Research Article

Nina Hutnik, Anna Stanclik*, Krzysztof Piotrowski, Andrzej Matynia

Size-dependent growth kinetics of struvite crystals in wastewater with calcium ions

<https://doi.org/10.1515/chem-2020-0015>

received February 15, 2019; accepted November 7, 2019.

Abstract: Kinetic parameters describing continuous reaction crystallization of struvite from aqueous solutions containing also calcium ions (from 100 to 2000 mg Ca²⁺/kg) were estimated. Test results were compared with kinetic data of struvite manufactured from real cattle liquid manure. Kinetic model for ideal MSMR (Mixed Suspension Mixed Product Removal) crystallizer was used assuming dependence of crystal growth rate G on its size L (size-dependent growth, SDG MSMR model). Based on nonlinear regression and statistical analysis, one from within five considered $G(L)$ models was selected – Rojowski exponential (RE) model – rendering the experimental population density distributions the best. It was concluded, that calcium ions influenced all components of struvite manufacturing process disadvantageously. A rise of Ca²⁺ concentration in a feed from 100 to 2000 mg/kg increased nucleation rate *ca.* 160-time, whereas growth rate of nuclei up to macroscopic size G_0 decreased more than 10-time. Linear (larger) crystal growth rate G_v was nearly two-times smaller: 1.71·10⁻⁸ m/s (100 mg Ca²⁺/kg) – 9.10·10⁻⁹ m/s (2000 mg Ca²⁺/kg). Resulting in a product with deteriorated quality. Mean size of the crystals decreased nearly two-times (to 18.4 μm), non-homogeneity within product population enlarged and calcium fraction in the product increased. The product, beside struvite MgNH₄PO₄·6H₂O, also contained hydrated amorphous calcium phosphate(V) Ca₃(PO₄)₂·*n*H₂O (ACP). It was observed, that 5-times smaller concentration of phosphate(V) ions in a feed and magnesium ions excess in relation to phosphate(V) and ammonium ions (1.2 : 1 :

1) influenced all kinetic parameters of continuous struvite reaction crystallization advantageously.

Keywords: struvite; phosphate(V) ions; calcium ions; continuous reaction crystallization; SDG MSMR kinetic model; phosphorus recycling.

1 Introduction

Modern technologies designed for efficient phosphate(V) ions recovery from various wastewaters [1] or from liquid manure [2] are commonly based on fixing of these ions into sparingly soluble magnesium and ammonium salt MgNH₄PO₄·6H₂O – struvite (phosphorus recycling) [3]. The process should be operated under rational technological control, resulting in struvite of the possibly best quality [4, 5]. The crystalline product should not contain excessive amount of impurities, which are present in wastewater, especially heavy and toxic metals [3, 6]. If wastewater contains additionally calcium ions, calcium phosphates also co-precipitate during struvite reaction crystallization. These form different crystalline or amorphous phases, like CaHPO₄·2H₂O (brushite, DCPD), Ca₄H(PO₄)₃·2.5H₂O (OCP), Ca₃(PO₄)₂·*n*H₂O (ACP, *n* may be also 0), Ca₅(PO₄)₃OH (hydroxyapatite, HAP) and other compounds depending on adjustable process control parameters (mainly pH and process / residence time) and specific chemical composition of wastewater [7]. The effect of the calcium ions presence on struvite reaction crystallization run and product properties was investigated by Le Corre [8] (batch variant of reaction crystallization) and Hutnik [9, 10] (continuous approach). Both chemical and phase composition of such product change significantly [3]. Calcium fraction itself can reach even up to 30 mass % [11].

Liquid manure is wastewater representing high calcium load [2, 6]. Crystal product manufactured from liquid manure should be thus regarded as a blend of struvite and calcium phosphates(V) [12, 13], what essentially influences its application as mineral fertilizer

*Corresponding author: Anna Stanclik, Faculty of Chemistry, Wrocław University of Science and Technology, 50–370 Wrocław, Poland, E-mail: anna.stanclik@pwr.edu.pl

Nina Hutnik, Andrzej Matynia, Faculty of Chemistry, Wrocław University of Science and Technology, 50–370 Wrocław, Poland
Krzysztof Piotrowski, Department of Chemical Engineering and Process Design, Silesian University of Technology, 44–101 Gliwice, Poland

Table 1: Effect of calcium ions on crystal product characteristic [9, 10] and kinetic parameters values [11] of continuous struvite reaction crystallization process. Nucleation rate B and crystal linear growth rate G calculated with SIG MSMR model. Process temperature: 298 K, pH 9, mean residence time of suspension in a crystallizer τ 900 s.

No.	Feed solution		Product characteristic ^a			Kinetic parameters (SIG MSMR model)		
	$[\text{PO}_4^{3-}]_{\text{RM}}$	$[\text{Ca}^{2+}]_{\text{RM}}$	L_m	CV	k_v	[Ca]	B^b	G
	mass %	mg/kg	mm	%	–	mass %	1/(sm ³)	m/s
Molar proportions of substrate ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$								
1	1.0	100	34.2	83.0	0.049	0.3	$3.8 \cdot 10^8$	$1.60 \cdot 10^{-8}$
2	1.0	500	32.6	85.1	0.045	1.8	$4.9 \cdot 10^8$	$1.45 \cdot 10^{-8}$
3	1.0	1500	28.9	85.4	0.042	5.9	$6.4 \cdot 10^8$	$1.36 \cdot 10^{-8}$
4	1.0	2000	18.4	85.5	0.045	8.4	$2.7 \cdot 10^9$	$8.55 \cdot 10^{-9}$
5	0.20	1500	46.7	87.5	0.042	29.2	$7.1 \cdot 10^7$	$1.58 \cdot 10^{-8}$
CLM	0.34	1200 ^c	12.4	101.0	–	6.2	$1.7 \cdot 10^{10}$	$5.09 \cdot 10^{-8}$
Molar proportions of substrate 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	1.0	1500	29.3	85.6	0.047	6.0	$5.7 \cdot 10^8$	$1.39 \cdot 10^{-8}$
7	0.20	1500	48.6	86.2	0.049	29.6	$6.2 \cdot 10^7$	$1.60 \cdot 10^{-8}$

^a After drying, without water washing of solid phase on a filter

^b For $k_v = 1$

^c and: Cu 3.3, Fe 2.3, K 2800, Mn 15.0, Mo 0.1, Na 1200, Zn 18.0 (in mg/kg) – cattle liquid manure (CLM) [15, 16]. A semi-quantitative science performed on source-dependent data, where error limits may vary with sample sources.

