OXIDATION OF REFRACTORY GOLD CONCENTRATES AND SIMULTANEOUS DISSOLUTION OF GOLD IN AERATED ALKALINE SOLUTIONS

By

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I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institute

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The oxidation of refractory gold concentrates containing arsenopyrite and pyrite and the simultaneous dissolution of gold in aerated alkaline solutions at ambient temperatures and pressures without the addition of cyanide has been studied. It involves the following aspects: the chemistry of the oxidation of pure arsenopyrite and pyrite minerals in aerated alkaline solutions; the kinetics of oxidation of arsenopyrite and the simultaneous dissolution of gold in such solutions; the kinetics of simultaneous dissolution of gold during the alkaline oxidation of refractory gold concentrates; the electrochemistry of gold in alkaline solutions containing thiosulfate or monothioarsenate; the effect of copper on the leaching of gold in alkaline thiosulfate solutions; and the leaching of gold in alkaline solutions with thioarsenites.

The nature and proportions of the products of the oxidation of arsenopyrite in aerated alkaline solutions have been studied using high pressure ion chromatography techniques that have shown that thiosulfate and a new species, monothioarsenate, are the main oxidation products of arsenopyrite apart from arsenate and sulfite. The alkaline oxidation of pyrite primarily yields thiosulfate and sulfite. A kinetic investigation of the oxidation of arsenopyrite with air or oxygen has shown that the initial rate of arsenopyrite oxidation is proportional to the concentration of dissolved oxygen. A reaction mechanism for the oxidation of arsenopyrite has been proposed, which involves an anodic oxidation of the mineral involving hydroxyl ions coupled to a cathodic process for oxygen reduction which is partially controlled by mass transfer of dissolved oxygen to the mineral surface.
Detailed studies of the dissolution behaviour of gold in aerated alkaline solutions in the presence of thiosulfate or monothioarsenate by electrochemical and leaching methods have demonstrated that the dissolution rate is very low as compared to that of gold in alkaline cyanide or ammoniacal thiosulfate solutions. It has been found that copper ions catalyze the dissolution of gold in the thiosulfate solutions in the absence of ammonia. The leaching experiments also have shown that gold may dissolve in alkaline thioarsenite solutions, which provides a possible new process option for the leaching of gold.

The oxidation of refractory arsenical gold concentrates in aerated alkaline solutions results in the formation of thiosulfate, arsenate and sulfate as well as the dissolution of gold, copper and iron. It appears that the dissolution of gold is due to the complex reactions of gold with thiosulfate ions promoted by the catalytic effect of copper ions. Up to 80% of the gold may be extracted during the oxidation of selected refractory arsenical gold concentrates, which suggests a possible one-step process for the extraction of gold.
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CHAPTER 1 INTRODUCTION

1.1 Background to this Study

Almost all gold currently produced from ores in the world is extracted by the cyanidation process, which was firstly recognized as early as 1783 and studied in the 1840's and 1850's. Between 1887 and 1888, the cyanidation process was patented and later developed into a commercial process in 1889 (Marsden and House, 1992). The process depends on the fact that gold forms an exceptionally strong bond with cyanide ions to give the aurous di-cyanide complex. Indeed, the stability constant for this species is sufficiently large for gold to be oxidized by oxygen in the presence of cyanide ions. Thus the leaching of gold from its ores is accomplished by bubbling air through a slurry of crushed ore in alkaline (pH=10) cyanide solution. The cyanidation process is so simple, efficient and economical that it has spread rapidly all over the world and has been the most important extraction process for the extraction of gold and silver from their respective ores for over a century.

Although it is an effective technique for the treatment of a wide range of ores, the cyanidation process has several drawbacks and is not suitable for the direct extraction of gold and silver from some kinds of ores and concentrates, for the following reasons:

(1) Cyanide is an extremely toxic compound, creating the need for expensive transportation, storage and cleanup procedures and resulting in a series of environmental and health problems related to the industrial use of cyanide and the
disposal of toxic cyanide waste. The cyanidation process is under scrutiny and more stringent environmental and health standards are being established. Several countries no longer allow the construction of new gold processing plants using cyanide (Han and Meng, 1992).

(2) The leaching kinetics of gold and silver with cyanide is slow, with the leaching rate being controlled by the diffusion of oxygen that has limited solubility in water. Under most plant conditions, the leaching of gold normally takes at least 24 hours for an economically acceptable recovery of gold.

(3) Gold occurs in refractory ores and concentrates.

The word, “refractory”, literally means “difficult to treat”. The so-called refractory gold ores cannot be easily and/or economically treated directly by conventional cyanidation processes, yielding unsatisfactorily low extractions of gold and silver. Generally, three basic causes account for the “refractory” characteristics of ores (Kontopoulos and Stefanakis, 1990):

a) Gold is often locked in oxidizable gangue minerals, often sulfides, and cannot be adequately liberated, even by fine grinding, so that it is not accessible to the leaching reagents, resulting in low recovery. This appears most commonly as physical encapsulation of very finely disseminated gold particles within a mineral that is unreactive and impermeable to the cyanide leaching solution. A typical mineral of this type is arsenopyrite (Rapson, 1997, Marsden and House, 1992).

b) Reactive constituents present in the mineral matrix consume unacceptable quantities of cyanide and/or oxygen in side reactions, for example, pyrrhotite, arsenopyrite, copper oxides (Davis and Tran, 1991).
c) Carbonaceous materials naturally occurring in some ores can adsorb the aurocyanide complex during cyanide leaching and result in low extraction of gold from ores. This phenomenon is known as pre-robbing (Thomas, 1991b).

The “easily cyanidable“ gold ores with exploitable grades are becoming rapidly depleted around the world and more and more ore bodies are proving to be refractory to some extent. Since refractory gold ores are not amenable to direct cyanidation, particular pretreatment processes are required prior to conventional cyanidation in order to improve the recovery of gold. Numerous pretreatment processes have been developed to overcome the refractory nature of some gold ores and to increase the extraction of gold and silver (Souza and Ciminelli, 1992; Wu, et al., 1999; Xu et al., 1999; Corrans and Angove, 1991; Luganov et al., 1996; Dunn and Chamberlain, 1997; Koslides and Ciminelli, 1992; Van Weert et al., 1986; Syrtlanova et al., 1979; Kostina and Chernyak, 1979; Thomas, 1991b, c; Kontopoulou and Stefanakisa, 1990; Dunn et al., 1989; Linge and Welham, 1997; Li et al., 1992). Some of these techniques are pre-aeration, chlorination, roasting, pressure oxidation, bacterial oxidation, ultra-fine grinding, chemical oxidation, electrochemical oxidation and high-pressure cyanidation. All the additional pretreatment techniques result in an increase in the overall production cost and thus are often not economically viable. Of these techniques, high temperature roasting, pressure oxidation and bacterial oxidation have found application in the gold industry, although each of them is subject to its particular advantages and shortcomings.

Alkaline oxidation may be the preferred treatment option for arsenical sulfide ores in certain situations. Thermodynamically, oxidation occurring in alkaline media would be advantageous because arsenopyrite and pyrite are not stable at low potentials (Ciminelli, 1987; Ciminelli and Osseo-Asare, 1995a, b; Tao et al., 1994; Kostina and
Chernyak, 1979; Wang et al., 1992). The use of an alkaline oxidation pretreatment process has several technical merits such as the following (Deng, 1995; Deng, 1992):

- Simpler flowsheet for gold recovery by cyanidation;
- Lower operating temperature (usually less than 100 °C);
- Fewer corrosion problems with materials of construction;
- Lower capital and operating costs, and
- Suitability for acid-consuming ores and concentrates.

However, in comparison with many developed acid pretreatment processes, the alkaline oxidation route has received very limited attention for refractory gold ores and only the Barrick Mercur Gold Mine, Nevada, used alkaline pressure oxidation on a commercial scale for the pretreatment of refractory gold ores (Thomas and Williams, 2000; Thomas, 1991a, b; Hiskey and Sanchez, 1995). The drawbacks of alkaline oxidation such as the use of relatively expensive reagents, e.g. sodium hydroxide (NaOH) and higher operating pressures have restricted the commercial application of this process (Deng, 1995). Additionally, gold extraction by cyanidation after pretreatment by alkaline oxidation normally does not exceed 85%, although some investigators reported 90 to 99% recoveries of gold by cyanidation from products of autoclave oxidation in NaOH solutions (Koslides and Ciminelli, 1992; Bhakta et al., 1989).

To overcome the above shortcomings, several new attempts have been made to increase gold recovery and decrease the operating and capital costs of alkaline oxidation processes, including:

- Simultaneous fine-grinding and leaching of gold by hypochlorite (Mao et al., 1997);
- Simultaneous fine-grinding and leaching of gold by cyanide (Min et al., 1999);
- Simultaneous pressure oxidation and gold leaching by thiosulfate (Lulham, 1989);
• Ultra-fine grinding and oxidation under ambient conditions (Syrtlanova et al., 1979; Rossovsky, 1993);
• Gold leaching by a lime-sulfur mixture (Lan and Zhang, 1996), and
• Gold leaching by oxidation products of sulfur in lime solution with oxygen (Fang and Han, 2002).

More recently, it has been found that during the alkaline oxidation by dissolved oxygen of refractory arsenopyrite bearing gold concentrates, the gold in the concentrates was simultaneously dissolved by a reaction which has not yet been identified (Zhang and Nicol, 1999). Independent Metallurgical Laboratories (Anon., 1999) in Western Australia also performed similar experiments and observed a similar phenomenon. They attributed the dissolution of gold to possible leaching by thiosulfates formed during the oxidation process or the complexation of gold with chlorides present in the water used.

1.2 Scope of this Study

As mentioned above, gold was simultaneously leached out during the alkaline oxidation of the refractory arsenopyrite bearing gold concentrates. It is necessary to study the chemistry of the alkaline oxidation of gold concentrates and relevant pure minerals such as arsenopyrite (FeAsS), pyrite (FeS$_2$) and chalcopyrite (CuFeS$_2$), especially FeAsS because arsenic and sulfur in the arsenopyrite mineral both can dissolve in alkaline solutions, forming species which might influence the behaviour of gold. Rossovsky (1993) has proposed that thioarsenites (AsS$_3^{3-}$) and thiosulfates (S$_2$O$_3^{2-}$) are present in such solutions. On the other hand, there is no consensus on the oxidation products of arsenopyrite and little is known about the formation of arsenic-sulfur compounds during the oxidation of arsenopyrite and their effects on the dissolution of gold which might take place during the oxidation. Therefore, part of this study focuses
on the chemistry of the oxidation of arsenopyrite and gold concentrates in alkaline solutions and the reaction of some arsenic-sulfur compounds with gold.

Another part of the study is devoted to the dissolution behavior of gold during the alkaline oxidation of arsenopyrite and refractory gold concentrates, and to the effects of some process variables on the kinetics of the dissolution of gold.

Since thiosulfate is a probable oxidation product of refractory sulfidic gold ores in alkaline solutions, part of this study is also engaged in a study of the dissolution of gold in alkaline solutions containing thiosulfate. Although extensive studies on the kinetics and mechanism of gold dissolution in ammoniacal thiosulfate media have been carried out (Aylmore and Muir, 2001), the thiosulfate leaching system for gold and silver has been found to be very complicated and is not fully understood, which in turn hinders its development and application in the gold industry. The successful development and utilization of the thiosulfate leaching system will depend on a detailed knowledge of the leaching mechanism. Further research on reactions of thiosulfate with gold is necessary so as to better understand the reaction mechanism and control the solution chemistry. In this part, the effect of copper on the dissolution of gold is investigated because of the common presence of copper bearing minerals like chalcopyrite in refractory sulfidic gold ores.
1.3 Objectives of this Study

The following are the main objectives of the research project:

1) To study the effects of various parameters on the kinetics of the oxidation of refractory gold concentrates containing arsenopyrite and pyrite at ambient temperatures and pressures;

2) To investigate the simultaneous dissolution of gold, arsenic and sulfur species in aerated alkaline solutions;

3) To establish the chemistry (including electrochemistry) of the reaction system so that optimization and control of the process can be accomplished on a rational basis.

1.4 Overview of this Thesis

The thesis is sub-divided into the following main sections:

Chapter 2 presents an overview of the relevant chemistry of gold, arsenic and sulfur and reviews the literature on the dissolution of gold in thiosulfate and arsenic bearing solutions, and on the oxidation of refractory sulfidic gold ores.

Chapter 3 describes the experimental set up and the analyses and test procedures used.

Chapter 4 deals with the studies of the electrochemical dissolution of gold in alkaline solution. It discusses the mechanism of the dissolution of gold and the effects of various parameters.
Chapter 5 considers the effect of copper and grinding on the dissolution of gold in alkaline thiosulfate solutions without ammonia.

Chapter 6 summarizes the results of a study of the behaviour of gold in alkaline arsenic bearing solutions by means of electrochemical and leaching techniques.

Chapter 7 deals with the kinetics of dissolution of gold, arsenic and sulfur during the alkaline oxidation of the pure sulfide minerals, arsenopyrite and pyrite. The effects of some parameters on the oxidation of arsenopyrite are also investigated.

Chapter 8 reports on the alkaline oxidation of selected refractory gold concentrates and the dissolution of gold during the oxidation.

Chapter 9 provides some conclusions and recommendations.
CHAPTER 2  REVIEW OF THE LITERATURE

2.1  The Chemistry of the Hydrometallurgy of Gold

2.1.1  General Properties of Gold

Gold is the noblest of all metals. From ancient times, it has been valued as the ‘king of metals’, excelling all others in its beautiful yellow color, bright luster, ductility and stability in air. Even today its special interest is connected with its value as a metal (Remy et al., 1956). It is a soft metal and is usually alloyed to give it more strength. Metallic gold also has high electrical and conductivity properties that have led to its widespread use in modern industries in more recent decades. Table 2.1 lists some of the physical properties of gold.

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Physical properties of gold (after Greenwood and Earnshaw, 1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar atomic weight / g mol⁻¹</td>
<td>196.967</td>
</tr>
<tr>
<td>Melting point / °C</td>
<td>1064</td>
</tr>
<tr>
<td>Boiling point / °C</td>
<td>2808</td>
</tr>
<tr>
<td>Density / g cm⁻³ at 20 °C</td>
<td>19.32</td>
</tr>
<tr>
<td>Electrical resistivity / μ Ω cm at 20 °C</td>
<td>2.35</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Gold is the only metal that is generally found in nature in the metallic state, and the only gold compounds that exist in a natural state are the tellurides and stibnites, AuTe$_2$ and AuSb$_2$. It is almost invariably associated with quartz or pyrite, both in veins and in alluvial or placer deposits (Greenwood and Earnshaw, 1997). Gold is the only metal that is not oxidized in air (even at high temperatures) or water by either oxygen or sulfur, and is not attacked under the most corrosive conditions (Bailar et al., 1973).

Of greater importance in gold hydrometallurgy is the chemistry of gold complexes in aqueous solutions. It has been well known that gold can occur in one of six oxidation states, from -1 to +5 (Puddephatt and Vittal, 1994), which can be related to its relatively high electronegativity, i.e. tendency to attract bonding electrons. The most ubiquitous forms of gold compounds and those of hydrometallurgical interest are those in the aurous (+1) or auric (+3) oxidation state.

### 2.1.2 Chemistry of the Dissolution of Gold

The dissolution of gold in aqueous solutions is a combined process of oxidation and complexation. In the presence of a complexing ligand, aurous or auric cations will form stable complexes or be reduced by water to metallic gold (Nicol, et al., 1987). It is also often necessary to add a pH modifier, either acid or alkali, to maintain an optimum pH for the dissolution of gold. From an electrochemical viewpoint, the dissolution of solid metallic materials is an electrochemical process, which involves separate anodic (oxidative) and cathodic (reductive) reactions (Nicol, 1993). For the dissolution of gold in aqueous solutions, the anodic process involves oxidation of the gold according to the following reactions:

\[
\text{Au}^+ + e^- = \text{Au}^0 \quad \quad \quad E^0 = 1.691 \text{ V} \quad (2.1)
\]
Chapter 2 Review of the Literature

\[ \text{Au}^{3+} + 3e^- = \text{Au}^0 \quad E^o = 1.498 \text{ V} \quad (2.2) \]

\( E^o \) is the standard reduction potential (King, 1994). The cathodic process that occurs simultaneously with the above reactions involves reduction of an appropriate oxidant.

In the absence of complexing ligands, the aurous ion (\( \text{Au}^+ \)) is thermodynamically unstable under all potential-pH conditions, as indicated by its higher reduction potential than the auric ion (\( \text{Au}^{3+} \)) reduction potential. At these high potentials, both the aurous and the auric ions will undergo spontaneous reduction to gold with the oxidation of water to oxygen, given that \( E^o = 1.229 \text{ V} \) (King, 1994) for the following reaction:

\[ \text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O} \quad (2.3) \]

This means that gold can not be oxidized in aqueous solutions in the absence of complexing ligands.

The stability of the ions can, however, be increased in the presence of appropriate ligands, such as cyanide, chloride and thiosulfate ions, by forming stable complexes,

\[ \text{Au}^+ + 2\text{L} = \text{AuL}_2^+ \quad (2.4) \]

\[ \text{Au}^{3+} + 4\text{L} = \text{AuL}_4^{3+} \quad (2.5) \]

where \( \text{L} \) is a complexing ligand. The stability constants, \( \beta_2 \) and \( \beta_4 \), for the \( \text{Au}^+ \) and \( \text{Au}^{3+} \) complexes can be expressed as follows:

\[ \beta_2 = [\text{AuL}_2^+]/[\text{Au}^+][\text{L}]^2 \quad (2.6) \]

\[ \beta_4 = [\text{AuL}_4^{3+}]/[\text{Au}^{3+}][\text{L}]^4 \quad (2.7) \]

By combining Equations 2.1 and 2.4, Equation 2.8 is obtained and the standard reduction potential at 25 °C is given by Equation 2.9 according to the Nernst equation (Nicol et al., 1987):

\[ \text{AuL}_2^+ + e^- = \text{Au} + 2\text{L} \quad (2.8) \]

\[ E^o_{\text{AuL}_2^+ / \text{Au}} = E^o_{\text{Au}^+ / \text{Au}} - \left( \frac{0.0592}{n} \right) \log \beta_2 \quad (2.9) \]
where \( n \) is the number of electrons involved in the reaction (here \( n = 1 \)). Similarly, Equations 2.10 and 2.11 can be obtained (\( n = 3 \)).

\[
\text{AuL}_4^{3+} + 3e^- = \text{Au} + 4L \quad (2.10)
\]

\[
\text{E}_\text{AuL}_4^{3+}/\text{Au} = \text{E}_\text{Au}^{3+}/\text{Au} - \left( \frac{0.0592}{n} \right) \log \beta_4 \quad (2.11)
\]

There are a number of ligands that can form aurous or auric complexes with a wide range of stability. However, only a limited number of ligands form aqueous complexes of sufficient stability for use in gold extraction processes. Some of these complexes are listed in Table 2.2 in which the stability constants and the standard reduction potentials of the corresponding reduction reactions are given. The stability of the gold complexes is related not only to the properties of the complexing ligand, but also more specifically to the donor atom of the ligand that is bonded directly to the gold atom. Two general rules apply (Nicol et al., 1987). The first is that the stability of gold complexes tends to decrease when the electronegativity of the donor atom increases. For example, the stability for the gold halide complexes in aqueous solution follows the order \( \Gamma > \text{Br}^- > \text{Cl}^- > \text{F}^- \). The second rule is that Au(III) is generally favored over Au(I) with hard ligands and Au(I) over Au(III) with soft ligands. Thus soft polarizable ligands containing less electronegative donor atoms such as S, C, Se, P, As and I form more stable complexes with Au(I), whereas hard (more electronegative) electron donor ligands with F, Cl, Br, O, N donor atoms prefer Au(III). The preferred co-ordination number of Au(I) is 2 and that of Au(III) is 4, with Au(I) tending to form linear complexes and Au(III) tending to form square planar complexes. In water, aurous and auric ions exist in the hydrated state as complexes \( \text{Au(H}_2\text{O)}_2^+ \) and \( \text{Au(H}_2\text{O)}_4^{3+} \), although they are generally represented as \( \text{Au}^+ \) and \( \text{Au}^{3+} \).
Table 2.2  Stability constants for selected Au(I) and Au(III) complexes and standard reduction potentials for the corresponding reactions at 25 °C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Log $\beta$</th>
<th>Reduction Reaction</th>
<th>$E^\circ$/V</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}^+ + e^- = \text{Au}$</td>
<td>-</td>
<td>-</td>
<td>1.69</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Au(CN)}_2^-$</td>
<td>38.3</td>
<td>$\text{Au(CN)}_2^- + e^- = \text{Au} + 2\text{CN}^-$</td>
<td>-0.57</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Au}_2(\text{HS})_2\text{S}^2-$</td>
<td>72.9</td>
<td>$\text{Au}_2(\text{HS})_2\text{S}^2- + 2e^- = 2\text{Au} + \text{S}^{2+} + 2\text{HS}^-$</td>
<td>-0.47*</td>
<td>c</td>
</tr>
<tr>
<td>$\text{AuS}^-$</td>
<td>36.3</td>
<td>$\text{AuS}^- + e^- = \text{Au} + \text{S}^{2-}$</td>
<td>-0.46</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au(HS)}_2^-$</td>
<td>32.8</td>
<td>$\text{Au(HS)}_2^- + e^- = \text{Au} + 2\text{HS}^-$</td>
<td>-0.25*</td>
<td>c</td>
</tr>
<tr>
<td>$\text{Au(SO}_3)_2^{3-}$</td>
<td>26.8</td>
<td>$\text{Au(SO}_3)_2^{3-} + e^- = \text{Au} + 2\text{SO}_3^{2-}$</td>
<td>0.11*</td>
<td>c</td>
</tr>
<tr>
<td>$\text{Au(S}_2\text{O}_3)_2^{3-}$</td>
<td>26.0</td>
<td>$\text{Au(S}_2\text{O}_3)_2^{3-} + e^- = \text{Au} + 2\text{S}_2\text{O}_3^{2-}$</td>
<td>0.15</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au(CSe(NH}_2)_2^{2+}$</td>
<td>25.3*</td>
<td>$\text{Au(CSe(NH}_2)_2^{2+} + e^- = \text{Au} + 2\text{CSe(NH}_2)_2$</td>
<td>0.20</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au(CS(NH}_2)_2^{2+}$</td>
<td>22.0</td>
<td>$\text{Au(CS(NH}_2)_2^{2+} + e^- = \text{Au} + 2\text{CS(NH}_2)_2$</td>
<td>0.38</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au(NH}_3)_2^{+}$</td>
<td>19.0*</td>
<td>$\text{Au(NH}_3)_2^{+} + e^- = \text{Au} + 2\text{NH}_3$</td>
<td>0.57</td>
<td>b</td>
</tr>
<tr>
<td>$\text{AuI}_2^-$</td>
<td>19.0*</td>
<td>$\text{AuI}_2^- + e^- = \text{Au} + 2\text{I}^-$</td>
<td>0.57</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au(SCN)}_2^-$</td>
<td>17.1</td>
<td>$\text{Au(SCN)}_2^- + e^- = \text{Au} + 2\text{SCN}^-$</td>
<td>0.66</td>
<td>a</td>
</tr>
<tr>
<td>$\text{AuBr}_2^-$</td>
<td>12.0</td>
<td>$\text{AuBr}_2^- + e^- = \text{Au} + 2\text{Br}^-$</td>
<td>0.98*</td>
<td>a</td>
</tr>
<tr>
<td>$\text{AuCl}_2^-$</td>
<td>9.0*</td>
<td>$\text{AuCl}_2^- + e^- = \text{Au} + 2\text{Cl}^-$</td>
<td>1.16</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au}^{3+} + 3e^- = \text{Au}$</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Au(CN)}_4^- + 3e^- = \text{Au} + 4\text{CN}^-$</td>
<td>~56</td>
<td>-</td>
<td>0.40*</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Au(NH}_3)_4^{3+}$</td>
<td>~59</td>
<td>$\text{Au(NH}_3)_4^{3+} + 3e^- = \text{Au} + 4\text{NH}_3$</td>
<td>0.33</td>
<td>d</td>
</tr>
<tr>
<td>$\text{AuI}_4^-$</td>
<td>47.7</td>
<td>$\text{AuI}_4^- + 3e^- = \text{Au} + 4\text{I}^-$</td>
<td>0.56*</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Au(SCN)}_4^-$</td>
<td>42</td>
<td>$\text{Au(SCN)}_4^- + 3e^- = \text{Au} + 4\text{SCN}^-$</td>
<td>0.62</td>
<td>a</td>
</tr>
<tr>
<td>$\text{AuBr}_4^-$</td>
<td>32</td>
<td>$\text{AuBr}_4^- + 3e^- = \text{Au} + 4\text{Br}^-$</td>
<td>0.87*</td>
<td>a</td>
</tr>
<tr>
<td>$\text{AuCl}_4^-$</td>
<td>26</td>
<td>$\text{AuCl}_4^- + 3e^- = \text{Au} + 4\text{Cl}^-$</td>
<td>1.00</td>
<td>a</td>
</tr>
</tbody>
</table>

a. from Nicol et al., 1987;
b. from Hiskey and Atluri, 1988;
c. from Webster, 1986;
d. from Skibsted and Bjerrum, 1974a, b;
* calculated from $E^\circ$ values or $\beta$ values with Equations 2.9 or 2.11.
As can be seen in Table 2.2, the most stable complex is that with cyanide and this has been of greatest importance in gold industry with the establishment of the cyanidation process. Other non-cyanide gold complexes of hydrometallurgical interest are those involving thiourea, thiocyanate, thiosulfate, sulfide and the halide complexes. These ligands are potential competitive alternatives to cyanide which has come under scrutiny due to increased environmental and occupational health pressures in recent years. Despite extensive laboratory studies, none has found commercial application on a large scale (Sparrow and Woodcock, 1995). The leaching of gold by cyanide and other ligands in aqueous solutions will be briefly summarized in the following Section 2.1.3, except for thiosulfate which will be reviewed in detail in Section 2.2. In Section 2.3, some gold bearing compounds formed with arsenic are also briefly reviewed.

2.1.3 The Leaching of Gold with Various Lixiviants

2.1.3.1 Cyanidation

Cyanidation is the most common method by which gold is recovered from its ores. After more than 100 years in use, a substantial body of empirical experience has been published and a solid theoretical framework has been established (Sparrow and Woodcock, 1995). In the cyanidation process for the extraction of gold, gold is oxidized and dissolves in aqueous alkaline cyanide solution in the presence of dissolved oxygen as an oxidant, forming the Au(I) cyanide complex, Au(CN)₂⁻. The overall reaction for the leaching of gold may be expressed by the following equation:

\[ 4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{Au(CN)}_2^- + 4\text{OH}^- \] (2.12)
In order to represent the equilibrium chemistry of the cyanidation reaction, it is often convenient to use the Eh-pH diagram (also called as Pourbaix diagram) which is widely utilized in hydrometallurgical processes (Burkin, 1966; Marsden and House, 1992). Figure 2.1 gives an Eh-pH diagram for the gold-water-cyanide-oxygen system at 25 °C and [CN⁻] = 10⁻³ M. The two dashed lines indicate the equilibria for the reduction of water to hydrogen (lower line),

\[ 2H_2O + 2e^- = H_2 + 2OH^- \quad E^\circ = - 0.0591 \text{ pH} - 0.0295 \log (pH_2) \quad (2.13) \]

and for the reduction of oxygen to water (upper line),

\[ O_2 + 4 H^+ + 4e^- = 2H_2O \quad E^\circ = 1.23 - 0.0591 \text{ pH} + 0.0147 \log (P_{O_2}) \quad (2.14) \]

respectively, where pH₂ and Po₂ are the partial pressure of hydrogen and oxygen gas respectively (Marsden and House, 1992). Between the two dashed lines is the area in which water is stable. The shaded region indicates the area of stability of gold as the \( \text{Au(CN)}_2^- \) complex in aqueous cyanide solutions over a wide range of pH values. As illustrated in Figure 2.1, gold may be oxidized by oxygen at a potential of about -0.52 V and will be soluble in alkaline cyanide solutions at high pH (>10). For practical purposes, the stoichiometry of the dissolution reaction of gold is given by

\[ \text{Au(CN)}_2^- + e^- = \text{Au} + 2CN^- \quad E^\circ = - 0.57 \text{ V} \quad (2.15) \]

while the reductive reaction of oxygen may be generally assumed to be as following:

\[ O_2 + 2H_2O + 4e^- = 4OH^- \quad E^\circ = + 0.401 \text{ V} \quad (2.16) \]

Of greater importance in practice are the kinetic considerations that apply to the leaching of gold. Thus, electrochemical techniques have been used to study the kinetics and mechanism of gold dissolution in that the anodic oxidative reactions of gold and the cathodic reductive reactions of oxygen may be studied separately (Kudryk and Kellogg, 1954). Accordingly, much work has been published on the anodic behaviour of gold in alkaline cyanide solutions and reviewed by Nicol (1980a, b).
It is generally accepted that the dissolution of gold occurs by way of the following mechanism:

\[ \text{Au} + \text{CN}^- = \text{AuCN}_{\text{ads}} + e^- \quad (2.17) \]

\[ \text{AuCN}_{\text{ads}} + \text{CN}^- = \text{Au(CN)}_2^- \quad (2.18) \]

The formation of an adsorbed intermediate species, AuCN, is believed to cause passivation of the gold surface. A number of foreign heavy metal ions such as Pb, Hg or Tl at low concentrations have been found to disrupt the formation of such a passivating layer and thus greatly increase the dissolution rate of gold in alkaline cyanide solutions (Nicol \textit{et al.}, 1987; Jeffrey and Ritchie, 2000).
The cathodic reduction of oxygen in alkaline solutions has been experimentally shown to proceed through the intermediate formation of peroxide by the reaction (Damjanovic et al., 1967; King, 1994)

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- = \text{HO}_2^- + \text{OH}^- \quad E^\circ = -0.076 \text{ V} \quad (2.19) \]

The hydrogen peroxide formed is a strong oxidizing agent which may take part in further oxidation reactions:

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2e^- = 3\text{OH}^- \quad E^\circ = 0.878 \text{ V} \quad (2.20) \]

Oxygen may be directly reduced to hydroxide ions, rather than to \( \text{HO}_2^- \) as in Equation 2.16. Generally, these reactions require a large overpotential and are very slow.

It is well established on the basis of electrochemical measurements that the overall rate of gold dissolution in aerated alkaline cyanide solutions is controlled by the rate of diffusion of the reactants from the bulk solution to the surface of gold i.e. the reaction is mass transport controlled. Therefore, the leaching rate of gold can depend on oxygen concentration, cyanide concentration, temperature and the agitation rate (Nicol et al., 1987).

### 2.1.3.2 Chlorination

Chlorination was extensively applied in the nineteen century for the treatment of ores and gold occurring with sulfides. With the advent of the cyanide process and steadily decreasing reserves of high grade of gold ores, this method has essentially disappeared and is used nowadays only in the refining of gold. Over the past 10 years, the leaching of gold with chlorides has gained renewed attention due to considerable emphasis on protection of the environment from pollution and on the treatment of
refractory gold ores which are not amenable to traditional cyanide process (Wang et al., 1998; Rapson, 1997; Pangum and Browner, 1996; Zyryanov and Doshlov, 1995; Li et al., 1992; Linge and Welham, 1997; Yen and Pindred, 1989; Liu and Nicol, 2002).

As can be seen in Table 2.2, the gold chloride complexes are not as stable as the Au(I) cyanide complex but one advantage of this is that they are therefore more easily reduced to gold metal. The oxidation of gold in chloride media depends on the concentration of chloride and the temperature but only occurs at potentials above about 1.2 V. Therefore, a strong oxidant such as chlorine, chlorate, hypochlorite or ozone is required to dissolve gold at a reasonable rate. Nitric acid may also be used to achieve fast dissolution rates. Cyclic voltammetry for the oxidation of gold in chloride solutions has shown (Nicol, 1980a) that the anodic dissolution rate of gold is proportional to the chloride ion concentration. Furthermore, the rate of dissolution of gold by chlorination can be faster than that achievable in aqueous alkaline cyanide solutions because the solubility of oxidants such as chlorine can be greater than that of oxygen in aqueous solutions. Under the strong oxidizing conditions used during chlorination, other metals and/or sulfide minerals may also be appreciably oxidized, thus resulting in excessively high consumption of chlorine and poor economics of the process. Chlorination has been suggested for gold ores containing less than 0.5% sulfur (Von Michaelis, 1987).

Other halide systems, such as bromine-bromide and iodine-iodide, are capable of dissolving gold at very fast rates and have been studied by Dadger (1989) and Davis et al. (1993). These systems are strongly oxidizing and able to dissolve many sulfide minerals as the chlorine-chloride system. However, the commercial application of bromine and iodine for gold leaching is restricted by the high cost of the reagents, the
high cost of materials of construction to withstand the severe conditions and health risks associated with their use (Marsden and House, 1992).

### 2.1.3.3 Sulfide/Polysulfides

Sulfide or polysulfide ions as lixiviants for gold have been extensively studied and recently reviewed by Sparrow and Woodcock (1995) and Hiskey and Atluri (1988). This subject has received considerable attention by geochemists due to its proposed importance in the mobilization and transport of gold in the environment and in the presence of gold in valuable minerals (Weissberg, 1970; Seward, 1973; Renders and Seward, 1989; Shenberger and Barnes, 1989; Seward, 1993; Nekrasov, 1996). It is well known that elemental sulfur dissolves readily in alkali sulfide solutions forming a mixture of different alkali polysulfides, with HS\(^-\) being the predominant species and small fractions of S\(_n\)\(^{2-}\) species becoming evident at pH values greater than 13. The polysulfides may also be formed slowly by atmospheric oxidation of alkali sulfide solutions with the color of the solution changing from colorless to yellow (Adams, 1994).

As shown in Table 2.2, the Au(I) complexes with polysulfides are closest to cyanide in the relative order of stability, thus gold can readily dissolve into the polysulfide solutions at low potentials. Krauskopf (1951) has suggested the gold complex formed in sulfide solutions is AuS\(^-\), but now it is commonly accepted, after the work of Seward (1973), that the gold complex Au\(_2\)(HS)\(_2\)S\(_2\)\(^-\) is predominant in strongly alkaline solutions while the Au(HS)\(_2\)\(^-\) ion predominates in less alkaline solutions. The maximum solubility of gold is about 220ppm at neutral pH at 300 °C in 0.2 M NaHS solution (Seward, 1973). At ambient temperatures, about 10 ppm Au may dissolve (Tan and Bell,
Gold can also dissolve in aqueous solutions of ammonium polysulfides and its dissolution rate is dependent on the temperature and composition of the solution (Kakovskii and Tyurin, 1962; Yang et al., 1992).

Zhang et al. (1992a, b) used a lime sulfur synthetic solution (LSSS) to dissolve more than 90% of the gold from ores and concentrates at 25 °C with the aid of ammonia and cupric ions. The LSSS solution, containing polysulfides and thiosulfate, was synthesized from calcium hydroxide, elemental sulfur and other additives. Zhu et al. (1994b) also used a mixed thiosulfate/polysulfide solution to leach 90% of the gold from ores at 25 °C with addition of ammonia, cupric catalyst and oxygen under pressure. More recently, bio-catalyzed bisulfide leaching of gold from its ores has been reported by Hunter et al. (1996 and 1998). Fang and Han (2002) used in situ oxidation products of elemental sulfur in a lime slurry to leach about 86% gold from a sulfidic flotation concentrate in an autoclave with oxygen.

2.1.3.4 Other lixiviants

Thiourea is a relatively non-toxic, reactive organic reagent for the dissolution of heavy metals in addition to gold and silver, and thus has been proposed as an alternative to cyanide for the treatment of sulfidic, cyanide-consuming ores, or for use in locations where environmental concerns make the use of cyanide difficult (Marsden and House, 1992). Extensive studies on the dissolution of gold and silver with thiourea have been reviewed by Groenewald (1975), Hiskey and Atluri (1988), Von Michaelis (1987), Sparrow and Woodcock (1995) and recently by Zhang (1997).
The ability of thiocyanate to dissolve gold was first reported by White (1905). The leaching of gold with thiocyanate has been investigated subsequently by Fleming (1986) and more recently by Chen and Pang (1997) and Barbosa-Filho and Monhemius (1994a, b and c) who reported in detail the chemistry and kinetics of the dissolution of gold in thiocyanate aqueous solutions.

Ammonia as a lixiviant for gold has been studied by Han and Meng (1992), Meng and Han (1993) and Guan and Han (1996). Gold dissolves as the Au(I) di-ammine complex Au(NH$_3$)$_2^+$ in ammoniacal solutions. Meng and Han (1993) have reported that the kinetics of gold dissolution are negligibly slow at low temperatures and an acceptable rate of dissolution occurs at temperatures above 120 °C in the presence of an oxidant. Several oxidants such as oxygen, Cu(NH$_3$)$_4^{2+}$, Co(NH$_3$)$_4^{3+}$ and OCl$^-$, alone or in combination, have been tested for gold leaching, with the cupric ammine ions in conjunction with dissolved oxygen being the best of all the oxidants used.

Sulfurous acid as a lixiviant for gold recovery from refractory gold ores has also been reported (Touro and Wiewiorowski, 1992). Zhang et al. (1996) studied the solubility of gold in amino acid solutions at pH 6-8 and temperatures from 20-80 °C. Other leaching systems using organic lixiviants such as nitriles, cyanamide, cyanoform and CSUT(I) (an unpublished synthetic organic compound, Wang et al., 1993) for gold dissolution have been proposed. However, despite some potential advantages, there is little prospect for commercial development and they are at present of academic interest only (Marsden and House, 1992).
2.2 The Leaching of Gold with Thiosulfate

2.2.1 The Chemistry of Thiosulfate

2.2.1.1 Structure and use

Thiosulfate ($S_2O_3^{2-}$) is an anion formed by full deprotonation of the strong acid, thiosulfuric acid ($H_2S_2O_3$) which is one of many oxo-acids of sulfur:

$$H_2S_2O_3 = H^+ + HS_2O_3^- \quad \text{pKa}_1 = 0.3 \quad (2.21)$$

$$HS_2O_3^- = H^+ + S_2O_3^{2-} \quad \text{pKa}_2 = 1.7 \quad (2.22)$$

where pKa is the negative logarithm of the dissociation constant Ka. (Sullivan and Kohl, 1997). However, pure $H_2S_2O_3$ is too unstable to be isolated. In aqueous acidic solutions, it rapidly decomposes with deposition of sulfur and evolution of sulfur dioxide. A series of thiosulfuric salts is known most of which are stable even in solution (Remy, 1956). There are two commercially available salts of thiosulfate namely, sodium thiosulfate (also known as “hypo”), $Na_2S_2O_3 \cdot 5H_2O$ and ammonium thiosulfate, $(NH_4)_2S_2O_3$.

Thiosulfate ion has a structure comparable to that of the sulfate ion with one oxygen atom replaced by a sulfur atom, as illustrated by the following structures (Remy, 1956):

\[
\begin{array}{c}
\text{Thiosulfate ion} \\
\text{Band } S - S = 2.01 \text{ Å} \\
\text{Band } S - O = 1.47 \text{ Å}
\end{array}
\]

\[
\begin{array}{c}
\text{Sulfate ion} \\
\text{Band } S - S = 2.01 \text{ Å} \\
\text{Band } S - O = 1.47 \text{ Å}
\end{array}
\]
It is this sulfide-like sulfur atom that dominates the unique chemistry of thiosulfate which has reducing properties, strong complexing tendencies and sulfide forming capabilities (Hiskey and Atluri, 1988). Hence, thiosulfate is widely applied in a range of areas including chemistry, photography, paper industry, pharmaceuticals, nuclear industry, and medicine (Dhawale, 1993). Thiosulfate has a low toxicity with a LD$_{50}$ (dose needed to kill 50% of a population) of $7.5 \pm 0.752$ g kg$^{-1}$ for mice (Langhans et al., 1992). Ammonium thiosulfate has also been used as a fertilizer for soils low in sulfur for many decades. Therefore, thiosulfate is regarded as an environmentally friendly reagent (Aylmore and Muir, 2001; Dhawale, 1993).

### 2.2.1.2 Redox properties and stability

Sulfur is an active element and forms numerous compounds that exist over a range of oxidation states from $-2$ to 7 (Zhdanov, 1975). To illustrate the oxidation-reduction properties of thiosulfates, it is convenient to use the Eh-pH diagram for the metastable S-H$_2$O system as shown in Figure 2.2 (Peters, 1986; Osseo-Asare, 1989). This Eh-pH diagram does not include sulfate and bisulfate, as these are thermodynamically more stable than thiosulfate, tetrathionate, sulfite, hydrogen sulfite and sulfurous acid.

As can be seen in Figure 2.2, thiosulfate is located in a narrow elongated stability field in the neutral and alkaline pH region and is a metastable anion that tends to undergo chemical decomposition in aqueous solutions. It may undergo oxidation to sulfite (SO$_3^{2-}$), polythionates (S$_n$O$_6^{2-}$, $n = 2-5$) and sulfate (SO$_4^{2-}$), or reduction to elemental sulfur (S$^0$) and sulfide (S$^2$) depending on the potential and pH of the solutions. Thiosulfate acts mainly as a reducing agent because it is oxidized to tetrathionate (S$_4$O$_6^{2-}$) at pH values above about 4 due to the relatively low reduction potential of the tetrathionate to...
thiosulfate reaction ($E^\circ = 0.08$ V). Trithionate and pentathionate are thermodynamically less stable than either tetrathionate or thiosulfate, and do not appear on the Eh-pH diagram. Given time, all sulfur species will ultimately be oxidized to sulfate, the most stable and final degradation product. Some selected important redox reactions involving thiosulfate are given in Table 2.3.

![Eh-pH diagram for the metastable S-H₂O system at 25 °C. [S]= 1 M. The thermodynamically stable species (i.e. sulfate ions) are omitted from consideration to reveal the metastability domain of species such as thiosulfate, sulfite ($SO_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$).]
Table 2.3  Selected redox reactions involving thiosulfate

<table>
<thead>
<tr>
<th>Redox Reactions</th>
<th>$\Delta G^{o}_{298K}$* /kJ mol$^{-1}$</th>
<th>Ref.</th>
<th>Equation No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2S_2O_3^{2-} + I_3^- = S_4O_6^{2-} + 3I^-$</td>
<td>-88.0</td>
<td>a</td>
<td>(2.23)</td>
</tr>
<tr>
<td>$S_2O_3^{2-} + 4Cl_2 + 5H_2O = 2SO_4^{2-} + 8Cl^- + 10H^+$</td>
<td>-829.1</td>
<td>a</td>
<td>(2.24)</td>
</tr>
<tr>
<td>$2S_2O_3^{2-} + 2Cu^{2+} = S_4O_6^{2-} + 2Cu^+$</td>
<td>-14.1</td>
<td>a</td>
<td>(2.25)</td>
</tr>
<tr>
<td>$S_2O_3^{2-} + 2Fe^{3+} = S_4O_6^{2-} + 2Fe^{2+}$</td>
<td>-133.3</td>
<td>a</td>
<td>(2.26)</td>
</tr>
<tr>
<td>$2S_2O_3^{2-} + \frac{1}{2}O_2 + H_2O = S_4O_6^{2-} + 2OH^-$</td>
<td>-61.9</td>
<td>c</td>
<td>(2.27)</td>
</tr>
<tr>
<td>$3S_2O_3^{2-} + 2O_2 + H_2O = 2S_5O_6^{2-} + 2OH^-$</td>
<td>-437.2</td>
<td>c</td>
<td>(2.28)</td>
</tr>
<tr>
<td>$S_2O_3^{2-} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O</td>
<td>-887.8</td>
<td>c</td>
<td>(2.29)</td>
</tr>
<tr>
<td><strong>Reduction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_2O_3^{2-} + CN^- = SO_3^{2-} + CNS^-$</td>
<td>-44.0**</td>
<td>c</td>
<td>(2.30)</td>
</tr>
<tr>
<td>$S_2O_3^{2-} + AsO_3^{3-} = SO_3^{2-} + AsO_3S_3^{2-}$</td>
<td>?</td>
<td>f</td>
<td>(2.31)</td>
</tr>
<tr>
<td><strong>Dissociation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_3O_6^{2-} + H_2O = S_2O_3^{2-} + SO_4^{2-} + H_2O</td>
<td>-18.7</td>
<td>a</td>
<td>(2.32)</td>
</tr>
<tr>
<td>$S_2O_3^{2-} + 2OH^- = SO_4^{2-} + S^{2-} + H_2O</td>
<td>-53.8</td>
<td>a</td>
<td>(2.33)</td>
</tr>
<tr>
<td>$S_3O_6^{2-} + 2H_2O = S_2O_3^{2-} + SO_4^{2-} + 2H^+$</td>
<td>-65.5</td>
<td>d</td>
<td>(2.34)</td>
</tr>
<tr>
<td>$2S_5O_6^{2-} + 6OH^- = S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O</td>
<td>-313.3</td>
<td>d</td>
<td>(2.35)</td>
</tr>
<tr>
<td>$S_4O_6^{2-} + 2OH^- = S_2O_3^{2-} + SO_4^{2-} + S^{0} + H_2O</td>
<td>-161.2</td>
<td>c</td>
<td>(2.36)</td>
</tr>
<tr>
<td>$4S_2O_3^{2-} + 6OH^- = 5S_2O_3^{2-} + 3H_2O</td>
<td>-189.4</td>
<td>b</td>
<td>(2.37)</td>
</tr>
<tr>
<td>$2S_5O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 3H_2O</td>
<td>-449.7</td>
<td>b</td>
<td>(2.38)</td>
</tr>
<tr>
<td>$4SO_3^{2-} + 2S^{2-} + 3H_2O = 3S_2O_3^{2-} + 6OH^-</td>
<td>-29.5</td>
<td>e</td>
<td>(2.39)</td>
</tr>
<tr>
<td>$S_4O_6^{2-} + SO_3^{2-} + 2OH^- = 2S_2O_3^{2-} + SO_4^{2-} + H_2O</td>
<td>-194.3</td>
<td>e</td>
<td>(2.40)</td>
</tr>
<tr>
<td>$S_4O_6^{2-} + SO_3^{2-} = S_2O_3^{2-} + S_2O_6^{2-}$</td>
<td>31.0</td>
<td>b</td>
<td>(2.41)</td>
</tr>
<tr>
<td>$S_4O_6^{2-} + S_2O_3^{2-} = SO_3^{2-} + S_3O_6^{2-}$</td>
<td>99.1</td>
<td>b</td>
<td>(2.42)</td>
</tr>
</tbody>
</table>

a. from Tykodi, 1990;
b. from Byerley et al., 1975;
c. from Suzuki, 1999;
d. from Naito et al., 1975;
e. from Wan, 1997;
f. from Bailar et al., 1973;

* calculated using the thermodynamic data from Pourbaix (1974) except the $\Delta G^{o}_{298K}$ for $S_2O_3^{2-}$ which is calculated from the redox potential $E^o$ (0.08 V) for the $S_4O_6^{2-}/S_2O_3^{2-}$ couple.

** calculated using the $\Delta G^{o}_{298K}$ data from Hiskey and Atluri (1988).
Equations 2.32 and 2.33 show that thiosulfate has a tendency to disproportionate at low pH to sulfur and sulfur dioxide or in alkaline solutions to sulfide and sulfate. The decomposition of thiosulfate may also be promoted by the presence of certain bacteria and exposure to ultraviolet light (Suzuki, 1999; Tykodi, 1990; Dhawale, 1993). Thus, efforts have been made to stabilize the thiosulfate as suggested in Equations 2.39 and 2.40 in which the addition of sulfite may inhibit the decomposition of thiosulfate (Kerley, 1981; 1983). The use of sulfate in the stabilization of thiosulfate has been reported (Hu and Gong, 1991) but the mechanism is unclear.

Thiosulfate will also be quantitatively oxidized by iodine (Equation 2.23), which forms the basis of iodimetry in analytical chemistry. The reaction of thiosulfate with chlorine (Equation 2.24) is used in the paper industry (Tykodi, 1990), while the reactions shown in Equations 2.30 and 2.31 are employed for detoxification of cyanide and arsenic containing solutions (Dhawale, 1993). As indicated by Equation 2.26, ferric ions can also promote the oxidation of thiosulfate in near neutral solutions. This reaction takes place in two stages, with a deep violet complex anion \( \text{Fe(}S_2\text{O}_3\text{)}_2^- \) being formed almost immediately, followed by a slower decomposition of this intermediate anion (Tykodi, 1990).

The oxidation of thiosulfate by cupric ions deserves special attention because of the use of copper ions as a catalyst and oxidant in the ammoniacal thiosulfate leach process for gold and silver. As indicated by the Equation 2.25, the reaction of thiosulfate with cupric ions is thermodynamically favored. In addition, copper(II) has long been known to greatly accelerate the oxidation of thiosulfate by a variety of oxidizing agents in aqueous solutions (Rabai and Epstein, 1992). The kinetics of the reaction (Equation 2.25) has been studied in a pure aqueous solution without any additional complexing
agent by Rabai and Epstein (1992) who have found that the reaction is not immeasurably fast and proceeds in steps, with the extremely rapid formation of the yellow \( \text{Cu(S}_2\text{O}_3\text{)}_2^{2-} \) complex and then the rapid, but relatively slower (in seconds), redox reaction forming tetrathionate and the copper(I) thiosulfate complex. The respective reactions can be represented by the following equations:

\[
\text{Cu}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \text{Cu(S}_2\text{O}_3\text{)}_2^{2-} \quad (2.43)
\]

\[
2\text{Cu(S}_2\text{O}_3\text{)}_2^{2-} = 2\text{CuS}_2\text{O}_3^{3-} + \text{S}_4\text{O}_6^{2-} \quad (2.44)
\]

The Cu(I) ions are stabilized by the excess thiosulfate in the form of the mono- or di-thiosulfato complexes (\( \text{Cu(S}_2\text{O}_3\text{)}_2^{3-} \) or \( \text{CuS}_2\text{O}_3^{3-} \)), most likely the \( \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} \) complex (see Table 2.4 in the following Section 2.2.1.3). When the thiosulfate is insufficient, the fast redox reaction is followed by slower side reactions that result in the formation of copper sulfide and sulfate (Rabai and Epstein, 1992):

\[
2\text{Cu}^{2+} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} = \text{Cu}_2\text{S} + \text{SO}_4^{2-} + 2\text{H}^+ 
\]  (2.45)

In alkaline ammoniacal solutions, however, the oxidation of thiosulfate by Cu(II) is much slower and the rate is inversely dependent on the concentration of ammonia (Byerley et al., 1973). Copper(II) ions, predominantly as the cupric tetra-ammine complex, \( \text{Cu(NH}_3\text{)}_4^{2+} \), oxidize thiosulfate initially to tetrathionate (Equation 2.25); the latter then undergoes a subsequent disproportionation reaction to yield trithionate and thiosulfate (Equation 2.37). The mechanism has been suggested to involve the formation of an intermediate \( \text{Cu(NH}_3\text{)}_3\text{S}_2\text{O}_3 \) complex which gives rise to copper(I) ions and the \( \text{S}_2\text{O}_3^{3-} \) radical, the latter dimerizing to tetrathionate ions. Therefore, Equation 2.25 is best described as follows in ammoniacal solutions (Abbruzzese et al., 1995; Wan, 1997):

\[
2\text{Cu(NH}_3\text{)}_4^{2+} + 8\text{S}_2\text{O}_3^{2-} = 2\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + \text{S}_4\text{O}_6^{2-} + 8\text{NH}_3 
\]  (2.46)
The Cu(S₂O₃)₃⁵⁻ complex is the most stable copper(I) species. If the ammoniacal solution is exposed to oxygen, the Cu(NH₃)₄²⁺ ions will be rapidly reformed by oxidation of copper(I) ions with oxygen as described in following equation:

\[
2\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 8\text{NH}_3 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{Cu(NH}_3\text{)}_4^{2+} + 6\text{S}_2\text{O}_3^{2-} + 2\text{OH}^- \tag{2.47}
\]

The mechanism of this re-oxidation has been suggested to occur via the intermediate formation of the amminethiosulfatocopper(II) species associated with axially coordinated dioxygen, with the following structures (Byerley et al., 1975; Breuer and Jeffrey, 2003):

![Structure Image]

Alternatively, ammonium sulfamate and ammonium sulfate have been reported to be the chief products of oxidation of thiosulfate by oxygen in high ammonia concentrations with copper (Naito et al., 1970). The oxidation of thiosulfate in aqueous solutions by molecular oxygen (Equations 2.27-2.29) under normal pressures and temperatures is very slow (Dhawale, 1993). Thus, the concentration of cupric ions is an important factor in determining the stability of thiosulfate and the management of the reagent suite. Increasing temperature and hydroxyl ion concentration will also promote the oxidation of thiosulfate to sulfate by oxygen in alkaline solutions (Rolia and Chakrabarti, 1982). In addition, the presence of sulfide minerals such as pyrite may catalyze the oxidation of thiosulfate by dissolved oxygen in aqueous solutions (Xu and Schoonen, 1995).
2.2.1.3 Metal complexation

Thiosulfate forms strong complex ions with a variety of metals including gold, silver, copper, iron, cadmium, nickel, cobalt, platinum and mercury (Hiskey and Atluri, 1988; Tykodi, 1990). Several of the relevant metal complexes of thiosulfate and their stability constants are listed in Table 2.4.

Table 2.4 Stability constants for selected metal thiosulfate complexes at 25 °C.

