

Kinetics of pyrite oxidation by hydrogen peroxide in phosphoric acid solutions

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The kinetics of pyrite oxidation by hydrogen peroxide in phosphoric acid solutions were investigated. The effects of stirring, temperature, and particle size, as well as of the hydrogen peroxide and phosphoric acid concentrations were studied. The effect of phosphate ion addition was also examined. The oxidation kinetics was found to follow a shrinking core model, with the surface chemical reaction as the rate-controlling step. This is in accord with an activation energy of 57 kJ/mol and a linear relationship between the rate constant and the reciprocal of the particle radius. The reaction order with respect to the hydrogen peroxide concentration was found to be equal to unity. Variation of the phosphoric acid concentration had practically no effect on the rate of pyrite oxidation. Addition of the phosphate ion in the relatively low concentration range (0.005–0.1 mol/dm³) had a highly negative influence on the rate of pyrite oxidation, indicating that this ion has an inhibiting effect on the oxidation of pyrite by hydrogen peroxide.

Key words: pyrite, oxidation, reaction kinetics, hydrogen peroxide, phosphoric acid.

Pyrite is the most abundant of the sulphide minerals and is found in a variety of geological settings. It occurs most often in base metal sulphide deposits, in sulphide concentrates (generally as an impurity) produced by flotation of sulphide ores and in the discarded overburden of open cut base metal mining operations.¹ Pyrite is also the major sulphur-bearing mineral in some refractory gold ores and in coal. The gold is frequently finely disseminated in the pyrite matrix and cannot be extracted by conventional cyanidation. Pyrite present in coal leads to an increased sulphur content and inferior quality.^{2,3}

As a result, the separation of pyrite from valuable minerals has attracted a great deal of attention. Undoubtedly, one of the effective ways of separation is leaching. Leaching of bulk sulphide concentrates is aimed at leaching valuable minerals using reagents which leave pyrite unattacked. Conversely, in the desulphurization of coal, as well as in the extraction of gold from pyrite the aim is dissolution of pyrite. The leaching of pyrite is based on its oxidation by a convenient reagent. Since pyrite is an inert sulphide,⁴ strong oxidants must be

employed for efficient dissolution to be achieved. One such oxidant is hydrogen peroxide.

The oxidative action of hydrogen peroxide in acids solutions is based on its reduction according to the equation:⁵



Hydrogen peroxide can also act as a reducing agent, undergoing oxidation according to the equation.



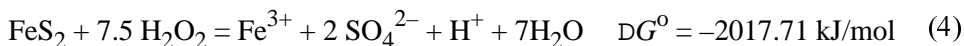
Hydrogen peroxide is known to be a relatively unstable compound, whose decomposition can be catalysed by Fe^{3+} ion, metal surfaces (Pt, Ag), dust, *etc.*⁵ The products of decomposition are oxygen and water:



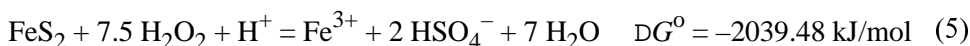
This equation is the sum of Eqs. (1) and (2).

Hydrogen peroxide has been used as a leaching agent for uranium ores,^{6–8} and its use has been studied with a zinc-lead bulk sulphide concentrate,⁹ as well as with concentrates of chalcopyrite,¹⁰ sphalerite¹¹ and pyrite.^{12–14}

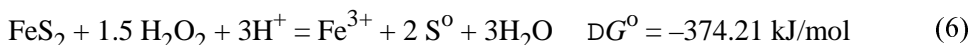
The dissolution of pyrite by hydrogen peroxide in acids solutions is characterized by the reaction:^{15,16}



and in highly acidic solutions by the reaction:



In addition, pyrite dissolution reactions yielding elemental sulphur are thermodynamically possible, for example:



However, these reactions were unlikely to occur during the experiments conducted in this study as some of the conditions that favour the formation of elemental sulphur, such as high temperature (373 K) and low anodic potentials ($< 8 \text{ V vs. SCE}$)¹⁷ were not fulfilled.

This paper is a continuation of previous work in which pyrite was leached with hydrogen peroxide in perchloric,¹³ sulphuric¹⁴ and hydrochloric acid media.¹⁸ As the rate of pyrite oxidation was different in these acids, despite the fact that the oxidant was the same, it seemed of interest to study the oxidation kinetics of pyrite by hydrogen peroxide in another medium and therefore phosphoric acid was selected.

