

# Application of a continuous FB MSZ type crystallizer with jet pump driven by compressed air for recovery of phosphate(V) ions from mineral fertilizer industry wastewater

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**Abstract:** New original construction of continuous FB MSZ (*Fluidized Bed with Mixed Suspension Zone*) crystallizer with internal circulation of suspension driven by jet pump fed with compressed air was used for continuous reaction crystallization of struvite  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  from phosphorus fertilizers industry wastewater by magnesium and ammonium ions addition. This wastewater of  $\text{pH} < 4$  contained 0.445 mass % of phosphate(V) ions and impurities: aluminium, calcium, copper, iron, potassium, magnesium, titanium, zinc, fluosilicate, fluoride and sulphate(VI) ions. Tests were carried out in 298 K, in stoichiometric conditions and at 20% excess of magnesium ions. Crystals of mean size. 27 – 43  $\mu\text{m}$  were produced. Struvite crystals of the largest sizes and acceptable homogeneity were produced at 20% excess of magnesium ions, at  $\text{pH} 9$  and elongated mean residence time of suspension 3600 s. Corresponding crystal linear growth rate was  $8.52 \cdot 10^{-9}$  m/s according to SIG MSMR (*Size Independent Growth, Mixed Suspension Mixed Product Removal*) kinetic model. Concentration of phosphate(V) ions decreased from 0.445 mass % in a feed to  $9.3 \cdot 10^{-4}$  mass % in a postprocessed mother solution. In a product, besides main crystalline component – struvite, also all impurities from wastewater appeared in a form of hydroxides, phosphates(V) and other salts.

**Key words:** Struvite, FB MSZ crystallizer, industrial wastewater, continuous reaction crystallization, product quality, kinetics, phosphorus recycling.

## Introduction

In most DTM (*Draft Tube Magma*) type crystallizers internal circulation of suspension is an effect of stirrer or pump action (Mullin, 1993). These can be, however, alternatively replaced by liquid jet pump devices (Synowiec, 2008). In typical constructions of liquid jet pump crystallizers (Matynia, 1997) driving agent is a possible fines-free mother solution collected from the crystallizer overflow and then redirected through the external circulation pump back into the feeding nozzle of a jet pump device. It is possible, however, to replace the circulating mother solution with the air (Matynia, 2009). Compressed air (or other gaseous medium) provided into feeding nozzle of a jet pump device becomes under these conditions working medium driving the internal circulation and mixing of suspension in the apparatus working volume. Troublesome in operating and control elements like crystallizer overflow and external circulation loop with the pump become thus unnecessary.

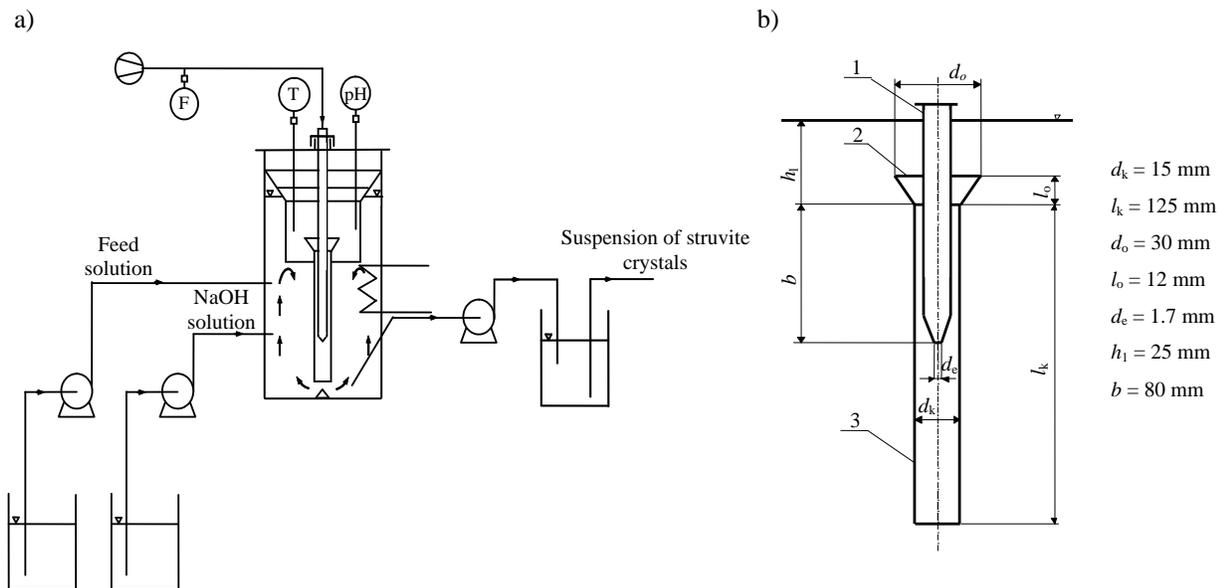
Laboratory research stand with a continuous FB MSZ (*Fluidized Bed with Mixed Suspension Zone*) type crystallizer were designed and constructed. This stand is especially destined for the tests concerning effectiveness, kinetics and optimisation of continuous reaction crystallization processes of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP) from diluted aqueous solutions, wastewaters, liquid manure, etc. containing phosphate(V) ions (Parsons, 2001; Doyle, 2002). Chemical recovery of phosphates(V) from various waste solutions can be numbered among phosphorus recycling (Le Corre, 2009), and resulting products – sparingly soluble crystalline calcium or magnesium salts – can be practically utilized as a mineral fertilizer (de-Bashan, 2004).

