Phosphates (V) recovery from phosphorus mineral fertilizers industry wastewater by continuous struvite reaction crystallization process

Nina Hutnik [a], Anna Kozik [a], Agata Mazienczuk [a], Krzysztof Piotrowski [b,*], Boguslawa Wierzbowska [a], Andrzej Matynia [a]

[a] Wroclaw University of Technology, Faculty of Chemistry, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
[b] Silesian University of Technology, Department of Chemical & Process Engineering, ks. M. Strzody 7, 44-101 Gliwice, Poland

ARTICLE INFO

ABSTRACT

Continuous DT MSMPR (*Draft Tube Mixed Suspension Mixed Product Removal*) crystallizer was provided with typical wastewater from phosphorus mineral fertilizers industry (pH < 4, 0.445 mass % of PO_4^{3-}, inorganic impurities presence), dissolved substrates (magnesium and ammonium chlorides) and solution alkalising the environment of struvite $MgNH_4PO_4 \cdot 6H_2O$ reaction crystallization process. Research ran in constant temperature 298 K assuming stoichiometric proportions of substrates or 20% excess of magnesium ions. Influence of pH (8.5–10) and mean residence time (900–3600 s) on product size distribution, its chemical composition, crystals shape, size–homogeneity and process kinetics was identified. Crystals of mean size ca. 25–37 μm and homogeneity CV 70–83% were produced. The largest crystals, of acceptable homogeneity, were produced using 20% excess of magnesium ions, pH 9 and mean residence time 3600 s. Under these conditions nucleation rate did not exceed 9×10^7 1/(s m^3) according to SIG (*Size Independent Growth*) MSMPR kinetic model. Linear crystal growth rate was 4.27×10^{-9} m/s. Excess of magnesium ions influenced struvite reaction crystallization process yield advantageously. Concentration of phosphate(V) ions decreased from 0.445 to 9.2×10^{-4} mass %. This can be regarded as a very good process result. In product crystals, besides main component – struvite, all impurities from wastewater were detected analytically.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Recovery of phosphate(V) ions from postprocessed liquors, wastewaters or liquid manure may be based on precipitation followed by mass crystallization of sparingly soluble phosphate(V) salts. The most frequent it is magnesium ammonium phosphate(V) hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$ (MAP, struvite –

solubility product pK_{sp} = 9.4–13.26) (Le Corre et al., 2009). Struvite precipitates after contacting magnesium ions (e.g. magnesium chloride) and ammonium ions (e.g. ammonium chloride) with the solution containing phosphate(V) ions, after its alkalization (7 < pH < 11) (Parsons, 2001). Increase in pH produces decrease of struvite solubility (minimum K_{sp} value corresponds to pH 10.3 (Ohlinger et al., 1998) or 10.7 (Snoeyink

* Corresponding author. Tel.: +48 32 237 1900; fax: +48 32 237 1461.
E-mail addresses: nina.hutnik@pwr.wroc.pl (N. Hutnik), anna.kozik@pwr.wroc.pl (A. Kozik), agata.mazienczuk@pwr.wroc.pl (A. Mazienczuk), krzysztof.piotrowski@polsl.pl (K. Piotrowski), boguslawa.wierzbowska@pwr.wroc.pl (B. Wierzbowska), andrzej.matynia@pwr.wroc.pl (A. Matynia).

Nomenclature

B	nucleation rate, 1/(s m^3)
d_{dt}	draft tube diameter, m
d_m	stirrer diameter, m
D	crystallizer diameter, m
G	crystal linear growth rate, m/s
h_{dt}	draft tube height, m
H	crystallizer height, m
K_{sp}	solubility product
L	crystal characteristic size, m
L_a	crystal length, m
L_b	crystal width, m
L_d	dominant (mode) crystal size, m
L_m	mean crystal size, m
L_{50}	median crystal size, m
M_T	solid phase content in a product crystal suspension, kg crystals/m^3
$[Mg^{2+}]_{RM}$	concentration of magnesium ions in a feed, mass %
n	population density, 1/(m m^3)
n_0	nuclei population density, 1/(m m^3)
$[NH_4^+]_{RM}$	concentration of ammonium ions in a feed, mass %
$[PO_4^{3-}]_{crystals}$	concentration of phosphates(V) in a crystal phase, mass %
$[PO_4^{3-}]_{RM}$	concentration of phosphates(V) in a feed, mass %
$[PO_4^{3-}]_{solution}$	concentration of phosphates(V) in mother solution, mg/kg
V_t	total volume of the crystallizer, m^3
V_w	working volume of the crystallizer, m^3
τ	mean residence time of suspension in a crystallizer working volume, s
CV	coefficient of crystal size variation, %
DT	Draft Tube
MAP	Magnesium Ammonium Phosphate(V) hexahydrate (struvite)
MSMPR	Mixed Suspension Mixed Product Removal crystallizer
SIG	Size Independent Growth kinetic model

and Jenkins, 1980)) and increase in its precipitating potential (Parsons, 2001). Course and results of a continuous struvite reaction crystallization process can be also affected by feed composition, temperature, mixing intensity, crystallizer construction, spatial distribution of inlet/outlet ports, as well as presence, phase and concentrations of impurities (Doyle and Parsons, 2002; Matynia et al., 2006; Kozik et al., 2011; Hutnik et al., 2012; Mazienczuk et al., 2012). Process should be carried out under strict technological control, providing the possibly best quality of struvite (Le Corre et al., 2009). Crystalline struvite can be used e.g. as a mineral fertilizer (NPMg) in agriculture (Bridger, 2001; de–Bashan and Bashan, 2004).

