The mechanisms of pyrite oxidation and leaching: A fundamental perspective

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Abstract

Pyrite is the earth's most abundant sulfide mineral. Its frequent undesirable association with minerals of economic value such as sphalerite, chalcopyrite and galena, and precious metals such as gold necessitates costly separation processes such as leaching and flotation. Additionally pyrite oxidation is a major contributor to the environmental problem of acid rock drainage. The surface oxidation reactions of pyrite are therefore important both economically and environmentally.

Spatially resolved surface characterisation of fresh and reacted pyrite surfaces is needed to identify site specific chemical processes. Scanning photoelectron microscopy (SPM) and photoemission electron microscopy (PEEM) are two synchrotron based surface spectromicroscopic and microspectroscopic techniques that use XPS- and XANES-imaging to correlate chemistry with topography at a submicron scale. Recent data collected with these two techniques suggests that species are heterogeneously distributed on the surface and oxidation to be highly site specific.

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1. Introduction

Pyrite (FeS₂, iron disulfide) is the most abundant and widespread of the earth’s sulfide minerals and is frequently found in hydrothermal deposits, veins and replacements, igneous rocks and sedimentary beds [12]. Pyrite has little economic value but is frequently associated with valuable minerals such as sphalerite, chalcopyrite and galena. Occasionally pyrite may also carry dispersions of valuable metals such as gold and is sometimes mined for this [3], in addition pyrite is commonly used for production of sulfuric acid [4].

Pyrite oxidation is economically important in mineral flotation and leaching, two industrial methodologies used to separate pyrite from other minerals of value. Oxidation can impart hydrophobicity or hydrophilicity to pyrite surfaces and hence influences interactions with collectors during flotation [5]. Inadvertent flotation of pyrite leads to reduced concentrate grades, increased superfluous and possible methods of obtaining spatially resolved surface and possible methods of obtaining spatially resolved surface chemical information.

2. The structure of pyrite

2.1. Chemical structure

FeS₂ is composed of a ferrous (Fe²⁺) cation and an S²⁻ anion with an ideal Fe:S ratio of 1:2 [4]. Deviations (<1%) from this stoichiometric relationship with either a higher cation or anion concentration are frequently reported [7]. Paszkowicz and Leiro [12] using the Rietveld refinement method found the S:Fe ratio of two different pyrite samples to be 1.978(6) and 2.027(6). Long and Dixon [13] reported the S:Fe ratio of 1.92 for a pyrite sample from Mexico. A greater S:Fe ratio is reported by Hu et al. [14] and Peng et al. [15]. These deviations are present due to lattice substitutions of the Fe²⁺ or the S⁻ ion with atoms of similar radius and charge or net polarity [4]. These minor and trace elements, listed in Abratis et al. [7], can introduce significant variations in the semi-conducting bulk properties of pyrite which can directly affect the reactivity of the pyrite surfaces [7,9]. The distribution of these impurity elements is not homogeneous [16] therefore site specific electronic variations are likely to exist. This, in turn, can have significant implications for the leaching and flotation behaviour of pyrite samples [17].

2.2. Crystal structure

FeS₂ exists in two polymorphic forms, pyrite which is cubic, and marcasite which is orthorhombic [6] of which marcasite is the less stable and also the less widespread [4]. Pyrite has a face-centred crystallographic arrangement similar to that of rock salt, halite (NaCl), with Na⁺ replaced by Fe²⁺ and the centre of the S–S bond being located at the Cl⁻ position [18–21]. Each Fe²⁺ is coordinated to six S in a distorted octahedral arrangement while each S is coordinated to one S and three Fe²⁺ in a distorted tetrahedral arrangement. The S²⁻ dumbbells are diagonally oriented and alternate in orientation in each crystal layer. This arrangements results in a reduction in the high symmetry close-packed NaCl structure [3]. Despite this the pyrite structure is still very dense, approximately 5.02 g/cm³ [4,22] and has a space group of Pa₃ [19,23].

Apart from the usual cubic (100) morphology, pyrite also forms as a dodecahedron [210] with pentagonal shaped faces known as pyritohedron, and octahedral [111] crystals with triangular faces [4]. The crystal faces are usually striated as a result of microscopic alternation of (100) and (210) growth [3]. Natural pyrite is found as a single morphology or in a varied combination of these structures [4]. Unlike other minerals of similar structure pyrite shows poor (100) fracture which is frequently conchoidal [4,21]. Paszkowicz and Leiro [12] reported crystallographic data of two different pyrite samples, a unit cell parameter of 5.41784(2) Å and x fractional coordinate of S (free positional parameter) of 0.3848(1) from Spain and a of 5.41819(2) Å and x of 0.3840(1) from Russia. These variations were attributed to deviations from ideal stoichiometry. While standard deviations (provided in parentheses) in values of a and x were reported by Paszkowicz and Leiro [12], no discussions were made regarding the contribution of estimated standard deviations.
2.3. Electronic structure

The electronegativity difference between Fe and S suggests predominantly covalent bonding which is defined by the overlap of the 3d valence electrons of Fe and the 3p valence electrons of S [7, 22]. Pyrite has a relatively high rest potential of approximately 0.66 V [25] making it the most electrochemically inert of the common sulfide minerals (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Sulfide mineral</th>
<th>Rest potential (SHE) V</th>
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<tbody>
<tr>
<td>Pyrite</td>
<td>0.66</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.56</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.46</td>
</tr>
<tr>
<td>Covellite</td>
<td>0.45</td>
</tr>
<tr>
<td>Bornite</td>
<td>0.42</td>
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<tr>
<td>Galena</td>
<td>0.40</td>
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X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy, ultra-violet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) together with first-principles quantum chemical calculations (ab initio) have been used to study the electronic structure of pyrites [7,17,22,24,26–33]. The shortest interatomic distance occurs between the two anion pairs with lengths calculated as \(d_{\text{S-S}}\) of 2.20 Å [24] and \(d_{\text{S-S}}\) of 2.14 Å [28]. The lengths between the Fe and S is reported as \(d_{\text{Fe-S}}\) of 2.26 Å [24] and \(d_{\text{Fe-S}}\) of 2.27 Å [28]. Unlike other sulfides such as chalcopyrite and sphalerite, where there is no S to S bonding, the short S-S distance in pyrite splits the S 3s orbital into bonding \(\sigma^+\) and antibonding \(\sigma^-\) orbitals with a gap of approximately 3 eV [24,28]. Using XPS and Mössbauer studies, van der Heide et al. [26] and Folmer et al. [27] constructed a molecular orbital (MO) diagram showing the 3s and 3p overlap of the S atoms and the subsequent σ–p hybridisation. The 3s overlap results in a bonding 3s(\(\sigma_2^+\)) and an antibonding 3s(\(\sigma_2^-\)) molecular orbital with two electrons in each orbital. The 3p orbitals form an occupied bonding 3p(\(\pi_2^+\)) and an unoccupied 3p(\(\pi_2^-\)) molecular orbital while the 3p\(\sigma\) orbitals form occupied bonding (\(\pi_2^+\)) and antibonding(\(\pi_2^-\)) molecular orbitals. There is also extensive splitting of the Fe 3d orbitals by the strong field S ligands resulting in the formation of triply degenerate \(t_{2g}\) and doubly degenerate \(e_{2g}\) molecular orbitals. Only the \(t_{2g}\) molecular orbital is occupied as Fe retains the spin-paired d\(^6\) configuration [27]. This \(t_{2g}\) molecular orbital is almost nonbonding in pyrite [26]. Moreover, as both the anion (\(S_2^2-\)) and the cation (Fe\(^{2+}\)) in the pyrite structure have paired electrons, pyrite is a low-spin diamagnetic compound with no magnetic moment [7,27,28,34]. The diamagnetic electronic configurations of the cation and the anion are shown in Fig. 1a and b respectively.

Edelbro et al. [28] presented a complete band structure of Fe\(S_2\) calculated by a full potential density functional approach and state that the band structure determines the strength of chemisorption bonds. This was similar to the calculations made by Cai and Philpott [24]. The structure showed that the valence band (valence spread, across 1.25 eV) just below the Fermi level is mainly composed of Fe \(t_{2g}\) states with some anion states. The main bonding band is located just 0.91 eV below the valence band and consists of S 3p orbitals and some Fe 3d orbitals, spread over 5 eV. Moreover, the \(t_{2g}\) orbitals also overlap with empty S 3d orbitals resulting in electron delocalisation [7]. The conduction band located approximately 0.9–0.95 eV above the valence band is a mixture of antibonding \(\sigma^+\) and the Fe \(e_g^*\) states [17,35]. Folmer et al. [27] showed that the \(\pi^*\) branch of the valence band lies across the Fermi level and possible Fe \(e_g^*\) and S \(\pi^*\) mixing exists as the \(\pi^*\) orbital is oriented towards the metal \(e_g^*\) orbitals. Furthermore, Oertzen et al. [36] conducted ab initio quantum-chemical calculations of the optical and electronic properties of pyrite, using density-functional, Hartree–Fock and hybrid functional methods, and compared the resulting band structure to the shape of S 1s-edge X-ray absorption spectra of pyrite, measured using synchrotron radiation. Based on the analysis it was shown that the conduction band consisted of S p and Fe p and d states. Further structural details can be found elsewhere [37]. Ferrer et al. [38] cautioned on the use of certain theoretical approximations for determining the electrical band gap as they cite this reason for the widely reported band gap values. According to them most approximations used are valid only for parabolic band edges while for pyrite the band edges appear flat. While this is a valid argument, electrical variations between different samples and even within the same samples can exist, as a result of heterogeneous impurity distributions. As discussed in subsequent paragraphs the apparent disparity between bulk and surface chemical states, and possibly within surface states can also be contributing factor.

The photoelectron spectra of the pyrite valence band is generally characterised by two distinct regions, the outer valence band and the inner valence band which are separated by a minimum at about 2 eV [30,31]. The outer valence band is characterised by a strong peak near 0.6–1 eV while the inner valence band stretches from the minimum to about 20 eV [30]. The inner valence band has an almost broad contribution from the minimum to about 8–10 eV and a doublet like (of the region between 0 to approximately 10 eV) feature from 10 to 20 eV [30,31].

Using both conventional and synchrotron XPS Nesbitt et al. [30] obtained a series of valence band spectra of the vacuum fractured pyrite surface that ranged from surface sensitive to bulk sensitive. In order to test previous theoretical calculations of the pyrite valence band, the incident photon energy was carefully varied during successive measurements and qualitative information on the relative contributions by the S 3s and 3p and Fe orbitals was obtained. From this range of valence band spectra, seven peaks were identified from 0.8 eV to 16 eV. Two peaks were identified in the doublet-like region, at 16 and 13 eV, which were found to arise entirely from S 3s molecular orbitals as bonding \(\sigma\) and antibonding \(\sigma^+\) respectively. There was no evidence to suggest any sp\(^3\) hybridisation of S molecular orbitals, hence it was concluded that the hybridisation concept cannot be used to explain tetrahedral S geometry in pyrite. The broad contribution of inner valence band was found to contain four distinguishable peaks, at 7, 5, 4 and 2.5 eV. The peak at 7 eV was attributed to the mixing of S 3p atomic orbitals to form bonding \(\sigma\) molecular orbital responsible for the S–S dimer, while the peak at 5 eV was attributed to contributions from S 3p derived orbitals possibly from the S–S \(\pi\) bond. Negligible Fe 3d contributions to the 7 and 5 eV peaks were also found. The peak at 4 eV results from mixing of Fe 3d–S 3p molecular orbitals and has a more S 3p character than Fe 3d. This represents the bonding \(\sigma\) molecular orbitals of Fe–S bonds. The 2.5 eV peak also results from mixing of Fe 3d–S 3p molecular orbitals however it has a more Fe 3d character than S 3p and results mostly from Fe–S \(\pi\) bonding. The single peak of the outer valence band, which is also the most prominent valence band peak, at approximately 0.8 eV, is attributed to result largely from Fe 3d. The peak position and shape was found to vary slightly in spectra taken at different incident photon energies, and it was concluded that there were additional contributions from S 3p and Fe 3d.
surface states. The Fe-S $\pi^+$ bonding was suggested to contribute to the high binding energy side of this peak at about 1 eV while the Fe 3d of surface Fe atoms was suggested to contribute to the lower binding energy side of this peak at about 0.5 eV. The surface Fe contributions may arise from Fe 3d$_{xy}$ (non-bonding orbitals) dangling bonds as a result of Fe-S bond fracture.

The most commonly found cubic pyrite morphology, terminates with the (100) surface while pyritohedral and octahedral morphologies terminate with (210) and (111) surfaces respectively [4]. Rare (110) surface terminations are also found [23]. All of these surfaces are of lower coordination as compared to the bulk structure as bonds are fractured during cleavage. The (100) surface is frequently found to have five-fold coordinated surface Fe due to the loss of $S_{2}^{2-}$ [17,23,39]. This leads to a square pyramidal field (point group $C_{4v}$) around the Fe atom resulting in the loss of degeneracy of the Fe $e_g^2$ orbitals [24]. Thus, the band gap reduces from about 0.9 eV in the bulk to only approximately 0.16 eV at the (100) surface (Fig. 1a) inducing a more metallic character in the surface as compared to the semi-conducting character of the bulk [17,23].

The (110) surface contains Fe of even lower coordination (<5) with four-fold coordination being the most frequent [23]. As seen in Fig. 1a, this leads to a further reduction in band gap and results in the (110) surface (<5 coordination) becoming spin polarised (paramagnetic) unlike the 5-fold coordinated and bulk Fe. Even though the (110) surface is rare, the 4-fold coordination typical of this surface also occurs on parts of the more common (100) pyrite surface. The (100) surface is the most stable of the terminating surfaces however, cleavage results in a high density of defects and imperfections (steps and kinks) which have low coordination (<5) Fe sites similar to the (110) surface [23,24,39]. The (111) and (210) surface have also been shown to terminate with low coordinated (<5) Fe atoms with similar structures to those shown in Fig. 1a [40].

The loss of coordination at the surfaces results in higher dangling bond density, making such sites highly reactive. Surface structures undergo considerable relaxation to stabilise these low coordinated sites [17,40]. This tends to shorten the S-S and Fe-S bond lengths as compared to the bulk [24]. Hung et al. [23], through their density functional calculations, suggested that low coordination sites (<5) tend to be spin polarised (while sites of normal coordination are spin neutral) and that species such as triplet molecular oxygen ($O_2^-$) which is paramagnetic will be more inclined to react with these low coordination defect sites. Qiu et al. [17] propose that during oxidation reactions the transfer of electrons will be much faster as a result of the reduced band gap and enhanced metallic character and will occur preferentially from the Fe rather than surface S species, which may result from bond cleavage during fracture (refer Section 3.1). This is in agreement with previous studies by Rosso et al. [33] who revealed for the first time the surface electronic heterogeneity of UHV fractured surfaces using STM microscopy and spectroscopy together with LEED, UPS and $ab$ initio calculations. It was concluded that surface redox processes are initiated by first quenching of high energy dangling bonds (at Fe sites) and leading to the formation of new surface species.

