Evaluation of Temporal Leachability of Strontium from Building Materials to Environment

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Abstract. The presented article covers very current issues regarding the assessment of trace element release from building materials to the natural environment. Strontium belongs to the trace elements mentioned in the group of potential reference chemical markers of the building materials. The leachability of strontium from monolithic samples was determined on sedimentary and igneous stone materials as well as ceramic materials: bricks. 40 samples were analyzed in which the leachability of the subjective element for 8 temporal fractions was determined. The research methodology was implemented in accordance with the applicable standard requirements. Execution of water extracts took place in accordance with EN NEN 7375:2004 standard. The mineralization of aquatic eluates was prepared according to the PN-EN ISO 11885 standard. The strontium concentration was determined using the ICP sequential plasma-emission spectrometer. Research for pH measurement was performed using a pH-meter CP-105 waterproof IP67 ELMATRON calibrated with buffer solutions of pH 4 and 7. The highest strontium content in the aquatic eluates was identified in bricks ranging from 0.06-0.47 mg/l. From the group of the sedimentary rocks the highest leachability of this element was determined in the opoka-rocks at its maximum content of 0.28 mg/l and in the sandstones 0.05 mg/l. Water extracts from the igneous stone materials did not show the presence of strontium.

1. Introduction
The presented article covers very current issues regarding the assessment of the release of trace elements from building materials to the natural environment. The European Committee for Standardization works on a system of ecological assessment of building materials. Construction products, apart from technical and functional description, should take into account the entire period of use of a given material with the possibility of its use after the end of the so-called technical life. Monitoring in its scope should also include control of the content and emissions of harmful components such as trace elements to the natural environment. As part of work on the content of the trace elements in building materials, the article presents the results of leachability of strontium from commonly used stone and ceramic materials. The leachability process of the present elements in the
material matrix depends on many components. One of them is the form in which the material occurs, whether it is a monolithic form or a comminution form [1]. The work involved analysis of monolithic samples in which the release of elements takes place mainly in the process of diffusion, advection and surface leaching. An important role in these processes is played by physical and chemical environmental factors. The main physical factors are the structural-textural features of the monolithic material. Porosity, presence of micro-fractures and crevices, shape and size of pores increase or decrease the phenomenon of immobilization of the trace elements in the material. Chemical factors that accelerate leaching of the trace elements from monolithic construction components are water, pH of the environment, duration of water influence on the monolith, solubility of the salt, or buffer capacity [1]. The purpose of the conducted research was to analyze the temporal leaching of strontium from genetically diverse rocks, formed under natural conditions in various geological environments and material created as a result of the production process. In the carried out studies, the factor of pH of the aquatic environment was also taken into account.

2. Strontium geochemistry and mineralogy

Strontium Sr-element from the group of beryllium is classified as poorly distributed elements that forms minerals of Celestine SrSO₄ and Strontianite SrCO₃. This element is not present in the free state, however, it is part of animal and human organisms, replacing calcium in bone tissue as a result of diadochia. Its excess causes decalcification and bone deformation. Its average content in the earth's crust is 0.045 wt.%. It is the product of the main stage of magma crystallization. In igneous rocks it is a dispersed element and its average content in these rocks in the continental crust is about 350 mg / kg. In the postamagmatic phase, its concentration decreases and in the hydrothermal stage Sr occurs as a dispersed element and is part of calcium minerals such as calcite ( up to 2% Sr), aragonite (2.5% Sr), fluorite (0.85% Sr), calcium zeolites as e.g. heulandite (up to 2.5% Sr). In addition, the admixtures of this element are recorded in feldspars, barite (6% Sr), and witherite (4% Sr) [2].

There rarely occurs in these conditions to create their own minerals. In sedimentary rocks its content is formed in limestones from 50-375 mg / kg, with an average value of 171 mg / kg; opoka-rocks from 223-396 mg / kg with an average value of 293 mg / kg, marls 203-308 mg / kg with an average value of 243 mg / kg [3]. In some types of limestone and evaporates, the minerals of strontium most often as a result of diagenesis, they can accumulate in large quantities. Gypsum rocks were found where the average strontium content was even 1800 mg/kg [4,5]. Environmental analyzes in the eastern belt of the EU have allowed to observe areas where the highest concentration of strontium in soils was found around cement production plants [6,7]. According to European data, the highest concentration of strontium was recorded in sediments of 126 mg / kg, in soil the value is higher in the lower part of the soil (95 mg / kg) than in the upper soil layer (89 mg / kg). Waters are characterized by an average content of this element in the range of 0.11 mg / l (table 1) (FOREGS 2016) [8].

| Strontium [mg/kg ] | Count | Minimum | Maximum | Median | Mean | Standard deviation | Percentile 90 |
|-------------------|-------|---------|---------|--------|------|-------------------|---------------|
| Stream sediment   | 852   | 31.0    | 1352    | 126    | 171  | 147               | 314           |
| Subsoil           | 787   | 6.00    | 2010    | 95.0   | 143  | 150               | 270           |
| Topsoil           | 845   | 8.00    | 3120    | 89.0   | 130  | 153               | 246           |
| Humus             | 367   | 1.10    | 205     | 17.4   | 22.4 | 20.7              | 40.7          |
| Water             | 808   | 0.001   | 13.6    | 126    | 171  | 147               | 314           |
| Floodplain sediment| 747   | 15.0    | 1660    | 131    | 166  | 140               | 293           |
3. Material and methodology

