter* cells use the energy from the stored PHB for cell functions and to reaccumulate orthophosphate for storage as polyphosphate. In this process, a large amount of orthophosphate is released into solution during anaerobic conditions, followed by a subsequent aerobic uptake of phosphate in excess of that released during anaerobic conditions, resulting in the net removal of phosphorus from wastewater.

The anaerobic/aerobic sequence is required to stimulate excess phosphate uptake. When exposed to aerobic conditions only, the Acinetobacter species do not synthesize polyphosphate since it can use glucose for energy and growth. When exposed to the anaerobic/aerobic process, however, the organism does not consume glucose; instead, it synthesizes fatty acids. Wentzel et al. (3) explained that the synthesis of fatty acids for substrate storage as PHB during the anaerobic climate gives Acinetobacter an advantage over other organisms in the competition for substrate in the aerobic zone. This advantage allows Acinetobacter to develop a larger population than it would under normal, strictly aerobic conditions.

The development of excess phosphate removal does not occur instantaneously when the organisms are exposed to the anaerobic/aerobic sequence. Manning and Irvine (4) found that 4-6 weeks of exposure are required for Acinetobacter to develop the pathway and population required for the efficient removal of phosphorus.

Cations must be co-transported across the cell membrane with orthophosphate to maintain electroneutrality of the organism and bulk solution during the uptake and release of orthophosphate. The literature presents conflicting findings regarding the identity of the ions co-transported with orthophosphate. Harold (5) reported that orthophosphate accumulation was prevented in the absence of Ca^{2+}, but took place when Ca^{2+} was added. His analysis of the intracellular phosphate granules called volutin, did not reveal the presence of Ca^{2+}, but indicated the presence of Mg^{2+} instead. Buchan (6) determined that volutin had a Ca:P ratio of 0.15-0.36 and concluded that Ca^{2+} played the predominant role in charge stabilization. However, Comeau et al. (7) reported that Mg^{2+}, K^{+}, and Ca^{2+} are co-transported with phosphate and provided a table of the molar ratios observed by several researchers (Table 1). These data indicate that Mg^{2+} and K^{+} play the dominant role in orthophosphate transport.

CHEMICAL PRECIPITATION DURING ANAEROBIC CONDITIONS

Given that anaerobic conditions favor the release of phosphate from BPR sludge, the formation of phosphate containing precipitates is likely to occur when the sludge is exposed to anaerobic conditions. Precipitation of a carbonate containing apatite in the anaerobic basin of a BPR reactor was reported by Arvin and Kristensen (8). Arvin (9) further concluded that precipitation of calcium phosphate in the anaerobic/aerobic reactors was favored by low

Table 1. Molar Ratios for the Release and Uptake of Phosphorus Across the Cell Membrane

	1	2	3	4	5
Mg^{2+}/P	0.26	0.32	0.24	0.28	0.27
K^{+}/P	0.27	0.23	0.34	0.20	0.23
Ca^{2+}/P	0.00	--	0.06	0.09	0.12
Na^{+}/P	--	--	0.00	0.00	0.00
Sum of Charges/P	0.79	0.87	0.94	0.94	1.01
P transport	release	release	release	release	release

P transport = Direction of transport across cell membrane

(1) Miyimato-Mills et al., 1983.
(2) Arvin and Kristensen, 1983.
(3), (4) Comeau et al., 1985.
(5) Brannan, 1985.

concentrations of Mg^{2+}, alkalinity, and pyrophosphate; a Ca^{2+} concentration of 50 mg/L or greater; and a pH of 7.5 or greater.

Anaerobic digestion also provides the conditions necessary for complete release of soluble phosphate from the phosphorus-rich sludge and a long contact time with many metal ions that form preciptates and others will be discussed in further detail.

Calcium Phosphate Precipitates

Menar and Jenkins (10) reported that the residual phosphate concentration in wastewater is governed by calcium phosphate equilibrium. They determined that tricalcium phosphate (TCP) and hydroxyapatite (HAP) were the calcium phosphate species precipitated in biological treatment systems. Using a thermodynamic model, Nancallos (11) predicted that at a pH of 7 and a temperature of 37 C, the order of calcium phosphate stability is as follows:

$Ca_{10}(PO_4)_6(OH)_2(s)$	>	$Ca_3(PO_4)_2(s)$ >
Hydroxyapatite Phosphate (HAP)		Tricalcium Phosphate (TCP)
$Ca_4(H(PO_4)_3) \cdot 5H_2O(s)$	>	$CaHPO_4 \cdot 2H_2O(s)$
Octacalcium Phosphate (OCP)		Dicalcium Phosphate (DCP)

In actual situations involving high degrees of supersaturation, Nancallos (11) concluded that the first formed phase is the unstable $Ca_9(PO_4)_6(s)$ precipitate known as ACP. With time, this precipitate forms OCP, which then evolves to the most stable calcium phosphate precipitate HAP. At very low degrees of supersaturation, HAP can be formed direclty with no precursor.

Nucleation plays an important role in the development of calcium phosphate precipitates; Jenkins et al. (12) studied this aspect. Data presented in Figure 1 show that seeding greatly decreases the time required for the formation of calcium phosphate precipitates because of the reduction in time required for nucleation. Given the diverse components of wastewater sludges, some calcium phosphate seeding would

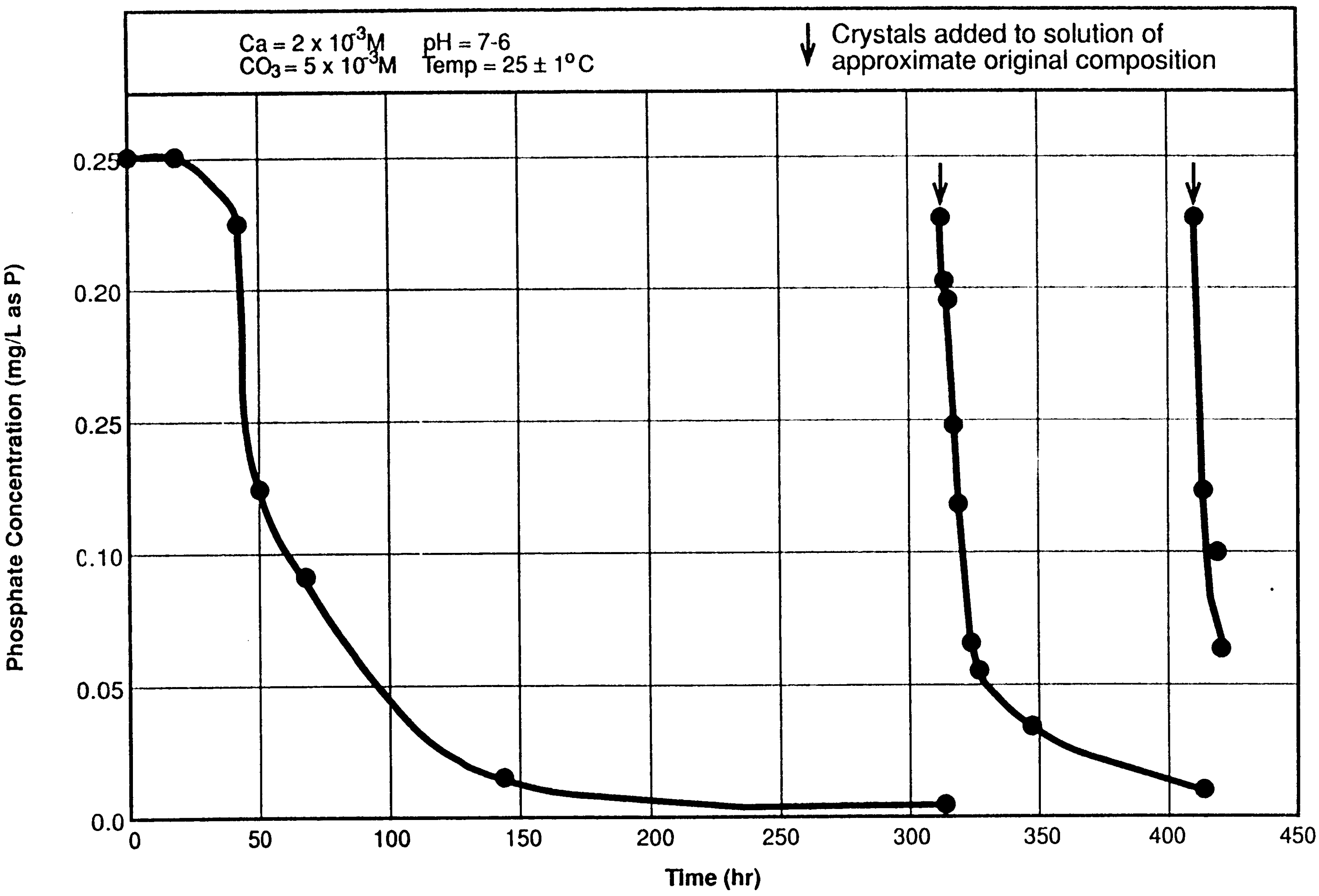

FIGURE 1. Effect of Crystal Seeding on the Rate of Calcium Phosphate Precipitation (from (3)).

be expected to occur in the reactor basins and digesters of wastewater treatment plants.

Natural water systems and wastewaters contain many soluble components other than calcium and phosphate. Some of these components have a significant effect on the type of calcium phosphate formed and the extent of calcium phosphate formation. Jenkins et al. (12) reported that the calcium phosphate precipitates in actual water systems have a much greater solubility than predicted by chemical thermodynamics as a result of the substitution of foreign ions in the crystal lattice. The identity and effect of several of these ions will subsequently be discussed.

Magnesium appears to increase the solubility of calcium phosphate at pH values below 9 (13). Ferguson and McCarty (13) reported that the presence of magnesium inhibits the nucleation and crystallization of hydroxyapatite by stabilizing the ACP phase and causing the precipitation of TCP rather than hydroxyapatite. Legeros (14) determined that a Mg/Ca molar ratio of 0.45 or greater will cause ACP stabilization.

The presence of carbonate also increases the solubility of calcium phosphate precipitates. Jenkins et al. (12)

determined thermodynamically that calcite ($CaCO_3(s)$) precipitation competes with hydroxyapatite between pH 9-10.5, but has little to no effect on hydroxyapatite formation between ph 7.5-8.5 and pH > 10.5. Ferguson et al. (15) reported that the rate of calcium phosphate precipitation is inversely proportional to carbonate concentration. At elevated carbonate concentrations, carbonate ions substitute for phosphate ions in the crystal lattice, forming carbonate containing apatites. These apatites are much more amorphous that hydroxyapatite and have a slower crystal growth rate. Further, the presence of carbonate inhibits apatite formation, with the net result being stabilization of the ACP phase as opposed to hydroxyapatite. Legeros (14) reported that magnesium greatly enhances the effect of carbonate. With no magnesium present, a $HCO_3^-/PO_4^=$ molar ratio of 20 will cause the production of ACP, however, if the Mg/Ca molar ratio is >0.1, a $HCO_3^-/PO_4^=$ molar ratio of 5:1 or greater will cause ACP production.

Other compounds also have an effect on calcium phosphate formation. Legeros and Legeros (16) reported that the presence of pyrophosphates stabilize the ACP phase and prevent the formation of hydroxyapatite. Other ions that inhibit hydroxyapatite formation are Zn^{2+}, Al^{3+}, Fe^{3+}, and Fe^{2+}

as a result of the incorporation of these ions into the crystal lattice of the precipitate (16). In contrast, the fluoride ion (F^-) promotes the growth of apatite crystals and decreases the solubility of apatites. This is accomplished by retarding the formation of ACP while accelerating the conversion of OCP to HAP (16). Arends and Ten Cate (17) found that the effect of F^- is significant at concentrations as low as a few ppm.

Iron Phosphate Precipitates

In an oxidizing (aerobic) environment, iron exists in the ferric (Fe^{3+}) state. The ferric iron precipitates formed in the presence of phosphate are stringite ($FePO_4(s)$) and ferric hydroxide, ($Fe(OH)_3(s)$). Thermodynamically, the optimum pH of stringite formation is 5 while that of ferric hydroxide is 9 (18).

In a reduced environment such as anaerobiasis, soluble iron exists in the ferrous (Fe^{2+}) state. Some solid species formed with ferrous iron in the presence of phosphate are vivianite, $Fe_3(PO_4)_2(s)$; ferrous hydroxide, $Fe(OH)_2(s)$; ferrous carbonate, $FeCO_3(s)$; and ferrous ammonium phosphate, $FeNH_4PO_4(s)$ (18).

Questions have arisen as to the fate of $FePO_4(s)$ formed in the aeration basin once it encounters the reducing conditions of the anaerobic digester. These reducing conditions favor the transformation of Fe^{3+} to Fe^{2+}, which could resolubilize $FePO_4(s)$ precipitates. Previous literature noted that when ferric salts have been added to the aeration basin for $FePO_4(s)$ precipitation, little release of soluble phosphate in the digester occurred (19). Singer (19) reported that the reason for this is the formation of $Fe_3(PO_4)_2(s)$ from $FePO_4(s)$. The existence of $Fe_3(PO_4)_2(s)$ was confirmed using x-ray diffraction on anaerobically digested sludge from a plant adding ferric salts in the aeration basin.

Magnesium Precipitates

The effect of magnesium on calcium phosphate precipitates has already been discussed, but magnesium also forms precipitates with phosphate. Struvite ($MgNH_4PO_4(s)$) is the magnesium phosphate precipitate most commonly found in anaerobic digesters. Newberyite, ($MgHPO_4$ $3H_2O(s)$) is sometimes formed along with struvite; however, the formation of newberyite is easily inhibited by the presence of strontium, copper, manganese, and pyrophosphate (16). Using equilibrium chemistry, Snoeyink and Jenkins (20) determined that the pH range favoring struvite formation in the recycle lines of anaerobic digesters is 8 to 12. The authors (20) also commented on the problems of struvite formation in the recycle lines of anaerobic digesters. Pipe elbows and pump suctions present special problem areas because of an increase in pH at these areas caused by a loss of CO_2 from solution. The presence of calcium inhibits the formation of struvite. The effects of calcium on struvite formation were quantified by Legeros and Legeros (16) and are presented in Table 2. The precipitates $MgCO_3(s)$ and $Mg(OH)_2(s)$ are also formed with magnesium. The formation of these precipitates also increases the solubility of struvite (16).

ANAEROBICALLY DIGESTED SLUDGE CONDITIONING ISSUES

Conflicting results have been reported as to the effect of anaerobic digestion on the dewaterability of wastewater sludge. Lawler et al. (21) found that anaerobic digestion improved the dewatering of municipal wastewater sludge, while others have reported the opposite effect (22). Literature sources generally agree, however, that particle size is the factor that most influences sludge dewatering rates.

Table 2. Phosphate Precipitation in the Presence of Calcium and Magnesium

Ca:Mg Molar Ratio	Metal Precipitate Favored
1.1:1.0	$MgNH_4PO_4(s)$ (Struvite)
1.5:1.0	$CaHPO_4 \cdot 2H_2O$ (Dicalcium Phosphate)
4.0:1.0	$Ca_3(PO_4)_2$ (Tricalcium Phosphate)

Karr and Keinath (22) found that the supracolloidal fraction of particles (1-100 um) had the most significant effect on dewatering. Lawler et al. (21) suggested that anaerobic digestion improved the dewatering of anaerobically digested sludge by destroying small particles (<2.5 um), while others suggest that digestion forms smaller particles in this same range from larger particles, thus making the sludge more difficult to dewater (22).

Typically, anaerobically digested sludges are difficult to dewater and chemical conditioning is required to yield an efficient dewatering sludge. Chemical conditioning improves dewatering by aggregating the small particles present in a sludge into a larger floc. This aggregation can be accomplished with two mechanisms: charge neutralization and particle bridging.

Charge neutralization involves the addition of positively charged chemical conditioners that neutralize the negatively charged sludge particles. The neutralized particles aggregate from the influence of Van Der Waals forces when they come in contact (23). Particle bridging involves the collection of negatively charged sludge particles onto the positively charged sites of long chained polymeric molecules. These processes can work separately or together to improve dewatering rates.

The most popular conditioners for anaerobically digested sludge are ferric chloride, ferric chloride with lime, and cationic organic polymers (23). Tenney et al. (24) attributed the success of ferric chloride as a conditioner to the formation of positively charged hydroxo-iron polymers by the Fe^{3+} ion. Spiro et al. (25) studied the formation of these polymers extensively and reported that the addition of pre-formed, hydroxo-iron polymers directly to sludge more effectively conditioned sludge than ferric chloride did. Christiansen and Stulc (26) explained that upon the dissociation of ferric chloride in sludge, the Fe^{3+} ion can precipitate as ferric hydroxide or be reduced to the ferrous state, effectively reducing the amount of hydroxo-polymer formed.

Low pH values favor the reduction of ferric ion to the ferrous state. The optimum pH for the formation of ferric hydroxide is 9. Tenney et al. (24) determined that the optimum pH range for sludge conditioning with ferric chloride was between 6-7, while Christiansen and Stulc (26) reported the optimum range to be between 5.2-6.0.

Lime added with ferric chloride is reported to condition sludge more effectively than ferric chloride alone. Christiansen and Stulc (26) found that lime with ferric chloride was more effective in conditioning mixed raw sludge in comparison to pre-formed hydroxo-iron polymers. The mechanism responsible for the effectiveness of the lime/ferric chloride combination has been explained to be a function of the increase in pH and the presence of positively charged calcium ions. Webb (27) suggested that the positively charged calcium ions bond negatively charged sludge particles to negatively charged ferric hydroxide precipitates. Eden (28) suggested that calcium precipitates provide a granular structure that assists in dewatering. Treating a mixed raw sludge, Christiansen and Stulc (26) reported that the lime/ferric chloride combination was most effective at pH 12 and above. EPA recommended dosages of ferric chloride and calcium oxide to condition anaerobically digested sludge for vacuum filtration are 3.0-6.0 and 14.8-20.7 percent by weight, respectively (29).

Organic polymers have become popular as chemical conditioners. Although they are more expensive, a much smaller dosage (on a weight basis) than inorganic chemicals is required for sludge conditioning. Organic polymers also have a BTU value making them much more energy-efficient than inorganic chemicals when sludge incineration is practiced. The organic polymers used for anaerobically digested sludge conditioning are usually long-chained, cationic polymers that aggregate particles by bridging.

Cole and Singer (30) reported that cationic polymers with molecular weights greater than 10^6 are required to dewater anaerobically digested sludges efficiently and that charge neutralization of the sludge particles was not required for effective conditioning. Polymer dosages of 2.2-8.8 lb polymer/ton dry sludge solids are recommended by the EPA (29) for conditioning anaerobically digested sludge dewatered by a belt filter press.

The effect of soluble phosphorus on required conditioning chemical dosages has been studied by Tenney et al. (24), who found that the effectiveness of a given dose of ferric ion as a conditioner decreased with increased phosphate concentration because ferric iron forms phophate complexes and precipitates. Stumm and Morgan (31) determined that Fe^{3+} ion has a stronger affinity for OH^- than $HPO_4^=$ or $PO_4^{\equiv}$ and that the extent of ferric- hydroxy complex formation depends on the $HPO_4^=/OH^-$ and $PO_4^{\equiv}/OH^-$ ratios. As pH decreases, they concluded, iron phosphate complex formation will increase. These results suggest that greater amounts of inorganic chemical may be required to condition sludge if phosphate is present.