The FB MSZ type crystallizer of working volume  $V_w$  1.2  $\text{dm}^3$  with jet pump fed with compressed air was used. Feeding nozzle of a jet pump was installed inside mixing chamber where compressed air flow was directed downward. In a space between the jet pump mixing chamber and crystallizer body pseudofluidal layer of struvite crystals

self-established. The crystallizer was used for struvite continuous reaction crystallization process using real wastewater from phosphorus mineral fertilizers industry (leachate from phosphogypsum slag heap in Z. Ch. POLICE S.A., Poland, containing 0.445 mass % of  $\text{PO}_4^{3-}$ ). It was continuously provided with feed solution (wastewater and reagents premixed) of the assumed molar ratio  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}}$  as 1 : 1 : 1 or 1 : 1.2 : 1. Process ran in a constant temperature 298 K. Influence of pH (8.5 – 10) and mean residence time of suspension in a crystallizer  $\tau$  (900 – 3600 s) on the product crystals quality was identified. Fundamental process kinetic parameter values were estimated from the product crystal size distributions. The most simplified model of mass crystallization process kinetics in a continuous MSMPR (*Mixed Suspension, Mixed Product Removal*) crystallizer – SIG (*Size Independent Growth*) – was used for the calculations. Characteristics of crystalline products and kinetic calculation results are presented and discussed below.

### Materials and Method

Scheme of the research stand is presented in Figure 1a. The FB MSZ crystallizer with jet pump driven by compressed air was cylindrical tank of diameter  $D$  90 mm and total height  $H_t$  330 mm, made with *Plexiglas*.



**Figure 1:** Scheme of laboratory stand with a continuous FB MSZ crystallizer with a gas-liquid jet pump: working volume of crystallizer  $V_w$  1.2 dm<sup>3</sup>, crystallizer’s geometrical parameters:  $D$  90 mm,  $H_t$  330 mm,  $H_w$  220 mm (a). Jet pump element in a FB MSZ crystallizer: 1 – feeding nozzle; 2 – confusor; 3 – mixing chamber (b).

Inside the crystallizer body gas-liquid jet pump was installed, presented schematically in Figure 1b. Feeding nozzle of a jet pump was provided with experimentally adjusted, minimal volumetric stream of the compressed air,  $q_{ve}$  0.43 dm<sup>3</sup>/s, indispensable only to keep all solid particles in a permanent movement. Resulting intensity of suspension circulation was thus also minimal. Geometrical proportions within a jet pump system are presented in Figure 1b. Owing to relatively small unit power of a feeding gaseous stream, relatively large struvite crystal density ( $\rho$  1710 kg/m<sup>3</sup>) and specific flow hydraulic conditions, the phenomenon of crystal suspension sucking into the mixing chamber space is not observed in a crystallizer. In such defined process conditions the pseudofluidal layer of crystals forms in a space between mixing chamber and crystallizer body.

