

## PHOSPHOGYPSUM SURFACE CHARACTERISATION USING SCANNING ELECTRON MICROSCOPY

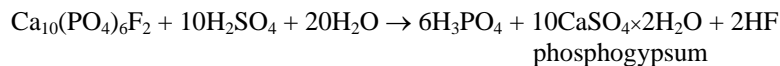
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*This paper presents the results of application of Scanning Electron Microscopy (SEM) to examinations of the samples of natural gypsum and phosphogypsum. Phosphogypsum has a well developed crystalline structure, and appear in two polymorphous forms, of rhombic and hexagonal shape crystals. Natural gypsum has a poorly crystalline structure. The differences in crystalline structure influence the chemical behavior of these raw materials.*

KEYWORDS: scanning electron microscopy (SEM), natural gypsum, phosphogypsum

### INTRODUCTION

Phosphogypsum is a by-product of the phosphate fertilizer which is produced in large quantities world-wide during the production of phosphoric acid. The wet phosphoric acid process is the most common process used to produce phosphoric acid. It can be summarized by the following equation (1):



Phosphogypsum consist mainly of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), but may also contain minor quantities of environmentally sensitive constituents such as heavy metals and naturally-occurring radionuclides (2). The presence of these minor constituents has raised some concerns regarding the stockpiling of phosphogypsum and its utilization in the other industries.

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The determination of elementary structure of matter, whether it is known or if it is necessary to verify the composition of a new or a well-known material to be used in further work, presents a frequent demand in the contemporary analytical practice. Sometimes these demands are combined with the need to determine the morphology or the structure of the surface roughness of a sample, its homogeneity or the presence of defects in the structure. The electron microscopic and spectroscopic techniques, whose rapid development to the commercial systems has been enabled first of all by the achievements in the electronic and computer technologies since the seventies to date, have become powerful tools to date for attaining the above requirements (3,4,5).

This paper presents the results of application of the Scanning Electron Microscopy (SEM) to examinations of the samples of natural gypsum and phosphogypsum, for the purpose of characterizing the composition and defining the morphological composition (6).

## EXPERIMENTAL

All investigations were performed with phosphogypsum obtained from Chemical Industry IHP Prahovo by a technological procedure in which raw phosphates are treated with  $H_2SO_4$ . Phosphogypsum purification was carried out by the following procedure (7,8): solution of  $H_2SO_4$  in water was made, with concentration of 28 wt.%, which was heated up to  $90^\circ C$ . Phosphogypsum was added to the solution and an emulsion was made with continuous stirring. After phosphogypsum,  $BaSO_4$  was added also at continuous stirring, until the temperature reached  $85^\circ C$ . Then the mixture was cooled. After cooling, it was filtered through a special Buchner funnel. Grinding of the purified phosphogypsum was carried out in a laboratory mixer to the particle size mainly between 100 and 200  $\mu m$ , with only 12% particles bigger than 200  $\mu m$ .

Phosphogypsum samples were analysed using scanning electron microscopy SEM, JSM-840A, JEOL, Tokyo, Japan, with the possibility of enlargement by 180.000 times and the resolution of 10 nm.

The adsorbed, specially sprayed and secondary electrons make it possible to obtain the picture by the scanning electron microscopy. For that reason, the sample does not have to be thin, which simplifies its application, and the energy of electrons of the primary beam does not have to be high, because electrons do not have to pass through the sample. Besides, the additional electromagnetic field (of the scanning coil) enables a controlled and programmed shifting of the electron beam. In such way, particularly small areas of a sample may be, line by line, examined – scanned (5).

X-ray diffraction analysis was carried out with a powder diffractometer SIEMENS D-500 with Ni-filtered  $CuK_\alpha$  radiation. Identification of crystalline phases in recorded samples has been carried out by matching position and intensity of diffraction profiles with the JC PDS data.

Thermogravimetric analyses of phosphogypsum were performed on a Dermatograph STANTON, England, with a heating rate up to  $7^\circ C/min$  in air stream in mixture with  $Al_2O_3$ . Samples were analysed in ceramic crucibles at temperature up to  $500^\circ C$ .

## RESULTS AND DISCUSSION

The results of the analysis of chemical and mineralogical composition of natural gypsum, phosphogypsum taken from filter from the process of phosphoric acid production by "wet procedure" and previously processed and purified phosphogypsum by the new procedure (9) are presented in Table 1.

