New crystallizers with a compressed air-driven jet pump in the process of precipitating struvite from diluted water solutions containing phosphate ions

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Introduction

In the majority of crystallizers, the regulation of the working supersaturation is achieved by causing a controlled, internal suspension circulation in the apparatus (DTM (*Draft Tube Magma*) - type crystallizers) [1]. The movement of the suspension causes the leveling of temperature and concentrations of the center, maintains the precipitating and growing crystals in the suspension, as well as prevents their agglomeration. A mechanical device that forces the internal flow of the suspension in the apparatus is usually the mixer or internal circulation pump. In terms of construction, a device that forces the set circulation of the suspension in the crystallizer a lot easier, although still rarely used in practice, is the jet pump [2÷4]. In typical apparatus constructions with a jet pump, the working element is a possibly clear mother solution taken from the overflow of the crystallizer, which is then directed via an external circulation pump to the jet pump's feeding nozzle [4÷7]. An alternative solution might be to substitute the circulated mother solution with air. Compressed air, added to the feeding nozzle, becomes an operating factor which forces the internal circulation/mixing of the suspension in the working volume of the apparatus [8÷14]. In such a case, the closed circulation system of the mother solution, encompassing the clarifying zone and external circulation (with the pump) may be substituted with a system open to the atmosphere (intake of atmospheric air through a compressor, its compression, feeding the jet pump's feeding nozzle, decompressing in the working volume of the apparatus, releasing the decompressed air to the atmosphere). In the case of using a different medium than atmospheric air (e.g. nitrogen), there exists the possibility of using a closed circuit of the gas working medium in which the compressor will compensate pressure losses related to decompressing the medium in the apparatus.

Below, new, original constructions of crystallizers with a compressed air-driven jet pump were presented, designed bearing in mind their application in continuous precipitation and crystallization processes of slow-soluble phosphate salts from diluted water solutions. Laboratory experimental installations with crystallizers with a continuous effect were designed and performed: DTM MSMPR (*Draft Tube Magma, Mixed Suspension Mixed Product Removal*) and FB MSZ-type (*Fluidized Bed with Mixing Suspension Zone*). These installations are used especially for testing the efficiency, kinetics and optimization of crystallization processes with the chemical reaction of struvite precipitation ($MgNH_4PO_4{\cdot}6H_2O$, MAP) from diluted water solutions, pre-purified domestic waste, industrial waste, liquid manures, etc., containing phosphate(V) ions [15, 16]. The chemical recovery of phosphates from waste solutions is treated as so-called phosphorus recycling [17÷19], while the products obtained as a result of these processes – difficult-to-dilute calcium or magnesium salts in crystal form, especially struvite – may be used as an inorganic fertilizer [20, 21].

The precipitation of struvite in the proposed crystallizers with a gaseous-liquid jet pump was carried out from diluted water solutions with the preservation of fixed process parameters in each of the apparatus. This enabled to compare the quality of the obtained products and the kinetics of struvite crystallization, as well as the assessment of the crystallizers' work.

Both crystallizers were fed in a continuous way with a feeding solution of a 0.2 or 1.0% concentration of phosphate(V) ion masses, and – in stoichiometric proportions – with the remaining reactants of the following concentrations: $[Mg^{2+}] = 0.0512$ or 0.256 and $[NH_4^+] = 0.0380$ or 0.190% of mass. The process was carried out in a temperature of 298 K with values of pH = 9, 10 or 11. The average assumed time of the suspension in the working volume of the crystallizers equaled $\tau = 900 – 3600$ s. Based on the crystal size distribution (CSD) of the obtained products, values of basic kinetic parameters of the process were assessed. For the calculations, the most simplified kinetics model of mass crystallization was assumed in the MSMPR (*Mixed Suspension Mixed Product Removal*) crystallizer – the so-called SIG (*Size Independent Growth*) model – in which it is assumed that under given process conditions the growth rate of all crystals is constant and does not depend on their sizes. The characteristics of the obtained products and the results of kinetic calculations were presented below.

