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The dissolution and leaching of minerals Mechanisms, myths and misunderstandings

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ABSTRACT

The dissolution of minerals is of importance to a number of fields of endeavour. In particular, it is the rate of dissolution that is important. Knowledge of the kinetics might allow the rate to be accelerated or retarded, depending on the field of endeavour. In understanding the mechanism of dissolution, it is the order of reaction that is of particular interest. The kinetics of dissolution of minerals are frequently found to be close to one-half order in the oxidant. The electrochemical mechanism of dissolution describes this dependence. However, a number of misunderstandings about the dissolution of minerals and the electrochemical mechanism recur, and need to be addressed. This paper addresses seven of these misunderstandings, and makes the following conclusions: (i) mechanism is not the same as chemical pathway, (ii) there is no separation of the surface into anodic sites and cathodic sites, (iii) there is no flow of electrons across the bulk of the mineral, (iv) the oxidation and reduction reactions are coupled by the transfer of electrons, not by a chemically bonded activated state, (v) polysulphides do not passivate the surface, (vi) the first step of the dissolution reaction is not by acid, and (vii) the solids do not need to be electrical conductors to dissolve by the electrochemical mechanism.

1. Introduction

Leaching is a central unit operation in the hydrometallurgical processing of minerals (Crundwell et al., 2011). Often a leaching stage is one of the initial operations in the process, and as a result the efficiency of leaching has a primary effect on the technical and economic success of a hydrometallurgical business. For this reason a great deal of attention has been focused on the study of dissolution reactions, and particularly on the kinetics of these reactions. An accurate understanding of the kinetics of dissolution is required in order to interpret the complex behaviour of leaching reactors, and to optimise the performance of a hydrometallurgical operation.

All dissolution reactions in aqueous solutions involve the movement of charge across the solid–solution phase boundary (Crundwell, 1987, 1988a,b; Verbaan and Crundwell, 1986). In this sense all dissolution reactions have an electrochemical step, and the mechanism of the reaction is electrochemical in nature.

Significant progress has been made towards the understanding of the mechanism of these leaching reactions as a result of the intense focus that dissolution reactions have received. This progress has been driven by the need to improve processing operations and has been delivered by research that has integrated knowledge from fields as diverse as metallurgy, chemistry, mineralogy, electrochemistry and microbiology. Like all fields of endeavour, this progress has not been linear. In searching for new knowledge, hypotheses are advanced. Sometimes hypotheses become accepted before being tested. On other occasions, simplifications that aid in explanation become the accepted view. The purpose of this paper is to discuss some of these persistent misconceptions. In particular, the following questions are addressed:

1. Is 'mechanism' the same as chemical pathway?
2. Is the surface divided into separate sites for the oxidation and reduction half-reactions?
3. Is there flow of electrons across the bulk of the mineral during dissolution?
4. How are the oxidation and reduction reactions coupled?
5. Do polysulphides cause passivation of the surface?
6. Is the first step of the dissolution reaction an acid attack?
7. Does the solid need to be an electrical conductor to dissolve by the electrochemical mechanism?

The paper is structured in the following manner. In the next section, the meaning of mechanism in the context of dissolution is clarified. The background electrochemistry is summarised in the section following this. Following this, the electrochemical mechanism of dissolution is derived. Several misunderstandings of the electrochemical mechanism are clarified. The correspondence between the model and the theory is then confirmed and several case studies are presented. Finally, two hypotheses on mechanism are challenged.

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2. What is meant by "the mechanism of dissolution"?

The term mechanism can be construed to mean different things in chemistry. One meaning might be that the mechanism is the pathway by which the reaction occurs. A second meaning might be that the mechanism is the rate-controlling step, in other words, the mechanism of the reaction is the more accurately described by the term "kinetic mechanism".

While the reaction pathway is undoubtedly important in several areas of chemistry, it is the rate of reaction and the kinetic mechanism, that is of primary interest. We wish to determine what controls the rate of reaction so that we can understand it, manipulate it, and alter it. Such information is critical to the design and interpretation of hydrometallurgy reactions so that these processes might be improved and controlled with confidence. It is also critical to our scientific knowledge. How can we say we know the mechanism of reaction if we do not know how to accelerate or retard its rate? Knowledge only of the pathway does not provide us with sufficient information to understand the factors that influence the rate of reaction.

In order to determine the kinetic mechanism of a reaction, one usually needs to propose or determine the reaction pathway up to the point of the slowest step in a series of reaction steps. This step is referred to as the "rate-controlling step". Steps beyond the rate-controlling step usually have little or no influence on the rate of the overall reaction, and as a result are of lesser importance. Thus, knowledge of the reaction pathway is not sufficient to determine the kinetic mechanism.

The assertion and its justification that we are interested in the kinetic mechanism have important consequences. It means that, in order to determine the mechanism, a researcher needs kinetic parameters. An observation of a chemical species on the surface or in solution does not necessarily mean that this chemical species is important or influences the rate of reaction. We discuss the general assertion by numerous researchers that polysulphides passivate the dissolution reaction later in this paper. Polysulphides are undoubtedly present on the mineral surface of sulphides. However, little or no evidence is presented by these researchers that the rate of dissolution of these materials is actually hindered by polysulphides. In terms of mechanism, the observation of surface species is not helpful in itself. In order to assist in the understanding of mechanism, the researchers must also show that the observed chemical species influences the rate of reaction. In other words, the observed surface species might not influence the kinetics of reaction. To say that the observed species does without supporting evidence is unjustifiable. In order to propose a mechanism of dissolution, the mechanism must be supported by the measured kinetic parameters.

The rates of dissolution or leaching reactions are influenced by the concentration of reagents in solution and the temperature. Consequently, the two kinetic parameters are the order of reaction and the activation energy. These two kinetic parameters are described in the following equation for the rate of reaction:

$$\text{rate} = k[c]^n \exp(-E_A/RT) \quad (1)$$

where [c] represents the concentration of a reagent, k the rate constant, n the order of reaction, E_A the activation energy, R the gas constant, and T the temperature.

The two parameters are the activation energy E_A and the reaction order n. Generally, the activation energy is below 20 kJ/mol for diffusion-controlled reactions in the aqueous phase, and it is above 40 kJ/mol for chemical-controlled reactions. Unfortunately, the activation energy conveys no more information that is useful in the determination of the mechanism of dissolution than this.

The kinetic parameter that is of most importance in determining the mechanism of dissolution is the order of reaction. It describes how the rate is dependent on the concentration of reagent. If the reagent is dependent on oxygen and the value of n is one, then the reaction is said to be "first order in the concentration of oxygen"; if n is one half, the reaction is "one-half order in oxygen."

For example, diffusional processes always have an order of reaction that is one. If the order of reaction is not one, then the rate-determining step in the mechanism of dissolution cannot be diffusion.

If the order of reaction is the important kinetic parameter for the mechanism of dissolution, what are the orders of the reaction for oxidative and reductive dissolution reactions? Is there any pattern? These questions are considered in the next section.

3. What do the kinetic parameters for mineral dissolution suggest?

The orders of reaction for a large number of oxidative and reductive dissolution reactions are shown in Tables 1 and 2. These systems cover a great range of minerals and dissolution chemistry, from metals to

Table 1
Orders of reaction for the oxidative dissolution of some minerals.

Mineral	Oxidant	Medium	Reactants		Order of reaction		Ref.
Au	O_2	Cyanide	O_2	CN^-	0.5	0.5	Crundwell and Godorr (1997)
Au	I_3^-	Iodide	I_3^-	I^-	0.5		Angelidis et al. (1993)
Au	$C_2H_6N_4S_2$	Acid thiourea	$C_2H_6N_4S_2$		0.5		Li and Miller (1999)
Ag	Cu^{2+}	NH_3	$Cu(NH_3)_4^{2+}$		0.5		Guan and Han (1994)
Si	Cr^{6+}	Fluoride	Cr^{6+}	HF	0.5	−0.5	Heimann (1984)
Ge	H_2O_2	Fluoride	H_2O_2	HF	0.5	0.7	Schwartz (1967)
UO_2	Fe^{3+}	Sulphate	Fe^{3+}		0.5		Nicol et al. (1975)
FeS_2	O_2	Sulphate	O_2	H^+	0.5	−0.5	McKibben and Barnes (1986), Bailey and Peters (1976)
FeS_2	O_2	Alkali	O_2		0.31		Koslides and Ciminelli (1992)
FeS_2	O_2	Alkali	O_2		0.5		Ciminelli and Osseo-Asare (1995)
FeS_2	Fe^{3+}	Sulphate	Fe^{3+}	Fe^{2+}	0.5	−0.5	Williamson and Rimstidt (1994), Holmes and Crundwell (2000)
ZnS	Fe^{3+}	Sulphate	Fe^{3+}		0.45		Crundwell (1987, 1988c), Souza et al. (2007)
ZnS	Fe^{3+}	Chloride	Fe^{3+}		0.5		Dutrizac and MacDonald (1978), Crundwell (1988a,c)
$CuFeS_2$	O_2	Sulphate	O_2		0.35		Yu et al. (1973)
$CuFeS_2$	Fe^{3+}	Chloride	Fe^{3+}		0.5		Majima et al. (1985)
$CuFeS_2$	Cu^{2+}	Chloride	Cu^{2+}	Cu^+	0.45	−0.5	Hirato et al. (1987)
Ag_2S	O_2	Cyanide	O_2		0.5		Burkin (1966)
PbS	O_2	Hydroxide	O_2		0.5		Anderson et al. (1963)
PbS	Fe^{3+}	Nitrate	Fe^{3+}		0.5		Fuerstenau et al. (1987)
PbS	Fe^{3+}	Chloride	Fe^{3+}		0.21		Warren et al. (1987)
FeS	O_2	Sulphate	O_2		0.5		Filippou et al. (1997)
CuS	Fe^{3+}	Chloride	Fe^{3+}		0.5		Hirato et al. (1989)
$NiFeS_{1.8}$	O_2	Sulphate	O_2		0.5		Corrans and Scholtz (1976), Schneerson et al. (1966)
Ni matte	Fe^{3+}	Sulphate	Fe^{3+}		0.5		Dry (1984), Dry and Bryson (1987)

Table 2
Orders of reaction for the reductive dissolution of some minerals.

Mineral	Reductant	Medium	Reactants		Order of reaction		Ref.
MnO_2	SO_2	Sulphate	SO_2		0.5		Miller and Wan (1983)
MnO_2	Fe^{2+}	Sulphate	SO_2	H^+	0.5	0.5	Tekin and Bayramoglu (1993)
FeOOH	SO_2	Sulphate	SO_2	H^+	0.5	0.5	Kumar et al. (1993)
Fe_2O_3	Fe^{2+}	Sulphate	Fe^{2+}	Fe^{3+}	0.5	−0.5	Bruyere and Buesa (1985)
$ZnOFe_2O_3$	Fe^{2+}	Sulphate	Fe^{2+}	Fe^{3+}	0.6	−0.5	Elgersma et al. (1992)

elemental semiconductors through base metal sulphides. The variation in the solution chemistry is also large, with chloride, sulphate, fluoride and other systems represented.

It is remarkable that most of the values for the order of reaction for these systems are consistently close to 0.5 for the oxidant and −0.5 for the reductant. The concentration of the acid is important in very few of these reactions.

There are two conclusions that can be drawn from this information: (i) the data suggests that the mechanism that controls the rate of reaction of all these reactions is the same; and (ii) the rates of these reactions do not seem to be affected by the concentration of H^+ in solution.

Because the concentrations of the oxidant and reductant are important, these results also suggest that the rate-determining step might be the transfer of electrons at the mineral surface during leaching. Consequently, the electrochemical theory of dissolution, which is based on the transfer of electrons being the rate-determining step, is discussed in the next section.

4. What theory describes the kinetic parameters for the dissolution of minerals?

The value of the order of reaction with a value of one half is very significant, because it is difficult to imagine a series of elementary reactions at the mineral surface that combine to give an overall value of one half.

