



Utilization of Blast Furnace Slag for Immobilization of Copper Ions from Solution

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Abstract

Disposal of wastes containing metal ions such as Cu(II) ions is serious problem nowadays. Various materials are utilized for the purpose of immobilization of Cu(II) ions. Attractive type of material is represented by slags – waste from the metallurgical industry. Raw and alkali-activated blast furnace slag were studied for the purpose of immobilization of Cu(II) ions from the aqueous solution and for disposal of Cu(II) containing wastes. Slags were saturated by Cu(II) ions. Amount of Cu(II) deposited on the raw slag was 6.35 ± 0.12 mg/g and amount deposited on the alkali-activated slag was 151.37 ± 0.95 mg/g. The saturated materials were thermally treated at 100, 500, and 1000°C. The thermal treatment leads to the slight structural changes in the case of raw slag and to the significant structural changes in the case of alkali-activated slag. Cu(II) ions probably incorporate to the matrix of materials. The materials based on alkali-activated slag exhibit higher stability to the leaching of Cu(II) ions compared to raw slag based materials when only 0.13% of the total immobilized amount of Cu(II) ions was released to the solutions during the leaching experiment in the case of alkali activated slag compared to 12% in the case of raw slag. The higher temperature of treatment leads to more stable material in the case of both initial slags. The studied materials are less stable under the acidic conditions in comparison with the neutral and alkaline conditions. Alkali-activated blast furnace slag could be promising material for the Cu(II) ions immobilization and for the safe disposal of Cu(II) containing wastes.

Keywords: slag, solidification, desorption, copper ions, thermal treatment

Introduction

Aluminosilicates of natural and artificial origin (clay minerals, slags) have been used in the field of waste processing and deposition for a long time. Attractive type of silicate material is represented by slag – waste needed to be safely deposited, but, on the other hand it finds its utilization in the building industry. Slag could be also used for the toxic waste immobilization (solidification) and thus to the hazardous waste disposal, e.g. the treatment of the contaminated waters (removal of inorganic and organic contaminants) (Shi et al., 2006; Repo et al., 2015). Number of studies (Dimitrova and Mehanjiev, 2000; Xue et al., 2009; Song et al. 2013) present slags as a cheap adsorbent of metals from the polluted waters. However, the slag adsorbents exhibit considerable heterogeneity and low stability of slag in the sorption processes (from disruption and change of structure up to matrix dissolution, leaching of some components causing the enormous pH enhancement of sorption medium, changes of chemical and mineralogical composition). Stabilization of slag for its application as adsorbent is necessary (Repo et al. 2015; Van Zomeren et al. 2011, Runti et al. 2016). The stabilization can be (in addition to other ways) performed by above mentioned alkali activation (Rovnaníková and Krmíčková, 2015; Pacheco-Torgal et al. 2015).

The aluminosilicate structure of slag creates with alkali activator (carbonates, hydroxides, sulphates) a solid matrix enabling to intercalate or encapsulate undesirable ions

(Rovnaníková and Krmíčková, 2015). This way alkali activated slags are used to fixing and immobilization of contaminants in wastes (Jin and Al-Tabbaa, 2014; Zhang et al., 2017). In addition to the improvement of mechanical properties, the reduction of matrix dissolution represents a great advantage of the alkali activated slags (Kim et al. 2017). The formed hardened material (geopolymer) can be therefore suitable to the wastes processing (Shi et al. 2006; Wang et al. 2016; Liew et al. 2016). The utilization of the waste material – slag for the disposal of another local wastes represents a positive aspect from the point of view of the Ostrava Agglomeration.