Solid phase content in a product suspension M_i ca. 24.8 kg/m³ (tests No. 1–4, 6) and M_i ca. 4.9 kg/m³ (tests No. 5, 7)

Concentration of PO_4^{3-} ions in a postprocessing mother solution: 10 – 27 mg/kg [9, 10]

L_m – mean crystal size, $L_m = \sum x_i L_i$, where: x_i – mass fraction of crystals of mean fraction size L_i ; $\text{CV} = 100(L_{84} - L_{16}) / (2L_{50})$, where: L_{84} , L_{16} , L_{50} – crystal sizes corresponding to: 84, 16 and 50 mass % undersize fractions in cumulative distribution; k_v – crystal volume shape factor = V_{crystal} / L^3 (V_{crystal} – crystal volume, L – crystal size)

[14]. Also hydroxides and salts of some impurities co-present originally in liquid manure were detected in a product [15, 16]. Final phase and chemical composition of the product, as well as its crystal size distribution (CSD) depend mainly on liquid manure composition and on assumed parameters of continuous reaction crystallization [15, 17]. From cattle liquid manure (CLM), of composition shown in Table 1, solid products representing from 58 to 62 mass % of struvite, from 33 to 36 mass % of amorphous hydrated calcium phosphate(V) (ACP), 3.2 – 3.6 mass % of halite and 1.2 – 1.6 mass % of sylvine [16] were obtained.

The results of experimental research and corresponding kinetic modeling data concerning continuous reaction crystallization process of sparingly soluble phosphates from aqueous solutions containing originally phosphate(V) and calcium ions are presented. Process tests ran in a continuous laboratory DT MSMR (Draft Tube, Mixed Suspension Mixed Product Removal) type crystallizer [18] with internal circulation of suspension driven by propeller mixer. From the product CSDs

nucleation rates and linear crystal growth rates of struvite (for nuclei and for larger crystals) were determined. Kinetic model of continuous mass crystallization in MSMR crystallizer, SDG (Size-Dependent Growth) MSMR model was used in calculations [19–23]. Generally, the SDG model is based on assumption of nonlinear $G(L)$ function, where G – crystal linear growth rate, L – linear crystal size. Struvite crystals, based on experimental $\ln n(L)$ data observation, satisfy assumptions of this phenomenon. The results were also compared with kinetic parameters [11] estimated with the most simplified SIG (Size Independent Growth) MSMR kinetic model [18]. Kinetic data from both models were also related to struvite nucleation and crystal growth observed in real cattle liquid manure (CLM) [24]. Knowledge of kinetic relations in struvite continuous reaction crystallization process can be practically utilized e.g. for elaboration of phosphates recovery technology based on aqueous solutions with high calcium content, including liquid manure.

2 Experimental

2.1 Setup and procedure

The research was carried out in a continuous laboratory experimental plant with automatic data processing (IKA Labortechnik). Operation, monitoring and recording of the experimental data were done with PC computer (IKA Labworldsoft and BioScadaLab software). The continuous process ran in DT MSMR type crystallizer (constructional details presented elsewhere [18]), of working volume V_w 0.6 dm³. Mixing intensity, temperature, inflow streams of feed and alkalizing solution, as well as outflow rate of product crystals suspension from the crystallizer unit were strictly centrally controlled and adjusted by PC computer. The crystallizer was continuously provided with aqueous solution of predetermined concentrations of phosphate(V), magnesium and ammonium ions, as well as calcium ions. Moreover, alkalizing solution (20 mass % aqueous solution of NaOH) was injected when necessary for stabilization of the predetermined pH level. Experimental stand and details of testing method were presented elsewhere [10], whereas calculation procedures are presented in [17].

The effects of three process parameters on struvite continuous reaction crystallization process: molar ratio of substrates in a feed ($\text{PO}_4^{3-} : \text{Mg}^{2+} : \text{NH}_4^+$ as 1 : 1 : 1 and 1 : 1.2 : 1), inlet concentration of phosphate(V) ions (0.20 and 1.0 mass % of PO_4^{3-}), as well as concentration of calcium ions (from 100 to 2000 mg Ca^{2+} /kg of solution) were investigated. Process temperature was set as 298 K, pH as 9 and mean residence time of suspension in a crystallizer τ as 900 s. For comparison, struvite was also manufactured from real liquid manure derived from animal-breeding farm [15], containing 0.34 mass % of phosphate(V) ions and calcium ions (1200 mg Ca^{2+} /kg solution), together with other accompanying impurities (Cu, Fe, K, Mn, Mo, Na, Zn and others) (CLM in Table 1). For each product CSD was determined using solid particle analyzer Coulter LS 230 and Beckman Coulter LS 13 320. On this basis distribution parameters were determined and then used for estimation of nucleation rate B and linear growth rate of struvite $G(L)$ (for nuclei and larger crystals). Identification of product crystals shape, as well as calculation of crystal volume shape factor k_v were done based on images provided by scanning electron microscope JEOL JSM 5800LV. Chemical compositions of mother liquor 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, the X-ray fluorescence spectrometer PANalytical Magi'X PW2424 was used for solid phase analysis (phosphorus and metals). Identification of product phases and quantification of their fractions were done with X-ray diffractometer PANalytical XPERT PRO MPD and Rietveld method (Figure 1).

