Alkali-Activation of Blast Furnace Slag as Possible Modification for Improving Sorption Properties of Heavy Metals

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Abstract

New direction of research uses the alkali-activated slags as sorbents for removing metals cations from the solution. Slag materials modified by alkali-activation were prepared by interaction of blast furnace slag (BFS Basic) with water glass. The prepared alkali-activated slags were dried under different conditions to form new structure in slag. The slag dried at room temperature for 7 days (AA BFS) and in a dryer at 105°C for 8 hours (AA BFS 105) were prepared and characterized with the aim to study their sorption properties. Characterization of the prepared slags by means of infrared spectrometry (with diffuse reflectance method) demonstrates that the alkaline activation forms a new structure. The new structures are products of hydration processes and structural changes after contact with water glass. Changes are significant in the comparison with original blast furnace slag. The influence of this new structure on the sorption properties was studied for the copper Cu(II) and lead Pb(II) cations. The sorption experiments were performed by batch method in the aqueous solutions without pH treatment for the concentration range 2–140 mmol/L. The maximum removal amounts of Cu(II) on the alkali-activated slags were almost three times higher and the maximum removal amounts of Pb(II) were at least twice higher in comparison to the BFS Basic. Removal efficiency achieved almost 100% to initial concentration 20 mmol/L for Cu(II) and Pb(II). The removal efficiency for both cations decreases with increasing concentration of metals cations. The removal efficiency is higher for both alkali-activated blast furnace slags in the comparison with BFS Basic. A mechanism of the metal cations removing is influenced by self-alkalization and the removing is mainly due to precipitation and complexation of copper and lead cations on the surface of slags. The alkaline activated slags can be possibly used for remediation of wastewater containing metals ions.

Keywords: sorption, slag, metal cations, alkali-activated slag

Introduction

Slags as secondary products of metallurgical processes are recycled for extraction of metals which they contain and further they are applied in the construction industry: aggregate, filler or admixture to the concrete (Collins and Sanjayan, 1999; Das et al., 2007). Slag is formed by mixing of alkaline and acid oxides. Their ratio influences the structure and physical and chemical properties of slag. The structure of slags depends on the type and process course of pig iron production and on the cooling process. The slags utilized as admixtures to concretes are often modified by process called alkali-activation. Treatment with alkali-activation is only possible with materials containing silicon and aluminium (Li et al., 2010). Slags represent the multicomponent materials with silicates and aluminosilicates as major components enabling their alkali-activation. Concretes obtain higher resistance to the reagents and pressure by utilization of alkali-activated slags (Bakharev et al., 2001).

The alkali-activated materials represent high strength binder under high alkaline conditions (pH value of 12–14.5). The addition of alkali-silicate solution (e.g. waterglass, Na_2SiO_3 or K_2SiO_3) to the slag can increase the rate of strength development as well as largely enhance the final strength by promoting hydrolysis of the siliceous and aluminum species of the raw materials. Alkali-silicate solution also provides additional silicate species, sodium or potassium ions required for geopolymerization (Oh et al., 2010). Material structure after alkali-activation depends on the slag composition and alkali-activation properties (type of activator, concentration, pressure, contact time). Amorphous or crystalline phases – such as zeolites or zeolitic precursors and hydrotalcites – may be formed as a result of activation (Bernal et al., 2014; Oh et al., 2010).

Slags have been already used for removal of metals from aqueous solutions (Bláhová et al., 2015; Dimitrova, 1996; Dimitrova and Mehanjiev, 2000; Kim et al., 2008; Xue et al., 2009) but sorption of heavy metals on the alkali-activated slags is new research direction. Utilization of slags in this way solves global problems namely recycling of waste and removal of heavy metals from the environment.

The aim of this work was to prepare alkali-activated materials with aim to test their adsorption capacity. The alkali-activated blast-furnace slags were studied as adsorbents of Cu(II) and Pb(II). The higher adsorption capacity was expected due to the structural changes of the alkali-activated slags.