There are five highly significant factors that any mechanism of dissolution needs to account for:

1. The mechanism is not dependent on the reaction stoichiometry, because the stoichiometry of the reactions given in Tables 1 and 2 is different.
2. The mechanism is not be dependent on the nature of the mineral surface, because the order of reaction is the same for minerals that are metals, sulphides, oxides, and elemental semiconductors.
3. The mechanism is not dependent on the products, because the products of the dissolution reactions shown in Tables 1 and 2 are different.
4. The mechanism has the same rate-determining step, because the orders of reaction are the same for all these reactions.
5. The mechanism is not dependent on whether the reactions are oxidation or reductive, because Tables 1 and 2 show that the orders of reaction are the same for both oxidative and reductive reactions.

These five factors place a significant burden on any proposed mechanism.

One general theory that might be proposed is that of surface adsorption. Surface adsorption is described by adsorption isotherms, such as the Langmuir, Temkin and Freundlich isotherms. Langmuir isotherms give rise to kinetic expressions that are either first order or zero order. Freundlich isotherms are non-linear, but there is no reason why they would give rise to a consistent value for the order of reaction of one half.

Two other theories have been proposed and are currently invoked on a frequent basis in the case of the dissolution of sulphides:

(i) that polysulphide layers limit the diffusion of ions at the surface, and
(ii) that there is an initial attack by protons to form hydrogen sulphide.

Diffusional processes can only be first order. Consequently, diffusional processes cannot describe the one-half order kinetics shown in Tables 1 and 2. Thus, diffusion through the polysulphide layer is rejected.

The proposal that the initial step is proton attack should produce rates of reaction that are highly dependent on the concentration of acid (or the pH). However, such a dependency is not observed. An additional factor is that it is frequently found that the rate of the proton attack is slower than that with an oxidant. This means that as an initial step, proton attack is too slow to sustain the rate of the overall reaction.

Both these proposals, which are discussed in further detail later in this paper, are rejected.

In contrast, the electrochemical mechanism of dissolution has a clear and natural explanation for the consistency of the prime kinetic parameters, that is, the orders of reaction. This theory, which will be discussed in detail in the next section, posits that it is the transfer of charge between the mineral and the oxidant at the surface that is the rate-determining step.

5. A model that describes the kinetic parameters: the electrochemical mechanism of dissolution

Dissolution reactions involve the breaking of bonds on the surface of the mineral to form a charged ion. This charged ion moves from the solid phase to the aqueous phase, where bonds are formed in the solution. Thus, dissolution is concerned with the movement of charge from the solid phase to the aqueous phase. In this section, the dissolution of a mineral by either an oxidative or a reductive reaction will be described in terms of the movement of ions and electrons between the mineral and the solution.

The boundary between the mineral and the leaching solution is charged. This charge across this boundary arises because bonds at the solid surface are unsatisfied, and hence there is an excess charge at the surface. This excess charge is balanced by an equivalent charge in the solution close to the solid surface. In addition, there may be an exchange of charged species between the two phases that contributes to the balancing of charge at the solid surface. The balancing of excess charge on the solid surface with excess charge in the solution is referred to as the double layer. The charged nature of the boundary between mineral and solution can be measured as an electrical potential difference. This electrical structure of the interface including the balancing of charge by the double layer is shown in Fig. 1.

5.1. Transfer of ions across the mineral–solution phase boundary

The rate of transfer of an ion from a position on the solid surface to a position in the solution is dependent on the potential difference across the double-layer (Butler, 1924, 1932; Erdey-Grusz and Volmer, 1930).

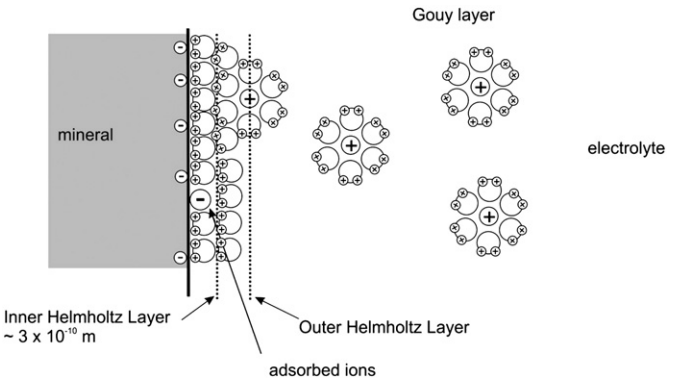

Fig. 1. A schematic diagram of the interface between the surface of a mineral and the solution.

As the ion moves from the surface into the solution the bonding with the solid is diminished and the interaction with the solvent becomes stronger. This change in bonding has an activation barrier with a saddle point within the double-layer. The height of the activation barrier is influenced by the potential difference across the double layer. This means that the rate of reaction, in this case the transfer of ions from the solid to the solution, can increase or decrease by increasing or decreasing the potential difference. Experimentally it has been found that there is an exponential relationship between the rate of transfer of ions and the applied potential difference.

The simplest ion transfer reaction is that which considers an elemental solid, A, undergoing dissolution (Gerischer, 1970). An atom of the solid at the surface has unsatisfied chemical bonds (because it is at the surface) and, hence is charged. This atom moves across the charged interface (double layer) from the solid surface to the solvent. This movement is the charge-transfer reaction:

$$A^{+}_{lat} + \text{solvent} = A^{+}(\text{solvent}) \tag{2}$$

where $A^{+}{}_{lat}$ is an atom of the lattice of the solid at the surface.

In this reaction, the surface ion, $A^{+}{}_{lat}$, is transferred from a position on the surface of the solid lattice to a position in the solution. In moving across the phase boundary, the ion is transferred over the potential-dependent activation barrier within the double layer. The rate of this ionic-transfer reaction is described by the Butler–Volmer equation (Butler, 1924, 1932; Erdey-Grusz and Volmer, 1930), and is given by the expression:

$$r = k_a\left[A^{+}_{lat}\right]\exp(\alpha z F V_H/RT) - k_c\left[A^{+}\right]\exp\{-(1-\alpha)zFV_H/RT\} \tag{3}$$

where $[A^{+}{}_{lat}]$ and $[A^{+}]$ refer to the surface and solution concentrations of A^{+}, V_H is the potential difference across the double layer with respect to a reference electrode, α is the transfer coefficient, and k_a and k_c are the rate constants for the forward (anodic dissolution) and backward (cathodic deposition) reactions, respectively.

The value of α is expected to be close to 0.5. It can be interpreted in the following terms. The activated state occurs when bonds with the surface are breaking and bonds with the solution species are forming. The solution species are located at the outer Helmholtz plane. The value of α is the distance that the activated complex is from the surface as a fraction of the distance between the surface and the solution species. Since the activated complex is probably halfway between the two, the value of α is expected to be one-half.

Eq. (3) can be re-written in the following more familiar form:

$$r = k^{1}{}_{a}\left[A^{+}_{lat}\right] - k^{1}{}_{c}\left[A^{+}\right]. \tag{4}$$

Comparison of Eqs. (3) and (4) indicates that the Butler–Volmer equation is the same as the kinetic expression for a first-order reversible reaction, except that the rate constants are dependent on the potential difference across the solid–solution interface.

5.2. Transfer of electrons across the mineral–solution boundary

Electrons, unlike atomic ions, are quantum particles, and the mechanism of transfer across the phase boundary is different to that of ions. Ions require sufficient energy to rise over the activation barrier. Electrons do not rise over an activation barrier; rather, they 'tunnel' through the barrier. The rate of electron transfer across the solid–solution boundary is dependent on the probability of tunnelling through the barrier (Gurney, 1931). This probability depends on the number of electronic energy levels on either side of the interface, and on the occupancy of these energy levels. The probability of an energy level in the solid being occupied is given by the Fermi distribution, and the probability of an energy level in the solution being occupied is given by the fluctuating-energy-level model (Gerischer, 1970; Green, 1959; Marcus, 1964; Morrison, 1980).

The simplest electron-transfer reaction is that in which a redox couple (A^{2+} / A^{+}) in solution interacts with an electron in an inert solid:

$$A^{2+}(aq) + e(\text{solid}) = A^{+}(aq). \tag{5}$$

If changes in the potential difference across the phase boundary are manifested predominantly as changes in the double layer, then it can be shown that an equation similar in form to the Butler–Volmer equation describes the rate of electron transfer (Gurney, 1931):

$$r = k_a\left[A^{+}\right]\exp(\alpha F V_H/RT) - k_c\left[A^{2+}\right]\exp\{-(1-\alpha)FV_H/RT\}. \tag{6}$$

The value of α is expected to be close to one-half at metal–solution interfaces. It is also expected to be one half for semiconductors if the Fermi level of the semiconductor is pinned (Green, 1959) or if the semiconductor is degenerate (Morrison, 1980).

Dissolution and corrosion reactions often result in a change in oxidation state, and these reactions can be separated into an anodic half-reaction and a cathodic half-reaction. Other dissolution reactions, such as the non-oxidative dissolution of oxides and sulphides can be analysed in terms of the transfer of anions and cations across the phase boundary. Both the transfer of ions and the transfer of electrons contribute to the dissolution of minerals.

These electrochemical equations are used in the next section to derive a theory of dissolution.

5.3. Kinetic mechanism for oxidative leaching

The main features of the electrochemical mechanism of dissolution reactions are illustrated by considering the dissolution of a mineral M in an aqueous solution containing the oxidant B^{2+}. The reaction may be written as:

$$M(s) + B^{2+}(aq) \rightarrow M^{+}(aq) + B^{+}(aq). \tag{7}$$

The half-reaction for the dissolution of the mineral is irreversible, and is given by:

$$M(s) \rightarrow M^{+}(aq) + e \tag{8}$$

and the half-reaction for the reduction of the oxidant might be reversible. This half-reaction is given by:

$$B^{2+}(aq) + e^{-} = B^{+}(aq). \tag{9}$$

The general requirement for the dissolution of a particle is that the sum of the rates of the anodic reactions is equal to the sum of the rates of the cathodic reactions (Wagner and Traud, 1938). This means that:

$$r_a = r_c \tag{10}$$

where r_a and r_c are the rate of the anodic and cathodic reactions. This condition means that there is no accumulation of charge: every electron donated by Eq. (8) is *instantaneously* accepted by Eq. (9).

The rate of the dissolution half-reaction is given by Eq. (6). If the half-reaction is considered to be irreversible, then the rate of the anodic half-reaction is given by:

$$r_a = k_a \exp(\alpha_a F V_H/RT). \tag{11}$$

The rate of the cathodic half-reaction is given by Eq. (6), and if this half reaction is considered reversible, then the rate of the cathodic half-reaction is given by:

$$r_c = k_c\left[B^{2+}\right]\exp\{-(1-\alpha_c)FV_H/RT\} - k_c^1\left[B^{+}\right]\exp(\alpha_c FV_H/RT). \quad (12)$$

The substitution of these expressions for r_a and r_c, into Eq. (10) gives the following expression:

$$k_a\exp(\alpha_a FV_H/RT) = k_c\left[B^{2+}\right]\exp\{-(1-\alpha_c)FV_H/RT\} - k_c^1\left[B^{+}\right]\exp(\alpha_c FV_H/RT). \quad (13)$$

The values of α_a and α_c are close to one half. If it is assumed that $\alpha_a = \alpha_c = \alpha$, the potential of the dissolving surface is given by the following equation for the potential of the corroding surface:

$$V_H = \frac{F}{RT}\ln\left(\frac{k_c\left[B^{2+}\right]}{k_a + k_c^1[B^{+}]}\right). \quad (14)$$

The potential of the dissolving surface is also referred to the mixed potential, after the corrosion theory of Wagner and Traud (1938). It can be measured independently, providing an additional source of information on the mechanism of dissolution.

The substitution of this expression for V_H back into Eq. (11) yields the following result for the rate of dissolution:

$$r_{diss} = k_a\left(\frac{k_c\left[B^{2+}\right]}{k_a + k_c^1[B^{+}]}\right)^{0.5} \quad (15)$$

where r_{diss} represents the rate of dissolution (which is equal to r_a and r_c). It has been assumed that $\alpha_a = \alpha_c = 0.5$ in this derivation, which is justified because the values of both α_a and α_c are expected to be about 0.5.

