Research Article

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Recovery of phosphates(V) from wastewaters of different chemical composition

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Abstract: Phosphate(V) ions were recovered from wastewaters of different chemical compositions in a continuous reaction crystallization of struvite. Two real wastewaters were represented by an effluent sample from the phosphorus mineral fertilizer industry and by liquid manure derived from a cattle-breeding farm. Two other wastewaters were prepared under laboratory conditions. Impurities present in the wastewaters caused the precipitation of solid products of distinctly different quality. The mean size of struvite crystals varied from *ca.* 18 to *ca.* 40 μm. Homogeneity within their populations, quantified by the coefficient of variation *CV*, varied from satisfactory (*CV ca.* 75%) to unfavorable (*CV ca.* 100%), which resulted in the elongation of necessary filtration time. Calcium ions in wastewater precipitated as amorphous hydrated calcium phosphates ACP. Their content in the products varied from 33.4 up to 73.1 mass %. Also 28.32 – 32.74 mass % of P_2O_5, 6.35 – 14.12 mass % of MgO and 4.35 – 16.94 mass % of CaO were confirmed in the products, together with hydroxides of some metals and salts of other impurities. Based on the chemical composition of the products derived from the investigated wastewaters, their application in agriculture as valuable mineral fertilizers is recommended.

Keywords: phosphate(V) ions; continuous reaction crystallization; industry wastewater; cattle liquid manure; phosphorus recycling; struvite.

1 Introduction

Recovery of phosphate(V) ions from industry wastewaters [1] or from agricultural liquid manure [2] is most often solved technologically by precipitating them as sparingly soluble magnesium and ammonium salt, $MgNH_4PO_4{\bullet}6H_2O$ – struvite (a variant of phosphorus recycling) [3, 4]. Struvite precipitates after direct contact of the following species: magnesium ions (*e.g.* magnesium chloride), ammonium ions (*e.g.* some ammonium salt) and phosphate(V) ions, provided that the solution's pH is appropriately raised [5]. The process should be driven under control, thus providing the possibly best quality struvite [6]. The solid product should not contain excessive doses of impurities derived from wastewater, especially heavy and toxic metals [3]. Struvite may be practically utilized as a competitive and balanced mineral NPMg fertilizer, slowly introducing its nutrient components into the soil [7]. If treated wastewater contains, among others, calcium ions, calcium phosphates also co-precipitate in a batch [8] or continuous [9] struvite reaction crystallization process modes. Depending on the process parameters (mainly pH and mean residence time of suspension), as well as on the specific chemical composition of wastewater, different crystalline or amorphous phases may form, like $CaHPO_4{\bullet}2H_2O$ (brushite, DCPD), $Ca_4H(PO_4)_3{\bullet}2.5H_2O$ (OCP), $Ca_3(PO_4)_2{\bullet}nH_2O$ (ACP or TCP, *n* may be also 0), $Ca_5(PO_4)_3OH$ (hydroxyapatite, HAP) [10]. The chemical and phase composition of the product manufactured from wastewater with calcium ions undergoes significant changes [11]. Calcium content in some products can reach even up to 30 mass % [12].

Wastewaters of high phosphate(V) ions load (from 0.2 to even above 1.0 mass % of PO_4^{3-}) usually derive from phosphoric acid production (wet process) and from the phosphorus mineral fertilizers industry [13]. A characteristic feature of these wastewater systems is, among others, a high concentration of silicon and fluorine compounds, as well as the presence of sulfuric acid [1]. Liquid manure is equally rich in phosphates [14]. Depending on its origin (cattle or pig liquid manure), the

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phosphorus content can be 0.2 – 0.4 mass % (presented as phosphates(V): 0.6 – 1.2 mass %) [2, 3]. High phosphorus content is connected with high nitrogen (0.45 – 0.64 mass %), potassium (0.3 – 0.6 mass %), magnesium (0.1 mass %) and calcium (0.3 mass %) concentrations [15, 16]. Since concentrations of these components are similar, recovery of phosphate(V) ions from liquid manure is regarded to be an extremely complex technological challenge [4]. It results, among others, from competitive reactions of magnesium and ammonium phosphate(V), as well as calcium phosphate precipitation. This process is also affected by impurities, iron and nutrient microelements present in liquid manure [3]. These are mainly: boron, cobalt, copper, manganese, molybdenum and zinc compounds [2, 17].

