

UNIVERSIDADE FEDERAL DE MINAS GERAIS
Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas

Tese de doutorado

“Investigation of pyrite oxidation in alkaline
solutions by thermodynamic modeling and
analyses by X-ray diffraction, infrared and
Raman spectroscopy”

“Estudo da Oxidação de Pirita em meio Alcalino
através de Modelagem Termodinâmica e de Análises
por Difração de Raios-X, Espectroscopia de
Infravermelho e Raman”

Autora: Cláudia Lima Caldeira
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Kwadwo Osseo-Asare

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LIST OF CHEMICAL FORMULAS

Compounds	Chemical formula
Corundum	Al_2O_3
Feroxyhite	$\delta\text{-FeOOH}$
Ferrihydrite	$\text{Fe}_4(\text{O},\text{OH},\text{H}_2\text{O})$ - 2-line and $\text{Fe}_{4.6}(\text{O},\text{OH},\text{H}_2\text{O})$ - 6-line (notation $\text{Fe}(\text{OH})_3$)
Ferric oxyhydroxycarbonate	$\text{Fe}(\text{III})_6\text{O}_{(2+x)}(\text{OH})_{(12-2x)}(\text{H}_2\text{O})_x(\text{CO}_3)$ – (notation - $\text{Fe}(\text{III})\text{-GRCO}_3$)
ferrous-ferric hydroxide carbonate - Green rust 1 – carbonate	$\text{Fe}_4^{(\text{II})}\text{Fe}_2^{(\text{III})}(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O}$ (notation - GR1 - CO_3)
Goethite	$\alpha\text{-FeOOH}$
Hematite	Fe_2O_3
Iron(II) carbonate hydroxide	$\text{Fe}(\text{II})_2(\text{OH})_2\text{CO}_3$
Iron (III) hydroxycarbonates	$\text{Fe}(\text{III})(\text{OH})\text{CO}_3$
Lepidocrocite	$\gamma\text{-FeOOH}$
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
Magnetite	Fe_3O_4
Pyrite	FeS_2
Pyrrhotite	FeS
Siderite	FeCO_3

ABSTRACT

An investigation of pyrite oxidation in alkaline solutions by thermodynamic modeling and analyses by X-ray diffraction, infrared and Raman spectroscopy was carried out. The effect of pH and solution composition on the nature of the oxide product and complex formation is explained. A mechanism is proposed to explain the increase of the oxidation rates in carbonate/bicarbonate solutions due to the formation of the iron carbonate complexes. According to thermodynamics, hematite is the expected iron oxide phase produced during oxidation. As ferrihydrite is considered to be the initial product of the rapid hydrolysis of Fe^{+3} solutions, the predominance area of this metastable phase was also investigated as a possible product of pyrite oxidation in alkaline solutions. The Eh–pH diagrams indicated that ferrihydrite predominates in the pH range from 2 to 14 and potentials (Eh) of 0.25 V and higher. In the presence of carbonate, the stability diagrams show that soluble iron-carbonate complexes may be formed at pH below 8-12, coexisting with pyrite in the same region. At pH higher than 11 and oxidizing conditions, only $\text{Fe}(\text{OH})_4^-$ predominates even in the presence of carbonate/bicarbonate ions. X-ray diffraction analyses, infrared and micro-Raman spectroscopy indicate that the products formed are determined by solution composition and pH. In hydroxide solutions (pH 8.5 and 10), hematite and feroxyhite were identified as the major and minor solid phases, respectively. At pH 12.5, only ferrihydrite is identified. Conversely, Fe(III)-green rust/ferrihydrite are found as the main products of pyrite oxidation in bicarbonate/carbonate media. It is proposed that the formation of soluble Fe(II)/Fe(III)- CO_3 complexes modify the hydrolysis and precipitation pathways of the iron released from pyrite. Two distinct precipitation pathways are proposed. In hydroxide solutions and in conditions of low iron solubility (pH 8.5 and 10), pyrite oxidation leads to the formation of hematite. As pH increases up to pH 12.5, iron solubility increases due to the formation of $\text{Fe}(\text{OH})_4^-$ and ferrihydrite becomes the predominant oxyhydroxide. Similarly, in the presence of carbonate/bicarbonate, Fe(III)- GRCO_3 is the main phase identified. The formation of these products was attributed to the increase of iron solubility in the presence of carbonate associated with the formation of the soluble Fe(II) and Fe(III) carbonate, and hydroxyl complexes. Ferrihydrite transformation to more stable phases (e.g. hematite or goethite) was prevented due to the high concentration/adsorption of soluble silicate ions. The identification of carbonate compounds among the products formed during pyrite oxidation was possible, by the first time, by the use of diffuse reflectance infrared spectroscopy. It is also important to note that the conditions where the carbonate compounds are identified correspond to those in which the fastest rate of pyrite oxidation in carbonate solutions is reported. Concerning the mechanism of pyrite oxidation, the formation of Fe(II)- CO_3 soluble complexes favors the

oxidation of iron, which in turn favors the overall kinetics of pyrite oxidation in carbonate solutions.

RESUMO

A oxidação de pirita em soluções alcalinas foi investigada através de modelagem termodinâmica e análises por difração de raios-X, espectroscopia por infravermelho e Raman. Os efeitos do pH e da composição da solução na formação de diferentes fases sólidas e solúveis foram explicados com base na solubilidade do ferro e na formação de complexos. Um modelo consistente foi proposto para explicar o aumento da taxa de oxidação da pirita em meio bicarbonato /carbonato, baseando-se na formação de complexos de ferro-carbonato. Evidências termodinâmicas e experimentais da formação das diferentes fases são apresentadas. De acordo com a termodinâmica, a hematita é o principal produto sólido formado na oxidação de pirita em meio alcalino. Em condições metaestáveis, os diagramas Eh-pH mostram a possibilidade de formação de ferridrita (produto inicial da rápida hidrólise de Fe(III)) na faixa de pH entre 2 e 14, e potencial redox superiores a 0,25. Os diagramas de estabilidade indicam, ainda, que complexos solúveis de ferro-carbonato podem ser formados entre pH 8-12, coexistindo com a pirita. Para valores de pH > 11 e condições oxidantes, apenas a espécie $\text{Fe}(\text{OH})_4^-$ é estável, mesmo na presença de íons carbonato/bicarbonato. As análises por difração de raios-X, espectroscopia por infravermelho e micro-Raman mostram que diferentes produtos de oxidação são formados em função da composição da solução e do pH. Em soluções de hidróxido de sódio (pH 8,5 e 10), a hematita e a feroxihita são identificadas como fases principal e minoritária, respectivamente. Em pH 12,5, apenas a ferridrita foi identificada. Na oxidação da pirita em sistema bicarbonato/carbonato, Fe(III)-**green rust** e ferridrita aparecem como os principais produtos formados. Propõe-se que os processos de hidrólise, oxidação e precipitação dos íons ferrosos gerados no processo de oxidação de pirita sejam afetados pela formação de complexos solúveis de Fe(II)/Fe(III)- CO_3 . Dois caminhos distintos explicam os resultados obtidos. Em sistema hidróxido e em condições de baixa solubilidade de íons ferro (pH 8,5 e 10), a oxidação de pirita leva à formação de hematita. Com o aumento do pH até 12,5 e o conseqüente aumento da solubilidade do ferro, pela presença de $\text{Fe}(\text{OH})_4^-$, a ferridrita torna-se o óxido predominante. Em sistema carbonato/bicarbonato, ferridrita e Fe(III)-GR CO_3 foram as principais fases identificadas. A formação desses produtos também foi relacionada ao aumento da solubilidade de íons ferro através da formação de complexos solúveis de Fe(II) e Fe(III) com os íons carbonato e hidroxila. A transformação de ferridrita em uma fase mais estável (por ex., hematita e goethita) foi impedida pela elevada concentração / adsorção de íons silicatos, liberados pelo contato da solução com o reator de vidro. A identificação de compostos de carbonato nos produtos de oxidação de pirita foi possível, pela primeira vez, com a utilização da espectroscopia por infravermelho – reflectância

difusa. É importante destacar que os complexos de ferro-carbonato são formados em condições similares àsquelas nas quais as maiores taxas de oxidação de pirita são relatadas. Considerando-se o mecanismo de oxidação, entende-se que a formação de complexos solúveis de Fe(II)-CO_3 favorece a oxidação de ferro, que por sua vez favorece a cinética global de oxidação de pirita em sistema carbonato.

1 INTRODUCTION

The kinetics and mechanisms of pyrite oxidation are important in order to understand and control the reactions in ore processing, metal extraction, acid mine drainage (AMD), among other processes (Stenhouse and Armstrong, 1952; Bailey and Peter, 1976; Moses et al. 1987; Mishra and Osseo-Asare, 1988; Crundwell, 1988; Ciminelli and Osseo, 1995a,b; Holmes and Crundwell, 2000; Chernyshova, 2004). Acid mine drainage (AMD) is a severe environmental pollution problem commonly related to sulfide-containing ore mining operations, such as pyrite oxidation in coal wastes and ore tailings. The kinetics and mechanism of pyrite oxidation have received much attention for many decades, especially in acidic solutions (Bailey and Peters, 1976; Lowson, 1982; Crundwell, 1988; Mishra and Osseo-Asare, 1988; Wei and Osseo-Asare, 1997; Holmes and Crundwell, 2000; Rimstidt and Vaughan, 2003). Pyrite oxidation is usually described by an electrochemical mechanism, thus implying that the overall reaction can be written in terms of half-cell reactions. The anodic oxidation of pyrite produces ferrous and sulfate ions and the oxidant (e.g. molecular oxygen or ferric ion) is reduced on the cathodic site. The specific mechanisms depend on the nature of the oxidizing agent (O_2 , Fe^{+3} , H_2O_2) as well as on the presence of other constituents of the aqueous phase. A main difference between pyrite oxidation under acidic and alkaline conditions is the hydrolysis and precipitation of ferrous/ferric ions as pH increases. The nature and properties of this solid product will be determined by the conditions in which the reaction takes place. The neutralization with lime is often expected to reduce pyrite oxidation due to the formation of an oxide layer. Long-term oxidation in carbonate solutions promoted the coating formation, which significantly reduced the rate of pyrite reaction (Nicholson et al., 1990). However, this coating's effect was shown to be highly dependent on solution composition (e.g. presence of calcium ions). The relatively slower rate of pyrite oxidation found in CaO solution was explained by the formation of an adherent layer of calcium carbonate (Caldeira et al., 2003).

The increase of the rate of pyrite oxidation with the increase of pH, alkaline reagent concentration and temperature is well established (Moses et al., 1987; Nicholson et al., 1988 and 1990; Hood, 1991; Moses and Herman, 1991; Ciminelli and Osseo-Asare, 1995 a, b; Descostes et al., 2002). Previous works (Nicholson et al., 1988 and 1990; Hood, 1991; Moses and Herman, 1991; Ciminelli and Osseo-Asare, 1995a, b) also showed a significant increase in the rate of pyrite oxidation by molecular oxygen in sodium carbonate solutions in comparison with the rate in other alkaline media, such as sodium hydroxide and sodium

borate. However, the specific role of bicarbonate/carbonate ion during the aqueous oxidation of pyrite is not available yet. The main hypothesis to explain this behavior is the possible formation of soluble iron carbonate complexes in neutral and alkaline solutions. Ciminelli (1987), Hood (1991) and Ciminelli et al. (1994) attempted to identify iron-carbonate complexes in the products of pyrite aqueous oxidation by FTIR, but none was able to find the characteristic bands related to the carbonate species. Evangelou and Huang (1994) and Evangelou et al. (1998) only identified Fe(II)-CO₃ complexes and carboxylic groups on the surface of pyrite samples exposed to atmospheric oxidation, due to carbon dioxide complexed at pyrite surface. Nevertheless, no carbonate species were identified on pyrite samples oxidized in aqueous bicarbonate media. Descostes et al. (2002) suggested the formation of siderite by FTIR analyses, but only in very concentrated carbonate/bicarbonate solutions (1 mol/L). These results can be questioned by the poor quality of the spectra and the possible precipitation of other metal carbonates, at such high concentrations. Until now, there is no clear evidence to support the role of aqueous or solids carbonate complexes on the reported faster kinetics of pyrite oxidation. One of the aims of the present investigation was to provide these evidences.

Recently, the carbonate complexation of Fe(II) and Fe(III) in solution has been investigated by Bruno et al. (1992a, b), through studies involving the solubility of siderite (FeCO₃) and hematite (Fe₂O₃) in acid, neutral and alkaline medium. The formation of iron carbonate complexes, as well as their equilibrium constants, has been reported by Bruno et al. (1992a, b), and their values were revisited by King (1998) and by Hummel (2000). A final set of data is presented by Bruno and Duro (2000). The determination of equilibrium constants for the Fe(II), Fe(III)-carbonate complexes makes possible now the establishment of their stability areas as a function of pH and redox potential.

Pyrite decomposition in alkaline solutions allows the neutralization of the acid formed during the oxidation reaction and maintains a favorable pH condition for the precipitation of iron (Burkin and Edwards, 1963; Nicholson et al., 1988 and 1990; Ciminelli and Osseo-Asare, 1995 a,b; Descostes et al., 2002). It may be possible that at a microscopic scale pyrite oxidation in the presence of alkaline material is controlled by the presence of Fe(III) near the surface of pyrite and not by the solubility of Fe(OH)₃ in pure solutions (Luther et al., 1992). The extension of Singer and Stumm (1970) model was proposed by Moses et al. (1987) and Moses and Herman (1991), which claims the Fe(III) is the major pyrite oxidant even at circumneutral pH. Regardless Fe(III) is the preferred reactant, the reaction can only be sustained in the presence of O₂. The role of ferric ion in alkaline oxidation of pyrite is not well understood.

The iron oxide/hydroxide layer formed during pyrite oxidation has been characterized mainly by X-ray photoelectron spectroscopy (XPS) and FT-infrared analyses (Evangelou and Huang, 1994; Evangelou et al. 1998; Bonissel-Gissing et al., 1998; Descostes et al., 2000, 2001; Todd et al., 2003). However, the XPS technique only provides information about the binding energy of the compounds found on oxidized samples (e.g., Fe-O, Fe-S, Fe-OH, S-O). Considering the proximity of the Fe-O values for the iron oxide/hydroxides, the precise identification of the phase formed is not unambiguous. In addition, most oxidized samples described in the aforementioned works using XPS or FTIR were obtained in long-term experiments. Thus, it is expected that ageing, phase transformations and secondary precipitation may occur. In addition, bulk infrared analyses are not the best option to discern a mixture of iron oxide/hydroxide phases. On the other hand, the successful identification of surface-bound sulfate and thiosulfate species (Sasaki et al., 1997; Borda et al., 2003a and 2004) encourages further attempts to identify carbonate on the oxidized pyrite. In this context, diffuse reflectance infra-red spectroscopy-DRIFT was employed.

There is a certain analogy between the reactions that can be involved during the pyrite oxidation and those found in the precipitation of iron compounds and in the iron corrosion process (Bewick et al., 1991; Blengino et al., 1995; Oblonsky and Devine, 1997; Legrand et al., 2000, 2001 a,b; Savoye et al., 2001; Music et al., 2004). Most of the iron oxides and oxide hydroxides can be produced from Fe(II) solutions by oxidation followed by hydrolysis. In general, the oxidation and hydrolysis of Fe^{+2} leads to Fe(III) oxides either directly or via soluble green rust complexes and solid green rusts or $\text{Fe}(\text{OH})_2(\text{aq})$. The latter is converted to the oxides either by a solid state or via a solution (reconstructive-dissolution and precipitation) transformation (Cornell and Schwertmann, 1996). The effect of bicarbonate/carbonate ions on the formation of iron oxide/hydroxide layer in aqueous corrosion of metallic iron has been reported by many authors (Odziemkowski et al., 1998; Legrand et al., 2000; Savoye et al., 2001; Bonin et al., 2000; Music et al., 2004).

Characterization of the oxide layer formed in iron/steel corrosion is found at a relatively advanced stage if compared with that of pyrite oxidation. Many techniques of surface analyses have been employed in order to further characterize iron compounds, such as Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS), FT-infrared and Raman spectroscopy. Raman spectroscopy presents the advantage of providing a fingerprint of the compound. In the case of incipient pyrite oxidation, micro-Raman spectroscopy provides the possibility to select target areas according to image features, a special advantage in analyzing complex oxide mixtures.

The present work aims to investigate the reaction of pyrite oxidation by molecular oxygen in NaOH and Na₂CO₃ solutions with the help of thermodynamic modeling and product analyses by X-ray diffraction, infra-red and Raman spectroscopy. The identification of the solid products and the iron carbonate complexes are emphasized. The thesis is organized in 6 chapters. A comprehensive review of pyrite oxidation is presented in Chapter 2. In this chapter, aspects of mechanism and kinetics involved in pyrite oxidation, emphasizing the reaction in alkaline media, are reported. The nature of the oxide layer obtained in alkaline pyrite oxidation is discussed in detail. The experimental approach adopted in this study is described in Chapter 3. The thermodynamic stability of the iron-carbonate complexes was evaluated with the help of Eh-pH diagrams. For characterization of the pyrite oxidation products, X-ray diffraction, infrared and micro-Raman spectroscopy were employed. In Chapter 4, the results obtained in this work are presented as follows: through Eh-pH diagrams for the Fe-S-CO₃-H₂O system, the thermodynamic stability of the iron-carbonate complexes, as well iron oxide/hydroxide phases, are discussed, in order to correlate the predominance areas of these phases with the mechanism of pyrite oxidation. The product layer formed during pyrite oxidation is analyzed by X-ray diffraction (XRD), infrared spectroscopy (diffuse reflectance and transmission techniques) and micro-Raman spectroscopy. These results are discussed in Chapter 5, with the focus on how the iron carbonate complexes and pH increase affect the mechanism of pyrite oxidation and the nature of the solid iron oxyhydroxide formed. The main conclusions of the present work are presented in Chapter 6.

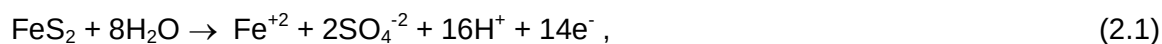
2 LITERATURE REVIEW

2.1 Pyrite Oxidation

The kinetics and mechanism of the oxidation of pyrite (FeS_2) mostly in acidic solutions are reported in a number of reviews (Lowson, 1982; Evangelou, 1995; Rimdist and Vaughan, 2003). McKibben and Barnes (1986), Moses et al. (1987), and Holmes and Crundwell (2000) studied the rate of the oxidation of pyrite by ferric ions and dissolved oxygen. In general, the rate of oxidation of pyrite increases with the concentration of ferric ions, and decreases with the concentrations of ferrous and H^+ ions. Bailey and Peters (1976), McKibben and Barnes (1986), Hood (1991), Williamson and Rimstidt (1994), Koslides and Ciminelli (1992); Ciminelli and Osseo-Asare (1995 a, b) and Holmes and Crundwell (2000) proposed different empirical expressions for the rate of oxidation of pyrite. The form of the rate expressions has been discussed in terms of adsorption theory (Bailey and Peters, 1976, Goldhaber, 1983) and molecular theory (Luther 1987, Osseo-Asare, 1993). A summary of the current understanding of FeS_2 oxidation is presented in the following paragraphs.

Pyrite is a semiconductor, and since the kinetics of dissolution is usually described by an electrochemical mechanism. The semiconducting properties influence the kinetics of dissolution (Crundwell, 1988; Mishra and Osseo-Asare, 1988; and Osseo-Asare, 1992). Thus, depending on the conductivity of the material, the electron transfer will occur via a chemical redox or an electrochemical pathway. Semiconductors, with their intermediate electronic conductivities, will be expected to be susceptible to both chemical and electrochemical redox dissolution (Osseo-Asare, 1993). In order to understand the model of chemical redox oxidation, an approach was proposed by Luther (1987) and Osseo-Asare (1993) in terms of molecular orbital theory. The chemical redox dissolution pathway exhibits many of the characteristics of homogeneous electron transfer, which may proceed via an outer-sphere or an inner-sphere pathway. This model will be discussed later.

The electrochemical oxidation of pyrite involves several key reactions and intermediates (Bailey and Peters, 1976; Mishra and Osseo-Asare, 1988; Holmes and Crundwell, 2000). The overall reaction can be written in terms of the half-cell reactions, which are the anodic oxidation of pyrite forming ferrous and sulfate ions,



or producing Fe^{+2} and S^0 when the acid strength increases, as shown in the reaction below:



and the cathodic reduction of ferric ions or dissolved oxygen,



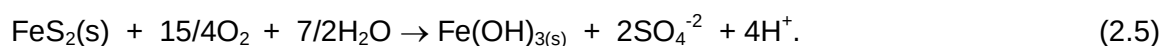
It should be noted that dissolved O_2 and Fe^{+3} behave only as electron acceptors in the separate cathodic reaction. By isotope studies, Bailey and Peters (1976), Taylor et al. (1984), Reedy et al. (1991) and Usher et al. (2004) observed that the oxygen in the sulfate product originates from water rather than molecular oxygen. This observation is a direct consequence of the electrochemical mechanism - the existence of anodic and cathodic sites on pyrite surface, the electrons moving from one part of the mineral to another, in order the reactions to occur. According to this mechanism thiosulfate is formed as an intermediate phase during pyrite oxidation. Thus, an important step is the breaking of the Fe-S bond and the formation of the intermediate thiosulfate, from which the final products of sulfate and elemental sulfur are formed. This approach is based on the model of Johnston and McAmish (1973), by which sulfur is formed from the decomposition of thiosulfate; while sulfate is formed by an electrochemical or homogeneous oxidation of thiosulfate in the presence of oxidants (e.g. Fe^{+3} and O_2) (Luther, 1987; Mishra and Osseo-Asare, 1988). Despite some arguments of Kelsall et al. (1999) and Holmes and Crundwell (2000) saying that the sulfate yields obtained from the anodic dissolution of pyrite provide evidence that sulfur is not formed by acid decomposition of thiosulfate. Recent studies reinforce that the step-wise oxidation of the disulfide group with the presence of intermediate thiosulfate species at the pyrite surface (Luther, 1997; Borda et al., 2003a and 2004; Descostes et al., 2004). In acidic solutions, disproportion of thiosulfate ions into sulfur and tetrathionate ions ($\text{S}_4\text{O}_6^{2-}$) and bisulfite (HSO_3^-) is consistent with thermodynamic considerations (Descostes et al., 2004).

2.2 Kinetics of Pyrite Oxidation in Alkaline Media

Some studies have been published focusing the kinetics and mechanism of pyrite oxidation in alkaline solutions (sodium carbonate/bicarbonate, sodium hydroxide and sodium borate reagents) (Stenhouse and Armstrong, 1952, Burkin and Edwards, 1963; Smith and Shumate,

1970; Moses et al., 1987; Nicholson et al., 1988 and 1990; Hood, 1991; Koslides and Ciminelli, 1992; Ciminelli and Osseo-Asare, 1995 a,b; Descostes et al., 2002 and Chernyshova, 2004). These authors observed an increase in the rate of pyrite oxidation with the increase of pH, reagent concentration and temperature.

The overall reaction of pyrite oxidation in neutral-alkaline solutions, assuming complete oxidation of iron and sulfur, is:



The main net products of pyrite oxidation are sulfate and a ferric hydroxide precipitate. Thus, at pH > 3.5, the rate of pyrite oxidation could be limited by the low solubility of Fe(OH)₃. It may be possible that at a microscopic scale pyrite oxidation in the presence of alkaline material is controlled by the accessibility of Fe⁺³ near the surface of pyrite and not by the solubility of Fe(OH)₃ in pure solutions. A similar conclusion was drawn by Moses et al. (1987). Luther et al. (1992) pointed out that the solubility of amorphous Fe(OH)₃ may control pyrite oxidation as long as there is physical contact between pyrite and the amorphous hydroxide. According to Eggleston et al. (1996), the rate constant for electron transfer from surface-exposed pyrite-Fe⁺² to O₂ is small. Fe⁺² in oxide form is a better reductant than Fe⁺² in pyrite, so the electron transfer to O₂ from oxide is faster. Electron transfer is also assumed to be faster from Fe(II)-pyrite to Fe⁺³ present as an oxidation product.

Ciminelli and Osseo-Asare (1995 a, b) have studied the kinetics of pyrite oxidation in the presence of different alkaline reagents and concentrations, temperatures (50-85°C) and oxygen partial pressures (0-1 atm). Under alkaline conditions (pH 8 - 12) and in the early stages, they found that the reaction rate in sodium carbonate solutions is faster relatively to the rate in other alkaline media (CaO and NaOH). Two possible reasons for the differences caused by the addition of carbonate ions have been considered: *(i)* alteration of the chemical nature of the product layer through precipitation of a distinct phase such as iron carbonate and *(ii)* modification of the oxide precipitation conditions through the formation of soluble iron-carbonate complexes and increase of ionic strength (Ciminelli, 1987). Hood (1991) observed that the rate of pyrite oxidation increases with increasing carbonate concentration (0.002 to 0.05 mol/L). No similar effect was obtained with borate solutions. Brown and Jurinak (1989) investigated the rate of pyrite oxidation in aqueous media at 25°C for periods up to 3 weeks. The authors reported constant oxidation rates as a function of time in the presence of NaClO₄, CaCO₃ and NaHCO₃.

Some kinetic parameters of pyrite oxidation determined by the different authors are shown in Table II.1. The dependence upon $[O_2]$ in either carbonate and hydroxide media obtained by Ciminelli and Osseo-Asare (1995 a, b) and Koslides and Ciminelli (1992) are in agreement with the 0.46 ± 0.05 dependence determined by Hood (1991) in various alkaline solutions and with the 0.5 dependence reported by Stenhouse and Armstrong (1952) for pyrite alkaline oxidation under high pressure and temperature. Also, these results are in agreement with the 0.5 dependence observed by McKibben and Barnes (1986), Williamson and Rimstidt (1994) and Holmes and Crundwell (2000) for pyrite oxidation in acidic solutions. It is important to mention that Stenhouse and Armstrong (1952) and Smith and Shumate (1970) measured the reaction rate from oxygen consumption, but this measurement requires a defined stoichiometry that was not stated by the authors. In addition, it is known that many reactions

Table II.1 – Kinetic parameters of pyrite oxidation in alkaline solution

Experimental Conditions	Ea (kcal/mol)	Rate expression	Reference
1.5 mol/L NaOH, 90-170 °C, 0-27 atm O_2 , $d_0 = 10.9 \mu m$	2 to 4	$r = k[O_2]^{0.5}$	Stenhouse and Armstrong, 1952
0.5 mol/L NaOH, 60-150 °C, 2.7 atm O_2 , $d_0 = 40-120 \mu m$, pH = 13.5	8.6 to 9.2	Not determined	Burkin and Edwards, 1963 ³
pH 2 to 10, 20-35 °C, 0-1 atm O_2	13.9	$r = f([O_2]^{0.7} [OH^-]^{0.12})$	Smith and Shumate, 1970 ^{1, 2}
NaHCO ₃ , pH 7-8.7, 10-55 °C, 62-1223 $\mu mol/L$, $d_0 = 75-106 \mu m$	19.8±1	$r = k[O_2]^{0.46} [OH^-]^{0.3}$	Hood, 1991
NaOH, pH 10 to 13.5, 100- 160 °C, 1-10 atm O_2 , $d_0 = 38-212 \mu m$	12.9 (T<100 °C) 2.9 (T>100 °C)	$r = k[O_2]^{0.31} [OH^-]^{0.23}$	Koslides and Ciminelli, 1992
NaOH, pH 5 to 12.5, 50-80 °C, 0-1 atm O_2 , $d_0 = 10-106 \mu m$	13.3	$r = k'' \frac{[O_2]^{0.5} [OH^-]^{0.25}}{1 + k''' pO_2^{0.5}}$	Ciminelli and Osseo-Asare, 1995
NaHCO ₃ /Na ₂ CO ₃ , pH 10- 12.5, 50-85 °C, 0-1 atm O_2 , $d_0 = 10-106 \mu m$	13.7±2.9	$r = k[O_2]^{0.5} [OH^-]^{0.11}$	

¹reaction order for oxygen concentration was indicated by McKibben and Barnes (1986).

²reaction order of hydroxyl ion concentration was calculated by (Ciminelli and Osseo-Asare, 1995b) from reported data.

³pH was indicated by Ciminelli and Osseo-Asare (1995).

may occur during pyrite oxidation and, in most cases, no total oxidation takes place (not only sulfate is formed). Thus, the accuracy of their experimental results can be argued. In hydroxide solutions, the rate expression proposed by Ciminelli and Osseo-Asare (1995a) follows a Langmuir type equation with $n=0.5$, indicating that oxygen adsorbs on pyrite as

dissociated species. More recently, theoretical calculations and STM (scanning tunneling microscopy) analyses provided additional evidences for the dissociative reaction of molecular oxygen on pyrite surface (Rosso et al., 1999; Becker et al., 2001).

The activation energy of 19.8 ± 0.9 kcal/mol (25 to 55°C) for pyrite oxidation was determined by Hood (1991). This is in the upper end of a range of activation energies reported in the literature, 9.3 – 21 kcal/mol (Lowson, 1982), and in good agreement with the value of 21 kcal/mol obtained by Nicholson et al. (1988) under very similar experimental conditions. Ciminelli and Osseo-Asare (1995 a, b) (50 to 80°C) report that the activation energy values obtained with either hydroxide or carbonate media are very close ($E_a = 13.3$ and 14.5 kcal/mol, respectively). All activation energies reported by these authors indicate chemical control, while that found by Stenhouse and Armstrong (1952) is typical of diffusion control. The apparent discrepancies concerning the reported controlling mechanisms may reflect a change in the mechanism from chemical control at temperatures below 100°C to diffusion control at higher temperatures, as suggested by Koslides and Ciminelli (1992).

Hood (1991) observed that the reaction oxidation rate increases slightly with increasing pH in the range pH = 7 to 9. A dependence upon $[\text{OH}^-]$ of 0.3 ± 0.1 was observed for runs in various alkaline solutions. The author suggested that the fact the dependence was very similar in different solutions indicates that the pH effect is associated to the primary mechanism, which is not affected by the different medium effects. Hood's results are in agreement with the 0.23 and 0.25 dependence determined by Ciminelli and Osseo-Asare (1995 a, b) and Koslides and Ciminelli (1992) in hydroxide solutions. In carbonate solutions, Ciminelli and Osseo-Asare (1995 a, b) found a dependence upon $[\text{OH}^-]$ of 0.11. Smith and Shumate (1970) studied the effect of pH (1.5-10) on the oxidation of coal pyrite in water. The reaction rate increases with pH above 4 and is practically independent of pH in acidic solutions. Analysis of the Smith and Shumate's data indicates a reaction order of 0.12 with respect to the hydroxyl ion concentration (Ciminelli and Osseo-Asare, 1995a). In acidic conditions, it has been reported that the rate is independent of proton concentration (Bailey and Peters, 1976 and McKibben and Barnes, 1986). After these, Williamson and Rimstidt (1994) and Holmes and Crundwell (2000) found a weak dependence of the rate on $[\text{H}^+]$ as indicated by reaction orders of -0.11 and -0.18, respectively. These dependences are within the range established in other works in alkaline media (Ciminelli and Osseo-Asare, 1995 a,b).

2.3 Mechanisms Aspects

Goldhaber (1983) investigated pyrite oxidation in circumneutral pH (6-9) and unbuffered solutions. The essential feature of the reaction mechanism proposed by Goldhaber (1983) is the initiation of pyrite oxidation by a direct attachment of an O_2 molecule to the partially protonated pyrite surface. According to Singer and Stumm (1970), Fe^{+3} is the major pyrite oxidant in the acidic pH region, while O_2 is expected to be the direct pyrite oxidant in neutral and alkaline pH due to the low solubility of Fe^{+3} under these conditions. However, Moses et al. (1987), Brown and Jurinak (1989) and Moses and Herman (1991) showed that Fe^{+3} may be a very effective pyrite oxidant even at circumneutral pH, the conclusion being supported by theoretical considerations based on magnetic properties and on molecular orbital theory of the reactants involved (Moses et al. 1987; Luther, 1987; and Osseo-Asare, 1993).

Moses et al. (1987) and Moses and Herman (1991) have also investigated pyrite oxidation at circumneutral pH. The experimental results indicated that pyrite oxidation over the pH range 2-9 was favored in the presence of Fe^{+3} as opposed to dissolved O_2 , and low concentration of Fe^{+3} was very effective in oxidizing pyrite (Moses et al., 1987; and Moses and Herman, 1991). According to the authors, the reaction was accompanied by adsorption of Fe^{+2} from the reaction solution. The adsorbed Fe^{+2} apparently blocked the surface reaction sites at which either Fe^{+3} or O_2 would oxidize pyrite because the oxidation rates slowed down when Fe^{+2} accumulated on the surface. Although Fe^{+3} is evidently the preferred reactant, the reaction could only be sustained in the presence of O_2 . Therefore, the proposed reaction mechanism involves electron transfer from adsorbed Fe^{+2} to O_2 followed by electron transfer from pyrite to the resulting adsorbed Fe^{+3} . Oxygen added to pyrite S comes from water in the hydration sphere of the adsorbed Fe, and the adsorbed Fe cycles between (II) and (III) oxidation states, alternately accepts an electron from pyrite and passes electron to O_2 . This mechanism extends the Singer-Stumm model for pyrite oxidation (Singer and Stumm, 1970), now stating that the oxidation of Fe^{+2} limits the rate of pyrite oxidation at low as well as at circumneutral pH. Fe^{+2} oxidation is rate limited at low pH because the reaction is much slower than the oxidation of pyrite by $Fe^{+3}_{(aq)}$ (Singer and Stumm, 1970). At circumneutral pH, Fe^{+2} oxidation is rate limiting because Fe^{+2} is adsorbed at pyrite surface and prevents the attack by $Fe^{+3}_{(aq)}$ or O_2 . The adsorbed Fe^{+2} must be oxidized by O_2 to generate Fe^{+3} at the pyrite surface (Figure 2.1). The reaction inhibition by Fe(II) is not fully understood. Coming directly from the electrochemical mechanism, an alternative explanation for the detrimental effect of ferrous ions on pyrite oxidation is that the build-up of Fe(II) species favors the reverse reaction of Fe(III) reduction in the cathodic sites (Osseo-Asare, 2005).

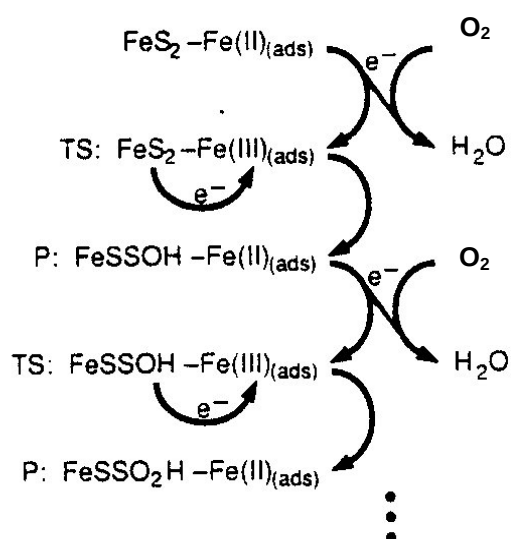


Figure 2.1 – Cycling Fe^{+2} and Fe^{+3} during pyrite oxidation. TS (transition state) = Fe(III) -pyrite; and P (product) = Fe(II) -pyrite. The product of one step in the cycle is the starting point for the next step (Moses et al., 1991).

The faster rate of pyrite oxidation by Fe^{+3} was explained by the fact that Fe^{+3} is bound chemically to pyrite surface whereas O_2 is physically adsorbed. This difference can be explained on the basis of molecular orbital theory (Luther, 1987; Osseo-Asare, 1993). This approach involves a model of chemical redox dissolution. Pyrite is a diamagnetic solid, which has Fe^{+2} in a d^6 electron configuration (Figure 2.2a). The Fe^{+2} is low spin and all electrons reside in t_{2g} orbital as described by the crystal field theory. In the Lewis acid-base model, the fragment would be (I) where a lone pair of electrons from S_A has been donated to Fe^{+2} :



The interaction between the ferric ion and the disulfide ion may be viewed in terms of a two step process involving the inner-sphere complexation of Fe^{+3} by S_2^{-2} , followed by an outer sphere electron transfer. Fe^{+3} has a vacant orbital, so it binds to the pyrite surface via sulfur to form a persulfido bridge. Through this bridge an electron can be transferred from the highest occupied molecular orbital (HOMO) of S_2^{-2} to the lowest unoccupied molecular orbital (LUMO) of Fe^{+3} . Three primary steps are necessary to initiate the electron transfer process from FeS_2 to the oxidant. The first step in the mechanism is fast and involves the removal of a water ligand from $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ or its hydrolysis product $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{+2}$:



Because Fe^{+3} is a d^5 high spin ion ($t_{2g}^3 e_g^2$), ligand exchange is relatively fast and the Fe^{+3} aquo complex is termed labile. After this first step, Fe^{+3} in eq. 2.7 is missing at least one ligand and is coordinately unsaturated. This species is a Lewis acid and could bind in a second step to the surface of FeS_2 through $S_B(\text{Fe}-S_A S_B)$, a Lewis base, as in (II):



In this case, the intermediate formed depends upon the persulfido ligand being able to bridge the two iron atoms, A (d^6 , from pyrite) and B(d^5 , from the Fe^{+3}). Other labile metal complexes such as aqueous Fe^{+2} can attach to the surface in this manner as well. The third, remaining step is electron transfer by an inner sphere type mechanism. For this transfer to occur, the intermediate in (II) formed requires all molecular orbitals to have the appropriate symmetry. In fact, this is possible because Fe^{+2} has t_{2g} orbitals (formally π type orbitals), the S_2^{-2} has two π^* molecular orbitals and Fe^{+3} has three t_{2g} orbitals which are π orbitals when a weak field

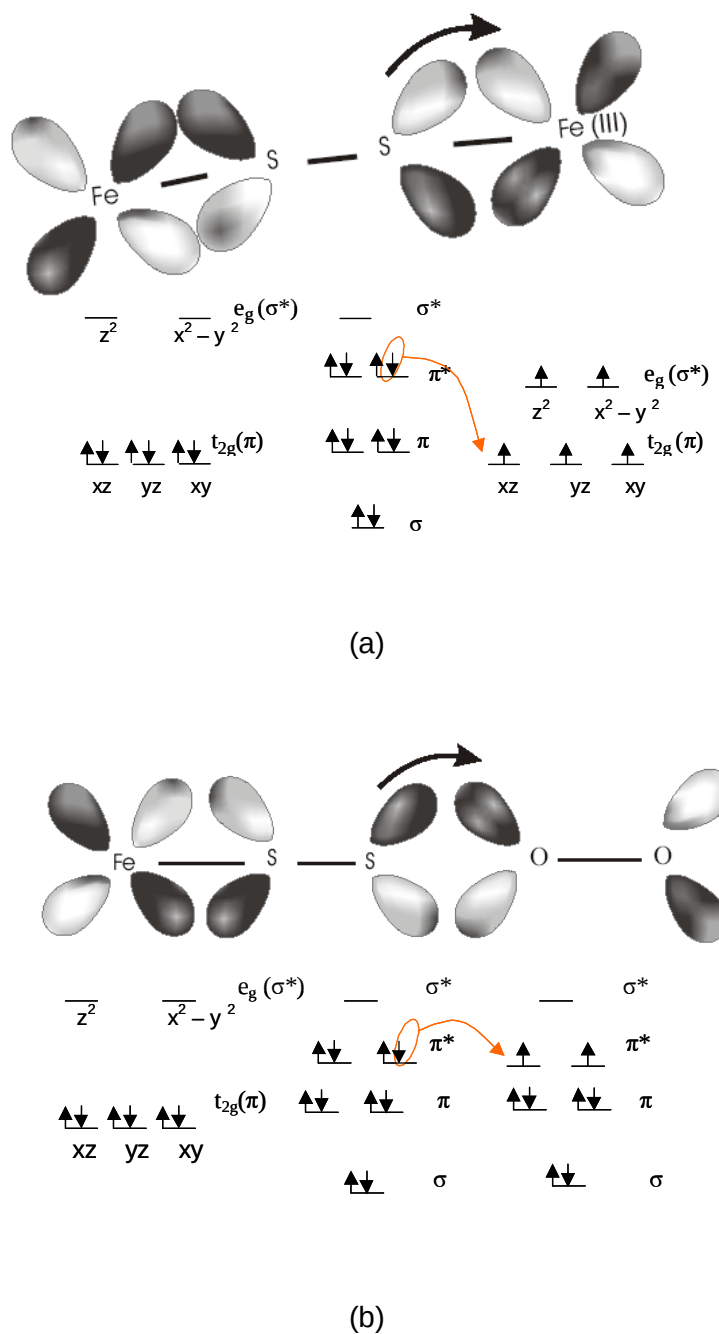
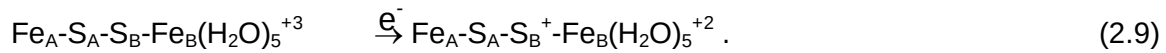
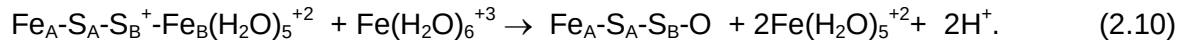


Figure 2.2 – Frontier molecular orbital diagram illustrating the mechanisms of oxidation of pyrite by a) Fe^{+3} and b) O_2 . Note that the proposed intermediate formed between a FeS_2 surface and a $\text{Fe}(\text{H}_2\text{O})_5^{+3}$ complex ion with vacant σ orbital and that there is no σ bond between molecular oxygen and the terminal sulfur in FeS_2 (Luther, 1987).

ligand (e.g. H₂O) binds Fe⁺³. Note that the e_g orbitals for the metals are σ* orbitals and cannot enter into an interaction with the π* orbitals of the S₂⁻² because there is no possible overlap in a linear arrangement of atoms for π and σ* orbitals. The Fe⁺² t_{2g}(π) orbitals and the S₂⁻² π* orbitals are filled. Electron transfer can only occur from a π* orbital (HOMO) of S₂⁻², the bridging ligand, to partially filled t_{2g}(π) orbital (LUMO) of Fe⁺³ from the aquo complex. The Fe⁺³ reduces to Fe⁺² (d⁶, t_{2g}⁴e_g² ion). The electron transfer results in (i) no loss of molecular orbital stabilization energy for the Fe⁺³ to Fe⁺² reduction, and (ii) the strengthening of the S-S bond in S₂⁻² because one electron is lost from a π* orbital. The bond order for the persulfido bridge increases from 1.0 to 1.5 (S₂⁻² to S₂⁻)



The radical ion intermediate in eq. 2.9 is still on the FeS₂ surface. It can further react with another Fe⁺³ complex ion and its water to give



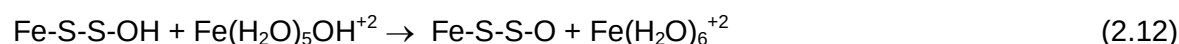
FeS₂O is likely to be unstable. Transfer of the π* electrons (HOMO) in FeS₂O to two π orbitals (LUMO) of Fe⁺³ ions would be too easy. These reactions repeat until FeS₂O₃ is formed at pyrite surface. Thus, oxygen from water forms S-O bonds with oxidation states -2 and +6 on pyrite surface.

