

# Recovery of Struvite from Phosphorus Mineral Fertilizer Industry Wastewater in Continuous Jet Pump Crystallizer

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**Abstract**—Research results concerning struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP – Magnesium Ammonium Phosphate) reaction crystallization process from phosphorus mineral fertilizer industry wastewater with the use of magnesium and ammonium ions are presented. 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. Laboratory tests were carried out in temperature 298 K, both under stoichiometric conditions and at 20% excess of magnesium ions in relation to phosphate(V) and ammonium ions feed concentrations. Original continuous DTM (*Draft Tube Magma*) type crystallizer with internal circulation of suspension driven by jet pump fed with compressed air was used. Effect of pH and mean residence time of suspension in a crystallizer on the product crystals quality was determined. Product crystals of mean size from ca. 23 to ca. 40  $\mu\text{m}$  were manufactured. The largest struvite crystals, of acceptable homogeneity, were produced at 20% excess of magnesium ions, pH 9 and for mean residence time elongated up to 3600 s. Concentration of phosphate(V) ions decreased from 0.445 mass % in a feed to  $9.0 \cdot 10^{-4}$  mass % in a postprocessed mother liquor. In a product, besides main component – struvite, also amorphous calcium phosphate(V) (ACP) was detected, accompanied with hydroxides of some metal impurities present in wastewater.

**Index Terms**—Struvite, industrial wastewater, continuous reaction crystallization, continuous DTM crystallizer, jet pump, compressed air, product quality, phosphorus recycling.

## I. INTRODUCTION

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , MAP) precipitates in ambient temperature from supersaturated aqueous solutions of magnesium phosphate(V) in presence of ammonium ions, within pH 7–11 (solubility product  $\text{p}K_{\text{sp}} = 9.0 - 13.26$ ) [1]. Process course and results are mainly influenced by: pH, working supersaturation in mother solution, temperature, presence of impurities, mixing intensity and crystallizer construction [2]. In modern processes of phosphorus recycling struvite production results from contacting magnesium and ammonium ions (e.g. aqueous solution of magnesium chloride and some ammonium salt) with

preliminary purified municipal, industrial or agricultural (liquid manure) wastewaters containing phosphate(V) ions. Process runs under precisely determined and controlled hydrodynamic conditions, inside an appropriately designed crystallizer [3]. Besides crucial for environmental protection effect of wastewater purification (eutrophication prevention), separated crystal product is regarded as an important, secondary phosphorus source. Recovered struvite can be further converted or used directly as mineral fertilizer for agriculture [3], [4].

Efficiencies of struvite nucleation and mass crystallization processes are strongly dependent on crystallizer, including: appropriate construction [5], spatial arrangement of reagent inlet places [6] and proper selection of its continuous work parameters [7], [8]. In most DTM (*Draft Tube Magma*) type crystallizers adjustment of working supersaturation can be achieved by arrangement of controlled internal circulation of suspension inside the apparatus [9]. Suspension flow produces homogenisation of temperature and concentration within the process environment, maintains the newly formed and already growing crystals in suspension, as well as prevents their agglomeration. Mechanical device responsible for internal suspension flow in apparatus is usually mixer or circulating pump. Significantly simpler approach, although still rarely used in practice, is application of liquid or gas-liquid jet pump [10]. Hydraulic system of jet pump provides intensive circulation of suspension, thus its good mixing, what affects simultaneous mass and heat transfer processes in a crystallizer advantageously [11].

In typical constructions of liquid jet pump crystallizers [10], [11] working medium is clear mother solution collected from the crystallizer's overflow and introduced through external circulating pump back into crystallizer via the jet pump's feeding nozzle. Circulated mother solution can be, however, replaced with compressed air [12]. Compressed air (or other gaseous factor of required properties) provided into jet pump's feeding nozzle becomes working medium responsible for internal circulation and mixing of suspension. Crystallizer's overflow and external circulating pump are thus redundant. Moreover, the apparatus construction makes removal of suspension of representative, in respect to interior, size distribution (CSD) possible. With some simplifications one can assume, that DTM crystallizer with jet pump fed with compressed air satisfies, approximately, theoretical assumptions of a model MSMR (*Mixed Suspension Mixed Product Removal*) crystallizer [9].