Impurities present in wastewaters or in liquid manure may catalyze or inhibit the nucleation of struvite and calcium phosphates, as well as influence the formation of other sparingly soluble salts or/and hydroxides. These may also influence particle growth up to macroscopic size range, affecting not only their sizes, but also homogeneity, shape and agglomeration abilities. Phase and chemical composition of the products may undergo significant changes, which is of primary importance in their further utilization.

Experimental results comparing the effect of impurities present in real wastewater from the phosphorus mineral fertilizer industry, IWW (leachate from slag heap of phosphogypsum in chemical industrial plant Police S.A., Poland) [1] and impurities identified in real cattle liquid manure CLM (derived from cattle-breeding farm near Wroclaw, Poland) [2, 18] on the quality of manufactured struvite are presented. Reaction crystallization of struvite ran continuously at magnesium ions excess in relation to phosphate(V) ions, in temperature 298 K, at pH 9 and for mean residence time of suspension in a crystallizer 3600 s, thus modeling the conditions recommended for industrial application [3, 4]. The parameters of crystal size distribution (CSD), as well as phase and chemical compositions of the products were determined experimentally based on instrumental analysis techniques. Test results were then related to the products manufactured from laboratory-prepared wastewaters, where combinations of impurities approached those found in real wastewaters (termed: synthetic wastewaters) – SWWP (Synthetic Wastewater of Phosphoric Acid Industry) [11] and SABW (Synthetic Animal Breeding Wastewater) [19]. Moreover, properties of these products were compared with the characteristics of struvite produced in comparable process conditions, but from a raw solution without any impurities, WI [20]. All presented tests were mainly focused on the identification of struvite product properties (especially chemical composition) in respect to its possible application as a mineral fertilizer, considering the current demand in the agricultural market.

2 Methods

2.1 Materials

Chemical compositions of wastewaters tested are presented in Table 1. Synthetic wastewaters SWWP and SABW were prepared from crystalline substances (*p.a.* – analytically graded, POCH Gliwice, Poland) and deionised water (Barnstead–NANOpure DIamond). These were aqueous solutions of ammonium dihydrogenphosphate(V) $NH_4H_2PO_4$, magnesium chloride hexahydrate $MgCl_2{\cdot}6H_2O$, chlorides of impurity cations ($AlCl_3{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $FeCl_3{\cdot}6H_2O$, KCl, $MnCl_2{\cdot}4H_2O$, NaCl, NH_4Cl and $ZnCl_2$) and sodium salts of impurity anions (NaF, Na_2SO_4 and Na_2SiF_6). Boron and molybdenum were introduced as standard solutions H_3BO_3 and $(NH_4)_6Mo_7O_{24}$ (CertiPUR, Merc, Germany). SWWP wastewater contained phosphate(V) ions of concentration 1.0 mass % and inorganic impurities (Al, Ca, Cu, Fe, K, Zn, as well as F^-, SiF_6^{2-} and SO_4^{2-}) being usually co-present in industry-derived wastewaters from the production of phosphoric acid and phosphorus mineral fertilizers [11]. The composition of SABW wastewater approached the animal-derived wastewater (liquid manure). Besides phosphate(V) ions (0.208 mass %) it also contained relatively large amounts of calcium, sodium, potassium and ammonium ions (attaining 0.451 mass %) [19]. Real samples of wastewater from the phosphorus mineral fertilizer industry IWW contained 0.445 mass % of phosphate(V) ions and impurity species, not only in a form of typical metal ions, but also as fluorides, fluosilicates and sulphates(VI) [1]. Liquid manure from cattle-breeding CLM contained 0.340 mass % of phosphates(V) and impurities typical for liquid manure with a high concentration of ammonium, calcium and sodium [2]. Detailed chemical compositions of these wastewaters are presented in Table 1, together with other substrates of struvite synthesis (magnesium and ammonium ions) dosed to satisfy a molar proportion of $PO_4^{3-} : Mg^{2+}$ as 1 : 1.2 (magnesium ions excess). Synthetic wastewaters provided some theoretical information about the individual effects of precisely known combinations of components, whereas from real wastewaters some data useful in design practice can be gained.

Table 1: Chemical compositions of synthetic and industry wastewaters containing phosphate(V) ions and struvite synthesis substrates of molar proportion PO_4^{3-} : Mg^{2+} as 1 : 1.2.

