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NATURAL PYRRHOTITE DISSOLUTION IN AQUEOUS SOLUTION

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ABSTRACT

The effects of some metal (II) ions on the natural pyrrhotite dissolution in hydrochloric acid solutions were studied. Our results suggest that the rate of pyrrhotite dissolution increases in the presence of Sn^{2+} *ion. Ions like* Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} *do not appear to have any effect on pyrrhotite dissolution in hydrochloric acid solutions. The magnitude of the activation energy (23.31 kJ* mol^{-1}*) is in agreement with a mechanism controlled by a diffusion process.*

RESUMO

Foram estudados os efeitos de vários íons metálicos (II) sobre a dissolução do mineral pirrohotita em soluções aquosas de ácido clorídrico. Os resultados experimentais indicam que a presença de íons de Sn^{2+} aumenta a dissolução deste mineral de ferro. Po outro lado, íons como Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} não tem nenhum efeito sobre a dissolução. A magnitude da energia de ativação (23.31 kJ mol^{-1}) está de acordo com um mecanismo controlado por processos de difusão.

KEYWORDS: pyrrhotite, nonoxidative dissolution, activation energy, iron minerals

INTRODUCTION

Pyrrhotite is an nonstoichiometric[1] compound, with the general formula $Fe_{1-x}S$, based on Fe(II) and S^{2-} ions. Values of x vary within the range $0<x<0.125$. The forms of the hexagonal pyrrhotite most commonly found in natural samples arise from vacancy ordering with numerous hexagonal and orthorhombic superstructures across Fe_9S_{10}, $Fe_{10}S_{11}$, - - - (or $Fe_{1-x}S$).

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There have been numerous studies on pyrrhotite dissolution in the literature[2-8]. Literature values for activation energy of pyrrhotite dissolution in acidic condition vary widely. On the basis of iron release, Janzen et al.[5] reported that the activation energies for pyrrhotite oxidation by oxygen and ferric iron ranged from 47 to 63 kJ mol^{-1}. Ingrham et al.[8] reported 29 kJ $\cdot mol^{-1}$ for dissolution in oxygen free condition at a pH less than one. This value is in the energy range for diffusion control. In addition to temperature, the crystal structure, trace metal content and specific surface area have also been reported to be controlling factors in the reaction kinetics of pyrrhotite dissolution.[9] Pyrrhotite dissolution mechanism and its dependence on aqueous solution composition is of fundamental importance in understanding mineral processing and the treatment of resulting waste mineral. Recovery of copper, nickel, gold and platinum often involves the processing of an iron sulfide rich matrix. Waste from the processing of sulfide ores are typically rich in pyrrhotite and other iron sulfides. These materials are a major contributor to acidic run off, commonly at pH 3 or lower.

The objective of this study is to compare the dissolution behavior of pyrrhotite as function of temperature and dissolved metal concentration. From these experiments we expect to improve the understanding of the mechanism of pyrrhotite dissolution in acidic solutions.

EXPERIMENTAL

Reagent grade tin (II) chloride ($SnCl_2 \cdot 2H_2O$), cobalt (II) chloride ($CoCl_2 \cdot 6H_2O$), nickel (II) chloride ($NiCl_2 \cdot 6H_2O$), cupric chloride ($CuCl_2 \cdot 2H_2O$) and zinc chloride ($ZnCl_2$) were obtained from Aldrich. The stock solutions of metal (II) chloride with a concentration of 0.1 mol L^{-1} were prepared by dissolving appropriate metal chloride in water containing 0.1 mol L^{-1} HCl. These solutions were diluted further with 0.1 mol L^{-1} HCl solution to obtain the required concentrations. The deoxygenated solutions were prepared by bubbling nitrogen for at least 2 hours.

The pyrrhotite was crushed and the particles ranging in size from 50 to 80 μm were recovered by sieving. This size fraction was used for the experiments.

