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TOXIC AND HYDRAULIC ACTIVITY OF BLAST FURNACE SLAG AS THE MAIN CRITERIA FOR CHOOSING THE TECHNOLOGY OF THEIR UTILIZATION

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Abstract

Aim. The purpose is to determine the hazard class and hydraulic activity of the blast-furnace slag fractions and substantiate the way of their utilization. The study deals with the blast furnace slags from Zaporizhstal, Dnieper Metallurgical Combine (DMC), ArcelorMittal Kryvyi Rig, Illich Iron & Steel Works (Mariupol Metallurgical Combine - MMC) and Alchevsk MC (AMC). Methods. The mineral composition of the slags was determined using X-ray phase analysis on a Siemens D500 diffractometer. The elemental composition of the slag fractions was determined by electron probe microanalysis on a JSM-6390 LV scanning electron microscope with an X-ray microanalysis system. The hazard class was determined by calculating the toxicity indices. Results. In the fractions of blast furnace slags, silicate minerals of three systems were found: $CaO-SiO_2$, $CaO-Al_2O_3-SiO_2$ and $CaO-MgO-SiO_2$. The hydraulic activity of slags is quite high, it is determined by the mass fraction of hydraulically active minerals: bredigite, larnite, akermanite, pseudowollastonite; by titrimetry according to the amount of absorbed lime and the content of unbound CaO. The impurity elements S, F, Cl, P, Mn, and Ti were found in slags. The calculation of the total hazard indices showed that all the studied fractions of blast furnace slags belong to hazard class III (moderately hazardous). Conclusions. The analyzed slag fractions can be used as sorbents in the treatment of waste water and secondary raw materials at roasting and hydration when producing binders, which ensures a decrease in the content of toxic components in the finished product to comply with hazard class IV.

Keywords: blast furnace slag; mineral; hydraulic activity; toxicity; hazard class; recycling; binder.

ТОКСИЧНА І ГІДРАВЛІЧНА АКТИВНІСТЬ ДОМЕННИХ ШЛАКІВ ЯК ОСНОВНІ КРИТЕРІЇ ВИБОРУ ТЕХНОЛОГІЇ ЇХ УТИЛІЗАЦІЇ

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Анотація

Мета. Визначити клас небезпеки і гідравлічну активність фракцій доменних шлаків і обґрунтувати напрям їх утилізації. Дослідження стосується доменних шлаків Запоріжсталі, Дніпровського металургійного комбінату (ДМК), АрселорМіттал Кривий Ріг, Маріупольського МК і Алчевського МК. Методи. Мінеральний склад шлаків визначали за допомогою рентгенофазового аналізу на дифрактометрі Siemens D500. Елементний склад фракцій шлаків визначали електронно-зондовим мікроаналізом на скануючому електронному мікроскопі JSM-6390 LV з системою мікрорентгеновского аналізу. Клас небезпеки визначали при розрахунку індексів токсичності і сумарних індексів небезпеки. Результати. У фракціях доменних шлаків виявлені силікатні мінерали трьох систем: $CaO-SiO_2$, $CaO-Al_2O_3-SiO_2$ і $CaO-MgO-SiO_2$. Гідравлічна активність шлаків досить висока, вона визначена по масовій частці гідравлічно активних мінералів: бредигіта, ларніта, окерманіта, псведоволастоніта; титруванням за кількістю поглиненого вапна і вмістом незв'язаного CaO. Як елементи-домішки в шлаках знайдені S, F, Cl, P, Mn і Ti. Всі досліджені фракції доменних шлаків відносяться до III класу небезпеки (помірно небезпечні). Висновки. Досліджені шлакові фракції можуть використовуватися в якості сорбентів при очищенні стічних вод і вторинної сировини у виробництві в'яжучих матеріалів при випалюванні і гідратації, що забезпечує зниження вмісту токсичних компонентів у готовій продукції до відповідності IV класу небезпеки.

Ключові слова: доменний шлак; мінерал; гідравлічна активність; токсичність; клас небезпеки; утилізація; в'яжучий матеріал.