The research results concerning continuous reaction crystallization process of sparingly soluble phosphate(V) salt  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , struvite, are presented. Phosphorus mineral fertilizer industry wastewater containing

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phosphate(V) ions was used as a feed. Research ran in a continuous DTM type crystallizer with gas-liquid jet pump fed with compressed air. Feeding nozzle of a jet pump was located in the apparatus bottom, providing thus upward suspension flow in mixing chamber. Crystallizer was continuously provided with a feed (leachate from phosphogypsum dump in Z.Ch. POLICE S.A., Poland containing 0.445 mass %  $\text{PO}_4^{3-}$  and reacting substances: magnesium chloride and ammonium chloride) 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 isothermal conditions (298 K). Influence of pH (8.5 – 10) and mean residence time of suspension in a crystallizer  $\tau$  (900 – 3600 s) on the product quality was investigated.

## II. MATERIALS AND METHODS

### A. Setup and Procedure

Experimental plant scheme is presented in Fig. 1a. DTM crystallizer with jet pump fed with compressed air was an cylindrical tank made of transparent *Plexiglas* of  $D$  90 mm diameter and of  $H_t$  330 mm total height. Inside the crystallizer jet pump, schematically presented in Fig. 1b, operated. Jet pump's feeding nozzle was provided with experimentally determined [12], minimal volumetric stream of compressed air  $q_{\text{ve}} 0.37 \text{ dm}^3/\text{s}$ , indispensable only for maintaining all solid particles in a permanent movement. Circulation intensity was thus also minimal, so effect of boundary (lower) hydraulic parameters on the process course and results was identified directly. Geometrical details and dimensions of the jet pump system are presented in Fig. 1b.

Raw materials for continuous struvite reaction crystallization process involved: crystalline magnesium chloride hexahydrate  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , crystalline ammonium chloride  $\text{NH}_4\text{Cl}$  (analytical grade, POCh, Gliwice, Poland) and wastewater from phosphorus mineral fertiliser industry (Z.Ch. POLICE S.A., Poland) of pH 3.8 and composition presented in Table I. All raw materials (wastewater,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$ ) were provided into the mixer, where substrates dosed in crystalline form totally dissolved. Mass streams resulted from the assumed: molar ratio  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}}$ , mean residence time  $\tau$  of suspension in a crystallizer and working volume  $V_w$  of the crystallizer applied. Clear solution of the mixed and totally dissolved compounds, of pH 3.6 (stoichiometric ratio of the reagents) or 3.5 (20% magnesium ions excess) was introduced via pump into the crystallizer. Crystallizer was also provided with aqueous solution of NaOH (5 mass %) for adjustment of pH of struvite reaction crystallization environment.

Inlet places of raw materials mixture, alkalisng solution and product suspension outlet are presented in Fig. 1a. Temperature, inlet (feed and alkalisng solution) and outlet (product crystal suspension) streams were strictly controlled and adjusted by computer (software: BioScadaLab). Research ran in temperature  $298 \pm 0.2 \text{ K}$  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). Reagent concentrations in a feed were:

$[\text{PO}_4^{3-}]_{\text{RM}} = 0.445 \text{ mass \%}$ ,  $[\text{Mg}^{2+}]_{\text{RM}} = 0.114 \text{ mass \%}$  and  $[\text{NH}_4^+]_{\text{RM}} = 0.0844 \text{ mass \%}$ , providing their molar ratio 1 : 1 : 1 or 0.445, 0.137 and 0.0844, appropriately, for 20% magnesium ions excess. After stabilization in a crystallizer of the assumed parameter values, process in a steady state ran through the next  $5\tau$ .

