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Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan

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Dulatbek Turysbekov

Satbayev University, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan.

E-mail: d.turysbekov@satbayev.university

ORCID ID: <https://orcid.org/0000-0003-0904-1565>

Larissa Semushkina

Satbayev University, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan.

E-mail: l.semushkina@satbayev.university

ORCID ID: <https://orcid.org/0000-0001-8925-5250>

Zhamihan Kaldybayeva

Satbayev University, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan.

E-mail: zh.kaldybaeva@satbayev.university

ORCID ID: <https://orcid.org/0000-0001-5763-9655>

Nessipbay Tussupbayev

Satbayev University, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan.

E-mail: n.tussupbayev@satbayev.university

ORCID ID: <https://orcid.org/0000-0002-6110-0772>

Sabira Narbekova

Satbayev University, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan.

E-mail: s.narbekova@satbayev.university

ORCID ID: <https://orcid.org/0000-0002-7325-754X>

Aynur Mukhamedilova

Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan

E-mail: a.muhamedilova@satbayev.university

ORCID ID: <https://orcid.org/0000-0002-0124-8046>

Effect of modifier reagent on sulfite ion oxidation during selective separation of copper and lead sulfides

Abstract: Oxidation of minerals and reagents, the mechanism of interaction of components of the liquid phase of the pulp between themselves and with the surface of ore-forming minerals have the greatest impact on selective flotation. The study of redox processes occurring in sulfide ores and pulps and leading to changes in the physical and chemical surface properties of minerals is an urgent task. The influence of divalent and trivalent forms of iron on the oxidation of sulfite ions in the pH range of 6-12 at different flotation conditions has been studied. It was found that 95-98% of sulfite ions are oxidized in the pH range of 6-8.5 in the presence of a mixture of divalent and trivalent iron oxides under aeration conditions for 8-10 min.

Keywords: flotation, modifier, selection, oxidation, sulfite ions.

Introduction

Most concentrators processing polymetallic ores operate according to the following scheme: collective flotation of copper and lead minerals from the initial ore with suppression of sphalerite and pyrite, followed by separation of the copper-lead concentrate; sphalerite and sometimes pyrite are extracted from the tailings of the copper-lead cycle.

The separation of copper, lead and zinc concentrates from polymetallic ores is very challenging (Mei et al., 2012; Kenzhaliyev, 2019; Chepushtanova et al., 2022; Dihanbaev et al., 2019; Yessengaziyev et al., 2020; Gladyshev & Nurhadiyanto, 2021). The quality of the homogeneous concentrates, which can only be achieved by flotation enrichment, is very important for metallurgical processing. Currently, there are several common techniques for separating the collective copper-lead concentrate. Cyanide and sulfite technologies (Bakinov, 1962; Kosherbaev, 1975; Viduetsky et al., 2009; Turysbekov et al., 2018) have found industrial applications. Cyanide technology is not environmentally safe, and at the sulfite method of separation, there is a large consumption of sodium sulfite (3-4 kg/t) and iron sulfate (5-6 kg/t). The development of new methods of separation of collective concentrates with the use of new reagents-modifiers is an important task in the flotation enrichment of non-ferrous metal ores.

Modifiers are of great importance in the flotation process (Bocharov et al., 2022; Kong et al., 2024; Kyaw et al., 2024; Miao et al., 2024). Numerous studies with various iron-containing reagents (Turysbekov

et al., 2020) were carried out to replace sodium sulfite and iron sulfate. As a result, a new iron-containing galena modifier was found, which has a depressing effect and more actively hydrophilizes lead sulfide minerals.

Such processes as oxidation of minerals and reagents, the mechanism of interaction of components of the liquid phase of the pulp between themselves and with the surface of ore-forming minerals, sorption of the collector and sulfur-containing modifiers have the greatest influence on selective flotation (Abramov, 1984; Eliseev et al., 1992; Bocharov, 1994; Kayumov et al., 2023). In addition, in the process of oxidation of sulfides and components of ore pulps, such products as sulfide ions, iron ions, metallic iron, their oxidation products, and waste rock minerals are formed. These products most effectively affect the flotation performance.

When using sulfite technology for the separation of copper-lead concentrate, sulfite ion, being a good reducing agent, creates a redox medium in the pulp, which is intensively oxidized in water with oxygen. Both sulfite ion and iron cations, being present in the pulp, always have a certain effect on the process, given which undesirable consequences can be eliminated to a certain extent. Currently, there is no consensus on the mechanism of action of minerals of both the sulfite ion and its joint action with iron cations.

