

INTRODUCTION

Need for Removal of Phosphorus from Waste Lagoon Effluent

Livestock manure or waste, which contains nutrients such as carbon, nitrogen, and phosphorus, is often flushed with water from animal confinement areas into a lagoon for treatment and storage. From the lagoon, wastewater is recycled back into the confinement area for flushing. In addition, to avoid the over-filling of the lagoon that would otherwise result from the net inputs of waste and possibly rainwater, an effluent stream is withdrawn and directed as irrigation water onto soil supporting crops.

In the lagoon, anaerobic microbes remove carbon by converting it into the volatile gases carbon dioxide and methane. These gases may escape to the atmosphere or be collected as biogas and combusted for energy recovery.

Nitrogen, which exists primarily in forms of ammonia in the lagoon, may partly volatilize into the atmosphere from the lagoon or during irrigation. The crop acreage is typically calculated to allow for uptake by the crops of the applied nitrogen from the soil, thus minimizing movement of nitrogen in ground and surface water beyond the farm's boundaries. In addition, to reduce the amount of ammonia escaping to the atmosphere and/or to reduce the demand for nitrogen uptake by crops, processes are under development for removal of nitrogen by microbes. In these processes, aerobic microbes convert ammoniacal forms of nitrogen to oxidized forms such as nitrate, followed by conversion of the oxidized forms to nitrogen gas by anaerobic microbes. The nitrogen gas escapes to the atmosphere, thus removing nitrogen.

Unlike carbon and nitrogen, phosphorus cannot volatilize from the system. In the lagoon, it exists partly as organic phosphorus and partly as orthophosphate phosphorus (OP), neither of which can evaporate or be converted by microbes to gaseous forms. Some phosphorus may be removed from the wastewater by settling of phosphorus-containing solids to the lagoon bottom; however, this

process does not ultimately remove the nutrient from the system, and appreciable phosphorus remains dissolved in the lagoon water. The irrigated crops typically take up from the soil less phosphorus than that applied in the irrigation water, because the acreage has been calculated for nitrogen removal, which requires less acreage. The soil absorbs phosphorus, but over time reaches saturation. Additional application of phosphorus can then cause release of phosphorus to surface waters beyond the farm's boundaries, risking oxygen depletion of those waters by accelerating growth of oxygen-consuming water organisms. New processes mentioned above for nitrogen removal will, if anything, worsen the phosphorus excess as the acreage requirements for nitrogen removal shrink. Measures to reduce the phosphorus content of the lagoon effluent must therefore be considered.

Means for Removal of Phosphorus from Anaerobic Treatment Effluent

Methods to remove solids, such as centrifuging and settling, will remove phosphorus that is contained in the solids. For removing the soluble phosphorus, four methods may be considered: (1) removal by aerobic microbes; (2) removal by phosphate-accumulating microbes; (3) precipitation by iron or calcium addition; and (4) precipitation as struvite.

Phosphorus can be removed from the effluent by subjecting it to the action of aerobic microbes, which assimilate the phosphorus into their cell mass, and then removing those cells from the system. This method suffers from three drawbacks. First, phosphorus removal may be limited because the phosphorus-to-carbon ratio in the effluent may exceed the ratio at which the microbes can take in the nutrients. Second, the cells are typically removed in a sludge-like form, leading to high costs for handling and transportation. Third, aeration is necessary, resulting in additional energy and equipment costs.

Phosphate-accumulating organisms are bacteria that outcompete other organisms in conditions that cycle between aerobic and anaerobic. These organisms are able to take up

phosphorus in excess of their needs during aerobic periods and use it to store energy. During anaerobic periods, they consume the stored energy and release the phosphorus in the process. If these bacterial cells are removed from the system just at the time they have completed their phosphorus uptake phase, the net result will be removal of phosphorus and carbon in a ratio considerably greater than the cells' overall phosphorus-carbon use ratio. Higher phosphorus removal for a given carbon content is thus possible than that achievable with purely aerobic microbes. While energy requirements may be decreased as a result of aeration being required only part of the time, the increased complexity may result in additional equipment costs that offset lower energy costs. Finally, costs related to sludge will be incurred because of the need to remove cells from the system.

Addition of soluble iron or calcium leads to precipitation of the phosphorus in the form of iron phosphate or calcium phosphate salts. Chemicals must be added to provide the iron or calcium ions, which can introduce new environmental concerns. In addition, the precipitated phosphorus-bearing salts are usually finely-divided, resulting again in a sludge-like waste product that is expensive to handle and transport.

Struvite (magnesium ammonium phosphate hexahydrate) precipitation could also be used to remove phosphorus from anaerobic treatment effluent. In this process, the concentration of magnesium (Mg) ions, ammonium, and phosphate ions must be brought high enough that the equilibrium solubility product of struvite is exceeded. In addition, there must be enough Mg and ammonium ions present in comparison with the phosphate that, as the precipitation occurs, the solubility product will continue to be exceeded until the phosphorus reduction goal has been met. Although anaerobic waste effluent usually contains ammonium and some Mg, Mg may still have to be added to remove the targeted amount of phosphorus. In addition, pH raising, and thus chemical addition, may be necessary to achieve a state of low struvite solubility. The main advantage of this method is that the precipitate can be made to form a coarse-grained material that is easily drained of

its water and thus less expensive to handle and transport. In addition, the product can be used as a slow-release fertilizer. Finally, if part of the Mg in the product can be separated and recycled to the raw effluent, the need for obtaining Mg elsewhere could be avoided.

Previous Work by Others Relevant to Struvite Precipitation

Given the advantages that struvite precipitation can potentially offer in treatment of lagoon effluent, a literature review was undertaken to support planning of research on that subject. The review focused on five points: (1) the factors promoting and inhibiting struvite crystallization; (2) the degree of nutrient removal achievable by struvite crystallization; (3) the form and manner of precipitation; (4) thermodynamics; and (5) kinetics. Results of the review are summarized below, organized according to the five points.

