

Precipitation and crystallization of struvite in the presence of iron(III) ions

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Please, cited as: CHEMIK 2010, **64**, 12, 816-823

Introduction

One of the possible ways of recovering phosphates from waste solutions, municipal sewage, industrial wastewater, liquid manure, etc. is by chemical precipitation in the form of soluble salts [1, 2]. The final result of this process—a population of crystals of defined chemical purity and crystal size distribution obtained in a satisfactory yield—depends on many parameters associated with the environment in which the process proceeds, on the values of these parameters, and also on the design of equipment and apparatus [3÷7]. One of the factors that have an effect on the course of the process, and consequently on the quality of the product obtained, is the contamination of the waste solutions, particularly by metal ions, sulphates, nitrates, fluorides, fluorosilicates [2, 4]. These contaminants inhibit or catalyze the precipitation reaction, have an impact on the rate of crystal nucleation and growth, affect crystal shape and possible particle agglomeration [8÷12]. Some metal ions in an alkaline precipitating environment may form sparingly soluble hydroxides or phosphates, which gravely deteriorates the chemical composition of the product and limits the possibilities of its further use [13, 14].

One of the contaminants present in wastewater, e.g. from the wet process of phosphoric acid manufacture [15], are iron ions. Below are the results of experimental studies of the effect of iron(III) ions' presence and concentration on the precipitation and crystallization of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, MAP) in a continuous DT MSMPR (*Draft Tube, Mixed Suspension Mixed Product Removal*) crystallizer with a propeller agitator. The efficiency of the process expressed as the final concentration of PO_4^{3-} in the mother solution was measured, statistical parameters of solution size distribution (CSD) (L_m , L_{50} , CV) were determined, shape and agglomeration of crystals was assessed, and the isolated solid phase was identified. The results of the tests were used to develop a concept of a plant for the recovery of phosphate ions from fertilizer industry wastewater [16, 17].

Experimental setup and procedure

A schematic drawing of the setup for studying the precipitation and crystallization of struvite in the presence of iron(III) ions is shown in Figure 1. Control, monitoring and data logging were done with the use of a computer. IKA labworldsoft software was used to precisely control the operation of the measuring system in the steady state. The working volume of the crystallizer was 0.6 dm^3 .

Points of reagent feeding and crystal suspension collection are indicated in Figure 1. The crystallizer was fed in a continuous manner with a water solution of magnesium chloride MgCl_2 , ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ and iron chloride FeCl_3 . The solution was fed into the circulating tube (mixer revolution number: $6.6 \pm 0.1 \text{ 1/s}$; downward flow of suspension). A 20% wt. aqueous solution of sodium hydroxide NaOH was fed into the space between the crystallizer shell and the tube (upward flow of suspension) in proportions warranting the set controlled value of pH required to precipitate phosphates. All tests were performed at the temperature of 298 K and pH = 9 and with mean residence time of suspension in the

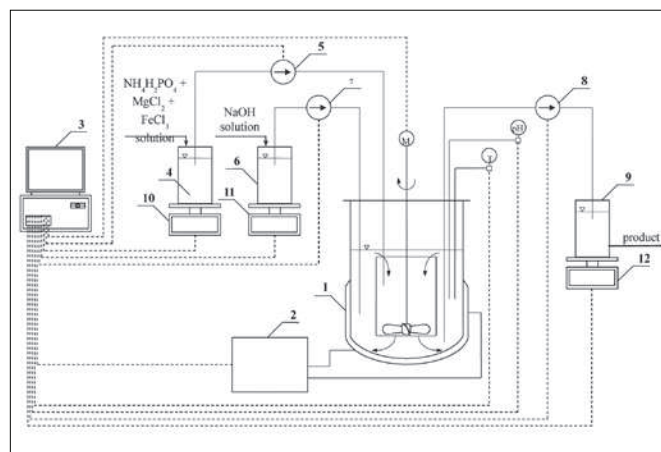


Fig. 1. Scheme of laboratory test stand with a continuous crystallizer with a propeller mixer for reaction crystallization of struvite, 1 – DT type crystallizer with internal circulation of suspension, 2 – thermostat, 3 – computer, 4 – reservoir of a feeding mixture: water solution of $\text{NH}_4\text{H}_2\text{PO}_4$, MgCl_2 and FeCl_3 , 5 – feed proportioner (pump), 6 – alkalinity agent tank: water solution of NaOH , 7 – proportioner of NaOH solution, 8 – receiver (pump) of a product crystal suspension from the crystallizer tank, 9 – storage tank of a product crystal suspension, 10, 11, 12 – balances, M – stirrer speed control, pH – alkaline/acid reaction control, T – temperature control

