MANAGEMENT OF NUTRIENTS AT CENTRAL VALLEY WATER RECLAMATION FACILITY

by

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STATEMENT OF THESIS APPROVAL

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ABSTRACT

Activated sludge process (ASP) is the most common method for wastewater treatment of domestic wastewater. In ASP, a consortium of microbes is used to consume different contaminants of concern using redox chemistry in which case, microbes gain energy through substrate partitioning. The main contaminants of concern are carbon, nitrogen (N) and phosphorus (P) in municipal wastewater with the latter two collectively known as nutrients. ASP is a robust process with proven performance metrics.

Between nitrogen and phosphorus, phosphorus is the main nutrient of concern because it is often cited as a limiting nutrient for biota. Furthermore, as a useful fertilizer, phosphorus is essential for plants and as a result, there is a global demand for P. Unfortunately, P is limited in nature with only five countries in the world supplying the total P demands. Hence, the focus of wastewater treatment management is changing from the removal of P to the recovery of P.

A study was conducted at Central Valley Water Reclamation Facility (CVWRF) to evaluate the P recovery potential at different segments of the treatment train. A P mass balance was also conducted under a hypothetical scenario, where enhanced biological P removal was assumed at CVWRF.

Results show that while aluminum was the superior chemical at removing phosphorus, all chemicals were successful at a rate of over 80% P removal at the optimum pH value. Magnesium, on the other hand, was superior at nitrogen removal. The sludge and filtrate have higher dissolved P loads, making them ideal areas for phosphorus removal and recovery. The installation of a Biological Nutrient Recovery (BNR) system with Enhanced Biological Phosphorus Removal (EBPR) would also release up to 7 times the amount of phosphorus and make it available for recovery in the sludge handling phase compared to a classic ASP. Based on these results, the ideal system for recovery of phosphorus and nitrogen would be a BNR process combined with a struvite recovery system.

The overall evaluation of a combination of analyses concluded that shifting to a form of recovery that includes a combination of EBPR on the liquids stream followed by precipitation on the solids stream could recover a vast amount of the phosphorus coming into the treatment plant. This would not only make Central Valley Water Reclamation Facility more sustainable and efficient, but could imply an economic value as well, if phosphorus was sold to other industries.

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CHAPTER 1

INTRODUCTION

Activated sludge process is the most widely used method of wastewater treatment, and is possibly the most complex microbial system engineered for a specific purpose (Orhon, 2014). The basic scheme of an ASP system consists of an aeration tank followed by a settling clarifier (Figure 1.1). The aeration tank contains suspended microorganisms that reduce the organic contaminants (BOD/COD) in the wastewater. The tank is supplied with oxygen that the organisms then use to degrade the biological matter. In the settling tank, the biological floc is separated from the treated wastewater by gravity settling. The clear water left at the top of the clarifier is the treated effluent, which can continue on for further processing. According to Metcalf and Eddy, more than 99% of the suspended solids can be removed through the ASP system. The basic ASP system removes COD/BOD as well as some ammonia (Hreiz et al., 2015). The removal of these contaminants is successful in the ASP system due to the oxygenated environment.

The main problem with conventional ASP systems is the lack of phosphorus removal. This, in turn, leads to diminished potential for phosphorus recovery. With a conventional ASP system, the phosphorus goes out in the effluent or within the biomass of the sludge. The nutrients are not removed or recovered to a significant extent.

Phosphorus is an important nutrient, and 90% of the world’s phosphorus is used for food production by the agriculture industry (Brunner, 2010; Cieslik and Konieczka, 2016). The world population is rapidly increasing, most notably in developing countries, and sustaining this growing population with adequate food and water becomes a serious concern for global well-being and sustainability. Because of this strain between supply and demand, upgraded treatment systems that recover nutrients for reuse are a necessity.

Phosphorus, a nonrenewable resource, is derived from phosphate rock (Geissler et al., 2015). Unlike coal and oil, however, it can be recovered and reused. Reserves of phosphorus obtained through mining are quickly depleting, although projections on how quickly vary by source (Cieslik and Konieczka, 2016). Currently, around 70% of phosphorus used is mined in China, Morocco, and the United States, which causes an economic imbalance globally (United States Geological Survey, 2016). Substantial amounts of phosphorus are lost through disposal, much of it in the water systems, making water treatment plants a promising resource for recovery.

Phosphorus comes into the treatment plant largely from urine but also from fertilizers and household items, such as detergents. If phosphorus is left untreated, several problems occur within the treatment plant and receiving waters, with the main problems being eutrophication in receiving waters and struvite formation on plant equipment. Eutrophication occurs when phosphorous feeds algae and cyanobacteria and pushes them into a cycle of overgrowth that consumes the oxygen available for the other organisms. Struvite is a compound that results from chemical precipitation and readily forms from ions that are available in the influent (Equation 1). It has the chemical formula $NH_4MgPO_4 \cdot 6H_2O$, forms at a 1:1:1 molar ratio, and precipitates in an alkaline environment (Figure 1.2). Uncontrolled struvite precipitation in the solids processing portion of the wastewater treatment train results in crystallized build-up on equipment and decreased efficiency of the solids-handling phase equipment, notably dewatering equipment such as centrifuges and belt filter presses. When solids degrade during digestion, magnesium, ammonium, and phosphate are released. This release, along with the higher pH that is commonly found in digesters, creates an ideal atmosphere for the formation of struvite (Ohlinger et al., 1998).

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O = Mg(NH_4)PO_4 \; x \; 6H_2O \tag{1.1}$$

Chemical and biological upgrades to the conventional ASP paradigm can help manage the problems of nutrient excess. These upgrades include controlled struvite precipitation and recovery, as well as enhanced biological nutrient removal systems (EBPR). Struvite can be used as a nutrient recovery method as it includes both phosphorus and nitrogen in its chemical makeup. The Airprex system, a product of CNP, is a struvite recovery system that can be installed between the digester and dewatering area. This placement takes advantage of the nutrient release in the digester and also helps curb struvite buildup on the dewatering equipment. The process and savings can be seen in Figure 1.3.

Enhanced biological phosphorus removal (EBPR) is a method that uses phosphorus accumulating organisms (PAOs) for release and uptake of phosphorus in anaerobic and aerobic/anoxic zones, respectively (Figure 1.4). Most organisms can store about 1-2% of their dry weight as phosphorus. PAOs can store over 5% (Egle et al., 2015). In the first phase, under anaerobic conditions, stored phosphorus is released as the

PAOs consume acetic and propionic acids from the incoming biodegradable COD. Orthophosphate is released as used energy, while the VFAs are assimilated to poly-β-hydroxyalkanoate (PHA). In the second phase, under aerobic conditions, the stored PHA releases energy from oxidation and forms bonds with the orthophosphates.

Orthophosphates are incorporated back into the cell from solution and cell growth occurs (cells get bigger). The POAs now have a high capacity for orthophosphate storage, and P removal takes place within the biomass (Metcalf and Eddy, 2014). An EBPR system can be used within a total biological nutrient removal (BNR) system for phosphorus and nitrogen removal. A portion of the biomass is wasted (as some is recycled), and at this point, phosphorus is in a biologically bound form in the sludge. To release the phosphorus for removal and recovery, anaerobic conditions would be desired. At this point, sludge handling methods become important for nutrient recovery (Morse et al., 1998).

Central Valley Water Reclamation Facility (CVWRF) in Salt Lake City, Utah was used as a model plant for the following research. CVWRF has been a forerunner in Utah towards becoming an efficient and sustainable wastewater treatment plant, using a mixture of digester gas and natural gas for cogeneration. Currently, the plant is focused on improving phosphorus removal as well as secondary nitrogen removal. Another goal is to implement nutrient recovery. CVWRF is also having problems with struvite build-up on their belt presses that needs to be addressed. The plant uses the trickling filter/solids contact process and is successful at carbon and nitrogen removal, removing 96% of the BOD and ammonia in the influent. The phosphorus and ammonia removal requirements for CVWRF are 1.0 mg/L and 3.7-5.9 mg/L, respectively. Currently, the phosphorus concentration in the effluent of CVWRF is 3.0 mg/L. The objective of this research was to analyze the best method or combination of methods for nutrient removal and recovery for CVWRF.