The first electron transfer step as well as subsequent steps results in a strengthening of the S-S bond and a weakening of the Fe-S bond in pyrite, which is essential if Fe⁺² is to be released to solution. The surface species, Fe-S-S-O₃, can dissociate to form Fe⁺² and S₂O₃⁻² because S₂O₃⁻² induces high spin Fe⁺², which is labile. The Fe⁺² in pyrite is low spin because of the interaction of the empty sulfur “d” orbital band with the t_{2g} band of Fe⁺². Thus, Fe⁺² in pyrite does not dissociate with release of Fe⁺² into solution unless the Fe-S bond is weakened by oxidation of the S₂⁻² species. Unlike Fe⁺³, O₂ cannot form a transition state intermediate onto the pyrite surface (Figure 2.2b). This Fe⁺³ pyrite oxidation mechanism, suggested by Luther (1987), is also consistent with the following well known experimental observations: (i) sulfoxo species S₂O₃⁻² are intermediates produced during the process of pyrite oxidation by either Fe⁺³ or O₂; (ii) O₂ does not oxidize S₂O₃⁻² as readily as Fe⁺³, so that when O₂ is the sole pyrite oxidant sulfoxo compounds are more prevalent; (iii) water is the source of oxygen for the sulfoxo intermediates and sulfate.

Brown and Jurinak (1989) found that the presence of diethylenetriamine pentaacetic acid (DTPA) causes the inhibition of pyrite oxidation at high pH (3.7-9). This effect was explained by the coordination of Fe^{+3} with DTPA, thus blocking electron transfer via the disulfide bridge. Oxidation does continue, but it is limited to slower, outer-sphere electron transfer reactions involving FeDTPA complexes or O_2 . Therefore, the authors inferred that Fe^{+3} was the rate-controlling oxidant even under alkaline conditions when Fe^{+3} solubility is low. Hood (1991) also observed that the presence of phosphate causes a dramatic decrease in the observed rate because, by strongly or irreversibly binding to the Fe^{+3} , thus “poisoning” the cathodic sites on pyrite surface. Very low concentrations of phosphate are necessary to create this effect. According to Brown and Jurinak (1989), the formation of Fe^{+3} by the homogeneous oxidation of Fe^{+2} with O_2 is not necessarily the rate-determining step. The rate is limited by a surface reaction involving Fe^{+3} as the oxidant. The effect of OH^- , that increases the oxidation rate, in contrast with Cl^- , SO_4^{-2} and DTPA, that decrease, is explained by the inhibition of the electron transfer from pyrite to Fe^{3+} . The species Cl^- and SO_4^{-2} form Fe^{+3} complexes that do not permit inner-sphere electron transfer. It is suggested that OH^- is bridging ligand between Fe^{+3} and the pyrite surface. One mechanism consistent with these data is inner-sphere electron transfer via the disulfide of Fe-S-S , which is promoted by an OH^- bridging ligand. It is possible to occur a typical inner-sphere electron transfer mechanism where OH^- and an electron are exchanged simultaneously between $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{+2}$ and the disulfide (Brown and Jurinak, 1989):



It is noted that the hydrolysis occurs in solution rather than at the pyrite surface. This differs from the mechanisms proposed by Luther (1987) and Moses et al. (1987), in that the surface reaction has been described for the oxidation of pyrite by the hexaquo-complex of Fe^{+3} via electrons transfer through the disulfide. Six electron transfers are required before $\text{S}_2\text{O}_3^{-2}$ can leave the pyrite accompanied by Fe^{+2} as proposed by Moses et al. (1987) and Luther (1987). The reaction eq. 2.11 is sufficient to explain the transfer of three electrons by the addition of OH^- . Three more electrons are added by the removal of H^+ from Fe-S-S-OH and formation of H_2O , which coordinates with the Fe^{+2} cation:



The effect of Cl^- and SO_4^{-2} on pyrite oxidation is that, when coordinated with Fe^{+3} , these do not transfer electrons from the disulfide bridge as readily as OH^- , at least partly because

bonding of Cl^- and SO_4^{2-} with the disulfide is not favored. Thus, outer-sphere electron transfers may still occur, but the reaction rate would be slower.

2.4 Effect of Carbonate/bicarbonate Ions on Pyrite Oxidation

The rate of pyrite oxidation was observed to vary with the solution composition. It increased with increasing bicarbonate buffer concentration, and decreased upon the addition of seawater divalent cations (Mg^{+2} and Ca^{+2}) (Hood, 1991). Both of these results can be modeled in terms of the dependence upon $[\text{CO}_3^{2-}]$, the concentration of free carbonate ion. A model in which the formation of a $\text{Fe(II)}\text{-CO}_3$ complex on the pyrite surface facilitates the oxidation of the pyritic sulfur by molecular oxygen was proposed (Hood, 1991). In this model, the pyritic iron basically acts as cathodic sites for oxygen reduction, with anodic oxidation of adjacent sulfur sites. The proposed model involves initial adsorption and reduction of molecular oxygen at the iron site. Thus, the Fe^{+3} formed oxidize the “electrochemically nearby” pyritic sulfur, returning to the Fe^{+2} state. This cycle continues until all of the adjacent sulfur has been oxidized; and at this point iron remains in the Fe^{+3} state and forms an increasingly thick layer of iron oxyhydroxide. Although the results show an increase in pyrite oxidation rate in carbonate/bicarbonate systems, no experimental evidences of the proposed mechanism have been provided. Some authors (Hood, 1991; Ciminelli and Osseo-Asare, 1995 a; Evangelou et al., 1998; Descostes et al., 2002) have suggested that the cause of the observed increase in pyrite conversion is the formation of pyrite /surface iron-carbonate complexes. This complex would facilitate the formation of Fe^{+3} on the pyrite surface.

To explain the potential enhancement of pyrite oxidation by HCO_3^- or CO_2 gas, Evangelou et al. (1998) postulated a model involving the formation of a ferrous-bicarbonate complex as follows:



The formation of a ferrous-bicarbonate complex on pyrite surface would increase the basicity of Fe^{+2} leading to a rapid oxidation:



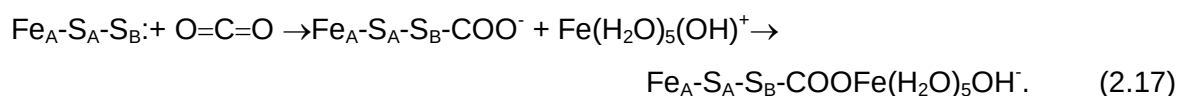
The surface adsorbed species spontaneously forms a persulfido bridge after Fe^{+2} oxidation followed by decarboxylation. Pyrite oxidation initiates as shown below:



The following steps of this process resemble those proposed by Luther (1987) (eqs 2.8-2.10). This leads to a continuous loss of electrons until thiosulfate is formed.

According to Millero and Izaguirre (1989), Fe^{+2} oxidation is promoted in the presence of bicarbonate/ carbonate due to Fe(II) -carbonate complex formation. Luther et al. (1992) postulated and then demonstrated that Fe^{+2} complexation by any ligands containing oxygen promotes Fe^{+2} oxidation due to the potential increase in frontier molecular orbital electron density. The latter increases Fe^{+2} basicity and, consequently, the latter acts as a stronger electron donor. Luther (1992) showed that oxygen ligands stabilize Fe^{+3} relatively to Fe^{+2} when oxygen is present. The number of ligands bound to iron also affects the redox potentials. This behavior can be explained via molecular orbital theory viewed through the oxidation of Fe^{+2} . The formation of complex between Fe^{+2} ion and a oxygen-containing ligand results in weak field or high spin complexes. Thus, the oxidation of Fe^{+2} and the stabilization of the resulting Fe^{+3} is now more likely to occur. To reinforce this, Millero and Izaguirre (1989) reported that the change in the rate of oxidation of Fe^{+2} due to various anions has important implications in the kinetics of pyrite oxidation in neutral to alkaline conditions. In the presence of anions, the oxidation rate of Fe^{+2} decreases in the order of $\text{HCO}_3^- > \text{Br}^- > \text{NO}_3^- > \text{ClO}_4^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{B(OH)}_4^-$. The strong decrease in the rate of Fe^{+2} oxidation due to the addition of SO_4^{2-} and B(OH)_4^- was attributed to formation of $\text{FeSO}_{4(\text{aq})}$ and $\text{Fe[B(OH)}_4]^+$ pairs, which are more difficult to oxidize. The dependence of Fe^{+2} is first order with respect to HCO_3^- . This dependence could be related to the formation of FeHCO_3^+ pair which has a faster rate of oxidation than $\text{Fe(OH)}_{2(\text{aq})}$ pair.

An alternative approach to the CO_2 involvement in pyrite oxidation is through formation of a pyrite/surface carboxylic group (Evangelou, 1995):



The complex promotes Fe^{+2} oxidation due to the fact that the carboxylate ligand contains oxygen as the ligating atom (Luther et al., 1992). Oxidation of Fe^{+2} to Fe^{+3} , however, is

expected to produce a metastable pyrite/surface Fe(III)-carboxylate complex, leading to pyrite/surface decarboxylation and formation of a persulfido bridge as proposed by Luther (1987) and Moses and Herman (1991). The latter facilitates electron transfer from S_B to Fe^{+3} .

The pyrite oxidation model proposed by Moses and Herman (1991) was deduced from macroscopic pyrite oxidation data and no direct molecular evidence on most of the intermediates (e.g. iron carbonate complexes) was presented. However, their pyrite oxidation model is consistent with the frontier molecular orbital theory (Luther, 1990) and classical redox reaction theory. The complementary pyrite oxidation model proposed by Evangelou and Huang (1994) (involving CO_2) is consistent with the model proposed by Moses and Herman (1991) and the effect of carbonate pyrite/ Fe^{+2} oxidation rate enhancement reported by Hood (1991), Millero and Izaguirre (1989), Luther et al. (1992), and Ciminelli and Osseo-Asare (1995a).

The carbonate complexation of Fe(II) and Fe(III) in solution has been investigated by Bruno et al. (1992a, b), through studies involving the solubility of siderite ($FeCO_3$) and hematite (Fe_2O_3) in acid, neutral and alkaline medium. The authors attributed to the presence of carbonate/bicarbonate ions the increased in the solubility of siderite and hematite, due to the iron-carbonate complexes formation, as well as to the increase of the rate of hematite dissolution. The reactions equilibria with their respective formation constants were determined (Bruno et al. 1992a; King, 1998). Values for the Fe(III)-carbonate complexation constants are poorly defined (Hummel, 2000; Bruno and Duro, 2000), due to the difficulty to know exactly which solid phase is involved in the equilibrium at the solid-solution interface: hematite or an amorphous Fe(III) solid such as ferrihydrite, probably formed at hematite during the experiment. Therefore, the equilibrium constants were recalculated considering ferrihydrite as the solid in equilibrium with the aqueous phase (Bruno and Duro, 2000). The determination of equilibrium constants for the Fe(II), Fe(III)-carbonate complexes makes possible now the establishment of their stability areas as a function of pH and redox potential.

2.5 The Effect of the Product Layer

At $pH < 12$ and longer reaction times (26 h), Ciminelli and Osseo Asare (1995a) observed that the conversion obtained in the carbonate system approximates to that obtained in sodium hydroxide solutions. This behavior was related to a growing oxide coating that covers the pyrite particles and hinders the accessibility of the reactants (eg. hydroxyl and carbonate

ions and oxygen) to pits. In sodium carbonate solutions, the particles are initially covered by a non-uniform and coarse granular oxide coating. The coating grows, with further oxide precipitation on the existing nuclei, thus increasing oxide coverage of pyrite surface, thereby slowing down the reaction rate. This behavior was also observed by Nicholson et al. (1988 and 1990), who investigated the kinetics of pyrite oxidation in bicarbonate-buffered system at pH values between 7.5 and 8.5, over a period over 10,000 hours in which a carbonate-buffered solution and air (20 % O₂) flowed continuously. The oxidation rate initially increases, reaches a maximum value and then decreases. The authors concluded that ferric oxyhydroxide formation and its accumulation on pyrite surface resulted in a significant reduction in the oxidation rate. Over the time periods studied (<200 hours), Hood (1991) also observed that the rate changes with time. But contrarily to the previous findings, after an initial period where the rate was constant, the rate increased with time, with a maximum increase of approximately 100%. A similar increase of rate with time within this time frame was also observed by Nicholson et al. (1990). This rate increase is consistent with the interpretation that increasing levels of iron (oxide or aqueous complex form) on pyrite surface initially promotes faster oxidation of pyrite. Differently from the carbonate media, in sodium hydroxide solutions, Ciminelli and Osseo-Asare (1995b) proposed that the precipitation seems to occur mainly in the bulk, resulting in pyrite particles uniformly covered by a thin, fine texture oxide layer and a stable colloidal suspension. The coating breaks down after some time and has no effect on the reaction rate.

According to Ciminelli and Osseo-Asare (1995 a,b), results from pyrite oxidation in hydroxide solutions, up to 24 h (~50 % oxidation), show that the oxidation is not inhibited by the product layer and, therefore, the unreacted core model for chemical reaction control is phenomenologically consistent with the long term leaching behavior. The results indicating chemically controlled reaction were expected for the low temperatures employed (50-80°C). The hypothesis of chemical control was also supported by the fractional orders with respect to oxygen pressure and hydroxyl ion concentration (0.5 and 0.25, respectively), the magnitude of the activation energy (13.28 kcal/mol), and the dependence of the rate constant on the reciprocal of particle diameter. Similar conclusions were obtained by Koslides and Ciminelli (1992), employing the pressure oxidation of pyrite and arsenopyrite in NaOH solution.

In carbonate solution, Ciminelli and Osseo-Asare (1995a) observed that the rate of pyrite oxidation was fitted by a stochastic model for chemically controlled reaction. This model assumes that surface heterogeneity leads to localized reaction. So, this model implies that pyrite reactivity decreases with time. As observed by the authors, the presence of the oxide

film decreases the rate of pyrite oxidation. Despite this, the hypothesis of chemical control is also supported by the independence of rate on the stirring speed, the magnitude of the activation energy ($E_a = 14.5 \text{ Kcal/mol}$), the dependence of rate constants on the inverse of particle diameter, the fractional reaction orders with respect to oxygen partial pressure and hydroxyl concentration (0.48 ± 0.10 and 0.11 ± 0.09 , respectively), and the adjusted kinetic model. The authors propose that the presence of the coating decreases reactivity by interfering with pit formation. Nicholson et al. (1990) also attributed the decreasing in the pyrite oxidation rate to effects of the surface rate constant plus the diffusive resistance to oxygen through a growing reaction layer as oxidation proceeds.

Ciminelli and Osseo-Asare (1995a) have discussed the role of iron-complexes in the oxide precipitation and proposed that the morphological differences observed in the iron oxide produced during pyrite oxidation in the carbonate and hydroxide systems is related to the kinetics of iron precipitation, rather than to a distinct chemical nature of the solid product. For the oxide precipitation to occur, it is necessary that supersaturation ratio must be attained. By complexing of $\text{Fe}^{+2}/\text{Fe}^{+3}$ ions, the concentration of free ions is reduced, thereby decreasing the supersaturation. Thus, it is to be expected that the rate of oxide nucleation will be lower in the carbonate systems, compared with hydroxide system. A lower nucleation rate will result in larger particles.

During pyrite oxidation in carbonate solutions, Descostes et al. (2002) reported the importance of ferrous carbonate complexes which tend to prevent the surface from coating. After 30 days, carbonate pH buffers properties seem to be limited and effective for moderated carbonate concentrations (0.112 mmol/L and 0.1 mol/L). Pyrite dissolution is more intense in diluted and concentrated carbonate medium (1 mmol/L and 1 mol/L) with respectively $\Delta\text{pH} = 5.06$ and $\Delta\text{pH} = 1.99$. In both cases, the coating removal allows pyrite oxidation to proceed. In the first case, due to acidic conditions that hinder the formation of the oxide coating and in the second, probably due to the iron complexes formation.

2.6 The Nature of the Product Layer

Many authors recognize the formation of solid ferric and/ or ferrous oxyhydroxides through pyrite oxidation in different alkaline media, but these products have not been clearly identified as well as their role on the reaction rate. Nicholson et al. (1990), using XPS analysis, suggested that maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is formed. This phase is known to be a dehydration

product of lepidocrocite (γ -FeOOH) and a metastable phase with respect to hematite. Therefore, the authors believed that the hydrous lepidocrocite is the most likely product of pyrite oxidation, and the dehydration occurred during sample preparation for XPS analysis (high vacuum). Despite the color differences observed in the oxidized samples, Hood (1991) suggested the formation of ferrihydrite (amorphous phase) in the different solutions. The color differences were attributed to the variation of metal substitution and crystallinity. In the presence of CO₂/carbonate, goethite or hematite may be formed, the latter with increasing temperature. Ciminelli and Osseo-Asare (1995a,b) reported that the solution composition affects both the morphology and the nature of the products of pyrite oxidation in alkaline solutions. The oxide coating was described as an amorphous ferric or ferrous oxyhydroxide phase, not completely identified.

In previous transmission infrared spectroscopy studies, Ciminelli (1987), Hood (1991) and Ciminelli et al. (1994) attempted to identify iron-carbonate complexes in the products of pyrite aqueous oxidation, but none was able to identify the characteristic bands of carbonate species. A direct experimental evidence for the proposed role of carbonate on pyrite oxidation is not available, yet. Evangelou et al. (1998) identified the formation of Fe(II)-CO₃ complexes and carboxylic groups by DRIFT only on pyrite samples exposed to atmospheric oxidation; no evidences of carbonate complexes were found in the samples submitted to oxidation in aqueous solutions.

Recently, Descostes et al. (2000, 2001) characterized pyrite oxidation layers in acidic and carbonate media using XPS. In acidic medium, only Fe(II)-sulfate was detected. The oxidation layer was shown to be more complex in carbonate medium than in acid medium. In carbonate medium, iron has mainly a (+2) oxidation state under siderite or Fe(II)-sulfate form. To a minor extent, a (+3) oxidation state (α -FeOOH form) from the first oxidized pyrite layers was detected by XPS analyses. The O1s and C1s photoelectron peaks confirm the presence hydroxide and carbonate groups. Sulfur oxidation induces intermediate species (polysulfides and sulfoxyanions as S₂O₃⁻² also identified in solution) indicating that oxidation occurs at solid state. In carbonate medium, the nature of oxidation products varies, as shown by the formation of intermediate species of sulfur as S₂O₃⁻² and the presence of iron carbonate complexes.

Descostes et al. (2002) also investigated the pyrite dissolution in carbonate ions in batch experiments in presence of atmospheric oxygen (20%) and in different bicarbonate concentrations (0.001 – 1 mol/L) and reaction time varying from 6 hours to 30 days. Carbonate bands were found in FT-IR spectra for higher bicarbonate concentration (1 mol/L)

and long reaction time. These bands are attributed to presence of siderite that tends to be transformed into goethite with adsorption of sulfate and carbonate ions (0.1 and 1 mol/L of bicarbonate concentration). Other iron phases are suggested, such as akaganeite or feroxyhite (Fe-O-H oxyhydroxy ferric sulfate).

There is a certain analogy between the reaction of pyrite oxidation and those found in the precipitation of iron compounds and in the iron corrosion process (Bewick et al., 1991; Blengino et al., 1995; Oblonsky and Devine, 1997; Legrand et al., 2000, 2001 a,b; Savoye et al.; 2001; Music et al., 2004). Most of the iron oxides and oxide hydroxides can be produced from Fe(II) solutions by oxidation followed by hydrolysis.

In several iron corrosion studies in bicarbonate/carbonate containing solutions, the occurrence of carbonate green rust ($\text{GR}(\text{Fe}(\text{II})\text{Fe}(\text{III})\text{CO}_3)$), and Fe(II)-Fe(III)-hydroxy-carbonate as intermediate products has been well described. $\text{GR}(\text{Fe}(\text{II})\text{Fe}(\text{III})\text{CO}_3)$ was reported as a transient compounds between the initials ferrous hydroxide and final ferric oxyhydroxides, goethite or lepidocrocite (Blegino et al., 1995; Legrand et al., 2000, 2001a, and 2001b; and Savoye et al., 2001). For the characterization of the corrosion products, different techniques were employed such as infrared (Blegino et al., 1995; Legrand et al., 2000; and Savoye et al., 2001) Raman (Bonin et al., 2000; Legrand et al., 2001b; and Savoye et al., 2001; and Music et al., 2004) and Mössbauer (Abdelmoula et al., 1996) spectroscopies. Various compounds have been identified by infrared and Raman spectroscopies: siderite, magnetite, am- $\text{Fe}(\text{OH})_3$ with adsorbed carbonate or bicarbonate ions, ferrihydrite, hematite and lepidocrocite.

Recent studies of Legrand et al. (2004) propose that the oxidation of green rust carbonate, $\text{GR}(\text{CO}_3^{2-})$, in bicarbonate solutions can proceed by two pathways: solid-state oxidation (SSO) leading to a ferric oxyhydroxycarbonate ($\text{Fe}(\text{III})_6\text{O}_{(2+x)}(\text{OH})_{(12-2x)}(\text{H}_2\text{O})_x(\text{CO}_3)$) as the end product, and a dissolution-oxidation-precipitation (DOP) mechanism leading to a ferric oxyhydroxides such as lepidocrocite, goethite or ferrihydrite. The DOP mechanism involves transformation via solution with the occurrence of soluble ferrous-ferric intermediate species. The the ferric oxyhydroxycarbonate, $\text{Fe}(\text{III})\text{GRCO}_3$, remains stable even after large periods of ageing, either as a dry powder or as particles in solution. In the presence of Si and phosphate species, the dissolution step is inhibited due to adsorption onto $\text{Fe}(\text{III})\text{GRCO}_3$ surface.

3 EXPERIMENTAL PROCEDURE

Thermodynamic analyses

Potential (Eh) vs. pH diagrams for the Fe-S-CO₃-H₂O system were prepared with the software, HSC Chemistry, version 4.0, from Outokumpu Research Oy (HSC Chemistry, 1999). The thermodynamic data were mostly based on a compilation from Naumov (1974) and HSC Chemistry software database (HSC Chemistry, 1999). Selected values are presented in the Appendix I. The redox potential (Eh) is based on the standard hydrogen electrode and has the units of volts.

Sample preparation

Pyrite samples from Huanzala, Peru, were supplied by Ward's Natural Science Establishment, Inc., Rochester, N.Y., USA. Chemical quantitative analyses were carried out by atomic absorption spectroscopy and carbon and sulfur analyzer (Leco) indicated that the sample contained 98.3% FeS₂, with minor silicon and other elements. This analysis was confirmed by X-ray fluorescence (Phillips model PW 2510), which indicated Fe and S as major constituents, Si as minor, As as trace and Ca, Al, Zr, Cr, Mn, Cu, P and Zn as very rare elements. The pyrite samples were ground, classified into various size fractions by wet-dry screening and only the fraction 95 % below 38 µm was used (particle size distribution in Appendix II). To remove the silicates and oxide layers, samples of the ground material were leached with concentrated hydrofluoric acid for two days. After filtration, this material was treated with a hot hydrochloric acid solution (3 mol/L) for 30 minutes, and maintained in this solution for 48 hours at ambient temperature. This treatment was followed by filtration and washing with N₂-purged deionized water and acetone. After that, X-ray fluorescence analysis showed Si as a rare element; no Cr, Mn, P and Zn were detected. The other elements maintained their concentrations prior to treatment. The samples were stored in a desiccator under vacuum. Prior to the oxidation experiments, the treatment sequence with hydrochloric acid was repeated in order to remove any oxidized iron or sulfur species that could be formed on pyrite surface.

Oxidation experiments

The oxidation experiments were performed in a 2 L glass reaction vessel immersed in a controlled temperature bath. The four-hole cover was fitted to a condenser, a fritted glass gas inlet, a pH probe and a shaft at the center connected to a constant speed motor. At the start of a run, the pyrite sample (1g of ground solids) was added to 1 L of a sodium carbonate / bicarbonate solution or sodium hydroxide solution (at desired concentration and pH), that had been previously thermally equilibrated at 80°C and saturated for 30 minutes with oxygen. During the experiments, oxygen (minimum 99.8% purity) was continuously bubbled and the pH was checked periodically and, when necessary, adjusted with the addition of drops of 0.5 mol/L sodium hydroxide solution. Finally, the solid residues were separated from the solution by using a 0.8 μm membrane filter (from Millipore, Inc.), washed with a pH 9 sodium hydroxide solution, dried with acetone and stored in a desiccator under vacuum. Carbonate concentration, pH and time were varied in the range of 0.001-1 mol/L; 8.5-12.5; 30-360 min, respectively. All solutions were prepared with water from Milli-Q, previously N_2 -bubbled to remove residual O_2 and CO_2 , and certified reagents (Aldrich Na_2CO_3 99.5% and NaHCO_3 99.7%) and gases (O_2 99.99 % and N_2 99.999 %). In order to minimize carbonate contamination in hydroxide reagents, different grades of reagents were tested (Aldrich - NaOH 99.99 % and Na_2CO_3 <1%). The dried oxidized samples were also stored in a desiccator under vacuum.

Solid Analyses

The diffraction patterns of unreacted and oxidized samples were obtained with a Philips model PW1710 diffractometer, fitted with a Cu tube ($\lambda=1.5418 \text{ \AA}$, 40 kV and 20 mA, Si standard, graphite monochromator, Ni filter, step size $0.02^\circ 2\theta$, 5 s/step).

Morphological studies on individual samples and their elemental analyses were undertaken using a scanning electron microscope (SEM; JEOL model JSM-6360LVI) equipped with an energy dispersive X-ray spectrometer (EDS; model Quest Thermo Noran). Prior to SEM and EDS microanalyses the unreacted and oxidized pyrite samples were dispersed on aluminum stubs with a silver adhesive tape without any carbon coating process. Spot mode analyses were carried out with the EDS technique.

Infrared analyses were carried out in a BOMEM DA8 FTIR spectrometer, under the following conditions: 64 scans of accumulation; 2 cm^{-1} resolution; MCT detector; KBr beamsplitter; Globar source. The measurements occurred under vacuum, in the spectral range of 400-

4000 cm^{-1} . For the diffuse reflectance technique, the dried samples were analyzed and a gold mirror was used as a reference spectrum. For the transmission measurements, the dried samples were mixed with KBr powder in very low concentrations (1 wt.%). The mixture was pressed under vacuum into disks of 13 mm diameter, under an applied pressure of 750 MPa. In these measurements, a pure KBr disk was used for the reference spectrum.

Micro-Raman spectroscopy analyses were performed on dried samples using a Jobin Yvon/Horiba model LabRam HR 800, coupled to an optical microscope Olympus BX41. The detector was a 1024 x 256 pixel liquid nitrogen cooler charge coupled device (CCD). A He-Ne laser with 632.8 nm wavelength and power output of 20 mW measured at the laser head was used as the excitation source. In order to avoid sample degradation, the laser power was always kept below 0.12 mW at the sample. The sample was targeted by the laser beam through a high-aperture microscope objective (Olympus 100x, 0.9 NA), and the scattered light was collected through the same objective in a back scattering configuration. The entrance slits to the spectrograph were 100 μm with a correspondent resolution of 2.0 cm^{-1} . Holographic grating was of 600 g/mm. Frequency calibration was achieved using the 520 cm^{-1} line of silicon. A small quantity of sample was placed on a glass slide on the microscope stage. The acquisition time ranged from 60 to 300s, and 8 to 25 scans. After each spectrum had been recorded, a careful visual inspection was performed using white light illumination on the XY microscope stage in order to detect any change that could have been caused by the laser. Collected Raman spectra were analyzed and optimized with Labspec 1.1, Peak Fit and Origin 5.0 softwares. Spectra collected were averaged, the background was corrected and if necessary they were normalized and peak deconvoluted.

Chemical analyses

Total concentrations of metals in the solid and aqueous samples were determined by atomic absorption spectroscopy (Perkin Elmer Aanalyst 300) coupled to a graphite furnace (Perkin Elmer HGA-800) or inductive plasma spectroscopy coupled to mass spectroscopy (ICP-MS) (Perkin Elmer Elan 9000). On solid samples, total sulfur contents were determined using Carbon and Sulfur analyzer (LECO model CS-244).

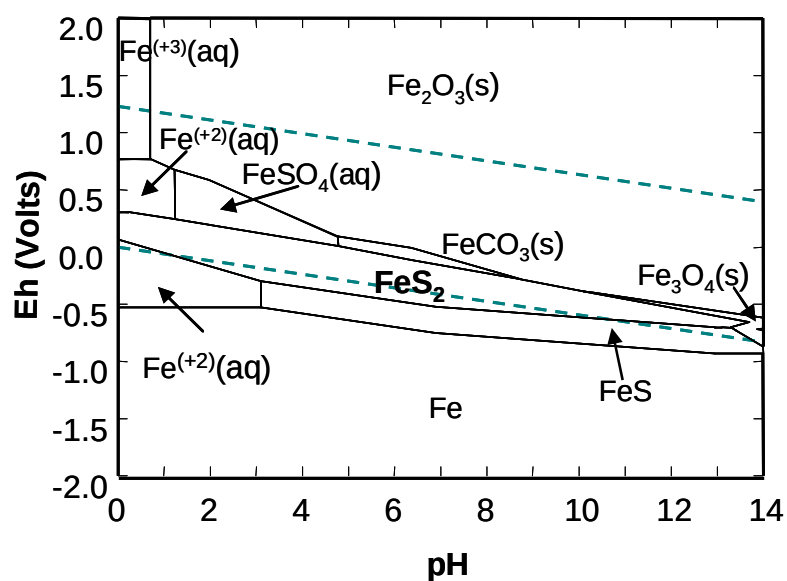
4 RESULTS

4.1 Thermodynamic Analysis

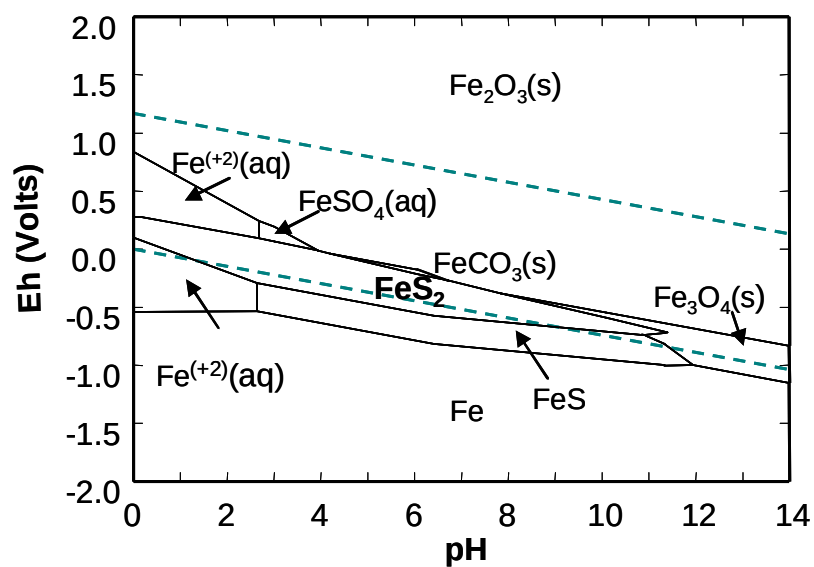
The thermodynamics of the Fe-S-CO₃-H₂O system was studied with the help of Eh-pH diagrams. Under oxygen partial pressure of 1 atm and pH 8.5-12.5, experimental conditions maintained in the present investigation, the main product of pyrite decomposition is α -Fe₂O₃, hematite (Figure 4.1a). Siderite (FeCO₃) is formed around neutral pH, and relatively lower Eh. Figure 4.1a also indicates that at pH < 4 and mild oxidizing conditions (Eh~0.5 V) pyrite would decompose to soluble ferrous or ferrous sulfate ions. Stronger oxidation conditions (higher Eh) would lead to ferric ion (pH < 1) or hematite formation. A list of selected species used in this and the following diagrams, with their respective standard free energy of formation (ΔG_f°) are shown in the Appendix I.

To be consistent with the temperature (80°C) maintained in the oxidation experiments, an Eh-pH diagram at 100°C has been also developed (Figure 4.1b). The thermodynamic data were mostly based on the compilation of Naumov (1974) and HSC Chemistry software database (HSC Chemistry, 1999). This diagram indicates that as temperature increases, the stability region of FeCO_{3(s)} decreases. Similar trend is observed with the soluble species Fe⁺², FeSO₄ and Fe⁺³, the stability region of the latter completely disappearing at 100°C. Conversely, the stability of Fe₃O₄ increases.

Metastable hydrated oxides are expected to be formed preferentially to the oxides in short-time experiments such as those carried out in this work. Depending on goethite crystallinity, values of standard free energy of formation are found to vary from the -111.20 kcal/mol for the amorphous FeOOH to the -117.2 kcal/mol of well crystallized goethite (Naumov, 1974; Cornell and Schwertmann, 1996). Detournay et al. (1975) suggested fresh goethite as the most probable species to be formed in experiments with pure solutions ($\Delta G_f^\circ = -114.8$ kcal/mol), this data being used in the present work. No data for feroxyhite (δ -FeOOH) is available yet. Several formulae have been proposed for ferrihydrite, such as 5Fe₂O₃.9H₂O, Fe₅HO₈.4H₂O and Fe₂O₃.2FeOOH.2.6H₂O. They are all equivalent and can be reduced to 5FeOOH.2H₂O, which is, in fact, a hydrated oxyhydroxide (Fe(OH)₃). In general, ferrihydrite is represented as Fe(OH)₃. Eggleton and Fitzpatrick (1988) reported that bulk compositions of ferrihydrite prepared from ferric nitrate solutions are Fe₄(O,OH,H₂O) for the 2-line variety, and Fe_{4.6}(O,OH,H₂O) for the 6-line type.



(a)



(b)

Figure 4.1 – Eh-pH diagram for the Fe-S-CO₃-H₂O system at (a) 25°C and (b) 100°C. [Fe] = 0.017 mol/L; [S] = 0.033 mol/L; [CO₃] = 0.4 mol/L (the activity coefficient was considered equal to 1). Water stability region is indicated within the dashed lines.

In the present work, ferrihydrite's standard free energy of formation was calculated from the solubility constant of $\text{Fe}(\text{OH})_3$ provided by Bruno and Duro (2000) as -167.7 kcal/mol. The standard free energy of formation of stoichiometric carbonate-containing green rust 1, $\text{GR1CO}_3 (\text{Fe}_4^{\text{(II)}}\text{Fe}_2^{\text{(III)}}(\text{OH})_{12}\text{CO}_3)$ was estimated to be -856.98 kcal/mol (Drissi et al., 1995).

The effects of carbonate and bicarbonate on the reaction rates and on oxidized products of pyrite oxidation and metallic iron corrosion have been studied (Nicholson et al., 1988 and 1990; Ciminelli and Osseo-Asare, 1995a; Descostes et al., 2002; Legrand et al., 2000; Music et al., 2004). The observed effects are related to the ability of carbonate and bicarbonate ions to form metastable complexes with ferric and ferrous ions. The formation of these iron complexes will be discussed with the aid of Eh-pH diagram developed for the aqueous species. The formation of Fe(II)/Fe(III)-carbonate species, as well as their equilibrium constants, has been reported by Bruno *et al.* (1992 a, b) and revisited by King (1998) using activity coefficients based on the interaction parameters of Millero and Hawke (1992). Table IV.1 indicates these species with their respective equilibrium reactions, and the standard free energy of formation (ΔG_f°). King (1998) pointed out that the results are in reasonable agreement with those reported by Bruno (1992b), but a slightly improved fit to the data is obtained if the $\text{Fe}(\text{OH})\text{CO}_3^{-1}$ species is considered (Table IV.1). Evidence of this species' formation is supported indirectly from the modeling of Fe^{+2} oxidation rate data described by King (1998). Values for the Fe(III)-carbonate complexation constants are poorly defined (Hummel, 2000; Bruno and Duro, 2000).

Table IV.1 – Equilibrium constants and standard Gibbs free energy of formation data for Fe(II)/Fe(III) ion - carbonate complexes (King, 1998; and Bruno and Duro, 2000)

Reactions	log K (25 °C)	ΔG_f° (kcal/mol) Fe-Carbonate species
$\text{Fe}^{+2} + \text{CO}_3^{-2} = \text{FeCO}_3 (\text{s})$	10.80	-162.95
$\text{Fe}^{+2} + \text{HCO}_3^- = \text{FeHCO}_3^+ (\text{aq})$	1.47	-164.31
$\text{Fe}^{+2} + \text{CO}_3^{-2} = \text{FeCO}_3 (\text{aq})$	5.69	-155.97
$\text{Fe}^{+2} + 2\text{CO}_3^{-2} = \text{Fe}(\text{CO}_3)_2^{-2} (\text{aq})$	7.45	-284.70
$\text{Fe}^{+2} + \text{CO}_3^{-2} + \text{OH}^- = \text{FeCO}_3(\text{OH})^- (\text{aq})$	9.97	-199.41
$\text{Fe}^{+3} + 2\text{CO}_3^{-2} = \text{Fe}(\text{CO}_3)_2^- (\text{aq})$	19.6	-283.34

Based on solubility measurements of hematite in NaHCO_3 solutions, Bruno et al. (1992) suggested the formation of two aqueous complexes, Fe(OH)CO_3 and $\text{Fe(CO}_3)_2^{-1}$. But the selection of hematite has been criticized due to a process of oxyhydroxide formation by dissolution/precipitation at the iron oxide surface. In view of that, the equilibrium constants have been recalculated considering the freshly precipitated amorphous ferrihydrite as the solid phase. After further discussion, Hummel (2000) and Bruno and Duro (2000) suggested to ignore the mixed complex Fe(OH)CO_3 and to rely solely on the complex $\text{Fe(CO}_3)_2^{-1}$. The stability constant for the formation of the $\text{Fe(CO}_3)_2^{-1}$ complex was reevaluated as $\log \beta_2 = 19.6$.

In order to reveal the metastable iron oxy-hydroxides and carbonate complexes, the stable phases (FeS_2 , $\text{FeCO}_{3(s)}$, Fe_2O_3 and Fe_3O_4) were removed from the data base. The pseudo-equilibrium diagrams are shown in Figure 4.2. Due to the lack of data for some of the complexes (heat capacity $-C_p$, enthalpy and entropy), only the diagram at 25°C is presented. In the region of water stability, FeOOH , fresh goethite, predominates in the pH range from 1.5 to 14 and potentials (Eh) 0.25 V and higher. In the pH range 8-12, the solids GR1CO_3 and Fe(OH)_2 and the soluble Fe(II)-carbonate complexes ($\text{FeCO}_{3(aq)}$ and $\text{Fe(OH)CO}_3^{-1(aq)}$) are shown in the region previously occupied by pyrite, i.e. relatively lower Eh (Figure 4.2a), and therefore are possible products of pyrite oxidation in alkaline solutions. In the absence of GR1CO_3 and fresh goethite, the stability regions of Fe(II)-carbonate complexes become even more evident (Figure 4.2b), maintaining the predominance of the species $\text{FeCO}_{3(aq)}$ and $\text{Fe(OH)(CO}_3)_2^{-1(aq)}$ at pH 8-11. The region occupied by ferrihydrite (Fe(OH)_3) is indicated as goethite is removed. Majzlan et al. (2004) reported the occurrence of ferrihydrite in a similar predominance region. Ferrihydrite is considered as the initial product of the rapid hydrolysis of Fe^{+3} solutions and therefore can also be formed during pyrite oxidation in alkaline solutions. Figure 4.2b shows the metastable iron (II) carbonate complexes coexisting with ferrihydrite. The stability areas of soluble Fe(III) carbonate complexes become evident only in the absence of the solid phases (Figure 4.2c).

