ON THE ROLE OF LOW-CONCENTRATION NITRITE
IN OXIDATIVE-LEACHING
WITH OXYGEN

by
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During the last two decades the NSC (Nitrogen Species Catalyzed) Process (Anderson, 2003) has received a great deal of attention for hydrometallurgical processing of concentrates from a variety of gold-bearing complex-sulfide ores, as well as gold-bearing by-products from several metallurgical processes. However, the fundamental chemical-reaction mechanisms responsible for the enhancements that the process offers, relative to existing competitive-processes, have only been addressed cursorily. The primary focus of the research reported in this thesis was to provide elucidation of the reaction mechanisms in the oxidation of ferrous ion, to ferric ion, by oxygen in the presence of low-concentration nitrite in a sulfuric-acid electrolyte whereby a dramatic enhancement in the oxidation rate is realized compared to when only oxygen is employed. To this end, the cyclic (“catalytic”) reaction mechanisms involving oxy-nitrogen species (HNO₂, N₂O₃, NO, and NO₂) as well as the ferrous-nitrosyl complex ([Fe(NO)]²⁺) were explored by providing the concentration-time trajectories of the prominent species (Fe²⁺, Fe³⁺, NO, NO₂, NO₃⁻) in the system. REDOX potential measurements and chemical analysis were performed. Preliminary (sealed system) and definitive (pressurized system with oxygen gas) experiments were conducted with FeSO₄–NaNO₂–H₂SO₄ electrolytes to visually observe and monitor the oxidation rate of ferrous to ferric at 25°C and 80°C. Dissolution of chalcopyrite mineral with nitrite at 80°C was also conducted. A mathematical chemical-reaction rate-model was developed to simulate the concentration-time trajectory of the prominent species in the system. The simulations were performed by employing COMSOL software for numerical solution of the model equations.

The applicability of the results of the research, conducted and reported in this thesis, to the leaching of gold-bearing complex sulfides by the NSC process is addressed in Section 6.2 of the Conclusion.
The results of the research conducted have shown that:

1.A. The oxidation rate of ferrous to ferric was dramatically higher, approximately (400) times, at high pressure ($p_\text{O}_2 \approx 4.0 \text{ atm.}$) in the presence of small concentrations of nitrite (3.89 mM; 266 mg NaNO$_2$ per liter and 4.5 mM; 311 mg NaNO$_2$ per liter) compared to when nitrite was absent. In contrast, these same small (molar) concentrations of nitrate did not result in enhanced oxidation-rates; this was readily apparent, since upon addition of the nitrate salt (KNO$_3$), there was no visual evidence of the formation of the ferrous-nitrosyl complex (FeNO$_2^+$), indicating that nitric oxide was not present at a significant concentration level in the electrolyte. This behavior was attributed to a proton activity in the electrolyte that was not high enough to promote the formation of the reactive HNO$_3$ species in the electrolyte – increasing the sulfuric acid concentration from 1.0 M to 3.0 M resulted in oxidation of ferrous ion and concomitant formation of ferrous-nitrosyl complex. While ferrous is oxidized by nitrite, higher potential values were obtained in shorter time with 4.5 mM NO$_2^-$ relative to 3.89 mM NO$_2^-$ and the active REDOX couple was attributed to HNO$_2$/NO$_3^-$ with higher concentration of nitrite. The nitrogen species that evolve in the electrolyte from the sodium-nitrite reagent (NO$_2^-$, NO, NO$_2$, NO$_x$) were all oxidized to nitrate (N(V)).

The experiments performed on oxidation of ferrous with oxygen and with nitrite at 80°C indicated that oxidation rate of ferrous with nitrite was approximately three times higher compared to when the oxidation is performed at 25°C. The black-green color of ferrous nitrosyl complex progressively became less intense over a period of 60 minutes (1 h) at this higher temperature. At 25°C the complex persisted for approximately 3 hours.

Preliminary experiments had revealed that when a small leak of gas from the gas-phase above the electrolyte was present in the reactor (IBM cell) gaseous nitrogen species (NO$_{(g)}$ and NO$_2(g)$) was allowed from the gas space at barometric pressure, REDOX potential indicating concentration ratio of ferrous to ferric decreased. However, the concentration of NO$_{(g)}$ and NO$_2(g)$
in the gas phase at high pressure were three orders of magnitude smaller that the initial nitrite concentration and gas concentrations decreased continuously. These results of analyses were interpreted as the oxidation of NO\(_{\text{g}}\) with oxygen to NO\(_{2\text{g}}\). Then NO\(_{2\text{g}}\), dissolved in the electrolyte, is disproportionated to HNO\(_2\) and NO\(_3^-\).

1.B. Computer simulations (COMSOL software) were performed to mimic the laboratory bench scale experiments provided concentration-time profiles of eight (8) species (Fe\(^{2+}\), Fe\(^{3+}\), HNO\(_2\), N\(_2\)O\(_3\), NO, NO\(_2\), NO\(_3^-\), FeNO\(_2^+\)). The oxygen (O\(_2\)) partial pressure was maintained at either 1.0 atm or approximately 4.0 atm. (the concentration in the electrolyte was correlated to the system temperature according to the (temperature dependent) Henrian Equilibrium Coefficient) and the proton activity (H\(^+\) concentration) was maintained at a value commensurate with the H\(_2\)SO\(_4\) concentration of the electrolyte (thus the sulfuric acid served as an Ionic Strength buffer in the system). These simulations revealed that the time-scale of the predictions, focused selectively on the conversion of ferrous to ferric, was six (6) times shorter than that observed in the laboratory experiments. It was therefore evident that the rate coefficients for the set of simultaneous reactions, obtained from the literature and are the constituents of the mathematical model, will require significant reassessment in order for the two “experiments” (physical and virtual) to be aligned. Nonetheless, an “optimum” NaNO\(_2\) (HNO\(_2\)) concentration was determined from an objective function designed on the basis of two competing-considerations: the cost of the nitrite reagent as manifested by the (feed) concentration employed in the processing scheme, and the processing costs as manifested by the time for 99.9% conversion of ferrous to ferric. Thus, the minimum in the ratio \( \frac{C_{\text{NaNO}_2}}{t_{99.9}} \) (should it exist) would identify the “optimum” concentration of nitrite that should be employed for the oxidation process. Simulation-trials were performed for a range of nitrite concentrations (0.100 mM to 100 mM), from which a minimum in the objective function was identified at a nitrite concentration of 4.5 mM. This concentration was selected for
the nitrite concentration employed in all subsequent laboratory bench-scale experiments as well as COMSOL simulations performed.

In general, the results of the simulation revealed that the (4.5 mM) nitrous acid (via the NaNO₃ feed reagent), in a 1.0M sulfuric acid electrolyte and a pO₂ ~ 4.0 atm, disproportionates to produce N₂O₃, NO, NO₂ and subsequently these oxy-nitrogen species are all oxidized to NO₃⁻. This final nitrate concentration reached the same as the concentration of the feed-nitrite: 4.5 mM; thereby validating the mass-balance closure for the simulation.

The oxidation behavior of ferrous with oxygen (and nitrite absent) was simulated at 25°C and 80°C. The rate coefficient for the oxidation of ferrous with oxygen at 25°C was derived by incorporating the concentration-time profile of the ferrous species obtained from laboratory-scale experiment (DE-1) into the COMSOL Parameter Estimation dialog box. The apparent activation-energy for the ferrous oxidation with oxygen was thus calculated based on an Arrhenius equation by using the rate coefficient at 120°C available in the publication by Baldwin and Van Weert (1996). The rate coefficient was based on a rate-expression that is first order with respect to the partial pressure of oxygen and second order with respect to the ferrous concentration. For these simulations the oxygen concentration in the aqueous electrolyte was determined from the (temperature dependent) Henrian Equilibrium Coefficient. The Parameter Estimation module of the COMSOL software thus determined the apparent activation-energy for ferrous oxidation with oxygen to be 54 kJ.mol⁻¹.

For the simulation of the oxidation rate of ferrous with oxygen at 80°C, rate coefficient was determined based on the activation energy of 54 kJ.mol⁻¹. The results of simulation indicated that the time for (99%) conversion of ferrous to ferric was achieved in 5 hours, which is twenty (20) times higher at 80°C compared to 25°C.

Simulation of ferrous oxidation with 4.5 mM nitrate at 25°C predicted that the ferrous oxidation rate was five (5) times lower compared to when 4.5 mM nitrite was the oxy-nitrogen
species. Ferrous nitrosyl complex increased continuously for 100 minutes and NO production from HNO₂ lasted for 120 minutes. It was interpreted that the catalytic effect of NO complexed with ferrous was prevented due to the presence of ferrous-nitrosyl complex in the electrolyte for a long time.

2. Oxidative leaching of a sample of chalcocite mineral (Cu₂S) (≈0.80g in 100mL of electrolyte) with 4.5 mM nitrite at 80°C and pO₂ ≈ 4.5 atm (P_{Tot} = 60 psig) resulted in an electrolyte (cupric) copper concentration of 0.065 mM, corresponding to 65% dissolution of the mineral sample. after 4 hours. FESEM images of partially-leached, larger (≈60 μm), chalcocite particles revealed islands of coalesced (amorphous) sulfur adjacent to leached regions that exhibited a lamillate grate-like structure. There was no evidence of sulfur entities in the particulate residue collected. It is apparent that the cuprous ion of the chalcocite (Cu₂S) is directly oxidized to cupric while the associated sulfide is oxidized by a two stage process that appears to be related to the particle size of the chalcocite. Thus, in the case of the sulfide there is an intermediate oxidation to elemental (solid) sulfur and subsequent oxidation to sulfate. The role of nitrite in the oxidation of the “sulfur” could not be readily elucidated. Cuprous ion is readily oxidized (homogeneously) in the electrolyte by oxygen and since EDS analysis conducted with the electron microscope, on leached surfaces of the residue sample, revealed a “Cu” to “S” ratio of two to one (2:1) there was no evidence of solid cupric-sulfide (CuS; covolite) being present. Therefore, the sulfide (S²⁻) accompanying the dissociation of the chalcocite (Cu₂S), in principle, can be oxidized either by the “high” oxidation-state oxy-nitrogen species (NO₂⁻, NO₂(aq), and NO₃⁻) or by O₂(aq); stage wise (depending on the particle size), first to S⁰ and then SO₄²⁻, or such that the intermediate S⁰ is short-lived and does not condense on the particle surface. The coalesced islands of sulfur observed (on the “large” particles) could be as a result of surface diffusion between neighboring
sites where the cuprous ion in the lattice was lost due to oxidation to cupric ion while at the same time the sulfide is oxidized to the zero-valence (solid) species.
# TABLE OF CONTENTS

ABSTRACT ......................................................................................................................................... iii  

LIST OF FIGURES ........................................................................................................................... xiii  

LIST OF TABLES ............................................................................................................................ xvi  

ACKNOWLEDGEMENTS ............................................................................................................ xvii  

CHAPTER 1  INTRODUCTION ....................................................................................................... 1  
  1.1 Scope of the Research ................................................................................................ 3  
  1.2 Focus of Research Conducted ............................................................................. 5  
  1.3 Organization of the Thesis .................................................................................... 5  

CHAPTER 2 LITERATURE AND FUNDAMENTALS REVIEW ............................................. 7  
  2.1 Properties and Uses of Gold ............................................................................. 7  
  2.2 Extractive Metallurgy of Gold........................................................................... 8  
    2.2.1 Free Milling Gold-Bearing Ores ................................................................. 10  
    2.2.2 Complex Gold-Bearing Ores ..................................................................... 10  
    2.2.3 Refractory Gold-Bearing Ores ................................................................. 11  
  2.3 Nitric Acid Oxidative Pressure Leaching ............................................................ 13  
  2.4 Nitrogen Species Catalyzed (NSC) Pressure Leaching ....................................... 22  
  2.5 Industrial Applications of NSC Pressure Leach Process ................................... 27  
    2.5.1 Silver-Bearing Copper Concentrates ....................................................... 27  
    2.5.2 Chalcopyrite Concentrates ........................................................................ 29  
    2.5.3 PGM Concentrates .................................................................................... 30  

CHAPTER 3 THEORETICAL CONSIDERATIONS .................................................................. 32  
  3.1 Kinetics of Oxidation of Ferrous Iron by Molecular Oxygen ............................ 32  
  3.2 Kinetics of NOx Species in Acidic Solution ...................................................... 34  
  3.3 Electrochemical Measurements ......................................................................... 38
CHAPTER 4 DETAILS OF EXPERIMENTS PERFORMED ........................................... 42

4.1 Reagents and Mineral Sample ................................................................. 42

4.2 Chemical Analysis Procedure ................................................................ 43

4.2.1 Titanium Analysis .............................................................................. 43

4.2.2 Spectrophotometric Analysis ............................................................... 44

4.2.3 Chemiluminescence (NOx) Gas Analyzer .......................................... 45

4.2.4 Filed Emission Scanning Electron Microscope (FESEM) .................. 45

4.2.5 REDOX Potential Measurement for Fe^{2+}/Fe^{3+} Concentration
    Determination .......................................................................................... 46

4.3 Equipment Details .................................................................................. 47

4.3.1 Electrodes ............................................................................................ 47

4.3.2 Ambient-Pressure Stirred-Reactor ...................................................... 48

4.3.3 Pressurized Stirred-Reactor ............................................................... 49

4.3.4 High Temperature Pressurized Reactor ............................................ 50

4.4 Procedure Employed ............................................................................... 51

4.4.1 Preliminary Experiments (PE) ............................................................. 51

4.4.2 Definitive Experiments (DE) ............................................................... 53

CHAPTER 5 RESULTS AND INTERPRETATION ............................................... 55

5.1 REDOX Potential Measurement for C_{Fe^{2+}}/C_{Fe^{3+}} Determination ....... 55

5.2 Preliminary Experiments (PE) ............................................................... 56

5.2.1 PE-1: Ferrous Oxidation with Sodium Nitrite in
    Controlled-Leak Reactor System ............................................................ 56

5.2.2 PE-2: Ferrous Oxidation with Sodium Nitrite in
    Leak-Tight Reactor System ..................................................................... 57

5.2.3 PE-3: Ferrous Oxidation with Potassium Nitrate in
    Leak-Tight Reactor .................................................................................. 59

5.3 Definitive Experiments (DE) .................................................................. 59
APPENDIX B  REACTION RATE CONSTANTS FOR THE REACTION RATE EXPRESSIONS ................................................................. 100

APPENDIX C  REACTION MECHANISMS FOR NON-ELEMENTARY RATE-EXPRESSIONS PERTAINING TO THE Fe$^{2+}$-HNO$_2$-H$_2$SO$_4$ SYSTEM AT 25°C ......................................................................................... 101

APPENDIX D  DEVELOPMENT OF NET REACTION RATE EXPRESSIONS FROM ELEMENTARY REACTION STEPS FOR REACTION 5, 6, 7 AND 8 ........................................................................................................ 102

APPENDIX E  DEVELOPMENT OF DIFFERENTIAL EQUATIONS FOR COMSOL SIMULATION ................................................................................................................................. 106

APPENDIX F  RESULTS OF THE ELECTROCHEMICAL MEASUREMENTS AND CHEMICAL ANALYSES FOR LABORATORY-SCALE EXPERIMENTS .................................................................................. 108

APPENDIX G  CONCENTRATION OF ACTIVE SPECIES IN 1 M H$_2$SO$_4$ ELECTROLYTE OBTAINED BY COMSOL-AIDED COMPUTER SIMULATION .................................................................................. 114

APPENDIX H  CHALCOCITE MINERAL DATA .............................................................................................................................. 115

BIOGRAPHICAL SKETCH ................................................................................................................................................................. 116
<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>General pretreatment processesing flowsheet applied for refractory ores</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Copper concentrate leach by nitric acid</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>NO and NO₂ gases distributions as a function of HNO₃ concentration at 95°C</td>
<td>18</td>
</tr>
<tr>
<td>2.4</td>
<td>Sunshine Mine Silver Refinery Flow Sheet</td>
<td>28</td>
</tr>
<tr>
<td>2.5</td>
<td>Flowsheet of NSC Partial Sulfide Oxidation of Gold Bearing Chalcopyrite</td>
<td>29</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic representation of a mixed potential system</td>
<td>40</td>
</tr>
<tr>
<td>3.2</td>
<td>Snapshot of COMSOL Reaction Engineering Lab GUI and Reaction Settings dialog box</td>
<td>41</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic of IBM PYREX cell showing electrodes in place</td>
<td>48</td>
</tr>
<tr>
<td>4.2</td>
<td>Electrochemical system including IBM PYREX cell and Standard pH meter</td>
<td>49</td>
</tr>
<tr>
<td>4.3</td>
<td>High Pressure PYREX vessel and titration set-up</td>
<td>50</td>
</tr>
<tr>
<td>4.4</td>
<td>High Temperature Pressurized PYREX vessel, IR-heat lamp and water bath</td>
<td>51</td>
</tr>
<tr>
<td>5.1</td>
<td>Measured potential as a function of activity ratios of ferrous to ferric ions in the H₂SO₄ electrolyte</td>
<td>56</td>
</tr>
<tr>
<td>5.2</td>
<td>Measured potential as a function of time for Experiment No: PE-1</td>
<td>57</td>
</tr>
<tr>
<td>5.3</td>
<td>Measured potential as a function of time for Experiment No: PE-2</td>
<td>58</td>
</tr>
<tr>
<td>5.4</td>
<td>Time trajectories of concentration of Ferrous in solution for Experiment No: DE-1</td>
<td>60</td>
</tr>
<tr>
<td>5.5</td>
<td>Time trajectories of concentration of Ferrous in solution for Experiment No: DE-2 and DE-3A and DE-3B</td>
<td>61</td>
</tr>
<tr>
<td>5.6</td>
<td>Time trajectories of concentration of Nitrite, Nitrate and Ferrous in solution for Experiment No: DE-3A and DE-3B</td>
<td>62</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.7</td>
<td>Time trajectories of concentration of NO(_{(g)}) and NO(_2(g)) in the gas phase above nitrite electrolyte for Experiment No: DE-3C</td>
<td>64</td>
</tr>
<tr>
<td>5.8</td>
<td>Measured potential as a function of time for Experiment No: DE-4</td>
<td>65</td>
</tr>
<tr>
<td>5.9</td>
<td>Measured potential as a function of time for Experiment No: DE-5A</td>
<td>66</td>
</tr>
<tr>
<td>5.10</td>
<td>Time trajectories of concentration of Ferrous in solution for Experiment No: DE-5A</td>
<td>66</td>
</tr>
<tr>
<td>5.11</td>
<td>Measured potential as a function of time for Experiment No: DE-5B</td>
<td>67</td>
</tr>
<tr>
<td>5.12</td>
<td>Time trajectories of concentration of cupric in solution for Experiment No: DE-6A and DE-6B</td>
<td>68</td>
</tr>
<tr>
<td>5.13</td>
<td>FESEM photomicrograph of unleached chalcocite at magnification 300X</td>
<td>68</td>
</tr>
<tr>
<td>5.14</td>
<td>FESEM photomicrograph of unleached chalcocite at magnification 1000X</td>
<td>69</td>
</tr>
<tr>
<td>5.15</td>
<td>FESEM photomicrograph of unleached chalcocite at magnification 2500X</td>
<td>70</td>
</tr>
<tr>
<td>5.16</td>
<td>FESEM photomicrograph of reacted chalcocite particles with nitrite at magnification 300X</td>
<td>71</td>
</tr>
<tr>
<td>5.17</td>
<td>FESEM photomicrograph of reacted chalcocite particles with oxygen at magnification 2500X</td>
<td>71</td>
</tr>
<tr>
<td>5.18</td>
<td>FESEM photomicrograph of reacted chalcocite particles with nitrite at magnification 2000X</td>
<td>72</td>
</tr>
<tr>
<td>5.19</td>
<td>FESEM photomicrograph of reacted chalcocite particles with oxygen at magnification 5000X</td>
<td>73</td>
</tr>
<tr>
<td>5.20</td>
<td>Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation, Initial electrolyte concentrations: (C_{\text{NaNO}<em>2} = 4.50 \text{ mM}, C</em>{\text{H}_2\text{SO}_4} = 1.0 \text{ M})</td>
<td>75</td>
</tr>
<tr>
<td>5.21</td>
<td>Time trajectories of concentration of ferrous and ferric ions in solution obtained by COMSOL-aided computer simulation, Initial electrolyte concentrations: (C_{\text{FeSO}<em>4} = 0.1 \text{ M}, C</em>{\text{H}_2\text{SO}_4} = 1.0 \text{ M})</td>
<td>76</td>
</tr>
<tr>
<td>5.22</td>
<td>Time trajectories of concentration of ferrous and ferric ions in solution obtained by COMSOL-aided computer simulation for 80°C, Initial electrolyte concentrations: (C_{\text{FeSO}<em>4} = 0.1 \text{ M}, C</em>{\text{H}_2\text{SO}_4} = 1.0 \text{ M})</td>
<td>76</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>5.23</td>
<td>Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation, Initial electrolyte concentrations: ( C_{\text{FeSO}<em>4} = 0.1 \text{ M} ), ( C</em>{\text{NaNO}_2} = 3.89 \text{ mM} )</td>
<td>78</td>
</tr>
<tr>
<td>5.24</td>
<td>Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation, Initial electrolyte concentrations: ( C_{\text{FeSO}<em>4} = 0.1 \text{ M} ), ( C</em>{\text{NaNO}<em>2} = 4.50 \text{ mM} ), ( C</em>{\text{H}_2\text{SO}_4} = 1.0 \text{ M} )</td>
<td>79</td>
</tr>
<tr>
<td>5.25</td>
<td>Objective function, Min ( z ), as function of electrolyte concentration</td>
<td>80</td>
</tr>
<tr>
<td>5.26</td>
<td>Comparison of ( \text{Fe}^{2+} ) concentration-time trajectories determined by COMSOL-aided simulation with that derived from analysis of samples collected from Experiment No: DE-3</td>
<td>81</td>
</tr>
<tr>
<td>5.27</td>
<td>Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation, Initial electrolyte concentrations: ( C_{\text{KNO}<em>3} = 4.50 \text{ mM} ), ( C</em>{\text{H}_2\text{SO}_4} = 1.0 \text{ M} )</td>
<td>82</td>
</tr>
<tr>
<td>5.28</td>
<td>Concentration-Time profile for ferrous oxidation with ( \text{NO}_3^- ) (( \text{KNO}_3 )) and ( \text{HNO}_2 ) (( \text{NaNO}_2 )) predicted by COMSOL-aided computer simulation</td>
<td>83</td>
</tr>
<tr>
<td>5.29</td>
<td>Correlation of recorded REDOX potential obtained from ex-situ REDOX measurement conducted for Experiment No: DE-3 with REDOX potentials derived from COMSOL-aided computer simulation</td>
<td>84</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Gold Content of Naturally Occuring Gold Minerals</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Mineralogical Techniques for Locating Gold in the Ore</td>
<td>9</td>
</tr>
<tr>
<td>2.3</td>
<td>Leaching Systems for Gold Leaching</td>
<td>13</td>
</tr>
<tr>
<td>2.4</td>
<td>Standard Potentials of Relevant REDOX Reaction</td>
<td>27</td>
</tr>
<tr>
<td>3.1</td>
<td>Kinetics Data of Ferrous Iron Oxidation by Molecular Oxygen</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>obtained from literature</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>List of Chemical Reagents and Mineral Used in Experiments</td>
<td>42</td>
</tr>
<tr>
<td>4.2</td>
<td>Specifications listed in the Standard Methods of Water Analysis</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>with Hach Spectrophotometer</td>
<td></td>
</tr>
</tbody>
</table>
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CHAPTER 1

INTRODUCTION

Dissolution of gold using cyanide as a complexing ligand has been practiced for over 120 years since it was patented in 1888 by McArthur and Forrest (MacArthur et al., 1888). Cyanide has featured prominently as a leach-reagent at gold mines because of the strong gold-complexes that it forms and its relatively low cost (Hilson and Monhemius, 2006). The debate surrounding the use of cyanide in the mining industry has fuelled considerable investigation into the development of more environmentally benign, alternative gold leaching technologies which use chlorine, thiourea, thiocyanate, thiosulfate, bromine, and iodine as reagents as described by Marsden and House in their recent text “The Chemistry of Gold Extraction” (Marsden and House, 2006).

The “chlorination” process requires expensive materials of construction due to its highly corrosive nature. This process is not widely used due to the poor overall economics it offers (Marsden and House, 2006).

Thiourea is often specified today for operations where environmental regulations are particularly stringent. Although it is relatively non-toxic, it is suspected to be a carcinogen. High consumption characteristics of thiourea contribute to it being more costly than that of cyanide, as the complexing ligand.

Thiocyanate operations are conducted at a pH between 2.0 to 3.0. Silver, if present, cannot be extracted and this precious metal value does not contribute to favorable economics. In contrast, the thiosulfate process employs an alkaline electrolyte and is performed over a relatively wide (alkaline) pH range. Bromine and iodine systems perform at higher rates than the cyanide/oxygen system but are seldom economically viable. Similar to the chlorination process,
high cost construction materials are required for these halogens as well. Thus, it is seen that, not surprisingly, the process economics become the deciding consideration in the specification of the process to be adopted.

Although those lixiviants can provide for the basic chemical-extraction requirements, pre-treatment process are often necessary to modify the structure of "refractory" gold bearing ores in order to provide for access of the lixiviant to the contained gold species. Nitric acid pressure-leaching, one of several pretreatment methods, was proposed at the beginning of the 20th century by Kingsley (1909) for extraction of metal values from sulfide ores. In later studies, researchers employed sulfuric acid to which a small amount of nitric acid was added, with air as oxidant, to solubilize sulfide minerals with the simultaneous recovery of elemental sulfur (Bjorling and Kolta, 1966). The first, patented, commercial process using sulfuric/dilute nitric acid to leach silver and copper bearing ores was employed by Sunshine Mining Company, (Caldon, 1978). Subsequently, "nitric-acid" leaching was practiced under various process acronyms such as NSL (Brennecke et al., 1981), NITROX (Van Weert et al., 1986), Arseno and REDOX (Beattie, 1989).

More recently, NSC (Nitrogen Species Catalyzed pressure leaching) process, – sulfuric-acid oxidative pressure-leach – was commissioned and operated successfully on an industrial scale (Anderson et al., 1994; Anderson, 1992), at Sunshine Precious Metals, in Kellogg, Idaho. It is reported that silver and copper were recovered successfully from a complex sulfide concentrate with this nitrous/sulfuric acid leach process.