Materials and methods

Blast furnace slag (BFS) was kindly provided by ArceorMittal Ostrava a.s. (Ostrava, Czech Republic). Slag was milled in the laboratory mill (Testchem, Poland) and sieved through the sieve 0,5 mm. Alkali-activation was performed by the water glass (Kittfort Ltd., Prague, Czech Republic) solution which was treated by NaOH (Mach chemicals Ltd., Ostrava, Czech Republic) to obtain ratio $\text{SiO}_2:\text{Na}_2\text{O}$ on the value 1:1. The portion of 250 g of slag was mixed with 250 mL of activation solution and the suspension was left for the 7 days with occasional mixing. The resulting gel was transferred to the plastic dishes and it was dried in the dryer at 60°C to the constant weight (7 days). The alkali-activated slag (AA BFS) was then milled and sieved to obtain particles below 0,5 mm. Both materials (raw and alkali-activated slag)

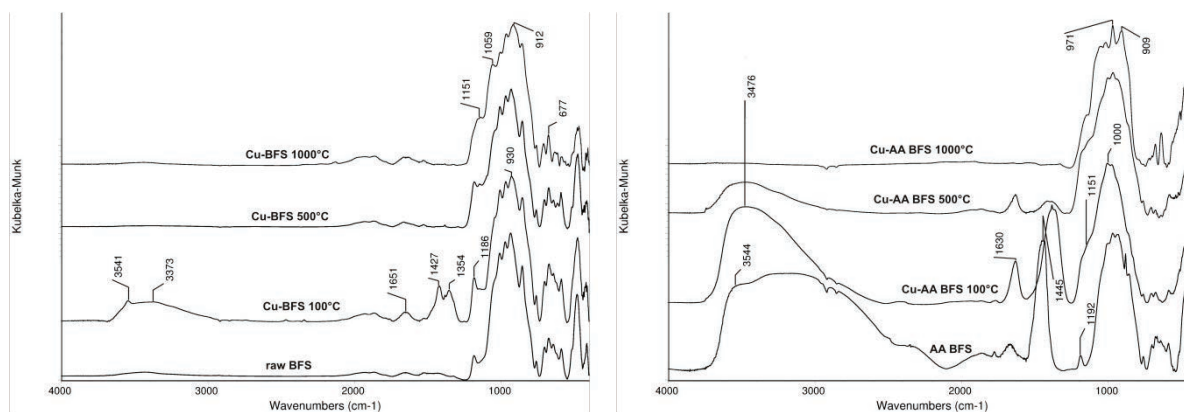


Fig. 1. Infrared spectra of the studied materials (BFS – blast furnace slag, AA BFS – alkali-activated blast furnace slag, prefix Cu – materials saturated by Cu)
 Rys. 1. Widma w podczerwieni badanych materiałów (BFS – żużel wielkopiecowy, AA BFS – żużel wielkopiecowy aktywowany alkali, Cu – materiały nasycone jonami Cu

were saturated by Cu(II) ions when 100 g of slag was mixed with 2.5 L of Cu(II) solution of concentration 80 mmol/L (5084 mg/L) prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ (Lachema, Brno, Czech Republic). Contact time 24 hours and ratio slag:solution 1:25 were selected according to the previous experiments (Bláhová et al., 2018). The suspensions were filtered after 24 hours and the solid materials were dried in the air. After that the Cu(II) saturated materials were milled and divided to the 3 groups which were thermally treated at 100 (6 hours), 500 (2 hours) and 1000°C (2 hours) in the furnace (LAC Ltd, Rajhrad, Czech Republic). Samples were then milled and the structural changes were characterized by infrared spectroscopy at Nicolet 6700 (Thermo scientific, USA) spectrometer equipped with KBr beamsplitter and DTGS/KBr detector. Samples were measured by diffuse reflectance technique, 128 scans were accumulated, the resolution was set to 4 cm^{-1} and apodization Happ-Genzel was used. Experiments with leaching of Cu(II) ions were performed for all prepared samples of slag saturated by Cu(II) ions and thermally treated. Demineralized water with pH value adjusted to 3, 7 and 10 by HCl or NaOH (Mach chemicals Ltd., Ostrava, Czech Republic) and solution of NaNO_3 (Lachema Brno, Czech Republic) of concentration 0.05 mol/L were used as leaching solutions. Amount of materials weighted to the centrifugation tubes was 1 g. Then 50 mL of leaching solution was added to the tube and the suspensions were left for 24 hours with occasional shaking. The suspensions were centrifuged on the Jouan BR4i multifunction centrifuge (Thermo scientific, USA) on the 6000 rpm for 15 minutes after the 24 hours of contact time. The content of Cu(II) in all solutions after saturation of slags by Cu(II) ions and after leaching experiments were measured by the atomic absorption spectrometry (AAS, Varian AA240FS, Varian, USA) at the wavelength 324.8 nm with air-acetylene flame, with limit of quantification 0.034 mg/L.

