

Relative Contributions of Biological and Chemical Reactions to the Overall Rate of Pyrite Oxidation at Temperatures between 30°C and 70°C

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The stoichiometry and kinetics of the spontaneous, chemical reaction between pyrite and ferric iron was studied at 30, 45, and 70°C in shake flasks at pH 1.5 by monitoring the ferrous iron, total iron, elemental sulfur, and sulfate concentration profiles in time. It was found that the sulfur moiety of pyrite was oxidized completely to sulfate. Elemental sulfur was not produced in detectable amounts. The iron moiety of pyrite was released as ferrous iron. All observed initial reaction rates could be fitted into an empirical equation. This equation includes the concentrations of ferric iron and pyrite, and a constant which is dependent on the temperature and the nature of the main anion present. It was observed that ferrous iron formed during the reaction slowed down the oxidation of pyrite by ferric iron. The extent of this effect decreased with increasing temperature. With the aid of the empirical equation, the contribution of the chemical oxidation of pyrite by ferric iron to the overall oxidation in a hypothetical plug-flow reactor, in which biologically mediated oxidation of pyrite and ferrous iron by oxygen also takes place, can be assessed. At 30, 45, and 70°C, respectively, 2, 8–17, and 43% of the pyrite was oxidized chemically by ferric iron. Therefore, it is expected that only in reactors operating at high temperatures with extremely thermophilic bacteria, will chemical oxidation cause a significant deviation from the apparent first order overall kinetics of biological pyrite oxidation.

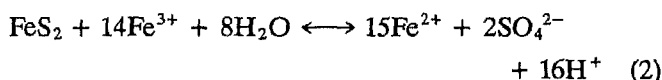
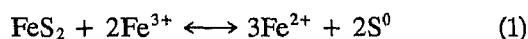
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INTRODUCTION

In 1986, a Dutch feasibility study on the microbial desulfurization of low-sulfur coal (<1% pyritic sulfur) was completed. Although the slow growth of the biomass and the pyrite (FeS₂) oxidation kinetics mean that the process will require huge reactors, cost analysis suggested that it might be of economic interest.⁷ Simple suspension reactors, such as cascades of Pachucatanks, appeared to be appropriate to fulfil the requirements for adequate aeration and bulk mixing, and to prevent sedimentation at the bottom of the reactors.⁸ Recently, an investigation into the potential of this process design for the treatment of high-sulfur coals was started.⁵

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As the oxidation of pyrite by oxygen is a highly exothermic reaction ($\Delta H_r^0 = -1481$ kJ/mol FeS₂), microbial desulfurization of high-pyritic coal would result in an increase of the temperature in the reactor such that the growth of, and pyrite oxidation by, mesophilic bacteria would be partially or completely inhibited unless the reactor was cooled. In fact, the cooling of such a large reactor would be uneconomical. In this case, thermophilic, pyrite-oxidizing bacteria would be more appropriate to desulfurize coal. However, operation at higher temperatures has several consequences for the process of leaching, which should be considered. Recently, we have evaluated the effect of the increase of temperature on oxygen and carbon dioxide mass transfer.⁴ Another important temperature-dependent parameter, which is the subject of this article, is the rate of the chemical oxidation of FeS₂ by ferric iron. According to the Arrhenius equation, it is expected that the rate of chemical oxidation of pyrite by (biologically produced) ferric iron would increase with increasing temperature. Chemical oxidation of pyrite by ferric iron is, generally, presented as two different reactions^{12,17,24,27,30}:



In eq. (1), the sulfur moiety of pyrite is oxidized incompletely to elemental sulfur, whereas in eq. (2) it is oxidized completely to sulfate. In order to measure to which extent chemical oxidation plays a part in the overall kinetics of pyrite oxidation, a study of the chemical reaction between pyrite and ferric iron as a function of the temperature has been made. This article describes an empirical equation that predicts the initial rate of chemical oxidation of pyrite by ferric iron as a function of the temperature and the concentrations of pyrite and ferric iron.

