

# Precipitation and Crystallization of Struvite from Synthetic Wastewater under Stoichiometric Conditions

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## ABSTRACT

Phosphate (V) ions were continuously removed from synthetic wastewater containing inorganic impurities using magnesium and ammonium ions. The product was magnesium ammonium phosphate (V) hexahydrate, struvite,  $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$ . Research ran in stoichiometric conditions in DT MSMPR type crystallizer with internal circulation of suspension. Increase in process environment pH from 9 to 11 resulted in 3-time decrease of mean struvite crystals size (from 40.1 to 12.6  $\mu\text{m}$ ). Elongation of mean residence time of suspension in a crystallizer up to 3600 s resulted in improvement of the product quality. Mean size of struvite crystals enlarged up to 50.2  $\mu\text{m}$ . Based on kinetic calculations results (SIG MSMPR model) it was concluded, that linear struvite crystal growth rate varied within  $5.04 \times 10^{-9} - 1.69 \times 10^{-8}$  m/s range, whereas nucleation rate within  $1.4 \times 10^7 - 1.7 \times 10^{10}$  1/(s m<sup>3</sup>) limits. In solid product, besides struvite, also all impurities present in wastewater were identified analytically as hydroxides, phosphates and other salts.

**Keywords:** Struvite; Precipitation; Continuous Reaction Crystallization; Phosphate(V) Ions; Impurity Ions; Continuous DT MSMPR Crystallizer; Crystal Size Distribution; Kinetics

## 1. Introduction

Inexpensive and easily available, secondary phosphorus sources can be industrial, municipal liquid wastes, liquid manure, urine and other waste solutions containing phosphate (V) ions [1]. Technological idea of recovery from them some useful phosphorus compounds is based on reaction crystallization of sparingly soluble phosphate salts, mainly struvite  $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$  (MAP) [2, 3]. Controlled reaction crystallization of struvite is not simple process. Its course and final results are strongly affected by temperature, concentrations of main reacting substances (phosphate(V), magnesium and ammonium ions), process environment's pH, reaction crystallization of not only expected product, but also co-precipitating sparingly soluble salts or/and hydroxides of some metals present in wastewaters [1, 4-6]. Process success depends also on the continuous crystallizer construction and its work mode/parameters, including: mean residence time of suspension in working volume of the crystallizer, intensity of mixing and circulation of suspension inside the apparatus, inlet places and contact method of the reacting substances, etc. [1, 7-9].

The experimental test results concerning recovery of phosphate(V) ions from solution of similar chemical

composition to agricultural, animal breeding or mineral fertilizer industry wastewater are presented. Precipitation of phosphate (V) ions with magnesium and ammonium ions in alkaline aqueous environment, followed by struvite mass crystallization was carried out in a laboratory continuous DT MSMPR (*Draft Tube, Mixed Suspension Mixed Product Removal*) type crystallizer with propeller stirrer. Crystallizer was provided with feed solution of determined chemical composition, prepared earlier in a mixer from chemically pure substances and deionized water. The solution contained, besides phosphate (V) ions, also: magnesium, ammonium, aluminium, calcium, copper, iron, potassium, zinc and nitrate (V) ions. In this environment also sodium and chloride ions were present from dissolved in water crystalline salts from which synthetic wastewater was made. Concentration of phosphate (V) ions was assumed to be 1.0 mass %. This concentration is ca. 2 - 5-time higher than reported in real wastewaters. However, one can thus compare the presented results with the data concerning struvite production process from solutions containing phosphate (V) ions only, of concentration 1.0 mass % [10]. The research was carried out at molar ratio of the substrates  $\text{PO}_4^{3-} : \text{Mg}^{2+} : \text{NH}_4^+$  as 1 : 1 : 1 in temperature 298 K. Influence of pH (from 9 to 11) and mean residence time of suspension in a crystallizer (from 900 to 3600 s) on product crystal size distri-

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butions, mean size and homogeneity within product population were investigated. Linear growth rate of struvite crystals and its nucleation rate were estimated. Calculations were based on the simplified model of mass crystallization kinetics in MSMPR crystallizer – SIG (*Size Independent Growth*) model.