Factors Promoting and Inhibiting Struvite Crystallization

The pH for struvite precipitation from wastewater has been reported at values from 6.5 to more than 10. Beal et al., 1999, reported phosphorus removal at pH 8.5 and slightly less at 9.0. Liao et al., 1995, tested various pH levels in combination with other factors, and found an optimum of 7.5 for swine wastewater and an optimum of 10.0 for synthetic wastewater. Ohlinger et al. (1998) predicted (but did not measure) the pH for minimum struvite solubility at just over 10. Schulze-Rettmer (1991) specified the pH range no more narrowly than 8 - 10. Although Webb and Ho (1992) did not conduct tests in the 9.0 to 9.5 pH range, their results were consistent with an optimum in that range: they found struvite solubility to decrease throughout the 6.5 to 8.2 pH range. Zdybiewska and Kula (1991) found the optimum pH for one of the three wastes they tested to be slightly above 9.5. The fact that tests on real wastewater reveal a lower optimum pH than that indicated by tests on synthetic wastewater and by theoretical predictions suggests that real wastewater contains species excluded from the synthetic wastewater and from the theoretical model.

Temperature for struvite precipitation has not often been tested. Experiments have been conducted generally near room temperature, which approximates the average temperature at which waste treatment systems are likely to operate, with no treatment of temperature as an independent variable. Webb and Ho (1992) did predict that the solubility product of struvite would be slightly lower at 25 degrees Celsius ($^{\circ}\text{C}$) than at 30°C . Beal et al. (1999) heated their samples to 35°C at the beginning before the reaction period, but did not report the temperature during the reaction and settling period.

For Mg supplementation, Beal et al. (1999) used magnesium oxide (MgO). Brionne et al. (1994) recommended magnesium sulfate or MgO and also tested magnesium chloride and magnesium carbonate. Liao et al. (1995) and Webb and Ho (1992) used magnesium chloride. Zdybiewska and Kula (1991) used magnesium chloride and MgO , and found the former to work better. Wrigley et al. (1992) used magnesium sulfate.

For phosphate supplementation, Brionne et al. (1994) proposed phosphoric acid, and also tested potassium hydrogen phosphate and potassium dihydrogen phosphate. Liao et al. (1995) and Webb and Ho (1992) used potassium dihydrogen phosphate. Schulze-Rettmer (1991) proposed phosphoric acid and Zdybiewska and Kula (1991) reported using it.

Various additives for pH adjustment are also reported. Momberg and Oellermann (1992) used lime, while Beal et al. (1999), Liao et al. (1995), Webb and Ho. (1992), and Wrigley et al. (1992) used sodium hydroxide. Brionne et al. (1994) independently tested lime, sodium hydroxide, and potassium hydroxide. Zdybiewska and Kula (1991) mentioned that pH was adjusted but did not identify the agent. Beal et al. (1999) observed higher phosphate removal when they added no sodium hydroxide.

Regarding nucleating agents, Webb and Ho (1992) report using borosilicate glass filings. Momberg and Oellermann (1992) used sand. There was no variation of amounts or types of

nucleating agents in their experiments to evaluate their effects, and in other articles, nucleating agents were apparently not used.

The time permitted for precipitation of struvite is often mentioned. Beal et al. (1999) allowed 15 minutes (min). Brionne et al. (1994) proposed two hours (h), while Liao et al. (1995) allowed 1 h. Webb and Ho (1992) took measurements all the way out to 200 h. Zdybiewska and Kula (1991) tested various reaction times between zero and 30 min, finding the optimum to be 25 min.

Degree of Nutrient Removal Achievable by Struvite Crystallization

In Liao et al. (1995) ammonia removal reached near 92 percent (%) when the other two ions were supplemented to 0.9 of stoichiometric equivalence with ammonia. With the same conditions except for dropping the phosphate concentration proportion to 0.6, ammonia removal was less complete, reaching 39% to 88%. Despite the authors' indication that nutrient removal occurs via struvite, there must have been some other ammonia removal mechanism, because 88% removal could not have been achieved at the lower phosphate level--struvite could only have removed 60% of the ammonia. Furthermore, the authors state that no phosphate was removed at the higher phosphate level. If any of the ammonia removal at the higher phosphate level had occurred via struvite precipitation, then phosphate should have been removed.

Ammonium removal reached 97.6% in Brionne et al. (1994). They focused on ammonium removal and hence did not report phosphate reduction.

Beal et al. (1999) achieved up to 98% phosphorus reduction. Reduction of other nutrients was small in percentage terms. The authors attribute this result to the fact that the starting levels of the other nutrients were high in comparison with phosphate.

Momberg and Oellermann (1992) focused on phosphate rather than ammonium, reducing phosphate from 198 to 5 milligrams (mg) per liter (L), or 97.5%. It should be noted that the authors

indicated that operation in the high end of the pH range was necessary to achieve this removal rate. It should also be noted that lime was used for pH adjustment in this experiment, raising the possibility that some of the phosphate removal occurred via formation of calcium phosphate salts. Ammonium was reported only to have been reduced from 296 to 173 mg/L. Even though the experimenters were focusing on phosphate rather than ammonium removal and thus ammonium removal would be expected to be less, associated text stating that "more than half the ammonia was removed" points to the possibility that the ammonium concentration figures, through a typographical error, understate the reduction.

Wrigley et al. (1992) achieved 90% reduction of phosphate in solution, down to about 1 mg/L, in continuous digester effluent. In batch digester effluent, removal was not as effective. They suggest that less successful removal from the liquid of struvite solid, rather than failure of phosphate to crystallize into struvite solid, may explain at least part of the comparative lack of effectiveness of phosphate removal from batch digester effluent. The phosphate concentrations constituted only a small portion of total phosphorus (TP) content. Unfortunately, the reductions in TP were not reported.

Zdybiewska and Kula (1991) focused on nitrogen removal. Their removal efficiencies reached only 31-82%, despite relatively high starting concentrations and supplementation of the other ions to reach up to 100% excess.

Form and Manner of Precipitation

Beal et al. (1991) reported the precipitated solid to be a "white flake-like" precipitate. They also observed that it formed within 15 minutes.

Brionne et al. (1994) state that the magnesium ammonium phosphate precipitate forms very quickly. They also state that an anionic flocculating agent was used to hasten separation of the precipitate. Their use of such an agent suggests that the precipitate was sufficiently small-grained

that settling or filtration of non-aggregated particles would present some difficulty. They do not report its composition other than referring to it as magnesium ammonium phosphate.