The raw materials in a continuous struvite reaction crystallization process were: crystalline magnesium chloride hexahydrate  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and crystalline ammonium chloride  $\text{NH}_4\text{Cl}$  (p.a., POCh, Gliwice, Poland), as well as wastewater from phosphorus mineral fertilizers industry (Z.Ch. POLICE S.A., Poland) of pH 3.8 and detailed

composition presented in Table 1. The reagents (wastewater,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$ ) were first introduced into the mixer, in which the struvite precipitation reaction substrates dosed in a crystalline form dissolved. Mass stream values of these reagents resulted from the assumed molar ratio  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}}$ , assumed mean residence time  $\tau$  of suspension in a crystallizer working volume and from working volume  $V_w$  of the crystallizer used. Clear solution of blended and totally dissolved reagents, of pH 3.6 (stoichiometric proportions of the reagents) or 3.5 (20% excess of magnesium ions), was introduced via pump into the crystallizer working volume. Crystallizer was also provided with aqueous solution of NaOH of concentration 5 mass %, responsible for stabilization of the required pH in struvite continuous reaction crystallization environment. Inlet places of reagents and alkalinizing solution, as well as crystalline product suspension removal port are marked in Figure 1a. Temperature and inflow/outflow streams were strictly controlled and adjusted by computer system (BioScadaLab program).

**Table 1:** Chemical composition of phosphorus mineral fertilizers industry wastewater.

Component	Concentration, mass %
$\text{PO}_4^{3-}$	0.445
Al	$6.4 \cdot 10^{-4}$
Ca	0.044
Cu	$0.25 \cdot 10^{-4}$
Fe	$8.9 \cdot 10^{-4}$
K	$4.6 \cdot 10^{-3}$
Mg	0.0306
Si	$5.1 \cdot 10^{-3}$
Ti	$0.2 \cdot 10^{-4}$
Zn	$2.2 \cdot 10^{-4}$
$\text{F}^-$	$4.2 \cdot 10^{-3}$
$\text{SO}_4^{2-}$	0.0703

The research tests ran in temperature  $298 \pm 0.2$  K assuming pH 8.5, 9 or 10 ( $\pm 0.1$ ) and mean residence time of suspension in a crystallizer  $\tau$  900, 1800 or 3600 s ( $\pm 20$  s). The reagent concentrations in a feed solution were:  $[\text{PO}_4^{3-}]_{\text{RM}} = 0.445$  mass %,  $[\text{Mg}^{2+}]_{\text{RM}} = 0.114$  mass % and  $[\text{NH}_4^+]_{\text{RM}} = 0.0844$  mass % securing their molar ratio 1 : 1 : 1 or 0.445, 0.137 and 0.0844 for 20% excess of magnesium ions, appropriately. After stabilisation in a crystallizer the predetermined parameter values, process in a steady state ran through  $5\tau$ . After this time there were determined using standard analytical methods: concentration of solid phase in a crystal product suspension ( $M_T$ ), chemical composition of mother solution and solid phase (among others: atomic absorption spectrometer iCE 3000, spectrophotometer UV-VIS Evolution 300), struvite crystal size distribution (solid particle analyser Beckman Coulter LS 13 320) and their habit (computer analysis of scanning electron microscope JEOL JSM 5800LV images). Accuracy of measurement data concerning continuous struvite reaction crystallization process in the described laboratory plant was estimated to be ca. 10%.

Kinetic parameter values of the process were estimated based on the population density distributions  $n(L)$  of the product crystals (Mullin, 1993). The most simplified kinetic model valid for continuous MSMMPR crystallizer, SIG kinetic model (Randolph and Larson, 1988), was assumed for the calculations. Equation of crystal population density distribution resulting from the assumed SIG kinetic model is in a form of Eq. (1):

$$n(L) = n_0 \exp\left(-\frac{L}{G\tau}\right) \quad (1)$$

from which for  $L = 0$  one can determine the nuclei population density  $n_0$  value and, from the slope in  $\ln n - L$  coordinate system, linear crystal growth rate  $G$  for the known mean residence time  $\tau$  of suspension in a crystallizer. Nucleation rate  $B$  can be calculated from Eq. (2):

$$B = n_0 G \quad (2)$$

## Results and Discussion

From FB MSZ crystallizer properly shaped product crystals were removed. Statistical parameter values of size distribution of these crystals are presented in Table 2. From the table it results (tests No. 1, 2 and 3 in Table 2), that increase in pH of mother solution in a crystallizer from 8.5 to 10 resulted in decrease of crystal mean size  $L_m$  from 37.2 to 26.7  $\mu\text{m}$  (by ca. 28%). The CV coefficient increased from 90.1 up to 99.3%. Crystal products manufactured under pH 10 characterised thus by not only smaller particle sizes, but also their higher variability. With the pH value increase nuclei population density also increases (see Table 4), what produces shifts in characteristic sizes of struvite crystals:  $L_m$ ,  $L_{50}$  and  $L_d$  towards smaller values. Elongation of mean residence time of suspension in a crystallizer caused, however, increase in mean sizes of product crystals, by ca. 18%. Struvite crystals reached mean size  $L_m$  41.8  $\mu\text{m}$  for mean residence time  $\tau$  3600 s and pH 9. With the mean residence time elongation average supersaturation in solution decreased, producing as a result decrease of both kinetic components of the process: nucleation rate of solid phase and their linear growth rate values (see Table 4).

