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A NEW PROCEDURE FOR OBTAINING CALCIUM SULPHATE α-HEMIHYDRATE ON THE BASIS OF WASTE PHOSPHOGYPSUM

NOVI POSTUPAK DOBIJANJA KALCIJUM-SULFATA α-POLUHIDRATANA BAZI OTPADNOG FOSFOGIPSA

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Izvod

Ispitivanja, izvršena u radu pokazala su da otpadni fosfogips-dihidrat *predstavlja balast koji se ne sme čak ni odlagati na deponiju usled njegove velike količine u odnosu na glavni* proizvod - *fosfornu kiselinu, kao i mogućih uticaja deponije fosfogipsa na životnu sredinu. Predloženim postupkom kalcijum-sulfat dihidrat prevodi se u daleko čistiji α*-poluhidrat *koji se po svojim fizičko-hemijskim karakteristikama približava prirodnom gipsu i sadrži još komponente koje omogućavaju građenje sitnozrnog fosfogipsa koji se može upotrebiti u građevinskoj industriji.* Pilot *postrojenje, opisano u radu je instrumentizovano i projektovano da sa njim rukuje samo jedan čovek.* Dobijeni *α-poluhidrat može da se* iskoristi *za dobijanje gipsnih blokova i suvog poluhidrata.*

Ključne reči: *kalcijum-sulfat, fosfogips, dihidrat.*

Abstract

Investigations, conducted in this study showed that waste phosphogypsum-dihydrate represents a burden which even must not be kept in deposits because of its large quantity in relation to the main product – phosphoric acid, as well as because of great impact of a phosphogypsum deposit on the environment. By the proposed procedure, calcium-sulphate dehydrate is transformed into a far purer α-hemihydrate which, with its physic-chemical characteristics, approaches natural gypsum and contains additional components which enable formation of small-grain phosphogypsum which may be utilised in construction industry. Test installation, given in this study, is highly automated and designed in such way to be operated by only one person. The obtained α-hemihydrate may be utilised for obtaining of gypsum blocks and dry hemihydrate.

Key words: *Calcium-sulphate, phosphor-gypsum, dyhydrate.*

1. INTRODUCTION

Phosphogypsum is by-product of the phosphate fertilizer which is produced in large quantities world-wide during the production of phosphoric acid [1-3]. The ”wet” phosphoric acid process from phosphate rock, $Ca_{10}(PO_4)_6F_2$ or $[Ca_3(PO_4)_2]\cdot CaF_2$, is the most common process used to produce phosphoric acid, it can be summarized by the following equation [4]:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \xrightarrow{75\text{–}80^{\circ}C} 6H_3PO_4 + 10CaSO_4\cdot 2H_2O + 2HF$$
(1)

e.g. by scheme on Figure 1. [23].

