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1. The Effects of Sulfate Ions and Temperature on the Leaching of Pyrite.

1. Electrochemistry

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Abstract

A detailed study of the electrochemical behavior of pyrite under typical bio-leaching conditions has been carried out with the focus on the effect of the concentration of sulfate ions on the mixed potential, cyclic voltammetric and potentiostatic measurements.

The mixed potential decreases with increasing sulphate ion concentration and the addition of iron(II) and increases as expected with increasing iron(III) concentration and agitation at constant pH. Temperature, pH and the concentration of dissolved oxygen have minimal effects on the mixed potential in the presence of iron(III).

Cyclic voltammetric and potentiostatic data confirm that the rate of anodic oxidation of pyrite decreases with increasing sulphate ion concentration and increases with increasing temperature. The pH and dissolved oxygen concentration have little effect while addition of chloride ions inhibits the anodic oxidation of pyrite.

Studies of the cathodic reduction of iron(III) and dissolved oxygen have shown that the rate of the former is several orders of magnitude more reversible (rapid) than that of dissolved oxygen which only exhibits measurable reactivity at potentials well below the mixed potentials in the presence of iron(III). The reduction of iron(III) is inhibited by sulfate ions due to the formation of electrochemically less reactive sulfate complexes.
Keywords: pyrite, dissolution, electrochemistry, voltammetry, potentiostatic, sulphate ion

1. Introduction

Thermophilic bacterial leaching is a promising alternative for heap leaching of primary copper sulphides. However, in order to achieve and retain the temperatures required for thermophilic bacterial activity, exothermic oxidation of pyrite in the ore is the preferred method. However, the oxidation of pyrite results in the production of significant quantities of sulfate ions which accumulate in the leach solutions. Leaching studies (Antonijevic et al., 1996) have shown that the rate of oxidation of pyrite is reduced in the presence of high concentrations of sulfate ions. The mechanism of this inhibition was suggested to involve the common unsubstantiated explanation of inhibition of the reaction by some sort of adsorption of sulfate ions on the pyrite surface. A detailed study of the electrochemistry of this system under typical bioleaching conditions could assist in establishing the magnitude and mechanism of this effect. This first paper presents the results of mixed potential, voltammetric and potentiostatic measurements related to the oxidation of pyrite and reduction of iron(III) and dissolved oxygen under various conditions with an emphasis on the effects of the sulphate ion concentration and temperature. Part II deals with the use of the electrochemical measurements to estimate the rates of oxidation which are compared with the results from batch abiotic leaching of particulate pyrite. Part III summarizes the results of the effects of sulfate ion concentration and temperature on the kinetics of batch bioleaching of a pyrite concentrate.

Although there have been several published reports on the electrochemistry of pyrite (Peters and Majime, 1968; Biegler et al., 1975; Biegler and Swift, 1979; Misra and
Osseoasare, 1988, 1992; Kelsall et al., 1996; Ahlberg and Broo, 1997; Fowler et al., 1999; Antonijevic et al, 2005), none of these have addressed in any detail the electrochemistry under conditions appropriate to the bioleaching of pyrite. The only detailed study (Holmes and Crundwell, 2000) presented useful information on the electrochemistry of pyrite under various conditions at low temperatures and the authors developed a conventional mixed-potential model for the oxidative dissolution of pyrite in sulfate solutions containing iron(III), iron(II) and dissolved oxygen which correlated well with the observed electrochemical data. However, no actual rates of dissolution were derived or comparison made with actual leaching studies and, although limited data showed that the mixed potential decreased in solutions containing high sulfate concentrations, this was not further studied and no comment was made on this observation.

