



Modelling and simulation of inorganic precipitation with nucleation, crystal growth and aggregation: A new approach to an old method



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HIGHLIGHTS

- A process model describing key facets of inorganic precipitation is developed.
- Novel discretised population balance is used to better describe nucleation.
- Thermodynamic model is validated for synthetic struvite solutions.
- Model is used to simulate struvite crystallisation at various operating conditions.

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ABSTRACT

A process model is developed to simulate the recovery of inorganic mineral phosphates through precipitation, incorporating nucleation, crystal growth and aggregation mechanisms. The model includes a detailed description of solution thermodynamics, nucleation, growth and aggregation kinetics, a population balance and dynamic mass conservation. A discretised population balance (DPB) is used to describe changes to the particle size distribution (PSD) caused by nucleation, growth and aggregation. A sigmoid function is incorporated into the DPB to produce a better description of small-particle dynamics. The model is applied in the context of nutrient removal and recovery, with specific focus on a recovery pathway for phosphorus based on chemical precipitation. The model is used here to simulate a mixed suspension, mixed product removal (MSMPR) reactor and explore the relationship between operating conditions and thermodynamics. A validation for the solution thermodynamics portion of the model is also performed and the model is found to successfully predict solution pH.

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1. Introduction

Nutrient removal and recovery from wastewater streams is an important contribution to sustainable development. The release of nutrients such as nitrogen and phosphorus to receiving waters can lead to eutrophication, making the removal of these nutrients mandatory in many countries [1]. However, there are potential opportunities to recover these nutrients for reuse. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation is one opportunity that allows for the simultaneous removal and recovery of key nutrients, nitrogen and phosphorus [2], and is formed by Eq. (1). The product struvite can then be used directly as a fertiliser or as a feedstock in other industries requiring phosphorus [3,4]. The development of ecological sanitation technologies for implementation in the developing world, such as urine diverting toilets, is another application of struvite precipitation. The major advantage of using urine is that

precipitation can occur in urine without the costly treatment steps associated with traditional municipal wastewater [5].



The imperative for recovering phosphorus is heightened when considering its predicted scarcity. Currently, the raw material for phosphorus-based fertilisers is phosphate rock. Estimates suggest the reserves of economic phosphorus could be exhausted by the end of the century [6,7] and a peak in production is expected around the mid twenty-first century [8]. Furthermore, between 32% and 72% of phosphorus deposits are in the geopolitically sensitive Morocco/West Saharan region which could lead to future conflicts [9]. It is therefore important that nutrient recovery technologies, like struvite precipitation, be available for deployment in the coming decades.

Process modelling is an important tool in better understanding any chemical process. The ability to predict process behaviour for process design leads to improved start-up, steady state operation and process optimisation. This article reports on the development

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of a process model for struvite precipitation that describes the key chemical and physical processes that influences its precipitation.

Many experimental studies of struvite thermodynamics and kinetics have been conducted to better understand the system. However, little progress has been made in developing a process model for this system. This work addresses this shortcoming in order to deliver more confident process design, control and optimisation of nutrient recovery systems. The development of a modelling framework will also enable more rigorous and meaningful analysis of laboratory, pilot or full-scale experimentation.

2. Materials and methods

This work focuses primarily on process modelling and so the following sections describe the method of developing the process model. The process model is composed of four interconnected components, which, when combined, uniquely describe the operation of a struvite Mixed Suspension Mixed Product Removal (MSMPR) crystalliser. These components are: real solution thermodynamics; nucleation, crystal growth and aggregation kinetics; dynamic population balances and mass balances, represented diagrammatically in Fig. 1. The resultant set of equations are solved using gPROMS.¹

The process flow diagram and nominal feed conditions for the MSMPR model are given in Fig. 2. The struvite constituents (magnesium, ammonium and phosphate) are fed by the stream subscripted MAP and the sodium hydroxide, used to increase pH, is fed by the stream subscripted NaOH. The flows and concentrations are specific to struvite precipitation and laboratory-scale reactors. However, the number of streams, constituents, flow rates and reactor size could be changed to model any system. One advantage of formulating a continuous process model is that other operating schemes, batch or fed-batch can also be achieved by setting out-flow and/or inflows to zero.

