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CATALYTIC ACTIVITY IN OXIDATION REACTIONS OF COPPER FURNACE SLAG AND CONVERTER SLAG

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ABSTRACT

The aim of the present study is to examine the catalytic activity of two types of copper slag – flash smelting furnace slag (FS) and converter slag (CS). Two typical slag compositions different in chemical composition and way of production were selected, in order to clarify how these differences affect their catalytic properties. The analysis of the samples of the slag was conducted using Scanning electron microscopy, Element distributions mapping, Electron probe micro analysis and BET surface area analysis. The catalytic activity of the samples was measured in two types of reactions: oxidation of CO and oxidation of toluene.

Keywords: catalytic activity, copper slags, flash smelting furnace slag, converter slag.

INTRODUCTION

The utilization of metallurgical slag as a byproduct from the production of ferrous and nonferrous metals is relevant to the optimization of production and protection of the environment. Metallurgical slags are most often used as construction materials [1, 2], in the production of glass-ceramics [3-5] and for other purposes [6-8].

Many studies [9-12] have shown that metallurgical slag from the production of ferrous metals (production of iron) has adsorption properties and can be used for purification of polluted water contaminated with heavy metals, such as lead and copper. It was found that the metallurgical slag can also be used as a media for the synthesis of catalysts in reactions of complete oxidation with the aim of purification of waste CO and organic substances gases. [13-14]. Slag photocatalysts have been obtained [15, 16]. Copper content in copper flash smelting furnace and converter slag amounts to a few percents [17-19]. It is well known that copper oxide massive and deposit catalysts are among the most active ones in reactions of complete oxidation [20-23]. A preliminary research was carried out on the phase composition and structure of these slags [19]. Therefore, the aim of the present study is to establish the level of catalytic activity of flash smelting furnace slag (FS) and converter slag (CS) in reactions of complete oxidation. This could lead to the discovery of another method for their disposal. The catalytic activity of slags was studied in reactions of complete oxidation of CO and toluene.

EXPERIMENTAL

Two kinds of copper slags have been examined – slag from flash-smelting furnace process (FS) and converter slag (CS). Samples were taken from the slag fields used for crystallization of the liquid slag by spraying with water. The samples of copper flash smelting furnace slag and converter slag are denoted as FS and CS, respectively. The samples of the slag were characterized using X-ray diffraction (DRON 3M X-ray diffractometer), Fourier transformation infrared spectroscopy (FTIR spectrophotometer Bruker EQUINOX 55), Light optical microscopy in transmitted and reflected light (polarizing microscopes Laboval – pol – u). Quantitative determination of elements in the samples was carried out by Gravimetric analysis, Complexonometry, Atomic absorption spectrometry (AAS) and Inductively coupled plasma (ICP-OES) (Teledyne Leeman Labs Prodigy High Dispersion). Sample data analysis is presented in detail in [19]. Additional investigations have been carried out using Scanning electron microscopy, Element distributions mapping, Electron probe micro analysis and BET surface area analysis.

Slag samples structures were observed using SEM on SEM Philips 525/EDAX 9900 equipment. Element distribution mapping was generated (of Cu, S, Fe, Si, Pb, etc.) in selected sections of the samples. The image is a backscattered (BS) electron image, and the X-Ray Mapping - of the respective spectral line of the element.

Electron probe micro analysis (EPMA) was performed on a JEOL JSM 35 CF Scanning Electron Microscope with a TRACOR NORTHERN TN – 2000 Energy-Dispersive Spectrometry (EDS) X-Ray Analyzer. JEOL company patterns have been used. The analysis was applied to establish the composition of copper and sulfide inclusions in the samples.

The determination of the specific surface area of samples was carried out by nitrogen adsorption at the boiling temperature of liquid nitrogen (77.4 K) using the BET equation.