The results of tests on the application of crystallizers with a clear mother solution-driven jet pump in the process of continuous crystallization with the chemical reaction of struvite precipitation from diluted solutions and waste from the fertilizer industry was presented in the works of authors [5÷7, 22, 23]. The application of compressed air as the working factor of the jet pump installed in the DTM MSMPR-type crystallizer was discussed in [9, 10, 14], while in the FB MSZ crystallizer – in [11÷13].

Workstations and methodology of tests

Figure 1 presents diagrams of laboratory testing installations with a DTM MSMPR and FB MSZ crystallizer. The working volumes of both crystallizers were the same and equaled 1.2 dm^3. The steering, control and recording of measuring data was performed via a computer. The compressed air added to the jet pump's nozzle was supplied by the Medic-Air 150-25 Silent compressor.

In the first crystallizer, the compressed air was fed directly to the feeding nozzle of the jet pump, mounted at the bottom of the crystallizer, and the movement of the suspension in the mixing chamber was upward. In the second proposed construction, the feeding nozzle of the jet pump system was situated below the free surface of clarified mother solution in the crystallizer, inside the jet pump's mixing chamber, while the movement of the compressed air was downwards. Because of the small unit value of the gaseous feeding stream power, the large density of struvite (1710 kg/m^3) and the hydraulic flow conditions, in this case no suction of the crystal solution to the mixing chamber occurred. In such defined process conditions, a pseudo-fluidal layer of crystals would form in the space between the mixing chamber and the crystallizer body.

Next, initially mixed reactants were fed to the crystallizers: ammonium dihydrogenphosphate(V), magnesium chloride and

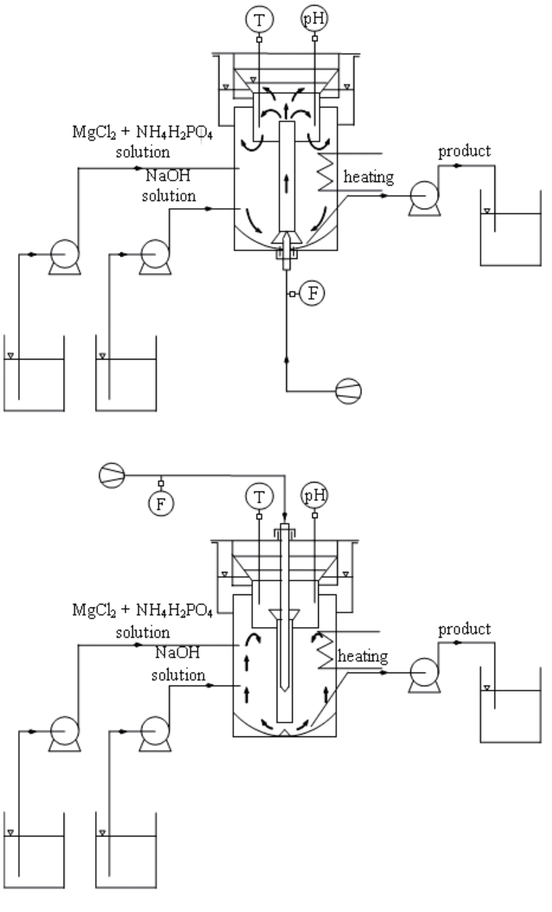

Fig.1. Scheme of laboratory–scale plant with continuous gas–liquid jet pump crystallizer of DTM MSMPR (a) and FB MSZ (b) type

deionized water, as well as a water solution of a NaOH 5% mass concentration providing the desired pH value of the struvite precipitation and crystallization environment. The points of introducing reactants, the alkalizing solution and the reception of the crystalline product suspension were marked in Figure 1. The feeding nozzle of the jet pump was fed with an experimentally determined, minimum stream of compressed air volume with a value of 0.37 dm^3/s (DTM MSMPR) and 0.43 dm^3/s (FB MSZ), necessary only for maintaining all solid particles in motion or suspension. The intensity of circulation and mixing was also minimal. The geometric proportions of crystallizers and the jet pump system, their detailed description and methodology of performing measurements and analyses of products were presented in detail in [8].

The process of continuous struvite precipitation and crystallization was carried out for a time of 5τ (counting from the moment of stabilizing the given process parameters). After this time, it may be assumed that the obtained values of crystal ratio in suspension (M_T), as well as the distributions of their sizes (CSD), correspond to the process parameters (so-called stationary state). After separating the product crystals, their washing and drying, a chemical analysis of the mother solution and the solid phase was performed, the crystal size distribution was set (COULTER LS-230 solid particle analyzer) and their pictures were taken (JEOL JSM 5800LV scanning electron microscope).

