Adaptation of the SAVMIN process for mine water treatment

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Abstract. The article presents the thermodynamic substantiation of the necessary and sufficient basicity of calcium aluminates for the formation of the preferred form of ettringite during purification of mine water from sulfate ions, the selection results based on the data obtained and studying the phase composition of aluminothermic slags by X-ray phase analysis of the preferred precipitating reagent. It has been established that mainly basic calcium aluminates are present in the chromium metal production slags, while ferrotitanium and ferrochrome production slags contain up to 35% majenite - 12CaO 7Al2O3, the presence of which in the precipitator increases the feasibility of precipitation from ettringite in the form of calcium mono-hydrosulfoaluminates. The results of the experimental verification of the feasibility and effectiveness of the purification of the model sub-waste water are presented. It is shown that it is possible in principle to reduce sulfates to MAC in mine waters using two-stage sedimentation using ferrotitanium production after liming as a reagent-precipitant of mechanically activated slag.

1. Introduction
One of the most important tasks of the rational use of natural resources in the activities of mining enterprises is the purification of technogenic waters with the extraction of valuable components from them [1-3] and, very importantly, with obtaining demanded products and easily recycled [3,4]. The main difficulty lies in the need to clean large volumes of water. This leads to high economic and material costs in the implementation of various cleaning schemes.

Mine water contamination – quarrying, mine, and bottom-drainage – is associated primarily with the oxidation of sulfides as unstable minerals in hypergene conditions. sulfate ions [5-7]. Thus, technogenic waters are complex multicomponent systems, which, in addition to solutes, include colloids, suspended solids of inorganic and organic origin [1,8,9].

The most polluted are acidic mine waters [9,10]. In terms of their chemical composition, acidic mine waters do not meet the standards of water quality for water bodies of fisheries value in many respects, including the following:

- high mineralization (up to 3 g / l), in connection with which about 2 million tons of mineral salts are discharged into reservoirs and rivers annually;
- contamination with suspended substances (90-110 mg / l), which causes siltation of water bodies;
- high content of heavy metal ions (1.5-15 times).
Environmental damage from discharging sulfates ions into reservoirs with acid mine waters is comparable less compared to other pollutants dissolved in these waters, therefore, until recently, mining enterprises did not pay serious attention to their monitoring and conditioning. The situation has changed due to changes in the environmental legislation of our country. The changes provide for a significant increase in fees for discharges exceeding the limits by 25 times instead of 5 to date. The factor 25 is applied to emissions and discharges exceeding the limits set by the permit for emissions and discharges, as well as the maximum allowable emissions and VAT - if the limits are not set [11,12]. In addition, in recent years, almost all the rivers that receive the treated waters of mining enterprises have been transferred to the category of reservoirs of fisheries value. That in itself tightens the requirements for water purification, including the salt composition.

In connection with the foregoing and the state’s transition to economic management under the rules of Green Logistics [13], many enterprises are showing an increased interest in methods and technologies for reducing sulfate in waters for their application to conditioning mine, sub-basement and other types of industrial waste to be discharged after treatment in surface water.

Currently, the most popular are reagentless methods, namely, membrane and ion-exchange technologies. However, the use of these methods for the treatment of large volumes of acid mine water is hampered by unsatisfactory technical and economic indicators: high capital and operating costs and not fully resolved environmental problems associated with waste disposal [14].

Practically at all mining and processing enterprises a traditional and economical method of purifying acidic waters is used by raising the pH to 9-11 by liming, to form poorly soluble compounds of heavy metals. In the schemes of purification of mine water by liming, gypsum is formed, but the required concentration of sulfates, namely 0.1 g / dm³, is not achieved when using only milk of lime. Therefore, a further decrease in the concentration of sulfates through the introduction of lime is ineffective. In this connection, to achieve the MPC requirements for sulfate ions, it is necessary to introduce an additional reagent to intensify the process. In this regard, the technology of sulfate removal by precipitation as a component of ettringite (1), proposed in 1999 by J. R. Smith and called the SAVMIN process [15] (Figure 1).

\[
Ca_6Al_2\left(SO_4\right)_3(\text{OH})_{12} \cdot 26H_2O
\]

**Figure 1.** Scheme SAVMIN-process.

Despite the attractiveness of the technology, today its use is not economically justified. This method can be used in mining enterprises subject to the use of relatively inexpensive technical reagents and optimization of the kinetics of the processes. Therefore, the adaptation of technology to the conditions of mining enterprises is urgent.