Component	Concentration in wastewaters, in mass %			
	SWWP	IWW	SABW	CLM
PO_4^{3-}	1.0	0.445	0.208	0.340
Mg^{2+}	0.307	0.137	0.064	0.1044
NH_4^+	0.190	0.085	0.451	0.28
Al	0.01	$6.4\bullet10^{-4}$	–	–
B	–	–	$1.62\bullet10^{-4}$	–
Ca	0.150	0.044	0.127	0.120
Cu	$0.5\cdot10^{-4}$	$0.25\bullet10^{-4}$	$6.35\bullet10^{-4}$	$3.3\cdot10^{-4}$
Fe	$5.0\cdot10^{-4}$	$8.9\bullet10^{-4}$	$2.2\bullet10^{-4}$	$2.3\cdot10^{-4}$
K	0.10	$46.0\bullet10^{-4}$	0.19	0.28
Mn	–	–	$19.0\bullet10^{-4}$	$15.0\cdot10^{-4}$
Mo	–	–	$0.62\bullet10^{-4}$	$0.1\cdot10^{-4}$
Na	–	–	0.05	0.12
Si	–	$51.0\bullet10^{-4}$	–	–
Ti	–	$0.2\bullet10^{-4}$	–	–
Zn	$0.5\cdot10^{-4}$	$2.2\bullet10^{-4}$	$31.2\bullet10^{-4}$	$18.0\cdot10^{-4}$
F^-	$20.0\cdot10^{-4}$	$42.0\bullet10^{-4}$	–	–
SiF_6^{2-}	0.03	0.025	–	–
SO_4^{2-}	0.50	0.0703	–	–

SWWP – Synthetic Phosphoric Acid Industry Wastewater
IWW – Industry Wastewater; Phosphorus Mineral Fertilizers Industry Wastewater
SABW – Synthetic Animal Breeding Wastewater
CLM – Cattle Liquid Manure

2.2 Setup and procedure

The recovery of phosphate(V) ions from wastewaters presented in Table 1 was carried out in a continuous DT MSMPR (Draft Tube, Mixed Suspension Mixed Product Removal) type crystallizer (of working volume V_w 0.6 dm^3) [21], in two different, fully automated experimental plants. Steering, control and multichannel recording of output data streams were organized and centrally synchronized by a PC computer unit, using original drivers. The SABW and CLM wastewaters were directed to a Mettler Toledo plant (iControl LabMax 4.0 drivers) [2, 18, 19], whereas SWWP and IWW wastewaters – to IKA Labortechnik experimental plant (IKA Labworldsoft and BioScadaLab drivers) [1, 11]. Constructional details of the crystallizers integrated with experimental plants were presented elsewhere [1, 2, 11, 19]. Each time the specified wastewater together with dissolved substrates of struvite synthesis (Table 1) were introduced into crystallizer's circulation pipe (downward movement of suspension). Aqueous solution of sodium hydroxide was dosed between the crystallizer body and centrally located circulation profile (upward movement of suspension) providing the necessary, controlled pH of a continuous struvite reaction crystallization environment. Research tests ran at temperature T 298 ±0.2 K assuming pH 9 (±0.1) and the mean residence time of suspension in a crystallizer t 3600 (±20) s (in case of IWW, SABW, CLM) or t 900 (±20) s (for SWWP). After stabilization of the predetermined parameter values in a crystallizer, a stable steady-state process ran through the additional time of 5t (here 5 h). After this period, the whole working volume was transferred onto a vacuum filter. Product crystals were not washed.

2.3 Analytical

After the air-drying of solid products in ambient temperatures their size distributions were determined with the use of instrumental analysis. Mean struvite crystal size, $L_m = Sx_iL_i$, was determined, where: x_i – mass fraction of crystals of mean size L_i. Coefficient of crystal size variation, characterizing its non-homogeneity, was calculated as $CV = 100(L_{84} - L_{16})/(2L_{50})$, where: L_{84}, L_{16}, L_{50} – crystal sizes limiting undersize fractions representing: 84, 16 and 50 mass %, appropriately. Also, the mode crystal size L_d, the value corresponding to maximum in differential crystal size distribution, was identified. Crystal shape was analyzed and quantified by planimetric determination of its length L_a to width L_b ratio, based on 50 crystals representing each product population, randomly selected from 3 scanning electron microscope (JEOL JSM 5800LV) images. On this basis, the geometrical coefficient of crystal shape k_v (= $V_{crystal}/L^3$) was calculated, where $V_{crystal}$ – crystal volume, L – its linear size. The chemical composition of the mother solution and solid product were identified analytically using an atomic absorption spectrometer iCE 3000 (metals), spectrophotometer UV–VIS Evolution 300 (phosphates(V)) and by titration (ammonium, formalin analytical method). Moreover, for the solid phase analysis, an X-ray fluorescence spectrometer PANalytical Magi'X PW2424 (phosphorus and metals) was used (procedure of melting of powder samples with lithium borates was used, calibration and ZAF correction, PN EN ISO 12,677: 2011). For phase identification in a product, an X-ray diffractometer PANalytical XPERT PRO MPD was applied (equipped

