Design and optimization of a reactive crystallization process for high purity phosphorus recovery from sewage sludge ash

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ABSTRACT

In this work, a reactive crystallization process was designed and optimized for separating high purity phosphorus (P) in the form of $CaClH_2PO_4 \cdot H_2O$ crystals from sewage sludge ash (SSA). The conceptual design procedure applied in the present work ensured to eliminate the co-precipitation of the undesired impurities as well as the optimal P recovery yield. Furthermore, the optimization of the key operating parameters for the crystallization process improved the particulate properties, which facilitated the separation of the crystals from the mother liquor in the down-stream filtration process. The experimental results showed that high purity crystals (Al and Fe impurities ~0.021 wt%) can be produced from the SSA with a high P-yield ($\geq$61.2%, based on the P in SSA). The production cost of US$ 3.0/(kg P) has been estimated for the proposed process.

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1. Introduction

Phosphorus is an essential element for the ecosystem, because it serves as a crucial nutrient for plants and livestock production [1–4]. The commercial phosphates are derived from phosphate rock, which is a limited and non-renewable deposit. The largest phosphorus rock deposits are located only in Morocco and Western Sahara, China, USA and Algeria [5]. It is predicted that the current exploitable reserves of phosphate rock will run out within 300 years [5]. European has only limited resources (in Finland) and thus 95% of phosphorus production to sustain EU population is largely dependent on imports [6]. The European Commission has added phosphate rock into the list of 20 critical raw materials of high economic importance and supply risk [7]. Meanwhile, a large percent of mined P loses to the environment. For instance, in 2005, 47% of phosphorus has been inefficiently used and lost to the waste streams [8]. According to Environmental Protection Agency of Denmark, it is possible to recycle 4200–5600 tons phosphorus from Danish wastewater treatment plant annually, which accounts for 21–37% of total phosphorus imports into Denmark per year [9]. Therefore, phosphorus recovery from waste streams provides an opportunity of supplying phosphorus with sustainable development. Environmental Protection Agency of Denmark has set up a new resource strategy aiming at recycling 80% of phosphorus from sewage sludge in 2018 [10].

The major constraint preventing the use of sewage sludge in agriculture is the heavy metal content [11]. The Outotec (formerly known as ASH DEC) has developed a thermochemical treatment to remove the heavy metals from sewage sludge ash by heating at >1000 °C in the furnace [12]. The method of wet acid leaching to recover P without heavy metals from SSA has been reported. Petzet et al. [13] reported a process named SESAL to separate P from the heavy metals: first, Al-P precipitate and the soluble heavy metals were separated at pH 3 by adding HCl acid; second, the Al-P precipitate was then dissolved at pH 13 by treating with NaOH; last, the P was recovered as Ca-P precipitate with dosing of $CaCl_2$. Franz [14] reported that more than 90% of P was extracted with a three-step process: (1) SSA was leached with 14 wt% H_2SO_4 at L/S ratio of 2 for 10 min; (2) the co-dissolved heavy metals were then removed either with ion exchange or with sulfide precipitation; (3) P was recovered as Ca-P precipitates with lime water. The primary objective of these technologies is to remove the hazardous heavy metals; the recovered P products are solely for agriculture application. For establishing a more sustainable P-cycle for phosphorus supply, more advanced technologies that can recover phosphorus from SSA and can furthermore convert it to high purity fine chemicals that can be used as industrial materials are required.

As one of the few separation technologies that can deliver high purity products, reactive crystallization has been used in the present work to recover crystalline phosphate from the SSA. In this study, one major challenge for crystallizing high purity P arises from the high concentrations of Al and Fe in the sewage sludge ash (SSA), because the frequently use of Al and Fe compounds in the WWTP as precipitating agents. The solubility of either Al

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phosphate or Fe phosphate is rather low in pH range of 0–5, and there is a high potential of getting these substances co-precipitate together with calcium phosphate. Furthermore, the SSA contains various hazardous substances with a relatively low concentration (Zn, Cd, Cr, Pb, Hg etc.) [15,16]. Although these substances have little possibility to precipitate together with the target P product, they may contaminate the P product if the crystallized P has poor filterability and is difficult to be filtered out from the mother liquor. To overcome the challenges, a novel conceptual design and optimization methodology has been suggested in the present work for the reactive crystallization of calcium phosphate from SSA. The novelty of this design methodology lies in the two-fold strategy to ensure the high purity of the phosphate product and the maximum P-yield of the process. First, the solid-liquid equilibrium in the multi-component system was established by considering the dissociation of the anions and cations as well as the low solubility phosphate compound. Based on the established solid-liquid equilibrium of the relevant species, the target phosphate product and the optimal operating pH range of the reactive crystallization process can be selected. In this optimal pH range, the solubility of the target phosphate product is lower than that of the undesired impurities (e.g. $AlPO_4$ and $FePO_4$). Second, the filterability of the phosphate product was optimized by performing the process with the optimal key parameters that promote the crystal growth. Consequently, the down-stream filtration process will be facilitated, and the mother liquor that contains large amount of soluble metals can be removed out from the filter cake. Accordingly, this two-fold strategy can ensure the high purity of the final phosphate product.

2. Experimental methods

2.1. Conceptual design of reactive crystallization

The formation of the phosphate salt via reactive crystallization occurs only when the concentration product of the constituent ions exceeds its thermodynamic solubility product (K_{sp}). In practice, the maximum amount of substance can be dissolved in the solution depends on its corresponding conditional solubility product P_s, which is a function of pH and takes into account the solubility product of substance as well as the dissociation of the ions (e.g. dissociation of H_3PO_4).