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ТОКСИЧНОСТЬ И ГИДРАВЛИЧЕСКАЯ АКТИВНОСТЬ ДОМЕННЫХ ШЛАКОВ КАК ОСНОВНЫЕ КРИТЕРИИ ВЫБОРА ТЕХНОЛОГИИ ИХ УТИЛИЗАЦИИ

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Аннотация

Цель. Определить класс опасности и гидравлическую активность фракций доменных шлаков и обосновать направление их утилизации. Исследование касается доменных шлаков Запорожстали, Днепровского металлургического комбината (ДМК), АрселорМиттал Кривой Рог, Мариупольского МК и Алчевского МК. Методы. Минеральный состав шлаков определяли с помощью рентгенофазового анализа на дифрактометре Siemens D500. Элементный состав фракций шлаков определяли электронно-зондовым микроанализом на сканирующем электронном микроскопе JSM-6390 LV с системой микрорентгеновского анализа. Класс опасности определяли при расчете индексов токсичности и суммарных индексов опасности. Результаты. Во фракциях доменных шлаков обнаружены силикатные минералы трех систем: $CaO-SiO_2$, $CaO-Al_2O_3-SiO_2$ и $CaO-MgO-SiO_2$. Гидравлическая активность шлаков достаточно высока, она определена по массовой доле гидравлически активных минералов: бредигита, ларнита, окерманита, псевдоволластонита; титриметрически по количеству поглощенной извести и содержанию несвязанной CaO. Как элементы-примеси в шлаках найдены S, F, Cl, P, Mn и Ti. Все исследованные фракции доменных шлаков относятся к III классу опасности (умеренно опасные). Выводы. Исследованные шлаковые фракции могут использоваться в качестве сорбентов при очистке сточных вод и вторичного сырья в производстве вяжущих материалов при обжиге и гидратации, что обеспечивает снижение содержания токсичных компонентов в готовой продукции до соответствия IV классу опасности.

Ключевые слова: доменный шлак; минерал; гидравлическая активность; токсичность; класс опасности; утилизация; вяжущий материал.

Introduction

Solution of environmental problems, introduction of processing and disposal of slag dumps of metallurgical plants can save resources and minimize environmental pollution [1]. The directions of slag utilization are various. Metallurgical slags are used as crushed stone for road construction [2], concrete filler and a component of the raw mix in the production of various binders [3; 4], as raw materials for manufacturing glass and mineral wool [1]. The hydraulic activity of granulated blast-furnace slags of various storage periods decreases with time [5]. In agriculture, slags are used for liming, soil conditioning, increasing crop yields and stabilizing heavy metals in soils [6]. The use of slags as sorbents in wastewater treatment technologies is promising [7–13]. Slags from the production of Fe-Ni alloy have proved efficient in the sorption of organic dyes [7; 8; 13], slags from the production of cast iron and steel absorb cations and anions from industrial waters and CO_2 in a blast-furnace process [9; 10]. Activation of blast furnace slag increases its sorption activity as related to Pb and Cr ions [11]. The number of surface calcium groups of blast furnace slag is sufficient for binding phosphates; an increase in the basicity of the slag reduces its sorption capacity [12].

The chemical and mineralogical composition of slags affects the direction of their disposal. The number of polluting elements does not always correspond to the chemical composition; therefore, it is necessary to carry out leaching tests of slags, which predict their behaviour in various environments [14]. The effect of non-ferrous metallurgy slags on the environment is more negative compared to slags from ferrous metals production [14]. Granular blast-furnace slag and concrete composite samples having it in their content [3], converter slag and crushed blast-furnace stones [15] have shown low eco- and phytotoxicity. Most slags contain admixtures of toxic elements: As, Pb, Cd, Co, Cr and Ni [1]. Metals Fe, Ti and Cu were found in the composition of the Zaporizhstal dump blast furnace slag [16; 17]. When steelmaking slag is used as crushed stone for road construction, the activation of soil pollution with heavy metals with an increase in soil acidity has been proven [2]. Leaching of Zn from granulated and dump blast furnace and steelmaking slag and Pb from dump blast furnace slag was registered [18]. When using blast-furnace slags as sorbents, the simultaneous input of Al, Cd, Co, and Hg into water was recorded [12].

