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Research on Temporal Leachability of Trace Elements from Opoka-Rocks in The Aspect of Geochemical Environmental Indicators

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Abstract. As part of the work on the trace element concentration in building materials and their leachability to the environment, the analyses of the temporal release of the trace elements group that could play a role as environmental chemical indicator were carried out. For a period of about half a year, in water eluates with different temporal fractions the leachability for: Sr, Ba, Mg, Mn, Zn were determined. Lumpy varieties of the opoka-rocks from the pre-industrial deposits and historical buildings were the material subjected to the analyses. The research methodology covered studies using broad analytics. The phase methods were used in order to uniquely identify the crystalline components of the studied rocks. Mineralogical and petrographic investigations were performed using Olympus BX-51 polarizing microscope and (SEM) FEI Quanta 200FEG electron microscope equipped with an X-ray spectrometer (EDX Genesis) and a backscattered electron detector (BSE). The concentration of these trace elements in water eluates in 8 temporal fractions was carried out in accordance with EA NEN 7375: 2004 and PN-EN ISO 11885 standards using the ICP sequential plasma spectrometer. It was found that the series of leachability of the studied elements in decreasing succession is as follows: Mg> Sr> Zn> Ba> Mn. The highest leachability from the selected elements was found for Mg, which ranged from 0.22 to 1.14 ppm

1. Introduction

The carried out environmental analyses in the current research work in the eastern belt of the EU have allowed to observe areas with a significant concentration of trace elements in soils neighboring around building material production plants. This phenomenon mainly concerned the concentration of strontium [1,2]. Strontium belongs to the trace elements listed in the group of potential standard chemical markers of building materials. According to European data, among others CEMBUREAU [3], besides strontium, they also include Ba, Mn, Mg, Zr, Ti, V and Zn [4,5].

The purpose of the research was to determine the quantitative and qualitative concentration of Sr, Mn, Zn, Mg and Ba in a stone material (opoka-rock), both of pre-industrial origin as well as subjected to the environmental impact factor. In addition, the concentration of these elements was determined in water eluates in eight fractions determined at specific time intervals to take into account the level of emissivity of the studied elements to the environment. Chemical analyses have been carried out for a group of elements considered as standard chemical markers, those that can be identified and measured -quantitatively or qualitatively by analytical methods. Each of the analyzed rock materials was also subjected to basic mineralogical and petrographic analyses in order to obtain an accurate information about the nature of the studied rocks. From the geochemical results, an attempt was made to determine the contamination index for the tested materials.

2. The material used in the research

The research material was represented by opoka- rocks, sedimentary rocks and transitional rocks between carbonate and siliceous rocks. Depending on the percentage ratio between silica and carbonaceous minerals, we can distinguish heavy opoka-rocks, light opoka-rocks and silicate opok-rocks [6,7]. The presence of the opoka-rocks is common in marine series of Mesozoic age, especially Upper Cretaceous. They form interbeddings with marls and limestones. Within the EU area, the opoka-rocks occur in all Upper Cretaceous stages. Outside Poland, we meet them in the Czech Republic, Slovakia, Lithuania, France, Germany and England. In Germany, the opoka-rocks can be found in Saxony in the region of Dresden and in Westphalia. Their age is estimated at Cenomanian and Turonian. In Lithuania, this stone was exploited in the Stoniškiai mining district. In the Czech Republic, rich deposits of the opoka- rocks extend from Kadań, east of Prague and end in the region of Moravia. These rocks are also common in Russia among the lower Neogene sediments in the Volga basin, on the eastern slopes of the Urals, in Upper Cretaceous formations of the Eastern European part of Russia, to the chalk deposits of the Paris Basin [8]. In Poland, their occurrence is common in the vast areas of the Lublin Upland, in the Mogilno-Łódź Basin and the Nidzica Basin. They include a lithostratigraphic profile from Turonian to Maastrichtian. The opoka-rocks can be used as a construction stone. This raw material was used already from the Paleolithic through the Middle Ages and until today it is an important rock raw material. Its largest use falls on the period from the sixteenth to the nineteenth century. Castles, churches, fences, roadside shrines were erected from white stone.

