

Research of slag sorbents in treatment of industrial wastewater

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The sorption properties of metallurgical slag from the following enterprises were determined: Pobuzhsky Ferronickel Plant (PFNP), PJSC Nikopol Ferroalloy Plant (NFP) and blast furnace slag from PJSC ArcelorMittal Kryvyi Rih. The slag from PFNP (production of FeNi alloys) and NFP (production of FeSiMn) contain mineral diopside $\text{CaSiO}_3 \cdot \text{MgSiO}_3$, and NFP slag additionally contains titanite $\text{Ca}(\text{Ti}_{0.818}\text{Al}_{0.182})(\text{O}_{0.818}\text{F}_{0.182})(\text{SiO}_4)$. The minerals okermanite $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, rankinite $3\text{CaO} \cdot 2\text{SiO}_2$ and microcline KAlSi_3O_8 , oldhamite CaS and calcite CaCO_3 were identified in the composition of granular slag from ArcelorMittal. Some phases are in an amorphous sorption-active state. The possibility of chemical activation of slags with water, alkali and acid solutions for 1 day was shown; as a result, the slag surface area increases, hydroxyl and silanol groups form and dissociate with the formation of a negative surface charge, which is typical for Ca and Mg aluminosilicates. The most appropriate acid activation is in 0.5 M H_2SO_4 at 20 °C. It has been shown that adsorption is determined not only by the degree of loosening and charge of the slag surface, but also by the nature of organic dyes as sorbates. Dyes cationic forms are sorbed more efficiently. The nature of the interaction of slag adsorbents and organic compounds indicates the occurrence of specific, irreversible activated adsorption.

Keywords: slag, minerals, amorphous condition, sorption, activation, desorption, specific activated adsorption.

Дослідження шлакових сорбентів для очищення промислових стічних вод.
Еліна Хоботова, Інна Грайворонська

Визначено сорбційні властивості металургійних шлаків підприємств: «Побузський феронікелевий завод» (ПФНК), ПАТ «Нікопольський завод феросплавів» (НФЗ) та доменного шлаку ПАТ «АрселорМіттал Кривий Ріг». Шлак ПФНК (виробництво сплавів FeNi) і НФЗ (виробництво FeSiMn) містить мінерал діопсид $\text{CaSiO}_3 \cdot \text{MgSiO}_3$, а шлак НФЗ додатково містить титаніт $\text{Ca}(\text{Ti}_{0.818}\text{Al}_{0.182})(\text{O}_{0.818}\text{F}_{0.182})(\text{SiO}_4)$. У складі гранульованого шлаку ArcelorMittal ідентифіковано мінерали окерманіт $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, ранкініт $3\text{CaO} \cdot 2\text{SiO}_2$ та мікроклін KAlSi_3O_8 , ольдгаміт CaS та кальцит CaCO_3 . Деякі фази знаходяться в аморфному сорбційно-активному стані. Показано доцільність хімічної активації шлаків водою, розчинами лугу та кислоти протягом доби, в результаті якої збільшується площа поверхні шлаку, утворюються та дисоціюють гідроксильні та силанольні групи з утворенням негативного поверхневого заряду, характерного для Ca і Mg алюмосилікатів. Найбільш прийнятна кислотна активація в 0,5 M H_2SO_4 при 20 °C. Показано, що адсорбція визначається не тільки ступенем розпушення і зарядом поверхні шлаку, а й природою органічних барвників як сорбатів. Ефективніше сорбуються катіонні форми барвників. Характер взаємодії шлакових адсорбентів і органічних сполук свідчить про виникнення специфічної, необоротної активованої адсорбції.

1. Introduction

The current ecological situation in Ukraine is characterized by a high anthropogenic load on the environment. Environmental problems are so numerous and deep that they can only be solved comprehensively. This approach is economic and environmental [1, 2]. It is characterized by two aspects: improving the environmental situation in areas of accumulation of metallurgical slag and ensuring environmental safety due to the reduction of effluents when using metallurgical slag in treatment technologies.

Of particular importance is the use of valuable components that are part of metallurgical slag [3]. At the current technological level, the resource value is represented by about 120–150 million tons of waste generated annually, which is a significant reserve and can create a basis for replacing components of critical imports of Ukraine. These wastes form man-made deposits, which, according to a number of estimates, are suitable for industrial development. To identify the resource value of slag waste, it is necessary to study the basic properties of environmentally hazardous dumps of enterprises [4]. Industrial wastes that accumulate in dumps, in many cases, have valuable technical properties, so they can be considered as secondary resources [5, 6].