**Table 2:** Influence of selected technological parameters of continuous struvite reaction crystallization process from phosphorus mineral fertilizers industry wastewater in FB MSZ crystallizer on the product quality. Process temperature: 298 K.

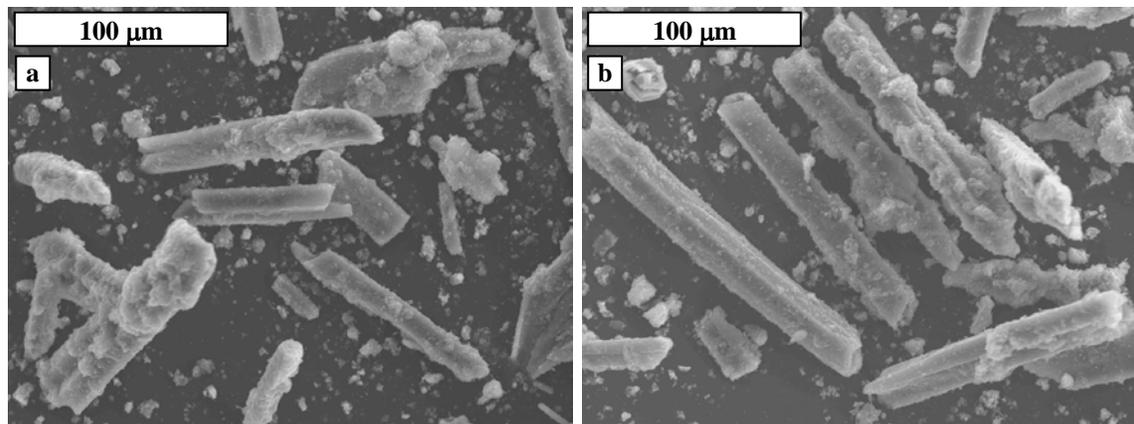
No.	Process parameters		Suspension in crystallizer			Crystal characteristic				
	pH	$\tau$	$M_T$	$[\text{PO}_4^{3-}]_{\text{solution}}$	$[\text{PO}_4^{3-}]_{\text{crystals}}$	$L_m$	$L_{50}$	$L_d$	CV	$L_a/L_b$
	–	s	kg crystals/m <sup>3</sup>	mg/kg	mass %	$\mu\text{m}$	$\mu\text{m}$	$\mu\text{m}$	%	–
Molar proportions of reagent ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$										
1	8.5	900	10.9	63.0	39.2	37.2	25.3	29.6	90.1	5.2
2	9	900	11.0	45.0	39.3	35.5	24.6	28.9	92.6	5.0
3	10	900	11.0	37.6	40.2	26.7	22.6	24.5	99.3	4.7
4	9	1800	11.1	31.8	40.1	41.7	30.3	36.1	92.6	5.1
5	9	3600	11.2	22.0	42.0	41.8	31.1	36.8	90.9	5.2
Molar proportions of reagent ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$										
6	9	900	11.3	18.6	39.2	37.9	26.6	30.1	93.9	5.2
7	9	3600	11.4	9.3	42.1	43.2	33.3	37.2	92.1	5.3

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

Longer residence time of crystal population in supersaturated solution caused, however, that their sizes increased significantly. In solution of lower average supersaturation crystals grew slower, however more stable. Longer contact time of crystal phase with supersaturated mother solution influenced also struvite final crystal size distribution advantageously. Homogeneity within product crystal population increased slightly. The CV value decreased from 92.6 to 90.9%, in spite of increase in intensity of co-running processes of attrition and breakage of crystals with the elongation of their residence time in a mixed and circulated suspension.

Excess of magnesium ions in relation to phosphate(V) and ammonium ions concentrations in a crystallizer feed resulted in increase in mean size  $L_m$  of product crystals: from 35.5 to 37.9  $\mu\text{m}$  (pH 9,  $\tau$  900 s), as well as from 41.8 to 43.2  $\mu\text{m}$  (pH 9,  $\tau$  3600 s) (tests No. 2 and 6, 5 and 7 in Table 2, respectively). Crystal population homogeneity decreased slightly since the CV values increased from 92.6 to 93.9% and from 90.9 to 92.1%, respectively. In pure aqueous solutions of phosphate(V) ions excess of magnesium ions influences final sizes of struvite crystals

disadvantageously (Kozik, 2012). Presence of impurities in a process system (Table 1) resulted, however, that final result of continuous struvite reaction crystallization process was more advantageous (Table 2). Some of ionic impurities inhibit struvite nucleation, other can catalyse nuclei or crystals growth, while some other can significantly affect their shape and habit (Hutnik, 2011; Hutnik, 2012).



