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Chemical and radiochemical characterization of phosphogypsum from Poland

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Abstract. The current study presents the results of the chemical and the radiochemical characterization of phosphogypsum obtained from the former Wizów Chemical Plant in Poland. Phosphogypsum is a residue obtained from phosphoric acid production. Phosphogypsum mainly contains calcium sulfate dihydrate and impurities originating from the source phosphate rock, including toxic trace elements and natural radionuclides. The phosphogypsum stacks occupy a large area and are an environmental issue today. The project "Phosphogypsum Processing to Critical Raw Materials", currently realized at the Institute of Nuclear Chemistry and Technology, focuses on the use of phosphogypsum from the Polish stacks as material to recover rare earth elements (REEs). The remaining gypsum matrix can be used as an inexpensive material in construction. The chemical and radiological characterization of the radioactive isotopes present in phosphogypsum was performed by using inductively coupled plasma mass spectrometry (ICP-MS) and the gamma spectrometry technique. The radioactivity of the Polish phosphogypsum was then compared with the radioactivity of the phosphogypsum waste present worldwide.

Keywords: Gamma spectrometry • Phosphogypsum • Radionuclides analysis • REEs

Introduction

Over 75% of the global phosphate fertilizers is produced using phosphoric acid as an intermediate, which is produced via the wet-phosphoric acid process, generating 4–5 tons of the byproduct phosphogypsum per ton of the phosphoric acid Eq. (1) [1]. The amount of phosphogypsum produced worldwide is estimated at about 100–280 million tons per year. In Poland alone, 2–3 million tons of phosphogypsum are produced annually [2].

$$(1)\quad \left[Ca_3(PO_4)_2\right]_3 CaF_2 + 10H_2SO_4 + 20H_2O \longrightarrow 6H_3PO_4 + 10(CaSO_4 * 2H_2O) + 2HF$$

Phosphogypsum contains approximately 96% of calcium sulfate dihydrate ($CaSO_4 \times 2H_2O$) [3, 4], various impurities such as phosphates, sulfates, fluorides, heavy metals, and trace elements such as lead, arsenic, cadmium, zinc, chromium, copper, and antimony [5]. The impurities content varies widely, influenced by phosphate rock origin and production-process factors. Phosphate rocks also contain radioactive elements (mainly uranium and thorium), which partially remain in the phosphogypsum as a result of the "wet process". The purification is challenging and expensive due to the chemical similarities of radium, often occurring

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in this material, with calcium [6]. The concentration of the radionuclides present usually exceeds that of the natural background. As a result, phosphogypsum can be classified as a technologically enhanced naturally occurring radioactive material (TENORM) [3].

Phosphogypsum, typically stored in expansive open heaps, poses environmental threats such as water, land, and atmospheric pollution. Nevertheless, with proper management, it does not need to be classified as waste. Ongoing efforts aim to repurpose phosphogypsum for applications such as construction materials, agricultural soil amendments, and industrial processes, minimizing its environmental impact [4, 7]. Phosphogypsum can possess the potential to be an important source of rare earth elements (REEs) and be a viable alternative of flue gas desulfurization (FGD) gypsum [8]. The radioactivity of phosphogypsum is usually relatively low, and it meets most national regulations to be used as a building material [4].

To comprehensively grasp the radiological and chemical attributes of phosphogypsum, a diverse array of analytical methods is essential, e.g., gamma and alpha spectrometry techniques for radioisotopes and mass spectrometry for other elements. Polish phosphogypsum from the former Chemical Wizów Plant is notable for its low radioactivity, because it predominantly originates from the processing of Kola Peninsula apatite [9, 10]. Apatite belongs to igneous phosphates, which are characterized not only by a very low content of radioactive elements, but also by a higher concentration of REEs (approximately 1%) than sedimentary phosphate rocks.

The main objective of this work is the examination of the chemical and radiochemical characterization of Wizów phosphogypsum stacks and the assessment of their potential as an important source of REEs and a viable alternative of gypsum. The consortium of Institute of Nuclear Chemistry and Technology with partners from Europe and Morocco is actively implementing the "Phosphogypsum Processing to Critical Raw Materials" project under ERA-MIN3. This project aims to develop innovative technologies for processing phosphogypsum stacks, leveraging its richness in REEs to meet the growing demand in the European high-tech industry, while simultaneously repurposing the gypsum matrix for cost-effective construction materials, aligning with EU's critical raw materials list [11]. The stacks of the former Wizów Chemical Plant contain 5–12 million tons of phosphogypsum from the processing of apatite from the Kola Peninsula. It is suspected that there are 6000–10 000 tons of REEs in the Wizów phosphogypsum stacks.