Intensive development of industry leads to a significant increase in the amount of wastewater. Discharging them into reservoirs causes pollution of the latter, reduction of clean fresh water resources, deterioration of the environment. In Ukraine, decisions have been repeatedly made at the state level to increase the effectiveness of measures for nature protection and rational use of water resources. One of the dangerous water pollutants are synthetic dyes that have a carcinogenic effect on humans and hydrobionts. The volume of use of organic dyes in industry is constantly increasing, and the amount of wastewater contaminated with dyes is correspondingly increasing. For example, the volume of wastewater from each stage of a textile operation is approximately 50.0 l/kg of product [7]. Hazardous dyes are the result of emissions from such industries as textile, printing, paper and pulp, oil refining, metallurgical industries, production of paints, pharmaceuticals, and plant protection products [8]. Organic dyes remain stable under various conditions due to their synthetic origin and complex aromatic structure and are not subject to biological degradation. That is why the problem

of cleaning polluted wastewater from dyes is of primary interest throughout the world [9].

Industrial waste contains mineral phases with sorption activity; they can be used in sorption technologies for wastewater treatment [10–12]. The part of glass in slag reaches 80 % [13]. The introduction of low-waste technologies stimulates the implementation of environmental protection measures: identification of resource value and useful properties of metallurgical slags of LLC Pobuzhsky Ferronickel Plant (PFNP), PJSC Nikopol Ferroalloy Plant (NFP) and PJSC ArcelorMittal Kryvyi Rih as technical materials and sorbents in the treatment of industrial wastewater.

2. Results and Discussion

Composition of crystalline components of slag

The composition of the crystalline part of the slag was determined by the powder X-ray phase analysis method [14] on a D500 Siemens diffractometer in copper radiation with a graphite monochromator for slag samples from PFNP and ArcelorMittal, and with nickel filter for slag samples from NFP. To account for the instrumental function of the profile, a diffraction pattern of lanthanum hexaboride was obtained under identical conditions in order to determine the microstructural characteristics of the specified phases: the average size of crystallites and the presence of microstrains. The initial phase search was performed on the PDF-1 file [15], followed by the calculation of diffraction patterns by the Rietveld method using the program FullProf [16].

The slags were pre-crushed to the following granulometric fractions (mm): <2.5; 10–20; > 20 using several types of crushers: destruction of slag stone in a jaw (conical) crusher and grinding in a roll crusher.

Thus the slag samples of PFNP (production of FeNi alloys) and NFP (production of FeSiMn) contain mineral diopside $\text{CaSiO}_3\text{-MgSiO}_3$ and the NFP slag additionally contains titanite $\text{Ca}(\text{Ti}_{0.818}\text{Al}_{0.182})(\text{O}_{0.818}\text{F}_{0.182})(\text{SiO}_4)$.

At metallurgical enterprises, both dump and granular slags are formed simultaneously. Their chemical composition and properties were compared using the example of ArcelorMittal blast furnace slag. Common minerals for the two types of slag are okermanite $2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$, rankinite $3\text{CaO}\cdot 2\text{SiO}_2$ and microcline KAlSi_3O_8 . The granular slag is not

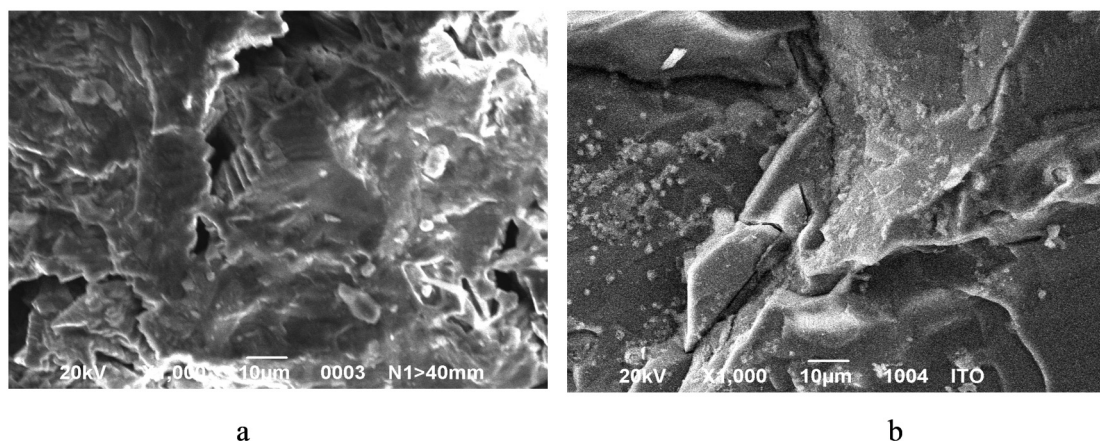


Fig. 1. Micrographs of the surface of the particles: a – slag fraction >20 mm (PFNP); b – NFP slag. Magnification 1000.

