



Characterisation of Purified Gypsum and Insoluble Impurities Obtained from Phosphogypsum Waste

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Abstract

In this study, the chemical and phase composition of two samples of phosphogypsum from the waste dumps of the Industry of Chemical Products “Elixir – Prahovo” (Serbia) were examined, as well as the possibility of recrystallization of gypsum from an aqueous suspension of phosphogypsum. The negative effect of higher temperatures on the solubility of calcium sulfate (13.08 mmol/dm^3 at 95°C vs. 15.43 mmol/dm^3 at 40°C) was utilized. In several repeated cycles, calcium sulfate component was progressively dissolved in water at room temperature and then precipitated at 100°C , using the same liquid phase throughout the experiment. Therefore, phosphogypsum was separated into recrystallized (purified) gypsum, insoluble residue and supernatant, and the mass balance for the experiment was calculated. Elemental, XRD and SEM-EDS analyses were performed on raw phosphogypsum, purified gypsum and insoluble residue. The whiteness of raw phosphogypsum and purified gypsum were determined and compared. The main objective of the study was to investigate the nature of insoluble impurities, in order to define and optimize the methods for their removal during a potential industrial processing of phosphogypsum.

Keywords: phosphogypsum, recrystallization, purified gypsum, insoluble impurities

Introduction

Phosphogypsum (PG) is a by-product of the production of phosphoric acid, during sulfuric acid digestion of phosphate rock. Currently, the annual PG production worldwide is about 160 million tons, of which 50 million tons are produced in China and 40 million tons in USA, according to the International Atomic Energy Agency (IAEA, 2013). It consists of hydrated calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and impurities such as P_2O_5 , fluorides, organic substances, and alkali metals (Hua et al., 2016; Walawalkar et al., 2016). A significant quantity of toxic and harmful elements (including U, Ra and Th) are transferred from phosphate rock into the phosphogypsum, thus limiting its commercial use (López et al., 2016).

Agriculture and road construction are areas where PG can be applied effectively and a large quantity of this material can be consumed; however, there is still a lack of information about the potential release of metals and radionuclides during the life time of certain applications (Cánovas et al., 2018). PG is also increasingly used by the cement industry and other building material manufactures (Hua et al., 2016).

The Industry of Chemical Products “Elixir – Prahovo” was founded in 1960, producing the superphosphates as a part of the Mining and Smelting Basin of Bor (Serbia). The production of phosphoric acid is achieved by dihydrate process, i.e. raw phosphates are dissolved by sulfuric acid, producing calcium sulfate dihydrate as a by-product. Phosphoric acid produced in “Elixir – Prahovo” is used for the production of NPK fertilizers in Prahovo and mineral fertilizers in Šabac, Serbia (<http://www.elixirprahovo.rs/en/node/142>).

Calcium sulfate and its hydrated species show the highest solubility between 30 and 50°C , with noticeable decrease both towards lower and towards higher temperatures. The negative effect of higher temperatures on the solubility of calcium sulfate is a general cause of the formation of gypsum scales in the industrial processes (Amjad, 1988). In this study, the difference in gypsum solubility at 25°C (15.19 mmol/dm^3) and 100°C (11.97 mmol/dm^3 ; Cohen, 1989) was utilized as a driving mechanism for a recrystallization process. Using this laboratory method, it was possible to extract purified gypsum and also to isolate insoluble impurities from PG, which allowed their characterization. This could further help to select and optimize appropriate methods for their removal, during a potential industrial processing of PG.

Materials and methods

Raw phosphogypsum samples were obtained from the waste dumps of the Industry of Chemical Products “Elixir – Prahovo” (Serbia). The samples were dried at 50°C during a period of 48 h, homogenized and several probes of 10 g were taken. The first probe was used for ICP-OES, XRD and SEM-EDS characterization, the second one for whiteness measurement and the third for a recrystallization experiment. For that experiment, a 10g probe was mixed with 2 L of distilled water in a beaker. Using a magnetic stirrer, the mixture was stirred during 2h at 40°C and subsequently filtered through a filter-paper. Then the filtrate was heated in another beaker at 95°C , stirred using a magnetic stirrer during 1 h and allowed to settle for 7 h at the same temperature, allowing excess calcium sulfate to crystallize. Recrystallized gypsum was

Tab. 1. SEM-EDS elemental analysis of investigated samples [1 – Calculated by stoichiometry; 2 – Below detection limit; 3 – Quantitative results normalized to 100%]