<table>
<thead>
<tr>
<th>Complex formation</th>
<th>log K</th>
<th>Ionic strength</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}^+ + 2\text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3)_2^{3-}$</td>
<td>26</td>
<td>dilute</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Au}^+ + \text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3)^-$</td>
<td>10.4</td>
<td>-</td>
<td>d</td>
</tr>
<tr>
<td>$\text{Ag}^+ + \text{S}_2\text{O}_3^{2-} = \text{Ag(S}_2\text{O}_3)^-$</td>
<td>9.2</td>
<td>1</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Ag}^+ + 2\text{S}_2\text{O}_3^{2-} = \text{Ag(S}_2\text{O}_3)_2^{3-}$</td>
<td>12.5</td>
<td>1</td>
<td>b</td>
</tr>
<tr>
<td>$\text{Ag}^+ + 3\text{S}_2\text{O}_3^{2-} = \text{Ag(S}_2\text{O}_3)_3^{5-}$</td>
<td>12.8</td>
<td>1</td>
<td>a</td>
</tr>
<tr>
<td>$2\text{Ag}^+ + 3\text{S}_2\text{O}_3^{2-} = \text{Ag}_2\text{(S}_2\text{O}_3)_3^{4-}$</td>
<td>24.5</td>
<td>1</td>
<td>b</td>
</tr>
<tr>
<td>$2\text{Ag}^+ + 4\text{S}_2\text{O}_3^{2-} = \text{Ag}_2\text{(S}_2\text{O}_3)_4^{6-}$</td>
<td>26.3</td>
<td>4</td>
<td>a</td>
</tr>
<tr>
<td>$3\text{Ag}^+ + 4\text{S}_2\text{O}_3^{2-} = \text{Ag}_3\text{(S}_2\text{O}_3)_4^{5-}$</td>
<td>38.2</td>
<td>1</td>
<td>b</td>
</tr>
<tr>
<td>$3\text{Ag}^+ + 5\text{S}_2\text{O}_3^{2-} = \text{Ag}_3\text{(S}_2\text{O}_3)_5^{7-}$</td>
<td>39.8</td>
<td>4</td>
<td>a</td>
</tr>
<tr>
<td>$6\text{Ag}^+ + 8\text{S}_2\text{O}_3^{2-} = \text{Ag}_6\text{(S}_2\text{O}_3)_8^{10-}$</td>
<td>78.6</td>
<td>4</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Cu}^+ + \text{S}_2\text{O}_3^{2-} = \text{Cu(S}_2\text{O}_3)^-$</td>
<td>10.4</td>
<td>1.6</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Cu}^+ + 2\text{S}_2\text{O}_3^{2-} = \text{Cu(S}_2\text{O}_3)_2^{3-}$</td>
<td>12.3</td>
<td>1.6</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Cu}^+ + 3\text{S}_2\text{O}_3^{2-} = \text{Cu(S}_2\text{O}_3)_3^{5-}$</td>
<td>13.7</td>
<td>1.6</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2\text{S}_2\text{O}_3^{2-} = \text{Cu(S}_2\text{O}_3)_2^{2-}$</td>
<td>4.6</td>
<td>0.2</td>
<td>c</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} + \text{S}_2\text{O}_3^{2-} = \text{Fe(S}_2\text{O}_3)^+$</td>
<td>1.98</td>
<td>0.1</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Pd}^{2+} + 4\text{S}_2\text{O}_3^{2-} = \text{Pd(S}_2\text{O}_3)_4^{6-}$</td>
<td>35.0</td>
<td>0.3</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Hg}^{2+} + 3\text{S}_2\text{O}_3^{2-} = \text{Hg(S}_2\text{O}_3)_3^{4-}$</td>
<td>33.3</td>
<td>1</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 3\text{S}_2\text{O}_3^{2-} = \text{Cd(S}_2\text{O}_3)_3^{4-}$</td>
<td>6.4</td>
<td>1</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Pb}^{2+} + 3\text{S}_2\text{O}_3^{2-} = \text{Pb(S}_2\text{O}_3)_3^{4-}$</td>
<td>6.2</td>
<td>3</td>
<td>a</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 3\text{S}_2\text{O}_3^{2-} = \text{Zn(S}_2\text{O}_3)_3^{4-}$</td>
<td>3.3</td>
<td>3</td>
<td>a</td>
</tr>
</tbody>
</table>

a. from Smith and Martell (1976);
b. from Hogfeldt (1982);
c. from Rabai and Epstein (1992);
d. from Webster (1986).
These complexes are formed by coordination through the sulfide-like sulfur atom in the thiosulfate molecule. There are two complexes of gold with thiosulfate, i.e. \( \text{Au(S}_2\text{O}_3\text{)}_2^{3-} \) and \( \text{Au(S}_2\text{O}_3\text{)}^{-} \) with the former being more stable. Silver forms stable complex ions which is why thiosulfate is used as a fixing agent in photography. Either Cu(I) or Cu(II) may form complexes with thiosulfate but the Cu(I) complexes are much more stable in aqueous solutions, with the \( \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} \) complex being most stable. Fe(III) complexes with thiosulfate are unstable and are suggested as intermediates during the oxidation of thiosulfate by Fe(III) (Tykodi, 1990; Sillen and Martell, 1964). The complexation of Fe(II) by thiosulfate is weak and generally not considered. Other transition metals have also been reported to form complexes with thiosulfate, with \( \text{Hg(S}_2\text{O}_3\text{)}_3^{4-} \), \( \text{Pd(S}_2\text{O}_3\text{)}_4^{6-} \) and \( \text{Tl(S}_2\text{O}_3\text{)}_4^{5-} \) being very stable (Sillen and Martell, 1964; Martell and Smith, 1982). Of importance to this study are the gold and copper complexes which are involved in the thiosulfate leach process for gold.

### 2.2.1.4 Generation of thiosulfate

Thiosulfate can be commercially generated by boiling aqueous solutions of sulfite with an excess of elemental sulfur (Equation 2.48). Of technical importance for the preparation of thiosulfate also is the partial oxidation of polysulfides \( \text{S}_n^{2-} \) by air (Equation 2.49, \( n = 2, 3, 4, \ldots \)), with full oxidation forming sulfate (Bailar et al., 1973). Thiosulfate can also be prepared by the oxidation of a mixture of sulfides and sulfites with iodine (Equation 2.50), by dissolving elemental sulfur in strong alkali solutions (Equation 2.51; Tykodi, 1990; Pryor, 1960) or weak alkali (\( \text{NH}_4\text{OH} \) or \( \text{Ca(OH)}_2 \) slurries) solutions (Equation 2.52; Peters, 1976). Under anhydrous conditions thiosulfuric acid may be produced (see Equation 2.53; Bailar et al., 1973; Cotton and Wilkinson, 1988). Kerley (1983) described a method of generating thiosulfate by Equation 2.54:
Thiosulfates and other metastable sulfur species have been known to be intermediate products in the inorganic and bacterial oxidation of sulfide minerals and of great relevance to the mobilization of gold in geological environments (Lakin et al., 1974; Peters, 1976; Rolia and Tan, 1985; Webster, 1986; Lulham, 1989).

2.2.1.5 Determination of thiosulfate

The best known method for the determination of thiosulfate is the iodimetric titration, which is based on the quantitative oxidation of thiosulfate by iodine (Equation 2.23) and widely finds application in the titrimetric determination of oxidizing agents (Vogel, 1962). Soluble starch is used to give a better determination of the end point or alternatively the end point can be determined potentiometrically or amperometrically.

A comprehensive review of methods used to determine thiosulfate and other sulfur species in solution has been made (Szekeres, 1974; Williams, 1979). Recently, chromatographic and electrophoretic analytical techniques with particular emphasis on ion chromatographic methods have been reviewed by O’Reilly et al. (2001) for the separation of inorganic sulfur species in aqueous matrices. As thiosulfate ions are
Chapter 2 Review of the Literature

metastable in aqueous solutions, aqueous samples from metallurgical processes often contain various sulfur ions including thiosulfate. For the determination of individual sulfur species, normal wet chemical analytical techniques including titrimetric iodimetry and gravimetry suffer problems because they are time-consuming and generally only applicable to the determination of one analyte ion at a time. Ion chromatography can be used to detect a range of sulfur ions in a single analysis with good reproducibility and detection limits down to 10 $\mu$M in concentration and is widely used for this purpose. Most researchers use anion exchange columns with a mixture of acetonitrile and/or sodium carbonate as the mobile phase to selectively separate sulfur species. A broad range of detection techniques has been used in conjunction with the ion chromatography methods, with by far the most popular being UV spectrophotometry and conductivity. Normally, ion chromatography techniques can take up to thirty minutes per sample to analyze all the species in solution (Steudel and Holdt, 1986; Barkley et al., 1993; Weir et al., 1994; Zou et al., 1993; Miura et al., 1997).

2.2.2 The Electrochemistry of Gold in the Presence of Thiosulfate

The study of the behaviour of gold in thiosulfate solutions is complicated by the reactivity of thiosulfate itself to oxidation and this aspect will therefore initially be briefly reviewed.

2.2.2.1 Electrochemical oxidation of thiosulfate

Few studies have dealt with the electrochemical oxidation of thiosulfate ions on platinum electrodes (Zhdanov, 1975). Glasstone and Hickling (1932) have examined the anodic oxidation of thiosulfate to tetrathionate and sulfate, and obtained tetrathionate in
the highest yield at a platinum electrode in slightly acid or neutral solutions (pH = 5-7) at a relatively high current density (0.2 A cm\(^{-2}\)). They have proposed that the thiosulfate is oxidized by H\(_2\)O\(_2\) produced at the anode, and not via a direct electrochemical process involving the discharge of thiosulfate ions. Similarly, Klemenc (1939) has argued that thiosulfate is oxidized to tetrathionate by free hydroxyl radicals created at the anode during the discharge of the OH\(^-\) ions. Voltammetric studies on a rotating platinum wire electrode suggest that in neutral solution, thiosulfate is firstly oxidized to tetrathionate which in turn is oxidized to dithionate through an electrochemical mechanism involving molecular oxygen (Kuzmina and Songina, 1963). More recently, Loucka (1998) has reported that in acidic thiosulfate solutions the platinum electrode is covered by sulfur layers which can subsequently be oxidized to soluble sulfate.

Pedraza et al. (1988) first reported the oxidation of thiosulfate on gold in neutral solutions in the double layer region where the gold is free of oxide layers. They have found that thiosulfate ions decompose when in contact with gold at open circuit, leaving a film of at least three sulfur-containing species tightly bound to the surface. A layer of sulfur builds up during the anodic oxidation of thiosulfate, which eventually blocks the surface of the gold electrode. However, the authors ignored the fact that gold might have dissolved at the same time as thiosulfate oxidized because gold is not inert in thiosulfate solutions. Recently, Zhuchkov and Bubeev (1994) studied the electrochemical oxidation of thiosulfate ions in order to determine the dissolution kinetics of gold based on current efficiency measurements. They have found that the current efficiency is strongly dependent on the anodic polarization and cannot be used alone for reliable determination of the dissolution rate of gold in thiosulfate solutions.
2.2.2.2 Electrochemical oxidation of gold

White (1905) first studied the direct oxidative dissolution of gold metal in an alkaline or near neutral solution of thiosulfate. This has been followed by several studies associated with the use of thiosulfate for gold leaching, and the role of thiosulfate in the mobilization of gold in geological environments (Kakovskii, 1957; Tyurin and Kakovskii, 1960; Panchenko and Lodeishchikov 1971; Umetsu and Tozawa 1972; Berezowsky et al., 1978; Kerley, 1981). The redox reaction for gold oxidation in thiosulfate media is known to be

\[
\text{Au(S}_2\text{O}_3)_2^{3-} + e^- = \text{Au} + 2\text{S}_2\text{O}_3^{2-}
\]  

(2.55)

with a standard reduction potential of \( E^\circ = 0.153 \) V at 25 °C (Schmid and Curley-Fiorino, 1975; Pouradier and Gadet, 1969; Sullivan and Kohl, 1997).

The electrochemical oxidation of gold in thiosulfate solutions has been studied by several researchers (Zhuchkov and Bubeev, 1990; Jiang et al., 1993a; Zhu et al., 1994a; Chen et al., 1996; Breuer and Jeffrey, 2002). Jiang et al. (1993a) have found that there are two current peaks in the steady-state anodic polarization curve for gold in thiosulfate solutions, as shown in Figure 2.3. They suggested that the smaller current peak I (at a potential of about 0.05 V vs. SCE) corresponds to the dissolution of gold while the current peak II (about 0.62 V vs. SCE) is associated with the anodic oxidation of thiosulfate ions. However, they did not provide practical evidence for the dissolution of gold.
The studies by Zhu et al. (1994a) have produced similar results using anodic voltammetry. In solutions of low concentration of thiosulfate (0.1 M) the anodic current is extremely low suggesting that the dissolution rate of gold in thiosulfate alone solutions is very slow. The same authors have established by the use of electrochemical impedance spectroscopy (EIS) that the anodic voltammetric response of a gold electrode in thiosulfate solutions includes reactions other than the dissolution of gold such as the oxidation of thiosulfate and the formation of passivating films of elemental sulfur on the surface of the gold electrode.

Zhuchkov and Bubeev (1990) focused on the current peak II in Figure 2.3 during their study on the mechanism of gold dissolution in thiosulfate media at 20 °C. They proposed that the dissolution of gold at higher potentials could be limited by the rate of
chemical dissolution of a passive surface film, which was suggested as being a hydrated auric oxide. Their study shows that increasing the pH value of the solution lowers the maximum anodic current while the rest potential becomes more positive. Although the activation energy for the dissolution of gold was measured by the authors, the use of the total anodic current as the dissolution rate of gold without considering the simultaneous oxidation of thiosulfate makes this data questionable.

Ammonia has been found to increase the anodic peak currents of gold in thiosulfate solutions in the absence of copper ions (Jiang et al., 1993a; Zhu et al., 1994a; Breuer and Jeffrey, 2002) and is more effective than ammonium ions for the oxidation of gold. Zhu et al. (1994a) suggested that ammonia prevents the passivation of the gold electrode with sulfur films by being adsorbed on gold surface to form the aurous di-ammine complex $\text{Au(NH}_3\text{)}_2^+$. The latter reacts with thiosulfate ions in the solution to form the aurous di-thiosulfate complex, $\text{Au(S}_2\text{O}_3\text{)}_2^{3-}$ as shown in Figure 2.4. In the presence of copper ions which have long been known to catalyze the oxidative dissolution of gold in thiosulfate solutions (Tyurin and Kakovskii, 1960; Umetsu and Tozawa, 1972; Von Michaelis, 1987), another important role of ammonia is to stabilize copper(II) ions as the cupric tetra-ammine complex, $\text{Cu(NH}_3\text{)}_4^{2+}$ for the oxidation of metallic gold to aurous ions (Byerley et al., 1973; Breuer and Jeffrey, 2002). Thus, based on their detailed studies for gold-copper-thiosulfate-ammonia system, Jiang et al. (1993a) proposed an electrochemical mechanism for the copper catalyzed leaching of gold with ammoniacal thiosulfate as displayed in Figure 2.4. The anodic oxidative reaction of gold is coupled to a cathodic process in which the cupric tetra-ammine complex ($\text{Cu(NH}_3\text{)}_4^{2+}$) is reduced to cuprous di-ammine complex ($\text{Cu(NH}_3\text{)}_2^+$), which is in turn re-oxidized by oxygen to the cupric tetra-ammine complex to complete the copper cycle.
However, the available data in the literature do not support this mechanism. For example, the standard reduction potential for the \( \text{Au(NH}_3\text{)}_2^+/\text{Au} \) couple is high (\( E^o = 0.57 \) V) (see Table 2.2 in Section 2.1.2; Guan and Han, 1995), and the kinetics of the oxidative dissolution of gold in ammoniacal solutions is extremely slow at ambient temperatures and measurable gold dissolution occurs only at temperatures greater than 120 °C (Meng and Han, 1993; Guan and Han, 1996). Measurements in thiosulfate solutions have shown that the rest potential of gold varies with the thiosulfate concentration instead of the ammonia concentration, suggesting that the predominant gold species in thiosulfate solutions is a gold thiosulfate species (Wan, 1997). Thus, Aylmore and Muir (2001) have proposed a revised electrochemical mechanism, in which gold reacts with thiosulfate to form \( \text{Au(S}_2\text{O}_3\text{)}_2^{3-} \) complex ions.
2.2.3 Leaching of Gold with Ammoniacal Thiosulfate Solutions

2.2.3.1 Thermodynamics of gold leaching

The Eh-pH diagram is a convenient way to illustrate the thermodynamics of hydrometallurgical leaching processes. However, its use requires a good understanding of the chemistry of the leaching system. It is known that the dissolution of gold in aqueous thiosulfate solutions with dissolved oxygen as an oxidant is very slow and the overall reaction can be illustrated as follows:

\[ 4\text{Au} + \text{O}_2 + 8\text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O} = 4\text{Au(S}_2\text{O}_3)_2^{3-} + 4\text{OH}^- \]  

(2.56)

For leaching of gold to occur at a reasonable rate, thiosulfate, ammonia and copper(II) must be present in solution which complicates the leaching process (Umetsu and Tozawa, 1972; Abbruzzese et al., 1995; Wan, 1997; Jeffrey, 2001).

An Eh-pH diagram for the gold-thiosulfate-ammonia-water system has been constructed showing the regions of stability of two main soluble gold complexes, namely the di-ammine (\(\text{Au(NH}_3)_2^{+}\)) and the di-thiosulfate complexes (\(\text{Au(S}_2\text{O}_3)_2^{3-}\)) as displayed in Figure 2.5 (Wan, 1997; Aylmore and Muir, 2001; Zipperian et al., 1988). Construction of this Eh-pH diagram was based on a stability constant for the aurous di-ammine complex ion of \(\beta_2 = 10^{26}\) which is of a very similar magnitude as that of the aurous di-thiosulfate complex (see Table 2.2 in Section 2.1.2).
Figure 2.5  Eh-pH diagram for Au-NH₃-S-H₂O system at 25 °C (0.05 mM Au, 0.1 M S₂O₃²⁻, 0.1 M NH₃/NH₄⁺) (after Wan, 1997).

Figure 2.6  Eh-pH diagram for Au(0)-Au(I)-Au(III)-NH₃-S₂O₃²⁻-H₂O system at 25 °C; [Au(I)]= 10⁻⁵ M, [Na₂S₂O₃]= 0.1 M, [NH₃+NH₄⁺]= 1 M. (after Senanayake et al., 2003).
However, recent reviews of this data and recalculation for the stability constants have shown that the stability constant for the di-ammine complex has been overestimated by several orders of magnitude, being about $10^{19}$ (see Table 2.2 in Section 2.1.2; Skibsted and Bjerrum, 1977; Guan and Han, 1995) or about $10^{13}$ (Senanayake et al., 2003). Therefore, the area of stability of the di-ammine complex of gold shown in Figure 2.5 should be much reduced and the di-thiosulfate complex exists over the whole pH range under alkaline conditions. Thus, Senanayake et al. (2003) recently constructed a new Eh-pH diagram shown in Figure 2.6 indicating that the Au(S$_2$O$_3$)$_2$$^{3-}$ is the predominant species over the entire range, particularly in the range of pH 9-11 and Eh 0 to 0.2 V which are likely to be encountered in a gold leaching circuit using the thiosulfate-ammonia system.

As shown above, ammoniacal thiosulfate solutions containing copper ions are very complex with many species present. An Eh-pH diagram for the copper-ammonia-thiosulfate-water system has been established by Wan (1997) as shown in Figure 2.7. Metallic copper is not stable in ammoniacal thiosulfate solutions. Various copper oxides, sulfides and other species may form depending on the potential and pH of the solution. In the presence of ammonia, copper(II) ions exist in the form of Cu(NH$_3$)$_4$$^{2+}$ in a narrow stability region while copper(I) ions are mainly present as Cu(S$_2$O$_3$)$_3$$^{5-}$. Oxygen can oxidize Cu(S$_2$O$_3$)$_3$$^{5-}$ to Cu(NH$_3$)$_4$$^{2+}$ (see Equation 2.47) which in turn oxidizes metallic gold to aurous ion as follows:

$$\text{Au} + \text{Cu(NH}_3)_4^{2+} + 5\text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3)_2^{3-} + \text{Cu(S}_2\text{O}_3)_3^{5-} + 4\text{NH}_3 \quad (2.57)$$

In addition, some thiosulfate degradation to tetrathionate occurs according to the simplified overall reaction shown in Equation 2.58 (Breuer and Jeffreys, 2000):

$$2\text{Cu(NH}_3)_4^{2+} + 8\text{S}_2\text{O}_3^{2-} = 2\text{Cu(S}_2\text{O}_3)_3^{5-} + 8\text{NH}_3 + \text{S}_4\text{O}_6^{2-} \quad (2.58)$$
Therefore, for efficient leaching of gold it is very important to maintain an optimum concentration of the cupric tetra-amine ion in the system by controlling the pH of the solution, the concentrations of ammonia and thiosulfate (Zipperian et al., 1988).

![Eh-pH diagram for Cu-NH₃-S-H₂O system at 25 °C (0.5 mM Cu, 0.1 M S₂O₃²⁻, 0.1 M NH₃/NH₄⁺) (after Wan, 1997).](image)

**Figure 2.7** Eh-pH diagram for Cu-NH₃-S-H₂O system at 25 °C (0.5 mM Cu, 0.1 M S₂O₃²⁻, 0.1 M NH₃/NH₄⁺) (after Wan, 1997).

### 2.2.3.2 Kinetics of the Leaching of Gold

As early as the 1880’s, the recovery of gold and silver proposed by Russell and the Von Patera process made use of thiosulfate (Von Michaelis, 1987). Copper was found to enhance the leaching of gold. However, it was not until the late 1970s that the work on the leaching of gold with thiosulfate was revived by Berezowsky and Sefton (1979) who proposed the use of ammonium thiosulfate and oxygen under pressure to recover gold, and by Kerley (1981, 1983) who developed a patented process using copper ions and sulfites to improve the leaching of gold in ammoniacal thiosulfate solutions. In recent years due to the environmental constraints on the use of cyanide,
extensive studies on the kinetics and mechanism of gold dissolution with thiosulfate have been carried out in order to understand and improve the atmospheric ammoniacal thiosulfate leach process (Hiskey and Atluri, 1988; Barbosa-Filho et al., 1995; Sparrow and Woodcock, 1995; Wan, 1997; Breuer and Jeffrey, 2000; Jeffrey et al., 2001). A comprehensive review on the fundamental chemistry and extractive processes of gold and silver in alkaline thiosulfate solutions has been published by Aylmore and Muir (2001). In the following sections of this review, some factors affecting the kinetics, efficiency and economics of the thiosulfate leaching processes are outlined.

1) Effect of Oxidants  Since thiosulfate is readily oxidized and disproportionates in acidic solutions, the process is required to be conducted in alkaline solutions for which the number of potential oxidants is limited. The most economic oxidant is molecular oxygen in air but it has been proven to be less effective under ambient conditions due to its limited solubility in aqueous solutions and the slow reduction of oxygen at the gold surface in the absence of copper (Webster, 1986; Jiang et al., 1993a). Thus, Berezowsky and Sefton (1979) promoted the use of oxygen under pressure to leach gold using ammonium thiosulfate. However, other work has not confirmed the beneficial effect of pressure alone (Hemmati et al., 1989; Langhans et al., 1992), while the oxidative degradation of thiosulfate is increased by the use of excessive oxygen (Byerley et al., 1973). Hence there should only be sufficient oxygen to convert the copper (I) to copper(II) for further gold leaching. Hydrogen peroxide and ozone oxidize thiosulfate rapidly thus increasing the consumption of thiosulfate (Naito et al., 1970). The dissolution of gold by thiosulfate using oxygen generated electrochemically has been reported by Panayotov et al. (1994).
2) Effect of Copper  Copper ions are effective catalytic agents for the dissolution of gold with thiosulfate as previously discussed. It is known that a freshly prepared solution of sodium cuprous thiosulfate can be used to extract silver but not gold from sulfide ores, which is attributed to the greater reactivity of cuprous ions for oxygen (Mellor, 1929; Flett et al., 1983). Copper ions also catalyze the oxidation of thiosulfate by oxygen or other oxidants. Consequently there should only be sufficient copper present to maximize leaching of gold and minimize thiosulfate consumption. It has been found that the initial rate of gold extraction but not the ultimate extraction is enhanced by increasing the copper(II) concentration (Abbruzzese et al., 1995; Zipperian et al., 1988). On the other hand, Jeffrey (2001) has reported that the leaching rate of gold (of $10^{-5}$ mol m$^{-2}$ s$^{-1}$ magnitude) increases linearly with copper concentration at low concentrations of less than 5 mM while at higher copper concentrations the rate of dissolution becomes almost independent of copper concentration. Such results are consistent with that of Langhans et al. (1992). Jeffrey (2001) suggested that the leaching rate of gold is limited by diffusion of copper(II) to the surface of gold at low concentrations of copper but at high copper concentrations the reaction is chemically controlled.

3) Effect of Thiosulfate Concentration  Since the stability of gold complexes with thiosulfate depends upon the concentration of thiosulfate in solution, increasing the thiosulfate concentration is expected to increase the recovery of gold. Many investigators have found the positive role of thiosulfate concentration (up to 2 M) in increasing the leaching rate of gold in ammoniacal solutions (Tozawa et al., 1981; Zipperian et al., 1988; Hemmati et al., 1989; Abbruzzese et al., 1995; Langhans et al., 1992; Breuer and Jeffrey, 2000). However, the concentration of thiosulfate has to be controlled by maintaining the appropriate concentration ratio of ammonia to thiosulfate in solution so that copper can play the catalytic role involving the facile transfer between the cupric and
cuprous states (see Section 2.2.1.2). In some cases, excess thiosulfate may result in a negative effect on the leaching of gold. In addition, higher thiosulfate concentrations increase thiosulfate consumption, which cause an increase in the concentrations of degradation products such as sulfate, trithionate and tetrathionate (Byerley et al., 1973 and 1975; Cao et al., 1992). Therefore, it is important to use an optimum thiosulfate concentration. Sulfite ions at a concentration of at least 0.05% have been used to stabilize thiosulfate by preventing the formation of any free sulfide ion and the precipitation of gold or silver from solution (Kerley, 1983).

4) Effect of Ammonia Concentration Ammonia is important in the leaching of gold in thiosulfate solutions. In the absence of copper, ammonia has been suggested to promote the leaching of gold by eliminating a passivating film of sulfur resulting from the decomposition of thiosulfate (Jiang et al., 1993a; Chen et al., 1996). In the presence of copper, ammonia stabilizes copper in the cupric state for the oxidation of gold. Therefore, changing the ammonia concentration influences the stability of the copper(II) complexes, alters the potential of the copper(II)-copper(I) redox couple and in turn affects the dissolution rate of gold in thiosulfate solutions (Wan, 1997). This might explain why there have been diverse reported effects of ammonia on the kinetics of leaching of gold in thiosulfate media. For example, it has been reported that increasing ammonia concentration increases the ultimate gold recovery, while lower gold recoveries are obtained when the ammonia concentration is higher than 4 M (Abbruzzese et al., 1995; Langhans et al., 1992; Hemmati et al., 1989). Jeffrey (2001) has reported that the leaching rate of gold decreases with the increase in the concentration of ammonia whereas Langhans et al. (1992) reported no effect of ammonia concentration on gold extraction from a low-grade gold ores. At high concentrations of ammonia and high pH, some solid copper species such as CuO, Cu$_2$O and (NH$_4$)$_5$Cu(S$_2$O$_3$)$_3$ may form, possibly
hindering gold dissolution by coating the gold ore particles (Abbruzzese et al., 1995; Flett et al., 1983; Chen et al., 1996).

5) **Effect of Temperature** Temperature has a significant effect on the rate of gold dissolution in thiosulfate leach solutions. The leaching rate of gold has been reported to increase with temperature in the range of 25 to 60 °C (Breuer and Jeffrey, 2000; Cao et al., 1992; Tozawa et al., 1981; Flett et al., 1983; Zipperian et al., 1988). In contrast, Abbruzzese et al. (1995) have observed in their studies that temperature has a negative effect on the dissolution of gold, which was ascribed to the passivation by cupric sulfide formed on the surface of gold and to loss of thiosulfate due to decomposition. Gold dissolution decreases between 65-100 °C and increases once again between 100-140 °C. Above 140 °C, the oxidation of thiosulfate is extremely rapid resulting in a decrease in gold dissolution (Tozawa et al., 1981). High temperatures will also cause the loss of ammonia in solution to the atmosphere by volatilization (Kerley, 1981). In order to maintain the ammonia concentration it may be necessary to leach at ambient temperatures in a sealed reactor at an appropriate pH. An apparent activation energy of the leaching of gold in ammoniacal thiosulfate solutions has been found of about 60 kJ mol⁻¹, suggesting that the rate of the reaction is chemically controlled (Kim and Sohn, 1990; Breuer and Jeffrey, 2000).

6) **Effect of pH** Alkaline conditions must be used to prevent the decomposition of thiosulfate at low pH. Furthermore, in order to prevent the solubilization of some impurities such as iron, manganese, nickel and cobalt, the pH of the solution should not be greater than 10 (Perez and Galaviz, 1987; Niinae et al., 1996). Hemmati et al. (1989) showed that the gold recovery generally increased with increasing pH over the pH range of 9 to 10.5, while Breuer and Jeffrey (2000), Jiang et al. (1993b) and Yen et al. (1999)
reported a slight decrease in leaching of gold at pH values greater than 10.5. It appears that a pH of about 10 is appropriate for the dissolution of gold with thiosulfate.

7) Comparison with Cyanidation A number of comparative studies on the leaching of gold in alkaline ammoniacal thiosulfate solutions and cyanide solutions have been conducted (Hemmati et al., 1989; Langhans et al., 1992; Jeffrey et al., 2001). Two apparent advantages of the ammoniacal thiosulfate leach system over cyanidation are its non-toxicity and the higher initial leaching rate for gold. Jeffrey et al. (2001) have measured the dissolution rate of pure gold in both media using a rotating electrochemical quartz crystal microbalance and found that the reaction rate ($4 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$) is substantially higher in freshly prepared ammoniacal thiosulfate solution containing copper(II) than in cyanide solution ($1 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$), although the leach rate decreases as the copper(II) reacts with thiosulfate. Extensive studies have been conducted on pure gold (Tozawa et al., 1981; Barbosa-Filho et al., 1995; Breuer and Jeffrey, 2000), copper sulfide concentrates (Berezowsky and Sefton, 1979; Cao et al., 1992; Yen et al., 1999), manganese ores (Kerley, 1981 and 1983; Zipperian et al., 1988; Hu and Gong, 1991), silver sulfides (Flett et al., 1983), oxidized ores (Langhans et al., 1992; Abbruzzese et al., 1995; Kim and Sohn, 1990) and carbonaceous gold ores (Hemmati et al., 1989; Wan and Brierley, 1997; Wan, 1997; Schmitz et al., 2001). Most of these studies have shown that 80% of gold can be extracted within 1-4 hours. Hemmati et al. (1989) compared the cost for gold extraction from a carbonaceous ore using both thiosulfate and cyanide leach system. They have concluded that the thiosulfate leach system has considerable economical advantage over cyanidation, while Langhans et al. (1992) have indicated that the copper-catalyzed thiosulfate leaching system may be competitive with conventional cyanidation methods for heap, dump, or in situ leaching techniques where longer leach times are normally utilized.
Newmont Gold was the first company to attempt a pilot scale thiosulfate heap leach process as a means of recovering gold from the residue of a bio-oxidation heap process (Wan, 1997). Because of the preg-robbing characteristics of the ore, the low-grade carbonaceous sulfidic ore cannot be heap leached with cyanide solution after the bio-oxidation. A thiosulfate leach system was found to be effective for extracting gold from this carbonaceous ore and successfully applied in three pilot scale plants, which were followed by further process development with a 300,000 ton low-grade ore heap leach using ammonium thiosulfate. However, the process has not yet been commercialized.

Another advantage of thiosulfate leaching is that the use of ammonia at pH values of about 10 hinders the dissolution of iron oxides, silica, silicates and carbonates, the most common gangue minerals found in gold-bearing ores (Abbruzzese et al., 1995). The low affinity of the gold thiosulfate complex ions for activated carbon is an important advantage over cyanidation for extracting gold from carbonaceous gold ores. Unlike gold cyanide, gold thiosulfate complexes do not adsorb on carbonaceous material and much higher recoveries of gold can be achieved (Gallagher, 1990). This is why Newmont Gold and Barrick Gold Corporation re-examined the thiosulfate leaching of gold for their refractory carbonaceous ores (Wan, 1997; Schmitz et al., 2001). On the other hand, this can be a disadvantage in terms of recovery of gold from leach pulps.

The main disadvantage associated with the thiosulfate leach process is the decomposition of the thiosulfate, which results in other problems including lower reaction rates due to passivation after an initial rapid stage of leaching, low extraction and high consumption of thiosulfate. The pilot scale tests at Newmont Gold Company
have shown (Wan, 1997) that the average gold recovery from a 300,000 ton low-grade ore heap is approximately 55%. Ammonium thiosulfate consumption is about 5 kg t\(^{-1}\) for low sulfide carbonaceous ores (without bio-oxidation) and 12-15 kg t\(^{-1}\) for bio-oxidized ores. Ammonium thiosulfate consumption depends on the sulfide content, ore characteristics and leach duration times. Another disadvantage of the thiosulfate leach process is the lack of an economical process for recovering gold from pregnant pulps or solutions, although a number of methods for gold recovery have been studied, including precipitation by metals (copper, zinc, iron or aluminum) and sulfides (Aylmore and Muir, 2001), solvent extraction (Chen et al., 1996; Virnig and Sierokoski, 1997), anion exchange resins (Thomas et al., 1998; Nicol and O’Malley, 2001; Fleming et al., 2002), and direct electrowinning (Gallagher et al., 1990; Abbruzzese et al., 1995). Activated carbon commonly used for recovering gold from cyanide solutions cannot be used in ammoniacal thiosulfate leach system due to its low affinity for gold thiosulfate complexes.

2.2.4 Summary

Thiosulfate is a promising alternative to cyanide due to its low toxicity and competitive leaching rate of gold in copper bearing ammoniacal solutions. Thiosulfate leaching also decreases the interference from cations such as lead, zinc, iron and copper commonly encountered in conventional cyanidation processes. However, the high rate of consumption of reagents is a disadvantage which has contributed to the lack of a successful application in the gold industry on a commercial scale. Many studies have shown that reagent consumption and the leaching rate of gold depend upon the composition of the leach solution, ore characteristics, temperature and leach time. The
thiosulfate leach process is potentially applicable to refractory ores such as carbonaceous or sulfidic ores for which cyanide is not suitable.

The chemistry of the ammoniacal thiosulfate system for the leaching of gold and silver is complicated due to complex interactions among thiosulfate, copper, ammonia and gold or silver. Decomposition of thiosulfate also complicates the thiosulfate leach process. A satisfactory mechanism for the dissolution of gold has not been established, meaning that more fundamental work is required to be carried out. For example, the fundamental electrochemistry of the anodic oxidation of gold and of the cathodic reduction of oxygen and redox mediators such as the copper(II)/copper(I) couple have not been satisfactorily explored. The effect of ammonia on the anodic oxidation of gold in thiosulfate solutions has not been fully established. An appropriate recovery method for gold from thiosulfate leach pulps is required to be developed based on a more complete understanding of the chemistry of the system.

2.3 Arsenical Complexes of Gold

This review on the arsenical complexes of gold was initiated by an observation that gold dissolution occurred during the alkaline oxidation of arsenical refractory gold concentrates during work carried out in 1999 in the A. J. Parker Cooperative Research Centre for Hydrometallurgy at Murdoch University. It was also inspired by the work of Williams and Anthony (1990) who have found that arsenic apparently influences the leaching of platinum group metals from ores, and the studies of Nagy et al. (1966) and Rossovsky (1993) who reported that the thioarsenite anion, \( \text{AsS}_3^{3-} \), existed in solutions produced by the alkaline leaching of refractory arsenical gold concentrates.
2.3.1 Oxy-Salts of Arsenic

Arsenic is very widely distributed in nature. In aqueous solution, the commonly encountered oxidation states of arsenic are +3, as in $\text{H}_3\text{AsO}_3$, and +5, as in $\text{H}_3\text{AsO}_4$. Formally, a $-3$ oxidation state can be assigned in $\text{AsH}_3$ (Zingaro, 1994).

Arsenious acid, $\text{H}_3\text{AsO}_3$, is formed by dissolving arsenic trioxide in water, but the free acid has never been isolated. It can dissociate in three steps forming the three anions $\text{H}_2\text{AsO}_3^-$, $\text{HAsO}_3^{2-}$, and $\text{AsO}_3^{3-}$. The $\text{pKa}$ for the dissociation of the first proton is 9.2, which means that $\text{H}_3\text{AsO}_3$ is a very weak acid. Alkali metal arsenites, being soluble in water, are frequently isolated in solid state as meta-arsenites, typically $\text{NaAsO}_2$.

Arsenic acid, $\text{H}_3\text{AsO}_4$, can be formed by the dissolution of arsenic pentoxide in cold water and obtained as a hydrate $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$, by the evaporation of a cold aqueous solution. It is about as strong an acid as $\text{H}_3\text{PO}_4$ and forms the three anions $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, and $\text{AsO}_4^{3-}$ depending the pH value of the aqueous solutions. The acid dissociation constants are $\text{pKa}_1 = 2.25$, $\text{pKa}_2 = 6.77$, $\text{pKa}_3 = 11.4$ respectively. An Eh-pH diagram for the As-H$_2$O system is shown in Figure 2.8. The thermodynamically stable species in alkaline solutions are $\text{HAsO}_4^{2-}$, $\text{AsO}_4^{3-}$, $\text{H}_2\text{AsO}_3^-$ and $\text{AsO}_3^{3-}$.
As can be seen in Figure 2.8, arsenite ion is a reducing agent in alkaline solutions while arsenate ion can thermodynamically behave as a relatively strong oxidizing agent in acidic solutions as shown below (E° from King, 1994).

\[
\begin{align*}
H_3AsO_4 (aq) + 2H^+ + 2e^- &= H_3AsO_3 (aq) + H_2O & E^0 &= + 0.56 \text{ V} \\
AsO_4^{3-} + 3H_2O + 2e^- &= H_2AsO_3^- + 4 OH^- & E^0 &= - 0.68 \text{ V}
\end{align*}
\]

Therefore, arsenite ions in basic solutions can be oxidized by species containing S-S bonds such as thiosulfate (S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}), polythionates (S\textsubscript{n}O\textsubscript{6}\textsuperscript{2-}) and polysulfides (S\textsubscript{n}\textsuperscript{2-}), forming thioarsenates. For example (Mellor, 1929; Bailar \textit{et al.}, 1973),

\[
\begin{align*}
AsO_3^{3-} + S_{2}O_3^{2-} &= AsO_3S^{3-} + SO_3^{2-} \\
AsO_3^{3-} + S^{2-} &= AsO_3S^{3-} + S^{2-}
\end{align*}
\]
In acid solutions, arsenite ions undergo reaction with thiosulfate forming the yellow di-arSENic tri-sulFide (As$_2$S$_3$). An induction period has been observed in the study of this reaction which has been attributed to the formation of an intermediate arsenic thiosulfate, As(S-SO$_2$-OK)$_3$, which subsequently undergoes decomposition (Zingaro, 1994):

$$2\text{As}(S_2O_3)_3\text{K}_3 = \text{As}_2\text{S}_3 + 3\text{SO}_2 + 3\text{S}^0 + 3\text{K}_2\text{SO}_4 \quad (2.62)$$

Arsenate ions can be reduced in a solution containing a non-oxidizing acid to arsenious state by a number of reductants such as Cu$^+$, Ti$^{3+}$, Fe$^{2+}$, Sn$^{2+}$, S$^2$-, SO$_2$ and I$_2$. For example,

$$\text{H}_3\text{AsO}_4 + \text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{H}_3\text{AsO}_3 \quad (2.63)$$

$$2\text{H}_3\text{AsO}_4 + 5\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 2\text{S}^0 + 8\text{H}_2\text{O} \quad (2.64)$$

There are a great number of metal salts containing arsenite or arsenate ions (Mellor, 1929; Greenwood and Earnshaw, 1997). Generally alkaline earth metal salts are less soluble than those of the alkali metals and heavy metal salts tend to be insoluble. Normally, iron arsenites and arsenates are insoluble in water. Guibourt (Mellor, 1929) has reported that some ferrous hydroxide dissolves in solution when the freshly precipitated hydroxide is digested with an aqueous solution of arsenic trioxide. When ferric sulfate, chloride, or nitrate is treated with a solution of arsenic trioxide or an alkali arsenate, all the ferric salt will not be precipitated. Guibourt has also found that when ferric hydroxide is mixed with a saturated solution of arsenic trioxide and sodium hydroxide, after cooling and standing for 24 hours, a yellow substance is obtained with the composition of ferric pyroarsenite, Fe$_4$(As$_2$O$_5$)$_3$·7H$_2$O which forms a deep red solution with sodium hydroxide. Neutral and acid ferric arsenates are quickly and completely dissolved by concentrated ammonia, yielding a blood-red solution while the basic ferric arsenates, however, do not dissolve. The above phenomena indicate that the chemistry of iron arsenic compounds is complex and not well understood.
There are very few simple inorganic compounds of gold with arsenic. Stavenhagen (Mellor, 1929) reported gold arsenite, \( \text{AuAsO}_3 \cdot \text{H}_2\text{O} \) to be formed when a solution of auric chloride in 50 percent of alcohol is treated with potassium arsenite. This gold arsenite is freely soluble in water, in an excess of the precipitating agent, in aqueous ammonia and in diluted acids. When a warm solution of auric chloride is mixed with sodium orthoarsenate, a yellow-white precipitate of gold arsenate, \( \text{AuAsO}_4 \) is produced (Mellor, 1929). \( \text{Au}_3\text{AsO}_4 \) exists with a free energy of formation at 25 °C \( (\Delta G^{\circ}_{298K}) \) of \( -297.7 \text{ kJmol}^{-1} \) (Barin, 1989).

2.3.2 Sulfides and Thiosalts of Arsenic

Realgar, \( \text{As}_4\text{S}_4 \) and orpiment, \( \text{As}_2\text{S}_3 \) are naturally occurring arsenic sulfides and can also be prepared artificially from aqueous solutions by reaction of As(III) and As(V) with \( \text{H}_2\text{S} \). For example,

\[
2\text{As}^{3+} + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 6\text{H}^+ \quad (2.65)
\]
\[
2\text{As}^{5+} + 5\text{H}_2\text{S} = \text{As}_2\text{S}_5 + 10\text{H}^+ \quad (2.66)
\]

They are insoluble in water but sufficiently acidic to dissolve in alkali sulfide solutions to form thiosalts with \( \text{S}^{2-} \) acting as the base (Remy et al., 1956; Zingaro, 1994).

\[
\text{As}_2\text{S}_3 + 3\text{S}^{2-} = 2\text{AsS}_3^{3-} \quad \text{(thioarsenite ion)} \quad (2.67)
\]

If arsenic trisulfide is allowed to react with ammonium polysulfide, the sulfur dissolved in the reagent brings about oxidation to thioarsenate:

\[
\text{As}_2\text{S}_3 + 3\text{S}^{2-} + 2\text{S}^0 = 2\text{AsS}_4^{3-} \quad \text{(thioarsenate ion)} \quad (2.68)
\]

The thioarsenite and thioarsenate anions are stable in alkali, but the free acids \( \text{H}_3\text{AsS}_3 \) and \( \text{H}_3\text{AsS}_4 \) are not and spontaneously decompose into arsenic sulfides and \( \text{H}_2\text{S} \).
Thioarsenite and arsenite ions can be formed simultaneously by the action of alkalis on arsenic trisulfide:

\[ \text{As}_2\text{S}_3 + 6\text{OH}^- = \text{AsS}_3^{3^-} + \text{AsO}_3^{3^-} + 3\text{H}_2\text{O} \quad (2.69) \]

Thioarsenite is expected to be present to some extent during the oxidation of arsenopyrite in alkaline solutions (Nagy et al., 1966; Rossovsy, 1993).

The details of the chemistry of thioarsenite are poorly understood. There is a lack of general agreement with regard to the speciation and molecular form of thioarsenite complexes and a variety of stoichiometries have been proposed (Mellor, 1929; Sillen and Martell, 1964; Sypcher and Reed, 1989; Webster, 1990; Eary, 1992; Helz et al., 1995; Young and Robins, 2000). Table 2.5 gives some selected complexes of thioarsenite and their free energies of formation at 25 °C.

Young and Robins (2000) suggested that the reactions of amorphous As$_2$S$_3$ in water could be written:

\[ 2\text{As}_2\text{S}_3 \text{(am)} + 3\text{H}_2\text{O} = \text{As}_3\text{S}_6^{3^-} + \text{H}_2\text{AsO}_3^- + 2\text{H}^+ \quad \text{pH > 9.2} \quad (2.70) \]
\[ 2\text{As}_2\text{S}_3 \text{(am)} + 3\text{H}_2\text{O} = \text{As}_3\text{S}_5(\text{SH})^2^- + \text{H}_3\text{AsO}_3 \text{(aq)} + 2\text{H}^+ \quad \text{pH 6.5-9.2} \quad (2.71) \]
\[ 2\text{As}_2\text{S}_3 \text{(am)} + 3\text{H}_2\text{O} = \text{HAs}_3\text{S}_4(\text{SH})_2 \text{(aq)} + \text{H}_3\text{AsO}_3 \text{(aq)} \quad \text{pH < 6.5} \quad (2.72) \]

while Helz et al. (1995) have proposed that in sulfide solutions at a pH less than 7, As$_2$S$_3$ dissolves via the following reactions:

\[ 1.5\text{As}_2\text{S}_3 + 1.5\text{H}_2\text{S} = \text{As}_3\text{S}_4(\text{SH})_2^- + \text{H}^+ \quad (2.73) \]
\[ \text{As}_3\text{S}_4(\text{SH})_2^- + \text{H}^+ + 3\text{HS}^- = 3\text{AsS(SH)}_2^- \quad (2.74) \]

At higher pH values, As$_2$S$_3$ is formed from AsS(SH)$_2$ by deprotonation. Zakaznova-Iakovleva and Seward (2002) have reported spectroscopic evidence for H$_3$AsS$_3^0$ and H$_2$AsS$_3^-$ from 25 to 300 °C in a brief abstract. However, Wood et al. (2002), in a Raman study, found that while general conditions could be defined under which
thioarsenite species were dominant with respect to their oxo analogues, the system appeared to be more complex than previously thought. They could not precisely identify the thio components in solution.

Table 2.5 A selection of proposed thioarsenite species

<table>
<thead>
<tr>
<th>Complexes Proposed</th>
<th>$\Delta G_{298K}^\circ$ / kJ mol$^{-1}$</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsS$_3^{3-}$</td>
<td>-</td>
<td>$&gt;12$</td>
<td>d</td>
</tr>
<tr>
<td>AsS$_2^{2-}$</td>
<td>-47.28</td>
<td>6 - 9</td>
<td>a</td>
</tr>
<tr>
<td>As$_3$S$_6^{3-}$</td>
<td>-55</td>
<td>$&gt;9.2$</td>
<td>a</td>
</tr>
<tr>
<td>As$_3$S$_3$(SH)$_2^{2-}$</td>
<td>-106</td>
<td>6.5 – 9.2</td>
<td>a</td>
</tr>
<tr>
<td>As$_3$S$_4$(SH)$_2^{2-}$</td>
<td>-139</td>
<td>1 - 7</td>
<td>a</td>
</tr>
<tr>
<td>HAS$_3$S$_4$(SH)$_2$</td>
<td>-180</td>
<td>$&lt;6.5$</td>
<td>a</td>
</tr>
<tr>
<td>As(SH)$_2^{2-}$</td>
<td>-38</td>
<td>8 - 12</td>
<td>c</td>
</tr>
<tr>
<td>AsS$_2$(SH)$_2^{2-}$</td>
<td>-</td>
<td>8 - 12</td>
<td>c</td>
</tr>
<tr>
<td>As$_3$S$_4^{2-}$</td>
<td>-23.90</td>
<td>2 - 10</td>
<td>b</td>
</tr>
<tr>
<td>HAS$_2$S$_4^{2-}$</td>
<td>-71.11</td>
<td>2 - 10</td>
<td>b</td>
</tr>
<tr>
<td>As$_4$S$_7^{2-}$</td>
<td>-102.63</td>
<td>4 - 9</td>
<td>b</td>
</tr>
<tr>
<td>As$_3$S$_5^{4-}$</td>
<td>-</td>
<td>10.5</td>
<td>d</td>
</tr>
</tbody>
</table>

a. from Young and Robins, 2000;
b. from Akinfiev et al., 1992;
c. from Helz et al., 1995;

A variety of thioarsenate tetrahedral ions As$_n$O$_{4-n}^{3-}$ are also known and may be isolated depending on the precise reaction conditions (Mellor, 1929; Schwedt and Rieckhoff, 1996), as indicated by Equations 2.31, 2.61 and 2.68. The acids of these thioarsenate ions are mild as shown in Table 2.6 in which the dissociation constants of the acids and relevant salts are given.
Table 2.6 Dissociation constants of the acids of thioarsenates at 25 °C (after Schwedt and Rieckhoff, 1996; Macintyre, 1992)

<table>
<thead>
<tr>
<th>Thioarsenate</th>
<th>Acid</th>
<th>Dissociation Reaction</th>
<th>pKs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃AsO₃S·12H₂O, Na₃AsO₃S·11H₂O, Na₃AsO₃S·6H₂O</td>
<td>H₃AsO₃S</td>
<td>H₃AsO₃S = H₂AsO₃S⁻ + H⁺</td>
<td>pKs₁ = 3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂AsO₃S⁻ = HAsO₃S²⁻ + H⁺</td>
<td>pKs₂ = 7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HAsO₃S²⁻ = AsO₃S³⁻ + H⁺</td>
<td>pKs₃ = 11.0</td>
</tr>
<tr>
<td>Na₃AsO₂S₂·11H₂O, Na₃AsO₂S₂·7H₂O, Na₃AsO₂S₂·2H₂O</td>
<td>H₃AsO₂S₂</td>
<td>H₃AsO₂S₂ = H₂AsO₂S₂⁻ + H⁺</td>
<td>pKs₁ = 2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂AsO₂S₂⁻ = HAsO₂S₂²⁻ + H⁺</td>
<td>pKs₂ = 7.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HAsO₂S₂²⁻ = AsO₂S₂³⁻ + H⁺</td>
<td>pKs₃ = 10.9</td>
</tr>
<tr>
<td>Na₃AsO₂S³·11H₂O</td>
<td>H₃AsOS₃</td>
<td>H₃AsOS₃ = H₂AsOS₃⁻ + H⁺</td>
<td>pKs₁ = 10.8</td>
</tr>
<tr>
<td>Na₃AsS₄·8H₂O</td>
<td>H₃AsS₄</td>
<td>H₃AsS₄ = H₂AsS₄⁻ + H⁺</td>
<td>pKs₃ = 5.2</td>
</tr>
</tbody>
</table>

Studies of the chemistry of thioarsenates are few. The monothioarsenate and dithioarsenate anions have structures as described by the following forms (Macintyre, 1992).

\[
\text{AsO}_3S^{3-} \quad \text{ion} \quad \text{Bond length: As-O 167, As-S 214, S-O 314 pm} \quad \text{Bond angles: OAsO 107.5-109.3°, OAsS 107.5-113.3°.}
\]

\[
\text{AsO}_2S_2^{3-} \quad \text{ion} \quad \text{Bond length: As-O 169, As-S 212-215, S-O 312-315 pm} \quad \text{Bond angles: OAsO 107.0°, OAsS 109.6°, SAsS 110.8°.}
\]
Schwedt and Rieckhoff (1996) have reported that monothioarsenate is the most stable of the thioarsenates over the entire pH range although acid solutions of monothioarsenate become turbid (Mellor, 1929). Dithioarsenate has maximum of stability at pH 3, 5-6 and 10, while decomposing to H$_2$S and a yellowish precipitate in acid solutions (Mellor, 1929). Tetrathioarsenate is stable in solution only at pH values higher than 10. It may also be oxidized to arsenate and sulfate by several oxidizing agents such as iodine, peroxide and K$_3$Fe(CN)$_6$ (Bailar et al., 1973; Macintyre, 1992). For example,

$$\text{AsO}_3\text{S}^3^- + 4\text{I}_2 + 10\text{OH}^- = \text{AsO}_4^{3^-} + \text{SO}_4^{2^-} + 8\text{I}^- + 5\text{H}_2\text{O} \hspace{1cm} (2.75)$$

Several compounds of transition metals formed with thioarsenite or thioarsenate are probably double salts: for example, enargite, CuAsS$_4$ as 3Cu$_2$S·As$_2$S$_5$; Proustite, Ag$_3$AsS$_3$ as 3Ag$_2$S·As$_2$S$_3$; lorandite, Tl$_2$As$_4$S$_7$ as Tl$_2$S·2As$_2$S$_3$ (Mellor, 1929). Gold compounds are few. Berzelius has reported that a yellow precipitate of gold sulfarsenite, 2AuS$_3$·3As$_2$S$_3$ (suspect formula) is formed when a solution of sodium sulfarsenite and a gold salt are mixed together (Mellor, 1929). When sodium orthosulfarsenate is used, gold orthosulfarsenate, AuAsS$_4$ can be precipitated from an aqueous solution of an auric gold salt. The dark brown precipitate is soluble in water and the solution can be decolorized by ferrous sulfate with a yellowish-brown precipitate being formed. If sodium pyrosulfarsenate is the precipitant, then gold pyrosulfarsenate, Au$_4$(As$_2$S$_7$)$_3$ is obtained as a reddish-brown precipitate that is soluble in water. Loeken and Tremel (1998) have recently reported evidence of one gold thioarsenate compound, K$_3$AuAsS$_4$. This compound forms orange, plate-like crystals that were found to be slightly air-sensitive and decompose in water.
2.3.3 Effect of Arsenic on the Dissolution of Gold

The behaviour of gold in hydrothermal solutions has been of great interest to economic geologists and geochemists, and arsenical complexes of gold have received considerable attention in the hydrothermal transport and deposition of gold because of the discovery of gold-arsenic deposits in rocks with high arsenic concentrations throughout the world (Nekrasov, 1996; Seward, 1993).

Thioarsenites have long been assumed to play a role in the complexation of elements of Group 1B (Cu, Ag, Au) in a variety of sulfide-rich environments when arsenic is present (Clarke and Helz, 2000; Tossell, 2000a) since arsenic is a very soft donor atom and forms its most stable complexes with soft metals such as Au, Pt, Pd (McAuliffe, 1987). A number of geochemists (Grigor’yeva and Sukneva, 1981; Nekrasov and Gamyanin, 1978; Akhmedzhakova et al., 1988 and 1991) have measured the solubility of gold in aqueous solutions in the presence of stibnite (Sb$_2$S$_3$) and/or orpiment (As$_2$S$_3$) in the temperature range from 200 to 300 °C. Nekrasov and Gamyanin (1978) studied the effect of arsenic as a metal or orpiment (As$_2$S$_3$) on the solubility of gold in alkaline sodium hydroxide (NaOH) solutions at 200 °C. They reported that the solubility of Au in alkaline arsenic solutions at 200 °C was greater by a factor of $10^3$ than in the same solution without arsenic, with the values being 0.003-0.007 and 4.9-8.6 ppm respectively. They have suggested that gold in alkaline solutions may occur in complexes of the type Au(As$_2$)$_2^{2-}$ (suspect formula), Au(As$_2$)$_2$ or Au(As$_2$)$_2^{2-}$, Au(AsS$_3$)$_2^{2-}$ and Au(AsS$_2$)$_0$. Figure 2.9 gives the relationship between the solubility of gold and concentration of As in alkaline (0.5 M NaOH) solution at 200 °C in the presence of orpiment.
Grigor’eva and Sukneva (1981) measured the solubility of gold in 0.1 M solutions of NaOH, Na₂S and Na₂Sn (n ≥ 2) at 200 °C in the absence or presence of As₂S₃. They also found that the addition of As₂S₃ to the NaOH solution increased the solubility of gold by 2-3 orders. The mechanism for the solubility enhancement by As₂S₃ is not known. Akhmedzhakova et al. (1988) studied the solubility of gold in acidic aqueous chloride-sulfide solutions in the presence of orpiment at 200 and 300 °C. Their results indicate that the solubility of gold increases with increasing arsenic concentration. They proposed that addition of arsenic to Au-S-Cl-H₂O system may lead to the formation of a heteropolynuclear compound of the type H₂(AuAs)S₃⁰ at 200 °C. However, the complexity of the system makes their results inconclusive.
Nekrasov (1996) synthesized an unknown gold sulfoarsenide with empirical formula \( \text{Au}_4\text{AsS}_3 \) while determining the solubility of gold in sulfide-arsenic solutions at 300 °C. They have suggested that gold migration in hydrothermal solutions is more probable in the form of heteropolynuclear complexes of the type \( \text{Au(AsS}_3\text{)}^2^- \) and \( \text{Au(AsS}_2\text{)}^0 \). Seward (1981) also suggested the probable existence of such polynuclear complexes. \( \text{As}_3\text{S}_6^{3-} \) and \( \text{Sb}_2\text{S}_6^{3-} \) are possible ligands which may play an important role in hydrothermal gold transport (Seward, 1993). Nutt and co-workers (Nekrasov, 1996) have suggested that the formation of gold-pyrite-arsenopyrite ore bodies in the jaspilite deposits of Broomstock in Zimbabwe is associated with the presence of the \( \text{Au(AsS}_3\text{)}^2^- \) complex.

