

# THE STUDY OF NEUTRALIZATION OF THE DIHYDRATE PHOSPHOGYPSUM IMPURITIES

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*The paper presents the characterization of dihydrate phosphogypsum impurities, both in laboratory and in industrial scale, and chemical process of their neutralization in the lime suspension. The fastest and controlling processes of transfer water soluble impurities to insoluble compounds of calcium orthophosphates  $\{Ca_3(PO_4)_2 \cdot nH_2O$  and  $Ca_5(PO_4)_3OH \cdot mH_2O\}$ ,  $CaF_2$ ,  $CaSiF_6$ ,  $Ce(OH)_3$  were determined. The impurities in the phosphogypsum crystals were neutralized under hydrothermal conditions (in an autoclave). The increased quantity of alkalis in the recycling water did not have influence on the phosphogypsum neutralization process and on the properties of the plaster made from phosphogypsum. Neutralized phosphogypsum may be used in the production of gypsum binding materials.*

## INTRODUCTION

Phosphogypsum is a by-product of the phosphoric acid industry and consists of 65-70 % gypsum, 25-30 % water and 5-10 % impurities, i.e. phosphoric acid and its salts, hydrofluoric acid and its compounds,  $R_2O_3$  ( $Al_2O_3 + Fe_2O_3$ ), quartz, apatite, alkali, organic matter, and others. The  $P_2O_5$  and F impurities are found in three different forms: on the surface of gypsum crystals as water-soluble compounds ( $H_3PO_4$ ,  $Ca(H_2PO_4)_2 \cdot H_2O$ ,  $H_2SiF_6$ ), substituted in the lattice of gypsum crystals (effectively solid solutions of  $CaHPO_4 \cdot 2H_2O$ ,  $SrSO_4$  or  $Na_2SiF_6$ ) and as insoluble compounds, i.e. apatite and quartz. These impurities, particularly hydrofluoric acid and its salts, contaminate an environment. Soluble phosphates  $\{H_3PO_4$  and  $Ca(H_2PO_4)_2 \cdot H_2O\}$  and soluble fluorides had maximum influence on the fall of compressive strength of plaster [1-3].  $CaHPO_4 \cdot 2H_2O$  had small influence [3, 4], but with the present of  $Ca(OH)_2$  it had great influence on the plaster properties [4]. The most impurities in phosphogypsum can be found in the particle size fractions above 160 and below 25  $\mu m$ . There are more than few plants (those of "Onoda" in Japan, "Giulini chemic GmbH", "Knauf" in Germany, etc.) where the impurities are eliminated by washing phosphogypsum with water or separating off coarse and very fine particles. Up to 4  $m^3$  of water is necessary for 1 ton of phosphogypsum. The phosphogypsum admixtures are also eliminated by using a combined method when phospho-

gypsum is washed with a smaller amount of water, and the rest of the acid admixtures are neutralized by adding the following additives:  $Ca(OH)_2$ ,  $CaCO_3$ ,  $K_2CO_3$ , KOH, Portland cement,  $NH_4OH$ , etc. [5-9]. The acid impurities are not fully eliminated from the phosphogypsum crystals [6, 8]. The insoluble phosphates  $\{Ca_3(PO_4)_2$ ,  $Ca_5(PO_4)_3OH\}$  and fluorides ( $CaF_2$  and  $CaSiF_6$ ) did not influence the plaster properties [3, 10].

The objective of the work is to investigate the neutralization process of the acid impurities of dihydrate phosphogypsum into lime suspension.

## EXPERIMENTAL

### Materials

*Phosphogypsum* (calcium sulfate dihydrate) is a by-product which is formed during the reaction of sulfuric acid with ground Kola apatite. The chemical composition of the dihydrate phosphogypsum samples (calculated for the dry product) is (%): 31-37 CaO, 44-45  $SO_3$ , 0.3-0.6  $SiO_2$ , 0.5-1.5  $R_2O_3$ , 0.24-0.32  $Na_2O$ , 0.04-0.08  $K_2O$ , 0.91-2.86  $P_2O_5$  common (c), 0.52-2.65  $P_2O_5$  water soluble (w.s.), 0.14-0.48 F common (c.), 0.015-0.33 F water soluble (w.s.), 1.8-2.0 SrO, 0.3-0.35  $Ce_2O_3$ . The phosphogypsum moisture is 20-25 %; loss on ignition at 400°C is 37-42 %; density is 750-800  $kg/m^3$  and specific surface by Blain is 260-290  $m^2/kg$ . The X-ray diffraction pattern is shown in figure 1 curve 1.

*Lime.* The ground calcite quicklime from the JSC "Kalcitas" has been used for the neutralization of phosphogypsum, the CaO + MgO amount is 60-67 %, specific surface is 210-560 m<sup>2</sup>/kg.

