Struvite recovery from solution containing phosphate(V) and sulphate(VI) ions

Abstract: The research results concerning the application of magnesium and ammonium ions for continuous removal of phosphate(V) ions from solution containing 1.0 or 0.20 mass% of \( \text{PO}_4^{3-} \) and from 0.10 to 0.50 mass% of \( \text{SO}_4^{2-} \) are presented. A continuous struvite reaction crystallization process was carried out both under stoichiometric conditions and using 20% excess of magnesium ions. The research was conducted in a DT MSMPR type crystallizer with internal circulation of suspension driven by a propeller stirrer, in constant temperature 298 K. The pH varied from 9 to 11 and mean residence time of suspension in a crystallizer \( \tau \) varied from 900 to 3600 s. It was concluded, that sulphate(VI) ions influenced product quality disadvantageously. Depending on process parameter combinations struvite crystals of mean size from ca. 18 to ca. 44 \( \mu \text{m} \) and of moderate homogeneity: CV 7–95% were produced. Presence of sulphate(VI) ions favored crystallization of struvite as prismatic crystals, but tubular forms were also identified. The best shaped struvite crystals were produced at relatively low concentration of sulphate(VI) ions, pH 9 and for mean residence time of suspension in a crystallizer elongated up to 3600 s.

Keywords: struvite, phosphate(V) ions, sulphate(VI) ions, continuous reaction crystallization, crystal product quality

1 Introduction

Chemical separation of phosphate(V) ions from industrial, municipal wastewaters or from liquid manure is most often based on binding of these species in a form of sparingly soluble magnesium and ammonium salt \( \text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O} \), struvite, MAP (corresponding solubility product \( pK_{sp} = 9.0–13.26 \)) [1]. Raw substrates necessary for this process can be crystalline magnesium and ammonium compounds, their aqueous solutions, as well as liquid waste mixtures in which these reagents are present in satisfactory concentrations [2]. Arrangement of optimal conditions for controlled, integrated continuous precipitation and mass crystallization of struvite is a complex technological challenge [3]. The final product of this process – a crystal population of specified chemical purity and particle size distribution (CSD) – depends on many parameters defining together the environment in which these processes run [4], on the parameter values [5], as well as on the apparatus construction and plant configuration [6].

One of the factors significantly affecting the struvite reaction crystallization course, and thus the product quality, are impurities present in wastewaters. These are mainly metal ions, but also include sulphates(VI), nitrates(V), fluorides, fluosilicates and others. These inhibit or catalyze, sometimes in unpredicted way, the precipitation reaction course, modify nucleation and crystal growth kinetics, solid product’s shape and possibly cause agglomeration effects [7]. Some metal ions in an alkaline environment of struvite precipitation can form sparingly soluble hydroxides or phosphates [8,9], which essentially modifies the chemical composition of the product [10,11] and usually limits the possibilities of its further application in agriculture [12].

One of the impurities present in phosphorus mineral fertilizer industry wastewaters [13] is sulphate(VI) ions. Analytically identified concentration of these ions can be relatively high: from 0.1 up to even 0.5 mass%. Their influence on the continuous struvite reaction crystallization process is practically unknown. In this work we present the experimental research results concerning the effects
of the presence and concentration of sulphate(VI) ions on the struvite reaction crystallization process in a continuous laboratory DT MSMPR (Draft Tube, Mixed Suspension Mixed Product Removal) type crystallizer with propeller stirrer. We determined process yield defined as final concentration of PO$_4^{3-}$ ions in a postprocessed mother liquor, product crystal size distributions (CSDs) and their statistical parameters ($L_m$, $L_d$, CV). We also evaluated crystal shapes ($L_a/L_b$) and their agglomeration effects.

2 Experimental procedure

2.1 Experimental apparatus

The general scheme of the experimental apparatus is presented in Fig. 1. It is a fully automated continuous IKA Labortechnik plant. Steering, control and on-line acquisition of data streams were done with the use of a PC (IKA Labworldsoft software). The continuous struvite reaction crystallization process ran in a DT MSMPR type crystallizer of working volume $V_w$ 0.6 dm$^3$.