Table 2: Comparison of SWWP, IWW, SABW, CLM and WI wastewaters feeding the continuous DT MSMPR crystallizer in respect to the particle product characteristic.

Wastewater type	Characteristic properties of product population				
	L_m	L_{50}	L_d	CV	L_a/L_b
	μm	μm	μm	%	–
SWWP	24.5	15.9	16.4	99.0	3.9
IWW	36.8	30.1	33.3	74.7	4.3
SABW	18.1	14.0	28.7	82.1	–
CLM	40.2	29.6	39.8	98.8	–
WI	48.5	42.4	44.6	64.6	7.7

Process parameters: molar proportions of substrate ions in a feed $PO_4^{3-} : Mg^{2+} = 1 : 1.2$, pH 9, T 298 K and mean residence time of suspension in a crystallizer t 900 s (SWWP) and t 3600 s (IWW, SABW, CLM, WI).

with Cu anode, X'Celerator RTMS detector, X-ray pattern within 5–80° 2θ range, X-ray tube settings: 40 kV and 30 mA, PANalytical High- Score software with ICDD PDF 4+ database, Rietveld method and Siroquant software were also in use). Size distributions of product particles, together with statistical parameters of these distributions were determined with laser solid particle analyzer Beckman Coulter LS 13 320. Also, thermogravimetric TG, differential thermal analysis DTA, as well as educed gases EGA research tests were done. Accuracy of the process data determination was estimated to be 10 – 12%.

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

3 Results and Discussion

3.1 Crystal size distribution

Statistical and planimetric parameters of the product's size distributions corresponding to the investigated wastewaters are presented in Table 2. Properties of pure struvite manufactured from solution without impurities, WI [20], were also added for comparison. From Table 2 it can be seen, that the best formed product crystals were manufactured from the pure aqueous solution of phosphate(V) ions (without any other impurities) (WI) of concentration 0.20 mass %. The mean size L_m of this product was 48.5 μm, whereas the mode size L_d reached 44.6 μm. Maximal value of the homogeneity coefficient CV reached *ca.* 65%. Thus, it was product of the highest quality. Contrarily, the product representing the worst size distribution parameters corresponded to synthetic animal breeding wastewater, SABW. The mean size L_m of this population was 18.1 μm only, thus was nearly 2.5-time smaller than the L_m of struvite manufactured from WI. Homogeneity within the population deteriorated; CV increased up to 82.1%. Maximal product crystal size was only 78 μm, while from the WI solution some struvite crystals exceeding even 200 μm were obtained. Since the product from SABW also contained small particles (product fraction < 5 μm represented 22.6 mass %, whereas the product from WI – 3.8 mass % only [20]), the separation of solid phase from the mother liquid was difficult. Vacuum filtration was long, and the product after filtration still contained ca. 30 mass % of mother liquid. A relatively significant agglomeration of product particles was observed; especially after drying, caking and agglomeration were observed (see Figure 1c).

Size dispersion ranges within the compared products can be classified in the following sequence, according to the CV indicator value: 64.6% (WI) < 74.7% (IWW) < 82.1% (SABW) < 98.8% (CLM) < 99.0% (SWWP). The least homogeneous products were obtained from real liquid manure CLM, and synthetic wastewater from the phosphoric acid industry SWWP (CV reached ca. 100%). The effect of impurities and their individual concentrations/ratios on struvite nucleation and its crystals growth is thus manifested [3, 4]. A similar sequence can also be demonstrated for the mean sizes of solid products, L_m: 48.5 μm (WI) > 40.2 μm (CLM) > 36.8 μm (IWW) > 24.5 μm (SWWP) > 18.1 μm (SABW). The effects of individual impurities (mainly metal ions) on size and homogeneity within struvite crystal populations in some cases may be generally favorable (*e.g.* aluminum [22], copper [23], potassium [24], as well as boron, cobalt and molybdenum ions [17]), in other cases -unfavorable (*e.g.* calcium [11, 12], manganese [17], iron [25], zinc [26] ions). Calcium [9, 12] and zinc [26] ions are especially disadvantageous in respect to struvite crystals growth and their size-homogeneity. Calcium ions also co-precipitate forming phosphates [11] of smaller sizes than struvite crystals. The shifting of the mean product size towards smaller values was reported. Zinc ions [26], similar to iron [25] and manganese [17] ions, precipitate in a form of hydroxide, also of small size. Their net effect is usually unfavorable [11, 19]. From the synthetic wastewater SWWP [11] struvite crystals of mean size L_m more than 12 μm smaller than L_m of the product from the real wastewater IWW [1] were obtained. Similarly, from synthetic liquid manure SABW [19], solids of more than 2-times smaller mean size L_m than from real liquid manure CLM [2] were