2. Experimental

2.1. Pyrite sample

Pyrite electrodes were prepared from museum grade cubic single crystals which were cut into small cubes of side about 10mm one of which is shown mounted in an XRD holder in Fig. 1(A). Fig. 2 shows the result of the XRD measurements which confirms that the sample is monocrystalline pyrite with the 200 face exposed. The XRD trace of polycrystalline material was obtained using a crushed sample. The cubes were mounted on a steel stub with conductive silver epoxy and the assembly then imbedded in resin as shown in Fig. 1(B) and (C). Two electrodes were prepared with different crystal faces exposed to the solution as shown.
2.2. *Electrochemical measurements*

Electrochemical measurements were carried out using a standard three-electrode system with a rotating working pyrite electrode. Potentials and currents were measured and controlled by a Solartron potentiostat operated with corrosion measurement software. The mercury/mercurous sulfate reference electrode (0.645 V versus SHE) was separated by a Luggin capillary from the solution in the cell and the potentials were measured and controlled relative to this electrode at room temperature. Electrolytes were prepared using sulphuric acid solutions with various concentrations of iron(III), aluminium(III) and magnesium(II) to simulate real bacterial leach solutions. The pH was adjusted to 1.2 unless otherwise stated. Iron(III), aluminium(III) and magnesium(II) were added as ferric sulphate (Fe$_2$(SO$_4$)$_3$·xH$_2$O), aluminium sulphate Al$_2$(SO$_4$)$_3$·18H$_2$O and magnesium sulphate (MgSO$_4$·7H$_2$O) respectively. Iron(III) concentrations of either 3 g/L or 15 g/L were used and the sulphate ion concentration was adjusted to 17 g/L, 40 g/L, 80 g/L or 120 g/L by addition of aluminium sulphate and magnesium sulphate to maintain a molar ratio of Al/Mg of 1.6. The required concentrations were calculated from the expected species using HSC Chemistry software prior to make up of the solutions.

Electrochemical measurements were carried out using the following procedure. 100 cm$^3$ of electrolyte of the required composition was added to the cell and, if required, nitrogen bubbled through the solution for 10 min to deaerate the solution and allow the temperature to stabilize. The solution potential was measured using a platinum electrode/mercury-mercurous sulfate reference electrode combination. The polished pyrite electrode was immersed into the electrolyte and the mixed potential of the stationary electrode recorded for a period of 20 to 30 min after which the pyrite electrode was rotated at 500 rpm and the potential recorded for an additional 10 min.
After measurements of the mixed potential, cyclic voltammetry was carried out at 1 mV/s from the rest potential in a negative direction and reversed when the potential became 200 mV less than the rest potential. The scan was limited to 200 mV negative and positive to the rest potential. Potentiostatic experiments were conducted by immersing a freshly polished electrode in the appropriate solution, the potential set to the desired value and the resulting current recorded for 1 hour. Unless otherwise stated, the electrode was rotated at 500 rpm during the cyclic voltametric and potentiostatic experiments. All potentials are shown relative to the standard hydrogen electrode.

3. Results and discussion

3.1. Formal and mixed potential measurements

The solution (Eh) and pyrite mixed potentials (Em) were measured in solutions containing 1.5 g/L of iron(II) and 1.5 g/L iron(III) at two total sulfate concentrations and various temperatures at pH 1.2 and the results shown in Table 1. In the case of the Eh measurements, these values correspond to formal (equal concentrations of oxidised and reduced forms) potentials for the iron(III)/iron(II) couple. Under these conditions, the mixed potential is almost identical to the formal potential which confirms that the current due to the anodic oxidation of pyrite at these potentials is negligible compared to the exchange currents for the iron(III)/iron(II) couple (see below) as predicted previously (Nicol and Lazaro, 2002). Note that the potentials are lower in the solution containing a higher sulfate concentration due to the greater stability of the iron(III) sulfate complexes relative to those with iron(II) (Martell and Smith, 2004)
The following is a brief introduction to mixed-potential theory as applied in this case. Assuming for simplicity that the overall reaction involved under these conditions is

$$\text{FeS}_2 + 2\text{Fe(III)} = 3\text{Fe(II)} + 2\text{S}$$

(1)

which is made up of the two half reactions

$$\text{FeS}_2 = \text{Fe(II)} + 2\text{S} + 2\text{e}^- \quad E^o = 0.39 \text{ V (sulfate)}$$

(2)

$$2\text{Fe(III)} + 2\text{e}^- = 2\text{Fe(II)} \quad E^o = 0.70 \text{ V (sulfate)}$$