2.2 Crystal product characteristic

Solid particles were manufactured from the aqueous solutions containing phosphate(V) and calcium ions not only of diverse crystal sizes, but also representing different chemical composition (Table 1). Mean size of struvite crystals varied from 12.4 to 48.6 μm . Particles of amorphous calcium phosphate were small, with size below 2 μm , the most often forming agglomerates on struvite crystal surface (Figure 1). Depending on crystallizer feed composition and its work parameters, struvite crystals with shape coefficient k_v 0.042 – 0.049 were obtained. Crystals length to width ratio varied from 4.0 (k_v 0.049) to 4.3 (k_v 0.042), thus within relatively narrow range. In scanning electron microscope images (Figure 1) one can distinguish dominating tubular crystals, some with longitudinal fractures (in respect to axis, trough), all with deformed, shredded ends. Only a few crystals demonstrated the prismatic shape, which is specific for struvite. Presence of not only crystalline struvite $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, but also hydrated amorphous calcium phosphate(V) $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ was confirmed in the products. Calcium content in solid phase varied from 0.3 up to even 29.6 mass % (Table 1). Product from cattle liquid manure (CLM) represented 58.6 mass % of struvite, 36.2 mass % of amorphous phase, 3.6 mass % of halite, as well as 1.6 mass % of sylvite [16].

From experimental CSDs of products the particle number distributions were calculated (population density distributions, $n(L)$). From these distribution courses (presented in [11]) one can observe, that for struvite crystals of size $L > 40 \mu\text{m}$ these relationships can be modeled with linear function, representing the most simplified SIG MSMR kinetic model [18, 25]. Linear growth rates G of struvite crystals and nucleation rates B calculated [11, 17] with this model are presented in Table 1. These results should be thus regarded as the estimated values only.

Figure 1: Struvite crystals produced from solution in the presence of: a) calcium ions in synthetic wastewater (experiment No. 6 in Table 1) [11], b) calcium ions in a real cattle liquid manure (CLM in Table 1) [16], c) calcium ions and inorganic impurities in synthetic wastewater [11], d) XRD pattern of crystal product – identification of struvite.

2.3 Size Dependent Growth (SDG) kinetic model

For struvite crystals of size $L < 40 \mu\text{m}$ population density distributions $n(L)$ in $\ln n(L) - L$ coordinates show significant nonlinearity (Figure 2). This characteristic, curved course may be interpreted as manifestation of some more complex kinetic mechanisms of crystal phase growth than it could result from the most simplified SIG MSMPR approach. In particular, this shape of population density distribution can result from dispersion of crystal growth rates within investigated population (*Growth Rate Dispersion* – GRD, where crystals of the same size in the same environment grow with different rates), complex secondary nucleation phenomena, size-dependent solubility in small size range or size-dependent relative slip velocities in crystal–solution system modifying by hydrodynamic action the convection/diffusion conditions of mass transfer from liquid phase into solid structure. Individual contributions of all these phenomena are, however, undistinguishable based on analysis of crystal population density distribution shape only. Nevertheless, one can assume, that for the process design all these partial phenomena may be considered together because all these produce qualitatively identical nonlinear effect in $\ln n(L) - L$ coordinates [18, 25]. This way their net effect may be described using size-dependent growth (SDG) kinetic models – as convenient, practical mathematical approach for determination of “conventional” kinetic parameters of the process.

For continuous mass crystallization, assuming steady state in a crystallizer with perfectly mixed suspension and removal of not classified, representative product (ideal MSMPR crystallizer), crystal population balance can be written in a form of differential equation (1) [25]:

$$-\frac{dn(L)}{n(L)} = \frac{dL}{G(L)\tau} + \frac{dG(L)}{G(L)} \quad (1)$$

Considering in crystal population balance (Eq. (1)) kinetic mechanism of size-dependent crystal growth rate ($G(L) \neq \text{const}$, SDG MSMPR model) requires preliminary assumption of some form of $G(L)$ dependence, following by solving of corresponding equation (2):

$$-\int_{n_0}^n \frac{dn}{n(L)} = \int_0^L \frac{dL}{G(L)\tau} + \int_{G_0}^G \frac{dG(L)}{G(L)}$$

Figure 2: Comparison of population density distribution courses of struvite crystals manufactured from feeding solutions of different calcium ions concentrations (Rojkowski exponential RE SDG MSMPR kinetic model, Eq. (8) [21], tests No. 1, 3 and 4 in Table 1 and 4).

(2)

where: n – population density, n_0 – nuclei population density. Some solutions of Eq. (2), obtained as $n(L)$ analytical expressions corresponding to theoretical $G(L)$ models assumed, are presented in Table 2 [26].

Knowing nuclei population density, n_0 , and their linear growth rate, G_0 , nucleation rate B can be calculated from the following relation (13):

$$B = n_0 G_0 \quad (3)$$

Two available SDG MSMPR models – Table 2, Canning and Randolph (CR) model (Eq. (3)) and ASL model (Eq. (5)) – predict monotonic rise of crystal linear growth rate with crystal size increment. Such prediction is, however, inconsistent with the results of experimental research. These demonstrated, that beyond some limiting crystal size, corresponding G practically stabilizes. This way the best approach is provided by three Rojkowski SDG models (Eqs. (7), (9) and (11) in Table 2), predicting both finite, minimal growth rate for nuclei (of size $L = 0$) and finite, maximal growth rate for large crystals.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

Experimental CSDs (Table 1) were recalculated into corresponding population density distributions, $n(L)$.

Table 2: Size-dependent growth $G(L)$ kinetic models and corresponding analytical $n(L)$ forms.

