

A probabilistic approach to modeling struvite precipitation with uncertain equilibrium parameters



N.J. Barnes*, A.R. Bowers

Department of Civil and Environmental Engineering, Vanderbilt University, 289 Jacobs Hall, PMB 351831, Nashville, TN 37235, USA

HIGHLIGHTS

- Published constants related to struvite solubility can vary by an order of magnitude.
- Significant uncertainty also exists in wastewater concentrations and parameters.
- Struvite precipitation model uncertainty was evaluated in a Monte Carlo framework.
- Model projections and associated uncertainty agreed with treatment plant data.
- Proposed method can be used to evaluate uncertainty in any design situation.

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ABSTRACT

The precipitation and accumulation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) within anaerobic processes has been a costly problem for wastewater facilities. To anticipate and mitigate struvite buildup, solubility models have been developed that employ equilibria software for the evaluation of equilibrium equations. Unfortunately, these programs run under the assumption that chemical equilibrium constants are single, universally accepted values when, in reality, a wide range of values have been published for these constants.

In this study, a struvite solubility model was developed in which the equilibrium constants were treated as empirically distributed variables within a Monte Carlo simulation to understand the effect of uncertainty on precipitation potential over a range of pH (6–8.5), temperature (0–60 °C), and ionic strength (0–1 M). Using field conditions measured at a struvite-afflicted treatment plant as model input parameters, the resulting uncertainty in the struvite supersaturation ratio was found to be highly consequential, with the 90 percent confidence interval spanning well over an order of magnitude. Additionally, a sensitivity analysis was performed on the model, identifying the third orthophosphate equilibrium constant and the struvite solubility product as the most significant source of uncertainty.

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1. Introduction

Precipitation and subsequent accumulation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) within sludge digestion and postdigestion processes has been a costly and enigmatic problem for wastewater facilities. Struvite crystals commonly form on the surface of pipes, mixers, and submerged mechanical equipment, limiting their efficacy and necessitating frequent maintenance. Fouling is often so extensive that processes are rendered inoperable and entire pipe systems have to be replaced (Ohlinger et al., 1998; Mamais et al., 1994; Horenstein et al., 1990). Benisch et al. estimated that main-

tenance and capacity reduction related to struvite deposits could cost a midsize (95 MLD/25 MGD) plant more than \$100,000 per year (Benisch et al., 2000).

Though conditions of struvite supersaturation within a wastewater stream often promote fouling, they can also be ideal for the extraction of struvite for phosphorus recovery. This can be of commercial use where the phosphate and ammonia-rich crystals have been shown to be an effective slow-release fertilizer (Durrant et al., 1999).

Predicting the precipitation of struvite is tantamount to efficient and cost-effective design and operation of wastewater plants. More specifically, it is necessary to have an accurate model of struvite solubility that can be adapted to the highly variable conditions within a wastewater stream (Ohlinger et al., 2000). Similar consid-

* Corresponding author.

E-mail addresses: nathaniel.j.barnes@vanderbilt.edu (N.J. Barnes), alan.bowers@vanderbilt.edu (A.R. Bowers).

erations must be made when intentionally precipitating struvite for environmental or agriculture purposes.

1.1. Uncertainty

The efficacy of a deterministic model for struvite solubility is diminished by three unique sources of uncertainty—a problem that has not been adequately evaluated. These sources of uncertainty—wastewater composition, measurement errors, and equilibrium parameters—all affect struvite prediction in different ways.

1.1.1. Uncertainty in concentrations

In struvite precipitation modeling, representative concentrations—usually a grab sample or an average of several grab samples—are commonly selected for each wastewater constituent (Ohlinger et al., 1998; Doyle and Parsons, 2002). Then, predictions are made using single, deterministic values under the pretense that average inputs will give an average output. This method, though simple and straightforward, does not evaluate the spatial and temporal variability of the constituents. Variability may be more prevalent in some constituents than others, and its effect on the conditional solubility product at different pHs, temperatures, and ionic strengths may be unevaluated.

While existing struvite equilibrium models are used for solutions of known/fixed concentrations, this idealized scenario is uncommon in wastewater. Instead, concentrations are in constant flux, rendering any deterministic predictions made from single or averaged values insufficient and obsolete the moment they are made.

The range of variability of constituent concentrations and wastewater properties are plant- and process-specific, so these must be evaluated on a case-by-case basis. As such, site-specific data must be collected to adequately characterize the spatial and temporal uncertainties.

1.1.2. Uncertainty due to errors in measurement

All things measured physically, i.e. evaluation of concentrations and equilibrium constants, are affected by measurement error. However, measurement errors accrued in the modern laboratory are rendered inconsequential compared to the uncertainty introduced by reported literature values. For example, the errors expected from different methods of measuring total phosphorus concentrations were all less than 0.05 mg/L (Greenberg et al., 1985, p. 440). This is inconsequential compared to concentrations in wastewater streams on the order of 100 mg/L (Doyle and Parsons, 2002; Ali and Schneider, 2008). Measurement errors for orthophosphate, ammonia, total nitrogen, total magnesium, pH, and temperature were similarly insignificant, especially when compared to equilibrium parameter uncertainty for struvite. Therefore, the uncertainty due to measurement error was considered negligible.