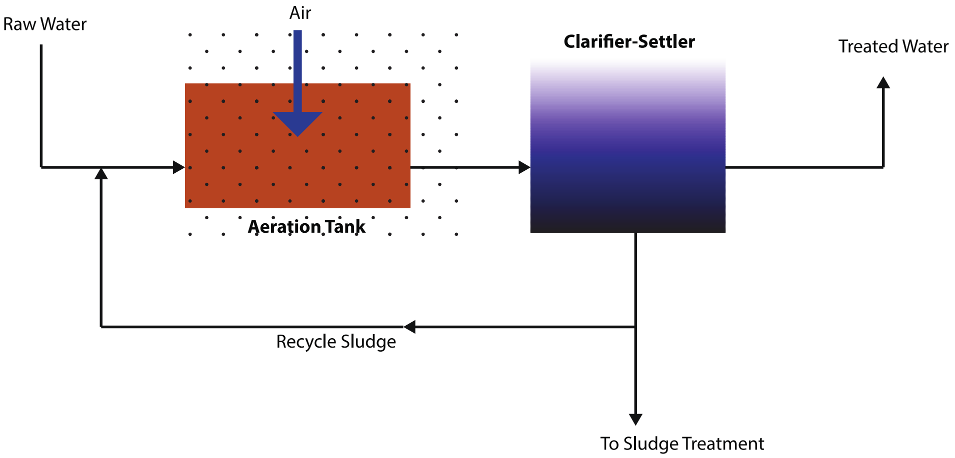


Figure 1.1 Schematic of Classic Activated Sludge Process

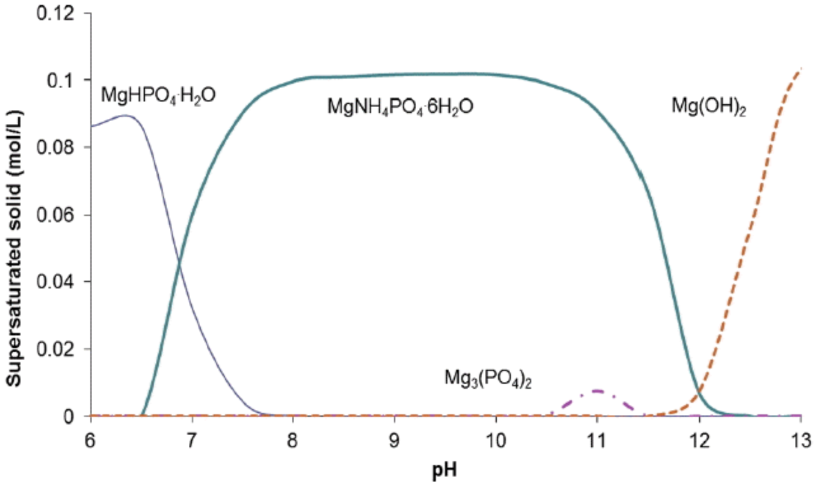


Figure 1.2 pH Range for Struvite Removal (Kim et al., 2017, reproduced with permission)

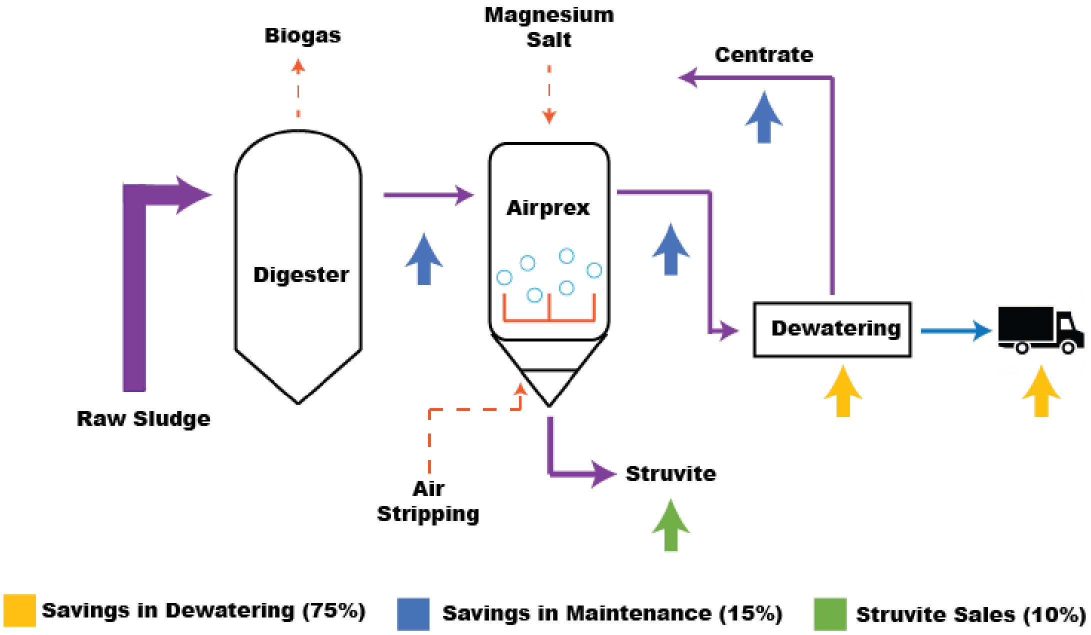


Figure 1.3 Airprex System

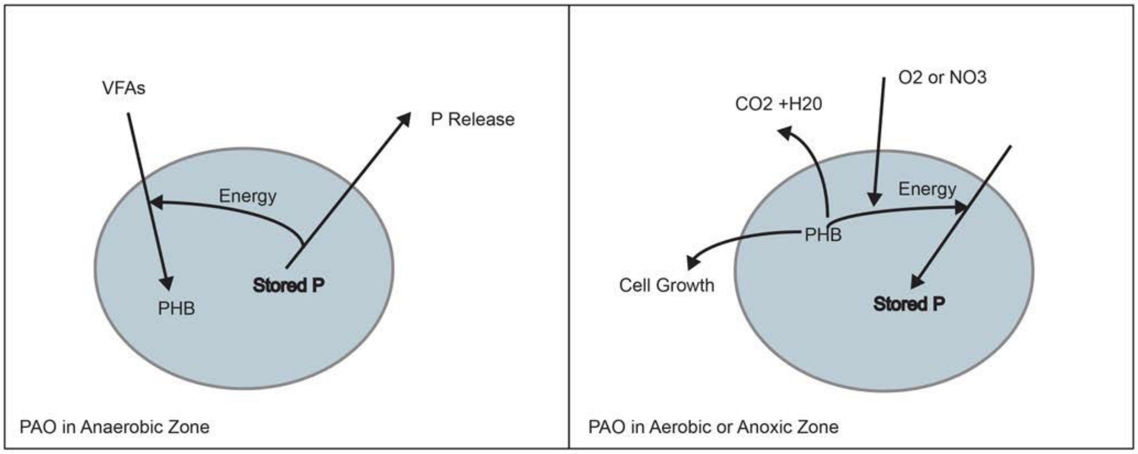


Figure 1.4 PAO Uptake and Release

CHAPTER 2

MATERIALS AND METHODS

To obtain an overall analysis of the current operational issues as well as the proposed improvements, two main experimentation methods were used. These methods also analyzed nutrient removal versus nutrient recovery. The methods included precipitation experiments and the resulting analyses, as well as a phosphorus mass balance study. The evaluation of these experiments gave an overview of how the plant would improve with the proposed additions of the Bardenpho BNR and Airprex processes.

2.1 Precipitation Experiments

The precipitation experiments were conducted to analyze the advantage of using struvite precipitation over other common precipitation compounds. There are four metal salts that are routinely used for nutrient precipitation – iron, calcium, aluminum and magnesium. Iron is commonly added before primary and secondary clarifiers, calcium is added to the dewatering filtrate, while aluminum is added as a final polishing step before the final clarifier. These chemicals are used for removal. Magnesium is the fourth common chemical used, but is unique in that it is used for both nutrient removal and recovery. When it comes to chemical precipitation, there are different precipitation parameters to take into account for optimal success. The parameters tested include pH levels, oxygen concentration, reaction time for precipitation, and molar ratio in moles of metal salt to moles of phosphorus. Aerobic environments were attained in an open air container while anaerobic environments were achieved by nitrogen purging. Optimum pH values and molar ratios can be found in literature. The results were recorded in percentage of phosphorus and ammonia removed from initial concentrations.

The samples were tested at their optimum pH value as well as at an alternative pH value for comparison (Table 2.1). The amount of metal salt added to each sample depended on the optimum molar ratio obtained from literature. The actual molar amount of metal salt added was slightly more than the optimum amount, to account for additional reactions occurring in the sample. The precipitation parameters can be found in Table 2.2, while the amounts added to the influent and filtrate are given in Table 2.3. There is much more added to the filtrate than the effluent based on phosphorus concentrations in each sample.

The precipitation experiments were conducted in two phases. In phase one, samples were collected from the mixed liquor of the digested sludge. This location was selected because the digester precedes the belt press, where the main struvite build-up is occurring. Three additional samples were added in phase 2 – influent, effluent, and filtrate. The objective was to compare the results at different points of the treatment train, investigating whether the same precipitation parameters were successful at all points. The experiments were run in 100 ml bench top tests. Each metal salt was made into a separate stock solution of the amount 1 g/L. The compound containing each salt (Table 2.2) was mixed with deionized water. To maintain an experimental amount of 100 ml, the volume of stock solution to be added must first be removed from the sample. Initial and post-experimental samples were filtered through a 0.45 uL filter and tested in triplicate for PO4-P and NH3-N using a spectrophotometer.

To elaborate on the experimental protocol, magnesium addition to filtrate will be used as an example for the procedure. The molar ratio from literature for magnesium to phosphorus is 1:1. The molar amount of magnesium added in the precipitation experiments, to account for other reactions, was 1.5:1. Filtrate had a phosphorus concentration of 36 mg/L, so the amount of magnesium stock solution added was 4.2 mL into 95.8 ml of filtrate sample to obtain 100 ml. A graph demonstrating an increased molar ratio in relation to percentage precipitated can be seen in Figure 2.1.

Additional experiments were performed on the filtrate using x-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS). XRD is an analysis method that determines the structural makeup of a crystalline compound which can include salts, minerals, metals, and semiconductors, as well as inorganic, organic, and biological compounds. The overall analysis determines what the chemical makeup of an unknown compound is based off of a known database. ICP-MS is used to detect metals and some non-metals in a liquid sample at very small amounts—as low as one part per trillion and sometimes lower.