The distribution of crystal sizes obtained from the granulometric analysis of the product was recalculated to the distribution of their population density. The calculated values were used to set kinetic parameters of the examined process. A kinetic model for the MSMPR crystallizer with a continuous operation [1] was adopted in which it is assumed that the crystallization process occurs in a state set in an ideally mixed crystal suspension. With an additional simplifying premise that the linear growth rate of crystals does not depend on their sizes ($G(L) = G = \text{const}$ for a given supersaturation, so-called SIG model), the equation of the crystal population balance may be written down as [24]:

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

The equation enables the specification of the basic kinetic parameters' values of the mass crystallization process in an ideal MSMPR crystallizer. The graphic $\ln n(L)$ dependence assumes in this case the form of a straight line whose point of intersection with the y-axis for $L = 0$ is interpreted as $\ln n_0$, while its inclination as $-1/(G\tau)$. If the mean time spent by the τ suspension in the crystallizer's working volume is known then the G linear growth rate of crystals may be determined directly from the value of this straight line's inclination. The B nucleation rate value is calculated from the density value of the n_0 nuclei population and the G linear growth rate of crystals from the following formula:

$$B = n_0 G \tag{2}$$

Test results and their discussion

Selected test results were presented in Table 1. From it, it stands that together with the increase of the pH of the struvite precipitation and crystallization environment the sizes of product crystals decrease. The increase of pH from 9 to 11 causes the average L_m crystal size to decrease even twice (from approx. 27 to approx. 15 μm for $\tau = 900$ s). This results from the fact that together with the increase of pH the solubility of struvite decreases, and together with it its precipitation potential, increases [15]. Also the induction time, necessary for initiating the nucleation process in the process system, decreases. As an effect, density values of nuclei populations and smaller struvite crystals increase which leads to the shifting of the average crystal size towards smaller values.

Table 1

Influence of selected technological parameters on product mean size L_m, nucleation rate B and crystals linear growth rate G – continuous reaction crystallization of struvite from water solutions of phosphate-(V) ions in DTM MSMPR and FB MSZ type crystallizers

Crystallizer type	$[PO_4^{3-}]_{init.}$, % of mass.	Process parameters		Resulting process parameters			Bibliography
		pH	τ, s	L_m, μm	G, m/s	B, 1/(s m³)	
DTM MSMPR	0.2	9	900	26.0	$1.41\cdot10^{-8}$	$9.1\cdot10^{7}$	[9, 10]
		11	900	21.3	$9.37\cdot10^{-9}$	$4.8\cdot10^{8}$	
		9	3600	41.3	$4.60\cdot10^{-9}$	$1.5\cdot10^{7}$	
	1.0	9	900	27.3	$1.45\cdot10^{-8}$	$4.1\cdot10^{8}$	[14]
		11	900	14.4	$7.69\cdot10^{-9}$	$3.2\cdot10^{9}$	
		9	3600	38.1	$4.83\cdot10^{-9}$	$5.1\cdot10^{7}$	
FB MSZ	0.2	9	900	27.1	$1.34\cdot10^{-8}$	$6.0\cdot10^{8}$	[11, 13]
		11	900	15.1	$7.31\cdot10^{-9}$	$4.1\cdot10^{9}$	
		9	3600	41.2	$3.15\cdot10^{-9}$	$3.3\cdot10^{7}$	
	1.0	9	900	26.1	$1.33\cdot10^{-8}$	$5.7\cdot10^{8}$	[12]
		11	900	14.8	$6.62\cdot10^{-9}$	$5.9\cdot10^{9}$	
		9	3600	39.0	$4.21\cdot10^{-9}$	$1.4\cdot10^{8}$	