Eq. (15) has two limiting forms: (i) if $k_a \gg k_c^1[B^+]$, then the rate of dissolution is given by the following equation:

$$r_{diss} = (k_a)^{0.5}\left(k_c\left[B^{2+}\right]\right)^{0.5} \quad (16)$$

and (ii) if $k_a \ll k_c^1[B^+]$, then the rate of dissolution is dependent on the ratio of the concentrations of the oxidant, B^{2+}, and its reduced form, B^+, and the corresponding expression for the rate of reaction is given by:

$$r_{diss} = k_a\left(\frac{k_c\left[B^{2+}\right]}{k_c^1[B^{+}]}\right)^{0.5}. \quad (17)$$

If k_a and $k_c^1[B^+]$ are of similar magnitude, then the full form of Eq. (15) is required.

The rates of the anodic and cathodic reactions as a function of the potential across the phase boundary are illustrated in Fig. 2. The mineral dissolves at the potential at which Eq. (14) is obeyed, that is, at the mixed potential. The mixed potential is determined by the reaction processes occurring at the mineral surface as a result of the condition given by Eq. (10). The rate of dissolution is given by either r_a or r_c at the mixed potential.

Eq. (15) was first presented by Nicol et al. (1975) in their studies of the dissolution of UO_2 in ferric sulphate solutions. Bailey and Peters (1976) soon afterward derived a rate equation that was half-order in the concentration of the oxidant in their study of the dissolution of pyrite, while Jones and Peters (1976) showed that the mixed potential of chalcopyrite was described by Eq. (14).

5.4. Kinetic mechanism for reductive leaching

The kinetics of reductive leaching, such as the reduction of pyrolusite (MnO_2) by sulphur dioxide, is rarely discussed in the context of the electrochemical mechanism of dissolution. However, these types of reactions have a similar mechanism to oxidative dissolution. It is straightforward to show that the rate of dissolution for a reductive leaching reaction is given by the following expression:

$$r_{diss} = k_c\left(\frac{k_c[B^{+}]}{k_c + k_a^1[B^{2+}]}\right)^{0.5} \quad (18)$$

where $[B^+]$ is the concentration of the reductant reacting with the mineral, and $[B^{2+}]$ is the concentration of its oxidized form.

The order of reaction with respect to the reductant is expected to be close to 0.5.

6. Verifying the electrochemical mechanism of dissolution

The expression for the rate of dissolution of a mineral undergoing oxidative dissolution:

$$r_{diss} = k_a\left(\frac{k_c\left[B^{2+}\right]}{k_a + k_c^1[B^{+}]}\right)^{0.5}. \quad (15)$$

The results shown in Table 1 indicate that this mechanism broadly describes the oxidative dissolution of many dissolving minerals. The primary kinetic parameter, the order of reaction, is elegantly described by Eq. (15).

Similarly, the rate of the reductive dissolution is given by the expression:

$$r_{diss} = k_c\left(\frac{k_c[B^{+}]}{k_c + k_a^1[B^{2+}]}\right)^{0.5}. \quad (18)$$

This rate expression, derived from the principle that the rate determining step is the charge transfer across the mineral solution interface, elegantly describes the primary parameter for determining the mechanism of reaction, that is, the order of reaction, values of which are given in Table 2.

We placed five conditions on the required mechanism in Section 4 above. The electrochemical mechanism of dissolution meets all of these criteria:

(i) the mechanism is not dependent on the reaction stoichiometry;
(ii) the mechanism is not be dependent on the nature of the mineral surface;
(iii) the mechanism is not dependent on the products of the reaction;
(iv) the mechanism has the same rate-determining step for all oxidative and reductive reactions; and,
(v) the mechanism is not dependent on whether the reactions are oxidation or reductive.

The electrochemical mechanism of dissolution meets all of these criteria.

Although there are views to the contrary, such those of Habashi (2002) and Tributsch (1999) who assert that there is no transfer of electrons and the breaking of bonds is due to the forces of hydration, the evidence is weighted in favour of the electrochemical mechanism.

7. Clarification of some common misunderstandings

At this point it is worth discussing several common misunderstandings of the electrochemical mechanism of dissolution. These misunderstandings are the belief that there are separate anodic and cathodic sites,

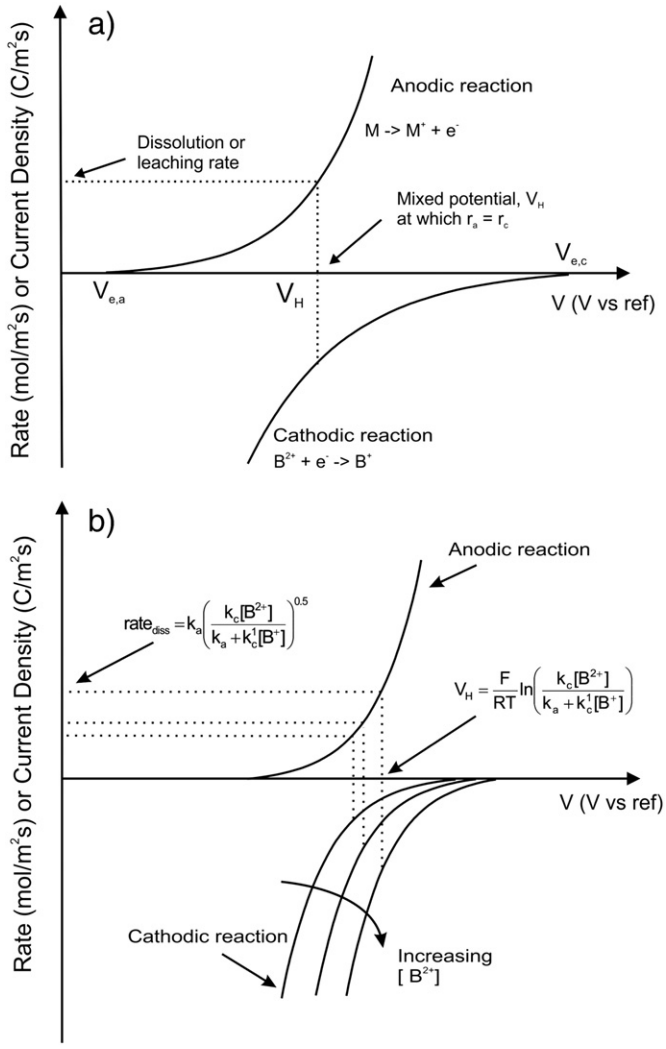

Fig. 2. The dissolution of a mineral by the electrochemical mechanism. (a) Anodic and cathodic processes, showing the formation of the mixed potential and the rate of dissolution. (b) The effect of changing the concentration of the oxidant in solution on the mixed potential and the rate of dissolution.

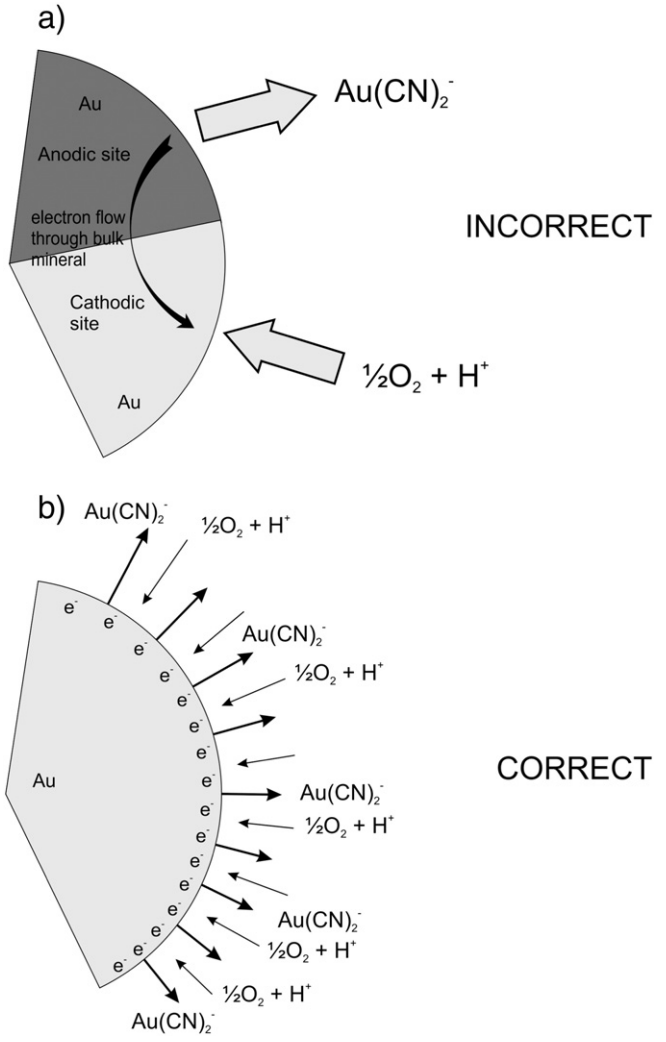

Fig. 3. The dissolution of a mineral. (a) The separation of the anodic and cathodic sites, which is incorrect. (b) The whole surface is both anodic and cathodic — it is at one potential, the mixed potential.

that there is bulk transfer of electrons across the solid, and that there are chemical intermediates that bond the reactants to another. Although these three aspects are related, they are discussed separately in the sections that follow.

7.1. Are there anodic and cathodic sites?

One of the classic diagrams for the explanation of the electrochemical mechanism of dissolution shows the anodic and cathodic sites separately, and electrons flowing from the one type of site to the other through the bulk of the mineral. This type of diagram is shown in Fig. 3.

Several authors propose separate anodic and cathodic sites. For example, Rimstidt and Vaughan (2003) talk extensively of anodic and cathodic sites, and of the flow of electrons from the anodic site to the cathodic site through the bulk of the material. The derivation of the rate of gold dissolution by Habashi (1966) explicitly accounts the areas of the surface that are devoted to the anodic sites and that to the cathodic sites.

Unfortunately, this view implies two things that are flawed:

(i) that the anodic and cathodic sites exist and are physically separated, and
(ii) that there is flow of electrons through the bulk of the material.

The first flaw, that the sites are physically separated, requires that the anodic and cathodic sites be at different electrical potentials. This is because a driving force, an electrical potential, is required to drive the electrons from the anodic sites to the cathodic sites.

The electrochemical mechanism of dissolution does not envisage different potentials at different points on the surface — the entire surface is at the same potential, the mixed potential, given by Eq. (14). The anodic dissolution and cathodic reduction half-reactions are envisaged as occurring at all points on the mineral surface (unless the mineral is clearly heterogeneous, as in the case of galvanic couples — see Holmes and Crundwell, 1995). Every point on the surface is both an anodic site and a cathodic site.

In summary, the electrochemical mechanism of dissolution requires that all parts of the surface of the mineral simultaneously entertain the anodic and cathodic half-reactions.

7.2. Is there flow of electrons across the bulk of the solid?

The second flaw in the "separate sites" explanation discussed above is that there is bulk flow of electrons through the mineral. Bulk flow of electrons cannot occur because there is no driving force between anodic and cathodic points. All points are at the same potential, the mixed potential, which means that there is nothing to drive electrons from one end of the mineral to the other. In addition, bulk flow of electrons

is not required for the electrochemical mechanism of dissolution, because dissolution is a surface phenomenon, not a bulk phenomenon.

Neither do the anodic and cathodic half-reactions occur at different times. Quite the contrary — since there is no accumulation of charge by Eq. (10), the anodic and cathodic half-reactions must occur simultaneously.

In summary, the electrochemical mechanism of dissolution is a surface phenomenon and does not require flow of electrons in the solid.

