

Growth Rate Kinetics for Struvite Crystallisation

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The crystallisation of struvite is one means of removing phosphate (and nitrogen) from nutrient-rich wastewater. As with all crystallisation processes, the growth rate of the crystals and its dependence on supersaturation is of considerable interest in designing processing equipment. Modelling of struvite solubility using the computer package MINTQA2 showed that struvite exhibits a minimum solubility in moderately alkaline conditions, with increasing solubility in acidic and strongly alkaline solutions, while temperature has only a minimal effect on struvite solubility. To measure the growth rate of struvite crystals, laboratory measurements were conducted in an isothermal batch 1 L stirred seeded crystallizer. Experiments were performed in aqueous solution at three pH levels (7.5, 8.0 and 8.5) and three temperatures (25, 35 and 40 °C) for similar initial ionic concentrations with phosphate being the limiting ion. These conditions were chosen to cover the pH values at which struvite readily crystallises without excessive adjustment of the wastewater pH, and at temperatures typical of many wastewaters. The increase in crystal size with time together with the decrease in the concentration of the ionic species in solution were followed. Rapid crystallisation kinetics were observed in the solution, with growth rates over 20 µm/min at pH 8.5. A second order dependence of growth rate on supersaturation (as phosphate concentration) was observed, and the growth rate constant increased as pH increased but was insensitive to temperature over the range of conditions used. Results from a 200 L pilot-scale trial of struvite crystallisation at a local abattoir were consistent with the laboratory results.

1. Introduction

Struvite (magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) readily crystallises from aqueous solution at neutral to alkaline pH, and is a well known nuisance in pipe-work and associated machinery (pumps and aerators) at wastewater treatment plants. Struvite deposition in pipes was reported as early as 1939 (Rawn et al., 1939). Numerous wastewater treatment plants around the world have reported its occurrence since, including the Hyperion facility in Los Angeles (Borgerding, 1972); the Oakland sewage treatment plant in California (Snoeyink and Jenkins, 1980), and a piggery near Mandurah, Western Australia (Webb and Ho, 1992). In the past decade, mandatory nutrient removal (mainly phosphorus and nitrogen) requirements and an

increase in the value of these nutrients have created interest in extracting these nutrients in the form of struvite. Predicting and controlling struvite nucleation and growth rate from wastewater is fundamental in crystalliser design. Previous studies have shown an influence of pH, mixing energy, and solution type on struvite growth rate (Koralewska et al., 2009; Nelson et al., 2003; Kofina & Koutsoukos, 2005; Ohlinger et al., 1999; Bouropoulos and Koutsoukos, 2000). However, none of these studies incorporated the mean particle size and the growth of struvite crystals as a function of solution supersaturation in a stirred batch crystalliser. The purpose of the present study was to estimate growth rate parameters of struvite crystallisation in a stirred batch crystalliser while examining the influence of pH, temperature and supersaturation on struvite growth kinetics.

2. Solubility of Struvite in Water

Struvite has a very low solubility in water of around 160 mg/L at pH 7 and 25 °C, with a solubility product (K_{sp}) between 10^{-10} and $10^{-13.3}$ (Burns and Finlayson, 1982; Taylor et al., 1963; Buchanan et al., 1994; Webb and Ho, 1992; Bhuiyan et al., 2007). Simulations of struvite equilibrium chemistry and analysis of ionic information for magnesium, ammonium and phosphate were performed using MINTEQA2 version 3.11 (USEPA, 1991). This program calculates equilibrium concentrations of all ionic species present in an aqueous mixture as defined by the user. The equilibrium concentrations of magnesium, ammonium, phosphate and struvite were determined at pH values between 6 and 12 (Figure 1). The flattening of the struvite ion activity product (IAP) between pH 7 and 11 indicates the formation of struvite crystals. IAP is defined as $a_{Mg}[Mg^{2+}] \cdot a_{NH4}[NH_4^+] \cdot a_{PO4}[PO_4^{3-}]$, where a_i is the activity coefficient of ionic species i (dimensionless) and $[i]$ is the molar concentration of species i (mol/L).

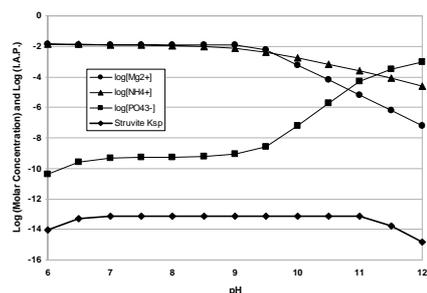


Figure 1: Effect of pH on ionic concentrations when solids are allowed to crystallise, calculated using MINTEQA2. Ionic strength was fixed at 0.1M at 25 °C.

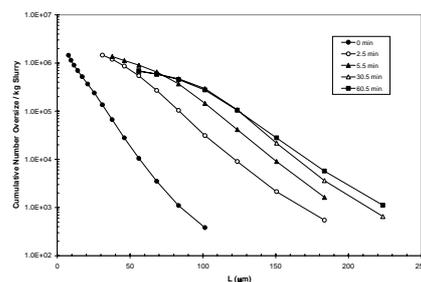


Figure 2: Cumulative number size distributions for the seeded batch crystallisation experiment performed at pH 8.5 and 35 °C.

