Studies on the transformation of calcium sulphate dihydrate to hemihydrate in the wet process phosphoric acid production

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The influence of the process temperature from 85°C to 95°C, the content of phosphates and sulphates in the wet process phosphoric acid (about 22–36 wt% P_2O_5 and about 2–9 wt% SO_4^{2-}) and the addition of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei (from 10% to 50% in relation to $CaSO_4 \cdot 2H_2O$) on the transformation of calcium sulphate dihydrate to hemihydrate has been determined. The wet process phosphoric acid and phosphogypsum from the industrial plant was utilized. They were produced by reacting sulphuric acid with phosphate rock (Tunisia) in the DH-process. The X-ray diffraction analysis was used to determine the phase composition and fractions of various forms of calcium sulphates in the samples and the degree of conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ and $CaSO_4$. It was found that the transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ should be carried out in the presence of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei as an additive (in the amount of 20% in relation to $CaSO_4 \cdot 2H_2O$), at temperatures 90±2°C, in the wet process phosphoric acid containing the sulphates and phosphates in the range of 4±1 wt% and 27±1 wt%, respectively.

Keywords: wet process phosphoric acid; phosphogypsum; transformation; calcium hemihydrate.

INTRODUCTION

The world phosphoric acid production amounted to 39.8 million tons of P_2O_5 in 2009, and, according to forecasts, will increase to 46.9 million tons of P_2O_5 by 2013 [1,2]. The largest consumption of phosphoric acid in 2009 was in Asia (30%), United States (22%) and Southwest Asia (10%) [3]. The phosphoric acid is produced by two commercial methods: wet process and thermal process. In the wet process the phosphate rock is extracted by acids (hydrochloric, nitric, sulphuric acids). The wet process phosphoric acid is utilized in 80–85% in the production of fertilizers, mainly triple superphosphate and ammonium phosphates [1].

The wet process phosphoric acid can be obtained by the decomposition of phosphate rock with sulphuric acid by the following methods: dihydrate (DH-process), hemihydrate (HH-process) and by combined processes [4–15]. The latter group includes various variants of process operation such as hemi-dihydrate transformation (HDH-process), di-hemihydrate transformation process (DHH-process) and hemi-di-hemihydrate transformation (HDHH-process). The primary objective of these processes was the achievement of high degree of phosphate rock conversion, a reduction of the phosphates content (phosphate losses) in waste $CaSO_4 \cdot nH_2O$, an enhancement of the degree of phosphates conversion from phosphate rock to the product, and the generation of waste with purity as high as possible [4,5]. The phosphates content in the calcium sulphate hydrate depends on the production method used. Their content results from the presence in this waste of unreacted phosphoric raw material, unwashed phosphoric acid and due to the co-crystallization of $CaHPO_4 \cdot 2H_2O$ with $CaSO_4 \cdot nH_2O$ [4,5].

In the wet process phosphoric acid production by the DH-process as much as 4–5 tons of phosphogypsum (PG) is generated per each ton P_2O_5 in the acid. Phosphogypsum is a waste by-product mainly disposed in landfills. Throughout the world in numerous landfills (some ac-

tive, some closed, some lost or abandoned) located in 50 countries there are about 5 billion tons of PG and the annual production is estimated to be 100–200 million tons [16]. For example, in China alone there are more than 200 million tons of PG in landfills and this quantity increases annually by 20 million tons. The phosphogypsum is characterized by the particles size in the range of 5–300 μm, significant humidity 10–40 wt% H_2O and it contains various impurities, such as phosphates, silicates, alkali-earth metals, fluorides, toxic and radioactive elements [4,5]. The actual content of these elements depends on the particular method of processing. With regard to above-mentioned physicochemical properties, the degree of utilization of the considerable quantities of phosphogypsum generated annually still remains below 15% [5,16]. More than 50 different methods have been proposed for phosphogypsum utilization in agriculture (as a source of calcium and sulphur, soil conditioner, filler in the production of fertilizer), construction (as setting regulator in cement, plaster, plasterboard, gypsum blocks), road building, industrial (as filler/pigment, production of ammonium sulphate and sulphuric acid), other (mine leveling, land reclamation) [16–19].

Only limited amounts of phosphogypsum are presently used for purposes such as building construction materials or road pavements. Currently in Europe, only PG produced by Prayon SA Company (DHH-process, Belgium) is used as plaster on a commercial scale (80% of the total production). In Finland (Kemira GrowHow) some phosphogypsum is applied in the paper industry [5,11].

