A FUNDAMENTAL STUDY OF THE ACIDIC PRESSURE
OXIDATION OF ORPIMENT AND PYRITE
AT HIGH TEMPERATURE

by

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ABSTRACT

The acidic pressure oxidation of pyrite (FeS$_2$) and orpiment (As$_2$S$_3$), as a pretreatment of refractory gold ores, has been studied by investigating the reaction chemistry and kinetics. The effects of retention time, temperature, particle size, oxygen partial pressure, pulp density, sulfuric acid concentration, and cupric ions were evaluated for both minerals. The effect of ferric ions on the oxidation rate of As(III) to As(V) was also examined. Also, the effects of mole ratio of Fe/As on the oxidation of pyrite and orpiment mixtures were evaluated.

During the acidic pressure oxidation of orpiment, most of the arsenic was found to be in the trivalent state after 2 hours oxidation at temperatures ranging from 170 to 230°C, and subsequent oxidation to As(V) with oxygen was very slow. Cupric ions do not affect the oxidation of As(III). However, the rate of oxidation of As(III) to As(V) is rapid in the presence of ferric ions. Sulfate becomes the predominant product species only at temperatures above 190°C. The oxidation kinetics are controlled by product layer diffusion with an Arrhenius activation energy of 22.2 kJ/mol (5.31 kcal/mol) over the temperature range of 170 to 210°C. However, as temperature increases above 210°C, the rate-controlling step switches to a surface chemical reaction with an Arrhenius activation energy of 50.0 kJ/mol (12.0 kcal/mol). The initial reaction rate is approximately $-1/5$ order with respect to pulp density, and $1/4$ order with respect to oxygen partial pressure in the system studied.
During the acidic pressure oxidation of pyrite, ferric, instead of ferrous, is the initial product at high temperatures. No elemental sulfur was found at temperatures above 190°C. An activation energy of 33.2 kJ/mol (7.94 kcal/mol) was observed over the temperature range 170 to 230°C. The reaction order with respect to oxygen partial pressure was found to be 1/2 at 210°C, which indicates an electrochemical mechanism of oxidation. The oxidation kinetics follow shrinking particle behavior. The surface chemical reaction is the rate-controlling step. The passivating shrinking sphere model was developed to represent the pressure oxidation of pyrite in the system studied at high temperature, based on the batch experimental data, which can be used to further develop a mathematical model to simulate continuous autoclave oxidation.

During the acidic pressure oxidation of mixtures of pyrite and orpiment, As(III) generated from orpiment was oxidized rapidly to very low levels in the presence of pyrite or the Fe(III)/Fe(II) couple. However, the oxidation rate of ferrous decreased in the presence of orpiment. Iron arsenate was generated in all tests conducted for the mixture, which is of critical importance in view of the current controversy surrounding the environmental stability of these compounds. Elemental sulfur was produced only at low ratios of Fe/As.

The pressure oxidation of orpiment is much slower than that of pyrite due to the formation of elemental sulfur. However, when the two minerals are mixed together, preferential leaching for orpiment is feasible due to galvanic effects. Thus orpiment oxidation is accelerated, while oxidation of the nobler pyrite is slowed.
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CHAPTER 1

INTRODUCTION

Gold was the first metal mankind discovered and used, followed by silver [1]. Because of its noble or unreactive nature, gold occurs in nature mostly in metallic form either by itself or alloyed with silver as electrum [2]. The early metallurgical methods for the recovery of gold were gravity separation and amalgamation. The cyanidation process came to commercial use in the late 19th century, and is still the conventional process used today. However, there are large deposits in the United States, Canada, South Africa, and Brazil [3, 4], which are refractory to conventional methods. Most of these ores contain sulfides, of which pyrite (FeS$_2$) and arsenopyrite (FeAsS) are the most common host minerals for gold. Their refractory nature is due to the dissemination of fine grained gold with pyrite, arsenopyrite and/or other sulfide minerals such as orpiment (As$_2$S$_3$), realgar (As$_2$S$_3$), stibnite (Sb$_2$S$_3$), chalcopyrite (CuFeS$_2$), and tetrahedrite (Cu$_3$SbS$_3$) [5]. The difficulty in treating these types of ores is not only incomplete liberation, but also the presence of soluble arsenic, antimony, and iron which consume dissolved oxygen and cyanide during their decomposition to retard gold dissolution [6, 7]. Therefore, an efficient method of treating these types of sulfide ores should involve the breakdown of their lattices for gold liberation and the elimination of soluble arsenic, antimony, and iron sulfide minerals to avoid their interference in the subsequent cyanidation process. In practice, this may be achieved by both pyrometallurgical and hydrometallurgical methods.
Historically, roasting has been used to oxidize such refractory ores, with the object of enhancing the exposure of gold particles to the leaching solution [8, 2]. Practical experience, however, has shown that the roasting is not completely successful as the calcined materials are refractory to some extent to the leaching medium and consequently the maximum gold recovery is limited [9]. Furthermore, the roasting operation is sensitive to the antimony and lead content in the concentrate, and the generation of sulfur, arsenic, antimony, and mercury containing gases is most undesirable from an environmental standpoint [10].

The significant increase in exploration activity during the past few decades has resulted not only in the development of many new amenable ore bodies, but also in the delineation and development of more refractory ore bodies. This, together with the disadvantages of roasting, has spurred the development of more efficient processes. Most of these processes are hydrometallurgical, including atmospheric oxidation in alkaline media with chlorine [11], atmospheric biological oxidation in acid media, and pressure oxidation in both alkaline and acid media. Other hydrometallurgical processes, such as the Artec/Cashman process [12], the Redox process [13, 14], and the Nitrox process [15, 16], have been investigated up to pilot plant scale. Among all the processes, acidic pressure oxidation is the prime commercial choice for pretreatment of many refractory sulfidic gold ores and concentrates, especially in North America.
Acid pressure oxidation is considered to be the most effective because of its metallurgical and environmental advantages [17]. Typical operating conditions include temperatures from 170 to 225°C with retention times from 1 to 3 hours at oxygen partial pressures from 350 to 700 kPa [18]. Oxidation of refractory ores involves very complex reactions including several oxidation and hydrolytic reactions which occur in series and/or in parallel.

Sulfide minerals have different oxidation reactivities in autoclaves. Thus, incomplete oxidation of the sulfides may take place with changes in the feed mineralogy, because there is typically little control over autoclave operation (such as retention time). Gold recovery in the subsequent cyanidation step is then decreased. This situation is fairly common, for instance, at the Barrick Goldstrike Mine.

The typical gold extraction at Barrick Goldstrike is about 92 percent from ores with sulfidic mineral fractions consisting mainly of pyrite (FeS₂) with some arsenopyrite (FeAsS). However, as mining progresses, increasing amounts of ore are being encountered with a much larger proportion of sulfur and high arsenic and antimony levels, predominantly as orpiment, realgar, and stibnite. Blending and feeding these ores to the autoclave can lead to decreases in gold recovery in the subsequent carbon-in-leach (CIL) step, sometimes by as much as 15 to 20 percent, which translates to the loss of hundreds of thousands of dollars per day. However, the exact causes for the decreased gold extraction associated with these mineral feeds is unknown.
A survey of the literature indicated that no information concerning the behavior of orpiment and realgar during acid pressure oxidation has been reported. Previous studies have been limited only to arsenopyrite. Since the nature and composition of minerals and reaction products have a considerable impact on autoclave operations and the downstream operations of gold recovery and waste management, an understanding of their solution chemistry is greatly needed.

A research project was proposed to carry out an extensive study of the chemistry and oxidation kinetics of orpiment during acid pressure oxidation as a step toward understanding, and eventually optimizing, the operation. It was found that although extensive investigations on pyrite have been performed by previous researchers, all of the reported work has been conducted at temperatures lower than 180°C. No data is available on the kinetics of pyrite dissolution during acid pressure oxidation over the temperature range of 180 to 230°C, which is the range employed by most commercial plants. From a process optimization standpoint it is important to know the behavior of pyrite during acidic pressure oxidation at temperatures above 180°C. Therefore, the behaviors of two sulfide minerals, orpiment and pyrite, both separately and in mixtures, over the temperature range of 170°C to 230°C, were studied in this work.

The objectives of this study are:

1. To study the reaction chemistry of orpiment and pyrite during pressure oxidation in sulfuric acid solution under varying conditions, such as retention time, temperature,
particle size, oxygen partial pressure, the concentration of sulfuric acid, and pulp density. Also, to examine the effects of foreign ion addition on the oxidation rate of As(III) to As(V) and Fe(II) to Fe(III).

2. To determine the reaction kinetics and rate controlling phenomena of these minerals under varying conditions of agitation speed, temperature, oxygen partial pressure, particle size, pulp density, the concentration of sulfuric acid, and the addition of foreign ions.

3. To determine the dissolution mechanism of these minerals during acidic pressure oxidation.

4. To determine the effects of these minerals on each other during acidic pressure oxidation.
References


CHAPTER 2

LITERATURE SURVEY

In this chapter a general survey of the literature written on the subject is presented. The chapter is divided into three sections. In the first two sections, the mineralogy of gold ores and the behavior of arsenic and antimony sulfide minerals in alkaline cyanide solution are presented, respectively. In the third section, the pretreatment of refractory sulfidic gold ores and concentrates is briefly reviewed. Finally, previous work relative to the chemistry and kinetics of iron and arsenic sulfide minerals during pressure oxidation is discussed in the fourth section.

2.1 Mineralogy of Gold Ores

Mineralogical studies of gold ores and metallurgical products containing gold in economic amounts are difficult and time consuming. For this reason, metallurgical testing is usually done simply by trial and error without understanding the causes for failure or success. Mineralogical studies, if appropriately conducted and combined with test work, provide an efficient means of improving recoveries through the understanding of gold losses derived from the use of the wrong technique for separation. The information they provide is, therefore, the first step in the development of recovery techniques, for those ores where the test work alone failed to produce positive results.
Gold-bearing minerals may be classified as native gold, electrum, alloys, and tellurides, and compounds of gold with sulfur, antimony, and selenium. Gold-bearing minerals are shown in Table 2-1. It has been found that most gold-bearing minerals listed in Table 2-1 occur in association with most of the common rock forming minerals such as iron oxides, uranium minerals, silicates and carbonates, carbonaceous material, sands and gravel (placer deposits), sulfides, and sulphosalts [1]. Table 2-2 lists the host minerals for gold. Among these host minerals, the more common host minerals are pyrite, arsenopyrite, and quartz [1, 2]

Magnetite and secondary iron oxides are relatively common hosts for gold in oxidized environments, in which grains of native gold are coated by fine rims of secondary iron oxide. Occurrence of gold in uranium minerals is common in South Africa and North America [3]. Gold enclosed in silicate and carbonate minerals or distributed along grain boundaries can be expected in ores where sulfides are absent or scarce. Gold is found associated with graphite and other carbonaceous matter, forming fine disseminated particles of native gold. In association with sands and gravel, gold occurs as loose detrital grains in sediments of variable mineralogical composition. The grain size is normally coarse, ranging from a few hundred microns to a few millimeters. In the presence of sulfides, native gold is normally associated with the sulfide minerals. Schwartz [4] examined the relationship between the presence of gold and various sulfides in 115 different sulfide gold ores. He reported that in 48 cases the presence of gold was related to the presence of pyrite and that, in 45 other cases, gold was related to arsenopyrite.
Table 2-1 Gold-bearing minerals [2]

<table>
<thead>
<tr>
<th>Native Gold</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrum</td>
<td>(Au, Ag)</td>
</tr>
<tr>
<td><strong>Alloy</strong></td>
<td></td>
</tr>
<tr>
<td>Cuproauride</td>
<td>(Au, Cu)</td>
</tr>
<tr>
<td>Porpezite</td>
<td>(Au, Pd)</td>
</tr>
<tr>
<td>Rhodite</td>
<td>(Au, Rh)</td>
</tr>
<tr>
<td>Iridic gold</td>
<td>(Au, Ir)</td>
</tr>
<tr>
<td>Platinum</td>
<td>(Au, Pt)</td>
</tr>
<tr>
<td>Bismuthian gold</td>
<td>(Au, Bi)</td>
</tr>
<tr>
<td>Maldonite</td>
<td>(Au₂Bi)</td>
</tr>
<tr>
<td>Auricupride</td>
<td>(AuCu₃)</td>
</tr>
<tr>
<td><strong>Tellurides</strong></td>
<td></td>
</tr>
<tr>
<td>Calaverite</td>
<td>(AuTe₂)</td>
</tr>
<tr>
<td>Krennerite</td>
<td>(Au, Ag)Te₂</td>
</tr>
<tr>
<td>Montbrayite</td>
<td>(Au, Sb)₂Te₃</td>
</tr>
<tr>
<td>Petzite</td>
<td>(Ag₃AuTe₂)</td>
</tr>
<tr>
<td>Muthamannite</td>
<td>(Ag, Au)Te</td>
</tr>
<tr>
<td>Sylvanite</td>
<td>(Au, Ag)Te₄</td>
</tr>
<tr>
<td>Kostovite</td>
<td>(AuCuTe₄)</td>
</tr>
<tr>
<td>Nagyagite</td>
<td>(Pb₂Au(Te, Sb)₄S₂₄)</td>
</tr>
<tr>
<td><strong>Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>Uytenbogaardite</td>
<td>Ag₃AuSb₂</td>
</tr>
<tr>
<td>Aurostibnite</td>
<td>AuSb₂</td>
</tr>
<tr>
<td>Fishchesserite</td>
<td>Ag₃AuSe₂</td>
</tr>
<tr>
<td>Rozhkovite</td>
<td>(Cu, Pd)₃Au₂</td>
</tr>
</tbody>
</table>
### Table 2-2  Host minerals for gold [1]

<table>
<thead>
<tr>
<th>Sulfides and Sulphosalts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>FeS_2</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>FeAsS</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>CuFeS_2</td>
</tr>
<tr>
<td>Orpiment</td>
<td>As_2S_3</td>
</tr>
<tr>
<td>Realgar</td>
<td>As_2S_2</td>
</tr>
<tr>
<td>Stibnite</td>
<td>Sb_2S_3</td>
</tr>
<tr>
<td>Jamesonite</td>
<td>2PbS.Sb_2S_3</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Cu_2S</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Linnaeite</td>
<td>Co_3S_4</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS_2</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>Cu_3SbS_3</td>
</tr>
<tr>
<td>Antimony-arsenic-bismuth-lead sulphosalts</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxides</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO_2</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe_3O_4</td>
</tr>
<tr>
<td>Secondary iron oxides</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Silicates and Carbonates</th>
<th></th>
</tr>
</thead>
</table>

| Carbonaceous materials             |   |
The manner of occurrence of the gold in the host mineral varies greatly. Metz [5] reviewed the different manners of occurrence of gold in pyrite and arsenopyrite. He found that the native gold grains are locked between the mineral grains, distributed along fine and medium size fractures of the minerals, or completely enclosed within the minerals. An explanation for different manners of occurrence of gold in pyrite and arsenopyrite was provided by Boyle [2]. He postulated that early formed high temperature sulfides (mainly pyrite and arsenopyrite) probably take up gold largely in solid solution, or as atomic layers on the growing faces of the sulfide minerals. At lower temperatures, the presence of foreign constituents such as gold and silver, distort the pyrite lattices, with a consequent rise in the free energy. In order to reduce the free energy of the system to a minimum under the prevailing conditions, gold migrates to nearby low chemical potential sites such as fractures and grain boundaries to be crystallized as native gold (and electrum). This appears to explain the frequent occurrence of invisible gold in relatively unfractured and unrecrystallized pyrite and arsenopyrite.

Gold associated with pyrite and/or other arsenical and antimonical minerals often give incomplete gold recovery by conventional grinding and cyanidation. This type of ore is termed refractory gold ore. Up to one-third of the world’s total production of gold is now estimated to come from underlying refractory deposits [6]. The degree of refractoriness and the fundamental causes vary from ore to ore. Gold ore can be either physically or chemically refractory to conventional cyanidation. Three main causes of refractoriness of gold are identified [7, 8, 9]. First, fine gold particles can be locked up in the mineral matrix so that leach reagents are unable to reach it. Secondly, reactive minerals in the gold ore can
consume the leach reagents in side reactions and there may be insufficient cyanide and/or oxygen in the pulp to leach the gold. Thirdly, components of the gold ore may adsorb or precipitate the dissolved gold cyanide complex so that it is lost from the leach liquor. The majority of refractory gold ores are related to the first cause, therefore, an oxidation pretreatment step is required before cyanidation to break up the mineral lattice and render the gold particles accessible to the leach reagents.

2.2 Behavior of Arsenic and Antimony Sulfide Minerals in Alkaline Cyanide Solution

Arsenic and antimony sulfide ores are common hosts for gold and exist in many parts of the world, including numerous mines in Canada and the western United States [10]. In these kinds of ores, arsenic exists as realgar (As$_2$S$_2$), orpiment (As$_2$S$_3$), and arsenopyrite (FeAsS), while antimony occurs mostly as stibnite (Sb$_2$S$_3$). Boyle [2] gave a comprehensive description of the manner of occurrence of the gold in arsenides, sulfo-arsenides, and antimonite. The manner of occurrence of the gold in these minerals is similar to that described above for the pyrite and arsenopyrite, and is mainly dependent on the general textural features of the ore.

Neither arsenic nor antimony forms stable complexes with cyanide and consequently the presence of cyanide in solution has no appreciable effect on the stability of the arsenic and antimony species formed.
Hedley and Tabachnick [11] demonstrated that orpiment, realgar, and stibnite decompose and introduce sulfide ions into cyanide solution. The extent of decomposition is higher for orpiment and increases with increasing pH. Orpiment decomposition during cyanidation may be expressed as:

\[
2 \text{As}_2\text{S}_3 + 6 \text{Ca(OH)}_2 \rightarrow \text{Ca}_3(\text{AsO}_3)_2 + \text{Ca}_3(\text{AsS}_3)_2 + 6 \text{H}_2\text{O} \tag{2.1}
\]

\[
\text{Ca}_3(\text{AsO}_3)_2 + \text{O}_2 \rightarrow \text{Ca}_3(\text{AsO}_4)_2 \tag{2.2}
\]

\[
\text{Ca}_3(\text{AsS}_3)_2 + 6 \text{NaCN} + 3 \text{O}_2 \rightarrow 6 \text{NaCNS} + \text{Ca}_3(\text{AsO}_3)_2 \tag{2.3}
\]

The attack on realgar is suggested to proceed with an initial oxidation to orpiment:

\[
6 \text{As}_2\text{S}_2 + 3 \text{O}_2 \rightarrow 2 \text{As}_2\text{O}_3 + 4 \text{As}_2\text{S}_3 \tag{2.4}
\]

after which the decomposition follows equations (2.1) to (2.3).

The chemistry of stibnite oxidation is thought to be analogous to that of orpiment [12].

The decomposition of realgar, orpiment, and stibnite during cyanidation, however, may be more complex than described above. Species such as \(\text{AsS}_3^{3-}\), \(\text{SbS}_3^{3-}\), \(\text{AsO}_3^{3-}\), \(\text{SbO}_3^{3-}\), \(\text{AsO}_4^{3-}\), \(\text{SbO}_4^{3-}\), \(\text{S}^{2-}\), \(\text{S}_2\text{O}_3^{2-}\), \(\text{SO}_4^{2-}\), and \(\text{CNS}^-\) have been identified as reaction products in such solutions [11, 12]. The mechanism of inhibition of gold dissolution by these minerals,
besides the chemical effects of cyanide consumption (reaction (2.3)), lime consumption (reaction (2.1)), and deoxygenation of the solution (reactions (2.2) and (2.3)), is believed to be the physical effect of the formation of passivating films of thioarsenite (AsS$_3^{3-}$), or thioantimonite (SbS$_3^{3-}$) on gold surfaces [13]. The passivating films inhibit the diffusion of both cyanide and oxygen to the surface. In some industrial plants, promoters such as lead salts can be added to remove soluble sulfide (S$_2^{2-}$) by forming PbS, thus keeping the gold surface clean and reducing passivation. It is further believed that these minerals and/or their oxidation products may lower the E$_h$ of the leach slurry to the point where gold cyanidation essentially stops [14]. However, these beliefs have yet to be verified experimentally. In addition to the chemical and physical factors, the presence of sulfide minerals may also cause electrochemical passivation of gold (galvanic effects) [15, 16].

Based on the above discussion, an effective treatment of the gold ores associated with arsenic and antimony minerals should, therefore, involve the chemical breakdown of these minerals and the elimination of all soluble arsenic and antimony prior to cyanidation. In practice, this may be achieved by both pyrometallurgical and hydrometallurgical processes.

2.3 Pretreatment of Refractory Sulfidic Gold Ores

The highly refractory gold ores have to be pretreated prior to conventional cyanidation in order to improve recovery of gold to economically acceptable levels. The treatment of refractory gold ores depends upon several factors such as the modes of occurrence, host
minerals and associations, and the causes for the refractoriness. The ability to treat a specific ore is a question of economics, and ultimately the choice is made based on the relative profitability of the various process possibilities. Several pretreatment methods involving both pyrometallurgical and hydrometallurgical processes have been practiced or proposed for refractory gold ores or concentrates [17, 18, 19].

The pyrometallurgical method, which has been extensively practiced for the treatment of refractory gold ores since early in the twentieth century, is an oxidation roast of a flotation concentrate to produce a porous calcine, the latter being more amenable to cyanidation. However, with today's standards for high product recovery and a clean environment, oxidation roasting is not considered particularly attractive, despite its established practice. Roasting is known to be very sensitive to heating parameters and feed composition, and deviation from optimum conditions can result in a reduction of permeability, which is translated into incomplete gold liberation. Thus, hydrometallurgical methods are the preferred refractory gold extraction routes. There are basically three aqueous oxidation approaches available:

- Pressure oxidation
- Biochemical oxidation
- Chemical oxidation
The aqueous oxidation methods can be applied to ores and concentrates equally. In chemical oxidation, strong oxidants, such as nitric acid (Nitrox, Redox, and Nitric acid/Salt leach process), or chlorine (Artech/Cashman process), are used to decompose the refractory minerals. In biochemical oxidation, which has been employed for refractory gold ores in recent years, autotrophic bacteria are used to catalyze the oxidation of minerals by air and Fe(III). Finally, in pressure oxidation, which has been applied industrially since the 80’s, oxygen is used at high temperatures and pressures to increase the oxidation kinetics and ensure complete oxidation of sulfide to sulfate, without elemental sulfur surviving. The pretreatment processes for refractory gold ores are summarized in Table 2-3.

Table 2-3 Pretreatment processes for refractory gold ores

<table>
<thead>
<tr>
<th>Process name</th>
<th>Temperature  °C</th>
<th>Total pressure, kPa</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrometallurgical Process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roasting</td>
<td>400–700</td>
<td>Atmospheric</td>
<td>[20]</td>
</tr>
<tr>
<td>Hydrometallurgical Processes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure oxidation</td>
<td>180–225</td>
<td>1400–3200</td>
<td>[19, 21, 22, 23, 24]</td>
</tr>
<tr>
<td>Bacterial oxidation</td>
<td>28–75</td>
<td>Atmospheric</td>
<td>[25]</td>
</tr>
<tr>
<td>Artec/Cashman</td>
<td>110</td>
<td>400</td>
<td>[26]</td>
</tr>
<tr>
<td>Redox</td>
<td>90</td>
<td>600</td>
<td>[27,28]</td>
</tr>
<tr>
<td>Nitrox</td>
<td>90</td>
<td>Atmospheric</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>Nitric Acid/Salt Leach</td>
<td>100</td>
<td>&lt;1400</td>
<td>[31]</td>
</tr>
</tbody>
</table>
2.3.1 Pressure Oxidation

When pressure hydrometallurgy is used the chemical reactions can be conducted above the boiling point of water, if desired, in autoclaves. Advances in the field of inorganic chemistry made early in the twentieth century have led to the rapid development of kinetic and thermodynamic information to bring pressure leaching from a theoretical possibility to a commercial reality. Pressure leaching has been used to meet the objectives of extracting metal and rendering waste streams acceptable for disposal to waste repositories and the environment.

The Bayer process for aluminum was the first industrial application of pressure leaching starting in 1880's. A process for oxidizing mixed sulfides with oxygen or air at 200 to 300 psi and 200°C was patented in 1927 [32]. In the fifties, the ammonia pressure leach process was published [33], and Chemical Construction Co. (Chemico) was granted several patents arising from its developmental work on pressure leaching of cobalt arsenides. One of Chemico's patents dealt specifically with the enhanced recoverability of gold by cyanidation of the residues generated by the pressure oxidation of concentrates [34]. Soon afterward Mitchell [35] described a leaching process to recover cobalt from arsenical sulfide ore with oxygen at 200°C and 500 psi pressure. In 1957, the application of high-pressure oxidation to refractory gold ores and concentrates was first demonstrated and patented by American Cyanamid Company [36]. Since that time pressure hydrometallurgy has become one of most important processes for the extraction of metals, especially non-ferrous metals. In
1985, Homestake’s McLaughlin gold plant became the first full scale industrial application of pressure oxidation pretreatment of a refractory gold ore [37, 38, 39].

Pressure hydrometallurgical unit operations can be conducted in kettles, spheres, pressurized pachucas, towers [40], tubular reactors [41], and vertical and horizontal autoclaves [42]. In industry, the selection of autoclaves to leach ore slurries at high temperature and pressure is an important step in the design for economic operation. For most purposes the horizontal autoclave is the system of choice. Horizontal autoclaves can take many forms and can be made of many types of materials. The horizontal autoclave is an extremely versatile piece of equipment for use in pressure hydrometallurgical applications. Figure 2.1 shows a schematic of a horizontal autoclave.
Currently, pressure oxidation appears to be one of the best approaches for oxidation of refractory ores. It offers a number of advantages over roasting, both from the processing and environmental points of view. Strict control of environmental pollution is not a critical factor in the operation of a pressure leach plant, as is the case in a roasting facility. Pressure leaching almost always renders the refractory material amenable to cyanidation and consistently high gold recoveries are realized. Finally, pressure oxidation is not associated with air pollution by $\text{SO}_2$ or arsenic emissions.