Redox processes that occur in sulfide ores and pulps and lead to a change in the physicochemical surface properties of minerals are the main cause of difficulties in the separation of selective concentrates during selective flotation (Avdokhin & Abramov, 1989; Bogdanov et al., 1983). The purpose of the work is to study the effect of the flotation modifier reagent, which is a mixture of divalent and trivalent forms of iron, on the oxidation of sulfite ions in the flotation system.

Materials and research methods

To study the effect of the reagent-modifier on the oxidizability of sulfite ions at different pH of the medium, sodium sulfite solution with an initial concentration of 400 mg/dm³ was used. The studies were carried out at different pH of the medium, which varied from 6 to 12. The pH was monitored using a pH-meter of pH-150 type. Sulfuric acid and caustic soda were used as medium regulators. The residual concentration of sodium sulfite [$\omega_{\text{residual}}(\text{SO}_3^{2-})$] was determined by inverse iodometric titration. The concentration of iodine solution for titration was 12.7 g/dm³ or 0.05 n. Test experiments were carried out in the flotation chamber in agitation and agitation-aeration modes without and with the addition of a reagent-modifier. The volume of the working chamber of the flotation machine was 50 cm³.

A mixture of divalent and trivalent forms of iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) was used as a reagent-modifier. The reagent was introduced into the solution in the form of powder with different dosages of 0.5-3.0 g.

The effect of Fe^{2+} divalent iron ions was investigated as a comparison. Iron sulfate solution of the concentration used in production conditions was used in the work.

Oxidation of sulfite ion was studied not only at different pH of the medium, and different modes of operation of the flotation machine but also at different agitation times with the reagent-modifier.

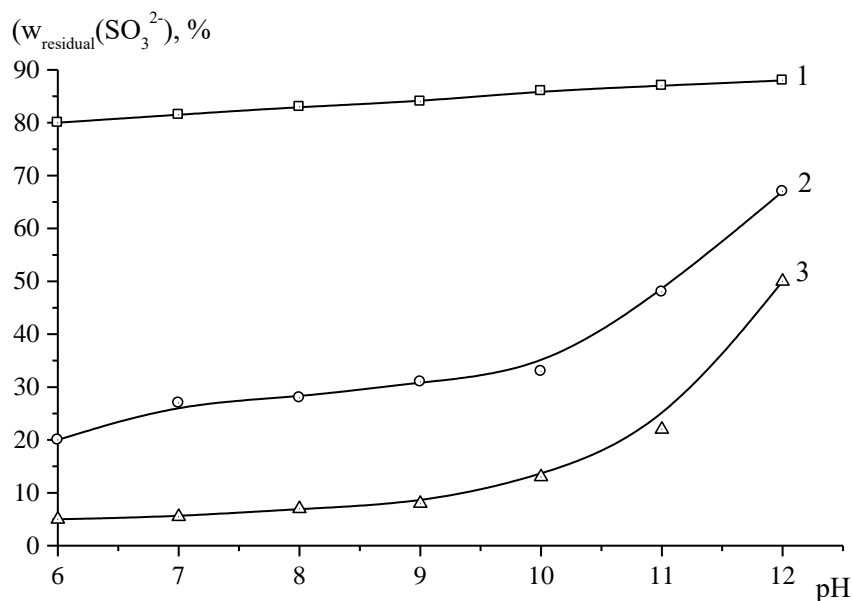
Results and Discussion

Test experiments were carried out to study the effect of solution pH on the oxidizability of sulfite ions in agitation and agitation-aeration modes without and with the addition of a reagent-modifier. The results of the experiments are presented in Figure 1.

It is known that under sulfite regime conditions the $(\text{SO}_3)^{2-}$ ion, reducing the galena surface, enhances the hydrophilic properties of the mineral. Based on the data of analysis of the residual concentration of sulfite ions ($\omega_{\text{residual}}(\text{SO}_3^{2-})$) in solution, it is shown that under agitation-aeration conditions in distilled water, the degree of its oxidation is insignificant (curve 1, Figure 1). Under the agitation-aeration regime in the absence of the modifier reagent, the oxidation of $(\text{SO}_3)^{2-}$ -ion is markedly increased compared to the agitation regime, which is due to the increased oxygen content. In the presence of the modifier reagent under the same treatment regime, the degree of sulfite ion oxidation is markedly enhanced (curve 2, Figure 1), as there is physical sorption of oxygen on the surface of the material, which promotes the oxidation of sulfite ions. At agitation-aeration mode in the region of pH above 10, the lowest degree of oxidation of $(\text{SO}_3)^{2-}$ ions is observed, which is consistent with the results of E.V. Adamov's studies on the