Results and discussion

Raw and alkali-activated slag were saturated by Cu(II) ions. Initial solution as well as solutions after contact with slags were analysed by the atomic absorption spectrometry to determine immobilized amount of the Cu(II) ions. The immobilized amount of Cu(II) ions on the raw blast furnace slag (BFS) was $6.35 \pm 0.12 \text{ mg/g}$ and the amount of Cu(II)

immobilized on the alkali-activated blast furnace slag (AA BFS) was $151.37 \pm 0.95 \text{ mg/g}$. Thus it can be stated that alkali-activation leads to increase of the ability to immobilize Cu(II) ions from the aqueous solution.

The decrease of weight of the samples saturated by Cu(II) ions was observed after the thermal treatment. The decrease was insignificant (maximum 0.8% of initial weight) in the case of BFS. In the case of AA BFS the increase was higher (maximum 11.7% of initial weight before thermal treatment). Thus thermal treatment of AA BFS sample could lead to changes in the mineralogical composition probably with release of chemically bonded water (dehydroxylation process) which is present in the structure due to the alkali-activation process (Shi et al. 2006; Kim et al. 2017).

Infrared spectra of the starting materials (raw BFS and AA BFS) and materials after the saturation by Cu(II) ions and the thermal treatment are shown on the Fig. 1. It can be concluded according to comparison of the spectra of raw BFS and AA BFS that alkali activation leads to increase of the -OH groups content in the material (increase of the absorbance of bands around 3200 cm^{-1}) and it leads to increase of carbonates content (band around 1445 cm^{-1}) which can be caused by interaction with air during drying. The band of stretch vibrations of silicates (around 1000 cm^{-1}) exhibits less particular isolated bands and shoulders, which can be caused by increase of amorphous character after activation. The slight changes occur in the spectra of BFS saturated by Cu(II) and thermally treated. The material treated at 100°C contains the higher amount of the structural -OH groups (3541 cm^{-1}) as well as free water (3373 and 1651 cm^{-1}). Band 1427 cm^{-1} belongs to the carbonates probably formed during drying of material. Band 1354 cm^{-1} belongs probably to nitrates which are present in the material due to utilization of copper nitrate for the saturation of materials. Materials treated at higher temperatures (500 and 1000 cm^{-1}) do not contain water, structural -OH groups, carbonates, and nitrates. These temperatures are high enough to release of these components. The little changes can be observed in the area of Si-O, Si-O-Si, Si-O-Al and Si-O-H stretch vibrations ($1200\text{--}850 \text{ cm}^{-1}$) for the materials treated at 500 and 1000°C , which can indicate incorporation of Cu to the mineral matrix of slag. The spectra of the AA BFS based materials exhibit larger changes in the compar-

