

COPPER SMELTER SLAG LEACHING BY USING H_2SO_4 IN THE PRESENCE OF DICHROMATE

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ABSTRACT

The system H_2SO_4 - $K_2Cr_2O_7$ is examined for leaching copper, zinc and iron from the copper smelter slag. The presence of dichromate has a positive effect on the copper recovery, which reaches 68 % under the following conditions: 0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4 , solid-to-liquid ratio = 15 g: 1 L, 120 min, 298 K. The calculated values of E_a of Cu recovery amounts to 34.60 kJ/mol, that of Zn – to 43.96 kJ/mol, while that of Fe - to 44.33 kJ/mol. The recovery of zinc and iron decreases significantly with the presence of $K_2Cr_2O_7$, and is only 4 % - 5 % under the conditions specified. This fact can be associated with the selective adsorption of dichromate ions on the surface of the minerals containing zinc and iron. It prevents the recovery of these metals into the solution. This circumstance can be used to separate copper from zinc and iron during the leaching process. About 68 % - 70 % of the copper present can be recovered during the first stage; the leaching residue can be used for further extraction of zinc.

Keywords: copper smelter slag, sulfuric acid leaching, dichromate.

INTRODUCTION

The exhaustibility of copper ore has become evident at present. The decline of the explored ore reserves with the growth of current copper consumption creates a threat of this metal deficit in the long term. The acuteness and the urgency of this problem require seeking the most accessible sources of copper raw materials as an ore alternative. The copper smelter slag is a prospective raw material resource in this respect. It is a by-product of the pyrometallurgical copper production [1, 2]. The production of a single ton of copper is accompanied by the formation of about 2.2 tons -3.0 tons of slag. The following content of valuable metals in the copper smelter slag is observed depending on the melting conditions of the copper concentrates: 0.5-2.0 wt. % of Cu, 2-5 wt. % of Zn, 0.2 ~ 1.0 wt. % Pb [3]. Thus, the copper smelter

slag can be considered a valuable raw material resource for the production of non-ferrous metals.

The hydrometallurgical methods are considered promising for processing copper slags. Aqueous solutions of acids (sulfuric, hydrochloric, nitric, acetic, etc.) and ammonium salts are widely used as leaching reagents on a laboratory scale [4-10]. However, due to various reasons, the hydrometallurgical method has not yet found industrial application for copper slag processing.

For more than 70 years, more than 31 million tons of copper smelter slag are been accumulated at the Balkhash copper plant (Central region of Kazakhstan) due to the lack of effective ways of processing this type of waste. More than 500 thousand tons of slag is recently produced annually. This circumstance encourages the investigation of new hydrometallurgical methods of copper smelter slag treatment.

A solution of potassium dichromate in sulfuric acid is found a capable agent for copper leaching from copper converter slag [11, 12]. 99.66 % of Cu recovery is achieved after slag leaching for 120 min at 70°C [12] in case of using a solution containing 0.25 M acid and 0.1 M $K_2Cr_2O_7$ of 10 g/L of solid/liquid ratio. However, the smelter and the converter slag differ somewhat in their composition. A higher content of copper and a lower content of zinc are observed in the converter slag. Differences in the content of iron oxides and silicates also occur. Therefore, it is of interest to apply H_2SO_4 - $K_2Cr_2O_7$ aqueous system for leaching copper smelter slag.

EXPERIMENTAL

On the slag sample used

The copper smelter slag sample used in this research was obtained from a copper smelting plant of the town of Balkhash town located in the central part of Kazakhstan. Fayalite (Fe_2SiO_4), ferrosilite ($FeSiO_3$), magnetite (Fe_3O_4), and zinc ferrite ($ZnFe_2O_4$) were identified by XRD analysis (DRON-3) as major components of the slag sample. Most of the copper was in the form of copper sulfides, such as chalcocite (Cu_2S), bornite (Cu_5FeS_4), and chalcopyrite ($CuFeS_2$), as presented in Table 1.

The chemical composition of the slag given in Table 2 was determined by ICP-AES (Perkin Elmer, Optima 8000).

The slag sample was crushed and then sieved. The fraction of – 200 mesh of the slag was subjected to further treatment. The bulk density of the slag sample obtained by dividing the weight of the sample by its volume was 3100 kg m⁻³.