**Table 1.** Chemical and mineralogical composition of natural gypsum, phosphogypsum taken from plant's pipe and purified phosphogypsum

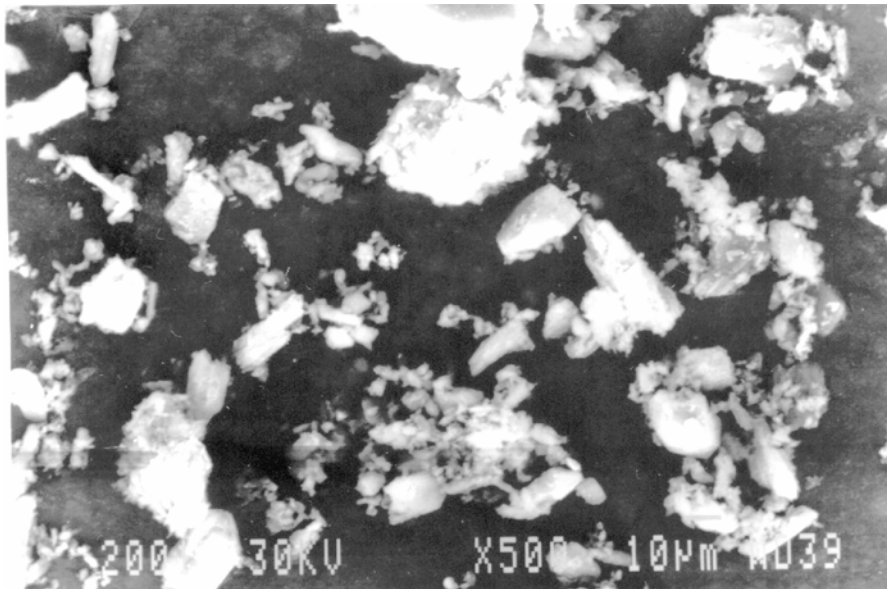
Chemical composition	Natural gypsum (in wt. %)	Phosphogypsum taken from plants's pipe (in wt. %)	Phosphogypsum (in wt. %)
CaSO <sub>4</sub> ×2H <sub>2</sub> O	–	74.16	11.54
CaSO <sub>4</sub> ×1/2H <sub>2</sub> O	81.34	–	77.26
CaSO <sub>4</sub> , anhydride	6.16	–	–
Bonded (fixed) water, H <sub>2</sub> O	5.38	18.02	7.21
CaSO <sub>4</sub> , total	82.12	56.14	81.59
	Excess:		
Free CaO	0.70	0.77	0.29
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 <sub>2</sub> +insoluble residue	4.15	21.75	4.55
Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	0.06	0.04	0.17
CaCO <sub>3</sub>	5.09	–	4.48
P <sub>2</sub> O <sub>5</sub>	–	0.84	0.09
Sum:	11.58	25.15	10.92
Total:	99.78	100.08	100.01

From Table 1, it can be seen that phosphogypsum is in the form of dihydrate, immediately after separation from filters (74.16 wt.%), while the natural gypsum is essentially hemihydrate (81.34 wt.% CaSO<sub>4</sub>×1/2H<sub>2</sub>O), and all the remaining parameters are far closer to natural gypsum than to phosphogypsum.

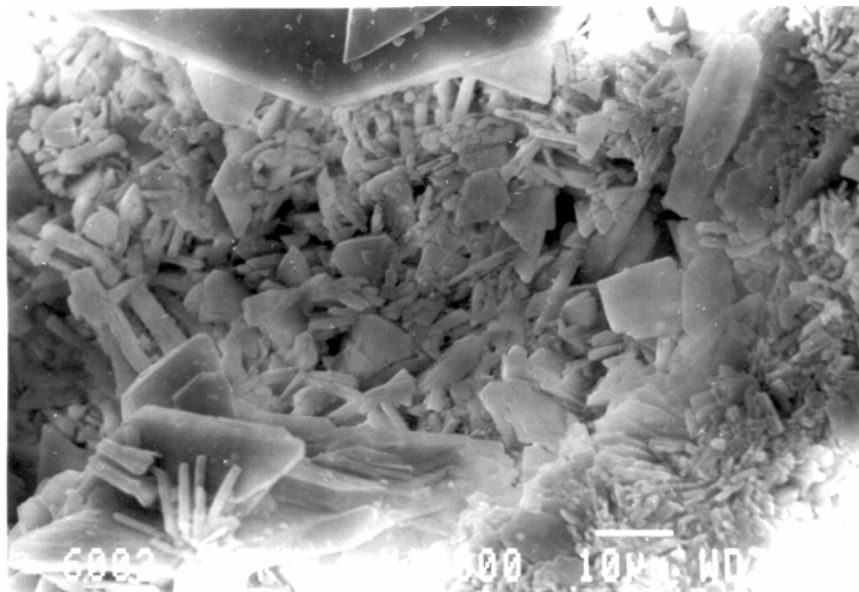
In both unpurified and purified phosphogypsum, P<sub>2</sub>O<sub>5</sub> contents are 0.84 and 0.09 wt.%, respectively, the content in natural gypsum being lower. A positive characteristics of purified phosphogypsum is the presence of CaO (as CaCO<sub>3</sub>, like that in natural gypsum 5.09%). The advantageous feature of phosphogypsum is the proportion of CaO and SO<sub>3</sub>, which indicates the presence of other salts with sulphur – MgSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeSO<sub>4</sub>.