7.3. How are the two half-reactions coupled to one another?

The overall reaction, Eq. (7), is separated into anodic and cathodic half-reactions, Eqs. (8) and (9), for the derivation of the model. This separation of reaction is an abstract construct that has been created to show the participation of electrons in the overall reaction. An interesting question arises: how are these two half reactions coupled to each other? Is the oxidant chemically bound to the surface? Is there a chemical intermediate state that links the surface and the oxidant during the reaction?

Consider, for example, the dissolution of pyrite by oxygen. This reaction is given as follows:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+. \quad (19)$$

Bailey and Peters (1976) showed that the atomic oxygen in the sulphate product comes from water, not from oxygen. This means that the separation of the reaction into the following half reactions has merit:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 16H^+ + 14e^- \quad (20)$$

$$O_2 + 4H^+ + 4e^- = 2H_2O. \quad (21)$$

Most importantly, the results of Bailey and Peters (1976) mean that the coupling between the two half reactions is not through a chemical intermediate or 'activated state', as one would expect from other types of chemical reactions. The coupling is through the transfer of electrons at the surface.

An interesting aspect of electron transfer is that electrons can transfer across distances that are several atoms or molecules thick. Electron tunnelling, as it is known, can occur at distances that are up to 30 Å, that is, up to 30×10^{-10} m (Morrison, 1980). Since the size of atoms is of the order of several Angstroms, there is no requirement for direct contact with the surface or chemisorption of the oxidant on the surface. The interaction can be at a distance with a layer or more of water molecules between the surface and the oxidant.

This aspect of electron transfer is remarkable. The 'activated state' is not the formation of a chemical that is halfway between the reactant and product, but the simultaneous stretching of the bonds in the surface and the solution so that electron transfer can occur at a distance.

This aspect of electron transfer distinguishes the kinetic study of dissolution reactions from other types of chemical reactions. The most important step in the reaction, and the mechanism by which the reactants interact to become products, is the transfer of electrons across the solid–solution interface.

In summary, there is no requirement for chemical coupling of the reactants as an activated state. Rather, the reactants interact through the transfer of electrons, which can occur across considerable distance.

7.4. Does the electrochemical mechanism of dissolution only apply to metal-like conductors?

There is a common misunderstanding that the electrochemical mechanism of dissolution applies only to metallic conductors. This is not true — Crundwell (1988a) derived the electrochemical mechanism of dissolution for the sphalerite, an insulator, using fundamental quantum electrochemistry. The derivation by Crundwell (1988a) showed the electronic coupling to be synchronous: electrons are removed by the oxidant directly from the bond that is breaking.

This model of synchronous coupling of electron transfer is illustrated in Fig. 4. The atoms on the surface of the mineral are only partially bonded to the bulk of the mineral because of the termination of the crystal structure. Due to thermal vibration, they are in constant motion, a motion that stretches and stresses this partial bond with the bulk of the mineral. As the bond stretches, it reaches a point where the electron forming the bond is able to transfer or 'tunnel' to the oxidant. The atom that is leaving the surface stretches the bond to a point where the electron can be captured by the oxidant. This results in the simultaneous dissolution of the ion in solution and the reduction of the oxidant.

This view is interesting because there is no need to invoke a metallic surface for the electrochemical mechanism of dissolution to apply. This understanding of the electrochemical mechanism of dissolution is particularly important in the interpretation of the dissolution of minerals in which the electrical conductivity is low.

There is no requirement that only minerals that are metallic conductors can dissolve by the electrochemical mechanism of dissolution.

8. Case studies

The development of the theory discussed in Section 5 was for a generalized reaction. The case studies presented in this section are chosen to demonstrate the application of the theory to specific reactions, and show in more detail the application of the model. In particular, four case studies of both chemical and bacterial leaching are discussed.

8.1. Dissolution of gold by cyanide and oxygen

Gold is most often leached in cyanide solutions in the presence of oxygen. The reaction occurs according to the stoichiometry:

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^-. \quad (22)$$

It has often been argued that the dissolution of gold in cyanide solutions is controlled by the diffusion of the cyanide and oxygen reactants to the surface of the gold particles. However, diffusion processes control

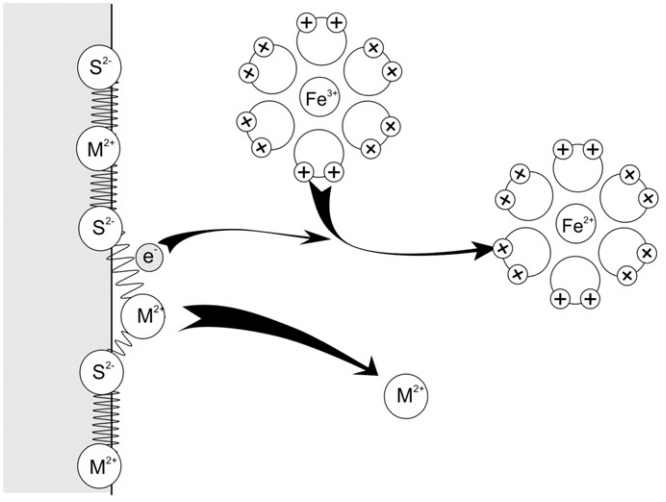

Fig. 4. The synchronous model of electrochemical dissolution. The bond in the solid stretches to the point where the energy level of the electron is equal to the energy level in the oxidant, at which point electron transfer takes place by tunnelling through the energy barrier at a distance to the oxidant in solution. There is no need for bonding, either fully or partially, between the surface and the oxidant. See Crundwell (1988a,c) for a derivation of this model.

the rate of dissolution for reactions that are rapid. For example, the dissolution of sugar and table salt is diffusion-controlled processes, and their rates of reaction are rapid in comparison to the leaching of gold and other minerals.

Crundwell and Godorr (1997) proposed that the charge transfer at the particle surface, rather than the diffusion of reactants to the gold surface, controls the rate of reaction.

The reaction may be separated into its electrochemical half-reactions. The anodic half-reaction is:

$$Au + 2CN^- \rightarrow Au(CN)_2^- + e^- \quad (23)$$

and the cathodic reaction is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-. \quad (24)$$

The kinetics of the anodic half-reaction may be described by Eq. (5). The anodic dissolution reaction has been found to be first order in cyanide, possibly because the first step in the reaction sequence is the adsorption of cyanide onto the gold surface (see Crundwell and Godorr, 1997). If we consider the reaction to be far from equilibrium so that the reverse reaction does contribute, then the rate of the anodic half-reaction may be given by:

$$r_a = k_a[CN^-]\exp(\alpha_a F V_H/RT). \quad (25)$$

The kinetics of the cathodic half-reaction may be described by Eq. (5). If the reaction is far from equilibrium, then the rate of the cathodic half-reaction is given by:

$$r_c = k_c[O_2]\exp\{-(1-\alpha_c)FV_H/RT\}. \quad (26)$$

The rate of production of electrons is equal to the rate of the consumption of electrons, so that $r_a = r_c$, given by Eq. (10). Eliminating V_H from Eqs. (25), (26) and (10), and rearranging to obtain a solution for the rate of reaction give:

$$r_{diss} = (k_a[CN^-])^{1-x}(k_c[O_2])^x \quad (27)$$

where $x = \alpha_a / (1 - \alpha_c + \alpha_a)$ and the values of α_a and α_c have been assumed to be close to 0.5, as suggested by electrochemical theory. Thus, the rate of the dissolution of gold is given by:

$$r_{diss} = k[CN^-]^{0.5}[O_2]^{0.5}. \quad (28)$$

The effect of the concentrations of cyanide and oxygen on the rate of gold leaching is shown in Figs. 5 and 6. This data, from Crundwell and Godorr (1997) and McLaughlin and Agar (1991), shows that the rate of dissolution is given by:

$$r = k[CN^-]^{0.47}[O_2]^{0.51}. \quad (29)$$

The rate of reaction has a one-half order dependence on the concentrations of cyanide and oxygen.

The electrochemical theory and the experimental data are in good agreement, suggesting that the rate of leaching of gold in cyanide solutions is controlled by the transfer of charge at the surface of the particle rather than by the diffusion of cyanide and oxygen to the surface, which has previously been thought to be the controlling mechanism. The order of reaction would be first order if the reaction was controlled by diffusion.

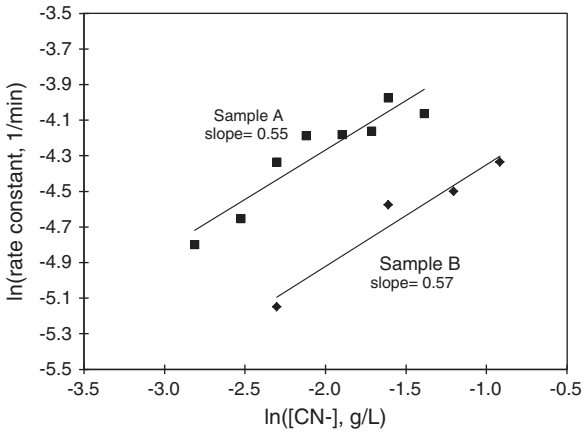

Fig. 5. Effect of the concentration of cyanide on the rate of dissolution (Crundwell and Godorr, 1997). Conditions: 21 °C, pH 10.3, 5 g/L boric acid, 50% solids, 7.1 mg/L O_2.

8.2. Dissolution of pyrite (FeS_2)

Pyrite is the most common sulphide mineral, and its dissolution is of great significance due to its role in the formation of acid mine drainage. Pyrite dissolves by the following reactions:

$$FeS_2 + 8H_2O + 14Fe^{3+} \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (30)$$

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+. \quad (31)$$

The overall reaction can be written in terms of the half-reactions for the oxidation of pyrite and the reduction of ferric ions and oxygen. The half-reaction for the oxidation of pyrite is given by:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 16H^+ + 14e^- \quad (32)$$

and the reduction of ferric ions and oxygen is given by:

$$Fe^{3+} + e^- = Fe^{2+} \quad (33)$$

$$O_2 + 4H^+ + 4e^- = 2H_2O. \quad (34)$$

Holmes and Crundwell (2000) extensively investigated each of these half-reactions and investigated the overall reaction. These measurements

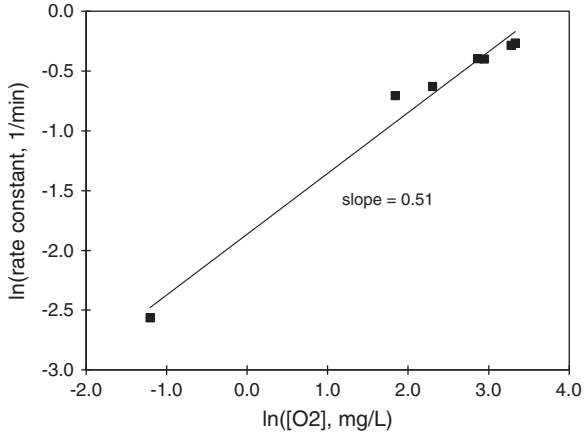

Fig. 6. Effect of the concentration of oxygen on the rate of dissolution (Crundwell and Godorr, 1997).

showed that the kinetics of the half-reaction for the anodic dissolution of pyrite is given by:

$$r_{FeS_2} = k_{FeS_2}\left[H^+\right]^{-1/2}\exp\left(\alpha_{FeS_2}FV_H/RT\right) \quad (35)$$

and that the half-reaction for the reduction of ferric ions is given by:

$$r_{Fe} = k_{Fe}\left[Fe^{3+}\right]\exp\{-(1-\alpha_{Fe})FV_H/RT\} - k^1_{Fe}\left[Fe^{2+}\right]\exp(\alpha_{Fe}FV_H/RT). \quad (36)$$

The order of reaction of −0.5 with respect to H^+ for the anodic reaction indicates that reaction consists of some steps, possibly involving adsorbed hydroxide ions, prior to the rate-determining step. (As an aside, the order of reaction with respect to H^+ has not been satisfactorily explained for several different types of reactions involving H^+ and iron. For example, the oxidation of ferrous ions by dissolved oxygen has an order of reaction with respect to H^+ of between −0.25 and −0.35 (Verbaan and Crundwell, 1986). This order of reaction has not been explained, and awaits some diligent research to unlock the steps in the mechanism.)

