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The Special Features of the Kinetics of Oxidation of Divalent Iron during Sulfuric Acid Leaching of Pyrrhotine with the Participation of Nitrous Acid

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Abstract—The kinetics of oxidation of divalent iron ions with molecular oxygen during pyrrhotine leaching in sulfuric acid solutions with the participation of nitrous acid as an activator was studied. The oxidation of Fe^{2+} to Fe^{3+} only occurred at the second slow stage of the process, when the degree of solid phase stripping reached almost 80% of the value maximum under given conditions. The order of the reaction with respect to sulfuric acid was negative (-1.1 ± 0.1), as is characteristic of sulfate media. A substantial change in effective activation energies from 7 ± 5 kJ/mol at $c^{\text{o}}_{H_2SO_4} = 0.25$ mol/l to 31 ± 5 kJ/mol at $c^{\text{o}}_{H_2SO_4} = 1.02$ mol/l could be caused by different contents of the pyrrhotine solid phase in the system at the beginning of the second leaching stage. It was assumed that the oxidation of Fe^{2+} to Fe^{3+} occurred with much lower energy expenditures in the presence of a sulfide solid phase.

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INTRODUCTION

The oxidation of divalent iron salts with molecular oxygen in acid media is the limiting factor of many natural processes and hydrometallurgical technologies. One of the methods for increasing the rate of this reaction under laboratory and industrial conditions is the use of various nitrogen compounds (oxides, nitrates, nitrites, etc.) as activators [1–5]. The mechanism of catalysis is very complex and has not been determined in detail. During oxidation, the system contains quite a number of nitrogen compounds (NO, N_2O_3, NO_2, N_2O_4, HNO_2, NO_2^-, HNO_3, NO_3^-, NO^+, and NO_2^+) having various catalytic activities. According to many experimental studies, the form most reactive kinetically is nitrous acid and the products of its dissociation. At low concentrations (<0.1 M), the activating action of HNO_2 exceeds the catalytic activity of all the other oxygen compounds of nitrogen severalfold [2, 4, 5].

Another approach to solving the problem of the acceleration of Fe^{2+} oxidation is based on the use of a heterogeneous rather than homogeneous mechanism of molecular O_2 activation. This approach takes the advantage of the ability of certain solids to sorb dissolved oxygen on active centers of their surface [6].

A study of the behavior of divalent iron in the $Fe_{0.88}S + H_2O + H_2SO_4 + O_2 + HNO_2$ system during the stripping of the sulfide solid phase capable of chemisorbing dissolved oxygen was therefore of certain interest.

EXPERIMENTAL

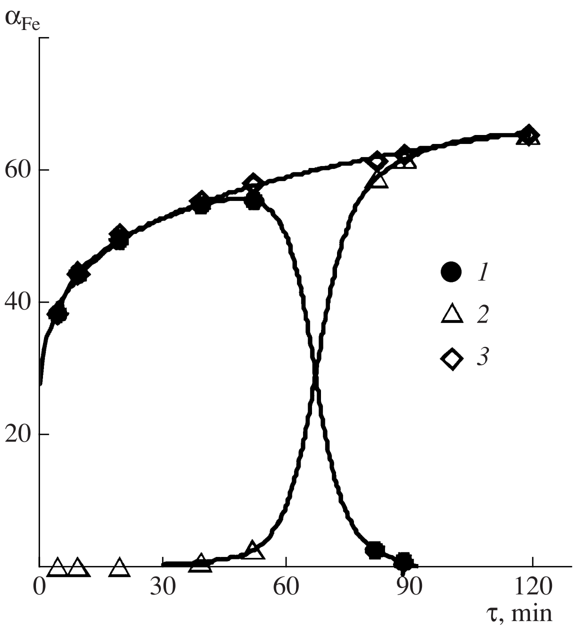
Studies of the kinetics of oxidation of Fe^{2+} in sulfuric acid solutions containing nitrous acid were performed for disperse selective pyrrhotine concentrate samples from Noril'sk deposit. The samples contained 93.2% $Fe_{0.88}S$, 1.5% $CuFeS_2$, and 4.5% SiO_2. A weighed amount of sulfide was leached under temperature-controlled conditions with continuous stirring (an upper drive) in a closed reaction vessel equipped with a sampler with a finely porous filter, a feeder for introducing activator solutions, and a system for supplying and removing gases, which could be used for the introduction of oxygen into the reaction zone at a pressure of 1 atm.

Nitrous acid was obtained by the exchange reaction

$$2NaNO_2 + H_2SO_4 = 2HNO_2 + Na_2SO_4.$$

A solution of sodium nitrite was dosed directly into the reaction slurry in certain time intervals. The conditions for feeding the catalyst were developed taking into account the occurrence of parallel processes in the oxidation system and allowed the concentration of nitrous acid to be maintained as close as possible to the required value 0.001 M.