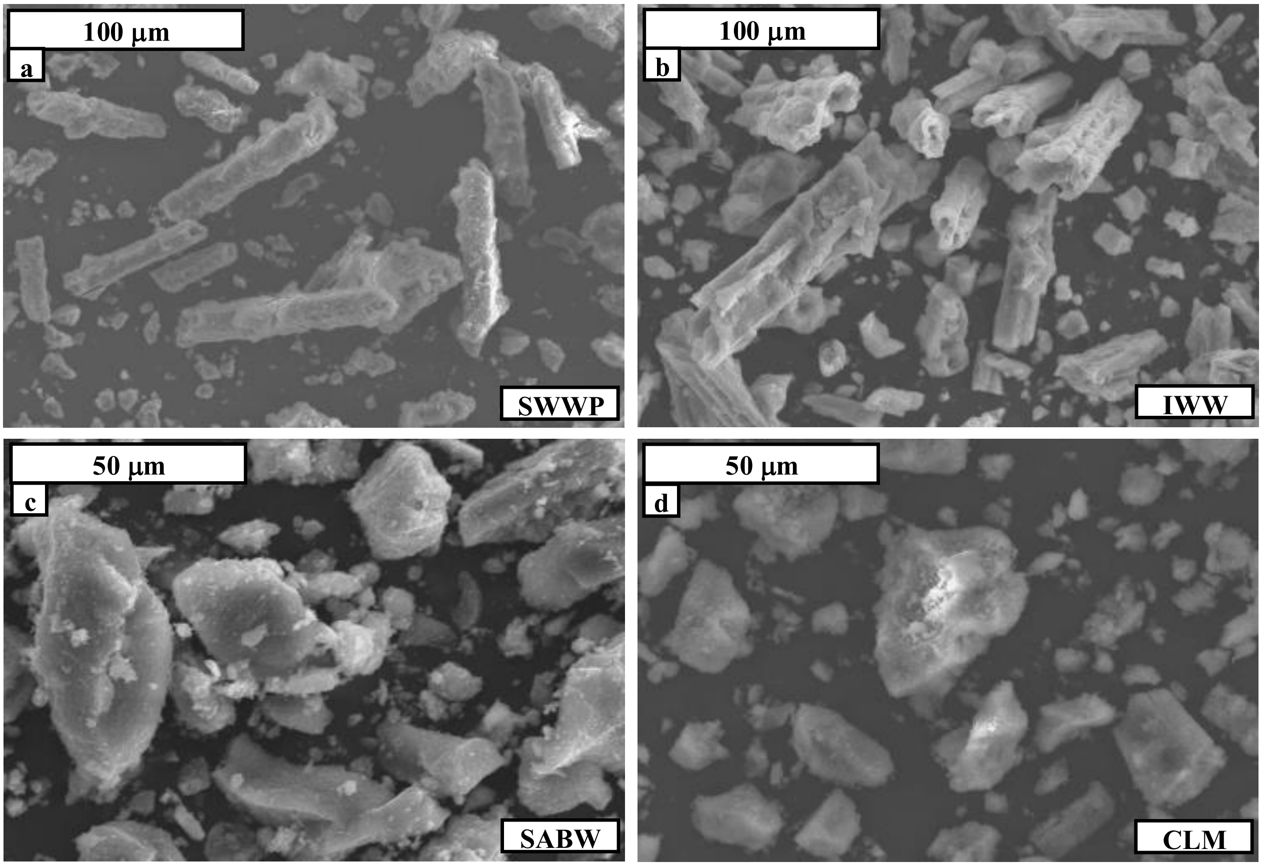

Figure 1: Scanning electron microscope images of struvite crystals produced from: synthetic wastewater of phosphoric acid industry SWWP (a), real phosphorus mineral fertilizer industry wastewater IWW (b), synthetic animal breeding wastewater SABW (c) and real cattle liquid manure CLM (d).