$G(L)$ kinetic model	Corresponding analytical $n(L)$ form [26]
Canning and Randolph (CR) model [19] $G = G_0(1 + aL)$	$n = n_0(1 + aL)^{-\left(\frac{1}{G_0 a \tau} + 1\right)}$ (4)
Abegg, Stevens, Larson (ASL) model [20] $G = G_0(1 + aL)^b$	for $b = 1$: $n = n_0(1 + aL)^{-\left(\frac{1}{G_0 a \tau} + 1\right)}$ for $0 < b < 1$: (5)
	$n = n_0 \exp \left[- \left(\frac{1}{G_0 a \tau (1 - b)} \left[(1 + aL)^{1-b} - 1 \right] + b \ln(1 + aL) \right) \right]$ (6)
Rojkowski (exponential model RE) [21] $G = G_\infty - (G_\infty - G_0) \exp(-aL)$	$n = n_0 \exp \left[- \left(\ln \frac{G_\infty - (G_\infty - G_0) \exp(-aL)}{G_0} \left[\frac{1}{G_\infty a \tau} + 1 \right] + \frac{L}{G_\infty \tau} \right) \right]$ (7)
Rojkowski (hyperbolic model RH) [22] $G = G_\infty - \left(\frac{G_\infty - G_0}{1 + aL} \right) = \frac{G_0 + aG_\infty L}{1 + aL}$	$n = n_0 \exp \left[- \left(\frac{1}{\tau} \frac{G_\infty - G_0}{aG_\infty^2} \ln \left(\frac{aG_\infty L + G_0}{G_0} \right) + \frac{1}{\tau} \frac{L}{G_\infty} + \ln \left(\frac{G_0 + aG_\infty L}{(1 + aL)G_0} \right) \right) \right]$ (8)
	(9)
Rojkowski (hyperbolic model II, RH II) [23] $G = \frac{G_0 G_\infty^2 \tau + G_\infty (G_\infty - G_0) L}{G_\infty^2 \tau + (G_\infty - G_0) L}$	$n = n_0 \exp \left[- \left(\ln \left(\frac{G_\infty (G_\infty - G_0) L + G_0 G_\infty^2 \tau}{G_0 G_\infty^2 \tau} \right) + \frac{L}{\tau G_\infty} + \ln \left(\frac{G_0 G_\infty^2 \tau + G_\infty (G_\infty - G_0) L}{G_\infty^2 \tau G_0 + (G_\infty - G_0) L G_0} \right) \right) \right]$ (10)
	(11)
	(12)

These distributions, presented graphically as $\ln n(L)$, demonstrated concave upward for the smallest particles, of size $L < 40 \mu\text{m}$. For modeling of $n(L)$ data courses five SDG MSMMPR models were preliminary tested. Their $G(L)$ functions and corresponding analytical equations of population density distributions $n(L)$ are presented in Table 2.

Eqs. (4), (6), (8), (10) and (12) were then fitted (using nonlinear regression analysis) to experimentally determined population density distributions of struvite crystals (7 experimental $n(L)$ distributions). For each experimental data set and for each model (Table 2) the parameters of $n(L)$ distributions were calculated, making determination of variance (Eq. (14)) possible:

$$(\text{RMSD})^2 = \frac{\sum \left(\ln n^{\text{calc}}(L) - \ln n^{\text{exp}}(L) \right)^2}{p - 1} \quad (4)$$

where RMSD^2 – variance, n^{calc} is population density value calculated by the model, n^{exp} is experimental population density value, p is number of experimental data.

Comparison of sum of variances $\Sigma(\text{RMSD})^2$ for all test runs made selection of $n(L)$ form modeling of experimental data the best possible (assumed criterion – minimal $\Sigma(\text{RMSD})^2$). This way selection of corresponding theoretical $G(L)$ model (Table 2) was possible. These verifying calculation results are presented in Table 3. From the table it results, that two SDG MSMMPR models described experimental data the best. These were: Rojkowski exponential RE (Eqs. (7) and (8), Table 2)

and Rojkowski hyperbolic RH (Eqs. (9) and (10), Table 2) models; $(\Sigma(\text{RMSD})^2 = 0.1363$ and 0.2225 , respectively). Quality of other models was significantly worse, $\Sigma(\text{RMSD})^2$ varied from ca. 1 to 3.6. For further calculations, covering determination of kinetic parameters of the continuous process, the best model was selected. It was Rojkowski exponential – RE SDG MSMMPR model (Eqs. (7)–(8)), because of the smallest sum of variances $\Sigma(\text{RMSD})^2$ and relatively simple $G(L)$ dependency form. Parameters of both RE SDG MSMMPR model equations – (7) and (8), namely: nuclei population density n_0 , minimal linear growth rate (of nuclei, zero-size crystals) G_0 , maximal linear growth rate (for the largest crystals, of theoretical infinite size) G_∞ , nucleation rate $B (= n_0 G_0)$, as well as model constant a – are all presented in Table 4.

Exemplary graphical comparison of experimental population density distributions $n^{\text{exp}}(L)$ of solids produced from aqueous solutions of phosphate(V) ions (1 mass %) with 100, 1500 and 2000 mg Ca^{2+}/kg (inlet concentration) and $n^{\text{calc}}(L)$ courses predicted by Rojkowski exponential RE SDG MSMMPR kinetic model (Eq. (8), tests No. 1, 3 and 4 in Table 1 and 4) is demonstrated in Figure 2. From the comparison it results, that RE SDG MSMMPR model precisely renders curvature of the $n(L)$ course in $\ln n(L)$ – L coordinates. The calculated kinetic parameter values (see Table 4) may be thus regarded as reliable numerical data for nominal description of kinetics of continuous reaction crystallization process of struvite in presence of calcium ions.

From the analysis of kinetic data presented in Table 4 it results, that calcium ions affected all kinetic components of struvite reaction crystallization process disadvantageously.

Table 3: (RMSD)² for each model/experimental case, as well as $\Sigma(\text{RMSD})^2$ for each SDG MSMMPR model (for all experimental data sets).

Experiment (see Table 1)	(RMSD) ² for selected SDG MSMMPR models				
	CR	ASL	RE	RH	RH II
1	0.2741	0.1258	0.0256	0.0307	0.5173
2	0.2846	0.1197	0.0223	0.0240	0.5485
3	0.3843	0.1677	0.0145	0.0294	0.5259
4	0.2506	0.0971	0.0288	0.0338	0.4022
5	0.3712	0.1592	0.0132	0.0326	0.5413
CLM	0.4927	0.2699	0.0239	0.0612	0.6491
6	0.3982	0.1762	0.0116	0.0329	0.5100
7	0.2816	0.1711	0.0203	0.0391	0.5602
$\Sigma(\text{RMSD})^2$	2.7373	1.2867	0.1602	0.2837	4.2545

CR: Canning and Randolph model [19]; ASL: Abegg, Stevens and Larson model [20]; RE: Rojowski exponential model [21]; RH: Rojowski hyperbolic model [22]; RH II: Rojowski hyperbolic II model [23]

Table 4: Kinetic parameters calculated with RE SDG MSMMPR model (Eqs. (7) and (8)): nuclei population density n_0 , nucleation rate B , minimal G_0 and maximal G_∞ crystal linear growth rate, as well as RE SDG MSMMPR model parameter a – estimated for continuous struvite reaction crystallization process in DT MSMMPR crystallizer. Corresponding process conditions – see Table 1.