Liao et al. (1995) do not explicitly report the form of the precipitate. However, their experiments apparently yield a fine-grained precipitate, because they mention using a microscope to compare precipitate grain size from synthetic wastewater to that of real wastewater. Grain size was smaller when real wastewater was used, a fact that the authors attribute to breakage of grains by suspended organic particles. An alternate explanation would be that the organic particles in the real wastewater provided more crystallization nuclei. The same amount of precipitate deposited upon more nuclei would result in smaller, more numerous grains. The article implies the precipitate is struvite, but composition is not explicitly reported, and stoichiometric calculations do not support the supposition that the precipitate is all struvite.

Momberg and Oellermann (1992) supplemented in part with calcium, so their precipitate contained some calcium along with the struvite. They did not report composition, but explain that the calcium could be in the form of calcium carbonate and/or hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$]. Wrigley et al. (1992) report that up to 7 mg/L of the phosphate in batch digester effluent treated to precipitate struvite may exist as struvite in the 10-40 micron grain size range. By comparing with the starting and ending phosphate contents of the effluent, it is possible to deduce that 20-25% of the struvite formed exists in this very small grain size.

Thermodynamics

Thermodynamics, which revolves around concepts of equilibrium, thermodynamic potential, and stability, can be applied in two ways that are particularly useful in contemplating a system for removing phosphorus from lagoon effluent by struvite precipitation. One is equilibrium among chemical species, and the other is thermodynamics of precipitate nucleation. The literature review results and findings are organized accordingly.

Equilibrium Among Chemical Species

Snoeyink and Jenkins (1980), demonstrate that, in a closed system at equilibrium and at a given temperature and pressure, chemical species that can react with one another will distribute themselves in a particular way to minimize Gibbs energy. Specifically, they will distribute themselves to satisfy the equilibrium constant, K , for each reaction. The K is equal to the product of the activities of the output species of the reaction (each activity raised to the power of its stoichiometric reaction coefficient) divided by a similar product for the input species. For aqueous systems that are very dilute (as are the systems dealt with in this paper, ranging from 0.005 to 0.05 mol/L [moles per liter] of solute), activities of solutes can be approximated by their molar concentrations. Furthermore, K is linked to the standard molar Gibbs energy of reaction (ΔG_r°), the absolute temperature (T), and the gas constant (R) by:

$$\Delta G_r^\circ = -RT \ln(K) \quad (1)$$

The ΔG_r° is equal to the standard molar Gibbs energy of formation (ΔG_f°) of the products minus that of the reactants. Water and solid substances have an activity near unity. The K for a reaction in which a solid substance dissolves into component ions is often called "solubility product."

These relations support analysis of the present practical problem because they enable one to predict whether, and to what extent, particular reactions will occur in the system of interest, if we have enough thermodynamic data related to the species of interest. Predictions of particular use are the extent to which phosphorus will be removed by struvite precipitation, and whether a sequence of reactions envisioned to separate the Mg from the struvite for recycle will actually occur.

To attempt the predictions, thermodynamic data (free energy of formation, equilibrium constants, solubility products, and related information) for species and reactions relevant to the predictions were sought from a variety of texts and reference works. Data yielded by the review are listed in Table 1. In the third column, sources are indicated by letters that key to a list immediately

following the table. Related information for some species in the table includes pK, which is the negative base-10 logarithm of the specified K; pKa, which is the pH at which an acid at equilibrium is half protonated and half de-protonated; and dissociation constants, which are products of the concentrations of the dissociated constituents of the specified molecule. Energy data is primarily in kilocalories per mole (kcal/mol).

**TABLE 1: LIST OF THERMODYNAMIC DATA
(all species aqueous unless otherwise noted)**

Species	Value	Source (see table endnote)
Mg ⁺⁺	$\Delta G_f^\circ = -108.9$ kcal/mol	A
HPO ₄ ⁻⁻	$\Delta G_f^\circ = -261.4$ kcal/mol	B
HPO ₄ ⁻⁻ /PO ₄ ⁻⁻⁻	pKa = 12.3	A
CO ₃ ⁻⁻	$\Delta G_f^\circ = -126.22$ kcal/mol	A
HCO ₃ ⁻ /CO ₃ ⁻⁻	pKa = 10.3	A
MgCO ₃ (solid)	$\Delta G_f^\circ = -246$ kcal/mol	B
MgCO ₃ (solid/liquid)	pK, solubility product = 5.0	A
H ₂ CO ₃	$\Delta G_f^\circ = -149.00$ kcal/mol	A
H ₂ CO ₃ /HCO ₃ ⁻	pKa = 6.3	A
MgNH ₄ PO ₄	$\Delta G_f^\circ = -390.0$ kcal/mol	E
MgNH ₄ PO ₄ (solid/liquid)	pK, solubility product = 12.6	G
MgNH ₄ PO ₄ (solid/liquid)	pK, solubility product = 13.2	H
H ₃ PO ₄	$\Delta G_f^\circ = -1123.6$ kilojoules/mol	C
H ₃ PO ₄ / H ₂ PO ₄ ⁻	pKa = 2.1	A
Mg ₃ (PO ₄) ₂ (solid)	$\Delta G_f^\circ = -904.2$ kcal/mol	B
Mg(OH) ₂ (solid)	$\Delta G_f^\circ = -199.27$ kcal/mol	D
Mg(OH) ₂ (solid/liquid)	pK, solubility product = 10.74	A
H ₂ PO ₄ ⁻	$\Delta G_f^\circ = -271.3$ kcal/mol	B
H ₂ PO ₄ ⁻	$\Delta G_f^\circ = -260.7$ kcal/mol	F
H ₂ PO ₄ ⁻ / HPO ₄ ⁻⁻	pKa = 7.2	A
3(MgCO ₃). (OH) ₂ . 3H ₂ O (solid)	$\Delta G_f^\circ = -1108.3$ kcal/mol	B
Mg(HCO ₃) ⁺	$\Delta G_f^\circ = -250.88$ kcal/mol	B
MgCO ₃ [°]	$\Delta G_f^\circ = -239.85$ kcal/mol	B
Mg(OH) ⁺	$\Delta G_f^\circ = -150.1$ kcal/mol	B
MgO (solid)	$\Delta G_f^\circ = -136.13$ kcal/mol	B
PO ₄ ⁻⁻⁻	$\Delta G_f^\circ = -245.1$ kcal/mol	B
NH ₄ ⁺	$\Delta G_f^\circ = -19.00$ kcal/mol	B
NH ₃	$\Delta G_f^\circ = -6.37$ kcal/mol	B

