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Opportunities for Nutrient Recovery from Post-Digestion Sludge Handling: Analysis and Feasibility Study Using Municipal Scale Aerobic and Anaerobic Digesters

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Opportunities for Nutrient Recovery from Post-Digestion Sludge Handling: Analysis and Feasibility Study Using Municipal Scale Aerobic and Anaerobic Digesters

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering
Department of Civil and Environmental Engineering
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Opportunities for Nutrient Recovery from Post-Digestion Sludge Handling: Analysis and Feasibility Study Using Municipal Scale Aerobic and Anaerobic Digesters

David Starman

ABSTRACT

The wastewater treatment process has developed with the primary goals of protecting receiving water ecosystems and human health. Over time, there have been continuous innovations in process efficiencies, energy recovery, and nutrient removal. Wastewater offers opportunity for recovery of resources of various economic values, and recent research aims at process innovation to optimize resource recovery while still achieving the primary goals of the treatment process. The objective of this study is to assess the logistical and economic feasibility of recovery of nitrogen and phosphorus at two municipal treatment plants in the Tampa Bay area, one employing aerobic digestion and the other anaerobic digestion. The study is conducted using literature review of applicable processes, mass balance on the fate of nutrients (N and P) through the treatment plants and special attention to sludge handling.

Based on the whole-plant mass balance conducted at the facilities, it is estimated that over 80% of the nutrient influent is routed to the solids handling side of the plant, warranting special attention to this area for nutrient recovery. Sludge digested through anaerobic and anaerobic processes have distinctly different characteristics and opportunities for resource recovery are specific to each process. Mass balances for nitrogen in the anaerobic digestion process show a high concentration of dissolved ammonia. The feasibility of struvite precipitation by addition of phosphate and magnesium compounds is evaluated through batch reaction using anaerobic sludge filtrate. Aerobic sludge contains most of the nutrient resources in the solid phase, ready for recovery if handled properly. Phosphorus release is a potential concern and specific phosphorus release rates are evaluated for a municipal scale aerobic digester.

1 Introduction

The term sewer comes from the English “seaward”. Intercepting this seaward flow for public health is the original impetus behind the development of wastewater treatment. Protection of rivers, lakes and the sea from eutrophication has brought about another level of wastewater treatment regulations and technology. The early history of wastewater treatment was a development of technology to accomplish removal: removal of oxygen demand, removal of nutrients which can cause eutrophication, and removal of pathogens.

It has been recognized that resources of value exist in wastewater. The following is excerpted from a sewage treatment textbook from the 1950’s: ” It is true that there are recoverable constituents in sewage, but, like the extraction of gold from seawater, the process of recovery is more costly than the value of the recovered constituents.” (Babbitt 1953)

Recovery of resources has been steadily growing in the wastewater treatment industry. Biosolids are land applied and reclaimed water is piped throughout many municipalities. Methane recovery for energy production is a common practice at anaerobic digestion facilities throughout the developed world.

Most “recovery” efforts result from convenient byproducts of the removal process, and are not the focus of technology development. But, with rising energy costs, depletion of mineral reserves, increasing fertilizer costs, and increasing population stress on resources, is Babbitt still correct? Are focused efforts to recover resources such as energy, nitrogen, and phosphorus now becoming worth the investment? Are we on the cusp of a paradigm switch where recovery of resources from wastewater makes sense?

This thesis investigates the value of nitrogen and phosphorus as resources in wastewater and the feasibility of recovery.

2 Background

2.1 Nitrogen and Phosphorus Resources – Discussion of Value

2.1.1 Nitrogen

Nitrogen is the most abundant element in the earth’s atmosphere and is an element crucial to many biological processes. Nitrogen cycles from the atmosphere into biota, journeying through the biosphere as an essential nutrient passing between living systems and inorganic forms and eventually back to the atmosphere in its elemental form, nitrogen gas. The “nitrogen cycle” is studied in a beginning biology curriculum and is most easily understood with a graphic representation of the various forms of nitrogen and how they transfer from one form to another.

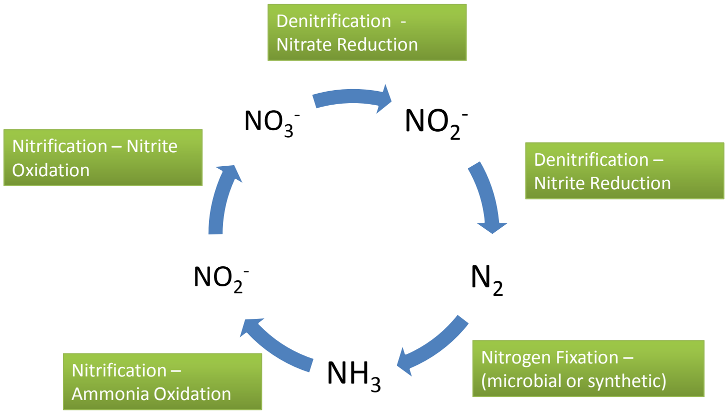

Figure 1: Nitrogen Cycle in Nature

Ammonia is the primary nitrogen compound used to make fertilizer for the world's agriculture. The world makes its ammonia and drives its agricultural economy by the energy intensive Haber - Bosch process, producing anhydrous ammonia. Under sufficient temperature, methane in natural gas will reform into hydrogen and carbon monoxide. The carbon monoxide is separated and the hydrogen reacts with atmospheric nitrogen to form ammonia. This process uses large quantities of natural gas. The natural gas is used as the fuel to create high temperature and pressure and also as the feedstock for hydrogen.

Production of nitrogen fertilizer constitutes approximately one percent of global energy expenditures (Worrell et al. 2000). The US is a net importer of ammonia, mostly from countries with abundant natural gas such as Trinidad and Canada (Worrell et al. 2000).

2.1.2 Phosphorus

Like nitrogen, phosphorus is a crucial element to biological processes. It is involved in the cellular energy currency, ATP, and is part of the polymer bonding of the backbone of DNA. However, unlike nitrogen, phosphorus is in limited supply as a resource to the biota. The only source of phosphorus is the weathering of phosphorus-containing rocks. Prior to mining of phosphate rock agriculturists made use of many strategies to conserve this resource, understanding that it was a limiting factor to agricultural productivity. Thus plants, animals and man were in competition for this limited resource and those that could locate, store and recycle phosphorus were successful (Driver et al. 1999).

Modern man has enjoyed a relative abundance of phosphorus by mining operations which accelerate the natural weathering and release of available phosphorus to the biosphere. The following is quoted from Driver et al. (1999) and summarizes the abuse of the phosphorus resource by our society.

"Only modern man, far removed from the process of primary production, has forgotten the importance of conserving and re-using this precious resource."

Mining efficiency and the resulting price of the phosphate product depends on the ease of access to the rock and the quality or percentage of phosphate available in the rock. There are limited reserves of phosphate around the world. Florida and Idaho represent the bulk of the USA's production and the US, China and Morocco represent approximately two –thirds of the world's production (Steen 1998). Currently the world extracts approximately 40 million tons of phosphate per year from 140 million tons of rock (Steen 1998). Morocco contains over 50% of the world's reserves of phosphate rock.

Projections of the extent of phosphorus reserves went from 160 years in 1996 to 90 years in 2001. US reserves are only projected at 25 years and the US will soon be a major importer rather than a major exporter. (Doyle and Parsons 2002)

Phosphate rock quality is on the decline as the highest grade resources are being depleted (Steen 1998). Phosphate quality is also adversely affected by increasing concentration of heavy metals in the rock. Interestingly, the phosphate rock is typically formed in seabeds and has a high affinity for metals and easily absorb cadmium, uranium, nickel, chromium and copper from seawater during the geological formation millennia ago (Driver et al. 1999).

Projections for worldwide phosphate resources look dismal with significant depletion of known reserves expected in the current century. Total phosphate consumption is driven by agriculture with approximately 80% of mined phosphate routed towards this use (Steen 1998). Most models show world population, agricultural production and fertilizer continuing a steep increase over the next century.

With increasing demand expected and depleting supply and quality, it is expected that phosphate costs will increase over the next century and the value of phosphate as a resource will also increase.

2.1.3 Summary of Resource Values

The objective of this study is to evaluate both the technical and financial feasibility for recovery of phosphorus and nitrogen from treatment plant operations. Based on comparison to equivalent products and market prices the value of nitrogen can be estimated at $1000 per ton of ammonia (compare to anhydrous ammonia) and the value of phosphate can be estimated at $1000 per ton of phosphate (compare to diammonium phosphate fertilizer).

Typical influent wastewater contains between 20-85 mg/L of Total Nitrogen and between 4-15 mg/L of Total Phosphorus. To gain an idea of the mass and value of nitrogen and phosphorus which pass through wastewater treatment plants on a daily basis, we can use median values of these ranges and plant flow data from the Howard F. Curren Advanced Wastewater Treatment Plant (HFCAWTP) in Tampa, FL which handles approximately 50 million gallons of wastewater per day or 189 million liters per day. There are approximately 10,868 kg of nitrogen and 1,781 kg of phosphorus passing through a plant of this size on a daily basis.

It is estimated that the world uses approximately 95 million tons of fertilizer nitrogen per year to support a population of 6 billion people, resulting in a per capita usage of 0.015 tons per person per year. If Howard Curren AWTP handles 10 tons/ day of nitrogen 365 days per year serving a population of 515,780 (according to plant operators), then we can estimate this influent at 0.007 tons of N/ person per year. Thus if all N were recovered from treatment plants (assuming all the world has treatment plants with similar characteristics to HFCAWTP) and the N were in a fertilizer form, something like 47% of the worlds fertilizer demand could be extracted from wastewater. This figure is hypothetical assuming both that all of the nitrogen could be recovered and that all of the world's population was connected to treatment plants.

2.2 Resource Partitioning in the Treatment Plant

In considering the recovery of resources from municipal-scale wastewater treatment, a preliminary step must be taken to quantify how the resources partition amongst the different treatment processes in the plant. In a simplistic model, the treatment plant can be divided into two treatment trains, solids and liquids. The two treatment trains from a typical wastewater treatment plant are shown in Figure 3.

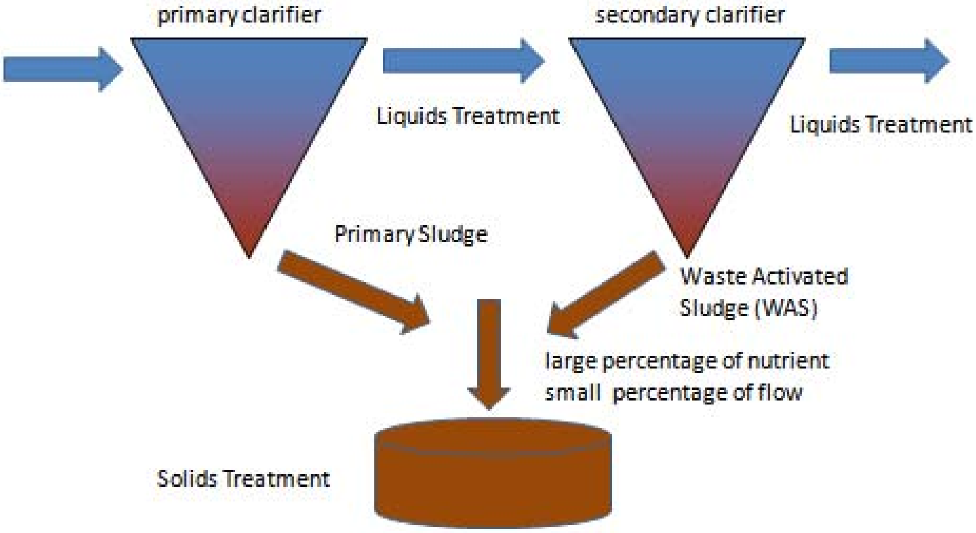

Figure 2: Concept of Liquids and Solids Treatment Trains

Typical values of municipal wastewater characterization, primary sedimentation efficiencies, and primary sludge solids content have been taken from Tchobanoglous and Burton (1991) and an estimation of the portioning of solids between the liquid and solid trains of the treatment plant can be calculated. It is assumed for this preliminary calculation that partitioning of resources will generally follow the partitioning of solids. Values used for estimation include a medium strength wastewater with 500 mg/L TDS and 220 mg/L TSS with a primary clarifier that is 60% efficient in removal of TSS and a resulting sludge with solids content of 6% by mass.

Using these parameters and balancing the mass of total solids around the primary clarifier we can show that approximately 18% of Total Solids (dissolved + suspended) is routed to the solids side of the treatment plant in 0.2% of the flow volume. The liquid side of the plant handles approximately 99.8% of the flow and 82% of the total solids.

A large portion of the solids initially diverted to the liquid side of the plant is biologically incorporated and sent to the solids side at a second clarifying step, where Waste Activated Sludge (WAS) is separated and sent to solids. Thus the percentage of total solids sent to the digester increases from 18%, with little increase in the total flow percentage.

Although the total solids (TS) sent to the solids side is less than half of the total influent TS, the high concentration of solids in relatively low flow volume warrants focusing attention to the solids side of the plant for resource recovery. While resources of particular interest resources of particular interest (nitrogen, phosphorus, carbon, energy) may not partition in exact accordance with total solids, solids partitioning analysis should give a general idea of resource partitioning and encourage further study. Further assessment of the partitioning between the solids and liquid side of typical treatment plants is discussed in more detail below.

2.3 Fate of Nutrients in Digester - Nitrogen

If we can establish that the solids side of the plant should offer the greatest opportunity for resource recovery, the fate of the resources in the solids digestion process should be understood in order to evaluate potential for resource recovery. Wastewater treatment facilities typically employ one of two solids digestion strategies, aerobic or anaerobic.

Bioenergetic half-reaction modeling is an approach which can be used to provide a stoichiometric representation of a microbial reaction. Development of these stoichiometric representations is conducted by selecting and combining half-reactions for an electron donor, electron acceptor, and cell synthesis reaction, each reduced to single electron equivalent. The half reactions are combined using an energetic partitioning coefficient which is specific to how a particular microbial reaction partitions the electrons between growth of new biomass and cellular metabolism. These energetic coefficients, f_s (synthesis) and f_e (energy) are specific to the various microbial reactions (or consortium of reactions which occur in the digestion process) and are developed empirically through monitoring of biomass growth.

Development of a stoichiometric representation of the digestion process also requires that the complicated influent streams used as carbon source and electron donors be approximated as a single compound. Influent streams into the digester systems are primary sludge, represented as $C_{10}H_{19}O_3N$ and waste activated sludge, represented as $C_5H_7O_2N$.

The following sections provide the resulting stoichiometric representations for the aerobic and anaerobic digestion of primary sludge and waste activated sludge, using half-reactions and energetic partitioning coefficients provided by Rittman and McCarty (2001).

Before discussing the results, several significant limitations to this approach should be noted.

Reduction of the complex mixture of suspended and dissolved, organic and non-organic compounds into one formula deemphasizes the complex disintegration and hydrolysis reactions necessary to make compounds biologically available for the microbially catalyzed reaction.   The estimated f_s values used to determine the partitioning cell growth versus cell maintenance energy have a significant effect on the partitioning of the resources, and these f_s values were taken from literature describing general classes of organisms. The reaction as written in equation 2-1 proceeds to completion, where all primary sludge is fully digested to cells and carbon dioxide, when in reality we expect many compounds to leave the reactor in various stages of breakdown and intermediate products.

However, understanding these limitations on this approach, it is also understood that the f_s values and characterization of primary sludge are the result of empirical studies and following through with this analysis should provide a valuable initial approximation on the partitioning of resources through the reactor.

There is an enormous difference in the typical f_s values for aerobic and anaerobic digestion processes, spanning more than an order of magnitude. High values for the aerobic process indicate a building of cell mass incorporating influent material into cell mass while low values for the anaerobic process indicate a slow growth rate and a breakdown of influent products into compounds other than incorporated cellular material.

Phosphorus is a small portion of the overall mass of primary and waste activated sludges and is not typically tracked in the half reaction methodology described above. Thus the methodology allows for an estimation of the fate of the nitrogen, but not phosphorus. The fate of phosphorus is discussed in the following section.

2.3.1 Aerobic Digestion

Using an f_s value of 0.6 and ammonia as the nitrogen source for cell synthesis, equation 2-1 is developed. The derivation of equation 2-1 is included as an example calculation in Appendix E-1.

$$C_{10}H_{19}O_3N + 0.75NH_4 + 3.75O_2 + 0.75HCO_3^- \rightarrow 1.75C_5H_7O_2N + 2CO_2 + 5.25H_2O$$

Where: $C_{10}H_{19}O_3N$: represents typical primary sludge

$C_5H_7O_2N$: represents new bacteria cell mass

Equation 2-1: Aerobic Degradation of Primary Sludge

Appendix E-2 shows calculations in determining the partitioning percentages of the resources from Equation 2-1 and results for nitrogen partitioning in the aerobic digestion of primary sludge are displayed in Figure 4.

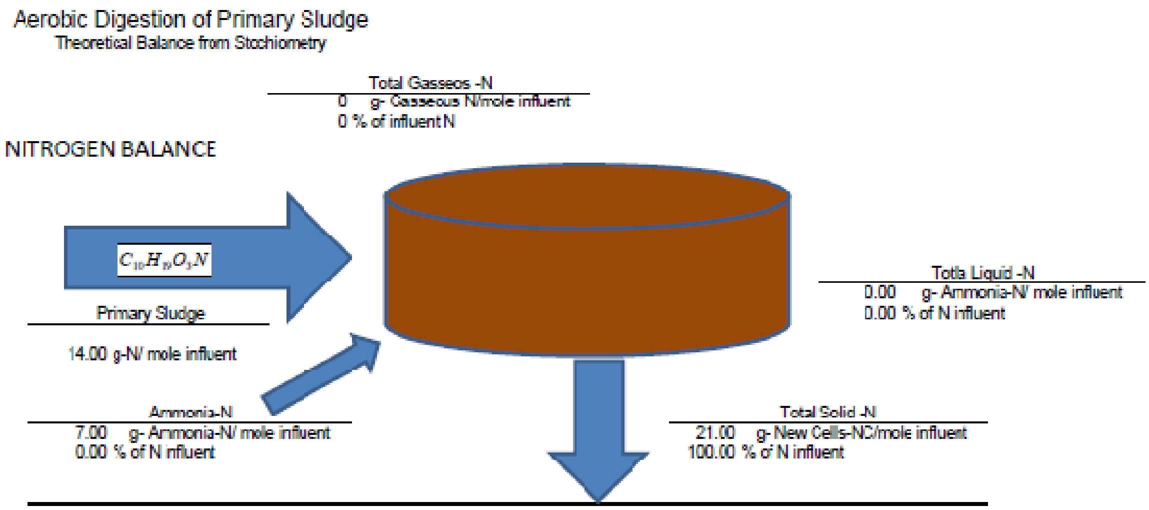

Figure 3: Theoretical Aerobic Degradation of Primary Sludge

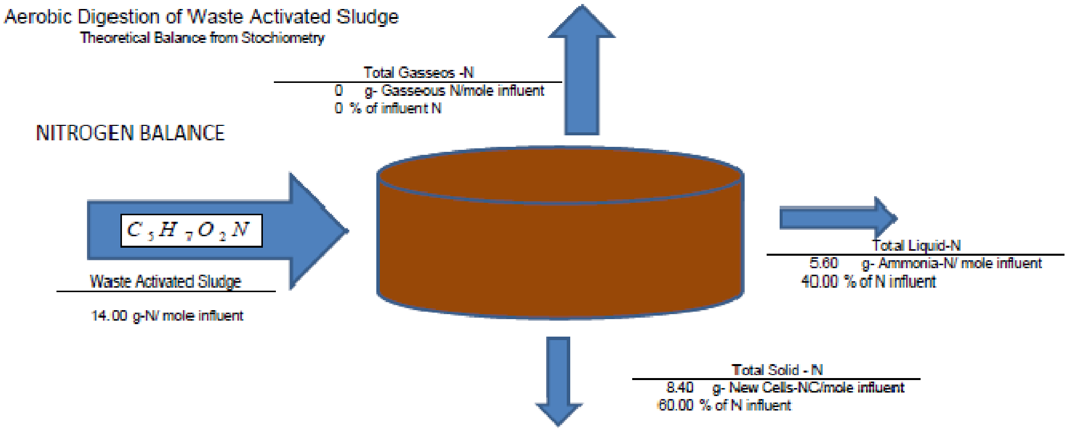

Figure 4: Theoretical Aerobic Degradation of WAS

An equation representing the aerobic digestion of Waste Activated Sludge (Equation 2-2) has been created according to similar methodology presented in Appendix E-1 from data taken from Rittman and McCarty (2001). WAS is represented by a typical formula for cells. Since the formula for cells ($C_5H_7O_2N$) would be the same on the left and right hand side of the equation, the right hand side has been modified to read “new cells”.

$$C_5H_7O_2N + 2O_2 \rightarrow 0.4H_2O + 1.6CO_2 + 0.4NH_4{}^{+} + 0.4HCO_3{}^{-} + 0.6NewCells$$

Where: $C_5H_7O_2N$: represents bacteria cell mass degraded

New Cells ($C_5H_7O_2N$): cells growing from the digestion of WAS

Equation 2-2: Aerobic Degradation of WAS

According to this analysis, aerobic digestion of WAS should release ammonia nitrogen and reduce the total cell mass to approximately 60%. Graphical representations of the distribution of the nitrogen are shown in Figure 5.

Aerobic digestion of primary sludge and WAS at the treatment plant often occur together simultaneously and in the same reactor. Therefore, the partitioning of the compounds in the total digestion process at a typical treatment plant would be expected as a weighted combination of the two analyses above, considering the relative contributions of primary sludge and WAS.

2.3.2 Anaerobic Digestion

Using the same methodology of estimation of stoichiometry for the microbial catalyzed digestion reaction and then calculating partitioning percentages, the fate of the nitrogen resource in anaerobic digestion of primary sludge and WAS has been calculated. An estimation of the anaerobic digestion of primary sludge has been estimated using half reactions provided by Rittman and McCarty, an f_s value of 0.05, ammonia as the nitrogen source for cell synthesis, and the same representation for primary sludge as used for the aerobic estimation. The sample calculation Appendix E-1 provides the basic strategy for determining the following equation:

$$C_{10}H_{19}O_3N + 4.95H_2O \rightarrow 5.91CH_4 + 2.54CO_2 + 0.14C_5H_7O_2N + 0.86NH_4^+ + 0.86HCO_3^-$$

Where: $C_{10}H_{19}O_3N$: represents typical primary sludge

$C_5H_7O_2N$: represents new bacteria cell mass

Equation 2-3: Anaerobic Degradation of Primary Sludge

Again, it should be noted that there are significant limitations to the power of prediction of the resource partitioning using this equation, even more significant than in the case of the aerobic digestion. In this case, using the carbon dioxide as the terminal electron acceptor and this general formula for primary sludge as the donor, there are many steps ignored in the breakdown of organic material to acetate, including disintegration, hydrolysis, acidogenesis, and finally acetogenesis. However, again, the f_s values and characterization of primary sludge were determined from empirical data and this methodology should provide a valuable preliminary predictive tool. Figure 6 depicts the nitrogen resource partitioning using similar methodology to Appendix E-2.

Equation 2-4 has been prepared using the methodology of the sample calculation in Appendix E-1.

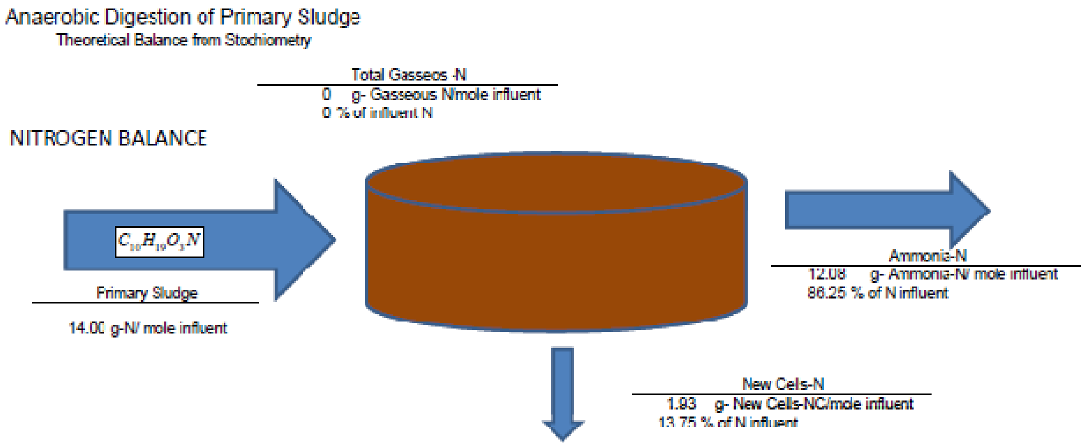

Figure 5: Theoretical Anaerobic Degradation of Primary Sludge

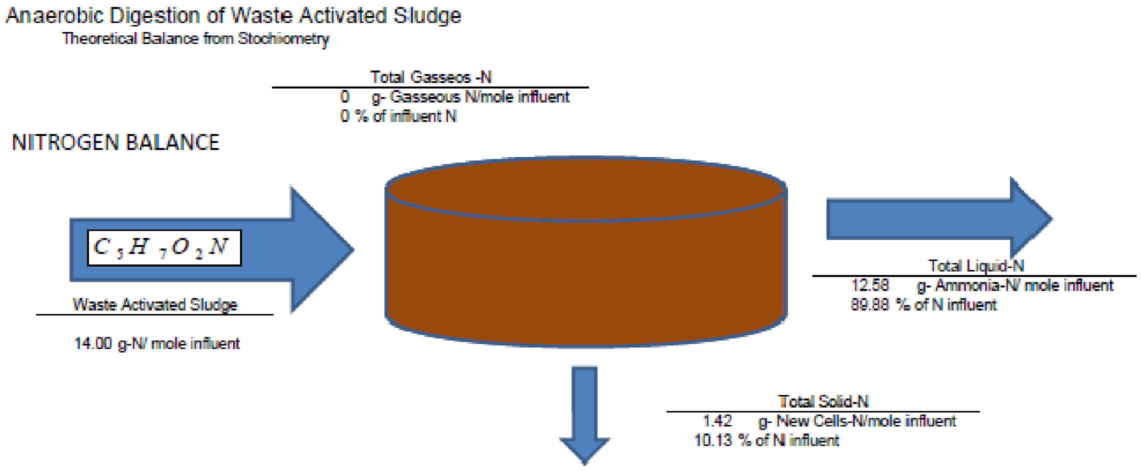

Figure 6: Theoretical Anaerobic Degradation of WAS

$$C_5H_7O_2N + 3.6H_2O \rightarrow 2.25CH_4 + 1.35H_2O + 0.1NewCells + 0.9NH_4^{\ +} + 0.9HCO_3^{\ -}$$

Where: $C_5H_7O_2N$: represents bacteria cell mass degraded

New Cells ($C_5H_7O_2N$): cells growing from the digestion of WAS

Equation 2-4: Anaerobic Degradation of WAS

Partitioning of resources based on Equation 2-4 has been calculated similarly to example Appendix E-2 and is graphically represented in Figure 7.

2.4 Fate of Nutrients in Digester – Phosphorus

Phosphorus is typically not tracked in the half reaction methodology used above to track nitrogen. However, using the same stoichiometric equations developed above, we can do some very rudimentary prediction of the fate of the phosphorus in the two digestion systems by using known content of phosphorus in typical wastewater influent and typical cellular material. Cell material typically contains 2-3% P by dry weight and this can be represented as $C_5H_7O_2NP_{0.1}$. Typical wastewater influent or primary sludge will typically contain approximately 0.5-2% P and this can be represented by adding a P term to our previous representation of primary sludge, as $C_{10}H_{19}O_3NP_{0.07}$. Then, using the molar ratios of products and reactants developed above with the bioenergetics method, we can estimate a percentage of influent phosphorus that is incorporated into cellular material. For example, equation 2-5 modifies equation to 2-3 to include phosphorus.

$$C_{10}H_{19}O_3NP_{0.07} + 4.95H_2O \rightarrow 5.91CH_4 + 2.54CO_2 + 0.14C_5H_7O_2NP_{0.1} + 0.86NH_4^{+-} + 0.86HCO_3^{-}$$

Where: $C_{10}H_{19}O_3NP_{0.07}$: represents typical primary sludge

$C_5H_7O_2NP_{0.1}$: represents new bacteria cell mass

Equation 2-5: Anaerobic Degradation of Primary Sludge

Using a similar methodology to the calculation of nitrogen partitioning in Appendix E-2, we see that there are 2.16 grams of phosphorus per mole of influent primary sludge and 0.43 grams of phosphorus incorporated into new cells per mole of influent primary sludge. This represents 20% of influent phosphorus incorporated into solids.

The significant limitation to this estimation is that non cellular phosphorus, typically present in the ortho-Phosphate forms is reactive and there is no methodology presented here which can estimate whether the remaining 80% is complexed into solids or remains as liquids.

But, continuing with this estimation procedure we find the following results. Aerobic digestion of primary sludge will result in 100% incorporation of influent P into cellular material, if all material is digested. Aerobic digestion of WAS will result in 60% incorporation of influent P into cellular material. Anaerobic digestion of primarily sludge will incorporate 20% of influent P into cellular matter and anaerobic digestion of WAS will incorporate 10%.

Again, as was evident in the nitrogen analysis, the fate of phosphorus in the digester is directly tied to the energetic partitioning coefficients for the processes. The high f_s of the aerobic process yields higher masses of cellular materials, incorporating the phosphorus into the biomass while the low f_s in the anaerobic process yields a slower microbial growth, a reducing environment, and a breakdown of influent material without significant build-up of biomass which sequester nutrient into a solid, recoverable form.

2.5 Current Nitrogen Removal Technology

2.5.1 Biological Nitrogen Removal

Biological Nitrogen Removal (BNR) is a well established technology. The process involves several steps to oxidize ammonia to nitrite then nitrate and then reduce nitrate to nitrite and then to nitrogen gas. Figure 8 illustrates the nitrogen cycle which is encouraged by the wastewater treatment plant for removal of nitrogen from the liquid train effluent.