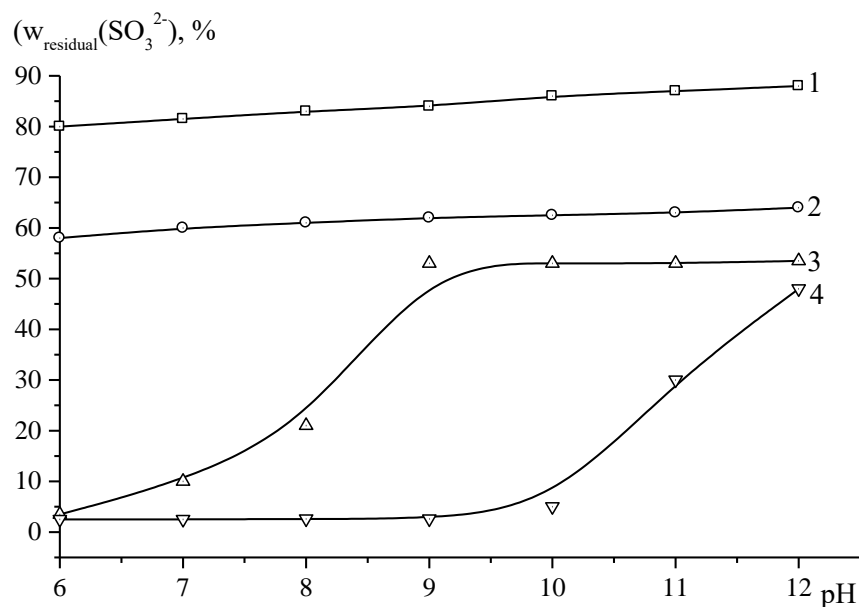
stability of sulfite ions in flotation conditions (Avdokhin, 2008). The results show that the most intensive oxidation occurs in agitation-aeration mode in the presence of a reagent-modifier (curve 3, Figure 1).

To obtain comparative data on the effect of mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) and divalent iron ions on the oxidation of sulfite ions, the corresponding experiments were set up. The results are shown in Figure 2.



1 - agitation mode; 2 - agitation-aeration mode; 3 - agitation-aeration mode in the presence of reagent-modifier

Figure 1. Influence of medium pH on oxidation of sulfite ions in different flotation modes



1- in agitation mode without reagent; 2 - in agitation mode in the presence of mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$);
3 - in aeration mode in the presence of iron sulfate; 4 - in aeration mode in the presence of a mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$)

Figure 2. Influence of pH of the medium and iron-containing reagents on oxidation of sulfite ions in different flotation modes

Judging from the residual concentration of the SO_3^{2-} ions in solution (Figure 2) in the presence of a mixture of ($\text{Fe}^{2+}+\text{Fe}^{3+}$) under agitation conditions, the sulfite ion does not undergo appreciable transformations in the pH=6-12 range. This is apparently due to the insignificant content of oxygen activated on the surface of the material. When the process is carried out in the aeration mode, the

oxidation of sulfite ions proceeds much deeper. The influence of iron ions on the oxidation of sulfite ions in solution in the aeration mode of treatment is manifested to a much lesser extent in the considered pH range. Hence, we can conclude about the essential role of the mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) in the complex redox processes occurring in the flotation system.

It is established that at aeration mode of treatment sulfite ion oxidation is intensified due to the increase of oxygen content in the solution. It is shown that sulfite ion oxidizability is intensified in the presence of a mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) at the aeration mode of treatment (curve 4, Figure 3).

Test experiments were carried out to study the effect of the dosage of the mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) on the oxidizability of sulfite ions. The dosage of the mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) was varied from 0.5 to 3 g. The results are presented in Figure 3.

