

## Development and Commissioning of Controlled Struvite Crystallization in Pilot Scale

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### Abstract

This paper focuses on the design of a nutrient recovery scheme, conducted in a fed-batch controlled crystallization technique, leading to the formation of struvite (Magnesium Ammonium Phosphate). The controlled crystallization technique included the control of solution pH and concentration during each experiment. Characterization of struvite crystal growth was conducted by CSD (crystal size distribution) analysis of growing struvite. Controlled crystallization showed significant growth of struvite crystals by surface diffusion, whereas faulty control initiated significant amount of fines.

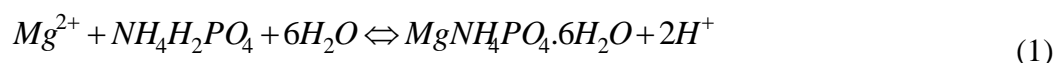
*Keywords: Struvite, Growth, Fed-batch crystallization, CSD analysis.*

### 1.0 Introduction

Crystalline deposits of struvite form in high turbulence zones of nutrient rich wastewaters. Due to increasing concentration of nutrient loadings, threats of environmental disasters causing eutrophication in surface water-body and burning of root of trees are possible. Recovery of struvite from nutrient-rich wastewater provides a value-added product and helps to minimize environmental impacts. Struvite crystallization is a novel technique proposed to recover phosphate and ammonium along with magnesium. Crystallization occurs in supersaturated solution.

Commercialization of struvite production relates to the production of good quality of crystals. High purity of crystals is not often sufficient since uniform crystal size distribution (CSD), compactness and durability of crystal is more desirable considering the commercial value, ease of transport and handling. In this regard, process control measures can help to ensure product quality.

On the basis of equation (1), each recordable unit of pH drop in the supersaturated struvite system represents the occurrence of reaction by means of 2 moles of H<sup>+</sup> release with resulting 1 mole of struvite formation when reaction takes place [1].



Moreover, precise stability of process control is highly desirable to accomplish improved understanding of growth rate formulations [2, 3]. The control system in struvite crystallization employs a feedback controller, incorporating pH as the key control variable [4-7]. pH-based control in hydroxyapatite crystallization was applied by van der Houwen and

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Valsami-Jones [8]. Bouropoulos and Koutsoukos [1] approached the control of struvite crystallization employing a scheme whereby stoichiometric quantities of reactants were metered into the reactor, based on a hydrogen ion balance. This pH-based control, used to maintain constant supersaturation for hydroxyapatite/struvite crystallization, was implemented in small-scale (several hundreds millilitres) [1, 8, 9].

This paper includes controlled struvite crystallization in pilot scale, maintained at constant supersaturation mode (constant pH as well as constant composition). Struvite was used as seeds, since mother crystal acts as efficient diffusive media in struvite crystallization [10].

## 2.0 Materials and Methods

This paper incorporates struvite crystallization in constant supersaturation mode. Experimental development of struvite recovery on pilot scale is a challenging proposition. A properly designed reactor and the commissioning of several factors such as controlled temperature, adequate hydrodynamics (mixing) and the selection of appropriate seeds, can lead to a suitably controlled supersaturation. Development of such a pilot plant has been a step-wise, trial and error procedure.

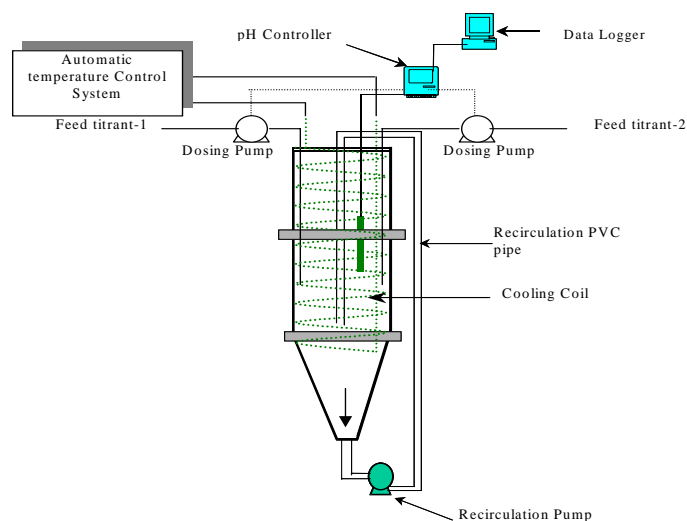


Figure 1 Schematic of Struvite Reactor

### 2.1 Design of the Struvite Reactor

A schematic diagram of struvite fed-batch system is shown in Figure 1. Unfortunately no standard design approach exists on struvite crystallization. However, some common techniques such as suspension bed, seeding and dosing of feed solution are widely practiced [1, 8, 11, 12]. The struvite reactor of 44-liter volume was manufactured from clear perspex. The reactor was operated in suspended bed condition, allowing seeds and crystals to keep in uniform suspension. A pH controller ( $\alpha$  2000W) monitored solution pH and triggered feed addition when solution pH dropped below set point. Two dosing pumps (Grundfos DME-12) were operated for titrants (feed solution) additions based on two matched output signals from the pH controller. The pH controller was operated in pulse frequency control mode using a PI feedback controller.

