

Adsorption capacity of modified metallurgical slag

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A study was conducted of the adsorption capacity of slag samples obtained by crystallization of granulated blast furnace slag with and without Al₂O₃ and MgO additions in aqueous solutions of Cu (II), and a comparison was made between the original amorphous slag and the synthesized samples with main phases gehlenite and åkermanite. The purpose of the study was to make evaluation of the adsorption of heavy metal ions by the main phases (crystalline and amorphous) of blast furnace slag. The comparative analysis of adsorption and XRD data showed that the formation in slag of melilite crystal phases (gehlenite and åkermanite) and merwinite results in an almost double increase of Cu (II) adsorption, compared to amorphous slag. The addition of Al₂O₃ alone and in combination with MgO leads to crystallization of a sorption inactive spinel phase.

Key words: blast furnace slag, Cu (II) adsorption, crystallization, merwinite, melilite.

INTRODUCTION

The disposal of a large volume of metallurgical slags as by-products in iron and steel industry is an important environmental and economic problem. Its solution should be sought in three directions: 1) use in construction (production of cement, concrete, railroad ballast, roof coverings, mineral wool, glass, etc.); 2) extraction of useful components 3) water treatment reagents (neutralization and precipitation systems for purification of industrial water contaminated by heavy metals, adsorbents).

The good adsorption capacity of blast-furnace slag (BFS) for heavy metals, phosphates, arsenic (V and III) and organic pollutants [1-6] provides good opportunity for the use of slag in locally based processes of waste water treatment. Slag low price and large quantities are a prerequisite for the economic efficiency of such treatment processes. The BFS chemical composition and structure play a key role in the adsorption activity. Previous research on sorp-

tion-active phase/phases in BFS [7, 8] has shown the positive effect of the thermal treatment of granulated blast furnace slag (GBFS) due to the crystallization of melilite – a crystal phase typical for BFS. The term melilite is used to denote the representatives of isomorphic series gehlenite (Ca₂Al₂SiO₇) – åkermanite (Ca₂MgSi₂O₇). However, in its broad sense the term also encompasses other crystalline phases of a melilite-type structure. The melilite structure tolerates isomorphic substitutions; therefore, the formation of a melilite phase with a complex composition is highly probable, given the complex composition of Kremikovtsi BFS (presence of Mn, Fe, Ba, Na, etc.). In addition to components such as gehlenite (Ca₂Al₂SiO₇) and åkermanite (Ca₂MgSi₂O₇), amounts of Ca₂MnSi₂O₇, Ca₂Fe²⁺Si₂O₇, Ca₂Fe³⁺₂SiO₇ as well as partial substitutions in the structural positions of Ca by Ba and Na should also be expected. Similar-type melilites containing barium and manganese have been found in Kremikovtsi BFS crystal samples [9]. Furthermore, synthetic melilites with a higher Ca content have been reported to exhibit large stoichiometric deviations [10]. For these reasons, the quantity of the formed melilite phase often exceeds the expected quantity based on preliminary calculations.

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The formation of melilites in Kremikovtsi BFS is limited by its low Al_2O_3 and MgO content. It could be assumed that an appropriate ratio modification of the major oxides CaO , MgO , Al_2O_3 and SiO_2 would enhance the crystallization of adsorption-active phases with a melilite structure. Therefore, the goal of the study was to add Al_2O_3 and MgO in amounts that promote melilite crystallization. The amounts to be added in slag were calculated based on the chemical composition of the original slag. The effect of these additions on the adsorption capacity of BFS was evaluated in terms of adsorption capacity to remove copper ions from aqueous solutions.

EXPERIMENTAL

Synthesis of samples

The samples were synthesized using GBFS with the following composition (in %_{mass}): SiO_2 – 34.0; CaO – 44.0; Al_2O_3 – 6.40; MnO – 2.33; MgO – 2.45; BaO – 3.2. In the present study the original granulated slag sample is denoted as sample GBFS.

