

Kinetics of Aqueous Pyrite Oxidation by Potassium Dichromate - An Experimental Study

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The kinetics of pyrite oxidation in perchloric acid solutions were investigated at temperatures ranging from 30°C to 40°C, potassium dichromate concentration from 0.001 to 0.05 mol L⁻¹, particle size fractions from 50 to 150 μm and pH values down to 2.83. The rate of the oxidation reaction is described by the following expression:

$$r = bkS^{0.51}[K_2Cr_2O_7]^{0.64}[H^+]^{0.22}$$

where S is the surface area of reacting solid, r represents the amount of Fe release in solution per unit surface area per unit time, b is a stoichiometric factor, k is the rate constant, and [K₂Cr₂O₇] and [H⁺] are the potassium dichromate and hydrogen ion concentrations respectively. The magnitude of the activation energy (74.83 kJ mol⁻¹) and the direct relationship between the rate constant and initial pyrite specific surface area are in agreement with a mechanism controlled by a chemical reaction. Trace element content had no statistically significant effect on the oxidation rate.

Key Words: pyrite oxidation, potassium dichromate, activation energy, reaction order, trace element content

Introduction

The decomposition of pyrite (FeS₂) constitutes an essential step in many mineral, metal, and coal-processing schemes. Although the oxidation of pyrite by oxygen and ferric iron has been studied in detail¹⁻⁴, limited information is available on the reaction kinetics by other oxidants (*e.g.* H₂O₂, KMnO₄ or K₂Cr₂O₇), and rate parameters have not been established. There is also a scarcity of detailed studies on the effect of different trace metal content of pyrite on the oxidation rates.

Pyrite has a structure based on a face-centered cubic array of ions with an NaCl-type structure. Nickel, cobalt, copper and other metals were found to occur in the pyrite structure as trace elements substituting for iron⁵. The trace metal content and the specific surface area have been reported to be a controlling factor in the reactions kinetics of pyrite^{2,6}.

The separation of pyrite in flotation in the mining industry is entirely based on differences in the surfaces properties among sulfide minerals. The specific sorption capacities of flotation collectors can be

influenced by the oxidation of pyrite surface in acidic systems with oxidants like Fe(III), H₂O₂, KMnO₄ etc.⁷.

The objectives of the current study were to determine the role of K₂Cr₂O₇ in pyrite oxidation reaction and clarify the differences in oxidation behavior among pyrite samples of different trace metal content. The effects of variables such as oxidant concentration, pH, temperature and particle size on rate of oxidation by K₂Cr₂O₇ were quantified and the mechanism of pyrite oxidation examined.

Experimental

The measurements were performed in a 2 L glass reaction vessel immersed in a controlled-temperature bath. The lid of the reaction vessel contained ports for the stirrer and for sampling. Crystalline pyrite samples were obtained from several locations across Romania. This pyrite was characterized by X-ray diffraction. Trace elements in the pyrite matrix were determined for 6 pyrite samples by electron microprobe analysis. The analytical results appear in Table 1. Samples were crushed in a jaw crusher and classified into various size fractions by screening. The material below 150 μm, was further separated into three fractions: 50-80 μm, 80-100 μm, and 100-150 μm and treated with a hot solution of 3 M HCl (following the methods outlined in Ciminelli and Osseo-Assare⁸) in order to produce a very clean pyrite surface.

Table 1. Trace element content of the 6 pyrite samples as determined by electron microprobe.

Sample	Co (%)	Ni (%)	Cu (%)	Zn (%)	As (%)	Total trace element (%)
Py - 1	0.01	0.03	0.02	0.00	0.13	0.19
Py - 2	0.03	0.04	0.00	0.00	0.15	0.22
Py - 3	0.03	0.00	0.01	0.02	0.10	0.16
Py - 4	0.02	0.01	0.01	0.00	0.10	0.14
Py - 5	0.04	0.01	0.00	0.00	0.16	0.21
Py - 6	0.02	0.00	0.02	0.00	0.17	0.21

K₂Cr₂O₇ run solutions were prepared by mixing aliquots of an acidified 0.2 M K₂Cr₂O₇ solution into oxygen-free distilled water and adjusting to a final pH (< 2.84) using reagent grade HClO₄. The pH was checked prior to each experiment.

