Struvite Scale Potential Determination Using a Computer Model

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Struvite-Computer-Model

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Abstract

A computer model was developed and tested to predict struvite precipitation mass potential. The model validity was tested using results from a fluidized bed precipitation reactor processing wastewater treatment plant sludge liquor. Increasing interest in controlled struvite precipitation to protect wastewater treatment infrastructure and to harvest nitrogen and phosphorus from wastewater will make the model useful to engineering and plant operation practitioners.

Introduction

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) scaling in post-digestion wastewater treatment processes can cause costly operation and maintenance problems. Cost impacts result from reduced capacity, equipment damage, and system downtime. One significant problem for designers and operators faced with struvite scaling problems is quantification of the struvite scaling potential for a particular waste stream. Although recent work has enabled investigators to determine the presence or absence of struvite scaling potential, designers need to quantify that scaling potential to design remediation or preventative systems or processes (Miles and Ellis, 2001; Ohlinger et al., 1998).

Accurate quantification of struvite scaling potential for a particular waste stream has historically been a complex calculation process. The literature contains much of the information needed to determine scaling potential but no commonly accepted standard calculation methodology.

Therefore, it has been up to the designer to extract components of the calculation process from different literature sources and piece them together into a method to complete a laborious calculation process.

The complexity of the calculation process has been a deterrent to the use of struvite precipitation potential quantification as a process planning and operation tool. Calculation of struvite equilibrium is an iterative process involving solution of a series of non-linear algebraic equations containing multiple variables, any of which can have a significant impact on the accuracy of the result. Many of the parameters are interdependent, making accurate determination of a correct solution dependent upon a thorough understanding of and an accounting for those interdependencies. This is not intended to imply that the process described cannot be readily handled by individuals with a thorough understanding of struvite chemistry and use of chemical equilibrium software. It can. Those individuals, however, are not generally the ones who need the information to make routine design and process decisions regarding struvite precipitation.

The objective of the current work is to provide a robust tool for designers and process controllers to efficiently and accurately quantify struvite precipitation potential using input parameters from the user's process.

In assessing struvite precipitation potential, it is often desirable to vary the values of process variables in the calculations to determine the impacts of process changes. Such "what if" exercises enable calculation of the impacts of changing important process variables such as the limiting ion concentration and the pH on the potential struvite mass production in the system. Current methods require laborious recalculation for each proposed change, a time consuming process. A tool that enables users to readily determine the impact of changing process variables on the struvite mass

precipitation potential will provide designers, process control engineers, and operators with the ability to easily determine the parameter settings to optimize struvite control processes.

Struvite scaling has historically been viewed as a nuisance problem and efforts at control have focused on methods to prevent or delay precipitation. More recently, struvite has been viewed as a potential source of valuable nitrogen and phosphorous minerals. During the past ten years, researchers, primarily in Europe and Japan, have studied struvite precipitation from wastewater as a method of recovering phosphate, a mineral that is in short supply in many areas of the world. Whereas struvite scale prevention entails methods designed to delay or prevent precipitation, struvite recovery entails maximizing precipitation within a reactor to optimize the amount of nitrogen and phosphorus-containing struvite recovered from the waste stream.

Whether interest is in preventing scale formation resulting from struvite precipitation or in recovering nitrogen and phosphorous from wastewater using struvite precipitation, quantification of struvite precipitation potential is critical information for process control and design. Many factors influence struvite precipitation from wastewater. Thermodynamic factors include absolute and relative constituent concentrations, pH, temperature, and the concentrations of organic and inorganic materials in the complex wastewater matrix. Kinetic factors include mixing energy and temperature. For a quantification tool to be accurate and useful, it must have the capability to account for all of these factors.

Determining struvite scaling potential involves first determining struvite equilibrium under the conditions of the process stream. The activity quotient for struvite is calculated as:

$$Q_{SP} = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\}$$

where: Q_{SP} = activity quotient for struvite (solubility product under all conditions).

$\{Mg^{2+}\}$ = free magnesium ion activity.