The following samples were synthesized:

- Sample GBFS/1050 – the sample of granulated blast furnace slag was crushed with a mortar and then heated at 1050 °C for 6 hours in air.
- Sample GBFS/1400 – using the same procedure, heated at 1400 °C.
- Sample GBFS+ Al_2O_3 – mixture of 2 g slag and 0.72 g of aluminum oxide crushed and heated for 6 hours at 1400 °C.
- Sample GBFS+ MgO – mixture of 2 g slag and 0.3 g magnesium oxide heated at 1400 °C for 6 hours.
- Sample GBFS+ Al_2O_3 + MgO was obtained by using the above procedure plus additions of 0.24 g aluminum oxide and 0.15 g magnesium oxide to amount of 2 g of the original slag.

The synthetic gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) was obtained through solid-state synthesis using the following high purity (over 98.5%) reagents: CaCO_3 , Al_2O_3 and SiO_2 . A stoichiometric mixture of 1.56 g CaCO_3 , 1.02 g Al_2O_3 and 0.60 g SiO_2 , crushed in an agate mortar and placed in a corundum crucible, was heated successively at 1000, 1200 and 1400 °C for 6 hours with intermediate grinding of the product. The same procedure was used to synthesize synthetic åkermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), by mixing 1.56 g CaCO_3 , 0.403 g MgO and 1.20 g SiO_2 . The synthesis of samples was performed in a high-temperature *Kanthal Super* furnace with Temperature Controller/Programmer. The XRD analysis showed that the synthesis of both minerals occurred at temperatures above 1200 °C. The synthesis was conducted at the maximum temperature (1400 °C) at

which they are treated slag samples. Under these conditions, the main phases in the samples are, respectively, gehlenite and åkermanite.

Experimental methods

Structural characterization was performed by powder X-ray diffraction (XRD) using a Bruker D8 Advance Powder Diffractometer with $\text{CuK}\alpha$ radiation and a SolX detector. XRD spectra were recorded at room temperature. Data were collected in the 2θ range from 10 to 80 degree with a step 0.04 degree and 1s/step counting time. The crystalline phases were identified using the powder diffraction files PDF 35-0755, PDF 35-0592, PDF 79-2422, PDF 79-2423, PDF 79-2424, PDF 74-0874, PDF 35-591, PDF 33-0302, PDF 70-2144, PDF 34-1350 and PDF 82-2424 from database JCPDS - International Centre for Diffraction Data PCPDFWIN v.2.2. (2001) [11]

Adsorption evaluation of Cu (II) cations by the synthesized samples was conducted through an adsorption test under the following static conditions: 9 samples of 0.1 g of each sample and 100 ml of CuSO_4 solution; Cu (II) concentration of 25.45 mg/L; pH 5.40, placed for 48 hours in an oven thermostat at 25 °C to establish equilibrium.

Then samples were filtered and the values of the pH of the filtrate and Cu (II) concentration were measured. The concentration of Cu (II) was determined photometrically at $\lambda = 560$ nm using DR 2800 Spectrophotometer.

The adsorption capacity was calculated as:

$$A = \frac{(C_0 - C) \times V}{m}$$

Where: A – adsorption capacity (mg/g); C_0 – original Cu(II) concentration in the solution (mg/L); C – Cu(II) concentration in solution after 48 h. (mg/L); V – Cu (II) solution volume (L); m – mass of the sample (g).

RESULTS AND DISCUSSION

Figures 1 and 2 represent the X-ray diffraction patterns of the studied samples. In Fig. 1 (Sample GBFS XRD pattern) a halo is observed between 20 and 40° 2θ , which points to the predomination of an amorphous phase in the sample, i.e. slag glass. The diffraction peaks are related to the early stages of melilite crystallization. Heat treatment of blast furnace slag at 1050 °C (sample GBFS/1050) leads to melilite (PDF 79-2423) crystallization, accompanied by crystallization of calcium silicate CaSiO_3 pseudowollastonite (PDF 74-0874). The increase