2.4. Semiconductor properties of pyrite

Pyrite is a potential photovoltaic absorber material for solar cells due to its high electron mobility ($230 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$) and high optical absorption coefficient ($\alpha > 6.0 \times 10^5 \text{ cm}^{-1}$ for $h\nu > 1.3 \text{ eV}$) [38,39,41]. However, considerable variations exist in the semi-conductor properties of natural pyrites which affect the physico-chemical processes of pyrite dissolution [42]. Abraitis et al. [7] comprehensively reviewed the semi-conducting properties of pyrite and found that reported conductivities vary by four orders of magnitude. Depending on geological conditions, natural pyrite can exist as either a n-type semiconductor or as a p-type semiconductor [43,44]. Pyrite formed at relatively high temperatures normally exhibits n-type character while pyrite formed at relatively low temperatures are p-type [7,22].

Abraitis et al. [7] calculated the mean conductivities of n- and p-type pyrites from the data they reviewed. Their calculations clearly illustrate that n-type pyrites have higher conductivities with a mean of 56.8 ($\Omega\text{cm})^{-1}$ while p-type pyrites are of lower conductivity with a mean of 0.53 ($\Omega\text{cm})^{-1}$. The variations in semi-conductor properties arise from deviations in stoichiometry and the presence of trace elements [9,22]. Trace elements can either have electron donating (n-type) or electron accepting (p-type) properties and hence impart the same to pyrites. Pyrites high in arsenic are found to be p-type semi-conductors while those low in As are n-type [7,44]. Pyrites high in cobalt have also been found to behave as a n-type semiconductor [44]. Similarly, pyrites with S:Fe stoichiometric ratios less than 2 are usually n-type while those above 2 are p-type. Buckley and Woods [5] found evidence of the coexistence of S-deficient and Fe-deficient regions on abraded pyrite surfaces. Moreover, according to Lowson [22], Rimstidt and Vaughan [9] and Abraitis et al. [7] natural pyrites have been reported to contain alternating n and p type properties. In fact, overall n or p behaviour of pyrites may result from a net of n or p properties.

Fig. 1. Molecular orbital diagram showing diamagnetic configuration of (a) Fe in pyrite, bulk and surface (b) $S_{2}^{2-}$ anion. Source: Fig. 1(a) redrawn from Ref. [23].
Using n-type pyrites as microelectrodes, Wei and Osseo-Asare [42] investigated anodic and cathodic dissolution in 1 M HNO₃ solution at a given potential. The dissolution rate was seen to be much faster under anodic current compared to cathodic current. Illumination of the pyrite microelectrode was found to increase anodic dissolution with no effect on cathodic dissolution. Hence, it was concluded that n-type pyrites dissolve anodically through a hole transfer (valence band) pathway. Moreover, Abraitis et al. [7] add that in mixed sulfide mineral pulps (without kinetic considerations), pyrite with a comparatively higher rest potential will be anodic while more reactive sulfides will be anodic. However, the resulting rates of preferential dissolution of the anodic sulfides will be dependent on variations in the pyrite’s rest potential resulting from impurities or semiconductor type.

3. Pyrite oxidation

3.1. Atmospheric oxidation

Oxidation of pyrite surfaces may occur upon exposure to atmospheric O₂ and water [5]. The oxidation layer formed can passivate against further oxidation, and hence determine subsequent aqueous phase oxidation processes [45]. The atmospheric reactivity of a pyrite surface is dependant on the different surface species and the abundance of such species on a freshly fractured pyrite surface.

XPS studies of vacuum fractured pyrite surfaces have shown that three different S species are present, disulfide (S²⁻), monosulfide (S⁻) and polysulfide (Sₙ⁻, n > 2) [11, 46–49]. The main disulfide peak for pyrite (fully coordinated S²⁻) occurs at the S 2p3/2 binding energy range of 162.3–162.7 eV [45–51]. During pyrite fracture, which is conchoidal, the rupture of the Fe-S bonds creates surface S²⁻ where the outermost (surface layer) S in S²⁻ is in a decreased 3-fold coordination of two bonds to Fe and one bond to S [46,49]. The reduction in coordination to Fe and the resulting decrease in attractive electrostatic potential cause a negative binding energy shift of about 0.7 eV compared to fully coordinated disulfide [46,49]. Surface S²⁻ has an S 2p3/2 binding energy of approximately 162.0 eV [46,49].

On the basis of bonding energy considerations Nesbitt et al. [46] suggested that S–S bonding in pyrite is weaker than Fe–S bonding and that therefore during pyrite fracture, appreciable amounts of S–S bonds are broken. The breaking of S–S bonds gives rise to one S⁻ species on each fracture face. According to Nesbitt et al. [46] this highly reactive mononuclear species undergoes relaxation through transfer of an electron from the Fe⁴⁺ to form one S⁻ and one ferric iron (Fe³⁺). The existence of Fe³⁺ on the surface has been confirmed through synchrotron XPS and quantum chemical calculations [52,53]. It is also possible that the S⁻ species can be stabilised through transfer of an electron from another nearby S⁻ species, resulting in the formation of one S⁻⁻⁻ and one S²⁻. Nesbitt et al. [46] suggest that the elemental sulfur (S⁰) produced can undergo further reactions to form the polysulfide species Sₙ⁻. The monosulfide, S⁻, S 2p3/2 binding energy occurs around 1.4 eV below the bulk S²⁻ binding energy in the range of 161.3–161.8 eV [45–49]. The intensity ratio (XPS) of surface Fe⁴⁺ to Fe³⁺ was found to be 1.7:1 in a vacuum fractured pyrite surface [49], indicating the presence of surface S²⁻. Moreover, any surface loss of S atoms due to cleavage reduces the ideal surface S:Fe stoichiometry of 2:1 and this can add to the electrical discrepancies between the surface and bulk structures. Therefore, in addition to Fe³⁺ and fully coordinated (4-fold S) S²⁻, freshly fractured (vacuum) pyrite surfaces also contain surface (3-fold S) S²⁻, Fe⁴⁺, S⁻, and S⁻⁻⁻ type species. Leiro et al. [54] however report the existence of an additional surface S state (in addition to surface S²⁻ and S⁻⁻⁻) shifted by 2.0 eV to a lower binding energy of 160.8 eV. They conducted synchrotron S 2p XPS measurements using 3 different incident photon energies, 210, 350 and 780 eV, while cooling the sample with liquid N₂ to reduce phonon broadening. It was found that the extra component at 160.8 eV reduced in intensity with increasing incident photon energy. Estimated effective attenuation lengths (λ) were 4 ± 1 Å for 210 eV, 8 ± 2 Å for 350 eV and 13 ± 1 Å for 780 eV photon energies at the take-off angle of 45°. It was concluded that this extra component was due to S⁻⁻⁻ species that occurred only near steps and kinks between terraces on a fractured pyrite surface. The pyrite surface is therefore highly heterogeneous with each of these species having different reactivity which may influence the nature and direction of initial oxidation.

Numerous studies have been conducted to identify oxidation products formed after exposure to atmospheric gases. Synchrotron and conventional XPS have been widely used to examine shifts in the binding energy of S 2p, Fe 2p and O 1s electrons [5,45,48,49,55,56]. In addition synchrotron-based X-ray absorption spectroscopy examination of the S 2p3/2 and 2p1/2, Fe 2p3/2 and 2p1/2, O 1s and Fe 1s absorption edges [45] along with DRIFTS (diffuse reflectance Fourier transform IR), UV spectroscopy and high performance liquid chromatography [55] have all been used to study pyrite surface oxidation. Sulfate has been shown to be a major surface oxidation product with the possible presence of Fe oxo-hydroxide species [22,49] however controversy still exists as to the presence of elemental sulfur (S⁰) and polysulfides (Sₙ⁻) [49,55].

Pyrite oxidation begins within minutes of exposure to the atmosphere, commencing with the oxidation of S⁻⁻⁻ species. Schaufler et al. [48] studied the reactivity of S⁻⁻⁻, S⁻⁻⁻(surface), and S²⁻⁻⁻(bulk) species by exposing pristine fractured pyrite surfaces to the atmosphere for various times. Nearly 80% of the S⁻⁻⁻ was oxidised to sulfate within 1 min exposure to the atmosphere. Buckley and Woods [5] also found evidence of Fe²⁺– sulfate production within a few minutes of atmospheric exposure. Schaufler et al. [48] concluded that the S⁻⁻⁻ species is the most reactive species with an initial oxidation rate of 0.77 min⁻¹, with the S⁻⁻⁻(surface) species being the second most reactive species while the bulk coordinated S²⁻⁻⁻(bulk) is the least reactive. Buckley and Woods [5] also exposed pyrite surfaces to the atmosphere for just a few seconds but found no evidence of sulfate formation, although the O 1s spectrum (XPS) revealed appreciable amounts of oxygen containing species on the surface which was attributed to the presence of chemisorbed water and/or hydroxide. Oxidation to sulfate also occurs within minutes even if the pyrite is exposed to limited amounts of atmospheric gases [48] however Schaufler et al. [48] add that under such conditions intermediate sulfur and oxy-sulfur species dominate sulfate formation.

As stated previously sulfate is the main oxidation product of prolonged atmospheric exposure. de Donato et al. [55] found sulfate to represent 36%–39% of all surface oxidation products. Todd et al. [45] and de Donato et al. [55] identified that this to be largely present as Fe²⁺ sulfate, Fe₂(SO₄)₃. Schaufler et al. [48] and Todd et al. [45] found Fe³⁺– oxo-hydroxide (FeOOH) to be the main oxidation product after sulfate and to extend below the uppermost Fe layer. This view is however not shared by de Donato et al. [55] who found Fe²⁺– hydroxide, Fe(OH)₃, and Fe³⁺– oxide, FeO, to be much more prolific than FeOOH. Buckley and Woods [5] also found Fe oxide on air-exposed pyrite surfaces which they expected to be hydrated. Furthermore with the appearance of possible Fe–oxy species on the surface they theorised that a metal–deficient sulfide must be forming in addition to the sulfate, given that the ratio of S to Fe is nearly 2. This conclusion was made on the basis that no elemental S signal was evident from S 2p spectra and no gaseous SO₂ formed. Although not identified by Buckley and Woods [5] this Fe-deficient compound could have been polysulfide. Using
show the diagrammatic representation of the formation of an intermediate S-OH species followed by the curse separately from sulfate formation and that therefore polysulfuroxidation by an $H_2$ mechanism proposed by Eggleston et al. [49]. This is consistent with the observation by Schaufuß et al. [48] in moist air, and found that the reaction rate decreased with time.

Using data from XPS, UPS (ultraviolet photoelectron spectroscopy), STM (scanning tunnelling microscopy) and Monte Carlo simulation studies of atmospherically oxidised pyrite, Eggleston et al. [59] proposed an air oxidation mechanism involving surface cycling of $Fe^{2+}$ and $Fe^{3+}$ along borders of oxidised and unoxidised areas. Patches of $Fe^{3+}$ hydroxide or oxide products form upon initial oxidation and these $Fe^{3+}$ products serve as a conduit for electron transfer from the pyrite surface to molecular oxygen. This involves the transfer of electrons from the pyrite valence band to the oxide conduction band, which effectively is transfer of an electron from pyrite $Fe^{2+}$ to oxide $Fe^{3+}$. The process takes place preferentially from pyrite $Fe^{3+}$ adjacent to the oxide. Electron transfer then takes place between oxide $Fe^{2+}$ to $O_2$ resulting in the formation of $O_2^2$. Electron transfer rate calculations estimate that the transfer of electrons from oxide $Fe^{2+}$ is nine orders of magnitude faster than the transfer from pyrite $Fe^{2+}$ [59]. The $O_2$ species then forms $H_2O$ via the formation of highly oxidising intermediates, $OH$ and $H_2O_2$. Fig. 2 shows the diagrammatic representation of the mechanism proposed by Eggleston et al. [59] which includes an outer-sphere sulfur oxidation by an $H_2O$ film adsorbed from the atmosphere. The mechanism shows that polysulfide formation occurs separately from sulfate formation and that therefore polysulfide is not an intermediate to sulfate formation.

Sulfur (surface) oxidation to sulfate proceeds through the formation of an intermediate S-OH species followed by the formation of thiosulfate, sulfite and finally sulfate [49]. The bulk disulfide is not directly oxidised, however there may be transfer of electrons from the bulk disulfide to surface $Fe^{3+}$ [49]. This leads to the formation of electron-deficient disulfide which may rearrange to form polysulfides. Continued oxidation will also result in rupture of further Fe-S and S-S bonds and formation of resulting surface species. S oxidation also leads to the formation of patches (“islands”) of products with in surrounding unreacted regions [48].

Schaufuß et al. [48,49] also provide an explanation for the initial formation of $Fe^{3+}$ oxides on fresh pyrite surfaces, similar to that suggested in the Eggleston et al. [59] model. The surface monosulfide attached to a $Fe^{3+}$ site (resulting from $e^-$ transfer to S) readily oxidises into sulfate. The sulfate is then displaced by competitive adsorption of $H_2O$, $O_2$ and $OH^-$. An electron is then transferred from an adjacent $Fe^{2+}$ (through attached S-bridge) to the attached $O_2$ resulting in the formation of $O_2^2$. Species. A second $Fe^{3+}$ adjacent to the first results and $Fe^{3+}$ oxide propagation occurs. Further electron transfer may rupture Fe-S bonds at the initial $Fe^{3+}$ site resulting in the formation of FeOOH.

Becker et al. [60] provides a mechanism of adsorption and reaction of surfaces species through what they call the “proximity effect”. Since pyrite is a semi-conductor and its surface electronic properties are affected by defect sites (steps and kinks) and impurities, surface reactions at different sites are coupled through electron transfer. The proximity effect suggests that the oxidation of one site near terraces renders the nearest neighbor more susceptible to oxidative attack in comparison to some site further away. This leads to the enlarging of the existing oxidation patches rather than the creation of new ones.

Information as to the correlation between topography and surface chemistry would benefit the development and substantiation of the proposed mechanisms however there is currently a lack of such a data set.