chemically inert probably due to the presence of oldhamite CaS and calcite CaCO_3 . It can be assumed that these components react with wastewater, creating a chemically aggressive medium in the slag bulk, under the action of which non-crystalline components are formed from other slag components. The latter can be gradually washed away with water from the slag bulk. Comparative analysis of the mineralogical composition of white and gray particles of the slag fraction >10 mm showed that the white particles lack microcline KAlSi_3O_8 , have a lower content of calcite and oldhamite, and a higher total mass fraction of calcium and magnesium aluminosilicates: 94.3% versus 45.2%. This served as the main criterion for selecting white particles of fraction >10 mm as the object of study of sorption properties.

ArcelorMittal blast furnace slag differs significantly in its mineralogical composition from granulated slag. Minerals composition of the dump blast furnace slag is: bredigite $\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$, larnite $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$, jacobsonite MnFe_2O_4 and srebrodolskite $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$; the mass fraction of the latter is significant – 29.8%. Based on the total content of calcium and magnesium aluminosilicates of 59.6%, the dump slag can be considered a promising sorbent.

Characterization of the surface of slag particles

The micrographs of the surface of slag particles were obtained on a scanning electron microscope JSM-6390 LV with a system of micro-X-ray analysis INCA [17]. The micrographs (Fig. 1) indicate the presence of a glass phase and liquid pores on the surface of PFNP and NFP slag samples. This is the so-called structure-forming porosity, in which the size of the

pores compared to the size of the mineral individuals is 3–25 μm .

The morphology of the surface of ArcelorMittal blast furnace slag varies depending on the method of its cooling, which is confirmed by micrographs in Fig. 2. The surface of the dump slag (Fig. 2 a, b), in comparison with granular slag (Fig. 2 c-e), is more fluffy with a large amount of fragmentary material. The micrographs show structurally formed porosity. From the standpoint of choosing an effective sorbent based on the characteristics of the surface layer, all the studied slags are good adsorbents with a developed surface, with numerous microscopic protrusions and depressions.

The charge of particles and the magnitude of the electrokinetic potential were determined during macroelectrophoresis of suspensions. Granulometric slag fractions $(1.0\text{-}6.3)\cdot 10^{-4}$ m were used.

Sorption properties of slags

Sorption properties of slags were determined under static and dynamic conditions by changing the concentrations of absorbing substances (sorbates) in the solution. The following organic dyes were used as sorbates: methylene blue (MB), Congo red (CR) and methyl violet (MV). The organic dyes chosen for the experiment differ in their nature and physicochemical properties. MV and CR are acid-base indicators with stable color in the alkaline medium. MV is a cationic dye and CR is an anionic dye. MB is a redox indicator that is sensitive to changes in pH and ionic strength of the solution. Thus, we were able to study the sorption of dyes of various natures and physicochemical properties.

Sorption of organic dyes by slags was studied spectrophotometrically using a SPEKOL 11