Aqueous pressure oxidation of refractory gold ores can be conducted in either alkaline [43, 44] or acidic media [45, 46, 47]. Acid pressure oxidation is more common than alkaline pressure oxidation. Aqueous pressure oxidation has been employed commercially in several plants in the world. Table 2-4 lists the commercial plants employing pressure oxidation for refractory gold ores and concentrates [19, 48, 49, 50, 51]. Some of them have been shut down now because the ore depleted.
<table>
<thead>
<tr>
<th>Mine</th>
<th>Country</th>
<th>Medium</th>
<th>Feed Type</th>
<th>Nominal Rate (t/d)</th>
<th>Number of Autoclaves</th>
<th>Start Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>McLaughlin</td>
<td>U.S.</td>
<td>Acid</td>
<td>Ore.</td>
<td>2,700</td>
<td>3</td>
<td>1985</td>
</tr>
<tr>
<td>Sao Bento</td>
<td>Brazil</td>
<td>Acid</td>
<td>Conc.</td>
<td>240</td>
<td>2</td>
<td>1986</td>
</tr>
<tr>
<td>Mercur</td>
<td>U.S.</td>
<td>Alkaline</td>
<td>Ore.</td>
<td>680</td>
<td>1</td>
<td>1988</td>
</tr>
<tr>
<td>Getchell</td>
<td>U.S.</td>
<td>Acid</td>
<td>Ore.</td>
<td>2,730</td>
<td>3</td>
<td>1989</td>
</tr>
<tr>
<td>Goldstrike</td>
<td>U.S.</td>
<td>Acid</td>
<td>Ore.</td>
<td>1,330</td>
<td>1</td>
<td>1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acid</td>
<td>Ore.</td>
<td>5,850</td>
<td>3</td>
<td>1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acid</td>
<td>Ore.</td>
<td>16,000</td>
<td>6</td>
<td>1993</td>
</tr>
<tr>
<td>Porgera</td>
<td>PNG*</td>
<td>Acid</td>
<td>Conc.</td>
<td>1,350</td>
<td>3</td>
<td>1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acid</td>
<td>Conc.</td>
<td>2,700</td>
<td>4</td>
<td>1994</td>
</tr>
<tr>
<td>Campbell</td>
<td>Canada</td>
<td>Acid</td>
<td>Conc.</td>
<td>70</td>
<td>1</td>
<td>1991</td>
</tr>
<tr>
<td>Con Mine</td>
<td>Canada</td>
<td>Acid</td>
<td>Conc.</td>
<td>100</td>
<td>1</td>
<td>1992</td>
</tr>
<tr>
<td>Lone Tree</td>
<td>U.S.</td>
<td>Acid</td>
<td>Ore.</td>
<td>2,270</td>
<td>1</td>
<td>1994</td>
</tr>
<tr>
<td>Lihir Gold</td>
<td>PNG</td>
<td>Acid</td>
<td>Ore.</td>
<td>13,250</td>
<td>6</td>
<td>1996</td>
</tr>
<tr>
<td>Twin Creeks</td>
<td>U.S.</td>
<td>Acid</td>
<td>Conc.</td>
<td>360</td>
<td>2</td>
<td>1997</td>
</tr>
<tr>
<td>Gold and</td>
<td>New Zealand</td>
<td>Acid</td>
<td>Conc.</td>
<td>480</td>
<td>1</td>
<td>1999</td>
</tr>
</tbody>
</table>

* Papua New Guinea.
Alkaline Pressure Oxidation

Alkaline pressure oxidation has been proposed for the treatment of arsenical ores [52, 53, 54, 55, 56]. One commercial application of this process was at the Barrick Mercur Mine in Utah [57, 58]. The Mercur Mine's flow sheet is shown in Figure 2.2. Recoveries of gold are about 85% compared to about 35% for conventional carbon in leach (CIL) processing. Oxidation of arsenopyrite and pyrite with oxygen in an aqueous solution with limestone at elevated temperature takes place according to the following reactions:

\[
\begin{align*}
2 \text{FeAsS} + 5 \text{CaCO}_3 + 7 \text{O}_2 & \rightarrow \text{Ca}_3(\text{AsO}_4)_2 + \text{Fe}_2\text{O}_3 + 2 \text{CaSO}_4 + 5 \text{CO}_2 \quad (2.5) \\
2 \text{FeS}_2 + 4 \text{CaCO}_3 + 15/2 \text{O}_2 & \rightarrow 4 \text{CaSO}_4 + \text{Fe}_2\text{O}_3 + 4 \text{CO}_2 \quad (2.6)
\end{align*}
\]

These reactions show that alkaline pressure oxidation yields a residue composed primarily of Fe\textsubscript{2}O\textsubscript{3} while the sulfur and arsenic are precipitated completely as calcium sulfate and arsenate salts. Alkaline oxidation using caustic soda (NaOH) has also been investigated [43, 44], but not implemented commercially.
Figure 2.2. Mercury simplified flowsheet, with oxide and refractory circuits.
The extent of oxidation depends on the solubility of oxygen in solution and the alkaline concentration. The higher the solubility of oxygen in the solution and the higher the alkaline concentration, the higher the extent of oxidation. Solubility of oxygen decreases with increasing alkaline concentration. Therefore, optimum conditions exist [59].

The economic advantage of the alkaline process may be derived from a relatively low temperature condition (about 180°C), a relatively less corrosive environment, and the absence of a subsequent neutralization step. However, insoluble iron oxides/hydroxides may coat gold and sulfide mineral surfaces, reducing both gold leachability and the extent of sulfide oxidation [12]. The limitation of alkaline autoclave oxidation is that it is only suitable for ores or concentrates containing relatively high amounts of basic constituents. Most refractory sulfidic gold ores do not satisfy this criteria, therefore, the development of the alkaline pressure leach route has been hampered by the high cost of reagents (NaOH). Alkaline pressure leaching has also been limited by the problem of arsenic isolation (Na₃AsO₄), and the release of undesirable contaminants such as mercury and thallium [60, 61]. A better choice for these kinds of ores is the acidic (H₂SO₄) pressure oxidation route.

**Acidic Pressure Oxidation**

Pressure oxidation in sulfuric acid medium is conducted at relatively high temperature (170 to 225°C) with a retention time of 1–3 hours and an oxygen partial pressure of 140–700 kPa in a 4 or 5-compartment horizontal autoclave. After autoclaving, the residues are neutralized
and leached using conventional carbon-in-leach or carbon-in-pulp cyanidation technology. Table 2-5 gives typical operating conditions for some commercial pressure oxidation plants. A typical flowsheet of the Goldstrike acidic autoclave circuit is shown in Figure 2.3[62]. Prior to pressure oxidation, the feed is acidified to remove carbonate minerals which might reduce the oxygen partial pressure. Following pressure oxidation, the oxidized solids, which contain the precious metals, are subjected to several stages of cooling and neutralization prior to cyanidation. Cyanidation residues are disposed of in a tailings pond.

Pressure oxidation appears to work very effectively. It has been reported [24] that for highly refractory ores, gold recovery increases from less than 10 percent by using conventional cyanidation to over 90 percent by using acidic pressure oxidation followed by cyanidation. Even if the ore itself is easily leached, pressure oxidation can reduce the reagent requirements by reducing the amount of heavy metals that can act as cyanicides during the leaching process [24].
<table>
<thead>
<tr>
<th>Plant</th>
<th>McLaughlin</th>
<th>Sao Bento</th>
<th>Goldstrike</th>
<th>Getchell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Media Type</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
</tr>
<tr>
<td>Feed Type</td>
<td>Ore</td>
<td>Concentrates</td>
<td>Ore</td>
<td>Ore</td>
</tr>
<tr>
<td>Feed Rate (mt/d)</td>
<td>2700/3</td>
<td>240/2</td>
<td>16000/6</td>
<td>2700/3</td>
</tr>
<tr>
<td>Particle Size</td>
<td>80% -75μm</td>
<td>90% -44μm</td>
<td>75% -105μm</td>
<td>80% -75μm</td>
</tr>
<tr>
<td>Sulfide Sulfur (%)</td>
<td>3.0</td>
<td>18.0</td>
<td>2.5-3.0</td>
<td>2.0-4.0</td>
</tr>
<tr>
<td>CO₃⁺ (%)</td>
<td>--</td>
<td>8.0</td>
<td>4.0-6.0</td>
<td>1.5-7.5</td>
</tr>
<tr>
<td>Organic Carbon (%)</td>
<td>--</td>
<td>--</td>
<td>0.75</td>
<td>0.4</td>
</tr>
<tr>
<td>Total Pressure (kPa)</td>
<td>1700-2200</td>
<td>1600</td>
<td>2500-3000</td>
<td>3200</td>
</tr>
<tr>
<td>Oxygen Pressure (kPa)</td>
<td>140-280</td>
<td>--</td>
<td>340</td>
<td>700</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>180</td>
<td>190</td>
<td>225</td>
<td>210</td>
</tr>
<tr>
<td>Retention Time (min.)</td>
<td>90</td>
<td>120</td>
<td>75/45</td>
<td>90</td>
</tr>
<tr>
<td>Sulfide Oxidation (%)</td>
<td>&gt;85</td>
<td>--</td>
<td>86-97</td>
<td>--</td>
</tr>
<tr>
<td>Reference</td>
<td>(24)</td>
<td>(21)</td>
<td>(22)</td>
<td>(23, 24)</td>
</tr>
</tbody>
</table>

-- not available
Figure 2.3 A Simplified flowsheet for the Goldstrike autoclave circuit
2.4 Acidic Pressure Oxidation of Iron and Arsenic Sulfide Minerals

Among the iron and arsenic sulfide minerals, pyrite and arsenopyrite are the principal refractory gold mineral carriers. There are numerous studies on pyrite dissolution reported in the literature [63, 64, 65, 66, 67]. Aqueous oxidation of pyrite has been reviewed thoroughly by Lowson [63] and Hiskey [64]. In most of the pressure leaching experiments reported [65, 66, 67] the oxidation of pyrite was found to yield only the following products: ferrous sulfate, ferric sulfate, sulfuric acid and elemental sulfur. No sulfur products of intermediate oxidation state, such as thiosulfate or thionates, were detectable under any conditions. Hamilton and Woods [68] proposed that elemental sulfur is produced initially as an intermediate species of pyrite oxidation, and is subsequently oxidized to sulfate. Other investigators [65, 66, 69] proposed mechanisms for pyrite oxidation suggesting that the formation of elemental sulfur and sulfate are independent processes, i.e., the sulfur formed during the oxidation of pyrite is a stable end product, rather than an intermediate species in the sulfate reaction pathway. The oxidation of pyrite may be represented by the following two competing reactions [66]:

\[
\begin{align*}
2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} & \rightarrow 2 \text{FeSO}_4 + 2 \text{H}_2\text{SO}_4 \quad (2.7) \\
\text{FeS}_2 + 2 \text{O}_2 & \rightarrow \text{FeSO}_4 + \text{S}^\circ \quad (2.8)
\end{align*}
\]

Reaction (2.7) is the dominant one at all temperatures below and above the melting point (119°C) of sulfur [66, 70]. High oxygen pressures appear to have, indirectly, a suppressing
effect on elemental sulfur formation by raising the mixed potential of the system [47]. Increased acidities on the other hand are known to favor the formation of S° [65, 66].

The formation of elemental sulfur in acidic pressure oxidation is undesirable. The molten sulfur may occlude unreacted sulfides, which prevents complete oxidation of sulfides, and the molten sulfur may also occlude gold particles, which prevents extraction of gold. Elemental sulfur formed can increase consumption of cyanide by the formation of thiocyanates during subsequent cyanidation. Therefore, it is important to avoid the formation of elemental sulfur during pressure oxidation. Formation of elemental sulfur is strongly temperature dependent (Figure 2-4) [71]. It is avoided at high temperature. Typically, autoclaves are operated in the range of 180–225°C, to allow for localized temperature variations and to minimize elemental sulfur formation.

Figure 2. 4. Oxidation of Sulfides at pH ≤ 3
Ferrous iron produced by reactions (2.7) and (2.8) is subsequently oxidized to ferric by the following reaction

\[ 4 \text{FeSO}_4 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O} \] (2.9)

The role of ferric ions on the distribution of the S\(^0\) oxidation products or for that matter in catalyzing the kinetics of pyrite decomposition does not appear to have been established unambiguously [66, 70, 72]. Upon formation, ferric ion undergoes hydrolysis, the extent of which depends on the prevailing solution conditions (i.e., Fe\(^{3+}\) and H\(_2\)SO\(_4\) concentration, temperature, etc.). At temperatures above 150°C the following two principal hydrolysis reactions occur [73]:

\[ \text{Fe}_2(\text{SO}_4)_3 + 3 \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{SO}_4 \] at lower acidity (2.10)

\[ \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O} \rightarrow 2 \text{FeOHSO}_4 + \text{H}_2\text{SO}_4 \] at higher acidity (2.11)

Precipitation of jarosite-type compounds is also known to occur [74], but to a lesser degree than Fe\(_2\)O\(_3\) and FeOH\(_2\)SO\(_4\):

\[ 3 \text{Fe}_2(\text{SO}_4)_3 + 14 \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 + 5 \text{H}_2\text{SO}_4 \] (2.12)
Table 2-6 lists the experimental conditions, the order of reaction for oxygen partial pressure, and the reported activation energies from the most relevant studies on pressure oxidation of pyrite in sulfuric acid solution. A number of conclusions may be drawn from Table 2-6.

Table 2-6 Summary of pyrite pressure oxidation studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions</th>
<th>Order of $P_{O_2}$</th>
<th>Activation energy (kJ/mol)</th>
<th>Mechanism</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upgraded pyrite Concentrate</td>
<td>0.075</td>
<td>100–130</td>
<td>0–4</td>
<td>1</td>
<td>55.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>chemisorption</td>
<td></td>
</tr>
<tr>
<td>Natural pyrite</td>
<td>0.2</td>
<td>60–130</td>
<td>0–15.5</td>
<td>1</td>
<td>54.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>chemisorption</td>
<td></td>
</tr>
<tr>
<td>Natural pyrite</td>
<td>1</td>
<td>85–130</td>
<td>0–20</td>
<td>1</td>
<td>51.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20–66.4</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Natural pyrite</td>
<td>0.5</td>
<td>140–160</td>
<td>5–20</td>
<td>1</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>160–180</td>
<td>5–10</td>
<td>1</td>
<td>110.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160–180</td>
<td>10–20</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) It is accepted by all researchers that the pressure oxidation rate of pyrite is controlled by the surface chemical reaction. The reaction orders with respect to oxygen partial pressure depend on the temperature and pressure. First order dependence is exhibited predominantly at lower oxygen pressures (< 20 atm) and at all temperatures employed, and one half order dependence is found at higher oxygen pressures and temperatures.
McKay and Halpern [65], Gerlach and his coworkers [70], and Cornelius and Woodcock [75] interpreted their experimental results as evidence of an oxygen chemisorption mechanism followed by a slow chemical reaction. However, Bailey and Peters [66] convincingly demonstrated the mechanism of pressure oxidation of pyrite to be electrochemical, involving coupled anodic (pyrite oxidation) and cathodic (oxygen reduction) reactions.

Activation energies between 46 and 55 kJ/mol are reported at temperatures below 160°C. Interestingly, Papangelakis and Demopoulos [67] reported an activation energy of 110.5 kJ/mol in the region of 160 to 180°C, which is more than twice the value reported by them and others at temperatures below 160°C. The reason for this significant shift in the activation energy is not clear.

The oxidation chemistry of arsenopyrite in an acidic medium at elevated temperatures has been studied by several investigators. The chemistry of arsenopyrite oxidation as reported by Berezowsky and Weir [34] can be represented by reactions (2.13) and (2.14).

\[
4 \text{FeAsS} + 11 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{H}_3\text{AsO}_3 + 4 \text{FeSO}_4 \quad (2.13)
\]

\[
\text{2H}_3\text{AsO}_3 + \text{O}_2 \rightarrow \text{2H}_3\text{AsO}_4 \quad (2.14)
\]
Trivalent arsenic produced from reaction (2.13) is further oxidized to arsenate. Jin [76] supported this postulation on the basis of his study of arsenopyrite in the temperature range of 180-210°C. No elemental sulfur was found in his tests.

However, Papangelakis and Demopoulos [77] proposed that pentavalent arsenic in the form of H₅AsO₄ is the direct product of the heterogeneous oxidation reaction (reaction (2.15)) rather than the result of a subsequent homogeneous reaction (reaction (2.14)) in the temperature range of 130-180°C. Their opinion is based on a test in which O₂/Fe(III) failed to oxidize a synthetically prepared H₃AsO₃ solution. Elemental sulfur was postulated to form through a parallel reaction path (reaction (2.16)). Reaction (2.15) is dominant in the temperature range studied:

\[
4 \text{FeAsS} + 13 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{H}_5\text{AsO}_4 + 4 \text{FeSO}_4 \quad (2.15)
\]

\[
4 \text{FeAsS} + 13/2 \text{O}_2 + \text{H}_2\text{SO}_4 + 5 \text{H}_2\text{O} \rightarrow 4 \text{H}_5\text{AsO}_4 + 4 \text{FeSO}_4 + \text{S}^0 \quad (2.16)
\]

Thus, the solution chemistry of arsenic at high temperature does not appear to have been established unambiguously.

It has been accepted by all investigators [74, 76, 77] that ferrous generated from reactions (2.13) and (2.16) is further oxidized to ferric. Finally, ferric combines with arsenate to form FeAsO₄•2H₂O (reaction (2.17)), which precipitates as crystalline scorodite, and excess ferric
may hydrolyze to hematite (reaction (2.10)), basic ferric sulfate (reaction (2.11)), and hydronium jarosite (reaction (2.12)).

\[
\text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_3\text{AsO}_4 + 4 \text{H}_2\text{O} \rightarrow 2 \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + 3 \text{H}_2\text{SO}_4
\]  

(2.17)

The kinetics of pressure oxidation of arsenopyrite has been found [76, 78] to be chemically controlled, exhibiting first order dependence on oxygen partial pressure. Jin [76] pointed out that at higher temperature (210°C), the reaction may shift towards diffusion control. Activation energies were reported in the range of 66 kJ/mol (triclinic arsenopyrite) to 72 kJ/mol (monoclinic arsenopyrite) in the temperature range 120–180°C [78] and 43 kJ/mol in the temperature range of 180–210°C [76]. Papangelakis and Demopoulos [78] postulated the true rate determining step to be electrochemical in nature, involving the first electron transfer during reduction of surface-adsorbed oxygen. The results of arsenopyrite pressure oxidation studies in acidic media are listed in Table 2-7.

Table 2-7. Summary of arsenopyrite pressure oxidation studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions</th>
<th>Order of O₂</th>
<th>Activation energy (kJ/mol)</th>
<th>Mechanism</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural arsenopyrite</td>
<td>0.1</td>
<td>1</td>
<td>43.01</td>
<td>Surface chemical electrochemical</td>
<td>76</td>
</tr>
<tr>
<td>Natural arsenopyrite</td>
<td>0.5</td>
<td>1</td>
<td>66–72</td>
<td>Surface chemical electrochemical</td>
<td>78</td>
</tr>
</tbody>
</table>
It was found from the survey that although pyrite has been investigated extensively by previous researchers, all of the reported work has been conducted at temperatures lower than 180°C. No data is available on the kinetics of pyrite dissolution during acid pressure oxidation over the temperature range of 180 to 230°C, which is the range employed by most commercial plants. The rate equations determined at the lower temperatures by previous researchers can not be used as the basis of developing a model suitable for design and performance optimization of large-scale industrial process reactors. From a process optimization standpoint it is important to know the behavior of pyrite during acidic pressure oxidation at temperatures above 180°C and to determine the governing rate law.

A survey of the literature indicated that no information concerning the behavior of orpiment and realgar during acid pressure oxidation has been reported. This is all the more surprising given the fact that one gold producer, namely the Getchell Mine in northern Nevada, autoclaves an ore, under acidic conditions, that has a sulfide mineral content made up almost exclusively of these minerals [79]. Since the nature and composition of minerals and reaction products have a considerable impact on the autoclave operations and the downstream operations of gold recovery and waste management, an understanding of their solution chemistry is needed.

In conclusion, commercial hydrometallurgical processes for pretreatment of refractory sulfidic gold ores and concentrates are described above; new methods are still being developed to meet the requirements of the treatment of refractory gold ores. All processes
are based on the thermodynamics and kinetics of reactions between minerals and reagents, which will be described in the next chapter.
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CHAPTER 3

FUNDAMENTALS OF OXIDATION

The efficiency of hydrometallurgical processes depends partly on selectivity and kinetics. Kinetic considerations may be of primary importance in low temperature processes where reaction rates are normally slow. However, at high temperatures where activation energy barriers are small and therefore many reactions are favored, thermodynamic parameters which determine the relative chemical stabilities of various species present in an aqueous system are of predominant importance. In this chapter, thermodynamics and kinetic considerations are presented.

3.1 Thermodynamics

Thermodynamic relationships involving pyrite and orpiment in an aqueous environment are conveniently illustrated by $E_h$–pH diagrams, which are actually graphical expressions of the fundamental reaction thermodynamics. For an oxidation–reduction reaction

$$\text{oxidized state} + n \text{e}^- \rightarrow \text{reduced state} \quad (3.1)$$

the free energy of reaction is given by the following expression
\[ \Delta G_{298} = \Delta G_{298}^\circ + RT \ln K \]  \hspace{1cm} (3.2)

where \( \Delta G_{298}^\circ \) is the standard free energy; \( R \) the universal gas constant; \( T \) absolute temperature; and \( K \) the equilibrium constant. The standard free energy is related to the standard half-cell potential \( E^\circ \) by:

\[ \Delta G^\circ = -nFE^\circ \]  \hspace{1cm} (3.3)

where \( n \) denotes the number of electrons involved in the half-reaction, and \( F \) is the Faraday constant. Similarly, the relationship between the free energy change for the reaction and the half-cell potential is:

\[ \Delta G = -nFE \]  \hspace{1cm} (3.4)

Then \( E_h = E \) and the oxidation potential for the half-cell is expressed as follows

\[ E_h = E^\circ - \frac{RT}{nF} \ln K \]  \hspace{1cm} (3.5)

This is the fundamental Nernst equation which relates \( E_h \) to the activities of species involved.
The basis of pressure oxidation as applied to refractory sulfidic gold ores is the manipulation of the relative stabilities of gangue minerals and gold-bearing sulfides in solution at elevated temperature. To achieve selectivity requires knowledge of the behavior of the predominant gangue elements such as iron, sulfur, and arsenic in aqueous systems.

The solubility of iron, the most predominant element in most refractory ores, in sulfate aqueous media is dependent on both temperature and pH. In the Fe-S-H$_2$O system, at high temperatures (>150°C), basic salts (Fe(OH)SO$_4$) and hematite (Fe$_2$O$_3$) are formed at high and low acidity, respectively.

Thermodynamically stable forms of sulfur in aqueous systems include elemental sulfur (S°), sulfate (SO$_4^{2-}$), bisulfate (HSO$_4^{-}$), and soluble sulfides (H$_2$S, HS$^-$, S$_2^{2-}$), depending on pH and $E_h$.

The important oxidation states of arsenic are +5, +3, and −3, as in arsenic acid, arsenuous acid, and arsine, respectively. The solubility of arsenic and its oxidation state are both dependent on the environmental conditions ($E_h$ and pH) [1]. In hydrometallurgical systems only arsenic (+5) and (+3) are of interest since arsenic metal rarely occurs and arsenic (−3) is stable only at extremely low $E_h$ values. Although the pentavalent form is the thermodynamically stable species under oxidizing conditions, the trivalent form may also exist due to the extremely low oxidation rate of arsenic (+3) to (+5) [2].
In industrial systems where iron, arsenic, and sulfur co-exist, the stabilities of various species are influenced by both physical and chemical interactions among species of other elements. Physical interactions may include co-precipitation of arsenates and arsenites with iron oxides as a result of physical adsorption of these ions onto iron oxides [3]. Aqueous arsenic species may also adsorb onto undissolved metal sulfides [4]. The effects of chemical interactions among species of different elements on their stabilities may be studied thermodynamically in terms of $E_H$-pH diagrams. The following $E_H$-pH diagrams were drawn using the STABCAL program [5]. All species thermodynamic data are shown in Appendix I.

Figure 3.1 shows an $E_H$-pH diagram for the Fe–S–H$_2$O system under standard conditions (298°K, 1 atm total pressure) illustrating that oxidizing conditions are required to dissolve pyrite. Equilibrium relationships for the various sulfur species are plotted in Figure 3.2.

At pH less than 4, pyrite is oxidized to soluble iron and sulfur species initially. The reactions are

$$\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{HSO}_4^- + 14 \text{H}^+ + 14 \text{e}^- \quad (\text{pH} < 2) \quad (3.6)$$

$$\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 14 \text{e}^- \quad (2 < \text{pH} < 4) \quad (3.7)$$

Pyrite can be oxidized to produce elemental sulfur and Fe$^{2+}$ according to the following reaction

$$\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{HSO}_4^- + 14 \text{H}^+ + 14 \text{e}^- \quad (\text{pH} < 2) \quad (3.6)$$

$$\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 14 \text{e}^- \quad (2 < \text{pH} < 4) \quad (3.7)$$

Pyrite can be oxidized to produce elemental sulfur and Fe$^{2+}$ according to the following reaction

$$\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{HSO}_4^- + 14 \text{H}^+ + 14 \text{e}^- \quad (\text{pH} < 2) \quad (3.6)$$

$$\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 14 \text{e}^- \quad (2 < \text{pH} < 4) \quad (3.7)$$
FeS₂ → Fe²⁺ + 2 S° + 2 e⁻ \hspace{1cm} (3.8)

It might be expected from purely thermodynamic considerations that sulfur should be relatively easily oxidized to sulfate or bisulfate over a wide range, as indicated by the small region of sulfur stability in Figure 3.2. In practice, elemental sulfur was found in the residue during oxygen pressure oxidation in acid media, even at temperatures up to 190°C. The range of sulfur stability is thus considerably larger than that predicted by thermodynamics because of kinetic constraints [6].

Figure 3.1 Eₘ-pH equilibrium diagram for the Fe-S-H₂O system at 25°C

with a_{Fe} = 0.01 M and a_{S} = 0.02 M
The stability regions of arsenic species in the As-H\textsubscript{2}O system are shown in Figure 3.3. The diagram indicates that the arsenic oxides, As\textsubscript{2}O\textsubscript{3} and As\textsubscript{2}O\textsubscript{5}, are both unstable at a total arsenic activity of 10\(^{-2}\) M. This is because of their high solubilities [7]. The upper boundary of the arsenic stability region is above the lower boundary of water stability, thus elemental arsenic is stable at normal conditions at all pH values.
It is found that the available thermodynamic data for crystalline orpiment (As$_2$S$_3$) varies significantly. The major thermodynamic compilations give free energies of formation for orpiment that range from $-40.34$ kcal/mol [8] to $-22.80$ kcal/mol [9], as shown in Table 3–1. In contrast, the free energies of formation for orpiment that have been derived from experimental studies are generally lower than those listed in the major thermodynamic compilations. For example, Barton [10] reported a value of $-22.99$ kcal/mol for orpiment from studies of equilibrium in the Fe–As–S system at high temperatures, whereas Johnson et al [11] obtained a value of $-21.68$ kcal/mol by calorimetric methods. Mironova et al. [12] reported a value of $-23.83$ kcal/mol, which is derived from solubility measurements. The
solubility data reported by Webster [13] yield a value of $-23.02 \text{ kcal/mol}$. Robins and Glastras [14] have determined the solubility of $\text{As}_2\text{S}_3$ to be $28.5 \text{ mg/L As}$ in the pH range of 1 to 4. This solubility is several orders of magnitude greater than that which has been calculated based on the free energy given by Wagman et al [8]. Based on these findings, it was decided to choose the free energy reported by Johnson et al [11] in the present work. Their value of the free energy of formation of $\text{As}_2\text{S}_2$ was also chosen. The free energies of other species were taken from other literature [15, 16].