**Figure 2:** Scanning electron microscope images of struvite crystals produced from phosphorus mineral fertilizers industry wastewater in a continuous FB MSZ type crystallizer. Process parameters:  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$  in a feed, pH 9,  $\tau$  900 s (a) and  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$  in a feed, pH 9,  $\tau$  3600 s (b). Magnification: 500 $\times$ .

In Figure 2 there are presented the scanning electron microscope images of exemplary product crystals. Diverse sizes of struvite crystals are clearly observable. Also other solid particles, co-precipitated from a complex wastewater system in the process conditions, are visible. The most often they form agglomerates on the struvite parent crystals surfaces. Struvite crystals are just stuck the co-precipitated hydroxides of metal impurities, hydroxyapatite and other salts around. Excess of magnesium ions favoured not only production of struvite crystals of larger sizes (Figure 2b), but also efficiency of phosphate(V) ions removal from wastewater. Concentration of phosphate(V) ions in a postprocessed mother solution  $[\text{PO}_4^{3-}]_{\text{solution}}$  decreased from 45.0 to 18.6 mg/kg (pH 9,  $\tau$  900 s) and from 22.0 to 9.3 mg/kg (pH 9,  $\tau$  3600 s) (see Table 2). The best-formed struvite crystals were produced at low pH value (8.5 – 9), elongated mean residence time  $\tau$  (3600 s) and at 20% excess of magnesium ions in a feed solution. In the process conditions tested, crystal length  $L_a$  to their width  $L_b$  ratio varied from 4.7 to 5.3 (Table 2). The  $L_a/L_b$  simplex values were calculated from planimetric measurements covering 50 crystals randomly selected from three different scanning electron microscope images of the same product sample. Based on microscope images analysis one can conclude, that struvite crystals surface was taken up by solid particles of impurity hydroxides and salts co-precipitated with struvite, what produced generation of significant tensions in parent struvite crystals structures. In result numerous crystal fractures and cracks, irregular surfaces, deformed edges, presence of characteristic tubular and trough-shaped crystals, etc. are observed (Figure 2). Product crystals habit distinctly deviated from the classical shape of struvite crystals produced from pure solutions of phosphates(V) ( $L_a/L_b$  ca. 6) or manufactured in the presence of single impurities (Hutnik, 2011; Hutnik, 2012). One can assume, that struvite crystal sizes and shapes are the resulting net effect of impurities presence in the investigated wastewater system and parameters of struvite continuous reaction crystallization process. From the microscope images it also results, that agglomeration within the struvite crystals was not significant, while attrition and breakage of crystal phase during their mixing and circulation in a crystallizer can be regarded moderate. Generally it speaks advantageously about process conditions established in a crystallizer working volume for struvite nucleation and its crystals growth. Original construction of FB MSZ crystallizer (lack of moving/rotating parts and elements), its work mode (formation of pseudofluidal crystal layer) and relatively low concentration of solid phase in suspension ( $M_T$  ca. 11 kg of struvite/m<sup>3</sup> of suspension) did not contribute to excessive attrition and breakage within crystal phase. Considering, however, all components of a complex process of continuous struvite reaction crystallization process in a FB MSZ crystallizer one can conclude, that main factor influencing the process course is solution supersaturation, very strongly dependent (assuming constant: feed solution composition,

process temperature and mixing/circulation intensity) on process environment's pH and mean residence time of suspension in a crystallizer working volume.

**Table 3:** Chemical compositions of solid phase and mother solution after filtration of crystal suspension removed from continuous FB MSZ crystallizer (see Table 2).