Temperature in the crystallizers: 298 K.
The molar ratio of reactants $[PO_4^{3-}] : [Mg^{2+}] : [NH_4^{+}] = 1 : 1 : 1$
The average concentration of phosphate ions in the liquor solution 0,012 ±0,002% mas.
The average content of crystalline phase in suspension M_T: 4,80 ±0,1 i 24,6 ±0,2 kg crystals/m^3 suspension (respectively for $[PO_4^{3-}]_{init.} = 0{,}2$ i 1,0% of mass.)
$L_m = \Sigma x_i L_i$, where: x_{i-} the participation of the mass fraction of crystals of medium size L_i

Extending the average time of the suspension in the crystallizer (from 900 to 3,600 s) causes the average crystal size to increase by approx. 50% (from 26 ÷ 27 μm to 38 ÷ 41 μm with pH = 9). The working supersaturation of the solution decreases (with constant values of the remaining process parameters), and thus the nucleation rate related to it in a non-linear way decreases (Tab.1). The linear growth rate of crystals also decreases (Tab. 1) together with the drop of the solution supersaturation, however the extension of the crystals' average time in the apparatus compensates for this decrease by providing a longer and more stable process of increasing the size through particles. Moreover, it also causes – especially with longer times – the increase of abrasion and breaking of the crystals [9÷14]. Microscopic pictures of exemplary products were presented in Figure 2.

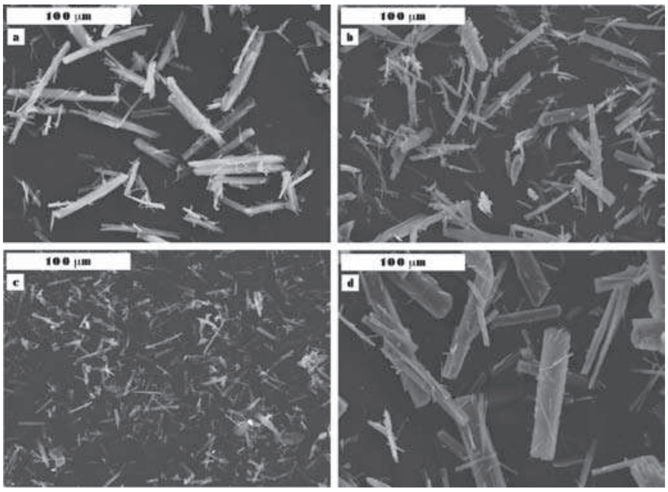

Fig. 2. Exemplary scanning microscope images of struvite crystals produced in DTM MSMPR (a) and FB MSZ (b ÷d) crystallizers with gas–liquid jet pump: a) L_m = 26.0 μm (pH = 9, τ = 900 s), b) L_m = 27.1 μm (pH = 9, τ = 900 s), c) L_m = 15.1 μm (pH = 11, τ = 900 s), d) L_m = 41.2 μm (pH = 9, τ = 3600 s). Feed concentration: 0.2 mass % of PO_4^{3-} ions. Magnification 500x

The simultaneous impact of the environment's pH in the range 9 ÷ 11 and the average time of the suspension in the crystallizers 900 < τ < 3600 s on the average size of the struvite crystals was worked out in the form of correlations (equation (3), (5), (9) and (11)) presented in Table 2. The values were given of R^2 correlation coefficients of nine measurement results for feeding crystallizers with a solution of a 0.2 or 1.0% mass concentration of PO_4^{3-}, as well as values of an average relative error. The graphic course of these dependencies was presented in Figure 3. Taking into account an additional variable in the worked out equations – the contents of M_T struvite crystals in the suspension mixed in the crystallizer – leads to a (7) and (13) dependency for the DTM MSMPR and FB MSZ crystallizers, respectively (Tab. 2).

From the data analysis (Tab. 1 and 2, Fig. 2 and 3) it stands that inhomogeneous products with different particle sizes were removed from the crystallizers. The CV inhomogeneity coefficient of the crystal population assumed high values within the range of 80 ÷ 100% [9÷14]. Generally, it may be observed that, together with the increase of pH values of the struvite precipitation and crystallization environment, the population homogeneity of its crystals decreased. The extension of the suspension's time in the crystallizer had a similar effect. One might think that this is the effect of a complex, overall impact of pH and the average time of the suspension in the crystallizer, as well as the abrasion and breaking of crystals on the level of mother solution supersaturation. The original crystallizer constructions (no movable parts), their working manner (mixing with the use of compressed air, pseudo-fluidal layer of crystals), as well as the small content of the solid phase in the suspension (M_T = 4.8 ÷ 25 kg struvite/m^3 of suspension), did not contribute to excessive abrasion and breaking of crystals (Fig. 2). Single broken crystals, damages to their surfaces, rounded edges were observed, however the number of such crystals was not big.