(3)

i.e. the product of oxidation is elemental sulphur, then one can schematically draw the current-potential curves for the anodic (positive currents) and cathodic (negative currents) reactions as shown in Fig. 3. The mixed potential will be that potential at which the sum of the currents for the anodic half reactions are equal but opposite to those for the cathodic reactions. The rate of dissolution of pyrite will be proportional to the current density \((i_a)\) for the anodic reaction at the mixed potential as shown. Note that the assumption that oxidation results in elemental sulfur as the product is only partially true given that it is well known that the relative proportions of sulfur and sulfate ions formed as products is variable and depends on the conditions during oxidation (Holmes and Crundwell, 2000). As will be demonstrated below, greater than 80% of the sulfide is oxidized to elemental sulfur under the conditions of the present study. It should be pointed out that these curves are drawn for particular concentrations of soluble species at the surface of the pyrite. While the curve for the oxidation of pyrite
will not change except for very high concentrations of iron(II) in solution, the curves for the oxidation of iron(II) and the reduction of iron(III) will change with changing surface concentrations of these ions. Thus the rate of oxidation of iron(II) will increase as the surface concentration of iron(II) increases i.e. the total current curve will shift to the left while the opposite will be true for the reduction of iron(III). It could therefore be expected that the mixed potential could increase with increasing agitation as a result of a decreasing surface concentration of iron(II) and increasing surface concentration of iron(III).

The effects of the sulfate concentration on the variation of the measured mixed potentials with time of immersion of a stationary pyrite electrode at 50°C are shown in Fig. 4. It is apparent that the potential increases initially and stabilizes after about 1000 s. Agitation results in an immediate increase in the potential of between 20 and 30 mV in every case. This is as expected on the basis of the above model in that, due to the reaction of the pyrite with iron(III), the surface concentration of iron(III) decreases but that of iron(II) increases both of which will decrease the mixed potential. Increasing agitation will increase the surface concentration of iron(III) and decrease that of the product iron(II) both of which will increase the mixed potential.

Fig. 5 summarizes the effect of sulphate ion concentration on the mixed potentials of the rotated electrode. As shown, the potential decreases with increasing sulfate concentration at all temperatures with the greatest effect between 40 and 80 g/L sulfate. As will be demonstrated in a later section, this effect is mainly due to inhibition of the rate of cathodic reduction of iron(III) at high sulfate concentrations. Temperature does not appear to have a significant effect on the mixed potential except
at high sulfate concentrations at 65 °C for which the potential is about 10-20 mV lower. This should also result in reduced rates of dissolution under these conditions. The effect of pH on the mixed potentials in solutions containing 17 and 80 g/L sulfate at 50 °C is shown in Fig. 6. It is apparent that there is little effect of pH on the potential in the range of pH from 1.0 to 1.5 while the potential is again lower in solutions containing high concentrations of sulfate ions.

The presence of dissolved oxygen has little effect on the mixed potential in the presence of iron(III) as shown by the curves for 40 g L⁻¹ sulfate in Fig. 7. Thus, under these conditions iron(III) is considerably more effective than dissolved oxygen in the dissolution of pyrite. In the absence of iron(III), the mixed potential in solutions saturated with oxygen is below 0.6 V at which potential the rate of dissolution is very low. As could be expected on the basis of the mixed potential model, a decrease in the concentration of iron(III) from 15 g/L to 3 g/L results in a decrease in the mixed potential of some 30 mV. Similarly, addition of iron(II) would be expected to reduce the potential as shown in Fig. 8. In this case, agitation had no observable effect on the potential suggesting that the rate of dissolution is not great enough to perturb the surface concentrations of iron(II) and iron(III) which would be the same as in the bulk solution.

The data in Fig. 9 show that the addition of relatively low concentrations of chloride ion has little effect on the mixed potential but that 10 g/L chloride reduces the potential by about 25 mV at low sulfate concentrations. However, there is no effect at high sulfate concentrations. This is probably due to the fact that both chloride (log K₁ = 0.6 at μ = 1) and sulfate (log K₁ = 1.96 at μ = 1) (Martell and Smith, 2004) ions form
weak complexes with ferric ions and that these species are electrochemically less reactive than the uncomplexed ion. The weaker ligand chloride will compete with sulfate ions only at high ratios of chloride to sulfate.