3.2. Aqueous oxidation

Studies have proposed that aqueous oxidation may involve chemical, electrochemical or bacterially catalysed pathways [1,9,22,61]. The latter normally involves catalysis of an oxidation reaction step by Thiobacillus bacteria such as T. ferrooxidans, however we do not review this here as it is not within the scope of this article.

The aqueous oxidation of pyrite is generally described by the following overall stoichiometric chemical reactions which were originally characterised by Garrels and Thompson [62] and Singer and Stumm [63].

$$\begin{align*}
FeS_2 + \frac{7}{2}O_2(aq) + H_2O &\rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ & (1) \\
Fe^{2+} + \frac{1}{4}O_2(aq) + H^+ &\rightarrow Fe^{3+} + \frac{1}{2}H_2O & (2) \\
FeS_2 + 14Fe^{3+} + 8H_2O &\rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ & (3)
\end{align*}$$

According to Moses and Herman [64] the pyrite oxidation reactions are far from equilibrium with essentially no reverse rate.

$O_2$ and $Fe^{2+}$ have been recognised as the two most important oxidants for pyrite oxidation [1,11,61,64–66]. Moses et al. [11] studied rates of pyrite oxidation at 22–25 °C, in oxygen saturated (DO—dissolved $O_2$) and $Fe^{3+}$ saturated solutions with initial pH values from 2 to 9, by monitoring the increase in either sulfate or total S concentrations over the oxidation period. In $Fe^{3+}$ saturated experiments, an initial rapid increase in sulfate concentration was observed at all pH values (2–9) which slowed considerably after a relatively short period of time. A similar observation was made by Moses and Herman [64] in experiments conducted at circumneutral pH with only $Fe^{3+}$ addition, however,
linear sulfate production was seen to resume after O₂ purging. The experiments conducted with DO saturated solutions, [11] on the other hand showed linearity throughout the oxidation period and in addition to sulfate, a number of different sulfury intermediates \((\text{SO}_3^{2-}, \text{S}_2\text{O}_5^{2-}, \text{SO}_4^{2-})\) were observed to be formed during the DO experiments which were absent in the Fe⁺⁺ saturated experiments especially at low pH. McKibbon and Barnes [65], in a similar experiment at 30 °C and low pH found sulfate to be the dominant product along with tetra-, penta- and hexa-thionates. It was further shown that no Fe⁺³ production occurs (by Eq. (2)) during short term (1–4 days) DO saturated oxidation of pyrite at low pH [65] while at pH 7 no Fe⁺³ is evident throughout the oxidation process [64].

An investigation by Moses et al. [11] of overall rates showed that rates due to the presence of Fe⁺⁺ were two orders of magnitude higher than those due to DO at low pH. Even at higher pH, where Fe⁺⁺ solubility diminishes, rates were almost an order of magnitude higher than the rates observed in DO saturated media. Therefore, with the lack of observed intermediates, it was apparent that Fe⁺⁺ is a more aggressive and effective than O₂ for pyrite oxidation. This is also true even at circumneutral and higher pH where the solubility of Fe⁺⁺ diminishes [64]. However, the presence of DO is critical to sustain the oxidation process. The reduced oxidation rate observed in Fe⁺⁺ saturated experiments occurred as a result of Fe⁺⁺ depletion [11]. It was seen that aqueous Fe⁺⁺ made available (through Fe(III)-oxo-hydroxides) to pyrite was less than what could be consumed. Hence, O₂ or DO is needed to replenish the diminishing Fe⁺⁺ through Fe⁺⁺/Fe⁺⁺ cycling.

Moses et al. [11] postulated that since O₂ in the ground state is paramagnetic (two unpaired electrons, triplet), its reaction with diamagnetic pyrite (no unpaired electrons) would not be possible due to spin restrictions. However, as mentioned previously, density functional calculations by Hung et al. [23] have shown the presence of low coordination (<5) sites on pyrite surfaces which can have unpaired electrons and may become sites of preferential attack by O₂. Fe⁺⁺ is also a paramagnetic species however it has been proposed that it is able to react readily with pyrite surfaces as it is usually complexed to a maximum of six diamagnetic \(\text{H}_2\text{O}\) molecules in solution. It is suggested that the resulting aquo-Fe⁺⁺ complex can react with a diamagnetic surface by transferring hydroxyl radical from its complexed water molecules to the surface [11]. This proposal by Moses et al. [11] does not explain how a paramagnetic Fe⁺⁺ is able to react with diamagnetic water other than by dipole interaction. An alternate explanation is that the Fe⁺⁺ also reacts with paramagnetic sites on the pyrite surface but that the activation energy required for this reaction, in comparison to that required to break O-O bonds is significantly lower and hence the reaction proceeds much more readily.

In the experiments conducted by Moses et al. [11], solution pH was seen to decrease in DO saturated experiments while surprisingly it increased slightly in experiments saturated with Fe⁺⁺. Moreover, only a slight pH rate dependency was observed for DO saturated experiments while McKibbon and Barnes [65] found no pH rate dependency in the pH range 2–4. The presence of intermediates seen during the DO saturated experiments was however pH-dependent with most appearing above pH 3.9 at high stirring speeds. The presence of intermediates was described by the Wackenroder reaction (Eq. (4)) with reaction balance shifting left above pH 7 and right below 7 [11].

\[
\text{SO}_4^{2-} + \text{S}_2\text{O}_5^{2-} \leftrightarrow \text{S}_n\text{O}_{3n+1}^{2-} + \text{SO}_3^{2-}.
\]  

(4)

In addition to Fe⁺⁺ and O₂, McKibbon and Barnes [65] also investigated pyrite oxidation by hydrogen peroxide at 30 °C and low pH. Pyrite oxidation by hydrogen peroxide can be represented by Eq. (5).

\[
\text{Fe}_2\text{S}_3 + \frac{15}{2} \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + 25\text{SO}_4^{2-} + \text{H}^+ + 7\text{H}_2\text{O}.
\]  

(5)

Even Fe⁺⁺ and sulfate were the only two detectable species with no metastable sulfur oxynitrides detected. Fe⁺⁺ was only detected initially while some Fe hydroxide precipitates were found towards the end of the experiments. No pH dependency was observed for the range of pH 2–4. However the initial rate of peroxide consumption was nearly double the rate of initial total Fe production, implying significant catalytic peroxide decomposition by Fe⁺⁺.

SEM studies have indicated oxidant attack on pyrite surfaces at only specific sites of high surface energy [65]. Thus, it appears that “effective” or “reactive” surface area is more significant than total surface area in determining rates of reaction. Such reactive sites are related to the grain edges and corners, defects, solid and fluid inclusion pits, cleavages and fractures. The preponderance of these features and their geometry may significantly vary from grain to grain, introducing variations in the observed rates of reaction on this spatial scale.

Atomic O reacted with pyritic S and subsequent products is believed to originate mostly from water molecules [64,67]. The identification of the source of O can provide valuable insights into the actual mechanism of aqueous pyrite oxidation [66]. Reedy et al. [67] showed that the majority of the sulfate formed (90%) derived all four O atoms from water rather than O₂ (under conditions of atmospheric O₂ with and without added Fe⁺⁺, at pH 1 and 20 °C or 70 °C) using \(^{18}\text{O}_2\) and \(^{18}\text{H}_2\text{O}\) and that the major product formed under all conditions was \(^{34}\text{SO}_4^{2-}\). Significant amounts of two other isotopomers, \(^{30}\text{SO}_4^{2-}\) and \(^{30}\text{SO}_4^{2-}\) were also formed when Fe⁺⁺ was not added while only \(^{30}\text{SO}_4^{2-}\) was formed as a minor product when Fe⁺⁺ was added. This was felt to strengthen the notion that Fe⁺⁺ is the dominant oxidant. According to Holmes and Crundwell [66], the fact that O atoms are mostly derived from water molecules during the oxidation process, points directly to an electrochemical mechanism of reaction, where electrochemical reaction steps at the mineral-solution interface control the dissolution rate of pyrite. The detection of significant levels of two sulfate isotopomers may also indicate mechanisms involving different intermediate sulfoxyl species [67].

Moreover, the Fe(III)-O and Fe hydroxides found on the surface are the result of the oxidation processes and not from precipitation of dissolved Fe from solution. Fe hydroxides and oxides have previously been found not only on pyrite surfaces from aqueous oxidation [5,45,50,68–70] but also on surfaces exposed to atmospheric gases [45,47,49,51,55,59,71]. Such Fe species on the surface are suggested to occur as an accumulation of oxidation products or as part of the oxidation mechanism. From Fe 2p XPS analysis of air-exposed pyrite, Eggleston et al. [59] concluded that hematite-like oxide or hydroxide type oxidation products form in patches on the surface. Such products promote electron transfer process from the valence band of pyrite to the conduction band on the oxide/hydroxide products and therefore aid in electrochemical oxidation of pyrite. Nesbitt and Muir [69] also made a similar observation on naturally weathered pyrite samples from mine dumps. Fe 2p and O 1s XPS were used to confirm the existence of goethite or hematite like products on tarnished pyrite surfaces. It was concluded that such Fe(III)-O or oxyhydroxide products represented oxidant reservoirs that helped in oxidation. Fe-hydroxy products have however been found to effectively passivate chalcopyrite surfaces during bioleaching [72]. Proposed electrochemical oxidation mechanisms of pyrite also suggest the occurrence of Fe(IV) oxide/hydroxide as one possible species (possibly cathodic) involved in electron transfer steps [8,59,70,73]. The Fe(III)-O and hydroxide/oxy-hydroxide type products seen on the samples leached under different conditions are therefore as a result of the direct oxidation process and not as a result of precipitation of
dissolved Fe from solution. Precipitation of dissolved Fe on pyrite surfaces has been shown to occur under neutral to alkaline conditions, where a thick coating of goethite retards oxidation by blocking oxidant diffusion [122,45,74].

Pyrite leaching has been studied under conditions of varying pH, Eh, oxidant (Fe$^{3+}$ and O$_2$), stirring speeds, grain size and temperatures [11,13,14,61,64–66,75,76]. These experiments have generally shown that the addition of oxidants, Fe$^{3+}$ and O$_2$, significantly increases the rate of pyrite dissolution. King and Lewis [75] found that O$_2$ partial pressures up to 120 psig and initial Fe$^{3+}$ concentrations up to 0.5 M had a significant influence, while rates at ambient PO$_2$ were similar to rates under N$_2$. Moreover, it was also established that the addition of both oxidants yielded better results than just one oxidant alone [11,65,66,75].

King and Lewis [75] further found that increased temperature (80–100 °C) also positively affected pyrite dissolution while stirring speeds above 680 rpm had no effect. Long and Dixon [13] also studied pyrite leaching at stirring speeds of 650, 800 and 950 rpm. They found that maintaining or increasing speeds above 800 rpm had no significant effect on the initial rate of dissolution. Apart from the effect on rates, speeds below 800 rpm were ideal to minimise Fe-species precipitation through solution splashing. Long and Dixon [13] also established that increasing temperature had a significant influence on the rate of dissolution. They found that at 230 °C nearly all the pyrite dissolved within 20 min. King and Lewis [75] achieved a 90% conversion in 4 h at 100 °C, with 120 psig O$_2$, 0.5 M Fe$^{3+}$ and 20 g/L pyrite loading.

To a lesser extent, the acidic anions in solutions can also exert an influence on leach rates. Previous studies of aqueous oxidation of pyrite by H$_2$O$_2$ with different leach media found oxidation rates to vary according to HClO$_4$, HCl < H$_2$SO$_4$ [77–80]. It was found that increasing HCl or H$_2$SO$_4$ concentrations in their respective leaches had a negative effect on oxidation rates [77,80]. Additions of Cl$^-$ or SO$_4^{2-}$ had a similar effect. It was suggested that Cl$^-$ and SO$_4^{2-}$ adsorb onto the pyrite surface and inhibit the access of oxidants. Increasing HClO$_4$ concentration or addition of ClO$_4^-$ had no effect on the oxidation rates, while addition of SO$_4^{2-}$ in HClO$_4$ leach solutions decreased oxidation rates [79]. CI 2p XPS measurements of pyrite samples leached in Cl$^-$ solutions with Fe$^{3+}$ oxidant showed evidence of Cl$^-$ adsorption on to the leached surfaces [81]. However, Cl$^-$ intensity was found to be independent of solution Cl$^-$ concentrations. In addition limited SO$_4^{2-}$ was found (through XPS) on pyrite surface in SO$_4^{2-}$ rich leach solutions which was also independent of SO$_4^{2-}$ solution concentrations. Studies by Lehmann et al. [82] have suggested a role of Cl$^-$ ions in inhibiting the deposition of S$^0$ and S$^{2-}_n$ on reacting pyrite surfaces and also preventing the buildup of passive Fe hydroxide/oxide coatings. Using ring-disk (made of pyrite) voltammetry and in-situ Raman spectroelectrochemistry they propose that Cl$^-$ promotes oxidation of thiosulfate intermediate into tetrathionate which readily dissolves. In absence of Cl$^-$ (experiment conducted in H$_2$SO$_4$ solution) thiosulfate undergoes acid decomposition to form S$^0$ which accumulates on the surface. Furthermore, Cl$^-$ ions are aggressive anions and readily adsorb on to the surface [82]. Being a strong Lewis base, Cl$^-$ is able to replace hydroxyl ions or water molecules in the hydrated Fe hydroxide/oxide surface layers. This results in the formation of Fe-chloride complexes which readily dissolve in solution. Lehmann et al. [82] further suggest that the adsorption of Cl$^-$ may also inhibit pyrite oxidation by blocking reactive sites for Fe$^{3+}$ adsorption. It may however be argued that the removal of S$^0$, S$^{2-}_n$ and Fe oxhydroxides/oxides from the surface by Cl$^-$ may prevent the inhibition of oxidation by Cl$^-$ by allowing continued diffusion of oxidants to the surface and removal of products into the solution and may as such be beneficial to oxidation rate. Beneficial effects of Cl$^-$ has been noted in chalcopryite leaching. It has been shown that leaching in Cl$^-$ media has a faster rate with more metallic dissolution compared to leaching conducted in SO$_4^{2-}$ media [83–85]. Inhibition of pyrite oxidation by Cl$^-$ has not been widely noted in the literature. In fact experiments conducted by Williamson and Rimstidt [8] did not show any appreciable difference in the reaction rates of pyrite oxidation conducted in Cl$^-$ and SO$_4^{2-}$ solutions. Investigations of electrochemical properties (such as rate of establishment and value of corrosion potential, Tafel’s slope, corrosion current and electrode order) of pyrite oxidation also found negligible difference upon anodic oxidation in HCl, H$_2$SO$_4$ or HClO$_4$ solutions [78,86].

