Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism

J. DONALD RIMSTIDT1,* and DAVID J. VAUGHAN2

1Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
2Department of Earth Sciences and Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester M13 9PL, UK

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Abstract—The oxidation of pyrite to release ferrous iron and sulfate ions to solution involves the transfer of seven electrons from each sulfur atom in the mineral to an aqueous oxidant. Because only one or, at most, two electrons can be transferred at a time, the overall oxidation process is quite complex. Furthermore, pyrite is a semiconductor, so the electrons are transferred from sulfur atoms at an anodic site, where oxygen atoms from water molecules attach to the sulfur atoms to form sulfoxy species, through the crystal to cathodic Fe(II) sites, where they are acquired by the oxidant species. The reaction at the cathodic sites is the rate-determining step for the overall process. This paper maps out the most important steps in this overall process.

1. INTRODUCTION

The oxidation of pyrite, the most abundant of all metal sulfide minerals, is the dominant process giving rise to the acidification of natural waters. Whether the source of the pyrite is shale or other rock with substantial accessory iron sulfide mineralogy, or dumps of waste material from a mining operation, the weathering of this pyrite can result in the acidification of large tracts of stream, river, and lake systems and the destruction of living organisms. Where anthropogenic influences have been involved, this is termed acid mine drainage (AMD), whereas the more general case is termed acid rock drainage (ARD). There is now a very substantial literature dealing with all aspects of AMD and ARD. Reviews and more general articles on this subject include those by Alpers and Blowes (1994), Banks et al. (1997), Evangelou (1995), Evangelou and Zhang (1995), Gray (1996), Jambor and Blowes (1994), (1998), Keith and Vaughan (2000), Nordstrom and Alpers (1999), and Salomons (1995).

In spite of many decades of research, the key controls of reaction mechanisms and hence rates of the oxidation of pyrite remain poorly understood. This is largely because the processes of aqueous oxidation, which are relevant here, involve a complex series of elementary reactions. Basolo and Pearson (1967) pointed out that elementary steps of redox reactions almost always involve the transfer of only one electron at a time so that the oxidation of monosulfide minerals (e.g., sphalerite, galena) to release sulfate must require as many as eight elementary steps, and the oxidation of disulfides (e.g., pyrite and marcasite) must require up to seven elementary steps, depending on how elementary steps are defined. This process is further complicated by the fact that the minerals are semiconductors and the reactions are electrochemical in nature. This means that electrons can move from one part of the mineral to another so that the various reactions happen at different sites. Furthermore, the semiconducting properties of sulfide minerals such as pyrite are in turn critically dependant upon the precise composition of the particular pyrite sample or even the zone or region of a particular sample. Thus, as further discussed below, subtle differences in stoichiometry influence electrical properties and may in turn significantly affect reactivity. This is certainly the case for electrochemical oxidation processes; however, the situation regarding chemical oxidation is less clear. As discussed below, there are differences in rates of oxidation for pyrite samples from different sources, although grain size (and hence surface area) differences may exert a greater control. Further studies are needed to resolve these issues.

The question that we wish to address in this article is how we can dissect the process of aqueous oxidation to reveal each of the elementary reaction steps and hence determine the key controls of reaction mechanisms and rates. Drawing upon our and our collaborators’ research and upon other published material, we present our ideas in answer to this question in ways that have not previously been laid out in the literature. The emphasis here is on pyrite (FeS2) oxidation, with some brief discussion of the oxidation of pyrrhotite (Fe1-xS), as it is the iron sulfides that dominate natural systems. However, the principles developed below should apply to most, if not all, sulfide minerals.

2. REACTION MECHANISM

Pyrite oxidation is an electrochemical process that consists of three distinct steps, as illustrated in Figure 1. These three steps are the (1) cathodic reaction, (2) electron transport, and (3) anodic reaction. Each step will be discussed separately to simplify this presentation, but the steps must occur more or less simultaneously in the actual oxidation process.