Experimental research results concerning continuous reaction crystallization of struvite from typical phosphorus mineral fertilizers industry wastewater (leachate from slag heap of phosphogypsum in Z. Ch. POLICE S.A., Poland, containing 0.445 mass % PO_4^{3-}) are presented and discussed. Tests were carried out in a laboratory DT MSMPR (*Draft Tube, Mixed Suspension Mixed Product Removal*) type crystallizer with internal circulation of suspension driven by propeller stirrer (Mullin, 1993). Crystallizer was provided with a feed (raw wastewater with appropriate substrates premixed) of assumed molar ratio $PO_4^{3-}:Mg^{2+}:NH_4^+$ set as 1:1:1 or 1:1.2:1. Process ran in constant temperature 298 K. Influence of pH (8.5–10) and mean residence time of suspension in a crystallizer (τ 900–3600 s) on the product quality was identified. From the product crystal size distributions nucleation rates and linear growth rates were estimated. Simplified model of mass crystallization kinetics in a continuous MSMPR crystallizer – SIG (*Size Independent Growth*) model was adopted for kinetic data estimation (Mullin, 1993; Randolph and Larson, 1988).

2. Materials and methods

The raw materials applied for struvite continuous reaction crystallization were: crystalline magnesium chloride hexahydrate, $MgCl_2 \cdot 6H_2O$, crystalline ammonium chloride NH_4Cl (p.a., POCh, Gliwice, Poland), aqueous solution of NaOH and typical wastewater from phosphorus mineral fertilizers industry (Z.Ch. POLICE S.A., Poland) of pH 3.8 and composition presented in Table 1. Reacting substances (wastewater, $MgCl_2 \cdot 6H_2O$ and NH_4Cl) were introduced into the mixer where substrates dosed in crystalline form dissolved. Mass streams of these resulted from the assumed molar ratio $PO_4^{3-}:Mg^{2+}:NH_4^+$, mean residence time τ of suspension in a crystallizer and its working volume V_w. Clear solution of premixed and totally dissolved compounds, of pH 3.6 (for stoichiometric proportions between the substrates) or 3.5 (for 20% excess of magnesium ions) was systematically dosed with a pump into the crystallizer which construction is presented schematically in Fig. 1.

Process ran in continuous DT MSMPR type crystallizer of working volume V_w 0.6 dm^3 (total volume V_t 1.3 dm^3). It was a glass cylindrical tank (D 120 mm, H 123 mm), in a bottom part equipped with external heating/cooling coil thermostated with independent water circulation system. In a central apparatus axis cylindrical circulation profile was placed (*Draft*

Table 1 – Chemical composition of typical phosphorus mineral fertilizers industry wastewater.

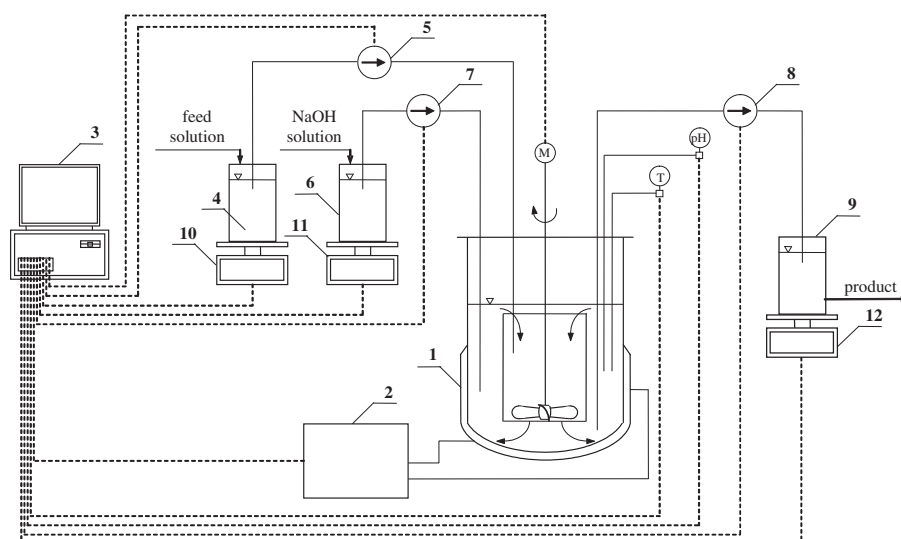| Component	Concentration, mass %
PO_4^{3-}	0.445
Al	6.4×10^{-4}
Ca	0.044
Cu	0.25×10^{-4}
Fe	8.9×10^{-4}
K	4.6×10^{-3}
Mg	0.0306
Si	5.1×10^{-3}
Ti	0.2×10^{-4}
Zn	2.2×10^{-4}
F^-	4.2×10^{-3}
SO_4^{2-}	0.0703

Fig. 1 – Schematic diagram of the experimental plant. 1 – DT MSMPR type crystallizer with internal circulation of suspension, 2 – thermostat, 3 – PC computer, 4 – feed reservoir: wastewater, $MgCl_2$ and NH_4Cl, 5 – feed proportioner (pump), 6 – alkalinity agent tank: aqueous solution of NaOH, 7 – proportioner (pump) of NaOH solution, 8 – receiver (pump) of product crystal suspension from the crystallizer tank, 9 – storage tank of a product crystal suspension, 10, 11, 12 – electronic balances, M – stirrer speed control/adjustment, pH – alkaline/acid reaction control/adjustment, T – temperature control/adjustment.