The material used in the research was represented by two groups of the opoka-rocks. The first group were sediments from pre-industrial period collected from the drilling cores. These opoka-rocks represent a material matrix with an original, uncontaminated composition. Researched in them element concentration can be considered as natural. The analyzed drilling cores came from the central region of Poland and samples for the tests were taken from a depth of 180 m below ground level. The age of the opoka-rocks was determined for the period of the Upper Cretaceous. In total, 50 samples of pre-industrial material were tested. The second group of the rocks were opoka- rocks subjected in a natural way to the influence of various environmental factors. The material came from a demolished nineteenth century residential house in the area of Kazimierz Dolny, (central-eastern Poland). The rock material is also attributed to the period of the Maastrichtian. Ten samples were taken and tested from the residential building.

3. Research methodology

Mineralogical tests to determine the phase composition of the tested materials were carried out with the use of:

- digital microscope Hirox - RH - 2000-EN,

- polarizing microscope Olympus BX-51,
- electron microscope (SEM) FEI Quanta 200FEG equipped with an X-ray spectrometer (EDX Genesis) and backscattered electron detector (BSE).

The chemical concentrations of Sr, Mn, Mg, Ba, Zn in materials and water eluates were carried out in accordance with the valid standards (EA NEN 7375: 2004, PN-EN ISO 11885) [9,10], using the sequential plasma-emission spectrometer ICP Ultima 2 Horiba Jobin Yvon.
The assessment of the impact of anthropogenic factors in environmental samples was carried out using different geochemical criteria. The paper attempts to determine whether the material originating from a demolished residential building could be negatively influenced by the environment over time. To do this, it was tried to apply the pollution factor. This ratio is determined by determining the ratio between the average concentration of a given element in the samples, divided by the pre-industrial concentration of the element [11]:
• Coefficient of contamination, CF (contamination factor) (1):

$$\text{CF} = \frac{Ca}{C_i} \quad (1)$$

C_a - The average concentration of the element in samples taken from at least 5 test sites
C_i - concentration of the element from the pre-industrial period (mg / kg of dry matter)

Table 1. The classifications according to CF [11]

Contamination Factor	Classification
CF<1	Low
1≤CF<3	Moderate
3≤CF<6	Considerable
CF≥6	Very high

4. Results

The studied opoka-rock has a highly porous texture. The voids and pores of the rock surface show both an oval shape and a spindle-like shape (photo 1). In the microscope image there is visible a micrite-organogenic or micrite-detritus structure in these rocks. The rock background is made up by a carbonate substance, created in the form of a micrite and silica represented by a opal. The detritic material is represented by numerous archaeological remnants, represented by the shells of foraminifers, fragments of molluscs and echinoderms. Locally, there are met sponge needles, made of chalcedony or opal. In the studied opoka-rocks there is observed in organic debris, symptoms of the processes of replacing carbonate minerals by chalcedony. In the rock background, besides bioclasts, the presence of quartz grains from sharp-edged forms to well-rounded with a variable size from the aleurite to the pelite fraction was found. Furthermore in the microscopic image it was possible to observe numerous grains of glauconite and sporadic relicts of hydro muscovite (photo 2).
In the carried out chemical analyses, among the marked elements: Sr, Ba, Zn, Mn and Mg in the collected material, the highest values were reached by magnesium. Its average maximum concentration in the material from historical cores is 3.5 %wt., while in the building material it is 2.18 %wt. These values do not exceed the values reported in the literature, in the carbonate rocks, the concentration of magnesium reaches 4.7 %wt. [12]. The slightly lower result achieved than for limestones is undoubtedly related to the mineral character of the opoka- rocks.