There were eight compounds tested using XRD analysis. Four of the compounds were taken from problem areas at CVWRF and included the belt filter press (BFP) rollers, BFP feed pump, BFP pump, and BFP drain. The other four compounds came from the precipitate of the filtrate precipitation experiments, one for each metal salt. The samples were analyzed by the Energy and Geoscience Institute at the University of Utah.

The analysis required at least 3 grams of each sample. For the filtrate samples, the amount obtained was around 0.6 grams due to the laboratory scale of the experiments. Because of this, silica, also known as sand (SiO_2), was added to each precipitate compound to add weight. The sand can be seen in the analysis but isn't taken into consideration when analyzing the makeup of the samples. For ICP-MS, 5 samples each were tested from the influent and filtrate experiments. These included initial as well as post-precipitation samples with each metal salt. Each sample was evaluated for 25 different elements. The overall analyses of the precipitation experiments, XRD, and ICP-MS gives a broad picture of what is happening chemically at the beginning and at the end of the precipitation experiments.

2.2 Phosphorus Mass Balance Study

The phosphorus mass balance experiment analyzed how the installation of a BNR process would improve the current treatment paradigm at CVWRF in regards to phosphorus removal. Figure 2.2 shows the current schematic at CVWRF, while Figure 2.3 shows the proposed schematic. In this potential scheme, a BNR system is added and the trickling filters have been removed. There are several configurations of BNR processes that differ based on the desired outcome. The process that CVWRF is thinking of installing is similar to the 5-stage modified Bardenpho process (Figure 2.4).

The first anaerobic tank is where fermentation takes place. Influent is mixed with return activated sludge. Stored phosphorus is released by the PAOs. The second tank is anoxic and has a recycle line where nitrate is recycled from the aerobic tank. In this tank, nitrate is denitrified to nitrogen gas, which completes the nitrogen cycle. In the aerobic tank, BOD removal as well as nitrification (oxidizing ammonia to nitrates) takes place. Phosphorus uptake also occurs in the aerobic stage. This is the anaerobic/aerobic PAO sequence mentioned in Chapter 1. In the next anoxic tank, denitrification polishing occurs for any leftover nitrate, and then the final aerobic tank provides oxygen to the microorganisms as well as restricting phosphorus release from the PAOs. As can be seen, there are a lot of tanks in the process, so the modified Bardenpho requires an ample amount of space. The trickling filters should be taken out, which would free up some space. As previously mentioned, they interfere with the rbCOD needed in the BNR process. The multiple tanks and need for space is where much of the cost comes from for the installation of the BNR process.

Samples were collected from 13 points of the Central Valley treatment train. As samples were collected from the various points, the corresponding flows were recorded in millions of gallons per day. Each sample was filtered through a 0.45 uL filter and tested with the spectrophotometer, in triplicate, for dissolved phosphorus. The mass balance was conducted three times. Each time was during a different month to analyze differences in wastewater makeup between months and seasons. Different factors can change the wastewater make-up during different times of year, such as weather and seasonal industries.

Using bioprocess design equations with the values in Table 2.4 and Table 2.5, the phosphorus mass balance was used to evaluate how altering CVWRF treatment train away from a TF/ASP system and towards a BNR/Airprex system would enhance nutrient removal and recovery, increase the quality of the effluent, and remedy the problem of struvite buildup on the equipment. The following equations were used to determine the improvement between the current and future paradigms.

2.2.1 Amount of rbCOD Used as Energy Source by Cells

Because rbCOD isn't necessarily a known influent factor, a relative relationship between rbCOD and COD was taken from Metcalf and Eddy. This ratio is about 0.25. In the case of CVWRF with a COD value of 255.4 mg/L, the rbCOD would be 63.85 mg/L.

2.2.2 Phosphorus Removed by the BNR Process

Another ratio taken from Metcalf and Eddy is the ratio of rbCOD to P. This ratio is 8 and represents the amount of phosphorus removed by the PAOs. In the case of CVWRF, the amount that can be removed would be 63.85/8 = 8.0 mg P/L.

2.2.3 Phosphorus Removed by Heterotrophic Biomass

Phosphorus used for heterotrophic biomass synthesis = Px,bio:

$$Px, bio = A + C \tag{2.1}$$

where A equals the heterotrophic biomass (kg/day) and C equals the nitrifying bacteria biomass (kg/day). The uptake of non-PAO bacteria can be determined by multiplying the Px,bio by 0.015, which is the phosphorus content of the heterotrophic biomass.

2.2.4 Phosphorus Wasted in the Sludge

The phosphorus that goes to the digestion phase and is available for recovery:

$$Total\ P\ in\ sludge = P\ removed * Q/1000 \tag{2.2}$$

where Q is the flow (m^3/day). This is the amount in kg/day of the biomass going into the solids handling phase. For the current ASP paradigm, the phosphorus in the biomass would only be the phosphorus removed by the heterotrophic biomass or non-PAOs (section 2.2.3). For the upgraded BNR system, the amount would be the amount in heterotrophic biomass as well as the phosphorus removed by BNR (section 2.2.2).

2.2.5 Percentage of Phosphorus in the Sludge

To determine the percentage of phosphorus in the sludge, divide the total P in sludge by the solids production (Px, TSS):

$$Px, TSS = \frac{A}{0.85} + \frac{B}{0.85} + \frac{C}{0.85} + D + Q\,\frac{(TSS - VSS)}{1000} \tag{2.3}$$

where B is cell debris (kg/day), D is nonbiodegradable VSS in influent, TSS is total suspended solids (mg/L) and VSS is volatile suspended solids (mg/L).

2.2.6 Concentration of Phosphorus in the Effluent After BNR Installation

The current concentration of phosphorus in the effluent is around 3.0 mg/L. To estimate how a BNR process would decrease this concentration, there are a few simple equations that can be used. The effluent TSS for CVWRF is 5.2 mg/L. An estimate of the

VSS would be 75% of this amount, which is 3.9 mg/L. If a mid-range percentage of PAO luxury uptake is used (7%), the effluent concentration of P would be estimated at 0.27 mg/L. This is well below the requirement of 1.0 mg/L.

Table 2.1 pH Values Tested for Each Chemical

Metal	*Ideal pH Value (Literature)*	*Alternative pH Value (for comparison)*
Mg^{2+}	9.5	8.5
Ca^{2+}	9.5	7.5
Fe^{3+}	7.0	9.5
Al^{3+}	6.0	9.5

Table 2.2 Precipitation Experiment Parameters

Metal	*Molar Ratio*	*Increased Molar Ratio*	*Ideal pH*	*Compound*	*Reaction with Metal*[a]	*Ksp Value*[a]
Mg^{2+}	1:1[a]	1.5:1	9-10[a]	$MgCl_2*6H_2O$	$Mg^{2+}+NH_4+PO_4^{3-}+6H_2O =Mg(NH_4)PO_4*6H_2O$	$7.59*10^{-14}$
Ca^{2+}	2:1[b]	2.5:1	8-11[b]	$CaCl_2*2H_2O$	$5Ca^{2+}+3PO_4^{3-}+OH^- = Ca_{10}(PO_4)_6(OH)_2$	$2.34*10^{-59}$
Fe^{3+}	1.2:1[c]	2:1	7[c]	$FeCl_3$	$Fe^{3+}+PO_4^{3-} = FePO_4$	$1.60*10^{-26}$
Al^{3+}	2.3:2[a]	3:1	4-6[a]	$Al_2O_{12}S_3*18H_2O$	$Al^{3+}+PO_4^{3-} = AlPO_4$	$3.0*10^{-34}$

[a] (Gong, 2014)
[b] (Le Corre, Valsami-Jones, Hobbs, & Parsons, 2005),
[c] (Mudragada, et al., 2014)

Table 2.3 Amount of Metal Salt Added to the Effluent and Filtrate in Mg/L

Sample	*Influent*	*Influent*	*Influent*	*Influent*	*Filtrate*	*Filtrate*	*Filtrate*	*Filtrate*
Metal	Mg	Ca	Fe	Al	Mg	Ca	Fe	Al
Amount Added mg/L	3.3	9.2	10.2	7.4	43	128	143	103

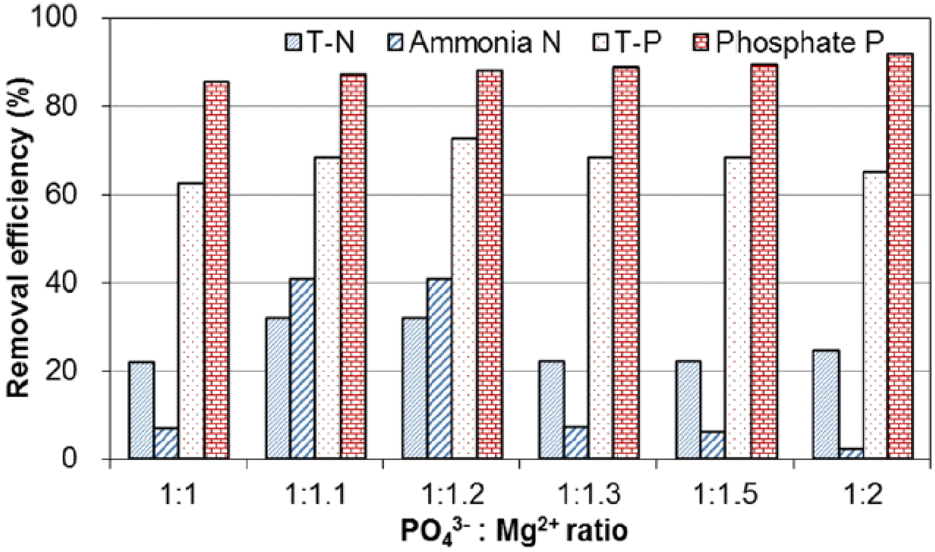


Figure 2.1 Nutrient Removal at Varying Mg Molar Ratios (Kim et al., 2017, reproduced with permission)