The catalytic activity of the samples was measured in an isothermal plug-flow reactor enabling operation under steady-state conditions without any temperature gradients. The size of the catalyst particles (0.3 – 0.6 mm) was chosen taking into account the reactor diameter (6 mm) and the hourly space velocity (20 000 h^{-1}). The gas feed flow rate was 4.0 l h^{-1}, the catalyst bed volume was 0.2 cm^3 and the mass of the charged catalyst was 0.2 – 0.25 g. The catalytic oxidation was performed within the temperature interval 200 – 400°C, the oxidizing agent used being oxygen from the air (gas mixture: 21 % O_2 and 79 % N_2). The preliminary treatment of the catalysts included heating in air flow at 300°C for 1 hour. The initial concentration of carbon monoxide was 0.5 vol. %. The carrier gas was air (a mixture of 21 % O_2 and 79 % N_2). A Maihak gas analyzer (O_2, CO, CO_2) was used to measure the CO and CO_2 concentrations with an accuracy of ±0.1 ppm, while the oxygen measurement accuracy was ± 100 ppm. The catalytic activity tests of samples with respect to the complete oxidation of toluene, were carried out in a flow reactor, with a catalyst volume 0.2 cm^3 (0.2 – 0.25 g), a space velocity 20000 h^{-1}, and concentration of toluene 0.03 vol. %). The inlet and outlet gas mixtures were analyzed by a THERMO-FID analyzer. The flow of CO and toluene was fed into the reactor by an Ismatex M62/6 pump (Switzerland).

RESULTS AND DISCUSSION

The major crystalline phases determined by XRD analysis in both FS and CS slag were fayalite Fe_2SiO_4 and magnetite Fe_3O_4 [19], with a higher magnetite content in CS compared to that in FS. The ratio of magnetite/fayalite phases in slag determined by X-ray diffraction using Powder Cell 2.4 [24] was approximately 7:3 in FS and 6:4 in CS [19]. Other phases found in the samples have been the amorphous silica phase and inclusions of copper sulfide, as well as metallic copper in CS.

Fig. 1 shows SEM images of CS sample. The brightest phases are copper and copper-sulfide inclusions. The light grey isometric idiomorphic cross-sections correspond to magnetite, while fayalite crystals are not fully formed and contain amorphous inclusions (dark grey). Fayalite crystals and the amorphous phase form a matrix, containing magnetite, copper and sulfides.

Fig. 1c, d, e and f show the distribution of copper, sulfur and iron in a section of converter slag. Cu, Fe and S are denoted under the magnification marker on the corresponding figures. Increased concentrations of a given element in the area under investigation are marked by white dots, which become more visible with the increase of the picture size. Iron was the main element present in fayalite, magnetite and the amorphous phase. It was less present in copper sulfide inclusions, which in turn are marked by higher concentrations of copper and sulfur. Fig. 1d also shows the presence of some copper in oxide and silicate phases. In Fig. 1c are clearly visible copper droplets formed within the boundaries of the large copper sulfide inclusion. They are also heterogeneous and the composition of the light areas is PbS.

A typical structure of the FS sample is presented in Fig. 2. The main phase is fayalite present in axial and