CONDITIONING OF WASTE BPR SLUDGE FOR PHOSPHATE REMOVAL

Deakyne et al. (32) studied the use of ferric choloride and lime to precipitate soluble phosphate from waste BPR plant sludge. At the Poapsco Wastewater Treatment Plant in Baltimore, Md., a waste activated sludge phosphorus content of 5 percent by weight was achieved using the A/O process. The sludge had a total suspended solids concentration of 12,800 mg/L and a total phosphorus concentration of 724 mg/L, with 13 mg/L of the phosphorus soluble. After 96 hours of exposure to anaerobic conditions, the soluble phosphorus content in the sludge increased to 428 mg/L. Treatment with 7.5 percent $FeCl_3$ followed three minutes later by 10 percent $Ca(OH)_2$ achieved a soluble phosphorus concentration of 0.93 mg/L in ten minutes. Another treatment scenario with 7.5 percent $FeCl_3$ followed three minutes later by 15 percent $Ca(OH)_2$ yielded a soluble phosphorus level of 0.16 mg/L after five minutes.

This source was the only one found which specifically addressed the issue of inorganic chemical dosages necessary for the conditioning of digested BPR sludges. It is clear that the work of this present study is necessary to help address this important issue related to the dewatering of such sludges.

CHAPTER III

METHODS AND MATERIALS

PLANT PROCESS DESCRIPTION

At the time of this study, the York River Wastewater Treatment Plant (York River, Virginia) was a conventional activated sludge plant treating 6 to 8 million gallons per day (mgd) before modification to include BPR. The treatment process began with grit removal followed by preaeration and primary clarification. Before modification, effluent from the primary clarifier underwent step aeration in the activated sludge basin. The basin consisted of six individual tanks operating in parallel, with each tank divided into four sub-units for the step aeration process. Effluent from the aeration basin flowed to a secondary clarifier for sludge settling; secondary clarifier effluent was then chlorinated before being discharged from the plant.

Sludge from the primary clarifiers was sent to a pair of gravity thickeners, while waste activated sludge from the secondary clarifier was thickened by dissolved air flotation. The thickened sludges were then anaerobically digested for stabilization and solids reduction. The digestion process consisted of primary digestion in the primary digester for initial stabilization and solids reduction followed by retention in the secondary digester. The solids retention time of the process was approximately 120 days at a digestion temperature of 35°C. The underflow from the secondary digester was conditioned with potassium permanganate and Percol 757 polymer before being dewatered with a belt filter press. Filtrate from the press was mixed with the supernatant from the gravity thickeners and dissolved air flotation units and sent back to the headworks of the plant.

For the addition of BPR, two of the six aeration tanks were modified. The first quarter of the tanks were divided into three equal anaerobic chambers. The second quarter of each tank was divided into two anoxic chambers, with the second chamber being twice the size of the first. The final half of these tanks remained aerobic as before the BPR modification. No other plant modifications were required. The layout of the plant including the BPR process is shown in Figure 2.

SAMPLING PROCEDURE

On July 31, 1986, anaerobically digested sludge sampling began at the York River site and continued approximately

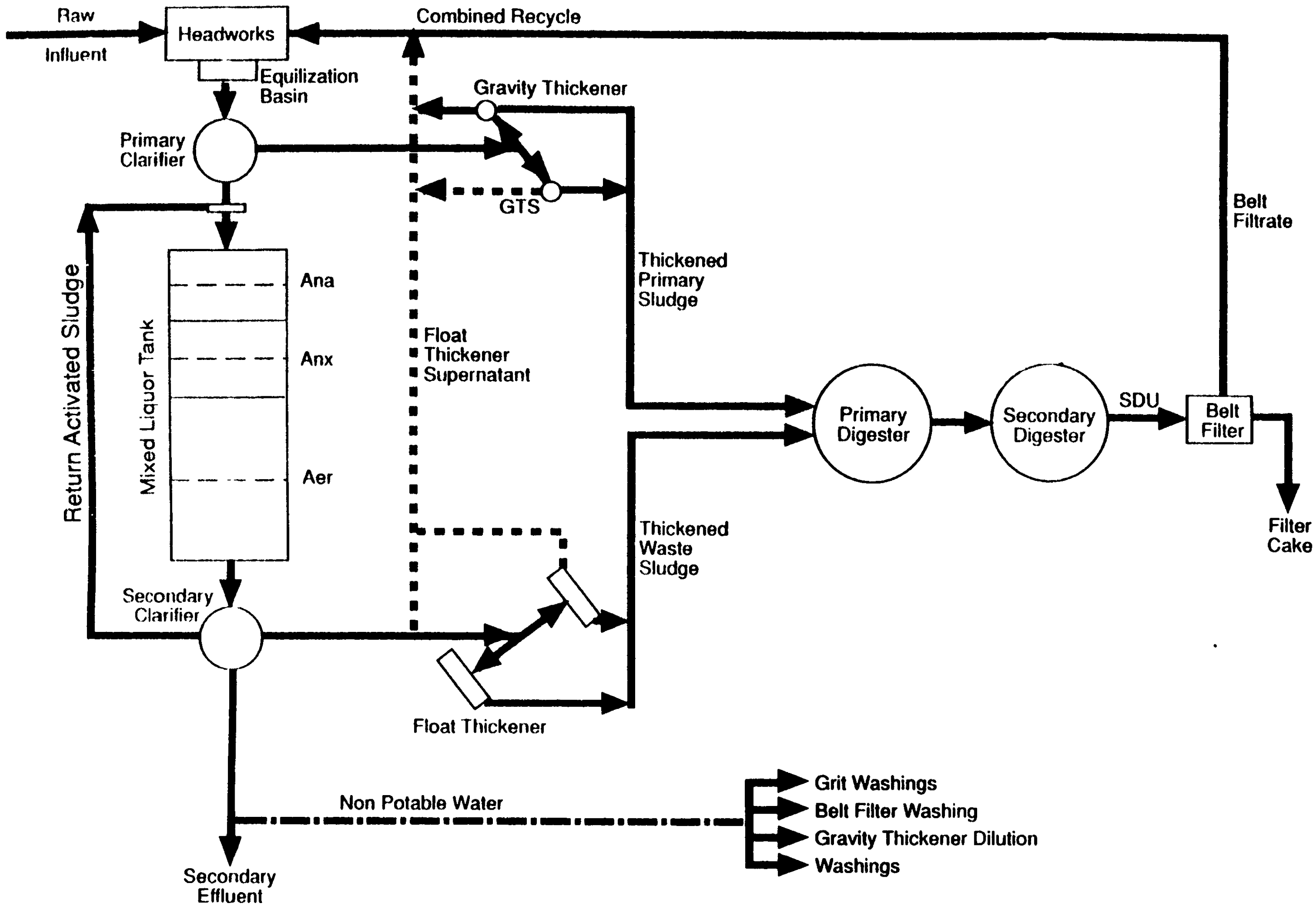

FIGURE 2. Schematic of York River Plant after Modification to BPR.

bimonthly until June 30, 1987. The purpose of the year-long sampling period was to study the changes in sludge characteristics from before BPR began to after the BPR process stabilized.

Unconditioned anaerobically digested sludge samples were collected from the secondary digester sampling port. Since the samples were in an anaerobic state for 120 days before collection, the sludge could be transported without changing its composition significantly. Therefore, the sludge was stored in five gallon carboys and transported to Virginia Tech for testing.

The characteristics of the anaerobically digested sludge led to an interest in the origins of the cations and phosphate present in the digester and their state before entering the digestion process. This led to the sampling of thickened primary sludge, flotation thickened sludge, and activated sludge on June 30, 1987. Thickened primary sludge was obtained from the gravity thickener underflow sampling port. Since this sludge exists in an anaerobic state before entering the digesters, it did not require treatment on the plant site to preserve its composition. Thus, the sample was stored at room temperature and transported to Blacksburg for chemical precipitate studies, The flotation thickened sludge samples were collected off the top of the flotation thickener because the sampling port was not operational. Activated sludge samples were obtained from the entrance to the secondary clarifier by submerging a one-gallon container into the basin. After 30 minutes of settling, the supernatant was poured off of the top of the activated sludge, and the remaining sludge used for testing.

Both the activated sludge and flotation thickened sludge were under aeration when they were collected. Since transporting these samples would expose them to anaerobic conditions for a long period of time, these sludges were tested on-site. Thus, after collection, portions of both samples were immediately filtered through 0.45 um filters and acidified with nitric acid for analysis in Blacksburg. The remaining sludge was used for chemical precipitate studies performed at the plant laboratory.

Phosphorus precipitation from the belt filtrate was also considered in this study. On January 20, 1987, samples of the belt filtrate were collected from sampling ports located on the belt filter press. The filtrate from these ports contained an unknown amount of wash water used in the operation of the press. Again, since these samples could be transported without changing their composition, they were stored at room temperature and taken to Blacksburg for phosphorus precipitation studies.

SLUDGE CONTITIONING AND PHOSPHORUS CONTROL STUDIES

The sludge conditioning experiments were designed to find the optimum dosages of chemicals required for removal of soluble phosphorus and improved dewatering. To achieve this, 250-mL aliquots of anaerobically digested sludge were placed in beakers and mixed using a Phipps and Bird jar testing apparatus. The samples were treated with varying amounts of ferric chloride, calcium hydroxide, and/or Percol 757 cationic polymer. Ferric chloride was added as a 40 g/L solution and calcium hydroxide was added as a 40 g/L slurry. The polymer was added as a 3-percent-by-weight solution, which is the current practice at the York River facility. All of the solutions were made with de-ionized/distilled water to prevent the introduction of excess metal cations and phosphate.

The chemical addition conditions at the plant were simulated by adding all of the solutions simultaneously to the sludge while the sludge was being mixed by the jar testing apparatus at approximately 200 revolutions per minute (rpm). Following chemical addition, the sludge was allowed to mix at this rate for one minute followed by two minutes of mixing at 25 rpm. The conditioned sludge samples were then transferred to a Buchner funnel device for specific resistance testing; the filtrate from the test was used for residual phosphorus analysis.

Phosphorus removal studies from the belt filtrate were performed with ferric chloride and calcium hydroxide. The procedure of chemical addition to the belt filtrate was the same as for the sludge except the 2-minute mixing time at 25 rpm was increased to 30 minutes. After conditioning, the belt filtrate was filtered through a 0.45-um filter, acidified, and analyzed for soluble phosphorus.

The Specific Resistance Test

The dewatering rates of conditioned sludge samples were measured using the Specific Resistance Test. The specific resistance of a sludge is determined by the following equation:

$$r=\frac{2PbA^2}{uC} \qquad [2]$$

where,

r = specific resistance, (m/kg)

P = vacuum pressure, (N/m^2)

b = slope of t/V vs. V, (s/m^6), where

t = time to collect a volume of filtrate, (s)

V = volume of filtrate collected, (m^3)

u = dynamic viscosity of sludge, ($N*s/m^2$)

A = area of filter, (m^2)

C = cake deposited/volume of filtrate, (kg/m^3)

C is calculated from the following equation:

$$C = \frac{C_R \quad C_o}{100\ (C_R - C_o)} \qquad [3]$$

where,

C_o = total solids of sludge before filtering, (% by weight)

C_K = total solids of sludge cake after filtering, (% by weight)

To measure the parameters required to calculate specific resistance, 100 mL of the conditioned sludge samples were placed in a porcelain funnel containing a Whatman 40 ashless filter with a 9.0-cm diameter. A vacuum differential of 20 in Hg was applied the filter and the amount of filtrate collected vs. time recorded until no more filtrate could be collected or the sludge cake began to crack or fail. The resulting sludge cake was analyzed for total solids; the value of b was determined by preparing a t/V versus V plot (Figure 3).

In the case of a poorly dewatering sludge, no cake could be achieved. When this occurred, filtration was stopped after ten minutes to prevent damage to the vacuum pump. For these sludge samples, the calculation of b was made over the range of filtrate collected and a final cake solids of 15 percent was assumed. The value of 15 percent was chosen because it was the average value achieved when a conditioned sludge sample dewatered to a final sludge cake. Information in Figure 3 shows the difference in the t/V vs. V plots for a poorly dewatering sludge that did not form a cake versus one that dewatered well and formed a cake. A final assumption

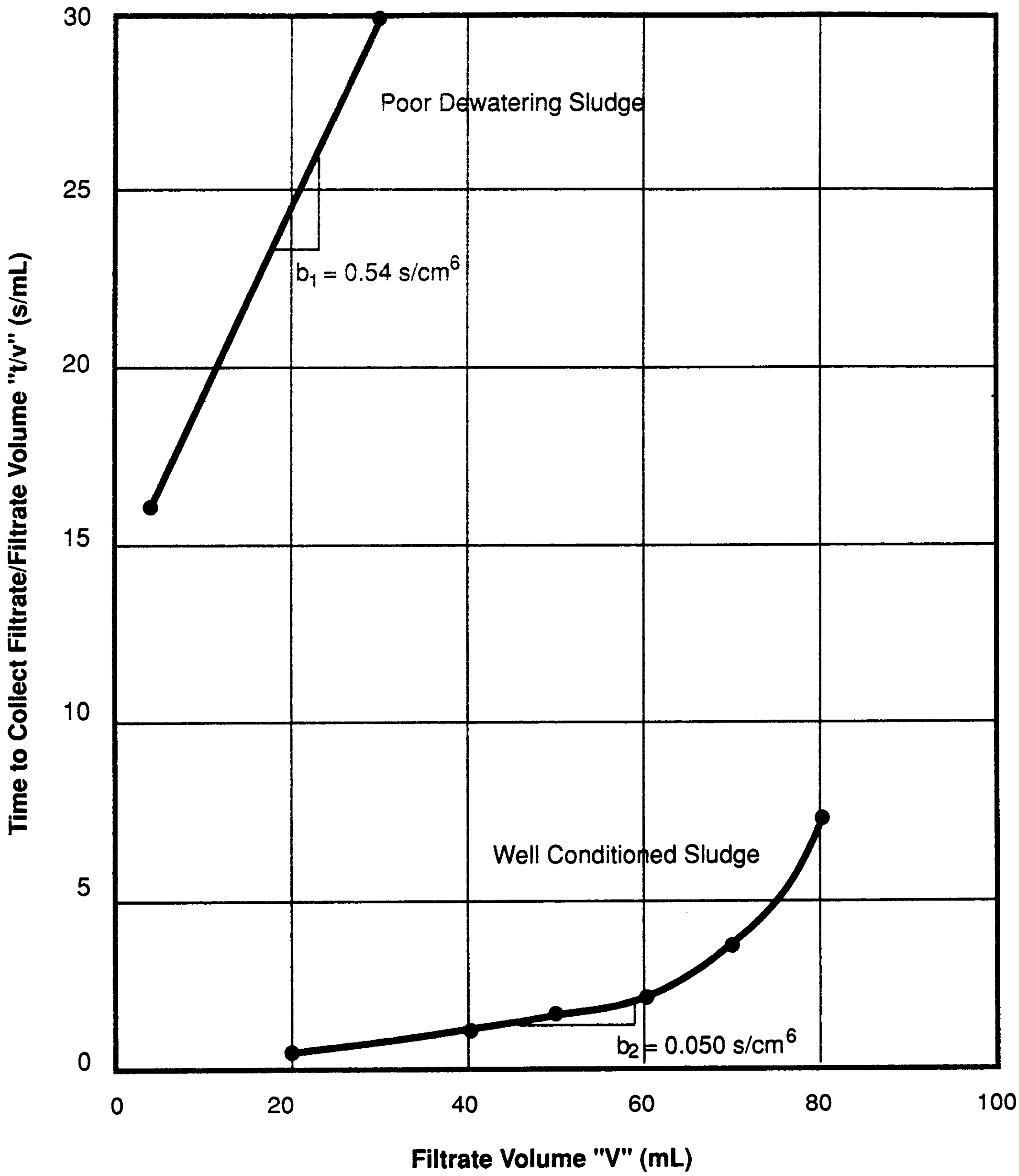

FIGURE 3. Representative Filtrate Volume and Dewatering Rate Data for Poor Dewatering and Well Conditioned Sludge Samples.

involved in the calculation of the specific resistance was that the viscosity of the sludge filtrate was equal to the viscosity of water at the same temperature.

CHEMICAL PRECIPITATE STUDIES

The equilibrium chemistry of activated sludge, flotation thickened sludge, thickened primary sludge, and anaerobically digested sludge was studied in an attempt to identify the solid precipitates entering and forming within the anaerobic digester. First, the pH of each sludge was varied and the release or uptake of Ca^{2+}, Mg^{2+}, K^{+}, Fe^{2+}, Fe^{3+}, and phosphate at each pH value determined. The pH of the anaerobically digested and thickened primary sludge samples was adjusted by dripping nitric acid and/or sodium hydroxide into 250-mL sludge samples during mixing with a magnetic stirrer. Once the desired pH was reached, the sample was allowed to mix for thirty minutes without any further addition of acid or base. If the pH changed after the mixing period, it was re-adjusted to the target pH value and allowed to mix for another thirty minutes. The samples were then placed in centrifuge tubes, capped, and allowed to equilibrate for 24 hours.

After 24 hours, the pH of each sample was measured, and the samples were centrifuged at 15,000 rpm for ten minutes for suspended solids separation. Centrate samples were subsequently filtered through a 0.45 um filter, acidified with nitric acid, and analyzed for the components of interest.

The pH of the activated sludge and the flotation thickened sludges was adjusted in the York River laboratory. For these sludges, 250 mL aliquots were treated with nitric acid and sodium hydroxide while being aerated by a small air sparger. Once the desired pH was reached, the samples were allowed thirty minutes to equilibrate. After thirty minutes, the samples were re-adjusted to the target pH and allowed to aerate for four more hours. Four hours was chosen as the final equilibration period because of time restrictions on the plant lab space. Upon completion of the four hour period, the samples were filtered through a 0.45 um filter, acidified with nitric acid, and sealed in centrifuge tubes for soluble species´ analyses in Blacksburg.

Analysis of Chemical Precipitation Studies

The first step in identifying the metal precipitates present in the sludges was to calculate the solubility product of many possible metal hydroxide, metal carbonate, and metal phosphate species at each pH value. This was accomplished by inserting the concentrations found at each pH value into a computer program designed by Sen (33) to calculate the solubility products and saturation conditions of metal precipitates under the conditions of anaerobic digestion. Once the saturation condition of each precipitate was found, the precipitates that were supersaturated and undersaturated at each pH value were listed. The second step of the identification process was the calculation of the molar changes of each metal cation and phosphate between the pH values. From both of these pieces of information, an attempt was made to associate the release of phosphate with the dissolution of specific chemical precipitates. The following example presents the approach that was attempted for this endeavor.