MATERIALS AND METHODS

Measurement of the Chemical Oxidation of Pyrite by Ferric Iron

Serum-bottles (300 mL) were filled with 50 mL medium. The medium had the same composition and was adjusted to the same pH as used in biological experiments⁶ performed with moderately thermophilic bacteria and contained (per L): 0.1 g yeast extract, 0.2 g $(\text{NH}_4)_2\text{SO}_4$, 0.25 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.07 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and 0.27 g KH_2PO_4 . The flasks were supplemented with 0.5% (w/v) or 1.0% (w/v) FeS_2 . The pyrite-particles (10 μm mean diameter) were 88% pure. After addition of FeS_2 , the pH was adjusted to 1.5 with HCl or H_2SO_4 . Subsequently, the bottles were sterilized for 20 min at 120°C. The reaction was started by adding a small volume of sterile, concentrated stock-solution of FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$. The flasks were incubated at 30, 45, or 70°C on rotary shakers at 130 rpm. Samples were taken and then centrifuged at 15,000g for 3 min. The resulting supernatants were analyzed for Fe^{2+} , Fe_{tot} (Fe^{2+} and Fe^{3+} together), and SO_4^{2-} . In some experiments, the pellets were analyzed for elemental sulfur.

Measurement of Ferrous Iron and Total Soluble Iron

Ferrous and ferric iron together (Fe_{tot}) were determined by the orthophenanthroline method.¹ Ferrous iron alone was determined by the same method, except for the omission of the reducing step with hydroxylamine. Ferric iron was determined as the difference between the Fe_{tot} and Fe^{2+} analyses.

Measurement of Sulfate

The SO_4^{2-} was determined by high-pressure liquid chromatography (HPLC) on an anion-exchange column as follows: the column was an ionosphere-tm-A (10 cm length, 3 mm internal diameter; Chrompack BV, The Netherlands); the eluent was Na-salicylate (4 g/L), pH 7.0; the elution rate was 0.8 mL/min; the temperature was 30°C; and the pressure was 80–100 atm. Prior to injection into the column, all soluble iron compounds had to be removed, otherwise iron precipitates would be immediately formed at the neutral pH of elution. Iron was therefore removed by adjusting the pH of the sample to 9–10 with NaOH and centrifuging at 15,000g for 3 min in order to remove the Fe precipitates. Subsequently, 10 μL of the supernatant was injected.

That the calibration curve for sulfate (0–10 mM) was not affected significantly by this procedure was confirmed as follows: after addition of 5 mM FeCl_3 to calibration samples containing 0, 2, 5, 7.5, or 10 mM Na_2SO_4 at pH 1.5, subsequent addition of NaOH and removal of the iron precipitates formed, the concentration of sulfate in the supernatant was determined.

Comparison of this calibration curve with the normal calibration curve revealed that more than 95% of the sulfate was recovered. Although formation of crystalline sodium jarosite or amorphous ferrisulfates was expected to occur, and cause the underestimation of the sulfate concentration, it apparently did not take place. A similar observation was made by Lazaroff et al.,¹⁸ who showed that at pH 9, spontaneous oxidation of even 200 mM ferrous sulfate in the presence of 200 mM sodium sulfate resulted in the formation of the iron-oxide magnetite (Fe_3O_4), and the precipitate contained only very little sulfate.

Measurement of Elemental Sulfur

The content of S^0 was determined by extraction of the pellets of samples with acetone¹³ and subsequent cyanolysis with cyanide. The thiocyanate formed was measured spectrophotometrically²⁹ at 460 nm as $[\text{FeSCN}]^{2+}$.

RESULTS

Stoichiometry of the Reaction between Pyrite and Ferric Iron at 30–70°C

The first experiments were designed to investigate whether the products of the chemical reaction between pyrite and ferric iron at different temperatures would support or invalidate either one or both of the equations shown in the introduction. Concentration ranges of 20–90 mM ferric iron and 0.5–1.0% (w/v) pyrite were tested, as such concentrations of Fe^{3+} and FeS_2 would be relevant for large-scale microbial desulfurization of high-pyritic coals. At 70°C, the production of Fe^{2+} and SO_4^{2-} was measured after the addition of 21, 55, and 89 mM FeCl_3 to shake flasks containing 1% FeS_2 at pH 1.5. In Figure 1, the production of ferrous iron (divided by 7.5) is given as a function of time, together with the concomitant sulfate production. At each concentration of ferric iron, the Fe^{2+} and SO_4^{2-} curves coincide reasonably well. Similar results were obtained in a full series of essentially identical experiments with 0.5% FeS_2 (not shown). Control experiments showed that accumulation of ferrous iron did not occur when either FeS_2 or Fe^{3+} was omitted.