*CaO* has been used for the testing of model systems. It was produced when calcined the "C" (clean) mark Ca(OH)<sub>2</sub> at the temperature 900°C for 2 h.

*Acids.* Orthophosphoric acid and hydrofluoric acid have been used in quality "analytical grade".

#### Equipments

The following equipment has been used in the testing of model systems: magnetic mixer MM-5; a universal-purpose ion meter EV-74; a 100 ml burette; an analytic balance VLR-200; a three-neck 2 l content flask; a conical flask with a funnel and vacuum pump VV-461M; a drying cupboard SNOL-3.5; heating furnace SNOL-1.5; X-ray apparatus DRON-6.

The equipment used for the neutralization of phosphogypsum under laboratory conditions: a 250 l neutralization reactor; a general-purpose ion meter EV-74 and laboratory vacuum drum-type filter. In the experimental production, the following devices have been used: a bunker with the screw phosphogypsum dosing tank; a belt-type transporter; four 6.8 m<sup>3</sup> capacity reactors; industrial pH-meters with self-recorders KSP2-004 and a drum-type vacuum filter.

#### Methods

*Impurities of phosphogypsum.* To determine the amount of water-soluble impurities; dihydrate phosphogypsum was mixed with distilled water in the ratio 1:2. After half-hour of mixing the pulp was drained through a thick filter. Some part of water-soluble admixtures formed phosphogypsum crystals. Phosphogypsum washed by the mentioned procedure was mixed with distilled water. The solution should not be saturated with CaSO<sub>4</sub>, i.e. the CaSO<sub>4</sub> concentration is not higher than 2.0 g/l. After the filtration the admixture amount in the solution was measured. The insoluble part was examined with the help of X-ray and chemical methods. The amount of P<sub>2</sub>O<sub>5</sub> common, assimilated, water soluble and free orthophosphoric acid in phosphogypsum was determined according to EN 196-2 by using the yellow phosphor-vanadium-molybdenum complex. The total amount of other impurities was determined with the complete chemical analysis according to EN 196-2.

*CaO-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system.* At certain rate following some order certain amounts of orthophosphoric acid, calcium dihydrogen phosphate and CaO solution or CaO suspension were poured into a three-neck 2 l content flask. The content was mixed with the magnetic mixer; pH measured with the ion meter. Samples were

taken at determined intervals, they were filtered, and the deposit poured over with 100 % ethyl alcohol and examined using the methods of X-ray and chemical analysis.

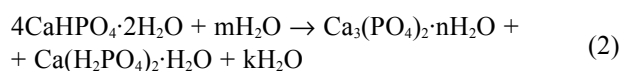
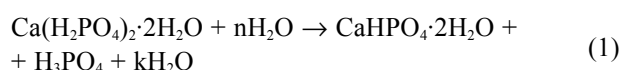
*Fluoride isolation.* Gas evolved from phosphogypsum was absorbed with the three-section water absorber. During the experiment, the variation of temperature was recorded with the self-recorder and the samples were taken in order to determine the degree of dehydration in phosphogypsum.

*Dehydration of dihydrate phosphogypsum.* The laboratory tested phosphogypsum was dried on the hearth dryer constantly stirring it, then boiled in the boiler of 50 l content or dried in 100 l drum-type dryer and then boiled in 30 l content autoclave. During the experimental production neutralized phosphogypsum was dried in the drum-type 5 t/h efficiency dryer SB-1.6-81 and boiled in 4.5 m<sup>3</sup> capacity gypsum boiler or in 63 l capacity autoclave.

## RESULTS AND DISCUSSION

### Impurities of phosphogypsum

Most impurities in phosphogypsum consists from a phosphate impurities remaining when orthophosphoric acid is washed out. The analysis of phosphogypsum showed that water soluble P<sub>2</sub>O<sub>5</sub> consists of free orthophosphoric acid H<sub>3</sub>PO<sub>4</sub>, calcium dihydrogen phosphate Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and calcium hydrogen phosphate CaHPO<sub>4</sub>·2H<sub>2</sub>O. The latter two compounds hydrolyze with water:



When acid phosphogypsum is dissolved in the water, the insoluble impurities, preserve the initial form of the phosphogypsum crystal. Both the X-ray diffraction patterns (Fig.1, roentgenogram 2) and chemical analysis demonstrated that the insoluble phosphogypsum admixtures are strontium sulfate and calcium hydrogen phosphate. The dimensions of the crystal lattice of these compounds are very close to the dimensions of the gypsum crystal lattice. In the solution there is up to 0.41 % P<sub>2</sub>O<sub>5</sub>.

