# Impact of non-stoichiometric conditions on the growth rates of struvite recovered from synthetic waste (RRS13)

*Energy and resource recovery*

Re-Inventing the Nation's Urban Water Infrastructure (ReNUWIt)

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## Background

Wastewater treatment plants (WWTP) are negatively affected by the accumulation of sludge, specifically in the form of struvite. The crystallization of struvite occurs naturally when levels of magnesium, ammonium, and phosphate. approach equimolar concentrations. The formation of struvite is affected by the pH, ion concentrations, mixing energy and temperature of the WWTP. Learning about the growth rate kinetics of struvite is an essential step in being able to recover it. The benefits of struvite recovery, however, go beyond preventing the accumulation of it in WWTP. The recovery of struvite can also prevent the runoff of phosphorus into water systems and by extension eutrophication. Furthermore, the phosphorus base composition of struvite makes it an excellent form of fertilizer.

$$Mg^{+2} + NH^{+} + PO_4^{-3} + 6H_2O \leftrightarrow \text{Struvite}$$

- Crystallization of struvite will not occur until supersaturation is achieved.
- Phosphate and ammonium have different pKa values that make finding the optimal pH for struvite growth difficult
- The optimal pH for struvite precipitation will be affected by the solubility and supersaturation of the ions within the WWTP

**Objective:**
This project aims to observe the different nucleation rates of struvite at different ionic concentrations starting with equimolar concentrations and then progressing to non equimolar concentrations of magnesium, ammonium, and phosphate..

## Approach

In order to create a trend line that would predict the growth rates of struvite seed at different saturation indices, experiments were carried out at various ionic concentrations. The general approach was maintained consistent with the exception of varying concentration levels while maintaining saturation indices, to measure the effects of non-stoichiometric concentration on the growth rate.

For each experiment two solutions of magnesium chloride hexahydrate ($MgCl_2$) and ammonium phosphate monobasic ($NH_4H_2PO_4$) were made at different concentrations. The solutions were then bubbled with nitrogen gas for seven minutes. The pH of the ammonium phosphate monobasic solution is then adjusted with sodium hydroxide to approach a pH of 8. Then the solutions would be synthesized in a bench chemostat reactor.

The chemostat reactor set-up included:

- 800 mL of each of the struvite based mineral solutions
- 1 g of seed ( struvite )
- Two titrants
  - $Na_3PO_4 12H_2O$
  - $NH_4Cl$ and $MgCl_2$

The chemostat would synthesize the solutions for one hour and samples from the chemostat were taken at five different occasions: before the seed was added, immediately after the seed was added, twenty, forty-five, and sixty minutes after the seed was added.

## Results

| Omega -1 | Mg | P | N(-3) | Ion activity (Mg+2) | Ion activity (NH4+) | Ion activity (PO4-3) | (Mg+2)/(PO4-3) | (NH4+)/(PO4-3) | si_Struvite |
|---|---|---|---|---|---|---|---|---|---|
| 0.03 | 2.00E-03 | 2.00E-03 | 2.00E-03 | 9.25E-04 | 1.73E-03 | 3.67E-08 | 2.52E+04 | 4.72E+04 | 0.03 |
| 0.13 | 2.20E-03 | 2.18E-03 | 2.18E-03 | 9.89E-04 | 1.88E-03 | 3.88E-08 | 2.55E+04 | 4.85E+04 | 0.12 |
| 0.23 | 2.40E-03 | 2.39E-03 | 2.39E-03 | 1.04E-03 | 2.06E-03 | 4.14E-08 | 2.52E+04 | 4.97E+04 | 0.21 |
| 0.41 | 2.75E-03 | 2.74E-03 | 2.74E-03 | 1.14E-03 | 2.35E-03 | 4.54E-08 | 2.52E+04 | 5.18E+04 | 0.35 |
| 0.60 | 3.13E-03 | 3.11E-03 | 3.11E-03 | 1.24E-03 | 2.66E-03 | 4.93E-08 | 2.52E+04 | 5.39E+04 | 0.47 |
| 0.13 | 1.60E-03 | 2.50E-03 | 2.50E-03 | 6.50E-04 | 2.17E-03 | 5.14E-08 | 1.26E+04 | 4.21E+04 | 0.12 |
| 0.24 | 2.00E-03 | 2.59E-03 | 2.59E-03 | 8.17E-04 | 2.24E-03 | 4.93E-08 | 1.66E+04 | 4.55E+04 | 0.22 |
| 0.41 | 2.20E-03 | 2.99E-03 | 2.99E-03 | 8.47E-04 | 2.58E-03 | 5.58E-08 | 1.52E+04 | 4.62E+04 | 0.35 |
| 0.60 | 2.51E-03 | 3.40E-03 | 3.40E-03 | 9.21E-04 | 2.91E-03 | 6.08E-08 | 1.51E+04 | 4.79E+04 | 0.47 |

**Table 1: Experimental Conditions - For trials 6-9, nonstoichiometric concentrations were used. Calculations performed using PHREEQC V2.**

### Case 1: Stoichiometric growth conditions

The first set of experiments was conducted at various saturation indices composed of equimolar concentrations of the growth solutions, $MgCl_2$:$6H_2O$ and $NH_4H_2PO_4$. The results indicate a linear increase in growth rates as a function of saturation index (Figure 2).