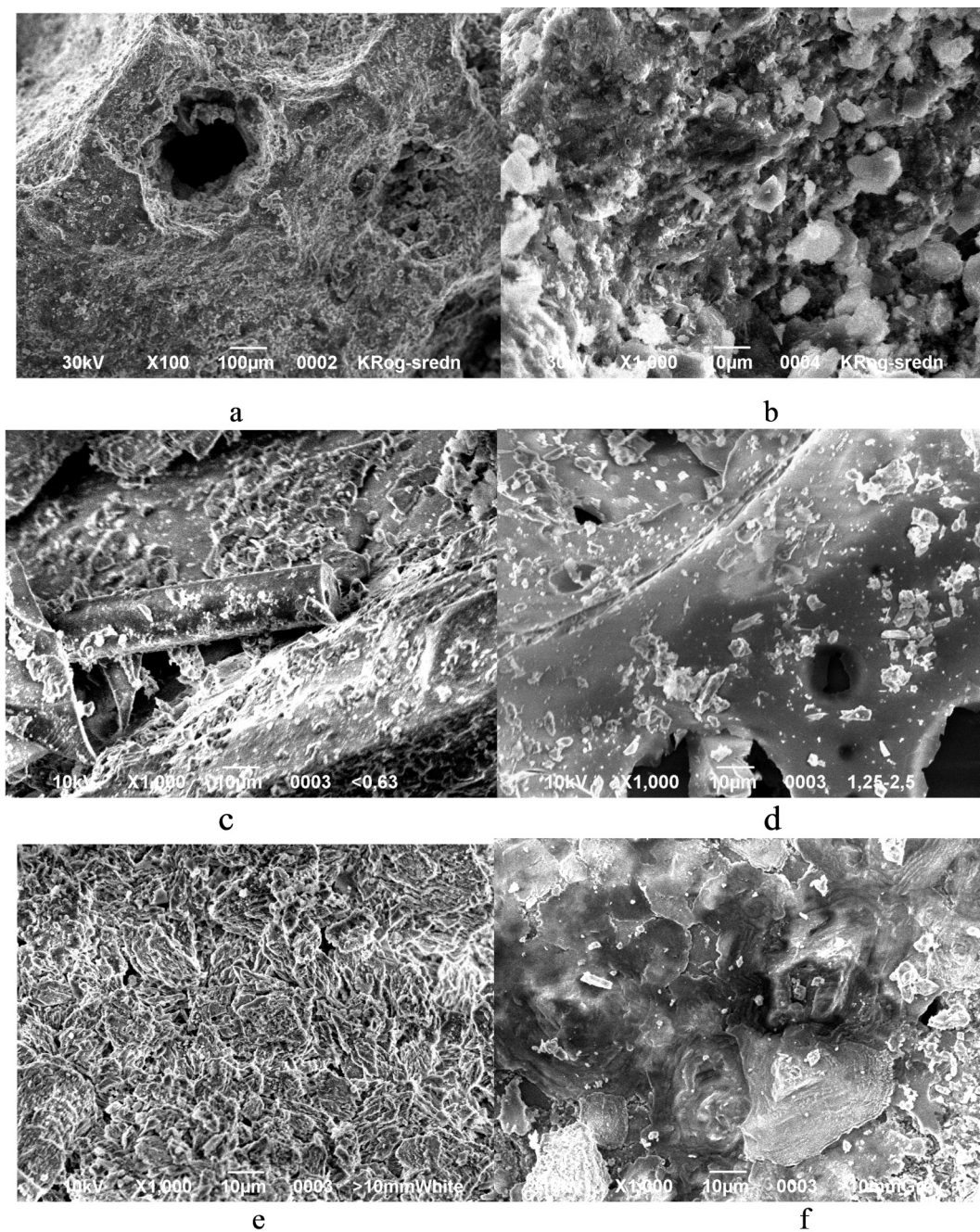


Fig. 2. Micrographs of the surface of ArcelorMittal blast furnace slag particles: a, b – waste, the average sample at magnifications: a – $\times 100$; b – $\times 1000$; (c, d) – granular different fractions $\times 1000$: c – $< 0.63\text{ mm}$; d – $(1.25\text{--}2.5)\text{ mm}$; e – $>10\text{ mm white}$; f – $>10\text{ mm gray}$.

instrument relative to distilled water at wavelengths of $\lambda = 620\text{ nm}$ and 500 nm for different sorbates depending on the color of the solution. The optical densities (D) of the MB solutions (blue color) and MV solutions (purple color) were measured at a wavelength of $\lambda = 620\text{ nm}$. The D values of the CR solutions (red color) were measured at a wavelength of $\lambda = 500\text{ nm}$. Concentrations of organic compounds were determined by a pre-constructed calibration curve

of D versus concentration. The limit of basic error is 5%. The adsorption value of slag (a) was calculated by the formula:

$$a = (C_1 - C_2) \cdot V / m, \text{ mg/g,}$$

where C_1 and C_2 are the concentrations of sorbate before and after sorption, mg/dm^3 ; V is the volume of solution, dm^3 ; m is the mass of sorbent, g.

Concentrations of cations and anions in the aqueous phase were determined by capillary

Table 1 – Change in the value of MB adsorption by PFNP slag during its acid and alkaline activation. The initial concentration of MB $C = 0.01 \text{ g/dm}^3$