3.2. **Cyclic Voltammetry**

Cyclic voltammograms were recorded after each mixed potential measurement with the sweep started in a negative direction from the mixed potential. It should be pointed out that qualitative comparisons can be made of the rate of dissolution in such a mixed potential system by comparison of the slopes of the curves at zero current. (see Part II). The effects of the sulfate ion concentration on the voltammograms at two of the three temperatures in the presence of 3 g/L iron(III) are shown in Fig. 10.

There are several aspects of these curves that should be emphasised

a) Both the anodic (oxidation of FeS$_2$) and the cathodic branches reveal that increasing sulfate ion concentrations result in reduced rates of both electrochemical reactions with the effect being more noticeable on the cathodic process particularly at the lower temperature. In the case of the cathodic reduction of iron(III), it is possible to explain this effect of sulfate in terms of the formation of increasing fractions of sulfate complexes of iron(III). Thus, Fig. 11 is a calculated (HSC Chemistry) distribution for the iron(III) species in a solution of 3 g/L iron(III) as a function of the total sulfate concentration at a constant pH of 1.23. As expected, the uncomplexed ferric ion and the mono-sulfate complex concentrations decrease significantly while that for the di-sulfate complex increases as the sulfate concentration increases. While all species could be involved in the cathodic reaction, the results appear to suggest that the complexed species are less reactive.

b) Increasing temperature results in increased rates of both processes at low sulfate concentrations. However, at high temperature and sulfate concentrations both
processes become less reversible (rapid) and the rate at 65°C is expected to be similar to that at 35°C at the high sulfate concentrations.

c) There is a remarkable lack of hysteresis in the anodic curves (which suggests that these are approximately steady-state currents) except at the higher temperatures and sulfate concentrations for which lower currents are observed on the negative-going sweep. This suggests the possible formation of a surface species (such as a jarosite) at higher potentials under these conditions that inhibits the anodic reaction. An analysis of the voltammetric data in terms of Tafel plots will be presented in Part II of this series.

The effect of increasing the concentration of iron(III) from 3 g/L to 15 g/L on the voltammograms is shown in Fig. 1. The increased currents in the cathodic branch are expected given that the rate of the reduction of iron(III) is expected to be first order in iron(III), i.e. the current at any potential will be proportional to the concentration of iron(III). The small increase in the currents in the anodic branch could be due to oxidation of small amounts of iron(II) produced by reaction of the pyrite and also to reduced free sulfate ion concentration as a result of complexation with the higher concentration of iron(III). As can be seen from the slopes of the curves at the mixed potentials, the rate of dissolution should be significantly greater at the higher iron(III) concentration. The effect of the addition of iron(II) is also shown in Fig. 12. As noted above, the mixed potential is significantly lower in the presence of only 10% of the dissolved iron as iron(II). It is apparent that in the presence of iron(II), the rate of dissolution of pyrite will be significantly lower and that the mixed potential is effectively determined by the iron(II)/iron(II) couple as shown by the data in Table 1.
Voltammograms (not shown) obtained at pH values in the range from 1.0 to 1.5 showed very little effect of the pH in this range on the dissolution of pyrite as confirmed by the negligible effect of pH on the mixed potential.

The effect of the addition of chloride ions on the voltammograms is shown in Fig. 13. At the lower sulfate ion concentrations, addition of chloride results in a measurable decrease in the rate of both the anodic oxidation of pyrite and the cathodic reduction of iron(II). This will result in decreased dissolution rates in the presence of chloride ions. The effect is not apparent at the higher sulfate ion concentration. Previous studies (Dimitrijevic et al, 1998; Nicol and Liu, 2003) have demonstrated a similar effect of chloride ions on the dissolution of pyrite under ambient and pressure leaching conditions.