Dissolution experiments were performed in a reaction vessel immersed in a controlled temperature bath. The vessel consisted of glass to minimize adsorption of pyrrhotite particles on the walls. The cap of the reaction vessel contained borings for sampling and for the stirrer. An agitation rate of 600 revolutions per minute (rpm) was chosen as a standard condition for the experiments. The experiments used 0.25 g pyrrhotite in 250 mL 0.1 mol L^{-1} HCl solutions with different metal (II) clorides.

The dissolution rate was monitored by determining the amount of total iron in solution. Periodically, 10 mL samples were extracted via a filter unit, to remove fine particles. The concentration of total Fe in solution was determined by Atomic Absorption Spectroscopy (AAS) with a Perkin Elmer AAS 3100 spectrometer. Reaction rates were measured experimentally by determining the slopes of concentration-time curves.

Identification of pyrrhotite by X-ray powder diffraction analysis was performed using an Inel Compteur Courbe X-ray diffractometer, with Co X-rays generated at 40 kV and 25 mA. The related X-ray diffractogram is shown in Figure 1; peak positions are consistent with reported ASTM data of hexagonal pyrrhotite. This sample composition was characterized by electron microprobe beam techniques (accelerating voltage of 25 kV and beam current 20.130 nA). The results gave a composition of $Fe_{1-0.11}S$. Trace elements content (Co, Zn and As) in the pyrrhotite matrix was below 0.32 %.