Kinetic measurements

Approximately 5 g of pyrite was used for each experiment. The oxidation rate was monitored by determining the amount of soluble iron in solution. Periodically, 10 mL samples were extracted via a filter unit, to remove fine particles. Total Fe was determined by atomic absorption spectrometry (AAS) using a Perkin-Elmer AAS 3100 spectrophotometer. Reacted pyrite was observed by scanning electron microscope (SEM) Jeol JSM 6400.

Determination of dissolution rate

Dissolution rates were determined by fitting the experimental amount of Fe release in solution per unit surface area of pyrite to a second-order polynomial regression equation:

$$\{\text{Fe}\} = \alpha + \beta t + \chi t^2 \quad (1)$$

The coefficient β represents the value of dissolution rate (r), and is given by the derivative of $\{Fe\}$, with respect to time; *i.e.*,

$$r = d\{Fe\}/dt = \beta \quad (2)$$

The second-degree polynomial (Eq. 1) fit the experimental data well; coefficients of correlation above 0.99 characterized the majority of the data.

Results and Discussion

The rate of heterogeneous reaction between a solid and an aqueous species A can be expressed by the following equation⁸:

$$(-1/S)(dN/dt) = kb[A]^a \quad (3)$$

where S is the surface area of the reacting solid, dN/dt represents the moles of reacting solid consumed per unit time, b is a stoichiometric factor, k is the rate constant, [A] is the concentration of reactant, and a is the reaction order.

Equation (3) was modified to provide a relationship between oxidation rate, r , defined in terms of amount of Fe release in solution per unit surface area of pyrite, $\{Fe\}$, the potassium dichromate concentration, and hydrogen ion concentration. If the rate is dependent on the fractional power of the surface area, the equation must be corrected for the surface area dependence.

Then

$$r = d\{Fe\}/dt = bkS^s [K_2Cr_2O_7]^n [H^+]^m \quad (4)$$

where $[K_2Cr_2O_7]$, and $[H^+]$ are the potassium dichromate concentration and hydrogen ion concentration respectively, and s, n and m are the orders of reaction with respect to surface area, potassium dichromate, and hydrogen ion, respectively.

The results of experimental oxidation of pyrite by potassium dichromate are listed in Table 2.

Effect of potassium dichromate concentration

The results of a series of runs conducted at different potassium dichromate concentrations are plotted in Figure 1. These measurements were performed in de-aerated solutions at $pH = 1$ and $30^\circ C$ with potassium dichromate concentrations in the range of 0.001 to 0.05 mol L^{-1} . The rate decreases with decreasing potassium dichromate concentration.

The reaction order with respect to potassium permanganate was estimated from the slope of $-\log_e r$ vs. $-\log_e [K_2Cr_2O_7]$ plot (Figure 2) as 0.64, indicating the reaction is fractional order with respect to $[K_2Cr_2O_7]$.

Effect of surface area

A series of experimental runs were made to evaluate the effects of pyrite surface area on the reaction rate. As expected, the rate of iron release from pyrite increased with decreasing grain size and hence increasing specific surface area. A straight line was obtained (Figure 3), which indicates a direct relationship between the rate

and the initial particle surface area. The reaction order with respect to initial mean pyrite surface area is 0.51. The deviation of the surface area of the reaction rate from unity is consistent with the observations suggesting that the rate-controlling reaction is the surface chemical reaction. The rate is dependent on the reactive surface area rather the geometric surface area of the reactant pyrite.

Table 2. Experimental results for pyrite oxidation by potassium dichromate.

