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Sulfides removal from slag infiltrate with layered double hydroxides

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ABSTRACT

Special place among a wide range of pollution sources of water bodies is occupied by industrial wastewater as they contain a huge amount of harmful substances. Sulfides are present in such substances list and can get into water bodies directly with industrial wastewater. Slag infiltrate is formed as a result of contact of metallurgical slag with water. Sulfides concentrations in the slag infiltrate can be around 500 mg/L. Sorption methods are perspective for wastewater treatment from sulfur compounds. A method based on the use of Mg/(Mg + Al) layered double hydroxides (LDHs) with 0.72 mol/mol Mg and Al molar ratio as sorbents is proposed for the removal of sulfides from the slag infiltrate. Prospects for their using for purifying slag infiltrate from sulfides as well as the kinetics of sulfides removal in the presence of proposed sorbents using model solutions and slag infiltrate samples are presented. It was found that the effectiveness of using Mg/(Mg + Al) LDHs with 0.72 mol/mol molar ratio of Mg and Al for the slag infiltrate treatment from sulfides is over 40% and for model solutions is over 90%.

Keywords: Infiltrate; Layered double hydroxides; Metallurgy; Slag; Sulfides

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1. Introduction

A large amount of water is used in the technological cycle of metallurgical enterprises. It determines their location near water bodies. Accordingly, the majority of metallurgical slag is stored in open disposals not far from rivers and seas [1,2].

Granulated blast-furnace slag is good material for road construction. Slag mixed with gravel and processed by viscous bitumen (product of coke oven gas processing) is an effective substitute for hot asphalt concrete mixtures. At the same time, bitumen slag roads are 2.5 times cheaper than asphalt [3,4]. Slag can also be used in the basic oxygen steelmaking for fixing damaged sites in the refractory lining [5]. The bulk of slag can be successfully used in construction engineering. One of the potential large consumers of metallurgical slag may be hydraulic construction engineering primarily marine [6]. Slag crushed stone can be a substitute for natural granite rubble when dumping dams, moorings, strengthening the coast, significantly reducing building costs. Metallurgical slag is successfully used in Japan to improve the quality of bottom sea sediments and the formation of artificial reefs [7]. Slag can be used to form artificial islands or concrete platforms for gas production installations [8]. Slag advantage in this case can be its property to harden with time like cement. An obstacle of slag using in marine construction engineering and an obvious reason for its limited use for these purposes is the danger of harmful substances transfer, primarily sulfur and its compounds, from slag into the aquatic environment [9,10].

Slag storages require significant areas. Until relatively recently, the industry disposed of the slags at poorly protected dumping sites without any environmental monitoring from the moment of disposal onward [9]. According to the fact, metallurgical slag is mainly stored in dumps near rivers and seas in an open way. That is why metallurgical

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slag disposals are sources of secondary environmental pollution due to emissions of pollutants into the air, hydrosphere, and soil. Leaching of heavy metal ions and other ions from slag occurs under the influence of atmospheric precipitation and as a result of weathering. It leads to an increase in such compounds content in water bodies compared to background [11]. The problem of slag dumps influence on the environment is of global importance. Many industrialized countries around the world have slag disposal sites, including Australia, the USA, China, Turkey, Chile, some African countries (e.g. Zambia, Namibia), Saudi Arabia as well as European countries (Poland, France, the Czech Republic, Belgium, Portugal, Ukraine, etc.) [9,12,13]. Reduction of slag disposals can be achieved by utilizing and recycling slag in an environmental friendly way, however, environmental risks and economic aspects must be taken into account [14].

Currently, more than 15 million tons of slag per year is produced at Ukrainian metallurgical enterprises [3,15,16]. However, slag consumption has significantly decreased due to the limited construction volumes in Ukraine at present time. This is due to both the environmental policy and the economic situation in the country. At the same time, slag sorting and transportation are economically inexpedient, but perspective for environmental situation improvement. In this regard, more than 100 million tons of slag have been accumulated by Ukrainian metallurgical enterprises [17,18]. For comparison, industrial wastes recycling level is more than 70% in Germany that ranked 7th in the world steel production [19]. In this work, an example of the slag disposal situated on the territory of AZOVSTAL IRON & STEEL WORKS (city of Mariupol, Ukraine) is presented. The protective dam to prevent the negative impact of the slag disposal on the coastal zone of the Sea of Azov was built. Slag infiltrate storage reservoir (Fig. 1) was formed as a result of contact with precipitations as well as natural cooling processes:

- average daily infiltrate discharge from the protective dam is 5,200 m^3/d;
- average sulfides concentration is 500 mg/L.