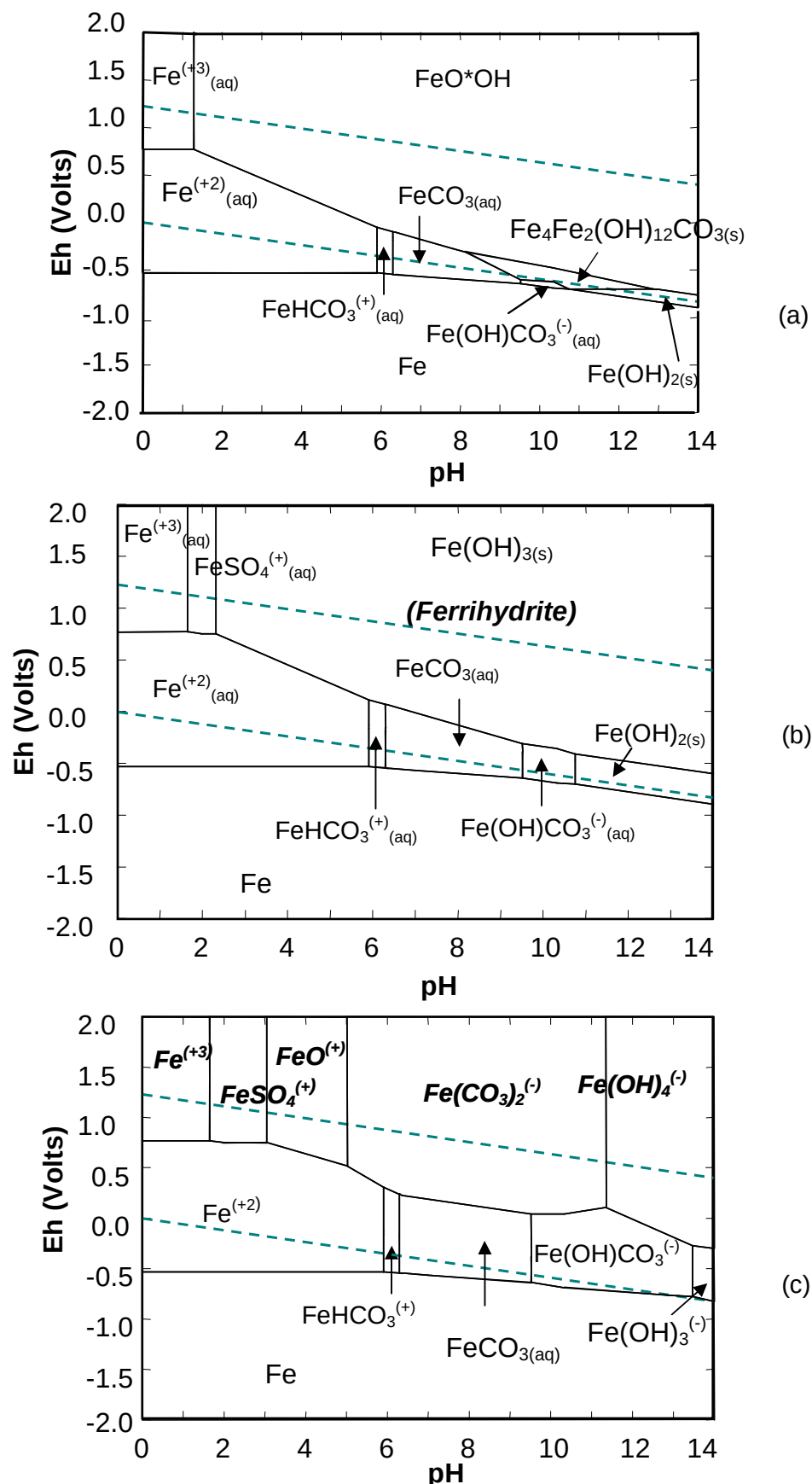


Figure 4.2 – Eh-pH diagram for the Fe-S-CO₃-H₂O system pseudo-equilibria at 25°C, showing (a) GR1CO₃ (Fe₄Fe₂(OH)₁₂CO₃) region and amorphous FeOOH(s) (b) Ferrihydrite and Fe(II)-carbonate complexes regions; (c) predominance areas of soluble iron species – Fe(III) species in *italic*. [Fe] = 0.017 mol/L; [S] = 0.033 mol/L; [CO₃] = 0.1 mol/L (the activity coefficient was considered equal to 1). FeS₂, Fe₂O₃ and FeCO₃(s) not considered. Water stability region is indicated within the dashed lines.

4.2 Macroscopic Analyses: XRD and SEM/EDS

In order to characterize the products of pyrite oxidation in alkaline media, X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy analyses (EDS) were carried out and the results are presented below.

The XRD patterns of unreacted pyrite and oxidized pyrite in carbonate and hydroxide solutions (pH 10) are shown in Figure 4.3. The XRD patterns for oxidized pyrite show that the most intense and well-defined peaks are assigned to pyrite, indicating that oxidation was incomplete. In both media, the oxidation products exhibit peaks with relatively lower intensities. No significant differences were observed in the peak positions for the samples obtained after longer reaction times but the peak intensities increased. Higher bicarbonate/carbonate concentrations led to poorly defined peaks. It is important to note the different oxidation products obtained in the presence and absence of carbonate. In the absence of carbonate, mainly hematite was formed, while in carbonate solutions, ferrihydrite was identified. Note that the peaks match very closely the reference patterns of both compounds (Figure 4.3b and c). At higher bicarbonate/carbonate concentrations, the presence of a peak at 3.02 Å suggests the formation a calcium carbonate-like phase (Figure 4.3d, 4.5a and 4.6a).

The products of pyrite oxidation obtained under different pH and concentration conditions are shown in Figure 4.4 to 4.6. For pH 8.5 and 10, a comparison between the XRD patterns obtained in the different alkaline media clearly shows distinguishable oxidation products. Hematite was identified in sodium hydroxide solution (Figure 4.4a and 4.5a); the inversion of the peak intensities at 1.69 and 1.51 Å was associated with the presence of minor δ -FeOOH (feroxyhite). The formation of hematite was predicted by thermodynamics (Figure 4.1).

In sodium carbonate/bicarbonate solution, the main product of pyrite oxidation was identified as ferrihydrite (Figure 4.3-4.6). A clear broad background at 2.5 Å (Figure 4.3c) characterizes amorphous hydrated iron oxide phases. The most poorly crystallized form of ferrihydrite, typical of room temperature precipitation, has been named the “2 line ferrihydrite” as its XRD pattern shows only two broad diffraction lines at 2.5 and 1.5 Å. It does not apply to the present case, as the four most intense lines of the named “6-line ferrihydrite”- 6L-FH were found to match quite well the diffraction patterns shown in Figure 4.3 to 4.6. Furthermore, the formation of the 6L-FH is favored at the above-room temperatures used in the present investigation. The diffraction line at 1.96 Å is considered to be highly characteristic of

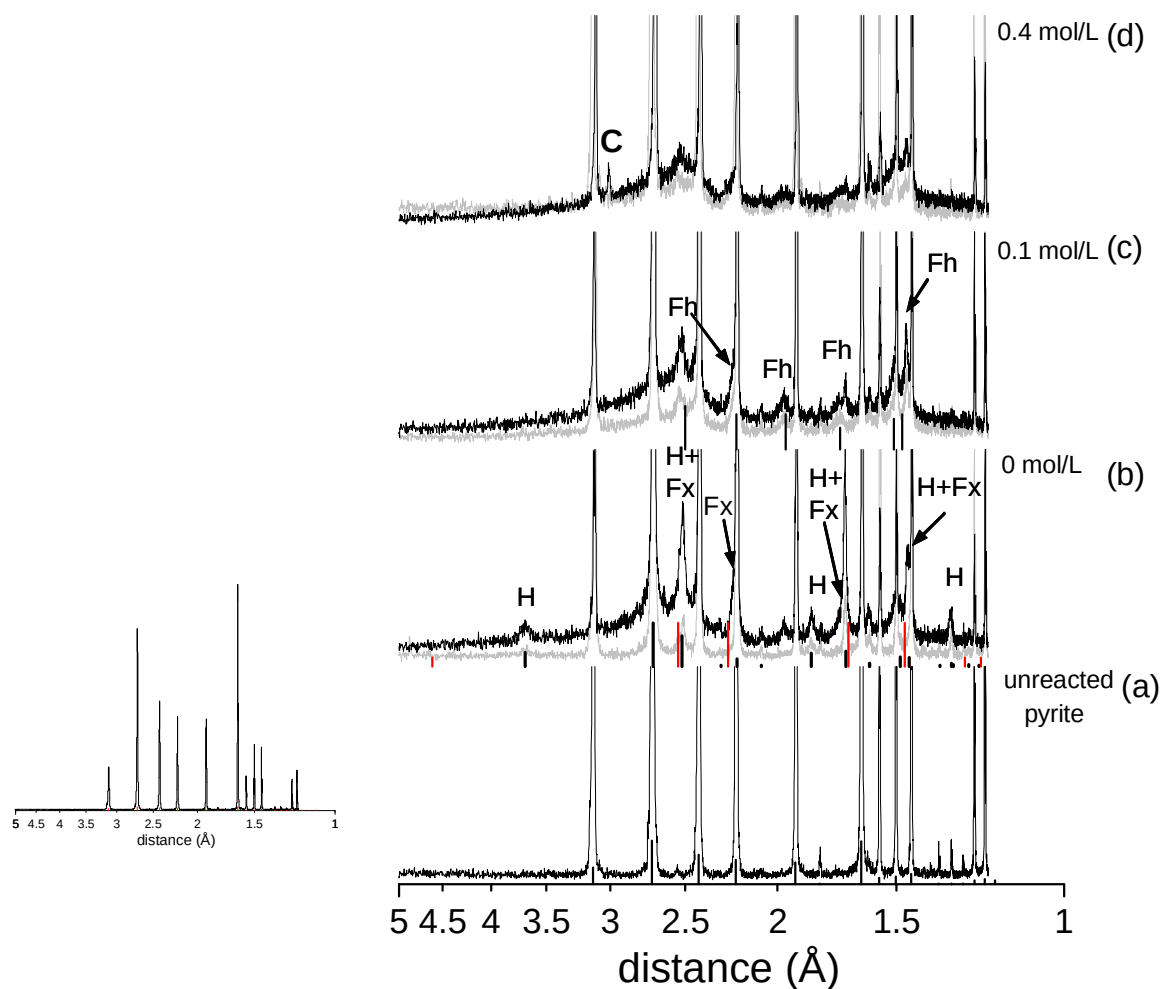


Figure 4.3 – XRD patterns for unreacted pyrite (a); oxidized pyrite pH 10 and in $[\text{CO}_3^{2-}]$ ($\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$) varying: 0 mol/L (corresponds to NaOH solution-0.1mmo/L (b)); 0.1 mol/L (c) and 0.4 mol/L (d). Reaction time: 1 h (gray) and 12 h (black). See vertical lines: P – Pyrite (ICDD 06-0710) in (a), H – Hematite (ICDD 33-0664) thick lines and Fx – feroxyhite, red or thin lines (ICDD 13-0087) in (b), Fh - Ferrihydrite (ICDD 29-0712) in (c); C – calcite (ICDD 72-1214). Insert figure shows the whole unreacted pyrite XRD pattern.

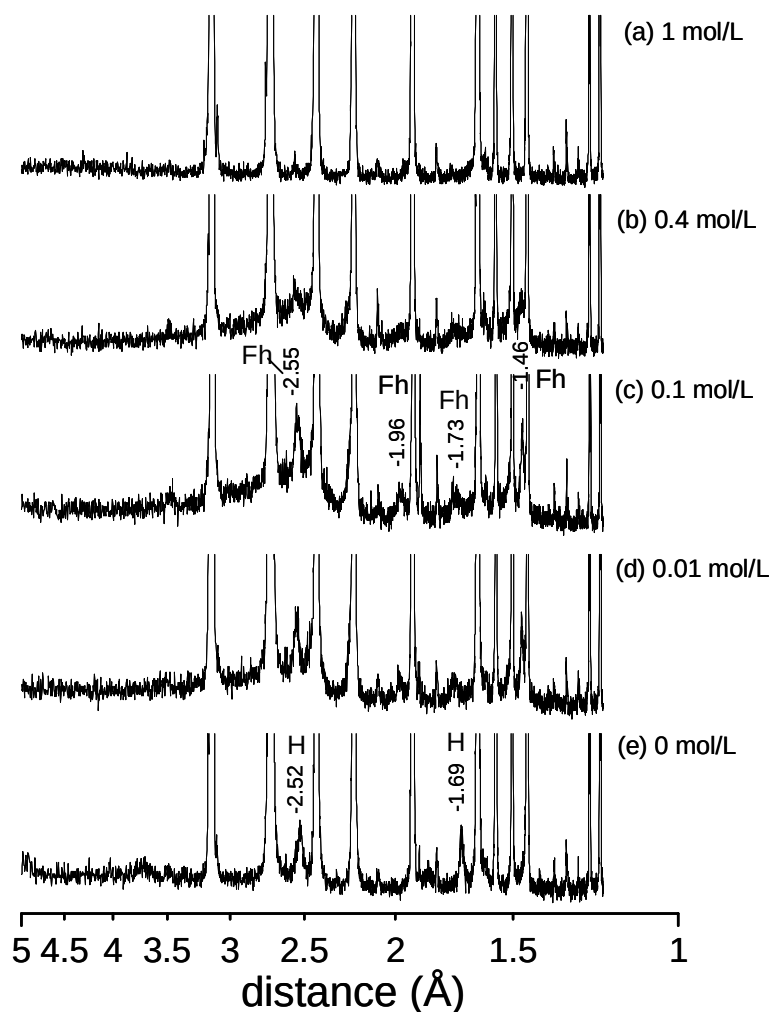


Figure 4.4 – XRD patterns for oxidized pyrite in pH 8.5 and different bicarbonate concentrations ($[\text{CO}_3^{2-}]$): 0 mol/L (corresponds to NaOH solution); 0.01 mol/L, 0.1 mol/L; 0.4 mol/L and 1 mol/L. Conditions: Temperature 80 °C, 1 h. H – Hematite (ICDD 33-0664) and Fh - Ferrihydrite (ICDD 29-0712).

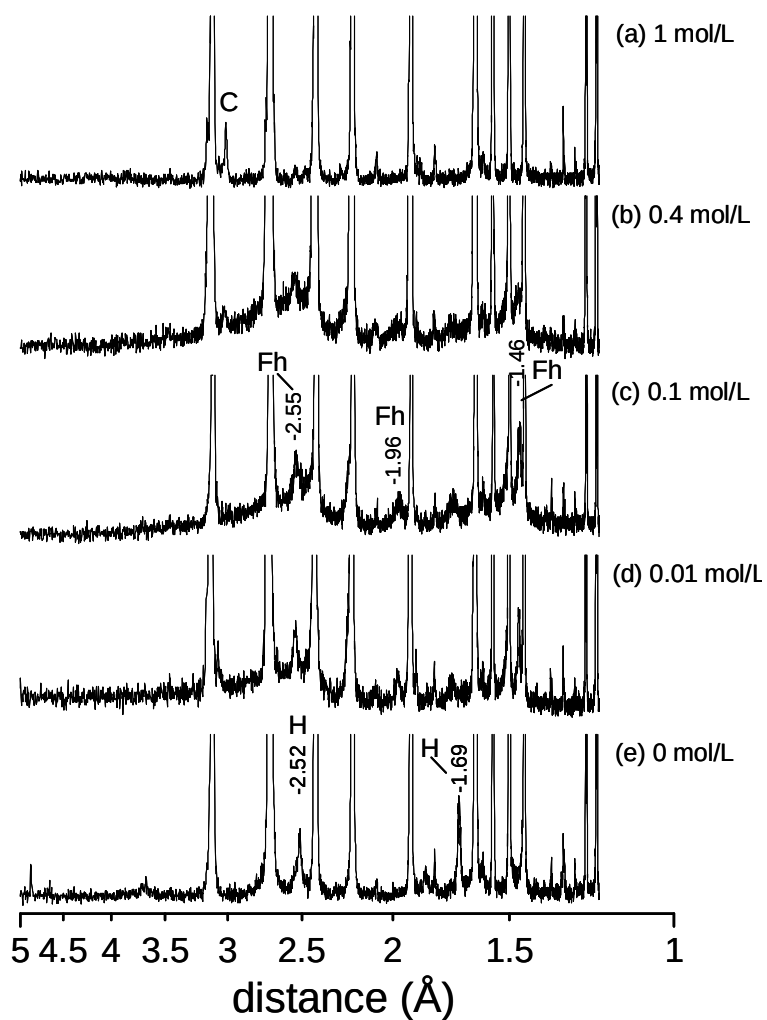


Figure 4.5 – XRD patterns for oxidized pyrite in pH 10 and different bicarbonate/carbonate concentrations ($[\text{CO}_3^{2-}]$): 0 mol/L (corresponds to NaOH solution); 0.01 mol/L, 0.1 mol/L; 0.4 mol/L and 1 mol/L. Conditions: Temperature 80 °C, 1 h. H – Hematite (ICDD 33-0664), Fh - Ferrihydrite (ICDD 29-0712) and C – calcite (ICDD 72-1214).

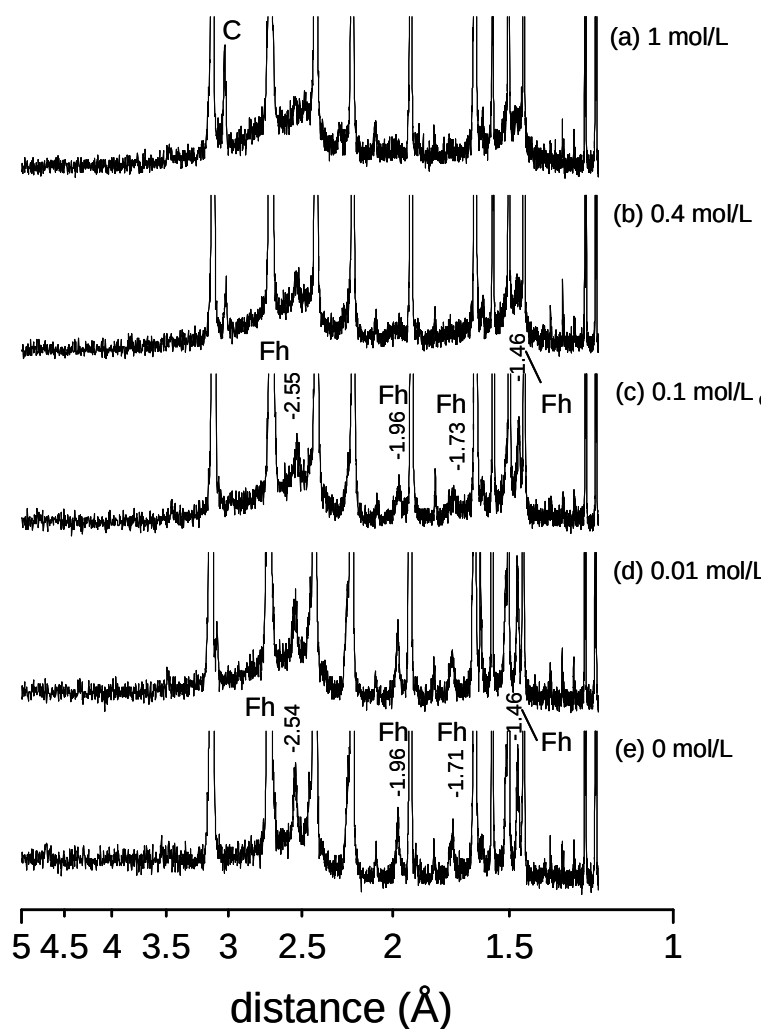


Figure 4.6 – XRD patterns for oxidized pyrite in pH 12.5 and different carbonate concentrations ($[\text{CO}_3^{2-}]$): 0 mol/L (corresponds to NaOH solution; 0.01 mol/L, 0.1 mol/L; 0.4 mol/L and 1 mol/L. Conditions: Temperature 80 °C, 1 h. Fh - Ferrihydrite (ICDD 29-0712) and C – calcite (ICDD 72-1214).

ferrihydrite, and used to distinguish this compound from the poorly crystalline ferroxihite (Jambor and Dutrizac, 1998). Therefore, the presence of ferroxihite in bicarbonate /carbonate media was excluded. At pH 12.5, ferrihydrite was the main oxidation product in both the hydroxide and carbonate solutions.

The formation of metastable carbonate compounds such as iron carbonate hydroxide ($\text{Fe}_2(\text{OH})_2\text{CO}_3$), siderite (FeCO_3) and ferrous-ferric hydroxide carbonate known as green rust1, GR1- CO_3 , ($[\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}][\text{CO}_3 \cdot 2\text{H}_2\text{O}]$) is supported by thermodynamics. Green rust containing carbonate, GR1- CO_3 , has been identified as a product of metallic iron corrosion in the presence of carbonate ions (Abdelmoula et al., 1996; Legrand et al., 2001a). However, no carbonate phase matched completely the diffraction patterns obtained in the present investigation. In view of that, techniques more specific to surface analyses, such as Infrared and Raman spectroscopy were employed. These results will be presented in the sections 4.3 and 4.4.

In all investigated pH range (Figure 4.4 to 4.6), the peaks of the oxidized phases become widened and poorly defined with the increase of the bicarbonate/carbonate concentration up to 0.4 mol/L (Figure 4.4-4.6), which is consistent with ferrihydrite formation. But surprisingly, no iron oxide/hydroxide phases were identified by XRD at 1 mol/L carbonate concentration and pH 8.5 and 10 (Figure 4.4a and 4.5a). This finding is in agreement with visual and optical microscope observations of the solid residues that showed no product layer. At pH 12.5 and 1 mol/L of carbonate concentration (Figure 4.6a), the XRD pattern exhibits similar peaks to those observed in other carbonate concentrations and pH values. At pH 12.5, ferrihydrite was the main oxidation product in both hydroxide and carbonate solutions.

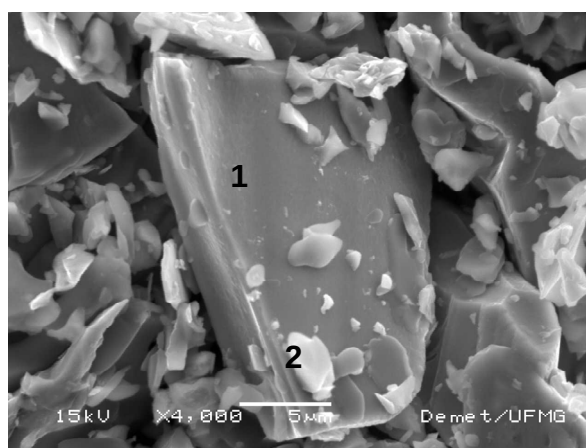
Soluble thiosulfate or sulfate ions (Mishra and Osseo-Asare, 1988; and Borda et al., 2003a and 2004) as well as solid iron oxyhydroxides are expected to be formed (Nicholson et al., 1988 and 1990; Ciminelli and Osseo-Asare, 1995 a,b) as a result of pyrite oxidation in alkaline solutions. But only minor amounts of soluble iron are likely to remain in solution. Considering that no iron product was identified after pyrite oxidation at 1 mol/L bicarbonate/carbonate (pH 8.5 and 10), quantitative chemical analyses were carried out (Table IV.2) in the aqueous phase. The results show the increase of soluble iron concentration with the increase of carbonate concentration, with significant values obtained at 1 mol/L bicarbonate/carbonate solution (pH 8.5 and 10). These findings clearly demonstrate the formation of soluble iron-carbonate complexes. It is worth noting that the predominance of iron carbonate complexes in this pH range was predicted by thermodynamics (Figure 4.2b). The absence of iron soluble complexes at pH higher than 12

is also in agreement with the results shown in Table IV.2. So, iron remains soluble at higher carbonate/ bicarbonate concentrations, due to the formation of iron complexes in the pH range 8.5 to 10. The increase of iron solubilization in the presence of carbonate concentration was also reported by Descostes et al. (2002). Dissolution of silica from the glass reactor (apparatus) usually occurs during the experiments carried out in alkaline solutions (Legrand et al., 2004). The Si concentration increases with the increase of bicarbonate /carbonate concentration and with pH (Table IV.2). At pH 12.5, Si dissolution is extensive and will affect iron precipitation, as will be discussed later.

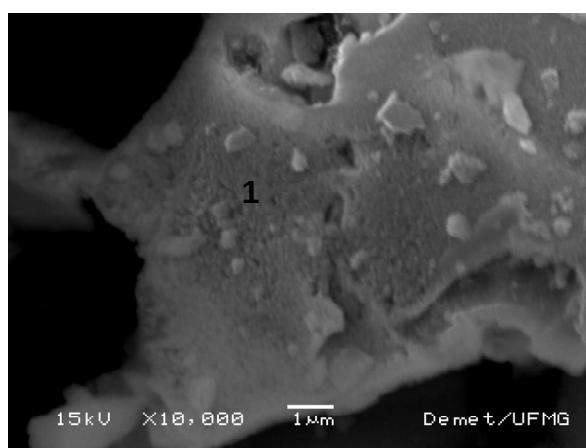
Table IV.2 – Iron and silicate concentrations in solutions of pyrite oxidation

Condition [CO ₃ ²⁻] _T (mol/L)	Reaction Time (h)	pH					
		8.5		10		12.5	
		Concentration (mg/L)					
		Fe total	Si	Fe total	Si	Fe total	Si
0 (NaOH solution)	1	< 0.05	2.4	0.6	3.9	< 0.05	104
	12	-	-	1.4	12.1	-	-
0.1 mol/L	1	0.2	8.4	0.3	9.3	0.4	58.3
	12		-	0.7	23.8	-	-
0.4 mol/L	1	1.6	11.8	3.5	10.7	0.5	41.6
	12	-	-	11.2	24.1	-	-
1 mol/L	1	28.0	20.4	58.3	12.0	1.2	48.4

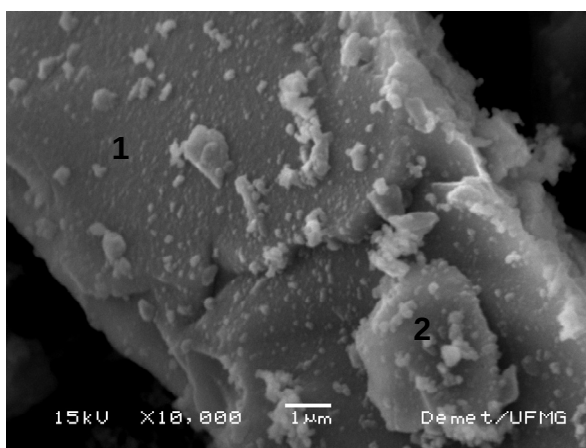
In order to evaluate the morphology of the products of pyrite oxidation, unreacted and oxidized pyrite samples were examined using scanning electron microscope (SEM) (Figures 4.7 and 4.8). SEM images revealed pyrite particles with a dense structure, sharp edges and broad particle size distribution. Semi-quantitative chemical analyses performed by energy dispersive X-ray spectrometer (EDS) showed 44% Fe and 56% S as typical composition of unreacted particles (Figure 4.7a); an incipient oxidation is already observed in the analyses of the small pyrite particles (42% Fe, 48% S and 10% O). It is noticeable that the oxide layers formed in both media contain Si, a fact that can be attributed to the dissolution of the glass apparatus. Contents as high as 4-7% Si were found in samples oxidized in higher bicarbonate /carbonate concentration (0.4 mol/L [CO₃²⁻]_T) and longer reaction time (12h). Confirming the XRD results (Figure 4.4a and 4.5a), no significant iron oxide layer is formed



(a)

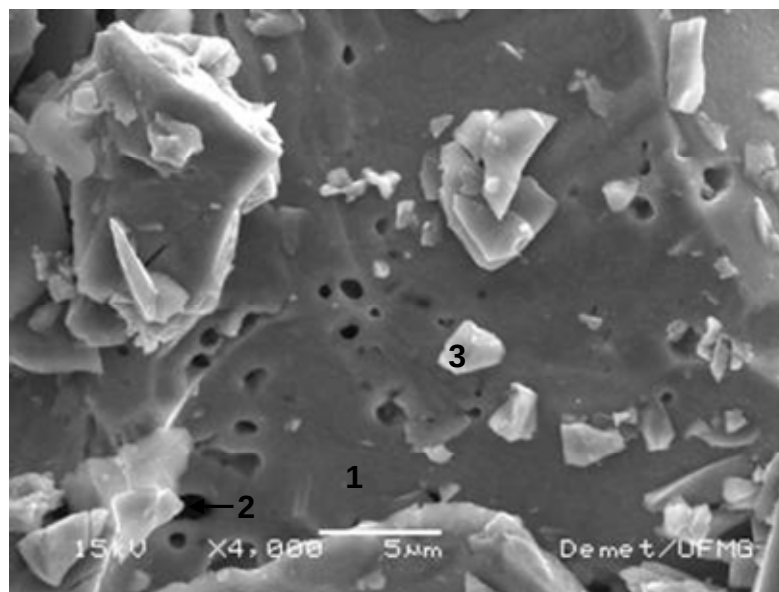


(b)

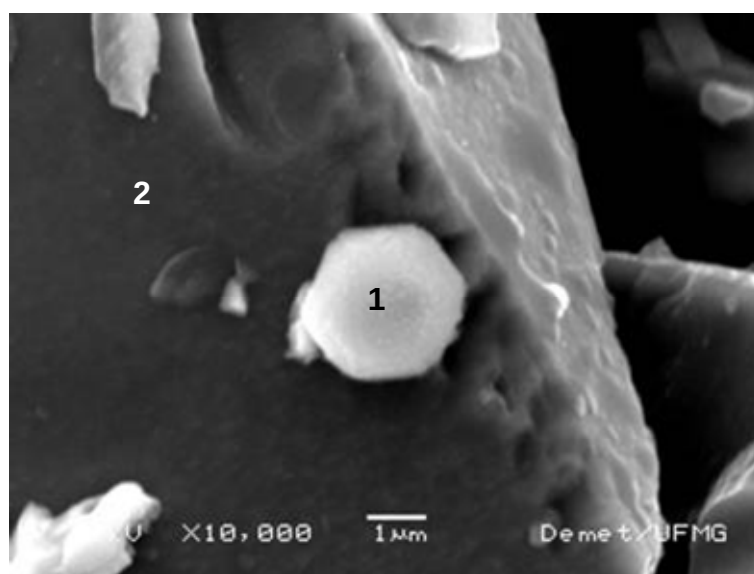


(c)

Figure 4.7 - Scanning electron microscope micrographs of unreacted pyrite (1 - Fe = 44%, S =56%; and 2 - Fe = 42%, S =48%, O =10%) (a); typical oxidized pyrite in hydroxide media (0 $[\text{CO}_3^{2-}]$ mol/L) – (1) - Fe = 79%, S = 6 %, O = 12%, Si = 3%) (b); and bicarbonate/carbonate media (0.4 mol/L $[\text{CO}_3^{2-}]$ (1) - Fe = 88%, S =2%, O =9%, Si = 1%, (2) - Fe = 80%, S =2%, O =14%, Si = 3%, (c). Conditions: pH 10, 12 h and 80 °C.



(a)



(b)

Figure 4.8 - Scanning electron microscope micrographs of typical oxidized pyrite in 1 mol/L of $[\text{CO}_3^{2-}]$ (1) Fe = 44%, S = 49%, O = 5%, Si = 1%, (2) - Fe = 49%, S = 45%, O = 4%, Si = 1%, (3) - Fe = 42%, S = 50%, O = 6%, Si = 1% (a); and detail showing small particle contents higher content of calcium (1) Fe=9%, Ca=74%, S=17%, (2) Fe = 48%, S = 52%, (b). Conditions: pH 10, 1 h and 80 °C.

on pyrite particles oxidized in 1 mol/L of bicarbonate /carbonate solutions (pH 8.5 and 10) (Figure 4.8). Note that the EDS analyses are very close to that of unreacted pyrite: 42-49% S in the residues and 44% S in the unreacted. The slightly rounded particles and the formation of pits on the surface distinguish the residues from the unreacted pyrite particles. In some samples oxidized at high bicarbonate/carbonate concentrations (0.4 and 1 mol/L), very small crystallites, rich in calcium (74% Ca, 9% Fe and 17% S) were identified. The presence of sulfur may be ascribed not only to residual sulfides but to sulfate species as well.

4.3 Infrared Spectroscopy Analyses

Diffuse reflectance (DRIFT) and transmission (FTTIR) spectra of unreacted and oxidized pyrite in carbonate and hydroxide media, in different reaction times, are shown in Figures 4.9 and 4.10. For the unreacted pyrite, characteristic bands of this sulfide, sulfate compounds and adsorbed water can be identified in both DRIFT and FTTIR spectra. A strong infrared absorption band at approximately 440 cm^{-1} is assigned to the disulfide (S-S) group in pyrite lattice (Evangelou, 1995). The multiple absorption bands observed in the DRIFT at 1040, 1120 and $1180\text{-}1210\text{ cm}^{-1}$ and FTTIR spectra at 1080, 1140 and 1230 cm^{-1} would correspond to the splitting of the asymmetric triply degenerate S-O stretching, ν_3 vibration, of the sulfate species. In addition to the ν_3 vibration of sulfate, the transmission spectra exhibit bands that can be attributed to sulfate bending mode (ν_2) at 610 cm^{-1} and the band characteristic of symmetric S-O stretching vibration (ν_1 sulfate mode) at 1000 cm^{-1} , that becomes fully active due to surface-complexed sulfate species. The broad band centered about 3400 cm^{-1} and the band at 1630 cm^{-1} are assigned to O-H stretching and bending modes of water or metal hydroxo groups, respectively (Nakamoto, 1997). The presence of hydroxo groups and sulfate indicates the onset of sulfide oxidation of the “unreacted” samples. A small band at 1430 cm^{-1} is assigned to the ν_3 symmetric stretching vibration of C-O bond, similar to that of carbonate ion (CO_3^{2-}) (Evangelou, 1995 and Nakamoto, 1997). The results obtained by IR analyses will be discussed in detailed in the following paragraphs.

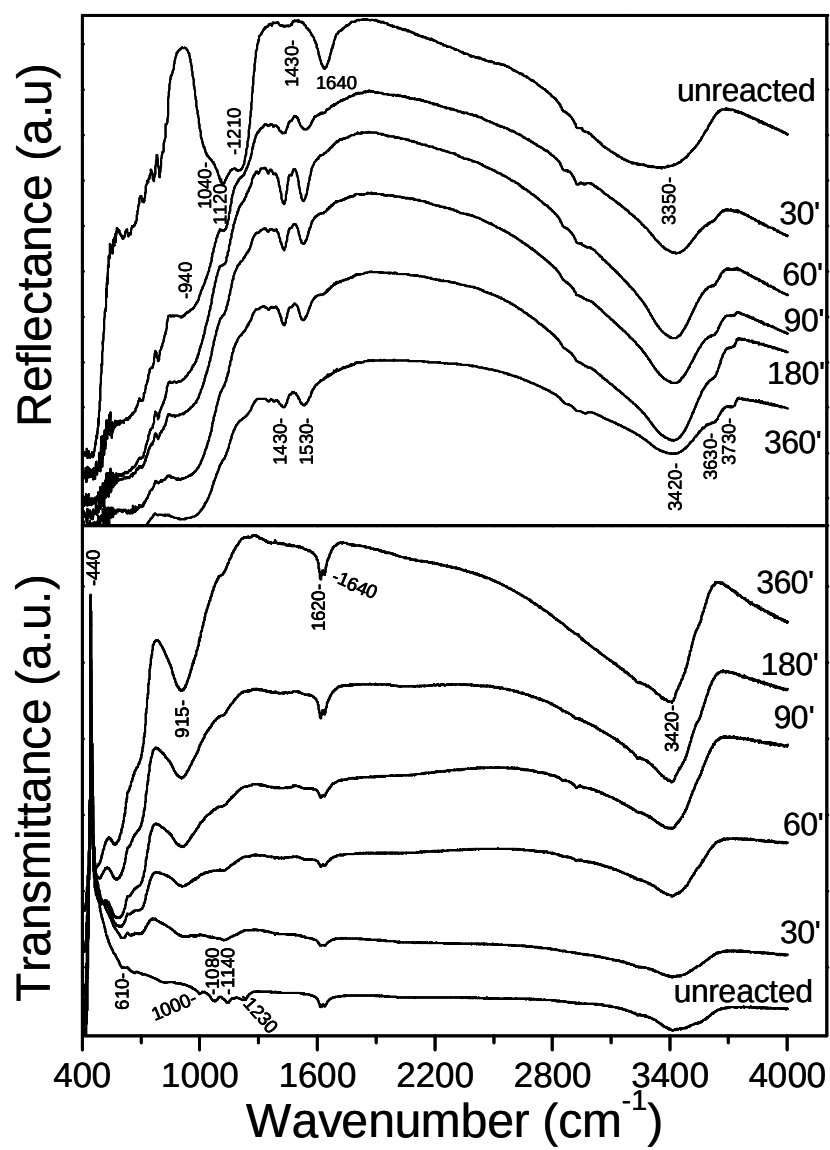


Figure 4.9 – For carbonate/bicarbonate media, diffuse reflectance and transmission spectra for unreacted and oxidized pyrite in different times, pH 10, T = 80°C, (a) 30, (b) 60, (c) 90, (d) 180 and (e) 360 min.

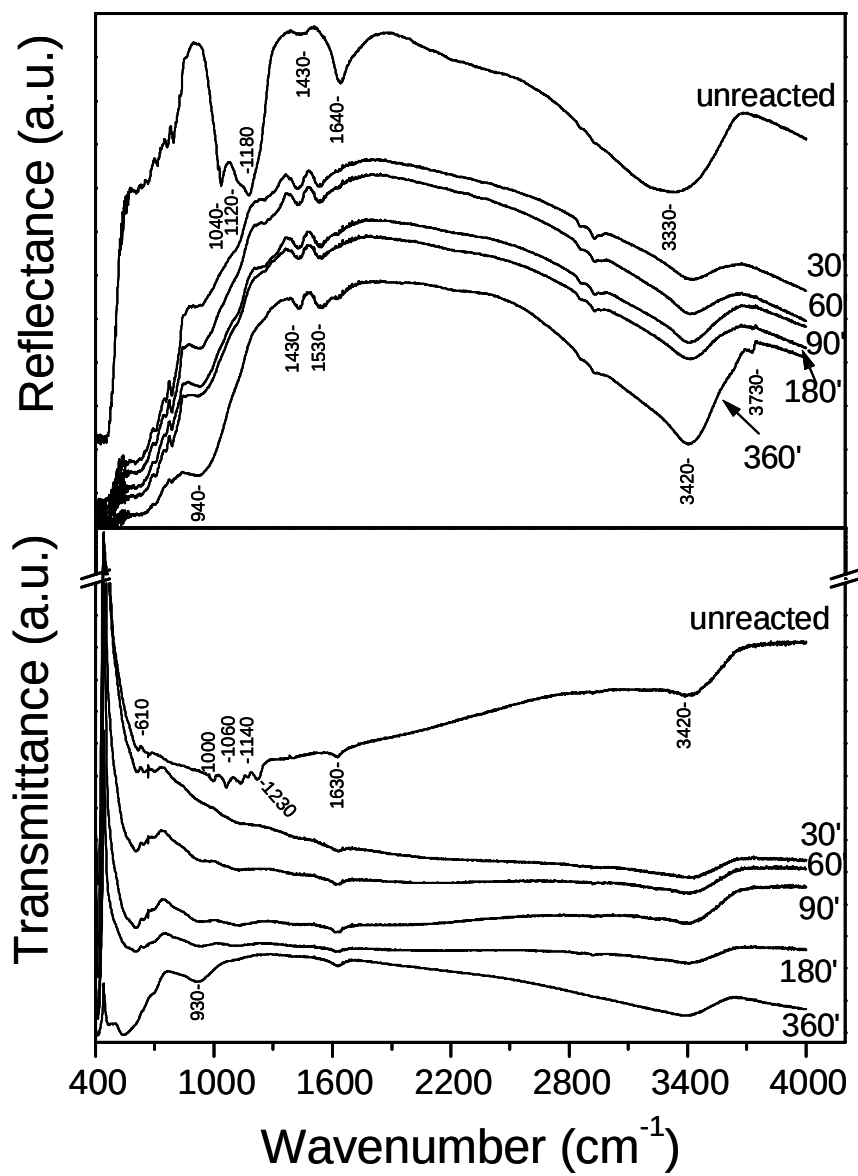


Figure 4.10 – For hydroxide media, diffuse reflectance and transmission spectra for unreacted and oxidized pyrite in different times, pH 10, $T = 80^{\circ}\text{C}$, (a) 30, (b) 60, (c) 90, (d) 180 and (e) 360 min.

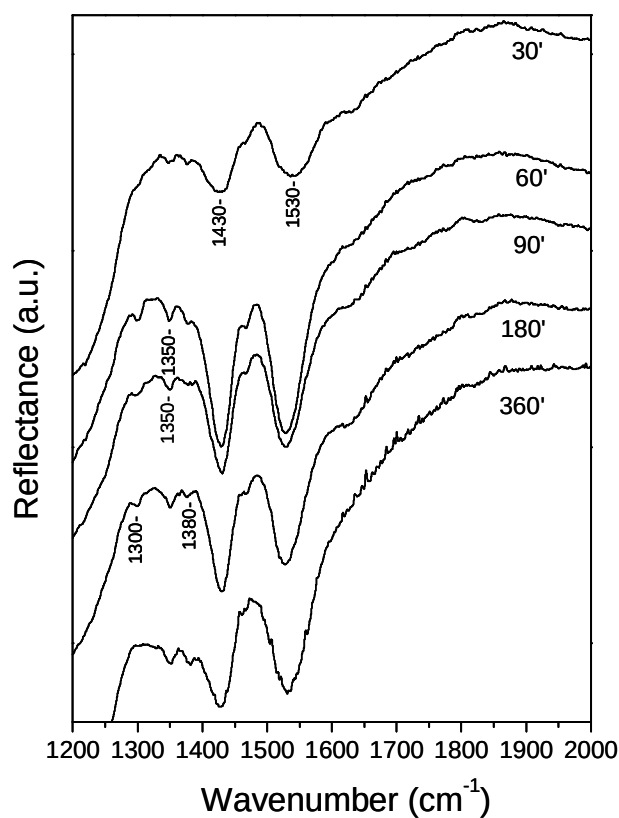
4.3.1 DRIFT vs transmission spectra for the oxidized samples

A comparison of the DRIFT and FTTIR spectra of oxidized pyrite samples, in pH 10, in both carbonate and hydroxide media, indicates two main differences. The first one is the presence of two well-defined peaks in the DRIFT spectra: one near 1430 (assigned to the ν_3 symmetric stretching vibration of C-O bond) and the other at 1530 cm^{-1} (C-O asymmetric stretching vibration), both being more intense in carbonate medium (Figure 4.9a and 4.10a). It is important to observe that these typical carbonate vibrations do not appear in the FTTIR spectra. This absence explains why carbonate species were not identified in previous works (Ciminelli, 1987, and Hood, 1991). As far as the authors are aware of, the results reported in the present work represent the first time that carbonate species have been identified, by infrared techniques, as a product of pyrite oxidation in aqueous solutions (Caldeira et al, 2001, 2003 and 2004).