For dilute solutions, the activity coefficients have been assumed equal to unity and the ion activity product is calculated as the product of the concentrations of each ion. When the solution is in equilibrium with the solid phase, the ion activity product is equal to the solubility product constant, K_{sp} . Solubility products were found to lie in the range $10^{12.96}$ to $10^{-13.32}$ over the pH range from 6.61 to 8.72 (Taylor et al., 1963; Bhuiyan et al.,

2007). An assumed value of the struvite solubility product of $10^{-13.15}$ was used in the MINTEQA2 calculations.

3. Struvite Crystal Growth Rate

Struvite growth rate studies were performed at nine different conditions, three pH levels (7.5, 8.0 and 8.5) and three temperatures (25 °C, 35 °C and 40 °C), with four experiments performed in duplicate for repeatability testing. Samples were taken during crystallisation for analysis using spectrophotometric methods for NH_4^+ and PO_4^{3-} and atomic absorption for Mg^{2+} . Crystal size distributions (CSD) were measured using a Malvern Mastersizer/E. Crystal growth rates were calculated from analysis of CSDs by determining the change in the volume equivalent crystal size between two sample intervals at a fixed value of cumulative number of crystals. Figure 2 shows the change in CSD with time for the seeded batch crystallisation conducted at pH 8.5 and 35 °C. The data are given in the form of cumulative number density against volume equivalent size (L). During growth, the CSD curves move progressively to the right. The CSD at zero time represents the CSD of the struvite seed crystals added to the crystalliser.

The coincidence of the CSD curves at approximately common total number values near the y-intercept confirms the absence of significant nucleation, agglomeration or breakage during the crystallisation experiment. The CSD curves in Figure 2 show a moderate degree of broadening with time, which suggests that growth rate dispersion (GRD, the growth rate of some crystals being higher than that of others) is present.

The change in concentration of each ionic species with time and the average molar consumption of nutrients during crystallisation were input into a batch crystallisation model written in MATLAB. For each of the crystallisation experiments the model was solved by minimising the sum of squares error between the experimental and predicted concentrations to find the reaction order (n) and kinetic growth rate constant (k_G) for a power law expression $G = k_G S^n$, where G is the growth rate (in $\mu\text{m}/\text{min}$) of crystals with the volume median mean size and S is the supersaturation (taken as $C_p - C_p^*$, the phosphate concentration in excess of the solubility value at the test conditions in mg/L). Phosphate is the limiting species in these experiments. Other measures of supersaturation can be used e.g. Ali and Schneider, (2005). Figure 3 compares growth rates versus supersaturations for duplicate experiments for two sets of conditions.

The slopes of the line of best fit for the two experiments are 2.1 and 1.9, suggesting a second order growth rate and this will be accepted for further data analysis. Growth rate orders of above 1.4 has been observed in the literature (Ali and Schneider, 2008) suggesting a dominant surface integration growth kinetics for struvite.

Figure 4 shows the growth rate versus supersaturation data for all runs. The results showed no significant dependence on temperature but a significant dependence on pH. The initial runs (solid symbols) were undertaken in 1999 (Harrison, 1999), the more recent with new equipment (open symbols) in 2010. The lines are the best fit second

order models at the three pH levels studied. There is over a thousand fold range of growth rates.

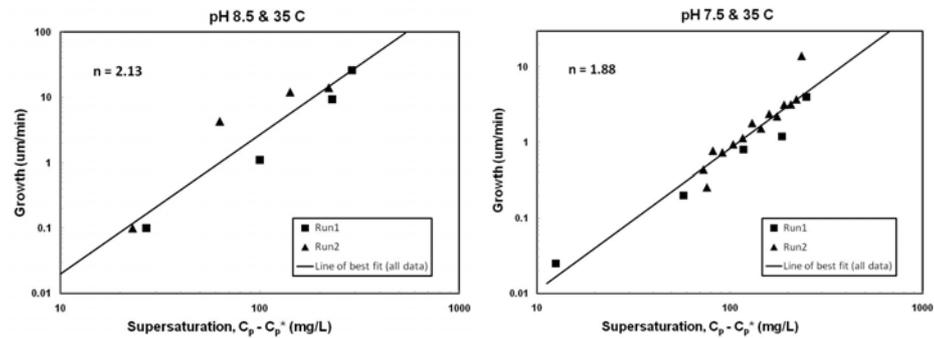


Figure 3: Comparison of growth rates at various supersaturations between duplicate experiments conducted for two conditions at 35 °C, pH 8.5 and pH 7.5.

