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Copper smelter slag leaching with hydrochloric acid in isopropyl alcohol: kinetic study

Abstract. The solvometallurgical approach was applied for the first time for processing copper smelter slag. A comparative analysis of the processes of slag leaching with hydrochloric acid dissolved in water, as well as in isopropanol is presented. The use of isopropanol as a solvent leads to an increase in the extraction of copper in comparison with an aqueous solution (84 and 66%, respectively, at 348 K). The rate constants of leaching processes in an alcohol environment are an order of magnitude higher than those in aqueous solutions at 298, 328 and 348 K. The calculated activation energy values were 28.1±0.8 and 15.7±0.5 kJ/mol for aqueous and alcohol environments, respectively. Diffusion and chemical reactions are the limiting stages of the leaching in aqueous solution while the only diffusion limits the leaching rate in alcohol environment, according to the shrinking core model. The much higher leaching ability of the isopropanol solution is explained by the lower energy of acid solvation in alcohol in comparison with the energy of hydration in an aqueous solution.

Key words: copper smelter slag, copper dissolution, leaching, solvometallurgy.

Introduction

Pyrometallurgical copper production is accompanied by the formation of smelter slag, with about three tons of slag being formed for each ton of copper produced. The copper content in the slag is on average about 1%, depending on the smelting mode used [1]. Being under the open air and exposed to temperature changes and atmospheric precipitation, the slag components partially dissolve and pass into the soil and water. Thus, copper smelter slag should be considered in two aspects: as a raw material for copper production and as a potential source of environmental pollution [2, 3]. Slag is currently processed in three ways: (i) flotation (mainly); (ii) pyrometallurgy; (iii) hydrometallurgy. All these routes have significant disadvantages: flotation loses up to 50% of copper; pyrometallurgy is energy-intensive and an expensive way of processing raw materials with low content of valuable metals. Hydrometallurgical processing of slag seems to be attractive [4-6]. However, the action of the acid on the silicon-containing components of the slag dissolves silicon in the form of silicic acid [7-10]. The dissolved silicon undergoes polymerization to form a gel. This gel makes it practically impossible to separate the pulp into solid and liquid phases [11-12]. Dissolved silicon is a problem not only in acid leaching but also in alkaline processing.

For the formation of silicic acid, water is required; thus, the use of non-aqueous solvents for leaching will avoid the problems associated with the formation of siliceous gels.

Solvometallurgy is a promising approach to the processing of metallurgical raw materials containing a significant amount of silicon. The difference between this approach and the hydrometallurgical one lies in the use of non-aqueous solutions for leaching raw materials [13-16]. Despite the well-known examples of use, solvometallurgy is today considered a new branch of extractive metallurgy [17].

We assumed the possibility of using solvometallurgy for processing copper smelter slag. Isopropyl alcohol was used as a non-aqueous solvent. Aliphatic alcohols are known as ionizing solvents capable of dissolving ionic and covalent compounds; in this case, the molecules and ions of the solute in the solution are strongly solvated [18]. Hydrochloric acid was used as a leaching agent, which is an effective reagent for leaching copper minerals [19, 20]. To the best of our knowledge, the solvometallurgical approach has not previously been used to process copper smelter slag.

Materials and methods

Copper smelter slag samples. Copper smelter slag was sampled at the slag dump of the «Kazakhmys Smelting» copper smelter (Balkhash, Central Kazakhstan), by hand. XRD analysis demonstrated that the major minerals were fayalite (Fe_2SiO_4) and quartz (SiO_2); copper presented mostly as chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S). The chemical composition of the slag sample determined by ICP-AES (Perkin Elmer, Optima 8000) was, wt %: Fe 35.17, Si 15.28, Zn 2.73, Al 1.12, Cu 1.09, S 0.85. After milling, slag was sieved; samples with particle size 90% ≥ 200 mesh were used for leaching experiments.