The production of wet process phosphoric acid by DH-process is carried out within the crystallization region of metastable $CaSO_4 \cdot 2H_2O$ whereas that carried out by HH-process within the crystallization region of metastable $\alpha CaSO_4 \cdot 0.5H_2O$ [*,4,5,7,8,11,12,15]. The crystallization regions of both calcium sulphate hydrates are separated by metastable equilibrium curve $CaSO_4 \cdot 2H_2O \Leftrightarrow CaSO_4 \cdot 0.5H_2O$[*]. The location of this curve depends on the concentration

of sulphates and various impurities in the liquid phase of the reaction mixture[4,5,20–23]. Along with an increase in the of SO_4^{2-} concentration the equilibrium curve is shifted in the direction at lower temperatures and lower phosphate concentration. Therefore, the production of wet process phosphoric acid by dihydrate method at a higher concentration of sulphates should be carried out at lower temperatures. For the pure system containing 30 wt% P_2O_5 and 5 wt% SO_4^{2-} the conversion temperature for $CaSO_4 \cdot 2H_2O \Leftrightarrow CaSO_4 \cdot 0.5H_2O^*$ is approximately 68°C, whereas at 10 wt% SO_4^{2-} is only 56°C. On the other hand, an increase in the sulphate concentration in the liquid phase of the reaction mixture affects the crystal habit of $CaSO_4 \cdot 2H_2O$ formed and leads to lowering the decomposition degree of phosphate raw material to the caused by encapsulation of raw material particles by calcium sulphate hydrate[1,5]. Moreover the crystal habit influences on the efficiency of filtration and washing the precipitate as well as on losses of phosphate in the phosphogypsum due to incomplete washing of H_3PO_4.

According to Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals in Europe a wet process phosphoric acid should be obtained using the following techniques: modified DH-process, transformation processes (HDH and DHH processes) on existing installations[5]. However, the transformation process with double-stage filtration should be applied in new installations.

The DHH route involves the decomposition of phosphate material and crystallization of $CaSO_4 \cdot 2H_2O$ at temperature of 80°C, the separation of precipitate from wet process phosphoric acid (32–38 wt% P_2O_5) on the filter, the transformation of calcium sulphate dihydrate to hemihydrate at temperature 100°C with enhanced content of sulphates (10–20 wt% H_2SO_4, 20–30 wt% P_2O_5), the separation of $\alpha CaSO_4 \cdot 0.5H_2O^*$ precipitate on the filter followed by washing, and the phosphoric is recycled to the first stage of process. In this process a high P_2O_5 efficiency (98%) is achieved and a relatively pure hemihydrate is obtained[4,5]. For comparison, the traditional DH-process gives lower P_2O_5 efficiency (94–96%), lower phosphate content (26–32 wt% P_2O_5) in the wet process phosphoric acid and impure calcium sulphate dihydrate containing 0.75 wt% P_2O_5[4,5].

The aim of the study was to investigate the possibilities to perform the transformation of calcium sulphate dihydrate to hemihydrate at temperature lower than 100°C and with a lower sulphate content (< 10 wt% H_2SO_4) in the wet process phosphoric acid. The influence of process temperature, the content of phosphates and sulphates in the wet process phosphoric acid and the presence of additives of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei on the transformation of calcium sulphate dihydrate to hemihydrate has been determined.

MATERIAL AND METHODS

Characteristics of utilized raw materials

The wet process phosphoric acid and phosphogypsum from an industrial installation were used in the study. They were obtained as a result of phosphate rock (Tunisia) decomposition with sulphuric acid in DH-process

Table 1. The chemical composition of phosphate rock Tunisia and the products of decomposition of phosphorite by sulphuric acid

Component	Tunisia phosphorite	Unwashed PG	Wet process phosphoric acid
	content (wt%)		
H_2O	1.97	35.72	
total P_2O_5	29.20	13.90	22.30
SO_4^{2-}	5.10	52.99	2.00
CaO	49.70	30.92	0.12
MgO	0.55	0.28	0.53
Al	0.20	0.10	0.15
Fe	0.19	0.09	0.17
F	3.44	2.85	0.95
SiO_2	3.10	2.18	0.44

(Table 1). In order to increase the content of phosphates and sulphates in the wet process phosphoric acid both phosphoric acid (61.5 wt% P_2O_5) and sulphuric acid (95 wt% SO_4^{2-}) of analytical grade were added.

The crystallization nuclei of calcium sulphate hemihydrate were prepared from washed phosphogypsum in the transformation process in phosphoric acid solution (26 wt% P_2O_5 and 6.8 wt% SO_4^{2-}) at 95°C for 2 h in a laboratory shaker with water bath (type 357 Elpinplus, 200 cycles/min, amplitude 5). The fraction of calcium sulphate phases in such obtained crystallization nuclei was the following: 96.2% $\alpha CaSO_4 \cdot 0.5H_2O$, 0.3% $CaSO_4 \cdot 2H_2O$, and 3.5% $CaSO_4$.

Sample preparation procedure

The transformation of calcium sulphate dihydrate to hemihydrate in the wet process phosphoric acid was carried out at the mass ratio of the liquid phase to the solid phase of 3 : 1. The transformation temperature was varied in the range from 85°C to 95°C. The content of phosphates and sulphates in the phosphoric acid was changed from about 22 wt% P_2O_5 to 36 wt% P_2O_5 and from about 2 wt% SO_4^{2-} to 9 wt% SO_4^{2-}, respectively. The addition of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei was varied from 10% to 50% (in relation to $CaSO_4 \cdot 2H_2O$). The nuclei were added to a phosphogypsum suspension in the phosphoric acid at the process temperature.