2.1. Cathodic Reaction

The cathodic reaction involves an aqueous species that accepts electrons from an Fe(II) site on the mineral surface. There are many oxidants that can accept electrons from iron sulfide minerals, including NO3−, Cl2, and H2O2, but the most important ones in nature are O2 and Fe3+. These react with pyrite by the following overall reactions:
Cathode

\[ \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2e^- = \text{H}_2\text{O} \]

Fe\(^{3+}\) + e\(^-\) = Fe\(^{2+}\)

Anode

\[ >\text{S} + \text{H}_2\text{O} = >\text{S-OH} + \text{H}^+ + e^- \]

These balanced reactions show that the oxidation process does not oxidize iron (it is Fe\(^{2+}\) in the mineral and remains Fe\(^{2+}\) as it is released into the solution), but rather, it oxidizes sulfur.

It is now clear that the cathodic reaction is the rate-determining step for sulfide mineral oxidation (e.g., Brown and Jurinak, 1989). Williamson and Rimstidt (1994) showed that the pyrite oxidation rate depends on the concentration of Fe\(^{3+}\) or O\(_2\) (Figs. 2 and 3). Because the oxidant is involved in the activated complex, we can deduce that electron transfer from the sulfide to the oxidant, at the cathodic site, is the rate-determining step. Studies of the oxidation of galena, sphalerite, chalcocyprite, and arsenopyrite (Rimstidt et al., 1994) show that this is also true for these minerals, and it is likely to be generally true. The exact nature of the cathodic site and the structure of the activated complex have not yet been documented, but there is evidence that electrons are transferred to the oxidant from metal sites in the mineral surface rather than from sulfur sites. For example, studies of the interaction of the pyrite [001] surface with O\(_2\) and H\(_2\)O conducted under ultrahigh vacuum conditions using scanning tunneling microscopy, along with ultraviolet photoelectron spectroscopy, support this view (Rosso et al., 1999). Surfaces exposed to O\(_2\) show oxidative consumption of low-binding-energy electrons occupying dangling bond surface states localized on surface Fe atoms. When O\(_2\) is combined with H\(_2\)O, there is a more aggressive oxidation of the surface, with discrete oxidation "patches" where reacted surface Fe sites have lost surface state density to the sorbed species. Thus, for pyrite, the activated complex might involve the transfer of an electron to a hydrated Fe\(^{3+}\) adsorbed from solution from Fe\(^{2+}\) in the mineral surface.

\[ \text{py-Fe}^{2+} + \text{Fe}^{3+}(\text{H}_2\text{O})_6 = \text{py-Fe}^{3+} \cdot \text{Fe}^{2+}(\text{H}_2\text{O})_6. \]

The Fe\(^{2+}\) is then released back to the solution, and an electron moves from an anodic site (described below) to reduce the Fe\(^{3+}\) back to Fe\(^{2+}\). Likewise, Lowson (1982) proposed a Fenton-type mechanism for the reduction of O\(_2\) at the surface of oxidizing pyrite. First, O\(_2\) adsorbs at the Fe\(^{2+}\) site, and this
is followed by the transfer of an electron from this site to the O$_2$:

$$\text{py-Fe}^{3+} + \text{O}_2 = \text{py-Fe}^{3+} + \text{O}_2^- \quad (4)$$

Then, a hydrogen ion reacts with the oxygen to produce HO$_2^-$, and concurrently, an electron moves from an anodic site (described below) to reduce the Fe$^{3+}$ back to Fe$^{2+}$. This allows another electron to be transferred to the oxygen.

$$\text{py-Fe}^{2+} + \text{O}_2^- = \text{py-Fe}^{2+} + \text{O}_2 \quad \text{H}^+ \quad (5)$$