The goal of the research is to determine the hazard class and hydraulic activity of fractions of blast furnace slags from metallurgical plants of Ukraine, which makes it possible to substantiate the direction of their utilization. This study deals with the blast furnace slags from the Public Joint-Stock Company (PJSC) “Zaporizhzhia Metallurgical Plant “Zaporizhstal” (Zaporizhstal), PJSC Dnieper Metallurgical Combine (DMC), PJSC “ArcelorMittal Kryvyi Rig”, Private joint stock company Illich Iron & Steel Works (Mariupol

Metallurgical Combine - MMC) and Open Joint Stock Company Alchevsky Metallurgical Combine (AMC). Granulometric fractions of slags, which are promising as a raw material component for the production of binders [4], have been selected for toxicological assessment.

Research objectives are determination of the mineralogical and elemental composition of the fractions of blast-furnace slags; calculation of the total hazard index of slag fractions and their assignment to a certain hazard class; determination of hydraulic activity of the slag fractions; substantiation of the direction for blast-furnace slags utilization.

The novelty of the work lies in the assessment of the toxicity and hydraulic activity of the fractions of dump and granular slags, for which the prospect of using as a raw material component of the production of binders was preliminarily determined, through the use of a set of experimental and calculated research methods.

Materials and methods of research

The separation of slags into granulometric fractions was carried out using a set of sieves.

The mineral composition of the slag fractions was determined by means of X-ray phase analysis [19] using a Siemens D500 powder diffractometer in copper radiation with a graphite monochromator. Full-profile diffraction patterns were measured in the angle range $5<2\theta<100°$ with a step of 0.02° and an accumulation time of 30 s. The primary search for phases was performed using the PDF-1 card index [20]; the calculation of X-ray diffraction patterns was carried out according to the Rietveld method using the FullProf program [21].

The chemical elemental composition of the slag fractions was determined by electron probe microanalysis (EPMA) on a JSM-6390 LV scanning electron microscope with an INCA micro-X-ray analysis system. The errors in determining the mass fractions of elements were 1.5–5.5 %.

The hydraulic activity of the slag fractions was determined by the amount of absorbed lime CaO from a 5.83 % CaO solution. In order to determine the content of unbound CaO, the extracts from blast furnace slags were obtained by keeping in water for 3 days. CaO concentration was determined by titrimetry with 1 N solution of HCl.

Methods to determine the hazard class of industrial waste using the toxicity index. For a quantitative assessment of the slags impact on the environment, a calculation method to determine the hazard class of industrial waste using the toxicity index was applied [22]. A calculation option for the development of a technology for the utilization and neutralization of industrial waste, causing a decrease in their negative impact on the soil has been chosen. Initially, the indices of K_i toxicity of chemical ingredients included in the composition of slags were calculated:

$$K_i = \frac{\lg(LD_{50})_i}{(S + 0.1F + C_s)}, \quad (1)$$

where $\lg(LD_{50})$ is the logarithm of the average lethal dose of a chemical compound when administered into the stomach; S is a coefficient reflecting the solubility of a chemical ingredient in the water; F is the coefficient of volatility of the substance; C_s is the amount of this compound in the total waste mass, in t/t; i is the ordinal number of the ingredient.

If there are no LD_{50} values for slag ingredients, but it is known that industrial waste components have a certain hazard class and are present in the air of the working area [23], then conventional LD_{50} values determined by the hazard class indicators in the air of the working area are substituted into formula (1): I hazard class $\lg LD_{50} = 1.176$ ($K_\Sigma < 1.3$); II –2.176 ($K_\Sigma = 1.3–3.3$); III - 3.699 ($K_\Sigma = 3.4–10$); IV - 3.778 ($K_\Sigma > 10$) [24].

After calculating K_i for the ingredients of the waste, no more than 3, but not less than 2 leading ones having the smallest K_i are chosen. The following conditions must be met: $K_1 < K_2 < K_3$ and $2K_1 > K_3$. The total hazard index K_Σ is calculated by the formula:

$$K_\Sigma = \frac{1}{n^2}\sum_{i=1}^{n} K_i, \; n \leq 3. \quad (2)$$

If the condition $2K_1 > K_3$ is not met, then the calculation of K_Σ is carried out according to the values of K_1 and K_2. After calculating the hazard index, the hazard class of industrial waste is determined. For the investigated fractions of blast-furnace slags, the following conditions were adopted [24]:

– Ca and Mg aluminosilicates belong to hazard class III in the air of the working area, therefore $\lg(LD_{50}) = 3.699$; the above compounds are insoluble and non-volatile ($S = 0$ and $F = 0$). Thus, when calculating K_i only the content of minerals in the slags of C_s is taken into account.