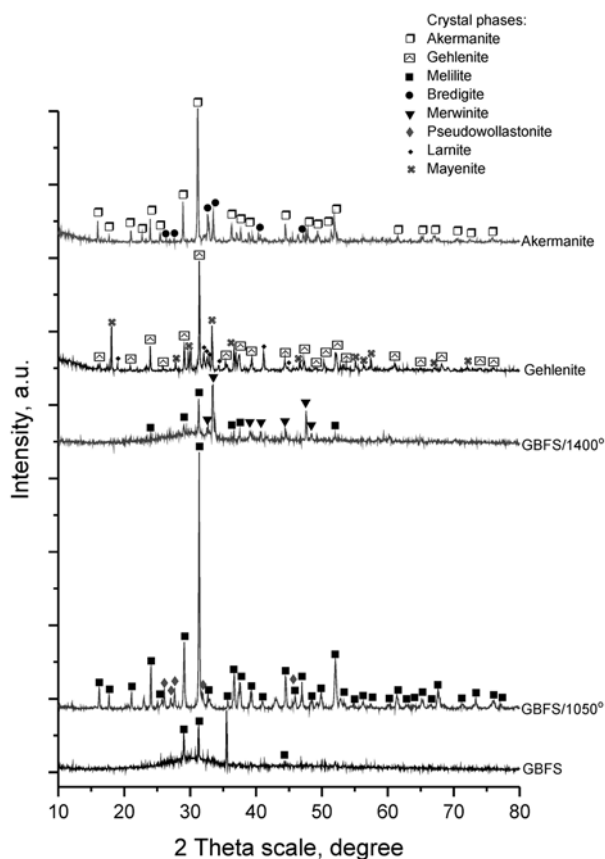


Fig. 1. XRD patterns of thermal treated slag samples and synthesized samples with main phases åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and gehlenite ($\text{Ca}_2\text{AlSiO}_7$)

of treatment temperature up to 1400 °C (sample GBFS/1400) resulted in melt crystallization of merwinite $\text{Ca}_3\text{Mg}[\text{SiO}_4]_2$ (PDF 35-591) and melilite (79-2424). The separate or simultaneous addition of MgO and Al_2O_3 affected differently the phase formation. The X-ray diffractograms of sample GBFS+ Al_2O_3 (with added Al_2O_3) and GBFS/1050 sample are similar in the predomination of melilite (PDF 79-2423 and PDF 79-2422) in both samples. Differences are found in the other crystal phases. The addition of Al_2O_3 leads to crystallization of some amounts of spinel (PDF 82-2424) in sample GBFS+ Al_2O_3 . Melilite (PDF 79-2423) is also the main phase in sample GBFS+ Al_2O_3 +MgO and the amount of the accompanying spinel is higher. The X-ray diffraction pattern of sample GBFS+MgO shows increased amounts of merwinite (PDF 35-591, compared to sample GBFS/1400 (without additions), both samples treated at the same temperature.

Figure 1 shows the X-ray diffraction patterns of the synthesized minerals gehlenite and åkermanite. The XRD patterns show successful synthesis of the specified minerals, but intermediate

phases are also found. In Gehlenite sample these are gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (PDF 35-0755), larnite Ca_2SiO_4 (PDF 33-0302), and mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (PDF 70-2144). In Åkermanite sample åkermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (PDF 35-0592) is the predominant crystal phase, but bredigite $\text{Ca}_7\text{Mg}[\text{SiO}_4]_4$ (PDF 34-1350) is also present.

Adsorption-capacity (AC) data is given in Tables 1 and 2. It can clearly be seen that slag AC is determined by the level of crystallization and the type of the crystalline phases. The lowest capacity is shown by the original sample, which is (according to XRD data) amorphous for the most part and contains small amount of melilite. The sample (sample GBFS/1050) heat treatment up to 1050 °C for 6 hours induces a higher level of crystallization. Melilite and pseudowollastonite are formed and the adsorption capacity (AC) is raised by 9%, compared to the original sample (GBFS). Heat treatment at 1400°C results in a sharp 83% increase in the retained Cu (II) compared with the original sample. Apart from melilite, in sample (GBFS/1400) merwinite is also present. The amount of melilite in sample GBFS/1400 is significantly smaller than in

