

INVESTIGATION OF CHEMICAL AND MORPHOLOGICAL COMPOSITION AND RADIOACTIVITY OF PHOSPHOGYPSUM

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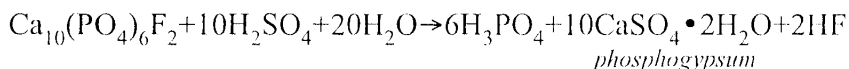
Phosphogypsum is a waste product in the manufacture of phosphoric acid from phosphorite and sulphuric acid by so-called "wet process" and represents a refuse that is as such simply thrown away. This paper describes our investigations of the actual fundamental problem: obtaining new material - chemical gypsum from phosphogypsum. The structure of phosphogypsum was determined by applying different instrumental techniques: scanning electron microscope, X-ray diffraction analysis, thermogravimetric analysis, investigations of phosphogypsum content and radioactivity. The obtained results showed similarity between phosphogypsum and natural gypsum, but also the significant difference that should be taken in account when phosphogypsum is used instead of natural gypsum. A process for reducing radioactive contamination of phosphogypsum has been used. The process of reducing radioactive contamination in waste product gypsum consisted of reacting it with dilute sulphuric acid containing barium sulphate to form an acidic slurry at an elevated temperature, the slurry was preferably cooled, and the resulting solid was separated into a fine fraction and a coarse fraction. In the fine fraction predominated barium sulphate and radioactive contamination, while in the coarse fraction predominated a purified gypsum product of reduced radioactivity.

Thus the chemical gypsum manufactured on the basis of phosphogypsum material was found suitable for use in the building industry as preparing plaster, gypsum wallboards and other constructional materials. Also, it can be useful as soil meliorate in agriculture and in production of ammonium-sulphate, as natural gypsum substitute.

KEY WORDS: phosphogypsum, scanning electron microscopy, thermogravimetric analysis, X-ray diffraction analysis, gamma-spectrometry

INTRODUCTION

The production of phosphoric acid by dehydrated process, the so-called "wet process", at low temperatures ($< 100^{\circ}\text{C}$), which is used later to manufacture phosphoric and other mixed fertilizers, is followed by separation of enormous quantities of phosphogypsum: about 4.5 t of phosphogypsum (proceed to one) per tone of the fertilizers (P_2O_5 equivalent) (1-3).



Phosphogypsum as waste-product is usually deposited close to phosphoric acid plants or into rivers and oceans. It represents a refuse that is from the environmental viewpoint of particular concern because of its toxic components such as fluorides, uranium and the uranium-series elements mainly ^{226}Ra , ^{222}Rn and ^{110}Po .

In our previous works, investigations of phosphogypsum have been carried out, and its characteristics were compared to natural gypsum (4-6) and detailed possibilities of phosphogypsum usage as semiproduct and final product have been analyzed.

The process of reducing radioactive contamination in waste product phosphogypsum will be apparent from the following description. This work concerns with the application of instrumental techniques for investigation of chemical characteristics, electrical surface properties and radioactivity of modified phosphogypsum.

EXPERIMENTAL

Phosphogypsum - waste product obtained from the phosphoric acid plant IHP Prahovo was used for all investigations (5). It was prepared for the analysis by the following procedure (6,16): samples were sieved on vibration screen and only fractions smaller than $200 \mu\text{m}$ were taken. The sample was rinsed with distilled water then with ethanol and ether, and then was dried at 60°C to constant mass. After calcination at 160°C during 2-3 hours the analyses were carried out.

Phosphogypsum samples were analyzed using scanning electron microscopy SEM, JSM-840A, JEOL, Japan. X-ray diffraction analysis was carried out using the diffractometer for powder SIEMENS D-500 with Ni-filtered $\text{CuK}\alpha$ radiation. Identification of crystalline phases in recorded samples has been carried out by position and intensity comparison of diffraction profiles with JC PDA data.

Thermogravimetric analyses of phosphogypsum were performed on Dermatograph Stanton, England, with a heating rate up to $7^{\circ}\text{C}/\text{min}$ in air stream in mixture with Al_2O_3 , samples were analyzed in ceramic crucibles at temperatures up to 500°C .