$\{NH_4^+\}$ = free ammonium ion activity.

$\{PO_4^{3-}\}$ = free phosphate ion activity.

The struvite saturation condition is determined by calculating the saturation index, S:

$$S = \frac{Q_{SP}}{K_{SP}}$$

where: K_{SP} = equilibrium solubility product for struvite = $10^{-13.26}$ (Ohlinger, et al., 1998)

A system is oversaturated when S > 1, meaning struvite precipitation potential exists. If S ≤ 1, the system is at equilibrium or undersaturated for struvite and precipitation cannot occur.

The greatest challenge in determining the saturation index is accurately determining the activities of the struvite constituent ions, which cannot be measured directly. Rather, the activities must be calculated, taking many factors into account in the calculations. The factors are dynamic in a precipitating system, making an iterative solution necessary; hence, the need for a computer solution. Using magnesium as an example, ion activity is calculated as:

$$\{Mg^{2+}\} = \gamma_{Mg^{2+}}[Mg^{2+}] = \gamma_{Mg^{2+}}\alpha_{Mg^{2+}}C_{T_{Mg}}$$

where:

$\gamma_{Mg^{2+}}$ = activity coefficient for free magnesium ion.

$\alpha_{Mg^{2+}}$ = ionization fraction for free magnesium ion.

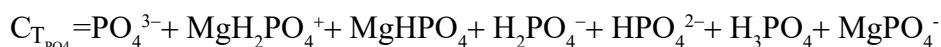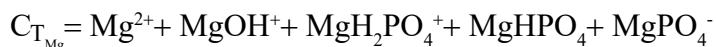$C_{T_{Mg}}$ = total dissolved concentration of magnesium (measured).

$[Mg^{2+}]$ = concentration of free magnesium ion.

The activity coefficient and the ionization fraction must be accurately determined to correctly calculate the ion activity for each dissolved constituent. Activity is strongly influenced by the concentration of all charged ions in solution and can be quantified based on calculation of ionic strength using specific conductance measurements (Russell, 1976). Ionization is strongly influenced by solution pH. In the case of magnesium and phosphate, it is also influenced by the relative concentrations of each constituent due to the presence of magnesium-phosphate complexes. In a system where struvite precipitation is occurring, causing constituent concentrations to change, the only method to accurately determine ionization fractions is through an iterative mass balance calculation of all struvite constituents, usually performed using commercially available chemical equilibrium software running on a desktop computer.

In prior studies, investigators have reported using the equilibrium software packages to determine struvite equilibrium conditions and thereby determine the saturation index (Ohlinger et al., 1998; Doyle and Parsons, 2002). Wrigley, et al. (1992) reported development of a Fortran- based equilibrium model. The objective of the current work is to calculate the amount of struvite that can precipitate from a process stream under given conditions. Although the saturation index accurately indicates saturation conditions, it does not quantify the potential mass of struvite that can precipitate, information that is needed by designers and process controllers. Further calculations, which incorporate process flows, are necessary to quantify the precipitation potential on a mass basis.

Methods

Calculating struvite mass precipitation potential requires a dynamic evaluation tool capable of responding to varied input parameters and induced parameter changes resulting from precipitation. A computer program was written to perform the described calculations through an iterative process of determining constituent concentrations, testing for precipitation potential, allowing precipitation (or dissolution) by adjusting constituent concentrations, and continuing to test until equilibrium conditions are attained. The following constituent mass balance equations are used in the program:

$C_{T_{Mg}}$ = Mg^{2+}+ $MgOH^+$+ $MgH_2PO_4^+$+ $MgHPO_4$+ $MgPO_4^-$

$C_{T_{NH4}}$ = NH_4^++ NH_3

$C_{T_{PO4}}$ = PO_4^{3-}+ $MgH_2PO_4^+$+ $MgHPO_4$+ $H_2PO_4^-$+ HPO_4^{2-}+ H_3PO_4+ $MgPO_4^-$

User inputs include measured constituent concentrations ($C_{T_{Mg}}$, $C_{T_{NH4}}$, $C_{T_{PO4}}$), solution pH, temperature, and specific conductance. The program calculates an estimate of the ionic strength from the specific conductance using the correlation derived by Russell (1976). Ion activity is calculated from the ionic strength using the Davies approximation of the Debye-Huckel limiting law and used to adjust the

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equilibrium constants for each species. Corrections for temperature using the Van't Hoff equation are also made to the equilibrium constants. The adjusted equilibrium constants are inserted into the matrix used in the iterative mass balances.