Table 2

Dependence of mean size L_m of struvite crystals and crystals linear growth rate G on selected process parameters in continuous DTM MSMPR and FB MSZ type crystallizers

Crystallizer type	$[PO_4^{3-}]_{init.}$, % of mass	Correlation	R^2	Average relative error, %
DTM MSMPR	0.2	$L_m = 4.83\cdot10^3 pH^{-2.67}\tau^{0.125}$, μm (3)	0.775	12.4
		$G = 1.06\cdot10^{-2} pH^{-3.29}\tau^{-0.907}$, m/s (4)	0.965	11.5
	1.0	$L_m = 5.17\cdot10^4 pH^{-3.83}\tau^{0.141}$, μm (5)	0.978	4.8
		$G = 3.34\cdot10^{-2} pH^{-3.72}\tau^{-0.420}$, m/s (6)	0.989	12.7
	0.2 – 1.0	$L_m = 2.03\cdot10^4 pH^{-3.25}\tau^{0.133}M_T^{-0.106}$, μm (7)	0.883	10.4
		$G = 2.10\cdot10^{-2} pH^{-3.53}\tau^{-0.914} M_T^{-0.047}$, m/s (8)	0.976	9.5
FB MSZ	0.2	$L_m = 8.94\cdot10^3 pH^{-3.17}\tau^{0.187}$, μm (9)	0.933	7.3
		$G = 6.68\cdot10^{-4} pH^{-1.89}\tau^{-0.975}$, m/s (10)	0.948	12.8
	1.0	$L_m = 5.68\cdot10^3 pH^{-3.07}\tau^{0.211}$, μm (11)	0.960	5.6
		$G = 3.41\cdot10^{-3} pH^{-2.89}\tau^{-0.894}$, m/s (12)	0.948	9.4
	0.2 – 1.0	$L_m = 7.53\cdot10^3 pH^{-3.12}\tau^{0.199}M_T^{-0.023}$, μm (13)	0.946	6.5
		$G = 1.60\cdot10^{-3} pH^{-2.39}\tau^{-0.934} M_T^{-0.025}$, m/s (14)	0.942	14.1
Scope of application: pH = 9 – 11, τ = 900 – 3600 s, M_T = 4.8 – 25.0 kg struvite/m^3 of suspension				

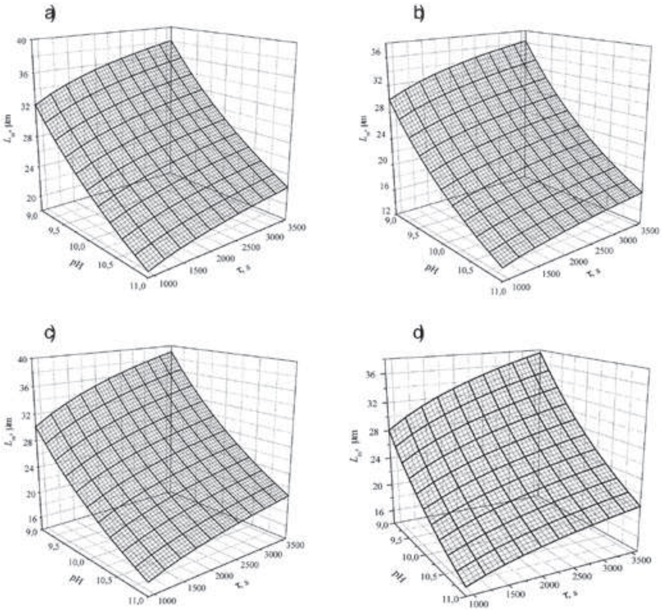

Fig. 3. Influence of reaction crystallization process pH and mean residence time of suspension in DTM MSMPR (a, b) and FB MSZ (c, d) crystallizers on mean size L_m of struvite product crystals. Concentration of phosphate(V) ions in a feed: 0.2 mass % (a, c) and 1.0 mass % (b, d)

This is a positive sign of the process conditions which were created in crystallizers for the nucleation and growth of struvite crystals. Taking into account all the elements of the precipitation and crystallization of struvite, it may be observed that the main element influencing the results of the process is the supersaturation of the solution, very strong dependencies (with a constant composition of the feeding solution, constant temperature and constant mixing/circulation intensity) on the environment pH and the average time of the suspension in the crystallizer's working volume.