The crystallizer was a glass cylindrical tank ($D$ 120 mm, $H$ 123 mm), in a bottom part equipped with an external heating/cooling coil, providing isothermal process conditions resulting from the externally controlled flow of thermostated water. In the central axis of the crystallizer we mounted a cylindrical circulation profile (Draft Tube, DT, $d_{dt}$ 57 mm, $h_{dt}$ 53 mm), inside which the three-paddle propeller stirrer ($d_m$ 55 mm) operated. Inlet port for reagent feed and alkalizing solution and outlet port for product crystal suspension removal are presented in Fig. 1.

2.2 Materials and methods

The crystallizer feed contained aqueous solution of ammonium dihydrogenphosphate(V) NH$_4$H$_2$PO$_4$, magnesium chloride hexahydrate MgCl$_2$·6H$_2$O and sodium sulphate(VI) Na$_2$SO$_4$. We prepared the feed mixture in an external mixer using the above presented substances in a crystalline form (analytically pure, POCh Gliwice, Poland) and deionised water (Barnstead–NANOPure Diamon). The concentration of phosphate(V) ions was adjusted to be 0.20 or 1.0 mass%, which is the typical range for phosphorus mineral fertilizer industry wastewaters [10, 13]. Concentrations of other substrates for struvite synthesis resulted from the assumed molar ratio PO$_4^{3-}$:Mg$^{2+}$:NH$_4^+$ = 1:1:1 (stoichiometry) or 1:1.2:1 (magnesium ions excess).

Chemical compositions of all eight feed alternatives are presented in Table 1. The solution was continuously
Table 1: Chemical composition of solutions feeding the continuous DT MSMPR crystallizer.

| Molar proportions of substrate ions in a feed | Concentration (mass%) |
|---------------------------------------------|-----------------------|
| PO₄³⁻:Mg²⁺:NH₄⁺ | PO₄³⁻ | Mg²⁺ | NH₄⁺ | SO₄²⁻ |
| 1:1:1 | 0.20 | 0.0512 | 0.0380 | 0.10 or 0.50 |
| 1.0 | 0.256 | 0.193 | 0.10 or 0.50 |
| 1:1.2:1 | 0.20 | 0.0614 | 0.0380 | 0.10 or 0.50 |
| 1.0 | 0.307 | 0.193 | 0.10 or 0.50 |

introduced into the DT subvolume (mixer speed: 6.6 ± 0.1 s⁻¹; suspension movement – downward). Between the crystallizer body and circulation profile (DT) (suspension movement – upward) aqueous solution of sodium hydroxide of concentration 20 mass% NaOH was carefully dosed in amounts conserving the assumed and strictly controlled pH value. Research was ran in a constant temperature 298 ± 0.2 K assuming pH 9, 10 or 11 (± 0.1) and mean residence time of suspension in a crystallizer τ 900, 1800 or 3600 (± 20) s. After stabilisation in a crystallizer of the required parameter values (initial ca. 5τ), process in a steady state ran through the next 5τ. After this time we transferred the whole crystallizer content onto the vacuum filter. Product crystals were not washed with water, but immediately dried at room temperature.

2.3 Measurement methods

After convective drying we determined crystal size distributions (CSDs) with the use of laser particle size analyser Coulter LS 230 and Beckman Coulter LS 13 320. Crystal shapes were quantified based on images from scanning electron microscope JEOL JSM 5800LV. We determined the mean size of struvite crystals as

\[ L_m = \sum x_i \times L_i \]

where: \( x_i \) – mass fraction of crystals of fraction’s mean size \( L_i \), dominant particle size \( L_d \) – size corresponding to maximum in differential CSD, as well as the coefficient characterizing particle size homogeneity

\[ CV = 100 \left( \frac{L_{50} - L_{10}}{2L_{50}} \right) \]

