

Sorption Properties of Slags

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Abstract

The aim of this work was to find if slags could be multifunction sorbents. Investigated slags were blast-furnace slag and steel making slag. The contribution is aimed at characterization of slags and their sorption properties. The characterization of slags were performed by X-ray fluorescence spectroscopy and infrared spectroscopy. It was found by infrared analysis that blast furnace slag contains mainly silicates and a small amount of carbonates. Steel making slag has lower content of silicate minerals and a higher amount of carbonates. The characterized samples of the blast furnace and steel making slags were tested as possible sorbents. The sorption experiments were carried out by batch method in aqueous medium. The selected metal cations (Cu(II) and Zn(II)) and anions (CrO_4^{2-}) were used as adsorbates. The sorption experiments were performed with standards of slags to find the best ratio for sorption of metals cations and chromates. The best ratio for sorption metals cations was 1:200 (solid:liquid) for both slags. The best ratio for sorption of chromates was 1:100 for steel making slag and 1:200 for blast-furnace slag. It was found that metal cations removing is influenced by alkalization property of slags. Maximum adsorbent amount of cooper is 0.23 mmol/g on the blast-furnace slag and 0.38 mmol/g on the steel making slag. Maximum adsorbent amount of zinc is 0.17 mmol/g on the blast-furnace slag and 0.35 mmol/g on the steel making slag. The maximum adsorbed amount of chromates for the blast-furnace slag is 15 $\mu\text{mol/g}$ and for steel making slag is 89 $\mu\text{mol/g}$. The mechanism of the metal cations removing is supposed to be an adsorption combined with precipitation indicated by a high pH after sorption experiments. Slags can be possibly used for remediation of wastewater containing metal ions.

Keywords: sorption, slag, metal cations, chromates

Introduction

Slags as secondary products of metallurgical processes are often applied in the construction industry as admixture to the concrete. They could be also used for wastewater purifying according to their structural properties. The contamination of soil and water by metals cations and other substances is serious problem in the global scale. The most used method for water purifying from metals cations is adsorption on various matrix e.g. natural based on silicates (Li et al., 2009; Sdiri et al., 2014; Dascălu et al., 2014) or on special prepared materials (Yavari et al., 2014; Cretescu et al., 2014). The Cr(VI) is considered to be toxic for organisms and it is commonly known as carcinogen. Many studies for Cr(VI) removal from aqueous solutions on natural materials (Baig et al., 2014; Zou et al., [in press]) or on special prepared materials (Pshinko et al., 2014; Zou et al., [in press]) have been widely documented.

Slags as secondary products of metallurgy were used previously for pollutants adsorption studies from wastewater (Dimitrova, 1996; Dimitrova and Mehanjiev, 2000; Kostura et al., 2005; Xue et al., 2009). Slag is a multicomponent material, where silicates are the major component. Composition,

structure, physical and physico-chemical properties of slag depend on the type of metallurgical process, on the raw materials introduced to the furnace, temperature or individual conditions of slag production.

Blast-furnace slag (formed by basic and acid oxides depending on a type of iron production) contains non-metallic components of furnace batch from the metallurgic process. Steel making slag is formed by production of steel, where it acts as a refining factor. The structural and chemical composition of slag is affected by removal of undesirable impurities from melted iron. Amounts and types of impurities affect also physical-chemical properties of steel slag (Hübner and Chvátal, 1988).

The article deals with sorption of Cu(II), Zn(II) and CrO_4^{2-} on two types of slag – steel making and blast-furnace slag. Their adsorption isotherms were measured in the solution with untreated pH and at given pH value of the sorption solution. The slags were characterized with infrared spectroscopy (IR) and X-ray fluorescence spectroscopy (XRF).