Thus, based on calculations sulfides daily amount inflow into the Sea of Azov in case of emergencies or overflow of the slag infiltrate storage reservoir can be about 3 tons, and the annual amount is 1,200 tons. Ammonia, iron, and chlorides were also found in the infiltrate.

CaS main part in the interaction with water is subjected to hydrolysis reaction [20]:

$$2CaS + 2H_2O \rightarrow Ca(HS)_2 + Ca(OH)_2 \tag{1}$$

Also, complete hydrolysis of sulfides interacting with water can occur with the formation of calcium hydroxide and hydrogen sulfide segregation by the reaction:

$$CaS + 2H_2O \rightarrow Ca(OH)_2 + H_2S\uparrow \tag{2}$$

The presence of sulfur and its compounds in reservoirs adversely affects not only the state of the environment (reduction of the population of living organisms that are in the reservoir) but also can harm human health (from dizziness at low concentrations to the development of cancer at high concentrations) [21,22].

The high content of sulfides in the slag infiltrate does not allow to purify it with other types of wastewater using biological treatment methods. Existing treatment methods are energy-intensive, expensive, and may contribute to secondary pollution. Known methods of industrial wastewater treatment from sulfides, such as stripping, degassing, carbonization require high energy costs and may cause additional environmental pressure due to air pollution with hydrogen sulfide and sulfur dioxide [23,24].

Using of sorbents in world practice is recognized as very promising for a number of environmental protection

Fig. 1. Slag disposal of AZOVSTAL IRON & STEEL WORKS: 1 – slag disposal; 2 – the Sea of Azov; 3 – protective dam; 4 – slag infiltrate storage reservoir.

measures. Sorbents can be used not only for wastewater cleaning or post-treatment [25] but also for neutralizing gas emissions [26], eliminating oil spills [27], and other chemical products. Currently, sorbents are mainly produced from coal of various grades, peat, and charcoal [28].

Activated carbon is an effective sorbent, but its use is limited by high exploitation costs [29]. In addition, the sorption processes are physical, and fixed anions are not linked to the matrix by chemical bonds. It makes the disposal processes risky due to the possible reverse desorption process. Also, the modified carbon sorbents [30] have such disadvantages as the long-term establishment of sorption equilibrium and a small degree of adsorption. In some countries, methods have been developed for obtaining cheaper sorbents from various wastes [7,15]. Therefore, it is necessary to search for new alternative sorbents, which would have a high degree of extraction and would not have a high cost [28–30].

Significant progress has been achieved in the research and development of layered double hydroxides (LDH) application in environmental protection, such as their use as environmental catalysts in removing organic and inorganic wastes [31–42]. There are also studies that present the efficiency of gas-phase purification from hydrogen sulfide using LDHs [43]. Studies devoted to the effectiveness of using LDHs for the purification of the aqueous phase from heavy metals are of interest [44]. However, studies on the selective removal of sulfides from a saturated salt solution, which is slag infiltrate, have not been previously presented. Thus, this work will present the investigation of using LDHs as a sorbent for reducing sulfides high concentrations.

The aim of the article is to study sulfide removal kinetics in the presence of LDHs with Mg and Al different content from a saturated salt solution (using slag infiltrate as an example of real solution), as well as to determine the most effective molar ratio of Mg and Al in the LDHs for these purposes.

2. Materials and methods

LDHs as a commercial product are produced by SASOL (Germany) and Kyowa (Japan) companies. In addition, LDHs can be synthesized in laboratory conditions.

In this work, LDHs based on Mg and Al with a molar ratio of 0.72 mol/mol of "SASOL" company and samples synthesized under laboratory conditions were used. Mg/(Mg + Al) LDHs can be obtained from the chemical production wastes containing Mg and Al salts.

Syntheses were performed by coprecipitation.

Metals salts $Mg(NO_3)_2$ and $Al(NO_3)_3$ solution with concentrations close to 100 g/L, taken in stoichiometric ratios, was poured into a solution containing about two times excess alkali and carbonates with stirring (final pH value = 8–10). The precipitate crystallizes under heating for at least during 18 h. Solutions of NaOH and Na_2CO_3 were used as a precipitant.

Precipitation time was 24 h, and crystallization time was 96 h at 80°C. The obtained samples were washed until no alkaline reaction and dried at 120°C to constant weight.

