

TOXIC PROPERTIES AND HYDRAULIC ACTIVITY OF DUMP WASTE BLAST FURNACE SLAG

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Abstract. Metallurgical slags accumulate in large quantities. For further disposal, they must have the certain technical properties. Among the main factors there are chemical and mineral compositions of slags, which affect their final properties. Elemental composition of Zaporozhstal dump blast furnace slag, determined by electron probe microanalysis, makes it possible to characterize the slag fractions in terms of toxicity. Potassium, sodium, sulfur, chlorine, copper and titanium, which are not part of the minerals, are recorded by scanning electron microscope; this suggests that they are sorbed by mineral particles surface. The maximum content of potassium, sodium and titanium is typical for the 2.5 – 5.0 mm fraction. Slag contains an insignificant (less than 1 %) amount of metals – iron, titanium and copper, which belong to the third hazard class of the substance; this does not impede further use of the slag. The third hazard class of dump blast furnace slag has been identified. Volume activities and effective volume activities of granulometric slag fractions have been determined by gamma-spectrometric method. ^{40}K , ^{226}Ra and ^{232}Th natural radio nuclides have been found. It has been proven that slag and its individual fractions belong to the first class of radiation hazard and can be used in construction without restrictions. Zaporozhstal dump blast furnace slag is characterized by high hydraulic activity with an increase in absorption of calcium oxide CaO over time. Dump blast furnace slag can be recommended for production of binders (Portland cement and slag Portland cement) in terms of combination of chemical parameters: to moderately hazardous production wastes of the first class of radiation hazard with manifestation of high hydraulic activity.

Keywords: dump blast furnace slag, elemental content, toxicity, class of a substance hazard, radioactivity, natural radionuclides, hydraulic activity.

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INTRODUCTION

Metallurgical slags accumulate in large quantities. For further disposal, they must have the necessary technical properties, chemical and mineral composition. Metallurgical enterprises adjust the quality of slag when choosing raw materials, optimizing the processing of liquid slag and the entire technological process [1]. Granulated blast furnace and steelmaking slags are used in civil and road construction, concrete and cement production, as reinforcing stones for hydraulic structures, during coastal stabilization as sorbents in wastewater treatment [2]. The effect of various cooling conditions on the properties of glassy steel slag in terms of their leaching and volume stability was studied [3]. The changes in the structure of steel slag reflect the process of gradual dissolution and reaction of lime with SiO_2 to formation of $3\text{CaO}\cdot\text{SiO}_2$ [4].

The dump blast furnace slags are not so thoroughly studied. They replace Portland cement in concrete materials aiming to increase durability and strength, conserve resources and save energy [5]. A study of the physical and chemical properties of blast furnace dust has shown its suitability for asphalt mixtures in road construction [6]. In paper [7] the chemical composition, basicity, hydraulic properties, melting temperature, and surface morphology of the particles of blast-furnace and domed slag, which determine the differences in their use, are compared. In some cases, the hydraulic activity of dump blast furnace slag is sufficient for use in the manufacture of binders: pozzolanic cement, ash-slag-lime binder, and additives to Portland cement [8, 9]. Hydraulic activity determines the use of slag. On the example of granulated blast furnace slags, a decrease in hydraulic activity over time is proved; the obtained analytical dependence allows us to determine the slag activity at a certain point in time [10]. The cool-

ing method may affect the hydraulic properties of the slag, which correlate with the glass phase content. A higher concentration of amorphous compounds was recorded in slags cooled by water or liquid nitrogen [11]. The heat conservation time is a factor determining hydraulic activity, and the glass phase content depends on temperature of the slag discharge [12].

The chemical composition significantly affects the latent hydraulic activity of dump blast furnace slag. Optimum hydraulic activity was recorded with the following composition of slag 47 CaO : 20 Al₂O₃ : 33 SiO₂ [13]. The reactivity of blast furnace slag depends on the chemical and particle size distribution, glass phase content, heat of hydration, and microstructure development [14]. The hydraulic activity of blast furnace slag can be increased upon activation in several ways [15]: in a strongly alkaline medium with pH > 1 or at pH = 11.8 – 12.2 with the addition of calcium hydroxide and its soluble salts – chloride, bromide, nitrate, formate and acetate. The presence of hydraulic activity of slags formed the basis for the development of methods for producing slag-alkali binders based on them [16].

Metallurgical slags contain impurities that can be toxic and pose an environmental hazard. So, in the composition of dump blast furnace slag, the following elements were detected, mg/kg: Ba – 611, Pb – 8 [17]; secondary and micro-elements: As, Au, Ba, Ce, Co, Cr, Cu, Fe, Hf, La, Mn, Mo, Rb, Sb, Sc, Sm, V, W, and Zn [18]; S, P, Mn, Cr, Sr, Zn, Ba, Ti [19]. No correlation was found between the mineral composition, the crystalline fraction of the substance, the structure of blast furnace and steel slag, and the concentration of impurity elements [20]. In the blast furnace slags Nb concentrations vary widely, but do not exceed 15 mg/kg, Ta concentration is <1 mg/kg, Sc <17 mg/kg, Y is about 30 mg/kg. Besides, rare earth elements were detected in concentrations of 0.5 – 36.6 mg/kg [20].