### CaO-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O system

When various synthesized phosphogypsum impurities were added to the gypsum plaster and the gypsum-cement-puzzolan binding material, it was found that in the alkaline medium, which is typical of the bindings

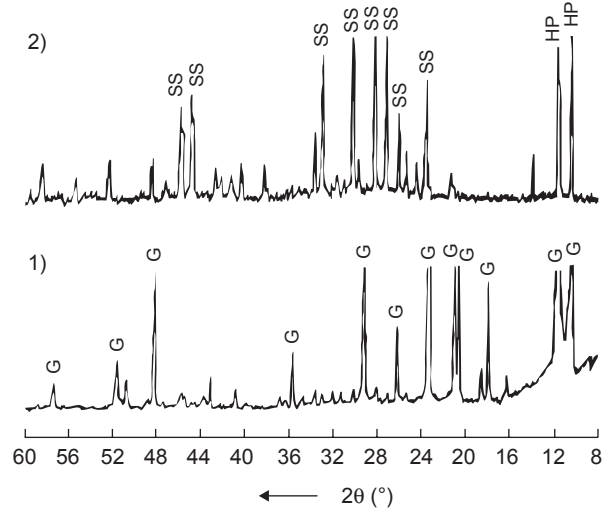


Figure 1. The X-ray diffraction patterns: 1 - phosphogypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), 2 - the residuum of acid phosphogypsum which remained after the dissolving of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; SS -  $\text{SrSO}_4$ , HP -  $\text{CaHPO}_4$ , G -  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

and many other building materials, calcium orthophosphates of the hydroxyl apatite group  $\{\text{Ca}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}, \text{Ca}_5\text{OH}(\text{PO}_4)_3 \cdot m\text{H}_2\text{O}, \text{etc.}\}$ ,  $\text{CaF}_2$ ,  $\text{CaSiF}_6$  and  $\text{Ce}(\text{OH})_3$  remain stable and do not affect their hydration.

Tests of the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  in the solutions show that at proportions of  $\text{CaO}/\text{P}_2\text{O}_5$  from 2 up to 3.33 calcium orthophosphate is formed firstly. This formation when orthophosphoric acid or calcium dihydrogen phosphate solution reacts to lime suspension ( $\text{CaO}/\text{P}_2\text{O}_5 = 3.33$ ) determines the duration of calcium orthophosphates of hydroxyl apatite group. If the concentration of the dissolved  $\text{CaO}$  is bigger than the concentration of  $\text{P}_2\text{O}_5$  (the suspension  $\text{pH}$  remains alkaline until the end of the reaction, Fig. 2 curve 2), then calcium orthophosphate (figure 2, the X-ray diffraction patterns 2-1) is formed in the solution far from the lime surface. It crystallizes into calcium orthophosphates of the hydroxyl apatite group (figure 2, the X-ray diffraction patterns 2-2; 2-3,) without interrupting the process of lime dissolution. On the contrary, if the concentration of dissolved  $\text{CaO}$  is smaller than the concentration of  $\text{P}_2\text{O}_5$ , the place of the formation of X-ray amorphous calcium orthophosphate comes closer to the lime surface.