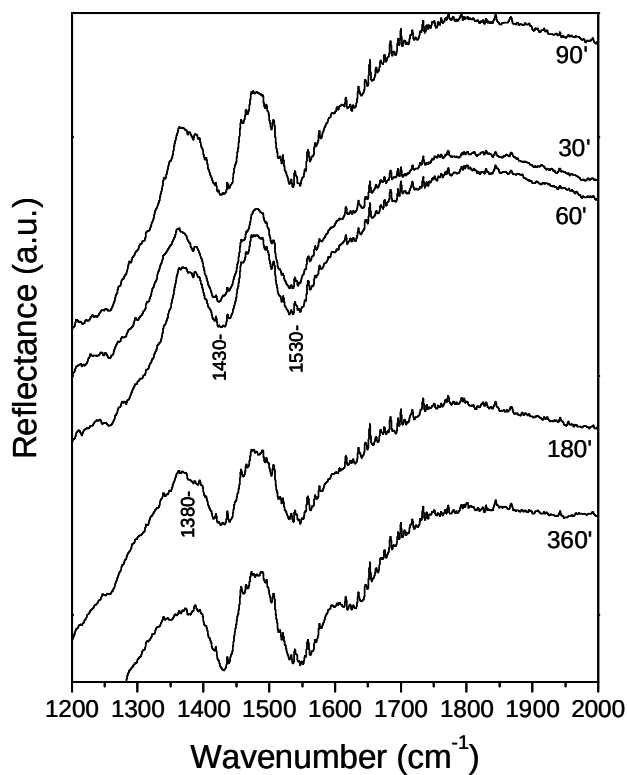
The second difference is the fact that the peak at 1640 cm^{-1} (water OH bending) in the DRIFT spectra (Figure 4.9a and 4.10a) practically disappears after pyrite oxidation. The peaks at 1620 and 1640 cm^{-1} in the FTTIR spectra were related to residual humidity in the KBr disks (Figure 4.9b and 4.10b). The FTTIR spectra also exhibited well-defined bands at 915 cm^{-1} in carbonate media, attributed to Fe-OH bending mode of iron oxyhydroxide (e.g. ferrihydrite), and at 930 cm^{-1} in the hydroxide media, attributed to Fe-O-Fe bond of hematite (Davydov et al., 1998) or feroxyhite (Weckler and Lutz, 1998).

4.3.2 Carbonate group

Aqueous (free) carbonate and bicarbonate ions exhibit the typical absorption bands in the spectral region between 1200 and 1700 cm^{-1} , the so-called C-O stretching region, denoted here as $\nu_3(\text{CO})$. The uncoordinated carbonate ion belongs to the D3h symmetry group with four fundamental modes of vibration. ν_2 , ν_3 , and ν_4 are infrared active while ν_1 , ν_3 and ν_4 are Raman active (Nakamoto, 1997). A strong $\nu_3(\text{CO})$ stretch vibration band appears at 1390-1415 cm^{-1} . If the D3h symmetry is broken (e.g. by protonation and adsorption), this doubly degenerate $\nu_3(\text{CO})$ stretch mode can split into other bands, such as those at 1430 and 1530 cm^{-1} (Figure 4.11). The following vibrational modes for bicarbonate aqueous ions are reported (Wen and Brooker, 1995): the 1360 cm^{-1} band assigned to the ν_3 symmetric C-O stretch and 1630 cm^{-1} to asymmetric C-O stretch, the 1300 cm^{-1} to the ν_4 COH bend, and the small band at 1017 cm^{-1} to the ν_4 C-OH stretch. The latter is the most important for



(a)



(b)

Figure 4.11 – Detail of the DRIFT spectra for oxidized pyrite in different times from Figures 5.9a and 5.10a showing the frequency range 1200-2000 cm⁻¹ in bicarbonate/carbonate media (a), hydroxide media (b).

diagnostic by Raman spectroscopy, while the band at 1360 cm^{-1} is the most intense in IR spectra. Considering the nearer position of their most characteristic bands, the distinction between surface-bound carbonate and bicarbonate is not trivial.

The identification of the coordination state of the carbonate in complexes is usually based on the degree of splitting of the $\nu_3(\text{CO})$ stretch vibration (Jolivet et al., 1982, Wijnja and Schulthess (1999); and Hiemstra et al., 2004). The magnitude $\Delta\nu_3(\text{CO})$ is influenced by polarization of the cation and additional field effects, for instance to H bonding. The schematic representation of the several different coordination states of carbonate are shown in Figure 4.12. In general, the following ranges for the degree of splitting have been used in surface and coordination chemistry to identify the type of coordination in carbonate complexes: no splitting for non-coordinated, $80\text{--}110\text{ cm}^{-1}$ for monodentate coordination, $310\text{--}340\text{ cm}^{-1}$ for bidentate-mononuclear coordination, and $400\text{--}750\text{ cm}^{-1}$ for bidentate-binuclear coordination.

In the present study, the band at 1430 cm^{-1} was assigned to the symmetric $\text{O}_{\text{II}}\text{CO}_{\text{II}}$ -stretch vibration ($\nu_s(\text{CO})$) and the band at 1530 cm^{-1} to the asymmetric $\text{O}_{\text{II}}\text{CO}_{\text{II}}$ -stretch vibration ($\nu_{as}(\text{CO})$) of adsorbed carbonate anion at the oxidized pyrite surface. The observed difference between the two bands ($\Delta\nu(\text{CO})$) is of 100 cm^{-1} . Based on a correlation between cation polarization and the degree splitting proposed by Hiemstra et al. (2004), the magnitude of $\nu_3(\text{CO})$ becomes representative of a bidentate complex on the Fe^{2+} from pyrite and of a monodentate complex on the Fe^{3+} from the iron oxihydroxides.

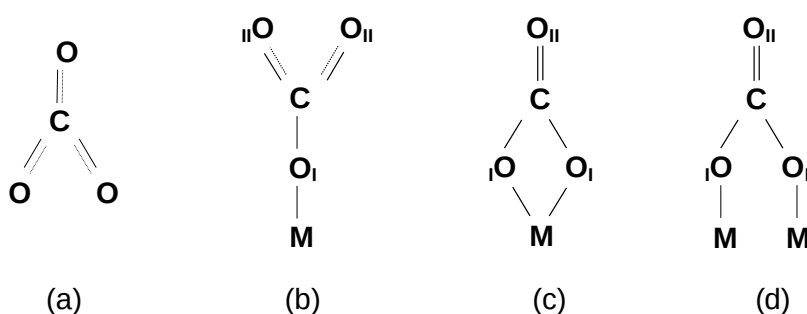


Figure 4.12 - Schematic representation of the various possible surface complexes of carbonate: (a) free ion (D_{3h}); (b) monodentate (C_s); (c) bidentate- mononuclear (C_{2v}); (d) bidentate-binuclear. The I and II subscripts are designations for the oxygens that are coordinated to metal (O_{I}) and not metal-coordinated (O_{II}). Adapted from Wijnja and Schulthess (1999).

Using attenuated total reflectance (ATR-FTIR) spectroscopy, Su and Suarez (1997) suggested that a monodentate carbonate is the species complexed to amorphous iron hydroxides in 1.0 mol/L NaHCO_3 suspensions. Using ATR-FTIR at experiments with 1 mmol/L NaHCO_3 solutions and pH 4.8-7, Wijnja and Schulthess (2001) also suggest that carbonate only exists in a monodentate coordination state with the goethite surface. However, if the effect of cation polarization is considered, as proposed by Jolivet et al. (1982), a bidentate structure is formed. Using this approach in combination with determination of charge distribution of carbonate complexation on goethite surface, Hiemstra et al. (2004) revisited the adsorption of carbonate on goethite and concluded that a bidentate-mononuclear complex is the structure more likely to occur.

The DRIFT spectra shown in Figure 4.11 highlight the bands at 1430 and 1530 cm^{-1} . Both increase with carbonate concentration and time (up to 90 min) and then decrease at longer reaction times (Figure 4.11a). In hydroxide medium (Figure 4.11b), no significant difference in peak intensities with time is observed. Bands at 1300, 1350, and 1380 cm^{-1} also appear in carbonate solutions. The multiplicity of bands indicates the presence of more than one carbonate/bicarbonate complex on pyrite surface, as discussed later in this chapter. At fixed time, the increase of carbonate concentration increases the perturbations on the carbonate region, with the appearance of a number of ill-defined bands (Figure 4.13), as those shown in Figure 4.11. As time increases (up to 12 hours), the bands at 3430 cm^{-1} (OH stretching) become sharper and more intense in both media (Figure 4.13), as a result of oxyhydroxides formation. The multiple bands in the 1350-1550 cm^{-1} region are highlighted in Figure 4.14. It can be observed that as carbonate concentration increases, the band at 1550 cm^{-1} (Fe-OH bending) decreases while the carbonate bands increase. The results suggest a replacement of the Fe-OH groups by carbonate.

Now it will focus on the effect of pH and carbonate concentration. The complete spectra are shown in Figure 4.15-4.18; the carbonate region is highlighted in Figure 4.19. In the absence of carbonate, the bands at 1410 and 1550 cm^{-1} appear at pH 8.5 (Figure 4.19a). According to various authors (Nakamoto, 1997; Busca and Lorenzelli, 1980; and Lorenzelli and Busca, 1982) the bands at 1410 cm^{-1} and 1552 cm^{-1} are assigned adsorbed O_2/O_2^- species on pyrite and hematite surfaces, respectively. This is consistent with the formation of hematite in hydroxide solutions at pH 8.5 and 10.

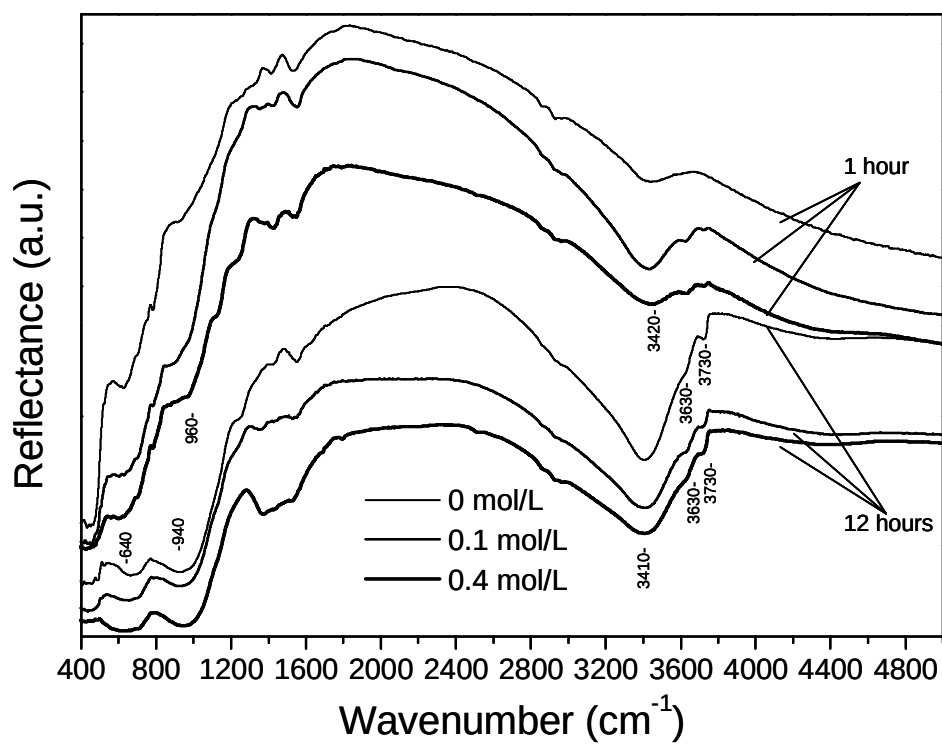


Figure 4.13 – Diffuse reflectance spectra (DRIFT) for unreacted and oxidized pyrite in pH 10 and in different carbonate/bicarbonate concentrations: 0 mol/L (corresponds to NaOH solutions- 0.1 mmol/L); 0.1 mol/L and 0.4 mol/L. Reaction time: 1 and 12 hours.

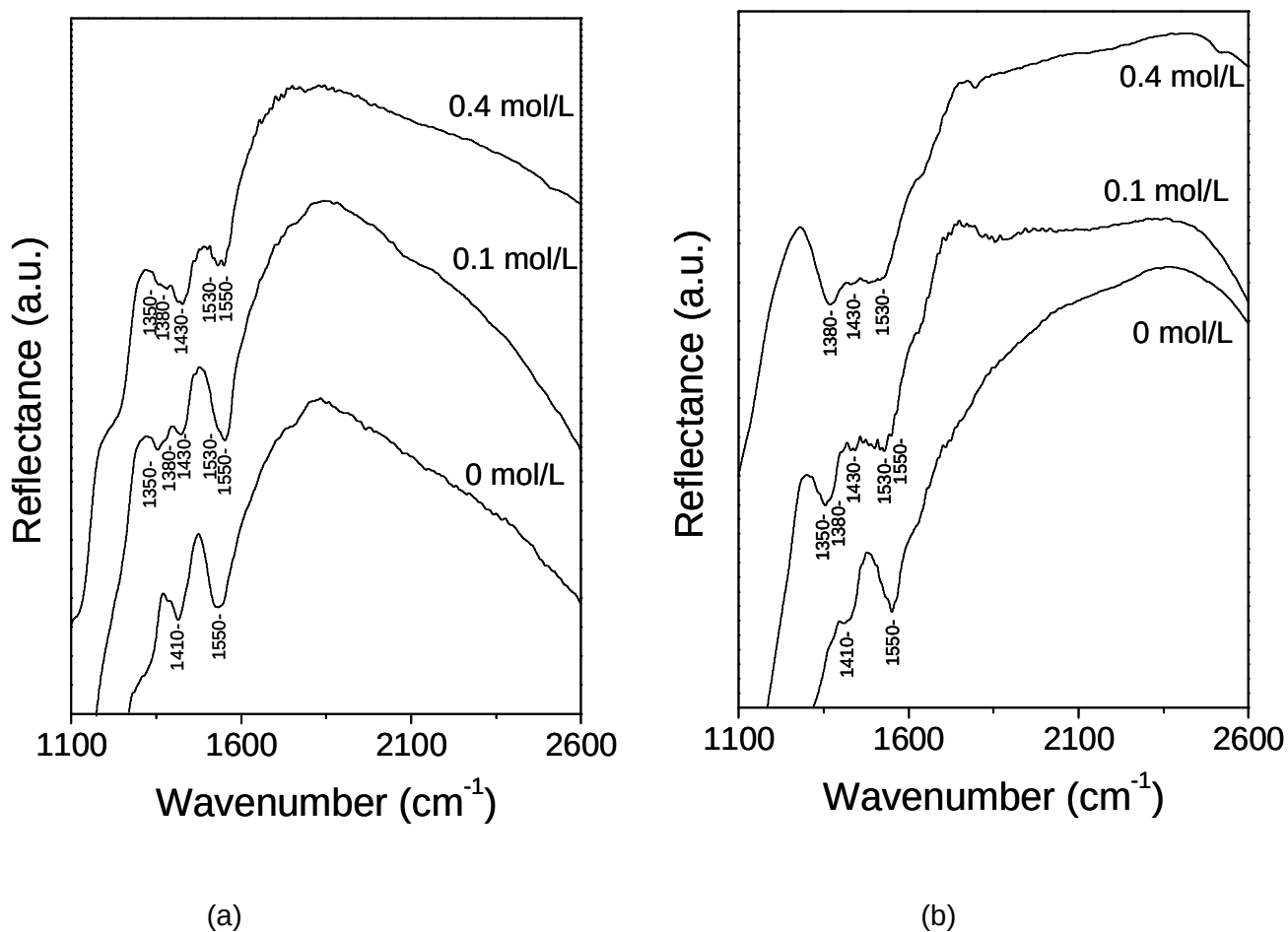


Figure 4.14 – Detail of the DRIFT spectra from Figures 4.13 showing the frequency range 1100-2600cm⁻¹ for reaction time 1 h (a), 12 h (b).

The results obtained under various bicarbonate/carbonate concentrations and pH values indicate bands at 1300, 1350, 1380, 1430, 1530 and 1550 cm^{-1} . The bands at 1300 (Figure 4.11) and at 1350 cm^{-1} are assigned to the COH bending mode (ν_4) and to the symmetric CO stretch (ν_3) vibration of the bicarbonate ion, respectively. In this case, their intensity would be expected to decrease as bicarbonate deprotonates with the increase of pH; this is not evident in the results shown in Figure 4.19. Thus, the band at 1350 cm^{-1} may be assigned more likely to the symmetric vibrational mode of carbonate ions. The band at 1380 cm^{-1} can be related to the presence of hydrogen peroxide, which would be an evidence of the hydroxyl radical mechanism of pyrite oxidation (Mishra and Osseo-Asare, 1988 and Borda et al., 2001 and 2003). The spontaneous formation of H_2O_2 or OH radical in the pyrite/water system was observed by Borda et al. (2003). Finally and more likely, the bands at 1350 (ν_3 C-O symmetric) and 1380 cm^{-1} (ν_3 C-O asymmetric) can be assigned to the presence of green rust - GR1CO_3 / ferric oxyhydroxycarbonate (Fe(III) GRCO_3) (Legrand et al., 2004; Savoye et al., 2001; and Drissi et al., 1995). The ferric oxyhydroxycarbonate (Fe(III) GRCO_3) was identified as a stable product of oxidation of the green rust - GR1CO_3 (Legrand et al., 2004). Considering green rust stability (Legrand et al., 2000) the effect of pH on these bands is expected to be less pronounced.

The characteristic and very strong broader band at 1430 cm^{-1} is assigned to the ν_3 vibrational mode of free carbonate ion, such as occurs in siderite (FeCO_3) or other metal-carbonate compounds. Nonsplitting of the carbonate band (at 1430 cm^{-1}) indicates the formation of weak carbonate complexes on pyrite and iron oxides surface or the formation of a carbonate compound. As bicarbonate/carbonate concentration increases, all typical carbonate bands are replaced by a broad and strong band at 1430 cm^{-1} (Figure 4.14 and 4.19). These modifications (intensities and shifts) indicate changes in carbonate coordination on the solid surface. At 0.4 and 1 mol/L carbonate/bicarbonate solutions the formation of a metal carbonate compound becomes evident. The presence of siderite and adsorbed carbonate ions on goethite formed during pyrite oxidation (0.1 and 1 mol/L of bicarbonate concentration) has been reported (Descostes et al., 2002).

At 1 mol/L bicarbonate/carbonate media (pH 8.5 and 10), no iron oxyhydroxides were identified by XRD or SEM. Hence, DRIFT spectra (4.19d) showed only the presence of the surface-bound carbonate ions (pH 8.5) or a metal carbonate compound (pH10), similar to those identified on the "unreacted" sample. Only in this condition (Figure 4.18), another typical carbonate band appears at 875 cm^{-1} due to out of plane bending of carbonate

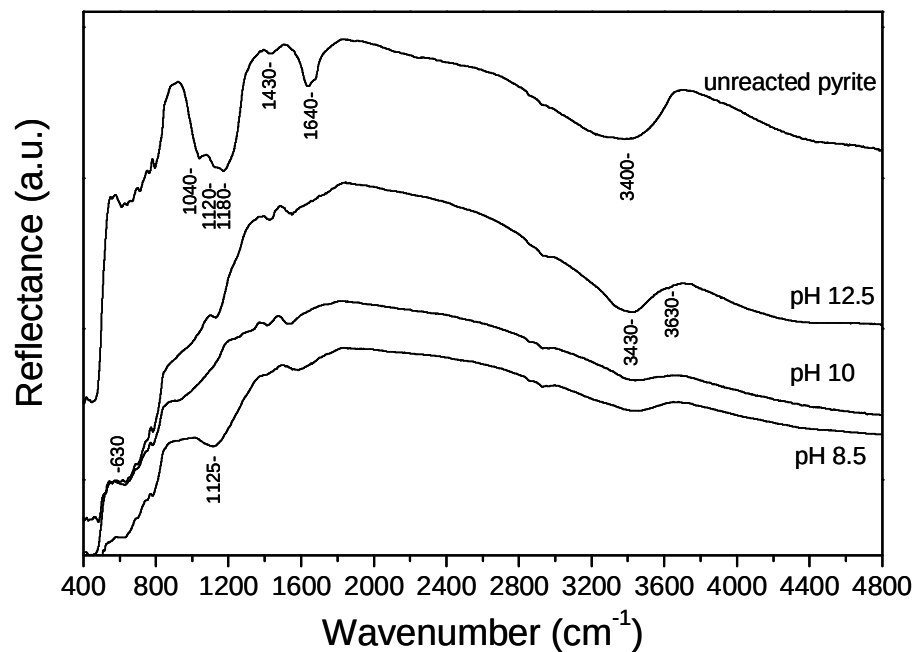


Figure 4.15 – Diffuse reflectance spectra (DRIFT) for oxidized pyrite in different pH values for 0 mol/L of carbonate/bicarbonate solution (corresponds to NaOH solution), $T = 80\text{ }^{\circ}\text{C}$ and 1 hour.

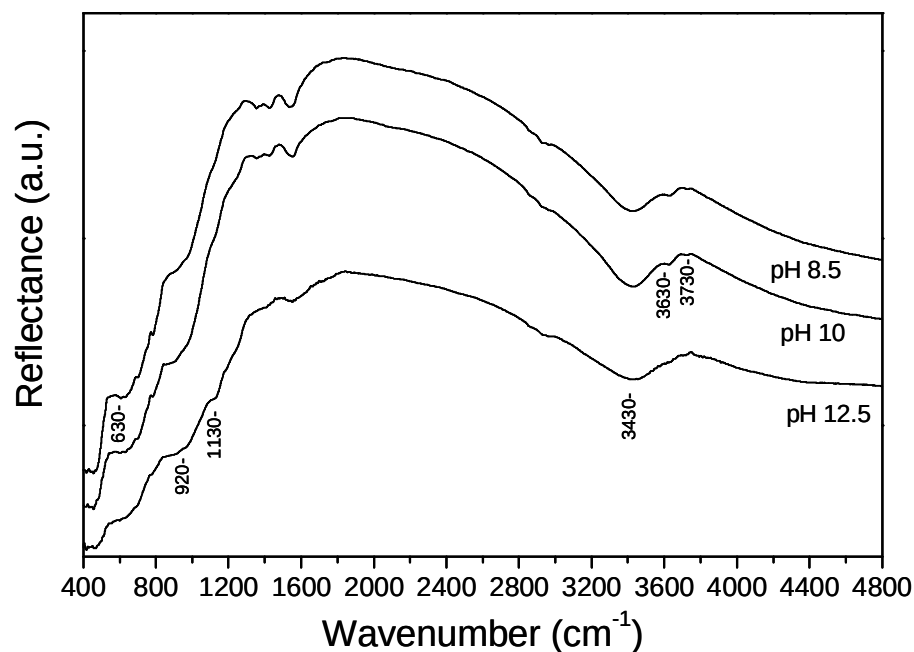


Figure 4.16 – Diffuse reflectance spectra (DRIFT) for oxidized pyrite in different pH values for 0.1 mol/L of carbonate/bicarbonate solution, 1 hour and $T = 80\text{ }^{\circ}\text{C}$.

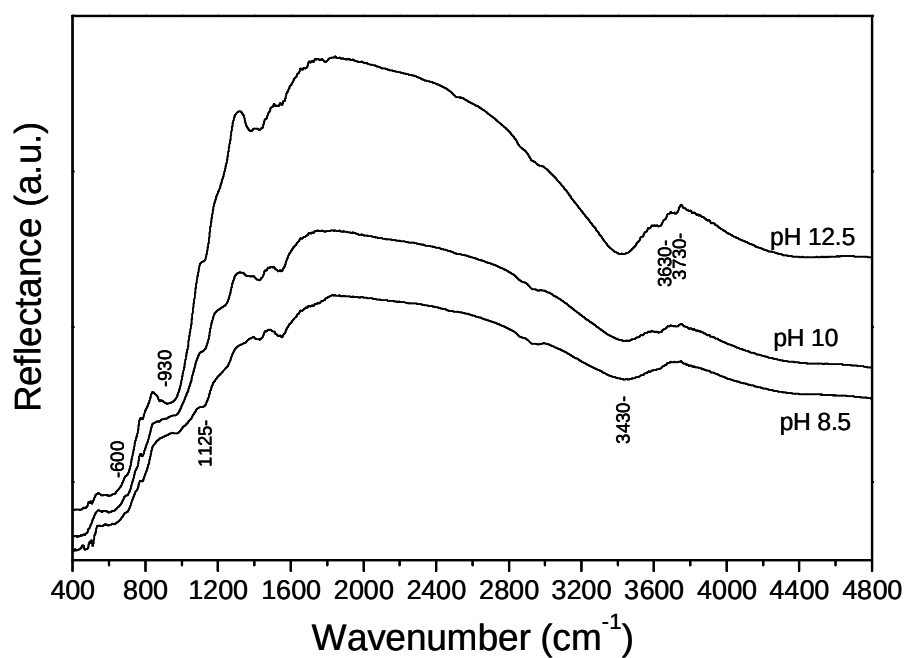


Figure 4.17 – Diffuse reflectance spectra (DRIFT) for oxidized pyrite in different pH values for 0.4 mol/L of carbonate/bicarbonate solution, 1 hour and $T = 80\text{ }^{\circ}\text{C}$.

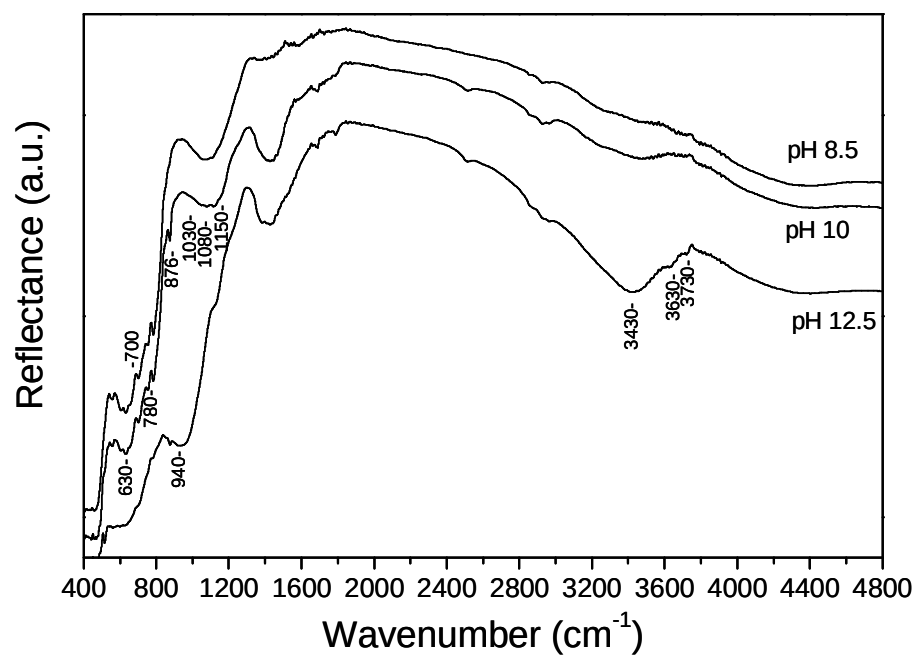


Figure 4.18 – Diffuse reflectance spectra (DRIFT) for oxidized pyrite under different pH values for 1 mol/L of carbonate/bicarbonate solution, $T = 80\text{ }^{\circ}\text{C}$ and 1 hour.

(ν_2 vibrational mode). The band at 1530 cm^{-1} is attributed to the “C-O” asymmetric stretching vibration of carbonate ions. This broad band exhibits a shoulder (1550 cm^{-1}) at pH 8.5. As pH increases, the band at 1530 cm^{-1} decreases whereas the 1550 cm^{-1} (Fe-OH bending) increases (Figure 4.19a and b).

In summary, the presence of two well-defined peaks in the spectra of oxidized pyrite in carbonate/bicarbonate solution has been identified by DRIFT spectroscopy. The first one, at near 1430 cm^{-1} , was assigned to the ν_3 symmetric stretching vibration of C-O bond, and the other, at 1530 cm^{-1} , was assigned to the C-O asymmetric stretching vibration. Regardless the source of carbonate (reagent addition or air), these bands are highly diagnostic for a surface-bound carbonate species. The magnitude of the splitting of the ν_3 stretching vibration of the C-O group indicated the formation bidentate mononuclear complex on pyrite surface. In carbonate solutions, new bands appear within the characteristic spectral range of carbonate ($1300\text{-}1600\text{ cm}^{-1}$). These bands (1350 and 1380 cm^{-1}) were assigned to green rust, GRCO_3 or more likely to Fe(III)GRCO_3 , due to the absence of a strong band at 1380 cm^{-1} , typical of the former. These bands arise under conditions where ferrihydrite is also identified, thus some carbonate adsorption can not be neglected. At high carbonate concentrations, a broad band at 1430 cm^{-1} indicates the formation of a metal carbonate compound.

4.3.3 Hydroxo (OH) group

According to Nakamoto (1997), lattice water (H_2O) absorbs at $3220\text{-}3550\text{ cm}^{-1}$ (asymmetric and symmetric stretching) and at $1600\text{-}1630\text{ cm}^{-1}$ (HOH bending). The absence of the HOH bending vibration mode around 1600 cm^{-1} indicates that this vibrational mode may be less evident by the DRIFT technique (Figure 4.9a and 4.10a). The well-defined peaks at 1620 and 1640 cm^{-1} in the FTTIR spectra are attributed to the residual moisture of the KBr disks and to the Fe-OH bending mode (Figure 4.9b), respectively.

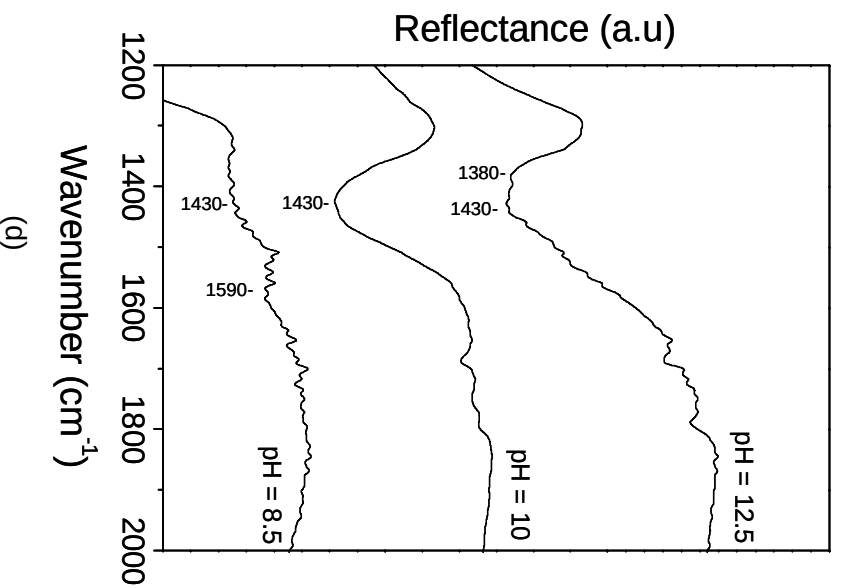
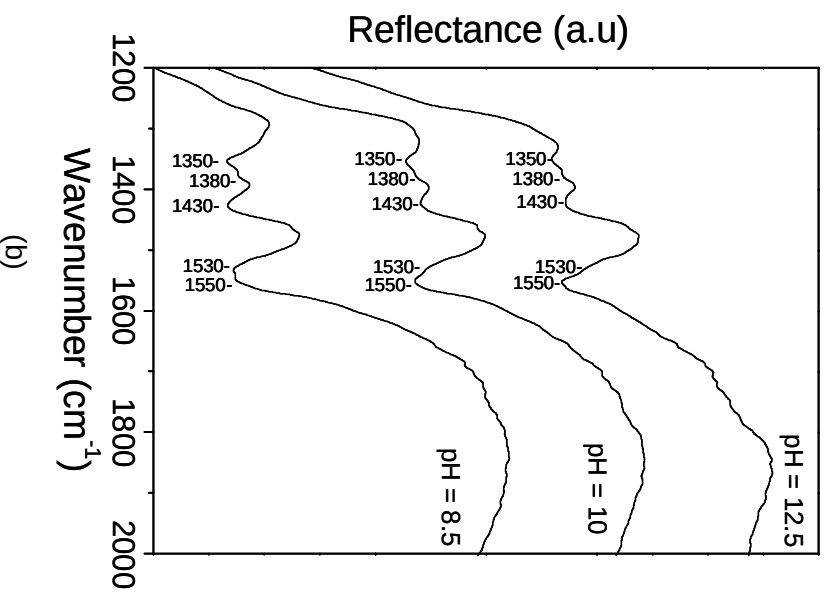
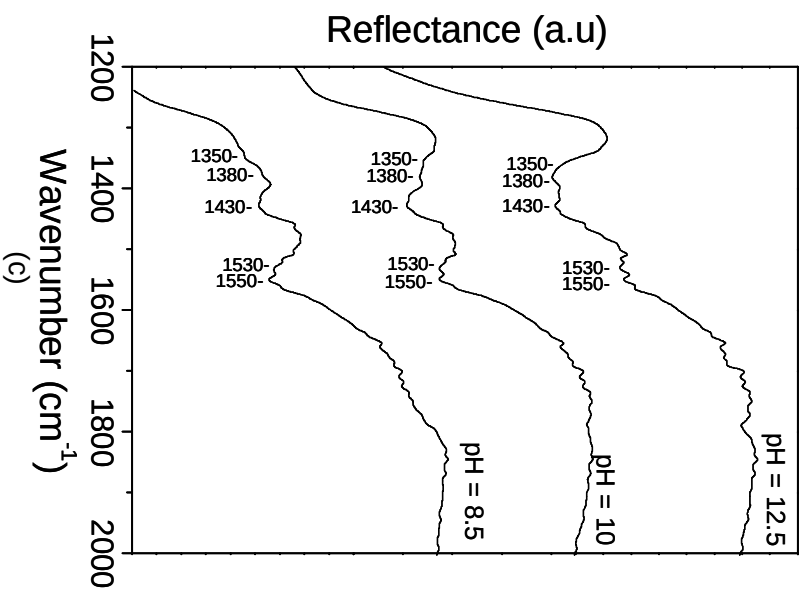
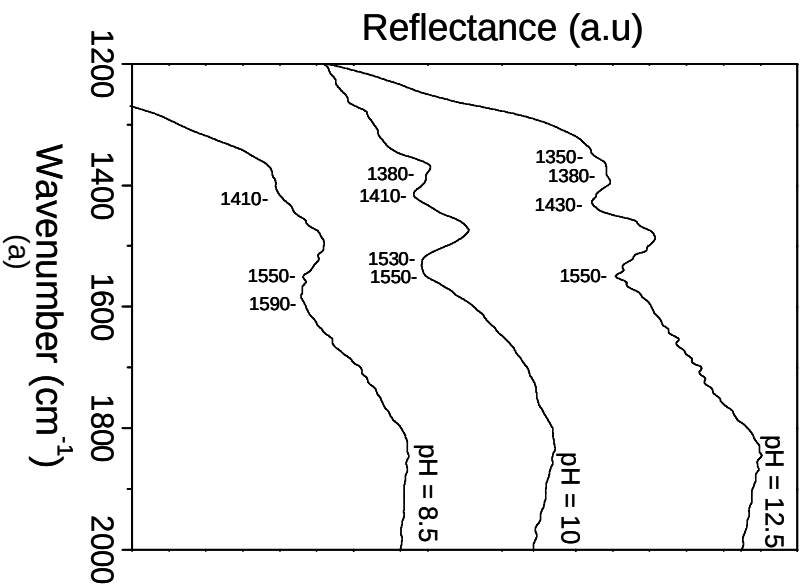


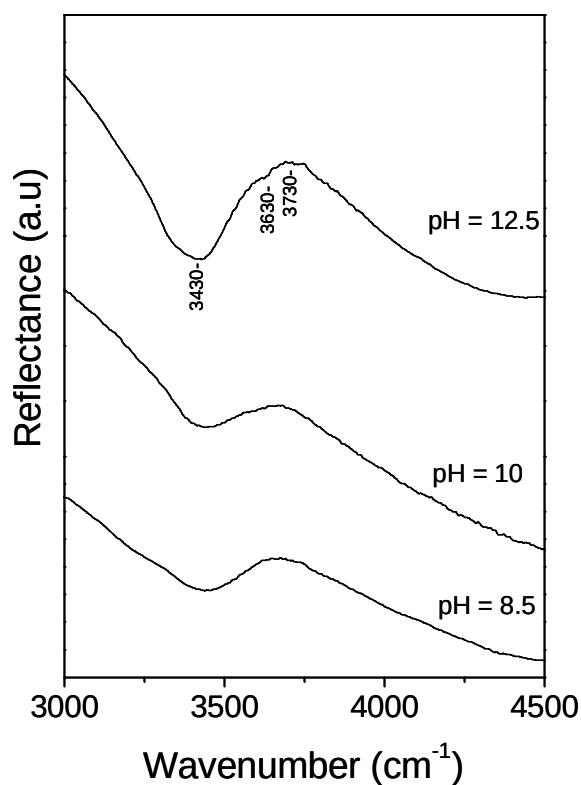
Figure 4.19 – Detail of the DRIFT spectra from Figures 4.15-4.18 showing the frequency range 1200-2000 cm^{-1} for different bicarbonate/carbonate concentrations: 0 mol/L (a), 0.1 mol/L (b), 0.4 mol/L (c) and 1 mol/L (d).

The band at 3420 cm^{-1} (Figure 4.9 and 4.10) is usually attributed to lattice water. Recently this band has been also associated to the stretching of OH groups of ferrihydrite (Mazzetti and Thistlethwaite, 2002). The results presented here corroborate this finding. The absence of iron oxide products in the residues of pyrite oxidation at 1 mol/L carbonate/bicarbonate solution, pH 8.5 and 10, was previously shown by XRD and SEM analyses (Figure 4.4a, 4.5.a and 4.8a). The lack of the band at 3420 cm^{-1} only in the DRIFT spectra of reacted pyrite under these experimental conditions (Figure 4.18 and 4.20d) is a strong indication that the band at 3420 cm^{-1} is more likely associated to iron oxide/hydroxides phases, such as ferrihydrite, rather than to adsorbed water on pyrite. The intensity of this band increases, as well as pyrite oxidation and ferrihydrite formation, with time and carbonate/bicarbonate concentrations (Figure 4.13).

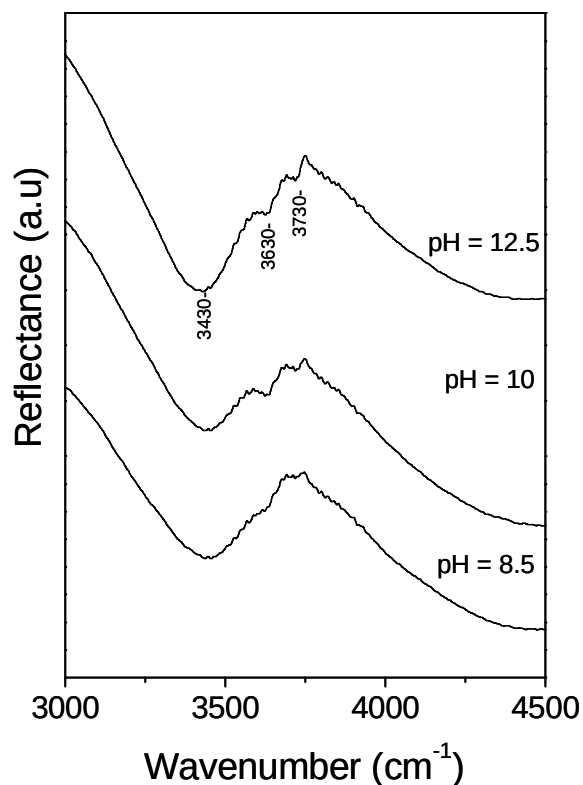
In carbonate medium, bands at 3630 and 3730 cm^{-1} (DRIFT spectrum) (Figure 4.20) are due to surface hydroxyl ion, singly coordinated to iron (Cornell and Schwertmann, 1996). The presence of two bands may indicate hydroxyl coordination to iron ions in both octahedral and tetrahedral sites, as reported for maghemite (Watanabe et al., 1994). It is suggested here that similar hydroxyl coordination may take place on ferrihydrite, knowing that this phase contains also a combination of octahedral or tetrahedral iron sites (Cornell and Schwertmann, 1996). Consistently with the presence of ferrihydrite identified by XRD, the bands at 3630 and 3730 cm^{-1} appear for different carbonate concentrations (Figure 4.16-4.18), regardless of pH (Figure 4.20) and in hydroxide solution only at pH 12.5. The presence of the band at 1550 cm^{-1} identified by DRIFT in both media (Figure 4.19) is also attributed to a surface Fe-OH species (at pyrite or at the iron oxide/hydroxide surface). This band was assigned by Legrand et al. (2000, 2003) to OH deformation (in plane bending) in green rust 1 – carbonate compounds and remained after its oxidation to $(\text{Fe(III)})\text{GRCO}_3$.

4.3.4 Fe-O group

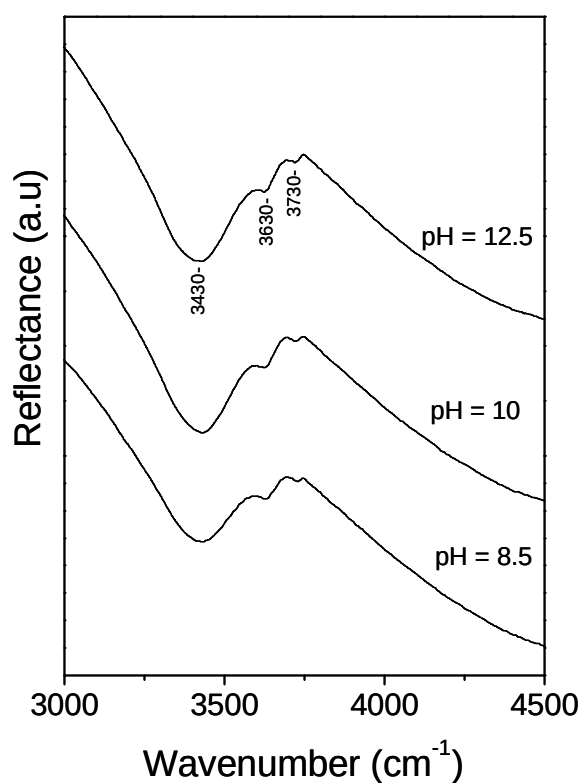
In both media, the regions below 1000 cm^{-1} show bands (Figure 4.21) that can be assigned to the iron oxide hydroxides, identified by XRD as ferrihydrite, in carbonate media, and hematite and feroxyhite ($\delta\text{-FeOOH}$), in hydroxide media. The peak at 915 cm^{-1} (Figure 4.21a) is typical of ferrihydrite (Parfitt et al., 1992; Music et al., 1993; Cornell and Schwertmann, 1996). Natural and synthetic ferrihydrite samples containing traces of Si show a broad, intense band around 940 cm^{-1} . Low frequencies correspond to silicate forming Fe-O-Si bonds, while higher frequencies arise from Si-O-Si bonds (Parfitt et al., 1992; Cornell and Schwertmann, 1996). The presence of Si in the oxide layer was identified by SEM analyses (Figure 4.7) and in solution (Table IV.2).