The number of elements released into the environment does not always correspond to the volumetric chemical composition of the slags. Leaching metal impurities from blast furnace slags is less intense than from non-ferrous metallurgy slags resulting from the formation of an alkaline medium in them [21]. Metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, and Zn were leached from steel slag. Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn showed less leachability. Toxic metals As, Cd, Se, and V were not leached using leaching and toxicity tests [22]. Most metals are firmly bound to the slag matrix; therefore, their concentration in soils near slag dumps is lower than in slag [23].

Slags of various origins are concentrators of natural radionuclides (NR). The possibilities of using metallurgical slag in civil and road construction according to radioactivity indicators are shown [24]. The concentrations of NR: U, Th, and K in the slags of iron and steel production can be compared with the radioactivity of limestone and dolomite. It was determined that the activity of NR is below the maximum allowable levels established by the norms

of Romania [18]. For waste blast furnace slag (UK) there are ²¹⁰Pb < 50 Bq/kg, ²²⁶Ra – 240 Bq/kg [17].

The purpose of the research is to study the toxicity and hydraulic activity of Zaporozhstal dump blast furnace slag as the parameters determining the slag resource value.

The objectives of the research are to study the elemental and radionuclide composition of dump blast furnace slag; to calculate the toxicity index and the hazard class of the slag; to determine the hydraulic activity of the slag.

RESEARCH METHODOLOGY

The elemental composition of dump waste blast furnace slag was determined by electron probe microanalysis using the JSM-6390 LV scanning electron microscope with the INCA microroentgen analysis system.

The gamma-ray spectrometric analysis of slag was carried out with the scintillation gamma-ray spectrometer SEG-001.

The identification of the acidity of slag particle surface layers was made with the pH-meter—the millivoltmeter that contains a hard phase selective electrode and a modified reference electrode in polypropylene cases.

Hydraulic activity was determined by the amount of absorbed lime CaO [25].

ELEMENTAL COMPOSITION OF DUMP

WASTE BLAST FURNACE SLAG

According to the results of electron probe microanalysis, the elemental composition of slag fractions is calculated (Table, Fig. 1). It reflects general content of the elements which enter the composition of crystalline and amorphous substances.

The results of microroentgen analysis of slag fractions clearly correlate with the results of the X-ray and phase analysis [26]. The chemical elements: K, Na, S, Cl, Cu and Ti, that are not part of the minerals, are registered with a scanning electron microscope; it enables us to suggest that mineral particle surfaces sorb them. For example, the maximum content of K, Na and Ti is characteristic of the fraction 2.5 – 5.0 mm. Zaporozhstal slag contains minor amount (<1 %) of the compounds of metals Fe, Ti and Cu (Table), which belong to the third class of a substance hazard. However, it does not prevent slag from further utilization.

A HAZARD CLASS OF ZAPOROZHSTAL

DUMP WASTE BLAST FURNACE SLAG

In order to quantitatively estimate the impact of dump waste slag on the environment, the method to assess the hazard class of industrial wastes is used, taking into consideration a toxicity index [27]. Calculations indicate that a toxicity index varies within a range of 4.3 – 5.4; it is

Micro-X-ray analysis of Zaporozhstal waste blast furnace slag fractions

Микрорентгеновский анализ фракций отвального доменного шлака ПАО «Запорожсталь»

Elemental composition parameters	Blast furnace slag fraction, mm		
	< 0.63	2.5 – 5.0	> 20
Si	10.42	10.80	8.69
Ca	30.81	25.67	28.53
Al	1.65	1.87	1.10
Fe	0.92	0.66	0.18
S	2.12	2.04	2.64
Mg	0.84	0.97	0.72
K	0.53	0.57	0.33
Na	0.33	0.38	–
Cu	0.50	–	–
Ti	0.17	0.18	0.10
Cl	–	–	0.08
O	51.70	51.69	57.63

hazard class III (moderately hazardous wastes), i. e. this dump waste blast furnace slag can be used as secondary raw materials in construction engineering.

