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ISSN 0543-5846
METABK 62(1) 29-32 (2023)
UDC – UDK 666.88.002.23:66.014:66.097:539.26=111

RESEARCH OF COMPONENT COMPOSITION AND CATALITIC REACTIVITY OF METALLURGICAL INDUSTRY SLAG

Received – Primljeno: 2022-03-29
Accepted – Prihvaćeno: 2022-06-30
Original Scientific Paper – Izvorni znanstveni rad

The article deals with the research of component composition and catalitic reactivity of metallurgical waste products. The slags component composition was investigated by X-ray fluorescence analysis. The slag stuff has been modified with alkali (NaOH) and mineral acids (HNO_3, H_2SO_4, HCI and H_3PO_4), and their catalytic reactivity in the catalytic decomposition of ethyl alcohol and hydrogen peroxide has been determined for the first time. The revealed catalytic reactivity of the slag staff for the decomposition of ethyl alcohol and hydrogen peroxide indicates the need for a more detailed research and development of an industrial non-ferrous waste treatment technology.

Key words: slag, modification, component composition, catalitic reactivity, X-ray research.

INTRODUCTION

Currently nonutilizable waste from various industries ar routinely stored on slurry sites with unfavourable environmental effect. Such wastes often contain valuable components and can be considered as technogenic deposits.

Slags are important by-products of pyrometallurgical steel and non-ferrous metal production, and annually hundreds of millions of tons of them are produced worldwide. Depending on the chemical and mineralogical composition of the slags, they can be recycled as waste, which can then be weathered and released into the environment. Their utilization is not only promising in terms of saving raw materials, but also improves the environmental situation [1].

So far, a number of scientists have studied slag materials. For example, the article [2] discusses the types, application and metal recovery from slag. The article considers gravimetric, magnetic, flotation, pyrometallic and hydrometallurgical slags processing for extraction of ions of various metals. The authors [3] describe detailed various experimental tests used to determine the characteristics of the slag. Moreover, thermo–chemical properties of slags, thermophysical properties and correlations between them are measured and modeled. The work [4] focuses on improving the catalytic performance of the modified steel slag to increase efficiency, purity and low cost.

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According to [5], there are two ways of recycling of slags from metallurgical industries. The first is the use of precipitation as a component of raw materials for production of building materials. The second is the use of modified precipitation in production making the most of the specific properties of compounds including iron, nickel, zinc, copper, chromium, as the most common components in slag. According to the metallurgical slags analysis many of them have compositon with the ratio of iron oxides to non-ferrous metals approximates the composition of mineral pigments for ceramic paints and colored glazes [5]. At the same time, metallurgical waste is rich in metal content and can be used as a promising technogenic raw materials. Taking into account the crisis phenomena in the economy, issues of development and early introduction of advanced waste disposal technologies and the use of secondary material resources in the metallurgical industry have become urgent.

Our research needed to study the catalitic reactivity of non-ferrous metallurgy slags to obtain certain beneficial effect, which could contribute to solving the problems of accumulation and growh of industrial wastes and their impact on the environment.

EXPERIMENTAL PART

The slag materials are fine black crystals. Slag sampling was carried out by the point technique. Spot samples of slags were taken by the “diagonal envelope”. Samples of slag up to 0,5 kg were taken from the points of the controlled “elementary” section, layer by layer from a depth of 20 cm using a tubular sampler. Pooled samples were formed from spot samples.

The samples were ground in a Puluerisette 6 ball mill (Gemany), sifted through a sieve (400 mesh) and