EXPERIMENTAL

A sample of pyrite concentrate from the Veliki Krivelj copper mine (Serbia) was used for studying the pyrite oxidation. The concentrate assayed 45.38% Fe, 52.17% S and 0.88% SiO₂. X-ray diffraction analysis revealed the presence of pyrite and a small amount of quartz. The sample was sieved into several size fractions. The experiments were carried out with the 0.050–0.063 mm fraction unless otherwise stated. All the solutions used were prepared using analytical grade chemicals and distilled water.

The experiments were carried out in a 0.5 dm³ glass reactor immersed in a thermostated water bath. The reactor was equipped with a condenser, thermometer and stirrer. The reactor was filled with 0.25 dm³ of acidic peroxide solution which was then heated to the desired temperature. After the desired temperature had been attained, a charge of 0.500 g of pyrite was added to the peroxide solution, stirring was started and the temperature of the reaction mixture was then maintained constant.

One milliliter of solution was withdrawn from the reactor with a pipette at various time intervals and diluted to 0.05 dm³ in a volumetric flask. The reaction kinetics was determined by measuring the total iron dissolved in the solution as a function of time. The total iron dissolved in the solution was analysed using AAS. The reaction residues after oxidation were washed with distilled water, dried and examined by X-ray diffraction analysis.

For the calculation of the degree of oxidation of the pyrite, *i.e.*, the fraction of pyrite reacted, a formula developed by Papangelakis and Demopoulos¹⁸ was used, which includes in itself correction factors to account for the volume and mass losses due to sampling. The degree of oxidation of pyrite was calculated by dividing the amount of solubilized iron (Fe²⁺ + Fe³⁺) at the moment of sampling by the amount of iron contained in the pyrite at the beginning of the reaction. The following correction formula was used:¹⁸

$$X_i = \frac{(c_i \cdot V_i + A_i) \cdot M_{\text{FeS}_2} \cdot d}{m_{\text{FeS}_2} \cdot M_{\text{Fe}} \cdot 10^6} \quad (7)$$

where: $V_i = V_{i-1} - V_{\text{si}1}$ and $A_i = A_{i-1} - c_{i-1} \cdot V_{\text{si}1}$, i = the number of the sample corresponding to time t , X_i = oxidation degree of FeS₂, c_i = iron concentration (mg/cm³), V_i = volume of the oxidation solution prior to the i th sampling (cm³), A_i = total amount of iron withdrawn with previous samples (mg), V_{si} = total sampling volume (cm³), M_{FeS_2} = molar mass of pyrite (g/mol), M_{Fe} = molar mass of iron (g/mol), m_{FeS_2} = mass of charged solids (g), d = dilution (50·), and at $t = 0$, $i = 0$, $V_0 = 250 \text{ cm}^3$ and $A = c_0 = V_{\text{so}} = 0$.

If the correction had not been applied, the maximal error would have been about 8%.

RESULTS AND DISCUSSION

Effect of stirring

The effect of stirring on the oxidation of pyrite was investigated at a stirring speed of 600 min⁻¹ as well as without stirring. The experiments were carried out with 3.0 mol/dm³ H₂O₂ in 0.2 mol/dm³ H₃PO₄, at 313 K.

The obtained results showed that the rate of pyrite oxidation was slightly higher in the absence of stirring (Fig. 1, Table I). This is in accord with our previous studies conducted in different acids (perchloric,¹³ sulphuric,¹⁴ hydrochloric¹⁸), although the differences in the degrees of oxidation observed in these studies were more pronounced than in the present one.

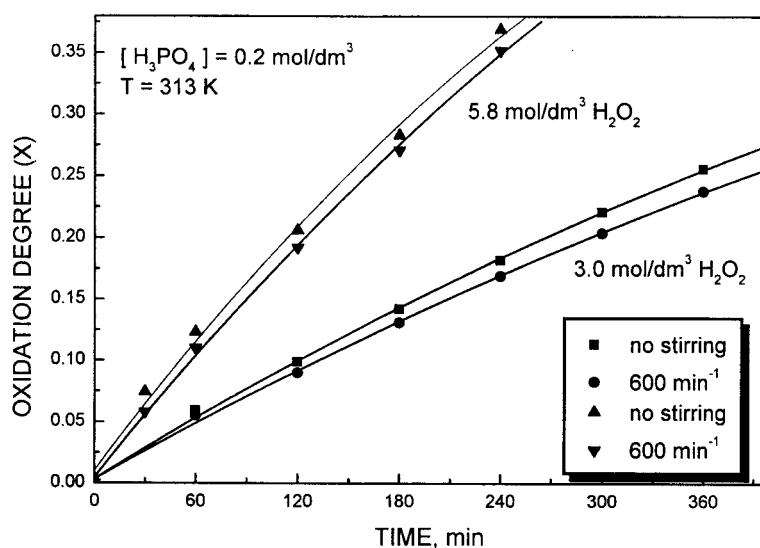


Fig. 1. Effect of stirring speed on pyrite oxidation.