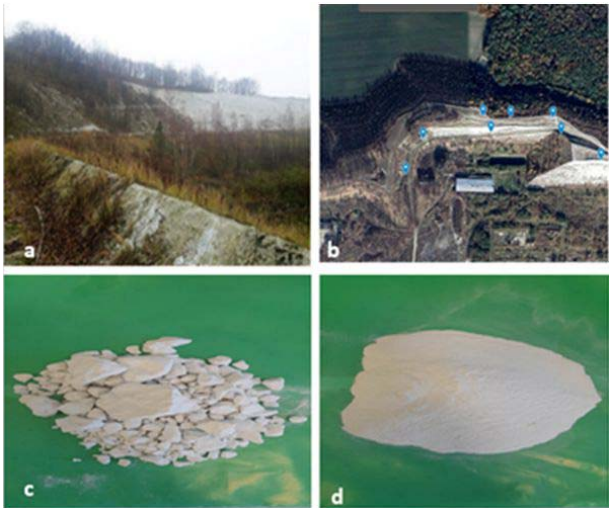


Fig. 1. (a) Phosphogypsum waste stack of the former Wizów Chemical Plant in Poland. (b) Phosphogypsum sampling points. (c) Raw sample of phosphogypsum. (d) Dried phosphogypsum.

Materials and methods

Ten representative samples of phosphogypsum were collected from various locations within all the three Wizów's stacks (Figs. 1a and 1b). Phosphogypsum is characterized by its off-white color, dampness, and a powdery or granular texture as shown in Figs. 1c and 1d. Additionally, it contains 50–75% of particles finer than 0.08 mm and maintains a moisture content of approximately 11%.

The studied samples were grounded to a grain size ≤200 μm, homogenized thereafter, oven dried at 65°C for 5 h, and analyzed as shown in Fig. 2.

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed using the Perkin-Elmer ELAN DRC II mass spectrometer with specific components and operational settings, including radio frequency power, lens voltage, dual detector mode, and argon flow rates. An indium internal standard was applied at a concentration of 5 ng/ml.

Prior to the ICP-MS analysis, mineralization is necessary (procedure: step 1: 120 mg of sample, 6 ml conc. HNO_3 + 2 ml conc. HF, 240°C, time 2 h;

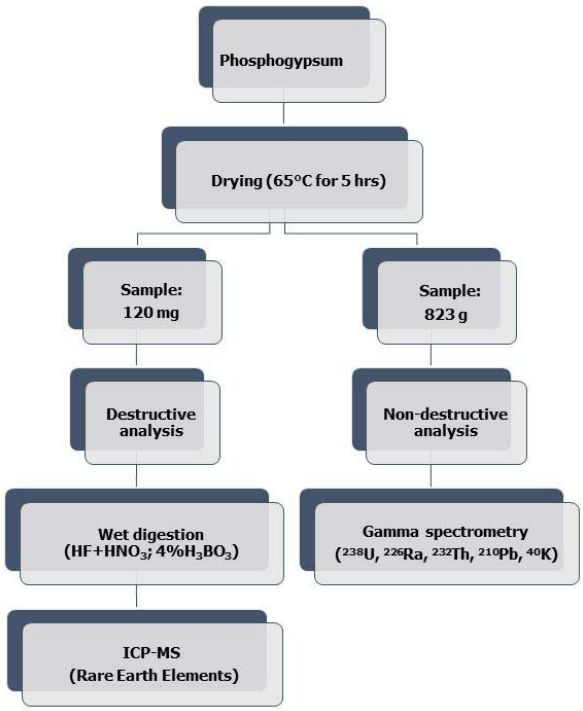


Fig. 2. Illustration of phosphogypsum sample laboratory preparation steps for analysis.

step 2: excess of fluoride complexing with 12 ml of 4% H_3BO_3, 200°C, time 80 min).

High purity germanium (HPGe) radiation detectors were used to measure the radioactivity in the samples (for the radionuclides determined after two months of equilibrium establishment). Efficiency was calibrated with standard sources and the background was subtracted. The method ensured accuracy and minimized self-absorption effects. The concentrations of ^{235}U, ^{226}Ra, ^{232}Th, and ^{40}K in the samples were determined using a slightly modified standard method in sample-preparation techniques and data analysis. The EFFTRAN algorithms for enhanced background subtraction and peak identification in the spectral analysis were used. The results were referred to a certified reference material (IAEA-443). Samples ranged from 800 g to 850 g, with a measurement time of 250 000 s. The measurements were repeated two times to confirm the correctness of the obtained results.

