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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Behavior of Chalcosine in Leaching of Carbonyl Nickel Synthesis Residues with Copper(II) Chloride Solutions

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Abstract—The behavior of chalcosine in leaching of carbonyl nickel synthesis residues with copper(II) chloride solutions was studied. The chalcosine leaching was examined in relation to the chloride background concentration, and kinetic features of the process were elucidated.

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At the present time, the annual world production of nonferrous metals by pyrometallurgical method tends to steadily decline [1–3]. Implementation of hydrometallurgical processing of sulfide materials was greatly motivated by the need to solve interconnected problems of environmental protection, exhaustion of rich deposits, reliance on sulfuric acid sales, and the need for complex processing of raw materials and utilization of harmful impurities. The main advantage offered by leaching in chloride solutions consists in that it allows sulfur to be virtually exhaustively oxidized to elemental form. Also, the process can be run at atmospheric pressure because of high leaching rate and utilizes smaller volumes of solutions in subsequent stages because of high solubility of metals.

Since the middle XX century, comprehensive efforts have been dedicated to commercial use of hydrochloride leaching of copper sulfide-based minerals. These efforts culminated in development of the known processes that are described in sufficient detail in [2–6]. Depending on the first stage of decomposition of the sulfide materials, the hydroochloride processes can be classed as leaching with concentrated solutions of iron(III) and/or copper(II) chloride or as leaching with solutions characterized by high concentration of the chloride ions, containing iron(III) and/or copper(II) chloride solutions, whose oxidative power is restored, e.g., by supplying gaseous chlorine or air to the solution regeneration stage [2, 5–14].

In aqueous solutions, iron is stable both as Fe^{3+} and Fe^{2+}, the standard redox potential of the Fe^{3+}/Fe^{2+} pair being 0.57 V (relative to silver chloride electrode), which makes iron(III) solutions suitable for leaching of sulfide minerals [15]. Earlier studies [6, 16–18] were concerned with the use or hydrochloric acid and iron(III) chloride solutions for leaching of carbonyl nickel synthesis residues (SR). Meant by the latter is a sulfide product whose phase composition is represented by chalcosine Cu_2S, cobalt pentlandite $(Co,Fe)_9S_8$, and pentlandite $(Ni,Fe)_9S_8$. Those studies revealed conditions at which over 99% copper passes into solution.

The standard redox potential of the Cu^{2+}/Cu^{+} pair is 0.044 V, which makes copper(II) chloride solutions unsuitable for leaching of sulfide minerals [19]. However, Cu^{+} ions can form stable chloride complexes in chloride media, thereby increasing the redox potential of the Cu^{2+}/Cu^{+} pair to 0.53–0.7 V, depending on the chloride ion concentration. Thus, concentrated copper(II) chloride solutions are also suitable as efficient oxidants in leaching of sulfides.

The advantages offered by copper(II) chloride as oxidant in hydrochloride leaching of sulfide minerals are soft oxidation conditions and simple regeneration of the leaching agent [14]. Also, copper(II) chloride solutions

are preferred for leaching of copper sulfide minerals, chalcosine Cu_2S, covellite CuS, and chalcopyrite $CuFeS_2$, because of a smaller amount of iron contained in the leaching solutions.

Here, we elucidate the possibility and the features of leaching of chalcosine Cu_2S from carbonyl nickel synthesis residues with copper(II) chloride solutions with a view to development of a hydrometallurgical technology for this intermediate of copper-nickel production process.

EXPERIMENTAL

For characteristics of the initial material and experimental technique of SR leaching, see [6, 16–18]. Elemental composition of the initial material, wt%: Ni 3.8; Co 16.0; Cu 33.0, Fe 4.4; S 18.9; ΣPM ~ 0.2. There is about 50% chalcosine in the phase composition of SR.

The X-ray phase analysis of the samples was carried out on a DRON-2.0 diffractometer with $Cu_{K\alpha}$ radiation. The content of the main components in solutions and leaching residues was determined by known techniques [17]. The mineralogical analysis of the samples by reflected light microscopy was carried out with an Ultrafot-3 Opton microscope with 0.2-μm resolution. The main phases were examined by the X-ray spectral micro analysis on an MS–46 Cameca microprobe analyzer.