Table 3-1 Thermodynamic data for orpiment at 25 °C

<table>
<thead>
<tr>
<th>$\Delta G_{f,25}$ (kcal/mol)</th>
<th>$\Delta H_{f,25}$ (kcal/mol)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40.34</td>
<td>-40.39</td>
<td>-</td>
<td>[8]</td>
</tr>
<tr>
<td>-40.25</td>
<td>-40.39</td>
<td>-</td>
<td>[17]</td>
</tr>
<tr>
<td>-32.46</td>
<td>-34.99</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>-22.80</td>
<td>-22.99</td>
<td>-</td>
<td>[9]</td>
</tr>
<tr>
<td>-24.35</td>
<td>-26.51</td>
<td>Solubility</td>
<td>[18]</td>
</tr>
<tr>
<td>-23.02</td>
<td>-33.29</td>
<td>Solubility</td>
<td>[13]</td>
</tr>
</tbody>
</table>

Note: DTA refers to differential thermal analysis of equilibria in the Fe-As-S system.

The $E_h$-pH diagram for the As–S–H$_2$O system at 25°C is shown in Figure 3.4. The activities of all species were taken at 0.01 M. Figure 3.4 indicates that both orpiment ($\text{As}_2\text{S}_3$) and realgar ($\text{As}_2\text{S}_2$) are stable under normal conditions (water stability zone) in both acidic and basic solution. It is obvious that these minerals can be decomposed at low oxidation potential in basic solution.
It must be remembered that the stability of a chemical species is dependent on the equilibrium constant (K) of the reactions of concern. Species stability domains would change with changing log K, which is a function of temperature. Thus, a stable species at one temperature may be unstable at another. The application of a stability diagram is therefore only meaningful when the diagram is constructed at the temperature of interest.

Effect of temperature on $E_h$–pH diagrams

For solid species, elements, and neutral compositions, if $\Delta H^o_T$ and $\Delta S^o_T$ are available, the free energy at elevated temperature can be obtained by using the following equations.
\[
\Delta G_T^o = \Delta H_T^o - T \Delta S_T^o
\]  
(3.9)

\[
\Delta H_T^o = \Delta H_{T_o}^o + \int_{T_o}^{T} \Delta c_p^o dT
\]  
(3.10)

\[
\Delta S_T^o = \Delta S_{T_o}^o + \int_{T_o}^{T} \frac{\Delta c_p^o}{T} dT
\]  
(3.11)

where \( \Delta c_p^o \) is the standard heat capacity change for the reaction, which is available as a power function derived from experimental data:

\[
\Delta c_p^o = a + bT + cT^2
\]  
(3.12)

The experimental power functions for iron and arsenic species are available in the literature [19, 20].

For aqueous ion species, by taking \( \Delta c_p^o(T, T_o) \) as the average of \( \Delta c_p^o \) between the two temperatures considered, the free energy \( (\Delta G_T^o) \) at an elevated temperature can be determined by

\[
\Delta G_T^o = \Delta G_{T_o}^o + \Delta c_p^o(T, T_o)(T - T_o - T \ln\left(\frac{T}{T_o}\right))
\]  
(3.13)

The standard state is conventionally taken as 298 K.
The average heat capacities for the ionic species can be calculated by use of the Criss and Cobble entropy correspondence principle [21, 22]. This principle shows that if a standard state is chosen properly by fixing the entropy of hydrogen ion at each temperature, the partial molal ionic entropies at that temperature are linearly related to their corresponding entropies at the same reference temperature. The entropy of an ion at elevated temperature, according to the correspondence principle, can be determined by

\[ S_{T, abs}^o = a_T + b_T S_{T_0, abs}^o \]  

(3.14)

where \(a_T\) and \(b_T\) are constants dependent on the class of ions (cations, anions, oxyanions, and acid oxyanions) and on the temperature considered. The values \(a_T\) and \(b_T\) for ions in solution at different temperatures are shown in Table 3.2. \(S_{T, abs}^o\) refers to the ionic partial molal entropies on an “absolute” scale for which was chosen the standard state at 298 K \(T_0\), corresponding to an entropy for hydrogen ion of -5 cal mole\(^{-1}\) deg\(^{-1}\).

\[ S_{298, abs}^o = S_{298}^o - 5.0z \]  

(3.15)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Simple Cations M(^{m+})</th>
<th>Simple Anion X(^m) and OH(^-)</th>
<th>Oxyanion XO(^{m-})</th>
<th>Acid Oxyanion HXO(^{m-})</th>
<th>Stand. State Entropy of H(^+)</th>
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</thead>
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<tr>
<td>(T) K</td>
<td>a(T)</td>
<td>b(T)</td>
<td>a(T)</td>
<td>b(T)</td>
<td>a(T)</td>
</tr>
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<td>0.0</td>
<td>1.000</td>
<td>0.0</td>
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</tr>
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<td>0.711</td>
<td>-30.2</td>
<td>0.981</td>
<td>-67.0</td>
</tr>
<tr>
<td>483*</td>
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<td>0.706</td>
<td>-30.5</td>
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<td>-68.0</td>
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<td>523</td>
<td>29.9</td>
<td>0.630</td>
<td>-38.7</td>
<td>0.978</td>
<td>-86.5</td>
</tr>
</tbody>
</table>

* Values obtained by linear extrapolation.
The values of standard free energy and entropy at room temperature are available in the literature [19, 20, 23, 24]. The average heat capacity ($\Delta c_p^o(T,T_o)$) can be obtained by the following equation:

$$\Delta c_p^o(T,T_o) = \frac{a_T - S_{T,obs}^o(1-b_T)}{\ln\left(\frac{T}{T_o}\right)}$$

(3.16)

Based on the above estimation techniques, high temperature stability diagrams were developed for the Fe-S-H$_2$O and As-S-H$_2$O systems at 210°C. The thermodynamic data of the species for both systems at high temperature are shown in Appendix II.

Figure 3.5 shows the $E_m$-pH equilibrium diagram for the Fe-S-H$_2$O system at 210°C. In contrast to that at 25°C, both stable areas of ferrous and pyrite are diminished. Also, ferrous could be oxidized at lower potential.
Figure 3. 5  $E_h$-pH equilibrium diagram for the Fe–S–H$_2$O system at 210°C

with $a_Fe = a_S = 0.01$ M

The $E_h$-pH equilibrium diagram for the As–S–H$_2$O system at 210°C is illustrated in Figure 3.6. It indicates that at high temperature (210°C), in contrast to that at 25°C, As$_2$S$_2$ has vanished from the diagram. Also, the stable area of As$_2$S$_3$ is diminished. It is no longer stable above pH 8. The diagram suggests that the increase in temperature from 25 to 210°C lowers the oxidation potential required to decompose orpiment.
Figure 3.6 Eh-pH equilibrium diagram for the As–S–H₂O system at 210°C with $a_{As} = a_{S} = 0.01$ M

The Eh-pH diagram shown in Figure 3.6 suggests that orpiment will be oxidized first to arsenite:

$$As_2S_3 + 6 O_2 + 6 H_2O \rightarrow 2 H_3AsO_3 + 3 H_2SO_4 \quad (3.17)$$

Arsenite will be subsequently oxidized further to arsenate:

$$H_3AsO_3 + \frac{1}{2} O_2 \rightarrow H_3AsO_4 \quad (3.18)$$
However, there is little data available to confirm this reaction mechanism and no information concerning the relative rates of oxidation, the effects of iron/arsenic/antimony ratios, the resulting solution chemistry, or any other factor of potential interest.

3.2 Kinetic Considerations

In general, rate studies provide information that aids in the determination of reaction mechanisms and in the prediction of process results under various conditions. If they are carried out under conditions comparable to those encountered in industrial practice, rate studies will provide valuable engineering data which are useful in the design of full-scale reactors.

In a typical oxidation pressure leaching process the mass transfer that is required to sustain heterogeneous reaction takes place by the following steps: a) dispersion of oxygen into the pulp by agitation and dissolution in the solution; b) advection of dissolved oxygen through the bulk aqueous phase; c) diffusion of dissolved oxygen through a fluid film to a product layer/fluid film interface; d) diffusion of dissolved oxygen through a product layer to an unreacted core/product layer interface; e) adsorption of dissolved oxygen onto the reaction core surface; f) chemical reaction at the unreacted core/product layer interface; g) diffusion of reaction product back through product layer and fluid film into the bulk solution; and h) advection of product through the bulk solution. Figure 3.7 shows a schematic diagram of sequential process steps for the leaching reaction of a solid particle. The rate-determining
step is considered to be the slowest of the above steps. However, in practice one or more of these process steps may be rate controlling.

1. Dispersion of oxygen into the pulp;
2. Advection of dissolved oxygen through bulk aqueous phase;
3. Fluid film mass transfer;
4. Diffusion of dissolved oxygen through a product layer;
5. Chemical reaction;
6. Diffusion of reaction product back through product layer;
7. Diffusion of reaction product through fluid film into the bulk solution;
8. Advection of product through the bulk solution.

Figure 3.7 Schematic diagram of sequential process steps for leaching of a solid particle
In an irreversible leaching reaction involving a solid particle and a fluid, the reaction equation may be written as:

\[ aA(s) + bB(aq) = cC(s) + dD(aq) \]  

(3.19)

where no product layer is formed, the rate-determining step may be a chemical reaction at the solid-fluid interface, diffusion through a fluid boundary layer, or both. The rate of disappearance of \( A \) due to chemical reaction may be expressed for a first-order reaction as:

\[ \frac{dn}{dt} = -A_s k_C C' \]  

(3.20)

where \( n \) is the number of moles of \( A \) in the solid at time \( t \), \( A_s \) is the surface area of the solid, \( k \) is the heterogeneous reaction rate constant, \( C_s \) is the concentration of potential reaction surface sites which takes into account the surface roughness factor, and \( C' \) is the surface concentration of aqueous reacting species \( B \). Equation (3.20) may be written as:

\[ \frac{dn}{dt} = -A_s k'C' \]  

(3.21)

where \( k' = kC_s \).

The flux of reacting species \( B \) through the fluid boundary layer, \( J \), may be expressed as:

\[ J = -\frac{A_s D(C - C')}{\delta} \]  

(3.22)
where $D$ is the solution diffusion coefficient of B, $C$ is the bulk solution concentration of aqueous reaction species B, and $\delta$ is the constant thickness of the fluid boundary layer.

Under steady-state conditions:

$$\frac{dn}{dt} = -A_k C' = -\frac{DA_k (C - C')}{\beta\delta}$$

(3.23)

where $\beta (b/a)$ is a stoichiometric factor. Rearranging equation (3.23):

$$C' = -\frac{D}{\beta\delta}$$

(3.24)

Substituting equation (3.24) into (3.21) gives:

$$\frac{dn}{dt} = -\frac{A_k C}{\beta\delta} \frac{1}{D + \frac{1}{k'}}$$

(3.25)

Equation (3.25) represents the general rate expression for mixed kinetics which may be written as:

$$\frac{dn}{dt} = -A_k k'' C$$

(3.26)

where $k'' = \left(\frac{\beta\delta}{D} + \frac{1}{k'}\right)^{-1}$. 

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In cases where mass transport through the boundary layer is the limiting factor, \( k' \) is large and therefore \( 1/k' \approx 0 \). Equation (3.26) becomes:

\[
\frac{dn}{dt} = -\frac{A_k D C}{\beta \delta} = -A_k' C
\]  

(3.27)

where \( k'' = \frac{D}{\beta \delta} \).

For chemical reaction controlled kinetics, \( D \) is large and therefore equation (3.27) becomes:

\[
\frac{dn}{dt} = -A_k' C = -A_k'' C
\]  

(3.28)

where \( k'' = k' = C_k \).

The rate controlling factor can be either diffusion control or chemical control, which is a function of temperature. The effect of temperature on the rate of reactions is described by Arrhenius' law:

\[
k = A \exp\left(-\frac{E_a}{RT}\right)
\]  

(3.29)

where \( k \) is the reaction rate constant, \( A \) is the frequency factor, \( E_a \) is the activation energy for the reaction, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. If the
logarithm of the reaction rate is plotted against $1/T$, the relationship is a straight line function and the slope of the straight line gives the value of the activation energy.

Thermodynamic and chemical kinetic considerations indicate that the rate of reaction is determined by activation energy and temperature. Chemically controlled processes have high activation energy (usually larger than 10 kcal/mole), but processes in which the rate is controlled by adsorption and diffusion, such as those which are dependent on agitation and partial pressure of oxygen, are characterized by low activation energy (usually 2 to 10 kcal/mole). A change of activation energy within the experimental temperature range signifies that the rate-controlling mechanism changes from one region to the other. In general, the overall reaction rate increases with increasing temperature. But chemically controlled processes are more temperature-sensitive than those controlled by adsorption and diffusion.

### 3.2.1 Kinetic Models

Almost all metallurgical reactions are heterogeneous in nature. A number of studies have been done on these types of reactions, and several general mathematical models have been developed [25, 26, 27]. Two of the most commonly used models are described as follows:
The Shrinking Particle Model:

The development of this model is based on a non-porous spherical particle reacting in an agitated fluid medium with no product layer formation (Figure 3.8), such that the radius decreases with time as the reaction proceeds.

![Diagram of Shrinking Particle Model](image)

Figure 3.8 Schematic diagram for the Shrinking Particle Model
Consider a particle of initial radius \( r_0 \) and containing \( n_0 \) moles of a certain solid-phase reacting species \( M \) of molecular volume \( V \) (cm\(^3\)/mol). Let \( M \) react with an aqueous species \( B \) to give an aqueous soluble reaction product \( P \).

\[
m \, M_{(s)} + b \, B_{(aq)} = p \, P_{(aq)} \tag{3.30}
\]

The general rate expression for a first-order kinetics is given by equation (3.31).

\[
\frac{dn}{dt} = -A \, k \, C = -4\pi r^2 \, k \, C \tag{3.31}
\]

where \( n \) is the number of moles of \( M \) present in the solid at any time \( t \). But

\[
n = \frac{4}{3\pi r^3} \tag{3.32}
\]

where \( V \) is molar volume. It follows that:

\[
\frac{dn}{dt} = \frac{4\pi r^2}{V} \, \frac{dr}{dt} \tag{3.33}
\]

Combining equations (3.31) and (3.33):

\[
\frac{dr}{dt} = -k \, n \, V \tag{3.34}
\]

Integrating equation (3.34) with the initial boundary conditions of \( r = r_0 \) at \( t = 0 \) and \( r = r \) at \( t = t \) yields:
\[ r_0 - r = k' CVt \quad (3.35) \]

Defining \( X \), the fraction of solid reacted in time \( t \), as:

\[ X = \frac{n - n}{n_0} \quad (3.36) \]

Then from equations (3.32) and (3.36), one obtains:

\[ r = r_0 (1 - X)^{\frac{1}{3}} \quad (3.37) \]

Substituting equation (3.37) into (3.35) yields:

\[ 1 - (1 - X)^{\frac{1}{3}} = \frac{k'' CVt}{r_0} \quad (3.38) \]

If the aqueous phase concentration is kept constant, then equation (3.38) may be written as:

\[ 1 - (1 - X)^{\frac{1}{3}} = \frac{k^* t}{r_0} \quad (3.39) \]

where \( k^* = k'' CV \) (linear rate constant) is the rate of movement of the reaction interface.

Thus, for a reaction whose kinetics are controlled by either chemical reaction, mass transport through a fluid boundary layer, or both, the plot of \( 1 - (1 - X)^{\frac{1}{3}} \) against \( t \) (reaction time)
should give a straight line with the slope equal to \( k^*/r_0 \). Thus, to determine whether the rate is controlled by solution diffusion or surface reaction, it is necessary to examine the effect of agitation speed and temperature on the constant \( k^* \).

The Shrinking Core Model:

In the shrinking core model, the heterogeneous reaction first occurs at the external surface of the particle and the well defined reaction surface then moves towards the interior of the solid, leaving behind the solid product and/or inerts. This type of reaction may in general be described by:

\[
\begin{align*}
    m M(s) + b B(aq) &= p P(aq) + q Q(s) \\
    \text{where } M &\text{ is the solid reacting species, } B \text{ is the oxidizing reagent, } P \text{ is the aqueous product,} \\
    &\text{and } Q \text{ is the solid product.}
\end{align*}
\]

The formulation of the mathematical model is based on the following assumption:

1) The system may be considered isothermal because the rate of heat production by the reaction is much less than the rate of heat removed by the solution.

2) The particle is considered spherical and maintains its shape and size during the entire leaching process.
3) Given the low reaction and product concentrations in the solution, the net flux due to
diffusion is considered to be negligible.

4) The surface reaction is assumed to be of first order and irreversible with respect to
the oxidizing agent concentration.

5) The oxidizing agent is in excess and its concentration may be considered constant
during the entire leaching process.

6) The system may be considered to be in quasi-steady state.

If \( J \) is the flux of \( B \) in moles diffusing across the product layer in time \( t \), then from Fick's
first law:

\[
J = -4n r^2 D_s \frac{dC}{dr}
\]  \hspace{1cm} (3.41)

where \( D_s \) is the effective diffusion coefficient of \( B \) through the product layer and \( C \) is the
concentration of \( B \).

Assuming \( J \) to be constant (steady-state approximation) and using the boundary conditions:
\( C = C_c \) when \( r = r_e \), and \( C = C_o \) when \( r = r_o \). Then equation (3.41) can be integrated to

\[
J = -4\pi D_s (C_c - C_o) r_e \frac{r_e}{(r_e - r_o)}
\]  \hspace{1cm} (3.42)

Under steady-state conditions the rate of disappearance of the core volume of \( M \) may be
related to \( J \) by
\[ J = \frac{\nu dV_c}{dt} \]  

(3.43)

where \( \nu \) is the moles of solute per unit volume.

Equating equations (3.42) and (3.43):

\[-\nu \left( \frac{dV_c}{dt} \right) = -4\pi \left\{ \frac{D_s (C_c - C_o) r_c r_c}{(r_c - r_o)} \right\} \]  

(3.44)

Rearranging and integrating both sides of equation (3.44) yields:

\[ \int_{V_o}^{V_c} \frac{r_c (r_c - r_o)}{r_c} dV_c = \int_0^{4\pi D_s (C_c - C_o) r_o \frac{dt}{\nu}} \]  

(3.45)

We know \( \frac{r_o}{r_c} = (\frac{V_o}{V_c})^{\frac{1}{3}} \), so equation (3.45) can be written as:

\[ \int_{V_o}^{V_c} \left\{ 1 - \left( \frac{V_o}{V_c} \right) \right\} dV_c = \int_0^{4\pi D_s (C_c - C_o) r_o \frac{dt}{\nu}} \]  

(3.46)

after integrating,

\[ V_c + \frac{1}{2} V_o - \frac{3}{2} \frac{1}{V_o^3} V_c^2 = \frac{4\pi D_s (C_c - C_o) r_o t}{\nu} \]  

(3.47)

From equation (3.36), we obtain

\[ X = \frac{n_c - n}{n_o} = \frac{V_o - V_c}{V_o} \]
or

\[(1 - X) = \frac{V_c}{V_0}\]  \hspace{1cm} (3.48)

where \(X\) is the fraction of solid reacted in time \(t\). Then equation (3.48) becomes:

\[
(1 - X) + \frac{1}{2} - \frac{2}{3} (1 - X)^{\frac{2}{3}} = \frac{3D_s (C_e - C_0)t}{r_0^2 v}
\]  \hspace{1cm} (3.49)

or

\[
1 - \frac{2}{3} X - (1 - X)^{\frac{2}{3}} = \frac{2D_s (C_e - C_0)t}{r_0^2 v}
\]  \hspace{1cm} (3.50)

Thus, for reactions controlled by the diffusion of reacting species through a product layer, the plot of the left-hand side of equation (3.50) against reaction time \(t\) should give a straight line. From the slope of the line it may be possible to determine the diffusion coefficient \(D_s\).
References


5. Huang, H. H., 1994, Stability Calculation Program for Aqueous Systems (STABCAL), Department of Metallurgical Engineering, Montana Tech, USA


19 Roine, A., 1994, HSC Chemistry Software, Ver. 2.03, Outokumpu Research Oy, Pori, Finland.


In this investigation, relatively pure minerals were leached in an autoclave in sulfuric acid medium with oxygen. The study of pure minerals can eliminate the effects of impurities on the oxidation of minerals. Only highly pure orpiment was used in this work. Based on reaction (2.4) in Chapter 2, it was assumed that realgar would exhibit the same behavior during acidic pressure oxidation, except that it would consume more oxygen. Reaction variables considered were: agitation speed, temperature, oxygen partial pressure, particle size, pulp density, and initial sulfuric acid concentration. The effects of cupric and ferric ions were also examined.

4.1 Materials

4.1.1 Minerals

High-grade massive pyrite and orpiment specimens were obtained from Ward's Natural Science Establishment, Inc. of Ontario, originating from Zacatecas, Mexico and Hanaatan, Nevada respectively. The samples were crushed, ground, and sieved to different narrow size fractions, namely \(-100 +140\), \(-140 +200\), \(-200 +270\), \(-270 +325\) mesh (Tyler). The samples were then washed to remove any fines adhering to particle surfaces which might interfere with the interpretation of the results, and air-dried at ambient temperature.
The mineral samples were analyzed by Chem Met Consultants Inc. (CMC) and International Plasma Laboratory (IPL), respectively. Tables III-1 and III-2 in Appendix III list the analytical results of pyrite composition in the different particle sizes, and Tables III-3 and III-4 in Appendix III list the analytical results of orpiment composition in the different particle sizes.

The results for pyrite indicate that the mole ratio of sulfur to iron is very close to the stoichiometric value for pyrite, and that iron and sulfide sulfur compositions in each size fraction show little variation. The pyrite structure was confirmed by X-ray diffraction, with traces of quartz and FeSO₄·2H₂O (as shown in Figure IV.1 in Appendix IV). The scanning electron micrograph of the -200+270 mesh particles is shown in Figure V.1 in Appendix V.

Analytical results of orpiment show that there is little variation except for arsenic from the two labs, which shows about a 5% difference between the two labs. Arsenic and sulfide sulfur compositions in each size fraction show a very slight variation. The mole ratio of sulfur to arsenic is also very close to the stoichiometric value for orpiment. The results from X-ray diffraction analyses show that the samples consist mainly of orpiment, with traces of realgar and quartz (as shown in Figure IV.2 in Appendix IV).
4.1.2 Reagents

All solutions were prepared with reagent grade chemicals and deionized water. The reagents used in this investigation were:

- Ferric sulfate pentahydrate (Fe$_2$(SO$_4$)$_3$.5H$_2$O) with 97% purity,
- Ferrous sulfate (FeSO$_4$.7H$_2$O) with 100.5% purity,
- Cupric sulfate (CuSO$_4$) with 98.5% purity,
- Sulfur (S) with 99.99% purity,
- Sulfuric acid (H$_2$SO$_4$) with 95-98% purity,
- Medical grade pressurized oxygen with minimum 99.5% purity,
- Ceric sulfate (Ce(SO$_4$)$_2$) solution with the concentration of 0.099-0.101 N,
- 1,10-phenanthroline ferrous sulfate complex solution with the concentration of 0.025 molar.

4.2 Equipment

4.2.1 Pressure Leaching

All pressure oxidation experiments were conducted in a 2-liter Parr titanium autoclave. Agitation was provided by a dual 4-pitched-blade impeller agitator. Heating was provided by an electrical resistance coil around the reaction chamber. Agitation speed and temperature were controlled by a Parr controller unit. The temperature was monitored using a thermocouple probe to an accuracy of about ±1°C and maintained at desired set points by
external heating and by passing cooling water through the internal cooling coils. Cooling water flow was regulated by a solenoid valve. Oxygen was introduced into the autoclave near the bottom through a dip tube which was also connected to an autoclave sampler. Oxygen input rates to the autoclave were measured by an OMEGA mass flowmeter (range from 0-2 SLPM) and recorded using the Labtech Notebook software package. A sampler, which can withdraw a 20 ml slurry sample during runs, was fitted to the reactor. The experimental setup is represented schematically in Figure 4.1.

Figure 4.1 Schematic representation of experimental setup
4.2.2 Examination of Solids

X-ray diffraction

X-ray diffraction patterns of ore samples and leaching residues were conducted using a Siemens D5000 X-ray diffractometer equipped with a PC X-ray pattern processing software program for mineral identification in the Department of Earth and Ocean Science at UBC. For all mineral samples and leaching residue samples, a program with a scan step of 0.03° of 2θ, a counting time of one second per step, and a scanning range from 10 to 65° of 2θ was used with a copper target at the test conditions of 40 kV and 30 mA. The peaks were matched with computer data files to identify the various minerals. Background subtraction and data smoothing were applied on all spectra reported here. Because of the limitations of the X-ray diffraction, peaks of minerals occupying less than 5% of the mixture may not appear in the scan. In the present study, minerals which can be identified by the X-ray diffraction pattern of the bulk sample are reported as major constituents of the sample.

SEM-EDX

A scanning electron microscope (SEM) was utilized to study the morphology of the leached mineral particles. A Kevex 8000 energy dispersive X-ray spectrometer (EDX) in the Department of Metals and Materials Engineering at UBC was employed to provide semi-quantitative to quantitative information. For the analysis, powder particles were mounted on
a stand with double stick and coated with carbon. EDX-spectra were collected with the following conditions: accelerating voltage 20 KV, live time 200 seconds (30% dead time), time constant 12 ms.

4.3 Methods and Procedures

4.3.1 Methods

For the pyrite tests, the slurry used for most experiments had a standard composition of 1 g/L pyrite and 0.5 M H\textsubscript{2}SO\textsubscript{4}. The acidity was fixed at 0.5 M H\textsubscript{2}SO\textsubscript{4} for all the experiments in order to obtain high solubility of Fe\textsubscript{2}O\textsubscript{3} and thereby to avoid Fe(OH)SO\textsubscript{4} precipitation. The proper amount of pyrite to charge into the autoclave was determined by a set of tests at different pulp densities at 230°C. The results showed that when 1 g/L FeS\textsubscript{2} was charged, even if pyrite was dissolved completely, the precipitated amount of iron corresponded to only about 5% pyrite conversion, mostly owing to solution splashing onto the heated walls of the reaction vessel above the solution line. At lower temperatures the precipitated amount was considerably less, so 1 gram FeS\textsubscript{2} per liter of solution was used in all experiments.

All pressure leaching tests were conducted in a 2-liter Parr titanium autoclave. It was found that the titanium corroded if the low pulp density (1 g/L) pyrite pressure oxidation experiments were conducted in the absence of copper. It was critical to the testwork to identify conditions that minimized titanium corrosion in order to avoid a dangerous exposure of reactive titanium metal to oxygen. Table 4-1 shows the effect of the concentration of
sulfuric acid on the corrosion of titanium at the conditions of 210°C, 800 rpm, 0 min., and 1 liter solution.