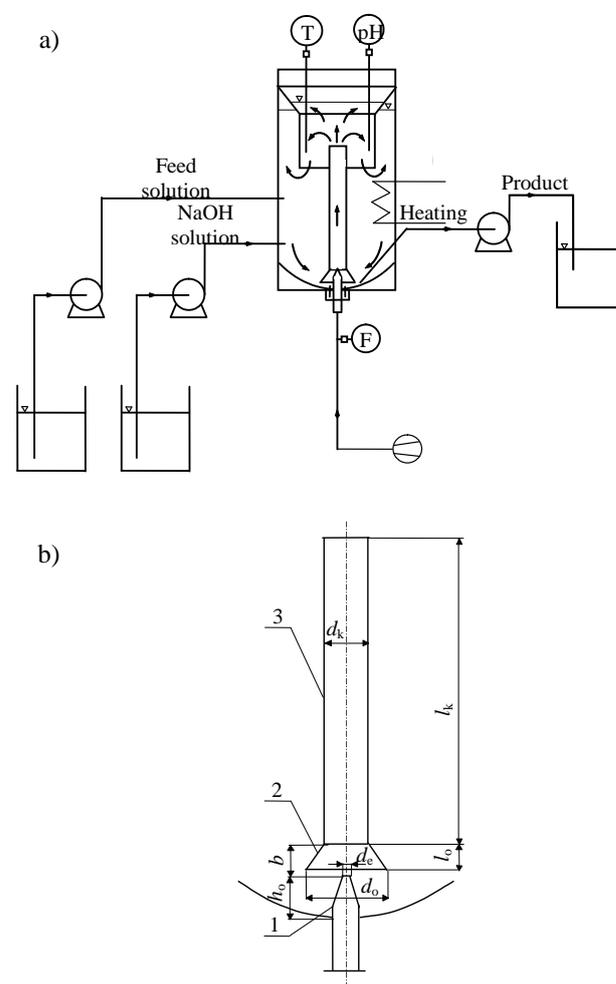


Fig. 1. Scheme of experimental stand (a) and jet pump device driven by compressed ambient air (b): 1 – feeding nozzle, 2 – confusor, 3 – mixing chamber;  $d_k = 15 \text{ mm}$ ,  $l_k = 125 \text{ mm}$ ,  $d_o = 30 \text{ mm}$ ,  $l_o = 12 \text{ mm}$ ,  $d_e = 1.7 \text{ mm}$ ,  $h_o = 25 \text{ mm}$ ,  $b = 0 \text{ mm}$ .

TABLE I: 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	$2.2 \cdot 10^{-4}$
F <sup>-</sup>	$4.2 \cdot 10^{-3}$
$\text{SO}_4^{2-}$	0.0703

## B. Analytical Methods

Chemical composition of mother solution and solid product were determined with atomic absorption spectrometer iCE 3000 (metals), spectrophotometer UV-VIS Evolution 300 (phosphates(V)) and by titration method (ammonium, formalin method). Additionally, for solid phase analysis the X-ray fluorescence spectrometer PANalytical Magi'X PW2424 (phosphorus and metals) was used. Phases identification and quantification in a product were done with X-ray diffractometer PANalytical XPERT PRO MPD according to Rietveld method. Product CSDs were determined with solid particle laser analyser Beckman Coulter LS 13 320. Particle shapes were quantified and evaluated based on computer-aided image analysis (scanning electron microscope JEOL JSM 5800LV). Accuracy in process data determination was estimated to be ca.  $\pm 10\%$ .