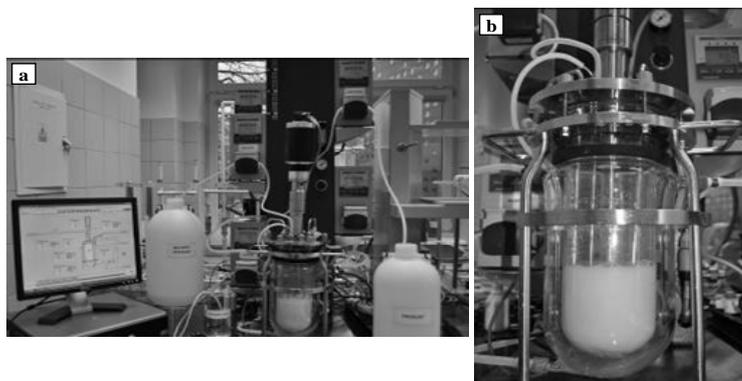
## 2. Material and Methods

Photo of experimental plant is shown in **Figure 1**. It is fully automated. Continuous Bioengineering RALF plus Solo plan. Steering, control and acquisition of measurement data streams were carried out with the use of PC computer (driven by BioScadaLab software). Process ran in DT MSMPR type crystallizer of working volume  $V_w$  0.6 dm<sup>3</sup> (total volume  $V_t$  1.3 dm<sup>3</sup>). Crystallizer, made of glass, was equipped with heating/cooling coat providing stable process temperature, as well as with the system delivering compressed air, required for stripping of absorbed CO<sub>2</sub> and oxidation of possible organic substances present in struvite continuous reaction crystallization environment. Crystallizer diameter was  $d$  100 mm, its working part height  $h_w$  90 mm, total height  $h_t$  200 mm. Inside the crystallizer circulation profile (DT, *Draft Tube*,  $d_{dt}$  52 mm,  $h_{dt}$  50 mm) was installed, inside which four-paddle propeller stirrer of diameter  $d_m$  48 mm operated. Mixer speed, process temperature, inlet stream of air, inflows of feed and alkalis solution, as well as outflow of product crystal suspension from the crystallizer were strictly controlled and adjusted by computer.

Synthetic wastewater feeding the crystallizer was aqueous solution of ammonium di hydrogen phosphate (V) NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, magnesium chloride MgCl<sub>2</sub>×6H<sub>2</sub>O, chlorides of impurity cations (AlCl<sub>3</sub>×6H<sub>2</sub>O, CaCl<sub>2</sub>×2H<sub>2</sub>O, CuCl<sub>2</sub>×2H<sub>2</sub>O, FeCl<sub>3</sub>×6H<sub>2</sub>O, KCl and ZnCl<sub>2</sub>), as well as sodium salt of impurity anion (NaNO<sub>3</sub>). The mixture was prepared in external mixer using crystalline substances (p.a., POCh Gliwice, Poland) and deionized water (Barnstead–NANOpure DIamond). Concentrations of main substrates: phosphate (V) ions (1.0 mass %) [10], magnesium

