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

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INTRODUCTION

The world phosphoric acid production amounted to 39.8 million tons of P₂O₅ in 2009, and, according to forecasts, will increase to 46.9 million tons of P₂O₅ by 2013.¹ The largest consumption of phosphoric acid in 2009 was in Asia (30%), United States (22%) and Southwest Asia (10%) ². 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 ³.

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 ⁴⁻⁶. The latter group includes various variants of process operation such as hemi-di-hydrate 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 CaSO₄·nH₂O, 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 ⁷⁻⁹. 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 CaHPO₄·2H₂O with CaSO₄·nH₂O ⁴⁻⁷.

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 P₂O₅ in the acid. Phosphogypsum is a waste by-product mainly disposed in landfills. Throughout the world in numerous landfills (some active, 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 ¹⁰. 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% H₂O and it contains various impurities, such as phosphates, silicates, alkali-earth metals, fluorides, toxic and radioactive elements ⁴⁵. 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% ¹⁵. 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 CaSO₄·2H₂O whereas that carried out by HH-process within the crystallization region of metastable αCaSO₄·0.5H₂O ⁴⁺²⁻¹¹⁻¹³. The crystallization regions of both calcium sulphate hydrates are separated by metastable equilibrium curve CaSO₄·2H₂O ↔ CaSO₄·0.5H₂O ¹⁴. The location of this curve depends on the concentration...
of sulphates and various impurities in the liquid phase of the reaction mixture\textsuperscript{4,5,20–23}. Along with an increase in the of $\text{SO}_4^{2-}$ 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\% $\text{P}_2\text{O}_5$ and 5 wt\% $\text{SO}_4^{2-}$ the conversion temperature for $\alpha\text{CaSO}_4\cdot2\text{H}_2\text{O}$-$\alpha\text{CaSO}_4\cdot0.5\text{H}_2\text{O}$ is approximately 68°C, whereas at 10 wt\% $\text{SO}_4^{2-}$ 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 $\alpha\text{CaSO}_4\cdot2\text{H}_2\text{O}$ 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\textsuperscript{4,5}. 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 $\text{H}_3\text{PO}_4$.

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\textsuperscript{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 $\alpha\text{CaSO}_4\cdot2\text{H}_2\text{O}$ at temperature 80°C, the separation of precipitate from wet process phosphoric acid (32–38 wt\% $\text{P}_2\text{O}_5$) on the filter, the transformation of calcium sulphate dihydrate to hemihydrate at temperature 100°C with enhanced content of sulphates (10–20 wt\% $\text{H}_2\text{SO}_4$, 20–30 wt\% $\text{P}_2\text{O}_5$), the separation of $\alpha\text{CaSO}_4\cdot0.5\text{H}_2\text{O}$ precipitate on the filter followed by washing, and the phosphoric is recycled to the first stage of process. In this process a high $\text{P}_2\text{O}_5$ efficiency (98\%) is achieved and a relatively pure hemihydrate is obtained\textsuperscript{45}. For comparison, the traditional DH-process gives lower $\text{P}_2\text{O}_5$ efficiency (94–96\%), lower phosphate content (26–32 wt\% $\text{P}_2\text{O}_5$) in the wet process phosphoric acid and impure calcium sulphate dihydrate containing 0.75 wt\% $\text{P}_2\text{O}_5$\textsuperscript{45}.

