

Technical Note

Pyrite oxidation by hydrogen peroxide in phosphoric acid solutions

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Received 18 February 2003; accepted 20 July 2004

ABSTRACT

Oxidation characteristics of natural pyrite were investigated in phosphoric acid solutions. Using hydrogen peroxide as an oxidant, the effect of particle size, reaction temperature, and hydrogen peroxide concentration were examined. The oxidation process can be described by the heterogeneous kinetic model in which the surface decomposition reaction is the rate-determining step. An activation energy of 49kJ/mol for pyrite oxidation is estimated. It was found that the smaller the particle size or the higher the reaction temperature, the faster the oxidation proceeds, as anticipated. © 2004 SDU. All rights reserved.

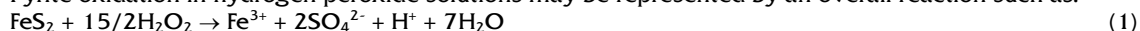
Keywords: Pyrite; Hydrogen peroxide; Oxidation; Surface reactivity

1. INTRODUCTION

Pyrite is a major sulfur-bearing mineral in various gold ores and in coal. The current use of cyanide leaching of gold ores is undesirable from environmental and economical perspectives. In recent years, cyanidation method has been abandoned in many regions because of several disadvantages. Cyanide solutions have an acute toxicity and create disposal problems, while the leaching rates are low. Where the method is still in use, the treatment of aqueous effluents resulting from cyanidation process is one of the main problems (Carrillo-Pedroza and Soria-Aguilar, 2001; Akcil, 2002; Dabrowski *et al.*, 2002). Additionally, direct cyanidation of gold ores is incomplete because a large portion of the fine gold remains within the host mineral and never comes in contact with the cyanide solution.

Hydrogen peroxide leaching processes are increasingly studied for gold recovery from various gold ores that cannot be processed economically by conventional methods (Groenewald, 1976; Sampaio *et al.*, 1997).

Pyrite oxidation in hydrogen peroxide solutions may be represented by an overall reaction such as:



Reaction (1) describes the overall stoichiometry of pyrite oxidation to sulfate by hydrogen peroxide, but it does not describe the individual steps involved, because of the large number of electrons that is transferred. Since electron transfer reactions are normally limited to one or, at most, two electrons, the overall oxidation of pyrite by H_2O_2 is composed of a number of intermediate steps even though only one elementary reaction is rate limiting under a given set of conditions.

According to the findings by McKibben and Barnes (1986) and Dimitrijevic *et al.* (1996 and 1999), the rate of pyrite oxidation by hydrogen peroxide is negligibly dependent on the proton concentration at low values of pH, and the ferric iron and sulfate are the only detectable reaction products. Values of activation energy reported in literature, from a variety of experimental conditions, vary from 33.5 to 68kJ/mol (Dimitrijevic *et al.*, 1999). These values are high enough to support a chemical control of rate limiting step.

This paper describes the oxidation of pyrite (FeS_2) by hydrogen peroxide in 0.6mol/l phosphoric acid solution. This medium was selected in order to avoid the oxidative action of ferric iron (King and Davidson, 1958; Sasaki *et al.*, 1995), resulted from oxidative dissolution of pyrite, and the decomposition of hydrogen peroxide (Negoiu, 1972). Rate data for the oxidation of pyrite are collected and analyzed to determine the effects of variables such as hydrogen peroxide concentration, temperature, and particle size on the reaction rate.

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2. EXPERIMENTAL

The samples used in this study were large crystals of natural pyrite, averaging 2cm in diameter, collected from Baia-Mare, Romania. X-ray diffraction (XRD) showed the material to be cubic pyrite. No other phase could be detected. The crystals were ground, classified in three fractions and treated with a hot solution of 3mol/l HCl (Ciminelli and Osseo-Asare, 1995) in order to produce very clean pyrite surface.

