

Kinetics of Pyrrhotine Leaching with Sulphuric Solutions under Oxidative Conditions with the Participation of Nitrous Acid

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Abstract

The kinetics of leaching pyrrhotine solutions in sulphuric solutions containing small amount of nitrous acid was investigated. It was shown that pyrrhotine treatment under the given oxidative conditions proceeds through the stages of intensive initial and subsequent slow dissolution. The first stage is likely to correspond to the dissolution of the oxidized layer on sulphide surface and to intensive non-oxidative leaching with the formation of hydrogen sulphide. A decrease in the process rate at the second stage is due to the transition to the oxidative regime of leaching and the formation of a film of difficultly soluble compounds (oxidized iron with oxygen, elemental sulphur) on the reaction surface. The activating action of nitrous acid is likely to be exhibited at the second stage when FeSO₄ solutions are oxidized with molecular oxygen. It was shown experimentally that even small concentration of HNO₂ (0.001 M) at low temperature (293 K) causes a substantial increase in the intensity of regeneration of the active agent of chemical weathering of hypergenesis zone, namely, Fe³⁺ ions. In this connection, the system H₂O + O₂ + HNO₂ + H₂SO₄ can play a substantial part in oxidative processes in sulphide tailings. Pyrite remained almost completely non-solved in this oxidative system within the experiment duration.

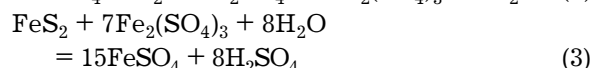
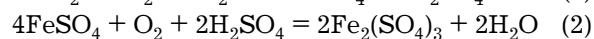
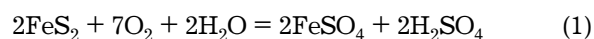
INTRODUCTION

Sulphide-containing solid waste products of metal mining industry are one of the main sources of uncontrollable environmental pollution with heavy metals. With the modern technology of ore processing, the prevailing fraction of impurities does not get concentrated in any ore dressing product, which provides especially toxic wastes. Under hypergenic conditions, they are actively affected by the agents of chemical and microbiological weathering [1].

The most widespread sulphide mineral in the waste materials of metal mining industry and metallurgy is pyrite; pyrrhotine occupies the fifth position [2]. The behaviour of iron sulphides in various oxidative systems of hypergenesis zone is of substantial interest for deeper understanding of the processes in the

system of sulphide tailings in natural environment.

According to the results of numerous field and experimental investigations, oxidation of sulphide minerals is a set of chemical and biogeochemical processes [3]. Oxidation of pyrite, the main acid-producing mineral, occurs in three consecutive stages:



An opinion exists that the first two reactions are catalyzed by mesophilic carbothionic bacteria, especially those of *Thiobacillus ferrooxidans* species which are usually present in the gob tailings and in drainage water. The intensity of oxidation is determined by the second stage [3].

An important factor of the acceleration of oxidation with molecular oxygen in aqueous solutions is the presence of catalysts, for example those causing the formation of active oxygen forms. The part of catalysts in a corresponding medium can be played by the elements with the valence state prone to change in the presence of oxygen, for example Fe^{3+} or Cu^{2+} ions. These substances also include nitrogen oxides and the products of their transformation in aqueous solutions (for example, nitric and nitrous acids) [4, 5].

It was stressed in [6, 7] that the acceleration of oxidation processes under the effect of molecular oxygen proceeds according to the ion-radical mechanism. In this case the process is driven by the products of dissociation of nitrous acid, in particular nitrozonium ion NO^+ . Nitrogen oxides evolved during the process are easily oxidized in the presence of oxygen and form an acid [8]; as a result, the catalytic activity of HNO_2 manifests itself even for its insignificant concentration in solution (0.001–0.01 M) [9, 10].

The above-described mechanism of catalysis of the oxidative processes participated by oxygen-containing compounds of nitrogen can take place in various natural and technology-related systems (in the atmosphere, soil, oxidation zones of sulphide deposits, in mining tailings). Oxygenated compounds of nitrogen are permanent components of acid rain; they are taken into account when evaluating the ecological situation only as acid-forming compounds. However, their contribution into the acceleration of oxidation reactions during weathering of minerals (for instance, sulphides and Fe(III) salts) is not taken into account at present.

The mechanisms of iron sulphide treatment in acid media are complicated and diverse. To achieve a more correct interpretation of the results obtained in the present work, let us consider modern experimental literature data on the transformations of the reaction surface during leaching.

According to the results of recent investigations [11–14], pyrrhotine leaching in acids is considered as a sequence of stages of the oxidative (slow) and non-oxidative (rapid) dissolution. The duration and order of the indicated stages in to a large extent determined by the initial state of sulphide surface,

temperature and the oxidative potential of the medium.

