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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Pentlandite Leaching in the $FeCl_3$– $CuCl_2$–HCl System

E. S. Kshumaneva[a], A. G. Kasikov[a], Yu. N. Neradovskii[b], and A. T. Belyaevskii[a]

[a]*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Scientific Center, Russian Academy of Sciences, Apatity, Murmanck oblast, Russia*
[b]*Geological Institute, Kola Scientific Center, Russian Academy of Sciences, Apatity, Murmanck oblast, Russia*

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Abstract—Pentlandite leaching in binary and ternary systems comprised of $FeCl_3$, $CuCl_2$, and HCl was studied. The degree of decomposition and recovery of pentlandite, as well as the kinetic characteristics of the process were examined in relation to the composition of solution.

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Pentlandite (Pnt) $(Fe,Ni)_9S_8$ is the main nickel-containing mineral which, in association with chalcopyrite and pyrrhotite, constitutes copper-nickel sulfide ores. Nickel is traditionally recovered from sulfide raw materials by flotation into a collective copper-nickel concentrate to be processed by pyrometallurgic methods into converter matte. At Russian enterprises, the latter is separated into nickel and copper concentrates to be once again subjected to pyrometallurgic refinement into crude nickel and copper anodes with formation of sulfuric acid [1]. The existing technology is power-intensive, bulky, and environmentally hazardous; certain problems are generated by sales and transportation of sulfuric acid.

Also, rich deposits are exhausted around the world; the available raw materials are characterized by increased complexity, and the minerals occur in the form unsuitable for enrichment and efficient recovery into high-quality concentrates by conventional methods. All this makes the latter impractical in the actual economic situation and necessitates the search for new methods of processing. These activities are promoted by rising prices and steady increase in demand for nonferrous metals [2, 3].

Up to the present time, pentlandite-containing materials have been processed commercially by two hydrometallurgical procedures: the ammonia procedure developed by Sherritt Gordon and the autoclave sulfuric acid procedure for processing of nickel-pyrrhotite concentrates, employed at Noril'sk Nickel, Polar Branch, Mining and Metallurgical Combine. In recent years, new processes were developed and passed pilot tests: Activox™ (Botswana), PLATSOL™ (US), and Inco's Voisey Bay (Canada). In Activox™ and PLATSOL™ autoclave processes, sulfur from sulfides is oxidized with oxygen to sulfates. In the sulfate-chloride two-phase process implemented at Voisey Bay most of sulfur is transferred to elemental form. The first stage of the process is run at atmospheric pressure with gaseous chlorine as oxidant, and the second stage of decomposition, under pressure in the presence of oxygen [1, 3, 4].

Copper(II) and iron(III) chloride solutions are suitable as oxidants for decomposition of the minerals at atmospheric pressure with virtually exhaustive removal of sulfur in the elemental form. Of special significance is the fact that platinum group metals, which are often part of copper-nickel ores, are concentrated in the leaching residues. For details on other benefits of hydrochloride processing of sulfide materials, see [5, 6].

The existing hydrochloride procedures are tailored primarily for nickel concentrates with heazlewoodite Ni_3S_2 as the main nickel-containing phase, since it exhibits acceptable dissolution rates in chloride media at low potentials [1, 7].

Published data are indicative of researchers' attempts to use various oxidants and procedures for preliminary processing of the initial material with the aim to develop efficient methods for dissolution of Pnt. For example, Warner et al. [8] reported that Pnt leaching with iron(III)

chloride at atmospheric pressure is an extremely slow process, with the mass transfer through the layer of the resulting elemental sulfur being the rate-limiting stage of the reaction. In leaching of pentlandite-containing concentrates this process can be accelerated in the presence of carbon tetrachloride, in which elemental sulfur is dissolved, or after mechanical activation of the material [9–11].