The pictures of product crystals in Figure 2 clearly illustrate smaller particle sizes corresponding to a higher pH value of struvite precipitation and crystallization environment (Fig. 2c). From the analysis of pictures it also stands that together with the pH increase, struvite crystals also become thinner and their agglomeration degree increases slightly. Together with the extension of the suspension's average time spent in the crystallizer, crystals become better developed, with larger sizes (sizes of some particles even above 200 μm) and less agglomerated (Fig. 2d).

In Table 1, the analytically specified average value of phosphate ions' concentration was given: 0.012 ±0.002% of mass in the post-process mother solution discharged from the crystallizers together with product crystals. It may be assumed that the concentration of phosphate ions in the mother solution was maintained at a relatively constant and low level. Thus, the effectiveness of removing phosphate ions equaled 93 ÷ 94% ($[PO_4^{3-}]_{init.} = 0.2\%$ of mass) or 98 ÷ 99% ($[PO_4^{3-}]_{init.} = 1.0\%$ of mass).

Analyzing the kinetic data presented in Table 1 one may notice the decrease of the *G* value of linear growth rate of crystals together with the increase of the environment pH value and the extension of the average time of the suspension in the crystallizer. Generally, higher crystal growth rate values are observed for their shortest average times spent in the apparatus which is consistent with the observations concerning classical, continuous mass crystallization processes. The average *G* value for $\tau = 900$ s equals 1.43×10^{-8} and 1.34×10^{-8} m/s, and for $\tau = 3600$ s – only 4.72×10^{-9} and 3.68×10^{-9} m/s, in the DTM MSMPR and FB MSZ crystallizers, respectively. On the other hand, the relative decrease of the crystal growth rate value, caused by the increase of the environment pH value from 9 to 11 ($\tau = 900$ s), equals 33 and 47% and 45 and 50% respectively for $[PO_4^{3-}]_{init.} = 0.2$ and 1.0% of mass. This is not a favorable phenomenon. The considerable value decrease of this rate results in obtaining a product with considerably smaller crystal sizes (Tab. 1) [9÷14]. The simultaneous impact of environmental pH within the range 9 ÷ 11 and the suspension's average time in crystallizers $900 < \tau < 3600$ s on the linear growth rate of struvite crystals was presented in the form of correlations (equations (4), (6), (10) and (12)) which were shown in Table 2 and illustrated in Figure 4. The additional impact of the M_T solid phase in specific crystallizers was shown in dependencies (8) and (14).

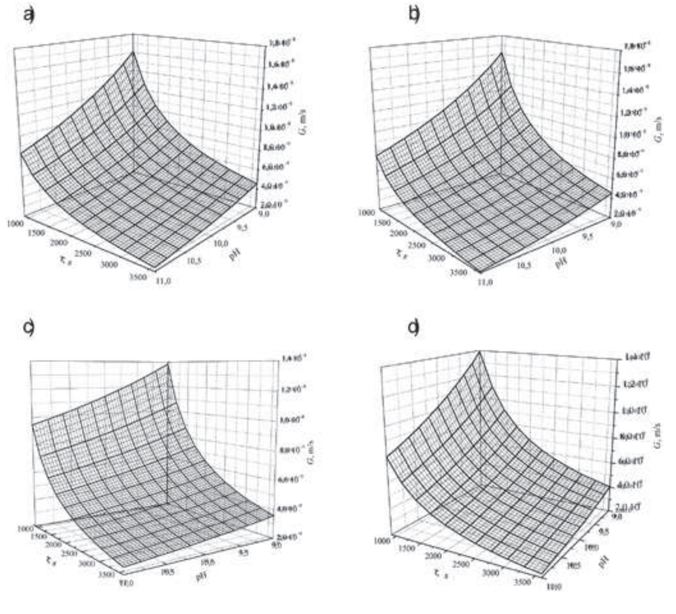

Fig. 4. Influence of reaction crystallization process pH and mean residence time of suspension in DTM MSMPR (a, b) and FB MSZ (c, d) crystallizers on linear growth rate of struvite crystals. Concentration of phosphate(V) ions in a feed: 0.2 mass % (a, c) and 1.0 mass % (b, d)