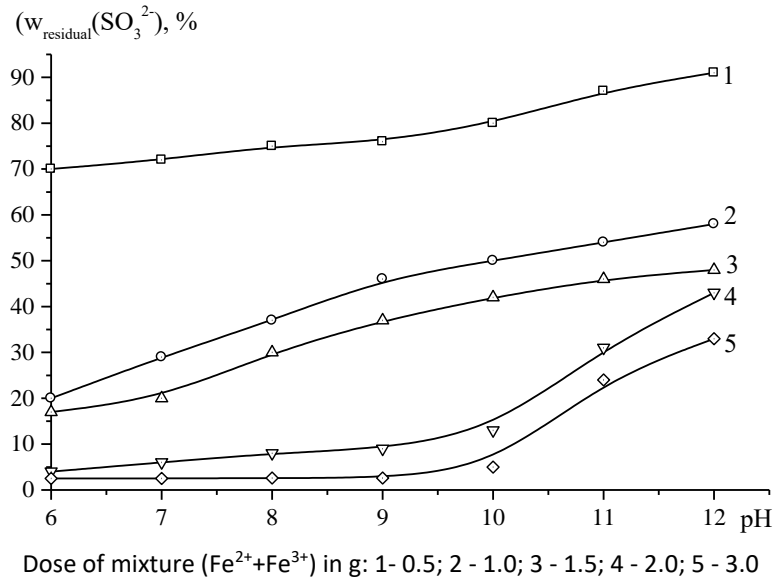


Figure 3. Influence of pH of medium and mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) on oxidation of sulfite ions at aeration flotation regime

The results of test experiments (Figure 3) show that increasing the dose of par magnetic material, i.e. ($\text{Fe}^{2+}+\text{Fe}^{3+}$) mixture, promotes the oxidizability of sodium sulfite especially in the pH range of 6-10.

Studies were also carried out to investigate the oxidizability of sulfite ions as a function of agitation duration with ($\text{Fe}^{2+}+\text{Fe}^{3+}$) mixture under aeration flotation regime. The results are presented in Figure 4.

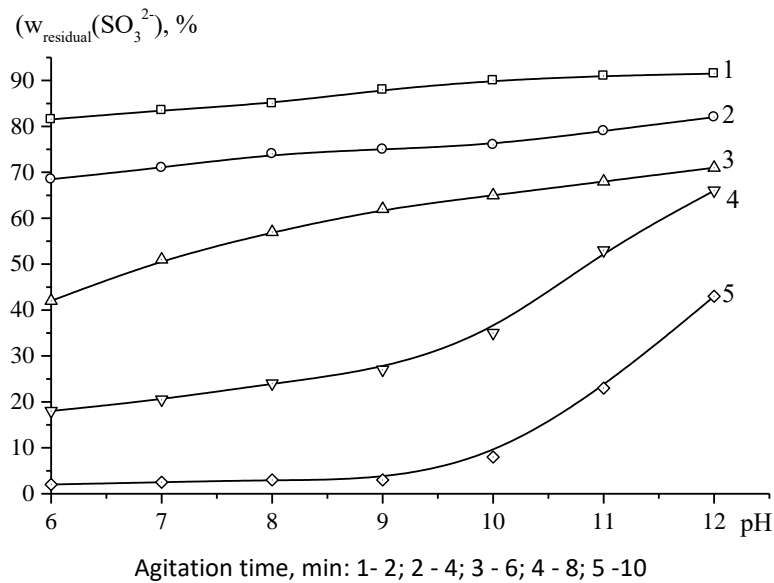


Figure 4. Influence of medium pH and agitation time with the mixture ($\text{Fe}^{2+}+\text{Fe}^{3+}$) on oxidation of sulfite ions at aeration flotation mode

Studies on the oxidation kinetics of sulfite ions (Figure 4) showed that within 8-10 min the residual concentration of sodium sulfite reaches 2-5 % of its initial concentration of 400 mg/dm³ at pH 6-8.5.

Conclusions

When using sulfite technology for the separation of collective copper-lead concentrates, it is important to know the kinetics of oxidation of sulfite ions in the presence of a modifier reagent. Paramagnetic material, which is a mixture of divalent and trivalent iron, was used as a modifier. The influence of the pH of the medium on the oxidation of sulfite ions in different flotation modes was studied. The most intensive oxidation occurs in agitation-aeration mode in the presence of modifier reagent: at pH 6-9, the residual concentration of sulfite ions is 5-8%.

Comparative data on the influence of the mixture (Fe²⁺+Fe³⁺) and divalent iron ions on the oxidation of sulfite ions showed that divalent iron ions have an effective oxidizing effect at pH 6-8.5; and the mixture (Fe²⁺+Fe³⁺) - in the whole range of pH 6-12.

The study of the influence of the dosage of the mixture (Fe²⁺+Fe³⁺) on the oxidation of sulfite ions showed that an increase in the dosage of paramagnetic material promotes the oxidizability of sodium sulfite in the pH range 6-10. In addition, it was found that for oxidation of sulfite ions in the aeration mode in the presence of paramagnetic material is sufficient for 8-10 min.

CRedit author statement: D.Turysbekov: Conceptualization, Methodology, Software; L. Semushkina: Software, Validation; Zh. Kaldybayeva: Reviewing and Editing; N. Tussupbayev: Data curation, Writing draft preparation; S. Narbekova: Visualization, Investigation, Supervision; A. Mukhamedilova: Investigation, Supervision..

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