An additional hydrogen reacts with this peroxide group to produce H$_2$O$_2$, and concurrently, an electron moves from an anodic site (described below) to reduce the Fe$^{3+}$ back to Fe$^{2+}$. The transfer of a third electron from the Fe$^{2+}$ to the peroxide converts one of the oxygen atoms to a hydroxyl ion that is released to the solution and the other to a $\cdot$OH radical:

$$\text{py-Fe}^{2+} + \text{O}_2^- + \text{H}^+ = \text{py-Fe}^{2+} + \text{OH}^- + \text{OH}^\cdot \quad (6)$$

The Fe$^{3+}$ is again recycled to Fe$^{2+}$ by the transfer of another electron from the anodic site, and this electron moves to the $\cdot$OH radical to convert it to $\text{OH}^-$, which is released to the solution:

$$\text{py-Fe}^{2+} + \cdot \text{OH} = \text{py-Fe}^{2+} + \text{OH}^- \quad (7)$$

Then, a final electron moves from an anodic site to reduce the Fe$^{3+}$ back to Fe$^{2+}$, leaving the site the same as it was in the beginning of the process, even though four electrons were transferred through it.

### 2.2. Electron Transport

Clearly, the transport of electrons through the pyrite from the anodic site to the cathodic site from which they are transferred to the oxidant is a very important step in the oxidation process. Pyrite, like other sulfide minerals, is a semiconductor. The conductivity of pyrites varies widely between 0.02 and 562 (Ω cm)$^{-1}$, with an average value of 48 (Ω cm)$^{-1}$ (Pridmore and Shivey, 1976; Doyle and Mirza, 1996). The conductivities of p-type pyrites are generally much lower than those of n-type samples, the mean conductivities being 0.5 and 56 (Ω cm)$^{-1}$ for p-type pyrites and n-type pyrites, respectively. Presumably, much of this variation in conductivity is related to the trace element composition. Pyrite exhibits considerable variability in terms of chemistry and electrical properties (Abraitis et al., 2003). Minor elements actually held within the lattice may include As (9.6 wt.%), Co (2.2 wt.%), Sb (0.7 wt.%), Au (0.3 wt.%), and Ni (0.2 wt.%), where the values in parentheses are the maximum reported values. Cu, Ag, and Sn may also occur as minor elements in the lattice but are typically present within mineral inclusions. Trace elements in pyrite include Ag, Bi, Cd, Hg, Mo, Pb, Pt, Ru, Sb, Se, Te, Ti, and Zn. Pyrite exhibits both n-type and p-type semiconducting behavior, and within a single pyrite specimen, there may exist zones exhibiting alternate n- and p-type behavior. Maps of typical trace element zoning in pyrite are shown in Craig et al. (1998). The S:Fe ratios of p-type pyrites are often > 2. These materials also often contain significant quantities of As. The n-type pyrites may be sulfur deficient (i.e., have S:Fe ratios < 2) and may be relatively rich in Co and Ni.

Although there have often been claims of significant differences in the reactivity of pyrite and marcasite, the experimental evidence currently available does not bear them out. One of the few studies that has compared the reactivity of pyrite and marcasite from several sources (Wiersma and Rimstidt, 1984) showed that the most extreme difference between the rates of oxidation of pyrite and marcasite samples from several different sources was less than an order of magnitude and that the differences between most samples are approximately within the uncertainty of the rate measurements ($\pm 50\%$) (see Fig. 4). The relatively good correlation between the rate data from experiments done in several different laboratories with several
The free energy of formation of marcasite and pyrite is only 1.7 J/mol, or 
\( \Delta G^\circ = -1180.8 \text{ kJ/mol} \) (data from Robie and Hemmingway, 1995), but the difference in the
free energy of formation of marcasite and pyrite is only 1.7 
kJ/mol, or \(-0.14\%\) of this total. Thus, there is only a tiny
difference between the chemical potential driving the oxidation of
marcasite and pyrite so that any difference in their rates of
oxidation would be best explained as either the result of vari-
ations in the reaction mechanism or the speci-
cies. Rosso (2001), who provided an extensive review
of the reactivity of semiconducting minerals, reported that the
band gap of pyrite is 0.95 eV, whereas that of marcasite is 0.34 
eV, so that there should be more electrons in the conduction
band of marcasite, relative to pyrite, that would be available to
transfer to the oxidant. Variation in the band gap of different
samples resulting from impurity contents may be sufficient to
explain the relatively narrow range of observed oxidation rates
within and among pyrite and marcasite samples. However, it is
also possible that the trace element sites themselves participate
as cathodic sites so that the number of cathodic sites varies as
a function of trace element content. Together, these effects
could easily account for the \( \sim 1 \) order of magnitude range of
observed oxidation rates for pyrite and marcasite samples.

