Reaction crystallization of struvite in a continuous draft tube magma (DTM) crystallizer with a jet pump driven by recirculated mother solution

A. Mazienczuk\textsuperscript{a}, A. Matynia\textsuperscript{a} a*, K. Piotrowski\textsuperscript{b}, B. Wierzbowska\textsuperscript{a}

\textsuperscript{a}Wroclaw University of Technology, Faculty of Chemistry, Wybrzeze Wyspianskiego 27, 50–370 Wroclaw, POLAND
\textsuperscript{b}Department of Chemical & Process Engineering, Silesian University of Technology, ks. M. Strzody 7, 44–101 Gliwice, POLAND

Abstract

Reaction crystallization of struvite from water solutions containing 1.0 mass % of phosphate(V) ions by means of magnesium and ammonium ions action was investigated experimentally. The process was carried out in a DTM type crystallizer with liquid type jet pump in temperature 298 K assuming stoichiometric conditions. Struvite crystals of mean size $L_m$ from 4 to 22.4 $\mu$m were produced depending on pH (pH from 9 to 11) and mean residence time of suspension in a crystallizer vessel ($\tau$ from 900 to 3600 s). In such process conditions linear growth rate of struvite crystals, calculated with SIG MSMPR kinetic model, decreases 2-time with the increase in pH level and 3-time with the elongation of mean residence time of suspension in a crystallizer, namely from $7.15 \times 10^{-9}$ m/s (pH 9, $\tau$ 900 s) to $1.16 \times 10^{-9}$ m/s (pH 11, $\tau$ 3600 s). Nucleation rate changed within the $9.3 \times 10^8$ – $9.0 \times 10^9$ 1/(sm$^3$) range. Crystal product of the best formed crystals, which maximal sizes reached 90 $\mu$m while content of crystals of sizes below 3 $\mu$m was ca. 12%, corresponded to pH 9 and mean residence time of suspension in a crystallizer 3600 s.

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Keywords: Struvite; crystal size distribution; reaction crystallization kinetics; continuous DTM type crystallizer; jet pump

* Corresponding author. Tel.:+48–71–320–34–97.
E–mail address: andrzej.matynia@pwr.wroc.pl
Nomenclature

- $B$ – nucleation rate, $1/(m^3s)$;
- $CV$ – coefficient of (crystal size) variation, defined as $100(L_{84} - L_{16})/(2L_{50})$, %;
- $G$ – linear growth rate of crystals, $m/s$;
- $H_t$ – total height of a crystallizer, $m$;
- $H_w$ – height of the crystallizer’s working part, $m$;
- $k_v$ – volumetric shape factor of crystal;
- $K_{sp}$ – struvite solubility product;
- $L$ – characteristic linear size of crystal, $m$;
- $L_d$ – dominant crystal size, $m$;
- $L_i$ – mean size of $i$–th crystal fraction, $m$;
- $L_m$ – mean size of crystal population, defined as $\Sigma x_i L_i$, $m$;
- $L_{50}$ – median crystal size for 50 mass % undersize fraction, $m$;
- $\Delta L_i$ – size range of $i$–th crystal fraction, $m$;
- $m_i$ – mass of $i$–th crystal fraction, kg;
- $m(L)$ – mass crystal size distribution;
- $M_T$ – crystal content in suspension (suspension density), $kg_{cryst}/m^3$;
- $[Mg^{2+}]_{RM}$ – inlet concentration of magnesium ions, mass %;
- $[NH_4^+]_{RM}$ – inlet concentration of ammonium ions, mass %;
- $[PO_4^{3-}]_{RM}$ – inlet concentration of phosphate(V) ions, mass %;
- $n_0$ – nuclei (zero–size crystals) population density, $1/(m \cdot m^3)$;
- $n_i$ – population density of $i$–th crystal fraction, $1/(m \cdot m^3)$;
- $n(L)$ – population density (number of crystals within the specified size range in unit volume of the suspension per this size range width), $1/(m \cdot m^3)$;
- $P_{eu}$ – unit power of the liquid stream feeding the jet pump, W/kg;
- $q_v$ – volumetric (out)flow rate of crystal suspension from the crystallizer, $m^3/s$;
- $T$ – process temperature, K;
- $V_i$ – volume of $i$–th crystal fraction, $m^3$;
- $V_w$ – crystallizer working volume, $m^3$;
- $V(L)$ – volumetric crystal size distribution;
- $x_i$ – mass fraction of the crystals of mean fraction size $L_i$. 
Greek letters
\( \tau \) – mean residence time of suspension in a crystallizer working volume, defined as \( V_w/q_w \), s;
\( \rho \) – density of crystals, kg/m³.