Reagents. Isopropyl alcohol (≥98%) and hydrochloric acid (37%) were purchased from Sigma-Aldrich and used without further purification.

Leaching. The leaching tests were performed in a thermostated 1-L flask. The slag sample (15 g) was placed in the flask filled with aqueous or alcohol solution of hydrochloric acid with pre-determined concentration. A magnetic stirrer was used to stir the pulp. After pre-determined leaching time, quantitative analysis of copper ions in the leachate was performed by using ICP-AES (Perkin Elmer, Optima 8000). All experiments were repeated 3 times; the averaged results were used further.

Results and discussion

Dissolution of copper-bearing minerals present in the slag sample. In the presence of hydrochloric acid, the following basic reactions are possible with the participation of copper-containing minerals:

$$CuFeS_2 + 4HCl = CuCl_2 + FeCl_2 + 2H_2S \quad (1)$$

$$CuFeS_2 + 3CuCl_2 = 4CuCl + FeCl_2 + 2S \quad (2)$$

$$Cu_2S + 2HCl = 2CuCl + H_2S \quad (3)$$

Leaching of chalcopyrite with hydrochloric acid leads to the formation of copper (II) chloride, which, in turn, is also a leaching agent.

In general, the above reactions are rather slow because chalcocite and (especially) chalcopyrite are refractory minerals. Besides, the vitreous matrix of the slag prevents the leaching agent from accessing the copper minerals. Acceptable leaching rates and recovery rates are achieved only when the slurry is heated.

Slag leaching in the aqueous and isopropanol solutions. To reveal the role of isopropyl alcohol in the process of copper leaching from slag, comparative experiments were carried out in aqueous and alcoholic media. The concentrations of hydrochloric acid in both media were kept the same for correct comparison.

Figure 1 demonstrates the dependences of the degree of copper extraction into an aqueous solution on the hydrochloric acid concentration and the leaching duration. Solution temperature was maintained at 298 K, the liquid-to-solid ratio was 20: 1, and the stirring rate was kept at 600 rpm.

Increasing both the leach time and the acid concentration increased the copper recovery to a certain limit. After 240 minutes of leaching and using 1M HCl, copper recovery reached 42%; further, the increase in acid concentration and leaching duration did not increase copper recovery.

It should be noted that as a result of leaching, a hard-to-filter slurry was formed; the separation of the solids from the liquid was a difficult task.

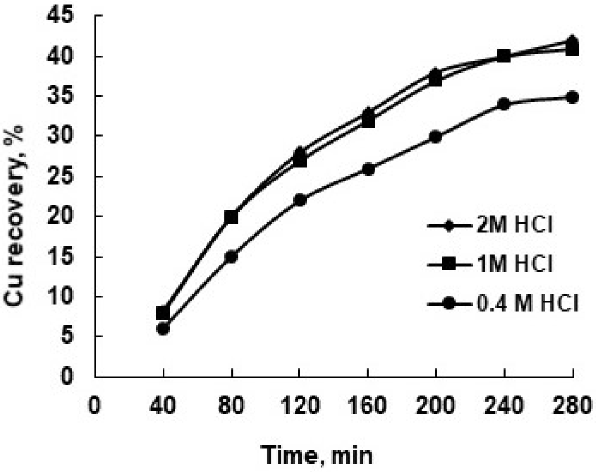

Figure 1 – Effect of hydrochloric acid concentration and leaching duration on copper recovery (%) into an aqueous solution (298 K, liquid-to-solid ratio = 20:1, 600 rpm)

A similar series of experiments were also performed for an alcoholic solution of hydrochloric acid. The results are presented in Figure 2.