No.	Kinetic parameters – RE SDG MSMMPR model				
	n_0	G_0	G_∞	a	B
	1/(m m ³)	m/s	m/s	1/m	1/(sm ³)
1	$4.35 \cdot 10^{24}$	$2.30 \cdot 10^{-11}$	$1.71 \cdot 10^{-8}$	32217.25	$1.00 \cdot 10^{14}$
2	$1.83 \cdot 10^{26}$	$6.85 \cdot 10^{-12}$	$1.69 \cdot 10^{-8}$	32862.98	$1.25 \cdot 10^{15}$
3	$1.70 \cdot 10^{27}$	$4.09 \cdot 10^{-12}$	$1.47 \cdot 10^{-8}$	38071.00	$6.95 \cdot 10^{15}$
4	$7.72 \cdot 10^{27}$	$2.09 \cdot 10^{-12}$	$9.10 \cdot 10^{-9}$	63184.43	$1.61 \cdot 10^{16}$
5	$9.26 \cdot 10^{26}$	$5.11 \cdot 10^{-12}$	$1.72 \cdot 10^{-8}$	37011.12	$5.66 \cdot 10^{15}$
CLM*	$2.99 \cdot 10^{26}$	$6.46 \cdot 10^{-12}$	$8.48 \cdot 10^{-9}$	65918.50	$1.93 \cdot 10^{15}$
6	$1.22 \cdot 10^{27}$	$4.87 \cdot 10^{-12}$	$1.49 \cdot 10^{-8}$	37620.72	$5.94 \cdot 10^{15}$
7	$6.45 \cdot 10^{26}$	$7.06 \cdot 10^{-12}$	$1.76 \cdot 10^{-8}$	35216.03	$4.55 \cdot 10^{15}$

* according to [24]

Increase in concentration of these ions from 100 to 2000 mg Ca²⁺/kg caused rise of nucleation rate B of struvite from $1.00 \cdot 10^{14}$ up to $1.61 \cdot 10^{16}$ 1/(sm³), what produced significant enlargement of the nuclei number in a crystallizer – nuclei population density n_0 raised nearly 1800-time. Linear crystal growth rate G_∞ of larger crystals decreased by

nearly 2-times as much, from $1.71 \cdot 10^{-8}$ to $9.10 \cdot 10^{-9}$ m/s. Also growth rate of nuclei G_0 decreased, *ca.* 10-times, from $2.30 \cdot 10^{-11}$ to $2.09 \cdot 10^{-12}$ m/s. In result, number of small crystals in agitated suspension enlarged. In effect mean size of solids removed from the crystallizer decreased from 34.2 to 18.4 μm (see Table 1), thus by 46%. Calcium content in a product increased, however, from 0.3 to 8.4 mass %, what additionally raised the non-homogeneity within product population (coefficient of variation CV 83.0 $\rightarrow$ 85.5%, Table 1). Especially concentration of small amorphous particles of calcium phosphate, ACT, increased [11]. Lower concentration of phosphate(V) ions in a feed (0.20 mass %) together with 20% excess of magnesium ions in a process system influenced the continuous struvite reaction crystallization process advantageously. In such conditions lower nucleation rates B and higher crystal growth rates G_∞ were observed. From this comparison it results, that stronger effect on raise of struvite crystals growth resulted from concentration of phosphate(V) ions. The 5-time lower concentration caused 17 – 19% increase in growth rate G_∞ (tests 3 and 5, 6 and 7 in Table 4). Under these conditions final mean size of struvite crystals enlarged by 62 – 65% (crystal mean size L_m reached *ca.* 47 – 49 μm). However, in presence of 20-proc. magnesium ions excess linear struvite crystals growth rate G_∞ raised by 1 – 2% only (tests 3 and 6, as well as 5 and 7 in Table 4). Product quality, however, slightly improved (L_m in Table 1). Compared data corresponded to presence of 1500 mg Ca²⁺/kg in a feed, where pH of mother liquor was 9 and mean residence time of suspension – 900 s, while process temperature – 298 K.

Kinetic calculations results of struvite continuous reaction crystallization in a real cattle liquid manure (CLM) [16] containing 0.34 mass % of phosphate(V) ions, 1200 mg/kg of calcium ions and specific impurities, which concentrations were provided in detail in Table 1, are also presented in Table 4 for comparison. Despite many impurities in CLM, kinetic parameters values of struvite reaction crystallization process did not deviate significantly from the ones corresponding to simple systems with calcium ions (tests No. 1 – 7 in Table 4). Nuclei population density n_0 of struvite crystals from CLM was *ca.* $3 \cdot 10^{26}$ 1/(m m³), their growth rate G_0 exceeded $6 \cdot 10^{-12}$ m/s, whereas nucleation rate B was below $2 \cdot 10^{15}$ 1/(sm³). These represent advantageous values, for which one should expect manufacturing of properly shaped struvite crystals. However, experimental data are different. Struvite of small sizes, non-homogeneous, of deformed shapes and with clear trend to caking and agglomeration (see Figure 1b) were removed from the crystallizer. Mean size of these crystals reached 12.4 μm only, and CV exceeded 100% (CLM, Table 1). The reason explaining the observed poor

