Research on the Process of Sulphatizing Roasting of Copper Slag Flotation Tailings Using Iron Sulphates

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Abstract. The paper presents a study of sulphatizing roasting using iron (II) and (III) sulphates of copper slag flotation tailings of JSC “SUMZ” (Sredneuralsk Copper Smelter) with high content of silica. Temperature ranges of sulphatizing roasting and necessary amounts of Fe₂(SO₄)₃ and FeSO₄ for sulphation of zinc and copper were calculated by thermodynamic software HSC Chemistry 9.9. The laboratory experiments have shown that the degree of extraction of zinc and copper from the roasted samples during water leaching is in the range of 60-79%, while the degree of dissolution of iron is less than 1.1%. The obtained results are better or comparable to the results of direct leaching of copper tailings by strong sulfuric acid.

1. Introduction
Currently copper ores generally contain 0.4-0.8% Cu [1]. The depletion of natural raw materials and the simultaneous accumulation of waste induce to process generated and dump slag of copper smelting. Such slag contains 0.5-2% Cu [2]. To extract copper from slag wastes, froth flotation method is frequently used [3, 4] due to its relatively low cost. Flotation process also forms tailings with higher contents of zinc and copper than in natural ores. In Russia only JSC “SUMZ” (Sredneuralsk Copper Smelter) has accumulated several million tons of such tailings that hold 0.3-0.45% Cu, 2.7-3.2% Zn, 33-37% Fe [5], that makes them a promising raw material for the extraction of metals. These tailings are called “technical sand” due to a high content of silicate phases. The sand contains copper and zinc in mainly in the form of hardly soluble ferrites and silicates and have a complex mineralogical structure, therefore well-known industrial methods are ineffective for their processing.

Internationally, copper tailings are used in the production of cement [6] and concrete [7, 8]. However, significant contents of nonferrous metals can often limit their usage in the construction industry. Currently, hydrometallurgical methods of recovery of copper and associated components from the tailings based on sulfuric acid leaching are most commonly studied [9]. The choice of sulfuric acid is due to its low cost and conventional availability at copper smelter plants. To increase efficiency of the method, bioleaching [10-12], fractional precipitation [13] and different oxidants [10,11, 14-16] were studied. One of the most widely used oxidants is ferric sulphate [10, 11, 14]. However, ferric sulphate can apply not only for leaching, but also for roasting. The approach for transforming zinc and copper into water soluble form by sulphatizing roasting with addition of iron...
sulphates was suggested for zinc leach residue [17, 18], copper converter slag [19] and electric arc furnace dust [20]. In the current paper, we tested the approach based on sulphatizing roasting with addition of iron sulfates and subsequent water leaching for copper tailings with high content of silica phases.

2. Materials and methods
Elemental and mineralogical compositions of tailings from copper slag processing of the Sredneuralsk Copper Smelter were analyzed by X-ray fluorescence spectrometer Axios Advanced (Netherlands) and X-ray diffractometer ARL XTRA (Switzerland) with Cu-Kα X-rays respectively. The content of carbon was analyzed by LECO CS-400 (USA).

Table 1 shows the elemental composition of the tailings sample, fig. 1 – its XRD pattern.

| Material | Fe | Cu | Zn | S | Si | Ca | Mg | Al | Pb | Ba | K | Mn | Ti | As | C |
|----------|----|----|----|---|----|----|----|----|----|----|---|----|----|----|---|
| Composition, % | 42.32 | 0.44 | 4.40 | 1.2 | 12.36 | 2.35 | 0.38 | 1.98 | 0.26 | 0.22 | 0.72 | 0.06 | 0.06 | 0.17 | 0.08 |

![Figure 1](image)

**Figure 1.** XRD pattern of the copper tailings sample.

Figure 1 points out that the main phases of the tailings are fayalite Fe₂SiO₄, zinc-copper ferrite ZnₓCuₓFe₂O₄, sphalerite Zn₁₋ₓFeₓS, diopside CaMgSi₂O₆, pyroxene CaFeₓZn₁₋ₓSi₂O₆ and amorphous phase.

Fig. 2 and 3 point out the flowsheets for selective dissolution of different copper and zinc phases [22].
Figure 2. Flowsheet for selective dissolution of copper compounds from the tailings sample.

Figure 3. Flowsheet for selective dissolution of zinc compounds from the tailings sample.
The analysis shows that 54.6% of copper is in the form of sulphide minerals, where only 2.4% is chalcopryite, 15.3% of copper is in the form of sulphates, 1% is in oxide form and about 29.1% is in ferrite form, 29.8% of zinc is in silicate form, 5.3% is in sulphate form, 7% is in oxide form, 8.6% is in sulphide form and 49.3% is in ferrite form.

The HSC Chemistry 9.9 was used for thermodynamic calculation [23]. The equilibrium states were calculated at 25-900°C in 79 mol.% N₂ + 21 mol.% O₂ atmosphere at P = 1 atm. The calculations were performed with preset value of 100 kg of the tailings, the components of small contents were excluded. Based on elemental and phase compositions, the following amounts of compounds was included in the calculations: 72.85% Fe₂SiO₄; 8.32% ZnFe₂O₄; 0.59% ZnS; 2.33% Zn₂SiO₄; 0.60% ZnSO₄; 0.40% ZnO; 0.50% CuFe₂O₄; 0.03% CuFeS₂; 0.31% Cu₂S; 0.18% CuSO₄; 0.01% CuO; 1.67% K₂SO₄; 3.86% Ca₂SiO₄; 0.31% PbS; 0.38% BaSO₄; 3.53% CaMgSi₂O₆; 3.90% Al₂O₃; 0.23% As₂O₃.