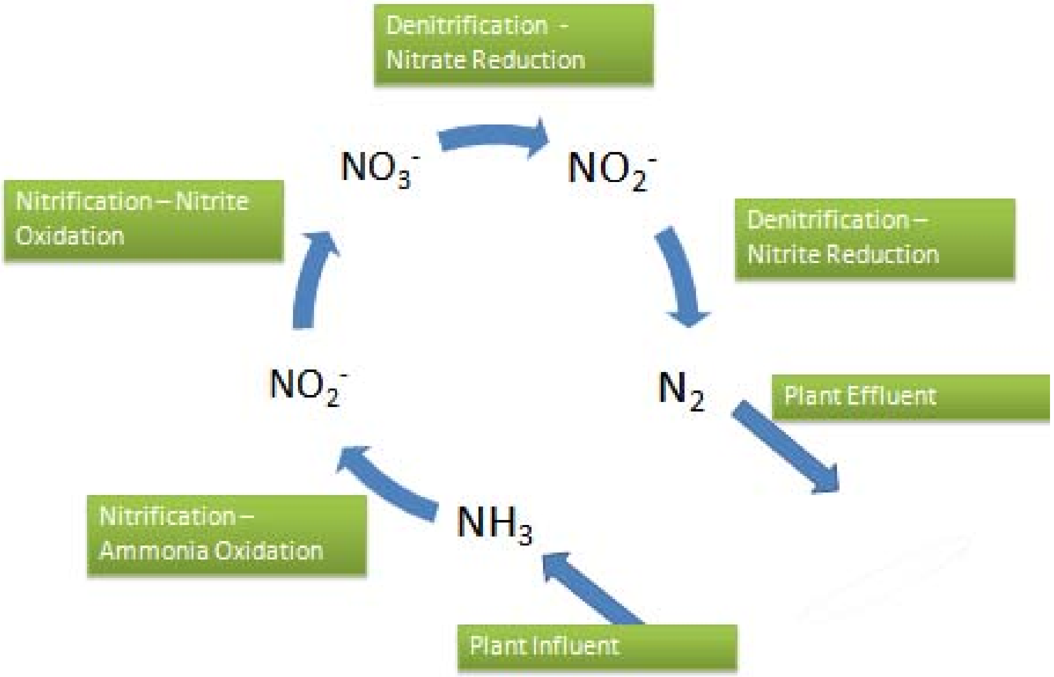

Figure 7: Nitrogen Cycle in WWTP

Ammonia-oxidizing bacteria include *Nitrosomonas* and other genera, and Nitrite oxidizing bacteria include *Nitrobacter*, *Nitrospira* and others. Nitrification requires energy input for aeration to supply oxygen to engineered systems culturing aerobic autotrophic ammonia-oxidizing bacteria and nitrite-oxidizing bacteria. Nitrifying bacteria are slow growing in comparison to heterotrophic microbes which dominate in carbonaceous BOD removal. As a result of the differences in growth rates of the two aerobic microbial systems employed in the treatment plant, the nitrification is sometimes separated from BOD removal and conducted in a separate aeration basin with longer solid retention times.

Once nitrogen compounds are dominated by nitrate an anoxic denitrification process is undertaken to reduce the nitrate to nitrogen gas. Denitrification requires a carbon source and electron donor for the anoxic heterotrophic denitrifying bacteria. Costs to provide the electron donor as methanol are typically a great expense to the plant.

The end result of the BNR process is release of the nitrogen to the atmosphere as nitrogen gas. In the context of resource recovery, this process represents a loss of the nitrogen resource.

2.5.2 BNR Nitrification/ Denitrification Efficiency Improvements

It has long been recognized in the field of wastewater treatment that the traditional BNR process includes some apparent inherent inefficiencies. Energy input is needed to nitrify and then energy input is needed to denitrify. Nitrite is an intermediate product in both processes. Biological nitrogen removal is under constant development for improvement in efficiency and reduction in operating costs. Several technologies and processes have been developed to reduce energy and material inputs of the nitrification and denitrification process. Although these improvements still result in a loss of the resource, they are developed to accomplish the removal of the nitrogen at reduced energy expenditure and operating cost. Figure 9 shows the revised nitrogen cycle, employing the advanced biological nitrogen removal technologies. Technologies such as MAUREEN, SHARON, ANNAMOX, DEMON, and STRASS create a short cut in the nitrogen cycle, allowing for significant savings in the nitrification and denitrification process.

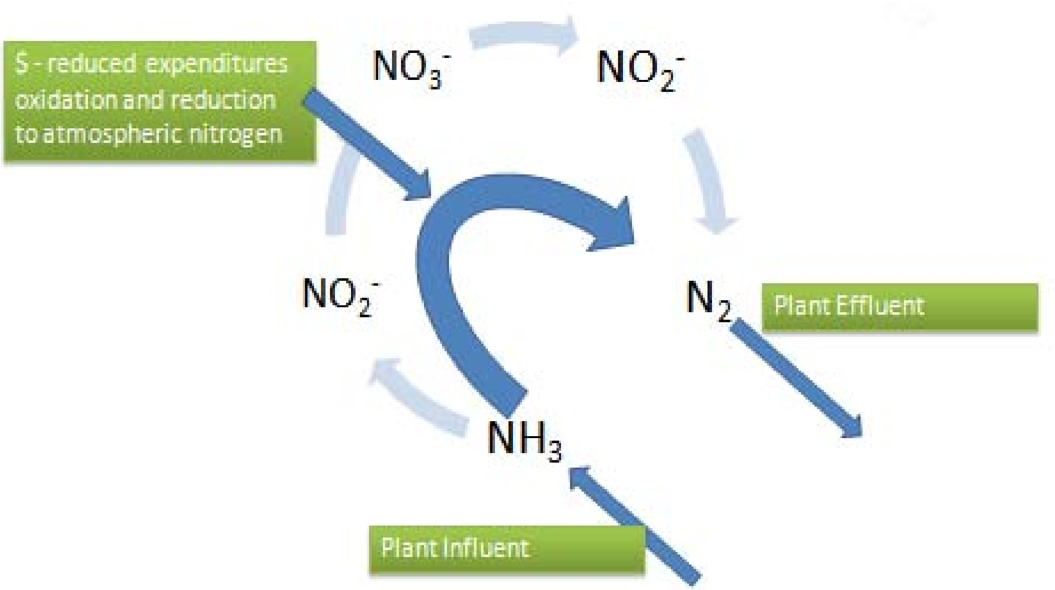

Figure 8: Nitrogen Cycle Shortcut in Enhanced BNR

2.5.3 Struvite

It is possible to precipitate ammonia nitrogen as a compound called struvite. Struvite contains equimolar concentrations of Ammonia, Phosphate and Magnesium. Removal of nitrogen by precipitation of struvite represents a recovery of the resource. Struvite is an effective non-burning slow release fertilizer.

Because in most wastewater treatment situations, ammonia is in molar excess (estimate 8:1) over phosphorus, only a small portion of the ammonia can be easily removed while high percentages of the phosphorus can be removed. Most of the available literature on struvite treats it as a phosphorus removal technology. Struvite is discussed in more detail in the next section as a phosphorus removal technology.

2.6 Current Phosphorus Removal Technology

2.6.1 Metal Salt Precipitation

Under appropriate conditions, various metal cations will precipitate phosphate from solution with iron the most common. This is a typical practice at waste water treatment plants which must meet phosphorus limit and do not employ the biological phosphorus removal scheme. Addition of iron and precipitation of ferrous phosphate is the most common metal salt precipitation for phosphorus removal.

Ferrous phosphate has applications in railway brake blocks, but its economic value is low. (Driver et al. 1999). The phosphorus industry typically regards iron in phosphate as undesirable, as most valued phosphate end products are difficult to derive from ferrous phosphate (Driver et al. 1999).

2.6.2 Biological Phosphorus Removal (BPR)

Bacteria utilize phosphate in typical cellular processes. It is estimated that typical aerobic organisms present in activated sludge contain 2-3% P on a dry weight basis (Rittmann and McCarty 2001). Bacteria in the genera of *Acinetobacter*, *Pseudomonas*, *Arthrobacter*, *Nocardia*, *Beyerinkia*, *Ozotobacte*r, *Aeromonas*, *Microlunatus*, *Rhodocyclus*, and others have been shown to uptake phosphate in concentrations which exceed a typical phosphate concentration. These organisms are known as Bio-P organisms and are utilized for biological phosphorus removal (BPR) in engineered systems.

The crucial design component to facilitate BPR is a cycling of the cells between aerobic and anaerobic conditions. The Bio-P organisms have the ability to “invest” in energy storage during the aerobic cycles and use the stored energy during anaerobic cycles to ferment volatile fatty acids and sequester electrons. The energy storage medium is intracellular polyphosphate (poly P) and phosphate is uptaken during the aerobic cycles and released during anaerobic cycles.

The Bio-P organisms outcompete organisms which do not have the ability to invest in energy in aerobic conditions to spend during the anaerobic conditions. The cycling between aerobic and anaerobic phases induces the uptake and release of phosphorus but it also serves to exert ecological pressure to select for the Bio-P organisms.

Phosphate uptake occurs in the aerobic stage when electron acceptors oxygen and nitrate are available for synthesis of adenine tri-phosphate (ATP). Polyhydroxybutyrate (PHB) stored in the cell is hydrolyzed to acetyl coenzyme A (HSCoA) and then oxidized in the TCA cycle. Released electrons from the oxidation are used for ATP synthesis and then ATP is used to synthesize poly P for energy storage. Thus for the formation of the poly P, the organism must uptake phosphorus from the environment.

In the anaerobic zone, electrons are sequestered in PHB using HSCoA which consumes energy. Energy comes from ATP through hydrolysis of stored poly P. The hydrolysis of poly-P for ATP and energy releases phosphorus.

The strategy at BPR treatment plants is to cycle solids between an anaerobic and aerobic zone allowing them to accumulate and release phosphorus from influent wastewater and then waste solids immediately following the aerobic stage when the intracellular polyphosphate and thus solid phase P is at its maximum.

2.6.3 Struvite

Unintentional precipitation of struvite in treatment plants has long been a problem where reactors, piping and equipment become fouled with the crystallized product. It is estimated, based on measured formation rates, that struvite accumulation can bring a 12 inch pipe to 50% capacity within three years.

Controlled and intentional precipitation of struvite (magnesium ammonium phosphate (MAP)) is a potential resource recovery technology, studied thoroughly on lab and pilot scales and implemented in a few cases on the scale of municipal treatment plants. Struvite requires equal molar concentrations of ammonium, phosphate and magnesium. With increased regulation on phosphorus effluent limits, there have been many studies on phosphorus removal through struvite precipitation. Typically, in anaerobic digester effluents, ammonium is in molar excess and depending on magnesium concentration, phosphorus can be removed with minimal addition of chemicals. Struvite reactors have a smaller footprint and have less operational problems than BPR reactors (Wang et al. 2005).

$$Mg^{2+} + NH_4^{\ +} + PO_4^{\ 3-} \leftrightarrow MgNH_4PO_4 \bullet 6H_2O$$

Equation 2-5: Basic Struvite Formation

The key control parameters to facilitate precipitation of struvite are solution super saturation and pH (Ali et al. 2005). Estimations for the solubility product for struvite range significantly in the literature. Values are reported ranging from 9.4 to 13.26 (Doyle and Parsons 2002). A conditional solubility product is defined for struvite precipitation and the interaction between a conditional solubility product and pH is modeled to control struvite solubility. The conditional solubility product is defined as follows:

$$\mathrm{Ps} = [\mathrm{C}_{\mathrm{t\,Mg}}][\mathrm{C}_{\mathrm{t\,PO4}}][\mathrm{C}_{\mathrm{t\,NH4}}]$$

Equation 2-6: Definition of Conditional Solubility

(Ohlinger et al. 2000)

When the solution's conditional solubility product is greater than the equilibrium conditional solubility product the solution is in supersaturation and precipitation of struvite is possible. Several investigators have developed curves for the equilibrium conditional solubility vs. pH, an example shown below in Figure 10 is adapted from Ohlinger et al. (2000), relating the negative log of the conditional solubility to pH.

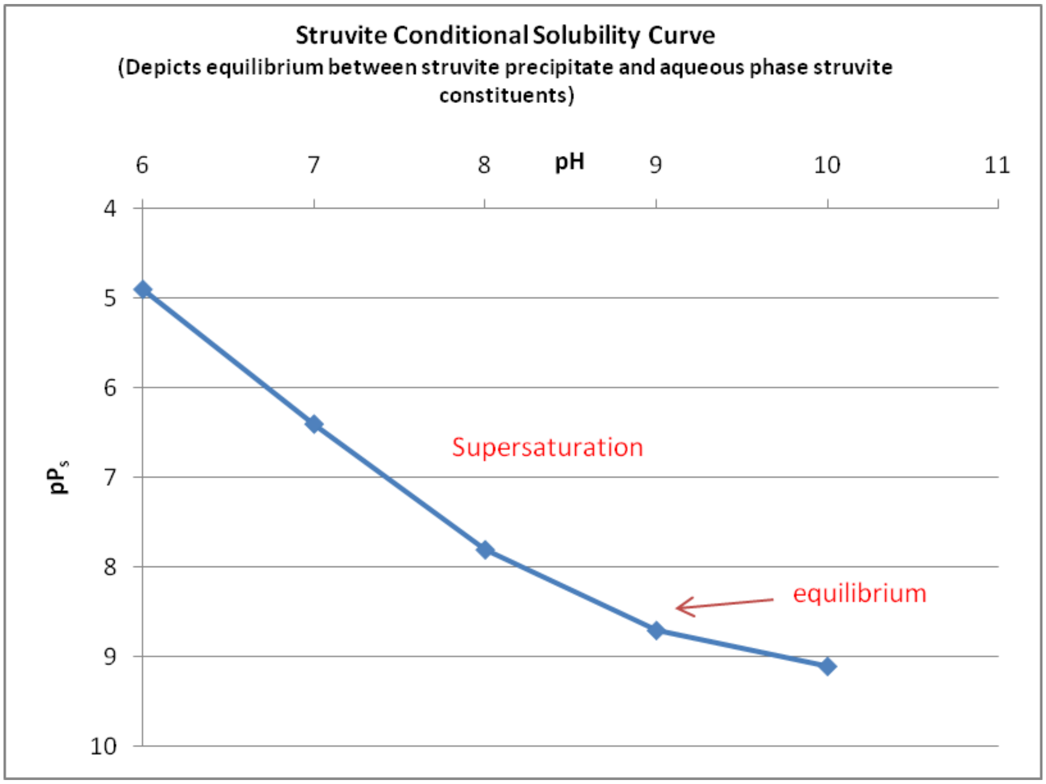

Figure 9: Struvite Conditional Solubility Curve
(adapted from Ohlinger et al. (2000))

As shown above in the solubility curve, the super saturation zone is achieved at lower reactant concentrations as pH increases. Optimum pH for minimum struvite solubility has been reported in the literature to range between 8.0 and 10.7 (Doyle and Parsons 2002). Control of pH in pilot scale and full scale reactor has been handled in two ways, via aeration for carbon dioxide stripping or via addition of an alkaline agent. Aeration and carbon dioxide stripping should be the least expensive pH control measure. Italian investigators are using aeration only with reported success (Battistoni et al. 1997). However, Japanese investigations report reduction in alkali agent requirement by stripping, but not elimination (Fujimoto et al. 1991).

As the pH approaches 11, struvite production is inhibited by two factors. Ammonia volatilization will occur at higher pH and $Mg(OH)_2$ may precipitate (Wang et al. 2005). Many investigations use MgO as the magnesium source as it also provides alkalinity and thus reduces chemical costs for pH control (Booker et al. 1999).

Solution chemistry may produce preferential precipitation of other compounds and the presence of calcium ions is the primary inhibitory ion (Wang et al. 2005). Increasing the magnesium to calcium ion ratio will result in more efficient struvite production (Battistoni et al. 1997). Studies have shown that an excess molarity of ammonia drives the reaction towards a pure struvite, while an excess molarity of magnesium yields a less pure product (Wang et al. 2005).

Fluidized bed reactors (FBR) appear to be the most established technology to facilitate precipitation in pilot scale and full scale systems. At the time of publication in 2001, a treatment plant in Japan had been operating a FBR for three years successfully producing struvite and achieving significant phosphorus removal (Ueno and Fuji 2001). The Japanese system used sodium hydroxide for pH control.

Italian investigators have developed a treatment process which accomplishes pH adjustment with carbon dioxide stripping and have implemented this on a full scale plant (Battistoni et al. 1997). Britton et al. (2005) could consistently recover

over 90% of phosphate in a pilot scale plant using anaerobic digester filtrate and sodium hydroxide for pH control.

Precipitation of phosphorus by struvite represents a recovery of the resources. One investigator estimates that with only 55% recovery of phosphate and with 50% of the world attached to sewers, 1.6% of the world's annual phosphate consumption could be supplied by recovery (Shu et al. 2005)! If 100% of the world were served by wastewater treatment plants and 100% of phosphate were recovered, phosphate mining could be reduced by 5.75% (Shu et al. 2005).

3 Study Treatment Plants: Preliminary Evaluation

In Chapter 2, the following points are discussed regarding resource recovery in wastewater treatment plants:

- Nitrogen’s value as a resource is derived from its biological significance and the energy consumption to create ammonia from atmospheric nitrogen.
- Phosphorus’s value as a resource is derived from its biological significance, its finite and limited quantity on earth, and production costs to mine it from rock.
- Based on a preliminary assessment, it appears that a significant fraction of the nitrogen and phosphorus should end up in the solids handling portion of a typical wastewater treatment plant, if nutrient partitioning follows solids partitioning.
- Based on a preliminary investigation and literature review, it appears that the fate of the resources is different within the typical aerobic and anaerobic digesters utilized at treatment plants.
- Various technologies are discussed which have potential for recovery of nitrogen and phosphorus.

In order to further evaluate the potential for resource recovery in the wastewater treatment plant, one operating municipal plant utilizing aerobic digestion and one plant utilizing anaerobic digestion have been chosen to study.

3.1 Process Descriptions

3.1.1 Howard Curren Treatment Plant

The Howard F. Curren Advanced Wastewater Treatment Plant serves the municipality of Tampa, FL as well as several surrounding suburban municipalities. Typical plant influent flow hovers around 50 million gallons per day (MGD).

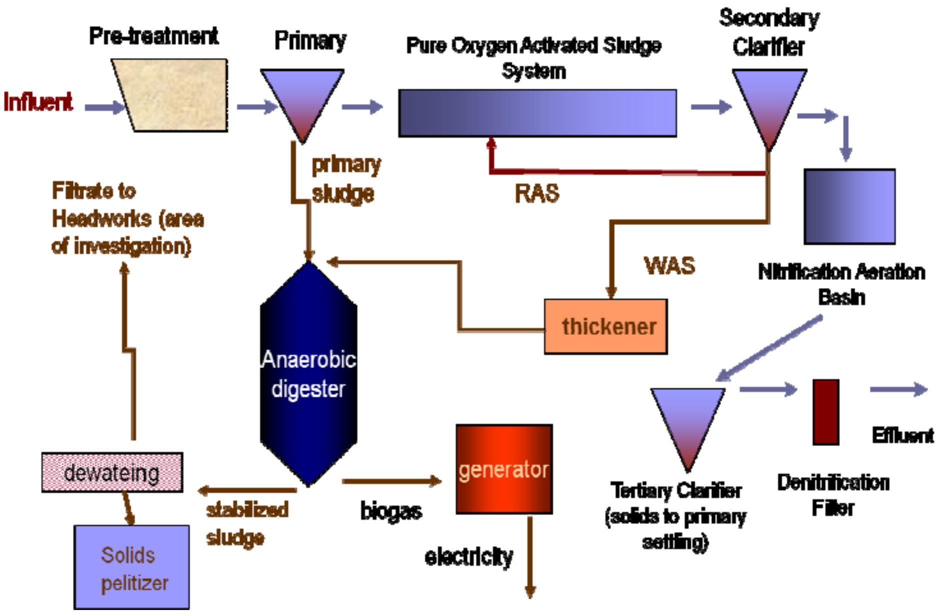

Figure 10: Howard F. Curren Advanced Wastewater Treatment Plant

Carbonaceous BOD removal of the primary effluent is accomplished with high purity oxygen supplied to activated sludge. Waste activated sludge is thickened and then sent to anaerobic digesters. Primary sludge is collected in primary settling tanks and digested along with the WAS. The facility maintains six digesters and alternates flow between them. The facility conducts nitrification using typical aeration basins and operates anaerobic denitrification filters using methanol as the carbon source and electron donor. Wasted sludge from the nitrification tanks is pumped to the primary settling tanks, and thus is indirectly diverted to the anaerobic digesters.

Biogas is collected from the anaerobic digesters and sent to a cogeneration facility. This facility burns the biogas in generators for production of electricity. Jacket cooling water is diverted to a heat exchanger where the digester sludge is heated.

Effluent sludge from the digesters is pumped to a solids handling facility. Solids are dewatered using a series of belt filter presses. Filtrate water is gravity fed to the high purity oxygenation tanks along with filter press wash water. This water then undergoes nitrification and denitrification before discharge. Currently no phosphorus discharge limit for the HFCAWTP and no removal or recovery of phosphorus is practiced other than the typical accumulation of P in biomass. Figure 11 shows a simplified schematic of HFCAWTP.

According to plant operators, the plant experiences problems with high nitrogen (ammonia) concentrations in the filtrate water returning to the head of the plant. The plant is currently investigating options to deal with the filtrate in a sidestream operation.

As part of this study, it is decided to include an investigation into the specific potential of recovering the anaerobic digester filtrate ammonia through struvite precipitation. The feasibility of recovering struvite should be compared financially to the current nitrification and denitrification process that treats the digester filtrate.

3.1.2 Largo

The Largo Advanced Wastewater Treatment Plant (LGAWTP) services the municipality of Largo, FL and handles approximately 12 million gallons per day if influent wastewater. Primary sludge is collected in primary settling tanks and sent to an Aerobic Digester.

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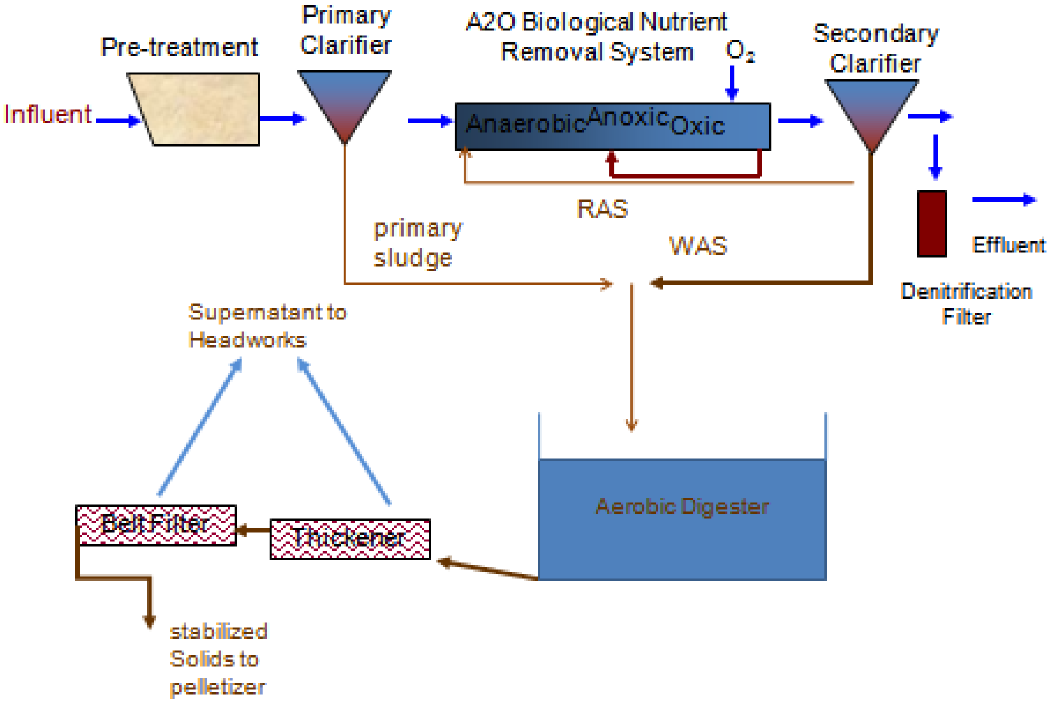


Figure 11: Largo Advanced Wastewater Treatment Plant

Primary effluent is sent into an A^2O reactor system facilitating biological nitrogen removal through nitrification and denitrification with biological phosphorus removal through PAO. Waste Activated Sludge is also sent to the aerobic digesters. Liquid effluent from the A^2O process undergoes further denitrification, final filtration and chlorination prior to discharge.

Digested sludge is gravity thickened and then sent to a solids processing facility. Filtrate from the thickener is returned to the head of the plant. Figure 12 represents a simplified schematic of the Largo Treatment Plant.

According to plant operators, there are sometimes problems with achieving the phosphorus discharge limits. One possible explanation is P-release in the thickener and high P concentrations in the filtrate overloading the A2O system. Further investigation into the possibility and rates of P-release in the thickener are incorporated into the study.

3.2 Further Plant Specific Background –LGAWTP

3.2.1 Potential for Phosphorus Release from Sludge

There are no significant gaseous forms of phosphorus to be considered under wastewater treatment conditions. Therefore, when considering the fate of phosphorus through the system boundaries of a treatment plant, all incoming P must either be discharged in the liquid state or recovered as a solid.

Wasting sludge from the aeration basin effectively removes P from the dissolved phase and out of the liquid side of the plant, hopefully to a level to achieve its primary goal of meeting the Total P effluent standard (typically 1 mg/L). Wasted sludge from BPR is typically sent to the solids handling side of the plant and at the time of wasting it contains P in a recoverable form, bound in cell mass. However, conditions in solids handling have potential to instigate release of the P.

The potential for P release is well established. It is the cycling of uptake and release of P at increasing capacity that facilitates the BPR process. Anaerobic conditions will cause a release of P. In the case of the Largo Treatment Plant WAS is sent to the aerobic digester where there is continuous aeration and should not reach anaerobic conditions until a gravity thickening stage between the digester and the solids processing facility. The rate at which this phosphorus release occurs in this thickener will determine the quantity of phosphorus release.

3.2.2 Rate of Phosphorus Release

Rates of P-release have been quantified by several studies and using several different units for quantification.

In a study on extended aeration times in the aerobic cycle of the BPR process, Brdjanovic et al. (1998) measure specific P-release rates ranging from 0.059 to 0.092 (mg-P/mg-active biomass)/hour (Brdjanovic et al. 1998). The Brdjanovic experiments were conducted in controlled sequencing batch reactors with simulated wastewater.

In another experiment conducted by Brdjanovic et al. (2000), specific P-release rates were calculated at 6 mg – P/ g VSS-hour. In this study it is interesting to note that the model correlation of P-release was one of the poorest aspects of the model.

In a study to quantify the affect of nitrate in the anaerobic zone on P-release rates and subsequent P-uptake and BPR performance, Artan et al. (1998) quantified the P-release rate ranging from 5-37 mg PO_4^{3-}/ g VSS-h.

The three studies above quantify P-release rates but each of them uses a laboratory scale reactor with a synthesized wastewater consisting of a carbon source and phosphate source. Two of the P-release rates are specific to VSS and one is specific to active biomass. All three studies quantify P-release rates in a cycling system similar to the BPR process, not after P-rich WAS has undergone an extended aeration/ digestion process. Although the rates above provide a starting point, they are derived from conditions distinctly different from those at the Largo Treatment Plant thickener and application of these rates to our system would be difficult.

Kuba et al. (1997) investigates the kinetics of the phosphorus removal process and how it is affected by shortening the cycling times. The study discusses numerous factors which affect the P uptake rate and the overall growth rate of the Poly P organisms. Although the study conducted by Kuba et al. (1997) was primarily concerned with phosphate uptake rate and capacity he does provide P-release rate data. However the P-release data is specific to acetate uptake rates and would be tough to apply to another system. Most notably, the P release rate appears to rise and fall with the P-uptake rate and total uptake capacity. We see in the experimental data considerable variation in P release rates but it appears to show a strong dependency on the uptake rate (Kuba et al. 1997).

Many studies which provide P concentration vs. time show a similar and characteristic shape to the curve, giving an indication of the P release behavior under anaerobic conditions. Figure 13 shows a typical curve adapted from previous literature (Kuba et al. 1997).

From this curve we see a rapid and nearly linear increase in phosphate concentration until it nears the maximum concentration. It is this characteristic shape that allows quantification of a P-release rate by approximating the bottom of the curve as linear. From this curve we also see that P-release occurs on the order of minutes, rather than hours once the phosphate accumulating organisms (PAO) are introduced to anaerobic conditions.

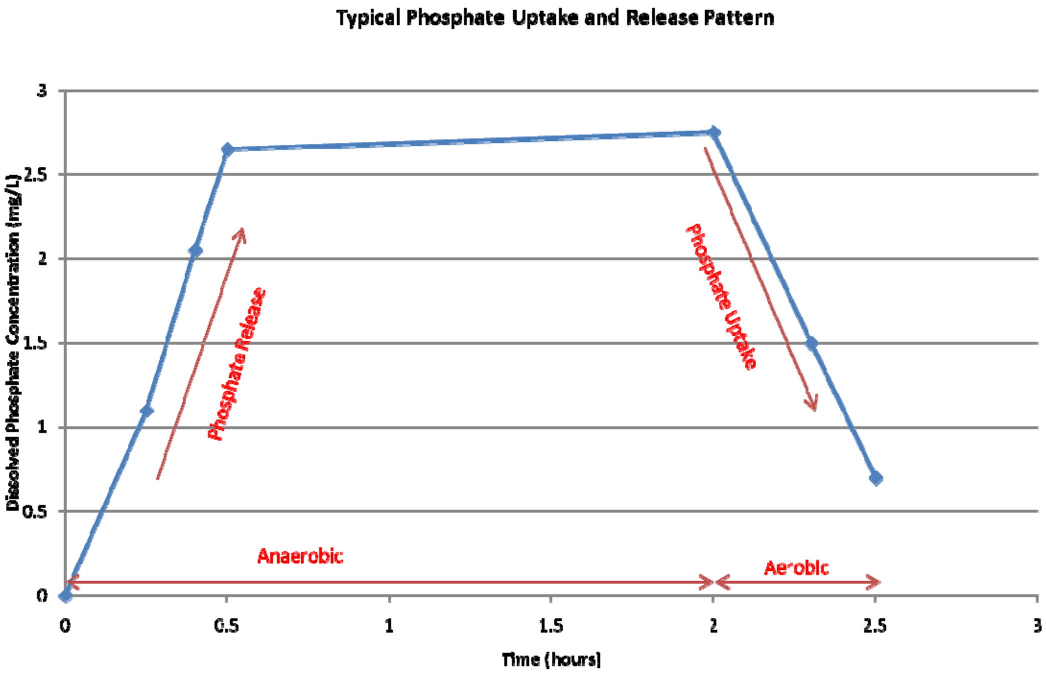


Figure 12: Phosphorus Release Curve

3.2.3   Correlation Between P-Release and P-Uptake Rates

Although Kuba et al (1997) does not discuss this explicitly, it appears from the experimental data that more effective P-uptake in the aerobic phase results in more rapid release of P in the anaerobic phase. At the Largo treatment plant, this result may prove somewhat counterproductive where effective P-uptake in the cycling A^2O system could result in rapid P-release in the digested sludge gravity thickener.

Mulkerins et al. (2003) also discuss the correlation between P-uptake and P-release rates and the strong dependence between the two, but restricts the correlation to a temperature dependence at 15-25 C. This study discusses cases where at lower temperatures, P-release rates do not correlate with uptake rates and overall BPR performance is diminished (Mulkerins et al. 2003).

3.2.4 Phosphate Release During Aerobic Digestion

As discussed, the PAO in the BPR system accumulate phosphate during aerobic cycles and release it during anaerobic. It may be assumed that if the WAS is kept aerobic, that it should hold onto the P. However, it has been noted by plant operators that over extended aeration periods, the accumulated P in the cells is released. Through experience in Johannesburg South Africa BPR plants, Pitman states that endogenous hydrolysis of P-rich WAS will release P in an aerobic digester (Pitman 1998). Pijuan et al. (2005) further characterize the P-release rate in periods of extended aeration showing P-release rates increasing significantly between day 8 and day 11.

3.2.5 Summary of Literature Review on Phosphorus Release

The following summary points are drawn from the literature review on P-release as it relates to the sludge handling at the Largo Treatment Plant:

- Phosphorus release rates are quantified in the literature, but no values were found which were directly applicable to the specific situation at Largo where aerobically digested P-rich WAS is gravity thickened.