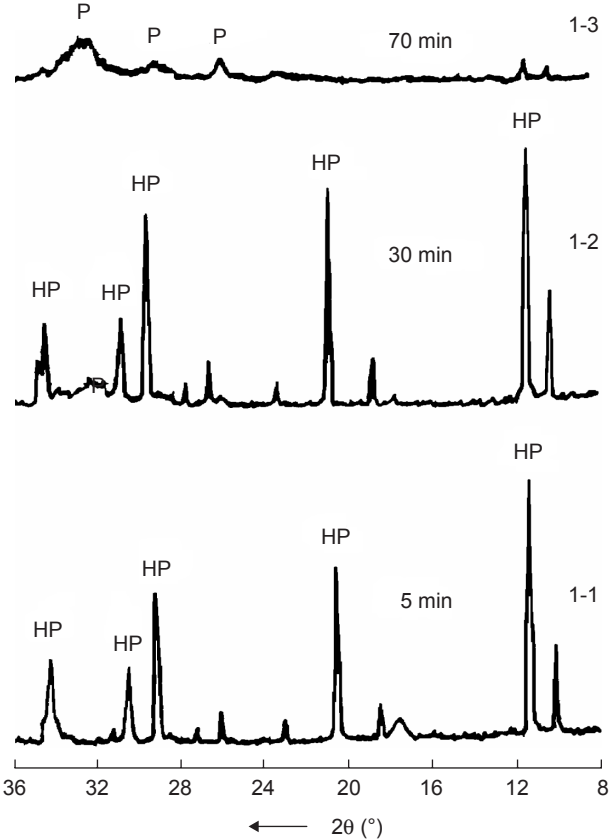
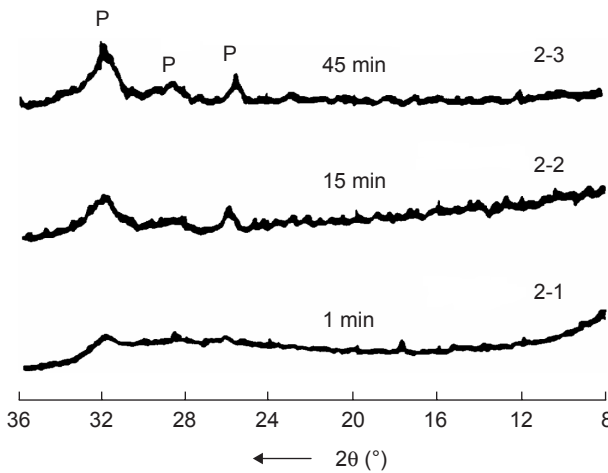
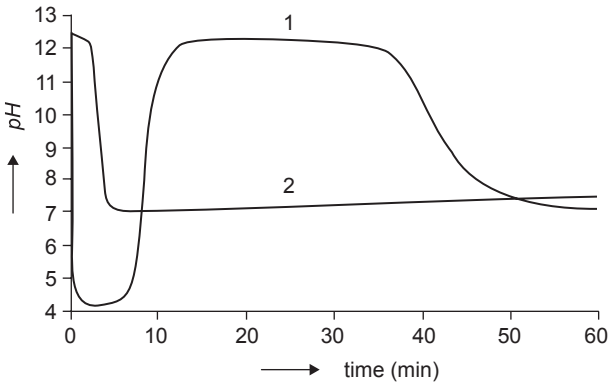


Figure 2. The suspension  $\text{pH}$  changes (curves 1 and 2) and X-ray diffraction patterns of solid phase: 1 - swift pouring of 1 %  $\text{H}_3\text{PO}_4$  solution into lime cream and the reaction products after 5, 40 and 70 min. (1-1; 1-2; 1-3 the X-ray diffraction patterns); 2 - pouring of 1 %  $\text{H}_3\text{PO}_4$  solution into lime cream for 2 min. and the reaction products after 1, 15 and 45 minutes (2-1; 2-2; 2-3 the X-ray diffraction patterns); HP -  $\text{CaHPO}_4$ , P -  $\text{Ca}_3(\text{PO}_4)_2$ .

Stable colloidal new compounds cover the lime particles, preventing them from dissolving. The suspension  $pH$  suddenly moves to the acid range (figure 2, curve 1). Under such conditions, X-ray amorphous calcium orthophosphate converts to calcium hydrogen phosphate (figure 2; the X-ray diffraction patterns 1-1; 1-2), thus releasing the lime particles from the colloidal layer. The lime starts dissolving freely, and the suspension  $pH$  suddenly increases. The decrystallized calcium hydrogen phosphate crystals in the alkaline lime medium react to form orthophosphates of the calcium hydroxyl apatite group (figure 2, X-ray diffraction patterns 1-3). However, this process is about 50 times slower than the direct one (figure 2, 1 and 2 curves).

In order the direct reaction could take place reliably, the pouring of acid phosphates into lime suspension is necessary, constantly watching the suspension  $pH$  and regulating the pouring efficiency. It is necessary for the movement of  $pH$  to the acid side up to the end of the reaction. While examining the effect of the lime suspension concentration (figure 3) it has been found that when it is less than 0.4 % CaO, the acid solution of  $P_2O_5$  may be swiftly poured into lime suspension because there are too few of X-ray amorphous calcium orthophosphates to form a non-permeable layer around the insoluble lime particles. That's why they dissolve easily. If phosphogypsum is washed until not more than 0.5 % of water soluble  $P_2O_5$  remains, the phosphogypsum neutralization process may be carried out with the constant stirring of lime suspension with phosphogypsum. Then the direct reaction of orthophosphate formation is uninterrupted. With the use of lime suspension greater concentration (0.4 % and CaO of greater concentration), during the neutralization process it is necessary to pour less water is solved orthophosphates into the reactor in order the suspension  $pH$  could remain alkaline.