Phosphoric acid, 0.6mol/l H_3PO_4 , was used in all experiments. The dissolution experiments were done in a 2000ml, stirred, air-tight glass reactor held at a constant temperature by use of a thermostatically controlled bath. Solutions were stirred at an agitation rate of 600rpm, with an overhead stirrer. The cap of the reaction vessel contained ports for inlet, outlet of nitrogen, and for sampling. At the start of a run, 0.60g pyrite was added to 1000ml solution that had been previously thermally equilibrated to the desired temperature.

The hydrogen peroxide solutions were prepared by adding the necessary volume of reagent grade H_2O_2 (33%) solution to deoxygenated 0.6mol/l H_3PO_4 solutions immediately before a run started. The oxygen-free water was prepared by bubbling nitrogen through the high purity water, which was obtained from Millipore Milli-Q system, for at least 5h. After adding the solution to the reactor, oxygen free conditions were maintained by passing nitrogen gas over the solution.

The dissolution of pyrite during the leaching experiments was followed by monitoring the concentration of dissolved iron present in solution as a function of time. In the time intervals, 5ml liquid sample was taken from reaction solution with a syringe connected to a $0.45\mu m$ filter. The concentration of the dissolved Fe in solution was determined by atomic adsorption spectrometry (AAS). Reaction rates were calculated by the differential method (*i.e.*, initial rate). Oxidation rates (R) were easily calculated by determining the slopes of dissolved iron (mol) vs. time (min) curves, because the instantaneous oxidation rates were maintained constant with time.

The solid residues after completing the leaching tests were separated from the liquids and stored in an evacuated desiccator until were examined for surface features. The examination was performed with Jeol JSM-6400 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Pyrite oxidation rates by hydrogen peroxide were measured at various reaction conditions. In order to calculate oxidation rates, the dissolved iron (mol) was plotted against the dissolution time (min). Leaching conditions and oxidation rates obtained for each experiment are listed in Table 1.

Table 1
Experimental results for pyrite oxidation by hydrogen peroxide

Temperature °C	Initial [H_2O_2] mol/l	Particle size range μm	Rate of oxidationx 10^7 mol/min
30	0.1	80-100	2.005
30	0.1	50-80	2.525
30	0.1	10-50	5.837
35	0.1	80-100	2.381
40	0.1	80-100	2.865
45	0.1	80-100	5.228
30	0.05	50-80	1.307
30	0.12	50-80	2.686
30	0.15	50-80	2.883
30	0.2	50-80	3.008

3.1. Effect of particle size

A series of experimental runs was done in order to evaluate the effect of pyrite particle size on the reaction rate. The reactant pyrite was divided into three size fractions by sieving: 100-80 μm , 80-50 μm , and 50-10 μm . The initial hydrogen peroxide concentration (0.1mol/l), solid to liquid ratio (0.6g of solid per 1000ml of solution), and reaction temperature (30°C) were kept constant. The results obtained are presented in Fig. 1.

The data from this figure indicate the significant increase obtained in the oxidation rates of pyrite with the decrease of particle size. Then, the oxidation rates were plotted against the reciprocal of the initial diameter, d_0 . This plot is linear and passes through the origin (Fig. 2). Because the limit of $1/d_0$ is zero as d_0 approaches to infinity (*i.e.*, when the specific surface area is zero), it is expected that any plot relating $1/d_0$ to the experimental rate should pass through the origin (Nicholson *et al.*, 1990).