Component	Concentration in mother solution mg/kg	Concentration in solid phase* mass %
PO <sub>4</sub> <sup>3-</sup>	9.3 – 63.0**	39.2 – 42.1**
Mg <sup>2+</sup>	30 – 240	9 – 10
NH <sub>4</sub> <sup>+</sup>	75 – 115	6.5 – 7.0
Al	0.1 – 0.3	(4.8 – 5.5)·10 <sup>-2</sup>
Ca	< 50	2.5 – 4.0
Cu	0.02 – 0.10	(0.6 – 1.3)·10 <sup>-4</sup>
Fe	0.03 – 0.07	0.10 – 0.20
K	25 – 39	0.12 – 0.22
Si	25 – 42	(8.6 – 9.7)·10 <sup>-2</sup>
Ti	< 0.2	< 2·10 <sup>-5</sup>
Zn	< 0.5	(1.6 – 1.9)·10 <sup>-2</sup>
F <sup>-</sup>	2 – 24	0.35 – 0.48
SO <sub>4</sub> <sup>2-</sup>	400 – 560	1.5 – 1.8

\* after drying, without water washing of crystals on a filter

\*\* see Table 2

In Table 3 there are presented the components concentration ranges identified in the postprocessed mother solution and in solid phase (without water washing of crystals on a filter and after their drying) removed from FB MSZ crystallizer (see Table 2). Crystalline product, as it results from Table 3, besides main component MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O, contained also all impurities present in wastewater, among others: phosphates(V) and metal hydroxides, fluosilicates, fluorides and sulphates. From these data analysis it results, that at magnesium ions excess practically total precipitation of aluminium, calcium, copper, iron and zinc ions is observed (compare these ions concentrations in raw wastewater (Table 1) and in postprocessed mother solution (Table 3)). One can also notice, that phosphate(V) ions concentration in a postprocessed mother solution varied from 63.0 (pH 8.5, τ 900 s) to 22.0 mg/kg (pH 9, τ 3600 s) (tests No 1 – 5 in Table 2). These concentration values decreased systematically with the pH raise and with elongation of mean residence time τ of struvite crystals suspension in a crystallizer. From the comparison it results, that phosphate(V) ions concentration decreased even 3-time. It is attributed to struvite solubility decrease with the increase in pH of reactive mixture or longer contact time of crystals with the supersaturated solution in a crystallizer (more thorough discharge of the generated supersaturation). The [PO<sub>4</sub><sup>3-</sup>]<sub>solution</sub> values can be regarded small, thus efficiency of phosphate(V) ions removal from feed solution (above 98%) as a fully satisfactory.

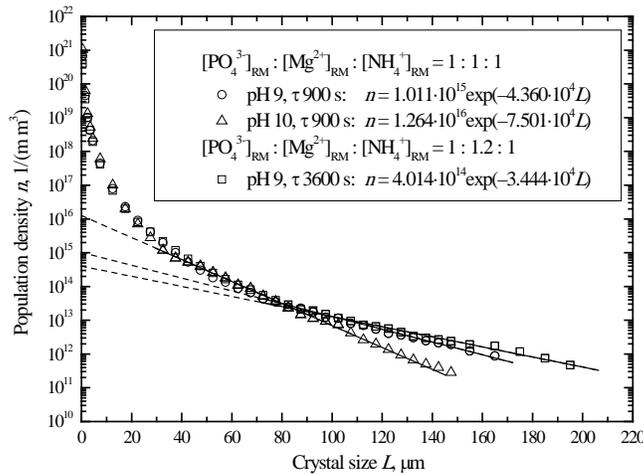
Excess of magnesium ions with relation to concentration of phosphate(V) and ammonium ions influenced the process yield advantageously. Concentration of phosphate(V) ions in a postprocessed mother solution was ca. 2-time smaller than in stoichiometric conditions (see tests No 6 and 7 in Table 2).

In Figure 3 there are presented the exemplary experimental population density distributions of crystals produced at pH 9 and 10 for mean residence time of suspension in a crystallizer 900 s (stoichiometric conditions) and at pH 9, τ 3600 s (20% excess of magnesium ions). From these distribution courses, presented in  $\ln n - L$  coordinate system it results, that for particles of sizes  $L > 70 \mu\text{m}$  (pH 8.5 and 9) or  $L > 30 \mu\text{m}$  (pH 10) these dependencies can be, with satisfactory precision, approximated with linear function. From Eq. (1) one can calculate linear crystals growth rate  $G$  value, and from Eq. (2) their nucleation rate  $B$ .

**Table 4:** Nucleation rate  $B$  and crystal linear growth rate  $G$  values estimated for continuous struvite reaction crystallization process in a FB MSZ crystallizer. Kinetic parameters calculated with SIG MSMPR model. Process conditions – see Table 2.