The NSC pretreatment process, which operates at lower temperatures and pressures (compared to other competitive processes), in conjunction with alkaline sulfide leaching, it is claimed stands as an economic and engineering advancement in pressure leaching and non-
cyanide treatment of gold ores and concentrates, especially in the treatment of gold bearing chalcopyrite ores and concentrates (Anderson, 2003). The application and economics of this technology for extraction of gold, silver, palladium, rhodium, zinc, germanium, gallium, cobalt, copper and nickel were discussed in detail in the article authored by the inventor (Anderson, 2008).

Although the NSC process fundamentals describing the so called catalytic effect of small concentrations of nitrites were reported in the articles and patents cited, the reaction mechanism by which the nitrogen species in a leaching system containing ferrous ions (for example) has not been definitively elucidated in the open literature as of 2009. It was therefore in an effort devoted to this objective that the research reported in this Thesis was focused. Specifically: elucidation of the reaction mechanisms in the oxidation of ferrous ion, to ferric ion, by oxygen in the presence of low-concentration nitrite in a sulfuric-acid electrolyte whereby a dramatic enhancement in the oxidation rate is realized compared to when only oxygen is employed. Economic analyses of the process have been addressed in several publications by Anderson (2003), and are not presented in this thesis.

1.1 Scope of the Research

Already alluded to, during the last four decades there has been significant research conducted on alternatives to: i) cyanidation-leaching for recovery of gold from gold bearing ores, and ii) pretreatment processing-strategies for modifying “refractory” gold-ores. In most instances the impetus that fueled this research stemmed from the potential hazard associated with the use of sodium cyanide in the gold-mining industry. Needless to say, improper management of cyanide can have a detrimental impact on the environment surrounding mine sites. A vast collection of papers have been published on these several replacement candidates (thiosulfate, thiocyanate,
halides, thiosulfate, and polysulfides). Also, there are ores that are not amenable to conventional cyanide leaching, and pretreatment of the ore is necessary before cyanidation. Recently (1990's), Nitrogen Species Catalyzed (NSC) Pressure Leaching was proposed as a potential alternative process which is capable of providing for: “modest” process-temperatures and -pressures (125-170°C and 6-10 atm.) as well as with lower oxygen-demand (associated with partial oxidation of sulfide to zero-valence sulfur). The process employs sulfuric acid to achieve a high proton-activity and oxygen/air as the primary oxidant with small nitrite concentration serving, in a broad (non-specific) sense, what must be the “catalytic” role.

During the past three decades, since the discovery of the “catalytic” role of nitric acid/nitrite in the leaching of refractory gold ores, the mechanism for the enhancement of oxidation by oxygen gas has been investigated by several researchers. To date, the proposed mechanisms reported in the open literature have been primarily speculative. The research conducted for this Thesis is intended to provide for definitive elucidation of the NSC Pressure Leach Pretreatment Process fundamentals and cyclic (“catalytic”) pathway involved in the leaching process. Reaction mechanisms involving the oxy-nitrogen species, which have been considered, include: nitrous acid (HNO₂) including its anhydride (N₂O₃), nitric oxide and nitrogen dioxide (NO and NO₂), the disproportionation behavior that nitrous acid and nitrogen dioxide exhibit, as well as the ferrous-nitrosyl complex ([Fe(NO)]²⁺) have been considered. The formation of nitrate (NO₃⁻) and the role of nitrite and nitrosonium ions (NO₂⁻ and NO⁺) in the system have also been addressed. Simultaneous reaction-rate expressions have been developed to provide for mathematical simulation of the oxidation process including the cyclic process-interaction between nitric oxide and oxygen. A robust software module (COMSOL) has provided the engine for performing these modeling-experiments by which the physical experiments performed could be simulated.
1.2 **Focus of Research Conducted**

In the research conducted for this thesis, the role of nitrite for enhancement of the oxidation of ferrous to ferric in a sulfuric-acid electrolyte was investigated. The conversion of ferrous ion to ferric ion as a function of time was determined in laboratory bench-scale experiments by measuring the ferrous concentration in the system, either by titration or by electrochemical REDOX potential measurements. Subsequently, the COMSOL software computer-simulations derived from chemical-kinetics rate-models developed as a component of the research were employed to provide concentration-time profiles for the complete set of species comprising the system. Both qualitative and quantitative correlation between the performance obtained from the laboratory experiments and that obtained by the computer simulations were performed. A statement on the applicability of the result of the research conducted to leaching of gold-bearing complex sulfide by the NSC process is provided in Section 6.2 of Chapter 6.

1.3 **Organization of the Thesis**

The thesis is comprised of six chapters:

Chapter 1: Provides brief background on the hydrometallurgical techniques for processing of gold ores. A scope of the research topic is presented followed by the objectives of the research conducted. This chapter is concluded with details on the organization of the manuscript.

Chapter 2: Contains properties/uses of gold and a compilation of well-established acidic oxidative pressure-leaching processes including details on fundamental aspects of “Nitrogen Species Catalyzed” (NSC) Pressure Leaching that have been published.

Chapter 3: Contains a selection of theoretical considerations directly related to the research, including the kinetic aspects pertaining to the NSC process.
Chapter 4: Provides details related to the laboratory bench-scale experiments performed including a listing of the experiments conducted.

Chapter 5: The results of the experiments are reported together with interpretation/discussion of the observations.

Chapter 6: This is the conclusion to the thesis; consists of a summary and retrospective of the research conducted, enumerated conclusions and recommendations of topics which warrant further study.
CHAPTER 2
LITERATURE AND FUNDAMENTALS REVIEW

The NSC process was developed for pretreatment of refractory gold-bearing ores/concentrates. Consequently, since gold recovery is the overall objective of this hydrometallurgical process, this chapter first provides a brief synopsis on physical and chemical properties, application/uses of gold. This is followed by a concise review of the extractive metallurgy of gold-bearing ores. A comprehensive literature review of nitric acid oxidative pressure-leaching processes is then provided. Early research efforts on oxidation of metals with nitric/sulfuric acid resulted in the development of “Nitrogen Species Catalyzed” (NSC) Pressure Leaching and the details on the fundamentals aspects of NCS Pressure Leaching Process that have been published are also included.

2.1 Properties and Uses of Gold

Gold (Au), atomic number 79 and average atomic mass of 196.9665 g/mol, is a soft and ductile metal with a characteristic yellow color. The Vickers hardness is the range of 40 to 95 kg/mm² and Mohs hardness numbers of 2.5 to 3.0. These unusual physical properties are a result of the face-centered cubic crystal structure. The freezing/melting point of gold is 1064 °C and its vapor pressure at 2808°C (its normal boiling point) is 1 atm. It is unaffected by air, water, alkalis and acids, with the exception of “aqua regia”, HNO₃/HCl. The two most common gold compounds are auric chloride (AuCl₃) and chlorauric acid (HAuCl₄) (Marsden, 2006).

Gold is primarily used for; coinage and jewellery. Coinage gold (USA) or standard gold (UK) contains gold and copper in slightly different amounts, while Australian gold (Australia) contains silver instead of copper. Green gold which is used for jewellery is an alloy of gold,
silver, and copper, and is graded from 14 to 18 karats. Other uses for gold include: those related to the textile industry; gold flake is used for a radiation-control coating for spacecraft, in electronic tubes, as gold-plated grid wire, for high conductivity and suppressing secondary emissions; gold powder and gold sheet is used for soldering semiconductors, with gold providing good wettability on silicon at 371°C (725°F). Gold is also used as a plating material, where sodium gold-cyanide \([\text{NaAu(CN)}_2]\) serves as the (aqueous) gold plating electrolyte. The plating is characterized by excellent chemical resistance and electrical properties, but lacks wear-resistance; this is achieved by utilizing gold-indium deposition for applications where this property is required. Gold alloys are also employed in several applications: for example; gold-gallium and gold-antimony are common in the electronic industry (primarily as wire). Alloys are also used for dental applications referred to as dental gold, where gold is alloyed with silver, platinum and also palladium. Iridium is also incorporated as a hardening alloy constituent (Marsden, 2006).

2.2 Extractive Metallurgy of Gold

Gold is widely distributed in the earth’s crust at a background level of 0.03 g/1000 kg (0.03 ppm by weight). Its inertness and high density are responsible for it being concentrated in streambeds, either as small flakes or in larger nuggets, from which it may be recovered by panning. Gold is found in nature as the free metal and in tellurides. Gold is typically mined and is found associated with gravels and quartz veins and also with pyrite deposits. Some of gold minerals and their gold contents are shown in the Table 2.1. Mineralogical examination techniques can be used for specifying ore type and for location of the gold in the ore and these techniques are listed in Table 2.2 (Marsden, 2006).
Table 2.1 Gold content of naturally occurring gold minerals

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Au Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native Gold (Au)</td>
<td>&gt; 75%</td>
</tr>
<tr>
<td>Electrum (Au, Ag)</td>
<td>45-75%</td>
</tr>
<tr>
<td>Calaverite (AuTe₂)</td>
<td>39.2-42.8%</td>
</tr>
<tr>
<td>Sylvinite (Au,Ag)₂Te₄</td>
<td>24.2-29.9%</td>
</tr>
<tr>
<td>Kostovite (CuAuTe₄)</td>
<td>25.2%</td>
</tr>
<tr>
<td>Arsenopyrite (FeAsS)</td>
<td>&lt; 0.2-15200 g/tone</td>
</tr>
<tr>
<td>Pyrite (FeS₂)</td>
<td>&lt; 0.2-132 g/tone</td>
</tr>
<tr>
<td>Tetrahedrite (Cu₁₂Sb₈S₃₃)</td>
<td>&lt; 0.2-72 g/tone</td>
</tr>
<tr>
<td>Chalcopryite (CuFeS₂)</td>
<td>&lt; 0.2-7.7 g/tone</td>
</tr>
</tbody>
</table>

Table 2.2 Mineralogical techniques for locating gold in the ore

<table>
<thead>
<tr>
<th>Technique</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Microscopy</td>
<td>Suitable for coarse (&gt;0.5 μm) gold particles</td>
</tr>
<tr>
<td>X-Ray Diffraction</td>
<td>Identification of Free Mineral Grains</td>
</tr>
<tr>
<td>SEM*</td>
<td>Elemental Analysis</td>
</tr>
<tr>
<td>Electron Microprobe</td>
<td>Detection limits of gold in solid solution (10-20 ppm)</td>
</tr>
<tr>
<td>Ion Microprobe</td>
<td>Detection limits of gold in solid solution (&gt;1 ppm)</td>
</tr>
</tbody>
</table>

*Scanning Electron Microscopy

Two thirds of the world's supply is produced in South Africa, and 60% of USA production is from South Dakota and Nevada. Other important mining regions are in Canada and Russia. World production in the neighborhood of 2500 tonnes per year, and reserves are estimated to be tens of thousands of tonnes (Marsden, 2006).

Methods utilized to recover gold from its ores/concentrates vary from primitive to sophisticated, depending on the nature of gold's association. Gold ores can be broadly classified as "free milling", "complex" or "refractory" (La Brooy et al., 1994).
2.2.1 Free Milling Gold-Bearing Ores

Placer (oxide) ores do not require any pretreatment. They can be recovered by physical methods such as gravity treatment. Knelson and Falcon concentrators, separate gold by gravitational and centrifugal forces to enable capture of “fine” gold particles. Alluvial ores can be also treated by a physical process of coal-oil agglomeration. Pretreatment prior to the cyanidation is usually limited to crushing and grinding. Free milling ores (sized 80% < 75 μm) give a gold recovery ≈ 95% with a conventional 20-30 hours cyanidation leach in agitated or Pachuca-type tanks, after comminution by conventional multistage crushing and ball milling, or by semi-autogenous grinding (SAG). Cyanide is added to provide for a concentration of 100-250 ppm of free cyanide at pH 10 at the completion of leaching. Similar to oxide ores some primary sulfide ores can be similarly processed but head grades are generally higher and often there are refractory components in the ore (La Brooy et al., 1994).

2.2.2 Complex Gold-Bearing Ores

Complex ores contain a range of sulfide minerals such as: pyrrhotite (FeS), marcasite (FeS₂), covellite (CuS), digenite (Cu₁₈S), chalcocite (Cu₂S), arsenic and antimony sulfides and zinc sulfide. Leaching reagents consumption increases due to sulfide content and completing-reactions cause lower-rate gold-leaching kinetics. Reactive sulfides (pyrrhotite etc.) require oxygen-in-air supply whereby Fe²⁺ is oxidized to Fe³⁺ and sulfide is oxidized to sulfate. Economic consideration may warrant the use of oxidants such as pure oxygen, hydrogen peroxide, calcium peroxide. Selective flotation is also employed to reject readily oxidized sulfides in the float tail if the reactive sulfides are barren (La Brooy et al., 1994).

Another complex ore class is “preg-robbing” ores including natural carbonaceous materials and clays in the ore, which adsorb gold as the Au(CN)²⁻ complex. Roasting and
bacterial pretreatment can obviate the preg-robbing behavior and gold recovery is then possible by conventional cyanide, bromine, chlorine or thiourea leaching (La Brooy et al., 1994).

2.2.3 Refractory Gold-Bearing Ores

The “refractory” nature of ores arise from: 

i) Physical occlusion of gold in sulfides, oxides, silicates;

ii) Chemical association as gold alloys or compounds (electrum, gold tellurides, aurostibnite (AuSb₂), moldonite (Au₅Bi));

iii) Gold substitution in the sulfide lattice (solid solution gold in arsenopyrite);

iv) Gold surface passivation due to formation of a chemical layer.

Arsenopyrite, pyrite, and chalcopyrite are the principal primary-sulfide minerals for which the gold is not readily accessible and categorized as refractory ores. The processing options for sulfidic ores depend greatly on location and mineralogy. Pre-treatment strategies for processing refractory ores are shown in Figure 2.1 (La Brooy et al., 1994).

![Figure 2.1 General pretreatment processing flowsheet applied for refractory ores](image-url)
Current gold recovery methods include gravity concentration, amalgamation, cyanide leaching, chlorination, zinc precipitation and carbon/charcoal adsorption are used based on techniques that have been known for centuries or established during the last century. All hydrometallurgical gold-extraction routes incorporate a leach step to produce a gold-bearing solution as an intermediate stream. Leaching is defined as the extraction of materials by dissolution from a solid phase (Hilson and Monhemius, 2006).

Currently, dilute alkaline, cyanide-solution is the primary “solvent” employed for gold dissolution, where the cyanide anion serves as a strong complexing-ligand with gold, and also because of its relatively low cost. Chlorine/chloride media have also been employed. The oxidized gold-species Au⁺, is complexed by the cyanide ion (CN⁻) and forms, predominantly, the di-cyanide species. This is referred to the “pregnant solution” from which gold is subsequently processed to recover the gold in metallic form. Oxygen is used as the oxidant in the process and the overall reaction can be written as:

\[
4\text{Au}(s) + 8\text{CN}^- + 0_2(aq) + 2\text{H}_2\text{O} = 4\text{Au(CN)}_2^- + 4\text{OH}^- \quad (2.1)
\]

The toxicity of cyanide is dependent on the “compound” being considered. Free cyanide being potentially the most toxic, and metal cyanide-complexes being less- or non-toxic. Weak cyanide-complexes, decompose, releasing hydrogen-cyanide gas when the pH of the solution is decreased. Despite the use of cyanidation for more than a century, there has been continued interest in non-cyanide gold technologies because of complex-ore types. For example, copper-bearing gold ores consume cyanide because carbonaceous “preg-robbing” material adsorbs gold cyanide complex thereby decreasing the solubilization of gold. Also, the neutralization of acidic solutions prior to cyanidation increases the cost due to lime reagent and material-handling requirements. Another reason for the promotion of alternative techniques is the potential impact of cyanide on the environment. Several replacement candidates have been proposed; the most
notable being thiourea, thiocyanate, coal-oil agglomeration, halides, thiosulfate and polysulfides leaching. In addition, pressure acid-leaching, prior to the cyanidation, is employed in the treatment of complex ores. The lixiviants and oxidants used in gold leaching and process pH values employed are listed in Table 2.3 (Woodcock, 1988).

Table 2.3  Leaching systems for gold leaching

<table>
<thead>
<tr>
<th>Leaching Reagent</th>
<th>Oxidant</th>
<th>Gold Complex</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkaline Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyanide</td>
<td>O₂</td>
<td>Au(CN)₂⁻</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Calcium Cyanamide</td>
<td>O₂</td>
<td>Au(OCN)₂⁺️</td>
<td>&gt;10</td>
</tr>
<tr>
<td><strong>Neutral Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>O₂</td>
<td>Au(S₂O₃)₂⁺️</td>
<td>&gt;7</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br₂</td>
<td>AuBr₄⁻️</td>
<td>7</td>
</tr>
<tr>
<td><strong>Acidic Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>Fe³⁺</td>
<td>AuCl₄⁻</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Aqua Regia</td>
<td>HNO₃</td>
<td>AuCl₄⁻</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>Fe³⁺, H₂O₂</td>
<td>Au(SCN)₄⁺️</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Thiourea</td>
<td>Fe³⁺, H₂O₂</td>
<td>Au(NH₂(SNH₂)₂⁺️</td>
<td>1-2</td>
</tr>
</tbody>
</table>

2.3  Nitric Acid Oxidative Pressure Leaching

The use of nitric acid in extracting metal values from sulfide ores was proposed as early as 1909 by Kingsley (1909). The basic principle underlying HNO₃ leaching is recovery of the valuable metal (occluded within sulfide mineral grains, in sub-microscopic form as inclusions, or in solid solutions) by oxidizing sulfide either to elemental sulfur or sulfate with an oxidant (for example, HNO₃) and thereby annihilating the sulfide lattice. The published literature reports on the leaching of heavy metals (As, Cu, Fe, Au, Ag, Pb) with HNO₃ for a range of operating temperature, pressure, and pulp ratio. Although the primary goal was to recover the metal,
economical and environmental aspects have also received attention. Pioneering studies in this field were published by Kingsley (1909), Rankin (1915), Pauling (1940), Bjorling and Kolta (1966).

Rankin (1915) used concentrated nitric acid at 100°C to completely solubilize the mineral values, thus oxidizing sulfide, the anion of the metal sulfide, to sulfate. The primary reactions were presented (from a purely stoichiometric perspective) as:

$$3\text{CuS} + 8\text{HNO}_3 = 3\text{CuSO}_4 + 8\text{NO} + 4\text{H}_2\text{O}$$  \hspace{1cm} (2.2)

$$8\text{NO} + 4\text{H}_2\text{O} + 6\text{O}_2 = 8\text{HNO}_3$$  \hspace{1cm} (2.3)

Kingsley, in a later patent, disclosed a process to recover the sulfur in elemental form by employing “milder” conditions, specifically 5% HNO₃ and 80°C. The attribute that this process offers, it is claimed, is that it avoids (or minimizes) disposal treatment of the sulfates associated with the Rankin process. However, the Kingsley patent did not disclose the minerals treated, neither the percentage of elemental sulfur recovered (Habashi, 1973).

Pauling (1940) reported that mild leaching-conditions resulted in high (≈80%) elemental sulfur recoveries for FeS, PbS, and ZnS; and much smaller (≈10%) for pyrite and marcasite. The recovery was intermediate (≈50%) for chalcopyrite. Furthermore, the yield of elemental sulfur could be increased for pyrite, marcasite, and chalcopyrite by thermal pretreatment in an inert atmosphere to partially desulfurize these minerals. For example, it was cited that when pyrite or marcasite was heated in an “inert” atmosphere, the following reaction takes place (shown amended in brackets):

$$\text{FeS}_2 \rightarrow \text{FeS} + \text{S} \hspace{1cm} (\text{FeS}(s) \rightarrow \text{FeS}(s) + \frac{1}{2} \text{S}_2(g))$$  \hspace{1cm} (2.4)

$$\text{Cu}_2\text{S}.\text{Fe}_2\text{S}_3 \rightarrow \text{Cu}_2\text{S}.2\text{FeS} + \text{S}$$  \hspace{1cm} (2.5)
These thermally-treated solids, when leached with dilute HNO₃, at moderate temperature, yielded most of their sulfur content in elemental form. Instead of nitric acid, sulfuric acid has been used to achieve the oxidation of sulfides by air at 110°C. However, significant corrosion problems were reported. The benefit that is realized in using HNO₃, is that under these “highly oxidizing” conditions stainless steel can be employed for the high-pressure leaching vessels (Habashi, 1973).

Bjorling and Kolta (1966) employed sulfuric acid, to which a small amount of HNO₃ was added, with air as oxidant, to solubilize sulfides with the simultaneous recovery of elemental sulfur. In this study, “nitric acid catalysis”, the dissolution behavior of pyrhotite, sphalerite, galena and molybdenite, in addition to pyrite and chalcopyrite, was characterized by lower pressure (1 atm) and moderate temperature (90°C). Nickel and cobalt were extracted with “suitable” promoter (HNO₃) whereby sulfide was oxidized to elemental sulfur. Selectively iron hydrolyzed in aqueous solution. It was claimed that nitric acid was an “excellent promoter” since during leaching, nitric-oxide gas (NO) is liberated which, in the presence of oxygen and water, is converted back to HNO₃ according to the following reactions:

\[ 3\text{MeS} + 2\text{HNO}_3 + 6\text{H}^+ \rightarrow 3\text{Me}^{2+} + 3\text{S}^0 + 2\text{NO} + 4\text{H}_2\text{O} \] (2.6)

\[ 2\text{NO} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \] (2.7)

In a later paper, Bjorling (1973) employed several oxidant species (Fe³⁺, Cu²⁺, HNO₃) in acidic leach solution, with air as primary oxidant, to solubilize sulfides with the simultaneous recovery of elemental sulfur. Ferric oxidation required the removal of iron as hydroxides and in the case of cupric oxidation, chloride salts of iron and copper were processed by electrodialysis.

It was reported that the oxidation of sulfides by ferric or cupric ions had the advantage of performing the reactions in open vessels, in contrast to nitric acid which required the use of a low-pressure reactor.
MeS + 2Fe^{3+} \rightarrow Me^{2+} + 2Fe^{2+} + S^0 \quad (2.8)

CuFeS_2 + 3CuCl_2 \rightarrow 4CuCl + FeCl_2 + 2S^0 \quad (2.9)

At pH below (1.0):

3CuFeS_2 + 5HNO_3 + 15H^+ \rightarrow 3Cu^{2+} + 3Fe^{3+} + 5NO + 10H_2O + 6S^0 \quad (2.10)

At pH above (1.5):

3CuFeS_2 + 5HNO_3 + 6H^+ \rightarrow 3Cu^{2+} + 3Fe(OH)_3 + 5NO + H_2O + 6S^0 \quad (2.11)

Researchers at Kennecott Copper in Utah built a pilot plant for treating chalcopyrite concentrate with HNO_3-H_2SO_4 mixture. Similar work, but on a small scale, was also conducted independently at Anaconda and other laboratories (Queneau and Prater, 1974). The flowsheet of the copper-concentrate leach-process by nitric acid and regeneration of nitric acid is shown in Figure 2.2. The chemical reactions and oxidation by nitric acid were emphasized in the report on the research. The oxidation was classified as being stepwise; firstly the oxidation of sulfide to elemental sulfur which leads to soluble iron and copper salt formation, followed by the oxidation of S^0 to sulfate. The yield of elemental sulfur was enhanced by increased temperature and decreased acid concentration (H_2SO_4 and HNO_3) associated with the predominant oxidation of sulfur to sulfate.

The experiments performed based on NO production demonstrated a maximum of 600 mL/min NO(g) produced with 20% HNO_3 at 90°C during a period of 1 h. The major effect on efficient utilization of reagents or regeneration of HNO_3 was the production of NO_2(g) rather than NO(g). The same amount of nitric acid was capable of extracting three times as much copper according to following reactions under conditions where the reaction product was NO(g) compared to when NO_2(g) was produced.

3CuS + 2HNO_3 + 3H_2SO_4 \rightarrow 3CuSO_4 + 3S^0 + 2NO(g) + 4H_2O \quad (2.12)

CuS + 2HNO_3 + H_2SO_4 \rightarrow CuSO_4 + S^0 + 2NO_2(g) + 2H_2O \quad (2.13)
Figure 2.2 Copper concentrate leach by nitric acid (Queneau and Prater, 1974)
The reactions by which NO\(_{(g)}\) and NO\(_2\)\(_{(g)}\) were produced were performed at 95°C. Pure NO\(_{(g)}\) was produced below 25% HNO\(_3\), and NO\(_2\)\(_{(g)}\) yield was 90% with the use of 70% HNO\(_3\). Figure 2.3 displays the concentrations of NO\(_{(g)}\) and NO\(_2\)\(_{(g)}\) as a function of HNO\(_3\) concentration (Queneau and Prater, 1974).

![Figure 2.3](image.png)

**Figure 2.3** NO and NO\(_2\) gases distributions as a function of HNO\(_3\) concentration at 95°C

The regeneration of nitric acid was performed by contacting oxygen and NO-NO\(_2\) gas (2.14 and 2.15) within the aqueous phase at pressures up to 100 psig, in cooled 304L stainless steel absorption towers (Queneau and Prater, 1974).

\[
\begin{align*}
2\text{NO} \rightarrow \text{NO}_2 + \text{O}_2 & \quad \Delta H^\circ = -27 \text{ kcal/mol} \\
3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} & \quad \Delta H^\circ = -32.9 \text{ kcal/mol}
\end{align*}
\]

Tail gases consisting of 0.15-0.3% NO was “burned” by mixing with natural gas in the presence of platinum catalyst at 900°C and the nitric oxide content was reduced to less than \%0.01 (100 ppm). Caldon (1978), developed a patented commercial process using sulfuric/dilute
nitric acid to leach silver and copper bearing ores at Sunshine Mining Company. The metal bearing ore was pretreated by an aqueous solution containing 0.31-1.22 M H₂SO₄ and 1.6x10⁻³ – 2x10⁻² M (0.01-0.15% by weight) HNO₃ at 90-100°C and ambient pressure for 1 hour to remove acid soluble metals carbonates (manganese carbonate). Pretreatment followed by pressure leaching performed with 1.83 M H₂SO₄ and 3x10⁻² M (0.2% by weight) HNO₃ at 150°C with oxygen overpressure pressure of 35 psi and total pressure of 90 psig for 2 hours. Silver recovery, obtained by both acid pretreatment and pressure leaching was reported to be 90% which was 1.4 times higher than the amount recovered by pressure leaching excluding acid pretreatment step. While copper and zinc recovery was 95%, arsenic and antimony, lead and iron remained undissolved material in oxide and sulfate forms, respectively.