## III. RESULTS AND DISCUSSION

### A. Crystal Size Distribution

Product crystals were removed from the DTM crystallizer. Statistical parameters values of their CSDs are presented in Table II. From the table it results (tests No. 1-3) that rise of mother liquor's pH from 8.5 to 10 effected in decrease of crystal mean size  $L_m$  from 33.7 to 23.2  $\mu\text{m}$  (by ca. 31%). The CV coefficient increased from 83.5 to 97.3%. Crystal products manufactured at pH 10 are thus characterized by not only smaller particle sizes, but also lower homogeneity. With the pH increase also nuclei population density increases, resulting in shift of  $L_m$ , and  $L_d$  towards smaller values. Contrary, elongation of mean residence time of suspension in a crystallizer resulted in product mean sizes increase by ca. 18% (tests No. 2, 4 and 5 in Table II). Struvite crystals reached mean size  $L_m$  38.3  $\mu\text{m}$  for mean residence time  $\tau$  3600 s and pH 9. With the mean residence time elongation average supersaturation in mother solution decreased, producing thus decrease of nucleation rate and linear growth rate.

Longer residence time of crystals in supersaturated solution produced, 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 liquor influenced also final CSD advantageously. Homogeneity within product crystals slightly increased. The CV coefficient decreased from 87.8 to 83.3%, despite increase in intensity of co-running attrition and breakage processes in a mixed and circulated suspension.

Magnesium ions excess (related to phosphate(V) and ammonium ions concentrations in a crystallizer feed) produced increase in mean product crystals size  $L_m$ : from 32.5 to 33.8  $\mu\text{m}$  (pH 9,  $\tau$  900 s) and from 38.3 to 39.5  $\mu\text{m}$  (pH 9,  $\tau$  3600 s) (tests No. 2 and 6, 5 and 7 in Table II, respectively). Homogeneity within crystal population slightly decreased. The CV values enlarged from 87.8 to 92.4% and from 83.3 to 85.7%, appropriately. In "pure" aqueous solutions of phosphates(V) excess of magnesium ions influences final struvite crystal sizes disadvantageously [13]. Presence of impurities in a process system (Table I) caused, that final result of continuous struvite reaction crystallization process

was more advantageous (Table II). Some of ionic impurities inhibit struvite nucleation, others catalyse crystals growth and/or modify their shape significantly [14], [15].

Struvite crystals of very diversified sizes were removed from the crystallizer. As it results from Table II, coefficient of crystal size variation CV demonstrated large values within 83.3 – 97.3% range. It may be concluded, that it is net effect of pH and mean residence time of suspension, attrition and breakage within struvite crystals, as well as competitive co-precipitation processes of sparingly soluble hydroxides and impurity salts on the self-establishing working supersaturation level. Attention should be also put on unavoidable oscillations of crystallizer work parameters. These are often reported during tests in spite of permanent computer control/steering of the plant. Also measurement errors during off-line analysis of the dried product's CSD can contribute, as well. Exemplary volumetric (mass) crystal size distributions (CSDs) of the products manufactured under stoichiometric conditions are presented in Fig. 2a-Fig. 2b (pH 9 (Fig. 2a) and pH 10 (Fig. 2b) for  $\tau$  900 s) whereas at 20% magnesium ions excess – Fig. 2c (pH 9 for  $\tau$  3600 s). From comparison of these CSDs it results, that local maxima in differential distribution curves are not observed. Thus in the whole range of crystal sizes no excessive number of particles was reported. It speaks well for stable (steady-state) run of continuous reaction crystallization process of main component – struvite. Mixing degree of crystal suspension in a crystallizer can be thus regarded as satisfactory in respect to concentration/ working supersaturation homogenisation in mother liquor. One can also assume, that potential local supersaturation maxima (at alkalisng solution and feed inlet places) are instantaneously and effectively discharged through the mixed and circulated suspension. With the pH increase dominant crystal size  $L_d$  (corresponding to maximum in differential size distribution) shifts towards smaller values: 31.5  $\mu\text{m}$  (pH 8.5), 28.7  $\mu\text{m}$  (pH 9) and 23.8  $\mu\text{m}$  (pH 10) ( $\tau$  900 s, Table II). Number and size of the largest crystals in a product decrease. The largest size of struvite particles produced at pH 8.5 is ca. 165  $\mu\text{m}$ , at pH 9 – ca. 160  $\mu\text{m}$  (Fig. 2a), while at pH 10 only ca. 140  $\mu\text{m}$  (Fig. 2b). Simultaneously fraction of the smallest particles enlarges. In a product manufactured at pH 8.5 crystal fraction of sizes below 5  $\mu\text{m}$  was 10.5 vol. %, at pH 9 – 12.9 vol. %, while at pH 10 it increased up to 18.3 vol. %, thus enlarged nearly 2-time. In effect crystal mean size  $L_m$  considerably decreased from 33.7 to 23.2  $\mu\text{m}$  (see Table II). Elongation of mean residence time of suspension in a crystallizer from 900 to 3600 s (at constant pH 9) resulted that dominant crystal size  $L_d$  increased from 28.7 to 37.2  $\mu\text{m}$ , while the largest particles sizes – from ca. 160 to 185  $\mu\text{m}$ . Crystal fraction of sizes < 5  $\mu\text{m}$  decreased (from 12.9 to 12.2 vol. %), despite that crystals attrition and breakage in circulated suspension are more pronounced with elongation of mean residence time. Excess of magnesium ions, together with the possible longest mean residence time  $\tau$  3600 s, influenced product's CSD advantageously (Fig. 2c). Dominant size  $L_d$  enlarged by 0.8  $\mu\text{m}$ , the largest crystals reached 190  $\mu\text{m}$ , while fraction of sizes < 5  $\mu\text{m}$  shrank by 1.8% (to 10.4 vol. %) (tests No. 5 and 7, Table II).