More recently, the ternary complex, \( \text{CuAsS(SH)(OH)} \) has been found to have an unusually high stability and makes a large contribution to the total concentrations of both Cu and As in sulfide solutions equilibrated with Cu and As sulfide minerals (Clarke and Helz, 2000; Tossell, 2000a, 2001). Based on quantum mechanical calculations, Tossell (2000b) has found that complexes with similar structures exist for \( \text{Au}^+ \) and \( \text{TI}^+ \) coordinated to \( \text{AsS(SH)(OH)}^– \), and \( \text{AuAsS(HS)(OH)(OH)} \) is considerably more stable than the aquo ion \( \text{Au}^+ \). He suggested that the \( \text{Au}^+ \) and \( \text{AuSH} \) complexes of \( \text{AsS(SH)(OH)}^– \) or \( \text{AsS(SH)}_2^– \) may be implicated in “invisible gold” in arsenical pyrite. Unfortunately, their work on thioarsenite chemistry has been of a theoretical nature.

In summary, the presence of arsenic in solution could have some influence on the dissolution of gold in aqueous solutions but the mechanism for this function is not clear and has not been satisfactorily investigated, although the existence of some complexes of gold with thioarsenites has been suggested.
Chapter 2 Review of the Literature

2.4 Alkaline Oxidation of Refractory Sulfide Gold Ores

2.4.1 Gold Recovery from Refractory Sulfide Ores

One of the major challenges currently experienced by the gold industry is the efficient recovery of precious metals from refractory ores containing arsenopyrite (FeAsS) and pyrite (FeS₂) which are important host minerals for gold. The most common association of gold with these sulfide minerals are in gaps and fractures of the minerals, along boundaries between sulfides and other minerals, locked within sulfide mineral grains, in sub-microscopic form as inclusions or in solid solution and possibly as a lattice constituent of the minerals (Gasparrini, 1983). Gold normally occurs as discrete grains with particle size from 200 microns to fractions of a micron. In arsenopyritic minerals, gold can be invisible as solid solution even when present at levels of 1% (Craig and Vaughan, 1990; Vaughan et al., 1989). The treatment of sulfide deposits has been of major interest in recent years due to continued exhaustion of oxidized gold ores (Marsden and House, 1992; Deng, 1995; Sparrow and Woodcock, 1995).

Gold can be recovered via direct cyanidation if it exists as liberated or exposed discrete grains. But gold in solid solution or as minute inclusions in sulfides responds poorly to conventional cyanidation or other alternative lixiviants, even after ultra-fine grinding of ores to 5 microns (Dunn et al., 1989; Corrans and Angove, 1991). Therefore, gold recovery from arsenopyrite-pyrite bearing ores requires breakdown of the crystal structure of the host minerals by oxidation, followed by conventional cyanidation. A more complex process is therefore required to affect the recovery of gold from such ores.
There are pyrometallurgical and hydrometallurgical options for arsenical sulfide oxidation. Extensive studies on the treatment of arsenical sulfide gold ores have been carried out worldwide, that have led to the industrial establishment and application of roasting, pressure oxidation and bacterial oxidation processes (Fraser et al., 1991; Robins and Jayaweera, 1992; Deng, 1995; Sparrow and Woodcock, 1995; Fleming, 1998). These processes have individual advantages and disadvantages. Almost all hydrometallurgical and pyrometallurgical processes for gold recovery utilize the cyanidation process as a means of gold dissolution from the residues after the above pretreatment processes, resulting in higher costs for the overall process and the increasing environmental pressure associated with disposal of cyanide.

2.4.1.1 Roasting

Roasting is a traditional option for oxidation of arsenical sulfide ores, which involves high temperature combustion in the presence of oxygen, resulting in the conversion of sulfur to sulfur dioxide and arsenic to arsenic trioxide. Equation 2.76 shows the reaction for the roasting of arsenopyrite.

\[ 2\text{FeAsS} + 5\text{O}_2 = \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 + 2\text{SO}_2 \]  

Roasting is simple in principle but has two major disadvantages. Firstly, gold recovery may still be low; for example, only 60-70% extraction is achieved in some cases (Dunn et al., 1989). Secondly, the highly toxic arsenic-bearing gases from the roaster cause severe environmental problems and impose strict legal regulations regarding their emissions (Schraufnagel, 1983; Robins and Jayaweera, 1992). These gases must be scrubbed and treated, which can result in increased costs and this in turn has led to the development of alternative hydrometallurgical processes (Thomas, 1991a, b and c; Sparrow and Woodcock, 1995; Van Weert et al., 1986; Nagpal et al., 1994; Deng, 1995).
2.4.1.2 Bio-oxidation

Bio-oxidation uses iron- and sulfur-oxidizing bacteria in acid solutions to destroy the sulfide lattice and thereby expose the gold (Lawrence and Bruynesteyn, 1983). Arsenopyrite is oxidized to Fe(III), As(V) and sulfate through the intermediates Fe(II), As(III) and S(0) (Malatt, 1999). One advantage of bio-oxidation over roasting is that toxic arsenic can be precipitated from solution using lime, which limits the environmental hazards of arsenic. Other advantages are that it is carried out under ambient conditions and has relatively low reagent costs (Gilbert et al., 1987). However, bacterial oxidation generally produces acid and lime must be used to thoroughly neutralize and raise the pH to values required for cyanidation. Furthermore, it is subject to large residence times and sensitivity to operating conditions, which can give rise to inconsistent plant performance and periodic high operating costs.

2.4.1.3 Chemical oxidation

Chemical oxidation processes use soluble chemical oxidants to oxidize the sulfide minerals faster than bacterial oxidation. The best known is pressure acid oxidation that uses high pressures and temperatures to increase the oxygen solubility and the oxidation rate of sulfide minerals. Pressure acid oxidation generally has acceptable operating costs, but the complexity and capital cost of a pressure leaching plant make it a more expensive option. It also requires the use of lime to raise the pH to cyanidation levels (Kontopoulos and Stefanakis, 1989; Deng, 1995). Therefore, alternative processes have been developed including the Cashman, Arseno, Nitrox, electrolytic and alkaline oxidation processes (Deng, 1995; Van Weert et al., 1986; Beattie et al., 1985; Linge and Jones, 1993; Bhakta
et al., 1989; Thomas and Williams, 2000; Thomas, 1991a, b and c; Souza and Ciminelli, 1992) none of which have been successfully applied commercially.

2.4.1.4 Alkaline oxidation

Alkaline oxidation was first proposed and commercially used in the late 1950’s for treating arsenical sulfide materials (Sill, 1958; Chilton, 1958; Plaksin and Masurova, 1959). Alkaline pressure oxidation was also used to treat sulfidic gold ore (Arkhipova et al., 1975; Mason et al., 1984; Bhakta et al., 1989; Thomas, 1991a, b and c; Souza and Ciminelli, 1992; Hiskey and Sanchez, 1995). More recently, new processes have been proposed for the oxidation of arsenical sulfidic gold ores in alkaline solutions to extract gold in either one or two steps (Mao et al., 1997; Min et al., 1999; Rossovsky, 1993; Lan and Zhang, 1996; Fang and Han, 2002). The use of alkaline oxidation pretreatment has several technical merits including the use of lower temperatures, less severe corrosion problems and suitability for acid-consuming ores (Deng, 1995; Deng, 1992), although the high reagent costs may be considered as a disadvantage.

2.4.2 Alkaline Oxidation of Arsenopyrite

2.4.2.1 The nature of arsenopyrite

Arsenopyrite or arsenical pyrite is the most common mineral containing arsenic and occurs worldwide in considerable abundance in many localities. Its composition generally deviates from its theoretical formula of FeAsS with some variation in As and S contents ranging from FeAs$_{0.9}$S$_{1.1}$ to FeAs$_{1.1}$S$_{0.9}$ (Morimoto and Clark, 1961). It has a molecular mass of 162.83 with a theoretical chemical composition of 34.29% Fe, 46.01%
As and 19.69% S. It has been suggested that Fe in arsenopyrite is present as both Fe$^{2+}$ and Fe$^{3+}$ with Fe$^{2+}$ predominant (Nesbitt et al., 1995; Tossell et al., 1981; Nickel, 1968), and the formula of arsenopyrite is described as Fe$^{2+}$(AsS)$^{2-}$ with a minor contribution from Fe$^{3+}$(AsS)$^{3-}$ (Nesbitt et al., 1995; Shuey, 1975). The As and S in arsenopyrite exist predominantly as a dianionic group because of the covalent bond between As and S. Arsenic is present as As$^{0}$ and As$^{-}$, with the last predominant (Nesbitt et al., 1995). Most sulfur is present as S$^{-}$ (78%) with S$^{2-}$ (15%) and S$^{2-}_{n}$ as minor species. The separation of the arsenic from the sulfur is more difficult than the separation of the iron from the arsenic-sulfur group (Nickel, 1968).

Arsenopyrite almost always occurs as an intergrowth of two or more single crystals in its mineral forms, which complicates the determination of its structure by X-ray diffraction (XRD) because of the difficulty of obtaining a single crystal (Vreugde, 1982). A fairly accurate quantitative XRD analysis for arsenopyrite can be obtained from the $d_{131} = 1.6106$ diffraction peak (Morimoto and Clark, 1961). It has a silver-white color and specific gravity of 6.07 (Cornelis et al., 1985). Arsenopyrite is a narrow band-gap semiconductor, and it is n-type when deficient in arsenic while p-type when it is arsenic-rich (Shuey, 1975). Its free energy of formation is $-109.6$ kJ mol$^{-1}$ (Vreugde, 1982; Barton, 1969).

Arsenopyrite has considerable economic importance when it carries the major portion of gold in the ore. The oxidation of arsenopyrite is of practical and theoretical importance in the processing of gold ores and concentrates. However, the chemistry of arsenopyrite in relation to its dissolution, flotation and electrochemistry has received little attention compared with other sulfide minerals, although there are a number of
published studies on the oxidation of arsenopyrite in acid and alkaline solutions. In the following section a review of work on the alkaline oxidation of arsenopyrite is outlined.

2.4.2.2 Thermodynamics of oxidation of arsenopyrite

Oxidation in alkaline media is advantageous thermodynamically because lower potentials are required to oxidize arsenopyrite as indicated by the Eh-pH diagram for Fe-As-S-H2O system shown in Figure 2.10 (Bhakta et al., 1989; Vreugde, 1982). The potential stability range for arsenopyrite is from about −0.6 to +0.2 V. The rest potential of arsenopyrite has been found to increase with decreasing pH from about -0.01 V at pH 12 to 0.15 V at pH 9 (Beattie and Poling, 1987; Sanchez and Hiskey, 1991). Thus, in alkaline media, normal oxidants such as oxygen can oxidize arsenopyrite readily to ferric hydroxides, arsenate (HAsO$_4^{2-}$ or AsO$_4^{3-}$ depending on pH), and sulfate with ferrous hydroxides and arsenites as intermediates. The overall reaction for the alkaline oxidation of arsenopyrite can be described by the following equation (Bhakta et al., 1989; Papangelakis and Demopoulos, 1990; Ciminelli, 1987):

$$2\text{FeAsS} + 10\text{OH}^- + 7\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{AsO}_4^{3-} + 2\text{SO}_4^{2-} + 5\text{H}_2\text{O} \quad (2.77)$$
2.4.2.3 Mechanism of the oxidation of arsenopyrite

Most studies have concentrated on the electrochemical mechanism of arsenopyrite oxidation. Kostina and Chernyak (1976) have studied the electrochemical oxidation of arsenopyrite in concentrated caustic soda solution at 20 °C, and reported that the oxidation of arsenopyrite starts at -0.2 V. The potential for arsenopyrite oxidation shifts negatively with increasing temperatures, and the oxidation rate of arsenopyrite increases with the increase of temperature and NaOH concentration. Sanchez and Hiskey
(1991) have observed that the main anodic oxidation peak for arsenopyrite appears at about 0.3 V.

The studies by Beattie and Poling (1987) indicate that oxidation of arsenopyrite results in the formation of ferric hydroxide films on the surface of the mineral at pH values greater than 7. Arsenic and sulfur are oxidized to arsenate and sulfate respectively. Bhakta et al. (1989) reported electrochemical studies that have shown that the hydrated iron oxide film appears to be porous and partially hinder further oxidation of arsenopyrite. At pH 13.5, thick and apparently porous layers of iron oxide precipitate on the sulfide particles, while at pH 7, thin and dense oxide coatings are formed (Koslides and Ciminelli, 1992; Sisenov et al., 1988; Yu and Fang, 2000). Hematite is the principle phase in the residue after pressure oxidation by oxygen (Koslides and Ciminelli, 1992; Hiskey and Sanchez, 1995). Bhakta et al. (1989) have found that the lowest potentials for arsenopyrite oxidation occur in caustic soda solutions.

Sanchez and Hiskey (1991) reinvestigated the electrochemical behaviour of arsenopyrite in alkaline media using cyclic voltammetry at pH 8-12 at room temperatures. Their work suggests that the anodic oxidation of arsenopyrite proceeds by a two-step dissolution mechanism. The first step is described by Equation 2.78:

$$\text{FeAsS} + 6\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{H}_2\text{AsO}_3^- + \text{S}^0 + 7\text{H}^+ + 6\text{e}^- \quad (2.78)$$

with the formation of a FeOOH surface layer, elemental sulfur, and arsenite ($\text{H}_2\text{AsO}_3^-$). The second step involves the oxidation of arsenite ($\text{H}_2\text{AsO}_3^-$) to arsenate ($\text{HAsO}_4^{2-}$) and sulfur to sulfate according to the following reactions:

$$\text{H}_2\text{AsO}_3^- + \text{H}_2\text{O} = \text{HAsO}_4^{2-} + 3\text{H}^+ + 2\text{e}^- \quad (2.79)$$

$$\text{S}^0 + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 3\text{H}^+ + 6\text{e}^- \quad (2.80)$$
The overall reaction involves 14 electrons, confirming stoichiometric determinations of the extent of dissolution of arsenopyrite. They have also found that the rate of oxidation is sensitive to the pH of the medium.

Wang et al. (1992) have argued that the initial oxidation of arsenopyrite produces ferric hydroxide and a realgar-like compound according the following reaction:

$$\text{FeAsS} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{As} + 3\text{H}^+ + 3\text{e}^- \quad (2.81)$$

At higher potentials, the oxidation of arsenopyrite results in elemental sulfur and arsenate according to the following overall reaction:

$$\text{FeAsS} + 7\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{HAsO}_4^{2-} + \text{S}^0 + 10\text{H}^+ + 8\text{e}^- \quad (2.82)$$

Ferric hydroxide is precipitated and arsenate stays on the surface. Both elemental sulfur and realgar (AsS) are retained on the arsenopyrite substrate.

It is interesting to note that Bou et al. (1998) suggested a possible mechanism for arsenopyrite oxidation, after studying the cementation of the gold chloride complex $\text{AuCl}_4^-$ on arsenopyrite, involving the formation of arsenothioate (or thioarsenate), $\text{AsS(OH)}_3$ or $\text{As(OH)}_3\text{S}$, on the surface of arsenopyrite mineral and the oxidation of arsenothioate to sulfate and arsenate. But more detailed fundamental studies are required to assess these claims.

Some studies have been reported on the atmospheric oxidation of arsenopyrite surfaces by X-ray Photoelectron Spectroscopy (XPS). Buckley and Walker (1988) have examined the surface oxidation of FeAsS in air-saturated alkaline solutions. Oxidation in air-saturated alkaline solutions produces iron oxide, As(III) oxide, and a metal deficient sulfide structure. Richardson and Vaughan (1989) conducted a spectroscopic investigation of arsenopyrite surfaces leached in a variety of solutions, and observed the
presence of arsenite, arsenate and iron in the forms of Fe(III)-arsenates and Fe(III)arsenites. Nesbitt et al. (1995) carried out more detailed studies on the atmospheric oxidation of the arsenopyrite surface by XPS. They have found that surfaces reacted with air-saturated distilled water for eight hours undergo extensive oxidation. Fe(III)-oxyhydroxides are the dominant surface species of iron. Polysulfide, sulfate and thiosulfate are present on surfaces as intermediates or the final oxidation products of sulfur. The oxidation of As(-I) in arsenopyrite proceeds via numerous intermediates, including As(I) and As(III), and possibly As(0), with As(V) as the final oxidation state of As. The oxidation rates of Fe(II) and As(-I) are similar and much more rapid than that of S(-I). The rate of production of As(III), relative to As(V), is sufficiently rapid to maintain an appreciable concentration of As(III) as arsenite at the mineral surface. Arsenic apparently diffuses rapidly from the interior of the mineral to the surface during oxidation.

Nicol and Guresin (2000 and 2003) have recently studied the electrochemistry of arsenopyrite in strongly alkaline solutions with either ferrate(VI) or dissolved oxygen as the oxidant. They have shown that arsenic(III) is the main product of the anodic process at potentials in the region of the rest potential (-0.7 to -0.3 V) during oxidation by either ferrate(VI) or oxygen, and that the rate determining step in the anodic oxidation involves transfer of a single electron with one or more hydroxyl ions also involved. The initial stage of oxidation by ferrate(VI) has been shown to be mass-transport controlled and this is also true of the oxidation by oxygen in dilute solutions of sodium hydroxide. The cathodic reduction of oxygen can be strongly inhibited when increasing the alkalinity of reaction solutions. The authors suggested that reduction of oxygen to peroxide might precede reduction to water. They also pointed out that both the anodic and cathodic
reactions could be partially passivated due to the formation of a thick passive layer produced by a dissolution-precipitation process.

As a cathodic process for arsenopyrite oxidation by oxygen, the reduction activity of oxygen on arsenopyrite in basic media has been studied electrochemically (Rand, 1977). At pH 9.06, the reduction of oxygen on arsenopyrite occurs at a potential below 0.0 V (vs. SCE) and is slower than that on pyrite and chalcopyrite surfaces. Arsenopyrite will act as an anode when contact with pyrite and chalcopyrite.

There is little work reported on the leaching chemistry of arsenopyrite in oxygenated alkaline media. The formation of thioarsenite \( \text{AsS}_3^{3-} \) ions in alkaline solutions has been found during the atmospheric oxidation of gold bearing arsenical ores (Nagy et al., 1966; Rossovsky, 1993). The oxidation reactions taking place in aerated NaOH solutions are suggested as:

\[
3\text{FeAsS} + 9\text{NaOH} + 4\text{O}_2 = \text{Na}_3\text{AsS}_3 + 2\text{Na}_3\text{AsO}_4 + 3\text{Fe(OH)}_3 \quad (2.83)
\]

with the subsequent oxidation of \( \text{AsS}_3^{3-} \) to \( \text{SO}_4^{2-} \) and \( \text{AsO}_4^{3-} \).

### 2.4.2.4 Kinetics of the oxidation of arsenopyrite

The kinetics of acid pressure oxidation of arsenopyrite has been studied in detail by Papangelakis and Demopoulos (1990). In alkaline media, some aspects of the kinetics of arsenopyrite oxidation have also been studied (Plaksin and Masurova, 1959; Kakovskii and Kosikov, 1975; Bhakta et al., 1989; Koslides and Ciminelli, 1992; Hiskey and Sanchez, 1995; Yang et al., 1997). The oxidation rate of arsenopyrite depends upon the concentrations of oxygen and the alkali used, temperature, surface area or particle size of the mineral, slurry density, agitation and reaction time.
It has been found that the initial oxidation rate of arsenopyrite in alkaline media is proportional to the surface area of the mineral, dissolved oxygen concentration and hydroxyl ion concentration. This initial oxidation rate can be described by the following rate equation:

\[- \frac{1}{S} \frac{dN(\text{FeAsS})}{dt} = k e^{(K_{a'})/RT} [\text{OH}^-]^a \text{Po}_2^b\]  

(2.84)

where \(S\) is the surface area of arsenopyrite, \(dN/dt\) the number of moles of arsenopyrite consumed per unit time, \(k\) the apparent constant, \(K_{a'}\) the reaction activation energy (J mol\(^{-1}\)), \(R\) the universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)), \(T\) the temperature (K), \(a\) and \(b\) are the respective reaction orders related to hydroxyl ion concentration and partial pressure of oxygen. Table 2.7 gives reported data for \(K_{a'}\), \(a\) and \(b\) from the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>(K_{a'}/\text{kJ mol}^{-1})</th>
<th>(a)</th>
<th>(b)</th>
<th>(T/\text{K})</th>
<th>(\text{Po}_2/\text{kPa})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kakovskii and Kosikov, 1975</td>
<td>41.3</td>
<td>~1</td>
<td>0.5</td>
<td>298-323</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Taylor and Amoah-Forson, 1987</td>
<td>23.8</td>
<td>-</td>
<td>-</td>
<td>353-423</td>
<td>280-1400</td>
</tr>
<tr>
<td>Bhakta et al., 1989</td>
<td>20.3</td>
<td>-</td>
<td>-</td>
<td>353-413</td>
<td>275-1380</td>
</tr>
<tr>
<td>Koslides and Ciminelli, 1992</td>
<td>15.1</td>
<td>0.27</td>
<td>~0</td>
<td>373-433</td>
<td>265-1053</td>
</tr>
<tr>
<td>Yang et al., 1997</td>
<td>24.4</td>
<td>-</td>
<td>-</td>
<td>283-333</td>
<td>Electrooxidation</td>
</tr>
</tbody>
</table>

As seen in Table 2.7, the activation energy for arsenopyrite oxidation in alkaline media is low, suggesting a diffusion control mechanism. The diffusion of reactants (OH\(^-\) or \(\text{O}_2\)) through the hydrous iron oxide layer on the partially reacted arsenopyrite may be the rate-controlling factor. There is a clear difference between the reaction orders with
respect to relevant reactants, which probably is associated with the use of different pressures of oxygen. The negligible effect of oxygen pressure at high pressures on the oxidation rate may indicate the occurrence of an adsorption reaction as described by a Langmuir isotherm (Koslides and Ciminelli, 1992; Plaksin and Masurova, 1959). The apparent fractional order for the hydroxyl ion concentration is typical of electrochemically controlled reactions, involving the oxidation of arsenopyrite, hydrolysis of iron and the reduction of oxygen (Koslides and Ciminelli, 1992).

Increasing temperature increases the rate oxidation of arsenopyrite up to about 140 °C, after which the As and S are precipitated from solution at high temperatures (Plaksin and Masurova, 1959; Bhakta et al., 1989). Generally, longer leaching time results in higher arsenic extraction from the pressure oxidation of arsenopyrite (Bhakta et al., 1989), while under atmospheric conditions the oxidation rate decreases with time, probably because of the formation of surface layers (Kakovskii and Kosikov, 1975). Bhakta et al. (1989) have reported that the use of higher density of solids (more than 15%) in solution leads to substantially lower extraction of arsenic. The oxidation rate of arsenopyrite increases with increasing agitation up to about 900 rpm above which the rate becomes virtually independent of the stirring speed (Koslides and Ciminelli, 1992).

Since the ultimate purpose of the oxidation of arsenopyrite is to enable extraction of precious metal values, a linear relationship between the extent of arsenic extraction from gold ores and subsequent gold extraction by cyanidation has been established by Hiskey and Sanchez (1995). It was observed that gold extraction after arsenopyrite oxidation never exceeded 85%, which is consistent with the operating results at Barrick Mercur (Thomas, 1991a, b). The reason was explained in terms of the formation of passivating oxide layers on the surface of arsenopyrite.
2.4.3 Alkaline Oxidation of Pyrite

The aqueous oxidation of pyrite is an oxidative process involving an increase in the sulfur valence state. This subject has been extensively studied, since the understanding of its behaviour in aqueous solutions is important for many applications such as the separation of pyrite from complex sulfide ores by flotation, desulfurization of coal, production of acid mine drainage and the leaching of pyrite. A number of excellent reviews have been published on the oxidation of pyrite (Lowson, 1982; Hiskey and Schlitt, 1982; Ciminelli, 1987; Zhu et al., 1993). The dissolution behaviour of pyrite has been investigated using various techniques, including electrochemical techniques (Meyer, 1979; Hamilton and Woods, 1981; Wadsworth et al., 1993; De Jager and Nicol, 1997), chemical analytical techniques (Goldhaber, 1983; Taylor et al., 1984; Moses et al., 1987; McKibben and Barnes, 1986; Ciminelli and Osseo-Asare, 1986, 1995a, b), XPS (Buckley and Woods, 1987; Mycroft et al., 1990), Raman Spectrometry (Li and Wadsworth, 1993; Mycroft et al., 1990; Caldeira et al., 2003) and other instrumental analytical techniques (Caldeira et al., 2003; Mishra and Osseo-Assare 1988; Wei and Osseo-Asare, 1996; Ennaoui et al., 1986; Michell and Woods, 1978). In the following section, attention is focused on the alkaline oxidation of pyrite.

2.4.3.1 The nature of pyrite

Pyrite is the most widespread and abundant of naturally occurring metal sulfides. It is represented chemically by the formula FeS$_2$ and is a binary transition metal sulfide found in association with various ores (Hiskey and Schlitt, 1982; Ciminelli, 1987). The iron component of pyrite has an oxidation state of +2. Consequently, it can be deduced
that pyritic sulfur is present as the sulfide di-anion $S_2^{2-}$ (Vaughan and Tossell, 1983). Pyrite occurs in two distinct crystal structures, cubic and frambooidal, which respond quite differently to oxidation (Lowson, 1982; Mishra and Osseo-Asare, 1988). The frambooidal form decomposes easily while the cubic structure is more stable. The pyrite mineral has a characteristic brass-yellow color, and is a diamagnetic semiconductor. Some physical properties of pyrite are given in Table 2.8.

Table 2.8  Some physical properties of pyrite (Lowson, 1982)

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Mass</td>
<td>g mol$^{-1}$</td>
<td>119.98</td>
</tr>
<tr>
<td>Density</td>
<td>g cm$^{-3}$</td>
<td>5.0</td>
</tr>
<tr>
<td>$\Delta G^\circ_{298K}$</td>
<td>kJ mol$^{-1}$</td>
<td>-166.94</td>
</tr>
<tr>
<td>Resistivity: n-type mean</td>
<td>$\Omega \cdot m$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Resistivity: p-type mean</td>
<td>$\Omega m$</td>
<td>$2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

2.4.3.2  Thermodynamics of the oxidation of pyrite

The oxidation behaviour of pyrite is determined by both equilibrium and kinetic considerations. The Eh-pH diagram as given in Figure 2.11 for the FeS$_2$-H$_2$O system may be used to determine the theoretical thermodynamic relationships for the behaviour of pyrite in an aqueous system (Tao et al., 1994; Ciminelli, 1987). It can be seen that pyrite is stable in a relatively broad range from approximately pH 1 to pH 13.

The potential range for pyrite stability is from approximately $-0.6$ to $+0.3$ V. It is interesting to note that above pH 13, pyrite is no longer thermodynamically stable at any potential. The rest potential of pyrite is about 0.3 V at pH 9.2, 0.2 V at pH 10 and -0.07
V at pH 11 (Tao et al., 1994; Ahlberg et al., 1990; Ahmed, 1978). Thus, normal oxidants such as oxygen can oxidize pyrite in alkaline media yielding iron hydroxides and sulfate ions. At high pH values, the iron exists in the form of hydrated iron oxide species (Hamilton and Woods, 1981, Caldeira et al. 2003). It should be emphasized that this diagram does not show the presence of metastable sulfur species as shown in Figure 2.2.

Elemental sulfur may be obtained as an end product of pyrite dissolution in acidic solutions, but it is not stable in alkaline media. Mishra and Osseo-Asare (1988) detected the formation of thiosulfate as an intermediate product in the anodic dissolution process for pyrite. Mycroft et al. (1990) have suggested that the electrochemical oxidation of pyrite surfaces between 0.15 and 0.75 V (vs. SCE) in near-neutral aqueous solutions

Figure 2.11  Eh-pH diagram for the pyrite-water system at 25 °C and for 10^{-5} M dissolved species (after Tao et al., 1994). The dashed line indicates the regional boundary within which certain species are metastable.
results in the formation of polysulfides and sulfur. Li and Wadsworth (1993) confirmed, by Raman spectroscopy studies, that the formation of sulfur and polysulfides on pyrite surface could only be detected at high potentials above about 0.8 V (vs. SCE) in alkaline solutions. However, Hamilton and Woods (1981) suggested the formation of a monolayer of sulfur on oxidized pyrite surface in solutions with pH 9.2 at a potential of about 0.0 V.

2.4.3.3 Oxidation by oxygen in alkaline solutions

The aqueous oxidation of pyrite by molecular oxygen has attracted scientific interest for more than 100 years (Lawson, 1982). It is generally believed that the overall stoichiometry for aqueous oxidation by molecular oxygen in alkaline solutions may be represented as

$$4\text{FeS}_2 + 15\text{O}_2 + 16\text{OH}^- = 4\text{Fe(OH)}_3 + 8\text{SO}_4^{2-} + 2\text{H}_2\text{O}$$ (2.85)

The iron hydroxide may form goethite (FeOOH), and then hematite (Fe$_2$O$_3$), as the water of hydration is removed at higher temperatures (Marsden and House, 1992; Goldhaber, 1983). In hydroxide medium, hematite is the main product of iron oxidation while in contrast the main constituent is ferrihydrite in carbonate medium (Caldeira et al., 2003).

The formation of iron hydroxide layers hinders the rate of further oxidation by oxygen. In hydroxide media, pyrite particles are initially covered by a thin oxide layer that fractures after longer reaction times with most of the oxide reporting to the aqueous phase (Caldeira et al., 2003). In carbonate solutions, the particles of pyrite after oxidation are initially covered by a discontinuous oxide coating that grows with reaction time, thus increasing the overall pyrite surface coverage.
Metastable sulfur oxyanions such as thiosulfate, polythionates and sulfite can form as intermediates in the oxidation of sulfur to sulfate, depending on the pH and potential of the medium (Goldhaber, 1983; Rolia and Tan, 1985; Moses et al., 1987; Luther III, 1987; Lulham, 1989; Rossovsky, 1993; Mishra and Osseo-Asare, 1988). Goldhaber has observed that at pH values greater than 7, the major sulfur oxidation products are thiosulfate (65-80%) and sulfite. The ultimate oxidation of thiosulfate to sulfate is delayed by an “induction period”, the duration of which increases with alkalinity (Rolia and Chakrabarti, 1982). However, pyrite itself is an electrocatalyst for the oxidation of thiosulfate to sulfate by oxygen in aqueous solutions (Xu and Schoonen, 1995). The production of thiosulfate may be described by the overall equations

\[
4\text{FeS}_2 + 7\text{O}_2 + 8\text{OH}^- = 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O} + 4\text{S}_2\text{O}_3^{2-} \tag{2.86}
\]

\[
4\text{FeS}_2 + 11\text{O}_2 + 6\text{CO}_3^{2-} = 2\text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 2\text{S}_2\text{O}_3^{2-} + 6\text{CO}_2 \tag{2.87}
\]

Use of lime, compared to NaOH or Na\textsubscript{2}CO\textsubscript{3}, appears to reduce the rate of thiosulfate formation, presumably because it can form less soluble intermediates, e.g., polysulphanes (Rolia and Tan, 1985). The formation of thiosulfate is of great importance because gold in pyritic ores may be complexed with thiosulfate and can therefore dissolve in alkaline solutions as reported by Lulham (1989).

Despite the possible formation of elemental sulfur in alkaline media (Hamilton and Woods, 1981; Rolia and Tan, 1985; Lowson, 1982), Buckley and Woods (1987) found from an XPS study that no elemental sulfur was formed on the surface of pyrite exposed to air-saturated alkaline environments.
2.4.3.4 Kinetics of the oxidation of pyrite by oxygen

As the principal reaction between oxygen and pyrite is a heterogeneous surface reaction between a dissolved gas and a solid surface, the reaction rate may be limited by the oxygen transfer from the gas phase to the liquid phase. However, this limitation can be removed by the use of high pressures.

As in the case of arsenopyrite, the initial oxidation rate of pyrite can be described by the following rate equation

\[- \frac{(1/S) \, dN(FeS_2)/dt}{k} = e^{(-Ka')/RT} [OH]^a P_{O_2}^b\]  \hspace{1cm} (2.88)

A variety of reaction orders have been reported. A fractional order of about 0.5 with respect to oxygen partial pressure has been found (Ciminelli and Osseo-Asare, 1986 and 1995a, b; Stenhouse and Armstrong, 1952; Lin et al., 1986) while Koslides and Ciminelli (1992) obtained a reaction order of 0.31. According to Wheelock (1981), the reaction rate becomes nearly independent of oxygen partial pressure above 810 kPa in sodium carbonate solutions. Fractional order kinetics is usually viewed as evidence that the rate-controlling step involves an adsorption or desorption process, with the surface concentrations being defined by a nonlinear, typically Langmuir, isotherm (Lowson, 1982; Hiskey and Wadsworth, 1981). A fractional order dependence on hydroxyl ion concentration has also been reported in alkaline media. Koslides and Ciminelli (1992) found an order of 0.23 in NaOH media while Ciminelli and Osseo-Asare (1986 and 1995a) obtained an order of 0.1 in Na\(_2\)CO\(_3\) solutions. The activation energies for the alkaline oxidation of pyrite by oxygen have been calculated to range from 40 to 90 kJ mol\(^{-1}\), indicating a chemical rather than a mass transport rate-determining step (Lowson 1982; Ciminelli and Osseo-Asare, 1986). However, Koslides and Ciminelli (1992) have
suggested that the rate-determining step changes from chemical control to diffusion control when the temperature is above 100 °C.

The initial oxidation rate of pyrite by oxygen in sodium carbonate solutions has been found to be inversely proportional to the diameter of the particles (Ciminelli and Osseo-Asare, 1986). An inverse first order relationship characterizes reactions controlled by either mass transfer in the liquid phase or by chemical reaction. If the reaction were limited by diffusion in the solid product, i.e. the iron oxide coating, an inverse relationship between initial rate and the square of particle size would be expected (Ciminelli and Osseo-Asare, 1986; Levenspiel, 1999).

2.4.3.5 Mechanism of the oxidation of pyrite

There are a number of reaction mechanisms that have been suggested (Lowson 1982; Goldbaber, 1983). Bailey and Peters (1976) have demonstrated, using $^{18}$O as a marker, that sulfate oxygen originates from water rather than molecular oxygen while 100% of the reactant oxygen becomes product water in pyrite pressure leaching. Rolia and Tan (1985) have found that very little dissolved oxygen is necessary to generate thiosulfate indicating an electrochemical process involving water. Thus, an electrochemical mechanism for the dissolution of pyrite has been proposed (Mishra and Osseo-Asare, 1988), which involves the formation of thiosulfate as an intermediate product. The following steps have been suggested for the anodic oxidation of pyrite in aqueous solutions:

\[
\begin{align*}
\text{FeS}_2(s) + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}\text{S}_2(s) + \text{H}^+ + \text{e}^- \\
\text{Fe(OH)}\text{S}_2(s) & \rightarrow \text{FeS}_2\text{(OH)}(s) \\
\text{FeS}_2\text{(OH)}(s) + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2\cdot\text{S}_2\text{(OH)}_2(s) + 3\text{H}^+ + 3\text{e}^-
\end{align*}
\]
\[
\text{Fe(OH)}_2\cdot\text{S}_2\text{(OH)}_2(\text{s}) \rightarrow \text{Fe}^{2+}_{\text{(aq)}} + \text{S}_2\text{O}_3^{2-}_{\text{(ads)}} + 2\text{H}^+ + \text{H}_2\text{O} + 2e^- \quad (2.92)
\]

Thiosulfate is either further oxidized to sulfate through a series of sulfur oxyanions or may decompose to produce elemental sulfur and bisulfite (see Section 2.2.1.2). With oxygen as the oxidant in alkaline media, the cathodic process on the pyrite surface is suggested to occur as in Equations 2.16, 2.19 and 2.20 (see Section 2.1.3.1), with the formation of hydrogen peroxide as the rate-controlling step.

### 2.4.4 Alkaline Oxidation of Chalcopyrite

This part of the literature review only briefly outlines the oxidation of chalcopyrite in alkaline media due to the possible presence of minor amounts of chalcopyrite in refractory arsenopyrite-pyrite containing gold ores and the effects of copper on the dissolution of gold in alkaline thiosulfate solutions.

Chalcopyrite is the major source of copper metal. It has a chemical formula \(\text{CuFeS}_2\) that is represented as a ionic structure \(\text{Cu}^+\text{Fe}^{3+}(\text{S}^2^-)_2\) (Hiskey and Wadsworth, 1981). It has a tetragonal crystal structure and is an n-type semiconductor. It has a lower rest potential than pyrite, suggesting that it will act as an anode when contact with pyrite in aqueous solutions (Hiskey and Wadsworth, 1981; Rand, 1977).

The Eh-pH diagram (Peters, 1976) indicates that chalcopyrite is unstable at high pH values. The relevant oxidation reaction in alkaline media is suggested as (Trahar, 1984):

\[
\text{CuFeS}_2 + 3\text{H}_2\text{O} = \text{CuS} + \text{Fe(OH)}_3 + \text{S}^0 + 3\text{H}^+ + 3e^- \quad E^0 = + 0.547 \text{ V} \quad (2.93)
\]

Thiosulfate has been detected during the oxidation of \(\text{CuFeS}_2\) by oxygen in solutions with pH 9.8 and its concentration in the slurry is reduced in the presence of pyrite,
presumably due to its reduction by Fe$^{2+}$ ions from the oxidation of pyrite (Rao et al., 1976). Elemental sulfur has also been detected on the surface of CuFeS$_2$.

In the case of leaching with oxygen in ammoniacal solutions, the generally observed leaching reaction for chalcopyrite is expressed as (Hiskey and Wadsworth, 1981):

$$2\text{CuFeS}_2 + 8.5\text{O}_2 + 4\text{OH}^- = 2\text{Cu}^{2+} + \text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 2\text{H}_2\text{O} \quad (2.94)$$

$$\text{Cu}^{2+} + 4\text{NH}_3 = \text{Cu(NH}_3)_4^{2+} \quad (2.95)$$

Thiosulfate and polythionates are found to be intermediates and subsequently oxidized to sulfate (Peters, 1976). It has been found that the kinetics for the ammoniacal leaching of chalcopyrite is approximately half order with respect to hydroxyl, cupric ions and oxygen at low pressures. At high pressures, the rate becomes zero order with respect to oxygen. The electrochemical reactions proposed include the anodic dissolution of CuFeS$_2$:

$$2\text{CuFeS}_2 + 38\text{OH}^- = 2\text{Cu}^{2+} + \text{Fe}_2\text{O}_3 + 4\text{SO}_4^{2-} + 19\text{H}_2\text{O} + 34\text{e}^- \quad (2.96)$$

and two parallel cathodic reactions involving the discharge of oxygen without and with the cupric ion autocatalytic effect (Equation 2.16).

The oxidative leaching of chalcopyrite, either in acid or ammoniacal systems, has drawn substantial interest from a number of investigators with the aim of developing a new process to extract copper and noble metals from chalcopyrite concentrates.

### 2.4.5 Eh Measurements

The oxidation or reduction conditions to which sulfide minerals are exposed in aqueous solutions may be monitored by measuring the potential of an indicator electrode.
such as platinum or gold metal placed in the solution (Woods, 1976; Rand and Woods, 1984). The potential measured with a reference electrode such as silver/silver chloride electrode is generally called the 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 (1938) and extended by several investigators (Nicol et al., 1975; Rand and Woods, 1984; Nicol, 1993; Nicol and Lazaro, 2002) 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 Red$_1$/Ox$_1$ and Red$_2$/Ox$_2$ as given by the Nernst equation are not equal:

\[
E_{\text{Red}_1/\text{Ox}_1}^R = E_{\text{Red}_1/\text{Ox}_1}^0 + \frac{RT}{n_1F} \ln\left(\frac{[\text{Ox}_1]}{[\text{Red}_1]}\right) \tag{2.97}
\]

\[
E_{\text{Red}_2/\text{Ox}_2}^R = E_{\text{Red}_2/\text{Ox}_2}^0 + \frac{RT}{n_2F} \ln\left(\frac{[\text{Ox}_2]}{[\text{Red}_2]}\right) \tag{2.98}
\]

\[
E_{\text{Red}_1/\text{Ox}_1}^R \neq E_{\text{Red}_2/\text{Ox}_2}^R \tag{2.99}
\]

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 (see Figure 2.12). 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 another words, the sum of the rates of anodic reactions must be equal to that of the rates of the cathodic
reactions at the mixed potential, since the net current flow is zero. This is illustrated in Figure 2.12 (Rand and Woods, 1984).

![Figure 2.12 Schematic representation of a mixed potential system (Rand and Woods, 1984).](image)

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 by 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 measured by a gold electrode (Woods, 1976).

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 indicator
electrodes to be cleaned before transfer from one system to another in order to obtain clean, reproducible surfaces (Rand and Woods, 1984).

The mixed potential of an inert electrode in the bulk of a leach solution or pulp is not identical to that experienced by an oxidizing mineral surface in the same solution because there can be additional anodic processes involving the mineral surface or reactions of the mineral with dissolved species in the pulp. Only the mixed potential measured using the mineral electrode is representative of the dissolution processes (Woods, 1976; Nicol et al., 1975). However, in some cases such as sulfide flotation, the mixed potential of sulfide minerals is frequently close to that of a platinum or gold electrode because both respond in a similar manner (Trahar, 1984). The platinum or gold electrode employed in a concentrated sulfide mineral slurry may act as a slurry electrode and take up the potential of the sulfides rather than the potential which the metal electrode would report in filtered solution (Woods, 1976). Thus, the Eh determined by a noble metal electrode may, in favourable cases, monitor the relevant electrochemical condition of the sulfide surface.

2.4.6 Electrochemical Interactions between Sulfide Minerals

Most sulfides are good semiconductors. There are considerable differences between the reactivities of these sulfides. It has been found that pyrite is a good electrocatalyst for reduction of oxygen and the evolution of hydrogen, being much more active than most other sulfide minerals (Rand, 1977). The more active minerals, namely pyrite, pentlandite, and copper sulfides, are only slightly less active for oxygen reduction than gold. The order of reactivity for reduction of oxygen at pH 9.06 is pyrite > chalcopyrite > arsenopyrite > pyrrhotite > galena (Rand, 1977). Thus, pyrite will act as a
cathode when in contact with other sulfides including arsenopyrite and chalcopyrite while these sulfides act as an anode in oxygenated alkaline media. Galvanic coupling between pyrite and other sulfide minerals can result in an accelerated oxidation rate of these minerals and passivation of pyrite under leaching conditions (Hiskey and Wadsworth, 1981).

### 2.4.7 Effect of Fine Grinding on Sulfide Oxidation

Grinding in steel mills is a common practice in the mineral processing industry, but the normal ball or autogenous mills become increasingly inefficient at sizes below about 45 microns. In some gold ores, an important fraction of the gold is locked in gangue minerals smaller than 45 microns and is therefore not readily amenable to cyanidation. Ultra fine grinding is particularly useful when treating refractory pyritic gold ores and calcines in which gold is coarser in size, ranging from 1 to 20 microns (Corrans and Angove, 1991). A number of studies have been reported using the ultra-fine grinding technology to leach gold and/or oxidize sulfide minerals in a one step process (Liddell, 1989; Rossovsky, 1993; Min et al., 1999; Wang et al., 1998; Huang et al., 1999; Mao et al., 1997). Thus, the use of fine grinding has become a promising treatment option for some refractory gold ores in recent years and has been extensively reviewed (Balaz and Liddell, 1999; Balaz, 2000).

It has been claimed that fine grinding will create disorder in the crystal structures of sulfide minerals, increase the surface area of mineral particles, produce new surfaces of the minerals, and thus influence the chemical reactivity of the sulfide minerals (Balaz, 2000). Inert pyrite has been found to be more active for oxidation after ultra-fine grinding and thus fast kinetics of oxidative dissolution of pyrite can be achieved (Huang
et al., 1999; Balaz, 2000). Bocharov and Golikov (1967) studied the kinetics of oxidation of some sulfide minerals during wet-grinding with free access of oxygen. They have found that grinding pyrite and quartz in a steel mill abrades the metallic iron, which is little oxidized in alkaline media. The presence of the metallic iron phase establishes reducing conditions (Rolia and Tan, 1985), and the larger is the relative area of metallic iron phase in galvanic contact with the sulfide mineral, the greater is the reduction in the potential of the mineral surface (Rao et al., 1976). Thus, during the grinding of pyrite, sulfur species of low valence state may be formed, including FeS, SO$_3^{2-}$, S$_2$O$_3^{2-}$, polythionates and possible elemental sulfur, the amount of which depends on grinding conditions (Bocharov and Golikov, 1967; Rolia and Tan, 1985). Cases et al. (1993) detected by XPS the presence of iron oxyhydroxides and oxidized iron-sulfur compounds (FeSO$_4$·nH$_2$O) on the surface of pyrite after wet-grinding in an iron rod mill and a stainless steel mill. The surface of arsenopyrite after wet-grinding contains S(-2) and S(+6) with sulfate sulfur prevailing (Balaz, 2000). Welham (2001) has studied the fine grinding of a gold-bearing pyrite/arsenopyrite concentrate, and found that the selective oxidation of arsenopyrite over pyrite is possible by grinding in oxygen, with arsenopyrite decomposing to arsenic oxide and iron sulfate and pyrite remaining essentially unreacted. Chalcopyrite was found to be oxidized at a higher rate than pyrite at various pH values (Bocharov and Golikov, 1967).

2.4.8 Effects of Sulfide Minerals on the Dissolution of Gold

Gold is associated with a variety of minerals in its ores including conductive sulfide minerals and thus its dissolution could be affected by the presence of these minerals. Lorenzen and Deventer (1992) have found that the leaching behaviour of gold in cyanide solutions depends largely on the galvanic interaction between gold and the
sulfide minerals and partially on the formation of a passivating film on the gold surface. Gold in contact with conducting minerals will passivate as a result of the enhanced magnitude of the cathodic current, resulting in decreased gold dissolution rates. Chalcopyrite, pyrite and pyrrhotite cause the largest decrease in the rate of gold leaching when in contact with gold. Galena strongly enhances the dissolution rate owing to the positive action of dissolved Pb\(^{2+}\) ions on the surface oxidation of gold. In contrast, Liu and Yen (1995) reported that their results were contrary to those of Lorenzen and Deventer in oxygen-enriched cyanide solutions. They have concluded that the leaching behaviour of gold and silver in the presence of various sulfide minerals depends strongly on both the solubility of the sulfides and the oxygen concentration in solution.

Zhuchkov and Bubeev (1992) studied the effect of the contact of gold with sulfide minerals on its behaviour in thiosulfate solutions by electrochemical techniques. They concluded that the presence of sulfide minerals increased the dissolution rate of gold in the sequence chalcopyrite < pyrrhotite < arsenopyrite < pyrite. The optimum particle size ratio of sulfide minerals to gold was 5.

2.4.9 Summary

Refractory gold ores containing arsenopyrite and pyrite require breakdown of the sulfide minerals to liberate the gold for further extraction by cyanidation or other processes because the gold frequently is very fine and even “invisible”. Ultra-fine grinding technology may benefit gold leaching from some pyritic ores, but has no major beneficial effect on the recovery of gold from ores containing arsenopyrite during the leaching of gold by cyanidation. Ultra-fine grinding can greatly accelerate the oxidation of sulfides but the possible presence of abraded iron metal may reduce the potential of
the leaching system, resulting in the formation of sulfur compounds of low valence state, such as thiosulfate or polysulfides.

Alkaline oxidation may be the preferred process for the oxidation of sulfide minerals owing to the instability of these minerals at high pH values. However, it has received little attention compared with acid oxidation. Arsenopyrite is more easily oxidized by oxygen than pyrite in alkaline media, but its oxidation chemistry and mechanism remain unclear although a number of electrochemical studies have been carried out. For example, it is not known how the arsenic and sulfur components in the FeAsS mineral are oxidized. Are thiosulfate and elemental sulfur the intermediates of sulfur oxidation to sulfate? Pyrite is a noble sulfide mineral and not easily oxidized. The alkaline oxidation of pyrite by oxygen will yield iron hydroxides (or oxides) and sulfate ions, forming thiosulfate, polythionates, sulfite, and possible sulfur as the intermediates. Chalcopyrite can also be oxidized at high pH values, forming sulfur, thiosulfate, sulfate and iron hydroxides. In alkaline systems containing arsenopyrite, chalcopyrite and pyrite arsenopyrite will be the first to be oxidized and pyrite will be the last.

Thiosulfate formed during the alkaline oxidation of pyrite by oxygen may react with gold particles, forming dissolved gold complexes. The dissolution rate of gold in thiosulfate solutions may be influenced by the presence of sulfide minerals, depending on the nature, amount and particle size of the mineral used. It is not known to what extent gold dissolves during the alkaline oxidation of arsenopyrite with oxygen.
CHAPTER 3 MATERIALS AND METHODS

3.1 Materials and Reagents

Table 3.1 lists the chemical reagents and mineral materials used in this study. All chemicals except those artificially synthesized in this study were used without further purification. The details of the mineral materials are described in the respective chapters.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold wire, 0.5mm diameter</td>
<td>99.9+</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>Gold rod, 3.5mm diameter</td>
<td>99.9+</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>Gold powder, spherical, 1.5-3um</td>
<td>99.9+</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>Platinum wire, 0.5mm diameter</td>
<td>99.9+</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>Platinum wire, 2mm diameter</td>
<td>99.9+</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>Na₂S₂O₃·5H₂O</td>
<td>AR, 99.5</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>NaOH</td>
<td>AR, 97</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>AR, 99.0</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>NH₃·H₂O</td>
<td>AR, 28</td>
<td>APS Chem</td>
</tr>
<tr>
<td>O₂ gas</td>
<td>Industrial grade</td>
<td>AIR LIQUIDE (WA)</td>
</tr>
<tr>
<td>N₂ gas</td>
<td>High purity grade</td>
<td>AIR LIQUIDE (WA)</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>AR, 99.5</td>
<td>APS Chem</td>
</tr>
<tr>
<td>Na₃Au(S₂O₃)₂·2H₂O</td>
<td>AR, 99.9, Au=35.78%</td>
<td>ALFA Chem</td>
</tr>
<tr>
<td>NaAuCl₄·2H₂O</td>
<td>LR, 99.0</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>AR, 98.0</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>Cu wire, 1mm diameter</td>
<td>99.9</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>Cu metal powder</td>
<td>LR, Precipitated</td>
<td>BDH Chem</td>
</tr>
<tr>
<td>CuO</td>
<td>AR, 97.5</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>CuS</td>
<td>LR</td>
<td>HOPKIN &amp; WILLIAMS</td>
</tr>
<tr>
<td>Cu₂S (Djurleite)</td>
<td>Mineral</td>
<td>Warburton Mission (WA)</td>
</tr>
<tr>
<td>CuCl</td>
<td>LR, 90.0</td>
<td>AJAX Chem</td>
</tr>
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</table>
Table 3.1 Chemicals and minerals (continued)

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S·9H$_2$O</td>
<td>AR, 98.0</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>S, sublimed</td>
<td>LR</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>AR, 99.5</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>AR, 98.0</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>AR, 99.99</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>NaAsO$_2$</td>
<td>LR, 98.0</td>
<td>BDH Chem</td>
</tr>
<tr>
<td>Na$_2$HAsO$_4$·7H$_2$O</td>
<td>AR, 98.0</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>As$_2$S$_3$, amorphous</td>
<td>Synthesized, 84.3%</td>
<td>This Study</td>
</tr>
<tr>
<td>Na$_3$AsO$_4$S·12H$_2$O</td>
<td>Synthesized, crystal</td>
<td>This Study</td>
</tr>
<tr>
<td>As standard solution</td>
<td>AR, 1000 mg l$^{-1}$</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>AR, 99.5</td>
<td>BDH Chem</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>AR, 99.8</td>
<td>APS Chem</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>HPLC grade</td>
<td>ALDRICH Chem</td>
</tr>
<tr>
<td>HOOC·C$_6$H$_4$·COOK</td>
<td>AR, 99.9</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>KBr</td>
<td>AR, 99.5</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>KCl</td>
<td>AR, 99</td>
<td>APS Chem</td>
</tr>
<tr>
<td>Br$_2$ liquid</td>
<td>AR, 99</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$·FeSO$_4$·6H$_2$O</td>
<td>AR, 99.0</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>Fe$_2$(SO$_4$)$_3$·9H$_2$O</td>
<td>AR</td>
<td>AJAX Chem</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>AR, 70%</td>
<td>APS Chem</td>
</tr>
<tr>
<td>HCl</td>
<td>AR, 32%</td>
<td>SIGMA Chem</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>AR, 98%</td>
<td>APS Chem</td>
</tr>
<tr>
<td>Arsenopyrite (FeAsS)</td>
<td>Crystal</td>
<td>Socklich, Gemhouse (WA)</td>
</tr>
<tr>
<td>Pyrite (FeS$_2$)</td>
<td>Crystal</td>
<td>Murdoch University</td>
</tr>
<tr>
<td>Gold concentrates</td>
<td>Mineral mixtures</td>
<td>Wiluna, Macraes, etc.</td>
</tr>
</tbody>
</table>

De-ionized water from a Millipore Milli-Q system was used for the electrochemical studies and distilled water for the oxidation of sulfide minerals and the dissolution of gold powders.

**Synthesis of amorphous orpiment.** The amorphous orpiment used for preparing thioarsenites was chemically synthesized according to Eary (1992). The preparation includes the following major steps:
a) Preparation of 1000 ml solution containing 0.1 M potassium hydrogen phthalate (HOOC·C₆H₄·COOK) and 0.15 M NaAsO₂ followed by deoxygenation using nitrogen for 0.5 hours and control of pH at 4.0.

b) Preparation of 1000 ml 0.23 M Na₂S solution followed by deoxygenation.

c) Mixing the Na₂S solution with the NaAsO₂ solution and stirring the mixture under nitrogen atmosphere.

d) Addition of diluted hydrochloric acid to the mixture and control of the pH at 4.0 at 25 °C. The amorphous orpiment immediately precipitates from solution as a bright yellow orange solid according the following reactions:

\[ 3\text{Na}_2\text{S} + 2\text{NaAsO}_2 + 8\text{HCl} = \text{As}_2\text{S}_3 + 8\text{NaCl} + 4\text{H}_2\text{O} \quad (3.1) \]

(e) The precipitate is aged for one day at room temperature, then filtered and washed with deoxygenated distilled water to remove phthalate and other salts before drying in a vacuum desiccator.

X-ray diffraction patterns of the precipitated orpiment showed only the broad increase in background scatter that is characteristic of amorphous solids. Diffraction peaks characteristic of crystal orpiment, realgar, native arsenic or native sulfur were not observed. After digestion in an acidic bromine-bromide mixture solution (see Appendix A2) followed by chemical element analyses using ICP (see Section 3.4.2) for As and S, the synthetic orpiment yielded a molar ratio of S:As of 1.44, giving an overall composition of As₂S₂.₈₈, which is in agreement with Eary (1992) and Helz et al. (1995). In this study, the formula As₂S₃ is used for convenience. The synthetic orpiment had a purity of 84.3%, with the balance being mainly moisture.
3.2 Apparatus

3.2.1 Electrochemical Set-up

3.2.1.1 Rotating gold disk electrode

The gold rotating disk electrode was made in the workshop at Murdoch University using a pure gold rod with a diameter of 3.5 mm and 10 mm length, with a surface area of 0.0962 cm². The gold rod was attached to a stainless steel holder using silver epoxy resin followed by mounting in araldite resin (Araldite LY 568), after which it was given a post-cure process that permitted this electrode to be used at temperatures as high as 90 °C. The gold disk electrode is graphically shown in Figure 3.1.