The copper(II) chloride solutions were prepared from chemically pure-grade $CuCl_2 \cdot 2H_2O$. The chloride background was created by dissolving reactive chemically pure-grade NaCl, HCl, or $NiCl_2 \cdot 6H_2O$, depending on the required chloride background concentration.

The redox potentials of the solutions were measured using a V7–77 voltmeter, with an Ag/AgCl silver chloride reference electrode and a platinum indicator electrode. The published standard redox potentials are also given relative to Ag/AgCl.

To assess how the mathematical models we used fit the experimental data with the significance level of 0.05, expressed as the determination coefficient R^2, we employed STATISTICA 6 program.

Studies dedicated to complexing of copper in chloride solutions showed that Cu^+ in concentrated solutions forms chloride complexes $CuCl^0$, $CuCl_2^-$, $CuCl_3^{2-}$, $CuCl_4^{3-}$, and even dimers $Cu_2Cl_4^{2-}$ and trimers $Cu_3Cl_6^{3-}$. In dilute chloride solutions (0.001–0.1 M Cl^-) near the boiling point of the solution, the dominating species is $CuCl^0$ complex, and in more concentrated solutions, $CuCl_2^-$ and $CuCl_3^{2-}$ complexes. At chloride concentrations above 7 M, $CuCl_4^{3-}$ complex can be formed [19–21].

Table 1. Standard free Gibbs energies of formation of copper sulfides and Cu(I) and Cu(II) chloride complexes according to [9, 21, 28]

Formula	ΔG°_{298}, kJ mol^{-1}	Formula	ΔG°_{298}, kJ mol^{-1}
$Cu_2S_{(sol)}$	–85.35	$Cl^-_{(soln)}$	–131.14
$CuS_{(sol)}$	–53.55	$Cu^+_{(soln)}$	+50.20
$Cu^{2+}_{(soln)}$	+64.96	$CuCl^-_{2\,(soln)}$	–248.03
$CuCl^+_{(soln)}$	–66.80	$CuCl^{2-}_{3\,(soln)}$	–373.46
$CuCl^0_{2\,(soln)}$	–196.95	$CuCl^{3-}_4$	–511.20

The available data about complexing by the Cu^{2+} ion are somewhat inconsistent. At low chloride concentrations, the dominating species are aqua complexes, and in more concentrated solutions, $CuCl^+$ and $CuCl_2^0$ [22]. At Cl^- concentration of 2.5 M, $CuCl_3^-$ is formed, and at 5–10 M Cl^-, $CuCl_4^{2-}$. At the same time, Collins et al. [23] showed that, at $T < 75$°C and chloride concentrations within 0.2–2.2 M, there is no complexing; at 5 M Cl^-, the $CuCl^+$ complex dominates; and at temperature increased to 125°C, $CuCl_3^-$ and $CuCl_4^{3-}$ are formed.

Nevertheless, the most recent EXAFS (Extended X–Ray Absorption Fine Structure) data

[21, 23] suggest that, under the conditions chosen for studying the behavior of the phase components of the carbonyl nickel synthesis residues with copper(II) chloride, free chloride concentration in solution of 4–8 M and temperatures within 20–95°C, the Cu^+ and Cu^{2+} ions occur mainly as $CuCl_2^-$, $CuCl_3^{2-}$, $CuCl_4^{3-}$ and Cu^{2+}, $CuCl^+$, $CuCl_2^0$, respectively.

Numerous studies [6, 24–27] showed that leaching of chalcosine Cu_2S under oxidative conditions involves formation of covellite CuS which is further dissolved to yield elemental and/or sulfate sulfur.

Based on the above-said and the Gibbs energies ΔG°_{298} of the chemical reactions calculated with the use of the data from Table 1, we estimated the thermodynamic probability of decomposition of chalcosine in copper(II) chloride solutions.