TABLE I. Effect of stirring on the final degree of oxidation of pyrite and on the final consumption of hydrogen peroxide (0.2 mol/dm³ H₃PO₄, 313 K)

Initial concentration of H ₂ O ₂ , mol/dm ³	3.0		5.8	
Stirring speed, min ⁻¹	0	600	0	600
Initial oxidation degree of pyrite	0.26	0.24	0.37	0.35
Final consumption of H ₂ O ₂ , mol	0.417	0.406	0.821	0.809

For this reason, the experiments were repeated with an increased hydrogen peroxide concentration of 5.8 mol/dm³ in order to reach higher degrees of oxidation and thus a greater difference between them. As can be seen in Fig. 1 and in Table I, similar results to the previous ones were obtained. By titrating the final solutions, the final consumption of H₂O₂ was found to be slightly higher in the absence of stirring (Table I), which is consistent with the higher degrees of oxidation. This is in accord with the results obtained in sulphuric acid solutions.¹⁴

The faster dissolution of pyrite in the absence of mechanical stirring could be attributed to the possibility of better contact between the pyrite and H₂O₂, rather than to a decrease in the H₂O₂ concentration due to its decomposition as first thought.

As the pyrite dissolution was faster in the absence of stirring, all further experiments were carried out without mechanical stirring, which was only used to homogenize the solution prior to sampling.

It was pointed out previously¹⁴ that, during pyrite dissolution by hydrogen peroxide, mixing of pyrite occurs, optionally termed 'self-mixing', as a result of oxygen bubbles rapidly rising. The bubbles of molecular oxygen are produced by hydrogen peroxide decomposition, which is catalysed by solid particles, in this case

by pyrite particles, as well as by Fe^{3+} ions generated by pyrite oxidation.^{15,20,21} The bubbles, generated predominantly on the pyrite particles rise, lifting in a large number of instances the particles with them. When such an aggregate reaches the solution surface the oxygen passes into the atmosphere, releasing the particles, which fall back to the bottom of the reaction vessel.

Effect of temperature

The experiments were carried out in the 293–323 K temperature range at an initial H_2O_2 and H_3PO_4 concentration of 3.0 and 0.2 mol/dm³, respectively. The dissolution curves are illustrated in Fig. 2, from which it can be seen that the pyrite conversion increases with increasing temperature.

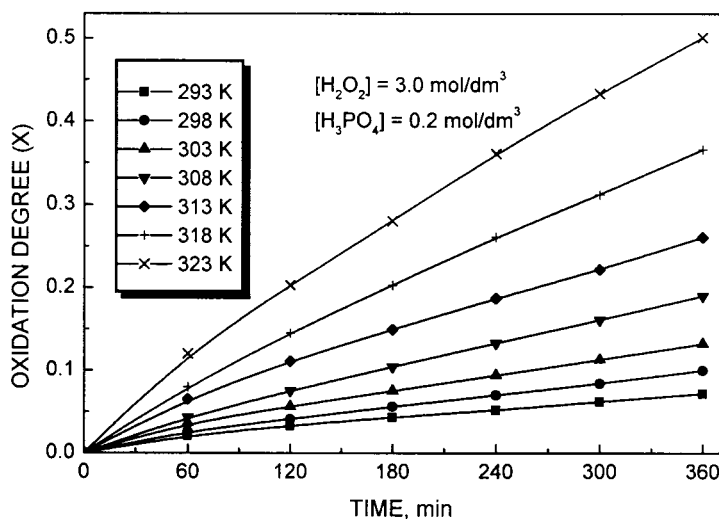


Fig. 2. Effect of temperature on pyrite oxidation.

Pyrite oxidizes to form soluble species (Fe^{3+} and SO_4^{2-}). However, during the course of the experiments, traces of elemental sulphur were observed floating on the solution surface and adhering to the reaction vessel walls at all temperatures. XRD analysis of the solid residue after 3 hours of oxidation revealed only the presence of pyrite and quartz, which was also confirmed by optical microscopy. Therefore, it is probable that the elemental sulphur is generated by reactions in the liquid phase during degradation of sulphur anions.