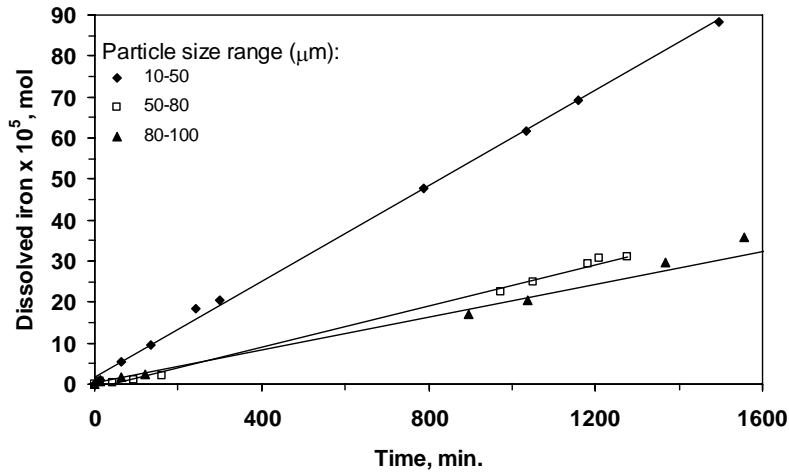


Figure 1. Effect of particle size on the oxidative dissolution of pyrite

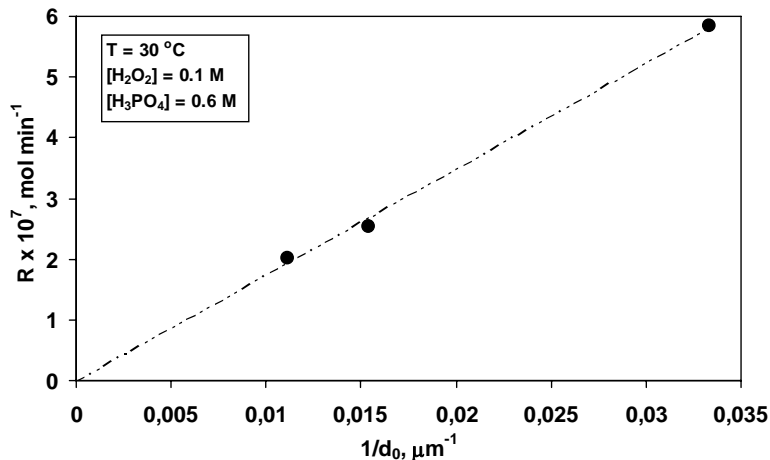


Figure 2. Rate of pyrite dissolution (mol/min) vs. the reciprocal of particle size (μm^{-1})

The foregoing results have demonstrated that the initial particle size is a notable factor for pyrite leaching by H_2O_2 . More importantly, the linear dependence of the oxidation rate vs. $1/d_0$ suggests that the rate-controlling reaction is a surface chemical reaction.

3.2. Effect of temperature

The experiments were performed in the 30-45°C temperature range at initial hydrogen peroxide and phosphoric acid concentrations of 0.1 and 0.6mol/l. In each oxidation experiment, soluble iron concentration was monitored in order to quantify the rate of pyrite oxidation. The results obtained are shown in Fig. 3. It is of interest to note that, the oxidation profiles for pyrite oxidation retained a linear dependence at the four temperatures studied. This fact can be attributed to the stability of hydrogen peroxide in phosphoric medium. H_3PO_4 stabilizes H_2O_2 by either precipitating (effect not observed in these experiments) or sequestering the ionic Fe species, and acts as an effective stabilizer.

In general and according to the results in Fig. 3 and Table 1 the oxidative dissolution of pyrite by hydrogen peroxide in acidic media is characterized by the fact that rate of oxidation increases with temperature. The quantitative expression of the temperature influence can be obtained by the Arrhenius relation represented in Fig. 4 for the applied 0.1mol/l initial concentration of hydrogen peroxide. The slope of the line in Fig. 4 yields an activation energy of 49kJ/mol which is consistent with published data.