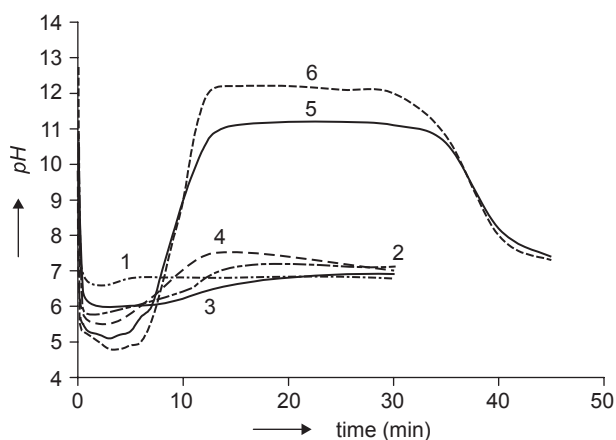


Figure 3. The  $pH$  alteration after the swift pouring of orthophosphoric acid solution of 1 % concentration into lime cream of various concentration; CaO %: 1 - 0.1; 2 - 0.2; 3 - 0.3; 4 - 0.35; 5 - 0.4; 6 - 0.8.

## Neutralization of phosphogypsum

The results show that the acid impurities of dihydrate phosphogypsum can be neutralized in the lime suspension. The process of neutralization can be controlled with estimation of the  $pH$  value. The concentration of lime suspension was changed according to the amount of water soluble  $P_2O_5$  in phosphogypsum, calculating that the relation of water in the neutralized phosphogypsum pulp and hard particles (W/G) were 1.0-1.2 after reacting them into calcium orthophosphates of the hydroxyl apatite group (under these conditions the drum-type vacuum filters are most effective). For this purpose, the calculated amount of the ground quicklime was poured into the lime cream preparation reactor as well as lime slaked for 30 minutes and later poured into the phosphogypsum neutralization reactor. Constantly recording  $pH$  with the self-recorder, acid phosphogypsum is poured into lime suspension. The efficiency of its provision is regulated in order  $pH$  of the pulp stirred in the reactor would not decrease below 7. The model system test results completely proved correct while neutralizing phosphogypsum both with the laboratory equipment and in the institute's experimental production line of phosphogypsum processing. The curves of typical  $pH$  variation during phosphogypsum neutralization are given in figure 4.

As it is obvious in the curves, the danger of lime particle screening increases at the end of phosphogypsum neutralization process when the surface of soluble lime particles extremely decreases as the soluble CaO stream decreases, too. In this neutralization period it is necessary to pour much smaller amount of phosphogypsum into the reactor. Sometimes its provision must be stopped for a short time. The neutralization is finished when phosphogypsum pulp reaches  $pH = 7-9$ . In case the neutralization takes place in the alkaline medium

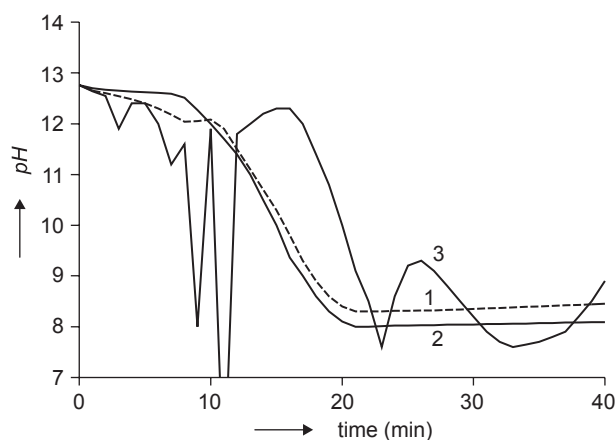


Figure 4. Curves showing  $pH$  changes during phosphogypsum neutralization: 1 and 2 - evenly decreasing the efficiency of supplied phosphogypsum; 3 - when the efficiency is too strong and when the phosphogypsum supply is interrupted time after time.

decreasing the phosphogypsum provision ( $pH$  decreased uniformly) even if the stirring of the neutralized phosphogypsum pulp lasts long,  $pH$  increases insignificantly. It means that soluble  $P_2O_5$  impurities during the neutralization process are transferred into insoluble calcium orthophosphates hydroxyl apatite group.

On the contrary, if  $pH$  in the pulp falls down below 7 because of various reasons, with the further stirring of the neutralized phosphogypsum pulp, the significance of  $pH$  in it starts growing intensively. In this case, as mentioned before, the concentration of dissolved CaO is smaller than the concentration of  $P_2O_5$ , amorphous calcium orthophosphate converts to calcium hydrogen phosphate. The process of this phosphate conversion to orthophosphates is many times slower than the direct one. It is not clear when the neutralization process should be finished.