Orange trend line

- Magnesium to phosphate activity ratios were similar for all Case 1 experiments
- Ammonium to phosphate activity ratios increased with increasing SI values

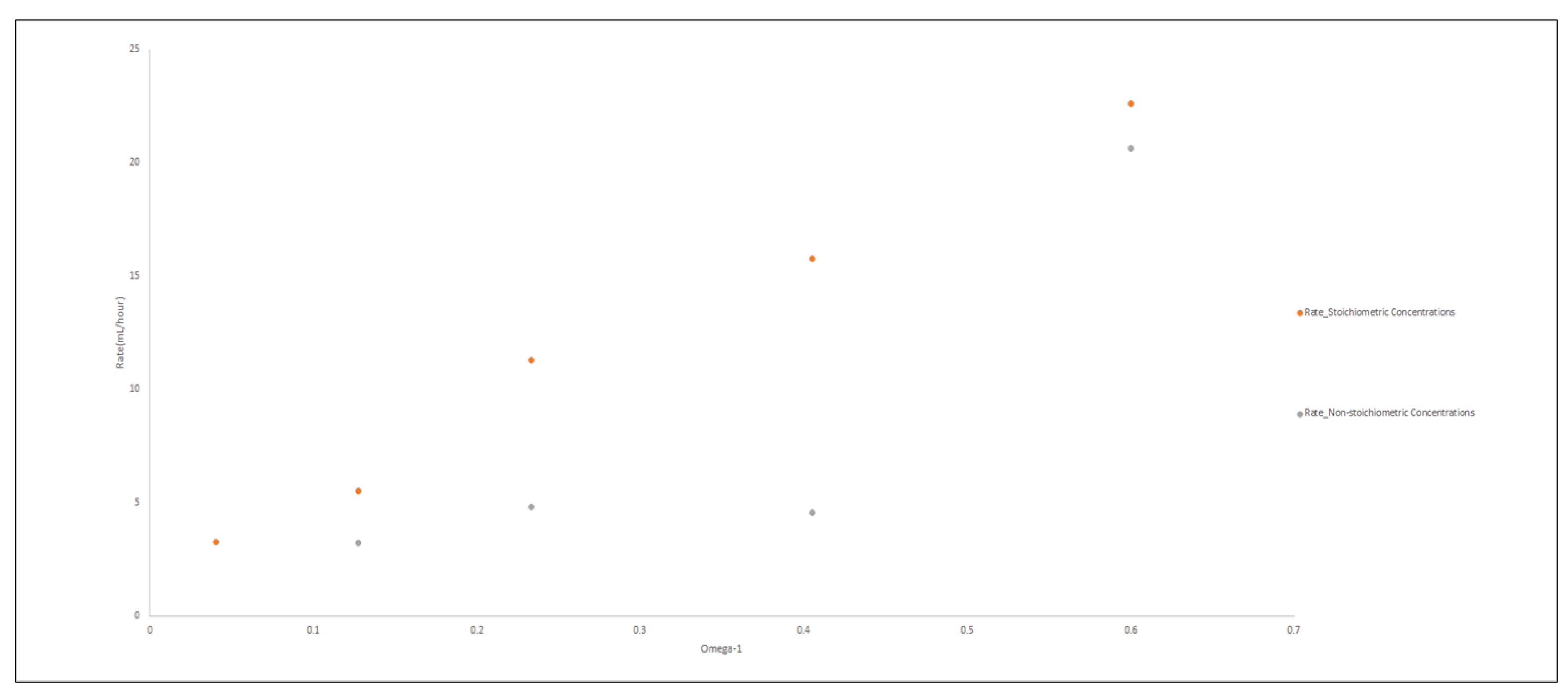


**Figure 1: Struvite growth rates as a function of relative supersaturation (Omega-1). Omega = ($IAP/K_{so}$), IAP = Ion Activity Product, SI = $Log_{10}$ (Omega).**

### Case 2: Non-stoichiometric growth conditions

The second set of experiments was conducted at various saturation indices composed of nonstoichiometric concentrations of the growth solutions, $MgCl_2$:$6H_2O$ and $NH_4H_2PO_4$. The results indicate that growth rates remain relatively constant at increasing relative supersaturation (Figure 2).

Gray trend line

- At low and high super saturation indices the struvite reflects similar growth rates as the struvite with stoichiometric growth conditions
- Growth rates at intermediate SI values did not follow a particular trend

## Conclusions

While comparing the first case of experiments to the second rate of experiments, the magnesium to phosphate activity ratios were significantly higher for the first set. The growth rate for the first set of experiments also remained constant at the different supersaturation indices. The second case of experiments did not have an evident pattern. The ammonium to phosphate activity ratios increased with increasing SI values for both cases. Generally, the activity rates were all higher for the first case of experiments.

- Equimolar concentration led to linear increase of struvite growth rates.
- Ammonia to phosphate ratios will have a bigger effect on the growth rate of struvite than the magnesium to phosphate ratio

At first glance it may seem like stoichiometric conditions are ideal for struvite recovery, but the growth rate of struvite at a a high saturation index of the non-stoichiometric condition was very similar to the stoichiometric conditions.
In order to form stronger conclusions and rule out potential experimental errors, experiments need to be replicated.

## Next Steps

Many of the complexities of the growth rate kinetics of struvite are still far from being understood, and still there is much to be learned. Consequently, this project is a very small portion of all the work that needs to be done in order to reap the full events of struvite recovery.

Improvements for this Experiment:

- Run experiments at temperatures that are representative of those in WWTPs
- Examine the struvite recovered from the chemostat with X-ray diffraction to further analyze the properties of the struvite recovered
- Calculate specific surface area of struvite recovered to draw comparisons with the results of other literature values

Future Points of Consideration:

- Which soils which can be complemented by the fertilizing properties of struvite?
- What can incentivize WWTP to upgrade their systems for struvite recovery?
- How can we promote the transition between current fertilizers to using struvite?

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