The numerical solution for the system of non-linear equilibrium equations was developed using the Damped Newton's method (Conti and de Boor, 1980). The algorithm can be described by the following pseudo-code (as listed by Conti and de Boor).

For m = 0, 1, 2, …, until satisfied, do:

$$h := - f'\left(x^{(m)}\right)^{-1} f\left(x^{(m)}\right)$$

$$i := \min\left\{ j: 0 \le j, \left\| f\left(x^{(m)} + \frac{h}{2^j}\right)\right\|_2 < \left\| f\left(x^{(m)}\right)\right\|_2 \right\}, j = 1,2,..., j_{max}$$

$$x^{(m+1)} := x^{(m)} + \frac{h}{2^i}$$

where,

$f'(x^{(m)})^{-1}$ = is the inverse of the Jacobian matrix estimated at iteration m.

$f(x^{(m)})$ = is the vector of the functions estimated at iteration m.

h = is the vector of the estimated increment for the next iteration

$\|x\|_2$ = is the Euclidean norm for the function vector, which can be expressed as:

$$\|x\|_2 = \sqrt{x^T x} = \sqrt{\sum x_i^2}$$

The Jacobian matrix is defined as:

$$\begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} & \cdots & \dfrac{\partial f_1}{\partial x_n} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} & \cdots & \dfrac{\partial f_2}{\partial x_1} \\ \vdots & \vdots & \cdots & \vdots \\ \dfrac{\partial f_n}{\partial x_1} & \dfrac{\partial f_n}{\partial x_2} & \cdots & \dfrac{\partial f_n}{\partial x_n} \end{bmatrix}$$

where,

n = number of unknowns, and

f_i = the ith nonlinear equation.

The Damped Newton's method has the advantage of controlling the size of the step (h) for the next iteration by controlling the Euclidean norm of the function. That is, the future iteration $x^{(m+1)}$ is not allowed to stray too far from the previous iteration $x^{(m)}$ by constantly monitoring the Euclidean

norm for the function vector. The numerical iteration stops when the successive iterations are within 10^{-6} as measured by the norm of the step vector (h). The algorithm was coded using Visual Basic in Microsoft $^{©}$ Excel.

Once the equilibrium concentrations $[Mg^{2+}]$, $[NH_4^+]$, and $[PO_4^{3-}]$ are calculated, their product is compared to the adjusted solubility constant of struvite. If the product of the concentrations is less than the solubility constant, the system is under saturated and the equilibrium concentrations are used. If the product of the concentrations is greater than the solubility product, the system is over-saturated. In that case, the molar concentrations of the three struvite constituents are reduced on an equimolar basis and the equilibrium concentration is recalculated repeating the same process until the equilibrium concentrations converge to the solubility product. The convergence criterion is based on the difference between the logarithms of the product of equilibrium concentrations and the solubility constant to be within 10^{-5}. The algorithm is shown below:

For $j = 0, 1, 2,\ldots$, until satisfied*, do:

$$\text{If } \prod_{i=1}^{nc} C_i > (K_{struvite})^{-1} \text{ then,} \qquad \text{elseif } \prod_{i=1}^{nc} C_i < (K_{struvite})^{-1} \text{ then,}$$

$$\text{For } i = 1,\ldots, nc \qquad\qquad\qquad \text{For } i = 1,\ldots, nc$$

$$C_{min}^{j} = 0.05 * \min\{CT^{j}\} \qquad\qquad C_{min}^{j} = 0.5 * C_{min}^{j-1}$$

$$CT_i^{j+1} = CT_i^{j} - C_{min}^{j} \qquad\qquad\quad CT_i^{j+1} = CT_i^{j} - C_{min}^{j}$$