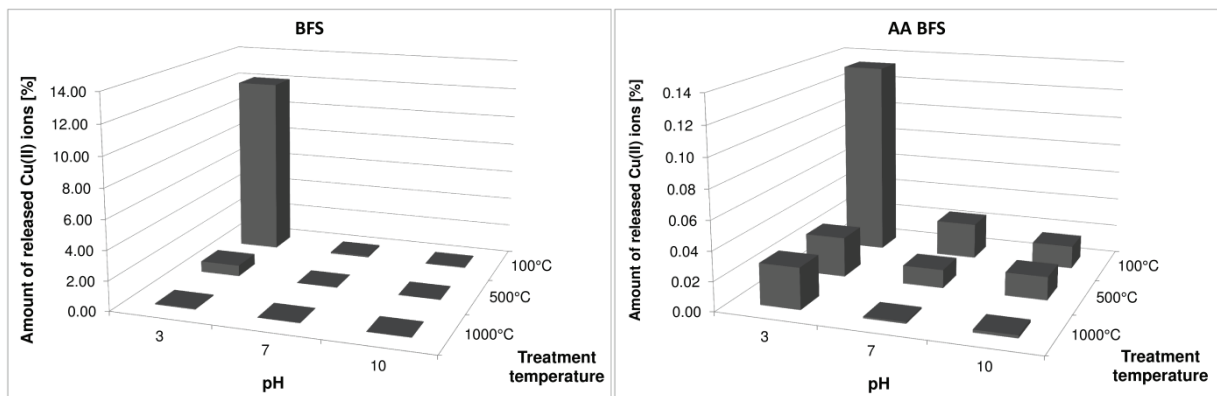


Fig. 2. Released amount of Cu(II) ions in the dependence on the pH value of the leaching solution. The released quantity is related to the content of immobilized Cu(II) ions in the individual materials

Rys. 2. Uwolniona ilość jonów Cu (II) w zależności od wartości pH roztworu ługującego.

Uwolniona ilość jest związana z zawartością unieruchomionych jonów Cu (II) w poszczególnych materiałach

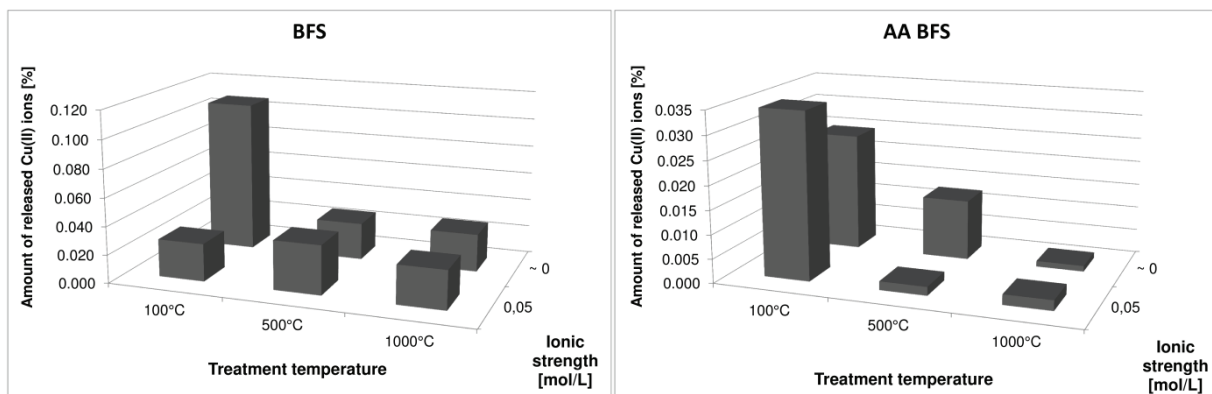


Fig. 3. Released amount of Cu(II) ions in the dependence on the ionic strength of the leaching solution. The released quantity is related to the content of immobilized Cu(II) ions in the individual materials

Rys. 3. Uwolniona ilość jonów Cu (II) w zależności od siły jonowej roztworu ługującego.

Uwolniona ilość jest związana z zawartością unieruchomionych jonów Cu (II) w poszczególnych materiałach

ison to the BFS based materials. The amount of free water (broad band around 3200 cm^{-1}) after treating of the Cu(II) saturated AA BFS material at 100°C decreases significantly compared to AA BFS and the shape of the band changes as well. These changes were probably caused by interaction of AA BFS with Cu(II) ions and by release some water during the thermal treatment. The decrease of the bands area in the O-H stretch vibration region is much higher than the decrease observed by the BFS based materials and it corresponds to the decrease of the materials weight after the thermal treatment mentioned above. The content of carbonates decreases and their mineral phase changes during the thermal treatment. It can be deduced from the decrease and shift of the band 1445 cm^{-1} . The broad band of Si-O, Si-O-Si, Si-O-Al and Si-O-H in the range $1200\text{--}850\text{ cm}^{-1}$ changes significantly during the thermal treatment, which can indicate the incorporation of Cu(II) to the mineral matrix of material as well as the increase of crystalline phases amount (Socrates, 2007).