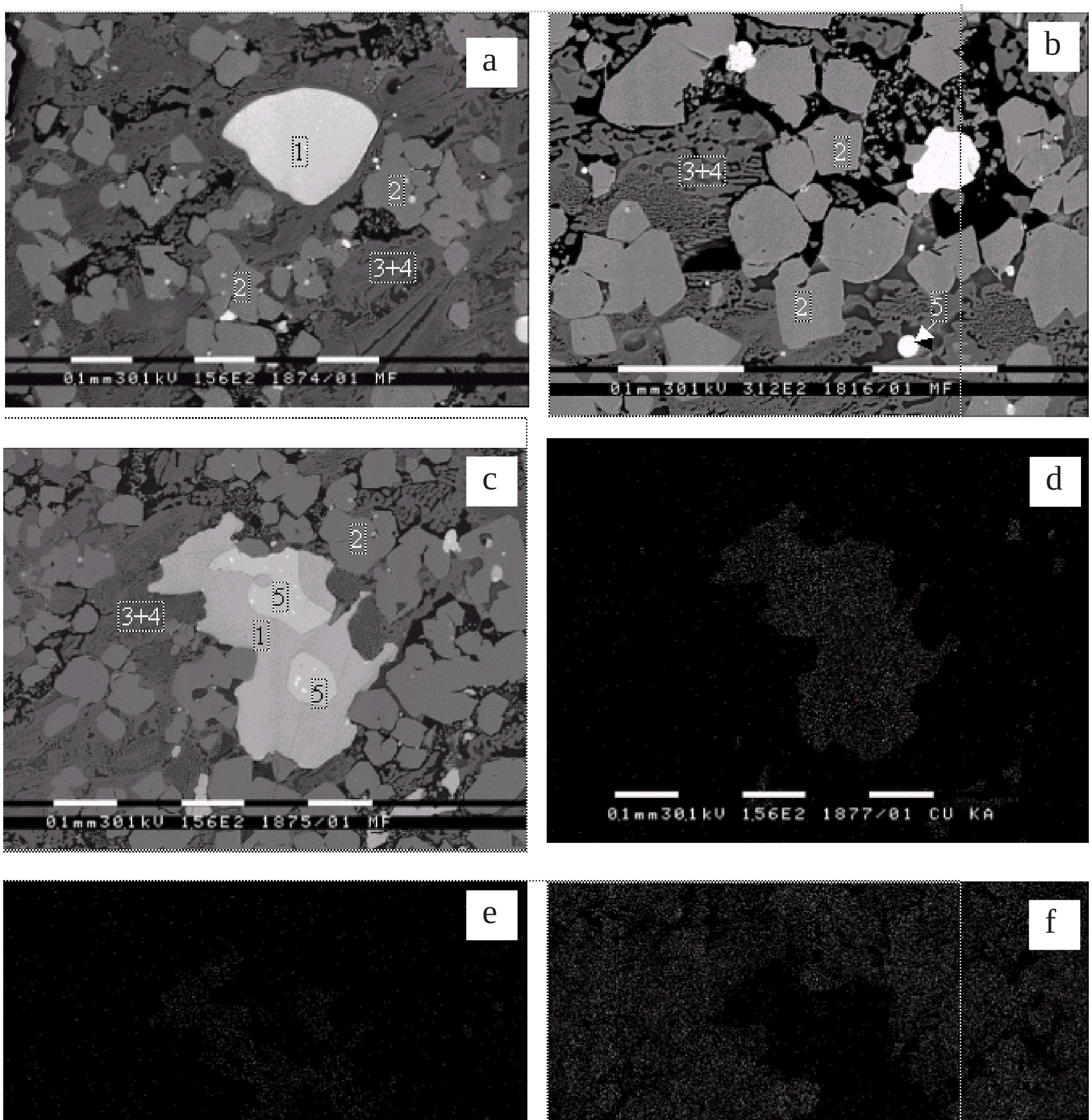

Fig. 1. A typical microstructure of the CS sample - a, b , c; The distribution of Cu, S and Fe - d, e and f, in the section shown in c. Denotations: 1 – copper sulfide phases; 2 - magnetite; 3+4 – a section built of fayalite and amorphous phase; 5 - copper.

slab cross-sections. Crystals are well-formed and with a different morphology compared with fayalite crystals of converter slag. Skeletal growth forms are typical of magnetite. The copper sulfide inclusions (bright spots) are rounded and heterogeneous. Again, sulfide inclusions (light areas of the structure) show higher content of Pb. Fig. 2(d), (e) and (f) gives the distribution of Cu, S and Fe in the section shown in (c). The distribution of copper and sulfur clearly indicates copper sulfide inclusions, though low concentrations of copper are contained