The transformation was carried out in a tightly closed Erlenmeyer flask placed in a laboratory shaker with water bath (type 357 Elpinplus, 200 cycles/min, amplitude 5). The transformation of calcium sulphate dihydrate was carried out for 2 h or 1.5 h. After completing the process the wet process phosphoric acid was separated from calcium sulphate hydrate. The precipitate was washed three times with distilled water at ambient temperature (the mass ratio of the solid phase to the liquid phase was 1 : 1) and then dried in a drier at 70°C for 1.5 h. It was experimentally found that during the drying at temperatures 50–80°C within 5 h calcium sulphate hemihydrate did not dehydrate to anhydrite. The diagram showing the method in which the experiment was conducted is presented on Fig. 1.
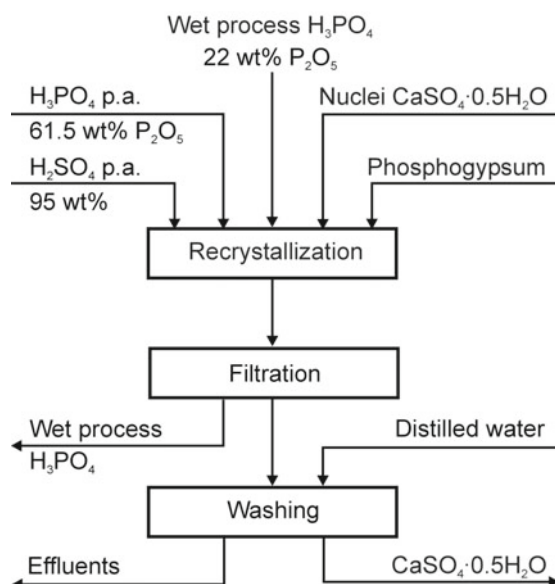
Figure 1. Diagram of the experimental method

Sample characterization

The X-ray diffraction analysis (X'Pert PRO Philips diffractometer with CuK_α radiation) was used to determine the fraction of different forms of calcium sulphates and phase composition in the samples. The relative abundance of $CaSO_4 \cdot 2H_2O$, $\alpha CaSO_4 \cdot 0.5H_2O$ and $CaSO_4$ phases were calculated from the (101) reflection of $CaSO_4 \cdot 2H_2O$, the (121) reflection of $\alpha CaSO_4 \cdot 0.5H_2O$ and the (020) reflection of $CaSO_4$. The fraction of $CaSO_4 \cdot 2H_2O$, $\alpha CaSO_4 \cdot 0.5H_2O$, $CaSO_4$ in the samples and the degree of conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ and $CaSO_4$ were determined from the following equations:

$$F_{DH} = \frac{I_{DH} \cdot 100}{I_{DH} + I_{HH} \cdot k_1 + I_{AH} \cdot k_2} \qquad (1)$$

$$F_{HH} = \frac{I_{HH} \cdot k_1 \cdot 100}{I_{DH} + I_{HH} \cdot k_1 + I_{AH} \cdot k_2} \qquad (2)$$

$$F_{AH} = \frac{I_{AH} \cdot k_2 \cdot 100}{I_{DH} + I_{HH} \cdot k_1 + I_{AH} \cdot k_2} \qquad (3)$$

$$\alpha = \frac{(I_{HH} \cdot k_1 + I_{AH} \cdot k_2) \cdot 100}{I_{DH} + I_{HH} \cdot k_1 + I_{AH} \cdot k_2} \qquad (4)$$

where: F_{DH}, F_{HH} and F_{AH} are the fractions of $CaSO_4 \cdot 2H_2O$, $\alpha CaSO_4 \cdot 0.5 H_2O$ and $CaSO_4$ in the samples, α is the conversion degree of $CaSO_4 \cdot 2H_2O$, I_{DH}, I_{HH} and I_{AH} are the peak intensities of $CaSO_4 \cdot 2H_2O$ (121), $\alpha CaSO_4 \cdot 0.5H_2O$ (110) and $CaSO_4$ (020), k_1 and k_2 are the coefficients (the ratio of peak intensity (110) 100 wt% of $\alpha CaSO_4 \cdot 0.5H_2O$ to the peak intensity (121) 100 wt% of $CaSO_4 \cdot 2H_2O$ and the ratio of peak intensity (020) 100 wt% of $CaSO_4$ to the peak intensity (121) 100 wt% of $CaSO_4 \cdot 2H_2O$).

The sulphate content in the wet process phosphoric acid was determined by a weight method according to PN-ISO 10084:2004 whereas the phosphates content by a spectrophotometric method according to PN-88/C-87015).