where: \( L_{50}, L_{10}, L_{50} \) – crystal sizes for undersize fractions representing: 84, 16 and 50 mass %, respectively. The authors evaluated the crystal shape of each product after its quantification by calculation of crystal length \( L_d \) to width \( L_w \) ratio based on 50 crystals randomly selected from three scanning electron microscope images. On this basis we also calculated the geometrical crystal shape coefficient \( k_g = \frac{V_{crystal}}{L^3} \). The accuracy of measurement data concerning the complex continuous struvite reaction crystallization process in a computer-controlled laboratory plant was estimated by us to be ca. 10%. The authors determined solid phase content in a product crystal suspension (\( M_p \)) based on crystal mass after filtration of 0.6 dm³ suspension (whole crystallizer’s working volume). For the determination of chemical compositions of mother liquor and solid phase we used plasma emission spectrometer ICP-AES CPU 7000, spectrometer IR PUG712, atomic absorption spectrometer iCE 3000, as well as spectrophotometer UV–Vis Evolution 300.

3 Results and discussion

3.1 Effect of sulphate(VI) ions

The research results are presented in Table 2. From the table it can be concluded, that the concentration of sulphate(VI) ions influenced both struvite crystal product sizes and population homogeneity disadvantageously (see the tests No. 1–2, 7–8, 9–10 and 11–12 in Table 2).

Feeding the crystallizer with solution containing 1.0 mass% of phosphate(V) ions, under stoichiometric conditions, and increasing sulphate(VI) ion inlet concentration from 0.10 to 0.50 mass% resulted in a decrease of mean struvite crystal size by ca. 13%: from 27.9 to 24.4 µm (at pH 9, τ 900 s; see tests No. 1–2 in Table 2) [14]. From the data analysis it is observed that this decrease was (in average) ca. 3.5 µm in the case of stoichiometric conditions and ca. 2.5 µm for excess of magnesium ions in a feed. Influence of phosphate(V) ion concentration (0.20 or 1.0 mass % \( \text{PO}_4^{3-} \)) in a feed solution on ∆\( L_m \) can be thus regarded as small. The difference does not exceed 1 µm, thus is practically within the experimental error limits. Homogeneity within product population manufactured in the presence of sulphate(VI) ions can be regarded as moderately satisfactory. Coefficient of crystal size homogeneity CV increased regularly with the increase in feed concentration of sulphate(VI) ions. It generally varied from 78 to 95% (Table 2). Higher feed concentration of sulphate(VI) ions caused growth of CV values by 1–3% (1.9% in average).

Decrease of the mean size \( L_m \) of struvite crystals with the increase in feed concentration of sulphate(VI) ions is connected with a general increase in the number of the smallest particles in a product population while both number and size of the largest crystals decreased. As a result the dominant crystal size shifted towards smaller values: \( L_d 23.8 \to 21.7 \) µm for \( \text{SO}_4^{2-} \) 0.10 – 0.50
mass%. The maximum size of struvite crystals produced in the presence of 0.10 mass% of sulphate(VI) ions was 130 µm, while for 0.50 mass% of SO$_4^{2-}$ it decreased to 120 µm. Simultaneously, the fraction of the smallest particles increased. For [SO$_4^{2-}$]$_{mM}$ 0.10 mass% crystal fraction of size < 5 µm represented 13.4%, while for [SO$_4^{2-}$]$_{mM}$ 0.50 mass% this fraction grew up to 16.3%, thus relatively increasing by more than 20%.

In Fig. 2a example size distribution of struvite crystals manufactured in the presence of 0.10 mass % of sulphate(VI) ions in a feed (process parameters: pH 9, τ 900 s, PO$_4^{3-}$:Mg$^{2+}$:NH$_4^+$ = 1:1:1) was presented. This distribution can be also evaluated visually, analyzing the scanning electron microscope image of the product sample (Fig. 3a), where diverse sizes of struvite crystals are clearly visible.

Taking under consideration all research results one can generally conclude, that sulphate(VI) ions did not inhibit struvite nucleation rate, as well as not favoring it’s crystal growth. Agglomeration within product crystals can be regarded as less than moderate (Fig. 3a).