Furthermore, the formation of different complexes in different leach media and their ability to act as an oxidant could also be a factor causing the observed variation in the leach rates. The acidic anions in solutions tend to complex with free Fe$^{3+}$ and limit its availability for pyrite oxidation. Sasaki et al. [81] studied the effect of anionic ligands on the oxidation of pyrite by Fe$^{3+}$ ions in acidic solutions where dissolution experiments were conducted in N$_2$ purged and uncontrolled (pH and Eh) solutions, with varied concentrations of different ligands at room temperature. It was found that ligands suppressed pyrite oxidation in the order Cl$^-$ < SO$_4^{2-}$ ≪ PO$_4^{3-}$ > CO$_3^{2-}$. This ligand behaviour was explained by comparing the standard redox potential ($E°$) of different Fe$^{3+}$ complexes formed during the dissolution reactions and the potential of dominant complexes to act as oxidants. Generally, a more positive $E°$ signifies a greater tendency to accept electrons and act as oxidants. Oxidation was found to be extremely low in oxalate and phosphate anion solutions. In oxalate solutions this was due to a sharp decrease in complexes with higher (more positive) $E°$ and emergence of complexes with lower $E°$. In PO$_4^{3-}$ solutions it was due to the formation of colloidal or polynuclear Fe$^{3+}$ species with further suppression through deposition of such colloidal species on the pyrite surface. The dissolution was relatively faster in SO$_4^{2-}$ and Cl$^-$ solutions due to the formation of complexes with higher $E°$ than those formed in either PO$_4^{3-}$ or CO$_3^{2-}$ solutions. Cl$^-$ solutions caused less suppression than SO$_4^{2-}$ solutions due to formation of Cl$^-$ complexes with higher $E°$ compared to SO$_4^{2-}$ complexes.

The exact effect of acidic anions on the aqueous oxidation rate remains poorly understood, in part due to other more predominant factors such as solution Eh not being controlled during experiments, which may mask effects due to anions. There are contrasting views on the effect of Cl$^-$, whether it has a positive or negative effect on rates and the actual mechanism involved is unknown. Further studies in this area are needed to resolve these issues.

Moses and Herman [64] pointed out that the reaction progress variable (RPV) is a critical factor for judging the pyrite dissolution process. Most studies have used either different forms of S or Fe as the RPV or a combination of these. Sulfate has been widely used as the RPV in many studies [11,64–66,87] and so has the sum of aqueous S species [11,65]. The emergence of sulfoxide intermediates (thiosulfate and polythionates) may reduce the accuracy of sulfate as a the RPV, as accumulation of sulfate may not reflect the rate of pyrite oxidation [64]. Under such conditions the sum of S may prove to be a better RPV [65]. However, under certain conditions (such as low pH or anoxic Fe$^{3+}$) where little or no intermediates are evident, $ES = [SO_4^{2-} ]$ [11]. Total Fe, Fe$^{3+}$ concentrations and Fe$^{3+}$/Fe$^{2+}$ ratios have also been used as the RPV [13,65,75]. There are however concerns that some Fe (Fe$^{3+}$) may be lost from the solution due to precipitation as oxhydroxides [64].
3.3. Mechanism and kinetics of aqueous oxidation

Formulating an accurate mechanism of reaction generally involves successive collection of chemical data such as species controlling the reaction rate, rate law formulation (as a function of potential, reagent concentration, isotopic constitution of reagents and temperature), reaction products and intermediate identification, tracing of product/intermediate speciation, activation energy, bond cleavage and the influence of free energy on the rate [8, 88]. While numerous mechanisms of abiotic aqueous oxidation of pyrite have been proposed, it is very difficult to prove any specific mechanism with a high degree of certainty. Table 2 provides kinetic data and proposed mechanisms from some leach studies conducted with pyrite samples over the last two decades.

Most of the studies reported in Table 2 have used Fe\(^{3+}\), O\(_2\) or H\(_2\)O\(_2\) as oxidants while a range of pH, particle size, temperature and leach medium has been used. High activation energies (33–92 kJ/mol) are reported which suggests chemical or electrochemical control and not physical or diffusion control of the oxidation process. Most of these studies have either identified pyrite oxidation as being controlled by a chemical process with molecular adsorption reactions of chemical nature occurring on the surface or by an electrochemical process with electron transfer reactions from distinct anodic and cathodic sites on the pyrite surface. The rate dependencies do not however agree well between the studies reported in Table 2 especially where Fe\(^{3+}\) is used as the oxidant.

According to Bockris and Reddy [89] and Bockris et al. [90] there are fundamental differences between chemical and electrochemical reactions. For a chemical reaction to occur the reactants collide directly to form a product while in electrochemical reactions reactants do not directly meet but collide with an electronically conducting substrate (electrode), such as a mineral surface. The direct collision and product formation that occurs for the chemical reaction produces heat while the free energy change in electrochemical reactions produces electricity without heating the surroundings. However according to Bockris and Reddy [89] it is difficult to separate electrochemical reactions from heterogeneous chemical reactions occurring at a solid-solution interface, such as aqueous pyrite oxidation. Heterogeneous processes on surfaces (both chemical and electrochemical) may in general involve a catalyst surface (electrocatalyst for electrochemical reactions), transport and adsorption of reactants to the surface, reaction between adsorbed species (charge transfer for electrochemical reactions) and finally release of products. Furthermore Bockris and Reddy [89] state that since both processes involve “potential-energy-distance relations and barriers and activated states”, both may follow the same mathematical expression for the rate (Eq. (6)):

\[
 r = \frac{kT}{h} \prod \varepsilon_i e^{-\Delta G^0_{\text{re}}/RT}
\]  

(6)

where \(\prod \varepsilon_i\) refers to product of reactant concentrations and \(\Delta G^0_{\text{re}}\) is the standard free energy of activation. However, in contrast to chemically controlled reactions, electrochemical reactions involve a net charge transfer and have potential dependant rates, normally expressed in terms of current density, \(i\), given by Eq. (7).

\[
 \text{rate}_{\text{electrode}} = \frac{i}{F}
\]  

(7)

where the rate of the electrode reaction is expressed as moles m\(^{-2}\)s\(^{-1}\) and \(F\) is Faraday’s constant.

Eq. (7) can further be expanded and expressed in terms of anodic current density and surface area, given by Eq. (8).

\[
 r = \frac{i_0 A}{Z \varepsilon F}
\]  

(8)

where \(i_0\) is the anodic current density, \(A\) is the surface area and \(Z\varepsilon\) is the moles of electrons transferred during mineral oxidation.

According to Bockris and Reddy [89] the rate of the electrochemical reaction is normally expressed in A cm\(^{-2}\) however the current density, \(i\), is divided by the amount of charge, \(F\), transferred per mole of reactant. Pyrite oxidation is however complex as it is a multi-step process with the possibility of both homogenous and heterogeneous processes. “Purely chemical” reactions do not form a major part of most natural processes, including corrosion, photosynthesis and biological respiration [90]. According to Koryta et al. [91] chemical reactions can be part of electrochemical reactions in that they may produce an electroactive species prior to an electrochemical step, consume a product after an electrochemical step or occur simultaneously to regenerate original species from products. If this is the case for pyrite oxidation than the rate determining step in this multi-step oxidation process can either be a chemical reaction or an electrochemical transfer process. Depending on the leaching conditions such as, pH, Eh, oxidants and their concentrations, solution to mass or volume ratios, and even the type of pyrite sample, the rate control may change from electrochemical to chemical and vice-versa.

Apart from those listed in Table 2, earlier studies also posed conflicting views on pyrite oxidation rate control processes. Using pyrite samples from three different localities (Utah, Vermont and Spain) to study pyrite oxidation Garrels and Thompson [62] proposed that the instantaneous rate was controlled by adsorption of Fe\(^{3+}\) and Fe\(^{2+}\) on to the pyrite surface while Singer and Stumm [63] showed that rate is controlled by Fe\(^{2+}\) oxidation to generate Fe\(^{3+}\) in a cyclic oxidation process. These two articles have since been amongst the most cited in pyrite oxidation research.

Garrels and Thompson [62] conducted their experiment in stirred acid (H\(_2\)SO\(_4\)) Fe\(^{3+}\) sulfate solution at 33°C in a nitrogen (N\(_2\)) purged environment. The Fe\(^{3+}\) was generated from Fe\(^{2+}\) sulfate through quantitative potentiometric titration with cerate or permanganate prior to the experiment. The solution potential for each experiment was recorded as a function of time. According to Garrels and Thompson [62] the solution potential may be related to Fe\(^{3+}\) and Fe\(^{2+}\) molalities according to Eq. (9):

\[
 \text{Eh} = E^\circ + 0.059 \log \frac{m_{\text{Fe}^{3+}}}{m_{\text{Fe}^{2+}}}
\]  

(9)

This relationship and results from various potential versus time plots of each experiment, with different pyrite and different initial Fe\(^{3+}\) concentrations, was used to trace the reduction of Fe\(^{3+}\). The reduction of Fe\(^{3+}\) was used as an indicator of pyrite oxidation. It was found that pyrite of different origin oxidised at distinctly different rates albeit following a common mechanism. It was also found that the average rate of Fe\(^{3+}\) reduction was independent of total Fe in solution while the instantaneous rate decreased with time and Fe\(^{2+}\) molality. It thus appeared that the overall oxidation rate is dependent on the oxidation potential of the solution or the Fe\(^{3+}\) to Fe\(^{2+}\) ratio. Garrels and Thompson [62] proposed that the rate is proportional to the portion of the surface occupied by Fe\(^{3+}\) which would be a function of the relative Fe\(^{3+}\) to Fe\(^{2+}\) adsorption and the surface area available. The fraction of Fe adsorbed as Fe\(^{3+}\) would in turn be proportional to the fraction of Fe\(^{3+}\) in solution. Fe\(^{3+}\) would normally (that is at condition of high Fe\(^{3+}\) concentration or solution potential) oxidise pyrite irreversibly to Fe\(^{2+}\) and sulfate according to Eq. (1). However, under equilibrium conditions (low Eh approx. 250–300 mV), S\(^0\) may be produced according to Eq. (10). If an excess of Fe\(^{3+}\) is present the S\(^0\) will be further oxidised to sulfate via a number of intermediate steps. In addition Garrels and Thompson [62] also found that pH does not exert a significant influence on pyrite oxidation rate in the range of pH 0–2, however it may be significant at higher pH where Fe(OH)\(_3\) is an additional oxidation product.

\[
 \text{FeS}_2 \rightarrow \text{Fe}^{2+} + 2\text{S}^\circ + 2e.
\]  

(10)
<table>
<thead>
<tr>
<th>Pyrite type (size µm)</th>
<th>T °C/pH</th>
<th>Leach medium</th>
<th>Oxidant used</th>
<th>Rate dependence</th>
<th>Activation energy, kJ/mol (T °C)</th>
<th>Rate constant (k)</th>
<th>Mechanism</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various natural (75–150)</td>
<td>25/2.0 (HCl adjusted)</td>
<td>FeCl₃ sol.</td>
<td>Fe³⁺ 10⁻³ M</td>
<td>[Fe³⁺]²</td>
<td>92 (25–50)</td>
<td>1 x 10⁻⁴⁻².7 x 10⁻⁴ s⁻¹</td>
<td>Surface chemical controlled and mass transport</td>
<td>[6]</td>
</tr>
<tr>
<td>Natural (125–250)</td>
<td>30/1.98 (HCl adjusted)</td>
<td>FeCl₃ and FeSO₄₂ (O₂ or N₂ purged) sol.</td>
<td>Fe³⁺</td>
<td>For N₂ purge: [Fe³⁺]⁻³⁻, [Fe³⁺]⁻⁰⁻⁻</td>
<td>–</td>
<td>1 x 10⁻⁵⁻¹ cm⁻² min⁻¹</td>
<td>None proposed suggested surface chem. and electrochem. possibilities</td>
<td>[65]</td>
</tr>
<tr>
<td>Various natural (108)</td>
<td>25/6.7–8.5</td>
<td>Carbonate-buffered sol. (5 mM NaHCO₃)</td>
<td>O₂, 0.06–0.94%</td>
<td>Non-linear with-respect-to [O₂]</td>
<td>56.9 ± 7.5 (20–40)</td>
<td>1 x 10⁻⁶⁻⁷ cm⁻² min⁻¹</td>
<td>Surface controlled by product decomposition</td>
<td>[61]</td>
</tr>
<tr>
<td>Natural (38–45)</td>
<td>23–23.5/6–7</td>
<td>Oxidant used</td>
<td>Rate dependence</td>
<td>Activation energy, kJ/mol (T °C)</td>
<td>Rate constant (k)</td>
<td>Mechanism</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>Various natural (150–250)</td>
<td>25/≈2 (HCl adjusted)</td>
<td>FeCl₃ sol.</td>
<td>Fe³⁺</td>
<td>[Fe³⁺]²</td>
<td>–</td>
<td>3 x 10⁻⁵ m⁻² s⁻¹</td>
<td>Non proposed. Suggests inhibitor amongst the products</td>
<td>[92]</td>
</tr>
<tr>
<td>Natural (150–250)</td>
<td>25/≈3 (HCl and H₂SO₄ adjusted)</td>
<td>FeCl₃ and Fe₂(SO₄)₃ sol. (O₂ or N₂ purged)</td>
<td>Fe³⁺ and O₂</td>
<td>For O₂ purge: [Fe³⁺]⁻³⁻, [Fe³⁺]⁻⁰⁻⁻, [O₂]²⁺</td>
<td>–</td>
<td>1.0 x 10⁻⁸⁻⁸ m⁻² s⁻¹</td>
<td>Surface Electrochemical controlled</td>
<td>[8]</td>
</tr>
<tr>
<td>Natural (50–63)</td>
<td>20–50 acidic</td>
<td>Acidified (HClO₄) peroxide sol.</td>
<td>H₂O₂</td>
<td>[H₂O₂]²⁻</td>
<td>57</td>
<td>–</td>
<td>Chemically controlled</td>
<td>[78]</td>
</tr>
<tr>
<td>Natural</td>
<td>20–50 acidic</td>
<td>Acidified (H₂SO₄) peroxide sol.</td>
<td>H₂O₂</td>
<td>[H₂O₂]²⁻</td>
<td>68</td>
<td>–</td>
<td>Surface chemical control by shrinking core model</td>
<td>[77]</td>
</tr>
<tr>
<td>Natural Spain</td>
<td>35/≈1.6–3.5 (H₂SO₄ adjusted)</td>
<td>Fe₂(SO₄)₃ sol. (O₂ or N₂ purged) and O₂ purged sol.</td>
<td>Fe³⁺ and/or O₂</td>
<td>Anodic dissolution [H⁺]⁻⁰⁻⁻</td>
<td>79.9</td>
<td>45</td>
<td>Electrochemical control with anodic oxidation and cathodic reduction</td>
<td>[66]</td>
</tr>
<tr>
<td>Natural (various fractions from 149–44)</td>
<td>170–230</td>
<td>O₂ purged 0.5 M H₂SO₄ sol.</td>
<td>O₂</td>
<td>[O₂]²⁻ (at 210 °C)</td>
<td>33.2 (170–230)</td>
<td>–</td>
<td>Electrochemical controlled</td>
<td>[13]</td>
</tr>
<tr>
<td>Natural ≈84% Py (&lt;38)</td>
<td>45–75 acidic</td>
<td>0.1 M Fe (Fe³⁺/Fe²⁺) in 0.5 M H₂SO₄ sol.</td>
<td>KMnO₄</td>
<td>[Fe³⁺⁺Fe²⁺]²⁻</td>
<td>83</td>
<td>–</td>
<td>Electrochemical with fast ferric reduction</td>
<td>[87]</td>
</tr>
</tbody>
</table>
Singer and Stumm [63] studied the relative rates of pyrite oxidation using both Fe$^{3+}$ and O$_2$ as oxidants, in a bid to identify the rate determining step in order to control acid mine drainage. They considered pyrite oxidation as a cyclic process involving first an initiation step (Eq. (1)) which produces Fe$^{2+}$. After the initiation step a cycle is established where Fe$^{2+}$ is oxidised (Eq. (2)) to form Fe$^{3+}$ which then is responsible for continued pyrite oxidation (Eq. (3)). Investigations of the rate of reduction of Fe$^{3+}$ by pyrite, with and without O$_2$ (DO) at pH 1, demonstrated Fe$^{2+}$ to be the dominant and more rapid oxidiser of pyrite. Experiments examining Fe$^{2+}$ oxidation rates as a function of pH demonstrated the following rate expression (Eq. (11)) at pH values above 4.5:

$$\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}][O_2][OH^-]^2 \quad (11)$$

where $k$ = 8.0 $\times$ 10$^{-13}$ l$^2$ mole$^{-2}$ atm$^{-1}$ min$^{-1}$ at 25 $^\circ$C. However at pH values below 3.5 Fe$^{3+}$ oxidation is independent of pH; a similar observation to that of Garrels and Thompson [62] for the overall pyrite oxidation rate between pH 0 and 2. Below pH 3.5 Fe$^{2+}$ oxidation follows the following rate law (Eq. (12)):

$$\frac{-d[Fe^{2+}]}{dt} = k'[Fe^{2+}][O_2] \quad (12)$$

where $k'$ equals 1.0 $\times$ 10$^{-7}$ atm$^{-1}$ min$^{-1}$ at 25 $^\circ$C. The Fe$^{2+}$ oxidation by O$_2$ was identified as the rate limiting step [63]. Further investigation by Singer and Stumm [63] with natural mine waters showed increased pyrite oxidation rates due to microbial acceleration of Fe$^{2+}$ oxidation by a factor of more than 10$^6$. The authors suggest use of kinetic control measures to suppress bacterial action and retard Fe$^{2+}$ oxidation to control acid mine drainage.

Three to four decades of exhaustive research has since been conducted into identifying the control mechanisms of this economically and environmentally important process. The remainder of this section in most part examines the important studies conducted in this period. As there are countless variables involved within each experiment, it is best to consider each study individually first before collating relevant important comparable information.

McKibben and Barnes [65] carried out pyrite oxidation in low temperature acidic chloride solutions to determine the rate laws for oxidation of pyrite by solution Fe$^{2+}$, O$_2$ and peroxide. They found that the dissolution rates generally obey the following rate law (Eq. (13)):

$$R_{\text{vol}} = -k \frac{A}{V} \prod_i (M_i^n) \quad (13)$$

where $R_{\text{vol}}$ is the volumetric dissolution rate, $k$ is the rate constant, $A$ is total mineral surface area, $V$ is solution volume, $M_i$ are molarities of species $i$ affecting rate and $n_i$ the order of dependence. Using this approach McKibben and Barnes [65] used the initial rate method to determine the rate laws as they reasoned that this was a more sound approach than the integration method as a rate law is not assumed and there are no large variations in $A$ and $V$ during the initial periods of the reaction in contrast to the longer periods required for the integration method. In addition to the data given in Table 2, McKibben and Barnes [65] obtained the following rate laws (Eqs. (14)–(16)) for the three oxidants examined:

$$R_{\text{sp,Fe}^{2+}} = -10^{-0.974}M_{Fe^{3+}}^{0.5}M_{OH}^{-0.5} \quad (14)$$

$$R_{\text{sp,O}_2} = -10^{-6.77}M_{O_2}^{0.5} \quad (15)$$

$$R_{\text{sp,H}_2O_2} = -10^{-1.43}M_{H_2O_2} \quad (16)$$

McKibben and Barnes [65] suggest that a rate law containing a factor of M$_{Fe}^{0.5}$ involves the surface dissociation of a species. While this is not the case for Fe$^{3+}$, O$_2$ may undergo such a dissociation process. The authors have proposed a partial mechanism which involves the dissociation of O$_2$ adsorbed on the pyrite surface into individual O species or peroxide (Eqs. (17) and (18)).

$$O_2 \rightarrow 2O \quad (17)$$

$$O_2 + 2H_2O \rightarrow 2H_2O_2 \quad (18)$$

They further propose that this form of molecular mechanism should be “reconciled” with electrochemical mechanisms involving cathodic reduction of O$_2$ (Eqs. (19) and (20)) and anodic oxidation of pyrite.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (19)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (20)$$

Wiersma and Rimstidt [6] identified chemical control as rate limiting from their leach studies on three different categories of pyrite samples (lower-temperature/early diagenetic, marcasite, and higher-temperature hydrothermal/metamorphic) in acidic FeCl$_3$ solutions to determine the dependence of pyrite oxidation rate on Fe$^{3+}$. It was shown that the Fe$^{3+}$ data was best described by the following rate law (assumed, Eq. (21)) that is first order with respect to Fe$^{3+}$:

$$-dm_{Fe^{3+}}/dt = k(A/M)m_{Fe^{3+}} \quad (21)$$

where $k$ is the rate constant, $A/M$ the ratio of surface area of the reacting solid to mass of solution and $m_{Fe^{3+}}$ is the molar concentration of uncomplexed Fe$^{3+}$. A high activation energy of 92 kJ mol$^{-1}$ was found from an Arrhenius plot and it was concluded that the rate determining step was the breaking of the relatively strong covalent bonds at the surface, and hence a chemically controlled reaction. It was also noted that the activation energy fell to 25 kJ mol$^{-1}$, at low stirring (400 rpm) speeds and high temperatures (>35 $^\circ$C), indicating a change in rate control from surface chemical control to solution mass transport control. Other studies under similar conditions did not witness any dependence of rate of reaction on stirring speeds and thus ruled out solution mass transport as being rate limiting [65,79]. Because a surface chemical control was identified, Wiersma and Rimstidt [6] also emphasised the need to incorporate the surface area to mass of solution ratio when calculating rate constants.

Dimitrijevic et al. [79] and Antonijevic et al. [77] conducted similar experiments and also found the pyrite oxidation process to be chemically controlled. Using H$_2$O$_2$ as the oxidant, Dimitrijevic et al. [79] studied the kinetics of pyrite oxidation in perchloric (HClO$_4$) acid solutions while Antonijevic et al. [77] used sulfuric (H$_2$SO$_4$) acid solutions. Both studies found that pyrite dissolution was best described by a surface reaction controlled shrinking core model with a reaction order of one with respect to peroxide, which was the same as the reaction order found by McKibben and Barnes [65]. In addition a high activation energy (Table 2) and inverse relationship between rate constant was found. Both studies concluded that the reaction was surface chemically controlled. Dimitrijevic et al. [79] proposed a mechanism involving pyrite oxidation by peroxide through a ‘thio’ intermediate (S$_2$O$_5^-$ and S$_2$O$_3^{2-}$) formation followed by either oxidation to sulfate or decomposition to elemental sulfur and bisulfite in perchloric acid solutions. Antonijevic et al. [77] also proposed a similar mechanism for oxidation in sulfuric acid solution, however in addition they suggested that the initial peroxide adsorption onto the pyrite surface or the subsequent formation and decomposition of a pyrite-peroxide activated complex could be the rate determining step.
Numerous studies have suggested that electrochemical processes control the rate of pyrite oxidation and dissolution [8, 13, 22, 64, 66, 87]. Moses and Herman [64] conducted numerous pyrite leach experiments at circumneutral pH using either Fe(II) or O₂, with or without added initial Fe(III), as oxidants. They developed the following rate law (Eq. (22)) which is first order with respect to the ratio of surface area to solution volume:

\[
rate = k \left( \frac{A}{V} \right)^n.
\] 

(22)

To derive this rate law they assumed zero-order kinetics with respect to [SO₄²⁻] and [Fe(II)(aq)], which are products of the oxidation process. They also assumed zero-order with respect to [Fe(III)(aq)], [O₂] and [H⁺], although the rate of change of these species was not determined during their experiment. Linear dependency of pyrite oxidation rate on surface area has also been reported under buffered carbonated conditions at pH 6.7–8.5 [61].

McKibben and Barnes [65] have cautioned against assuming linear dependency of pyrite oxidation rates on surface area. As stated previously, SEM studies by McKibben and Barnes [65] showed that pyrite oxidation is mostly confined to regions with high excess surface energies, which results from the mineral growth history and surface preparation techniques. Their results demonstrated that “effective” or “reactive” surface area was more important and significantly different from total surface area. In experiments purged with O₂ and with added initial Fe(II), Moses and Herman [64] found that there was a very rapid loss of Fe(II) during the initial stages of the reaction which oxidation (to Fe(III)) alone could not account for. Moreover, in experiments with Fe(II) alone, they found that the reaction ceased after a rapid initial rate, despite the reaction solution having enough Fe(II) to sustain the reaction, with far less Fe(II) in solution then expected from Fe(II) reduction on the pyrite surface. From these results they concluded that Fe(III) was preferentially (over Fe(II)) adsorbing onto reactive surface sites and blocking Fe(II) attachment. They also suggested that Fe(III) adsorption also affects oxidation by O₂ (alone) but less severely as the amount of Fe(III) produced by O₂ oxidation is far less than that produced by Fe(II) (Eqs. (1) and (3)).

Rimstidt and Newcomb [92] also suggest the existence of an inhibitor amongst the oxidation products but rule out Fe(II), sulfate or chloride. From their results Moses and Herman [64] proposed an electrochemical mechanism of pyrite oxidation, which they considered as an extension of the model proposed by Singer and Stumm [63]. Since Fe(II) will always be present in natural systems, their mechanism involves Fe(II) adsorption on to the reactive sites as the first step followed by oxidation to Fe(III) by O₂. A schematic of the mechanism is shown in Fig. 3. The hydrated Fe(II) first adsorbs onto an electron-rich anodic site on the pyrite surface and then forms a termolecular complex with O₂ through hydrogen bonding. Electron from the Fe(II) then flow to the O₂ to produce an O₂ reduction product and Fe(III) (Fig. 3b).

from the pyrite surface to the Fe(III) to reduce it back to Fe(II) and cause a transfer of a hydroxyl to the surface sulfur group (Fig. 3c). After rehydration the Fe(III) (Fig. 3c) can repeatedly undergo the steps shown in Fig. 3a, b and c until a stable sulfoxyl species dissociates into the solution. According to Moses and Herman [64] the rate limiting step of this mechanism at circumneutral pH is the oxidation of Fe(III) to produce Fe(II). However if Fe(III) is not present then the first S to O bond formation becomes rate limiting. Williamson and Rimstidt [8] argued that at pH 2 the oxidation of Fe(III) to produce Fe(IV) for pyrite oxidation is not significant. The mechanism shown in Fig. 3 indicates that O₂ does not directly attack the pyrite surface (although this may be possible) and that the oxygen added to the sulfur group originates from water. Isotopic tracer studies by Reedy et al. [67] have shown this to be correct. Fe(III) is the dominant oxidant and if adsorbed prior to Fe(II) begins the oxidation process from Fig. 3b.

Williamson and Rimstidt [8] compiled the available literature rate data and combined it with their own experimental data to produce rate laws using multiple linear regression analysis. Their rate laws also showed dependence on Fe(II) concentration when Fe(III) was present, thus highlighting the importance of Eh in the control of the rate of reactions. When DO was present during pyrite oxidation by Fe(III), rates were only affected by Fe(II) and Fe(III) concentrations (Eq. (23)):

\[
r = 10^{-8.58(\pm 0.15)} \frac{m_{Fe(II)}}{m_{Fe(III)}}^{0.3(\pm 0.02)} \frac{m_{Fe(III)}}{m_{Fe(II)}}^{0.45(\pm 0.03)} \frac{m_{H^+}}{m_{Fe(III)}}^{0.32(\pm 0.04)},
\] 

(23)

When only DO is present as the oxidant, rates are predominantly dependant on DO concentration and with minor contribution from pH (Eq. (24)):

\[
r = 10^{-8.19(\pm 0.10)} \frac{m_{Fe(II)}}{m_{H^+}}^{0.5(\pm 0.04)} \frac{m_{H^+}}{m_{Fe(II)}}^{1.1(\pm 0.07)},
\] 

(25)

Moreover, Williamson and Rimstidt [8] also found that the rate of pyrite oxidation by Fe(III) increases when DO is present at high Fe(III) to Fe(II) ratios, however the rate is faster when DO is not present at low Fe(II) to Fe(III) ratios. The rates were also seen to positively correlate with Fe(III) and negatively with Fe(II) concentrations, which indicated a dependence of rate on the Eh of the solution. Williamson and Rimstidt [8] developed rate laws dependant on solution Eh for Fe(II) oxidation. When DO was also present the rate is given by Eq. (26):

\[
r = 10^{-19.71(\pm 0.86)} \text{Eh}^{12.93(\pm 1.04)} \text{pH}^{1.0(\pm 0.29)},
\] 

(26)

And for N₂ purged solutions the rate is given by Eq. (27):

\[
r = 10^{-12.7(\pm 0.11)} \text{Eh}^{6.10(\pm 0.19)} \text{pH}^{6.37(\pm 0.04)}.
\] 

(27)

These rate laws show that solution Eh plays a significant role in controlling the rate of pyrite oxidation by Fe(III), which may provide evidence for an electrochemical rate determined oxidation process. According to Williamson and Rimstidt [8] the leach mechanism may not follow a site specific adsorption process as they found that the reaction kinetics (fractional orders) and saturation of the mineral surface by oxidants cannot be explained by a simple Langmuir isotherm model and therefore adsorption of oxidants or desorption of products may not control the...
rate of reaction as suggested by McKibben and Barnes [65]. Williamson and Rimstidt however found that the data could better be represented by a Freundlich isotherm with a multilayer non-site-specific process. Williamson and Rimstidt [8] proposed an electrochemical mechanism for aqueous oxidation of pyrite with non-site specific, multilayer adsorption of oxidants with electron transfer from the pyrite surface as the rate limiting step. This electron transfer was proposed to occur at a cathodic site on the pyrite surface with the oxidant not necessarily directly binding to the surface. The electron transfer may occur within a “discrete zone” of solution in close proximity to the cathodic site. Williamson and Rimstidt also suggest an analogous anodic reaction, at a separate site, involving electron-deficient sulfur and water resulting in the release of a stable sulfur product. This electrochemical mechanism is different from the one suggested by Moses and Herman [64] in that the oxidants approach/adsorb on the cathodic site and not on the reduced (anodic) site. Also there is no termolecular complex (Fig. 3) formation and the sulfoxyl species are produced at a different site from the site approached by the oxidants.