On the basis of the amount of Fe^{2+} produced, as shown in Figure 1, the theoretical increase in soluble, ionic Fe species can be calculated according to eqs. (1) or (2). It should be noted that reaction (1) would predict a clear increase in total ionic iron species, whereas this increase according to eq. (2) would be only marginal. In Figure 2, these theoretical Fe_{tot} concentrations are given, together with the experimentally observed increase of the Fe_{tot} concentration. It is evident that the experimental curves (closed symbols) fit much better with the theoretical curves calculated for eq. (2) (Δ) than for eq. (1) (\square). Similar results were obtained in comparable experiments with 0.5% FeS_2 (not shown).

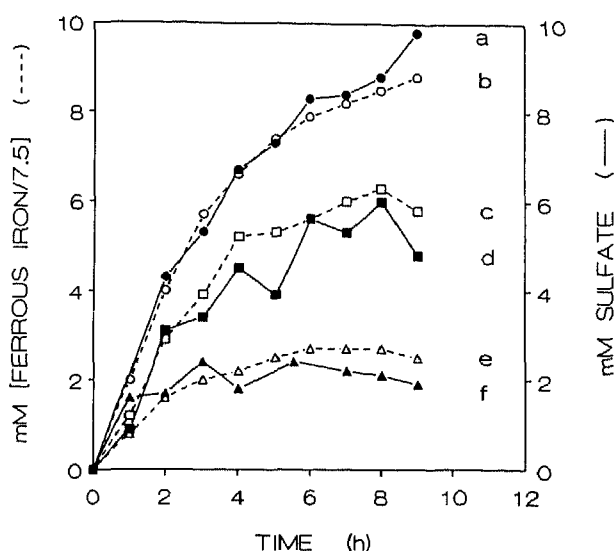


Figure 1. Production of ferrous iron, divided by 7.5, and sulfate during the oxidation of pyrite by ferric chloride at 70°C in shake flasks. The reaction was started by the addition of FeCl_3 at $t = 0$ h to a flask containing 73 mM FeS_2 at 70°C and pH 1.5. The production of Fe^{2+} (mM), divided by 7.5 (solid lines), and the production of sulfate (broken lines) is given as a function of time (h) for three different concentrations of FeCl_3 . Symbols show 21 mM FeCl_3 (Δ); 55 mM FeCl_3 (\square); and 89 mM FeCl_3 (\circ).

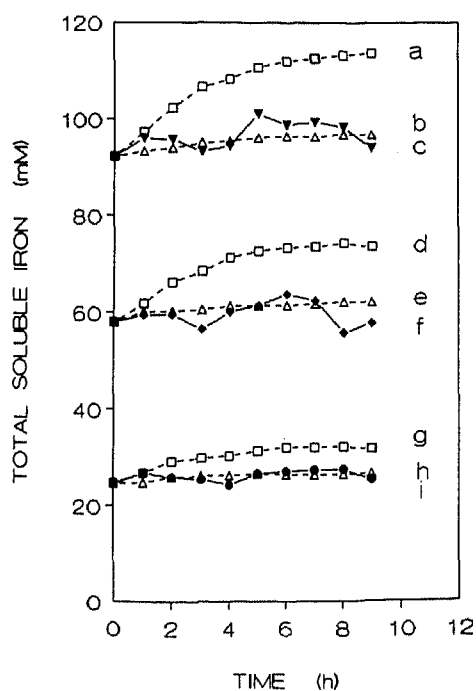


Figure 2. Theoretical and measured concentration of total, soluble ionic iron during the oxidation of pyrite by ferric chloride at 70°C. The Fe_{tot} concentrations (mM), measured during the experiments, described in Figure 1, are given as a function of time (h). Symbols show Fe_{tot} , calculated on the basis of eq. (1) (curves a, d, and g) (\square); Fe_{tot} , calculated on the basis of eq. (2) (curves b, e, and h) (Δ); and measured Fe_{tot} (curves c, f, and i) (∇ , \diamond , \bullet).

Taken together, these results strongly indicate that, at 70°C and pH 1.5, pyrite is oxidized by ferric iron according to reaction (2). In order to determine whether this hypothesis can be maintained at lower temperatures, the chemical oxidation of pyrite by ferric iron was

also studied at 30 and 45°C. The observed increase in soluble ionic iron was more in agreement with reaction (2) than with reaction (1), for each combination (see Table I) of FeS_2 and FeCl_3 concentrations (not shown). Furthermore, the production of elemental sulfur in the experiments performed at 30°C was measured. It was found that at any time, with each of the six combinations of FeS_2 and Fe^{3+} (see Table I), the reaction produced less than 1% of the amount of S^0 that could be theoretically expected on the basis of reaction (1).