crystallizer of $\tau = 900 \text{ s}$. The concentration of reagents in the solution fed was constant: 1.0% wt. PO_4^{3-} , 0.256% wt. Mg^{2+} and 0.190% wt. NH_4^+ (molar ratio of reagents 1 : 1 : 1). The concentration of iron(III) ions was varied in the range of 1×10^{-4} to 10×10^{-4} wt. (1 to 10 mg/kg of solution). For selected Fe^{3+} ion concentrations measurements were also made at pH 10 and 11 and $\tau = 1800$ and 3600 s (Table 1). After stabilizing the set parameters in the crystallizer the process was continued in the steady state for the time of 5τ . After that time the following parameters were determined by analytical methods: concentration of solids in the crystal suspension (M_T), struvite crystal size distribution (COULTER LS-230 laser particle size analyzer), chemical composition of mother solution and solid phase (Philips PU 7000 ICP-AES spectrometer, Philips PU 9712 IR spectrometer, etc.) and crystal shape (analysis of images obtained from a JEOL JSM 5800LV scanning electron microscope).

Results and discussion

The results of tests and analyses are presented in Table 1. The table shows that the presence of iron(III) ions in the solution fed to the crystallizer has an adverse effect on the product crystal size distribution. Both statistical parameters of that distribution, L_m and L_{50} , had decreased. The mean crystal size L_m decreased from 35.5 to 26.0 μm (i.e. by ca. 27%), whereas the median value of crystal size L_{50} decreased from 30.9 to 19.4 μm (i.e. by more than 37%) – see Figure 2. Moreover, a ten-fold increase of the concentration of iron(III) ions caused a decrease in the homogeneity of the struvite crystals population. The value of CV, which is a measure of the inhomogeneity of crystal size, increased from 71 to ca. 97%.

Table I
Influence of iron(III) ions concentration and selected parameters of the continuous reaction crystallization process on the size characteristics of struvite product crystals and their chemical purity

Item	Concentration of Fe ³⁺ ions in feed solution, % wt.	pH	τ , s	Characteristics of crystals			Contents Fe (total) in the product mg/kg
				L_m , μm	L_{50} , μm	CV, %	
1	1·10 ⁻⁴	9	900	35,5	30,9	71,1	41
2	2·10 ⁻⁴	9	900	33,9	29,0	73,9	80
3	3·10 ⁻⁴	9	900	29,9	24,0	81,2	123
4	5·10 ⁻⁴	9	900	28,2	23,1	79,1	202
5	10·10 ⁻⁴	9	900	26,0	19,4	96,8	418
6	2·10 ⁻⁴	10	900	25,4	19,6	89,1	82
7	2·10 ⁻⁴	11	900	19,7	13,8	92,0	84
8	5·10 ⁻⁴	10	900	21,4	16,5	86,3	206
9	5·10 ⁻⁴	11	900	20,0	13,9	82,0	206
10	5·10 ⁻⁴	9	1800	37,1	26,6	80,9	200
11	5·10 ⁻⁴	9	3600	43,4	28,9	86,6	205

Crystallization process temperature: 298 K

Concentrations of reagent ions in a feed: 1.0 of PO₄³⁻, 0.256. of Mg²⁺, 0.190 % wt. of NH₄⁺ (stoichiometric conditions)

Average crystal content in suspension: $M_T = 23.6 \pm 0.4$ kg of struvite/m³ of suspension

Concentration of iron(III) ions in mother solution (as total Fe): 0.05 – 0.07 mg/kg

Concentration of phosphate(V) ions in mother solution: 0.011 ± 0.003 % wt.

$L_m = \sum x_i L_i$, where: x_i – mass fraction of the crystals of mean fraction size L_i ; L_{50} – median crystal size for 50 % wt. undersize fraction; $CV = 100(L_{84} - L_{16})/2L_{50}$, where: L – crystal sizes corresponding to 84, 16 and % wt. undersize fraction

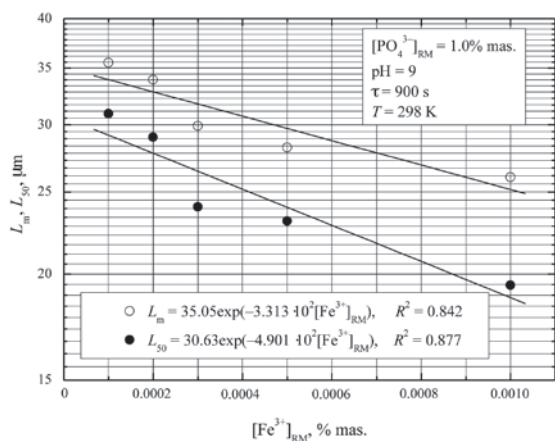


Fig. 2. Influence of iron(III) ions concentration in a feed on mean L_m and median L_{50} product crystal size