Holmes and Cruddwell [66] conducted electrochemical experiments to study the kinetics of pyrite dissolution by Fe$^{3+}$ and/or DO through steady-state voltammetric measurements from a standard three electrode (pyrite working electrode, platinum counter electrode and saturated calomel electrode, SCE) cell. The pyrite used in the electrode was from Logrono, Spain and was determined by thermoelectric and Hall Effect measurements to be an n-type semiconductor. The oxidation and reduction processes were studied separately by applying anodic and cathodic potentials with respect to the rest potential while measuring the current produced. The mixed potential of the pyrite electrode leached for 14 days in acidic (pH 1.6) Fe$_2$(SO$_4$)$_3$ (9 g/L total Fe) solutions at 35 °C with solution redox potential of 0.65 V (vs SCE) was determined with and without DO. The mixed potential is defined as a spontaneous process where “two or more coupled redox reactions occur at equal but opposite rates at the same interface, one component being oxidised and the other reduced” [93]. According to Holmes and Cruddwell [66] pyrite dissolution involves anodic oxidation of pyrite and cathodic reduction of oxidants (Fe$^{3+}$ and/or O$_2$) which occur simultaneously on the pyrite surface. Thus pyrite dissolution may be represented by the following half reactions which show the anodic oxidation of pyrite by water (Eq. (28)) and cathodic reduction of the oxidants (Eqs. (19) and (29)).

\[
\begin{align*}
\text{FeS}_2 + 8\text{H}_2\text{O} & \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^- \\
\text{Fe}^{3+} + \text{e}^- & \rightarrow \text{Fe}^{2+}.
\end{align*}
\]

(28)

(29)

It was proposed that the anodic and cathodic processes are dependent on the potential across the mineral-solution interface and the overall process occurs at the mixed potential or corrosion potential ($E_m$) where the current due to the anodic and cathodic processes are equal with no net electron production. The rates of the individual half reactions determine the mixed potential for pyrite dissolution and may be given by Eq. (30) in the presence of anode $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$, with out O$_2$. This equation was derived from the individual half reactions and their relationship to current density, $i$.

\[
E_m = \frac{RT}{F} \ln \left( \frac{k_{\text{Fe}^{3+}} [\text{Fe}^{3+}]}{k_{\text{Fe}^{2+}} [\text{Fe}^{2+}] (k_{\text{Fe}^{3+}} [\text{Fe}^{3+}] + k_{\text{Fe}^{2+}} [\text{Fe}^{2+}])^{\frac{1}{2}}} \right)
\]

(30)

where $k_{\text{Fe}^{3+}}$ is the rate constant for anodic oxidation, $k_{\text{Fe}^{2+}}$ is the cathodic oxidation rate constant and $k_{\text{Fe}^{3+}}$ the cathodic reduction rate constant. According to Holmes and Cruddwell [66] under conditions where $k_{\text{Fe}^{3+}} [\text{H}^+]^{-\frac{1}{2}} \gg k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]$, the mixed potential and rate become independent of $\text{Fe}^{2+}$ concentration and dependent on pH. This occurs at low $\text{Fe}^{2+}$ concentrations typical of acid mine drainage conditions. However, under conditions where $k_{\text{Fe}^{3+}} [\text{H}^+]^{-\frac{1}{2}} \ll k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]$, the mixed potential depends on both $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ concentrations, and approaches the value of the redox potential of the solution which is given by the following Nernst equation (Eq. (31)).

\[
E_{\text{redox}} = \frac{E_0^{\text{redox}} RT}{F} \ln \left( \frac{a(\text{Fe}^{3+})}{a(\text{Fe}^{2+})} \right)
\]

(31)

where $a(\text{Fe}^{3+})$ and $a(\text{Fe}^{2+})$ represents $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ solution activities. The authors have cautioned against the assumption that the mixed potential, which is a kinetic quantity, and redox potential, which is a thermodynamic quantity, are the same. At constant $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ ratios the mixed potential is independent of total solution Fe concentration. When both $\text{Fe}^{3+}$ and O$_2$ are present the expression for the mixed potential of pyrite modifies to (Eq. (32)).

\[
E_m = \frac{RT}{F} \ln \left( \frac{k_{\text{Fe}^{3+}} [\text{Fe}^{3+}] + k_{\text{O}_2} [\text{O}_2] [\text{H}^+]^{14}}{k_{\text{Fe}^{2+}} [\text{H}^+]^{-\frac{1}{2}} + k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]} \right)
\]

(32)

where $k_{\text{O}_2}$ is the cathodic reduction rate constant. Examination of the pyrite anodic electrode (used to study pyrite oxidation) using Raman spectroscopy and XPS showed increasing amounts of polysulfides ($\text{S}_n^-$) on the surface with increasing applied potential. No apparent reduction in oxidation rates was observed due to the accumulation of these surface products as current was seen to increase exponentially with applied potential. Moreover the mixed potential of samples leached for different time periods and an unleached sample were the same. The study of the cathodic pyrite electrode for $\text{Fe}^{3+}$ or O$_2$ reduction showed that both processes are controlled by reaction kinetics and not by mass transfer, which is also evident from the high activation energies for these processes (Table 2). The cathodic study and mixed potential measurements further showed that pyrite dissolution occurs much more slowly as a result of oxidation by O$_2$ as compared with $\text{Fe}^{3+}$. Holmes and Cruddwell [66] developed the rate laws for pyrite dissolution by expanding the Eq. (7). The electrochemical rate law for pyrite dissolution with only $\text{Fe}^{3+}$ is given by Eq. (33).

\[
r_{\text{Fe}^{3+}} = \frac{k_{\text{Fe}^{3+}} [\text{H}^+]^{-\frac{1}{2}}}{14F} \left( \frac{k_{\text{Fe}^{3+}} [\text{Fe}^{3+}]}{k_{\text{Fe}^{2+}} [\text{H}^+]^{-\frac{1}{2}} + k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]} \right)^{\frac{1}{2}}
\]

(33)

and for dissolution by only DO:

\[
r_{\text{Fe}^{3+}} = \frac{k_{\text{Fe}^{3+}} [\text{H}^+]^{-0.18}}{14F} \left( \frac{k_{\text{Fe}^{3+}} [\text{Fe}^{3+}]}{k_{\text{Fe}^{2+}} [\text{H}^+]^{-\frac{1}{2}} + k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]} \right)^{\frac{1}{2}}
\]

(34)

and for dissolution by both $\text{Fe}^{3+}$ and DO the rate law is (Eq. (35)).

\[
r_{\text{Fe}^{3+}} = \frac{k_{\text{Fe}^{3+}} [\text{H}^+]^{-\frac{1}{2}}}{14F} \left( \frac{k_{\text{Fe}^{3+}} [\text{Fe}^{3+}] + k_{\text{O}_2} [\text{O}_2] [\text{H}^+]^{0.14}}{k_{\text{Fe}^{2+}} [\text{H}^+]^{-\frac{1}{2}} + k_{\text{Fe}^{2+}} [\text{Fe}^{2+}]} \right)^{\frac{1}{2}}
\]

(35)

The study finally concluded that pyrite dissolution was entirely governed by the proposed electrochemical/mixed potential process and the rate determining step is the charge transfer at the surface-solution interface.

Recent studies by Long and Dixon [13] and Bouffard et al. [87] have also pointed to an electrochemical control mechanism of pyrite oxidation. Long and Dixon [13] conducted a pressure oxidation study of pyrite from Zacatecas, Mexico (obtained from...
Wards Natural Science Establishment, Ontario, Canada) in sulfuric acid solutions and at O2 partial pressures from 345 to 1035 kPa in the temperature range of 17–230 °C. Their results showed that at low pulp densities (1 g dm−3) pyrite oxidation initially conforms to shrinking sphere model given by Eq. (36):

$$\frac{dX}{dt} = \frac{3(1-X)^2}{\tau} \quad \text{or} \quad \frac{d\sigma}{d\tau} = -\frac{1}{\tau}$$  \hspace{2cm} (36)

where \(\sigma = (1 - X)^{1/3} = d/d_{0} (d = \text{particle diameter}, d_{0} = \text{initial particle diameter}, X = \text{pyrite conversion}, \tau = \text{time} \ (\text{mins}) \) for complete oxidation.

However at later stages (at low pulp densities) the oxidation follows a “passivating shrinking sphere” model, proposed by Long and Dixon [13], as a result of possible passivation of the pyrite surface by elemental sulfur (S0). Earlier studies have also proposed possible rate control by product decomposition on the surface [61]. According to Long and Dixon [13] this surface passivation may be related to a decrease in surface electrochemical potential evident from the low Fe3+ to total Fe ratio. Moreover, they suggest that the electrochemical component of pyrite oxidation can be represented by Eq. (37). The thiosulfate (S2O32−) produced is unstable in acid solutions and may readily convert to elemental sulfur, and sulfite (SO32−, Eq. (38)). The sulfite may further be oxidized by Fe3+. They further postulate that the potential near the surface may decrease as a result of the possible increase in local concentration of Fe2+, causing a build-up of the passivating elemental sulfur film on the surface. It was further shown that increasing pulp density to 20 g dm−3 also prevented the onset of surface passivation in addition to increasing the rate of oxidation. According to Long and Dixon [13] the increased surface area relative to Fe concentration most likely maintained the electrochemical potential at a level that prevented passivation. This together with the evidence of the dissolution rate being proportional to oxygen partial pressures to the power of 0.5 led Long and Dixon [13] to suggest that the pyrite oxidation mechanism may be consistent with anodic dissolution and cathodic reduction with the rate controlled by the initial charge transfer step of both half-cell reactions represented by Eqs. (37) and (38).

$$4\text{FeS}_2 + 7\text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 4\text{S}_2\text{O}_3^{2−} + 2\text{H}_2\text{O}$$  \hspace{2cm} (37)

$$\text{S}_2\text{O}_3^{2−} \rightarrow \text{S}^{0} + \text{SO}_3^{2−}. \hspace{2cm} (38)$$

Bouffard et al. [87] studied the leaching kinetics and stoichiometry of pyrite oxidation in acidic Fe3+ sulfate (Fe2(SO4)3) solutions under controlled conditions (isokinetic) in the temperature range of 45–75 °C. KMnO4 was used as the oxidising agent which also served as a medium for controlling solution potential (Eh) and for tracing leaching progress. Fe3+ to Fe2+ ratios from 10 to 300 were used in a range of experiments. The sample used in this study contained 84.0 wt% pyrite, 11.2 wt% marcasite, 2.7 wt% arsenopyrite and 0.6 wt% chalcopyrite, determined through quantitative XRD, Rietveld analysis. It was found that the leach data, under all conditions studied, conformed well to the shrinking sphere model. The stoichiometry of dissolution was only slightly dependant on solution potential and independent of temperature, with nearly 64% sulfate formed from each unit of sulfide sulfur that was oxidised. The remaining proportion was found to be elemental S0 particles of 2 μm diameter. On the basis of the leach data a rate expression for pyrite oxidation based on mixed potential theory, an Arrhenius temperature function and shrinking sphere model was developed. The authors considered that Fe3+ reduction and mineral oxidation, occur simultaneously on the pyrite surface, and are governed by surface mixed potentials with no net electron production. The Eq. (8) was further expanded by including surface galvanic contributions from Fe(III) and Fe(II), and including effects of changing grain morphology (shrinking sphere model) and temperature (Arrhenius function) to develop the following overall rate law (Eq. (39)):

$$\frac{dX}{dt} = 0.0176 \exp \left[ -9937 \left( \frac{1}{T} - \frac{1}{333} \right) \right] \left( \frac{C_{\text{Fe(III)}}}{C_{\text{Fe(II)}}} \right)^{0.572} \frac{\mu \text{m}}{h}$$  \hspace{2cm} (39)

where \(\frac{dX}{dt}\) is the particle shrinkage rate, \(C_{\text{Fe(III)}} \) and \(C_{\text{Fe(II)}} \) are molal concentrations of Fe(III) and Fe(II) respectively and \(T\) is absolute temperature. In addition to the rate law Bouffard et al. [87] also created a mathematical expression for pyrite leaching:

$$1 - X (t, d_0) = \left[ 1 - \frac{t}{d_0} \left( 0.0176 \exp \left[ -9937 \left( \frac{1}{T} - \frac{1}{333} \right) \right] \left( \frac{C_{\text{Fe(III)}}}{C_{\text{Fe(II)}}} \right)^{0.572} \right) \right]^{3} \hspace{2cm} (40)$$

where \(X\) is pyrite dissolution and \(d_0\) is initial particle diameter. The pyrite oxidation rate was found to be dependent on temperature and proportional to the square root of the potential determining couple, Fe3+/Fe2+ ratio. According to the authors fast Fe3+ reduction occurs at the pyrite surface where mixed potentials approach the reversible potential of the Fe3+/Fe2+ couple.