Adequate mixing of the reactive solution was achieved using a recirculation pump through 1-inch diameter PVC pipe. The top portion of PVC pipe was connected with an adjustable and flexible arm to prevent short-circuiting. It is worthwhile pointing out that short-circuiting of the recirculated stream impedes full suspension of crystals and thus has an adverse affect on mixing and uniform supersaturation.

This research incorporated struvite crystals as seeds for all experiments. It is important to use air-dried struvite crystals, since over drying leads to decreased structural integrity of the seed crystals, which leads to crystal break-up within the reactor. Therefore, previously generated air-dried struvite crystals (size classified) were used as seeds. Samples of growing struvite crystals were collected and filtered using 0.45- $\mu\text{m}$  filter paper.

The fed-batch system was maintained using two feed solutions. The first was a solution of  $\text{NH}_4\text{H}_2\text{PO}_4$  (the ammonia and phosphate source) and  $\text{NaCl}$  (to maintain ionic strength), pH-adjusted to 6.0. The second was composed of  $\text{NaOH}$  (for pH maintenance) and  $\text{MgCl}_2$  (the magnesium source). Composition factor of the feed solutions are  $12x_1$  ( $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ ) and  $18x_1$  ( $\text{NaOH}$ ), where  $x_1$  is the equimolar reactive solution concentration.

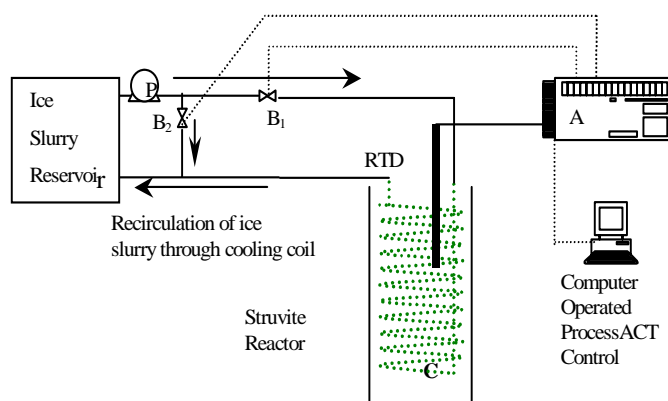


Figure 2 Schematic of Automatic Temperature Control System

Continuous operation of the recirculation pump caused significant temperature rise, since this was a closed system. This increase of solution temperature affected the overall solution thermodynamics, thus it was necessary to implement a temperature controller. A constant operating temperature was maintained by an automated temperature control system (Figure 2), encompassing an epoxy-coated copper cooling coil, resistive temperature device (RTD) and solenoid-activated valves. The epoxy-coating minimized the corrosion of the annealed copper tubing.

## 2.2 Temperature Control System

The automated temperature control system was implemented using ProcessACT1, a software-based advanced control and prototyping system. The flow of chiller water to the cooling coils was actuated using on-off solenoid valves under a pulse-width modulated proportional controller. Ice slurry recirculation stream through copper coil acted as coolant. The recirculation system was comprised of a normally-open solenoid valve (B1), a normally-closed solenoid valve (B2), a recirculation pump (P) and the chilled water supply. A resistive

temperature device (RTD) was used to monitor the temperature. Logic within ProcessACT was set-up to close solenoid valve (B1) and open solenoid valve (B2) simultaneously, so that coolant flows through the bypass loop (PB2) by default. When the system temperature increased above set point, the a pulse-width-modulated PID controller in ProcessACT closed the solenoid valve (B2) and opened the solenoid valve (B1) so that coolant flow through cooling coil, maintaining the set-point temperature. Controlling the process temperature reduced temperature offsets in the pH reading, which would otherwise have an adverse affect on process control.