Table 1 (continued)

OH-	$\Delta G_f^\circ = -37.595 \text{ kcal/mol}$	B
NH ₄ OH	$\Delta G_f^\circ = -63.04 \text{ kcal/mol}$	F
MgCO ₃ (solid)	$\Delta G_f^\circ = -241.9 \text{ kcal/mol}$	F
3(MgCO ₃). ₃ (OH) ₂ .3H ₂ O (solid)	$\Delta G_f^\circ = -1100.8 \text{ kcal/mol}$	F
PO ₄ ⁻⁻⁻	$\Delta G_f^\circ = -243.5 \text{ kcal/mol}$	F
HPO ₄ ⁻⁻	$\Delta G_f^\circ = -260.7 \text{ kcal/mol}$	F
Mg ₃ (PO ₄) ₃ (solid)	solubility product = 1.04×10^{-24}	C
MgPO ₄ .3H ₂ O (solid/liquid)	solubility = slight; soluble in dilute acid	C
water	dissociation constant = 10^{-14}	A
MgOH ⁺	dissociation constant = $10^{-2.58}$	I

Table Endnote (Sources):

- A. Snoeyink and Jenkins, 1980
- B. Garrels and Christ, 1965
- C. Handbook of Chemistry and Physics, 1999
- D. Dictionary of Inorganic Compounds, 1992
- E. Latimer, 1952
- F. National Bureau of Standards Tables of Chemical Thermodynamic Properties, 1982
- G. Bube, 1910
- H. Taylor et al, 1963
- I. Stock and Davies, 1948

In addition to the data in Table 1, reports were found on two studies modeling struvite solubility. In the first study, Buchanan et al. (1994) reported results obtained from a model simulating equilibrium between solid and dissolved ions in waste treatment effluent at various pH values. The study related total phosphate, Mg, and ammonia concentrations to struvite solubility. The model took into account the fact that not all phosphate, ammonia, and Mg ions in solution exist as free ions whose concentrations should be included fully in the solubility product. It adjusted the concentrations in three ways.

First, it recognized variation of speciation of phosphate—i.e., how total phosphate concentration would be partitioned among free phosphate, hydrogen phosphate, dihydrogen phosphate, and un-ionized phosphoric acid--and other ions with varying pH. Second, it recognized

the effect that ionic strength of the effluent has upon the activities of ions. Finally, the model included partitioning of ions between their free forms and complexed forms with which they are in equilibrium--most notably magnesium, which for example can form the MgOH^{+1} and MgPO_4^{-1} complexes.

The model found a minimum absolute solubility for struvite at a pH of 9.0. It also developed a solubility product estimate of $\text{pK}=13.2$, which as can be seen in Table 1 agrees well with the Taylor et al., 1963, value but not so well with the Bube, 1910, estimate.

In the second study, Ohlinger et al. (1998) modeled a system of Mg, ammonium, phosphate, hydrogen, hydroxide, and carbonate ions (the last three because they are present in natural water) and their various species and complexes in water, using equilibrium solubility products for struvite and other inorganic salts and equilibrium constants for formation of dissolved species. The modeling was done to predict how the equilibrium conditional solubility product for struvite varies with respect to pH. Figure 1 shows the model-predicted struvite solubility as a function of pH.

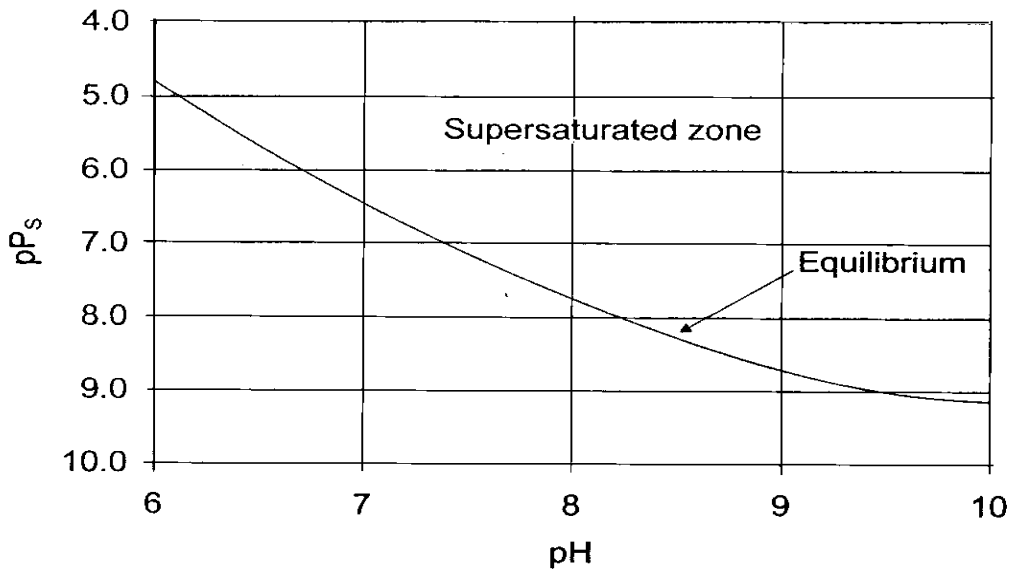


Figure 1: Variation of Equilibrium Conditional Solubility versus pH for Struvite (from Ohlinger et al., 1998)

In the figure, the solubility is indicated as pPs, the negative base-10 logarithm of the equilibrium conditional solubility product. This quantity is the product of total Mg concentration (not just free Mg ion), total ammonia concentration (not just ammonium), and total phosphate (including all species and complexes) in a solution that is in equilibrium with solid struvite. The equilibrium conditional solubility product is easier to determine in the laboratory because total Mg, ammonia, and phosphate concentrations can be determined through simple testing. Unlike the equilibrium conditional solubility product, equilibrium solubility products of the conventional type remain constant with pH. However, determining the free ion concentrations composing the equilibrium solubility products of the conventional type presents a challenge due to the ability of the ions to protonate, deprotonate, and complex.