Our results suggest (Table 2) that the first stage of the reaction of Cu_2S with the solution components, involving recrystallization to CuS, can proceed already under the standard conditions [reactions (1–4)]. However, the route of the process is governed both by the initial state of the

Table 2. Gibbs energies of the reactions of dissolution of chalcosine with copper(II) chloride in chloride solutions under standard conditions

Reaction	ΔG^{o}_{298}, kJ mol^{-1}
First stage	
$Cu_2S_{(sol)} + CuCl^{+}_{(soln)} + 3Cl^{-}_{(liq)} = CuS + 2CuCl^{-}_{2\,(liq)}$ (1)	–4.04
$Cu_2S_{(sol)} + Cu^{2+}_{(soln)} + 4Cl^{-}_{(liq)} = CuS + 2CuCl^{-}_{2\,(liq)}$ (2)	–4.66
$Cu_2S_{(sol)} + CuCl_2 + 2Cl^{-}_{(liq)} = CuS + 2CuCl^{-}_{2\,(liq)}$ (3)	–5.03
$Cu_2S_{(sol)} + CuCl_2 + 6Cl^{-}_{(liq)} = CuS + 2CuCl^{3-}_{4}$ (4)	–6.81
$Cu_2S_{(sol)} + CuCl^{+}_{(soln)} + 5Cl^{-}_{(liq)} = CuS + 2CuCl^{2-}_{3\,(soln)}$ (5)	+ 7.38
$Cu_2S_{(sol)} + CuCl_2 + 4Cl^{-}_{(liq)} = CuS + 2CuCl^{2-}_{3\,(liq)}$ (6)	+6.39
$Cu_2S_{(sol)} + Cu^{2+}_{(soln)} + 6Cl^{-}_{(liq)} = CuS + 2CuCl^{2-}_{3\,(liq)}$ (7)	+6.76
Second stage	
$CuS_{(sol)} + CuCl_2 + 6Cl^{-}_{(liq)} = 2CuCl^{3-}_{4} + S_{(sol)}$ (8)	+14.94
$CuS_{(sol)} + CuCl_2 + 2Cl^{-}_{(liq)} = 2CuCl^{-}_{2\,(liq)} + S_{(sol)}$ (9)	+16.72
$CuS_{(sol)} + Cu^{2+}_{(soln)} + 4Cl^{-}_{(liq)} = 2CuCl^{-}_{2\,(liq)} + S_{(sol)}$ (10)	+17.09
$CuS_{(sol)} + CuCl^{+}_{(soln)} + 3Cl^{-}_{(liq)} = 2CuCl^{-}_{2\,(liq)} + S_{(sol)}$ (11)	+17.71
$CuS_{(sol)} + CuCl_2 + 4Cl^{-}_{(liq)} = 2CuCl^{2-}_{3\,(liq)} + S_{(sol)}$ (12)	+28.14
$CuS_{(sol)} + Cu^{2+}_{(soln)} + 6Cl^{-}_{(liq)} = 2CuCl^{2-}_{3\,(liq)} + S_{(sol)}$ (13)	+28.51
$CuS_{(sol)} + CuCl^{+}_{(soln)} + 5Cl^{-}_{(liq)} = 2CuCl^{2-}_{3\,(soln)} + S_{(sol)}$ (14)	+29.13

Cu^{2+} complexes and the resulting chloride complexes of Cu^{+}, i.e., by the equilibrium of the system. Dissolution of covellite under the standard conditions [reactions (8–14)] is thermodynamically hardly probable.

At the same time, Lundström et al. [12, 19] reported that, at 363 K, an increase in the copper(II) concentration

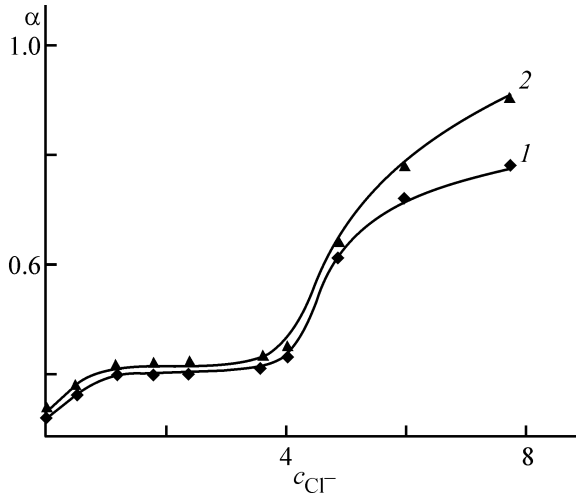

Fig. 1. Copper(II) recovery α from SR vs. chloride concentration in leaching solution c_{Cl^-}, M. τ = 2 h, T = 363 K, $CuCl_2$: Cu = 1 : 1. Composition of the solution: (*1*) $NiCl_2$ and (*2*) NaCl + HCl.