Materials and methods

Two types of slags, steel making slag (Soc) and blast-furnace slag (Sv), were kindly provided

Tab. 1. Chemical composition of slags

Tab. 1. Skład chemiczny żużła

Proportional composition	Blast-furnace slag	Steel making slag
	%	%
Na ₂ O	0.43	0.42
MgO	12.70	8.80
Al ₂ O ₃	7.20	1.69
SiO ₂	38.20	15.10
P ₂ O ₅	0.20	1.62
SO ₃	1.68	0.15
K ₂ O	0.43	0.00
CaO	37.30	26.40
TiO ₂	0.42	0.38
MnO	0.44	5.70
Fe ₂ O ₃	0.39	43.70

by ArcelorMittal Ostrava a.s. and they were used for experiments. Two types of standards of slags were used for study, steel making slag – BCS No. 381 BASIC SLAG (Soc std.) and blast-furnace slag – Slovak reference material No. 7-1-005 (Sv std.). All used chemicals were of analytical grade. Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O (Lach-Ner, s.r.o. Czech Rep.) were used for preparation of metals cations solutions and K₂CrO₄ (Lach-Ner, s.r.o. Czech Rep.) was used for preparation of CrO₄²⁻ solution. The standards of metals cations for atomic absorption spectrometry (Cu, Zn – Sigma-Aldrich) and K₂CrO₄ (Lach-Ner, s.r.o. Czech Rep.) were used for AAS analysis of the metals.

The characterization of slags was performed by XRF and IR spectroscopy. XRF analyses were carried out at Nanotechnology centre, VŠB-Technical university of Ostrava. Infrared spectra of the studied slags were recorded on spectrometer FTIR Nicolet 6700 (TermoNicolet, USA) equipped with the DTGS/KBr detector in the middle IR range. The KBr pressed-disc (13 mm diameter) technique (2 mg of sample and 250 mg of KBr) was used. The spectra were measured in the spectral range 4000–400 cm⁻¹ (64 scans, 4 cm⁻¹ resolution, apodization Happ-Genzel) with baseline correction.

The sorption experiments were performed by batch technique. In the first instance, experiments for finding the best ratio (ratio solid : liquid) were performed for further sorption experiments. Standards of slags (Soc std. and Sv std.) were used for these experiments and the ratios 1:50, 1:100 and 1:200 were investigated and the best ratio was used for the sorption experiments on the real samples of slags. The conditions for sorption of metals cations for Cu(II) and Zn(II) were used: the ratio 1:200, the concentration in the range 10⁻⁴–10⁻²

mol/L, 24 hours contact time and ambient temperature. The conditions for sorption CrO₄²⁻ were: the ratios 1:100 (Soc) and 1:200 (Sv), concentration in the range 10⁻⁵–10⁻⁴ mol/L, 24 hours contact time and ambient temperature. The metal concentrations in the supernatants after the sorption were determined by means of atomic absorption spectrometry (AA240FS Varian, USA).

Results and discussion

Characterization of slags

The Table 1 shows the results of the elemental composition of slags performed by XRF analysis. The trace composition of slags is very similar, but the differences are in the content the major substances SiO₂, CaO, Al₂O₃, Fe₂O₃. These differences have the major impact on the properties and the structure of the slags.

The infrared spectra of the studied slags are compared in Figure 1. As it was found by XRF analysis the slags contain mainly SiO₂, Fe₂O₃, CaO, Al₂O₃.

The spectrum of blast-furnace slag contains broad band between 1100 and 850 cm⁻¹ which can be assigned to the valence vibration of Si-O, Si-O-Si and Si-O-Al bonds. The vibrations at 853 and 760 cm⁻¹ can be vibrations of quartz. Band around 1415 cm⁻¹ is due to vibration of carbonate ion. Shoulder at 3538 cm⁻¹ is probably caused by structural –OH vibration. The absorption bands of water valence (3425 cm⁻¹) and deformation (1620 cm⁻¹) showed the presence of some molecular water in the material.

The steel making slag have a smaller amount of silicates, but their presence could be approved from the broad band with several shoulders in the range 1100–800 cm⁻¹. The content of carbonates is

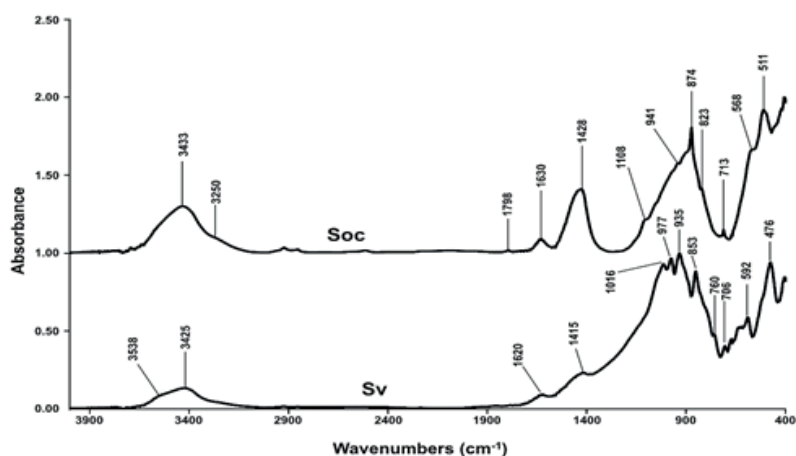


Fig. 1. Infrared spectra of the studied slags
 Rys. 1. Spektrum w podczerwieni badanych żużli