(0.256 mass %) and ammonium (0.190 mass %) resulted from their assumed molar ratio 1 : 1 : 1. Detailed chemical composition of the feed was presented in **Table 1**. This solution was continuously introduced into circulation profile (mixer speed: 4.0 1/s; suspension movement – downward). Between crystallizer body and circulation profile (suspension movement – upward) aqueous solution of sodium hydroxide, of concentration 3 mass % NaOH was dosed in amount providing the assumed, controlled pH of continuous struvite reaction crystallization environment. Tests ran in temperature 298 ±0.2 K assuming pH 9, 10 or 11 (±0.1) and mean residence time of suspension in a crystallizer  $\tau$  900, 1800 or 3600 (±20) s. Compressed air flow was established on the 100 Ndm<sup>3</sup>/h level (pressure ca. 2.5 bar). After stabilisation in a crystallizer the assumed parameter values, process in a steady state ran through another 5 $\tau$ . After this time whole crystallizer content was transferred on vacuum filter. Product crystals were not washed. Using appropriate analytical methods and procedures there were determined: solid phase concentration in product crystals suspension ( $M_T$ ), chemical composition of mother solution and solid phase (using, among others, plasma emission spectrometer ICP–AES CPU 7000, spectrometer IR PU9712, atomic absorption spectrometer iCE 3000, spectrophotometer UV–Vis Evolution 300), product crystal size distributions (solid particle laser analyser Beckman Coulter LS 13 320) and crystal habit (scanning electron microscope JEOL JSM 5800LV). Accuracy of process data determination in the continuous plant used was estimated to be ca. 10%.

Kinetic parameters of the investigated continuous struvite reaction crystallization process were determined based on population density distributions  $n(L)$  of product crystals [11]. The most simplified kinetic model for continuous MSMPR crystallizer – SIG model [12], was used for the calculations. Crystal population density distribution equation resulting from the assumed SIG kinetic model constraints can be presented in the form of Eq. (1):



**Figure 1. Photo of experimental plant for continuous reaction crystallization of struvite: (a) general view, (b) continuous DT MSMPR type crystallizer unit with internal circulation of suspension.**

**Table 1. Chemical composition of synthetic wastewater from fertilizer industry.**

Component	Concentration mass %
PO <sub>4</sub> <sup>3-</sup>	1.0
Mg <sup>2+</sup>	0.256
NH <sub>4</sub> <sup>+</sup>	0.190
Al <sup>3+</sup>	0.002
Ca <sup>2+</sup>	0.05
Cu <sup>2+</sup>	2·10 <sup>-5</sup>
Fe <sup>3+</sup>	2·10 <sup>-4</sup>
K <sup>+</sup>	0.025
Zn <sup>2+</sup>	2·10 <sup>-5</sup>
NO <sub>3</sub> <sup>-</sup>	0.02
pH	3.7

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

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

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

### 3. Results and Discussion

Statistical parameter values of product crystal size distributions are presented in **Table 2**.

From the table it results, that diversified struvite crystals of mean size  $L_m$  from 12.6 to 50.2  $\mu\text{m}$  ( $L_{50}$  from 10.7 to 38.7  $\mu\text{m}$ ) were produced from the synthetic wastewater depending on pH of reaction crystallization process

environment and mean residence time of suspension in a crystallizer. These are large differences, speaking about significant influence of process parameters on product crystal sizes. With the pH increase homogeneity within product crystals population increased (as CV decreased by more than 10%, from 78.4 to 69.6%), simultaneously their mean size significantly decreased. Rise of pH from 9 to 11 caused, that  $L_m$  values decreased from 40.1 to 12.6  $\mu\text{m}$ , thus more than 3 times. Also second statistical parameter of crystal size distribution  $L_{50}$  decreased analogously by ca. 67%. With the pH increase struvite solubility decreases (minimal value corresponds to pH 10, 3 [13] or 10,7 [14]), and its precipitation potential increases [2,3]. All these make, that nuclei population density enlarges (**Table 3**), shifting of mean or median crystal size towards smaller values.

**Table 2. Experimental test results concerning continuous struvite reaction crystallization process in DT MSMPR type crystallizer. Process temperature: 298 K.**

No.	Process parameters		Crystal product characteristics				
	pH	$\tau$ s	$L_m$ $\mu\text{m}$	$L_{50}$ $\mu\text{m}$	$L_d$ $\mu\text{m}$	CV %	$L_a/L_b$
1	9	900	40.1	32.9	38.0	78.4	5.4
2	10	900	15.6	13.3	13.6	71.1	4.6
3	11	900	12.6	10.7	11.6	69.6	4.4
4	9	1800	43.9	36.4	41.7	79.7	5.6
5	9	3600	50.2	38.7	43.7	82.5	6.1