### 2. Research methods

In order to adapt the technology for the conditions of mining enterprises, together with specialists from CJSC UralOmega, LLC Evrosintez, LLC Sredny Volga, an approach was used based on the thermodynamic substantiation of the necessary and sufficient basicity of calcium aluminates to form the preferred form of ettringite, the choice based on data obtained from mining and metallurgical
production, the most responsible in composition and basicity to obtain from it a precipitating agent and conducting experiments on water purification from sulfates.

In order to assess the possibility and priority of the reaction between calcium aluminates of different basicity and sulfate ions, [16] carried out thermodynamic calculations for five calcium aluminates possible in the CaO – Al₂O₃ system according to the following stages of ettringite formation [17,18]: hydrolytic decomposition of calcium aluminates, being in solid phase (stage 1); the formation of calcium hydroaluminates in water of different basicity (stage 2); the interaction of calcium hydroaluminates with sulfate anions with the formation of calcium hydrosulfoaluminates (stage 3). The values of the thermodynamic characteristics of the reactants are taken from [19,20].

The phase composition of aluminothermic slags and sludge from sulfates water was studied using X-ray phase analysis on a D2 PHASER diffractometer (manufactured by BRUKER AXS GmbH, quantitative analysis was performed using a licensed version of the TOPAS 4.2 program. Sludges were studied using electronic microscopy. Scanning electron microscope JSM-6490 (Japan).

Sulfate was precipitated from wastewater under laboratory conditions on model bottom water, typical of enterprises producing pyrite copper ores, using the principles of physical modeling. Studied the effect of the precipitator consumption, the duration of the reagent conditioning with water, the method of preparing the reagent on the removal efficiency of sulfate - ion from the model solution.

3. Results and discussion
As a result of the reaction of the interaction of sulfates with calcium cations and aluminum ions, insoluble four-component compounds of the following chemical formula (2) are formed:

\[ 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \gamma \text{CaSO}_4 \cdot \chi \text{H}_2\text{O}, \text{where } \gamma = 1 + 3, \chi = 12 + 32 \]  

(2)

The calculations were performed for five calcium aluminates of the composition (3)

\[ \text{CaO} \cdot \text{Al}_2\text{O}_3, \text{CaO} \cdot 2\text{Al}_2\text{O}_3, \text{CaO} \cdot 6\text{Al}_2\text{O}_3, 3\text{CaO} \cdot \text{Al}_2\text{O}_3, 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \]  

(3)

From the values of the Gibbs energy, it was determined that when they are hydrolyzed, four types of calcium hydroaluminates can be formed (4):

\[ \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}, 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}, 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}, 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O} \]  

(4)

It should be noted that with an increase in the basicity of calcium aluminate, the value of the Gibbs energy of the hydrolysis reaction decreases (Table 1) and the maximum negative values are obtained for majenite (5)

\[ 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \]  

(5)

| Calcium Aluminates | Calcium hydroaluminates (hydrolysis products) |
|-------------------|-----------------------------------------------|
| CaO · 6Al₂O₃      | [-90.71, -105.84, -142.25, -55.39] (kJ/mol)  |
| CaO · 2Al₂O₃      | [-7.25, -22.37, -35.66, -37.92]               |
| 3CaO · Al₂O₃      | [-11.73, -26.86, -34.36, -42.40]              |
| 3CaO · Al₂O₃      | [-156.62, -163.91, -167.01, -202.80]          |
| 12CaO · 7Al₂O₃    | [-384.22, -450.89, -511.89, -637.68]          |

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Table 1. Values of ΔG°₂₉₈ calcium hydroaluminates formation reactions.
As a result of the performed thermodynamic calculation (Table 2), it can be argued that all varieties of calcium hydroaluminates in an aqueous medium can interact with sulfate ions. Most of the reaction with calcium dicalcium octahydroaluminate ($\Delta G_{298}^0 = -305.66 \text{ kJ / mol}$), the formation of which is most thermodynamically likely from twelve calcium aluminate (magenite) $\Delta G_{298}^0 = -450.89 \text{ kJ / mol}$. It should be noted that at the same time, two types of calcium hydrosulfoaluminates can be formed simultaneously: mono- and tri-sulfate forms.

