Analysis of the Toxic Element Concentrations in the Mesozoic Siliceous Rocks in Terms of the Raw Material Importance

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Abstract. As part of an integrated system of environmental protection at every stage of the product life cycle such as: raw material extraction, its transportation and processing as well as the subsequent use and development is required to carry out actions towards reducing or completely eliminating products that contain harmful substances to the environment. The purpose of the presented paper is an analysis of the toxic element concentrations in the extracted siliceous minerals at the initial stage of the raw material recognition. The research material is constituted by rocks collected from the Mesozoic bedrock from the Belchatów lignite deposit. A group of the studied rocks is represented by diatomites, gaizes, opoka-rocks and light opoka-rocks, enriched with minerals from the group of SiO₂. Most of the recognized petrographic sediments have a real possibility of potential applications in the building material industry, but it needs to carry out a detailed and thorough research.

The studies of the chemical composition were determined by atomic absorption spectroscopy (AAS) using Philips PU 9100Xi Camera SX-100 spectrometer and an atomic emission spectroscopy with inductively coupled plasma (ICP AES) using PLASMA 40 spectrometer. There were carried out a chemical analyses and determined the content of some toxic elements: Pb, Cr, Cd, Ni, Zn, Cu, Co, As, Sr, Ba, Zr. in the studied sedimentary rocks.

The analysis of the results draws attention to the high content of cadmium in the case of the studied sediments. The concentration of this element in the described rocks is an average of 0.22 mg/kg –the diatomites, 0.05 mg/kg –the gaizes, 0.4 mg/kg –the opoka-rocks, 2.23 mg/kg –the light opoka-rocks. It was moreover registered varied concentration of arsenic in diatomites, that is formed in the range of 0.05 - 9.6 mg/kg, an average of 6.3 mg/kg. The content of the other designated elements with toxic properties in the analysed groups of rocks does not exceed the limit values. An increased concentration of cadmium and arsenic should be considered as an important information in resource research of the studied rocks. The both elements belong to the easily soluble elements as a result of weathering processes. Cadmium is one of the most dangerous toxicological environmental elements. It is easily absorbed and relatively long stopped in humans and animal’s organism. It also seems that the increased concentration in the siliceous rocks results from the nature of the lignite from the Belchatów lignite deposit, outstanding higher cadmium content in relation to the observed lignite of the world.

1. Introduction
In the present 40 years the Belchatów mine still not fully resolved problem of the issue of comprehensive use of all varieties of minerals extracted during exploitation operations. The opencast nature of lignite
mining in the Bełchatów lignite deposit is conducive to acquiring new varieties of the petrographic rocks with the raw material importance and makes access to them much easier.

As part of an integrated environmental protection system, rock material which is stored on slag heaps and providing a raw material perspective to accurately assess its suitability and potential impacts on environment requires the determination of mineral and chemical composition. The carried out mineralogical and petrographic studies have made it possible to distinguish within the investigated zone the Mesozoic substrate rocks represented by limestone, opoka-rocks, gaizes, diatomite, flints, marls and medium grain rocks, as well as sediments of the weathering complex: decalcified opoka-rocks, kaolin clays and sedimentary breccia’s [1].

The purpose of the presented paper is to carry out chemical studies in the evaluation of the determination of concentrations of toxic elements in the Mesozoic siliceous rocks originating from the Belchatów lignite deposit. An analysis of rare and trace elements, not covered by common indications in rocks, is being made more and more often due to the presence in their composition many elements harmful to the environment.

1.1. The mineralogical characteristics of the Mesozoic rocks

The analysed Mesozoic rocks are represented by: the diatomites, the opoka- rocks, the decalcified opoka- rocks and the gaizes. Their mineral composition was as follows:

- The diatomites are composed of silica in the form of opal type CT and quartz. In addition, it was found the presence of calcite, montmorillonite, illite, muscovite and minerals from the zeolite group. The silica built a rocky background and was a part of biloclasts, such as diatoms and sponges, it was accessory found quartz grains. Pyrite has also been found in the mineral composition of the diatomites. Observations in the scanning microscope showed that it generally has adopted framboid forms (nodular) with characteristic oval shapes. Such occurrences of the pyrite are formed by colonies in silica - argillaceous background (figure 1a), filling various types of voids, channels after infaun. Some of the microframboides have distinctly sharp edges (figure 2b).

- The opoka-rocks are composed of carbonate substance, formed in the form of a micrite together with opal. There are also numerous carbonate bioclasts, mainly represented by foraminifera shells, fragments of molluscs and echinoderms. The sponge needles are less common, made of chalcedony or opal. In this group of rocks, within the organic remains, the symptoms of processes of substitution of carbonate minerals by the minerals from the SiO₂ group - chalcedony were observed. In the rocky
background besides bioclasts the presence of quartz grains among detritus materials has been showed.