Results and discussion

Chemical characterization

Ten samples were collected from three stacks in Wizów. The results of the chemical analysis of the metal samples are presented in Table 1, which reveal notably high levels of cerium (2234 mg/kg) and lanthanum (1545 mg/kg), indicating the presence of significant quantities of these REEs in the phosphogypsum. Additionally, other elements such as iron (1124 mg/kg), neodymium (752.5 mg/kg), gadolinium (128.6 mg/kg), and copper (21.69 mg/kg) were found in significant amounts. In contrast, certain elements like thallium (0.02 mg/kg) and uranium (0.72 mg/kg) were detected in trace quantities.

Radiological characterization

The radionuclides present in Wizów's phosphogypsum sample were detected by gamma spectrometry. The results are presented in Table 2.

The gamma spectrometry results for the Wizów's phosphogypsum sample showed the presence of various radionuclides with distinct energy levels and radiological impacts. The ^{214}Bi isotopes, with energies at 79.7, 609.3, 768.4, and 934.1 keV, collectively exhibit an activity of 1.33 ± 0.001 Bq/kg, underscoring their substantial radiological influence in precision radiometric measurements. The $A/A_{background}$ ratio of 2.5 highlights their significance in radiometric assessments. ^{214}Pb isotopes, spanning energies from 53.2 keV to 351.9 keV, show a combined activity of 2.13 ± 0.004 Bq/kg, emphasizing their considerable radiological impact, approximately 2.7 times the background. Additionally, ^{208}Tl exhibits a moderate activity of 1.25 ± 0.002 Bq/kg at 84.9 keV, with an $A/A_{background}$ ratio of 1.9, while ^{40}K, with an energy level of 1460.8 keV, has a modest activity of 0.132 ± 0.000 Bq/kg, with an $A/A_{background}$ ratio of 3, making

Table 1. The content of selected metals in Wizów's phosphogypsum

Elements	Concentration (mg/kg)	Elements	Concentration (mg/kg)
Antimony	0.12–0.15	Manganese	22.96–25.18
Arsenic	4.76–5.23	Molybdenum	2.14–2.36
Barium	476.3–522.5	**Neodymium**	685.9–752.5
Beryllium	0.27–0.31	Nickel	12.54–13.75
Cadmium	0.06–0.08	**Praseodymium**	200.5–220.0
Cerium	2036–2234	**Samarium**	97.4–106.8
Cobalt	3.35–3.69	Selenium	6.46–7.10
Copper	19.77–21.69	Silver	0.61–0.67
Dysprosium	41.92–45.97	**Terbium**	10.23–11.23
Erbium	15.45–16.95	Thallium	0.01–0.02
Europium	26.98–29.58	Thorium	9.92–10.88
Gadolinium	117.2–128.6	**Thulium**	1.21–1.32
Holmium	6.26–6.87	Uranium	0.67–0.72
Iron	1024–1124	Vanadium	12.27–13.46
Lanthanum	1408–1545	**Ytterbium**	5.46–5.99
Lead	3.36–3.72	Zinc	14.57–15.99
Lutetium	0.54–0.61		

Table 2. The content of radionuclides in phosphogypsum sample related to sea sand as natural background

Isotope	Energy (keV)	Combined activity ± uncertainty (Bq/kg)	$A/A_{background}$
^{214}Pb	53.2, 241.9, 258.8, 351.9	2.13 ± 0.004	2.7
^{214}Bi	79.7, 609.3, 768.4, 934.1	1.33 ± 0.001	2.5
^{208}Tl	84.9	1.25 ± 0.002	1.9
^{212}Pb	87.3, 115.2, 238.6	1.16 ± 0.004	2.1
^{235}U	89.95, 93.9, 109.2, 185.7	0.192 ± 0.011	1.48
^{228}Ac	99.5, 129.1, 129.1, 153.9, 199, 209.2	5.76 ± 0.068	1.8
^{40}K	1460.8	0.132 ± 0.001	3.0

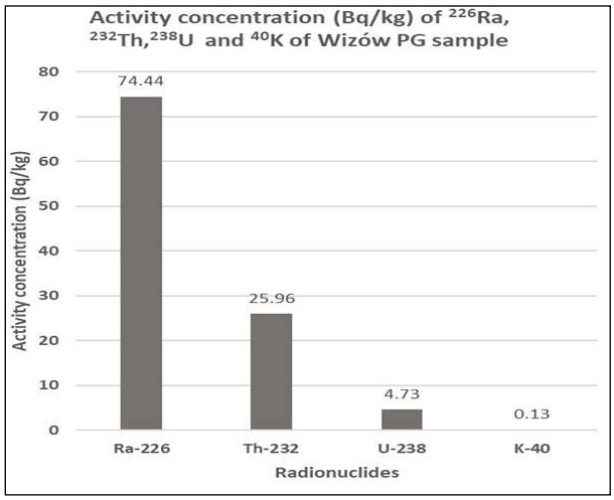


Fig. 3. Activity concentrations of ^{226}Ra, ^{232}Th, ^{238}U, and ^{40}K in Wizów's phosphogypsum sample.

it relevant in geophysical and geological investigations. Notably, self-absorption correction techniques were applied, enhancing the precision and reliability of radiometric measurements by addressing low-energy photo peaks of ^{210}Pb and ^{234}Th, dependent on the sample's composition and accomplished using EFFTRAN for efficiency correction.