Compared with other conversion functions tested, the best straight lines were obtained using the surface reaction control shrinking core model:^{22,23}

$$1-(1-X)^{1/3} = \frac{b}{\tau} \frac{k}{r_0} \frac{c^n}{M} t = k_s t \quad (8)$$

where: X is the degree of oxidation, b is the stoichiometry factor, k is the intrinsic rate constant (m/min), c is the liquid reagent concentration (mol/dm³), n is the

reaction order with respect to the liquid reagent, M is the molar mass of the solid reagent (kg/mol), ρ is the density of the solid reagent (kg/m³), r_0 is the initial particle radius (m), t is the time (min) and k_s is the apparent rate constant (1/min).

The variation in $1 - (1-X)^{1/3}$ with time is shown in Fig. 3. The apparent constants were calculated as the slopes of the straight lines. An activation energy of 57 kJ/mol was determined from the Arrhenius diagram depicted in Fig. 4.

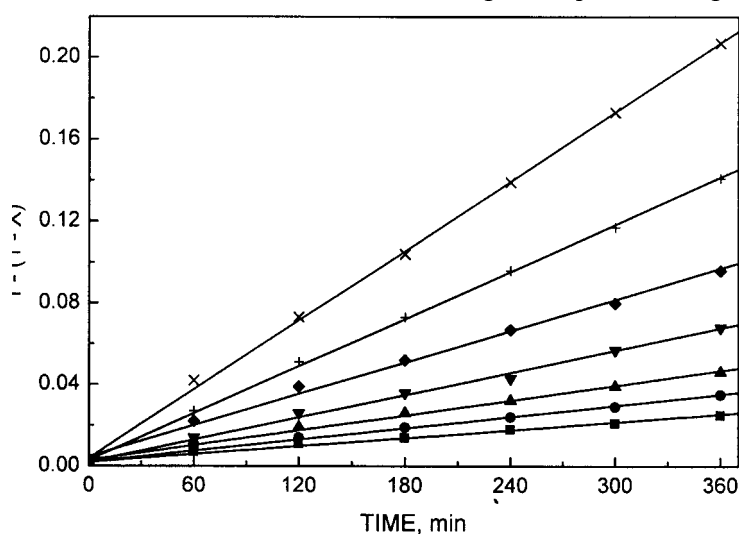


Fig. 3. Variation of $1 - (1-X)^{1/3}$ with time at various temperatures.

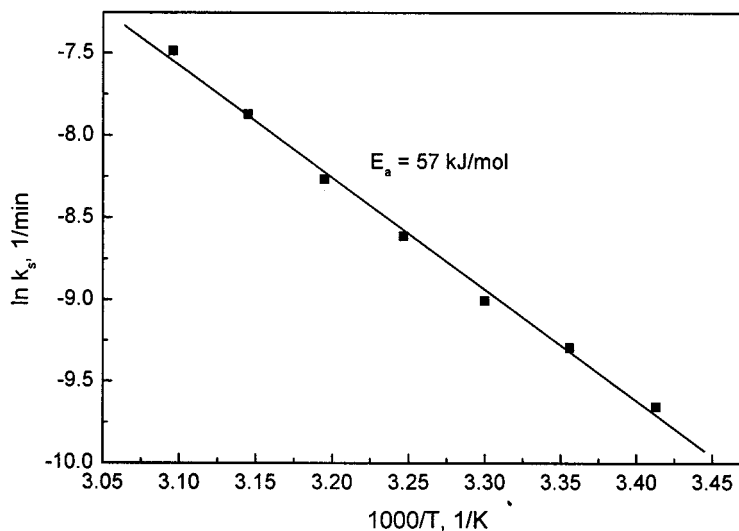


Fig. 4. Arrhenius plot for pyrite oxidation.

Based on the value of the activation energy it could be concluded that a chemical reaction at the pyrite surface is the rate-controlling step for the dissolution of pyrite by

H_2O_2 in H_3PO_4 solutions. Similar values of the activation energy were found for the dissolution of pyrite by H_2O_2 in HClO_4 (57 kJ/mol),¹³ H_2SO_4 (68 kJ/mol)¹⁴ and HCl (65 kJ/mol),¹⁸ while McKibben¹⁶ determined an activation energy of 33.5 – 12.6 kJ/mol for pyrite dissolution by millimolar concentrations of H_2O_2 in acidic solutions.