Figure 1. Opoka-rock - Porous texture -Digital microscopy (Photo. A. Pękala)

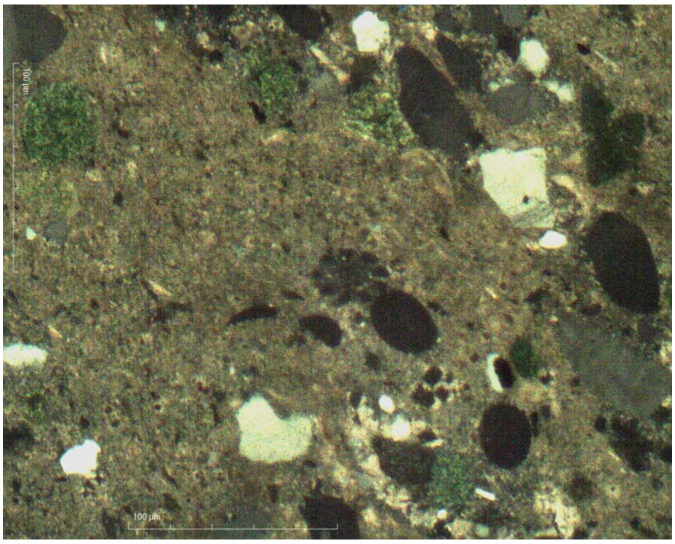

Figure 2. Opoka rocks - Detritus material in a silica - carbonate rock background. (Photo A.Pękala)

The presence of silica in them affected reducing of the magnesium content. The next of the analyzed elements, strontium reached the maximum average value of 293 mg / kg, while in the construction object the value is about 160 mg / kg. The average maximum concentration for barium is 153 mg / kg in the historical material and 120 mg / kg in the building material. The opposite situation was observed in the case of zinc. This element achieved higher values in the material coming from the building, subjected to the influence of the natural environment. The concentration of zinc in the construction material exceeded almost twice (16 mg / kg) in relation to the concentration in the historical material of 8.53 mg / kg. The concentration of manganese was very similar in both of the analyzed cases table 2.The average values of the calculated pollutant index indicate the average accumulation of Zn in the building material (table.2). In the case of these elements, the index was 2.1 for zinc.

Table.2. Concentration of trace elements in the opoka- rocks [own research]

Trace elements			a	b	c
Mg [% wag]		C_i	4.40	1.7	3.50
		C_a	2.25	1.5	2.18
Sr	**[mg/kg]**	C_i	396	223	293
		C_a	267	30	160.4
Ba		C_i	314	38	153
		C_a	200	40	120
Zn		C_i	9.05	7.99	8.53
		C_a	20.0	10	16
Mn		C_i	222	70	125
		Ca	130	55	120

*/ Explanations: Ci-concentration from the pre-industrial period, Ca-current concentration, a- maximum, b- minimum, c – average.

The carried out tests of the leachability of elements from the opoka-rocks showed that the highest concentrations were recorded for Mg, the maximum value of leachability after 216 h was 1.14 mg / l. After 1536h the concentration of this element decreases gradually reaching the value of 0.84 mg / l in the last attempt. Subsequent leachability studies of magnesium showed a downward trend (figure 3).