Figure 3.1 Cross-section of a rotating disk electrode
3.2.1.2 Rotating platinum disk electrode

The platinum rotating disk electrode was prepared following the method above described, using a platinum wire with a diameter of 2 mm and length of 10 mm. The disk surface area was 0.0314 cm².

3.2.1.3 Counter electrode

This electrode was a platinum wire of 0.5 mm diameter and 150 mm length. It was coiled and put in a glass tube with a glass frit that separated the cathodic compartment from the anodic compartment as illustrated in Figure 3.2.

3.2.1.4 Reference electrode

All measurements were carried out using a silver/silver chloride electrode (saturated potassium chloride solution, Model PJFO, IONODE) with a potential of 0.199 V (25 °C) against the standard hydrogen electrode (SHE). However, for the sake of convenience all potentials reported in this work have been converted to the SHE scale. The measured potential with respect to SHE (Eh) can be obtained by addition of the potential of this reference electrode against SHE (EhAg/AgCl) to the potential measured with respect to this reference electrode (E) as described in following equation:

\[ Eh = E + Eh_{Ag/AgCl} = E + 0.199 \text{ (V, at 25 °C)} \]  \hspace{1cm} (3.2)

At other temperatures, a temperature coefficient \(\frac{dE}{dT} = -1.01 \text{ mV K}^{-1}\) for the saturated KCl, Ag/AgCl electrode was used for potential correction (Reiger, 1994):

\[ Eh_{Ag/AgCl} = 0.199 - 1.01 \times 10^{-3} (T-273) \text{ (V)} \]  \hspace{1cm} (3.3)
3.2.1.5 Electrochemical cell

The electrochemical cell as shown in Figure 3.2 was a typical 100-ml water-jacketed glass vessel suitable for three electrodes, i.e. a working rotating disk electrode, a counter electrode and a reference electrode. The cell was fitted with an entry port at the base for the Luggin capillary which was used to separate the reference electrode from the working solutions.

3.2.1.6 Electrochemical system

The electrochemical set-up is shown in Figure 3.2. The working disk electrode was rotated using a stand and a speed controller manufactured in the workshop at Murdoch University. The potential of the working electrode was controlled with a Model 362 scanning potentiostat (Princeton Applied Research Company, USA) that was linked initially to a Bausch & Lomb Model 2000 X-Y recorder (Houston Instrument, USA) and in the later stage of this work to a LabView™ data acquisition system (National Instruments, USA). The potential of the working electrode and the current passed through it were monitored and recorded using the above system. The plots from the X-Y recorder were digitized using a UMAX Scanner (Model Astra 600S) and WinDig2.5 data digitizer software. To calculate the charge passed through the working electrode, Origin5.0 software (Microcal, USA) was used to integrate the area under the relevant curve in the recorded current-potential or current-time graphs.
3.2.2 Oxidation and Leaching System

3.2.2.1 Reactor system

The oxidation and leaching experiments were carried out in a specially designed 1-liter glass reactor with a water jacket, four baffles symmetrically fixed on the inside wall of the glass vessel, and a plastic (PVC) lid on the center of which a stationary motor was mounted to control the speed of the agitator by means of a direct current (DC) power supply. The detailed assembly of the reactor is shown in Figure 3.3. The rotation speed was calibrated using a tachometer. The reactor was designed to use air for lubrication of the seal. It had ports on the lid for various probes to monitor pH, dissolved oxygen, and the potentials of different electrodes in the reaction system. The reactor was also equipped with inlets for gas injection and for a cooling condenser for use at higher temperatures. The temperature of the reactor was controlled by circulation of thermostatted water through the water jacket as shown in Figure 3.4.

3.2.2.2 Gas supply system

In this work, commercially available high pure nitrogen, industrial grade oxygen and pressured air (400 kPa, meter reading) from the compressed air system at Murdoch University were used. The gas flow rate was measured using an air flowmeter (GAP Meter, England) and controlled by adjusting the gas regulators and valves. Prior to entering the reactor, the gases were pre-saturated with water vapor by bubbling through a gas scrubber. The oxygen partial pressure in the reaction system was controlled by adjusting the flowrates of oxygen and nitrogen under same pressures.
Figure 3.2 A schematic presentation of electrochemical set up.
Figure 3.3 Assembly of reactor and agitating units.
Figure 3.4 A schematic presentation of reactor system for oxidation of sulfide minerals and dissolution of gold.
3.2.2.3 Monitoring system

a) pH measurement. An Activon pH probe was mounted in the reactor and immersed in the reaction solution or slurry throughout an experiment. The pH signal was monitored by an Activon pH meter (Model 101) and recorded with the computer based LabView™ data acquisition system. No attempt was made to control the pH at a constant value. BDH colour coded buffers of pH 7 and pH 10 were used for the calibration of the pH probe before each use. In the case of pH measurements in alkaline solutions, a pH value higher than 12 is not considered accurate due to the limited working range of the pH probe.

b) Eh measurement. The solution or slurry potential during reaction was continuously monitored and recorded with the LabView™ data acquisition system using platinum and gold electrodes. In some experiments involving the oxidation of sulfide minerals, arsenopyrite or pyrite electrodes were used to monitor the potential response of the mineral in solutions.

A platinum electrode with a combined Ag/AgCl reference electrode (Metrohm, Switzerland) was used for the determination of the solution or slurry potential. The potential response of a gold wire electrode that was constructed in the workshop at Murdoch University was also recorded simultaneously with the same reference electrode. Aarsenopyrite and pyrite electrodes were made by embedding a small rectangular chip (about 3 × 3 × 10 mm) of crystalline arsenopyrite or pyrite mineral in a glass tube filled with epoxy resin. Conducting silver glue was employed to connect the mineral chip to a copper wire that was used for exterior connection. Figure 3.5 shows a schematic diagram of these electrodes. The potential of the arsenopyrite or pyrite electrode was recorded
against the Ag/AgCl reference electrode. However, all potentials reported in this study have been converted to the SHE scale according to Equations 3.2 and 3.3. It should be pointed out that the reported Eh is generally a mixed potential because there are many reactions involved during the oxidation of sulfide minerals and the leaching of gold in the reactor (see Section 2.4.5 for mixed potential).

c) Measurement of dissolved oxygen. Dissolved oxygen in solution was measured using a TPS dissolved oxygen sensor (Model ED1) which was connected to the LabView™ data acquisition system. The relationships between the concentrations of dissolved oxygen ($C_{aq}$) and the potentials recorded ($E$) at various temperatures were established by recording the potentials of the oxygen probe in solutions of different concentrations of dissolved oxygen. Zero concentration of dissolved oxygen was achieved by the addition of a concentrated sulfite solution. The solutions of different oxygen concentrations were obtained by bubbling compressed air continuously into solutions of different sodium hydroxide concentrations at various temperatures. Then the dissolved oxygen concentration was calculated using the following equation established by Tromans (1998).

$$C_{aq} = (1 + \kappa C^y)^{-\eta} P_{O_2} f(T)$$  

(3.4)

where $C_{aq}$ is the molal concentration of dissolved oxygen in a solution of an inorganic solute; $C$ is the molality of the solute (mol per kg water); $P_{O_2}$ is the partial pressure of oxygen; $f(T)$ is a temperature-dependent function (Tromans, 1998); the coefficient $\kappa$ and the exponents $y$ and $\eta$ are solute-specific and have positive values. For NaOH solute, $\kappa = 0.102078$, $y = 1.00044$, $\eta = 4.308933$. At various temperatures, linear relationships between the dissolved oxygen and the recorded potential of the oxygen sensor were calculated and are shown in Table 3.2.
Chapter 3 Materials and Methods

Figure 3.5  Schematic presentation of combined Pt-Ag/AgCl electrode, gold and mineral electrodes.

Table 3.2  Relationships between O₂ concentration and the potential of O₂ sensor

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Relationship (C_{aq} / mg l⁻¹; E / V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>C_{aq} = 43.43 E − 0.48</td>
</tr>
<tr>
<td>35</td>
<td>C_{aq} = 35.02 E − 0.59</td>
</tr>
<tr>
<td>40</td>
<td>C_{aq} = 30.92 E − 0.45</td>
</tr>
<tr>
<td>45</td>
<td>C_{aq} = 26.82 E − 0.32</td>
</tr>
<tr>
<td>55</td>
<td>C_{aq} = 21.12 E − 0.27</td>
</tr>
</tbody>
</table>
3.3 Experimental Methods

3.3.1 Electrochemical Measurements

For electrochemical studies, de-ionized water from a Millipore Milli-Q system was used for all purposes. Prior to each experiment, the working disk electrode was polished using P1200 and P2400 grade silicon carbide waterproof paper and rinsed with de-ionized water, and then put in the test solution in the electrochemical cell when dry. Nitrogen or oxygen was bubbled through the solution throughout the experiment.

3.3.1.1 Open circuit potential (OCP) measurement

The open circuit potential, or rest potential is that exhibited by an electrode when immersed in solution without any externally applied potential. It is determined by the individual reversible potentials and kinetics of all the contributing half-cell reactions which occur on the electrode so that no net current flows. Therefore, it is a so-called mixed potential and indicates the potential region for possible reactions on the electrode in solution. In this work, the OCP was measured under nitrogen or oxygen atmospheres, using a rotating disk electrode and the Ag/AgCl reference electrode. The potential difference between the rotating disk electrode and the reference electrode was recorded as a function of time using the LabView™ system.

3.3.1.2 Cyclic voltammetry

This electrochemical technique is commonly used to identify the potential region of possible anodic and cathodic processes taking place on an electrode. In this technique
the current is measured as the potential applied to an electrode (by means of a potentiostat) is changed linearly with time over a potential range, and plotted against the applied potential on a X-Y chart resulting in a current-potential curve which is called as cyclic voltammogram as shown in Figure 3.6. A rate of a particular electrode reaction is indicated by the sign and magnitude of the current and the potential is an indicator of the equilibrium potential of the reaction. A current peak or plateau generally indicates that the rate is limited by diffusion of reactants or passivation of the surface (Rieger, 1994).

For diffusion-controlled reactions, the peak current is proportional to the reactant concentration and to the square root of the potential scan rate (V s$^{-1}$). If only a single anodic (positive) or cathodic (negative) sweep is performed, the technique is usually called linear potential sweep voltammetry (Rieger, 1994).

![Figure 3.6 A cyclic voltammogram at 5 mV s$^{-1}$ of a rotating (500 rpm) gold electrode in 0.1 M NaOH solution at room temperature. E$_{pa}$ = anodic peak potential; E$_{pc}$ = cathodic peak potential; i$_{pa}$ = anodic peak current; i$_{pc}$ = cathodic peak current. The arrows indicate direction of the potential sweep.](image)

Figure 3.6 A cyclic voltammogram at 5 mV s$^{-1}$ of a rotating (500 rpm) gold electrode in 0.1 M NaOH solution at room temperature. E$_{pa}$ = anodic peak potential; E$_{pc}$ = cathodic peak potential; i$_{pa}$ = anodic peak current; i$_{pc}$ = cathodic peak current. The arrows indicate direction of the potential sweep.
All voltammograms in this work were initiated after one minute of immersion of gold or platinum electrode in relevant solutions at room temperatures. The solution in the electrochemical cell for each voltammetric experiment was purged with high purity nitrogen gas for 30 minutes prior to the experiment, and during the whole experiment.

### 3.3.1.3 Constant potential coulometry

This technique is based on Faraday’s laws of electrolysis, i.e. to measure the charge passed through the electrochemical cell when a constant potential is applied to the working electrode. If an anodic reaction occurs on the working electrode and N moles of species R are oxidized to species O (Rieger, 1994),

\[
R - n\,e^- = O \quad (3.5)
\]

the electric charge through the cell, Q, should be equal to \( N \, n \, F \) (Coulombs), i.e.

\[
Q = N \, n \, F \quad (3.6)
\]

where F is Faraday constant (96485 Coulombs mol\(^{-1}\)) and n is the number of moles of electrons per mole of reaction (mol mol\(^{-1}\)). If Q and n are known, N can be determined. If the measured \( Q' \), on the other hand, is larger than the calculated Q according to Equation 3.6 for known values of n and N, there must be other anodic reactions taking place on the working electrode. Thus, a current efficiency, \( \xi \) for the oxidation of R is given as the following

\[
\xi = \frac{Q}{Q'} \quad (3.7)
\]

In this work, coulometry was used to study the electrochemical dissolution of gold in alkaline solutions at potentials lower than 0.4 V which is the standard reduction potential of oxygen at pH 14, to establish whether gold could dissolve in the solutions with oxygen. In the coulometric experiments, 30-ml of solution was used in the cell and
it was purged with nitrogen gas for 30 minutes. The polished dry gold rotating disk electrode was then immersed in the solution and the constant potential was applied. The current was recorded as a function of time using a LabView™ data acquisition system. Thus, the charge passed through the cell could be calculated by integration of the area under the recorded current-time curve using Origin 5.0 software. During some experiments, a solution sample of 3 ml was taken from the cell at intervals and a fresh 3 ml solution of the same electrolyte concentration was returned to the cell to keep the solution volume approximately constant. The samples and the final solution were analyzed for gold by atomic absorption spectrometry (AAS).

3.3.2 Dissolution of Gold

Experiments involving the dissolution of fine gold powder in thiosulfate or thioarsenate solutions were carried out in the glass reactor shown in Figures 3.3 and 3.4. Before the run, a known amount of fine gold powder was added into the reactor either as is or after wet-milling for 30 minutes in a small porcelain ball mill as shown in Figure 3.7. An alkaline solution containing thiosulfate or thioarsenate was added with nitrogen gas initially bubbled into the reactor. In the study of the effect of copper ions, the required amount of concentrated cupric sulfate solution was added before adjusting the pH of the aqueous solution. When the required temperature of 25 °C was achieved, oxygen was bubbled into the solution to initiate the dissolution of gold. The agitation was controlled at 800 rpm. During the leaching experiments, samples (5 ml) of the reacting solution were taken at given intervals and filtered through a 0.45 µm nylon membrane filter for analysis of gold by AAS. In some tests, gold powder was milled together with copper metal or copper oxide before addition to the reactor.
Chapter 3 Materials and Methods

1. Rotating motor
2. Balance blocks
3. Centrifugal ball mill
4. Transparent safety cover

Material:
- Mill vessel: Stainless steel or porcelain, Φ 150 mm, 500 ml
- Mill Balls: Stainless steel or porcelain, Φ 8 mm, 85 balls

Figure 3.7 Mechanical mill for ultra-fine grinding of sulfide minerals and/or gold powder (from Retsch, Germany).
The experiments on the reaction of gold with thioarsenites were carried out prior to the manufacture and setup of the reactor shown in Figures 3.3 and 3.4. In this case, a 500 ml Pyrex glass vessel with a water jacket was used. The lid of the vessel had several ports for an impeller, a tube for air injection, a platinum electrode, a reference electrode, and for sampling. In some experiments, the agitation of the solutions was provided using an IKA-WERK model RW20 overhead stirrer and a Pyrex impeller. A rotating speed of 600 rpm was used to keep the gold power suspended. The temperature of the reaction system was controlled via a water bath and the water jacket of the reactor. Unless otherwise stated, tests were performed at 25 °C. The gas used (air or N₂) was bubbled into the reactor after passage through a water-containing bottle immersed in the water bath and the amount of the gas was controlled by adjusting the flow rate. When the thioarsenite solution was added into the reactor, nitrogen gas was injected to remove the dissolved oxygen for 30 minutes. After the required temperature was achieved, a given amount of fine gold powder was added into the reactor and air was sparged into the solution to initiate the reaction. During the experiment, the pH of the solution was measured using an Action pH meter and the mixed potential of the solution was determined using a multimeter. Aqueous samples were taken from the reaction system at intervals of time and filtered using a 0.45 µm nylon filter followed by analysis of gold using AAS. In other experiments without any gas bubbling, a magnetic stirrer was used to keep the gold powder in suspension and the reactor was covered with a plastic film.

3.3.3 Oxidation of Sulfide Minerals and Gold Concentrates

For the oxidation of pure sulfide minerals, the weighed mineral sample was milled in a stainless steel ball mill as shown in Figure 3.7 with distilled water (water to solid mass ratio = 1) in the presence or absence of fine gold powder for 60 minutes. The
particle size of the mineral after milling was about 80% passing 4.2 µm as determined using a laser size analyzer (see Section 3.4.8). The mineral slurry was then immediately transferred into the reactor shown in Figure 3.4 with constant stirring and nitrogen gas sparging to prevent possible oxidation by oxygen for 30 minutes. Then the required amount of concentrated sodium hydroxide solution was added when the preset temperature was achieved. The experiment was initiated by introducing compressed air or oxygen gas into the reaction system through a flowmeter and a gas sparger. For oxidation of refractory gold concentrates, the above procedure was followed without the addition of fine gold powder. The particle sizes of the Wiluna concentrate samples milled for 20, 60 or 120 minutes were measured using the laser size analyzer and were found to be about 80% passing 12.4, 6.0 or 4.7 µm respectively (see Appendix A5). Distilled water was used throughout these experiments.

During the oxidation experiments, samples (about 17ml) of the reaction slurry were taken at various stages and filtered through a 0.45 µm nylon membrane filter (Millipore, USA). The solid residues were returned to the reaction system and about 13 ml distilled water (17 ml × ¾ ≈ 13 ml) was added to keep the reaction volume approximately constant. The filtrates were analyzed by AAS for As, Au, Cu and Fe, and by ICP for As and S. The final oxidation products (including filtrate, washings and residue) were also analyzed for Au, As, S and Fe. For oxidation of refractory gold concentrates, the quantities of arsenopyrite and pyrite minerals in the residues were also analyzed and estimated by the wet chemical digestion-ICP analysis, the details of which can be found in Appendix A2.
3.4 Analyses

All chemicals except those artificially synthesized in this study were used without further purification. A detailed description of the reagents employed in the analyses can be found in Table 3.1. The thioarsenates used in this study were synthesized in the laboratory. This section describes the methods and procedures employed for the various analyses conducted.

3.4.1 Atomic Absorption Spectrometry (AAS)

This technique was applied to determine the concentrations of gold, arsenic, copper and iron in solution using a GBC Avanta AAS Model 933AA and an air/acetylene flame.

3.4.1.1 Analysis for gold

Gold standard solutions for AAS were prepared dissolving Na$_3$Au(S$_2$O$_3$)$_2$·2H$_2$O (AR, 99.9%, Au = 35.78%) in 0.1 M Na$_2$S$_2$O$_3$ solution to produce a concentration of 100 mg l$^{-1}$ Au and then diluting to 2, 5, 10 mg l$^{-1}$ Au using 0.1 M Na$_2$S$_2$O$_3$ solution. At the recommended wavelength of 242.8 nm, the detection limit is 0.08 mg l$^{-1}$ Au. It was found that arsenic also absorbed at this wavelength. Therefore, when analyzing samples containing both gold and arsenic, arsenic was first determined by AAS and then the absorbance from arsenic of the same concentration was subtracted from the total absorbance of the samples to obtain the concentrations of gold. The error associated with this technique for gold was found to be less than 5%.
3.4.1.2 Analysis for arsenic

An arsenic standard solution of 1000 mg l\(^{-1}\) As from ALDRICH was employed to prepare 20, 40, 60, 80, 100 mg l\(^{-1}\) As solutions for analysis by AAS. At the recommended wavelength of 193.7 nm, the detection limitation of As was 0.7 mg l\(^{-1}\). The analysis of As by AAS had an uncertainty of \(\pm 5\%\).

3.4.1.3 Analysis for copper and iron

Dissolved iron standards were prepared from AR grade FeSO\(_4\cdot(NH_4)_2SO_4\cdot6H_2O\) dissolved in HCl solution and diluted to 2, 4, 6, 8, 10 mg l\(^{-1}\) Fe. Dissolved copper standards were prepared from CuSO\(_4\cdot5H_2O\) having 1, 2, 4, 5, 10 mg l\(^{-1}\) Cu. At the wavelengths for copper and iron of 324.8 nm and 248.3 nm respectively, the detection limits for copper and iron are 0.05 mg l\(^{-1}\). The analysis uncertainty is less than \(\pm 3\%\).

3.4.2 Inductively Coupled Plasma Spectrometry (ICP)

This instrumental analysis technique was employed mainly for determination of total dissolved sulfur in solution. It also used for analysis of arsenic in some cases, for example, for comparison with results by AAS. The instrument is a Varian ICP Model Liberty 200 located in Environmental Science at Murdoch University and wavelengths of 193.7 nm for arsenic and of 180.7 nm for sulfur were used. The uncertainty of the analysis for sulfur was \(\pm 5\%\).

3.4.3 UV/Visible Spectrophotometry
This technique was used to qualitatively detect any possible dissolved species that have absorbance in UV/Visible regions. The instrument was a Shimadzu MultiSpec-1500 UV/Visible spectrophotometer. It was found using this technique that thiosulfate, sulfide, sulfite, arsenite, arsenate and thioarsenates all have a positive absorbance while sulfate has negative absorbance in the 195-300 nm region.

### 3.4.4 High Pressure Liquid Chromatography (HPLC)

This instrumental analysis technique was used to simultaneously determine dissolved arsenic species such as arsenite, arsenate, thioarsenates and sulfur species such as sulfate, sulfite, thiosulfate, tetrathionate and other polythionates. The analysis method was based on the work reported by Schwedt and Rieckhoff (1996) for thioarsenate determination, Tan and Dutrizac (1987) for As(III) and As(V) determination and Weir et al. (1994) for sulfur species.

#### 3.4.4.1 Instrumentation for HPLC

The instrumentation for HPLC consisted of an in-line degassing system (Alltech, USA), a Waters 501 HPLC pump, a Rheodyne 7725i manual injector valve, a 20-µl sample loop, a separation column, a Waters 481 LC spectrophotometer, a Waters System Interface Module (SIM), and a Waters Millenium 32 workstation. Two separation columns were used: the main analysis column was a PRP-X100 polymer anion exchange column (Hamilton, USA), 150 mm x 4.1 mm ID, particle size 10 µm; the other was an Allsep™ SS anion column (from Alltech), 100 mm x 4.6 mm ID, particle size 7 µm, which was used in some cases for tetrathionate analysis. An All-guard column from Alltech was employed to protect the separation column. The chromatographic analysis
for all species except tetrathionate was carried out using 10 mM bicarbonate/carbonate buffer solution (8 mM NaHCO₃ + 2 mM Na₂CO₃) with a pH of 9.7 at a flow rate of 2.0 ml min⁻¹ at 19 ± 1 °C using a detector wavelength of 205 nm. A 50-µl syringe was used to introduce samples to the analysis system. The output was recorded and processed using Waters Millennium 32 software. A schematic presentation of the instrumentation is shown in Figure 3.8.

3.4.4.2 Solutions for HPLC

In this work AR grade chemicals were used for preparing standard solutions and buffer eluants except thioarsenates which were synthesized according to Schwedt and Riechhoff (1996). De-ionized water from Millipore Milli-Q system was used for all solutions. All solutions were filtered through a 0.45 um nylon membrane filter (Millipore, USA) before use.

a) Synthesis of thioarsenates. The thioarsenates (Na₃AsO₃S and Na₃AsO₂S₂) was synthesized in the laboratory because of the lack of commercially available reagents. To prepare sodium monothioarsenate (Na₃AsO₃S), 1.44 grams of sublimed elemental sulfur (0.045 mol S) was added to a mixture of 5.00 grams of As₂O₃ (0.050 mol As) and 6.00 grams of NaOH (0.150 mol Na) in 20 ml distilled water and then the solution was heated to 100 °C. After 2 hours, the excess sulfur was filtered off and the solution was cooled slowly to 4 °C. Colorless needle-shaped crystals were obtained and dried in a vacuum desiccator. This material was mainly Na₃AsO₃S·12H₂O with 16.73% As and a purity of 98.3% as determined by analysis by AAS and HPLC. The impurities consisted of minor amounts of Na₂SO₃, Na₂S₂O₃ and Na₃AsO₃. The ion chromatogram for a solution containing 3.03 mM Na₃AsO₃S is shown in Figure 3.9. The synthesis of
dithioarsenate followed a similar procedure to the above but with an increased amount of sulfur (Schwedt and Rieckhoff, 1996). This material was found to be a mixture of 34.1% (by mass) Na$_3$AsO$_2$S$_2$ and 16.7% Na$_3$AsO$_3$S as determined by AAS and HPLC. Figure 3.10 shows the ion chromatogram for a 0.25mM Na$_3$AsO$_2$S$_2$ solution prepared using the synthesized salt.

b) **Standard solutions.** The standard solutions of thioarsenates for HPLC were made up by preparing first a solution of 10 mM and then diluting as appropriate using the eluant. All standard solutions are given in Table 3.3. An arsenite solution of 10 mM was prepared from As$_2$O$_3$ dissolved in 30 mM NaOH solution and diluted as appropriate. All other AR chemicals were salts of sodium of the relevant ions (see Table 3.1). It is noteworthy that the formula of some species has been modified to reflect their form in a buffer of pH 9.7.

c) **Buffer eluants.** Sodium hydrogen carbonate, sodium carbonate and acetonitrile were used to prepare mobile buffer solutions for HPLC. The main eluant was 10 mM bicarbonate/carbonate buffer solution (8 mM NaHCO$_3$ + 2 mM Na$_2$CO$_3$) with a pH of 9.7. In the analysis of tetrathionate, a solution of acetonitrile-water (50:50 volume ratio) with 8 mM bicarbonate/carbonate (4 mM NaHCO$_3$ + 4 mM Na$_2$CO$_3$) was employed as a buffer solution. Prior to use for HPLC, the eluant was filtered through a 0.45 µm nylon membrane filter and degassed for 30 minutes in an ultrasonic apparatus.

d) **Sample solutions.** Sample solutions without any pretreatment were first diluted to appropriate concentrations using the buffer solution and filtered through a 0.45 µm nylon membrane filter to protect the separation column. Thereafter, a 20 µl sample was injected into the HPLC system using a 50-µl syringe.
Figure 3.8  Instrumentation set-up for high pressure liquid chromatography.
Figure 3.9  Ion chromatogram for a 3.03 mM solution of Na₃AsO₃S using CO₃²⁻·HCO₃⁻ eluant with UV detection. (a) H₂AsO₃⁻, (b) SO₃²⁻, (c) HAsO₃S₂⁻, (d) S₂O₃²⁻.

Figure 3.10  Ion chromatogram for a 0.25 mM Na₃AsO₂S₂ solution prepared using the synthesized Na₃AsO₂S₂ with UV detection and CO₃²⁻·HCO₃⁻ eluant. (a) HAsO₃S₂⁻, (b) HAsO₂S₂²⁻.
Table 3.3   Standard solutions for HPLC (Unit: mM)

<table>
<thead>
<tr>
<th></th>
<th>HAsO₃S²⁻</th>
<th>HAsO₂S₂²⁻</th>
<th>H₂AsO₃⁻</th>
<th>HAsO₄²⁻</th>
<th>SO₃²⁻</th>
<th>SO₄²⁻</th>
<th>S₂O₃²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 1</td>
<td>0.10</td>
<td>0.25</td>
<td>0.02</td>
<td>0.5</td>
<td>0.05</td>
<td>0.5</td>
<td>0.10</td>
</tr>
<tr>
<td>Standard 2</td>
<td>0.20</td>
<td>0.50</td>
<td>0.04</td>
<td>1.0</td>
<td>0.10</td>
<td>1.0</td>
<td>0.50</td>
</tr>
<tr>
<td>Standard 3</td>
<td>0.60</td>
<td>0.75</td>
<td>0.06</td>
<td>2.0</td>
<td>0.20</td>
<td>2.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.4.4.3 Calibration and determination

Calibration curves for each species were established by plotting the peak areas of the recorded traces as shown in Figures 3.11 and 3.12 against the standard concentrations using the Waters Millenium 32 software. Linear relationships between the concentrations and peak areas were obtained and are given in Table 3.4. Also shown are the detection limits for these species and their retention times on a Hamilton PRP-X100 column with an eluant containing 2 mM sodium carbonate and 8 mM sodium hydrogen carbonate. It should be pointed out that the exact retention time for each species is sensitive to the concentrations of the constituents and the flow rate of the eluant. Note that the peak for sulfate ions is negative due to its negative absorption in the UV region.

From Figures 3.11 and 3.12, it can be seen that simultaneous analysis of arsenic species and sulfur species using HPLC is possible on the Hamilton PRP-X100 column using the sodium carbonate/sodium hydrogen carbonate eluant. The peaks for H₂AsO₃⁻, HAsO₃S²⁻, S₂O₃²⁻, HAsO₂S₂²⁻ are good, but the peaks for HAsO₄²⁻, SO₃²⁻, SO₄²⁻ tend to overlap which results in a larger uncertainty in their concentrations, being of the order of ± 10% while the analysis error for H₂AsO₅⁻, HAsO₃S²⁻, S₂O₃²⁻, HAsO₂S₂²⁻ was found to be less than 5%.
Figure 3.11  Ion chromatogram showing peaks for (a) 0.10 mM $\text{H}_2\text{AsO}_3^-$, (b) 2.0 mM $\text{HAsO}_4^{2-}$, (c) 2.0 mM $\text{SO}_4^{2-}$, (d) 0.60 mM $\text{HAsO}_3\text{S}_2^{-}$, (e) 1.0 mM $\text{S}_2\text{O}_3^{2-}$ using UV detection and $\text{CO}_3^{2-}-\text{HCO}_3^-$ eluant.

Figure 3.12  Ion chromatogram showing peaks for (a) 0.20 mM $\text{HAsO}_4^{2-}$, (b) 0.25 mM $\text{SO}_3^{2-}$, (c) 0.40 mM $\text{HAsO}_3\text{S}_2^{-}$, (d) 1.0 mM $\text{S}_2\text{O}_3^{2-}$ using UV detection and $\text{CO}_3^{2-}-\text{HCO}_3^-$ eluant.
Table 3.4 Calibration curves for various species using HPLC

<table>
<thead>
<tr>
<th>Species</th>
<th>Peak Location / min</th>
<th>Detection Limit / mM</th>
<th>Relationship (A: area; C: concentration / mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$AsO$_3^-$</td>
<td>1.15</td>
<td>0.008</td>
<td>$A = 1450000 , C - 9180$</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$</td>
<td>6.8</td>
<td>0.1</td>
<td>$A = 543000 , C - 14500$</td>
</tr>
<tr>
<td>SO$_3^{2-}$</td>
<td>7.5</td>
<td>0.05</td>
<td>$A = 1090000 , C - 44800$</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>9.6</td>
<td>0.08</td>
<td>$A = 68800 , C + 476$</td>
</tr>
<tr>
<td>HAsO$_3$S$_2^{2-}$</td>
<td>13</td>
<td>0.005</td>
<td>$A = 1520000 , C + 3610$</td>
</tr>
<tr>
<td>S$_2$O$_3^{2-}$</td>
<td>25</td>
<td>0.02</td>
<td>$A = 1480000 , C - 16900$</td>
</tr>
<tr>
<td>HAsO$_3$S$_2^{2-}$</td>
<td>36</td>
<td>0.005</td>
<td>$A = 4241700 , C$</td>
</tr>
</tbody>
</table>

For the detection of sulfide ions or polysulfides, a new Hamilton PRP-X100 anion column was employed because, on the older Hamilton PRP-X100 column used for the separation of most arsenic and sulfur species, peaks for sulfide ions occur very close to that of hydroxyl ions. Sulfide ions were found being well separated from the hydroxyl ions on the new Hamilton column using the same 10 mM bicarbonate/carbonate eluant but the retention time was longer. The detection limit for sulfide ions was about 0.2 mM.

For analysis of real samples, arsenic and sulfur species except tetrathionate were quantitatively determined simultaneously on the Hamilton PRP-X100 column. Concentrations of each species were calculated from the peak areas of their relevant peaks on the ion chromatogram using Waters Millennium 32 software. Figure 3.13 gives a typical ion chromatogram for a real aqueous sample obtained during the oxidation of arsenopyrite after 3 hours in aerated 0.625 M NaOH at 25 °C. It clearly shows that monothioarsenate and thiosulfate are the two major products under these conditions.
Figure 3.13 Ion chromatogram for a solution obtained during the oxidation of arsenopyrite in aerated 0.625 M NaOH at 25 °C after 3 hour. (a) H$_2$AsO$_3^-$, (b) HAsO$_4^{2-}$, (c) SO$_3^{2-}$, (d) HAsO$_3$S$_2^{2-}$, (e) S$_2$O$_3^{2-}$, (f) HAsO$_2$S$_2^{2-}$.

3.4.5 X-Ray Diffraction (XRD) Analysis

This technique was employed to qualitatively analyze the composition and structure of crystal or powder samples such as minerals, residues and gold concentrates. Detailed results of XRD analysis using a Philips Model 1050 XRD spectrometer for these solid samples can be found in Chapter 7, Chapter 8 and Appendix A4.

3.4.6 Scanning Electron Microscopy (SEM) Analysis

This instrumental technique was applied for the surface analysis of solid samples and the surfaces of the disk electrodes. A Philips Model XL20 Scanning Electron Microscope was used.
3.4.7 Optical Microscopy

A Nikon Model EPIPHOT 200 optical microscope was employed to examine the surface of solid materials, particularly the gold disk electrode before and after dissolution in various solutions.

3.4.8 Particle Size Analysis

A MICROTRAC Model SRA150 laser size analyzer was used to measure the particle size distribution after wet-milling of minerals and gold concentrates in the Retsch centrifugal ball mill (Section 3.3.3).

3.4.9 Wet Chemical Analysis

Wet chemical techniques, followed by AAS and/or ICP were used to quantify arsenic, sulfur, iron and/or copper in solid samples such as minerals, gold concentrates, oxidized residues and the synthetic orpiment. The powdered sulfide materials were digested in an acidic bromine-bromide mixture before AAS or ICP analysis. The procedures for the preparation of the bromine-bromide mixture and digestion of sulfide materials can be found in Appendix A2.

3.4.10 Miscellaneous Analyses

Head assays for gold concentrates and some mineral samples were carried out by UltraTrace Laboratory, WA. The elemental sulfur content of the leached residues was
measured by carbon disulfide (CS$_2$) extraction and weighing after evaporation of the CS$_2$ solvent (sensitivity 0.2 mg) (Fernandez et al., 1996a, b; Papangelakis and Demopoulos, 1990).
CHAPTER 4 ELECTROCHEMICAL DISSOLUTION OF
GOLD IN ALKALINE THIOSULFATE
SOLUTIONS

4.1 Introduction

As reviewed in Chapter 2, one of the most promising alternatives to cyanide is thiosulfate which is considered as a non-toxic lixiviant, especially for ores and concentrates which cannot be economically treated due to excessive consumption of cyanide or which contain so-called preg-robbing components which adsorb the aurocyanide complex ion. Much work has been carried out with the aim of understanding and improving the atmospheric ammoniacal thiosulfate leaching process for gold and silver. Aylmore and Muir (2001) have recently provided a comprehensive review of the chemistry involved. However, the thiosulfate leaching system has been found to be very complicated and its process is still not fully understood, which in turn hinders the development and application of the technology. In particular, the fundamental electrochemistry of the anodic oxidation of gold and of the cathodic reduction of oxygen and redox mediators such as the copper(II)/copper(I) couple have not been satisfactorily explored.

As will be reported in Chapters 7 and 8, thiosulfate was detected as one of the major oxidation products of arsenopyrite and refractory gold ores containing arsenopyrite in strongly alkaline solutions. It was suspected that this species could be responsible for
the observation that gold was found to dissolve simultaneously with oxidation of these minerals i.e. in the absence of cyanide. This chapter therefore summarizes the results of a study of the anodic dissolution of gold in alkaline thiosulfate solutions by using a rotating gold disk and electrochemical techniques. This work focuses on the anodic oxidation of gold at potentials in the region of the mixed potential of gold in oxygenated solutions, in order to establish whether this process could be responsible for the oxidative dissolution of the gold by oxygen.

4.2 Results

As reviewed in Chapter 2, the dissolution of gold in aqueous solutions is an electrochemical process and thus the rate of gold dissolution would be expected to be dependent upon the potential of the leaching solutions (Nicol, 1993). Since dissolved oxygen which could oxidize gold in thiosulfate solutions has a standard reduction potential of 0.401 V at pH 14 (see Section 2.1.3.1), electrochemical studies were focused on the potential range below 0.4 V.

4.2.1 Open Circuit Potentials

The potential attained by a gold electrode in aerated thiosulfate solutions should be a mixed potential because of the expected reactions involving oxidation of gold and reduction of oxygen (see Section 2.4.5). Therefore, open circuit potential (OCP) measurements were carried out by recording the potential of a rotating gold disk in alkaline thiosulfate solutions to establish the relevant potential region for anodic oxidation of gold in alkaline thiosulfate solutions. Figure 4.1 shows the potential of the gold electrode in a solution containing 1 M Na₂S₂O₃ plus 0.1 M NaOH with nitrogen and
oxygen bubbling respectively. It can be seen that the potential of gold increases from 0.0 V to a value of 0.05 V when exposed to solutions saturated with oxygen. The latter can be considered as a mixed potential which is within the potential range for the anodic region observed in the cyclic voltammogram obtained for gold in a solution of 1 M Na$_2$S$_2$O$_3$ plus 0.1 M NaOH as shown in Figure 4.4. The value of this mixed potential is consistent with the rest potential of gold in thiosulfate solutions reported by Wan (1997). However, the relevant current at the mixed potential is extremely low and not suitable for accurate coulometric measurements. Thus subsequent electrochemical dissolution experiments were performed at slightly more positive potentials (≥ 0.2 V).

![Figure 4.1](image1.png)

**Figure 4.1** OCP of a rotating (1000 rpm) gold electrode in 1 M Na$_2$S$_2$O$_3$ + 0.1 M NaOH solutions under nitrogen and oxygen at 23 °C.

Open circuit potentials of the gold electrode in deoxygenated and oxygenated thiosulfate solutions at a lower pH of 10.6 were also measured in the presence or absence of ammonia and are shown in Figures 4.2 and 4.3. 0.1 M ammonium sulfate was used as
a supporting electrolyte and the pH adjusted by the addition of ammonia. From Figure 4.2 it can be seen that the OCP of gold in deoxygenated ammonia solution is higher than in deoxygenated solutions containing thiosulfate at the same pH. Particularly, addition of ammonia makes the OCP of gold in deoxygenated thiosulfate solution more negative. This difference of the OCP of gold in deoxygenated solutions suggests that thiosulfate ions are adsorbed on the surface of gold.

![Graph: Open circuit potentials of a rotating (200 rpm) gold disk electrode in deoxygenated solutions of pH 10.6 at 25 °C. (a) 1 M Na₂S₂O₃ + 0.1 M (NH₄)₂SO₄; (b) 1 M Na₂S₂O₃; (c) 0.1 M (NH₄)₂SO₄. The pH of solutions a) and c) was adjusted with ammonia.](image)

Figure 4.2 Open circuit potentials of a rotating (200 rpm) gold disk electrode in deoxygenated solutions of pH 10.6 at 25 °C. (a) 1 M Na₂S₂O₃ + 0.1 M (NH₄)₂SO₄; (b) 1 M Na₂S₂O₃; (c) 0.1 M (NH₄)₂SO₄. The pH of solutions a) and c) was adjusted with ammonia.

On the other hand, as shown in Figure 4.3, gold attains a higher potential in oxygenated solution containing ammonia alone than in the solution containing thiosulfate at the same pH. More important is that in the presence of ammonium and ammonia, the potential of gold in oxygenated thiosulfate solution increases, which suggests that the addition of ammonia may increase the dissolution rate of gold with oxygen as an oxidant.
Figure 4.3 Mixed potentials of a rotating (200 rpm) gold disk electrode in oxygenated solutions of pH 10.6 at 25 °C. a) 1 M Na₂S₂O₃ + 0.1 M (NH₄)₂SO₄ ; b) 1 M Na₂S₂O₃ ; c) 0.1 M (NH₄)₂SO₄. Solutions a) and c) were adjusted to pH 10.6 with ammonia.

4.2.2 Cyclic Voltammetry of Gold

4.2.2.1 Thiosulfate solutions

Cyclic voltammograms of gold and platinum electrodes in deoxygenated 1 M Na₂S₂O₃ and/or 0.1 M NaOH solutions are shown in Figure 4.4. Gold oxidizes in 0.1 M NaOH solution at a potential higher than 0.6 V (Nicol, 1980b; Wierse et al., 1978) and no reactions take place on platinum in 0.1 M NaOH solution in this potential range. In the presence of thiosulfate there are noticeable oxidation currents on both gold and platinum electrodes at the potentials above about 0.4 V. In the case of gold there is a current peak at about 0.25 V in the solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH,
which is similar to that reported by Jiang et al. (1991; 1993a), Zhu et al. (1994a) and Chen et al. (1996). Jiang et al. (1991, 1993a) have suggested that the current peak at about 0.25 V corresponds to the anodic dissolution of gold by comparison with the thermodynamic potential but they did not provide evidence for this conclusion. This current peak can be attributed to either oxidation of thiosulfate or dissolution of gold, or both.

![Cyclic voltammograms of the gold and platinum electrodes in a more dilute solution containing 0.1 M Na₂S₂O₃ plus 0.1 M NaOH are shown in Figure 4.5 from which it is apparent that the current at about 0.25 V is very small compared to that in the more concentrated solution. This result is in agreement with Zhu et al. (1994a) who reported that there was no obvious anodic peak in dilute aqueous thiosulfate solution.](image)

Figure 4.4  Cyclic voltammograms at 5 mV s⁻¹ of rotating (200 rpm) gold and platinum electrodes in deoxygenated 0.1 M NaOH solutions with and without 1 M Na₂S₂O₃ at 23 °C. Sweeps were initiated in a positive direction from the rest potential.
The anodic current at the same potential is somewhat higher on the gold than the platinum electrode.

![Cyclic voltammograms](image)

Figure 4.5 Cyclic voltammograms at 5 mV s\(^{-1}\) of rotating (200 rpm) gold and platinum electrodes in deoxygenated solutions containing 0.1 M Na\(_2\)S\(_2\)O\(_3\) and 0.1 M NaOH at 23 °C.

4.2.2.2 Formation of sulfur film

Anodic oxidation of thiosulfate to tetrathionate and sulfate has been found to occur in slightly acid or neutral solutions by Glasstone and Hickling (1932). Previous studies with regard to the electrochemical oxidation of thiosulfate in acid or neutral solutions on gold and platinum electrodes (Loucka, 1998; Pedraza et al., 1988) have shown that thiosulfate oxidizes at the potentials investigated, with the formation of a film consisting of several sulfur bearing species on the electrodes.
The possibility of formation of a sulfur containing film during the anodic oxidation of thiosulfate in alkaline solutions was investigated in this study by using the method reported by Pedraza et al. (1988). After sweeping the potential of the gold electrode for three cycles from 0 to 0.35 V in positive direction starting at 0 V in 1 M Na₂S₂O₃ solution containing 0.1 M NaOH, the gold electrode was transferred, after rinsing, to another electrochemical cell containing only 0.1 M Na₂SO₄ solution for a potential sweep in the negative direction from 0 V as shown in Figure 4.6. The sweep was reversed at −0.8 V and reversed again at 1.6 V at 25 °C. The cathodic processes at potentials less than −0.5 V are supposed to be related to the reduction of the sulfur film, whereas the higher anodic peaks appearing at potentials greater than 1 V are also evidence of sulfur species according to Pedraza et al. (1988). Similar behaviour was reported by Wierse et al. (1978) and Hamilton and Woods (1983) for the reduction of a sulfur-covered gold electrode in alkaline solutions. Hamilton and Woods (1983) assumed that mono-layer sulfur coverage on polycrystalline gold involved $0.72 \times 10^{15}$ atom cm$^{-2}$, equivalent to a deposition charge of 0.23 mC cm$^{-2}$. In this case, estimation of the charge involved in the oxidation of the sulfur species indicates that there is a multiple layer of sulfur on the surface of gold, which is consistent with the results obtained by Louck a (1998). Wierse et al. (1978) have suggested that the sulfur-like film on the gold surface is insulating and probably responsible for the reported inhibition of redox reactions on a gold electrode with such a film.
Figure 4.6  Cyclic voltammogram at 10 mV s$^{-1}$ of a stationary gold electrode in 0.1 M Na$_2$SO$_4$ solution at 25 °C. The sweep starts from 0.2 V in negative direction. The gold electrode was previously swept in 1 M Na$_2$S$_2$O$_3$ and 0.1 M NaOH between 0 V and 0.35 V for three cycles without rotation.

Figure 4.7  Cyclic voltammograms at 5 mV s$^{-1}$ of a rotating (200 rpm) gold disk electrode in deoxygenated solutions of pH 10.6 at 25 °C containing a) 0.1 M (NH$_4$)$_2$SO$_4$ plus NH$_3$; b) 1 M Na$_2$S$_2$O$_3$ plus NaOH; c) 1 M Na$_2$S$_2$O$_3$, 0.1 M (NH$_4$)$_2$SO$_4$ plus NH$_3$. Solutions a) and c) were adjusted with ammonia.
4.2.2.3 Effect of ammonia

Since it appears that a sulfur-like film may cover the surface of gold and therefore retard the dissolution of gold in alkaline thiosulfate solutions, it would be desirable to eliminate or reduce the passivation of the gold in some ways. Addition of ammonia has been found to increase the anodic current of gold in thiosulfate solutions (Jiang et al., 1991 and 1993a; Zhu et al., 1994a; Chen et al., 1996). Hence, cyclic voltammetric experiments were carried out with deoxygenated thiosulfate solutions in the presence and absence of ammonia and the results are shown in Figure 4.7. Also shown is the voltammogram of gold in ammonia solution without thiosulfate. As seen in Figure 4.7, the anodic current in the solution containing only ammonia and ammonium ions is very low at potentials below 0.4 V, which is in consistent with the results of leaching experiments by Meng and Han (1993). However, when ammonia is added into the thiosulfate solution, the anodic current markedly increases as compared to that in the thiosulfate solution alone. The reason for this enhancement of the anodic current by ammonia is possibly due to elimination or reduction of the sulfur film on the surface of gold electrode as suggested by Figure 4.2.

4.2.2.4 Oxygen reduction

Oxygen reduction on the surface of gold in alkaline thiosulfate solution was measured by cyclic voltammetry and is shown in Figure 4.8. Clearly, the cathodic reduction current of oxygen on gold is very small in the mixed potential region of 0 to 0.1 V. This extremely low current suggests that the rate of oxidation of gold by oxygen in alkaline thiosulfate solution would be very slow.
4.2.3 Coulometric Experiments

To verify the extent of anodic dissolution of gold in alkaline thiosulfate solutions, coulometric experiments were carried out by applying a constant potential to the rotating gold disk in the electrochemical cell containing alkaline thiosulphate solution for several hours. The current passed through the cell was recorded and the electric charge was calculated by integration of the current-time transient. After the run, the solution was analyzed for gold by AAS.

4.2.3.1 Effect of potential

Figure 4.9 and Table 4.1 show the average measured dissolution rates of gold over a period of 12.5 hours in 1 M Na₂S₂O₃ plus 0.1 M NaOH solutions for potentials in
the range 0.2-0.35 V at 23 °C. Also shown are the rates calculated from the measured charge assuming a one-electron process (see Chapter 3). It is apparent that the trend in the data in Figure 4.9 is similar to that observed in the voltammogram of gold shown in Figure 4.4 with a peak at about 0.25 V. This suggests that the partial passivation on gold observed in Figure 4.4 is a steady-state effect (Rieger, 1994).

Figure 4.9 Anodic dissolution of a rotating (1000 rpm) gold electrode in 1 M Na₂S₂O₃ plus 0.1 M NaOH solutions at different potentials at 23 °C for 12.5 hours. (◊) Calculated from charge; (□) Measured from dissolved gold.

Table 4.1 Average dissolution rates of gold in 1 M Na₂S₂O₃ and 0.1 M NaOH solutions at various potentials over 12.5 hours at 23 °C, 1000 rpm rotation

<table>
<thead>
<tr>
<th>Potential / V, SHE</th>
<th>Average Charge / F cm⁻² s⁻¹</th>
<th>Dissolution Rate / mol cm⁻² s⁻¹</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1.49 × 10⁻¹⁰</td>
<td>4.53 × 10⁻¹¹</td>
<td>0.30</td>
</tr>
<tr>
<td>0.26</td>
<td>4.31 × 10⁻¹⁰</td>
<td>2.56 × 10⁻¹⁰</td>
<td>0.59</td>
</tr>
<tr>
<td>0.30</td>
<td>3.51 × 10⁻¹⁰</td>
<td>1.82 × 10⁻¹⁰</td>
<td>0.52</td>
</tr>
<tr>
<td>0.35</td>
<td>6.13 × 10⁻¹⁰</td>
<td>2.44 × 10⁻¹⁰</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Note: F is Faraday (96485 C mol⁻¹)
Figure 4.9 shows that in the potential range under study, the average measured charge is larger than the dissolution rate of gold in 1 M Na₂S₂O₃ plus 0.1 M NaOH solutions over 12.5 hours, indicating that competing processes occur, which confirms the conclusion of Zhuchkov et al. (1994) that the anodic current cannot be used without adjustment to determine the rate of gold dissolution in thiosulfate solutions. As shown in Table 4.1, the average coulombic efficiency for the dissolution of gold increases from 30% at 0.2 V to 59% at 0.25 V before declining to 40% at 0.35 V. The competing process involving the oxidation of thiosulfate therefore becomes more prominent at the higher potentials as was suggested by the results in Figure 4.4.

To better understand the kinetic behaviour of the anodic dissolution of gold in thiosulfate solution, a similar experiment was performed in a deoxygenated solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH at a potential of 0.25 V. The results shown in Figure 4.10 demonstrate that the current passed through the cell increases rapidly at the start of the experiment achieving a plateau at about 60 µA cm⁻² followed by a progressive decrease to about 15 µA cm⁻² after 5 hours, suggesting that the passivation process is relatively slow at this potential. The measured dissolution rate of gold followed a similar pattern with a decrease after 5 hours. At 0.5 hour, however, dissolved gold was not detected indicating that there is an induction period for the dissolution of gold. Figure 4.11 gives the calculated coulombic efficiency during this experiment. Clearly, the oxidation of thiosulfate is favored during the first 3 hours after which the coulombic efficiency for dissolution of gold stabilized at about 55%. Visual and microscopic examination of the gold electrode after this experiment (Figure 4.12) revealed the presence of a brown film in addition to corrosion pits on the surface.
Figure 4.10  Anodic dissolution of a rotating (200 rpm) gold disk in a solution containing 1 M Na₂S₂O₃ plus 0.1 M NaOH at 0.25 V and 25 °C.

Figure 4.11  Coulombic efficiency during anodic oxidation of a rotating (200 rpm) gold disk in a deoxygenated solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH at 0.25 V and 25 °C.
Figure 4.12 Optical microscope image of a gold disk after anodic oxidation in 1 M Na$_2$S$_2$O$_3$ and 0.1 M NaOH solutions for 12.5 hours at 0.25 V and 25 °C.

The method of Pedraza et al. (1988) as described above was again utilized to confirm the existence of the sulfur-like film on the gold electrode. The results of the voltammograms in 0.1 M Na$_2$SO$_4$ solution are shown in Figure 4.13. The current peak at a potential of about 1.4 V shown in Figure 4.13 is due to the oxidation of the sulfur-like film on the gold electrode. An untreated gold electrode gives a much lower current in this potential region. As before, the charge associated with the peak at 1.4 V is such that multi-layers are involved. Attempts to collect sufficient material for either chemical or XRD analysis were not successful.
Figure 4.13 Cyclic voltammograms (10 mV s\(^{-1}\)) for gold in 0.1 M Na\(_2\)SO\(_4\) solutions. The sweeps start from 0 V in the positive direction. (---) fresh gold electrode; (——) gold electrode oxidized at 0.25 V in 1 M Na\(_2\)S\(_2\)O\(_3\) and 0.1 M NaOH solutions for 12.5 hours at 25 °C.

Figure 4.14 Effect of rotation on anodic dissolution of gold in alkaline 1 M Na\(_2\)S\(_2\)O\(_3\) solutions for data from Table 4.2. (□) measured charge; (◊) measured dissolution of gold.
4.2.3.2 Effect of rotation speed

Figure 4.14 and Table 4.2 show that rotation of the gold disk electrode has little effect on the anodic dissolution of gold, with the rate without rotation being only slightly lower than that at rotation speeds of 200 rpm and 1000 rpm. This result suggests the rate of dissolution of gold is controlled by the rate of the electrochemical reaction rather than diffusion.

Table 4.2 Effect of rotation speed on the average anodic dissolution rate of gold in a solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH at 0.25 V, 25 °C over 12.5 hours

<table>
<thead>
<tr>
<th>Rotation Speed / rpm</th>
<th>Average Charge / F cm⁻² s⁻¹</th>
<th>Dissolution Rate / mol cm⁻² s⁻¹</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.58 × 10⁻¹⁰</td>
<td>1.45 × 10⁻¹⁰</td>
<td>0.56</td>
</tr>
<tr>
<td>200</td>
<td>3.13 × 10⁻¹⁰</td>
<td>1.66 × 10⁻¹⁰</td>
<td>0.53</td>
</tr>
<tr>
<td>1000</td>
<td>5.07 × 10⁻¹⁰</td>
<td>2.71 × 10⁻¹⁰</td>
<td>0.53</td>
</tr>
</tbody>
</table>

4.2.3.3 Effect of temperature

The effect of temperature on the anodic dissolution of gold was investigated by carrying out the coulometric experiments at a constant potential of 0.25 V at various temperatures over 12.5 hours in a solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH. The results are shown in Table 4.3 which demonstrates that, as expected, a higher temperature results in a higher average anodic current and dissolution rate of gold. The coulombic efficiency does not appear to show a consistent trend with temperature but is generally about 50%. Figure 4.15 shows the current-time transients during these
experiments. It can be seen that the reaction rate is much higher in the initial stage and after some time decreases to a lower level, which may be due to the formation of a partially passivating film on the gold surface.

Table 4.3  Effect of temperature on the average anodic dissolution rate of gold in 1 M Na₂S₂O₃ and 0.1 M NaOH solutions at 0.25 V, 200 rpm over 12.5 hours

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Average Charge / F cm⁻² s⁻¹</th>
<th>Dissolution Rate / mol cm⁻² s⁻¹</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.13 × 10⁻¹⁰</td>
<td>1.66 × 10⁻¹⁰</td>
<td>0.53</td>
</tr>
<tr>
<td>35</td>
<td>7.42 × 10⁻¹⁰</td>
<td>3.77 × 10⁻¹⁰</td>
<td>0.51</td>
</tr>
<tr>
<td>45</td>
<td>15.6 × 10⁻¹⁰</td>
<td>9.78 × 10⁻¹⁰</td>
<td>0.63</td>
</tr>
<tr>
<td>55</td>
<td>42.0 × 10⁻¹⁰</td>
<td>17.5 × 10⁻¹⁰</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Figure 4.15  Current-time transients during the anodic dissolution of a rotating (200 rpm) gold disk in a solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH at various temperatures at 0.25 V.
Based on these results, the activation energy of anodic dissolution of gold in 1 M Na₂S₂O₃ solutions can be estimated as follows. The reaction rate may be expressed by the Arrhenius equation:

\[ r = A \exp\left\{-\frac{E_a}{RT}\right\} \]  \hspace{1cm} (4.1)

where \( r \) is the average rate of the reaction (from Table 4.3); \( A \) is a pre-exponential factor; \( E_a \) is the activation energy (J mol\(^{-1}\)); \( R \) is the universal gas constant and \( T \) is the absolute temperature (K). A plot of \( \ln r \) vs \( T^{-1} \) shown in Figure 4.16 gives an apparent activation energy of about 65 kJ mol\(^{-1}\) for the dissolution of gold in the alkaline thiosulfate solutions suggesting that, as expected from the minimal effect of rotation speed on the rate, the rate of dissolution is chemically controlled at this potential, since diffusion controlled reactions usually have an activation energy of less than 25 kJ mol\(^{-1}\) (Power and Ritchie, 1975).