Still, there is no doubt that samples of pyrite and marcasite from
different sources seem to deteriorate at much different
rates during storage. Museum curators have long recognized
that different samples of pyrite and marcasite display a wide
range of reactivity (Howie, 1992). The best explanation for this
observation available at this time was provided by Caruccio
(1975), who pointed out that the one factor that seems to most
affect the acid production rates for coal mine wastes is the size
of the pyrite grains. Laboratory measurements have consistently
shown that the oxidation rate is directly proportional to
the exposed surface area. Therefore, it is not surprising that
rocks that contain frambooidal pyrite, which consists of micron-
or submicron-sized crystals that have very high specific surface
areas, produce acid at much higher rates than rocks containing
larger sized pyrite or marcasite grains. Furthermore, when
pyrite or marcasite oxidizes in moist air, salt weathering tends
to fracture the crystals to increase the surface available for
reaction. Salt weathering occurs because the molar volume of
pyrite, 23.9 cm\(^3\), is much smaller than the molar volume of
melanterite, 146.5 cm\(^3\) (Robie and Hemmingway, 1995), so
when pyrite oxidation produces melanterite, or a similar hy-
drous iron sulfate salt, that crystallizes in the fractures and
wedges the crystal apart, more and more surface area is created
as the oxidation proceeds. This results in the well-known phe-
nomenon of “pyrite disease,” which destroys museum samples
of pyrite and marcasite. Thus, it appears that variations in
exposed surface area, which can be different by many orders of
magnitude, are a much more important factor in controlling
oxidation rate than composition or crystal structure, which
seem to cause rate variations of \(< 1 \) order of magnitude.

2.3. Anodic Reaction

2.3.1. Oxidation Products

Sulfide mineral oxidation removes seven electrons from di-
sulfide sulfur or eight electrons from sulfide sulfur to form
sulfate. This means that the sulfur atoms must pass through
several oxidation states during the oxidation process, so many
different sulfur compounds might be involved. Because of the
importance of sulfur in technology and in the environment,
there have been many studies of the oxidation of aqueous sulfur
species (e.g., Bamford and Tipper, 1972; Braga and Connick,
1982; Golodets, 1983; Martin and Hill, 1987; Anderson et al.,
1989; Viaravanmurthy and Zhou, 1995), and minor amounts of
some of these aqueous species have been identified in labora-
tory experiments (e.g., Goldhaber, 1983; Moses et al., 1987).
However, most evidence suggests that aqueous sulfur species
other than sulfate are not present at significant concentrations in
AMD where Fe\(^{3+}\) is the most important oxidant and the pH is
low. If a significant amount of sulfur species other than sulfate
were produced under AMD conditions, there would be two or