\*Without product crystal washing;  $L_m = \sum x_i L_i$ , where:  $x_i$  – mass fraction of crystals of mean fraction size  $L_i$ ;  $L_{50}$  – median crystal size for 50 mass % undersize fraction;  $L_d$  – crystal mode size;  $CV = 100(L_{84} - L_{16})/(2L_{50})$ , where:  $L_{84}$ ,  $L_{16}$ ,  $L_{50}$  – crystal sizes corresponding to 84, 16 and 50 mass % undersize fractions).

**Table 3. Nucleation rate  $B$  and crystal linear growth rate  $G$  estimated for struvite reaction crystallization process in a continuous DT MSMPR type crystallizer with SIG MSMPR model. Process conditions – see Table 2.**

No.	Kinetic parameters of the process (SIG MSMPR model)			
	$n(L)^{*}$	$R^2$ (for linear segment*)	$G \times 10^{-9}$ m/s	$B \times 10^9$ 1/(s m <sup>3</sup> )
1	$n = 2.344 \times 10^{16} \exp(-6.570 \times 10^4 L)$	0.986	16.9	0.39
2	$n = 6.218 \times 10^{17} \exp(-1.489 \times 10^5 L)$	0.994	7.46	4.6
3	$n = 3.406 \times 10^{18} \exp(-2.206 \times 10^5 L)$	0.982	5.04	17
4	$n = 1.348 \times 10^{16} \exp(-5.793 \times 10^4 L)$	0.992	9.59	0.12
5	$n = 2.045 \times 10^{15} \exp(-3.797 \times 10^4 L)$	0.971	6.98	0.014

\*for  $L > 50 \mu\text{m}$  (pH 9),  $L > 20 \mu\text{m}$  (pH 10),  $L > 10 \mu\text{m}$  (pH 11).

Elongation of mean residence time of suspension in a crystallizer was responsible for growth of product crystals sizes, even by more than 25%. Struvite crystals reached mean size  $L_m$  50.2  $\mu\text{m}$  for mean residence time  $\tau$  3600 s and pH 9. With the elongation of mean residence time of suspension mean supersaturation in solution decreased, resulting thus in decrease of both kinetic components of the process: nucleation rate of solid phase and its linear growth rate (Table 3). Longer residence time of crystals in supersaturated solution produced, however, that their sizes enlarged significantly. In solution of lower mean supersaturation crystals grew slower, however longer and more stable. Homogeneity within crystal population, however, decreased (CV increased from 78.4 to 82.5%), resulting mainly from increase in intensity of co-running crystal attrition and breakage processes correlated with the elongation of their residence time in a mixed and circulated suspension. From aqueous solutions containing only phosphate (V) ions of concentration 1.0 mass % at the same crystallizer struvite of generally larger crystal sizes (by ca. 15% on average) was produced [10]. These crystals were also more homogeneous. The largest differences were observed for mean residence time of suspension in a crystallizer elongated up to 3600 s. For example, for pH 9 and  $\tau$  3600 s:  $L_m$  63.0  $\mu\text{m}$ , CV 63.2% (system without impurities, [10]) and  $L_m$  50.2  $\mu\text{m}$ , CV 82.5% (synthetic wastewater, Table 2). Main reason of these differences is impurities presence. Individual influence of each impurity is different. Some of these affect shape and sizes of struvite crystals advantageously [5], while others, for example, raise nucleation rate or limit linear growth rate [15]. Their interaction – effect of not only presence, but also concentration of particular impurities in a process system, is usually disadvantageous [6,9]. In the discussed case study (see Table 2) net effect of impurities also turned out to be unfavourable.