Abbreviations
CSD – Crystal Size Distribution
DTM – Draft Tube Magma (crystallizer)
MSMPR – Mixed Suspension Mixed Product Removal (crystallizer)
SIG – Size–Independent Growth (kinetic growth model)

1. Introduction

Running low of natural phosphorus resources leans towards searching of efficient methods of its recovery from abundant secondary sources, including industrial, municipal and agricultural liquid wastes. Attractive method of phosphorus recycling can be based on controlled reaction crystallization of struvite resulting from appropriate contacting of magnesium and ammonium ions (e.g. water solution of magnesium chloride and ammonium salt) with sewages of various origins, as well as with liquid manure rich in phosphate(V) ions \[1\]. Struvite, magnesium ammonium phosphate(V) hexahydrate \( \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \), MAP, precipitates as a sparingly soluble salt (solubility product \( pK_{sp} = 9.4 \sim 13.26 \)) within pH 7 – 11 range \[2, 3\]. Struvite reaction crystallization course and results are mainly dependent on pH, concentrations of components in solution, working supersaturation level and mixing intensity/crystallizer vessel configuration \[1\sim6\]. The crystalline product can be directly used in agriculture as a valuable, balanced mineral fertilizer, slowly releasing its nutrient contents \[7\].

In most crystallizer constructions adjusting/control of working supersaturation level is achieved by induction inside the apparatus the controlled internal circulation of suspension (Draft Tube Magma – DTM crystallizers). Permanent magma movement produces better even out of temperature and concentrations within the whole process environment, suspends nucleated and growing up crystals, as well as effectively prevents their aggregation/agglomeration \[8\]. Mixing device responsible for required internal flow of recirculated magma in the apparatus working volume is usually mixer or internal circulation pump \[8, 9\]. Also jet pump can be effectively applied for such purpose \[9\sim11\]. In jet pump crystallizers, working medium can be a possibly clarified mother solution, collected from the crystallizer’s overflow and referred further via external circulation pump loop back into the jet pump feeding nozzle.

The experimental research results concerning reaction crystallization of struvite from diluted water solutions of phosphate(V) ions in a continuous DTM type crystallizer with internal circulation of suspension resulting from liquid jet pump action, inducing ascending flow of suspension in a mixing chamber are presented and discussed. In such constructional arrangement feeding nozzle of jet pump was fixed at the bottom of DTM crystallizer.

From the product crystal size distributions (CSDs) the fundamental kinetic parameter values of the process, corresponding to various technological conditions, were estimated. Calculations were based on the most simplified kinetic model of continuous mass crystallization in MSMPR (Mixed Suspension
Mixed Product Removal) crystallizer configuration – SIG (Size Independent Growth) model, assuming that linear growth rate of all crystals is identical, size-independent, and resulting only from the process conditions (supersaturation) [12].

2. Experimental

2.1. Setup and Procedure

A flow scheme of the measurement stand designed for the experiments, covering reaction crystallization of struvite, is presented in Fig. 1a. Total height of the whole crystallizer construction was \( H_t = 330 \text{ mm} \), while its working part’s was \( H_w = 220 \text{ mm} \). Crystallizer working volume was \( V_w = 1.2 \text{ dm}^3 \). A liquid jet pump device installed in a laboratory crystallizer is presented in Fig. 1b.