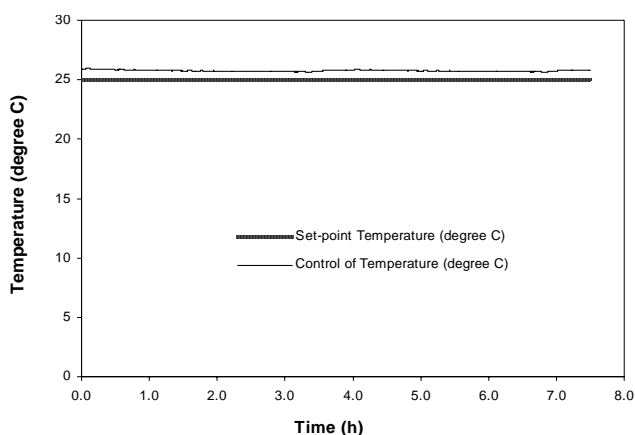


Figure 3 Control of temperature by automated temperature control system

### 3.0 Results and Discussion

#### 3.1 Experimental Response of the Control

Experiments conducted with the temperature control system enabled precise control of the process temperature during extended batch times. Without the temperature control system, increases of batch temperature in the order of 5°C/hr were observed, leading to inaccurate monitoring of system pH. The temperature control system maintained the operating temperature as shown in Figure 3.

Start-up of the process is critical to a successful experiment, particularly in establishing the solution supersaturation. Figures 4A and 4B illustrate the control profile of struvite system at different process conditions. In order to start-up the process, pH was manually altered through the addition of a base, until the onset of crystallisation occurred. Once crystallisation commenced, there was a commensurate demand for more base (NaOH) addition to the system, due to the pH controller. Since the addition of extra base was accompanied by the crystallising reactants, the process then essentially drove itself.

Care should be taken in preparing the feed solution to avoid preliminary loss of reactant during the start-up. A step-wise elevation of pH to the desired set point would eliminate preliminary reduction of reactant concentration. Another issue of the controlled fed-batch experiment was the acid-base neutralization, due to excessive difference of pH between titrant-1 and reactive solution. In this circumstance, excessive addition of feed solution occurred during the start-up of control leading to ruin of control. Experimental observation showed that the approximate difference of pH between titrant-1 and reactive solution must be within the pH limit of 1.25 for smoother control.

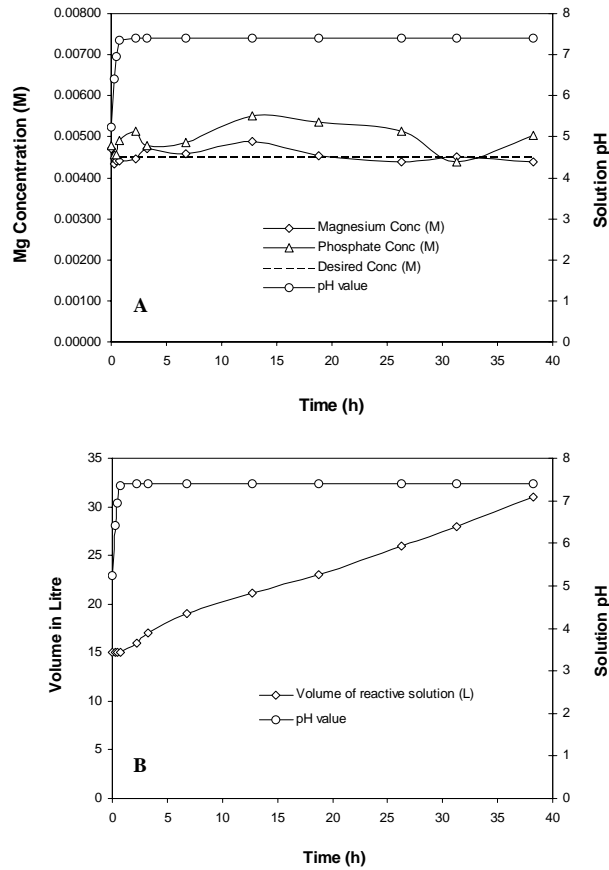


Figure 4 Experimental Process Control (A), Experimental Volume of Reactive Solution during Process Control (B).

Struvite crystals were separated from mother liquor using an ASTM standard sieve of aperture 63- $\mu\text{m}$ . Collected struvite was air dried and dry sieved to separate further fines of size smaller than 63- $\mu\text{m}$ . A recovery of 65-70% of expected mass of struvite was found in each experiment. For perfect diffusion integration mechanism, it was expected that 100% of the generated struvite would be larger than 63- $\mu\text{m}$ . However experimental observation showed that 30-35% of the generated struvite was composed of smaller crystal size than expected. The generation of sub-63  $\mu\text{m}$  struvite crystals was due to production of fines due to lack of perfect diffusion and possibly the breakage of crystals due to impeller action of the recirculation system (pumps, pipe etc).