Exemplary volumetric (mass) crystal size distributions of the products are presented in Figure 2. From these it results, that raise of pH from 9 (Figure 2(a)) up to 11 (Figure 2(b)) resulted in shift of crystal dominant size ( $L_d$ , maximum of differential distribution), towards smaller values: from 38.0 to 11.6  $\mu\text{m}$ . Size and amount of the largest struvite crystals in a product decreased. The largest crystal size at pH 9 reached 210  $\mu\text{m}$  and then decreased to 50  $\mu\text{m}$  – at pH 11, thus decreased more than four times. Simultaneously the smallest crystals fraction in the product enlarged from 7.4% (pH 9) up to 22.7% (pH 11) – for the particles of size smaller than 5  $\mu\text{m}$ . In result mean size of struvite crystals shrank more than 3 time ( $L_m$  40.1  $\rightarrow$  12.6  $\mu\text{m}$ ). Elongation of mean residence time of suspension up to 3600 s (at pH 9) produced, however, increase in  $L_d$  value of struvite crystals: from 38.0  $\mu\text{m}$  (Figure 2(a)) to 43.7  $\mu\text{m}$  (Figure 2(c)). Maximal crystal size reached 250  $\mu\text{m}$ , larger by 40  $\mu\text{m}$  com-

pared to results for  $\tau$  900 s. Particle fraction of sizes smaller than 5  $\mu\text{m}$  practically not modified in comparison to  $\tau$  900 s (Figure 2(a)) and was 7.3 – 7.4% (Figure 2(c)). In net result, mean crystal size increased by ca. 10  $\mu\text{m}$  (Table 2).

Population density distributions of product crystals which size distributions are presented in Figure 2 are presented in Figure 3. From these distribution courses, presented in  $\ln n - L$  coordinates it results, that for struvite particles of size  $L > 50$   $\mu\text{m}$  (pH 9) and  $L > 10$   $\mu\text{m}$  (pH 11) these courses can be with satisfactory accuracy approximated with linear function. Applying Equation (1) one can thus calculate linear crystals growth rate  $G$ , while from Equation (2) their nucleation rate  $B$ . Parameters of population density distribution functions for struvite crystals of size  $L < 50$   $\mu\text{m}$  or  $L < 10$   $\mu\text{m}$  (Equation (1)) and calculated on this basis  $G$  and  $B$  values are presented in Table 3. Nonlinearity in population density distribution courses for the crystals of size  $L < 50$   $\mu\text{m}$  or  $L < 10$   $\mu\text{m}$  (in  $\ln n - L$  coordinates, Figure 3) speaks about more complex process kinetics than it results from the preliminary assumed SIG MSMPR model [11,12]. Determined this method kinetic parameter values should be regarded as the estimated ones only. It especially concerns nucleation rate values calculated with Equation (2), with the use of significantly devaluated nuclei population density  $n_0$  ( $n(L)$  for  $L = 0$ ). As it results from Figure 3, the differences between  $n_0$  values predicted by

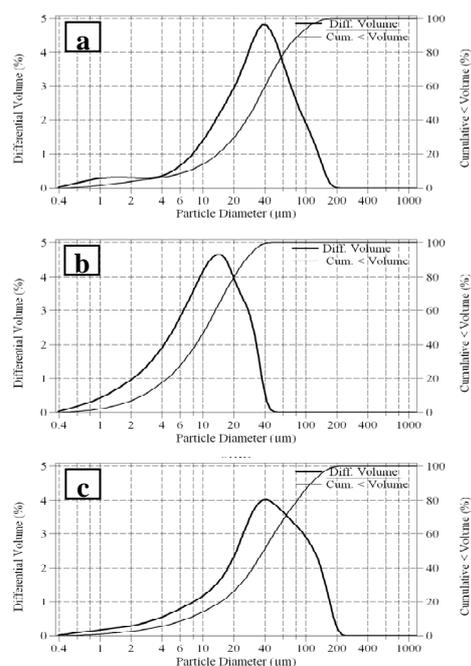
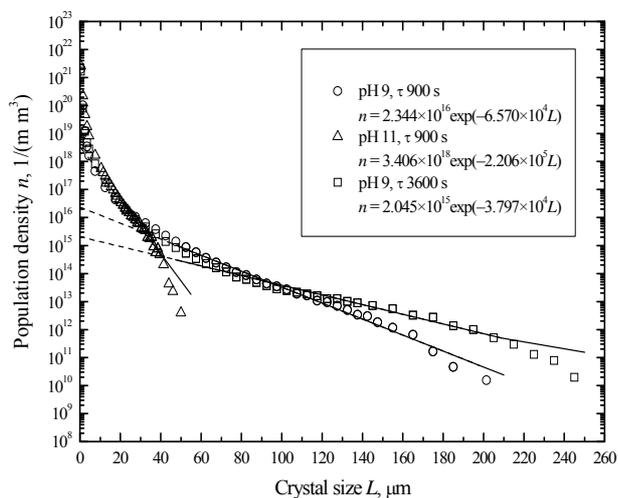