TABLE II: INFLUENCE OF SELECTED TECHNOLOGICAL PARAMETERS OF CONTINUOUS STRUVITE REACTION CRYSTALLIZATION PROCESS ON THE PRODUCT QUALITY (PHOSPHORUS MINERAL FERTILIZERS INDUSTRY WASTEWATER PROCESSED IN DTM CRYSTALLIZER WITH A JET PUMP DRIVEN BY COMPRESSED AIR PROCESS TEMPERATURE: 298 K)

No.	Process parameters		Suspension in a crystallizer		Crystal characteristic			
	pH (–)	$\tau$ (s)	$[\text{PO}_4^{3-}]_{\text{solution}}$ (mg/kg)	$[\text{PO}_4^{3-}]_{\text{crystals}}$ (mass %)	$L_m$ ( $\mu\text{m}$ )	$L_d$ ( $\mu\text{m}$ )	CV (%)	$L_a/L_b$ (–)
Molar proportion 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	64.1	39.8	33.7	31.5	83.5	4.8
2	9	900	48.0	39.9	32.5	28.7	87.8	4.8
3	10	900	36.1	41.1	23.2	23.8	97.3	4.6
4	9	1800	32.0	40.9	36.7	34.6	83.9	5.0
5	9	3600	22.1	41.3	38.3	37.2	83.3	5.2
Molar proportion 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	18.5	40.8	33.8	32.6	92.4	5.2
7	9	3600	9.0	42.0	39.5	38.0	85.7	5.5

Average crystal content in suspension:  $M_T 11.1 \pm 0.3$  kg of crystals/ $\text{m}^3$  of suspension;

$L_m = \sum x_i L_i$ , 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;  $L_a$  – crystal length;  $L_b$  – crystal width.