Table 4-1 Effect of the concentration of sulfuric acid on the corrosion of titanium

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. of H$_2$SO$_4$, g</th>
<th>Wt of Pyrite, g</th>
<th>Total Pressure, psi</th>
<th>Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>P217</td>
<td>54.5</td>
<td>20</td>
<td>450</td>
<td>yes</td>
</tr>
<tr>
<td>P218</td>
<td>20</td>
<td>20</td>
<td>330</td>
<td>yes</td>
</tr>
<tr>
<td>P219</td>
<td>11.2</td>
<td>20</td>
<td>295</td>
<td>yes</td>
</tr>
<tr>
<td>P220</td>
<td>5.5</td>
<td>20</td>
<td>290</td>
<td>yes</td>
</tr>
</tbody>
</table>

As can be seen, the corrosion still happened at 5.5 g/1 H$_2$SO$_4$. It should be mentioned that the steam pressure is 280 psi at 210°C. So the higher the total pressure, the more serious the corrosion. The extraction and the analysis results of the residues for these experiments are given in Table 4-2. It has been clearly shown that elemental sulfur did not form. All sulfur from the decomposition of pyrite formed H$_2$S gas. From Tables 4-1 and 4-2, it can be seen that the higher the sulfuric acid concentration, the more serious the corrosion, and the higher the extraction.

Table 4-2 Extraction and analysis of the residues

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe, %</th>
<th>S$^0$, %</th>
<th>S$^2$, %</th>
<th>S$_T$, %</th>
<th>Extraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P217</td>
<td>18.8</td>
<td>&lt;0.01</td>
<td>20.7</td>
<td>20.7</td>
<td>40.75</td>
</tr>
<tr>
<td>P218</td>
<td>28.4</td>
<td>&lt;0.01</td>
<td>32.1</td>
<td>32.1</td>
<td>22.53</td>
</tr>
<tr>
<td>P219</td>
<td>36.4</td>
<td>&lt;0.01</td>
<td>42.1</td>
<td>42.1</td>
<td>13.75</td>
</tr>
<tr>
<td>P220</td>
<td>42.8</td>
<td>&lt;0.01</td>
<td>49.5</td>
<td>49.5</td>
<td>7.39</td>
</tr>
</tbody>
</table>
From the results shown above, the small amount of pyrite cannot be mixed with sulfuric acid solution at high temperature in the absence of an oxidizing agent. A method had to be developed in order to conduct the experiments in the absence of copper.

The first idea was to use an acid injector to inject sulfuric acid at the desired temperature. The acid injector, made of stainless steel (316SS), was fabricated and used to inject the acid in the experiments. However, the results of experiments showed that the concentration of ferrous was very high in the samples which were withdrawn at 0, 5, 10 minutes respectively. Ferrous levels also increased with high temperatures. The concentration of ferrous was twice as much as the total iron input at high temperatures (above 210°C). The extra iron was clearly a corrosion product. An inspection revealed that a part which connected the acid injector to the autoclave was seriously corroded, therefore, the acid injector could not be used in the experiments.

The second idea was to use an ampoule to seal pyrite and then break it at the desired temperatures. This method avoids the reaction between pyrite and sulfuric acid during heating. However, the corrosion of titanium still happened at the experimental conditions (i.e. 210°C and 50 g/l H₂SO₄), even when oxygen was injected into autoclave prior to heating.

The third approach involved sealing the acid in ampoules instead of pyrite. Oxygen was injected into the autoclave prior to breaking the ampoules. This technique eliminated the
corrosion. Therefore, for the experiments conducted in the absence of Cu\(^{2+}\) at low pulp density, concentrated sulfuric acid was sealed in ampoules during heating to avoid the corrosion of titanium, while for the experiments conducted in the presence of Cu\(^{2+}\), pyrite was sealed in an ampoule to avoid any oxidation of pyrite during heating.

For the orpiment tests, the slurry used for most experiments had a standard composition of 2 g/L orpiment and 0.1 M \(\text{H}_2\text{SO}_4\). Orpiment was sealed in an ampoule to avoid any oxidation of orpiment during heating. Corrosion did not occur during these tests.

### 4.3.2 Procedures

A slurry with ampoules containing sulfuric acid, or a solution with an ampoule containing pyrite was placed in the autoclave, which was then sealed and heated. Once the desired temperature was reached, an initial sample was taken, then the unit was pressurized with oxygen for one minute. Finally, the ampoules were broken by the agitator blades when the agitator was switched on and the test was thus initiated. Samples were withdrawn periodically through the dip tube during a run. The withdrawn sample was cooled to room temperature immediately (in less than 5 seconds) and suction filtered. The volume of each sample withdrawn was determined by weighing, assuming a density of 1 g/ml (since the percent solid was very low). At the end of a run, the system was cooled quickly to room temperature with the cooling coil (less than 15 minutes). The slurry was removed and
suction filtered. The residue was washed thoroughly with deionized water and dried in an oven at 50°C overnight. Both solids and solution were analyzed.

If any precipitate was found on the walls of the bomb and internal parts after each experiment, the autoclave was soaked in 15% HCl for 30 minutes and washed with water, then soaked overnight in a solution of 10% HNO₃, with 5 g/L ferric added in order to encourage the formation of a TiO₂ film, and then washed thoroughly with water. Pressure tests with water for safety and leak detection were conducted periodically.

4.4 Analytical

Pyrite and orpiment consist of three elements: iron, arsenic, and sulfur. These elements may exist in different states in both solution and solids at the different conditions. Therefore, different analytical methods were required for the different forms. All solid samples were analyzed by Chem Met Consultants Inc. (CMC) and International Plasma Laboratory (IPL). Solution samples were analyzed at the hydrometallurgical laboratory at UBC.

Total dissolved iron and arsenic in solution samples were analyzed by an atomic absorption spectrometer (AAS), Model Unicam 929. Fe(II) and As(III) were analyzed by redox titration with ceric sulfate solution using ferroin as an indicator [1]. The methods for titration of Fe(II) and As(III) are listed in Appendix VI. The time elapsed from sampling to Fe(II) and As(III) titration was not longer than 1 hour, during which time no significant
difference in titration results was found from the preliminary tests. Fe(III) and As(V) were taken as the difference between total iron and Fe(II), and total arsenic and As(III), respectively.

Before the ceric sulfate titrimetric method was used in this study to determine As(III), the interference of other ions, such as As(V), Fe(III), and Fe(II), on the measurement was evaluated. Four pure Fe(III), Fe(II), As(III), and As(V) standard solutions were prepared using $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{As}_2\text{O}_3$, and $\text{As}_2\text{O}_5$ reagents, respectively. All solutions were analyzed for total iron and total arsenic by means of AAS to verify the concentration of each solution. The solutions containing various quantities of Fe(III), Fe(II), As(III) and As(V) were subsequently prepared by mixing specific aliquots of the pure standard solutions. These solutions were immediately analyzed using the ceric sulfate titrimetric method. The results for the analyses of Fe(II) and As(III) are summarized in Table 4-3.

<table>
<thead>
<tr>
<th>Composition of standard solutions g/l</th>
<th>Analytical results g/l</th>
<th>Relative errors %</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Fe(II)</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>Fe(II)</td>
<td>As(III)</td>
</tr>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.000</td>
<td>1.000</td>
<td>1.000</td>
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<tr>
<td>0.000</td>
<td>0.600</td>
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<tr>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
</tr>
</tbody>
</table>

where: ND = not determined, NA = not applicable

The results indicate that As(III) and Fe(II) interfere slightly with each other in the determination when using the ceric sulfate titrimetric method, with relative errors of < 3.5%
being obtained at the concentration of 1 g/L for both ions. Relative maximum errors of < 4% and 3.7% for the determination of Fe(II) and As(III) respectively were obtained in the presence of Fe(III) and As(V). These results clearly indicate that the ceric sulfate titrimetric method is sufficiently accurate for monitoring Fe(II) and As(III) in solution.

4.5 Data Reduction and Rate Determination

Experimental dissolution rates in batch reactor studies usually obey rate laws of the form:

\[ r = -kA \prod_i (P_i^{n_i}) \]  

(4.1)

where:

- \( r \): the dissolution rate (moles mineral per unit time);
- \( k \): the rate constant;
- \( A \): total mineral surface area;
- \( P_i \): parameter i, which affects the rate;
- \( n_i \): orders of dependence of the rate on the parameter i.

The most widely used methods of determining rate laws for mineral dissolution are the initial rate and integration methods [2, 3]. The integration method makes use of run data over relatively large extents of reaction, because the orders of dependence \( n_i \) or rate constant \( k \) are determined by integrating equation (4.1) over time. A rate law must be assumed in
order to calculate the rate constant, and *vice versa*. Additionally, because the total surface area of mineral may vary significantly with large extents of reaction, use of the integration method can erroneously incorporate such changes in the derived orders of dependence or rate constant by assuming that the total surface areas are constant throughout a run. The initial rate method, in contrast, makes use of only the initial period of the reaction, where relatively minor changes in the total surface area occur. Also, the initial rate method does not require that a rate law be assumed. For these reasons the initial rate method is best for dissolution experiments.

Initial rates for individual runs were determined by measuring the conversion \((X_i)\) of a mineral *versus* time in this study, where \(i\) was a parameter such as pressure, particle size or pulp density. The order of dependence of the rate on a parameter \(i\), \(n_i\), was determined by conducting a series of runs at different values of parameter \(i\) while other parameters were held constant. From equation (4.1), it is easily seen that a plot of log initial rate \((r)\) *versus* log parameter \(i\) \((P_i)\) for the series will yield a slope equal to \(n_i\).
References


CHAPTER 5

BEHAVIOR OF ORPIMENT DURING PRESSURE OXIDATION

In the past no information has been reported on the behavior of orpiment (As$_2$S$_3$) during aqueous oxidation in sulfuric acid solution at high temperatures (>180°C). The important contribution of the present work is the first systematic study of the oxidation of orpiment in sulfuric acid solution. In this chapter the reaction chemistry and kinetics of aqueous oxidation of orpiment during pressure oxidation at high temperature are discussed.

5.1 Reaction Chemistry of Orpiment

According to the $E_h$-pH diagram shown in Chapter 3 (Figure 3.6), orpiment may be oxidized at relatively mild oxidation potentials at low pH values. Once orpiment is decomposed, arsenic reports to the liquid phase as As(III), where it may be further oxidized to As(V), while sulfur may form elemental sulfur or sulfate depending on the conditions. However, there is frequent uncertainty over the exact chemical nature of phases formed at high temperatures. Therefore, it is necessary to get confirmative data experimentally.

The following parameters were investigated: retention time, temperature, pulp density, the concentration of sulfuric acid, particle size, and oxygen partial pressure. The standard conditions for the pressure oxidation tests were 210°C, 800 rpm, 100 psi $P_{O_2}$, -200 + 270
mesh, 2 hours and 20 g/L orpiment at 0.1 M H$_2$SO$_4$. The solution and residue after each test were analyzed to identify the reaction products.

In this study, the conversion of orpiment was calculated from the total mass of arsenic in solution divided by the total mass input, which was obtained from the mass balance. The ratio of As(III)/As was calculated from the concentration of trivalent arsenic divided by the total concentration of arsenic in solution. The ratio of elemental sulfur to total sulfur (S°/S$_r$) was calculated from the mass of elemental sulfur in the residue divided by the total mass of sulfide sulfur oxidized.

5.1.1 Effect of Retention Time

Figure 5.1 shows the effect of retention time on the product distribution and conversion of orpiment. The data in Figure 5.1 were obtained from one set of pressure oxidation tests conducted over periods of 1, 2, and 4 hrs under the standard conditions. It is very interesting to see that most of the arsenic in solution is in the trivalent state and a high percentage of elemental sulfur is formed in the early stages of oxidation. As the oxidation of orpiment progresses with time, both the ratios of As(III) to total dissolved arsenic and of elemental sulfur to total sulfur oxidized decrease. However, more than 85% As(III) and 10% elemental sulfur were still found even after 4 hours of retention time.
Figure 5.1 Effect of retention time on product distribution and conversion at 210°C, 800 rpm, 100 psi $P_{O_2}$, -200 + 270 mesh, and 20 g/L orpiment at 0.1 M $H_2SO_4$.

5.1.2 Effect of Temperature

Figure 5.2 illustrates the effect of temperature on the product distribution and conversion of orpiment. The tests were conducted over the temperature range of 170 to 230°C under the standard conditions. Both the product distribution and the conversion of orpiment are strongly temperature dependent. The higher the temperature, the higher the conversion, the lower the ratio of As(III) to total dissolved arsenic, and the lower the yield of elemental sulfur. It is of interest to observe that all arsenic in solution is in the trivalent state with more than 50% elemental sulfur yield in the temperature range of 170 to 190°C. At 230°C, only a very small amount of elemental sulfur was detected, and orpiment was completely
oxidized. However, more than 85% As(III) in solution was still found. A very low conversion of orpiment was obtained at 170°C, namely 36% after 2 hours oxidation.

Figure 5.2 Effect of temperature on product distribution and conversion at 800 rpm, 100 psi $P_{O_2}$, -200 + 270 mesh, 2 hours and 20 g/L orpiment at 0.1 M $H_2SO_4$.  

5.1.3 Effect of Pulp Density

The effect of pulp density on the product distribution and conversion of orpiment is illustrated in Figure 5.3. Three pulp densities were studied, namely 2, 10 and 20 g/L, under the standard conditions. The higher the pulp density, the higher the ratio of elemental sulfur to total sulfur oxidized, and the lower the conversion of orpiment. Orpiment can be oxidized completely at pulp density of 2 g/L, and oxidized almost completely at pulp density of 10
g/L after 2 hour oxidation. The pulp density only slightly affected the ratio of As(III) to total arsenic in solution, apparently. Again, most of the arsenic in solution exists in the trivalent state.

Figure 5.3 Effect of pulp density on product distribution and conversion at 210°C, 800 rpm, 100 psi P_{O_2}, -200 + 270 mesh, and 2 hours at 0.1 M H_{2}SO_{4}.

5.1.4 Effect of Acid Concentration

Figure 5.4 shows the effect of sulfuric acid concentration on the product distribution and conversion of orpiment. The tests were conducted at sulfuric acid concentrations of 10, 30, and 50 g/L, under the standard conditions. It is evident that both the relative proportion of As(III) to total dissolved arsenic and elemental sulfur to total sulfur oxidized decrease with
increasing sulfuric acid concentration while the conversion of orpiment increases with the acid concentration. Again, most of the arsenic in solution exists in the trivalent state.

![Diagram showing the effect of acid concentration on product distribution and conversion.]

Figure 5.4 Effect of the acid concentration on product distribution and conversion at 210°C, 800 rpm, 100 psi P O₂, -200 + 270 mesh, 2 hours and 20 g/L orpiment.

5.1.5 Discussion

Figure 5.5 shows conversions calculated on the basis of both sulfur and arsenic analyses. It is obvious that the values of conversion based on arsenic are very close to the values based on sulfur. It was found that the mole ratio of arsenic to sulfide sulfur in the residue is still very close to the stoichiometry of orpiment. This indicates that no arsenic precipitates or intermediate sulfur compounds are formed during pressure oxidation. This was further
confirmed by using X-ray diffraction to identify the residues (as shown in Figure III.3 in Appendix III).

![Temperature vs. Conversion Based On S, %]

**Figure 5.5** Conversion based on sulfur measurements vs. conversion based on arsenic measurements at the various conditions

With regard to sulfur species, from Figures 5.1 through 5.4, it can be seen that elemental sulfur and sulfate are produced at all the temperatures investigated. Elemental sulfur is the predominant species at low temperature (170 to 190°C). Sulfate becomes gradually more predominant at temperatures above 190°C. However, 25% elemental sulfur was still found in the residue generated at the conditions of 210°C, 100 psi of oxygen partial pressure, 800 rpm agitation speed, and 2 hours retention time in 0.1 M H₂SO₄ solution. Separate sulfur blebs were also found in the residue. This behavior is unlike pyrite (FeS₂), for which sulfate
was reported to be the predominant species over the temperature range of 100 to 180°C by all investigators [1, 2, 3], and for which no elemental sulfur has been detected at temperatures above 190°C [4].

The products of a reaction usually depend on oxidative potential of the system. If the oxidative potential is not high enough, sulfide in the mineral may only be oxidized to elemental sulfur.

The oxidation of a mineral sulfide can be thought of as the sum of two half reactions. Here it is assumed that the oxidation product of S\(^2^-\) is S°.

\[
MS + \frac{1}{2}O_2 + 2H^+ \rightarrow M^{2+} + S^0 + H_2O
\]  

(5.1)

Anodic reaction

\[
MS \rightarrow M^{2+} + S^0 + 2e^-
\]  

(5.2)

Cathodic reaction

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O
\]  

(5.3)

The surface of the solid is taken to consist of anodic and cathodic sites. Each half reaction has its own intrinsic kinetics. The kinetics of O\(_2\) reduction (equation 5.3) depend on the properties of the mineral.
According to thermodynamics, the standard reduction potential of oxygen is 1.229 volts. However, molecular oxygen is an inert reactant exhibiting high activation overpotential, the exact value of which depends on the electrocatalytic properties of the substrate or mineral undergoing oxidation [5]. Some typical values of oxygen overpotential ($\eta_a$) in acid media are given in Table 5-1. The overpotential of the half reaction (5.3) depends on the substrate. So it is not surprising to observe that in some cases the yield of elemental sulfur from one mineral to the other varies considerably.

Table 5-1 Some typical $\eta_a$ values of O$_2$/H$_2$O in acidic media [5]

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>$\eta_{O_2}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS</td>
<td>1330</td>
</tr>
<tr>
<td>Fe$_{1-x}$S</td>
<td>1060</td>
</tr>
<tr>
<td>CuFeS$_2$</td>
<td>1000</td>
</tr>
<tr>
<td>FeAsS</td>
<td>880</td>
</tr>
<tr>
<td>FeS$_2$</td>
<td>840</td>
</tr>
<tr>
<td>Au</td>
<td>700</td>
</tr>
<tr>
<td>Pt</td>
<td>400</td>
</tr>
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</table>

Elemental sulfur can be further oxidized to sulfate sulfur, at least at 210°C in the system investigated, although this reaction is relatively slow. This opinion is on the basis of the decrease in the ratio of elemental sulfur to reacted sulfide with retention time (Figure 5.1). Also, a test was conducted to oxidize elemental sulfur powder at the conditions of 210°C, 100 psi oxygen partial pressure, 800 rpm agitation speed, two hours of retention time and 6 grams of elemental sulfur in one liter of 0.1 M H$_2$SO$_4$ solution. The results of the test show that about 20% of the elemental sulfur was oxidized, which further supports the opinion.
Moreover, it is well known that elemental sulfur is unstable thermodynamically under pressure oxidation conditions.

Based on the findings of arsenic species from the experiments, it is clear that trivalent arsenic is a predominant species under all conditions investigated. Extrapolation to time zero indicates that all arsenic is initially extracted as trivalent arsenic and is subsequently oxidized very slowly to pentavalent arsenic in the aqueous phase. Dutrizac and Morrison [6] reported the dissolution of niccolite (NiAs) in FeCl$_3$ media to yield As(III) instead of As(V) in solution.

In an attempt to confirm the findings of arsenic speciation observed above, another series of pressure oxidation tests were performed under varying conditions of temperature, agitation speed, particle size, and oxygen partial pressure at low pulp density (2 g/L). The standard conditions for these low pulp density tests were 210 °C, 800 rpm, 100 psi, -200 + 270 mesh, 2 hours and 2 g/L orpiment at 0.1 M $\text{H}_2\text{SO}_4$. The results of the experiments are shown in Figures 5.6 through 5.9. It bears noting that elemental sulfur was not determined because of the small amounts of residue generated. However, elemental sulfur was visible on the wall of the reactor over the temperature range of 170 to 190°C.

Figure 5.6 shows the effect of temperature (170 to 230°C) on the ratio of As(III) to total dissolved arsenic. It is evident that all the arsenic in solution is in the trivalent state at low temperature (170 to 190°C), and more than 85% trivalent arsenic was found at 230°C, which
is the same result as at high pulp density. Figures 5.7 and 5.8 show the effect of particle size
(−100 +140 to −270 +325 mesh) and oxygen partial pressure (50 to 150 psi) on the ratio of
As(III) to total dissolved arsenic. It can be seen that all the arsenic in solution is in the
trivalent state at the large particle size range from −100 +140 to −140 +200 mesh and at low
oxygen partial pressure (50 psi). When particle size is reduced to −200 +270 mesh or
oxygen partial pressure is increased to 100 psi, As(III) is gradually oxidized to As(V).
However, further reducing particle size or increasing oxygen partial pressure does not affect
the ratio of As(III) to total dissolved arsenic significantly. The effects of agitation speed
(600 to 1000 rpm) on the ratio of As(III) to total arsenic in solution at 210°C were found to
be marginal (Figure 5.9). Most of the dissolved arsenic is in the trivalent state over the
range of agitation speed investigated.

It is obvious from the results that all the arsenic extracted is initially in the trivalent state and
is subsequently oxidized to the pentavalent state. The oxidation rate of As(III) to As(V)
seems very slow in the system studied. Consequently, most of the arsenic in solution
remains in the trivalent state, which verifies the results obtained at high pulp density.
Figure 5.6 Effect of temperature on the ratio of As(III) to total dissolved arsenic at 800 rpm, 100 psi P_{O_2}, -200 + 270 mesh, and 2 g/L orpiment at 0.1 M H_2SO_4.

Figure 5.7 Effect of particle size on the ratio of As(III) to total dissolved arsenic at 210°C, 800 rpm, 100 psi P_{O_2}, and 20 g/L orpiment at 0.1 M H_2SO_4.
Figure 5.8  Effect of oxygen partial pressure on the ratio of As(III) to total dissolved arsenic at 210°C, 800 rpm, -200 + 270 mesh, and 20 g/L orpiment at 0.1 M H₂SO₄

Figure 5.9  Effect of agitation speed on the ratio of As(III) to total dissolved arsenic at 210°C, 100 psi P₀₂, -200 + 270 mesh, and 20 g/L orpiment at 0.1 M H₂SO₄
The oxidation of a synthetic As(III) solution was attempted under the standard conditions. The solution, consisting of 0.5 g/L As(III) and 0.1 M H$_2$SO$_4$, was charged into the autoclave. Also, the effects of cupric and ferric ions on the oxidation of As(III) were investigated. The synthetic solution is the same as above except that 1 g/L of cupric and 2 g/L of ferric were added, respectively. The results are shown in Figure 5.10. It is clear that As(III) can be also oxidized to As(V) partially in the synthetic solution without any addition, although the reaction is very slow. This result further confirms that As(V) is derived from the oxidation of As(III) during the oxidation of orpiment. It is obvious that cupric ion has no effect on the oxidation rate of As(III). However, ferric has a significant effect. The ratio of As(III) to total dissolved arsenic drops to less than 7% after two hours in the presence of Fe(III). At the same time, 93% of the arsenic was removed from solution. Hematite and scorodite were identified in the precipitate. It is noticed from Figure 5.10 that the ratios of Fe(II)/Fe$_T$ and As(III)/As$_T$ are not zero and 100%, respectively, at the initial time, which indicates that ferric oxidized As(III) during heating. Therefore, we can conclude that As(III) can be oxidized rapidly by ferric, but not by oxygen, under the conditions studied. However, oxygen can help to regenerate the “catalyst” Fe(III) to maintain a high ratio of Fe(III)/Fe(II), or a high potential in solution.
Based on the results of the present work, the chemistry of pressure oxidation of orpiment in sulfuric acid medium seems to consist of the following reactions:

$$\text{As}_2\text{S}_3(\text{s}) + 6 \text{O}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{aq}) \rightarrow 2 \text{H}_3\text{AsO}_3(\text{aq}) + 3 \text{H}_2\text{SO}_4(\text{aq}) \quad (5.4)$$

$$2 \text{As}_2\text{S}_3(\text{s}) + 3 \text{O}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{aq}) \rightarrow 4 \text{H}_3\text{AsO}_3(\text{aq}) + 6 \text{S}(\text{s}) \quad (5.5)$$

$$\text{H}_3\text{AsO}_3(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{AsO}_4(\text{aq}) \quad (5.6)$$

$$\text{S}(\text{s}) + 3/2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) \quad (5.7)$$
During pressure oxidation of orpiment, the formation of products is postulated via two parallel and competing reactions (5.4) and (5.5). At low temperature, reaction (5.5) is predominant. However, reaction (5.4) becomes predominant as the temperature increases above 190°C. As(III) as arsenious acid (H$_3$AsO$_3$) generated by reactions (5.4) and (5.5) is subsequently oxidized to arsenic acid (H$_3$AsO$_4$) very slowly according to reaction (5.6), although this reaction is rapid in the presence of ferric. Elemental sulfur formed through a parallel reaction path (reaction 5.5) can be further oxidized to sulfate (reaction (5.7)), especially at high temperature.
5.2 Reaction Kinetics of Orpiment

Pressure oxidation tests were performed under different experimental conditions including agitation speed, temperature, and oxygen partial pressure. The standard conditions for the pressure oxidation tests were 210°C, 800 rpm, 100 psi $P_{O_2}$, -200 + 270 mesh, 2 hours and 2 g/L orpiment at 0.1 M $H_2SO_4$. The initial reaction rates mentioned in this study are slopes of tangents of percent arsenic extracted versus retention time curves taken at time zero. A third-order polynomial regression was used to find equations for the experimental data curves. The orpiment conversion is based principally on total arsenic measurements as mentioned above. During the calculation of the percent orpiment conversion, correction factors were applied to account for the volume and mass losses due to sampling. Hence, for any sample $i$:

$$X_i = \frac{C_i V_i + \alpha_i}{m - \frac{M_{As}}{M_{AsS}_3} \gamma} \times 100\% \quad (5.8)$$

where

- $X$ percentage conversion of orpiment, %;
- $C_i$ arsenic concentration of the $i$th sample, g/L;
- $V_i$ volume of leaching solution prior to taking the $i$th sample, L;
- $\alpha_i$ total amount of arsenic withdrawn prior to the $i$th samples, g;
- $m$ mass of charged solid, g;
$M_{As}$  molecular weight of arsenic, g/gmol;

$M_{AsS}$ molecular weight of orpiment, g/gmol;

$\gamma$  orpiment purity;

hence, $V_j = V_0 - \sum_{i=1}^{n} V_{si}$, and $\alpha_i = \sum_{i=1}^{n} C_i V_{si}$

$V_{si}$  volume of sample, L;

$n$  number of total samples;

and at $t = 0$,

$V_0 = 1$ L, and $C_0 = V_{s0} = 0$.

5.2.1 Effect of Agitation Speed

The results of leaching experiments conducted at various agitation speeds under the standard conditions are shown in Figure 5.11. From the figure, it is observed that there is no significant effect of agitation speed between 600 and 1000 rpm; although increasing the agitation speed has a small positive effect on the rates of the reactions. For consistency throughout the work, 800 rpm was chosen as a standard agitation speed.
Figure 5.11 Effect of agitation speed on orpiment conversion at 210°C, 100 psi P_\text{02}, -200 + 270 mesh, 2 hours and 2 g/L orpiment at 0.1 M H_2SO_4

5.2.2 Effect of Temperature

The effect of temperature on the reaction rate was studied in a series of experiments at 170°C, 190°C, 210°C, 220°C and 230°C under the standard conditions. The results obtained from experiments are shown as percent orpiment conversion versus retention time plots in Figure 5.12.
It is evident that the leaching rates are strongly temperature dependent. Complete oxidation of orpiment could be achieved within short times (45 min.) at temperatures above 210°C. However, orpiment conversion reached only about 80% after 2 hours at the lowest temperature (170°C). Initial rate values for the dissolution of orpiment were determined from the curves in Figure 5.12. An Arrhenius plot of the initial rate data for dissolution of orpiment is presented in Figure 5.13. Two distinct regions are observed in the plot. The first, between 170 and 210°C, has an experimental activation energy of 26.1 kJ/mol (6.25 kcal/mol) with a correlation coefficient of 0.9953, which suggests that the kinetics may be controlled by product layer diffusion. The other region, between 210 and 230°C, has a value of 55.20 kJ/mol (13.21 kcal/mol), which suggests that the kinetics may be controlled by
surface chemical reaction. It appears that a temperature near 210°C may be of critical importance.