Pyrrhotine dissolution under oxygen-free conditions has an induction period before the stage of a sharp (by 2–3 orders of magnitude) increase in the process rate. Air exposure of pyrrhotine samples ground in an inert atmosphere (N_2) results in a substantial increase in the induction period from several seconds to 2 h [11]. These changes are explained by the formation of a zonal structure on sulphide surface in the oxidative atmosphere: zone A – the upper layer (with the length up to $5 \cdot 10^{-4} \mu\text{m}$) enriched with the compounds of oxygen with Fe(III) and S, and zone B – the intermediate metal-depleted layer (up to $30 \cdot 10^{-4} \mu\text{m}$ long) containing di- and polysulphide forms of sulphur. The zones are formed by means of migration of electrons and iron atoms from the bulk unreacted pyrrhotine phase through the metal-deficient layer to the oxidation boundary [15].

The slow stage of oxidative leaching of the layer of zone B is preceded by a short-time overshoot of the process rate (without the formation of hydrogen sulphide), which is considered by the authors of [11] to be connected with the dissolution of the upper oxidized layer (zone A). According to the data of X-ray photoelectron spectroscopy, mainly ferric sulphate, ferrous hydroxides and oxyhydroxides pass into the liquid phase in this case; ferric oxides turn out to be the least soluble in this situation. The maximal rate of iron transfer into solution at the stage of hydrogen sulphide formation is quite comparable with that at the stage of dissolution of the oxidized layer [11].

The transfer from the oxidative to non-oxidative dissolution of FeS is accompanied by the accumulation of the negative charge in the surface layer of the mineral and, as a consequence, by reduction of di- and polysulphide sulphur to the monosulphide form S^{2-} which stimulates non-oxidative dissolution [14]. Further development of the process leads to a sharp increase in the rate of extraction of iron and sulphur (by a factor of 7 and 1200, respectively) into solution in the form of H_2S and to the substantial amorphization of the sulphide surface – the formation of a massive (up to hundreds micrometres) non-equilibrium

metal-deficient layer (with the ratio $S/Fe > 2$) [11, 12]. Pyrrhotine leaching is controlled at this stage by the rate of chemical reaction at the interface. The experimental activation energy of the process ($E_a = 70$ kJ/mol) corresponds to the kinetic regime [11].

For pyrrhotine ground in the inter atmosphere and leached in the acid electrolyte saturated with air (by means of aeration), the oxidative mechanism dominates in the process except the initial stage (from 0 to 7 min) which corresponds to the dissolution of the upper oxidized layer (zone A). This regime is characterized by the minimal formation of sulphate and the absence of H_2S . Only a thin non-equilibrium layer is formed in the process on the sulphide surface; the major part of iron in this layer is represented by O-Fe(III) form prevailing under the conditions of passivation. In this case, the reaction rate is limited by the diffusion of iron ions from the bulk solid phase through the layer enriched with sulphur (zone B) to the surface of the mineral. The process rate is directly proportional to the square root of leaching time ($E_a = 21$ kJ/mol) [11].

An excess of oxidizing particles (O_2 or Fe^{3+}) in the system results in substantial changes in the mechanism of pyrrhotine leaching: the induction period increases substantially, and the composition of the final products becomes different. According to the data of X-ray photoelectron spectroscopy, the forms of sulphur in the surface layer are represented by the sorts: $\alpha-S^0$ (77 %), S_n^{2-} (17 %) and O-S (6 %) [11].

This fact can be explained as follows. The key moment of FeS dissolution with the formation of H_2S is predominance of the kinetically active monosulphide sulphur on the reaction surface over the passive di- and polysulphide forms. One of the reasons of the formation of such centres is connected with the accumulation of the surface charge in the metal-deficient layer (zone B). In the presence of oxygen or ferrous ions – acceptors of electrons – the excess negative charge on the interface is likely to be insufficient to reduce S_n^{2-} into S^{2-} , so sulphur passes into solution in the form of sulphate.

For leaching of dispersed and polished pyrite samples under the conditions similar to those of pyrrhotine treatment, the authors of [14]

did not discover any confirmations of the accumulation of a negative charge in the surface layer of the mineral. The reductive mechanism of FeS_2 dissolution manifests itself only when a substantial cathode potential is applied [14, 16].

Recently, much attention of researchers has been paid to the investigation of the mechanisms and kinetics of the processes widely occurring both in nature and in chemical technologies: oxidation of pyrite and pyrrhotine [11, 16–18] and ferric salts [19–22] by molecular oxygen in the presence of various catalysts. Publications on the experimental investigation of iron sulphide leaching with sulphuric acids under oxidative conditions with the participation of nitrous acid are almost absent from literature. Because of this, investigation of the physicochemical features of the behaviour of $Fe_{0.88}S$ and FeS_2 in the oxidative system $H_2O + O_2 + HNO_2 + H_2SO_4$ was of definite interest.