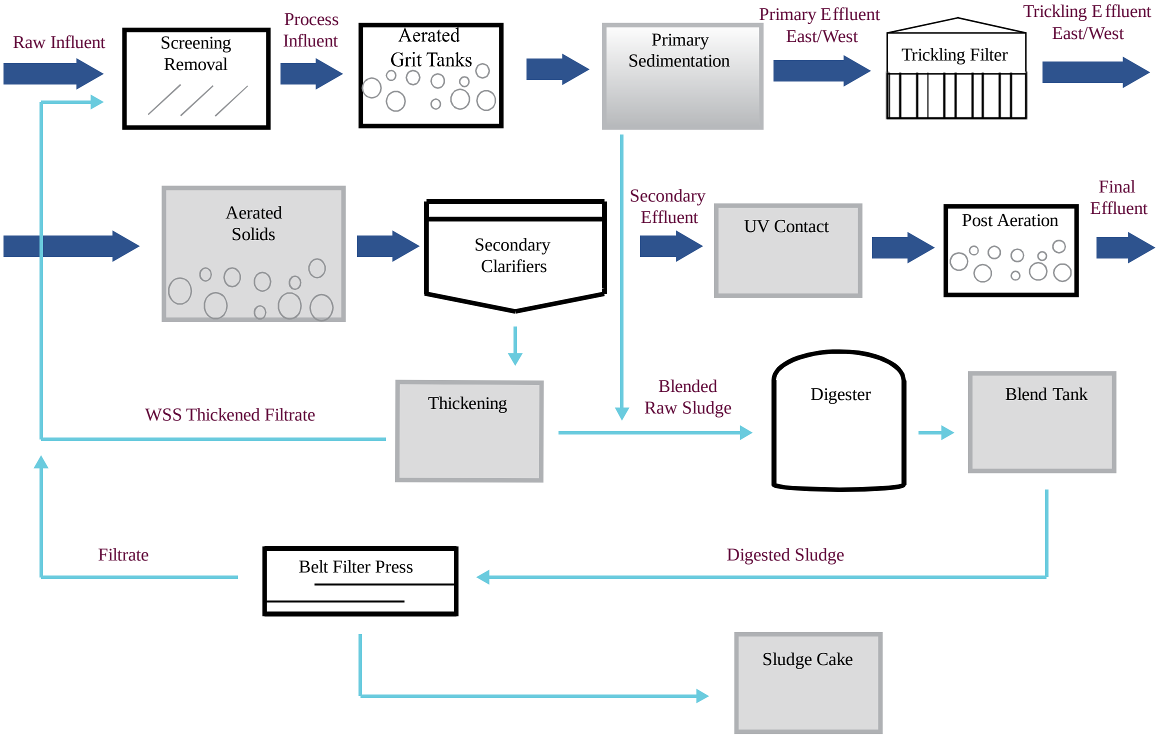


Figure 2.2 Current Schematic at Central Valley Water Reclamation Facility

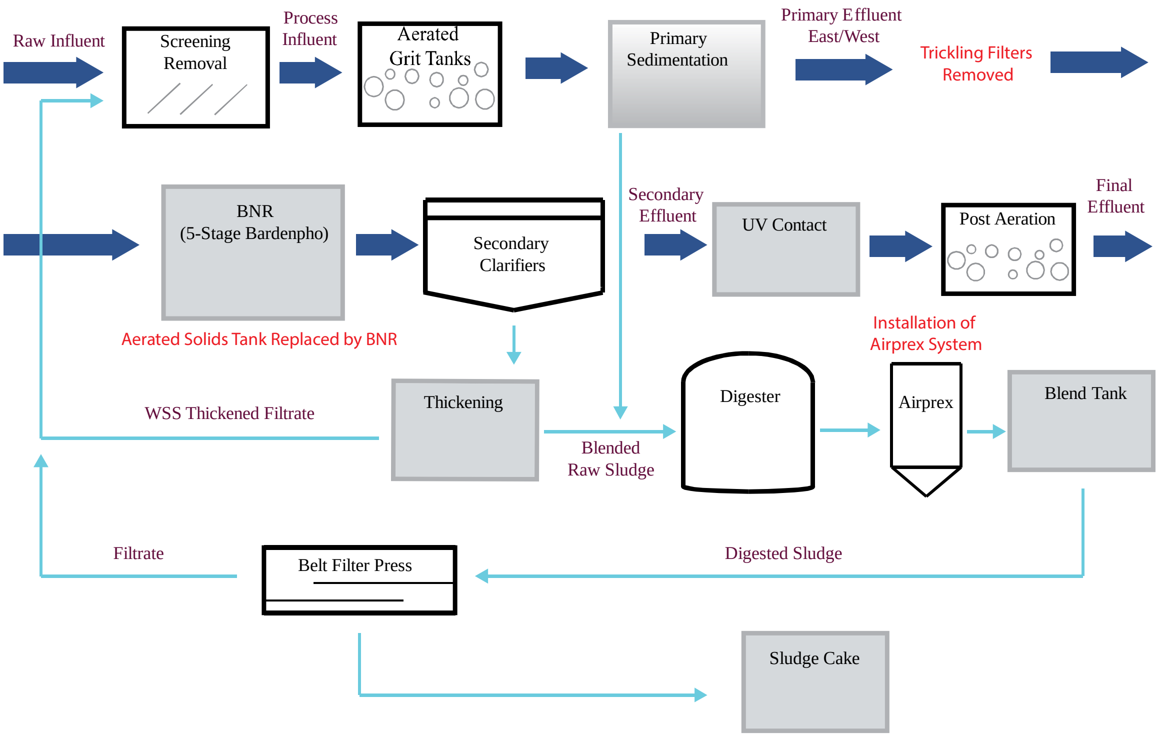


Figure 2.3 Proposed Schematic for Central Valley Water Reclamation Facility

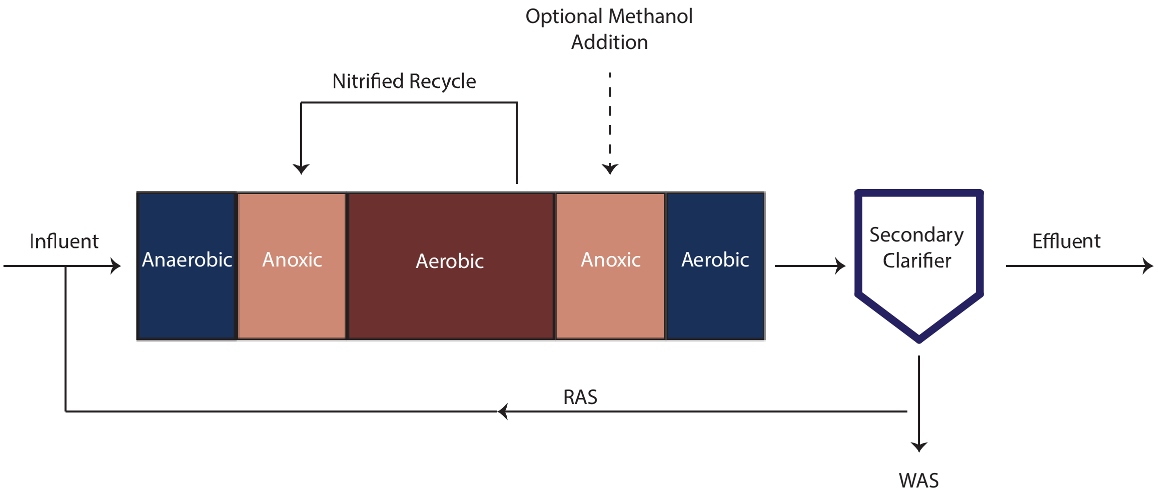


Figure 2.4 5-Stage Modified Bardenpho BNR Process

Table 2.4 Concentrations of the Constituents of CVWRF Wastewater

Parameter	*Raw Influent*	*Primary Influent*	*Final Effluent*
*BOD (mg/L)**	210	105.3	8.1
*COD (mg/L)**	455	255.4	29.2
*TSS (mg/L)***	231	55.6	5.2
*VSS (mg/L)***	205	48	_
TKN (mg/L)	-	36.8	-
*NH3 (mg/L)**	26.0	25.5	0.9
*Dissolved P (mg/L)****	3.3	3.0	2.9
*Flow (MGD)****	58.7	59.2	60
*pH**	7.5	-	7.15
*Temp (ºC)**	19/20	-	20

* CVWRF Reports for the Month of June
** 2013 Brown and Caldwell Report
*** Total P and Flow are from P Mass Balance

Table 2.5 Design Variables and Constants

Parameter	*Value*
S_0 = *Influent Substrate is cBOD (mg/L)*	105.3
Y_N *(Kg VSS/Kg NH4 + - N nitrified)**	0.12
K_d *(g VSS/g VSS*d)**	0.12
F_d *(unitless)**	0.15
K_{dn} *(g VSS/g VSS.d)**	0.08
Q = Flow (m^3*/day)*	216,904
Y = g VSS/g bCOD (g)	0.45
*SRT (days)**	5.7
*S = Effluent Substrate (mg/L)***	8.1
*NOx (mg/L)****	28.7

* Metcalf & Eddy
** Central Valley WRF Future Effluent Limitations Design Criteria
*** NOX/TKN = 0.78

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Precipitation in Mixed Liquor From Anaerobic Digester in Phase One

The experiments from phase one produced inconclusive results that were expanded upon in phase two. Figure 3.1 and Figure 3.2 show the phosphorus and nitrogen results of phase one, respectively. The results from phase one were used to reduce the number of parameters in phase two.