Figure 5.13 Arrhenius plot using the data at the lower pulp density

The data given in Figure 5.12 were analyzed with the aid of established leaching models. The surface reaction control (shrinking sphere) plots are shown in Figure 5.14, while the respective product layer diffusion (shrinking core) plots are shown in Figure 5.15. Analysis of the results indicated that only data obtained at 220°C and 230°C were in good correlation with the surface reaction control model (Figure 5.14), which suggests that the oxidation reaction may be controlled by the chemical reaction at the particle surface. Near perfect linearity of the plots for the product layer diffusion control model are found for the data obtained at temperature between 170 to 190°C (Figure 5.15), which suggests that orpiment
oxidation is controlled by product layer diffusion. These observations agree with the finding of two distinct regions in the Arrhenius plot.

It appears that liquid sulfur formation, especially at the lower temperature range investigated, interferes with the kinetics of orpiment oxidation. In other words, liquid sulfur forms a protective, impervious or semi-pervious layer around the orpiment particles. Under such conditions, continued oxidation of the orpiment would involve the reaction of the bulk orpiment by oxidant migration through the surface layer. In addition, the surface sulfur layer might undergo oxidation on its own. At high temperature, elemental sulfur could be oxidized relatively quickly. So even though the liquid sulfur layer is impervious, parts of the particle surfaces would be exposed after the liquid sulfur layer is oxidized.

![Figure 5.14 Test for chemical reaction control at different temperatures](image)

Figure 5.14 Test for chemical reaction control at different temperatures
5.2.3 Effect of Particle Size

Leaching tests under standard conditions were conducted using different particle size samples. The effect of particle size on oxidation rate is shown in percent orpiment conversion versus retention time plots for various sizes in Figure 5.16. It is obvious that the leaching rates are also particle size dependent. The reaction rate is observed to increase with decreasing particle size.
Figure 5.16 Effect of particle size on orpiment oxidation at 210°C, 800 rpm, 100 psi P_O_2, 2 hours and 2 g/L orpiment at 0.1 M H_2SO_4

Figure 5.17 is a plot of 1 - (1 - X)^{1/3} versus time at different particle sizes, while Figure 5.18 is a plot of 1 - 2/3 X - (1 - X)^{2/3} versus time at different particle sizes. The linear relationship is maintained roughly for product layer diffusion model at fine particle size (-270+325 mesh). A relationship between the logarithm of the initial particle size radius (r_o) and the logarithm of the initial rates is shown in Figure 5.19. A straight line relationship with a slope of -1.49 is found, which is not very close to the value of -2 for the product layer diffusion model. These results indicate that orpiment oxidation may be controlled by mixed control (i.e. the product layer diffusion and the chemical reaction).
Figure 5. 17 Test for chemical reaction control at different particle sizes

Figure 5. 18 Test for product layer diffusion control at different particle sizes
5.2.4 Effect of Oxygen Partial Pressure

The effect of oxygen partial pressure on the reaction rates was determined over the range of 50 to 150 psi under the standard conditions. The vapor pressure of water above the solution is very sensitive to temperature, especially at high temperature. A slight change in temperature, caused by the heat of reaction, results in a dramatic change in pressure. In order to avoid this problem, an internal water-coil cooling system was used to carefully control the temperature and maintain the desired pressure. The oxygen overpressure was added based on the vapor pressure at the desired temperature. A digital pressure gauge was used for accuracy.
The results are given in Figure 5.20, which indicates that there is no significant difference in orpiment oxidation rate over the oxygen partial pressure range of 50 to 150 psi.

![Graph showing orpiment conversion vs retention time for different oxygen partial pressures.]

Figure 5.20 Effect of oxygen partial pressure on orpiment extraction at 210°C, 800 rpm, -200 + 270 mesh, 2 hours and 2 g/L orpiment at 0.1 M H₂SO₄

As proposed above, the oxidation of orpiment may be expressed as:

\[ \text{As}_2\text{S}_3 + 6 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{AsO}_3 + 3 \text{H}_2\text{SO}_4 \]  \hspace{1cm} (5.4)

\[ 2\text{As}_2\text{S}_3 + 3 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{H}_3\text{AsO}_3 + 6 \text{S} \]  \hspace{1cm} (5.5)
By combining reactions (5.4) and (5.5), one obtains:

\[ \text{As}_2\text{S}_3 + 3 \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{AsO}_3 + \text{H}_2\text{SO}_4 + 2 \text{S} \quad (5.9) \]

The rate of oxidation of orpiment expressed as the mole of oxygen disappearing per unit time, per particle is:

\[ -\frac{dN_{O_2}}{dt} = A_s k [O_2]^n \quad (5.10) \]

where:

- \( N_{O_2} \): number of mole of oxygen at time \( t \);
- \( A_s \): total surface area of un-reacted core at time \( t \);
- \( k \): apparent intrinsic rate constant;
- \([O_2]\): bulk concentration of dissolved oxygen, \( \text{mol/cm}^3 \);
- \( n \): reaction order with respect to oxygen concentration.

The bulk concentration of oxygen in sulfuric acid solution may be calculated using Tromans' model [7]:

\[ [O_2] = \phi P_{O_2} f(T) \quad (5.11) \]

where \( P_{O_2} \) is oxygen partial pressure, \( f(T) \) is a temperature dependent function, which is given by
\[ f(T) = \exp \left\{ \frac{0.046T^2 + 203.35T \ln(T/298) - (299.378 + 0.092T)(T - 298) - 20.591 \times 10^3}{83144T} \right\} \]

where \( T \) is absolute temperature, and \( \phi \) is a solute-dependent factor given by

\[ \phi = \left\{ \frac{1}{1 + 2.01628 \times (C_{\text{H}_2\text{SO}_4})^{1.253475}} \right\}^{0.168954} \]

where \( C_{\text{H}_2\text{SO}_4} \) is the molal concentration of sulfuric acid in solution.

Substituting equation (5.11) into (5.10) gives:

\[ \frac{dN_{O_2}}{dt} = A_k \phi \rho_o f(T)^n \]

(5.14)

From the stoichiometry of reaction (5.9):

\[ \frac{dN_{O_2}}{dt} = 3 \frac{dN_{\text{As}_2\text{S}_3}}{dt} \]

(5.15)

where \( N_{\text{As}_2\text{S}_3} \) is number of moles of orpiment present at time \( t \). On the other hand, the conversion of orpiment, \( X \), is given by the following equation:

\[ X = \frac{N_{\text{As}_2\text{S}_3}^0 - N_{\text{As}_2\text{S}_3}}{N_{\text{As}_2\text{S}_3}^0} \]

(5.16)
where \( N_{A_{2}S_{3}}^0 \) is the initial number of moles of orpiment. By differentiating equation (5.16) and combining it with equation (5.14) and equation (5.15), the following equation is obtained:

\[
\frac{dX}{dt} = \frac{A_{4}[\phi f(T)]^n}{3N_{A_{2}S_{3}}^0} kP_{O_{2}}^n
\]  

(5.17)

A plot of the logarithms of \( \frac{dX}{dt} \) versus the logarithms of oxygen partial pressure, \( P_{O_{2}} \), would result in a straight line with slope \( n \). By taking the logarithms of the initial rates from the curves in Figure 5.20 and plotting them against the logarithms of the respective oxygen partial pressures, the resulting straight line with a slope of 0.25 (or \( 1/4 \)) is shown in Figure 5.21, indicating that the initial reaction rate is one quarter order with respect to oxygen partial pressure.

It should be noted that the temperature function, \( f(T) \), not only affects solubility of oxygen, but also affects the apparent activation energy because it changes with temperature. Therefore, the apparent activation energy cannot be calculated simply as logarithm of initial rate vs. \( 1/T \), temperature function \( f(T) \) has to be considered. A new Arrhenius plot of the initial rate data for dissolution of orpiment is illustrated in Figure 5.22. The value of 22.21 kJ/mol (5.31 kcal/mol) between 170 and 210°C, and 50.01 kJ/mol (11.96 kJ/mol) between 210 and 230°C were obtained, which are smaller than the values calculated before in the same range, respectively. These values are the true activation energy for dissolution of orpiment at high temperature.
Figure 5.21 Ln(oxygen partial pressure, psi) vs. Ln(initial rate, \%/min.)

\[
y = 0.247x + 1.0875 \\
R^2 = 0.984
\]

Figure 5.22 Arrhenius plot for orpiment oxidation

E = 50.0 kJ/mol (12.0 kcal/mol)
E = 22.2 kJ/mol (5.3 kcal/mol)
5.2.5 Effect of Pulp Density

Experiments to study the effect of pulp density on orpiment oxidation were run over the range of 2 g/L to 20 g/L under the standard conditions. -200+270 mesh samples at 2 g/L, 10 g/L and 20 g/L were used. It was found that the reaction rate decreased with increasing orpiment concentration, as shown in Figure 5.23. The reason is because more elemental sulfur was formed at the higher pulp density, which may partially or entirely cover the particle surfaces and isolate the oxygen contact with orpiment surfaces.

Figure 5.23 Effect of pulp density on orpiment oxidation rate at 210°C, 800 rpm, 100 psi P02, -200 + 270 mesh, and 2 hours at 0.1 M H2SO4
When the pulp density is considered, the rate of oxidation of orpiment can be expressed as the mole of oxygen disappearing per unit time:

\[
-\frac{dN_{O_2}}{dt} = A_{r} \phi f(T) \frac{k}{P_{O_2}^\gamma \phi_{As_2S_3}^m} 
\]  
(5.18)

where:

- \(\phi_{As_2S_3}\): pulp density of orpiment, g/L;
- \(m\): reaction order with respect to pulp density.

As in the section 5.2.4, by differentiating equation (5.16) and combining it with equation (5.15) and equation (5.18), the following equation is obtained:

\[
\frac{dX}{dt} = \frac{A_{r} \phi f(T) \frac{k}{3N_{As_2S_3}^0}}{P_{O_2}^\gamma \phi_{As_2S_3}^m} 
\]  
(5.19)

A plot of the logarithms of \(dX/dt\) versus the logarithms of pulp density, \(\phi_{As_2S_3}\), would result in a straight line with slope \(m\). By taking the logarithms of the initial rates and plotting them against the logarithms of the respective pulp density, the resulting straight line has a slope of \(-0.22\) (about \(-1/5\)), as shown in Figure 5.24, indicating that the initial reaction rate is about negative one fifth order with respect to pulp density.
Figure 5. 24 Logarithm of initial rate versus logarithm of pulp density

Based on the findings above, the reaction rate equation for dissolution of orpiment in the system studied at the baseline (e.g. 210°C, -200+270 mesh, 0.1 M H$_2$SO$_4$, and low pulp density) was formulated as

$$-r_{As_j} = \gamma A_j k [\phi f(T)P_{O_2}]^{1/4} \phi_{As_j}^{5/4}$$

where

- $\gamma$ : a stoichiometric factor;
- $A_j$ : total surface area of un-reacted core at time t;
- $k$ : apparent intrinsic rate constant;
- $\phi$ : a solute-dependent factor;
\[ P_{O_2} \text{: oxygen partial pressure; } \]
\[ f(T) \text{: a temperature dependent function; } \]
\[ \phi_{As_2S_3} \text{: pulp density of orpiment, g/L. } \]

5.3 Summary

The acid pressure oxidation of orpiment with oxygen was studied under various experimental conditions in the temperature range 170 to 230°C, and the reaction products were determined. Orpiment reacts with oxygen yielding elemental sulfur, sulfate, As(III) and As(V). Elemental sulfur is produced under all conditions tested. Most of the dissolved arsenic is in the trivalent state after two hours of oxidation, even at temperatures up to 230°C and oxygen partial pressures up to 150 psi. As the oxidation of orpiment progresses with time, both the ratio of As(III) to total dissolved arsenic and the ratio of elemental sulfur to total sulfur oxidized decrease.

It is postulated that both elemental sulfur and sulfate are direct products of orpiment oxidation via two parallel and competing reactions. The predominant species at temperatures below 190°C is elemental sulfur, and sulfate is predominant above 190°C. Elemental sulfur can be further oxidized to sulfate. This reaction is slow at low temperature, but fast at high temperature (> 210°C).
Oxidation of orpiment yields $\text{H}_3\text{AsO}_3$ in solution, and not $\text{H}_3\text{AsO}_4$, which is the thermodynamically stable species. It appears that As(III) enjoys a considerable degree of metastability in the sulfuric acid system. Cupric ions do not affect the oxidation of As(III). However, the oxidation of As(III) is rapid in the presence of ferric ions, resulting in the precipitation of ferric arsenate.

The kinetics of pressure oxidation of orpiment were studied under various conditions in the temperature range of 170 to 230°C. A number of conclusions may be drawn from the foregoing results:

1. The reaction rate of orpiment dissolution is strongly temperature and particle size dependent. The higher the temperature or the smaller the particle size, the faster the reaction rate,

2. The oxidation kinetics are controlled by product layer diffusion with an Arrhenius activation energy of 22.2 kJ/mol (5.31 kcal/mol) over the temperature range of 170 to 210°C. However, as temperature increases from 210 to 230°C, the rate controlling step is switched to surface chemical reaction with an Arrhenius activation energy of 50.0 kJ/mol (12.0 kcal/mol).
3. The reaction rate is decreased with pulp density because more elemental sulfur is formed at high pulp density. It was found that the initial reaction rate is about negative one fifth order with respect to pulp density.

4. The rate of oxidation of orpiment is not affected significantly by agitation speed and oxygen partial pressure. The results indicate that the initial reaction rate is one quarter order with respect to oxygen partial pressure.

5. The reaction rate equation for dissolution of orpiment in the system studied at the baseline (e.g. 210°C, -200+270 mesh, 0.1 M H₂SO₄, and low pulp density) was formulated as

\[ -r_{As_{3}S_{3}} = γA_s k [φ f(T) P_{O₂}]^\frac{1}{4} \phi_{As_{3}S_{3}} \]

where

- \( γ \): a stoichiometric factor;
- \( A_s \): total surface area of un-reacted core at time t;
- \( k \): apparent intrinsic rate constant;
- \( φ \): a solute-dependent factor;
- \( P_{O₂} \): oxygen partial pressure;
- \( f(T) \): a temperature dependent function;
- \( \phi_{As_{3}S_{3}} \): pulp density of orpiment, g/L.
References


CHAPTER 6

BEHAVIOR OF PYRITE DURING PRESSURE OXIDATION

In the past no information has been reported on the aqueous oxidation behavior of pyrite (FeS₂) in sulfuric acid solution at high temperature (>180°C). The important contribution of the present work is the first systematic study of the oxidation of pyrite in sulfuric acid solution under oxygen pressure at high temperature (170 to 230°C). In this chapter the aqueous oxidation behavior of pyrite is presented.

6.1 Reaction Chemistry

The standard conditions for the oxidation tests were 210°C, 800 rpm, 100 psi P₀₂, -200 + 270 mesh, 2 hours and 20 g/L pyrite at 0.1 M H₂SO₄. The solution and residue after each test were analyzed to identify the reaction products. The term “percent iron extracted” is equal to the term “percent sulfide oxidation”. The ratio of ferrous or ferric iron to total iron (Fe(II)/Fe or Fe(III)/Fe) was calculated from the concentration of ferrous or ferric divided by the total concentration of iron in solution.
6.1.1 Effect of Temperature

Figures 6.1 and 6.2 show the effect of temperature on the chemistry of pressure oxidation of pyrite. Four temperatures, namely 170, 190, 210, and 230°C, were tested under the standard conditions. Figure 6.1 is the percent iron extracted and the percent iron precipitated versus temperature, which shows how the extent of pyrite oxidation and iron precipitation increase with temperature. The oxidation of pyrite is not complete under the investigated conditions only at 170°C. The most dramatic effect of temperature is on precipitation. At temperatures below 190°C, more than half of the dissolved iron exists in the solution. However, at temperatures above 210°C, about 90% of the iron product reports to the leach residue. Figure 6.2 shows the distributions of iron and sulfur products. Elemental sulfur, almost 3%, was only found at 170°C after 2 hours pressure oxidation. A higher percent ferrous, 13%, is found at 170°C, while about 3% ferrous is found after 2 hours at higher temperatures (>190°C).
Figure 6.1 Effect of temperature on iron extraction and precipitation at 800 rpm, 100 psi $P_{O_2}$, -200 + 270 mesh, 2 hours and 20 g/L pyrite at 0.1 M $H_2SO_4$

Figure 6.2 Effect of temperature on product distribution at 800 rpm, 100 psi $P_{O_2}$, -200 + 270 mesh, 2 hours and 20 g/L pyrite at 0.1 M $H_2SO_4$
6.1.2 Effect of Retention Time

The effect of retention time on the extraction of pyrite (or iron extracted) and on the distribution of products is illustrated in Figures 6.3 and 6.4. The experiments were conducted under the standard conditions. It can be seen that both the extent of pyrite oxidation and iron precipitation increase with time. The complete oxidation of pyrite can be expected in about one hour in this system, and more than 90% of the iron precipitates during pressure oxidation.

Figure 6.3 Effect of time on iron extraction and precipitation at 210°C, 800 rpm, 100 psi P_{O_2}, -200 + 270 mesh, and 20 g/L pyrite at 0.1 M H_2SO_4
Regarding product distributions, as shown in Figure 6.4, about 1% of elemental sulfur is found at the beginning of the reaction (15 minutes). As the oxidation of pyrite progresses with time only trace amounts of elemental sulfur are found, which indicates that elemental sulfur generated at the beginning of the reaction could be oxidized with time at high temperature. It is clear that most of the iron is in the ferrous state during the initial oxidation stage of pyrite (15 minutes). As the oxidation of pyrite progresses with time the value of $\text{Fe(II)}/\text{Fe}$ reacted decreases. After two hours oxidation, about 3.5% ferrous remained in solution.
6.1.3 Sulfur Species

During the acidic pressure oxidation of pyrite, it was postulated that the reactions follow two parallel and competing paths [1, 2, 3]: the first yielding sulfate and the second yielding elemental sulfur. The reaction yielding sulfate is the dominant reaction at all temperatures below and above the melting point of sulfur. Several investigations gave further support to this postulation [4, 5]. From the $E_h$-pH diagram presented in Chapter 3, elemental sulfur in this system is thermodynamically unstable. The dominant product is sulfate although decreased temperature favors the formation of elemental sulfur. The results observed in this work showed that almost all sulfur was in the sulfate form. Comparing the results obtained in this research with those reported in the literature, the elemental sulfur yields observed in this work are much lower than those reported elsewhere due to the differences in temperature and acidity. The temperature range used in this work was from 170 to 230°C, while the temperature range used by Bailey and Peters was from 85 to 130°C, and the initial acidity in this work is 0.1 M $H_2SO_4$, which is much less than 1 M $H_2SO_4$ used by them. As we know, increased acidities favor the formation of elemental sulfur [3].

6.1.4 Iron Species

Ferrous was postulated as the initial iron product in all experiments of pressure oxidation of pyrite. The results shown in Figure 6.3 also agree with this postulation. However, it was surprising to find in another set of leaching experiments that most of the iron is in the ferric state, instead of ferrous, during the early stages (5 minutes) of pressure oxidation of pyrite.
These experiments, including the effects of temperature, agitation speed, particle size and oxygen partial pressure on the ratio of ferric to total iron, were conducted using 1 g/L of pyrite in one liter 0.5 M H$_2$SO$_4$ solution under the different conditions. The effects of each of the parameters are shown below.

**Effect of Temperature**

Four temperatures were tested, namely 170, 190, 210, and 230°C with other variables kept constant (i.e. 100 psi, 800 rpm, −200 + 270 mesh, and 0.5 M H$_2$SO$_4$). Figure 6.5 shows the relationship between the ratio of ferric to total dissolved iron in solution (Fe(III)/Fe$_T$) and temperature. It is interesting to see that the ratios of Fe(III)/Fe$_T$ are high at the beginning (5 minutes), which means that most of the iron is in the ferric state. As oxidation progresses, the ratios decreased, and reached their lowest values after about 10 minutes, then increased with time. This observation may indicate that iron in pyrite is oxidized to Fe(III) directly, and not Fe(II), initially at high temperature. Fe(III) then oxidizes pyrite or sulfur and sulfur products of intermediate oxidation state, such as thiosulfate, to be reduced to Fe(II).

It is clearly shown that the higher the temperature, the faster the rate of ferrous oxidation. However, more than 40% ferrous was detected at the end of pressure oxidation at 170°C, and nearly 20% ferrous remained even at 230°C after complete oxidation of pyrite. The reason that ferrous persists in solution may be because the pyrite was depleted.
In order to confirm this view, a test of ferrous oxidation with oxygen was conducted under the conditions of 210°C, 100 psi of oxygen partial pressure, 800 rpm of agitation speed, 0.6 g/L of ferrous at 0.5 M H₂SO₄. The result of ferrous oxidation is shown in Figure 6.6. It is clear that ferrous was oxidized in the absence of pyrite and approximately 20% of the ferrous remained in solution after pressure oxidation. The oxidation and final ferrous levels are very similar to the results of ferrous oxidation in the presence of pyrite at the same temperature. It can be concluded from this comparison that the high percentage of ferrous is not because of the absence of pyrite, although pyrite may catalyze ferrous oxidation. It is important to point out that all ferrous data plotted in Figures 6.5 and 6.6 was obtained by titrating the samples which were taken at the desired temperatures and cooled in seconds. However, the final filtrate was cooled in the autoclave in which it took about 15 minutes.

Figure 6.5 Effect of temperature on the ratio of ferric to total dissolved iron at 800 rpm, 100 psi P₂O₅, –200 + 270 mesh, 2 hours and 1 g/L pyrite at 0.5 M H₂SO₄
Figure 6.7 shows the data of the ratios of Fe(II)/Fe$_r$ in the final filtrates (solid line) and in the samples (dash line) after 2 hours oxidation at the various temperatures. The data of the ratios of Fe(II)/Fe$_r$ in the filtrate and the sample for the test of ferrous oxidation at 210°C were also included in Figure 6.7. Obviously, the ratios of Fe(II)/Fe$_r$ in the final filtrates were lower than those in the samples. The cause of this phenomenon was because the solubility of ferrous sulfate dropped to low levels at high temperature. Thus, any solid salt of ferrous sulfate would be difficult to oxidize at high temperature. However, when the solubility of ferrous increased with decreasing temperature, the dissolved ferrous could be oxidized in an autoclave. The drop in solubility of ferrous sulfate at high temperature was also observed in the work of Dreisinger and Peters [6].

![Graph](image_url)

**Figure 6.6** Oxidation of ferrous with oxygen at 210°C, 800 rpm, 100 psi $P_{O_2}$, and 2 hours at 0.5 M $H_2SO_4$
Figure 6.7 Effect of taking sample methods on the ratio of Fe(II)/Fe$_T$

**Effect of Agitation Speed**

Three agitation speeds were tested, namely 650, 800, and 950 rpm, with the other variables kept constant (i.e. 210°C, 100 psi, -200 + 270 mesh). Figure 6.8 shows the effect of agitation speed on the ratio of ferric to total dissolved iron. It was also found that the ratio of Fe(III)/Fe$_T$ decreased with time at the beginning (5 to 10 minutes), then increased with time. The higher the agitation speed, the faster the ferrous oxidation rate.
Effect of Particle Size

The relationship between the ratio of ferric to total iron and particle size, which was determined under a set of runs at the different particle size, is shown in Figure 6.9. It was also found that the ratio of Fe(III)/Fe₇ decreased with time at the beginning, then increased with time. It is known that the smaller the pyrite particles, the faster the oxidation of pyrite. Therefore, the longer the time of oxidation of ferrous, the lower the terminal ferrous concentration in the solution.
Figure 6.9 Effect of particle size on the ratio of ferric to total dissolved iron at 210°C, 800 rpm, 100 psi P$_{O_2}$, 2 hours and 1 g/L pyrite at 0.5 M H$_2$SO$_4$

**Effect of Oxygen Partial Pressure**

In order to determine the effects of oxygen partial pressure on ferrous oxidation, three pressures were tested, namely 50, 100, and 150 psi, with the other variables kept constant. Figure 6.10 shows that the higher the pressure, the faster the oxidation of ferrous to ferric and the lower the terminal concentration of ferrous. It was found again that the ratio of Fe(III)/Fe$_{x}$ decreased with time at the beginning, then increased with time.
Other studies have demonstrated that ferric was the only form of iron produced by pyrite oxidation. Peters and Majima [7] studied the anodic oxidation of pyrite at 0.81 volts in 1M HClO₄ solution and found that ferric was the only iron species found. The anodic reaction is as follows:

\[
\text{FeS}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 15e^- \quad (6.1)
\]

Biegler and Swift [4] also found that ferrous was not detected after pyrite was oxidized in their study of the anodic oxidation of pyrite in 1M H₂SO₄ solution. These findings were further supported by Ahlberg and Broo [8]. Furthermore, ferric and sulfate are the only detectable products of pyrite oxidation by hydrogen peroxide [9]. At high potential, ferrous
may be oxidized as soon as the Fe-S bond is broken. It could be as Meyer [10] proposed that oxidation of Fe(II) to Fe(III) occurs in a thin surface layer within the solid phase. At low potential ferrous is found initially during the oxidation of pyrite because the oxidation of Fe(II) to Fe(III) is relatively slow, therefore, the initial iron product depends on potential on the particle surface. Similarly, ferric could be the initial product at high temperature.

From the results above, we may conclude that ferric, instead of ferrous, is the initial product during pressure oxidation of pyrite at high temperature.

The precipitates, formed at 210°C and at both high (0.5M H₂SO₄) and low (0.1M H₂SO₄) acidities, were analyzed by X-ray diffractometry. A white-yellow precipitate, formed at high acidity, was identified as basic ferric sulfate (Fe(OH)SO₄), while a red precipitate, formed at low acidity, was identified as hematite (Fe₂O₃). These findings confirm the results of Tozawa and Sasaki [11]. The results of X-ray diffraction analysis are shown in Figures IV-4 and IV-5 in Appendix IV.

6.1.5 Chemical Reactions

Based on the results of this work, the following steps (overall reactions) are proposed to describe the reaction mechanism of pressure oxidation of pyrite in sulfuric acid at high temperature:

*Step 1.*
\[ 4 \text{FeS}_2(\text{s}) + 15 \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{aq}) \rightarrow 2 \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + 2 \text{H}_2\text{SO}_4(\text{aq}) \quad (6.2) \]

Pyrite is initially oxidized to ferric sulfate, instead of ferrous sulfate, by dissolved oxygen at high temperatures. The oxygen is chemisorbed on the pyrite surface at the beginning.