To establish morphological composition and structure, their homogeneity and the presence of faults in their structure of samples of natural gypsum and various phosphogypsum, previously prepared (7,10), and mixtures of natural gypsum–phosphogypsum were subjected to SEM analysis.

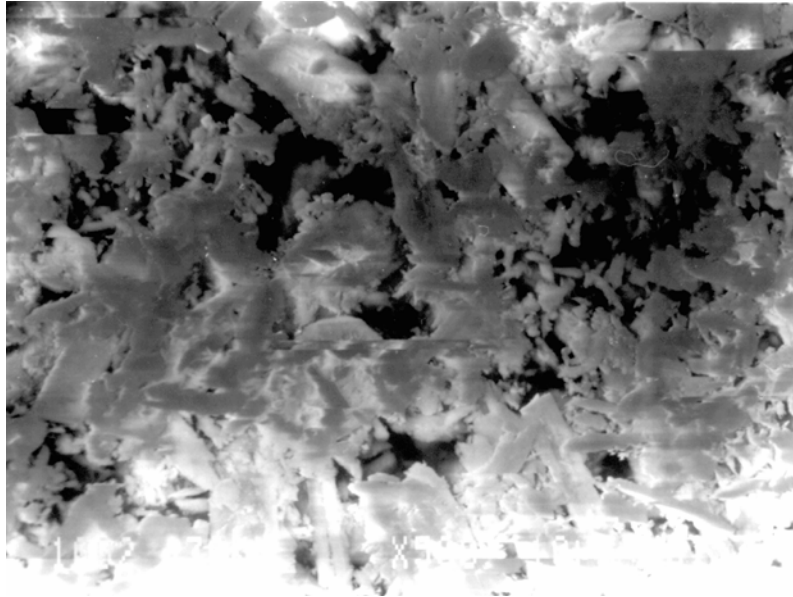
The obtained micrographs are presented in Figs. 1 – 5.



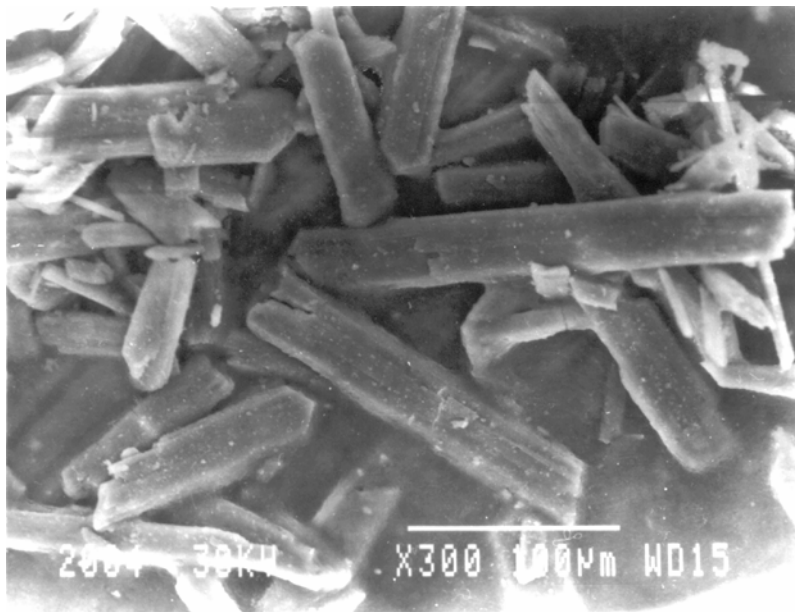
**Fig. 1.** SEM micrograph of crystalline structure of natural gypsum ( $\times 500$ )



**Fig. 2.** SEM micrograph of crystalline structure of phosphogypsum taken from plant's pipe ( $\times 1,000$ )



**Fig. 3.** SEM micrograph of crystalline structure of mixture of 75 wt. % natural gypsum and 25 wt. % phosphogypsum ( $\times 500$ )