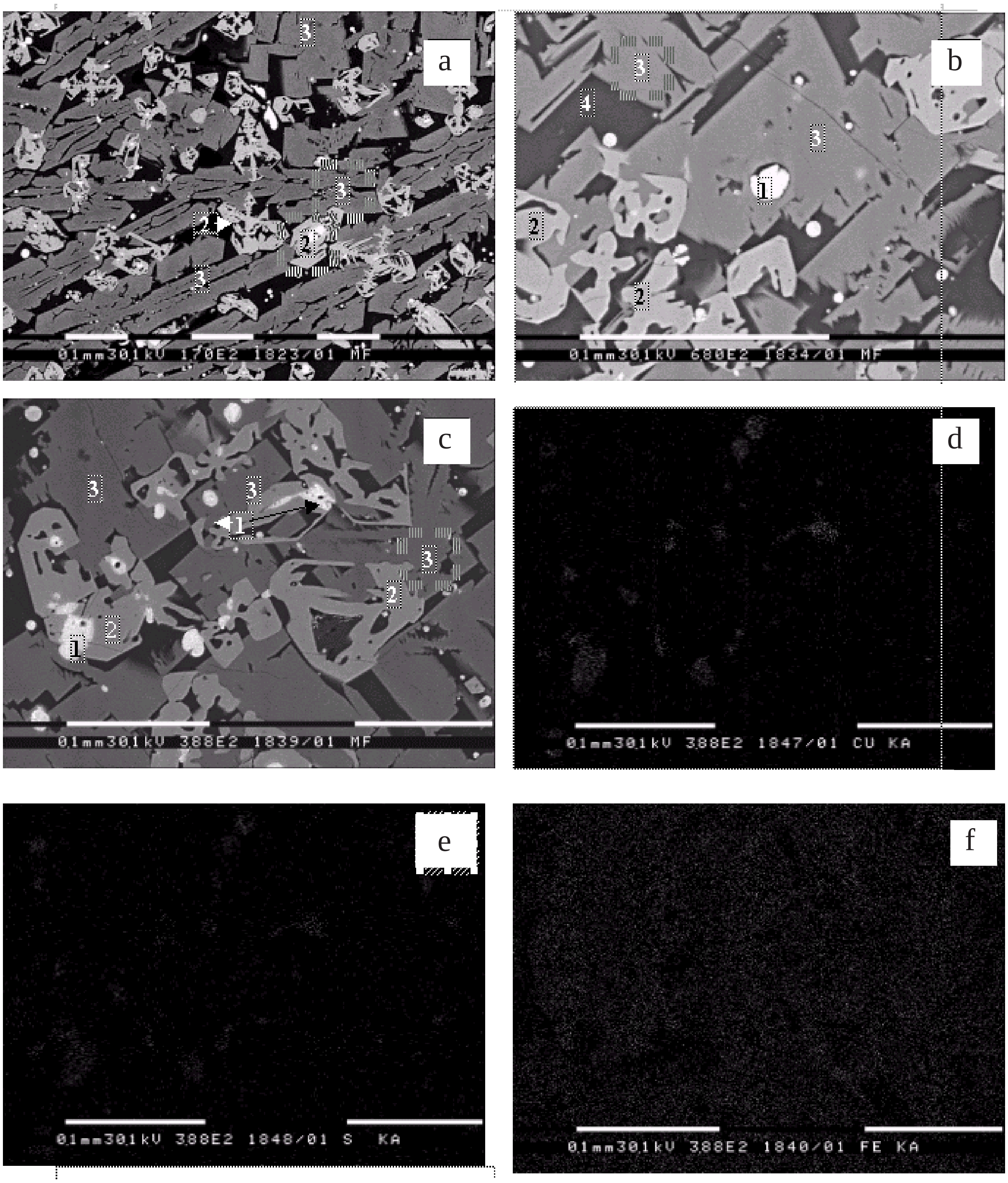

Fig. 2. A typical microstructure of the FS sample - a, b and c; The distribution of Cu, S and Fe - d, e and f, in the section shown in c. Denotations: 1 – copper sulfide phases; 2 – magnetite; 3 – fayalite; 4 – amorphous phase.

in other phases too. Data from the analysis confirms quantitatively the presence of copper in fayalite, magnetite and amorphous phases, but does not allow to determine whether the distribution of copper in these phases was equal or there were some preferences. Concerning the distribution of iron, we can determine with a higher degree of certainty that its content in fayalite and magnetite is higher than in the amorphous mass. Analysis of the chemical composition of the FS sample established the presence of Zn, not only in the sulfide phases, but also in the silicate ones.

Table1. Chemical composition of copper and copper-sulfide phases found in FS and CS samples using EPMA.

Slag analysis No	Cu $\%_{mass}$	Fe $\%_{mass}$	S $\%_{mass}$	As $\%_{mass}$
FS-1	40.27	28.07	31.66	
FS-2	52.51	22.04	25.45	
FS-3	62.75	12.64	24.61	
Bornite $Cu_5Fe^{2+}S_4$	*63.31*	*11.13*	*25.56*	
Chalcopyrite $CuFe^{2+}S_2$	*34.63*	*30.43*	*34.94*	
CS-3	92.81	2.72	-	4.37
CS-2	91.18	2.86	0.27	5.69
CS-1	80.49	0.34	19.17	
Chalcocite Cu_2S	*79.85*		*20.15*	

Most of the copper contained in slag is incorporated into sulfide and metal phases. Table 1 shows some specific compositions of copper and copper-sulfide phases observed in FS and CS samples using EPMA. FS contains copper-containing sulfides of a variable composition. For CS also typical are metallic copper droplets, except for the copper-sulfide phases. The chemical compositions of bornite, chalcopyrite and chalcocite are shown for comparison.