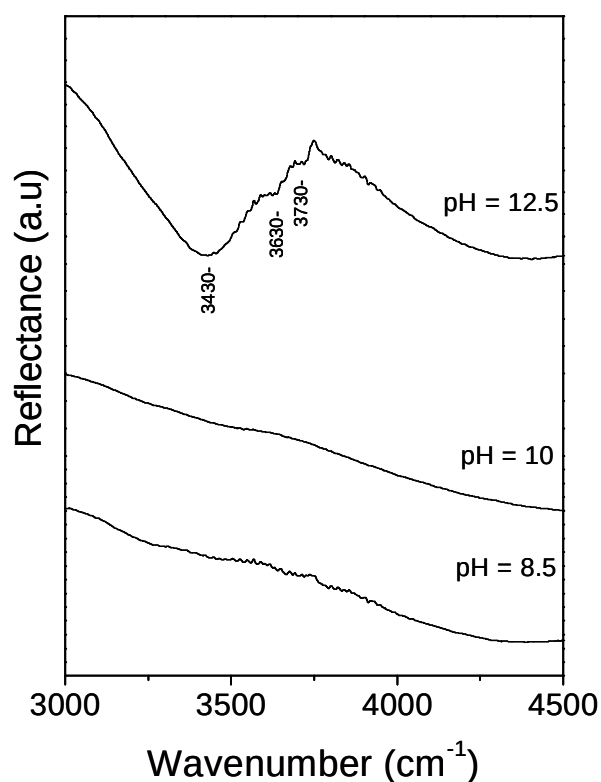
(a)



(c)



(b)



(d)

Figure 4.20 – Detail of the DRIFT spectra from Figures 4.15-4.18 showing the frequency range 3000-4500 cm^{-1} for different bicarbonate/carbonate concentrations: 0 mol/L (a), 0.1 mol/L (b), 0.4 mol/L (c) and 1 mol/L (d).

The band at 480 cm^{-1} can be assigned to Fe-O stretching mode in the Fe-O(OH) group, which is present in ferrihydrite, iron (III) hydroxycarbonates (Markov et al., 1990), ferrous-ferric hydroxide carbonate and in GR-CO₃ (Blengino et al., 1995; Drissi et al., 1995; Legrand et al. 2000). GR-CO₃ also exhibits bands at 484 and 515 cm^{-1} attributed to Fe-OH lattice modes, which are coincident with bands of ferrihydrite. With increasing time, the band at 490 cm^{-1} is shifted to 460 cm^{-1} , and this and those at 460 , 580 , 700 , 3420 and 3630 cm^{-1} become sharper, suggesting the formation of ferrihydrite. Comparison of the spectra shown in Figure 4.21 with those shown by Mazzetti and Thistlethwaite (2002) supports the formation of a 6-line ferrihydrite; the 2-line and 6-line phases exhibit strong bands at 475 and 585 cm^{-1} and a shoulder at $\sim 710\text{ cm}^{-1}$, more prominent in the 6-line case. In hydroxide medium, the small bands at 550 , 600 and 650 cm^{-1} are attributed to hematite (Figure 4.21b). The presence of δ -FeOOH is suggested by the bands at 650 , 700 , 930 , 1125 cm^{-1} . These results are in agreement with the XRD patterns shown in Figure 4.3-4.6.

4.3.5 S-O group

The multiple absorption bands observed in the DRIFT at 1040 , 1120 and 1180 - 1210 cm^{-1} and FTIR spectra at 1060 - 1080 , 1140 and 1230 cm^{-1} correspond to the splitting of the asymmetric triply degenerate S-O stretching, ν_3 vibration, of the sulfate species at unreacted pyrite (Figures 4.9 and 4.10). The splitting of the degenerate ν_3 vibration and the formerly forbidden ν_1 band (at 1000 cm^{-1}) indicates that the sulfate symmetry is lowered by coordination with cations (Nakamoto, 1997; and Hug, 1997). In addition to the ν_3 vibration of sulfate, the transmission spectra exhibit bands which can be attributed to sulfate bending mode (ν_2) at 610 cm^{-1} and the band characteristic of symmetric S-O stretching vibration (ν_1 sulfate mode) at 1000 cm^{-1} , that becomes fully active due to surface-complexed sulfate species. After oxidation, the strong split bands assigned to sulfate vibrations, 1000 - 1200 cm^{-1} range (Figure 4.9a and 4.10a), in the spectra of unreacted pyrite disappear, leaving only a very weak peak at 1125 cm^{-1} and at 610 cm^{-1} (Figure 4.21a). Only the DRIFT spectra of those samples showing no oxide product (Figure 4.18, pH 8.5 and 10), depicted the broad bands centered at 630 cm^{-1} and 1080 cm^{-1} (splitting in 1045 and 1118 cm^{-1}), and thus resembling those identified in the unreacted pyrite. The presence of thiosulfate ion could not be determined either due to the absence of its characteristic bands, ν_1 at $\sim 1000\text{ cm}^{-1}$ and ν_3 , at 1150 cm^{-1} (Nakamoto, 1997; Borda et al., 2004) on most of the reacted samples or due to overlapping with sulfate bands, as in Figure 4.18.

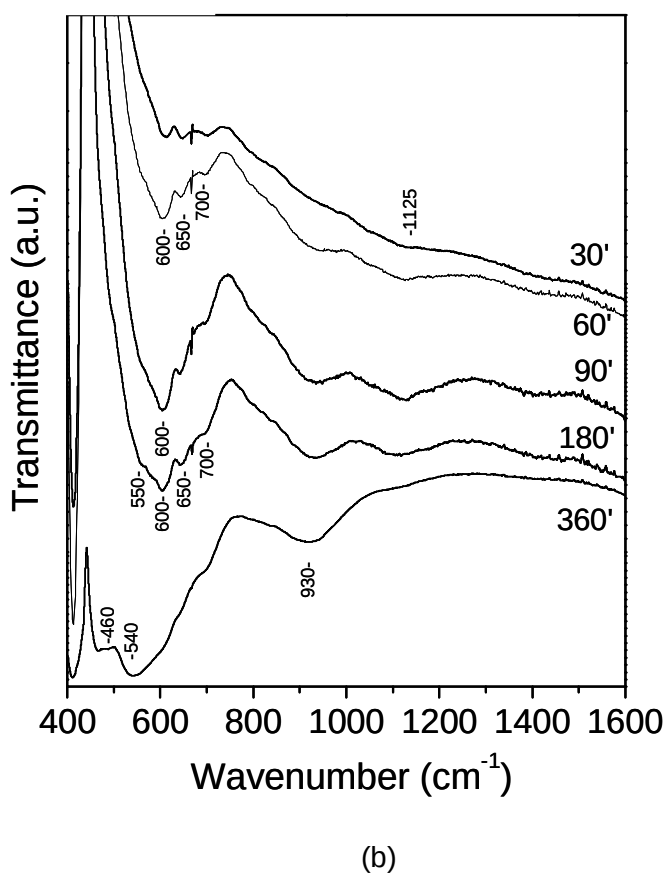
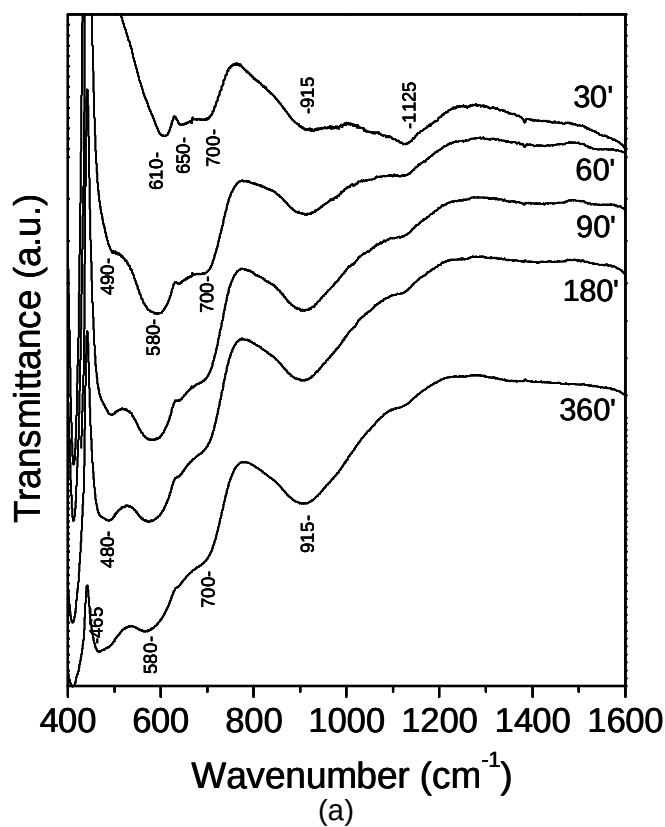


Figure 4.21 – Detail of the DRIFT spectra from Figures 4.9B-4.10B showing the frequency range $400\text{-}1600\text{ cm}^{-1}$ for different reaction times in 0.1 mol/L of bicarbonate/carbonate media (a), hydroxide solutions (b).

4.4 Micro-Raman Spectroscopy Analyses

The use of infrared spectroscopy for the identification of the products of pyrite oxidation is limited by the overlapping of bands exhibited by mixtures of iron oxides. Raman spectroscopy coupled with optical microscopy was used in order to help the identification of these products.

Optical microscopy images of unreacted pyrite and oxidized samples obtained under different experimental conditions are shown in Figure 4.22. Unreacted pyrite sample exhibits particles with shiny yellow color and smooth surfaces (Figure 4.22a). The oxidized pyrite samples appeared as heterogeneous and colorful powders (Figure 4. 22b-e). The presence of distinct regions in the oxidized samples in carbonate/bicarbonate and hydroxide media indicates different levels of pyrite oxidation. In hydroxide medium, the dark-reddish (DR) regions represent more intense pyrite oxidation while the yellow (Y) and green (G) regions, less reacted areas. In carbonate/bicarbonate medium mainly brown (BR) and orange (OR) regions, as well as minor yellow, green and pink regions have been identified. It is suggested that the green and pink regions correspond to less intense pyrite oxidation. In these regions, the oxidation product exhibits a fine texture and adherent coatings. As the oxidation increases, the green and yellow regions transform into dark-reddish or brown-color regions, exhibiting a coarse texture and poorly adherent coatings. The oxidized layers seem to be loose from the surface.

4.4.1 Laser power and pyrite oxidation

The micro-Raman spectrum was recorded for the unreacted pyrite samples (Figure 4.23a). Curve fitting analysis showed the following centered bands: 343, 350, 376, 379, 430 cm^{-1} (Figure 4.24a). This spectrum agrees well with that reported by Vogt et al. (1983). Pyrite crystal has five Raman active modes. One of them is totally symmetric, corresponding to S_2 dumbbells stretching vibration mode ($\sim 379 \text{ cm}^{-1}$); one is doubly degenerate, corresponding to displacements of the sulphur atoms perpendicular to S-S bond axis ($\sim 343 \text{ cm}^{-1}$), the phonon is a libration (S-S rotation); and the last three are triply degenerate, and corresponds to various librational and stretching modes or combinations of them ($\sim 350, 377$ and 430 cm^{-1}). No significant bands are found in frequencies higher than 500 cm^{-1} (Vogt et al., 1983).

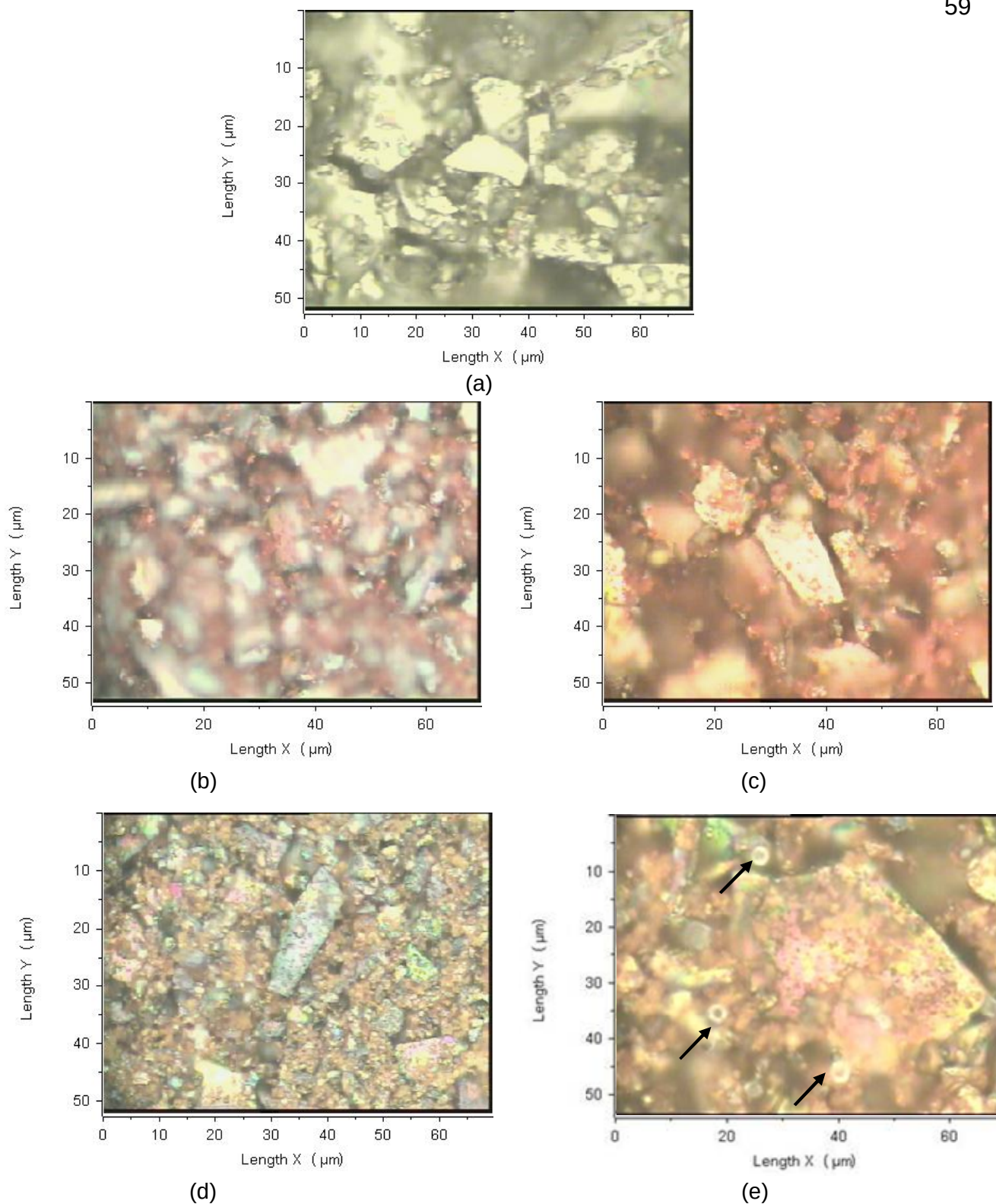


Figure 4.22 – Light micrograph showing the typical regions found in the samples analyzed by micro-Raman spectroscopy coupled to optical microscopy: the unreacted pyrite (a); oxidized pyrite sample in hydroxide medium 50x (b) and 100x (c); oxidized pyrite sample in bicarbonate/ carbonate medium 50x (d) and 100x (e). Oxidations conditions: pH 10 and 12 hours, 80 °C. Arrows is indicating transparent particles (see text).

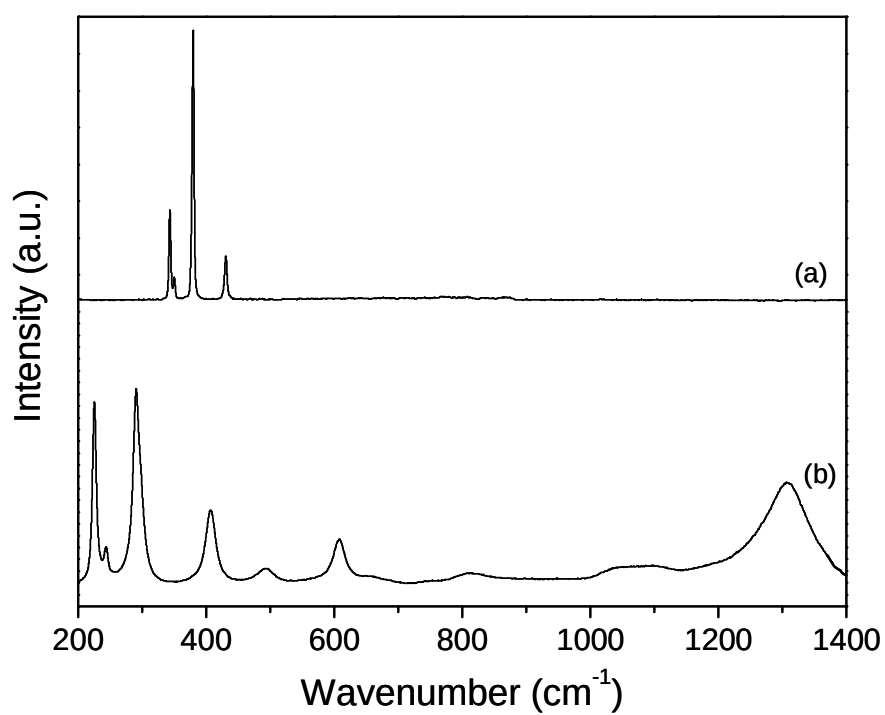
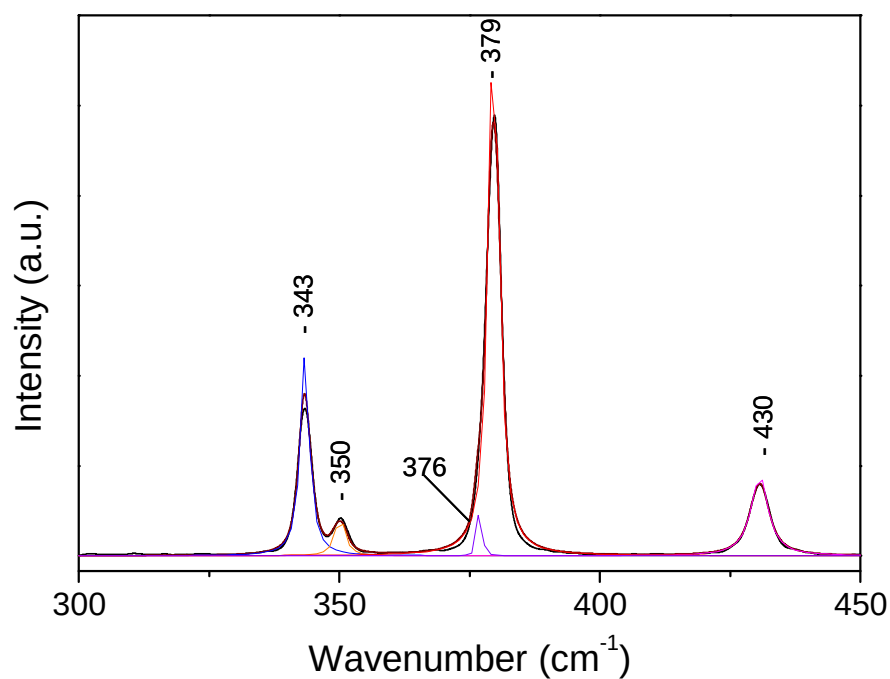
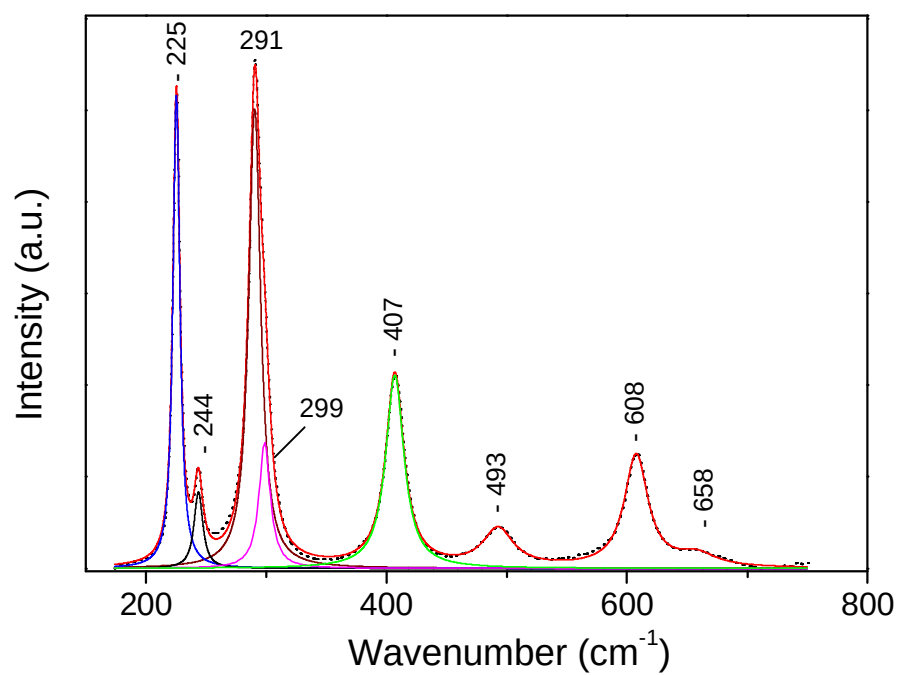


Figure 4.23 – Micro-Raman spectra of unreacted pyrite sample recorded with laser power (a) 0.12 mW; (b) 3 mW.



(a)



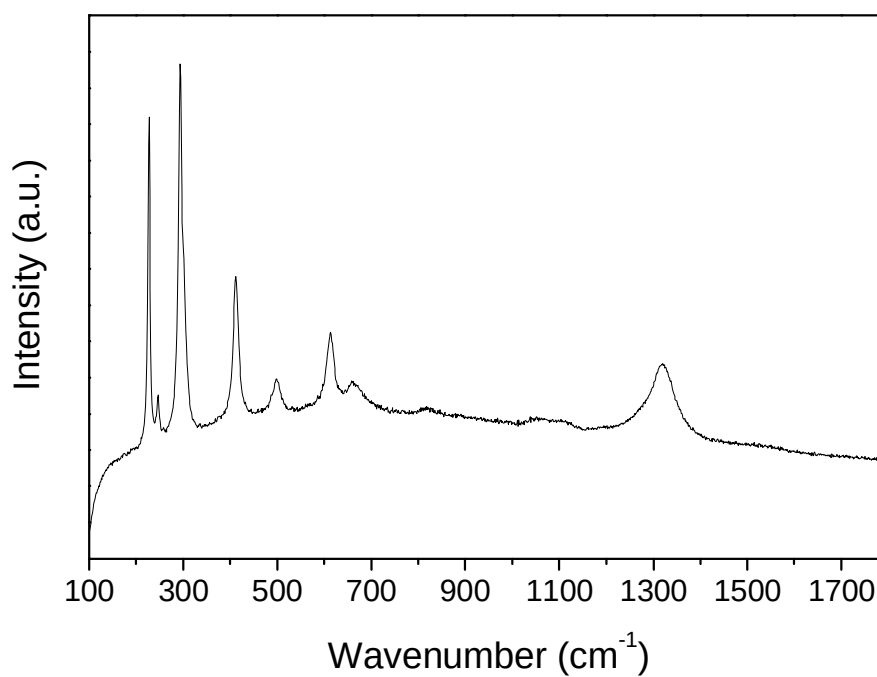
(b)

Figure 4.24 – Deconvoluted of the micro-Raman spectrum of (a) unreacted pyrite (Figure 4.22a) showing the pyrite bands; (b) after thermal transformation with laser power 3 mW (Figure 4.22b) showing the hematite band positions (see positions and FWHM Appendix III- Table AIII.1).

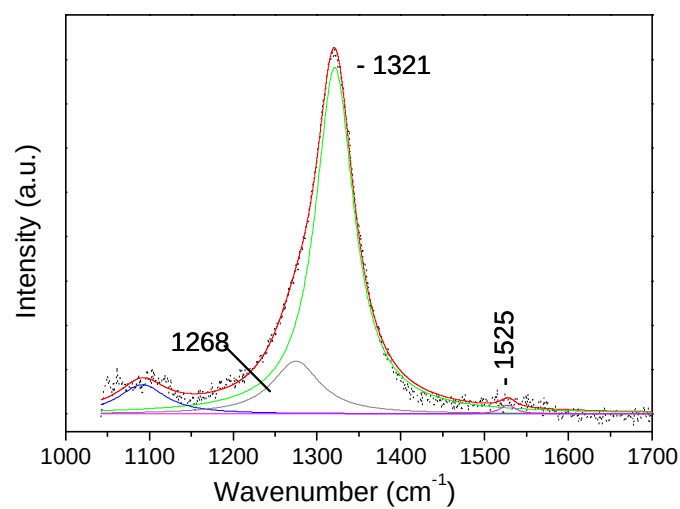
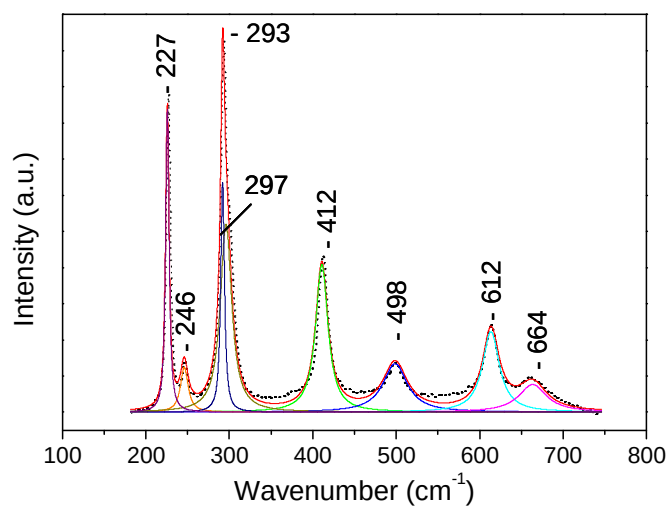
Prior to the analyses, some experiments were carried out in order to evaluate how Raman analysis of pyrite is sensitive to the laser power, and thus to establish adequate experimental conditions. Figure 4.23b shows the micro-Raman spectrum recorded with 3 mW. Curve fitting analysis of this spectrum showed now clearly bands at 225, 244, 291, 299, 407, 493, 608, 658 and 1315 cm^{-1} (Figure 4.24b). These bands are similar to those obtained from the micro-Raman spectrum of a sample of finely ground hematite ($< 38\mu\text{m}$), shown in Figure 4.25. The former values are a few cm^{-1} lower than those of mineral hematite. Faria et al. (1997) reported the laser power influence on the band wavenumber of thermally produced hematite. Hematite is expected to show seven Raman-allowed phonons. The phonons can be further classified as five “internal modes” involving motion within a single Fe_2O_3 unit that correspond to bands at 228, 296, 413, 500 and 612 cm^{-1} , and two “external” modes, the bands at 248 and 296 cm^{-1} (Shim and Duffy, 2002). For the sample of mineral hematite, deconvolution of the micro-Raman spectrum indicates the following centered bands: 227, 246, 293, 297, 412, 498, 612, 1268, and 1525 cm^{-1} (Figure 4.25b). In addition to the Raman-allowed phonons, this spectrum also exhibits two others bands at 664 and 1321 cm^{-1} . The former is Raman-forbidden, but IR- allowed, labeled LO (longitudinal optical) phonon. This band may become active due to a strong resonance on the surface where the solid may not have the complete symmetry of the bulk structure or due to defects in the structure induced by stress. The stronger line at roughly twice this frequency (at 1321 cm^{-1}) is labeled 2LO. According to group theory, the 2LO line is the first overtone ($660 \times 2 = 1320 \text{ cm}^{-1}$) and is Raman active. The large strength is apparently due to a resonance enhancement (Massey et al., 1990; Shim and Duffy, 2002). Once the thermal transformation of pyrite into hematite was shown, the laser power was kept below 0.12 mW, in order to avoid sample decomposition or alteration that could lead to misleading interpretation.

4.4.2 Hydroxide solutions

Now, the results obtained with the analyses of oxidized pyrite samples will be discussed. All the compounds were identified through comparison of observed and reference spectra. Figure 4.26 shows the micro-Raman spectra obtained after pyrite oxidation in hydroxide solutions. In order to compare the bands obtained in different regions, curve fitting analyses were done for the spectra obtained for green (G) and dark-red (DR) regions of oxidized samples (Figure 4.27). In addition to the reminiscent pyrite bands (343, 379 and 431 cm^{-1}), the main bands found at 225, 295, 409, 484-493, 608 and 664 cm^{-1} were attributed to hematite (Figure 4.27a and Table IV.3). No bands of pyrite are shown in the spectrum obtained in the DR region (Figure 4.27b). Despite the apparent spectra differences, the



(a)



(b)

Figure 4.25 – Deconvoluted of micro-Raman spectrum of a mineral hematite sample (a), showing the hematite band positions range 700 cm^{-1} and range 1300 cm^{-1} (b). (See positions and FWHM Table AIII.2).

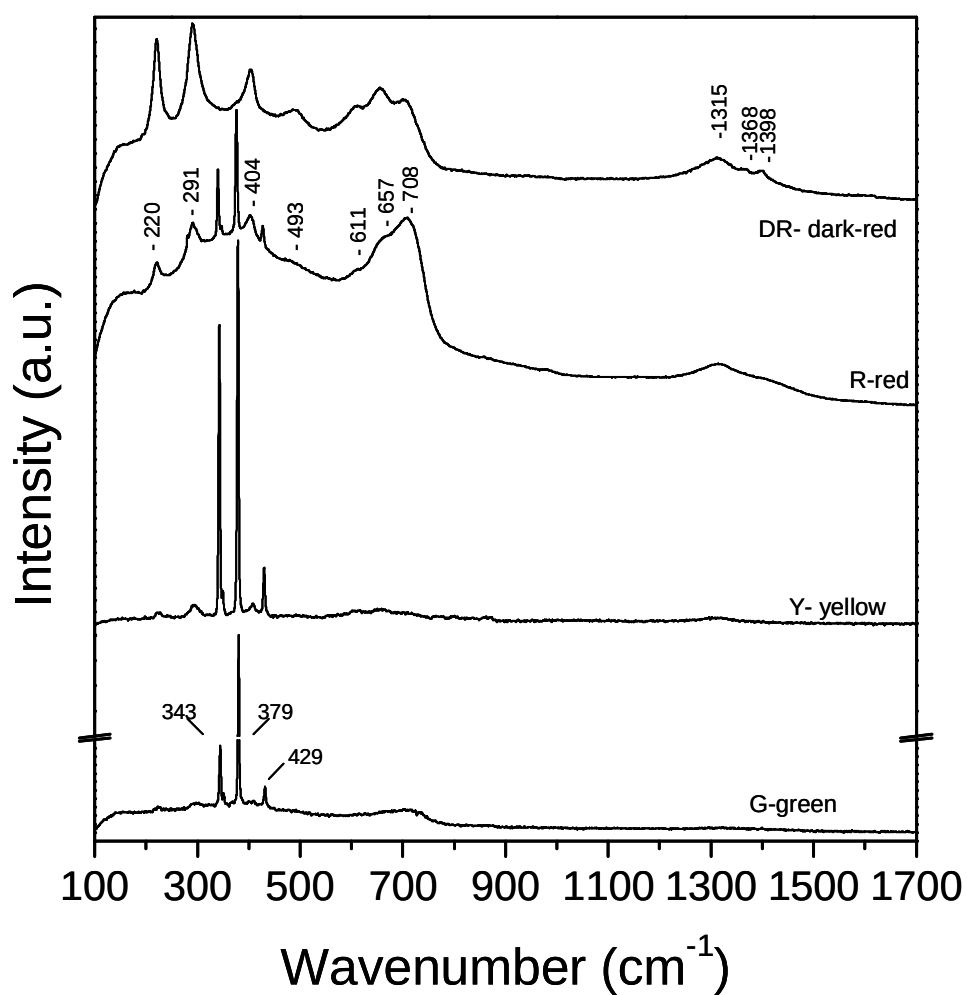


Figure 4.26 – Typical micro-Raman spectra obtained in different regions of oxidized pyrite samples in hydroxide media (0.1 mmol/L). Conditions: $[\text{CO}_3^{2-}]_{\text{T}} = 0 \text{ mol/L}$, pH 10, 12 h.

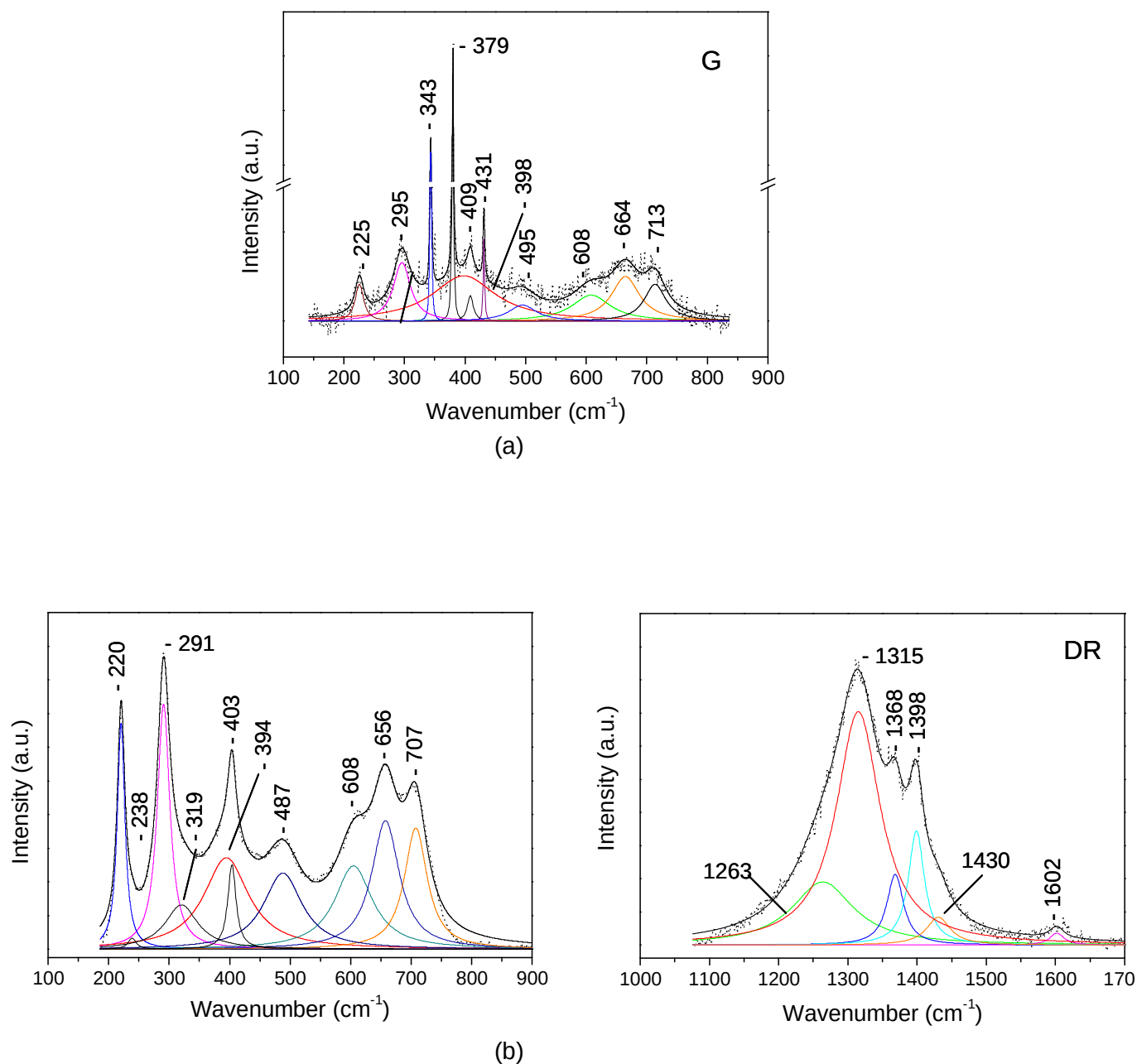


Figure 4.27 – Deconvoluted of Raman spectra of the samples G (a) and DR (b) regions of the Figure 4.26, showing the hematite bands as main oxidation product in hydroxide media.

characteristic vibrational modes of pyrite and hematite were identified in all selected areas. Even in the green and yellow regions, where the particles resemble those of unreacted pyrite, the micro-Raman spectra showed the incipient bands of hematite (Figure 4.27). As pyrite oxidation increases, the DR region is developed and hematite becomes the main identified phase. In general, the bandwidths in Raman spectra of crystalline solids are of the order of only a few tens of cm^{-1} . The full widths at half-maximum (FWHM) values of the Raman bands, $\sim 100 \text{ cm}^{-1}$, may indicate band overlap and therefore that no single species of known stoichiometry can account for the observed features. It may also indicate the presence of a highly disordered structure (amorphous phase or poorly crystalline) or the microcrystalline nature of the products.

Table IV.3 – Band positions and FWHM for spectra of G and DR regions
(Figure 4.27)

G-region			DR region		
$\nu \text{ (cm}^{-1}\text{)}$	FWHM(cm^{-1})	phase	$\nu \text{ (cm}^{-1}\text{)}$	FWHM(cm^{-1})	phase
225	16	Hematite	220	15	Hematite
295	34	Hematite	238	16	Hematite
343	2	Pyrite	291	25	Hematite
379	2	Pyrite	319	64	Feroxyhite
398	127	Feroxyhite	394	96	Feroxyhite
409	11	Hematite	403	17	Hematite
431	3	Pyrite			
495	53	Hematite	487	75	Hematite
608	69	Hematite	608	85	Hematite
664	58	Hematite + feroxyhite + magnetite?	656	48	Hematite + feroxyhite + magnetite?
713	43	Feroxyhite	707	54	Feroxyhite
			1263	108	Hematite
			1315	77	Hematite+ feroxyhite
			1368	29	Cr-lines
			1398	28	Cr-lines
			1430	41	Feroxyhite
			1602	25	OH group

Curve fitting indicated broad and stronger bands centered at 319, 394-398, 656-664, 707-714, 1315 and 1430 cm^{-1} (Figure 4.27 and Table IV.3). The broad band near to 660 cm^{-1} was found to be stronger than usual Raman spectrum of nanocrystalline hematite (Wang et al. 2000). A comparison of Raman bands observed with those of known iron oxides or oxyhydroxides suggests that these may be attributed to maghemite (double bands at 660 and 719 cm^{-1}), $\text{Fe}(\text{OH})_3$ (696 cm^{-1} and 710 cm^{-1}), feroxyhite (680 cm^{-1}) or magnetite (670 cm^{-1}) (Table IV.4 and Appendix IV). However, the absence of a band at $\sim 510 \text{ cm}^{-1}$ makes unlikely the presence of maghemite and ferrihydrite (Faria et al., 1997; Mazzetti and Thistlethwaite, 2002). The presence of feroxyhite is also supported by a very broad feature near 400 cm^{-1} that is as intense as the feature near 680 cm^{-1} (see Figure 4.27b). Of all known iron oxides and oxyhydroxides, only feroxyhite could account for the all broad bands that appear in Figure 4.27 and Table IV.3.

Therefore, it is concluded that the products of pyrite oxidation in hydroxide media are mainly hematite, with minor feroxyhite and possibly magnetite. In addition to hematite, already identified by XRD, Raman spectroscopy confirmed the indication of the formation of feroxyhite and suggested the presence of magnetite.

Hematite has a hexagonal close packed array (hcp). All Fe(III) is octahedrally coordinated with oxygen. The structure of feroxyhite is based on a disordered hcp arrangement of hydroxyl and oxygen sheets with Fe(III) distributed between octahedral and tetrahedral sites. There are some evidences that 80% of the Fe(III) are randomly distributed in octahedral sites and 20% in tetrahedral sites; goethite has 100% of the Fe(III) in octahedral sites (Cornell and Schwertmann, 1996; Keiser and Brown, 1983). As feroxyhite and hematite have a similar anionic framework (hcp), it is expected that the conversion feroxyhite $\rightarrow$ hematite proceeds relatively easily, then leading to hematite as the final product of pyrite oxidation in hydroxide solutions.