Crystallizer was continuously provided with a feed of concentration 1.0 mass % of phosphate(V) ions and – in stoichiometric proportions – with other ions of concentrations: [Mg\(^{2+}\)]\(_{RM}\) = 0.256 and [NH\(_4^+\)]\(_{RM}\) = 0.190 mass %, respectively. Initially blended liquid reagents were introduced into the process environment as ammonium dihydrogenphosphate(V) NH\(_4\)H\(_2\)PO\(_4\), magnesium chloride MgCl\(_2\)·6H\(_2\)O (both from p.a., POCh, Gliwice, Poland) and deionized water (Barnstead – NANOpure Diamond). Process temperature was 298 ±0.2 K, while environment’s pH was adjusted with water solution of NaOH (5 mass %) to 9, 10 and 11 (±0.1), depending on the current test requirements. Mean residence time \( \tau \) of suspension in a crystallizer working volume was changed from 900 to 3600 s (±20 s). Process temperature, pH and inlet/outlet stream flows (feed solution / product crystal magma) were strictly controlled with PC computer driven by IKA Labworldsoft software. Inlet ports of the reagents mixture and alkaline agent solution, as well as isokinetic product suspension’s outlet are schematically marked in Fig. 1a. For providing effective enough and stable internal circulation of suspension, the possibly minimal value of unit power of the liquid stream feeding the jet pump was assumed, \( P_{eu} = 0.25 \text{ W/kg} \) [13]. The resulting internal circulation intensity was thus also minimal, what limited attrition and breakage within the bulk crystal magma advantageously.

![Fig. 1. Scheme of experimental stand (a) and jet pump device in the DTM type crystallizer (b): 1 – feeding nozzle, 2 – confuzor, 3 – mixing chamber; \( d_k = 15 \text{ mm}, l_k = 125 \text{ mm}, d_o = 30 \text{ mm}, l_o = 12 \text{ mm}, d_e = 2 \text{ mm}, h_o = 25 \text{ mm}, b = 0 \text{ mm} \)](image-url)
assumed process parameter values). After this time the whole crystallizer content was transferred into a vacuum filter for mother liquor drainage. The crystals – not washed – were weighed before and after drying. Also mass and volume of mother solution were determined analytically. This way solid phase content in a product crystal suspension \( (M_T) \) could be calculated. Product CSD was determined with solid particle analyzer COULTER LS–230, whereas crystal habits were evaluated from scanning electron microscope JEOL JSM 5800LV images. Chemical composition of mother solution and solid phase were determined applying, among others, plasma emission spectrometer ICP–AES CPU 7000, spectrometer IR PU9712, and spectrophotometer UV–VIS Evolution 300. Accuracy of measurement data collected in this continuous laboratory plant was estimated to be 10–15%. Thus in Table 1 mean values of \( M_T \) and phosphate(V) ions concentration in a postprocessed mother solution are provided.

2.2. Kinetic parameters

Automatically determined with the use of solid particle analyzer COULTER LS–230 product CSDs were then converted into population density distributions \( n(L) \) [1]. Individual population density values, \( n_i \), were determined based on the original mass \( m(L) \) (or volumetric, \( V(L) \)) size distribution data according to Equation (1):

\[
n_i = \frac{m_i}{k_i \rho L_i^3 \Delta L_i V_w} = \frac{V_i}{k_i L_i^3 \Delta L_i V_w}
\]

Elaboration of the experimental data was based on a SIG kinetic model, Equation (2) [12]:

\[
n(L) = n_0 \exp \left( -\frac{L}{G \tau} \right)
\]

Equation (2) enables one to determine the values of fundamental kinetic parameters of a continuous mass (reaction-)crystallization process in a theoretically idealized MSMPR crystallizer configuration – nucleation and growth rates. Plot of \( \ln n \) versus \( L \) gives a straight line with an intercept at \( L = 0 \) equal to \( \ln n_0 \), while its slope is interpreted as \( -1/G \tau \). If the mean residence time of suspension, \( \tau \), can be experimentally adjusted with satisfactory accuracy (e.g. by computer control system), linear growth rate of crystals, \( G \), can be calculated directly.

From the nuclei population density, \( n_0 \), and linear growth rate, \( G \), the value of nucleation rate \( B \) can be determined, Equation (3):

\[
B = n_0 G
\]

3. Results and Discussion

The research results are presented in Table 1. From these data it results, that with the increase in pH of struvite reaction crystallization environment, product crystal sizes decrease. Raise of pH from 9 to 11 produces ca. 3-time decrease of mean crystal size, \( L_m \) (for \( \tau = 900 \) s: \( L_m = 12.9 \rightarrow 4.0 \) \( \mu m \), for \( \tau = 3600 \) s: \( L_m = 22.4 \rightarrow 8.6 \) \( \mu m \)).