Tube, DT, d_{dt} 57 mm, h_{dt} 53 mm), with a three-paddle propeller stirrer operating inside (d_m 55 mm). Stirrer speed, process temperature, inflow rates of feed and pH-adjusting solution, as well as outflow rate of product crystal suspension were strictly controlled by PC computer driven by BioScadaLab software.

Feed solution was introduced into the circulation profile interior (stirrer speed: 6.6 ± 0.1 1/s; suspension movement – downward). Between the crystallizer body and circulation profile (suspension movement – upward) aqueous sodium hydroxide solution of concentration 5 mass % NaOH was

dosed providing the assumed, controlled pH. Research was carried out in temperature 298 ± 0.2 K. For stoichiometric conditions tests ran at pH 8.5, 9 or 10 (±0.1) assuming mean residence time of suspension in a crystallizer τ 900 s (±20 s). For pH 9 additional measurements were done at mean residence time elongated up to 1800 and 3600 s (±20 s). For 20% excess of magnesium ions in a feed process parameters were set as pH 9, τ 900 and 3600 s. The pH 9 was assumed as reference condition since for it the individual effects of separate ionic impurities in a feed were determined, both in the same crystallizer (Hutnik et al., 2011a,b, 2012) and in other

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

No.	Process parameters		Suspension in a crystallizer			Crystals characteristic sizes				
	pH	τ	M_T	$[PO_4^{3-}]_{solution}$	$[PO_4^{3-}]_{crystals}$	L_m[a]	L_{50}[b]	L_d[c]	CV[d]	L_a/L_b
–	–	s	kg crystals/m^3	mg/kg	Mass %	µm	µm	µm	%	–
Molar proportions of substrate ions in a feed: PO_4^{3-}:Mg^{2+}:NH_4^+ = 1:1:1										
1	8.5	900	10.8	62.8	39.2	26.1	22.0	23.6	73.9	3.9
2	9	900	11.0	46.0	39.4	25.5	21.6	22.5	79.8	3.8
3	10	900	11.1	36.8	40.9	24.7	19.3	21.7	83.3	3.4
4	9	1800	11.2	32.6	40.5	28.6	23.3	24.8	74.2	4.0
5	9	3600	11.3	20.8	41.2	30.9	25.7	26.8	70.1	4.2
Molar proportions of substrate ions in a feed: PO_4^{3-}:Mg^{2+}:NH_4^+ = 1:1.2:1										
6	9	900	11.3	18.5	38.4	34.2	27.5	31.5	80.9	4.9
7	9	3600	11.4	9.2	41.5	36.8	30.1	33.3	74.7	4.3

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

crystallizer constructions (jet pump DTM, Mazienczuk et al., 2012). The research results make thus direct comparison of the process results possible. The substrate concentrations in a feed were: $[PO_4^{3-}]_{RM} = 0.445$ mass %, $[Mg^{2+}]_{RM} = 0.114$ mass % and $[NH_4^+]_{RM} = 0.0844$ mass % (molar ratio 1:1:1) or 0.445, 0.137 and 0.0844 mass % for 20% excess of magnesium ions. After stabilization of the assumed parameter values, process ran in a steady state through additional 5τ. After this time solid phase content in a product crystal suspension (M_T), as well as chemical composition of mother solution and solid phase were determined using appropriate analytical methods. Concentration of phosphate(V) ions was determined with photometric method as phosphormolybdenum blue (spectrophotometer UV–VIS Evolution 300) and, additionally, with plasma optical emission spectrometer ICP–OES Varian Vista − MPX. Ammonium ions content was determined with volumetric method (formalin method). Concentrations of other substances in raw material and in products were determined with atomic absorption spectrometer iCE 3000 and plasma optical emission spectrometer ICP–OES Varian Vista − MPX. Crystal size distribution of product was determined with solid particle analyser Beckman Coulter LS 13 320 while particles habit(s) − using computer aided analysis of scanning electron microscope JEOL JSM 5800LV images. Analytical tests and assays were done in authors own laboratory and in Certified Chemical Laboratory of Multielemental Analyses, Faculty of Chemistry, Wroclaw University of Technology (www.lcaw.pwr.wroc.pl.). Accuracy of measurement data in a described laboratory plant was estimated to be ca. 10%.

Kinetic parameters of the continuous struvite reaction crystallization process were calculated from population density distributions $n(L)$ of the product crystals (Mullin, 1993). The most simplified kinetic model derived for the continuous MSMPR crystallizer − SIG kinetic model (Randolph and Larson, 1988) was adopted for the calculations. Population density distribution of product crystals resulting from the assumed SIG kinetic model is (Eq. (1)):

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

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

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

3. Results and discussion

3.1. Crystal size distribution

Statistical parameters of product crystal size distributions are presented in Table 2. From the table it results, that increase in mother solution pH from 8.5 to 10 resulted in decrease of mean crystal size L_m from 26.1 to 24.7 μm (by ca. 7.5%). The CV coefficient raised from 73.9 to 83.3%. Crystals produced at pH 10 characterized thus by not only smaller particles, but also

higher size−diversity. Increase in pH produces higher nuclei population densities (Table 4). In consequence shift of L_m, L_{50} and L_d towards smaller values is observed. Elongation of mean residence time of suspension in a crystallizer caused growth of mean product crystal sizes, even by more than 20%. Struvite crystals reached mean size L_m 30.9 μm for mean residence time τ 3600 s and pH 9. With the mean residence time elongation average supersaturation in solution decreases. In result the values of both kinetic components: nucleation rate and crystal linear growth rate decrease, as well (Table 4). Longer residence time of crystals in supersaturated solution produced, however, that their sizes enlarged significantly. In solution of smaller average supersaturation crystals grew slower, however longer and more stable. Longer contact time of crystal phase with supersaturated mother solution influenced also final product size distribution advantageously. Homogeneity of product population increased. The CV decreased from 79.8 to 70.1% (by ca. 9%), in spite of higher intensity of attrition and breakage processes − effect of elongation of suspension residence time in a mixed working volume of a crystallizer.