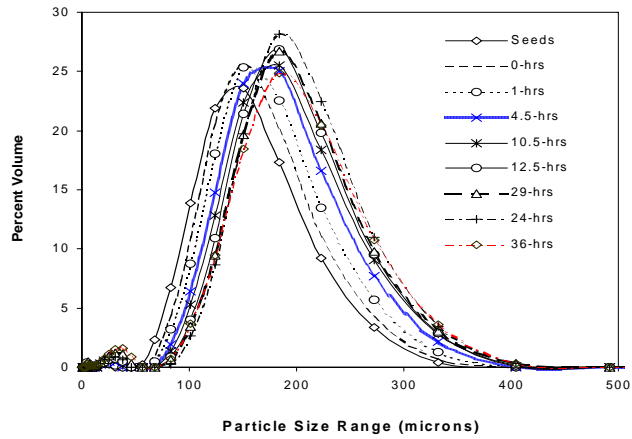


Figure 5 Crystal Size Distribution (CSD) of Generated Struvite

The size distribution curves of the harvested crystal show size-independent growth, since the frequency curves are almost identical, except that they are shifted to the right (Figure 5). Minor agglomeration, among the fine particles, is also observed which causes the elevation of peakedness of these frequency curves.

### 3.2 Sensitivity to reactant feeding points

Fed-batch controlled crystallization conducted using solution concentration of 0.005-M along with the operating pH of 7.35 imparted significant production of fines due to the close proximity of the two feeding points (Figure 6). Floc/fines formation was most likely due to poor mixing of solution, which resulted nonuniform supersaturation conditions [1, 13-15]. Therefore feed points should remain well apart.

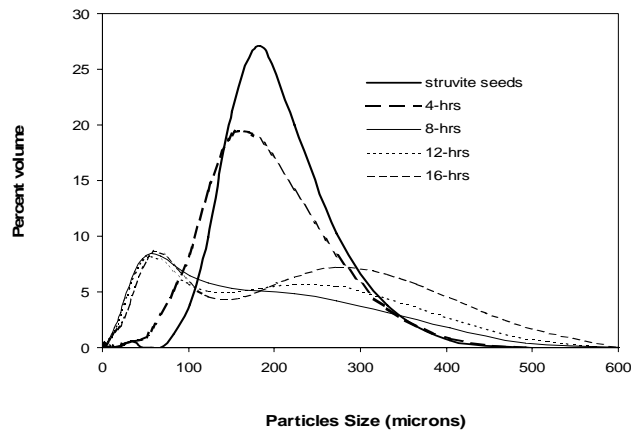


Figure 6 Crystal Size Distribution of Struvite due to faulty dosing

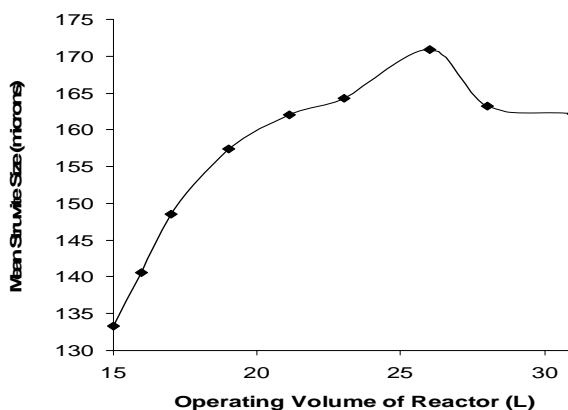


Figure 7 Mean crystal size vs operating volume

One of the major problems, observed late in each experiment, was the decline of struvite growth at close-to-full reactor volume. The graphical presentation (Figure 7) of mean particle size against operating volume shows the reduction of particle size when the operating volume exceeds 25-L. In this circumstance significant amounts of fines are produced, which decreases the mean particle size. The most liable reason of fines production was the insufficient mixing caused by the remoteness of inlet and outlet of recirculation stream in larger operating volume, which made reactive solution somewhat stagnant. Therefore, local supersaturation fluctuation caused the generation of fines. Improved mixing is required if this problem is to be overcome.

#### 4.0 Conclusions

The strategy described here has potential to cope with struvite crystallization at constant supersaturation, since pH and reactant concentration can be maintained precisely constant. This control system maintained the system temperature and pH, and indirectly the composition of the system. Sufficient mixing intensity of the reactive solution must be provided to effect growth of seed crystals. Moreover, care should be taken to keep the dosing point apart from each other to avoid local fluctuation of supersaturation.

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