Lu et al. [12] and Park et al. [13] showed that dissolution of sulfide minerals, in particular Pnt, is significantly accelerated in solutions containing copper(II) chloride. After 6-h leaching, ca. 95% nickel is recovered, the process being unaffected by carbon tetrachloride [13].

Our previous studies concerned with the behavior of the phase components of carbonyl nickel synthesis residues (SR), pentlandite and cobalt pentlandite, in iron(III) chloride solutions [14, 15] showed that copper(II) chlorides cause the degree of dissolution of Pnt to substantially increase. Additional experiments showed that the synergistic effect was also observed for dissolution of Pnt concentrate under conditions similar to those in SR leaching by iron(III) chloride solutions. These conditions were provided by introduction of either chalcosine (Cu_2S) in the amount identical to that in the SR or of copper(II) chloride in the amount identical to that in the SR leaching solution.

Here, we studied the degree of decomposition of Pnt in relation to the composition of binary systems $FeCl_3$–HCl and $CuCl_2$– $FeCl_3$ and ternary system $CuCl_2$– $FeCl_3$–HCl. This is essential for predicting the behavior of Pnt under various conditions and achieving high recoveries at the optimal composition of the leaching system. Studies into decomposition of sulfide minerals with iron(III) and copper(II) chloride solutions attract much interest because hydrochloride leaching is being assessed as an alternative to pyrometallurgic processing of straight nickel ores and complex nickel sulfide concentrates.

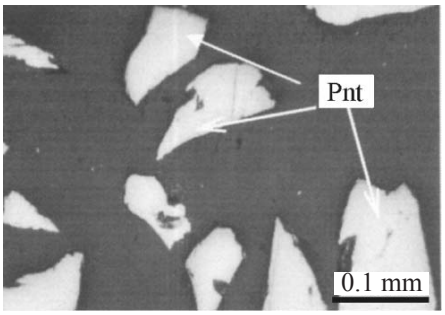

Fig. 1. Electron image of the initial sample of natural pentlandite: pentlandite grain morphology (grain size 0.02–0.20 μm).

EXPERIMENTAL

We used pentlandite concentrate with the following phase composition: pentlandite (90%), pyrite (5–10 %), chalcopyrite (up to 0.5 %), and pyrrhotite (individual grains). The mineralogical analysis of the samples by reflected light microscopy was carried out on an Ultrafot-3 Opton microscope with 0.2-μm resolution (Fig. 1). In all the experiments we used the –50 + 20 μm fraction; the chemical composition of the concentrate, wt%, was as follows: Ni 39.4, Fe 35.5, and Co 0.6. We described the experimental technique of pentlandite leaching earlier [15]. The solid : liquid ratio in each experiment was constant, 1 : 50. The X-ray phase analysis of the samples was carried out on a DRON-2.0 diffractometer in $Cu_{K\alpha}$ radiation.

The particle morphology was examined by raster electron microscopy on an SEM Leo-420 electron microscope. The content of the main components in leaching solutions and residues was determined by atomic-absorption spectrometry on an AAS (Karl Zeiss, Germany) instrument. Model solutions for leaching were prepared from chemically pure-grade $FeCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and HCl. The composition of the $CuCl_2$–$FeCl_3$–HCl mixture was modeled using STATISTICA 6.0 program [16].

The experiments on Pnt leaching with $FeCl_3$–HCl and $CuCl_2$– $FeCl_3$ solutions at isomolar ratios of the components of the system and their total concentration of 4 M (Fig. 2) are indicative of synergistic effect in each of the systems examined: $FeCl_3$: HCl = 3 : 1 and $CuCl_2$: $FeCl_3$ = 2 : 2.