Consider the data presented in Table 3 for the release of various chemical species as the sludge pH decreased from 6.3 to 5.2. The solubility program calculated that, at a pH of 6.3, the liquid phase of the sludge was supersaturated with

Table 3. Example Soluble Ion Concentration Data

	Soluble Species´ Concentration (mM/L)					
pH	Ca^{2+}	Mg^{2+}	K^{+}	Fe^{3+}	Fe^{2+}	Ortho-P
			A. Solubilization Results			
6.3	2.40	2.11	0.50	0.01	0.01	13.88
5.2	10.00	3.38	0.50	0.11	0.21	20.31
			B. Amounts of Each Species Released (mM/L)			
6.3-5.2	7.60	1.27	0	0.10	0.11	6.43

respect to $MgNH_4PO_4(s)$, $Ca_3(PO_4)_2(s)$, $Ca_{10}(PO_4)_6(OH_2)(s)$, $CaHPO_4(s)$, $Fe_3(PO_4)_2(s)$, and $FePO_4(s)$ and undersaturated with respect to $MgCO_3(s)$, $Mg(OH)_2(s)$, $CaCO_3(s)$, $Ca(OH)_2(s)$, $FeCO_3(s)$, and $Fe(OH)_2(s)$. Thus, in making further calculations for this sample, the following assumptions were made:

1. The $Fe^{2+}/PO_4^{=}$-P molar release ratio is 3/2 (based upon $Fe_3(PO_4)_2(s)$);

2. The $Fe^{3+}/PO_4^{=}$-P molar release ratio is 1/1 (based upon $FePO_4(s)$); and

3. The $Mg^{2+}/PO_4^{=}$-P molar release ratio is 1/1 (based upon $MgNH_4PO_4(s)$).

Calculating the amount of phosphate released by these metal precipitates yields the following:;

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2(s)$ = (0.11 mM Fe^{2+} released (2/3) = 0.07 mMP

2. $PO_4^{=}$-P release from $Fe(PO_4)(s)$ = (0.10 mM Fe^{3+} released (1.0) = 0.10 mMP

3. $PO_4^{=}$-P release from $MgNH_4PO_4(s)$ = (1.27 mM Mg^{2+} released (1.0) = 1.27 mMP

Total = 1.4 mMP

This would indicate that, of the 6.43 mM of phosphate released, 4.99 mM of phosphate was due to calcium phosphate precipitates.

Dividing the moles of calcium released by the moles of phosphate released gives a $Ca^{2+}/PO_4^{=}$-P molar ratio of 1.52, suggesting that $Ca_3(PO_4)_2$ is a significant calcium phosphate precipitate in this pH range. In most of the cases, the computer program calculated that many precipitates were present based upon equilibrium calculations, making identification of individual precipitates difficult.

ANALYTICAL TESTS

Total Solids Analysis

The total solids concentration of each sludge sample (expressed on a dry weight percentage basis) was determined by use of procedures described in Section 209A of Standard Methods (34).

pH

pH values for all samples were determined using either a Corning Model 7 pH meter or a Fisher Accumet Model 610 pH meter.

Soluble Phosphorus Analysis

Soluble phosphorus concentrations were determined using the ascorbic acid test found in Standard Methods (34). The detection limit of the test was 0.1 mg P/L; this procedure was linear in response up to 1.0 mg P/L. A Beckman Model DU6 spectrophotometer was used to measure the appropriate absorbance values.

Soluble Cations

Soluble Ca^{2+}, Mg^{2+}, K^{+}, and soluble Fe (Fe^{2+} and Fe^{3+}) concentrations were determined by atomic absorption techniques using a Perkin-Elmer Model 703 atomic absorption spectrophotometer.

Ferrous Iron Analysis

The concentration of soluble ferrous iron was determined using the Bathophenanthroline method described by Lee and Stumm (35). This method was chosen over the 1,10 Phenanthroline Method in Standard Methods (34) for two reasons:

1. The sensitivity is better, detecting between 0.1 mg Fe^{2+}/L and 1.0 mg Fe^{2+}/L in the presence of ferric iron; and,

2. The method is less subject to interferences than the 1,10 Phenanthroline method.

A typical standard response curve for the ferrous iron analysis is shown in Figure 4. A Klett-Summerson Model 900-3 photoelectric colorimeter was used with a No. 42 filter to determine the absorbance of the samples.

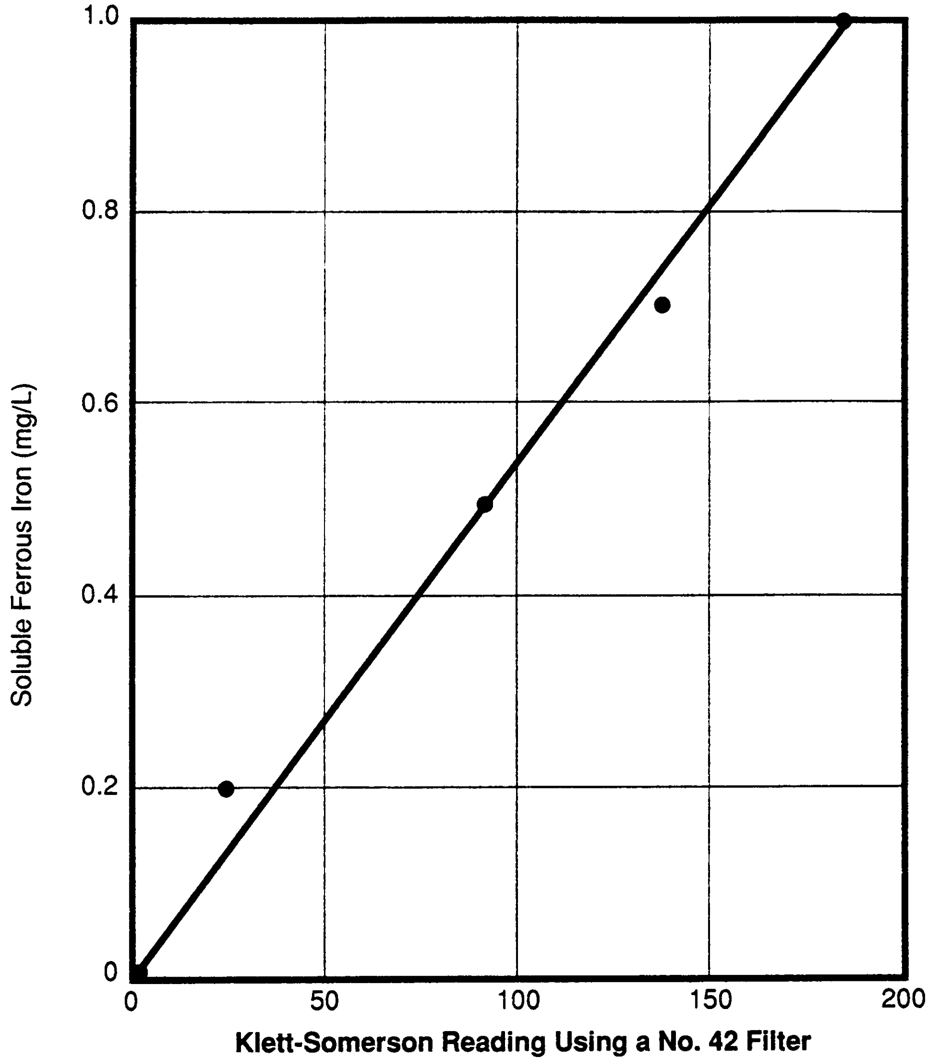

FIGURE 4. Standard Curve for Ferrous Iron Analysis using the Bathophenanthroline Method.

CHAPTER IV

EXPERIMENTAL RESULTS

THE EFFECT OF BPR ON CHEMICAL SPECIES PRESENT IN THE ANAEROBIC DIGESTER

Data collected from the anaerobic digester (presented in Figure 5) show that both the soluble and total phosphorus content of the secondary digester underflow increased significantly after the BPR process began. The total phosphorus concentration increased from approximately 400 mg/L during conventional treatment to 1,050 mg/L after three months of BPR; the soluble phosphorus concentration increased from 50 mg/L to 400 mg/L during the same time period.

These data indicate that the BPR process successfully accumulated the phosphorus removed from the wastewater into the sludge. The total phosphorus concentration in the digester increased to a greater extent than did the soluble phosphorus concentration. Assuming the organisms completely released the accumulated phosphorus, this difference between the total phosphorus concentration and the soluble phosphorus concentration suggested that much of the excess

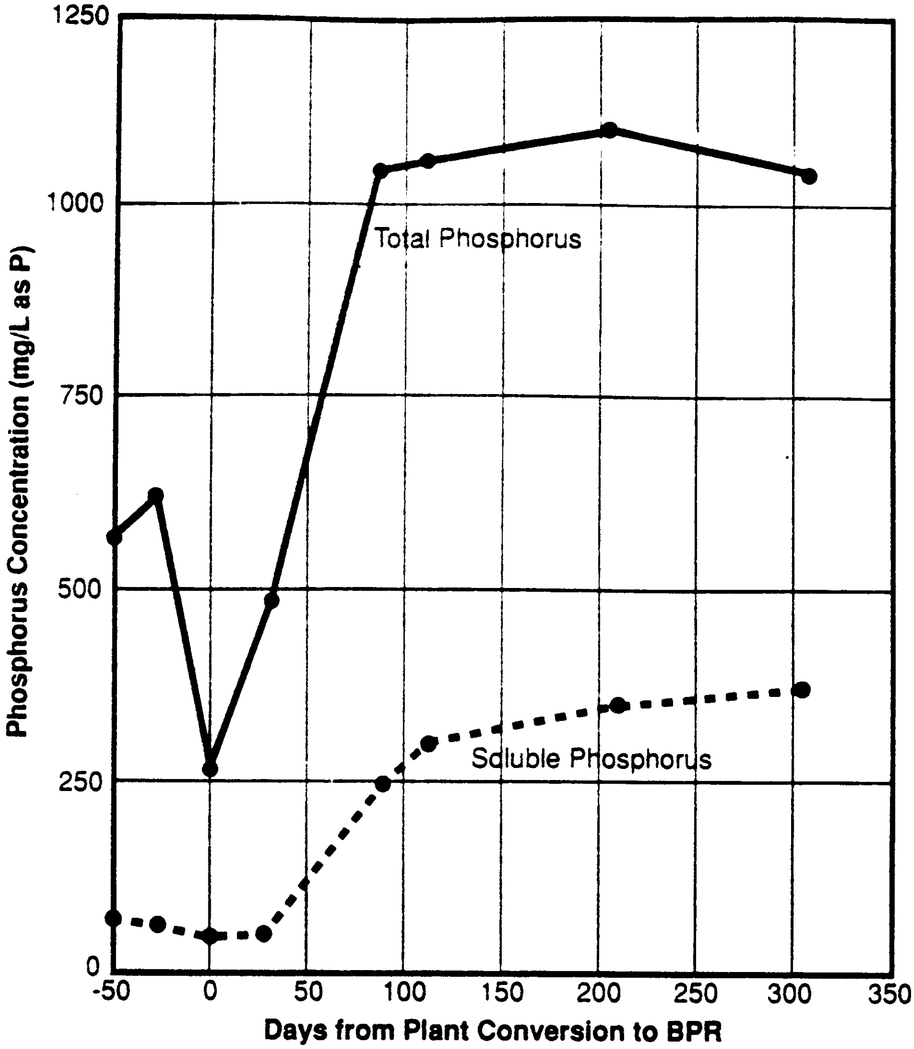

FIGURE 5. Phosphorus Concentration in the Digester with the Onset of BPR.

phosphorus accumulated during the BPR process was subsequently precipitated within the digester.

The change in various total cation concentrations (Ca^{2+}, Fe, Mg^{2+}, and K^{+}) within the digester are presented in Figures 6 and 7. The total concentrations of Mg^{2+} and K^{+} increased significantly after conversion to BPR while the total concentrations of Ca^{2+} and Fe showed no consistent trend. This increase in total Mg^{2+} and K^{+} is consistent with the literature (7) concerning the co-transport of Mg^{2+} and K^{+} with phosphate in BPR systems.

However, the soluble concentrations of these ions behaved differently. Data presented in Figure 8, show that the soluble Mg^{2+} concentrations remained unchanged while the soluble concentration of Ca^{2+} significantly decreased. These results suggest that metal-phosphate precipitates were forming in the anaerobic digester because of the increase in total phosphorus in the sludge. The soluble concentration of K^{+} increased in proportion to the total increase in K^{+}, suggesting that K^{+} does not form any precipitates with phosphate under the conditions in the digester.

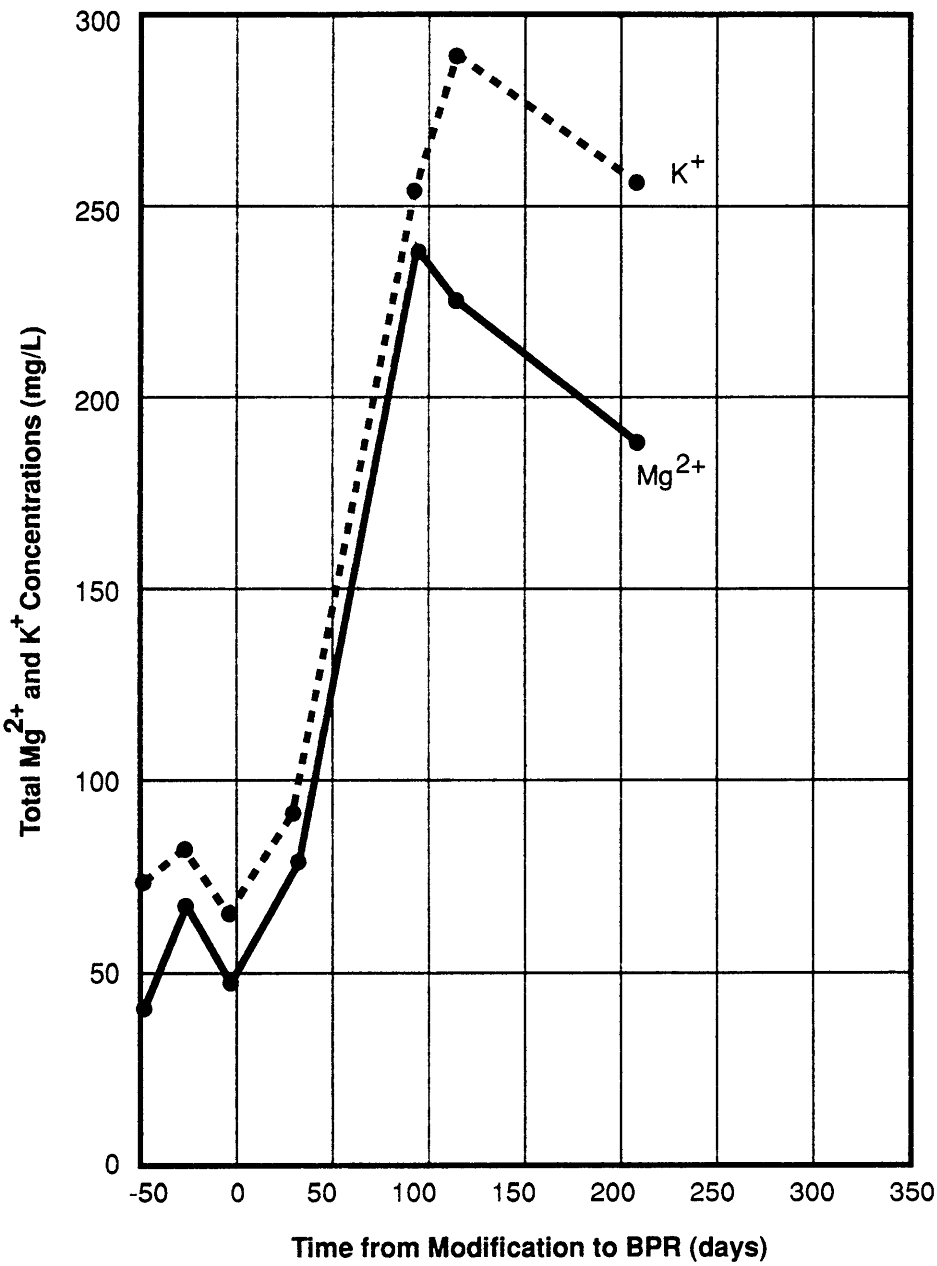

FIGURE 6. Total Mg^{2+} and K^+ Concentrations in the Anaerobic Digester.

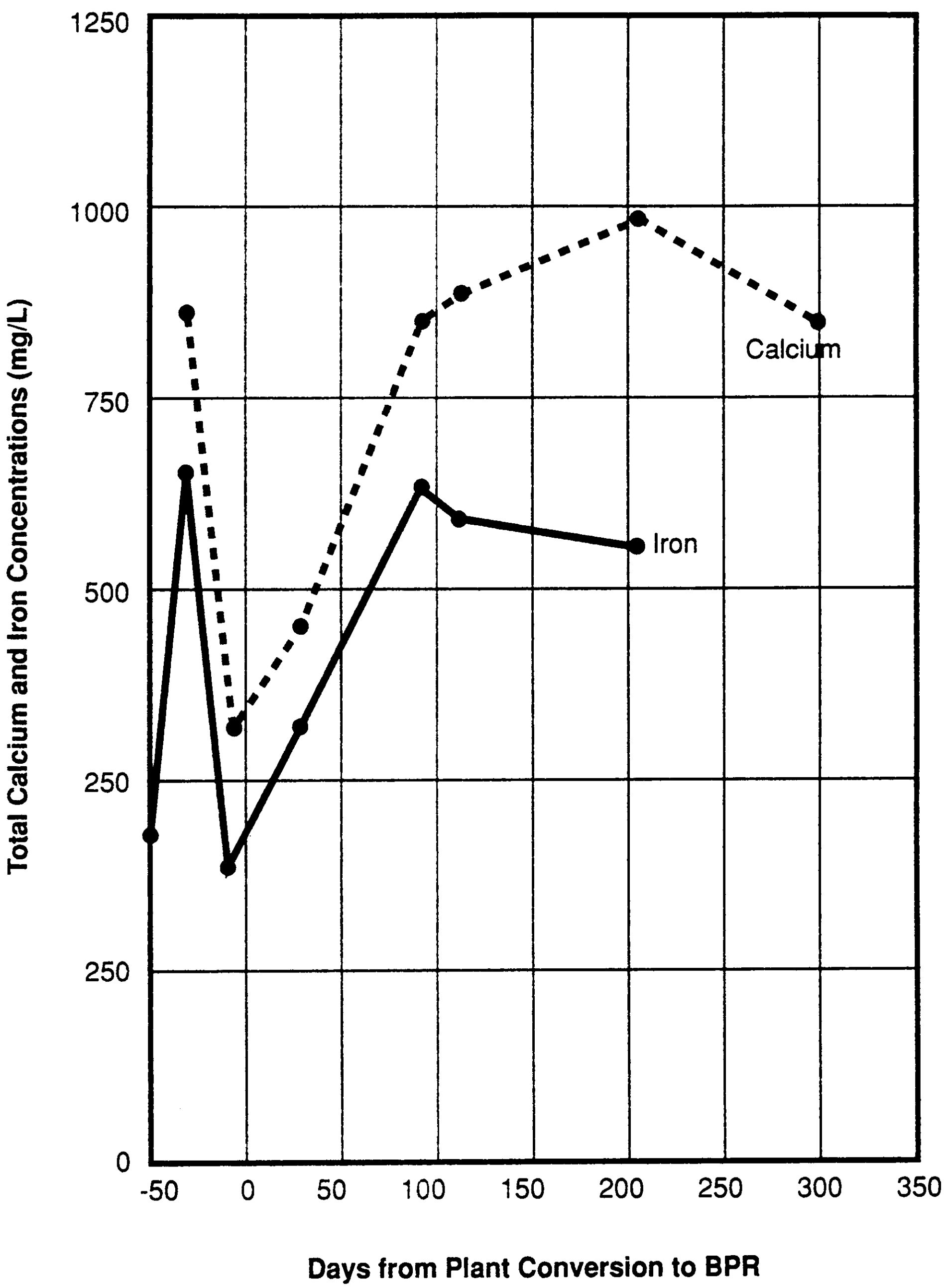

FIGURE 7. Total Calcium and Iron Concentrations in the Anaerobic Digester.