![Arrhenius plot for data from Table 4.3.](image)
4.2.3.4 Effect of pH

Table 4.4 and Figure 4.17 summarize the effect of pH on the anodic dissolution rate of gold in a solution of 1 M Na₂S₂O₃ at various pH values adjusted by the addition of sodium hydroxide at a potential of 0.25 V. The results indicate that the dissolution rate of gold increases significantly with increasing pH value of the solution.

Table 4.4 Effect of pH on the average anodic dissolution rate of gold in 1 M Na₂S₂O₃ solutions at 0.25 V, 25 °C and 200 rpm rotation over 12.5 hours

<table>
<thead>
<tr>
<th>pH</th>
<th>Average Charge / F cm⁻² s⁻¹</th>
<th>Dissolution Rate / mol cm⁻² s⁻¹</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.6</td>
<td>1.03 × 10⁻¹⁰</td>
<td>0.66 × 10⁻¹⁰</td>
<td>0.63</td>
</tr>
<tr>
<td>12</td>
<td>1.27 × 10⁻¹⁰</td>
<td>0.88 × 10⁻¹⁰</td>
<td>0.69</td>
</tr>
<tr>
<td>13</td>
<td>3.13 × 10⁻¹⁰</td>
<td>1.66 × 10⁻¹⁰</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Figure 4.17 Effect of pH on anodic dissolution of gold in the alkaline 1 M Na₂S₂O₃ solutions for data from Table 4.4. (□) Measured charge; (◊) Measured dissolution rate of gold.
4.2.3.5 **Effect of thiosulfate concentration**

The effect of the concentration of thiosulfate was studied by repeating the experiment in solutions containing 0.1, or 0.5 M Na₂S₂O₃ and 0.1 M NaOH in order to compare with the results obtained in 1 M Na₂S₂O₃ solution under same conditions. The results shown in Table 4.5 and Figure 4.18 indicate that there is very little gold dissolution in the dilute 0.1 M Na₂S₂O₃ solution confirming the result obtained by cyclic voltammetry in 0.1 M Na₂S₂O₃ solution. The anodic dissolution rate of gold increases linearly with thiosulfate concentration while the coulombic efficiency decreases as the thiosulfate concentration increases, which suggests that the reaction order for the dissolution of gold is one and that the order for thiosulfate oxidation is greater than one.

![Figure 4.18](image)

**Figure 4.18** Effect of Na₂S₂O₃ concentration on anodic oxidation of gold at 0.25 V for data from Table 4.5. (◊) Measured charge; (□) Dissolved gold.
Table 4.5  Effect of Na$_2$S$_2$O$_3$ concentration on the average anodic dissolution rate of gold in 0.1 M NaOH solutions at 0.25 V, 25 °C, 200 rpm over 12.5 hours

<table>
<thead>
<tr>
<th>[Na$_2$S$_2$O$_3$] / M</th>
<th>Average Charge / F cm$^{-2}$ s$^{-1}$</th>
<th>Dissolution Rate / mol cm$^{-2}$ s$^{-1}$</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>6.01 × 10$^{-12}$</td>
<td>5.98 × 10$^{-12}$</td>
<td>0.99</td>
</tr>
<tr>
<td>0.5</td>
<td>9.52 × 10$^{-11}$</td>
<td>7.44 × 10$^{-11}$</td>
<td>0.81</td>
</tr>
<tr>
<td>1</td>
<td>3.13 × 10$^{-10}$</td>
<td>1.66 × 10$^{-10}$</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Figure 4.19  Current-time transients during anodic oxidation of gold at 0.25 V in (a) 1.0 M, (b) 0.5 M, (c) 0.1 M Na$_2$S$_2$O$_3$ solutions at 25 °C, 200 rpm.

Figure 4.19 shows the variation of anodic current during the oxidation of gold in different concentrations of thiosulfate. In the 0.1 M Na$_2$S$_2$O$_3$ solution, the anodic current is very small whereas the current is much higher in the 0.5 M or 1 M Na$_2$S$_2$O$_3$ solution. In all cases, the anodic current increases to a high level initially and then gradually decreases after some time. Considering the results given in Table 4.5, it appears that the higher current in the initial stage of the anodic oxidation is mainly due to the oxidation of...
thiosulfate ions and it depends on the concentration of thiosulfate. The decrease of the anodic current in the late stage may be attributed to the formation of a partially passivating film on the surface of gold as suggested in Section 4.2.3.1.

### 4.2.3.6 Effect of ammonia concentration

The data in Table 4.6 show that the addition of ammonia leads to a higher rate of dissolution of gold at 0.25 V in thiosulfate solutions compared to the rate in thiosulfate solutions adjusted to the same pH of 10.6 with NaOH. The rate of oxidation of thiosulfate also apparently increases in the presence of ammonia. In the absence of thiosulfate, no gold was detected after 12.5 hours at a potential of 0.25 V.

The current-time transients obtained during these experiments are shown in Figure 4.20. It is apparent that the anodic oxidation current increases quickly to a maximum before decreasing over a period of several hours to a steady value which is significantly greater in the presence of ammonia. In the absence of thiosulfate, there is a negligibly small current in aqueous ammonia solution.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Average Charge / F cm$^{-2}$ s$^{-1}$</th>
<th>Dissolution Rate / mol cm$^{-2}$ s$^{-1}$</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M $\text{S}_2\text{O}_3^{2-}$ + 0.2 M $\text{NH}_4^+$ + NH$_3$</td>
<td>$2.13 \times 10^{-10}$</td>
<td>$1.42 \times 10^{-10}$</td>
<td>0.66</td>
</tr>
<tr>
<td>1 M $\text{S}_2\text{O}_3^{2-}$ + NaOH</td>
<td>$1.03 \times 10^{-10}$</td>
<td>$0.66 \times 10^{-10}$</td>
<td>0.63</td>
</tr>
<tr>
<td>0.2 M $\text{NH}_4^+$ + NH$_3$</td>
<td>$5.17 \times 10^{-12}$</td>
<td>&lt; $10^{-12}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.20 Current-time transients during anodic dissolution of a rotating (200 rpm) gold disk at 0.25 V in solutions of pH 10.6 containing (a) 1 M Na₂S₂O₃, NH₃ and 0.1 M (NH₄)₂SO₄; (b) 1 M Na₂S₂O₃ and NaOH; (c) NH₃ and 0.1 M (NH₄)₂SO₄ without Na₂S₂O₃ at 25 °C.

The appearance of the electrode was different when examined after each experiment in that, without the addition of ammonia, a visible yellowish brown film was present which can be easily rubbed from the surface. On the other hand, no visible film was observed on the pitted surface after the experiment in the presence of ammonia.

4.3 Discussion

4.3.1 Gold in Thiosulfate Solutions

Measurements of the open circuit potentials of gold in alkaline thiosulfate solutions without ammonia in the presence or absence of oxygen have shown (Figures
4.1 and 4.3) that the mixed potential of gold in oxygenated thiosulfate solutions is in the range of 0 to 0.1 V. The cyclic voltammograms shown in Figures 4.4 and 4.5 have indicated that in this mixed potential region the anodic oxidation rate of gold in thiosulfate solutions is very low. The reduction of oxygen on gold is also very slow in this mixed potential region as shown in Figure 4.8. These results suggest that gold could dissolve in alkaline thiosulfate solutions with oxygen as an oxidizing agent in the absence of copper ions and ammonia but that its dissolution rate would be extremely slow.

The dissolution rate of gold at the mixed potential can be estimated from the experimental results obtained in the coulometric studies. The rate of anodic dissolution of gold in alkaline thiosulfate solutions in the potential range from 0.2 to 0.35 V has been established as shown in Table 4.1 and Figure 4.9. It is reasonable to extrapolate the data in Figure 4.9 to the mixed potential in an oxygenated thiosulfate solution to give a rate of less than \(10^{-11}\) mol cm\(^{-2}\) s\(^{-1}\). This value is very low as compared to that in aerated cyanide solutions of about \(5 \times 10^{-9}\) mol cm\(^{-2}\) s\(^{-1}\) (Jeffrey and Ritchie, 2000). In a preliminary study reported by Webster (1986), dissolution of gold was detected in 0.1 M Na\(_2\)S\(_2\)O\(_3\) solutions without ammonia and copper after reaction with oxygen for 9 weeks. Zhang and Nicol (2002) have estimated the actual dissolution rate of gold in neutral 0.1 or 1 M Na\(_2\)S\(_2\)O\(_3\) solutions to be of the magnitude of \(10^{-13}\) mol cm\(^{-2}\) s\(^{-1}\) which is similar to the rate obtained in a 0.2 M Na\(_2\)S\(_2\)O\(_3\) solution with pH 12 in this study (see Chapter 5). These estimated dissolution rates of gold in thiosulfate solutions are much lower than that obtained by Jeffrey (2001) of about \(4 \times 10^{-9}\) mol cm\(^{-2}\) s\(^{-1}\) in ammoniacal thiosulfate solutions containing copper ions.
The very low dissolution rate of gold in alkaline thiosulfate solutions may be associated with the passivation of the surface of gold by a film containing sulfur species. Figure 4.2 shows that adsorption of thiosulfate ions on the surface of gold occurs which is reflected by the immediate decrease of the potential of a gold electrode when contacted with thiosulfate solution. The cyclic voltammograms of gold in alkaline thiosulfate solutions shown in Figures 4.4 and 4.5 suggest the possibility of adsorption on the surface of gold (refer to Rieger, 1994) and also the absence of cathodic processes suggests that the oxidation products are either dissolved or that the anodic process at potentials studied is irreversible. The current-time transients (Figure 4.10) have confirmed that the passivation process is relatively slow at a potential of 0.25 V. During the pre-passive period, oxidation of thiosulfate and adsorption of thiosulfate ions on the gold surface predominates, as there is an induction period for the dissolution of gold. The passivation can only be observed several hours later and has been confirmed by the existence of a multi-layer sulfur film on the surface of gold electrode (Figures 4.6, 4.12 and 4.13). The onset of passivation appears to occur more rapidly at higher temperatures as shown in Figure 4.14.

From the viewpoint of thermodynamics, it is possible for thiosulfate to undergo many reactions in the potential region studied. Some possible reactions involving thiosulfate in alkaline solutions are given in Table 4.7 (Lyons and Nickless, 1968; Pryor, 1960). Thus, the anodic process on the surface of gold in alkaline thiosulfate solution possibly involves an absorption reaction as the first step:

\[ \text{Au} + \text{S}_2\text{O}_3^{2-} = \text{Au} | \text{S}_2\text{O}_3^{2-} \text{(ads)} \quad (4.2) \]

and oxidation reactions as the second step:

\[ 2\text{S}_2\text{O}_3^{2-} \text{(ads)} = \text{S}_4\text{O}_6^{2-} \text{(ads)} + 2\text{e}^{-} \quad (4.3) \]

\[ \text{S}_4\text{O}_6^{2-} \text{(ads)} = \text{S}_4\text{O}_6^{2-} \text{(aq)} \quad (4.4) \]
Chapter 4 Electrochemical Dissolution of Gold in Alkaline Thiosulfate Solutions

\[
\text{Au} \mid \text{S}_2\text{O}_3^{2-} \text{(ads)} = \text{Au(S}_2\text{O}_3^-) \text{(ads)} + e^- \quad (4.5)
\]

\[
\text{Au(S}_2\text{O}_3^-) \text{(ads)} + \text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3)_2^{3-} \quad (4.6)
\]

The tetrathionate could undergo subsequent rapid decomposition to other sulfur species under alkaline conditions:

\[
\text{S}_4\text{O}_6^{2-} + 2\text{OH}^- = \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + \text{S}^0 + \text{H}_2\text{O} \quad (4.7)
\]

\[
4\text{S}_4\text{O}_6^{2-} + 6\text{OH}^- = 5\text{S}_2\text{O}_3^{2-} + 2\text{S}_3\text{O}_6^{2-} + 3\text{H}_2\text{O} \quad (4.8)
\]

Reaction 4.8 has been reported to be catalyzed by the presence of thiosulfate ions and the rate is sensitive to temperature and pH, with higher temperatures and pH leading to rapid decomposition (Rolia and Chakrabarti, 1982; Byerley et al., 1975). Reaction 4.7 is thermodynamically possible, thus producing elemental sulfur on gold surface.

### Table 4.7 Some possible reactions of thiosulfate in alkaline aqueous solutions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E^\circ / \text{V})</th>
<th>(\Delta G^\circ_{298K} / \text{kJ mol}^{-1})</th>
<th>Equation No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{S}_4\text{O}_6^{2-} + 2\text{OH}^- = \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + \text{S}^0 + \text{H}_2\text{O})</td>
<td>-161.2</td>
<td>(4.7)</td>
<td></td>
</tr>
<tr>
<td>(4\text{S}_4\text{O}_6^{2-} + 6\text{OH}^- = 5\text{S}_2\text{O}_3^{2-} + 2\text{S}_3\text{O}_6^{2-} + 3\text{H}_2\text{O})</td>
<td>-189.4</td>
<td>(4.8)</td>
<td></td>
</tr>
<tr>
<td>(\text{S}_4\text{O}_6^{2-} + 2e^- = 2\text{S}_2\text{O}_3^{2-})</td>
<td>0.08</td>
<td>(4.9)</td>
<td></td>
</tr>
<tr>
<td>(2\text{SO}_3^{2-} + 3\text{H}_2\text{O} + 4e^- = \text{S}_2\text{O}_3^{2-} + 6\text{OH}^-)</td>
<td>-0.571</td>
<td>(4.10)</td>
<td></td>
</tr>
<tr>
<td>(\text{S}^0 + 2e^- = \text{S}^{2-})</td>
<td>-0.476</td>
<td>(4.11)</td>
<td></td>
</tr>
<tr>
<td>(\text{S}_2\text{O}_3^{2-} + 2\text{OH}^- = \text{SO}_4^{2-} + \text{S}^{2-} + \text{H}_2\text{O})</td>
<td>-53.8</td>
<td>(4.12)</td>
<td></td>
</tr>
</tbody>
</table>

Note: \(\Delta G^\circ_{298K}\) data were calculated by using standard free energy data from Pourbaix (1974) except that for \(\text{S}_2\text{O}_3^{2-}\) which was calculated from the redox potential \(E^\circ\) (0.08 V) for the \(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}\) couple (King, 1994).

The sulfur could also be formed by discharge of sulfide ions (Chen et al., 1996; Hamilton and Woods, 1983) in the potential range of 0-0.4 V:

\[
\text{S}^{2-} + \text{Au} = \text{Au} \mid \text{S}^0 + 2e^- \quad (4.13)
\]

The sulfide ions may be produced from decomposition of thiosulfate on the surface of gold according to Equation 4.12, particularly at higher temperatures (Pryor, 1960):
Figure 4.15 has shown that the passivation on gold occurs more rapidly at higher temperatures. Hamilton and Woods (1983) have suggested that the sulfur layer on gold is stable in alkaline solutions, though elemental sulfur is not under these conditions. Wierse et al. (1978) reported that the adsorbed sulfur layer on gold was insulating and therefore probably responsible for the inhibition of redox reactions on gold electrodes.

Coulometric studies have shown that the anodic oxidation of gold in thiosulfate solutions is accompanied by the anodic oxidation of thiosulfate. The maximum possible rate of these reactions would be controlled by mass transport of thiosulfate to the electrode surface. This rate can be estimated using the Levich equation for a rotating disk electrode (Rieger, 1994):

\[ I_L = 0.62 n F A C_0^* D_0^{2/3} v^{-1/6} \omega^{1/2} \]  

where \( I_L \) is the limiting current in Ampere (A); \( n \) the number of electrons transferred; \( F \) the Faraday constant, 96485 C mol\(^{-1}\); \( A \) the disk area, cm\(^2\); \( D_0 \) the diffusion coefficient, cm\(^2\) s\(^{-1}\); \( v \) the kinematic viscosity, cm\(^2\) s\(^{-1}\) (\( v = \eta_s / \rho_s \); \( \eta_s \) is the coefficient of viscosity of solvent, kg cm\(^{-1}\)s\(^{-1}\) and \( \rho_s \) the density of the solution, kg cm\(^{-3}\); \( \omega \) the angular speed, s\(^{-1}\) (2\( \pi \) times the rotation frequency in hertz); \( C_0^* \) the molar concentration of bulk solution, mol cm\(^{-3}\). By considering a one-electron process such as Equation 4.5 and assuming a diffusion coefficient for thiosulfate of 1.16 \( \times \) 10\(^{-5}\) cm\(^2\) s\(^{-1}\) (calculated from the molar ionic conductivity of thiosulfate in aqueous solutions at infinite dilution and 25 °C) and \( \eta_s = 8.9 \times 10^{-6} \) kg cm\(^{-1}\)s\(^{-1}\) for water (Rieger, 1994), the limiting current density on a rotating (200 rpm) disk electrode in an aqueous solution of 1 M Na\(_2\)S\(_2\)O\(_3\) (calculated \( \rho_s = 1.16 \times 10^{-3} \) kg cm\(^{-3}\)) can be estimated to be 0.31 A cm\(^{-2}\) or 3.2 \( \times \) 10\(^{-6}\) F cm\(^{-2}\) s\(^{-1}\) which is very much higher than the current densities actually observed. This supports the idea that the
rates of oxidation of thiosulfate and gold are limited by an electrochemical process on the surface of gold.

The above mechanism for the anodic dissolution reaction of gold in thiosulfate solutions (Equations 4.5 and 4.6) suggests that the rate of dissolution of gold will be proportional to the concentration of thiosulfate i.e. first order in thiosulfate. This has been confirmed by the experimental results in Figure 4.18. The activation energy for anodic oxidation of gold in thiosulfate solutions has been estimated to be 65 kJ mol\(^{-1}\), which is close to the value of 60 ± 10 kJ mol\(^{-1}\) estimated by Breuer and Jeffrey (2000) in 0.1 M Na\(_2\)S\(_2\)O\(_3\) solutions containing copper ions and ammonia and to that of 53.6 kJ mol\(^{-1}\) for gold dissolution in 50 g l\(^{-1}\) Na\(_2\)S\(_2\)O\(_3\) solution at pH 8.3 obtained by Zhuchkov and Bubeev (1990). However, it is much larger than the value of 28.0 kJ mol\(^{-1}\) reported by Jiang \textit{et al.} (1993b) which was calculated using the total current at a gold electrode in 1 M Na\(_2\)S\(_2\)O\(_3\) solution without copper ions and ammonia. The high activation energy supports the conclusion that the dissolution of gold with thiosulfate is characteristic of chemically controlled reaction, which is further supported by lack of any effect of the rotation speed of the electrode on the rate (Figure 4.14).

Figure 4.17 has shown that higher concentrations of hydroxyl ions result in higher rates of dissolution at a fixed potential. Such results are in consistent with those of Jiang \textit{et al.} (1993b) and Chen \textit{et al.} (1996), but are contrary to those of Zhuchkov and Bubeev (1990) who observed that the maximum dissolution current decreased with increasing pH. According to the above proposed mechanism for the anodic processes on gold, it is possible that the increase of the dissolution rate with pH may be attributed to partial elimination of the sulfur film on gold surface in solutions with high concentration of hydroxyl ions, particularly at high temperatures (Pryor, 1960):
4S^0 + 4OH^- = 2HS^- + S_2O_3^{2-} + H_2O \quad (4.15)

The current-time transients shown in Figure 4.15 have suggested partial elimination of the passivating film on the surface of gold.

4.3.2 Effect of Ammonia

With addition of ammonia to an oxygenated thiosulfate solution, the mixed potential of gold becomes more positive than that in a solution containing only thiosulfate as shown in Figure 4.3. It is therefore expected that the rate of dissolution would increase in the presence of ammonia. As seen in Table 4.6 and Figure 4.7, ammonia does increase the rate of gold dissolution in aqueous thiosulfate solutions, which confirms the conclusion of Zhu et al. (1994a).

According to Jiang et al. (1993a), the effect of ammonia on the dissolution of gold is due to the following reactions:

\[
\text{Au} + 2\text{NH}_3 = \text{Au(NH}_3)_2^{+} + e^- \quad (4.16)
\]

\[
\text{Au(NH}_3)_2^{+} + 2\text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3)_2^{3-} + 2\text{NH}_3 \quad (4.17)
\]

in which gold is anodically oxidized to form the aurous di-amine complex, namely, \(\text{Au(NH}_3)_2^{+}\) which reacts with thiosulfate ions after entering the solution to form the aurous di-thiosulfate complex, \(\text{Au(S}_2\text{O}_3)_2^{3-}\). It is possible that this mechanism was suggested in the light of published data for the stability constants for the di-amine and di-thiosulfate gold complexes which appeared to be of a very similar magnitude of \(10^{26}\) (Jiang et al., 1992; Aylmore and Muir, 2001). However, predicted stability constant based on the linear free energy relationship between the stability constants for the formation of a number of silver(I) and gold(I) complexes (Hancock et al., 1974) suggests a much lower stability constant of \(10^{13}\) for \(\text{Au(NH}_3)_2^{+}\) than that for \(\text{Au(S}_2\text{O}_3)_2^{3-}\). Very
recently, Senanayake et al. (2003) studied and reviewed the thermodynamics of aqueous gold-ammonia-thiosulfate system at 25 °C. They have suggested that more reliable stability constants for Au(NH$_3$)$_2^+$ and Au(NH$_3$)$_4^{3+}$ could be $10^{13}$ and $10^{33}$ respectively, and that the reason for large discrepancy between predicted stability constants and the measured values (Guan and Han, 1995; Skibsted and Bjerrum, 1974a, b) is due to the inherent problems associated with the possibility of the disproportionation of gold(I) to metallic gold and gold(III) as described below:

$$3\text{Au(NH}_3\text{)}_2^+ = \text{Au(NH}_3\text{)}_4^{3+} + 2\text{Au} + 2\text{NH}_3$$  \hspace{1cm} K_{e, 298K} = 10^{3.7} \quad (4.18)$$

where $K_{e, 298K}$ is the equilibrium constant at 25 °C calculated from the predicted stability constants. Thus the Au(NH$_3$)$_4^{3+}$ ions must be the major species in aqueous ammonia and a much higher concentration of ammonia is required to stabilize Au(NH$_3$)$_2^+$. In addition, with the much lower stability constant of $10^{13}$ for Au(NH$_3$)$_2^+$, the standard reduction potential for reaction 4.16 can be calculated to be 0.922 V which is much higher than those reported by Guan and Han (1995) and Skibsted and Bjerrum (1974a, b). This high potential suggests that the formation of Au(NH$_3$)$_2^+$ is not favored at low potentials in aqueous ammonia solutions.

If the formation of the gold(I) ammine complexes is important, a measurable rate of dissolution of gold should be obtained in the potential region studied in solutions containing only ammonia. This was not observed in present study, supporting the view that Au(NH$_3$)$_2^+$ is not formed under these experimental conditions. The cyclic voltammogram of gold in ammonia solution at 25 °C shown in Figure 4.7 indicates that there is an extremely low anodic current below 0.4 V. This is in agreement with Breuer and Jeffrey (2002) and was confirmed by the potentiostatic measurements at 0.25 V that resulted in no measurable dissolution of gold in that solution as shown in Table 4.6. Furthermore, Meng and Han (1993) have reported the kinetics of the oxidative
dissolution of gold is very poor at room temperatures and significant gold dissolution in ammonia solutions occurs only at temperatures greater than 120 °C. Guan and Han (1996) have used galvanostatic tests to show that dissolution of gold in 1 M ammonia solutions at pH 10 does occur at 135 °C.

Thus, it appears unlikely that the above mechanism is responsible for the role of the ammonia but that the primary role of the ammonia in enhancing the dissolution of gold is associated with its ability to reduce the partial passivation of the gold surface. Figure 4.2 suggests that ammonia may reduce the adsorption of thiosulfate ion and thereby the passivation of the dissolution reaction. This is supported by the fact that a film on the surface of gold was not visually observed after anodic oxidation at 0.25 V in ammoniacal 1 M Na₂S₂O₃ at pH 10.6, whereas under the same conditions the gold surface was covered by an obvious film in a 1 M Na₂S₂O₃ solution containing NaOH. The possible role of ammonia may be described by the following reaction (Peters, 1976):

\[ 12S^0 + 6OH^- = 2S_5^{2-} + S_2O_3^{2-} + 3H_2O \]  

(4.19)

4.4 Conclusions

The cyclic voltammetric and coulometric studies have shown that anodic dissolution of gold can be measured in alkaline thiosulfate solutions at ambient temperatures at potentials above about 0.2 V. Thiosulfate ions undergo oxidative decomposition on the gold surface in the same potential region with the formation of a sulfur-like surface film which acts to partially passivate the surface for the dissolution of gold. The rate of the anodic dissolution of gold at constant potential has been found to be electrochemically controlled with activation energy of 65 kJ mol⁻¹, and the rate is
enhanced by increases in pH, concentration of thiosulfate and temperature of the solutions.

Addition of ammonia to the thiosulfate solution results in increased dissolution of gold at fixed potentials due possibly to the partial elimination of the passivating film.

Measurement of the mixed potential of a gold electrode in oxygenated thiosulfate solutions has shown that open circuit dissolution of the gold will occur with a rate which is significantly lower than that achieved by conventional cyanidation or the copper-catalyzed dissolution in ammoniacal thiosulfate solutions.
CHAPTER 5 EFFECT OF COPPER ON THE DISSOLUTION OF GOLD IN ALKALINE THIOSULFATE SOLUTIONS

5.1 Introduction

As reviewed in Chapter 2, thiosulfate appears to be the most promising alternative to cyanide for gold leaching, although much research work on thiosulfate leaching of gold over the last three decades has not resulted in its commercial introduction (Aylmore and Muir, 2001). Perhaps the main reason for this is the poor understanding of the thiosulfate leaching system which has been found to be very complicated (Wan, 1997), thus in turn hindering the development and application of the technology. In particular, the fundamental electrochemistry of the anodic oxidation of gold and of the cathodic reduction of oxygen and the role of redox mediators such as the copper(II)/copper(I) couple have not been satisfactorily explored.

The results presented in Chapter 4 have confirmed that dissolution of gold is very slow in the absence of ammonia due to formation of a sulfur-like film as a result of decomposition of thiosulfate on the surface of gold. It has been known that for leaching to occur at a reasonable rate, thiosulfate, ammonia and copper(II) must be present in solution (Wan, 1997; Abbruzzese et al., 1995; Zipperian et al., 1988). Copper(II) ions have been found to have a strong catalytic effect on the dissolution rate of gold in the presence of ammonia (Tyurin and Kakovskii, 1960; Ter-Arakelyan et al., 1984; Breuer
Chapter 5 Effect of Cu on Dissolution of Au in Alkaline Thiosulfate Solutions

The main role of copper(II) ions in the dissolution of gold is believed to be the oxidation of metallic gold by the cupric tetra-ammine complex ions as expressed in the following reaction:

\[ \text{Au} + 5\text{S}_2\text{O}_3^{2-} + \text{Cu(NH}_3\text{)}_4^{2+} = \text{Au(S}_2\text{O}_3\text{)}_2^{3-} + 4\text{NH}_3 + \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} \]  (5.1)

On the other hand, cupric tetra-ammine ions can also be reduced to cuprous thiosulfate complex ions by thiosulfate as shown in the reaction (Breuer and Jeffrey, 2003):

\[ 2\text{Cu(NH}_3\text{)}_4^{2+} + 8\text{S}_2\text{O}_3^{2-} = 2\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 8\text{NH}_3 + \text{S}_4\text{O}_6^{2-} \]  (5.2)

Consequently, the concentration of copper(II) ions present in the leaching solution is an important factor in determining both the stability of thiosulfate and the leaching of gold. Oxygen is required to convert copper(I) to copper(II) for further gold leaching. The oxidation of copper(I) by oxygen in ammoniacal thiosulfate solutions is known to occur readily and represented by reaction 5.3 (Byerley et al., 1973; 1975):

\[ 2\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 8\text{NH}_3 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{Cu(NH}_3\text{)}_4^{2+} + 6\text{S}_2\text{O}_3^{2-} + 2\text{OH}^- \]  (5.3)

However, recent results (Van Wensveen and Nicol, 2003) have shown that the copper(I) thiosulfate complexes are only oxidized at very slow rates relative to those of the copper(I) ammine complexes.

A freshly prepared solution of sodium thiosulfate containing copper(I) ions is known to be able to dissolve silver metal and silver sulfide from sulfidic ores even in the absence of ammonia. The dissolution rate of silver metal in a solution of sodium cuprous thiosulfate is nine times higher than that in a solution containing sodium thiosulfate alone (Mellor, 1929). The enhanced solvent power of sodium cuprous thiosulfate for silver metal compared with that of sodium thiosulfate has been attributed to the redox mediating effect of the copper ions. On the other hand, gold apparently does not dissolve in the sodium cuprous thiosulfate solution any more rapidly than in a solution of sodium thiosulfate alone (Mellor, 1929). Although the role of copper ions in the copper-
ammonia-thiosulfate leaching system for gold is generally accepted, the behaviour of gold in thiosulfate solutions containing copper without ammonia is less clear despite some published work on the leaching of gold in thiosulfate solutions (Breuer and Jeffrey, 2000 and 2002; Breuer et al., 2002).

As will be reported in Chapters 7 and 8, thiosulfate was detected as one of the major oxidation products of sulfide minerals in strongly alkaline solutions. In addition, up to 1 mM copper was also detected in the leaching solutions. It was suspected that these species could be responsible for the observation that gold was found to dissolve simultaneously with oxidation of these minerals in the absence of cyanide and ammonia. An electrochemical study of the dissolution of gold in alkaline thiosulfate solutions without copper has been reported in Chapter 4. This Chapter will report on an investigation of the dissolution of gold in copper bearing thiosulfate solutions in the absence of ammonia.

Detailed experimental can be found in Chapter 3. Unless otherwise stated, all experiments were carried out in solutions containing 0.2 M thiosulfate at 25 °C using a gold disk rotated at 400 rpm. The potential scan rate in the electrochemical experiments was 5 mV s⁻¹.

### 5.2 Chemistry of Copper in Thiosulfate Solutions

As reviewed in Chapter 2, copper ions in aqueous solutions containing excess of thiosulfate exist in the form of stable (thiosulfato)copper(I) complexes. In a small excess of thiosulfate, cuprous sulfide may be formed as a result of the decomposition of thiosulfate. An Eh-pH diagram for the copper-thiosulfate-water system at 25 °C shown in
Figure 5.1 summarizes the stability regions of the various copper species under different conditions. It can be seen that metallic copper is not stable in aqueous thiosulfate solutions. Various copper oxides, sulfides and other species may exist depending on the solution potential and pH. Cuprous thiosulfate is the predominant species in solution at the potentials normally encountered in the leaching of gold.

![Eh-pH diagram for Cu-S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}-H\textsubscript{2}O system at 25 °C](image)

It has been long known that copper(II) can catalyze the oxidation of thiosulfate by a variety of oxidizing agents, including oxygen in aqueous solutions while the oxidation of thiosulfate by oxygen under ambient conditions in the absence of copper ions is
known to be extremely slow (Rabai and Epstein, 1992; Rolia and Chakrabarti, 1982). The catalytic activity of copper is usually explained by assuming that the copper(II) ion undergoes a facile, rapid reduction by the thiosulfate ion to copper(I), followed by a fast oxidation of copper(I) to copper(II) as described in reactions 5.4 and 5.5:

\[ 2\text{Cu}^{2+} + 2\text{S}_2\text{O}_3^{2-} = 2\text{Cu}^+ + \text{S}_4\text{O}_6^{2-} \quad (5.4) \]
\[ 2\text{Cu}^+ + \text{Ox} = 2\text{Cu}^{2+} + \text{Ox}^{2-} \quad (5.5) \]

Reaction 5.4 is thermodynamically favored. From the redox potentials of 0.08 and 0.153V for $\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}$ and $\text{Cu}^{2+}/\text{Cu}^+$ respectively (King, 1994), its standard reaction free energy $\Delta G^\circ$ is evaluated to be -14.1 kJ mol$^{-1}$ at 25 °C. The formation of stable copper(I) thiosulfate complexes further decreases the free energy change for reaction 5.4. Reaction 5.5 in which the thiosulfate complexes are involved has been found to be very slow (Van Wensveen and Nicol, 2003).

5.3 Results

5.3.1 Mixed Potential Measurements

Figure 5.2 shows the mixed potential of a rotating gold disk electrode in aerated 0.2 M Na$_2$S$_2$O$_3$ solutions containing different copper sulfate concentrations at pH 7 and 12 at room temperature. In the solutions of pH 7, the potential of the gold electrode reaches a maximum before decreasing to a steady value of about 0.1 V at longer times. Initially, the potential increases with an increase in the concentration of copper. In the solutions of pH 12, the initial potential of the gold similarly increases with copper concentration but this is not true after longer times. It also appears that the final potential is lower at the higher pH value. At pH 7, the final potentials are very similar suggesting
that there should be little effect of copper on the rate of dissolution at this pH value. At pH 12, the trend with copper concentration is not clear. These results suggest that copper could initially increase the dissolution rate of gold in thiosulfate solutions and that a higher pH may have a negative effect on the rate of dissolution.

![Diagram of potential variation](image)

Figure 5.2 Variation of the potential of a rotating gold electrode in aerated 0.2 M thiosulfate solutions at different pH values and copper concentrations.

In other experiments, the effect of copper on the mixed potential of a gold electrode can be clearly seen in aerated 0.2 M Na₂S₂O₃ solutions at pH 7 as shown in Figure 5.3. In these experiments, a given amount of cupric sulfate or cuprous thiosulfate solution was added to the solution at the times indicated to produce a concentration of 2 mM copper. The mixed potential of gold increases immediately to a higher value and then gradually decreases to the normal level. By comparison, the mixed potentials of a
platinum electrode under same conditions do not change measurably on addition of copper ions. It is also obvious that platinum has a higher potential than gold in thiosulfate solutions, suggesting that platinum is more inert than gold in aerated thiosulfate solutions. It is possible that the increase in the potential of gold is associated with the formation of an intermediate copper(II) complex which can act to oxidize the gold. It is well known that the oxidation of thiosulfate by copper(II) ions involves the intermediate formation of a copper(II) thiosulfate complex, \( \text{Cu}(\text{S}_2\text{O}_3)_2^{2-} \) (Rabai and Epstein, 1992; see Figure 5.1).

Figure 5.3  Effect of the addition of copper ions (2 mM Cu) on the mixed potentials of rotating gold and platinum electrodes in aerated 0.2 M thiosulfate solutions at pH 7.
5.3.2 Anodic Polarization

Anodic polarization experiments were carried out to investigate the anodic behaviour of gold and platinum in thiosulfate solutions with and without copper ions. The results are shown in Figures 5.4 - 5.7. It is apparent that the anodic current becomes larger in the presence of copper than in its absence on both gold and platinum electrodes. The increase in anodic current is more obvious on the gold electrode, which suggests that copper ions could assist in the dissolution of gold in the thiosulfate solutions. Clearly, with 5 mM copper the anodic current appears to increase with the potential with a peak at a potential of about 0.28 V. This result indicates that the surface may become partially passivated during oxidation.

Figure 5.4 Anodic polarization of a rotating platinum electrode in deoxygenated 0.2 M thiosulfate solutions containing 0 mM (······), 0.5 mM (——) and 5 mM (-----) Cu ions at pH 7.
Chapter 5 Effect of Cu on Dissolution of Au in Alkaline Thiosulfate Solutions

Figure 5.5 Anodic polarization of a rotating gold electrode in deoxygenated 0.2 M thiosulfate solutions containing 0 mM (······), 0.5 mM (——) and 5 mM (-----) Cu ions at pH 7.

Figure 5.6 Anodic polarization of a rotating platinum electrode in deoxygenated 0.2 M thiosulfate solutions containing 0 mM (······), 0.5 mM (-----) and 5 mM (——) Cu ions at pH 12.
Figure 5.7  Anodic polarization of a rotating gold electrode in deoxygenated 0.2 M thiosulfate solutions containing 0 mM (·······), 0.5 mM (-----) and 5 mM (——) Cu ions at pH 12.

Figure 5.8  Anodic polarization curves of a rotating gold electrode in deoxygenated 0.2 M thiosulfate solutions containing 0.5 mM Cu ions at various pH values.
The effect of pH on the anodic oxidation of gold electrode in 0.2 M thiosulfate solutions with 0.5 mM copper is summarized in Figure 5.8. It is apparent that pH has a significant influence only at potentials above about 0.3 V, which could be due to the more favourable formation of copper(II) species at higher potentials and pH values (Figure 5.1). The effect of copper ions on the anodic behaviour in the region of the mixed potential in aerated solutions is, however, significant at both pH values.

### 5.3.3 Coulometric Measurements

It has been shown that gold dissolves during anodic oxidation in alkaline thiosulfate solutions in the absence of copper and ammonia (Chapter 4). The anodic current of the gold electrode in thiosulfate solutions containing copper shown above could be associated with either the oxidative dissolution of gold, the oxidation of copper(I) to copper(II) and/or the oxidation of thiosulfate. Coulometric measurements were therefore carried out in deoxygenated 0.2 M thiosulfate solutions containing copper ions at pH 12 by applying a constant potential of 0.3 V to the gold electrode and recording the anodic current as a function of time. After potentiostatic oxidation, the thiosulfate solutions were analyzed for Au by AAS. The average dissolution rates of gold and current efficiencies (assuming a one-electron process) were calculated and are shown in Table 5.1.

<table>
<thead>
<tr>
<th>Copper / mM</th>
<th>Average Charge / F cm⁻² s⁻¹</th>
<th>Au Dissolution / mol cm⁻² s⁻¹</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$5.17 \times 10^{-12}$</td>
<td>$2.07 \times 10^{-12}$</td>
<td>0.40</td>
</tr>
<tr>
<td>0.5</td>
<td>$6.46 \times 10^{-12}$</td>
<td>$2.11 \times 10^{-12}$</td>
<td>0.33</td>
</tr>
<tr>
<td>5</td>
<td>$2.50 \times 10^{-11}$</td>
<td>$6.50 \times 10^{-12}$</td>
<td>0.26</td>
</tr>
</tbody>
</table>
As seen in Table 5.1, gold dissolves and its dissolution rate increases slightly with increasing concentration of copper at 0.3 V. However, the coulombic efficiency decreases with increasing copper concentration. This fact suggests that the presence of copper in thiosulfate solutions enhances not only the dissolution of gold but also the oxidation of thiosulfate. The potentiostatic current-time transients shown in Figure 5.9 reveal that the anodic currents are high initially and then decrease gradually to very low levels, suggesting that, as in the absence of copper ions, passivation of both the oxidation of gold and of thiosulfate occurs in this potential region.

![Figure 5.9 Current-time transients at the gold electrode in 0.2 M thiosulfate solutions with and without copper at 0.3 V, pH 12 and 20 °C.](image)
5.3.4 Gold Dissolution in Thiosulfate Solutions Containing Copper

To further investigate the effect of copper on the dissolution of gold, leaching experiments were performed in oxygenated thiosulfate solutions in the presence or absence of copper. The effect of milling of the gold particles on the rate of dissolution was also investigated. Figure 5.10 shows the dissolution rate of unmilled and milled fine gold powder in 0.2 M Na₂S₂O₃ solutions at pH 12 with or without copper. Obviously, copper (in the form of either ions, metal or oxide) enhances the rate of gold dissolution. The effect appears to be greatest with dissolved copper although higher concentrations of copper ions appears to be disadvantageous, which is possibly due to the instability of copper in alkaline solutions. It is noteworthy that the rate of gold dissolution decreases after a relatively rapid reaction in the early stages, which is consistent with the results in Figure 5.9. Apparently, milling of gold powder assists with the dissolution of gold especially in the presence of copper. The appreciable effect of milling on the dissolution of gold is probably associated with the increased surface area of gold. The potential of a gold electrode in the leach solutions was found to be about 0.11 V which is similar to the mixed potential of gold reported in Figure 5.2.

5.4 Discussion

5.4.1 Electrochemical Oxidation

Electrochemical experiments have shown that even without ammonia, copper in thiosulfate solutions has a positive effect on the anodic behaviour of gold. The presence of copper in thiosulfate solutions enhances not only the dissolution of gold but also the oxidation of thiosulfate at constant potentials, which is similar to that observed in the
presence of ammonia (Breuer and Jeffrey, 2002). In the presence of ammonia, the role of copper is relatively well understood in terms of the chemistry of the copper ammine complexes. However, in the absence of ammonia, the role of copper is not obvious.

![Graph showing dissolution of gold powder](image)

**Figure 5.10** Dissolution of gold powder in oxygenated 0.2 M thiosulfate solutions at pH 12 with (solid line) and without (dashed line) copper at 25 °C. Fine gold powder (0.1 g) was wet-milled (diamonds) in a porcelain mill or added without milling (circles). The copper was used as (♦), 0.5 mM CuSO₄, ( ●) 2 mM CuSO₄, (♦) 20% CuO (by mass, milled with gold) and (♦) 20% Cu powder (by mass, milled with gold) respectively.

A stability constant \((3.6 \times 10^4 \text{ M}^{-2})\) for the unstable bis(thiosulfato)copper(II), \(\text{Cu(S}_2\text{O}_3\text{)}_2^{2-}\), has been determined by Rabai and Epstein (1992). Using this stability constant and relevant thermodynamic data in Appendix A.1, the standard free energy of formation of \(\text{Cu(S}_2\text{O}_3\text{)}_2^{2-}\) can be calculated to be \(-998.7 \text{ kJ mol}^{-1}\). By using this value and assuming that the thiosulfatocopper(I) complexes are oxidized to \(\text{Cu(S}_2\text{O}_3\text{)}_2^{2-}\), standard reduction potentials can be calculated as shown for the following half reactions.
\[
\begin{align*}
    \text{Cu(S}_2\text{O}_3\text{)}_2^{2-} + e^- &= \text{Cu(S}_2\text{O}_3\text{)}^+ + S_2\text{O}_3^{2-} & E^o &= 0.499 \text{ V} \\
    \text{Cu(S}_2\text{O}_3\text{)}_2^{2-} + e^- &= \text{Cu(S}_2\text{O}_3\text{)}_2^{3-} & E^o &= 0.611 \text{ V} \\
    \text{Cu(S}_2\text{O}_3\text{)}_2^{2-} + S_2\text{O}_3^{2-} + e^- &= \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} & E^o &= 0.694 \text{ V}
\end{align*}
\]

Thus in the present electrochemical studies with copper ions in 0.2 M thiosulfate solutions at pH 12, the concentration of the copper(II) complex, \(\text{Cu(S}_2\text{O}_3\text{)}_2^{2-}\) at an applied potential of 0.3 V can be calculated to be very low. Although this copper(II) species is not shown at pH about 12 in the Eh-pH diagram of Figure 5.1, it is nevertheless possible that it could be formed and therefore account for the oxidation of thiosulfate.

The role of copper in the oxidation of thiosulfate may also be due to the participation of other forms of copper(II) formed from the oxidation of copper(I) ions. From Figure 5.1, it can be seen that at pH about 12 and potential of 0.3 V, the most stable aqueous species of copper(II) is \(\text{HCuO}_2^-\) which may oxidize thiosulfate to tetrathionate given that the standard reduction potential for the \(S_4\text{O}_6^{2-}/S_2\text{O}_3^{2-}\) couple is 0.08 V. The reaction between \(\text{HCuO}_2^-\) and thiosulfate could be described as:

\[
2\text{HCuO}_2^- + 2\text{H}_2\text{O} + 8\text{S}_2\text{O}_3^{2-} = 2\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 6\text{OH}^- + S_4\text{O}_6^{2-}
\]

The effect of copper on the dissolution of gold may also be explained in terms of the above copper(II) species. Given that the standard reduction potential for the \(\text{Au(S}_2\text{O}_3\text{)}_2^{3-}/\text{Au}\) couple is 0.153 V (refer to Chapters 2 and 4; Bard, 1975), both \(\text{Cu(S}_2\text{O}_3\text{)}_2^{2-}\) and \(\text{HCuO}_2^-\) may oxidize gold at a pH value of 12. Thus, possible reactions between gold and these two copper(II) species could be given by

\[
\begin{align*}
    \text{Cu(S}_2\text{O}_3\text{)}_2^{2-} + \text{Au} + 3\text{S}_2\text{O}_3^{2-} &= \text{Au(S}_2\text{O}_3\text{)}_2^{3-} + \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} & (5.10) \\
    \text{HCuO}_2^- + \text{Au} + \text{H}_2\text{O} + 5\text{S}_2\text{O}_3^{2-} &= \text{Au(S}_2\text{O}_3\text{)}_2^{3-} + \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 3\text{OH}^- & (5.11)
\end{align*}
\]
The higher currents and lower current efficiency for gold dissolution shown in Table 5.1 in copper-containing thiosulfate solutions are possibly associated with the oxidation of copper(I) to copper(II) followed by rapid reactions of the copper(II) species with thiosulfate, i.e. catalysis of the thiosulfate oxidation by copper.

On the other hand, the role of copper is possibly also associated with the partial elimination or reduction of the sulfur-like passivating film on the surface of gold. As suggested in Chapter 4, gold in thiosulfate solutions could be covered by a sulfur-like film resulted from the decomposition of thiosulfate and oxidation of sulfide ions. Cuprous ions in thiosulfate solutions could react with the $S^{2-}$ ion to form cuprous sulfide, $Cu_2S$ as shown in the reaction:

$$2Cu(S_2O_3)^{5-} + S^{2-} = Cu_2S + 6S_2O_3^{2-} \quad (5.12)$$

The standard free energy $\Delta G^\circ$ at 25 °C for this reaction was calculated to be -122.0 kJ mol$^{-1}$, suggesting that it is thermodynamically favorable. Thus, copper may partially prevent the oxidative adsorption of sulfur and in turn enhance the dissolution of gold.

### 5.4.2 Dissolution of Gold with Oxygen

Leaching experiments have confirmed the catalytic effect of copper on the dissolution of gold in thiosulfate solutions without ammonia. The Eh-pH diagram in Figure 5.1 suggests that at the mixed potential ($< 0.12$ V) in oxygenated thiosulfate solutions, copper exists in the form of the copper(I) thiosulfate complexes. Thus the possible explanation for the dissolution of gold in the coulometric studies at 0.3 V may not apply to the dissolution of gold with oxygen.
The role of copper in the dissolution of gold in oxygenated thiosulfate solutions could be due to formation of a copper-thiosulfate-oxygen intermediate which has a higher reduction potential. Figure 5.2 shows that gold attains a higher potential when initially contacting an aerated thiosulfate solution in the presence of copper. Figure 5.3 shows that after copper ions (either cuprous or cupric) are added into aerated thiosulfate solutions, the potential of gold electrode immediately increases to a higher value before gradually decreasing to a lower value of about 0.1 V. The increase in the potential of gold electrode probably implies the formation of an intermediate which has a higher reduction potential. The intermediate could be formed from a cuprous thiosulfate complex and oxygen:

$$\text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + \text{O}_2 = [(\text{S}_2\text{O}_3\text{)}_3\text{Cu} \cdot \text{O}_2]^{5-} \quad (5.13)$$

in which oxygen molecule is bound to copper(I) which has an apparent coordination number of 4. In this way cuprous thiosulfate acts as a carrier of oxygen to expedite redox reactions as in the case of dissolution of silver metal in cuprous thiosulfate solutions (Mellor, 1929). Similar intermediates have been suggested in the reactions between oxygen and other cuprous complex ions in copper-catalyzed autoxidation reactions in aqueous solutions (Hopf et al., 1983; Pecht and Anbar, 1968; Nord, 1955; Zuberbuhler, 1967). However, these intermediates have not been identified chemically or spectrophotometrically in their free or complexed forms during copper(I) autoxidation (Zuberbuhler, 1983). This is not unexpected given the high reactivity of these intermediates (Zuberbuhler, 1983). In the current study, the increase in the potential of the gold electrode could be an indicator of the presence of this intermediate which probably acts as an oxidant for the dissolution of gold and oxidation of thiosulfate. The possible overall reactions between this intermediate and gold or thiosulfate could be given by the reactions:
\[
([S_2O_3)_3Cu \cdot O_2]^{5-} + 4Au + 8S_2O_3^{2-} + 2H_2O = 4Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4OH^- \quad (5.14)
\]

\[
([S_2O_3)_3Cu \cdot O_2]^{5-} + 4S_2O_3^{2-} + 2H_2O = 2S_4O_6^{2-} + Cu(S_2O_3)_3^{5-} + 4OH^- \quad (5.15)
\]

The initial rate of dissolution per unit area of gold in oxygenated thiosulfate solutions can be estimated as follows, assuming that all the gold particles are spherical and have the same size (3 µm).

Initial rate = - (1/S) \(dN_{Au}/dt\) \quad (5.16)

where S is the total surface area of all gold particles; \(dN_{Au}/dt\) is the dissolution rate of gold in moles per unit time. The value of S can be calculated from

\[
S = n_p S_p = S_p W_{Au} / (\rho V_p) \quad (5.17)
\]

where \(n_p\), \(S_p\), \(V_p\) are the number of gold particles, the surface area and volume of one gold particle respectively; \(W_{Au}\) is the mass of the gold powder used; \(\rho\) is the specific gravity of gold (\(\rho = 19.32\) g cm\(^{-3}\)). For spherical particles with a diameter of \(d\), Equation 5.17 can be rewritten as

\[
S = \pi d^2 W_{Au} / (\rho \pi d^3/6) = 6W_{Au} / (\rho d) \quad (5.18)
\]

Thus, the initial dissolution rate can be described as

Initial rate = - (\(dN_{Au}/dt\)) (\(\rho d\)) / (6\(W_{Au}\)) \quad (5.19)

The dissolution fraction of gold at time \(t\), \(X = 1 - N/N_0\) and \(W_{Au} = N_0 M_{Au}\) where \(N\) is the number of moles of gold at time \(t\) and \(N_0\) the initial number of moles of gold. Thus

Initial rate = (\(dX_{Au}/dt\)) (\(\rho d\)) / (6\(M_{Au}\)) \quad (5.20)

where \(M_{Au}\) is the molar weight of gold (196.97 g mol\(^{-1}\)). Based on the above and the data in Figure 5.10, the initial dissolution rate of wet-milled gold powder in oxygenated alkaline 0.2 M thiosulfate solution in the presence of 0.5 mM copper was calculated to be \(3.5 \times 10^{-11}\) mol cm\(^{-2}\) s\(^{-1}\). Similarly, the rate of wet-milled gold powder in oxygenated 0.2
M thiosulfate solution without copper was estimated to be about $1.5 \times 10^{-13}$ mol cm$^{-2}$ s$^{-1}$, while the rate of unmilled gold powder in oxygenated 0.2 M thiosulfate solution without copper was only about $6 \times 10^{-15}$ mol cm$^{-2}$ s$^{-1}$. These values indicate that a small amount of copper can significantly accelerate the initial rate of dissolution of gold. However, this rate in the presence of copper is still low compared with that obtained by Jeffrey (2001) of about $4 \times 10^{-9}$ mol cm$^{-2}$ s$^{-1}$ in ammoniacal thiosulfate solutions containing copper ions. The appreciable effect of milling on the dissolution of gold is probably associated with the increased surface area of gold.

Figure 5.10 shows that gold initially dissolves relatively rapidly in copper bearing thiosulfate solutions but that the rate gradually decreases with time, which is consistent with results in Figure 5.9. As suggested in Chapter 4, it is possible that a sulfur-like film could be formed on the oxidized gold surface in thiosulfate solutions, which inhibits further dissolution of gold. Some yellow brownish spots were observed under the microscope on a gold disk after it had been reacted with oxygenated copper bearing thiosulfate solutions at room and elevated temperatures, supporting passivation of the surface of gold.

5.4.3 Possible Complex of Gold with Copper in Thiosulfate Solutions

It has been shown that copper accelerates the dissolution of gold in thiosulfate solutions in the presence of oxygen. A possible reason has been suggested above for this observation. However, some consideration should be given to the possibility of the formation of a mixed gold-copper-thiosulfate complex of the type $(\text{Au},\text{Cu})(\text{S}_2\text{O}_3)_2^{3-}$. Webster (1986) suggested that gold might substitute into the silver-thiosulfate complex to form a thiosulfate complex of the type $(\text{Au},\text{Ag})(\text{S}_2\text{O}_3)_2^{3-}$ in his study on the solubility
of gold and silver in thiosulfate solutions. In the current study, similar evidence for a combined gold-copper-thiosulfate complex has been obtained in experiments aimed at the precipitation of copper from solutions used in the leaching of gold by sulfide ions. When sulfide ($S^{2-}$) ions were added into solutions containing gold-thiosulfate and copper-thiosulfate and mixed for 15 minutes, almost all the gold and copper precipitated, but no precipitation of gold occurred from the solutions containing only gold (Table 5.2). The co-precipitation of gold with copper is unlikely to be a consequence of adsorption onto the cuprous sulfide ($Cu_2S$) precipitate because after mixing with either cupric sulfide ($CuS$) reagent, djurleite($Cu_{1.98}S$) mineral or freshly prepared $Cu_2S$ (obtained from mixing of cuprous thiosulfate with sulfide ions), the concentration of gold in thiosulfate solutions containing both gold and copper remained constant while that of copper increased (Table 5.2). In the absence of copper, gold-thiosulfate appears to be stable in the presence of sulfide ions. From these results it is tentatively concluded that gold is precipitated by the decomposition of the combined gold-copper-thiosulfate complex in the presence of sulfide ions. However, more evidence for a possible gold-copper-thiosulfate complex needs to be obtained to confirm this postulate.

Table 5.2  Atomic absorption assay of gold- and copper-thiosulfate bearing solutions, before and after reaction with selected reagents

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Initial Concentration / mg l$^{-1}$</th>
<th>Final Concentration / mg l$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
<td>Cu</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>28</td>
<td>0.2</td>
</tr>
<tr>
<td>CuS</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>Djurleite($Cu_{1.98}S$)</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>Fresh $Cu_2S$</td>
<td>5.8</td>
<td>21</td>
</tr>
</tbody>
</table>
5.5 Conclusions

Both electrochemical and dissolution experiments have shown that copper ions enhance the rate of gold dissolution in the absence of ammonia at ambient temperatures. Electrochemical studies have shown that copper has a positive effect on the anodic dissolution of gold with increasing concentrations of copper resulting in higher dissolution rates of gold at a potential of 0.3 V. The pH of thiosulfate solutions containing copper appears to affect the anodic currents only at potentials above about 0.3V. Studies on the dissolution of gold powder in alkaline oxygenated thiosulfate solutions containing low concentrations of copper have shown that the role of copper in enhancement of the dissolution rate of gold is probably associated with the formation of a copper-thiosulfate-oxygen intermediate which has a higher reduction potential, but the mechanism for this remains unclear. On the other hand, the possibility of the formation of mixed copper-gold-thiosulfate complexes could not be ruled out and this possibility needs to be further investigated using other techniques. As expected, milling of gold powder assists with the dissolution of gold in thiosulfate solutions, especially in the presence of copper.
CHAPTER 6  THE DISSOLUTION OF GOLD IN
THIOARSENATE/THIOARSENITE
SOLUTIONS

6.1 Introduction

Analyses of the solutions from the alkaline oxidation of pure arsenopyrite (in Chapter 7) will show that thioarsenates are present. Thioarsenites are also possible components of the solution (Nagy et al., 1966; Rossovsky, 1993) although these ions were not detected in this study. As reported in Section 2.3, several possible gold thioarsenite complexes have been suggested as being formed during the dissolution of gold in arsenic sulfide solutions at 200-300 °C. It is, therefore, reasonable to investigate the possibility of reaction of gold with these ions in alkaline solutions at ambient temperatures and pressures in order to explain the dissolution of gold during the alkaline oxidation of arsenopyrite by oxygen (see Chapter 7).