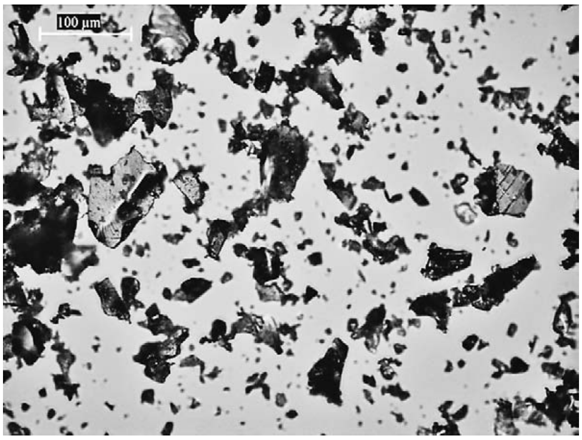

Figure 1 Slag photomicrography

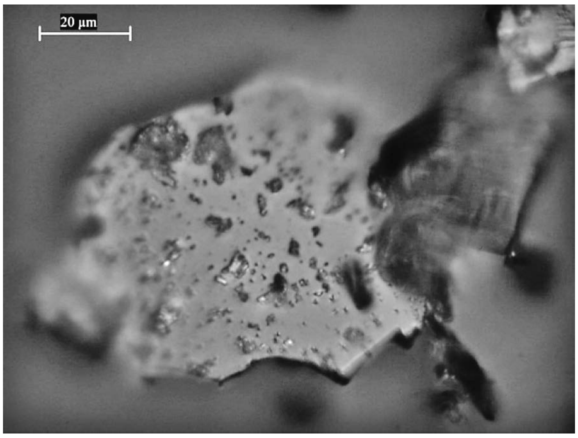

Figure 2 Photomicrography of a slag granule

homogenized. The composition of the samples was determined by X-ray fluorescence analysis.

Photomicrographies of slag and slag granules were obtained with a Leica DM 6000M optical microscope (Figures 1 and 2).

Slag granules are of various shapes and sizes, characterized by a purple hue. With an increase in the resolution of the microscope, inclusions of glassy transparent substances, apparently silicon compounds, are observed in the slag granules.

Further the component composition of unmodified slags and slag materials treated with distilled water is presented.

Table 1 presents the results of the fractional analysis of unmodified and slag materials treated with distilled water.

The research results proved that slag materials contain large quantities of iron - 43,901 %, zinc - 20,163 % and silicon - 16,064 %. There is also small amount of calcium - 9,071 and aluminum - 2,343 %, and trace amount of lead, copper, indium, arsenic and some other substances.

After treatment of slags with distilled water, no fundamental change in the component composition was observed (Table 1).

In the following studies, the slag has been modified in distilled water, with the following mineral acids (concentration of 0,1 n): sodium hydroxide, nitric, sulfuric, hydrochloric and phosphoric acids without pre-cleaning.

Table 1 **Component composition of unmodified slags and treated with distilled water slag materials**

Slag materials			
unmodified, mslag = 1,6720 g		distilled water treated, m_{slag} = 1,083 g	
components	quantity/%	components	quantity/%
Mg	0,509	Mg	0,508
Al	2,343	Al	2,259
Si	16,064	Si	15,874
P	0,705	P	0,463
K	0,964	K	0,927
Ca	9,071	Ca	8,876
Zn	20,163	Zn	19,487
Mn	0,268	Mn	0,276
Fe	43,901	Fe	43,050
Cu	0,987	Cu	0,939
In	0,022	In	0,152
Pb	0,986	Pb	0,905
As	0,176	As	0,174

Crushed slag material with a mass of 5g was added separately into HNO_3, H_2SO_4, HCI and H_3PO_4 dissolved in distilled water by alkali (NaOH) and acids, and heated with intensive agitation to a temperature of 50 ^{0}C for 3 - 5 hours. The resulting mixture was filtered by the Büchner funnel and repeatedly washed with water to remove the acid residues (when using hydrochloric acid). Then the filtered slag material was dried in the drying chamber at a temperature of 100 - 110 ^{0}C for 2 - 3 hours.

The modified slag samples were studied by X-ray fluorescence analysis and atomic emission spectroscopy to determine its composition after modification.

The component composition of slag materials is given in Table 2. The component composition of slag materials undergoes certain changes after modification with mineral acids and alkali. There is a decrease in light metals, which is associated with their interaction with acids. An increase of silicon and a slight decrease in the amounts of iron and zinc are found. This is apparently due to the fact that the hydrochloric acid treatment of slag is accompanied by the release of monomeric silicic acid. These results were proved by the analysis of atomic emission spectroscopy of acid solutions after modification of slag materials (Table 2).

Table 2 (column 1) show the study results of the slag chemical compound after alkali modification, where changes in amphoteric metal content, i.e. lead and zinc, are observed. Solutions obtained after modification with mineral acids and alkali have been subjected to atomic emission spectroscopy (Table 3).