### 3.2 Effect of pH and mean residence time

Increase in pH of the continuous struvite reaction crystallization process environment produced a decrease of crystal size (compare tests 1, 3 and 4 in Table 2). Elevation of pH from 9 to 11 – at constant feed concentration of sulphate(VI) ions 0.10 mass% – resulted in mean product size $L_m$ decreasing by nearly 35%: from 27.9 to 18.3 µm. Increase in pH also did not favor homogeneity within product crystals population. The CV increased from 86.6% to 95.0%. Dominant crystal size $L_d$ shifted towards lower values: from 23.8 µm (pH 9) to 13.6 µm (pH 11). Both number and size of the largest struvite crystals in a product population decreased. Their maximal size at pH 9 was 130 µm (Fig. 2a), whereas at pH 11 – only 85 µm (Fig. 2b). Simultaneously, the fraction of the smallest particles increased. At pH 9 the crystal fraction of size < 5 µm was 13.4%, whereas at pH 11 it increased up to 19.2%. As a result the mean crystal size $L_m$ decreased by ca. 10 µm. A scanning electron microscope image of such product crystals is shown in Fig. 3b, of corresponding CSD presented in Fig. 2b. Smaller sizes of struvite crystals produced at pH 11 are easily observable (compare Fig. 3a and 3b). It is an effect of lower struvite solubility at higher pH values (minimal value corresponds, however, to pH 10.3 [15] or 10.7 [16]). Under these conditions struvite precipitation potential increases [2]. Additionally, induction time necessary for nucleation process initiation shortens [17]. All of these factors contribute to an increase in nuclei population density, shifting $L_m$ and $L_d$ towards smaller values.

### Table 2: Effects of feed concentration of sulphate(VI) ions and selected technological parameters of continuous struvite reaction crystallization process on the product quality. Process temperature: 298 K.

| No. | $[\text{PO}_4^{3-}]_{\text{mM}}$ (mass%) | $[\text{SO}_4^{2-}]_{\text{mM}}$ (mass%) | pH | τ (s) | $M_{\text{a}}$ | $[\text{PO}_4^{3-}]_{\text{ML}}$ (mg kg$^{-1}$) | $[\text{Mg}^{2+}]_{\text{ML}}$ (mg kg$^{-1}$) | $[\text{SO}_4^{2-}]_{\text{ML}}$ (mass%) | $L_m$ (µm) | $L_d$ (µm) | CV (%) | $L_d/L_m$ |
|-----|----------------------------------|----------------------------------|-----|-------|------------|----------------------------------|----------------------------------|----------------------------------|----------|----------|-------|------------|
| 1   | 1.0                              | 0.10                             | 9   | 900   | 0.103     | 23.6                             | 2152                             | 37                               | 27.9     | 23.8     | 86.6  | 7.5        |
| 2   | 1.0                              | 0.50                             | 9   | 900   | 0.513     | 40                               | 24.4                             | 21.7                             | 87.6     | 7.8      |       |            |
| 3   | 1.0                              | 0.10                             | 9   | 1000  | 0.102     | 14                              | 22.7                             | 18.0                             | 88.4     | 7.7      |       |            |
| 4   | 1.0                              | 0.10                             | 10  | 900   | 0.102     | 34                               | 29                               | 13.6                             | 95.0     | 7.8      |       |            |
| 5   | 1.0                              | 0.10                             | 10  | 1800  | 0.102     | 37                               | 29.8                             | 34.8                             | 84.2     | 8.2      |       |            |
| 6   | 1.0                              | 0.10                             | 9   | 3600  | 0.102     | 32                               | 44.2                             | 50.2                             | 80.0     | 9.0      |       |            |
| 7   | 0.20                             | 0.10                             | 9   | 900   | 0.101     | 37                               | 38.5                             | 35.0                             | 78.0     | 7.4      |       |            |
| 8   | 0.20                             | 0.50                             | 9   | 900   | 0.503     | 37                               | 35.1                             | 30.2                             | 80.2     | 7.8      |       |            |

* $M_{\text{a}}$ – solid phase content in a product crystal suspension, kg crystals m$^{-2}$ suspension