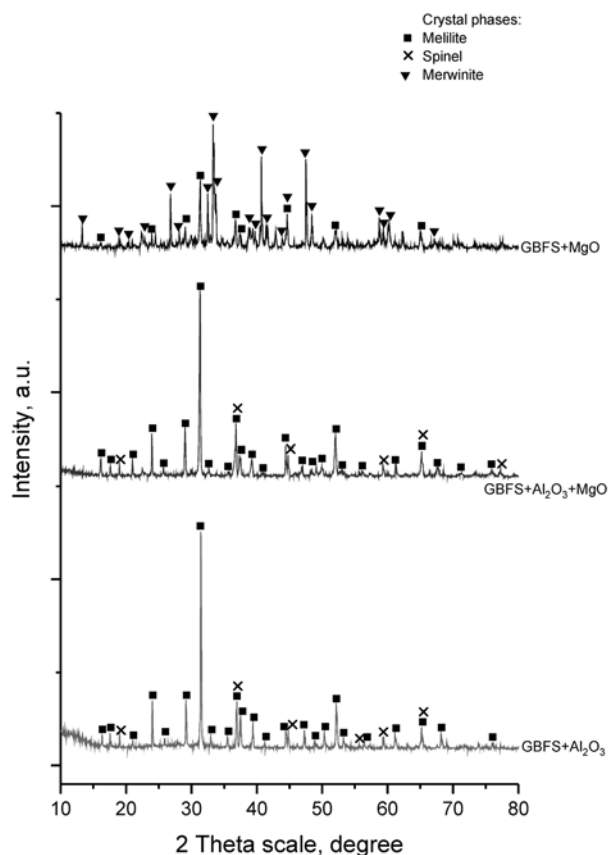


Fig. 2. XRD patterns of thermal treated slag samples with Al_2O_3 and MgO additions

Table 1.

Sample	A, mg/L	Phases
GBFS	13.3	amorphous phase + melilite
GBFS/1050	14.5	melilite + pseudowollastonite
GBFS/1400	24.4	amorphous phase + merwinite + melilite
Gehlenite	23.4	gehlenite + mayenite + larnite
Åkermanite	21.6	åkermanite + bredigite

sample GBFS/1050. Therefore, the higher AC of the slag sample treated at higher temperature can be related to the formation of a merwinite crystal phase and/or a residual glass phase.

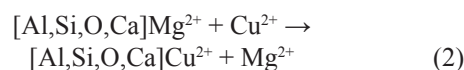
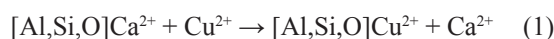
The AC of slag samples with Al₂O₃ and MgO additions is generally lower when compared to the sample GBFS/1400 without additions, treated at the same temperature (Table 2). One exception is sample GBFS+MgO, which shows the maximum AC increase of 88 %, compared to the original slag material. The phase composition of this sample also differs, merwinite being its main phase. This leads to a conclusion that the presence of merwinite improves the adsorption properties of slag materials. AC data for the remaining slag samples with Al₂O₃ and MgO additions is similar and corresponds to their close phase composition. It is evident that additions in slag do not lead to an increase of the amount of melilite. The amount of the melilite phase in pure slag treated at 1050 °C is higher. In most of the samples, the additions react with other components in slag and new adsorption-inactive phases are formed: spinels. The synthetic samples with gehlenite and åkermanite as predominant phases also have a high AC. The obtained results are in complete accordance with previous findings [7, 8] reporting that increase of the level of crystallization and the presence of melilite phases (such as gehlenite and åkermanite) result in significant increase of slag AC. On the other hand, one should bear in mind the presence of other crystal phases in the samples that also affect the AC. Therefore, we can not make firm conclusions about the roles played by åkermanite and gehlenite.

Table 2.