from 0.1 to 1.0 M results in stabilization of the Cu(II) and Cu(I) ions, which makes formation of $CuCl^{+}$ and $CuCl_2^{-}$ chloride complexes most probable. Simultaneously with increase in the free Cl^{-} concentration from 1.2 to 2.7 M, the $CuCl_3^{2-}$ chloride complex is stabilized, and the redox potential of the $CuCl^{+}/CuCl_3^{2-}$ pair increases to 0.53 V. Further increase in the free Cl^{-} concentration to 12 M caused formation of $CuCl_2$ and $CuCl_4^{3-}$ complexes, the redox potential of the $CuCl_2/CuCl_4^{3-}$ pair being 0.7 V. The equilibrium rate constant of the redox reaction

$$Cu_2S_{(sol)} + 2CuCl_2 + 12Cl^{-}_{(liq)} = 4CuCl_4^{3-} + S_{(sol)} \quad (15)$$

can increase by eight orders of magnitude, as follows from the equation $\ln K_a = nF\Delta DE°/RT$, where n is the number of electrons participating in the conversion of the substance from the reduced to oxidized form; F, Faraday number; R, gas constant; and T, temperature of the process. The standard electrode potential of chalcosine is 0.31 V [29, 30].

Based on the above-said, we carried out experiments to elucidate how the amount of the copper(II) chloride spent and the chloride concentration affect the degree of decomposition of chalcosine from SR. We found that, at chloride concentration of 4 M and temperature 368 K, an increase in the copper(II) chloride concentrations beyond the stoichiometric amount for the overall reaction (15) leaves virtually unaffected the degree of copper passing into solution (47–52%).

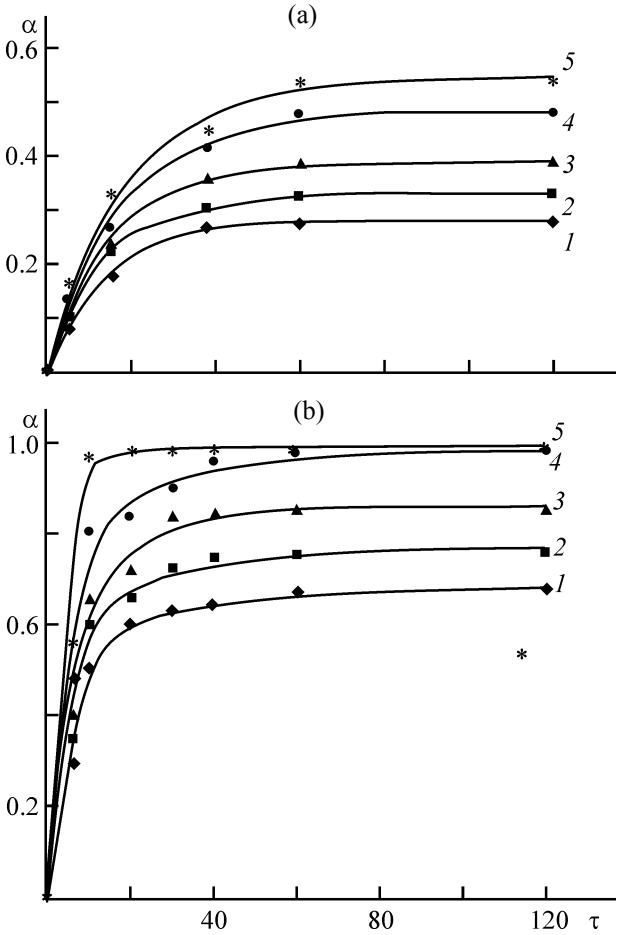

Fig. 2. Kinetic curves of dissolution of chalcosine with copper(II) chloride: (α) recovery and (τ) leaching time, min. (a) $c_{Cl^-} = 4$, $c_{CuCl_2} = 0.4$, $c_{HCl} = 0.5$ M; sol : liq = 1:10 and (b) $c_{Cl^-} = 8$, $c_{CuCl_2} = 0.4$, $c_{HCl} = 0.5$ M; sol : liq = 1:10. Temperature, K: (*1*) 293, (*2*) 313, (*3*) 333, (*4*) 353, and (*5*) 373.