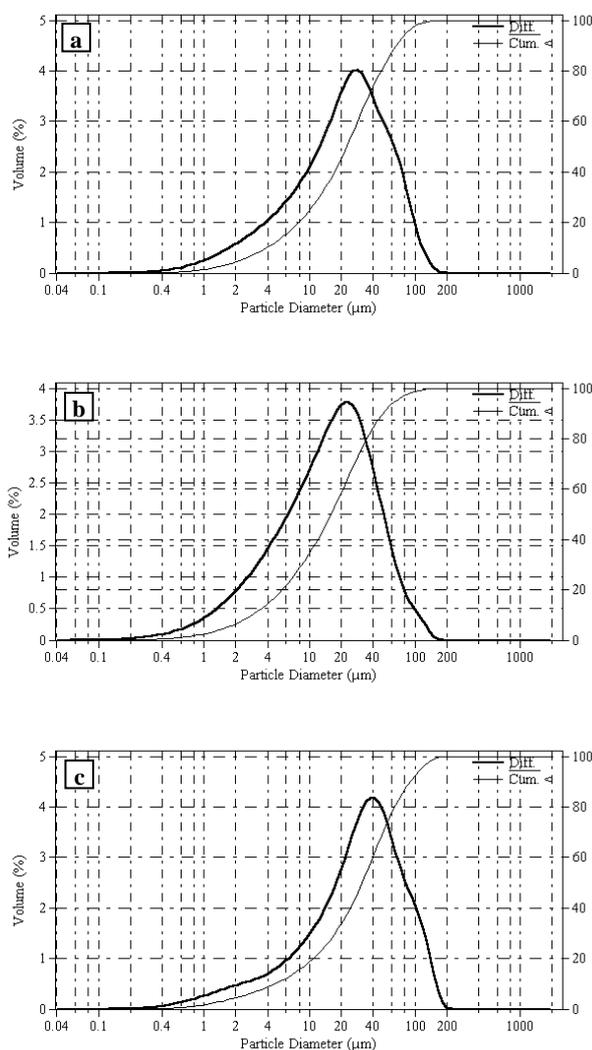


Fig. 2. Exemplary differential (left scale) and cumulative (right scale) volumetric (mass) crystal size distributions (CSDs) of struvite produced from phosphorus mineral fertilizers industry wastewater in a continuous DTM crystallizer with a jet pump driven by compressed air stream. Process parameters:  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$ , pH 9,  $\tau$  900 s, (a), and pH 10,  $\tau$  900 s (b);  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$ , pH 9,  $\tau$  3600 s, (c) (see No. 2, 3 and 7 in Table II).

### B. Crystal Shape

Scanning electron microscope images of exemplary crystal products are presented in Fig. 3 (corresponding CSDs – Fig. 2a, c). Diverse sizes of struvite particles are clearly observable. Also other solids, co-precipitated from wastewater in identical process conditions can be identified. The most often these form surface agglomerates on the parent struvite crystal surfaces. Struvite crystals are just totally covered with co-precipitated hydroxides of metal impurities, calcium phosphates(V) and other salts. The best formed struvite crystals, of the most advantageous size distribution (like presented in Fig. 2c), were manufactured at low pH (8.5 – 9), elongated mean residence time  $\tau$  (3600 s) and at 20% excess of magnesium ions in a feed (Fig. 3b). Moreover, in the conditions tested crystals length  $L_a$  to their width  $L_b$  ratio varied from 4.6 to 5.5 (Table II).

The  $L_a/L_b$  values were calculated based on planimetric measurements covering 50 crystals randomly selected from three different microscope images of the same product sample. Based on analysis of these images one can conclude, that surface of parent struvite crystals was “insulated” by co-precipitated hydroxides and impurity salts. It possibly generated large tensions in struvite crystal structures. In result numerous crystal ruptures, irregular surfaces, deformed edges, presence of tubular crystals and trough-shape crystals, etc. were observed (Fig. 3). Crystals shape, however, did not clearly deviate from classical shape of struvite crystals produced from pure aqueous solutions of phosphates(V) ( $L_a/L_b$  ca. 6). One can assume, that struvite crystal sizes and shapes demonstrate the net effect of impurities present in the investigated wastewater, as well as net effect of struvite reaction crystallization process parameters. From microscope images it also results, that agglomeration within struvite crystals was not significant. Attrition and breakage during mixing and circulation in a crystallizer can be regarded moderate. It speaks generally advantageously about process conditions established in a crystallizer in respect to nucleation and growth of struvite crystals. Original construction of jet

pump DTM crystallizer (absence of moving parts), its work mode (suspension mixing and circulation by jet pump fed with compressed air) and relatively small solid phase content in suspension ( $M_T$  ca. 11 kg struvite/m<sup>3</sup>) did not contribute excessive crystal attrition and breakage. Taking under consideration all components of struvite reaction crystallization process in DTM crystallizer one can notice, that main factor influencing the process course is solution supersaturation, very strongly dependent (at constant: feed composition, temperature and mixing/circulation intensity) on pH and mean residence time of suspension in a crystallizer working volume.