** After drying, without water washing of crystals on a filter 1 and 2 [14]
Elongation of mean residence time of suspension in a crystallizer up to 3600 s caused, however, the product crystal size to increase by more than 58% (compare the tests 1, 5 and 6 in Table 2). In the presence of 0.10 mass% of sulphate(VI) ions in a feed struvite crystals reached a mean size $L_m$ of 44.2 µm (pH 9, $\tau$ 3600 s). With the elongation of mean residence time of suspension supersaturation in solution decreases, thus decreasing the values of both kinetic components of the process: nucleation rate of struvite crystals and their linear growth rate. Longer residence time of crystals in supersaturated solution produced a better final product. Crystals grew slower, but for longer, thus becoming more stable and reaching considerably larger sizes. Homogeneity within their population improved (CV 86.6% ($\tau$ 900 s) → 84.2% ($\tau$ 1800 s) → 80.0% ($\tau$ 3600 s)).

Residence time of suspension up to 3600 s caused the dominant size $L_d$ of struvite crystals to shift towards larger values: from 23.8 µm ($\tau$ 900 s) up to 50.2 µm ($\tau$ 3600 s). The largest crystals reached 130 µm ($\tau$ 900 s, Fig. 2a) and 250 µm ($\tau$ 3600 s, Fig. 2c). The fraction of the smallest
3.3 Effect of phosphate(V) ion concentration in a feed and magnesium ion excess

Reduction to 20% phosphate(V) ion concentration in the feed (from 1.0 to 0.20 mass%) resulted in enlargement of mean struvite crystal size \( L_a \) by ca. 10 \( \mu \)m, thus by ca. 30–40% (tests 1, 2 and 7, 8 under stoichiometric conditions, as well as 9, 10 and 11, 12 at magnesium ion excess in Table 2). This change meant that the local solution’s supersaturation at the crystallizer inlet proportionally decreased. As a result the struvite nucleation rate, very strongly dependent on supersaturation, also lowered. It produced a decrease in nuclei number, thus higher mean size of crystals removed from the crystallizer, as well as smaller diversification within their sizes (coefficient of crystal size homogeneity CV decreased by ca. 6%).

Excess of magnesium ions related to inlet concentrations of phosphate(V) and ammonium ions (\( \text{PO}_4^{3-}:\text{Mg}^{2+}:\text{NH}_4^+ = 1:2:1 \)) influenced process results advantageously (compare tests 9–12 in Table 2). For example, the mean size of struvite crystals \( L_a \) enlarged from 38.5 to 43.1 \( \mu \)m (by 12%) and from 35.1 to 41.0 \( \mu \)m (by 17%) for \( [\text{PO}_4^{3-}]_{\text{SM}} \) 0.20 mass % and \( [\text{SO}_4^{2-}]_{\text{SM}} \) 0.10 and 0.50 mass%, respectively. It may be generally concluded, that higher supersaturation of magnesium ions affected all partial phenomena involved in the continuous struvite reaction crystallization process advantageously. Their total effect (higher nucleation rates compensated in excess by higher crystal growth rates) influenced product sizes advantageously (\( L_a, L_b \)). Nevertheless, these also slightly deteriorated product homogeneity (see the corresponding CV values).

3.4 Crystal shape

From the analysis of scanning electron microscope images of the products, (example images are presented in Fig. 3) it is found that the majority of struvite crystals were not stable. Based on the planimetric measurements involving 50 crystals randomly selected from three electron microscope images (for each product) we concluded, that their mean length \( L_a \) to width \( L_b \) ratio varied from 74 to 9.0 depending on process parameters (Table 2). An increase in feed concentration of sulphate(VI) ions resulted in struvite crystals length \( L_a \) increasing with their width \( L_b \) practically unmodified (the \( L_a/L_b \) ratio increased from 7.5 to 7.8) (stoichiometric conditions, \( [\text{PO}_4^{3-}]_{\text{SM}} \) 1.0 mass%, pH 9, \( \tau \) 900 s). Increase in pH of the struvite continuous reaction crystallization process environment resulted in crystal length \( L_a \) and width \( L_b \) decreasing, however \( L_b \) clearly decreased more: \( L_a/L_b \) 7.5, 7.7 and 7.8 – at pH 9, 10 and 11 (\( \tau \) 900 s and \( [\text{SO}_4^{2-}]_{\text{SM}} \) 0.10 mass %, Fig. 3a and b). However, with the enlargement of mean residence time of suspension in a crystallizer, crystal length \( L_a \) and width \( L_b \) increased, but not proportionally. Thus the \( L_a/L_b \) ratio distinctly increased from 7.5 to 9.0 (Figs. 3a and c). Lower feed concentration of phosphate(V) ions and magnesium ions excess did not make any essential modifications in mean \( L_a/L_b \) ratio values.