No. (see Table 2 for details)	Process kinetic parameter values (SIG MSMPR model)				
	$n(L)^*$	$R^2$ (for linear segment)	$n_0$ 1/(m m <sup>3</sup> )	$G$ m/s	$B$ 1/(s m <sup>3</sup> )
Molar proportions of reagent ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$					
1	$n = 7.783 \cdot 10^{14} \exp(-4.098 \cdot 10^4 L)$	0.983	$7.8 \cdot 10^{14}$	$2.71 \cdot 10^{-8}$	$2.1 \cdot 10^7$
2	$n = 1.011 \cdot 10^{15} \exp(-4.360 \cdot 10^4 L)$	0.993	$1.0 \cdot 10^{15}$	$2.55 \cdot 10^{-8}$	$2.6 \cdot 10^7$
3	$n = 1.264 \cdot 10^{16} \exp(-7.501 \cdot 10^4 L)$	0.995	$1.3 \cdot 10^{16}$	$1.48 \cdot 10^{-8}$	$1.9 \cdot 10^8$
4	$n = 4.075 \cdot 10^{14} \exp(-3.453 \cdot 10^4 L)$	0.989	$4.1 \cdot 10^{14}$	$1.61 \cdot 10^{-8}$	$6.6 \cdot 10^6$
5	$n = 4.014 \cdot 10^{14} \exp(-3.444 \cdot 10^4 L)$	0.987	$4.0 \cdot 10^{14}$	$8.06 \cdot 10^{-9}$	$3.2 \cdot 10^6$
Molar proportions of reagent ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$					
6	$n = 6.682 \cdot 10^{14} \exp(-4.134 \cdot 10^4 L)$	0.987	$6.7 \cdot 10^{14}$	$2.69 \cdot 10^{-8}$	$1.8 \cdot 10^7$
7	$n = 3.610 \cdot 10^{14} \exp(-3.261 \cdot 10^4 L)$	0.991	$3.6 \cdot 10^{14}$	$8.52 \cdot 10^{-9}$	$3.1 \cdot 10^6$

<sup>\*</sup>) for  $L > 70 \mu\text{m}$  (pH 8.5 and 9),  $L > 30 \mu\text{m}$  (pH 10)



**Figure 3:** Exemplary population density distributions of crystals produced in a FB MSZ type crystallizer fed with a phosphorus mineral fertilizers industry wastewater assuming stoichiometric ratio between the main reagents and at 20% excess of magnesium ions. The points – experimental data, solid lines – values calculated with Eq. (1) (see Table 4) for crystals of sizes  $L > 70 \mu\text{m}$  (pH 8.5 and 9) and  $L > 30 \mu\text{m}$  (pH 10), dashed lines – linear extrapolations of SIG model to  $L = 0$ .

Determined parameters of population density distribution function  $n(L)$  (Eq. (1)) for struvite product crystals and calculated on this basis  $G$  and  $B$  values are presented in Table 4. Nonlinearity in population density distribution courses for the crystals of size  $L$  smaller than 30 or 70  $\mu\text{m}$  (in a  $\ln n - L$  coordinate system, Figure 3) points on more complex process kinetics than it results from the assumed “linear” SIG MSMPR model. Thus the presented kinetic parameter values of the investigated process should be regarded only as the estimated ones. It especially concerns nucleation rate value  $B$  calculated with Eq. (2), with the use of strongly devaluated values of nuclei population density

$n_0$  ( $n(L)$  for  $L = 0$ ). As it results from Figure 3, the differences between  $n_0$  values predicted by extrapolation with linear SIG MSMPR kinetic model and real population density values for the smallest crystals are in the order of  $10^5$ . Calculated values of nucleation rate  $B$  are thus useful only for relative, conventional comparison of the investigated process parameter effects on its course and final results.

Analyzing the kinetic data presented in Table 4, one can notice regular decrease of struvite crystal linear growth rate  $G$  with the increase in process environment pH and with elongation of mean residence time of suspension in a crystallizer. Generally higher crystal growth rate values are observed for the shortest mean residence times in apparatus, what is in accordance with the observations concerning classical continuous mass crystallization processes. Exemplary, increase in pH of process environment in a crystallizer from 8.5 to 10 for  $\tau$  900 s results in decrease of linear growth rate of struvite crystals from  $2.71 \cdot 10^{-8}$  to  $1.48 \cdot 10^{-8}$  m/s. It is large decrement of  $G$  value (by ca. 45%). It is additionally accompanied by significant increase in nuclei population density  $n_0$  value, thus nucleation rate  $B$  (from  $2.1 \cdot 10^7$  to  $1.9 \cdot 10^8$  1/(s m<sup>3</sup>)). In result final crystal mean size  $L_m$  decreased ( $37.2 \rightarrow 26.7$   $\mu$ m). Elongation of mean residence time of suspension in a crystallizer limited struvite nucleation rate  $B$  (from  $2.6 \cdot 10^7$  to  $3.2 \cdot 10^6$  1/(s m<sup>3</sup>) for  $\tau$  900  $\rightarrow$  3600 s, pH 9). Linear crystal growth rate also decreased ( $G$   $2.55 \cdot 10^{-8} \rightarrow 8.06 \cdot 10^{-9}$  m/s), however longer contact time with supersaturated mother solution caused, as it was mentioned earlier, increase in mean struvite crystal size.