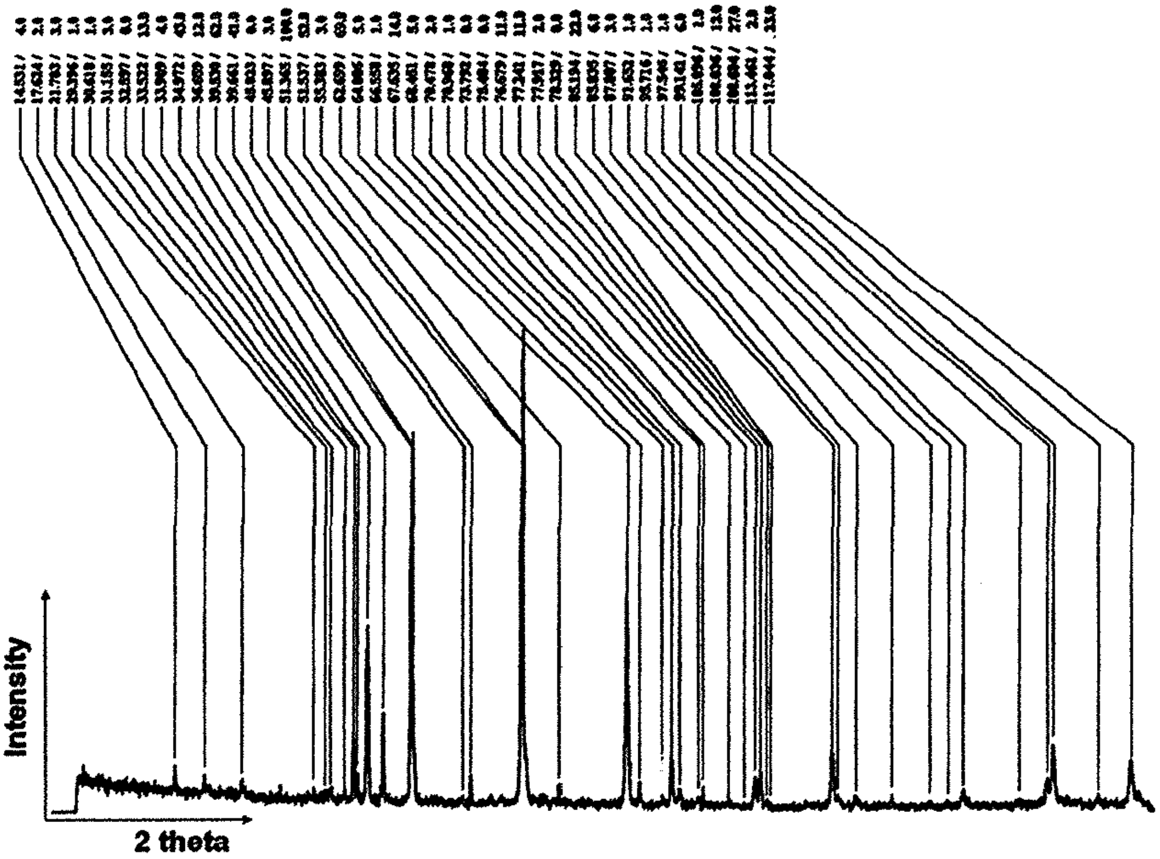

Figure 1. X-ray diffractogram of the pyrrhotite sample.

RESULTS AND DISCUSSION

Typical results of the dissolution experiments are shown in Figure 2. These results exhibit high iron fluxes during early times, with a decline to more consistent rates over short periods of time. The time over which rates were calculated for each experiment corresponds to intervals containing relatively consistent rate values. The initially high iron concentrations appear to be the result of preexperimental oxidation of the pyrrhotite surfaces that is difficult, if not impossible to avoid. This is the reason that the rate data was ignored prior to about 600 s into experimental runs.

The pyrrhotite dissolution rate in acidic conditions and in presence of Sn^{2+} ions is affected by changes in temperature (Table 1). A plot of the - ln Rate against 1/T yields a straight line in temperature range 30-65°C and an activation energy of 23.31 $kJ \cdot mol^{-1}$. This value of activation energy point to diffusion controlled mechanism. The activation energy is much closed from value obtained by Ingrahmm et al.[7] than others values from literature.

Table 1. Data for rate dependence on temperature for pyrrhotite dissolution in the presence of $SnCl_2$.

$[Sn^2]$ (mol L^{-1})	**T (°C)**	**d* (µm)**	**Rate (mol s^{-1} g^{-1})**
5×10^{-3}	65	50-80	1.733×10^{-7}
5×10^{-3}	50	50-80	1.218×10^{-7}
5×10^{-3}	40	50-80	1.017×10^{-7}
5×10^{-3}	30	50-80	6.402×10^{-8}
0	65	50-80	1.180×10^{-8}

*d = diameter of pyrrhotite particles.

