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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Kinetic Regularities of Recovery of Metals from Raw Materials of Industrial Origin

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Abstract—Kinetics of recovery of metals from the wastes and poor ores, which contain oxide and sulfide minerals of copper, vanadium, and silver with an azomethine solution in organic solvent was studied. The optimal parameters of the recovery were suggested.

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Many industrial plants are the source of wastes containing metal elements. These are mining, metallurgical, and electroplating tailings, spent catalysts from organic synthesis, and wastes from abrasive processing of metals. A significant amount of metal elements is present in dust emissions of mechanical engineering plants.

Presently, processing of wastes and ores with a low content of metal elements is economically disadvantageous or impossible due to lack of appropriate technologies. The increased demand for various non-ferrous metals and the depletion of ore deposits stimulate searching for new ways of processing [1–7].

As known, azomethines can form complex compounds with many transition metals in dissolved form, particularly with metal acetates in alcohol medium on boiling [8]. It was established that azomethines in aprotonic solvents with a large Dimroth–Reichardt electrophilicity parameter E_T at temperature not higher than 30°C can recover metals directly from metals, oxides, sulfides, carbonates, silicates, phosphates and spinels in solid phase. This made it possible to use as starting raw material metal-containing wastes and dust, out-off-balance ores of native metals, and poor ores containing both sulfide and oxide minerals.

In this work, the kinetics and mechanism of interaction of the mineral components of poor ores and wastes of industrial origin with a 2-oxy-1 benzylideneaniline (salicylal aniline, SA) in organic solvents were studied and the optimal parameters of the extraction of metals by this reagent were determined.

EXPERIMENTAL

We studied recovery of copper from dust emissions formed in a number of plants. Objects of study were spinels $CuFe_2O_4$ and ores of cuprite Cu_2O, tenorite CuO, malachite $Cu (OH)_2 \cdot CuSO_3$, chalcosine Cu_2S, covellite CuS, chalcopyrite $CuFeS_2$, and bornite Cu_5FeS_4. Also, we studied recovery of vanadium from vanadinite $Pb_5[VO_4]_3Cl$ and recovery of silver from argentite Ag_2S. The concentration of metals in the samples was 0.1–0.7 wt %. Samples were immersed into a solution of 2-oxy-1 benzylideneaniline in dimethylformaldehyde (DMFA) at agitation. The agitation rate was 200 rpm, temperature 25°C, and the liquid-solid ratio, 60 : 1 or 30 : 1.

Lump leaching was performed during 5 days in packed pulp without agitation (the liquid-solid ratio 10 : 1 or 5 : 1). Samples were ores containing 50% of 7.8-mm fractions.

The process rate was determined from change in the optical density of colored solutions of the complex metal compounds being formed. After the metal recovery was complete, the solution was separated from surrounding rock, the solvent was distilled and recovered into the extraction process.

Kinteic study was performed in a thermostated cuvette of an LMF-82 nephelometer. The optical density of colored solutions of complex compounds was recorded automatically. The kinetic curves were constructed with an EPP-09M3 device. Loss of metal during the oxidation was determined simultaneously by the gravimetric method.

The optical density was determined from data obtained in at least 10 experiments

The reaction of copper with a ligand yields copper(II) bis(2-oxy-1-benzylideneanilinate in one stage.

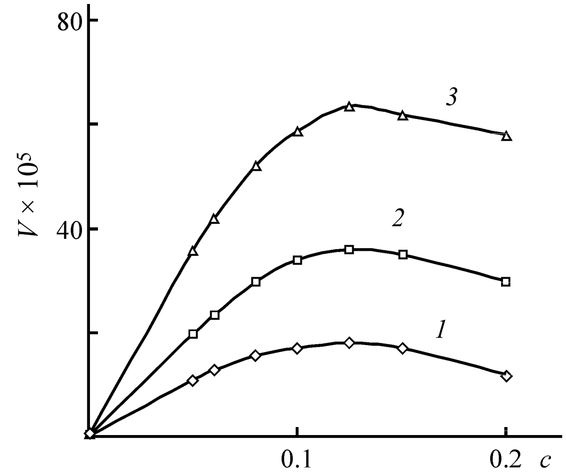
Individuality of the obtained complex compound crystals, recrystallized from a chloroform–heptane mixture, was confirmed by data on the elemental analysis and IR spectroscopy. Found(%): C 68.2, H 4.56, N 6.24, O 6.84, Cu 14.12. Calculated (%): C 68.42, H 4.34, N 6.14, O 7.02, Cu 13.96.