1.1.3. Uncertainty in equilibrium parameters

Several models for struvite precipitation have been developed using chemical equilibria and solubility, for example, those outlined by Ohlinger et al. (1998) and Doyle and Parsons (2002). As is common practice in chemical modeling, equilibria software such as MINEQL+ and MINTEQA2 are regularly employed. Unfortunately, these assume that equilibrium constants for the speciation and solubility of constituents are single, universally accepted values. This assumption is further promoted by the existence of reference materials, such as Smith and Martell (1976), that report only a single selected, or “critical”, stability constant for each reaction. In reality, each of these constants (K_{sp} , K_{a1P} , K_{a2P} , K_{a3P} , K_{a1N} , K_{1Mg} , K_{MgP} , K_{MgHP} , and K_{MgH2P}) is associated

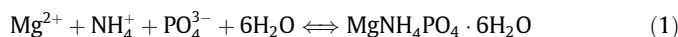
with a variety of published values, many with substantial differences, so they are not explicitly known. This inconsistency adds a level of uncertainty to the models that has not been investigated or quantified for struvite. This problem is readily apparent in the significant inconsistencies between equilibrium solubility products. For example, Snoeyink and Jenkins (1980), Stumm and Morgan (1970), Mamais et al. (1994) and Loewenthal et al. (1994) reported a struvite solubility product, pK_{sp} , of 12.6; Buchanan et al. (1994) reported 12.36; and Ohlinger et al. (1998) and Ali and Schneider (2008) found a value of 13.26. In addition, Borgerding (1972) found a pK_{sp} of 9.41 for struvite solids resuspended in ammonium acetate solution.

With almost four orders of magnitude difference, this uncertainty threatens the validity of struvite precipitation calculations. Furthermore, the significance of each constant depends on the pH and constituent concentrations of the waste stream (all variable over time) as well as the values of other constants. It is important to understand under which circumstances this uncertainty will be problematic and invalidate solubility predictions.

The purpose of this study was to develop a struvite solubility model in which the equilibrium constants could be treated with uncertainty (Monte Carlo variables) in order to understand the effects of uncertainty on struvite precipitation estimation. In addition, a sensitivity analysis was performed to identify which uncertainties have the most affect on equilibrium solubility predictions.

2. Chemistry of struvite precipitation

Struvite precipitation is dependent on the available concentrations of magnesium, ammonium, and phosphate, and forms as follows:



When concentrations of dissolved Mg^{2+} , NH_4^+ , and PO_4^{3-} exceed the struvite solubility limit, precipitation may occur. The equilibrium precipitation of struvite has been considered by a variety of researchers and can be described as follows (Stumm and Morgan, 1970; Ohlinger et al., 1998; Doyle and Parsons, 2002; Snoeyink and Jenkins, 1980; Ali and Schneider, 2008):

$$K_{sp} = [\text{Mg}_T][\text{N}_T][\text{P}_T](\alpha_{\text{Mg}^{2+}}) \cdot (\alpha_{\text{NH}_4^+}) \cdot (\alpha_{\text{PO}_4^{3-}}) \quad (2)$$

$$K_{sp\text{cond}} = \frac{K_{sp}}{\alpha_{\text{Mg}^{2+}} \cdot \alpha_{\text{NH}_4^+} \cdot \alpha_{\text{PO}_4^{3-}}} \quad (3)$$

where K_{sp} is the solubility product of struvite, $K_{sp\text{cond}}$ is the pH-conditional solubility product, Mg_T , N_T , and P_T are the total magnesium, ammonia, and orthophosphate concentrations, and α_i denotes the fraction for each component described generically by:

$$\alpha_i = \frac{\text{free ion concentration}}{\text{total dissolved species concentration}} \quad (4)$$

For struvite, the free ion concentrations consist of NH_4^+ , Mg^{2+} , and PO_4^{3-} , and the total dissolved species concentrations (Mg_T , N_T , and P_T) are:

$$\text{Mg}_T = \text{Mg}_f + \text{MgPO}_4^- + \text{MgHPO}_4 + \text{MgH}_2\text{PO}_4^+; \quad (5)$$

$$\text{N}_T = \text{NH}_3 + \text{NH}_4^+ \quad (6)$$

and,

$$\text{P}_T = \text{P}_f + \text{MgPO}_4^- + \text{MgHPO}_4 + \text{MgH}_2\text{PO}_4^+; \quad (7)$$

where Mg_f and P_f represent the free magnesium and orthophosphate species, respectively, or:

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