It can be observed that there is some ambiguity in regards to whether aerobic or anaerobic is more successful in these initial experiments. This could imply that dissolved oxygen is not as crucial of a parameter when it comes to phosphorus precipitation. Because of this, it is important to see how oxygen affects the ammonia nitrogen results to see whether it will be a determining factor in overall precipitation. Ammonia removal was most successful in an aerobic environment, as can be seen in Figure 3.2. There was a possible concern between the ammonia levels in aerobic and anaerobic environments due to ammonia stripping from N_2 purging. The Free Ammonia (NH_3^+-N) equation from Metcalf and Eddy was used to determine the NH_4/NH_3 ratios for each environment. The findings concluded that there was not a significant difference in the NH_4/NH_3 ratio between aerobic and anaerobic environments. The anaerobic environment had approximately 100 mg/L more of NH_3 after experimentation. There does appear to be significant ammonia stripping at the higher pH, however, as would be expected. Because of these findings, the anaerobic phase was eliminated and phase two was done solely in an aerobic environment to reduce the unnecessary step of nitrogen purging. This experimental plan was conducted to compare the advantage of struvite precipitation using the Airprex system, a system that uses an oxygenated environment.

$$NH_3\text{-}N = \frac{TAN\ (10^{pH})}{\left(\frac{1}{Ka}\right) + (10^{pH})} \qquad (4.1)$$

The parameter of time was also solidified in phase one. Struvite needs at least 20-40 minutes to precipitate (Crutchik and Garrido, 2016). 30 minutes falls squarely within this time frame, while 60 minutes exceeds the high end of this spectrum. Ammonia removal by magnesium was more successful at 60 minutes, suggesting this timeframe gives the chemicals ample time to form precipitates. Calcium was most successful at 30 minutes, however, Calcium has been shown to precipitate quickly and even out-compete magnesium for phosphorus precipitation (Wu et al., 2018).

In the study done by Kozik et al., a longer mean residence time resulted in larger struvite crystals. This study tested residence times up to one hour with one hour being the most successful. A factor that was not tested in the CVWRF experiments but could possibly fluctuate between experiments was temperature. When it comes to temperature, the bench top experiments were performed at room temperature in the lab. The time requirement could have fluctuated based on what day the experiments were run due to a temperature change in the lab. The labs do not stay at the exact same temperature every day. Because of this fluctuation, and to keep the time parameter constant, 60 minutes was chosen over 30 minutes as the standard time to run the phase two experiments.

The precipitation parameters that were tested more thoroughly in phase two were optimum pH value and metal salt. There was some ambiguity with both of these parameters in phase one. In regards to pH, some of the trials were more effective at a higher pH than anticipated. As mentioned previously, the ideal pH values from literature can be found in Table 2.2. Because of this ambiguity, the phase two experiments expanded the number of pH values tested from two values to four values (pH of 7.5, 8.2, 9.0, and 10.0) for each metal salt. This was to solidify the best pH value for each metal within the four sampling points.

In regards to the chemical additive, magnesium was the superior chemical for phosphorus and nitrogen overall. As can be seen in Figure 3.1, magnesium, as well as iron, recovered 90% of the phosphorus in the sludge. This recovery was under aerobic conditions at a pH value of 9.5. For nitrogen removal, magnesium, as well as calcium, had the highest removal rate at 54% (Figure 3.2). The parameters for this removal was a pH of 9.5-10, and an aerobic atmosphere.

3.2 Precipitation in Waste Samples From Four Sampling Points in Phase Two

The experiments in phase two were run solely in an aerobic environment for 60 minutes. These parameters were the most successful in phase one. The samples tested from CVWRF were influent, effluent, filtrate, and sludge. The general results of influent were very similar to effluent due to the dissolved phosphorus content being fairly steady throughout the liquid treatment process, at around 3 mg/L. In the solids handling process, the dissolved concentration of P is much higher and fluctuates significantly.

Because filtrate is produced from sludge in the sludge dewatering process of the treatment train, the results are consistent between these two samples. Calcium and magnesium were more successful at a higher pH of 9.5 while iron and aluminum were more successful at a pH of 7.0 and 6.0, respectively. This was the anticipated outcome. The experiments in phase two investigated how the four metal salts compare with one another as successful precipitants. The most successful phosphorus and nitrogen results for all samples can be seen in Table 3.1.

3.2.1. Influent and Effluent Results

The two samples from the liquids treatment process have similar results. Both samples have an initial value of 3 mg/L for dissolved phosphorus. After comparing metal salts, aluminum was the superior metal salt, removing about 100% of dissolved phosphorus in both samples. Calcium and magnesium removed at least 80% of phosphorus in the influent and at least 98% in the effluent at a pH of 9.5-10. This removal percentage dropped dramatically once the pH was lowered to 9.0 and below. Iron also removed at least 80% of dissolved phosphorus in the influent and at least 98% of dissolved phosphorus in the effluent. The difference with iron was that it was successful at all pH levels. This makes all four chemicals extremely successful in the effluent sample. An explanation for the higher success rate of precipitation in the effluent could be due to the simple fact that there aren’t many contaminants to interfere with the precipitation reactions on a concentration basis, at the final stage of treatment.

The percentage of nitrogen removed is substantially less than the percentage of phosphorus removed for all samples. However, this is misleading. When the concentration is converted to molarity, there is approximately three times the amount of ammonia being removed, on a molar basis, as compared to phosphorus. While aluminum was the most successful at phosphorus removal, it removed the least amount of nitrogen. An explanation for this can be seen when analyzing the make-up of the resulting compounds. While magnesium precipitates as struvite, which contains ammonia, aluminum does not precipitate as a compound containing nitrogen. Influent removed more nitrogen than effluent, but also had about six times the amount available, initially. Effluent is completely treated, so much less nitrogen is available due to the processes of precipitation, nitrification, and free ammonia already occurring in previous stages of the treatment train.

3.2.2. Sludge Results

The dissolved phosphorus results of the sludge experiments were slightly different than that of the influent, effluent, and filtrate samples. The similarities included optimum pH values for magnesium, iron, and aluminum at 9.5, 7.0, and 6.0, respectively. This is congruent with the other three samples. The outlier in this set of experiments was calcium. While the more successful phosphorus removal with calcium was at a higher pH for influent, effluent, and filtrate, the most successful calcium, in sludge, occurred at the lower pH value of 7.5. Because of this anomaly, several more experiments were run solely on the sludge, and the same results were obtained multiple times. The reason for this inconsistency is not known.

There are some possible explanations that come from the research done by Manas et al. (2012). In their paper, the precipitation of calcium is greatly affected by initial concentrations and the final pH after precipitation. They found that under certain molar ratios, the maximum phosphorus removed was at a pH of 8.0. The pH of the sludge was normally around 7.5-7.7, which is relatively close to pH of 8.0. The initial concentrations were most likely at a ratio that precipitates best around the lower pH.

The percentage of nitrogen removed in the sludge was higher than in the other three samples. Magnesium had the highest removal rate at 70%, while aluminum had the lowest removal rate at 46%. This implies that the digestion phase of treatment has the best concentrations of dissolved phosphorus and ammonia for controlled struvite precipitation. As mentioned previously, although there is a lower percentage of ammonia removed compared to phosphorus, when the concentrations are converted to molar ratios, more nitrogen was removed than phosphorus. This is true in the filtrate as well, and once again points towards other reactions occurring that involve nitrogen.

3.2.3. Filtrate Results

The results for filtrate are similar to the other three samples. The anomaly found in the sludge sample was not found in the filtrate sample, which points to different concentrations of calcium than that found in the sludge. Magnesium removed at least 85% of the initial phosphorus at both pH 8.5 and 9.5. This is a slightly different result from influent and effluent, where the success of phosphorus precipitation with magnesium dropped significantly at pH of 9. The difference, however, is beneficial for struvite recovery in the filtrate. The lower pH value is more economical, because it is closer to the initial pH of the water sample, which was around 7.70. By not having to increase the pH level, overall costs are reduced. Calcium had 80-90% removal at pH of 9.5, which dropped by about 20-30%, from pH of 9.5 to pH of 7.5. Iron had a high removal rate of around 90% at pH of 9.5 and 7.5. This is similar to phase one where iron was successful at both pH values. In literature, however, a lower pH is more desirable for iron. Even more successful than iron was aluminum. It was the most successful chemical and removed just under 100% of phosphorus at a lower pH of 6. Aluminum, overall, was the most successful chemical in all experiments from phase one and phase two.