Increase in pH level produces increase in population density of struvite nuclei (see Table 2, No 4–9), resulting thus in a corresponding shift of mean crystal size towards lower values.

The 2-time elongation of mean residence time of suspension in a crystallizer (from 900 to 1800 s) at pH 9 makes that mean crystal size increases by ca. 67%: \( L_m = 12.9 \rightarrow 21.6 \) \( \mu m \). Such change in the process conditions (assuming constant values of other parameters) produces decrease of working
supersaturation in a process medium, thus lowering the nonlinearly correlated with it nucleation rate $B$ (see Table 2).

Table 1. Influence of selected technological parameters of struvite reaction crystallization process in a continuous DTM crystallizer with a liquid jet pump on the crystal product properties.

<table>
<thead>
<tr>
<th>No.</th>
<th>Process parameters</th>
<th>Crystal product characteristics</th>
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<tbody>
<tr>
<td></td>
<td>pH</td>
<td>$\tau$, s</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>900</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>900</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>900</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>1800</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>1800</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>1800</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>3600</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>3600</td>
</tr>
<tr>
<td>9</td>
<td>11</td>
<td>3600</td>
</tr>
</tbody>
</table>

Reagent concentrations in a crystallizer feed (RM): $[\text{PO}_4^{3-}]_{\text{RM}} = 1.0$ mass %, $[\text{Mg}^{2+}]_{\text{RM}} = 0.256$ mass %, $[\text{NH}_4^+]_{\text{RM}} = 0.190$ mass %

Mean concentration of phosphate(V) ions in a postprocessed (outlet) mother solution: 0.012 ±0.002 mass %

Mean concentration of crystal phase in a product magma $M_{\text{f}}$: 25.0 kg of struvite/m$^3$ of suspension

Longer mean residence time of suspension in a flow apparatus is, however, also responsible for the establishment of more advantageous conditions for the crystals growth. Reduction of supersaturation level in mother solution causes also decrease of linear crystal growth rate, nevertheless elongation of mean residence time compensates this fall in excess, providing longer and more stable growth process within crystalline solids. It is also responsible for, especially at longer mean residence times, increase in attrition and breakage intensities within larger crystals (e.g. for $\tau$ 3600 s at pH 9: $L_{\text{mm}} = 22.4$ $\mu$m, thus increase in this size by ca. 4% only in relation to $L_{\text{mm}} = 21.6$ $\mu$m for $\tau$ 1800 s was reported). At higher pH levels (10 – 11) smaller increments in mean particle size with the elongation of mean residence time of magma in a crystallizer were observed (see Table 1). Elongation of this time from 900 up to 1800 s produced, at pH 10, increase in $L_{\text{mm}}$ by ca. 35%. This way the disadvantageous influence of process environment’s pH on linear growth rate of struvite crystals is demonstrated in such defined process conditions (see Table 2).

Simultaneous influence of reaction crystallization environment’s pH (within the 9 – 11 range) and mean residence time of suspension in a crystallizer ($900 < \tau < 3600$ s) on mean crystal size of struvite (in $\mu$m) can be presented in a form of empirical design correlation, Equation (4):

$$L_{\text{mm}} = 2.49 \times 10^5 \text{pH}^{-5.72} \tau^{0.422}$$

with $R^2 = 0.888$ and mean relative error ±19.8%. Graphical projection of equation (4) is presented in Fig. 2.