As already mentioned [17], the sulfide inclusions, mainly related to loss of copper in furnace slag, are of variable compositions, which do not correspond to the stoichiometries of the known crystalline phases in the systems Cu - S and Cu - Fe - S.

The composition of typical sulfide inclusions in CS samples is close to that of chalcocite, Cu_2S. On the other hand, our previous studies of converter slag [18] have identified a wide variety of copper-iron sulfide phases. Typical impurities in copper-containing inclusions are As, Sb, Fe, Zn, Pb, Ni, however, these elements can form their own phases [18].

FS and CS include phases of variable composition and structures, as figures show. Phases containing copper and iron could play a decisive role in terms of catalytic activity.

Table 2 contains data on the chemical composition, specific surface and forsterite number ($Fo_{\#}$). Iron predominates in slag, as seen in the table, and its content is slightly higher in CS. Next to iron, copper has the second highest concentration, which is three times higher in FS. Other transition metals that could play a catalytic role have low concentrations (below 0.1 %), with the exception of Co (0.16 %). These metals cannot be expected to have a significant influence on the catalytic activity, given their highly probable distribution between different slag phases. The total content of transition metals in CS is 0.239 %, which is considerably higher than in FS - 0.061 %. The amount of the forsterite component Mg_2SiO_4 in the fayalite phase of FS is higher compared to CS, which can be deduced from the higher value of the forsterite number (Table 2). The forsterite number of samples calculated on the basis of chemical composition is denoted in Table 2 as $Fo_{\#}$ calculated; the experimentally determined forsterite number based on band positions in FTIR spectra – as $Fo_{\#}$ experimental.

Fig. 3 presents the levels of oxidation of CO to CO_2 (η, %) and toluene to CO_2 and H_2O, depending on temperature. Although FS and CS samples contain silicates (fayalite and glass phase) as main phases, they nevertheless show relatively high catalytic activity, especially in the case of CO oxidation. The conversion of CO to CO_2 at 330°C is 100 %. We should have in mind the high space velocity of the catalytic process, which is 20000 h^{-1}. The complete oxidation of toluene is observed at higher temperatures, as expected. This is typical for catalysts based on 3d-transition metals. However, the catalytic activity of this harmful component is also high, considering both the relatively difficult complete oxidation of toluene and its low concentration in the gas mixture (300 ppm). Similar results are observed in Fig. 4, which shows the catalytic activity of samples in terms of the amount of oxidized CO and toluene per gram of catalyst per hour, depending on temperature (Fig. 4). The FS sample has a slightly higher operating efficiency than the CS sample, both in the case of the dependency η - T (Fig. 3) and Ig – T. More precise information can be obtained by presenting the dependence of the amount of oxidized CO and toluene

Table 2. Data on the chemical composition [19] and the specific surface of copper slag samples.

Sample	$Fo_{\#}$ calculated	$Fo_{\#}$ experimental	So m^2/g	Cu $\%_{mass}$	Fe $\%_{mass}$	Ni $\%_{mass}$	Co $\%_{mass}$	Cr $\%_{mass}$
FS	4.5	8.3	10.0	1.14	46.63	0.017	0.04	0.004
CS	1.4	5.5	11.0	5.07	47.71	0.036	0.16	0.043

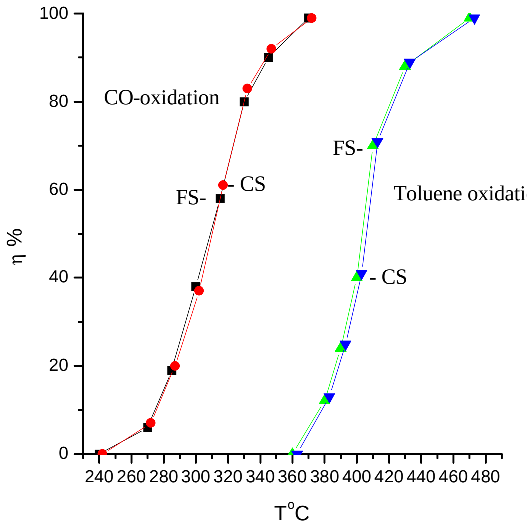

Fig. 3. Amount of oxidized CO and toluene η (%) depending on temperature (°C); Samples of a copper slag: flash smelting furnace slag (FS) and converter slag (CS).