It can be noted that the nature of the curves in Figure 2 is similar to that for Figure 1. An increase in the leaching duration, as well as an increase in the acid concentration from 0.4 M to 1.0 M, led to an increase in the copper extraction into solution. Meanwhile, the maximum achievable copper recovery is higher than in aqueous solution (46% vs 42%); besides, the maximum copper recovery in an alcoholic solution was achieved in less time than in an aqueous one (200 min vs 240 min). Thus, it can be assumed that the isopropanol medium favours the leaching of copper from the slag from both thermodynamic (increased recovery) and kinetic (decrease in leaching duration) points of view.

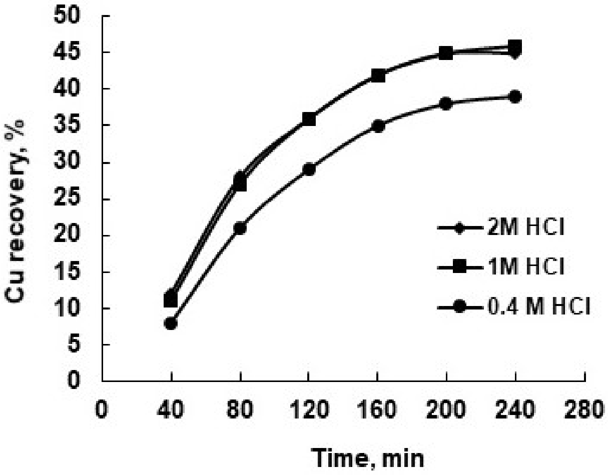

Figure 2 – Effect of hydrochloric acid concentration and leaching duration on copper recovery (%) into alcohol solution (298 K, liquid-to-solid ratio = 20:1, 600 rpm)

In contrast to the aqueous solution, the alcoholic solution after leaching was filtered quite easily. Visually, no siliceous gel was observed, as in the case of an aqueous environment.

In the next series of experiments, the temperature was varied; acid concentration was maintained at 1M (since further increase in acid concentration did not increase copper recovery, see Figs. 1 and 2), the liquid-to-solid ratio was 20: 1, and the stirring rate was kept at 600 rpm.

Figures 3 and 4 demonstrate the dependences of the degree of copper recovery into aqueous and alcoholic solutions, respectively.

It can be seen that with increasing temperature, the degree of copper extraction into solution also increases, in both media. Upon reaching 200 min (in an aqueous medium) and 160 min (in an alcoholic medium), the curves reached a plateau. The maximum extraction of copper in solution was 66% (aqueous solution) and 84% (an alcohol solution).

To determine the limiting stage of leaching in both studied media, as well as the kinetic parameters, the shrinking core model [21] was applied. According to this model, slag particles were considered as ideal spheres, the radius of which decreased over time. Depending on which stage of leaching is the limiting one, one of the following straight-line relationships can be observed:

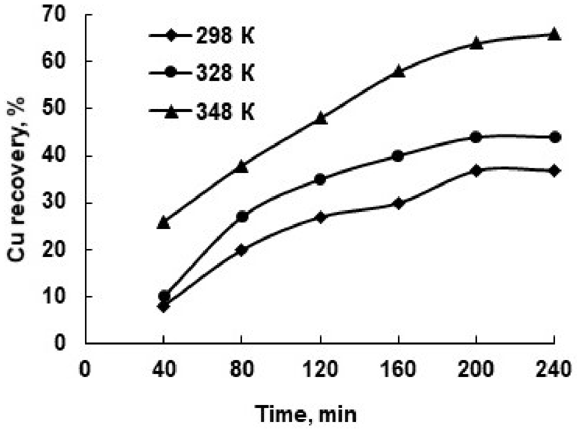

Figure 3 – Effect of leaching duration and temperature on copper recovery (%) into an aqueous solution (1 M HCl, liquid-to-solid ratio = 20:1, 600 rpm)

