# A review of struvite nucleation studies

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**Abstract** A review of struvite nucleation studies is given. Low supersaturation induction time experiments are presented. A thermodynamic solver was developed in Engineering Equation Solver (EES) which was validated against PHREEQc. This solver allowed meaningful comparisons to be made by processing the raw data under consistent thermodynamic conditions. Differences in the results that still remained are attributed to hydrodynamic variations. An image capture and analysis experimental method proved successful for the low supersaturation induction time experiments. Previous studies were unable to predict induction times at low supersaturation.

## INTRODUCTION

Intentional struvite crystallisation, formed via Equation (1), is an attractive processing route for nutrient recovery from a variety of wastewater streams because of its potential as a sustainable fertiliser (Driver *et al.*, 1999; Li and Zhao, 2003). However, effective process design and optimisation requires the investigation of crystallisation mechanisms. This paper focuses its attention on struvite crystal nucleation by reviewing contributions to this field and conducting a nucleation study.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (1)$$

## BACKGROUND

Before the analysis of previous and current work it is important to address the solution thermodynamics that govern struvite precipitation. Some background theory to nucleation will also be given as well as in introduction to the previous research.

### Solution thermodynamics

The formation of struvite is not as simple as Equation (1) suggests. There are complicated thermodynamics influencing the precipitation reaction. Free magnesium, ammonium and phosphate ions that react to form struvite are subject

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to a range of speciations that are pH dependant. It is therefore important to understand these equilibria in order to calculate the free ion concentrations and other thermodynamic properties of the system.

### *Thermodynamic equilibria*

In water chemistry equilibrium reactions take place between various dissolved species in solution (Snoeyink and Jenkins, 1980). These equilibria form the basis for all subsequent thermodynamic calculations and measurements, the most important of these being supersaturation which is the most significant variable in any nucleation study (Mullin, 1993).

An early investigation of struvite thermodynamics conducted by Snoeyink and Jenkins (1980) based their calculations on the following species; $Mg^{2+}$, $MgOH^{+}$, $NH_4^{+}$, $NH_3$, $PO_4^{3-}$, $HPO_4^{2-}$, $H_2PO_4^{-}$ and $H_3PO_4$. As computing improved the list of species included in thermodynamic calculation expanded in subsequent research (Ohlinger *et al.*, 1998; Ali and Schneider, 2005). The species included for this work were taken from Ohlinger *et al.* (1998) which were used in the nucleation investigations by Ohlinger *et al.* (1999). The equations and constants corresponding to the equilibrium reactions are located in Table 1.

Some other species that have been included in previous research are $MgNH_3^{2+}$, $Mg(NH_3)_2^{2+}$ and $Mg(NH_3)_2^{2+}$ (Bouropoulos and Koutsoukos, 2000). However, these complexes have little influence due to their low equilibrium constants, compared with other species (Ali and Schneider, 2005).

The various equilibria require activity coefficients to be calculated in order to determine ion species activities. These calculations are performed with Equations (2), (3) and (4).

$$I = \frac{1}{2}\sum C_i Z_i^2 \tag{2}$$

$$-\log \gamma_i = AZ_i^2\left(\left[\frac{\sqrt{I}}{1+\sqrt{I}}\right] - 0.3I\right) \tag{3}$$

$$\{i\} = \gamma_i C_i \tag{4}$$

where $I$ = Ionic Strength, $C_i$ = Concentration of species $i$, $Z_i$ = Valency of species $i$, $\gamma_i$ = Activity coefficient of species $i$, $A$ = DeBye-Hückel constant (0.509 at 25°C, (Mullin, 1993)). Equation (3) is the DeBye-Hückel equation