Struvite crystals of strongly diversified sizes were removed from the crystallizer. As it results from the data presented in Table 1, the coefficient of crystal size variation (CV) reached high values, however concentrated within the relatively narrow range: 88.6 – 99.6%. None unequivocal dependence of size-homogeneity within the product crystal population on main process parameters (pH, $\tau$) could be determined statistically. It may be assumed, that it is a resulting complex, net effect of pH and mean residence time of suspension, accompanied by attrition and breakage within the bulk struvite crystal
magma on the level of working supersaturation in a crystallizer, provided by intrinsic process feedbacks. It should be also noticed, that some contribution results from unavoidable oscillations of crystallizer working parameters ($T \pm 0.2$ K, pH $\pm 0.1$, $\tau \pm 20$ s), in spite of permanent computer-aided control of experimental plant, as well as from systematic errors in dried products analysis and elaboration of its CSDs.

Both crystallizer construction and its characteristic work mode are responsible for the fact, that some fraction of the smallest struvite crystals reaches the crystallizer’s external loop and circulation pump interior, where these elongated crystals are subject of additional attrition and breakage – not reflecting the hydrodynamic conditions established within the crystallizer working volume itself. In result, crystals of lower size-homogeneity and demonstrating lower mean sizes compared to solid products from other types of crystallizers with internal circulation of suspension are produced [4, 6]. To possibly maximally confine this phenomenon, minimal value of unit power of a jet pump feeding stream ($P_{eu} = 0.2$ W/kg) was assumed for the experiments.

Some exemplary volumetric (mass) struvite CSDs produced at pH 9 for $\tau$ 900 s and 3600 s are presented in Fig. 3. With the increase in mean residence time of suspension in a crystallizer, crystal dominant size ($L_{dm}$, corresponding to maximum in differential distribution) shifts towards larger crystal sizes: from 12.4 $\mu$m ($\tau$ 900 s) up to 26.1 $\mu$m ($\tau$ 3600 s). Both number and size of the largest crystals in the product population increase. The largest size of struvite crystals produced at pH 9 and $\tau$ 900 s is ca. 70 $\mu$m (Fig.
3a), while at $\tau = 3600$ s – ca. 90 $\mu$m (Fig. 3b). Simultaneously fraction of crystals of the smallest sizes decreases. In struvite crystals produced at $\tau = 900$ s crystal fraction of sizes below 3 $\mu$m was 16.7%, while for $\tau = 3600$ s it decreased to 12.3% (thus 26% drop is observed). In result, mean crystal size $L_m$ increased considerably from 12.9 to 22.4 $\mu$m (see Table 1).

![Scanning electron microscope images of struvite crystals](image)

Fig. 4. Exemplary scanning electron microscope images of struvite crystals produced in DTM MSMPR crystallizer with a liquid jet pump for pH 9: a) $L_m = 12.9$ $\mu$m ($\tau = 900$ s), b) $L_m = 22.4$ $\mu$m ($\tau = 3600$ s), magnification 2500x, cf. Fig. 3 for size distribution details.

Scanning electron microscope images of struvite crystals, corresponding to CSDs from Fig. 3, are presented in Fig. 4. Larger sizes of particles produced at longer residence time of suspension in a crystallizer are observed clearly (Fig. 4b). From the analysis of crystal images it also results, that with the elongation of mean residence time the struvite crystals become thinner and longer. Their agglomeration degree decreases, as well. Attrition and breakage of crystals during their mixing and circulation in a crystallizer system can be regarded moderate. Only single broken crystals and the ones manifesting some surface defects or rounded edges were observed, however generally their number was not large. It speaks advantageously for the process conditions established in the crystallizer, facilitating integrated, continuous processes of nucleation and growth of struvite crystals.

![Population density distributions](image)

Fig. 5. Population density distributions of struvite crystals produced in a continuous DTM crystallizer with a liquid jet pump: the points – experimental data (Equation (1)), solid lines – values calculated with Equation (2) (Table 2) for the crystal size $L > 20\ \mu$m (SIG MSMPR kinetic model applied).

Selected experimental population density distributions of struvite crystals produced at pH 9 and for mean residence time of suspension in a crystallizer 900 and 3600 s, are presented in Fig. 5. Individual
population density values \( n(L) \) were calculated from Equation (1) assuming crystal volumetric shape factor \( k_v = 1 \). From these distribution courses, presented in \( \ln n - L \) coordinate system, it results that for struvite crystals of size \( L > 20 \, \mu m \) these dependencies can be with satisfactory accuracy approximated with linear function. Thus from Equation (2) – SIG kinetic model – one can calculate linear crystal growth rate \( G \), while from Equation (3) nucleation rate \( B \) can be determined. The parameter values in struvite population density distribution functions \( n(L) \) (Equation (2)) defined by this method, as well as the extracted \( G \) and \( B \) values corresponding to process conditions No 1–9 (Table 1) are presented in Table 2.