- Phosphorus release rates appear directly correspond to phosphorus uptake rates, indicating that the more effective phosphate uptake is in the A^2O system, the more rapid the P-release should be when the sludge encounters anaerobic conditions. This correspondence may be affected by extended aeration in the digester.
- Even while maintaining aerobic conditions, P-release may be occurring in the digester.

Based on these summary points, it is decided that a study should be conducted to evaluate the specific phosphorus release rates in the Largo AWTP thickener. Concurrent to this study an evaluation of the settling rate of the sludge can be conducted. Comparison of these two studies should provide an optimum residence time in the thickener to minimize P-release and maximize thickening. Also, the mass balance of P around the digester system should reveal whether P is released from solid to liquid during the solids retention time in the digester.

3.3 Further Plant Specific Background – HFCAWTP

3.3.1 Struvite Potential for Ammonia Recovery

According to Howard F. Curren AWPT plant operators, digester filtrate contains a high concentration of ammonia nitrogen and is periodically causing problems with nitrogen loading when pumped to the head of the plant. Attempts at ammonia recovery in wastewater treatment through struvite precipitation are scarce, because ammonia is typically in molar excess with respect to the phosphate and magnesium and significant chemical additions are required. But, when examining the nitrogen cycle which occurs in the treatment plant and combined with the synthetic fixation of ammonia by the Haber Bosch process, it is apparent that society is paying to circumnavigate the nitrogen cycle, as outlined in Figure 13.

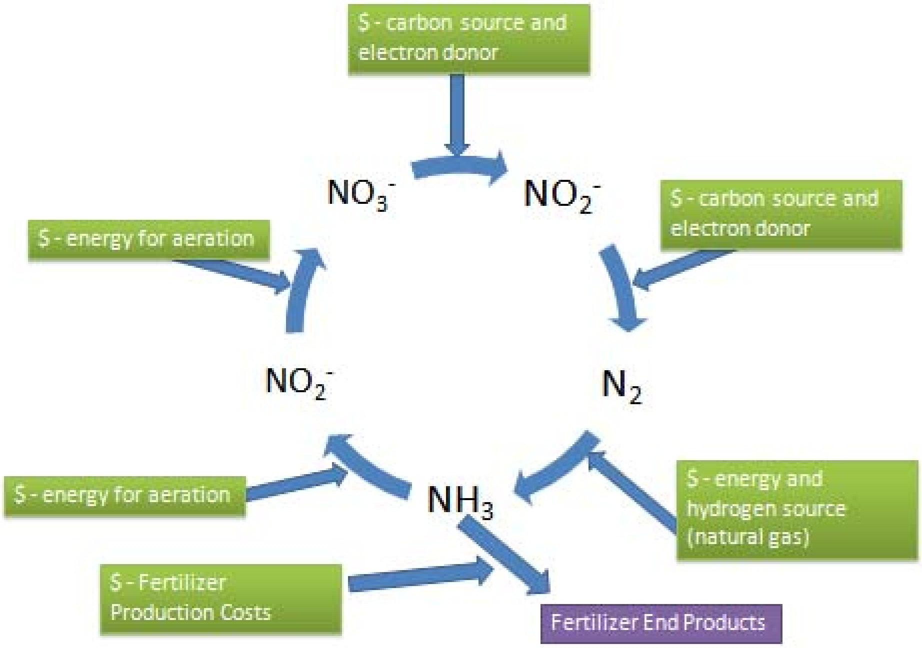


Figure 13: Circumnavigate the Nitrogen Cycle

Struvite precipitation has the potential to cut out the loop in this process recover the valued nitrogen resource.

Celen and Turker (2001) evaluate the potential for full nitrogen removal from digester effluents. Their study uses batch reactors and quantifies costs for chemical additions to achieve full nitrogen removal and show effective ammonia reduction, but the ammonia source is laboratory chemicals simulating effluent concentration.

There is no literature found which provides pilot scale or full scale operational data which would be applicable to the Howard Curren Plant. There is no study which attempts a full ammonia recovery from a high ammonia concentration waste stream from anaerobic digestion supernatant by addition of phosphate, magnesium and pH control. Phosphate is a limited and expensive chemical and its discharge is regulated. Addition of phosphate into the wastewater stream is at high quantities is not desirable.

3.3.2 Estimates of Struvite Recovery Costs

Estimates are given in previous literature for the material and operating costs to remove struvite. A lower range is \$8.50 per kilogram of NH_4-N (Celen and Turker 2001). A higher range is estimated at \$9.72 per kilogram of NH_4-N (Siegrist 1996). Doyle and Parsons (2002) provide a review of struvite literature and tabulate various reported costs to produce and sell struvite. Production costs ranged from \$140 - \$460 per ton. These costs do not include attempting to remove nitrogen, but were developed in systems where ammonia was left in excess of phosphate concentration and removal of phosphate was the objective. Struvite resale costs varied even more significantly than the production costs, ranging from $198-$1885 per ton.

Siegrist evaluated struvite precipitation costs versus other nitrogen removal costs in 1996 and concluded that struvite precipitation was more expensive than nitrification/ denitrification by a factor of 4 (Siegrist 1996). However, the Siegrist evaluation did not include resale potential for the recovered struvite.

3.3.3 Summary of Struvite Potential Literature Review

From the literature review on struvite and its potential for a sidestream treatment technology for nitrogen and phosphorus recovery from anaerobic digester filtrate, the following summary points are provided:

- Recovery of nitrogen and phosphorus should be possible by creating appropriate conditions and providing appropriate concentrations of constituents. There is ample data in the literature which provide ranges of operating conditions plus discussion of inhibitory constituents.
- The variability of wastewater conditions coupled with variability in literature values for optimum pH and solubility product for struvite precipitation suggests that bench and pilot testing is required prior to any system implementation.

- If ammonia recovery is attempted, reported problems associated with the Ca : Mg ratio should be easily avoided as large quantities of magnesium would be added.
- It does not appear that many investigators or treatment plants are pursuing ammonia recovery through struvite, likely due to fear of adding a phosphate compound to the wastewater stream which must later be removed.

Evaluations of financial aspects to struvite recovery in the literature vary widely. From the literature, it appears that using phosphoric acid as the phosphate source, magnesium oxide as the magnesium source, and aeration for carbon dioxide stripping and a fluidized bed reactor would be the most cost effective system for struvite recovery.

Based on the summary points above it was decided to conduct a study of struvite precipitation using digester effluent filtrate. Bench scale batch tests of precipitation potential, required chemical additions, and recovery potential of nitrogen and phosphorus were conducted. From this initial investigation, further assessment of financial considerations can be made to evaluate the overall feasibility of struvite as a sidestream filtrate treatment technology for the Howard Curren treatment plant.

4 Rationale and Outline of Assessment and Experimental Plan

Chapters 2 and 3 represent a background discussion to serve as a starting point for further analysis of resource recovery potential at the Howard Curren and Largo Treatment Plants. The following basic points were established:

- There are resources of value in wastewater
- The value of the resources in wastewater will likely increase relative to operating costs, and if this occurs, financial benefits of resource recovery may become increasingly attractive.
- An initial attempt is made to understand the partitioning of the resources through the wastewater treatment plant and from this understanding it is suggested that the solids side of the plant will be the most effective area to focus resource recovery efforts.
- We attempt to understand the partitioning of resources through the two common digestion processes, aerobic and anaerobic digestion.
- We discuss some of the ways that the resources are treated, recovered or removed in various technologies associated with the solids side of the treatment plant.

- Two operational treatment plants are chosen to evaluate the potential for resource recovery in aerobic and anaerobic digestion systems and specific target areas of investigation are identified at each of the two study plants.
- At the anaerobic digestion system of the Howard Curren Treatment Plant, investigation into the feasibility of struvite precipitation is suggested as a means for ammonia removal and recovery from filtrate.
- For the aerobic digestion system at the Largo Treatment Plant, a study of specific phosphorus release kinetics is suggested in order to better design retention time in the gravity thickener to maximize sludge settling and minimize phosphorus release to the supernatant.

The following sections outline the rational and investigative plan to further evaluate the points above.

4.1 Evaluation of Resource Content in Solids vs. Liquids

The objective of this study is to provide an estimate of the partitioning of nitrogen and phosphorus into the solids and liquid side of the treatment plant. Samples from the primary effluent, primary sludge, and waste activated sludge of each plant were collected in order to quantify the total nitrogen and phosphorus in the dissolved and suspended phases. From this data, an estimation of the partitioning between the solids train and liquid train can be estimated. Analysis of partitioning was conducted on a mass per time basis. Thus, the following equations are used for each of the resources.

$$\dot{m}_{\text{solids}} = \dot{m}_{PS} + \dot{m}_{WAS}$$
$$\dot{m}_{\text{liquids}} = \dot{m}_{PE} - \dot{m}_{WAS}$$

Where :

$\dot{m}$ = mass of nutrient per time (kg/day)
PS = Primary Sludge
WAS = Waste Activated Sludge

Equation 4-1: Solid Train and Liquid Train Partitioning

4.2 Mass Balance: Nitrogen and Phosphorus in Digesters

The objective of this study is to quantify the fate of the resources through two digestion systems, one anaerobic and the other aerobic using the Howard Curren Treatment Plant and Largo Treatment Plant reactors. A quantification of resource partitioning through these systems will allow for evaluation of resource recovery potential after the digestion process. A thorough evaluation of resource partitioning may also allow for decision making in technology selection, if resource recovery potential factors into financial decisions for municipal treatment plants and farm scale treatment operations.

An experimental plan was developed in order to determine the fate of the resources in an aerobic digestion and an anaerobic digestion system. Samples were collected from two digester influent streams, primary sludge (PS) and waste activated sludge (WAS). Samples were also collected from one digester effluent stream, effluent sludge (ES). Solids and liquids were separated from each sludge sample and analyzed for nitrogen and phosphorus. Mass balance calculations were performed according to the following equation, shown as an example for nitrogen mass balance:

$$\begin{aligned}&\left[\left(\mathrm{q}_{\mathrm{ps\text{-}s}} * \mathrm{TS}_{\mathrm{ps}}\right) + \left(\mathrm{X}_{\mathrm{ps\text{-}aq}} * \mathrm{TL}_{\mathrm{ps}}\right)\right] Q_{ps} + \left[\left(\mathrm{q}_{\mathrm{was\text{-}s}} * \mathrm{TS}_{\mathrm{was}}\right) + \left(\mathrm{X}_{\mathrm{was\text{-}aq}} * \mathrm{TL}_{\mathrm{was}}\right)\right] Q_{was} \\ &= \left(\mathrm{Y} * Q_{gas}\right) + \left[\left(\mathrm{q}_{\mathrm{es\text{-}s}} * \mathrm{TS}_{\mathrm{es}}\right) + \left(\mathrm{X}_{\mathrm{es\text{-}aq}} * \mathrm{TL}_{\mathrm{es}}\right)\right] Q_{es}\end{aligned}$$

Where:

Y = concentration of nitrogen in biogas (mg - N/L - biogas) - (from lab analysis)

$\overline{\mathrm{Q}}_{\mathrm{gas}}$ = average flowrate of biogas - (data from plant operations)

$\overline{\mathrm{Q}}_{\mathrm{ps}}$ = average flowrate of primary sludge - (data from plant operations)

$\mathrm{X}_{\mathrm{ps\text{-}aq}}$ = concentration of aqueous nitrogen in primary sludge (mg - N/L) - (data from lab analysis)

$\mathrm{q}_{\mathrm{ps\text{-}s}}$ = concentration of solid nitrogen in primary sludge (mg - N/ mg - solid) - (data from lab analysis)

$\mathrm{TS}_{\mathrm{ps}}$ = Total Solids in Primary Sludge (mg solids/ L - sludge) - (data from lab analysis)

$\mathrm{TL}_{\mathrm{ps}}$ = Total Liquids in Primary Sludge (L - liquid/ L - sludge) - (data from lab analysis)

Equation 4-2: Example Mass Balance Using Nitrogen

Each bracketed term in the equation 4-2 results in a mass per time of the resource. The mass balance equation was developed without accumulation, sink or source. This generalization is made, ignoring the small quantity of ammonia vaporization in the anaerobic digester. Thus flow in for any resource (nitrogen and phosphorus) should equal the flow out.

Following evaluation of the mass balance above, the partitioning of total nitrogen into the solid, liquid and gas phases is calculated from the different terms in the above equation. From this data many calculations can be made regarding the fate of the resources, percentages recovered, percentage recoverable and value of the resources. Digester supernatant or filtrate is pumped to the head of the plants at both of the study plants. The percentage of resource loading resulting from this filtrate is calculated.

4.3 Evaluation of N and P Recovery by Struvite

The objective of this study is to determine the percentage of phosphate and nitrogen recovery possible through struvite precipitation in batch reaction, using actual anaerobic digester supernatant from the Howard Curren AWTP. This study will also provide specific chemical input requirements for the magnesium, phosphorus, and pH control needed to facilitate struvite precipitation. Specific chemical input requirements will provide data to allow for financial calculations to assess the feasibility of struvite production in comparison to more traditional methods.

4.4 Financial Analysis of Struvite Production

Given the percentage recovery obtained in the above experiments and specific chemical input requirements, a calculation methodology is developed in order to assess the financial feasibility of struvite precipitation at the Howard Curren Treatment Plant. Actual ammonia and phosphate recovery rates and actual plant data are utilized. Market prices for chemical additions are used. The production costs of struvite are analyzed and compared to the current method of sidestream nitrogen removal including aeration for nitrification and methanol driven denitrification.

4.5 Aeration for Struvite pH Adjustment

Based on results and conclusions from the financial analysis, a revised methodology for struvite production was evaluated. The costs for pH adjustment through chemical addition of a strong base are a significant portion of the total production costs. Therefore investigation into a less expensive pH adjustment is desired and the literature provides examples of pH adjustment for struvite precipitation through aeration (Battistoni et al. 1997). However, because the aim of the work by Battistoni et al. (1997) is phosphate recovery, the stripping of ammonia is not investigated during the aeration process. Therefore, this study will investigate the adjustment of pH through aeration for carbonate stripping while monitoring ammonia stripping as a potential negative side effect, as full ammonia recovery is the desired result. This section includes a theoretical calculation of mass transfer of carbonate and ammonia through aeration. The experimental objectives are to:

- observe pH and ammonia concentrations as a result of aeration
- quantify a relationship between aeration and reduction in lime addition for pH control
- Conduct further financial feasibility study on the struvite precipitation process using aeration and lime together as a pH adjustment.

4.6 Evaluation of Specific Phosphorus Release Rate – LGAWTP

The objective of the phosphorus release and sludge settling tests were to understand the kinetics of phosphate release (if any) when aeration ceases and quiescent conditions are induced by the plant for sludge settling and dewatering. The tests were conducted in jars test in order to mimic the quiescent conditions in the gravity thickener employed at the Largo treatment plant. An understanding of the kinetics of phosphorus release may assist in plant operation schemes to maximize phosphate recovery while balancing with the need to dewater sludge prior to entering the belt filter press.

5 Materials and Methods

5.1 Analytical Methods

Sludge samples were collected from the two treatment plants on various dates. Samples were collected from various sampling ports or dipped from the digesters.

The liquid portion of sludges were separated from solids for dissolved constituent analysis. Sludge samples were centrifuged in 50 mL centrifuge tubes at 3500 RPM for 20 minutes. Supernatant was extracted with a pipette and then passed through a 0.45 micron glass fiber filter on a vacuum pump assembly.

Total Nitrogen in liquid was analyzed using the Shimadzu TOC-V with the TNM-1, Total Nitrogen Measuring Unit using calibration curves generated with known concentrations of urea.

Total Suspended Solids was measured according to Standard Method 2540, subtracting Total Dissolved Solids from Total Solids.

Ammonium was analyzed by Ion selective probe manufactured by Cole-Palmer Instrument Co. and a Corning 350 pH/ ion analyzer man. Calibration curves were created according to the probe manufacturer specification using known concentrations of ammonium chloride.

Nitrate was analyzed by Ion selective probe manufactured by Cole-Palmer Instrument Co. and a Corning 350 pH/ ion analyzer. Calibration curves were created according to the probe manufacturer specification using known concentrations of sodium nitrate.

Reactive Phosphate (ortho-Phosphate) in liquid was analyzed using the Standard Method 8114 (molybdovanadate method) using a HACH spectrophotometer. Adsorbance is measured at 420 nm.

Total Phosphate in liquid and mixed liquor suspended solids was analyzed by the molybdovanadate method with acid persulfate digestion using a test kit provided by HACH. Potassium persulfate was added to the sample and then heated. After digestion and release of bound phosphate, molybdovanadate was added to affect color change and the sample was analyzed using the spectrophotometer at a wavelength of 420 nm.

The pH was measured using a pH probe and the Corning 350 pH/ ion analyzer.

5.2 Experimental Methods

5.2.1 Preparation of Struvite by Batch Reaction

Initial concentrations of ammonia, ortho-Phosphate, and magnesium were analyzed. Calculations were conducted for addition of chemicals in order to bring all three reactants to equimolar concentrations in the solution. Phosphate was added in the form of phosphoric acid and magnesium was added in the form of magnesium sulfate. The solution was stirred and a pH meter measured pH continuously as pH was adjusted with sodium hydroxide or aeration or both. When the pH reached 9.75, adjustment was stopped and stirring continued. After approximately 5 minutes, stirring was stopped and solids were allowed to settle. Final concentrations of ammonia and phosphate were measured in the solution. Portions of the solid was collected on a filter paper, dried, re-dissolved in deionized water and analyzed for ammonium and phosphate concentration for analysis of struvite content.

5.2.2 Phosphorus Release and Sludge Settling

Aerobic digester sludge was collected and put in beakers to evaluate sludge settling and collect phosphate release samples. As a clear interface between settling sludge and “clear” supernatant developed, the volume that the sludge occupies was recorded with time. During settling samples of supernatant are collected at various times with a syringe and filtered using a 0.45 micron glass fiber syringe filter. Supernatant total phosphate concentrations are analyzed and dissolved concentration of total phosphate is plotted versus time.

6 Results and Discussion

6.1 General

Significant variability in samples was observed. The inconsistencies in plant influent and operating conditions were appreciated during this study. It should be noted that the Largo Treatment Plant and Howard Curren Treatment Plant employ different digestion systems (aerobic vs. anaerobic) but also different activated sludge and nutrient removal systems in the liquid side of the plant. The BPR and BNR system at Largo generates a WAS of different composition than that of Howard Curren which uses a high purity oxygen aeration system. However, collection of primary sludge at each of the plants is very similar.

6.2 Resource Partitioning Between Solid and Liquid Streams

Worksheet 1 attached in Appendix A-1 outlines the calculation methodology and input parameters for estimation of the resource partitioning between the solid and liquid streams of the treatment plant. Results are shown in Table 2. Only one sample was collected of primary effluent for input into this calculation and the results are displayed on Worksheet 1. Mean values were used for input in to Worksheet 1, taken from the summary of analytical data, Tables 3 and 4.

Table 1: Summary of Resource Partitioning Results

Plant	Stream	Flow %	Nitrogen %	Phosphate %
Howard Curren	Solids	2.3	38	93
	Liquids	97.7	62	7
Largo	Solids	0.8	45	122
	Liquids	99.2	55	-22

Partitioning of resources in both the Howard Curren Treatment Plant and the Largo treatment plant show that although handling a very small percentage of the flow rate, the solids side of both facilities handle a significant portion of the nutrient mass flow (see Table 2). Phosphate partitions into the solids stream in higher proportions than nitrogen, with over 90% of the phosphate in the solids stream and 38%-45% of the nitrogen. The high percentage of nutrients routed to “solids” was expected from literature values and solids flow analysis and only one sample was collected from each treatment plant for confirmation. This result encouraged continued investigations in to the solids side of the plant for evaluation of the resource recovery potential of the two digester systems plus opportunities for further resource recovery from post digestion sludge handling.

6.3 Fate of Resources in Aerobic and Anaerobic Digesters

Tables 2 and 3 provide a summary of all analytical data collected during the investigation with statistical analysis. From this data and from flow rate data provided by the plant operations, calculations and mass balances were conducted for the fate of nitrogen and phosphorus at the Howard Curren and Largo Treatment Plants.

The initial intent for mass balancing was to collect samples and flow rates in and out of the digesters and conduct a mass balance on a daily basis. However during the investigation, it was learned that flow out of the digesters to solids handling at each of the facilities did not match the daily input. This is most prevalent at Largo, where primary sludge (PS) and waste activated sludge (WAS) are pumped to the digester over the weekends, but no effluent sludge (ES) is taken for processing into biosolids. During the week, more ES is taken from the digester than PS+WAS put in to make up for the weekends.

Therefore, daily flow volumes proved to be an insufficient length of time to ensure equalized flow and no “accumulation” term in the mass balance. It was decided to average flow rates and average analytical constituent concentrations and conduct one mass balance over the entire study period for each constituents.

Worksheets in Appendix A-1 provide the mass balance calculations. All analytical data is taken from mean values, provided on Tables 2 and 3. Flow data represents the average daily flow volume for PS, WAS, and ES provided by plant operations. Figures 15 through 18 in provide graphic representations of the fate of the resources through the digestion system.

Table 2: Cumulative Analytical Data for Anaerobic Digester at HFCAWTP

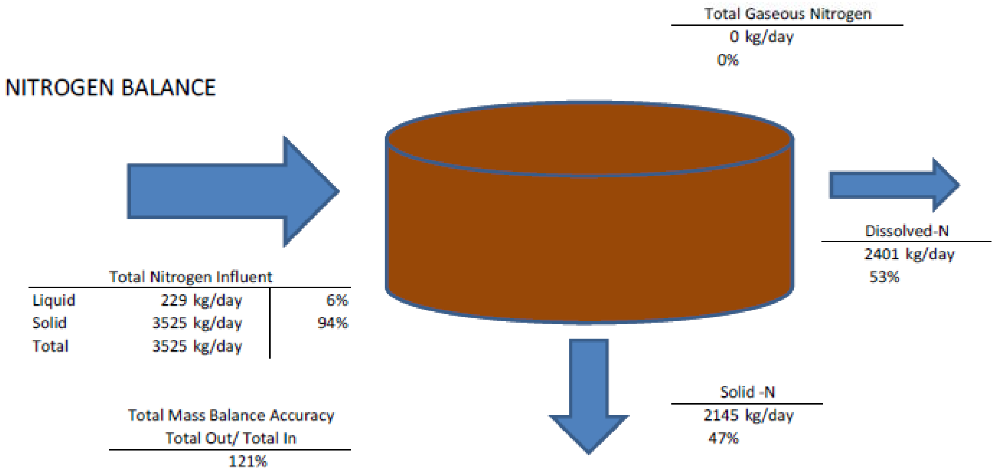
		Primary Sludge					Waste Activated Sludge					Effluent Sludge				
		17-Dec	12-Jan	30-Jan	25-Feb	Cumulative	17-Dec	12-Jan	30-Jan	25-Feb	Cumulative	17-Dec	12-Jan	30-Jan	25-Feb	Cumulative
Dissloved Nitrogen (mg/L - filtered supernatant)	mean	43	18.5	34.5	73	42	282	149.4	193.1	362	247	1552	1188.1	1160	2223	1531
	sd	3.83	0.47	4.6	16.7	23	7.24	0.97	17.5	45	95	13.07	6.22	40.7	2.42	495
	cv	0.09	0.03	0.13	0.23	0.54	0.03	0.01	0.09	0.12	0.38	0.01	0.01	0.04	0.00	0.32
	n	2	2	2	2	4	2	2	2	2	4	2	2	2	2	4
Total Nitrogen (mg/L - total sludge)	mean	1664	1370	1365	1215	1403.50	3100	3589	3300	2970	3239.75	2699	2652	3210	2805	2841.50
	sd	31.3	134	21.2	21.2	188	330	388	0	127.3	270	397	313	0	63.6	254
	cv	0.02	0.10	0.02	0.02	0.13	0.11	0.11	0.00	0.04	0.08	0.15	0.12	0.00	0.02	0.09
	n	2	2	2	2	4	2	2	2	2	4	2	2	2	2	4
Dissolved Phosphate (mg/L - filtered supernatant)	mean		31.8	105	100.25	79		131	223.5	276.25	210		218	309	219.75	249
	sd		0.51	NA	1.06	41		0.51	NA	1.77	74		NA	NA	1.06	52
	cv		0.016038	NA	0.01	0.52		0.003893	NA	0.006407	0.35		NA	NA	0.004	0.21
	n		2	1	2	3		2	1	2	3		1	1	2	3
Total Phosphate (mg/L - total sludge)	mean	1665	1178	2385	1343	1643	2883	3180	4870	4915	3962	1705	1715	2615	1793	1957
	sd	219	95.5	NA	39	535	753	566	NA	141	1081	339	7.07	NA	11	440
	cv	0.13	0.08	NA	0.03	0.33	0.26	0.18	NA	0.03	0.27	0.20	0.00	NA	0.01	0.23
	n			1	2	2			1	2	2			1	2	2
Dissolved COD (mg/L)	mean	534	1160	2220		1305	2220	1896	3188		2435	1096	1924	1976		1665
	sd	NA	NA	NA		852	NA	NA	NA		672	NA	NA	NA		494
	cv	NA	NA	NA		0.65	NA	NA	NA		0.28	NA	NA	NA		0.30
	n	1	1	1		3	1	1	1		3	1	1	1		3
Total COD (mg/L)	mean	72300	65000	114700		84000	63600	43050	85500		64050	31100	27690	32400		30397
	sd	NA	NA	NA		26836	NA	NA	NA		21229	NA	NA	NA		2432
	cv	NA	NA	NA		0.32	NA	NA	NA		0.33	NA	NA	NA		0.08
	n	1	1	1		3	1	1	1		3	1	1	1		3
Total Suspended Solids (mg/L)	mean	28,957	35,893	49740	38148	38185	30,603	41,285	39440	38050	37345	19,933	18,042	19550	20855	19595
	sd	2085	1322	1047	977	8640	1209	962	57	1662	4686	696	220	156	220	1171
	cv	0.07	0.04	0.02	0.03	0.23	0.04	0.02	0.001	0.04	0.13	0.03	0.01	0.01	0.01	0.06
	n	3	3	2	3	4	3	3	2	3	4	3	3	2	3	4

Table 3: Cumulative Analytical Data for Aerobic Digester at LGAWTP

		Primary Sludge					Waste Activated Sludge					Effluent Sludge				
		17-Dec	8-Jan	30-Jan	23-Feb	Cumulative	17-Dec	12-Jan	29-Jan	23-Feb	Cumulative	17-Dec	12-Jan	30-Jan	23-Feb	Cumulative
Dissloved Nitrogen (mg/L - filtered supernatant)	mean	35	37.1	32.7	49.5	39	9	2	4.1	0	4	11	2.7	2.9	24.9	10
	sd	0.21	0.62	0.9	3	8	0.11	0.02	0.1	0	4	0.18	0	0.1	0.12	10
	cv	0.01	0.02	0.03	0.06	0.19	0.01	0.01	0.02	0.00	1.02	0.02	0.00	0.03	0.00	1.00
	n	2	2	2	2	4	2	2	2	2	4	2	2	2	2	4
Total Nitrogen (mg/L - total sludge)	mean	364	1015	645	670	777	977	848.2	960	920	926	758	951.4	810	690	802
	sd	33	71	21.2	42.4	207	30	2.97	0	28.3	57	24	65	84.9	14.1	111
	cv	0.09	0.07	0.03	0.06	0.27	0.03	0.00	0.00	0.03	0.06	0.03	0.07	0.10	0.02	0.14
	n	2	2	2	2	3	2	2	2	2	4	2	2	2	2	4
Dissolved Phosphate (mg/L - filtered supernatant)	mean	8.2		96.5	73	59	149		66.5	110.5	109	173		101.5	207.5	161
	sd	1.5		NA	NA	46	4.8		NA	NA	41	6.3		NA	NA	54
	cv	0.18		NA	NA	0.77	0.03		NA	NA	0.38	0.04		NA	NA	0.34
	n	2		1	1	4			1	1	4	2		1	1	4
Total Phosphate (mg/L - total sludge)	mean	93	1041	910	690	880	1505	1251	1941	1985	1671	1074	1223	1731	1200	1307
	sd	0	30	NA	NA	177	78.5	27	NA	NA	354	21	7	NA	NA	290
	cv	0	0.03	NA	NA	0.20	0.05	0.02	NA	NA	0.21	0.02	0.01	NA	NA	0.22
	n	2		1	1	3	2	0	1	1	4	2		1	1	4
Dissolved COD (mg/L)	mean	306	503	830		546	148	33	40		74	167	56	70		98
	sd	NA	NA	NA		265	NA	NA	NA		64	NA	NA	NA		60
	cv	NA	NA	NA		0.48	NA	NA	NA		0.88	NA	NA	NA		0.62
	n	1	1	1		3	1	1	1		3	1	1	1		4
Total COD (mg/L)	mean	9016	45100	33500		39300	13620	12975	15180		13925	12112	17940	18570		16207
	sd	NA	NA	NA		18421	NA	NA	NA		1134	NA	NA	NA		3561
	cv	NA	NA	NA		0.47	NA	NA	NA		0.08	NA	NA	NA		0.22
	n	1	1	1		2	1	1	1		3	1	1	1		4
Total Suspended Solids (mg/L)	mean	5798	28,775	17930	19088	21931	10,497	9423	12950	11595	11116	9212	12433	12540	9000	10796
	sd	222	503	636	979	9419	123	145	14	213	1510	323	189	283	64	1954
	cv	0.04	0.02	0.04	0.05	0.43	0.01	0.02	0.001	0.02	0.14	0.04	0.02	0.02	0.01	0.18
	n	3	3	2	3	3	3	3	2	3	4	3	3	2	3	4

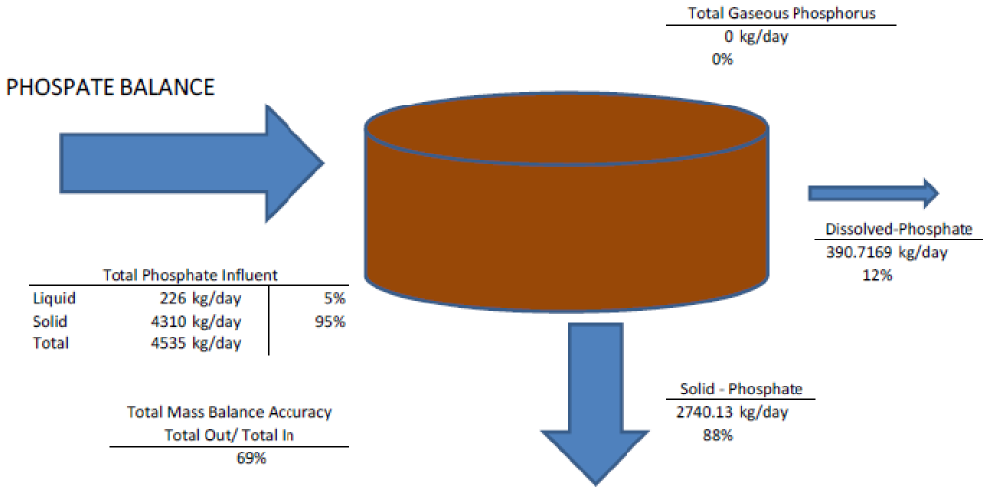
The following discussion represents a comparison of the fate of the various resources through the aerobic and anaerobic digestion processes and an evaluation of the resource recovery potential. It is noted that there was significant variability in the data collected. The statistical analyses shown on Tables 2-3 show a high coefficient of variation for several of the analyses. The majority of the variability is attributed to variations in the plant. Daily fluctuations in influent flow and concentrations are a well established factor in sewage treatment. Additionally, instantaneous constituent concentrations can also fluctuate significantly based on changes in industrial use inputs.