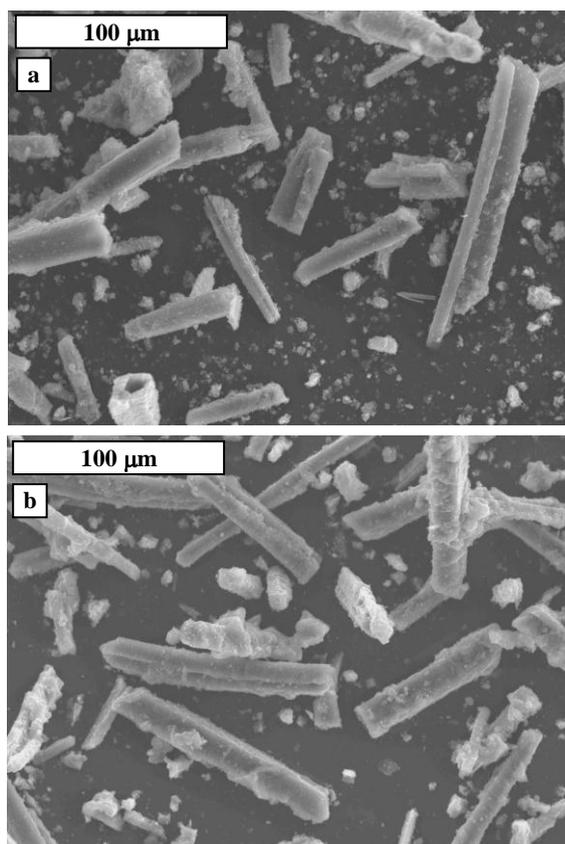


Fig. 3. Scanning electron microscope images of struvite crystals produced from phosphorus mineral fertilizers industry wastewater in continuous DTM crystallizer. Process parameters:  $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$  in a feed, 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).

### C. Chemical Composition

Product phase composition was determined with X-ray tests (X-ray diffractometer). It resulted, that the product contained 58 – 63 mass % of struvite  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , as well as amorphous calcium phosphate(V) (ACP) (37 – 42 mass %). Component concentrations in a postprocessed mother liquor and in solid phase (without water washing of crystals on a filter and after their drying) are presented in Table III.

Crystal product, as it results from Table III, besides struvite and calcium phosphate(V) contained practically all impurities from the wastewater: metal hydroxides, fluosilicates, fluorides, sulphates and others. At magnesium ions excess practically total precipitation of aluminium, calcium, copper, iron and zinc ions was reported (compare initial concentrations of these ions in wastewater (Table I) and in postprocessed mother liquor (Table III)). Concentration of

phosphate(V) ions in a postprocessed mother liquor varied from 64.1 mg/kg (pH 8.5,  $\tau$  900 s) to 22.1 mg/kg (pH 9,  $\tau$  3600 s) (tests range: No 1 – 5 in Table II). Generally these concentration values decreased systematically with pH rise and with elongation of mean residence time  $\tau$  of struvite crystal suspension in a crystallizer. From the comparison it results, that concentration of phosphate(V) ions decreased even 3-time. It results from decrease of struvite solubility with the increase in reacting mixture's pH and longer contact time of crystals with supersaturated solution (more thorough discharge of the supersaturation). The  $[\text{PO}_4^{3-}]_{\text{solution}}$  values can be regarded small, while overall efficiency of phosphate(V) ions removal from the feed (above 98%) as a fully satisfactory.