Pyrite sample	Initial pH	Temp. °C	Initial $[\text{K}_2\text{Cr}_2\text{O}_7]$ mol L ⁻¹	Surface area m ²	Rate mol h ⁻¹ m ⁻²
Py - 1	1.00	30	0.01	0.0185	1.049×10^{-4}
Py - 1	1.03	35	0.01	0.0185	1.503×10^{-4}
Py - 1	1.05	40	0.01	0.0185	2.714×10^{-4}
Py - 1	0.96	30	0.05	0.0185	2.854×10^{-4}
Py - 1	1.00	30	0.005	0.0185	6.162×10^{-5}
Py - 1	1.02	30	0.001	0.0185	2.378×10^{-5}
Py - 1	1.06	30	0.01	0.0133	8.321×10^{-5}
Py - 1	0.98	30	0.01	0.0096	7.5×10^{-5}
Py - 1	1.51	30	0.01	0.0185	7.417×10^{-5}
Py - 1	1.83	30	0.01	0.0185	5.514×10^{-5}
Py - 1	2.35	30	0.01	0.0185	4.973×10^{-5}
Py - 1	2.83	30	0.01	0.0185	4.108×10^{-5}
Py - 4	1.02	30	0.01	0.0185	1.022×10^{-4}
Py - 3	1.02	30	0.01	0.0185	9.472×10^{-5}
Py - 5	0.99	30	0.01	0.0185	9.725×10^{-5}
Py - 6	1.07	30	0.01	0.0185	9.951×10^{-5}
Py - 2	1.04	30	0.01	0.0185	1.034×10^{-4}

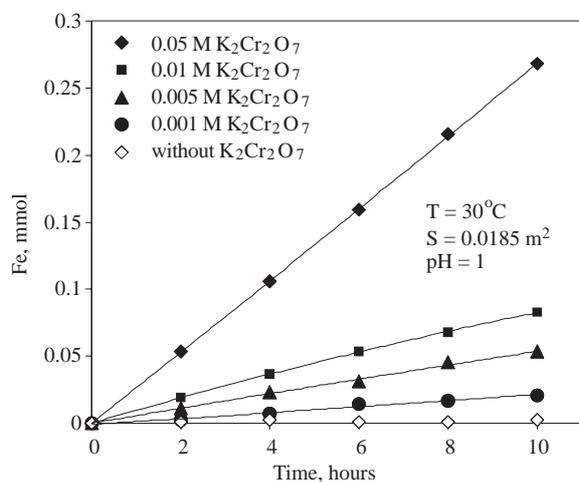


Figure 1. Effect of potassium permanganate concentration on pyrite oxidation at 30°C.

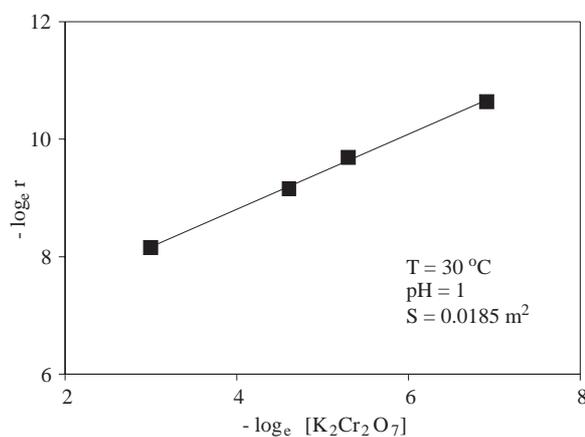


Figure 2. Plot of the $-\log_e r$ vs. $-\log_e [\text{K}_2\text{Cr}_2\text{O}_7]$.

Effect of pH

The influence of pH on the oxidation of pyrite is evident from the results shown in Figure 4. The oxidation rate decreases with increases in pH. An order of reaction with respect to hydrogen ion concentration equal to 0.22 was obtained when the pH 1.00 to 2.83 data from Table 2 were replotted as $-\log_e r$ vs. $-\log_e [\text{H}^+]$

(or 2.303pH). It can be seen (Figure 4) that there is a decrease in the reaction rate as the pH varies from 1.00 to 2.83.