Table IV.4 – Raman wavenumbers of selected iron oxides, hydroxides and oxyhydroxides
(Raman spectra in Appendix IV)

Species	Wavenumbers (cm ⁻¹) according to different workers										Ref.
Fe(OH) ₂					460		550				1
Fe(OH) ₃				395				696 ^{br}		1335	1
Fe ₂ O ₃ Hematite	<u>225</u>	247	<u>293</u>	299	412	498		613		1320	3
γ-Fe ₂ O ₃ Maghemite				360 ^{br}		495 ^{br}		<u>680</u> -	<u>720</u> ^{br}	1378	2
Fe ₃ O ₄ Magnetite				301		513	533	<u>662</u>			3
α-FeOOH Goethite		243	299	<u>385</u>	479		550	685		993	3
γ-FeOOH Lepidocrocite	<u>245</u>			373	493 ^{sh}	522		650 ^{sh}	719	1303	3
δ-FeOOH Feroxyhite			296 ^{sh}		<u>400</u>			680		1160 1314	3
Ferrihydrite (2 and 6 line)				370 ^{br}		510 ^{br}			710 ^{br}		5

(Underlined bands exhibit the strongest intensities. ^{sh} shoulder, ^{br} broad bands)

1- Oblonsky and Devine (1997); 2- Sousa et al. (2000); 3 – Faria et al. (1997); 4 – Dunnwald and Otto (1989); 5 – Mazzetti and Thistlewaite (2002)

4.4.3 Carbonate solutions

Now, the micro-Raman spectra from pyrite oxidation in bicarbonate/carbonate media will be discussed. Note that the Raman spectra exhibit similar band profiles regardless of the region analyzed (Figure 4.28). The differences observed are mainly due to band intensities, and therefore to the extension of pyrite oxidation. The deconvoluted micro-Raman spectra are characterized for bands of pyrite (340, 347, 377, and 427 cm^{-1}) and broad bands at 366-369, 514-510, 679-689 and 720 cm^{-1} (strongest) and 1329-1434 cm^{-1} (Figure 4.29a-b and Table IV.5). In the brown region (BR), where total conversion of pyrite is observed, the broadness increases and no pyrite bands appear. In contrast to the results obtained in hydroxide media, one of the features of the deconvoluted spectra (Figure 4.29) is the exceptionally large bandwidths (FWHM 100-200 cm^{-1}) that are required to match the measured spectra of the oxidized pyrite in carbonate media. The oxidation products obtained in bicarbonate/carbonate media are characterized by a disordered and poorly crystalline material.

The broad bands at ~ 370 , ~ 510 , ~ 720 cm^{-1} (strongest) and 1329-1434 cm^{-1} can be attributed to 2-line ferrihydrite or 6-line ferrihydrite, as both show a very similar Raman profile (Table IV.4). Maghemite also exhibits a Raman pattern similar to that of ferrihydrite, with double bands at 650 and 710 cm^{-1} . However, maghemite can be distinguished from ferrihydrite by the two relatively stronger and broader maghemite bands at 1378 and ~ 1580 cm^{-1} (Faria et al., 1997 and Sousa et al., 2000), not found in the present work (Figure 4.29b). The Raman features reported here - showing a slight asymmetry of the single Raman band at 720 cm^{-1} , due to a weaker band at 689 cm^{-1} , and the relatively greater intensity of the band at ~ 370 cm^{-1} (Figure 4.29 a,b and Table IV.5) - indicates the predominance of 6-line ferrihydrite (Mazzetti and Thistlethwaite, 2002). The formation of a 6-line ferrihydrite is consistent with the XRD patterns shown previously.

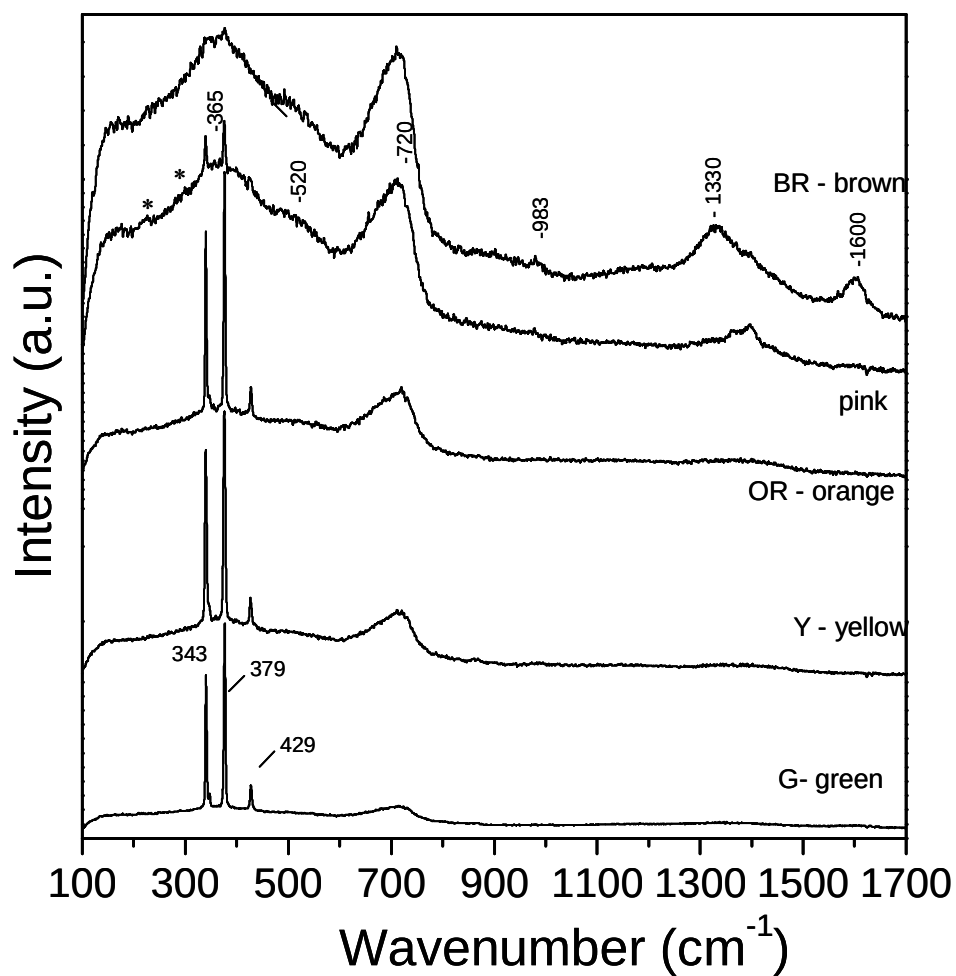


Figure 4.28 – Typical micro-Raman spectra obtained in different regions of oxidized pyrite samples in bicarbonate/carbonate media. * - Hematite lines? Conditions: $[\text{CO}_3^{2-}]_{\text{T}} = 0.1 \text{ mol/L}$, pH 10, 12 h.

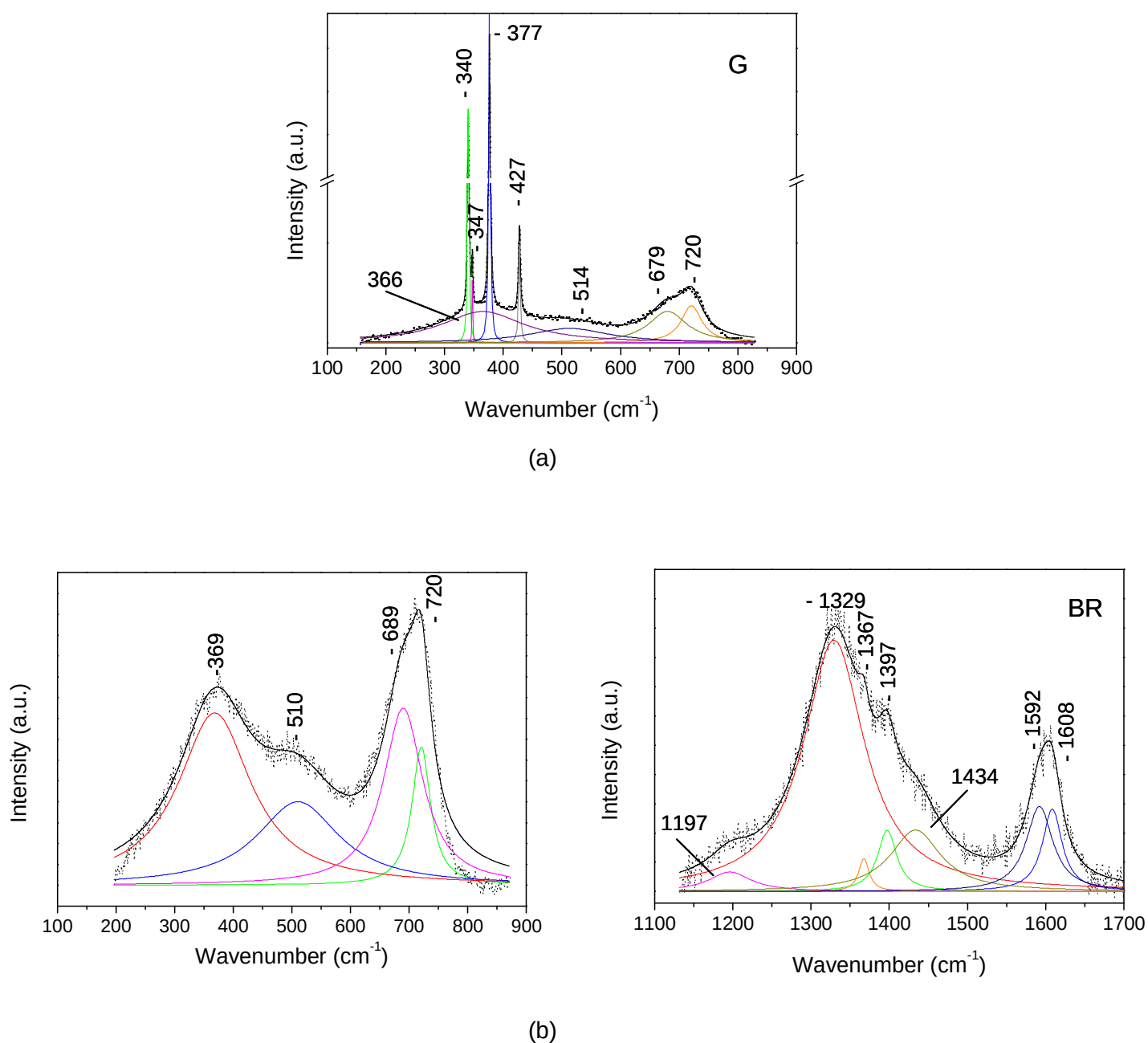


Figure 4.29 – Deconvoluted of Raman spectra of the G region (a) and BR regions (b) of the Figure 4.28, showing the ferrihydrite bands as main oxidation product in bicarbonate/carbonate media.

Table IV.5 – Band positions and FWHM for spectra of G and BR regions
(Figure 4.29)

G-region			BR region		
ν (cm ⁻¹)	FWHM (cm ⁻¹)	phase	ν (cm ⁻¹)	FWHM (cm ⁻¹)	phase
340	1.8	Pyrite	369	151	Ferrihydrite
347	1.9	Pyrite	510	170	Ferrihydrite
366	170	Ferrihydrite	689	81	Ferrihydrite
377	2.2	Pyrite	720	39	Ferrihydrite
427	3.5	Pyrite	1197	65	Ferrihydrite
514	163	Ferrihydrite	1329	95	Ferrihydrite
679	79	Ferrihydrite	1367	16	Cr-lines
720	44	Ferrihydrite	1397	29	Cr-lines
			1434	79	Ferrihydrite
			1592	41	OH group
			1608	30	OH group

It is important to point out the resemblance of the micro-Raman spectra obtained in bicarbonate/carbonate media with the “in situ” Raman spectrum of a ferric oxyhydroxycarbonate, Fe(III)GRCO₃, which exhibits bands at 250, 310, 400, 505, 725 (strong) and 1050 cm⁻¹ (Legrand et al., 2003). The difference between the spectrum obtained by the authors and here is the presence of the main bicarbonate band (at 1050 cm⁻¹) by the former. Considering that Legrand et al. (2003) recorded the spectrum “in situ”, the small bicarbonate Raman band (at 1050 cm⁻¹) may have been created by the signal from solution (0.4 mol/L NaHCO₃ solution). Summarizing, the formation of ferrihydrite and possibly Fe(III)-GRCO₃ are suggested by the Raman spectra of the oxidized pyrite samples in bicarbonate/carbonate media.

The effect of carbonate concentration on pyrite oxidation, at pH 8.5, 10 and 12.5, is shown in Figure 4.30, 4.31 to 4.33. The targeted areas have been selected with the criteria of the apparent highest pyrite oxidation. Hematite is confirmed as the main product of pyrite oxidation in sodium hydroxide solution (0 mol/L carbonate) (Figure 4.30 and 4.31). In all the investigated pH range (Figure 4.30 - 4.33) the increase of the bicarbonate/carbonate concentration promoted an increase of pyrite oxidation and the broadening of bands of the main oxidized phases, Fe(III)GRCO₃. For 1 mol/L of bicarbonate/carbonate concentration at pH 10 and pH 8.5 (not shown here) only pyrite is identified. This finding is in agreement with XRD and infrared analyses (Figure 4.4, 4.5 and 4.18) and with visual and optical microscope observation (Figure 4.32). At pH 12.5 (Figure 4.33), ferrihydrite is the main phase formed in hydroxide solutions and Fe(III)GRCO₃ in carbonate solutions.

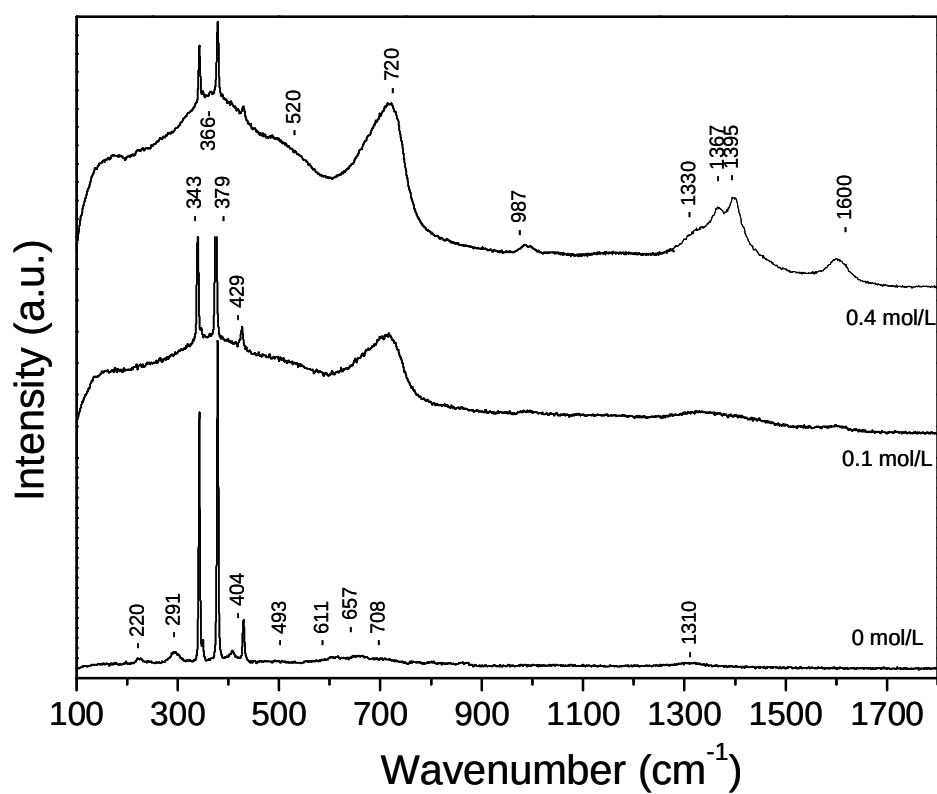


Figure 4.30 – Micro-Raman spectra obtained in pH 8.5 in different bicarbonate concentrations, $T = 80\text{ }^{\circ}\text{C}$, 1 hour. Hydroxide medium corresponds to the 0 mol/L $[\text{CO}_3^{2-}]_{\text{T}}$.

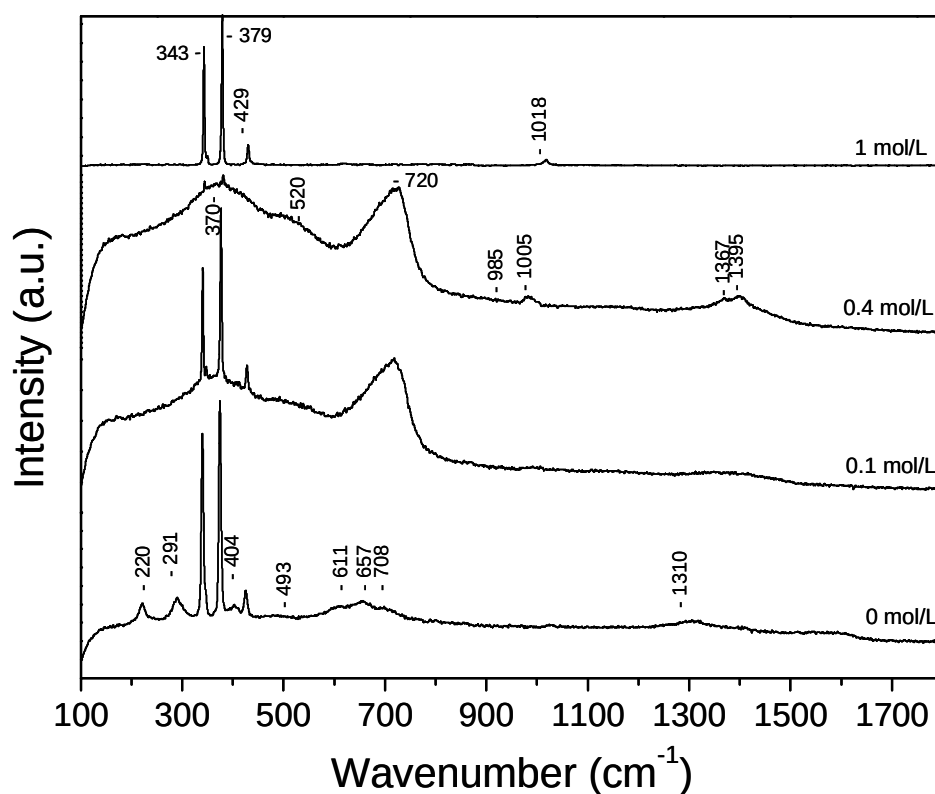


Figure 4.31 – Micro-Raman spectra obtained in pH 10 in different bicarbonate/ carbonate concentrations. $T = 80\text{ }^{\circ}\text{C}$, 1 hour. Hydroxide medium corresponds to the 0 mol/L $[\text{CO}_3^{2-}]_{\text{T}}$.

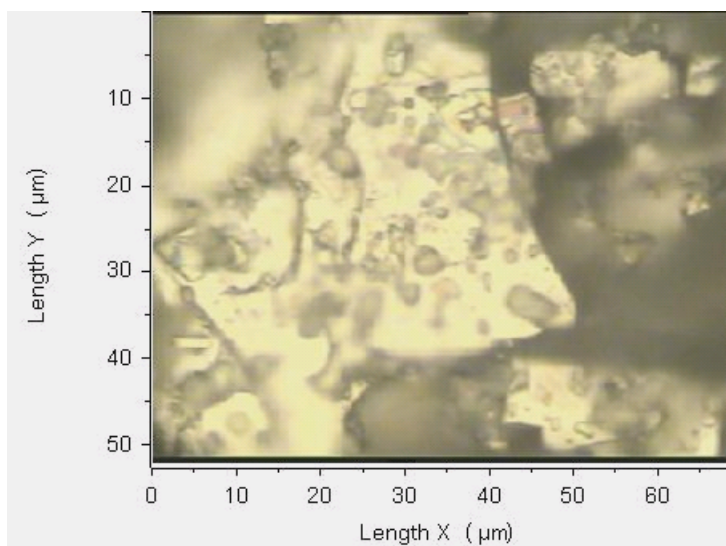


Figure 4.32 – Light micrograph showing typical particles found on oxidized pyrite sample in 1 mol/L of carbonate/ bicarbonate solution, pH 10 and 1 hour. Obj. 100x.

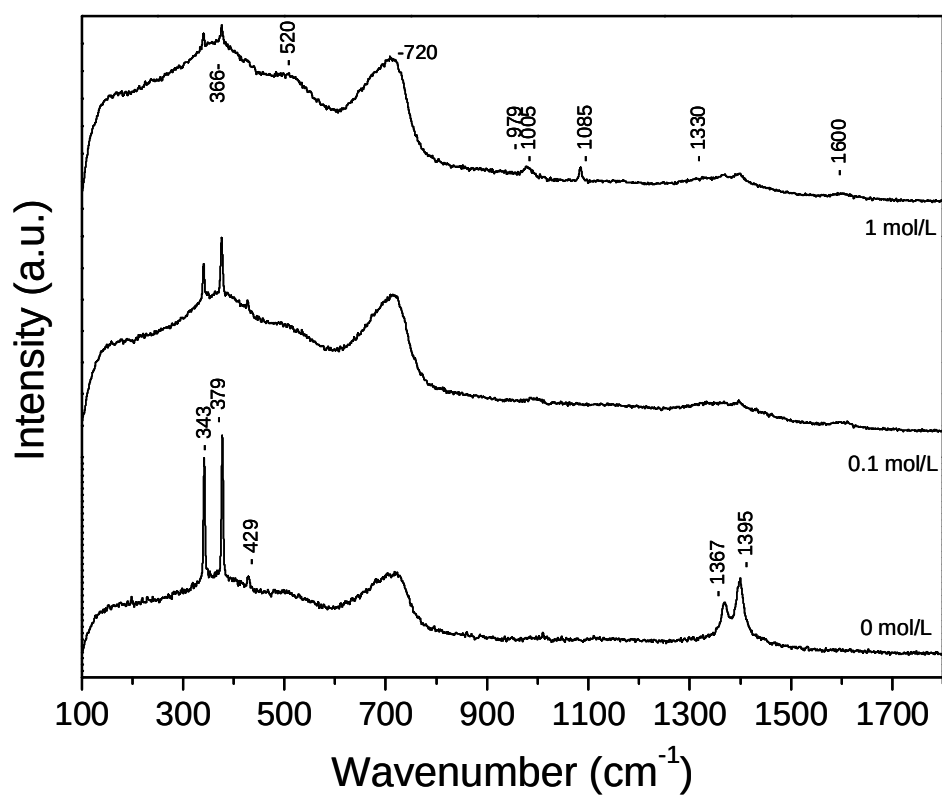


Figure 4.33 – Micro-Raman spectra obtained in pH 12.5 in different bicarbonate/ carbonate concentrations. $T = 80\text{ }^{\circ}\text{C}$, 1 hour. Hydroxide medium corresponds to 0 mol/L $[\text{CO}_3^{2-}]_{\text{T}}$.

As mentioned before, one of the main features of the deconvoluted spectra obtained in the present work are the exceptionally large bandwidths (FWHM 100-200 cm^{-1}), specially in bicarbonate/carbonate media, that are required to match the measured spectra of the oxidized pyrite. The broadening is related to structural disorder, which is characteristic of compounds with a spinel structure, such as maghemite, and in a lesser degree, ferrihydrite and feroxyhite. Both the 6-line and 2-line ferrihydrite are dominated by iron in octahedral coordination ($\text{Fe}(\text{O},\text{OH})_6$) with minor amounts of iron in tetrahedral coordination. In the former, the 15% of maghemite-like crystals coexist with three others in a 90% crystalline material, with over 80% of that exhibiting hexagonal close packing (Janney et al., 2000, 2001). Therefore, in analogy with Al(III) coordination proposed by Busca et al. (1993), the broad bands observed in the micro-Raman spectra at 650 – 730 cm^{-1} (Figure 4.27 and 4.29) are suggested to be related to the disorder caused by partial Fe(III) coordination on tetrahedral sites in compounds such as ferrihydrite and feroxyhite. Hematite and goethite (single octahedral coordination) show Raman bands only at wavenumbers < 650 cm^{-1} .

4.4.4 Additional features

For samples oxidized at high bicarbonate/carbonate concentrations (0.4 and 1 mol/L), small and white shiny (transparent) particles are found as shown in the Figure 4.22e. These particles were identified as calcium carbonate precipitate due to the presence of the bands at 150, 278, 709 and 1085 cm^{-1} (Figure 4.34), which are very similar to that reported by Herman et al. (1987). The most intense active band (1085 cm^{-1}) is attributed to ν_1 stretching vibrational mode of carbonate ion (Nakamoto, 1997). Although FeCO_3 and CaCO_3 exhibit similar bands, the presence of FeCO_3 is unlikely due to absence of a band at 509 cm^{-1} , which is characteristic of iron carbonate (Herman et al., 1987). The presence of calcite was previously indicated by XRD (Figures 4.3, 4.5 and 4.6) and EDS (Figure 4.8b) analyses. The characteristic bands of pyrite and ferrihydrite were also identified in association with the calcite bands. The band at 1018 cm^{-1} , attributed to an intense C-OH stretching mode ν_5 of bicarbonate ion, was identified in Figure 4.31.

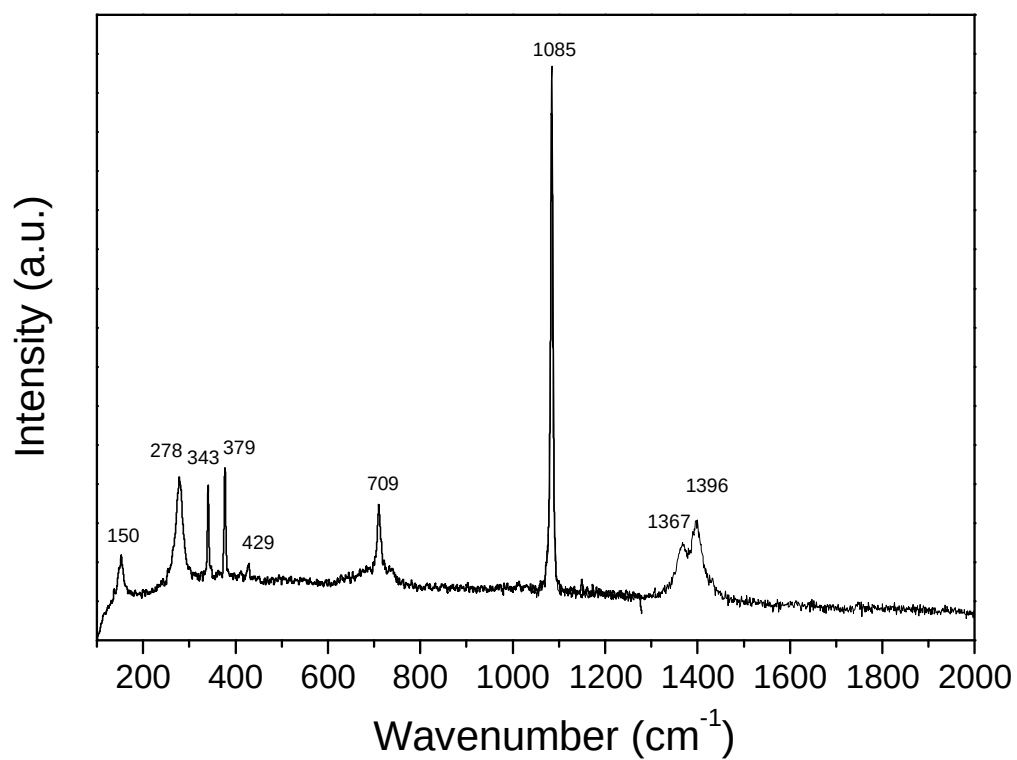


Figure 4.34 – Typical micro-Raman spectra of transparent particles formed during pyrite oxidation in the 0.4 molar bicarbonate/carbonate solution, pH 12.5.

A small broad band around 980 cm^{-1} appeared in some micro-Raman spectra (Figures 4.28, 4.30, 4.33) and was attributed to the ν_1 vibrational mode of sulfate ion (Nakamoto, 1997). The presence of thiosulfate species on oxidized pyrite samples may also be considered due the presence of the band at $995\text{--}1005\text{ cm}^{-1}$ in association with the sulfate band (980 cm^{-1}) (Rintoul et al., 1997).

Some spectra show a small bands at 1590 and 1602 cm^{-1} (Figure 4.27 and 4.29), these being higher in bicarbonate/carbonate media. These bands can be attributed to OH bending vibration of the water molecule. Carey and Korenowski (1998) suggest that the OH bending Raman near 1640 cm^{-1} for liquid water can be decomposed into two peaks: 1641 and 1581 cm^{-1} ; the former may correspond to partially hydrogen bonded water, whereas the other, near 1581 cm^{-1} , may correspond to water molecules engaged in fully hydrogen bonded configurations.

Finally, the presence of the bands at 1367 and 1395 cm^{-1} (Figure 4.30, 4.31, 4.33), not characteristic of either pyrite or iron oxide hydroxide, was investigated. These bands are very similar to the R-lines ascribed to Cr(III) luminescence in octahedral sites (Cr-corundum or Ruby) (Shoval et al., 2003). In order to investigate this possibility, one reacted pyrite sample was submitted to laser beams at 647.1 and 568.2 nm and the spectra compared with that obtained with the 632.8 nm laser. The Raman spectra (Figure 4.35) was shifted according to the laser source while emission characteristics of Cr(III) remained fixed around 692 and 694 nm , as an indication of Cr(III) luminescence. The presence of trace amounts of chromium in the solids was confirmed by X-ray fluorescence analysis (See chapter 3).

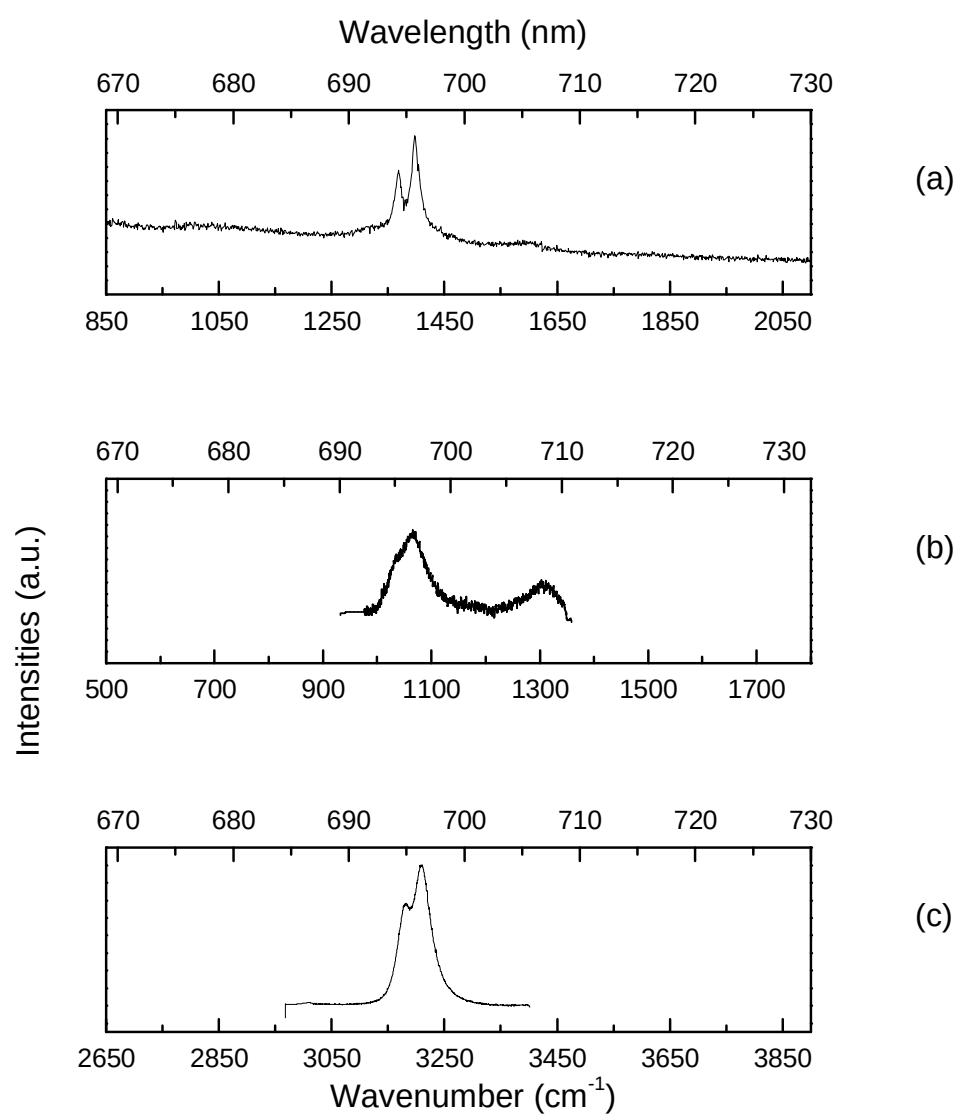


Figure 4.35 – Micro-Raman spectra showing the laser line effect for the oxidized pyrite in hydroxide sodium solution (0 mol/L $[\text{CO}_3^{2-}]$), pH 12.5. Laser lines: (a) 632.8 nm, (b) 647.1 nm and (c) 568.2 nm.

5 DISCUSSION

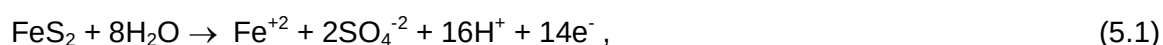
5.1 Mechanism of Pyrite Oxidation in Acid and Circumneutral pH

In the discussion of the effect of Fe(II)/Fe(III) – carbonate complexes on pyrite oxidation, some relevant aspects of the reaction mechanisms will be summarized in the following paragraphs. A comprehensive review is presented in Chapter 2.

The kinetics and mechanism of pyrite oxidation have received much attention for many decades, especially in acidic solutions (Bailey and Peters, 1976; Lowson, 1982; Mishra and Osseo-Asare, 1988; Wei and Osseo-Asare, 1997; Holmes and Crundwell, 2000).

Pyrite is a semiconductor, and therefore, may be susceptible to both chemical and electrochemical redox dissolution. The chemical redox dissolution pathway was reported to exhibit the characteristics of a homogeneous electron transfer, which may proceed via an inner-sphere or an outer-sphere pathway (Osseo-Asare, 1992 and 1993).

Pyrite oxidation is usually described by an electrochemical mechanism, thus implying that the overall reaction can be written in terms of half-cell reactions. The anodic oxidation of pyrite produces ferrous and sulfate ions (Bailey and Peters, 1976; Wei and Osseo-Asare, 1997; and Holmes and Crundwell, 2000):



Fe^{+2} and S^0 can also be formed under strongly acidic conditions:



O_2 and Fe^{3+} behave as electron acceptors in separate cathodic reactions:



Using isotope markers, Bailey and Peters (1976), Taylor et al. (1984), Reedy et al. (1991) and Usher et al. (2004) demonstrated that the oxygen in the sulfate product originates from water (see Eq. 5.1) rather than from molecular oxygen. This observation is a direct

consequence of the electrochemical mechanism - the presence of anodic and cathodic reactions on pyrite surface, the electrons produced by the anodic reaction being consumed by cathodic step. A schematic representation of the conventional electrochemical mechanism is shown in Figure 5.1. The oxidant (molecular oxygen or ferric ion) is reduced in the cathodic reaction. The anodic reaction, described by equation (5.1), involves the transfer of seven electrons from each pyrite-sulfur to the oxidant (ferric ion or oxygen) in the aqueous phase. It is known that the maximum electron transfer is of one or two in each elementary step. Therefore, the electrochemical oxidation of pyrite involves a complex mechanism comprised of various elementary reactions and the formation of both aqueous and solid intermediate products. Figure 5.1 shows thiosulfate as the main sulfur product released to the aqueous phase (Luther, 1987; Mishra and Osseo-Asare, 1988).

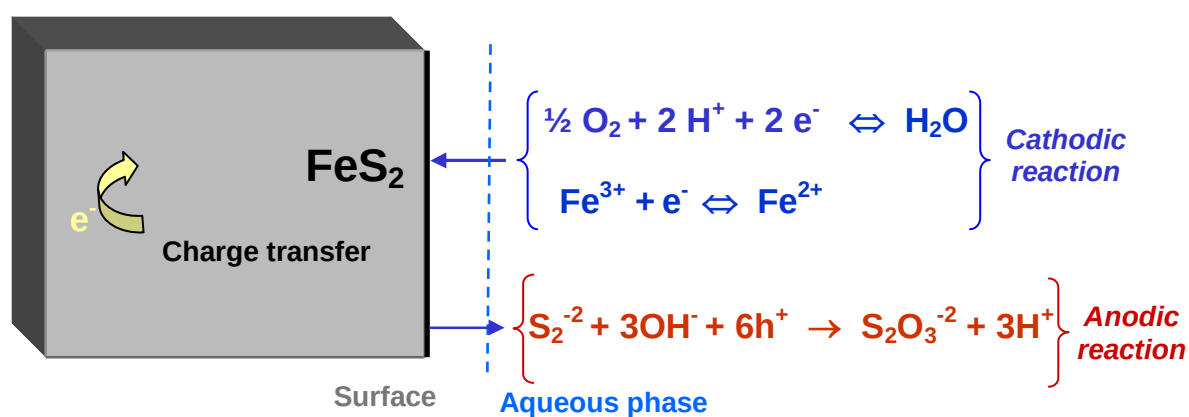
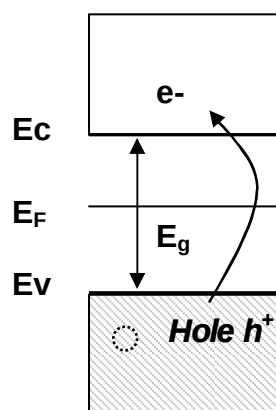


Figure 5.1 - Representation of the electrochemical reactions involved in pyrite oxidation: (i) anodic oxidation releases electrons (or consumes holes (h^+) - that are transported through the solid), and protons and thiosulfate to solution; (ii) electrons are captured by the oxidant at the cathode.

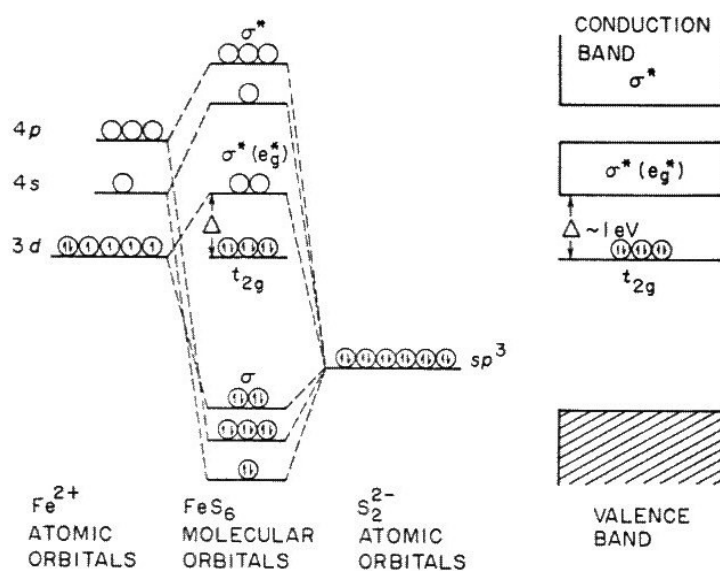
An electrochemical reaction at the solid/aqueous interface involves interfacial electronic charge carriers (i.e. electrons and holes) transfer. In order to allow charge transfer to occur, the energy level of the aqueous species must fluctuate at the same energy as the conduction or valence band in the solid. The electron-energy states are grouped into bands. The lower, or valence band - results from the overlap of filled valence orbitals of individual atoms - and the upper, or conduction band - results from the overlap of partially filled or empty higher orbitals of the atoms involved. An energy gap (E_g), usually of $E_g < 2\text{eV}$, separates the valence band from the conduction band in the semiconductors (Figure 5.2). For pyrite the band gap is near 1 eV, due to the atypical existence of nonbonding orbitals. For semiconductors, the Fermi level* lies in the forbidden band (band gap) between the conduction and valence bands. When an electron is excited across the energy gap to the conduction band, an unoccupied energy state, or hole (lack of electron), is left behind in the normally full valence band (Bockris and Reddy, 1977). The uppermost level of pyrite's valence band consists of occupied Fe 3d t_{2g} (nonbonding t_{2g} orbitals) states, with the S 3p states deeper in the valence band (bonding orbitals). The bottom of the conduction band is composed by unoccupied Fe 3d e_g^* (antibonding orbitals) states and S 3p states (Tributsch, 1986; Osseo-Asare 1992) (Figure 5.2b).

When the surface of a semiconductor is brought into contact with an aqueous solution, there will be a transfer of electrons or holes between the energy bands of the solid and the energy bands of the available aqueous phase redox couples. At equilibrium, the electrochemical potential of the electron must be the same in both the solid and aqueous phases (Crundwell, 1988; Mishra and Osseo-Asare, 1992). The resulting alignment of the energy levels in the solid and aqueous species allows charge transfer via holes or electrons to occur without an energy change. Other electronic levels rather than the Fermi energy, i.e. surface states, can exist on the semiconductor surface due to adsorbed species or surface reorganization. In the case of pyrite, surface states may originate from structural defects in pyrite lattice as well as the holes generated on Fe d-states in the valence band. These states facilitate electron transfer between semiconductor surface and electrolyte (Mishra and Osseo-Asare, 1992).

*According to Koryta et al. (1993) "In a solid states physics, the electrochemical potential of the electron is mostly replaced by the equivalent energy of the Fermi level (E_F). While the electrochemical potential is usually related to one mole of particles, the Fermi energy is related to a single electron."



(a)



(b-1)

(b-2)

Figure 5.2 – (a) Representation of band edges at an intrinsic semiconductor. E_c = energy level at lower conduction band; E_v = energy level at upper valence band; E_g = energy gap; E_F = Fermi energy level. (b) Relationship between atomic orbitals, molecular orbitals, and the band model. Molecular orbital diagram for the FeS_6 cluster (b-1). Band model for FeS_2 (b-2) (From Osseo-Asare, 1992, after Vaughan and Craig, 1978).

Anodic Reaction

Mishra and Osseo-Asare (1988) and Wei and Osseo-Asare (1997) have demonstrated the important role of holes in the anodic dissolution of pyrite and explain the pathway involved in sulfur oxidation. According to the authors, the initial step of the anodic reaction involves the reversible adsorption of $\text{H}_2\text{O}/\text{OH}^-$ ions via interaction with of iron 3d t_{2g} , nonbonding orbital in the valence band of pyrite:

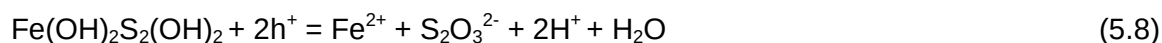
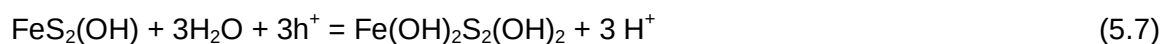


The presence of a hole in the valence band (corresponding to Fe(III)-pyrite) makes stronger the interaction of iron 3d t_{2g} orbitals with H_2O or OH^- . It is important to stress that unlike other sulfides, the iron-sulfur bond is not weakened with the creation of holes, as it occurs in the nonbonding orbitals (Figure 5.2b) (Tributsch, 1986; Crundwell, 1988). In a further step, the $\bullet\text{OH}$ radical is transferred to sulfur sites at pyrite surface



Recent studies corroborate the above mechanisms involving an OH radical. Borda et al. (2003) proposed that pyrite oxidation proceeds via the OH radical formed by the interaction of H_2O with defect sites at pyrite surface. Experimental evidence of this mechanism as obtained by measuring the OH radical concentration and the conversion of Fe(III) to Fe(II) at defect sites shown by XPS spectroscopy.