Brennecke et al. (1981) introduced a similar process referred to as the NSL (Nitric-Sulfuric Leach) for chalcopyrite pressure leaching with nitric/sulfuric acid in brick-lined vessels with stainless steel trim. The operating temperature was 90-105°C below the melting point of sulfur (≈120°C). Recovery of copper was 99%. Nitric oxide (NO(g)) collected from the pressure reactor was transferred to an absorption tower to be oxidized to NO₂ and to reproduce nitric acid by absorption into water. Residual nitrate in the solution was removed by reducing nitrate to NO by iron (Fe²⁺), at a temperature above 150°C, according to the following reaction.

\[
\begin{align*}
\text{NO}_3^- + 4\text{H}^+ + 3\text{Fe}^{2+} & \rightarrow \text{NO}_2(g) + 2\text{H}_2\text{O} + 3\text{Fe}^{3+} & \Delta H = -19\text{kcal/mol} \\
3\text{Fe}^{3+} + \text{NH}_3 + 6\text{H}_2\text{O} + 2\text{SO}_4^{2-} & \rightarrow \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6(s) + 5\text{H}^+ & (2.17)
\end{align*}
\]

The specific Fe²⁺/NO₃⁻ molar ratio of 3 was maintained in the system. Ammonojarosite was precipitated to remove iron (Fe³⁺) from solution. More recently Van Weert et al. (1986) developed the NITROX process, and subsequently introduced improvements to it.

This process utilizes nitric acid to pre-treat refractory pyrite and arsenopyrite gold-ores and convert the sulfides into oxides according to reaction of 2.18. It was noted that pyrite and
arsenopyrite dissolve rapidly in “hot” nitric acid (80°C, 12% w/w) solutions which produces a REDOX potential of 750 mV. The “liberated” gold is occluded within a residue consisting mainly of elemental sulfur. Nitric oxide (NO(g)) gas produced is directly oxidized to nitrogen dioxide by oxygen in air, that is supplied to the reactor. The nitrogen dioxide dissolves in the solution and reacts with water to form nitric acid (HNO₃), thereby completing the NITROX cycle.

This process was developed to pilot-plant scale where it was demonstrated on the leaching of a selection of ores. The most significant problem identified was that of high sulfate-production. The overall reaction was stated as:

$$2\text{FeS}_2 + 10\text{HNO}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + 10\text{NO} + 4\text{H}_2\text{O} \quad (2.18)$$

The NITROX cycle was completed with the production of nitric acid from NO(g) by employing several stages that were required due to the low rate of oxidation NO(g) to NO₂(g). The first 7 stages of 20, recovered 90% HNO₃, while the remaining 13 stages were required to recover an additional 8%. The remaining 2% was not economical to recover by this scheme and was oxidized to N₂O₃ and could be absorbed as nitrite in alkaline solution.

Arseno Processing Ltd. developed a nitric-acid based process for treating refractory gold ores and concentrates in 1981. The Arseno and Redox processes were developed to pilot plant scale to treat pyrite and arsenopyrite containing gold that was not amenable to direct cyanidation. These are both low pressure (1 atm total pressure) oxidation processes operating in the neighborhood of 100°C. Ultrafine grinding to 5-15 microns (µm), depending on the particular feedstock was a process flowsheet component. Once the minerals are dissolved in 3N HNO₃, gold was liberated and now accessible to cyanidation (Beattie et al., 1989). Copper recovery was accomplished by SX/EW.

The process has been practiced for the leaching of chalcopyrite and chalcocite for copper extraction, and gold is recovered by cyanidation of the residue. Advantages claimed for this low-
pressure process include lower capital cost for the pressure reactors and related equipment, production of elemental sulfur which minimizes oxygen consumption, operation below the melting point of sulfur and precipitation of most of the iron as hematite or goethite. Cyanide consumption for gold recovery from the residue is reported to be “acceptable” (Taylor and Jansen, 1999).

The rate enhancement effect of nitrite has been also investigated in other fields besides hydrometallurgy such as Environmental and Medical Sciences. The chemistry of nitrogen oxides in the atmosphere is important not only because these species ultimately form nitric acid that contributes much of the strong acid deposited to the earth surface but also because they play pivotal roles in the formation of secondary photooxidants, such as ozone, hydroxyl radical, and hydrogen peroxide, that in turn control, in a major way, the oxidation of sulfur dioxide and other atmospheric species such as hydrocarbons. Consequently, it was recognized that a systematic characterization of the chemistry of nitrogen species is necessary to gain a full understanding of the overall role that these play in atmospheric chemistry (Park and Lee, 1988).

In addition, there is significant research being conducted on the in vivo production and effects of nitric oxide on ischemic tissue, regional blood flow and skin. Sodium nitrite is used as a vasodilator and also as an antidote to cyanide poisoning. It is thought that the vasodilator effect is due to nitrite conversion into nitric oxide after protonation. In a recent publication, research on the rate at which NO forms from nitrite in a closed system, such as circulating blood plasma with a physiological pH of 7.4, was conducted (Butler and Ridd, 2004).

It is apparent, from the literature review presented, that the use of nitric acid in sulfide oxidation is not new. However, only the (“catalytic” nitrogen species) NSC process, – sulfuric-acid oxidative pressure-leach – has ever been commissioned and operated successfully on an industrial scale for a significant length of time. Moreover, it has been extensively researched and
has found successful application in oxidation of other feedstocks (besides refractory gold-ores) as well.

2.4 Nitrogen Species Catalyzed (NSC) Pressure Leaching

Nitrogen Species Catalyzed (NSC) is the name (acronym) that the inventors assigned to this processing scheme (pressure-leaching) (Anderson, 2003). The process employs sulfuric acid to achieve a high proton-activity and oxygen/air as the primary oxidant with small nitrite concentration serving, in a broad (non-specific) sense, what must be the “catalytic” role.

The (NSC) process development can be traced to early research efforts on oxidation of metals with nitric acid. Abel and Schmid (1928) investigated the aqueous-phase reaction between nitric acid and the lower oxidation-state nitric-oxide product that was formed by the oxidation of the metal. They (correctly) identified the autocatalytic reaction step to be:

\[ \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} = 3\text{HNO}_2 \]  

in which, nitric oxide (NO), a product species, serves as a catalyst and is responsible for the resulting autocatalysis. A decade later, Abel, Schmid, and Pollak (1936) reported on ferrous oxidation by \( \text{HNO}_2 \) (nitrous acid) rather than \( \text{HNO}_3 \) in an aqueous phase and proposed the following reaction mechanism:

\[ \text{Fe}^{2+} + \text{HNO}_2 + \text{H}^+ = \text{Fe}^{3+} + \text{NO} + \text{H}_2\text{O} \]  

More recently, Baldwin and Van Weert (1996) reported that ferrous oxidation-rate by oxygen was enhanced significantly in the presence of minor concentration of nitrite compared to similar concentration of nitrate. Researchers from various disciplines (chemical, medical, environmental) have devoted significant efforts to investigating the autocatalytic reaction-mechanism(s) associated with oxynitrogen species over a period spanning more than seven decades now (2009). At high concentration, nitrous acid is unstable, consequently, researchers have provided for \( \text{HNO}_2 \) by employing nitrite salts (\( \text{KNO}_2 \), \( \text{NaNO}_2 \)) for the experiments in their
studies. It was already known that the acid is produced by the protonation of NO$_2^-$ to form HNO$_2$, the concentration of which is dependent on the hydrogen-ion activity. The acid dissociation constant provides the basis for calculating the equilibrium concentrations in the aqueous electrolyte (Vogel, 1961). It is apparent that a high proton activity promotes a high concentration of HNO$_2$ according to the reaction:

$$\text{H}^+ + \text{NO}_2^- = \text{HNO}_2$$

$$K_a = \frac{c_{\text{HNO}_2}}{c_{\text{NO}_2^-}c_{\text{H}^+}} = 2.51 \times 10^3 \text{ M (25 °C)} \quad (2.21)$$

Subsequently, and again at “high proton-activity”, disproportionation of nitrous acid occurs to produce NO(aq) and NO$_2$(aq). Markovits et al. (1981) considered two reaction steps, (2.21) and (2.22) for NO production from HNO$_2$. This nitrogen species, with 3+ oxidation state, N$_2$O$_3$ (anhydrous nitrous acid), is a short-lived species with a Henry’s law solubility-coefficient (25°C) of 0.7 M.atm$^{-1}$. The rate of homolysis (disproportionation) of N$_2$O$_3$ to NO and NO$_2$ was found to be much greater than its hydrolysis to HNO$_2$ (Park and Lee, 1988).

$$2\text{HNO}_2 = \text{N}_2\text{O}_3(aq) + \text{H}_2\text{O} \quad K = \frac{c_{\text{N}_2\text{O}_3(aq)}}{c_{\text{HNO}_2}^2} = 3 \times 10^{-3} \text{ M}^{-1} \text{ (25°C)} \quad (2.22)$$

$$\text{N}_2\text{O}_3(aq) = \text{NO(aq)} + \text{NO}_2(aq) \quad K = \frac{c_{\text{NO}}c_{\text{NO}_2}}{c_{\text{N}_2\text{O}_3}} = 1.07 \times 10^{-4} \text{ M (25°C)} \quad (2.23)$$

The elucidation of the mechanism by which the production of NO and NO$_2$ occurs in the electrolyte by disproportionation of “nirite”, now presented another consideration concerning NO in a closed reactor; namely how it is distributed between the aqueous-electrolyte and gas phase. Anderson (2003) reported that the solubility of NO$_{(g)}$ in an aqueous solution was “low” and consequently would be expected to report to the gas phase. However, the Henry’s law solubility-coefficient for NO$_{(g)}$, published earlier, is $1.9 \times 10^{-3}$ M.atm$^{-1}$ (25°C) which in fact is greater than that for O$_{(g)}$ at the same conditions of experiments performed (of $1.2 \times 10^{-3}$ M.atm$^{-1}$) (Wrinkler, 1901; Dean, 1999).
Also, the published Henry’s law solubility-coefficient for \( \text{NO}_2 \) is \( 2.88 \times 10^{-2} \text{ M atm}^{-1} \) (Bosio et al., 1985). Moreover, the mass transfer rate of \( \text{NO}_2 \) would be expected to be 15 times higher than that for \( \text{NO} \), on the basis that the gas-phase concentrations and liquid-phase diffusivities are similar in magnitude (Bosio et al., 1985).

\[
\text{NO}_{(aq)} + \frac{1}{2} \text{O}_2(aq) = \text{NO}_2(aq)
\]  \hspace{1cm} (2.24)

The cyclic \( \text{NO}_x \) redistribution-mechanism was still unclear due to the unknown “catalytic” species responsible for regeneration of \( \text{HNO}_2 \). Recently, Anderson (2003) has proposed the reactive species to be \( \text{NO}^+ \), and that the formation of this nitrosonium ion occurred according to the reaction:

\[
\text{HNO}_2 + \text{H}^+ = \text{NO}^+ + \text{H}_2\text{O}
\]  \hspace{1cm} (2.25)

In their study, the “autocatalytic” reaction step was reported to be the result of the reduction of \( \text{NO}_2 \) and the concomitant oxidation of \( \text{NO} \) within the acidic electrolyte to regenerate \( \text{NO}^+ \). This reaction was stated thus:

\[
2\text{NO}_2 + 2\text{NO} + 4\text{H}^+ = 4\text{NO}^+ + 2\text{H}_2\text{O}
\]  \hspace{1cm} (2.26)

It was also noted as that \( \text{NO}^+/\text{NO} \) REDOX couple is capable of an extremely high potential, and consequently, \( \text{NO}^+ \) is readily formed from nitrous rather than nitric acid. “Overall, the nitrogen intermediates serve as an expedient means to transport oxygen to the surface of the solid particle and allow the resulting reaction to take place at an increased REDOX potential” (Anderson, 2003). However, Turney and Wright (1959) have shown that conditions required to produce nitrosonium ion (\( \text{NO}^+ \)) from \( \text{HNO}_2 \) correspond to extremely high hydrogen-ion activity or, correspondingly, low water activity. This is evident from the following reaction:

\[
\text{HNO}_2 + \text{H}^+ = \text{NO}^+ + \text{H}_2\text{O} \hspace{1cm} K = \frac{c_{\text{NO}^+}a_w}{c_{\text{HNO}_2}a_{\text{H}^+}} = 2 \times 10^{-7} \text{ (25°C)}
\]  \hspace{1cm} (2.27)
Topol et al. (1965), supported this finding on the basis of results of a study on the cathodic reduction of nitric acid to nitrous acid, an important consideration in the elucidation of the “autocatalytic” characteristics of the (several oxidation states) nitrogen species in acidic solutions. They performed electrochemical measurements on platinum (and mercury) working-electrodes and presented the voltammograms generated, for the reduction of nitrous acid in acidic medium (>6 M H₂SO₄). Under high acidic conditions, nitrite originally present as NO⁺ is rapidly converted into N₂O₄ (dimer of NO₂ species) when sufficiently large concentration of HNO₃ was added. The investigation demonstrated unequivocally that in dilute-acid electrolytes (1 M H₂SO₄) the nitrosonium ion, NO⁺, is not an (electro-) active species.

Over a decade ago (1996), Baldwin and Van Weert (1996) also discussed the role of the “oxygen carrier”, NO₂(g), which is responsible, most likely, for the oxygen transfer by which the HNO₂ is regenerated. Heckner (1973) performed an experiment on the chemical species produced upon dissolution of NO₂ in dilute perchloric-acid solutions (1 M) and described the formation of HNO₂ by the disproportionation reaction:

\[ 2\text{NO}_2(aq) + \text{H}_2\text{O} = \text{HNO}_2(aq) + \text{HNO}_3(aq) \quad K = 8.5 \times 10^8 \text{ M}^{-1}; \ (25^\circ\text{C}) \quad (2.28) \]

It is to be noted that, at this high proton-activity, the conversion of NO₂ to HNO₂ and HNO₃, from an equilibrium perspective, is quantitative due to the large value of K.

In the presence of, for example, ferrous ion, should NO be selected/identified as the catalytic species, its role is moderated because of the formation of ferrous-nitrosyl complexes which is the complex formed in the well-known brown ring test for nitrates (Baldwin and Van Weert, 1996). This complex, green-black in color, is stable at ambient conditions. However, the experiments, performed at 120°C, for several ferrous concentrations and initial ferrous/ferric concentration ratios, have indicated that the increased initial ferrous concentrations did not adversely affect the reaction rates, “due to binding of NO in a ferrous-nitrosyl complex”. This
suggested that most of the nitrogen species were in solution, bound perhaps as Fe(NO)\(^{2+}\), and that oxidation must somehow take place there and not in the gas phase. Furthermore, gas-venting experiments indicated that depressurizing and re-pressurizing of the reactor (with oxygen) did not result in any significant decrease in the reaction rate. It was postulated that this could be attributed to most of the nitrogen being in solution, in the form of the nitrosyl complex Fe(NO)\(^{2+}\) (Baldwin & Van Weert, 1996), the equilibrium of which is described by the reaction:

\[
Fe^{2+} + NO = Fe(NO)^{2+} \tag{2.29}
\]

The ferrous-nitrosyl complex formation-reaction was studied by Epstein et al. (1982) and in their paper it is referred to as a clock reaction (this term can be traced back to an 1886 publication by Hans Heinrich Landolt (1886). A REDOX potentiometric technique was employed to monitor the progress of the reaction. A potential of 700 mV (SCE) (25°C) was observed when a 0.025 M ferrous had been completely converted to ferric (by 1 M nitric acid) and the nitrosyl complex no longer present.

It is appropriate to introduce remarks concerning standard REDOX potentials at this juncture. Several selected oxynitrogen- species (including O\(^{2-}\)) and the Fe\(^{2+}/Fe^{3+}\) couple are listed in Table 2.4. These potentials have, on a relative basis, been employed for ranking the effectiveness of an oxidant for an intended application (Park and Lee, 1988). However, this can lead to erroneous conclusions. For example, NO\(^+\)/NO couple has the highest standard potential listed, but in general, these species are not present at unit activity in the system being considered. In fact, species such as NO, and more so NO\(^+\), are at relatively low concentrations in the NSC process. Consequently, the REDOX potential would be expected to be smaller than the value listed. In addition, kinetic limitations can further confound such a forecast.
Table 2.4 Standard potentials of relevant REDOX reactions (Anderson, 2003; Dean, 1999)

<table>
<thead>
<tr>
<th>Redox Equation</th>
<th>$E^0_{b}$ (pH=0, $H_2$ ref) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe^{3+} + e^- \rightarrow Fe^{2+}$</td>
<td>0.77</td>
</tr>
<tr>
<td>$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$</td>
<td>0.94</td>
</tr>
<tr>
<td>$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$</td>
<td>0.96</td>
</tr>
<tr>
<td>$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$</td>
<td>1.00</td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td>
<td>1.23</td>
</tr>
<tr>
<td>$NO^+ + e^- \rightarrow NO$</td>
<td>1.45</td>
</tr>
</tbody>
</table>

2.5 Industrial Applications of NSC Pressure Leach Process

Industrial-scale applications of NSC (Nitrogen Species Catalyzed) pressure leaching processes of Silver-Bearing Copper Concentrates, Chalcopyrite Concentrates, and PGM Concentrates are reviewed. The application details (e.g. process conditions, flowsheets) are also presented in following sections.

2.5.1 Silver-Bearing Copper Concentrates

Nitrogen Species Catalyzed (NSC) Pressure Leaching was operated at Sunshine Mine Silver Refinery from 1984 until 1995. The primary purpose was to selectively solubilize silver and copper values from a copper concentrate obtained after selective alkaline sulfide-leaching of antimony from the ore containing silver, copper and antimony which occur in association with tetrahedrite mineralization. The solution obtained by NSC pressure leaching contained three major products: i) silver and copper values along with other soluble metals most notably iron, ii) Sulfur pellets contained most of the oxidized portion of the sulfide mineral, iii) Fine leach residue which was the oxidized and finely divided insoluble metallic portion (lead sulfate and antimony
oxide) of the feed. Sunshine Mine Silver Refinery flowsheet is illustrated in Figure 2.4 (Ackerman, 1993).

Figure 2.4 Sunshine Mine silver refinery flowsheet

Silver was recovered from the leach solution as insoluble precipitate of silver chloride. The silver chloride was separated and washed by filtration and was reduced to silver metal. The resulting silver powder (sponge) was cast into a suitable shape for anodes and then placed in an electrolytic refining circuit. The pure silver electrodeposit produced by the refining cells were
cast into bars and prepared for market. In the final step copper recovered from silver free leach solution by treating with solvent extraction and copper electrowinning.

2.5.2 Chalcopyrite Concentrates

The application of complete oxidation and partial NSC pressure leaching were demonstrated on chalcopyrite concentrates at a laboratory scale. The flow sheet is presented in Figure 2.5.

Figure 2.5 Flowsheet of NSC partial sulfide oxidation of gold bearing chalcopyrite
For complete oxidation, sulfide in the mineral matrix oxidized to sulfate. Excess acid and ferric iron in-situ are facilitated which could be used to enhance heap leaching of associated copper-oxide deposits. Conventional cyanide leaching could then be applied to recover gold or silver remaining in the leached solids. For partial oxidation, sulfide is oxidized to elemental sulfur instead of complete oxidation to the sulfate. This processing scheme requires a lower temperature and pressure. Furthermore leaching is accomplished in a minimum amount of time. Silver in the leach solution is recovered directly by established industrial practice without the use of cyanide since the gold is occluded in the elemental sulfur residue (Anderson, 2000).

### 2.5.3 PGM Concentrates

Partial NSC pressure leaching was investigated for treating PGM smelting-concentrate and palladium bearing ore. The objective of this laboratory scale research was to selectively recover the palladium and rhodium. Alternatively, PGM’s can also be retained in the solid phase by controlling operating parameters. The conditions of which the experiments were performed are listed in the publication by Anderson (2008).

The advantages claimed for NSC pressure leaching and stated by Anderson (2008) are:

i) It is the only proven industrial process over the long term for pressure leaching of copper sulfides and direct recovery of precious metals without the use of cyanide; ii) The rate of reaction is much higher and subsequent required reactor volume is thus smaller; iii) The process does not require excessively high temperatures or pressures; iv) The oxidation/reduction potential (ORP) in the electrolyte can be adjusted and controlled to be extremely high so it oxidizes elemental sulfur at low oxygen overpressures; v) Stainless steel autoclaves can be employed instead of titanium cladding or brick with lead liners. Thus, the capital and maintenance costs are less. Also, because of the simpler internal design, direct heat exchange can be utilized in-situ for
optimal temperature control. Further, in a manner analogous to existing Ni/Co laterite HPAL (high-pressure acid-leaching) systems, the energy from the in-situ heat exchanger can be readily utilized for optimizing the plant heat balance or co-generating electrical power resulting in significant process operating cost-savings; vi) There is no need for a dip tube or special design radial agitators with cowlings and the like. Oxygen transfer is innate with the enhanced nitrogen species chemistry. So, without titanium, or a titanium dip tube in particular, there is much less oxygen fire danger. vii) The design of the feed pump system is far less of a challenge as is the flash system and the choke systems; vii) Similar to a smelter, precious metals recovery can be high and direct; ix) Chloride chemistry and resultant corrosion issues are avoided; x) By-product elemental sulphur formation, handling and treatment for contained gold recovery was proven and readily accomplished and value added by-products such as sodium sulphate, sodium hydroxide sulfuric acid and gypsum can be produced from the waste streams; xi) There is minor amount of nitrogen species utilized which reports almost entirely to the gas phase upon autoclave flashing. This is readily destroyed and scrubbed using commercially available equipment. So, there are no major economic or environmental issues with the use of the small amount of nitrogen species utilized (Anderson, 2008).
CHAPTER 3
THEORETICAL CONSIDERATIONS

This chapter is devoted to the fundamentals relevant to the leaching of gold-bearing ores with nitric/sulfuric acid. The topics covered include: i) kinetics of oxidation of ferrous iron by molecular oxygen; ii) kinetics of NOx species in acidic solution; iii) electrochemical measurements; and iv) Computer Simulation for Mathematical Modeling. Discussed under item ii) are kinetic aspects of the NSC process, which will be revisited in Appendix A1.

3.1 Kinetics of Oxidation of Ferrous Iron by Molecular Oxygen

The oxidation of ferrous iron plays an important role in either commercial leaching operations or natural weathering of sulfide minerals. The rate of ferrous oxidation by molecular oxygen has been reported under a variety of acid solution (HCl, HClO4, HNO3, H3PO4, H2SO4) and temperature conditions. Ferrous sulfate can be oxidized in acidic sulfate solutions according to the following overall reaction formula (Rönnholm et al., 1999):

\[ 4\text{FeSO}_4 + 2\text{HSO}_4^- + \text{O}_2 + 2\text{H}_3\text{O}^+ = 2\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} \]  
(3.1)

or, expressed with the participating species,

\[ \text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}_3\text{O}^+ = \text{Fe}^{3+} + \frac{3}{2} \text{H}_2\text{O} \]  
(3.2)

Major factors affecting the rate at which the ferrous oxidation by molecular oxygen reaction proceeds are the concentration of the ferrous iron and dissolved oxygen, pH of electrolyte, temperature, and certain catalytic materials (Lowson, 1982).

McBain (1901) and Lamb and Elder (1931) reported that at ambient temperatures, and in sulfuric acid solutions below pH 2, the reaction rate was very slow, independent of pH, first order with respect to the partial pressure of oxygen and second order with respect to ferrous iron, resulting in the rate equation:
-r_{Fe^{2+}} = kC_{Fe^{2+}}^2P_{O_2} \quad (3.3)

Huffman and Davidson (1956) observed a dependence of the reaction rate on the sulfate concentration at a fixed pH and ionic strength. Also researchers demonstrated that the kinetics of ferrous iron oxidation by molecular oxygen in 1 M sulfuric acid at 140-180°C proceeds simultaneously by second-order and first-order paths with respect to ferrous iron, giving an overall rate equation:

- r_{Fe^{2+}} = k_1C_{Fe^{2+}}P_{O_2} + k_2C_{Fe^{2+}}^2P_{O_2} \quad (3.4)

And that the reaction reverts to the single second-order reaction with respect to ferrous iron at 30°C. Matthew and Robins (1972) indicated a slight drop in reaction rate with increasing acidity over the pH range 2-0.5 with a fractional order of C_{H+}^{1/4}. A slight increase in reaction rate was observed for concentrated acid solutions.

Chmielewski and Charewicz (1984) determined that the rate of pressure oxidation of ferrous in H$_2$SO$_4$ solution was dependent on ferrous concentration according to a second-order kinetic equation at concentrations exceeding 0.05 M, but according to a first-order equation at lower concentrations. The study showed that the ferrous oxidation rate increases linearly with the partial oxygen pressure at constant temperature and increases with the temperature at constant partial oxygen pressure. The activation energy involved was reported to be equal to 13.6 kcal/mol (56.9 kJ/mol).

In the study of 0.1 M ferrous sulfate oxidation with small amounts of nitrites (3.89 mM) in 1 M H$_2$SO$_4$, Baldwin and Van Weert (1996) found the oxidation rate coefficient to be 0.0192 L.mol$^{-1}$.min$^{-1}$.atm at 120°C. Researchers, quoting from the study of Dreisinger and Peters (1989), reported that the oxidation rate of ferrous was slower at higher acidities, but faster in the presence of other metal sulfates. The last two observations were explained by the postulation that ferrous complexed species are oxidized faster than free ferrous ion, the relative concentrations of which
are influenced by solution chemistry. Table 3.1 lists the conditions of the studies conducted on the ferrous oxidation by molecular oxygen, the proposed rate laws, rate constants and the activation energies for some of the more important studies.