RESULTS AND DISCUSSION

Study on transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$

On the basis of the preliminary investigations it was found that the transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ should be carried out at temperature higher than 85°C. This conclusion was based on the results of experiments, in which the $CaSO_4 \cdot 2H_2O$ transformation proceeded in the phosphoric acid containing 21–30 wt% P_2O_5 and 4–9 wt% sulphates, at temperature of 80°C and 85°C for 2 h. Under these conditions, in only few cases, a small degree of conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ not higher than 28% was obtained in few experiments.

The transformation of calcium sulphate dihydrate at 90°C, 92°C and 95°C was carried out in the phosphoric acid containing 21–36 wt% P_2O_5 and 4–9 wt % sulphates for 2 h. The X-ray diffraction analysis was used to determine the fraction of the particular phases present in the products and the degree of $CaSO_4 \cdot 2H_2O$ dehydration was calculated. It is worthy to note that, in many experiments conducted the low degree of $CaSO_4 \cdot 2H_2O$ transformation to anhydrite was obtained. The fraction of this phase in the conversion products in relation to the remaining phases amounted to maximum 9%, and in the majority of cases this fraction was within the range 1–4%. Therefore, the main phases in the products comprise either $CaSO_4 \cdot 2H_2O$ or $\alpha CaSO_4 \cdot 0.5H_2O$ or both simultaneously. The XRD pattern of one of the transformation products is shown in Figure 2.
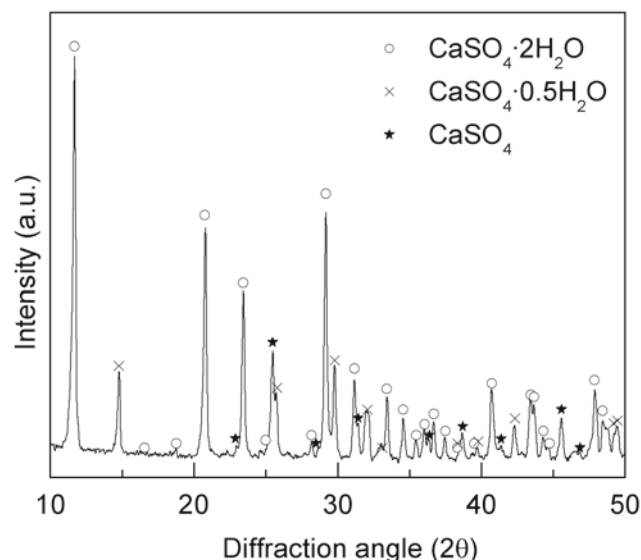

Figure 2. XRD pattern of transformation product $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$

The relationships obtained, determining the influence of phosphates and sulphates in wet process phosphoric acid on the degree of $CaSO_4 \cdot 2H_2O$ conversion were expressed mathematically by means of a nonlinear regression model with two independent variables in the form:

$$Y = b_0 + b_1 X_1 + b_2 X_1^2 + b_3 X_2 + b_4 X_2^2 + b_5 X_1 X_2 \qquad (5)$$

where: X_1 is the content of P_2O_5 in phosphoric acid (wt%), X_2 is the content of sulphates in phosphoric acid (wt%) and Y is the degree of $CaSO_4 \cdot 2H_2O$ conversion (%).

Table 2. Compilation of coefficients in the regression equations and their statistical estimation for particular conversion systems

No.	Temp.	Nuclei	Polynomial equation coefficients								
	°C	wt%	b_0	b_1	b_2	b_3	b_4	b_5	R^2	F	$F_{0.05}$
1	90	0	-3409.49	204.7054	-2.5272	0	10.1826	-4.3666	0.84	16.20	3.26
2	92	0	-515.05	0	0.5507	0	2.7946	0	0.81	19.32	4.26
3	95	0	23.40	0	-0.1536	-65.6485	0	3.3590	0.78	30.76	2.98
4	88	20	-99.87	4.8581	0	0	0	0.4436	0.91	45.89	4.26
5	90	20	-899.50	60.2030	-0.9771	71.9758	-2.9089	-1.4646	0.92	14.23	4.39
6	92	20	-556.04	34.8714	-0.4625	79.3817	-2.7631	-2.0066	0.96	31.49	4.39

The equation coefficients for particular series of experiments, calculated for independent variables and their statistical estimation where R^2 is the square of multiple correlation coefficients, F is the calculated value of Snedecor's test for regression equation, and $F_{0.05}$ is the boundary value of F test for significance level $\alpha = 0.05$ are compiled in Table 2.

The regression relationship was estimated by the method of stepwise regression with entering of variables. The significance of multiple regression was validated using the F Fisher-Snedecor test. The values of the coefficients of this function were determined using the Marquardt method and their significance was verified using the t-Student test.