Effect of particle size

The effect of particle size on the rate of pyrite dissolution was studied by treating four size fractions (0.040–0.050, 0.050–0.063, 0.063–0.080 and 0.080–0.100 mm) at 313 K in solutions containing 3.0 mol/dm³ H_2O_2 and 0.2 mol/dm³ H_3PO_4 . The results showed that the smaller the pyrite particles, the faster the pyrite dissolution. The kinetic curves were linearized by means of Eq. (8). The apparent rate constants calculated are shown as a function of the inverse of the particle radius in Fig. 5. The linear relationship between k_s and $1/r_o$ confirms that a chemical reaction on the pyrite surface is the rate-controlling step.

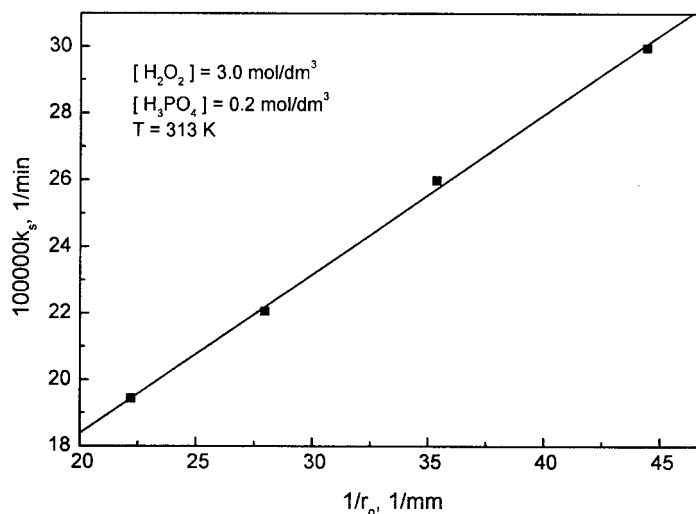


Fig. 5. Plot of k_s versus $1/r_o$.

Effect of hydrogen peroxide concentration

The effect of the hydrogen peroxide concentration was examined by varying the initial H_2O_2 concentration in the 1.0–5.0 mol/dm³ range at 313 K in 0.2 mol/dm³ H_3PO_4 . Increasing H_2O_2 concentration increased the rate of pyrite oxidation (Fig. 6). It can also be seen that the dissolution curves are linear after 60 min.

The kinetic data were linearized by means of Eq. (8). The rate constants were calculated from the slopes of the straight lines obtained. By constructing, a $\ln k_s$ versus $\ln [\text{H}_2\text{O}_2]$ plot a reaction order of 1.05 with respect to the H_2O_2 concentration was determined (Fig. 7). In our previous studies, reaction order of 1.26, 1.09 and 1.32 were found for pyrite dissolution by H_2O_2 in HClO_4 , H_2SO_4 and HCl , respectively. Similarly a first order reaction with respect to the H_2O_2 concentration was found by McKibben¹⁶ for pyrite dissolution by H_2O_2 in HCl .

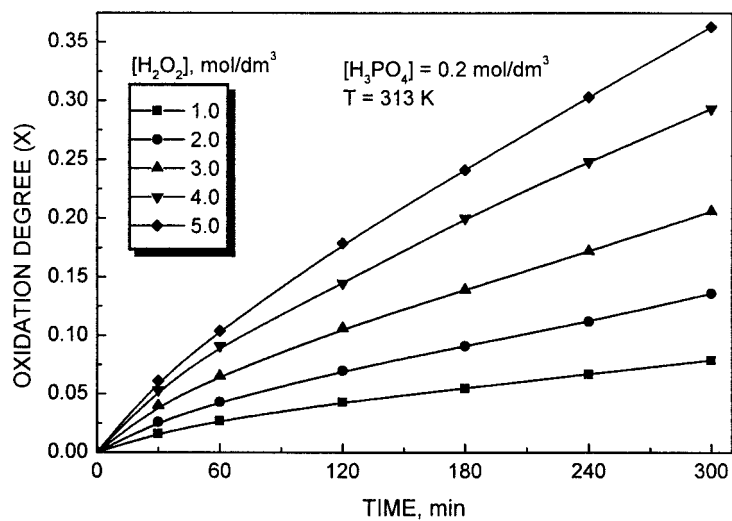
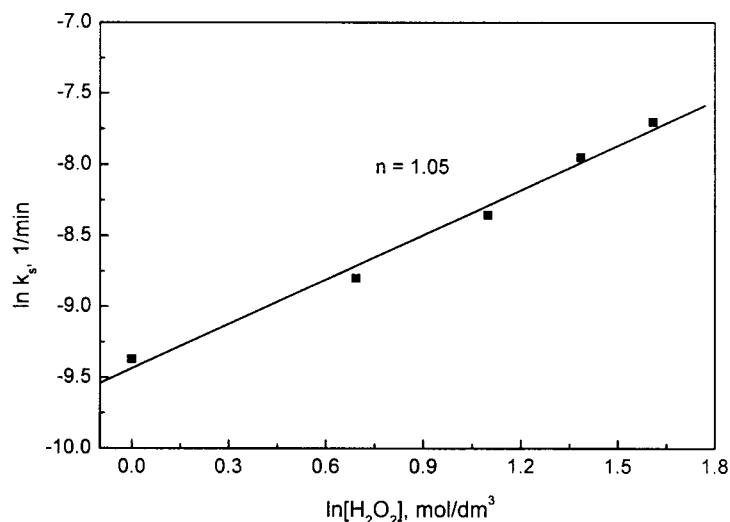