collected. In both compared cases chemical compositions of inorganic impurities in wastewaters were similar (Table 1), nevertheless the parameters of product size distributions were clearly different. One can assume that the reason for these differences was the co-presence of other impurities, especially organic ones. Their action on the struvite reaction crystallization process turned out to be advantageous. Products of higher quality were manufactured from the real wastewaters than from synthetic wastewaters.

3.2 Crystal shape

Solid products contained mainly struvite, but also calcium phosphates, hydroxides and salts of impurities present originally in wastewaters (Table 1). Scanning electron microscope images of these product crystals are demonstrated in Figure 1. Diverse sizes of struvite are distinct. Also, other solids, co-precipitated from wastewaters in the process conditions arranged are observable. As it was mentioned earlier, the best shaped struvite crystals, representing the most favorable size distribution, were produced from real wastewaters IWW (Figure 1b) and CLM (Figure 1d); these are of the worst quality – from synthetic wastewaters SWWP (Figure 1a) and SABW (Figure 1c). Based on the analysis of scanning electron microscope images, one can conclude that the struvite crystals surface was occupied by various combinations of co-precipitated hydroxides and impurity salt fines, generating strong tensions within the struvite crystals microstructure. For this reason numerous crystal cracks and fractures, irregular surface morphology, randomly deformed edges, *etc.* are observed. From the analysis of microscope images, it can also be seen that the crystal habit was not constant. Based on planimetric measurements of 50 crystals from each product, selected randomly from three scanning electron microscope images, it was concluded, that the mean length L_a to width L_b ratio was 3.9 (SWWP) and 4.3 (IWW) (Table 2). Contrarily, struvite manufactured in the same crystallizer from aqueous solution of phosphate(V) ions without impurities WI demonstrated the L_a/L_b ratio of 7.7 [20]. The L_a/L_b ratios for solids derived from synthetic and real liquid manure were impossible to estimate, since the product was lumped and agglomerated (Figure 1c and d). Microscope images of the products (Figure 1) show struvite crystals of a prismatic, needle shape, as well as even tubular-form crystals. These crystals were more or less deformed, with surface defects and damaged edges. Inside and outside these are covered by the fines representing hydroxides of impurity metals and different salts. Generally cross-section of these crystals was ring-shaped, however not in each case. The volumetric shape coefficient k_v for typical struvite crystals varies usually from 0.010 to 0.040 for $L_a : L_b : L_c$ 10 : 1 : 1 and 5 : 1 : 1, correspondingly [27]. Assuming that struvite crystals are cylindrical (Figure 1a and b), their mean shape coefficient k_v was calculated as: 0.052 (L_a/L_b 3.9; SWWP) and 0.042 (L_a/L_b 4.3; IWW). The experimentally determined k_v of struvite crystals produced from aqueous solutions of phosphate(V) ions without impurities was 0.013 [20]. Struvite content in this product was 99.6 mass %. The appearance of tubular-form crystals in the process environment suggests that process kinetics is diffusion-limited [28].

3.3 Product phase and chemical composition

Table 3: Product phase composition.

Component	Content, in mass %			
	Product from wastewater type:			
	SWWP	IWW	SABW	CLM
Struvite, $MgNH_4PO_4·6H_2O$	65.0 ±0.2	61.1 ±0.1	26.5 ±0.2	62.2 ±0.2
Amorphous phase	33.9 ±0.8	37.9 ±0.6	73.1 ±0.4	33.4 ±0.6
Halite, NaCl	1.2±0.1	1.0 ±0.1	0.4 ±0.1	3.2 ±0.1

T 298 K, pH 9, $PO_4^{3-} : Mg^{2+} : NH_4^+ = 1 : 1.2 : 1$, τ 900 s (SWWP), τ 3600 s (IWW, SABW, CLM)