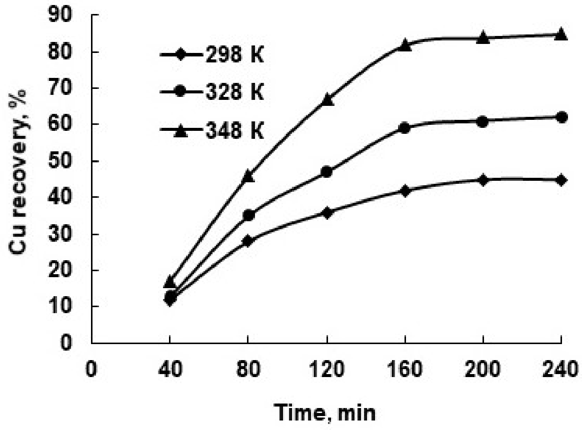

Figure 4 – Effect of leaching duration and temperature on copper recovery (%) into alcohol solution (1 M HCl, liquid-to-solid ratio = 20:1, 600 rpm)

$$1 - (1\text{-}X)^{2/3} = k\tau \tag{4}$$

$$1 - (1\text{-}X)^{1/3} = k\tau \tag{5}$$

$$1 - 2(1\text{-}X)^{1/3} + (1\text{-}X)^{2/3} = k\tau \tag{6}$$

where X is the fraction of the recovered component at the leaching time τ, and k is the apparent rate constant.

Eqs. 4, 5 and 6 correspond to diffusion, kinetic and mixed control leaching processes, respectively. By substituting the values of the degree of copper extraction (X) into the above equations, it was determined which equation led to the straight-line dependence.

Calculations demonstrated that for an aqueous solution, a linear dependence was observed corresponding to the equation (6), see Fig.5.

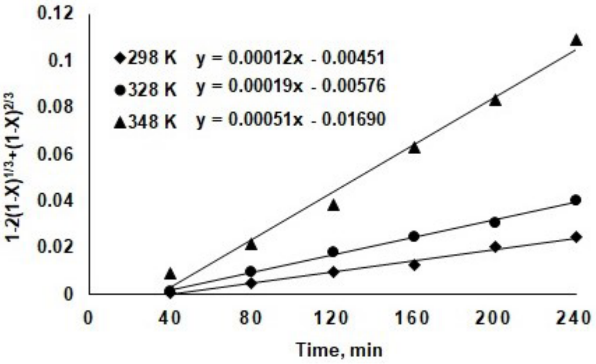

Figure 5 – Plot of $1\text{-}2(1\text{-}X)^{1/3}+(1\text{-}X)^{2/3} = k\tau$ vs time for leaching in aqueous solution(1 M HCl, liquid-to-solid ratio = 20:1, 600 rpm)

This fact indicates a mixed, diffusion-kinetic control of the process of dissolution of copper in an aqueous solution of hydrochloric acid. The apparent rate constants for these reactions have been found as 0.00012, 0.00019, and 0.00051 min^{-1} for 298, 328 and 348 K, respectively.

For the alcoholic solution, a different rectilinear relationship was observed (Fig. 6), that can be described by Eq.(4).

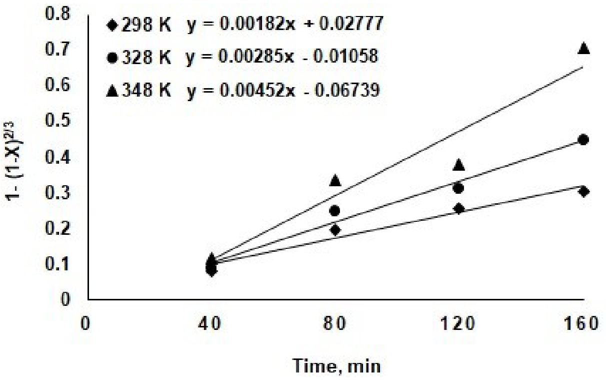

Figure 6 – Plot of $1\text{-}2(1\text{-}X)^{1/3}+(1\text{-}X)^{2/3} = k\tau$ vs time for leaching in alcohol solution (1 M HCl, liquid-to-solid ratio = 20:1, 600 rpm)

This fact testifies in favour of diffusion control of the copper dissolution process in isopropanol solution of hydrochloric acid. The apparent rate constants for these reactions have been found as 0.00182, 0.00285, and 0.00452 min^{-1} for 298, 328 and 348 K, respectively.