**Table 1.** Thermodynamic equilibria and their governing equations.

| Compound | Equilibrium Equation | Equilibrium Constant ($K_i$) | Reference |
|---|---|---|---|
| $HPO_4^{2-}$ | $\frac{\{H^+\}\{PO_4^{3-}\}}{\{HPO_4^{2-}\}} =$ | $10^{-12.35}$ | (Morel and Hering, 1993) |
| $H_2PO_4^-$ | $\frac{\{H^+\}\{HPO_4^{2-}\}}{\{H_2PO_4^-\}} =$ | $10^{-7.20}$ | (Morel and Hering, 1993) |
| $H_3PO_4$ | $\frac{\{H^+\}\{H_2PO_4^-\}}{\{H_3PO_4\}} =$ | $10^{-2.15}$ | (Martell and Smith, 1989) |
| $MgPO_4^-$ | $\frac{\{Mg^{2+}\}\{PO_4^{3-}\}}{\{MgPO_4^-\}} =$ | $10^{-4.80}$ | (Martell and Smith, 1989) |
| $MgHPO_4$ | $\frac{\{Mg^{2+}\}\{HPO_4^{2-}\}}{\{MgHPO_4\}} =$ | $10^{-2.91}$ | (Martell and Smith, 1989) |
| $MgH_2PO_4^+$ | $\frac{\{Mg^{2+}\}\{H_2PO_4^{3-}\}}{\{MgH_2PO_4^+\}} =$ | $10^{-0.45}$ | (Martell and Smith, 1989) |
| $MgOH^+$ | $\frac{\{Mg^{2+}\}\{OH^-\}}{\{MgOH^+\}} =$ | $10^{-2.56}$ | (Childs, 1970) |
| $NH_4^+$ | $\frac{\{H^+\}\{NH_3\}}{\{NH_4^+\}} =$ | $10^{-9.25}$ | (Taylor *et al.*, 1963) |
| $H_2O$ | $\frac{\{H^+\}\{OH^-\}}{\{H_2O\}} =$ | $10^{-14}$ | (Harris, 2003) |

with Davies approximation and was chosen due to its simplicity and accuracy at moderate ionic strengths (Mullin, 1993).

### *Supersaturation*

Supersaturation is a term used to describe a solution where the solute concentration is greater than its value at equilibrium; precipitation is a direct result of supersaturation. As struvite contains three constituent ions, its solute concentration is defined by the ion activity product (IAP), see Equation (4). When the IAP is greater than the minimum solubility product ($K_{so}$) the system is supersaturated and struvite may nucleate and grow, returning the system to equilibrium.

When dealing with non-ideal, multi-component systems a more complex expression for supersaturation is required, such as supersaturation index, SI (Allison *et al.*, 1991; Parkhurst, 1999; Ali, 2005; Bhuiyan *et al.*, 2008), or supersaturation ratio, $S_a$ (Snoeyink and Jenkins, 1980; Ohlinger *et al.*, 1999; Bouropoulos and Koutsoukos, 2000). Both expressions incorporate the ion activity product and the minimum solubility product. The equations for SI and $S_a$ are given below in Equations (6) and (7), respectively.

$$IAP = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\} \tag{5}$$

$$SI = \log\left(\frac{IAP}{K_{SO}}\right) \tag{6}$$

$$S_a = \left(\frac{IAP}{K_{SO}}\right)^{1/3} \tag{7}$$

The minimum solubility product of struvite used in this research was that published by Ohlinger *et al*. (1998) where $pK_{so} = 13.26$. This value was used by Ohlinger *et al*. (1999) and Bouropoulos and Koutsoukos (2000). Bhuyian *et al.* (2008) used a Kso value of 13.36 (Bhuyian *et al.*, 2007).

### *Thermodynamic solvers*

In order to solve these equations simultaneously a computer program is required. Some common packages used in struvite research are PHREEQC (Bhuyian *et al.*, 2008), MINTEQA2 or VisualMINTEQ (Ali, 2005), MINEQL+ (Ohlinger *et al.*, 1999) and ChemEQL (Bouropoulos and Koutsoukos, 2000). These programs use the initial conditions of the system and a database of equilibrium information to calculate the concentration of all species in solution. For the purposes of understanding struvite thermodynamics more thoroughly, Engineering Equation Solver (EES) was used to solve the relevant nonlinear equation set that specifies the solution thermodynamics. The output from the EES solver was validated by comparing the ionic concentration of $Mg^{2+}$, $NH_4^+$ and $PO_4^{3-}$ against the outputs of PHREEQC as seen in Figure 1. The outputs from both solvers are almost identical showing the EES solver to be numerically robust in handling these complex thermodynamic calculations.