Increase of pH of the struvite precipitation and crystallization medium caused a decrease in the product crystal size. An increase of pH from 9 to 11 caused a decrease of the mean crystal size L_m by ca. 42%: from 33.9 to 19.7 μm at an iron(III) ions concentration of 2·10⁻⁴% wt. in the solution fed, and from 28.2 to 20.0 μm at a 2.5-fold higher iron(III) ions concentration. This trend is more evident when the values of the median crystal size L_{50} are compared (Tab. I). Increase of pH in the crystallizer had also an impact on the homogeneity of the product crystals. With pH increase the solubility of struvite decreases, while its precipitation potential increases [2, 4]. The induction time necessary to initiate the nucleation process is also shortened [18]. The effect of all of this is the increase in the

population density of struvite crystal nuclei, the consequence of which is the shift of the mean or median crystal size towards lower values [7].

On the other hand, the extension of the residence time of the suspension in the crystallizer increased the size of product crystals, even by more than 50% (Table I). In the presence of 5·10⁻⁴ % wt. iron(III) ions, the struvite crystals attained an mean size L_m of even more than 43 μm (pH 9, $\tau = 3600$ s). With the extension of the residence time the supersaturation of the solution decreased and in effect the values of both kinetic components of the process decreased: the rate of solid phase nucleation and the linear rate of its growth. However, the extended residence time of crystals in the supersaturated solution makes the final effect more advantageous: crystal growth is slower, but it is more stable and thereby the crystals attain larger sizes. However, the homogeneity of the crystals population decreased slightly (Tab. I), which was caused by increased attrition and breaking of crystals during extended residence time in agitated suspension.

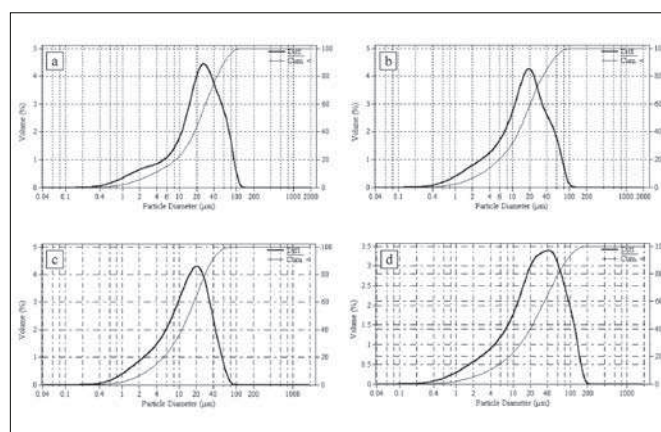


Fig. 3. Exemplary differential (left scale) and cumulative (right scale) volumetric (mass) size distributions of struvite crystals produced in continuous reaction crystallization process in presence of 5·10⁻⁴% wt of iron(III) ions (a, b, c and d – corresponding to No. 4, 8, 9 and 11 in Table I)

Figure 3 shows examples of volumetric (weight) distribution of crystal sizes of product obtained in the crystallizer at pH 9, 10 and 11 for $\tau = 900$ s (Fig. 3, a, b and c, respectively) and at pH 9 for $\tau = 3600$ s (Fig. 3d). The concentration of iron(III) ions in the solution fed was 5·10⁻⁴% wt. For very small crystals (0.4 – 4 μm) of product obtained at pH 9 and $\tau = 900$ s (Fig. 3a) a distinct change is observed in the shape of the differential curve of distribution (local maximum). In this range of crystal sizes there is an overabundance of crystals, which is, as shown by physicochemical analysis (Tab. I), the effect of the presence in the crystals population of other particles than struvite crystals. The presumption is that these are predominantly particles of iron(III) hydroxide (solubility product of Fe(OH)₃ at the temperature of 298K: $K_{sp} = 1.1 \times 10^{-36}$, $pK_{sp} = 35.96$). With rising pH the local maximum in the distribution differential curve becomes less distinct (pH 10, Fig. 3b), and even disappears (pH 11, Fig. 3c). This is associated with the overall increase of the number of the finest struvite crystals in the population of product particles. At pH 11 struvite crystals of less than 4 μm are virtually undistinguishable from iron(III) hydroxide crystals of similar size. In consequence, the prevailing size of crystals (L_d , which corresponds to the maximum of differential distribution) is shifted towards lower values (25.0, 18.5 and 14.3 μm at pH 9, 10 and 11, respectively), while the number and size of the largest crystals in the product decreases. The largest size of struvite crystals obtained is ca. 125 μm at pH 9 (Fig. 3a), ca. 100 μm at pH 10 (Fig. 3b), and only ca. 83 μm at pH 11 (Fig. 3c). The proportion of the smallest particles is increased at the same time. At pH 9 the proportion of crystals smaller than 10 μm was 22.8%,