**Step 2.**

\[ \text{FeS}_2(\text{s}) + 7 \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + 8 \text{H}_2\text{O}(\text{aq}) \rightarrow 15 \text{FeSO}_4(\text{aq}) + 8 \text{H}_2\text{SO}_4(\text{aq}) \quad (6.3) \]

Ferric produced from step 1 then oxidizes the sulfide in the pyrite to produce ferrous sulfate and sulfuric acid.

It can be seen from equation (6.3) that 14 moles of Fe(III) are required to oxidized one mole of pyrite, and 15 moles of Fe(II) is generated. This could explain why the ratio of Fe(III) to total dissolved iron decreases with time at the beginning.

**Step 3.**

\[ 2 \text{FeSO}_4(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \quad (6.4) \]

Ferrous sulfate produced from step 2 is oxidized to ferric sulfate by dissolved oxygen. Ferric sulfate thus formed oxidizes pyrite again by step 2.
Ferric sulfate produced in steps 1 and 3 also tends to hydrolyze, resulting in the precipitation of ferric oxide ($\text{Fe}_2\text{O}_3$) or basic ferric sulfate ($\text{Fe(OH)}\text{SO}_4$) depending on acidity as mentioned by Tozawa and Sasaki [11].

In acidic solution, the oxidation of pyrite is a complex process. There may be a number of series and parallel reactions occurring during the oxidation of pyrite. Some investigators have suggested that the end product of sulfate may be produced via intermediate sulfoxyl anions, such as sulfite ($\text{SO}_3^{2-}$), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), and polythionates ($\text{S}_n\text{O}_6^{2-}$, $n=4, 5, \text{and} 6$) [12, 13, 14, 15]. The sulfur intermediates were found during the oxidation of pyrite in alkaline solution [16]. However, there were no intermediates detected during acidic oxidation of pyrite [17]. Direct detection of the intermediate species is difficult due to the inherent limitations of the specific analytical instruments, and the low stability and the small amount of the reaction products.
6.2 Reaction Kinetics

As described in the previous section, the dominant products of oxidation of pyrite in sulfuric acid pressure oxidation at high temperature (210°C) are: ferric, ferrous, sulfuric acid, and hematite (Fe₂O₃) or basic ferric sulfate (Fe(OH)SO₄), depending on the acidity. In this section, the effect of agitation speed from 650 to 950 rpm, temperature from 170 to 230°C, particle size (diameter) from 49 to 125 μm, oxygen partial pressure from 345 to 1035 kPa (50 to 150 psi), and pulp density from 1 to 20 g/L on the reaction rates are presented and discussed. The standard conditions for the leaching experiments were 210°C, 690 kPa (100 psi), -74+53 μm, and 1 gram of pyrite in one liter 0.5 M H₂SO₄ solution.

Initial reaction rates, as mentioned in this study, are the slopes of curves of percent iron extracted vs. retention time at time zero. A third-order polynomial regression was used to find equations for the experimental data curves. For the low pulp density tests (1 g/L), pyrite conversion was calculated from the total weight of iron in solution divided by the weight of iron in the head. The calculation of pyrite conversion included correction factors which were applied to account for the volume and mass losses due to sampling. The equation is the same as used in the study of orpiment, which is:

\[ X_t = \frac{C_{V_t} + \alpha}{m \frac{M_{Fe}}{M_{FeS}}} \times 100\% \]  

(6.5)
For the tests at high pulp density, an oxygen mass flow meter was used to record the consumption of oxygen during pressure oxidation. Thus, pyrite conversion was calculated from the oxygen consumed according to reactions (6.2) and (6.4).

The mean particle size in this study was taken as the square root of the product of two adjacent sieve sizes (i.e., the geometric mean sieve opening).

6.2.1 Effect of Agitation Speed

In two phase (solid-liquid) systems, mass transfer can play an important role. It is therefore important to assess its relative effect by changing the hydrodynamic conditions of the system. Increasing the agitation speed is the simplest way of effecting this change. The effect of agitation speed on pyrite oxidation was studied at 650, 800, and 950 rpm under the standard conditions (i.e. 210°C, 100 psi, -200+270 mesh, 1g/L of pyrite at 0.5 M H₂SO₄). 800 rpm is the minimum speed which gave adequate solids suspension at ambient temperature and pressure. This was determined visually in a series of agitation tests carried out in a transparent plastic autoclave mock-up. Figures 6.11 and 6.12 show the effect of agitation speed on the pyrite conversion and the initial rates of pyrite conversion, respectively. It was observed that agitation speed has no significant effect on the initial kinetics when the agitation speed is greater than 800 rpm. For consistency throughout the work, 800 rpm was chosen as the standard agitation speed.
Figure 6.11 Effect of agitation speed on pyrite conversion at 210°C, 100 psi, -200+270 mesh, 1g/L of pyrite at 0.5 M H₂SO₄.

Figure 6.12 Effect of agitation speed on the initial rate of pyrite oxidation.
6.2.2 Effect of Temperature

The effect of temperature on pyrite oxidation was studied over the temperature range of 170 to 230°C under the standard conditions. The effect of temperature on pyrite conversion is shown in Figure 6.13. It is evident that the leaching rate is strongly temperature dependent. At 230°C, the reaction rate was so fast that nearly all of the pyrite dissolved within 20 minutes. However, longer retention times were needed to oxidize pyrite at lower temperatures.

The reproducibility of the initial reaction rate was found to be in the region of 6% for the three runs, which were conducted at 210°C under the standard conditions. Variability in this work was expected, because crushed pyrite is not homogeneous, in terms of its elemental composition and surface structure.

An Arrhenius plot, shown in Figure 6.14, was constructed using the initial rate data for the dissolution of pyrite, determined from the curves in Figure 6.13. The apparent activation energy for the dissolution of pyrite, calculated from Figure 6.14, is 41.25 kJ/mol (9.87 kcal/mol) with a correlation coefficient of 0.992, which may reflect a transition from chemical reaction to mixed control. Therefore, the pressure oxidation of pyrite may be controlled either by chemical reaction or by a combination of both chemical and diffusion mechanisms.
Figure 6.13 Effect of temperature on pyrite oxidation at 800 rpm, 100 psi, -200+270 mesh, 1g/L of pyrite at 0.5 M H$_2$SO$_4$

Figure 6.14 Arrhenius plot of the initial rates calculated from the curves shown in Figure 6.13

$E = 41.25$ kJ/mol (9.87 kcal/mol)
6.2.3 Effect of Particle Size

The effect of particle size on pyrite oxidation, which was determined in a set of runs under the standard conditions, is illustrated in Figures 6.15. It is apparent that particle size has a pronounced influence on the pressure leaching rate of pyrite. The reaction rate is observed to increase with decreasing particle size.

An inverse relationship between the initial mean particle radius, $r_0$, and the initial rate of dissolution of pyrite, obtained from Figure 6.15, is shown in Figure 6.16. A straight line relationship through the origin is found. This inverse dependency suggests that the initial stage of dissolution of pyrite may be controlled by heterogeneous processes at the mineral surface.

![Figure 6.15 Effect of particle size on pyrite oxidation](image)

Figure 6.15 Effect of particle size on pyrite oxidation
at 210°C, 800 rpm, 100 psi, 1g/L of pyrite at 0.5 M H₂SO₄

![Graph](image)

Figure 6.16 Initial rate versus reciprocal particle radius

6.2.4 Effect of Oxygen Partial Pressure

The effect of oxygen partial pressure, taken as the total pressure of the reactor minus the vapor pressure of water at temperature, on pyrite oxidation was determined over the range of 345 to 1035 kPa (50 to 150 psi) under the standard conditions. The results of the tests are illustrated in Figures 6.17 and 6.18. Figure 6.17, which shows pyrite conversion vs. retention time, reveals that the rate of dissolution of pyrite increases with increasing oxygen partial pressure.
As was proposed above, the oxidation of pyrite may be expressed as:

\[
4 \text{FeS}_2 + 15 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{SO}_4
\]  

(6.2)

The rate of oxidation of pyrite expressed as the moles of oxygen disappearing per unit time, per particle is:

\[
-\frac{dN_{O_2}}{dt} = A_s k [O_2]^n
\]  

(6.6)

where:

\[N_{O_2} \text{ : number of mole of oxygen at time } t;\]
The bulk concentration of oxygen in sulfuric acid solution is calculated using equation (5.11) in Chapter 5.

Substituting equation (5.11) into (6.6) gives:

\[
- \frac{dN_{O_2}}{dt} = A_{i} k \phi P_{O_2} f(T) \]

(6.7)

From the stoichiometry of reaction (6.2):

\[
4 \frac{dN_{O_2}}{dt} = 15 \frac{dN_{FeS_2}}{dt}
\]

(6.8)

where \(N_{FeS_2}\) is the number of moles of pyrite present at time \(t\). On the other hand, the conversion of pyrite, \(X\), is given by the following equation:

\[
X = \frac{N_{FeS_2}^0 - N_{FeS_2}}{N_{FeS_2}^0}
\]

(6.9)

where \(N_{FeS_2}^0\) is the initial number of moles of pyrite. By differentiating equation (6.9) and combining it with equations (6.7) and (6.8), the following equation is obtained:
\[
\frac{dX}{dt} = \frac{4A_0[\phi f(T)]^n}{15N_{\text{FeS}_2}^n} kP_{O_2}^n
\]  

(6.10)

A plot of the logarithms of \(dX/dt\) versus the logarithms of oxygen partial pressure, \(P_{O_2}\), would result in a straight line with slope \(n\). Taking the logarithms of the initial rates from the curves in Figure 6.17 and plotting them against the logarithms of the respective oxygen partial pressures yields a straight line with a slope of 0.49, as shown in Figure 6.18. This indicates that the initial reaction rate is one half order with respect to oxygen partial pressure. One half order dependency suggests that the diffusion of dissolved oxygen to the pyrite surface is not rate-controlling.

\[y = 0.4924x - 0.1737\]
\[R^2 = 0.9979\]

Figure 6.18  Logarithm of initial rate versus logarithm of oxygen partial pressure
6.2.5 Effect of Pulp Density

Pulp density is defined here as the mass of pyrite per liter of solution. Experiments to study the effect of pulp density on pyrite oxidation were run over the range of 1 g/L to 20 g/L under the standard conditions. It was found that the reaction rate increased with increasing amounts of pyrite, as shown in Figure 6.19. The explanations for this are:

a). the initial ferric concentration increases with increased pyrite concentration. As described above, ferric is the initial product of the oxidation of pyrite, and the higher the concentration of ferric, the faster the initial rate;

b). iron solubility increases as the solution acidity increases, and the higher the pulp density, the higher the acidity;

c). the oxidation rate of ferrous increases with increased pyrite concentration.
When the pulp density of pyrite is considered, the rate of oxidation of pyrite can be expressed as the moles of oxygen disappearing per unit time as:

\[- \frac{dN_{O_2}}{dt} = A_r k[\phi f(T)] \frac{1}{P_o} \varphi_{FeS_2}^{m} \]  \hspace{1cm} (6.11)

where:

- \( \varphi_{FeS_2} \): pulp density of pyrite, g/L;
- \( m \): reaction order with respect to weight of pyrite per liter.

As in section 6.2.4, by differentiating Equation (6.9) and combining it with Equation (6.8) and Equation (6.11), the following equation is obtained:
A plot of the logarithms of $\frac{dX}{dt}$ versus the logarithms of pulp density, $\varphi_{\text{FeS}_2}^m$, would result in a straight line with slope $m$. By taking the logarithms of the initial rates and plotting them against the logarithms of the respective pulp density, the resulting straight line has a slope of 0.14 or $1/7$, as shown in Figure 20, indicating that the initial reaction rate is one seventh order with respect to pulp density.

\[
\frac{dX}{dt} = \frac{4A_1[\phi f(T)]^2}{15N_{\text{FeS}_2}^0} kP_{\text{O}_2}^2 \varphi_{\text{FeS}_2}^m
\] (6.12)
6.2.6 Effect of Cupric Ion

The effect of cupric ion, added as 5 g/L CuSO₄, on pyrite and ferrous oxidation at low pulp density (1 g/L) under the standard conditions is illustrated in Figure 6.21. It is obvious that the oxidation of ferrous and pyrite are fast in the presence of cupric. The ratio of ferrous to total iron decreases to about 6% in the presence of cupric ion compared to only 20% in the absence of cupric. These observations indicate that cupric is not an oxidant for pyrite, but that it catalyzes the oxidation of ferrous to ferric. The rate of pyrite oxidation is increased by virtue of more ferric or a higher ratio of ferric to ferrous in solution.

King and Lewis [18] used ferric sulfate and oxygen to oxidize pyrite in the temperature range from 80 to 100°C. They found that the rate of pyrite oxidation with both oxygen and ferric ion present was significantly greater than with either oxygen or ferric alone, and the higher the concentration of ferric, the faster the rate of pyrite oxidation. However, the highest concentration of ferric is limited by its solubility at high temperature. Experimental data indicates that the higher the oxygen pressure or in the presence of cupric, the higher the rate of ferrous oxidation, and the higher the conversion of pyrite.

Figure 6.22 shows the effect of cupric on pyrite oxidation at high pulp density (20g/L), which is more apparent than that at low pulp density. It is clear from these results that the ratio of ferric to ferrous has a significant effect on the dissolution of pyrite during pressure oxidation.
Figure 6.21 Effect of cupric ions on pyrite oxidation and the ratio of ferrous to total dissolved iron at low pulp density (1g/L)

Figure 6.22 Effect of cupric ions on pyrite oxidation at high pulp density (20g/L)
6.3 Reaction Mechanism

The electrochemical phenomena involved in the dissolution of sulfides in hydrometallurgical processing of minerals has received extensive study in the past. Bailey and Peters [7] investigated the reaction mechanism of oxygen pressure leaching of pyrite over the temperature range 85 to 130°C. They found that the dissolution mechanism of pyrite under pressure oxidation was electrochemical. Lin, Sohn, and Wadsworth [19] interpreted the pressure leaching of chalcopyrite as an electrochemically controlled process.

The electrochemical dissolution of pyrite can be expressed by the following anodic and cathodic reactions:

\[
\text{Fe}_2\text{S}_2 + 8 \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 15e^- \quad (6.13)
\]

\[
2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4e^- \quad (6.14)
\]

The cathodic reduction of dissolved oxygen at the pyrite surface, according to reaction (6.14), is the key process effecting the overall reaction kinetics. The reaction paths considered here are the chemical adsorption of dissolved oxygen on the pyrite surface and the subsequent electrochemical reaction on the surface.

The electrochemical bias for charge transfer in simple reversible reactions may be expressed quantitatively by the Butler-Volmer equation [20]. This equation relates the current density
at a solid-solution interface to the established overpotential. The Butler-Volmer expression for the net anodic, $i_a$, and net cathodic, $i_c$, current densities for reactions (6.13) and (6.14) are

$$i_a = n_a F k_{af} \exp\left(\frac{\phi_a Z_a F E_a}{RT}\right) - n_a F k_{ar} [Fe^{3+}][SO_4^{2-}][H^+] \exp\left(-\frac{(1 - \phi_a) Z_a F E_a}{RT}\right)$$  \hspace{1em} (6.15)

$$i_c = n_c F k_{cf} \exp\left(\frac{\phi_c Z_c F E_c}{RT}\right) - n_c F k_{cr} [O_2][H^+] \exp\left(-\frac{(1 - \phi_c) Z_c F E_c}{RT}\right)$$  \hspace{1em} (6.16)

where:

- $i_a, i_c$: anodic and cathodic current densities, respectively.
- $n_a, n_c$: total charge transfer for anodic and cathodic reaction, respectively.
- $k_{af}, k_{ar}$: the rate constants for forward and reverse directions for anodic reaction.
- $k_{cf}, k_{cr}$: the rate constants for forward and reverse directions for anodic reaction.
- $E_a, E_c$: potentials for anodic and cathodic reactions, respectively.
- $\phi_a, \phi_c$: charge transfer coefficients for anodic and cathodic reactions, respectively.
- $Z_a, Z_c$: number of charges transferred in the rate-determining steps in anodic and cathodic reactions, respectively.
- $[O_2]$: bulk concentration of dissolved oxygen.
- $F$: Faraday constant.
- $R$: universal gas constant.
- $T$: absolute temperature.
Commonly, single electron transfer processes are favored. This assumption makes $Z_a = Z_c = 1$. The activation barrier is symmetrical, and the values of the transfer coefficient fall generally in the range 0.4 to 0.6, with values commonly near 0.5. So $\phi_a = \phi_c = \phi = 0.5$. The assumptions made here are only for purposes of simplification.

If we neglect the effect of the ions on the back anodic reaction, then $i_a$ and $i_c$ can be rewritten as:

$$i_a = n_a F k_{af} \exp\left(\frac{\phi_a F E_a}{RT}\right)$$  \hspace{1cm} (6.17)

$$i_c = n_c F k_{cf} \exp\left(\frac{\phi_c F E_c}{RT}\right) - n_c F k_{cf} [O_2] [H^+] \exp\left(-\frac{(1 - \phi_c) F E_c}{RT}\right)$$  \hspace{1cm} (6.18)

At the mixed potential $E_m$, $E_m = E_a = E_c$, and the sum of all anodic currents, $\Sigma I_a$, is equal to the negative sum of all cathodic currents, $\Sigma I_c$, such that

$$\Sigma I_a = \Sigma I_c.$$

where $I_a = i_a A_a$ and $I_c = i_c A_c$.

The terms $A_a$ and $A_c$ are the respective anodic and cathodic areas. During pyrite oxidation, both anodic and cathodic reactions occur on the same surface, so $A_a = A_c$, which gives $i_a = -i_c$. Accordingly equations (6.17) and (6.18) may be combined giving

$$\exp\left(\frac{F E_m}{RT}\right) = \frac{n_c k_{cf} [O_2] [H^+]}{n_a k_{af} + n_c k_{cf}}$$  \hspace{1cm} (6.19)
Substituting equation (6.19) into equation (6.17), yields

\[ i_a = n_a F k_{of} \left[ \frac{n_c k_{cr} [O_2] [H^+]^{1/2}}{n_a k_{of} + n_c k_{cr}} \right] \]  

(6.20)

Substituting equation (5.11) for the concentration of dissolved oxygen into equation (6.20), gives:

\[ i_a = n_a F k_{of} \left[ \frac{n_c k_{cr} f f(T)}{n_a k_{of} + n_c k_{cr}} \right] \left[ H^+ \right]^{1/2} P_{O_2}^{1/2} \]  

(6.21)

and assigning \( K(T) \) for all constants, the dissolution rate of pyrite can be written as:

\[ \frac{-dN_{FeS}}{dt} = K(T) \left[ H^+ \right]^{1/2} P_{O_2}^{1/2} \]  

(6.22)

Equation (6.22) suggests half-order dependency on the hydrogen ion concentration and on oxygen partial pressure. The experimentally determined order was found to be 0.5 for \( P_{O_2} \) (Figure 6.18). This suggests that the dissolution of pyrite in acidic pressure oxidation systems may be electrochemically controlled at high temperature.
6.4 Controlling Step and Model

In the case of spherical (or more precisely equiaxed) particles, the following shrinking core models are available for single particles and constant solution concentration:

\[ 1 - X = \left( 1 - \frac{t}{\tau_s} \right)^3 \quad \text{or} \quad \frac{dX}{dt} = \frac{3(1-X)^2}{\tau_s} \tag{6.23} \]

for surface reaction control,

\[ 3(1-X)^3 - 2(1-X) = 1 - \frac{t}{\tau_D} \quad \text{or} \quad \frac{dX}{dt} = \frac{1}{2 \tau_D} \frac{(1-X)^{\frac{1}{3}}}{1-(1-X)^3} \tag{6.24} \]

for product layer diffusion control, where \( X \) is the conversion at time \( t \) and \( \tau_s \) or \( \tau_D \) is the total time required for complete dissolution of a particle, which are given by the following equations:

\[ \tau_s = \frac{\rho_m D_0}{2bk[O_2]^n} \tag{6.25} \]

and

\[ \tau_D = \frac{\rho_m D_0^2}{24bD_3[O_2]^n} \tag{6.26} \]

where:

\[ b: \quad \text{stoichiometric coefficient;} \]
\[ k: \quad \text{intrinsic rate constant, cm/sec;} \]
\[ [O_2]: \quad \text{the oxygen concentration, mol/cm}^3; \]
\[ n: \quad \text{the order of oxygen concentration;} \]
$D_0$: initial particle diameter, cm;

$D_S$: the effective diffusivity of $O_2$(aq) through the product layer;

$\rho_m$: the mole density of pyrite, mol/cm$^3$.

The equations (6.23) and (6.24) can be written simply as following:

$$1 - \sigma = \frac{t}{\tau_S}$$  \hspace{1cm} (6.27)

and

$$1 - 3\sigma^2 + 2\sigma^3 = \frac{t}{\tau_D}$$  \hspace{1cm} (6.28)

where $\sigma = (1 - X)^{\frac{1}{3}}$.

Substituting equation (5.11) for the concentration of dissolved oxygen into equation (6.25) yields

$$\tau_S = \frac{\rho_m D_0}{2b[(\phi P_{O_2} f(T))]^{\mu}}$$  \hspace{1cm} (6.29)

The shrinking core model was used to test the degree of fit for the data given in Figure 6.13, which shows the effect of temperature on the oxidation of pyrite. Figure 6.23 shows the surface reaction control plots of $1 - \sigma$ vs. retention time, and Figure 6.24 shows the product layer diffusion plots of $1 - 3\sigma^2 + 2\sigma^3$ vs. retention time. It can be seen that good linear fits were obtained from Figure 6.23, which suggests that the rate controlling step may be a
chemical reaction at the particle surface. The slopes of these lines represent $1/\tau_s$ in min$^{-1}$.

The non-linearity of the plots in Figure 6.24 indicates that pyrite pressure oxidation is not controlled by product layer diffusion. Examination with a scanning electron microscope (SEM) found no product layer on the particle surface at room temperature (Figure V.2 in Appendix V).

![Figure 6.23 Test for chemical reaction control at different temperatures](image)

Figure 6.23 Test for chemical reaction control at different temperatures
The shrinking core model was also used to test the degree of fit for the data given in Figure 6.15, which shows the effect of particle size on the oxidation of pyrite. The data only conform to the model for chemical reaction control, as shown in Figure 6.25, which further suggests that pressure oxidation of pyrite is under chemical reaction control.
A relationship between the logarithm of the initial mean particle diameter ($D_0$) and the logarithm of slopes ($1/\tau$) of the surface reaction control model lines from Figure 6.25 is shown in Figure 6.26. A straight line relationship is found, with a slope of $-1.12$, which is somewhat higher than the expected value of $-1.0$ for the shrinking core model for chemical reaction control, although still within range. This suggests that the dissolution of pyrite may be controlled by heterogeneous processes at the mineral surface.
Again, the shrinking core model was also used to test the degree of fit for the data given in Figure 6.17, which shows the effect of oxygen partial pressure on the oxidation of pyrite. Linear fits were only obtained for the surface reaction control plots, as shown in Figure 6.27, which further suggests that pressure oxidation of pyrite is under chemical reaction control.

Figure 6.26 Logarithm of $1/\tau_s$ vs. logarithm of initial particle diameter
Figure 6.27 Test for chemical reaction control at different oxygen partial pressures

According to equation (6.29), a plot of the logarithms of $1/\tau_s$ versus the logarithms of oxygen partial pressure, $P_{O_2}$, would result in a straight line with slope $n$. By taking the slopes ($1/\tau$) of lines in Figure 6.27 and plotting them against the logarithms of respective oxygen partial pressures, the resulting a straight line with a slope 0.49 is shown in Figure 6.28. It is obvious that the value of order with respect to oxygen partial pressure obtained using the shrinking core model is exactly the same as the value obtained using initial rate.
As mentioned in Chapter 5, the temperature function, \( f(T) \), not only affects the solubility of oxygen, but also affects the calculation of the apparent activation energy because it changes with temperatures. A new Arrhenius plot was constructed by plotting the differential of logarithms of the slopes of the surface reaction control model lines from Figure 6.23 and one half logarithms of \( f(T) \) for respective temperatures versus \( 1/T \times 1000 \). The resulting plot is shown in Figure 6.29. The apparent activation energy calculated from this plot is 33.2 kJ/mol (7.9 kcal/mol) with a correlation coefficient of 0.993, which is smaller than the value determined in Section 6.2. However, this is the true apparent activation energy for dissolution of pyrite at high temperature.
According to the observed activation energy (33.2 kJ/mol) and the shrinking core model for surface reaction, the following equation is proposed to represent the reaction extent as a function of reaction time, temperature, oxygen partial pressure, temperature function, particle size, and pulp density for the pressure oxidation of pyrite in the system studied at high temperature:

\[
\sigma = 1 - 1.56 \phi_{FeS_2} \frac{1}{\sqrt[3]{P_{O_2}f(T)}} \left[ \exp \left( \frac{-3990}{T} \right) \right] t
\]  

(6.30)

where \( \sigma = (1 - X)^{\frac{1}{3}} \)

\( X \) the conversion of pyrite

\( \phi_{FeS_2} \) pulp density, g/L of pyrite
$P_o$, the oxygen partial pressure, psi

$f(T)$ a temperature dependent function

$D_0$ an initial particle diameter, cm

$T$ temperature of the slurry, K

It should be mentioned that shrinking sphere model (SS Model) fits the data well only for the first 20 minutes of leaching, as shown in Figures 6.30 through 6.32, then deviates from it more or less severely as a function of temperature, partial pressure, and particle size. This deviation can be attributed to passivation of the mineral surface, most likely by elemental sulfur. Indeed, traces of elemental sulfur were detected in the residue of the test run at 170°C, which also displayed the most severe passivation behavior.

![Figure 6.30 SS Model for pyrite conversion data at various temperatures](image)

Figure 6.30 SS Model for pyrite conversion data at various temperatures
Figure 6. 31 SS Model for pyrite conversion data at various particle sizes

Figure 6. 32 SS Model for pyrite conversion data at various oxygen partial pressures
So, the question is, now that we know about this passivation phenomenon, how can we represent it mathematically?