EXPERIMENTAL PROCEDURE AND INSTRUMENTATION

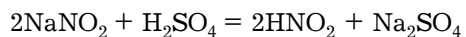
The choice of the acidic and temperature regimes of the experiment was made on the basis of literature data on the processes that occur in the refuse heaps of gobs and concentrating tailings of metal mining industry and metallurgy. According to the published results of investigations [3], acid sulphate water ($pH \leq 2$) prevails in the oxidative horizon of sulphide dumps. Exothermal character of the major part of sulphide oxidation processes promotes temperature rise inside the dumps (up to 330 K and above [23]). Taking into account the above considerations, we varied the experimental conditions within the following ranges: $C_{H_2SO_4} = 0.25-1.02$ M, $T = 293-333$ K, $\omega = 58-168$ s⁻¹, where ω is the angular velocity of mixer rotation. The concentration of HNO_2 equal to 0.001 M and oxygen pressure ($1.01 \cdot 10^5$ Pa) were maintained through an experiment in all the cases.

Experiments were carried out with the pyrrhotine concentrate from the Ozernoye deposit. Iron sulphides were ground in a vibratory abrasive machine with steel cylinders under the oxidative atmosphere (air). The

ground material was subjected to the sieve analysis. The size of fractions was 74 μm in all the experiments. Specific surface area and granulometric composition of the disperse samples were not determined in the present work. The results of X-ray phase analysis showed the presence of relatively pure pyrite (FeS_2 98 %) and pyrrhotine ($\text{Fe}_{0.88}\text{S}$ 93.2 %) containing 1.5 % CuFeS_2 . Sulphides have the following elemental composition, mass %: pyrite – Fe 45.73, S 52.24, Zn 0.006, Cu 0.003, Pb 0.009, Si 0.42, O_2 0.48; pyrrhotine – Fe 56.97, S 37.33, Cu 0.52, Si 1.88, O_2 2.14.

The experiments were carried out in a closed glass reaction vessel 0.4 dm^3 in volume under continuous mixing with the overhead drive. A thermometer and sampler equipped with a fine porous ceramic filter were built into the cap of the reactor. Oxygen was admitted into the reaction pulp through a special tube under a pressure of $P_{\text{O}_2} = 1$ atm. Two glass-communicating cylinders filled in part with the saturated NaCl solution were used for this purpose. One of the cylinders was connected to the oxygen-containing balloon and the reaction vessel through a two-way cock, another one was left open. To prevent emission of nitrogen oxides into the atmosphere, the hydroseal system was used. It was connected through a buffer vessel with the gas withdrawal hole in the reactor cap. This gas admission and withdrawal unit allowed us to prevent overpressure in the reactor and to provide oxygen into the reaction zone as necessary. Temperature in the reaction zone was maintained automatically. In all the experiments, the mass of the weighed portion of sulphide was 2 g, the volume of sulphuric solution was 0.2 dm^3 .

Nitrous acid was obtained according to the reaction



by dosing sodium nitrite (0.16 ml of 10 % solution for each run) directly into the reaction pulp in definite time intervals (12 min). The regime of NaNO_2 solution supply was developed by us on the basis of preliminary investigation of the behaviour of nitrous acid under similar oxidative conditions; the regime allowed us to maintain HNO_2 concentration as close to the required one (0.001 M) as possible.

Analysis of solutions for iron content was carried out by means of chelatometric titration (determination error did not exceed 5 %) and atomic absorption spectroscopy using the generally accepted procedures [24]. X-ray analysis methods were used to determine macro- and microstructure of sulphides.

It is impossible to describe the experimental results within the entire time range using the existing kinetic models of leaching of a disperse material (for example, a shrinking sphere model, *etc.*). Total rate of pyrrhotine dissolution was determined by graphic differentiation (on the basis of slope ratios of tangent straight lines) of the initial regions of kinetic curves ($\tau \rightarrow 0$) when the surface area of the reacting particles has not yet undergone any substantial changes [25]. This method allows one to estimate leaching regime only at the initial stage and does not give any view of the process character, which can change substantially during the experiment.

The factor characterizing the rate of Fe^{2+} transformation into Fe^{3+} was accepted to be the moment of time when the concentrations of the reduced and oxidized forms of iron reached the same value (τ_{eq} is time within which equal concentrations were achieved). Determination of the kinetics of iron (II) oxidation using the proposed procedure is somewhat conventional because the concentration of Fe^{2+} in solution increases while pyrrhotine gets dissolved. Nevertheless, the dependencies of τ_{eq} on T and $C_{\text{H}_2\text{SO}_4}$ depict specific features of the oxidative process.

The procedure of calculating the main process parameters (activation energy, reaction orders with respect to the reagents) and statistical processing of the experimental results were the same and those generally accepted [26].

RESULTS AND DISCUSSION

The effect of nitrous acid on pyrrhotine leaching is shown in Fig. 1. Two stages are clearly distinguished on the kinetic curve: intensive initial dissolution (from 0 to 10 min) followed by slow dissolution (from 10 to 120 min). Deceleration of the process rate at the second

stage is likely to be due to the formation of a film of difficultly soluble compounds (oxidized iron with oxygen, elemental sulphur) on the reaction surface.

X-ray phase analysis of the solid residue of leaching showed that a part of sulphide sulphur is oxidized to the elemental form during pyrrhotine oxidation (the quantitative yield of $\alpha\text{-S}^0$ was not determined in the present work).