The relationships described by regression equations are exemplified in Figs. 3a and 3b. It was found that the fraction of calcium sulphate hemihydrate in the precipitate increases in relation to the remaining phases with increasing the process temperature or the content of phosphates and/or sulphates in the liquid phase of the reaction mixture. The higher the process temperature, the higher degree of $CaSO_4 \cdot 2H_2O$ crystallization was obtained in the phosphoric acid with a lower content of phosphates and/or sulphates.

For example: i) when the sulphate content in the initial phosphoric acid was 6 wt% then along with the increase in the phosphate concentration in the range of 28–35 wt% P_2O_5, the fraction of $\alpha CaSO_4 \cdot 0.5H_2O$ in the solid phase increased from 0% to 97.7% (at 90°C), ii) when the sulphate content in the initial phosphoric acid amounted to 5 wt% then along with the increase of phosphate concentration 27–32 wt% P_2O_5, the fraction of $\alpha CaSO4 \cdot 0.5H_2O$ in the solid phase increased from 0% to 96.8% (at 92°C), iii) when the phosphate content in the initial phosphoric acid was 26 wt% P_2O_5 then along with sulphate increase by 4–7 wt% the fraction of $CaSO_4 \cdot 0.5H_2O$ in the solid phase increased from 0% to 97.7% (at 95°C).

On the basis of obtained results, the minimum content of P_2O_5 and SO_4^{2-} in the phosphoric acid needed to achieve practically complete (96–98%) conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ at 90, 92 and 95°C was determined. The conversion isotherms were shown in the system: phosphate content/sulphate content in the phosphoric acid (Fig. 4). The regions over the plotted curves (and including the curves) are the regions, in which the conversion of calcium sulphate dihydrate to hemihydrate took place at a given temperature. The particular curves separate from each other the regions of metastable stability of $CaSO_4 \cdot 2H_2O$ and $\alpha CaSO_4 \cdot 0.5H_2O$. The total conversion under study proceeded over certain
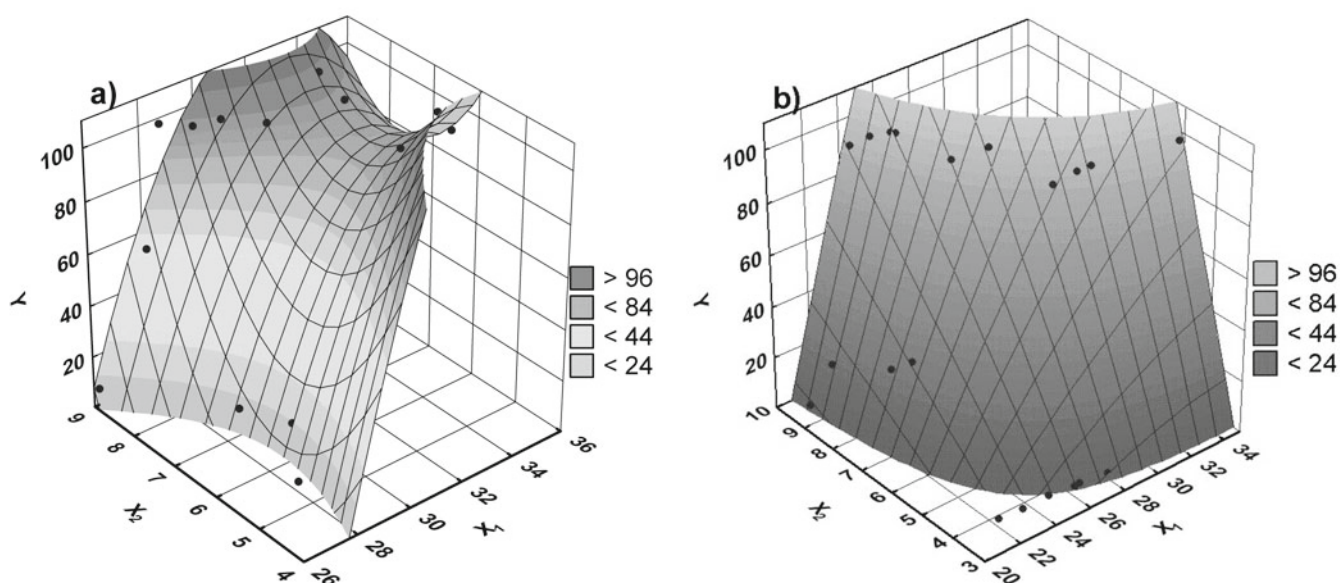