Knowledge of the equilibrium conditional solubility product at various pH values is particularly helpful in the present case because it allows estimation of how much struvite, and thus phosphorus, can be precipitated from the wastewater by changing pH and/or total concentrations of ammonia and/or Mg. For example, by looking at Figure 1, we can see that if we have a solution saturated with respect to struvite (that is, in equilibrium with solid struvite) at pH 7.5, and we raise the pH to 8.0, then the product falls from $10^{-7.1}$ to $10^{-7.75}$, a reduction by a factor of about 4.5 (equal to $10^{(-7.1 - -7.75)}$, or $10^{0.65}$). If we know the beginning total concentrations, then we can calculate the ending concentrations, including phosphate. It should be noted that the modeling that resulted in Figure 1 includes only Mg, ammonia, phosphate, hydrogen, hydroxide, and carbonate species and their various combinations. Actual wastewater may have other inorganic ions and organic species that will alter the solubility profile with respect to pH.

The data and models relevant to struvite solubility indicate that struvite precipitation does indeed offer the potential for reducing phosphorus in lagoon effluent. Comparing the Mg, ammonium, and phosphate ion product of typical lagoon effluent (as estimated from pH and

composition data from North Carolina lagoons) against the Taylor et al. (1963) value for the equilibrium solubility product, one can see that lagoon effluent is typically saturated or near-saturated in struvite. The same conclusion is reached by comparing the typical conditional solubility product with the saturation curve in the model of Ohlinger et al. (1998). This conclusion is consistent with reports that lagoon effluent readily forms struvite scale in systems that handle it (Mohajit et al., 1989; Sievers, 1997; Booram et al., 1975; and Battistoni et al., 1997). The equilibrium solubility product and the model also can be applied to estimate that greater than 90% of the OP in solution in the effluent can be precipitated if the starting Mg concentration is twice the starting OP concentration and pH is raised by 1 point.

Not only does the data on equilibrium among species address the question of whether struvite precipitation can remove phosphorus, but it also addresses the question of whether Mg can be separated from product struvite and re-used for supplementing the raw liquid. An analysis, conducted by the author of the present work, envisioned reactions first to drive ammonia and water from struvite by heating to yield magnesium hydrogen phosphate, followed by dissolution of the latter in water to a concentration of 1% by weight. These two reactions are already known to occur. However, no reports on the third proposed reaction, carbonation with biogas (10% to 50% carbon dioxide) to precipitate a magnesium carbonate salt, could be found. The final reaction, heating of magnesium carbonate to convert to MgO, which could be used to supplement the raw effluent, is well known. The analysis thus centered on the third reaction, precipitation of magnesium carbonate.

To conduct the analysis, a simple equilibrium model of the proposed method (dissolution of the magnesium hydrogen phosphate in water at 1%, followed by carbonation to achieve equilibrium with carbon dioxide in biogas) was conceived. The model consisted of sixteen unknowns and sixteen equations relating the unknowns to one another. The unknowns were concentrations of dissolved species (hydrogen, hydroxide, phosphate, hydrogen phosphate, dihydrogen phosphate,

phosphoric acid, Mg ion, magnesium monohydroxide ion, dissolved un-ionized magnesium carbonate, magnesium bicarbonate, monomagnesium monophosphate, un-ionized magnesium hydrogen phosphate, magnesium di-hydrogen phosphate, carbonic acid, bicarbonate ion, and carbonate ion.

The sixteen equations were mainly dissociation and other equilibrium constants taken from Table 1. In several cases, the constants were not available and thus were calculated by applying the relation between Gibbs energy of reaction (from formation energies in the table) and equilibrium constants. In addition an overall balance on Mg and phosphorus were used as linking equations. Ionic strength was considered negligible, permitting use of concentrations in place of activities.

Solving the sixteen equations yielded equilibrium concentration for each species. Two Mg and carbonate-containing salts were identified and judged most likely to have their solubility products approached, due to the large negative values of these compounds' Gibbs energy of formation. The two compounds were MgCO_3 (magnesium carbonate) and $3(\text{MgCO}_3)\cdot(\text{OH})_2\cdot 3\text{H}_2\text{O}$ (magnesium carbonate magnesium hydroxide trihydrate). For these two salts, solubility products were calculated from Gibbs energy of reaction, and the products were compared against the product of their component ions' concentrations at equilibrium from the model.

The result was that, unfortunately, the equilibrium solubility product of neither of the salts was achieved. This means that, for these salts and for these assumptions, the proposed process cannot split Mg for recycle and supplementation.

Thermodynamics of Precipitate Nucleation

Thermodynamics of nucleation figure into research on struvite crystallization because it helps in understanding the conditions that may lead to large-grained, easily manageable product as opposed to fine-grained sludge-like product. The following discussion summarizes relevant aspects, drawing upon concepts set forth in texts of Walton (1967), Nielsen (1964), and Van Hook (1961).

The free energy change of a substance passing from dissolved state into a precipitated particle equals the difference between the free energy of the precipitated particle and the free energy of the ions in solution. In addition to the dependence of the free energy of the ions in each phase upon their formation energy, the energy of the ions in solution also increases with increasing concentration, and the energy of the precipitated particle decreases with the size of the particle.