Pre-activation in solution	$t \text{ } ^\circ\text{C}$	Mass concentration of MB after sorption, g/dm^3	The efficiency of extraction of MB from solution, %	a , mg/g
1 M HCl	20	0.0028	72	0.144
1 M HNO ₃	20	0.0028	72	0.144
0,5 M H ₂ SO ₄	20	0.0023	77	0.154
0,25 M H ₂ SO ₄	20	0.0031	69	0.138
0,125 M H ₂ SO ₄	20	0.0032	68	0.136
0,05 M H ₂ SO ₄	20	0.0033	67	0.134
0,025 M H ₂ SO ₄	20	0.0038	62	0.124
0,005 M H ₂ SO ₄	20	0.0039	61	0.122
0,5 M H ₂ SO ₄	40	0.0049	51	0.102
0,5 M H ₂ SO ₄	50	0.0061	39	0.078
0,5 M H ₂ SO ₄	60	0.006	40	0.08
0,5 M H ₂ SO ₄	70-80	0.0056	44	0.088
1 M NaOH	20	0.0039	61	0.122
1 M NaOH	40	0.0056	44	0.088
1 M NaOH	50	0.0054	47	0.092
1 M NaOH	60	0.0052	48	0.096
1 M NaOH	70-80	0.003	70	0.14
H ₂ O	20	0.0046	54	0.108
H ₂ O	40	0.0044	56	0.112
H ₂ O	50	0.0051	49	0.098
H ₂ O	60	0.0059	41	0.082
H ₂ O	70-80	0.0054	46	0.092
H ₂ O (vapor)	100	0.0045	55	0.110

electrophoresis based on the separation of the components of a complex mixture in a quartz capillary under the action of an electric field. The device “Drops-104T” was used.

Activation of PFNP slag in the production of FeNi alloys

The slag was pre-prepared for sorption by keeping it in water, acid solutions or alkali NaOH for 24 hours at different temperatures. Sorption was carried out under static conditions. The ratio of “slag: MB solution” = 5 g : 100 cm³ ($C_{\text{MB}} = 0.01 \text{ g/dm}^3$). The sorption time of 3 days is quite sufficient to establish exchange equilibrium during the absorption of organic substances by a sorbent of inorganic nature. The results of the experiment are shown in Table 1.

Acid activation of slag as an MB adsorbent is more effective than alkaline or water treatment. For the studied acids, the highest efficiency of MB extraction from the solution is achieved by pre-activation in a 0.5 M sulfuric acid solution. Apparently, the acid concentration of 0.5 M is the most effective, since its increase causes excessive consumption of the reagent, and the decrease reduces the capacity of the slag.

The dependence of the slag activation efficiency on temperature was studied. When activated by water, the efficiency of MB extraction from the liquid phase changes slightly. The maximum activation efficiency is achieved at 40 °C, but increases by only 3.7 % compared to 20 °C. Steam treatment for 1 hour gives an adsorption value $a = 0.11 \text{ mg/g}$ close to that at 20 °C. In addition, the structure of the slag changes to dusty. This factor does not contribute to the use of slag as an adsorbent in drinking water supply.

When slag is activated in an acid solution, the minimum value of MB adsorption is observed in the temperature range of 50-60 °C. Increasing the temperature to 70-80 °C leads to a slight increase in a . The highest a value is observed at 20 °C.

For an alkali solution, the minimum a is observed in the temperature range of 40-50 °C, the maximum value of a is at 70-80 °C. Moreover, the value of this maximum, 0.14 mg/g, is lower than for acid activation at 20 °C (0.154 mg/g); the efficiency of extraction of MB from solution decreases by 7 %. Thus, chemical acid activation of slag at a temperature of 20 °C is most appropriate.

Table 2 – The effect of PFNP slag on the ionic composition of water after leaching

Ions	Mass concentration, mg/dm ³			
	Control sample	Water after exposure to slag	State industry standard [18]	Sanitary rules and norms [19]
Cl ⁻	23.6	18.7	350	350
SO ₄ ²⁻	58.2	45.3	500	500
NO ₃ ⁻	1.8	0.7	45	45
K ⁺	5.6	2.9	not normalized	not normalized
Na ⁺	37.8	34.7	not normalized	not normalized
Mg ²⁺	1.54	2.1	not normalized.	20
Sr ²⁺	< 0.5	< 0.5	7.0	7.0
Ca ²⁺	3.5	13.8	not normalized	not normalized
SiO ₃ ²⁻	0.135	2.93	not normalized	30
pH	6.65	8.15	-	-

Activation of slag from NFP production of FeSiMn alloy

Chemical activation of the slag from NFP production of FeSiMn alloys was carried out using acid and alkali solutions, as well by keeping in water for 1 day. In all cases, the ratio of “volume of activating agent: slag” was 20 ml : 5 g. Adsorption of MB occurred from solutions with a mass concentration of 0.01 g/dm³.