**Table 3.1 Kinetics data of ferrous iron oxidation by molecular oxygen obtained from literature**

<table>
<thead>
<tr>
<th>Rate equation, ( -r_{Fe^{2+}} )</th>
<th>Temp (°K)</th>
<th>pH</th>
<th>H(_2)SO(_4) Conc. (M)</th>
<th>Fe(^{2+}) Conc. (M)</th>
<th>Rate coefficient</th>
<th>Activation Energy</th>
<th>Ref.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( kC_{Fe^{2+}P_{O_2}}^2 )</td>
<td>303</td>
<td>~0</td>
<td>1 M</td>
<td>0.45-0.02</td>
<td>( k = 1.1 \times 10^6 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>( kC_{Fe^{2+}P_{O_2}}^2 )</td>
<td>303</td>
<td>~0</td>
<td>1 M</td>
<td>0.2-0.15</td>
<td>( k = 4.0 \times 10^6 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>( kC_{Fe^{2+}P_{O_2}}^2 )</td>
<td>303</td>
<td>~0</td>
<td>1 M</td>
<td>0.025-0.001</td>
<td>( k = 2.78 \times 10^6 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>( kC_{Fe^{2+}P_{O_2}^2 C_{H^+}^{1/4}} )</td>
<td>303</td>
<td>~1</td>
<td>1 N</td>
<td>0.01-1.0</td>
<td>( k = 5.1 \times 10^7 \text{ M}^{-1/25} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>73.7</td>
<td>293-353</td>
</tr>
<tr>
<td>( k_1 C_{Fe^{2+}P_{O_2}} + k_2 C_{Fe^{2+}P_{O_2}}^2 )</td>
<td>432</td>
<td>~1</td>
<td>1 M</td>
<td>0.025-0.001</td>
<td>( k_1 = 1.93 \times 10^5 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} ), ( k_2 = 1.60 \times 10^3 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>56±8</td>
<td>68±8</td>
</tr>
<tr>
<td>( kC_{Fe^{2+}P_{O_2}}^2 )</td>
<td>313</td>
<td>~0</td>
<td>0.41-0.82 M</td>
<td>0.54</td>
<td>( k = 1.52 \times 10^4 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>56.9</td>
<td>313-408</td>
</tr>
<tr>
<td>( kC_{Fe^{2+}P_{O_2}}^2 )</td>
<td>393</td>
<td>~0</td>
<td>1 M</td>
<td>0.1</td>
<td>( k = 3.2 \times 10^4 \text{ M}^{-1} \text{atm}^{-1} \text{s}^{-1} )</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
</tbody>
</table>


### 3.2 Kinetics of NO\(_x\) Species in Acidic Solution

Relatively little is known about ferrous oxidation by nitrite. Consequently, in order to elucidate the reaction mechanism, rate-data available on the reactions involving the various oxynitrogen species were retrieved from the literature. Three classifications were assigned to the principal reactions: I) Reactions which contribute to the oxynitrogen speciation in acidic
electrolyte, **II)** the oxidation of ferrous to ferric ion by nitrite (NO production) and **III)** Formation of FeNO$_2^+$ complex.

**I)** The published literature contains references to several other nitrogen species besides the ones already mentioned, e.g. NO$_2^+$, N$_2$O$_5$ which might be present in an acidic electrolyte containing nitrite. In order to render this exercise tractable, the reaction-rate data for only reactions involving the five prominent, relevant nitrogen-species identified (HNO$_2$, NO, NO$_2$, N$_2$O$_3$, NO$_3$) were reviewed.

The kinetics of HNO$_2$ disproportionation to NO and NO$_2$ can be described by the two step, homogeneous, elementary-reaction mechanism listed below:

\[
2\text{HNO}_2(aq) = \text{N}_2\text{O}_3(aq) + \text{H}_2\text{O}; \quad (3.5a)
\]

\[
-r_{\text{HNO}_2} = k_{1f}C_{\text{HNO}_2}^2 - 2k_{1b}C_{\text{N}_2\text{O}_3}; \quad (3.5b)
\]

where: $K_1 = 3.0 \times 10^{-3} \text{M}^{-1}$;

$k_{1f} = 17.7 \text{M}^{-1}\text{s}^{-1}$ and $k_{1b} = 2.9 \times 10^3 \text{s}^{-1}$; (25°C) \hspace{1cm} (3.5c)

\[
\text{N}_2\text{O}_3(aq) = \text{NO(aq)} + \text{N}_2\text{O}_2(aq); \quad (3.6a)
\]

\[
-r_{\text{N}_2\text{O}_3} = k_{2f}C_{\text{N}_2\text{O}_3} - k_{2b}C_{\text{NO}}C_{\text{NO}_2}; \quad (3.6b)
\]

where: $k_{2f} = 1.18 \times 10^5 \text{s}^{-1}$ and $k_{2b} = 1.1 \times 10^9 \text{M}^{-1}\text{s}^{-1}$; \hspace{1cm} (25°C) \hspace{1cm} (3.6c)

Markovits *et al.* (1981) investigated the hydrolysis of N$_2$O$_3$ in dilute acidic (0.1 M HCl) solution by ultraviolet absorbance. In dilute acid, the equilibrium concentration of N$_2$O$_3$ in the electrolyte is controlled by reaction (3.5). The equilibrium constant, $K_1$ (at 25°C), was determined and reported to be the value listed above under (3.5c). In addition, the forward reaction-rate coefficients for reaction (3.5 a) were reported in the study, by Bunton and Stedman (1959), on oxygen exchange between nitrous acid and water. They presented the intermediate reactions involved in the nitrosation, and also in the formation of NO which leads to the exchange of one
oxygen atom of nitrous acid with the aqueous solvent. The published value of \( k_{1f} \) is listed in (3.5 c). Butler et al. (2004) were thus able to determine \( k_{1b} \) from the value of \( k_{1f} \) and in conjunction with the reported value of the equilibrium constant provided by Markovitz et al. (1981) The rate of \( \text{N}_2\text{O}_3 \) homolysis, reaction (3.6a), had also been investigated by Markovitz et al. (1981) and the rate-coefficients \( k_{2f}, k_{2b} \) were reported to be those listed in (3.6c).

Awad and Stanbury (1993) investigated the irreversible reaction of NO with \( \text{O}_2 \), (2.18a), in 0.06 M HCl (pH 1.22) at 25°C. They reported the rate-coefficient shown in (3.7c).

\[
\begin{align*}
4\text{NO}^{(aq)} + \text{O}_2^{(aq)} + 2\text{H}_2\text{O} & \rightarrow 4\text{HNO}_2^{(aq)} \\ 
-\tau_{\text{NO}} = k_{3f} \text{C}_{\text{NO}}^2 \text{C}_{\text{O}_2} \quad (3.7b)
\end{align*}
\]

where: \( k_{3f} = 8.4 \times 10^6 \text{ M}^{-2} \text{ s}^{-1} \); (25°C) (3.7c)

Rabani and Mulac (1992) reported on research performed on the in-situ generation of \( \text{NO}_2^{(aq)} \), reaction (3.8a) and determined the rate of hydrolysis directly. The decomposition mechanism proved to be complex and they were only able to conclude that the hydrolysis was very “rapid”. In the same year, research published on the reaction of nitrous acid with 4-substituted phenols in aqueous solution, by Beake et al. (1992), reported the rate-coefficients, \( k_{4f} \) and \( k_{4b} \) listed in (3.8c).

\[
\begin{align*}
2\text{NO}_2^{(aq)} + \text{H}_2\text{O} & = \text{H}^+ + \text{NO}_3^- \text{(aq)} + \text{HNO}_2^{(aq)} \\ 
-\tau_{\text{NO}_2} = k_{4f} \text{C}_{\text{NO}_2}^2 - 2k_{4b} \text{C}_{\text{H}_2\text{O}} \text{C}_{\text{NO}_3^-}\text{C}_{\text{HNO}_2} \quad (3.8b)
\end{align*}
\]

where: \( k_{4f} = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) and \( k_{4b} = 5 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1} \); (25°C) (3.8c)

Epstein et al. (1982) has identified the reaction between NO and \( \text{NO}_3^- \) (3.9a) as being significant in controlling the speciation in electrolytes containing oxynitrogen species. The computer simulation performed in the study revealed that the \( t_{\text{max}} \) (the time at which the maximum in the absorbance-peak occurred) was directly related to the reaction rate. In view of the strong...
dependence of $t_{\text{max}}$ on hydronium concentration, $C_{H^+}$, they developed the non-elementary, “two rate coefficient”, rate equation listed under (3.9b). The rate-coefficients reported are shown in (3.9c):

$$\text{NO}_{(aq)} + \text{NO}_3^- + H^+ = \text{NO}_2(aq) + \text{HNO}_2(aq)$$ (3.9a)

$$r_{Fe^{3+}} = k_5 C_{\text{NO}_3} C_{\text{NO}} C_{H^+}^2 - k_5 C_{\text{HNO}_2} C_{\text{NO}_2} C_{H^+}$$ (3.9b)

where: $k_5 = 5.0 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$ and $k_5 = 9.7 \times 10^7 \text{M}^{-2} \text{s}^{-1}$; (25°C) (3.9c)

II) The oxidation of ferrous $Fe^{2+}$ occurs by three reversible, parallel reactions. This reaction mechanism was developed by Abel, Schmid and Pollak (1936) The reaction path in which nitrous acid is the oxidant, reaction (3.10a), is non-elementary and its rate is described by a “three rate-coefficient” rate-equation (3.10b). The corresponding three rate-coefficients are listed in (3.10c).

$$\text{Fe}^{2+} + \text{HNO}_2(aq) + H^+ = \text{Fe}^{3+} + \text{NO}(_{aq}) + \text{H}_2\text{O}$$ (3.10a)

$$r_{Fe^{3+}} = C_{\text{Fe}^{2+}} C_{\text{HNO}_2} (k_{6-1} C_{\text{Fe}^{2+}} + k_{6-2} C_{H^+} + k_{6-3} C_{\text{HNO}_2} / C_{\text{NO}})$$ (3.10b)

where: $k_{6-1} = 7.8 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$, $k_{6-2} = 2.3 \times 10^{-1} \text{M}^{-2} \text{s}^{-1}$

and $k_{6-3} = 7.6 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; (25°C) (3.10c)

The reaction with nitrogen dioxide serving as the oxidant is listed in (3.11a). It is also non-elementary with two rate-coefficients. The rate-expression is shown in (3.11b) with the rate-coefficients presented in (3.11c).

$$\text{Fe}^{2+} + \text{NO}_2(aq) + H^+ = \text{Fe}^{3+} + \text{HNO}_2(aq)$$ (3.11a)

$$r_{Fe^{3+}} = k_7 (C_{\text{Fe}^{2+}}) C_{\text{NO}_2} - k_7 (C_{\text{Fe}^{3+}}) C_{\text{HNO}_2} / C_{H^+}$$ (3.11b)

where: $k_7 = 1.2 \times 10^4 \text{M}^{-1} \text{s}^{-1}$ and $k_7 = 2.3 \times 10^{-5} \text{M}^{-1} \text{s}^{-1}$; (25°C) (3.11c)

Finally, the reaction with nitrate serving as the oxidant is listed in (3.12a). It, also, is non-elementary with two rate-coefficients. The rate-expression is shown in (3.12b) with the rate-coefficients presented in (3.12c).
\[ \text{Fe}^{2+} + \text{NO}_3^- + 2\text{H}^+ = \text{Fe}^{3+} + \text{NO}_2(\text{aq}) + \text{H}_2\text{O} \]  
\hspace{1cm} (3.12a)

\[ r_{\text{Fe}^{3+}} = k_{8.1}(C_{\text{Fe}^{2+}}) C_{\text{NO}_3^-} - k_{8.2} (C_{\text{Fe}^{3+}}) C_{\text{NO}_2}/C_{\text{H}^+} \]  
\hspace{1cm} (3.12b)

where: \( k_{8.1} = 1.0 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1} \) and \( k_{8.2} = 2.8 \times 10^{-4} \text{ M s}^{-1} ; (25^\circ\text{C}) \)  
\hspace{1cm} (3.12c)

Inherent in the rate-expression is that the \( \text{Fe}^{2+} \) oxidation with \( \text{NO}_3^- \) occurs in two elementary-reaction steps (3.13a-1 and 3.13a-2) that include the intermediate (N(IV)) species \( \text{NO}_3^{2-} \).

\[ \text{Fe}^{2+} + \text{NO}_3^- = \text{Fe}^{3+} + \text{NO}_3^{2-} \hspace{1cm} \text{(slow; rate controlling)} \]  
\hspace{1cm} (3.13a-1)

\[ \text{NO}_3^{2-} + 2\text{H}^+ = \text{NO}_2(\text{aq}) + \text{H}_2\text{O} \hspace{1cm} \text{(fast; in dynamic equilibrium)} \]  
\hspace{1cm} (3.13a-2)

\( \text{III) } \) The formation/decomposition rates of the dark-color ferrous-nitric oxide complex have been measured spectrophotometrically using a temperature-jump technique. (Epstein et al, 1982) The reaction is elementary as presented below in (3.14a), and the rate-coefficient as well as the rate-coefficients are listed in (3.14b) and (3.14c), respectively.

\[ \text{Fe}^{2+} + \text{NO} = \text{Fe(NO)}^{2+} \]  
\hspace{1cm} (3.14a)

\[ -r_{\text{Fe}^{2+}} = k_{9f}(C_{\text{Fe}^{2+}}) C_{\text{NO}} - k_{9b} (C_{\text{Fe(NO)}^{2+}}) \]  
\hspace{1cm} (3.14b)

where: \( k_{9f} = 6.2 \times 10^{5} \text{ M}^{-1} \text{ s}^{-1} \) and \( k_{9b} = 1.4 \times 10^{3} \text{ s}^{-1} ; (25^\circ\text{C}) \)  
\hspace{1cm} (3.14c)

### 3.3 Electrochemical Measurements

The oxidation or reduction conditions to which sulfide minerals are exposed in aqueous solutions may be monitored by measured the potential of an indicator electrode such as platinum or gold metal placed in the solution. The potential measured with a reference electrode such as silver/silver chloride electrode generally called Eh of the solution when it is converted to a potential against the standard hydrogen electrode (SHE). Despite its widespread use, the potential
so measured is not always necessarily a reversible equilibrium potential but can often be a mixed potential (Rand and Woods, 1984). The concept of mixed potential was first introduced by Wagner and Traud (1983) to explain the kinetics observed in many hydrometallurgical processes involving solids which are electron conductors, such as metals, metal sulfides and some oxides.

A mixed potential arises when there are two (or more) REDOX couples present in the system and they are not in equilibrium, i.e., the reversible potentials for the couples Fe\(^{2+}/Fe^{3+}\) and HNO\(_2\)/NO\(_3^-\) as given by the Nernst equation are not equal:

\[
E_{Fe^{2+}/Fe^{3+}} = E_{Fe^{2+}/Fe^{3+}}^0 + \frac{RT}{nF} \ln \frac{C_{Fe^{2+}}}{C_{Fe^{3+}}}
\]

\[
E_{HNO_2/NO_3^-} = E_{HNO_2/NO_3^-}^0 - \frac{RT}{nF} \ln \frac{C_{HNO_2}}{C_{NO_3^-}}
\]

\[
E_{Fe^{2+}/Fe^{3+}} \neq E_{HNO_2/NO_3^-}
\]

Thus, the REDOX condition in solution is not characterized by a unique Eh value, but rather it is represented by two potentials (i.e, those of the two REDOX couples present). When an indicator electrode is introduced into the solution, electrons can exchange with the two separate REDOX couples and the measured potentials will reach a value lying between the reversible potentials of the two couples at which the component anodic and cathodic processes proceed at equal and opposite rates. In other words, the sum of the rate of anodic reactions must be equal to that of the rates of the cathodic reaction at the mixed potential, since the net current flow is zero. This is illustrated in Figure 3.1 (Rand and Woods, 1984).

Mixed potentials in the same system can be different for different indicator electrodes because the rate of an electrode reaction is dependent on the nature of the electrode surface. The potential is not determined solely by thermodynamics but also the kinetics of the reactions at the electrode/solution interface. Hence the mixed potential can vary significantly from one electrode
surface to another. For example, the Eh measured by a platinum electrode can differ from that measure by a gold electrode (Woods, 1976).

![Diagram of mixed potential system](image)

**Figure 3.1** Schematic representation of a mixed potential system (Rand and Woods, 1984)

The mixed potential will also be influenced by other factors that affect the rate of each participating reaction. Stirring the solution will enhance the rates of mass-transport controlled but not chemically controlled processes. Adsorption of impurities can decrease the rate of an electrocatalytic process and it is often necessary for reference electrodes to be cleaned mechanically before each measurement in order to obtain clean, reproducible surfaces.

### 3.4 COMSOL Software for Mathematical Modeling

The numerical strategy embodied in the COMSOL Multiphysics 3.5-Reaction Engineering Lab Module can be used to solve the ODE's describing the concentration-time profiles (trajectories) of species. The COMSOL Reaction Engineering Lab® is a tool that uses
reaction formulas to create models of reacting systems. It is also capable of performing parameter estimation calculations. Using this feature, the kinetic data obtained from the definitive experiments can be used to extract the kinetic parameters. For parameter estimation calculations, Reaction Engineering Lab uses a nonlinear least squares (NLS) algorithm implementing the Gauss-Newton method. The Reaction Engineering Lab’s graphical user interface (GUI) and dialog box containing the reaction parameter setting is illustrated in Figure 3.2.

![Figure 3.2 Snapshot of COMSOL Reaction Engineering Lab GUI and Reaction Settings dialog box](image)

**Figure 3.2** Snapshot of COMSOL Reaction Engineering Lab GUI and Reaction Settings dialog box
CHAPTER 4

DETAILS OF EXPERIMENTS PERFORMED

The materials, reagents and methods of preparation of electrolytes/solutions, equipment, and protocols/procedures employed in performing the experiments performed are described in this chapter.

4.1 Reagents and Mineral Sample

Table 4.1 lists the chemical reagents and mineral (chalcolite) used in the research conducted.

Table 4.1 List of chemical reagents and mineral used in experiments

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Formula</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid</td>
<td>H₂SO₄</td>
<td>98.0</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Ferrous Sulfate</td>
<td>FeSO₄·7H₂O</td>
<td>N. A.</td>
<td>Mallinckrodt Chemicals</td>
</tr>
<tr>
<td>Ferric Sulfate</td>
<td>Fe₃(SO₄)₂·9H₂O</td>
<td>N. A.</td>
<td>Mallinckrodt Chemicals</td>
</tr>
<tr>
<td>Sodium Nitrite</td>
<td>NaNO₂</td>
<td>N. A.</td>
<td>Sigma Chemical</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>KMnO₄</td>
<td>N. A.</td>
<td>Baker Chemical</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>KCl</td>
<td>N. A.</td>
<td>Mallinckrodt Chemicals</td>
</tr>
<tr>
<td>Copper Sulfate</td>
<td>CuSO₄·5H₂O</td>
<td>98.0</td>
<td>Mallinckrodt Chemicals</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO</td>
<td>98.0</td>
<td>Mallinckrodt Chemicals</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>CuS₂</td>
<td>95.0</td>
<td>WARD Minerals</td>
</tr>
</tbody>
</table>

All solutions were prepared with analytical grade reagents and distilled water. The electrical conductivity of distilled water was always lower than 2.00 ± 0.05 μS.cm⁻¹.
4.2 Chemical Analysis Procedure

The procedures/protocols used in the chemical analyses for determination of iron and nitrogen species in the electrolyte and solid residue obtained from leaching of chalcocite are described in this section. The correlation of the electrochemical potential, based on calibration of the potential of a Pt-REDOX Electrode in conjunction with a calomel reference electrode, for determining Fe$^{2+}$/Fe$^{3+}$ concentration ratio (at a “standard” ionic strength) is also included. A copper selenide (CuSe; solid-state) ion-selective electrode/calomel electrode combination was employed for determination of the copper (cupric) concentration in the leaching experiment with chalcocite, and the correlation/calibration details of this electrochemical analysis system are also presented here.

4.2.1 Titration Analysis

This analysis procedure was employed to determine the concentration of Fe(II) and subsequently Fe(III) in the electrolyte during the course of an oxidation experiment. Potassium permanganate, KMnO$_4$, was used as the oxidizing agent for this volumetric-type analysis. In acid solution, MnO$_4^{-}$ ion undergoes reduction to Mn$^{2+}$ ion while Fe$^{2+}$ is oxidized to Fe$^{3+}$ according to the reaction:

$$\text{MnO}_4^{-} + 5\text{Fe}^{2+} + 8\text{H}^{+} = \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$$  \hspace{1cm} (4.1)

The titration involving the oxidation of Fe$^{2+}$ ion to Fe$^{3+}$ by 1x10^{-2} M KMnO$_4$, was conducted in sulfuric acid solution. A 2 mL sample of electrolyte containing Fe(II) diluted with 50 mL of deionized water and 5 mL of 3M H$_2$SO$_4$ was added. The KMnO$_4$ titrant was added one drop at a time while the solution was stirred continuously with a TEFLOWN magnetic impeller. The MnO$_4^{-}$ anion has a violet color and the Mn$^{2+}$ cation is nearly colorless. Thus, the end point in a titration using MnO$_4^{-}$ was taken as the first permanent pink color that appeared in the solution.
being titrated. For the calculation step, the number of moles of potassium permanganate used in the titration is equal to the product of the molarity of the KMnO₄ and the volume added to the end-point. The number of moles of Fe(II) present in the sample was obtained from the balanced equation for the reaction and the moles of permanganate added. Since the initial concentration of total iron in the sample was known, the concentration of Fe(III) was determined as follows:

\[ C_{Fe^{3+}} = C_{Fe\text{-Total}} - C_{Fe^{2+}}, \quad C_{Fe\text{-Total}} = 0.1 \text{ M} \]  

(4.2)

4.2.2 Spectrophotometric Analysis

Chemical analyses of Fe(II) and nitrogen species in the electrolyte (N(III), N(V)) were performed by Hach:UV/Visible Spectrophotometer (Model DR/2500). Nitrite and nitrate analyses employed NitriVer 3 and NitraVer 53 Reagent Sets containing reagent pillows and solution vials. Nitrite analyses were in the “Low” range (0.002 to 0.300 mg/L (ppm) NO₂⁻-N) diazotization method and nitrate analysis was “High” range (0.2 to 30.0 mg/L (ppm) NO₃⁻-N) chromotropic acid method. Ferrous iron in the electrolyte was analyzed by 1,10 Phenanthroline method which has detection limits of 0.02 to 3.00 mg/L. A reagent blank concentration-value for each lot of reagents was determined. This procedure consisted of using deionized water in place of the sample. A specified amount of sample was transferred into a vial and a specified reaction-time (listed in Table 4.2) was allowed to elapse.

**Table 4.2** Specifications listed in the Standard Methods of Water Analysis with Hach Spectrophotometer

<table>
<thead>
<tr>
<th><strong>Analyzed Species</strong></th>
<th><strong>Ferrous (Fe²⁺)</strong></th>
<th><strong>Nitrite (NO₂⁻)</strong></th>
<th><strong>Nitrate (NO₃⁻)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method No.</strong></td>
<td>8146</td>
<td>10020</td>
<td>8507</td>
</tr>
<tr>
<td><strong>Analysis Wavelength (nm)</strong></td>
<td>510</td>
<td>507</td>
<td>410</td>
</tr>
<tr>
<td><strong>Volume of Container (mL)</strong></td>
<td>25</td>
<td>10</td>
<td>Test’N Tube Vial</td>
</tr>
<tr>
<td><strong>Volume of Sample (mL)</strong></td>
<td>25</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td><strong>Visible Complex Color</strong></td>
<td>Orange</td>
<td>Pink</td>
<td>Yellow</td>
</tr>
<tr>
<td><strong>Reaction Time (min)</strong></td>
<td>3</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>
The program was selected from the *Hach Spectrophotometer* Menu and measured the absorbance. The instrument was converted absorbance value to concentration value (ppm: parts per million) automatically. The reagent blank value was subtracted from final concentration values.

### 4.2.3 Chemiluminescence (NO-NOₓ) Gas Analyzer

A chemiluminescence gas-analyzer was utilized to monitor the concentrations of nitric oxide (NO) and “oxides” of nitrogen (NOₓ≡NO+NO₂) in the gas space of the oxygen-pressurized reactor for ferrous-oxidation experiments conducted with 4.5 mM NO₂⁻ (DE-3C) electrolyte. The gas phase (NO and NO₂) was sampled from the reactor and fed to the analyzer (Thermoelectron Model 10-A) with the flowrate of 350 L.min⁻¹ by the carrier gas N₂.

The principle of this instrumental analysis is based on reaction of NO(₈) with ozone in an isothermal reactor. The resulting chemiluminescence is measured with a photodetector (by photoelectric amplification of the signal). NOₓ is measured by the reduction of NOₓ to NO with oxygen in the thermal molybdenum catalytic-converter operated at 650°C. Consequently, NOₓ converted to NO in addition to NO present is detected in the NOₓ configuration with the convert in series. The concentration of NO₂ is subsequently determined by difference between the two measurement-modes.

### 4.2.4 Field Emission Scanning Electron Microscope (FESEM)

Particulate samples of chalcocite were examined before and after oxidative leaching (Experiment: DE-6) by Field Emission Scanning Electron Microscopy (FESEM) (JEOL JSM-7000F). Particles comprising the sample were deagglomerated in an ultrasonically in a small beaker containing ethanol. A liquid sample containing a population of particles was extracted from the beaker with an “eye dropper” and placed on aluminum foil attached to a stub which was
then placed into the vacuum chamber of the microscope. The FESEM provided for image
magnifications in the range from 300X to 2500X. The electron accelerating voltage was
1500 keV. EDS analysis was used to obtain sulfur and copper atomic concentrations.

4.2.5 REDOX Potential Measurement for Fe\(^{2+}/Fe^{3+}\) Concentration Determination

Prior to the preliminary experiments, REDOX-potential measurements were conducted in
a de-oxygenated 1.0 M H\(_2\)SO\(_4\) containing FeSO\(_4\) and Fe\(_3\)(SO\(_4\))\(_3\) at a total concentration of 10\(^{-1}\) M,
with concentrations of each ranging from a low of 10\(^{-3}\) to a high of 10\(^{-1}\) M. This allowed,
subsequently, for correlation of the concentration ratio of C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) as a function of time during
the ferrous-oxidation experiments. Furthermore, in order for this REDOX-potential calibration to
be viable (have the desired resolution) for predicting ferrous-ferric ratios, the concentration of the
minor species present was selected to be equal to or greater than 10\(^{-3}\) M.

The IBM PYREX cell was charged with 50 mL 1.0 M H\(_2\)SO\(_4\) solution. The electrodes
were inserted into the IBM cell and the required mass of FeSO\(_4\),7H\(_2\)O salt was dissolved in 50
mL of 1 M sulfuric acid solution to prepare 1.0x10\(^{-3}\), 2.0x10\(^{-3}\), 1.0x10\(^{-2}\), 5x10\(^{-2}\) and 0.10 M
ferrous sulfate solution. Similarly, the same concentrations of the ferric sulfate solutions were
prepared from Fe\(_2\)(SO\(_4\))\(_3\),9H\(_2\)O added to 1.0 M H\(_2\)SO\(_4\) solutions. These electrolytes with various
Fe(II)/Fe(III) concentration ratios listed below.