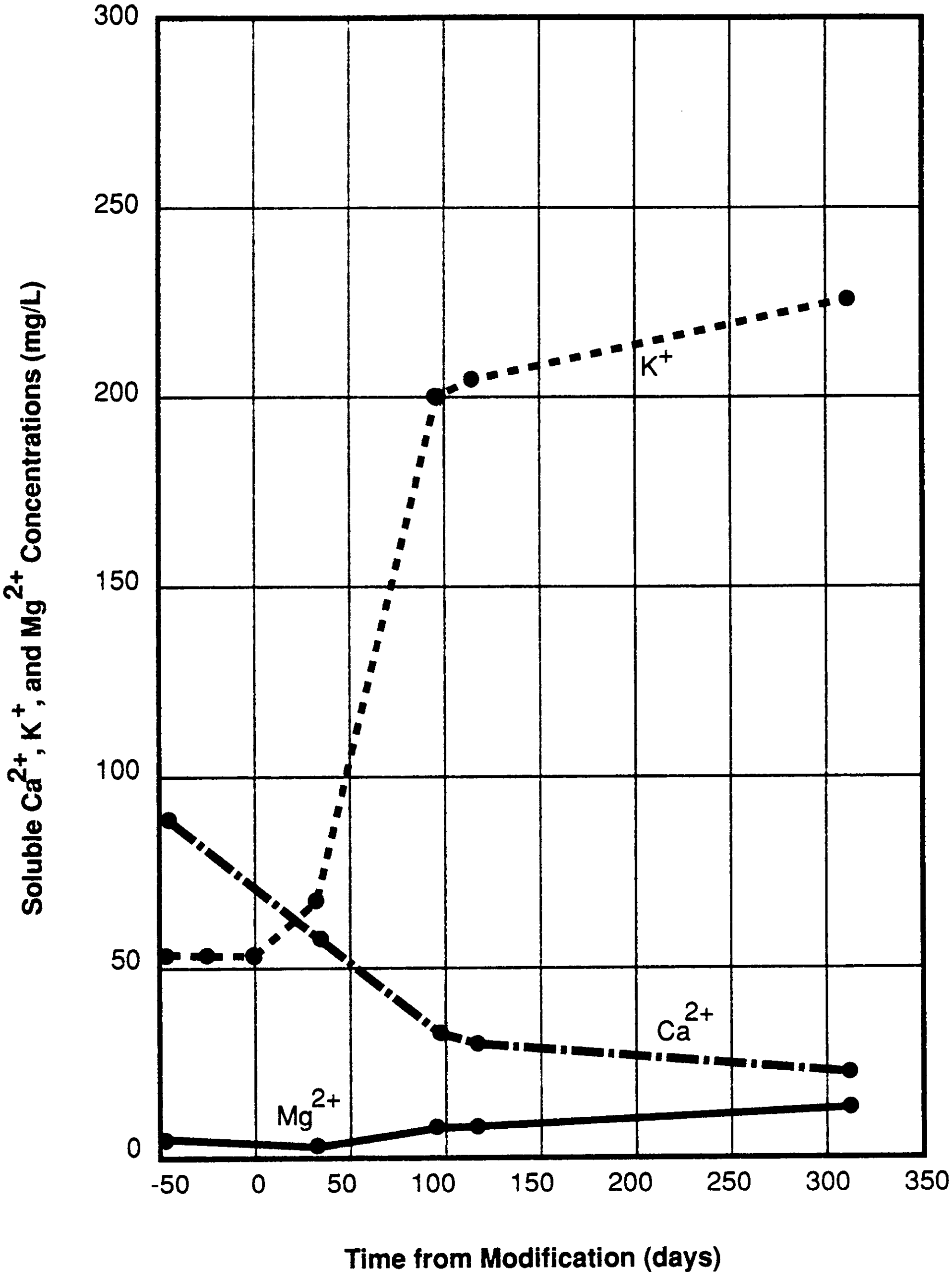

FIGURE 8. Soluble Ca^{2+}, Mg^{2+}, and K^{+} Concentrations in the Anaerobic Digester.

Analysis of pH Effects on Digester Sludge Constituents

Data included in Tables 4 and 5 show the changes in soluble ion concentrations as a function of pH in pre- and post-BPR digested sludges. As the pH of the sludge samples decreased, large amounts of orthophosphate were released. Since the cell mass does not undergo hydrolysis under the pH conditions used, most of the phosphate was assumed to be released directly from phosphorus-containing precipitates. This assumption is further justified by the accompanying release of Fe^{2+}, Fe^{3+}, Ca^{2+}, and Mg^{2+} ions. The post-BPR sludge contained a greater amount of precipitant than the pre-BPR sludge. This was expected because of the increase in phosphate in the cell mass entering the digester.

The solubility product of many precipitates containing these ions was calculated with an equilibrium program developed by Sen (33) to determine the specific precipitates responsible for the chemical binding of the phosphate. Coupled with the molar changes in the soluble metal and phosphate ions from pH value to pH value given in Appendix A, this method yielded some possible clues about these existing precipitates.

Magnesium-Phosphorus Precipitates

Data in Tables 4 and 5 indicate that the largest release of Mg^{2+} occurred between pH 7.0 and pH 5.0 for both sludges, with the post-BPR sludge releasing four times the amount of Mg^{2+} than the pre- BPR sludge in this pH range. The results of the equilibrium program showed that both pre- and post-BPR sludges were supersaturated with respect to struvite ($MgNH_4PO_4(s)$). Therefore, it was assumed that all of the Mg^{2+} released as the pH was lowered was from the solubilization of struvite. The existence of struvite in this sludge was confirmed by Sen (33), who identified its presence via x-ray diffraction.

Iron- Phosphorus Precipitates

Most of the iron release for both sludges occurred between pH 5.0 and pH 3.0 with 70-80 percent of the iron being in the reduced Fe^{2+} form. For purposes of calculation and the solubility program input, it was assumed that the remaining iron was in the ferric (Fe^{3+}) state. Only the total iron concentration was quantified at each pH for the pre-BPR sludge; therefore, the results of the tests on the post-BPR sludge were used to formulate the assumption that 80 percent of the iron in the pre-BPR sludge was in the ferrous form

Table 4. Soluble Ion Concentrations at Various pH Values for Pre-BPR Anaerobic Digested Sludge

pH	$PO_4^{=}$-P (mg/L)	Fe (Total) (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
2.7	320	208	836	50.6
3.9	270	65.7	725	46.9
5.0	200	0.18	478	41.2
6.0	68.5	0.05	94.7	14.3
6.9	54.5	0.09	67.6	10.1
7.9	49.0	0.23	51.9	11.9

Table 5. Soluble Ion Concentrations at Various pH Values for Post-BPR Anaerobic Digested Sludge

pH	$PO_4^{=}$-P (mg/L)	Fe (Total) (mg/L)	Fe^{2+} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)
3.2	988	371	--	1160	178	248
3.5	993	394	266	1160	173	246
5.3	694	61.4	--	569	140	206
6.0	450	4.33	2.89	211	85.2	242
7.0	297	0.38	--	55.0	22.3	232
7.7	270	0.72	0.37	19.8	3.63	222

and 20 percent was ferric. This was necessary to utilize the computer solubility program.

In the pH range 5.0-3.0, the results of the computer solubility program estimated that the sludge was supersaturated with respect to $Fe_3(PO_4)_2(s)$, $FePO_4(s)$, and $Fe(OH)_3(s)$, but not with respect to $FeCO_3(s)$ or $Fe(OH)_2(s)$ for both sludges. Therefore, the ferrous iron release in this pH range was assumed to be mostly the result of the presence of the iron phosphate complex $Fe_3(PO_4)_2(s)$; the ferric iron release was assumed to be equally caused by $Fe(OH)_3(s)$ and $FePO_4(s)$. The large fraction of reduced iron found in the sludge coupled with the results of the solubility program support the findings of Singer (19) who reported the existence of $Fe_3(PO_4)_2(s)$ in anaerobically digested sludge.

Calcium Phosphate Precipitates

The largest release of calcium for both sludges occurred between pH 6.0 and pH 3.5. The results of the equilibrium program predicted that the sludge was supersaturated with respect to $Ca_{10}(PO_4)_6(OH)_2(s)$ (hydroxyapatite), $Ca_3(PO_4)_2(s)$ (b-tricalcium phosphate), and $CaHPO_4(s)$ (brushite).

Since the molar amount of phosphate released by magnesium and iron could be estimated from the precipitates, it was possible to speculate on the specific calcium phosphate precipitates that were binding phosphorus in this pH range. Assuming the molar ratio of magnesium to phosphate released is 1:1, ferric iron to phosphate is 1:1, and ferrous iron to phosphate is 3:2, the molar ratio of calcium to the remaining phosphate released for various pH ranges was calculated for both sludges and is presented in Tables 6 and 7.

The data show that the $Ca^{2+}/PO_4^{=}$ molar ratios for the pre-BPR sludge are greater than those calculated for the post-BPR sludge and are not indicative of any particular calcium phosphorus precipitate. This suggests that much of the calcium entering the digester is bound in other precipitates such as $CaCO_3$. The $Ca^{2+}/PO_4^{=}$ molar ratios for the post-BPR sludge are consistently lower than that of the pre-BPR sludge, suggesting that much of the excess phosphate introduced by the BPR process is bound by calcium in the digester.

The calcium to phosphorus ratio of 1.68:1 in the pH range 7.0-6.0 is equal to the calcium to phosphorus molar ratio of hydroxyapatite. The molar ratios calculated in the other

Table 6. Calculated $Ca^{2+}/PO_4^{\equiv}$ Molar Release Ratios for Pre-BPR Anaerobic Digested Sludge

pH Range	$PO_4^{\equiv}$-P Released by Fe^{2+} (mM P/L)	$PO_4^{\equiv}$-P Released by Fe^{3+} (mM P/L)	$PO_4^{\equiv}$-P Released by Mg^{2+} (mM P/L)	$PO_4^{\equiv}$-P Released by Ca^{2+} (mM P/L)	$Ca^{2+}/PO_4^{\equiv}$ Molar Release Ratio
6.9-6.0	0	0	0.17	0.28	2.43
6.0-5.0	0	0	1.11	3.14	3.04
5.0-3.9	0.94	0.12	0.23	0.97	6.35
6.9-5.0	0	0	1.28	3.42	2.99
6.9-3.9	0.94	0.12	1.51	4.39	3.74
6.0-3.9	0.94	0.12	1.34	4.11	3.82

Table 7. Calculated $Ca^{2+}/PO_4^{\equiv}$ Molar Release Ratios for Post-BPR Anaerobic Digested Sludge

pH Range	$PO_4^{\equiv}$-P Released by Fe (mM P/L)	$PO_4^{\equiv}$-P Released by Fe (mM P/L)	$PO_4^{\equiv}$-P Released by Mg (mM P/L)	$PO_4^{\equiv}$-P Released by Ca (mM P/L)	$Ca^{2+}/PO_4^{\equiv}$ Molar Release Ratio
7.0-6.0	0.03	0.01	2.58	2.32	1.68
6.0-5.3	0.45	0.17	2.26	5.00	1.79
5.3-3.5	2.69	1.10	1.36	4.50	3.27
7.0-5.3	0.48	0.18	4.84	7.32	1.75
7.0-3.5	3.17	1.28	6.20	11.82	2.33
6.0-3.5	3.14	1.27	3.62	9.50	2.49

two pH ranges, however, are not representative of any of the calcium phosphate precipitates identified by the equilibrium program. This result is most likely because of the presence of some other magnesium, iron, or calcium precipitate that does not contain phosphate.

Metals, Phosphate, and Precipitates Entering the Digester

Tests involving species´ solubilization as a function of pH were performed on waste activated sludge, flotation thickened waste activated sludge, and gravity thickened primary sludge to estimate the source of the precipitates found in the digester. The soluble ion concentrations at various pH values for waste activated sludge, flotation thickened waste activated sludge, and gravity thickened primary sludge are shown in Tables 8 and 9. The data in these tables show that a significant release of phosphorus, potassium, and magnesium occurs from the waste activated sludge during the flotation thickening process at pH 7.0.

Because of the biological composition of the waste activated sludge, the release of phosphorus and metal ions can be assumed to be a result of the reaction of the microorganisms to the stress of the flotation thickening process. This stress causes the microorganisms to release accumulated

Table 8. Soluble Ion Concentrations at Various pH Values for Post-BPR Waste Activated and Flotation Thickened Sludges

pH	$PO_4^{\equiv}$-P (mg/L)	Fe^{3+} (mg/L)	Fe^{2+} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)
Waste Activated Sludge - 0.76% Solids						
4.5	46.1	0.50	0	187	31.7	30.0
7.0	7.32	0.06	0	108	12.8	11.8
Flotation Thickened Waste Activated Sludge - 3.94% Solids						
4.0	1243	45.9	13.9	859	717	524
6.0	777	2.69	0	342	406	324
7.0	564	2.04	3.33	161	245	228

Table 9. Soluble Ion Concentrations at Various pH Values for Post-BPR Primary Sludge

pH	$PO_4^{\equiv}$-P (mg/L)	Fe^{3+} (mg/L)	Fe^{2+} (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	K^{+} (mg/L)
1.7	354	51.2	611	2040	96.8	41.4
4.4	220	4.9	92.8	1610	65.4	36.6
5.2	156	1.61	1.39	500	46.0	32.0
5.9	92.7	0.45	0.25	180	27.5	30.0
6.9	79.6	1.73	1.67	106	21.9	31.0

phosphate and co-transport the associated metal ions. Another significant release of phosphate, magnesium, calcium, and potassium occurred when the pH of the flotation thickened sludge was lowered. Again, the release of phosphate, magnesium, and potassium in this sludge can be assumed to have resulted from the stress of lowered pH imposed on the microorganisms.

The results of the pH extraction tests for primary sludge show that the release of phosphate, magnesium, and potassium at each pH value was not as great as the release of these components from the flotation thickened sludge. However, large releases of calcium and iron occur as the pH of the primary sludge is decreased. This suggests that the phosphate entering the digester in the primary sludge is most likely bound in a calcium-phosphate or iron-phosphate precipitate. These results indicate that most of the phosphorus, potassium, and magnesium enters the digester in the flotation thickened sludge; most of the calcium and iron enters the digester in the gravity thickened sludge.

A final point of interest in these tests is the transition of ferric iron to ferrous iron in the digestion process. Less than 20 percent of the total iron in the waste activated sludge was in the reduced ferrous state. However, this value changes to 67 percent in the flotation thickened sludge, indicating that a transition of ferric iron to ferrous iron occurred during flotation thickening. The iron in the thickened primary sludge was 60 percent ferrous, showing that much of this iron is in the reduced state before entering the digestion process.

CHEMICAL CONDITIONING OF ANAEROBICALLY DIGESTED SLUDGE

Sludge Conditioning with Cationic Polymer

The BPR process appeared to have little effect on the amount of polymer required to optimally condition the resulting digested sludge. Data included in Figure 9 show that equivalent dosages of polymer achieved similar dewatering rates for pre- and post-BPR sludges. For the range of dosages tested, the optimum polymer dosage was found to be near 18 lb/ton dry solids, which achieved a specific resistance 5.0×10^{11} m/kg (representative of a good dewatering sludge), and a cake solids concentration of 15 percent by weight.

Actual plant operating data for the performance of the belt filter press during the first year following the modification to BPR are shown in Figure 10. Data presented in this

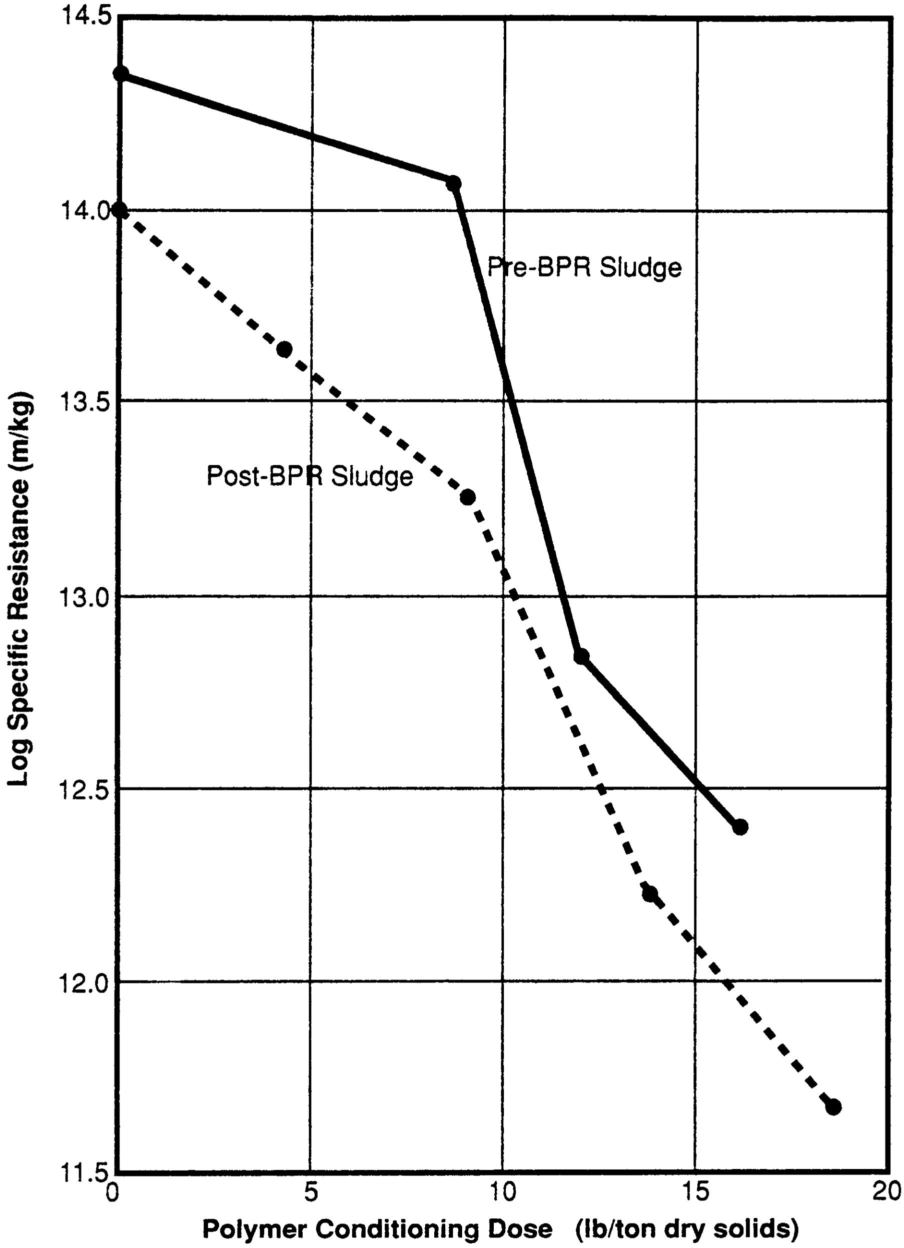

FIGURE 9. Effect of Percol 757 Cationic Polymer on Dewatering Rate for Pre- and Post-BPR Anaerobically Digested Sludges.