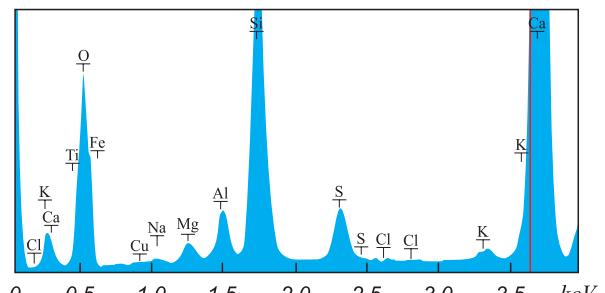
THE RADIONUCLIDE COMPOSITION OF ZAPOROZHSTAL DUMP WASTE BLAST FURNACE SLAG

Slags accumulate NR. The gamma-ray spectrometric method determines the specific activity of NR (C_i) and the effective specific activity (C_{ef}) of slag granulometric fractions. The results are presented on Fig. 1. The natural radionuclides discovered are as follows: ^{40}K , ^{226}Ra and ^{232}Th . A major contribution to Cef is made by radionuclide ^{226}Ra , the second contributor is ^{232}Th .

In the work [28] it was shown that heterovalent isomorphic replacement in the structures of minerals of blast-furnace slags in crystalline or amorphous state is the most probable mechanism of NR accumulation.

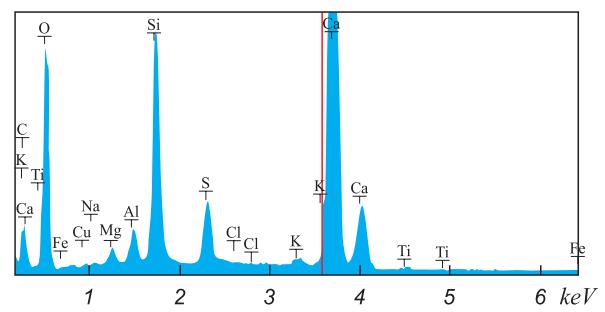
A major contributor to the total activity of Zaporozhstal dump waste blast furnace slag is isotope ^{40}K , the second contributor is ^{226}Ra which contribution exceeds 20 % and is hazardous because of radon release.

Slag fractions have different specific activation. The exceeding of specific activation is marked for fractions 1.25 – 2.5 mm and 2.5 – 5.0 mm. The most radiation-free fractions have the particles of a size more than 10 mm and less than 0.63 mm. The least value of C_{ef} and the low content of ^{226}Ra are more than 20 mm (74.3 Bq/kg) for the fraction of a particle size. According to C_{ef} , slag and its separate fractions, which are related to the first class of a radioactive hazard ($C_{ef} \leq 370$ Bq/kg [29]), can be used in construction engineering without restrictions.



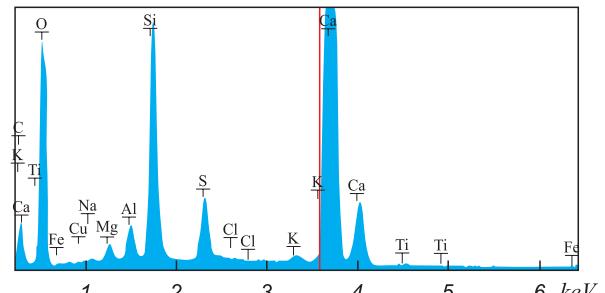
Full scale: 4045 cts; Cursor: 3.652 (6985 cts)

a



Full scale: 7415 cts; Cursor: 3.593 (1992 cts)

b



Full scale: 7415 cts; Cursor: 3.593 (1992 cts)

c

Fig. 1. Energy spectrum of dump blast furnace slag of fractions less than 0.63 mm (a) – spectrum 3, 2.5 – 5.0 (b) – spectrum 5 and more than 20 mm (c) – spectrum 5

Рис. 1. Энергетический спектр отвального доменного шлака фракций менее 0,63 мм (a) – спектр 3, 2,5 – 5,0 (b) – спектр 5 и более 20 мм (c) – спектр 5

DETERMINATION OF ACIDITY OF SLAG PARTICLE SURFACE LAYERS

Acidity slightly varies in slag fractions. More basic is <0.63 mm fraction ($\text{pH} = 9.67$), 2.5 – 5.0 ($\text{pH} = 9.11$), >20 ($\text{pH} = 8.17$).

HYDRAULIC ACTIVITY OF ZAPOROZHSTAL DUMP WASTE BLAST-FURNACE SLAG

The hydraulic activity of blast-furnace slags is an important factor determining the feasibility of their disposal in the production of slag Portland cement. Experimental results were obtained on determination of the hydraulic