Figure 3. The influence of phosphates and sulphates on the degree of conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ and to $CaSO_4$: a) 90°C and b) 95°C
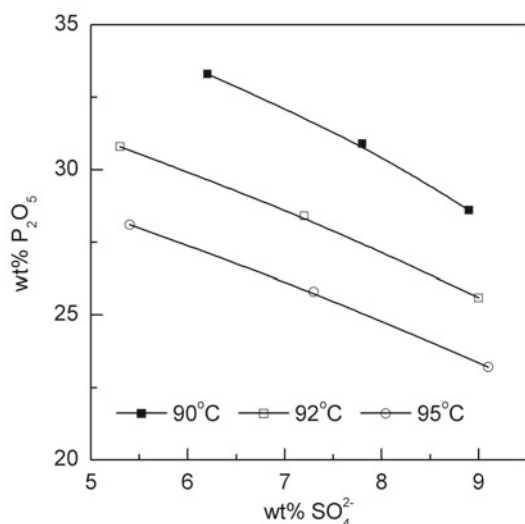
Figure 4. Conversion isotherms of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ in the order: P_2O_5 content/SO_4^{2-} content in wet process phosphoric acid

Figure 5. The influence of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei on the degree of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ conversion

isotherms under given process conditions (temperature, concentration of P_2O_5 and SO_4^{2-}), but not below them.

Therefore, a high concentration of phosphates and sulphates in the phosphoric acid, respectively, 29–31 wt% P_2O_5 and 8–9 wt% SO_4^{2-} should be maintain in order to carry out the transformation process at temperature of 90°C. By increasing the temperature to 95°C it is possible to decrease the content of both components down to 25–27 wt% P_2O_5 and 6–7 wt% SO_4^{2-}. It was found that the acid viscosity increases with increasing the content of phosphate and sulphate in the phosphoric acid. The difficulties occurred in washing the precipitate and a considerable quantity of phosphates remained in insufficient washed calcium sulphate hydrate.

The transformation process of $CaSO_4 \cdot 2H_2O$ should be carried out at the possibly lowest temperature and at a low content of sulphates in the phosphoric acid. This is associated with the influence of temperature and the reaction environment on the corrosion of equipment and installation as well as with the impact of sulphates on the crystal habit of calcium sulphate hydrates. Moreover, the wet process phosphoric acid with a high content of sulphates, for some applications, has to be subjected to desulphurization. In order to reduce these parameters, the influence of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei addition on the $CaSO_4 \cdot 2H_2O$ transformation was investigated.

Tests of transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ in the presence of calcium sulphate hemihydrate's crystallization nuclei

XRD analysis of transformation products of $CaSO_4 \cdot 2H_2O$ (22 wt% P_2O_5 and 3.8 wt% of sulphates in the phosphoric acid, temperature 95°C, time 2h) revealed a marked influence of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei on the conversion when their fraction in the initial solid phase was > 10% (Fig. 5). On the basis of the obtained results it was decided that subsequent experiments will be carried out at the weight ratio of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei in the initial solid phase equal to 4 : 1.

The transformation of calcium sulphate dihydrate was carried out at 88°C, 90°C and 92°C in the phosphoric
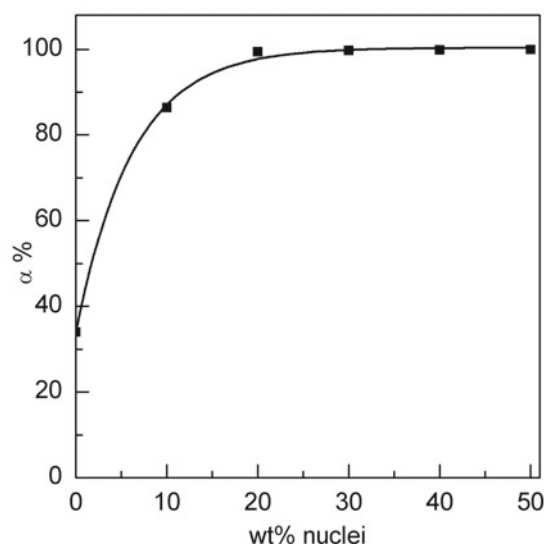
acid containing 22–28 wt% P_2O_5 and 2.2–6.1 wt% of sulphates for 1.5 h. Therefore, the following parameters: the temperature, the process time and the content of sulphates in the initial phosphoric acid were lower in relation to those used in the experiments discussed in section *Study on transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$.*

The obtained dependencies were expressed mathematically by means of a nonlinear regression model with two independent variables (Equation 5, Table 2). The appropriate relationships described by the regression equations are presented in Fig. 6.

In the experiments under study the transformation degree of $CaSO_4 \cdot 2H_2O$ to anhydrite was higher than that described in section *3.1*. The fraction of anhydrite in the products varied from 3% to 17%, while in the majority of cases it amounted to 3–7%. This could be caused by the presence of anhydrous calcium sulphate in $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei containing 3.5 wt% $CaSO_4$ which were added to the reactor.