Fig. 6. Effect of hydrogen peroxide concentration on pyrite oxidation.

Fig. 7. Determination of the reaction order with respect to [H₂O₂].

Effect of phosphoric acid and phosphoric ions concentration

Experiments were carried out in solutions containing different initial H₃PO₄ concentrations (0.05 – 1.0 mol/dm³) at 313 K in 3.0 mol/dm³ H₂O₂. The kinetic curves (Fig. 8) showed that the initial phosphoric acid concentration has essentially no effect on the degree of pyrite conversion, except at the lowest concentration (0.05 mol/dm³ H₃PO₄) where a considerably higher pyrite conversion is attained.

The reason for the faster rate of pyrite dissolution at lower concentrations of phosphoric acid (mol/dm³ H₃PO₄) is the increased catalytic decomposition of H₂O₂

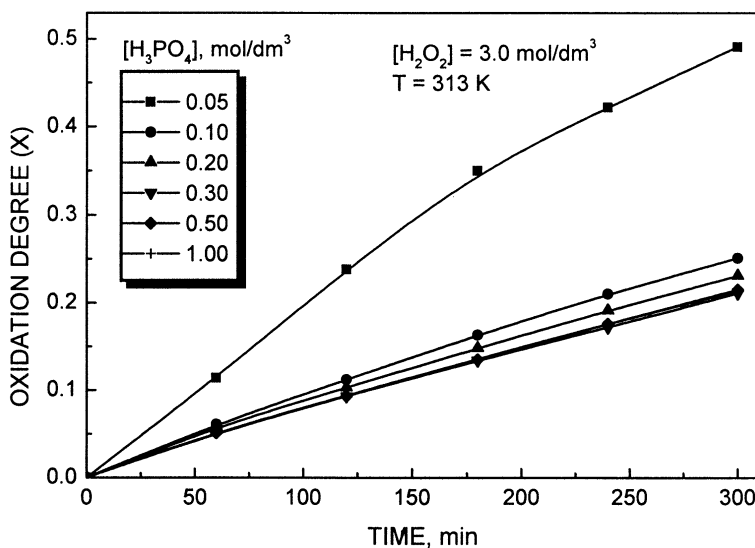


Fig. 8. Effect of phosphoric acid concentrations on pyrite oxidation.

caused by iron(III) ions. During our previous studies,¹⁸ the rate of pyrite oxidation was found to increase as the rate of hydrogen peroxide decomposition increases. Also, it is known that iron(III) ions, in the presence of phosphoric ions, form an uncoloured phosphato-complex $\text{Fe}(\text{HPO}_4)^+$ that is responsible for the stabilisation effect of phosphoric acid on H_2O_2 decomposition in solutions containing $\text{Fe}(\text{III})$ ions. Therefore, iron(III) ions, for the most part not complexed at lower acid concentrations ($\text{mol/dm}^3 \text{H}_3\text{PO}_4$), lead to an increased catalytic decomposition of hydrogen peroxide, which in turn results in increased pyrite dissolution.

Furthermore, owing to the low acid concentration and its consumption during the reaction, an increase of the solution pH ($\text{pH} > 2$) occurs. As a result, after 180 min of reaction, iron(III) hydroxide forms and precipitates on the pyrite particles, diminishing the reaction surface. This results in a slight slowdown of the reaction, which, after 180 min of oxidation, is manifested as a departure from the essentially linear dependence of conversion on time, for a H_3PO_4 concentration of 0.05 mol/dm^3 .