The chelate structure of the complex was confirmed by change in the IR spectra in comparison with the ligand spectrum. The IR spectra of the ligand have band of the C=N group at 1618 cm^{-1}. In the complex spectrum, this band is shifted by 14 cm^{-1} to lower frequencies, the band of Ph–O in the region 1278 cm^{-1} is shifted by 1324 cm^{-1} to higher frequencies, and band of OH and NH groups within 3100–3500 cm^{-1} is absent. Complex compounds obtained from oxide and sulfide ores have similar spectral characteristics.

Pure metal can be obtained by heating a complex compound, metal salicylal anilinate, at sufficiently low for metallurgy temperatures (180–200°C) without oxygen access, by recovery with hydrazine or by cathodic recovery from nonaqueous solvent. The elements of the incorporarting rock (*s*-elements, in particular) do not enter into reaction with the solvent.

The rate of the copper dissolution on the concentration is the complex dependence. At the low concentrations of the ligand (0.001–0.05 M) the process is described by the first-order consecutive reactions with respect to the ligand:

$$\mathrm{Cu(0)} \xrightarrow[\mathrm{L}]{k_1} \mathrm{Cu(I)L} \xrightarrow[\mathrm{L}]{k_2} \mathrm{Cu(II)L_2},$$



The rate V (mol cm^{-2} h^{-1}) of the oxidative dissolution of a compact copper vs. the 2-oxy-1-benzylideneaniline concentration c (M) at (*1*) 25 (*2*), 35, and (*3*), 40°C.

where $k_1 << k_2$.

The rate constants of the reactions ($k_1 = 0.0437\ \mathrm{h}^{-1}$ and $k_2 = 0.428\ \mathrm{h}^{-1}$) were calculated from experimental data. The maximum concentration of the intermediate product, Cu(I)L, is attained after 2 h 48 min (9.9×10^{-5} M) at the initial ligand concentration 0.01 M.

The kinetic curves pass through a maximum at the concentration 0.05–5 M (see the figure). This means the Langmuir– Hinshelwood mechanism, involving similar active centers of the metal surface [9]:

$$\mathrm{Sol} + \mathrm{S} \xrightarrow{K_{\mathrm{sol}}} \mathrm{SolS},$$

$$\mathrm{L} + \mathrm{S} \xrightarrow{K_{\mathrm{L}}} \mathrm{LS},$$

$$\mathrm{SolS} + \mathrm{LS} \xrightarrow{k'} \text{Reaction products}.$$

where Sol is the solvent, L is the ligand, S an active center on the surface of a metal, K_{Sol} and K_{L} are the adsorption equilibrium constants for a coordinating solvent and a ligand, respectively.

The equation for the process rate V has the form [9]

$$V = k' \frac{S_0{}^2[\mathrm{Sol}][\mathrm{L}]K_{\mathrm{Sol}}K_{\mathrm{L}}}{(1 + K_{\mathrm{Sol}}[\mathrm{Sol}] + K_{\mathrm{L}}[\mathrm{L}]^2},$$

where $k = k'S_0^2$, k is the rate constant of the surface reaction and S_0, the number of active centers per unit surface area.