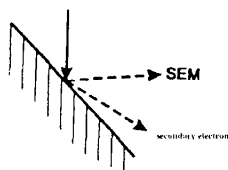
The radioactivity of phosphogypsum samples was analyzed by the following procedure (17): phosphogypsum samples were dried at 105°C (24 hours) to remove water due to the technological process and all measurement results are referred to dry substance. Samples were packed in small plastic vessels and hermetically closed to retain evolved radon. The measurement time for each spectrum was about 24 hours, and all measurements were repeated after 20 days to obtain radioactive equilibrium of the evolved radon (14). Low phonon measurements were carried out using CANBERRA Hp Ge coaxial detector with relative efficiency of 14%, FWHM of 1.7 keV, placed in vertical cryostat and protected with 2 cm of iron and 15 cm of lead. Total measured speed of phonon counting in the energy range of 20-2880 keV was 0.9 pulse/sec. The spectrometer was connected with a CANBERRA 8k ADC "MCA 35" multichannel analyzer which was connected with an HP Vectra ES/12 computer to treat the gam-

ma spectra using the "MicroSAMPO" program. Time for sample measurements was about 160 ks, while measurements of phonon spectra were significantly longer and were carried out regularly between sample measurements. Radium and potassium activity were determined by comparison with the standard SRM694 (Standard Reference Material 694, National Bureau of Standards, US) WPR (West Phosphate Rock), phosphate ore with known uranium content (141.4 ± 0.6 ppm) which is in equilibrium with its decay products.

RESULTS AND DISCUSSION

Granulometric analysis was carried out with phosphogypsum samples previously dried at 60°C . It was necessary to remove extreme fractions since they contain the greatest contaminants portion. Particle size of phosphogypsum varied over the range from 20 to $200 \mu\text{m}$ (average $80 \mu\text{m}$). The elimination of impurities has been carried out by sifting on sieve or with the aid of the agents for foam formation such as alkylarylsulphonates: dodecylbenzenesulphonate and tetrapropylbenzenesulphonate.

The adsorbed, specially scattered and secondary electrons make it possible to obtain the picture by scanning electron microscopy.



With the scanning electron microscopy the source of electrons is the electron gun (less powerful), and the entrance beam is focused on the sample by electromagnetic lenses whereas its deflection for the purpose of scanning the sample is also possible. The picture is obtained of the front surface of the sample and it is made by the repulsed and secondarily emitted electrons.

Photographs of gypsum and phosphogypsum obtained on scanning electron microscope are presented in Figures 1 - 3 (21).

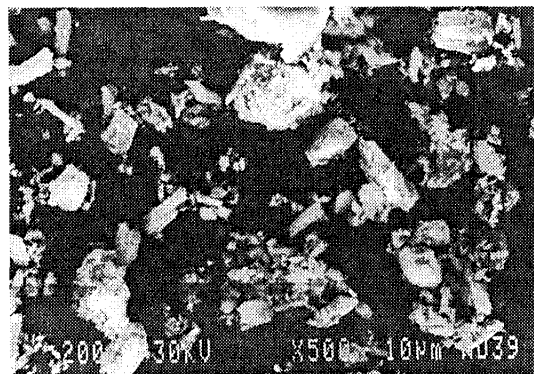


Fig. 1. SEM photograph of crystalline structure of natural gypsum (x500) (5)

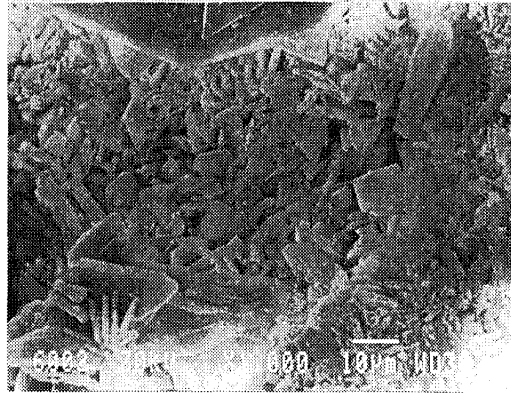


Fig. 2. SEM photograph of crystalline structure of phosphogypsum taken from plant pipe (x1,000)

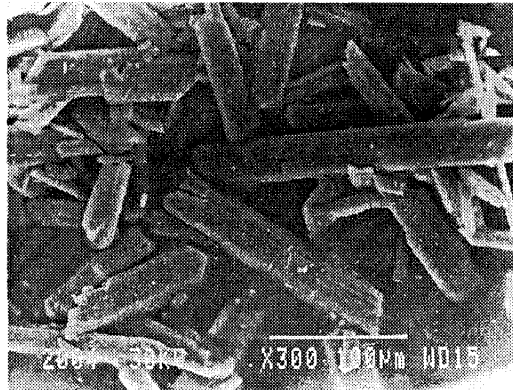


Fig. 3. SEM photograph of crystalline structure of purified phosphogypsum (x300) (6)

The SEM photograph of phosphogypsum presented in Fig.2 , shows that phosphogypsum has a well-defined crystalline structure with majority of rhombic and hexagonal crystal systems, pointing out to more complex composition in comparison with natural gypsum, which is in accordance with the literature data (7,8). The identification of the crystal phases in the analyzed samples was performed by comparing the position and the intensity of the diffraction profiles with the JS PDS data. The complexity of phosphogypsum is due to its crystalline structure and it influences its chemical behaviour.

