Alkali-activated coal fly ash as a matrix for heavy metals immobilization

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Nowadays, when the pace of industry development is as fast as never before, the environmental protection aspect has become extremely important. One of the key environmental problems is waste management. According to directive 2008/98/EC of the European Parliament (2008) the goal is to recycle waste as much as possible and eliminate waste generation. This requirement is hard to be met in case of materials that cannot be reused. Then, the material should be given a new function. Such materials include, among others, ash from coal burning and municipal waste. Until now, they have been used as an additive to cement pastes (Gougar *et al.*, 1996), bituminous materials (Cervinkova *et al.*, 2007), red ceramics (Liguori *et al.*, 2006) etc. However, the latest research shows that chemical reactions and corrosion occurring in these materials can cause leaching of harmful components to the environment (Shi *et al.*, 2009). Potential solution to this problem may be use of geopolymers as matrix for disposal of heavy metal ions.

Geopolymers – the alkali-activated aluminosilicates, are synthesized by treating reactive solid source of SiO_2 and Al_2O_3 with an alkaline solution. There are known various sources of SiO_2 and Al_2O_3, such as natural clays and synthetic industrial by-products: coal fly ash, ash from waste incineration, blast furnace slag etc. (Rożek *et al.*, 2019). The utilization of industrial by-products and wastes for the synthesis of materials that can be applied for different purposes is particularly important. For instance, the global production of coal combustion products (e.g. fly ash) in 2010 was 780 million tonnes, and its utilization rate was around 50% (Heidrich *et al.*, 2013). Therefore, the preparation of coal fly ash-based geopolymers provides a sustainable way for the disposal of this by-product which remains a worldwide challenge. Synthetic ashes, as combustion products, contain only inorganic compounds such as: silicates, aluminates and also heavy metals such as zinc, copper, lead, chromium and nickel (Jing *et al.* 2007, Saquib *et al.* 2016). Heavy metals, without proper treatment, are washed out of material, get into soil, groundwater and finally plants and animals. The accumulation of heavy metals in human body can lead to many serious diseases. In connection with the above, it is strived to develop a method of immobilization of heavy metals that would allow them chemical binding in the material and eliminate their leaching to ecosystem.

Zehua et al. (2020), in their study, successfully applied granulated blast furnace slag-based geopolymers in the immobilization of heavy metal ions (Cd^{2+}, Pb^{2+}, Zn^{2+}, AsO_4^{3-} and $Cr_2O_7^{2-}$), showing potential role of geopolymers in immobilization of heavy metals. On the other hand, Bagheri *et al.* (2018) and Nazari et al. (2014) show studies of a more environment-friendly type of alkali-activated materials-boroaluminosilicates. Nicholson *et al.* (2005) found that boron atoms have trigonal and tetrahedral coordination and maintain that the incorporation of boron in geopolymer structure is in the form of substitution with aluminum and silicon atoms. In the mentioned boroaluminosilicate geopolymers studies, the main goal was to decrease the use of sodium silicate by replacing it with borax, in order to decline the cost and energy.

The aim of this work was to use alkali-activated fly ash as a matrix for immobilization of heavy metals and to assess the role of boron in the immobilization efficiency. In this work, results of structural studies of boroaluminosilicate geopolymers, obtained using alkali-activation method, fly-ash and two different sources of boron, were presented. As activators, NaOH and borax were applied. The impact of using boron as a component of the alkalizing solution is currently undertaken in the related literature (Bagheri *et al.*, 2018, Nazari et al. 2014) and is considered to be environment-friendly additive influencing the mechanical properties. However, no descriptions of boroaluminosilicate geopolymers as matrix for disposal of ashes containing heavy metal ions were found.

Experimental Methods

Geopolymers were prepared by mixing coal fly ash with 10 M sodium hydroxide solution with addition of boron carrier (borax) and heavy metal salt (lead and nickel nitrates). Water to solid ratio was 0.4. All pastes compositions are collected in Table 1. The prepared samples were cured at 80°C for 24 h.

Table 1. Geopolymers composition.

Sample name	RS 0	BX 0.015	BX 0.030	BX 0.075	BX 0.150	BX 0.300
B/Al	0.000	0.015	0.030	0.075	0.150	0.300
Borax (wt.%)	0	1	2	5	10	20

Fourier transform infrared spectroscopy (FT-IR) was used to determine the structure of the obtained geopolymers. The phase composition was assessed by means of X-ray diffraction (XRD). The microstructure observations were carried out by the use a scanning electron microscope (SEM). The apparent density and compressive strength were also determined. The concentration of heavy metals leached from the samples was assessed with the use of Atomic absorption spectroscopy (AAS).

Results and Discussion

Compressive strength and bulk density of materials were measured. It was found that differences in bulk density of the samples studied were within an experimental error (about 1,26 g/cm^3). Thus, the influence of the sample composition on this parameter is insignificant. A small addition of boron increases the compressive strength from 16.0 MPa for reference sample to 16.3 MPa for the sample BX 0.015. The addition of heavy metals does not significantly affect strength parameters.

FT-IR spectroscopy were the main experimental method used, the results obtained were compared with XRD phase analysis and SEM observations. The exemplary results are shown in Figure 1. In the MIR spectra the bands due to the characteristic vibrations of bonds observed in all types of oxygen bridges: Si–O–Si, Si–O–Al, and Si–O–B, were assigned. These bridges constitute basic structural units, forming tetrahedral geopolymer chains. It was found that the slag composition influences the presence of the bands connected with the phases formed during the hydration in the MIR spectra. Additionally, significant effect of amorphous phases share on the spectra shape was established. Based on IR spectra, it was also possible to determine the influence of the activator type on the products formed, the role of boron in the structure, as well as the interrelations between heavy metals and structure of resulting material.

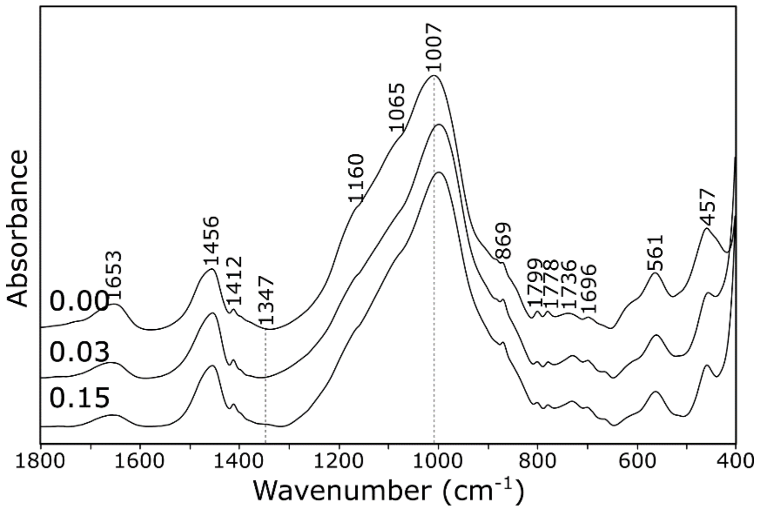

Figure 1. Exemplary FT-IR spectra of reference samples.

SEM observations show that microstructure of all composites is quite similar and typical for alkali-activated coal fly ash. Both boron and heavy metal cations influence the microstructure and the ordered state of the N–A–S–H phase.

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