- calcite and gypsum belong to hazard class IV in the air of the working area, therefore $\lg(LD_{50}) = 3.778$; the solubility coefficient S for calcite is 0.000012, for gypsum – 0.002.

The greatest danger is the fibrogenic effect of dust generated during the processing of aluminosilicate rocks, gypsum and calcite in the production of building materials. Entry through the gastrointestinal tract and the transcutaneous route are not important for determining the toxic effect on the body. Therefore, we used indicators of toxicity of harmful substances in the air.

Mineralogical composition of blast-furnace slag fractions. During the X-ray phase analysis, silicate minerals of three systems were found in the composition of blast-furnace slags (Table 1). The minerals of the $CaO–SiO_2$ system include rankinite $3CaO·2SiO_2$, bredigite α-$2CaO·SiO_2$, and pseudowollastonite α-$CaO·SiO_2$ [25]. Rankinite has no hydraulic properties. Bredigite is an α-modification of belite with high hydraulic activity. The hydraulic properties of the β-modification are less pronounced. Pseudowollastonite is metastable, which determines its hydraulic activity during slow hardening [25].

Helenite $2CaO·Al_2O_3·SiO_2$ belongs to the ternary system $CaO–Al_2O_3–SiO_2$ [24], it does not possess binding properties. Okermanite $2CaO·MgO·2SiO_2$ belongs to the $CaO–MgO–SiO_2$ system, it exhibits insignificant hydraulic activity. In addition to magnesium ions, it may contain iron (II) and manganese ions [25]. Helenite and okermanite are isostructural minerals in which Mg and Al can be substituted by transition metals.

Table 1

Initial data for calculating toxicity indices of blast furnace slag components

№	Phase	C_s, t/t	K_i
	Zaporizhstal bump blast-furnace slag, fraction > 20 mm		
1	*α-$2CaO·SiO_2$ bredigite	0.272	13.6
2	$2CaO·Al_2O_3·SiO_2$ helenite	0.41	9.02
3	*$2CaO·MgO·2SiO_2$ okermanite	0.034	108.8
4	*α-$CaO·SiO_2$ pseudowollastonite	0.114	32.4
5	$3CaO·2SiO_2$ rankinite	0.137	27.0
	DMC bump blast-furnace slag, average sample		
6	*$Ca_{14}Mg_2(SiO_4)_8$ bredigite	0.078	47.4
7	$Ca_2Al_2SiO_7$ helenite	0.33	11.2
8	*$Ca_2MgSi_2O_7$ okermanite	0.042	88.1
9	*$CaSiO_3$ pseudowollastonite	0.165	22.4
10	$Ca_3Si_2O_7$ rankinite	0.055	67.3
11	$Ca_3MgSi_2O_8$ merwinite	0.24	15.4
	ArcelorMittal bump blast-furnace slag, average sample		
12	*$Ca_{14}Mg_2(SiO_4)_8$ bredigite	0.016	231.2
13	*$Ca_2MgSi_2O_7$ okermanite	0.1	36.1
14	$Ca_3Si_2O_7$ rankinite	0.16	23.1
15	*β-Ca_2SiO_4 larnite	0.32	11.6
16	$MnFe_2O_4$ jacobsite	0.085	43.5
17	$Ca_2Fe_2O_5$ srebrodolskit	0.298	12.4
18	$KAlSi_3O_8$ microcline	0.025	147.1

	ArcelorMittal granulated blast-furnace slag, fraction >10 mm, colour				
		C_s, t/t		K_i	
		white	grey	white	grey
19	$CaCO_3$ calcite	0.053	0.332	71.3	11.4
20	CaS oldhamite	0.0048	0.151	770.6	24.5
21	$Ca_2Al_2SiO_7$ helenite	0.559	0.245	6,6	15.1
22	*$Ca_2MgSi_2O_7$ okermanite	0.095	0.055	38.9	67.3
23	*$CaSiO_3$ pseudowollastonite	–	0.043	–	86.02
24	$Ca_3Si_2O_7$ rankinite	0.289	0.048	12.8	77.06
25	$KAlSi_3O_8$ microcline	–	0.065	–	56.9