It was shown earlier [16–18] that the catalytic effect from hydrochloric acid and/or copper(II) chloride in iron(III) chloride solutions on various processes is associated with formation of complexes whose composition varies with the concentration of the components. In the $FeCl_3$–HCl system, $[FeCl_n]^{3-n}$, $[HFeCl_4]$, $[H_2FeCl_5]$, $[H(FeCl_5)]^-$, and $[H_2(FeCl)_6]^-$ complexes can be formed, and in the $CuCl_2$–$FeCl_3$ system, $CuFeCl_5$ complex in which the electron density is transferred from ligands and iron(III) onto the copper(II) ion. This decreases the effective charge of the copper(II) ion, thereby enhancing the catalytic activity. The logarithm of the stability constant of the complex is 1.374.

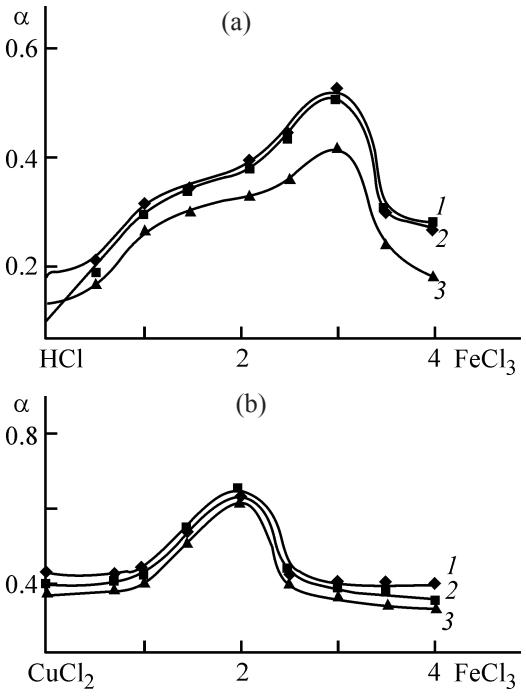

Fig. 2. Recovery of the main components α in leaching of natural pentlandite with binary mixtures, M: (a) $FeCl_3$–HCl and (b) $FeCl_3$– $CuCl_2$ at the HCl concentration of 1 M and different concentrations of the components. Experimental conditions: T = 80°C, = 2 h, solid : liquid = 1 : 50. (a) Iron(III) chloride and hydrochloric acid and (b) iron(III) chloride and copper(II) chloride taken in isomolar concentrations. (*1*) Ni; (*2*) Co; and (*3*) Fe.

A decrease in the concentration of the complex in the leaching solution (Fig. 3) against the background of the sodium chloride concentration of 5 M causes the degree of dissolution of Pnt to decrease.

Figure 4 shows the temperature dependence of the degree of nickel leaching at temperatures within 313–373 K in $CuCl_2$– $FeCl_3$ solution at the 2 : 2 ratio of the concentrations of the components. Hydrochloric acid was introduced into solution to avoid formation of various iron oxide and hydroxide species during leaching. The degree of dissolution of Pnt tends to noticeably increase with the temperature increasing beyond 333 K. In 5-h leaching at 373 K it was estimated at 90%.

Our experiments showed that, over the temperatures range examined, these dependences can be adequately described by the compressible sphere equation, derived for solid-state kinetically limited reactions: $k\tau = 1 - (1-\alpha)^{1/3}$, where α is the proportion of the reacted substance; k, reaction rate constant; and τ, reaction time. The apparent activation energy of the process was estimated at 78.1 kJ mol^{-1} from the slope of the Arrhenius curve. Hence, Pnt leaching with the synergistic mixture proceeds in the kinetic mode, while in the case of iron(III) chloride solution the process is limited by diffusion through the elemental sulfur layer [8].