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**Fig. 4.** Comparison of the rate of oxidation by ferric iron of pyrite and marcasite samples from various sources, showing that these rates do not vary systematically and differ by no more than \( \pm 1 \) log unit. Data from Weirsma and Rimstidt (1984).
more reservoirs of sulfur species, each with a different sulfur isotope fraction factor, and each of the resulting species, including sulfate, would have a sulfur isotope ratio that differs from the original sulfide mineral(s). Most studies of the sulfur isotope systematics of AMD show that the sulfur isotope ratio of the sulfide closely matches the sulfur isotope ratio of the sulfides (see the review by Toran and Harris, 1989). This evidence suggests that sulfate is the predominant oxidation product. Although some thiosulfate was found in the experiments of Moses et al. (1987) and Goldhaber (1983), it would not persist in AMD solutions. The laboratory studies of Williamson and Rimstidt (1993) showed that thiosulfate quickly forms a highly colored, purple complex with ferric iron so that even relatively small amounts of thiosulfate are visible in solutions that contain ferric iron. This complex decomposes to form tetrathionate and ferrous iron. In acidic solutions that lack significant amounts of dissolved ferric iron, thiosulfate reacts to form sulfite and very long chain polythionates that precipitate from solution as yellowish-white colloids (Davis, 1958). These polythionates eventually decompose to elemental sulfur. Neither tetrathionate nor elemental sulfur is found in significant amounts in association with weathering pyrite, leading us to suggest that aqueous sulfur species other than sulfate are not important players in the AMD environments, but they might occur in higher pH situations.

2.3.2. The Multistep Sulfur Oxidation Process

Because so many electrons must be removed from each sulfur atom to oxidize it to sulfate, this oxidation process is by far the most complex and difficult to understand process in sulfide mineral oxidation. Because it is unlikely that more than one electron is removed from the sulfur atom at a time (Basolo and Pearson, 1967), there must be several steps to this overall process. Williamson and Rimstidt (1992) investigated the thermodynamic stability of the aqueous species that might be intermediates in this oxidation process and showed that there is no simple step-by-step path whereby this reaction can occur via aqueous intermediates (Fig. 5). This is an argument in favor of the idea that almost all of the sulfur remains on the mineral surface throughout the oxidation process.

There is evidence that for many sulfide minerals, the first step in oxidation produces a sulfur-enriched surface, both on pyrite (Buckley and Woods, 1987) and on many other sulfide systems (see, e.g., Kartio et al., 1998). However, this is difficult to prove conclusively by experiment because sulfur, as a volatile species, is easily lost from the surface before analysis, particularly in standard ultrahigh vacuum surface analysis instruments. In the more extreme cases, this may involve the partial oxidation of sulfide sulfur to sulfide sulfur as in the oxidation of pyrrhotite (po) to form marcasite (mc) with ejection of Fe$^{2+}$ into solution to maintain charge balance:

$$2\text{Fe}_{1-x}\text{S}(\text{po}) + \left(\frac{1-x}{2}\right)\text{O}_2 + 2(1-x)\text{H}^+ = (1-x)\text{Fe}^{2+} + \text{FeS}_2(\text{mc}).$$

This type of “oxidative dissolution” reaction is common in sulfide minerals; for example, Goble (1981) showed that it is responsible for forming the so-called blaubleibender covellite:

$$\text{py-S-S} = \text{py-S-S}^+ + e^-, \quad \text{py-S-S}^+ + \text{H}_2\text{O} = \text{py-S-SOH} + \text{H}^+.$$  

so that the negative end of the water dipole can mount a nucleophilic attack on this electropositive sulfur to produce a S-OH and release a hydrogen ion to solution:

$$\text{py-S-S}^+ + \text{H}_2\text{O} = \text{py-S-SOH} + \text{H}^+.$$  

This hydrogen ion balances the positive charge lost from the solution at the cathodic site as an electron is transferred into the oxidant. The next electron removed from the mineral allows the S-S-OH group to release the second hydrogen to solution:

$$\text{py-S-S-OH} = \text{py-S-SO} + e^- + \text{H}^+. \quad \text{(11)}$$

This cycle is repeated to produce py-S-SO$_2$, two more electrons, and two more hydrogen ions,