quality of the product manufactured from CLM may be, among others, the smallest value of linear crystal growth rate G_∞ : only $8.48 \cdot 10^{-9}$ m/s (CLM, Table 4). In solution, where inlet concentration of calcium ions was higher by 300 mg Ca^{2+} /kg, while concentration of phosphate(V) ions was 1.0 mass % (0.34 mass % in liquid manure, CLM), linear crystal growth rate G_∞ was $1.47 \cdot 10^{-8}$ m/s (test No. 3 in Table 4). From this solution product of significantly higher quality: L_m 28.9 μm , CV 85.4% was manufactured (Table 1). In general, one can conclude, that impurities present in real liquid manure (CLM) influenced the continuous reaction crystallization of struvite in diverse way. These affected nuclei population density n_0 of struvite and growth rate of its nuclei G_0 advantageously. In consequence nucleation rate $B (= n_0 G_0)$ of struvite was smaller than the values calculated for the solutions with calcium ions of similar concentration (compare CLM and tests No. 3, 5–7 in Table 4). In liquid manure linear crystal growth rate G_∞ of struvite decreased by 2-times on average: to $8.48 \cdot 10^{-9}$ m/s. Composition of impurities observed in liquid manure influenced also struvite crystal shape disadvantageously (compare Figure 1a and 1b). In general, quality of the product manufactured from liquid manure CLM should be regarded as unsatisfactory in respect to market demands [27,28]. Improvement of the product quality is, however, possible, among others, through elongation of residence time of struvite suspension in a crystallizer [15, 16, 24].

Comparison of $G(L)$ courses predicted by RE SDG MSMR model (Eq. (7)) for different inlet concentrations of calcium ions: 100, 1500 and 2000 mg Ca^{2+} /kg (see No. 1, 3 and 4 in Tables 1 and 4) is presented in Figure 3, where $G(L)$ determined for struvite produced from cattle liquid manure CLM is also added for comparison. With the size enlargement of struvite crystals, linear growth rate increases from some finite growth rate of nuclei (crystals „formally” of $L = 0$) G_0 , in m/s: $2.30 \cdot 10^{-11}$ (100 mg Ca^{2+} /kg), $4.09 \cdot 10^{-12}$ (1500 mg Ca^{2+} /kg) and $2.09 \cdot 10^{-12}$ (2000 mg Ca^{2+} /kg) up to asymptotic, maximal G_∞ reaching: $1.71 \cdot 10^{-8}$, $1.47 \cdot 10^{-8}$ and $9.10 \cdot 10^{-9}$ m/s, appropriately. The limiting, constant G_∞ value, which beyond some initial L range is practically stable and size-independent, is visibly influenced by calcium ions concentration in a feed. The higher this concentration is, the more limiting value of G_∞ is shifted towards smaller crystals. For 100 mg Ca^{2+} /kg in a feed linear growth rate G_∞ stabilizes for the crystals of size larger than 140 μm , for 1500 mg Ca^{2+} /kg – for crystals of $L > 120 \mu\text{m}$, whereas for 2000 mg Ca^{2+} /kg – for the crystals of $L > 80 \mu\text{m}$. In liquid manure linear growth rate raises from G_0 $6.46 \cdot 10^{-12}$ up to $8.48 \cdot 10^{-9}$ m/s. For crystals of size $L > 100 \mu\text{m}$ it reaches practically constant value. From all presented data it results, that in struvite reaction crystallization

Figure 3: Size-dependent linear growth rate dependency courses observed in struvite crystals obtained for various calcium ions concentrations in a feed solution, as well as from real cattle liquid manure CLM [24] (RE SDG MSMR kinetic model, (Eq. (7) in Table 2 with model parameters values presented in Table 4).

process small crystals grow slower, larger ones – faster, up to maximal, stable value, practically dependent on concentration of calcium ions in a process system. All these affect product's CSD and homogeneity of its population. It is of great importance in practice, in elaboration of technology of phosphate(V) ions recovery from liquid manure, as well as in developing of rational strategy of this process steering in a continuous crystallizer.

Other divalent cation present in struvite reaction crystallization environment, Mg^{2+} , was also subject of the authors' more thorough research (e.g. [17]). However, Mg^{2+} ion is substrate in struvite synthesis reaction, thus should be analyzed together with other process parameters. The 20% excess of magnesium ions in respect to PO_4^{3-} and NH_4^+ ions results in lower values of mean (16.2–72.8 mm) and dominant (11.3–66.4 mm) crystal sizes (at nearly identical CV values) compared to stoichiometric ratio of reagents (23.2–110.2 mm, 28.7–140.1 mm, respectively) - for identical ranges of pH (8.5–10), mean residence time (900–3600 s) and inlet concentration of phosphate(V) ions (0.20 and 1.0 mass %). It modifies continuous process kinetics (SIG MSMR) disadvantageously towards lower G and higher B . Nevertheless, excess of Mg^{2+} ions shifts equilibrium of the struvite synthesis reaction towards product formation, thus affects process effectiveness advantageously. The observed postprocessed concentrations of PO_4^{3-} ions in mother liquor were ca. 2–7-times lower (19–92 mg/kg) compared to stoichiometric proportion of PO_4^{3-} , Mg^{2+} and NH_4^+ ions (130–220 mg/kg).

In diluted aqueous solutions of phosphate(V) ions, for $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$, increase in $[\text{PO}_4^{3-}]_{\text{RM}}$ from 0.20 to 1.0 mass % resulted in decrease of L_m from 42.9 to 37.9 mm, whereas for $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$ it resulted in decrease of L_m from 32.9 to 26.4 mm. In both cases CV deteriorates slightly (CV 76.6 $\rightarrow$ 80.9% and CV 72.3 $\rightarrow$ 86.8%) (corresponding to: T 298 K, pH 8.5 and t 900 s). The related kinetic parameters changes are: G $1.81 \times 10^{-8} \rightarrow 1.75 \times 10^{-8}$ m/s (stoichiometric ratio, by 3%) and G $1.68 \times 10^{-8} \rightarrow 1.49 \times 10^{-8}$ m/s (Mg^{2+} excess, by 11%), and B $5 \times 10^7 \rightarrow 3.1 \times 10^8$ 1/(sm³) (by 520 %), B $5.9 \times 10^7 \rightarrow 2.7 \times 10^8$ 1/(sm³) (by 358 %).