The experimental conditions were changed over the intervals $c^{\text{o}}_{H_2SO_4} = 0.25$–$1.02$ M and $T = 293$–333 K. The concentration of nitrous acid (0.001 M), the rate of stirrer rotations (168 s^{-1}), and oxygen pressure (1.01×10^5 Pa) were maintained constant in all experiments.



Kinetic curves for the degree of extraction of Fe^{2+} and Fe^{3+} ions into solution during pyrrhotine leaching; T = 293 K, $\omega = 168\ s^{-1}$; $c^{o}_{H_2SO_4} = 0.51$ mol/l, $c_{HNO_2} = 0.001$ mol/l, and $p_{O_2} = 1.01 \times 10^5$ Pa; (*1*) Fe^{2+}, (*2*) Fe^{3+}, and (*3*) $Fe^{2+} + Fe^{3+}$.

The initial solid : liquid ratio was 1 : 100 (2 g of sulfide per 200 ml of solution).

The contents of di- and trivalent iron ions in the liquid phase were determined by complexonometric titration [7]. The methods for calculating the main process parameters (activation energy and reaction orders with respect to the reagents) were quite traditional [8].

RESULTS AND DISCUSSION

We showed in [9] that the leaching of pyrrhotine in sulfuric–nitrous acid media includes two successive stages of intense (0–10 min) and slow (10–120 min) solution. The two-stage character of the process is likely caused by a change of the leaching mechanism from nonoxidative with the formation of hydrogen sulfide (which is substantiated by the absence of Fe^{3+} ions in solution) into oxidative,

$$FeS + H_2SO_4 = FeSO_4 + H_2S, \tag{1}$$

$$\begin{gathered} FeS + 2HNO_2 + H_2SO_4 + O_2 \\ = FeSO_4 + 2NO_2 + S^0 + 2H_2O, \end{gathered} \tag{2}$$

$$\begin{gathered} 2FeSO_4 + 2HNO_2 + H_2SO_4 + O_2 \\ = Fe_2(SO_4)_3 + 2NO_2 + 2H_2O. \end{gathered} \tag{3}$$

A decrease in the rate of the process at the second stage can be caused by the formation of a film of low-solubility products (iron oxides and elemental sulfur) on the reaction surface [9].

The evolution of the contents of Fe^{2+} and Fe^{3+} ions in solution during the stripping of pyrrhotine is presented in the figure. Such a shape of kinetic curves was observed under all experimental conditions. Note that the oxidation of divalent iron only occurred at the second slow stage, after the degree of pyrrhotine leaching reached 80% of the value maximum under given conditions.

We used the time at which the concentrations of the oxidized and reduced iron forms became equal (τ_p) as a factor characterizing the rate of Fe^{2+} transformation into Fe^{3+} [8]. Process parameters (reaction order with respect to sulfuric acid and activation energy) were determined taking into account changes in the initial experimental conditions by the time at which the second stage began, namely, a decrease in solution acidity and a nonuniform increase in the concentration of Fe^{2+} ions. The content of sulfuric acid in the system (at τ = 10 min) was calculated in each experiment using the kinetic equation for pyrrhotine leaching [9] (Table 1). The kinetics of oxidation of divalent iron with molecular oxygen in sulfuric acid solutions described in sev-

Table 1. Sulfuric acid concentration effects on the rate of oxidation of divalent iron ions (c_{HNO_2} = 0.001 mol/l, T = 293 K, and $p_{O_2} = 1.01 \times 10^5$ Pa)

$c^0_{H_2SO_4}$, mol/l	$c_{H_2SO_4}$, mol/l	α_{Fe}, %	$c_{Fe^{2+}}$, mol/l	τ_p, min	$1/\tau_p$, min^{-1}
0.25	0.22	29	0.034	47	0.021
0.51	0.46	44	0.050	68	0.015
0.75	0.67	50	0.056	96	0.010
1.02	0.95	60	0.067	113	0.009

Note: $c^0_{H_2SO_4}$ is the initial concentration of sulfuric acid, mol/l; $c_{H_2SO_4}$ is the concentration of sulfuric acid at the beginning of the second leaching stage (τ = 10 min), mol/l; $c_{Fe^{2+}}$ is the concentration of divalent iron ions at the beginning of the second leaching stage (τ = 10 min), mol/l; and α_{Fe} is the degree of iron ($Fe^{2+} + Fe^{3+}$) extraction into solution at the beginning of the second stage (τ = 10 min), %.