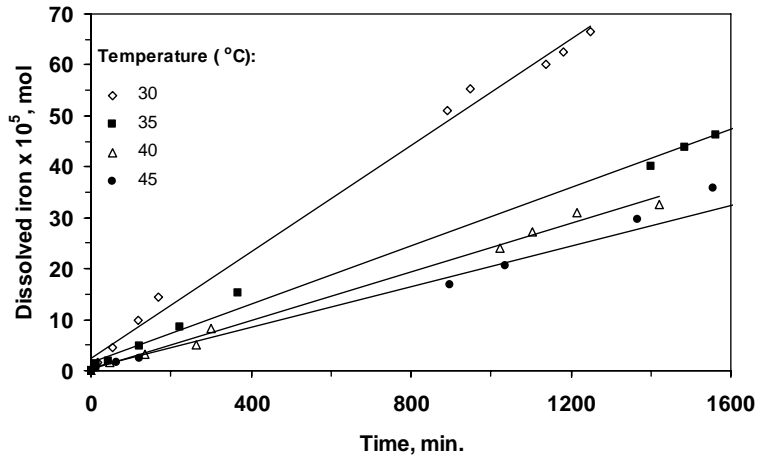


Figure 3. Effect of temperature on pyrite oxidation in phosphoric acid solutions at a hydrogen peroxide concentration of 0.1 mol/l

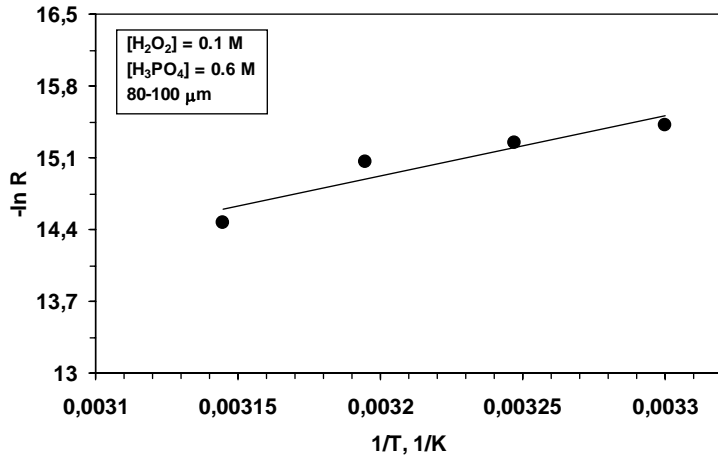


Figure 4. Arrhenius plot for pyrite leaching in 0.1 mol/l H₂O₂

The value of activation energy found in this investigation suggests that the rate is controlled by a surface chemical reaction because diffusion-controlled heterogeneous reactions tend to have Arrhenius activation energies in the range 12-27 kJ/mol (*i.e.*, 2.8-6.5 kcal/mol; Rickard, 1975). This occurs because the chemical rate of reaction increases substantially with temperature while the diffusion coefficient increases only slightly with an increase of temperature.

3.3. Effect of hydrogen peroxide concentration

The effect of hydrogen peroxide concentration on the leaching of pyrite in 0.6 mol/l H₃PO₄ solutions, when the particle size range was 50-80 μm and temperature was 30°C, is shown in Fig. 5. The concentration of dissolved iron increases when hydrogen peroxide concentration increases from 0.05 mol/l to 0.2 mol/l. After 0.12 mol/l, this influence is not so marked.

Fig. 6 shows the effect of hydrogen peroxide concentration on pyrite oxidation rates. The pyrite oxidation rates increased with increase in the hydrogen peroxide concentration. At a given temperature, the pyrite oxidative dissolution rates would no longer increase with increase in the hydrogen peroxide concentration beyond a certain value, as shown in Fig. 6. In the absence of hydrogen peroxide, no pyrite dissolution was observed.

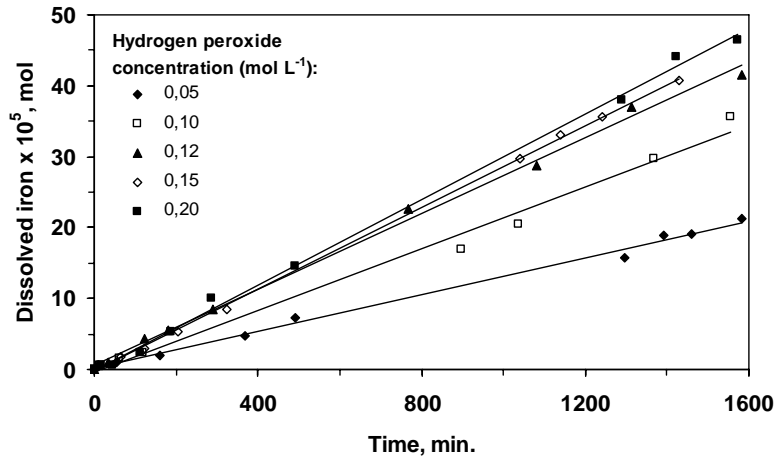


Figure 5. Effect of varying initial concentration of hydrogen peroxide on pyrite oxidation at 30°C