The complete hydroxylation of the surface, followed by oxidation of sulfur sites occurs according to the following reactions (Mishra and Osseo-Asare, 1988):



Note that according to this mechanism thiosulfate is formed as an intermediate species during pyrite oxidation, which is also supported by application of the concepts of molecular orbital theory (Luther, 1987). The surface species, Fe-S-S-O_3 dissociates into Fe^{+2} and $\text{S}_2\text{O}_3^{2-}$ because $\text{S}_2\text{O}_3^{2-}$ induces high spin Fe^{+2} , which is labile. The Fe^{+2} in pyrite is originally low spin in view of the interaction of the empty sulfur “d” orbital band with the t_{2g} band of Fe^{+2} . Thus, Fe^{+2} in pyrite does not dissociate with the release of Fe^{+2} into solution unless the Fe-S bond is weakened by oxidation of the S_2^{2-} species. At low pH, the thiosulfate ions decompose

to elemental sulfur and bisulfite (HSO_3^-) ions, which finally oxidizes to sulfate (Mishra and Osseo-Asare, 1988). At high pH and in the presence of oxidants such as Fe^{3+} and O_2 , thiosulfate is oxidized to sulfate by an electrochemical mechanism or by a chemical homogeneous reaction. Using in situ attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy, Borda et al. (2003a and 2004) concluded that although the initial step differs when O_2 and Fe^{3+} react with pyrite, the step-wise oxidation of the disulfide group should follow the same pathway regardless of the oxidant.

Cathodic Reaction

In the cathodic reaction, the oxidant receives electrons from the conduction band of pyrite. Singer and Stumm (1970) proposed that Fe(III) is the major pyrite oxidant in the acidic pH region. Moses et al. (1987) and Moses and Herman (1991) showed the reaction with Fe(III) is faster than that with oxygen even at circumneutral pH, the conclusion being supported by theoretical considerations based on molecular orbital theory (Luther, 1987; Luther et al., 1992; and Osseo-Asare, 1993). Based on the measurement of the mixed potentials of pyrite in the presence of both ferric ions and dissolved oxygen, Holmes and Crundwell (2000) also suggested that the rate of dissolution of pyrite with oxygen is much slower than that with ferric ions. Oxygen is reduced to water in a series of consecutive, one electron transfer steps that lead to the formation of intermediate species, such as hydroxyl and peroxide free radicals and hydrogen peroxide. The well-known inertness of molecular oxygen is related to the repulsive interaction of the incoming electron to those already present in the oxygen molecule, which implies in negative redox potential (unfavorable reduction) of the first electron transfer reaction (Osseo-Asare, 2005)

Regardless of whether or not Fe(III) is the preferred reactant, the reaction can only be sustained in the presence of O_2 and is affected by adsorption of Fe(II) from solution and the possible catalytic effect of pyrite surfaces on Fe(II) oxidation (Moses et al. 1987; Moses and Herman, 1991). Therefore, the reaction mechanism involves electron transfer from pyrite to the adsorbed ferric species followed by electron transfer from the adsorbed Fe^{+2} to O_2 in order to restore the oxidant. The Fe(II)/Fe(III) couple thus works as an electron transfer “pipeline” between pyrite and dissolved oxygen. This cycle involving the Fe(II)/Fe(III) couple extends the Singer-Stumm model for pyrite oxidation (Singer and Stumm, 1970), now implying that the oxidation of Fe(II) is the rate-limiting step both at low as well as at circumneutral pH; at low pH because the oxidation of Fe(II) by O_2 is slower than the oxidation of pyrite by $\text{Fe(III)}_{(\text{aq})}$. At circumneutral pH it is suggested that Fe(II) adsorbed at pyrite surface blocks the attack by either $\text{Fe(III)}_{(\text{aq})}$ or O_2 (Moses and Herman, 1991). The reaction

inhibition by Fe(II) is not fully understood. A plausible correlation of this inhibition with the formation of an oxide film is not supported by the studies carried out by Ciminelli (1987), showing similar reaction rates in the presence of a growing oxide film and when the oxide layer was removed in every 1 hour interval. This conclusion is not extended to the carbonate systems, in which the presence of an oxide layer does affect the reaction rate. Coming directly from the electrochemical mechanism, an alternative explanation for the detrimental effect of ferrous ions on pyrite oxidation is that the build-up of Fe(II) species favors the reverse reaction of Fe(III) reduction in the cathodic sites (Osseo-Asare, 2005).

Summarizing, the studies on the anodic pathway converge to a mechanism that involves the creation of holes at Fe 3d t_{2g} states, followed by the strong adsorption of $H_2O/OH^\cdot$. After that, the OH radical is transferred to the sulfur sites. Further complete hydroxylation takes place at the sulfur sites until thiosulfate is formed. Thiosulfate is either fully oxidized to sulfate (high pH) or may decompose into elemental sulfur and bisulfite (HSO_3^-)(low pH).

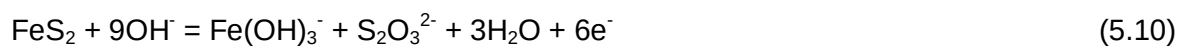
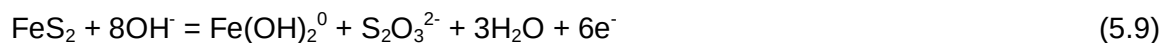
A definitive picture of the cathodic reaction is not available at this point. It will be adopted here the understanding that in oxygenated systems the electron acceptors can be either oxygen or ferric ions, both adsorbed on the Fe-pyrite sites. Oxidation of adsorbed Fe(II) by dissolved O_2 to generate Fe(III) at the pyrite surface (or in solution) is the rate-limiting step. The adsorbed Fe(III) is reduced to Fe(II), receiving electrons from the conduction band of pyrite. Thus the cycle of the Fe(II)/Fe(III) redox couple is formed, mediating the electron transfer from the sulfur atoms to dissolved oxygen. As a parallel reaction, oxygen is adsorbed on the iron sites and reduced to water in a series of consecutive, one electron transfer steps that produces intermediate hydroxyl and peroxide free radicals and hydrogen peroxide.

5.2 Oxidation of Pyrite in Oxygenated Alkaline Solutions

The mechanisms discussed in the previous paragraphs were mostly derived from studies carried out in acidic solutions. A main difference between pyrite oxidation under acidic and alkaline conditions is the hydrolysis and precipitation of ferrous/ferric ions as pH increases. The nature and properties of this solid product will be determined by the conditions in which the oxidation reaction takes place. In terms of the oxidation mechanism, alternative anodic or cathodic pathways can be favored. Therefore, the questions addressed in the present work

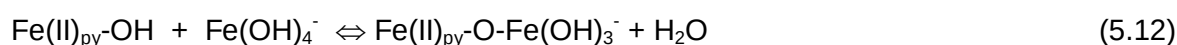
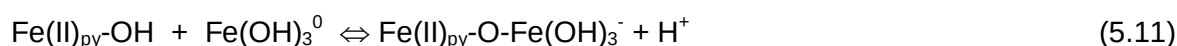
are: (i) how is the mechanism affected by the increase in pH and presence of carbonate ions and (ii) how is the nature of the solid iron oxyhydroxide affected by these conditions.

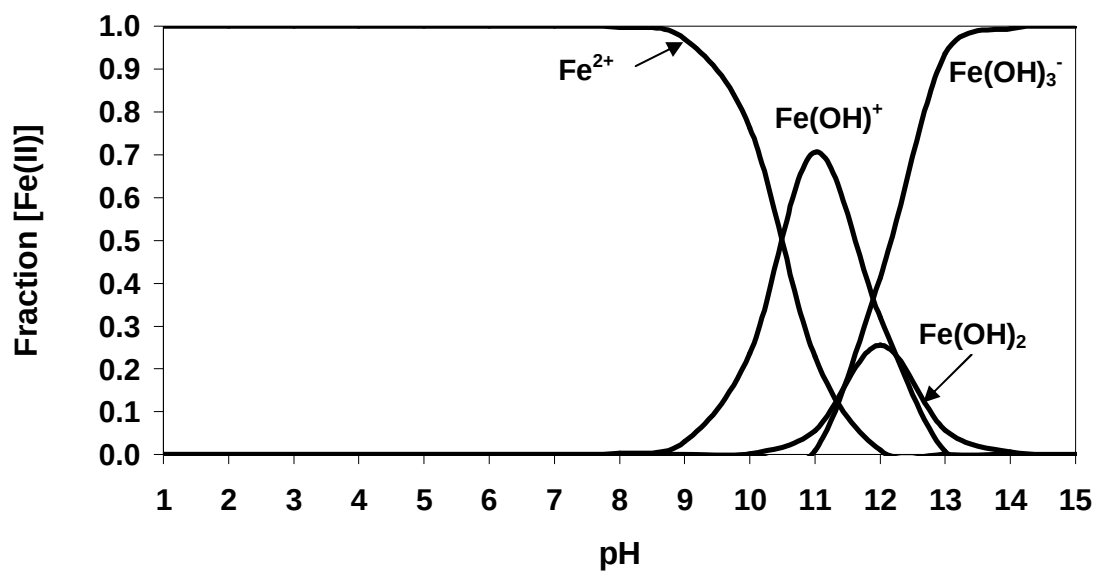
In light of the studies in acid and neutral pH, the anodic oxidation of pyrite in alkaline solutions is hypothesized also to involve an initial adsorption of water or hydroxyl ions on the iron sites, the hydroxyl ion being the favorable species at high pH. The presence of holes at the iron sites strengthens the adsorption of the OH⁻ species and is followed by the transference of the OH radical to the sulfur sites. Further hydroxylation takes place at the sulfur sites until thiosulfate is formed and eventually released to solution. The breakage of the Fe-S₂ bond leads to the release of the Fe(II)hydroxo complex that is the soluble iron species formed under alkaline conditions (Figure 5.3):



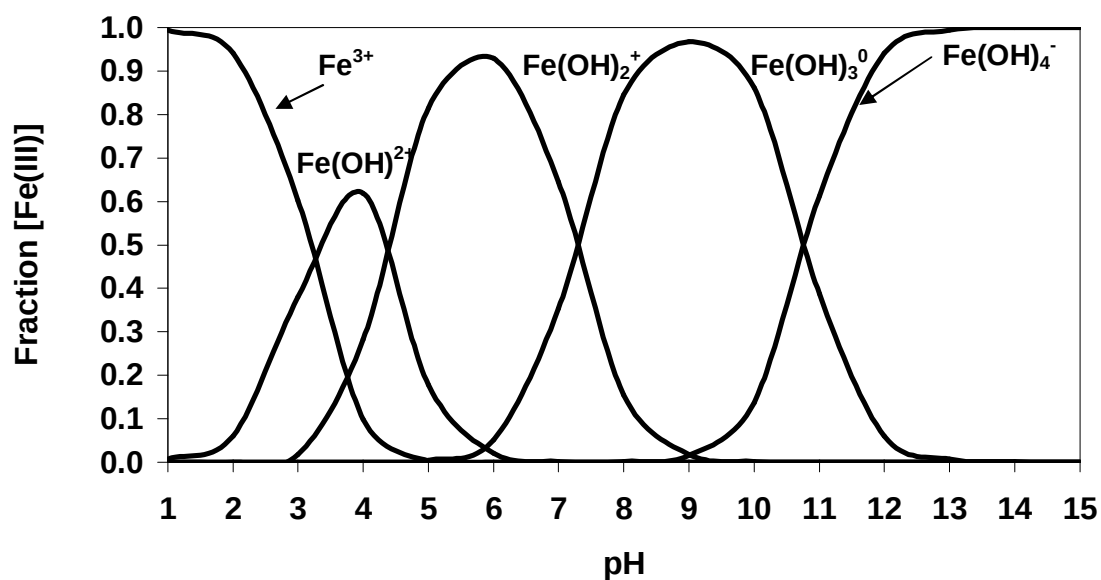
Further hydrolysis/oxidation of the Fe(II) hydroxo complex will lead to the formation of hematite and feroxyhite/magnetite (Chapter 4); thiosulfate is oxidized to sulfate. The formation of the insoluble oxide layer was shown not to affect the overall oxidation rate of pyrite (Ciminelli, 1987).

In oxygenated alkaline systems the electron acceptors will be considered to be either oxygen or ferric ions adsorbed on the pyrite iron sites. But at this point, the relative importance of these two possible cathodic reactions in alkaline solutions can not be determined. Evidences of oxygen and ferric ion adsorption on pyrite surface are provided by Becker et al. (2001) and Fornaserio and Ralston (1992), respectively. Measurements of eletrophoretic mobility (Monte et al., 1997) indicate adsorption of the positively charged ferric hydroxo complexes (Fe(OH)²⁺ and Fe(OH)₂⁺) on pyrite surface, with the consequent charge reversal at low pH (IEP – isoelectric point - from pH 2 to 5.5). Conversely, the increase of the negative surface charge, in the presence of hydrogen peroxide at high pH, is consistent with the adsorption of the neutral and negatively charged hydroxo complexes (Fe(OH)₃⁰ and Fe(OH)₄⁻):





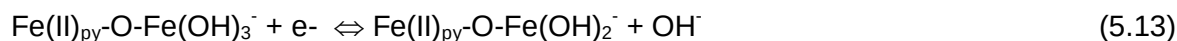
(a)



(b)

Figure 5.3 – Diagram of iron speciation with pH (a) Fe(II) and (b) Fe(III). Data from King and Farlow (2000), and Cornel and Schwertmann (1996).

The above reactions are based on the usual surface coordination pathway reported by oxide systems (Osseo-Asare, 2005). The soluble iron species $(\text{Fe}(\text{OH})_3^0$ and $\text{Fe}(\text{OH})_4^-$) in eq. (5.11-12) were selected according to the speciation diagram shown in Figure 5.3. The adsorbed Fe(III) is further reduced to Fe(II), as electrons are received from pyrite's conduction band:



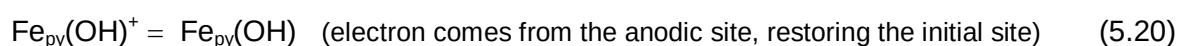
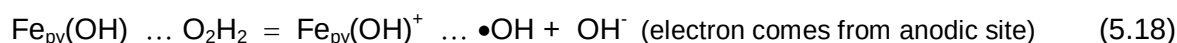
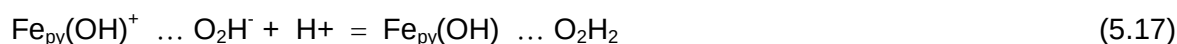
The regeneration of Fe(III) by oxidation with oxygen may take place either on pyrite surface or in solution. Thus the cycle of the Fe(II)/Fe(III) redox couple is formed, mediating the electron transfer from the sulfur atoms to dissolved oxygen. As a parallel cathodic reaction, oxygen is adsorbed on the iron sites and reduced to water in a series of consecutive one electron transfer steps that produces intermediate hydroxyl and peroxide free radicals and hydrogen peroxide. The following mechanism was based on the model suggested by Rimstidt and Vaughan (2003):



The hydrogen ion reacts with the oxygen to produce HO_2 radical, and simultaneously the Fe^{3+} receives an electron from an anodic site, and Fe^{2+} is produced. After this, another electron can be transferred to the oxygen:



An additional hydrogen ion reacts with the peroxide group to yield H_2O_2 . From the anodic site, another electron reduces Fe^{3+} back to Fe^{2+} .



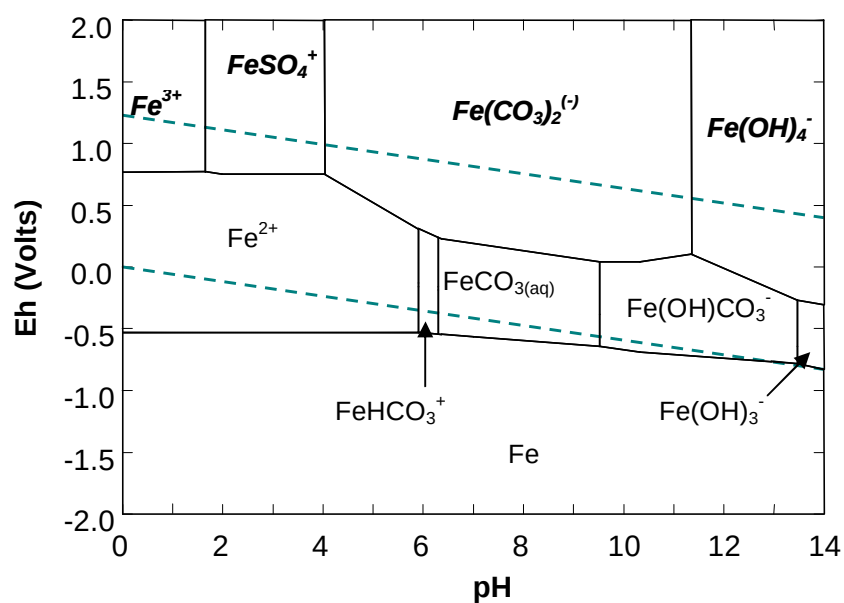
5.2.1 The effect of carbonate on pyrite oxidation

The presence of carbonate bound to pyrite surface was clearly demonstrated in the previous chapter. The two well-defined peaks in the DRIFT spectra of oxidized pyrite in carbonate/bicarbonate solutions - at near 1430 cm^{-1} and 1530 cm^{-1} - were assigned to the ν_3 symmetric and asymmetric stretching vibration of C-O bond, respectively. The magnitude of this splitting indicated the formation of a bidentate mononuclear complex. The bands at 1350 and 1380 cm^{-1} were assigned to Fe(III)GRCO_3 . The increase of iron solubility in the presence of carbonate (Table IV.2) was related to the formation of the soluble Fe(II) and Fe(III) complexes shown in Figure 5.4.

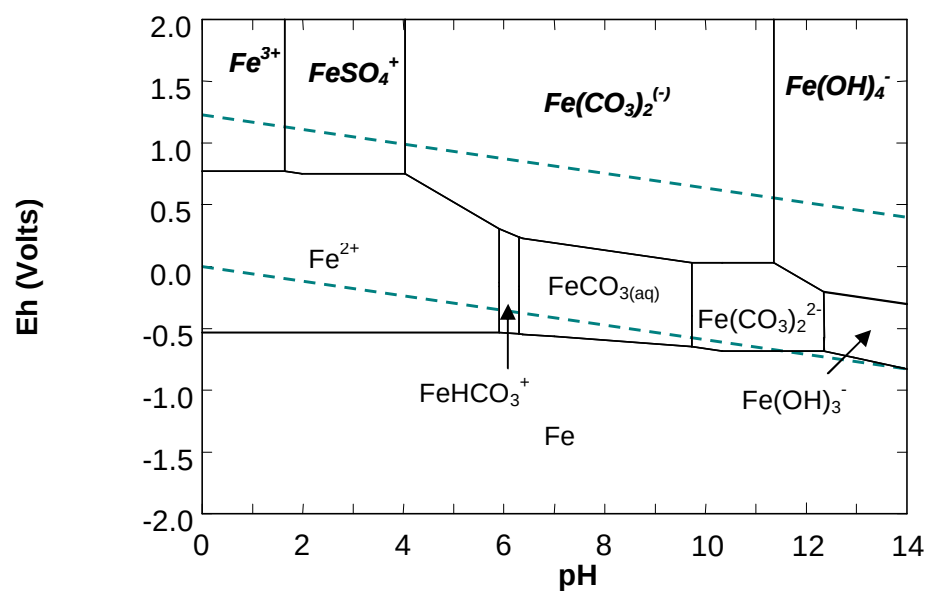
It is important to correlate these results with the kinetics aspects of pyrite oxidation in alkaline media reported in previous works (Ciminelli and Osseo-Asare, 1995a,b; Nicholson et al., 1988 and 1990; Hood, 1991). Ciminelli and Osseo-Asare (1995a,b) observed that under moderately alkaline conditions the reaction rate is faster in the presence of bicarbonate/carbonate ions. The difference with respect to the reaction rate in NaOH solutions is restricted to moderately basic solutions ($\text{pH} < 12$) and to the early stages of oxidation. It is interesting to note that this effect of carbonate correlates well with the pH range of formation of Fe(II)/Fe(III) – carbonate complexes (Figure 5.4). The presence of carbonate did not affect the reaction rate at pH 12.5 (Ciminelli and Osseo-Asare, 1995 a,b); Figure 5.4 shows no iron carbonate complex at this pH.

The increase of pyrite oxidation rate in the presence of carbonate ions is explained by a combination of factors:

(i) The formation of soluble Fe(II)-CO_3 complexes favors the oxidation to Fe(III) , which in turn favors the overall kinetics of pyrite oxidation. As indicated previously, one of the cathodic reactions of pyrite oxidation is the reduction of Fe(III) to Fe(II) , the former species being restored by oxidation with oxygen. Based on the results discussed in the next paragraph, it is proposed that the electron transfer to O_2 is facilitated by the formation of a Fe(II)-CO_3 complex at the pyrite surface or in solution. If the hypotheses of the Singer-Stumm model for pyrite oxidation (Singer and Stumm, 1970) is extrapolated to alkaline solutions, the oxidation of Fe(II) is the rate-limiting step.



(a)



(b)

Figure 5.4 - Eh-pH diagram for the Fe-S-CO₃-H₂O system pseudo-equilibria at 25°C, showing (a) predominance areas of soluble iron II and III species – Fe(III) species in italics; (b) predominance areas with metastable species Fe(CO₃)₂²⁻. [Fe] = 0.017 mol/L; [S] = 0.033 mol/L; [CO₃] = 0.1 mol/L. Water stability region is indicated within the dashed lines.

Millero et al. (1987) and King (1998) investigated the Fe(II) oxidation by molecular oxygen. Preliminary values of rate constants for various iron species are shown in Table V.1. The results illustrate how ligands containing oxygen increase the Fe(II) oxidation rate when compared to the oxidation of free Fe(II) ion, (i.e. $\text{Fe}(\text{H}_2\text{O})_6^{2+}$). When Fe(II) is bound to hydroxide ion or carbonate/bicarbonate ion, high spin complexes are formed and less energy is thus required to oxidize ferrous ion. The well-known increase of Fe(II) oxidation by molecular oxygen at $\text{pH} > 7$ can be related to the formation of $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3^-$. The strong dependence of Fe(II) oxidation rates on bicarbonate/carbonate concentration is also supported by the results shown in Table V.1. This behavior was related to the formation of Fe(II)-carbonate complexes. The $\text{Fe}(\text{CO}_3)_2^{2-}$ species was shown to be the main species involved in Fe(II) oxidation in NaHCO_3 solutions (King, 1998). The predominance region of this metastable species is shown in Figure 5.4. According to King (1998) the data for the $\text{Fe}(\text{OH})\text{CO}_3^-$ species was considered preliminary, due to the uncertainty in defining the equilibrium constant for this species and the minor influence of the species contributed to the kinetic fits.

Table V.1 – Fe(II) reaction rates with molecular oxygen at 25 °C and zero ionic strength (I)
(King, 1998)

Reactions	log k ($\text{mol}^{-1}\text{min}^{-1}$)
$\text{Fe}^{2+} + \text{O}_2 = \text{Fe}^{3+} + \text{O}_2^-$	-4.26
$\text{Fe}(\text{OH})^+ + \text{O}_2 = \text{Fe}(\text{OH})^{2+} + \text{O}_2^-$	2.62
$\text{Fe}(\text{OH})_2 + \text{O}_2 = \text{Fe}(\text{OH})_2^+ + \text{O}_2^-$	7.72
$\text{FeHCO}_3^+ + \text{O}_2 = \text{FeHCO}_3^{2+}(\text{aq}) + \text{O}_2^-$	< 1.9
$\text{FeCO}_3(\text{aq}) + \text{O}_2 = \text{FeCO}_3^+(\text{aq}) + \text{O}_2^-$	< 1.4
$\text{Fe}(\text{CO}_3)_2^{2-} + \text{O}_2 = \text{Fe}(\text{CO}_3)_2^- + \text{O}_2^-$	5.82
$\text{FeCO}_3(\text{OH})^- + \text{O}_2 = \text{FeCO}_3(\text{OH}) + \text{O}_2^-$	9.97

(ii) The complexation with bicarbonate/carbonate ions provides a stronger Fe(III)/Fe(II) redox couple by increasing Fe(III) solubility. The increasing in the availability of Fe(III) ions allow the role of Fe(III) as oxidant in alkaline medium to be enlarged. The presence of Fe(III)/Fe(II)-carbonate complexes redox couple increases the number of surface states due to the mixed potential formed in the interface between the mineral and solution. The presence of surface

states modifies the Fermi levels, which in turn facilitates the electron transfer between the mineral and the oxidants (Crundwell, 1988).

(iii) The buffering effect of carbonate minimizes the variation of pH at the reaction interface, thus maintaining more favorable conditions for pyrite oxidation (Ciminelli, 1987). Hydrogen ions are produced by the anodic reaction (eq. 5.1). As the reaction rate increases with pH, a smaller pH drop at the reaction interface can explain the faster initial rate of pyrite oxidation in sodium carbonate solutions.

(iv) Finally, the formation of Fe(II)/Fe(III)-CO₃ complexes modifies the hydrolysis and precipitation pathways of pyrite iron. Supported by the identification of solid products shown in chapter 4, two distinct precipitation pathways for systems containing carbonate or not are proposed in the following section. The effect of a growing oxide layer on the oxidation rate of pyrite was investigated by Ciminelli (1987). The author demonstrated that only the oxide layer produced in carbonate systems inhibits the oxidation rate. Nicholson et al. (1990) also showed that the formation of an oxide layer controls the oxidation rate of pyrite in carbonate-buffered solution. Therefore, this negative role of the oxide layer formed in carbonate solutions offsets the positive effect observed at short reaction times.

5.3 Product Layer Formation during Alkaline Pyrite Oxidation

The present work showed hematite as the major and ferroxhyte as the minor solid phase formed during pyrite oxidation at pH 8.5 and 10. At pH 12.5, only ferrihydrite was identified. Conversely, Fe(III)-green rust/ferrihydrite were found as the main products of pyrite oxidation in bicarbonate/carbonate media. Figure 5.5 summarizes the pathways of the product formation in both systems.

The release of iron into solution as a consequence of pyrite oxidation in alkaline solutions generates soluble iron (II) species complexed with OH⁻ and HCO₃⁻/CO₃²⁻. The presence of carbonate, and the consequent formation of Fe(II)/Fe(III)-CO₃ complexes increase iron solubility as well as introduces new possible reaction pathways until the oxide arises. There is a certain analogy between the reactions that can be involved during the pyrite oxidation

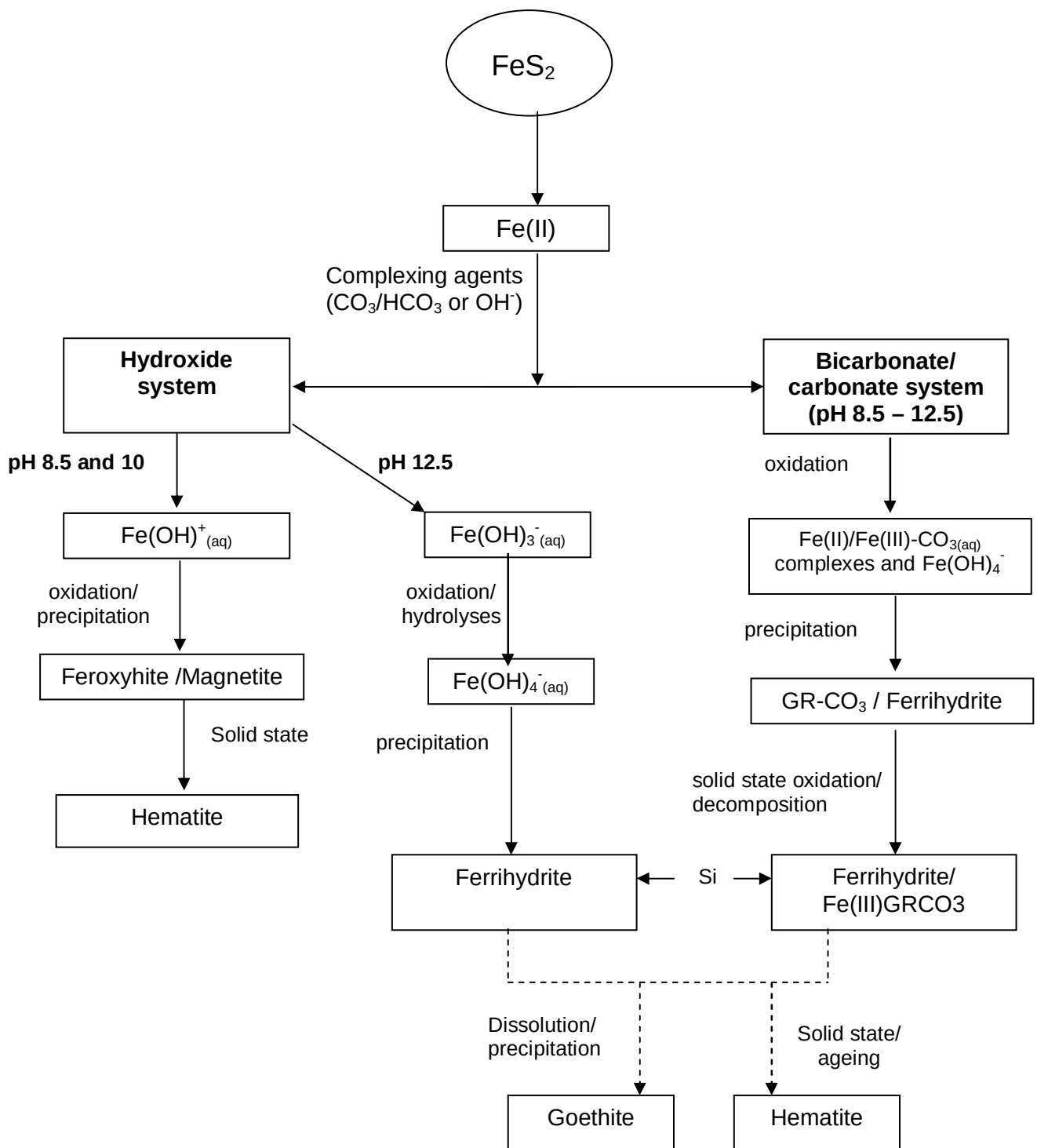


Figure 5.5 - A schematic representation of the reaction pathways proposed for the formation of the different solid phases during pyrite oxidation.

and those found in the precipitation of iron compounds and in the iron corrosion process (Bewick et al., 1991; Blengino et al., 1995; Oblonsky and Devine, 1997; Legrand et al., 2000, 2001 a,b; Savoye et al., 2001; Music et al., 2004). Most of the iron oxides and oxide hydroxides can be produced from Fe(II) solutions by oxidation followed by hydrolysis. The processes by which oxides form are governed by the pH, the rate of oxidation, the temperature, ferrous ion concentration and also by foreign compounds in the system (Cornell and Schwertmann, 1996). In general, the oxidation and hydrolysis of Fe^{+2} leads to Fe(III) oxides either directly or via soluble green rust complexes and solid green rusts or $\text{Fe}(\text{OH})_2(\text{aq})$. The latter is converted to the oxides either by a solid state or via a solution (reconstructive-dissolution and precipitation) transformation (Cornell and Schwertmann, 1996).

Pyrite oxidation in hydroxide media shows hematite as the main solid product at pH 8.5 and 10; and ferrihydrite in pH 12.5. Hematite and $\delta\text{-FeOOH}$ (feroxyhite) were identified by XRD, IR and Raman analyses. It is assumed that soluble Fe(II) ions (eg. $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3^-$) are rapidly oxidized, leading to feroxyhite formation, that is finally transformed to hematite, as the end product (Figure 5.5). As reported by Cornell and Schwertmann (1996), $\delta\text{-FeOOH}$ is formed over a wide pH range if the rate of oxidation is high. As $\delta\text{-FeOOH}$ and hematite have a similar anionic framework (hexagonal close packaged - hcp), the conversion proceeds relatively easily. Regardless the dehydroxylation of $\delta\text{-FeOOH}$ takes place in the dry state or in solution, the end product is hematite. Magnetite can also be obtained in alkaline aqueous systems by precipitation from mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution, by oxidation of Fe^{2+} solution via $\text{Fe}(\text{OH})_2$ and by interaction of Fe^{2+} with ferrihydrite (Cornell and Schwertmann, 1996). The conditions employed in the present work favor the formation of magnetite (Eh-pH diagram) as an intermediate product, which was identified by Raman spectroscopy as may also be present.

The strong influence of the pH on the nature of the product layer can be explained by the availability of Fe(III) in solution. The lowest solubility of Fe(III) ions is found near pH 7-8, and so is the predominance of hematite. Conversely, maximum concentration of $\text{Fe}(\text{OH})_4^-$ is found at pH 12, where the predominance of ferrihydrite is achieved (Cornell and Schwertmann, 1996). Ferrihydrite can be transformed to the more stable hematite or goethite phases as reported by Cornell and Schwertmann (1996). Hematite is formed by a solid state reaction, the details of which are not yet fully understood. Until recently, the consensus was that nucleation/growth of hematite involves a combination of dehydration and rearrangement processes, facilitated by the structural resemblance between ferrihydrite and hematite. In contrast to hematite, the formation of goethite from ferrihydrite in both acid and alkaline

media involves dissolution of ferrihydrite followed by nucleation and growth of goethite in solution. Recently, it was reported that the transformation to hematite would also require dissolution and reprecipitation (Jambor and Dutrizac, 1998). Thus, dissolution and precipitation process would operate during the formation of goethite, whereas both dissolution and the solid-state transformation would take place during the formation of hematite.

In the presence of carbonate and bicarbonate ions, the oxidation/hydrolysis of ferrous species into ferric oxyhydroxides takes place via an intermediate Fe(II)-Fe(III) hydroxy-salt designated as green rust-carbonate (GR-CO₃) (Fe₄^(II)Fe₂^(III)(OH)₁₂CO₃·2H₂O). Ferric hydroxycarbonate and GR-CO₃ have been identified as intermediate products of metallic iron oxidation (Blengino et al., 1995; Abdelmoula et al., 1996; Bonin et al., 2000; Legrand et al., 2000; Savoye et al., 2001; Music et al., 2004). The solid green rusts are double-layer hydroxide salts in which positively charged octahedral Fe hydroxy layers are linked by interlayer anions (e.g. CO₃⁻²). This phase is stable only at low redox potential. Upon oxidation, the green rust-carbonate is expected to be transformed to goethite, as predicted by the Eh-pH diagram (Figure 4.2a). It is proposed that carbonate anions favors the polymerization of the double bonds FeO₃(OH)₃ octahedra common to FeOOH compounds towards a corner-sharing arrangement, and thereby to goethite (α-FeOOH) (Music et al., 2004).

In the present work, the bands at 1350, 1380 and 1550 cm⁻¹, shown in carbonate solutions, can indicate the presence of Fe(III)GRCO₃ (ferric oxyhydroxycarbonate) (Figure 4.19). The bands at 1350 and 1380 cm⁻¹ are attributed to the symmetric and asymmetric vibrational modes of carbonate ions; and the band at 1550 cm⁻¹ can be associated with the hydroxyl group. According to the Eh-pH diagram (Figure 4.2a), the formation of GR1CO₃ is favored at pH around 10, at reducing conditions. Fe(III)GRCO₃ (no thermodynamic data available) is reported as an oxidation product of GRCO₃, via a solid state reaction. It is important to point out the resemblance of the micro-Raman spectra obtained in bicarbonate/carbonate media in the present work with the “in situ” Raman spectrum of a ferric oxyhydroxycarbonate, Fe(III)GRCO₃ reported by Legrand et al. (2003). These spectra are also similar to that of ferrihydrite. Ferrihydrite was reported by Benali et al. (2001) as being a metastable product of the oxidation of green rust-1 (GR1-CO₃) (Fe₄^(II)Fe₂^(III)(OH)₁₂CO₃·2H₂O).

Once formed, ferrihydrite can be transformed to the more stable hematite (solid state reaction) or goethite (dissolution-precipitation reaction). In bicarbonate/carbonate media, the ferrihydrite → hematite transformation is prevented due to the relatively higher iron solubility

(Fe(II) and Fe(III) –carbonate complexes species) (Figures 5.4 and 5.5) as compared to that in hydroxide media in the same pH range (8.5-10). Higher dissolution favors the development of goethite. However, it is found that the adsorption of silicate anions retards the transformation of ferrihydrite to the more crystalline goethite (Cornell and Schwertmann, 1996). The presence of soluble silicate ions (Table IV.2 and Figure 4.7) is correlated to the fact that goethite was not identified by XRD, infrared and micro-Raman analyses. By ageing, hematite is expected to be the end product of pyrite oxidation in alkaline media, as predicted by thermodynamics.

6 CONCLUSIONS

The thermodynamics of pyrite oxidation in alkaline solutions was studied with the aid of Eh-pH and speciation diagrams. The results indicated that the main product of pyrite decomposition is hematite; siderite is formed around neutral pH, and relatively lower Eh. At $\text{pH} < 4$ and mild oxidizing conditions ($\text{Eh} \sim 0.5 \text{ V}$) pyrite decomposes to soluble ferrous or ferrous sulfate ions. Ferrihydrite is produced by the rapid hydrolysis of Fe^{+3} solutions and therefore can be formed during pyrite oxidation in alkaline solutions. The Eh-pH diagrams showed that this metastable phase predominates in the pH range of 1.5 to 14 and potentials (Eh) 0.25 V and higher. In the presence of carbonate, soluble and solid Fe (II)-carbonate complexes are formed at pH 8-12, coexisting with pyrite and relatively low Eh values. These complexes are the solids GR1CO_3 and Fe(OH)_2 and the soluble Fe(II)-carbonate complexes ($\text{FeCO}_{3(\text{aq})}$ and $\text{Fe(OH)CO}_3^{-1}(\text{aq})$). The relatively less stable Fe(III) carbonate complexes predominate at pH 6-11 and oxidizing conditions. For $\text{pH} > 11$, only Fe(OH)_4^- prevails, even in presence of carbonate/bicarbonate ions.

The identification of carbonate compounds among the products formed during pyrite oxidation was possible, by the first time, by the use of diffuse reflectance infrared spectroscopy. Two well-defined peaks in the DRIFT spectra of oxidized pyrite in carbonate/bicarbonate solutions - at near 1430 cm^{-1} and 1530 cm^{-1} - were assigned to the ν_3 symmetric and asymmetric stretching vibration of C-O bond, respectively. The magnitude of this splitting indicates the formation of a bidentate mononuclear complex. The bands at 1350 and 1380 cm^{-1} were assigned to Fe(III)GRCO_3 . These bands arise under conditions where ferrihydrite is also identified, thus some carbonate adsorption can not be neglected.

The presence of sulfate and residual water on unreacted pyrite surface was shown by transmission (FTTIR) and diffuse reflectance spectroscopy. The FTTIR spectra of oxidized pyrite samples exhibit typical bands of iron oxides/hydroxides (in the spectral region $< 1000 \text{ cm}^{-1}$), but a definitive identification of these oxides was not provided by this technique.

The XRD patterns combined with micro-Raman analyses allowed the identification in detail of the main and minor oxide/hydroxide products of pyrite oxidation at short reaction times - prior to ageing and other factors that may lead to phase transformation. Hematite appeared as the major and feroxyhite as the minor solid phase formed during pyrite oxidation at pH 8.5 and 10. At pH 12.5, only ferrihydrite was identified. Conversely, Fe(III)-green rust was found

as the main product of pyrite oxidation in bicarbonate/carbonate media. The formation of hematite was ascribed to the low solubility of iron complexes at $\text{pH} < 11$ and in absence of carbonate. The formation of Fe(III)-green rust and ferrihydrite was explained by the increase of iron solubility due to the metal complexation with carbonate or hydroxyl ions, respectively. The increase of iron solubility in the presence of carbonate was also demonstrated by wet-chemistry analyses. Ferrihydrite transformation to more stable phases (e.g. hematite or goethite) was prevented due to the high concentration/adsorption of soluble silicate ions.

The conditions where the carbonate compounds are identified correspond to those in which the fastest rate of pyrite oxidation in carbonate solutions is reported. It is proposed that the formation of Fe(II)- CO_3 soluble complexes helps the oxidation of iron, which in turn favors the overall kinetics of pyrite oxidation in carbonate solutions.

7 ORIGINAL CONTRIBUTIONS TO KNOWLEDGE

1. The identification of carbonate compounds among the products formed during pyrite oxidation was possible, by the first time, by the use of diffuse reflectance infrared spectroscopy (DRIFT). This result as well the thermodynamic analysis provide evidences of the formation of Fe(II)/Fe(III)-carbonate complexes during pyrite oxidation.
2. A mechanism is proposed to explain the increase of the oxidation rates in carbonate/bicarbonate solutions due to the formation of the iron carbonate complexes. Previous works have attributed the increase of the oxidation rates of pyrite in carbonate media to the presence of the iron-carbonate complexes. However, no clear thermodynamic or experimental evidences to support this were presented.
3. The thermodynamic conditions (pH, potential redox) favoring the formation of the soluble Fe(II), Fe(III)-carbonate complexes were identified. Some works have already discussed Fe(II) and Fe(III) speciation, but without considering the stability in terms of redox potential, which is an essential variable in processes that involve oxidation.
4. The identification of the products of pyrite oxidation at short reaction time (small quantities yielded) was possible through the combination of XRD and micro-Raman analyses. By the first time, micro Raman spectroscopy was employed to identify the iron oxyhydroxides formed during pyrite oxidation. Micro-Raman spectroscopy provides the possibility of selecting target areas according to images features (in the present work, oxidized areas), thus enhancing Raman signal from trace constituents in complex mixtures. This advantage is not provided by other techniques based on "bulk" analyses.
5. The effect of pH and solution composition on the phases formed during pyrite oxidation was identified and explained. The detailed characterization of the oxidized products was possible through the combination of different analytical techniques with thermodynamic modeling.