The source of calcium aluminates can be aluminothermic slags. Only at Klyuchevsky Ferroalloy Plant OJSC for more than sixty years of activity in the dump accumulated over 2.5 million tons of slag.

| System | $\Delta H_{298}^0$ (kJ / mol) | $\Delta Z_{298}^0$ (kJ / mol) | $\Delta H_{298}^0$ (kJ / mol) | $\Delta Z_{298}^0$ (kJ / mol) |
|--------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ | 7456.43 | -108.73 | 10900.66 | -183.60 |
| $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ | 5942.79 | -305.66 | 10869.74 | -142.98 |
| $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ | 5911.03 | -31.72 | 10837.98 | -106.58 |
| $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$ | 6051.91 | 45.74 | 11437.2 | -29.71 |

The complexity of the slag mass makes it impossible to rationally use it in further processing at the plant itself, as well as in the sale to potential consumers. Analysis of the chemical composition of slags according to [21] shows a high content of $\text{Al}_2\text{O}_3$, which varies from 53 to 78.6%. For the research, five types of slag with the highest amount of alumina were chosen:
- №1 - slag metal chromium production from the slag heap;
- №2 – metallic chromium current production slag;
- №3 – slag production of ferrochrome alloy from the slag heap;
- №4 – ferrotitanium slag from slag heap;
- №5 – ferrotitanium current slag.

X-ray phase analysis showed (Table 3) that mainly basic calcium aluminates are present in slags from the production of metallic chromium, while in the slags of the production of ferrotitanium and ferrochrome there is magenite (5). The highest content of magenite in the absence of harmful impurities in the slags of ferrotitanium production.

| Slag | The phases that make up the slag |
|------|----------------------------------|
|      | calcium hexaaluminate and sodium | calcium dialuminate | majenite | spinel | titanium phases | chromium phases |
|      | $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ | $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ | $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ | $\text{MgO} \cdot (\text{Al}_3\text{Cr})_2\text{C}$ | $\text{CaTiO}_3$, $\text{FeCr}$, $\text{TiO}_2$, $\text{Ti}_2\text{O}_3$, ($\text{Al},\text{Cr})_2\text{O}_3$, $\text{TiO}_2$, $\text{FeTi}$ | $\text{Cr}$ |
| 1    | 65-70 | 4-5 | 2-3 | 2-3 | - | 16-22 |
| 2    | 55-60 | 3-4 | 2-3 | 3-4 | - | 31-37 |
| 3    | 30-35 | 8-10 | 8-10 | 55-60 | - | 2-3 |
| 4    | 35-40 | 20-25 | 8-10 | 8-10 | 26-35 | - |
| 5    | 35-40 | 30-35 | 8-10 | 8-10 | 19.5-26.5 | - |
According to data from microstructural studies of slags, inert minerals such as magnesium spinel, calcium titanates, and intermetallic compounds or intermetallic compounds were also found. Based on the phase composition of the slag, slag for the production of ferrotitanium was chosen as a reagent for precipitating sulfates from mine water. The X-ray diffraction pattern of slag (sample 5) is shown in Figure 2.

To use slag as a precipitant, it was crushed to a particle size of 100% -44 microns. An aqueous suspension was prepared and its mechanical activation was carried out to form calcium hydroaluminates necessary for the production of ettringite.

In laboratory studies, a mechanically activated suspension of finely ground slag was fed into the model water after the operation of liming. The change in the residual sulfate content depending on the time of conditioning the suspension with model water is presented in Figure 3. With the conditioning time of more than 120 minutes, the concentration of sulfate ions in the model water decreased below the MPC level and at 180 minutes was 20 mg / l.

Microscopic studies have confirmed that as a result of wastewater treatment using a suspension of finely divided slag, sulfate ions become insoluble and precipitate as a complex compound of high and low sulfate ettringite, presented in the form of thin hexagonal plates and needle tubes (Figure 4).

The use of mechanically activated slurry of aluminothermic slag after liming reduces the sulfate content in the model water to the level of the MPC, and the resulting ettringite can be used as an additive in concrete for special purposes.
4. Conclusion

Thus, a production waste containing the most active calcium aluminates for the production of ettringite in sulfate water purification processes was selected. Thus, a promising direction for the disposal of heavy-duty ferrous metallurgy was substantiated. It is shown that it is possible in principle to effectively bind a sulfate ion to ettringite by using mechatonotized slag production of ferrotitanium as a precipitating agent. The use of the prepared slag in the mine water purification schemes after the precipitation of metals with lime milk will lead to the formation of commodity ettringite and a decrease in the concentration of sulfate ion in the purified water to MPC.

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