The intention of this study was to provide a strict accounting of the fate of the resources through the two digester systems in order to evaluate the resource recovery potential. During the data analysis it was realized that a highly accurate mass balance would require an enormous amount of sampling, not feasible for this study. However, despite some of the high coefficients of variations,



Total Nitrogen Influent		
Liquid	229 kg/day	6%
Solid	3525 kg/day	94%
Total	3525 kg/day	

Figure 14: Nitrogen Balance at Anaerobic Digester



Total Phosphate Influent		
Liquid	226 kg/day	5%
Solid	4310 kg/day	95%
Total	4535 kg/day	

Figure 15: Phosphate Balance at Anaerobic Digester

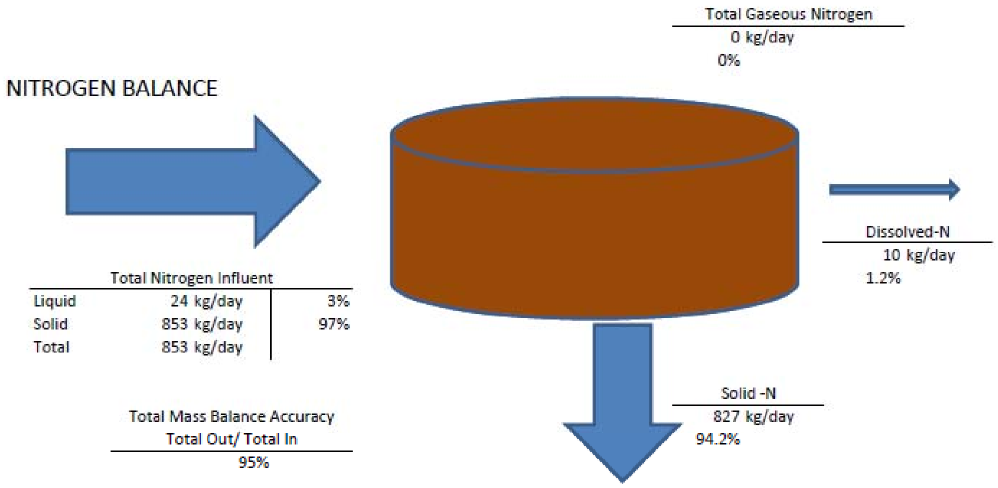
valuable discussion comparing the fate of resources in the aerobic and anaerobic digester can be facilitated.

6.3.1 Nitrogen

The most distinct differences between the aerobic and anaerobic system are in the fate of nitrogen through the digesters. In the aerobic system, there is a net solidification of nitrogen. At Largo, 24 kg/day of dissolved nitrogen enter the digester and only 10 kg/ day of dissolved nitrogen leave. The difference is incorporated into solids in the effluent.

This contrasts sharply to the nitrogen balance for the anaerobic system at Howard Curren where dissolved nitrogen influent is approximately 229 kg/ day but 2401 kg/day dissolved nitrogen exits the reactor. The percentage of solid phase nitrogen drops significantly, from 96% solid entering the reactor to 60% exiting. The majority of the liquid phase nitrogen is in the ammonia form.

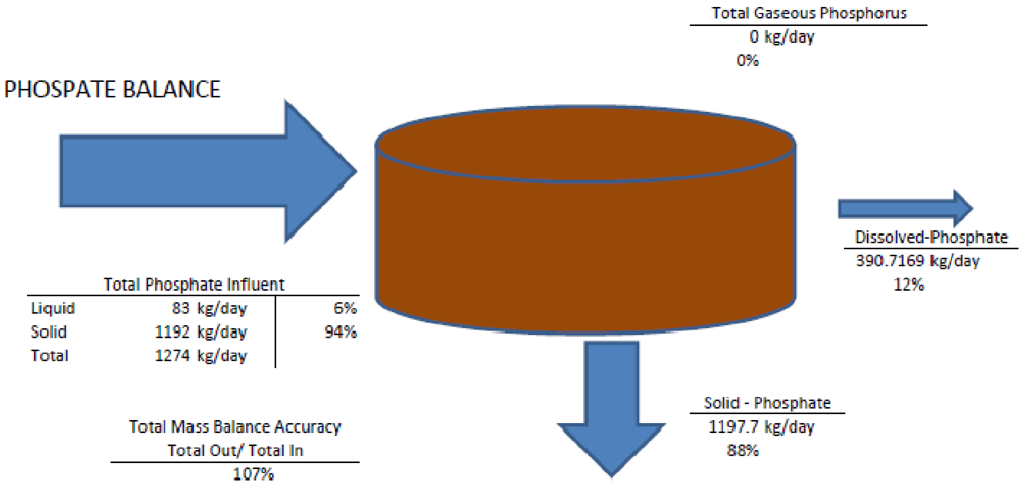
This ammonia stream returning to the head of the plant represents a signifant percentage (approximately ¼) of the plant's influent nitrogen loading estimated between 8,000 and 10,000 kg total nitrogen per day.



Total Nitrogen Influent		
Liquid	24 kg/day	3%
Solid	853 kg/day	97%
Total	853 kg/day	

Total Mass Balance Accuracy
Total Out/ Total In
95%

Figure 16: Nitrogen Balance at Aerobic Digester



Total Phosphate Influent		
Liquid	83 kg/day	6%
Solid	1192 kg/day	94%
Total	1274 kg/day	

Total Mass Balance Accuracy
Total Out/ Total In
107%

Figure 17: Phosphate Balance at Aerobic Digester

6.3.2 Phosphorus

The fate of phosphate in the two digestion systems appears to be similar. Both digestion systems lose phosphate from solid to liquid. However, the majority of the phosphorus in both systems enters in solid form (94-95%) and leaves in solid form (88%).

6.4 Whole Plant Mass Balancing

By using plant data and the mass balance data discussed in section 6.3 above, we can also gain an understanding of the fate of the nutrient resources through the treatment plant in order to discuss the current process and the “recoverability” of nutrients through the treatment plant.

Figure 18 shows a material balance with the system boundary around the entire treatment plant and a general accounting of the partitioning of resources through the various effluent streams in the plant: discharge in the liquid effluent, incorporation into solids, and gaseous release.

In both plants, a majority of the nitrogen is discharged through gaseous release to dinitrogen gas. This is accomplished through the Biological Nitrogen Removal processes. Nitrogen is lost to the atmosphere and this loss represents an opportunity for process change and recovery of the resource.

The fate of phosphorus through the treatment plant is in sharp contrast to the nitrogen. Because there are no gaseous forms of phosphorus, all influent phosphorus will leave the plant either in the liquid effluent or in the processed solid. Howard Curren does not utilize any phosphorus removal technology because the plant has a variance and no phosphate discharge limit (due to high background concentration in receiving water). Approximately 20% of the phosphorus is discharged in the effluent where at Largo almost all of the phosphorus leaves the plant in a recovered form, in the processed solids. Largo accomplishes this recovery through the phosphate accumulating organisms (PAO) which hyper accumulated phosphate into cellular compounds.

At Largo, there have been problems with overloading the BNR system with phosphorus and exceedances of the discharge limits. The mass balances shown in Figure 18 do not show internal recycle. Maintaining phosphate in its solid form in PAO through the digestion process is a component to reducing recycle of phosphate from the digester back into the BNR system. So, although most phosphate at Largo should eventually be recovered as solid even if it is released in the thickening system, the release of phosphate at this stage may contribute to higher percentages of phosphate leaving the plant in liquid phase and potentially incurring discharge fines on the plant.

6.5 Phosphorus Release and Sludge Settling vs. Time

Phosphate release and sludge settling were analyzed as aerobically digested sludge from the Largo AWTP was allowed to settle in conditions similar to the gravity thickener employed at the plant. Figures 19 through 24 provide data collected during six trials. Phosphorus concentration and sludge settling is plotted vs. time. Dissolved oxygen concentrations were monitored during three of the six trials, with results displayed in Figures 25 through 27. During trial 1, the effluent sludge was transported from the plant to the laboratory, thus the first phosphate analysis was conducted at 75 minutes. It was realized that phosphate data during the first 75 minutes would be critical and trials 2 through 4 were conducted at the plant so that sample collection could begin immediately.

Tables summarizing the phosphate concentrations and calculated release rates for the trials over various time period are included as Table 3. An analysis of the phosphate release significance compared to plant and digester phosphate loading is included as Table 4.

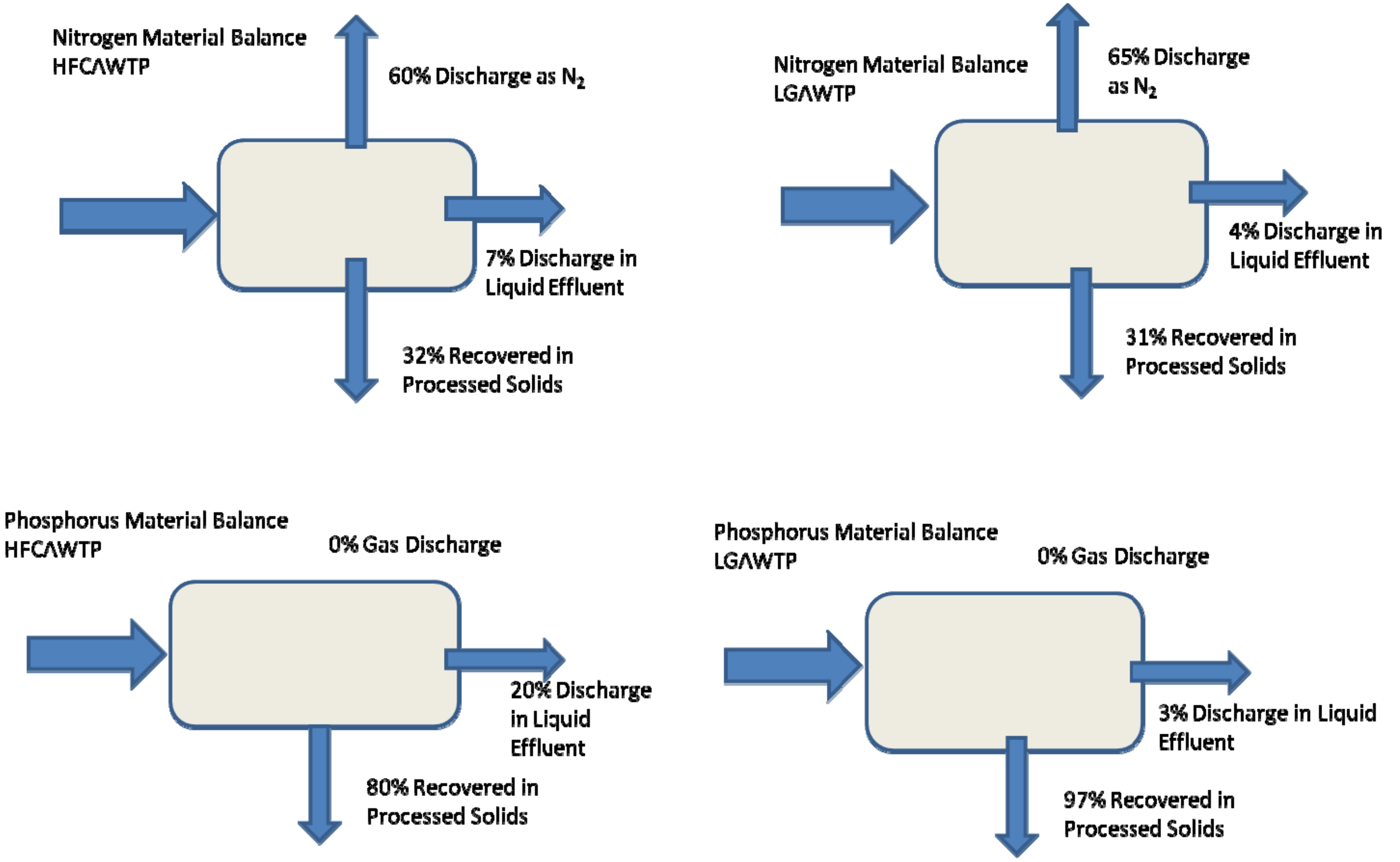


Figure 18: Nutrient Mass Balance for Treatment Plants

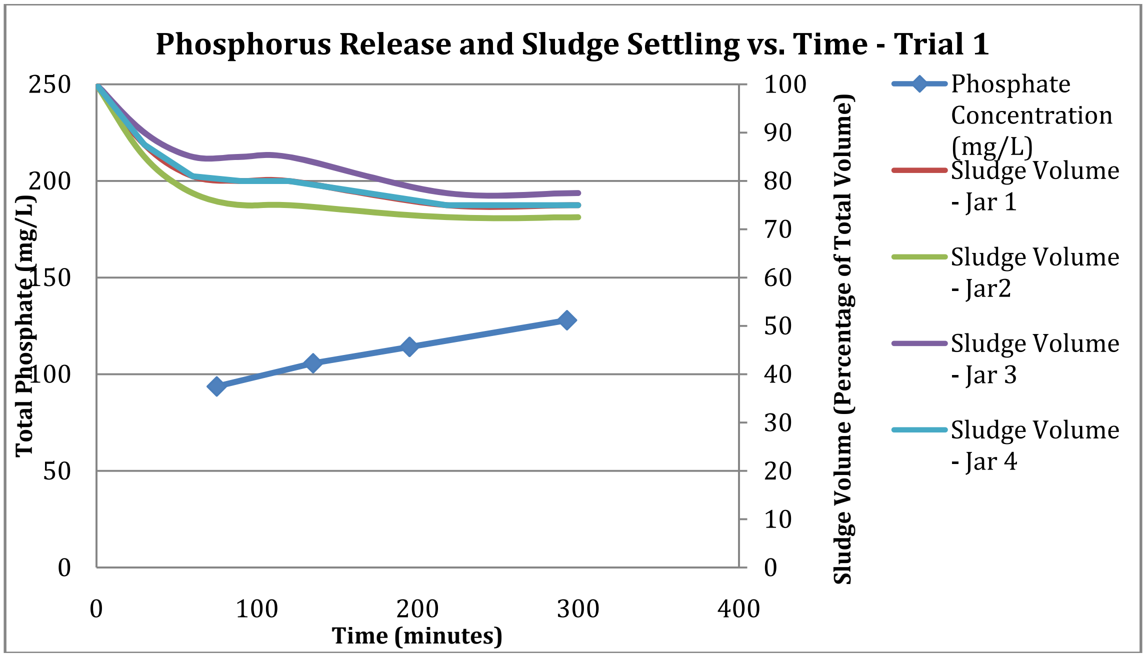


Figure 19: Trial 1 Phosphorus Release at Largo AWTP

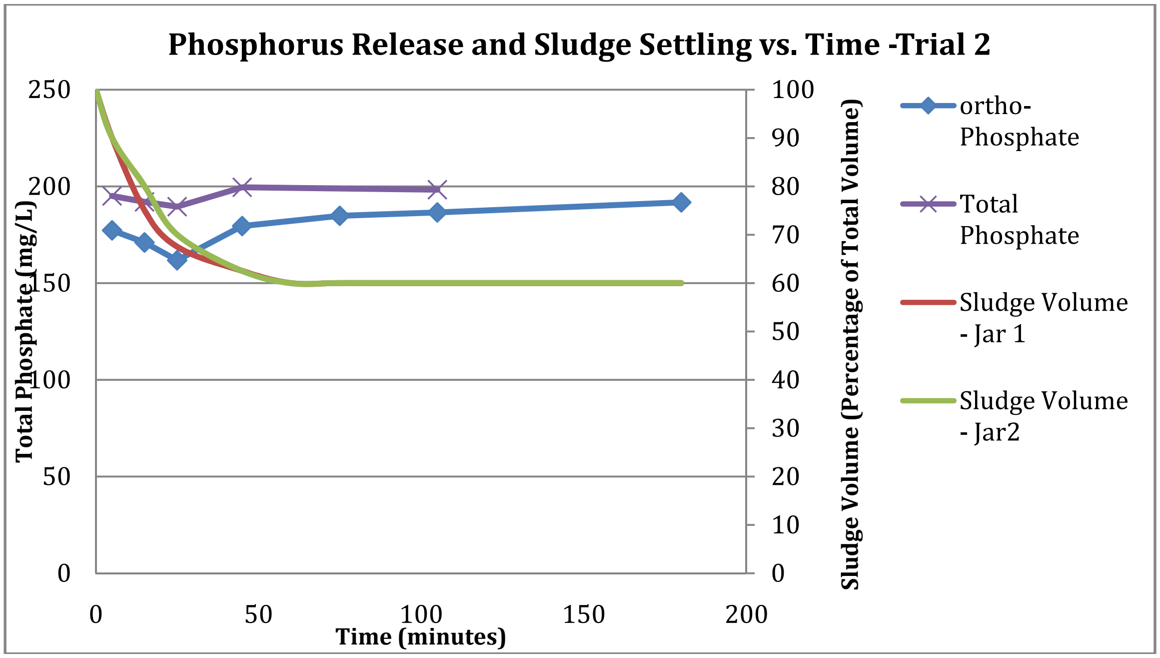


Figure 20: Trial 2 Phosphorus Release at Largo AWTP

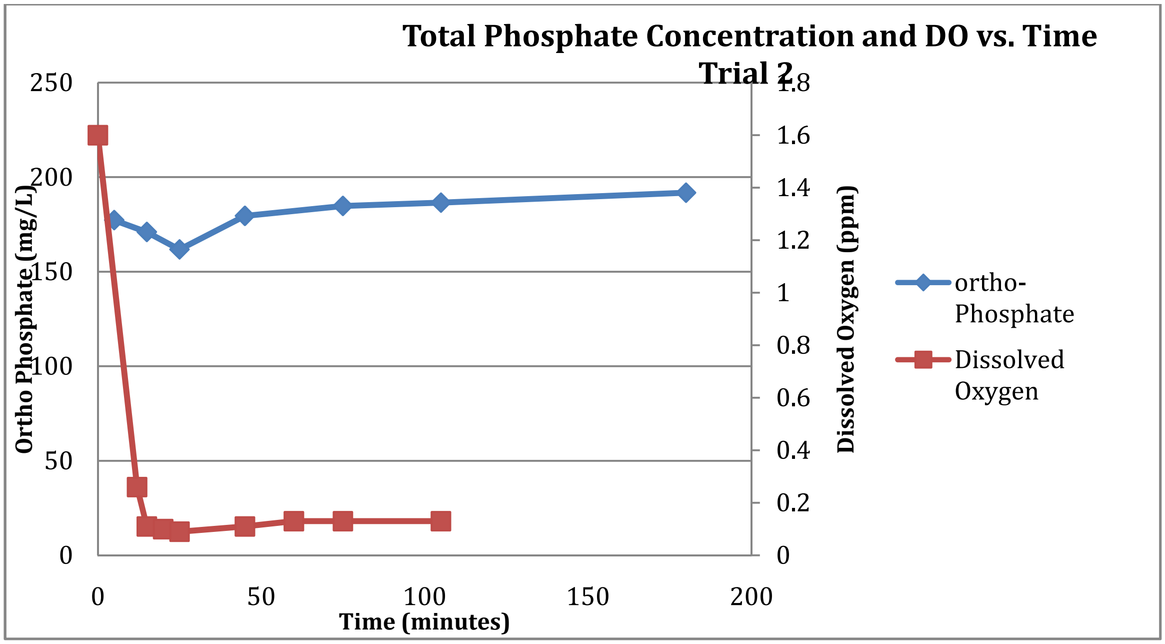


Figure 21: Trial 2 DO Analysis at Largo AWTP

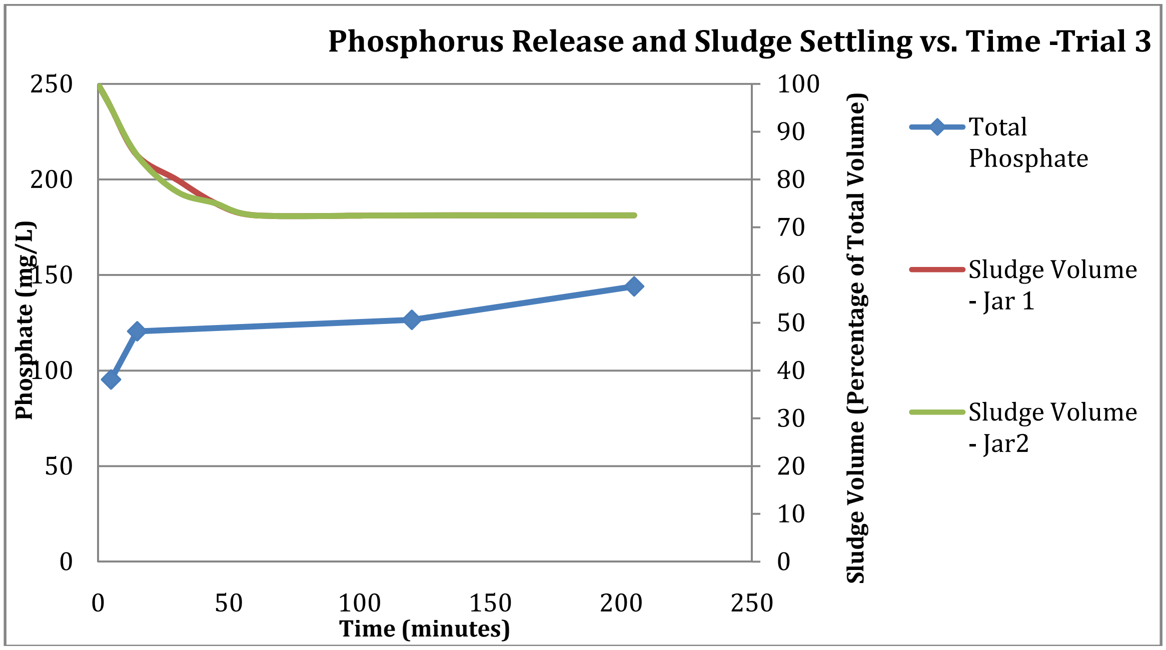


Figure 22: Trial 3 Phosphorus Release at Largo AWTP

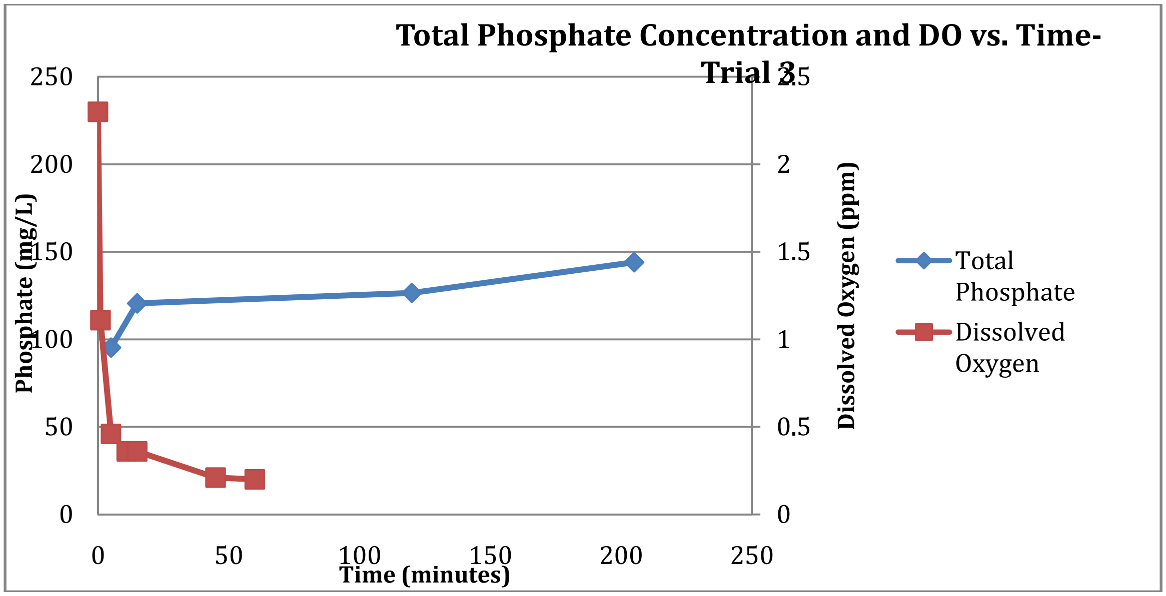


Figure 23: Trial 3 DO Analysis at Largo AWTP

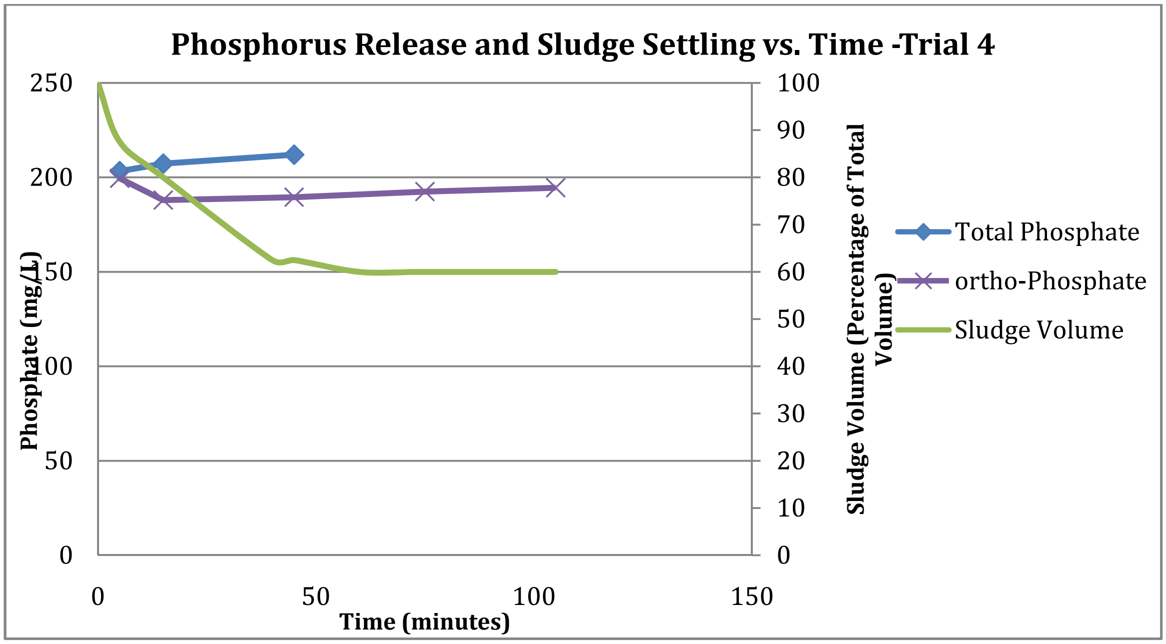


Figure 24: Trial 4 Phosphorus Release at Largo AWTP

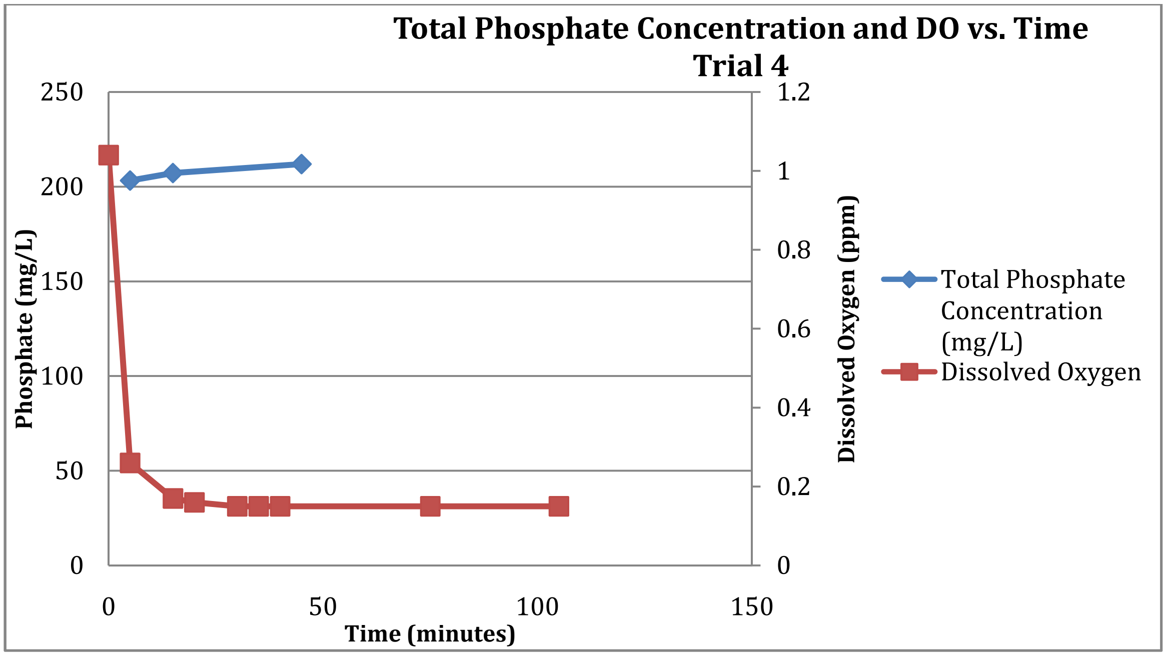


Figure 25: Trial 4 DO Analysis at Largo AWTP

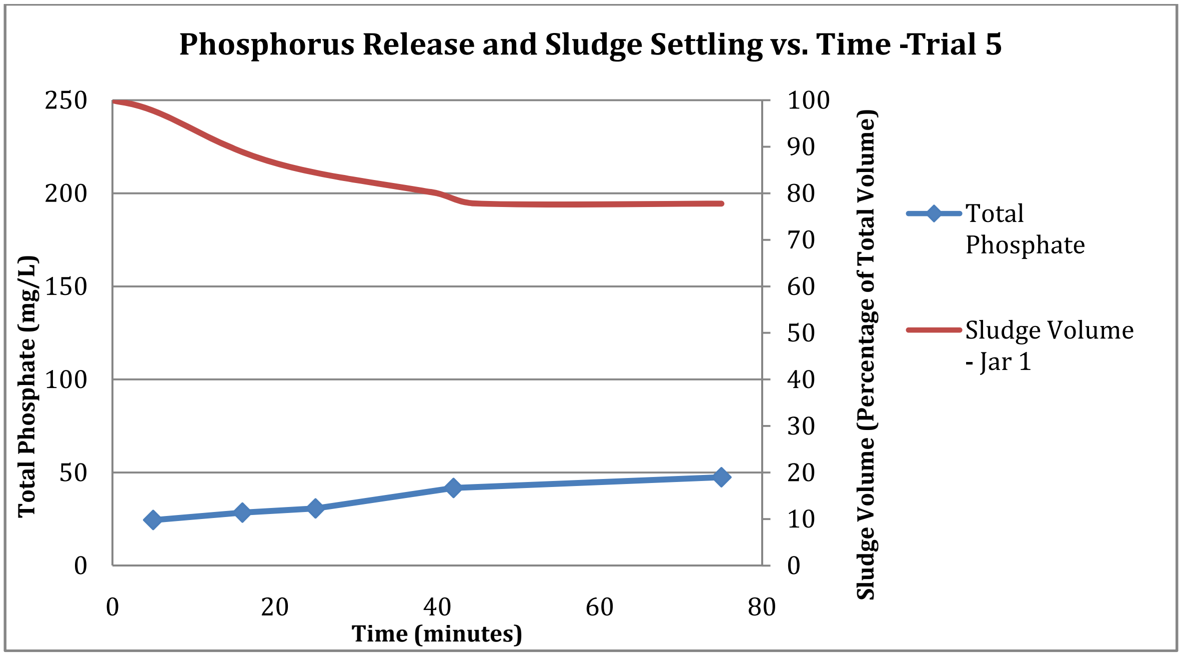


Figure 26: Trial 5 Phosphorus Release at Largo AWTP

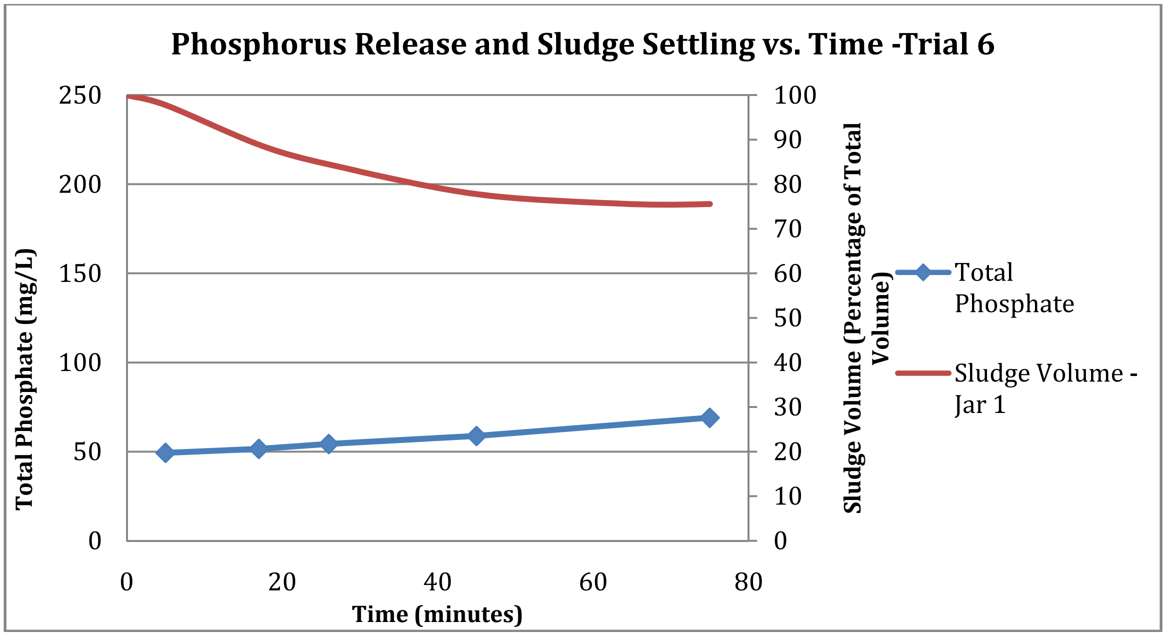


Figure 27: Trial 6 Phosphorus Release at Largo AWTP

Table 4: Summary of Phosphorus Release Trials

Trial	Date	Day of Week	Starting Concentration	Start Time	Ending Concentration	End Time	Change in Concentration	Elapsed Time	Linear Slope
			(mg/L)	minutes	(mg/L)	minutes	(mg/L)	minutes	(mg/L-minute)
2	23-Feb	Monday	195	5	199.5	45	4.5	40	0.11
3	27-Feb	Friday	95.25	5	122	45*	26.75	40	0.67
4	2-Mar	Monday	203.25	5	212	45	8.75	40	0.22
5	8-May	Friday	24.5	5	41.75	42	17.25	37	0.47
6	11-May	Monday	49.25	5	58.75	45	9.5	40	0.24
	* - extrapolated								