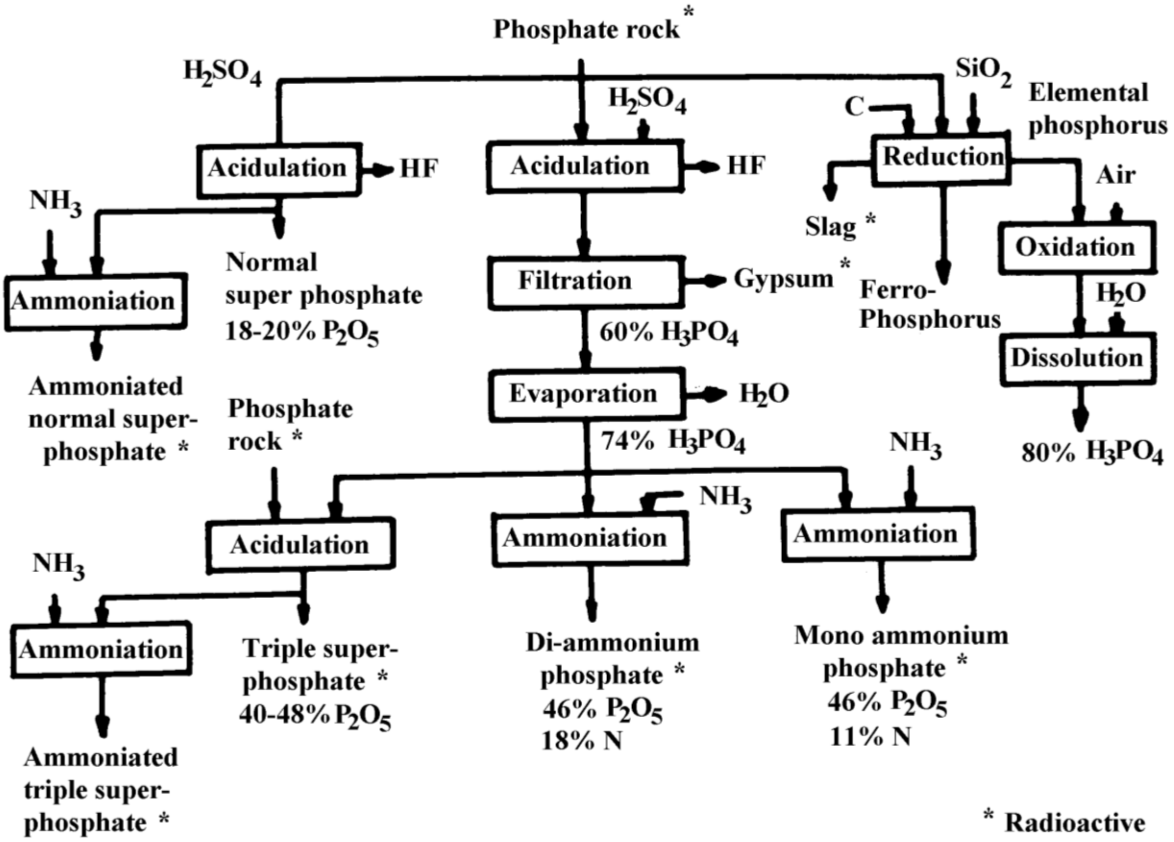

Figure 1. The production of phosphate fertilizers

Phosphogypsum is separated on filters from phosphoric acid, which is then concentrated and subsequently utilised for mineral fertiliser production, while the phosphogypsum is kept in deposits [5-7], or in the areas intended for this purpose (mines, opencasts) or is (temporarily) discarded as a very diluted (2 wt. %) dispersion into water flows. Considering that the ratio CaO/P_2O_5 in phosphates utilised for phosphoric acid production varies between 1.35 and 1.65, the mass of dry impure phosphogypsum produced during this procedure amounts to 4-5 tones per one tone of obtained P_2O_5 [8].Thus ”produced” phosphogypsum is not unable, and the widespread methods of disposal, like dispersing into rivers or seas (as 2 wt. % suspension) or storing at specially prepared deposits, become increasingly unacceptable, precisely because of large amounts of phosphogypsum, as well as a possibility of environment contamination [9,10]. Part of the impurities present in the phosphate is carried off with the gypsum stream after the separation of phosphoric acid and gypsum. The small amounts of soluble impurities in phosphogypsum (traces of free acids, acidic phosphates and silicofluorides; 0.1-1 wt. %) affect the quality of the phosphogypsum much more strongly than the insoluble impurities in natural gypsum, whose concentration may be as much as 10 wt. % (clay, $CaCO_3$, SiO_2, iron oxide - present asintertfillers). For this reason, a procedure is needed for processing and purification of phosphogypsum obtained in raw form and of removing of the present impurities [11]. In raw form, phosphogypsum contains 20-30 wt. % moisture and above 50 wt. % of impurities, like immanent organic compounds, soluble and insoluble phosphates, fluorine compounds, traces of sodium compounds, rare and even radioactive elements [12]. There are three types of soluble impurities in phosphogypsum: free phosphoric and sulphuric acids, salts of various acids, as for instance, mono- and di-calcium phosphates and fluorosilicates, sodium and potassium salts. Insoluble impurities may be divided into two groups: impurities already present in natural phosphates (rocks, silicates and organic compounds) and impurities formed in the second cycle of the reaction of phosphate processing, e.g. P_2O_5 syncrystalic, numerous insoluble phosphates and fluoride components [13]. Water-soluble P_2O_5 influences the set time and causes corrosion during burning of the phosphogypsum. Lattice P_2O_5 may evolve during burning and contribute to the corrosion. Fluorine may affect the efficiency of the setting retards. Na_2O and K_2O cause efflorescence, water-soluble salts reduce the strength of the hardened phosphogypsum. Organic material causes cause discoloration and irregular set time, adversely affects the mechanical properties of the end-product. Non-digested phosphate and silica particles (sand) have little influence on the quality of the end product, but increase the wear on processing equipment [14, 15].The distribution of impurities across the phosphogypsum fractions after wet purification is represented in Table 1. Purification and processing of phosphogypsum are extremely complex, not only due to the presence of various types and amounts of impurities, but also because of their different mutual ratios, which are in direct correlation with the type and origin of phosphates utilised in factories for phosphoric acid production.

Table 1. The distribution of impurities across the phosphogypsum fractions after wet purification

	Fine < 30 µm (removed by filtration)	**Medium 30-200 µm**	**Coarse > 200 µm (removed by flotation or with hydrocyclones**	**Phosphogypsum**
Wt. % of phosphogypsum	20	70	10	100%
Total P_2O_5	0.8	0.5	7.6	1.3%
SiO_2	0.45	1.0	8.0	1.3%
Na	0.15	0.07	0.3	0.15%
Fe_2O_3+Al_2O_3	0.5	0.45	1.8	0.7%
F	1.4	0.5	7.0	0.2%
Organic C	0.3	0.05	0.2	0.2%
Ra (Bq/g)	1.258	0.592	0.703	0.814

Types (or forms) of calcium sulphate

The basic form of phosphogypsum is dihydrate – $CaSO_4 \cdot 2H_2O$, characterised with monoclinic crystal system with three imagined axes with different lengths, two of which intersect mutually at sharp angle, and the third is perpendicular in relation to their plain. Of symmetry elements it possesses: one binary axis, centre of symmetry and one plain of symmetry. The basic form is an oblique prism, with a rectangular basis. In a stability diagram (Figure 2), there is presented $CaSO_4$ in $CaSO_4 \cdot H_2SO_4 \cdot H_2O$ system [11].