- 0.10 M Fe(II) + 1.0x10\(^{-3}\) M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 100
- 0.10 M Fe(II) + 5.0x10\(^{-2}\) M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 10
- 0.10 M Fe(II) + 2x10\(^{-3}\) M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 50
- 5.0x10\(^{-2}\) M Fe(II) + 5.0x10\(^{-2}\) M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 1
- 1.0x10\(^{-3}\) M Fe(II) + 0.10 M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 1/100
- 2.0x10\(^{-3}\) M Fe(II) + 0.10 M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 1/50
- 1.0x10\(^{-2}\) M Fe(II) + 0.10 M Fe(III), C\(_{Fe^{2+}}\)/C\(_{Fe^{3+}}\) = 1/10
Electrolyte was first deoxygenated with industrial grade nitrogen gas. All measurements were performed using a Pt electrode, in conjunction with a calomel reference-electrode was used to monitor the REDOX potential, primarily due to the Fe$^{2+}$/Fe$^{3+}$ couple in the electrolyte. The electrolyte temperature was 25°C.

4.3 Equipment Details

Total number of four equipments utilized for the experiments including the devices/instruments for performing the electrochemical measurements and chemical analysis are described in this section.

4.3.1 Electrodes

In the experiments, Pt electrode (Beckman Electrode Model No.39273) in conjunction with a reference-electrode was used to monitor the REDOX potential. REDOX electrode had 12 mm diameter and U.S. standard combination plug. Reference electrode was a single junction Standard Calomel Electrode (SCE), in which the liquid junction was saturated potassium chloride (KCl) electrolyte. The Radiometer manufactured standard calomel electrode had banana plug type connection and lower diameter was 7.5 mm. The calibration of the reference electrodes was performed by employing a Zobell electrolyte ($3.33 \times 10^{-3} \text{ M} \ K_4\text{Fe(CN)}_6$, $3.33 \times 10^{-3} \text{ M} \ K_3\text{Fe(CN)}_6$ and $0.10 \text{ M} \text{ KCl}$) at 20°C. A potential of 240 mV relative to the standard hydrogen electrode (SHE) was obtained.

All potentials reported in the research were converted to the SHE scale. The measured potential with respect to SHE ($E_{h}^{\text{SHE}}$) is obtained by addition of the potential of the reference electrode ($E_{h}^{\text{SCE}}$) according to the relationship:

$$E_{h}^{\text{SHE}} = E_{h}^{\text{SCE}} + 240 \text{ (mV, at 20°C)} \quad (4.3)$$
The potential of the electrode system in contact with the electrolyte was measured using a Radiometer type PHM 62 digital pH/mV meter. The analog output from the meter was recorded continuously by custom software written in Visual Basic 6.0 on a desk-top personal computer with analog/digital interface card. This provided for data acquisition.

4.3.2 Ambient-Pressure Stirred-Reactor

An IBM PYREX® electrochemical cell consisting of a 50 mL conical borosilicate glass vessel fitted with a polycarbonate cap to hold two electrodes was used in preliminary experiments. The cap of the vessel contains a groove to hold an O-ring which provided for sealing between the cap and body of the vessel.

![Schematic of IBM PYREX cell showing electrodes in place](image)

**Figure 4.1** Schematic of IBM PYREX cell showing electrodes in place

The cap had five O-ring-sealable ports. Two provided for insertion of REDOX (Pt) and reference (SCE) electrodes. Two ports allowed for connection of a TEFLON tube to introduce gas into the system and an orifice to allow for a small leak from the system. Nitrogen or oxygen
could be bubbled into the solution at a flow rate of 3 SCCM measured by a Hasting Mass Flowmeter. One port allowed for withdrawal of electrolyte samples. Figure 4.1 shows the schematic of the cell together with the ancillary equipment employed for performing the experiments.

A magnetic stirrer was utilized with a top-and-bottom four-blade Teflon impeller. The rotational speed was set at 400 RPM with Strobotac (General Radio Company). A photograph of the system is shown in Figure 4.2.

![Figure 4.2 (A) Electrochemical system including IBM PYREX cell and Standard pH meter (B) Five ports carrying 1) REDOX (Pt) electrode, 2) Reference (Calomel) Electrode, 3) Purge Gas (N₂/O₂), 4) Orifice, 5) Sampling Port](image)

### 4.3.3 Pressurized Stirred-Reactor

Definitive experiments were performed in a 250 mL pressurized PYREX® reactor with three baffles incorporated in the walls of the vessel. An O-ring provided a seat between the cover and vessel with three stainless steel bolts clamping the two parts together. The cap contained three Swagelock® fittings. One was used to introduce a sampling tube into the vessel. The
sampling tube was connected to a TEFLON® plug valve and a delivery tube. The liquid hold-up in the sampling arrangement was less than 1.0 mL. One fitting was provided for pressurizing the vessel with oxygen. The third fitting with cap was an auxiliary port for either inserting reagents into the reactor or depressurizing it. A magnetic stirrer was utilized in conjunction with a double-face four-bladed Teflon impeller for stirring the liquid in the reactor.

**Figure 4.3** (A) High Pressure PYREX vessel and titration set-up, (B) Cap carrying 1) O₂ inlet, 2) Sampling tube, 3) Auxiliary Port, 4) Sampling Valve

### 4.3.4 High Temperature Pressurized Reactor

The temperature of the reactor was controlled by circulation of hot water through the water jacket as shown in Figure 4.4. High temperature experiments were performed in a 250 mL pressurized PYREX® reactor with three baffles incorporated in the walls insulated by a heat jacket. An O-ring provided a seat between the cover and jacket with three stainless steel bolts clamping the three parts (Vessel cap, heating jacket and glass reactor) together. The configuration of the fittings on the cap was the same as pressurized stirred-reactor. Polycarbonate heat jacket was custom made and sealed with an O-ring placed between the cap and the heat jacket. The
heating fluid was water and heat jacket filled with hot water (80°C) obtained from water bath.

**Figure 4.4 (A) High Temperature Pressurized PYREX vessel, IR-heat lamp and water bath, (B) Cap carrying \( \text{O}_2 \) inlet, 2) Sampling tube, 3) Auxiliary Port, 4) Sampling Valve, 5) Water Jacket Inlet, 6) Water Jacket Outlet**

### 4.4 Procedure Employed

This section describes the procedures employed for conducting the research reported in the thesis. Laboratory-scale experiments were classified into two categories: preliminary and definitive experiments. Preliminary experiments were performed in an IBM cell. Subsequently, definitive experiments were designed and performed in a high pressure (≈5 atm) PYREX reactor which could be operated at ambient temperature (≈25°C) and also at higher temperature (≈80°C) by employing a water jacket with thermostated water-bath circulator.

#### 4.4.1 Preliminary Experiments (PE)

**PE-1: Ferrous Oxidation to Ferric with Sodium Nitrite in Controlled-Leak Reactor System**

The IBM PYREX cell was charged with 50 mL 1 M \( \text{H}_2\text{SO}_4 \) solution. Mass of 1.39 g of FeSO\(_4\) salt was added to provide for an electrolyte concentration of 0.1 M. A magnetically coupled impeller in the cell provided for stirring to dissolve the salt completely in the sulfuric
acid electrolyte. In preparation for conducting the experiment, the gas space in the cell was purged with industrial-grade (99.9%) nitrogen gas for approximately 10 minutes. The experiment was initiated by introducing 1.34 mg of NaNO₂ salt into the electrolyte to provide a concentration of 3.89 mM, followed by switching the gas supply to oxygen which was bubbled into the electrolyte at a flow rate of 3 SCCM. The orifice in the gas outlet provided for the flowrate indicated, while maintaining a small overpressure in the cell. REDOX potential measurements were performed in-situ using a Pt electrode and calomel reference-electrode and monitored continuously with an analog connection to the computer. The REDOX potentials were recorded for 20h.

**PE-2: Ferrous Oxidation to Ferric with Sodium Nitrite in Leak-Tight Reactor System**

The experiment was conducted in the same manner of PE-1, except that the orifice was replaced with a plug and system was operated with a small over-pressure above barometric pressure (≈ 2 inches Water Column). REDOX potentials were recorded for 13 h at which time the potential became asymptotic.

**PE-3: Ferrous Oxidation with Potassium Nitrate in Controlled-Leak Reactor**

An experiment was performed to oxidize ferrous with the same concentration (3.89 mM) of nitrate instead of nitrite in 1M H₂SO₄ system was operated with a small over-pressure above barometric pressure (≈ 2 inches Water Column). REDOX potentials were recorded for 12 h. REDOX potentials were recorded continuously with data acquisition.

Prior to and between each run, the IBM cell was washed, rinsed with deionized water, and allowed to dry. Also, the potassium chloride (KCl) level within the double-junction calomel electrode were checked and topped off as needed.
4.4.2 Definitive Experiments (DE)

**DE-1: Ferrous Oxidation to Ferric with (only) Oxygen at 25°C**

In this experiment 100 mL H$_2$SO$_4$ (1 M) – FeSO$_4$ (0.1 M) electrolyte was prepared, transferred to the reactor which was then pressurized with oxygen to 50 psig ($\approx$ 4 atm total pressure). Typically, a total of 5 electrolyte samples were collected for chemical analysis one each day for four days. Chemical analyses were performed volumetrically (titration) using 1x10$^{-2}$ M KMnO$_4$ for 96 h.

**DE-2: Ferrous Oxidation to Ferric with 3.89 mM Sodium Nitrite (25°C)**

The experiment were also conducted with 100 mL H$_2$SO$_4$ (1 M) – FeSO$_4$ (0.1 M) electrolyte. Once the electrolyte was transferred to the reactor, 3.89 mM NaNO$_2$ was injected into the vessel and the system was operated at oxygen pressure of 50 psig. Since the system is pressurized it was not possible, with the sealing-configuration available, to introduce electrodes to monitor the REDOX potential, continuously. Therefore, ex-situ REDOX potential measurements were performed. A total of 10 samples were collected one each hour for the first 8 hours and the two remaining samples at 22 and 24 hours elapsed time.

**DE-3A, DE-3B, and DE-3C: Ferrous Oxidation to Ferric with 4.5 mM Sodium Nitrite (25°C)**

Three experiments, identical to DE-2, except that a higher concentration of nitrite (4.5 mM NaNO$_2$) was employed. Samples were collected as before, but now ferrous, nitrite and nitrate were analyzed with Hach UV-Visible Spectrophotometer. Chemical analyses were performed one after 15 min and one each hour for the first 4 hours and last one at 24 hours elapsed time. DE-3B and DE-3C were a replicate of DE-3A. In DE-3C, the gaseous nitrogen species in reactor gas space was analyzed with Thermoelectron chemiluminescence (NO$_x$) gas analyzer for 2 hours.
The first sample was withdrawn after 15 minutes and six remaining samples every 30 minutes.

**DE-4A and DE-4B: Ferrous Oxidation to Ferric in the Presence of Solid Phase**

Two experiments with the same procedure of “DE-3” were conducted with quartz (silica) sand to provide for an inert solid-phase. 1 g of quartz (silica) sand sample was employed had a the particle size in the range of 100 to 200 mesh (74 to 149 μm) in the Ferrous-Nitrite electrolyte. DE-3B was a replicate of DE-3A.

**DE-5A and DE-5B: Ferrous Oxidation with Oxygen and Sodium Nitrite (80°C)**

Two ferrous oxidation experiments (with only oxygen (DE-5A) and with oxygen and nitrite (DE-5B)) were conducted at higher temperatures (80°C) to observe the increased rate of oxidation of ferrous and behavior of the ferrous-nitrosyl complex at a temperature higher than ambient. These experiments were conducted in the pressurized PYREX reactor-vessel, which was fitted with a thermostated water-jacket.

**DE-6A and DE-6B: Chalcocite (Cu₂S) Leaching with Oxygen and Sodium Nitrite (80°C)**

An experiment was performed on the oxidative dissolution behavior of chalcocite in an electrolyte containing 4.5 mM NaNO₂ and 1M H₂SO₄. Only oxygen was employed instead of sodium nitrite in Experiment No. DE-6B. Naturally occurring sample of chalcocite (Butte, Montana) was ground with a mortar and pestle. The cuprous copper and sulfide were expected to be oxidized to cupric and sulfur/sulfate, respectively. The experiment was performed in the high pressure PYREX vessel with a water jacket, at a temperature of 80°C (± 2°C). Oxygen gas with the pressure of 60 psig was used. The concentration of copper was analyzed by atomic absorption spectrophotometer.
CHAPTER 5
RESULTS AND INTERPRETATION

This chapter presents the results of the experiments conducted as well as predictions generated by the computer simulation of model developed in Appendix A1. Calibration of the REDOX potential measurement for Fe\textsuperscript{2+}/Fe\textsuperscript{3+} concentration ratio and for Cu\textsuperscript{2+} concentration are discussed in Section 5.1. Preliminary Experiments are presented in Section 5.2 and the results obtained from the experiments performed in the partially-sealed and sealed reactors are reported. The Definitive Experiments conducted in the pressurized reactor is discussed in Section 5.3. Also the results “high temperature” experiments and analysis results of species in the electrolyte are presented in this section. Besides, the concentration-time trajectories obtained from simulation are covered in Section 5.4 and the results compared with the one for related experiments.

5.1 \textbf{REDOX Potential Measurement for C_{Fe2+}/C_{Fe3+} Determination}

Prior to the preliminary and definitive experiments $E_h$ measurements were conducted to obtain calibration curve representing different C_{Fe2+}/C_{Fe3+} ratios. At a concentration ratio of ferrous to ferric at unity, time-independent equilibrium $E_h$ was 678 mV (SHE). This observed REDOX potential in Figure 5.1 is smaller, by approximately 100 mV, than the value of 771 mV reported in the literature (Dean, 1999) for “standard” conditions (activity ratio of unity); nonetheless, it should be noted that the purpose of the calibration was to allow for monitoring of the concentration of the iron species in the electrolyte. The reason for this behavior has been discussed by Natarajan and Iwasaki (1970).
5.2 Preliminary Experiments (PE)

Three preliminary experiments on ferrous oxidation with sodium nitrite were performed in partially-sealed and sealed reactor. Also, the experiment presenting ferrous oxidation with nitrate instead of nitrite was employed.

5.2.1 PE-1: Ferrous Oxidation with Sodium Nitrite in Controlled-Leak Reactor System

Ferrous oxidation was employed with 3.89 mM NO$_2^-$ in a partially-sealed reactor containing 1M H$_2$SO$_4$ electrolyte. In the partially-sealed system, a small leak was introduced by providing a small orifice in a plug inserted in one of the ports in the cap. Oxygen was bubbled continuously into the electrolyte (FeSO$_4$−NaNO$_2$−H$_2$SO$_4$) at a flowrate of 3 SCCM, with a back-pressure of approximately 2 in. Water Column in the reactor. A mass of 13.9 mg NaNO$_2(s)$ was transferred to the oxygenated 50 mL of 1M H$_2$SO$_4$ electrolyte containing 0.1 M FeSO$_4$. Once
nitrite salt was introduced, the FeNO$^{2+}$ complex (green-black color) formed. The REDOX potential was recorded for 20 hours by use of the data-acquisition system. The measured potential as a function of time is displayed in Figure 5.2. The calibration curve obtained previously for the concentration ratio ($C_{Fe^{2+}}/C_{Fe^{3+}}$) provided for the determination of the ferrous concentration in the system. The potential became asymptotic at 764 mV (SHE) and corresponds to a $C_{Fe^{2+}}/C_{Fe^{3+}}$ ratio of 1/36. The corresponding concentration of ferric ion (based on the total iron concentration, 0.1 M) was determined to be 0.097 M after 20h. The rate of oxidation of ferrous was observed to increase while the color progressively became less intense with a rapid change at the end as the asymptotic value was achieved.

![Figure 5.2](image_url)

**Figure 5.2** Measured potential as a function of time for Experiment No: PE-1. Electrolyte Composition: $C_{FeSO_4} = 0.1$ M, $C_{NaNO_2} = 3.89$ mM, $C_{H_2SO_4} = 1.0$ M, Ionic Strength $\approx 1$ M. Controlled-Leak Reactor System

### 5.2.2 PE-2: Ferrous Oxidation with Sodium Nitrite in Leak-Tight Reactor System

In order to assess the role of possible gas species (NO, NO$_2$) in the system, the experiment was now conducted in the sealed reactor which is the same reactor used in PE-1 but
with the orifice removed and the port plugged. Small leaks from the ports carrying electrodes were considered to be negligibly small. The ferrous-nitrosyl complex color persisted for approximately 3 hours. The observed asymptotic $E_h$ recorded (Figure 5.3) was 954 mV (SHE) after 13 h. This value is higher than could be supported by a Fe$^{2+}$/Fe$^{3+}$ REDOX couple with a "low" concentration of ferrous ion. This result could be interpreted that in PE-1, lower REDOX potentials were observed as a consequence of loss of NO$_{(g)}$ from the gas phase during the course of the experiment.

![Figure 5.3](image)

**Figure 5.3** Measured potential as a function of time for Experiment No: PE-2. Electrolyte Composition: $C_{FeSO_4} = 0.1$ M, $C_{NaNO_2} = 3.89$ mM, $C_{H_2SO_4} = 1.0$ M, Ionic Strength $\approx 1$ M. Leak-Tight Reactor System

Higher REDOX potentials indicated possible presence of a nitrogen species REDOX couple, since most (~99%) of the ferrous ($C_{Fe^{2+}} / C_{Fe^{3+}} > 0.01$) was oxidized above a sustaining potential of 792 mV (SHE) observed. Standard REDOX potentials of HNO$_2$/NO$_3^-$, NO/NO$_3^-$, NO/HNO$_2$ have been reported as 940, 960, 1000 mV (Dean, 1999). It is apparent that the continuous O$_2$ supply oxidizes the nitrogen species to the nitrate (NO$_3^-$). Thus, after oxidation of
97% Fe$^{2+}$, the platinum electrode responds to a nitrogen species REDOX couple. The specific REDOX couple cannot be unambiguously determined from this set of experiments, and was subsequently explored further in the section 5.4.5.

5.2.3 PE-3: Ferrous Oxidation with Potassium Nitrate in Leak-Tight Reactor

An experiment was conducted in the leak-tight reactor with O$_2$ overpressure (~2 in. Water Column) and 3.89 mM nitrate (KNO$_3$) instead of nitrite (NaNO$_2$) to determine the oxidation rates of ferrous with nitrate addition, compared to nitrite. The REDOX potentials were monitored for 12 h. The measured Eh was initially 556 mV (SHE). During the 12h elapsed time, the increase in Eh was insignificant (~1-2 mV). Furthermore, the ferrous-nitrosyl complex was not formed indicating the absence of significant concentration of NO species in the electrolyte. The hypothesis being tested was that nitrate, like nitrite, would be (ultimately) reduced to NO by ferrous, possibly via a nitrite species (HNO$_2$) intermediate. Since there was no evidence of this, it was apparent that nitrate cannot be reduced by ferrous ion or conversely ferrous cannot be oxidized by NO$_3^-$ . This being the case, it is must be stated that nitric acid (HNO$_3$) is capable of oxidizing ferrous ion, however a high proton activity (approximately by 3 M H$_2$SO$_4$) is required for nitrate protonation and the necessary HNO$_3$ concentration to be achieved.

5.3 Definitive Experiments (DE)

A total of six definitive experiments were performed. The last experiment in this series was performed on the leaching of chalcocite. Replicates were performed for three of these six experiments.

5.3.1 DE-1: Ferrous Oxidation with (only) Oxygen at 25°C

In this set of experiment, ferrous oxidation rate was examined with 50 psi of O$_2$ pressure when nitrite was absent. The experiment was performed at 25°C (±2 °C). No significant change in
the ferrous concentration was discernable during the first 24 hours. At the end of 96 h.
approximately 82% of the ferrous iron was still present, thus 0.018 M ferric iron had been
produced (Figure 5.4). The ferrous concentration of samples collected were analyzed
volumetrically (titration) using $1 \times 10^{-2}$ M KMnO$_4$, during an elapsed time of 96 h. Samples were
collected every 8 hours and subsequently each 24 hours following.

![Graph](image)

**Figure 5.4** Time trajectories of concentration of Ferrous in solution for Experiment No: DE-1.
Initial electrolyte concentrations: $C_{FeSO_4}$=0.1 M, $C_{H_2SO_4}$ = 1.0 M. Ionic Strength ≈ 1 M. Pressurized reactor ($P_{O_2}$= 50 psig ≈ 4 atm total pressure of $O_2$)

5.3.2 DE-2: Ferrous Oxidation with 3.89 mM Sodium Nitrite (25°C)

The same concentration of nitrite (3.89 mM) with in PE-1 and PE-2 was used to oxidize
0.1 M ferrous in 1M $H_2SO_4$ electrolyte. Oxygen was supplied into the reactor with 50 psi of
oxygen pressure. The ferrous-nitrosyl complex, evident from its color, had disappeared after,
approximately, an elapsed time of 3 hours. Ex-situ REDOX potential measurements exhibited the
same trend of increasing with elapsed time as was observed for the sealed (unpressurized) reactor
experiment (PE-2). At the conclusion of the experiment, the $E_h$ recorded was 976 mV (SHE). This higher potential has been interpreted as having effective nitrogen species recycle and oxidation to nitrate, as a result of increased solubility of $O_2$ due to high pressure (50 psig).

5.3.3 DE-3A, DE-3B and DE-3C: Ferrous Oxidation with 4.50 mM Sodium Nitrite (25°C)

Three experiments, identical to DE-2, except that higher concentrations of nitrite (4.5 mM NaNO$_2$) were employed. DE-3B was a replicate of DE-3A. This concentration was selected based on an "optimum concentration" devised in conjunction with the mathematical simulation (discussed in section 5.4.4). The REDOX potential output and chemical analysis results are presented in Figure 5.5 and 5.6.

![Figure 5.5](image)

**Figure 5.5** Time trajectories of concentration of Ferrous in solution for Experiment No: DE-2 and DE-3A and DE-3B. Initial electrolyte concentrations: $C_{FeSO_4}=0.1$ M, $C_{H_2SO_4} = 1.0$ M, Ionic Strength $\approx 1$ M. Pressurized reactor ($P_{O_2}=50$ psig $\approx 4$ atm total pressure of $O_2$)

At the end of elapsed time of 24 hours, the potential of 954 mV was observed. Higher potential values were obtained in shorter time (6 hours) with 4.5 mM NO$_2^-$ relative to 3.89 mM NO$_2^-$.
It was concluded that the higher oxidation rate of ferrous was accomplished and the active REDOX couple becomes nitrogen species with higher concentration of nitrite.

Figure 5.6 Time trajectories of concentration of Nitrite (A), Nitrate (B) and Ferrous (C) in solution for Experiment No: DE-3A and DE-3B. Initial electrolyte concentrations: $C_{\text{FeSO}_4} = 0.1 \text{ M}$, $C_{\text{NaNO}_2} = 4.5 \text{ mM}$, $C_{\text{H}_2\text{SO}_4} = 1.0 \text{ M}$. Ionic Strength $\approx 1 \text{ M}$. Pressurized reactor ($P_{\text{O}_2} = 50 \text{ psig } \approx 4 \text{ atm}$ total pressure of $\text{O}_2$)
The nitrite concentration decreased in higher rates than the one obtained from simulation (section 5.4.3). This decrease was interpreted as the formation of gaseous species (NO, NO₂, NOₓ) in the gas phase which couldn’t be analyzed by spectrophotometer. It is apparent during the course of reaction time the original nitrogen species (NO₂⁻, NO, NO₂, NOₓ) was converted to nitrate (N(V)) in the electrolyte.

The chemical analysis indicated that 50% of ferrous is oxidized in approximately 1 h and 99% conversion realized at the end of 17 h. Three ferrous oxidation experiments (DE-1, DE-2 and DE-3) showed that in the presence of nitrite, the rate of ferrous oxidation is 400 times higher compare to oxidation of ferrous with only O₂ present.

In the DE-3C experiment, similar to DE-3A and 3B, chemiluminescence analyzer was used to assess the concentration of gaseous nitrogen species (NOₓ; NO and NO₂) in the gas space of the reactor containing 4.5 mM nitrite. Figure 5.7 illustrates the concentrations of the NO(g) and NO₂(g) obtained from NOₓ gas analyzer for 3 hours.

During the course of the analysis time, the maximum concentration for NO(g) and NO₂(g) were 2.77x10⁻⁶ M and 1.66 x10⁻⁶ M, respectively. Concentrations of NO(g) and NO₂(g) were three orders of magnitude smaller that the initial nitrite concentration and decreased continuously. The gas species of nitrogen do not appear to be in the equilibrium with the species in the electrolyte. The continuous decrease was interpreted that the NO(g), transferred from the electrolyte to gas phase and reacted with O₂ to produce NO₂(g). Then NO₂(g) dissolved in the electrolyte, is disproportionate to HNO₂ and NO₃⁻.
Figure 5.7 Time trajectories of concentration of NO(g) and NO2(g) in the gas phase above nitrite electrolyte for Experiment No: DE-3C. Initial electrolyte concentrations: $C_{FeSO_4}$=0.1 M, $C_{NaNO_2}$ = 4.5 mM, $C_{H_2SO_4}$ = 1.0 M. Ionic Strength $\approx$ 1 M. Gas flowrate: 0.5 SCCM. Pressurized reactor ($P_{O_2}$= 50 psig $\approx$ 4 atm total pressure of O$_2$)

5.3.4 DE-4A and DE-4B: Ferrous Oxidation in the Presence of Solid Phase (Quartz Sand)

Two experiments were performed with the addition of quartz sand into the electrolyte containing 4.5 mM NO$_2^-$ in order to determine the role of a high surface-area solid-phase in the electrolyte. The Figure 5.8 presents the measured potentials of the REDOX couples in the electrolyte with and without quartz.