From the data obtained, the scheme of the copper extraction with a coordinating agent is described by the following equations:

$$\begin{array}{c} 4\ C_{13}H_{10}NOH + 4\ Cu + O_2 \rightarrow 4\ CuC_{13}H_{10}NO + 2\ H_2O\ , \\ 4\ C_{13}H_{10}NOH + 4\ CuC_{13}H_{10}NO + O_2 \rightarrow 4\ Cu(C_{13}H_{10}NO)_2 + 2\ H_2O\ , \\ \hline 4\ C_{13}H_{10}NOH + 2\ Cu + O_2 \rightarrow 2\ Cu(C_{13}H_{10}NO)_2 + 2\ H_2O\ . \end{array}$$

It was found that complex copper compounds obtained by the dissolution are identical, irrespective of the nature of starting material (metal in oxidation state (0), sulfide minerals containing chalcosine and covelline, or oxide minerals containing cuprite and tenorite). Therefore, the mechanism of the copper recovery from minerals can be described by the following schemes (HL is $C_{13}H_{10}NOH$):

Cuprite Cu_2O

$$Cu_2O + 2HL = 2\ Cu^IL + H_2O,$$

$$4Cu^IL + O_2 + 4HL = 4Cu^{II}L_2 + 2H_2O;$$

Tenorite CuO

$$CuO + 2HL = Cu^{II}L_2 + H_2O;$$

Chalcosine Cu_2S

$$Cu_2S + 2HL = 2Cu^IL + H_2S,$$

$$4Cu^IL + O_2 + 4HL = 4Cu^{II}L_2 + 2H_2O,$$

$$H_2S + 1/2O_2 = H_2O + S;$$

Covelline CuS

$$CuS + 2HL = Cu^{II}L_2 + H_2S,$$

$$H_2S + 1/2O_2 = H_2O + S;$$

Chalcopyrite, $CuFeS_2$ ($Cu_2S{\cdot}Fe_2S_3$)

$$2CuFeS_2 + 2HL = 2Cu^IL + Fe_2S_3\downarrow + H_2S,$$

$$4Cu^IL + O_2 + 4HL = 4Cu^{II}L_2 + 2H_2O,$$

$$H_2S + 1/2O_2 = H_2O + S\ ;$$

Bornite Cu_5FeS_4 ($5Cu_2S{\cdot}Fe_2S_3$)

$$2Cu_5FeS_4 + 10HL = 10Cu^IL + Fe_2S_3\downarrow + 5\ H_2S\ ,$$

$$10Cu^IL + 10HL + 5/2O_2 = 10Cu^{II}L_2 + 5H_2O,$$

$$H_2S + 1/2O_2 = H_2O + S.$$

Oxygen absorption was confirmed by the volumetric method. In dissolution of metallic copper and minerals containing copper in oxidation state (I) the process proceeds in two stages.

The electronic spectra for solutions of complex copper compounds poor in oxygen have two maxima assignable to $Cu^{II}L_2$ (λ^I_{max} = 490 nm) and copper compounds in oxidation state (I) (λ^{II}_{max} = 720 nm). Green solutions containing Cu^IL kept in air transformed into $Cu^{II}L_2$ compounds of brown color. Apparently, the Cu^IL $Cu^{II} \leftrightarrows L_2$ transformation is reversible, with equilibrium in the presence of oxygen shifted however toward $Cu^{II}L_2$.

Let us consider data on the dissolution of covelline and tenorite. The spectrum of covelline has, along with the maximum due to copper salicylal anilinates in DMFA (λ_{max} = 490 nm), a broad band at λ_{max}= 750 nm. Consequently, copper recovery from covelline is a more complex process. It can now be considered proven that covelline (CuS) has a very complicated structure, described by the formula $CuI_2(CuIIS_2)S$. Copper is present in it in oxidation states (I) and (II) and sulfur, in the form of sulfide and polysulfide ions (S^{2-} and S_2^{2-}, respectively) [1]. The solubility of H_2S and H_2S_2 in DMFA is reasonably high. The spectrophotometric study of the extracts of sulfur and H_2S_2 in DMFA revealed sulfur and polysulfane [$\lambda_{max\ (S)}$ = 286 nm and $\lambda_{max\ (H_2S_2)}$ = 348 nm].