In order to more easily separate the currents due to reduction of iron(III) from those due to reduction of dissolved oxygen, experiments were conducted at various sulfate concentrations and temperatures in the absence of iron(III). As a result of the low solubility of oxygen, the cathodic current densities involved are significantly lower than in the above voltammograms with iron(III) present. There is therefore a measurable “background” current in the absence of oxygen and the currents at any potential can be corrected by subtracting that observed under nitrogen. Fig. 14 shows corrected curves for the reduction of oxygen at various temperatures in oxygenated solution and Fig. 15 shows the effect of the sulfate ion concentration. A Tafel plot (not shown) for the data for oxygen from the curve for 35°C in Fig. 14 had a reasonable linear section with a slope of 130 mV/decade. Extrapolation of the line to the mixed potential gave a dissolution current density of about 3.2 x 10^{-2} A m^{-2} which
is about an order of magnitude lower than that in the presence of 3 g/L iron(III) (see Part II).

It is of interest to estimate the limiting current density for the reduction of dissolved oxygen. This can be accomplished by use of the Levich equation for a rotating disk

\[ i_L = 41.8nD^{2/3}CA\omega^{1/2} \]  

in which \( i_L \) is the limiting current density (A/cm²), \( n=4 \) is number of electrons involved in the reaction, \( D \) is diffusion coefficient of oxygen (1x10⁻⁵ cm²/s), \( C \) is the molar concentration of oxygen (mol/L), \( A \) is surface area of electrode (0.48 cm²), and \( \omega \) is rotation speed (500 rpm). The concentration of dissolved oxygen was estimated for the various conditions from published correlations (Tromans, 1998) and the diffusion coefficient also obtained from published data. Thus, at 35°C, the limiting current can be estimated to be 9.1 A m⁻² for a solution saturated with oxygen. This value is an order of magnitude greater than the current densities shown in Fig. 14 and Fig. 15. Thus, mass transport is not involved in the oxidation of pyrite by dissolved oxygen under ambient conditions.

It should be pointed out that the reduction of dissolved oxygen on pyrite is significantly slower at 65 °C than at 35 °C as can be seen from the curves in Fig. 14. This decrease in reactivity can be partially accounted for in terms of the reduced solubility of oxygen at the higher temperatures. Thus, the relative solubilities at 35, 50 and 65°C are approximately 1:0.85:0.76 (Tromans, 1998) whereas the currents for the reduction of oxygen are approximately seven times less at 65 °C than 35 °C. These results indicate that the pyrite surface may be partially oxidised and therefore has a
lower electrocatalytic activity for oxygen reduction at high temperatures. Although not as pronounced, the same behaviour at high temperature and sulfate concentrations is observed in Fig. 10 for the reduction of ferric ions.

3.3. Potentiostatic Measurements

Potentiostatic measurements were carried out in a solution without iron(III) present and the potential was set to the mixed potential observed under the same conditions in the presence of iron(III). Thus, according to the mixed potential theory, the steady-state anodic current under these conditions should be equivalent to the rate of dissolution of pyrite in the presence of iron(III). Initial experiments showed that the anodic currents were largely unaffected by the presence of dissolved oxygen as shown in Fig. 16 which also gives an indication of the reproducibility of these measurements. The initial current decays rapidly within a few minutes to a relatively stable value. This behaviour contrasts with that observed on other sulphide minerals such as chalcopyrite and covellite for which the current slowly decays over periods of days.

Transients at various potentials in the region of the mixed potential were obtained and the steady-state current density after 2 h is plotted as a function of potential in Fig. 17. A linear Tafel plot (not shown) can be obtained of the data in Fig. 17 with a slope of 107 mV/decade which is similar to the values obtained from the cyclic voltammetric measurements and in other studies (Holmes and Crundwell, 2000). In similar experiments, the total anodic charge passed over a period of 4 or 5 hours was measured as was the solution potential at the end of this period. The concentration of dissolved iron in the solution was analysed by ICP spectrophotometry. The final solution potentials of 0.71 to 0.74V indicate that essentially all of the iron present

after anodic oxidation at potentials of 0.82V and greater is in the form of iron(III) which suggests that one of the following reactions can be used to describe the anodic process,

\[ \text{FeS}_2 = \text{Fe}^{3+} + 2\text{S} + 3e \quad (5) \]

\[ \text{FeS}_2 + 8\text{H}_2\text{O} = \text{Fe}^{3+} + 2\text{HSO}_4^- + 14\text{H}^+ + 15e \quad (6) \]

At potentials below 0.82V, the final solution potentials were lower in the region of 0.68 to 0.70V which suggests that both iron(II) and iron(III) are products of oxidation under these conditions.