In this study, the behaviour of gold in monothioarsenate (AsO$_3$S$^-$) solutions and in solutions containing some thioarsenites is reported. The experiments were carried out at 25 °C in alkaline solutions of pH 12 with a gold disk electrode at a rotation speed of 1000 rpm unless otherwise stated. In voltammetric experiments, a potential sweep rate of 10 mV s$^{-1}$ was used.
6.2 Dissolution in Alkaline Monothioarsenate Solutions

As outlined in Chapter 2, the chemistry of thioarsenates is poorly understood and there do not appear to be any reports in the literature on the possible formation of gold thioarsenate complexes or the reaction between gold and thioarsenate ions in aqueous solutions. However, the monothioarsenate \((\text{AsO}_3\text{S}^3^-\) or \(\text{S-AsO}_3^3\)) ion resembles the thiosulfate \((\text{S}_2\text{O}_3^{2^-}\) or \(\text{S-SO}_3^{2^-}\)) ion in structure, which suggests that the monothioarsenate ion could react with gold in alkaline solutions. In the following sections, some aspects of the behaviour of gold in alkaline solutions of monothioarsenate are described.

6.2.1 The Electrochemical Behaviour of Gold

6.2.1.1 Mixed potential measurements

Mixed potentials for gold were measured by recording the potential of a rotating gold disk electrode in alkaline thioarsenate solutions to establish the relevant potential region for the oxidative dissolution of gold. Figure 6.1 shows the potentials of gold in oxygenated 0.1 M and 0.5 M \(\text{Na}_3\text{AsO}_3\text{S}\) solutions respectively. It appears that the mixed potential of gold is located between \(-0.05\) V and 0.16 V, which is within the potential range for anodic oxidation observed in the cyclic voltammogram shown in Figure 6.2. It is also apparent that the potential is lower in the solution containing the higher concentration of thioarsenate.
6.2.1.2 Cyclic voltammetry

Figure 6.2 shows the cyclic voltammogram of a stationary gold electrode in deoxygenated 0.1 M Na₃AsO₃S solution. It can be seen that an anodic process occurs in a potential region from about -0.1 V to 0.66 V. A partial passivation occurs at a potential of about 0.4 V and the anodic current increases again when the potential increases to about 0.6 V. Figure 6.3 compares the cyclic voltammograms of gold and platinum under the same conditions. It is apparent that the anodic current on gold is slightly higher than on the platinum at potentials below about 0.4 V. There is no indication of passivation in the case of platinum. The passivation of the gold electrode in 0.1 M Na₃AsO₃S solution can be seen more clearly in Figure 6.4. When the gold electrode is subjected to successive potential sweeps between -0.15 to 0.5 V, the current decreases with each successive sweep.

Figure 6.1 Mixed potentials for a rotating (400 rpm) gold electrode in oxygenated alkaline AsO₃S³⁻ solutions. (- - - -) 0.1 M Na₃AsO₃S solution, pH 12; (-----) 0.5 M Na₃AsO₃S solution, pH 13.
Figure 6.2  Cyclic voltammogram of a stationary gold electrode in deoxygenated 0.1 M Na$_3$AsO$_3$S solution at pH 12. Sweep initiated in negative direction from -0.1 V.

Figure 6.3  Cyclic voltammograms of rotating gold and platinum electrodes in deoxygenated 0.1 M Na$_3$AsO$_3$S solutions at pH 12. Sweeps were initiated in a positive direction from -0.15 V.
Figure 6.4  Successive voltammograms of a rotating gold electrode in deoxygenated 0.1 M Na₃AsO₃S solutions at pH 12.

Figure 6.5  Cyclic voltammograms of gold with and without rotation in deoxygenated 0.1 M Na₃AsO₃S solutions at pH 12.
The effect of rotation of the electrode is shown in Figure 6.5 from which it is apparent that the anodic current is higher at potentials above about 0.2 V at a stationary electrode, suggesting that the anodic process could involve the formation of a soluble species which undergoes further oxidation. By comparison with Figure 4.5 (see Section 4.2.2.1), it can be seen that the anodic current density is higher in monothioarsenate than in thiosulfate solutions.

![Figure 6.6 Variation with time of the anodic current on a rotating (200 rpm) gold electrode at 0.25 V in a deoxygenated 0.5 M Na₃AsO₃S solution at pH 13.](image)

6.2.1.3 Coulometric measurements

In order to establish the relative rates of oxidation of gold and of the monothioarsenate ion, a coulometric experiment was carried out by applying a potential of 0.25 V to the gold electrode in 0.5 M monothioarsenate solution at pH 13 and 25 °C for about 12.5 hours. It was found that gold dissolved with an average dissolution rate of $2.0 \times 10^{-11}$ mol cm$^{-2}$ s$^{-1}$, which is of the same order of magnitude as that of gold in 0.5 M
thiosulfate solution (Chapter 4). The anodic current recorded during the coulometric test is shown in Figure 6.6 from which it is clear that the current decreases with time, indicating a passivation process. The average current efficiency for the dissolution of gold was calculated to be 6% assuming a one-electron process. This indicates that the oxidation of monothioarsenate predominates at a potential of 0.25 V.

### 6.2.1.4 Cathodic reduction of oxygen

The mixed potential of gold in oxygenated monothioarsenate solutions is between –0.05 V to 0.1 V. The cathodic behaviour of oxygen on the gold electrode in monothioarsenate solutions was thus investigated in the potential range between –0.2 and 0.2 V. Figure 6.7 shows a cyclic voltammogram for the cathodic reduction of oxygen in 0.1 M AsO₃S³⁻ solution at pH 12. Apparently, the cathodic current of oxygen on gold is very small in the potential region of 0 to 0.1 V, confirming that the rate of oxidation of gold by oxygen will be very low.

![Cyclic voltammogram](image-url)

**Figure 6.7** Cathodic reduction of oxygen on a rotating (400 rpm) gold electrode in an oxygenated 0.1 M AsO₃S³⁻ solution at pH 12.
6.2.2 Dissolution of Gold in Monothioarsenate Solutions

Electrochemical studies suggest that dissolution of gold may occur in solutions containing monothioarsenate ion. This was confirmed by experiments (Figure 6.8) which show the dissolution rate of milled gold powder (1.5-3 µm size) in oxygenated alkaline (pH 12) solutions containing 0.2 M $S_2O_3^{2-}$ or 0.1 M $AsO_3S^{3-}$. Also shown in Figure 6.8 is the dissolution of gold in 1 mM $S_2O_3^{2-}$ solution at pH 12 for comparison because the 0.1 M $AsO_3S^{3-}$ solution was found to contain about 0.4 mM $S_2O_3^{2-}$ after analysis by HPLC. As can be seen, gold obviously dissolves more rapidly in the $AsO_3S^{3-}$ solution than in $S_2O_3^{2-}$ solutions, which is consistent with the results from the electrochemical studies.

Figure 6.8  Dissolution of gold in oxygenated alkaline solutions containing (○) 0.2 M $S_2O_3^{2-}$, (□) 0.1 M $AsO_3S^{3-}$ and (◇) 1 mM $S_2O_3^{2-}$ at 25 °C and pH 12. Before leaching, 0.10 grams of gold powder (1.5-3 µm) was wet-ground in a porcelain mill.
6.2.3 Discussion

Electrochemical studies have shown that gold may dissolve in alkaline monothioarsenate solutions with a rate which is comparable to that in alkaline thiosulfate solutions. The reactivity of monothioarsenate with gold could be associated with coordinating ability of the sulfur atom in the AsO$_3$S$_3^-$ ion because sulfur is a soft polarizable electron donor (see Section 2.1.2). By analogy with thiosulfate, the mechanism of the anodic reaction of gold with monothioarsenate could be:

\[
\begin{align*}
\text{Au} + \text{AsO}_3\text{S}_3^- &= \text{Au} \mid \text{SAsO}_3\text{S}_3^-(\text{ads}) \quad (6.1) \\
\text{Au} \mid \text{SAsO}_3\text{S}_3^-(\text{ads}) &= \text{Au(SAsO}_3\text{S}_3^2^-(\text{ads}) + e^- \quad (6.2) \\
\text{Au(SAsO}_3\text{S}_3^2^-(\text{ads}) + S\text{AsO}_3\text{S}_3^3^- &= \text{Au(SAsO}_3\text{S}_3^5^- \quad (6.3)
\end{align*}
\]

Figures 6.4 and 6.6 have shown that there is a passivation process which occurs on the surface of gold in monothioarsenate solutions. As the monothioarsenate ion has a similar structure as the thiosulfate ion, it is possible that this passivation is similar to that in thiosulfate solutions and could result from the formation of a sulfur-like film on the surface of gold, leading to a low anodic current efficiency for the dissolution of gold. By analogy with oxidation of thiosulfate (see Chapter 4), the anodic oxidation of monothioarsenate could involve the following reactions:

\[
\begin{align*}
\text{AsO}_3\text{S}_3^3^- (\text{ads}) + 2\text{OH}^- &= \text{AsO}_4\text{S}^3^- + \text{S}^0 (\text{ads}) + \text{H}_2\text{O} + 2e^- \quad (6.4) \\
2\text{SAsO}_3\text{S}_3^3^- (\text{ads}) &= (\text{O}_3\text{AsS-SAsO}_3)_{4}^4^- (\text{ads}) + 2e^- \quad (6.5) \\
(\text{O}_3\text{AsS-SAsO}_3)_{4}^4^- (\text{ads}) &= (\text{O}_3\text{AsS-SAsO}_3)_{4}^4^- (\text{aq}) \quad (6.6)
\end{align*}
\]

The (O$_3$AsS-SAsO$_3$)$_{4}^4^-$ ion could rapidly oxidize or decompose to other species:

\[
\begin{align*}
(\text{O}_3\text{AsS-SAsO}_3)_{4}^4^- + 4\text{OH}^- &= 2\text{AsO}_4\text{S}^3^- + 2\text{S}^0 + 2\text{H}_2\text{O} + 2e^- \quad (6.7) \\
(\text{O}_3\text{AsS-SAsO}_3)_{4}^4^- + 2\text{OH}^- &= \text{AsO}_3\text{S}_3^3^- + \text{AsO}_4\text{S}^3^- + \text{S}^0 + \text{H}_2\text{O} \quad (6.8)
\end{align*}
\]
However, more detailed work with respect to the chemistry of thioarsenate needs to be carried out in order to characterize the reactions of gold in monothioarsenate solutions.

The leaching experiments have shown that gold can dissolve in oxygenated alkaline monothioarsenate solutions at ambient temperatures and its dissolution rate is measurably higher than that in thiosulfate solutions under similar conditions. The dissolution reaction could be expressed as

$$4\text{Au} + \text{O}_2 + 8\text{AsO}_3\text{S}^{3-} + 2\text{H}_2\text{O} = 4\text{Au(AsO}_3\text{S)}_2^{5-} + 4\text{OH}^- \quad (6.9)$$

The initial rate of dissolution per unit area of gold in oxygenated AsO$_3$S$^{3-}$ solution may be estimated according to Equation 5.20 in Chapter 5, assuming that all the gold particles are spherical and have the same size (3 µm). Using the data in Figure 6.8, the initial dissolution rate of gold in oxygenated alkaline 0.1 M AsO$_3$S$^{3-}$ solution was calculated to be $1.3 \times 10^{-12}$ mol cm$^{-2}$ s$^{-1}$. Similarly, the leaching rate of gold in oxygenated 0.2 M thiosulfate solution at pH 12 was estimated to be about $1.5 \times 10^{-13}$ mol cm$^{-2}$ s$^{-1}$. These values are about an order of magnitude less than those found for the anodic oxidation at 0.25 V.

In many hydrometallurgical leaching systems involving dissolution of a solid, mass transfer of reactants to the solid-liquid interface is often rate controlling (Wadsworth and Miller, 1979; Nicol, 1987). If the overall dissolution rate of gold in oxygenated solutions containing 0.1 M AsO$_3$S$^{3-}$ is limited by the rate of mass transport of dissolved oxygen to the metal surface, the maximum rate of dissolution may be given by Fick’s first law of diffusion, and described by the following equation (Wadsworth and Miller, 1979):

$$R_{\text{max}} = k_L [\text{O}_2] \quad (6.10)$$
where $R_{\text{max}}$ is the maximum rate of dissolution per unit area, mol cm$^{-2}$ s$^{-1}$; $k_L$ the mass transfer coefficient of dissolved oxygen, cm s$^{-1}$; $[O_2]$ the concentration of dissolved oxygen, mol cm$^{-3}$. For suspended spherical particles of 3 µm diameter in aqueous solution, $k_L$ is about 0.065 cm s$^{-1}$ (Wadsworth and Miller, 1979; also see Appendix A3). If the solubility of oxygen in 0.1 M electrolyte solutions at 25 °C and one atmosphere partial pressure is assumed to be 32 mg l$^{-1}$, i.e. $10^{-6}$ mol cm$^{-3}$ (Tromans, 1998), the maximum rate of gold dissolution will be $6.5 \times 10^{-8}$ mol cm$^{-2}$ s$^{-1}$. This value is much higher than the measured rate in the above experiments. This calculation confirms that the rate of dissolution of gold in oxygenated monothioarsenate solution will be chemically controlled.

6.3 Dissolution in Alkaline Thioarsenite Solutions

As reviewed in Section 2.3.2 in Chapter 2, there are many forms of thioarsenite and the chemistry of thioarsenite is poorly understood. Synthetic solutions of thioarsenite generally contain various arsenic species (Young and Robins, 2000; Mellor, 1929), and, for this reason, the electrochemistry experiments on the behaviour of gold in thioarsenite solutions were not carried out. However, some experiments involving the dissolution of gold were carried out.

Two solutions containing thioarsenites were used in these experiments. Solution (A) was prepared by dissolving 13.29 grams of synthetic amorphous orpiment (As$_2$S$_3$, 84.3% purity) in a solution containing 26.84 grams of sodium sulfide (Na$_2$S·9H$_2$O) at a pH of 12. The molar ratio of Na$_2$S to orpiment was 2.45, so that the arsenic-sulfur species was stoichiometrically close to the form As$_2$S$_5^{4-}$, with a concentration of about 0.046 M.
Solution (B) was prepared by dissolving 7.00 grams of synthetic amorphous orpiment of 84.3% purity in 500 ml of a solution containing 9.00 grams of sodium hydroxide. According to Remy et al. (1956), this solution with pH 12.7 should contain 0.024 M AsS$_3^{3-}$ and 0.024 M AsO$_3^{3-}$ as suggested by the following equation (see Section 2.3.2):

$$\text{As}_2\text{S}_3 + 6\text{OH}^- = \text{AsS}_3^{3-} + \text{AsO}_3^{3-} + 3\text{H}_2\text{O}$$  \hspace{1cm} (6.11)

### 6.3.1 Dissolution of Gold

Figure 6.9 summarizes the results of an experiment in which fine gold powder (100 mg) was contacted with an aerated solution (300 ml) of solution (A) at 25 °C. The agitation of the solution was provided by a magnetic stirrer. It is apparent that the pH of the solution decreased gradually from 12 to 10.5 while gold dissolved to some extent with the concentration reaching 1 mg l$^{-1}$ after 21 hours. During the experiment, the potential of the solution increased gradually with time, achieving a stable value of about 0.1 V after 4 hours. This potential is similar to that observed during the alkaline oxidation of refractory gold concentrates containing arsenopyrite and pyrite (see Chapter 8).

The results of a similar experiment with solution (B) in the presence of air are shown in Figure 6.10. As can be seen, the pH and potential profiles are similar to those in Figure 6.9, while the dissolved gold concentration was much lower, at 0.3 mg l$^{-1}$ after 24 hours.
Chapter 6 The Dissolution of Gold in Thioarsenate / Thioarsenite Solutions

Figure 6.9 Variation of pH, potential, and gold concentration with time during reaction of gold powder with an aerated solution of \(0.046 \text{ M} \text{As}_2\text{S}_5^{4-}\) at 25 °C.

Figure 6.10 Variation of pH, potential and gold concentration during reaction of gold powder with an aerated solution of \(\text{AsS}_3^{3-}\) and \(\text{AsO}_3^{3-}\) at 25 °C.
Table 6.1 shows the effects of time, temperature and atmosphere on the extent of dissolution of gold in thioarsenite solutions. It is clear by comparison between Tests 2 and 3 that gold dissolution is favored by higher temperatures, while, as expected, the presence of oxygen has a positive effect on the dissolution of gold (see Tests 1, 2 and 4).

Table 6.1  Results of testwork on the dissolution of gold in thioarsenite solutions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Au used (mg)</th>
<th>Solution (100 ml)</th>
<th>Gas bubbling</th>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>[Au] (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>A</td>
<td>N₂</td>
<td>25</td>
<td>10</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>A</td>
<td>Air</td>
<td>25</td>
<td>10</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>A</td>
<td>Air</td>
<td>50</td>
<td>10</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>A</td>
<td>None</td>
<td>25</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>A</td>
<td>None</td>
<td>25</td>
<td>24</td>
<td>4.6</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>B</td>
<td>None</td>
<td>25</td>
<td>20</td>
<td>0.4</td>
</tr>
</tbody>
</table>

6.3.2 Discussion

It has been shown that gold dissolves in alkaline thioarsenite solutions but that the kinetics of the reaction is extremely slow. It is evident that the rate of dissolution is dependent on the composition, potential and temperature of the solution. Comparison of Figure 6.9 with Figure 6.10 indicates that under similar conditions the dissolution of gold is greater in the $\text{As}_2\text{S}_5^{4-}$ solution than the alkaline solution containing $\text{AsS}_3^{3-}$ and $\text{AsO}_3^{3-}$. Since the chemistry of thioarsenite is poorly understood, it is not certain which ions are responsible for the reaction i.e. coordinate with gold(I), although several possible gold complexes with thioarsenites have been suggested (see Section 2.3.3). According to
Webster (1990) and Eary (1992), amorphous orpiment dissolves under alkaline conditions to produce arsenite and sulfide ions while Young and Robins (2000) and Remy et al. (1956) suggest that the As\textsubscript{3}S\textsubscript{6}\textsuperscript{3–} or AsS\textsubscript{3}\textsuperscript{3–} ion could be formed in sulfide free alkaline solutions in addition to arsenite (see Equations 2.69 and 2.70 in Chapter 2). If the sulfide ion is formed, it will react with the auric ion to precipitate gold sulfide in oxygen free solutions, in addition to which the auric ion is not stable in alkaline solutions, forming a yellow brown precipitate, gold(III) hydroxide (Remy et al., 1956; Mellor, 1929).

\begin{align*}
8\text{AuCl}_4^- + 9\text{S}^{2-} + 8\text{OH}^- &= 8\text{AuS} + 32\text{Cl}^- + \text{SO}_4^{2-} + 4\text{H}_2\text{O} \quad (6.12) \\
\text{AuCl}_4^- + 3\text{OH}^- &= \text{Au(OH)}_3 + 4\text{Cl}^- \quad (6.13)
\end{align*}

Preliminary experiments, however, showed that no apparent reactions were observed when an auric chloride (NaAuCl\textsubscript{4}) solution containing 13.6 mg l\textsuperscript{–1} Au was mixed with an equal volume of the 0.024 M AsS\textsubscript{3}\textsuperscript{3–} solution at pH 12.7. The gold concentration of the resulting solution (pH 12) was found to be 6.5 mg l\textsuperscript{–1} gold, which indicates that almost all the gold remained in the solution. The fact that no precipitation occurred suggests that gold(III) ions possibly react with thioarsenite ions, forming stable soluble complexes or that auric ions are reduced by thioarsenite forming thioarsenite complexes of gold(I).

In alkaline 0.046 M As\textsubscript{2}S\textsubscript{5}\textsuperscript{4–} solutions which were prepared by dissolving As\textsubscript{2}S\textsubscript{3} in Na\textsubscript{2}S solution, the AsS\textsubscript{2}(SH)\textsuperscript{2–}, AsS(SH)\textsubscript{2} and AsS(SH)(OH)\textsuperscript{–} ions probably exist according to Helz et al. (1995). These ions could react with gold forming stable complexes. Thus, when a fresh 0.046 M As\textsubscript{2}S\textsubscript{5}\textsuperscript{4–} solution was mixed with an equal volume of NaAuCl\textsubscript{4} solution containing 13.6 mg l\textsuperscript{–1} Au, no precipitation was observed and all the gold was still present in solution at pH 12 even after 3 days. This explanation is also supported by the theoretical calculations of Tossell (2000b) who has suggested that the complex AuAsS(SH)(OH) is more stable than the aquo ion of Au(I) and that
other complexes of gold with the ligands AsS(SH)(OH)\(^{-}\) or AsS(SH)\(_2\)\(^{-}\) are possible. The
dissolution behaviour of gold in thioarsenite solutions is possibly associated with the
sulfur in thioarsenite as in the case of polysulfides, thiosulfate, thiocyanate, thiourea or
other sulfur bearing ligands which form complexes with gold(I).

6.4 Conclusions

Some aspects of the electrochemistry of gold in alkaline monothioarsenate
solutions and the dissolution of gold in monothioarsenate and thioarsenate solutions have
been studied. Electrochemical studies have shown that gold dissolves at a measurable
rate in monothioarsenate solutions at a potential of 0.25 V, which is confirmed by
leaching experiments in the presence of oxygen. The low current efficiency of about 6%
for the anodic oxidation of gold indicates that the oxidation of thioarsenate is the
predominant reaction in this potential region. There is evidence that the formation of a
passivating film inhibits the dissolution of the gold. It has also been found that gold
dissolves in thioarsenite solutions and its dissolution rate is dependent on the
composition, temperature and oxygen concentration of the solution. Possible forms of
gold complexes with these species have been discussed.
CHAPTER 7 SIMULTANEOUS OXIDATION OF SULFIDE MINERALS AND DISSOLUTION OF GOLD IN ALKALINE SOLUTIONS

7.1 Introduction

As mentioned in Chapter 1, one of the major challenges currently experienced by the gold industry is the efficient recovery of precious metals from refractory ores and concentrates containing arsenopyrite (FeAsS) and pyrite (FeS₂) which are important host minerals for gold. These minerals are required to be broken down by oxidation in order to expose the gold to cyanide or other lixiviants. Although several pretreatment options for the oxidation of these minerals have found industrial application such as roasting, pressure oxidation and bio-oxidation (Sparrow and Woodcock, 1995), they still have some drawbacks, particularly in their application to small or low grade operations.

Alkaline oxidation may be a preferred treatment option for arsenical sulfide ores in certain situations and has several technical merits (Deng, 1995). However, in comparison with many developed processes carried out under acidic conditions, the alkaline oxidation route has received very limited attention for refractory gold ores and only the Barrick Mercur Gold Mine, Nevada, used alkaline pressure oxidation on commercial scale as pretreatment of refractory gold ores (Thomas, 1991a; Thomas and Williams, 2000). The drawbacks of alkaline oxidation route such as the use of relatively expensive reagents, such as sodium hydroxide (NaOH) and higher operating pressure
have prevented the commercial application of this process (Deng, 1995). In recent years, novel attempts have been made to increase gold recovery and decrease the costs of alkaline oxidation processes, including simultaneous oxidation of ores and leaching of gold with cyanide (Mao et al., 1997; Min et al., 1999; Rossovsky, 1993) and leaching with a lime-sulfur mixture (Lan and Zhang, 1996; Fang and Han, 2002).

As reviewed in Chapter 2, the oxidation of pyrite has been extensively studied in acid and alkaline media (Ciminelli and Osseo-Asare, 1995a, b; Tao et al., 1994; Mycroft et al., 1990; Lowson, 1982; Goldhaber, 1983; Mishra and Osseo-Asare, 1988). In alkaline solutions, the predominant sulfur species produced during pyrite oxidation are thiosulfate and sulfite as described in reactions 7.1 and 7.2 (Goldhaber, 1983).

\[ 4\text{FeS}_2 + 7\text{O}_2 + 6\text{H}_2\text{O} = 4\text{FeOOH} + 8\text{H}^+ + 4\text{S}_2\text{O}_3^{2-} \] (7.1)

\[ 4\text{FeS}_2 + 11\text{O}_2 + 10\text{H}_2\text{O} = 4\text{FeOOH} + 16\text{H}^+ + 8\text{SO}_3^{2-} \] (7.2)

Unlike pyrite, there is less information available related to the aqueous alkaline oxidation of arsenopyrite in the literature. Although the chemistry of arsenopyrite oxidation in acid media has been studied by Papangelakis and Demopoulos (1990) and Fernandez (1992), and the electrochemical studies on the alkaline oxidation of arsenopyrite have been carried out, there is little work reported for the dissolution chemistry of arsenopyrite in oxygenated alkaline media. Generally, it is believed that the overall reaction for the arsenopyrite oxidation in strong alkalis is as follows (Kostina and Chernyak, 1979):

\[ 2\text{FeAsS} + 10\text{OH}^- + 7\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{AsO}_4^{3-} + 2\text{SO}_4^{2-} + 5\text{H}_2\text{O} \] (7.3)

But there still is some debate about the intermediate products of arsenopyrite oxidation. The formation of thioarsenite (AsS$_3^{3-}$) and thiosulfates in alkaline solutions has been reported during the atmospheric oxidation of gold bearing arsenical ores (Nagy et al., 1966; Rossovsky, 1993).
During an ongoing investigation into the oxidation of refractory gold ores containing arsenopyrite and pyrite, it was found (Zhang and Nicol, 1999) that gold dissolved simultaneously with oxidation of these ores by dissolved oxygen in alkaline solutions in the absence of cyanide. This study, therefore, was aimed at an investigation of the chemistry of oxidation of pure arsenopyrite and pyrite in alkaline solutions with dissolved oxygen, and the dissolution behaviour of pure gold during the oxidation of these minerals in order to develop an understanding of the chemistry of a possible new process for gold recovery from refractory sulfidic gold ores.

This chapter focuses on the characterization of the products of oxidation of sulfur and arsenic with a view to possible correlations of gold dissolution with the nature and concentration of the oxidation products. The minerals used in this study are described in the following section, and the detailed experimental procedure and analytical techniques can be found in Chapter 3.

During experiments aimed at the study of the kinetics of the reactions, experimental conditions were adjusted such that only one experimental parameter was varied at a time. Unless otherwise stated, all experiments were carried out in 500 ml of 1.25 M NaOH solution using 50 g l\(^{-1}\) mineral sample and 66 mg fine gold powder at 25 °C, 1400 rpm stirring speed and 1 l min\(^{-1}\) flow rate of air. Prior to oxidation, the gold was wet-ground together with the mineral for 60 minutes in a stainless steel mill.

### 7.2 Sulfide Minerals

In this study two arsenopyrite samples were used. One sample was obtained from China through Gemstone House in Western Australia. X-ray diffraction analysis (Figure
7.1) of this specimen shows the predominant mineral as being arsenopyrite with only minor amounts of quartz. Chemical analysis using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on a crushed sample after removing visible minor minerals such as quartz showed that this mineral is composed of 41.5% As, 35.4% Fe and 19.4% S which is equivalent to a stoichiometric composition of $\text{Fe}_{1.0}\text{As}_{0.9}\text{S}_{1.0}$. It appears that the specimen is arsenic deficient arsenopyrite.

Another arsenopyrite sample was obtained from a compact, crystalline block from China via Socklich Trading Company in Western Australia. X-ray diffraction analysis of this arsenopyrite specimen (Figure 7.2) shows the predominant mineral as arsenopyrite with minor minerals such as quartz, lepidolite, chalcopyrite, and calcite. Chemical analysis using AAS showed that a crushed sample after removing visible minor minerals like quartz is composed of 45.8% As, 34.3% Fe 19.7% S and 0.174% Cu which translates into a stoichiometric composition of $\text{Fe}_{1.0}\text{As}_{1.0}\text{S}_{1.0}$ and 0.41% of chalcopyrite. Crushed samples of these minerals were subjected to screening to obtain different particle sizes for use in the oxidation experiments. The size distribution of the crushed sample and its chemical composition are shown in Table 7.1.

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Arsenic%</th>
<th>Arsenopyrite%</th>
</tr>
</thead>
<tbody>
<tr>
<td>+75</td>
<td>43.5</td>
<td>94.6</td>
</tr>
<tr>
<td>+63-75</td>
<td>45.3</td>
<td>98.5</td>
</tr>
<tr>
<td>+53-63</td>
<td>43.1</td>
<td>93.8</td>
</tr>
<tr>
<td>+45-53</td>
<td>47.2</td>
<td>102.0</td>
</tr>
<tr>
<td>+38-45</td>
<td>43.6</td>
<td>94.9</td>
</tr>
<tr>
<td>-38</td>
<td>45.2</td>
<td>98.3</td>
</tr>
</tbody>
</table>
Figure 7.1  X-ray diffraction diagram for pure arsenopyrite sample from Gemstone House. Wavelength of 1.7902 Å (Co).

Figure 7.2  X-ray diffraction diagram for pure arsenopyrite sample from Socklich Trading Company. Wavelength of 1.7902 Å (Co).
A pyrite sample was obtained from the department of Extractive Metallurgy at Murdoch University. It was a golden yellowish crystalline block. XRD analysis (Figure 7.3) confirmed the absence of other phases. Chemical analysis of a crushed sample using ICP-OES showed the mineral specimen consisted of 47.4%Fe and 45.0%S with approximate stoichiometric composition of FeS$_{1.67}$.

Unless stated otherwise, all mineral samples were crushed and dry-ground using an iron ring mill to about 74 µm particle size prior to oxidation experiments.
7.3 Results

7.3.1 Oxidation of Pyrite and Gold in Alkaline Solutions

As many studies have been reported in relation to the oxidation of pyrite, only one experiment was carried out with pyrite in the presence of gold powder in order to observe the behaviour of gold and other species during the alkaline oxidation of pyrite with dissolved oxygen. Figure 7.4 shows the molar ratios of the main sulfur species to total dissolved sulfur obtained by analysis of aqueous solutions during the oxidation in aerated 1.25 M NaOH solution of pyrite which was milled with gold powder. In this experiment, about 60% of the pyrite sample was oxidized after 24 hours. Elemental sulfur was observed as a fine white dispersion in the slurry during the oxidation and found to constitute about 0.3% (by mass) of the final residue after 24 hours. This experiment confirmed the formation of thiosulfate and sulfite during the alkaline oxidation of pyrite by oxygen (Goldhaber, 1983). Sulfate is obviously formed as a product of the oxidation of sulfite after long leaching times.

Figure 7.4 Atomic molar ratios of sulfur species to total dissolved sulfur during the oxidation of pyrite by air. (◊) S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}; (Δ) SO\textsubscript{4}\textsuperscript{2-}; (□) SO\textsubscript{3}\textsuperscript{2-}. (pulp density =100 g l\textsuperscript{-1}, 56 mg gold powder).
Figure 7.5 shows the variations in the solution potential, pH, dissolved O\textsubscript{2} concentration, and Figure 7.6 gives the concentrations of Au, Cu, Fe and thiosulfate during the oxidation. The pulp potential reported during the oxidation is in the range –0.6 V to 0.2 V. Thiosulfate reached its highest concentration after 24 hours while 5.6% of the gold dissolved after 24 hours. Copper and iron were also detected in trace amounts in the leach solutions. The dissolution of copper is probably due to a trace amount of copper in the pyrite and its reaction with thiosulfate. Polysulfides were not detected by ion chromatography nor through the reaction of cupric ions with the solutions, which is consistent with the previous studies (Goldhaber, 1983). From these results it appears that gold is dissolved with thiosulfate as the lixiviant in the potential range of 0 to 0.2 V and the pH region of 10.5 to 13.5.

![Graph showing variations in solution potential, pH, concentration of gold, and dissolved oxygen during the oxidation of pyrite by air.](image-url)

Figure 7.5  Variation of solution potential (×), pH (□), concentration of gold (◊) and dissolved oxygen (△) during the oxidation of pyrite by air (pulp density =100 g l\textsuperscript{-1}, 56 mg gold powder).
Figure 7.6  Variation of concentrations of Au(◊), Cu(□), Fe(×) and thiosulfate(Δ) during the oxidation of pyrite by air (pulp density =100 g l\(^{-1}\), gold added =56mg).

7.3.2 Oxidation of Arsenopyrite in Alkaline Solutions

Alkaline oxidation of arsenopyrite was carried out under various experimental conditions of temperature, oxygen partial pressure, alkalinity, pulp density, particle size and stirring speed. Typical experimental results obtained for the reaction stoichiometry during oxidation are given in Figures 7.7 to 7.9 which show the molar ratios of the various soluble species obtained by analysis of aqueous samples taken at different stages of the oxidation in aerated 1.25 M NaOH solutions. The stoichiometric molar ratio of dissolved S/As has been found to be 1.0 (Figure 7.7) throughout the oxidation. After 24 hours about 95% of the arsenopyrite was oxidized by chemical analysis of the oxidation residue for arsenic and sulfur.
Figure 7.7  Molar ratio of total sulfur/total arsenic during the oxidation of arsenopyrite with air.

Figure 7.8  Molar fractions of sulfur species/total dissolved sulfur during the oxidation of arsenopyrite with air. (◊) S$_2$O$_3$$^-$; (△) AsO$_3$S$_3$$^-$; (□) SO$_3$$^-$.
It appears that monothioarsenate and sulfite are the initial products of arsenopyrite oxidation while thiosulfate is not. After 12 hours, the concentrations of various species tend to be constant, with the molar ratio of monothioarsenate to total dissolved sulfur or arsenic being 1/3 and that of thiosulfate to total dissolved sulfur and arsenate to total dissolved arsenic being 2/3. Other than the sulfur species, thiosulfate and sulfite, and the arsenic species, arsenate, arsenite and monothioarsenate, small amounts of dithioarsenate (AsO$_2$S$_2^{3-}$), sulfate and polythionates (S$_n$O$_6^{2-}$, n = 3-5) were also detected with concentrations less than 5 mM by ion chromatographic analysis of the solutions. As in the case of the oxidation of pyrite, sulfide or polysulfide ions were not detected by ion chromatography which is not unexpected because of the presence of significant amounts of iron in an oxidizing environment and high pH (Goldhaber, 1983). This study clearly shows that thiosulfate, monothioarsenate and arsenate are the predominant species in solutions, the relative ratios of which are dependant on the oxidation conditions such as alkalinity, oxygen pressure and reaction time.
In this typical experiment, elemental sulfur was neither observed nor determined in the oxidation residue as an intermediate product. Chemical analysis for iron and arsenic after dissolving the dried residue in 3 M HCl solutions indicated that the residue consisted predominantly of iron hydroxide possibly in the form of FeOOH with a very small amount of arsenic probably as iron arsenate (FeAsO₄). X-ray diffraction analysis of this residue showed that almost all the arsenopyrite minerals had been oxidized and that amorphous iron oxides were formed because there was no significant peak detected in the XRD analysis. Figure 7.10 shows a SEM photograph of the oxidized residue of milled arsenopyrite which indicates that the particles are very fine and porous.
Figure 7.11  Optical microscopic photograph of an arsenopyrite electrode after oxidation in an aerated 1.25 M NaOH solution. The yellowish bright spots are the surface of arsenopyrite and the brownish color indicates the presence of iron hydroxide.

Figure 7.11 shows the surface of an arsenopyrite electrode immersed in reacting pulp during oxidation of arsenopyrite in aerated 1.25 M NaOH solution. Clearly, the electrode is covered by an amorphous porous brownish iron hydroxide which may hinder the transport of reactants and products to and from the surface of the mineral during oxidation. This may explain why the extent of oxidation of arsenopyrite in alkaline media increases linearly and rapidly in the initial stage before decreasing at later stages as shown in the following sections.
7.3.3 Effect of Milling of Gold with Arsenopyrite

These experiments investigated the behaviour of milled or unmilled gold during the oxidation of arsenopyrite and were carried out in aerated 1.25 M NaOH solutions at 25 °C using 50 grams of pure arsenopyrite wet-milled with or without 55 mg gold fine powder for 1 hour. In the latter case, the gold powder was directly added into the pulp of milled arsenopyrite prior to oxidation. The results are shown in Figures 7.12, 7.13 and 7.14.

As seen in Figure 7.12, about 5% of gold wet-milled with arsenopyrite dissolves after 24 hours, whereas the gold directly added into the reaction system effectively does not dissolve. As expected, there are no marked differences in the dissolution rates of arsenic and iron between the two experiments. The extent of dissolution of arsenic increases with time, reaching about 60% in 12 hours and increasing slowly with time thereafter. Possible reasons for the slower dissolution rate of arsenopyrite in the later stages are the increase of the thickness of the iron hydroxide films on the surface of the arsenopyrite particles which may retard the mass transport of reactants such as oxygen and the consumption of the reactant, namely, sodium hydroxide. It is interesting to note that a significant and increasing amount of iron starts to dissolve when the pH becomes less than 12. Figures 7.13 and 7.14 show that there are small differences in the concentrations of oxygen, thiosulfate and monothioarsenate between the two experiments.
Figure 7.12  Dissolution of Au (◊), As (□) and Fe (ο) during oxidation of arsenopyrite milled with (white, dashed line) and without (black, solid line) gold powder (pulp density =100 g l⁻¹, 55 mg gold).

Figure 7.13  Variation of the potential (□), pH (Δ) and dissolved oxygen (ο) of the pulp during oxidation of arsenopyrite milled with (white) and without (black) gold (pulp density =100 g l⁻¹, 55 mg gold).
Figure 7.14  Variation of the concentrations of thiosulfate (□) and monothioarsenate (Δ) during oxidation of arsenopyrite milled with (white) and without (black) gold (pulp density =100 g l⁻¹, 55 mg gold).

The presence of dissolved iron in the solutions is possibly related to the presence of soluble arsenic species because ferric ions are not normally stable in alkaline media. This was tested by a preliminary investigation of the solubility of ferric ions in aqueous solutions of monothioarsenate or arsenate at various pH values by adjustment using dilute NaOH or sulfuric acid solutions. The experimental results shown in Table 7.2 indicate that ferric ions form clear stable or metastable complexes with monothioarsenate and arsenate in aqueous solutions with pH of 8 to 11. The brown solutions have remained stable even after one year.
Table 7.2  Solubility of ferric ions in monothioarsenate and arsenate solutions

<table>
<thead>
<tr>
<th>pH</th>
<th>[Fe] / g l⁻¹</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01 M AsO₃S₃⁻</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.31</td>
<td>1.48 Brown clear solution</td>
</tr>
<tr>
<td>10</td>
<td>0.38</td>
<td>1.18 Brown clear solution</td>
</tr>
<tr>
<td>9</td>
<td>1.30</td>
<td>- Brown clear solution</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>0.45 Brown clear solution</td>
</tr>
</tbody>
</table>

The higher dissolution rate of gold during the oxidation of arsenopyrite milled with gold could be attributed to a greater surface area and a better dispersion of the gold particles after wet-grinding. However, it is difficult to determine the size distribution of the gold particles before and after milling with the mineral, although an effort was made to analyze the arsenopyrite sample milled with the gold powder by using a Scanning Electron Microscope (SEM) technique. Figure 7.15 shows some fine gold particles found in the milled arsenopyrite and the surface components of one gold particle are listed in Table 7.3.

Table 7.3  Semi-quantitative SEM/EDAX analysis of a fine gold particle after wet-grinding

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
<th>Molar%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold (Au)</td>
<td>94.6</td>
<td>83.2</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>3.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>0.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure 7.15 SEM photograph of fine gold particles wet-milled together with arsenopyrite in a stainless steel mill. The white spots are gold particles. The original unmilled gold particles are 1.5 - 3 µm in size.

It can be seen that there is no apparent change in the sizes of gold particles after wet-grinding. However, the data shown in Table 7.3 indicate a molar ratio of As:S:Fe of around 1:1:3, which seems to suggest the occurrence of chemical reactions of arsenopyrite on the surface of gold. Thus, mechanochemical interactions between gold and the arsenopyrite mineral should be taken into account in the interpretation of the higher dissolution rate of gold during the alkaline oxidation of arsenopyrite. According to Balaz (2000), S(-2) and S(+6) can be found on the surface of mechanically activated arsenopyrite samples with sulfate sulfur prevailing. It is possible that some of the gold particles could react with sulfides or the As-S group forming solid compounds that are more easily soluble in thiosulfate solutions.
Figure 7.16 shows the X-ray diffraction patterns of the arsenopyrite mineral before and after wet-milling with gold powders. No obvious differences can be observed which is not unexpected given that the X-ray diffraction technique normally cannot detect components with a mass less than 5% of the total.

![XRD diagram](image)

Figure 7.16  XRD diagrams for wet-milled arsenopyrite minerals in the presence and absence of gold powder. Wavelength of 1.7902Å (Co).

### 7.3.4 Effect of Particle Size on the Dissolution of Arsenopyrite

The results of experiments conducted with three size fractions of arsenopyrite samples (-10 µm, +38-45 µm, and +63-75 µm) are shown in Figures 7.17 and 7.18. These experiments were carried out using 30 g l⁻¹ pulp density in aerated 1.25 M NaOH solutions without the addition of gold powder. As shown in Figure 7.17, the oxidation
rate of arsenopyrite increases as expected with decreasing particle size. With ultra-fine particles (less than 10 µm, average size 4.2 µm), the rate of oxidation is rapid and almost constant for the first 5 hours after which the rate reduces with time until complete oxidation is achieved after about 12 hours. In the cases of the coarser particle sizes, the rate of oxidation is significantly lower and remains nearly constant for 24 hours. Figure 7.18 shows that the concentrations of thiosulfate and monothioarsenate in the reacting slurry with ultra-fine particles of arsenopyrite are much higher than those with coarser sizes of arsenopyrite. These results suggest that ultra-fine milling of arsenopyrite could assist in the dissolution of gold because of the formation of higher concentrations of thiosulfate and monothioarsenate.

Figure 7.17  Dissolution rates of arsenopyrite with different particle sizes in aerated 1.25 M NaOH solutions (pulp density =30 g l⁻¹). (◊) -10 µm; (□) +38-45 µm; (Δ) +63-75 µm.
7.3.5 Effect of Stirring Speed on the Dissolution of Arsenopyrite and Gold

Stirring speed has a significant effect on the oxidation rate of arsenopyrite in alkaline or acid solutions under oxygen pressures (Ciminelli and Osseo-Asare, 1995a, b; Koslides and Ciminelli, 1992; Papangelakis and Demopoulos, 1990). Koslides and Ciminelli (1992) reported that over 800 rpm rotation in their reactor the reaction rate became independent of the stirring speed. In this study only two stirring speeds, 600 rpm and 1400 rpm, were selected to assess the effect of agitation on the rate of dissolution of arsenopyrite and gold.

The experimental results shown in Figure 7.19 highlight the noticeable differences in the dissolution rates of arsenopyrite and gold. At 600 rpm agitation, gold does not dissolve and only 41% of the arsenopyrite is oxidized after 24 hours, whereas with a strong agitation of 1400 rpm, 8.3% of the gold and 95.2% of the arsenopyrite
dissolve after 24 hours. Figures 7.20 and 7.21 show the concentrations of thiosulfate, oxygen and monothioarsenate and the potential of a gold electrode in the reaction slurry during these experiments.

Figure 7.19 Dissolution rate of arsenopyrite and gold in 1.25 M NaOH solutions with different agitation speeds (pulp density =50 g l\(^{-1}\), 66 mg gold).

It can be seen that at 600 rpm agitation, the concentrations of thiosulfate, monothioarsenate and oxygen in the pulp and the potential of gold electrode are much lower than those at the higher 1400 rpm stirring speed, which suggests that mass transfer of oxygen in the bulk solution could be limiting the reaction rates at the lower agitation speed. Thus, based on these data, the stirring speed of 1400 rpm was chosen as the standard condition for the experiments because it ensured more efficient mass transfer of oxygen as well as adequate suspension of the solid particles. From these results, it can also be concluded that at lower potentials the initial oxidation product is mainly monothioarsenate.
Figure 7.20  Variations of the concentrations of thiosulfate and oxygen during the oxidation of arsenopyrite in 1.25 M NaOH solutions with different agitation speeds (pulp density =50 g l⁻¹, 66 mg gold).

Figure 7.21  Potential of gold electrode and concentration of monothioarsenate during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions at two agitation speeds (pulp density =50 g l⁻¹, 66 mg gold). (□) 1400 rpm; (◊) 600 rpm.
7.3.6 Effect of Pulp Density on the Dissolution of Arsenopyrite and Gold

For a given amount of sodium hydroxide, changes in the solids concentration would lead to different concentrations of oxidation products which could influence the dissolution of the gold. Figures 7.22 to 7.27 show the variation with time of the dissolution rate of arsenopyrite, the concentrations of dissolved gold, thiosulfate and monothioarsenate, the solution potentials, pH and dissolved oxygen during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions at different pulp densities. Before the experiment, different quantities of the arsenopyrite mineral were wet-milled together with 60mg of gold powder and the same amount of NaOH was used for each experiment.

It can be seen that a lower solids concentration results in higher oxidation rates of both arsenopyrite and gold. On the other hand, lower concentrations of thiosulfate and monothioarsenate (Figure 7.24) are formed when a lower pulp density of arsenopyrite is used. The potentials of the slurries (Figures 7.26 and 7.27) are between –0.7 V and 0.12 V. It appears that gold starts to dissolve at potentials above -0.1 V. These results are rather unexpected and dissimilar to the behaviour of pyrite. Thus, if the concentration of thiosulfate is lower at the lower pulp densities, then one could expect a lower rate of gold dissolution. Perhaps other species involving arsenic, for example, monothioarsenate, could be involved in the dissolution of gold in the case of arsenopyrite.
Chapter 7 Simultaneous Oxidation of Sulfide Minerals and Dissolution of Au in Alkaline Solutions

Figure 7.22 Oxidation of arsenopyrite in aerated 1.25 M NaOH solutions at different pulp densities (60 mg gold).

Figure 7.23 Variation of the gold dissolved during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions at different pulp densities (60 mg gold).
Figure 7.24 Generation of thiosulfate and monothioarsenate during the oxidation of arsenopyrite in aerated 1.25 M NaOH solution at different pulp densities (60 mg gold). (◊) 30 g l⁻¹; (□) 50 g l⁻¹; (Δ) 100 g l⁻¹.

Figure 7.25 Variation of pH values and oxygen concentrations during the oxidation of arsenopyrite in aerated 1.25 M NaOH at different pulp densities (60 mg gold). (◊) 30 g l⁻¹; (□) 50 g l⁻¹; (Δ) 100 g l⁻¹.
Figure 7.25 shows the pH value and oxygen concentration of the pulp during the oxidation at different pulp densities. As expected, the pH of the pulp decreases more markedly with time at the higher pulp concentrations. The concentration of dissolved oxygen decreases in the initial stage indicating relatively rapid initial oxidation rate of arsenopyrite. During the later stages, the oxygen concentration increases to the saturated value, suggesting that the oxidation rate of arsenopyrite has decreased substantially due to either complete oxidation or depletion of the available alkali. From Figure 7.22 and 7.25, it can be seen that at the lowest pulp density the oxidation of arsenopyrite is completed in 12 hours after which a higher concentration of oxygen is observed, whereas at the highest pulp density the oxygen concentration is lower even during the later stages of oxidation.

The potentials of the gold, platinum and arsenopyrite electrodes during the oxidation of arsenopyrite with 30 g l⁻¹ pulp density were also recorded as shown in Figure 7.26. The difference between the potentials of the gold and platinum electrodes is small, with the potential of gold slightly lower than that of platinum as could be expected due to the dissolution of gold. The potential of arsenopyrite is, as expected in a mixed potential system, also lower and increases with time in the range of −0.5 V to 0 V which is in agreement with previous work on the anodic behaviour of arsenopyrite (Nicol and Guresin, 2000 and 2003). Figure 7.27 compares the mixed potentials of gold and arsenopyrite electrodes during oxidation at different pulp densities. It appears that the potential of arsenopyrite during the later stage of oxidation at 30 g l⁻¹ density is low, suggesting a strong dependence of the mixed potential of arsenopyrite on the alkalinity which is consistent with the studies by Nicol and Guresin (2000 and 2003).
Figure 7.26  Potentials of gold, platinum and arsenopyrite electrodes during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions (pulp densities = 30 g 1⁻¹).

Figure 7.27  Variation of potentials of gold (solid lines) and arsenopyrite (dashed lines) electrodes during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions at different pulp densities. (◊) 30 g 1⁻¹ ; (□) 50 g 1⁻¹ ; (Δ) 100 g 1⁻¹.
It can also be seen from Figure 7.27 that the mixed potential of gold in the later stage of the oxidation of arsenopyrite is lower at 30 g l\(^{-1}\) pulp density than at 100 g l\(^{-1}\) density whereas the dissolution of gold (Figure 7.23) is higher at 30 g l\(^{-1}\) pulp density than at 100 g l\(^{-1}\) pulp density. Given the data shown in Figure 7.25, the unexpected results could be due to a relatively strong dependence of the mixed potential of gold on the alkalinity which agrees with the electrochemical studies regarding to the mixed potentials of gold in alkaline thiosulfate solutions shown in Section 4.2.1 in Chapter 4, and due to the effect of the concentration of dissolved oxygen on the rate.

### 7.3.7 Effect of Oxygen Partial Pressure

Since as suggested by the above results the dissolved oxygen concentration may affect the rate of oxidation of both arsenopyrite and gold, the role of oxygen was determined by using air, a mixture of air and oxygen gas, a mixture of nitrogen and oxygen and pure oxygen at a flowrate of 1 l min\(^{-1}\) at 25 °C. The results of a series of tests conducted at various partial pressures of oxygen are plotted in Figures 7.28 and 7.29. It is clear that an increase in oxygen pressure favors the overall oxidation kinetics of both arsenopyrite and gold.

It is also apparent that the dissolution rate of gold is characterized by an induction period, followed by a rapid increase in the rate at higher oxygen partial pressures, whereas at lowest oxygen pressure i.e. air, the extent of dissolution of gold shows an approximately linear increase with time after a longer induction period. This phenomenon can be understood by considering the variation of the thiosulfate concentration during the oxidation at various oxygen partial pressures as shown in Figure
7.30. When higher oxygen pressures are employed, the thiosulfate concentration is higher in the initial stage of the oxidation than when air is used, thus resulting in a higher rate of dissolution of the gold. In support of this is the fact that when higher oxygen pressures were used, the potential of the slurries increased from -0.6 V at the beginning of the oxidation to about 0 V after 2 hours whereas the slurry potential reached the same level only after 7 hours when air was used.

![Figure 7.28](image-url)

**Figure 7.28**  Effect of oxygen partial pressure on the oxidation of arsenopyrite in 1.25 M NaOH solutions.

### 7.3.8 Effect of NaOH Concentration

Arsenopyrite requires hydroxyl ions for its oxidation (Equation 7.3). Thus, a series of runs were conducted at various initial NaOH concentrations to determine the effect of the NaOH concentration on the rate of oxidation of arsenopyrite and gold with air. Figures 7.31, 7.32 and 7.33 give the results of these experiments.
Figure 7.29  Effect of oxygen partial pressure on gold dissolution during the oxidation of arsenopyrite in 1.25 M NaOH solutions.

Figure 7.30  Variation of thiosulfate formed during the oxidation of arsenopyrite in 1.25 M NaOH solutions at various oxygen partial pressures.
Figure 7.31 Oxidation of arsenopyrite with air in solutions of different initial NaOH concentrations.

Figure 7.32 Dissolution rates of gold during the oxidation of arsenopyrite with air in different NaOH solutions.
Apparently, the extent of oxidation of arsenopyrite after 10 hours is greater when a higher initial concentration of NaOH is employed. However, higher concentrations of NaOH result in a slightly lower initial rate of oxidation of arsenopyrite, which may be due to the decrease in oxygen solubility in solutions of high ionic strength (Narita et al., 1983). In 0.625 M NaOH solution, 63% oxidation is achieved due to the lack of sufficient NaOH for the complete oxidation of the arsenopyrite. Thus, the stoichiometric requirement of NaOH for the oxidation of arsenopyrite by oxygen in these experiments is about 30 grams assuming that Equation 7.3 applies, whereas in the experiment with 0.625 M NaOH solution the quantity of NaOH used is only 12.5 grams which is only about 41% of the stoichiometric. In this comparison it should be noted that the oxidation reaction given by Equation 7.3 cannot apply because of the apparent difference in the extent of oxidation between that achieved (63%) and calculated (41%).

Figure 7.32 shows the significant effect of the initial NaOH concentration on the dissolution of gold during oxidation of arsenopyrite. Again an induction period can be observed. Gold starts to dissolve after 3 hours in 0.625 M and 1 M NaOH solutions and later in 2.08 M NaOH solution. As before, this phenomenon can be attributed to the slow formation of thiosulfate in the more concentrated NaOH solution as demonstrated in Figure 7.33. It is worth noting that there is a significant effect of hydroxyl ions on the dissolution rate of gold after 12 hours despite the fact that the concentrations of thiosulfate in the different solutions are similar after 12 hours (about 70 mM). This behaviour is in agreement with electrochemical studies of the dissolution of gold in thiosulfate solutions in which the anodic reactivity of gold increased with an increase in pH (Chapter 4).
Figure 7.33  Formation of thiosulfate during the oxidation of arsenopyrite with air in different NaOH solutions.

Figure 7.34  Oxidation of arsenopyrite in 1.25 M NaOH solutions with air at different temperatures (pulp density = 50 g l\(^{-1}\)).
7.3.9 Effect of Temperature

Figure 7.34 shows the variation of the extent of oxidation of arsenopyrite with time for temperatures from 25 °C to 55 °C. As expected, an increase in temperature improved the kinetics of oxidation of arsenopyrite. Figure 7.35 shows the variation of gold dissolved during the oxidation of arsenopyrite at different temperatures. In the initial stages of oxidation, no obvious difference can be seen between the experiments at increasing temperature. However, it is apparent that there is an optimum temperature of about 35 °C at which the extent of gold dissolution appears to attain the highest value, while at 55 °C gold appears to cease dissolution after 12 hours. The concentration of thiosulfate, however, does not appear to vary with the increasing temperature (Figure 7.36). On the other hand, as shown in Figure 7.37 the dissolved oxygen concentration decreases with an increase in temperature and this could account for the reduced rate at the higher temperatures. Figure 7.38 shows that there is no apparent difference in the mixed potential of the gold electrode at various temperatures but the potentials of gold are higher than those of arsenopyrite as expected.