Rimstidt and Vaughan [9] further strengthened the notion of electrochemical control by combining results from their previous studies and other published data to provide a detailed mechanism showing each elementary step involved in the cathodic reduction of oxidents (Fe3+ and O2) and anodic oxidation of pyrite. Their proposed mechanism is shown in Fig. 4, where the first step is the transfer of charge from a cathodic mineral surface to oxidant species followed by electron transport from an anodic site to the cathodic site and finally attachment of an oxygen atom of water to a positively charged S of disulfide sulfur (S22−) at an anodic site. The oxidants (Fe3+ and O2) react with pyrite according to Eqs. (1) and (3).

Rimstidt and Vaughan [9] propose that the electron transfer at the cathodic site occurs from a Fe2+ site on the pyrite surface to either a hydrated Fe3+ or O2 through formation of an activated complex between Fe2+ and the oxidant, and that this step is viewed as the rate determining step for the overall oxidation process. The adsorbed Fe3+ finally leaves the cathodic site as a Fe2+ after a single electron transfers while O2 is converted to 2 hydroxyl groups after the successive transfer of four electrons from the same surface Fe2+. After each successive electron transfer from the cathodic Fe2+ site on the mineral surface (which renders the cathodic Fe2+ to be a Fe3+), an electron is transferred from an anodic site to reduce the Fe3+ to reform as a Fe2+, to allow further cathodic electron transfer. This then leads to the final step to complete the oxidation process where the O of water attaches (through nucleophilic attack) to a terminal S of positive polarity (due to electron transfer to cathode) to form sulfate as the final product after 7 or 8 electron successive transfer steps. This S may pass through several oxidation states to produce S(VI)O72− from S(−I)S22−. Rimstidt and Vaughan [9] suggest that the last step of the multistep sulfate oxidation process depends on pH which can result in nearly 100% sulfate formation at low pH to substantial amounts of thiosulfate and other sulfur products as well at high pH. Along with the sulfate, Fe2+ from the anodic site will simultaneously be released into the solution where it will be coordinated by 6 water molecules which will change it to a high spin configuration thus easing its oxidation to Fe3+.

3.3.1. Summary

Recent studies seem to generally conclude that the control mechanism for pyrite oxidation follows an electrochemical process rather than a purely chemical reaction. In summary the following conclusions can be drawn.
In addition to Fe$^{3+}$, Fe$^{2+}$ also adsorbs onto the surface of reacting pyrite. One would expect that with continued leaching and with a limited supply of complexing ions in solution the concentration of Fe$^{2+}$ in the leach solution will increase (even with continued oxidation to Fe$^{3+}$) and this may increase the competition between Fe$^{2+}$ and Fe$^{3+}$ surface adsorption. What effect may this have on the rate of the oxidation process? Moses and Herman [64] and Garrels and Thompson [62] suggest that such Fe$^{2+}$ adsorption will reduce the rate and the effects may be more severe if Fe$^{3+}$ is present together with O$_2$. This is consistent with reported fractional rate law orders which are negative for Fe$^{2+}$ (Table 2). It is possible that oxidation may also proceed from adsorbed Fe$^{2+}$ sites by a similar mechanism to that proposed by Moses and Herman [64], or the adsorbed Fe$^{2+}$ may behave like surface Fe$^{2+}$ and follow the mechanism suggested by Rimstidt and Vaughan [9].

Rate control by decomposition of surface products has been suggested [61] and with the suggested presence of elemental sulfur [13,62,87] this seems highly likely. However very few studies have suggested the presence of surface leaching inhibitors [92] and such passivation has only been shown to occur under high pressure conditions [13]. The impact of the accumulation of surface products on rate may be greater under unstirred conditions which are typical of acid rock drainage however this seems to require further investigation and verification.

The rate is generally reported to be slightly inversely dependent on pH under acidic conditions but pH may play a greater role at high pH where Fe-oxy/hydroxide formation also occurs. Williamson and Rimstidt [8] showed that the rate dependence on pH was greater in the absence of O$_2$ when Fe$^{3+}$ was present and only slightly dependent on pH when O$_2$ was the only oxidant. While McKibben and Barnes [65] find similar results for the former case ($-\frac{1}{2}$ order dependence), no dependence on pH was found for the latter. Holmes and Crundwell [66], with their electrochemical study under acidic conditions, showed that pH can play a significant role in determining rates under certain conditions.

The surface area of the reacting pyrite in relation to solution volume or mass is another very important factor that determines the rate [6,64,65]. Studies [61] have reported a linear rate dependency on surface area (for O$_2$ oxidation) while others have found beneficial effects of increasing pulp densities, which increases surface area in relation to Fe concentrations [13]. Garrels and Thompson [62] have suggested a proportionality of rate to the surface area covered by the Fe$^{3+}$ which is consistent with the SEM results of McKibben and Barnes [65] who highlighted the importance of “reactive” surface area over total surface area. Studies suggesting chemical control [6,77,79] and electrochemical control [13,87] have both found a dependence of rate on the initial particle size where results conform to the shrinking sphere model. Certainly the surface plays a determining role for attachment of reactants and electron transfer processes. The ratio of surface area to solution volume needs to be sufficient to minimise solution transport effects and is an important consideration in rate law formulations.

Studies such as that reported by Wiersma and Rimstidt [6] and Holmes and Crundwell [66] suggest that under certain conditions, especially at low stirring speeds, solution transport can exert an influence on the rate. Note that nearly all studies reported here have conducted leach studies under sufficiently stirred conditions to overcome solution transport.
While industrial leaching is generally carried out with sufficient stirring to overcome bulk solution diffusion this will be quite different for acid rock drainage where transport control can exert a significant influence.

(6) \( \text{Fe}^{3+} \) is the dominant and the more rapid oxidiser compared to \( \text{O}_2 \) however \( \text{O}_2 \) is needed to sustain the oxidation reaction. Peroxide has also been shown to be also an important oxidiser with a reported first order rate dependency \([65,77,79]\).

(7) The \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) couple is rate determining even when \( \text{O}_2 \) is also present. Reported rate laws involving \( \text{Fe}^{3+} \) generally follow half order kinetics with a few studies reporting up to first order. Order with respect to \( \text{Fe}^{2+} \) is also generally half order but is negatively correlated with rate. The \( \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) ratio determines the solution’s redox potential \([62,87]\) and therefore leach rate depends on the solution \( \text{Eh} \) \([8]\).

(8) The situation is however less clear when only molecular oxygen is present as an oxidant. The rate dependence of oxidation on \( \text{O}_2 \) has not been shown to be dependent on \( \text{Eh} \). Oxidation by \( \text{DO} \) produces \( \text{Fe}^{2+} \) in solution and this has the potential to oxidise to \( \text{Fe}^{3+} \) to become a potential oxidiser itself. However, the rate of pyrite oxidation when only \( \text{O}_2 \) is present has been shown to be dependent only on \( \text{O}_2 \) concentration and \( \text{pH} \) (Table 2). It has also been shown that under such conditions \( \text{Fe}^{2+} \) oxidation to produce \( \text{Fe}^{3+} \) is not significant \([8,65]\). According to Williamson and Rimstidt \([8]\) the \( \text{O}_2 \) concentration apparently determines the solution \( \text{Eh} \) in absence of aqueous \( \text{Fe} \).

(9) Therefore when both \( \text{Fe}^{3+} \) and \( \text{DO} \) are present as oxidants the pyrite oxidation rate is directly correlated with \( \text{Eh} \) and this tends to support an electrochemical control mechanism. The rate of pyrite oxidation may be defined by mixed potential theory and expressed in terms of current density \([66,87]\) may follow a multistep electrochemical mechanism as suggested by Rimstidt and Vaughan \([9]\). However, with the strong evidence that surface area also plays a critical role this factor it needs to be incorporated into any proposed electrochemical rate laws, similar to Bouffard et al. \([87]\).

(10) The evidence for electrochemical control does not however rule out the presence of chemical processes amongst the electrochemical processes. The isotopic study conducted by Reedy et al. \([67]\) also showed that minor amounts of sulfate also derived at least one oxygen from molecular oxygen in addition to oxygen from water. The electrochemical mechanisms proposed do not however explain the existence of such sulfate-species.

Recent reviews by Chandra and Gerson \([94]\) have characterised the surface processes occurring during copper activation and flotation of pyrite and sphalerite. An electrochemical control of the process was also suggested especially under mixed mineral conditions where galvanic interactions may be rife. Mineral processing plants dealing with pyrite (for both leaching and flotation) can benefit positively by controlling electrochemically driven oxidation processes within the circuit. Further studies, resulting in the provision of information on product/intermediate speciation and spatial distribution, are required to further validate the existence of electrochemical processes as a dominant mechanism and to verify the co-existence of chemical processes and their impact under various different leach conditions. Spatially resolved surface studies are also needed to study site-specific variations in reactivity and speciation.

4. Spatially resolved surface characterisation

Pyrite (as well as many other minerals) has a very heterogeneous surface, both topographically and chemically. Numerous different \( \text{S} \) and \( \text{Fe} \) species have been suggested to occur on fresh and reacted pyrite surfaces. However, to date very few studies have focused on characterising the lateral chemical heterogeneity to get a better understanding of how distinct topographic sites react and how and what local speciation occur during reactions. Recent reviews have shown that pyrite surface studies have mostly been confined to macroscopic techniques \([95]\). Macroscopic techniques provide area averaged information and may miss critical site specific chemical variations. For example, it has been shown that a fresh pyrite surface contains four different main surface species, \( \text{S}^2_\text{(surface)} \) (3-fold coordinated), \( \text{S}^2_\text{(bulk)} \) (4-fold coordinated), \( \text{S}^2^- \) and \( \text{S}^2^- \) species \([46-49]\). However no information is so far available to see how each of these species is distributed on the surface and if there are particular regions of the surface where one species may be concentrated. If a particular species does have site-specific localisation then that area of the surface will react differently to other areas. Such information will be vital to the understanding of pyrite oxidation during leaching and acid rock drainage, and suggestions of electrochemical mechanisms may be able to be verified. Spatially resolved surface speciation information may also help in the understanding of copper activation and xanthate adsorption processes during mineral flotation.

Synchrotron based imaging and spectroscopic techniques are ideally suited for surface studies of heterogeneous materials. Synchrotrons offers a highly collimated and wide radiation energy range of high brightness (typically greater than \( 10^{18} \) photons/s/mm²/mrad²/0.1% bandwidth). The high brightness together with the high degree of collimation enables a considerable degree of demagnification and therefore high spatial resolution. The incident beam can be focused down to the sub-micron and nanometre scale while maintaining sufficient intensity to enable good quality analyses. Scanning photoelectron microscopy (SPEM) and X-ray photoemission electron microscopy (PEEM) provide spectromicroscopy and microspectroscopy with sub-micron scale spatial resolution with fast acquisition times that enables surface elemental and speciation imaging correlated to surface morphology.

4.1. Scanning photoelectron microscopy (SPEM)

Summary of capabilities:
- Highly surface sensitive imaging with high spatial resolution (>100–150 nm);
- Nano spot (150 nm) spectroscopy (XPS and XANES) with high spectral resolution;
- Chemical and elemental imaging;
- Ability to correlate topography with chemistry at a submicron scale;
- Ability to extract spectroscopic information from any region of the recorded image;
- In situ sample preparation with UHV sample fracture and exposure to atmospheric gases;
- The sample does not need to be atomically flat;
- However the focused beam can induce surface carbon deposition which may obstruct measurements.

SPEM measurements involve the use of X-ray optics to demagnify the incident photon beam to sub-micron size. Measurements are made by scanning the sample on an x–y stage with respect to the incident beam.

In a SPEM setup the sample is always normal to the incident beam while the hemispherical electron analyser (energy filter) has
Higherspatial resolution is possible (Conducting XANES imaging is easier; Problem of surface carbon contamination offset with XANES). Fig. 6 shows an image of a freshly fractured pyrite surface taken at the ESCA the sample’s surface, similar to an SEM image.

The microscopic and spectroscopic information is gathered through parallel measurements where detailed images are taken at each energy point across the absorption edge of the element examined the information depth can be in the order of Angstroms. The incident beam is focused to sub-micron size using a Fresnel zone plate lens. The two typical types of chromatic optical elements used to reduce photon beam size are reflective (such as Schwarzschild objectives) and diffractive (zone plates). Zone plates are however preferred for SPEM as they offer the optimal spatial resolution i.e. the smallest focal spot, while Schwarzschild objectives are mostly preferred for photon energies below 100 eV [96]. An order-sorting aperture (OSA) is used to block unwanted diffraction orders from reaching the sample’s surface, so that a high signal-to-noise ratio is maintained. The pressure in the SPEM chamber is maintained at a pressure in the order of $10^{-10}$ mbar.

SPEM can be used to either conduct imaging spectromicroscopy or selected microspot spectroscopy. In the spectroscopic mode it is possible to collect XPS spectra of selected elements in addition to conducting XANES measurements (as total electron yield). However, XANES measurements require a synchronised movement of the zone plate optics with changing the incident energy to keep the sample in focus [96]. The SPEM instrument incorporates a multi-channel electron detector where photoelectrons with specific kinetic energy are measured by each channel, within a specified energy window or pass energy [97]. During imaging mode an energy window is specified and multiple images (equal to the number of detector channels) of photoelectrons within this energy window are simultaneously recorded. This also provides the option of extracting XPS spectra, of energy range determined by the energy window, from any selected region of the total image.

Since intensities of photoelectrons with a particular kinetic energy within the energy window are stored in different channels, chemical maps showing chemical state information can be obtained from elemental maps by plotting information from only those channels corresponding to the energies of a particular component. Lateral chemical variations at different depths can also be imaged for a single element by using different core level transition energies, for example Fe 2p and Fe 3s images will provide information from different depths due the different kinetic energies of the resulting photoelectron.

Moreover, the final image contains topographical information (in addition to any possible artifacts as discussed below) of the sample’s surface, similar to an SEM image. Fig. 6 shows an image of a freshly fractured pyrite surface taken at the ESCA Microscopy beamline, Elettra, Italy. The image, recorded at the S 2p photoelectron energy shows the topography of the surface in a similar manner as to what would be observed with a SEM. This image also contains the elemental or chemical contrast information across the sample area, which is convoluted with the topographical effects. Processing of the image, such as division by a background image (taken at some energy below the target photoelectron peak) of the sample area, is necessary to remove the topographic effects and to reveal any chemical contrast present on the surface. To obtain the image in Fig. 7, the detector channels corresponding to $S_{2p}^+$ from Fig. 6 were chosen and normalised against the sum of the intensities of the detector channels of other energies. This removes the topographic contribution to the image and only intensities corresponding to disulfide energy are consequently displayed. Fig. 8 shows a micro-XPS spectrum with approximate energy/channel distribution and channels corresponding to different S species. Some topographic effects will remain if there is a significant difference between the kinetic energies of the background image and the elemental image as information will be from different depths. Division by a background image also helps to remove any variation in beam intensity which is essential for quantitative evaluations. Further details of artifact removal are available elsewhere [98,99]. The SPEM setup also enables in situ sample treatments, such as exposure to different gases, and pyrite surfaces before and after treatment can be studied.