Summarizing, it can be concluded that at pH 1.5, in the temperature range between 30 and 70°C, and at ferric iron concentrations relevant to microbial leaching systems, the sulfur moiety of FeS_2 is completely oxidized to SO_4^{2-} by Fe^{3+} , according to reaction (2).

Kinetics of the Reaction between Pyrite and Ferric Iron at 30–70°C

On the basis of the stoichiometry of reaction (2), the rate of the chemical reaction can be defined either as pyrite disappearance or ferrous iron appearance rate:

$$r_{\text{chem}} = -\frac{d[\text{FeS}_2]}{dt} = +\frac{1}{15} \cdot \frac{d[\text{Fe}^{2+}]}{dt} \quad (3)$$

The set of pyrite oxidation experiments described in the preceding section was used to calculate r_{chem} . The initial rate of ferrous iron production was calculated on the basis of the curves of the Fe^{2+} concentration versus time, for every combination of pyrite, ferric iron and temperature. The r_{chem} was calculated from these initial rates with the aid of eq. (3), as shown in Table I. From Table I, it is clear that the rate of chemical oxidation is

Table I. Initial rates of the oxidation of pyrite by ferric chloride at 30, 45, and 70°C in shake flasks.

$[\text{FeS}_2]$ (mM)	$[\text{FeCl}_3]$ (mM)	Temperature (°C)	Initial r_{chem} (mM FeS_2 /day)
37	18	30	0.11
37	45	30	0.31
37	70	30	0.36
73	18	30	0.20
73	44	30	0.36
73	67	30	0.48
37	19	45	1.67
37	67	45	3.27
73	19	45	2.00
73	46	45	3.93
73	70	45	5.20
37	21	70	5.6
37	51	70	13.1
37	89	70	15.3
73	21	70	9.2
73	55	70	16.7
73	89	70	22.4

Note: FeS_2 (mM) was oxidized by FeCl_3 (mM) at 30, 45, and 70°C in shake flasks at pH 1.5. The initial rate of FeS_2 oxidation (mM FeS_2 /day) was calculated from the ferrous-iron-versus-time curves. The amount of insoluble pyrite present is expressed in mM as if it were a soluble substance (see text).

strongly dependent on the temperature. Raising the temperature from 30 to 45 or 70°C caused the value of r_{chem} to increase by a factor 10 or 40, respectively. Furthermore, at each temperature the r_{chem} increased with increasing Fe^{3+} concentration at a constant percentage of FeS_2 . Finally, at each temperature, the value of r_{chem} increased if the percentage of FeS_2 was increased from 0.5 to 1.0% at a constant concentration of Fe^{3+} . The results presented in Table I clearly show that the reaction between pyrite and ferric iron cannot be described by simple first- or second-order kinetics. Apparently, saturation with respect to Fe^{3+} and FeS_2 occurs at each of the tested temperatures. Therefore, the following empirical equation was constructed:

$$r_{\text{chem}} = a \cdot \frac{[\text{FeS}_2]}{30 + [\text{FeS}_2]} \cdot \frac{[\text{Fe}^{3+}]}{95 + [\text{Fe}^{3+}]} \quad (4)$$

It must be emphasized that pyrite in eq. (4) is treated as if it were a soluble substance, the amount of which can be expressed in mmol/L. Of course, from a mechanistic point of view, the surface area of the insoluble pyrite-particles seems to be a more realistic parameter. Nevertheless, this concentration was used as a variable, because the sole intention of these experiments was to find a correlation between the data presented in Table I. Hence, eq. (4) has no general value, but is only valid for these experiments, performed with slurries consisting of small (10 μm) particles of pyrite in acid water. In this formula, the constant a (mM/day) is dependent on the temperature and has a value of 64 ± 6 (6) {mean \pm standard deviation (number of observations)} at 70°C, 16.6 ± 1.5 (6) at 45°C and 1.59 ± 0.18 (6) at 30°C.

In the experiments described above, Fe^{3+} was added as FeCl_3 and the pH was adjusted with HCl. However, it appeared that the nature of the anion was also an important parameter in the chemical oxidation of pyrite. It was observed that lower rates of chemical oxidation were obtained by using $\text{Fe}_2(\text{SO}_4)_3$ and H_2SO_4 . In experiments similar to those described above, it was found that in the presence of sulfate at 45°C and pH 1.5, the constant a had a value of 8.1 ± 1.1 (6), which is about two-times lower than in the presence of chloride.