2.1.1. Conditional solubility curves

The following equilibrium, Eq. (1), will be attained when the compound X_aY_b dissolves in water, forming a saturated solution.

$$X_aY_b \leftrightarrow aX^{b+} + bY^{a-} \tag{1}$$

The solubility product K_{sp} for X_aY_b (a sparingly soluble salt) is given in Eq. (2) [17].

$$K_{sp} = C^a(X^{b+}) C^b(Y^{a-}) \tag{2}$$

Table 1
Solubility product exponents.

Compound	pK_{sp} (298 K)
$CaClH_2PO_4 \cdot H_2O$	2.24 (current study)
$CaHPO_4$	6.7
$Ca(H_2PO_4)_2$	3.0
$Fe(OH)_3$	38.7
$FePO_4$	21.9
$Al(OH)_3$	33.7
$AlPO_4$	20.0
$CaSO_4$	4.3

where $C(X^{b+})$, $C(Y^{a-})$ represent the molar concentration of X^{b+} and Y^{a-} ions in the solution. In ideal dilute solution, the conditional solubility product, P_s, is defined in Eq. (3) [17].
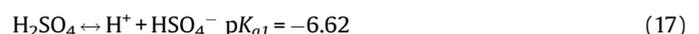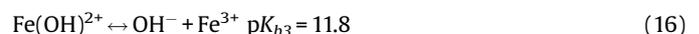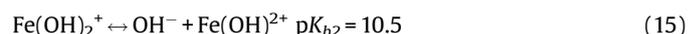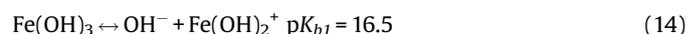
$$P_s = C^a(X) C^b(Y) = K_{sp}/(\alpha^a(X^{b+}) \alpha^b(Y^{a-})) \tag{3}$$

where $C(X)$, $C(Y)$ are the total molar concentration of all soluble X and Y species in the solution; $\alpha(X^{b+})$, $\alpha(Y^{a-})$ are the ionization fraction of X^{b+} and Y^{a-} in the solution, respectively, and are defined in Eqs. (4) and (5) [18].

$$\alpha(X^{b+}) = C(X^{b+})/C(X) \tag{4}$$

$$\alpha(Y^{a-}) = C(Y^{a-})/C(Y) \tag{5}$$

The dissociation equations and their corresponding dissociation constant exponents used to calculate the relative concentrations of the species in the solution system can be found in literatures [19–21], see Eqs. (6)–(18).

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \quad pK_{a1} = 2.1 \tag{6}$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \quad pK_{a2} = 7.2 \tag{7}$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-} \quad pK_{a3} = 12.3 \tag{8}$$

$$Ca(OH)_2 \leftrightarrow OH^- + Ca(OH)^+ \quad pK_{b1} = 2.4 \tag{9}$$

$$Ca(OH)^+ \leftrightarrow OH^- + Ca^{2+} \quad pK_{b2} = 1.4 \tag{10}$$

$$Al(OH)_3 \leftrightarrow OH^- + Al(OH)_2^+ \quad pK_{b1} = 14.8 \tag{11}$$

$$Al(OH)_2^+ \leftrightarrow OH^- + Al(OH)^{2+} \quad pK_{b2} = 10.3 \tag{12}$$

$$Al(OH)^{2+} \leftrightarrow OH^- + Al^{3+} \quad pK_{b3} = 9.0 \tag{13}$$

$$Fe(OH)_3 \leftrightarrow OH^- + Fe(OH)_2^+ \quad pK_{b1} = 16.5 \tag{14}$$

$$Fe(OH)_2^+ \leftrightarrow OH^- + Fe(OH)^{2+} \quad pK_{b2} = 10.5 \tag{15}$$

$$Fe(OH)^{2+} \leftrightarrow OH^- + Fe^{3+} \quad pK_{b3} = 11.8 \tag{16}$$

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^- \quad pK_{a1} = -6.62 \tag{17}$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-} \quad pK_{a2} = 1.99 \tag{18}$$
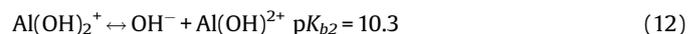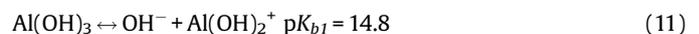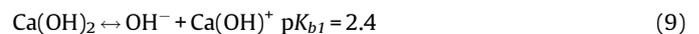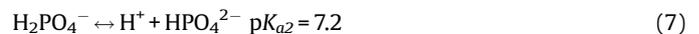
It must be noted that as the pH increases, $Al(OH)_3$ and $Fe(OH)_3$ will dissolve to form $Al(OH)_4^-$ and $Fe(OH)_4^-$, respectively. This formation can be detailed in four steps as follows (Eqs. (19)–(26)) [22]:

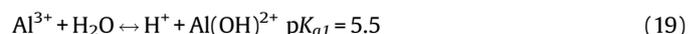$$Al^{3+} + H_2O \leftrightarrow H^+ + Al(OH)^{2+} \quad pK_{a1} = 5.5 \tag{19}$$

$$Al(OH)^{2+} + H_2O \leftrightarrow H^+ + Al(OH)_2^+ \quad pK_{a2} = 5.8 \tag{20}$$