It was found, similar to the previously discussed experiments, that with an increase of either the process temperature or the content of phosphates or sulphates in the liquid phase of the reaction mixture, the fraction of calcium sulphate hemihydrate in the precipitate was increasing in relation to the remaining phases. The higher the temperature of the process the higher degree of $CaSO_4 \cdot 2H_2O$ transformation was achieved in the phosphoric acid with a lower content of phosphates and/or sulphates. However, it was observed that in the presence of transformation nuclei the dehydration of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ proceeded with significant efficiency also at a lower temperature of 88°C. It was found that by increasing the phosphate concentration in the liquid phase of the reaction mixture from about 22 wt% P_2O_5 to 28 wt% P_2O_5, in which the sulphate concentration was 3.7 wt%, it is possible to obtain higher degrees of converting $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ increasing from 23% to about 85%. At 90°C, the degree of $CaSO_4 \cdot 2H_2O$ transformation to $\alpha CaSO_4 \cdot 0.5H_2O$ in the phosphoric acid containing 24 wt% P_2O_5 increased from 81% to 97% along with the increase of the sulphates
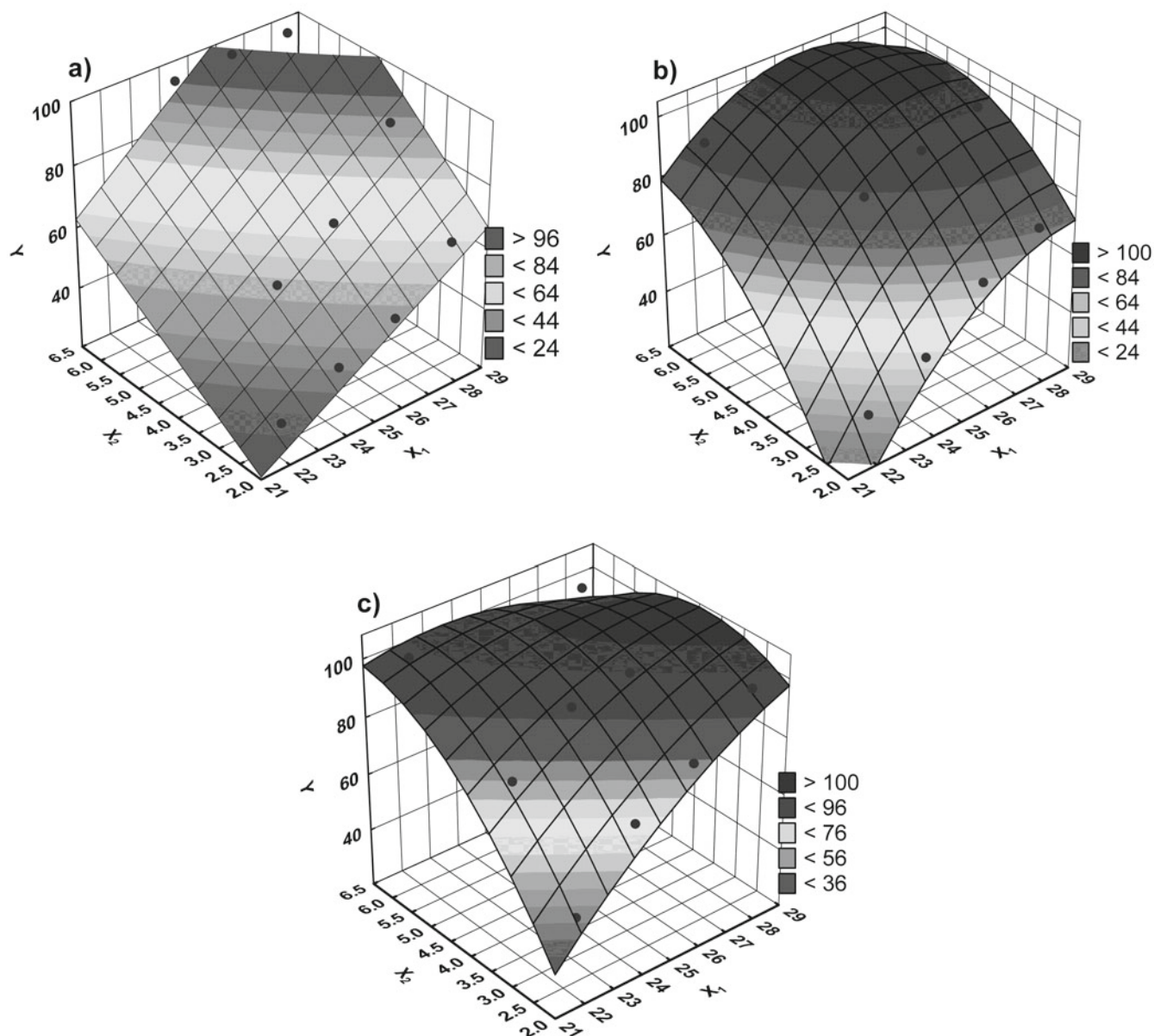
Figure 6. The influence of phosphates and sulphates on the degree of conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ and to $CaSO_4$ in the presence of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei: a) 88°C, b) 90°C and c) 92°C

content in this acid from 3.7 wt% to 6.1 wt%. The fraction of $\alpha CaSO_4 \cdot 0.5H_2O$ in the products obtained from $CaSO_4 \cdot 2H_2O$ conversion in the phosphoric acid containing about 22 wt% P_2O_5 and 3.7–6.1 wt% of sulphates, varied between approximately 72% and about 97%, when the process temperature was the highest (92°C). When the content of phosphates in the phosphoric acid solution was being raised from about 22 wt% P_2O_5 to 28 wt% P_2O_5 (with the sulphates content of 2.2 wt%) then the ratio of $\alpha CaSO_4 \cdot 0.5H_2O$ in the products was increasing gradually, depending on temperature of the process, within the following ranges: 18–54% (88°C), 21–66% (90°C) and 42–96% (92°C).