The decrease in the oxidation rate of ferrous was observed during the first 6.5 hours and REDOX potentials increased to the same values obtained from the measurements for the electrolyte with no quartz. The results were interpreted as the adsorption of FeNO$_2^+$ complex onto the quartz particles at the beginning of the ferrous oxidation mechanism. REDOX potential measurements showed that once the complex decomposed completely, the adsorption of FeNO$_2^+$ species onto the solid phase is no longer a rate limiting mechanism in the oxidation of ferrous.
**Figure 5.8** Measured potential as a function of time for Experiment No: DE-4. Composition of Electrolyte containing Quartz Sand: $C_{FeSO_4} = 0.1 \text{ M}$, $C_{NaNO_2} = 4.5 \text{ mM}$, $C_{H_2SO_4} = 1.0 \text{ M}$, Pulp Ratio 1%, Ionic Strength $\approx 1 \text{ M}$

### 5.3.5 DE-5A and DE-5B: Ferrous Oxidation with Oxygen and Sodium Nitrite (80°C)

The experiments DE-1 and DE-3 were repeated at the higher temperature (80°C) to observe the temperature effect on the ferrous oxidation rate. Figure 5.9 shows the REDOX potentials obtained from the experiment employed using only oxygen (DE-5A).

The highest REDOX potential was 590 mV (SHE) and this value represented the $C_{Fe^{2+}}/C_{Fe^{3+}}$ ratio of 40, found from the calibration curve. Figure 5.10 illustrating the titration analysis shows significant increase in the rate of ferrous oxidation the ferrous conversions to ferric at 25°C and 80°C were compared. The elapsed time was 5 hours to achieve the 20% conversion of ferrous at 80°C while the same conversion was found after 96 hours at 25°C.
**Figure 5.9** Measured potential as a function of time for Experiment No: DE-5A. Composition of Electrolyte: $C_{\text{FeSO}_4} = 0.1$ M, $C_{\text{H}_2\text{SO}_4} = 1.0$ M, Ionic Strength ≈ 1 M Pressurized reactor ($P_{\text{O}_2} = 50$ psig, $P_T \equiv 4$ atm at 25°C and 5 atm at 80°C)

**Figure 5.10** Time trajectories of concentration of Ferrous in solution for Experiment No: DE-5A. Initial electrolyte concentrations: $C_{\text{FeSO}_4} = 0.1$ M, $C_{\text{H}_2\text{SO}_4} = 1.0$ M, Ionic Strength ≈ 1 M. Pressurized reactor ($P_{\text{O}_2} = 50$ psig, $P_T \equiv 4$ atm at 25°C and 5 atm at 80°C)
In DE-5B, ferrous oxidation was employed with 4.5 mM nitrite at 80°C. The REDOX potential measurements showed that the same potential was obtained in 2.5 hours instead of 7 hours which was obtained at 25°C. The results indicated that oxidation rate of ferrous with nitrite was approximately three times higher compared at 25°C. The black-green color of ferrous nitrosyl complex progressively became less intense over a period of 1 h. at this higher temperature. The comparison of Eh potentials at 25°C and 80°C are illustrated in Figure 5.11.

Figure 5.11 Measured potential as a function of time for Experiment No: DE-5B. Composition of Electrolyte: $C_{\text{FeSO}_4} = 0.1$ M, $C_{\text{NaNO}_2} = 4.5$ mM, $C_{\text{H}_2\text{SO}_4} = 1.0$ M, Ionic Strength $\approx 1$ M Pressurized reactor ($P_{\text{O}_2} = 50$ psig, $P_T = 4$ atm at 25°C and 5 atm at 80°C)

5.3.6 DE-6A and DE-6B: Chalcocite (Cu$_2$S) Leaching with Oxygen and Sodium Nitrite

Oxidative leaching of a sample of chalcocite mineral (Cu$_2$S) ($\approx 0.80$g in 100mL of electrolyte) with oxygen and with 4.5 mM nitrite at 80°C and $P_{\text{O}_2} \approx 4.5$ atm ($P_{\text{tot}} = 60$ psig) resulted in an electrolyte (cupric) copper concentration of 0.072 mM, corresponding to 72% dissolution of the mineral sample with nitrite and 63% with oxygen after 4 hours. The concentration-time profile of cupric ion is presented in Figure 5.12.
Figure 5.12 Time trajectories of concentration of cupric in solution for Experiment No: DE-6A and DE-6B. Initial electrolyte concentrations: $C_{\text{NaNO}_2} = 4.5$ mM (DE-6A), $C_{\text{H}_2\text{SO}_4} = 1.0$ M, Ionic Strength $\approx 1$ M. Solid Concentration $\approx 1$ g per 100 g of solution. Temperature: $80^\circ$C ($\pm 2$ °C); Pressurized reactor ($P_{\text{TOT}} = 60$ psig; $\approx 5$ atm; $P_{\text{O}_2} = 4.5$ atm)

Figure 5.13-5.19 presents the FESEM images of partially reacted and unreacted chalcocite particles with nitrite.

Figure 5.13  FESEM photomicrograph of unleached chalcocite at magnification 300X
Figures 5.13, 5.14, and 5.15 show three assemblages of unreacted chalcocite particles at increasing magnifications in the size range of 200 μm to 5 μm. At the highest magnification the particles are angular with smooth fracture faces resulting from comminution of the sample. These particles are dense exhibiting neither porosity nor cracks. At the lower magnification representing the largest particles in the system, there are cleavages but these large particles remain intact.

FESEM images of partially-leached chalcocite particles (≈ 60 μm) indicated islands of coalesced (amorphous) sulfur adjacent to leached regions that exhibited a lamillate grate-like structure. Since there was no evidence of sulfur coating in the particulate residue, it could be concluded that the cuprous ion of the chalcocite (Cu₂S) is directly oxidized to cupric while the associated sulfide is oxidized by a two stage process that appears to be related to the particle size of the chalcocite. Thus, in the case of the sulfide there is an intermediate oxidation to elemental (solid) sulfur and subsequent oxidation to sulfate. The role of nitrite in the oxidation of the “sulfur” could not be readily elucidated.
Figure 5.15  FESEM photomicrograph of unleached chalcocite at magnification 2500X

EDS analysis conducted with the electron microscope at 500 keV, on leached surfaces of the residue sample, showed a “Cu” to “S” ratio of two to one (2:1) there was no evidence of solid cupric-sulfide (CuS; covolite) being present. Therefore, the sulfide (S²⁻) accompanying the dissociation of the chalcocite (Cu₂S), in principle, can be oxidized either by the “high” oxidation-state oxy-nitrogen species (NO₂⁻, NO₂(aq) and NO₃⁻) or by O₂(aq); stage wise (depending on the particle size), first to S⁰ and then SO₄²⁻, or such that the intermediate S⁰ is short-lived and does not condense on the particle surface. The coalesced islands of sulfur observed (on the “large” particles) could be as a result of surface diffusion between neighboring sites where the cuprous ion in the lattice was lost due to oxidation to cupric ion while at the same time the sulfide is oxidized to the zero-valence (solid) species.
Figure 5.16  FESEM photomicrograph of reacted chalcocite with nitrite at magnification 300X

Figure 5.17  FESEM photomicrograph of reacted chalcocite with oxygen at magnification 2500X
Figure 5.18 FESEM photomicrograph of reacted chalcocite particles with nitrite at magnification 2000X. Features identified are: Sulfur islands coalesced on a particle, and ii) lamellate grate-like leached structure on the same particle.
5.4 Model Development and Simulation

Six computer simulations were performed to mimic the laboratory bench-scale experiments provided concentration-time profiles of eight (8) species (\(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{HNO}_2, \text{N}_2\text{O}_3, \text{NO}, \text{NO}_2, \text{NO}_3^-, \text{FeNO}_2^{3+}\)). All relevant reactions, kinetic parameters and initial conditions were incorporated into the dialog box of the COMSOL Reaction Engineering Lab software. The oxygen (\(\text{O}_2\)), partial pressure was maintained at approximately 4.0 atm (the concentration in the electrolyte was correlated to the system temperature according to the (temperature dependent) Henrian Equilibrium Coefficient) and the proton activity (\(\text{H}^+\) concentration) was maintained at a value commensurate with the \(\text{H}_2\text{SO}_4\) concentration of the electrolyte (thus the sulfuric acid served as an Ionic Strength buffer in the system).

5.4.1 Simulation of HNO\(_2\)-\(\text{O}_2\) system

In the simulation of nitrous acid-oxygen system, ferrous oxidation is not included. Initial concentrations for \(\text{HNO}_2\) and \(\text{H}_2\text{SO}_4\) were set as 4.5 mM and 1 M, respectively and oxygen at a
total pressure of 4.0 atm. The concentration of nitrate increased as nitrous acid (HNO₂) decreased. After an elapsed time of seven minutes the two species were present at equal concentrations (2.1 mM). NO concentration increased over a period of 3 seconds and to a maximum of 4.73x10⁻² mM after which it decrease continously. NO₂ and N₂O₃ are present at very small concentrations (10⁻⁶ mM). Apparently, since nitrous acid disproportionates to NO and NO₂, in first few seconds their concentrations increase then NO is oxidized by oxygen to NO₂. NO₃⁻ production from the hydrolysis of NO₂ continues until the only nitrogen species present is nitrate. The concentration-time profiles are presented in Figure 5.20.

5.4.2 Simulation of Fe²⁺-O₂ system

Ferrous oxidation simulations were performed at 25°C and 80°C. The oxy-nitrogen species were not included in the simulations. The rate constant for the oxidation of ferrous with oxygen at 25°C was extracted by incorporating the concentration-time profile of ferrous species obtained from laboratory-scale experiment (DE-1) into the COMSOL Parameter Estimation dialog box. The activation energy for the ferrous oxidation with oxygen was calculated from Arrhenius equation by using the rate constant for 120°C available in the study of Baldwin and Van Weert (1996). The rate coefficient was reported with respect to first order of partial pressure of oxygen and second order of ferrous concentration. In the calculations, oxygen partial pressure was converted to the concentration in the electrolyte according to the (temperature dependent) Henrian Equilibrium Coefficient. As a result of calculations the activation energy for ferrous oxidation with oxygen was found as 54 kJ.mol⁻¹. In simulation of the oxidation rate of ferrous with oxygen at 80°C, rate constant for this temperature was calculated from Arrhenius equation based on the calculated activation energy. The results of simulation indicated that the time for (99%) conversion of ferrous to ferric is approximately twenty (20) times higher at 80°C compare to 25°C.
Figure 5.20: Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation. Initial electrolyte concentrations: $C_{\text{NaNO}} = 4.50 \text{ mM}$, $C_{\text{CsSO}} = 1.0 \text{ M}$, Ionic Strength $= 1 \text{ M}$. Pressurized reactor ($P_{\text{O}_2} = 50 \text{ psig}$, $T = 4 \text{ atm}$)
Ferrous concentrations obtained from those simulations were correlated with the concentrations found from experiments of DE-1 (25°C) and DE-5A (80°C). The concentration-time trajectories of ferrous and ferric ion are illustrated in Figure 5.21 and 5.22.

Figure 5.21 Time trajectories of concentration of ferrous and ferric ions in solution obtained by COMSOL-aided computer simulation. Initial electrolyte concentrations: $C_{FeSO_4} = 0.1 \text{ M}$, $C_{H_2SO_4} = 1.0 \text{ M}$, Ionic Strength $\approx 1 \text{ M}$. Pressurized reactor ($P_{O_2} = 50 \text{ psig; } \approx 4 \text{ atm}$).

Figure 5.22 Time trajectories of concentration of ferrous and ferric ions in solution obtained by COMSOL-aided computer simulation for 80°C. Initial electrolyte concentrations: $C_{FeSO_4} = 0.1 \text{ M}$, $C_{H_2SO_4} = 1.0 \text{ M}$, Ionic Strength $\approx 1 \text{ M}$. Pressurized reactor ($P_{O_2} = 50 \text{ psig; } \approx 4 \text{ atm, } P_{H_2O} = 7 \text{ psi}$)
5.4.3 Simulation of Fe$^{2+}$-HNO$_2$-O$_2$ system

In this simulation nine reactions and corresponding rate equations, presented in Appendix A1, were incorporated in the COMSOL software dialog box with initial concentrations of 0.1 M Fe$^{2+}$, 3.98 mM and 4.5 mM HNO$_2$ and 1 M H$^+$ and an aqueous-phase concentration of O$_2$ corresponding to a gas-phase total pressure of 4 atm. In Figure 5.21 for 3.89 mM NO$_2^-$, it can be seen that the concentration of NO$_3^-$ increases gradually and attains the same value as the decreasing HNO$_2$ concentration (0.73 mM) in 60 minutes. The NO concentration increases during a period of 18 minutes to a maximum concentration of 8.32x10$^{-2}$ mM after which it decreases continuously. The concentrations of NO$_2$ and N$_2$O$_3$ were not included on the graph because they attain a maximum concentration of 10$^{-7}$ M and subsequently decrease to very small concentrations (10$^{-9}$ M). The production of nitrate occurs at a lower rate because of the presence of ferrous which is oxidized preferentially. Nitrous acid reduction by ferrous leads to the higher concentration of NO compared to when ferrous is absent but the ferrous-nitrosyl complex controls the increase of un-complexed NO in the solution. Therefore, NO$_2$ production is limited. Low concentration of NO$_2$ in turn leads to a lower increase in NO$_3^-$ concentration. The concentration of FeNO$^{2+}$ complex is at a maximum of 2.79 x10$^{-3}$ M in 1 second and the complex decomposes thereafter to produce in-complexed NO. The Fe$^{2+}$ and Fe$^{3+}$ concentrations are equal after 15 minutes as the ferrous is consumed to produce ferric. Ultimately, 99% conversion of ferrous is achieved in 40 min.

The concentration-time trajectories showed similar trend for the simulation using 4.5 mM NO$_2^-$ but the oxidation rate of ferrous was found higher than the simulation using 3.8 mM NO$_2^-$ . The maximum concentration of NO increased to 9.29x10$^{-2}$ in 13 minutes. The 99% conversion of ferrous is achieved in 30 min (Figure 5.23).
Figure 5.23 Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation. Initial electrolyte concentrations: $C_{\text{FeSO}_4} = 0.1$ M, $C_{\text{NaNO}_2} = 3.89$ mM, $C_{\text{H}_2\text{SO}_4} = 1.0$ M. Ionic Strength $\approx 1$ M. Pressurized reactor ($P_{\text{O}_2} = 50$ psig; $\approx 4$ atm)
Figure 5.24 Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation. Initial electrolyte concentrations: $C_{SO_4^2-} = 0.1 \text{ M}$, $C_{NaSO_4} = 4.50 \text{ mM}$, $C_{HSO_4} = 1.0 \text{ M}$.  Pressurized reactor ($P_{CO_2} = 50 \text{ psig}$; $\approx 4 \text{ atm}$)
5.4.4 Estimation of Optimum HNO₂ Concentration by Objective Function

In the preliminary experiments 3.89 mM NO₂⁻ concentration had been selected based on the concentration in the research of Baldwin and Van Weert (1996). However, an optimum concentration can be determined from an objective function designed on the basis of two competing-considerations: the cost of the nitrite reagent as manifested by the (feed) concentration employed in the processing scheme, and the processing costs as manifested by the time for 99% conversion of ferrous to ferric. The objective function proposed is:

\[ z = \frac{C_{NaNO₂}}{C_{Fe^{2+}}} \times t_{99} \]

where, \( t_{99} \) is the time to oxidize 99.9% of Fe²⁺ to Fe³⁺ (sec) and the optimum value obtained from \( \min z \)

![Graph](Figure 5.25) Objective function, \( \min z = \frac{C_{NaNO₂}}{C_{Fe^{2+}}} \times t_{99} \) as function of electrolyte concentrations:

\[ C_{FeSO₄} = 0.1 \text{ M}, 10^{-4} \text{ M} \leq C_{NaNO₂} \leq 0.1 \text{ M} \text{ (var. inc.)}, C_{H₂SO₄} = 1.0 \text{ M}, \text{ Ionic Strength } \approx 1 \text{ M}. \] Pressurized reactor (\( P_{O₂} = 50 \text{ psig}; \approx 4 \text{ atm} \))

The optimum value was determined by performing multiple simulations with selected values of NaNO₂ concentration (0.1 mM to 100 mM), for a range of concentrations, in order to
generate corresponding values of the objective function, thereby allowing the minimum value (Figure 5.25) to be revealed. The optimum NaNO₂ concentration required for the oxidation of 0.1M Fe²⁺ in 1M H₂SO₄ at 50 psig O₂ was determined to be 4.5 mM. This concentration was selected for the nitrite concentration employed in all subsequent laboratory bench-scale experiments as well as COMSOL simulations performed.

![Graph](image)

**Figure 5.26** Comparison of Fe²⁺ concentration-time trajectories determined by COMSOL-aided simulation with that derived from analysis of samples collected from Experiment No: DE-3.

Figure 5.26 obtained from this simulation indicated that 50% of Fe²⁺ is oxidized in 10 min, whereas in the experiment performed, 1 hour was required to achieve the same conversion. Simulations revealed that the time-scale of the predictions, focused selectively on the conversion of ferrous to ferric, was six (6) times shorter than that observed in the laboratory experiments (DE-3A and DE-3B). It was therefore evident that the rate coefficients for the set of simultaneous reactions, obtained from the literature and are the constituents of the mathematical model, will require significant reassessment in order for the two “experiments” (physical and virtual) to be
aligned. It was concluded that the time scale of simulation must be expanded by approximately 6 times to obtain the same values that are aligned with the concentration behavior observed in the experiment.

5.4.5 Simulation of Fe\(^{2+}\)-NO\(_3^-\) - O\(_2\) system

A COMSOL-aided computer simulation of ferrous oxidation by nitrate was performed to investigate the extremely low oxidation rate observed in the experiment where KNO\(_3\) was employed instead of NaNO\(_2\). In Figure 5.27 it is seen that 2.5 hours are required to oxidize 99% of ferrous when 4.5 mM NO\(_3^-\) was employed for the simulation. This is in marked contrast to 30 minutes, when nitrite at the same concentration was employed for the simulation. When timescale alignment is introduced the corresponding times are 3 hours with nitrite and 15 hours with nitrate.

![Figure 5.27 Time trajectories of concentration of active species in solution obtained by COMSOL-aided computer simulation. Initial electrolyte concentrations: C\(_{\text{KNO3}}\) = 4.50 mM, C\(_{\text{H2SO4}}\) = 1.0 M, Ionic Strength \(\approx\) 1 M. Pressurized reactor (P\(_{\text{O2}}\) = 50 psig; \(\approx\) 4 atm)
In the experiment that was performed in the lab-scale reactor, with nitrate substituted for nitrite, there was no visual evidence of nitrosyl complex. The reason that the presence of the complex was not observed is linked to a low oxidation rate of ferrous and concomitant production of nitric oxide. The simulation revealed that the nitrosyl complex attained a maximum concentration of approximately 1.45 mM after 2 hours (12 hours with alignment) (Figure 5.28).

![Figure 5.28](image)

**Figure 5.28** Concentration-Time profile for ferrous oxidation with NO$_3^-$ (KNO$_3$) and HNO$_2$ (NaNO$_2$) predicted by COMSOL-aided computer simulation

5.4.6 REDOX Potentials of Fe$^{2+}$/Fe$^{3+}$ and HNO$_2$/NO$_3^-$ Couples

The ex-situ REDOX potentials measured in the experiment numerated as DE-3 and those obtained from the corresponding COMSOL-aided computer simulation were compared in order to explore the reason for the increase in $E_h$ to a value beyond that, which could be attributed to the Fe$^{2+}$/Fe$^{3+}$ REDOX couple. It had been observed that when the ferrous concentration became
smaller than 0.01 M (0.09 M ferric) the Pt electrode would no longer respond to the \( \text{Fe}^{2+}/\text{Fe}^{3+} \) couple. The REDOX couple must then be controlled by a nitrogen species pair.

![Graph showing REDOX potentials](image)

**Figure 5.29** Correlation of recorded REDOX potential obtained from ex-situ REDOX measurement conducted for Experiment No: DE-3 with REDOX potentials derived from COMSOL-aided computer simulation.

In Table 2.4, where these REDOX couples are listed, the \( \text{HNO}_2/\text{NO}_3^- \) couple when applied to the concentrations predicted by the simulation, higher \( E_h \) values recorded for the experiment performed with the containing 4.5 mM \( \text{NaNO}_2 \) and 0.1 M \( \text{Fe}^{2+} \) (Figure 5.29). This was interpreted as the mixed potentials occurring between \( \text{Fe}^{2+}/\text{Fe}^{3+} \) and \( \text{HNO}_2/\text{NO}_3^- \) couples present in the electrolyte. The \( E_h \) values were computed based on pseudo-equilibrium, employing the Nernst Equation.
CHAPTER 6
CONCLUSION

This chapter, the concluding chapter of the thesis, contains, in the first section, a summary of the results of the investigation. Enumerated conclusions which highlight the significant findings of the research are presented in the second section. The third, and last, section lists two recommendations of research topics which warrant further investigation.

6.1 Summary and Retrospective

The research conducted for this thesis has been focused on the elucidation of the reaction mechanisms in the oxidation of ferrous ion, to ferric ion, by oxygen in the presence of low-concentration nitrite in a sulfuric-acid electrolyte whereby a dramatic enhancement in the oxidation rate is realized compared to when only oxygen is employed. To this end, the cyclic ("catalytic") reaction mechanisms involving oxy-nitrogen species (HNO₂, N₂O₃, NO, and NO₂) as well as the ferrous-nitrosyl complex ([Fe(NO)]²⁺) were explored by developing the set of ODE’s that describe the concentration-time trajectories of the prominent species (Fe²⁺, Fe³⁺, HNO₂, N₂O₃, NO, NO₂, NO₃⁻, and [Fe(NO)]²⁺) in the system. These equations were incorporated into the COMSOL software module to provide for simulation of the laboratory bench-scale experiments that were performed.

Laboratory bench-scale (preliminary) experiments were first conducted on the oxidation of ferrous to ferric in an electrolyte containing 3.89 mM NaNO₂ and oxygen, which represented an ambient temperature and pressure investigation similar to that of Baldwin and Van Weert (1996). These preliminary experiments were performed primarily to develop an understanding of the behavior of the system including visual observations associated with the formation of ferrous-
nitrosyl complex in the system. A partially-sealed reactor (with controlled gas-phase leak present) as well as a “leak-tight” sealed reactor system was used to assess the role of oxy-nitrogen species in the system. REDOX potential was monitored in the experiments performed so as to obtain information on the concentration ratio of ferrous to ferric (and indirectly the individual concentrations of these two iron species). With the controlled gas-phase leak present in the system (IBM Cell), REDOX potential indicating concentration ratio of ferrous to ferric decreased.

A hypothesis tested was that the same small (molar) concentrations of nitrate as that of nitrite would be reduced to nitric oxide (NO) by ferrous, possibly via a nitrite species intermediate. However, nitrate did not result in an enhanced oxidation-rate. This could readily be discerned, since upon addition of the nitrate salt (KNO₃), there was no visual evidence of the formation of the ferrous-nitrosyl complex (FeNO₂⁺), indicating that nitric oxide was not present at a significant concentration level in the electrolyte. This behavior was attributed to a proton activity in the electrolyte that was not high enough to promote the formation of reactive HNO₃ species in the electrolyte – increasing the sulfuric acid concentration from 1.0 M to 3.0 M resulted in oxidation of ferrous ion and concomitant formation of ferrous-nitrosyl complex.

In the definitive ferrous oxidation experiments performed the oxidation rate of ferrous to ferric was dramatically higher, approximately two orders of magnitude (400 times), at high pressure (p₀₂ ≈ 4.0 atm) in the presence of small concentrations of nitrite (3.89 mM; 266 mg NaNO₂ per liter and 4.5 mM; 311 mg NaNO₂ per liter) compared to when nitrite was absent.

While ferrous was oxidized by nitrite at high pressure, the characteristic, asymptotic higher REDOX-potential was obtained in a shorter time (6 hours) with 4.5 mM NaNO₂ compared to 3.89 mM NaNO₂. The concentrations of nitrogen species in the electrolyte were determined spectrophotometrically, and nitric oxide and nitrogen dioxide were determined by chemiluminescence analysis.
The nitrogen species that evolve in the electrolyte from the sodium-nitrite reagent (HNO₂, N₂O₃, NO, and NO₂) were all oxidized to nitrate (NO₃⁻). The continuous decrease in the concentration of gaseous species indicated the dissolution of NO₂ and subsequent oxidation to nitrate in the electrolyte.

In addition, a solid phase, quartz (silica) sand, was introduced into two-phase system to investigate the rate of ferrous oxidation with nitrite in the presence of a solid phase. For the first seven hours, lower REDOX potentials were observed compare to the system with no quartz. After seven hours, the potential became asymptotic to the same value. The results were interpreted as adsorption of FeNO²⁺ complex onto the quartz particles during the initial stage of ferrous oxidation. REDOX potential measurements showed that once the complex decomposed completely, the adsorption of FeNO²⁺ species onto the solid phase is no longer a rate limiting mechanism in the oxidation of ferrous.

The experiments, conducted the ferrous oxidation at 80°C and a total pressure of 60 psig, resulted in a significant increase in rate for both oxidation with oxygen and absence of nitrite (≈20 times) and with oxygen and nitrite present (≈3 times). The black-green color of ferrous nitrosyl complex progressively became less intense over a period of 1 hour at this higher temperature of 80°C. At 25°C the complex persisted for approximately 3 hours.

Lastly, oxidative leaching of a sample of chalcocite mineral (Cu₂S) with 4.5 mM nitrite at 80°C and pO₂ ≈ 4.5 atm (P_tot = 60 psig) resulted in an electrolyte (cupric) copper concentration of 0.065 mM after 4 hours, corresponding to 65% dissolution of the mineral sample.

Images of partially-leached chalcocite-particles (≈60 μm) obtained by FESEM revealed sulfur-islands coalesced on a particle as well as lamellate grate-like leached structure on the same particle. Since there was no evidence of sulfur entities in the particulate residue collected, it was interpreted that the cuprous ion of the chalcocite (Cu₂S) is directly oxidized to cupric while the
associated sulfide is oxidized to sulfate. The role of nitrite in the oxidation of the “sulfur” could not be readily elucidated. EDS analysis conducted with the electron microscope, on leached surfaces of the residue sample, revealed a “Cu” to “S” ratio of two to one (2:1) and cupric-sulfide (CuS; covolite) was not observed. Therefore, the sulfide (S\(^2-\)) accompanying the dissociation of the chalcocite (Cu\(_2\)S), in principle, can be oxidized either by the “high” oxidation-state oxynitrogen species (HNO\(_2\), NO\(_2^{(aq)}\) and NO\(_3^-\)) or by O\(_2^{(aq)}\). This oxidation could occur stage wise (depending on the particle size), first to S\(^0\) and then SO\(_4^{2-}\), or such that the intermediate S\(^0\) is short-lived and does not condense on the particle surface. The coalesced islands of sulfur observed (on the “large” particles) could develop as a result of surface diffusion between neighboring sites where the cuprous ion in the lattice was lost due to oxidation to cupric ion while at the same time the sulfide was oxidized to the zero-valence (solid) species.