8.2.1. The dissolution of pyrite by ferric ions

A rate expression for the reaction of pyrite with *ferric ions* is derived first. The substitution of Eqs. (35) and (36) into Eq. (10) yields the following expression for the mixed potential:

$$V_H = \frac{F}{RT}\ln\left(\frac{k_{Fe}\left[Fe^{3+}\right]}{k_{FeS_2}[H^+]^{-1/2} + k^1_{Fe}\left[Fe^{2+}\right]}\right). \quad (37)$$

The substitution of this equation for the mixed potential into Eq. (35) yields the rate equation for the oxidative dissolution of pyrite by ferric ions:

$$r_{diss} = \frac{k_{FeS_2}[H^+]^{-1/2}}{14}\left(\frac{k_{Fe}\left[Fe^{3+}\right]}{k_{FeS_2}[H^+]^{-1/2} + k^1_{Fe}\left[Fe^{2+}\right]}\right)^{1/2}. \quad (38)$$

If $k_{FeS_2}\left[H^+\right]^{-1/2}$ is much less than $k^1_{Fe}[Fe^{2+}]$ (which Holmes and Crundwell, 2000 determined is valid when $[Fe^{2+}]$ is greater than 0.001 M) then Eq. (38) can be written as follows:

$$r_{diss} = k\left(\frac{\left[Fe^{3+}\right]}{[H^+]\left[Fe^{2+}\right]}\right)^{1/2}. \quad (39)$$

Eq. (39) predicts that the rate of dissolution of pyrite is one-half order in ferric ions and negative one-half order in H^+. Fowler et al. (1999, 2001) determined the rate of dissolution of pyrite. These results from these experiments, shown in Figs. 7 and 8, are in agreement with the theory of Holmes and Crundwell (2000).

A large number of experimental investigations of the rate of dissolution of pyrite by ferric ions have been completed. The results of the most recent of these investigations are compared with the electrochemical mechanism in Table 3. It is clear that the electrochemical mechanism derived by Holmes and Crundwell (2000) correctly describes the experimental rate equations.

8.2.2. The dissolution of pyrite by oxygen

The second rate expression is that for the dissolution of pyrite by *oxygen*. Holmes and Crundwell (2000) measured the cathodic reduction of oxygen on pyrite, and showed that the order of reaction with respect to H^+ is 0.14. Using this result, they derived an expression for the rate of dissolution of pyrite in the presence of oxygen, which is given as follows:

$$r_{diss} = \frac{k_{FeS_2}[H^+]^{-0.18}}{14}\left(\frac{k_{O_2}[O_2]}{k_{FeS_2}}\right)^{1/2}. \quad (40)$$

This result is compared with the experimentally determined rate equations in Table 4. The experimental expressions in Table 4 are closely related to the electrochemical mechanism, suggesting that the dissolution of pyrite occurs as described by the electrochemical mechanism derived by Holmes and Crundwell (2000). This result was confirmed by Rimstidt and Vaughan (2003).

A powerful feature of the electrochemical mechanism of dissolution is the prediction of the mixed potential, which can be used in addition to measurements of the rate of reaction to confirm the mechanism. Holmes and Crundwell (2000) conducted an extensive experimental investigation of the mixed potential of pyrite in the presence of both ferric ions and oxygen.

The effect of the concentrations of ferric and ferrous ions on the mixed potential of pyrite is shown in Figs. 9 and 10. The slope of the

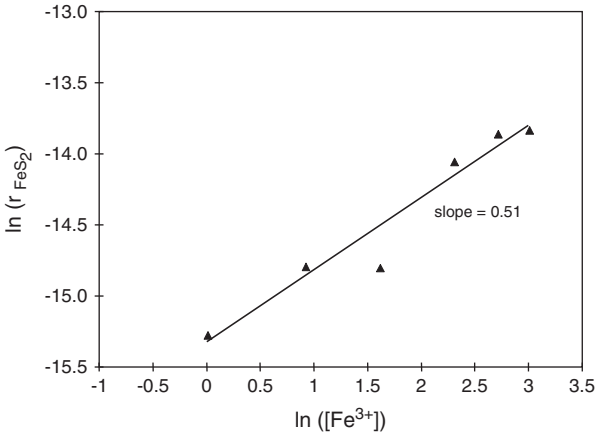

Fig. 7. Effect of the concentration of ferric ions on the rate of dissolution of pyrite, showing that the order of reaction is 0.5 (Fowler et al., 1999, 2001). It is important to note that the conditions, in particular the pH and the concentrations of Fe^{2+} and Fe^{3+}, were held constant for the entire duration of the experiment. Conditions: 35 °C; pH 1.3; 1.0 g/L Fe^{2+}; 10 g/L solids; 5.9 mg/L O_2.

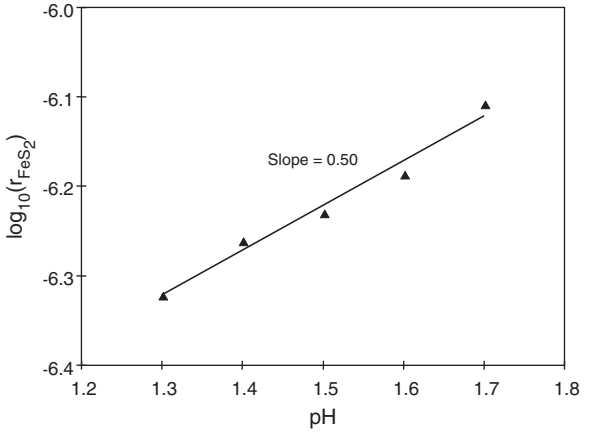

Fig. 8. Effect of the pH on the rate of dissolution of pyrite, showing that the order of reaction with respect to H^+ is −0.5 (Fowler et al., 1999, 2001). It is important to note that the conditions, in particular the pH and the concentrations of Fe^{2+} and Fe^{3+}, were held constant for the entire duration of the experiment. Conditions: 35 °C; pH 1.3; 1.0 g/L Fe^{2+}; 5.0 g/L Fe^{3+}; 10 g/L solids; 5.9 mg/L O_2.

Table 3
Comparison of experimentally measured rate expressions with the electrochemical mechanism for the dissolution of pyrite by ferric ions.

Description	Rate expression	Reference
Empirical rate	$\text{rate} = \frac{k[Fe^{3+}]^{0.58}}{[H^+]^{0.5}}$	McKibben and Barnes (1986)
Empirical rate	$\text{rate} = \frac{k[Fe^{3+}]^{0.3}}{[H^+]^{0.32}[Fe^{2+}]^{0.47}}$	Williamson and Rimstidt (1994)
Electrochemical mechanism with experiment validation	$\text{rate} = \frac{k[Fe^{3+}]^{0.5}}{[H^+]^{0.5}[Fe^{2+}]^{0.5}}$	Holmes and Crundwell (2000)

mixed potential is 0.059 mV/decade, which is in good agreement with the theoretical value. There are two limiting forms to the theoretical value of the mixed potential. If $k_{FeS_2}[H^+]^{-1/2}$ is much less than $k^1_{Fe}[Fe^{2+}]$, then the predicted value of the slope of the mixed potential is −0.059 mV/decade. Again, the experimentally determined value of −0.056 mV/decade is close to this theoretical value. Thus, the experiments of the mixed potential confirm the theory. The predicted effect of the pH was confirmed by Holmes and Crundwell (2000).

8.3. Dissolution of sphalerite (ZnS)

The dissolution of sphalerite in ferric sulphate or ferric chloride solutions occurs according to the reaction:

$$ZnS + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+} + S^\circ. \quad (41)$$

Verbaan and Crundwell (1986) and Crundwell (1987, 1988a,b) studied this reaction in both chloride and sulphate media and reported the results in a series of papers. Essentially, they demonstrated that the reaction was one-half order in ferric ion, and negative one-half order in ferrous ions.

Experimental results for the orders of reaction were determined by Fowler (2000). These results are shown in Figs. 11 and 12, which supports the earlier experimental work of Verbaan and Crundwell (1986).

These results show that the rate of reaction is described by the following kinetic expression:

$$r_{diss} = k_a \left(\frac{k_c[Fe^{3+}]}{k^1_c[Fe^{2+}]} \right)^{0.5}. \quad (42)$$

Consequently, Crundwell (1987, 1988a) concluded that the rate determining step is the transfer of charge at the mineral surface.

Iron occurs as an impurity in all natural samples of sphalerite. This iron has a pronounced effect on the rate of dissolution. Crundwell (1988a,c) presented experimental results that showed that the rate of dissolution is directly proportional to the iron content in the sphalerite. Values of the rate constant for four samples of sphalerite are shown in Fig. 5. Palencia-Perez and Dutrizac (1991) confirmed this result on a larger sample size.

Sphalerite is a semiconductor with a wide band-gap, which is another way of saying that it is an electrical insulator. The valence band is comprised of electron orbitals that are of bonding character, and the conduction band is comprised of electron orbitals that are of non-bonding character. In order for this material to be dissolved by an oxidative mechanism, electrons must be removed from the bonding orbitals, that is, from the valence band. The positive charge that arises from the removal of an electron from the valence band is referred to as a hole. As a result, for dissolution to occur bonding electrons must be removed from the valence orbital by the oxidant in solution.

Table 4
Comparison of experimentally measured rate expressions with the electrochemical mechanism for the dissolution of pyrite by oxygen.

Description	Rate expression	Reference
Empirical rate	$\text{rate} = k[O_2]^{0.5}$	McKibben and Barnes (1986)
Empirical rate	$\text{rate} = \frac{k[O_2]^{0.5}}{[H^+]^{0.11}}$	Williamson and Rimstidt (1994)
Electrochemical mechanism with experiment validation	$\text{rate} = \frac{k[O_2]^{0.5}}{[H^+]^{0.18}}$	Holmes and Crundwell (2000)

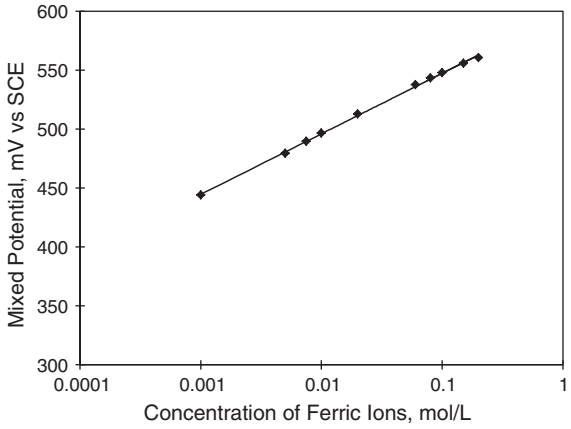

Fig. 9. Effect of the concentration of ferric ions on the mixed potential for pyrite. The slope of the line is in agreement with the theory proposed by Holmes and Crundwell (2000). Conditions: 0.037 M H_2SO_4, 1 M Na_2SO_4, 25 °C, N_2 sparged, pyrite electrode rotated at 250 rpm.

The presence of iron that substitutes for zinc atoms in the sphalerite lattice results in a *d*-orbital band within the band-gap of sphalerite. The iron *d*-orbitals of this band are of bonding character. This means that the removal of an electron from this band (injection of a hole) also results in dissolution of the solid. The iron impurity and its associated *d*-orbital band have two consequences for the dissolution of sphalerite: the *d*-orbital band presents a narrow localised band with which the transfer of electrons is energetically more favourable than it is with the valence band, and the *d*-orbital band 'pins' the Fermi level so that changes in the interfacial potential occur on the solution side of the interface rather than on the solid side.