8 SUGESTIONS TO FUTURE WORKS

1. To investigate the effect of reaction time (1 h, 24h, days) on the solid products, in order to identify (i) phase transformation, or secondary phases and (ii) the role of the oxidation layer on the rate of pyrite reaction.
2. To evaluate the role of reagents (e.g. phosphate) on the modification of the oxidation layer in order to obtain a dense and resistant oxidized product. The layer would hinder the access of O_2 e H_2O to pyrite surface, thus minimizing the formation of acid rock drainage.
3. To evaluate the buffer effect of carbonate on pyrite surface through pH measurements at the solid/liquid interface.
4. To investigate the presence of iron carbonate complexes in solution and at pyrite surface employing techniques that allow “in situ” analyses, such as infrared (***attenuated total reflectance*** -ATR) or Raman.
5. To evaluate the occurrence of preferential reaction on the different crystal planes by using monocrystals of pyrite.

REFERENCES

- Abdelmoula, M.; Refait, P.; Drissi, S. H.; Mihe, J. P. and Génin, J.-M. R. (1996). Conversion electron Mössbauer spectroscopy and X-ray diffraction studies of the formation of carbonate-containing green rust one by corrosion of metallic iron in NaHCO_3 and $(\text{NaHCO}_3 + \text{NaCl})$ solutions. ***Corrosion Science***, 38, p. 623-633.
- Bailey, L. K. and Peters, E. (1976). Decomposition of pyrite in acids by pressure leaching and anodization: The case for electrochemical mechanism. ***Canadian Metallurgical Quarterly***, 15, p. 333-344.
- Becker, U.; Rosso, K. M. and Michael F. Hochella, J. (2001). The proximity effect on semiconducting mineral surfaces: a new aspect of mineral surface reactivity and surface complexation theory? ***Geochimica et Cosmochimica Acta***, 65, p. 2641-2649.
- Benali, O.; Abdelmoula, M.; Refait, P. and Génin, J.-M. R. (2001). Effect of orthophosphate on the oxidation products of Fe(II)-Fe(III) hydroxycarbonate: The transformation of green rust to ferrihydrite. ***Geochimica et Cosmochimica Acta***, 65, p. 1715-1726.
- Bewick, A.; Kalaji, M. and Larramona, G. (1991). In-situ infrared spectroscopic study of the anodic oxide film on iron in alkaline solutions. ***Journal of Electroanalytical Chemistry***, 318, p. 207-221.
- Blengino, J. M.; Keddami, M.; Labbe, J. P. and Robbiola, L. (1995). Physico-chemical characterization of corrosion layers formed on iron in a sodium carbonate-bicarbonate containing environment. ***Corrosion Science***, 37, p. 621-643.
- Bockris, J. O. M. and Reddy, A. K. N. (1997). Modern electrochemistry. New York – USA: Plenum publishing corporation., 1432p.
- Bonin, P. M. L.; Odziemkowski, M. S.; Reardon, E. J. and Gillham, R. W. (2000). In Situ Identification of Carbonate-containing Green Rust on Iron Electrodes in Solutions Simulating Groundwater. ***Journal of Solution Chemistry***, 29, p. 1061-1074.
- Bonnissel-Gissinger, P.; Alnot, M.; Ehrhardt, J.-J. and Behra, P. (1998). Surface oxidation of pyrite as a function of pH. ***Environmental Science and Technology***, 32, p. 2839-2845.
- Borda, M. J.; Elsetinow, A. R.; Strongin, D. R. and Schoonen, M. A. (2003). A mechanism for the production of hydroxyl radical at surface defect sites on pyrite. ***Geochimica and Cosmochimica Acta***, 67, p. 935-939.
- Borda, M. J.; Strongin, D. R. and Schoonen, M. A. (2003a). A vibrational spectroscopic study of the oxidation of pyrite by ferric iron. ***American Mineralogist***, 88, p. 1318-1323.
- Borda, M. J.; Strongin, D. R. and Schoonen, M. A. (2004). A vibrational spectroscopic study of the oxidation of pyrite by molecular oxygen. ***Geochimica and Cosmochimica Acta***, 68, p. 1807-1813.
- Brown, A. D. and Jurinak, J. J. (1989). Mechanism of pyrite oxidation in aqueous mixtures.

- Journal of Environmental Quality***, 18, p. 545-550.
- Bruno, J.; Stumm, W.; Wersin, P. and Brandberg, F. (1992). On the influence of carbonate in mineral dissolution: I. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at $T=25^{\circ}\text{C}$. ***Geochimica et Cosmochimica Acta***, 56, p. 1139-1147.
- Bruno, J.; Wersin, P. and Stumm, W. (1992). On the influence of carbonate in mineral dissolution: II. The solubility of $\text{FeCO}_3(\text{s})$ at 25°C and 1 atm total pressure. ***Geochimica et Cosmochimica Acta***, 56, p. 1149-1155.
- Bruno, J. and Duro, L. (2000). Reply to W. Hummel's comment on and correction to "On the influence of carbonate in mineral dissolution: 1. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at $T=25^{\circ}\text{C}$ " by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. ***Geochimica and Cosmochimica Acta***, 64, p. 2173-2176.
- Burkin, A. R. and Edwards, A. M. (1963). The formation of insoluble iron oxide coatings during the alkali pressure leaching of pyrite. In: 6th International Congress of Mineral Processing, 1963, Cannes. p. 159-169
- Busca, G. and Lorenzelli, V. (1980). Infrared Study of Methanol, Formaldehyde, and Formic Acid Adsorbed on Hematite. ***Journal of Catalysis***, 66, p. 155-161.
- Busca, G.; Lorenzelli, V.; Ramis, G. and Willey, R. J. (1993). Surface sites on spinel-type and corundum-type metal oxide powders. ***Langmuir***, 9, p. 1492-1499.
- Caldeira, C. L.; Ciminelli, V. S. T.; Dias, A.; Moreira, R. L. and Osseo-Asare, K. (2001). Fourier transform infrared spectroscopy of the pyrite oxidation products under alkaline environments. ***VI SHMMT/XVIII ENTMME***, 1-6.
- Caldeira, C. L.; Ciminelli, V. S. T.; Dias, A. and Osseo-Asare, K. (2003). Pyrite oxidation in alkaline solutions: nature of the product layer. ***International Journal of Mineral Processing***, 72, p. 373-386.
- Caldeira, C.L.; Osseo-Asare, K.; Ciminelli, V.S.T. Oxidation of Pyrite in Alkaline Environments. In: REWAS'2004: Global Symposium on Recycling, Waste Treatment and Clean Technology, Madrid, Spain, ***Proceedings...***, TMS, Warrendale, PA, USA, 2004, V. III, p.2091-2101.
- Carey, D. M. and Korenowski, G. M. (1998). Measurement of the Raman spectrum of liquid water. ***Journal of Chemical Physics***, 108, p. 2669-2675.
- Chernyshova, I. V. (2004). Pyrite oxidation mechanism in aqueous solutions: an in situ FTIR study. ***Russian Journal of Electrochemistry***, 40, p. 69-77.
- Ciminelli, V. S. T. (1987). ***Oxidation of pyrite in alkaline solutions and heterogeneous equilibria of sulfur- and arsenic-containing minerals in cyanide solutions***. The Pennsylvania State University, University Park, PA, USA. 234.a doctoral thesis
- Ciminelli, V. S. T.; Miranda, R. T. and Castro, R. M. Z. (1994). Alkaline oxidation of a

- refractory gold ore. In: I. Wilkomirsky, M. Sánchez and C. Hecker. **Chemical Metallurgy**. Concepcion, Chile, University of Concepcion. III: p. 65-74.
- Ciminelli, V. S. T. and Osseo-Asare, K. (1995a). Kinetics of pyrite oxidation in sodium carbonate solutions. **Metallurgical and Materials Transactions B**, 26B, p. 209-218.
- Ciminelli, V. S. T. and Osseo-Asare, K. (1995b). Kinetics of pyrite oxidation in sodium hydroxide solutions. **Metallurgical and Materials Transactions B**, 26B, p. 677-694.
- Cornell, R. M. and Schwertmann, U. The Iron Oxides. New York: VCH, 1996 573p.
- Crundwell, F. K. (1988). The influence of electronic structure of solids on the anodic dissolution and leaching of semiconducting sulphide minerals. **Hydrometallurgy**, 21, p. 155-190.
- Davydov, A.; Chuang, K. T. and Sanger, A. R. (1998). Mechanism of H₂S oxidation by ferric oxide and hydroxide surfaces. **The Journal of Physical Chemistry B**, 102, p. 4745-4782.
- Descostes, M.; Mercier, F.; Thromat, N.; Beaucaire, C. and Gautier-Soyer, M. (2000). Use of XPS in the determination of chemical environment and oxidation state of iron and sulfur samples: constitution of a data basis in binding energies for Fe and S reference compounds and applications to the evidence of surface species of an oxidized pyrite in a carbonate medium. **Applied Surface Science**, 165, p. 288-302.
- Descostes, M.; Mercier, F.; Beaucaire, C.; Zuddas, P. and Trocellier, P. (2001). Nature and distribution of chemical species on oxidized pyrite surface: Complementarity of XPS and nuclear microprobe analysis. **Nuclear Instruments and Methods in Physics Research B**, 181, p. 603-609.
- Descostes, M.; Beaucaire, C.; Mercier, F.; Savoye, S.; Sow, J. and Zuddas, P. (2002). Effect of carbonate ions on pyrite (FeS₂) dissolution. **Bull. Soc. Géol. France**, 173, p. 265-270.
- Descostes, M.; Vitorge, P. and Beaucaire, C. (2004). Pyrite dissolution in acidic media. **Geochimica and Cosmochimica Acta**, 68, p. 4559-4569.
- Detournay, J.; Miranda, L. d.; Derie, R. and Ghodsi, M. (1975). The region of stability of green rust II in the electrochemical potential-pH equilibrium diagram of iron in sulphate medium. **Corrosion Science**, 15, p. 295-306.
- Drissi, S. H.; Refait, P.; Abdelmoula, M. and Génin, J. M. R. (1995). The Preparation and thermodynamic properties of Fe(II)-Fe(III) hydroxide-carbonate (green-rust 1); Pourbaix diagram of iron in carbonate-containing aqueous media. **Corrosion Science**, 37, p. 2025-2041.
- Dunnwald, J. and Otto, A. (1989). An investigation of phase transitions in rust layers using Raman spectroscopy. **Corrosion Science**, 29, p. 1167-1176.
- Eggleston, C. M.; Ehrhardt, J.-J. and Stumm, W. (1996). Surface structural controls on pyrite oxidation kinetics: and XPS-UPS, STM, and modeling study. **American Mineralogist**, 81, p. 1036-1056.

- Eggleton, R. A. and Fitzpatrick, R. W. (1988). New data and a revised structural model for ferrihydrite. **Clays and Clay Minerals**, 36, p. 111-124.
- Evangelou, V. P. and Huang, X. (1994). Infrared spectroscopy evidence of an iron(II)-carbonate complex on the surface of pyrite. **Spectrochimica Acta**, 50A, p. 1133-1340.
- Evangelou, V. P. B. Pyrite oxidation and its control. Boca Raton, Florida: CRC Press, Inc., 1995, 293p.
- Evangelou, V. P.; Seta, A. K. and Holt, A. (1998). Potential role of bicarbonate during pyrite oxidation. **Environmental Science and Technology**, 32, p. 2084-2091.
- Faria, D. L. A. d.; Venâncio Silva, S. and Oliveira, M. T. (1997). Raman microspectroscopy of some iron oxides and oxyhydroxides. **Journal of Raman Spectroscopy**, 28, p. 873-878.
- Farmer, V. C. The infrared spectra of minerals. London: Mineralogical Society, 1974, 539p.
- Fornasiero, D.; Eijt, V. and Ralston, J. (1992). An electrokinetic study of pyrite oxidation. **Colloids and Surface**, 62, p. 63-73.
- Goldhaber, M. B. (1983). Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6-9 and 30°C. **American Journal Science**, 283, p. 193.
- Herman, R. G., Bogdan, C. E., Sommer, A. J., Simpson, D. R. (1987). Discrimination among carbonate minerals by Raman spectroscopy using the laser microprobe. **Applied Spectroscopy**, 41, p. 437-440.
- Hiemstra, T.; Rahnemaie, R. and van Riemsdijk, W. H. (2004). Surface complexation of carbonate on goethite: IR spectroscopy, structure and charge distribution. **Journal of Colloid and Interface Science**, 278, p. 282-290.
- Holmes, P. R. and Crundwell, F. K. (2000). The kinetics of the oxidation of pyrite by ferric ions and dissolved oxygen: an electrochemical study. **Geochimica et Cosmochimica Acta**, 64, p. 263-274.
- Hood, T. A. (1991). **The kinetics of pyrite oxidation in alkaline systems**. University of Miami, Coral Gables, Florida. 223. thesis
- HSC Chemistry, (1999). Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database. Ver. 4.1, Outokumpu Research Oy, Pori, Finland
- Hug, S. J. (1997). In Situ Fourier Transform infrared measurements of sulfate adsorption on hematite in aqueous solutions. **Journal of Colloid and Interface Science**, 188, p. 415-422.
- Hummel, W. (2000). Comment on "On the influence of carbonate in mineral dissolution: 1. the thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T=25°C" by J. Bruno, W. Stumm, P. Wersin, and F. Brandberg. **Geochimica and Cosmochimica Acta**, 64, p. 2167-2171.
- Jambor, J. L. and Dutrizac, J. E. (1998). Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. **Chemical Reviews**, 98, p. 2549-2585.

- Janney, D. E.; Cowley, J. M. and Buseck, P. R. (2000). Structure of synthetic 2-line ferrihydrite by electron nanodiffraction. ***American Mineralogist***, 85, p. 1180-1187.
- Janney, D. E.; Cowley, J. M. and Buseck, P. R. (2001). Structure of synthetic 6-line ferrihydrite by electron nanodiffraction. ***American Mineralogist***, 86, p. 327-335.
- Johnston, F. and McAmish, L. (1973). ***Journal of Colloid and Interface Science***, 42, p. 112. (apud Mishra and Osseo-Asare (1988))
- Jolivet, J. P.; Thomas, Y.; Taravel, B.; Lorenzelli, V. and Busca, G. (1982). Infrared spectra of cerium and thorium pentacarbonate complexes. ***Journal of Molecular Structure***, 79, p. 403-408.
- Keiser, J. T. and Brown, C. R. (1983). Characterization of the passive film formed on weathering steels. ***Corrosion Science***, 23, p. 251-259.
- Kelsall, G. H.; Yin, Q.; Vaughan, D. J.; England, K. E. R. and Brandon, N. P. (1999). Electrochemical oxidation of pyrite (FeS₂) in aqueous electrolytes. ***Journal of Electroanalytical Chemistry***, 471, p. 116-125.
- King, D. W. (1998). Role of carbonate speciation on the oxidation rate of Fe(II) in aquatic systems. ***Environmental Science & Technology***, 32, p. 2997-3003.
- King, D. W. and Farlow, R. (2000). Role of carbonate speciation on the oxidation of Fe(II) by H₂O₂. ***Marine Chemistry***, 70, p. 201-209.
- Koryta, J.; Dvůrák, J. and Kavan, L. (1993). Principles of electrochemistry. 2nd. England: John Wiley & Sons Ltd., 486p.
- Koslides, T. and Ciminelli, V. S. T. (1992). Pressure oxidation of arsenopyrite and pyrite in alkaline solutions. ***Hydrometallurgy***, 30, p. 87-106.
- Legrand, L.; Savoye, S.; Chausse, A. and Messina, A. (2000). Study of oxidation products formed on iron in solutions containing bicarbonate/carbonate. ***Electrochimica Acta***, 46, p. 111-117.
- Legrand, L.; Abdelmoula, M.; Géhin, A.; Chaussé, A. and Génin, J.-M. R. (2001a). Electrochemical formation of a new Fe(II)-Fe(III) hydroxy-carbonate green rust: characterisation and morphology. ***Electrochimica Acta***, 46, p. 1815-1822.
- Legrand, L.; Sagon, G.; Lecomte, S.; Chausse, A. and Messina, R. (2001b). A Raman and infrared study of a new carbonate green rust obtained by electrochemical way. ***Corrosion Science***, 43, p. 1739-1749.
- Legrand, L.; Maksoub, R.; Sagon, G.; Lecomte, S.; Dallas, J. P. and Chausse, A. (2003). Electroanalytical and Kinetic Investigations on the Carbonate Green Rust-(Fe(III)) Redox System. ***Journal of The Electrochemical Society***, 150, p. B45-B51.
- Legrand, L.; Mazerolles, L. and Chausse, A. (2004). The oxidation of carbonate green rust into ferric phases: solid state reaction or transformation via solution. ***Geochimica and Cosmochimica Acta***, 68, p. 3497-3507.

- Lorenzelli, V. and Busca, G. (1982). Infrared Studies of the Diatomic Molecules O₂, N₂, NO and H₂ adsorbed on Fe₂O₃. **Journal of Molecular Structure**, 80, p. 181-186.
- Lowson, R. T. (1982). Aqueous oxidation of pyrite by molecular oxygen. **Chemical Reviews**, 82, p. 461-497.
- Luther III, G. W. (1987). Pyrite oxidation and reduction: molecular orbital theory considerations. **Geochimica et Cosmochimica Acta**, 51, p. 3193-3199.
- Luther III, G. W.; Kostka, J. E.; Church, T. M.; Sulzberger, B. and Stumm, W. (1992). Seasonal iron cycling in the salt-marsh sedimentary environment: the importance of ligand complexes with Fe(II) and Fe(III) in the dissolution of Fe(III) minerals and pyrite, respectively. **Marine Chemistry**, 40, p. 81-103.
- Luther III, G. W. (1997). Comment on "Confirmation of a sulfur-rich layer on pyrite after oxidative dissolution by Fe(III) ions around pH 2" by K. Sasaki, M. Tsunekawa, T. Ohtsuka, and H. Konno. **Geochimica et Cosmochimica Acta**, 61, p. 3269-3271.
- Majzlan, J.; Navrotsky, A. and Schwertmann, U. (2004). Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite (~Fe(OH)₃), schwertmannite (~Fe(OH)_{3/4}(SO₄)_{1/8}), and e-Fe₂O₃. **Geochimica et Cosmochimica Acta**, 68, p. 1049-1059.
- Markov, L.; Blaskov, V.; Klissurski, D. and Nikolov, S. (1990). The thermal decomposition mechanism of iron(III) hydroxide carbonate to alpha-Fe₂O₃. **Journal of Materials Science**, 25, p. 3096-3100.
- Massey, M. J.; Baier, U.; Merlin, R. and Weber, W. H. (1990). Effects of pressure and isotopic substitution on the Raman spectrum of alpha-Fe₂O₃: Identification of two-magnon scattering. **Physical Review B**, 41, p. 7822-7827.
- Mazzetti, L. and Thistlethwaite, P. J. (2002). Raman spectra and thermal transformations of ferrihydrite and schwertmannite. **Journal of Raman Spectroscopy**, 33, p. 104-111.
- McKibben, M. A. and Barnes, H. L. (1986). Oxidation of pyrite in low temperature acidic solutions: Rate laws and surface textures. **Geochimica et Cosmochimica Acta**, 50, p. 1509-1520.
- Millero, F. J., Sotolongo, S.; Izaguirre, M. (1987). **Geochimica et Cosmochimica Acta**, 51, p. 793-801. *apud* King (1998).
- Millero, F. J. and Izaguirre, M. (1989). Effect of ionic strength and ionic interactions on the oxidation of Fe(II). **Journal of Solution Chemistry**, 18, p. 585-599.
- Millero, F. J. and Hawke, D. J. (1992), **Marine Chemistry**, 40, p. 19-48. *apud* King, 1998.
- Mishra, K. K. and Osseo-Asare, K. (1988). Aspects of the interfacial electrochemistry of semiconductor pyrite (FeS₂). **Journal of the Electrochemical Society**, 135, p. 2502-2509.
- Mishra, K. K. and Osseo-Asare, K. (1992). Electroreduction of Fe⁺³, O₂, and Fe(CN)₆³⁻ at n-

- pyrite (FeS_2) surface. ***Journal of the Electrochemical Society***, 139, p. 3116-3120.
- Monte, M. B. M.; Lins, F. F. and Oliveira, J. F. (1997). Selective flotation of gold from pyrite under oxidizing conditions. ***International Journal of Mineral Processing***, 51, p. 255-267.
- Moses, C. O.; Nordstrom, D. K.; Herman, J. S. and Mills, A. L. (1987). Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. ***Geochimica et Cosmochimica Acta***, 51, p. 1561-1571.
- Moses, C. O. and Herman, J. S. (1991). Pyrite oxidation at circumneutral pH. ***Geochimica et Cosmochimica Acta***, 55, p. 471-482.
- Music, S.; Gotic, M. and Popovic, S. (1993). X-ray diffraction and Fourier transform-infrared analysis of the rust formed by corrosion of steel in aqueous solutions. ***Journal of Materials Science***, 28, p. 5744-5752.
- Music, S.; Nowik, I.; Ristic, M.; Orehovec, Z. and Popovic, S. (2004). The Effect of Bicarbonate/Carbonate ions on Formation of Iron Rust. ***Croatica Chemica Acta***, 77, p. 141-151.
- Nakamoto, K. (1997) Infrared and Raman Spectra of Inorganic and Coordination Compounds – Part B. 5th edition. New York: John Wiley & Sons, 384p.
- Naumov, G. B.; Ryzhenko, B. N. and Khodakovskiy, I. L. (1974). Handbook of Thermodynamic Data. Moscow, U.S. Geological Survey,
- Nicholson, R. V.; Gillham, R. W. and Reardon, E. J. (1988). Pyrite oxidation in carbonate-buffered solution: 1. Experimental kinetics. ***Geochimica et Cosmochimica Acta***, 52, p. 1077-1085.
- Nicholson, R. V.; Gillham, R. W. and Reardon, E. J. (1990). Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. ***Geochimica et Cosmochimica Acta***, 54, p. 395-402.
- Oblonsky, L. J. and Devine, T. M. (1997). Corrosion of carbon steels in CO_2 -saturated brine a surface enhanced Raman spectroscopic. ***Journal of the Electrochemical Society***, 144, p. 1252-1260.
- Odziemkowski, M. S.; Schuhmacher, T. T.; Gillham, R. W. and Reardon, E. J. (1998). Mechanism of oxide film formation on iron simulating groundwater solutions: raman spectroscopy study. ***Corrosion Science***, 40, p. 371-389.
- Osseo-Asare, K. (1992). Semiconductor electrochemistry and hydrometallurgical dissolution processes. ***Hydrometallurgy***, 29, p. 61-90.
- Osseo-Asare, K. (1993). Oxidants and catalysts in the aqueous dissolution of metal sulfides: influence of electronic structure on reactivity. In: J. B. Hiskey and G. W. Warren. ***Hydrometallurgy, Fundamentals Technology and Innovation***. AIME, TMS: p.173-187.
- Osseo-Asare, K. (2005). ***Unpublished paper***.
- Parfitt, R. L.; Gaast, S. J. v. d. and Childs, C. W. (1992). A structural model for natural

- siliceous ferrihydrite. **Clays and Clay Minerals**, 40, p. 675-681.
- Reedy, B. J.; Beattie, J. K. and Lowson, R. T. (1991). A vibrational spectroscopic ^{18}O tracer study of pyrite oxidation. **Geochimica et Cosmochimica Acta**, 55, p. 1609-1614.
- Rimstidt, J. D. and Vaughan, D. J. (2003). Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. **Geochimica et Cosmochimica Acta**, 67, p. 873-880.
- Rintoul, L.; Crawford, K.; Shurvell, H. F. and Fredericks, P. M. (1997). Surface-enhanced Raman scattering of inorganic oxoanions. **Vibrational Spectroscopy**, 15, p. 171-177.
- Rosso, K. M., Becker U., Hochella Jr., M. F. (1999). The interaction of pyrite {100} surface with O_2 and H_2O : Fundamental oxidation mechanism. **American Mineralogist**, 84, p. 1549-1561.
- Sasaki, K. (1997). Raman study of the microbially mediated dissolution of pyrite by *Thiobacillus ferrooxidans*. **The Canadian Mineralogist**, 35, p. 999-1008.
- Savoye, S.; Legrand, L.; Sagon, G.; Lecomte, S.; Chausse, A.; Messina, R. and Toulhoat, P. (2001). Experimental investigation on iron corrosion products formed in bicarbonate/carbonate- containing solutions at 90°C . **Corrosion Science**, 43, p. 2049-2064.
- Shim, S. and Duffy, T. S. (2002). Raman spectroscopy of Fe_2O_3 to 62 GPa. **American Mineralogist**, 87, p. 318-326.
- Shoval, S., Gaft, M., Panczer, G. (2003). Luminescence of Cr(III) in natural and calcinated diaspore. **J. of Thermal Analysis and Calorimetry**, 71, p. 699-706.
- Singer, P. C. and Stumm, W. (1970). Acidic mine drainage: the rate-determining step. **Science**, 167, p. 1121-.
- Smith, E. E. and Shumate, K. S. (1970). The sulfide to sulfate reaction mechanism, a study of sulfide to sulfate reaction mechanism as it relates to the formation of acid mine water. **Water Pollution Control Research Series**, 14010FPS02/70.
- Sousa, M. H.; Tourinho, F. A. and Rubim, J. C. (2000). Use of Raman micro-spectroscopy in the characterization of $\text{M(II)Fe}_2\text{O}_4$ (M=Fe, Zn) electric double layer ferrofluids. **Journal of Raman Spectroscopy**, 31, p. 185-191.
- Stenhouse, J. F. and Armstrong, W. M. (1952). The aqueous oxidation of pyrite. **The Canadian Mining and Metallurgical Bulletin**, 49-53.
- Su, C. M. and Suarez, D. L. (1997). In situ infrared speciation of adsorbed carbonate on aluminum and iron oxide. **Clays and Clay Minerals**, 45, p. 814-825.
- Taylor, B. E.; Wheeler, M. C. and Nordstrom, D. K. (1984). Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. **Geochimica et Cosmochimica Acta**, 48, p. 2669-2678.
- Todd, E. C.; Sherman, D. M. and Purton, J. A. (2003). Surface oxidation of pyrite under ambient atmospheric and aqueous (pH = 2 to 10) conditions: Electronic structure and

- mineralogy from X-ray absorption spectroscopy. ***Geochimica and Cosmochimica Acta***, 67, p. 881-893.
- Tributsch, H. (1986). In: Modern Aspects of Electrochemistry, v. 17. Eds.: J. O'M. Bockris, B. E. Conway, and R. G. White. New York: Plenum Press. p. 303. ***apud*** Mishra and Osseo-Asare (1988)
- Usher, C. R., Cleveland Jr, C. A., Strongin, D. R., Schoonen, M.A. (2004). Origin of oxygen in sulfate during pyrite oxidation with water and dissolved oxygen: an in situ total reflectance infrared- spectroscopy isotope study. ***Environ. Sci. Tech.***, 38, 5604-5606.
- Vaughan, D. J. and Craig, J. R. (1978). Mineral Chemistry of Metal Sulfides. New York: Cambridge University Press. ***Apud Osseo-Asare (1992).***
- Vogt, H.; Chattopadhyay, T. and Stolz, H. J. (1983). Complete first-order Raman spectra of the pyrite structure compounds FeS₂, MnS₂, and SiP₂. 44, p. 869-873.
- Wang, S.; Wang, W.; Wang, W.; Jiao, Z.; Liu, J. and Qian, Y. (2000). Characterization and gas-sensing properties of nanocrystalline iron (III) oxide films prepared by ultrasonic spray pyrolysis on silicon. ***Sensors and Actuators***, 69, p. 22-27.
- Watanabe, H.; Gutleben, C. D. and Seto, J. (1994). Sulfate ions on the surface of maghemite and hematite. ***Solid State Ionics***, 69, p. 29-35.
- Weckler, B. and Lutz, H. D. (1998). Lattice vibration spectra. Part XCV. Infrared spectroscopic studies on the iron oxide hydroxides goethite (alfa), akaganéite (beta), lepidocrocite (gama), and feroxyhite(delta). 35, p. 531-544.
- Wei, D. and Osseo-Asare, K. (1997). Semiconductor electrochemistry of particulate pyrite: Mechanisms and products of dissolution. ***Journal Electrochemical Society***, 144, p. 546-553.
- Wen, N. and Brooker, M. H. (1995). Ammonium carbonate, ammonium bicarbonate, and ammonium carbamate equilibria: a Raman study. ***Journal of Physical and Chemistry B***, 99, p. 359-368.
- Wijnja, H. and Schulthess, C. P. (1999). ATR-FTIR and DRIFT spectroscopy of carbonate species at the aged gamma-Al₂O₃/water interface. ***Spectrochimica Acta Part A***, 55, p. 861-872.
- Wijnja, H. and Schulthess, C. P. (2001). Carbonate adsorption mechanism on goethite studied with ATR FTIR, DRIFT and proton coadsorption measurements. ***Soil Science Society of America Journal***, 65, p. 324-330.
- Williamson, M. A. and Rimstidt, J. D. (1994). The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. ***Geochimica et Cosmochimica Acta***, 58, p. 5443-545.

APPENDIX I

Table AI-1

Selected standard free energies of formation (ΔG°_f), for iron, sulphur and carbonate species

– Figure 4.1

Species	Standard free energy (ΔG°_f), kcal/mol [§]	
	25°C	100°C
C	0.000	0.000
Fe	0.000	0.000
FeCO ₃	-162.600 ¹	-157.697
FeO	-58.730	-57.455
Fe ₂ O ₃	-177.413	-172.514
Fe ₃ O ₄	-242.645	-236.494
Fe(OH) ₂	-116.390	-111.488
Fe(OH) ₃	-166.464	-158.844
FeO*OH	-116.484	-112.243
FeS	-24.370	-24.403
FeS ₂	-38.259	-37.550
FeSO ₄	-197.154	-190.897
Fe ₂ (SO ₄) ₃	-540.811	-521.510
H ₂ SO ₄	-164.885	-157.489
S	0.000	0.000
CO ₃ ²⁻ (aq)	-126.173	-116.614
Fe ³⁺ (aq)	-4.107	-2.050
Fe ²⁺ (aq)	-21.875	-21.784
FeO(aq)	-50.715	-47.575
FeO ⁺ (aq)	-53.093	-50.711
FeOH ²⁺ (aq)	-57.830	-54.658
FeOH ⁺ (aq)	-65.845	-62.806
Fe ₂ (OH) ₂ ⁴⁺ (aq)	-111.743	-103.791
FeSO ₄ (aq)	-202.830 ¹	-192.137
Fe ₂ (SO ₄) ₃ (aq)	-536.087	-500.451
FeSO ₄ ⁺ (aq)	-184.657	-175.416
H ₂ CO ₃ (aq)	-148.948	-144.174
HCO ₃ ⁻ (aq)	-140.264	-133.839
H ₂ S(aq)	-6.516	-6.081
HS ⁻ (aq)	2.887	4.863
H ₂ SO ₃ (aq)	-128.553	-124.080
H ₂ SO ₄ (aq)	-177.947	-167.405
H ₂ S ₂ O ₃ (aq)	-128.008	-122.350
H ₂ S ₂ O ₄ (aq)	-147.387	-140.383
H ₂ S ₂ O ₈ (aq)	-266.487	-252.260
HSO ₃ ⁻ (aq)	-126.104	-119.970
HSO ₄ ⁻ (aq)	-180.611	-172.401
S ²⁻ (aq)	20.547	24.215
S ₂ ²⁻ (aq)	19.053	22.688
SO ₃ ²⁻ (aq)	-116.288	-106.615
SO ₄ ²⁻ (aq)	-177.908	-167.269
S ₂ O ₃ ²⁻ (aq)	-123.962	-115.467

[§]Data from HSC Chemistry software database, version 4.0 (HSC Chemistry, 1999), except for marked species (¹) taken from Naumov et al.(1974).

Table AI-2

Selected standard free energies of formation (ΔG°_f), for iron, sulphur and carbonate species

– Figure 4.2

Species	Standard free energy (ΔG°_f), kcal/mol [§]	Species	Standard free energy (ΔG°_f), kcal/mol [§]
Fe	0.000	FeO	-58.590
Fe ₂ O ₃	-177.713	Fe ₂ O ₃ *H ₂ O	-233.238
Fe ₃ O ₄	-242.645	Fe(OH) ₂	-116.300
Fe(OH) ₃	-170.800	FeO*OH	-114.800
Ferrihydrite	-167.70 ¹	FeS ₂	-38.900
FeSO ₄	-196.100	Fe ₂ (SO ₄) ₃	-537.000
H ₂ SO ₄	-128.560	S	0.000
Fe ⁽⁺³⁾	-4.270	Fe ₄ Fe ₂ (OH) ₁₂ CO ₃	-856.980 ³
Fe ⁽⁺²⁾	-22.050	FeOH ⁽⁺²⁾	-54.830
Fe(CO ₃) ₂ ⁽⁻⁾	-283.340 ¹	Fe(OH) ₃ (aq)	-161.900
Fe(OH)CO ₃ (aq)	-207.448 ¹	Fe(OH) ₂ ⁽⁺⁾	-104.700
HCO ₃ ⁽⁻⁾	-140.264	Fe(OH) ₄ ⁽⁻⁾	-193.020
CO ₃ ⁽⁻²⁾	-126.173	Fe ₂ (OH) ₂ ⁽⁺⁴⁾	-111.743
FeHCO ₃ ⁽⁺⁾	-164.310 ²	FeSO ₄ (aq)	-202.830
FeCO ₃ (aq)	-155.720 ¹	FeSO ₄ ⁽⁺⁾	-184.657
Fe(CO ₃) ₂ ⁽⁻²⁾	-284.080 ¹	H ₂ CO ₃ (aq)	-148.948
Fe(OH)CO ₃ ⁽⁻⁾	-199.414 ¹	H ₂ S(aq)	-6.660
FeO ⁽⁺⁾	-53.093	H ₂ SO ₃ (aq)	-128.553
FeO(aq)	-50.715	H ₂ S ₂ O ₃ (aq)	-128.008
FeO ₂ ⁽⁻⁾	-92.642	HSO ₄ ⁽⁻⁾	-180.611
FeOH ⁽⁺⁾	-69.540	S ⁽⁻²⁾	20.547
Fe(OH) ₂ (aq)	-107.330	SO ₄ ⁽⁻²⁾	-177.908
Fe(OH) ₃ ⁽⁻⁾	-148.480		
Fe(OH) ₄ ⁽⁻²⁾	-184.000		
Fe(OH)O(aq)	-105.700		
Fe ₂ (SO ₄) ₃ (aq)	-536.087		
Fe(SO ₄) ₂ ⁽⁻⁾	-364.400		
HS ⁽⁻⁾	2.887		
H ₂ SO ₄ (aq)	-177.947		
HSO ₃ ⁽⁻⁾	-126.104		
HS ₂ O ₃ ⁽⁻⁾	-127.185		
SO ₃ ⁽⁻²⁾	-116.288		
S ₂ O ₃ ⁽⁻²⁾	-123.692		

[§]Data from HSC Chemistry software database, version 4.0 (HSC Chemistry, 1999), except for marked species (*) taken from Naumov et al.(1974).

1 – Bruno and Duro (2000) and Hummel (2000)

2 – King (1998)

3 – Drissi et al. (1995)

APPENDIX II

Sizing distribution of unreacted pyrite ($< 38 \mu\text{m}$).

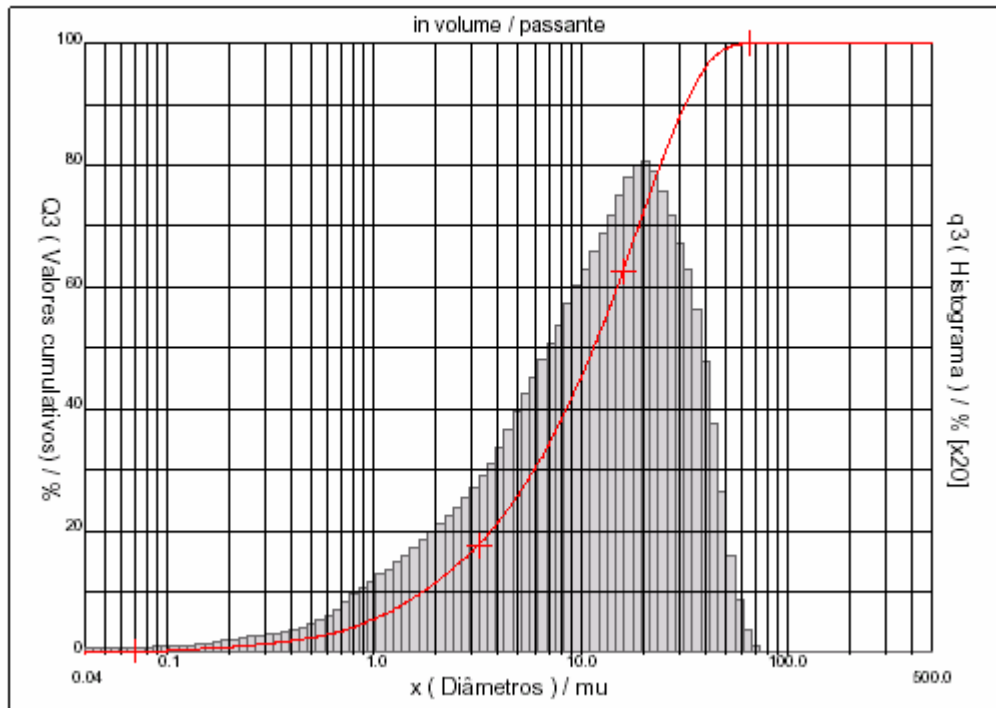


Figure All -1 – Sizing distribution of unreacted pyrite.

APPENDIX III

Table AIII.1

Band positions and FWHM for spectra of pyrite and pyrite after laser pretreatment (Figure 4.24)

<i>Pyrite</i>	
ν (cm⁻¹)	FWHM (cm⁻¹)
343	2.06
350	2.18
376	0.53
379	2.30
430	4.05
<i>Pyrite after laser treatment</i>	
225	6.5
244	8.5
291	11.8
299	11.3
407	18.2
493	30.5
608	23.6
658	38.4

Table AIII.2

Band positions and FWHM for spectrum mineral hematite (Figure 4.25)

ν (cm⁻¹)	FWHM (cm⁻¹)
227	5.3
246	6.3
293	7.2
297	11.8
412	15.8
498	54.1
612	21.8
664	47.2
1268	67.9
1321	59.4
1525	29.7

APPENDIX IV

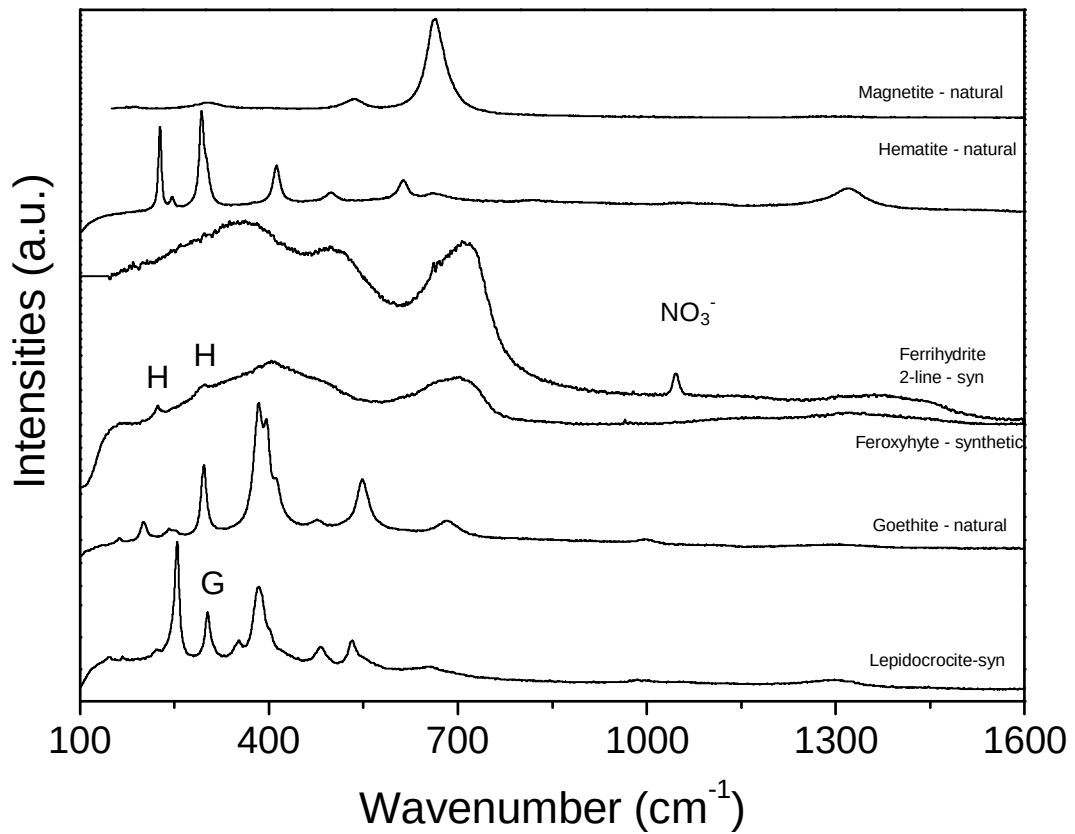


Figure AIV-1– Reference Raman spectra for iron oxides and hydroxides natural samples or synthesized. G – Band attributed to presence of goethite; H – bands attributed of hematite. Nitrate from synthesis solution. Raman conditions: Magnetite (10s, 10x, filter D1); Goethite (20s, 5x, filter D1); Hematite (10s, 10x, filter D2); Ferrihydrite, Feroxyhite and Lepidocrocite (300s, 10x, filter D2).