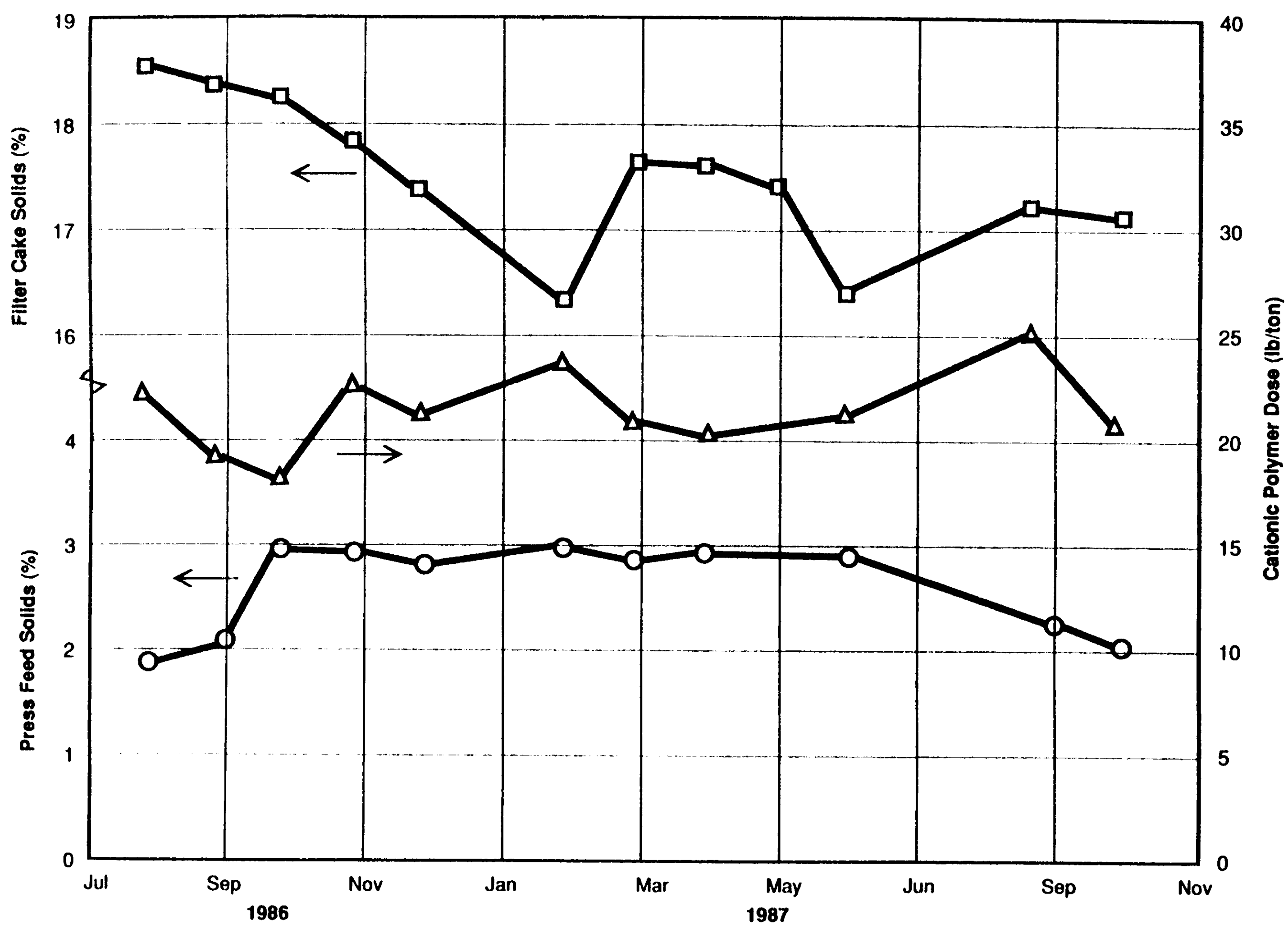

FIGURE 10. Full-Scale Belt Filter Press Performance Data During the BPR Modification Studies at the York River Plant. (BPR Conversion - August 1986)

figure show that only a slight decrease in performance was noted after the change to BPR. The addition of polymer did not affect the soluble phosphorus concentration of either sludge, as shown in Figure 11.

Sludge Conditioning with $FeCl_3$ Alone

Ferric chloride served a dual conditioning purpose of precipitating soluble phosphorus while improving the dewatering rate. The dosages of $FeCl_3$ required for phosphorus removal from sludge samples tested before and after the BPR process was online are compared in Figure 12. As would be expected, a much greater dosage of $FeCl_3$ was required for phosphorus removal from the BPR sludge than for the conventional sludge because of the higher initial concentration of phosphorus in the BPR sludge. A $FeCl_3$ dose of 2.6 percent by weight accomplished a soluble phosphorus concentration of 5 mg/L in the pre-BPR sludge while a $FeCl_3$ dose of 9.0 percent was required to achieve a soluble phosphorus concentration of 50 mg/L in the post-BPR sludge. Treatment with $FeCl_3$ doses recommended by EPA (4-10 percent by weight) only slightly improved the dewatering rate of both pre- and post-BPR sludges, as shown in Figure 13. Doses of up to 10 percent accomplished specific resistance values of only 7×10^{12} m/kg, compared with the specific

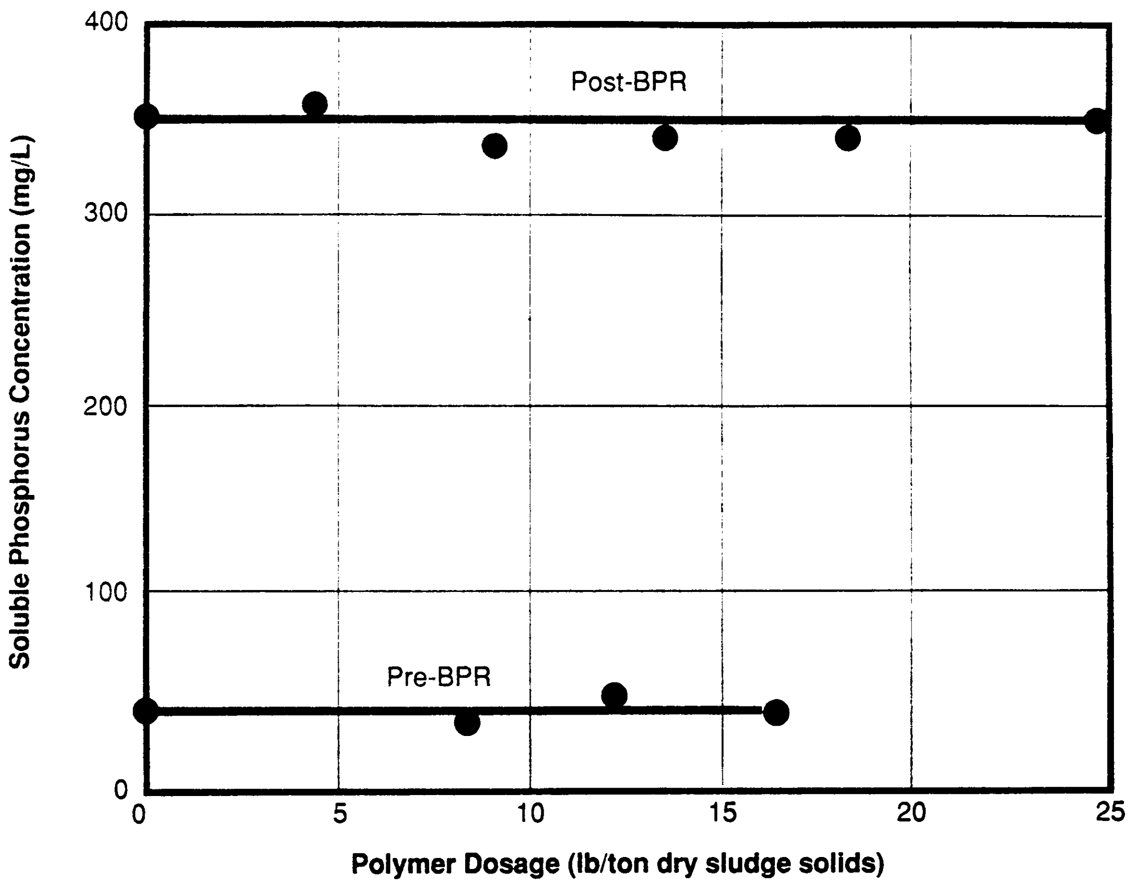

FIGURE 11. Soluble Phosphorus Concentration vs. Polymer Dosage for Pre- and Post-BPR Anaerobically Digested Sludges.

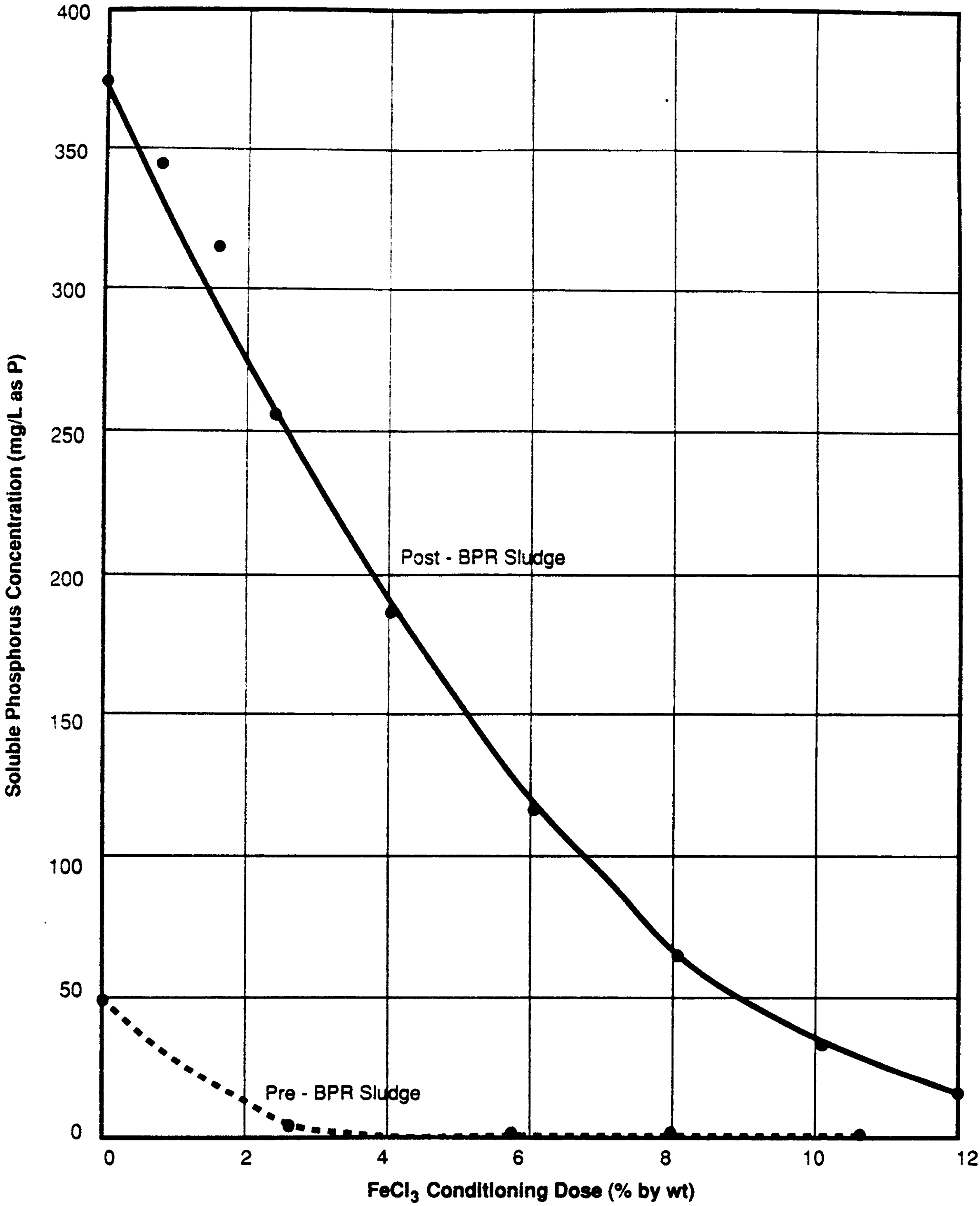

FIGURE 12. Effect of Ferric Chloride on Soluble Phophorus for Pre - and Post - BPR Anaerobically Digested Sludges.

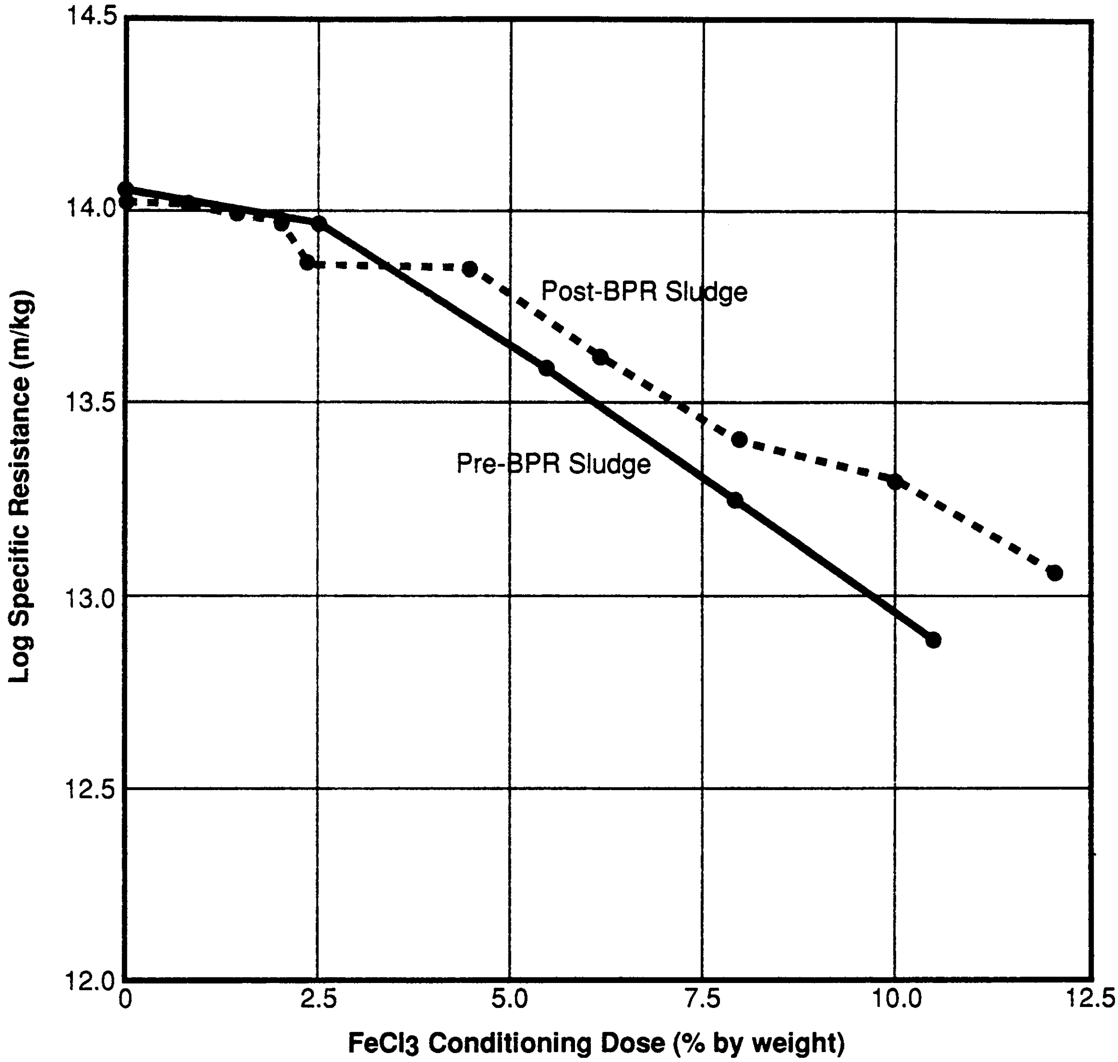

FIGURE 13. Effect of Ferric Chloride Addition on Dewatering Rate for Pre- and Post-BPR Anaerobically Digested Sludges.

resistance values of 5 x 10^{11} m/kg achieved with polymer treatment. The effect of BPR on the dose of $FeCl_3$ required for dewatering was not significant since both sludges dewatered poorly for the $FeCl_3$ doses tested. $FeCl_3$ addition also decreased the pH of the sludge samples, as shown in Figure 14. At the doses required for phosphorus removal from the post-BPR sludge, this decreased pH condition liberated noticeable amounts of hydrogen sulfide from the sludge sample.

Sludge Conditioning Using Both $FeCl_3$ and Polymer

The addition of both ferric chloride and polymer effectively removed soluble phosphorus and improved dewatering. Data presented in Figure 15 show that the addition of 3 percent $FeCl_3$ and 12 lb polymer/ton dry solids decreased the soluble phosphorus concentration of the filtrate from 350 mg/L as P to 180 mg/L as P and achieved a specific resistance value of 3.1 x 10^{12} m/kg. The cake solids concentration following vacuum filtration (16 percent) was equivalent to that achieved by the addition of polymer alone. The joint addition of the two chemicals did not appear to impair the effects of the other. For example, at the constant $FeCl_3$ dose of 3 percent, the soluble phosphorus concentration remained constant as the dosage of polymer was

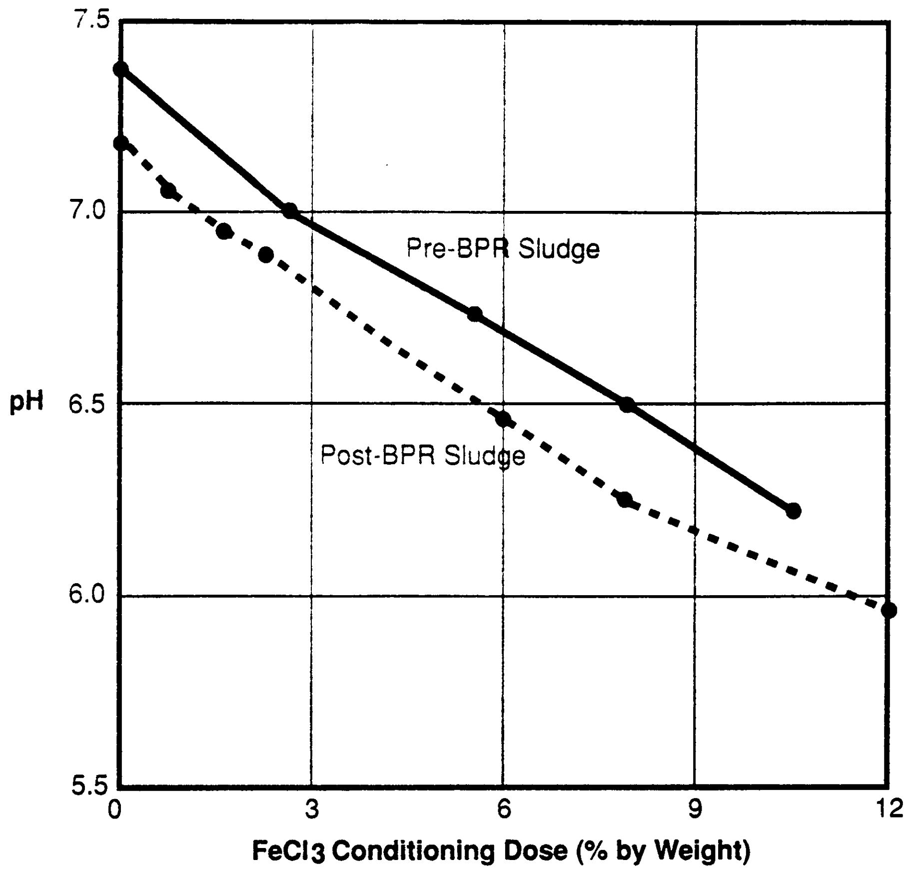

FIGURE 14. Effect of Ferric Chloride on Sludge pH for Pre- and Post-BPR Anaerobically Digested Sludges.