Retardation of the Reaction between Ferric Iron and Pyrite by Ferrous Iron

In the foregoing section, initial rates of oxidation of FeS_2 by ferric iron were measured. Clearly, as the reaction proceeds the rate tends to decrease because Fe^{3+} and, to a much lesser degree, FeS_2 are being consumed. With the aid of eq. (4), this decrease in the chemical reaction rate can be calculated. Such calculations were made for the oxidation of 1% FeS_2 (w/v) by ferric iron (19, 46, or 70 mM) at 45°C and pH 1.5. Taking the initial rate of oxidation as the 100% value, the percentage of the reaction rate was calculated as a function of the percentage of the ferric iron concentration initially present. In Figure 3, the solid lines represent these per-

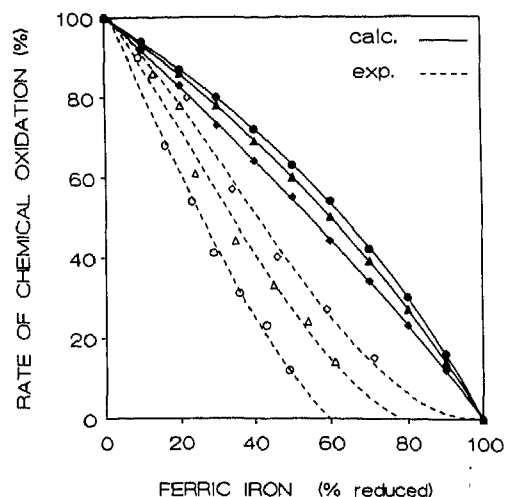


Figure 3. Calculated and experimental rates of pyrite oxidation during the reaction between pyrite and ferric iron. The calculated rates of FeS_2 oxidation (solid lines) were determined with the aid of equation 4 for oxidation of 1% FeS_2 by 19 (\blacklozenge), 46 (\blacktriangle), or 70 (\bullet) mM FeCl_3 at 45°C in shaken flasks at pH 1.5 (adjusted with HCl). The experimental rates of FeS_2 oxidation (broken lines) were determined from the tangent drawn at regular time intervals at the curve of ferrous iron versus time. The rates of oxidation (calculated and experimental) are given as a percentage of the initial rate of oxidation (0 to 100%). The 100% values are 2.00, 3.93, and 5.20 mM FeS_2 /day for 19, 46, and 70 mM FeCl_3 , respectively (see also Table I). The ferric iron concentration is given as the percentage reduced of the initial concentration of ferric iron (0–100%).

centages at different initial concentrations of FeCl_3 . However, lower rates were obtained during these experiments when the rate of oxidation was determined from the tangent (experimental rate) drawn at regular time intervals at the curve of ferrous iron versus time (Fig. 3; broken lines). This discrepancy was more substantial, and appeared sooner after the reaction was started, when higher initial concentrations of Fe^{3+} were used. Furthermore, comparable results were obtained with 0.5% FeS_2 and 19 or 67 mM FeCl_3 (not shown).

Similar calculations were also made on the basis of the experiments performed at 30 and 70°C and described in Table I. At these temperatures, the discrepancy between calculated and experimental rates was, respectively, more and less pronounced than at 45°C (not shown). Thus, the apparent retardation of the oxidation of pyrite by Fe^{3+} was inversely proportional to the temperature.

The occurrence of precipitate formation, that could be the cause of the observed retardation of the chemical reaction, can be excluded since no gaps in the element balances for Fe and S were observed (see Figs. 1 and 2). Alternatively, since the accumulation of ferrous iron, which is a product of the chemical oxidation of FeS_2 by Fe^{3+} , might slow down the reaction, this possibility was qualitatively investigated by measuring the effect of FeSO_4 on the oxidation of 1% FeS_2 by ferric iron at 45°C and pH 1.5. In Table II it can be seen that FeSO_4 , added at the start, severely retarded the oxidation of pyrite by ferric sulfate. In the presence of 22 mM

Table II. Retardation of the chemical oxidation of pyrite by FeSO_4 .