The presence of a small amount of HNO_2 in the solution (0.001 M) with $C_{\text{H}_2\text{SO}_4} = 1 \text{ M}$ and $T = 293 \text{ K}$ causes an insignificant (by 10 %, or by 0.1 in fractions of a unit) increase in the degree of iron extraction from the solid phase (α_{Fe}) at the second stage of the process (see Fig. 1).

Changes in the concentrations of the oxidized and reduced iron forms Fe^{3+} and Fe^{2+} during pyrrhotine treatment with $C_{\text{H}_2\text{SO}_4} = 0.25 \text{ M}$ and $T = 293 \text{ K}$ are shown in Fig. 2. A similar shape of kinetic curves was observed for all the experimental conditions. According to the results of chemical analysis, ferric ions are observed in all the experiments only at the second slow stage of sulphide leaching, after the degree of pyrrhotine treatment has almost reached the maximal value for the given conditions and after that changes only insignificantly. In the presence of nitrous acid (with $C_{\text{H}_2\text{SO}_4} = 1 \text{ M}$, $C_{\text{HNO}_2} = 0.001 \text{ M}$, $T = 293 \text{ K}$), the time of establishment of the equilibrium concentrations of Fe^{2+} and Fe^{3+} (τ_{eq}) is 113 min. Under the same conditions but without HNO_2 Fe^{2+} almost do not interact with

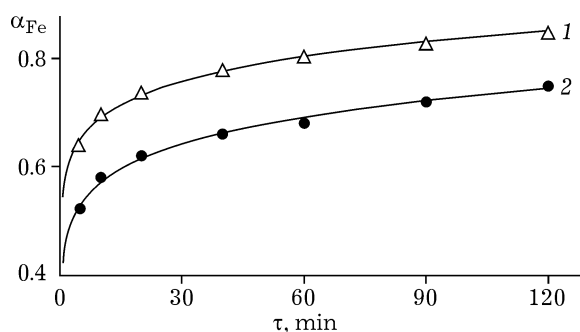


Fig. 1. Effect of nitrous acid on the kinetics of pyrrhotine leaching ($C_{\text{H}_2\text{SO}_4} = 1 \text{ M}$, $T = 293 \text{ K}$, $P_{\text{O}_2} = 1.01 \cdot 10^5 \text{ Pa}$, $\omega = 168 \text{ s}^{-1}$). C_{HNO_2} , M: 0.001 (1), 0 (2).

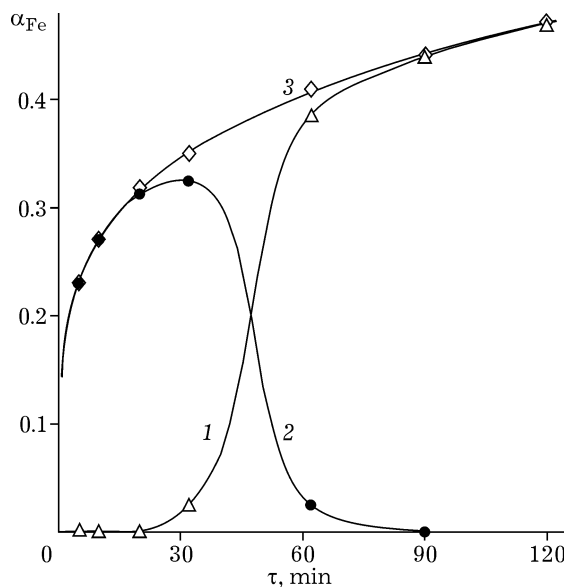
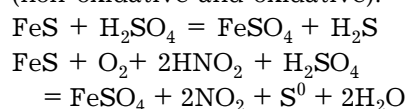


Fig. 2. Kinetic curves of changes in the concentrations of iron (II) and iron (III) during pyrrhotine leaching ($C_{\text{H}_2\text{SO}_4} = 0.25 \text{ M}$, $T = 293 \text{ K}$, $C_{\text{HNO}_2} = 0.001 \text{ M}$, $P_{\text{O}_2} = 1.01 \cdot 10^5 \text{ Pa}$, $\omega = 168 \text{ s}^{-1}$): 1 - Fe(II), 2 - Fe(III), 3 - Fe_{tot} .

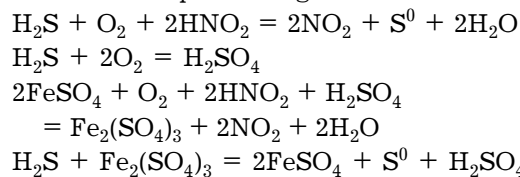
molecular O_2 within the time of experiment ($\tau = 120 \text{ min}$).

A two-stage character of the process is likely to be due to the change in leaching mechanism from non-oxidative dissolution regime with the formation of H_2S to the oxidative one.

Two constituents of the process can be formally distinguished: topochemical interaction of the sulphide with the components of solution (non-oxidative and oxidative):



and reactions proceeding in the solution volume:



The absence of iron (III) in the system at the initial stage of FeS dissolution is likely due to prevalence of the reductive process (10) over the oxidative reaction (9), which goes on until the main part of H_2S gets oxidized to elemental sulphur or sulphuric acid.