Excess of magnesium ions in relation to concentration of phosphate(V) and ammonium ions in a feed caused increase in mean size L_m of product crystals: from 25.5 to 34.2 μm (pH 9, τ 900 s) and from 30.9 to 36.8 μm (pH 9, τ 3600 s) (Table 2). Population's homogeneity slightly decreased. The CV values increased from 79.8 to 80.9% and from 70.1 to 74.7%, appropriately. In pure aqueous solutions of phosphates(V) excess of magnesium ions affects final struvite crystal sizes disadvantageously (Kozik et al., 2012a). It may be assumed, that main reason of this phenomenon is higher supersaturation in respect to magnesium ions at the crystallizer's inlet point (resulting from their excess in a feed). Higher supersaturation corresponds to increase in population density of struvite nuclei suggesting higher nucleation rate. All these together makes, that struvite crystals reach smaller sizes (Kozik et al., 2012a) compared to crystals produced in identical conditions, however assuming stoichiometric proportions between the main reagents (Kozik et al., 2012b). Presence of impurities in a process system (Table 1) can be thus regarded advantageous in respect to the final product properties (Table 2). Some ionic impurities inhibit struvite nucleation, while other can even catalyse nuclei formation or crystals growth processes. Simultaneously some of them can also significantly modify crystal habit (Kozik et al., 2011; Hutnik et al., 2012, 2011a). Individual concentrations of ionic impurities, concentration of phosphate(V) ions, continuous reaction crystallization process parameters (especially pH) − both under stoichiometric proportions (Hutnik et al., 2011a) and at magnesium ions excess (Hutnik et al., 2012) − are of decisive influence. For example, in a 1.0 mass % solution of phosphate(V) ions presence of 0.05 mass % of calcium ions in a comparable process conditions (crystallizer identical with presented in Fig. 1, stoichiometric proportions between the substrates, pH 9, τ 900 s) product crystals of mean size L_m 32.6 μm were obtained (Hutnik et al., 2011b). In identical conditions, from pure model solutions of phosphates(V), struvite of L_m 27.5 μm was removed (Hutnik et al., 2011a), while at 20% excess of magnesium ions it was 26.0 μm (Hutnik et al., 2012). From the wastewater tested (however fully representative for typical

phosphorus mineral fertilizers industry), containing among others 0.044 mass % of calcium ions (Table 1), mean product crystal size was 25.5 μm (reagents stoichiometry — see No. 2 in Table 2) and 34.2 μm (20% excess of magnesium ions — see No. 6 in Table 2).

In Fig. 2 there are presented volumetric (mass) crystal size distributions of the compared above products manufactured at pH 9 and τ 900 s, both in stoichiometric conditions (Fig. 2a, No. 2 in Table 2) and at 20% excess of magnesium ions (Fig. 2b, No. 6 in Table 2). Dominant crystal size L_d (corresponding to differential distribution maximum) shifts towards larger crystal sizes: 22.5 μm (Fig. 2a) and 31.5 μm (Fig. 2b). Number and size of the largest crystals in a product increase. The largest particle size observed under stoichiometric conditions is 120 μm, while at magnesium ions excess — 150 μm. Simultaneously shrinkage of the smallest size fraction is observed. In a first of the compared groups fraction of sizes below 3 μm was 9.4%, while in a second it decreased to 6.9%, thus by ca. 27%. In result mean crystal size L_m enlarged significantly from 25.5 to 34.2 μm (Table 2).

3.2. Crystal shape

Scanning electron microscope images of struvite product crystals, of size distributions shown in Fig. 2, are presented in Fig. 3. Diverse sizes of struvite particles are clearly observable. Also other co-precipitated solid particles are detectable. The most frequently they create agglomerates on the struvite parent crystal surfaces. Struvite crystals are just stuck around with them. Excess of magnesium ions favoured thus not only production of struvite crystals of larger sizes (Fig. 3b), but also co-precipitation of larger amount of impurities from the wastewater (see Table 3). Struvite crystals demonstrating the best shapes were produced at lower pH, elongated mean residence time and at excess of magnesium ions in a feed. Under these conditions mean struvite crystal size was L_m ca. 37 μm, dominant size L_d exceeded 33 μm and CV was lower than 75%. Crystal length L_a to their width L_b ratio was 4.3 in average (Table 2). The L_a/L_b values were calculated from planimetric measurements covering 50 crystals randomly selected from three different scanning electron microscope images of the same product sample. From the measurements it results, that for all product crystals L_a/L_b varied within the 3.4–4.9 range (Table 2). The shortest and thinnest crystals