The most effective type of chemical activation is treatment with a solution of 0.5 M H₂SO₄. The limit of *a* value was reached after 12 days, with a 95 % efficiency of cleaning the solution from MB. After alkaline activation and aqueous treatment, *a* reaches a maximum value after 27 days with a purification efficiency of 90 and 96 %. However, the prospects for the practical use of static adsorption should be assessed by quantitative criteria over a shorter period of time. In 3 days, the *a* value of the acid-activated slag is 97 % of the maximum value with a 92 % efficiency of MB extraction from solution, which is sufficient for removing organic compounds from industrial wastewater. Adsorption of MB using alkaline and aqueous slag activation is characterized by lower extraction efficiency over the same time interval compared to acid activation: 79 and 72 %, respectively. Thus, it is optimal to use acid activation of the slag.

Activation of granulated slag from ArcelorMittal

The conditions for slag activation are similar to those described above. The adsorption value of MB does not depend on the type of chemical

activation and in all cases is equal to 0.2 mg/m. The fastest adsorption occurs after acid activation of slag. Slower adsorption is typical for water pre-activation. However, differences in the rate of adsorption are insignificant. Based on this, in order to save chemical reagents and eliminate the stage of washing the slag from the activator, it is recommended to carry out preliminary activation with water.

Processes of leaching slag components in the liquid phase

Practical use of slag as adsorbents is possible in the absence of leaching of its own components or reaction of slag with the liquid phase. Checking the resistance of slag to water should be carried out for a long time, since in practice the slag can be used repeatedly until the sorbent is depleted.

The second condition for the use of slag sorbents is a sufficiently stable content of absorbed sorbates and the absence of their desorption into the volume of the solution, which is important for the efficiency of the adsorption process. This is important from the standpoint of possible secondary contamination of purified solutions, as well as during the disposal of spent slag adsorbents or their use in the production of building materials.

Diopside does not contain toxic elements, but its mineral components can be leached out with prolonged contact with water. For this purpose, the slag was aged in water for 1 month. A comparison of the results of the analysis of the control water sample and the water after slag

Table 3 – The effect of NFP and ArcelorMittal slags on the ionic composition of water

Ions	Control sam- ple	Mass concentration, mg/dm ³		State industry stan- dard [18]	Sanitary rules and norms [19]
		Water after slag production			
		NFP	ArcelorMittal		
Cl ⁻	12.6	13.7	16.9	350	350
SO ₄ ²⁻	4.8	21.7	21.1	500	500
NO ₃ ⁻	4.3	1.9	1.9	45	45
K ⁺	1.0	11.4	3.0	not standardized	not standardized
Na ⁺	3.7	11.0	12.7	not standardized	not standardized
Mg ²⁺	0.6	1.3	0.4	not standardized	20
Sr ²⁺	< 0.5	1.9	0.3	7.0	7.0
Ca ²⁺	11.3	27.4	57.4	not standardized	not standardized
Ba ²⁺	–	1.9	–	0.1	0.1
NH ₄ ⁺	–	1.3	0.6	not standardized	2.0
pH	8.0	8.7	11.5	–	–

leaching is given in Table 2. Dispersed compounds, silica, aluminum and magnesium ions are leached from the slag, and calcium is leached when kept in water for a long time, which helps to increase the adsorption of anions and cations of alkali metals. It can be assumed that the slag will also sorb other mineral components, which is due to the presence of an amorphous phase.

The concentrations of alkaline earth metal cations in water are low. The magnesium content of 2.1 mg/dm³ does not exceed the norm of 20 mg/dm³. The calcium mass concentration is standardized according to water hardness. A calcium concentration of 13.8 mg/dm³ corresponds to a very soft water. It can be assumed that in the dynamic sorption mode the mass concentrations of calcium and magnesium cations will be even lower. There are no exceedances of drinking water standards for cations and anions.

The alkalization of water after exposure to slag is explained by the transition of silicate ions into the solution and their hydrolysis. Thus, when slag is kept in water, parallel processes of leaching of cations and anions of the diopside mineral are observed. The ongoing processes lead to an increase in the sorption properties of the slag due to loosening its surface.

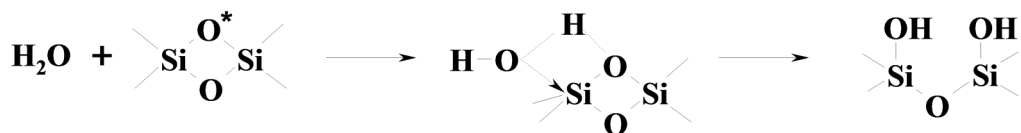
Desorption of organic dyes from slag after sorption was observed for 30 days. The efficiency of adsorption is confirmed by the practical absence of desorption of MB from PFNP slag without its pre-activation in water. When the slag was kept for a month after sorption

in distilled water, the MB was desorbed into water to a mass concentration of 0.3 mg/dm³, which corresponds to a decrease in slag capacity by 5.6 %. From this we can conclude that adsorption is ensured by the establishment of sufficiently strong bonds.