## Nucleation

Nucleation is the first step in the crystallisation process. It occurs when solute molecules come together in clusters and grow by accretion. They then coalesce to form large amounts of a new phase (Mullin, 1993). A period of time usually passes between the achievement of supersaturation and the appearance of crystal nuclei; this is called the induction time.

A common approach in nucleation studies and the one taken by the three studies being reviewed is measuring the induction time and applying classical nucleation theory which is based on homogeneous nucleation (Mullin, 1993).

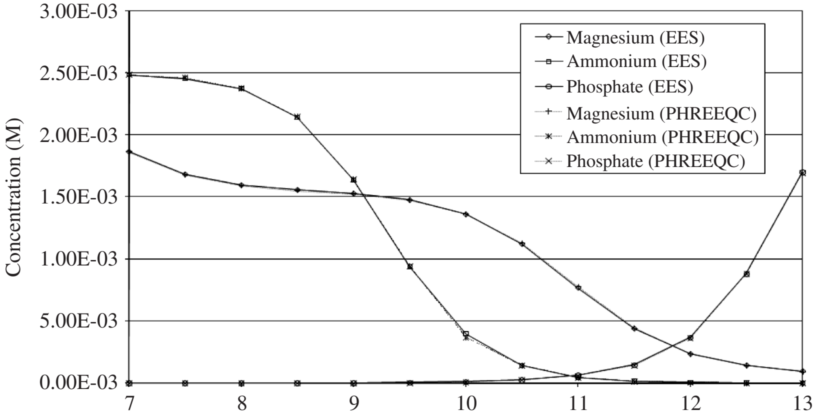

**Figure 1.** EES thermodynamic solver validated against PHREEQC at 0.0025M.

This produces a relationship between induction time and supersaturation shown in Equation (8), the derivation of this equation can be found in Mullin (2003). Homogeneous nucleation is the precipitation of nuclei in a solution free from foreign particles which is practically impossible to achieve in real solutions. However, the assumption of homogeneous nucleation is valid under conditions of high supersaturation (Mullin, 1993).

$$\log t_{ind} = \frac{A}{(\log S_a)^2} - B \tag{8}$$

A problem emerges in the relevance of this data to struvite reactor design as suspension reactors designed for crystal growth operate at low supersaturation in the metastable zone where crystal growth is favoured over nucleation. This is important as struvite reactors can encounter loss of product, fouling of process equipment, poor product quality and handling difficulties due to fines resulting from excess nucleation (von Munch and Barr, 2001, Battistoni *et al.*, 2005, Adnan *et al.*, 2003). Therefore it is a major aim of this work to gather nucleation data at low levels of supersaturation, which is relevant to reactor design and to compare these results with the predictions made by the other studies.

## Previous work

Because of the complex nature of struvite thermodynamics it can be difficult to compare the experimental results of previous work. It has already been established in thermodynamic equilibria that Ohlinger *et al.* (1999) and Bouropoulos and Koutsoukos (2000) included different species in the thermodynamics and the species included by Bhuyian *et al.* (2008) are not specified. This means that the same initial condition inputs would give three different supersaturation outputs. In order to perform a valid comparison the raw data from the three previous studies was processed using the EES solver. A summary of the experimental conditions and techniques used by all studies is detailed in Table 2.

**Table 2.** Summary of experimental conditions and techniques.

| | Ohlinger *et al.* (1999) | Bouropoulos and Koustoukus (2000) | Bhuyian *et al.* (2008) | This study (2008) |
|---|---|---|---|---|
| **Concentration** | 4.0–20.0 mM | 2.75–4.0 mM | 56, 70 mg/L at 1:1:10 Mg:$PO_4$:$NH_4$ | 1.0, 2.5 mM |
| **pH range** | 6.3–7.9 | 8.5 | 8.2–8.51 | 7.8–9.2 |
| **Temperature** | 22°C | 25°C | 25°C | 22°C |
| **Detection method** | Laser scintillations | pH change | pH change | Laser scintillations |
| **Thermodynamic solver** | MINEQL+ | ChemEQL v2.0 | PHREEQC | EES |
| **Induction time (sec)** | 13–2280 | 360–7500 | 12–500 | 999–26289 |