* The convergence criterion is:

$$\left| \log\left(\prod_{i=1}^{nc} C_i \right) - \log\left(\frac{1}{K_{struvite}} \right) \right| \leq 10^{-5}$$

where,

Π = product operator,

C_i^k = equilibrium concentration of component i at iteration k,

$K_{struvite}$ = the adjusted formation constant of struvite $(\gamma_{struvite} * 10^{-13.26})^{-1}$,

nc = number of components of interest, and

CT_i^k = total molar concentration of component i at iteration k.

Results returned from the calculations are the equilibrium concentrations of the struvite constituents. Using the equilibrium concentrations, the initial concentrations and the molecular weight for struvite, the program determines the mass precipitation potential for the process stream.

$$\text{Struvite Mass, } \frac{kg}{day} = \left(Q, \frac{m^3}{day} \right)\left(\Delta C_T, \frac{mol}{L} \right)\left(\frac{0.2454 \, kg}{mol} \right)\left(\frac{1,000 \, L}{m^3} \right)$$

where,

Q = volumetric flow rate of process stream

ΔC_T = calculated decrease in $C_{T, Mg}$ resulting from struvite precipitation.

0.2454 kg/mol = molecular weight of struvite ($MgNH_4PO_4 \cdot 6 H_2O$)

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To validate the program, operational data collected from the Sacramento Regional Wastewater Treatment Plant in northern California was utilized. The Sacramento facility routinely experiences struvite precipitation in the supernatant from its post-digestion, facultative sludge lagoons. Measurements of pH, temperature, specific conductance, and dissolved magnesium, ammonia-nitrogen, and orthophosphate concentrations were input to the program to determine the struvite mass precipitation potential. Subsequent runs were then conducted to determine the effect of parameter changes on the struvite mass precipitation potential. Parameters varied were temperature, pH, and limiting ion (magnesium) concentration.

Results

The nature of the current work allows for an unlimited number of proposed struvite precipitation problems to be solved using the computer tool. To confirm the validity of results produced by the program, bench-scale experiments were conducted using the fluidized bed reactor (FBR) described by Ohlinger et al. (2000) to precipitate struvite from Sacramento facultative sludge lagoon supernatant. Four experiments were conducted, all at 25°C. In the first two experiments, raw lagoon supernatant was used ($\mu = 0.07$ mol/L). In the second two experiments, magnesium sulfate was added to the lagoon supernatant to enhance struvite precipitation and thus, phosphate removal (magnesium was the limiting ion in the system). Influent and effluent struvite constituent concentrations were measured, along with pH, temperature, and specific conductance. The measured influent values were used as input parameters for the computer tool. The predicted equilibrium values from the computer program output and the measured effluent struvite constituent concentrations from the FBR effluent are listed in Table 1.

Table 1. Comparison of computer simulation predicted struvite constituent concentrations to measured values from struvite precipitation experiments using a fluidized bed reactor and post- digestion sludge supernatant.

Hydraulic Detention Time (Hr.)	pH	Concentration (mg/L)								
		Inlet (Measured)			Outlet (Measured)			Outlet (Predicted)		
		$C_{T, Mg}$	$C_{T, NH3}$	$C_{T, PO4}$	$C_{T, Mg}$	$C_{T, NH3}$	$C_{T, PO4}$	$C_{T, Mg}$	$C_{T, NH3}$	$C_{T, PO4}$
7.2	8.30	13	430	41	6.4	420	32	5.6	426	32
7.2	8.32	13	430	40	6.5	420	32	5.0	426	30
7.2	8.28	14	440	41	6.4	420	32	5.3	436	30
4.2	8.19	13	440	42	6.8	430	33	6.3	436	33
4.2	8.13	13	440	41	6.7	440	33	6.9	437	33
4.2	8.22	13	440	40	6.9	430	33	5.9	436	31
4.1	8.21	34	450	40	16	420	16	14	438	14
4.1	8.21	35	450	41	16	420	18	14	437	13
7.3	8.21	27	450	40	12	420	19	10	440	18
7.3	8.18	25	440	40	13	420	19	10	431	20