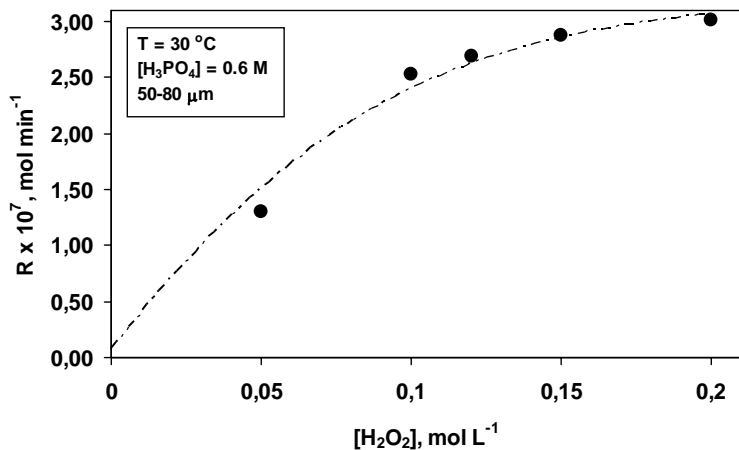


Figure 6. Effect of hydrogen peroxide concentration on the pyrite oxidation rates

A reaction order of 0.62 with respect to hydrogen peroxide concentration was obtained, when the $-\log(R)$ vs. $-\log[H_2O_2]$ plot (not shown) was constructed. However, as the initial concentration of oxidant increased, the dependence on hydrogen peroxide concentration significantly decreased.

3.4. Surface morphology of reacted pyrite

Since the morphology of reacted particles reveal the oxidation model, the leached pyrite samples were analyzed by scanning electron microscopy (SEM). The obtained images (Fig. 7) indicate that oxidant attack was non-uniform, occurring at specific locations of high excess surface energy (cracks, edges, and fractures of solids).

Inspection of particle faces revealed the presence of pits of various sizes beneath the surfaces (Fig. 7d). However, as seen in the SEM micrographs, there are significant numbers of grooves (with various sizes), which indicate the distribution of active sites of pyrite surface. These images are in good agreement with those obtained by McKibben and Barnes (1986) (Figs. 13c and 13d in their papers).

3.5. Suggested reaction mechanism

Fractional orders of reaction for heterogeneous process, such as aqueous pyrite oxidation by H_2O_2 , are often viewed as evidence for adsorption of reactants or desorption of products as rate limiting (Lasaga, 1981). This dependence is expected if the hydrogen peroxide adsorbs onto two sites. The hydrogen peroxide shows two centers with the same reactivity (each OH can adsorb onto a site) and so this

adsorption behavior is reasonable. Thus, the sorption of H_2O_2 as initial step for oxidation of pyrite can be represented as:



The second step, the rate determining step, is the decomposition of hydrogen peroxide into two entities. This process is expected to create very reactive intermediates such as HO radicals, which oxidize the pyrite surface.

Adsorption mechanism has been used to explain rate control phenomena for pyrite oxidation by hydrogen peroxide (McKibben and Barnes, 1986; Antonijevic *et al.*, 1997). The proposed adsorption mechanism is consistent with the rate being determined by the decomposition of H_2O_2 adsorbed at the pyrite surface.