Sample	A, mg/L	Crystal phases
GBFS+Al ₂ O ₃	15.2	melilite + spinel
GBFS+Al ₂ O ₃ +MgO	15.3	melilite + spinel
GBFS+MgO	25.0	merwinite + melilite

According to the XRD data (Fig. 1 and 2), many slag samples contain identical amounts of åkermanite and gehlenite in the melilite crystal phase of the synthesized samples. However, slag samples with a predominant melilite crystal phase exhibit lower AC compared to the synthesized samples. This means that besides the phase composition and respectively quantity of the melilite phase, other factors have a significant impact on the adsorption properties, most probably the structural characteristics of the samples and the chemical composition of formed melilite. The obtained experimental data does not permit to establish clear dependency between the amounts of melilite in samples and the AC value, but it is indisputable that a 9-15 % higher AC is observed in slag samples with a predominant melilite, compared to the original slag.

The presented experimental data allows finding a correlation between the phase composition and the adsorption properties of BFS. The presence of merwinite and melilite induces a higher AC of the slag samples. The results allow us to make a new and interesting conclusion – merwinite also exhibits a high AC, apart from the minerals gehlenite and åkermanite. This is proved by the fact that samples containing this mineral showed the highest AC. The addition of Al₂O₃ and Al₂O₃+MgO did not considerably influence the adsorption properties of slag samples. Only MgO addition positively affected the promotion of the merwinite crystallization. As already known [1, 7], the AC of metallurgical slag take place primarily by a cation exchange process. The adsorption is based on exchange reactions represented by the following scheme:



The possibility of exchange depends on the structure of slag and accordingly of the crystal structure of the formed minerals. Schematic diagrams of åkermanite and merwinite crystal structures are shown in Figs. 3 and 4. We have chosen åkermanite instead of gehlenite for its Mg²⁺ content. Both minerals belong to different structural types and the coordination of Mg²⁺ and Ca²⁺ cations differs. As shown earlier, [12, 13] åkermanite and gehlenite are tetragonal. The crystal cell data are: space group $P4_2m$, $a = 7.8288(8) \text{ \AA}$, $c = 5.0052(2) \text{ \AA}$ for åkermanite and. space group $P4_2m$, $a = 7.6850(4) \text{ \AA}$, $c = 5.0636(3) \text{ \AA}$ for gehlenite [13]. Åkermanite is part of the silicates with diorthogroups of silicon-oxygen tetrahedra. These structural units are linked with each other through the so-called “particular type” of tetrahedra [MgO₄]. The tetrahedral lay-