Figure 2. Exemplary differential (left scale) and cumulative (right scale) volumetric (mass) size distributions of crystals products: a) pH 9,  $\tau$  900 s, b) pH 11,  $\tau$  900 s, c) pH 9,  $\tau$  3600 s (corresponding to No. 1, 3 and 5 in Table 2).



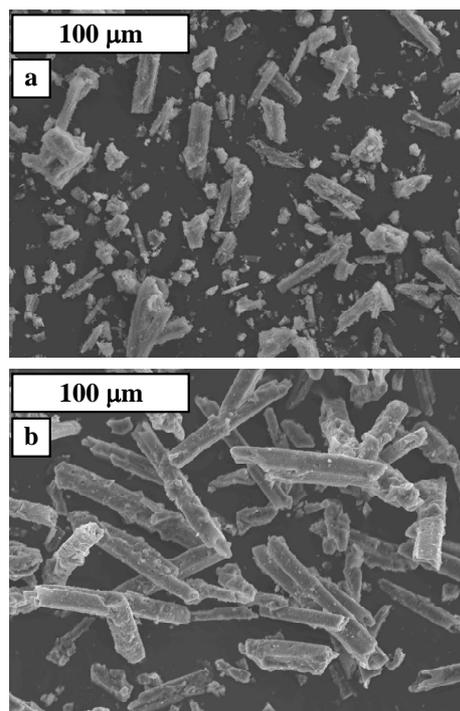
**Figure 3.** Influence of pH and mean residence time of suspension in DT MSPR type crystallizer on population density distribution of crystal product: points – experimental data, dashed lines –  $n(L)$  values calculated with Equation (1) (Table 3) for crystal fractions  $L > 50 \mu\text{m}$  (pH 9) and  $L > 10 \mu\text{m}$  (pH 11).

extrapolation using linear SIG kinetic model and real values reach even  $10^3 - 10^6$ . Calculated nucleation rates of struvite crystals  $B$  are thus useful only for relative, conventional comparison of process parameters influence on its course and results.

Analysing the kinetic data presented in Table 3, one can notice decreasing trend of linear struvite crystal growth rate  $G$  with the increase in environment's pH and with elongation of mean residence time of suspension in the crystallizer. Generally larger crystal growth rates are observed for the shortest mean residence times in apparatus, what is in conformity with the observations concerning the classical continuous mass crystallization processes [11]. Increase in environment pH from 9 to 11 results in decrease of linear struvite crystals growth rate from  $16.9 \times 10^{-9}$  to  $5.04 \times 10^{-9}$  m/s. It is significant decrease of this rate (by more 3 times). It is accompanied by increase in nuclei population density  $n_0$ , thus increase in nucleation rate  $B$  (from  $0.39 \times 10^9$  to  $17 \times 10^9$  1/(s m<sup>3</sup>)). As a consequence final mean crystal size  $L_m$  decreased ( $40.1 \rightarrow 12.6 \mu\text{m}$ ). Elongation of mean residence time of suspension in a crystallizer effectively confined struvite nucleation rate (Table 3). Crystal linear growth rate also decreased, however significantly lower nucleation rate and longer contact time of crystal phase with supersaturated mother solution resulted in visible growth of mean struvite crystal size (Table 2). With the elongation of mean residence time more convenient conditions of mass transfer between the liquid and solid phases established, additionally providing more stable growth of crystal phase. In process conditions characterized by relatively

long mean residence time of suspension in a crystallizer higher quality product is manufactured. However unit productivity is lower, thus economical effectiveness of the production plant is smaller.