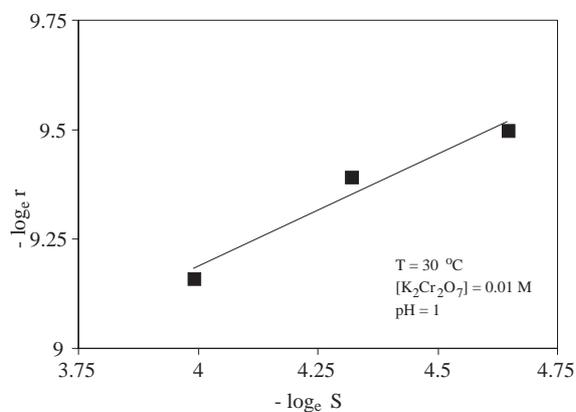


Figure 3. Effect of surface area on the pyrite oxidation at 30°C.

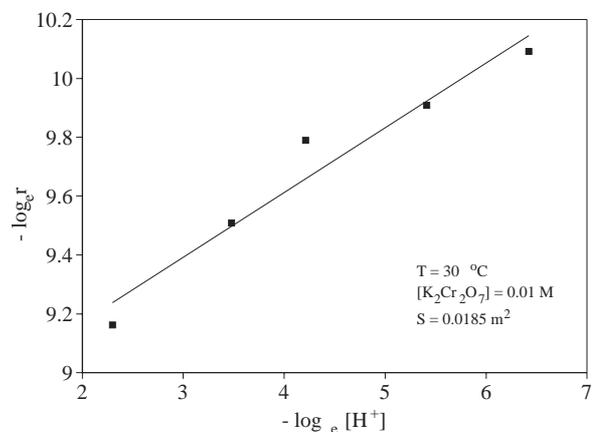


Figure 4. $-\log_e r$ vs. $-\log_e [H^+]$ (pH 1.00 to 2.83) for the data from Table 2.

Effect of temperature

The effect of temperature, T, on the reaction rate is defined by an Arrhenius plot:

$$E_a = -R\partial(\log_e r)/\partial(1/T) \quad (5)$$

where E_a is apparent Arrhenius activation energy (or critical increment of energy for a heterogeneous reaction⁹), R is universal gas constant, and T is the temperature in Kelvin. Figure 5 shows an Arrhenius plot of $-\log_e r$ vs. $1/T$ for the reaction between potassium dichromate and pyrite in perchloric acid solution (pH = 1) in the temperature range of 30-40°C. This yields an apparent Arrhenius activation energy of 74.83 kJ mol⁻¹. This magnitude is typical of reactions under chemical control.

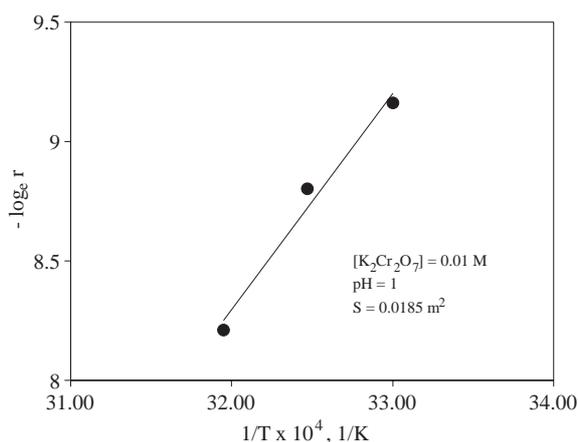


Figure 5. Arrhenius plot for the data from Table 2.