$$\text{py-S-SO} = \text{py-S-SO}_2 + 2e^- + 2\text{H}^+. \quad \text{(12)}$$

and then repeated again to produce py-S-SO$_3$, two more electrons, and two more hydrogen ions:

$$\text{py-S-SO}_2 = \text{py-S-SO}_3 + 2e^- + 2\text{H}^+. \quad \text{(13)}$$

At this point, if the cation in the sulfide mineral is a relatively soft acid, there is a tendency for this species to break away from the surface as a thiosulfate complex:

$$\text{py-S-S-O}_3 = \text{py} + \text{MS}_3\text{O}_4. \quad \text{(14)}$$

The final step in the sulfur oxidation process appears to depend upon the pH. At high pH, the terminal S-SO$_4$ completely ionizes, making the S-S bond stronger than the Fe-S bond. As a result, much of the sulfur is released to solution as S$_2$O$_3$$^{2-}$. At low pH, the majority of the terminal S-SO$_4$ groups retain a proton, so they have the stoichiometry, S-SO$_3$H. This encourages the transfer of electrons into the S-S bond, where they are more easily transferred to the cationic site, leaving the terminal sulfur with a very positive charge. This leads to a fourth nucleophilic attack by a water molecule to produce SO$_2$$^-$, which is released into the solution. Note that for cations that are soft bases, it is possible that an entire M-S-SO$_4$ moiety is released to the solution. Therefore, there appears to be a range of aqueous sulfur products ranging from almost 100% sulfate in
low-pH solutions to a fairly high proportion of thiosulfate and related products at higher pH.

Withdrawal of the last electron from the sulfoxyl group to produce py-S-S$^-$ and one more water molecule reacts with the terminal sulfur to produce bisulfate:

$$\text{py-S-S}^- + \left( \frac{1}{x} + \frac{1}{2} \right) \text{H}_2\text{O} + \left( \frac{3x - y - 1}{2x} \right) \text{O}_2 = \text{SO}_3^- + \left( \frac{2 - 2}{x} \right) \text{H}^+.$$  

(15)

This sequence of reactions consumes four water molecules and produces eight hydrogen ions per sulfur oxidized (see Eq. (2)) and accounts for the seven electrons that must be removed from each disulfide sulfur, S(-I), to produce sulfate sulfur, S(VI). This suggests that most, if not all, of the oxidation steps involve surface sulfur species. Figure adapted from Williamson and Rimstidt (1992).

2.4. A Specific Case: Pyrite Oxidation in Acid (1 mol/L HCl) Solution

The reactions at the anodic sites are the most difficult to document both because they are quite complex and because they cannot easily be studied using the standard kinetic methods for the rate-determining step. Instead, the nature of these reactions must be inferred by combining information from several sources. One of the most important of these is electrochemical study of pyrite oxidation.

The specific case of oxidation of pyrite in 1 mol/L HCl was discussed by Kelsall et al. (1999) in the light of electrochemical studies combined with spectroscopic investigations of the altered pyrite surface. This provides a useful example with which to develop the ideas presented above. The electrochemical data for the specific pyrite investigated showed very little reaction over a relatively wide range of potentials (between −0.4 and +0.6 V vs. S.C.E.). This was attributed to reversible adsorption/desorption of water and protons. Recalling that pyrite has a cubic crystal structure with Fe$^{2+}$ ions at the corners and face centers of the cube unit cell and dumbbell shaped disulfide S$_2$ ions at the center of the cube and the midpoints of the cube edges, when pyrite is immersed in 1 mol/L HCl, H$^+$ ions can approach a Lewis base site S$_2$ and be adsorbed on it.
whereas the oxygen atom of water will be liable to approach a Lewis acid site Fe$^{2+}$ and be adsorbed. However, as a positive potential is applied to the pyrite electrode, the electron cloud is pulled toward the bulk pyrite, leaving the positive end of a S$^{2-}$ dipole exposed to the electrolyte. The adsorbed H$^+$ ions will be forced to desorb from the disulfide sites, and the oxygen atom of water will turn to these disulfide sites and be adsorbed here instead:

$$\text{Fe-S-S} \cdot \text{OH}_2 - e^- = \text{Fe-S-SOH} + \text{H}^+. \quad (18)$$