were produced at high pH and short mean residence time (L_a/L_b 3.4). Reduction of pH and elongation of mean residence time resulted in significantly longer and thicker struvite crystals. Despite L_b raise, L_a/L_b was above 4. Based on microscope images analysis one can conclude, that struvite crystal surfaces were blocked by co-precipitating and co-crystallizing solid impurity particles of different specific volumes. It generated relatively large tensions within the struvite crystal structures. In effect numerous crystal cracks, irregular surfaces, deformed edges, as well as presence of tubular forms and crystals formed into the trough shape were identified (Fig. 3). Product crystal habit distinctly differed from classical shape of struvite crystals produced from pure phosphate(V) solutions (mean L_a/L_b ca. 6) (Hutnik et al., 2012), or from solutions with single impurities (mean L_a/L_b from 6 to 8.4), except for calcium and iron ions (mean L_a/L_b 4.2–4.6) (Hutnik et al., 2011a, 2012). Since calcium ions concentration in wastewater, as impurity, predominated (440 mg/kg), it may be assumed, that it mainly influenced final geometrical proportions of struvite crystals (Hutnik et al., 2011b). It can be supposed, that the observed struvite crystal sizes and habits are the net effects of impurities present in the wastewater and technological parameters of continuous reaction crystallization process. From the microscope images it also results, that agglomeration within struvite crystals population was insignificant. Crystal attrition and breakage during their mixing and circulation in a crystallizer working volume can be also regarded moderate. Generally, it speaks advantageously about process conditions established in a continuous DT MSMPR crystallizer for nucleation and struvite crystals growth.

3.3. Chemical composition

In Table 3 there are presented the concentration ranges of mother solution and resulting solid phase components (after drying, without water washing of the crystals on a filter (see Table 2)). Crystal product, as it results from Table 3, besides main component $MgNH_4PO_4 \cdot 6H_2O$, contains also all impurities present in wastewater. From these data it results, that impurity concentrations in postprocessed mother solution visibly decreased, especially of aluminium, calcium, copper, iron and zinc ions (see wastewater composition in Table 1). Excess of magnesium ions in a process system resulted in generally lower concentrations of these ionic species
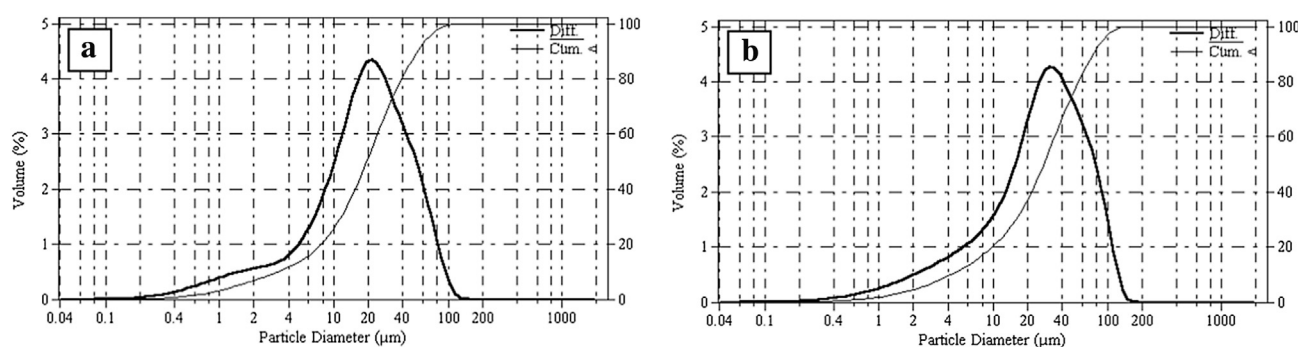

Fig. 2 — Differential and cumulative volumetric (mass) crystal size distributions of struvite produced from phosphorus mineral fertilizers industry wastewater in a continuous DT MSMPR crystallizer. Process parameters: pH 9, τ 900 s, $[PO_4^{3-}]_{RM}$: $[Mg^{2+}]_{RM}$: $[NH_4^+]_{RM}$ in a feed as 1 : 1 : 1 (a) and 1 : 1.2 : 1 (b) (see No. 2 and 6 in Table 2).
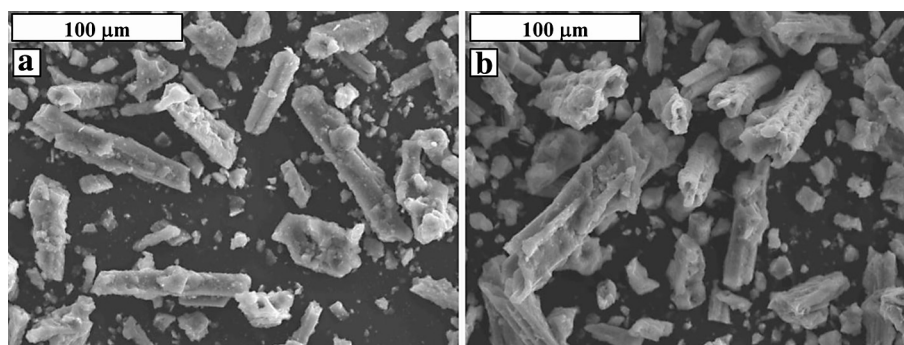
Fig. 3 – Scanning electron microscope images of struvite crystals produced from phosphorus mineral fertilizers industry wastewater in a continuous DT MSMPR crystallizer (crystal size distributions – see Fig. 2).