Morphology of reacted solids

The oxidation in perchloric acid solution appears to begin preferentially in corners and cracks in the solids. There are points of localized attack characterized by large pits (Figure 6A). These pits may exhibit defined

geometry and orientation. Figure 6B shows an SEM image of pyrite sample treated with 0.001 M $K_2Cr_2O_7$ solution. The image of this pyrite sample shows a particle with a relatively low degree of destruction. Therefore, I conclude that the sensitivity to the amount of oxidative dissolution increases with increasing potassium dichromate concentration. Pyrite particles are not covered by the oxide layer or by another phase (*i.e.* elemental sulfur).

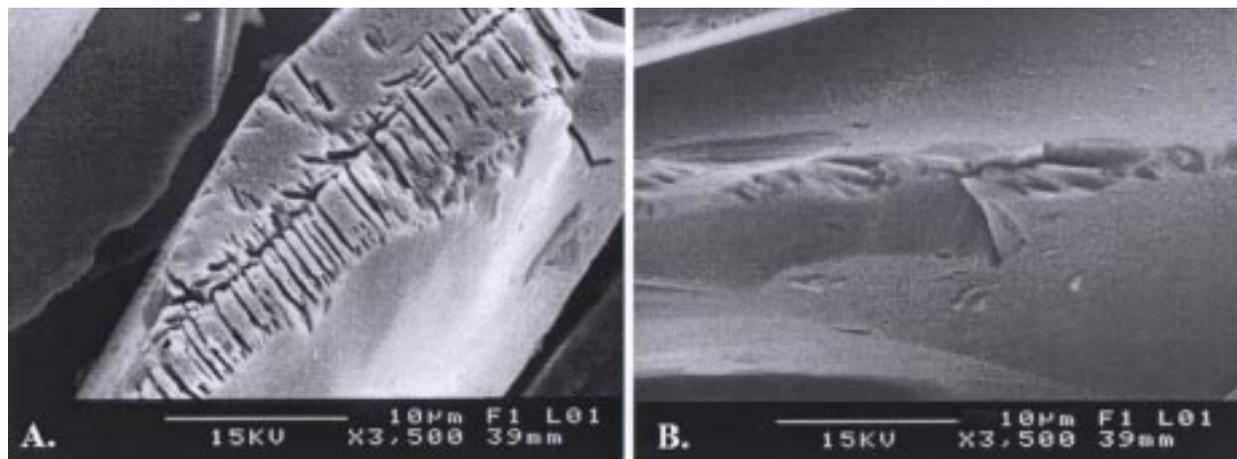


Figure 6. SEM images of pyrite reacted in: **A.** 0.01 M potassium dichromate solution, and **B.** 0.001 M potassium dichromate solution. $T = 30^\circ C$, $pH = 1$.

Trace element content

Figure 7 illustrates the effect of trace element content on pyrite oxidation by potassium dichromate. No apparent correlation is observed between pyrite oxidation and trace element content. The slope of the regression line for data in Figure 7 was not statistically significantly different from zero ($R^2 = 0.0201$).

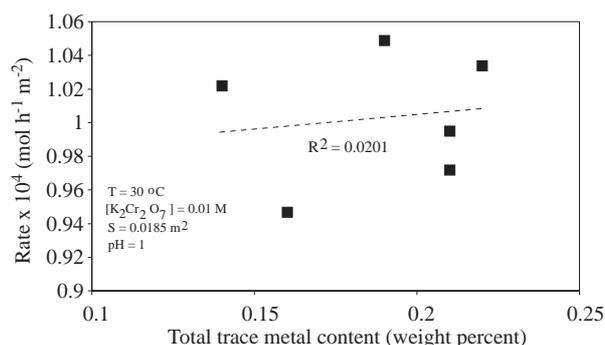


Figure 7. The influence of the trace element content on pyrite oxidation by potassium dichromate ($pH = 1$, $T = 30^\circ C$)

The five trace elements (Co, Ni, Cu, Zn and As) accounted for practically 100% of impurities in the pyrite samples (Table 1). Cobalt, and sometimes nickel, copper and zinc, substituted for iron. As is the only non-metallic element from pyrite matrix. A similar plot (not shown) was prepared using the trace metals as an independent variable. Pyrite trace element content does not appear to have a consistent effect on pyrite

oxidation by potassium dichromate in perchloric acid solutions. Quantitatively, the differences between the oxidation rates are no higher than 10.77%.