By analysing the kinetic data depicted in Fig. 8 with the aid of Eq. (8), a reaction order of -0.08 with the respect to H_3PO_4 concentration was calculated.

The effect of phosphoric acid on the oxidation of pyrite by hydrogen peroxide can be seen best by analysing Fig. 9. In this figure, the comparative results of pyrite oxidation by hydrogen peroxide in solutions of the four mineral acids so far studied (HClO_4 , HCl , H_2SO_4 , H_3PO_4) are presented, under the same experimental conditions. It can be seen that the rate of pyrite oxidation is lowest in the presence of phosphoric acid, and therefore it could be said that H_3PO_4 is an inhibitor of pyrite dissolution by H_2O_2 .

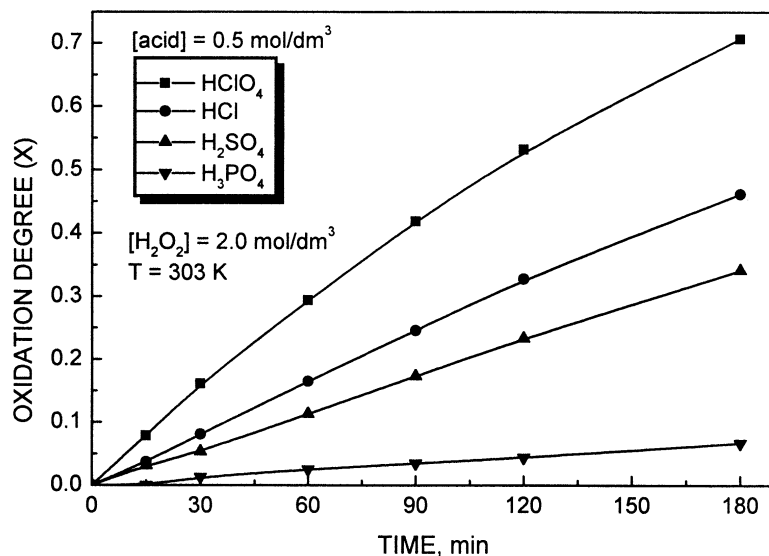


Fig. 9. Effect of various acids on pyrite oxidation by hydrogen peroxide.

As previous investigations^{13,24} have shown that H^+ ions have no effect on the oxidation of pyrite by H_2O_2 , it can be concluded that the anions (ClO_4^- , Cl^- , SO_4^{2-} and PO_4^{3-}) account for the different behaviour of pyrite that was observed in the acids used in the studies.

For this reason, the effect of phosphate ions on the oxidation of pyrite was examined, in solutions containing 2.0 mol/dm^3 H_2O_2 and 0.5 mol/dm^3 $HClO_4$, at 303 K . Phosphate ions were added as $Na_3PO_4 \cdot 12H_2O$.

Perchloric acid was chosen as the most convenient medium because of the facts that (i) the rate of pyrite oxidation by H_2O_2 in this acid was the highest (Fig. 8) and (ii) this acid, as well as ClO_4^- and H^+ ions, have no effect on the oxidation of pyrite by H_2O_2 .¹³

Low concentrations of phosphate ions were used ($0.005 - 0.100 \text{ mol/dm}^3$) since phosphate ions, at low concentrations, act as stabilisers for the decomposition of aqueous solutions of hydrogen peroxide. In addition it was found that phosphoric acid, at concentrations below 0.1 mol/dm^3 , has an effect on the oxidation of pyrite (Fig. 8).

The results obtained are shown in Fig. 10. As can be seen from this figure, the increase in phosphoric ions concentration results in a significant decrease in the rate of pyrite dissolution, indicating that these ions are inhibitors of pyrite oxidation by H_2O_2 .

After linearizing the dissolution curves and calculating the rate constants, reaction orders of -0.40 and -1.40 were found for low PO_4^{3-} concentrations ($0.005 - 0.020 \text{ mol/dm}^3$) and higher ones ($0.020 - 0.100 \text{ mol/dm}^3$), respectively.