From the charge passed and the total iron dissolved the average number of electrons involved in the anodic dissolution of 1 mole of iron can be estimated as can the fraction of sulfide sulfur oxidized to elemental sulfur assuming that the only products are sulfur and bisulfate ions. The results are shown in Figure 18 for experiments conducted at 35°C. It is apparent that little oxidation beyond elemental sulfur occurs at potentials below about 0.82V which is the region in which oxidation by iron(III) occurs. Thus, one can assume that reaction (5) is predominant under the conditions of these experiments. The results of preliminary experiments suggested that the extent of oxidation of sulfur increases with increasing temperature and decreasing sulfate ion concentration. Of course, it is possible that other products of oxidation such as thiosulfate and other oxy-anions of sulfur are formed in the anodic process (Schippers et al, 1999). A more detailed study of the products of anodic oxidation of pyrite will be presented in a future publication.

A number of similar potentiostatic experiments were carried out under various conditions and the results at different sulfate concentrations and temperatures are
given in Fig. 19. At 35°C the currents decay rapidly to steady values after a few minutes while the transients have a more complex shape at the higher temperatures and steady values are only attained after several hours. The complex shape at higher potentials (this is also observed at higher temperatures (see below)) is possibly associated with the nucleation and growth of elemental sulfur on the surface at short times while the broad increase in current density after about 1000 s is due to increasing amounts of oxidation to sulfate.

The decrease in the currents with increasing sulfate ion concentration is easily discernible from these data as is the effect of temperature. Increased agitation has a measurable positive effect and this is confirmed by the data shown in Fig. 20. The reason for this unexpected dependence on mass transfer is not known at this stage.

3.4. Effect of exposed crystal face

The above electrochemical measurements were carried out using a “normal” pyrite electrode in which a (presumably Fe-fcc) cubic face was exposed as shown in Fig. 1 (B). Another electrode (diagonal) was prepared in which the cube was rotated by 90° as shown in Fig. 1 (C). This should not produce the same exposed Fe-fcc face. The results of measurements of the mixed potentials of the two electrodes in a solution of 40g/L sulphate solution at 50°C with 3g/L iron(III) indicated (not shown) that the potentials are very similar for both electrodes without and with rotation. A comparison of the cyclic voltammetric behavior for the two electrodes is shown in Fig. 21.

The difference in the relative reactivities of the two electrodes as reflected in the cyclic voltammetry is a possible difference in the transient behaviour. As shown in
Part II, the steady-state behavior shows that there are no significant differences between the two exposed faces. It is likely that a milled pyrite mineral will consist largely of small cubes and that the normal cubic face will be the preferred crystal face exposed to any lixiviant. These results are in accord with published data (Ndlovu and Monhemius, 2005) who found that the rate of bacterial oxidation of pyrite was largely independent of the crystal face exposed to the solution.

4. Conclusions

As a result of an extensive investigation of the anodic and cathodic reactions taking place on the surface of pyrite during oxidative dissolution by iron(III) in sulfate solutions under typical bioleaching conditions, it has been confirmed that the dissolution of pyrite conforms to classical mixed-potential theory.

The effects of a number of process variables on the electrochemical response of pyrite have been studied and the results interpreted in terms of mixed potential theory. The mixed potential decreases with increasing sulphate ion concentration and the addition of iron(II) and increases as expected with increasing iron(III) concentration and agitation at constant pH. Temperature, pH and the concentration of dissolved oxygen have minimal effects on the mixed potential.

Cyclic voltammetric data confirmed that the rate of anodic oxidation of pyrite decreases with increasing sulphate ion concentration and increases with increasing temperature except at high sulfate concentrations. The pH and dissolved oxygen concentration had little effect while addition of chloride ions inhibits the anodic oxidation of pyrite.
Studies of the cathodic reduction of iron(III) and dissolved oxygen have shown that the former is several orders of magnitude more reversible (rapid) than that for dissolved oxygen which only exhibits measurable reactivity at potentials well below the mixed potentials in the presence of iron(III). Reduction of both iron(III) and dissolved oxygen is inhibited by high sulfate concentrations at elevated temperatures.