#### Alkalies accumulation

For the phosphogypsum neutralization technology to be wasteless, the filtrate after the neutralized phosphogypsum pulp filtration ( $pH = 7$ ) was used again and again for the preparation of lime cream. It has been noticed that the alkalies are accumulated in an often used filtrate (in phosphogypsum up to 0.4 %). The effect of this phenomenon on the neutralization process and the properties of the product have been analyzed. In the tested phosphogypsum 0.24 %  $Na_2O$  and 0.04 %  $K_2O$  were found. The results are presented in figure 5. Say, the humidity both of acid and neutralized phosphogypsum after filtration is nearly the same (25-30 %), then the maximum of theoretical alkali amount in the filtrate cannot exceed the following:  $Na_2O = 0.24/25 \times 1000 = 9.6$  g/l;  $K_2O = 0.04/25 \times 1000 = 1.6$  g/l. The curves presented in figure 5 asymptotically approached the given quantities. During the test much smaller alkali concentration has been reached. It shows that not all

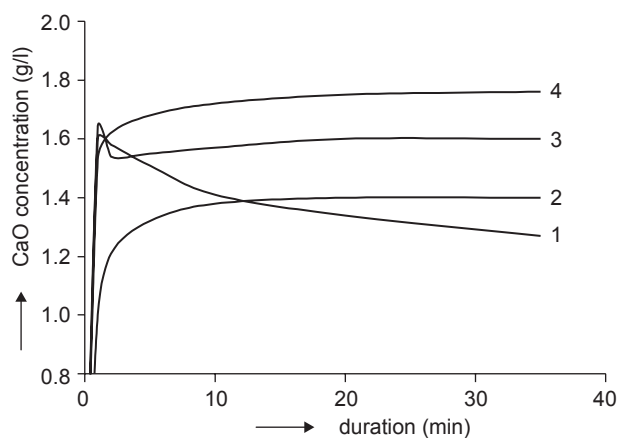


Figure 6. The effect of alkali concentration in the filtrate on the alteration of the dissolved CaO in lime cream: 1 - incline water; 2 - 0.9 g/l  $R_2O$ ; 3 - 1.8 g/l  $R_2O$ ; 4 - 3.9 g/l  $R_2O$ .

alkalies dissolve. The greater part is most probably in  $Na_2SO_4$  and  $K_2SO_4$  compounds, which are found in phosphogypsum crystals lattices.

The effect of the amount of alkalies in the filtrate on the amount of CaO in lime cream is seen in figure 6. The concentration of dissolved CaO in the filtrate of different alkalinity grows together with the increase of alkali concentration in them. The greater the concentration of dissolved CaO in lime suspension, the greater efficiency of phosphogypsum supply into the neutralization reactor which is achieved without interrupting (preserving the alkaline medium in the pulp) the direct reaction of converting soluble phosphates into insoluble calcium orthophosphates. The growth of alkali concentration in the filtrate allows the shortening of the duration of phosphogypsum neutralization.

After 30 cycles of neutralization there were no physical mechanical alterations in the finished production from successfully neutralized phosphogypsum when pure water and the filtrate after 30 cycle's neutralization were used. Therefore, the alkalies in the filtrate are not harmful.

#### Fluorine evolution

About 40 % of fluorides are eliminated from phosphogypsum during its drying and dehydration. These are injurious to health  $HF$ ,  $H_2SiF_6$  and  $SiF_4$  gas products. It has been determined that it is possible to avoid the evolution of these harmful kinds of gas. The evolution of fluorine compounds from heated phosphogypsum depends on the amount of water soluble  $P_2O_5$  and the temperature of phosphogypsum (figure 7).

The diagram data demonstrates that with the increase of soluble  $P_2O_5$  in phosphogypsum much greater amount of fluorine is isolated during dehydration. Two maxima of fluoride evolution were been detected, the first is dependent on the drying of phos-

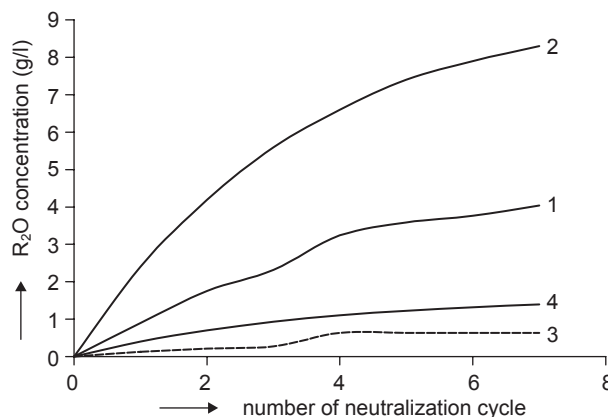


Figure 5. Alkalies accumulation in the filtrate when it is returned to the neutralization cycle: 1 - experimental  $Na_2O$ ; 2 - theoretical  $Na_2O$ ; 3 - experimental  $K_2O$ ; 4 - theoretical  $K_2O$ .

phogypsum and hemi-hydrate gypsum formation at temperatures 105-110°C, and the second on the beginning of the dehydration of hemihydrate gypsum at temperatures 150-180°C.