The catalytic action of oxygenated compounds of nitrogen (NO^+ , NO , NO_2 , which are the products of nitrous acid decomposition) on liquid-phase oxidation of hydrogen sulphide

with molecular oxygen under autoclave conditions was investigated in [7]. A new ion-radical mechanism of the catalysis of single-stage oxidation of H_2S into H_2SO_4 was proposed. It was shown that elemental sulphur is not an intermediate product of the reaction but it is formed as a result of recombination of radicals: $\text{HS}^\bullet + \text{HS}^\bullet = \text{H}_2\text{S} + \text{S}$. Chain termination manifests itself if the amount of the catalyst, nitrozonium ion NO^+ , is insufficient ($C_{\text{HNO}_3} = 0.23 \text{ M}$). The probability for such reactions to proceed in an oxidative system containing nitrous acid ($\text{HNO}_2 \leftrightarrow \text{NO}^+ + \text{OH}^-$) is very high.

For the dissolution of disperse material, the shape of kinetic curves is close to parabolic. A decrease in the process rate with time may be caused by different reasons: a decrease in the surface area of the solid phase during leaching (with dissolution of the narrow fraction of isometric particles), including complete dissolution of the fine fraction when a polydispersed material is used; changes in the mechanism of regime of leaching during the process, *etc.*

In the given work, the investigation was carried out with a polydispersed material containing the fine sulphide fraction. Complete dissolution of dust-like FeS particles should make a definite contribution into an increase in the intensity of leaching at the initial stage.

In addition, pyrrhotine grinding in the oxidative atmosphere (air) was likely to result in the formation of a substantial amount of oxygen-containing compounds of iron and sulphur (sulphates, oxides, hydroxides, and oxyhydroxides) (zone A). Dissolution of the oxidized layer also provides a substantial increase (by a factor of 9.5) in the extent of iron extraction into solution (from $550 \cdot 10^{-8}$ to $5200 \cdot 10^{-8} \text{ mol/m}^2$) for $C_{\text{HClO}_4} = 0.1 \text{ M}$, $T = 313 \text{ K}$ at the first stage of leaching (from 25 s to 7 min), which was observed in [11].

It should be noted that after special preparation of the pyrrhotine samples (washing off the fine fraction and removal of the oxidized layer by means of preliminary acidic etching) the kinetic curves of FeS leaching in acidic solutions (HCl) with various oxidizers (O_2 and Fe^{3+}) and under non-oxidative conditions are linear within a long time interval (100 h

[17]. In this case, the rates of pyrrhotine oxidation by oxygen and by ferric ions turn out to be higher in comparison with non-oxidative dissolution (by a factor of 8 and 70, respectively). For instance, for pH 2.75, FeS leaching rates are, $\text{mol}/(\text{m}^2 \text{ s})$: $5 \cdot 10^{-10}$ (non-oxidative leaching), $4 \cdot 10^{-9}$ (oxidation with O_2), $3.5 \cdot 10^{-8}$ (oxidation with Fe^{3+}). It is evident that the removal of the oxidized layer from the surface of reacting particles, as well as low initial acidity of solution (pH 2.75) have a substantial effect on the kinetics of pyrrhotine leaching. It is known that a definite pH value exists for each sulphide; above this specific value the formation of H_2S is extremely hindered [27]. The experimental activation energies of FeS treatment under oxidative conditions (47 to 63 kJ/mol for different pyrrhotine samples) are also characteristic for the kinetic regime.

Pyrrhotine dissolution at the oxidative stage (according to the data presented in [11, 12, 14]) causes the formation of a passive layer containing polysulphide sulphur ions and difficultly soluble compounds of Fe(III) with oxygen.

For leaching reactions complicated by the formation of the films of intermediate and final products, not all the indices provide unambiguous characterization of the region of process propagation. According to the theory of leaching kinetics, the dependence of reaction rate on the intensity of solution mixing is considered as the most reliable criterion of the process character [26]. An essential aspect is fulfillment of the condition of laminar streamline of the reaction surface with the leaching solution, which can be possible only if the rotating disc technique is used. In the case of dissolution of dispersed samples, different points of the sulphide particle surface are not equivalent to each other with respect to diffusion; the use of the dependence of process rate on mixing rate as a criterion becomes conditional to some extent. In addition, mutual friction of particles in a turbulent flow promotes partial renewal of the reaction surface; the degree of such a renewal is determined by the strength of the film, which also has an effect on the total leaching rate.

TABLE 1

Effect of the solution mixing intensity on the degree of iron extraction from pyrrhotine.