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\% $\text{H}_2\text{SO}_4$) 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 $\alpha\text{CaSO}_4\cdot0.5\text{H}_2\text{O}$ 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Tunisia phosphorite</th>
<th>Unwashed PG</th>
<th>Wet process phosphoric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>1.97</td>
<td>35.72</td>
<td>22.30</td>
</tr>
<tr>
<td>total $\text{P}_2\text{O}_5$</td>
<td>29.20</td>
<td>13.90</td>
<td>22.30</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>5.10</td>
<td>52.99</td>
<td>2.00</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>49.70</td>
<td>30.92</td>
<td>0.12</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>0.55</td>
<td>0.28</td>
<td>0.53</td>
</tr>
<tr>
<td>$\text{Al}$</td>
<td>0.20</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{Fe}$</td>
<td>0.19</td>
<td>0.09</td>
<td>0.17</td>
</tr>
<tr>
<td>$\text{F}$</td>
<td>3.44</td>
<td>2.85</td>
<td>0.95</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>3.10</td>
<td>2.18</td>
<td>0.44</td>
</tr>
</tbody>
</table>

(Table 1). In order to increase the content of phosphates and sulphates in the wet process phosphoric acid both phosphoric acid (61.5 wt\% $\text{P}_2\text{O}_5$) and sulphuric acid (95 wt\% $\text{SO}_4^{2-}$) 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\% $\text{P}_2\text{O}_5$ and 6.8 wt\% $\text{SO}_4^{2-}$) 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\% $\alpha\text{CaSO}_4\cdot0.5\text{H}_2\text{O}$, 0.3\% $\alpha\text{CaSO}_4\cdot2\text{H}_2\text{O}$, and 3.5\% $\alpha\text{CaSO}_4$.

#### 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\% $\text{P}_2\text{O}_5$ to 36 wt\% $\text{P}_2\text{O}_5$ and from about 2 wt\% $\text{SO}_4^{2-}$ to 9 wt\% $\text{SO}_4^{2-}$, respectively. The addition of $\alpha\text{CaSO}_4\cdot0.5\text{H}_2\text{O}$ crystallization nuclei was varied from 10\% to 50\% (in relation to $\alpha\text{CaSO}_4\cdot2\text{H}_2\text{O}$). 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.
Sample characterization

The X-ray diffraction analysis (X’Pert PRO Philips diffractometer with CuKα radiation) was used to determine the fraction of different forms of calcium sulphates and phase composition in the samples. The relative abundance of CaSO₄·2H₂O, αCaSO₄·0.5H₂O and CaSO₄ phases were calculated from the (101) reflection of CaSO₄·2H₂O, the (121) reflection of αCaSO₄·0.5H₂O and the (020) reflection of CaSO₄. The fraction of CaSO₄·2H₂O, αCaSO₄·0.5H₂O, CaSO₄ in the samples and the degree of conversion of CaSO₄·2H₂O to αCaSO₄·0.5H₂O and CaSO₄ were determined from the following equations:

\[ F_{\text{DHF}} = \frac{I_{\text{aw}} \cdot 100}{I_{\text{aw}} + I_{\text{aw}} \cdot k_1 + I_{\text{aw}} \cdot k_2} \]  

\[ F_{\text{HH}} = \frac{I_{\text{aw}} \cdot k_1 \cdot 100}{I_{\text{aw}} + I_{\text{aw}} \cdot k_1 + I_{\text{aw}} \cdot k_2} \]  

\[ F_{\text{AH}} = \frac{I_{\text{aw}} \cdot k_2 \cdot 100}{I_{\text{aw}} + I_{\text{aw}} \cdot k_1 + I_{\text{aw}} \cdot k_2} \]  

\[ \alpha = \frac{(I_{\text{aw}} \cdot k_1 + I_{\text{aw}} \cdot k_2) \cdot 100}{I_{\text{aw}} + I_{\text{aw}} \cdot k_1 + I_{\text{aw}} \cdot k_2} \]  

where: \( F_{\text{DHF}}, F_{\text{HH}} \) and \( F_{\text{AH}} \) are the fractions of CaSO₄·2H₂O, αCaSO₄·0.5H₂O and CaSO₄ in the samples, \( \alpha \) is the conversion degree of CaSO₄·2H₂O, \( I_{\text{DHF}}, I_{\text{HH}} \) and \( I_{\text{AH}} \) are the peak intensities of CaSO₄·2H₂O (121), αCaSO₄·0.5H₂O (110) and CaSO₄ (020), \( k_1 \) and \( k_2 \) are the coefficients (the ratio of peak intensity (110) 100 wt% of αCaSO₄·0.5H₂O to the peak intensity (121) 100 wt% of CaSO₄·2H₂O and the ratio of peak intensity (020) 100 wt% of CaSO₄ to the peak intensity (121) 100 wt% of CaSO₄·2H₂O).