	MMC bump blast-furnace slag, fraction 2.5–5.0 mm		
26	SiO_2 quarz	0.245	15.1
27	*$Ca_{14}Mg_2(SiO_4)_8$ bredigite	0.039	94.8
28	*$Ca_2MgSi_2O_7$ okermanite	0.244	15.2
29	*$CaSiO_3$ pseudowollastonite	0.0539	68.6
30	$Ca_3Si_2O_7$ rankinite	0.12	30.8
31	$KAlSi_3O_8$ microcline	0.15	24.7

32	$(Mg_{0.56}Fe_{0.44})_2(Si_2O_6)$ enstatite	0.085	43.5
33	$K_{0.94}Na_{0.06}Al_{1.83}Fe_{0.17}Mg_{0.03}(Al_{0.91}Si_{3.09}O_{10})(OH)_{1.65}O_{0.12}\ F_{0.23}$ muscovite	0.065	56.9
	AMC bump blast-furnace slag, fraction >10 mm		
34	$CaCO_3$ calcite	0.026	145.2
35	*$Ca_{14}Mg_2(SiO_4)_8$ bredigite	0.087	42.5
36	$Ca_2Al_2SiO_7$ helenite	0.318	11.63
37	*$Ca_2MgSi_2O_7$ okermanite	0.147	25.2
38	*$CaSiO_3$ pseudowollastonite	0.197	18.78
39	$Ca_3Si_2O_7$ rankinite	0.138	26.8
40	$CaSO_4{\cdot}2H_2O$ gypsum	0.038	94.45
41	$KAlSi_3O_8$ microcline	0.027	137
42	$Ca_{19.06}(Al_{8.82}Mg_{2.71}Fe_{1.45}Ti_{0.16})(SiO_4)_{10}(Si_2O_7)_4O(OH)(OH)_{6.56}F_{1.44})$ vesuvianite	0.011	336.27

* Hydraulically active minerals

It is interesting to compare the mineralogical compositions of ArcelorMittal granulated and dump blast-furnace slag. In the fraction >10 mm of granular slag, white and grey samples are present. In the white samples, the main minerals are helenite and rankinite, and in the grey samples these are calcite, helenite, and oldhamite. In terms of the content of hydraulically active minerals, the fractions are close: white – 9.5 % of okermanite; grey – 5.5 % of okermanite and 4.3 % of pseudowollastonite. The dump slag contains more hydraulically active minerals, 43.6 %: 10 % of okermanite + 1.6 % of bredigite + 32 % of larnite, and may show higher activity when interacting with water. This refutes the opinion about the low hydraulic activity of dump blast furnace slags and confirms the need for a mandatory assessment of the hydraulic properties of slags before using them in the production of binders.

Blast furnace slags can be used in the production of binders in two main areas: 1. as a raw material for the production of Portland cement clinker; 2. in the production of slag Portland cement (SPC) by joint grinding of cement clinker and slag. In the first case, slag minerals partially decompose with the formation of oxides at high burning temperatures. In this case, the hydraulic activity of slag minerals is of limited importance. The oxide composition of blast-furnace slags determines the choice of the first direction of utilization, it should be close to the oxide composition of the raw materials. According to [26], the use of granulated slags in the production of cements, concrete and mortars is possible if the following conditions are met: the ratio of oxides $(CaO+MgO)/SiO_2 > 1$, the slag must contain at least 67% by weight of the sum of oxides $(CaO+MgO+SiO_2)$, the rest should be Al_2O_3 together with a small amount of other compounds. White fraction> 10 mm of granulated slag has the following parameters: $(CaO+MgO)/SiO_2 = 1.7$; $(CaO+MgO+SiO_2) = 76.78$ %. Grey fraction> 10 mm: $(CaO+MgO)/SiO_2 = 2.38$; $(CaO+MgO+SiO_2) = 54.78$ %. On average, with a ratio of white and grey fractions of 1: 1, the indicators are: $(CaO+MgO)/SiO_2$ 2.04; $(CaO+MgO+SiO_2) = 65.78$ %. Thus, the fraction> 10 mm of granulated slag "ArcelorMittal" almost completely meets the requirements [26].