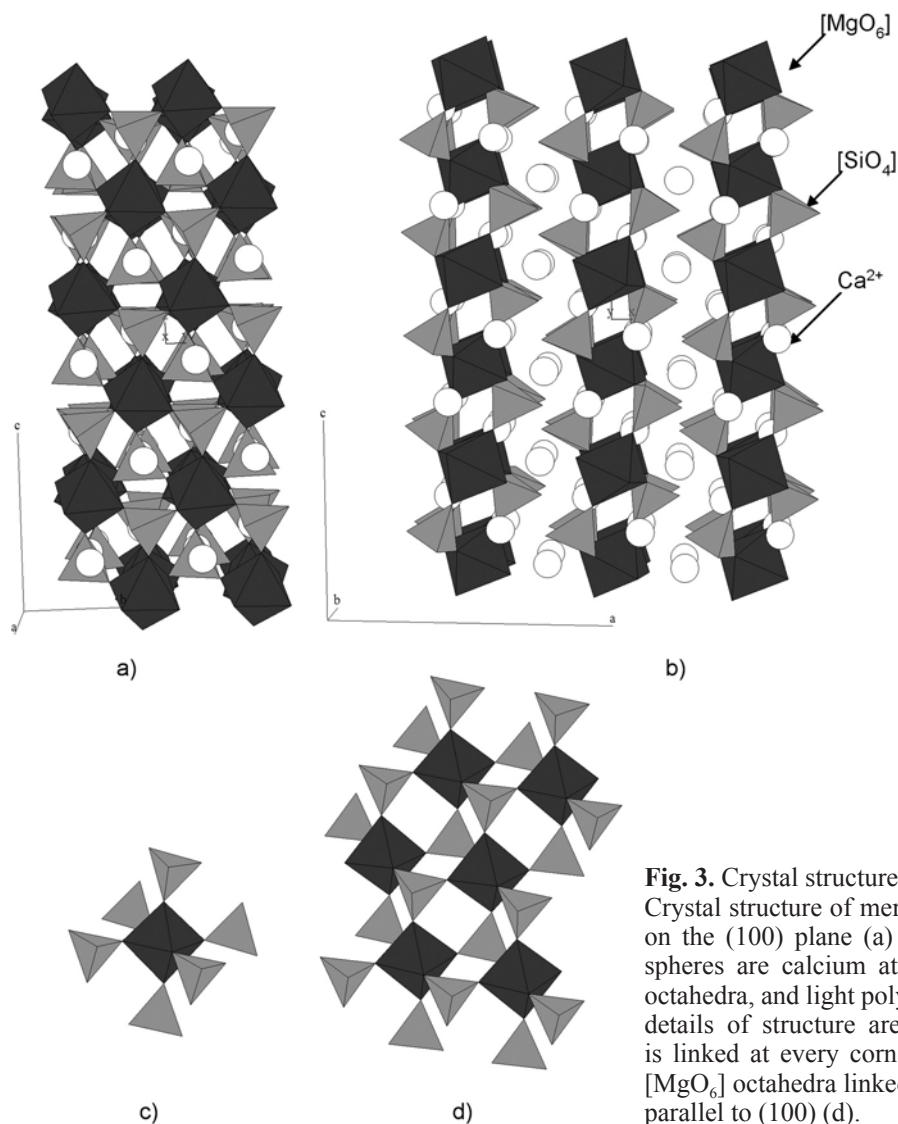


Fig. 3. Crystal structure of merwinite

Crystal structure of merwinite ($\text{Ca}_3\text{Mg}[\text{SiO}_4]_2$) projected on the (100) plane (a) and the (010) plane (b). White spheres are calcium atoms, dark polyhedra are MgO_6 octahedra, and light polyhedra are SiO_4 tetrahedra. Some details of structure are presented. $[\text{MgO}_6]$ octahedron is linked at every corner by $[\text{SiO}_4]$ tetrahedra (c). The $[\text{MgO}_6]$ octahedra linked by $[\text{SiO}_4]$ tetrahedra form slabs parallel to (100) (d).

ers alternate along c-axis with layers of calcium polyhedrons. The coordination number of Ca^{2+} is 8. Merwinite crystallizes in the orthorhombic space group $P2_1/a$ and the cell parameters are $a = 13.254(21) \text{ \AA}$, $b = 5.293(9) \text{ \AA}$, $c = 9.328(17) \text{ \AA}$, $\beta = 91.90(15)^\circ$. The structure of merwinite is an extreme example of dense packing where both O^{2-} and Ca^{2+} ions make up the dense-packed layers. The $[\text{MgO}_6]$ octahedra are linked at every corner by $[\text{SiO}_4]$ tetrahedra. The $[\text{MgO}_6]$ octahedra are linked by $[\text{SiO}_4]$ tetrahedra and form slabs parallel to (100). The Ca^{2+} ions have three structural positions with coordination numbers between 8 and 9 [15]. Despite the obvious differences, a common feature of both structures is the location of Ca^{2+} cations in layers between slabs of linked silicon and magnesium polyhedrons. Probably this structural feature permits the easy exchange of Mg^{2+} and Ca^{2+} cations, which increases the AC of slag containing these minerals.

The experimental results show that besides the melilite group, merwinite has certain adsorption capacity towards heavy metals, too. This finding extends the possible application of slag and slag based products in the purification of water contaminated by heavy metals.

CONCLUSIONS

The experimental results demonstrate the possibility to increase the AC of granulated blast furnace slag for heavy metals (CuII) with over 80% through crystallization.