Crundwell (1988a) used the principles of quantum electrochemistry to derive the following expressions for the rate of the anodic half-reaction:

$$r_a = k_a N_d \exp(\alpha_a F V_H / RT) \quad (43)$$

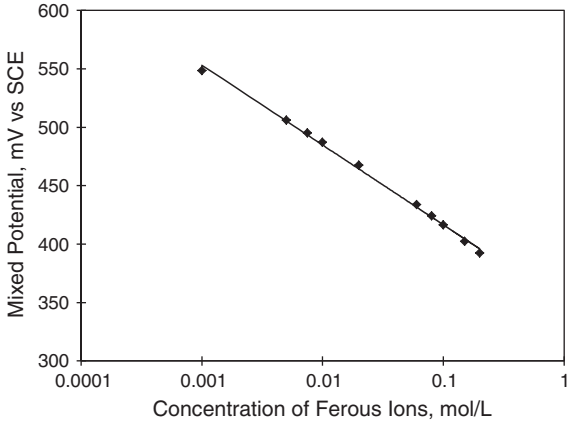

Fig. 10. Effect of the concentration of ferrous ions on the mixed potential for pyrite. The slope of the line is in agreement with the theory proposed by Holmes and Crundwell (2000). Conditions: 1 M Na_2SO_4, 0.025 M Fe^{3+}; 25 °C, N_2 sparged, pyrite electrode rotated at 250 rpm.

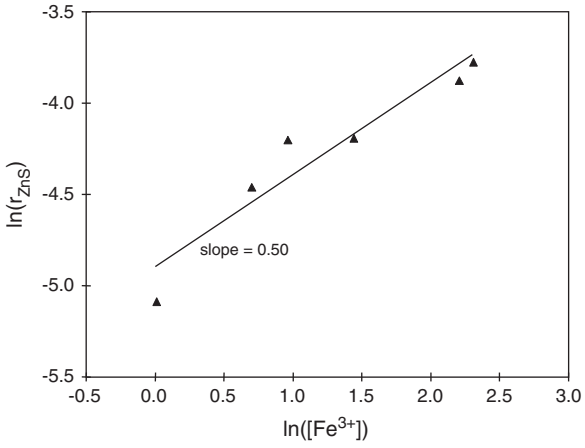

Fig. 11. The effect of the concentration of ferric ions on the rate of dissolution of sphalerite (Fowler, 2000). Conditions: 35 °C; pH 1.6; 1.0 g/L Fe^{2+}; 5.9 mg/L O_2; 5 g/L solids.

and for the cathodic half-reaction:

$$r_c = k_c N_d \left[Fe^{3+}\right] \exp\{-(1-\alpha_c)FV_H/RT\} - k_c^1 N_d \left[Fe^{2+}\right] \exp(\alpha_c FV_H/RT) \quad (44)$$

where N_d is the concentration of iron in the sphalerite (mol Fe/mol Zn).

Since $r_a = r_c$ by Eq. (10), V_H can be eliminated between Eqs. (43) and (44), giving the expression for the rate of the surface reaction:

$$r = kN_d \left(\frac{k_c\left[Fe^{3+}\right]}{k_c^1\left[Fe^{2+}\right]}\right)^{0.5} \quad (45)$$

where α_a and α_c have been assumed to be equal to one-half, in accordance with a rate determining step based on the transfer of charge.

This was the first extension of the electrochemical mechanism of dissolution to account for the effects of the composition of the mineral.

This equation indicates that the rate of reaction is proportional to the concentration of iron in the sphalerite and proportional to the square root of ferric ions in solution. This is consistent with the experimental results shown in Fig. 13 for the effect of the iron impurity, and the experimental results that focused on the orders of reaction with respect to species in solution shown in Figs. 11 and 12 previously.

An interesting feature is the effect of light on the rate of dissolution. Electrons can be excited from bonding orbitals at the surface by shining light on them if the energy of the light matches the band gap of the semiconductor. The results of such an experiment are shown in Fig. 14.

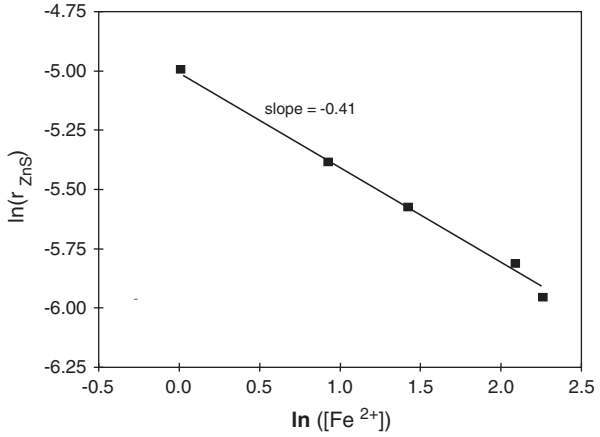

Fig. 12. The effect of the concentration of ferrous ions on the rate of dissolution of sphalerite (Fowler, 2000). Conditions: 35 °C; pH 1.6; 1.0 g/L Fe^{3+}; 5.9 mg/L O_2; 5 g/L solids.

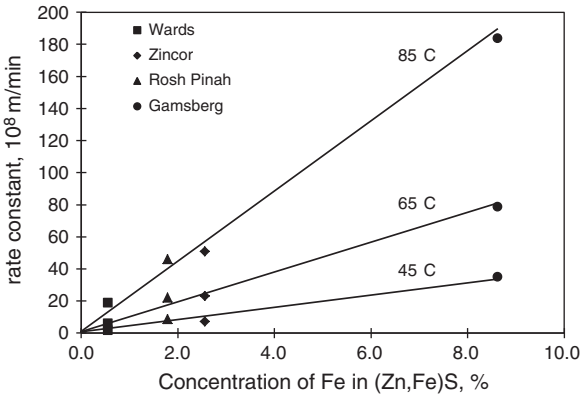

Fig. 13. The effect of the concentration of Fe as an impurity in the solid phase of sphalerite (Crundwell, 1988a). Conditions: 0.2 M $FeCl_3$, 0.3 M HCl, 0.005 M $FeCl_2$, 2 M NaCl.

Clearly, ultraviolet light increases the rate of reaction, which serves to confirm that the rate determining step in the dissolution of this mineral is the transfer of charge at the mineral surface. If the rate-determining step was not the transfer of charge, there would have been no effect as a result of shining ultraviolet light on the particles during dissolution.

8.4. Bacterial leaching

The technical arguments in determining a kinetic mechanism can be subtle; however, there is no area of kinetics more subtle than that where one of the reagents is a living organism.

The mechanism of the leaching of sulphide minerals by bacteria was the subject of continuous debate and conjecture from the time of the discovery of the organisms in 1950. One postulate was that bacteria attached to the surface of sulphides, and 'directly' leached the mineral. The alternative postulate was that bacteria enhanced the rate of oxidation of ferrous ions, and the resulting ferric ions leached the mineral.

The conceptual approach prevalent in the field for studying the mechanism of bacterial leaching was (i) observations of bacterial attachment, (ii) observations of surface changes after bacterial leaching, arguments based on stoichiometry, (iii) identification of biological agents that might possibly be responsible, and (v) leaching experiments with and without bacteria. This approach should have been profitable. However, the primary variable in the discussion of kinetic mechanism, the order of reaction, was not determined in any the previous work in the field of bacterial leaching and biohydrometallurgy. In addition, the concentration of the two of the primary reagents, that is, ferric and ferrous ions, varied considerably during the course of the reaction,

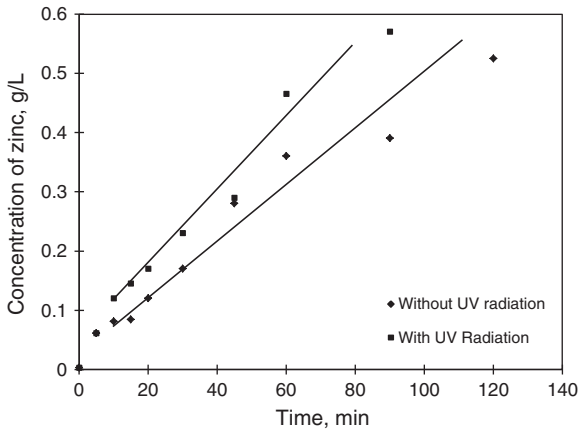

Fig. 14. The effect of UV radiation on the dissolution of the sphalerite sample from Ward's Scientific Museum. Conditions: 65 °C, 0.2 M $FeCl_3$, 0.3 M HCl, 0.005 M $FeCl_2$, 2 M NaCl.

invalidating direct comparison of experiments with and without bacteria.

Crundwell (1998) and Fowler et al. (1999, 2001) realized that a new approach was necessary to resolving this debate. In particular, their approach had four critical elements that were different from the approach adopted by others in the field of bacterial leaching:

(i) Crundwell (1998) and Fowler et al. (1999, 2001) re-defined the debate on bacterial mechanism from the participation of biological agents to the role of ferric ions in the reaction. If ferric ions were involved kinetically, they argued, then the mechanism was 'indirect', but if ferric ions were not involved, then the mechanism was 'direct'. In this formulation, the order of reaction with respect to ferric ions would be zero, because a biological agent, rather than ferric ions, would be more important. This was a crucial intervention, because it allowed the mechanism to be directly tested. Their re-definition of the terminology is illustrated in Fig. 15.

(ii) Fowler et al. (1999, 2001) realized that the standard experiments conducted in biohydrometallurgy could not determine the true effect of ferric ions because of the changing concentrations of ferric and ferrous ions during the experiments. In other words, the concentrations of ferric and ferrous ions varied widely over the experimental period, making it impossible to determine the kinetic parameters of the reaction.
In addition, the standard method in the field of bacterial leaching of comparing experiments with and without bacteria seriously prejudiced the chemical reaction because these experiments were, and still are, carried out with insufficient reagents. Thus, the chemical experiment ran out of oxidant, while the bacteria regenerated the oxidant.
As a result, Harvey and Crundwell (1997) developed a specialized reactor for measuring the rate of leaching while maintaining the concentrations of ferrous and ferric ions at a constant level. The rates of reaction were determined in a specially designed apparatus that maintained the concentrations of ferric and ferrous ions at a constant value throughout the duration of the experiment. This meant that the results from the chemical and bacterial experiments could be compared fairly, because the concentrations of ferric and ferrous ions were the same in both cases, and constant for the entire duration of the experiment. The experiments subsequently carried out by Fowler and Crundwell (1998), Fowler et al. (1999, 2001) and Holmes et al. (1999) in this apparatus probably rank as the most controlled dissolution studies ever carried out.

(iii) Fowler et al. (1999, 2001) and Holmes et al. (1999) made sure that these measurements were unbiased, in the sense that it tested the rate of reaction in the absence or presence of bacteria, and did so independently. If there was a biological contribution to the rate of reaction, it would show up clearly.

(iv) Fowler et al. (1999, 2001) and Holmes et al. (1999) adopted a conceptual approach based on the kinetic theory of leaching. They measured the kinetic parameters, the orders of reaction and the mixed potential, which up to that point had never been measured before for bacterial leaching systems.

These four steps represent a radical departure from the predominant paradigm of research in bacterial leaching.

The experimental results that were produced are clear and unambiguous: there is no direct biological attack of the mineral surface. The evidence for this unequivocal statement is first presented for sphalerite, and then for pyrite.

8.4.1. Bacterial leaching of sphalerite

The rate of leaching of sphalerite in the presence and absence of bacteria is shown in Figs. 16 and 17 as a function of the concentration of ferric and ferrous ions, respectively (Fowler, 2000). The results presented in these figures show that the rate of reaction and the orders of reaction for the dissolution of sphalerite do not change in the presence of bacteria. Because the orders of reaction and the rate of reaction are the same, the same mechanism is controlling the rate of reaction both in the presence and the absence of bacteria. This means that bacteria do not change the mechanism of reaction, which means that biological effects are limited to reaction steps that do not affect the rate-determining step.

In addition, the order of reaction is close to one-half, which is predicted by the electrochemical mechanism of leaching. In summary, the presence of bacteria does not change the mechanism of leaching since the rate and the order of reaction remain the same as they were in the absence of bacteria, and the leaching reaction is controlled by the electrochemical step for both with and without bacteria.