- The decalcified opoka-rocks are mainly composed of the chalcedony that builds the skeleton of the rock. Terrigenous quartz grains are an important component of the rocks. They represented about 30% of the volume of the rock. Clayey minerals were present in an amount of up to 18% wt. Low CaO content of less than 1% confirms the strong decalcification process of these rocks. Accessory minerals are represented by heavy minerals (zirconium, rutile, tourmaline), opaque ore minerals and framboid pyrite.

- The gaizes are composed among others of opal and chalcedony as well as an argillaceous substance. A detritus material is represented by silicon organic skeletal elements, mainly sponge needles, radiolabels or diatoms (figure 2b). The chalcedony also forms secondary fillings of rock pores. In these types of occurrences, chalcedony fibers are arranged in concentric-radial forms creating characteristic "rosette" forms (figure 2a).

![Figure 2](image_url)

> Figure 2. a) “Rosette” chalcedony forms in gaizes. The microscope picture 1P. b) Organic remains. SEM / EDX

### 1.2 The current directions of using of the rocks from the Mesozoic top surface.

Previous studies of the rocks from the Mesozoic top surface in the Bełchatów lignite deposit determined their use for sorption and desorption in the first place of petroleum substances and then heavy metal ions. Attention was also paid on their use in agriculture for the production of calcium fertilizers and fertilizer mixtures to change pH and water buffer in soils [2]. The later results of laboratory tests carried out by [3] proved a new direction of utilization of these minerals as an ingredient in the production of synthetic calcium silicate - wollastonite. Limestone raw materials, mainly marbles, could be used as low raw material for cement production [4]. The ongoing research on limestone is being used as a sorbent for dry methods of SO₂ emission reduction in grate, particulate hearths as well as fluid furnaces [5].

The siliceous raw materials from the Mesozoic-Neogene contact zone in the Bełchatów lignite deposit augurs hope to use them as an additive for cement production. The high value of the silicate module in the opoka-rocks qualifies them for use in the binding materials industry for the production of Portland cement with high strength as a component of cement clinker. In addition, the presence in them the silica in the amorphous form additionally has a positive effect on the clinker burning process. Taking into account the estimated and extraction resources of these rocks (the opoka-rock - 100-150 thousand m³/year, the decalcified opoka-rock - several million m³) and the narrow range of existing research works on their sorption capacity, it seems that they may be interesting as a new material in pro-ecological technologies [6].
2. The research material and methodology
The Belchatów lignite deposit is a tectonic, fault block depression deposit located in Central Poland. The opencast character of the extraction works led to the formation of a 300 m deep excavation and a length of about 3 km (figure 3). The research material was taken during fieldwork from the southern slope of the Belchatów opencast mine and during the testing of drilling cores preceding the exploitation front of the Szczerców field. A total of 26 drilling wells were tested and 29 samples were taken, including 19 samples from drilling cores and 10 from the escarpments. The diatomites - 8 samples, the opoka-rocks 10 samples, the decalcified opoka-rocks-6 samples as well as the geizes- 5 samples were given detailed investigations.

![Figure 3. The study area. The surface excavation of lignite from the Belchatów deposit with slag heap](image)

The examination of the concentration of toxic elements in the siliceous rocks was determined by atomic absorption spectrometry (AAS) using PHILIPS PU 9100Xi Camera SX-100 spectrophotometer and atomic emission spectroscopy with inductively coupled plasma (ICP AES) using PLASMA 40 spectrometer. In the discussed rocks, chemical analyses were carried out and it was determined the content of some trace elements: Pb, Cr, Cd, Ni, Zn, Cu, Co, As, Sr, Ba, Zr.