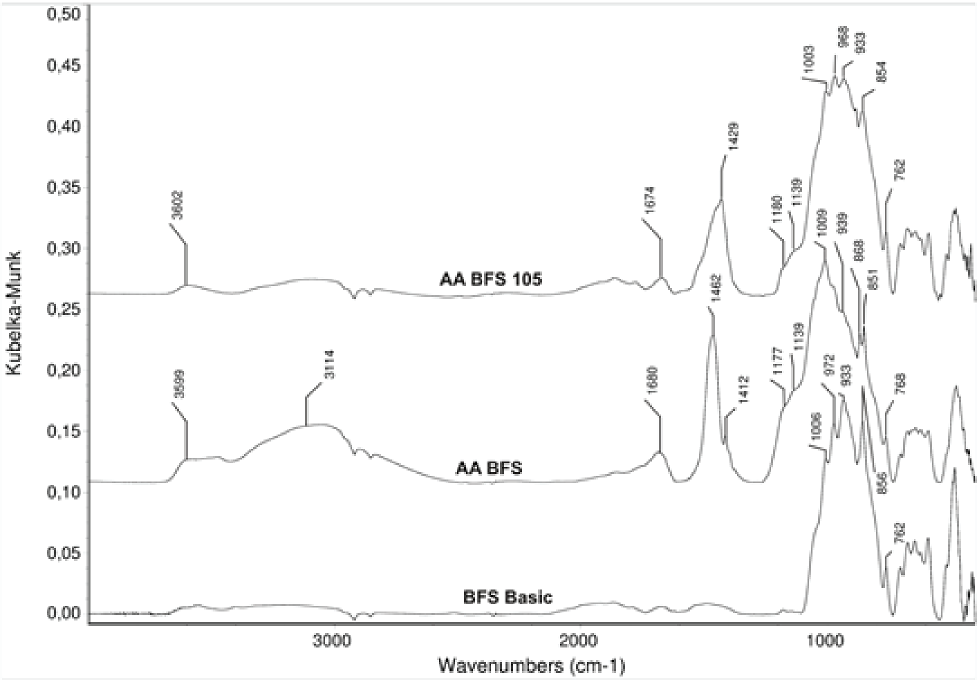

Fig. 1. Infrared spectra of BFS Basic and its alkali-activated modifications

Rys. 1 Spektrum w podczerwieni BSF Basic i jego aktywacja alkaliczna

Materials and methods

Blast furnace slag (BFS Basic) provided by ArcelorMittal Ostrava a.s. was used for experiments. Water glass (Na_2SiO_3) was used for the alkali-activation (KITTFORT s.r.o. Prague Czech Rep.). The content of SiO_2 and Na_2O in the water glass was necessary to determine. The content of SiO_2 was determined gravimetrically and the Na^+ content was determined by atomic absorption spectrometry. The alkali-activation was carried out with solution of water glass and sodium hydroxide (Lach-Ner, s.r.o. Czech Rep.). NaOH was added so that molar ratio SiO_2/Na_2O in the solution was equal to 1. The contact time of solution and slag was 7 days, then the suspension was filtered and the solid fraction was dried. Drying was carried out in two ways: at room temperature for 7 days (AA BFS) and in a dryer at 105°C for 8 hours (AA BFS 105).

All used chemicals – $Cu(NO_3)_2 \cdot 3H_2O$ and $Pb(NO_3)_2$ (Lach-Ner, s.r.o. Czech Rep.) for preparation of metals cations solutions – were of analytical grade. The standards of metals cations for atomic absorption spectrometry (Cu, Zn – Sigma-Aldrich) were used for AAS analysis of the metals.

The characterization of all studied slags was performed by IR spectroscopy. Infrared spectra were recorded on spectrometer FTIR Nicolet 6700 (Thermo Scientific, USA) equipped with the DTGS/KBr detector in the middle IR range. The diffuse reflectance method (DRIFT) was used. The spectra were measured in the spectral range 4000–400 cm^{-1} (128 scans, 4 cm^{-1} resolution, apodization Happ-Genzel). Baseline correction was carried out.

The sorption experiments were performed by batch technique. The optimal conditions for the sorption experiments were investigated on the BFS Basic (the contact time, the best ratio adsorbent dose : volume of solution) for both metals cations Cu(II) and Pb(II). The experiments for comparison of the sorption properties of materials were performed under the found optimal conditions.