Potentiostatic measurements have confirmed that the anodic oxidation of pyrite does not suffer from passivation which is characteristic of other sulfide minerals. The effects of the sulfate ion concentration, temperature and pH on the steady-state rates of anodic dissolution are similar to those observed in the cyclic voltammetric measurements. The major product of oxidation of sulfide sulfur is elemental sulfur at the potentials operative during oxidation by iron(III) at low temperatures.

There is little difference in the reactivity of the normal cubic face of pyrite and that obtained by exposing the diagonal of the face-centered cubic structure.

5. Acknowledgements

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6. References


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Table and Figures

Table 1  Formal and Mixed Potentials at pH 1.2

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Figure 3  Simulated curves of the mixed-potential model for the dissolution of pyrite

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Figure 5  The effect of sulphate concentration on the mixed potentials at various temperatures with 3g/L iron(III) at pH 1.2.

Figure 6  The effect of pH on the mixed potentials in solutions containing 3 g/L iron(III) at 50ºC.

Figure 7  Effect of dissolved oxygen and the iron(III) concentration on the mixed potentials in solutions containing 40 g/L sulfate at 50ºC.

Figure 8  Effects of iron(II) concentration on the mixed potential at 35ºC in a solution of 3g/L Fe(III) and 17g/L sulfate.

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Figure 12. The effect of iron(III) and iron(II) concentration on the voltammograms in a solution of 40 g L\(^{-1}\) sulfate at 50°C.

Figure 13. The effect of chloride ion concentration on the voltammograms at 50°C in a solution of 3 g L\(^{-1}\) iron(III) at (A) 17 g/L and (B) 80 g/L sulfate.

Figure 14. Corrected voltammograms for the reduction of dissolved oxygen in a solution of 17 g/L sulfate at 35°C and 65°C.

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Figure 17. Steady-state current/potential relationship for the oxidation of pyrite in a solution of 40 g L\(^{-1}\) sulfate at 50°C.

Figure 18. Stoichiometry of anodic dissolution of pyrite for 4 hours at various potentials in a solution containing 17 g L\(^{-1}\) sulfate at 35°C.

Figure 19. The effects of temperature and sulphate ion concentration on potentiostatic transients at 500rpm.

Figure 20. Effect of rotation speed of the electrode on the current density in a solution of 17 g/L sulfate at 0.816V and 65°C.

Figure 21. Comparison of cyclic voltammograms for normal and diagonal pyrite electrodes in a solution of 17 g/L sulfate and 3 g/L iron(III) at 35°C.
Table 1. Formal and Mixed Potentials at pH 1.2

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<th>[Sulfate] g/L</th>
<th>Temp. °C</th>
<th>Eh V</th>
<th>Em V</th>
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<td>65</td>
<td>0.671</td>
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</tr>
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</table>
Figure 1
Figure 2
Figure 3

- Fe(II) = Fe(III) + e
- FeS$_2$ = Fe(II) + S + 2e
- O$_2$ + 4H$^+$ + 2e = H$_2$O
- Fe(III) + e = Fe(II)
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8.
Figure 9.
Figure 10.
Figure 11

[Graph showing the concentration of FeSO4(+a), Fe(SO4)2(-a), and Fe(+3a) as a function of sulfate concentration.]
Figure 12.
Figure 13.
Figure 14.
Figure 15.
Figure 16
Figure 17
Figure 18
Figure 19
Figure 20
Figure 21
Highlights – Part I

- The dissolution of pyrite conforms to classical mixed-potential theory.
- The rate of anodic oxidation of pyrite decreases with increasing sulphate ion concentration and increases with increasing temperature except at high sulfate concentrations.
- The pH and dissolved oxygen concentration had little effect while addition of chloride ions inhibits the anodic oxidation of pyrite.
- Reduction of both iron(III) and dissolved oxygen is inhibited by high sulfate concentrations at elevated temperatures.
- The major product of oxidation of sulfide sulfur is elemental sulfur at the potentials operative during oxidation by iron(III) at low temperatures.
- There is little difference in the reactivity of the normal cubic face of pyrite and that obtained by exposing the diagonal of the face-centered cubic structure.