As it may be seen from Figure 2, the form $CaSO_4 \cdot 2H_2O$ is stable up to 45ºC and H_2SO_4 concentration of 28 wt. %. Within the temperature range between 45 and 100ºC, i.e. acid concentrations between 28-50 wt. %, the stable form is $CaSO_4$, and $CaSO_4 \cdot 2H_2O$ is transformed into a metastable form and for the first time appears as hemihydrate – $CaSO_4 \cdot 1/2H_2O$.

There are two forms of the hemihydrate: α- and β-hemihydrate. Although of the same composition, α- and β-hemihydrates express different physical and chemical properties because they crystallise within different crystal systems. While β-hemihydrate is stacked in form of an agglomeration, with distinguishable individual crystals, α-hemihydrate is completely defined crystal characterised with macroscopically visible forms of various sizes [11,12].

α-Hemihydrate is also much more stable than β-hemihydrate, because while staying in the absence of moisture, β-hemihydrate is slowly transformed into α-hemihydrate [3]. In the region II (Figure 2) within the temperature range between 100 and 120ºC, and acid concentrations between 50 and 55 wt. % of H_2SO_4, the stable form is anhydride – $CaSO_4$, the unstable one $CaSO_4 \cdot 2H_2O$, and the metastable $CaSO_4 \cdot 1/2H_2O$.

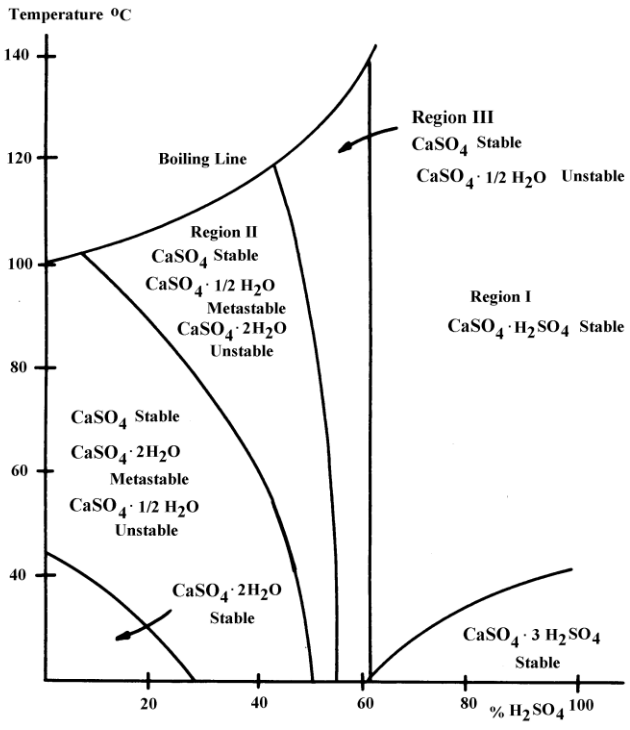

Figure 2. Stability diagram - $CaSO_4$ in $CaSO_4 \cdot H_2SO_4 \cdot H_2O$ system

In connection with anhydride $CaSO_4$, its forms should be mentioned: I, II and III, which are represented in Table 2. The first form to appear is anhydride III which crystallizes according to hexagonal system which has four crystallographic axes, three of which lie in one plain, are of equal length and intersect at the angle of 60ºC, and the fourth one is either longer or shorter and is normal to the plain containing the first three axes. Of the symmetry elements, it has: one sextery axis, 6 binary axes, a centre of symmetry and seven plains of symmetry. The main form is a straight prism with hexagonal basis. This anhydride III is soluble form and is also designated as γ-anhydride.

Table 2. $CaSO_4$ - H_2O crystal system

Formula	**Crystal system**	**Names**
$CaSO_4{\cdot}2H_2O$	Monoklinic	Natural gypsum
$CaSO_4{\cdot}1/2H_2O$	Hexagonal	Hemihydrate
$CaSO_4{\cdot}0H_2O$	Hexagonal	Anhydrit III, dehydrated hemihydrate
$CaSO_4{\cdot}0H_2O$	Orthorhombic	Anhydrit II, dead-burned gypsum
$CaSO_4{\cdot}0H_2O$	Cubic	Anhydrit I, (high-temperature form)

The α- and β-forms of hemihydrate and anhydrite differ not in crystal system, but in crystal size: the α-form is associated with large crystal (~ 0.1 mm); the β-for, with microcrystallinity (< 0.001 mm). Many physical properties of β-hemihydrate are explained by the very large specific surface. The next form is anhydride II, also designated as natural β-anhydride or ”dead-burned gypsum” and plays an undesirable role at phosphogypsum application, especially in construction industry. Anhydride II is transformed into anhydride I which is desirable and is easily activated, having thus a role of connective material. Anhydride I is also designated as α-anhydride. It is partly decomposed within the temperature range between 780 and 1200ºC, i.e. there occurs a thermal dissociation that includes transformation of $CaSO_4$ into CaO and SO_3. This reaction is slow at the beginning, and the produced CaO acts as a catalyzer and accelerates the reactions [11].