The influence of adsorbent dose was studied for finding the best ratio (ratio solid : liquid). The best ratio was used for the further sorption experiments. The ratios 1:25, 1:50, 1:100 and 1:200 were investigated. The influence of the adsorbent dose was studied for the contact time 24 hours. The contact time for these experiments was selected on the basis of the previous experiments (Bláhová et al., 2015). Then the influence of the contact time on the removal of the metals cations was studied with the best ratio 1:25 and for the contact times 6, 12, 16 and 24 hours. The optimal conditions for the further sorption experiments were: the ratio solid : liquid 1:25, the cations concentrations in the range 2 –140 mmol/L, a 24 hours contact time and the ambient temperature. The metal concentrations in the supernatants after the sorption were determined by means of atomic absorption spectrometry (AA 240FS Varian, USA).

Results and discussion

Characterization of alkali – activated slags

Tab. 1 Removal amounts and efficiency of metals removal with respect to type of slag and initial concentration

Tab. 1 Stopień redukcji metali dla różnych żuzli i różnych zawartości początkowych

Slag		**BFS Basic**		**AA BFS**		**AA BFS 105**	
Concentration [mmol/l]		a [mmol/g]	E [%]	a [mmol/g]	E [%]	a [mmol/g]	E [%]
Cu(II)	2	0.04	97.6	0.04	93.4	0.04	81.6
	3	0.08	98.6	0.07	95.0	0.07	88.8
	6	0.15	90.3	0.15	97.5	0.14	94.8
	8	0.18	87.3	0.19	97.9	0.18	94.2
	9	0.17	68.1	0.22	98.5	0.22	97.2
	11	0.17	56.7	0.26	98.3	0.26	96.8
	15	0.18	47.7	0.36	98.5	0.35	98.7
	20	0.20	43.7	0.48	99.5	0.51	99.9
	40	0.23	22.8	0.58	59.7	0.75	73.0
	60	0.27	18.1	0.73	51.4	0.88	58.6
	100	0.34	14.4	1.04	43.7	1.05	42.9
	120	0.38	13.1	1.19	40.6	1.26	40.6
	140	0.46	13.7	1.35	39.7	1.42	39.5
Pb(II)	2	0.05	99.2	0.04	88.7	0.03	88.0
	3	0.07	99.7	0.07	94.2	0.07	93.1
	6	0.15	91.2	0.16	99.5	0.13	96.9
	8	0.20	69.2	0.21	99.6	0.15	97.1
	9	0.23	60.4	0.23	99.5	0.17	98.2
	11	0.27	48.4	0.28	99.9	0.22	99.1
	15	0.37	28.2	0.37	99.9	0.31	99.7
	20	0.49	23.2	0.48	99.9	0.44	99.4
	40	0.18	17.7	0.71	68.3	0.59	60.0
	60	0.22	13.5	0.76	48.4	0.85	51.1
	100	0.34	13.2	0.85	33.2	0.80	32.4
	120	0.37	11.7	0.97	30.6	1.15	36.0
	140	0.45	12.1	1.03	27.3	1.23	35.5

The infrared spectra of BFS Basic and alkali-activated slags are shown on the Fig. 1. BFS Basic contains mainly silicates, which is confirmed by several bands in the range 1100–700 cm^{-1}. These bands belong to Si-O, Si-O-Si and Si-O-Al stretch vibrations in the various minerals. The weak band belonging to carbonates (around 1450 cm^{-1}) and very weak bands of adsorbed water (around 3400 cm^{-1} and 1650 cm^{-1}) can be seen in the spectrum of the BFS Basic.

The spectrum of alkali-activated slag dried at laboratory temperature (AA BFS) shows several significant changes in the comparison with BFS Basic. Bands of silicates broaden and are shifted to the higher wavenumbers. New bands appear at 1177 and 1139 cm^{-1}. These changes indicate probably the hydration process of activated slag which takes place during slow drying of material. Formation of the hydration products is confirmed by band of OH stretch vibrations at 3114 cm^{-1}. Another type of newly formed structural OH vibrations is indicated by band at 3599 cm^{-1}. AA BFS contains slightly higher amount of adsorbed water compared to BFS Basic. Adsorbed water is proved by bands around 3400 and 1680 cm^{-1}. Deformation band of free water (1680 cm^{-1}) is shifted to the higher wavenumbers, which can be caused by interactions of water molecules with material surface. Very intensive band of carbonates (1462 cm^{-1}) is present in the spectrum of AA BFS. Carbonates form probably during hydration process by the incorporation of carbon dioxide from the air. This process is called carbonation.