The synthesized sorbent based on Mg and Al have the following characteristics shown in Table 1 [32].

Table 1
Characteristics of synthetic sorbent [32]

Mg/(Mg + Al), mol/mol	0.72
d, Å	3.036
c, Å	22.67
Specific surface area, m^2/g	200
Pore volume, mL/g	0.2
Acidity, meq/g	0.32
Basicity, meq/g	0.54
E_{dyn}, meq/g	0.081
E_{st}, meq/g	0.41

The determination was performed by titration method in the presence of Gammet indicators. Thermal studies were carried out in a muffle furnace, in which ceramic containers were placed containing exactly measured amount of sorbent.

The temperature rise rate ranged from 1 to 10°C/min, the maximum temperature was 1,000°C, and the mass change was recorded with an accuracy of 0.0001 g. The specific surface area of LDHs was determined by low-temperature nitrogen adsorption by the chromatographic method with subsequent processing of the results obtained using the BET method. The interplanar distances in the sorbents were determined by X-ray diffraction analysis on a Siemens D-500 diffractometer. Sorption studies were performed under periodic conditions, loading the sorbent into a solution containing sulfides, and samples were taken after intensive mixing for a certain time.

The photometric method using N,N-dimethyl-n-phenylenediamine was chosen as the main method for determining sulfides [45].

Studies of S^{2-} anions sorption on Mg/(Mg + Al) LDHs showed that the reaction proceeds as in Fig. 2.

Kinetic studies of sorption were carried out to determine the parameters of the flowing process.

The sorption study of sulfide ions using LDHs was carried out in a mixing reactor with periodic sampling using model solutions prepared in the laboratory conditions and slag infiltrate samples taken from the slag infiltrate storage reservoir (Fig. 1). Sorbent mass was approximately from 0.1 to 0.4 g per 1 L of polluted water. Thus, within 5 min more than 90% of contaminants in the form of sulfide ions can be removed.

3. Results and discussion

Results of the sorption study of sulfide ions using LDHs are presented in Fig. 3. From the obtained data presented in Fig. 3, it can be seen that the sorption rate of sulfides is high, the system quickly comes to a state of equilibrium. The effectiveness of the use of a sorbent weighing 0.1 g was 65% while weighing 0.2 g was 90%.

The obtained experimental results are well linearized in coordinates $\ln C_0/C - \tau$ (Fig. 4), that shows the first concentration order by adsorbate:

$$\upsilon = k \cdot C_{S^{2-}} \tag{3}$$

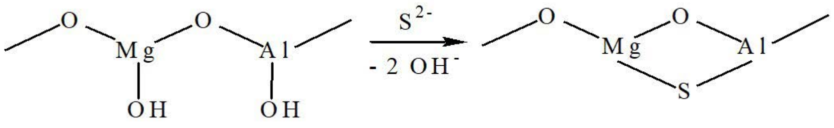

Fig. 2. Sulfides sorption on Mg/(Mg + Al) layered double hydroxides.

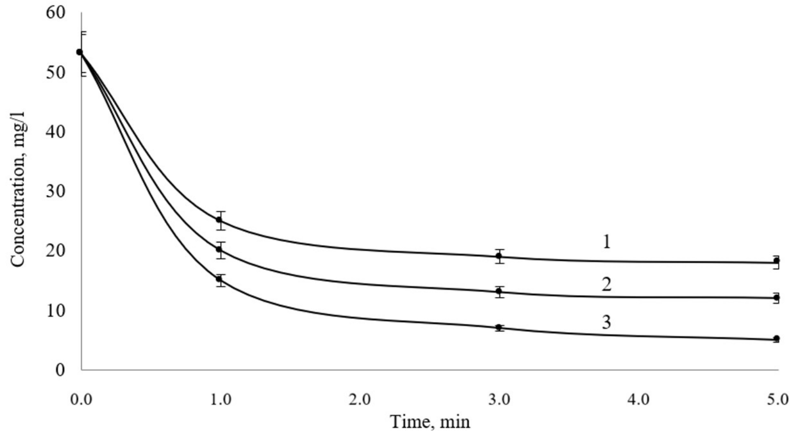

Fig. 3. Sulfide ions concentration change at different Mg/(Mg + Al) = 0.72 mol/mol LDHs mass: 1 – 0.1 g; 2 – 0.15 g; 3 – 0.2 g (t = 20°C).