higher in comparison with the blast-furnace slag. The peak at 1428 cm^{-1} is typical for the valence vibration of carbonate ions CO_3^{2-} . Calcite (1798 , 1428 and 874 cm^{-1}) is the major form of the carbonates present in the material. Shoulder 3250 cm^{-1} is probably band of structural $-\text{OH}$ group. Absorption bands of molecular water (3433 cm^{-1} and 1630 cm^{-1}) are also present in the spectrum.

Sorption of copper and zinc cations and chromates anions

The contact time (24 h for all experiments) was chosen to ensure that the sorption equilibrium will be achieved. It was found that the pH value of the sorption media increased in the case of both real slag types due to a self-alkalization property of the slags. The pH increase was found for all studied ratios solids: liquid and was higher in the case of the steel making slag. The pH changes at the blast-furnace slag are in the range of 1 pH unit for all concentrations of metals cations, but the pH changes at the steel making slag are in the range of 5 pH units. The similar conditions were observed for both metals cations. The increase of pH value is higher with the decreasing concentration of Cu(II) and Zn(II) . This is probably due to precipitation of metals cations on the surface in the form of complexes. The alkalization property of slags occurred also during the sorption of chromates, but the pH changes are in the range of 2 pH units, although the final pH value was 12. It can be assumed that the removing of the chromates is due to the adsorption than precipitation on the surface of the slags because the chromates do not create the precipitate in the high pH values.

The sorption experiments were performed with standards of slags with different ratios solid liq-

uid (1:50; 1:100; 1:200) for the determination of suitable ratio for the sorption of metals cations and chromates. The best ratio was chosen on the basis of these experiments and experiments were performed with real samples of slags. The best ratio was 1:200 for all samples except from copper and blast-furnace slag. The maximum adsorbed amounts of copper by standard of blast-furnace slag are very similar for different ratios (Fig. 2). The ratio 1:200 was chosen for all further experiments to save the material. The maximum adsorbed amounts on the real samples of slags do not reach the values obtained for standards but the real samples still achieve very good results for metals cations removal from the solution. The maximum adsorbed amount of copper cations on the blast-furnace slag is 0.23 mmol/g and 0.38 mmol/g on the steel making slag. The maximum adsorbed amount of zinc cations on the blast-furnace slag is 0.17 mmol/g and 0.35 mmol/g on the steel making slag.

When the slags get in the contact with sorption solutions as it is described above, the increase of pH has been found. The mechanism of the self-alkalization property represents acid-basic interactions in the heterogeneous system, which means mainly hydrolysis of calcium silicates (Dimitrova, 1996). The self-alkalization property of the slag caused that a certain part of Cu(II) is present as dissolved complex forms and insoluble copper(II) hydroxide (Xue et al. (2009) or other insoluble complexes during the sorption process. A presence of Zn(II) predominantly in the insoluble forms (hydroxide) suggests the Zn(II) sorption by means of its hydroxide precipitation on the slags surface (Xue et al. (2009)).