Table 2. Temperature effects of the rate of oxidation of divalent iron ions (c_{HNO_2} = 0.001 mol/l and p_{O_2} = 1.01 × 10^5 Pa)

T, K	$c_{H_2SO_4}$, mol/l	τ_p, min	$1/\tau_p$, min^{-1}	α_{Fe}	$c_{Fe^{2+}}$, mol/l	s : l
293	$\frac{0.219}{0.940}$	$\frac{47}{113}$	$\frac{0.021}{0.009}$	$\frac{27}{70}$	$\frac{0.031}{0.080}$	$\frac{1.46 : 200}{0.60 : 200}$
303	$\frac{0.207}{0.936}$	$\frac{28}{68}$	$\frac{0.036}{0.015}$	$\frac{38}{74}$	$\frac{0.043}{0.084}$	$\frac{1.24 : 200}{0.52 : 200}$
318	$\frac{0.189}{0.929}$	$\frac{16}{36}$	$\frac{0.062}{0.028}$	$\frac{54}{80}$	$\frac{0.061}{0.091}$	$\frac{0.92 : 200}{0.40 : 200}$
333	$\frac{0.171}{0.923}$	$\frac{10}{20}$	$\frac{0.010}{0.050}$	$\frac{70}{85}$	$\frac{0.079}{0.097}$	$\frac{0.60 : 200}{0.30 : 200}$

Note: $c^0_{H_2SO_4}$ = 0.25 mol/l in the numerator and 1.02 mol/l in the denominator; s : l is the solid to liquid ratio.

eral works [10, 11] (including processes with the participation of nitrous acid [2, 5] and in the presence of activated carbon as a solid phase [6]) led us to suggest that, under the conditions of our experiments, the rate of the reaction also linearly depended on the initial content of Fe^{2+} in solution.

The kinetic equation for the oxidation of divalent iron takes the form

$$1/\tau_p = kc_{Fe^{2+}}c^n_{H_2SO_4}, \tag{4}$$

where $c_{Fe^{2+}}$ and $c_{H_2SO_4}$ are the concentrations of divalent iron ions and sulfuric acid at the beginning of the second stage (τ = 10 min), mol/l, and k is an experimental constant.

According to the results presented in Table 1, an increase in the initial content of H_2SO_4 in solution from 0.25 to 1.02 M decelerates oxidation and increases the time of the attainment of equal concentrations τ_p by 2.4 times. The dependence written in the logarithmic coordinates has the form

$$\log(1/\tau_p) - \log c_{Fe^{2+}} = -1.09\log c_{H_2SO_4} - 0.92. \tag{5}$$

It follows that the order of the reaction with respect to sulfuric acid is –1.1 ± 0.1 (with the corrections discussed above). The dependence obtained in this work corresponds to the literature data [5, 10, 11]. It was convincingly shown in these works that an increase in the concentration of acid decelerated (in sulfate) and accelerated (in chloride media) the oxidation of iron, which was caused by an increased reactivity of $FeSO_4^+$ complexes.

The influence of temperature on the rate of Fe^{2+} transformation into Fe^{3+} was studied at initial H_2SO_4 contents of 0.25 and 1.02 M. The results are listed in Table 2. An increase in T from 293 to 333 K accelerated oxidation and decreased the time of the attainment of equal concentrations τ_p by 4.7 and 5.6 times at low and high sulfuric acid contents, respectively.

The dependences obtained are described in the Arrhenius coordinates as

$$1/\tau_p = k_1c_{Fe^{2+}}c^{-1.1}_{H_2SO_4}\exp(-E_a/RT), \tag{6}$$

where E_a is the activation energy, kJ/mol; R is the gas constant, J/(mol K); T is the temperature, K; and k_1 = k/exp(–E/RT). We have

$$\ln(1/\tau_p) - \ln c_{Fe^{2+}} + 1.1\ln c_{H_2SO_4} = -801.8/T + 0.7 \quad \text{for} \quad c^o_{H_2SO_4} = 0.25\text{ M}, \tag{7}$$

$$\ln(1/\tau_p) - \ln c_{Fe^{2+}} + 1.1\ln c_{H_2SO_4} = -3679.0/T + 10.3 \quad \text{for} \quad c^o_{H_2SO_4} = 1.02\text{ M}. \tag{8}$$

The effective activation energies of the reaction determined this way were 7 ± 5 and 31 ± 5 kJ/mol (Eqs. (7) and (8), respectively).

The substantial difference between the E_a values obtained can be caused by different contents of the pyrrhotine solid phase at the beginning of the second stage (Table 2). The solid : liquid ratio at $c^o_{H_2SO_4}$ = 0.25 M is two times higher than that at $c^o_{H_2SO_4}$ = 1.02 M.

Note that, for homogeneous oxidation of divalent iron salts under similar conditions, the effective activation energy has a still higher value, 59 kJ/mol [11].

Substantial changes in the kinetics of Fe^{2+} transformation into Fe^{3+} in the presence of activated carbon are evidence of the possibility of the oxidation of iron(II) ions by molecular oxygen in sulfate media not only in solution but also on the surface of a solid phase [5].

To summarize, the results obtained lead us to conclude that, at low degrees of sulfide leaching, that is, at a high solid : liquid ratio, the oxidation of divalent iron with molecular oxygen in sulfuric acid solutions with the participation of nitrous acid occurs with much lower energy expenditures.

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