Tab. 1. Analiza elementarna SEM-EDS badanych próbek [1 – Obliczone stechiometrycznie; 2 – Poniżej granicy wykrywalności; 3 – Wyniki ilościowe normalizowane do 100%]

Sample name	PG1	PG2	PG1R	PG2R	PG1P	PG2P
Sample description	Raw phosphogypsum, sample 1	Raw phosphogypsum, sample 2	Residue from sample 1	Residue from sample 2	Recrystallized gypsum from sample 1	Recrystallized gypsum from sample 2
Elements	wt. %					
O ¹	47.07	46.99	51.65	50.05	46.69	46.98
F	BDL ²	BDL	0.56	1.68	BDL	BDL
Na	BDL	BDL	0.08	0.11	BDL	BDL
Mg	BDL	BDL	0.03	0.07	BDL	BDL
Al	0.26	0.25	0.77	1.33	0.30	0.12
Si	2.23	2.25	41.19	39.35	0.06	BDL
P	0.34	0.31	0.65	1.02	0.14	0.09
S	21.77	21.67	1.15	0.42	22.86	23.40
K	BDL	BDL	0.07	0.08	BDL	BDL
Ca	28.13	28.37	2.13	2.18	29.95	29.43
Ti	BDL	BDL	0.22	0.29	BDL	BDL
Fe	0.15	0.16	1.34	2.97	BDL	BDL
Sr	0.04	BDL	BDL	0.13	BDL	BDL
Ba	BDL	BDL	0.15	0.31	BDL	BDL
Total	100.00 ³	100.00	100.00	100.00	100.00	100.00

Tab. 2. ICP-OES elemental analysis of raw phosphogypsum and recrystallized gypsum

Tab. 2. Analiza elementarna ICP-OES surowego fosfogipsu i rekrytalizowanego gipsu

Elements	Units	Sample name	
		PG1	PG1P
Na	ppm	94.54	14.52
Mg	ppm	18.70	0.24
Al	ppm	260.05	12.55
Si	ppm	3529	74.63
P	ppm	2904.80	2426.13
S	wt. %	18.687	20.295
K	ppm	67.44	22.51
Ca	wt. %	25.049	27.508
Ti	ppm	121.44	36.96
Fe	ppm	605.15	24.24
Sr	ppm	412.99	374.42
Ba	ppm	94.81	6.45

filtered and washed with boiling distilled water. Supernatant liquid was mixed with the rest of PG from the first part of the experiment and this cycle was repeated several times, until the PG was reduced to an insoluble residue. In this manner, phosphogypsum was separated into recrystallized gypsum, insoluble residue and supernatant.

Scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS analysis) was performed using a JEOL JSM-IT300 scanning electron microscope, coupled to an Oxford Instruments XMax 50 mm² SDD energy-dispersive spectrometer, in high vacuum mode, at accelerating voltage

of 20 kV and probe current of approximately 0.1 nA. SEM images were acquired on gold-coated samples, using magnification of 200×, while EDS elemental analyses were conducted on carbon-coated samples, using low magnification (50×) in order to avoid variations in chemical composition. SEM-EDS analysis was performed on raw phosphogypsum, recrystallized gypsum and insoluble residue.

The elemental composition of a raw phosphogypsum and a recrystallized gypsum was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Thermo Scientific iCAP 6500 Duo ICP-OES spectrometer