Fe^{2+} (mM)	Initial r_{chem} (mM FeS_2 /day)	
	17 mM Fe^{3+}	38 mM Fe^{3+}
5	0.67	1.07
22	0.35	0.50
45	0	0.11

Note: The oxidation of FeS_2 (73 mM) by ferric iron [8.5 or 19 mM $\text{Fe}_2(\text{SO}_4)_3$] was measured in shake flasks at 45°C at pH 1.5, after the addition of 0, 17, or 40 mM FeSO_4 . The initial rate of FeS_2 oxidation (mM FeS_2 /day) was calculated on the basis of the ferrous-iron-versus-time curves.

FeSO_4 , the initial rate of the reaction was only about half the rate observed without the addition of FeSO_4 . In the presence of 45 mM FeSO_4 , hardly any FeS_2 was oxidized. Calculation of the influence of mass action (not shown) revealed that this effect could only partly explain the observed decrease in the chemical oxidation rate. Therefore, the possibility cannot be excluded that ferrous iron inhibits the oxidation by competing with ferric iron for the formation of a σ bond to the FeS_2 surface which, in the case of Fe^{3+} , precedes electron transfer.²⁰

CALCULATIONS

Chemical and Biological Oxidation of Pyrite in a Plug-Flow Reactor

It is now, possible to predict the extent of the chemical oxidation of pyrite by ferric iron in a plug-flow reactor, in which the bacterial oxidation of pyrite and ferrous iron by oxygen also takes place. In the plug-flow reactor, the concentration of pyrite decreases, and the concentration of ferric iron increases, as the slurry progresses from the first to the last Pachucatanak.^{7,8} With the aid of the empirical formula, the value of r_{chem} can be calculated at 30, 45, and 70°C as a function of the conversion factor (ϕ) of pyrite.

In Figure 4, this calculation is presented for an input of 1% (w/v) pyrite particles (73 mM FeS_2) into the plug-flow reactor. It is assumed that the concentration of biomass is high enough to prevent accumulation of ferrous iron, so that the observed retardation of the chemical reaction by ferrous iron (Fig. 3 and Table II) does not have to be taken into account. It can be seen that the rate of chemical oxidation was maximal in all cases when about 60% ($\phi = 0.6$) of the pyrite is oxidized. Furthermore, at 30°C the rate of chemical oxidation is low. At 45°C, this rate is somewhat higher. The difference between the chemical oxidation at 45°C in the presence of SO_4^{2-} or Cl^- can be clearly seen.

Finally, at 70°C the maximal rate amounts to 10 mM FeS_2 /day, which is highly significant for the predicted situation, as will be shown in Figure 5. On the assumption that bacteria in the plug-flow exhibit oxidation kinetics showing a first order relationship with respect to

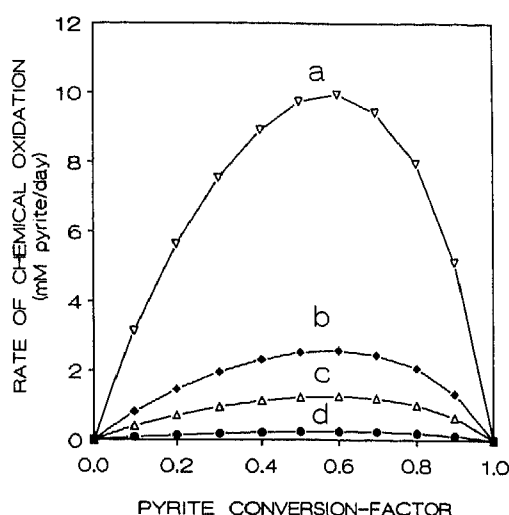


Figure 4. Rate of chemical oxidation of pyrite by ferric iron at different temperatures as a function of the conversion factor of pyrite in a plug-flow reactor. The theoretical rate of chemical oxidation (mM FeS_2 /day) in a plug-flow reactor is calculated with the aid of eq. (4) and plotted against the conversion factor for pyrite (Φ). It is assumed that FeS_2 is converted biologically to Fe^{3+} , without accumulation of Fe^{2+} in the reactor. The rate is calculated for three different temperatures: 70°C (∇ , curve a); 45°C (\blacklozenge and Δ , curves b and c); and 30°C (\bullet , curve d). In one case (curve c), ferric sulfate is assumed to be the oxidizing agent, and in the other three, ferric chloride (curves a, b, and d). The input-concentration of pyrite is 73 mM.