Table 5: Analysis of Phosphate Release Significance

	Average Release Rate for t = 5-45 min	Average Starting Concentration	Average Concentration after 45 min settling (based on Release Rate)	Supernatant Flow Rate (75% of sludge rate)	Daily PhosphateMass Released	Daily Return Load (Sent to Head of Plant)	Daily Mass Released/ Total Digester Load	Daily Return Load/ Total Plant Loading
	(mg/l-minute)	(mg/L)	(mg/L)	(L/day)	(kg/day)	(kg/day)	(%)	(%)
Monday	0.19	149.2	157.7	782647	6.7	123.4	0.5%	9.0%
Friday	0.57	71.2	96.7	782647	20.0	75.7	1.6%	5.5%

The objective of this portion of study is to quantify the phosphorus release rates in a quiescent clarifier environment relative to the rate of sludge settling in order to further an understanding on how to maximize recovery of phosphate as solid and maximize sludge dewatering through the clarifier. Additionally, because the Largo Treatment plant only operates the clarifier and solids handling facility during the business week, special attention was paid to differences in the release rates at the end of the week when mean sludge age would be significantly lower than at the beginning of the week.

Three of the trials included evaluation of dissolved oxygen levels after removal from the aeration. The results in the DO testing are consistent, with a very rapid drop in DO concentration, indicating microbial oxygen utilization.

There is significant variability in the initial concentration of total phosphate and in the rate of release when comparing all three “end of the week” trials, Trial 1, 3 and 5. Similarly, the “beginning of the week”, Trials, 2, 4 and 6 trials show significant variability in both initial phosphate concentration and release rates. However, it is noted that in the first 45 minutes the two highest phosphate release rates are on the two Friday samples and the lowest release rate.

The most useful comparisons to draw analysis come from comparison of the two pairs of trials which span a weekend. Trials 3 and 4 surrounded a single weekend and Trials 5 and 6 surrounded a single weekend.

In both of these pairs, the initial phosphate concentration on Friday was lower than on Monday and the initial rate of release on Friday was higher than on Monday. These results are consistent with two expectations gained from the literature. First, PAO’s can release phosphate when exposed to extended aeration and second, PAO’s which have not been exposed to extended aeration will rapidly release phosphate when stressed for oxygen as an electron acceptor.

In the context of the sludge settling rate, it appears that in all trials the sludge reached its maximum settling volume prior to 1 hour.   This observation is made by visual inspection of the sludge settling curves. Therefore if residence time in the clarifier can be held to less than 1 hour, the sludge will reach its maximum settling point and analysis of the total phosphate release rate for the time 0-45 minutes should be the most significant.

Table 5 provides an analysis of average phosphate release rates for Friday and Monday between t=5 minutes and t=45 minutes with a calculation of the total mass of phosphate released per day at the Largo Treatment Plant plus an estimation of the total mass of phosphate returned to the head of the plant in digester supernatant.

Based on the estimations made in this investigation, it appears that approximately 75 to 123 kg/day of dissolved total phosphate is returned to the plant headworks per day from digester supernatant. This represents approximately 5.5 to 9 percent of the total plant daily phosphorus loading, possibly significantly more on Mondays when the solids digestion facility is initiated.

In the broader context of aerobic digestion and phosphate recovery as a resource, the total phosphate mass released during a 45 minute sludge settling time is between 6.7 and 20 kg/ day. This represents 0.5% - 1.6% of the total load of phosphate sent to the digester. In other words, even with the sludge settling release, the digested material retains 98.4% to 99.5% of the total phosphate in the solid form as biosolids.

The total load of phosphate sent to the head of the plant from the digestion system may be a significant percentage (5.5%-9%), but little of this phosphate is released during post digestion sludge handling. The A^2O system followed by aerobic digestion appears to recover phosphate at the facility with good efficiency. There is some recycling and “looping” of phosphorus through the system, but closing the majority of this loop would require a modification to the digestion process rather than to post digestion sludge handling.

6.6 Struvite Precipitation from AnD Filtrate: Phosphorus Recovery

The initial area of investigation during this study was on the ability to add phosphate to actual filtrate and then recover the phosphate in a re-marketable form. The addition of phosphate is necessary to recovery ammonia, but recovery of the phosphate is crucial to the financial and regulatory feasibility of the process. Many trials were conducted in order to quantify the potential for struvite precipitation using filtrate from the Howard Curren Treatment Plant. Results of phosphate analysis are presented in Table 4 and illustrated graphically in Figure 28. A scanning electron micrograph of struvite crystallized during this investigation is shown as Figure 29 and solids analysis by X-ray diffractive analysis is shown in Figure 30.

Data in Table 6 analyzes the phosphate removal in several manners each resulting from a comparison of the final concentration of ortho-Phosphate in the liquid phase after precipitation with some initial concentration. The three initial concentrations used are the initial phosphate concentration in the supernatant solution, the total ortho-Phosphate concentration after addition of phosphate, and the concentration which was added. Table 4 shows promising results for all three analyses. In each of the trials, all added phosphate was removed from solution plus there was removal of phosphate originally in the solution.

Figure 28 provides a graphical look at the phosphate concentrations during the batch reactions. Large quantities must be added to facilitate precipitation, but the final concentration is below the initial in each batch.

Analysis of the product by Energy Diffractive Spectrophotometry (EDS) shown in Figure 30 shows a high phosphorus concentration in the solid product.

6.7 Evaluation of Struvite Production Using Aeration as pH Control

Once it is displayed that phosphate could be recovered if added, further financial analysis (discussed in Section 6.7) indicated that reducing costs for pH control would also be crucial to the feasibility of the struvite process. The objective of aeration is to reduce the acidity of the solution and reduce the chemical input for pH adjustment without stripping ammonia. The potential for ammonia stripping is first analyzed theoretically using mass transfer relationships. Our objective to facilitate carbonic acid stripping without ammonia stripping is assisted due to the fact that ammonia is in equilibrium with the gas phase in its deprotonated form, abundant at high pH, and carbonic acid is in equilibrium with the vapor phase in its protonated form, abundant at low pH.

Table 6: Summary of Phosphate Removal Results

Struvite Batch #	Initial Phosphate	Phosphate after Addition (Total)	Dissolved Phosphate after Precipitation (Final)	(Initial - Final)/ Initial	(Total - Final)/Total	(Total-Final)/(Total-Initial)
#	mg/L	mg/L	mg/L	%	%	%
13	347.5	1615	236	32%	85%	109%
14	250	3985	155	38%	96%	103%
15	204	2241	76.2	63%	97%	106%
16	204	2610	169.2	17%	94%	101%
17	204	1999	73	64%	96%	107%
18	204	2240	93	54%	96%	105%
19	505	4039	176.5	65%	96%	109%
20	440	5130	161	63%	97%	106%
21	440	4240	219	50%	95%	106%
22	400	3915	173	57%	96%	106%

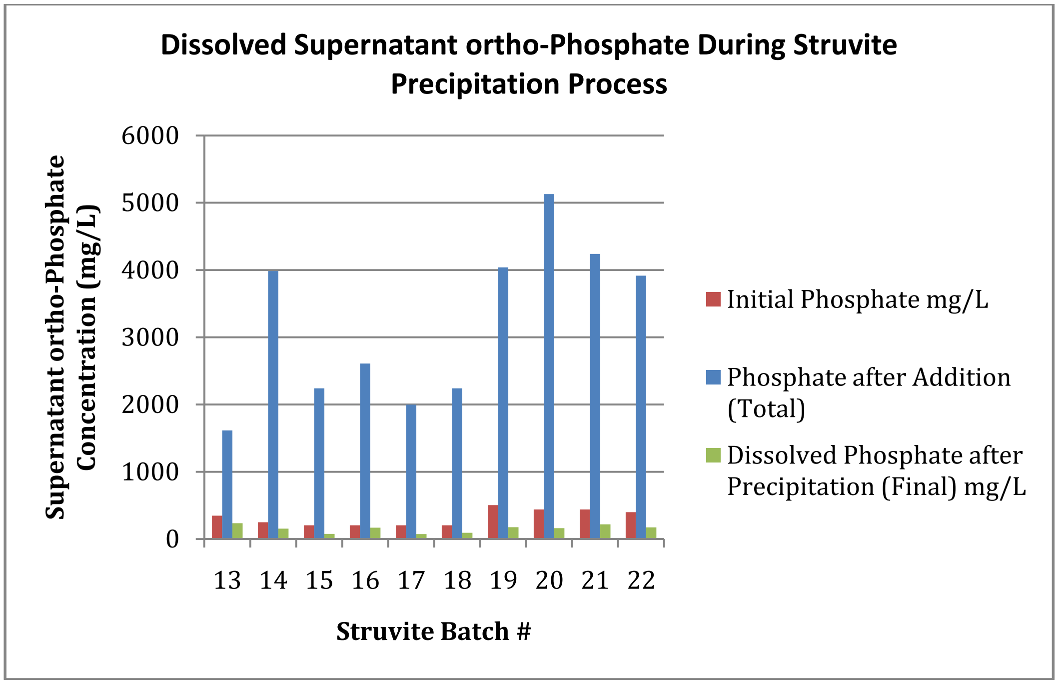


Figure 28: Phosphate Concentrations During Struvite Precipitation

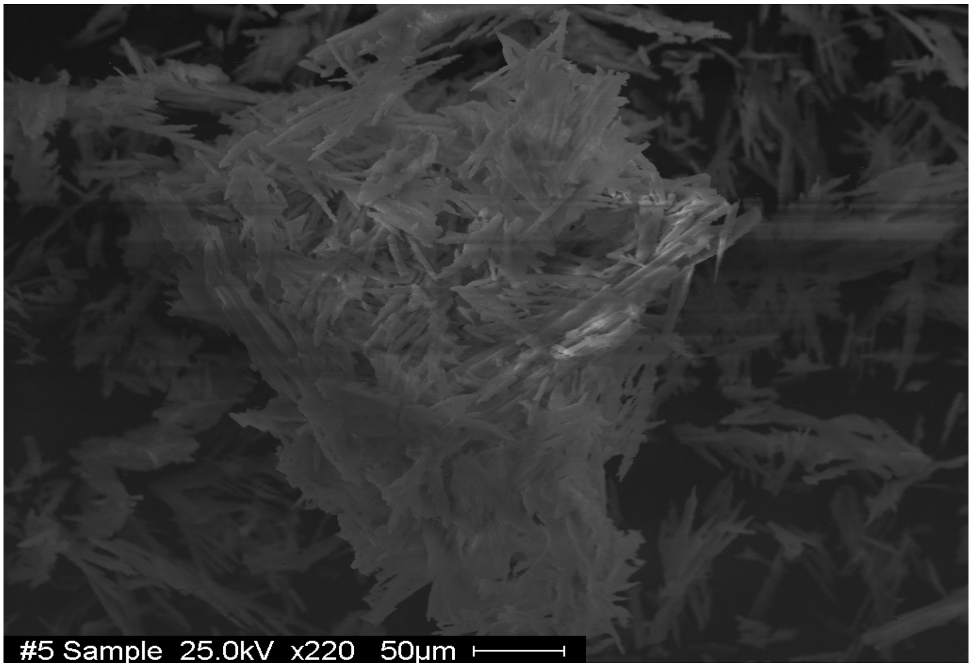


Figure 29: SEM Image of Crystallized Product
(courtesy of Russell Ferlita)

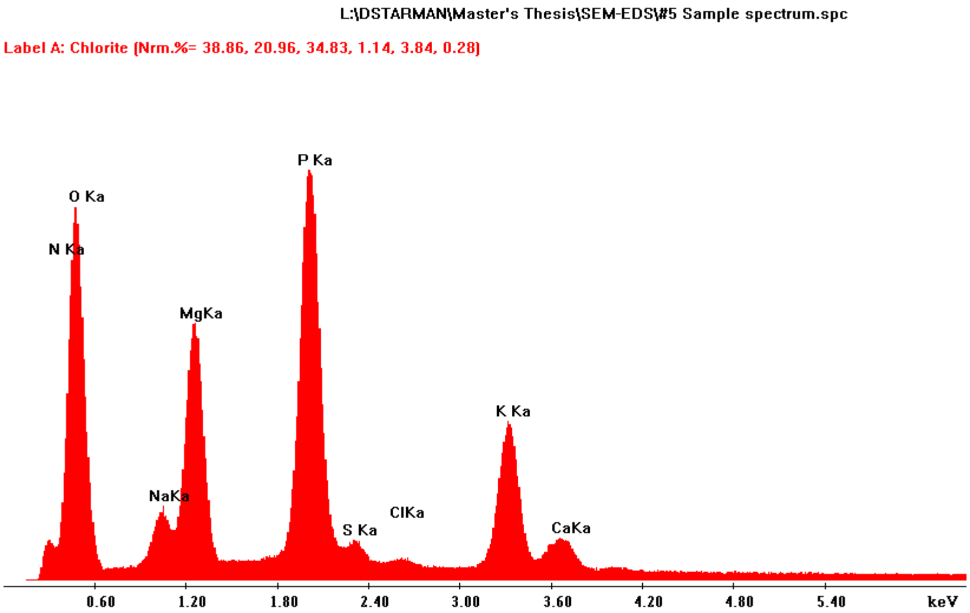


Figure 30: Solid Product Analysis by EDS (courtesy of Russel Ferlita)

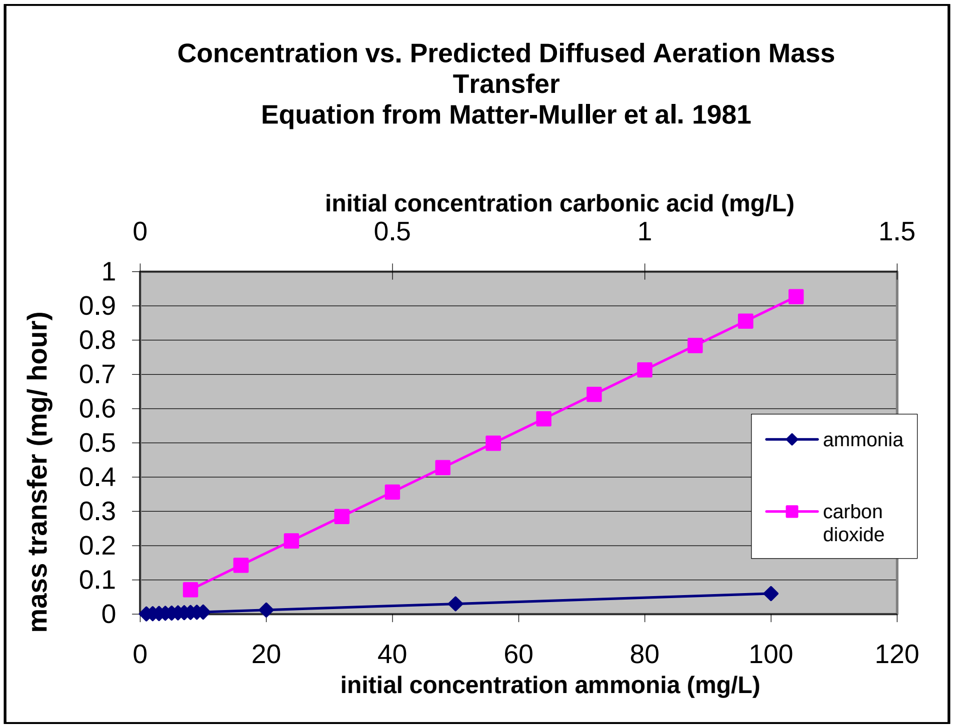


Figure 31: Prediction of Mass Transfer for Carbon Dioxide and Ammonia

Our objective is further facilitated by a difference in Henry's constants between the two compounds of over two orders of magnitude (0.006 and 1.6 for ammonia and carbon dioxide respectively). Thus, if our aeration occurs at a low pH the driving force for carbonic acid stripping should be at a maximum and the driving force for ammonia stripping should be at a minimum, given the total concentrations of each species in our solution. Some preliminary analysis was conducted using mass transfer relationships taken from literature (Matter-Muller et al. 1981). Typical oxygen transfer rates for diffused bubble aeration were taken also from the literature (Gilot et al. 2005). Example calculations using the Matter-Muller et al. (1981) relationship is provided in Appendix E-3. Figure 31 shows a plot of mass transfer rates vs. a range of concentrations for ammonia and carbonic acid which are expected. The result clearly shows that aeration should remove carbonic acid far more rapidly than ammonia, given the pH and concentration range expected.

Appendix B-1 shows plots ammonium and pH vs. time for each of the struvite batch reactions. Also in Appendix B-1 are plots of ammonium vs. pH for each of the batch reactions. These trials each use of combination of aeration followed by lye addition for pH control. Aeration at a power of 0.036 Watts is conducted first for a set duration and then NaOH added to complete the pH adjustment to above 9.75.

The ammonia vs. pH plots also contain a plot of ammonium ion vs. pH under theoretical acid/ base speciation conditions. This plot allows for reference of the measured ammonium concentration.

Table 7 displays a summary of data collected and calculated during aeration and lye struvite preparation trials.

"Acidity" is defined as the concentration in millieqivalents per liter of a strong base (NaOH) required to raise a solution pH to a set point. For this investigation, the set point is pH 9.75, determined by trial and error for struvite precipitation. Figure 32 shows a plot of post aeration solution acidity vs. specific aeration energy for the aeration trials.

Directly proportional to the acidity is a factor termed "specific alkaline addition" defined here as the mass of NaOH per liter of supernatant needed to raise pH to the operational set point (9.75) for struvite precipitation. This specific alkaline addition is a more useful term than acidity for financial analysis and for operational calculations. Figure 33 shows a plot of specific alkaline addition vs. aeration energy and also includes a plot of ammonia reduction vs. aeration energy.

Table 7: Summary of Struvite Precipitation Analysis

Struvite batch	Initial Ammonia to Phoshpate Ratio	Ammonia Reduction	Phosphate Reduction	Aeration pH Adjustment	Chemical pH Adustment	Calculated Acidity (after Aeration)	recovered solids molar ratio	Recovered Solid Phosphate "Purity"	Recovered Solid Ammonium "Purity"
#	$[NH_4^+]$: $[PO_4^{3-}]$	%	%	kWh/ L-Supernatant	g NaOH/ L supernatant	mequivalents [OH-]	$[PO_4^{3-}]$: [NH4+]	%	%
13	4.73	80.35	84.03	0	5	125	not analyzed	82%	57%
14	15.8	86.37	96.59	0	6.72	168	1.3	56%	61%
15	11	83.9	96.6	0	6.93	173	1.06	97%	43%
16	12.8	93.31	93.52	0.012	2.4	60	1.17	70%	39%
17	9.78	95.53	96.35	0.0105	1.65	41	2.94	40%	58%
18	10.78	91.85	95.85	0.0103	1.6	40	2.31	49%	49%
19	7.9	90.3	95.63	0.0072	2.88	72	0.89	44%	66%
20	11.69	87.86	96.86	0.0082	3.45	86	1.27	45%	56%
21	8.4	92.44	94.83	0.024	2.23	57	0.85	63%	45%
22	11.5	89.71	95	0.024	2.27	60	1.03	82%	44%

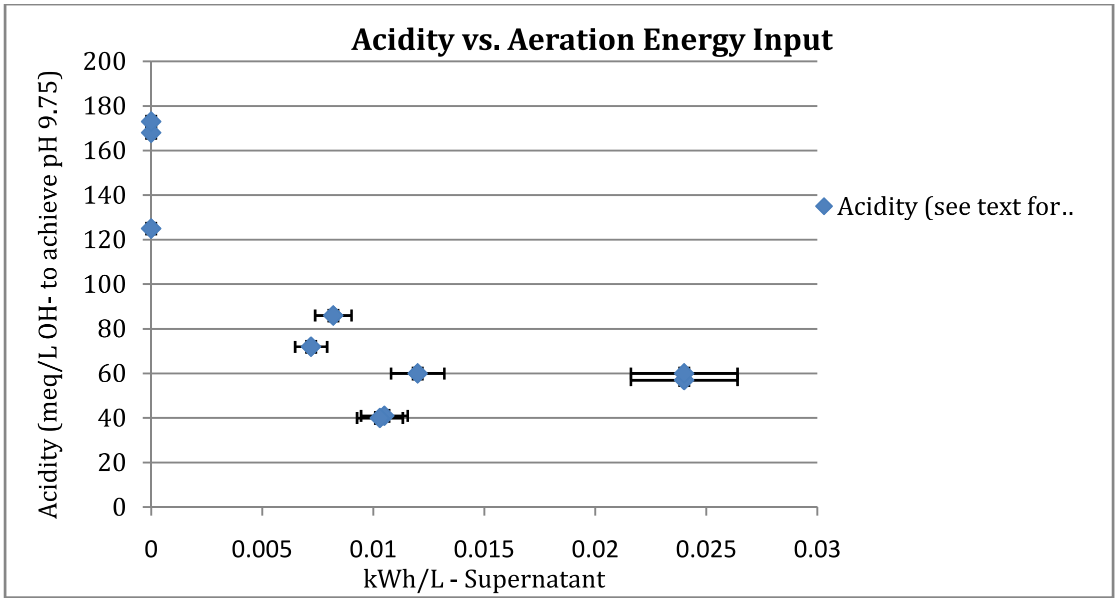


Figure 32: Acidity Analysis for Struvite Aeration Tests

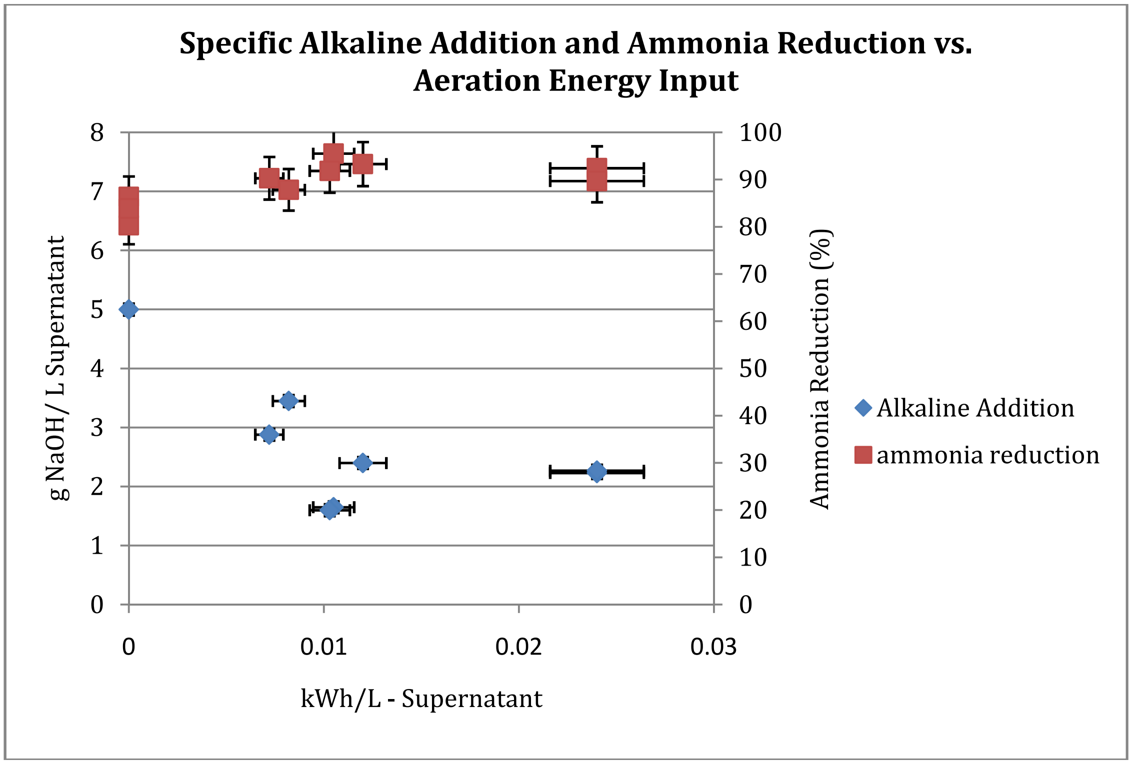


Figure 33: Alkaline Addition and Ammonia Reduction Analysis

Another graphical representation of the differences in acidity affected by aeration is shown on Figure 34. A titration curve for each of the trials is plotted on the same graph. Referencing Table 7 for each trial and the specific aeration energy, it can be clearly seen that the trials with no aeration (#13-#15) have less steep titration curves than those with extended aeration (#19-#20).

The results of the aeration trials show a relationship between aeration energy input and acidity with very little affect on the reduction of ammonia in the final solution supernatant. Aeration of the batch reaction solution clearly reduces the acidity and the specific alkaline addition needed to subsequently raise the pH to the struvite precipitation target. The acidity vs. aeration energy curve shown in Figure 32 appears to be moving toward an asymptotic shape. This would make sense as there is a finite mass of carbonic acid (and perhaps other volatile compounds contributing to acidity) to be removed. Thus, some guidance from this study can be gained towards optimizing aeration energy to minimize reactor size and aeration electricity while maximizing acidity reduction. For our small reactor size and tiny aeration power, approximately 0.5 hours of aeration resulting in approximately 0.010 – 0.012 kWh/ L of supernatant appears optimal. It would be expected that full scale systems would achieve similar mass transfer rates with greater efficiency resulting from larger blowers.

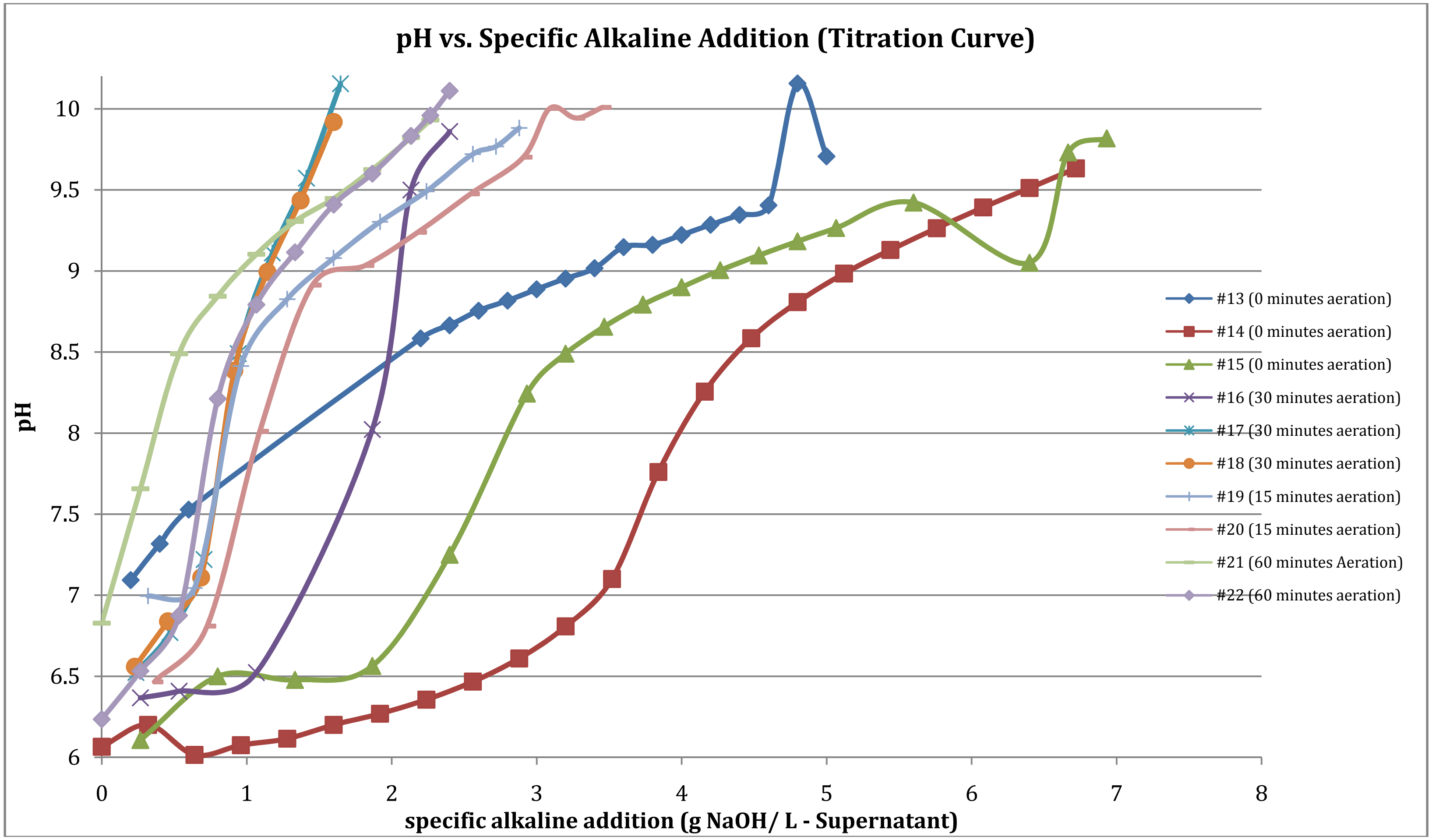


Figure 34: Titration Curves for Struvite Aeration Tests

While the reduction in acidity through aeration is clearly demonstrated, confirmation of the retention of the ammonia resource has proven more difficult. Examination of the ammonium vs. pH plots clearly show that as the pH is raised, something is occurring other than simple acid/ base speciation change from ammonium ion to ammonia. While our hope is that the difference between the observed ammonium vs. pH plot is attributed to precipitation and recovery, there is the possibility that volatilization has occurred.