Experiments were carried out as follows. The tailings and chemically pure reagents FeSO₄·7H₂O and Fe₂(SO₄)₃·9H₂O were ground to fraction of <0.1 mm in agate mortar. The mixtures were prepared in a V-shell blender for 24 hours. 7,5-12,5 g samples of the obtained mixtures were placed in a muffle furnace, heated at speed of 300°C/h to temperature of 625°C and held for 6 hours.

Water leaching of the roasted samples was performed by a magnetic stirrer. Leaching was carried out at 70°C with the ratio of solid to liquid of 1:160 and stirring time of 30 min. Zinc, copper and iron content in the obtained solutions after filtration were analyzed by Therm Fisher Scientific iCE 3500 (USA) atomic-absorption spectrometer.

3. Results and discussion

To choose the optimal conditions of zinc and copper sulphation, thermodynamic calculations were carried out at first. Fig. 4 and 5 show the results of calculations performed by HSC Chemistry software.

![Figure 4](image_url) Effect of temperature on equilibrium amounts of zinc and copper compounds in copper tailings at 25-900°C with addition of 100 kg Fe₂(SO₄)₃.

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Fig. 4 shows that zinc and copper contained in the tailings can transform into sulphates at 25-650°C. At higher temperatures copper and zinc compounds are substantially in the ferrite form, so it indicates that sulphation is impossible above 650°C. Fig. 5 shows that sulphation of more than 90% of zinc and copper is possible with addition of at least 58% $\text{Fe}_2(\text{SO}_4)_3$. Additional calculation pointed out that sulphation of more than 90% of zinc and copper is possible with addition of at least 82% $\text{FeSO}_4$.

The mechanism of sulphation of copper and zinc compounds is their oxidation by sulfur trioxide that generated during ferric sulphate decomposition [17, 23]. At the same time, sulphides are oxidized in air, so during roasting the following reactions may occur:

\[
\begin{align*}
\text{CuFe}_2\text{O}_4 + \text{SO}_3 & \rightarrow \text{CuSO}_4 + \text{Fe}_2\text{O}_3 \\
\text{CuO} + \text{SO}_3 & \rightarrow \text{CuSO}_4 \\
8/15\text{Cu}_2\text{S} + \text{O}_2 & \rightarrow 2/5\text{Cu}_2\text{O} + 4/15\text{CuSO}_4 + 4/15\text{SO}_2 \\
\text{ZnFe}_2\text{O}_4 + \text{SO}_3 & \rightarrow \text{ZnSO}_4 + \text{Fe}_2\text{O}_3 \\
1/2\text{Zn}_2\text{SiO}_3 + \text{SO}_3 & \rightarrow \text{ZnSO}_4 + 1/2\text{SiO}_2 \\
\text{ZnO} + \text{SO}_3 & \rightarrow \text{ZnSO}_4 \\
1/2\text{ZnS} + \text{O}_2 & \rightarrow 1/2\text{ZnSO}_4
\end{align*}
\]

Fig. 6 and 7 show the temperature dependences of Gibbs energy change of reactions (1)-(7) that indicate the possibility of these interactions under the conditions of sulphatizing roasting.

**Figure 5.** Effect of $\text{Fe}_2(\text{SO}_4)_3$ on equilibrium amounts of zinc and copper compounds in copper tailings at 625°C.
Figure 6. Temperature dependences of Gibbs energy change of reactions (1)-(3).

Figure 7. Temperature dependences of Gibbs energy change of reactions (4)-(7).
The calculations were verified experimentally with an excess of sulphates to the tailings compared to the calculated values. Table 3 shows the results of the experiments.

Table 2. The recovery rate of zinc, copper and iron from the roasted samples at 625°C during 6 hours after water leaching, %.

| Mixture components          | Ratio | Recovery rate, % |
|-----------------------------|-------|------------------|
| Tailings + FeSO₄·7H₂O       | 1:1.5 | 78.8 83.2 0.54   |
| Tailings + Fe₂(SO₄)·9H₂O    | 1:0.75| 66.8 60.6 1.12   |

The results show that the addition of iron (II) sulphate leads to a higher dissolution of zinc and copper than iron (III) sulphate. In both cases, the obtained recovery rates of zinc and copper are higher or comparable to the results presented in [10, 14, 16]. Compared to [10, 14, 16, 24], in this study the solutions with lower content of iron were obtained, that can facilitate their subsequent purification. In addition, water leaching can be carried out without the application of chemically resistant acid equipment. To increase the degree of extraction of zinc and copper in the solution it is necessary to optimize the temperature and time of the sulphatizing roasting, as well as type and amount of sulphatizing agents. The use of acid, alkaline or salt solutions for leaching can also increase the recovery of zinc and copper, but can also lead to the higher dissolution of undesirable impurities.

4. Conclusion

The obtained results have shown efficiency of sulphatizing roasting using iron sulphates with following water leaching to extract zinc and copper from copper tailings with high silica content. The recovery rates of zinc and copper are in the range of 60-79%, while the degree of dissolution of iron is insignificant. The application of the approach is possible for processing of other materials containing zinc and copper in hardly soluble forms.

5. References

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Acknowledgments
The reported study was funded by the program of the Presidium of the Russian Academy of Sciences №39 (project № AAAA-A18-118031490126-8).