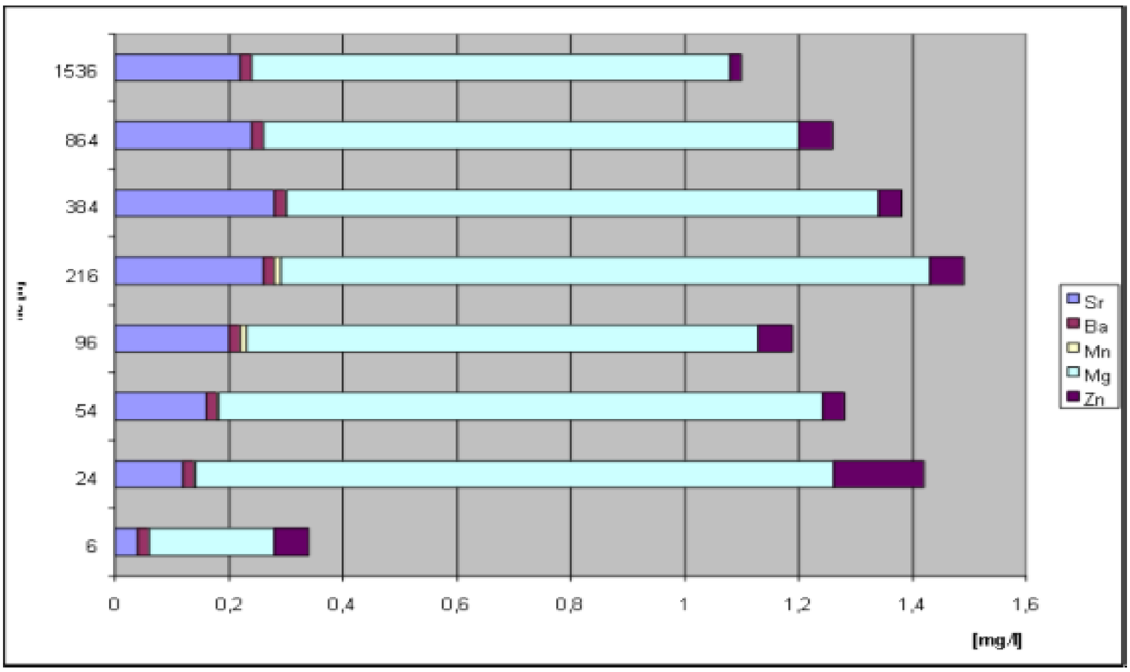

Figure 3. The leachability of elements from the opoka-rocks for 8 time fractions [own research]

The second element in terms of penetration into the eluates is strontium, whose concentration is between 0.04 - 0.28 mg / l. Its concentration increases uniformly until 384h reaching the maximum value of 0.28 mg / l. After a period of 16 days, its concentration gradually decreased. The results for zinc range from 0.16 mg / l to 0.02 mg / l. Its maximum value was achieved after 24 hours and further results show a downward trend to the minimum value achieved after 1536h. The leachability of Ba from the beginning to the end of the carried out tests was uniform and during all research periods oscillates at the value of 0.02 mg / l. From the analyzed elements, the lowest concentration in aqueous eluates was recorded for manganese. The leachability of this element was noticed until after 24 h and took the value of 0.001 mg / l. Its maximum value after 96h is 0.01 mg / l, with manganese being the only one from the analyzed elements after 384 reached the final result of the transition to the solution.

5. Conclusions

The carried out leaching tests for the trace elements such as Sr, Mg, Mn, Zn and Ba from the opoka-rocks showed that all of the analyzed elements are leached into the aquatic environment. A series of leachability for the studied elements in the ascending order was Mg> Sr> Zn> Ba> Mn. This and other results, however, do not exceed the permissible values of the trace elements in the waters specified in the Ministries Regulations [13,14]. Determined concentration of the studied elements in the building material showed that the highest concentration is attributed to magnesium and the next one is strontium. These values, however, do not exceed the concentrations determined in the pre-industrial material. Higher values were annotated for zinc. The concentration of zinc in the construction material exceeded value almost twice (16 mg / kg) in relation to the concentration in the historical material of 8.53 mg / kg. The average values of the calculated geochemical contamination index indicate the average accumulation of Zn in the building material (table.1). Enrichment of building material with zinc may be the result of biological weathering. The studied building material rich in carbonates is susceptible for physical and chemical processes. Over the years it has been subject to degradation resulting, for example, from the effect of lichens. Lichens accumulate primary metals by capturing insoluble solid particles. The average concentration of zinc in *H.physodes* from the area of three Polish National Parks is 71 mg / kg in Magurski N.P, 83 mg / kg in Świetokrzyskie N.P. and 67 mg / kg in Wigry N.P. [15].

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