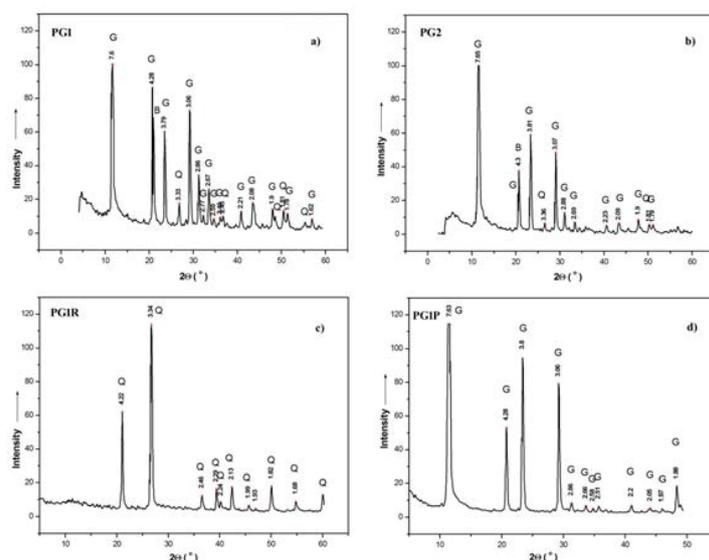


Fig. 1. XRD patterns of raw phosphogypsum (a, b), insoluble residue (c) and recrystallized gypsum (d). G – gypsum, B – brushite, Q – quartz
 Rys. 1. Wzory XRD surowego fosfogipsu (a, b), nierozpuszczalnej pozostałości (c) i rekrytalizowanego gipsu (d). G – gips, B – kruchy, Q – kwarc

(Thermo Fisher Scientific, Cambridge, UK), equipped with a RACID86 Charge Injector Device (CID) detector. The detection limit for the elements analyzed was ~0.1 mg/L. The digestion was performed on an Advanced Microwave Digestion System (ETHOS 1, Milestone, Italy) using HPR-1000/10S high pressure segmented rotor.

X-ray diffraction (XRD) analysis was conducted using a Philips PW 1710 automated diffractometer. X-ray patterns were collected on powdered samples using CuK α radiation ($\lambda = 1.54184 \text{ \AA}$), with tube current of 30 mA and voltage of 40 kV. 2θ angles ranged from 4 to 60°, with a step of 1°/min.

The whiteness index values of a raw phosphogypsum and recrystallized gypsum were obtained from the diffuse reflectance spectra, using a Thorlabs CCS200 spectrometer with R45/45 geometry, in the region between 400 and 700 nm, according to the CIE (1932) method. The white standard was BaS and the light source was illuminant C. The whiteness was determined from the luminous reflectance, as described by Milošević and Logar (2017).

Results and discussion

Elemental EDS analysis, as well as a short description of the investigated samples, are given in Table 1. The samples of raw PG are dominated by Ca, S and O, as expected for calcium sulfate-based material. The major impurity is represented by Si, followed by small amounts of P, Al, Fe and Sr, which is typical for PG material from different deposits in the world (Jalali et al. 2016; Kandil et al. 2017; Zhou et al. 2016). Recrystallized samples present a purer form of calcium sulfate, with only small amounts of Al, Si and P. On the other hand, insoluble residue is a silicon-oxide based material relatively enriched in Fe, F, Al, P, Ti, Ba, Sr, Na, K and Mg, as well as essentially depleted in Ca and S.

A more precise elemental analysis was performed for PG1 and PG1P samples using ICP-OES

(Table 2). ICP-OES and SEM-EDS analyses are in general accordance, showing an enrichment of Ca and S and a drastic depletion of Si and Fe after the recrystallization.

The XRD patterns of the investigated samples are dis-

played in Figure 1. The most abundant minerals in PG1 and PG2 samples are gypsum, brushite and quartz (Figs. 1a, b; identified according to Михеев, 1957). These phases have routinely been identified in PG by various researchers (e.g. Jalali et al., 2016; Roode and Strydom, 1990; Tian et al., 2016). The XRD pattern of PG1P is typical for pure gypsum (Fig. 1d). On the other hand, insoluble residue shows only the reflections of quartz (Fig. 1c). By means of XRD analysis, it was not possible to confirm the presence of other crystalline phases, which is in accordance with a low abundance of impurities, obtained by SEM-EDS and ICP-OES elemental analyses.

The mass balance of the recrystallization experiment for PG1 sample is given as follows: the yield of purified gypsum was 90.50%, leaving 4.29% of insoluble residue and 5.21% of original mass in the supernatant. These values are in accordance with elemental composition obtained by elemental analysis, i.e. with stoichiometrically calculated contents of calcium sulfate and insoluble oxides.

SEM image analysis revealed a significant increase in gypsum crystal size after the recrystallization (Fig. 2). Moreover, z/x axis ratio increased from 1–3 (PG1 sample) and 1–1.5 (PG2 sample) to >5 for recrystallized samples, producing long bladed crystals. A similar result was obtained by Sun et al. (2016), who synthesized calcium sulfate whisker from flue gas desulfurization gypsum using atmospheric acidification method. Insoluble residue is chiefly composed of coarse quartz particles: primary massive grains and secondary agglomerates, most probably resulting from an acid attack on primary silicates.