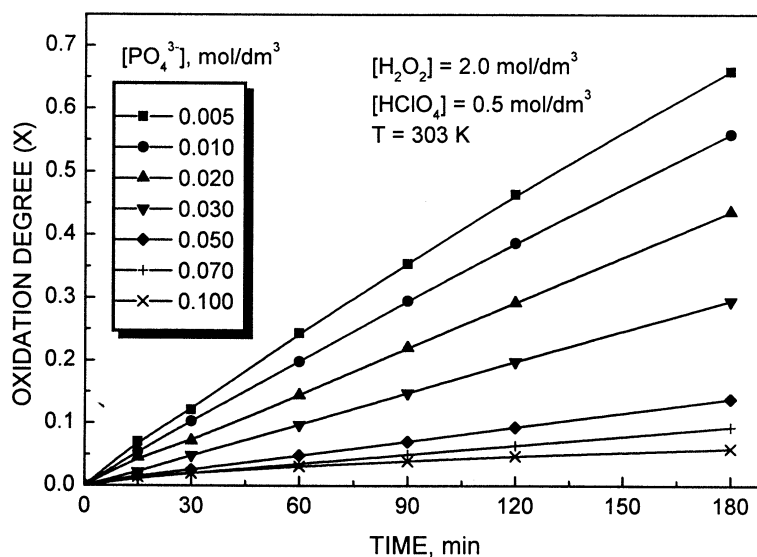


Fig. 10. Effect of phosphoric ions concentration on pyrite oxidation.

CONCLUSIONS

From the results of this study, the following conclusions can be drawn.

1. The rate of pyrite oxidation by H_2O_2 in H_3PO_4 solution is slightly higher in the absence of mechanical stirring.
2. The kinetics of pyrite oxidation by H_2O_2 in H_3PO_4 solution conform to the equation $1 - (1-X)^{1/3} = k_{s,t}$, which is valid when a surface chemical reaction is the rate-controlling step. This is supported by the magnitude of the activation energy of 654 kJ/mol and the linear relationship between k_s and $1/r_0$.
3. Increasing the H_2O_2 concentration results in accelerated pyrite oxidation. The reaction order with respect to H_2O_2 is equal to unity.
4. Phosphoric acid has no effect on pyrite oxidation in the 0.1 – 1.0 mol/dm³ concentration range, whereas below 0.1 mol/dm³ it has a positive influence. The rate of pyrite oxidation is the lowest in the presence of H_3PO_4 as compared to other mineral acids (HClO_4 , HCl and H_2SO_4).
5. The phosphate ion acts as an inhibitor of pyrite oxidation by H_2O_2 since at low concentrations (0.005 – 0.100 mol/dm³) it decrease significantly the rate of pyrite oxidation. The reaction order is – 0.40 for the 0.005 – 0.020 mol/dm³ concentration range and – 1.40 for the 0.020 – 0.100 mol/dm³ range.
6. Pyrite oxidation products are thought to be dissolved species (Fe^{3+} , SO_4^{2-}), whereas the traces of elemental sulphur detected in solution are probably generated by reactions in the liquid phase.

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ИЗВОД

КИНЕТИКА ОКСИДАЦИЈЕ ПИРИТА ВОДНИК-ПЕРОКСИДОМ У РАСТВОРИМА
ФОСФОРНЕ КИСЕЛИНЕМИЛЕ ДИМИТРИЈЕВИЋ,^{1*} МИЛАН М. АНТОНИЈЕВИЋ² и ВАЛЕНТИНА ДИМИТРИЈЕВИЋ¹¹Институт за бакар, Зелени булевар 35, 19210 Бор и²Технички факултет у Бору, Универзитет у Београду, ВЈ 12, 19210 Бор

Испитивана је кинетика оксидације пирита водоник-пероксидом у фосфорној киселини. Испитиван је утицај мешања, температуре, величине честица, концентрације водоник-пероксида и концентрације фосфорне киселине. Такође, испитиван је и додатак фосфатних јона. Нађено је да се оксидација пирита може представити помоћу модела неизреагованог језгра са хемијском реакцијом на површини која контролише брзину. То је у складу са одређеном енергијом активације од 57 kJ/mol и линеарном зависношћу константе брзине од реципрочне вредности полупречника честице. Одређен је ред реакције 1,05 у односу на концентрацију водоник-пероксида. Промена концентрације фосфорне киселине практично није имала утицаја на брзину оксидације пирита. Допатак фосфатних јона у релативно малим концентрацијама (0,005 – 0,1 mol/dm³) имао је јако негативан утицај на брзину оксидације пирита, што је указало да ови јони делују као инхибитори оксидације пирита водоник-пероксидом.

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