Nitrogen removal was within the range of 10-40% for for filtrate. Similar to other samples, magnesium and calcium were more successful at removing nitrogen than iron and aluminum. Like the sludge sample, the filtrate sample has higher initial values of phosphorus and nitrogen for reactions to occur.

3.3 XRD and ICP-MS Results on Precipitation Experiments

The results for XRD were give in weight percent out of 100. For the samples containing the sand additive for weight, the percentage of sand is disregarded, while all other compounds in the sample are comparatively analyzed. The sand dilution factors of each compound, as well as the chemical makeup of each compound, is listed in Table 3.2.

Struvite is the main component found from the CVWRF BFP samples. This outcome was expected, due to struvite being an ongoing problem on the belt press. The interesting findings came from filtrate samples. No struvite, phosphorus, iron, or aluminum compounds were detected, though many other compounds were found. A reason for the lack of struvite results could be due to the residence time and the XRD analysis itself. According to Kozic et al. (2013), when the mean residence time of precipitation is increased, larger struvite crystals were achieved. The samples taken from the BFP were building up on the equipment for much longer than the reaction time of the filtrate experiments. The XRD test itself is also prone to errors. Substances aren't detected if the resolution is poor, the peaks are not prominent, the crystals are too small or the crystal makeup is not adequately uniform (Ham and MaHam, 2015). The combination of the time of precipitation, affinity factor, and the possibility of small crystals could be why the XRD didn't pick up any of the desired compounds.

Anhydride, dolomite, and calcite were found in all four precipitation experiments. All of these compounds contain calcium while dolomite contains calcium as well as magnesium. As can be seen in the ICP-MS results in Table 3.3 there is already substantial amounts of magnesium and calcium in the initial filtrate, which is the reason why all four precipitation chemicals in filtrate have XRD results containing calcium and magnesium.

The ICP-MS tests were performed on influent and filtrate to analyze the beginning of treatment as well as the end of the sludge handling phase. The results were obtained for initial concentrations as well as final concentrations of the four metal salts. There were four recurring elements that were found in substantial concentrations during the ICPMS analysis. These elements were calcium, magnesium, potassium, and sodium. The concentrations are listed in Table 3.3. Aluminum and iron have very low concentrations in the water samples before and after experimentation, signifying that precipitation is not occurring with these metal salts. In the experiments where additional iron and aluminum are added, precipitation is occurring, observed by the decrease in concentration after experimentation. This is most likely due to pH optimization in the iron and aluminum experiments. As mentioned previously, however, there is no aluminum or iron found in the XRD results. There is a possibility it is in the precipitate but was not detected. As mentioned in the XRD analysis, the analysis of XRD is based on the most prominent factors. The peaks with aluminum and iron may have been less pronounced.

Magnesium and Calcium did not have this detection issue. Precipitates containing magnesium and calcium can be seen in the XRD analysis. When examining the ICP-MS tests, there is also a noted decrease of concentration of calcium and some decrease of concentration of magnesium. Calcium is precipitating in all experiments, signifying precipitation is freely occurring regardless of parameter optimization. For magnesium, the final concentrations are similar to the initial concentrations in the experiments without added magnesium. This signifies that precipitation is not freely occurring. However, in the experiment where magnesium is added, the added magnesium is precipitating out of solution. This could be occurring due to optimizing the precipitation parameters for that experiment. Conversely, after completing a mass balance in molar ratios, there is still a relatively high concentration of magnesium left after precipitation occurs. Reasons for this could be due to the reaction rate of magnesium compared to other chemicals, as well as the probability that calcium is out-competing magnesium for phosphorus precipitation (Wu et al., 2018).

Magnesium and calcium have a higher affinity to precipitation compared to aluminum or iron. Calcium could also have a much faster reaction rate than the other chemicals, seen in the precipitation experiments. Calcium is still very successful at the

30-minute time parameter. By examining the XRD and ICP-MS results, it could be concluded that calcium is precipitating much more successfully than the other chemicals. This is not the case from the precipitation experiment results where aluminum and iron are more successful. This variance could be the case of difference in molar ratios, as well as the detection efficiency of the XRD/ICP-MS tests. The main finding from these tests concluded that calcium is a main precipitate in all experiments regardless of precipitation parameters or added metal salts. This would be something to take into consideration if precipitation with magnesium is desired, as is the case with struvite precipitation.

3.4 Phosphorus Mass Balance Analysis

The results of the phosphorus mass balance can be seen in Figure 3.3. The dissolved phosphorus concentration stays under 4 mg/L until the digestion phase of treatment. As mentioned previously, the conditions of digestion instigate the release of dissolved phosphorus. Because of this, the dissolved phosphorus concentration is much higher in the raw primary sludge, up to 96 mg/L. As can be seen in the figure, there is some variations between the months in the sludge handling phase of treatment. This could be due to variations in the sludge make-up from month to month. May and June are relatively similar as they are both summer months. October varies slightly as part of a different season.

When analyzing the data of the mass balance, there is an interesting occurrence happening in the blended raw sludge. The concentration is much higher than the combination of the inputs, which are the raw primary sludge and the thickened WSS. For example, in the month of June, the raw primary sludge had 57 mg/L of dissolved phosphorus, while the thickened WSS had 10 mg/L. These two samples combine into the blended raw sludge, which had 96 mg/L. The explanation for this extra 20 mg/L could be due to the hydrolysis occurring in the blended sludge tank (Cheremisinoff, 2002). This could be causing release of phosphorus in the mix tank either from PAOs already in the WSS stream (not enhanced) or from breakdown of the blended raw primary sludge solids. The phosphorus mass balance was used to assess how much phosphorus the addition of an EBPR (within a BNR) system would recover at CVWRF. For this assessment, the mass balance from June was used.

In the non-BNR system that is currently in place at CVWRF, phosphorus is taken up primarily for cell synthesis by bacterial cells with the imperial makeup of $C_5H_7O_2NP_{0.2}$. The phosphorus take-up of these cells amounts to about 0.02 g P/g VSS. The flow of phosphorus for the current scenario is outlined in Figure 3.4. When PAO’s are added, the take-up of phosphorus includes the bacterial cells synthesis plus PAO synthesis, which is about 0.30 g P/g VSS (Metcalf and Eddy, 2014). The proposed scenario for increased phosphorus recovery is outlined in Figure 3.5. The visible difference between the two scenarios can be seen in the digestion phase. In the proposed schematic, using EBPR, noticeably more dissolved phosphorus is available for recovery.

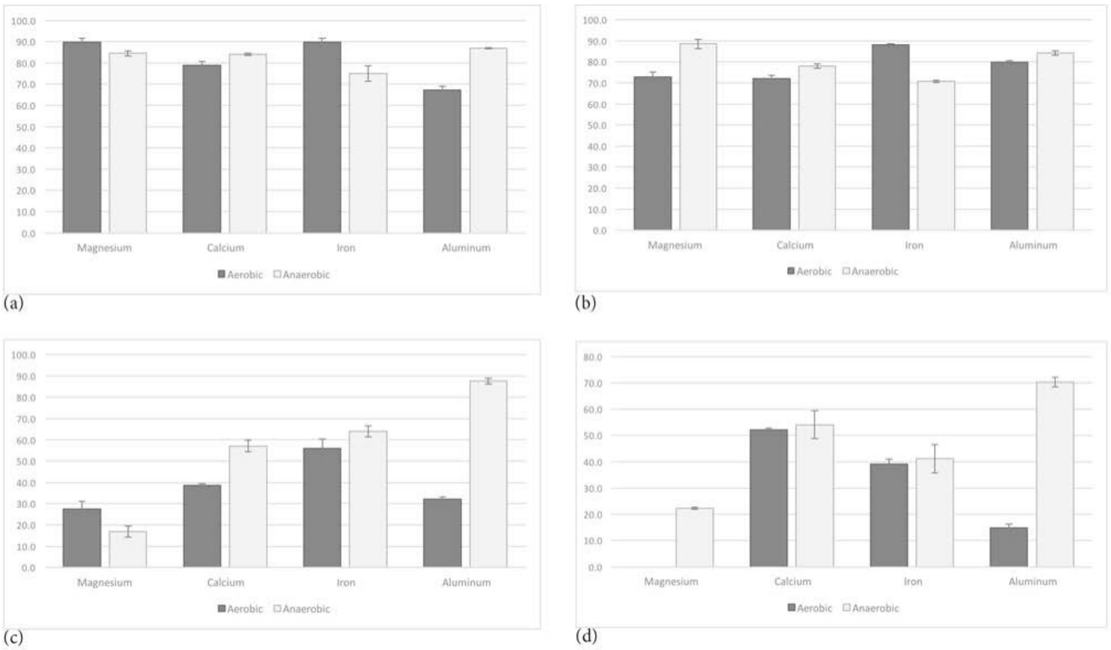

(a) (b) (c) (d)

Figure 3.1. PO4-P Removed (%) in Phase 1 Experiments Performed on the Mixed Liquor From the Digested Sludge. (a) 60 Minute Precipitation Time at pH of 9.5-10.0, (b) 30 Minute Precipitation Time at pH of 9.5-10.0, (c) 60 Minute Precipitation Time at pH of 6.0-7.5, (d) 30 Minute Precipitation Time at pH of 6.0-7.5.