Hydrogen sulfide, formed upon copper extraction from sulfide minerals, oxidizes with air oxygen to elementary sulfur, which can be easily separated from DMFA by filtration, and no pollution of the environment with hydrogen sulfide takes place. The H_2S concentration never exceeded MPC (0.01 mg m^{-3}).

The oxygen is involved into the leaching process. Upon replacement of air for oxygen the chemical reaction ceased. Hence, it follows that in the ligand reaction, copper oxide in the form of surface chemical compound is a reagent.

The solubility of oxygen in DMFA exceeds by approximately one order of magnitude its solubility in water (28×10^{-4} M in DMFA and 2.6×10^{-4} M in water at 20°C). The dissolution rate of metallic copper is independent of the pressure of oxygen or air over the solution. The kinetic curves (dependences of concentration of a complex compound on time) obtained under the oxygen pressure 0.2–2 atm have similar

Table 1. Kinetic characteristics of metal recovery from the wastes. SA concentration 0.05 M and temperature 298 K

Ore	Formula	Rate $V \times 10^5$, mol g^{-1} h^{-1}	E_a, kJ mol^{-1}	Extraction degree, %
Chalcopyrite	$CuFeS_2$	64	53.0 ± 2	37.61
Chalcosine	Cu_2S	148	18.3 ± 1	81.39
Covelline	CuS	76	38.9 ± 2	85.60
Bornite	Cu_5FeS_4	22	117 ± 3	47.60
Cuprite	Cu_2O	19	36 ± 1	63.33
Tenorite	CuO	59	68 ± 2	70.60
Malachite	$(CuOH)_2CO_3$	24	43 ± 4	79.89
Spinel	$CuFe_2O_4$	3.33	171 ± 3	72.47
Hematite	Fe_2O_3	3.75	98 ± 2	76.70
Magnetite	Fe_3O_4	0.13	87 ± 3	69.59
Siderite	$FeCO_3$	1.5	69 ± 2	72.34
Vanadinite	$Pb_5[VO_4]_3Cl$	58	45 ± 4	50.71
Argentite	Ag_2S	183	–	76.00

run at the ligand concentrations 0.01–1 M. Thus, the concentration of oxygen near a metal surface is excessive and the rate is limited solely by the concentration of a complex-forming reagent.

Table 1 collects kinetic data on the copper recovery from the wastes. Copper is extracted from sulfide ores at higher rate than from oxide ores. The extraction rate for chalcosine, covelline, and chalcopyrite is maximal (at the extraction degree 37–85%). Silver and vanadium also dissolve at considerable rates and extraction degrees, whereas iron extracts at low rate from siderire, hematite, and especially, magnetite. From ores containing iron and copper (chalcopyrite, bornite, and spinel), copper is recovered as major form. The selectivity of copper recovery is explained by the low rates of the iron extraction from the above minerals. The donor-acceptor systems may be applied for copper recovery from iron–copper spinel, which is obtained in pyrometallurgical processes and cannot be processed further.

This result can be ascribed to the standard free energies of formation of minerals (Table 2).

The study of complex iron compounds and complexation reactions of iron chloride(III) with 2-oxy-1-benzylideneaniline showed that the synthesized complex iron(III) compounds are not chelates. They belong to the molecular type $FeCl_3 \cdot 2NL$, in wich intramolecular hydrogen bond is preserved. Apparently, this impedes transition of iron from the solid phase into the solution, leads to the kinetic selectivity of metal extraction, and suggests that the method of metal coordination with typical chelating agents play a certain role in removing metals from the solid phase.