Unground granulated slag used for the production of cement must meet the requirements [27]: $(CaO+MgO+Al_2O_3)/SiO_2 \geq 1.2$, the slag must contain at least 67 % by weight of the sum of oxides$(CaO+MgO+SiO_2)$. For white fraction >10 mm $(CaO+MgO+Al_2O_3)/SiO_2=2.43$; for grey fraction $(CaO+MgO+Al_2O_3)/SiO_2=3.01$; the average value for the entire fraction $(CaO+MgO+Al_2O_3)/SiO_2=2.72$, which indicates the compliance of the slag with the requirements [27].

The second option for the use of blast-furnace slags in the production of binders provides for the presence of minerals with hydraulic properties in their composition. The initial hydraulic potential of the slag is used, since in the absence of burning, the amounts of glassy and crystalline phases and their mineralogical composition remain unchanged. During hardening, calcium silicates are hydrated to form Ca hydrosilicates.

Impurity elements in blast furnace slags

The results of electron probe microanalysis are in good agreement with the results of X-ray phase analysis for most elements (Table 1). Deviations are observed for impurity elements (Table 2). Compounds of S, Cl, P, Mn and Ti, which are not included in the composition of minerals, have been identified in the composition of Zaporizhstal blast-furnace slag. Discrepancies in the mineralogical and elemental compositions of the MMC blast-furnace slag are noted: the elemental composition is free of F. However, according to X-ray phase analysis, fluorine-containing minerals are present. From this it can be assumed that F is replaced in these phases by hydroxyl groups. S and Mn are present in elemental analysis. It is possible that S is present in the form of unstable Ca or Fe sulfide or hydrosulfide. The results of the chemical analysis of the AMC slag fraction >10 mm also slightly differ from the data of X-ray phase analysis. Elemental analysis additionally showed the presence of Mn, Cl in the fraction at zero F, registered in the vesuvianite mineral. Mass fraction of S is higher than expected for gypsum content.

Table 2

Results of electron probe microanalysis of blast furnace slag samples

Mass share of the element in slag fraction, %						
Fe	K	Ti	Mn	S	Cl	P
Zaporizhstal bump blast-furnace slag, fraction > 20 mm						
0.18	0.33	0.10	–	2.64	0.08	–
DMC bump blast-furnace slag, average sample						
0.38	0.42	0.22	0.36	1.95	–	–
ArcelorMittal bump blast-furnace slag, average sample						
15.38	0.28	0.19	5.34	0.80	–	–
ArcelorMittal granulated blast-furnace slag, fraction >10 mm, white colour						
–	0.25	–	–	0.61	–	–
ArcelorMittal granulated blast-furnace slag, fraction >10 mm, grey colour						
–	0.65	–	–	0.77	–	–
MMC bump blast-furnace slag, fraction 2.5–5.0 mm						
0.78	0.72	–	0.14	2.0	–	0.1
AMC bump blast-furnace slag, fraction >10 mm						
1.77	0.39	0.23	0.05	1.98	0.19	–

Thus, it can be assumed that impurity elements in the form of ions can be sorbed by the surface of mineral particles or be present in the amorphous part of the samples.

Assessment of the hazard of blast furnace slags in terms of their further disposal was carried out over silicates and aluminosilicates Ca (Mg) with a high mass contribution. The detected impurity elements cannot determine the danger of slags due to their low toxicity and low content. Table 2 shows the initial data and calculated values of K_i of the slag components, according to which the total slag hazard index was calculated. For the three lowest toxicity indices K_1, K_2 and K_3, the condition $2K_1 > K_3$ was not satisfied, therefore the total hazard index was calculated using the values of K_1 and K_2. For ArcelorMittal granulated blast-furnace slag (fraction> 10 mm) K_i are calculated separately for ingredients of fraction >10 mm of different colours (table 1). The total index is determined based on the equal content of fractions of different colours:

$$K_{\Sigma} = \frac{1}{2}(K_{\Sigma 1} + K_{\Sigma 2}) = 5.7.$$

All investigated fractions of blast-furnace slags belong to hazard class III, moderately hazardous (Table 3). For almost all samples, K_{Σ} was calculated using Ca and Mg silicates; for four slags, one of the ingredients for calculating K_{Σ} was helenite – Ca aluminosilicate. An exception is the average sample of ArcelorMittal dump blast furnace slag, for which K_{Σ} was calculated using $Ca_2Fe_2O_5$ srebrodolskit. Aerosols of these compounds have a fibrogenic effect without an acute toxic effect, for them contact with the respiratory organs and skin is possible, no control of the air in the working area is necessary [23].