The results of the analysis to determine the concentration of metal ions by atomic emission spectroscopy (Table 3) show that solutions obtained after the slags

Table 2 **The component composition of slag materials modified with various mineral acids and alkalis**

Slag materials									
NaOH modified, m_{slag} = 1,0080 g		HNO_3 modified, m_{slag} = 1,0885 g		H_2SO_4 modofied, m_{slag} = 1,1637 g		HCl modified, m_{slag} = 1,0816 g		H_3PO_4 modified, m_{slag} = 1,0774 g	
metals	%	metals	%	metals	%	metals	%	metals	%
Mg	1,009	Mg	0,021	Mg	0,011	Mg	0,011	Mg	0,002
Al	3,680	Al	4,086	Al	3,759	Al	4,042	Al	3,728
Si	12,873	Si	13,611	Si	15,075	Si	13,350	Si	17,521
P	0,529	P	0,566	P	1,585	P	0,495	P	1,342
K	2,018	K	0,025	K	0,012	K	0,013	K	0,016
Mn	0,837	Mn	0,818	Mn	0,821	Mn	0,800	Mn	0,819
Fe	42,662	Fe	42,790	Fe	42,010	Fe	42,467	Fe	40,161
Cu	1,017	Cu	1,372	Cu	1,847	Cu	2,522	Cu	1,414
Zn	0,024	Zn	3,205	Zn	3,136	Zn	3,036	Zn	3,280
Mo	0,053	Mo	0,057	Mo	0,056	Mo	0,057	Mo	0,053

Table 3 **Metal ion concentration of the solution obtained after the slag modification by different mineral acids and alkali**

Metals	NaOH	HNO_3	H_2SO_4	HCl	H_3PO_4
	Concentration/ mg/ml				
Fe^{3+}	0,165	7,260	0,366	4,530	0,022
Ca^{2+}	26,641	493,800	434,720	1350,900	430,020
Cu^{2+}	0,307	12,393	0,017	20,523	0,084
Mg^{2+}	0,138	54,871	29,904	50,238	26,287
Al^{3+}	3,178	8,447	0,143	24,059	0,266
Mn^{2+}	0,007	41,718	6,275	37,972	7,701
Zn^{2+}	10,497	75,284	0,407	63,773	2,463
Pb^{2+}	14,619	0,442	0,231	0,425	0,181

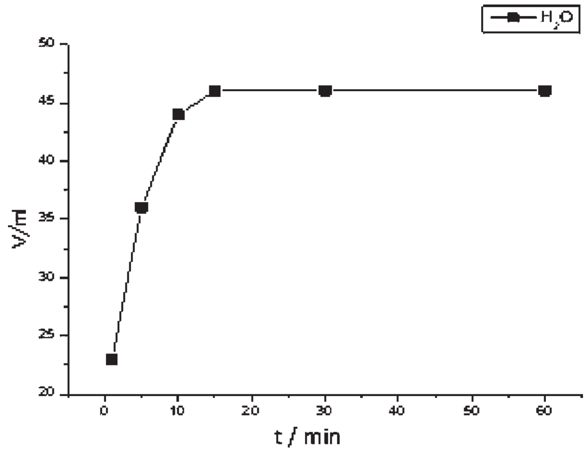

Figure 3 Ethyl alcohol decomposition kinetics with slag material washed with distilled water (m_{kt} = 0,03 g, V(C_2H_5OH 90 %) = 1 ml, t = 50 ^{0}C)

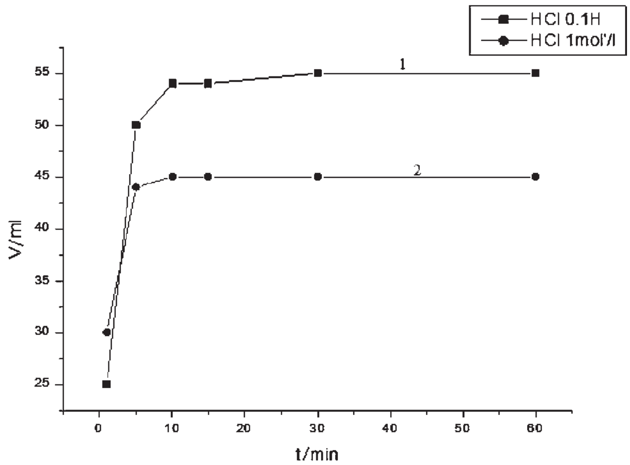

Figure 4 Ethyl alcohol decomposition kinetics with a hydrochloric acid-washed slag (m_{kt} = 0,03 g, V(C_2H_5OH 90 %) = 1 ml, t=50 ^{0}C)