The energy of the ions in the precipitated particle decreases with particle size because it includes not only its energy of formation, but also the surface energy of the particle. The surface energy reflects the net energy that is required to break bonds between solute molecules (water, in this case) as the particle forms and grows. The surface energy is the product of the tension at the surface between particle and solute (expressed in energy per area) and the area of the particle's surface. For a particle of constant density that is growing or shrinking yet maintaining its shape, the total energy content will not vary linearly with volume. One energy component (the energy of formation) will in fact vary proportionally with the number of molecules, and therefore volume. However, the other component (the surface energy) will vary only as the 2/3 power of the volume, because area varies as the 2/3 power with volume if shape holds constant. We may think of the free energy content of the particle, then, as the sum of two terms, each different functions of the number of ions in the particle:

$$\Delta G = -n\phi + n^{2/3}\psi \quad (2)$$

where ΔG = Gibbs energy difference between individual ions in solution and particle with n ions;

n = number of ions in a particle;

ϕ = Gibbs energy difference between individual ions in solution and ions in an infinite crystal; and

ψ = constant of proportionality relating free surface energy to $n^{2/3}$.

Figure 2 shows this relationship by graphing ΔG against n for four values of ϕ (a negative value; zero; and two different positive values, the greater of which appears as the lowest curve on the graph). From the graph, one can see that, for any value of ϕ less than zero, ΔG will always rise for increasing n . That is, equilibrium particle size is zero; if a particle consisting of multiple ions happens to form through collision of ions, the direction of spontaneous change is for it to decrease in size. Also, one can see that, for values of ϕ greater than zero, there exists a maximum in the curve, indicated as n^* , ΔG^* . At this point, free energy gained from size increase equals that lost from size increase. Above this point, growth decreases free energy, and below it, the reverse is true. This size, then, is a critical one. If no particles size n^* or larger exist in the solution, precipitation cannot spontaneously occur. If particles of size n^* or larger do exist, they will grow. The figure also reveals that n^* decreases as ϕ increases.

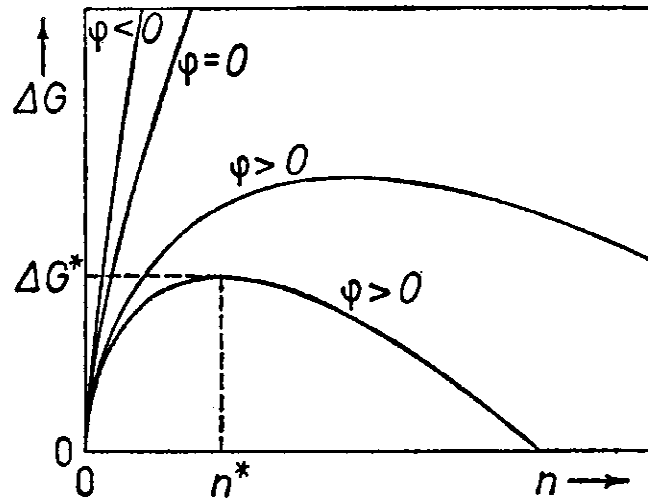


Figure 2: Free Energy versus Number of Particles in a Precipitating Crystal (from Nielsen, 1964)

Particles of size n^* are called critical nuclei; any particle size n^* or larger is called a nucleus. The provision or presence of nuclei is called nucleation. Nucleation can occur homogeneously or heterogeneously.

In heterogeneous nucleation, particles of a substance other than the precipitating substance serve as nuclei. In this case, the other substance must possess sufficient size and a crystalline structure similar to that of the precipitating substance.

In homogeneous nucleation, particles of the precipitating substance itself serve as nuclei. Even though the average particle size is near zero when averaged over all the molecules and over time, there still exists a distribution of particle sizes. Particles of size near zero (only one or a few ions) abound; those of critical size are very few if the critical size is large. Particles of many ions form by random collision of smaller particles and disintegrate quickly if they are smaller than the critical size. Occasionally, however, a particle of critical size or larger will form. For these particles, the slope of the free energy curve favors growth, and hence they will tend to grow rather than to disintegrate. As pointed out by Nielsen (1964), how frequently a particle of critical size or larger appears per cubic centimeter (cc) of volume depends on the relative size of ϕ and ψ , and can range from many per second to only one in many years.

For a given substance in solution, ϕ will increase with degree of supersaturation, while ψ holds constant, resulting in smaller and smaller n^* , and thus more frequent occurrence of nucleation. Also, if a solution contains particles that could serve as heterogeneous nuclei, the size to which those particles must be limited to prevent nucleation becomes smaller with increasing supersaturation. At some higher level of supersaturation, called the critical supersaturation, the critical size drops to just one ion, and nucleation will proceed immediately and in the form of many small particles.

Therefore, if struvite precipitates from a solution that is above its critical supersaturation level, many nuclei will form rapidly and simultaneously. This action will result in the undesired, small

particles of precipitate, because the available struvite will be distributed across a very large number of particles. In addition, even though a solution may not be critically supersaturated in struvite, precipitation could take the form of small particles if after reaching this level of supersaturation it is not exposed to already-existing large particles quickly enough to avoid precipitation onto homogeneously formed nuclei or small heterogeneous nuclei present in the wastewater.

Conversely, if the struvite precipitates from a solution in the range between saturation and critical supersaturation, and is exposed quickly enough to existing precipitate, then large crystals can be grown. Data on critical nucleus size or critical supersaturation level are needed to determine what particle size is to be avoided where precipitation is not wanted and what size is needed where precipitation is desired.

Unfortunately, the literature review identified no reports of experiments to estimate critical nucleus size or critical supersaturation. However, one study, Gunn and Murthy (1972) did monitor induction time (Δt_i) for struvite precipitation, a useful related characteristic. The quantity Δt_i , which may be considered to approximate the time for critical nuclei to be generated, was observed as a function of degree of the product of the concentrations of Mg ion, ammonium, and phosphate. Specifically, the study found a relation of:

$$\Delta t_i = (\text{constant}) \times \{[\text{Mg}^{++}][\text{NH}_4^+][\text{PO}_4^{---}]\}^{-1/3}{}^2 \quad (3)$$

This relation is graphed in Figure 3. From the figure, one can estimate the induction time for a wastewater of given magnesium, TAN, and OP concentrations.

For example, suppose that wastewater, immediately after Mg supplementation and adjustment to 9.2 pH, had dissolved in it a total Mg concentration of 60 parts per million (ppm), TAN of 600 ppm, and OP of 90 ppm as phosphorus. Assuming the Mg to be nearly all available as free Mg ion rather than complexed in some way, the Mg concentration would be about 0.00247 moles per liter

(mol/L). The total ammonium ion plus ammonia concentration would be 0.0429 mol/L, but at this pH only about 50% would be in the ammonium form, giving an ammonium ion concentration of about 0.0214 mol/L. The OP, totaling 0.0029 mol/L, would primarily exist (about 99%) as hydrogen phosphate ion, with about 1% as dihydrogen phosphate ion and 0.1%, or 0.0000029 moles per liter, as phosphate ion.