The *B* nucleation rate, similarly to the *G* linear growth rate of crystals, decreases together with extending the suspension's average time in the crystallizer. Extending this time significantly decreases the level of working supersaturation in the process system. For example, extending τ from 900 to 3600 s causes the nucleation rate to decrease several or even a dozen or so times, depending on the pH, phosphate ions' concentration in the solution feeding the crystallizers, as well as the type of crystallizer (Tab. 1, Fig. 4). Moreover, together with the increase of environment pH (within the range of 9 to 11) the nucleation rate, contrary to the crystals' growth rate, increases its values from 5 to 10 times. Higher nucleation rate means more small particles in the suspension and, as a result, a smaller average size of product crystals.

Comparing the results of tests and calculations (Tab. 1 and 2, Fig. 3 and 4) it may be noticed that the decrease in value of both analyzed kinetic parameters, *B* and *G*, together with the extension of the average time spent in the crystallizer, is accompanied by the increase of the L_m size of product crystals. The lower linear growth rate values are compensated with excess by a longer time of crystals' contact with the supersaturated mother solution. The simultaneously decreasing values of nucleation rate also favorably influence the process of crystalline phase growth and the size composition of the suspension setting in such conditions. As an effect, more favorable conditions of exchanging mass between the liquid and solid phases are created which enable an even more stable crystal growth. Under process conditions characterized by a relatively long average time of the suspension in the crystallizer, a high-quality product is created. However, at that time the unit process capacity is small and so the economic effectiveness of the production installation is also small.

From comparing the test results in both tested crystallizers it stands that under comparable process conditions the L_m average size of the obtained products' crystals, as well as the homogeneity of their population, were similar. The differences in L_m values were included within the 1 ÷ 2 μm range (Fig. 3), and the differences of CV inhomogeneity coefficients of crystals did not exceed 10%. The differences in crystal shape and habit, the degree of their agglomeration and mechanical damage were also small (Fig. 2a, b). Generally it may be assumed that the quality of struvite crystals discharged from both crystallizers was similar. It may be assessed as good, especially in comparison with the quality of products obtained (in comparable conditions) from crystallizers with a clear mother solution-driven jet pump [5÷7, 22, 23]. Here, the L_m average size of crystals was even twice as large. Thus, in the new crystallizer constructions being tested, more favorable conditions were obtained for the exchange of mass between the created and increasing solid phase and the supersaturated initial solution, with a simultaneous elimination of an intensive crystal damaging done by the circulation pump of the external circuit.

In the FB MSZ crystallizer, lower values of the *G* linear growth rate of crystals (Fig. 4), as well as higher values of the *B* nucleation rate (Tab. 1), were noted. These values are calculated from the size distribution of product crystals (SIG MSMPR model) thus it should be assumed that this is the effect of a total impact of all process elements in a given crystallizer: from producing the supersaturation, its discharge in the mixed and circulating suspension (DTM MSMPR) or in the pseudo-fluidal layer (FB MSZ), through the reception of the crystals in a solution with a residual supersaturation. It may be assumed that the initial cause of differences in kinetic parameters is a different hydrodynamics of the suspension in both crystallizers. In the FB MSZ crystallizer, the crystal suspension is not mixed intensively. Thus, there exists a higher probability of local supersaturation gradients occurring (and, at the same time, higher deviations from the ideal MSMPR crystallizer) which reflects on the intensity of nucleation, and in consequence – on the distribution of crystal sizes of the product. As a result, the kinetic parameter values calculated from this distribution are burdened with a relatively large error of the adopted kinetics model.