The degree of harmful effects of moderately hazardous blast-furnace slags on the environment is medium [28]. The ecological system at the storage sites is disturbed, the recovery period is at least 10 years after the reduction of the harmful effects from the existing source.

Moderately hazardous blast furnace slags can be utilized as sorbents and used in the production of construction materials. Experimental results on the determination of the hydraulic activity of blast furnace slags by the absorption of CaO (Table 3) confirm this prediction.

Table 3

Hydraulic activity for the absorption of CaO, the content of unbound CaO and the total hazard indices of blast furnace slags

Slag, fraction	Mass fraction of hydraulically active minerals in slag, %	The absorption of CaO (mg/g) at the time of contact of blast furnace slags with a $Ca(OH)_2$ solution per day.			CaO content in slags, determined by dissolution in water, mg/g	Total hazard index K_Σ	Hazard class
		3	7	14			
Zaporizhstal, > 20mm	42.0	183.5	226.7	359.5	13.44	5.7	III
DMC, average sample	28.5	209.5	–97.2	–162	31.1	6.7	III
ArselorMittal dump, average sample	43.6	–712.6	–1058	–1134	84.9	6.0	III
ArselorMittal granulated, >10mm	19.7	32.4	–64.7	–130	12.6	5.7	III
MMC, 2.5–5.0 mm	33.7	227.5	345.5	378	9.2	7.6	III
AMC, >5 mm	43.1	248.3	262.4	335	16.8	7.6	III

The samples of AMC, Zaporizhstal, MMC dump blast furnace slags exhibit high hydraulic activity, the absorption of CaO increases with time. The absorption of CaO by MMC slag is most effective. For dump and granulated ArcelorMittal slag and DMC dump slag the reverse process of CaO leaching from the solid phase is observed. Moreover, the dissolution of CaO from the ArcelorMittal waste blast-furnace slag is observed throughout the entire time of contact of the slags with the solution. ArcelorMittal granulated slag and DMC dump slag absorb CaO for 3 days, then release it. This phenomenon may be associated with the excess content of unbound CaO in the slags: free or included in minerals that react with water. According to X-ray phase analysis, the fraction >10 mm of ArcelorMittal granulated blast-furnace slag contains 10 % of CaS, which undergoes hydrolysis with the release of $Ca(OH)_2$; the dissolved fraction of the $CaCO_3$ mineral (19 %) is partially hydrolyzed.

The content of unbound CaO lime in the slags was determined by analyzing water extracts from the slags. According to the results of Table 3, CaO dissolves from all slags with different intensity. The investigated fractions of blast-furnace slags can be arranged in a row according to the increase in the content of unbound CaO form in them: MMC < ArcelorMittal, granular < Zaporizhstal < AMC < DMC < ArcelorMittal, dump. Since there is no direct correlation between the CaO content and the amount of hydraulically active minerals that split off CaO during hydration, it can be concluded that the DMC and ArcelorMittal blast furnace slags contain the greatest amount of free CaO. The high content of CaO determines the independent hydraulic properties of the slag, since the $Ca(OH)_2$ formed during hydration acts as an alkaline agent on the glassy part of the slag.

Thus, the studied industrial waste can be used as a secondary raw material in the construction industry for processing and hydration. In this case, conditions are provided to reduce the content of toxic components in finished products to comply with hazard class IV.

Conclusion

In the fractions of blast furnace slags, silicate minerals of three systems were found: $CaO–SiO_2$, $CaO–Al_2O_3–SiO_2$ and $CaO–MgO–SiO_2$. A sufficiently high hydraulic activity of slag fractions was determined in terms of the content of hydraulically active minerals (bredigite, larnite, okermanite, pseudowollastonite), and the content of unbound CaO. The impurity elements S, F, Cl, P, Mn, and Ti were found in slags. It was established that all investigated fractions of blast-furnace slags belong to hazard class III (moderately hazardous).

The investigated slag fractions can be used as sorbents during purification of waste water and as secondary raw materials at burning and hydration when producing binders, which ensures a decrease in the content of toxic components in the finished product to comply with hazard class IV.

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