Solid products, without water washing of crystals on the filter (ca. 20-25 mass % of mother solution in a filter cake) and after drying, contained mainly struvite, but also hydroxides and salts of impurities from mother solution (indirectly – from synthetic wastewater). In Figure 4 there are presented scanning electron microscope images of the exemplary crystalline products. Diversified sizes of struvite particles are clearly visible. Other solid particles, co-precipitated from wastewater in the process conditions are also visible. The most often these form agglomerates on struvite crystal surfaces. The best shaped struvite crystals, of the most advantageous size distribution, were produced at pH 9 and mean residence time of suspension elongated up to 3600 s (test No. 5 in Table 2, Figure 2(c) and Figure 4(b)). Based on microscope images analysis one can conclude, that struvite crystal surface was taken up by co-precipitated solid particles of hydroxides and impurity salts, what in turn generated large tensions and stresses within struvite crystal structures. Thus many crystal cracks, irregular surfaces, deformed edges, tubular crystals presence, etc. are observed (Figure 4).



**Figure 4.** Scanning electron microscope images of struvite crystals produced from synthetic wastewater in continuous DT MSPR type crystallizer. Process parameters: a) pH 11,  $\tau$  900 s, b) pH 9,  $\tau$  3600 s (corresponding to Figure 2b and c, respectively).

**Table 4. Chemical composition of solid phase and mother solution after filtration of crystal suspension removed from continuous DT MSMPR type crystallizer (see Table 2).**

Component	Concentration in:	
	Mother solution	Solid phase <sup>1</sup> mass %
PO <sub>4</sub> <sup>3-</sup>	15 – 66	37.2 – 40.2
Mg <sup>2+</sup>	31 – 66	8.6 – 9.6
NH <sub>4</sub> <sup>+</sup>	70 – 110	6.5 – 7.0
Al	0.05 – 0.5	0.05 – 0.16
Ca	20 – 60	1.8 – 3.4
Cu	0.002 – 0.004	(6 – 11) × 10 <sup>-4</sup>
Fe	0.005 – 0.008	0.006 – 0.018
K	63 – 160	0.20 – 0.66
Zn	< 0.1	0.09 – 0.18
NO <sub>3</sub> <sup>-</sup>	100 – 150	0.20 – 0.29

<sup>1</sup>after drying, without water washing of crystals on a filter.

Based on planimetric measurement results involving 50 crystals of each product, randomly selected from three scanning electron microscope images it was concluded, that average ratio of their length  $L_a$  to their width  $L_b$  varied from 4.4 to 6.1, depending on the process parameter values (Table 2). Struvite produced in the same crystallizer from aqueous solutions of phosphate (V) ions without impurities characterized with  $L_a/L_b$  ratio ca. 6 (for  $[\text{PO}_4^{3-}]_{\text{RM}}$  1.0 mass %, pH 9 and  $\tau$  900 s) [10]. Increase in pH from 9 to 11 caused, that struvite crystals became clearly shorter and thinner ( $L_a/L_b$  5.4  $\rightarrow$  4.4, see Figure 4(a)). Contrary, elongation of mean residence time of suspension up to 3600 s favoured production of longer and wider crystals, and length  $L_a$  increment was clearly larger than width  $L_b$  increment. The  $L_a/L_b$  ratio increased thus up to 6.1 (see Figure 4(b)). One can assume that struvite crystal sizes and their shape are the net result of wastewater impurities action and parameters of reaction crystallization process. From the microscope images it also results, that agglomeration within struvite crystals was not significant. It generally speaks advantageously about process conditions established in the crystallizer in respect to nucleation and growth of struvite crystals. Taking, however, under consideration all components of struvite continuous reaction crystallization process in DT MSMPR type crystallizer one can notice, that main factor influencing the process course is supersaturation in mother solution, very strongly dependent (at constant composition of feed solution, constant temperature and constant mixing/circulation intensity) on environment pH and on mean residence time of suspension in the crystallizer working volume.