Excess of magnesium ions in a feed mixture caused advantageous changes in kinetic parameters of struvite continuous reaction crystallization process: decrease of nucleation rate and increase in linear crystal growth rate (compare: No. 2 and 6, as well as No. 5 and 7 in Table 4). Net effect of all partial interactions within the analysed process turned out to be advantageous for manufacturing the product crystals of larger sizes.

## Conclusions

The research tests of struvite continuous reaction crystallization from phosphorus mineral fertilizers industry wastewater in a FB MSZ type crystallizer with internal circulation of suspension driven by jet pump fed with compressed air were carried out. Test results can be regarded satisfactory and advantageous. The FB MSZ crystallizer worked stable in a continuous work mode. Its original construction (absence of moving or rotating elements) and its work mode (formation of pseudofluidal crystals layer) did not arrange excessive attrition and breakage effects within the crystal phase. It was concluded, that the product crystals homogeneity was significantly influenced by technological process parameters (pH, mean residence time of suspension in a crystallizer, excess of magnesium ions in relation to phosphate(V) and ammonium ions in a feed), as well as intrinsic chemical composition of wastewater.

From FB MSZ crystallizer properly shaped struvite crystals of mean size  $L_m$  from ca. 27 to ca. 43  $\mu$ m were removed. It was experimentally proved, that increase in pH value (from 8.5 to 10) caused decrease of mean crystal size (by ca. 28%,  $L_m$   $37.2 \rightarrow 26.7$   $\mu$ m,  $\tau$  900 s). Contrary, elongation of mean residence time of suspension in a crystallizer from 900 to 3600 s produced significant increase in this size (by ca. 18%,  $L_m$  41.8  $\mu$ m at pH 9 and  $\tau$  3600 s). Products of low size homogeneity (CV  $\sim$  90 – 100%) were removed from the crystallizer. It is a net effect of a complex influence of pH and mean residence time of suspension, as well as crystals attrition and breakage on supersaturation level in mother solution.

For the process kinetic parameters estimation the simplest kinetic model developed for ideal MSMPR crystallizer was applied. It was concluded, that linear crystal growth rate values of struvite varied within the  $8.06 \cdot 10^{-9} - 2.71 \cdot 10^{-8}$  m/s range, while nucleation rate within the  $3.2 \cdot 10^6 - 1.9 \cdot 10^8$  1/(sm<sup>3</sup>) range. With the elongation of mean residence time of suspension both kinetic parameter values decreased. With the pH rise nucleation rate increased while simultaneously linear growth rate decreased. Reduction of both kinetic parameter,  $B$  and  $G$ , values with the elongation of mean residence time was correlated with increase in mean size  $L_m$  of product crystals. Lower values of linear growth rate are thus compensated with excess by longer contact time of crystals with supersaturated mother solution. Simultaneously decreasing nucleation rate values also advantageously affected the process of crystal phase growth and self-establishing in these conditions size distribution of the product suspension.

Excess of magnesium ions in a process system definitely advantageously influenced the struvite continuous reaction crystallization process yield. Concentration of phosphate(V) ions decreased from 0.445 mass % in a feed to  $9.3 \cdot 10^{-4}$  mass % in a postprocessed mother solution, what can be regarded as a very good result of their removal process from inlet solution. It was accompanied by rise of mean size of product crystals ( $L_m$  up to 43.2  $\mu$ m), crystal linear growth rate ( $G$  up to  $8.52 \cdot 10^{-9}$  m/s) and nucleation rate decrease ( $B$  to  $3.1 \cdot 10^6$  1/(sm<sup>3</sup>)).

In crystal product, besides main component – struvite, all impurities originally present in wastewater appeared in a form of hydroxides, phosphates(V) and other salts. Aluminium, copper, iron and zinc ions practically totally co-precipitated with struvite. Direct application of such crystalline mixture in agriculture is limited, however part of these impurities can be regarded as the soil enriching components (nutrients).

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