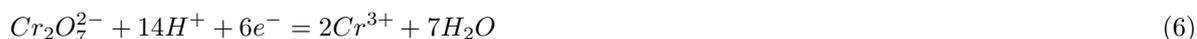
Some reports suggest that major differences in oxidation rates exist among pyrite specimens with different elemental content. It has also been suggested that crushed museum-grade types of pyrite were “relatively inert” whereas pyrite associated with sedimentary environments oxidizes rapidly¹⁰. There have been attempts by some authors to classify the reactivity of pyrite by texture and crystallinity. One investigation was conducted to compare the rates of oxidation among various specimens of pyrite by molecular oxygen¹¹. Those results indicated the small difference for the rates observed for crystalline pyrite specimens. These small differences occur even though pyrite specimens exhibit some differences in the chemical composition of pyrite. The small differences in rate among various pyrite samples shown here agree with those results.

Reaction mechanism

Much of the difficulty in formulating a reaction mechanism for the aqueous oxidation of pyrite by potassium dichromate is centered on whether a molecular adsorption process (effective chemical reactions at the pyrite surface) or other processes are operative. The evidence in this study may be used to address this dilemma and provide a convincing argument for the mechanism involving a surface chemical reaction and oxidation of the disulfide bond with the oxidant.

Central to molecular mechanism^{4,6,9-13} is site-specific adsorption of the oxidant on the pyrite S_2^{2-} sites. The rate of pyrite destruction is positively correlated with the concentration of the oxidant, stating that electron transfer from the disulfide group to the aqueous oxidant is rate-limiting. This is consistent with surface heterogeneity leading to preferential dissolution, supported by the SEM image of reacted pyrite particles, showing pits created by localized dissolution, and activation energies $E_a = 74.83 \text{ kJ mol}^{-1}$, which indicate that a chemical rather than physical barrier to reaction is rate-limiting.

Electrons are consumed by reduction of dichromate ions:



The proton will affect the electron density of $Cr_2O_7^{2-}$ and therefore the electron transfer rate between the disulfide group and dichromate ion.

Conclusions

The results of this study show that the rate of oxidation: (1) is a function of the surface area; (2) is a function of pH, and initial potassium dichromate concentration; (3) varies with temperature in an Arrhenius fashion, with activation energies of about $74.83 \text{ kJ mol}^{-1}$. It was also shown that the oxidation rate is the same for a number of different pyrite specimens that have different trace element content. This is consistent with the observations of Nicholson *et al.*¹¹ for crystalline pyrite oxidation by dissolved oxygen.

Rates of oxidation of pyrite with potassium dichromate decrease with increasing pH. In the pH range of 1.00 to 2.83, the order of the reaction is 0.22 with respect to proton, and 0.51 with respect to specific surface area, while the rate is of an order of 0.64 with respect to potassium dichromate concentration. These results can be combined to give an equation that describes the rate of oxidation of pyrite at low pH values under the given experimental conditions:

$$r = bkS^{0.51}[K_2Cr_2O_7]^{0.64}[H^+]^{0.22} \quad (7)$$

where S is the surface area of the reacting solid, r represents the amount of Fe release in solution per unit surface area per unit time, b is a stoichiometric factor, k is the apparent rate constant, and $[K_2Cr_2O_7]$ and $[H^+]$ are the potassium dichromate concentration and hydrogen ion concentration respectively.

The rate relationship with potassium dichromate suggests that the rate-controlling step during oxidation by potassium dichromate is the surface chemical reaction.

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