pyrite at 30, 45, and 70°C, and that the corresponding rate constant k has a realistic value^{6,9} of 0.010 h^{-1} at these three temperatures, the value of r_{biol} can be expressed as a linear function of the conversion factor of pyrite (Fig. 5, curve e). Moreover, the total rate of FeS_2 oxidation ($r_{\text{tot}} = r_{\text{chem}} + r_{\text{biol}}$) can now be calculated and the r_{tot} is also indicated in Figure 5 (curves a–d). On the

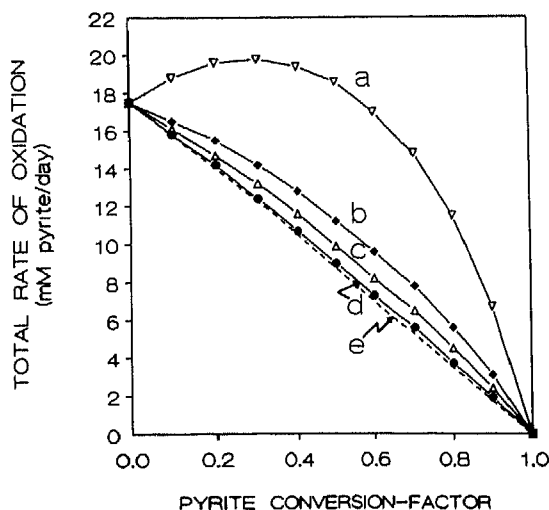


Figure 5. Overall rate of oxidation of pyrite as a function of the conversion factor for pyrite in a plug-flow reactor. The total rate of pyrite oxidation (mM FeS_2 /day) in a plug-flow reactor is given as a function of the conversion factor for pyrite (Φ). The r_{biol} is calculated assuming first order kinetics with respect to pyrite: $r_{\text{biol}} = k \cdot [\text{FeS}_2]$. The value of k is taken to be 0.010 h^{-1} at 30, 45, and 70°C (curve e). The r_{chem} is calculated with eq. 4. The r_{tot} is the sum of r_{chem} and r_{biol} . Symbols: see Fig. 4.

basis of this hypothetical figure, the contribution of the chemical oxidation to the overall oxidation of FeS_2 in the presence of chloride was calculated to be 2, 17, and 43% at 30, 45, and 70°C, respectively. This percentage was 8% at 45°C in the presence of sulfate.

DISCUSSION

In this article, it has been shown that at pH 1.5, with ferric iron concentrations between 20 and 90 mM, pyrite concentrations between 0.5 and 1.0% (w/v) and temperatures between 30 and 70°C, the sulfur moiety of pyrite is oxidized stoichiometrically to sulfate by ferric iron in the absence of bacteria. The formation of elemental sulfur during these experiments can be ruled out as it was not detected. Under these conditions sulfur is very stable. Oxidation to sulfate, although thermodynamically feasible, does not seem to take place at appreciable rates, even at elevated temperatures.^{3,11} Indeed, Brock and Gustafson¹⁰ observed that the reaction between colloidal sulfur and ferric iron was virtually undetectable at room temperature, and quite slow even at 70°C. Moreover, in several other articles^{12,21,22,32} complete oxidation of pyritic sulfur to sulfate by ferric iron was reported to take place under comparable experimental conditions. Therefore, in our opinion, the chemical oxidation of pyrite by ferric iron results in the formation of sulfate, and the release of ferrous iron under those conditions generally encountered in biohydrometallurgy, i.e., atmospheric pressure, temperature lower than 80°C, ferric iron concentration lower than 100 mM, and pH between 1 and 3.

At first sight, this conclusion seems to be at variance with other data presented in the literature. In the first place, in addition to sulfate, elemental sulfur was sometimes found to be, or was supposed to be produced during the chemical oxidation of pyrite.^{12,15,16,30} In the second place, the electrochemical oxidation of pyrite resulted in the formation of both sulfate and elemental sulfur.^{2,3,25} In the third place, the oxidation of metal sulfides, which contain a S^{2-} unit, generally produces elemental sulfur and only very little sulfate.¹¹ However, an explanation for these observations might be found in the specific crystal structure of pyrite. Sulfur in pyrite is present¹⁹ as the diatomic ion S_2^{2-} . The presence of an anion pair is unique, and it represents the unifying feature of the disulfide group of metalsulfides.³¹ Luther²⁰ proposed a mechanism for the chemical oxidation of pyrite by ferric iron on the basis of molecular orbital theory considerations, in which thiosulfate rather than elemental sulfur is expected to be formed as the initial oxidation product. Partial oxidation of the S_2^{2-} unit to a matrix-bound S_2 group would result in an increase of the bond order for the persulfido group from 1.0 to 2.0, and via hydrolysis, eventually, $\text{S}_2\text{O}_3^{2-}$ might be produced.²⁰ Similarly, Mishra²³ suggested, on the basis of electrochemical experiments, that thiosulfate might be an intermediate oxidation product.