Characterization of the precipitate product can give an indication of the presence of struvite and the relative purity of the product. Characterization of the precipitated product was carried out by dissolving a known mass into deioinized (DI) water, reducing pH and measuring phosphate and ammonium concentrations. Included in Table 7 are data which analyze the product. The molar ration of ammonium to phosphate should be 1:1 in a pure struvite product. And, if a known mass of a pure struvite product is dissolved in DI water, the concentrations of ammonium and phosphate should be known.

The “purity” figures shown in Table 7 are the ratio of the observed concentration of ammonium or phosphate divided by the predicted concentration if the precipitate were pure struvite.

The molar ratio of ammonium to phosphate observed in the re-dissolved precipitated solids indicates a significant variability. Several of the samples have a molar ratio of ammonia to phosphate which gives an indication that the ammonia and phosphate present could be from struvite, while others do not. However, analysis of the concentrations of ammonia and phosphate in comparison to a “pure” struvite product indicate that there is a significant mass of solids present which are not struvite.

The fact that ammonia is present in the dissolved product is a great indication that ammonia recovery is occurring, but quantification of this recovery has not been accomplished. Inspecting the ammonium vs. pH curves also gives an indication that ammonium is precipitating rather than volatilizing during aeration because pH remains low (near 6) during the aeration phase and the concentration of volatile ammonia (NH_3) should be low at this pH. Comparison of the data between the aeration batches (#16-24) and the NaOH only batches (#13-15) does not show significant differences in the ammonia: phosphate ration or the purity factors shown on Table 7. This gives further indication that ammonium is precipitating rather than volatilizing.

Although the factors above provide some hope that the desired result, (struvite precipitation rather than ammonia volatilization) is occurring, a strict mass balancing of ammonia species before and after the precipitation would be the best route to quantify recovery. However, the batch reaction process used for the precipitation creates some physical difficulties in recovering the product.

Product was inefficiently recovered through filtration onto glass fiber paper at high energy consumption.

The phosphorus recovery struvite efforts explained in the literature typically use a fluidized bed reactor to accomplish the precipitation, as this configuration encourages crystal growth and ease of the physical recovery of the precipitate. Further efforts in a feasibility study for struvite crystallization for ammonia recovery should move towards this configuration.

6.8 Financial Analysis of Struvite

There has been a continuing adjustment on several levels of financial analysis which have directed the struvite precipitation research throughout this study. The first questions involved an analysis of the economic feasibility of adding large quantities of phosphate to the system, if it was recoverable, and if so would it make financial sense. It was demonstrated that, given current market prices struvite precipitation could not compete as an ammonia removal technology with the current nitrification/ denitrification process at Howard Curren and would likely be far behind more advanced BNR technologies. The initial calculation showed that at current market prices struvite production less its resale value would cost the plant $3.07 per kg of influent nitrogen while the BNR process would cost $1.08 per kg of influent nitrogen.

However, since the struvite process has a marketable product where the others do not, a financial analysis of the potential effect of a general rise in commodity prices. This effect was approximated by simply linearly scaling the current prices of all commodities and examining the effect on struvite feasibility. The results of this exercise showed that the struvite actually became less competitive. Figure 35 displays this result.

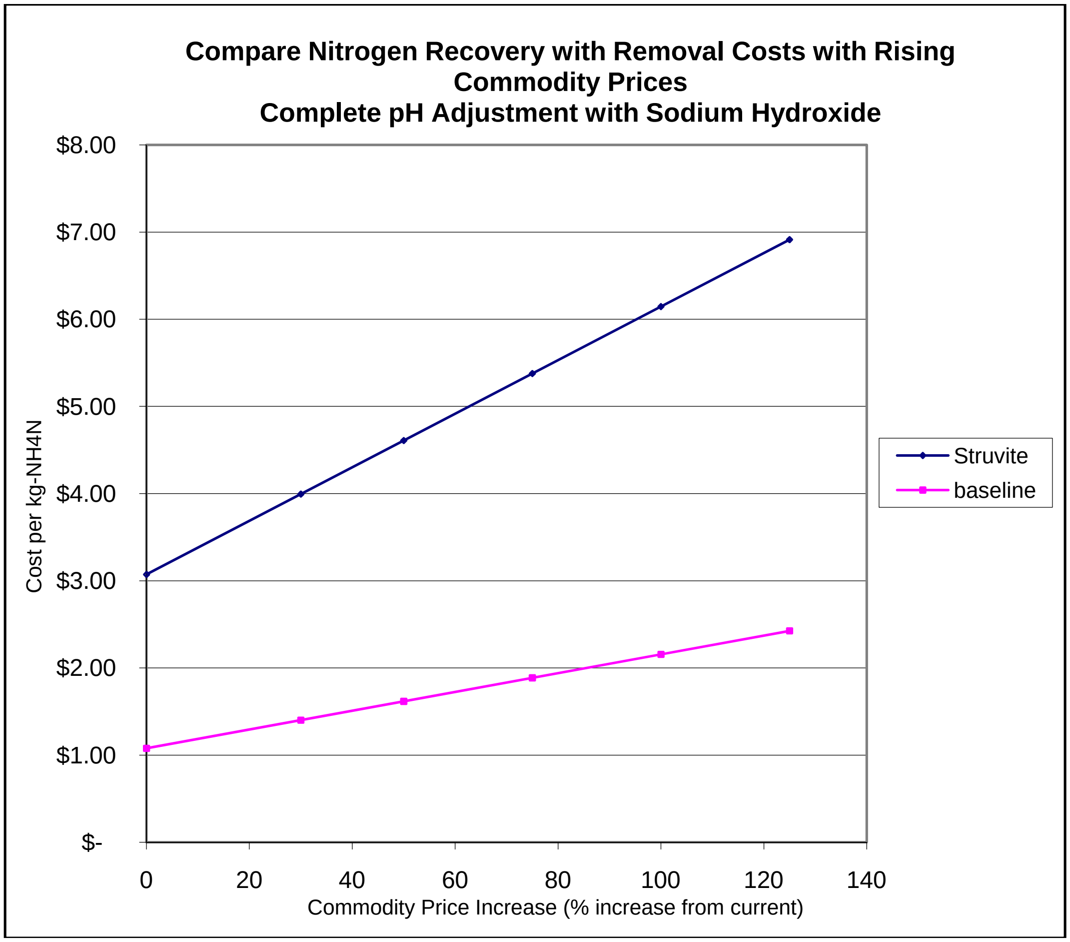


Figure 35: Analysis of Increasing Commodity Prices on Struvite Feasibility

However, it was observed that the pH adjustment costs comprised a large portion of the struvite production costs as shown in Figure 36.

Another level of financial analysis was conducted to evaluate the competitiveness of struvite precipitation if the pH adjustment costs could be reduced through aeration, while keeping a high ammonia recovery for resale.

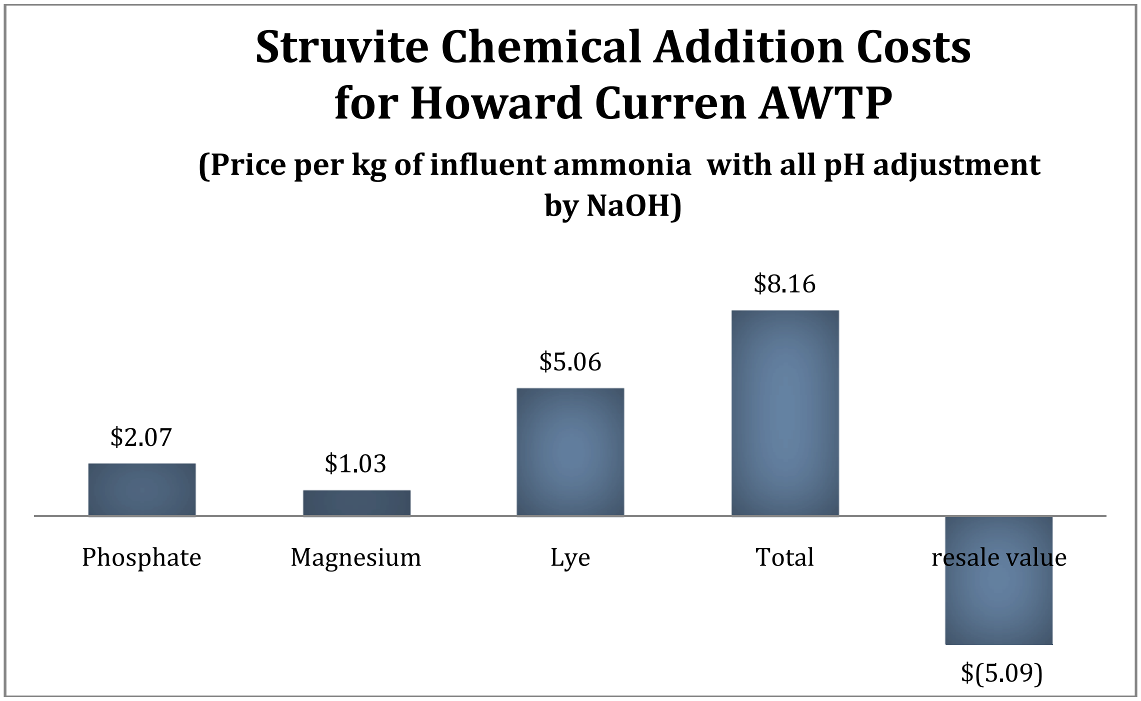


Figure 36: Assessment of Struvite Production Costs

This analysis showed significant promise for the technology both in its immediate competitiveness and also for its potential to buffer against rising commodity prices (see Figures 37 and 38). Figure 37 compares the price per kg-N at current prices if the ph adjustment cots can be reduced by varying percentages. Figure 38 shows that if pH can be cut to 40% of the full lye addition cost now, struvite production costs will not increase with rising commodity prices. This analysis encouraged the further experimentation into aeration and pH reduction described above.

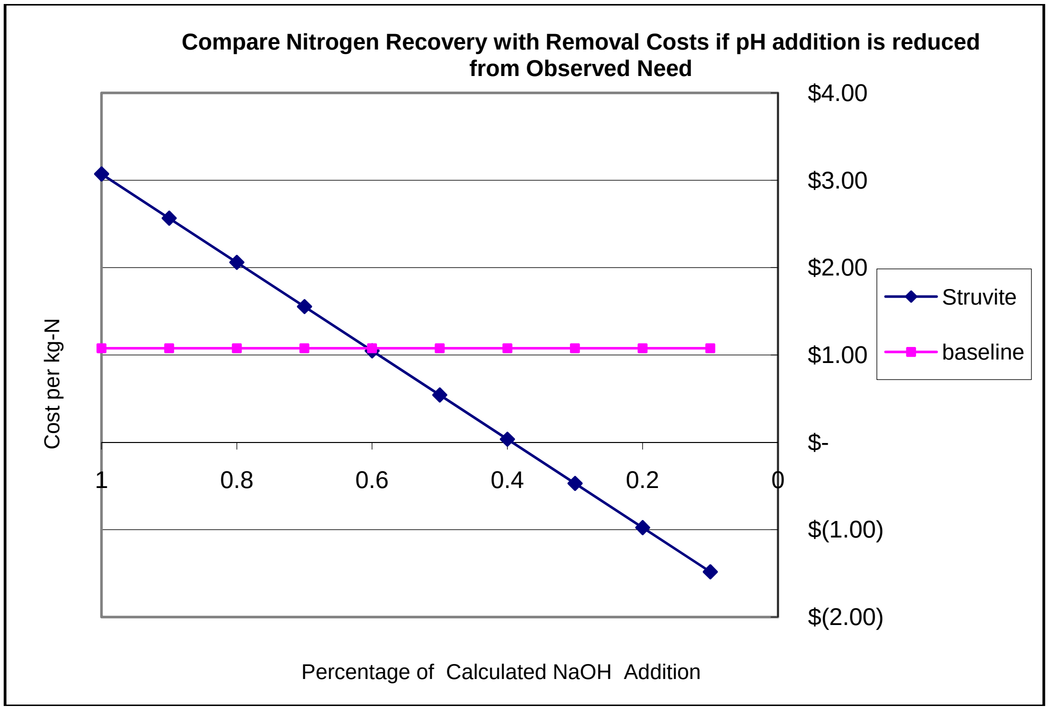


Figure 37: Assessment of pH Chemical Reduction Effects

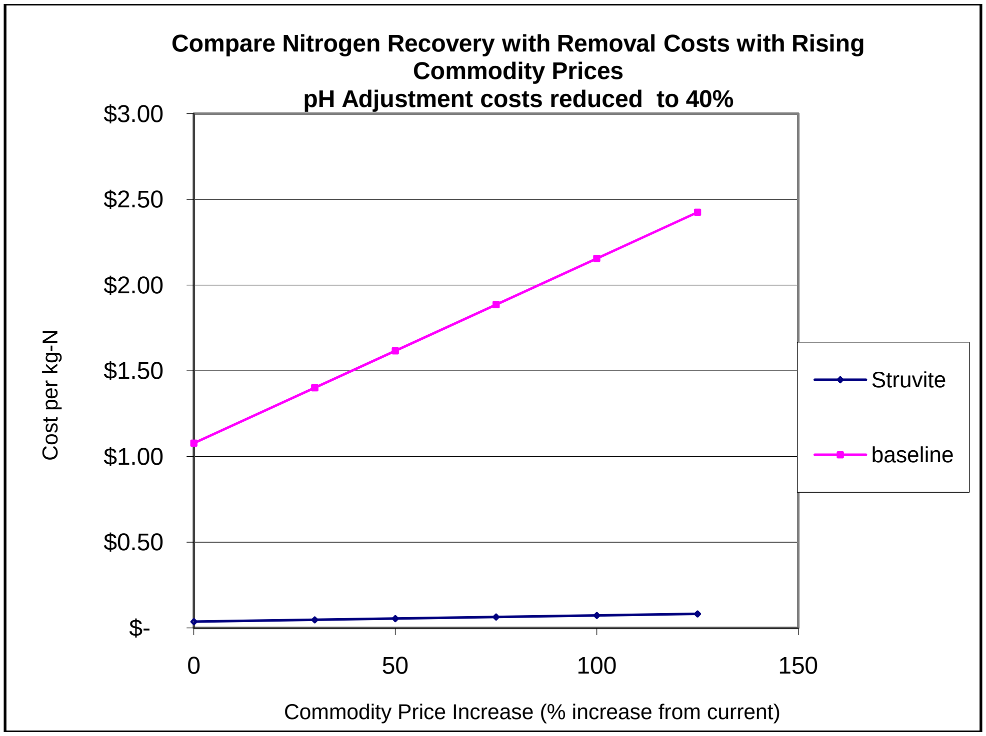


Figure 38: Rising Commodity Prices with Reduced pH Cost

A final effort at financial analysis has been conducted, incorporating all of the data collected during this investigation, including optimized aeration energy, specific alkaline addition, Howard Curren plant flow data, and estimates of phosphate and ammonia recovery percentages. Input parameters are shown in Table 8. The results of this analysis are shown in Figure 39. It should be noted that ammonia and phosphate recovery percentages were estimated from ammonia and phosphate removal rates observed in this study and recovery rates from previous literature. Quantification of the recovery rates in this study has not been accomplished. The financial feasibility is highly dependent on high recovery rates. The estimate in Figure 39 uses 90% recovery for both ammonia and phosphate and the financial feasibility of struvite recovery would be seriously compromised with significant reductions in this estimate.

Table 8: Input Parameters for Financial Analysis

Parameter	Value	Unit
Ammonia Concentration	1000	mg/L
Magnesium Concentration	100	mg/L
Phosphate Concentration	200	mg/L
Supernatant Flow rate	1000000	L/ day
Magnesium Unit Cost	0.5	$/kg Mg
Phosphate Unit Cost	0.5	$/kg Phoshpate
pH Adjustment Unit Cost	0.46	$/kg NaOH
pH Adjustment Requirement	1.6	g NaOH/ L Supernatant
phosphate recovery	0.9	percentage
ammonia recovery	0.9	percentage
resale value of struvite	1	$/kg N +P
Electricity Costs	0.11	$/kWh
Methanol Costs	1.5	$/ gallon
Aeration Power Requirement	0.005	kWh/ L Supernatant

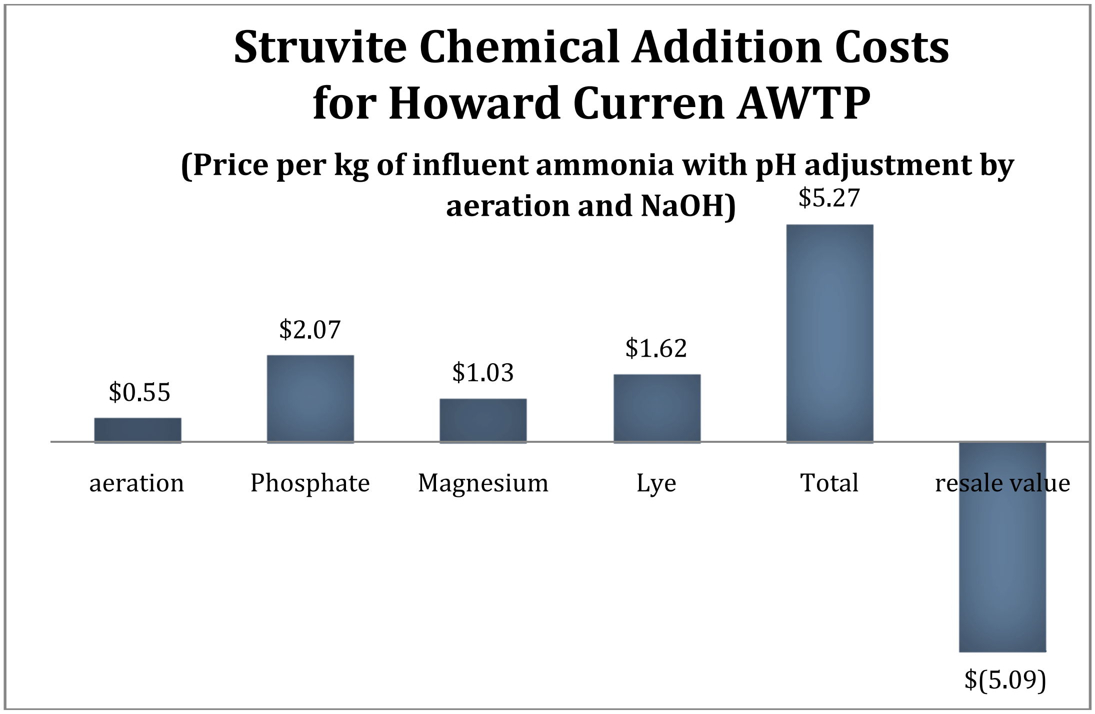


Figure 39: Resulting Financial Analysis from this Study
(with Nitrogen and Phosphorus Recovery Values from Literature)

7 Conclusions

From the literature review and data collected during this investigation, the following conclusions are made.

- As would intuitively be expected, the solids side of the typical waste water treatment plant is the place to look for resource recovery. Given the high flow rates and dilute resource concentrations on the liquid side, it is expected that it will be a long time before resource recovery considerations will compete with current removal technologies.
- Firm conclusions from the phosphate release study at the Largo Treatment Plant are difficult due to the enormous amount of variables which cannot be controlled when analyzing a treatment plant. However some observations can be made.
- Phosphorus release rates during the end of the week are slightly more rapid than the phosphorus release rates at the beginning of the week. This may be attributable to a higher percentage of PAO who have experienced short retention time and have retained the rapid phosphorus release characteristic acquired during the aerobic/ anaerobic cycling in the A2O system

- As sludge remains in the digester over the three day weekend period, it appears that phosphorus is released. This release may be a result of extended aeration of the PAO’s and release of the Poly-P during the extended periods with ample electron acceptors.
- Total phosphorus release during the anaerobic settling and thickening process during post digestion sludge handling at the Largo AWTP does not appear to release a significant percentage of the total phosphate in the digester sludge. Based on the data collected in six trials, 98.4-99.5% of the total phosphate is retained in the solid form during the settling process.
- The sludge at the Largo Treatment plant appears to settle to its fullest extent within 45 minutes to 1 hour. Although phosphorus release rates are relatively slow at this time, phosphate recovery can be maximized by limiting retention time in the settler to a minimum.
- Aeration has a clear effect on acidity and therefore the quantity of lye needed to raise the pH of a supernatant based struvite precipitation solution.
- Phosphate was added to the batch reaction solutions in order to increase the phosphate molar concentration to equal the ammonium concentration. Based on analysis of dissolved phosphate the conclusion of the batch tests, it appears that the added phosphate was removed and available for recovery as a precipitate.
- Struvite recovery could become financially feasible if the ammonia recovery rate can be kept high, while reducing lye addition for pH control. Further, if

struvite can be made financially feasible now, it will buffer plant operations against rising commodity prices in the future.

- Further study is needed to quantify the ammonia recovery and ammonia volatilization during the aeration process. There were data several indicators collected during this investigation that ammonium is precipitating rather than volatilizing during the batch reaction process, however a strict material balance on all ammonium species would be desirable.

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Appendices

Appendix A-1: Mass Balance Worksheets

WORKSHEET 1: Resource Partitioning Between Solids and Liquid

	Total Plant Flow (gal/day)	Total Primary Sludge Flow (gal/day)	Total WAS Sludge Flow (gal/day)	Total Flow to Solids (gal/day)	Total Flow to Liquids (gal/day)	Total Plant Flow (L/day)	Total Flow to Solids (L/day)	Total Flow to Liquids (L/day)	Flow to Solids %	Flow to Liquids %
Howard Curren	50,000,000	196,923	221,170	418,093	49,581,907	189000000	1580391.54	187419608.5	0.8%	99.2%
Largo	12,000,000	156,964	119,103	276,067	11,723,933	45360000	1043533.26	44316466.74	2.3%	97.7%

	Resource	Total Mass per Day - PE (kg/day)	Total Mass per Day - PS (kg/day)	Total Mass per Day- WAS (kg/day)	Total Mass/Day - Solids (kg/day)	Total Mass/ Day - Liquids (kg/day)	Resource to Solids %	Resource to Liquids %
Howard Curren	Nitrogen	7216	1045	2708	3753	4508	45%	55%
	Phosphorus	2483	1223	3312	4535	-829	122%	-22%
Largo	Nitrogen	1839	461	417	878	1422	38%	62%
	Phosphorus	842	522	753	1275	89	93%	7%

Calculation of Total Mass in Primary Effluent

		Total Eff (mg/L)	Peff Total (kg/day)
Howard Curren	Nitrogen	38.5	7216
	Phosphorus	13.25	2483
Largo	Nitrogen	41.5	1839
	Phosporus	19	842

Appendix A-1 (Continued)

Worksheet 2

Nitrogen Balance at HCAWTP

		Color Scheme
Sample Date	December	Plant Data
Sample Location	Howard Curren	Lab Analysis
Notes		Calculated Value

CALCULATION OF NITROGEN FLOW RATES

SLUDGE SAMPLES

Sample	Flow Rate (gallons/day)	Total Average Flow Rate (liters/ day)	Total Suspended Solids (mass solid/ volumesludge) (mg/L)	Total Liquid (volume liquid/ volume sludge)	Mixed Liquor Total Nitrogen (mg/L)	Supernatant Total Nitrogen (mg/L)	Total Nitrogen (kg/day)	Liquid Total Nitrogen(kg/day)	Solid Total Nitrogen (kg/day)
PS	196,923	744369	38,185	0.961815	1404	42	1045	30	1015
WAS	221,170	836023	37,345	0.962655	3240	247	2709	199	2510
ES	423,233	1599821	19,595	0.980405	2842	1531	4547	2401	2145

GAS SAMPLES

NITROGEN BALANCES

Total PS In (kg/day Nitrogen)	Total WAS In (kg/day Nitrogen)		Total ES Out (kg/day Nitrogen)	Total Gas Out (kg/day Nitrogen)	Total Out/ Total In
1045	2709	=	4547	0	1.2

NITROGEN PARTITIONING

	kg/day	percentage of influent	
Total N In	3754	100%	
Total Dissolved N In	229	6%	
Total Solid N In	3525	94%	
			Percentage of Effluent
Total N Out	4547	121%	
Total Dissolved N Out	2401	64%	53%
Total Solid N Out	2145.4	57%	47%
Total Gas NOut	0	0%	0%

Appendix A-1 (Continued)

Worksheet 3

Phosphate Balance at HCAWTP

Sample Date	December
Sample Location	Howard Curren
Notes	

Color Scheme
Plant Data
Lab Analysis
Calculated Value

CALCULATION OF PHOSPHORUS FLOW RATES

SLUDGE SAMPLES

Sample	Flow Rate (gallons/day)	Total Average Flow Rate (liters/ day)	Total Suspended Solids (mass solid/ volumesludge) (mg/L)	Total Liquid (volume liquid/ volume sludge)	Mixed Liquor Total Phosphate (mg/L)	Supernatant Total Phosphate (mg/L)	Total Phosphate (kg/day)	Liquid Total Phosphate (kg/day)	Solid Total Phosphate (kg/day)
PS	196,923	744369	38,197	0.961803	1643	79	1223	57	1166
WAS	221,170	836023	37,109	0.962891	3962	210	3312	169	3143
ES	423,233	1599821	19,175	0.980825	1957	249	3131	391	2740

GAS SAMPLES

PHOSPHATE BALANCES

Total PS In (kg/day Phosphate)	Total WAS In (kg/day Phosphate)		Total ES Out (kg/day PO4)	Total Gas Out (kg/day PO4)		Total Out/ Total In
1223	3312	=	3131	0		0.69

PHOSPHATE PARTITIONING

	kg/day	percentage of influent
Total PO4 In	4535	100%
Total Dissolved PO4 In	226	5%
Total Solid PO4 In	4310	95%

			Percentage of Effluent
Total PO4 Out	3130.849188	69%	
Total Dissolved PO4 Out	390.7169002	9%	12%
Total Solid PO4 Out	2740.1	60%	88%
Total Gas PO4 Out	0	0%	0%

Appendix A-1 (Continued)

WORKSHEET 4

Nitrogen Balance at LGAWTP

		Color Scheme
Sample Date	1/29/2009	Plant Data
Sample Location	Largo	Lab Analysis
Notes		Calculated Value

CALCULATION OF NITROGEN FLOW RATES

SLUDGE SAMPLES

Sample	Flow Rate (gallons/day)	Total Average Flow Rate (liters/ day)	Total Suspended Solids (mass solid/ volumesludge) (mg/L)	Total Liquid (volume liquid/ volume sludge)	Mixed Liquor Total Nitrogen (mg/L)	Supernatant Total Nitrogen (mg/L)	Total Nitrogen (kg/day)	Liquid Total Nitrogen (kg/day)	Solid Total Nitrogen (kg/day)
PS	156964	593324	21,931	0.978069	777	39	461	23	438
WAS	119103	450209	11,116	0.988884	926	4	417	2	415
ES	276066	1043529	10,796	0.989204	802	10	837	10	827

GAS SAMPLES

Nitrogen BALANCES

Total PS In (kg/day Nitrogen)	Total WAS In (kg/day Nitrogen)		Total ES Out (kg/day Nitrogen)	Total Gas Out (kg/day Nitrogen)	Total Out/ Total In
461	417	=	837	0	0.95

Nitrogen PARTITIONING

	kg/day	percentage of influent	percentage of effluent
Total Nitrogen In	878	100%	
Total Dissolved Nitrogen In	24	3%	
Total Solid Nitrogen In	853	97%	
Total Nitrogen Out	837	95%	
Total Dissolved Nitrogen Out	10	1%	1.2%
Total Solid Nitrogen Out	826.6	94%	98.8%

Appendix A-1 (Continued)

Worksheet 5

Phosphate Balance at LGAWTP

		Color Scheme
Sample Date	1/29/2009	Plant Data
Sample Location	Largo	Lab Analysis
Notes		Calculated Value

CALCULATION OF PHOSPHORUS FLOW RATES

SLUDGE SAMPLES

Sample	Flow Rate (gallons/day)	Total Average Flow Rate (liters/ day)	Total Suspended Solids (mass solid/ volumesludge) (mg/L)	Total Liquid (volume liquid/ volume sludge)	Mixed Liquor Total Phosphate (mg/L)	Supernatant Total Phosphate (mg/L)	Total Phosphate (kg/day)	Liquid Total Phosphate (kg/day)	Solid Total Phosphate (kg/day)
PS	156964	593324	21,931	0.978069	880	59	522	34	488
WAS	119103	450209	11,116	0.988884	1671	109	752	49	704
ES	276066	1043529	10,796	0.989204	1307	161	1364	166	1198

GAS SAMPLES

PHOSPHATE BALANCES

Total PS In (kg/day Phosphate)	Total WAS In (kg/day Phosphate)		Total ES Out (kg/day Phosphate)	Total Gas Out (kg/day Phosphate)		Total Out/ Total In
522	752	=	1364	0		1.07

PHOSPHATE PARTITIONING

	kg/day	percentage of influent	percentage of effluent
Total Phosphate In	1274	100%	
Total Dissolved Phosphate In	83	6%	
Total Solid Phosphate In	1192	94%	
Total Phosphate Out	1364	107%	
Total Dissolved Phosphate Out	166	13%	12.2%
Total Solid Phosphate Out	1198	94%	87.8%