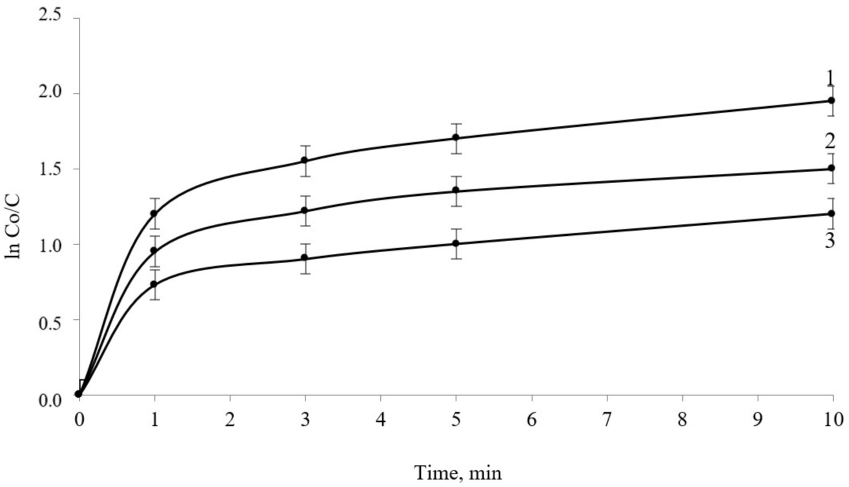

Fig. 4. Dependence of lnC_0/C on sorption time using Mg/(Mg + Al) = 0.72 mol/mol LDHs: 1 – 0.1 g; 2 – 0.15 g; 3 – 0.2 g (t = 20°C).

where k is the reaction rate constant and $C_{S^{2-}}$ is the sulfide ion concentration.

It was found that the reaction rate depends on sorbent mass. The first-order rate constants were determined by the calculation for various sorbent masses Mg/(Mg + Al) = 0.72 mol/mol. The dependence of the sorption rate constant on the mass of the sorbent was obtained using the values of the first-order rate constants (Fig. 5).

The presented kinetic dependence of sulfide ion sorption indicates the first order in mass of the sorbent. Therefore, the kinetic equation has the form:

$$\upsilon = k \cdot m \tag{4}$$

where k is the sorption reaction rate constant and m is the sorbent mass.

To replace sorbents mass on the concentration of active centers $C_{a.c.}$, the value of dynamic capacity E_{dyn} = 16.3 meq/g for 0.72 mol/mol Mg/(Mg + Al) LDHs, determined under conditions of dynamic equilibrium are used in solution volume.

Sorbent mass is multiplied by its exchange capacity and by the mass of the solution in order to calculate the main centers concentration at which the sorption process takes place in the solution volume. The final second-order kinetic equation is:

$$\vartheta = k'' \cdot C_{S^{2-}} \cdot C_{a.c.} \tag{5}$$

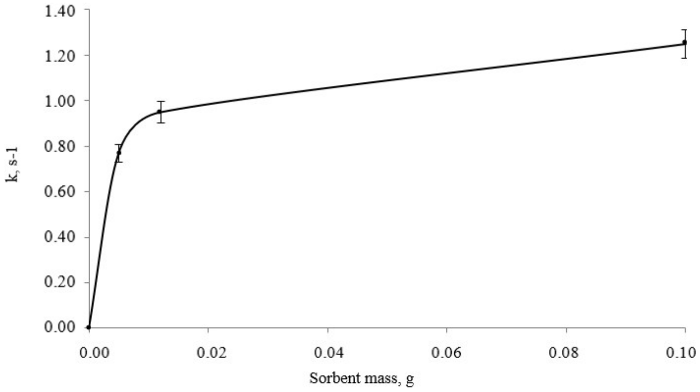

Fig. 5. Dependence of sorption rate constants of sulfide ion on LDHs mass (Mg/(Mg + Al) = 0.72 mol/mol; t = 20°C).

The adsorption capacity of the obtained sorbents was studied in the reaction of sodium sulfide with layered double hydroxides of the previously studied composition with the general formula is $Mg_xAl_y(OH)_z$, with varying degrees of isomorphous substitution. The kinetic parameters of ion exchange were studied, and the content of absorbed sulfide ions in the aqueous phase after the sorption process was recorded (Fig. 6). The effectiveness of LDHs using was about 40%.

First-order sulfide ion sorption rate constant value $k' = 0.04$ s^{-1} was calculated using Eq. (6) [46]:

$$k' = \frac{1}{\tau}\cdot\ln\frac{C_0}{C}, \tag{6}$$

where τ – time of the initial concentration of the substance C_0 change to C.