After 10 days of keeping the slag, previously activated in a 0.5 M H₂SO₄ solution, in water, MB entered the water at a concentration of 0.1 mg/dm³. Increasing the time of slag exposure in water to 30 days did not lead to increased MB desorption. After 10 days of exposure of the slag, previously activated in a 1 M NaOH solution, the MB was desorbed into water at a concentration of 0.4 mg/dm³. Minor fluctuations in concentration over the next 20 days are within the measurement error.

Similarly, we studied the desorption of CR and MV dyes using the slag from PFNP. After 10 days of slag exposure in water after sorption, the following maximum mass concentrations of sorbates were set depending on the type of activator: a solution of 0.5 M H₂SO₄ – 0.4 mg/dm³ CR and 0 g/dm³ MV; 1 M NaOH – 0.1 mg/dm³ CR and 0.08 mg/dm³ MV. Slight desorption of organic compounds from slag after sorption ensures the safety of their disposal and utilization in the production of building materials.

When kept in distilled water for a long time (1 month), some cations and anions from NFP and ArcelorMittal slags are sorbed from the water and simultaneously washed out into the water. The results of the analysis of the control



samples of water and water after exposure to slag are presented in Table 3.

The concentrations of the indicated ions do not exceed the requirements of [18] and [19] standards for wastewater for cations and anions, with the exception of the Ba^{2+} ion. After holding the NFP slag in water, the concentration of Ba^{2+} significantly exceeds the standard. Therefore, this slag can be recommended as a sorbent for the treatment of industrial wastewater only in the case of recycled water supply.

The exposure of slags in water that had absorbed MB until the maximum value of α was reached was carried out for 30 days, after which MB was not detected in control water samples. Thus, the efficiency of adsorption is confirmed by the lack of MB desorption from slag, which ensures the safety of its utilization.

The mechanism of adsorption

The slag has undergone high-temperature treatment, so most of the pores are closed. Based on the difference between the volume of a unit mass of PFPN slag and the true volume of the solid material, the open porosity was determined to be $0.0303 \text{ cm}^3/\text{g}$ or 3.03%. This factor, as well as the large size of dye molecules, practically eliminates sorption by the pores of the adsorbent.

A common factor that increases the efficiency of adsorption is the loosening of the slag surface upon activation, which increases the surface area of the adsorbent.

The mechanism of interaction of dyes with functional groups of slags is confirmed by analysis of their IR spectra. It was previously shown [11] that during the chemical activation of slags, the nature and the number of functional groups change. The initial slag is characterized by the presence of the Si–O–Si siloxane bonds, OH hydroxyl and Si–OH silanol groups. The presence of amorphous substances and the strong tension of the siloxane bonds make it possible for the chemical reaction of re-hydroxylation to occur in water, which is manifested in a slight increase in the band intensity of the free Si–OH groups in the IR spectra [11]

Three peaks at 1698, 1635, and 1585 cm^{-1} in the IR spectra were recorded in the area of

deformation oscillations of water molecules for the sample activated in sulfuric acid [11]. It can be assumed that the appearance of an additional peak is caused by a change in the coordination of water molecules by the diopside crystal lattice. The peak at 3430 cm^{-1} is the largest compared to the other samples. Based on this, it can be concluded that the most effective method of slag activation is treatment with sulfuric acid, which causes intensive slag hydration and rehydroxylation. Hydroxyl and silanol groups are potential adsorption sites. Their dissociation causes a negative charge on the slag surface (Table 4) and promotes the fixation of dye particles on the surface of the sorption material. The surface charge of slag particles is an important factor in adsorption water purification and determines the choice of organic sorbents. Indirect confirmation of this is the lower desorption of MV (cationic dye) and MB which has cationic forms $(\text{MB}^+)_2$ at pH 2-6 and MBH_2^+ at pH 0-5, after holding the slag, pre-activated with acid, in water. Less desorption of MV and MB compared to CR (anionic dye) indicates the formation of stronger bonds during the electrostatic interaction of cation forms of dyes with the negatively charged surface of slags.

The isotherm of MB adsorption by PFPN slag shows (Fig. 3) that within 24 hours, α reaches a value of 0.2 mg/g. The adsorption value does not reach the limiting value with an increase in the equilibrium concentration of MB (C_{eq}). This indicates a high efficiency of adsorption with the formation of a polymolecular layer of organic dye on the surface of the sorbent.