## EXPERIMENTAL METHOD

Experiments were conducted at 25°C with 250 mL solutions at two levels of equimolar concentration (0.001 M and 0.0025 M) of Mg, $NH_4$ and $PO_4$. Supersaturation was established by adjusting solution pH with sodium hydroxide. Induction times were determined by monitoring light scintillations from a HeNe laser directed through the supersaturated solution and recorded with a low-light CCD camera placed perpendicular to the laser.

Prior to nucleation the solution is clear and therefore no light will be reflected. The induction time is determined taking images of the solution at fixed time intervals and measuring the time until scintillations are detected. JPEG images from the CCD camera were automatically archived to a high capacity disk drive at a suitable sampling frequency. Experiments could therefore be conducted unsupervised over extended periods, enabling the investigation of induction at low solution supersaturation.

Image files were subsequently processed using a custom MATLAB script, yielding the time course of average red light intensity versus time. Regression of the rate of change of red light intensity was used to determine induction times. A typical plot of light intensity and pictures captured are shown in Figure 2.

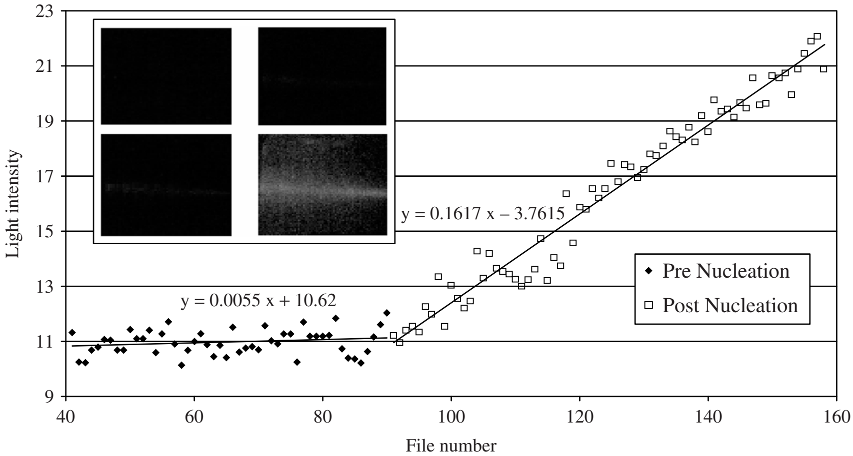

**Figure 2.** Light intensity versus the time stamped file number; the subfigure shows the light scintillations as nucleation onsets.

## RESULTS AND DISCUSSION

The results from processing the raw data from previous studies through the EES thermodynamic solver are demonstrated in Figure 3. The differences between the studies are apparent and none of the studies have overlapping results. This is to be expected due to the different detection methods used and varying hydrodynamic conditions. The results also support the assumption that homogeneous nucleation is valid at high levels of supersaturation. This is demonstrated by $R^2$ values of the linear regression.

The idea that this assumption is no longer valid at lower levels of supersaturation is also supported by the results. Bouropoulos and Koustsoukos (2000) decreased supersaturation to see where the assumption of homogeneous nucleation no longer applies. This can be clearly seen in Figure 3 by the change in gradient. Furthermore it can be seen that the Ohlinger *et al.* (1999) data points begin lie further away from the regressed line as supersaturation decreases.