while at pH 11 this proportion increased to 36.3% that is by ca. 60% (Figs. 3a and c). As a result of this the mean product crystal size decreased significantly from 28.2 to 20.2 μm (Tab. 1). On the other hand, the extension of the mean residence time of the suspension in the crystallizer to 3600 s ($[\text{Fe}^{3+}]_{\text{init.}} = 5 \times 10^{-4}\%$ wt., pH 9) resulted in the increase of the prevailing size L_d of struvite particles to 34.2 μm , and in the increase of the size of the largest crystals in the population to 188 μm . The proportion of the finest particles, however, did not decrease significantly. The content of particles smaller than 10 μm in the product was 22.0% (Fig. 3d). The presumption is that this is because of the overall effect of struvite nucleation, precipitation of iron(III) hydroxide particles and attrition of crystals.

When comparing the data presented here with the results of tests carried out under the same process conditions and in the same crystallizer, but in the presence of iron(II) ions [12], it was established that in the latter case the products obtained were of better quality and were more uniform. The mean size L_m and median size L_{50} of struvite particles were larger by more than 10% on the average. Higher was also the number and size of the largest crystals in the whole population. The presumption is that one of the reasons for these differences may be the higher value of the solubility product of iron(II) hydroxide ($K_{\text{sp}} = 1.8 \times 10^{-14}$, $\text{p}K_{\text{sp}} = 13.74$) than that of iron(III) hydroxide.

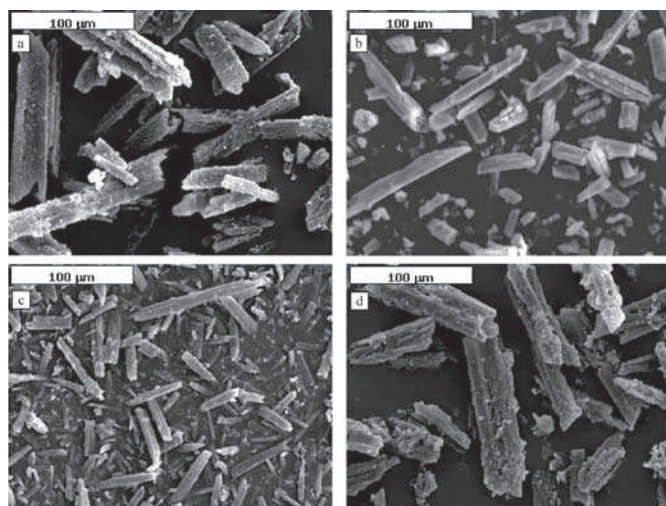


Fig. 4. Scanning electron microscope images of struvite crystals produced in presence of $5 \times 10^{-4}\%$ wt. of iron(III) ions. Process parameters: a) pH 9, b) pH 10 and c) pH 11 (τ 900 s), d) pH 9 (τ 3600 s). Corresponding crystal size distributions are presented in Fig. 3. Magnification: 500x

Figure 4 shows images of the product crystals, the size distributions of which are presented in Figure 3. Smaller struvite crystals formed in the crystallizer at higher pH values are apparent. The crystal habit, however, did not undergo any distinct change. On the basis of surface area measurements of 50 crystals randomly selected from each population obtained, it was found that the ratio of crystal length L_a to crystal width L_b was 4.7 ± 0.3 , irrespective of pH and concentration of iron(III) ions in the solution fed (in the presence of iron(II) ions the ratio L_a/L_b was 5.0 ± 0.2 [12]). On the surface of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals one may note the agglomeration of distinctly smaller particles of iron hydroxide (promoted by the presence of unevenness (roughness) of the crystal surfaces). Iron hydroxide particles are also observed in the whole population of crystals, predominantly in the form of agglomerates. In the case of struvite crystals, agglomeration is less than moderate, particularly with large crystals. It may therefore be said that the process conditions prevailing in the crystallizer were advantageous, in the sense that they prevented excessive bonding and fusion of crystals of the main product component.