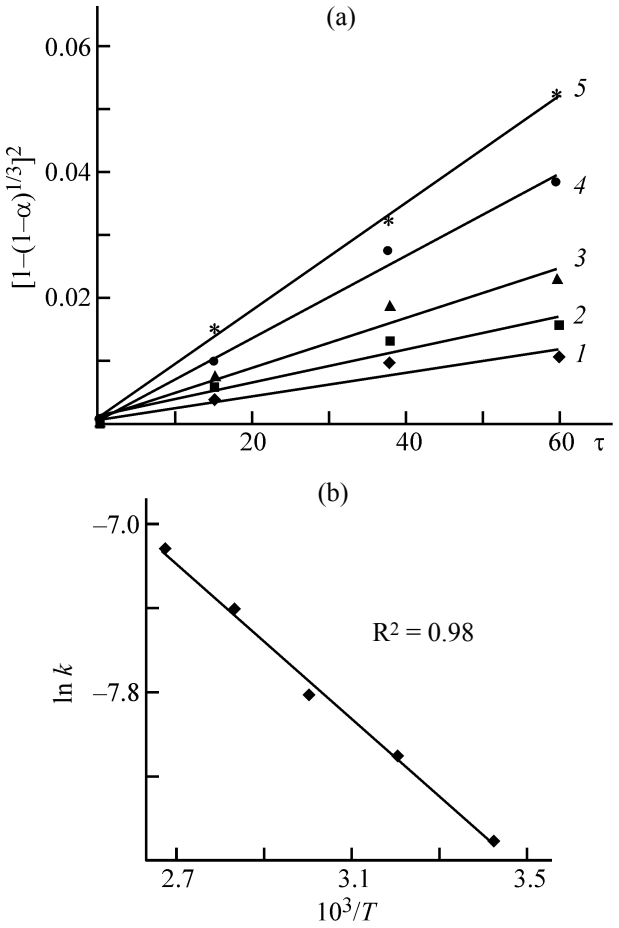

Fig. 3. Calculation of the kinetic parameters for dissolution of chalcosine with copper(II) chloride at chloride concentration of 4 M. (τ) Time, min; the same for Fig. 5. Temperature, K: (*1*) 293; (*2*) 313; (*3*) 333; (*4*) 353; and (*5*) 373; the same for Fig. 5. (a) Jander equation and (b) ln *K*–1/*T* dependence.

To elucidate how the dissolution of chalcosine from SR with copper(II) chloride is affected by the chloride background concentration (Fig. 1), the chloride background was created with nickel chloride solutions (curve *1*) and a 1:1 sodium chloride–hydrochloric acid mixture (curve *2*). It is seen that, with increasing chloride background concentration c_{Cl^-} to 8 M, the degree of copper passing into solution increases stepwise: Without chloride background, no greater than 32% copper passes into solution within 4 h at 95°C; at c_{Cl^-} within 1–4 M the copper recovery does not exceed 50%; and at c_{Cl^-} of 8 M 78–86% copper is recovered. The curves exhibit identical runs, with higher recovery achieved in the presence of hydrochloric acid.

Most likely, such pattern is due to the change in stability as $CuCl^+ < CuCl_2^0$ for the chloride complexes in the initial solutions and as $CuCl_2^- < CuCl_3^{2-}$ for the chloride complexes formed during the reaction. Mineralogical, X-ray phase, and X-ray spectral microprobe analyses showed that, at Cl^- concentration of 3–4 M, chalcosine is exhaustively substituted by covellite; insignificant amounts of $Cu_{2-x}S$ ($x \le 1$) sulfides are also present.

Figures 2a and 2b characterize the chalcosine leaching rate in relation to temperature within 293–373 K for the chloride concentrations of 4 and 8 M. The experiments aimed to elucidate the limiting stage of chalcosine dissolution from SR with a copper(II) chloride solution at the chloride concentration of 4 M showed (Fig. 2a) that, within 2-h leaching, the system attains equilibrium. The experimental data suggest (Figs. 3a, 3b) that, over the temperature range examined, the dependences obtained adhere to the Jander and Ginstling–Brounshtein equations

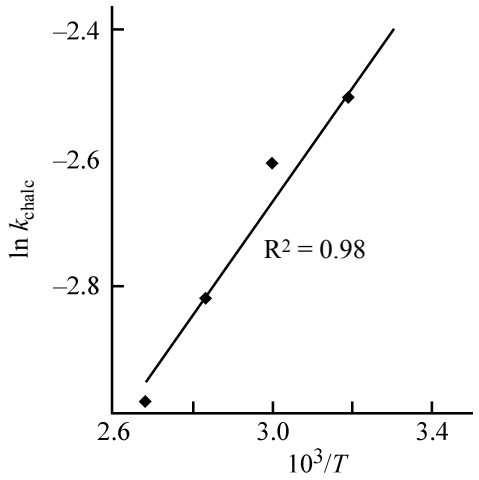

Fig. 4. The ln k_{chalc}–1/T dependence for the first stage of dissolution of chalcosine with copper(II) chloride at the chloride concentration of 8 M (E = 7.2 kJ mol^{-1}).