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 CaSO₄·2H₂O to αCaSO₄·0.5H₂O

On the basis of the preliminary investigations it was found that the transformation of CaSO₄·2H₂O to αCaSO₄·0.5H₂O should be carried out at temperature higher than 85°C. This conclusion was based on the results of experiments, in which the CaSO₄·2H₂O transformation proceeded in the phosphoric acid containing 21–30 wt% P₂O₅ 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 CaSO₄·2H₂O to αCaSO₄·0.5H₂O 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% P₂O₅ 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 CaSO₄·2H₂O dehydration was calculated. It is worthy to note that, in many experiments conducted the low degree of CaSO₄·2H₂O 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 CaSO₄·2H₂O or αCaSO₄·0.5H₂O or both simultaneously. The XRD pattern of one of the transformation products is shown in Figure 2.

\[ Y = b_0 + b_1X_1 + b_2X_1^2 + b_3X_2 + b_4X_2^2 + b_5X_1X_2 \]  

where: \( X_1 \) is the content of P₂O₅ in phosphoric acid (wt%), \( X_2 \) is the content of sulphates in phosphoric acid (wt%) and \( Y \) is the degree of CaSO₄·2H₂O conversion (%).
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 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$_4$·2H$_2$O 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$_2$O$_5$, the fraction of $\alpha$CaSO$_4$·0.5H$_2$O 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$_2$O$_5$, the fraction of $\alpha$CaSO$_4$·0.5H$_2$O 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$_2$O$_5$ then along with sulphate increase by 4–7 wt% the fraction of CaSO$_4$·0.5H$_2$O in the solid phase increased from 0% to 97.7% (at 95°C).

On the basis of obtained results, the minimum content of P$_2$O$_5$ and SO$_4^{2-}$ in the phosphoric acid needed to achieve practically complete (96–98%) conversion of CaSO$_4$·2H$_2$O to $\alpha$CaSO$_4$·0.5H$_2$O 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$_4$·2H$_2$O and $\alpha$CaSO$_4$·0.5H$_2$O. The total conversion under study proceeded over certain

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. °C</th>
<th>Nuclei wt%</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$R^2$</th>
<th>$F$</th>
<th>$F_{0.05}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>0</td>
<td>-3409.49</td>
<td>204.7054</td>
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<td>0</td>
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</tr>
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<td>2</td>
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<td>0</td>
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<td>0</td>
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</tr>
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</tr>
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</tr>
<tr>
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<tr>
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<td>-0.4625</td>
<td>79.3817</td>
<td>-2.7631</td>
<td>-2.0066</td>
<td>0.96</td>
</tr>
</tbody>
</table>

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$_4$·2H$_2$O 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$_2$O$_5$, the fraction of $\alpha$CaSO$_4$·0.5H$_2$O 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$_2$O$_5$, the fraction of $\alpha$CaSO$_4$·0.5H$_2$O 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$_2$O$_5$ then along with sulphate increase by 4–7 wt% the fraction of CaSO$_4$·0.5H$_2$O in the solid phase increased from 0% to 97.7% (at 95°C).
is associated with the low content of sulphates in the phosphoric acid. This can be carried out at the possibly lowest temperature and at a concentration down to 25–27 wt% P$_2$O$_5$ and 6–7 wt% SO$_4^{2-}$. It is possible to decrease the content of both components in desulphurization. In order to reduce these parameters, the sulphates, for some applications, has to be subjected to the wet process phosphoric acid with a high content of the crystal habit of calcium sulphate hydrates. Moreover, installation as well as with the impact of sulphates on the reaction environment on the corrosion of equipment and 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$_4$.2H$_2$O to CaSO$_4$.0.5H$_2$O crystallization nuclei equal to 4 : 1.