$C_{\text{H}_2\text{SO}_4} = 0.25 \text{ M}$, $T = 293 \text{ K}$, $C_{\text{HNO}_2} = 0.001 \text{ M}$,
 $P_{\text{O}_2} = 1.01 \cdot 10^5 \text{ Pa}$

Time (τ), min	Degree of iron extraction into solution (α) for ω , s^{-1}		
	58	100	168
5	0.15	0.19	0.23
10	0.19	0.24	0.28
20	0.24	0.28	0.32
40	0.27	0.31	0.36
60	0.31	0.35	0.40
90	0.37	0.40	0.44
120	0.39	0.42	0.47

Investigation of the effect of hydrodynamic conditions of leaching on the depth of pyrrhotine treatment was carried out with $C_{\text{H}_2\text{SO}_4} = 0.25 \text{ M}$, $T = 293 \text{ K}$. The intensity of mixing of the reaction mixture ω was varied within the range 58–168 s^{-1} . Experimental results are shown in Table 1. The dependence of process rate v on ω in the logarithmic form is expressed by equation $\ln v = 0.3 \ln \omega - 0.98$. Therefore, the intensity of FeS leaching is proportional to the velocity of mixer rotation to the power 0.30 ± 0.05 . In this case, the process under investigation is likely to go in agreement with the regularities of external diffusion or mixed kinetics. It should be noted that the obtained dependence characterizes the initial stage of non-oxidative dissolution of pyrrhotine (from 0 to 10 min). Mixing is also necessary to maintain pyrrhotine particles in suspended state, which to a definite extent provides equal accessibility of the solid phase surface. The mixer rotation velocity ω equal to 168 s^{-1} was chosen for all the subsequent experiments.

The effect of temperature on pyrrhotine leaching rate within the temperature range 293–333 K for $C_{\text{H}_2\text{SO}_4} = 0.25 \text{ M}$ is shown in Fig. 3, *a*. Temperature rise within the indicated range is accompanied by an increase in FeS dissolution degree from 0.41 to 0.80 within 1 h. The induction period preceding the stage of intensive dissolution of the sulphide is not exhibited under these experimental conditions. A temperature-related change in the rate of iron extraction into solution at the initial stage

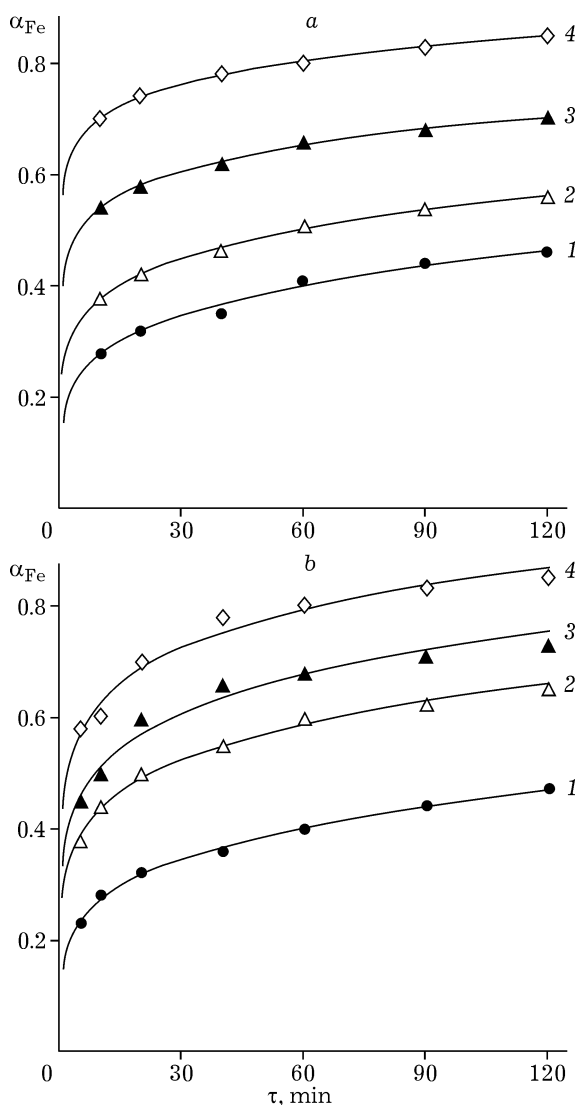


Fig. 3. Kinetic curves of pyrrhotine leaching at different temperatures (*a*) and concentrations of H_2SO_4 (*b*): *a* – T , K: 293 (1), 303 (2), 318 (3), 333 (4); $C_{\text{H}_2\text{SO}_4} = 0.25 \text{ M}$, $C_{\text{HNO}_2} = 0.001 \text{ M}$, $P_{\text{O}_2} = 1.01 \cdot 10^5 \text{ Pa}$, $\omega = 168 \text{ s}^{-1}$; *b* – $C_{\text{H}_2\text{SO}_4}$, M: 0.25 (1), 0.51 (2), 0.75 (3), 1.02 (4); $T = 293 \text{ K}$, $C_{\text{HNO}_2} = 0.001 \text{ M}$, $P_{\text{O}_2} = 1.01 \cdot 10^5 \text{ Pa}$, $\omega = 168 \text{ s}^{-1}$.

is described in the logarithmic form by equation $\ln v = -3249/T + 7.9$. The experimental activation energy of the process, calculated on the basis of the slope of Arrhenius curve, is $(27 \pm 4) \text{ kJ/mol}$, which slightly exceeds the upper limit characteristic of diffusion-controlled processes (20 kJ/mol) and corresponds to the mixed kinetics.