Leaching experiments

The batch leaching tests of the slag sample with a combination of H_2SO_4 and $K_2Cr_2O_7$ were performed by shaking 500 mL flasks. A mixture of a slag sample (15 g) and a leaching solution of a predetermined concentration of the aforementioned leaching agents was stirred at 450 min⁻¹ at the predetermined temperature. The solid residue obtained by the leaching was washed twice with distilled water and was completely dissolved in nitric acid using the device for microwave decomposition of solid samples “Minotaur - 2”. The quantitative analysis of the metal ions (Fe, Cu, Zn) in the leach liquor was determined by ICP-AES (Perkin Elmer, Optima 8000), while the dry residues were analysed by X-ray diffraction (DRON- 3).

RESULTS AND DISCUSSION

Two aspects of the process of copper slag leaching can be considered. The first one refers to the metal recovery completion in the solution studied. It is determined by chemical thermodynamics. The second aspect refers to the chemical kinetics that treats the rate of the slag sample dissolution.

Effect of leaching conditions on the degree of Zn, Cu, and Fe recovery

The dependences of Cu, Zn, and Fe recovery in a solution on H_2SO_4 and $K_2Cr_2O_7$ concentrations presented in Fig. 1 (a-c) demonstrate that the recovery of Fe and Zn increases significantly with increase of the acid concentration up to 0.5 M in absence of dichromate.

The maximum values of extraction of zinc and iron are 57 % and 56 %, respectively. The increase of Cu

Table 1. A mineralogical composition of the slag sample.

Fe_2SiO_4	$FeSiO_3$	$ZnFe_2O_4$	Fe_3O_4	Al_2SiO_5	$CaSiO_3$	ZnS	$CuFeS_2$	Cu_5FeS_4	$MgSiO_3$	Cu_2S
29.6	26.3	14.9	9.5	4.4	2.6	1.2	1.1	0.6	0.5	0.4

Table 2. A chemical composition of the slag sample.

Fe	Si	Zn	Al	Cu	S	Ca	Mg
13.88	39.79	4.52	1.49	1.20	1.11	0.76	0.18

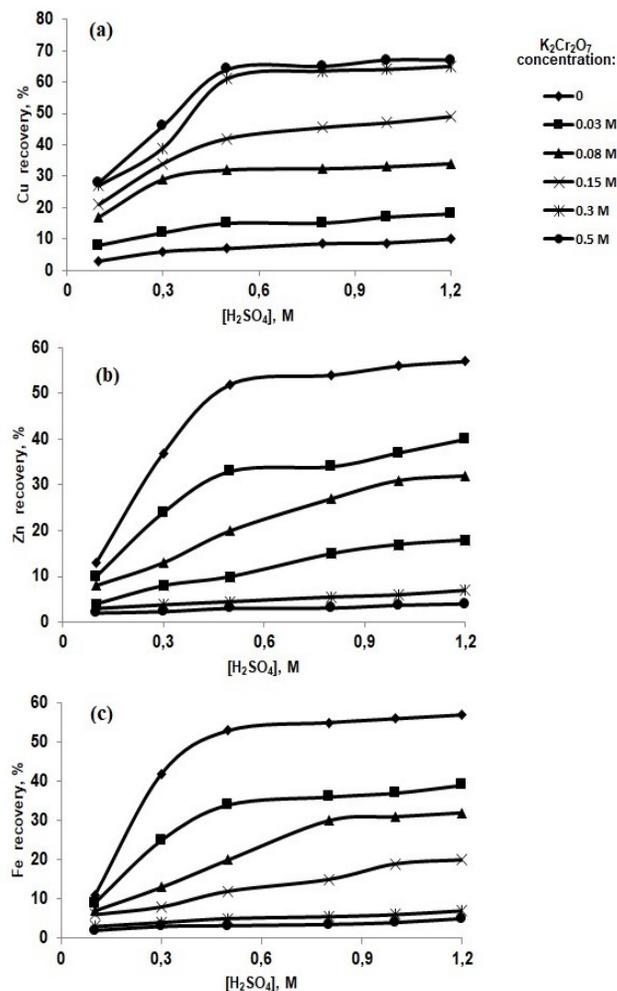
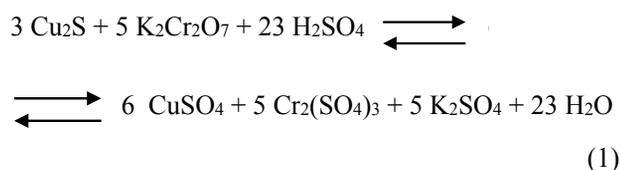
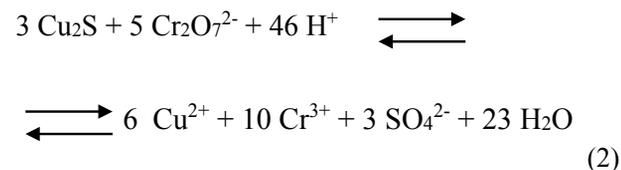