Formation of individual phosphogypsum forms is presented in Figure 3.

Conversions of phosphogypsum during phosphoric acid production

During technological procedure of phosphoric acid production by action of sulphuric acid on phosphoric acid, in dependence of H_2SO_4 concentration, as well as of reaction temperature, dihydrate and hemihydrate may be formed as a product (Figure 4).

In the conventional procedure for phosphoric acid production, the conditions are actually selected for dihydrate to be formed (temperature below 80ºC and sulphuric acid concentration of 25 wt. %), which would absorb all impurities by its large crystals and which could be easily filtered out on rotation filter. Thus, by the conventional ”wet” procedure, phosphogypsum is already prepared as waste material, because with the majority of absorbed impurities, approximately 20 wt. % of uranium and even up to 85 wt. % of radium-226 isotope pass into phosphogypsum [16]. Considering that, phosphogypsum is a predicted waste and is disposed in deposits. The problem arises from its quantity, because, for instance, a factory producing 1000 t/24h P_2O_5 needs an area of 1.2x1.2 km^2 for deposition of phosphogypsum during a period of 20 years, and the height of the deposit reaches about 15 m [17].

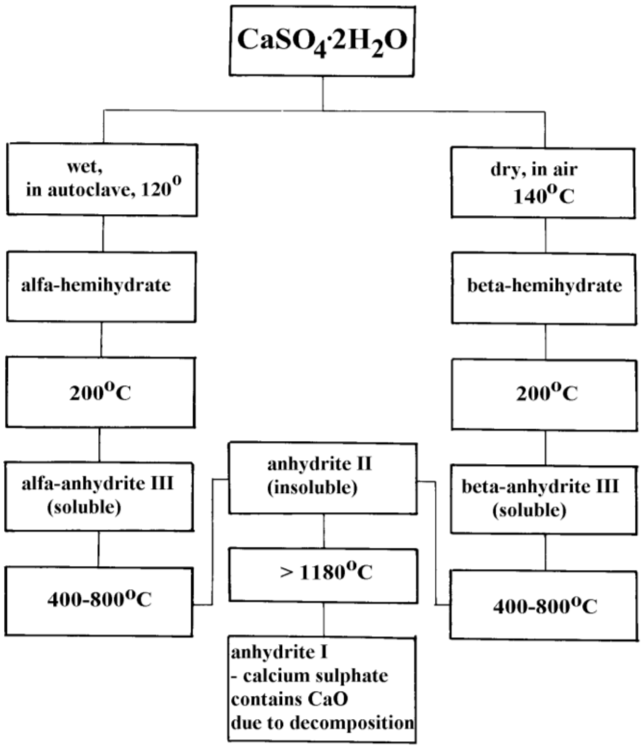

Figure 3. Phase transitions in $CaSO_4$ - H_2O system [15]

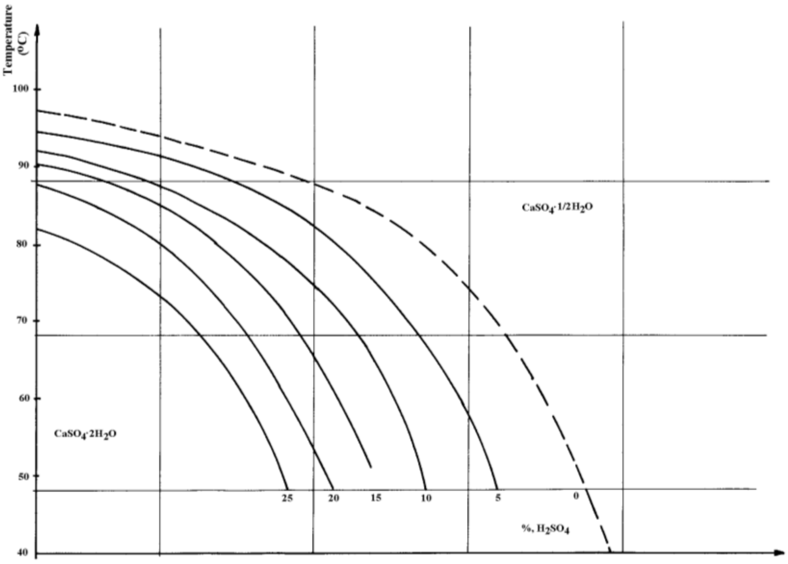

Figure 4. Forms of $CaSO_4$ as influenced by reaction temperature and H_2SO_4 concentration

During dry calcination (”dry burning”) β-hemihydrate is formed, which is a form convenient for further application of phosphogypsum due to the presence of various crystal impurities which are incorporated in gypsum crystals in reaction with P_2O_5. Because it is impossible to remove these impurities either before or during the dry calcination, phosphogypsum, even as hemihydrate, remains a burden. Thus, it is necessary to convert phosphogypsum dihydrate into α-hemihydrate, in order to obtain much purer phosphogypsum. At the same time, the reaction is much more easily controlled and may be adjusted so to obtain a hemihydrate with specific characteristics with a change of crystal state.