Mineralogical and X-ray phase analyses of the initial samples and solid residues from leaching of pentlandite concentrate, as well as electron microscopic examination showed that, under the actual conditions, Pnt is decomposed without formation of intermediate phases: The initial Pnt and elemental sulfur were identified. Figure 5 shows that the particle morphologies in $CuCl_2$– $FeCl_3$ and $FeCl_3$–HCl systems are totally different. During Pnt leaching in the $FeCl_3$–HCl system the solution diffuses deep inside the grains via micropores, and Pnt is dissolved with formation of sulfur. This precludes

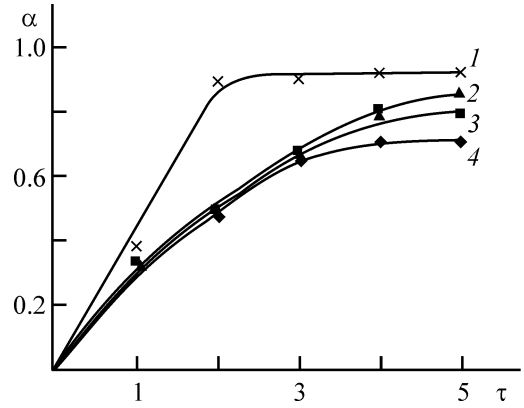

Fig. 3. Degree of dissolution of pentlandite α vs. leaching time, h, in relation and to the copper(II) and iron(III) chloride concentration at the sodium chloride concentration of 5 M. Experimental conditions: solid:liquid = 1 : 50. Concentration of components, M: (*1*) $CuCl_2$ 2, $FeCl_3$ 2, HCl 1; (*2*) $CuCl_2$ 1.0, $FeCl_3$ 1.0, HCl 0.5; (*3*) $CuCl_2$ 0.6, $FeCl_3$ 0.6, HCl 0.3; (*4*) $CuCl_2$ 0.4, $FeCl_3$ 0.4, HCl 0.2.

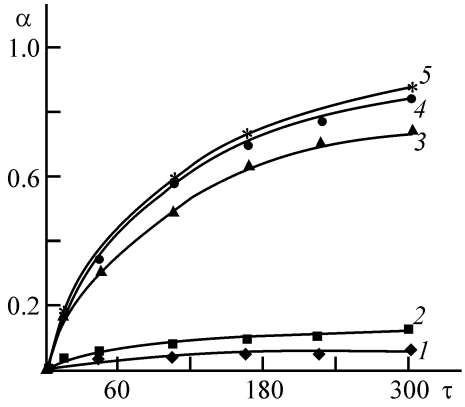

Fig. 4. Kinetic curves of pentlandite leaching in $CuCl_2$–$FeCl_3$–HCl solution. Experimental conditions: c_{CuCl_2} 2, c_{FeCl_3} 2, and c_{HCl} 1 M; α, degree of dissolution; and τ, time, min. Temperature, °C: (*1*) 40; (*2*) 60; (*3*) 80; (*4*) 90; and (*5*) 98.