2.1. Solution thermodynamics

The precipitation of any solid phase from an aqueous solution is governed by solution thermodynamics. The thermodynamic condition can also be used to determine the driving force for nucleation and crystal growth. Therefore, a description of solution thermodynamics is central to any model describing a precipitation process.

2.1.1. Supersaturation

A solution is supersaturated when the solute concentration exceeds its equilibrium concentration. In multi-ionic systems, defining solute concentration can be troublesome. Instead, solute concentration is defined in terms of the ion activity product (IAP), as per Eq. (2).

$$IAP = \{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\} \quad (2)$$

When the IAP is greater than the equilibrium solubility product, K_{sp} , the system is supersaturated and nucleation and/or crystal growth may occur, in a bid to return the system to equilibrium. This work employs the saturation index (SI) given by Eq. (3) as a representation of solution supersaturation [10,11]. The equilibrium solubility product used in this work is $pK_{sp} = 13.26$ [2], where pK_{sp} is the negative base ten logarithm of K_{sp} .

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \quad (3)$$

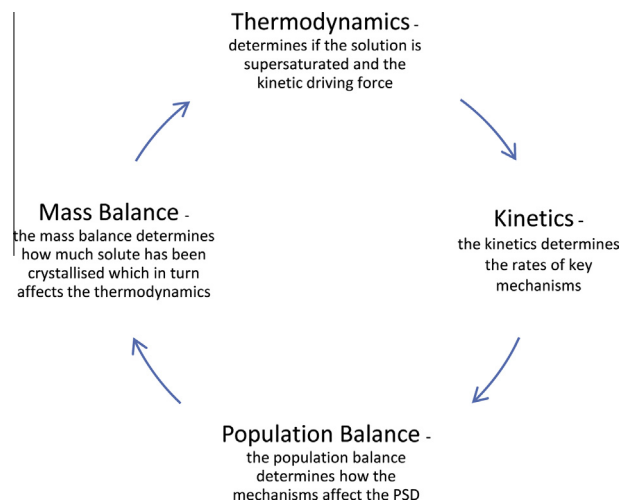


Fig. 1. Diagram of process modelling structure used for the struvite MSMPR crystalliser representing the highly coupled nature of the individual model components.

2.1.2. Speciation

The species considered can be defined in terms of the elements present in the system, with the exception of hydrogen and oxygen. The concentration of each element is equal to the molar sum of all species containing those elements, as defined by Eqs. (4)–(6), where square brackets represent the concentration of the species. The species considered in this analysis are based upon the work of Ohlinger et al. [2].

$$C_{Mg}^T = [Mg^{2+}] + [MgOH^+] + [MgPO_4^-] + [MgHPO_4] + [MgH_2PO_4^+] \quad (4)$$

$$C_N^T = [NH_4^+] + [NH_3] \quad (5)$$

$$C_P^T = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] + [MgPO_4^-] + [MgHPO_4] + [MgH_2PO_4^+] \quad (6)$$

Spectator ions (ions that do not participate in speciation), chloride and sodium, are added to the system through $MgCl_2 \cdot 6H_2O$ and NaOH additions. The spectator ions can also be written in terms of their elements, as shown in Eqs. (7) and (8).

$$C_{Cl}^T = [Cl^-] \quad (7)$$

$$C_{Na}^T = [Na^+] \quad (8)$$

The equilibria considered in this work to determine the speciation are listed in Table 1.

2.1.3. Activity models and ionic strength

Ionic species activity is related to concentration via an activity coefficient (Eq. (9)). Activity coefficients may be evaluated using some variant of the Debye–Hückel equation. The Davies approximation is used in this work, based on its upper limit of $I = 0.2$ M and its use in similar studies [12–14], and is given by Eq. (10). The ionic strength is defined by Eq. (11) and is a measure of the concentration of all ions in solution.

$$a_i = \gamma_i C_i \quad (9)$$

$$-\log \gamma_i = AZ_i^2 \left(\left[\frac{\sqrt{I}}{1 + \sqrt{I}} \right] - 0.3I \right) \quad (10)$$

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