2. EXPERIMENTAL

All investigations were performed with phosphogypsum obtained from chemical industry in IHP Prahovo by a technological procedure in which raw phosphates are treated with H_2SO_4. Phosphogypsum purification was carried out by the new procedure, which be explained in further part of paper. Phosphogypsum and natural gypsum samples were analysed using scanning electron microscopy SEM, JSM-84OA, JEOL, Japan. X-ray diffraction analysis was carried out using the diffractometer for powder SIEMENS D-500 with Ni-filtered CuK_α radiation. Identification of crystalline phases in recorded samples has been carried out by position and intensity comparison of diffraction profiles with JC PDS data. Thermogravimetric analysis of phosphogypsum were performed on Dermatograph STANTON, England, with speed of heating up to 7ºC/min in air stream in mixture with Al_2O_3, samples were analysed in ceramic crucible on temperature up to 500ºC.

Obtaining of α-hemihydrate

In order to perform transformation of phosphogypsum dehydrate into α-hemihydrate at least 98ºC temperature is needed, while it has been found that the transformation takes place with highest rate within the temperature interval between 150ºC and 160ºC. At higher temperatures, little is obtained by increasing the reaction rate, while at lower temperatures large reactors are needed to provide a complete transformation [18], which is represented in Figure 5. The procedure of the transformation is, on the basis of the diagram in Figure 2, carried out with 28 wt. % water solution of sulphuric acid which had been heated to the temperature of 90ºC. Phosphogypsum was added to the solution and the resulting emulsion has been vigorously stirred. After phosphogypsum addition, barium sulphate was added also with continual stirring, until the temperature reached 85ºC. Then the mixture was cooled. After cooling, it was filtered through a special Buchner funnel, separating the solid from the liquid phase. After drying and calcination, grinding of the purified phosphogypsum was carried out by laboratory mixer to the particle size mainly between 100 and 200 µm, with only 12% particles bigger than 200 µm.

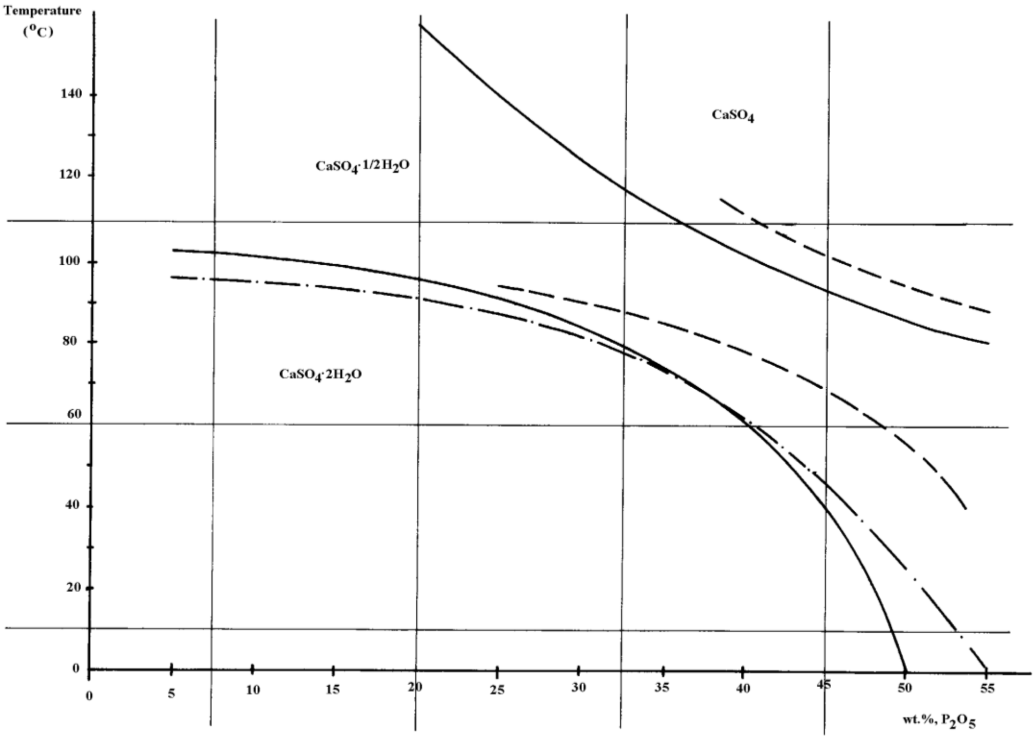

Figure 5. Dependence of calcium-sulphate form on mass ratio in wt.% P_2O_5 *and temperature (-) and (--) values obtained on industrial scales (-.-.) thermodynamic curve, according Slack* [2]