According to equation (6.23),

\[
\frac{dX}{dt} = \frac{3}{\tau} (1-X)^{\frac{2}{3}} \quad \text{or} \quad \frac{d\sigma}{dt} = \frac{3\sigma^2}{\tau}
\]

so

\[
\frac{d\sigma}{dt} = -\frac{1}{\tau} \quad \text{or} \quad -\tau \frac{d\sigma}{dt} = 1 \quad (6.32)
\]

However, plots of \(-\tau \frac{d\sigma}{dt}\) vs \(\sigma^2\), which represents the fraction of original particle surface area remaining, show a very different picture, as shown in Figures 6.33 through 6.35. Beyond a certain point (moving from right to left), the rate begins to decrease with decreasing particle surface area in a more or less linear fashion.
Figure 6. 33 Passivation test plots at various temperatures

Figure 6. 34 Passivation test plots at various particle sizes
If we define this point representing the onset of passivation on the x-axis as $\sigma_p$, then to the left of this point the rate is given thus:

$$-\tau \frac{d\sigma}{dt} = 1 - m (\sigma_p^2 - \sigma^2)$$  \hspace{1cm} (6.33)

where $m$ is the slope of the line, and represents the rate of the onset of passivation. The integrated form of this "passivating shrinking sphere model" (PSS Model) is:

$$\sigma = 1 - \frac{t}{\tau} \hspace{0.5cm} @ \hspace{0.5cm} \sigma \geq \sigma_p$$  \hspace{1cm} (6.34)
\[ \sigma = \lambda \left[ \frac{\sigma_p - \lambda \tan(\lambda \phi)}{\lambda + \sigma_p \tan(\lambda \phi)} \right] \quad @ \quad \sigma \leq \sigma_p \quad \text{and} \quad m\sigma_p^2 < 1 \quad (6.35) \]

\[ \sigma = \frac{\sigma_p}{1 + \sigma_p \phi} \quad @ \quad \sigma \leq \sigma_p \quad \text{and} \quad m\sigma_p^2 = 1 \quad (6.36) \]

\[ \sigma = \lambda \left[ \frac{(\sigma_p + \lambda) + (\sigma_p - \lambda) \exp(-2\lambda \phi)}{(\sigma_p + \lambda) - (\sigma_p - \lambda) \exp(-2\lambda \phi)} \right] \quad @ \quad \sigma \leq \sigma_p \quad \text{and} \quad m\sigma_p^2 > 1 \quad (6.37) \]

where \( \lambda = \left( \frac{1 - m\sigma_p^2}{m} \right)^{\frac{1}{2}} \) and \( \phi = m \left[ \frac{1 - \frac{t}{\tau}}{\sigma_p} \right] \)

When \( m\sigma_p^2 \leq 1 \), then the line intersects the y-axis and the reaction goes to completion, since the rate is still non-zero at 100% conversion; hence, incomplete passivation. However, when \( m\sigma_p^2 > 1 \), then the line intersects the x-axis and the reaction fails to go to completion, since the rate falls to zero before complete conversion is reached; hence, complete passivation. Instead, a limiting particle size is approached asymptotically; \( i.e.: \)

\[ \lim_{t \to \infty} \sigma = 0 \quad @ \quad m\sigma_p^2 = 1 \]

\[ \lim_{t \to \infty} \sigma = \lambda \quad @ \quad m\sigma_p^2 > 1 \]
Both situations can be seen in Figures 6.33 through 6.35. Complete passivation is achieved at the two lowest temperatures, at the two coarsest particle sizes, and at the lowest oxygen partial pressure, and this observation is borne out in the conversion data in Figures 6.30 through 6.32. Figures 6.36 through 6.38 show how well the passivating shrinking sphere model fits the data based on the best fit values of $m$ and $\sigma^2_p$ represented by the "predicted lines" of Figure 6.33 through 6.35.

![Figure 6.36 Test for the passivating shrinking sphere model at various temperatures](image-url)
Figure 6. 37 Test for the passivating shrinking sphere model at various particle sizes

Figure 6. 38 Test for the passivating shrinking sphere model at various oxygen partial pressures
6.5 Summary

The acid pressure oxidation of pyrite with oxygen was studied under various experimental conditions in the temperature range 170 to 230°C, and the reaction products were determined. Pyrite reacts with oxygen yielding elemental sulfur, sulfate, Fe(II) and Fe(III). Elemental sulfur is produced only at low temperature (<190°C).

For the reaction mechanism at high temperature it is postulated that pyrite is initially oxidized to ferric sulfate, instead of ferrous sulfate, by dissolved oxygen. The dissolved oxygen is chemisorbed on the pyrite surface at the beginning. Then, ferric produced during the early stages oxidizes the sulfide in the pyrite to produce ferrous sulfate and sulfuric acid. Therefore, ferrous generated during pressure oxidation of pyrite is not a direct product of the oxidation of pyrite by oxygen. The role of ferric in the overall reaction as the actual oxidizer is not obvious. Ferrous sulfate can be oxidized to ferric sulfate by dissolved oxygen. Ferric sulfate thus formed oxidizes the sulfide in the pyrite or hydrolyzes.

The kinetics of pressure oxidation of pyrite were studied under various conditions in the temperature range of 170 to 230°C. A number of conclusions may be drawn from the foregoing results:

1. Pyrite is oxidized electrochemically by dissolved oxygen and ferric ion during acid oxygen pressure leaching at high temperature.
2. The final products are ferric sulfate, sulfuric acid and ferrous sulfate, but no elemental sulfur at temperatures above 190°C.

3. The reaction rate of pyrite dissolution is strongly temperature and particle size dependent, and is one half order with respect to oxygen particle pressure.

4. The oxidation kinetics are controlled by the surface reactions with an Arrhenius activation energy of 33.2 kJ/mol (7.94 kcal/mol).

5. The reaction rate is increased by increasing the pulp density or adding cupric ions. These findings indicate that reproduction of ferric by oxygen conversion of ferrous significantly affects the distribution of products and the reaction rate of pyrite oxidation. Also, it suggests the importance of pyrite surface area to the overall kinetics.

6. The passivating shrinking sphere model was developed to represent the pressure oxidation of pyrite in the system studied at high temperature, which fits the experimental data very well. The equations are shown as following:

\[ \sigma = 1 - \frac{t}{\tau} \quad \text{at} \quad \sigma \geq \sigma_p \]

\[ \sigma = \frac{\sigma_p - \lambda \tan(\lambda \phi)}{\lambda + \sigma_p \tan(\lambda \phi)} \quad \text{at} \quad \sigma \leq \sigma_p \quad \text{and} \quad m \sigma_p^2 < 1 \]
\[ \sigma = \frac{\sigma_p}{1 + \sigma_p \phi} \quad @ \quad \sigma \leq \sigma_p & m\sigma_p^2 = 1 \]

\[ \sigma = \lambda \left[ \frac{(\sigma_p + \lambda) + (\sigma_p - \lambda) \exp(-2\lambda \phi)}{(\sigma_p + \lambda) - (\sigma_p - \lambda) \exp(-2\lambda \phi)} \right] \quad @ \quad \sigma \leq \sigma_p & m\sigma_p^2 > 1 \]

where \( \lambda = \left( \frac{1 - m\sigma_p^2}{m} \right)^{\frac{1}{2}} \) and \( \phi = m \left[ \sigma_p - \left( 1 - \frac{t}{\tau} \right) \right] \)

where \( \sigma_p \) represents the particle size at the onset of passivation, and \( m \) represents the passivation rate.
References


The behaviors of the individual minerals, orpiment and pyrite, during pressure oxidation have been presented in Chapters 5 and 6, respectively. However, real ores or concentrates tend to be assemblages of more than one mineral. Hence, the behavior of mixtures of the two minerals is perhaps more interesting, and will be discussed in this Chapter.

The interactions of pyrite and orpiment at different mole ratios of iron to arsenic were investigated. The conditions of the experiments were 210°C, 100 psi oxygen partial pressure, 800 rpm agitation speed, -100+140 mesh particle size, and 2 hours retention time in a solution containing 0.1 M H\textsubscript{2}SO\textsubscript{4}. The weight of the sample in each experiment was kept the same. Table 7-1 lists the mole ratios of Fe/As for the experiments.

<table>
<thead>
<tr>
<th>Test</th>
<th>Wt. of orpiment</th>
<th>Wt. of pyrite</th>
<th>Total wt.</th>
<th>Mole ratio of Fe/As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orpiment</td>
<td>168</td>
<td>0</td>
<td>168</td>
<td>0</td>
</tr>
<tr>
<td>Mix1</td>
<td>102</td>
<td>66</td>
<td>168</td>
<td>0.7</td>
</tr>
<tr>
<td>Mix2</td>
<td>72</td>
<td>96</td>
<td>168</td>
<td>1.5</td>
</tr>
<tr>
<td>Mix3</td>
<td>45</td>
<td>123</td>
<td>168</td>
<td>3</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0</td>
<td>168</td>
<td>168</td>
<td>∞</td>
</tr>
</tbody>
</table>
The study of pressure oxidation of a mixture of minerals is more difficult than a single mineral, especially for mixtures of pyrite and orpiment, because iron and arsenic generated from pyrite and orpiment precipitate iron arsenate during pressure oxidation. Also, iron will precipitate as hematite or basic iron sulfate. These precipitates make it difficult to determine the conversion of each mineral after pressure oxidation. A method was used to try to solve this problem, which was based on the mass balance of each mineral. The mass balances of arsenic and iron in orpiment and pyrite can be presented as in equations (7.1) and (7.2), respectively.

\[ W_{\text{Total As}} = W_{\text{As in orpiment}} + W_{\text{As in FeAsO}_4} + W_{\text{As in solution}} \]  
\[ (7.1) \]

\[ W_{\text{Total Fe}} = W_{\text{Fe in pyrite}} + W_{\text{Fe in hematite}} + W_{\text{Fe in FeAsO}_4} + W_{\text{Fe in solution}} \]  
\[ (7.2) \]

where

- \( W_{\text{Total As}} \) total arsenic inputted, gram
- \( W_{\text{As in orpiment}} \) arsenic in unreacted orpiment, gram
- \( W_{\text{As in FeAsO}_4} \) arsenic in iron arsenate, gram
- \( W_{\text{As in solution}} \) arsenic in solution, gram
- \( W_{\text{Total Fe}} \) total iron inputted, gram
- \( W_{\text{Fe in pyrite}} \) iron in unreacted pyrite, gram
- \( W_{\text{Fe in hematite}} \) iron in hematite, gram
- \( W_{\text{Fe in FeAsO}_4} \) iron in iron arsenate, gram
- \( W_{\text{Fe in solution}} \) iron in solution, gram
Total arsenic and iron in solution can be analyzed easily by an atomic adsorption spectrometer. If the amounts of arsenic in unreacted orpiment and iron in hematite are determined by dissolving them from residues selectively, then the amounts of arsenic in iron arsenate and iron in pyrite can be calculated according to equations (7.1) and (7.2), respectively. Thus the conversions of the individual minerals could be determined. In alkaline solution, only orpiment can be dissolved, while only hematite is dissolved selectively in hydrochloric acid.

In order to determine whether orpiment could be dissolved in alkaline solution completely, a set of tests was conducted by boiling 1 gram of orpiment in 1 and 3 M NaOH solution respectively for different times. The results of the tests are shown in Figure 7.1. It is evident that orpiment cannot be dissolved completely even in 3 M NaOH for 8 hours, in which conditions only about 78% of orpiment was dissolved. No other reagent was found for this purpose. Therefore, the method above could not be used for determining the conversions of minerals during pressure oxidation. However, the interaction of the minerals could be studied on the basis of the solution chemistry and the characteristics of the leaching residues during pressure oxidation.
7.1 Results and Discussion

7.1.1 Solution Chemistry

Figure 7.2 shows the ratio of ferrous to total iron in solution during the pressure oxidation of pyrite in the absence of orpiment. The ratio of Fe(II)/Fe decreases with time, which is the same finding as in Chapter 6 (Figure 6.4).
Figure 7.2 Iron distribution during pressure oxidation of pyrite at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 168 g/L pyrite with 0.1 M H₂SO₄.

Figure 7.3 shows the concentrations of total iron and ferrous in the solution during the pressure oxidation of pyrite. It is evident that the concentration of total iron in the solution was maintained at about 14 g/L after 30 minutes even though pyrite was further oxidized, which reflects the solubility of iron in the system. Any iron will precipitate when the concentration is beyond this point.
Figure 7.3 Concentrations of total iron and ferrous with time for the Pyrite test at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 168 g/L pyrite with 0.1 M \( \text{H}_2\text{SO}_4 \).

Figure 7.4 shows the ratio of As(III)/As(V) during pressure oxidation of orpiment in the absence of pyrite. It is obvious that As(III) is a predominant species (more than 96%) in solution after pressure oxidation. No As(III) was oxidized until 90 minutes. These findings are the same as in Chapter 5.
Figure 7.4 Product distribution of arsenic during pressure oxidation at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 168 g/L orpiment with 0.1 M H$_2$SO$_4$.

Figure 7.5 shows both ratios of Fe(II)/Fe and As(III)/As during pressure oxidation for the Mix1 test, which is the mixture of pyrite and orpiment at a mole ratio of Fe/As = 0.7. It is obvious that As(III) can be oxidized to As(V) quickly in the presence of pyrite, actually in the presence of ferric. This has been discovered already in Chapter 5. The ratio of Fe(II)/Fe declines more slowly than the ratio of As(III)/As and the ratio of Fe(II)/Fe in the absence of orpiment (see Figure 7.2), especially in the first 30 minutes. This may be because ferric is reduced by oxidizing As(III), orpiment, or pyrite.
Figure 7. 5 Ratios of Fe(II)/Fe and As(III)/As with time for the Mix1 test at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 0.1 M H_2SO_4

Figure 7.6 shows the concentrations of total iron and total arsenic in the solution during pressure oxidation. It can be seen that the concentration of arsenic increases rapidly in the first 15 minutes, then increases steadily. The high concentration of arsenic in solution indicates that orpiment may be oxidized preferentially in the mixture. The concentration of iron stays very low (less than 1 g/L) during pressure oxidation due to the formation of iron arsenate.
Figure 7.7 shows both ratios of Fe(II)/Fe and As(III)/As during pressure oxidation for the Mix2 test, which had a mole ratio of Fe/As = 1.5. Comparing Figures 7.5 and 7.7, it can be seen that the ratio of As(III)/As decreases even more quickly as the mole ratio of Fe/As increases. However, the ratio of Fe(II)/Fe decreases more slowly. Figure 7.8 shows the concentrations of total iron and total arsenic in the solution during pressure oxidation. It is evident that the concentration of arsenic increases more quickly, while the concentration of iron starts to increase only when the concentration of arsenic decreases. This finding further indicates that orpiment may be oxidized preferentially in the mixture.
Figure 7. 7 Ratios of Fe(II)/Fe and As(III)/As with time for the Mix2 test at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 0.1 M H₂SO₄

Figure 7. 8 Concentrations of total iron and arsenic with time for the Mix2 test at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 0.1 M H₂SO₄
Figure 7.9 shows both ratios of Fe(II)/Fe and As(III)/As during pressure oxidation for Mix3 test, which had a mole ratio of Fe/As = 3. Comparison Figure 7.9 to Figure 7.7, there is little effect of the mole ratio of Fe/As on the oxidation rate of As(III). However, the oxidation rate of ferrous decreases. It is interesting to see from Figure 7.9 that the ratio of Fe(II)/Fe stays at about the same level (70%) before the ratio of As(III)/As reaches its lowest level in 60 minutes. Then it starts to decline at a constant rate. The concentrations of total iron and total arsenic in the solution during pressure oxidation are illustrated in Figure 7.10. It is obvious that the concentration of iron only increases when the concentration of arsenic decreases. Now it can be concluded that orpiment is oxidized preferentially in the presence of pyrite.
Figure 7.10 Concentrations of total iron and arsenic with time for the Mix3 test at 210°C, 100 psi, 800 rpm, -100+140 mesh, and 0.1 M H$_2$SO$_4$

7.1.2 Solids Analysis

Figure 7.11 shows the percentage of sulfide oxidation for all the tests. It is obvious that pyrite can be oxidized completely in the absence of orpiment after pressure oxidation. However, only about half of the orpiment was oxidized in the absence of pyrite. In terms of kinetics, orpiment oxidation alone is slower than pyrite alone. Figure 7.12 shows comparative sulfide oxidation curves for the two minerals. Figure 7.13 shows cumulative oxygen consumption for each test. The oxidation rate of pure pyrite is very fast. It was oxidized completely in 90 minutes even though it contains the highest sulfide content among all the tests. The extent of sulfide oxidation increases with increasing additions of
pyrite. In other words, the oxidation of orpiment is accelerated in the presence of pyrite. This is so because the Fe(III)/Fe(II) couple, generated from pyrite, exhibits negligible overpotential in comparison to the O_2/H_2O couple, which makes the former a more effective oxidant for orpiment. Oxygen simply helps to regenerate the “catalyst” Fe(III), which in turn attacks orpiment and the leaching reaction is sustained at a high rate. A similar situation occurs during the pressure oxidation of zinc sulfide.

Besides the Orpiment test, elemental sulfur (3 %) was only found in the Mix1 test residue, which had a low mole ratio of Fe/As (= 0.7). When the mole ratio of Fe/As was equal to or more than 1.5, no elemental sulfur was found in the residues. This indicates that a certain amount of pyrite is required to prevent the formation of elemental sulfur in the mixture.

![Figure 7.11 Percentage of sulfide oxidation for all the tests](image)
Figure 7.12 Sulfide oxidation of the individual minerals

Figure 7.13 Cumulative oxygen consumption
Table 7-4 lists the minerals in the residues, which were identified by X-ray diffraction. The X-ray patterns for these residues are illustrated in Figures IV.6 to IV.10 respectively in Appendix IV.

Table 7-2  Results of X-ray analysis of residues after pressure oxidation

<table>
<thead>
<tr>
<th>Test I.D.</th>
<th>Minerals after pressure oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>Basic iron sulfate (FeOHSO₄)</td>
</tr>
<tr>
<td>Orpiment</td>
<td>Elemental sulfur, Arsenolite (As₂O₃), Orpiment</td>
</tr>
<tr>
<td>Mix1</td>
<td>Iron arsenate hydrate (FeAsO₄H₂O), Elemental sulfur, Pyrite, Orpiment, Quartz</td>
</tr>
<tr>
<td>Mix2</td>
<td>Iron arsenate hydrate (FeAsO₄H₂O), Hematite, Pyrite, Quartz</td>
</tr>
<tr>
<td>Mix3</td>
<td>Iron arsenate hydrate (FeAsO₄H₂O), Hematite, Quartz</td>
</tr>
</tbody>
</table>

Basic iron sulfate, instead of hematite, is the only product in the residue generated from the oxidation of pyrite. The formation of basic iron sulfate must be due to the generation of sulfuric acid during pressure oxidation of pyrite. Elemental sulfur and arsenolite were the products of pressure oxidation of orpiment. The presence of arsenolite in the residue was mainly because the residue was not well washed. Iron arsenate hydrate, one of the scorodite-class compounds, was identified in the residues after pressure oxidation of the mixtures. A SEM micrograph of typical iron arsenate crystals is presented in Figure 7.15. The property of well crystallized iron arsenate is of critical importance in view of the current controversy surrounding the environmental stability of these compounds. Krause and Ettel [1] have demonstrated that well crystallized iron arsenate exhibits two orders of magnitude lower solubility than reported previously in the literature [2]. Thus it can be
concluded that from the environmental standpoint pressure oxidation is expected to produce less troublesome arsenic residues than other hydrometallurgical processes, such as biological and chemical, operated under milder oxidation conditions.

Figure 7.14 Iron arsenate crystals produced from oxidation of the mixture

In the mixtures of pyrite and orpiment, elemental sulfur was identified only in the residue of the Mix1 test (Fe/As=0.7), which is consistent with the assay results. It disappeared as the mole ratio of Fe/As was increased to 1.5.
Both unreacted pyrite and orpiment were found in the Mix1 residue. X-ray diffraction analysis of the Mix1 residue failed to reveal the presence of hematite, which may indicate that iron precipitates with arsenic as iron arsenate preferentially. As the mole ratio of Fe/As increased to 1.5, orpiment was not found in the residue, but pyrite was still there. Pyrite disappeared from the residue as the mole ratio of Fe/As was further increased to 3. Now the products were iron arsenate and hematite. These results further support the conclusion that orpiment is oxidized preferentially in the mixture. These findings can be explained by galvanic interactions.

Galvanic effects, occurring in suspensions of electrically conducting minerals in aqueous solutions, play an important role in the wet processing of ores and minerals. These effects accelerate or retard the dissolution of minerals in hydrometallurgical systems. When two conducting minerals are in electrical contact in a slurry system, the one with the more negative rest potential will dissolve preferentially. The cathodic reduction takes place at the surface of the mineral with the more positive rest potential and there is a net flow of electrons between the minerals. Extensive investigations of the influence of galvanic effects on the kinetics of mineral dissolution have been carried out by several investigators [3, 4, 5, 6]. In gold extraction systems, galvanic interactions can affect both metal and sulfide dissolution rates.

Contact between two or more of sulfide minerals may lead to alteration of their electrochemical dissolution kinetics. This would depend again on the intrinsic electrochemical properties of the minerals involved. The evidence for the galvanic
effects was obtained by Peters [7] who combined mixtures of pyrite with galena, covellite, and sphalerite. His results showed that the presence of pyrite accelerated the oxygen pressure leaching of all these minerals, while the leaching rate of pyrite was substantially suppressed by the presence of the other minerals. Orpiment may also behave as these minerals when it contacts directly with nobler pyrite. The net result of this process is the cathodic protection of pyrite, which will then require more time to oxidize completely.

7.2 Comparison to Results of Real Ore Oxidation

In order to prove the findings above, experiments were conducted on real refractory sulfide ores. Two samples were provided by the Barrick Goldstrike Mine, denoted UBC-1 (high arsenic) and UBC-2 (blending material), respectively. UBC-1 sample was representative of ore giving low gold recoveries, while UBC-2 sample was representative of normal ore giving high recoveries. Before the experiments, the ore samples were pulverized from about 2 mm to 90% passing 100 mesh (about 150 μm) and well mixed. The compositions of each sample are listed in Table 7-2. Arsenic content in the UBC-1 ore is much higher than in the UBC-2 ore. The mole ratio of iron to arsenic is about 1.5 in the UBC-1 sample, and more than 7 in the UBC-2 sample.
Table 7-3  Compositions of the refractory sulfide gold ores

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CO$_3^-$ (%)</th>
<th>Total S (%)</th>
<th>S$^2-$ (%)</th>
<th>Al (%)</th>
<th>As (%)</th>
<th>Fe (%)</th>
<th>Ca (%)</th>
<th>Cu (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBC-1</td>
<td>2.64</td>
<td>4.81</td>
<td>3.64</td>
<td>1.05</td>
<td>3.23</td>
<td>3.63</td>
<td>2.3</td>
<td>48</td>
</tr>
<tr>
<td>UBC-2</td>
<td>6.20</td>
<td>2.69</td>
<td>2.34</td>
<td>2.60</td>
<td>0.58</td>
<td>3.10</td>
<td>2.7</td>
<td>48</td>
</tr>
</tbody>
</table>

Possible minerals identified by X-ray diffraction in both ore samples are presented in Table 7-3. Pyrite and realgar are the only sulfide minerals found in the UBC-1 sample. The minerals in the UBC-2 sample are the same as those in the UBC-1 sample except for realgar, which may occur, albeit in too small of a quantity to be detected by X-ray, in the former. Arsenic was assumed to exist primarily as realgar in the UBC-1 sample because no other arsenic mineral was identified. Although the behavior of pure realgar was not studied, it is believed that its behavior during acidic pressure oxidation should be similar to orpiment.

Table 7-4 Possible minerals in the UBC-1 and UBC-2 ore samples.

<table>
<thead>
<tr>
<th>UBC-1</th>
<th>Formula</th>
<th>UBC-2</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minerals</td>
<td>Formula</td>
<td>Minerals</td>
<td>Formula</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>Quartz</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS$_2$</td>
<td>Pyrite</td>
<td>FeS$_2$</td>
</tr>
<tr>
<td>Realgar</td>
<td>AsS</td>
<td>Dolomite</td>
<td>CaMg(CO$_3$)$_2$</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO$_3$)$_2$</td>
<td>Calcite</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>Muscovite</td>
<td>KAl$_2$Si$<em>3$AlO$</em>{10}$(OH)$_2$</td>
</tr>
<tr>
<td>Muscovite</td>
<td>KAl$_2$Si$<em>3$AlO$</em>{10}$(OH)$_2$</td>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$O$_5$(OH)$_4$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

202
The conditions for the tests were 210°C, 110 psi of oxygen partial pressure, 1000 rpm of agitation speed, and 40% pulp density. The slurry was acidified to destroy carbonate at room temperature, and pH was adjusted to 2.5 before autoclaving. Figure 7-15 shows the sulfide oxidation with time for both ores. The UBC-2 ore reached a higher degree of oxidation than the UBC-1 ore before 60 minutes. After 60 minutes, both ores are virtually completely oxidized. The UBC-1 ore needs more time to oxidize to the same extent as the UBC-2 ore. Figure 7-16 shows the concentrations of iron and arsenic in solution during pressure oxidation of the UBC-1 sample. It is clear that the concentration of arsenic is higher than that of iron before 60 minutes, and especially around 15 minutes. This is essentially the same behavior exhibited by the pyrite/orpiment mixtures.

![Sulfide oxidation for the samples](image)

Figure 7.15 Sulfide oxidation for the samples
Gold extraction from both ores at different autoclave retention times is shown in Figure 7-17, which indicates that the UBC-2 sample needed only 15 minutes oxidation in the autoclave to achieve more than 90% gold extraction, while the UBC-1 needed 30 minutes oxidation. Now it can be safely concluded that decreased gold extractions in the Barrick Goldstrike Mine circuit in the presence of high arsenic/high sulfur ores are primarily the result of inadequate residence time for complete oxidation of the gold-hosting pyrite, due to the preferential oxidation of (non-gold bearing) arsenic sulfides.

Figure 7. 16 Metal concentration with retention time for the UBC-1 sample
7.3 Summary

The acidic pressure oxidation of mixtures of pyrite and orpiment with oxygen was investigated under various experimental conditions and different ratios of Fe/As. Both solution chemistry and solid reaction products were studied. The pressure oxidation of the mixture yields sulfate, ferric, ferrous, arsenic (III), arsenic (V), iron arsenate, hematite, and elemental sulfur. Iron arsenate was generated in all tests conducted with the mixtures, which is of critical importance in view of the current controversy surrounding the environmental stability of these compounds. Elemental sulfur was produced only at the lowest mole ratio of Fe/As (= 0.7). Ferric and arsenic (V) are the predominant species in the final solution. The Fe(III)/Fe(II) couple plays a very
important role during pressure oxidation. In the presence of pyrite, As(III) generated from orpiment can be oxidized rapidly to very low levels. However, the oxidation rate of ferrous decreases in the presence of orpiment.