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Discussion

The algorithms used in the program converge quickly to a solution for struvite equilibrium problems. Accuracy of solutions was tested in two ways. During development, results were compared to the results from MINEQL+, a commercially available chemical equilibrium computer program, after adding the thermodynamic characteristics for struvite to its database. The two programs, which use different algorithms for solving the equilibrium matrices, produced identical results. Second, and more important, the program was used to predict struvite constituent concentrations for the fluidized bed reactor experiments using sludge liquor from a municipal wastewater treatment process stream. As shown in Table 1, the program accurately predicted the effluent concentrations of the struvite constituents.

The true utility of the tool is in predicting the mass of struvite that can be precipitated from a process stream under given conditions. Since the given conditions can be easily changed for subsequent runs, it is easy for a user to simulate changing physical parameters such as pH and limiting ion concentration to determine the impact on struvite precipitation. It is precisely that type of analysis that is of interest to an investigator trying to optimize struvite removal, either to harvest phosphorus or nitrogen from a waste stream or to protect downstream infrastructure from struvite scaling damage.

To illustrate the utility of using the tool to conduct a "what if" investigation into changing precipitation-affecting parameters, the tool was used to predict the effect of pH elevation at three different temperatures. This type of simulation would enable an investigator to determine the seasonal pH settings needed to achieve a desired struvite production rate from a precipitation reactor. The results, in Figure 1, illustrate the sensitivity of struvite production to pH elevation and the expected seasonal reduction in struvite production due to water temperature depression. The input parameters for the simulation were measured values from the Sacramento facility (Flow = 4,700 m^3/day, μ = 0.07 M, concentrations from Table 1).
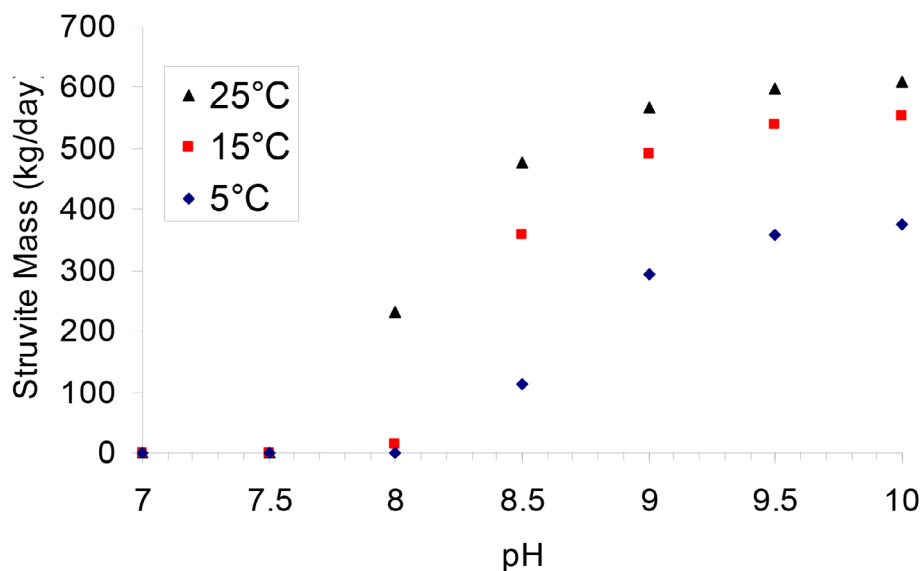

Figure 1. Predicted response of struvite precipitation potential to pH and temperature changes.