3. RESULTS AND DISCUSSION

Thermogravimetric analysis of natural gypsum and phosphogypsum from the filter indicated that natural gypsum is hemihydrate – $CaSO_4·1/2H_2O$, while is phosphogypsum dihydrate – $CaSO_4·2H_2O$ [19,20]. The results of chemical and mineralogical analyses of natural gypsum, phosphogypsum taken from the filter at phosphoric acid production by ”wet procedure” and previously processed and purified phosphogypsum by new procedure [3,19], are represented in Table 3. The results of investigation, presented in Table 3, confirmed that phosphogypsum is in the form of dihydrate (74.16 wt. %) immediately after separation from the filter, while natural gypsum is actually hemihydrate (81.34 wt. % $CaSO_4·1/2H_2O$). By suggested procedure, phosphogypsum is transformed into α-hemihydrate (77.26 wt. % $CaSO_4·1/2H_2O$), and all the other parameters are closer to natural gypsum than to the waste phosphogypsum.

Table 3. Chemical and mineralogical composition of natural gypsum, phosphogypsum taken from plant's pipe and purified phosphogypsum

Chemical composition	**Natural gypsum (in wt. %)**	**Phosphogypsum taken from plant's pipe (in wt. %)**	**Purified phosphogypsum (in wt. %)**
$CaSO_4 \cdot 2H_2O$	–	74.16	11.54
$CaSO_4 \cdot 1/2H_2O$	81.34	–	77.26
$CaSO_4$, anhydride	6.16	–	–
Bonded (fixed) water, H_2O	5.38	18.02	7.21
$CaSO_4$, total	82.12	56.14	81.59
	Excess:		
Free CaO	0.70	0.77	0.29
SO_3	–	–	–
Sum:	**88.20**	**74.93**	**89.09**
	Impurities:		
Free water, at 45°C	1.30	0.34	1.03
Calcination loss	0.98	2.18	0.60
SiO_2+insoluble residue	4.15	21.75	4.55
$MgCO_3$	–	–	–
Na_2O	–	–	–
K_2O	–	–	–
$Al_2O_3+Fe_2O_3$	0.06	0.04	0.17
MgO	–	–	–
$CaCO_3$	5.09	–	4.48
P_2O_5	–	0.84	0.09
Sum:	**11.58**	**25.15**	**10.92**
Total:	**99.78**	**100.08**	**100.01**

To establish morphological composition and structure, their homogeneity and the presence of faults in the structure, an inspection was performed by scanning electronic microscopy (SEM) of the natural gypsum and various phosphogypsum samples: phosphogypsum taken from plant's pipe and purified phosphogypsum α-hemihydrate, and the photographs are represented in our Figures 6, 7 and 8 [3,20-22]. The presence of increased Al concentration (0.17 versus 0.04 wt. % in phosphogypsum from filter) acts as a powerful modifier of crystal state, because Ca^{2+} ion is replaced by complex AlOH in crystal lattice of phosphogypsum. Present Al yields a series of Al(OH) species, the equilibrium of which are determined by pH value, up to pH = 4.0, above which this condition ceases to be valid.

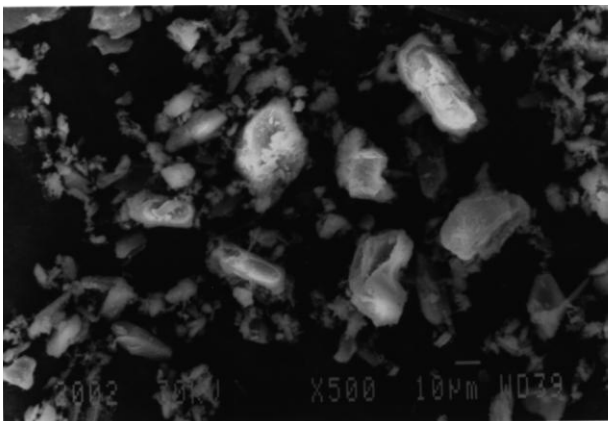

Figure 6. SEM photograph of crystalline structure of natural gypsum (x500)

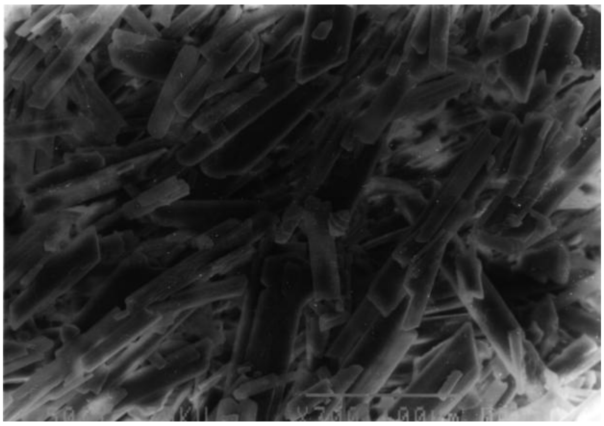

Figure 7. SEM photograph of crystalline structure of phosphogypsum – dehydrate taken from plant's pipe (x1,000)