The spectrum of AA BFS dried at 105°C indicates high impact of higher drying temperature. The spec-

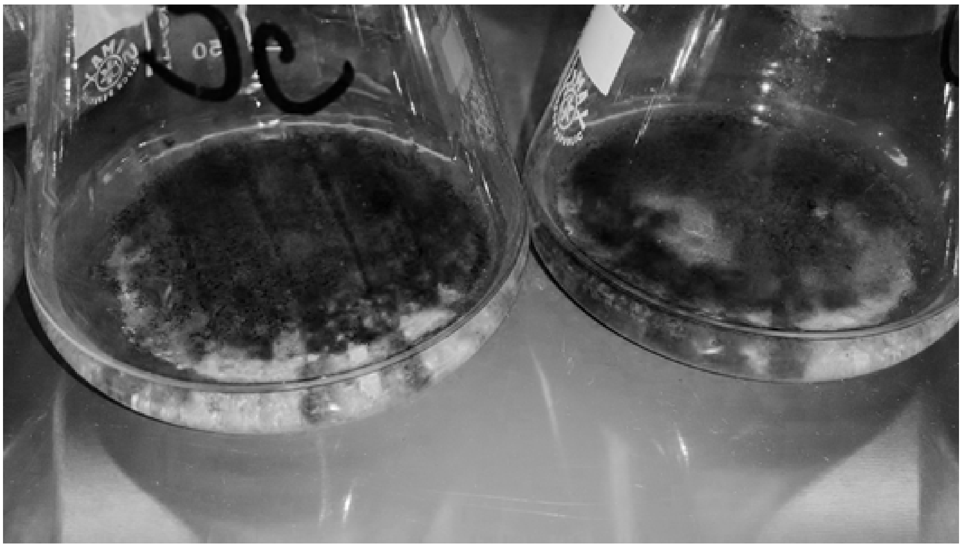

Fig. 2 Precipitation of Cu(II) (20 mmol/L, dark precipitate) on the surface of alkali activated slag (AA BFS, light grey)

Rys. 2 Osadzanie Cu(II) (20 mmol/L, ciemny osad) na powierzchni aktywowanego żużla (AA BFS, jasno szary)

trum is similar to the spectrum of BFS Basic, only slight changes (especially in the intensities) are present in the silicates bands. Bands of newly formed hydration products (1180 and 1139 cm^{-1}) can be seen in the spectrum. Intensity of these bands is lower than in the spectrum of AA BFS, which is probably caused by interruption of hydration process during drying at higher temperature. Lower amount of hydration products is confirmed by weak bands in the area of OH stretch vibrations. Also water content in the AA BFS 105 is significantly lower than in the AA BFS. The band of carbonates (1429 cm^{-1}) is intensive but the maximum is shifted to the lower wavenumbers compared to AA BFS, which indicates formation of different carbonate minerals.

Sorption of copper and lead cations

Table 1 presents the experimental data of the removal amounts [mmol/g] and the metals removal efficiency depending on the concentration of metals cations at the ambient conditions. The phase ratio was 1:25 and the contact time 24 hours.

The alkali-activation of slag has a positive effect on the ability to remove the metals cations from the solution. The removal efficiency of the AA BFS slag is almost 100% up to the metals concentration 20 mmol/L. The original BFS Basic has the same efficiency up to concentration 6 mmol/L. The similar results like for the AA BFS were found in the case of the Cu(II) sorption on the AA BFS 105. The results also show that the alkali activation increases the removal amounts almost threefold for Cu (II) and at least twice for Pb (II) in the comparison with the original BFS Basic for some of the studied concentrations. Of course, the efficiency of the metals removal is decreasing with the increased concentration of the metals cations.