![Graph showing the variation of gold dissolved with time for different temperatures.](image)

Figure 7.35 Dissolution rates of gold during the oxidation of arsenopyrite by air in 1.25 M NaOH solutions at different temperatures (pulp density = 50 g l⁻¹).
Figure 7.36  Variation of thiosulfate concentration during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions at different temperatures (pulp density = 50 g l$^{-1}$).

Figure 7.37  Variation of oxygen concentration during the oxidation of arsenopyrite by air in 1.25 M NaOH solutions at different temperatures (pulp density = 50 g l$^{-1}$).
7.3.10 Effect of the Addition of Thiosulfate or Sulfur

The above experimental results have suggested that thiosulfate could be the lixiviant of gold. Thus addition of thiosulfate to the reacting pulp could be expected to have a positive effect on gold dissolution during oxidation. It is possible that the addition of elemental sulfur could also have an effect on the rate of dissolution of gold. Therefore, three experiments were carried out in which arsenopyrite was oxidized in aerated 1.25 M NaOH solution in the presence or absence of 0.05 M added thiosulfate, and in the presence of 0.1 g elemental sulfur. It should be pointed out that the arsenopyrite sample used in these tests contained 0.174% Cu and that the elemental sulfur was wet-milled together with the mineral and gold powder.
Figure 7.39 Oxidation of arsenopyrite in 1.25 M NaOH solution in the presence and absence of 0.05 M thiosulfate, and in the presence of 0.1 g sulfur.

Figure 7.40 Concentrations of gold (solid lines) and copper (dotted lines) during the oxidation of arsenopyrite with 0.1 g sulfur (Δ), with (o) and without (◊) 0.05 M thiosulfate in 1.25 M NaOH solutions.
Figure 7.41 Effect of the addition of thiosulfate or elemental sulfur on the concentration of thiosulfate during the oxidation of arsenopyrite in aerated 1.25 M NaOH solutions.

The main experimental results are shown in Figures 7.39, 7.40 and 7.41. It can be seen that the extent and rate of oxidation of arsenopyrite is not changed when 0.05 M thiosulfate is initially added into 1.25 M NaOH solution. However, the dissolution of both gold and copper are improved in the presence of higher concentrations of thiosulfate as shown in Figure 7.40. Figure 7.41 suggests that oxidation rate of thiosulfate with air is rather slow because the difference of the concentrations of thiosulfate at the same reaction time during the two experiments is nearly constant. It is worth noting the dissolution of copper which is probably due to complexation of copper ions with thiosulfate ions. As found and reported in Chapter 5, the dissolved copper can catalyze the dissolution of gold in thiosulfate solutions.

It has been shown in Section 7.3.1 that small amounts of elemental sulfur may be formed during the alkaline oxidation of pyrite. It was suspected that sulfur could play a
role in the dissolution of gold in alkaline solutions. Figures 7.40 and 7.41 clearly demonstrate that addition of milled sulfur has increased the dissolution of gold and copper without increasing the concentration of thiosulfate. This observation implies that the sulfur could have reacted with gold and copper during milling, resulting in more rapid dissolution of gold and copper in the thiosulfate solution. Thus, additional experiments were carried out in which 50 mg gold fine powder was first wet-milled with 0.1 grams of elemental sulfur in a porcelain ball mill for 1 hour before being leached in the presence and absence of added thiosulfate. The results are shown in Table 7.4.

Table 7.4 Dissolution of gold in oxygenated alkaline NaOH solutions after milling with elemental sulfur (600 ml solution, pH 12, 25 °C, 0.1 g sulfur)

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>With no addition of S$_2$O$_3^{2-}$</th>
<th>With 0.1 M S$_2$O$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Au] /ppm</td>
<td>[S$_2$O$_3^{2-}$] /mM</td>
</tr>
<tr>
<td>16</td>
<td>0.00</td>
<td>0.2</td>
</tr>
<tr>
<td>19</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>48</td>
<td>0.00</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Obviously, no dissolution of gold is detected without the addition of thiosulfate even after the gold is wet-milled with sulfur. Oxidation of the elemental sulfur is obviously very slow at room temperatures as shown by the low concentrations of thiosulfate and sulfite formed. As expected, sulfide ions were not detected by ion chromatographic analysis. However, dissolution of gold does occur to some extent in the 0.1 M thiosulfate solution when the gold is wet-milled with sulfur followed by oxidation with oxygen. Therefore, it is believed that the dissolution of gold during the oxidation of pyrite and arsenopyrite is due to its reaction with thiosulfate.
7.3.11 Reactions between Arsenite and Sulfur Species

The above studies have shown that thioarsenates are important products of the oxidation of arsenopyrite with air under ambient temperatures and pressures. To better understand the dissolution mechanism of arsenopyrite, reactions between arsenite and sulfur species such as thiosulfate and polysulfides were studied by using ion chromatographic analysis to determine the species present in various solutions. The experiments were carried out by mixing arsenite solutions with thiosulfate solutions or polysulfide solutions to form a solution containing 2 mM $\text{AsO}_3^{3-}$, 2 mM $\text{S}_2\text{O}_3^{2-}$, 10 mM NaOH or a solution of 2 mM $\text{AsO}_3^{3-}$, 2 mM polysulfides, 10 mM NaOH. The polysulfide solution was prepared by dissolving equimolar amounts of elemental sulfur and base (as sodium hydroxide) solution with heating. Thus the polysulfide solution was a mixture containing $\text{S}_n^{2-}$ ($n \geq 2$), $\text{S}_2\text{O}_3^{2-}$ and $\text{SO}_3^{2-}$ with $\text{S}_2^{2-}$ probably predominant. The analysis of 2 mM polysulfide solution by HPLC indicated the presence of 0.64 mM $\text{S}_2\text{O}_3^{2-}$ and 0.26 mM $\text{SO}_3^{2-}$. After mixing, the solutions were analyzed using HPLC for various species at various times. The results are given in Table 7.5.

Table 7.5 clearly shows that the reaction between arsenite and thiosulfate is very slow at room temperatures. It appears that thiosulfate is formed after 4 days in the case of mixing arsenite with polysulfides and the dithioarsenate concentration decreases with time after its formation, implying that thiosulfate could be produced by the decomposition of dithioarsenate. The concentration of monothioarsenate appears to remain constant, suggesting a possible slow rate of monothioarsenate decomposition. An additional experiment (results not shown) on the oxidation of monothioarsenate with oxygen in an aqueous solution of pH 12 indicated that the concentration of monothioarsenate remained essentially constant over 24 hours, suggesting a very slow
oxidation of monothioarsenate. The formation of thiosulfate, therefore, could probably be attributed to the formation and decomposition of dithioarsenates.

Table 7.5 Concentrations of the various species formed in the reactions of arsenite with sulfur species at 25 °C (Units: mM)

<table>
<thead>
<tr>
<th>Time</th>
<th>0 hour</th>
<th>0.5 hour</th>
<th>4 days</th>
<th>8 days</th>
<th>6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction of ( \text{AsO}_3^{3-} ) with ( \text{S}_n^{2-} ), ( n \geq 2 )</td>
<td>( \text{AsO}_3^{3-} )</td>
<td>2.1</td>
<td>1.57</td>
<td>0.73</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>( \text{AsO}_3\text{S}^{3-} )</td>
<td>0</td>
<td>0.08</td>
<td>0.45</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>( \text{SO}_3^{2-} )</td>
<td>0.26</td>
<td>0.60</td>
<td>1.00</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>( \text{S}_2\text{O}_3^{2-} )</td>
<td>0.54</td>
<td>0.54</td>
<td>0.54</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>( \text{AsO}_2\text{S}_2^{2-} )</td>
<td>0</td>
<td>0.35</td>
<td>*</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>( \text{AsO}_4^{4-} )</td>
<td>0</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
<tr>
<td></td>
<td>( \text{SO}_4^{2-} )</td>
<td>0</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
<tr>
<td>Reaction of ( \text{AsO}_3^{3-} ) with ( \text{S}_2\text{O}_3^{2-} )</td>
<td>( \text{AsO}_3^{3-} )</td>
<td>2.1</td>
<td>*</td>
<td>2.10</td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>( \text{S}_2\text{O}_3^{2-} )</td>
<td>2.1</td>
<td>*</td>
<td>2.10</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>( \text{AsO}_3\text{S}^{3-} )</td>
<td>0</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
<tr>
<td></td>
<td>( \text{SO}_3^{2-} )</td>
<td>0</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
</tbody>
</table>

* Not Determined;  # Not Measurable.

7.4 Discussion

7.4.1 Chemistry of the Oxidation of Pyrite

Experimental results have shown that thiosulfate, sulfite and small amounts of elemental sulfur are formed during the alkaline oxidation of pyrite by oxygen or air at ambient temperatures and pressures, which are in agreement with the results reported by Goldhaber (1983), Mishra and Osseo-Asare (1988) and Hamilton and Woods (1981). An
approximate stoichiometry of the overall process of pyrite oxidation in alkaline solutions with air is given by the following reaction:

$$12\text{FeS}_2 + 11\text{O}_2 + 32\text{NaOH} + 2\text{H}_2\text{O} = 12\text{Fe(OH)}_3 + 8\text{Na}_2\text{S}_2\text{O}_3 + 8\text{Na}_2\text{SO}_3$$  \hspace{1cm} (7.4)

This is based mainly on the results (Figure 7.4) which show that in the initial stages of the oxidation, the atomic molar ratio of thiosulfate to total dissolved sulfur is about 2/3 and that of sulfite to total dissolved sulfur is about 1/3. Sulfate is believed to be formed as a product of the oxidation of sulfite by oxygen. Small amounts of polythionates ($\text{S}_n\text{O}_{6}^{2-}$, $n = 3-5$) as the oxidation products of thiosulfate could also be formed during the oxidation of pyrite in alkaline media as reported by Goldhaber (1983) and Xu and Schoonen (1995), although analysis for these species was not carried out in this study. However, the concentrations of polythionates in strongly alkaline solutions are well known to be low due to decomposition to thiosulfate and sulfite (Rolia and Chakrabarti, 1982).

As found by Goldhaber (1983), sulfide and polysulfides were not detected in the reacting solutions. The small amounts of sulfur found in this study probably resulted from the oxidation of sulfide or polysulfides with oxygen (Equation 2.49; Figure 2.2) under alkaline conditions as suggested by Chen and Morris (1972) and Goldhaber (1983).

### 7.4.2 Chemistry of the Oxidation of Arsenopyrite

#### 7.4.2.1 Speciation of arsenic and sulfur

The results of Figure 7.7 have confirmed that the alkaline oxidation of arsenopyrite at ambient temperatures and pressures is stoichiometric in regard to the
constituent elements of the mineral. There appears to be no formation of any intermediate sulfide-containing solid phase as suggested by Sanchez and Hiskey (1991) and Wang et al. (1992). The measured pulp potentials during the alkaline oxidation are in the range of -0.6 to 0.2 V (Figure 7.13), which is in agreement with the thermodynamic values (Figure 2.10 in Section 2.4.2.2) and the electrochemical measurements carried out by Nicol and Guresin (2000 and 2003), and corresponds to the initial oxidation step of arsenopyrite in alkaline solutions as suggested by Sanchez and Hiskey (1991) and Nicol and Guresin (2003). Thus, arsenic and sulfur species of low oxidation states would be formed.

However, ion chromatographic and chemical analyses in this study have shown that the arsenic and sulfur species formed as oxidation products of arsenopyrite, are very different from those suggested by most of the previous studies (Sanchez and Hiskey, 1991; Rossovsky, 1993; Wang et al., 1992; Nicol and Guresin, 2003). Thioarsenites as proposed by Rossovsky (1993) and elemental sulfur as suggested by Sanchez and Hiskey (1991) were not detected in this study. Figures 7.8, 7.9 and 7.14 clearly show that a new species, namely, monothioarsenate is one of the prominent products of the oxidation of arsenopyrite by oxygen in aqueous alkaline solutions. Furthermore, dithioarsenate as a minor ion has also been identified during the oxidation. Similar to the oxidation of pyrite, sulfide or polysulfides were not detected by either HPLC analysis or qualitative tests for sulfide ions in solution, which is not unexpected because of the presence of significant amounts of iron in an oxidizing environment and due to the rapid oxidation of sulfide and polysulfides to sulfite or thiosulfate (Chen and Morris, 1972). The absence of elemental sulfur in oxidized residues appears to be consistent with the thermodynamics of the oxidation of arsenopyrite as shown in the Eh-pH diagram (Figure 2.9) which shows that elemental sulfur would not be formed at pH values higher than 8. As will be
discussed below, elemental sulfur was not produced probably due to the presence of arsenate and thioarsenates.

This study evidently shows that thiosulfate, monothioarsenate and arsenate are the predominant species in solutions, although very small amounts of sulfite, sulfate, arsenites and polythionates are also detected. The sulfate and polythionates are believed to be the oxidation products of sulfite and thiosulfate respectively. According to Figures 7.8 and 7.9, therefore, the possible stoichiometry of the overall process of the oxidation of arsenopyrite in NaOH solutions by oxygen may be given by the following reaction:

$$6\text{FeAsS} + 13\text{O}_2 + 22\text{NaOH} = 6\text{Fe(OH)}_3 + 2\text{Na}_3\text{AsO}_3\text{S} + 4\text{Na}_3\text{AsO}_4 + 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}$$  \hspace{1cm} (7.5)

However, intermediate species such as arsenite and dithioarsenate may also be present in the oxidation process as suggested by Nicol and Guresin (2003). This study experimentally confirms the formation of monothioarsenate as proposed by Bou et al. (1998) for the possible anodic oxidation reactions of arsenopyrite in acid media. However, the mechanism proposed by Bou et al. (1998) ruled out the formation of thiosulfate.

The data in Figures 7.8 and 7.9 suggest that monothioarsenate is the principal product in the initial stage of arsenopyrite oxidation while thiosulfate and, to a lesser extent, arsenate, are produced by subsequent homogeneous oxidation of monothioarsenate in alkaline media, because the concentrations of thiosulfate and arsenate increase as the concentration of monothioarsenate decreases with time. However, the experimental results in Section 7.3.11 indicate that the reaction of arsenite with thiosulfate (Equation 2.31) and the oxidation of monothioarsenate in aqueous alkaline media by oxygen are kinetically very slow at room temperatures. Thiosulfate
probably comes from the decomposition and/or oxidation of dithioarsenates which could be formed either from the reactions of arsenite with polysulfides (Equations 7.6 and 7.7; Mellor, 1929) or from the reaction of monothioarsenate with polysulfides (Equation 7.8).

\[
\text{AsO}_3^{3-} + \text{S}_2^{2-} = \text{AsO}_3\text{S}_3^{3-} + \text{S}^{2-} \quad (7.6)
\]
\[
\text{AsO}_3^{3-} + \text{S}_2^{2-} + \text{H}_2\text{O} = \text{AsO}_2\text{S}_2^{3-} + 2\text{OH}^- \quad (7.7)
\]
\[
\text{AsO}_3\text{S}_3^{3-} + \text{S}_2^{2-} + \text{O}_2 = \text{AsO}_2\text{S}_2^{3-} + \text{SO}_3^{2-} \quad (7.8)
\]

Schwedt and Rieckhoff (1996) have reported that dithioarsenate is not stable in alkaline media. The possible reaction for the formation of thiosulfate from dithioarsenate could be:

\[
\text{AsO}_2\text{S}_2^{3-} + 2\text{O}_2 + 2\text{OH}^- = \text{S}_2\text{O}_3^{2-} + \text{AsO}_4^{3-} + \text{H}_2\text{O} \quad (7.9)
\]
in which arsenate is also produced. The rate of oxidation of dithioarsenate may be fast in the presence of oxygen. Thus, the formation of dithioarsenate may be important for the production of thiosulfate and this also suggests the possible presence of polysulfides or sulfur as intermediates on the surface of oxidized arsenopyrite particles.

Although polysulfides were not detected in aqueous solutions or solid residues in present work, Nesbitt and coworkers (1995) have reported, by using x-ray photoelectron and auger electron spectroscopy techniques, that reaction of arsenopyrite with air-saturated water produces polysulfides and thiosulfate on the surface of the reacted mineral, all primarily at the expense of disulfide (S$_2^{2-}$). In this case, the disulfide S$_2^{2-}$ ion should be represented more accurately as a dianionic group, (AsS)$_2^{-}$. They have also reported that on an unoxidized surface of arsenopyrite (Fe$_2^+(\text{AsS})^2$), sulfur is present as disulfide (S$_2^{2-}$, 78 atomic%), monosulfide (S$_2^{-}$, 15%), and as polysulfides (S$_n^{2-}$, 7%) while arsenic is predominantly present as As(-1) with 15% present as As(0). Buckley and Walker (1988) have reported that most of arsenic has an oxidation state of three rather than five in air-saturated alkaline solution and that sulfur also occurs on a reacted surface.
of arsenopyrite. Therefore, reactions 7.6 and 7.7 could occur on the surface of arsenopyrite in aerated alkaline solutions. Figures 7.8 and 7.9 show that in the early stage of oxidation about 60-70% (by atom) of AsO$_3$$^-$, 10% S$_2$O$_3$$^-$$^-$ and 15% SO$_3$$^-$$^-$ (probably from the oxidation of S$^2$-, Equation 7.10) are formed. The ratios of these species suggest that the monothioarsenate ion could have its origins in the (AsS)$_2$$^-$$^-$ group and that thiosulfate is produced from polysulfides with dithioarsenate being the intermediate. On the other hand, the sulfite could react with polysulfides, thus forming thiosulfate as described in Equation 7.11.

\[
2S^{2-} + 3O_2 = 2SO_3^{2-}
\]  
(7.10)

\[
SO_3^{2-} + S_2^{2-} = S_2O_3^{2-} + S^{2-}
\]

$\Delta G^{\circ}_{298K} = -23.8$ kJ mol$^{-1}$  
(7.11)

It is apparent that the oxidation of arsenopyrite in alkaline media is a complex process that involves many possible reactions such as the simultaneous dissolution and oxidation of arsenic and sulfur and the oxidation, hydrolysis and precipitation of iron. The actual reaction mechanism is not completely understood and should be further investigated.

### 7.4.2.2 Products of oxidation of iron

One important feature of the oxidation of iron-bearing sulfides in alkaline media is the precipitation of hydrated iron oxide compounds on the surface of the reacting mineral. The oxide often forms a coating whose properties depend on the experimental conditions as well as on the texture of the parent phase (Caldeira et al., 2003; Burkin and Edwards, 1963). The characteristics of the oxide coating determine the rate of mass transfer through the layer and, thus, the overall rate of decomposition of the minerals (Ciminelli and Osseo-Asare, 1986 and 1995a, b; Burkin and Edwards, 1963; Kostina and Chernyak, 1979). Examination of an almost completely oxidized residue of arsenopyrite by SEM (Figure 7.10) and chemical analyses, and an optical microscopic analysis of an
arsenopyrite electrode (Figure 7.11) have confirmed the formation of an amorphous porous iron oxide (such as ferrihydrite) or hydroxide (such as FeOOH) on the surface of arsenopyrite mineral (Koslides and Ciminelli, 1992; Hiskey and Sanchez, 1995 and Bhakta et al., 1989). In addition, small amounts of iron arsenate were detected in the oxidized residue, probably as FeAsO₄.

An interesting and unexpected feature found in this study is the dissolution of iron in alkaline solutions during the oxidation of arsenopyrite at pH values below 11 (Figure 7.12). Table 7.2 has confirmed the dissolution of ferric ions in alkaline solutions containing arsenate or monothioarsenate. This is unexpected because ferric ions usually precipitate as ferric hydroxides or iron arsenates under alkaline conditions (Robins, 1987; Krause and Ettel, 1989). In fact, the work of Krause and Ettel (1989) on the solubility of synthetic scorodite (FeAsO₄·2H₂O) at room temperatures has showed that the dissolution of iron and arsenic increases significantly with increasing pH above pH 5, with the iron concentration being 52 ppm at pH 7.92. However, the mechanism of iron dissolution in alkaline arsenic bearing solutions is not known. From the Table 7.2, it is possible that ferric ions react with arsenate or monothioarsenate forming metastable species. This feature of iron dissolution may assist with the further decomposition of arsenopyrite under certain conditions such as the catalytic role of the Fe(III)/Fe(II) couple in acid media for the oxidation of arsenopyrite (Ruitenber et al., 1999; Nicol and Lazaro, 2002). In this case, the dissolved metastable species of iron in alkaline arsenic solutions may act as catalysts for the oxidation of arsenopyrite by oxygen. Further studies of this aspect should be made.
7.4.3 Kinetics of the Oxidation of Arsenopyrite

The primary objective of this study was to investigate the chemistry and kinetics of the dissolution of gold. However, as gold dissolves simultaneously during the alkaline oxidation of arsenopyrite with oxygen, it is important to also establish the kinetics (and, if possible) the mechanism of the oxidation of the mineral. As an introduction, the general concepts of heterogeneous reaction kinetics and its relevance to this work are briefly summarized.

Heterogeneous reactions are reactions that occur at the interfaces of two or more phases in a system. Hydrometallurgical processes often involve heterogeneous reactions which take place between a solid phase and a solute in an aqueous solution. Some processes can involve three phases such as gold cyanidation and pressure oxidation of sulfides in which the gas phase is also implicated. These reactions usually contain the following major steps (Marsden and House, 1992):

1. Mass transport of gaseous reactants (where relevant) into the solution phase and subsequent dissolution;

2. Mass transport of reacting species through the solution/solid boundary layer, to the solid surface;

3. Chemical (or electrochemical) reaction at the solid surface, including adsorption and desorption at the solid surface;

4. Mass transport of produced species through the boundary layer into bulk solution.

The rate-limiting step for a sequential reaction path is determined by the slowest step in the sequence. If this slow step is mass transfer, the reaction is said to be diffusion
controlled. In contrast, when the slow step is a chemical (or electrochemical) reaction at the surface of the solid, the rate is referred to as being chemically controlled. The rate determining step may change for a reaction if conditions change: for example, if a reactant concentration is increased, a reaction may change from mass transport to chemically controlled as more reagent is available to be transported to the reaction surface. For chemically controlled reactions the Arrhenius activation energy (Ea) is large, typically greater than 40 kJ mol\(^{-1}\), while for mass transport controlled reactions Ea is small, between 5 and 20 kJ mol\(^{-1}\) (Marsden and House, 1992).

In heterogeneous solid-liquid reaction systems, rates of reactions are often proportional to both the total surface area of the solid and the concentrations of reacting species. For reaction between a solid, B, and a solute, A as described in the following simplified reaction:

\[
\text{bB (s) + A (aq) } \rightarrow \text{B----A (products)}
\]

the rate of reaction may be defined by the general expression

\[
\frac{dN_B}{dt} = - S b k_0 k' [A]^m
\]

where \(\frac{dN_B}{dt}\) is the rate of reaction in moles per unit time, \(S\) is the solid surface area, \(b\) is the stoichiometric number of moles of the solid reacting with one mole of the solute, \([A]\) is the solution concentration of the solute, \(k'\) is the rate constant, \(k_0\) is the concentration of reactive surface sites (in moles per unit area) and \(m\) is the reaction order with respect to \([A]\). Based on this general expression, various kinetic models for heterogeneous solid-liquid reactions have been developed, including shrinking sphere and shrinking core models for various solid geometries (Levenspiel, 1999).

In this study the oxidation of arsenopyrite was carried out at high pulp densities and the concentrations of NaOH and oxygen were not constant during the experiments
(see Figures 7.13, 7.20 and 7.37). In addition, iron oxide layers are formed on the reacting mineral surface and thus the simple kinetic models for heterogeneous solid-liquid reactions are not applicable to the present study. For this reason, initial reaction theory is utilized below in an attempt to derive rate equations for the oxidation reactions.

7.4.3.1 Initial reaction orders

The initial rate of arsenopyrite oxidation in NaOH solutions can be described by an expression of the following type:

\[- \frac{1}{S} \frac{dN}{dt} = b k [O_2]^m [OH^-]^n\]  

where \(S\) is the total interfacial area of arsenopyrite particles, m\(^2\); \(dN/dt\) is the number of moles of arsenopyrite reacted per unit time, mol s\(^{-1}\); \(b\) is the stoichiometric number of moles of arsenopyrite reacting with one mole of oxygen; \(k\) is the apparent rate constant; \([O_2]\) is the concentration of dissolved O\(_2\), mol l\(^{-1}\); \([OH^-]\) is the concentration of hydroxyl ion, mol l\(^{-1}\); \(m\) and \(n\) are the reaction orders for oxygen and hydroxyl ion respectively.

The fraction \((X)\) of arsenopyrite reacted at time \(t\), is given by the following equation

\[X = 1 - \frac{N}{N_0}\]  

where \(N\) and \(N_0\) are the respective numbers of moles of arsenopyrite present at time \(t\) and \(t = 0\). By differentiating Equation 7.15 and combining with Equation 7.14, one obtains

\[\frac{dX}{dt} = \frac{S b k [O_2]^m [OH^-]^n}{N_0}\]  

The partial pressure of oxygen \(P_{O_2}\) can be used to substitute for oxygen concentration in the above rate expression, since Henry’s law (Pray et al., 1952) i.e. \([O_2]\)
\[ R_0 = \frac{dX}{dt} = S b k K_h^{-m} \text{Po}_2^m [\text{OH}^-]^n / N_0 \]  

(7.17)

A plot of the logarithm of \( R_0 \) at \( t = 0 \) versus the logarithm of the partial pressure of oxygen, when other variables remain constant, would result in a straight line with slope \( m \), the reaction order with respect to oxygen partial pressure. \( R_0 \) in this case is the derivative at time zero, \( (dX/dt)_t = 0 \). This can conveniently be obtained by fitting a polynomial equation to the data of the reacted fraction \( X \) versus time \( t \). Third or fourth order (degree) polynomial regression using Excel program was performed to obtain the best fit parameters to the experimental data.

Therefore, based on initial reaction rates from Figure 7.28, Figure 7.42 was obtained which shows that the resulting straight line (correlation coefficient = 0.99) at low oxygen pressures has a slope of 1 while at high oxygen pressures the slope of the straight line is near zero. This result indicates that the oxidation reaction of pure arsenopyrite in NaOH solutions at low pressures is first order in oxygen whereas at high pressures oxygen has a negligible effect on the rate. It should be emphasized that the number of experimental points on which this conclusion is based is rather small.

The reaction order of zero found at higher oxygen partial pressures (> 66 kPa) agrees with the results of Koslides and Ciminelli (1992) who reported that the rate of alkaline oxidation of arsenopyrite is almost independent of oxygen partial pressure in the range of 132.7-1061.6 kPa. They suggested a possible Langmuir-type adsorption reaction occurring on the surface of arsenopyrite. The approximate first order dependence of arsenopyrite oxidation in alkaline media on \( O_2 \) for partial pressures less than 1 atmosphere has not been found in the literature, although Papangelakis and Demopoulos
(1990) reported a first order dependence of arsenopyrite oxidation on oxygen partial pressure in the range of 2 to 10 atmospheres in acid solutions. Similar results for the oxidation of pyrite by oxygen in aqueous solutions were found in some studies (Ciminelli and Osseo-Asare, 1995a, b; Lawson, 1982; Goldhaber, 1983). Goldhaber (1983) suggested that the first order dependence on O$_2$ at low P$_{O_2}$ for pyrite oxidation is actually a pseudo-first order dependence which breaks down at higher P$_{O_2}$. He further pointed out that the rate of pyrite oxidation could not be limited by an adsorption process. Accordingly, the behaviour of the oxidation rate of arsenopyrite with respect to oxygen in alkaline solutions may not necessarily suggest an adsorption-controlling mechanism.

![Figure 7.42](image_url)

**Figure 7.42** Effect of oxygen partial pressure on the initial rate of arsenopyrite oxidation (Data from Figure 7.28).

Using the polynomial regression method, initial rates calculated from Figure 7.17 are inversely proportional to the initial particle size, $d_0$, considered here as the average of the screen apertures used, as shown in Figure 7.43. An inverse first order relationship
Chapter 7 Simultaneous Oxidation of Sulfide Minerals and Dissolution of Au in Alkaline Solutions

characterizes reactions controlled by either mass transfer in the liquid phase or by chemical reaction (Levenspiel, 1999). If the reaction were limited by diffusion in the solid product, i.e., the iron oxide coating, an inverse relationship between initial rate and the square of the particle size would be expected.

![Graph](image_url)

Figure 7.43 Logarithms of initial rates versus logarithms of average particle sizes (Data from Figure 7.17).

The apparent activation energy for arsenopyrite oxidation by air in alkaline media can be described using the Arrhenius equation:

\[
k = A \exp\left\{-\frac{E_a}{RT}\right\} \tag{7.18}\]

where \(k\) is the apparent rate constant; \(A\) is a pre-exponential factor; \(T\) is the absolute temperature (K); \(E_a\) is the apparent activity energy (J mol\(^{-1}\)); \(R\) is the universal gas constant.
At a given temperature \( T \) and \( \text{NaOH} \) concentration \([\text{OH}^-] \), the oxygen concentration \([O_2]_T \) as a function of temperature can be calculated from the expression proposed by Narita et al. (1983):

\[
[O_2]_T = ([O_2]_{298K}) \exp(1336T^{-1} - 4.48) \tag{7.19}
\]

As the temperature increases, the actual concentration of dissolved oxygen in solution decreases. By substituting the oxygen concentration in Equation 7.16 with Equation 7.19 and \( m = 1 \) (first order), and substituting \( k \) with Equation 7.18, one obtains

\[
R_0 = \frac{dX}{dt} = (\frac{SA}{N_0})([O_2]_{298K} [\text{OH}^-]^n) \exp\{1336T^{-1} - 4.48 - \frac{E_a}{(RT)}\} \tag{7.20}
\]

Taking the logarithms of both sides of Equation 7.20 and rearranging it, one gets

\[
\ln R_0 - 1336T^{-1} = B - \frac{E_a}{(RT)} \tag{7.21}
\]

where \( B = \ln(\frac{SA[O_2]_{298K} [\text{OH}^-]^n}{N_0}) - 4.48 \)

![Arrhenius plot for the oxidation of arsenopyrite (Data from Figure 7.34).](image)

Thus, with the initial rates \( R_0 \) calculated as above using data in Figure 7.34, a plot of \( \ln R_0 - 1336T^{-1} \) versus \( T^{-1} \) was constructed as shown in Figure 7.44, from which an
activation energy of 15.8 kJ mol\(^{-1}\) can be calculated. This value is very similar to that of 15.1 kJ mol\(^{-1}\) obtained by Koslides and Ciminelli (1992), slightly lower than those reported by Bhakta et al. (1989) and Taylor and Amoah-Forson (1987) who quoted values of 20.3 kJ mol\(^{-1}\) and 23.8 kJ mol\(^{-1}\) respectively. This magnitude of the activation energy is typical of reactions under diffusion control, suggesting that mass transfer of reactants may be the rate-controlling step. Considering the effects of particle size and stirring, mass transport of oxygen could control the oxidation rate of arsenopyrite at low oxygen partial pressures.

If the rate of arsenopyrite oxidation is controlled by mass transfer of oxygen to the mineral, the actual mass transfer coefficient of oxygen calculated from the present study should be comparable with that which can be estimated from the semi-theoretical correlation for freely falling spherical particles suspended in a stirred reactor (Wadsworth and Miller, 1979). Calculation of the actual mass transfer coefficient of oxygen can be made as follows.

Figure 7.17 has shown that the dissolution rate of arsenopyrite for particles of +38-45 \(\mu\)m is approximately constant. For the small extent of reaction in this case the concentrations of O\(_2\) and OH\(^-\) during the experiment may be assumed to be constant. For a reaction controlled by diffusion of oxygen through a liquid boundary film, Equation 7.14 becomes

\[- \left(1/S\right) \frac{dN}{dt} = b k_m [O_2] = \text{constant} \quad (7.22)\]

\(k_m\) is the mass transfer coefficient of oxygen. Using Equation 7.15, one obtains

\[\frac{dX}{dt} = S b k_m [O_2]/N_0 \quad (7.23)\]

For spherical particles of radius \(r\), \(N_0 = 4\pi r_0^3 \rho/3\ M\) and \(S = 4\pi r^2\). Thus,

\[\frac{dX}{dt} = (3 b M r^2/r_0^3 \rho) k_m [O_2] \quad (7.24)\]
At time $t = 0$, 

$$(dX/dt)_{t=0} = (3 \cdot b \cdot M/r_0 \cdot \rho) \cdot k_m \cdot [O_2] \quad (7.25)$$

where $r_0$ is the radius of arsenopyrite particles at time $t = 0$; $M, \rho$ are the molar mass and specific density of arsenopyrite respectively. Some electrochemical studies (Nicol and Guresin, 2003; Sanchez and Hiskey, 1991; Beattie and Poling, 1987; Kostina and Chernyak, 1976) have suggested the electrochemical nature of the oxidation of arsenopyrite in aerated and oxygenated alkaline solutions. Thus, the anodic oxidation of arsenopyrite is assumed to be

$$\text{FeAsS} + 19\text{OH}^- = \text{Fe(OH)}_3 + \text{AsO}_4^{3-} + \text{SO}_4^{2-} + 8\text{H}_2\text{O} + 14\text{e}^- \quad (7.26)$$

The cathodic reduction of oxygen in alkaline solutions may be (Nicol and Guresin, 2003)

$$\text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2\text{O}_2 + 2\text{OH}^- \quad (7.27)$$

On this basis, the stoichiometric number $b$ would be $2/14$ or $1/7$. The concentration of dissolved oxygen in aerated 1.25 M NaOH solution ([OH$^-$] = 1.25 M) at 25 °C can be estimated according to Narita et al. (1983) (also see below):

$$[O_2] = 0.21 \times 3.12 \times 10^{-5} \times 40.2 \times \exp(-0.433[\text{OH}^-]) \text{, mol l}^{-1} \quad (7.28)$$

For the experiment using particles of $+38-45$ µm size with average diameter of 42 µm, $(dX/dt)_{t=0}$ can be calculated to be about $2.0 \times 10^{-2}$ hr$^{-1}$ or $5.5 \times 10^{-6}$ s$^{-1}$. For $M = 162.83$ g mol$^{-1}$ and $\rho = 6.0$ g cm$^{-3}$, the calculated mass transfer coefficient $k_m$

$$k_m = (dX/dt)_{t=0} (r_0 \cdot \rho)/(3 \cdot b \cdot M \cdot [O_2]) = 6.5 \times 10^{-3} \text{ cm s}^{-1} \quad (7.29)$$

This calculated mass transfer coefficient for oxygen is comparable to the minimum mass transfer coefficient $k^*$ estimated to be about $10.6 \times 10^{-3}$ cm s$^{-1}$ (See Appendix A3 and refer to Wadsworth and Miller, 1979). However, the stoichiometric number $b$, according to Equation 7.5, is $6/13$ which is larger than $1/7$ leading to an even smaller mass transfer coefficient of oxygen. This suggests that the oxidation rate of arsenopyrite by oxygen of low pressures in alkaline solutions may be only partially controlled by mass transport of oxygen, which is consistent with the results obtained by Nicol and Guresin (2003).
The rates of processes such as the cyanidation of gold, silver and copper, the dissolution of copper and nickel in ammoniacal solutions have been found to controlled by mass transport of oxygen (Wadsworth and Miller, 1979). However, in the present case, the reduction of oxygen requires more negative potentials because of the shift of the potential for the reaction

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^- \quad (7.30)$$

to lower potentials with increasing pH. This was confirmed by Nicol and Guresin (2003) in an electrochemical study of this reaction on arsenopyrite in concentrated alkaline solutions.

The effect of hydroxyl ions on the overall rate of arsenopyrite oxidation may be calculated after making corrections for the effect of the hydroxyl concentration on the solubility of oxygen. According to Narita et al. (1983), oxygen solubility as a function of NaOH concentration solution is expressed by the following:

$$[\text{O}_2] = 3.12 \times 10^{-5} \ [\text{O}_2]_0 \exp(-0.433[\text{OH}^-]) \quad (7.31)$$

where $[\text{O}_2]$ is the oxygen solubility in NaOH solution at 25 °C, mol l$^{-1}$; $[\text{O}_2]_0$ is the saturation solubility of O$_2$ in pure water at 25 °C (mg l$^{-1}$) at the given oxygen pressure; $[\text{OH}^-]$ is the NaOH concentration, mol l$^{-1}$. Thus, at constant oxygen partial pressures and temperatures, the concentration of dissolved oxygen will decrease exponentially with increasing NaOH concentration. By combining Equation 7.16 with Equation 7.31 and assuming $m = 1$, one gets

$$R_0 = \frac{dX}{dt} = 3.12 \times 10^{-5} \text{ S k} \ [\text{O}_2]_0 \exp(-0.433[\text{OH}^-]) \ [\text{OH}^-]^n/ N_0 \quad (7.32)$$

or

$$\ln R_0 + 0.433[\text{OH}^-] = n \ln[\text{OH}^-] + \ln(3.12 \times 10^{-5} \text{ S k} \ [\text{O}_2]_0/ N_0) \quad (7.33)$$

Considering the initial conditions in Figure 7.31, a plot of $\ln R_0 + 0.433[\text{OH}^-]$ versus $\ln[\text{OH}^-]$ would result in a straight line with slope $n$. By using the same procedure, an
apparent reaction order of about 0.09 was obtained as shown in Figure 7.45, which can be compared with that of 0.27 obtained by Koslides and Ciminelli (1992) for arsenopyrite oxidation during their studies on the pressure oxidation of a sulfide concentrate in NaOH solutions. A similar reaction order of 0.1 with respect to the hydroxyl ion has also been reported for the oxidation of pyrite in alkaline media (Ciminelli and Osseo-Asare, 1986 and 1995). These data indicate that the alkalinity has a negligible effect on the oxidation rate of arsenopyrite in aerated alkaline solutions. Considering the possible errors involved in the data, the variations in activity coefficients and the effect of oxygen on the rate, it seems reasonable to assume therefore that the oxidation of arsenopyrite is zero order with respect to the hydroxyl concentration. The apparent zero order for the hydroxyl ion concentration may be a result of the combined but converse effects of alkalinity on the anodic oxidation of arsenopyrite and cathodic reduction of oxygen as reported by Nicol and Guresin (2003).

![Graph](image)

**Figure 7.45** Determination of the apparent reaction order of arsenopyrite with respect to NaOH concentration (Data from Figure 7.31).
Summarizing the above calculations, the overall rate of arsenopyrite oxidation with oxygen at ambient temperatures and pressures in alkaline solutions is believed to be partially limited by the rate of mass transfer of dissolved oxygen to the surface of arsenopyrite, and the rate of reaction may be expressed as:

\[- \frac{dN}{dt} = S \ k' \ \exp(-15.8 \ \text{kJ/RT}) \ \text{Po}_2 = S \ k' \ \exp(-1900 \ \text{T}^{-1}) \ \text{Po}_2 \]  

(7.34)

where \( k' \) is a constant and \( \text{Po}_2 < 1 \ \text{atm} \).

### 7.4.3.2 Mechanism for arsenopyrite oxidation

The above observations on the chemistry and kinetics of arsenopyrite oxidation in aerated alkaline solutions may be integrated into a mechanistic interpretation of the reaction. Such a proposed mechanism must necessarily be highly speculative because evidence regarding the occurrence of some reactions is still weak or lacking. Yet it is nonetheless useful to suggest a possible mechanism as a basis for further studies.

Since arsenopyrite is a semiconducting mineral and behaves as an electrocatalyst for oxygen reduction, the acid pressure oxidation of arsenopyrite has been interpreted as an electrochemical process (Papangelakis and Demopoulos, 1990). Moreover, Bou et al. (1998) proposed an electrochemical reaction mechanism for gold deposition on the surface of arsenopyrite in acid solutions based on the electrochemical theory of Osseo-Asare (1992) for pyrite. It is therefore reasonable to assume that the alkaline oxidation of arsenopyrite with oxygen is also electrochemical in nature. Thus the surface of arsenopyrite is envisaged to consist of sites on which anodic and cathodic reactions are believed to occur. The cathodic process for the reduction of oxygen may involve the mass transfer of dissolved oxygen to cathodic sites, adsorption of oxygen on the active
sites and subsequent fast reduction reactions of oxygen as described in the following
equations, with the mass transfer of dissolved oxygen being the slowest reaction step:

1) Mass transfer of $O_2$

$$O_2 \text{(aq, bulk)} \rightarrow O_2 \text{(aq, surface)} \quad (7.35)$$

2) Physisorption of $O_2$

$$O_2 \text{(aq, surface)} + FeAsS \text{ (s)} \leftrightarrow FeAsS \cdot O_2 \text{ (ads)} \quad (7.36)$$

3) Electron transfer reactions

$$FeAsS \cdot O_2 \text{ (ads)} + H_2O + 2e^- \rightarrow FeAsS \text{ (s)} + H_2O_2 + 2OH^- \quad (7.37)$$

The anodic process for oxidation of arsenopyrite could involve physisorption of hydroxyl
ion and subsequent electron transfer reactions as given in the following:

1) Adsorption of OH$^-$ ion

$$FeAsS \text{ (s)} + OH^- \text{(aq)} \rightarrow FeAsS \cdot OH^- \text{(ads)} \quad (7.38)$$

2) First electron transfer

$$FeAsS \cdot OH^- \text{(ads)} \rightarrow Fe(OH)AsS \text{(ads)} + e^- \quad (7.39)$$

3) Transposition of OH to As or Fe sites

$$Fe(OH)AsS_{(ads)} \leftrightarrow FeAs(OH)S_{(ads)} \quad (7.40)$$

4) Further electron transfer

$$[FeAs(OH)S_{(ads)} \leftrightarrow Fe(OH)AsS_{(ads)}] + 5OH^- \rightarrow$$

$$Fe(OH)_3 + As(OH)_3S_{(ads)} + 5e^- \quad (7.41)$$

5) Formation and decomposition of thioarsenates

$$As(OH)_3S_{(ads)} \leftrightarrow H_3AsO_3S_{(ads)} \quad (7.42)$$

$$H_3AsO_3S_{(ads)} + 3OH^- \rightarrow AsO_3^{3-} + 3H_2O \quad (7.43)$$

$$2H_3AsO_3S_{(ads)} + 8OH^- \rightarrow AsO_3^{3-} + AsO_4^{3-} + S_2^{2-} + 7H_2O \quad (7.44)$$

$$AsO_3^{3-} + S_2^{2-} \rightarrow AsO_3^{3-} + S^{2-} \quad (7.45)$$

$$AsO_3^{3-} + S_2^{2-} + H_2O \rightarrow AsO_2S_2^{3-} + 2OH^- \quad (7.46)$$

6) Formation of thiosulfate, sulfite and arsenate
\[ S^{2-} + 6OH^- \rightarrow SO_3^{2-} + 3H_2O + 6e^- \quad (7.47) \]
\[ 2S^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 3H_2O + 8e^- \quad (7.48) \]
\[ AsO_2S_2^{3-} + 10OH^- \rightarrow S_2O_3^{2-} + AsO_4^{3-} + 5H_2O + 8e^- \quad (7.49) \]
\[ AsO_3^{3-} + 2OH^- \rightarrow AsO_4^{3-} + H_2O + 2e^- \quad (7.50) \]
\[ SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \quad (7.51) \]

The initial anodic oxidation of arsenopyrite may be expressed as:

\[ FeAsS + 6H_2O \rightarrow Fe(OH)_3 + H_3AsO_3S + 6H^+ + 6e^- \quad (7.52) \]

or in alkaline media:

\[ FeAsS + 6OH^- \rightarrow Fe(OH)_3 + H_3AsO_3S + 6e^- \quad (7.53) \]

The initial cathodic reduction of oxygen may be written as:

\[ O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (7.54) \]

The following information could support this mechanism:

1). The molar ratio of monothioarsenate to total dissolved arsenic is higher in the initial stage of the oxidation of arsenopyrite while the ratio of arsenate to total dissolved arsenic is initially lowest;

2). The molar ratio of thiosulfate to total dissolved sulfur increases with reaction time whereas the ratio of sulfite to total sulfur decreases with time at long times;

3). The first four anodic steps produce 6 electrons which is in agreement with the results of Sanchez and Hiskey (1991);

4). Most of the oxidized arsenic has an oxidation state of III rather than V and sulfur is not directly oxidized to elemental sulfur as reported by Buckley and Walker (1988);

5). The electrochemical studies reported by Nicol and Guresin (2003) suggest that the cathodic reduction of oxygen to peroxide may precede reduction to water.
7.4.4 Dissolution of Gold

Figures 7.5 and 7.6 have shown that gold dissolves during the alkaline oxidation of pyrite by air in the potential range of about 0-0.2 V at pH values less than 13. The concentration of thiosulfate in the slurry has been found to be greater than 0.1 M. These conditions under which gold dissolves are consistent with the results of the electrochemical study of the dissolution of gold in alkaline thiosulfate solutions as described in Chapter 4. The overall dissolution rate of the gold powder (1.5-3 µm) during the oxidation of pyrite was calculated to be about $2 \times 10^{-12}$ mol cm$^{-1}$ s$^{-1}$ which is also similar to the rate obtained in Chapter 4. Similar results have been reported by Lulham (1989) on the dissolution of gold during the oxidation of pyrite in aqueous carbonate solutions. Hence, the dissolution of gold is believed to be associated with the presence of thiosulfate generated by oxidation of the mineral.

The experimental results given in Chapter 5 have confirmed the dissolution of gold in oxygenated 0.2 M thiosulfate solution at pH 12 in the presence or absence of copper. However, the dissolution rate of gold in the absence of copper has been shown to be extremely slow being about $6 \times 10^{-15}$ mol cm$^{-2}$ s$^{-1}$ which is much lower than the rate of gold dissolution during the oxidation of pyrite. Although the leaching rate of gold was increased to about $1.5 \times 10^{-13}$ mol cm$^{-2}$ s$^{-1}$ after wet milling of the gold powder, this value is still relatively low. It has been shown in Chapter 5 that the presence of copper (in the form of either copper ions, oxides or metal) in alkaline thiosulfate solutions significantly accelerated the leaching rate of gold by oxygen with the rate being greater than $1 \times 10^{-12}$ mol cm$^{-2}$ s$^{-1}$. The data in Figure 7.6 has shown that a small amount of dissolved copper was detected during the alkaline oxidation of pyrite and it can be
assumed that copper plays an important role in accelerating the leaching rate of gold under these conditions by a mechanism which is not known and is beyond the scope of this study.

As reported in Section 7.3.1, small amounts of elemental sulfur were detected during the alkaline oxidation of pyrite, and in Section 7.3.10 no dissolution of gold was detected in oxygenated alkaline solutions without thiosulfate even after the gold powder was wet ground with elemental sulfur. However, gold was found to dissolve in oxygenated 0.1 M thiosulfate solution as shown in Table 7.4, which suggests that gold could have reacted with thiosulfate. At room temperature the kinetics of the oxidation of elemental sulfur by oxygen has been found to be very slow in alkaline solutions. The oxidation of elemental sulfur only resulted in very low concentrations of thiosulfate and sulfite (< 1 mM) and sulfide was not detected by HPLC analysis. Therefore, the complexing of gold with sulfide or polysulfides must be ruled out.

The results in Section 7.3 have also shown that gold dissolves into alkaline thiosulfate-bearing solutions during the oxidation of arsenopyrite by air and that the rate of dissolution of gold strongly depends on the temperature, stirring speed, concentrations of oxygen, NaOH and arsenopyrite in the reaction system. As in the case of pyrite, the dissolution of gold is believed to be due to the complexing of gold with thiosulfate. However, the possible reaction of monothioarsenate with gold should also been considered, because the results outlined in Chapter 6 have shown that gold may dissolve in alkaline monothioarsenate solutions in the presence of oxygen. In this work the concentrations of monothioarsenate were determined to be similar to those of thiosulfate, and the initial concentration of monothioarsenate was higher than that of thiosulfate during the oxidation of arsenopyrite.
The effect of milling on the rate and extent of dissolution of gold requires some consideration because it has been shown that gold dissolved only after the gold powder was wet milled with the arsenopyrite samples. There are probably several reasons for this observation, two of which are discussed below. The first is that the sulfide mineral itself has a positive effect on the dissolution of gold in thiosulfate solutions at various pH values, as reported by Zhuchkov and Bubeev (1992) who found that the rate-enhancing effect of sulfide minerals increased in the following sequence

chalcopyrite < pyrrhotite < arsenopyrite < pyrite

The second is the possible formation of gold sulfide intermediates which could explain the positive effect of elemental sulfur (when milled with the gold powder) on the dissolution of gold during the oxidation of arsenopyrite as reported in Section 7.3.10. According to Balaz (2000), S(-2) and S(+6) predominate on the surface of mechanically activated arsenopyrite samples with sulfate sulfur prevailing, while Nesbitt et al. (1995) reported that polysulfides could be present on the surface of reacted arsenopyrite. It is, therefore, possible that some of the gold particles could react with sulfide, polysulfides or an As-S group forming solid gold-sulfide intermediates that are more easily soluble in thiosulfate solutions. In another word, mechanical grinding may activate part of the gold particles to react with the arsenopyrite mineral and enable the dissolution of gold in alkaline thiosulfate solutions. However, this mechanism needs further investigation.

7.5 Summary and Conclusions

The alkaline oxidation of arsenopyrite and pyrite at ambient temperatures (25-55 °C) and pressures (1 atm) has been found to be accompanied by the simultaneous dissolution of gold without the addition of cyanide. The pertinent reaction products and
stoichiometries have been determined using chromatographic techniques. For the first time a new product of arsenopyrite oxidation, namely, monothioarsenate has been identified and quantitatively determined. Arsenopyrite reacts with oxygen yielding mainly thiosulfate, thioarsenates, arsenate and sulfite, with monothioarsenate being the principal product in the initial stage of oxidation. In alkaline media elemental sulfur is not a product of the oxidation of arsenopyrite but is one of the minor products of pyrite oxidation. Thiosulfate has been confirmed to be the dominant product of pyrite oxidation. The formation of porous coatings of ferric hydroxide has been confirmed in the oxidation of arsenopyrite. An approximate stoichiometry of the overall process of pyrite oxidation in alkaline solutions with air is given by the following reaction:

\[
12\text{FeS}_2 + 11\text{O}_2 + 32\text{NaOH} + 2\text{H}_2\text{O} = 12\text{Fe(OH)}_3 + 8\text{Na}_2\text{S}_2\text{O}_3 + 8\text{Na}_2\text{SO}_3
\] (7.4)

In the case of arsenopyrite, the reaction is more complex and the following reaction may be used to approximately express the overall process of arsenopyrite oxidation in alkaline solution with oxygen.

\[
6\text{FeAsS} + 13\text{O}_2 + 22\text{NaOH} = 6\text{Fe(OH)}_3 + 2\text{Na}_3\text{AsO}_3\text{S} + 4\text{Na}_3\text{AsO}_4 + 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}
\] (7.5)

The kinetics of the alkaline oxidation of arsenopyrite has been studied. Particle size, oxygen concentration and stirring speed are the variables that most affect the oxidation rate of arsenopyrite at ambient temperatures and pressures. Based on an analysis of the initial rate data, the rate of arsenopyrite oxidation with air in NaOH solutions may be represented by the following expression:

\[
- \frac{1}{S} \frac{dN}{dt} = k' \exp(-1900 \frac{1}{T}) \text{Po}_2
\] (7.55)

where \(N\) is the number of moles of arsenopyrite, \(t\) is the time, \(S\) the total surface area of arsenopyrite particles, \(k'\) a constant, \(T\) the absolute temperature and \(\text{Po}_2\) the oxygen
partial pressure. A reaction mechanism has been proposed and discussed based on this study.

Gold (added as powder) has been found to dissolve simultaneously during the alkaline oxidation of both arsenopyrite and pyrite, which reaction appears to be associated with the complex reactions between gold and thiosulfate. In the case of arsenopyrite, monothioarsenate possibly also plays a role in the dissolution of gold in the alkaline solutions. The dissolution rate of gold depends on wet-grinding of the reacting materials, temperature, stirring speed, and the concentrations of oxygen, NaOH and arsenopyrite in the reaction system.
CHAPTER 8 THE OXIDATION OF SULFIDE CONCENTRATES AND THE SIMULTANEOUS DISSOLUTION OF GOLD

8.1 Introduction

As discussed in Chapter 1, the objective of the oxidative treatment of arsenopyrite or pyrite is to breakdown the mineral and thereby to expose precious metals to cyanide or other lixiviants. There are a great number of studies reported in the literature on two-step processes for the extraction of gold/silver from refractory gold ores, involving the oxidation of sulfide minerals as a first step and the leaching of previous metals in the second step (Sparrow, and Woodcock, 1995; Souza and Ciminelli, 1992). In order to reduce capital and operating costs, one step processes for direct extraction of gold have been studied, including simultaneous chemical (and/or electrochemical) oxidation in acid solutions with strong oxidants (Deng, 1995; Linge and Welham, 1997), simultaneous oxidation of ores and leaching of gold with cyanide in alkaline solutions (Mao et al., 1997; Min et al., 1999), simultaneous oxidation of pyrite and leaching of gold in alkaline carbonate solutions (Lulham, 1989), and gold leaching with a lime-sulfur mixture (Lan and Zhang, 1996; Fang and Han, 2002).

Chapter 7 has shown that gold may dissolve simultaneously during the alkaline oxidation of arsenopyrite or pyrite by oxygen when gold is wet-milled with the mineral. This one-step method may form the basis for a novel process for extraction of gold from
refractory sulfidic gold concentrates. Thus it is necessary to investigate the extent of gold
dissolution during the alkaline oxidation of refractory gold concentrates in order to
evaluate the feasibility of the process. This chapter, therefore, highlights experimental
work carried out on the oxidation of selected refractory arsenical gold concentrates in
alkaline solutions and the simultaneous dissolution of gold. The effects of the
concentrations of sodium hydroxide and oxygen, particle size and temperature on the
recovery of gold were examined using a commercially available flotation concentrate
containing arsenopyrite. The characteristics of the flotation concentrates used are
described in the following section, and detailed experimental procedure and analytical
techniques can be found in Chapter 3.

The oxidation of arsenopyrite and pyrite by oxygen in alkaline media may be
expressed by Equations 7.4 and 7.5 respectively. Thus the required amount of sodium
hydroxide for complete oxidation of a given amount of the arsenopyrite or pyrite mineral
can be calculated and is given in Table 8.1. It is clear from Table 8.1 that if the gold
concentrate contains 20% of arsenopyrite, 180 kg sodium hydroxide per ton of the gold
concentrate is required theoretically for complete oxidation of arsenopyrite by oxygen.
Note that the values are very similar for arsenopyrite and pyrite.

Table 8.1  Sodium hydroxide required for complete oxidation of arsenopyrite or pyrite

<table>
<thead>
<tr>
<th>Concentration of Pyrite or Arsenopyrite in Gold Ores / %</th>
<th>Sodium Hydroxide Need / kg t⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Arsenopyrite</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td>135</td>
</tr>
<tr>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>25</td>
<td>225</td>
</tr>
<tr>
<td>30</td>
<td>270</td>
</tr>
<tr>
<td>35</td>
<td>315</td>
</tr>
<tr>
<td>40</td>
<td>360</td>
</tr>
</tbody>
</table>
8.2 Gold Concentrates

In this work several flotation gold concentrates containing arsenopyrite were utilized in the oxidation tests. Table 8.2 summarizes the samples and the chemical analyses for the main elements.