From the analysis of microscope images of the crystal products (Fig. 3) we also concluded, that the geometric shape of struvite crystals changed. The authors observed particles of prismatic (Fig. 4a), needle forms, and even tubular crystals with deformed edges (Fig. 4b). Volumetric shape factor \( k_v \) of these crystals varied, however, within typical limits: from 0.010 to 0.040 for \( L_a : L_c \) : \( r \) 10:3:1 and 5:1:1, respectively [18]. If the particles are elongated or needle-shaped, their volume may be calculated assuming formally that they are cylindrical [19]. Calculated under this assumption mean values of \( k_v \) were: 0.014 (pH 9, \( \tau \) 900 s, \( L_a/L_b \) 7.5, Fig. 3a), 0.013 (pH 11, \( \tau \) 900 s, \( L_a/L_b \) 7.8, Fig. 3b), 0.0097 (pH 9, \( \tau \) 3600 s, \( L_a/L_b \) 9.0, Fig. 3c).

Struvite crystals produced from solution containing only phosphate(V) ions and sulphate(VI) ions (Table 1 and 2, Fig. 3) differed in shape from the crystals produced from real, complex phosphorus mineral fertilizers industry wastewater, containing, among others, sulphate(VI) ions [10] (Fig. 5).

Significant influence on this shape was exerted by other impurities present in this specific wastewater [7]. Struvite recovered from this wastewater was characterized by \( L_a/L_b \) ratio varying from 3:4 to 4.9 [10]. Its crystals were thus shorter and simultaneously thicker. Moreover, their surface was partly blocked by co-precipitated and co-crystallized sparingly soluble impurity compounds (calcium phosphates, selected metal hydroxides).
3.5 Chemical composition

Analytically determined concentrations of phosphate(V) ions in a postprocessed mother liquor are presented in Table 2. We can practically assume, that this concentration stabilized at relatively constant and low level: $140 \pm 10 \text{ mg PO}_4^{3-} \text{ kg}^{-1}$ (under stoichiometric conditions) and $27 \pm 3 \text{ mg PO}_4^{3-} \text{ kg}^{-1}$ (at magnesium ions excess). The mean effectiveness of phosphate(V) ions removal from the feed stream varied thus from 93 to 99% depending on the process technological parameters assumed. Feed concentration of sulphate(VI) ions did not influence the concentration of phosphate(V) ions in a postprocessed mother liquor. The $[\text{PO}_4^{3-}]_{\text{ML}}$ values, however, diminished regularly with pH increase and with elongation of mean residence time of suspension in a crystallizer. This can be explained by decrease of struvite solubility with pH increase and longer contact time of crystals with supersaturated solution (more thorough discharge of supersaturation). However, the authors were not able to calculate the creditable value of working supersaturation in a crystallizer, thus supersaturation in a postprocessed, outflowing mother liquor with satisfactory accuracy. Most published works assume the solubility product of struvite $pK_{sp}^{\text{struvite}} = 13.26$ [15], for which – theoretically – equilibrium concentration of phosphate(V) ions is $3.6 \text{ mg kg}^{-1}$. However, $pK_{sp}^{\text{struvite}}$ value is practically unknown since it depends on many process, technological, and even constructional factors. Thus it usually significantly differs from the one provided by Ohlinger et al. [15]. Excess of magnesium ions related to phosphate(V) and ammonium ions concentrations influenced the process yield advantageously. The concentration of phosphate(V) ions in a postprocessed mother liquor varied from 24 to 30 mg kg$^{-1}$ and was distinctly lower (even from 4- to 6-time) compared to stoichiometric conditions. For comparison, in a process system without impurities, this concentration varied from 9 to 92 mg kg$^{-1}$ [20], whereas in the case of phosphorus mineral fertilizers industry wastewater processing – from 9.2 to 18.5 mg kg$^{-1}$ [10]. For pH 9 and mean residence time $\tau 900 \text{ s}$ the concentration of $\text{PO}_4^{3-}$ in mother liquor was: 25 mg kg$^{-1}$ [20], 18.5 mg kg$^{-1}$ [10] and 24 – 28 mg kg$^{-1}$ – present study. From these data comparison, it is concluded that the presence of sulphate(VI) ions practically did not influence the final concentration of phosphate(V) ions.