In Table 4 the concentration ranges of components in

the post processed mother solution and in solid phase (without water washing of crystals on the filter and after their drying) removed from the crystallizer were presented. Crystal product, as it results from Table 4, besides main component  $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$ , contained also all impurities present in synthetic wastewater (hydroxides, phosphates (V), chlorides, nitrates (V)). From the data analysis it results, that aluminium, calcium, copper, iron and zinc ions practically totally precipitated (compare concentration of these ions in wastewater (Table 1) and in post processed mother solution (Table 4)).

One can also notice, that concentration of phosphate (V) ions in a post processed mother solution varied from 66 mg/kg (pH 9,  $\tau$  900 s) to 15 mg/kg (pH 9,  $\tau$  3600 s). This concentration values decreased regularly with the pH raise and with elongation of mean residence time  $\tau$  of struvite crystals suspension in the crystallizer. From the comparison it results, that concentration of phosphate (V) ions can be decreased even 4 times. It is connected with decrease of struvite solubility with the rising of reacting mixture pH while longer contact time of crystals with mother solution in a crystallizer is responsible for more thorough discharge of the generated supersaturation. The values of phosphate (V) ions concentration in mother solution can be regarded small, thus effectiveness of their removal from the feed solution as fully satisfactory.

#### 4. Conclusions

The sparingly soluble salt,  $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$ , struvite was produced from synthetic wastewater, simulating wastewater from mineral fertilizer industry, agricultural industry or liquid manure. Process ran in continuous DT MSMPR type crystallizer. Struvite crystals of mean size  $L_m$  from ca. 13 to ca. 50  $\mu\text{m}$  were removed from the crystallizer. It was proved, that increase in pH (from 9 to 11) of struvite reaction crystallization process environment produced decrease of crystal mean size by more than 3 times ( $L_m$  40.1  $\rightarrow$  12.6  $\mu\text{m}$ ,  $\tau$  900 s). Contrary, elongation of mean residence time of suspension in a crystallizer from 900 to 3600 s produced significant enlargement of this characteristic size by ca. 25% ( $L_m$  50.2  $\mu\text{m}$  at pH 9,  $\tau$  3600 s). Products of moderate crystal homogeneity (CV ca. 76%) were removed from the crystallizer. It is complex, net effect of feed chemical composition, pH, mean residence time of suspension, as well as crystals attrition and breakage on the supersaturation level establishing in mother solution.

From the population density distribution of product crystals nucleation rate and linear growth rate of struvite were estimated. It was concluded, that linear crystal growth rate varied within  $5.04 \times 10^{-9} - 16.9 \times 10^{-9}$  m/s range, while nucleation rate changed within the  $0.014 \times 10^9 - 17 \times 10^9$  1/(s m<sup>3</sup>) limits depending on process parameter values. With the increase in environment pH

nucleation rate increased while linear crystal growth rate decreased, what influenced final size of struvite crystals disadvantageously. Elongation of mean residence time of suspension in a crystallizer caused, that both kinetic parameter ( $B$  and  $G$ ) values decreased. On the other hand longer contact time of crystals from the supersaturated mother solution compensated with excess lower crystal growth rate. In result struvite crystals of relatively large sizes were produced.

Concentration of phosphate (V) ions decreased from 1.0 mass % in a feed to 15 – 66 mg/kg in a postprocessed mother solution. It can be regarded as a very good result of their removal process from the feed. In solid product, besides main component – struvite, all impurities from wastewater appeared in form of hydroxides, phosphates and other salts.

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