TABLE III: CHEMICAL COMPOSITION – COMPONENT CONCENTRATION RANGES IN SOLID PHASE AND IN MOTHER SOLUTION AFTER FILTRATION OF CRYSTAL SUSPENSION REMOVED FROM CONTINUOUS DTM CRYSTALLIZER WITH A JET PUMP DRIVEN BY COMPRESSED AIR STREAM

Component	Concentration – mother solution (mg/kg)	Solid phase* (mass %)
$\text{PO}_4^{3-}$	9.0 – 64.1**	39.8 – 42.0**
$\text{Mg}^{2+}$	30 – 240	9 – 10
$\text{NH}_4^+$	75 – 115	6.5 – 7.0
Al	0.1 – 0.3	$(4.8 – 5.5) \cdot 10^{-2}$
Ca	< 50	2.5 – 4.0
Cu	0.02 – 0.10	$(0.6 – 1.3) \cdot 10^{-4}$
Fe	0.03 – 0.07	0.10 – 0.20
K	25 – 39	0.12 – 0.22
Si	25 – 42	$(8.6 – 9.7) \cdot 10^{-2}$
Ti	< 0.2	$< 2 \cdot 10^{-5}$
Zn	< 0.5	$(1.6 – 1.9) \cdot 10^{-2}$
$\text{F}^-$	2 – 24	0.35 – 0.48
$\text{SO}_4^{2-}$	400 – 560	1.5 – 1.8

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

\*\* see Table II

Magnesium ions excess influenced process yield advantageously (tests No. 6 and 7, Table II). Concentration of phosphate(V) ions in a postprocessed mother liquor was even ca. 2-time smaller than maximal result achievable under stoichiometric conditions.

### IV. CONCLUSIONS

Research results concerning struvite reaction crystallization from phosphorus mineral fertilizer industry wastewater are presented. Continuous DTM type crystallizer with internal circulation of suspension induced by jet pump fed with compressed air was used. The research results can be appraised positively. Crystallizer worked stable in a continuous work regime. Its original construction, lack of moving parts, mixing and circulation of suspension driven by compressed air did not cause excessive attrition and breakage within crystal phase. It was concluded, that crystal product homogeneity depended significantly on the technological parameters (pH, mean residence time of suspension, excess of magnesium ions in a feed), as well as on chemical composition of the wastewater.

Struvite crystals of mean size  $L_m$  from ca. 23 to ca. 40  $\mu\text{m}$  were removed from DTM crystallizer. It was identified, that increase in pH (from 8.5 to 10) of struvite reaction crystallization environment produced decrease of crystal mean size by ca. 31% ( $L_m$  33.7  $\rightarrow$  23.2  $\mu\text{m}$ ,  $\tau$  900 s). Contrary, elongation of mean residence time of suspension from 900 to 3600 s caused significant enlargement of this size by ca. 18% ( $L_m$  38.3  $\mu\text{m}$  at pH 9 and  $\tau$  3600 s). Crystal products of small size-homogeneity were removed from the crystallizer (CV 83 – 97%). It is effect of complex, net influence of pH and mean residence time of suspension, contributed by attrition and breakage, on the supersaturation level in mother liquor.

Excess of magnesium ions in a process system influenced the struvite reaction crystallization process yield strongly and advantageously. Concentration of phosphate(V) ions decreased from 0.445 mass % in a feed even to  $9.0 \cdot 10^{-4}$  mass % in a postprocessed mother liquor, what can be regarded as a very good recycling result. It was also correlated with enlargement of mean size of product crystals ( $L_m$  up to 39.5  $\mu\text{m}$ ).

Product consisted of crystal (struvite, MAP) and amorphous phases (calcium phosphate(V), ACP, as well as hydroxides of same metal impurities). Mean content of struvite in product samples was ca. 60%. Aluminium, copper, iron and zinc ions practically totally precipitated. Direct application of such product in agriculture is limited, however part of these impurities can be regarded as the soil enriching components.

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