The crystallization of granulated slag or a mixture of granulated blast-furnace slag with 13% addition of MgO leads to the formation of crystal phases – melilite and merwinite. The presence of both minerals in slag leads to an almost double increase in

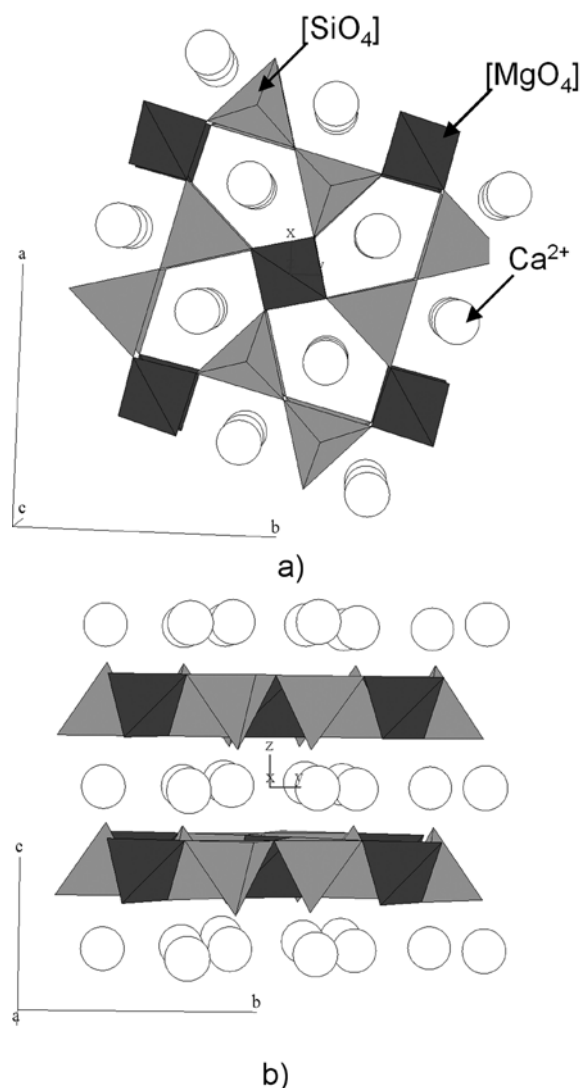


Fig. 4. Crystal structure of åkermanite
 Crystal structure of åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) projected on the (001) plane (a) and the (100) plane (b). White spheres are calcium atoms, dark polyhedra are MgO_4 tetrahedra, and light polyhedra are SiO_4 tetrahedra

adsorption activity compared to the original amorphous product.

The crystallization of a mixture containing granulated blast-furnace slag with addition of Al_2O_3

(alone and in combination with MgO) does not lead to an increase of the adsorption activity.

The minerals merwinite, gehlenite and åkermanite are adsorption-active phases determinative for the very high levels of adsorption of heavy metal ions by blast furnace metallurgical slag.

Slag samples with a main crystal phase merwinite exhibit the highest adsorption capacity. The promotion of merwinite crystallization would allow synthesizing materials with high adsorption capacity towards CuII .

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АДСОРБЦИОННА СПОСОБНОСТ НА МОДИФИЦИРАНА МЕТАЛУРГИЧНА ШЛАКА

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(Резюме)

Адсорбционният капацитет на шлакови образци, получени чрез кристализация на гранулирана доменна шлака без и с добавки на Al_2O_3 и MgO , беше изследван във водни разтвори на $Cu(II)$ и сравнен с този на изходна аморфна шлака и на синтезирани образци с основни фази геленит и акерманит. Целта на изследването беше: оценка на адсорбционната активност на основните фази в доменната шлака (кристални и аморфни) към тежки метални йони. Сравнителният анализ на адсорбционните данни и XRD показва, че формирането на кристалните фази мервинит и мелилит (геленит и акерманит) в шлаката предизвиква почти двойно увеличение на адсорбционният капацитет по отношение на $Cu(II)$ в сравнение с аморфната шлака. Добавката на Al_2O_3 самостоятелно, както и в комбинация с MgO води до кристаллизация на сорбционно неактивна фаза шпинел.