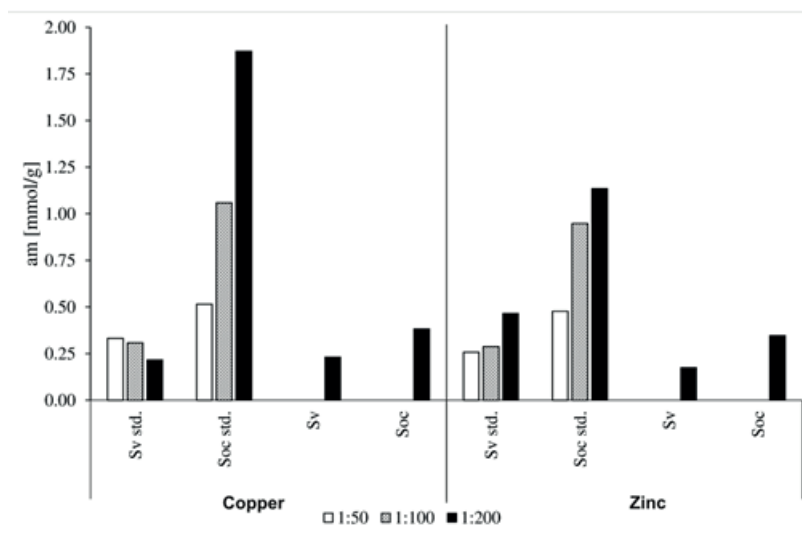


Fig. 2. Maximum adsorbed amount am [mmol/g] of Cu(II) and Zn(II)
 Rys. 2. Największa zaadsorbowana ilość am [mmol/g] Cu(II) and Zn(II)

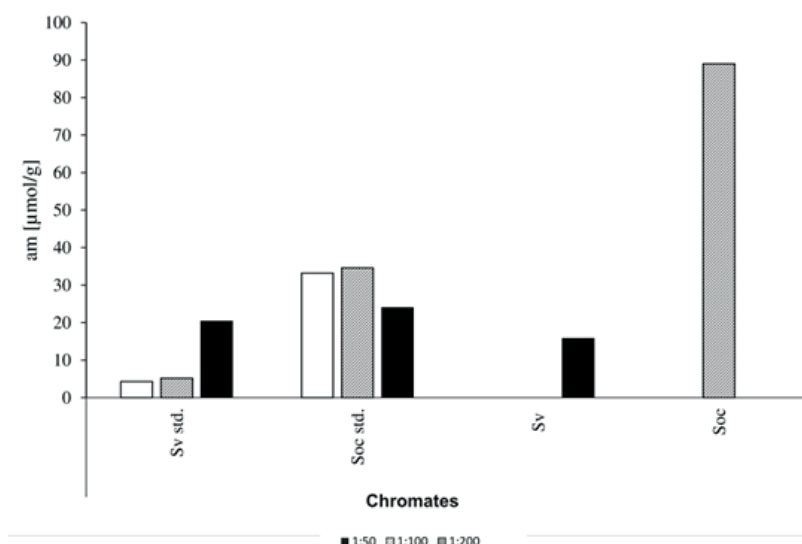


Fig. 3. Maximum adsorbed amount am [μmol/g] of Chromates
 Rys. 3. Największa zaadsorbowana ilość am [μmol/g] chromianów

However, it is not easy to suggest the removal mechanisms (precipitation or sorption) of the metals ions on the slags. Another probable mechanism is an ion exchange. Considering the fact that the products of the slag hydrolysis may be released into the sorption solution and this process is accompanied with the sorption of metals cations on the surface of slags, then mechanism could be the ion exchange (Dimitrova and Mehanjiev, 2000). The substances released into solution have very important influence to increase pH of solution and they are the reason of precipitation on the slags surface. Therefore it is not easy to identify simply and unambiguously a mechanism for removal of metal cations from solution.

The differences between the sorption capacities of the slags for both metals cations can be explained by composition of slag and thus their properties. The self-alkalization property of slag is more intense by the steel making slag. The differences between the sorption capacities of the slags for Cu(II) and Zn(II) can be explained by a presence of various forms of the metals in the aqueous solution (Xue et al. (2009)).

The sorption experiments of chromates were performed on the standards of slags and on base of these experiments the best ratio for the sorption experiments on the real samples of the slags was chosen.

The suitable ratio for the sorption on the blast-furnace slag is 1:200, but for the steel mak-

ing slag the best ratio is 1:100. The maximum adsorbed amounts for real samples of steel making slag achieve higher value than of the standards with the same ratio. The maximum adsorbed amount for the blast-furnace slag Sv is 15.8 $\mu\text{mol/g}$ and for the steel making slag Soc is 89 $\mu\text{mol/g}$ (Fig. 3).

The sorption capacities of the slags for the removal of chromates from the solution are very low in comparison with metal cations. It is probably as a result of the higher self-alkalization property of slags. As it was described above, the sorption system achieves the pH value about 12 after sorption. But the most authors claim (Baig et al., 2014; Pshinko et al. 2014; Zou et al., [in press]), that the best conditions for the removal Cr(VI) from the solution are the acid or weakly acid pH in the dependence on the material.