A mechanism of the metals cations removing on slag is supposed to consist of several different processes – precipitation of hydroxides (Kim et al. 20008), by formation of hydrated oxides or hydroxo-complexes and carbonato-complexes (Dimitrova, 1996), and by ion exchange (Dimitrova and Mehanjiev, 2000). The prepared alkali-activated slag exhibited very similar self-alkalization ability as original slag. The pH value increases to 11–12 after sorption when the low concentrations of metals cations are present in the solution. This fact suggests also precipitation of metal hydroxides on the surface of alkali-activated slag, which can be illustrated by precipitate on Fig. 2. On the other hand, the pH value is invariable (around 7) during sorption if solutions with higher concentrations of metals cations were added to the slags. The solutions with higher metals concentration act as buffer. The precipitation is supposed to represent the predominant mechanism of the cations removal in the case of the alkali-activated slags.

Conclusion

The sorption of the metals cations was carried out on the blast furnace slag and its alkali-activated equivalents. The characterization was performed by IR-spectroscopy with DRIFT technique. The alkali-activation leads to formation of new minerals in the materials. Bands of hydration products and carbonates were observed in the spectra of the alkali-activated slags. Drying temperature has significant impact on the structure of modified material. The higher drying temperature (105°C) leads to the interruption of hydration process (lower contents of hydration products compared to the material dried at laboratory temperature were detected by IR-spectroscopy) and to the different distribution of carbonate minerals. The results of the sorption studies confirm that the alkali-activation increases the removal amounts and efficiency of the removal of metals cations compared to the original slag (BFS Basic). The removal amount and efficiency is threefold higher for Cu(II) and at least twice higher for Pb(II) than on the BFS Basic at high concentrations levels (above 40 mmol/l). The efficiencies at the low concentrations levels (up to 9 mmol/l) are comparable for all studied materials.

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Aktywacja alkaliczna żużla wielkopiecowego w celu poprawy właściwości sorpcyjnych metali ciężkich

Nowy kierunek badań obejmuje wykorzystanie aktywowanych alkalicznie żużli jako sorbentów do usuwania kationów metali z roztworów. Żużle modyfikowane alkalicznie przygotowano w reakcji żużla wielkopiecowego (BFS Basic) ze szkłem wodnym. Przygotowane żużle aktywowane alkalicznie wysuszono w różnych warunkach, tworząc nową strukturę w żużlu. Żużel wysuszono w temperaturze pokojowej przez 7 dni (AA BFS) i suszarce w temperaturze 105°C przez 8 godzin (AA BFS 105), w celu zbadania ich właściwości sorpcyjnych. Charakterystyka przygotowanych żużli za pomocą spektrometrii w podczerwieni (metodą rozproszonego odbicia) wykazuje, że aktywacja alkaliczna tworzy nową strukturę. Nowe struktury są produktami procesów hydratacji i zmianami strukturalnymi po kontakcie ze szkłem wodnym. Zmiany są znaczące w porównaniu z żużlem wielkopiecowym. Wpływ nowej struktury na właściwości sorpcyjne zbadano dla kationów miedzi Cu (II) i ołowiu Pb (II). Eksperymenty sorpcyjne przeprowadzono metodą wsadową w wodnych roztworach bez obróbki pH w zakresie stężenia 2–140 mmol/l. Maksymalna redukcja Cu (II) w żużlach aktywowanych alkaliami była prawie trzy razy wyższa, a maksymalny stopien redukcji Pb (II) był co najmniej dwa razy wyższy w porównaniu do BFS Basic. Wydajność redukcji osiągnęła prawie 100% w stosunku do początkowego stężenia 20 mmol/l dla Cu (II) i Pb (II). Skuteczność redukcji kationów maleje wraz ze wzrostem stężenia kationów. Skuteczność redukcji jest większa w przypadku żużli wielkopiecowych w porównaniu z BFS Basic. Mechanizm usuwania kationów metali wpływa na samoalkalizację, a redukcja jest głównie spowodowana wytrącaniem się kationów miedzi i ołowiu na powierzchni żużla. Żużle alkaliczne mogą być używane do oczyszczania ścieków zawierających jony metali.

Słowa kluczowe: sorpcja, żużel, kationy metali, żużel aktywowany alkalicznie