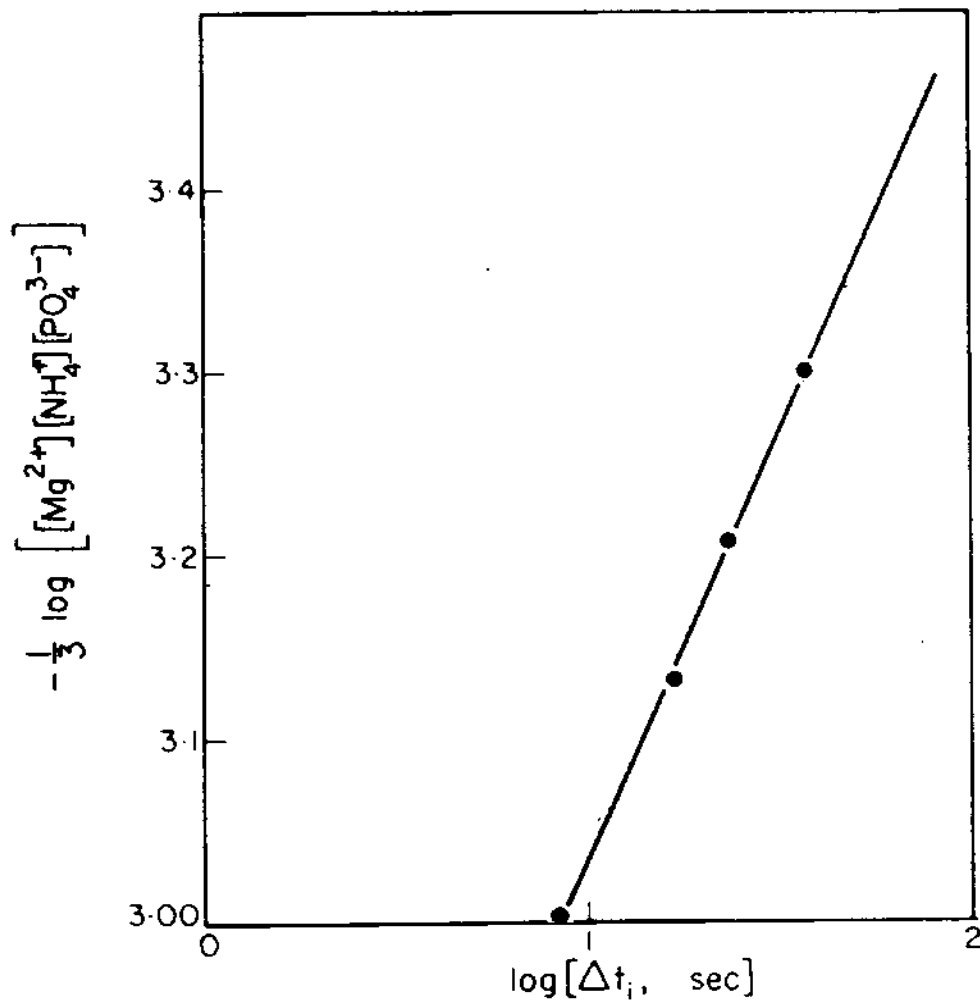


Figure 3: Concentration ($-1/3 \log$ of Ionic Product, Mol/L) versus Induction Time (Sec) for Struvite Precipitation (from Gunn and Murthy, 1972)

The product of the Mg, ammonium, and phosphate ion concentrations is $(0.00247) \times (0.0214) \times (0.0000029)$, or about 1.53×10^{-10} . Taking the logarithm and multiplying by negative one-third gives 3.27. Finding this value on the vertical axis in Figure 3 and reading down to the horizontal axis yields an estimate of 1.6 for the logarithm of the induction time in seconds, which means the induction time is about 40 seconds. Approximately this time may pass before spontaneous nucleation begins despite the high degree of supersaturation. Comparing with equilibrium solubility product of $10^{-13.2}$, we can see that the solution is supersaturated in struvite by a factor of 2000 or more.

If the concentration of Mg doubles and the other conditions remain the same, the estimated induction time from Figure 3 drops to about 22 seconds. If the TAN concentration is then doubled, the time drops to about 12 seconds.

These estimates suggest that the critical nucleus size may be large enough that spontaneous nucleation may be avoidable. The induction times indicate that there is a comfortable time cushion available between the point in time at which supersaturation is achieved by pH and content adjustment and the point by which the adjusted effluent must be exposed to the struvite particle surfaces on which the precipitation is intended to occur. However, the time estimates to self-nucleation at various conditions must be regarded as upper limits of the time available, because heterogeneous nuclei in the raw effluent could promote nucleation before the time period is exhausted. In addition, locally very high levels of supersaturation could occur at the point where the adjusting chemicals are mixed into the raw effluent, possibly exceeding critical supersaturation and thereby forming nuclei almost immediately.

Gunn and Murthy (1972), Buchanan et al. (1994), and Joko (1984), state that solutions supersaturated with respect to struvite can remain stable if they lie below the critical saturation level; however, the actual value of the level was not found in the literature review. Buchanan (1994) also

reports that increasing the pH of wastewater that is not precipitating struvite into the 8-11 range can result in induction and precipitation of struvite in a few minutes. The pH increase presumably increases, via pH-dependent speciation, the product of the concentrations of the required ions above the critical supersaturation level. The latter study also reports that a majority of phosphate can be precipitated via struvite.

Kinetics

Precipitation of a salt from a supersaturated solution occurs in either of two different modes. These are called nucleation and crystal growth.

If there are no surfaces of solid struvite present, the precipitation must first occur by forming nuclei. This mode of precipitation was reviewed above. It is desired that precipitation not occur by this mode in a struvite crystallizer, because it could lead to fine, sludge-like product and/or particles that are too small to be retained by gravity.