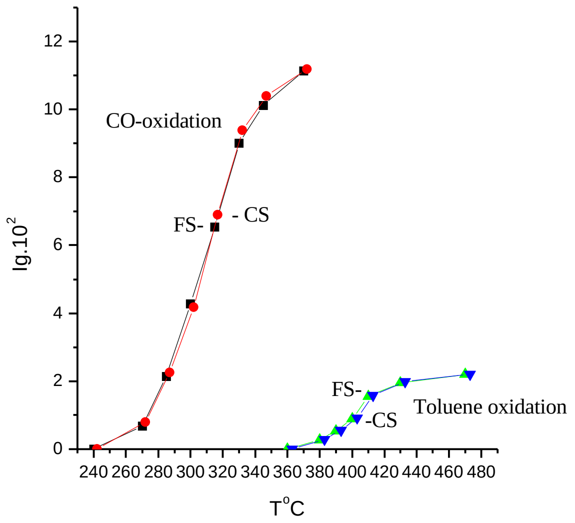

Fig. 4. Amount of oxidized CO and toluene (g) per gram of catalyst per hour (I_g) depending on temperature (°C); Samples of copper slag: flash smelting furnace slag (FS) and converter slag (CS).

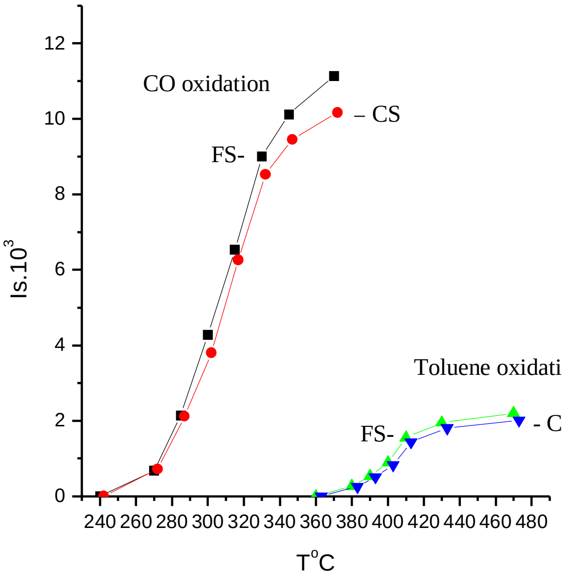

Fig. 5. Amount of oxidized CO and toluene (g) per m² per hour (I_s) depending on temperature (°C); Samples of copper slag: flash smelting furnace slag (FS) and converter slag (CS).

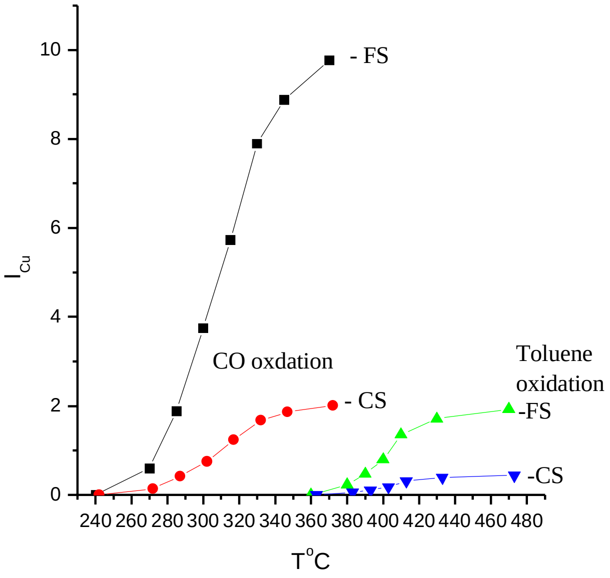

Fig. 6. Amount of oxidized CO and toluene (g) per g of copper in the catalyst (I_{Cu}) depending on temperature (°C); Samples of copper slag: flash smelting furnace slag (FS) and converter slag (CS).

per 1 m² of catalyst surface per hour, depending on temperature. The dependence is shown in Fig. 5. FS has a higher operating activity, as clearly visible in Fig. 5.