Thermogravimetric analysis of phosphogypsum sample was performed in air stream with a heating rate of 7°C/min, and the obtained results are presented in Fig. 4, showing the change of sample mass in % in dependence on temperature. The mass loss for phosphogypsum is 17.53% (gypsum loses 2 molecules of water), that would corresponds to a gypsum portion of 84% in the sample. For natural gypsum, which is hemihydrate ($\text{CaSO}_4 \times 1/2\text{H}_2\text{O}$) the mass loss is 5.75% that would corresponds to gypsum portion of 93%.

X-ray diffraction analysis was carried out by comparing the position and intensity of diffraction profiles with JC PDA data. The following crystalline phases were identified for phosphogypsum: $\text{CaSO}_4 \times 2\text{H}_2\text{O}$ (33-311); $\text{CaSO}_4 \times 1/2\text{H}_2\text{O}$ (33-310) spectra corresponded to natu-

Table 1. Chemical and mineralogical composition of natural gypsum and phosphogypsum

Chemical composition	Natural gypsum (in wt. %)	Phosphogypsum (in wt. %)
CaSO ₄ ·2H ₂ O	–	11.54
CaSO ₄ ·1/2H ₂ O	81.34	77.26
CaSO ₄ , anhydride	6.16	–
Bonded (fixed) water, H ₂ O	5.38	7.21
CaSO ₄ , total	82.12	81.59
	Excess:	
Free CaO	0.70	0.29
SO ₃	–	–
Sum:	88.20	89.09
	Impurities:	
Free water, at 45°C	1.30	1.03
Calcination loss	0.98	0.60
SiO ₂ +insoluble residue	4.15	4.55
MgCO ₃	–	–
Na ₂ O	–	–
K ₂ O	–	–
Al ₂ O ₃ +Fe ₂ O ₃	0.06	0.17
MgO	–	–
CaCO ₃	5.09	4.48
P ₂ O ₅	–	0.09
Sum:	11.58	10.92
Total:	99.78	100.01

In phosphogypsum P₂O₅ can be found P₂O_{5/total} ≈ 0.09 wt. % which the natural gypsum contains at a low level. The presence of the fraction P₂O_{5/sin} is unfavourable only if phosphogypsum is applied in construction, while in agriculture it can have a positive effect on the soil treatment. A positive attribute of phosphogypsum is the presence of CaO (as CaCO₃ like that in natural gypsum 5.09 wt.%). The advantageous feature of phosphogypsum is the portion of CaO and SO₃, that indicates the presence of other salts with sulphur (MgSO₄, Al₂(SO₄)₃, FeSO₄).

Organic substances cause great difficulties in the process of phosphoric acid production. The method of organic substance determination is the calculation of carbon portion, which is in the order of 0.1 wt. %.

The investigations obtained with different phosphogypsum samples (10) showed that chlorides are present only in traces.

The main obstacle, though is the presence of radionuclides in phosphogypsum. The quantitative presence of uranium has been established in samples of phosphogypsum and the specific activity originates from ²²⁶Ra (18). The analyzed samples of phosphogypsum show that the distribution of uranium and ²²⁶Ra in relation to the initial phosphate ore is such that the basic component of phosphogypsum is ²²⁶Ra.

Gamma-spectrometry results of unpurified and purified phosphogypsum samples are presented in Table 2.

Table 2. Gamma-spectrometry results of unpurified and purified phosphogypsum samples (Bq/kg) (23)

Radionuclide	Activity of unpurified phosphogypsum	Activity of purified phosphogypsum
^{226}Ra	379±20	439±20
^{232}Th	7.1±0.5	8.7±0.5
^{40}K	7.8±0.5	< 8.7
Radionuclides artificial origin	< 1.1	< 1.0

The process of reducing radioactive contamination in phosphogypsum will be apparent from the following description (19,20). It has now been discovered that the foregoing objects are accomplished for reducing the radioactive contamination in waste product gypsum in a process which comprises:

a) This can be accomplished by a procedure comprising mixing the phosphogypsum containing radioactive contamination with dilute sulphuric acid containing barium sulphate at an elevated temperature to form an acidic slurry, having a solid component comprised of a fine fraction and a coarse fraction;

b) Separating the fine fraction of solids from the coarse fraction;

c) It was found that the fine fraction contains the main portion of radioactivity, while the coarse phosphogypsum fraction is characterized by a reduced radioactivity.