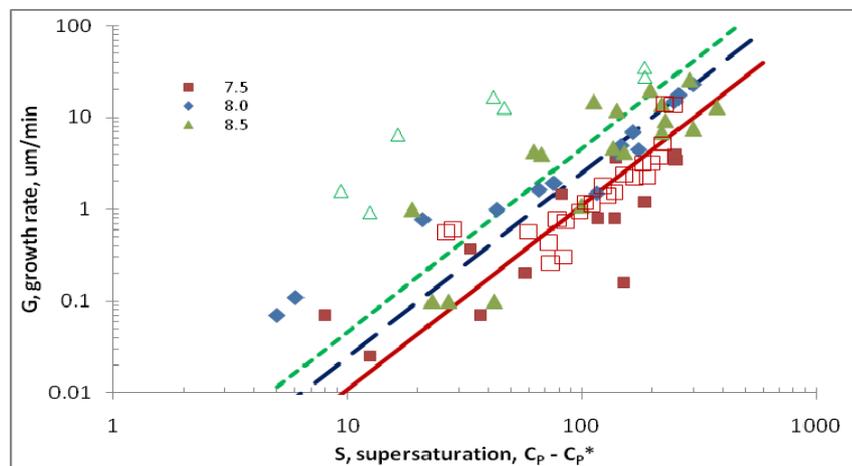


Figure 4: Growth rate versus supersaturation for all experiments. Filled symbols are 1999 data, hollow symbols 2010. Solid line, pH = 7.5, dashed, 8.0, dotted 8.5.

The k_G values for $n = 2$ for the batch crystallisation experiment at each temperature and pH were calculated (Figure 5). The plot illustrates the lack of dependence of k_G on temperature and its dependence on pH, with the growth rate constant increasing by over three times from pH 7.5 to 8.5. The pH trend may be fitted over the experimental range by $k_G = (2.5 \pm 1.2) \times 10^{-5} e^{(1.2 \pm 1.1)(\text{pH}-8)}$, where the \pm values are the 95% uncertainty on the parameters. This implies no effect of temperature on k_G . The complete growth rate equation can be represented as a function of pH and supersaturation as $G = (2.5 \pm 1.2) \times 10^{-5} e^{(1.2 \pm 1.1)(\text{pH}-8)} S^2$, where G is the growth rate of volume median crystals ($\mu\text{m}/\text{min}$) and S is the absolute supersaturation as phosphate (mg/L).

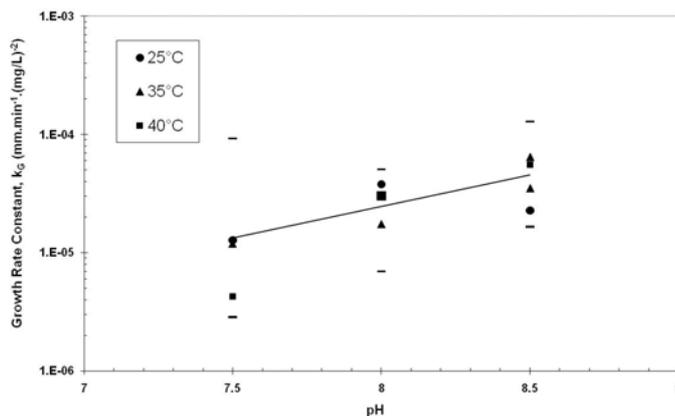


Figure 5: Second order growth rate constant as a function of pH. The line of best fit with pH is shown. The horizontal bars represent the lowest and highest 95 % confidence intervals of k_G at each pH.

Pilot scale studies on a wastewater stream at a local abattoir used a 200 L working volume stainless steel drum crystalliser. The concentrations of the nutrients (phosphate and ammonium) were greater than their respective solubility concentrations. Magnesium addition to the wastewater was required to achieve supersaturation and pH control was essential to maintain a constant pH due to the production of acid during crystal growth. The pilot scale growth rate constants ranged from $1.5 \cdot 10^{-5}$ to $1.0 \cdot 10^{-4}$, which are in fair agreement with laboratory results between pH values of 8.0 and 8.5. The initial growth rates in the pilot scale studies (0.45 to $0.8 \mu\text{m}/\text{min}$) were lower than those observed in the laboratory studies (10 to $24 \mu\text{m}/\text{min}$) at pH 8.5. The effects of suspended particles (which made crystal sizings difficult) and foreign ions (e.g. calcium) in the wastewater may have caused the slower initial growth rates.

4. Conclusions

Aqueous laboratory struvite crystallisation experiments showed that struvite probably shows GRD behavior. The average growth rate of struvite increased with an increase in pH (from 7.5 to 8.5) at a given supersaturation. The maximum measured crystal growth rate was over $20 \mu\text{m}/\text{min}$ at pH 8.5. The range of temperatures used in this study (from 25°C to 40°C) showed no significant effect on the growth rates. For the range of conditions used struvite crystallisation exhibited second order growth kinetics based on supersaturation expressed as phosphate concentration. Pilot-scale studies at a local abattoir showed that struvite crystals can be grown from abattoir wastewater, although the growth rates were somewhat lower than those obtained in the laboratory.

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