The higher the pH value indicate the lower sorption of Cr(VI) (Pshinko et al. 2014) and it is apparent, that the self-alkalization property of slags is very problematic for the sorption chromates on this materials. Adjustments of the sorption system pH will be necessary for the improvement of the sorption capacities. The pH value of the solution does not affect only the properties of the material for the removal of chromates from the solution, but in the same time it affects the species of Cr(VI) in the aqueous solution. The species are $\text{H}_2\text{Cr}_2\text{O}_7$ at $\text{pH} < 1$, HCrO_4^- at $1 < \text{pH} < 6$ and at $\text{pH} > 6$ is CrO_4^{2-} (Zou et al., [in press]).

Explanation of the higher sorption capacity of the real steel making slag in comparison with the

standard of steel making slag can consist in the slag composition. The presence of iron cations in the various forms depending on the composition and structure of the materials can affect the sorption of Cr(VI) and Cr(VI) may be removed by reduction with iron cations and the subsequent sorption as $\text{Cr}(\text{OH})_3$ on the surface of the slag (Baig et al. 2014).

Conclusion

The sorption of the metals cations and the chromates was carried out on two types of the slags – blast-furnace and steel making slag. The data in this paper shows that both types of slag are effective sorbent of chosen pollutants. The maximum adsorbed amounts for the blast-furnace slag are 0.23 mmol/g for copper and 0.17 mmol/g for zinc and for the steel making slag are 0.35 mmol/g for copper and 0.38 mmol/g for zinc. However, the accurate mechanism for the removal of metals cations is not identified but a combination of sorption and precipitation on the surface of slags is supposed. The maximum adsorbed amounts of chromates are 15.8 $\mu\text{mol/g}$ for the blast-furnace slag and 89 $\mu\text{mol/g}$ for the steel making slag. The higher amounts of the iron in the materials could increase the sorption properties of the materials for the removal chromates from the solution.

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Właściwości sorpcyjne żużla

Celem pracy było sprawdzenie czy żużle mogą być wielofunkcyjnymi sorbentami. Badaniu poddano żużel wielkopiecowy oraz żużel stalowniczy. W pracy skupiono się na przygotowaniu charakterystyki żużli i ich właściwości sorpcyjnych. Przeprowadzono badania spektroskopem fluorescencji rentgenowskiej oraz spektroskopem w podczerwieni. Dzięki analizie w podczerwieni odkryto, że żużel wielkopiecowy zawiera głównie krzemiany i niewielkie ilości węglanów. Żużel stalowniczy zawiera niższą wartość krzemianów i wyższą węglanów. Opisane próbki żużli wielkopiecowych i stalowniczych zostały sprawdzone jako potencjalne sorbenty. Testy sorpcji zostały przeprowadzone metodą partii w środowisku wodnym. Wybrane kationy metali (Cu(II) oraz Zn(II) oraz aniony (CrO₄-2) zostały użyte w charakterze adsorbatów. Badania sorpcji zostały przeprowadzone z zachowaniem standardów, aby znaleźć najlepszą proporcję kationów metali do chromianów dla przeprowadzenia sorpcji. Najlepszy stosunek dla sorpcji kationów metalu wyniósł 1:200 (faza stała: ciecz) w obydwu rodzajach żużla. Najlepszy współczynnik dla sorpcji chromianów wyniósł 1:100 dla żużla stalowniczego oraz 1:200 dla żużla wielkopiecowego. Odkryto, że na eliminację kationów metalu mają wpływ właściwości alkalinizujące żużli. Najwyższa wartość adsorpcji miedzi wynosi 0,23 mmola/g w przypadku żużla wielkopiecowego i 0,38 mmola/g w żużlu stalowniczym. Najwyższa wartość adsorpcji cynku wynosi 0,17 mmola/g przy żużlu wielkopiecowym i 0,35 mmola/g przy żużlu stalowniczym. Maksymalna wartość adsorpcji chromianów dla żużla wielkopiecowego wyniosła 15 μmola/g, a przy stalowniczym 89 μmola/g. Mechanizm usuwania kationów metalu powinien być połączeniem adsorpcji ze strącaniem przy wysokim pH. Wykazano, że można stosować żużle do oczyszczania wód ściekowych zawierających jony metali.

Słowa kluczowe: sorpcja, żużel, kationy metali, chromiany