compared to stoichiometric conditions. One can also notice, that concentration of phosphate(V) ions in mother solution varies from 62.8 mg/kg (pH 8.5, τ 900 s) to 20.8 mg/kg (pH 9, τ 3600 s) (stoichiometric conditions, No 1–5, Table 2). These concentration values decrease systematically with the pH raise and with elongation of mean residence time τ. From the comparison it results, that concentration of phosphate(V) ions can be lowered even nearly three times. It can be attributed, as it was mentioned earlier, to the decrease of struvite solubility with the rise of reactive mixture pH and longer contact time of crystals with supersaturated solution (more thorough discharge of generated supersaturation through induced mass transfer between both phases). The resulting $[PO_4^{3-}]_{solution}$ values can be regarded relatively small. Effectiveness of

phosphate(V) ions removal from the feed (of initial $[PO_4^{3-}]_{RM}$ in wastewater: 4450 mg/kg) is thus fully satisfactory, ranging from 98.6% (pH 8.5, τ 900 s) up to 99.5% (pH 9, τ 3600 s). It should be noticed here, that working supersaturation in a crystallizer, thus supersaturation in a postprocessed mother solution, couldn't be calculated with sufficiently high precision. In majority of published works solubility product of struvite in pure phosphate(V) solutions $pK_{sp} = 13.26$ is assumed (e.g. Ohlinger et al., 1998), for which corresponding concentration of phosphate(V) ions in an equilibrium is 3.6 mg/kg. However, in reality this value is unknown since it depends on the solution composition and on many other – process, technological and even constructional factors (Le Corre et al., 2009; Parsons, 2001; Doyle and Parsons, 2002).

Excess of magnesium ions at a feed point in relation to phosphate(V) and ammonium ions concentrations influenced process yield advantageously. Residual concentration of phosphate(V) ions in a postprocessed mother solution was ca. 2-time smaller than under stoichiometric conditions. It was 18.5 and 9.2 mg/kg for τ 900 and 3600 s, appropriately (pH 9) (Table 2).

3.4. Nucleation and crystal growth kinetics

In Fig. 4 there are presented the 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 distributions, presented in $\ln n - L$ coordinate system, it results, that for $L > 30 \ \mu m$ these dependencies can be with satisfactory accuracy approximated with linear function. After fitting Eq. (1) to experimental data one can estimate the nuclei population density n_0 and calculate crystal linear growth rate G, while from Eq. (2) – their nucleation rate B. Estimated values of population density distribution parameters, valid for struvite crystals of size $L > 30 \ \mu m$ ("linear" SIG kinetic model, Eq. (1)) and calculated on this basis G and B values are presented in Table 4. Nonlinearity in population density distribution courses observed for L smaller than 30 μm (in $\ln n - L$ coordinate system, Fig. 4) suggests more complex process kinetics than it would result from the initially assumed SIG MSMPR model background (Mullin, 1993; Randolph and Larson, 1988). Determined this method

Table 3 – Chemical composition of solid phase and mother solution after filtration of crystal suspension removed from continuous DT MSMPR crystallizer (see Table 2).

Component	Concentration in:		
	Mother solution, mg/kg		Solid phase, mass %
	a	b	c
PO_4^{3-}	20.8–62.8	9.2–18.5	38.4–41.5
Mg^{2+}	32–90	159–238	8.9–9.8
NH_4^+	92–118	54–76	6.6–7.0
Al	0.10–0.30	0.10–0.15	$(4.8–5.5) \times 10^{-2}$
Ca	<50	<50	2.8–3.6
Cu	0.03–0.09	0.02–0.04	$(0.6–1.3) \times 10^{-4}$
Fe	0.05–0.07	0.03–0.05	0.12–0.20
K	25–35	28–37	0.12–0.22
Si	28–39	24–30	$(8.6–9.7) \times 10^{-2}$
Ti	<0.2	<0.2	$<2 \times 10^{-5}$
Zn	<0.5	<0.5	$(1.7–1.9) \times 10^{-2}$
F^-	10–22	3–20	0.36–0.46
SO_4^{2-}	400–500	400–550	1.5–1.9

a Molar proportion of substrate ions in a feed: $PO_4^{3-}:Mg^{2+}:NH_4^+ = 1:1:1$.
b Molar proportion of substrate ions in a feed: $PO_4^{3-}:Mg^{2+}:NH_4^+ = 1:1.2:1$.
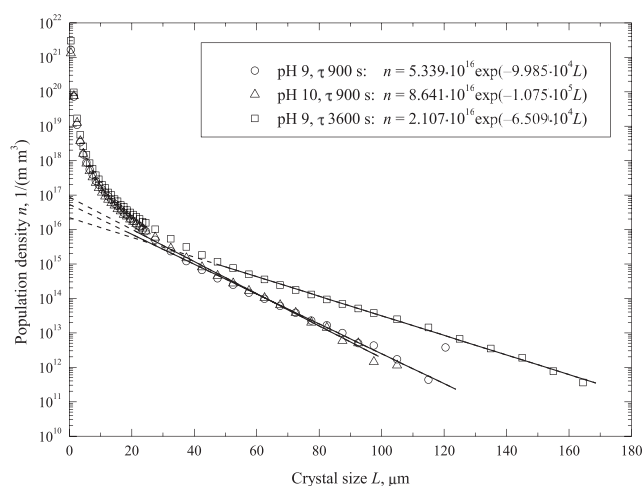c After drying, without water washing of crystals on filter.

Fig. 4 − Exemplary population density distributions of crystals produced in DT MSMPR crystallizer fed with phosphorus mineral fertilizers industry wastewater assuming stoichiometric ratio between the main substrates (○, △) and at 20% excess of magnesium ions (□). The points − experimental data, solid lines − values calculated with Eq. (1) (see Table 4) for crystal sizes $L > 30$ μm, dashed lines − linear extrapolations of SIG model.