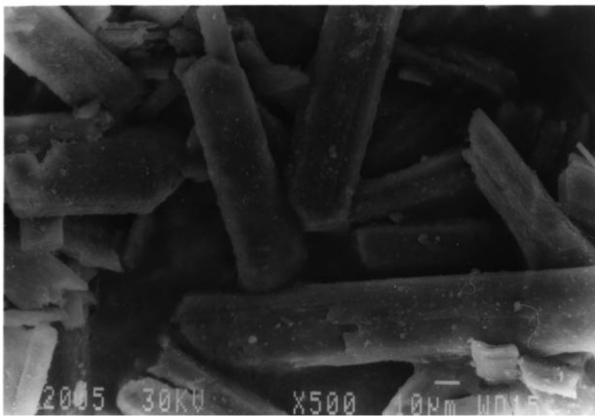

Figure 8. SEM photograph of crystalline structure of purified phosphogypsum α-hemihydrate (x300)

Industrial procedure for obtaining α-hemihydrate

Obtaining of α-hemihydrates in an industrial plant, instead of calcium sulphate dihydrate is hindered due to the formation of anhydride on the surface. With that aim, direct injection of vapour is performed into the container for mixing, achieving thus α-hemihydrate obtaining at optimal temperature for the reaction of 150-160ºC, without anhydride. In order to terminate conversion into α-hemihydrate, behind the reaction container for mixing there is mounted a flow continual reactor.

On the basis of investigations, a system was made of two mixing reactors in a series with the conversion of at least 80 wt. % in the first bigger container. Thus, the total time for conversion is less than 3 minutes. Conversion and conversion rate are also influenced by gypsum suspension concentration which may increase the degree of conversion even to 70 wt. %, although the concentration of gypsum suspension of 50 wt. % is practically the limit that may be achieved. Conversion rate may be additionally increased by acidification of the reaction precipitate, by sulphuric acid. The influence of sulphuric acid is explained by increasing of HSO_4^- concentration which accelerates crystal growing for crystallisation phase of the hemihydrate.

For a correct control of crystal state it is important to know the parameters which influence the reaction, because the crystallisation rate has a significant influence on the efficiency of a modifier for crystal state, the modifiers being either naturally present in the phosphgypsum or are specially added.

Low pH values are favourable for the formation of a modifier complex for crystal state, but at the same time they increase the rate of crystallisation, which enables formation of smaller crystals which decrees the efficiency of the modifier for crystal state. In phosphogypsum samples that contain greater quantities of impurities, crystal state may be modified by control of reaction conditions, enabling thus the action of already present modifier for crystal state. In dependence of the type of phosphates yielding the given phosphogypsum, it is necessary to control closely the reaction conditions in order to confirm obtaining of the desired crystal form, minimal waste of modifier for crystal state and the best possible physical characteristics of the obtained hemihydrate.

Test installations for α-hemihydrate production

Flow sheet diagram of semiindustrial process for obtaining of α-hemihydrate is represented in Figure 9. Phosphogypsum may be fed direct from a phosphoric acid plant or dump to the storage tank, where it is slurried to a 50 wt. % concentration. From there it is pumped to a second vessel, at which point the pH is adjusted and habit modifier added and the slurry continuously monitored to provide correst feedstock analysis. High-pressure pumps then feed the slurry to two autoclaves equipped with turbine-type stirrers and arranged in series. Here the phosphogypsum is convered to hemihydrate at 150ºC and 0.7 MPa.