8.4.2. Bacterial leaching of pyrite

The rate of leaching of pyrite in the presence and absence of bacteria is shown in Fig. 18 as a function of the concentration of ferric ions. The results clearly show that the order of reaction remains the same in the

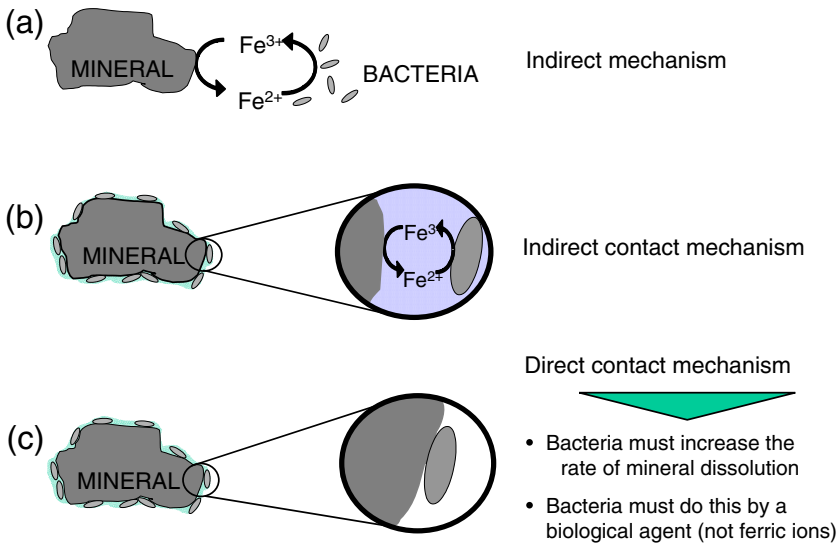

Fig. 15. The terminology developed to clarify the role of ferric and ferrous ions in the debate on bacterial leaching (Fowler et al., 1999, 2001; Holmes et al., 1999).

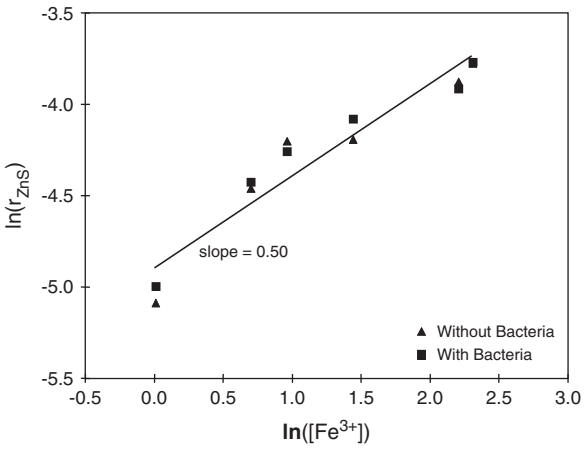

Fig. 16. The effect of the concentration of ferric ions on the rate of dissolution of sphalerite in the presence and absence of bacteria (Fowler, 2000). Since both reactions with and without bacteria have the same slope, hence the order of reaction, they have the same mechanism. Conditions: 35 °C; pH 1.6; 1.0 g/L Fe^{2+}; 5.9 mg/L O_2; 10% (vol/vol) *Acidothiobacillus ferrooxidans* inoculum; 5 g/L solids.

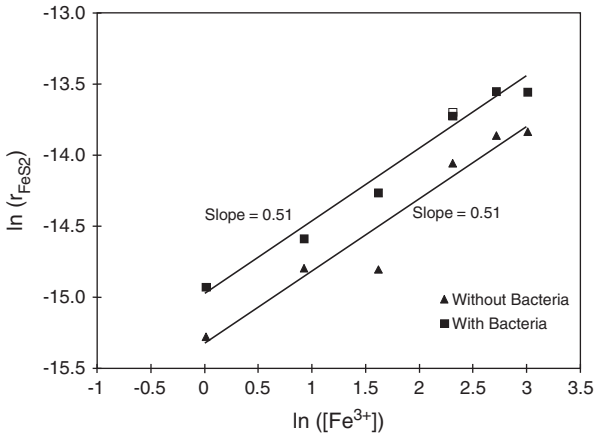

Fig. 18. The effect of the concentration of ferric ions on the rate of dissolution of pyrite in the presence and absence of bacteria (Fowler et al., 2001; Holmes et al., 1999). Bacteria enhance the rate, but since both reactions with and without bacteria have the same slope, hence the order of reaction, they have the same mechanism. Conditions: 35 °C; pH 1.3; 1.0 g/L Fe^{2+}; 10 g/L solids; 5.9 mg/L O_2; 10% (vol/vol) *A. ferrooxidans* inoculum.

presence and absence of bacteria, indicating that the rate-determining step is the same in both cases. In addition, the value of the order of reaction is one-half, which strongly indicates that the rate-determining step is the electrochemical dissolution step.

However, the results are more intriguing than the results presented for sphalerite because the rate is higher in the presence of bacteria. The order of reaction with respect to hydronium ions (H^+) is also slightly different in the presence of bacteria. At higher concentrations of ferrous ions, the theory presented earlier suggested that the rate of reaction should be given by the following expression:

$$r_{diss} = \frac{k\left[Fe^{3+}\right]^{0.5}}{[H^+]^{0.5}\left[Fe^{3+}\right]^{0.5}}. \quad (40)$$

The effect of pH on the rate of reaction is shown in Fig. 19. The results in the absence of bacteria are in agreement with Eq. (40). However, the order of reaction with respect to hydronium ions in the presence of bacterial changes slightly to −0.39. This is still within the ranges of values expected from Eq. (40), which indicates that the order of reaction with respect to H^+ should be in the range −0.25 to −0.5.

Fowler et al. (1999, 2001) and Holmes et al. (1999) complemented these leaching results with mixed potential results, which are shown in Fig. 20. These results indicate that the mixed potential in the absence of bacteria is stable over several days. In contrast, the mixed potential in the presence of bacteria drops over the same period.

This result is something of a conundrum, since one would expect, from a simplistic model of leaching, the mixed potential to increase when the rate increases. What the experimental results show, however, is that the mixed potential decreases and the rate increases in the presence of bacteria.

Fowler et al. (1999, 2001) and Holmes et al. (1999) offered an explanation for this result: they argued that the presence of the bacteria on the surface of the pyrite alters the pH at the pyrite surface, hence an increase in rate and decrease in mixed potential. The expression for the mixed potential that they presented is in agreement with this explanation.

To summarise: do the bacteria attach to the surface? Yes. Does this attachment influence the rate of dissolution of pyrite? Yes, by about 15%. Do the bacteria actively increase the rate of dissolution of pyrite by a separate (enzymatic) reaction? No, the bacteria do not change the mechanism of leaching.

The rate-determining step for both chemical and bacterial leaching is the transfer of charge between the mineral surface and the ferric ions in solution. The resolution of the debate on the mechanism of

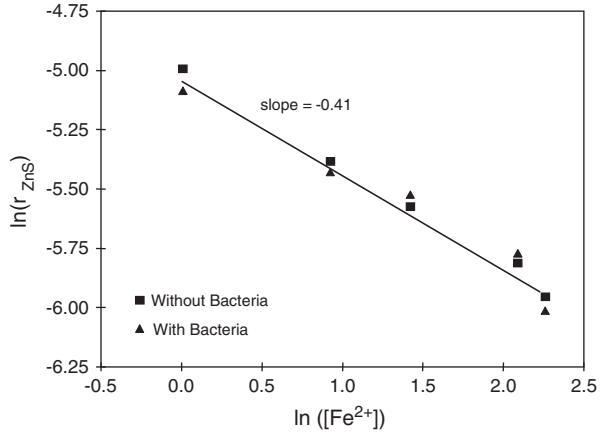

Fig. 17. The effect of the concentration of ferrous ions on the rate of dissolution of sphalerite in the presence and absence of bacteria (Fowler, 2000). Since both reactions with and without bacteria have the same slope, hence the order of reaction, they have the same mechanism. Conditions: 35 °C; pH 1.6; 1.0 g/L Fe^{3+}; 5.9 mg/L O_2; 10% (vol/vol) *A. ferrooxidans* inoculum; 5 g/L solids.

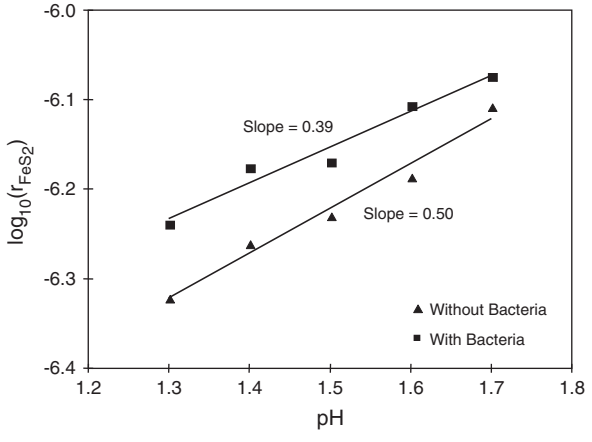

Fig. 19. The effect of the concentration of pH on the rate of dissolution of pyrite in the presence and absence of bacteria (Fowler et al., 2001; Holmes et al., 1999). Bacteria enhance the rate, probably by inadvertently affecting the pH at the surface, hence the difference in the reaction order between orders of reaction with and without bacteria. Conditions: 35 °C; pH 1.3; 1.0 g/L Fe^{2+}; 5.0 g/L Fe^{3+}; 10 g/L solids; 5.9 mg/L O_2; 10% (vol/vol) *A. ferrooxidans* inoculum.

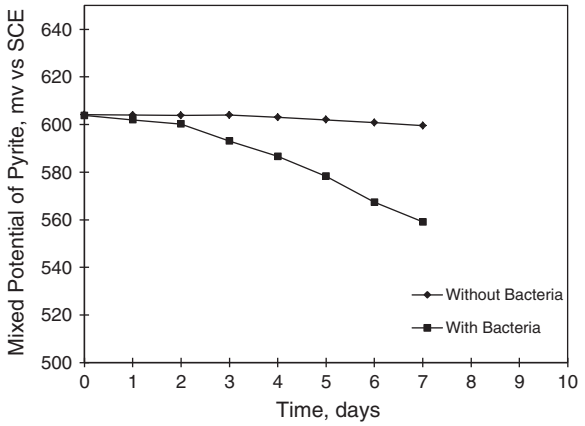

Fig. 20. The measured mixed potential of pyrite with and without bacteria over several days (Fowler et al., 1999, 2001; Holmes et al., 1999). Conditions: 35 °C; pH 1.6; 9 g/L total iron, redox potential 650 mV (vs. SCE).

bacterial leaching is a triumph for the electrochemical mechanism of dissolution.

9. Challenging two hypothesized mechanisms

Two common mechanisms are frequently advocated: (i) that sulphide minerals are passivated by polysulphides, and (ii) that the first step in the dissolution mechanism of sulphides is the attack of the mineral by acid. These two hypothesized mechanisms are addressed, using experimental data, in the sections that follow.

9.1. Do polysulphides really passivate the dissolution of sulphides?

A predominant paradigm in the research on the dissolution of minerals is that the rate is slow because the surface is "passivated". The prime suspect in the passivation model is polysulphide, a partially oxidized sulphur species, S_n^{2-}. This is at times expressed slightly differently by saying that a metal-deficient layer is responsible for passivation. Essentially, a polysulphide layer and a metal-deficient layer are two names for the same thing.

Polysulphides form on the surface of the sulphide mineral during dissolution and electrochemical studies. Mere observation of their presence seems to be sufficient to implicate them as the cause of passivation. However, the researchers who postulate the passivation of mineral surfaces by polysulphides usually provide no evidence that the presence of polysulphides inhibits the rate of reaction or controls the mechanism of dissolution.

An analogy with the dissolution of iron and stainless steel is appropriate. In both cases a reaction product forms on the surface of the corroding material. In the case of iron it is rust, and in the case of stainless steel it is an oxide layer. However, the rust has little effect on the continued corrosion of iron, whereas the oxide layer very effectively inhibits further dissolution. Are polysulphides like rust on iron, or like the oxide layer on stainless steel?