Moreover, the images of the product presented here indicate the presence of characteristic tubular crystals within the whole

of the struvite crystal population. According to Seckler *et al.* [19] struvite crystals of this structure occur at pH 7. In the case studied, in the presence of iron(III) ions, tubular crystals were abundant in the product. However, most of them, particularly those larger in size, had distinct fractures parallel to their longitudinal axis and on the surface, as well as distorted terminal parts, which indicated severe stresses occurring within their structure (Fig. 5). Crystals formed in this manner during unrestricted growth are particularly susceptible to shearing forces caused by turbulent flow of the solution, as well as to the phenomena of secondary contact nucleation (strong agitation, high crystal content in the circulating suspension). Struvite crystals of similar characteristic shape were also obtained in the presence of iron(II) ions [12].



Fig. 5. Characteristic tubular-shape crystal forms of struvite produced in the presence of iron(III) ions. Process parameters: $[\text{Fe}^{3+}]_{\text{RM}} = 0.001\%$ wt., pH = 10, $\tau = 900$ s, $T = 298$ K. Magnification: 1500x

Table I shows the concentrations of phosphate ions and iron ions determined analytically in the mother solution, as well as the iron content in the product. It may be stated that the concentration of phosphate ions in the mother solution was at a nearly constant and low level of $0.011 \pm 0.003\%$ wt. On the other hand, the concentration of iron ions (calculated as total Fe concentration) decreased to 0.05–0.07 mg/kg of solution. Therefore, these were precipitated almost completely in the form of iron hydroxide, which appeared in the solid phase in an amount of 41 to 418 mg/kg of product (calculated as iron) depending on the concentration of iron(III) ions in the solution fed to the crystallizer.

Summary and Conclusions

The paper presents the results of tests on continuous phosphate ions removal, using magnesium and ammonium ions from dilute solutions containing iron(III) ions. Tests were carried out under stoichiometric conditions in a DT type crystallizer with suspension circulation effected by means of a propeller agitator. It was found that with increasing concentration of iron ions in the solution fed to the crystallizer, the mean size of product crystals decreased by ca. 27% (from 35.5 to 26.0 μm at pH 9 and $\tau = 900$ s). The homogeneity of the crystals population had also deteriorated. Increased pH had also an adverse effect on quality of the product. Crystals smaller in size ($L_m = 19.7$ μm at pH 11 and $2 \times 10^{-4}\%$ wt. iron ions concentration in solution fed) and less uniform were obtained. On the other hand, the extension of the mean residence time of the suspension in the crystallizer (to 3600 s), equivalent to decreasing the supersaturation of the mother solution, caused increase of the size of product crystals obtained by more than 50%. Precipitation of phosphate ions in the presence of iron(III) ions, leads to formation of not only struvite crystals, but also of iron(III) hydroxide particles. The product

obtained is therefore contaminated, and its utility is reduced as its applicability in agriculture. Moreover, the presence of iron ions promotes the formation of the so-called tubular crystals of struvite. These crystals have fractures along their longitudinal axis and on their surface, and have frayed ends. Removal of mother solution from the inside of such tubular structures during filtration and washing is virtually impossible. Particles of iron hydroxide co-precipitated with struvite crystals were very small in size, even less than 1 μm , and formed agglomerates on the surface of struvite crystals and formed unbound agglomerates. The presence of the latter in the product suspension definitely hindered the separation of phases, extended filtration and cake washing time. The content of iron(III) hydroxide in the product, calculated as Fe, ranged from 41 to 418 mg/kg, depending on the concentration of iron(III) ions in the solution fed. The precipitation of iron ions was virtually complete, as the concentration thereof in the mother solution was less than 0.07 mg/kg. The concentration of phosphate ions in this solution was $0.01 \pm 0.003\%$ wt., meaning that it decreased by ca. 98% in relation to its concentration in the solution fed, which may be regarded as a good result of removal of these ions in the process of continuous reaction crystallization.

Physicochemical analyses of the crystalline phase and the mother solution were carried out at the Institute of Inorganic Chemistry in Gliwice.

This work was financed from the Polish science budget resources for the years 2008 – 2011 and 2009 – 2012 as research projects NN209 010834 and NN209 117437.

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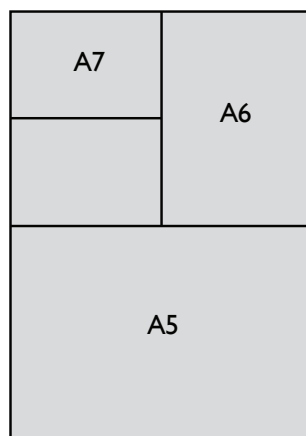
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