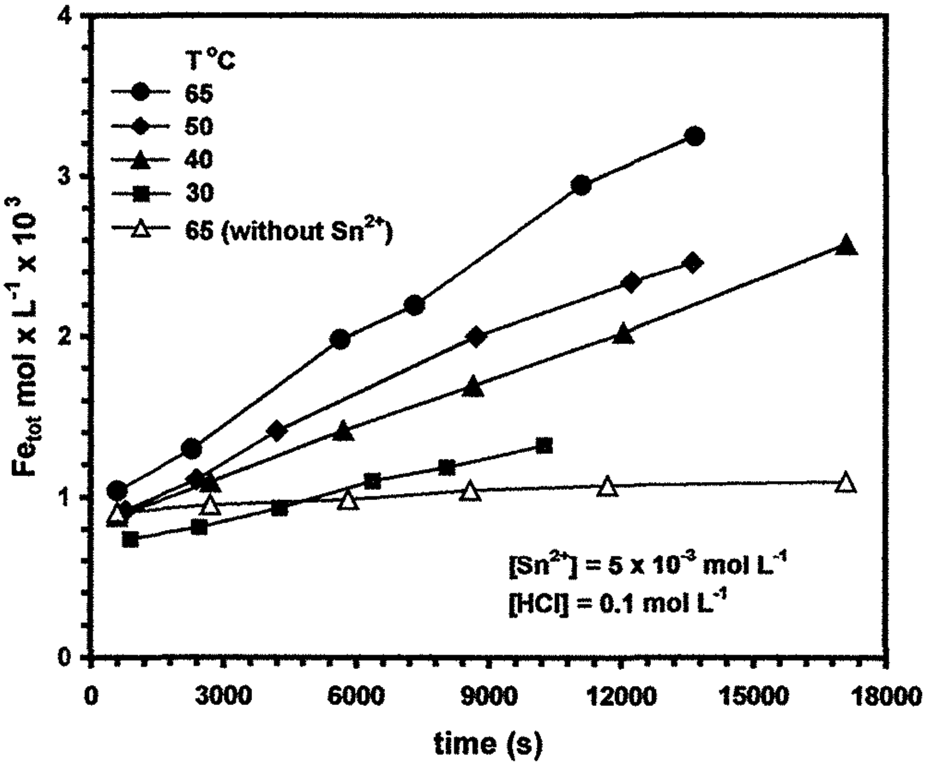

Figure 2. Effect of temperature on pyrrhotite dissolution in hydrochloric acid solution.

The addition of $SnCl_2$ with initial concentrations ranging from 2×10^{-4} to 5×10^{-3} mol L^{-1} causes an asympthotical increase of the pyrrhotite dissolution rate by a factor ~ 8 (Figure 3).

The release rates of iron indicate that the presence of the Sn^{2+} ions influences the dissolution of natural pyrrhotite. The results show that the Sn^{2+} is indeed able to increase the dissolution rate of pyrrhotite. The conclusion seems therefore obvious that the observed increase of dissolution rate of pyrrhotite in presence of Sn^{2+} is related to the reduction of ferric iron by Sn^{2+}.

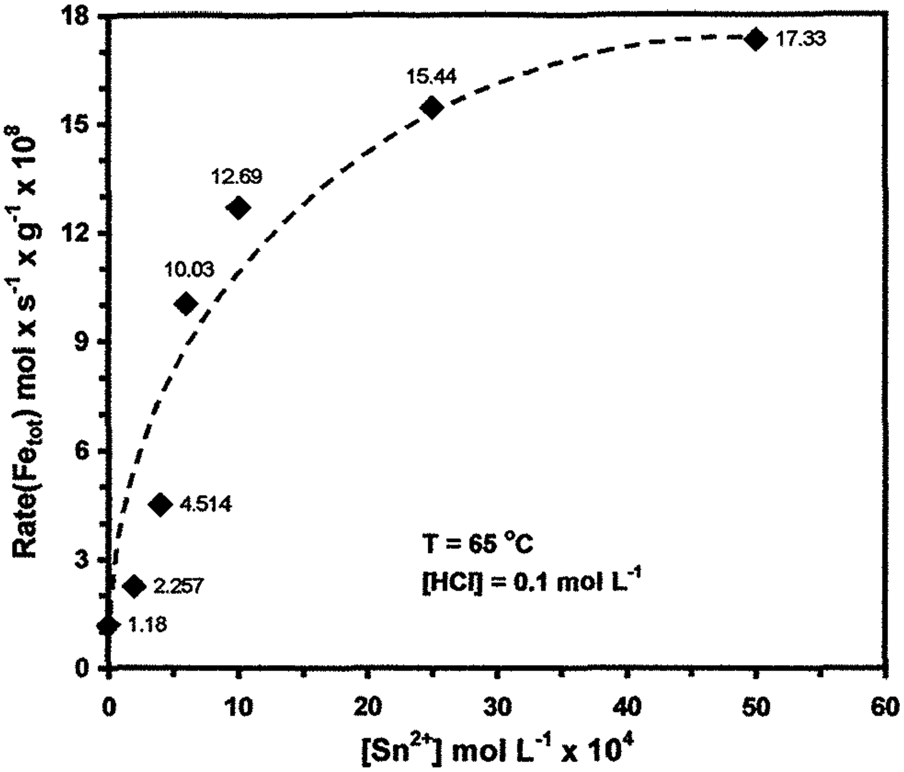

Figure 3. Rate for the dissolution of natural pyrrhotite in acidic solutions at various initial concentration of Sn^{2+}.