Appendix B-1: Struvite Batch Reaction Plots

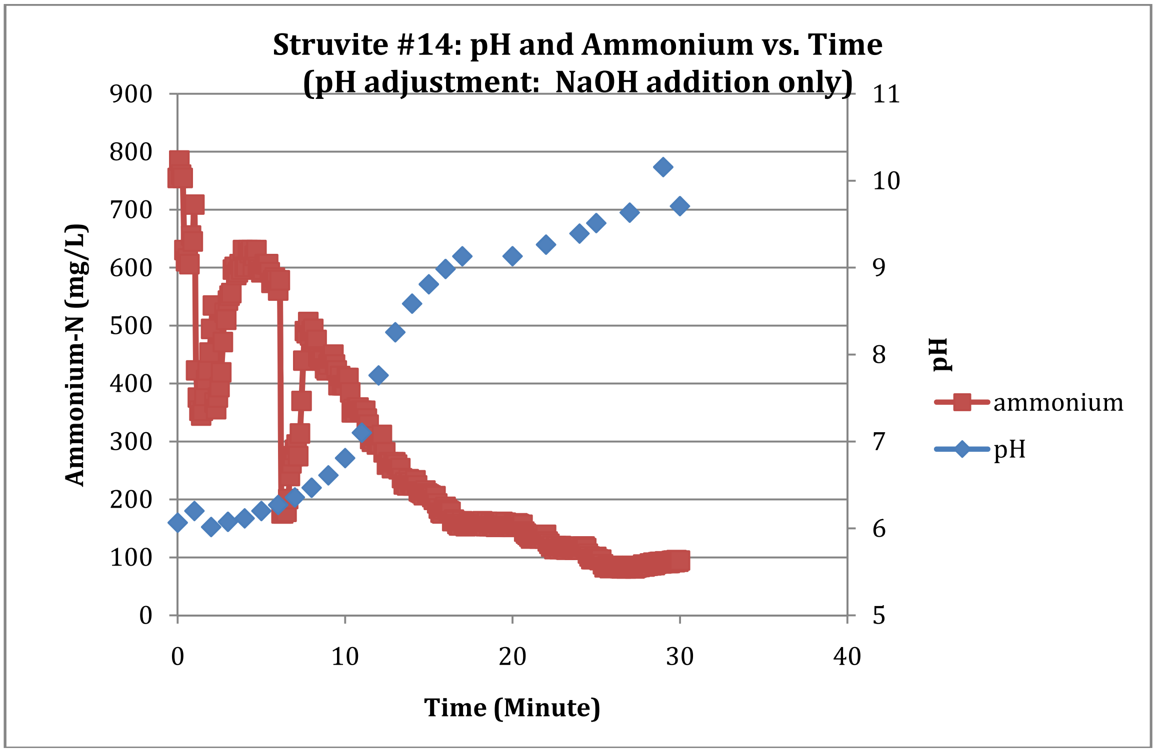

Figure 40: Struvite #14 pH and Ammonium vs. Time

Appendix B-1 (Continued)

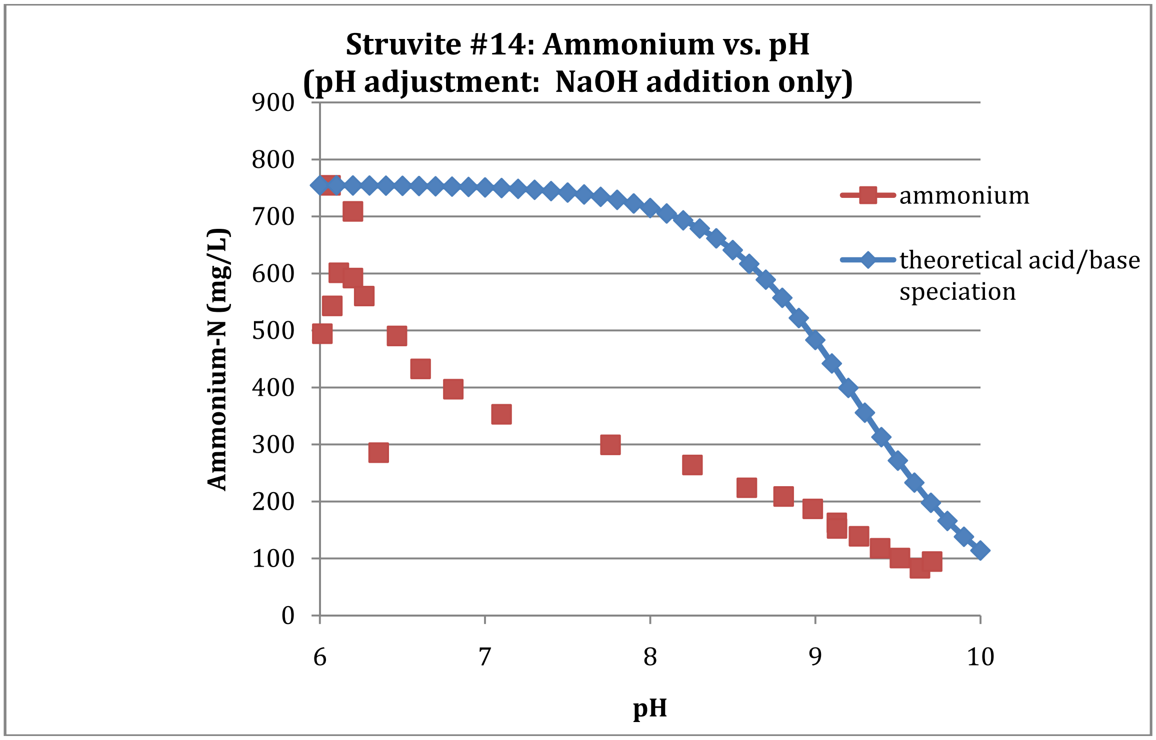

Figure 41: Struvite #14 Ammonium vs. pH

Appendix B-1 (Continued)

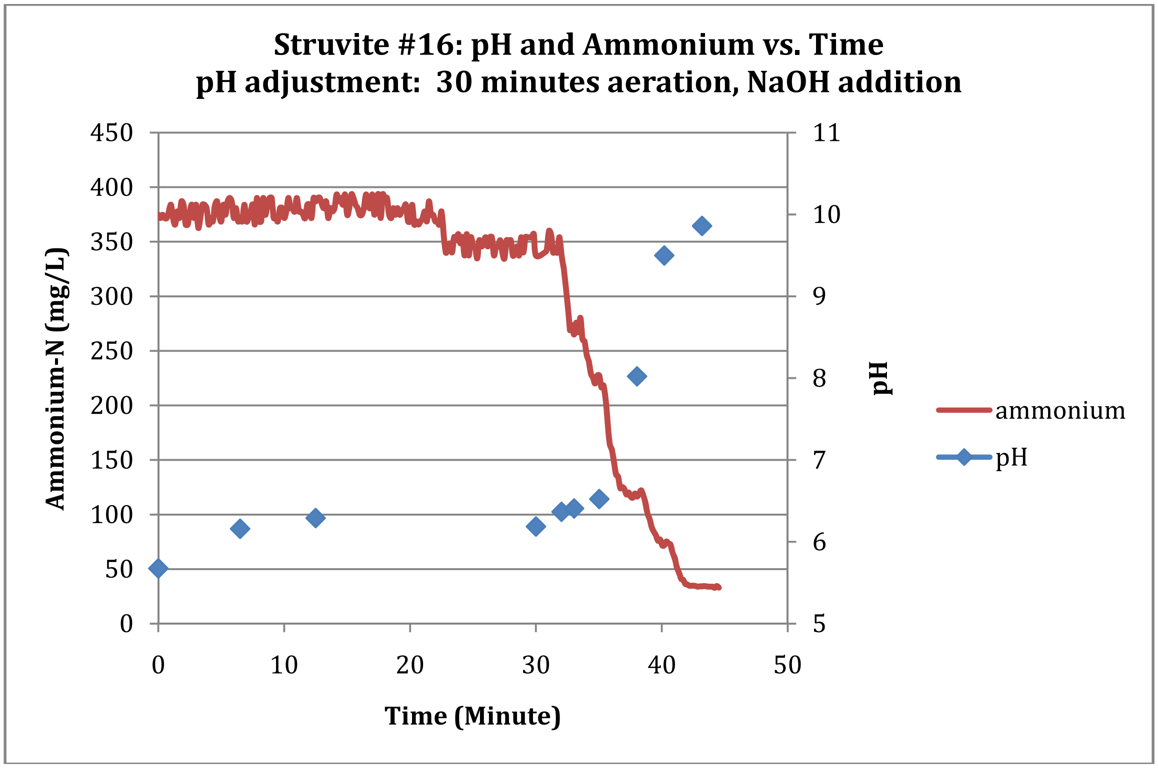

Figure 42: Struvite #16 pH and Ammonium vs. Time

Appendix B-1 (Continued)

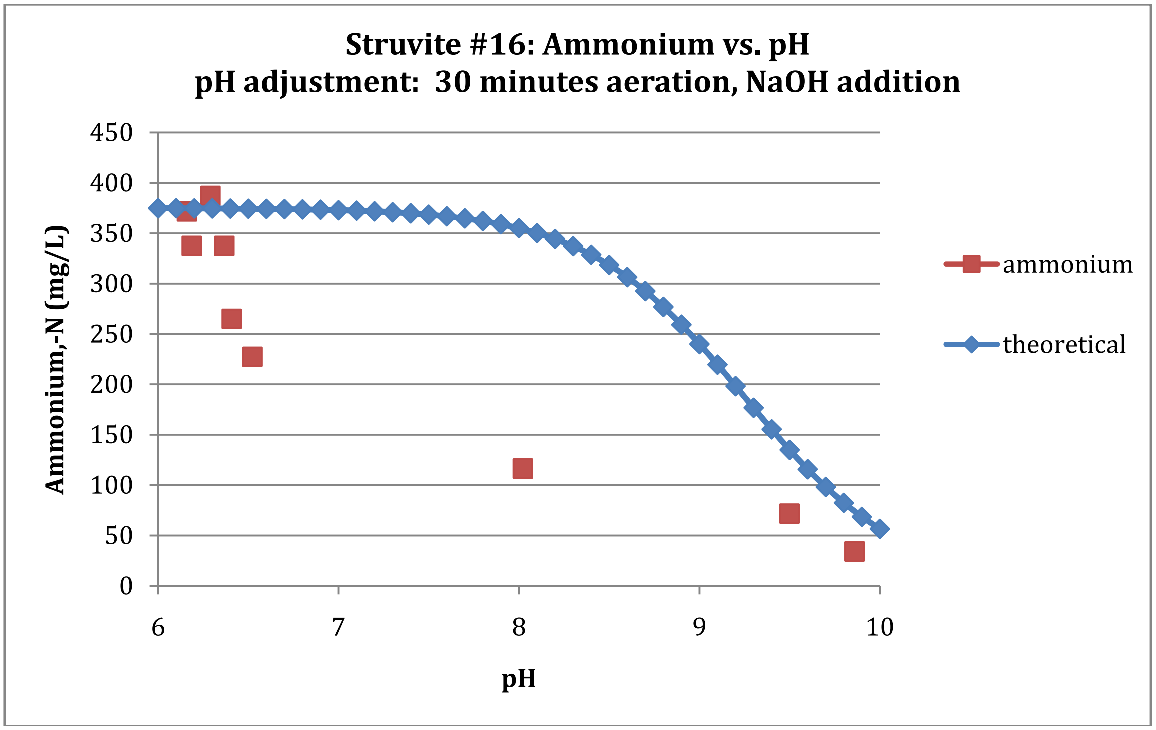

Figure 43: Struvite #16 Ammonium vs. pH

Appendix B-1 (Continued)

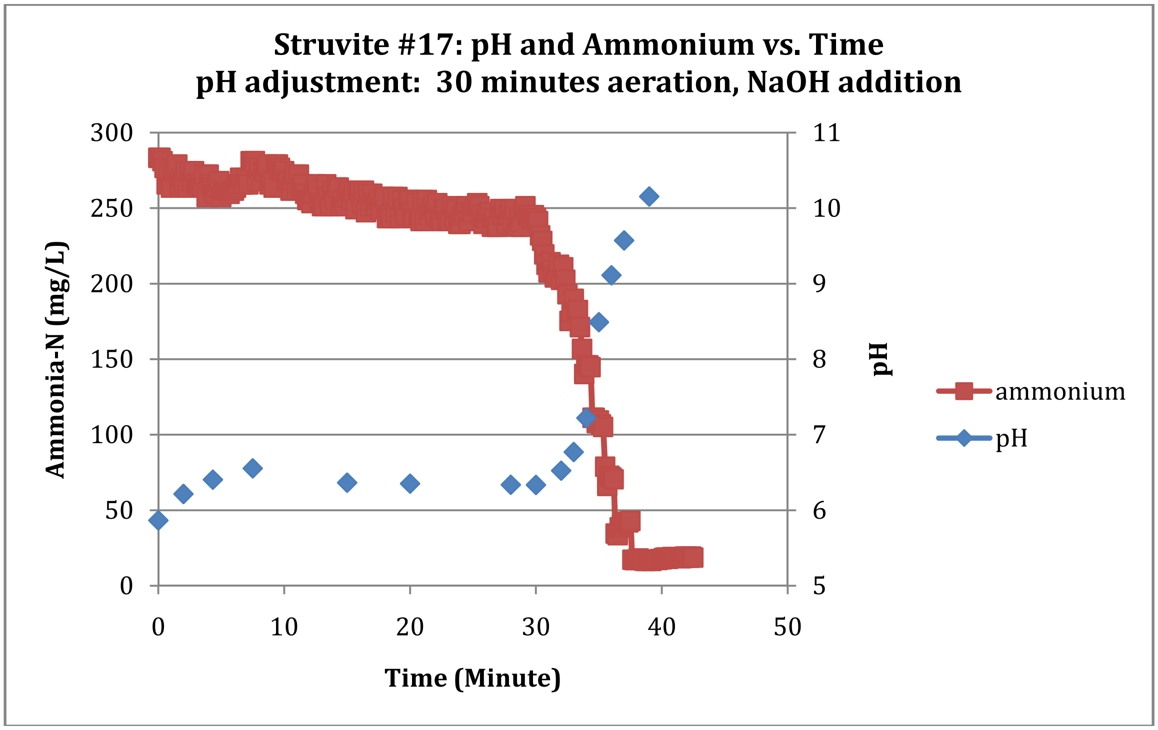

Figure 44: Struvite #17 pH and Ammonium vs. Time

Appendix B-1 (Continued)

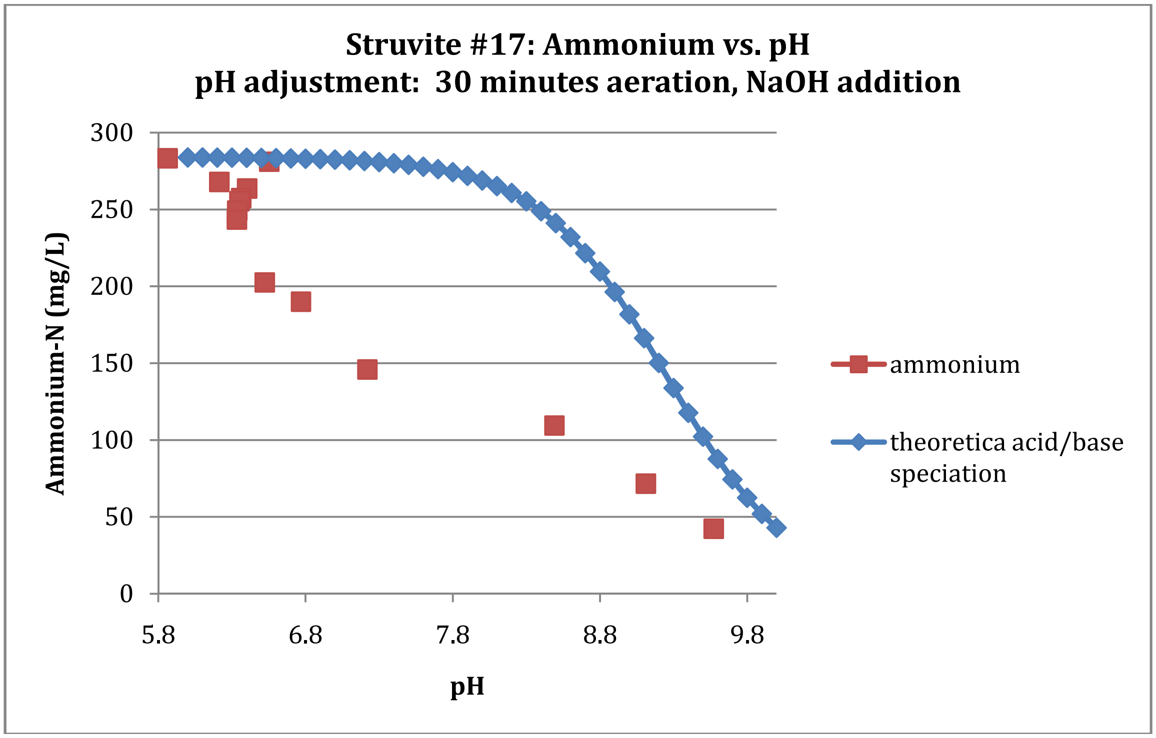

Figure 45: Struvite #17 Ammonium vs. pH

Appendix B-1 (Continued)

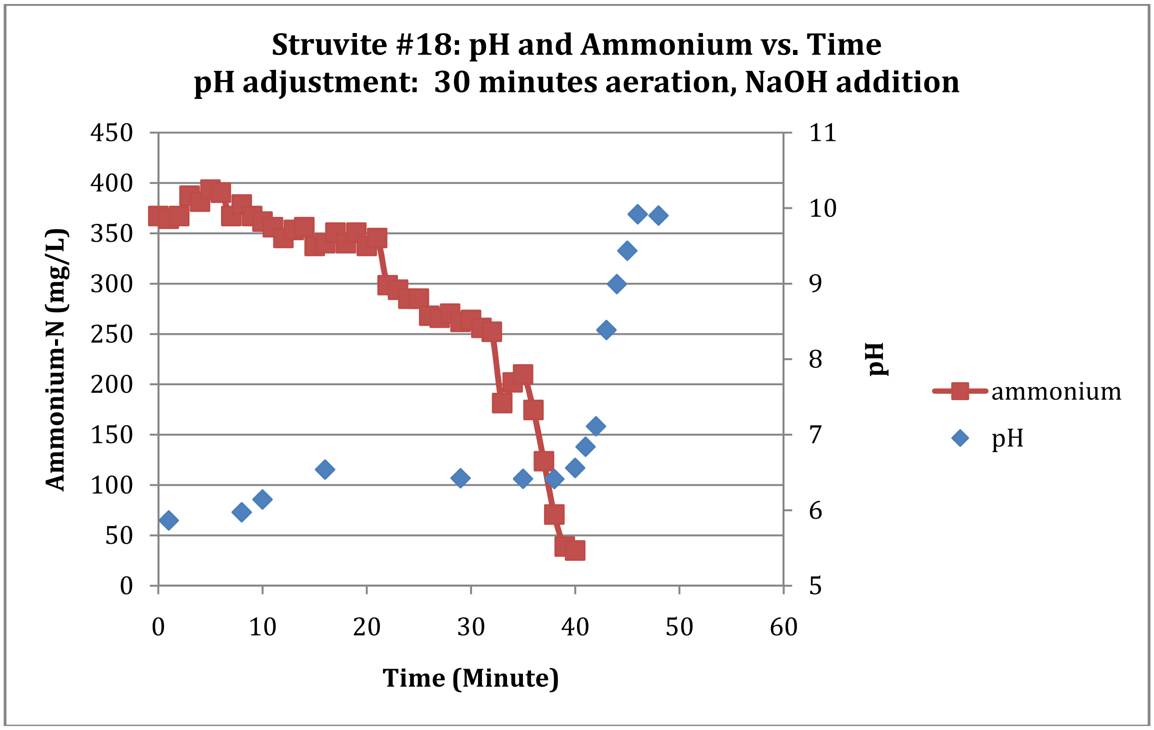

Figure 46: Struvite #18 pH and Ammonium vs. Time

Appendix B-1 (Continued)

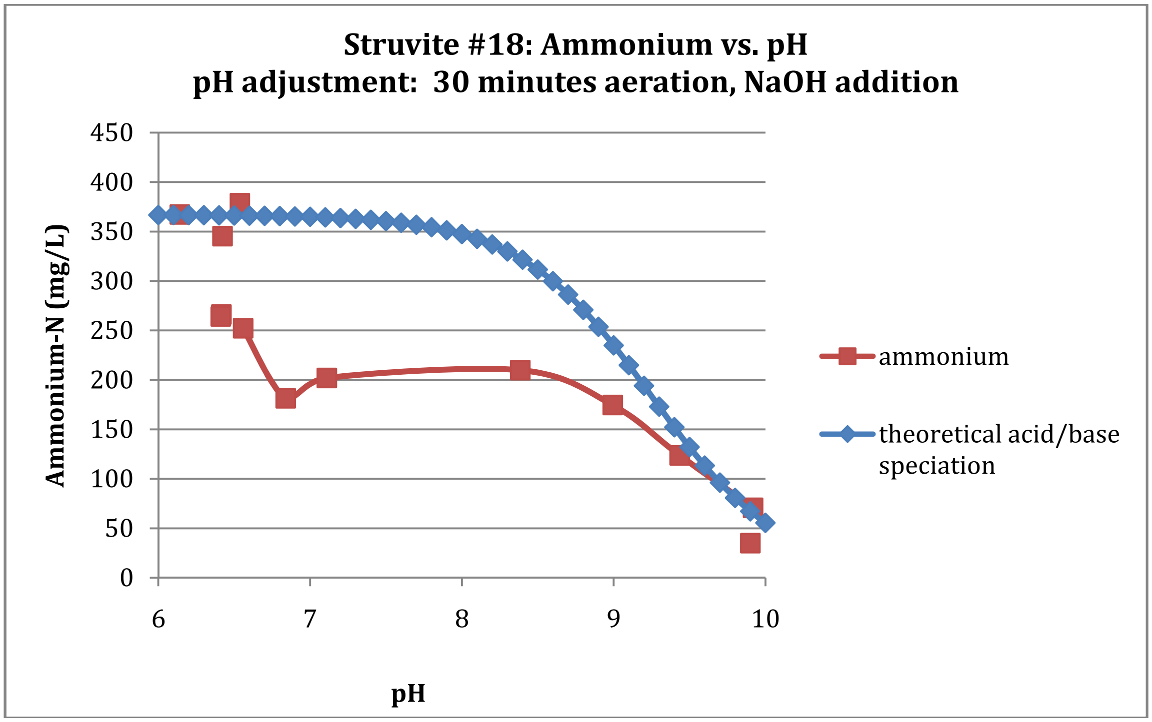

Figure 47: Struvite #18 Ammonium vs. pH

Appendix B-1 (Continued)

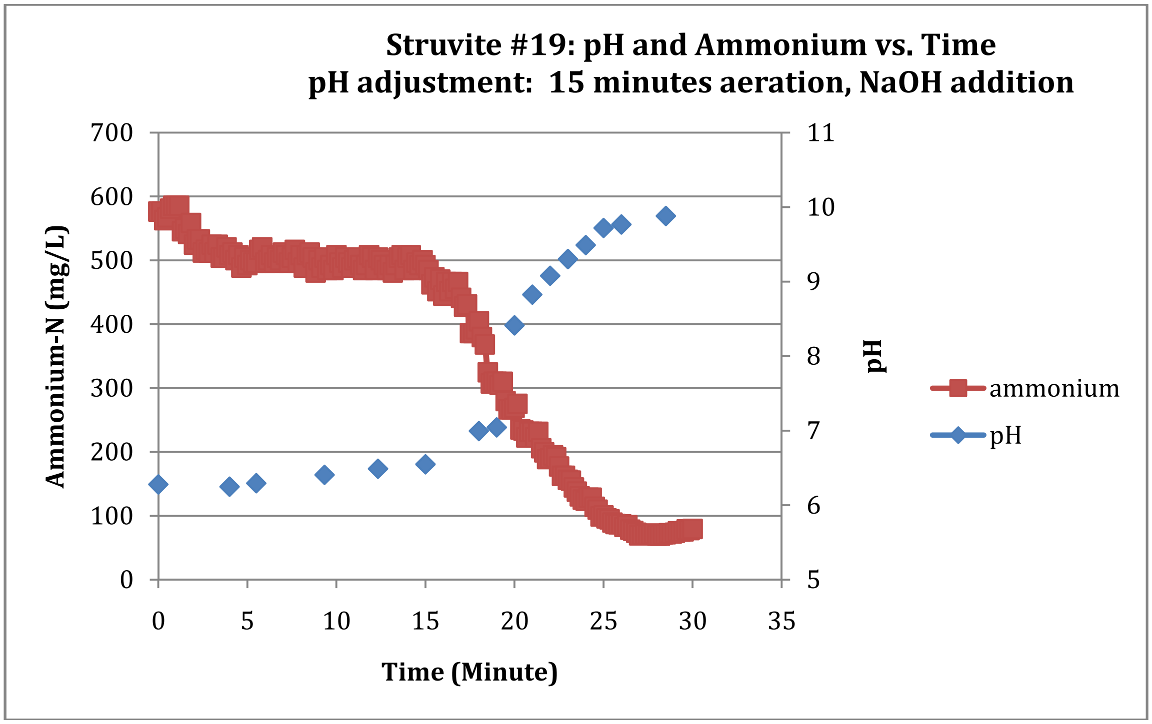

Figure 48: Struvite #19 pH and Ammonium vs. Time

Appendix B-1 (Continued)

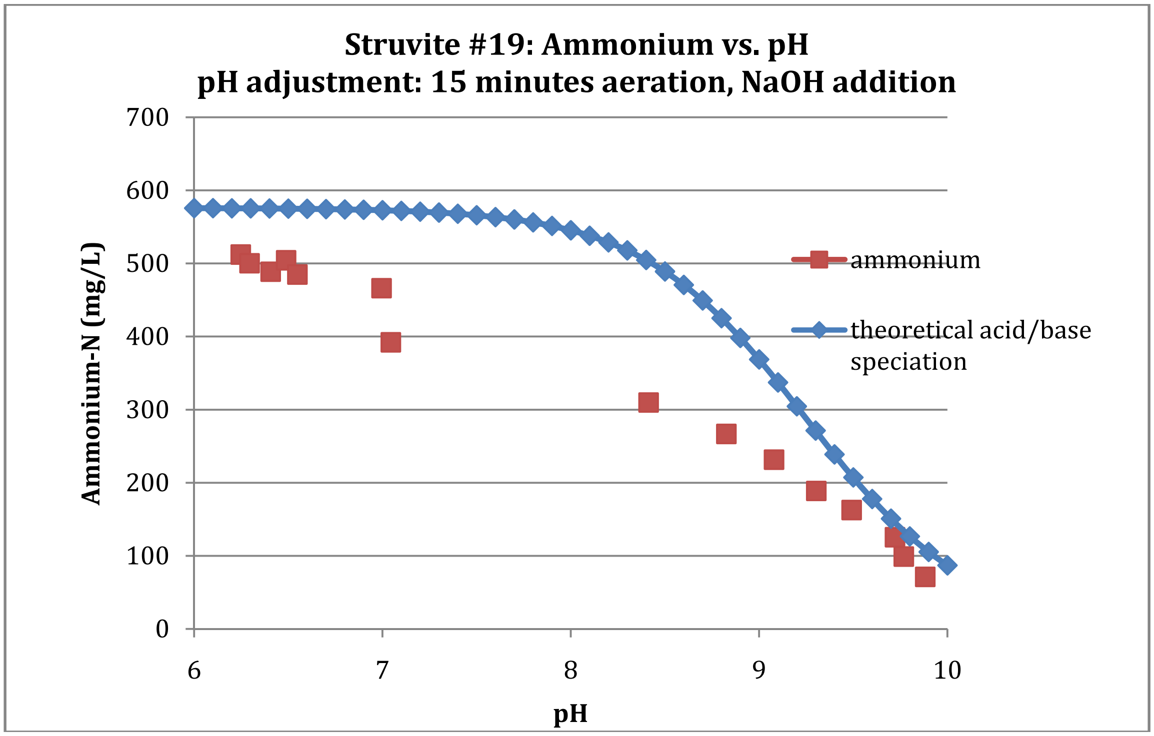

Figure 49: Struvite #19 Ammonium vs. pH

Appendix B-1 (Continued)

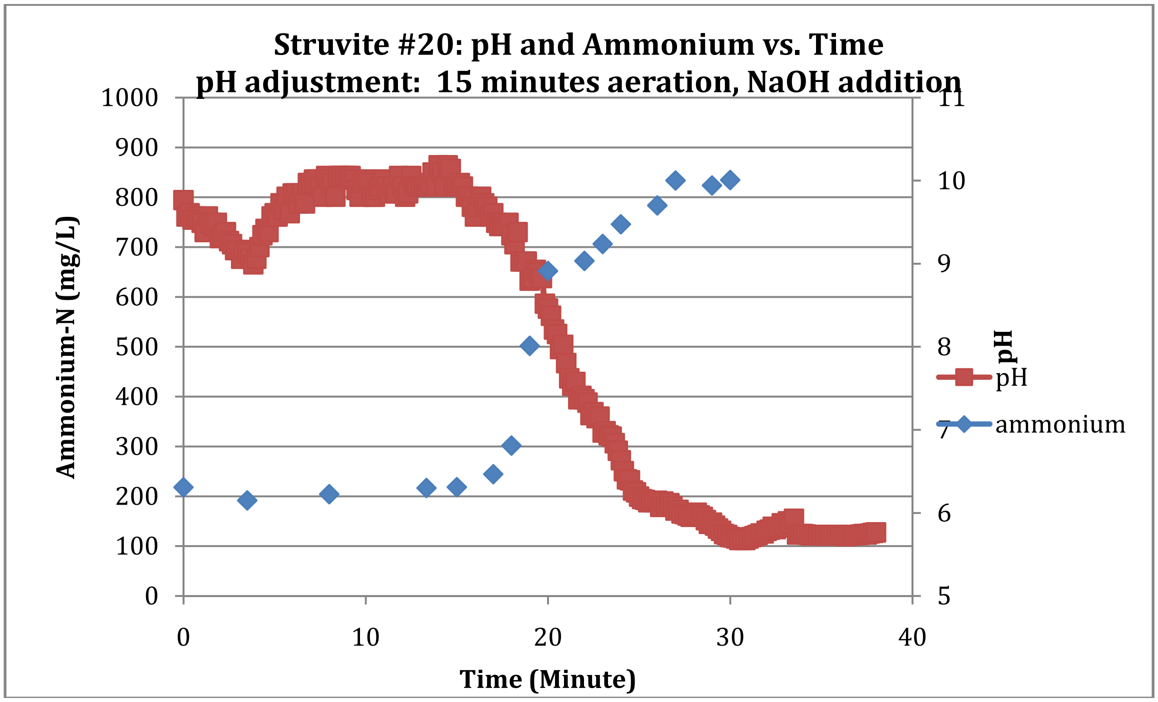

Figure 50: Struvite #20 pH and Ammonium vs. Time

Appendix B-1 (Continued)