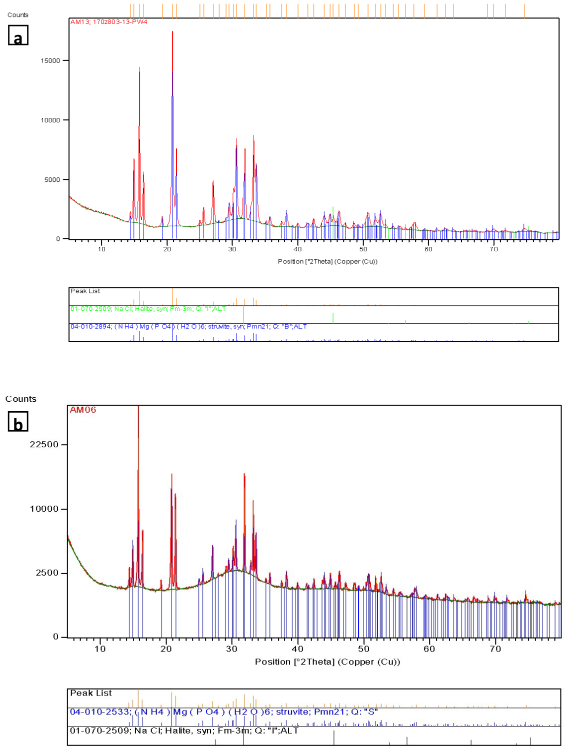

Figure 2: X-ray diffraction pattern of product from SWWP (a) and SABW (b) with characteristic peaks of crystalline phases: struvite and halite; a large amount of amorphous phase is visible as characteristic background hump.

Solid products of the process, without water washing of crystals on a filter (*ca.* 25 – 30 mass % of mother liquor remained within the post-filtration cake structure) and after drying, represented mixed struvite and calcium phosphates. Hydroxides of some metals and salts of impurities derived from the mother liquor (indirectly – from source wastewaters) were also identified. Phase composition of these products is presented in Table 3. The composition was determined in X-ray tests (X-ray diffractometer) and then these were independently confirmed based on thermal analysis methods (TG, DTG, DTA). It was concluded, that the products contained struvite $MgNH_4PO_4•6H_2O$ in amounts varying from 26.5 mass % (product from SABW) to 65.0 mass % (product from SWWP). Also, crystalline halite (NaCl) was identified, varying from 0.4 mass % (SABW) to 3.2 mass % (CLM). Moreover, an amorphous phase was isolated in amounts ranging from 33.4 mass % (product from CLM) up to 73.1 mass % (product from SABW). This amorphous phase is visible in a form of characteristic raised diffraction pattern background of X-ray test (Figure 2, exemplary products from SWWP (a) and SABW (b)). Comparing phase composition (Table 3) and chemical composition (Table 4) analyses with feed composition (Table 1) one may conclude, that the amorphous phase was represented mainly by a hydrated form of one from within calcium phosphates(V) (e.g. $Ca_3(PO_4)_2•nH_2O$, ACP) [10]. One can also suppose, that in this phase co-precipitated sparingly soluble hydroxides of some metal impurities were also present (Table 4). The presence of amorphous hydrated calcium phosphate(V) was independently confirmed

Table 4: Chemical composition of solid phase manufactured from SWWP, IWW, SABW and CLM wastewaters in a continuous reaction crystallization process.

Component	Content in product, in mass %			
	SWWP	IWW	SABW	CLM
P_2O_5	29.01	31.45	32.74	28.32
MgO	11.12	14.12	6.35	13.11
CaO	4.99	4.35	16.94	9.16
Al_2O_3	0.60	0.15	–	–
Fe_2O_3	0.05	0.29	0.09	0.06
K_2O	0.54	0.21	0.44	2.38
MnO	–	0.15	0.37	0.24
Na_2O	1.24	1.14	0.74	3.66
SiO_2	0.16	0.43	–	–
others	0.08	0.14	0.03	0.04
Weight loss during drying in temperature 378 K + weight loss during roasting in temperature 1298 K	52.22	47.57	42.30	43.12

during tests with thermal analysis methods (DTA, TG). This way calcium ions had a key effect on the reaction crystallization of struvite. Their presence in a process system induced a competitive chemical reaction of calcium phosphates synthesis [11]. Thus, the products formed may be generally termed as *struvite with the addition of hydrated calcium phosphate* (products from SWWP, IWW and CLM, see Table 3) or even, where this addition prevails, *hydrated calcium phosphate with struvite addition* (product from SABW, see Table 3). Each product was, however, contaminated with hydroxides and salts of metals derived from the crystallizer feed (Table 4). Magnesium content (as MgO) in the products varied from 6.35 mass % (SABW) to 14.12 mass % (IWW), calcium content (as CaO) – from 4.35 mass % (IWW) even up to 16.94 mass % (SABW). The P_2O_5 content varied from 28.32 to 32.74 mass % (Table 4). Thus, these products can be recommended as useful mineral fertilizers, slowly dosing their nutrient contents, which are valuable products in the world's fertilizers market [3, 7, 29, 30].