The main problem is to determine the key factors that affect this higher catalytic activity. Table 2 and Figs. 2 and 3 show higher iron content (respectively magnetite) in the CS sample, as well as of other 3d transition metals such as Cu, Co, Ni, Cr. It is well known that these metals or their compounds, more precisely oxides and spinels [21-23, 26-28], are catalytically active in reactions of complete oxidation. Therefore, we could draw the most general conclusion that the sample should have a higher operating efficiency.

However, it was observed that the catalytic activity of the FS sample was higher. This could be due to the different inclusion of copper in the system (the samples). Sulfur content is higher in the CS sample, which could negatively affect the catalytic activity. On the other hand, the content of Cu was significantly higher, and even in case of a blockage of copper as sulfide, the amount of copper unassociated with sulfur in CS would be higher.

The main FS parameters with higher values compared with those of CS are the amount of the primary phase (fayalite) and the characteristics relating to its composition ($Fo_{\#}$). Therefore, the content of the forsterite component (Mg_2SiO_4) in the composition of the solid solution based on the fayalite is higher. On the other hand, Mg_2SiO_4 is not an active catalyst in oxidation reactions. It could be assumed that the inclusion of Cu^{2+} as an isomorphic impurity in the fayalite phase determines the higher catalytic activity. In this case the operating efficiency of Cu^{2+} should be higher in the FS sample, compared to CS. Information about this can be obtained by building up the dependency of the amount of processed CO or toluene per one gram of copper contained in the catalyst, depending on temperature. The dependence is presented in Fig. 6. It clearly shows that the operating efficiency of copper in the FS sample is significantly higher than that in CS. This applies to the CO oxidation, as well as to the complete oxidation of toluene.

The question remains whether the hypothesis of presence of copper in the composition of fayalite is a well-reasoned one. All slag phases have a complex and variable composition. According to our previous studies [17, 18], the compositions of magnetite and fayalite include, apart from their main components, also Al, Mg, Zn, Cu, Pb as isomorphic impurities. It is noticeable that Cu contents in FS glass phase, fayalite and magnetite, although being variable, reach relatively high levels [17]. According to analyses, the amount of Cu in oxide and silicate phases typically ranges from 0 to about 0.4 %, however, phases with much higher content (~ 5 %) have been found. The composition of phases in the samples is variable and non-stoichiometric, and it varies not only between samples, but even within one section of the tested sample and the mineral grain. This makes difficult the exact quantitative assessment of the isomorphic impurities in the composition of phases, and consequently of the contained amount of Cu. Returning to the values of the forsterite number of samples calculated on the basis of the chemical composition and those experimentally determined based on the position of the bands in FTIR spectra. In both cases $Fo_{\#}$ value of FS is higher compared with that of CS. The value difference is higher at the calculated $\Delta = 3.1$ than at $\Delta = 2.8$ determined by FTIR.

We have stated that some deviations from data for the isomorphic series forsterite – fayalite are inevitable and may be also due to possible inclusion in the olivine crystal structure of other cations present in the slag. The infrared spectra of olivines exhibit a generally linear decrease in the wavenumber position of each band as the molar proportion of Fe increases, and this trend is attributed to the increasing radius and mass of the cation linking the SiO_4 tetrahedra [25]. Therefore, the inclusion of some copper in the olivine structure should lead to a more significant reduction in the wavenumber position of the bands and a registering of a lower value of $Fo_{\#}$. Thus the lower value of the difference between the experimentally determined $Fo_{\#}$ values compared to the expected value based on the chemical composition can be related to the higher copper content in the fayalite phase in FS compared with CS.

CONCLUSIONS

The results of the present study demonstrate that copper slag samples show relatively high catalytic activity in oxidation reactions. The activity is higher in terms of CO oxidation, however, toluene oxidation activity is also high. The sample of the flash smelting furnace slag (FS) has a higher operating efficiency compared with the sample of converter slag (CS). The results are surprising inasmuch as the higher contents of the spinel phase and Cu, Co, Ni, Cr in CS suppose a higher catalytic activity compared to FS. The higher catalytic activity of the FS sample may be due to the higher degree of copper incorporation as an isomorphic impurity into FS fayalite phase.

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