Fig.1. Influence of H₂SO₄ and K₂Cr₂O₇ concentrations on the copper, zinc and iron recovery from the slag sample (15 g sample was treated with 1 L solution for 120 min at 298 K).

recovery is not significant and these values remain at the level of 8 % – 9 % up to 1.2 M sulfuric acid. The presence of K₂Cr₂O₇ in the solution has a positive impact on the recovery of copper; this value reaches 68% when 0.5 M K₂Cr₂O₇ is added to the solution. The positive effect of the presence of potassium dichromate on copper recovery can be explained by the interaction of Cr₂O₇²⁻ with copper sulfide minerals in an acidic medium following Eq.1 (on an example of chalcocite dissolution):



To demonstrate the oxidation-reduction processes, Eq. (1) can be rewritten as follows:



The equilibrium constant of Reaction (1) can be used to estimate the completeness of its course under the conditions selected. The equilibrium constant of the reaction is determined in accordance with Eq. (3):

$$\Delta_r G_T^0 = -RT \ln K \quad (3)$$

where $\Delta_r G_T^0$ is the Gibbs free energy of the reaction, R is the universal gas constant, T is the absolute temperature, and K is the equilibrium constant of chemical reaction.

Table 3. A mineralogical composition of the solid residue after leaching (0.5 M K₂Cr₂O₇ + 1 M H₂SO₄, a solid:liquid ratio = 15 g : 1 L, 120 min, 298 K).

Compound	wt.%	Compound	wt. %
Fe ₂ SiO ₄	21.7	CaSiO ₃	2.1
FeSiO ₃	21.0	ZnS	1.0
ZnFe ₂ O ₄	12.2	CuFeS ₂	0.9
Fe ₃ O ₄	7.6	CaSO ₄	1.6
Al ₂ SiO ₅	3.5	KFe ₃ (CrO ₄) ₂ (OH) ₆	18.4

At 298 K the equilibrium constant of chemical reaction (1) is found equal to 0.113. This requires an excess of potassium dichromate and sulfuric acid in comparison with the stoichiometrically calculated amounts.

The recoveries of both Zn and Fe, on the contrary, decrease in presence of $K_2Cr_2O_7$ and reach 4%-5% when 0.5 M of dichromate is added. This fact is in agreement with the results obtained by Altundogan and co-workers [11] who studied the leaching of a converter slag under similar conditions. The mentioned scholars point out that the fact of Co, Fe, and Zn recovery decrease in presence of dichromate ions is due to passivation of the slag particles surface by adsorbed $Cr_2O_7^{2-}$ and/or $HCrO_4^-$. According to the authors' explanation, Co, Fe, and Zn are mostly present in silicate and ferrite matrices. The adsorption of $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions inhibits probably the contact of H_3O^+ ions with major mineral phases of the slag. In contrast to the metals mentioned, the copper is present in separate phases, and it is not affected by passivation. Another version of the very low extraction of iron reported in ref. [11] is the formation of a sparingly soluble jarosite analogue.

Table 3 demonstrates the mineralogical composition of the solid residue after leaching under the following conditions: 0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4 , a solid: liquid ratio = 15 g:L, 120 min, 298 K. The weight of the washed and the dried precipitate is 16.5 g. It is seen that a hardly soluble compound $KFe_3(CrO_4)_2(OH)_6$ is formed [13, 14] as a result of the solid precipitate leaching. According to the stoichiometric calculations, the iron content in $KFe_3(CrO_4)_2(OH)_6$ is 45 % of iron in the original slag. Thus, the extraction of iron from the slag into the solution during the leaching process amounts to 50 %. Thus 90 % of this amount is precipitated as $KFe_3(CrO_4)_2(OH)_6$. This fact confirms the version stated in ref. [11].