Generally, higher crystal growth rates are observed for shorter mean residence times. This is in accordance with the observations concerning classical continuous mass crystallization processes (Mullin, 1993). For example, increase in pH from 8.5 to 10, for τ 900 s, results in decrease of linear crystal growth rate from 1.14×10^{-8} to 1.03×10^{-8} m/s. It is relatively small G decrease (by ca. 10%). This effect was, however, accompanied by significant increase in nuclei population density n_0 (above two time), thus in nucleation rate B (from 4.8×10^8 to 8.9×10^8 1/(s m³)). In result final mean crystal size L_m decreased (26.1 → 24.7 μm). Elongation of mean residence time of suspension in a crystallizer confines nucleation rate B (from 5.9×10^8 to 1.6×10^8 1/(s m³) for τ 900 → 3600 s, pH 9). Crystal linear growth rate G also decreases, however longer contact time with the supersaturated mother solution causes increase in mean crystal size by more than 20% (L_m 25.5 → 30.9 μm).

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

In Table 4, for comparison, also struvite linear crystal growth rates and its nucleation rates were provided. These parameter values corresponded to continuous DT MSMPR crystallizer, fed with synthetic wastewater of phosphate(V) ions concentration 1.0 mass % (Kozik et al., 2012a,b). Synthetic wastewater did not contain any impurities. For identical technological parameter values generally higher (by ca. 30% on average) crystal linear growth rate and lower (by ca. 43% on average) nucleation rates were reported, despite nearly two-time higher concentration of PO_4^{3-} ions than in industrial wastewater. One can thus conclude, that impurities presence is responsible for the observed differences. Impurity presence, as it was mentioned earlier, made that final struvite crystals were shorter and thicker compared to particles produced from synthetic wastewater (Section 3.2). Its number in the process system was also considerably higher (resulting from higher nucleation rates), providing smaller mean size of product crystals (average L_m 29.5 μm − Table 2, average L_m 39.9 μm − Kozik et al., 2012a,b).

kinetic parameter values should be thus treated as the roughly estimated ones only. It especially concerns nucleation rates calculated with Eq. (2), based on the nuclei population density n_0 values ($n(L)$ for $L = 0$) strongly devaluated by SIG kinetic model. As it results from Fig. 4, the differences between n_0 values predicted by linear extrapolation with SIG kinetic model and experimental population density values attributed to the smallest crystals reach even 10^5. Calculated nucleation rate values B are thus useful only for relative, conventional comparison of the investigated process parameter influences on its course and final results.

Analysing the kinetic data presented in Table 4 one can notice systematic lowering of crystal linear growth rate G with the pH raise and with elongation of mean residence time.

Table 4 − Nucleation rate B and crystal linear growth rate G values estimated for continuous struvite reaction crystallization process in DT MSMPR crystallizer. Kinetic parameters calculated with SIG MSMPR model. Process conditions − see Table 2.

No.[a]	Process kinetic parameter values (SIG MSMPR model)					Synthetic wastewater[b]	
	$n(L)$ for $L > 30$ μm	R^2 (for linear segment)	n_0 1/(m m³)	G m/s	B 1/(s m³)	G m/s	B 1/(s m³)
1	$n = 4.247 \times 10^{16} \exp(-9.746 \times 10^4 L)$	0.990	4.2×10^{16}	1.14×10^{-8}	4.8×10^8	1.75×10^{-8}	3.1×10^8
2	$n = 5.339 \times 10^{16} \exp(-9.985 \times 10^4 L)$	0.992	5.3×10^{16}	1.11×10^{-8}	5.9×10^8	1.68×10^{-8}	3.1×10^8
3	$n = 8.641 \times 10^{16} \exp(-1.075 \times 10^5 L)$	0.994	8.6×10^{16}	1.03×10^{-8}	8.9×10^8	1.20×10^{-8}	4.7×10^8
4	$n = 6.922 \times 10^{16} \exp(-8.762 \times 10^4 L)$	0.992	6.9×10^{16}	6.34×10^{-9}	4.4×10^8	1.09×10^{-8}	2.0×10^7
5	$n = 4.734 \times 10^{16} \exp(-8.150 \times 10^4 L)$	0.991	4.7×10^{16}	3.41×10^{-9}	1.6×10^8	5.48×10^{-9}	6.6×10^7
6	$n = 2.507 \times 10^{16} \exp(-7.756 \times 10^4 L)$	0.996	2.5×10^{16}	1.43×10^{-8}	3.6×10^8	1.20×10^{-8}	4.6×10^8
7	$n = 2.107 \times 10^{16} \exp(-6.509 \times 10^4 L)$	0.990	2.1×10^{16}	4.27×10^{-9}	9.0×10^7	5.41×10^{-9}	7.6×10^7

a see Table 2 for details.
b References: Kozik et al., 2012a,b.

4. Conclusions

Typical wastewater from phosphorus mineral fertilizers industry, contacted with Mg^{2+} and NH_4^+ ions in continuous DT MSMPR type crystallizer, resulted in production of struvite crystals of mean size L_m from 24.7 to 36.8 μm. Increase in pH (8.5 → 10, τ 900 s) effected in decrease of mean crystal size by ca. 5.4% (L_m 26.1 → 24.7 μm). Contrary, elongation of mean residence time of suspension in a crystallizer from 900 to 3600 s (pH 9) induced increase in this size even by ca. 20% (L_m 25.5 → 30.9 μm). Crystal products of moderate size–homogeneity (CV 70–83%) were removed. It is complex net effect of pH and mean residence time, contributed by attrition and breakage on the resulting working supersaturation level in mother solution.