The optimum concentrations of the ligand were determined from the dependence of dissolution rate on the 2-oxy-1-benzylideneaniline concentration (0.125 M for copper, 0.030 M for vanadium, and 0.652 M for silver). It was unreasonable to increase further the concentration of a chelating agent because of the decreasing rate and recovery degree, which is due to

Table 2. Standard free energies of formation of minerals

Substance	ΔG, kJ mol^{-1}	Substance	ΔG, kJ mol^{-1}
FeO	–224.30	CuO	–127.28
Fe_2O_3	–741.05	Cu_2S	–86.25
Fe_3O_4	–1014.90	CuS	–49.00
FeS	–100.8	$CuFeS_2$	–178.78
Cu_2O	–146.45	Cu_5FeS_4	–353.37

the fact that energetically simlar active centers on the metal surface adsorb both the solvent and the ligand. Thus, the increase in the ligand concentration should be acceptable and individual for each metal.

The nature of the organic solvent plays the essential role. Reliable criterion for its choice may be the Dimroth– Reichardt electrophilicity parameter E_T, which is a quantitative measure of the capability of aprotonic solvent–ligand system to coordination leaching of metal. For systems with large E_T value, the tendency to chelate formation is larger. The obtained empiric equation depicting the dependence of the logarithm of the reaction rate constant on E_T is $\log k = -10.49 + 0.19E_T$.

The extraction rate as a function of temperature within 20–80°C is described by the exponential Arrhenius equation. The apparent activation energy of the process was determined from the $\ln V_0 == f(1/\tau)$ graphs (V_0 is dissolution rate (mol g^{-1} h^{-1}) and τ, time (h). Experimental data suggest that the reaction of an ore metal with the ligand is kinetically limited under agitation conditions (activation energy 40–70 kJ mol^{-1}). Exception is chalcosine (apparent activation energy 18 ± 1 kJ mol^{-1}). For this mineral, a temperature increase is less efficient than for other minerals, whereas the agitation intensity, on the contrary, increases with the extraction rate (diffusion control). For ores with other mineral components, the increase in the agitation intensity has no effect.

As the s : l ratio decreases to 5 : 1, the extraction degree and leaching rate decrease and then remain constant at larger ratios (60 : 1 or 30 : 1).

Analysis of the kinetic data warrants a conclusion to be made that these ores can be processed in non-aqueous solvents, but each type of the ore requires individual choice of the solvato-processing conditions in order to select the best parameters of the process. Solvato-processing can be carried out in leaching vats with agitation and by heap leaching without stirring. In the latter case however, the leaching time, at which an acceptable degree of metal recovery is reached, increases from 3 h to 5 days.

The mechanism of the chemical coordination extraction of metals with organic reagents, proceeding without dissociation, hydration, and hydrolysis at larger solubility of oxygen, is less complicated in comparison with the extraction with aqueous solutions. The proposed technological solution of leaching metals from waste is simple, proceeds at low temperatures, which is unusual for pyrometallurgical processes, and is characterized by the kinetic selectivity in the separation of metals and possibility of recovering the solvent.

The advantages of the technological methods using organic reagents and their ability to extract metals from industrial waste and poor ores with a low concentration of *d*-elements demonstrate wide possibilities of solvate-metallurgical processes and, presumably, will lead to a radical change in the classical schemes used in extraction of non-ferrous metals.

CONCLUSIONS

(1) The products formed in the reaction of 2-oxy-1-benzylideneaniline with poor ores containing native copper and different sulfide and oxide minerals upon leaching in the dimethylformaldehyde–azomethine system were determined

(2) The kinetic parameters of the process were studied. The rate constants of concecutive reactions, the optimum concentration of the ligand, and the mechanism of the recovery of copper in oxidation state 0 were determined. The reaction proceeds by the Langmuir–Hinshelwood mechanism, when the reagent and the solvent are adsorbed on energetically similar surface centers.

(3) Study of the kinetics and mechanism of the process and determination of the limiting stage gives ground to choose the processing conditions (pressure, temperature, time, solvent, and concentration of complexing agent) and determine ways for leaching intensification.

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