Tests of transformation of CaSO$_4$.2H$_2$O to CaSO$_4$.0.5H$_2$O in the presence of calcium sulphate hemihydrate's crystallization nuclei

XRD analysis of transformation products of CaSO$_4$.2H$_2$O (22 wt% P$_2$O$_5$ and 3.8 wt% of sulphates in the phosphoric acid, temperature 95°C, time 2h) revealed a marked influence of CaSO$_4$.0.5H$_2$O 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$_4$.2H$_2$O to CaSO$_4$.0.5H$_2$O 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$_2$O$_5$ 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$_4$.2H$_2$O to αCaSO$_4$.0.5H$_2$O.

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$_4$.2H$_2$O 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 CaSO$_4$.0.5H$_2$O 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$_4$.2H$_2$O 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$_4$.2H$_2$O to αCaSO$_4$.0.5H$_2$O 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$_2$O$_5$ to 28 wt% P$_2$O$_5$, in which the sulphate concentration was 3.7 wt%, it is possible to obtain higher degrees of converting CaSO$_4$.2H$_2$O to αCaSO$_4$.0.5H$_2$O increasing from 23% to about 85%. At 90°C, the degree of CaSO$_4$.2H$_2$O transformation to αCaSO$_4$.0.5H$_2$O in the phosphoric acid containing 24 wt% P$_2$O$_5$ increased from 81% to 97% along with the increase of the sulphates concentration.
content in this acid from 3.7 wt% to 6.1 wt%. The fraction of $\alpha$CaSO$_4$·0.5H$_2$O in the products obtained from CaSO$_4$·2H$_2$O conversion in the phosphoric acid containing about 22 wt% P$_2$O$_5$ 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$_2$O$_5$ to 28 wt% P$_2$O$_5$ (with the sulphates content of 2.2 wt%) then the ratio of $\alpha$CaSO$_4$·0.5H$_2$O 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$_2$O$_5$ and SO$_4^{2-}$ in the phosphoric acid which is necessary to obtain a high transformation of CaSO$_4$·2H$_2$O to $\alpha$CaSO$_4$·0.5H$_2$O (>85%) at 82, 90 and 92°C at the presence of $\alpha$CaSO$_4$·0.5H$_2$O 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$_4$·2H$_2$O to $\alpha$CaSO$_4$·0.5H$_2$O 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$_2$O$_5$ 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$_4$·2H$_2$O to $\alpha$CaSO$_4$·0.5H$_2$O, it was found that:
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$_2$O to CaSO$_4$.5H$_2$O.

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 CaSO$_4$.5H$_2$O crystallization nuclei enabled the achievement of a high degree of CaSO$_4$.2H$_2$O conversion to CaSO$_4$.5H$_2$O at lower process temperatures and at a lower content of phosphates and sulphates in H$_3$PO$_4$.

It was found that the transformation of CaSO$_4$.2H$_2$O to CaSO$_4$.5H$_2$O should be carried out in the presence of CaSO$_4$.5H$_2$O crystallization nuclei addition (in the amount of 20% in relation to CaSO$_4$.2H$_2$O), at a temperature of 90±2°C, and at the content of sulphates 4±1 wt% and phosphates 27±1 wt% P$_2$O$_5$ 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$_2$O dehydation to CaSO$_4$.5H$_2$O.

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$_2$O$_5$ in the phosphoric acid, which will result in lower impact of wet process phosphoric acid production on the environment.

ACKNOWLEDGEMENTS

This scientific work was funded from financial support on science as research project for 2010–2013.

LITERATURE CITED


IFA Technical Committee Meeting, Abu Dabi, October 2003.