Summary and conclusions

Two new crystallizer constructions with continuous operation were presented in which the movement of the suspension in each of them was forced by a compressed air-driven jet pump. The crystallizers are meant for carrying out crystallization processes with the chemical reaction of precipitating difficult-to-dilute phosphate salts, mainly $MgNH_4PO_4 \cdot 6H_2O$ struvite. In case of the first construction (DTM MSMPR-type crystallizer), the feeding nozzle of the jet pump was mounted at the bottom of the crystallizer – the process was carried out in a mixed and circulating suspension inside the apparatus. In the second construction (FB MSZ-type crystallizer), the jet pump's feeding nozzle was situated below the free surface of clarified mother solution in the crystallizer – struvite precipitation and crystallization occurred in a spontaneously created pseudo-fluidal layer of crystals raised by bubbling, decompressing air. In both types of crystallizers with an identical working volume of 1.2 dm^3 tests of struvite precipitation and crystallization from diluted water solutions containing 0.2 or 1.0% phosphate ions masses were conducted. The process was carried out under stoichiometric conditions (reactant proportions), in a temperature of 298 K, with a pH of 9, 10 or 11 and an average time of the suspension in the crystallizer's working volume equaling from 900 to 3,600 s.

Both crystallizers worked stably in continuous work regime. Well developed struvite crystals were obtained with an average size of L_m 14 ÷ 41 μm. It was stated that increasing the pH value (from 9 to 11) of the struvite precipitation and crystallization environment in crystallizers caused an almost double decrease of the average size of crystals. On the other hand, extending the average time of the suspension in crystallizers from 900 to 3,600 s caused a significant increase (even by 50%) of this size. Products were discharged from the crystallizers of a small crystal homogeneity. The analysis of test results in both tested crystallizers show that under comparable process conditions the average size of product crystals and their homogeneity were close to each other. Moreover, the differences in shape and habit of crystals, their agglomeration and abrasion degree were insignificant.

The simplest kinetics model for an ideal MSMPR crystallizer was adopted for calculating the kinetic parameters of the process. It was stated that the values of a linear growth rate of struvite crystals were included within the range $2.06 \cdot 10^{-9} \div 1.41 \cdot 10^{-8}$ m/s, while the nucleation rate – within the range of $1.5 \cdot 10^{7} \div 5.9 \cdot 10^{8}$ $1/(sm^3)$. Together with extending the average time spent in the crystallizer, the values of both kinetic parameters were decreasing. However, the longer contact time of the crystals with the supersaturated solution compensated with excess for their lower growth rates. Thanks to this, crystals of larger sizes appeared in the product. On the other hand, together with the increase of pH, the nucleation rate increased and at the same time the linear growth rate decreased. As a result, a product was obtained with significantly smaller crystal sizes. In the FB MSZ crystallizer, higher values of nucleation rates and lower values of a linear growth rate were noted than in the DTM MSMPR crystallizer. It must be assumed that the fundamental cause of these discrepancies is the different hydrodynamics of the suspension in both crystallizers. However, in the pseudo-fluidal layer of crystals created in the FB MSZ crystallizer the mixing is not as intensive as in the circulating suspension in the DTM MSMPR crystallizer. Deviations from the SIG MSMPR kinetics model adopted for calculations are considerable higher here.

The simultaneous impact of the environmental pH and the average time of the suspension in the crystallizers, as well as of the crystal contents in the suspension on the average size of product crystals and the linear rate of their growth, were worked out in the form of suitable correlations which were presented in Table 2. The graphic presentation of these dependencies was presented in Figures 3 and 4.

The proposed crystallizers with a compressed air-driven jet pump, taking into account the simplicity of their construction and the operation reliability, may be recommended for recovering phosphate ions from diluted solutions in the process of phosphorus recycling.

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Officer’s Cross of the Order of the Rebirth of Poland for Professor Jacek Kijeński

Polish President Bronisław Komorowski, gave the orders and decorations deserving activists and members of the Association of Polish Inventors and Innovators. Decoration of the Act, on behalf of the Polish President, made the Secretary of State Minister Olgierd Dziekoński, during the opening of the IV International Exhibition of Innovation, Warsaw - IWIS 2010. For outstanding achievements in acting on behalf of the Association of Polish Inventors and Innovators, for achievements in scientific and journalistic **Officer’s Cross of the Order of the Rebirth of Poliand** was awarded prof. Jacek Kijeński, PACE President, member of Initiative Programmatic Council of the magazine CHEMIK science•technique•market.

Congratulations!