Table 2. Influence of selected technological parameters of struvite reaction crystallization process in a continuous DTM crystallizer with a liquid jet pump on nucleation rate \( B \) and crystal linear growth rate \( G \) values – SIG MSMPR kinetic model applied

<table>
<thead>
<tr>
<th>No. (see Table 1)</th>
<th>Process kinetic parameters (SIG MSMPR model)</th>
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<tbody>
<tr>
<td></td>
<td>( n(L) ) for ( L &gt; 20 , \mu m )</td>
</tr>
<tr>
<td>1</td>
<td>( n = 8.951 \times 10^{7} \exp(-1.554 \times 10^{7} L) )</td>
</tr>
<tr>
<td>2</td>
<td>( n = 1.360 \times 10^{18} \exp(-1.678 \times 10^{7} L) )</td>
</tr>
<tr>
<td>3</td>
<td>( n = 9.357 \times 10^{17} \exp(-3.249 \times 10^{7} L) )</td>
</tr>
<tr>
<td>4</td>
<td>( n = 6.468 \times 10^{17} \exp(-1.382 \times 10^{7} L) )</td>
</tr>
<tr>
<td>5</td>
<td>( n = 9.948 \times 10^{17} \exp(-1.454 \times 10^{7} L) )</td>
</tr>
<tr>
<td>6</td>
<td>( n = 3.131 \times 10^{18} \exp(-2.806 \times 10^{7} L) )</td>
</tr>
<tr>
<td>7</td>
<td>( n = 3.859 \times 10^{17} \exp(-1.153 \times 10^{7} L) )</td>
</tr>
<tr>
<td>8</td>
<td>( n = 9.900 \times 10^{17} \exp(-1.447 \times 10^{7} L) )</td>
</tr>
<tr>
<td>9</td>
<td>( n = 2.759 \times 10^{18} \exp(-2.395 \times 10^{7} L) )</td>
</tr>
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</table>

From Fig. 5 it also results, that for crystal fractions of sizes \( L < 20 \, \mu m \) the corresponding population density distributions show significant nonlinearity in their courses. This characteristic, curved shape can be interpreted as the occurrence in the crystallizing system a more complex kinetics of crystal phase growth than it apparently results from preliminary assumed, the most simplified SIG model [8, 12]. A more detailed insight into this phenomenon will be presented in the next authors’ work.

Analysing the kinetic data presented in Table 2 one can observe decrease of linear crystal growth rate \( G \) value with the increase in pH level, as well as with elongation of mean residence time of suspension in a crystallizer. In general, higher crystal growth rates are observed for shorter mean residence times in apparatus, what is in accordance with the observations concerning classical, continuous mass crystallization processes [8–10]. Mean value of \( G \) for \( \tau = 900 \) s is \( 5.7 \times 10^{-9} \) m/s, while for \( \tau = 3600 \) s – it is only \( 1.8 \times 10^{-9} \) m/s. In turn, relative decrease of crystal growth rate resulting from increase in pH level from 9 to 11 (\( \tau = 900 \) s) is 52%. It is not an advantageous phenomenon. Large decrease of \( G \) results in production of significantly smaller crystals (Table 1). Simultaneous influence of environment’s pH within the 9 – 11 range and mean residence time of suspension in a crystallizer (900 < \( \tau < 3600 \) s) on struvite crystals linear growth rate \( G \) (in m/s) can be presented in a form of design, empirical correlation, Equation (5):

\[
G = 5.31 \times 10^{-3} \, \text{pH}^{-3.57} \, \tau^{-0.819}
\]

with \( R^2 = 0.948 \) and mean relative error ±13.5%. Graphical projection of this dependency is presented in Fig. 6.
8.0 \sim 10^{-9}