Thiosulfate is known to be unstable and to decompose to elemental sulfur and sulfite. The rate of decomposition increases with increasing acidity and temperature.¹⁴ Thus, elemental sulfur production can be expected whenever the rate of decomposition is faster than the rate of oxidation of thiosulfate.²³ Because only sulfate is detected as oxidation product under biohydrometallurgical conditions, the oxidation is apparently much faster than the decomposition. Moreover, elemental sulfur production was generally observed at pH values lower than about 1.0, low anodic over-potentials, or temperatures higher than about 100°C. These findings are in accordance with the expected fast rate of decomposition of thiosulfate under these conditions. However, one observation still cannot be readily explained. At high concentrations of ferric iron ($>0.1M$), the accumulation of elemental sulfur has been observed,^{15,16} although the oxidation rate of thiosulfate would be expected to be high.

The rate of the chemical oxidation of pyrite, present in the particles used in this study, by ferric iron ($<0.1M$) is dependent on the FeS_2 , Fe^{3+} , and Fe^{2+} concentrations, the temperature, and the nature of the anion present (this article). Several complex rate laws, including parameters such as Fe^{3+} , Fe^{2+} , Fe_{tot} , or H^+ concentrations, particle size, pyrite loading and surface area, and a number of rate constants, have been published.^{12,21,22,26,32}

The data presented in this article on this heterogeneous reaction at three different temperatures can all be accommodated to a simple, empirical equation. By means of this equation, it has been possible to predict the contribution of the chemical oxidation to the overall oxidation in a hypothetical plug-flow reactor, operating with a slurry of the small pyrite particles used in this study. In the presence of chloride, oxidation of pyrite by ferric iron in this reactor would constitute only a few percent of the total oxidation at 30°C, about 20% at 45°C and about 45% at 70°C. However, in the real situation, sulfate is the main anion present. On the assumption that the observation made at 45°C (but see ref. 21) that lower rates of oxidation occur in the presence of sulfate is representative for the whole range of temperatures between 30 and 70°C, the chemical oxidation in the presence of sulfate will constitute a smaller part of the overall oxidation than in the presence of chloride.

The chemical oxidation of pyrite by dissolved oxygen does not proceed fast enough^{19,24} to interfere significantly with the kinetics of oxidation of pyrite by ferric iron. Indeed, it has been shown that this chemical oxidation proceeds under aerobic conditions at the same rate as under anaerobic conditions.^{12,28} Moreover, on the basis of molecular orbital theory considerations it has been suggested that pyrite would be more easily oxidized by ferric iron than by oxygen.²⁰

Our former conclusion⁷ that, after an initial phase of aerobic, autotrophic growth, the overall oxidation of pyrite in coal at 30°C showed the features of first-order kinetics with respect to pyrite, can still be maintained,

because at this temperature the rate of chemical oxidation is low in comparison to the rate of biological oxidation generally⁹ found. However, at 70°C a significant deviation from the overall first-order characteristics is expected to be found, since at this temperature the rate of chemical oxidation of FeS₂ by Fe³⁺ can be similar (this article) to the rate of biological oxidation of FeS₂ by O₂, and apparently does not show first order features [see eq. (4)].

CONCLUSIONS

1. The sulfur moiety of pyrite is stoichiometrically oxidized to sulfate by ferric iron (<0.1M) at pH 1.5 and in the temperature range 30–70°C. Elemental sulfur was not produced.
2. The rate of oxidation of pyrite by ferric iron increases with increasing concentrations of ferric iron and pyrite, and with increasing temperatures.
3. All of the rates observed with small pyrite particles could be accommodated to a simple, empirical equation.
4. With the aid of this equation, the contribution of the chemical oxidation of pyrite to the overall oxidation in a biological plug-flow reactor was estimated to be negligible at 30°C, small at 45°C, but substantial at 70°C.
5. Therefore, it is expected that the overall kinetics of pyrite oxidation will show a significant deviation from first-order kinetics in reactors operating with pyrite-oxidizing, extreme thermophiles.

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