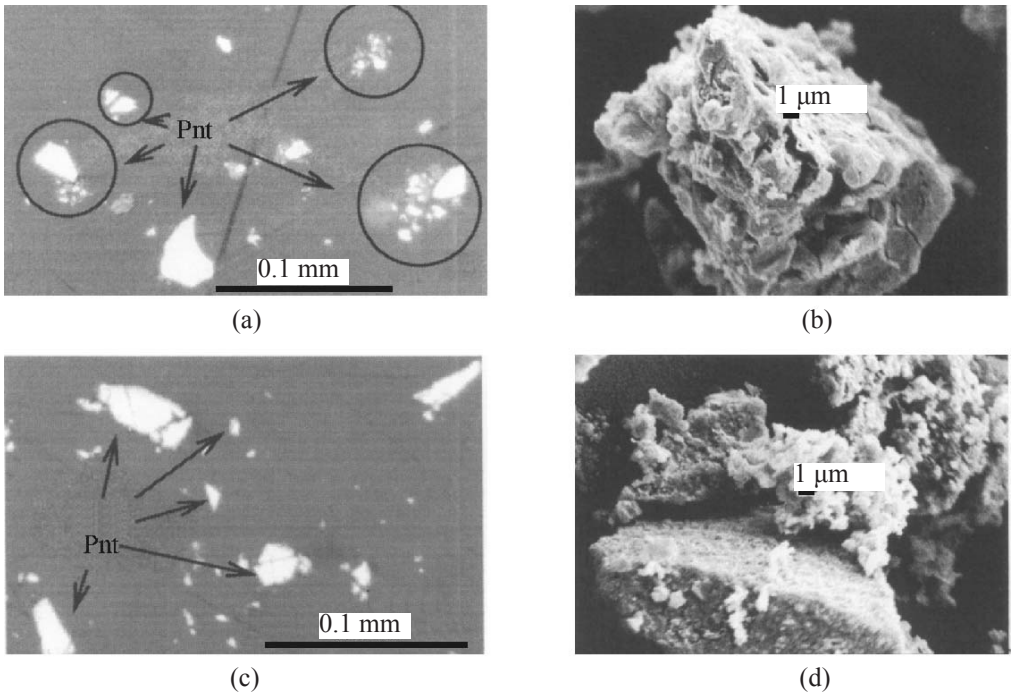

Fig. 5. Electron images of the leaching residues for natural pentlandite. Pentlandite grain morphology for leaching in solutions: (a) $FeCl_3$–HCl and (c) $CuCl_2$– $FeCl_3$. Electron images (SEM) of sulfur deposits for leaching in solution: (b) $FeCl_3$–HCl and (d) $CuCl_2$– $FeCl_3$.

further decomposition of the mineral, as suggested by deceleration of dissolution upon 2-h leaching. Warner et al. [8] found that the reaction

$$Fe_{4.5}Ni_{4.5}S_8(sol) = 4.5Fe^{2+}(aq) + 4.5Ni^{2+}(aq) + S(sol) + 18e$$

departs from equilibrium because of a slow solid-sate diffusion of the metal atoms inside the sulfur sublattice with formation of metastable amorphous sulfur. This is accompanied by occlusion of small Pnt grains by elemental sulfur, followed by aggregation of small particles around the initial grain (Figs. 5a, 5b). A distinctive feature of Pnt leaching at $CuCl_2$–$FeCl_3$ concentrations corresponding to the synergistic effect and in copper(II) chloride solution is that the nondecomposed mineral in the residues is not occluded by elemental sulfur: The grain surfaces are basically clean (Figs. 5c, 5d). Evidently, significant acceleration of the process prevents sulfur polymerization. The electron-microscopic data on the grain morphology agree well with the results of mineralogical analysis. The disperse sulfur particles formed on the Pnt grain surface pass into solution and are aggregated (Fig. 5d). The morphologies of the Pnt and elemental sulfur particles in the case of $CuCl_2$–HCl and $CuCl_2$–$FeCl_3$ systems are similar.

The composition of the $CuCl_2$– $FeCl_3$–HCl ternary mixture was modeled using simplex-lattices with inner points added in STATISTICA 6.0 program. The choice of the model was determined by its complexity. Preliminary studies revealed extrema of the function and inflections for the $FeCl_3$–HCl and $CuCl_2$– $FeCl_3$ binary systems. Hence, for the ternary system we chose the third-order model which allows estimating nonlinear effects in binary and ternary mixtures. The experimental design matrix is presented in the table. The total concentration of the components of the mixture was constant, 4 M. Leaching was run for 2 h at 98°C. As response function α, whose value depends on the composition of solution, we took the degree of decomposition of the mineral, calculated for its basic component, nickel. It was presumed that the degree of decomposition varies with the mixture composition solely. The dispersion analysis of the results in selecting the model out of the hierarchy of models of ever growing complexity (linear, quadratic, special cubic, and full cubic models) revealed a satisfactory agreement with the observed data for the full cubic model (determination coefficient $R^2 = 0.996$, $p = 0.024$, $F = 40.0$).