Table 8.2  Fire assay (Au) and ICP analyses of the flotation gold concentrates

<table>
<thead>
<tr>
<th>Samples</th>
<th>Head Grades</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au / g t(^{-1})</td>
</tr>
<tr>
<td>Wiluna Concentrate</td>
<td>94.2</td>
</tr>
<tr>
<td>Macraes Concentrate</td>
<td>82.3</td>
</tr>
<tr>
<td>Salsigne Concentrate</td>
<td>23.0</td>
</tr>
<tr>
<td>Unknown Concentrate</td>
<td>414</td>
</tr>
</tbody>
</table>

8.2.1 Wiluna Concentrate

The flotation concentrate obtained from Wiluna Gold Mines in Western Australia contained mainly pyrite and arsenopyrite as sulfidic minerals, with stibnite being a minor component. The non-sulfide (gangue) component of the concentrate was dominated by quartz and carbonate minerals. The XRD pattern of a Wiluna sample is given in Figure A4.1 in Appendix A4. By calculation from the chemical composition, the sample contained 18.0% arsenopyrite, 35.0% pyrite and 0.473% chalcopyrite.

In Wiluna primary sulfide ores approximately 95% of the gold was locked within the sulfide lattice, the remainder being very fine free native gold. About 70% to 80% of the gold in sulfides was in arsenopyrite, with pyrite and stibnite where present,
containing the balance (Guresin, 1999). This concentrate is treated using a bacterial oxidation process at Wiluna. The particle size of the concentrate was 80% passing 75 µm.

8.2.2 Macraes Concentrate

This came from the Macraes Gold Mine in New Zealand and the particle size was 80% passing 119 µm. The dominant components of the Macraes flotation concentrate were pyrite and arsenopyrite. Minor amounts of pyrrhotite, chalcopyrite, quartz and other gangue minerals were also present. The XRD diagram for a Macraes sample can be found in Figure A4.2 in Appendix A4. The concentrate had a black color because of the high carbonaceous mineral content which added to the refractory nature of the material. Almost all sulfur in the sample was present as sulfidic sulfur. The concentrate sample contained 23.3% arsenopyrite, 32.8% pyrite and 0.351% chalcopyrite according to the more detailed analysis shown in Table 8.3. The mineralogical deportment of the gold was not known.

8.2.3 Salsigne Concentrate

A sample of flotation concentrate from Mines d'Or de Salsigne, France was also used for the oxidation and dissolution of gold. The dominant components of the Salsigne concentrate were pyrite and arsenopyrite with other minor minerals such as pyrrhotite, chalcopyrite, chlorite, mica, quartz, siderite and a trace of rutile (Guresin, 1999). The amount of arsenopyrite was estimated to be about 32% based on the data in Table 8.2. The particle size of the original sample was nominally - 40 µm.
Table 8.3  Average head assays of the Macraes concentrate sample

<table>
<thead>
<tr>
<th>Element</th>
<th>Average Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au / g t⁻¹</td>
<td>82.3</td>
</tr>
<tr>
<td>Ag / g t⁻¹</td>
<td>5.8</td>
</tr>
<tr>
<td>Pt / g t⁻¹</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Pd / g t⁻¹</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>As / %</td>
<td>10.7</td>
</tr>
<tr>
<td>C_Total / %</td>
<td>3.92</td>
</tr>
<tr>
<td>C_Organic / %</td>
<td>3.30</td>
</tr>
<tr>
<td>Fe / %</td>
<td>25.8</td>
</tr>
<tr>
<td>S_Total / %</td>
<td>22.3</td>
</tr>
<tr>
<td>S_Sulfide / %</td>
<td>22.1</td>
</tr>
<tr>
<td>Al / %</td>
<td>4.45</td>
</tr>
<tr>
<td>Cu / g t⁻¹</td>
<td>1220</td>
</tr>
<tr>
<td>Sb / g t⁻¹</td>
<td>652</td>
</tr>
</tbody>
</table>

8.2.4 An Unknown Concentrate

A flotation concentrate of unknown origin containing arsenopyrite and pyrite was also used in this work. It was found to be coarser than the other samples used. By calculation from the chemical composition, the sample contained about 33.5% arsenopyrite, 54.4% pyrite and 0.10% chalcopyrite, assuming that all sulfur exists in the form of arsenopyrite, pyrite and chalcopyrite.

8.3 Results

An extensive set of experiments was carried out with the Wiluna concentrate and a more limited set (because of limited quantities of material) with the other concentrates.
In experiments to investigate the effects of various conditions on the rate of the process, all experimental conditions remained constant except for the parameter under investigation. Unless otherwise stated, all experiments were carried out in 600 ml of 1.56 M NaOH solution using 250 g l\(^{-1}\) solid sample (solid-liquid ratio = 1:4) at 25 °C, 1400 rpm stirring speed and 1 l min\(^{-1}\) flow rate of air. Prior to oxidation, each sample of the gold concentrate was wet-milled for 60 minutes in a stainless steel ball mill.

During each experiment, slurry samples were taken at various times and filtered. The filtrates were analyzed by AAS for Au, Cu and Fe, by ICP for As and S, and by HPLC for dissolved species of sulfur and arsenic. Cumulative dissolution rates at different reaction times of total Au, As, S, Cu and Fe were calculated based on the results of filtrate analyses and shown in the following sections. An example of calculation of the cumulative dissolution rates can be found in Appendix A6. In addition, the final oxidized residue after each experiment was analyzed for total Au, As, S and Fe, arsenopyrite and pyrite by wet chemical digestion-ICP analysis described in Appendix A2. The dissolution rates calculated from analyses of the residue for total Au, As, S and Fe were found to be within 10% of those calculated from the filtrate analyses.

### 8.3.1 Oxidation of Wiluna Concentrate

#### 8.3.1.1 Effect of milling time

The results shown in Chapter 7 have indicated that gold only dissolves when it is wet-milled with the arsenopyrite or pyrite mineral and it could be expected that milling of the concentrate sample (or its particle size) would have an effect on the extent of gold dissolution during alkaline oxidation. Figures 8.1 and 8.2 compare the dissolution of Au,
Cu, As, S and Fe as a function of reaction time after milling for various times. The particle sizes after wet-milling for 20, 60 and 120 minutes in a stainless steel ball mill were 80% less than 12.4, 6.0 and 4.7 µm respectively (refer to size analyses in Appendix A5). It can be clearly seen that increasing the milling time or decreasing the particle size of the sample significantly increases the dissolution rate of gold, copper, arsenic, sulfur and iron. Also apparent is an induction period for gold dissolution which is possibly related to the release of gold after oxidation of sulfide minerals or to the generation of a lixiviant for gold.

The higher dissolution rate of arsenic than sulfur suggests that the arsenopyrite mineral oxidizes more rapidly than pyrite under these conditions. The results of analyses of oxidized residues after 48 hours’ oxidation showed that more than 90% of the arsenopyrite minerals were oxidized while more than 60% of the pyrite minerals were left unoxidized in the residues. As the percentage of pyrite (35%) in original Wiluna gold concentrate is much higher than that of arsenopyrite (18%), the dissolution of sulfur is thus less than 50%. The fact that the oxidation rates of arsenopyrite are higher than the dissolution rates of arsenic suggests the formation of intermediate solid products of arsenopyrite and/or precipitation of arsenic probably as iron arsenates. The decrease in the arsenic concentration at long times as shown in Figure 8.2 confirms the precipitation of arsenic. It should be noted that copper dissolves in the later stage of arsenopyrite oxidation, which is important because copper can catalyze the dissolution of gold in alkaline thiosulfate solutions. Figure 8.3 shows that the rate of thiosulfate formation also increases with milling time. The concentration of thiosulfate is high (up to 0.25 M) while that of monothioarsenate is low and less than 0.05 M. A comparison of the extraction of gold with the potential of the slurry suggests that gold dissolution starts at potentials above about 0 V.
Figure 8.1 Effect of milling time on rates of extraction of Au (—) and Cu (········) during the oxidation of Wiluna concentrate with air. (Δ) 120 min; (◊) 60 min; (□) 20 min.

Figure 8.2 Effect of milling time on rates of extraction of As (——), S (−−−−−) and Fe (········) during the oxidation of Wiluna concentrate with air. (Δ) 120 min; (◊) 60 min; (□) 20 min.
Figure 8.3  Variation of concentrations of thiosulfate (——) and monothioarsenate (----) and the potential of gold (········) during the oxidation of Wiluna concentrate with air for various milling times. (Δ) 120 min; (◊) 60 min; (□) 20 min.

8.3.1.2 Effect of the concentration of NaOH

The oxidation of milled Wiluna concentrate was carried out in NaOH solutions of various concentrations. Figures 8.4, 8.5 and 8.6 show the results of these experiments. Figure 8.4 shows that the dissolution rates of gold and copper are higher in the 1.56 M NaOH solution than in the other solutions, suggesting a possible adverse effect of hydroxyl ions on the dissolution of gold. However, by comparison with the results in Figure 8.6, the lower dissolution of gold in solutions of high NaOH concentration appears to be due to the lower concentration of dissolved oxygen (see Section 8.3.1.3). The analyses of the oxidized residues indicated that the extent of oxidation of arsenopyrite after 48 hours was 92.4%, 93.9% and 94.2% and that of pyrite was 31.8%, 41.9% and 43.5% in NaOH solutions of 1.56 M, 1.88 M and 2.19 M respectively.
Figure 8.4  Dissolution of gold (——) and copper (········) during the oxidation of milled Wiluna concentrate in different NaOH solutions with air. (◊) 1.56 M; (□) 1.88 M; (△) 2.19 M.

Figure 8.5  Dissolution of arsenic (——) and sulfur (········) during the oxidation of milled Wiluna concentrate in different NaOH solutions with air. (◊) 1.56 M; (□) 1.88 M; (△) 2.19 M.
8.3.1.3 Effect of oxygen concentration

The results in Chapter 7 have shown that the oxygen partial pressure has a significant effect on the rate of oxidation of arsenopyrite and the dissolution of gold. In this case, only one experiment using pure oxygen gas was carried out to compare with the above experiments using air. The results are given in Figures 8.7, 8.8 and 8.9. It is apparent that the use of oxygen instead of air results in higher concentration of dissolved oxygen in the pulp and a corresponding higher oxidation rate of arsenopyrite and dissolution rate of gold and copper, especially in the early stages of the oxidation. The extents of oxidation of arsenopyrite and pyrite (by residue analyses) after 48 hours were 93.8% and 42.9% respectively when oxygen was used, while the rates with air were 92.4% and 31.8% respectively. The concentration of thiosulfate is also much higher.
initially when oxygen is used. These results are clearly in agreement with those found in Chapter 7.

Figure 8.7   Dissolution of gold (——), copper (− − − −) and iron (······) during the oxidation of milled Wiluna concentrate with air (◊) and oxygen (□).

Figure 8.8   Dissolution of arsenic (——) and sulfur (······) during the oxidation of milled Wiluna concentrate with air (◊) and oxygen (□).
8.3.1.4 Effect of temperature

The effects of temperature on the rates of oxidation of Wiluna concentrate and the dissolution of gold are shown in Figure 8.10, 8.11 and 8.12. When higher temperatures are used, the induction period for gold dissolution becomes longer (Figure 8.10) although the dissolution rate of gold increases at higher temperatures. Increasing temperature also results in the increase in the dissolution rates of copper and iron. The analyses of the final residues showed that the extent of oxidation of arsenopyrite at the various temperatures was 92.4% (25 °C), 93.8% (40 °C) and 93.6% (55 °C), and the corresponding quantities for pyrite were 31.8% (25 °C), 40.4% (40 °C) and 41.3% (55 °C). Examination of the variation in concentrations of dissolved oxygen and thiosulfate in the pulp (Figure 8.12), indicates that in the initial stage of reaction, the oxidation of the minerals at higher temperatures is faster so that there is insufficient dissolved oxygen.
available for the oxidation of gold, and that in the later stage, part of the dissolved oxygen is employed to oxidize soluble species such as thiosulfate.

Figure 8.10  Dissolution of gold (——), copper (········) and iron (−−−−−−) during the oxidation of milled Wiluna concentrate with air at various temperatures. (◊) 25 °C; (□) 40 °C; (Δ) 55 °C.

Figure 8.11  Dissolution of arsenic (——) and sulfur (······) during the oxidation of milled Wiluna concentrate with air at various temperatures. (◊) 25 °C; (□) 40 °C; (Δ) 55 °C.
The results shown above clearly indicate that temperature has two opposing effects on the rates of sulfide oxidation and gold dissolution. The first is to increase the oxidation rate of the minerals and gold, while the second is that lower solubility of oxygen at the higher temperatures and the increased oxidation rate result in lower concentrations of dissolved oxygen under the conditions of these experiments. Thus, to increase the rate of dissolution of gold, it is important to increase both the temperature and concentration of dissolved oxygen.

**8.3.1.5 Effect of extended reaction time**

The above results have indicated that both oxidation of sulfides and dissolution of gold may increase further after two days. It was therefore decided to carry out
experiments over extended reaction times. Figures 8.13, 8.14 and 8.15 show the effect of time on the oxidation of gold and sulfide minerals at 25 °C. These results also serve to illustrate the reproducibility of the experimental results. It can be seen that the dissolution rates of gold, copper, sulfur and arsenic gradually decrease after about 24 hours but that the dissolution of gold is still increasing above 70% even after 4 days. The analyses of the oxidized residues indicated that the extent of oxidation of arsenopyrite was 95.5% while that for pyrite was 41.7% after 4 days while after 2 days 92.4% of the arsenopyrite and 31.8% of the pyrite had been oxidized. The dissolved arsenic concentration decreases after 24 hours, which is probably related to the formation of some insoluble iron arsenate compounds. The concentration of thiosulfate also gradually decreases after 24 hours while that of sulfate increases, presumably as a result of the oxidation of thiosulfate.

![Figure 8.13](image-url)

**Figure 8.13** Dissolution of gold (◊) and copper (Δ) during the oxidation of milled Wiluna concentrate at different times. (······) 2 days; (——) 4 days.
Figure 8.14  Dissolution of arsenic (◊), sulfur (△) and iron (□) during the oxidation of milled Wiluna concentrate at different times. (········) 2 days; (——) 4 days.

Figure 8.15  Concentration profiles of thiosulfate (Δ), arsenate (□), sulfite (○) and sulfate (◊) during the oxidation of milled Wiluna concentrate at different times. (········) 2 days; (——) 4 days.
In summary, it has been demonstrated that in excess of 70% of the gold in the refractory Wiluna flotation concentrate is dissolved simultaneously during the oxidation of the concentrate in alkaline solutions. Partial oxidation is required before the dissolution of gold commences. Increasing oxygen concentration and temperature result in an increase in the dissolution rate of gold while a decrease in particle size leads to higher dissolution rate of gold. Excess amounts of sodium hydroxide reduce the concentration of dissolved oxygen in the reacting system, thus delaying the oxidation of gold. Copper and iron are also dissolved after partial oxidation of the sulfide minerals. The concentration of monothioarsenate is lower than 0.05 M while that of thiosulfate is high up to 0.25 M, and the thiosulfate is gradually oxidized to other species such as sulfate at longer reaction times.

### 8.3.2 Oxidation of Macraes Concentrate

Several experiments on the alkaline oxidation of the Macraes flotation concentrate and the simultaneous dissolution of gold were carried out at 25 °C. The results of a typical test are given in Figures 8.16 and 8.17. It can be seen that, as in the case of the Wiluna concentrate, gold starts to dissolve only after the mineral is partly oxidized after which the gold dissolves at an approximately linear rate to a maximum dissolution of about 72% after 48 hours.
Figure 8.16 Dissolution of gold (○), arsenic (◇), sulfur (□), copper (△) and iron (x) during the oxidation of milled Macraes concentrate with air at 25 °C.

Figure 8.17 Variation of concentrations of thiosulfate (◇), arsenate (△), sulfite (□) and monothioarsenate (○) during the oxidation of milled Macraes concentrate with air at 25 °C.
Figure 8.16 shows that the dissolution of arsenic is higher than that of sulfur, suggesting that the oxidation rate of arsenopyrite is higher than that of pyrite, which is also similar to the results obtained with the Wiluna concentrate. In fact, the extent of oxidation of arsenopyrite by analyses of the solid residue after 48 hours was 97% and that of pyrite was 36.2%. The dissolution of copper indicates partial oxidation of chalcopyrite. Figure 8.17 shows that the concentrations of thiosulfate and arsenate are high while those of monothioarsenate and sulfite are low, suggesting the faster oxidation rate of monothiosulfate and sulfite in this reacting system.

### 8.3.3 Oxidation of Salsigne Concentrate

A single experiment on the oxidation of the Salsigne concentrate sample was carried out at 25 °C for 48 hours in 300 ml 2.08 M NaOH solution with 100 grams of the sample milled to 90% passing 5 micron. The amount of NaOH used is equivalent to 250 kg per ton of the concentrate. The overall results of the experiment are given in Table 8.4 which shows that about 76% of the gold in the sample is dissolved with the dissolution of arsenic being about 70%. The calculated dissolution rates of gold by analyses of the solid residue and the solutions are consistent. Small amounts of iron were found in the solution after 48 hours.

**Table 8.4 Oxidation of Salsigne concentrate with air at 25 °C for 48 hours**

<table>
<thead>
<tr>
<th>Arsenic Dissolution / %</th>
<th>Gold Dissolution (by solution) / %</th>
<th>Gold Dissolution (by residue) / %</th>
<th>Iron in solution / g l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.3</td>
<td>76.0</td>
<td>76.8</td>
<td>0.49</td>
</tr>
</tbody>
</table>
8.3.4 Oxidation of Unknown Concentrate

A flotation concentrate of unknown origin was available with a high gold concentration of 414 g t\(^{-1}\) and was included in the test work. The experiment was carried out under the following conditions: 150 grams of the sample in 600 ml distilled water, 45.2 grams of sodium hydroxide (calculated from Table 8.1 according to the arsenopyrite content), 25 °C, 1400 rpm stirring speed, 1 l min\(^{-1}\) air flowrate. The sample was wet milled for 60 minutes.

The results are shown in Figures 8.18 and 8.19. The gold starts to dissolve after about 12 hours when more than 40% of arsenic is dissolved from the sample. The concentration of thiosulfate at 12 hours is about 0.16 M while that of monothioarsenate is low at 0.03 M. The concentration of thiosulfate at 50 hours increases to 0.4 M whereas that of monothioarsenate decreases to zero.

The dissolution of arsenic reaches 83% after 50 hours (the oxidation of arsenopyrite and pyrite by residue analyses being 97% and 28% respectively) at which time the extent of gold dissolution is only 21%. The relevant dissolution rates of copper and iron are 36% and 7% respectively.
Figure 8.18  Dissolution of gold (◊), arsenic (□), sulfur (×), copper (Δ) and iron (○) during the oxidation of milled unknown concentrate with air at 25 °C.

Figure 8.19  Variation of the concentrations of thiosulfate (Δ) and monothioarsenate (□) during the oxidation of milled unknown concentrate with air at 25 °C.
8.4 Discussion

Experimental tests on several refractory concentrates have shown that gold can be dissolved during the alkaline oxidation of these sulfide concentrates with air without addition of a lixiviant such as cyanide. The dissolution of gold appears to be correlated with the concentration of thiosulfate and probably occurs as a result of the complex reactions of gold with thiosulfate. The alternative reaction with monothioarsenate as a lixiviant does not appear likely given the low concentration of monothioarsenate during the oxidation process. This conclusion is in agreement with the studies of Lulham (1989) who reported the dissolution of gold from pyritic ores in Na₂CO₃ solutions in the presence of thiosulfate and the results of Fang and Han (2002) who studied the leaching of gold with sulfur and Ca(OH)₂ under oxygen pressures. The dissolution rate of gold in the gold concentrates can be estimated by considering the oxidation of the Wiluna sample (milled for 60 minutes) at 25 °C as shown in Figure 8.1 and using Equation 5.20 in Chapter 5 (assuming spherical particles of gold):

\[
R_{Au} = \frac{(dX_{Au}/dt) \cdot (\rho \cdot d)}{(6 \cdot M_{Au})} \quad (8.1)
\]

where \( R_{Au} \) is the initial dissolution rate of gold in moles per unit time per unit surface area (mol cm\(^{-2}\) s\(^{-1}\)); \( X_{Au} \) is the dissolution fraction of gold; \( M_{Au} \) is the molar weight of gold (196.97 g mol\(^{-1}\)); \( \rho \) is the specific gravity of gold (19.32 g cm\(^{-3}\)); \( d \) is the diameter of spherical gold particles (cm). From Figure 8.1 it can be seen that \( X \) increases approximately linearly with time at 25 °C. Thus \( dX_{Au}/dt \) can be assumed to be a constant and for \( X = 0.58 \) at 48 hours,

\[
dX_{Au}/dt = 0.58/(48 \times 3600) = 3.35 \times 10^{-6} \text{ (s}^{-1}) \quad (8.2)
\]

Assuming \( d = 1 \mu\text{m} = 10^{-4} \text{ cm}, R_{Au} = 5.5 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}. \) If \( d = 0.1 \mu\text{m}, R_{Au} = 5.5 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}, \) and \( d = 0.01 \mu\text{m}, R_{Au} = 5.5 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}. \) These estimated
values for the dissolution rate of gold in the concentrate sample are much higher than the
value of about $6 \times 10^{-15}$ mol cm$^{-2}$ s$^{-1}$ as estimated in Chapter 5 for the dissolution rate of
gold powder in oxygenated alkaline thiosulfate solutions without copper and ammonia.
These values are similar to the rate ($1.5 \times 10^{-13}$ mol cm$^{-2}$ s$^{-1}$) of wet-milled 1.5-3 µm gold
powder in oxygenated alkaline thiosulfate solutions without copper (Chapter 5). This
comparison suggests that the size of gold particles in the concentrates may be very fine
i.e. less than 0.1 µm so that gold in sulfide minerals dissolves much faster than with
powders, which is in consistent with the mineralogy of Wiluna gold concentrate in which
most of the gold occurs in arsenopyrite as microscopic or invisible grains.

There is an induction period for the dissolution of gold, which probably results
from the slow rate of formation of thiosulfate ions by oxidation of sulfide minerals but
also the requirement of oxidation of the minerals for occluded gold grains to be exposed
to thiosulfate and oxygen. Mineralogical analysis of the Wiluna concentrate has shown
that the gold is mostly locked in sulfide minerals (it is probable that other refractory gold
concentrates have similar features). Thus the oxidation or decomposition of the sulfide
minerals such as arsenopyrite or pyrite is required to release the gold in order for gold to
react with the thiosulfate formed during the oxidation of these minerals with dissolved
oxygen. From all the experimental results on the oxidation of Wiluna gold concentrate,
the relationship between the dissolution of gold and the dissolution of total sulfur and
arsenic in the concentrate have been established and shown in Figures 8.20. Based on the
analyses of the oxidized residues, the correlations of the dissolution of gold with the
oxidation of sulfidic sulfur, arsenopyrite and pyrite are given in Figure 8.21.
Figure 8.20  Correlation of the dissolution of gold with the dissolution of arsenic (+) and sulfur (o) during the oxidation of milled Wiluna concentrate at various conditions.

Figure 8.21  Correlation of the dissolution of gold with the oxidation of arsenopyrite (□) and pyrite (o) and with the dissolution of sulfur (Δ) and arsenic (+) based on analyses of residues after 48 hours' oxidation of milled Wiluna concentrate under various conditions.
It appears from Figure 8.20 that the dissolution of gold increases with the dissolution of sulfur. The analytical results of the final oxidation residues as given in Figure 8.21 also shows that the dissolution of gold correlates with the dissolution of sulfur. It was found from the analyses of the residues that, as expected, the extent of dissolution of sulfur varied approximately linearly with the oxidation of sulfidic sulfur. Thus the dissolution of gold increases with the extent of sulfur oxidation, suggesting that most of gold in the Wiluna concentrate is associated with the sulfide minerals. From Figure 8.20 it can be seen that in the initial stage of the oxidation the dissolution of arsenic rapidly increases up to about 90% while the extent of gold dissolution increases with the dissolution of arsenic but reaches only about 20%, suggesting that most of the gold probably is locked in arsenopyrite as very fine grains so that most of the arsenopyrite is required to be oxidized to release the gold. On the other hand, the low dissolution of gold at the beginning may be related to the low mixed potential of gold in the reacting slurry as shown in Figure 8.3. As the oxidation of the concentrate proceeds, the mixed potential of gold increases gradually and the dissolution of gold also increases up to 80%, while the rate of dissolution of arsenic decreases slowly. The faster increase in the dissolution of gold in this stage is believed to be associated with the reaction of released fine particles of gold with thiosulfate generated by the oxidation reaction, whereas the loss of arsenic is due to the precipitation of arsenic probably as iron arsenates and/or other intermediates. Figure 8.21 shows that almost all of the arsenopyrite actually is oxidized after 48 hours but the dissolution of arsenic is only about 60-70%, confirming the precipitation of arsenic into the residues. As seen from Figure 8.21, 80% of gold dissolution from the Wiluna concentrate can be achieved after more than 90% of arsenopyrite and only 40% of pyrite are oxidized, which also seems to
suggest that the dissolution of gold correlates mainly with the oxidation of arsenopyrite and not that of pyrite.

Figures 8.2 and 8.20 show that the dissolution rate of arsenic is higher than that of sulfur, suggesting that the oxidation rate of arsenopyrite is more rapid than that of pyrite despite the higher proportion of pyrite than arsenopyrite in the concentrate, which has been confirmed by the analyses of final oxidized residues for arsenopyrite and pyrite as shown in Figure 8.21. These results are in consistent with the published data (Hiskey and Wadsworth, 1981; Rand, 1977) which have indicated that pyrite is a more noble sulfide mineral oxidation and would act as a cathode when in contact with other sulfides including arsenopyrite and chalcopyrite and accelerate the oxidation of these minerals. The mixed potential of gold in the reacting slurry (Figure 8.3) is between -0.1 V and 0.2 V which value falls between the rest potential of arsenopyrite and that of pyrite in alkaline solutions (Vreugde, 1982), confirming the prior oxidation of arsenopyrite to pyrite.

The dissolution of copper shown in Figure 8.1 could result from the oxidation of chalcopyrite in the concentrates as suggested by Lazaro-Baez (2001) and Hiskey and Wadsworth (1981):

\[
\begin{align*}
\text{CuFeS}_2 &= \text{CuS} + \text{Fe}^{2+} + \text{S}^0 + 2e^- \\
\text{CuFeS}_2 &= \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^0 + 4e^- \\
\text{CuFeS}_2 + 3\text{H}_2\text{O} &= \text{Cu}^{2+} + \text{Fe}^{2+} + \text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 8e^- \\
\end{align*}
\]

and the formation of copper-thiosulfate complexes:

\[
\begin{align*}
2\text{Cu}^{2+} + 8\text{S}_2\text{O}_3^{2-} &= \text{S}_4\text{O}_6^{2-} + 2\text{Cu(S}_2\text{O}_3)_3^{5-} \\
4\text{CuS} + 10\text{S}_2\text{O}_3^{2-} + 3\text{O}_2 &= 4\text{Cu(S}_2\text{O}_3)_3^{5-} \\
\end{align*}
\]

\[\Delta G^{\circ}_{298K} = -170.5 \text{ kJ mol}^{-1} \quad (8.6)\]
\[\Delta G^{\circ}_{298K} = -954.0 \text{ kJ mol}^{-1} \quad (8.7)\]

The copper dissolved may accelerate the dissolution of gold as discussed in Chapter 5.
Since the dissolution of gold appears to be due to the reaction of gold with thiosulfate, the concentration of oxygen as the oxidant would be expected to have an important effect on the rate of gold dissolution. Experimental tests on the Wiluna concentrate sample have confirmed the positive role of dissolved oxygen and that increasing oxygen concentration or partial pressure would accelerate the rate of dissolution of gold.

The apparent minor detrimental effect of higher concentrations of sodium hydroxide can be attributed to the reduced levels of dissolved oxygen at the higher concentrations of sodium hydroxide and the shift to more negative potentials of the cathodic reduction of oxygen. Increasing temperature has two opposing effects on the rate of gold dissolution. An expected increase in the oxidation rate of arsenopyrite, pyrite and gold at higher temperatures is counteracted by a decrease in the concentration of dissolved oxygen under the conditions of the experiments. Therefore, the dissolution rate of gold at higher temperatures shown in Figure 8.10 is lower in the first 12 hours but increases in the later stages of oxidation as the concentration of oxygen increases.

Figure 8.13 shows that the dissolution rate of gold is low and constant after an initial rapid increase. This behaviour is very similar to that of gold found in the thiosulfate solutions with copper present as described in Chapter 5, suggesting the occurrence of passivation of gold in thiosulfate solutions.

The oxidation of the Macraes gold concentrate as shown in Figures 8.16 and 8.17 shows similar results to that of Wiluna concentrate, indicating that Macraes concentrate could probably have similar mineralogical features to those of the Wiluna concentrate.
However, the experimental results shown in Figure 8.18, for the oxidation of the unknown gold concentrate, indicate that the dissolution of gold (about 20% after 48 hours) is considerably low despite a high gold content of more than 400 g t\(^{-1}\) in the concentrate. One possible reason for the low recovery of gold could be that most of the gold in the unknown concentrate is associated with pyrite which needs to be completely oxidized before gold particles can be exposed to the thiosulfate lixiviant. In fact, the oxidation rate of pyrite by analysis of the residue after 48 hours was low with only about 28% oxidation while 97% of the arsenopyrite had been oxidized. Additionally, the gold in the unknown concentrate may not occur as microscopic grains or invisible gold as in arsenopyrite.

Therefore, the extraction of gold during the alkaline oxidation of refractory sulfide gold concentrates depends on not only the concentration of gold in the concentrates but also on the mineralogy and deportment of gold with the host minerals. More detailed investigations of this aspect need to be carried out.

### 8.5 Conclusions

Several refractory gold sulfide-bearing concentrates have been tested for the dissolution of gold during the alkaline oxidation of these concentrates without the addition of cyanide. For rapid and effective dissolution of gold, it is required to oxidize the gold-bearing sulfide minerals to release the gold particles in the minerals. Fine-grinding of the concentrate samples will increase the rate of oxidation of the sulfide minerals in alkaline solutions as will an increase in temperature and concentration of dissolved oxygen. The rate of oxidation of arsenopyrite is greater than that of pyrite under the conditions of these experiments.
The simultaneous dissolution of gold is attributed to the reaction of gold with thiosulfate ions generated during the alkaline oxidation of the sulfide minerals. It is suggested that the monothioarsenate ion could possibly play only a minor role in the dissolution of gold because of the low concentration of this species in the reacting pulp. Copper dissolved from the oxidation of copper minerals such as chalcopyrite may accelerate the dissolution of the gold.

The results obtained in this limited assessment of the applicability of the chemistry to the recovery of gold from selected sulfide concentrates have shown promise and could provide the basis of a new process for direct extraction of gold from refractory arsenical gold concentrates in one step without using lixiviants such as cyanide.
CHAPTER 9  SUMMARY AND RECOMMENDATIONS

This chapter summarizes the principal results of this study carried out on the simultaneous dissolution of gold during the alkaline oxidation of arsenopyrite and pyrite, the electrochemistry and leaching of gold in alkaline thiosulfate and thioarsenate solutions and on the practical extraction of gold from refractory sulfide concentrates without the use of cyanide. Recommendations for further work in this area are also made.

9.1 Summary

A major finding in this study is that the alkaline oxidation of refractory gold concentrates containing arsenopyrite and pyrite with oxygen at ambient temperatures and pressures is accompanied by the simultaneous dissolution of gold without the addition of cyanide. Studies of the alkaline oxidation of some selected refractory sulfide gold concentrates have shown that up to 80% of gold can be extracted in a one-step process without cyanide, suggesting a new possible approach for extraction of gold from refractory sulfide gold concentrates.

A detailed study on the chemistry of the products formed during the dissolution of arsenopyrite and pyrite in alkaline solutions has been carried out by way of high performance liquid chromatography (HPLC). Previously unidentified oxidation products of arsenopyrite, namely, thioarsenates, have been identified and quantitatively determined. Arsenopyrite reacts with oxygen yielding mainly thiosulfate, thioarsenates, arsenate and sulfite, with monothioarsenate being the principal product in the initial stage.
of arsenopyrite oxidation. Sulfur appears not to be the oxidation product of arsenopyrite but is one of the oxidation products of pyrite in alkaline media. Thiosulfate has been confirmed to be the dominant product of pyrite oxidation. Ferric hydroxide in the form of porous layers on the mineral particles is the oxidation product of both arsenopyrite and pyrite. An approximate stoichiometry for the overall process of pyrite oxidation in alkaline solutions with air is given by the following reaction:

$$12\text{FeS}_2 + 11\text{O}_2 + 32\text{NaOH} + 2\text{H}_2\text{O} = 12\text{Fe(OH)}_3 + 8\text{Na}_2\text{S}_2\text{O}_3 + 8\text{Na}_2\text{SO}_3 \quad (9.1)$$

In the case of arsenopyrite, the reaction below may be used to approximately express the overall process of arsenopyrite oxidation in alkaline solution with oxygen.

$$6\text{FeAsS} + 13\text{O}_2 + 22\text{NaOH} = 6\text{Fe(OH)}_3 + 2\text{Na}_3\text{AsO}_3\text{S} + 4\text{Na}_3\text{AsO}_4 + 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O} \quad (9.2)$$

The study of the kinetics of the alkaline oxidation of arsenopyrite has shown that variables such as particle size, oxygen concentration, and stirring speed have the most significant effect on the rate at ambient temperatures and pressures. The initial oxidation rate of arsenopyrite in NaOH solutions may be represented by the following expression:

$$- (1/S) \frac{dN}{dt} = k' \exp(-1900 \ T^{-1}) \ P_{O_2} \quad (9.3)$$

A reaction mechanism for the oxidation of arsenopyrite has been proposed, which involves an anodic process for arsenopyrite oxidation involving hydroxyl ions and a cathodic process for oxygen reduction. The overall rate of oxidation is partially controlled by mass transfer of dissolved oxygen.

Gold, either as added powder or as a constituent of the concentrates has been found to dissolve simultaneously during the alkaline oxidation of both arsenopyrite and pyrite, which appears to be associated with the complex reactions between gold and thiosulfate. The dissolution rate of gold is dependent on wet-milling of the reacting
materials, temperature, stirring speed, concentrations of oxygen, NaOH and arsenopyrite
in the reaction system. Small amounts of copper in the form of copper sulfide minerals in
the concentrates have also been found to dissolve simultaneously, most likely due to
reaction with thiosulfate. The solubility of iron from the sulfide minerals in weak
alkaline media appears to be a result of reaction of dissolved iron with arsenates.

Electrochemical studies of gold in thiosulfate solutions have shown that anodic
dissolution of gold can be measured in alkaline thiosulfate solutions at ambient
temperatures at potentials above about 0.2 V. Thiosulfate ions undergo oxidative
decomposition on the gold surface in the same potential region with the formation of a
sulfur-like surface film which acts to partially passivate the surface for the dissolution of
gold. The anodic dissolution of gold at constant potentials has been found to be
 electrochemically controlled with an activation energy of 65 kJ mol\(^{-1}\), and the rate has
been enhanced by increases in pH, temperature and concentrations of thiosulfate and
ammonia. Open circuit dissolution of gold in oxygenated thiosulfate solutions can occur
with a rate which is significantly lower than that achieved by conventional cyanidation or
by the copper-catalyzed dissolution in ammoniacal thiosulfate solutions.

The effect of copper on the dissolution of gold in alkaline thiosulfate solutions in
the absence of ammonia has been investigated by ways of electrochemical and leaching
techniques. It is found that while copper ions catalyze the reaction rate of gold with
thiosulfate they also accelerate the rate of oxidation of thiosulfate. It is proposed that the
catalytic role of copper in enhancing the rates of dissolution of gold and oxidation of
thiosulfate in oxygenated thiosulfate solutions in the absence of ammonia is possibly
associated with the formation of a copper-thiosulfate-oxygen intermediate species, which
acts as an oxidant. It is also possible that a mixed copper-gold-thiosulfate complex is
formed and plays a role in the increase of the dissolution rate of gold in ammonia-free thiosulfate solutions. As expected, milling of gold powder assists with the dissolution of gold in thiosulfate solutions, especially in the presence of copper. The positive effect of copper on the dissolution of gold may account for the simultaneous dissolution of gold during the alkaline oxidation of refractory gold concentrates containing arsenopyrite and pyrite.

A preliminary investigation into possible reactions of gold with arsenical compounds such as monothioarsenate and thioarsenites has been conducted using electrochemical and leaching approaches. Electrochemical studies have shown that gold dissolves at a measurable rate in monothioarsenate solutions at potential of 0.25 V, which is confirmed by leaching experiments in the presence of oxygen. It appears that the formation of a passivating film inhibits the dissolution of the gold. It is also found that gold dissolves in thioarsenite solutions, with the dissolution rate depending on the composition, temperature and oxygen concentration of the solution. The reactions of gold with thioarsenates and thioarsenites are attributed to be presence of the active sulfur atoms in these arsenical compounds that are soft electron donors as in the case of polysulfides, thiosulfate, thiocyanate, thiourea or other sulfur bearing ligands which can form complexes with gold. The reactivity of gold with monothioarsenate suggests that thioarsenates may play a role in the dissolution of gold accompanying the alkaline oxidation of refractory gold concentrate containing arsenopyrite.

In summary, the results of this study demonstrate that the alkaline oxidation of fine-ground refractory gold concentrates containing arsenopyrite and pyrite with air in the absence of cyanide is accompanied by the simultaneous dissolution of gold as a result of reactions of gold with thiosulfate. The fraction of gold dissolved depends on the
mineralogy and particle size of the ore sample, oxygen concentration, alkalinity, pulp density, agitation and the availability of copper in the sample. This work has suggested an alternative one-step process for the direct extraction of gold from refractory sulfide-bearing gold ores without the use of cyanide.

9.2 Recommendations for Future Work

As mentioned above, direct extraction of gold from refractory arsenical gold concentrates by alkaline oxidation with air at ambient temperatures and pressures is possible. However, it is worth noting that this study was carried out on a laboratory scale. For practical, commercial use, much further work is necessary to be conducted on a larger scale to examine the efficiency of the process investigated in this study. Each ore or concentrate has a characteristic mineralogy and deportment of gold and therefore the feasibility of the proposed process needs to be carefully evaluated for each particular ore. The following activities could be considered for further investigation.

1. A more extensive study of the mechanism of the dissolution of gold using thiosulfate as the lixiviant in order to increase the leaching rate of gold.
2. A detailed investigation aimed at a fuller understanding of the effect of ammonia on the dissolution of gold in thiosulfate solutions.
4. Extension of this work to higher temperatures and pressures such as those under consideration for pressure oxidation of arsenopyrite concentrates.
5. Examination of the use of some additives such as ammonia or sulfite to increase the recovery of gold from refractory concentrates.
6. Studies on the relationship between the mineralogy and the recovery of gold in order to establish the applicability of the process to concentrates from different sources.

7. An investigation into the recovery of gold from the pregnant solutions produced from the alkaline oxidation of refractory sulfide bearing concentrates.

8. Disposal of the arsenic-containing solutions to meet environmental regulations for health and safety.


10. Scale-up experiments using appropriate large reactors or vessels to evaluate the feasibility of the one-step gold extraction process for a selection of some refractory gold concentrates.

11. Minimization of reagent consumption for commercial use.
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APPENDIX

Appendix A1  Thermodynamic Data Used in this Study

Table A1  Free energies of formation (kcal mol\(^{-1}\)) (1 kcal = 4.184 kJ)

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta G_{298K}^0)</th>
<th>Reference</th>
<th>Species</th>
<th>(\Delta G_{298K}^0)</th>
<th>Reference</th>
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<tr>
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</tr>
<tr>
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<td>b</td>
</tr>
<tr>
<td>SO(_2)(aq)</td>
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<td>a</td>
<td>Cu(OH)(_2)(^{2-})</td>
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<tr>
<td>S(_3)O(_6)(^2-)</td>
<td>-229.00</td>
<td>a</td>
<td>Cu(S(_2)O(_3))(^{2-})</td>
<td>-252.80</td>
<td>e</td>
</tr>
<tr>
<td>S(_4)O(_6)(^2-)</td>
<td>-244.30</td>
<td>a</td>
<td>Cu(S(_2)O(_3))(^-)</td>
<td>-126.20</td>
<td>e</td>
</tr>
<tr>
<td>S(_5)O(_6)(^2-)</td>
<td>-228.50</td>
<td>a</td>
<td>Cu(S(_2)O(_3))(^{2-})</td>
<td>-238.7</td>
<td>e</td>
</tr>
<tr>
<td>Au(^+)</td>
<td>39.00</td>
<td>a</td>
<td>As(s)</td>
<td>0.00</td>
<td>b</td>
</tr>
<tr>
<td>Au(S(_2)O(_3))(^{2-})</td>
<td>-244.50</td>
<td>e</td>
<td>As(_3)(aq)</td>
<td>-152.88</td>
<td>b</td>
</tr>
<tr>
<td>CN(^-)</td>
<td>39.60</td>
<td>d</td>
<td>H(_2)AsO(_3)(_3)(aq)</td>
<td>-140.28</td>
<td>b</td>
</tr>
<tr>
<td>SCN(^-)</td>
<td>21.20</td>
<td>d</td>
<td>H(_2)AsO(_3)(_3)(^-)</td>
<td>-125.30</td>
<td>c</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>-31.35</td>
<td>a</td>
<td>HAsO(_3)(^2-)</td>
<td>-107.00</td>
<td>c</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>-2.53</td>
<td>a</td>
<td>AsO(_3)(^3-)</td>
<td>-183.08</td>
<td>b</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>-20.30</td>
<td>a</td>
<td>H(_2)AsO(_4)(aq)</td>
<td>-179.99</td>
<td>b</td>
</tr>
<tr>
<td>I(_3)(^-)</td>
<td>-12.31</td>
<td>a</td>
<td>H(_2)AsO(_4)(^-)</td>
<td>-170.76</td>
<td>b</td>
</tr>
<tr>
<td>I(_2)(^-)</td>
<td>-12.35</td>
<td>a</td>
<td>HAsO(_4)(^2-)</td>
<td>-154.93</td>
<td>b</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>-37.60</td>
<td>a</td>
<td>AsO(_4)(^3-)</td>
<td>-154.93</td>
<td>b</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>-56.69</td>
<td>a</td>
<td></td>
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</tr>
</tbody>
</table>

a. from Pourbaix (1974);
b. from Outokumpu HSC program database (Roine, 1994);
c. from Dove and Rimstidt (1985);
d. from Aylmore and Muir (2001) and Hiskey and Atluri (1988);
e. calculated from either the stability constant of species or the reduction potential \(E^0\).
Appendix A2  Wet Chemical Analysis of Sulfide Minerals and Oxidized Residues

A2.1  Preparation of a bromine-bromide mixture

The bromine-bromide (Br₂-KBr) mixture solution was made up according to Young (1971) and Vogel (1962) by dissolving 160 grams potassium bromide in a small quantity of water in a 2-liter beaker, adding 100 ml of bromine under a hood, stirring vigorously, and making up with water to 1 liter.

A2.2  Procedure for digesting sulfide materials

1) Weigh out about 0.2 grams sample into a 100-ml beaker.
2) Add 10-20 ml Br₂-KBr mixture followed by placing a watch glass on the beaker and allowing the sample to stand for about 10 minutes in a fume cupboard.
3) Add 10 ml concentrated nitric acid and allow to stand for 15 minutes at room temperature.
4) Place the beaker on asbestos on a hot plate and heat up to about 50 °C.
5) Digest for 0.5 - 1 hour until the red color of bromine fades.
6) Stop heating and add about 20 ml Milli-Q water to cool the solution.
7) Rinse the watchglass and filter all solutions in the beaker through Whatman No. 541 filter paper into a 200 or 250 ml volumetric flask.
8) Rinse the filter paper 5-6 times with water or 0.1 M nitric acid.
9) Make up to the mark of the flask for further analysis by AAS or ICP.
A2.3 Analysis of oxidized residues

1) Weigh out about 1.0 grams sample into a 100 ml beaker.

2) Add 20 ml 3 M HCl solution and shake the beaker gently to dissolve iron hydroxides, arsenates and other acid soluble materials in the residue.

3) Filter through Whatman No. 541 filter paper into a 500 ml volumetric flask and wash the paper 5-10 times using distilled water. Transfer all washings into the flask and make up to the mark of this first flask for further analysis by AAS or ICP of As, S and Fe.

4) Put the filter paper and its contents into a 100 ml beaker.

5) Add 15 ml Br₂-KBr mixture and 10 ml concentrated nitric acid to dissolve the remaining sulfide minerals according to the procedure in the above Section A2.2.

6) Filter through Whatman No. 541 filter paper into a 100 or 200 ml volumetric flask and rinse the filter paper 5-6 times with pure water.

7) Make up to the mark of this second flask for further analysis by AAS or ICP for As, S and Fe.

8) From the analyses of solutions in the two flasks for As, S and Fe, percentages of total As, S and Fe in the residue can be calculated. The percentage of arsenopyrite mineral in the residue can be calculated using Equation A2.1, assuming that all arsenic is in the form of arsenopyrite.

\[
\%\text{FeAsS} = \frac{m_{\text{As}}}{0.4601 \times W_{\text{sample}}} \tag{A2.1}
\]

where \(m_{\text{As}}\) is the total mass of arsenic in the second flask, g; \(W_{\text{sample}}\) is the mass of residue weighed, g; 0.4601 is the theoretical percentage of arsenic in pure arsenopyrite.
9) As most of the contained sulfide mineral is in the form of arsenopyrite and pyrite with minor amounts of chalcopyrite, it is assumed that all sulfidic sulfur in the residue is in the form of arsenopyrite and pyrite. Thus the percentage of pyrite of the oxidized residue can be estimated by using Equation A2.2.

\[
\% \text{FeS}_2 = \left( m_S - m_{\text{As}} \times 0.1969 / 0.4601 \right) / \left( 0.5345 \times W_{\text{sample}} \right)
\]  

(A2.2)

where \( m_S \) is the mass of total sulfur in the second flask, g; \( m_{\text{As}} \), \( W_{\text{sample}} \) and 0.4601 are as above; 0.1969 and 0.5345 are theoretical percentages of sulfur in pure arsenopyrite and pyrite respectively.
Appendix A3  Estimation of the Mass Transfer Coefficient of Oxygen

For reactions limited by diffusion through the mass transfer boundary layer, the hydrodynamic flow regime at the reacting surface is of considerable importance in understanding the reaction kinetics. Mass transfer in an aqueous phase has been analyzed in detail (Wadsworth and Miller, 1979). However, the theoretical treatment of mass transfer to particles suspended in a stirred reactor has not been fully developed. Nevertheless, the minimum mass transfer coefficient, $k^*$, in which the slip velocity would be equivalent to that for freely falling particles, can be calculated on a semi-theoretical basis for monosize spheres from the physical properties of the aqueous and solid phase and the diffusion coefficient of the reactant. Basically, the semi-theoretical correlation takes the following form for free-falling spherical particles (Wadsworth and Miller, 1979):

$$Sh = 2 + 0.6 \text{Re}^{0.5} \text{Sc}^{0.33} \quad (A3)$$

where

- $Sh =$ Sherwood number, $k^*d/D$;
- $Re =$ Reynolds number, $ud/ν$;
- $Sc =$ Schmidt number, $ν/D$;
- $u =$ velocity;
- $D =$ diffusion coefficient;
- $ν =$ kinematic viscosity; and,
- $d =$ particle diameter.

Equation A3 can be plotted in terms of the mass transfer coefficient vs. particle size and the resulting diagram is given in Figure A3 (Wadsworth and Miller, 1979). From this graph the value of $k^*$ for a suspended particle can be estimated. However, the actual coefficient depends on reactor design and stirrer speed or power input.
In this study, for arsenopyrite (specific density $\rho_s = 6.0$ g cm$^{-3}$) spherical particles of +38-45 µm (average 42 µm), the mass transfer coefficient is estimated to be about 0.0106 cm s$^{-1}$. 

Figure A3  Plot of mass transfer coefficient vs. particle diameter for freely falling spheres.
Appendix A4  XRD Patterns

Figure A4.1  XRD pattern for a Wiluna flotation concentrate sample. Wavelength of 1.7902Å (Co).

Figure A4.2  XRD pattern for a Macraes flotation concentrate sample. Wavelength of 1.7902Å (Co).
Appendix A5  Particle Size Analyses

Figure A5.1  Size distribution of particles resulted from wet-milling 150 grams of Wiluna gold concentrate in a stainless steel mill for 120 minutes. The heavy line denotes the percentage of particles passing a given size.

Figure A5.2  Size distribution of particles resulted from wet-milling 150 grams of Wiluna gold concentrate in a stainless steel mill for 60 minutes. The heavy line denotes the percentage of particles passing a given size.
Figure A5.3  Size distribution of particles resulted from wet-milling 150 grams of Wiluna gold concentrate in a stainless steel mill for 20 minutes. The heavy line denotes the percentage of particles passing a given size.

Figure A5.4  Size distribution of particles resulted from wet-milling 25 grams of pure arsenopyrite in a stainless steel mill for 60 minutes. The heavy line denotes the percentage of particles passing a given size.
Appendix A6  Calculation of Cumulative Dissolution Rates for the Oxidation of Sulfide Minerals and Gold Concentrates

During the alkaline oxidation of sulfide minerals or gold concentrates, slurry samples (about 17 ml) were taken from the reactor at various times and filtered through 0.45 micron nylon membrane paper. The clear filtrates (about 13 ml) were analyzed by AAS for Au, Cu and Fe, by ICP for As and S elements, and by HPLC for dissolved species of sulfur and arsenic. The residues were returned and about 13 ml distilled water was added each time to the reactor in order to keep the mass of the reacting slurry approximately constant. At the end of the experiment, the slurry in the reactor was filtered through Whatman No.541 filter paper by vacuum and washed three times with distilled water. The final filtrate and washings were collected for further analyses of As, Au, Cu, Fe and S. The final residue was oven dried at 110 °C and weighed before being analyzed for Au, As, Fe, S and sulfide minerals. Thus, cumulative dissolution rates at different reaction times of total Au, As, S, Cu, or Fe were calculated based on the results of filtrate analyses. An example of the calculation of the cumulative dissolution rate is shown below.

In the case of a typical experiment on the oxidation of Wiluna gold concentrate, the experiment was carried out in 600 ml water with addition of 150 g milled Wiluna sample and 37.5 g NaOH (solid-liquid ratio = 1:4) at 25 °C, 1400 rpm stirring speed and 1 l min⁻¹ flow rate of air. The results of analyses of aqueous samples taken at various times are given in Table A2. After 48 hours, the slurry was filtered and washed with the volume of the filtrate being 455 ml and that of the washings being 440 ml. The dried final residue was weighed as 144.2 grams. The percentages of total As, S and Fe in the residue are also given in Table A2, and the arsenopyrite and pyrite in the residue are estimated to be 1.2% and 22% respectively. Thus, the cumulative dissolution rates of Au,
As, S, Cu and Fe from solution analyses, and the dissolution rates of As, S and Fe from residue analyses were calculated and are also shown in Table A2.

### Table A2  Results of an experiment with Wiluna concentrate

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Au ppm</th>
<th>As g l⁻¹</th>
<th>S g l⁻¹</th>
<th>Cu ppm</th>
<th>Fe g l⁻¹</th>
<th>Au%</th>
<th>As%</th>
<th>S%</th>
<th>Cu%</th>
<th>Fe%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.2</td>
<td>1.6</td>
<td>0.4</td>
<td>0.001</td>
<td>0</td>
<td>5.8</td>
<td>2.9</td>
<td>0.1</td>
<td>0</td>
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<tr>
<td>3</td>
<td>0</td>
<td>4.0</td>
<td>3.8</td>
<td>0.3</td>
<td>0.001</td>
<td>0</td>
<td>19</td>
<td>6.8</td>
<td>0.08</td>
<td>0</td>
</tr>
<tr>
<td>6.5</td>
<td>0.33</td>
<td>7.5</td>
<td>7.5</td>
<td>0.3</td>
<td>0.001</td>
<td>1.4</td>
<td>37</td>
<td>14</td>
<td>0.08</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>2.27</td>
<td>12</td>
<td>12</td>
<td>0.98</td>
<td>0.001</td>
<td>9.7</td>
<td>59</td>
<td>22</td>
<td>0.2</td>
<td>0</td>
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<tr>
<td>24</td>
<td>10.3</td>
<td>13.5</td>
<td>20</td>
<td>4.45</td>
<td>0.73</td>
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<td>68</td>
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<tr>
<td>36</td>
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<tr>
<td>48</td>
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<td>10</td>
<td>22</td>
<td>90.8</td>
<td>3.15</td>
<td>78</td>
<td>61</td>
<td>44</td>
<td>22</td>
<td>5.7</td>
</tr>
<tr>
<td>Filtrate Vₖ</td>
<td>16.8</td>
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<td>22</td>
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<td>Wash Vₚ</td>
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<td>8.5</td>
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<td>440 ml</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residue Wₐ</td>
<td>-</td>
<td>3.5% As</td>
<td>13% S</td>
<td>-</td>
<td>24.6% Fe</td>
<td>-</td>
<td>59</td>
<td>44</td>
<td>-</td>
<td>5.4</td>
</tr>
<tr>
<td>144.2 g</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The calculation for the results in Table A2 is described as follows. Since the volume of the reacting slurry was kept approximately constant, the solution component of the slurry was assumed to be 0.6 liter during the experiment except when the experiment ended. The measured volumes of the final filtrate and washings were used for calculation of the cumulative dissolution rate. As about 13 ml aqueous solution was taken out each time for analysis, the loss of targeted elements in the slurry for the calculation of the cumulative dissolution rates should be considered. Thus,

\[
\text{Dissolution rate (at time } t) = \frac{(0.013 \times \sum C_{t-1} + 0.6 \times C_t)}{W_0 \times H_0}
\]

\[
\text{Dissolution rate (final) } = \frac{(0.013 \times \sum C_{t-1} + V_F \times C_F + V_W \times C_W)}{W_0 \times H_0}
\]
Dissolution rate (by residue) = 1 - \( \frac{(W_R \times H_R)}{(W_0 \times H_0)} \)

where \( C_t \) is the concentration of the targeted element at time \( t \), ppm or g l\(^{-1} \); \( \sum C_{t-1} \) is the sum of all concentrations of the targeted element before time \( t \); \( W_0, H_0 \) are the initial mass, g, and head analysis of the Wiluna concentrate, g l\(^{-1} \) or % (by mass); \( V_F, V_W \) are the volumes of final filtrate and washings respectively, l; \( C_F, C_W \) are the concentrations of final filtrate and washings respectively; \( W_R, H_R \) are the mass and the head analysis of the dried residue. The dissolution rate of arsenic at 24 hours, for example, is calculated by

\[
\% \text{As dissolved (at 24 hours)} = \left[0.013 \times (1.2 + 4.0 + 7.5 + 12) + 0.6 \times 13.5 \right] / (150 \times 8.29\%) = 68\%
\]

At 48 hours, the final extent of dissolution is calculated as follows:

\[
\% \text{As dissolved (at 48 hours)} = \left[0.013 \times (1.2 + 4.0 + 7.5 + 12 + 13.5 + 12) + 0.455 \times 10 + 0.44 \times 5.5 \right] / (150 \times 8.29\%) = 61\%
\]

The final extent of dissolution from analysis of the residue is calculated as

\[
\% \text{As dissolved (by residue)} = 1 - \left[144.2 \times 3.5\% \right] / (150 \times 8.29\%) = 59\%
\]

Similarly, the dissolution rates of gold, sulfur, copper and iron can be calculated. Furthermore, the oxidation rates of arsenopyrite and pyrite can also be calculated to be about 94% and 40% respectively.