In presence of Ca^{2+} ions (Table 1, for 1500 mg/kg) the same change in $[\text{PO}_4^{3-}]_{\text{RM}}$ provides decrease of L_m from 46.7 to 28.9 mm (stoichiometric proportion) and from 48.6 to 29.3 mm (Mg^{2+} excess), at smaller CV changes – from 87.5 to 85.4% and from 86.2 to 85.6% (corresponding to: T 298 K, pH 9 and t 900 s). Crystal growth rates G decrease from $1.58 \cdot 10^{-8}$ to $1.36 \cdot 10^{-8}$ m/s (by 14%) and from $1.60 \cdot 10^{-8}$ to $1.39 \cdot 10^{-8}$ m/s (by 13%), whereas nucleation rates B rise - from $7.1 \cdot 10^7$ to $6.4 \cdot 10^8$ 1/(sm³) (by 801%) and from $6.2 \cdot 10^7$ to $5.7 \cdot 10^8$ 1/(sm³) (by 819%).

From the comparison it results, that presence of calcium ions enhances changes in process kinetics for the nearly identical process conditions (T , pH, t).

4 Conclusions

Size-Dependent Growth (SDG) kinetic model for ideal MSMPR crystallizer was assumed for the modeling of experimental data derived from continuous reaction crystallization process of phosphate(V) ions recovery from aqueous wastewater solutions containing also calcium ions. The 5 different SDG MSMPR $n(L)$ models derived from 5 different theoretical $G(L)$ relations were considered. Based on results of nonlinear regression analysis the $n(L)$ equation the best modeling of population density distribution of solid product was selected. It was Rojkowski exponential (RE SDG MSMPR) model. Kinetic parameters of struvite continuous reaction crystallization in presence of calcium ions (from 100 to 2000 mg Ca^{2+} /kg of feed) were calculated based on this model.

Considering the experimental data and kinetic calculations it was generally concluded, that increase in inlet concentration of calcium ions produced increase in nucleation rate of struvite from $1.00 \cdot 10^{14}$ 1/(sm³) (100 mg Ca^{2+} /kg) up to $1.61 \cdot 10^{16}$ 1/(sm³) (2000 mg Ca^{2+} /kg), simultaneously observing decrease of growth rate of these nuclei G_0 : from $2.30 \cdot 10^{-11}$ to $2.09 \cdot 10^{-12}$ m/s. Linear

crystal growth rate G_∞ of struvite also decreased, from $1.71 \cdot 10^{-8}$ to $9.10 \cdot 10^{-9}$ m/s. These are significant changes in kinetic parameters of struvite continuous reaction crystallization. Nucleation rate higher by more than two orders of magnitude, at 2-time lower crystal growth rate G_∞ caused, that mean struvite product size L_m decreased from 34.2 to 18.4 μm , while calcium fraction in a product increased from 0.3 up to 8.4 mass %. Amorphous calcium phosphate ACP appeared in solid phase. The final product represents thus a mix of both these phosphates, what is not, however, essential drawback in practical application of such product in agriculture as a valuable mineral fertilizer slowly dosing its nutrient content [27, 28].

It was also concluded, that the decrease of concentration of phosphate(V) ions (from 1.0 to 0.2 mass % of PO_4^{3-}) in a feed, as well as magnesium ions excess in respect to phosphate(V) and ammonium ions inlet concentrations (as 1.2 : 1 : 1) constrained nucleation rate of struvite and influenced its crystal growth rate advantageously (G_∞ (1.72 – 1.76) $\cdot 10^{-8}$ m/s). Mean size L_m of solid product reached even 48.6 μm . However, in these conditions calcium content in a product was even 29.6 mass %.

Calculation results according to RE SDG MSMPR model can be regarded as moderately reliable for kinetic description of continuous, complex struvite reaction crystallization process from wastewaters containing calcium ions.

List of abbreviations

ACP	– hydrated amorphous calcium phosphate(V) $\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$,
ASL	– Abegg, Stevens, Larson (SDG kinetic model),
CLM	– cattle liquid manure,
CR	– Canning and Randolph (SDG kinetic model),
CSD	– crystal size distribution,
DCPD	– $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (brushite),
DT	– draft tube,
GRD	– growth rate dispersion,
HAP	– $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite),
MSMPR	– mixed suspension mixed product removal (crystallizer type),
OCP	– $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$
RE	– Rojkowski exponential (SDG kinetic model),
RH	– Rojkowski hyperbolic (SDG kinetic model),
RH II	– Rojkowski hyperbolic II (SDG kinetic model),
RMSD	– root mean squared deviation (RMSD^2 – variance),

SDG – size-dependent growth,
 SIG – size independent growth,

List of symbols

a – model constants in CR, ASL, RE, RH (SDG MSMMPR) kinetic models, 1/m
 b – ASL (SDG MSMMPR) model parameter,
 B – nucleation rate, 1/(m³s)
 $[Ca^{2+}]_{RM}$ – feed concentration of calcium ions, mg/kg
 $[Ca]$ – calcium content in a product, mass %
 CV – coefficient of (crystal size) variation, %
 G – crystal linear growth rate, m/s
 G_0 – linear growth rate of nuclei, m/s
 G_v – linear crystal growth rate (of larger particles), m/s
 k_v – crystal volume shape factor (coefficient),
 L – crystal size, m
 L_{84}, L_{16}, L_{50} – limiting crystal sizes corresponding to: 84, 16 and 50 mass % of undersize fractions in cumulative distribution, m
 L_i – mean size of i -th crystal fraction, m
 L_m – crystal mean size, m
 M_T – solid phase content in a product suspension, kg_{solids}/m³
 $[Mg^{2+}]_{RM}$ – feed concentration of magnesium ions, mass %
 $[NH_4^+]_{RM}$ – feed concentration of ammonium ions, mass %
 $n(L)$ – population density distribution, 1/(m m³)
 n – population density, 1/(m m³)
 n_0 – nuclei population density, 1/(m m³)
 n^{calc} – population density value calculated by the model, 1/(m m³)
 $n^{calc}(L)$ – population density distribution predicted by SDG MSMMPR model, 1/(m m³)
 n^{exp} – experimental population density, 1/(m m³)
 $n^{exp}(L)$ – experimental population density distribution, 1/(m m³)
 p – number of experimental data,
 $[PO_4^{3-}]_{RM}$ – feed concentration of phosphate(V) ions, mass %
 τ – mean residence time of suspension in a crystallizer, s
 T – process temperature, K
 $V_{crystal}$ – crystal volume, m³
 V_w – crystallizer working volume, m³
 x_i – mass fraction of crystals of mean fraction size L_i

Conflict of interest: Authors declare no conflict of interest.