**Fig. 4.** SEM micrograph of crystalline structure of purified phosphogypsum ( $\times 300$ ) (10)



**Fig. 5.** SEM micrograph of crystalline structure of phosphogypsum precipitate (×500)

The SEM micrographs of the natural gypsum and phosphogypsum show that these two kinds of gypsum, regardless of having the same chemical formulas, have different structures: the natural gypsum has a less distinct crystalline structure, and phosphogypsum has a well-defined crystalline structure with the majority of rhombic and hexagonal shape crystals. This indicates that it has a more complex composition than natural gypsum, which is in accordance with literature data (6,11,12). The photographs shows that, after phosphogypsum grinding, crystal phase is still dominant, because of the presence of various product mode during the production process, e.g.  $P_2O_5$  syncrist. All the complexity of phosphogypsum originates from its crystal structure, which eventually influences its chemical behaviour.

Thermogravimetric analyses of phosphogypsum sample were performed in air stream with a heating rate of  $7^\circ\text{C}/\text{min}$ , and the obtained results presented at Fig. 6 show the change of sample mass in % in dependence of temperature. The mass loss for phosphogypsum is 17.53 wt.% (gypsum loses 2 molecule of water), that would corresponds to gypsum portion of 84 wt.% in sample. For natural gypsum, which is a hemihydrate ( $\text{CaSO}_4 \times 1/2\text{H}_2\text{O}$ ) the mass loss is 5.75 wt.% that would corresponds to a gypsum content of 93 wt.% (7).

X-ray diffraction analysis was carried out on a powder diffractometer and the identification of the crystal phases in the investigated samples has been performed by comparing the position and the intensity of the diffraction profiles with the JS PDS 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 natural gypsum,  $\text{CaHPO}_4$  (9–80) or  $\text{CaHPO}_4 \times 2\text{H}_2\text{O}$  (9–77) spectra also corresponded to natural gypsum.

The X-ray diffractograms for natural gypsum and phosphogypsum sample are presented in Figs. 7 and 8.