The leachability of strontium from monolithic samples was determined on igneous and sedimentary stone materials as well as on ceramic material. The research was carried out on Strzegom granite, Lublin opoka-rock, Carpathian sandstone and brick. The selection of the research material resulted from the criterion of the most commonly used building material and diversity in terms of genesis, composition and production process. The magma rock-granite, represents a non-construction building material, the opoka-rock and sandstone belong to a group of sedimentary construction materials and the brick is classified into a group of construction materials created from the recycling of natural resources. During the study 40 samples were analyzed in which the leachability of the studied element for 8 time fractions were determined. The research methodology was implemented in accordance with the applicable standard requirements. Execution of water extracts took place in accordance with NEN 7375: 2004 [9]. The strontium concentration was determined using the ICP sequential plasma-emission spectrometer. Research for pH measurement was performed using a pH-meter CP-105 waterproof IP67 ELMATRON calibrated with buffer solutions of pH4 and 7 (PN-ISO 10390:1997) [10]. The mineralization of water eluates was prepared according to the PN-EN ISO 11885 standard [11]. The concentration of strontium was determined using a sequential plasma ICP spectrometer. ULTIMA 2 HORIBA JOBIN-YVON, with the possibility of retrospective analysis, operating in the spectral range from 160 to 800 nm with the possibility of extending them to the range of 120-800 nm at any time. The software cooperating with the ICP spectrometer enables the registration of the full spectrum in less than 200 s with the full resolution of the spectrometer. The study of quantitative concentration of strontium in water eluates was carried out at the Aerospace Materials Research Laboratory of the Rzeszów University and Technology. The laboratory is accredited by Nadcap (National Aerospace and Defense Contractors Accreditation Program), issued in March 2009 by the Performance Review Institute, USA and Polish Center for Accreditation.

![Figure 1. The resulting total strontium leachability in individual types of material](image-url)
Figure 2. Temporal distribution of strontium leachability from the studied materials.

4. Results
The highest Sr content in the tested materials was identified in the brick eluates, where its maximum value reached 0.47 mg / l. In total, within 3180 h 1.93 mg / l penetrated into the water solution. In addition, it was observed that over time more and more of this element was released, after the first 6 hours the solution exceeded 0.06 mg / l Sr and in the last test at the time of 1536 h its amount reached 0.47 mg / l. During the entire period of the strontium leaching from the brick, the growth tendency can be clearly observed figure1. From the group of sedimentary rocks the highest leachability of this element was determined in the opoka-rocks.

The nature of the strontium leaching to the aquatic environment in the opoka-rocks in the first months of research showed an increasing trend. Its concentration increases uniformly until 384h reaching the maximum value of 0.28 mg / l figure 2. After a period of 16 days its concentration began to gradually decrease to a value of 0.22 mg / l. The last of the obtained results did not indicate a downward trend. In the sandstones, the strontium leaching process started only at the third test after 54 hours. The value of 0.01 mg / l was registered, which changed only after 216h reaching the value of 0.04 mg / l. The maximum concentration of Sr in sandstone occurred after 1536h reaching 0.05 mg / l. The water extracts from the soil in none of the tests showed the presence of strontium. In this case, it can be assumed that strontium in igneous rocks is more strongly associated with the rock matrix than in the case of the other studied materials.

The pH of the water surrounding the building material and the pH of the pore liquid play an important role in the carried out studies. Depending on its nature, the release of trace elements to the natural environment is accelerated or slowed down. Due to the lowering of pH in materials such as cement, there is a change in the solubility of trace elements. Strongly alkaline environment favors the formation of sparingly soluble compounds while lower pH shows an increase in solubility. The analysis of the pH of aqueous solutions was performed in the study. The pH of the liquid in individual samples in a given temporal distribution did not show too much variation. The obtained results were similar to the pH of distilled water used in laboratory tests (pH 5.8). The determinations showed that in all solutions pH was in range from 6 to 8. It was observed that the increase in alkalinity direction of the solution increased uniformly with increasing time. In natural rock materials, the pH was in the
following ranges: (6.98-7.73) in the granite, (7.14-7.93) in the opoka-rock, (6.91-7.91) in the sandstone. In the ceramic material, the pH ranged from 6.86 to 7.21.

5. Conclusions
The results of the obtained tests allow to state that during leaching of strontium from the studied materials, the lowest concentrations were characterized by ceramic solution and brick. The total strontium content in the solution after the final time reached 1.93 mg / l. In silica-carbonate materials (opoka-rock), the content of strontium was 1.52 mg / l, while in sandstones 0.19 mg / l. It is noteworthy that strontium was not precipitated from the granite material matrix. In this case, it can be assumed that strontium in igneous rocks is more strongly associated with the rock matrix than in the case of the other studied materials.

Taking into account that all of the performed analyzes were characterized by the same environmental conditions, it can be assumed that the degree of release of trace elements will be largely influenced by the origin of the material. It can also be assumed that the presented total strontium content in the analyzed period presents only part of the element accumulated in the material that has passed into the solution. Each of the tested materials is characterized by a long operational period lasting several dozen years. The obtained results indicate that the concentration of strontium in all water eluates apart from-granite did not aim for zero. What does it mean that the extension of the research period would allow to obtain more complete information in the assessment of strontium leachability to the aquatic environment. The carried out analysis of strontium leachability confirms that in the case of igneous rocks, the studied element does not release. In the remaining materials, although strontium was found in aqueous eluates, its quantity does not exceed the norm values [12].

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