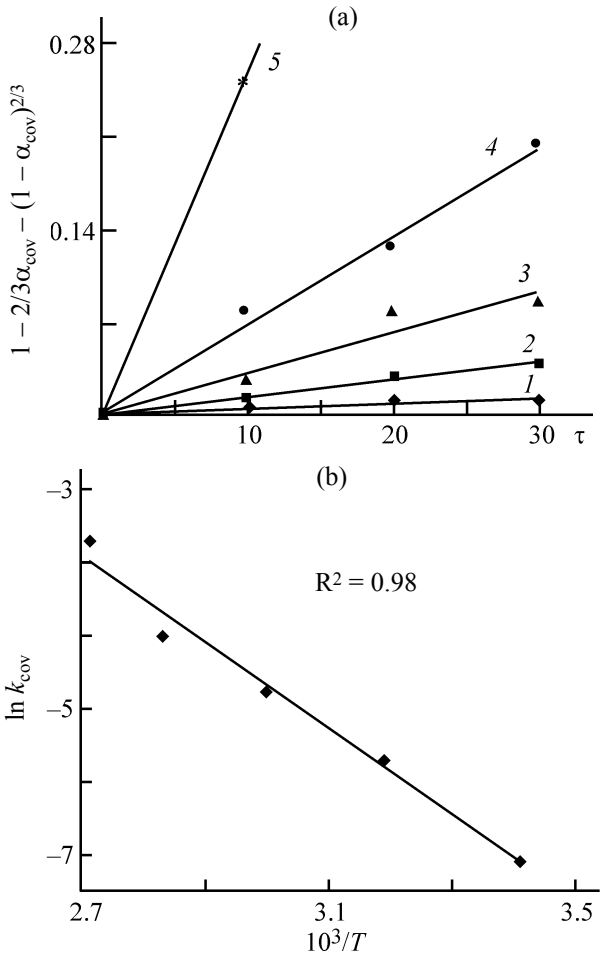

Fig. 5. Calculation of the kinetic parameters of dissolution of covellite with copper(II) chloride at the chloride concentration of 4 M: (a) Ginstling–Brounshtein equation and (b) ln k–1/T dependence, E = 49.4 kJ mol^{-1}.

[31] describing the kinetic features of heterogeneous processes with diffusion-limited rate:

$$[1 - (1 - \alpha)^{1/3}]^2 = K_{Ja}\,\tau$$

$$[1 - 2/3\alpha - (1 - \alpha)^{2/3}] = K_{G-B}\,\tau,$$

where α is the proportion of the spent substance; τ, reaction time; and k, reaction rate constant.

The plots of these functions for the achieved conversions exhibit virtually identical runs. The apparent activation energy of the process was estimated at 15.7 kJ mol^{-1}.

Herreros et al. [11] examined dissolution of djurleite $Cu_{1.97}S$, isostructural with chalcosine [28], in a copper(II) chloride solution at chloride concentrations ranging from 0.6 to 1.3 M at temperatures within 293–353 K. Those experiments showed that the process is controlled by the chemical reaction with the activation energy E_a = 35 kJ mol^{-1}.

A decrease in the activation energy in dissolution of chalcosine from SR is most likely due to an increase in the chloride concentration in the leaching solution. In this case, dissolution of chalcosine is controlled by diffusion of the oxidant through a layer of the freshly formed covellite, rather than by the chemical reaction.

At free chloride concentration increased to 8 M, chalcosine is dissolved virtually exhaustively (Fig. 2b). The first stage takes very brief time: Within 10 min at room temperature chalcosine is exhaustively recrystallized into covellite [reactions (1–7)]. The second stage consists in dissolution of covellite with formation of elemental sulfur during the reaction [reactions (8–14)]. This stage takes longer time: Only after 60 min of leaching at $T \leq$ 353 K the system attains the equilibrium. The two-stage nature of dissolution of chalcosine suggests a change in the leaching mechanism. Similar results were obtained by Ruiz et al. [24], Rajko et al. [25], and Cheng and Lawson [26].