The main arguments for proposing that S$^{2-}$ rather than Fe$^{2+}$ loses an electron first may be stated as follows:

1. The nonbonding t$_{2g}$ electrons in FeS$_2$ are localized and less reactive, whereas the antibonding t$_{2g}$ electrons are delocalized and more reactive (see, e.g., the discussion in Tossell and Vaughan, 1992).
2. The ionization energy required to transform Fe$^{2+}$ to Fe$^{3+}$ is 2957 kJ mol$^{-1}$, much greater than that required to transform S$^2-$ to S$^+$, 999 kJ mol$^{-1}$ (National Bureau of Standards, 1970).
3. The standard Gibbs functions and experiment results indicate that Fe$^{3+}$ ions can oxidize FeS$_2$ to S or SO$_4^{2-}$ (see, e.g., reaction 2).

Therefore, under a positive applied potential, electrons in $\Pi^a$ orbitals of S$^{2-}$ would be lost first rather than those in t$_{2g}$ orbitals of Fe$^{2+}$. Such electron transfer processes would continue if a positive external potential were applied to the pyrite, resulting in the following reactions:

$$\text{Fe-S-SOH} + \text{H}_2\text{O} - e^- = \text{Fe-S-S(OH)}_2 + \text{H}^+. \quad (19)$$

$$\text{Fe-S-S(OH)}_2 + \text{H}_2\text{O} - e^- = \text{Fe-S-S(OH)}_3 + \text{H}^+. \quad (20)$$

$$\text{Fe-S-S(OH)}_3 - e^- = \text{Fe-S-SO(OH)}_2 + \text{H}^+. \quad (21)$$

$$\text{Fe}(\text{OH})_2 - e^- = \text{Fe-SSO}_3(\text{OH}) + \text{H}^+. \quad (22)$$

$$\text{Fe-SSO}_3(\text{OH}) - e^- = \text{Fe-SSO}_4 + \text{H}^+. \quad (23)$$

At this stage, it would be difficult to attach further water molecules to the sulfur atom and achieve electron transfer until the Fe-S or S-S bonds are broken. The Fe-S bond is relatively weaker than the S-S bond, so that the former would be broken to produce

$$\text{Fe-SSO}_3 = \text{Fe}^{3+} + \text{SO}_4^{2-}. \quad (24)$$

On release into the electrolyte, six water molecules would octahedrally coordinate the Fe$^{2+}$ ions. The ligand field imposed by the six water molecules is weaker than that imposed by the six S$^{2-}$ in pyrite so that the six 3d electrons of Fe$^{2+}$ will change into a high-spin configuration. This will make the Fe(H$_2$O)$^+$ easier to oxidize to Fe$^{3+}$ than Fe$^{2+}$ in pyrite because the latter is in a low-spin configuration. As is well known, S$_2$O$_3^{2-}$ is unstable in acid solution (1 mol/L HCl) and will decompose very quickly to form

$$\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ = \text{S} + \text{H}_2\text{SO}_4. \quad (25)$$

There are, however, uncertainties remaining regarding the importance of thiosulfate as a product, particularly when ferric iron is the oxidant, and this is another aspect of the oxidation of pyrite requiring further investigation.

### 3. CONCLUSIONS

The oxidation of pyrite is a complex electrochemical process requiring the transfer of seven electrons from each sulfur atom through the semiconducting crystal to an oxidant. This paper provides a brief summary of our attempt to create an internally consistent chemical and electrochemical model of the steps that must occur as pyrite oxidizes to form ferrous iron and sulfate ions.

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