The temporal dependence of pyrrhotine leaching depth for different concentrations of H_2SO_4 in solution (from 0.25 to 1.02 M) and $T = 293 \text{ K}$ is shown in Fig. 3, *b*. The dependence of the process rate (for $\tau \rightarrow 0$) on the initial

concentration of H_2SO_4 is expressed in the logarithmic form by equation $\ln v = \ln C_{\text{H}_2\text{SO}_4} - 0.79$. So, the rate of pyrrhotine oxidation in sulphuric-nitrous solutions at the initial stage is proportional to $C_{\text{H}_2\text{SO}_4}$ to the power 1.0 ± 0.2 . According to the theory of leaching kinetics, the first order with respect to the dissolved reagent (H_2SO_4) does not contradict the criteria of the process running in the transient regime.

So, the obtained kinetic characteristics of pyrrhotine dissolution – rather large activation energy ((27 ± 4) kJ/mol), the first reaction order with respect to H_2SO_4 , and a weak dependence of the process rate on hydrodynamic conditions (to the power 0.30 ± 0.05) – allow assuming that FeS leaching at the initial stage obeys the regularities of mixed kinetics.

On the other hand, a large degree of iron extraction into solution at the stage of rapid dissolution (20 to 70 %) achieved within 10 min provides evidence of the high rate of the process at this stage, which is characteristic of the reaction of H_2S formation (which proceeds, according to the data of the majority of researchers, in the kinetic regime, $E_a \geq 40$ kJ/mol). It was shown in [28] that pyrrhotine dissolution in the acidic non-oxidative medium ($\text{pH} < 1$) takes place in the mixed regime ($E_a = 29$ kJ/mol). Similar low experimental activation energy (15 and 22.8 kJ/mol) were established for the oxidative leaching of pyrrhotine concentrate and for one of the 12 samples of natural pyrrhotines by ferric salts [17, 29]. A decrease in the experimental activation energy in our case may be due to the use of polydispersed material containing a substantial amount of the dust-like fraction with increased reactivity.

For a more detailed description of the mechanism of pyrrhotine treatment in the system $\text{H}_2\text{O} + \text{O}_2 + \text{HNO}_2 + \text{H}_2\text{SO}_4$, additional experimental investigation is necessary (monitoring of changes between different forms of sulphur – S^{2-} and SO_4^{2-} in solution during the process, determination of granulometric composition and specific area of disperse samples, etc.).

Investigation of the kinetic features of Fe^{2+} oxidation with molecular oxygen in sulphuric solutions containing nitrous acid was carried out in

parallel with studies of pyrrhotine treatment process.

Experimental results on the effect of solution acidity and temperature on the rate of changes in the relations between the oxidized form of iron (Fe^{3+}) and its reduced form (Fe^{2+}) during leaching (τ_{eq}) are presented in Table 2. One can see that at increase in the concentration of H_2SO_4 in solution from 0.2 to 1.02 M results in deceleration of the oxidative process and an increase in τ_{eq} by a factor of 2.4. A similar result has been already described in literature [30]. Analyzing rather numerous experimental data the authors concluded that an increase in the acid concentration causes braking of iron oxidation in sulphate media but accelerates it in chloride solutions. This fact is due to the higher reactivity of FeSO_4^+ complexes in comparison with Fe^{3+} . In chloride solutions, the FeCl^+ complex reacts with O_2 at a higher rate than Fe^{2+} , while the rates of FeCl^{2+} and Fe^{3+} interaction with O^{2-} are quite comparable with each other. The dependence of the logarithm of time within which equal concentrations of iron (II) and (III) are achieved on the logarithm of the initial H_2SO_4 concentration is expressed by equation $\log \tau_p = 0.6 \log C_{\text{H}_2\text{SO}_4} - 2.04$. Thus established order with respect to the acid is equal to 0.6 ± 0.1 .

An increase in temperature from 293 to 333 K accelerates the oxidative process and causes a 5.6-fold decrease in the time within which equal concentrations of Fe^{2+} and Fe^{3+} are achieved. Within the temperature range under investigation, an increase in iron (II) oxidation rate is described in Arrhenius coordinates by equation $\ln \tau_p = 4212/T - 9.6$. The experimental activation energy of this process is (35 ± 5) kJ/mol.

TABLE 2

Effect of H_2SO_4 concentration and temperature on the rate of iron (II) oxidation.
 $C_{\text{H}_2\text{SO}_4} = 1.02$ M, $C_{\text{HNO}_2} = 0.001$ M, $T = 293$ K,
 $P_{\text{O}_2} = 1.01 \cdot 10^5$ Pa

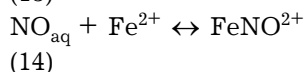
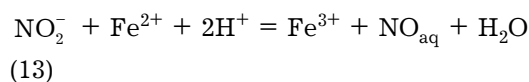
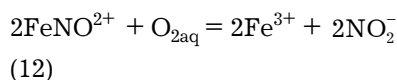
$C_{\text{H}_2\text{SO}_4}$, M	τ_{eq} , min	T , K	τ_{eq} , min
0.25	47	293	113
0.51	68	303	68
0.75	96	318	36
1.02	113	333	20

A fraction order of the reaction with respect to the dissolved reagent (0.6 ± 0.1), essential dependence of the reaction rate on temperature ($E_a = 35 \pm 5$ kJ/mol) allow us to assume that the oxidation of iron (II) in the sulphuric-nitrous medium proceeds in the transient or kinetic regime.