The minimum contents of P_2O_5 and SO_4^{2-} in the phosphoric acid which is necessary to obtain a high transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ (>85%) at 82, 90 and 92°C at the presence of $\alpha CaSO_4 \cdot 0.5H_2O$ crystallization nuclei were determined. Similarly, as previously, the conversion isotherms were plotted in the system: phosphate content/sulphate content in phosphoric

acid (Fig. 7).

It was found that the content of sulphates and phosphates in the phosphoric acid required for the appropriate course of the conversion of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$ can be efficiently reduced by the introduction of nuclei of calcium sulphate hemihydrate into the transformation reactor. Therefore, when the process is carried out in the phosphoric acid containing approximately 6 wt% sulphates and > 24 wt% P_2O_5, in the presence of nuclei in the amount of 20% (in relation to phosphogypsum) it is possible to lower the conversion temperature by 7°C (from 95 to 88°C).

CONCLUSIONS

While observing the influence of temperature and the content of phosphates and sulphates in the wet process phosphoric acid on the transformation of $CaSO_4 \cdot 2H_2O$ to $\alpha CaSO_4 \cdot 0.5H_2O$, it was found that:
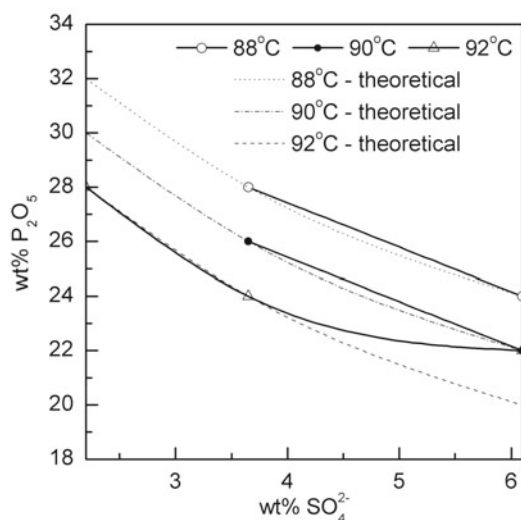
Figure 7. Conversion isotherms of $CaSO_4·2H_2O$ to $\alpha CaSO_4·0.5H_2O$ in the presence of $\alpha CaSO_4·0.5H_2O$ crystallization nuclei in the order: P_2O_5 content/SO_4^{2-} content in wet process phosphoric acid

1. an increase of the process temperature and/or the content of SO_4^{2-} and/or PO_4^{3-} in the phosphoric acid affected the increase of the degree of transformation of $CaSO_4·2H_2O$ to $\alpha CaSO_4·0.5H_2O$,

2. a higher reaction temperature enables to carry out the conversion under milder conditions in relation to the content of SO_4^{2-} and PO_4^{3-} in the phosphoric acid,

3. the addition of $\alpha CaSO_4·0.5H_2O$ crystallization nuclei enabled the achievement of a high degree of $CaSO_4·2H_2O$ conversion to $\alpha CaSO_4·0.5H_2O$ at lower process temperatures and at a lower content of phosphates and sulphates in H_3PO_4.

It was found that the transformation of $CaSO_4·2H_2O$ to $\alpha CaSO_4·0.5H_2O$ should be carried out in the presence of $\alpha CaSO_4·0.5H_2O$ crystallization nuclei addition (in the amount of 20% in relation to $CaSO_4·2H_2O$), at a temperature of $90\pm2°C$, and at the content of sulphates 4 ± 1 wt% and phosphates 27 ± 1 wt% P_2O_5 in the wet process phosphoric acid. By maintaining such conditions of the process it is possible to achieve a high degree of $CaSO_4·2H_2O$ dehydration to $\alpha CaSO_4·0.5H_2O$.

The final effect of our investigations will be the proposal for modernization of DH-process in the direction: enhancement of the degree of phosphates conversion from phosphate rock to the wet process phosphoric acid (an improvement of phosphate efficiency of the process), production of phosphoric acid with higher concentration, substantial improvement in purity of waste calcium sulphate hydrate and lowering its quantity. The indirect effect will be the prolongation of landfill exploitation period, the limitation of phosphoric raw materials consumption per 1 ton of P_2O_5 in the phosphoric acid, which will results in lower impact of wet process phosphoric acid production on the environment.

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