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A second type of simulation was run, again using the physical parameters from the Sacramento facility. The second simulation investigates the impact of supplementing magnesium, the limiting ion, on the struvite production rate at three different pH values. This type of simulation would be useful to an investigator interested in assessing the increased struvite, nitrogen, and phosphorus yields resulting from magnesium supplementation. Coupling the results of the simulation with chemical cost and struvite price data would enable the investigator to make process decisions based on cost-optimization. All simulations illustrated in Figure 2 were run at 25°C.
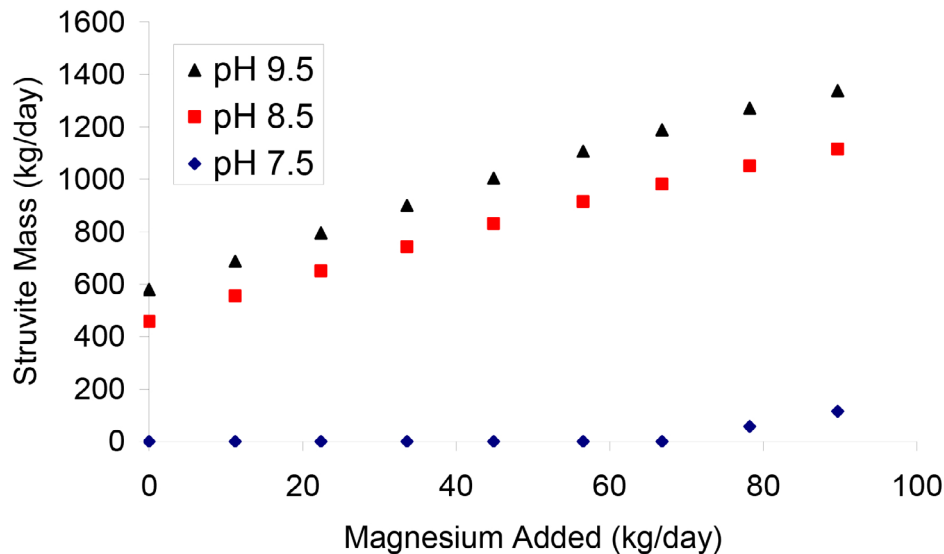

Figure 2. Predicted response of struvite precipitation potential to pH and limiting ion concentration changes at 25°C.

Conclusions

The struvite computer tool developed in this investigation accurately predicts equilibrium dissolved struvite constituent concentrations and mass struvite precipitation potential. Accuracy of the tool was verified by comparing the output to experimental data using process fluid from a municipal waste treatment facility. The tool should prove useful to engineering and plant operation practitioners interested in preventing struvite scale damage to infrastructure and in harvesting the nutrients nitrogen and phosphorus from municipal waste streams. In each case, the tool can quantify the amount of struvite that will be produced in a precipitation reactor, or, in the absence of a reactor, in the storage and conveyance system. The tool will be available through the Office of Water Programs at California State University Sacramento.

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References

Conti, S.D. and de Boor, C. (1980). *Elementary Numerical Analysis: An Algorithmic Approach.* 3rd Ed. McGraw-Hill, New York, NY.

Doyle, J.D. and S.A. Parsons (2002) Struvite formation, control and recovery. *Wat*. Res. **36**(16): 3925-3940.

Miles, A. and Ellis, T.G. (2001) Struvite precipitation potential for nutrient recovery from anaerobically treated wastes. *Wat. Sci. and Tech*. **43**(11): 259-266.

Ohlinger, K.N., Young, T.M., and Schroeder, E.D. (1998). "Predicting struvite formation in digestion." *Wat. Res*. **32**(12), 3607-3614.

Ohlinger, K.N., Young, T.M. and Schroeder, E.D. (2000) "Post Digestion Struvite Precipitation Using a Fluidized Bed Reactor," ASCE J. of *Env. Engr.* **126**(4), 361-368.

Russell, L.L. (1976) *Chemical Aspects of Ground Water Recharge with Wastewaters*. PhD Thesis, Department of Civil and Environmental Engineering, University of California, Berkeley.

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