3. The research results
The content of some trace elements: Pb, Cr, Cd, Ni, Zn, Cu, Co, As, Sr, Ba, Zr, was determined in the studied siliceous rocks from the Belchatów lignite deposit (table 1). The analysis of the obtained results draws attention to the high cadmium content in the case of the investigated sediments. The concentration of this element in the described rocks is on average: 0.22 mg / kg -the diatomites, 0.05 mg / kg -the geizes, 0.4 mg / kg –the opoka- rocks and 2.23 mg / kg –the decalcified opoka- rocks. Cadmium is a strongly dispersed element in the rocks. In weathering processes, it is easily activated and then bound by clayey minerals, iron hydroxides and organic matter. Its content in the sedimentary rocks appropriately is in clayey sediments -0.3 mg / kg, elastic rocks- 0.05 mg / kg and chemical and organochemical rocks- 0.035 mg / kg [7, 8].
In addition, different concentrations of arsenic in the diatomites were recorded, ranging from 0.05 to 9.6 mg / kg and averaging 6.3 mg / kg. These values exceed the indications given for arsenic. It is believed that its concentration in almost all rocks is within the range of 0.5 - 2.5 mg / kg. The concentration is usually up to 13 mg / kg only in clayey sediments. In the clastic rocks, its value is in the range 1 - 1.2 mg / kg. In the carbonate sediments it is slightly higher, reaching up to 2.4 mg / kg. All arsenic compounds and minerals are readily soluble. Its migration is however limited by strong sorption by clayey minerals, iron and aluminium hydroxides, and organic matter. In addition, some minerals such as micas or goethyt show particular tendency to bind arsenic and affect its distribution in sediments [7,8].

The content of the remaining determined elements with toxic properties in analysed rock groups does not exceed the permissible values.

| Elements | Rock name | Diatomite | Opoka-rock | Decalcified opoka-rock | Gaize |
|----------|-----------|-----------|------------|------------------------|-------|
|          |           | Obser. scope* | Geome. mean** | Obser. scope* | Geome. mean** | Obser. scope* | Geome. mean** | Obser. scope* | Geome. mean** |
| Pb       |           | 0 – 4.3 | 1.72 | 2.29-3.3 | 2.9 | - | - | 2.5 | -4.3 | 2.99 |
| Cr       |           | 0.72-18.76 | 10.23 | 5.36-9.40 | 6.69 | 0.01 | -0.05 | 0.02 | 0.02 | 5.36 | 3.91 |
| Cd       |           | 0-0.44 | 0.22 | 0.1-1.1 | 0.4 | 2.01 | -2.64 | 2.23 | 0.1-0.22 | 0.055 |
| Ni       |           | 0-18.56 | 5.51 | 3.25-6 | 4.79 | - | - | 2.22 | -8.12 | 3.74 |
| Zn       |           | 4.58-77.1 | 26.54 | 7.99-9.05 | 8.53 | 1.12 | -1.58 | 1.37 | 3-13.43 | 5.62 |
| Cu       |           | 2.8-11.2 | 7.7 | 1.9-9 | 4.39 | 1.6 | -2.8 | 2.38 | 1.95-22.4 | 7.48 |
| Co       |           | 1-4 | 2 | 0.1-2.21 | 0.85 | 0.01 | -0.02 | 0.003 | 0.1-4 | 1 |
| As       |           | 0 – 6.6 | 6.3 | 0.1-5.1 | 0.91 | - | - | 1.5-4.3 | 2.2 |
| Sr       |           | 0 0.05 | 0.025 | 223-396 | 293 | 320-396 | 35 | 49-222 | 11.5 |
| Ba       |           | 185-210 | 193.75 | 38-314 | 153 | 37-38 | 37.66 | 120-190 | 151.25 |
| Zr       |           | 19-20 | 19.125 | 8-81 | 33 | 7-10 | 8.33 | 17.5-100 | 40.37 |

* Observation scope
** Geometric mean
- means content below the detection limit

4. Conclusions

The detailed analysis of the sediments laying in the substrate of lignite series is very important because of stratigraphic, structural, lithological, raw material, mineralogical - petrographic and even environmental issues. These sediments are lithologically different from the overlying rocks in a fundamental way due to the extremely paleogeographical conditions prevailing at the Mesozoic and Cenozoic age, and especially the sedimentation condition associated with their forming. These sediments contain the resultant of diastrophic and sedimentation processes due to the presence and the effect of the lignite sedimentation on the substrate deposits. The intensity of the mineral and rock-forming processes is caused by the presence and the specificity of the physicochemical regimen of lignite sedimentation, had a strong influence on lithological forming and even on expansion of the forming sediments. Their character and intensity for a long time, also in the case of the Belchatów lignite deposit, were not fully identified.

The increased concentrations of cadmium and arsenic that was found in this work should be considered as important information in the raw material research of the studied rocks. Both elements are readily soluble as a result of weathering processes. Cadmium is one of the most toxic in effects environmental elements. It is easily absorbed and relatively long retained in humans and animals. It also
seems that its increased concentration in the Mesozoic substrate rocks is due to the character of lignite from the Belchatów deposit, distinguished by higher cadmium content in relation to the observed lignite of the world. It is assumed that its average concentration in Belchatów lignite is 0.6 mg / kg with a minimum value <0.2 and a maximum of 0.6 mg / kg [9,10].

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