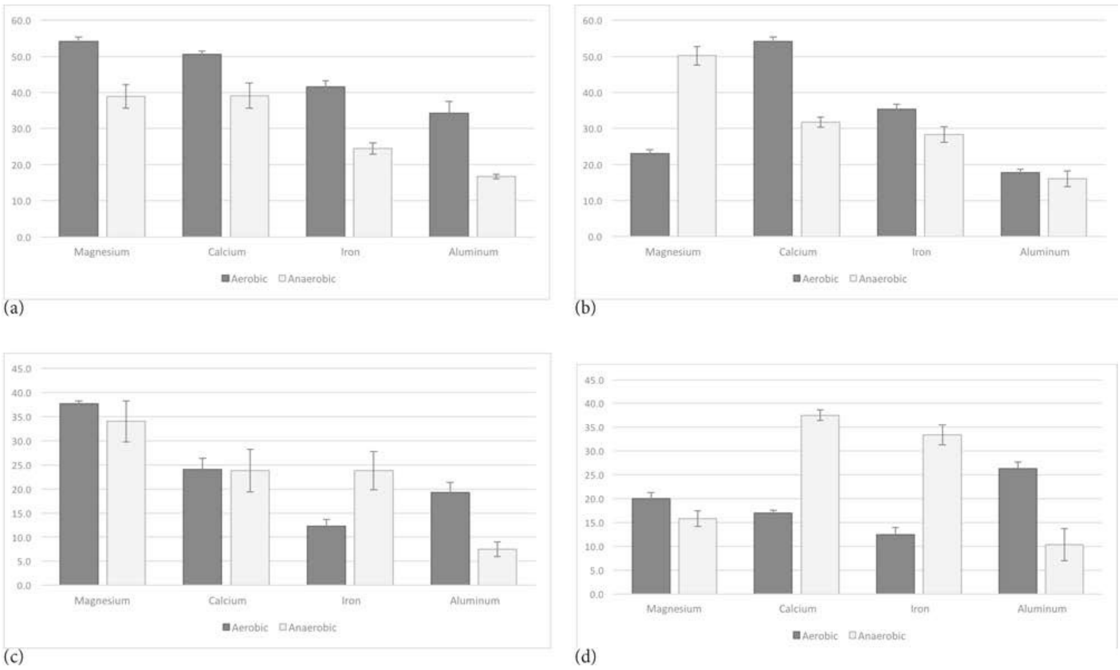
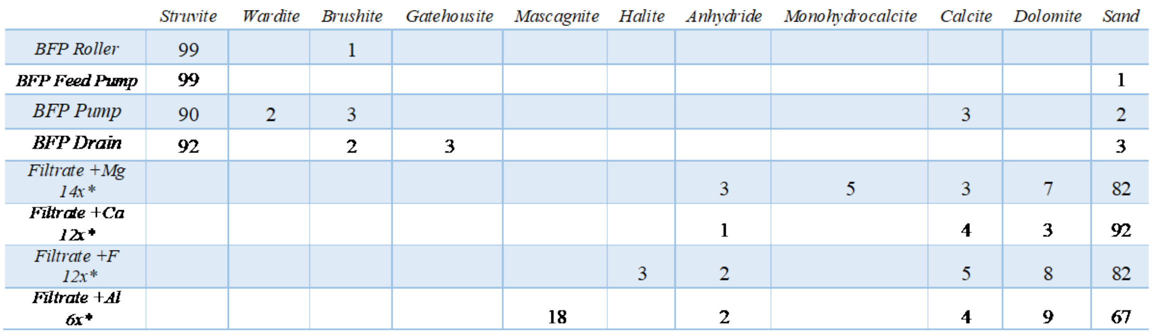


Figure 3.2. NH3-N Removed (%) in Phase 1 Experiments Performed on the Mixed Liquor From the Digested Sludge. (a) 60 Minute Precipitation Time at pH of 9.5-10.0, (b) 30 Minute Precipitation Time at pH of 9.5-10.0, (c) 60 Minute Precipitation Time at pH of 6.0-7.5, (d) 30 Minute Precipitation Time at pH of 6.0-7.5.

Table 3.1 Phosphorus and Nitrogen Results at the Optimum pH Value for Phase Two Experiments - Performed on the Influent, Effluent, Sludge, and Filtrate

	Magnesium	*Calcium*	*Iron*	*Aluminum*
Influent P	83.5±0.53	83.6±1.26	88.8±0.73	100.2±1.12
Effluent P	98.9±0.18	99.0±0.10	98.2±0.16	99.9±0.15
Sludge P	84.1±0.23	81.2±0.76	96.6±0.24	94.0±0.47
Filtrate P	89.3±0.31	84.8±0.67	96.5±0.25	100.0±0.47
Influent N	17.9±2.62	16.0±0.86	14.7±2.92	11.0±1.86
Effluent N	13.6±2.33	18.4±1.51	2.2±0.73	5.3±1.51
Sludge N	71.6±0.49	61.2±0.61	60.3±1.10	46.1±0.64
Filtrate N	40.3±1.47	34.2±1.25	28.7±0.0	15.7±1.46

Table 3.2 XRD Results by Sample and Compound
The Amount Given Represents Weight Percentage of the Sample

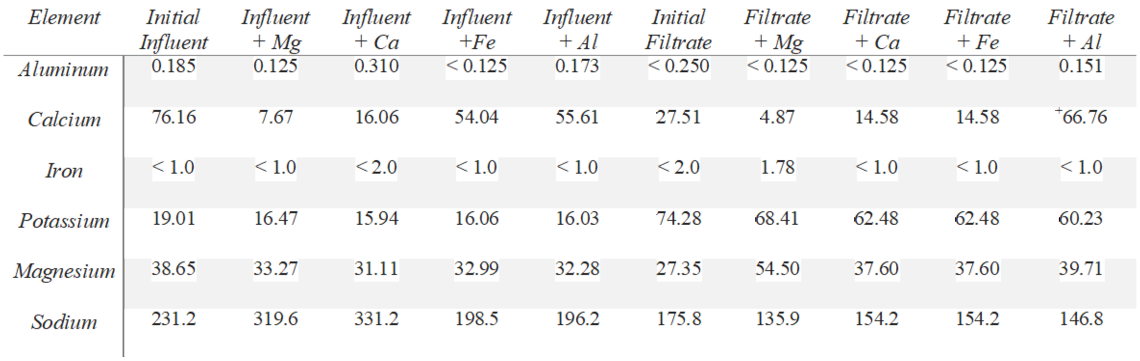


	Struvite	Wardite	Brushite	Gatehousite	Mascagnite	Halite	Anhydride	Monohydrocalcite	Calcite	Dolomite	Sand
BFP Roller	99		1								
BFP Feed Pump	**99**										**1**
BFP Pump	90	2	3						3		2
BFP Drain	**92**		**2**	**3**							**3**
Filtrate +Mg 14x*							3	5	3	7	82
Filtrate +Ca 12x*							**1**		**4**	**3**	**92**
Filtrate +F 12x*						3	2		5	8	82
Filtrate +Al 6x*					**18**		**2**		**4**	**9**	**67**

Struvite: $NH_4MgPO_4 \cdot 6H_2O$
Wardite: $NaAl_3(PO_4)_2(OH)_4 \cdot 2(H_2O)$
Brushite: $CaHPO_4 \cdot 2H_2O$
Gatehousite: $Mn_5(PO_4)_2(OH)_4$
Mascagnite: $(NH_4)_2SO_4$
Halite: $NaCl$
Anhydride: $CaSO_4$
Monohydrocalcite: $CaCO_3 \cdot H_2O$
Calcite: $CaCO_3$
Dolomite: $CaMg(CO_3)_2$

*Dilution Factor of Sand to Sample

Table 3.3 Amounts in Mg/L of Each Element in Eight Different Samples Using ICPMS



Element	*Initial Influent*	*Influent + Mg*	*Influent + Ca*	*Influent +Fe*	*Influent + Al*	*Initial Filtrate*	*Filtrate + Mg*	*Filtrate + Ca*	*Filtrate + Fe*	*Filtrate + Al*
Aluminum	0.185	0.125	0.310	< 0.125	0.173	< 0.250	< 0.125	< 0.125	< 0.125	0.151
Calcium	76.16	7.67	16.06	54.04	55.61	27.51	4.87	14.58	14.58	+66.76
Iron	< 1.0	< 1.0	< 2.0	< 1.0	< 1.0	< 2.0	1.78	< 1.0	< 1.0	< 1.0
Potassium	19.01	16.47	15.94	16.06	16.03	74.28	68.41	62.48	62.48	60.23
Magnesium	38.65	33.27	31.11	32.99	32.28	27.35	54.50	37.60	37.60	39.71
Sodium	231.2	319.6	331.2	198.5	196.2	175.8	135.9	154.2	154.2	146.8

*Other elements found in very small amounts were: silver, arsenic, boron, barium, beryllium, cadmium, cobalt, chromium, copper, mercury, manganese, molybdenum, nickel, lead, antimony, selenium, thallium, vanadium, zinc.