As an example: an aqueous sulphuric acid solution (*cca.* 2.97 dm³) having a concentration of 28 wt.% was mixed with a concentrated sulphuric acid solution (30 cm³) containing dissolved 3 g of barium sulphate at a temperature of 105°C. The phosphogypsum (750 g containing radium at *cca.* 26 pCi/g) (14,17) was agitated with the solution of sulphuric acid and barium sulphate for 12 minutes, while maintaining the temperature of the resulting slurry in the range of 98-105°C. At the end of this period, the slurry was cooled to 30-35°C, and then filtered. The filter cake was washed with 6.2 dm³ of water and the solids were dried at a temperature of 60°C. The weight of the dry solids was 695 g. 50 Grams of the dried solids was slurried with 1 dm³ of water and then wet screened on a 200 mesh (75 micron) screen. The solid gypsum material retained on the 200 mesh screen was collected and dried at 60°C. Analysis of the purified gypsum product showed that it had a radium concentration of 1.42 pCi (*cca.* 95 wt. % less than the initial sample) (22).

CONCLUSIONS

The investigations presented in this work showed the complexity of structure and content of phosphogypsum, which is of the same chemical formula as natural gypsum, CaSO₄×2H₂O, and also phosphogypsum is a typical raw material due to its impurities.

SEM photographs showed a different crystalline content of phosphogypsum in comparison to natural gypsum. The application of scanning microscopy to different samples, in the work of the electroactive (sulphide) coating of both gypsum and phosphogypsum, as well the obtained SEM photographs shows that this technique is becoming a powerful tool both for observing the morphological changes of the surface and for determining the quantitative composition.

X-ray diffraction analysis showed that phosphogypsum has a similar spectrum to that of natural gypsum and this could be decisive concerning potential usage of phosphogypsum as substituent of natural gypsum.

Thermogravimetric analysis indicated significant presence of water in mass, which suggests that the portion of CaSO_4 in phosphogypsum is in order of 84 wt.% (in natural gypsum up to 93 wt.%).

The investigations of radioactivity indicated the presence of ^{226}Ra and ^{40}K in phosphogypsum, which from the aspect of deposition (radon liberation) is not a problem, but if phosphogypsum is used without any treatment, that could yield a higher radioactivity at the environment.

Purified phosphogypsum - chemical gypsum material is suitable for use in preparing plaster, gypsum, gypsum wallboards and other construction materials. Also, chemical gypsum can be useful as a soil meliorate in agriculture and in the production of ammonium-sulphate as a natural gypsum substitute.

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ИСПИТИВАЊЕ ХЕМИЈСКОГ И МОРФОЛОШКОГ САСТАВА И РАДИОАКТИВНОСТИ ФОСФОГИПСА

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Фосфогипс је споредни производ који настаје при производњи фосфорне киселине диhidратним, *тзв.* "мокрим поступком", какав се примењује у нашој земљи. Услед присуства већег броја нечистоћа, као и производа радиоактивног распада урана, који се налази у почетној сировини за производњу фосфорне киселине - *фосфата*, фосфогипс се углавном одлаже на депоније на којима "стари". Због огромних количина фосфогипса, који настаје у односу 5:1 према главном производу - фосфорној киселини, депоније фосфогипса заузимају велику површину и временом могу да контаминирају околину, земљиште и ваздух.

У раду је предложен поступак рециклирања фосфогипса, који укључује пречишћавање фосфогипса уклањањем радионуклида и пречишћавање од присутних нечистоћа, које воде своје порекло из полазне сировине - фосфата, поступком калцинације и гранулисања. Предложеним поступцима пречишћавања добијени фосфогипс је био анализиран: извршена су физичко-хемијска испитивања фосфогипса, рендгенско дифракциона анализа, термогравиметријска анализа и гамаспектрометријска анализа. Такође, у раду су приказани резултати примене

скенирајуће електронске микроскопије (СЕМ) на испитивањима узорака природног гипса и фосфогипса, ради утврђивања морфолошког састава и структуре, њихове хомогености и присуства дефеката у структури. СЕМ снимци природног гипса и фосфогипса показују да ова два гипса, иако имају исте хемијске (молекулске) формуле, $\text{CaSO}_4 \times 2\text{H}_2\text{O}$, имају различиту структуру: природни гипс има слабије изражену кристалну структуру а фосфогипс има изразиту кристалну структуру, претежно ромбичног и хексагоналног облика, који указују на његов сложенији састав од природног, а што је у складу са литературним подацима.

Добијени резултати упоређени су са резултатима испитивања природног гипса, при чему је показано да се пречишћени фосфогипс по својим карактеристикама приближава природном гипсу. Хемијски састав фосфогипса и природног гипса одређен је стандардном силикатном анализом, методом алкалног топљења.

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