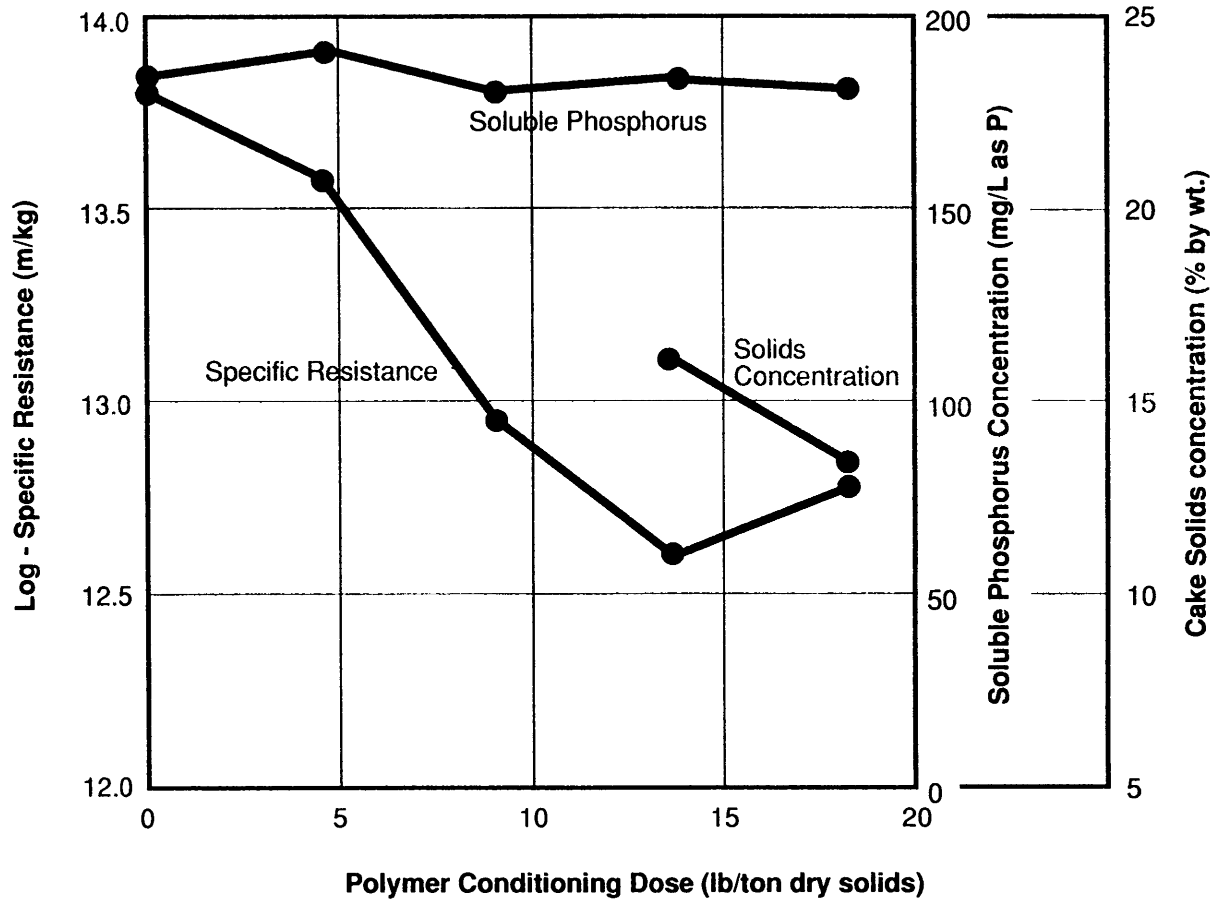

FIGURE 15. Polymer and Ferric Chloride Conditioning of Post -BPR Anaerobically Digested Sludge (Ferric Chloride Dose Held Constant at 3% by Weight).

increased, as shown in Figure 15. The addition of $FeCl_3$ did, however, appear to slightly decrease the amount of polymer required for efficient dewatering.

Sludge Conditioning with $Ca(OH)_2$ Only

The addition of $Ca(OH)_2$ alone did not significantly affect the dewatering rate of either the pre- or post-BPR sludge at the dosages tested. However, such chemical addition effectively removed soluble phosphorus from both sludges. Data presented in Figure 16 show the dosages of $Ca(OH)_2$ required for the removal of soluble phosphorus from both pre- and post-BPR sludge samples. The dosage of $Ca(OH)_2$ required to achieve a soluble phosphorus concentration of 50 mg/L as P in the post-BPR sludge was 12 percent by weight compared to a 9 percent by weight requirement when using $FeCl_3$. The addition of $Ca(OH)_2$ also effectively increased the pH of both sludges, as shown in Figure 17.

Sludge Conditioning Using Both $FeCl_3$ and $Ca(OH)_2$

Conditioning tests were performed using $FeCl_3$ and $Ca(OH)_2$ jointly for only post-BPR sludge. In these tests, the dosage of one chemical was held constant while varying the dosage of the other chemical. In the first test, the dosage

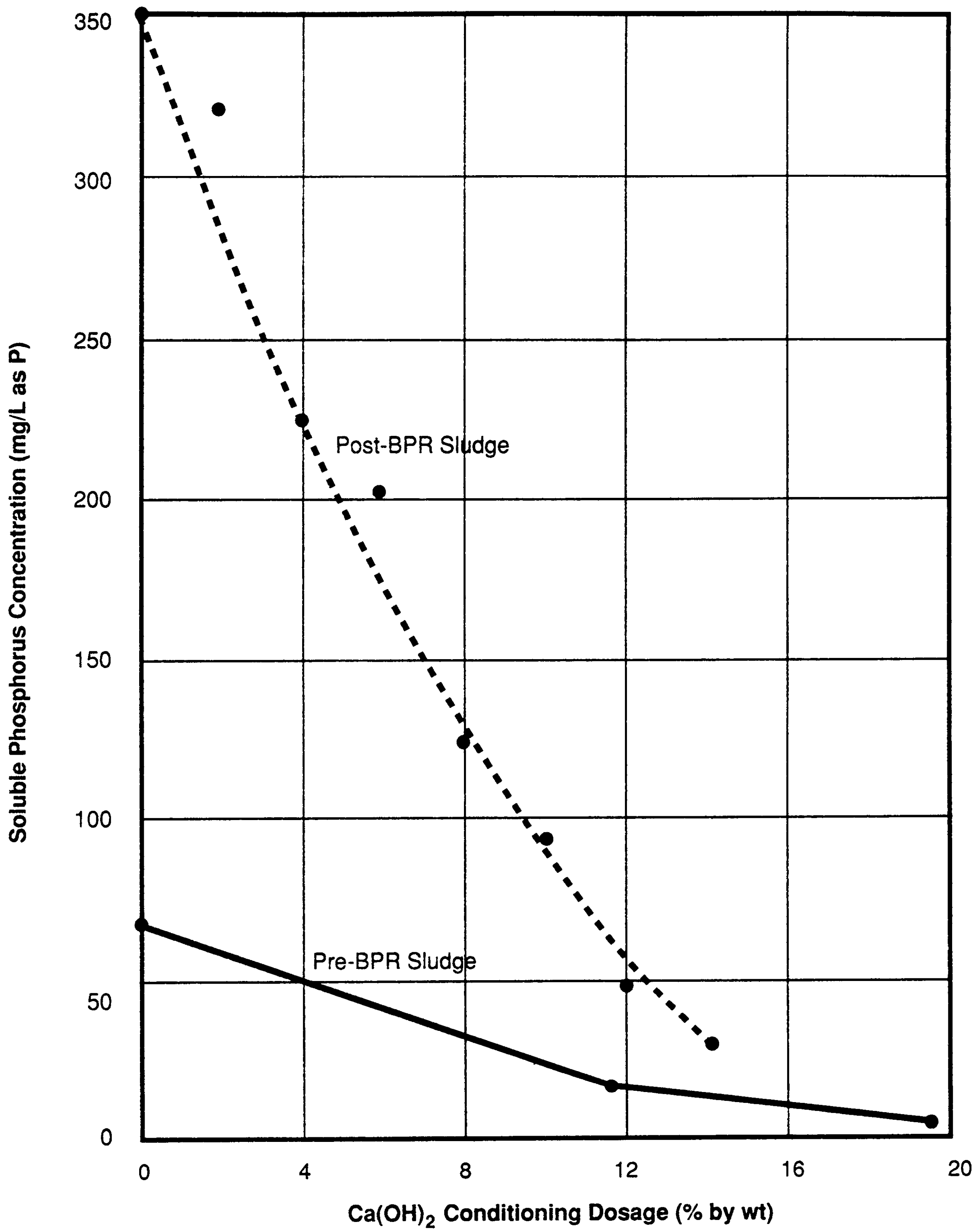

FIGURE 16. Effect of Calcium Hydroxide on Soluble Phosphorus Concentration for Pre- and Post-BPR Anaerobically Digested Sludges

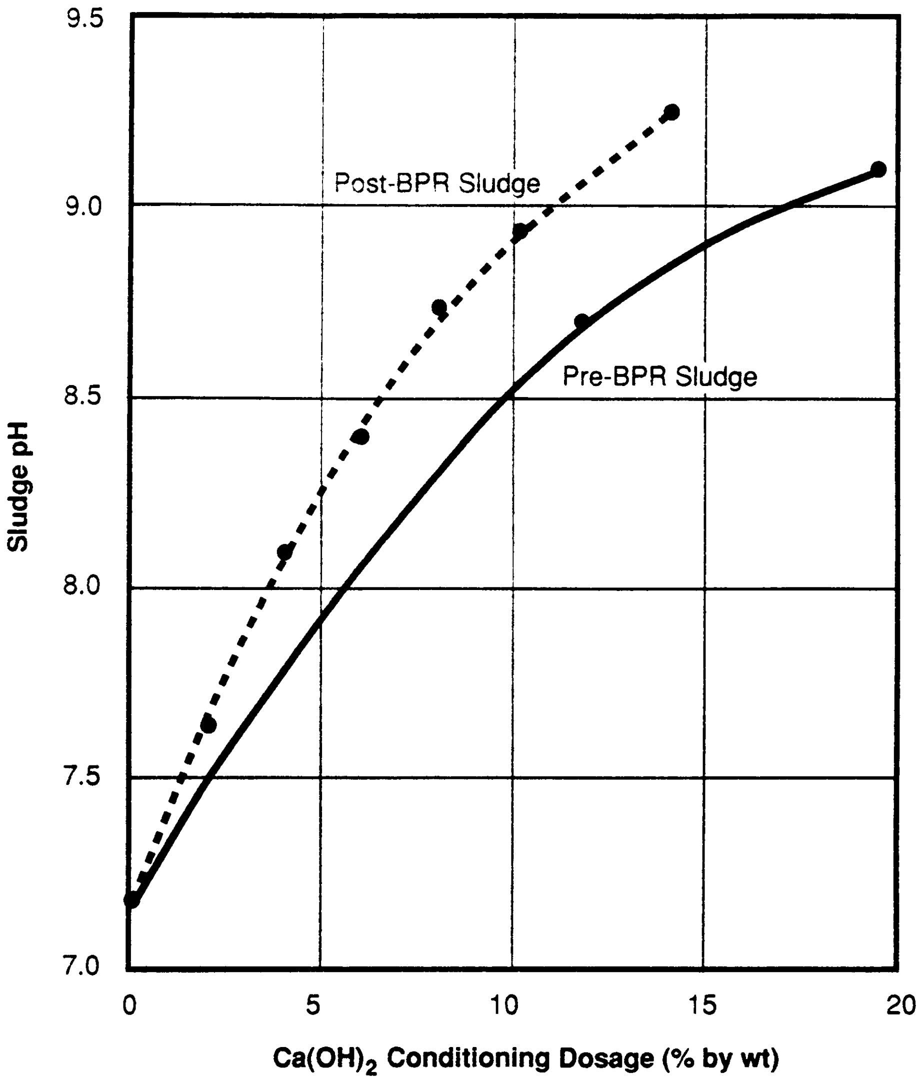

FIGURE 17. Effect of Calcium Hydroxide on pH for Pre- and Post-BPR Anaerobically Digested Sludges.

of $FeCl_3$ was held constant at 6 percent while the dosage of $Ca(OH)_2$ was varied. The second test was performed holding the dosage of $Ca(OH)_2$ constant at 12 percent while varying the dosage of $FeCl_3$.

Data included in Figures 18 and 19 indicate that, at a constant $FeCl_3$ dose of 6 percent, an increase in the amount of $Ca(OH)_2$ added consistently improved the dewatering rate of the sludge. This also yielded efficient removal of soluble phosphorus. The chemical dose of 6 percent $FeCl_3$ and 24 percent $Ca(OH)_2$ achieved a specific resistance of 2.2×10^{12} m/kg and a soluble phosphorus concentration in the filtrate of <1 mg/L as P. Data presented in Figures 20 and 21 indicate that, at a constant $Ca(OH)_2$ dose of 12 percent, an increase in the amount of $FeCl_3$ added consistently improved the dewatering rate of the sludge and the corresponding removal of phosphorus. For example, a chemical dose of 15 percent $FeCl_3$ and 12 percent $Ca(OH)_2$ achieved a specific resistance of 2.2×10^{12} m/kg and a soluble phosphorus concentration in the filtrate of <1 mg/L as P.

The cake solids concentration obtained following vacuum filtration increased for both studies as the chemical conditioning dosages increased, as shown in Figures 18 and

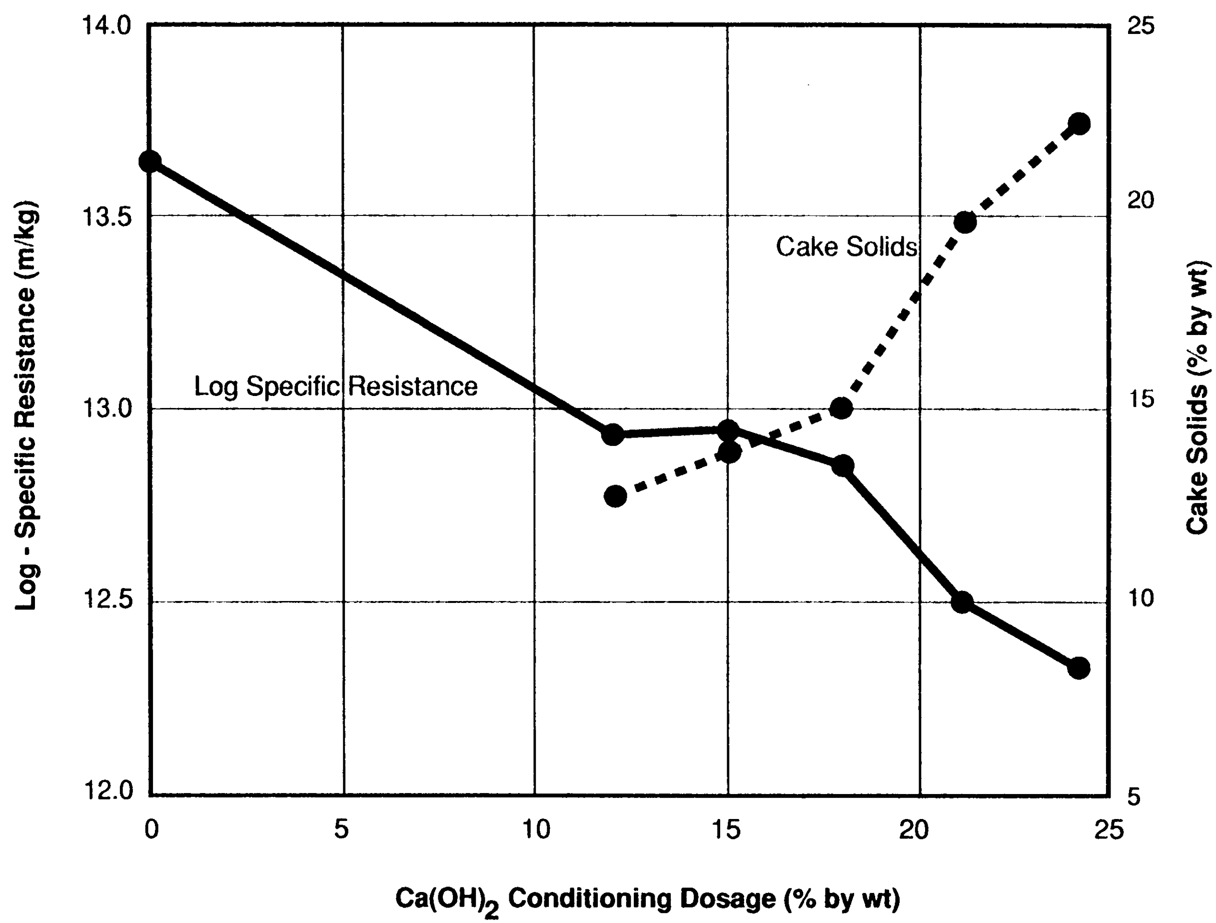

FIGURE 18. Effect of Ferric Chloride and Lime Conditioning on Post-BPR Anaerobically Digested Sludge Dewatering Rate and Cake Solids Concentration (Ferric Chloride Dosage Held Constant at 6% by Weight).

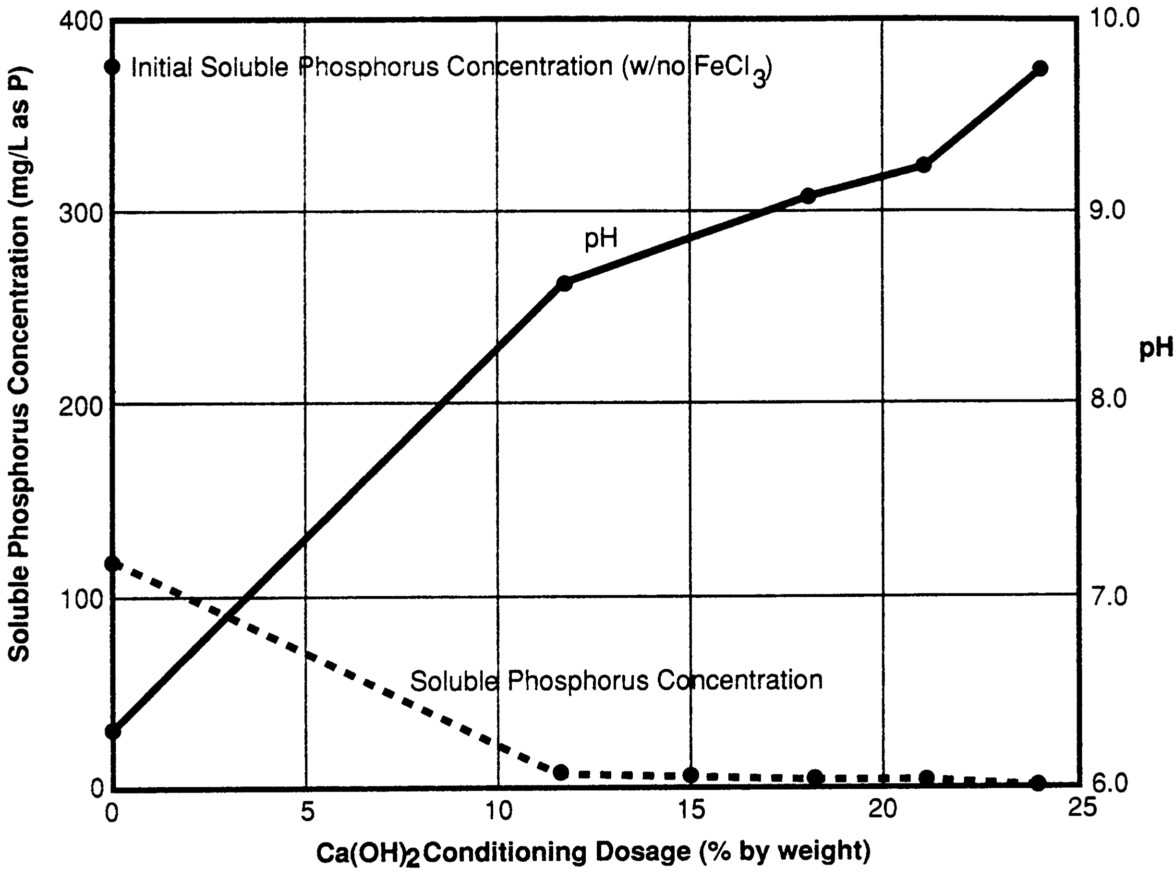

FIGURE 19. Effect of Ferric Chloride and Lime Conditioning on Residual Soluble Phosphorus Concentration and pH for Post-BPR Anaerobically Digested Sludge (Ferric Chloride Dosage Held Constant at 6% by Weight).