Figure 2b suggests that, over the temperature range examined, the copper recovery from chalcosine linearly varies with time up to 0.50, which corresponds to conversion of chalcosine, contained in the synthesis residues, to covellite:

$$\alpha = k_{chalc}t,$$

where α is the proportion of spent chalcosine, and k_{chalc}, reaction rate constant for the first stage.

Using the rate constants derived from the slopes of the straight lines in Fig. 2b, we estimated the experimental activation energy from the slope of the Arrhenius curve at 7.2 kJ mol^{-1}, which is characteristic for diffusion processes (Fig. 4).

For two consecutive stages, the proportion of dissolved covellite can be calculated by the method proposed by Ruiz et al. [24]:

$$\alpha_{cov} = (\alpha - 0.5)/0.5; \quad \alpha \geq 0.5$$

The leaching time in the second stage of the reaction is defined as $\tau_{cov} = \tau - \tau_{chalc}$, where τ is the total leaching time, and τ_{chalc}, time of exhaustive recrystallization of chalcosine into covellite.

Subsequent analysis of the experimental data showed (Figs. 5a, 5b) that, over the temperature range examined, the dependences adhere to the Ginstling–Brounshtein equation. The activation energy was estimated at 49.4 kJ mol^{-1}, and this suggests a kinetic mode of the process for the second stage.

Also, the kinetic curves of leaching of chalcosine with copper(II) chloride at chloride concentration of 8 M also adhere to the Erofeev–Kolmogorov equation $\alpha = 1 - e^{-k\tau n}$, where α is the proportion of the spent substance; τ, reaction time; and k and n, coefficients (coefficient n measures the deviation of the leaching process from the first-order kinetic relationships). The coefficient n for the first stage is close to unity, and that for the second stage was estimated at 0.1–0.2.

Thus, our study of the dissolution of chalcosine from SR in $CuCl_2$–Cl^-–H_2O solutions showed that its decomposition is governed to a greater extent by the chloride background concentration: At $c_{Cl^-} < 4$ M chalcosine is recrystallized into covellite, and at $c_{Cl^-} > 4$ M covellite is decomposed, with ca. 99% copper passing into solution at $c_{Cl^-} \sim 8$ M and 373 K.

Earlier [18], we studied in detail the behavior of cobalt pentlandite and pentlandite from SR in the $FeCl_3$–H_2O–HCl and $CuCl_2$–H_2O–HCl systems. Those experiments showed that, in oxidative leaching of SR, cobalt pentlandite is dissolved with formation of thiospinel (M_3S_4, where M = Co, Ni), which is associated with a defective structure of the initial cobalt pentlandite.

In decomposition of cobalt pentlandite, iron which isomorphically substitutes cobalt in the mineral structure virtually exhaustively passes into solution, which results in recrystallization of cobalt pentlandite into cobalt thiospinel. At the hydrochloric acid concentrations under 0.5 M and at copper(II) chloride concentration within 1–3 M no greater than 30–40% pentlandite was dissolved.

CONCLUSIONS

(1) Study of the behavior of the phase components of the carbonyl nickel synthesis residues in $CuCl_2$–HCl–Cl^- solutions showed that decomposition of chalcosine is governed to a greater extent by the chloride concentration in solution and the temperature of the process: At $c_{Cl^-} <$ 4 M chalcosine is dissolved with formation of covellite, and at $c_{Cl^-} > 4$ M covellite is decomposed, specifically by 99% at $c_{Cl^-} \sim 8$ M.

(2) At chloride concentrations in the leaching solution under 4 M recrystallization of chalcosine into covellite is controlled by diffusion, the apparent activation energy being 15.7 kJ mol^{-1}.

(3) At chloride concentration of 8 M in the leaching solution, dissolution of chalcosine proceeds in two stages. The apparent activation energy in the first stage is 7.2 kJ mol^{-1}. This suggests that the process is controlled by diffusion of the Cu^{2+} oxidant through the boundary layer of covellite to the external surface of the chalcosine particles. In the second stage, dissolution of covellite proceeds in a kinetic mode with the apparent activation energy of 49.4 kJ mol^{-1}.

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