Leaching kinetics

The shrinking core model is used to describe the kinetics of copper slag's leaching process [15]. The model assumes that the particles, being spherical, shrink uniformly during the leaching. It is found that the dependence of the degree of Cu recovery on the leaching duration at 298 K, 318 K and 358 K is determined by Eq. (4):

$$1 - (1 - X_{Me})^{2/3} = k_{exp} \tau \quad (4)$$

where X_{Me} is the metal fraction of the slag that has reacted, k_{exp} is the experimental apparent rate constant (min^{-1}), while τ is the time (min).

This fact means that the limiting stage of copper leaching from the slag refers to the mass transfer to the fluid layer that surrounds the solid particle.

The processes of extraction of zinc and iron are limited by the chemical reaction on the surface of the particle in accordance with Eq. (5):

$$1 - (1 - X_{Me})^{1/3} = k_{exp} \tau \quad (5)$$

The apparent rate constants of the reactions of copper, zinc and iron recovering at the three temperatures investigated are given in Table 4.

The Arrhenius equation is used [16] to determine the activation energies (E_a) of the chemical reactions leading to Cu, Zn, and Fe recovery to the solution. The calculated values of E_a refer to 34.60 kJ/mol for Cu, 43.96 kJ/mol for Zn and 44.33 kJ/mol for Fe. The kinetics of the nonferrous metals and iron extraction from the copper converter slag by sulfuric acid leaching in presence of

Table 4. Experimental apparent rate constants of the reactions of Cu, Zn, and Fe recovery from the slag.

Temperature, T/K	Experimental apparent rate constant, $k \times 10^{-3} / min^{-1}$		
	For Cu recovery	For Zn recovery	For Fe recovery
298	0.724	0.626	0.619
318	1.971	1.915	2.017
358	6.857	12.250	12.140

ammonium dichromate is studied [12]. The value of the activation energy of Cu recovery found by us is close to that found in ref. [12]. The values of E_a referring to Zn and Fe recovery under the conditions investigated are determined for the first time.

Recommendations on copper smelter slag treatment by using $H_2SO_4 - K_2Cr_2O_7$ system

The results obtained in the present work can be used for selective extraction of copper from copper smelter slag. A flow sheet of copper, nickel, zinc, and cobalt recovery from copper converter slag is proposed in ref. [12]. It involves processing of the original slag by lixiviate containing dichromate and sulfuric acid. However, the scheme does not take the advantage of selective copper recovery in presence of dichromate.

The flow sheet proposed in ref. [12] can be changed as follows. Up to 68 % – 70 % of copper is recovered during the first stage, while only about 5 % of iron and zinc passes into the solution. This circumstance is beneficial for the further processing of the copper-containing solution. The solid residue is leached with a sulfuric acid solution to extract zinc without the addition of dichromate. It is worth noting that iron is simultaneously extracted. Other operations, including regeneration of lixiviate remain as described in ref. [12].

CONCLUSIONS

The process of Cu, Zn and Fe recovery from copper smelter slag of Balkhash copper plant by leaching with $H_2SO_4 - K_2Cr_2O_7$ system is investigated. It is found that that the recovery of Fe and Zn increases significantly with increase of the acid concentration up to 0.5 M in absence of dichromate and reaches values of 57 % and 56 % for zinc and iron, respectively. The presence of dichromate has a negative effect on Zn and Fe recoveries. Presumably, this fact is due to adsorption of dichromate ions on the minerals surface. The copper recovery, on the contrary, increases in the presence of dichromate and reaches 68% in case of leaching under the following conditions: 0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4 , a solid-to-liquid ratio = 15 g:1 L, 120 min, 298 K. Some thermodynamic and kinetic characteristics of Cu, Zn, and Fe recovery are determined. The calculated values of the recovery activation energies refer to 34.60 kJ/mol for Cu, 43.96 kJ/mol for Zn and 44.33 kJ/

mol for Fe. Recommendations on copper smelter slag hydrometallurgical treatment are made in case of using $H_2SO_4 - K_2Cr_2O_7$ system providing copper separation from zinc and iron.

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