References

- [1] Le Corre KS, Valsami-Jones E, Hobbs P, Parsons SA. Phosphorus recovery from wastewater by struvite crystallization: a review. *Crit Rev Environ Sci Technol.* 2009;39(6):433–77.
- [2] Sommer SG, Christensen ML, Schmidt T, Jensen LS, editors. *Animal Manure Recycling. Treatment and Management.* New Delhi: Wiley; 2013. <https://doi.org/10.1002/9781118676677>.
- [3] Rahman MM, Salleh MA, Rashid U, Ahsan A, Hossain MM, Ra CS. Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review. *Arab J Chem.* 2014;7(1):139–55.
- [4] Parsons SA. Recent scientific and technical developments: struvite precipitation. *CEEP Scope Newslett.* 2001;41:15–22.
- [5] Hutnik N, Kozik A, Mazieniczuk A, Piotrowski K, Wierzbowska B, Matynia A. Phosphates (V) recovery from phosphorus mineral fertilizers industry wastewater by continuous struvite reaction crystallization process. *Water Res.* 2013 Jul;47(11):3635–43.
- [6] Tansel B, Lunn G, Monje O. Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: A review of magnesium-ammonia-phosphate interactions. *Chemosphere.* 2018 Mar;194:504–14.
- [7] Valsami-Jones E. Recent scientific and technical developments: calcium phosphate precipitation. *CEEP Scope Newslett.* 2001;41:8–15.
- [8] Le Corre KS, Valsami-Jones E, Hobbs P, Parsons SA. Impact of calcium on struvite crystal size, shape and purity. *J Cryst Growth.* 2005;283(3-4):514–22.
- [9] Hutnik N, Piotrowski K, Wierzbowska B, Matynia A. Continuous reaction crystallization of struvite from phosphate(V) solutions containing calcium ions. *Cryst Res Technol.* 2011;46(5):443–9.
- [10] Hutnik N, Wierzbowska B, Piotrowski K, Matynia A. Effect of calcium ions on quality of struvite produced in continuous reaction crystallization process. *Int. J. Adv. Chem. Technol.* 2013;2:1–6.
- [11] Hutnik N, Stanclik A, Matynia A. Influence of calcium ions on struvite precipitation and crystallization from wastewaters [in Polish]. *Przem Chem.* 2017;96:1864–8.
- [12] Kozik A, Hutnik N, Podworny J, Gerle A, Mazieniczuk A, Matynia A. Recovery of phosphate(V) ions from synthetic swine wastewater under stoichiometric conditions [in Polish]. *Przem Chem.* 2014;93:559–64.
- [13] Kozik A, Hutnik N, Mazieniczuk A, Wierzbowska B, Piotrowski K, Podworny J, et al. Phosphates(V) recovery from synthetic liquid manure by continuous struvite reaction crystallization process, 41st International Conference of SSCHE, Tatranské Matliare, Slovakia. 2014;853-861.
- [14] Latifian M, Liu J, Mattiasson B. Struvite-based fertilizer and its physical and chemical properties. *Environ Technol.* 2012 Dec;33(22-24):2691–7.
- [15] Kozik A, Hutnik N, Hoffmann K, Huculak-Maczka M. Phosphates(V) ions recovery from cattle manure [in Polish]. *Przem Chem.* 2015;94:938–42.
- [16] Kozik A, Hutnik N, Piotrowski K, Matynia A. Precipitation of calcium and magnesium phosphates(V) from cattle manure,

Acknowledgements: The work was supported by the National Science Center of Poland under grant No 2016/21/D/ST8/01694, 2017–2020.

- 43rd International Conference of SSCHE, Tatranské Matliare, Slovakia. 2016;508-515.
- [17] Kozik A, Hutnik N, Piotrowski K, Matynia A. Continuous reaction crystallization of struvite from diluted aqueous solution of phosphate(V) ions in the presence of magnesium ions excess. *Chem Eng Res Des.* 2014;92(3):481–90.
- [18] Mullin JW. *Crystallization*. 3rd ed. Oxford: Butterworth-Heinemann; 1993.
- [19] Canning TF, Randolph AD. Some aspects of crystallization theory: systems that violate McCabe's delta L law. *AIChE J.* 1967;13(1):5–10.
- [20] Abegg CF, Stevens JD, Larson MA. Crystal size distribution in continuous crystallizers when growth rate is size-dependent. *AIChE J.* 1968;14(1):118–22.
- [21] Rojkowski Z. New empirical kinetic equation of size dependent crystal growth and its use. *Krist. Tech.* 1977;12(11):1121–8.
- [22] Rojkowski Z. New hyperbolic empirical model of size dependent crystal growth. *Bull. Acad. Pol. Sci. Ser. Chim.* 1978;26:265–70.
- [23] Rojkowski Z. Two parameter kinetic equation of size dependent growth. *Krist. Tech.* 1978;13(11):1277–84.
- [24] Stanclik A, Hutnik N, Piotrowski K, Matynia A. Struvite nucleation and crystal growth kinetics from cattle liquid manure. *Chem Pap.* 2019;73(3):555–63.
- [25] Randolph AD, Larson MA. *Theory of Particulate Processes: Analysis and Techniques of Continuous Crystallization*. New York: Academia Press; 1988.
- [26] Machej K, Piotrowski K. Review and comparison of kinetic equations for mass crystallization design purposes [in Polish]. *Inz. Ap. Chem.* 2001;40:17–8.
- [27] Nongqwenga N, Muchaonyerwa P, Hughes J, Odindo A, Bame I. Possible use of struvite as an alternative phosphate fertilizer, J. *Soil Sci. Plant Nut.* 2017;1:581–93.
- [28] Nagy J, Mikola A, Pradhan SK, Zseni A. The utilization of struvite produced from human urine in agriculture as a natural fertilizer: A Review. *Period Polytech Chem Eng.* 2019;63:478–84.