The research conducted also include an extensive literature search on kinetics and reaction mechanisms associated with oxidation of ferrous to ferric by oxygen in the presence of oxy-nitrogen species. Kinetic data acquired from the sources uncovered in the search was incorporated in the development of rate equations (a total of nine ODE’s) that describe the concentration-time behavior including ten species. This allowed for (COMSOL Reaction Engineering Lab Module) computer simulation of conditions corresponding to those of the laboratory bench-scale experiments. Concentration-time profiles of eight (8) species (Fe\(^{2+}\), Fe\(^{3+}\), HNO\(_2\), N\(_2\)O\(_3\), NO, NO\(_2\), NO\(_3^-\), FeNO\(_2^+\)) were thus obtained. The oxygen (O\(_2\)), partial pressure was maintained at either approximately 4.0 atm (the concentration in the electrolyte was correlated to the system temperature according to the (temperature dependent) Henrian Equilibrium Coefficient) and the proton activity (H\(^+\) concentration) was maintained at a value commensurate with the H\(_2\)SO\(_4\) concentration of the electrolyte (thus the sulfuric acid served as an Ionic Strength buffer in the system). The predictions obtained from the simulations could thus be correlated with the bench-scale experiments.
These simulations revealed that the time-base of the predictions, focused selectively on the conversion of ferrous to ferric, should be scaled (increased) by a factor of approximately six in order to align with that observed in the laboratory experiments. It was therefore evident that the rate coefficients for the set of simultaneous reactions, obtained from the literature and are the constituents of the mathematical model, will require significant reassessment in order for the two “experiments” (physical and virtual) to be aligned.

An “optimum” NaNO₂ (HNO₂) concentration was determined from an objective function designed on the basis of two competing-considerations: the cost of the nitrite reagent as manifested by the (feed) concentration employed in the processing scheme, and the processing costs as manifested by the time for 99% conversion of ferrous to ferric. Thus, the minimum in the ratio \( \frac{C_{NaNO_2}}{t_{99.9}} \) (should it exist) would identify the “optimum” concentration of nitrite that should be employed for the oxidation process. Simulation-trials were performed for a range of nitrite concentrations (0.1 mM to 100 mM), from which a minimum in the objective function was identified at a nitrite concentration of 4.5 mM. This concentration was selected for the nitrite concentration employed in all subsequent laboratory bench-scale experiments as well as COMSOL simulations performed.

Two simulations for oxidation of ferrous with oxygen at 25°C and 80°C performed without including the oxy-nitrogen species in the simulations. The rate coefficients for the oxidation of ferrous with oxygen at 25°C were extracted by incorporating the concentration-time profile of ferrous species obtained from laboratory-scale experiment (DE-1) into the COMSOL Parameter Estimation dialog box. The activation energy for the ferrous oxidation with oxygen was calculated from Arrhenius equation by using the rate coefficient at 120°C available in the publication by Baldwin and Van Weert (1996). The rate coefficient was reported for an irreversible, elementary-reaction that is first order with respect to the partial pressure of oxygen
and second order with respect to the ferrous-ion concentration. In order to perform the Parameter Estimation, oxygen partial pressure was transformed to the oxygen concentration in the electrolyte according to the (temperature dependent) Henrian Equilibrium Coefficient. The apparent activation-energy for ferrous oxidation with (solely) oxygen was found to be 54 kJ.mol⁻¹.

In order to perform the simulation of the oxidation rate of ferrous with (solely) oxygen at 80°C, the rate coefficient for this temperature was calculated by employing the Arrhenius Equation with the apparent activation-energy of 54 kJ.mol⁻¹. The results of simulation indicated that the time for (99%) conversion of ferrous to ferric was twenty times higher at 80°C compared to that at 25°C.

Simulation of ferrous oxidation with 4.5 mM nitrate at 25°C predicted that the ferrous oxidation rate was five (5) times lower compared to when 4.5 mM nitrite was the oxy-nitrogen species. Ferrous nitrosyl complex increased continuously for 100 minutes to its maximum concentration (6x10⁻² mM) and NO production from oxidation of ferrous by HNO₂ lasted for 120 minutes.

6.2 Statement of Applicability of Results of Investigation to the Leaching of Gold-Bearing Complex Sulfides

A quantitative mathematical model, which describes the interaction between the product species NO(g) and O₂(g), to partially regenerate HNO₂ (the oxy-nitrogen precursor) as well as the evolution of the oxy-nitrogen species by several simultaneous reaction-paths that lead to higher-oxidation nitrogen species (NO₂(g) and NO₃⁻) has, of 2009, never been published in the open literature. This highly-coupled system of chemical reactions involving unique disproportionation mechanisms cannot be grasped without the aid of the (COMSOL) computer-simulation that was
performed as part of the research reported in this thesis. The regeneration of the highly reactive HNO2(aq) species by oxygen is only “partial” since the less reactive NO3(aq) species progressively increases and becomes the primary oxy-nitrogen species once the ferrous (for example) has been completely oxidized to ferric.

Notwithstanding that there remains parameter-estimation to be performed in order to resolve the time-scale alignment between the bench-scale experiments and their simulations, the ability to perform these virtual experiments represents a significant contribution to insight into the NSC process performance and process optimization.

6.3 Enumerated Conclusions

The conclusions representing the significant findings of the research are now enumerated.

1. The oxidation rate of ferrous to ferric at 25°C, with nitrite at a concentration of 4.5 mM, was dramatically higher at high pressure (pO2 ≈ 4.0 atm) compared to that obtained at ambient pressure.

2. The same small (molar) concentrations of nitrate did not result in an enhanced oxidation-rate, at 25°C. This behavior was attributed to a proton activity in the electrolyte that was not high enough to promote the formation of the reactive HNO3 species in the electrolyte. On increasing the sulfuric acid concentration from 1.0 M to 3.0 M resulted in oxidation of ferrous ion and concomitant formation of ferrous-nitrosyl complex, thereby confirming the hypothesis advanced.

3. On increasing the nitrite concentration from 3.89 mM to 4.5 M (pO2 ≈ 4.0 atm) resulted in a higher oxidation rate at 25°C. This was manifested by a high asymptotic REDOX potential (≈954 mV) being achieved in a significantly shorter time compared to when the lower nitrite concentration was employed. The asymptotic-potential observed was identified as being due to the HNO2/NO3− REDOX couple since as the ferrous conversion approaches 100%, the Fe2+/Fe3+
REDOX couple is overwhelmed by the aforementioned REDOX couple. Ultimately, the nitrogen species that evolve in the electrolyte from the sodium-nitrite reagent (HNO₂, N₂O₃, NO, NO₂) were all oxidized to nitrate (NO₃⁻), as the oxidation of ferrous to ferric proceeded to completion.

4. The oxidation rate of ferrous was enhanced approximately three times with nitrite at 80°C compared to when the oxidation is performed at 25°C.

5. The loss of nitrogen species from the gas phase of the reactor resulted (as expected) in lower ferrous-oxidation rates. It appears from the results of gas analysis employed by chemiluminescence NOₓ analyzer that NO(g) and NO₂(g) are not in the equilibrium with the species in the electrolyte. It is critical that the NO(g) produced during the oxidation process be available to complete the regeneration cycle by reaction with oxygen in the gas phase thereby producing NO₂(g) which is readily solubilized in electrolyte. The nitrogen dioxide subsequently disproportionates into HNO₂ and NO₃⁻, both of which serve as oxidants in the system.

6. The time-base of the predictions of the (ferrous) concentration-time trajectory obtained by the computer simulations (COMSOL software) had to be scaled (expanded) by a factor of six in order to align with that observed in the laboratory experiments conducted at 25°C with 4.5 mM nitrite and pO₂ ≈ 4.0 atm.

7. An optimum concentration of nitrite reagent, representing the minimum of the designed objective-function, was determined to be 4.5 mM. It is noted that this value is in the neighborhood of 3.89 mM employed by Baldwin and Van Weert (1996) in their research.

8. The activation energy for ferrous oxidation with oxygen was found to be 54 kJ.mol⁻¹ by employing the kinetic data at 25°C on COMSOL Parameter Estimation Module and correlating those with the value reported in the study of Baldwin and Van Weert (1996).
6.4 Recommendations for Further Research

The following two topics have been selected as warranting further research. The first is related to investigation of ferrous oxidation rates at higher temperatures (in the vicinity of 120°C) and at total pressures not exceeding 10 atm. The second is intended to complement the first by performing controlled laboratory bench-scale experiments with "pure" minerals, specifically: chalcocite, covolite and chalcopyrite. The data derived from these experiments would be employed to develop tenable models (based on electron microscope imaging of partially-reacted particles) that thus provide the necessary details for coupling the homogeneous kinetics in these systems with the heterogeneous kinetics associated with the oxidative dissolution of the particulate mineral-phase.

1. Higher temperature and pressure experiments on ferrous-oxidation are warranted in order to explore the full potential of the NSC process. These experiments must be performed in a "leak-tight" reactor in order that the oxy-nitrogen species in the gas phase remain in the system. The range of oxygen partial-pressures that should be investigated would be in the range 1.0 atm to 10 atm. In regard to nitrite reagent concentrations in the range 5.0 mM to 10 mM, is recommended bearing in mind the research conducted by Baldwin and Van Weert (1996) and the optimal value of 4.5 mM obtained by the optimization procedure employed in the research reported in this Thesis. The upper limit on temperature is expected to be in the vicinity of 120°C (above the melting point of sulfur) since in the leaching of sulfide minerals, the oxidized zero-valence sulfur (solid or liquid) may significantly influence the heterogeneous reaction between the liquid lixiviant and the particulate solid-mineral. A lower temperature limit of 50°C is recommended. In this manner, the behavior of the oxynitrogen species in the absence of confounding effects involving solid-particle/liquid electrolyte interactions can first be elucidated. In conjunction with
the laboratory experiments, the Parameter Estimation module of the COMSOL software would have to be employed for optimization of the chemical reaction rate-parameters (rate coefficients and their corresponding Arrhenius-Model parameters). Thus, chemical analysis of the electrolyte species (of “significant” concentration) as well as the gas-phase (NO and NO₂) species will have to be performed rigorously.

2. Complementary to the first topic is a research effort conducted with “pure” (natural) minerals, specifically: chalcocite, covolite and chalcopyrite. This research effort would include several components: a) laboratory bench-scale experiments conducted on oxidative leaching of each of these minerals at temperatures in the range 50°C to 120°C and oxygen partial pressures in the range 1.0 atm. to 10 atm. with the nitrite reagent concentration range 5.0 mM to 10 mM, similar to that indicated above, under 1., b) analyze the data derived from the experiments under a) to develop heterogeneous reaction rate model(s) for the oxidation/decomposition of these selected sulfide minerals. This development would be conducted based on details revealed by electron-microscopy imaging of partially reacted particles of the mineral being leached. In this manner, the oxidation behavior of the sulfide anion in each of the minerals would be characterized with respect to the formation of (intermediate) zero-valence sulfur (S°; solid and liquid) and the concomitant rate-enhancement that the valence 3+, 4+ and 5+ oxy-nitrogen species (HNO₂/N₂O₃, NO₂ and NO₃⁻) might provide in this regard.

3. Parameter-estimation, using the results obtained from bench-scale experiments on ferrous oxidation with nitrite, should also be performed in order to estimate the kinetic data for the system including ferrous ion and oxy-nitrogen species. Development of the reaction rate coefficient for this system could resolve the time-scale alignment between the bench-scale experiments and their simulations.
REFERENCES CITED


Lamb, A.B., and Elder, L. W. 1931. The electromotive activation of oxygen. J. Amer. Soc. 53: 137.


# APPENDIX A

## REACTIONS IN COMSOL SIMULATION AND NET RATE EXPRESSIONS FOR THE Fe$^{2+}$- HNO$_2$- H$_2$SO$_4$ SYSTEM AT 25°C

<table>
<thead>
<tr>
<th>Reaction No</th>
<th>Reaction</th>
<th>Reaction Rate-Expression</th>
<th>Reaction Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2HNO$_2$(aq) + N$_2$O$_3$(aq) + H$_2$O</td>
<td>$-r_{\text{HNO}<em>2\text{(net-1)}} = k</em>{1\text{f}} C_{\text{HNO}<em>2}^2 - k</em>{1\text{b}} C_{\text{N}_2\text{O}_3}$</td>
<td>Elementary</td>
</tr>
<tr>
<td>2</td>
<td>N$_2$O$_3$(aq) = NO$_3$(aq) + NO$_2$(aq)</td>
<td>$-r_{\text{N}<em>2\text{O}<em>3\text{(net-2)}} = k</em>{2\text{f}} C</em>{\text{N}<em>2\text{O}<em>3} - k</em>{2\text{b}} C</em>{\text{NO}} C_{\text{NO}_2}$</td>
<td>Elementary</td>
</tr>
<tr>
<td>3</td>
<td>4NO$_2$(aq) + O$_2$(aq) + 2H$_2$O $\rightarrow$ 4HNO$_2$(aq)</td>
<td>$-r_{\text{O}<em>2\text{(net-3)}} = k</em>{3\text{f}} C_{\text{NO}}^2 C_{\text{O}_2}$</td>
<td>Elementary</td>
</tr>
<tr>
<td>4</td>
<td>2NO$_2$(aq) + H$_2$O = H$^+$ + NO$_3^-$(aq) + HNO$_2$(aq)</td>
<td>$-r_{\text{NO}<em>2\text{(net-4)}} = k</em>{4\text{f}} C_{\text{NO}<em>2}^2 - k</em>{4\text{b}} C_{\text{H}<em>2\text{O}} C</em>{\text{NO}<em>3} C</em>{\text{HNO}_2}$</td>
<td>Elementary</td>
</tr>
<tr>
<td>5</td>
<td>NO$_2$(aq) + NO$_3^-$(aq) + H$^+$ = NO$_2$(aq) + HNO$_2$(aq)</td>
<td>$r_{\text{NO}<em>2\text{(net-5)}} = k</em>{5\text{f}} C_{\text{NO}<em>3} C</em>{\text{NO}<em>2} C</em>{\text{H}<em>2\text{O}} - k</em>{5\text{b}} C_{\text{H}<em>2\text{O}} C</em>{\text{NO}_2}$</td>
<td>Non-elementary</td>
</tr>
<tr>
<td>6</td>
<td>Fe$^{2+}$ + HNO$_2$(aq) + H$^+$ = Fe$^{3+}$ + NO$_3^-$ + H$_2$O</td>
<td>$r_{\text{Fe}<em>3\text{+}(\text{net-6})} = C</em>{\text{Fe}<em>2\text{+}} C</em>{\text{HNO}<em>2} (k</em>{6\text{f}-1} k_{6\text{f}-2} C_{\text{H}<em>2\text{O}} + k</em>{6\text{f}-3} C_{\text{HNO}<em>2}/C</em>{\text{NO}_3})$</td>
<td>Non-elementary</td>
</tr>
<tr>
<td>7</td>
<td>Fe$^{2+}$ + NO$_2$(aq) + H$^+$ = Fe$^{3+}$ + HNO$_2$(aq)</td>
<td>$r_{\text{Fe}<em>3\text{+}(\text{net-7})} = k</em>{7\text{f}-1} (C_{\text{Fe}<em>2\text{+}}) C</em>{\text{NO}<em>2} - k</em>{7\text{b}-2} (C_{\text{Fe}<em>3\text{+}}) C</em>{\text{HNO}<em>2}/C</em>{\text{H}_2\text{O}}$</td>
<td>Non-elementary</td>
</tr>
<tr>
<td>8</td>
<td>Fe$^{2+}$ + NO$_3^-$ + 2H$^+$ = Fe$^{3+}$ + NO$_2$(aq) + H$_2$O</td>
<td>$r_{\text{Fe}<em>3\text{+}(\text{net-8})} = k</em>{8\text{f}-1} (C_{\text{Fe}<em>2\text{+}}) C</em>{\text{NO}<em>3} - k</em>{8\text{b}-2} (C_{\text{Fe}<em>3\text{+}}) C</em>{\text{NO}<em>2}/C</em>{\text{H}_2\text{O}}$</td>
<td>Non-elementary</td>
</tr>
<tr>
<td>9</td>
<td>Fe$^{2+}$ + NO = Fe(NO)$_2^{2+}$</td>
<td>$-r_{\text{Fe}<em>2\text{+}(\text{net-9})} = k</em>{9\text{f}-1} (C_{\text{Fe}<em>2\text{+}}) C</em>{\text{NO}} - k_{9\text{b}-2} (C_{\text{Fe}(\text{NO}_2)^{2+}})$</td>
<td>Elementary</td>
</tr>
</tbody>
</table>
APPENDIX B

REACTION RATE CONSTANTS FOR THE REACTION RATE EXPRESSIONS

<table>
<thead>
<tr>
<th>Reaction No</th>
<th>Reaction Rate Coefficient (25°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$k_{1f}$: $17.7 \text{ M}^{-1}\text{s}^{-1}$</td>
<td><em>Bunton et al.(1959)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{1b}$: $2.9 \times 10^3 \text{ s}^{-1}$</td>
<td><em>Butler et al.(2004)</em></td>
</tr>
<tr>
<td>2</td>
<td>$k_{2f}$: $1.18 \times 10^5 \text{ s}^{-1}$</td>
<td><em>Markovitz et al.(1981)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{2b}$: $1.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$k_{3f}$: $2.1 \times 10^6 \text{ M}^{-2} \text{s}^{-1}$</td>
<td><em>Awad et al.(1993)</em></td>
</tr>
<tr>
<td>4</td>
<td>$k_{4f}$: $1.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$</td>
<td><em>Beake et al.(1992)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{4b}$: $2.7 \times 10^{-2} \text{ M}^{-2} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$k_{5.1}$: $7.5 \text{ M}^3 \text{s}^{-1}$</td>
<td><em>Epstein et al.(1982)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{5.2}$: $1.4 \times 10^4 \text{ M}^2 \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$k_{6.1}$: $7.8 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$</td>
<td><em>Abel et al.(1928)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{6.2}$: $2.3 \times 10^{-1} \text{ M}^{-2} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{6.3}$: $7.6 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{6.4}$: $5.6 \times 10^{-4} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{6.5}$: $1.6 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{6.6}$: $5.4 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$k_{7.1}$: $3.1 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$</td>
<td><em>Abel et al.(1928)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{7.2}$: $6.6 \times 10^{-4} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$k_{8.1}$: $1.5 \times 10^{-4} \text{ M}^{-2} \text{s}^{-1}$</td>
<td><em>Abel et al.(1928)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{8.2}$: $2.1 \times 10^{-2} \text{ M} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$k_{9.1}$: $6.2 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$</td>
<td><em>Epstein et al.(1982)</em></td>
</tr>
<tr>
<td></td>
<td>$k_{9.2}$: $1.4 \times 10^3 \text{ s}^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

$k_f$: Forward Reaction; $k_b$: Back Reaction
### APPENDIX C

**REACTION MECHANISMS FOR NON-ELEMENTARY RATE-EXPRESSIONS PERTAINING TO THE Fe²⁺-HNO₂-H₂SO₄ SYSTEM AT 25°C**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Mechanism (Elementary Steps)*</th>
</tr>
</thead>
</table>
| NO°(aq) + NO₃⁻ + H⁺ = NO₂(aq) + HNO₂(aq) | \(2H^+ + NO_3^- = H_2NO_3^+ ; K_{S(1)} \)
| | \(k_{5f}\) |
| | \(H_2NO_3^+ + NO \rightleftharpoons HNO_2 + NO_2 + H^+ ; k_{5b}\) |
| | P.Eq. – R.C. |
| H⁺ + OH⁻ = H₂O ; K₆(1) | \(k_{6f}(1)\) |
| Fe²⁺ + HNO₂ \rightleftharpoons Fe³⁺ + OH⁻ + NO \(k_{6b}(1)\) | P.Eq. – R.C. |
| HNO₂ + H⁺ = H₂NO₂⁺ ; K₆(2) | P.Eq. |
| H₂NO₂⁺ = H₂O + NO⁻ ; K₆(2ii) | P.Eq. |
| Fe²⁺ + NO⁺ \rightleftharpoons Fe³⁺ + NO \(k_{6f}(2)\) | R.C. |
| Fe²⁺ + NO⁻ \rightleftharpoons NO₂⁻ + Fe³⁺ \(k_{6b}(3)\) | R.C. |
| 2HNO₂ = NO₂ + NO + H₂O ; K₆(3) | P.Eq. |
| H⁺ + NO₂⁻ = HNO₂ ; K₆(3ii) | P.Eq. |
| Fe²⁺ + NO₂⁻ \rightleftharpoons NO₂⁻ + Fe³⁺ \(k_{6f}(3)\) | R.C. |
| Fe²⁺ + NO₂⁻ \rightleftharpoons NO₂⁻ + Fe³⁺ \(k_{6b}(3)\) | R.C. |
| Fe²⁺ + NO₂(aq) + H⁺ = Fe³⁺ + HNO₂(aq) | \(H^+ + NO_2^- = HNO_2(2aq) ; K_{7(1)} \)
| | \(k_{7f}\) |
| | \(Fe^{2+} + NO_2(2aq) \rightleftharpoons Fe^{3+} + NO_2^- \(k_{7b}\) |
| | P.Eq. – R.C. |
| NO₃⁻ + 2H⁺ = H₂O + NO₂ ; K₈(1) | \(k_{8f}\) |
| | \(Fe^{2+} + NO_3^- \rightleftharpoons Fe^{3+} + NO_3^2- \(k_{8b}\) |
| | P.Eq. – R.C. |

*P.Eq. : Pseudo-Equilibrium; R.C.: Rate Controlling*
APPENDIX D

DEVELOPMENT OF NET REACTION RATE EXPRESSIONS FROM ELEMENTARY REACTION STEPS FOR REACTION 5, 6, 7, and 8

Species Numerical-Template:

\begin{align*}
1 & = \text{HNO}_2, \\
2 & = \text{H}^+, \\
3 & = \text{NO}_2^-, \\
4 & = \text{N}_2\text{O}_3, \\
5 & = \text{NO(aq)}, \\
6 & = \text{NO}_2(aq), \\
7 & = \text{NO}_3^-, \\
8 & = \text{O}_2, \\
9 & = \text{Fe}^{2+}, \\
10 & = \text{Fe}^{3+}, \\
11 & = \text{FeNO}_2^+ \\
12 & = \text{OH}^-, \\
13 & = \text{NO}^+, \\
14 & = \text{H}_2\text{NO}_2^+, \\
15 & = \text{H}_2\text{NO}_3^+, \\
16 & = \text{NO}_2^-, \\
17 & = \text{NO}_3^{2-}
\end{align*}

\textbf{i)} \quad \text{NO(aq)} + \text{NO}_3^- + \text{H}^+ = \text{NO}_2(aq) + \text{HNO}_2(aq) \quad (5)

\begin{align*}
r_{5(\text{net-5})} &= k_{5-1}C_2^2C_5 - k_{5-2}C_1C_6C_2
\end{align*}

\textbf{ELEMENARY REACTIONS:}

\begin{align*}
\text{H}_2\text{NO}_3^- + \text{NO} &= \text{HNO}_2 + \text{NO}_2 + \text{H}^+ \quad \text{(R.C.)} \\
r_{5(\text{net-5})} &= k_{5f}C_{15}(t)C_5(t) - k_{5b}C_1(t)C_6(t)C_2(t)
\end{align*}

\begin{align*}
2\text{H}^+ + \text{NO}_3^- &= \text{H}_2\text{NO}_3^-; K_{5(1)} \quad \text{(P.Eq.)}
\end{align*}

\begin{align*}
K_{5(1)} &= \frac{C_{15}(t)}{C_7(t)C_5^2(t)}; C_{15}(t) = K_{5(1)}C_2^2C_7
\end{align*}

By combining those two equations:

\begin{align*}
r_{5(\text{net-5})} &= k_{5f}K_{5(1)}C_2^2(t)C_7(t)C_5(t) - k_{5b}C_1(t)C_6(t)C_2(t)
\end{align*}

\begin{align*}
k_{5-1} &= k_{5f}K_{5(1)}
\end{align*}

\begin{align*}
k_{5-2} &= k_{5b}
\end{align*}

\textbf{ii)} \quad \text{Fe}^{2+} + \text{HNO}_2(aq) + \text{H}^+ = \text{Fe}^{3+} + \text{NO(aq)} + \text{H}_2\text{O} \quad (6)

\begin{align*}
r_{10(\text{net-6})} &= C_9C_1(k_{6-1}C_2 + k_{6-2}C_2^2 + k_{6-3}C_1/C_5)
\end{align*}

\textbf{ELEMEMARY REACTIONS:}

\begin{align*}
(4) \quad \text{Fe}^{2+} + \text{HNO}_2 &= \text{Fe}^{3+} + \text{OH}^- + \text{NO} \quad \text{(R.C.)} \\
r_{10(\text{net-6}(4))} &= k_{6f(1)}C_9(t)C_1(t) - k_{6b(1)}C_{10}(t)C_{12}(t)C_5(t)
\end{align*}

\begin{align*}
\text{H}^+ + \text{OH}^- &= \text{H}_2\text{O}; K_{6(1)} \quad \text{(P.Eq.)}
\end{align*}

\begin{align*}
K_{6(1)} &= \frac{1}{C_2(t)C_{12}(t)}; C_{12}(t) = \frac{1}{K_{6(1)}C_2(t)}
\end{align*}
By combining those two equations:

\[ r_{10(\text{net-6}(1))} = k_{6f(1)}C_9(t)c_1(t) - k_{6b(1)} \frac{C_{10}(t)}{K_{6(1)}C_2(t)}C_5(t) \]

(2) \( \text{Fe}^{2+} + \text{NO}^+ = \text{Fe}^{3+} + \text{NO} \)  
(R.C.)

\[ r_{10(\text{net-6}(2))} = k_{6f(2)}C_9(t)c_{13}(t) - k_{6b(2)}C_{10}(t)C_5(t) \]

\[ \text{HNO}_2 + H^+ = \text{H}_2\text{NO}_2^+; \ K_{6(2i)} \]  
(P.Eq.)