With the help of the dehydration with various additives and the use of different methods, the evolution of fluorides decreases 30 times and more and stops when water soluble phosphates convert into calcium orthophosphates of the hydroxyl apatite group.

The data in the table show that in order to avoid fluoride evolution into the environment during the drying and boiling operations, the neutralization of phosphogypsum should be finished when in the pulp is  $pH \geq 7.5$ .

#### Neutralization of the impurities in phosphogypsum crystals

The water insoluble impurities which were formed in phosphogypsum pulp during the neutralization process settle down on phosphogypsum particles. When phosphogypsum is dried and boiled in the gypsum boiler, these impurities and the ones formed in phospho-

gypsum crystals -  $SrSO_4$  and  $CaHPO_4$  - preserve the form of phosphogypsum particles. Surrounded by the impurities,  $\beta - CaSO_4 \cdot 0.5H_2O$  crystals remain decrystallized the product with such porous and angular particles requires twice more water to get the gypsum dough of normal density (the relation of water and gypsum W/G varies from 1.0 to 1.3). Because of that, the duration of phosphogypsum binding becomes longer and its strength at pressing for 2 h does not reach 3 MPa. This rather weak admixture carcass is easily destroyed when the product is ground in the ball-shaped mill for a short time thus releasing the hemihydrate gypsum crystals. The binding time shortens W/G decreases to 0.55-0.7, and the strength at pressing increases twice - to 6 MPa. However, even after it W/G of gypsum plaster received from phosphogypsum remains greater and the strength smaller than that of gypsum plaster from natural resources. It depends on the difference in the size the particles of hemihydrate gypsum. The particles of gypsum plaster produced from phosphogypsum are much smaller than those of gypsum plaster produced from natural materials. Besides, there remains up to 0.3 % of

Table 1. Fluorine evolution during dehydration of neutralized phosphogypsum containing 2.7 %  $P_2O_5$ .

Neutralization conditions				Total amount of fluorine in phosphogypsum (%)	Evolved fluorine (% of total fluorine)
Neutralizer mark	Neutralizer amount	Neutralization method	10 % medium pH		
-	-	-	2.3	0.42	25.10
CaCO <sub>3</sub>	6.5	dry	4.2	0.41	0.23
CaCO <sub>3</sub>	5.4	wet	4.7	0.31	0.15
CaO	0.77	wet	4.5	0.42	0.23
CaO	2.8	dry	6.9	0.35	0.22
CaO	2.5	wet	6.9	0.41	0.17
CaO	2.9	wet	7.3	0.41	not found

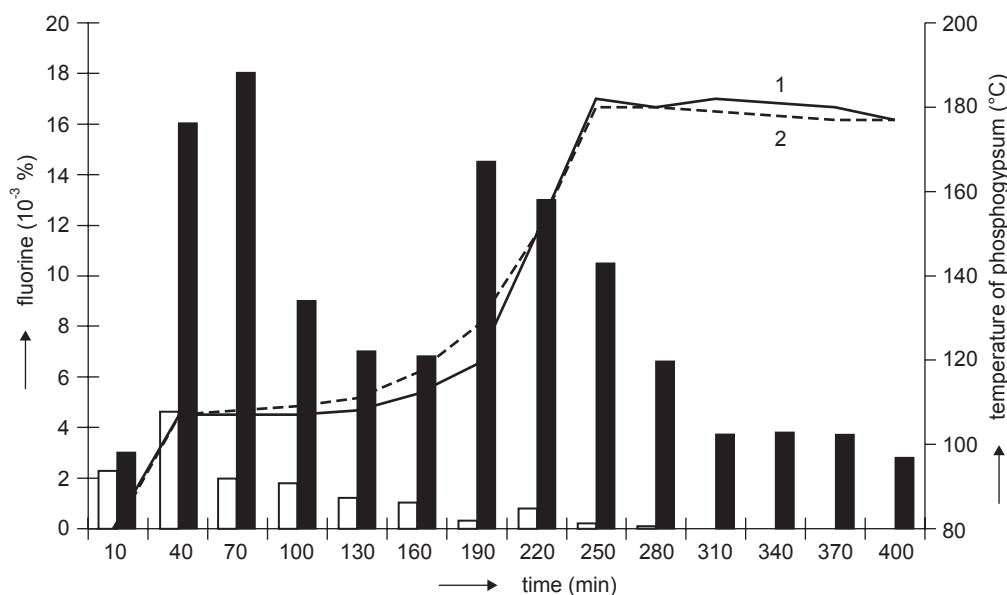


Figure 7. Fluorine evolution during dehydration of the phosphogypsum: 1 and white columns - 0.7 % water soluble  $P_2O_5$ ; 2 and black columns - 2.7 % water soluble  $P_2O_5$ .

unneutralized ortho-phosphoric acid, which was in phosphogypsum crystals. These drawbacks are removed during dehydration carried out under hydrothermal conditions - in autoclaves when phosphogypsum is neutralized in lime cream and when phosphogypsum pulp  $pH$  8.5-9.5, but not under atmospheric pressure in gypsum boilers.