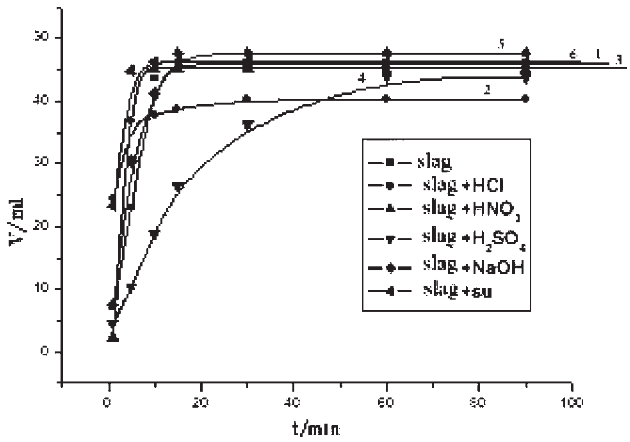

Figure 5 Comparative hydrogen peroxide decomposition kinetics with slag material, washed with distilled water, and modified with mineral acids and hydrochloric acid alkali (m_{kt} = 0,05 g, V(H_2O_2 30 %) = 1 ml, t = 45 ^{0}C)

modification with mineral acids have a high content of light metals, in particular calcium, magnesium, respectively, solutions obtained after slag treatment with alkali have a high content of ions such as zinc and lead. This once again proves that modification with acids decreases metal ions content of the first and second groups, the main subgroups of the periodic table.

Modified and unmodified slag materials were studied for the catalytic decomposition of ethanol and hydrogen peroxide by the volumetric method. During the research, we measured the decomposition rate of hydrogen peroxide of a given concentration in modified and unmodified slag materials at various temperatures.

Next, the kinetics of ethyl alcohol decomposition by slag material washed with distilled water and hydrochloric acid was studied (Figures 3 and 4). It should be noted that prior to this, the kinetics of zinc leaching from calamine and smithsonite with sulfuric acid [6–7] was investigated.

Higher catalytic activity is observed for slag materials washed with hydrochloric acid (Figure 4). At the same time, an increase in the hydrochloric acid concentration to 1n contributes to a decrease in the hydrogen output, which is associated with a change in the slag chemical composition towards the silicon compounds formation.

Figure 5 presents the comparative decomposition kinetics of hydrogen peroxide with a slag material washed with distilled water, also modified with mineral acids and hydrochloric acid alcali.

Non-ferrous metallurgy slag materials have been established to have catalytic activity for ethyl alcohol decomposition. The hydrogen output in the decomposition of ethyl alcohol with washed water-distilled slag material

According to the data obtained, except for slags modified with sulfuric and hydrochloric acids, all have much the same activity in the decomposition of hydrogen peroxide. The non-modified slag material for catalytic activity is not inferior to the modified material. This is apparently due to the fact that the content of transition metals, which are active components, decreases insignificantly during modification. The decomposition process is completed ten minutes after the start of the hydrogen peroxide decomposition reaction. In the case of sulphuric acid, equilibrium is established after sixty minutes.

RESULTS AND DISCUSSIONS

The component composition of slag materials after modification with mineral acids and alkali undergoes certain changes. There is a decrease in light metals associated with their interaction with acids. Also an increase in the silicon content and a slight decrease in the amounts of iron and zinc are observed. This is apparently due to the fact that the hydrochloric acid slag treatment is followed by the release of monomeric silicic acid.

It was determined that the solutions obtained after the modification of slags with mineral acids have a high content of light metals, in particular calcium and magnesium, respectively, solutions obtained after the alkalia slags treatment contain high content of such ions as zinc and lead. This proves that modification with acids leads to a decrease in metal ions of the first and second groups, the main subgroups of the periodic table.

It has been established that non-ferrous metallurgy slag materials have catalytic activity for the decomposition of ethyl alcohol and hydrogen peroxide.

CONCLUSION

The chemical composition and catalytic reactivity of non-ferrous metallurgy slag wastes have been investigated. The research has determined that slag materials contain iron in large quantities - 43,901 %, zinc - 20,163 % and silicon - 16,064 %; a small amount of calcium - 8,876 and aluminum - 2,343 %.

The component composition of slag materials was studied. The slag composition was modified with slag mineral acids and their catalytic reactivity was determined for the first time during the catalytic decomposition of ethyl alcohol and hydrogen peroxide.

The slag catalytic reactivity for the decomposition of ethyl alcohol and hydrogen peroxide has been identified, which indicates the need for more detailed research and development of an industrial non-ferrous waste treatment technology.

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Note: The responsible translator for English language is E.V.Popkova, Ust-Kamenogorsk, Kazakhstan