Concentration of magnesium ions in a postprocessed mother liquor varied in a narrow range 29–40 mg Mg$^{2+}$ kg$^{-1}$ (tests 1–8 in Table 2). One can observe clear correlation of this concentration with phosphate(V) ion concentration. Excess of magnesium ions related to feed concentrations.
of phosphate(V) and ammonium ions (PO$_4^{3-}$$:$Mg$^{2+}$$:$NH$_4^+$ = 1:1:2:1) caused the concentration of Mg$^{2+}$ ions to increase up to ca. 530 mg kg$^{-1}$ ([PO$_4^{3-}$]$_{in}$ 1.0 mass %) and up to ca. 110 mg kg$^{-1}$ ([PO$_4^{3-}$]$_{am}$ 0.20 mass %) (tests 9–12 in Table 2). The concentration of phosphate(V) ions in these solutions decreased (from 121–152 to 24–30 mg PO$_4^{3-}$ kg$^{-1}$). The equilibrium of the precipitation reaction therefore shifted towards struvite formation. Reaction crystallization process yield increased.

Sulphate(VI) ions do not take direct part in a struvite reaction crystallization process. These do not form any sparingly soluble sulphate(VI) salts because of the matching cations absence. Their concentrations in postprocessed liquors were, however, higher by ca. 2–3% in average compared to a feed. It is only the direct effect of the general decrease of mother solution mass that modifies component proportions in the system.

4 Conclusions

We continuously produced struvite from solution containing phosphate(V) (0.20–1.0 mass %) and sulphate(VI) ions (0.10–0.50 mass %). The authors observed, that with the increase in sulphate(VI) ion concentration in a feed, the mean size of struvite crystals $L_m$ decreased by ca. 13% (e.g. from 27.9 to 24.4 µm at pH 9 and τ 900 s). Homogeneity within the product population decreased and corresponding CV increased by ca. 2%. Increase in the pH of the struvite reaction crystallization process environment influenced process quality disadvantageously. The authors obtained crystals of smaller sizes ($L_m$ 18.3 µm at pH 11 and feed concentration of sulphate(VI) ions 0.10 mass %) and of lower homogeneity (CV 95%). Contrary, elongation of mean residence time of suspension in a crystallizer (up to 3600 s), despite the decrease of working supersaturation in the mother liquor, resulted in product crystal sizes increasing by more than 58%. Homogeneity within product crystals improved as well.

Based on microscope images of crystal products we concluded, that agglomeration within struvite crystals was less than moderate. Properly shaped product crystals were formed. The presence of sulphate(VI) ions and process conditions established in a crystallizer favored crystallization of struvite mainly in prismatic, needle and tubular forms (minor fraction).

Decrease of phosphate(V) ion concentration in a crystallizer feed down to 0.20 mass% caused an increase in mean struvite crystals size by ca. 10 µm. Similarly, excess of magnesium ions in relation to the concentration of phosphate(V) and ammonium ions influenced process results advantageously. The mean size of product crystals increased by 12–17%.

An excess of magnesium ions in a process system influenced the struvite reaction crystallization process yield strongly advantageously. Residual concentration of phosphate(V) ions in a postprocessed mother liquor decreased to 24–30 mg kg$^{-1}$ depending on the process technological parameters combination, which can be regarded as a very good result of their continuous removal from inlet solution.

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