Under hydrothermal conditions, when phosphogypsum crystals intensively dissolve, the liquid medium gets saturated both with  $Ca^{2+}$  and  $SO_4^{2-}$  ions and acid phosphates and fluorides, some amounts of which were isothermally interfered into the structure of  $CaSO_4 \cdot 2H_2O$  crystals. As  $OH^-$  ion concentration in phosphogypsum pulp is bigger, the further neutralization of acid admixtures takes place. The stable  $Ca_5(PO_4)_3OH \cdot nH_2O$ ;  $Ca_3(PO_4)_2 \cdot nH_2O$  and  $CaF_2$  which were formed in the alkaline medium remain among phosphogypsum admixtures, and the crystallization of  $\alpha$ - $CaSO_4 \cdot 0.5H_2O$  particles as well as their growth take place in the liquid medium free of admixtures. There are no phosphogypsum admixtures in the crystals of the product thus produced. When the product is dried and ground the W/G of the produced binding material is 0.38-0.43, and its strength at pressing for 2 h is 10-15 MPa.

## CONCLUSION

1. When the dihydrate phosphogypsum is neutralized in lime suspension, acid phosphogypsum impurities are transferred into insoluble  $Ca_5(PO_4)_3OH \cdot nH_2O$ ;  $Ca_3(PO_4)_2 \cdot nH_2O$ ;  $CaF_2$ ;  $CaSiF_6$  compounds. The rate of the direct formation of calcium orthophosphates hydroxyl apatite group from  $P_2O_5$  solution in lime suspension depends on the rate of lime dissolving process. These compounds in the alkaline medium, which is typical to mineral binding materials, remain stable and do not change the properties of the gypsum binding materials.
2. Water soluble fluorine present in phosphogypsum during the neutralization process is transferred into insoluble calcium fluoride and evolution of fluorine decreases many times during dehydration step.
3. The increase of alkali concentration in the filtrate circulating in an isolated manner does not disturb the phosphogypsum neutralization process. On the contrary, it accelerates the process. The alkalies do not deteriorate the properties of the product.

4. The impurities in phosphogypsum crystals may be neutralized. This makes possible to reduce their negative effect during the dehydration process under hydrothermal conditions (in an autoclave).

## References

1. Berry E. E.: J.Appl.Chem.Biotechnol. 22, 667 (1972).
2. Beretka J., Douglas N., Crook and George King A.: J.Chem.Technol.Biotechnol. 31, 151 (1981).
3. Singh M.: Cem.Conc.Res. 33, 1363 (2003).
4. Beretka J.: J.Chem.Technol.Biotechnol. 32, 607 (1982).
5. Geeraert E., De Lange G.: Cim.betons.platres.chaux. 2, 95 (1998).
6. Wirsching F.: TIZ -Fachberichte Rohstoff-Engineering 105, 382 (1981).
7. Stonis S., Kaziliunas A., Bacauskiene M.: Build.Mater. 3, 9 (1984). (in Russ.)
8. Gopakumar K., Mukundan P., Satyanarayana K. G.: Trans.J.Brit.Ceram.Soc. 82, 193 (1983).
9. Singh. M.: Cem.Conc.Res. 32, 1033 (2002).
10. Moldan D.: Cim.betons.platres.chaux. 2, 98 (1998).

## STUDIE NEUTRALIZACE NEČISTOT DIHYDRÁTU SÍRANU VÁPENATÉHO

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Dokument předkládá charakteristické vlastnosti nečistot dihydrátu síranu vápenatého (phosphogypsum), jak v laboratorních podmínkách a v průmyslovém měřítku chemické procesy jejich neutralizace ve vápenné suspenzi. Byly stanoveny nejrychlejší a řídicí procesy přenosu vodou rozpustných nečistot na nerozpustné směsi ortofosforečnanu vápenatého  $Ca_3(PO_4)_2 \cdot nH_2O$  a  $Ca_5(PO_4)_3OH \cdot nH_2O$ ,  $CaF_2$ ,  $CaSiF_6$ ,  $Ce(OH)_3$ . Nečistoty v krystalech síranu vápenatého byly neutralizovány v hydrotermálních podmínkách (v autoklávu). Zvýšená kvalita zásad v recyklované vodě neměla žádný vliv na proces neutralizace síranu vápenatého a na vlastnosti sádry vyrobené ze síranu vápenatého. Neutralizovaný síran vápenatý může být použit při výrobě sádrových spojovacích materiálů.