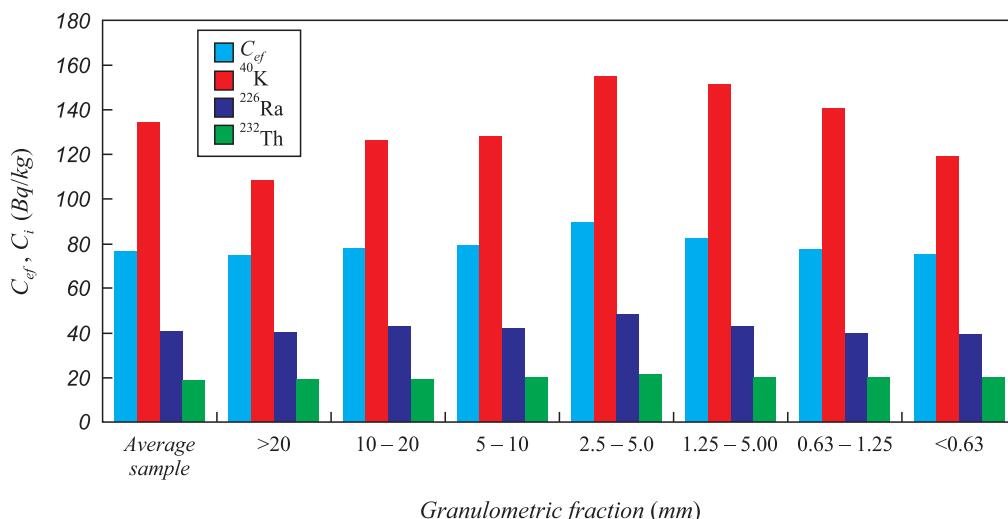


Fig. 2. Volume activity and effective volume activities for Zaporozhstal waste blast furnace slag fractions

Рис. 2. Удельная активность и эффективная удельная активность для фракций отвального доменного шлака ПАО «Запорожсталь»

activity of the slag fraction >20 mm by CaO absorption value (mg/g) at a certain time of blast furnace slag contact with $\text{Ca}(\text{OH})_2$: 1 day – 184; 7 days – 227; 14 days – 360. Zaporozhstal dump blast furnace slag shows high hydraulic activity, CaO absorption increases in time. The content of CaO in the slag, determined by dissolution in water, is 13.44 mg/g.

CONCLUSIONS

Elemental slag composition that is determined by the electron probe microanalysis enables to characterize its fractions in terms of toxicity. The third hazard class of dump waste blast furnace slag is determined.

A database containing data about natural radionuclides in technogenic raw material is expanded. It is determined that slag fractions contain ^{226}Ra , ^{232}Th and ^{40}K . It is proved that slag has the first class of radioactive hazard, which means the lack of restrictions to use technogenic raw material in construction engineering.

Dump blast furnace slag Zaporozhstal exhibits high hydraulic activity with an increase in CaO absorption over time.

Zaporozhstal dump waste blast furnace slag can be recommended to produce binders: Portland cement and Portland slag cement – in the totality of chemical parameters: relation to both moderately dangerous production wastes, the first radiation hazard class and high hydraulic activity.

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ТОКСИЧЕСКИЕ СВОЙСТВА И ГИДРАВЛИЧЕСКАЯ АКТИВНОСТЬ ОТВАЛЬНОГО ДОМЕННОГО ШЛАКА

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Аннотация. Металлургические шлаки накапливаются в больших количествах. Для дальнейшей утилизации они должны обладать необходимыми техническими свойствами. Как один из основных факторов выступает химический и минеральный составы шлаков, оказывающие влияние на их конечные свойства. Элементный состав отвального доменного шлака ПАО «Запорожсталь», определенный методом электронно-зондового микронализа, позволяет охарактеризовать фракции шлака с точки зрения токсичности. Элементы калий, натрий, сера, хлор, медь и титан, которые не входят в состав минералов, зарегистрированы сканирующим электронным микроскопом. Это позволяет предположить, что они сорбируются поверхностью минеральных частиц. Максимальное содержание калия, натрия и титана характерно для фракции 2,5 – 5,0 мм. Шлак содержит незначительное (менее 1 %) количество железа, титана и меди, которые относятся к третьему классу опасности вещества; это не препятствует дальнейшему использованию шлака. Определен третий класс опасности отвального доменного шлака. Гамма-спектрометрическим методом определены удельные активности и эффективные удельные активности гранулометрических фракций шлака. Обнаружены природные радионуклиды ⁴⁰K, ²²⁶Ra и ²³²Th. Доказано, что шлак и его отдельные фракции относятся к первому классу радиационной опасности и могут быть использованы в строительстве без ограничений. Отвальный доменный шлак ПАО «Запорожсталь» характеризуется

высокой гидравлической активностью с увеличением поглощения оксида кальция CaO во времени. Отвальный доменный шлак может быть рекомендован для производства вяжущих (портландцемента и шлакопортландцемента) по совокупности химических параметров: по отношению к умеренно опасным отходам производства, первому классу радиационной опасности и проявлению высокой гидравлической активности.

Ключевые слова: отвальный доменный шлак, элементный состав, токсичность, класс опасности вещества, радиоактивность, природные радионуклиды, гидравлическая активность.

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