\[ K_{6(2i)} = \frac{C_{14}(t)}{C_1(t)C_2(t)}; \ C_{14}(t) = K_{6(2i)} \cdot c_1(t) \cdot c_2(t) \]

\[ \text{H}_2\text{NO}_2^+ = \text{H}_2\text{O} + \text{NO}^+; \ K_{6(2ii)} \]  
(P.Eq)

\[ K_{6(2ii)} = \frac{C_{13}(t)}{C_{14}(t)}; \ C_{14}(t) = K_{6(2ii)} \cdot c_{13}(t) \]

By combining those three equations:

\[ r_{10(\text{net-6}(2))} = k_{6f(2)}K_{6(2i)} \cdot c_1(t) \cdot c_2(t) \cdot c_9(t) - k_{6b(2)}C_{10}(t)C_5(t) \]

(3) \( \text{Fe}^{2+} + \text{NO}_2 = \text{NO}_2^- + \text{Fe}^{3+} \)  
(R.C.)

\[ r_{10(\text{net-6}(3))} = k_{6f(3)}C_9(t)c_6(t) - k_{6b(3)}C_3(t)C_{10}(t) \]

\[ 2\text{HNO}_2 = \text{NO}_2 + \text{NO} + \text{H}_2\text{O}; \ K_{6(3i)} \]  
(P.Eq.)

\[ K_{6(3i)} = \frac{C_6(t) \cdot C_5(t)}{C_1^2(t)}; \ C_6(t) = \frac{K_{6(3i)}C_1^2(t)}{C_5(t)} \]

\[ \text{H}^+ + \text{NO}_2^- = \text{HNO}_2; \ K_{6(3ii)} \]  
(P.Eq.)

\[ K_{6(3ii)} = \frac{C_1(t)}{C_2(t) \cdot c_3(t)}; \ C_3(t) = \frac{C_1(t)}{K_{6(3ii)}C_2(t)} \]

By combining those three equations:

\[ r_{10(\text{net-6}(3))} = k_{6f(3)}C_9(t) \frac{K_{6(3i)}C_1^2(t)}{C_5(t)} - k_{6b(3)} \frac{C_1(t)}{K_{6(3ii)}C_2(t)}C_{10}(t) \]
Net Reaction (System) Rate Equation for Fe$^{3+}$ ion becomes:

$$r_{10(\text{net-6f})} = k_{6f(1)} C_5(t) C_1(t) + k_{6f(2)} K_{6(2i)}, C_1(t), C_2(t), C_9(t)$$

$$+ k_{6f(3)} C_9(t) \frac{K_{6(3i)}}{C_5(t)}$$

$$r_{10(\text{net-6b})} = k_{6b(1)} \frac{C_{10}(t)}{K_{6(1)}} C_2(t) C_5(t) + k_{6b(2)} C_{10}(t) C_5(t) + k_{6b(3)} \frac{C_1(t)}{K_{6(3i)}} C_2(t) C_10(t)$$

$$k_{6-1} = k_{6f(1)}; \quad k_{6-2} = k_{6f(2)} K_{6(2i)} K_{6(2ii)}; \quad k_{6-3} = k_{6f(3)} K_{6(3i)}$$

$$k_{6-4} = \frac{k_{6b(1)}}{K_{6(1)}}, \quad k_{6-5} = k_{6b(2)}; \quad k_{6-6} = \frac{k_{6b(3)}}{K_{6(3i)}}$$

$$iii) \quad \text{Fe}^{2+} + \text{NO}_2(\text{aq}) + \text{H}^+ = \text{Fe}^{3+} + \text{HNO}_2(\text{aq})$$

$$r_{10(\text{net-7})} = k_{7f} C_9(t) C_6(t) - k_{7b} C_{10}(t) C_{16}(t)$$

$$H^+ + \text{NO}_2^- = \text{HNO}_2(\text{aq}), \quad K_{7(1)} \quad \text{(P.Eq.)}$$

$$K_{7(1)} = \frac{C_1(t)}{C_2(t) C_{16}(t)}; \quad C_{16}(t) = \frac{C_1(t)}{C_2(t) K_{7(1)}}$$

By combining those two equations:

$$r_{10(\text{net-7})} = k_{7f} C_9(t) C_6(t) - k_{7b} C_{10}(t) \frac{C_1(t)}{C_2(t) K_{7(1)}}$$

$$k_{7-1} = k_{7f}$$

$$k_{7-2} = \frac{k_{7b}}{K_{7(1)}}$$

$$iv) \quad \text{Fe}^{2+} + \text{NO}_3^- + 2\text{H}^+ = \text{Fe}^{3+} + \text{NO}_2(\text{aq}) + \text{H}_2\text{O}$$

$$r_{10(\text{net-8})} = k_{8-1} C_9 C_7 - k_{8-2} C_{10} C_6 / C_2^2$$

**ELEMENTARY REACTIONS:**

$$\text{Fe}^{2+} + \text{NO}_3^- = \text{Fe}^{3+} + \text{NO}_3^- \quad \text{(R.C.)}$$
\[ r_{10(\text{net-8})} = k_{8f} C_7(t) C_9(t) - k_{8b} C_{10}(t) C_{17}(t) \]

\[
\text{NO}_3^{-} + 2\text{H}^{+} = \text{H}_2\text{O} + \text{NO}_2, \quad K_{8(1)} \quad \text{(P.Eq.)}
\]

\[
K_{8(1)} = \frac{C_6(t)}{C_{17}(t) C_7^2(t)}; \quad C_{17}(t) = \frac{C_6(t)}{C_7^2(t) K_{8(1)}}
\]

By combining those three equations:

\[
r_{10(\text{net-8})} = k_{8f} C_7(t) C_9(t) - k_{8b} C_{10}(t) \frac{C_6(t)}{C_7^2(t) K_{8(1)}}
\]

\[
k_{8,1} = k_{8f}
\]

\[
k_{8-2} = \frac{k_{8b}}{K_8}
\]

**Table D.1 Equilibrium Constants for Non-elementary Reactions, 5, 6, 7 & 8**

<table>
<thead>
<tr>
<th>Reaction No</th>
<th>Equilibrium Constant (25°C)</th>
<th>Equilibrium Constant (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( K_5 = 5.41 \times 10^{-4} , M )</td>
<td>( K_{5(i)} = 1.01 \times 10^{-5} , M )</td>
</tr>
<tr>
<td>6</td>
<td>( K_6 = 1.4 \times 10^{-1} , M )</td>
<td>( K_{6(i)} = 4.13 \times 10^{-2} , M )</td>
</tr>
<tr>
<td></td>
<td>( K_{6(ii)} = 1.03 , M )</td>
<td>( K_{6(ii)} = 2.41 \times 10^{-4} , M )</td>
</tr>
<tr>
<td></td>
<td>( K_{6(iii)} = 1.96 \times 10^{-3} , M )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( K_7 = 4.84 \times 10^{-7} , M )</td>
<td>( K_{7(i)} = 4.84 \times 10^{-7} , M )</td>
</tr>
<tr>
<td>8</td>
<td>( K_8 = 7.14 \times 10^{-1} , M^2 )</td>
<td>( K_{8(i)} = 1.03 \times 10^{-14} , M^2 )</td>
</tr>
</tbody>
</table>

*The protonated nitrous acid, \( \text{H}_2\text{NO}_2^+ \), is a somewhat speculative species. In fact, it is apparent that elementary reaction-steps shown, reaction 6(2i) and 6(2ii), only the combined reaction \( \text{HNO}_2(\text{aq}) + \text{H}^+ = \text{H}_2\text{O} + \text{NO}^+ \) \( (K_{b(2ii)}) \) is required in formulating the mechanism involving the nitrosonium ion \( \text{(NO}^+) \) as an intermediate species.*
APPENDIX E

DEVELOPMENT OF DIFFERENTIAL EQUATIONS FOR COMSOL SIMULATION

Species Numerical-Template:

\[ i \equiv \text{HNO}_2, 2 \equiv \text{H}^+, 3 \equiv \text{N}_2\text{O}_3, 4 \equiv \text{NO}_\text{(aq)}, 5 \equiv \text{NO}_2\text{(aq)}, 6 \equiv \text{NO}_3^-, 7 \equiv \text{O}_2, 8 \equiv \text{Fe}^{2+}, 9 \equiv \text{Fe}^{3+}, 10 \equiv \text{FeNO}_2^{2+} \]

\( r_i \) is defined as: the rate of formation of moles of species \( i \) per unit volume of solution (For a Batch Stirred-Reactor (BSR) and for a reaction system which there is no significant volume change \( \Delta V \) of the solution due to chemical reaction)

Thus:

\[
\frac{dN_i}{dt} = \frac{1}{V_s} \frac{d}{dt}(V_sC_i) = (V_s \frac{dC_i}{dt} + C_i \frac{dV_s}{dt})
\]

where; \( N_i \) is the number of moles of species \( i \) in the BSR

\( V_i \) is the volume of the solution in the BSR

\[
\frac{d}{dt} \text{ is the rate differential-operator}
\]

Net Rate Equations for System:

\[ -r_{\text{HNO}_2\text{(net-S)}} = -r_{1\text{(net-S)}} = -r_{1\text{(net-1)}} + r_{1\text{(net-3)}} + r_{1\text{(net-4)}} + r_{1\text{(net-5)}} - r_{1\text{(net-6)}} + r_{1\text{(net-7)}} \]

\[ -r_{\text{H}^+\text{(net-S)}} = -r_{2\text{(net-S)}} = r_{2\text{(net-4)}} - r_{2\text{(net-5)}} - r_{2\text{(net-6)}} - r_{2\text{(net-7)}} - r_{2\text{(net-8)}} \]

\[ -r_{\text{NO}_3\text{(net-S)}} = -r_{3\text{(net-S)}} = r_{3\text{(net-1)}} - r_{3\text{(net-2)}} \]

\[ -r_{\text{NO}_\text{(aq)(net-S)}} = -r_{4\text{(net-S)}} = r_{4\text{(net-2)}} - r_{4\text{(net-3)}} - r_{4\text{(net-5)}} + r_{4\text{(net-6)}} - r_{4\text{(net-9)}} \]

\[ -r_{\text{NO}_2\text{aq}(net-S)} = -r_{5\text{(net-S)}} = r_{5\text{(net-2)}} - r_{5\text{(net-4)}} + r_{5\text{(net-5)}} - r_{5\text{(net-7)}} + r_{5\text{(net-8)}} \]

\[ -r_{\text{NO}_3-(net-S)} = -r_{6\text{(net-S)}} = r_{6\text{(net-4)}} - r_{6\text{(net-5)}} - r_{6\text{(net-8)}} \]

\[ -r_{\text{O}_2\text{(net-S)}} = -r_{7\text{(net-S)}} = -r_{7\text{(net-3)}} \]

\[ -r_{\text{Fe}^{2+}\text{(net-S)}} = -r_{8\text{(net-S)}} = r_{8\text{(net-6)}} - r_{8\text{(net-7)}} - r_{8\text{(net-8)}} - r_{8\text{(net-9)}} \]

\[ -r_{\text{Fe}^{3+}\text{(net-S)}} = -r_{9\text{(net-S)}} = r_{9\text{(net-6)}} + r_{9\text{(net-7)}} + r_{9\text{(net-8)}} \]

\[ -r_{\text{FeNO}_2^{2+}\text{(net-S)}} = -r_{10\text{(net-S)}} = r_{10\text{(net-9)}} \]

Relationships between \( r_{\text{(net)}} \) for Reaction \( x \):

RXN 1: \(-\frac{1}{2} r_{1\text{(net-1)}} = r_{3\text{(net-1)}} \)
RXN 2: $-r_3^{(net-2)} = r_4^{(net-2)} = r_5^{(net-2)}$

RXN 3: $-\frac{1}{4} r_4^{(net-3)} = -r_7^{(net-3)} = \frac{1}{4} r_1^{(net-3)}$

RXN 4: $-\frac{1}{2} r_5^{(net-4)} = r_2^{(net-4)} = r_6^{(net-4)} = r_1^{(net-4)}$

RXN 5: $-r_4^{(net-5)} = -r_6^{(net-5)} = -r_2^{(net-5)} = r_5^{(net-5)} = r_1^{(net-5)}$

RXN 6: $-r_8^{(net-6)} = -r_1^{(net-6)} = -r_2^{(net-6)} = r_6^{(net-6)} = r_4^{(net-6)}$

RXN 7: $-r_8^{(net-7)} = -r_5^{(net-7)} = -r_2^{(net-7)} = r_9^{(net-7)} = r_1^{(net-7)}$

RXN 8: $-r_8^{(net-8)} = -r_6^{(net-8)} = -\frac{1}{2} r_2^{(net-8)} = r_9^{(net-8)}$

RXN 9: $-r_8^{(net-9)} = -r_4^{(net-9)} = r_1^{(net-9)}$
### APPENDIX F

RESULTS OF THE ELECTROCHEMICAL MEASUREMENTS AND CHEMICAL ANALYSES FOR LABORATORY-SCALE EXPERIMENTS

Table F.1 Measured potential as a function of time for experiment no: PE-1

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$E_{SCE}$ (mV)</th>
<th>$E_{SHE}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>340</td>
<td>584</td>
</tr>
<tr>
<td>5</td>
<td>316</td>
<td>560</td>
</tr>
<tr>
<td>10</td>
<td>355</td>
<td>599</td>
</tr>
<tr>
<td>20</td>
<td>365</td>
<td>609</td>
</tr>
<tr>
<td>50</td>
<td>383</td>
<td>627</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>644</td>
</tr>
<tr>
<td>150</td>
<td>412</td>
<td>656</td>
</tr>
<tr>
<td>200</td>
<td>422</td>
<td>666</td>
</tr>
<tr>
<td>250</td>
<td>430</td>
<td>674</td>
</tr>
<tr>
<td>300</td>
<td>436</td>
<td>680</td>
</tr>
<tr>
<td>450</td>
<td>466</td>
<td>710</td>
</tr>
<tr>
<td>600</td>
<td>493</td>
<td>737</td>
</tr>
<tr>
<td>900</td>
<td>520</td>
<td>764</td>
</tr>
<tr>
<td>1160</td>
<td>525</td>
<td>764</td>
</tr>
</tbody>
</table>
**Table F.2** Measured potential as a function of time for experiment no: PE-2

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$E_{SCE}$ (mV)</th>
<th>$E_{SHE}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>354</td>
<td>598</td>
</tr>
<tr>
<td>5</td>
<td>314</td>
<td>558</td>
</tr>
<tr>
<td>10</td>
<td>314</td>
<td>558</td>
</tr>
<tr>
<td>20</td>
<td>365</td>
<td>609</td>
</tr>
<tr>
<td>50</td>
<td>381</td>
<td>625</td>
</tr>
<tr>
<td>100</td>
<td>398</td>
<td>642</td>
</tr>
<tr>
<td>150</td>
<td>409</td>
<td>653</td>
</tr>
<tr>
<td>200</td>
<td>420</td>
<td>664</td>
</tr>
<tr>
<td>250</td>
<td>426</td>
<td>670</td>
</tr>
<tr>
<td>300</td>
<td>436</td>
<td>680</td>
</tr>
<tr>
<td>450</td>
<td>471</td>
<td>715</td>
</tr>
<tr>
<td>550</td>
<td>505</td>
<td>749</td>
</tr>
<tr>
<td>650</td>
<td>587</td>
<td>831</td>
</tr>
<tr>
<td>780</td>
<td>706</td>
<td>950</td>
</tr>
<tr>
<td>1110</td>
<td>710</td>
<td>954</td>
</tr>
</tbody>
</table>

**Table F.3** Concentration of ferrous in solution obtained by titration analysis as a function of time for experiment no: DE-1

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$C_{Fe^{2+}}$ (M)</th>
<th>$C_{Fe^{3+}}$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>24</td>
<td>0.095</td>
<td>0.005</td>
</tr>
<tr>
<td>48</td>
<td>0.091</td>
<td>0.009</td>
</tr>
<tr>
<td>96</td>
<td>0.080</td>
<td>0.020</td>
</tr>
</tbody>
</table>
Table F.4 Concentration of ferrous in solution as a function of time for experiment no: DE-2 and DE-3A and DE-3B

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>3.89 mM NO$_2^-$</th>
<th>4.5 mM NO$_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E^{\text{SCE}}$ (mV)</td>
<td>$E^{\text{SHE}}$ (mV)</td>
</tr>
<tr>
<td>15</td>
<td>380</td>
<td>620</td>
</tr>
<tr>
<td>60</td>
<td>412</td>
<td>652</td>
</tr>
<tr>
<td>120</td>
<td>440</td>
<td>680</td>
</tr>
<tr>
<td>180</td>
<td>458</td>
<td>698</td>
</tr>
<tr>
<td>240</td>
<td>484</td>
<td>724</td>
</tr>
<tr>
<td>300</td>
<td>512</td>
<td>752</td>
</tr>
<tr>
<td>360</td>
<td>532</td>
<td>772</td>
</tr>
<tr>
<td>420</td>
<td>555</td>
<td>795</td>
</tr>
<tr>
<td>1320</td>
<td>690</td>
<td>930</td>
</tr>
<tr>
<td>1440</td>
<td>692</td>
<td>932</td>
</tr>
</tbody>
</table>

Table F.5 Concentration of nitrite, nitrate and ferrous in solution obtained by spectrophotometric analysis as a function of time for experiment no: DE-3A and DE-3B

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Fe$^{2+}$ (mM)</th>
<th>HNO$_2$ (mM)</th>
<th>NO$_3^-$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>4.5</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>0.08</td>
<td>0.20</td>
<td>0.82</td>
</tr>
<tr>
<td>45</td>
<td>0.06</td>
<td>0.15</td>
<td>1.04</td>
</tr>
<tr>
<td>60</td>
<td>0.053</td>
<td>0.11</td>
<td>1.10</td>
</tr>
<tr>
<td>120</td>
<td>0.022</td>
<td>0.09</td>
<td>1.50</td>
</tr>
<tr>
<td>180</td>
<td>0.006</td>
<td>0.07</td>
<td>1.98</td>
</tr>
<tr>
<td>1020</td>
<td>0.001</td>
<td>0.05</td>
<td>3.93</td>
</tr>
</tbody>
</table>
Table F.6 Concentration of NO\(_{(g)}\) and NO\(_2(g)\) in the gas phase above nitrite electrolyte obtained by chemiluminescence for experiment no: DE-3C

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>NO (ppm)</th>
<th>NO(_2) (ppm)</th>
<th>C(_{NO}) (M)</th>
<th>C(_{NO2}) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>15</td>
<td>25</td>
<td>1.66x10(^{-6})</td>
<td>2.77x10(^{-6})</td>
</tr>
<tr>
<td>30</td>
<td>13</td>
<td>25</td>
<td>1.44x10(^{-6})</td>
<td>2.77x10(^{-6})</td>
</tr>
<tr>
<td>60</td>
<td>12</td>
<td>22</td>
<td>1.33x10(^{-6})</td>
<td>2.44x10(^{-6})</td>
</tr>
<tr>
<td>120</td>
<td>10</td>
<td>16</td>
<td>1.11x10(^{-6})</td>
<td>1.77x10(^{-6})</td>
</tr>
<tr>
<td>150</td>
<td>8.5</td>
<td>13</td>
<td>9.42x10(^{-7})</td>
<td>1.44x10(^{-6})</td>
</tr>
<tr>
<td>180</td>
<td>7.5</td>
<td>9.5</td>
<td>8.32x10(^{-7})</td>
<td>1.05x10(^{-6})</td>
</tr>
</tbody>
</table>

Table F.7 Measured potential as a function of time for experiment no: DE-4

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>4.5 mM NO(_2^)</th>
<th>4.5 mM NO(_2^) and Quartz -1</th>
<th>4.5 mM NO(_2^) and Quartz -2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>377</td>
<td>376</td>
<td>376</td>
</tr>
<tr>
<td>60</td>
<td>404</td>
<td>407</td>
<td>400</td>
</tr>
<tr>
<td>120</td>
<td>433</td>
<td>417</td>
<td>417</td>
</tr>
<tr>
<td>180</td>
<td>459</td>
<td>430</td>
<td>438</td>
</tr>
<tr>
<td>240</td>
<td>505</td>
<td>450</td>
<td>456</td>
</tr>
<tr>
<td>300</td>
<td>553</td>
<td>480</td>
<td>492</td>
</tr>
<tr>
<td>360</td>
<td>679</td>
<td>535</td>
<td>540</td>
</tr>
<tr>
<td>420</td>
<td>694</td>
<td>651</td>
<td>660</td>
</tr>
<tr>
<td>1320</td>
<td>710</td>
<td>710</td>
<td>710</td>
</tr>
<tr>
<td>1440</td>
<td>714</td>
<td>714</td>
<td>714</td>
</tr>
</tbody>
</table>
Table F.8 Measured potential as a function of time for experiment no: DE-5A

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$E_{SCE}$ (mV)</th>
<th>$E_{SHE}$ (mV)</th>
<th>$C_{Fe^{2+}}$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>272</td>
<td>512</td>
<td>0.10</td>
</tr>
<tr>
<td>60</td>
<td>306</td>
<td>546</td>
<td>0.10</td>
</tr>
<tr>
<td>120</td>
<td>323</td>
<td>563</td>
<td>0.095</td>
</tr>
<tr>
<td>180</td>
<td>339</td>
<td>579</td>
<td>0.090</td>
</tr>
<tr>
<td>240</td>
<td>345</td>
<td>585</td>
<td>0.083</td>
</tr>
<tr>
<td>300</td>
<td>350</td>
<td>590</td>
<td>0.078</td>
</tr>
</tbody>
</table>

Table F.9 Measured potential as a function of time for experiment no: DE-5B

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>25°C</th>
<th>Time (min)</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{SCE}$ (mV)</td>
<td>$E_{SHE}$ (mV)</td>
<td>$E_{SCE}$ (mV)</td>
</tr>
<tr>
<td>15</td>
<td>377</td>
<td>617</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>404</td>
<td>644</td>
<td>15</td>
</tr>
<tr>
<td>120</td>
<td>433</td>
<td>673</td>
<td>30</td>
</tr>
<tr>
<td>180</td>
<td>459</td>
<td>699</td>
<td>45</td>
</tr>
<tr>
<td>240</td>
<td>505</td>
<td>745</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>553</td>
<td>793</td>
<td>90</td>
</tr>
<tr>
<td>360</td>
<td>679</td>
<td>919</td>
<td>120</td>
</tr>
<tr>
<td>420</td>
<td>694</td>
<td>934</td>
<td>150</td>
</tr>
<tr>
<td>1320</td>
<td>710</td>
<td>950</td>
<td>180</td>
</tr>
<tr>
<td>1440</td>
<td>714</td>
<td>954</td>
<td></td>
</tr>
</tbody>
</table>
Table F.10 Concentration of cuprous ion in solution as a function of time for experiment no: DE-6

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$E^{\text{SCE}}$ (mV)</th>
<th>$E^{\text{SHE}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>56</td>
<td>296</td>
</tr>
<tr>
<td>60</td>
<td>72</td>
<td>312</td>
</tr>
<tr>
<td>120</td>
<td>80</td>
<td>320</td>
</tr>
<tr>
<td>180</td>
<td>83</td>
<td>323</td>
</tr>
<tr>
<td>240</td>
<td>83</td>
<td>323</td>
</tr>
</tbody>
</table>
APPENDIX G

CONCENTRATION OF ACTIVE SPECIES IN 1 M H₂SO₄ ELECTROLYTE, CONTAINING 4.5 mM HNO₂ AND 0.1 M Fe²⁺, OBTAINED BY COMSOL-AIDED COMPUTER SIMULATION

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>C_HNO₂ (M)</th>
<th>C_NO₂ (M)</th>
<th>C_N₂O₃ (M)</th>
<th>C_NO (M)</th>
<th>C_NO₂⁻ (M)</th>
<th>C_Fe²⁺ (M)</th>
<th>C_Fe³⁺ (M)</th>
<th>C_FeNO₂⁺ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.50 x 10⁻³</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.00 x 10⁻¹</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>1.27 x 10⁻³</td>
<td>5.71 x 10⁻⁹</td>
<td>4.30 x 10⁻⁹</td>
<td>7.82 x 10⁻⁵</td>
<td>1.80 x 10⁻²</td>
<td>9.05 x 10⁻²</td>
<td>6.38 x 10⁻³</td>
<td>3.13 x 10⁻³</td>
</tr>
<tr>
<td>5</td>
<td>1.58 x 10⁻³</td>
<td>9.44 x 10⁻⁷</td>
<td>7.60 x 10⁻⁷</td>
<td>8.42 x 10⁻⁶</td>
<td>5.34 x 10⁻⁴</td>
<td>7.47 x 10⁻²</td>
<td>2.25 x 10⁻²</td>
<td>2.78 x 10⁻³</td>
</tr>
<tr>
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APPENDIX H

CHALCOCITE MINERAL DATA

Crystal Data: Monoclinic, pseudo-orthorhombic. Point Group: 2/m or m. Crystals are short prismatic [001], thick to tabular {001}, to 12 cm across, and prismatic [100], to 25 cm long; {001} is striated [100]. Massive, compact, fine powdery. Twinning: Common on {110} yielding pseudohexagonal stellate forms; also on {032}, {112}. Seen as lamellar twinning in polished section.

Physical Properties: Cleavage: Indistinct on {110}. Fracture: Conchoidal. Tenacity: Brittle, somewhat sectile. Hardness = 2.5–3 VHN = 84–87 (100 g load). D(meas.) = 5.5–5.8 D(calc.) = 5.80

Cell Data: Space Group: $P2_1/c$ or $Pc$. $a = 11.82$, $b = 27.05$, $c = 13.43$, $\beta = 90^\circ$, $Z = 96$

X-ray Powder Pattern: Bristol, Connecticut, USA (close to djurleite).

1.8800 (100), 2.4030 (70), 1.9746 (70), 1.8811 (70), 2.4074 (50), 3.276 (35), 2.7256 (35)

Chemical Composition*:

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</table>

*Butte, Montana, USA; Fe present as pyrite (Palache et al., 1944)
BIOGRAPHICAL SKETCH

The author was born in Izmir, Turkey and completed the Bachelor Science Degree in Chemical Engineering at Ege University. She received her M.Sc degree in Chemical Engineering at Ege University and Mining Engineering at Dokuz Eylul University in Turkey.

In January 2004, she started to work as a research assistant in Mining Engineering Department at Dokuz Eylul University. After being awarded a scholarship to continue her graduate studies in United States by The Higher Council of Education (YÖK) and Dokuz Eylul University, the author enrolled at Colorado School of Mines in January 2007.