In radiometric analysis, the presence of ^{214}Bi and ^{214}Pb isotopes with specific gamma energies signifies the influence of the uranium decay series, particularly the uranium-238 chain. Their high activities and $A/A_{background}$ ratios highlight the radiological importance of these isotopes. Notably, the average activity concentration of ^{226}Ra in phosphogypsum samples is approximately 74.44 Bq/kg, which is about three times higher than the activity concentration of ^{232}Th in Wizów's phosphogypsum samples, as depicted in Fig. 3. Additionally, the presence of ^{208}Tl, representing the thorium decay series, further underscores the role of the thorium-232 chain. Although not part of these series, ^{40}K significantly contributes to geophysical and geological investigations. This radiometric analysis clearly illustrates the coexistence and impact of the uranium and thorium decay series in the Wizów's phosphogypsum sample.

The activity concentration index (I) for phosphogypsum was derived from the activities of potassium-40, radium-226, and thorium-232 using Eq. (1) and it yielded a value of approximately 0.378. This result suggests that phosphogypsum can satisfy the safety requirements specified in the European Union Council Directive 2013/59/EURATOM for building materials [12]. The value of the indicator >1 means that the reference level may be exceeded for external exposure of people to gamma radiation emitted by building materials indoors amounting to 1 mSv/year. However, it is important to note that the indicator applies to the building material, not to its constituents.

$$I = C_{\mathrm{Ra}\,226} / 300\ \mathrm{Bq/kg} + \mathrm{C}_{\mathrm{Th}\,232} / 200\ \mathrm{Bq/kg} + \mathrm{C}_{\mathrm{K}\,40} / 3000\ \mathrm{Bq/kg} \quad (2)$$

where C_{Ra226}, C_{Th232}, and C_{K40} are the activity concentrations in Bq/kg of the corresponding radionuclides in the building material.

The radioactivity of phosphogypsum varies globally (Table 3) due to differing radioactive isotopes and concentrations. Egyptian and US (Florida) phosphogypsum share similar ^{226}Ra and ^{232}Th levels, whereas Greek phosphogypsum shows higher ^{226}Ra and ^{40}K content. Wizów's phosphogypsum exhibits elevated ^{226}Ra and ^{232}Th, but its overall radioactivity remains relatively low compared to most global phosphogypsum sources.

Conclusion

The combined analysis of Wizów's phosphogypsum using ICP-MS and gamma spectrometry has yielded valuable insights. ICP-MS revealed diverse elemental concentrations, including significant cerium and lanthanum levels (2036–2234 mg/kg and 1408–1545 mg/kg, respectively), indicative of REEs. Iron, with concentrations ranging from 1024 mg/kg to 1124 mg/kg, also played a substantial role in the sample's composition.

Gamma spectrometry analysis of Wizów's phosphogypsum highlights the coexistence and impact of the uranium and thorium decay series. Radionuclide concentrations are low and do not exceed three times the background radioactivity. These parameters

Table 3. Comparison of the radioactivity of phosphogypsum collected from the former Wizów Chemical Plant, Poland, to phosphogypsum from other countries

Country/Radioisotope	Activity concentration (Bq/kg)				
	^{226}Ra	^{232}Th	^{238}U	^{40}K	Reference
Spain	670	2	220	39	[13]
Egypt	459	40	140	2	[14]
USA (Florida)	1140	2	130	14	[15]
Tunisia	188	2	600	3	[16]
Serbia	600	3	–	47	[16]
Croatia	811	8	–	13	[16]
Czech Republic	115	31	–	95	[16]
Morocco	160	20	190	10	[17]
Togo	100	13	150	3	[16]
Greece	573	2.2	29	562.4	[18]
Worldwide range	162–5126	2.1–35.2	15–60	15–1410	[17, 18]
Poland, Wizów	77.44	25.96	4.73	0.13	Current study

make Wizów's phosphogypsum a promising substitute for gypsum, given its significant REE metal concentrations and low diversity in radionuclide concentrations across the three stacks, indicating its potential as a valuable REE reserve. The demand for REEs is continuously growing due to their high requirement in many applications. The studies will be continued in the frame of the ERAMIN project.

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