For the process kinetic parameters estimation the simplest kinetic model of continuous mass crystallization, valid for the ideal MSMPR crystallizer, was adopted. It was concluded, that linear growth rates of struvite crystals varied within the $3.41 \times 10^{-9} - 1.14 \times 10^{-8}$ m/s range, whereas nucleation rate within the $1.6 \times 10^8 - 8.9 \times 10^8$ 1/s m^3 limits. With the elongation of mean residence time both kinetic parameters decreased. The pH raise produced, however, increase in nucleation rate while decrease of crystal linear growth rate was simultaneously observed. Decrease of both kinetic parameters, B and G, with the elongation of mean residence time of suspension is accompanied by L_m raise. Lower linear growth rates were compensated by longer contact times between the crystals and supersaturated mother solution. In a process conditions characterized by relatively long mean residence time of suspension in a crystallizer higher quality product is formed. However, in such process arrangement unit productivity is small, resulting in lower economical effectiveness of the whole production plant.

Excess of magnesium ions in relation to phosphate(V) and ammonium ions content (1.2:1:1) shifted the precipitation reaction's equilibrium right, towards struvite formation. In such modified process conditions concentration of phosphate(V) ions in mother solution decreased (to 9.2 mg PO_4^{3-}/kg of solution for pH 9, τ 3600 s), raising thus additionally the struvite reaction crystallization process yield. It was accompanied by increase in mean size of product crystals (L_m up to 36.8 μm), crystal linear growth rate (G up to 4.27×10^{-9} m/s) and decrease of nucleation rate (B to 9.0×10^7 1/(s m^3)). It is a result of complex feedbacks between higher supersaturation at the crystallizer inlet point and crystal size distribution of product outflowing from the crystallizer, through nucleation and crystal growth rates, depending, in turn, on the resulting supersaturation in mother solution (Randolph and Larson, 1988). These are also strongly affected by presence and concentrations of impurities in wastewater. On the basis of experimental data presented this complex influence can be generally regarded advantageous.

Presence of many impurities and their interactions in a process system produced, as a net effect, that product crystal size distribution can be regarded satisfactory. Crystal mean size L_m was higher than 35 μm. Crystal homogeneity did not differ significantly from this parameter for crystals produced from pure phosphate(V) solutions (CV 70–83%). Maximal crystal size was 120–150 μm while product crystal fraction of sizes below 3 μm was less than 10%. Main disadvantageous effect of wastewater feed is chemical purity of the resulting crystal product. Practically all impurities present in raw wastewater appeared in solid phase. Utilization of such product (e.g. in agriculture) is thus limited, although part of these impurities can be regarded as the soil enriching components (nutrients, especially: sulphur, calcium, iron and others).

REFERENCES

Bridger, G., 2001. Fertiliser value of struvite. CEEP Scope Newsletter 43, 3–4.

de–Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer. Water Research 38, 4222–4246.

Doyle, J., Parsons, S.A., 2002. Struvite formation, control and recovery. Water Research 36, 3925–3940.

Hutnik, N., Piotrowski, K., Gluzinska, J., Matynia, A., 2011a. Effect of selected inorganic impurities present in real phosphate(V) solutions on the quality of struvite crystals produced in continuous reaction crystallization process. Progress in Environmental Science & Technology 3, 559–566.

Hutnik, N., Piotrowski, K., Wierzbowska, B., Matynia, A., 2011b. Continuous reaction crystallization of struvite from phosphate(V) solutions containing calcium ions. Crystal Research and Technology 46, 443–449.

Hutnik, N., Wierzbowska, B., Matynia, A., 2012. Effect of inorganic impurities on quality of struvite in continuous reaction crystallization at the excess of magnesium ions. Przemysł Chemiczny 91, 762–766 (in polish).

Kozik, A., Piotrowski, K., Wierzbowska, B., Matynia, A., 2011. Recovery of phosphate(V) ions from wastewaters of different chemical composition. Progress in Environmental Science & Technology 3, 550–558.

Kozik, A., Matynia, A., Piotrowski, K., 2012a. Recovery o struvite from diluted aqueous solutions of phosphate(V) ions in the presence of magnesium ions excess. In: Markoš, J. (Ed.), Proceedings of the 39th International Conference of Slovak Society of Chemical Engineering, pp. 742–749. Slovakia.

Kozik, A., Matynia, A., Piotrowski, K., 2012b. Continuous reaction crystallization of struvite from diluted aqueous solutions of phosphate(V) ions in DT MSMPR crystallizer. Procedia Engineering 42, 344–355.

Le Corre, K.S., Valsami–Jones, E., Hobbs, P., Parsons, S.A., 2009. Phosphorus recovery from wastewater by struvite crystallization: a review. Critical Reviews in Environmental Science and Technology 39 (6), 433–477.

Matynia, A., Koralewska, J., Piotrowski, K., Wierzbowska, B., 2006. The influence of the process parameters on the struvite continuous crystallization kinetics. Chemical Engineering Communications 193, 160–176.

Mazienczuk, A., Hutnik, N., Piotrowski, K., Wierzbowska, B., Matynia, A., 2012. Continuous crystallizers with jet pump

driven by recirculated mother solution in production of struvite. Przemysł Chemiczny 91, 890—895 (in polish).

Mullin, J.W., 1993. Crystallization. Butterworth—Heinemann, Oxford.

Ohlinger, K.N., Young, T.M., Schroeder, E.D., 1998. Predicting struvite formation in digestion. Water Research 32, 3607—3614.

Parsons, S.A., 2001. Recent scientific and technical developments: struvite precipitation. CEEP Scope Newsletter 41, 15—22.

Randolph, A.D., Larson, M.A., 1988. Theory of Particulate Processes: Analysis and Techniques of Continuous Crystallization. Academia Press, New York.

Snoeyink, V.L., Jenkins, D., 1980. Water Chemistry. Wiley, New York.