In order to understand this pattern one has to recapitulate the mechanism for dissolution of pyrrhotite proposed in the literature. Unlike pyrite, pyrrhotite can dissolve both oxidatively and nonoxidatively. Any oxidative dissolution which occurs increases the iron deficiency of the pyrrhotite structure and thus decreases the probability of H_2S production and rapid release of Fe.[4]

It is generally accepted that ferric iron has an oxidant effect on pyrrhotite. Fe^{3+} may be directly released into solution from the pyrrhotite surface during the first stage of dissolution. Pratt et al.[10] and Mycroft et al.[11] have shown that when exposed to air, pyrrhotite surface oxidized rapidly to form a superficial layer of iron (III) oxyhydroxides, and later iron sulfate.

Partial oxidation of pyrrhotite by ferric iron may produce either elemental sulfur or increasingly sulfur-rich pyrrhotite:

$$Fe_{1-x}S + 2yFe^{3+} \rightarrow 3yFe^{2+} + Fe_{1-x-y}S \qquad (1)$$

Nonoxidative dissolution can occur in acidic conditions whenever there is exposed S^{2-} on the surface of a iron sulfide. The reaction which occurs is

$$FeS + 2H^{+} \rightarrow Fe^{2+} + H_2S \qquad (2)$$

Under these conditions the extra sulfur rich layer on the pyrrhotite is absent or is thin, and dissolution of pyrrhotite will be more rapid.

Any interference of Sn^{2+} on the pyrrhotite dissolution must be related to this model. In the presence of the Sn^{2+}, which reduce Fe^{3+}, the concentration of the iron species in solution and at the pyrrhotite surface will be altered. The reduction of the ferric iron will affect the oxidation of pyrrhotite, which is equivalent to avoid the extra sulfur rich layer formation on the pyrrhotite surface (Eq. 1). The activation energy value suggests that the rate-controlling step is a diffusive process rather than chemical reaction. The $Fe_{1-0.11}S$ can be considered like sulfur rich iron sulfide. Therefore, it is possible that in this experiment the release of Fe into solution may be influenced by the diffusion rate of iron through pyrrhotite.

Nicol and Scott[12] showed that nonstoichiometric iron-deficient sulfides dissolved spontaneously via nonoxidative dissolution once reduction to stoichiometric FeS had occurred via cathodic potential. The results shown here are in agreement with their observations.

The effect of some metals (Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) on the pyrrhotite dissolution rate was also examined. The experiments were conducted in 0.1 mol L^{-1} HCl solutions with 5×10^{-3} mol L^{-1} metal (II) concentration at 65°C. Runs made in these solutions showed little or no effect on the pyrrhotite dissolution rates (Table 2). The addition of these metals ions to the aqueous solution will not result in a change in the iron species present in solution and on the pyrrhotite surface. Addition of Sn^{2+} ions to a pyrrhotite suspension may results in the conversion of a ferric iron to ferrous iron.

Table 2. Effect of metals on the dissolution rates of natural pyrrhotite in 0.1 mol L^{-1} HCl at 65 °C.

Metal	$[M^{2+}]$ mol L^{-1}	Rate (mol s^{-1} g^{-1})
Ni^{2+}	5×10^{-3}	2.017×10^{-8}
Co^{2+}	5×10^{-3}	1.094×10^{-8}
Cu^{2+}	5×10^{-3}	3.952×10^{-8}
Zn^{2+}	5×10^{-3}	2.108×10^{-8}

As can be seen, attempts to fit our experimental results with the general mechanism remain somewhat speculative. Since laboratory work gave quite contrasting results on the rates of the oxidation of pyrrhotite with ferric iron,[5] the proposed mechanism needs further experimental confirmation. Future studies should therefore be designed to explain the interaction between the surface states and the solution composition.

CONCLUSIONS

The results of pyrrhotite dissolution experiments presented here indicate that the presence of Sn^{2+} affects its dissolution behaviour. The dissolution rates increased in the presence of Sn^{2+} ions in solution. This implies that in presence of reducing species the rate of pyrrhotite dissolution can be enhanced. On the other hand, ions like Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} do not appear to have any effect on pyrrhotite dissolution in hydrochloric acid solutions.

The activation energy (23.31 kJ·mol^{-1}) points to a diffusion controlled mechanism.

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