A value of the whiteness index (WI) changes from 52.5% for raw phosphogypsum PG1 to 80.5% for recrystallized gypsum PG1P (namely, the WI of 100% corresponds to a pure white color). A relatively low WI value of PG1 is caused by the significant content of iron (in the form of iron-oxide or iron-bearing minerals) that tends to produce brown to orange color. An increase of the value of WI after the recrystallization is in accordance with significantly lower content of iron in purified gypsum, as ICP-OES and SEM-EDS analyses confirmed.

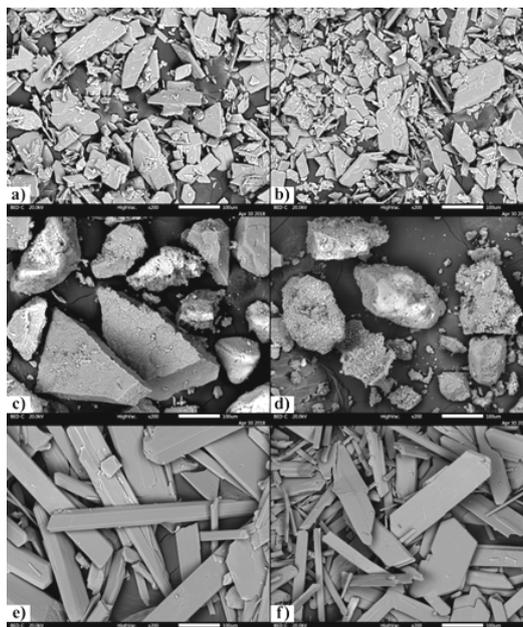


Fig. 2. SEM images of raw phosphogypsum (a, b), insoluble residue (c, d) and recrystallized gypsum (e, f). Magnification 200×, micron bar length 100 μm

Rys. 2. Obrazy SEM surowego fosfogipsu (a, b), nierozpuszczalnej pozostałości (c, d) i rekrytalizowanego gipsu (e, f). Powiększenie 200 ×, długość skali 100 μm

Conclusion

The samples of raw phosphogypsum are dominated by Ca and S, in the form of calcium sulfate dihydrate, i.e. gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The major impurity is represented by Si in the form of quartz. Relatively low value of the whiteness index (52.5%) is caused by the significant content of iron, which produces light brown to light orange color.

The yield of recrystallized gypsum is slightly higher than 90 wt. %. It is composed of very pure calcium sulfate dihy-

drate, containing only small amounts of phosphorus. Gypsum crystal size significantly increased after the recrystallization process, forming long bladed crystals. The whiteness index reached a value of 80.5%, thus promoting a potential use of recrystallized gypsum in the civil engineering. Insoluble phosphogypsum residue is composed mainly of quartz and it is relatively enriched in impurities that originate from the raw phosphogypsum (e.g. Fe, F, Al and P).

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Charakterystyka oczyszczonego gipsu i nierozpuszczalnych zanieczyszczeń uzyskanych z odpadów fosfogipsu

W artykule przedstawiono skład chemiczny i fazowy dwóch próbek fosfogipsu ze składowisk odpadów Przemysłu Chemicznego „Elixir – Prahovo” (Serbia), a także możliwość rekrytalizacji gipsu z zawiesiny wodnej fosfogipsu. Wykorzystano negatywny wpływ wyższych temperatur na rozpuszczalność siarczanu wapnia ($13,08 \text{ mmol/dm}^3$ w 95°C wobec $15,43 \text{ mmol/dm}^3$ w 40°C). W kilku powtarzających się cyklach siarczanu wapnia stopniowo rozpuszczano w wodzie w temperaturze pokojowej, a następnie wytrącano w 100°C , stosując tę samą fazę ciekłą w całym doświadczeniu. W ten sposób fosfogips został rozdzielony na rekrytalizowany (oczyszczony) gips, nierozpuszczalną pozostałość i supernatant, kolejno obliczono bilans masy dla doświadczenia. Analizy elementarne, XRD i SEM-EDS przeprowadzono na surowym fosfogipsie, oczyszczonym gipsie i nierozpuszczalnej pozostałości. Określono i porównano biel surowego i oczyszczonego gipsu. Głównym celem pracy było zbadanie natury nierozpuszczalnych zanieczyszczeń w celu określenia i zoptymalizowania metod ich usuwania podczas przemysłowego przetwarzania fosfogipsu.

Słowa kluczowe: fosfogips, rekrytalizacja, oczyszczony gips, zanieczyszczenia nierozpuszczalne