An example of the work of the advocates of passivation is that of Weisner et al. (2003) who diligently measure the formation of polysulphides on the surface of sphalerite. They measure a slowing of the rate of reaction after the first 5% of the reaction and argue that it might be associated with the formation of a metal-deficient layer on the surface. Following this excellent work, they then conclude that the slowing of the reaction is due to diffusion of either Zn^{2+} or H^+ through this layer. However, if diffusion through this layer controlled the rate of reaction, the reaction would not be one-half order in ferric ion, as outlined in Section 8. Rather, it would be first order in the diffusing species, either Zn^{2+} or H^+. Their conclusion must be challenged based on the observed order of reaction. (Note that the reaction orders mentioned in Section 8 were determined over much greater range than the first few percent of the reaction.)

Another example is pyrite. The dissolution and electrochemistry of pyrite have been interpreted as consisting of "passive" and "transpassive" regions. Li and Wadsworth (1993) identified a passive region at low potential, followed a transpassive region at higher potentials. Alhberg and Broo (1996) complemented this work, and drew the conclusion that polysulphides passivated the anodic dissolution of pyrite. Researchers continue to assert that pyrite is passivated and that the cause is polysulphides. Yun Liu et al. (2011) have recently concluded that polysulphides are the passivating agent on pyrite.

For the advocates of passivation, the observation of a surface species or metal-deficient layer is a sufficient proof that the reaction is controlled by this layer. But is it really?

Holmes (1998) performed experiments in which he dissolved samples of pyrite at different potentials and measured the thickness of the passivating layer using Raman spectroscopy.

At the same time, Holmes (1998) measured the current at these potentials due to dissolution. The results are shown in Fig. 21, from which it is clear that polysulphides are not a cause of passivation. The thickness of the polysulphide layer increases with potential, but so does the rate of reaction, which he measured in terms of the current.

The conclusion that must be drawn from these results is that polysulphides are not a cause of passivation. More polysulphide does not translate into lower rates of reaction. Polysulphides have no influence on the rate of reaction of the steadily dissolving surface. Without evidence to the contrary, the results of Holmes (1998) represent strong evidence that the passivation of the reaction by polysulphides or a metal-deficient layer does not occur.

9.2. Is the first step in the leaching of sulphides an acid attack?

A frequent assumption in the literature on dissolution of minerals is that the dissolution reaction commences with an attack of the surface by acid to form hydrogen sulphide, and this hydrogen sulphide is oxidized by the oxidant in solution.

The mechanism of acid attack was the basis proposed by Schippers and Sand (1999) for their interpretation of bacterial leaching of minerals. The first step in their mechanism was acid attack. They presented no data on the kinetic parameters of the reaction, and no data on whether the first reaction in their scheme, the acid attack, is fast enough to sustain the rate of the overall reaction. Schippers and Sand (1999) make no distinction between the minerals — according to them all sulphides dissolve by a mechanism in which acid attack is the first step.

The proposed mechanism of acid attack is in direct opposition to the electrochemical mechanism of dissolution, and consequently it is worth examining in more detail.

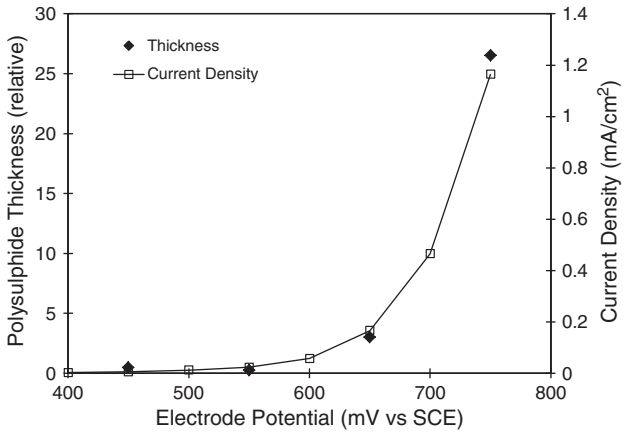

Fig. 21. The lack of an effect of polysulphides on the anodic dissolution of pyrite (Holmes, 1998; Holmes and Crundwell, 2013).

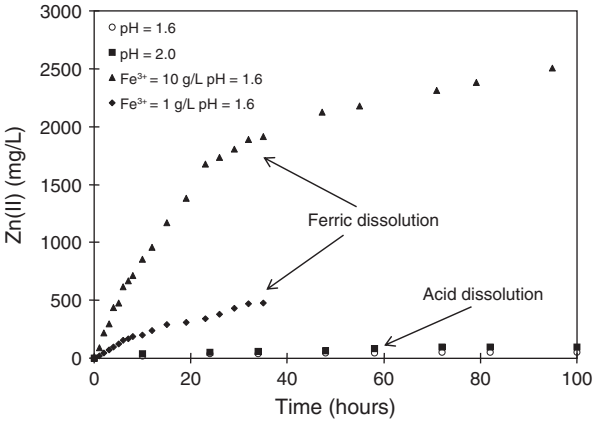

Fig. 22. The dissolution of sphalerite by acid and ferric ions, showing that the acid reaction is too slow to be the initial step in dissolution by ferric ions (Fowler, 2000).

The acid attack reaction scheme for pyrrhotite (Filippou et al., 1997), for example, is written as follows:

$$FeS + 2H^+ \rightarrow Fe^{2+} + H_2S \quad (46)$$

$$H_2S + 2Fe^{3+} \rightarrow 2H^+ + 2Fe^{2+} + S^\circ. \quad (47)$$

The overall reaction is the sum of these two reactions:

$$FeS + 2Fe^{3+} \rightarrow 3Fe^{2+} + S^\circ. \quad (48)$$

Similar reaction pathways have been proposed for sphalerite (Verbaan, 1977; Markus et al., 2004; Nicol, 2011; Schippers and Sand, 1999; amongst others) and other sulphide minerals.

Crundwell and Verbaan (1987a,b) studied the first reaction, Eq. (46), in detail. A unique feature of their work was that they studied the kinetics of both the forward reaction and the reverse reaction. They found that the forward reaction is first order in H^+ and the reverse reaction is one-half order in H_2S and one-half order in Zn^{2+}. The one-half orders for the reverse reaction are significant, because like the one-half orders for oxidative dissolution, they are difficult to explain by theories other than electrochemistry.

The problem with the reaction scheme like that given in Eqs. (46) and (47) is two-fold:

(i) the acid attack is too slow at the conditions found in leaching reactors, both chemical and bacterial, to sustain the rate of the overall reaction, and,
(ii) the acid attack does not describe the kinetic parameters (that is, the overall reaction is one-half order in ferric ions).

This first point is important: if the Eq. (46) is the first step in the overall scheme, it is at least as fast as the overall reaction. This is because the reaction scheme is a simple series:

$$A \xrightarrow{1} B \xrightarrow{2} C. \quad (49)$$

In a simple series with two steps, either step 1 or step 2 is at the same speed as the overall reaction. That means either step 1 is the slow step or step 2 is.

If an independent measurement of step 1 shows that it is slower than the overall rate, then step 1 cannot be part of the overall reaction. This is because it cannot produce B at a rate that is fast enough.

In other words, the rate of Eq. (46) cannot be slower than the rate of Eq. (48).

Fortunately, data is available that sheds light on this. Fowler (2000) measured the rate of dissolution of sphalerite, and these results are shown in Fig. 22.

Dutrizac (2006) measured the rate of dissolution both with and without ferric addition. The dissolution with ferric ions is faster than that with acid below an acid concentration of 100 g/L. This means that the acid attack mechanism is too slow to sustain the overall rate if the concentration of sulphuric acid is below 100 g/L.

The results from both Fowler (2000) and Dutrizac (2006) are in agreement: acid attack is too slow to sustain the overall rate of dissolution. Ferric ions, or any other oxidant, must interact with the mineral without the mediation of H_2S.

The results shown in Fig. 22 are corroborated with other measurements of the rate of dissolution. These results, shown in Table 5, indicated that the rate of dissolution by acid is significantly slower than the dissolution by ferric ions for both sphalerite and pyrrhotite.

An interesting feature of these results is the nearly two orders of magnitude increase in the rate of reaction with the addition of only 0.0002 M $FeCl_3$. Proponents of the acid attack mechanism might argue that the addition of ferric ions removes an inhibition due to the build-up of H_2S. However, this argument is flawed for two reasons — the pyrrhotite results shown in Table 5 are initial rates, before H_2S can accumulate, and secondly, H_2S strips very easily from the liquid phase to the gas phase, so the sparging of gas (either air or nitrogen, for example) easily removes H_2S.

Clearly, the mechanism based on acid attack is found wanting. However, this is not the only evidence against it.

The second, perhaps more important, objection to the acid attack mechanism that was mentioned earlier is that for a mechanism to gain acceptance it must make sense of the orders of reaction. The utilitarian test of a mechanism, and the theme of this paper, is that a mechanism *must* describe the orders of reaction.

The mechanism by acid attack does not explain the kinetic parameters of these reactions, that is, that the dissolution of these minerals is one-half order in ferric ions. Many of the alternative theories proposed pay no attention to the orders of reaction; instead, a mechanism is proposed without any account of the primary kinetic information, the orders of reaction.

If the acid attack mechanism did occur, one would expect that the rate of reaction would be strongly dependent on the concentration of acid. However, this is not the case, it is usually *independent* of acid (sphalerite) or *weakly inversely dependent* on acid (pyrite).

For sphalerite, in particular, the acid attack mechanism has no explanation for the effect of the iron impurity in the solid (see Fig. 13) and the effect of light (see Fig. 14). Both of these factors are explained by the electrochemical mechanism of dissolution (Crundwell, 1988a).

The acid attack mechanism is rejected because its rate of reaction is not fast enough, and it does not successfully describe the kinetic parameters.

Table 5
Rates of dissolution for pyrrhotite and sphalerite, showing that the acid reaction is too slow.

Mineral	Dissolution system	Medium	Conditions	Rate of reaction	Reference
Pyrrhotite	Acid only	HCl	pH 2.75	5.0×10^{-10} mol/m^2/s	Janzen et al. (2000)
	Oxygen	HCl	pH 2.75	4.0×10^{-9} mol/m^2/s	Janzen et al. (2000)
	Ferric chloride	HCl	0.0002 M $FeCl_3$, pH 2.75	3.5×10^{-8} mol/m^2/s	Janzen et al. (2000)
Sphalerite	Acid only	H_2SO_4	0.01 M H_2SO_4	0.0015 h^{-1}	Dutrizac (2006)
	Ferric sulphate	H_2SO_4	0.01 M H_2SO_4, 0.3 M $Fe(SO_4)_{1.5}$	0.24 h^{-1}	Dutrizac (2006)

10. Conclusions

This paper has made strong arguments, based on data, for the following points:

(i) Mechanism is not the same as chemical pathway
  – mechanism requires that the orders of reaction are correctly accounted for.
(ii) There is no separation of the surface into anodic sites and cathodic sites
  – the entire surface is both anodic and cathodic at the same potential.
(iii) There is no flow of electrons across the bulk of the mineral
  – there is no driving force for bulk flow.
(iv) The oxidation and reduction reactions are coupled by the transfer of electrons, not by a chemical intermediate
  – the 'activated state' is not a chemical intermediate with bonding between that of the reactants and the products. Rather, it is the stretching of bonds so that electrons can tunnel through the energy barrier at a significant distance.
(v) Polysulphides do not passivate the surface
  – polysulphides do not inhibit the dissolution; no evidence has been presented to show that they do indeed inhibit dissolution, like thickness versus rate data.
(vi) The first step of the reaction is not by acid
  – the acid reaction is too slow to sustain the overall rate of dissolution, so it cannot be the first step. Also, this mechanism does not explain the orders of reaction.
(vii) The solids do not need to be electric conductors to dissolve by the electrochemical mechanism.
  – the electrochemical model of dissolution applies to insulators.

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