4 Conclusions

Phosphate(V) ions were recovered from four wastewaters of different chemical composition. Two of them represented real wastewater from the phosphorus mineral fertilizer industry (IWW) and liquid manure from the cattle-breeding farm (CLM). Another two wastewaters were prepared under laboratory conditions (SWWP, SABW). The presence of impurities in a continuous crystallizer feed resulted in the precipitation of products of clearly different quality. The mean size L_m of the solids representing these products varied in a very broad range: from 18.1 μm (SABW) to 40.2 μm (CLM), similarly to the other two parameters of crystal size distribution (CSD): L_{50} (14.0 – 30.1 μm) and L_d (16.4 – 39.8 μm). The *CV* value, representing size non-homogeneity within product particles varied from a moderate (*CV* 74.7%; IWW) to an unfavorable (*CV* 98.8 – 99.0%; CLM, SWWP), which, in turn, significantly elongated the filtration time of the product suspension. It was concluded that the struvite crystal's surface was occupied by co-precipitating solid particles of hydroxides and salts of metal impurities. In consequence, large tensions were generated within the struvite crystal's structure. Externally these produced numerous crystal cracks, randomly irregular surface micromorphology, deformed edges, *etc*. Struvite crystals of a prismatic, needle habit were visible, as well as numerous, specific in shape and clearly exhibiting these effects, tubular crystals [28].

It was experimentally confirmed, that the reaction crystallization of struvite was affected by calcium ions. Their presence in a process system resulted in the co-synthesis of amorphous calcium phosphates (ACP). Solid products manufactured from investigated wastewaters contained struvite from 26.5 mass % (products from SABW) up to 65.0 mass % (product from SWWP) and amorphous hydrated calcium phosphate from 33.4 mass % (CLM product) to 73.1 mass % (SABW product), accompanied by other salts and hydroxides of metal impurities. Contents of the main components in the products were: P_2O_5 from 28.32 (CLM) to 32.74 mass % (SABW), magnesium (as MgO): from 6.35 (SABW) to 14.12 mass % (IWW) and calcium (as CaO) from 4.35 (IWW) to 16.94 mass % (SABW). The chemical composition of the products derived from the investigated wastewaters can be generally regarded as satisfactory. Their application in agriculture is thus possible and even recommended.

In future some investigation should focus on the optimization of the struvite manufacturing procedure, considering phase, chemical composition, as well as product size distribution towards combinations demanded in agriculture. Moreover, other promising sources of phosphates – wastewaters from other industry branches and from agricultural sources – should be experimentally investigated towards struvite synthesis abilities.

List of abbreviations

ACP – amorphous calcium phosphates, $Ca_3(PO_4)_2 \bullet nH_2O$
CLM – cattle liquid manure
CSD – crystal size distribution
DCPD – brushite, $CaHPO_4 \bullet 2H_2O$
DT MSMPR – Draft Tube, Mixed Suspension Mixed Product Removal crystallizer
HAP – hydroxyapatite, $Ca_5(PO_4)_3OH$
IWW – Industry Wastewater; Phosphorus Mineral Fertilizers Industry Wastewater
OCP – $Ca_4H(PO_4)_3 \bullet 2.5H_2O$
SABW – Synthetic Animal Breeding Wastewater (synthetic liquid manure)
SWWP – Synthetic Wastewater of Phosphoric Acid Industry
TCP – $Ca_3(PO_4)_2 \bullet nH_2O$
WI – solution without any impurities

List of symbols

CV – coefficient of (crystal size) variation, %
k_v – coefficient of crystal shape,
L – crystal linear size, m
L_{84}, L_{16}, L_{50} – crystal sizes limiting undersize fractions representing: 84, 16, 50 mass %, m
L_a – crystal length, m
L_b – crystal width, m
L_c – crystal height, m
L_d – mode crystal size, m
L_m – mean crystal size, m
$V_{crystal}$ – crystal volume, m^3
V_w – crystallizer working volume, m^3
T – process temperature, K
t – mean residence time, s
x_i – mass fraction of crystals of mean size L_i

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