Concentrations of sorbent active centers were used to find the second-order rate constants [47]. The second-order reaction rate constant $k'' = 245$ l/mol found using the equation:

$$k'' = \frac{k'}{C_{a.c.}} \tag{7}$$

The course of ion exchange at different temperatures was studied to determine the activation parameters of sulfide ion sorption on LDHs. The values of the sorption rate constant of sulfide ions for different temperatures were determined. The data obtained are presented in Table 2.

The obtained value of activation energy indicates that the reaction proceeds in the diffusion region, but already much closer to the kinetic region than the other sorbates understudy, which indicates a high acidity of sulfides.

The full kinetic equation for the sorption of sulfides by the Mg/(Mg + Al) sorbent with Mg and Al molar ratio 0.72 mol/mol has the form:

$$k = 0.5\cdot 10^3 \cdot e^{-23\cdot 10^3/RT} \tag{8}$$

$$\vartheta = 0.5\cdot 10^3 \cdot e^{-23\cdot 10^3/RT}\cdot C_{S^{2-}}\cdot C_{a.c.} \tag{9}$$

Mg/(Mg + Al) LDHs can be regenerated using alkali in the amount of tens cycles. Therefore, two sorption columns filled with LDHs should be installed during the

Table 2
Sorption rate of sulfide ions at different temperatures

T, K	293	313	328	338	348
k', s^{-1}	0.04	0.05	0.06	0.08	0.12
E = 23.28 kJ/mol			$k_0 = 0.5 \times 10^3$ 1/mol·s		

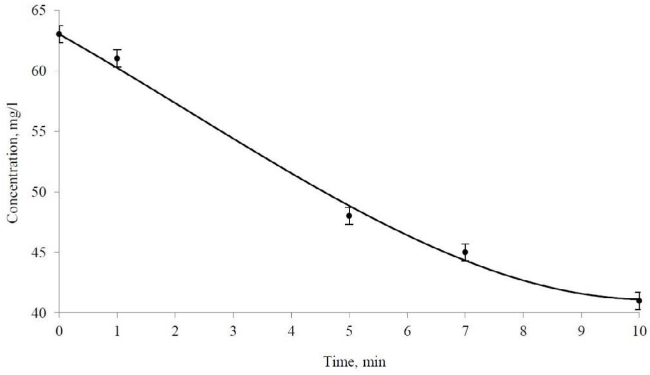

Fig. 6. Sulfide ions concentration change for LDHs Mg/(Mg + Al) = 0.72 mol/mol (m = 0.1 g; t = 20°C).

development of the technological concept for slag infiltrate treatment. One column will be used for the treatment process. In the second column, the sorbent will be regenerated. After the end of use, LDHs can be buried both in closed disposals and in the open air without the threat of a negative impact on the environment.

In conclusion, the effectiveness of using Mg/(Mg + Al) LDHs with 0.72 mol/mol molar ratio of Mg and Al for the slag infiltrate purification from sulfides is over 40%. However, at high sulfides concentrations, it will be necessary to use additional treatment methods in order to meet the legal requirements. There are also other pollutants in the infiltrate such as suspended solids, heavy metals, etc. [9,14]. Thus, it is promising to study the kinetics of sorption not only of sulfides, but also of other substances using LDHs as sorbents. It is also promising to conduct further research using the LDHs of an alternative composition (for example, Zr/Al) in order to purify slag infiltrate as well as saturated salt solutions from sulfur compounds.

4. Conclusions

The effectiveness of Mg/(Mg + Al) LDHs using as sorbents for purification from sulfur compounds was analyzed. Studies of sulfide removal kinetics were carried out using model solutions and slag infiltrate samples to determine the prospects of using Mg/(Mg + Al) LDHs as a sorbent for wastewater treatment and saturated salt solutions. Studies were conducted for LDHs with the content of Mg and Al is 0.72 mol/mol. The sorbents used by SASOL and samples synthesized in the laboratory during the implementation of the experiments allowed us to obtain results with a deviation of no more than 5%. Therefore, separate results are not presented for each of the samples in this article. The effectiveness of using Mg/(Mg + Al) LDHs with 0.72 mol/mol molar ratio of Mg and Al for the slag infiltrate purification from sulfides is over 40% and for model solutions are over 90%. It is also promising to conduct further research using the LDHs of an alternative composition (for example, Zr/Al) in order to purify slag infiltrate as well as saturated salt solutions from sulfur compounds.

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