+This value seems to be vastly incorrect due to an error or typo. The correct value is most likely 16.76.

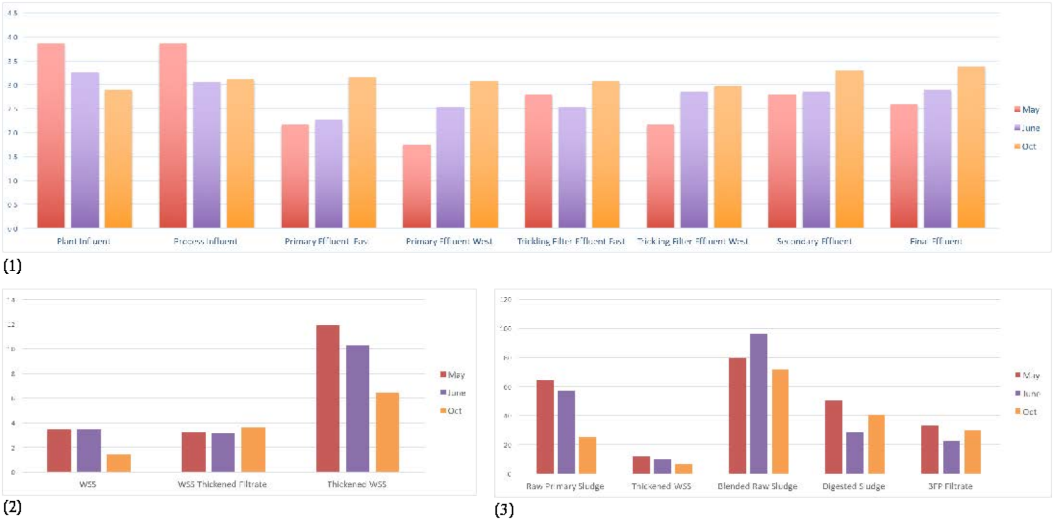


Figure 3.3 Dissolved Phosphorus Concentrations at Each of the 13 Sampling Points at Central Valley Water Reclamation Facility for May, June, and October.
(1) Liquid Stream (2), WSS, (3) Solids Processing.

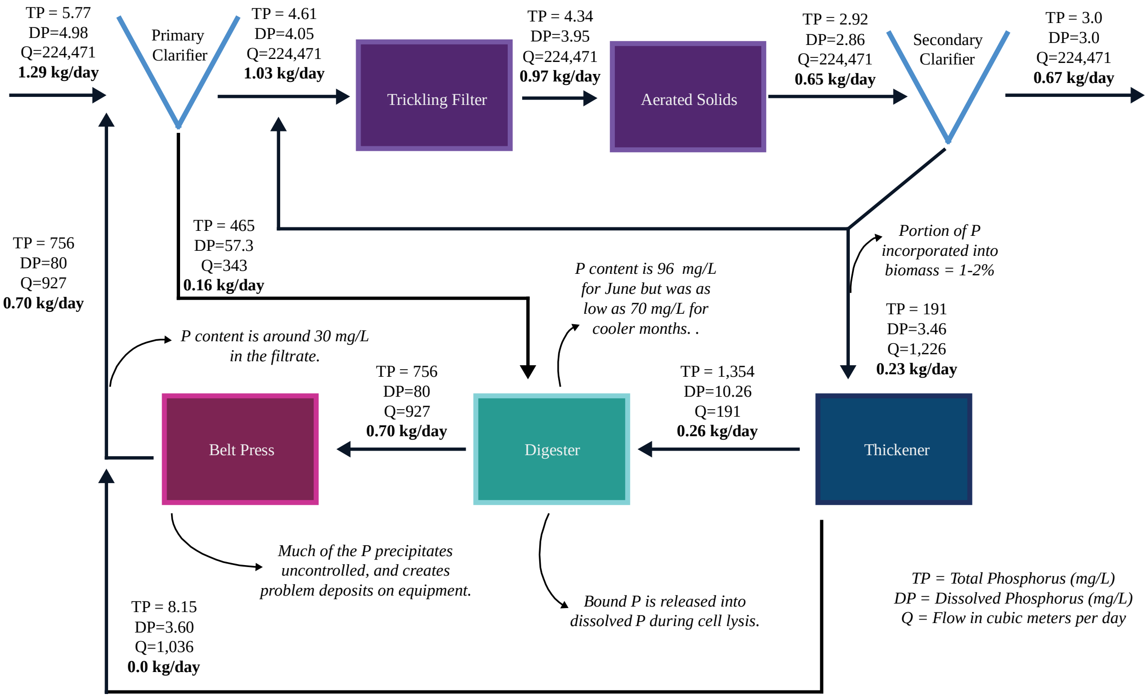


Figure 3.4 Flow of Dissolved Phosphorus in the Current Schematic of Central Valley Water Reclamation Facility

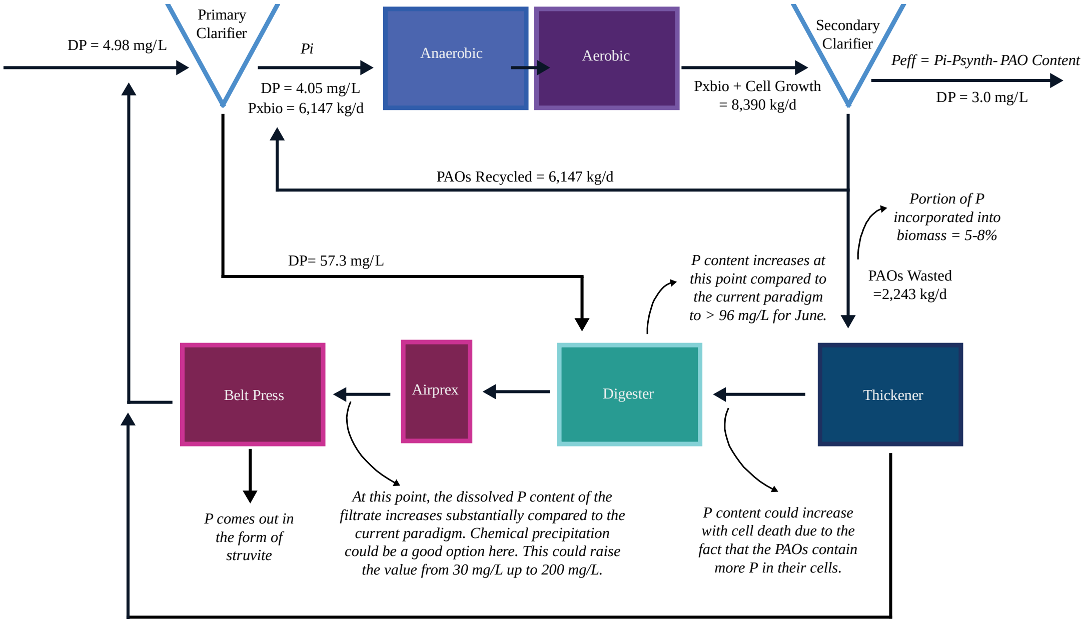


Figure 3.5 Flow of Dissolved Phosphorus in the Proposed Schematic of Central Valley Water Reclamation Facility

CHAPTER 4

CONCLUSION

In conclusion, CVWRF is efficient at BOD and ammonia removal. This leaves room for improvement in regards to phosphorus removal and phosphorus and nitrogen recovery. Installing an EBPR process coupled with an Airprex system would be advantageous in achieving these goals. The upgrades would have multiple benefits to the plant. The first benefit would be a reduction in the phosphorus concentration of the effluent, which is required by law to protect receiving waters. The second benefit would be the removal of conditions that favor struvite buildup in the solids process, which would decrease plant maintenance costs on the dewatering equipment. The installation of the Airprex system would also help decrease dewatering costs due to more P being removed. According to a study done by Mulder et al. (2017), precipitation of struvite decreased polymer usage in dewatering stage by 25% while the dry matter increased by 2%. The third benefit would be the recovery of phosphorus and nitrogen, which is environmentally conscious as well as monetarily beneficial.

The the 5-Stage Bardenpho Process and the Airprex system would require an initial installation cost as well as the only ongoing operational costs of $MgCl_2$ and increasing aeration for the BNR process. Currently, the trickling filters do not need to be aerated. Some of the costs of the new paradigm could potentially be offset by reducing the sludge handling costs, cost of the removal of struvite, repair of equipment, and economic benefits of selling the accumulated struvite. An additional study to add on to this research would be an extensive cost analysis of the current paradigm compared to the upgraded scheme. The prominent benefits of the upgraded paradigm are P reduction, a required environmental benefit, and P recovery.

It is important to look at the environmental benefits of upgrading wastewater treatment plants into reclamation and nutrient recovery facilities in regards to water and phosphorus sustainability and population. This crisis will inevitably have a domino effect on food production, water availability, and the sustainability of societies all over the world. It is crucial that wastewater treatment plants be upgraded to a more sustainable treatment train as a measure taken to offset the growing population. The benefits of transitioning to a sustainable treatment system far outweigh the negatives, the negatives being initial installation and ongoing maintenance costs. Environmental sustainability, especially in regards to the treatment of water, is not only necessary in the future, but is necessary today.

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