The released amounts of the Cu(II) ions related to the total amount of copper present in the materials in the dependence on the pH value of the leaching solution are presented on the Fig. 2. It can be concluded that stability of the materials increase with the increasing temperature of thermal treatment and all materials are less stable in the acidic conditions.

The absolute amount of Cu(II) ions released from the BFS material treated at 100°C was $0.771 \pm 0.018\text{ mg/g}$ in the case of the leaching solution with pH 3, which is 12% of the total amount immobilized on the material. The released amounts at the pH values 7 and 10 were near the limit of quantification of the used AAS method. The BFS materials treated at 500°C and 1000°C were more stable, the released amounts for the leaching solution with pH 3 were $0.048 \pm 0.019\text{ mg/g}$ (500°C) resp. $0.004 \pm 0.003\text{ mg/g}$ (1000°C). The values obtained for the leaching solutions with the pH values 7 and 10 were under the limit of quantification of the used AAS method. The AA BFS based materials show higher stability of the Cu(II) binding in the comparison to the BFS based materials. Only 0.13% of the total immobilized amount of Cu(II) ions was released to the leaching solution with pH value 3 from the material treated at 100°C . This value corresponds to the absolute amount of the released Cu(II) $0.213 \pm 0.134\text{ mg/g}$ of material. The amounts released from the above mentioned material by the solutions with the pH values 7 and 10 were around 0.05 mg/L . It can be stated that the materials based on the AA BFS and treated at 500°C and 1000°C are quite less stable than the materials based on BFS and treated at the same temperatures. The released amounts for the material AA BFS treated at 500°C and leached by the solutions with the higher

pH values (3 and 10) were around 0.02 mg/g whereas the BFS treated at 500°C shows values below 0.002 mg/g, which is value for the limit of quantification of the used AAS method. The amount released from the AA BFS treated at 1000°C leached by the solution with pH 3 is higher in the comparison to the BFS treated at the same temperature. Both basic materials (BFS and AA BFS) are suitable for the immobilization of Cu(II) ions from the sight of stability to leaching, the AA BFS material has advantage in the higher immobilized amount of Cu(II) ions compared to BFS.

The stability of the prepared materials in the solutions with various ionic strengths was studied for description of foreign ions influence on the stability of materials, e.g. influence of ionic exchange processes (Fig. 3). The demineralized water was used as leaching solution with very low ionic strength near to 0 (~ 0 mol/L) and NaNO₃ solution of concentration 0.05 mol/L was used as leaching solution with ionic strength 0.05 mol/L. The material BFS saturated by Cu(II) ions and thermally treated at 100°C is more stable in the case of the higher ionic strength when the absolute released amount of Cu(II) was 0.007 ± 0,003 mg/g in the case of solution with ionic strength ~ 0 mol/L and under 0.002 mg/g (under the limit of quantification of the used AAS method) in the case of the solution with the ionic strength 0.05 mol/L.

The other materials (treated at 500°C and 1000°C) show no significant difference among the studied values of ionic strength and the released amount of Cu(II) was under the limit of quantification of the used AAS method. The material AA BFS treated at temperature 100°C exhibits a little bit higher stability in the case of the lower ionic strength, the absolute released amount of Cu(II) ions is 0.040 ± 0.022 mg/g (ionic strength ~ 0 mol/L) and 0.056 ± 0.010 mg/L (ionic strength 0.05 mol/L). The AA BFS treated at 500°C exhibits an opposite trend but it is more stable than the material AA BFS treated at 100°C. In the case of material treated at 1000°C the released amount was very low and the difference between the ionic strengths was negligible.