6.0 \sim 10^{-9}

4.0 \sim 10^{-9}

11.0

10.0

10.5

9.5

Fig. 6. Simultaneous influence of pH and mean residence time of suspension in a continuous DTM crystallizer with a liquid jet pump on linear growth rate of struvite crystals, G, Equation (5). Process temperature 298 K, concentration of phosphate(V) ions in a feed: 1.0 mass 

Nucleation rate $B$, similarly to linear crystal growth rate $G$, decreases with the elongation of mean residence time of crystal suspension in a crystallizer. Increase in this time lowers working supersaturation level in the process system significantly. For example, in this case study elongation of $\tau$ from 900 up to 3600 s, at pH 9, results in ca. 7-time decrease of nucleation rate. Contrary, with the pH level increase nucleation rate, opposite to crystal growth rate, increases even more than 3-time ($\tau$ 3600 s). Higher nucleation rate, however, corresponds to enlarged crystal fines fraction in suspension, thus in smaller mean crystal product size.

4. Conclusions

From the continuous DTM type crystallizer with liquid jet pump device generating ascending flow of suspension in a mixing chamber the struvite crystals of mean size $L_m$ from 4.0 to 22.4 $\mu$m were produced. It was experimentally observed, that increase in pH level (from 9 to 11) within the struvite reaction crystallization environment resulted in, on average, 3-time decrease of mean crystal size. Contrary, elongation of mean residence time of suspension in a crystallizer from 900 up to 3600 s produced significant increase in this size (even by more than 70\% at pH 9). Product crystals of relatively small size-homogeneity (CV 90–100\%) were removed from the crystallizer. Such high CV is a net effect of complex feedbacks between pH level, mean residence time of suspension, attrition/breakage intensities within the bulk crystal magma and resulting working supersaturation in mother solution.

Original construction of DTM crystallizer, its working mode (internal circulation of suspension driven by liquid jet pump device with no moving parts), as well as small content of solid phase in suspension ($M_T$ ca. 25 kg of struvite/m$^3$ of suspension) do not contribute to excessive attrition and breakage of crystals. Main source of secondary nucleation turned out to be external circulation pump fed with relatively small mass stream of crystal fines (clarification zone ineffectiveness – Fig. 1a). Taking under consideration all components of a complex, continuous reaction crystallization process of struvite in a DTM crystallizer, one can notice that main factor influencing the process course is supersaturation value, strongly dependent (assuming constant composition of a feed solution, constant temperature and constant mixing/circulation intensity) on environment’s pH and on mean residence time of suspension in a working volume of the crystallizer.

Process kinetic parameter values were approximated using the simplest kinetic model of continuous mass crystallization, valid for ideal MSMPR crystallizer configuration. It was observed, that linear
growth rate of struvite crystals changed within the $1.16 \times 10^{-9} - 7.15 \times 10^{-9}$ m/s range, whereas nucleation rate varied within the $9.3 \times 10^{-8} - 9.0 \times 10^{-9}$ 1/sm³ extent. With the elongation of mean residence time the values of both kinetic parameters decreased. Contrary, with the increase in pH increase in nucleation rate and decrease of linear growth rate were reported.

Decrease of both kinetic parameter, $B$ and $G$, values with the elongation of mean residence time is accompanied by the increase in mean product crystal size, $L_m$. Lower $G$ values are thus compensated, with excess, by longer contact time of growing crystals with the supersaturated mother solution. Simultaneously decreasing $B$ values also advantageously influence the growth process in crystal phase and self-establishing under these conditions product’s CSD. In effect, more convenient conditions of mass transfer between liquid and solid phases are observed, additionally providing more stable crystal growth. In such process conditions, characterized by relatively long mean residence time of suspension in a crystallizer, higher quality crystals are produced. However, the corresponding unit process productivity is thus relatively small, lowering economical efficiency of a whole production plant.

Concentration of phosphate(V) ions in a postprocessed mother solution after reaction crystallization of struvite decreased by ca. 95%, what can be regarded as a very good result of the process of their selective removal form the inlet e.g. waste solution.

Acknowledgement

This work was supported by the Ministry of Science and Higher Education of Poland within a frame of statutory activity grant realized in Faculty of Chemistry, Wroclaw University of Technology.

References