The experiments conducted for this work investigated nucleation behavior at low supersaturation; the results can be seen in Figure 4. It can be clearly seen that concentration influences induction time at low supersaturation, this is contrary to classical theory which states induction time is only a function of

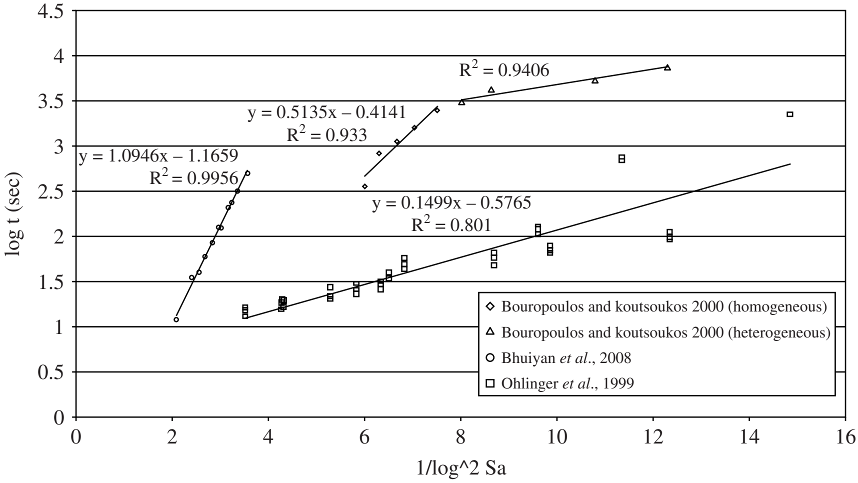

**Figure 3.** Logarithmic plots of induction time versus the inversed square of supersaturation ratio for the previous studies.

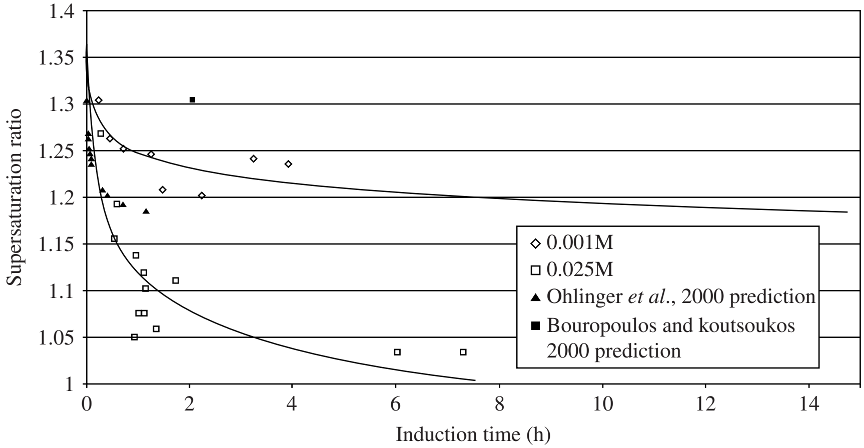

**Figure 4.** Induction time curves obtained by this study and predictions using previous studies.

supersaturation. This means that nucleation rates found at high supersaturation cannot be used for valid reactor design at low supersaturation.

Further evidence supporting this can be found by using the results of previous studies to predict the induction times at the levels of supersaturation used in this study. These predictions can be made by using Equation 8 which can be solved using the information in Figure 3. The results from these predictions were overlaid the results from this research in Figure 4.

It can be seen that the Ohlinger *et al.* (1999) predictions are in reasonable agreement at high supersaturation. Below $S_a = 1.2$ the induction time quickly approaches infinity though it is apparent in Figure 4 that nucleation does onset between 1 to 8 hours below $S_a = 1.2$. The Bouropoulos and Koutsoukos (2000) predictions only appear on Figure 4 at the highest level of supersaturation and the Bhuyian *et al.* (2008) predictions do not appear at all demonstrating predictions of infinite induction time at higher supersaturation levels than Ohlinger *et al.* (1999). The induction time curves themselves show clearly that, even at very low supersaturation, nucleation cannot be avoided indefinitely.

## CONCLUSIONS

The method of image capture and analysis can be used to determine induction times at low supersaturation and the results produced with this method indicated that nucleation of struvite could not be avoided indefinitely at low supersaturation. The comparison of previous studies in a common thermodynamic solver demonstrated that hydrodynamic conditions and detection methods may account for variations in observed induction times. Comparing the nucleation information from previous studies to this work showed that they cannot be used to design low supersaturation crystallisers. As nucleation is practically unavoidable in struvite crystallization it is also concluded that a means of dealing with fine nuclei is not an option but a necessity in the design of a struvite recovery unit.

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