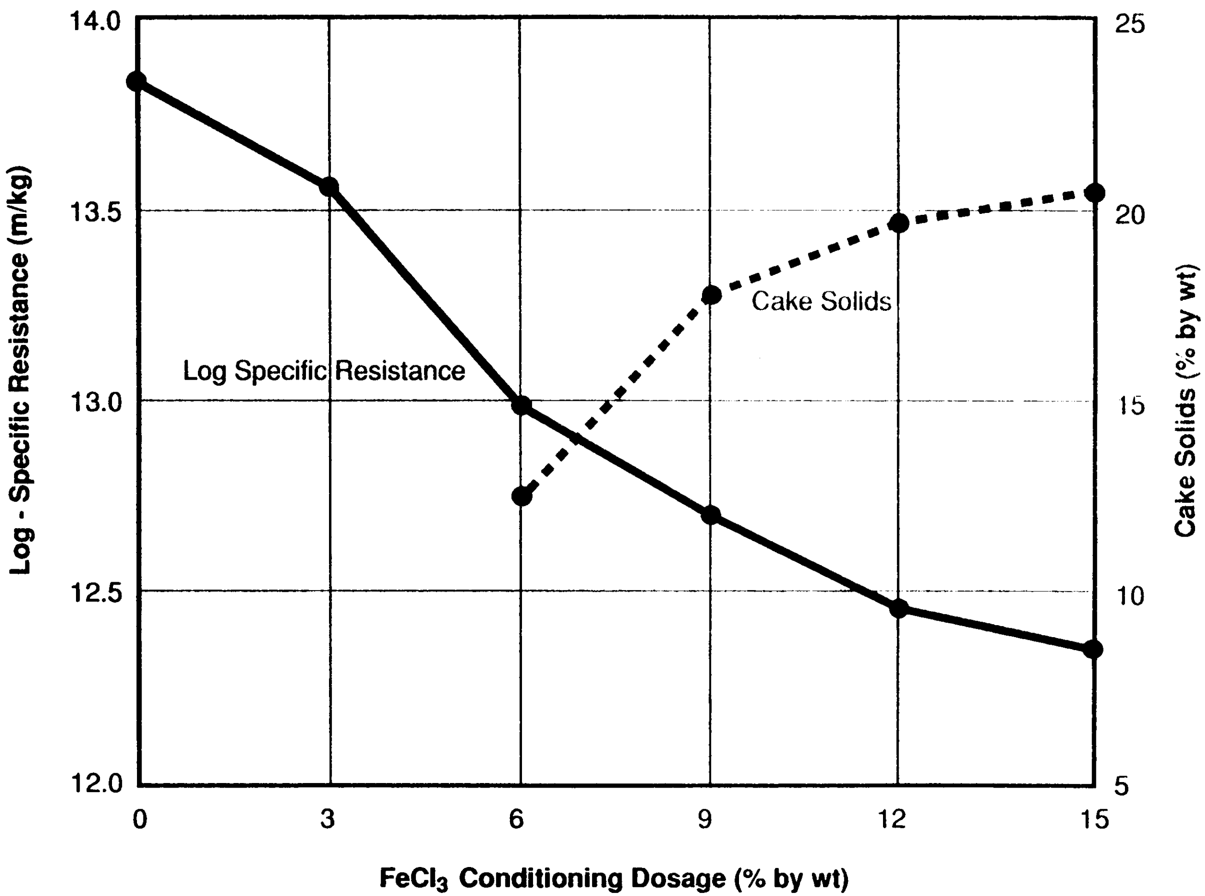

FIGURE 20. Effect of Ferric Chloride and Lime Conditioning on Dewatering Rate and Cake Solids Concentration for Post-BPR Anaerobically Digested Sludge (Lime Dosage Held Constant at 12% by Weight.

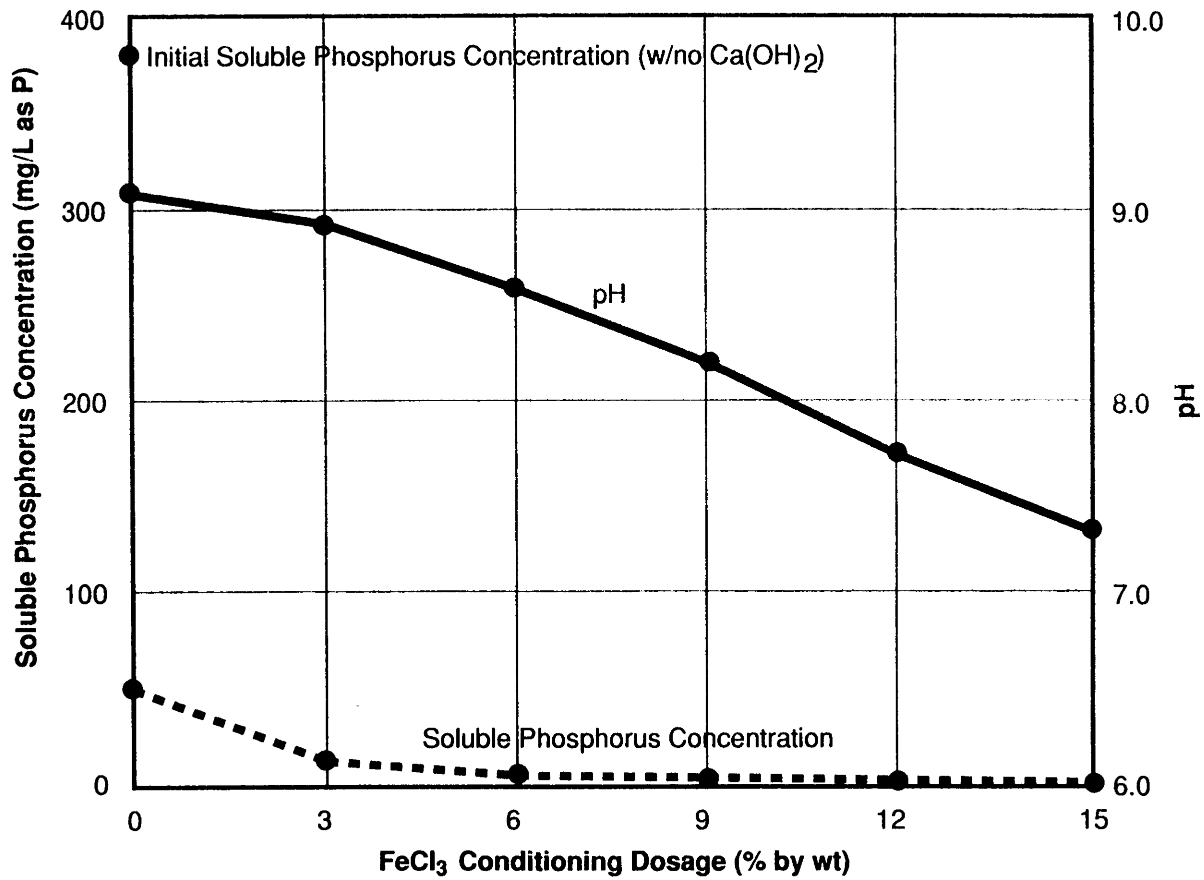

FIGURE 21. Effect of Ferric Chloride and Lime Conditioning on Residual Soluble Phosphorus Concentration and pH for Post-BPR Anaerobically Digested Sludge (Lime Dosage Held Constant at 12% by Weight).

20. The solids concentrations obtained from the use of these inorganic conditioners (20-22 percent) were significantly greater than the concentrations achieved with cationic polymers (15-16 percent) alone, as shown in Table 10. This increase in cake solids concentration may reflect the precipitation of additional dry solids within the cake structure [eg., $CaCO_3$(s), $Fe(OH)_3$(s), $Ca(OH)_2$(s), $FePO_4$(s), etc.].

Conditioning for Phosphorus Removal Alone Using $FeCl_3$ and $Ca(OH)_2$

An attempt was made to determine the dosages of $FeCl_3$ and $Ca(OH)_2$ required for phosphorus removal only. The target concentration of soluble phosphorus and sludge pH were established at 50 mg/L as P and a pH between 7.0 and 7.5 for the purposes of this study. These conditions were characteristic of the pre-BPR sludge samples. The test results, given in Figures 22 and 23, showed that 5 percent $FeCl_3$ combined with 3 percent $Ca(OH)_2$ achieved a pH of 7.0 and a soluble phosphorus concentration of 53 mg/L as P. The effect on the dewatering rate at these chemical dosages was minimal. It appears evident that the inorganic chemical dosages required to control soluble phosphorus

Table 10. Specific Resistance and Cake Solids Values Achieved by Various Conditioning Schemes

Conditioning Dosages	Specific Resistance (m/kg)	Cake Solids (% by wt)
18 lb polymer / ton dry solids	4.96×10^{11}	15.1
3% $FeCl_3$ (by wt) and 14 lb polymer / ton dry solids	3.12×10^{12}	16.1
6% $FeCl_3$ (by wt) and 24% $Ca(OH)_2$ (by wt)	2.17×10^{12}	22.2
15% $FeCl_3$ (by wt) and 12% $Ca(OH)_2$ (by wt)	2.26×10^{12}	20.4

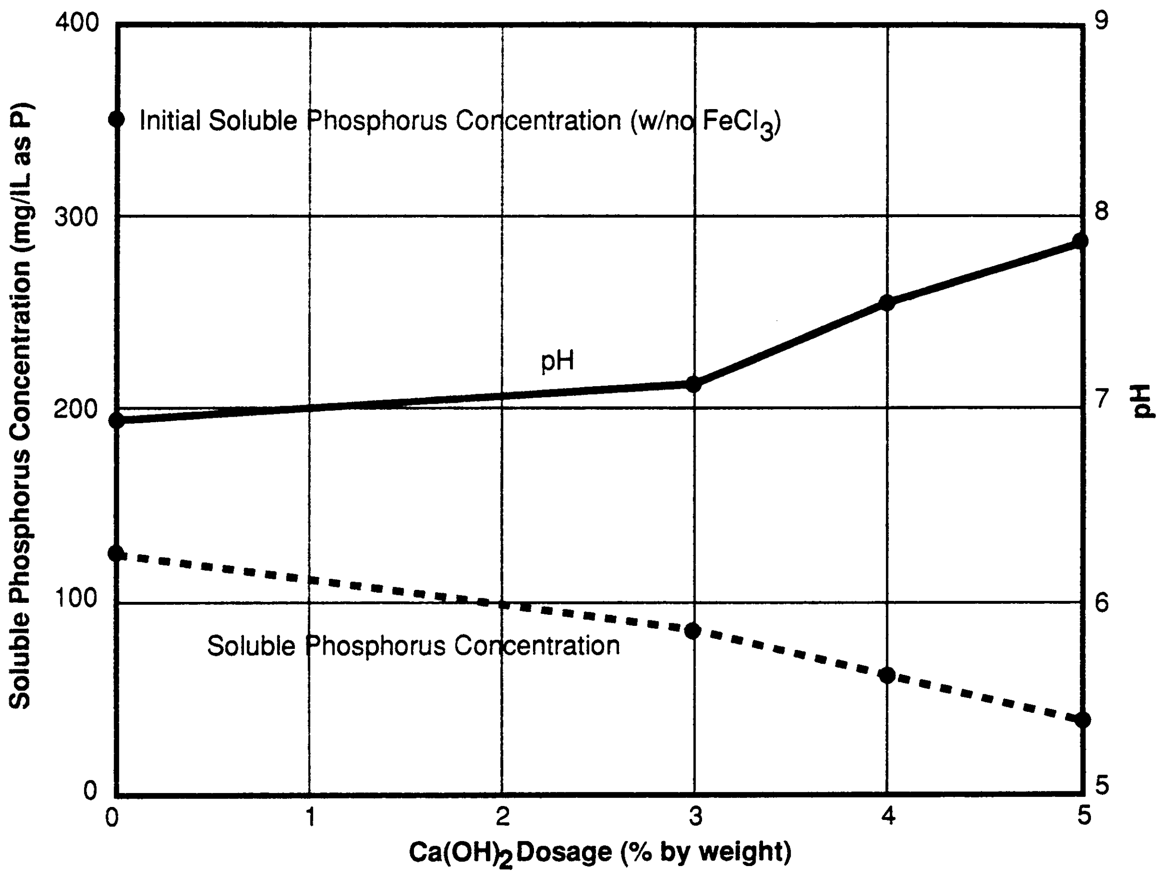

FIGURE 22. Residual Soluble Phosphorus Concentration and pH vs. Calcium Hydroxide Dosage for Post-BPR Anaerobically Digested Sludge (Ferric Chloride Dosage Held Constant at 4% by Weight).

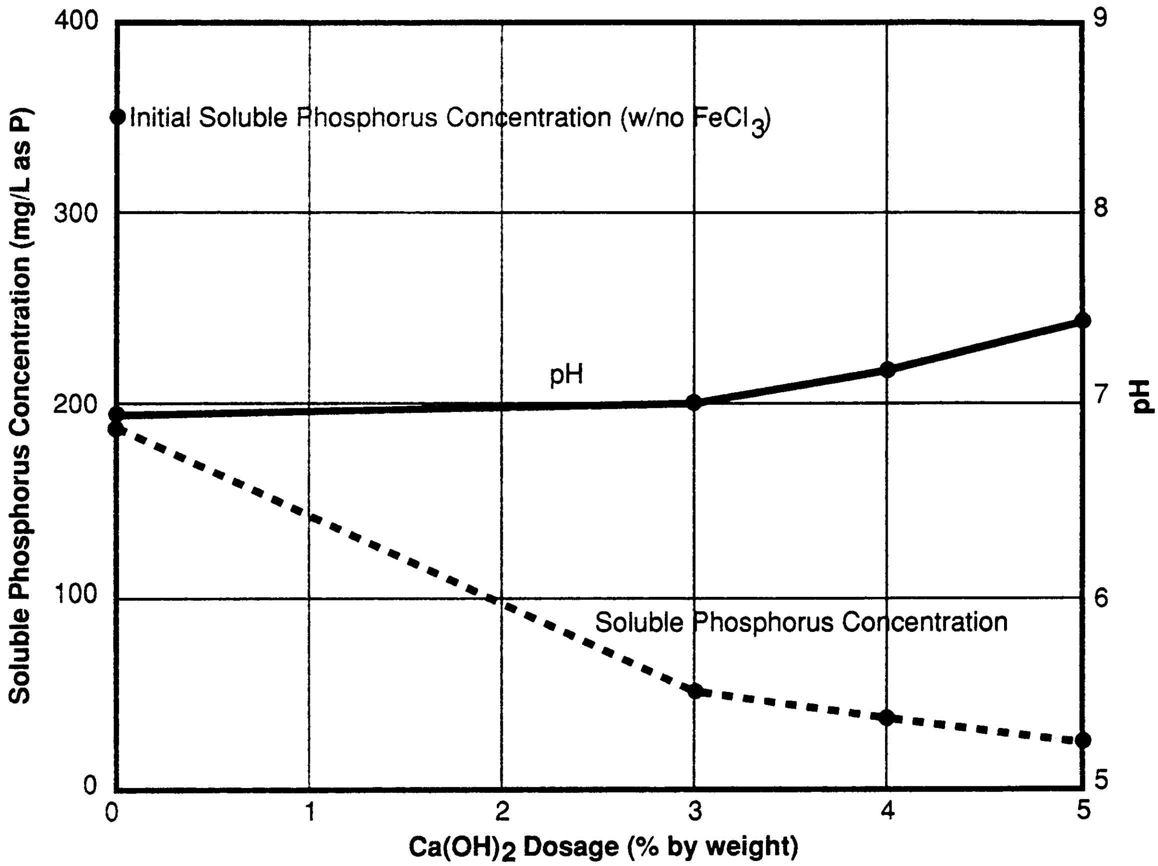

FIGURE 23. Residual Soluble Phosphorus Concentration and pH vs. Calcium Hydroxide Dosage for Post-BPR Anaerobically Digested Sludge (Ferric Chloride Dosage Held Constant at 5% by Weight).

concentrations are well below those routinely required to produce acceptable sludge dewatering rates.

Chemical Treatment of Belt Filtrate for Phosphorus Removal

Since the belt filter press filtrate from the dewatering of the secondary digester underflow is recycled to the headworks of the York River plant, treatment of the belt filtrate with $FeCl_3$ and $Ca(OH)_2$ for soluble phosphorus removal was tested. The soluble phosphorus concentration in the belt filtrate was 50 mg/L as P on June 29, 1986, 35 days before conversion to BPR. This concentration increased to 125 mg/L as P on March 24, 1987, 200 days after conversion to the BPR treatment system. Data presented in Figure 24 show the reduction in soluble phosphorus concentration achieved by $FeCl_3$ and $Ca(OH)_2$. As shown by the figure, higher amounts of $Ca(OH)_2$ than $FeCl_3$ are required to affect the same removal of soluble phosphorus. The dosage of $FeCl_3$ required to achieve a soluble phosphorus concentration less than 10 mg/L as P is approximately 650 mg/L of $FeCl_3$ compared to a $Ca(OH)_2$ dosage of approximately 1,100 mg/L. Examining the molar ratios of phosphate removed to chemical required reveals that the PO_4:Ca^{2+} molar ratio is 0.26, while that of PO_4:Fe^{3+} is 0.74, indicating that Fe^{3+} more effectively binds phosphate than Ca^{2+} in this water.