The efficiency of cleaning wash water with an MB concentration of $20 \text{ mg}/\text{dm}^3$ was tested over 5 days and was (%): 97.5 (1 day), 99.9 (3 days); 99.95 (5 days). The MB dye ion is positively charged and is adsorbed mainly on electronegative (acidic) adsorbents. Polar adsorp-

Table 4 – The electrokinetic potentials of slag particles

Metallurgical plant slag	ξ , mV
PFPN	22.2
NFP	15.1
ArcelorMittal	11.7

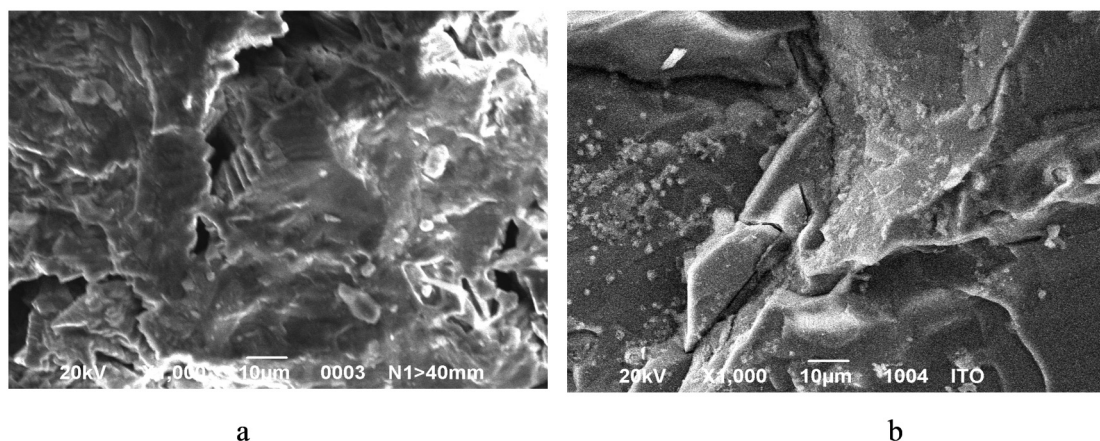


Fig. 3. Isotherm of MB adsorption by PFNP granular blast-furnace slag activated with water for 1 day ($T = 298 \text{ K}$, $C_0 \text{ MB} = 20 \text{ mg/g}$).

tion is accompanied by ion exchange between the sorbent and the solution. The retention of the large dye ion on the sorbent surface is facilitated by dispersion forces. The adsorbed aromatic compounds have a sufficiently large permanent dipole moment due to which induction electrostatic interaction with the sorbent surface occurs. Large enough organic dye ions are also capable of being adsorbed due to the lability of their electronic structure, which is easily polarized and changes the configuration of the ion, facilitating its penetration to the site of adsorption.

The nature of the interaction of slag adsorbents and organic compounds indicates the occurrence of specific, irreversible activated adsorption, which is confirmed by the insignificant desorption of organic compounds from the spent sorbent. The absence of leaching of sorbed dyes from waste slag allows for its disposal and use as a filler in the production of building materials.

3. Conclusions

It has been shown that the main factors determining the sorption properties of the studied metallurgical slags are the mineralogical composition, the presence of a sorption-active amorphous phase and the loosened surface of slag particles. The main mineral of the PFNP and NFP enterprises is diopside $\text{CaSiO}_3 \cdot \text{MgSiO}_3$; granulated blast furnace slag from ArcelorMittal is characterized by minerals okermanite $2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$, rankinite $3\text{CaO} \cdot 2\text{SiO}_2$, microcline KAlSi_3O_8 , oldhamite CaS and calcite CaCO_3 .

Using the example of MV, MB and KR dyes, it has been proven that chemical acid activa-

tion of slag with $0.5 \text{ M H}_2\text{SO}_4$ at a temperature of $20 \text{ }^\circ\text{C}$ is advisable to increase the efficiency of adsorption of organic compounds. As a result of activation, the number of protrusions and depressions on the surface of the slag increases, and hydroxyl and silanol groups are formed as adsorption centers.

Desorption of organic dyes from waste slags is insignificant, which indicates the formation of strong sorbent-sorbate bonds. The electrostatic interaction of cationic forms of dyes with a negatively charged surface during the dissociation of surface functional groups can be considered as one of the mechanisms of adsorption of dyes on slag particles. The shape of the adsorption isotherm indicates specific, irreversible activated adsorption with formation of a polymolecular sorbed layer of organic dye.

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