Conclusion

The utilization of raw and alkali-activated blast furnace slag for the immobilization of Cu(II) ions was investigated.

Alkali-activation was performed by solution of water glass and NaOH. Materials were saturated by Cu(II) ions. The immobilized amounts were 6.35 ± 0.12 mg/g in the case of raw slag and 151.37 ± 0.95 mg/g in the case of alkali-activated slag. The alkali-activated slag is more efficient in the immobilization of Cu(II) ions. The saturated materials were thermally treated at temperatures 100, 500, and 1000°C. The structural changes were studied by infrared spectroscopy. The thermal treating leads to the slight structural changes in the case of blast furnace slag but the changes of the material's structure were significant in the case of alkali-activated slag when dehydroxylation processes and decomposition of carbonates and nitrates probably take place. Changes in the silicate matrix structure were proved by infrared spectroscopy as well. The Cu(II) ions probably incorporate to the matrix of samples during the thermal treatment. Leaching of Cu(II) ions from the thermally treated materials by the solutions with various pH values (3, 7 and 10) and by the solutions with various ionic strengths (ionic strength set by the NaNO₃) was studied. The materials based on alkali-activated slag exhibit the higher stability to the leaching of the Cu(II) ions compared to raw slag based materials when only 0.13% of the total immobilized amount of the Cu(II) ions was released to the solutions during the leaching experiment in the case of alkali activated blast furnace slag compared to 12% in the case of raw blast furnace slag. The higher temperature of treatment leads to more stable material in the case of both types of slags. The studied materials are less stable at under the acidic conditions then under the neutral and alkaline conditions. Blast furnace slag, especially alkali-activated, can be promising material for the Cu(II) ions immobilization and for the safe disposal of the Cu(II) containing wastes.

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Wykorzystanie żużla wielkopiecowego do immobilizacji jonów miedzi z roztworów

Utylizacja odpadów zawierających jony metali, takich jak jony Cu (II), stanowi obecnie poważny problem. W celu immobilizacji jonów Cu (II) stosuje się różne materiały. Atrakcyjny rodzaj materiału reprezentują żużle – odpady z przemysłu metalurgicznego. Surowe i aktywowane alkalicznie żużle wielkopiecowe badano pod kątem immobilizacji jonów Cu (II) z roztworu wodnego i możliwości składowania odpadów zawierających Cu (II). Żużle były nasycone jonami Cu (II). Ilość Cu (II) osadzonego na surowym żużlu wynosiła $6,35 \pm 0,12$ mg/g, a ilość osadzona na żużlu aktywowanym alkaliami wynosiła $151,37 \pm 0,95$ mg/g. Nasycone materiały poddano obróbce termicznej w 100, 500 i 1000°C. Obróbka termiczna prowadzi do niewielkich zmian strukturalnych w przypadku surowego żużla i znacznych zmian strukturalnych w przypadku żużla aktywowanego alkaliami. Jony Cu (II) prawdopodobnie wypełniają matrycę materiałów. Materiały na bazie żużla aktywowanego alkaliami wykazują wyższą stabilność wymywania jonów Cu (II) w porównaniu z żużłami surowymi. Uzyskano immobilizację wynoszącą 0,13% całkowitej unieruchomionej ilości jonów Cu (II) dla żużla aktywowanego i 12% w przypadku żużla surowego. Obróbka w wyższej temperaturze prowadzi do uzyskania bardziej stabilnego materiału w przypadku obu rodzajów żużla. Badane materiały są mniej stabilne w warunkach kwasowych niż w warunkach obojętnych i alkalicznych. Żużel wielkopiecowy aktywowany alkaliami może być obiecującym materiałem do immobilizacji Cu (II) i do bezpiecznego usuwania odpadów zawierających Cu (II).

Słowa kluczowe: żużle, stabilizacja, zestalanie, desorpcja, jony miedzi, obróbka termiczna