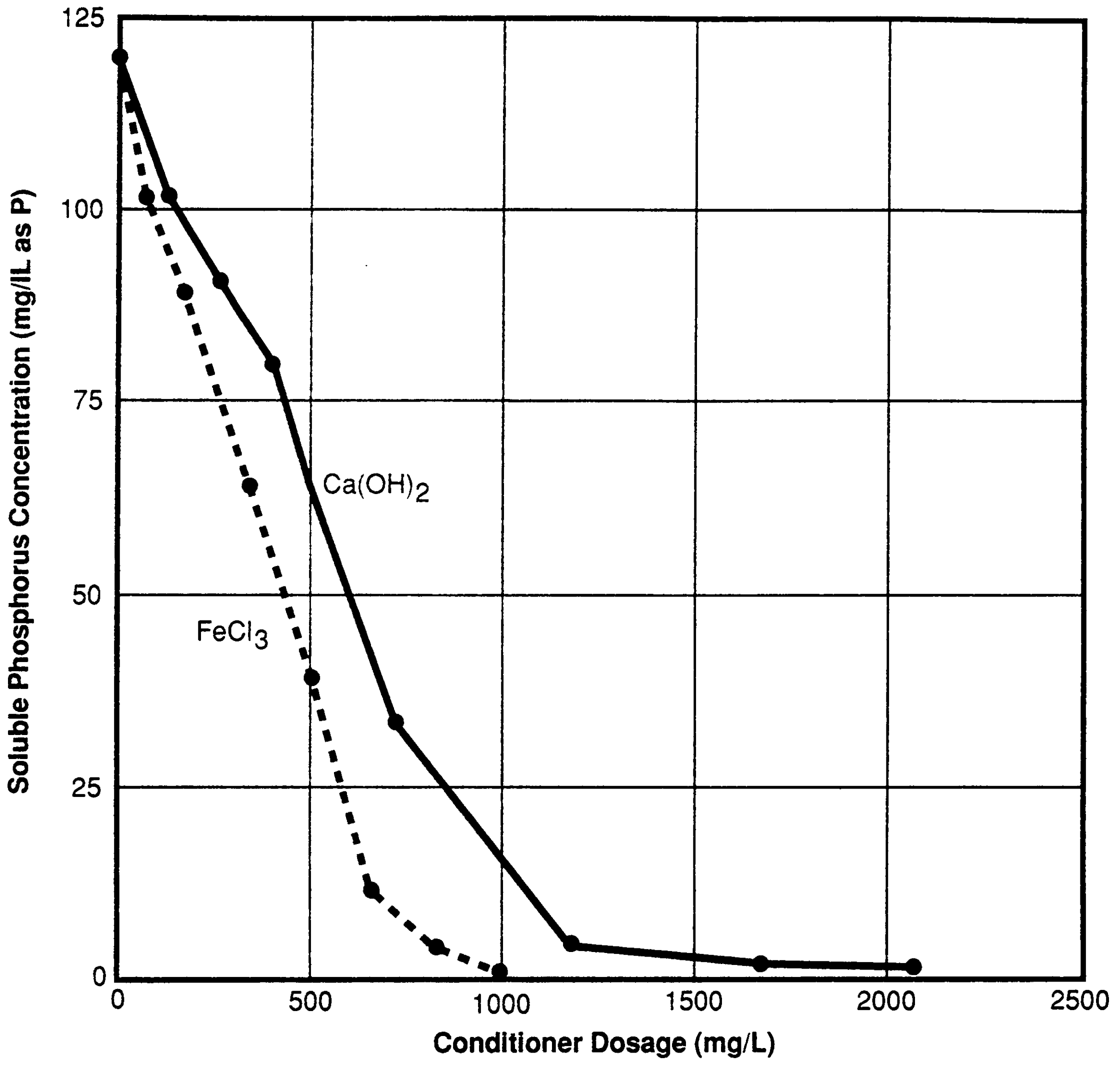

FIGURE 24. Ferric Chloride and Calcium HydroxideTreatment of Belt Filtrate from Post-BPR Anaerobically Digested Sludge.

CHAPTER V

DISCUSSION

CHEMICAL PRECIPITATES AND THE FATE OF ACCUMULATED PHOSPHORUS IN THE ANAEROBIC DIGESTER

In the pre-BPR sludge, approximately 85 percent of the phosphorus present in the digester is bound in chemical precipitates. Calcium phosphate precipitates appear to be the most prevalent metal precipitates in the pre-BPR sludge, accounting for approximately 65 percent of the precipitated phosphorus. The results of the equilibrium program suggested the presence of hydroxyapatite; the high calcium to phosphate molar release ratios calculated during the acid extraction studies suggested that much of the calcium present in the digester was bound in non-phosphorus containing precipitates such as $CaCO_3(s)$. Magnesium phosphate precipitates such as struvite accounted for approximately 20 percent of the phosphate bound in the pre-BPR sludge. Iron phosphate precipitates accounted for approximately 15 percent of the phosphorus bound in the digester, with ferrous phosphate being the most prevalent iron phosphate solid species.

In the post BPR sludge, approximately 65 percent of the total phosphorus present in the anaerobic digester is bound in chemical precipitates. This difference in the percentage of precipitated phosphorus from the pre-BPR sludge indicates that the increase in metal cations that form precipitates with phosphate with the onset of BPR is not as extensive as the increase in soluble phosphorus. Calcium phosphate precipitates such as hydroxyapatite, appear to be the most prevalent metal precipitates in the post-BPR sludge. These precipitates appear to be responsible for binding approximately 50 percent of the phosphate released during the conditions of the study. The calculated calcium to phosphorus molar release ratios were much lower than those for the pre-BPR sludge, indicating that a higher percentage of the calcium present was incorporated in calcium phosphate precipitates. The magnesium precipitate struvite bound approximately 30 percent of the phosphorus precipitated; vivianite 15 percent; and ferric phosphate 5 percent. These percentages show that a shift took place between the percentage of phosphorus precipitated by calcium phosphate precipitates and magnesium phosphate precipitates (struvite) from the pre- to post-BPR sludges. This increase in struvite formation could be a cause for concern due to its propensity to block pipelines. However, the work of Sen (33) reported that the struvite in this sludge was precipitated on the cell mass and not on the sides of the digester and piping.

It appears that the majority of the phosphorus, magnesium, and potassium present in the digester entered through the flotation thickened waste activated sludge. The extensive release of magnesium and potassium accompanying the release of soluble phosphorus during flotation thickening indicates that these ions are released into the soluble phase by cells and are not bound by chemical precipitates before reaching the anaerobic digester.

CONDITIONING OF POST-BPR ANAEROBICALLY DIGESTED SLUDGE

Based upon the results obtained during the study and the plant belt filter press operating data, it appears that the conversion to BPR did not significantly effect the polymer dosage required to optimally condition the resulting sludge after anaerobic digestion. Further, there was no significant difference between the specific resistance values for unconditioned sludge samples for both pre- and post-BPR sludges, indicating again that the BPR conversion did not affect sludge dewatering characteristics. The use of polymer for dewatering had no effect on the soluble phosphorus concentration, though, indicating that polymer addition alone was not sufficient for sludge conditioning if soluble phosporus removal was also required. Based on the results of the study joint conditioning for dewatering and phosphorus removal can be accomplished using one of four conditioning strategies:

1. Cationic polymer for improved dewatering plus $FeCl_3$ for soluble phosphorus control; chemical addition directly to the sludge prior to dewatering.

2. $FeCl_3$ and $Ca(OH)_2$ for improved dewatering and soluble phosphorus control; chemical addition directly to the sludge prior to dewatering.

3. Cationic polymer for improved dewatering and mixtures of $FeCl_3$ and $Ca(OH)_2$ for soluble phosphorus control; chemical addition directly to the sludge prior to dewatering.

4. Cationic polymer added to the sludge for improved dewatering; treatment of belt filtrate with $FeCl_3$ for P control.

The advantages of conditioning strategy #1 are that only two chemicals must be added to the sludge and the total amount of solids to be disposed of does not increase significantly over the addition of polymer alone. However, the addition of $FeCl_3$ reduces the sludge pH. Depending on the amount of $FeCl_3$ added for phosphate removal, the decrease in pH could be significant, causing a release of H_2S from the sludge.

The advantages of conditioning strategy #2 are that only two chemicals must be added and pH control is possible. However, very high chemical dosages are required to achieve acceptable dewatering rates. This may lead to higher chemical conditioner costs and will significantly increase the inorganic solids content of the sludge, possibly effecting the ultimate sludge disposal method.

Conditioning strategy #3 has the advantages of pH control and yields a sludge with a much lower inorganic solids content than strategy #2. Capitol and operations costs may be extensive due to the fact that three chemicals must be added to the sludge.

Conditioning strategy #4 has the advantage of no inorganic chemical addition to the sludge and a reduced amount of phosphorus to treat. The capitol cost of this system may be very high since a contact basin must be constructed to give the chemicals adequate mixing and contact time with the belt filtrate. This system will also produce an additional waste sludge that must be dewatered and disposed of. It is possible that the $FePO_4(s)/Fe(OH)_3(s)$ sludge produced by this treatment could be mixed with the anaerobically digested sludge and jointly dewatered. Further, such mixing might provide for partial conditioning of the digested sludge. This possibility should be reviewed in further studies.

The treatment process chosen would depend on the degree of phosphorus removal required. If a small degree of removal is required, treatment scheme #1 would most likely be the strategy of choice since the pH effects of increased inorganics would be minimal. If a large degree of phosphate removal is required, a cost analysis including the effect on the ultimate disposal of the sludge would be required to determine the optimum conditioning strategy.

CHAPTER VI

CONCLUSIONS

Based on the experimental results of the study, the following conclusions were formulated:

EFFECT OF BPR ON ANAEROBICALLY DIGESTED SLUDGE CHARACTERISTICS

1. The total and soluble phosphorus content of the anaerobically digested sludge increased significantly with the onset of BPR.

2. Much of the excess phosphate introduced into the digester by the BPR process formed precipitates with calcium, iron, and magnesium.

3. Calcium phosphorus precipitates were the most prevalent metal phosphate precipitates present in the pre- and post-BPR anaerobically digested sludges.

EFFECT OF BPR ON ANAEROBICALLY DIGESTED SLUDGE CONDITIONING REQUIREMENTS

4. The BPR process did not significantly alter the dewatering characteristics of the resulting anaerobically digested sludge. For example, cationic polymer requirements for optimum sludge conditioning were essentially the same for both pre- and post- BPR sludges.

5. Inorganic chemicals such as ferric chloride and lime were required to remove soluble phosphate from the filtrate. Polymer addition alone accomplished no P removal.

6. Ferric chloride (6% by weight) and lime (24% by weight) in combination achieved acceptable dewatering rates while removing soluble phosphorus.

7. The dosages of ferric chloride and calcium hydroxide required for acceptable dewatering caused a significant increase in the cake solids concentration over polymer conditioning due to the precipitation of additional inorganic solids.

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APPENDIX A

Calculation of the phosphate bound by phosphate containing precipitates for pre- and post-BPR anaerobic digested sludges

Pre-BPR sludge

pH Range 6.9-6.0

1. $PO_4^{\equiv}$-P release from $Fe_3(PO_4)_2$ (s)= (0.0 mM Fe^{2+} released)(2/3)= 0.0 mM P

2. $PO_4^{\equiv}$-P release from $FePO_4$ (s)= (0.0 mM Fe^{3+} released)(0.5)(1.0)= 0.0 mM P

3. $PO_4^{\equiv}$-P release from $MgNH_4PO_4$ (s)= (0.17 mM Mg^{2+} released)(1.0)= 0.17 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 0.17 mM P

$PO_4^{\equiv}$-P release due to calcium phosphate precipitates= 0.45 mM P - 0.17 mM P= 0.28 mM P

$Ca^{2+}/PO_4^{\equiv}$ molar ratio= 0.68 mM Ca^{2+}/0.28 mM P = 2.43

<u>pH Range 6.0-5.0</u>

1. $PO_4^{\equiv}$-P release from $Fe_3(PO_4)_2$ (s)= (0.0 mM Fe^{3+} released)(2/3)= 0.0 mM P

2. $PO_4^{\equiv}$-P release from $FePO_4$ (s)= (0.0 mM Fe^{2+} released)(0.5)(1.0)= 0.0 mM P

3. $PO_4^{\equiv}$-P release from $MgNH_4PO_4$ (s)= (1.11 mM Mg^{2+} released)(1.0)= 1.11 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 1.11 mM P

$PO_4^{\equiv}$-P release due to calcium phosphate precipitates= 4.25 mM P - 1.11 mM P= 3.14 mM P

$Ca^{2+}/PO_4^{\equiv}$ molar ratio= 9.56 mM Ca^{2+}/3.14 mM P = 3.04

<u>pH Range 5.0-3.9</u>

1. $PO_4^{\equiv}$-P release from $Fe_3(PO_4)_2$ (s)= (0.94 mM Fe^{2+} released)(2/3)= 0.63 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.23 mM Fe^{3+} released)(0.5)(1.0)= 0.12 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (0.23 mM Mg^{2+} released)(1.0)= 0.23 mM P

Total P released due to Fe^{2+}, Fe^{3+} and Mg^{2+} precipitates= 0.98 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 2.26 mM P - 0.98 mM P= 1.28 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 6.16 mM Ca^{2+}/1.28 mM P = 4.81

<u>pH Range 6.9-5.0</u>

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (0.0 mM Fe^{2+} released)(2/3)= 0.0 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.0 mM Fe^{3+} released)(0.5)(1.0)= 0.0 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (1.28 mM Mg^{2+} released)(1.0)= 1.28 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 1.28 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 4.70 mM P - 1.28 mM P= 3.42 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 10.24 mM Ca^{2+}/3.42 mM P = 2.99

<u>pH Range 6.9-3.9</u>

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (0.94 mM Fe^{2+} released)(2/3)= 0.63 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.23 mM Fe^{3+} released)(0.5)(1.0)= 0.23 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (1.51 mM Mg^{2+} released)(1.0)= 1.51 mM P

Total P released due to Fe^{2+}, Fe^{3+},and Mg^{2+} precipitates= 2.37 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 6.96 mM P - 2.37 mM P= 4.59 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 16.4 mM Ca^{2+}/4.59 mM P = 3.57

pH Range 6.0-3.9

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (0.94 mM Fe^{2+} released)(2/3)= 0.63 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.23 mM Fe^{3+} released)(0.5)(1.0)= 0.12 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (1.34 mM Mg^{2+} released)(1.0)= 1.34 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 2.09 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 6.51 mM P - 2.09 mM P= 4.42 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 15.72 mM Ca^{2+}/4.42 mM P = 3.56

Post-BPR sludge

pH Range 7.0-6.0

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (0.047 mM Fe^{2+} released)(2/3)= 0.031 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.023 mM Fe^{3+} released)(0.5)(1.0)= 0.0115 mM P

3. $PO_4^{=}$-P release from MNH_4PO_4 (s)= (2.58 mM Mg^{2+} released)(1.0)= 2.58 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 2.58 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 4.94 mM P - 2.62 mM P= 2.32 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 3.89 mM Ca^{2+}/2.32 mM P = 1.68

<u>pH Range 6.0-5.3</u>

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (0.68 mM Fe^{2+} released)(2/3)= 0.45 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.34 mM Fe^{3+} released)(0.5)(1.0)= 0.17 mM P

3. $PO_4^{\equiv}$-P release from $MgNH_4PO_4$ (s)= (2.26 mM Mg^{2+} released)(1.0)= 2.26 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 2.88 mM P

$PO_4^{\equiv}$-P release due to calcium phosphate precipitates= 7.88 mM P - 2.88 mM P= 5.00 mM P

$Ca^{2+}/PO_4^{\equiv}$ molar ratio= 8.94 mM Ca^{2+}/5.00 mM P = 1.79

<u>pH Range 5.3-3.5</u>

1. $PO_4^{\equiv}$-P release from $Fe_3(PO_4)_2$ (s)= (4.30 mM Fe^{2+} released)(2/3)= 2.87 mM P

2. $PO_4^{\equiv}$-P release from $FePO_4$ (s)= (2.20 mM Fe^{3+} released)(0.5)(1.0)= 1.10 mM P

3. $PO_4^{\equiv}$-P release from $MgNH_4PO_4$ (s)= (1.36 mM Mg^{2+} released)(1.0)= 1.36 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg_{2+} precipitates= 5.33 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates=
9.85 mM P - 5.33 mM P= 4.52 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 14.70 mM Ca^{2+}/4.52 mM P = 3.25

pH Range 7.0-5.3

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (0.727 mM Fe^{2+} released)(2/3)= 0.48 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (0.363 mM Fe^{3+} released)(0.5)(1.0)= 0.181 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (4.84 mM Mg^{2+} released)(1.0)= 4.84 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates=
5.50 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates=
12.82 mM P - 5.50 mM P= 7.32 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 12.83 mM Ca^{2+}/7.32 mM P = 1.75

pH Range 7.0-3.5

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (4.76 mM Fe^{2+} released)(2/3)= 3.17 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (2.56 mM Fe^{3+} released)(0.5)(1.0)= 1.28 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (6.20 mM Mg^{2+} released)(1.0)= 6.20 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 10.65 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 22.47 mM P - 10.65 mM P= 11.82 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 27.53 mM Ca^{2+}/11.82 mM P = 2.33

pH Range 6.0-3.5

1. $PO_4^{=}$-P release from $Fe_3(PO_4)_2$ (s)= (4.71 mM Fe^{2+} released)(2/3)= 3.14 mM P

2. $PO_4^{=}$-P release from $FePO_4$ (s)= (2.54 mM Fe^{3+} released)(0.5)(1.0)= 1.27 mM P

3. $PO_4^{=}$-P release from $MgNH_4PO_4$ (s)= (3.62 mM Mg^{2+} released)(1.0)= 3.62 mM P

Total P released due to Fe^{2+}, Fe^{3+}, and Mg^{2+} precipitates= 8.03 mM P

$PO_4^{=}$-P release due to calcium phosphate precipitates= 17.53 mM P - 8.03 mM P= 9.50 mM P

$Ca^{2+}/PO_4^{=}$ molar ratio= 23.64 mM Ca^{2+}/9.50 mM P = 2.49

Table A1 Change in Soluble Ion Concentrations at Various pH Values for Anaerobically Digested Sludge

pH Range	$PO_4^{≡}$-P (mM/L)	Fe^{3+} (mM/L)	Fe^{2+} (mM/L)	Ca^{2+} (mM/L)	Mg^{2+} (mM/L)	K^{+} (mM/L)
		Post-BPR				
7.7-7.0	0.87	-0.004	0.002	0.88	0.77	0.25
7.0-6.0	4.94	0.023	0.047	3.89	2.58	0.26
6.0-5.3	7.88	0.34	0.68	8.94	2.26	0.92
5.3-3.5	9.65	2.20	4.03	14.70	1.36	1.02
7.0-5.3	12.82	0.36	0.73	12.83	4.84	0.66
7.0-3.5	22.47	2.56	4.76	27.53	6.20	0.36
6.0-3.5	17.53	2.54	4.71	23.64	3.62	0.10
		Pre-BPR				
7.9-6.9	0.18	0	0	0.39	-0.07	-
6.9-6.0	0.45	0	0	0.68	0.17	-
6.0-5.0	4.25	0	0	9.56	1.11	-
5.0-3.9	2.26	0.23	0.94	6.16	0.23	-
3.9-2.7	1.61	0.51	2.04	2.77	0.15	-
6.9-5.0	4.70	0	0	10.24	1.28	-
6.9-3.9	6.96	0.23	0.94	16.40	1.51	-
6.0-3.9	6.51	0.23	0.94	15.72	1.34	-

Table A2 Change in Soluble Ion Concentrations at Various pH Values for Waste Activated Sludge, Flotation Thickened Waste Activated Sludge, and Gravity Thickened Primary Sludge

pH	$PO_4^{\equiv}$-P (mM/L)	Fe^{3+} (mM/L)	Fe^{2+} (mM/L)	Ca^{2+} (mM/L)	Mg^{2+} (mM/L)	K^{+} (mM/L)
			Waste Activated Sludge			
7.0-4.5	1.25	0.008	0	1.98	0.78	0.47
			Flotation Thickened Waste Activated Sludge			
7.0-6.0	6.88	0.012	-0.06	4.52	6.62	2.46
6.0-4.0	15.0	0.77	0.25	12.9	12.8	5.12
			Gravity Thickened Primary Sludge			
6.9-5.9	0.42	-0.023	-0.025	1.85	0.23	-0.026
5.9-5.2	2.04	0.021	0.020	7.98	0.76	0.051
5.2-4.4	2.07	0.89	1.64	27.70	0.80	0.118
4.4-1.7	4.33	6.56	9.28	10.73	1.01	0.123

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