There are some publications dealing with the investigation of the effect of oxygen-containing compounds of nitrogen on the oxidation of sulphate, chloride and sulphate-chloride solutions of iron (II) [8, 20, 31, 32]. The detailed mechanism of catalysis has not been established yet. Oxidative system $\text{NO}_x\text{-H}_2\text{O}$ is very complicated. A number of compounds can exist in solution (with different quantitative characteristics) at the same time: NO , N_2O_3 , NO_2 , N_2O_4 , HNO_2 , NO_2^- , HNO_3 , NO_3^- , NO^+ , NO_2^+ , as well as the products of their association and hydration.

Within the low concentration region (<0.1 M), the activating action of nitrous acid exceeds the catalytic activity of HNO_3 , which is convincingly demonstrated in [20]. Oxidation of sulphuric solutions of iron (II) by molecular oxygen under the autoclave conditions ($C_{\text{H}_2\text{SO}_4} = 1$ M, $C_{\text{Fe}^{2+}} = 0.2$ M, $T = 393$ K, $P_{\text{O}_2} = 8.10 \cdot 10^5$ Pa) with the same activator concentration (0.004 M) proceeds with a 4.8 times higher intensity for NaNO_2 and only with 2 times higher intensity for KNO_3 .

Nitrates and nitrites are usually reduced in oxidative processes to NO , which also causes a substantial acceleration of the transition of Fe(II) into Fe(III) . The catalytic action of nitrogen oxide is believed by the authors of [31] to be connected with the formation of nitrozyl complex of iron (II) FeNO^{2+} , which possesses 20 times as high reactivity toward O_2 as that of aqua complexes of Fe^{2+} . A substantial contribution into the acceleration of the oxidative process is brought by the following reactions:



The authors of [31] note that complete oxidation of iron (II) by oxygen of the air occurs within 12 h in the solutions saturated with NO at $T = 295$ K, $C_{\text{Fe}^{2+}} = 0.05$ M, $C_{\text{HCl}} = 0.1$ M. In the absence of nitrogen oxide under similar experimental conditions, the degree of Fe^{2+} oxidation is only 5 %.

The authors of [9] study the kinetics of iron (II) oxidation in sulphate-chloride media in the presence of sodium nitrite within a broad temperature range (295–363 K) and pH interval (1.5–3.5). It was established experimentally that the addition of NaNO_2 ($C_{\text{NaNO}_2} = 0.025$ M) causes a substantial acceleration of iron (II) oxidation with oxygen of the air (in an open reactor) in acidic medium. The rate of Fe^{2+} transformation into Fe^{3+} linearly depends on the solution acidity. The experimental activation energy (59 kJ/mol) is higher than E_a value obtained by us ((35 ± 5) kJ/mol); the former value is characteristic of the processes running in the kinetic regime. The observed discrepancy is likely to be due to the presence of a solid phase (pyrrhotine) in our experiments; molecular oxygen gets activated on the surface of this solid phase; as a result, further transformations in the reaction mixture occur with lower energy consumption.

Investigation of the kinetics of oxidative leaching of pyrite in sulphuric solutions containing nitric acid ($C_{\text{H}_2\text{SO}_4} = 0.25\text{--}1.02$ M, $C_{\text{HNO}_2} = 0.001$ M, $T = 293\text{--}333$ K, $P_{\text{O}_2} = 1.01 \cdot 10^5$ Pa) showed that FeS_2 is almost undissolved under these oxidative conditions within the time of experiment (2 h).

According to the literature data, leaching of FeS_2 in various oxidative environments proceeds in the kinetic regime ($E_a > 50$ kJ/mol). The high degree of iron extraction from the solid phase ($\alpha_{\text{Fe}} > 0.8$) during FeS_2 leaching with HNO_2 solutions is achieved only under the autoclave conditions at elevated temperature and increased concentration of the acid ($T > 363$ K и $C_{\text{HNO}_3} > 2$ M) [7, 14, 16].

CONCLUSIONS

It was established in the investigation that the activating action of small amounts of nitrous acid is likely to be exhibited during

pyrrhotine leaching with sulphuric solutions under oxidative conditions (O_2) for the oxidation of $FeSO_4$ by molecular oxygen. It was shown experimentally that even in the case of small (0.001 M) concentration of HNO_2 and low temperature (293 K) the intensity of regeneration of the active agent of chemical weathering of hypergenesis zone – Fe^{3+} ions – increases substantially (the limiting stage of pyrite treatment, eq. (2)). Because of this, the $H_2O + O_2 + HNO_2 + H_2SO_4$ system may play a substantial part in oxidative processes in sulphide dumps.

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