Figure 6 shows the response surface for regression equation.

$$\alpha = 1.00c_{CuCl_2} + 0.81c_{FeCl_3} + 0.76c_{HCl} + 0.18c_{CuCl_2}c_{FeCl_3} + 0.38c_{CuCl_2}c_{HCl} + 0.44c_{FeCl_3}c_{HCl} - 2.27c_{CuCl_2}c_{FeCl_3}(c_{CuCl_2} - c_{FeCl_3}) - 0.50c_{CuCl_2}c_{HCl}(c_{CuCl_2} - c_{HCl}) - 0.47\, c_{FeCl_3}c_{HCl} \times (c_{FeCl_3} - c_{HCl}) - 2.08\, c_{CuCl_2}c_{FeCl_3}c_{HCl}.$$

We revealed a decrease in the degree of dissolution of Pnt for solutions containing all the three components, and an increase for the binary systems $CuCl_2$– $FeCl_3$ and $FeCl_3$–HCl, as suggested by the observed synergistic effects. Comparison of the data for 80 and 98°C (Figs. 2, 6) suggests shifting of the maximal degree of decomposition of Pnt toward higher iron(III) chloride concentrations from 2 to 3 M for the $CuCl_2$– $FeCl_3$ system. At the same time, for the $FeCl_3$–HCl system it is shifted toward lower iron(III) chloride concentrations from 3 to 1.5 M.

Thus, our data allow predicting the behavior of pentlandite in hydrochloride processing of sulfide raw material and determining the optimal composition of leaching solutions that ensures the maximal recovery of valuable components.

CONCLUSIONS

(1) Pentlandite leaching in $FeCl_3$–HCl and $CuCl_2$–$FeCl_3$ binary systems at isomolar ratio of components, 3:1 and 2:2, respectively, and their total concentration of 4 M is accompanied by synergistic effect manifested in substantial acceleration of dissolution of the initial material.

(2) Leaching in the $FeCl_3$–HCl system is accompanied by occlusion of small pentlandite grains with elemental sulfur, followed by aggregation of small particles around the initial grain and is controlled by diffusion of the solution through the elemental sulfur layer. At the same time, leaching in the $CuCl_2$– $FeCl_3$ system is controlled by the chemical reaction with the apparent activation energy of 78.1 kJ mol^{-1}.

(3) For the ternary mixture $CuCl_2$– $FeCl_3$ –HCl, variation of the degree of dissolution of pentlandite can be adequately described by the full cubic model. The degree of dissolution of pentlandite decreases in the presence in solution of all the three components, while in the case of the binary interaction of the components in the $CuCl_2$– $FeCl_3$–HCl system it increases, as suggested by the observed synergistic effects.

Experimental design matrix

C_{CuCl_2}	C_{FeCl_3}	C_{HCl}	α
0	0	4	0.76
4	0	0	1.00
0	4	0	0.81
1	1	2	0.91
1	2	1	0.94
2	1	1	0.84
2	2	0	0.95
2	0	2	0.97
0	2	2	0.88
3	0	1	0.96
0	3	1	0.84
0	1	3	0.91

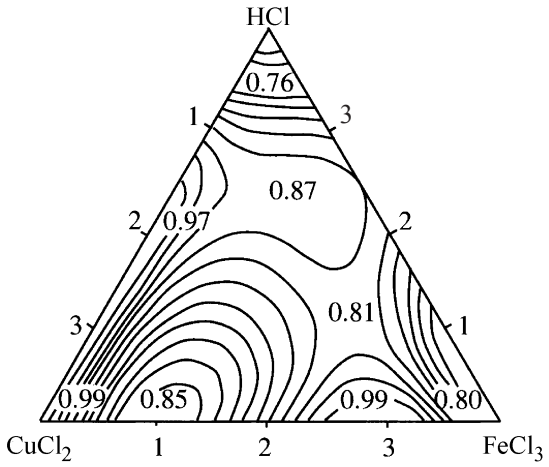

Fig. 6. Composition–degree of decomposition diagram for pentl

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