4.2. Photoemission electron microscopy (PEEM)

PEEM generally offers similar capabilities to SPEM. However, some differences are:

- Higher spatial resolution is possible (<100 nm down to <10 nm on new generation PEEM);
- Conducting XANES imaging is easier;
- Problem of surface carbon contamination offset with XANES imaging which has greater information depth than XPS imaging.

PEEM is a spectromicroscopic technique which is capable of providing surface images with high spatial resolution together with detailed spectroscopic information via the use of an electron imaging system for magnification and projection of emitted electrons. The microscopic and spectroscopic information is gathered through parallel measurements where detailed images are taken at each energy point across the absorption edge of...
a selected element. Spectroscopic information (XANES) is then derived from this series of images (or stacks) by first selecting an area (or areas) of interest and plotting the intensity of the region through the stack. A diagrammatic explanation is shown in Fig. 9. Prior to obtaining the spectroscopic information the images in the stack need to be normalised against the incident beam intensity to account for natural decay or any instabilities. The images also need to be aligned well as the sample position may shift during measurements as a result of vibrations or sample stage instability. In simple terms PEEM is usually capable of XAS (XANES)-imaging by measurement of a fixed electron kinetic energy as a function of incident X-ray energy and/or XPS-imaging by measurement of a range of kinetic energies as a function of fixed incident X-ray energy. Fig. 10 shows the incident beam and sample geometry inside a PEEM UHV chamber.

PEEM offers rapid imaging due to parallel detection (simultaneously acquisition of photoelectrons emitted from different regions of the microscopic field of view) with acquisition times of a few tenths of a millisecond. This capability makes it possible to undertake in situ studies of chemical and physical processes [100].

PEEM measurements can be performed using a variety of photon sources such as a UV-lamp, laboratory X-ray sources such as Al Kα, and synchrotron X-rays [101]. Imaging can also be done using other light sources such as Hg arc lamps which may provide better (than X-ray) image contrast due to the narrow energy distribution [102]. Contrast in PEEM images usually depends on the illumination source, sample surface composition and sample topography [103]. The most powerful attributes of this technique has been made possible through the development of 3rd generation synchrotron X-ray sources which produce a wide selectable energy X-ray range and a highly brilliant X-ray beam which can also be polarised (depending on the insertion device used) The chemical and magnetic sensitivity offered by PEEM makes this technique one of the most important in the areas of surface and material science, thin films, geology, medicine and biology [104].

In its simplest form a PEEM instrument contains an objective lens and a projective lens between the sample and the detector (Fig. 11). Further lenses, apertures, beam separator, astigmatism correctors and mirrors may be added to this basic set-up for better spatial and energy resolution and more spectroscopic options [98,102,104]. These lenses in PEEM instruments can either be electrostatic or magnetic with the latter having better spatial resolution due to smaller objective lens aberrations and higher transmission [102,104]. The sample in the PEEM UHV chamber is normal to the objective lens with homogenous illumination of a relatively large area of the sample by photons incident at a glancing angle. A strong electric field exists between the sample and the objective lens (known as cathode lens) which causes the emitted electrons to accelerate from the sample surface to the objective lens. The image of the sample within the field of view (FOV) is first magnified by the objective lens, after which the
image undergoes further magnification by a series of additional lenses and finally the projective lens magnifies it onto a 2D image detector. The detector is usually an image intensifier (multichannel plate electron multiplier) coupled with a phosphor screen which converts the electron image into visible light detectable by a CCD camera with high dynamic range and high sensitivity [98].

Three categories of PEEM designs exist; PEEM without an energy filter, PEEM with an energy filter and aberration-corrected PEEM with and without energy filters [98,102]. The current generation of PEEM instruments can achieve a spatial resolution of a few tens of nanometres and an energy resolution of a few tenths of an eV [102,104]. PEEM also offers picosecond scale time resolution [104].

The spatial resolution in PEEM is limited by chromatic and spherical aberrations of the objective lens. PEEM receives all photoelectrons emitted from the surface and PEEM images are dominated by low energy secondary electrons, the source of chromatic aberrations [103]. Aberration-corrected PEEM instruments such as SMART at BESSY II and PEEM-3 at ALS are now being commissioned. These incorporate an electron optical mirror with a highly symmetric beam separator for correcting the chromatic and spherical aberrations of the objective lens [100]. Spatial resolution below 2 nm is theoretically possible [98,100]. However, even with these aberration-corrected setups PEEM will not be able to achieve the 0.1 nm range resolution currently possible with TEM [102]. Spatial resolution also depends on the degree of contrast offered by the sample which is a function of the sample material and surface smoothness. The maximum resolution cannot be smaller than two pixels. The ALS PEEM currently does not have the correction mirrors installed, however spatial resolution below 150 nm is possible.

Fig. 12 shows a feature on a pyrite surface leached in HClO$_4$ solution at pH 1, 75 °C and controlled solution Eh of 700 mV (SHE), taken with the ALS PEEM 3 instrument, beamline 11.0.1. The image shown is part of the PEEM stack or series of images taken at the Fe 2p edge. The image shown is just above Fe edge at 710 eV.

The transmission of electrons through PEEM optics is proportional to 1/E, where transmission decreases quickly with increasing kinetic energy. The signal levels are higher when kinetic energy
is lower and optimum signals are obtained when electron kinetic energy is between 50 and 100 eV making the XPS-imaging mode PEEM highly surface sensitive. XPS-imaging is best done at energies above any secondary electron peak to avoid the resulting strong background [102]. Fig. 14 shows a 2p-edge image taken at 181.0 eV photoelectron kinetic energy at the PEEM endstation, SM beamline, Canadian Light Source from of an HCl leached pyrite sample. The CLS PEEM, known as CaPeRS PEEM (Canadian Photoemission Electron Research Spectromicroscope) is a commercial instrument purchased from Elmitec GmbH (www.elmitec.de). The setup includes an energy filter which allows XPS imaging in addition to XAS spectromicroscopy. The best resolution possible with an ideal sample (high contrast features and low topography) is 25 nm [106]. Using XPS spectromicroscopy, S 2p XPS spectra were obtained from within the 10 µm feature (Fig. 15) and outside the feature with the former being dominated by high binding energy S components.

X-ray absorption measurements are conducted by the measurement of the flux of the secondary electrons (resulting from filling of core holes created by the photoionisation process) which does not require an energy filter. Secondary electrons have a relatively large mean free path due to their low energies (< 10 eV) and therefore X-ray absorption measurements using PEEM have an approximate impendence range of 5–10 nm [104,105]. Diffraction measurements (X-ray photoelectron diffraction, XPD) may also be possible with PEEM setups that use magnetic lenses [102,104].

4.3. Topographic artifacts in SPEM and PEEM

The grazing angle geometry can introduce topographic artifacts due to the angular dependence of the emitted photoelectron probing depth [98]. This causes curved or protruding surface features to appear brighter on the side facing the analyser or the incident beam, due to enhanced flux while the side away from the analyser or incident beam appears darker (shadowing effect) as either the emitted photoelectrons or the incident beam are obstructed. Similar effects also occur around pits or depressions on the surface. Other artifacts due to diffraction, back-scattering and deflection of emitted photoelectrons may also occur [98]. A simple approach to removing these artifacts from the image is by division of the image with a background image (taken at some energy below the absorption edge or photoelectron peak), provided that the kinetic energies of the background and the image are similar. An example of a topographic artefact on a pyrite surface is shown in Fig. 16.

4.4. Sample preparation

Being photoelectron-based techniques, SPEM and PEEM require the sample to be conductive or of low resistance to avoid sample charging. Pyrite being a semi-conductor (band gap 0.95 eV) meets this requirement. One of the advantages SPEM has over PEEM is that it does not require the sample to be flat, hence is ideal for studying freshly (in situ) fractured surfaces.

Samples for PEEM measurements need, ideally, to be atomically flat with highly parallel front and back surfaces so that sample tilt can be optimised (only few degrees of angle adjustment is available) and so that the surface normal is parallel with the electron optic axis. This ensures a uniform sample illumination for a good focus of the field of view and sufficient signal. However, the most important reason for a highly flat surface is due to the possible field emissions that may be created by rough surface topography. The sample in the PEEM UHV chamber is part of the cathode lens and is usually maintained under a negative voltage (approx. −15 to −20 kV) while the objective lens is at ground, approximately 2 mm from the sample. This lens field can be distorted by sample charging or surface roughness. Sharp edges on the sample surface tend to field-emit very strongly and cause the field emission intensity to exceed safe levels for the image intensifier. In the most extreme case this can possibly lead to multi-channel plate damage or in more moderate cases field emissions may cause strange image patterns. Discharges from the sample may also cause contamination of the sample surface with objective lens material such as Fe, Ni and Cr. Imaging may still be possible with moderate sample topography however the collection efficiency will vary between depressions and hills causing false intensity variations and loss of spatial resolution. Mineral samples can be polished to a mirror finish using an automatic polisher which ensures parallel surfaces (Fig. 17).

5. Conclusion

Pyrite is often viewed as a “penalty” mineral that not only increases smelting costs but is also a significant contributor to acid rock drainage. Pyrite from different geographical regions can have different electrical properties with samples also exhibiting electrical structure variations between the surface and the bulk. Pyrite is composed of Fe"^2^+" cations and S"^2^-" anions (with covalent bonding) in an ideal stoichiometric ratio of 1:2, however this...
Fig. 16. S 2p SPEM image of pyrite surface collected at ESCA Microscopy beamline, Elettra, Italy. Image A is a raw image which shows a protruding surface feature which appears brighter towards the analyser while the side away from the analyser is dark. After normalising the image with background channel, image B is obtained which shows that there was no real chemical contrast but just an artifact of the glancing angle geometry.

Fig. 17. Pyrite crystal chunk and polished pyrite slab that can be used for SPEM and PEEM measurements.

rarely occurs in nature. Lattice substitution of these ions by other minor and trace elements is directly related to ore genesis and geographical location. This tends to introduce significant electronic variations due to band gap variability and may cause the pyrite to be either an n-type semiconductor or a p-type semiconductor. Furthermore with the possibility of electrochemical control of pyrite oxidation such variations may be the reason for the differing reaction rates observed for pyrites from different locations. Generally pyrite formed in an high temperature environment, with low arsenic content and with stoichiometric S to Fe ratios of less than 2 are n-type semiconductor while where the opposite is the case p-type semiconducting pyrite tends to form. The distribution of elemental inclusions within the pyrite structure does not seem to be uniform with evidence of alternating n and p semiconductivities within a single pyrite sample. On comminution this may result in the liberation of n and p-type particles, thus adding to the variability in reaction rates. The geographical origin, elemental composition and semi-conductor type of pyrites are therefore important considerations for the study of pyrite or in industrial plant processing.

Low coordination sites are present on the pyrite surface, compared to the bulk, as a result of conchoidal fracture. Ferrous iron, with low coordination, tends to be present at sites of defects and imperfections (steps and kinks) which have smaller band gaps and higher dangling bond densities. This makes these sites prone to oxidant (ferric iron and molecular oxygen) attack where the rate of charge transfer will be much faster compared to sites of normal (6-fold) coordination. Pyrite exists in a low-spin diamagnetic configuration with unoccupied Fe 3d states. If oxidants chemisorb to the pyrite surface then these empty 3d states will accommodate electrons from the adsorbates following strong hybridisation. Consequently ferrous iron is an ideal species for electron transfer reactions with oxidants, as is consistent with the electrochemical oxidation mechanism proposed by Rimstiidt and Vaughan [9].

Atmospheric oxidation of pyrite begins within minutes of exposure, resulting in the production of sulfate, iron oxyhydroxide species and possibly elemental sulfur and polysulfide. The oxidation reaction is more rapid when both molecular oxygen and water are present. The formation of ‘islands’ of surface products provides further evidence for the concept of reactive and less reactive surface areas.

Aqueous oxidation of pyrite generally results in the production of sulfate as the main product and the release of unoxidised ferrous iron into solution. It may also produce species such as elemental sulfur, polysulfide, hydrogen sulfide gas, ferric hydroxide precipitate, iron oxide, iron(III) oxyhydroxide and intermediates such as thiosulfate, sulfite and polythionates. However, the presence and abundance of these species depends on the oxidising conditions. Solution pH, Eh, oxidant type and concentration, stirring speeds, grain size and surface area in relation to solution volume, temperature and pressure are all critical and generally influence the rates of reaction. Of these, solution Eh and surface area or grain size exert a more significant influence on rates as compared to any one other factor. The direct correlation of rates with Eh strongly indicates the dominance of electrochemical reactions during pyrite oxidation. This may involve the anodic oxidation of pyrite with simultaneous cathodic reduction of oxidants with the overall process occurring at a mixed potential where the individual reactions are defined by current density. The proposed mechanism involves numerous charge transfers with a multi-step disulfide oxidation process to produce sulfate as the final product through several intermediates and release of ferrous iron. The proposed rate determining step is the transfer of charge from the pyrite surface at the cathodic site. Given the reactivity of other surface species (on freshly fractured surface) such as monosulfide, these species will be oxidised during atmospheric exposure or during the initial period of aqueous reaction.

The proposed mechanisms have not yet defined the nature of adsorption (if any) of the oxidants on to the surface. Furthermore, the proposed mechanisms do not account for the presence of sulfoxyl species with at least one oxygen atom abstracted from molecular oxygen. Therefore the simultaneous presence of minor chemical processes, with the possibility of chemisorption of oxidants, should also be considered.

While numerous detailed studies of the pyrite surface have been carried out, there is currently lack of any chemical information on a spatially resolved scale. Recent data suggests that species
are heterogeneously distributed on the surface and oxidation is seen to be site specific. A detailed characterisation of freshly fractured surfaces by imaging the spatial distribution of different surface species is required. Such a study should also be coupled with a spatially resolved examination of species evolution on reacted pyrite surfaces. It would then be possible to trace the reactivity of different surface regions and verify if the proposed electrochemical mechanism conforms to the spatially observed surface speciation. Scanning photoelectron microscopy (SPM) and photoemission electron microscopy (PEEM) are two synchrotron-based surface spectromicroscopic and microspectroscopic techniques that can provide such information. The two techniques use XPS-imaging and XANES-imaging to provide surface chemical maps enabling the correlation of chemistry and topography at a sub-micron scale.

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