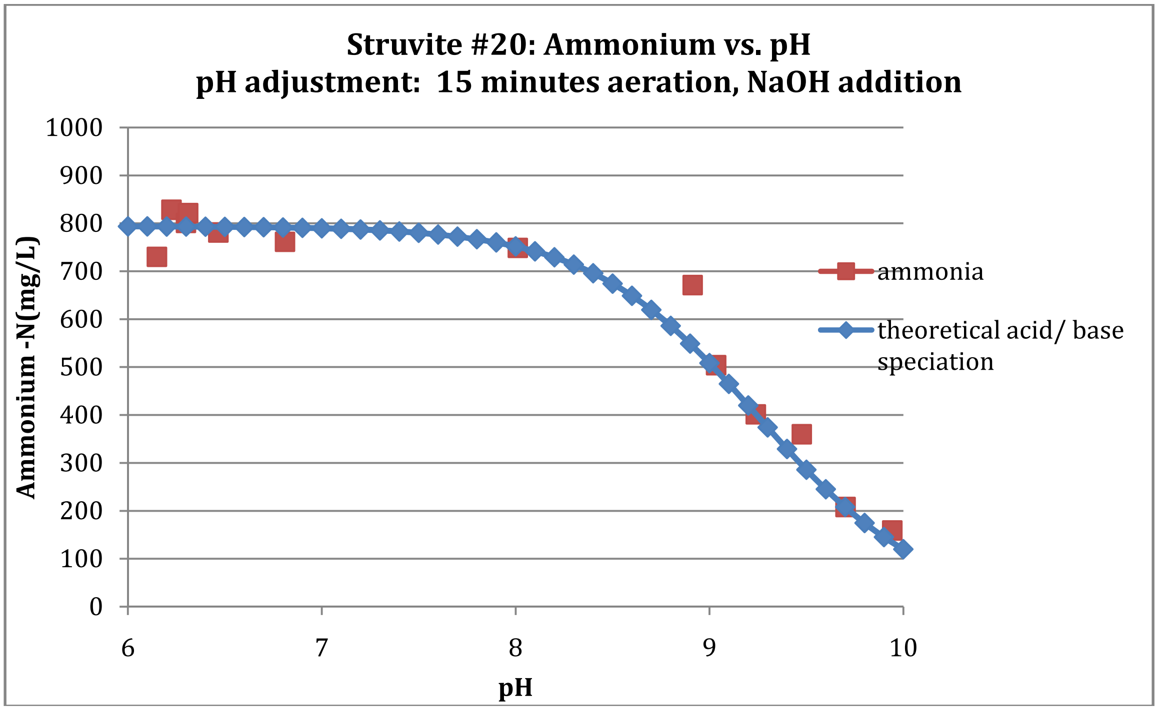

Figure 51: Struvite #20 Ammonium vs. pH

Appendix B-1 (Continued)

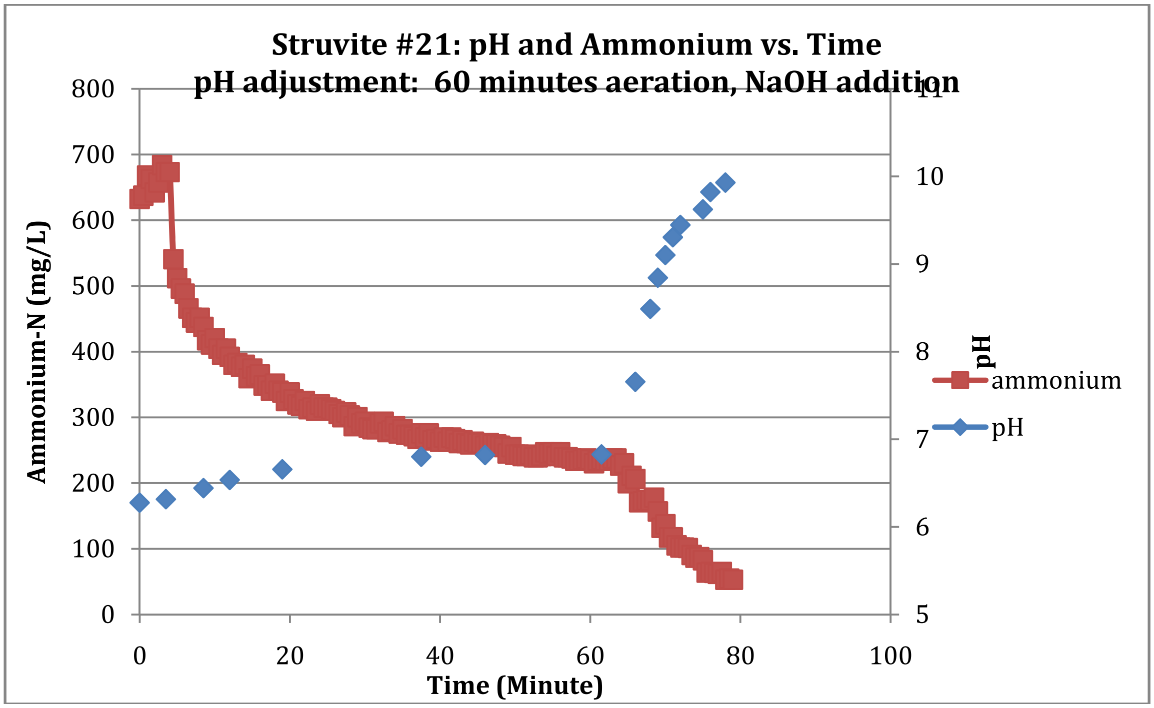

Figure 52: Struvite #21 pH and Ammonium vs. Time

Appendix B-1 (Continued)

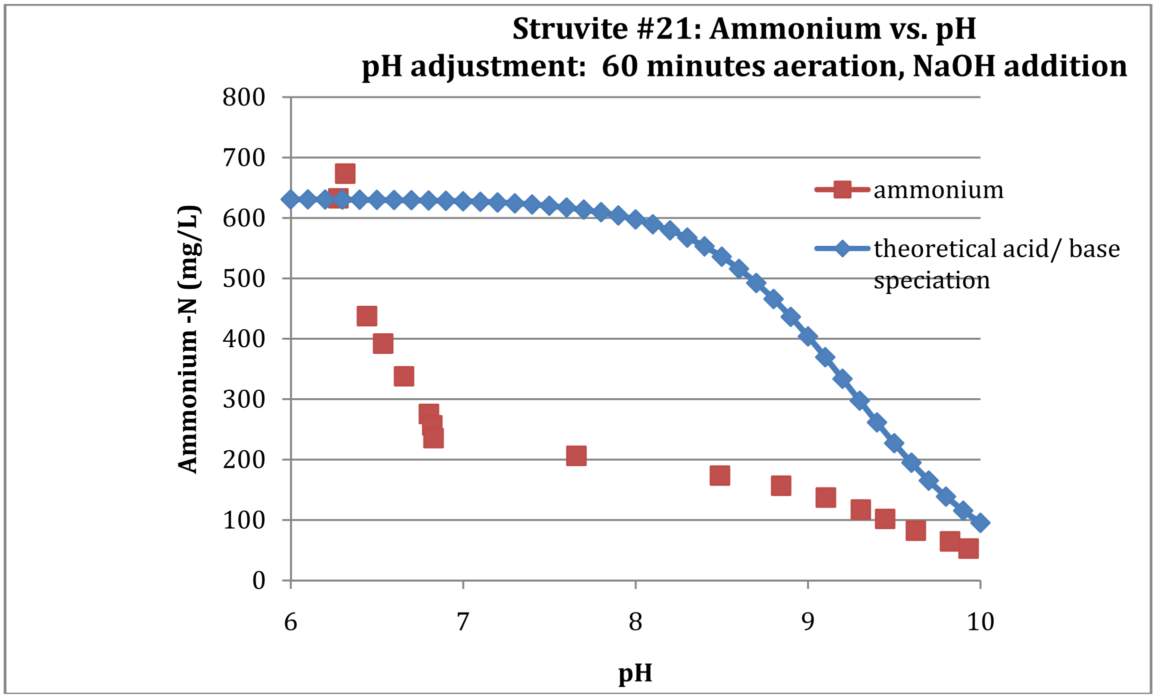

Figure 53: Struvite #21 Ammonium vs. pH

Appendix B-1 (Continued)

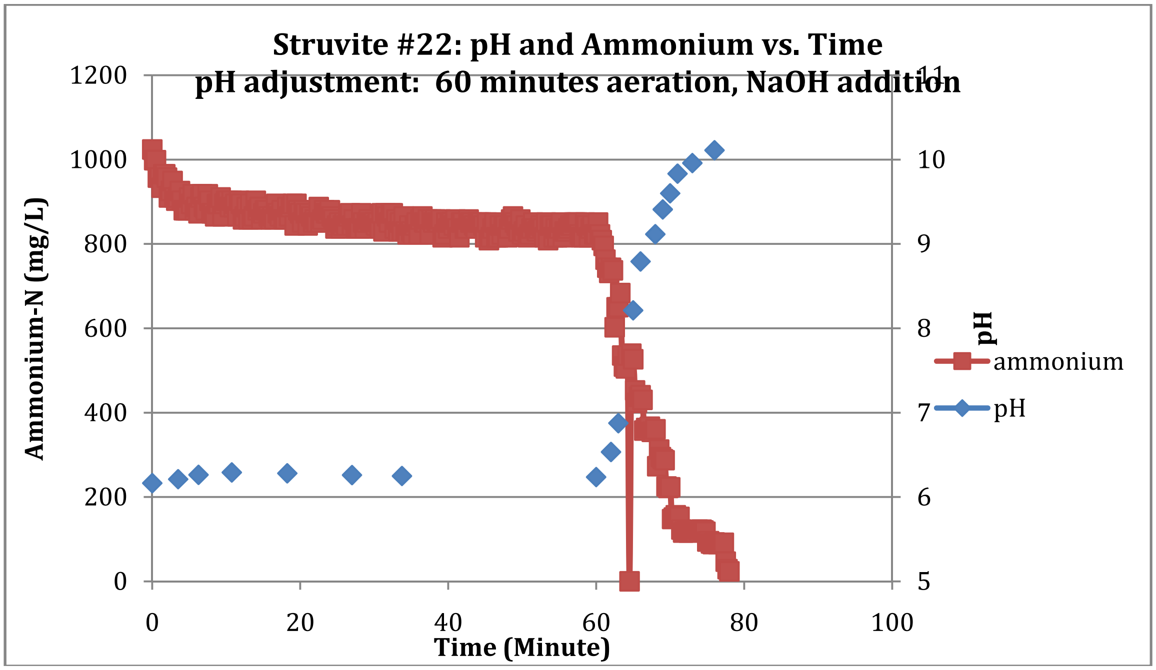

Figure 54: Struvite #22 pH and Ammonium vs. Time

Appendix C-1: Financial Analysis Worksheets

Financial Assessment of Struvite Feasibility - Worksheet Page 1

DATA INPUT

Ammonia Concentration	1000	mg/L
Magnesium Concentration	100	mg/L
Phosphate Concentration	200	mg/L
Supernatant Flow rate	1000000	L/ day
Magnesium Unit Cost	0.5	$/kg Mg
Phosphate Unit Cost	0.5	$/kg Phosphate
pH Adjustment Unit Cost	0.46	$/kg NaOH
pH Adjustment Requirement	0.016	L 2.5 M NaOH/L
phosphate recovery	0.9	percentage
ammonia recovery	0.9	percentage
resale value of struvite	1	$/kg N +P
Electricity Costs	0.11	$/kWh
Methanol Costs	1.5	$/ gallon
Aeration Power	0.005	kWh/ L

Convert g NaOH/L to L of 2.5 M NaOH/L Super

g NaOH/L - Super	g NaOH/L 2.5 M	L 2.5 M NaOH/L - Super
1.6	100	0.016

Assessment of Howard Curren Anaerobic Digester Sludge Supernatant

Compound	Measured Concentration (mg/L)	Molar Concentration (M)	Set Molarity (to highest) (M)
Ammonium	1000	0.056	0.056
Magnesium	100	0.004	
Phosphate	200	0.002	

Assessment of Required Chemical Additions for Equimolar Concentrations and Struvite Precipitation

Quantity of Compound Needed (M)	Quantity of Compound Needed (mg/L)	Source Compound	Total MW of Solid Source (g/mole)	Molarity of Liquid Source (M)	Moles Ion/ Mole Source Compound	Mass of Solid Source Needed (mg/L)	Volume Liquid Source Needed (L/L)
0	0	NH4Cl	53.4	NA	1	0	0
0.051440329	1250	MGO	40	NA	1	2.057613169	NA
0.053450292	5077.8	85% H3PO4	NA	15.2	NA	NA	0.003516467

Assessment of Ammonia Flow

Supernatant Flow (L/day)	Ammonia Concentration (mg/L)	Total Ammonia Mass Flow (kg/day)
1,000,000	1000	1000

Assessment of Chemical Addition Costs for Precipitation of Struvite

Compound	Total Mass Needed (kg/day)	Product Addition Cost ($/kg)	Total Cost/ Day ($/day)	Total Cost/ Year ($/year)	Chemical Addition Cost/ Kg NH4 ($/kg NH4)
Ammonium	0	$0.50	$0.00	$0.00	$0.00
Magnesium	2057.613169	$0.50	$1,028.81	$375,514.40	$1.03
Phosphate	3516.466605	$0.50	$2,068.51	$755,006.07	$2.07

Appendix C-1 (Continued)

Financial Assessment of Struvite Feasibility - Worksheet Page 2

Assessment of pH Control with Sodium Hydroxide to Facilitate Preciptiation of Struvite

pH Control Source	Molarity (M)	Addition Ratio (L NaOH/ L)	Addition (Moles NaOH/L)	Addition Mass (moles/day)	Addition Mass (kg/day)	Bulk NaOH Cost ($/lb)	Total Daily Cost ($/day)	Chemical Addition Cost/ Kg NH4 ($/kg)
NaOH	2.5	0.016	0.04	40000	1600.0000	$0.46	$1,619.2	$1.62

Assessment of Total Chemical Addition Costs for Struvite Precipitation at Howard Curren AWTP

Phosphate		Magnesium		Lye		Total Struvite Production Chemical Costs		aeration	aeration cost
$/day	$/kg NH4	$/day	$/kg NH4	$/day	$/kg NH4	$/day	$/kg NH4	kwH/L	$/kg-N
$2,068.51	$2.07	$1,028.81	$1.03	$1,619.20	$1.62	$4,716.52	$5.27	0.005	0.55

Assess Costs for Production of Struvite with Consideration to Struvite Resale

Supernatant Ammonia (kg NH4/ day)	Production Cost for Struvite ($/ kg - NH4)	Expenditure ($/day)	Expenditure Cost/ Year ($/year)	Struvite Value ($/kg - A+P)	Ammonia Recovery Percentage	Phosphate Recovery Percentage	Valued Struvite Production (kg NH4 + PO4/day)	Recovery value ($/day)	Total Cost/ Day ($/day)	Total Cost/Kg NH4 ($/kg)
1000	$5.82	$ 5,816.52	$ 2,123,028.47	$1	90.00%	90.00%	5085.0	$ 5,085.00	$ 731.52	$ 0.73

Assess Current Bilogical Nitrogen Removal Process Costs

Supernatant Ammonia NH4/ Day (kg NH4/ day)	Required Aeration Power (KW)	Electricity Price ($/KW)	Aeration Cost/ Day ($/day)	Methanol Usage (gal/kg NH4)	Methanol Price ($/gal)	Methanol Cost/ Day ($/day)	Total BNR Cost ($/day)	Total Cost/Kg NH4 ($/kg)
1000	67.3	0.11	$ 177.67	0.6	$ 1.50	$ 900.00	$ 1,077.67	$ 1.08

Comparison

Method	$/ kg ammonia-N
Struvite	$ 0.73
Baseline (BNR)	$ 1.08

Appendix D-1: Calibration Curves

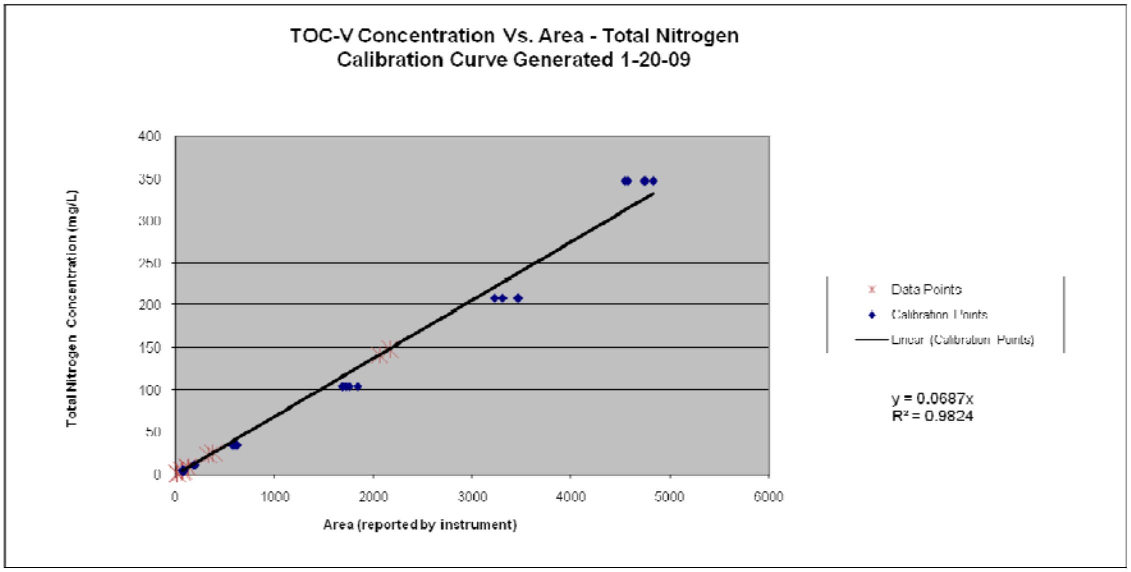

Figure 55: Typical Calibration Curve for Total N by TOC-V

Appendix D-1 (Continued)

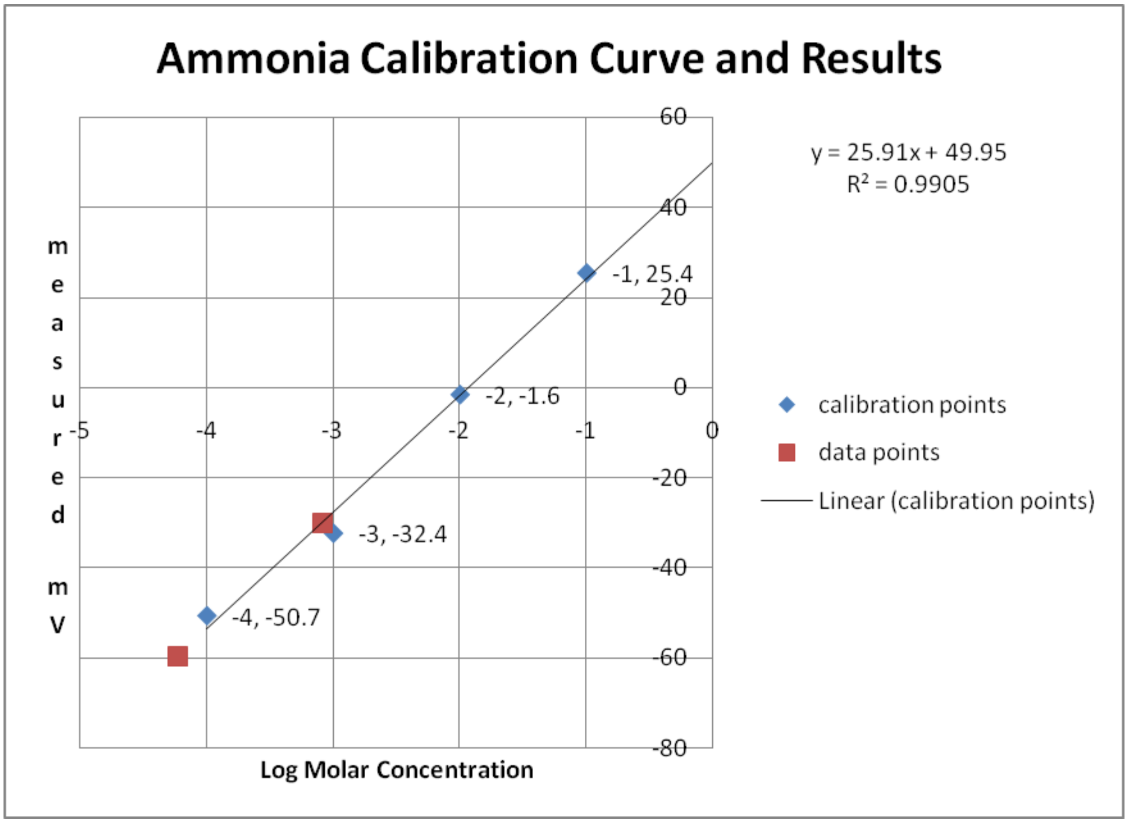

Figure 56: Typical Calibration Curve for Ammonia Probe

Appendix D-1 (Continued)

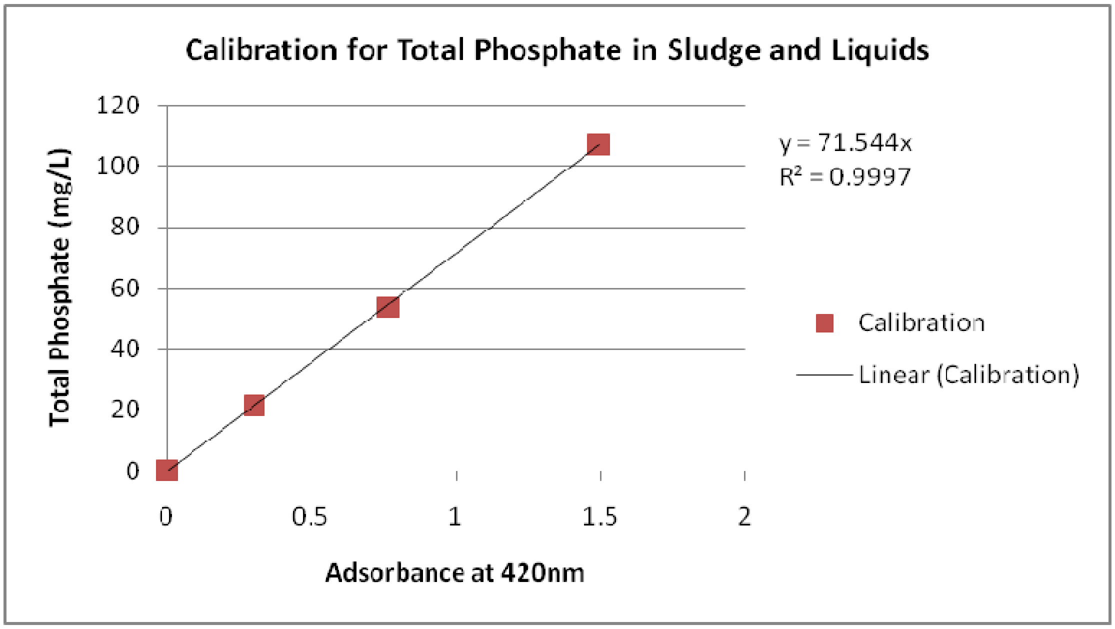

Figure 57: Typical Calibration Curve for Total Phosphate

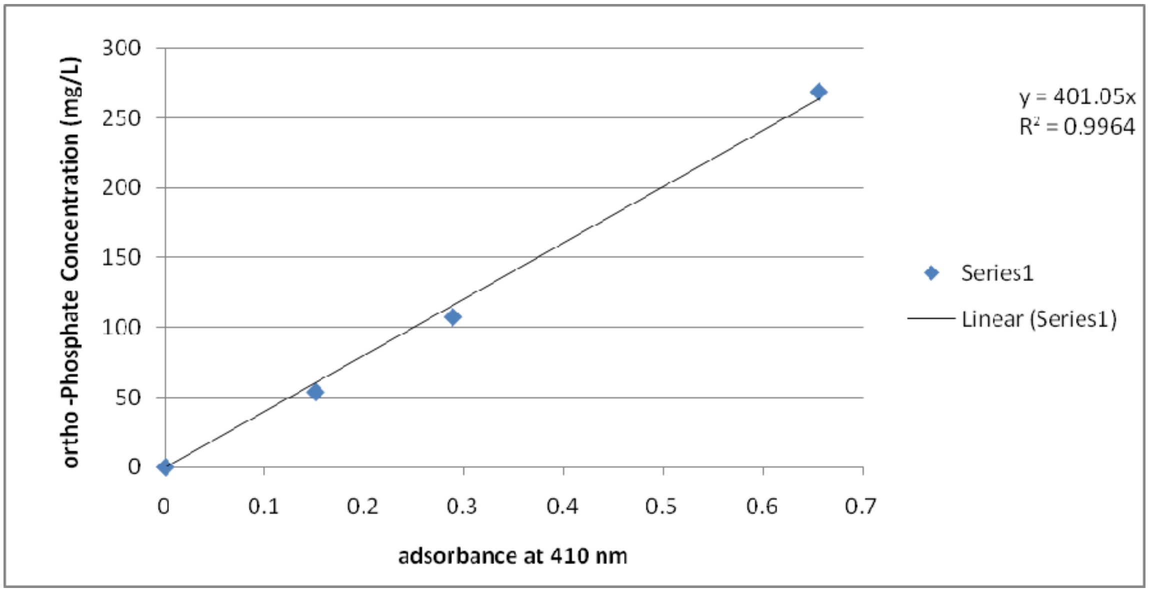

Figure 58: Typical Calibration Curve for Ortho-Phosphate

Appendix E-1: Bioenergetic Stoichiometry Determination

$$R = f_e R_a + f_s R_c - R_d$$

Where:

R = overall reaction
f_e = energetic partitioning coefficient
R_a = electron acceptor half reaction
f_s = synthesis partitioning coefficient
R_c = cell synthesis half reaction
R_d = electron donor half reaction

Equation E-1: Microbial Energetic Stoichiometry

For aerobic digestion of primary sludge, use the following values from Rittman and McCarty (2001). Primary sludge is represented as $C_{10}H_{19}O_3N$ and new bacteria cells are represented as $C_5H_7O_2N$.

Appendix E-1 (Continued)

$$f_s = 0.6$$

$$f_e = 0.4$$

$$-R_d : \frac{1}{50} C_{10}H_{19}O_3N + \frac{9}{25} H_2O = \frac{9}{50} CO_2 + \frac{1}{50} NH_4^{\ +} + \frac{1}{50} HCO_3^{\ -} + H^+ + e^-$$

$$R_c : \frac{1}{5} CO_2 + \frac{1}{20} HCO_3^{\ -} + \frac{1}{20} NH_4^{\ +} + H^+ + e^- = \frac{1}{20} C_5H_7O_2N + \frac{9}{20} H_sO$$

$$R_a : \frac{1}{4} O_2 + H^+ + e^- = \frac{1}{2} H_wO$$

Equation E-2: Determination of Aerobic Degradation of Primary Sludge

Converting fraction to decimal, multiplying by the appropriate half reactions by the energetic and synthesis coefficients and adding the reactions, we arrive at the following total reaction.

$$R : 0.02C_{10}H_{19}O_3N + 0.01NH_4 + 0.01HCO_3^{\ -} + 0.1O_2 = 0.11H_2O + 0.06CO_2 + 0.03C_5H_7O_2N$$

Equation E-3: Resulting Aerobic Degradation of Primary Sludge

And then converting to a one molar basis of the influent primary sludge we arrive at the equation presented in the text.

$$R: C_{10}H_{19}O_3N + 0.5NH_4 + 0.5HCO_3^- + 5O_2 = 5.5H_2O + 0.3CO_2 + 0.15C_5H_7O_2N$$

Equation E-4: Aerobic Degradation of Primary Sludge on Single Molar Basis

Appendix E-2: Partitioning Based on Stoichiometry

Beginning with equation F-5 from the previous appendix, we observe that the aerobic digestion of primary sludge as represented would require additional nitrogen source, shown as ammonia on the left side of the equation, in order to proceed fully. For this example we assume that sufficient supplemental nitrogen is available and the reaction proceeds.

Following N through the equation F-5, we see that there are 14 g N / mole of influent primary sludge and 14 g N/ mole of influent supplemental ammonia multiplied by 0.5 moles ammonia per mole influent primary sludge equals 7 grams of ammonia- N / mole of influent sludge. Therefore, the total influent is 21 g N/ mole of influent primary sludge.

Looking at nitrogen on the effluent side, we see that solid there is 14 g N/ mole of effluent cells multiplied by 1.5 mole of effluent cells per mole influent primary sludge. This N is considered solid, so that solid N equals 21 g N per mole of influent primary sludge. Thus solid N equals 100% the 21 g of influent N.

In this example, there is no N on the right side of the equation in a liquid form and liquid effluent N equals 0%. Similarly there is no gaseous N on the right side of equation F-5 and effluent gaseous N equals 0%.

Appendix E-2 (Continued)

Because all effluent N is in the form of cellular N, this is considered solid and the partitioning for this example is 100% solid and 0% liquid, 0%gas. Were there to be ammonia or any gaseous forms of nitrogen on the right hand side of the equation, the percentages would be calculated using the same methodology as above.

Appendix E-3: Mass Transfer Calculations

$$F_y = Q_G H_y C_{L,y}\left[1-\exp\left(\frac{-K_{OL,y} a V_l}{H_y Q_G}\right)\right]$$

Where:
F_y = mass transfer rate (M/T)
Q_G = gas flow rate (L^3/T)
$C_{L,y}$ =dimensionless Henry's Constant
$K_{OL,y}$ =liquid concentration of y (M/ L^3)
a = interfacial are aper unit volume of liquid (L^3/ L^2)
V_l = liquid volume (L^3)

Equation E-5: Mass Transfer for a volatile compound out of an aeration system (Matter-Muller et al. 1980)

Our objective is to compare mass transfer rates for carbon dioxide and ammonia out of solution in the same aeration system.

The overall mass transfer coefficient for each compound is calculated from liquid and gas phase mass transfer coefficients. The liquid phase mass transfer coefficient is estimated from the diffusivity of the compounds, the diffusivity of oxygen, and published values for the liquid phase mass transfer coefficient for oxygen in fine bubble aeration conditions. The following relationships are used.

Appendix E-3 (Continued)

$$\frac{k_{l,B}}{k_{l,A}} = \left(\frac{D_{L,B}}{D_{L,A}}\right)^{0.5} \quad \text{and} \quad \frac{1}{K_{OL,y}} = \frac{1}{k_L} = \frac{1}{k_g H_y}$$

Where:

$k_{l,B}$ = liquid phase mass transfer coefficient, compound B

$D_{L,B}$ = diffusivity of compound B

k_g = gas phase mass transfer coefficient

Equation E-6: Determination of Diffusion and Mass Transfer Coefficients

Gilot et al. (2005) estimate the liquid phase mass transfer rate for oxygen in fine bubble aeration to range from 3.2 – 13.4 hour^{-1}. For our purposes, we'll take the median and use 8.3 hour^{-1}.

Carbon dioxide and ammonia have the same diffusivity (2X 10^{-5}), but differing Henry's constants results in significantly different overall mass transfer coefficients.

Based on the equations and calculations outlined above, the following values were used for comparison of mass transfer rates using the Matter Muller equation. The gas flow rate, interfacial area per unit volume, and liquid volume should be the same for both compounds and not affect the result. These values were set arbitrarily.

Table 9: Parameters for Mass Transfer Comparison

Parameter	Ammonia	Carbon Dioxide
Henry’s Constant	0.0006	1.1
Overall Mass Transfer Rate	0.7/ hour	7.66/ hour
Gas Flow Rate	1 m^3/h	1 m^3/h
Liquid volume	0.15 L	0.15L
Interfacial area	1m	1m

With the values above, only concentration and the mass transfer rate are unknown in the equation and the plot in the text shows transfer rate vs. various concentrations of ammonia and carbon dioxide for a visual comparison of different scenarios.