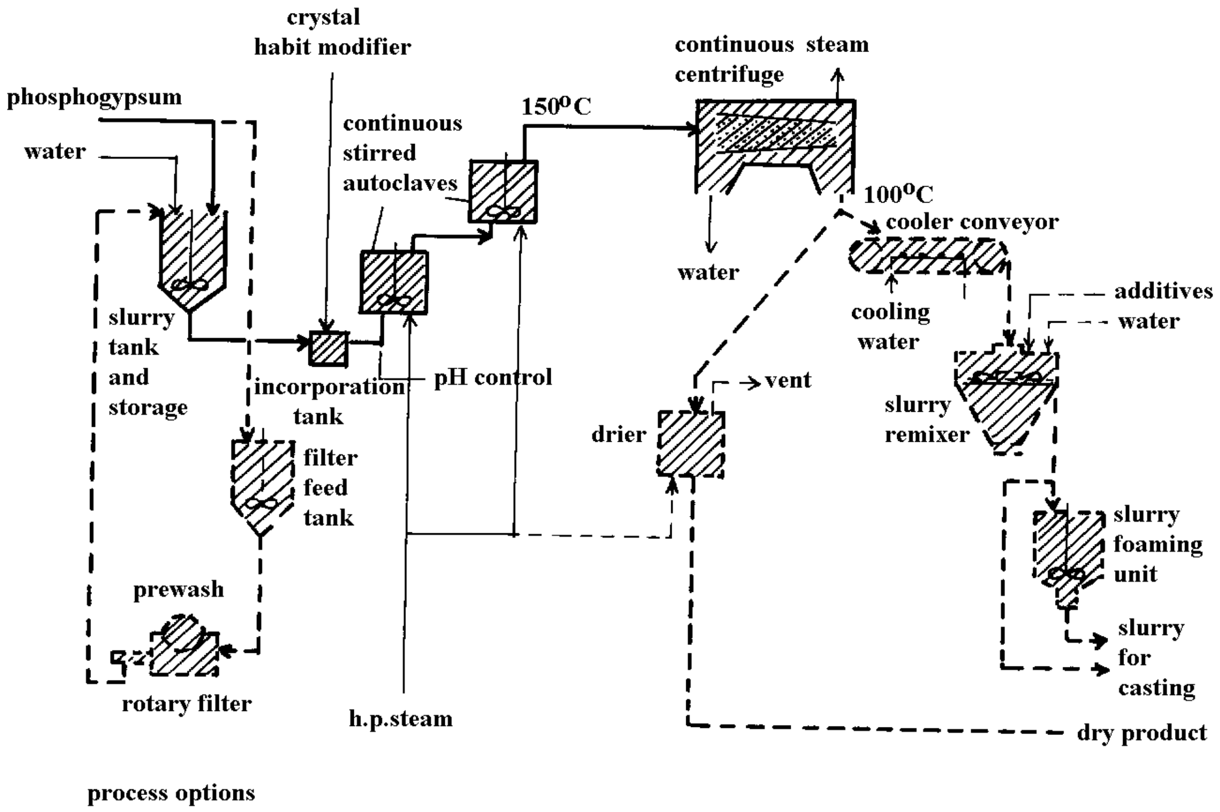

Figure 9. Flow sheet diagram of semi-industrial process for obtaining of α-hemihydrate

The amount of heat supplied by direct steam injection is controlled individually according to the temperature in each autoclave and the pressure is controlled at the exit of the second. Following conversion, the α-hemihydrate slurry is fed to a pressure let-down vessel (if heat recovery is used) and then to a continuous scroll discharge centrifuge where the liqor is separated, leaving a hemihydrate with a moisture content varying between 8 wt. % and 15 wt. % depending on crystal habit. The discharge casings and chute of the centrifuge are maintained at a temperature above 100°C to prevent the hemihydrate from becoming rehydrated and to avoid blockage. Effluent liquor typically contains less than 0.4 wt. % suspended solids and can be discharged to a drain pr, in some cases, used again. The α-hemihydrate may the be reslurried and used in a continuous casting process for manufacturing phosphogypsum blocks or fed direct to a drier for producting dry hemihydrate plaster. Normaly no pre-wash step is included unless the phosphogypsum is grossly contaminated or the hemihydrate is required to satisfy a particularly stringent specification.

Calculation of utilization of fuel and raw materials for α-hemyhydrate production

Calculation of utilization of fuel and raw materials for α-hemihydrate production, to be allowed by equation:

$$Bg = \frac{Gp \cdot (h_2 - h_1)}{Hd \cdot \eta} \qquad (2)$$

Where,

Bg - fuel consummation per hour,

Hd - lower thermal power of the fuel combusted in the boiler for production of dry-saturated steam,

h_1, h_2 - specific enthalpy of boiling liquid and dry-saturated steam, respectively, at the pressure p (0.7 MPa),

Gp - mass flow of the steam for heating,

η - the degree of the boiler usefulness (depends primarily on the fuel and heating rate; under the conditions of industrial application it amounts to approximately 0.80-0.95).

$$Costs = Bg \cdot PF \qquad (3)$$

where PF - price of the fuel.

Approximate costs of the production of 1 t of α-hemihydrate, with the condition of 50 wt. % *input* of sludge suspension and yield of about 97 wt. % are given in Table 4.

Table 4. Material and process requirements per ton α-hemihydrate

Phosphogypsum (in tons)	*H.p.steam* (in tons)	Electric power (in KWh)	Water (in tons)	Effluent (in tons)
1.22	0.35	45	1.50	1.70

4. CONCLUSIONS

Investigations, conducted in this study showed that waste phosphogypsum-dihydrate represents a burden which even must not be kept in deposits because of its large quantity in relation to the main product – phosphoric acid, as well as because of great impact of a phosphogypsum deposit on the environment. By the proposed procedure, calcium-sulphate dehydrate is transformed into a far purer α-hemihydrate which, with its physic-chemical characteristics, approaches natural gypsum and contains additional components which enable formation of small-grain phosphogypsum which may be utilised in construction industry. Test installation, given in this paper, is automated and designed in such way to be operated by only one person. Because of the simplicity of the process and short conversion time, of about 3 min, starting and terminating of the process is measured by minutes instead of hours, with the capacity of 1.8 t/h. The obtained α-hemihydrate may be utilised for obtaining of gypsum blocks and dry hemihydrate.

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