If there are solid struvite surfaces already present, then precipitation will occur by crystal growth. In this mode, the precipitation offers the possibility of being controlled to form large-grained product, which can be retained more easily by gravity and is easier to handle and dry. To create a process using crystal growth, it is helpful to understand the kinetics of the process. The kinetics of the process characterizes the rate at which it occurs, thus enabling some prediction of the dimensions required for a given reactor type, flow rate, composition, and phosphorus reduction target.

Some recent studies have reported on kinetics of struvite precipitation in the crystal-growing mode. The studies have generally found that the rate of precipitation varied proportionally with the extent of supersaturation expressed in $(\text{mol/L})^3$, and in some cases provide the measured rate constant. Unfortunately, those studies did not measure or did not report the amount of crystal surface area per volume of reacting solution. Knowing this last quantity is crucial in designing a struvite precipitating

device because it is not possible to calculate the total precipitation rate, and hence phosphate removal rate, from a known supersaturation degree and volume unless one knows the amount of crystal surface area present and the precipitation rate per surface area.

Ohlinger et al. (2000) did report the size, shape, and amount of crystals, and held the quantity constant through each experimental run, thus enabling a rough estimate of the surface-area-specific rate constant. The rate constant was not reported in the desired surface-area-specific form. Rather, it was reported as the constant of proportionality between the decrease in struvite ionic product per volume of liquid per time and the difference between the product of the total concentrations of the three constituent ions and that product for a saturated solution at that pH. However, from the data in the article regarding the size, shape, and amount of crystals, it is possible to estimate surface area and thus convert the reported constant into the desired form.

The result is an estimate that places the rate constant in the range of 13 to 19×10^{-6} (mol/L)³ decrease in struvite ionic product per hour per (mol/L)³ of supersaturation and per square millimeter (mm) of surface area per L of reacting solution. Canceling units where possible yields 0.13 to 0.19 decimeters (dm) per h as the estimate for the surface-area specific rate constant. While this estimate is uncertain because several assumptions were used in the conversion, it will serve as a starting point because no reports of the surface-area-specific rate constant were found in the review.

Research Goals for Applying Struvite Crystallization to North Carolina Lagoon Effluent

Completion of the literature review facilitated the setting of goals for research to apply it for removal of phosphorus from lagoon effluent in North Carolina. The goals were formulated to utilize the results of work reported by others and to advance knowledge beyond that work. Seven goals were set forth and are summarized below.

(1) Observe precipitation of phosphorus from actual lagoon effluent in batch tests.

Estimates yielded by the literature review for struvite solubility and the rate constant were based on others' experiments with laboratory reagents, synthetic wastewater, or actual wastewater from sources other than North Carolina livestock lagoon effluent. Batch tests for removal of phosphate using locally obtained lagoon effluent will aim not to quantify those constants precisely, but rather will aim to indicate whether precipitation is occurring when expected and approximately at the expected rate. If precipitation does not occur as expected, the assumptions and calculations used in interpreting the literature would have to be revisited to identify errors and, possibly, more precise solubility and rate measurements would have to be conducted.

(2) Investigate means of magnesium supplementation in batch tests.

The analysis of thermodynamic data in the literature review indicated that Mg cannot easily be recycled from the product struvite. Therefore, Mg from external sources will be needed for augmenting the content of the effluent. Ideally, Mg should be added in a MgO or carbonate form to avoid adding anions of environmental concern. Also, the Mg addition should be in solution form rather than in slurry form, because the latter would introduce heterogeneous nuclei. The literature review revealed that others have used MgO, but not in solution form. Batch tests are intended to develop a means for producing and introducing MgO or carbonate in solution. In addition, batch tests will explore the possibility of adjusting pH by manipulating pressure (to change the content of acidic and alkaline gases) and by adding ammonia. The former is desirable because it would require no purchase of pH-adjusting chemicals. The latter may be desirable because it adds no ions not already addressed by current treatment systems, and because it may be available in the future from on-site ammonia stripping systems.

(3) Set forth the basic design for a struvite crystallizer.

Using the results of the literature review and the research toward the first two goals, the basic design for a crystallizer appropriate to livestock lagoon effluent can be formulated. The design should aim for economy, simplicity, and effectiveness.

(4) Model the performance of hypothetical crystallizers adhering to the basic design.

Developing a model for the behavior of the crystallizer will help in understanding the crystallizer and in designing crystallizers for waste streams of various flow rates and characteristics. More than one model may result if uncertainty exists as to how the materials will behave in the crystallizer.

(5) Assemble and operate a laboratory-scale crystallizer adhering to the basic design.

Drawing upon the modeling from the previous objective, a design for a laboratory-scale crystallizer can be produced. Once assembled, the crystallizer can be used for studying struvite crystallization with the control and flexibility of the laboratory environment, yet using actual lagoon liquid from the field.

(6) Characterize the operation of the laboratory-scale crystallizer and compare with modeling.

The variation in performance of the crystallizer at different levels of Mg, pH, and flow rate can be evaluated using statistical analysis of the performance achieved at each level in a randomized series of short runs. The validity of the models can be evaluated by characterizing the behavior of the crystallizer during runs long enough to permit more complete data-taking and to ensure operation is near steady state. The model best fitting the observations can then be selected and/or modified if necessary.

(7) Design and Operate a field-scale crystallizer by applying results of goal 6.

The model as selected and/or modified can then be used to design and assemble a larger crystallizer for use at an actual livestock lagoon. The crystallizer can then be tested and its behavior evaluated at different levels of Mg, pH, and flow rate.

The next section, “Experiments in Batch-Mode and Resulting Design Elements for Struvite Crystallizer,” reports on work done to fulfill goals (1), (2), and (3). The subsequent section, “Modeling the Behavior of a Cone-Shaped, Fluidized Bed Struvite Crystallizer,” overviews work for goal (4). Next, “Experiments with a Laboratory-Scale Continuous Crystallizer” covers goals (5) and (6). “Design and Operation of Field-Scale Crystallizer” addresses goal (7). “Summary, Conclusions, and Recommendations for Future Work” then overviews and interprets the main outcomes of the research.