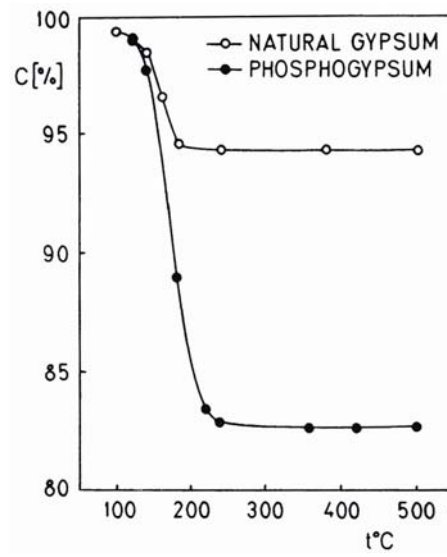


Fig. 6. Thermogravimetric analysis of gypsum samples

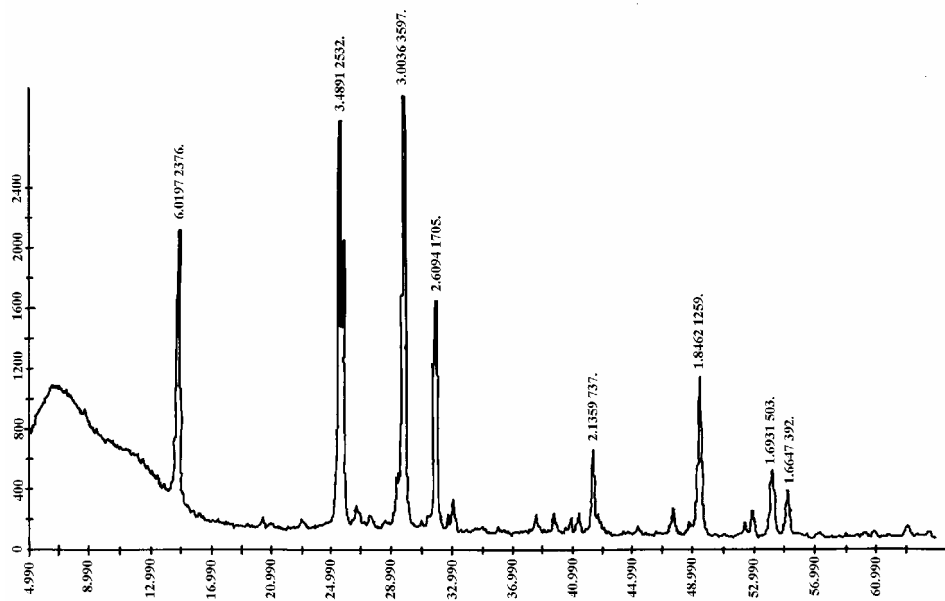
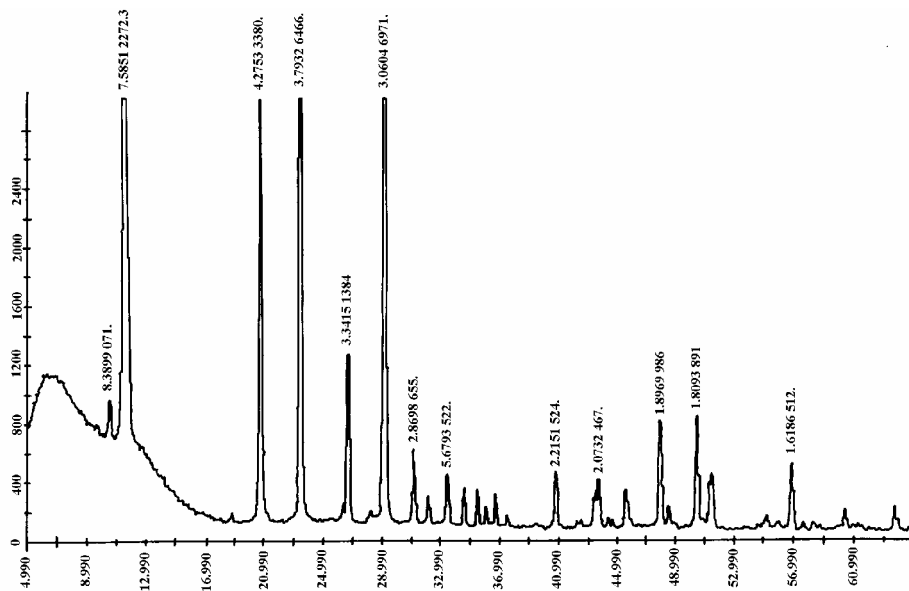


Fig. 7. Characteristic X-ray diffractogram of natural gypsum



**Fig. 8.** Characteristic X-ray diffractogram of phosphogypsum

The results of the investigation of phosphogypsum have been compared with the results obtained by the investigation of natural gypsum (2), whereby some similarities but also some differences have been observed in comparison with natural gypsum. The entire complexity of phosphogypsum is due to its crystalline structure and influences its chemical behavior.

## CONCLUSIONS

The advantage of SEM technique is that a sample need not be thin, which facilitates its preparation, and the energy of the electrons of the primary beam does not have to be high because the electrons need not pass through the sample.

SEM photographs of natural gypsum and phosphogypsum show that these two materials, regardless of having the same chemical composition, have different structures: natural gypsum has poorly expressed crystalline structure and phosphogypsum has a marked crystal structure, mostly of rhombic and hexagonal forms, which indicates its more complex composition than that of natural gypsum.

The application of the SEM method to samples of gypsum and phosphogypsum, as well the obtained SEM micrographs show that this technique is a powerful tool both for studying the morphological changes of the surface and for determining quantitative composition of such samples.



## ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the Ministry for Science, Technology and Development of Serbia (Project 1941).

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## ИСПИТИВАЊЕ ПОВРШИНСКИХ КАРАКТЕРИСТИКА ФОСФОГИПСА ПРИМЕНОМ СКЕНИРАЈУЋЕ ЕЛЕКТРОНСКЕ МИКРОСКОПИЈЕ (SEM)

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Елементарни састав материје, било да је непознат или да је потребно проверити састав новог или познатог материјала који ће се користити у даљем раду, представља чест захтев у савременој аналитичкој пракси. Некада се овим захтевима придружује и потреба да се утврди морфологија или структура површинске храпавости узорка, његова хомогеност или присуство дефеката у структури. Електронске микроскопске и спектроскопске технике, чији је нагли развој, све до комерцијалних система, од седамдесетих година до сада, омогућен пре свега достигнућима у електронским и компјутерским технологијама, постале су снажно оруђе за остваривање поменутих захтева.

У раду су приказани резултати примене скенирајуће електронске микроскопије (SEM) на испитивања површине узорака природног гипса и фосфогипса, ради карактеризације састава и дефинисања морфолошког састава.

SEM снимци природног гипса и отпадног фосфогипса указали су 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 отпадни фосфогипс има изразиту кристалну структуру, претежно ромбичног и хексагоналног облика, што указује на његов сложенији састав од природног, а што је у складу са литературним подацима.

Received 26 May 2003  
Accepted 24 September 2003