The decrease in the reaction order at high oxidant concentrations, the dependence of oxidation rates on the reciprocal of the initial diameter, d_0 , the value of activation energy and the observed preferred reaction at high energy sites are also consistent with an adsorption-decomposition mechanism.

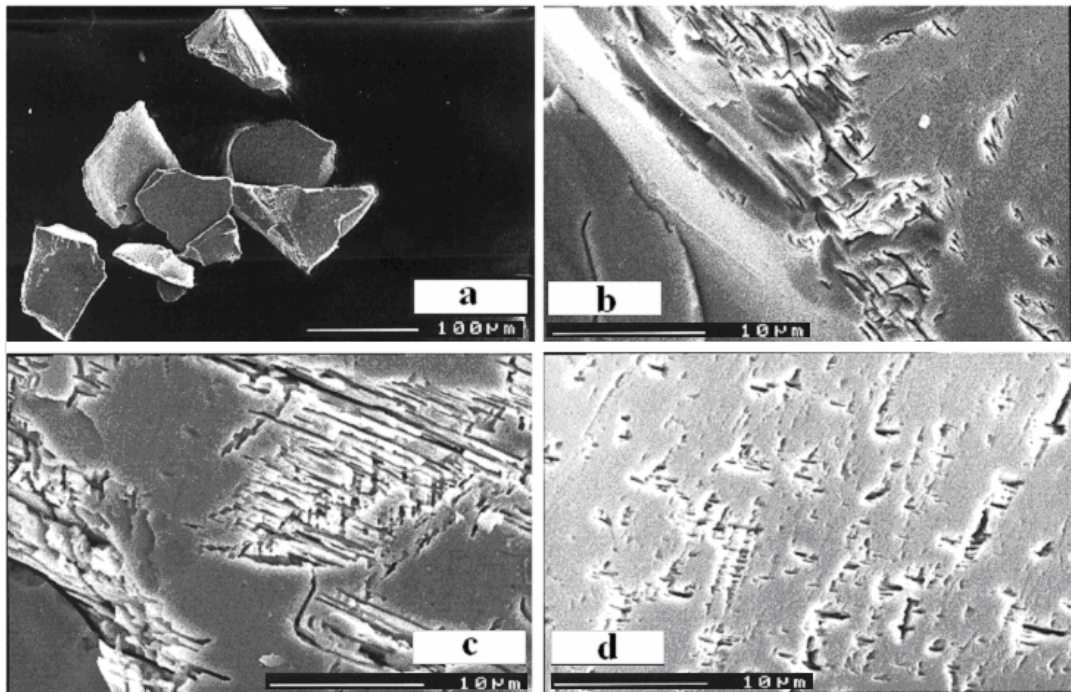


Figure 7. Micrographs of pyrite samples reacted at different conditions: (a) Low magnification SEM image for pyrite sample (50-80 μ m) after dissolution in 0.1mol/l H_2O_2 solution, at 30°C. (b) As in figure (a) but high magnification. (c) A pyrite surface (80-100 μ m) after dissolution in 0.1mol/l H_2O_2 solution, at 45°C. (d) A pyrite surface (80-100 μ m) after dissolution in 0.1mol/l H_2O_2 solution, at 30°C

4. CONCLUSIONS

Several different aspects of pyrite oxidation by H_2O_2 in H_3PO_4 solutions were evaluated in this study. From the results obtained, the following conclusion can be made. The pyrite oxidation is influenced by the size of particles. The smaller the particle size, the faster the leaching proceeds. The oxidation rate of pyrite is also temperature dependent. The activation energy over the range 30-45°C is approximately 49kJ/mol. It was also shown that the rate-dependence on hydrogen peroxide concentration is non-linear. The rate-controlling step during oxidation by hydrogen peroxide is the decomposition of H_2O_2 adsorbed at the pyrite surface. SEM micrographs indicate that oxidation is occurred on surface locations with high excess energy such as particle edges, fractures, and corners.

ACKNOWLEDGEMENTS

Support of this work by the National University Research Council Grant No. 33451/23C/2 is gratefully acknowledged.

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