It can be seen that the apparent rate constants in the case of an alcohol solution are an order of magnitude higher than those for an aqueous solution.

By using the Arrhenius plot (Fig.7), the activation energies have been calculated for copper leaching processes in both aqueous and alcohol environments.

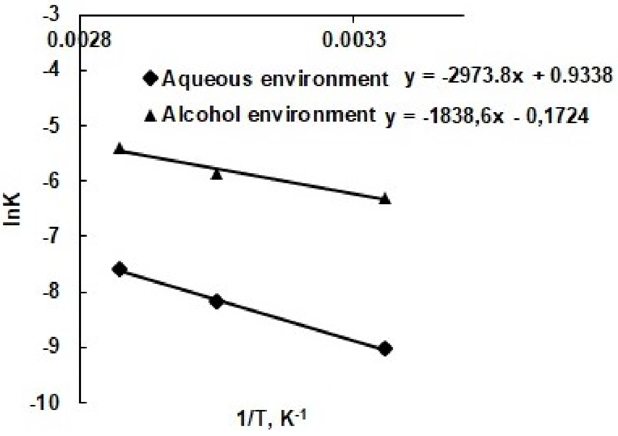

Figure 7 – Arrhenius plot for copper dissolution from slag in aqueous and alcohol environments (1 M HCl, liquid-to-solid ratio = 20:1, 600 rpm)

The activation energy values were 28.1±0.8 and 15.7±0.5 kJ/mol for aqueous and alcohol solutions, respectively. The activation energies values confirmed the initial assumptions about mixed control for a process in an aqueous environment and diffusion control for a process in an alcohol environment.

We assume that the higher capacity of hydrochloric acid in a non-aqueous (alcoholic) solution is due to the lower energy of acid solvation compared to its energy of hydration in an aqueous solution.

Thus, the use of isopropanol hydrochloric acid solution has the following advantages in comparison with an aqueous solution: (i) higher extraction of copper into solution, (ii) higher copper leaching rate, (iii) much easier filterability of the pulp.

The above advantages determine the promising use of the solvometallurgical approach for leaching the copper smelter slag.

Conclusion

The traditional ways of processing copper smelter slag are characterized by various disadvantages, such as significant losses of copper with tailings (flotation enrichment), energy intensity (pyrometallurgy), as well as the formation of hard-to-filter pulp due to acid dissolution of silicon (hydrometallurgy). In this work, a solvometallurgical approach to the processing of copper slag has been applied for the first time.

It was found that the use of isopropanol as a solvent for hydrochloric acid leads to an increase in the extraction of copper in comparison with an aqueous solution (84 and 66%, respectively, at 348 K).

The kinetic characteristics of slag leaching in aqueous and isopropanol hydrochloric acid solutions have been compared. The rate constants of leaching processes in an alcohol environment are an order of magnitude higher than those for an aqueous one at the three operating temperatures (298, 328 and 348 K). The calculated activation energy values were 28.1±0.8 and 15.7±0.5 kJ/mol for aqueous and alcohol solutions, respectively. It has been demonstrated that during leaching in an aqueous solution, diffusion process and chemical reactions are the limiting stages, while when using an isopropanol environment, the leaching process is controlled only by the diffusion stage.

The much higher ability of the isopropanol solution to leach copper from the slag is explained by the lower energy of acid solvation in alcohol in comparison with the energy of hydration in an aqueous solution.

In contrast to leaching with an aqueous solution, the use of an alcohol environment results in the formation of an easily filterable slurry.

The results obtained demonstrate the promise of applying the solvometallurgical approach to the processing of copper smelter slag.

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