The kinetics of pressure oxidation of orpiment are much slower due to the formation of elemental sulfur, while pyrite oxidation is very fast. However, when the two minerals are mixed together, preferential leaching for orpiment is feasible due to galvanic effects. Thus orpiment oxidation is accelerated, while pyrite oxidation is retarded. The net result of this process is the cathodic protection of pyrite, which will then require more time to oxidize completely. Based on the findings of the mixtures and the real Barrick gold ore sample, it can be concluded that decreased gold extractions in the Barrick Goldstrike Mine circuit in the presence of high arsenic/high sulfur ores are primarily the result of inadequate residence time for complete oxidation of the gold-hosting pyrite.
Reference


CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The autoclave oxidation of orpiment and pyrite as a pretreatment of refractory gold ores has been studied respectively in terms of investigating the dissolution behaviors of orpiment and pyrite in sulfuric acid system. Also, the interaction of pyrite and orpiment during pressure oxidation at the different mole ratios of Fe/As has been evaluated. The conclusions are summarized as follows:

8.1.1 Reaction Chemistry of Orpiment

In the acid pressure oxidation of orpiment system, the products are elemental sulfur, sulfate, As(III) and As(V). Elemental sulfur is produced under all conditions tested (temperature range from 170 to 230°C at 100 psi of oxygen partial pressure). Most of the dissolved arsenic is in the trivalent state after two hours of oxidation, even at temperatures up to 230°C and oxygen partial pressures up to 150 psi. As the oxidation of orpiment progresses with time, both the ratio of As(III) to total dissolved arsenic and the ratio of elemental sulfur to total sulfur oxidized decrease.
It is postulated that both elemental sulfur and sulfate are direct products of orpiment oxidation via two parallel and competing reactions. The predominant species at temperatures below 190°C is elemental sulfur, and sulfate is predominant above 190°C. Elemental sulfur can be further oxidized to sulfate. This reaction is slow at low temperature, but fast at high temperature (> 210°C).

Oxidation of orpiment yields $\text{H}_3\text{AsO}_3$ in solution, and not $\text{H}_3\text{AsO}_4$, which is the thermodynamically stable species. It appears that As(III) enjoys a considerable degree of metastability in the sulfuric acid system. Cupric ions do not affect the oxidation of As(III). However, the oxidation of As(III) is rapid in the presence of ferric ions, resulting in the precipitation of ferric arsenate.

8.1.2 Reaction Kinetics of Orpiment

The kinetics of pressure oxidation of orpiment were studied under various conditions in the temperature range of 170 to 230°C. A number of conclusions may be drawn from the foregoing results:

1. The reaction rate of orpiment dissolution is strongly temperature and particle size dependent. The higher the temperature or the smaller the particle size, the faster the reaction rate,
2. The oxidation kinetics are controlled by product layer diffusion with an Arrhenius activation energy of 22.2 kJ/mol (5.31 kcal/mol) over the temperature range of 170 to 210°C. However, as temperature increases from 210 to 230°C, the rate controlling step is switched to surface chemical reaction with an Arrhenius activation energy of 50.0 kJ/mol (12.0 kcal/mol).

3. The reaction rate is decreased with increasing pulp density because more elemental sulfur is formed at high pulp density. It was found that the initial reaction rate is about negative one fifth order with respect to pulp density.

4. The rate of oxidation of orpiment is not affected significantly by agitation speed and oxygen partial pressure. The results indicate that the initial reaction rate is one quarter order with respect to oxygen partial pressure.

5. The reaction rate equation for dissolution of orpiment in the system studied at the baseline (e.g. 210°C, -200+270 mesh, 0.1 M H₂SO₄ and low pulp density) was formulated as

\[-r_{A_{2}S_{1}} = \gamma A_{t} k[\phi f(T)P_{O_{2}}]^{1/4} \phi_{A_{2}S_{1}}^{1/2}\]

where

\(\gamma\) : a stoichiometric factor;

\(A_{t}\) : total surface area of un-reacted core at time \(t\);
8.1.3 Reaction Chemistry of Pyrite

The acid pressure oxidation of pyrite with oxygen was studied under various experimental conditions in the temperature range 170 to 230°C, and the reaction products were determined. Pyrite reacts with oxygen yielding elemental sulfur, sulfate, Fe(II) and Fe(III). Elemental sulfur is produced only at low temperature (<190°C).

For the reaction mechanism at high temperature it is postulated that pyrite is initially oxidized to ferric sulfate, instead of ferrous sulfate, by dissolved oxygen. The dissolved oxygen is chemisorbed on the pyrite surface at the beginning. Then, ferric produced during the early stages oxidizes the sulfide in the pyrite to produce ferrous sulfate and sulfuric acid. Therefore, ferrous generated during pressure oxidation of pyrite is not a direct product of the oxidation of pyrite by oxygen. The role of ferric in the overall reaction as the actual oxidizer is not obvious. Ferrous sulfate can be oxidized to ferric sulfate by dissolved oxygen. Ferric sulfate thus formed oxidizes the sulfide in the pyrite or hydrolyzes.
8.1.4 Reaction Kinetics of Pyrite

The kinetics of pressure oxidation of pyrite were studied under various conditions in the temperature range of 170 to 230°C. A number of conclusions may be drawn from the foregoing results:

1. Pyrite is oxidized electrochemically by dissolved oxygen and ferric ion during acid oxygen pressure leaching at high temperature.

2. The final products are ferric sulfate, sulfuric acid and ferrous sulfate, but no elemental sulfur at temperatures above 190°C.

3. The reaction rate of pyrite dissolution is strongly temperature and particle size dependent, and is one half order with respect to oxygen particle pressure.

4. The oxidation kinetics are controlled by the surface reactions with an Arrhenius activation energy of 33.2 kJ/mol (7.94 kcal/mol).

5. The reaction rate is increased by increasing the pulp density or adding cupric ions. These findings indicate that reproduction of ferric by oxygen conversion of ferrous significantly affects the distribution of products and the reaction rate of pyrite oxidation. Also, it suggests the importance of pyrite surface area to the overall kinetics.
6. The passivating shrinking sphere model was developed to represent the pressure oxidation of pyrite in the system studied at high temperature, which fits the experimental data very well. The equations are as follows:

\[
\sigma = 1 - \frac{t}{\tau} \quad @ \quad \sigma \geq \sigma_p
\]

\[
\sigma = \lambda \left[ \frac{\sigma_p - \lambda \tan(\lambda \phi)}{\lambda + \sigma_p \tan(\lambda \phi)} \right] \quad @ \quad \sigma \leq \sigma_p \quad & \quad m \sigma_p^2 < 1
\]

\[
\sigma = \frac{\sigma_p}{1 + \sigma_p \phi} \quad @ \quad \sigma \leq \sigma_p \quad & \quad m \sigma_p^2 = 1
\]

\[
\sigma = \lambda \left[ \frac{(\sigma_p + \lambda) + (\sigma_p - \lambda) \exp(-2\lambda \phi)}{(\sigma_p + \lambda) - (\sigma_p - \lambda) \exp(-2\lambda \phi)} \right] \quad @ \quad \sigma \leq \sigma_p \quad & \quad m \sigma_p^2 > 1
\]

where \( \lambda = \left( \frac{1 - m \sigma_p^2}{m} \right)^{1/2} \) and \( \phi = m \left( \sigma_p - \left( 1 - \frac{t}{\tau} \right) \right) \)

where \( \sigma_p \) represents the particle size at the onset of passivation, and \( m \) represents the passivation rate.
8.1.5 Interaction of Pyrite and Orpiment

The acidic pressure oxidation of mixtures of pyrite and orpiment with oxygen was investigated under various experimental conditions and different ratios of Fe/As. Both solution chemistry and solid reaction products were studied. The pressure oxidation of the mixture yields sulfate, ferric, ferrous, arsenic (III), arsenic (V), iron arsenate, hematite, and elemental sulfur. Iron arsenate was generated in all tests conducted with the mixtures, which is of critical importance in view of the current controversy surrounding the environmental stability of these compounds. Elemental sulfur was produced only at the lowest mole ratio of Fe/As (= 0.7). Ferric and arsenic (V) are the predominant species in the final solution. The Fe(III)/Fe(II) couple plays a very important role during pressure oxidation. In the presence of pyrite, As(III) generated from orpiment can be oxidized rapidly to very low levels. However, the oxidation rate of ferrous decreases in the presence of orpiment.

The kinetics of pressure oxidation of orpiment are much slower due to the formation of elemental sulfur, while pyrite oxidation is very fast. However, when the two minerals are mixed together, preferential leaching of orpiment is feasible due to galvanic effects. Thus orpiment oxidation is accelerated, while pyrite oxidation is retarded. The net result of this process is the cathodic protection of pyrite, which will then require more time to oxidize completely.
8.2 Recommendations for Future Work

This study revealed certain areas that require further study. The following recommendations are proposed:

A. Studies on the kinetics of each mineral were all conducted at a relatively low pulp density. However, in real systems very high pulp densities are employed. Hence, the data obtained in the present study should be verified at pulp densities similar to those used in real systems.

B. An effective way to determine the conversion of each mineral during pressure oxidation of mineral mixtures of pyrite and orpiment should be found.

C. The kinetics should be expanded into a model of continuous autoclave leaching and validated against actual plant operating data.
APPENDIX I

THERMODYNAMIC DATA FOR Eh-pH DIAGRAMS AT 25°C

Tables I-1 through I-4 show the complete set of species considered and thermodynamic data used for the calculations of Eh-pH diagrams in the different systems at room temperature (25°C) in Chapter 3.

Table I-1 Data for Fe-S-H₂O system at 25°C

<table>
<thead>
<tr>
<th>Name of the diagram:</th>
<th>Fe-S-H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td># Components</td>
<td>2</td>
</tr>
<tr>
<td>Temp °C</td>
<td>25</td>
</tr>
<tr>
<td>dG water</td>
<td>-56.67519</td>
</tr>
<tr>
<td>Dielect C.</td>
<td>78.54</td>
</tr>
<tr>
<td>Lowest Eh</td>
<td>-1</td>
</tr>
<tr>
<td>Highest Eh</td>
<td>1</td>
</tr>
<tr>
<td>Lowest pH</td>
<td>0</td>
</tr>
<tr>
<td>Highest pH</td>
<td>14</td>
</tr>
<tr>
<td>dG D-base</td>
<td>N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Species and Free Energy (kcal)</th>
</tr>
</thead>
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<tr>
<td>S</td>
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</tr>
<tr>
<td>1</td>
<td>S 2- A 20.507</td>
</tr>
<tr>
<td>4</td>
<td>HS - A 2.8872</td>
</tr>
<tr>
<td>7</td>
<td>HSO₄ - A -180.67</td>
</tr>
<tr>
<td>10</td>
<td>H₂SO₄ 0 A -177.97</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Fe 2+ A -22.05</td>
</tr>
<tr>
<td>14</td>
<td>Fe(OH)₂+ A -54.766</td>
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<tr>
<td>17</td>
<td>Fe(OH)₃ - A -148.48</td>
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<tr>
<td>20</td>
<td>Fe 0 S 0</td>
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<tr>
<td>23</td>
<td>Fe(OH)₃ 0 S -170.8</td>
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<tr>
<td>26</td>
<td>FeSO₄ 0 S -196.1</td>
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<table>
<thead>
<tr>
<th>Component</th>
<th>Species and Free Energy (kcal)</th>
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</thead>
<tbody>
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<td>S</td>
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<td>SO₃ 2- A -116.276</td>
</tr>
<tr>
<td>4</td>
<td>H₂SO₄ 0 A -6.65153</td>
</tr>
<tr>
<td>7</td>
<td>H₂SO₃ 0 A -128.54</td>
</tr>
<tr>
<td>10</td>
<td>SO₄ 2- A -177.9469</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Fe 3+ A -4.27</td>
</tr>
<tr>
<td>14</td>
<td>Fe(OH)₂+ A -108.42</td>
</tr>
<tr>
<td>17</td>
<td>Fe(OH)₃ 2- A -185.52</td>
</tr>
<tr>
<td>20</td>
<td>Fe(OH)₃ 0 S -177.44</td>
</tr>
<tr>
<td>23</td>
<td>Fe(OH)₃ 0 S -240.22</td>
</tr>
<tr>
<td>26</td>
<td>FeHSO₄ 2+ A -183.647</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Component</th>
<th>Species and Free Energy (kcal)</th>
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</thead>
<tbody>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SO₄ 2- A -177.9469</td>
</tr>
<tr>
<td>4</td>
<td>H₂SO₄ 0 A -6.65153</td>
</tr>
<tr>
<td>7</td>
<td>H₂SO₃ 0 A -128.54</td>
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<td>10</td>
<td>SO₄ 2- A -177.9469</td>
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<tr>
<td>Fe</td>
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<tr>
<td>11</td>
<td>Fe 3+ A -4.27</td>
</tr>
<tr>
<td>14</td>
<td>Fe(OH)₂+ A -108.42</td>
</tr>
<tr>
<td>17</td>
<td>Fe(OH)₃ 2- A -185.52</td>
</tr>
<tr>
<td>20</td>
<td>Fe(OH)₃ 0 S -177.44</td>
</tr>
<tr>
<td>23</td>
<td>Fe(OH)₃ 0 S -240.22</td>
</tr>
<tr>
<td>26</td>
<td>FeHSO₄ 2+ A -183.647</td>
</tr>
</tbody>
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216
Table I-2 Data for S-H₂O system at 25°C

Name of the diagram: S-H₂O

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<th>System data</th>
<th>Element</th>
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<th>Concentration</th>
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<th>cmpt#</th>
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<td>M</td>
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<td>10</td>
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<td>Temp oC</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dG water</td>
<td>-56.67519</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Dielect C.</td>
<td>78.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lowest Eh</td>
<td>-1</td>
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<tr>
<td>Highest Eh</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>I Strength</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dG D-base</td>
<td>N</td>
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Component | Species and Free Energy (kcal)

<table>
<thead>
<tr>
<th>Component</th>
<th>S 2- A</th>
<th>SO3 2- A</th>
<th>SO4 2- A</th>
<th>HS - A</th>
<th>H2S 0 A</th>
<th>HSO3 - A</th>
<th>H2SO3 0 A</th>
<th>SO S</th>
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<tbody>
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<td>4</td>
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<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
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<td>-128.5397</td>
<td>0</td>
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<td></td>
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</tbody>
</table>

217
Table I-3 Data for As-H₂O system at 25°C

<table>
<thead>
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<th>Name of the diagram:</th>
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</table>

<table>
<thead>
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<th>System data</th>
<th>Element</th>
<th>Unit</th>
<th>Concentration</th>
<th>spec</th>
<th>cmpt#</th>
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</tr>
<tr>
<td>Temp oC</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dG water</td>
<td>-56.67519</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dielect C.</td>
<td>78.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lowest Eh</td>
<td>-1</td>
<td></td>
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</tr>
<tr>
<td>Highest Eh</td>
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<tr>
<td>Highest pH</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I Strength</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dG D-base</td>
<td>N</td>
<td></td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Species and Free Energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>As</td>
</tr>
<tr>
<td>4</td>
<td>H₂AsO³ - A -140.327 5 H₂AsO₄ - A -180.0119 6 H₃AsO₃ 0 A -152.9159</td>
</tr>
<tr>
<td>7</td>
<td>H₃AsO₄ 0 A -183.078 8 As 0 S 0 9 As₂O₅ 0 S -186.9742</td>
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<td>10</td>
<td>As₄O₆ 0 S -275.796</td>
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</tbody>
</table>
Table I- 4 Data for As-S-H$_2$O system at 25°C

<table>
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<tr>
<th># Components</th>
<th>System data</th>
<th>Element</th>
<th>Unit</th>
<th>Concentration</th>
<th>#spec</th>
<th>cmpt#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp oC</td>
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<td>S</td>
<td>M</td>
<td>0.001</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>dG water</td>
<td>25</td>
<td>As</td>
<td>M</td>
<td>0.001</td>
<td>12</td>
<td>main</td>
</tr>
</tbody>
</table>

- $\Delta G$ water = -56.67519
- Dielect C. = 78.54
- Lowest Eh = -1
- Highest Eh = 1
- Lowest pH = 0
- Highest pH = 14
- I Strength = 0
- $\Delta G$ D-base = N

Component | Species and Free Energy (kcal)

<table>
<thead>
<tr>
<th>Component</th>
<th>Species</th>
<th>Free Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
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</tr>
<tr>
<td>1</td>
<td>S$^{2-}$</td>
<td>20.50669</td>
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<tr>
<td>4</td>
<td>HS$^{-}$</td>
<td>2.887189</td>
</tr>
<tr>
<td>7</td>
<td>HSO$_4^{-}$</td>
<td>-180.6668</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$SO$_4$ 0 L</td>
<td>-164.9147</td>
</tr>
<tr>
<td>As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>AsO$^{+}$</td>
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<tr>
<td>14</td>
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<tr>
<td>20</td>
<td>As$_4$O$_6$ 0 S</td>
<td>-275.7959</td>
</tr>
</tbody>
</table>

Component 3, 5, 6, 9, 13, 15, 18, 21
### THERMODYNAMIC DATA FOR Eh-pH DIAGRAMS AT 210°C

Tables II-1 and II-2 show the complete set of species considered and thermodynamic data used for the calculations of Eh-pH diagrams in the different systems at high temperature (210°C) in Chapter 3.

**Table II-1 Data for Fe-S-H$_2$O system at 210°C**

<table>
<thead>
<tr>
<th>Component</th>
<th>Species and Free Energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S 2- A 28.8946</td>
</tr>
<tr>
<td>2</td>
<td>SO3 2- A -89.8696</td>
</tr>
<tr>
<td>3</td>
<td>SO4 2- A -150.256</td>
</tr>
<tr>
<td>4</td>
<td>HS - A 9.5123</td>
</tr>
<tr>
<td>5</td>
<td>H2S 0 A -4.5981</td>
</tr>
<tr>
<td>6</td>
<td>HSO3 - A -112.553</td>
</tr>
<tr>
<td>7</td>
<td>HSO4 - A -161.649</td>
</tr>
<tr>
<td>8</td>
<td>H2SO3 0 A -121.3745</td>
</tr>
<tr>
<td>9</td>
<td>S 0 S 1.7855</td>
</tr>
<tr>
<td>10</td>
<td>H2SO4 0 A -151.2277</td>
</tr>
<tr>
<td>11</td>
<td>Fe 2+ A -18.8325</td>
</tr>
<tr>
<td>12</td>
<td>Fe 3+ A 4.91596</td>
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<tr>
<td>13</td>
<td>FeOH + A -59.9102</td>
</tr>
<tr>
<td>14</td>
<td>FeOH 2+ A -45.7673</td>
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<tr>
<td>15</td>
<td>Fe(OH)2 + A -90.5296</td>
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<tr>
<td>16</td>
<td>Fe(OH)3 - A -117.291</td>
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<tr>
<td>17</td>
<td>Fe 0 S -0.0062</td>
</tr>
<tr>
<td>18</td>
<td>Fe2O3 0 S -165.4647</td>
</tr>
<tr>
<td>19</td>
<td>Fe3O4 0 S -227.779</td>
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<tr>
<td>20</td>
<td>Fe(OH)3 0 S -147.7068</td>
</tr>
<tr>
<td>21</td>
<td>FeS 0 S -24.1727</td>
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<td>22</td>
<td>FeS2 0 S -37.8891</td>
</tr>
<tr>
<td>23</td>
<td>FeSO4 0 S -180.695</td>
</tr>
<tr>
<td>24</td>
<td>FeHSO4 2+ A -173.2344</td>
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<tr>
<td>25</td>
<td>FeHSO4 + A -184.362</td>
</tr>
<tr>
<td>26</td>
<td>FeSO4 + A -161.7198</td>
</tr>
</tbody>
</table>

**Name of the diagram:** Fe-S-H$_2$O

<table>
<thead>
<tr>
<th>System data</th>
<th>Element</th>
<th>Unit</th>
<th>Concentration</th>
<th>#spec</th>
<th>cmpt#</th>
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<td>2</td>
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<tr>
<td>210</td>
<td>Fe</td>
<td>M</td>
<td>0.01</td>
<td>16</td>
<td>main</td>
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Temp oC: 210

dG water: -49.824
Dielect C.: 32.89771
Lowest Eh: -1
Highest Eh: 1
Lowest pH: 0
Highest pH: 14
I Strength: 0

dG D-base: N
Table II-2 Data for As-S-H₂O system at 210°C

<table>
<thead>
<tr>
<th>Name of the diagram:</th>
<th>As-S-H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td># Components</td>
<td>2</td>
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<tr>
<td>Temp °C</td>
<td>210</td>
</tr>
<tr>
<td>Imose AQ?</td>
<td>N</td>
</tr>
<tr>
<td>dG water</td>
<td>-49.824</td>
</tr>
<tr>
<td>Dielect C.</td>
<td>32.89771</td>
</tr>
<tr>
<td>Lowest Eh</td>
<td>-1</td>
</tr>
<tr>
<td>Highest Eh</td>
<td>1</td>
</tr>
<tr>
<td>Lowest pH</td>
<td>0</td>
</tr>
<tr>
<td>Highest pH</td>
<td>14</td>
</tr>
<tr>
<td>I Strength</td>
<td>0</td>
</tr>
<tr>
<td>dG D-base</td>
<td>N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Species and Free Energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>S 2- A 28.8946 2 SO3 2- A -89.8696 3 SO4 2- A -150.256</td>
</tr>
<tr>
<td>4</td>
<td>HS - A 9.5123 5 H2S O A -4.5981 6 HSO3 - A -112.553</td>
</tr>
<tr>
<td>7</td>
<td>HSO4 - A -161.649 8 H2SO3 0 A -121.3745 9 S 0 S 1.7855</td>
</tr>
<tr>
<td>10</td>
<td>H2SO4 0 A -151.2277</td>
</tr>
<tr>
<td>As</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>H2AsO3 - A -120.912 15 H2AsO4 - A -156.5237 16 H3AsO3 0 A -139.461</td>
</tr>
<tr>
<td>17</td>
<td>H3AsO4 0 A -159.59 18 As O S -0.0129 19 As2O5 0 S -165.926</td>
</tr>
<tr>
<td>20</td>
<td>As2O3 0 S -126.311 21 As2S3 0 S -28.5966 22 As2S2 0 S -15.1448</td>
</tr>
</tbody>
</table>
**Entropy Estimations**

*Latimer's Method*

1. Arsenyl ion

According to Latimer [i], the standard entropy of a complex aqueous species can be approximated by adding the individual entropy contributions of the element and the ligand. Whereas the former is usually known, the latter may be calculated from available data for similar species. Thus, for the arsenyl ion, the entropy contribution of the ligand (oxygen) is calculated from the antimonyl ion. Table II-3 shows thermodynamic data used in the calculation of the standard entropy of the arsenyl ion.

Table II- 3 Thermodynamic data used in the calculation of the standard entropy of the arsenyl ion

<table>
<thead>
<tr>
<th>Species</th>
<th>$S_{298K}^o$ (species) J.mole$^{-1}$K$^{-1}$</th>
<th>$S_{298K}^o$ (element) J.mole$^{-1}$K$^{-1}$</th>
<th>$S_{298K}^o$ (ligand) J.mole$^{-1}$K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbO$^+$</td>
<td>22.33</td>
<td>45.522</td>
<td>-23.19</td>
</tr>
<tr>
<td>AsO$^+$</td>
<td>?</td>
<td>35.706</td>
<td>-23.19</td>
</tr>
</tbody>
</table>

Hence:

$$S_{298K}^o (\text{AsO}_2^+) = 35.706 + (-23.19) = 12.52 \text{ J.mole}^{-1}\text{K}^{-1} \quad (\text{II. 1})$$

If more entropy data for similar species are available, they all should be used to calculate a more accurate average value for the entropy contribution of the ligand.

2. Di-ortho-arsenite and ortho-arsenite ions

It is assumed that the stepwise decrease in entropy for the ortho-arsenious acid dissociation series is proportionally the same as for arsenic acid. Table II-4 shows thermodynamic data used in the calculation of the standard entropy of the arsenyl ion.

Table II- 4 Thermodynamic data used in the calculation of the standard entropy of the arsenyl ion

<table>
<thead>
<tr>
<th>Species</th>
<th>$S_{298K}^o$ (right species) J.mole$^{-1}$K$^{-1}$</th>
<th>$S_{298K}^o$ (left species) J.mole$^{-1}$K$^{-1}$</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$AsO$_4$</td>
<td>184.1</td>
<td>196.6</td>
<td>H$_3$AsO$_3$</td>
</tr>
<tr>
<td>H$_2$AsO$_4^+$</td>
<td>117.0</td>
<td>110.4</td>
<td>H$_2$AsO$_2^{2+}$</td>
</tr>
<tr>
<td>HAsO$_4^{2-}$</td>
<td>3.76</td>
<td>?</td>
<td>HAsO$_3^{2-}$</td>
</tr>
<tr>
<td>AsO$_4^{3-}$</td>
<td>-162.7</td>
<td>?</td>
<td>AsO$_3^{3-}$</td>
</tr>
</tbody>
</table>
Hence:

\[ S_{298}^o (\text{HAsO}_4^{2-}) = 110.4 - \frac{117.0 - 3.76}{184.1 - 117.0} (196.6 - 110.4) = -35.1 \text{ J.mole}^{-1}\text{K}^{-1} \]  

(II. 2)

\[ S_{298}^o (\text{AsO}_3^{3-}) = -35.1 - \frac{3.76 - (-162.7)}{184.1 - 117.0} (196.6 - 110.4) = -248.9 \text{ J.mole}^{-1}\text{K}^{-1} \]  

(II. 3)

**Helgeson's Theory**

In Helgeson’s analysis [ii] the total interaction between complex, ions, and solvent dipoles contributing to the entropy change of dissociation of an undissociated species in aqueous solution is regarded as the sum of electrostatic (long range) and non-electrostatic (short range) interaction, as shown in equation II.4.

\[ \Delta S_e^o (\text{diss}) = \Delta S_e^o (T) + \Delta S_e^o (T_r) f(T) + \Delta S_e^o (T_r) g(T) \]  

(II. 4)

where \( T_r \) is the reference temperature (25°C)

The combination of a general form of the Born or Bjerrum equation and a mathematical relationship expressing the variation of the dielectric constant of water with temperature in the 0 – 370°C interval gives the following equation for the electrostatic entropy term:

\[ \Delta S_e^o (T) = \Delta S_e^o (T_r) \exp \left[ \exp(b + aT) - \exp(b + aT_r) + \frac{T - T_r}{\Theta} \right] \times \frac{1 + a\Theta \exp(b + aT)}{1 + a\Theta \exp(b + aT_r)} \]  

(II. 5)

where \( a = 0.01875, b = -12.741 \), and \( \Theta = 219 \).

\( \Delta S_e^o (T) \) is equal to the net difference in the entropy change attending solvation of the neutral complex and its dissociated species as long as the hydration process is entirely electrostatic. The standard state adopted in Helgeson’s theory is based on infinite dilution. Consequently, ion-ion and ion-complex interaction are negligible, and \( \Delta S_e^o (T) \) refers solely to the electrostatic interaction of water dipoles with the complex and its dissociated ions.

Assuming that for dissociational reaction in aqueous solutions the non-electrostatic contribution to the heat capacity of dissociation can be represented by
\[ \Delta C_{p,n}^o(T) = \alpha + \beta T + \gamma T^2 \]  
\( (II. 6) \)

where \( \alpha, \beta, \) and \( \gamma \) are reaction dependent coefficients, then equation (II.4) can be divided by \( T \) and integrated to give the following approximation to the non-electrostatic entropy term:

\[ \Delta S_n^o(T) = \Delta S_n^o(T_r) + \alpha \ln \frac{T}{T_r} + \beta (T - T_r) + \frac{\gamma}{2} (T^2 - T_r^2) \]  
\( (II. 7) \)

Substituting equations (II.5) and (II.7) into equation (II.4) yields:

\[ \Delta S_e^o(T) = \Delta S_e^o(T_r) \exp \left[ \exp(b + aT) - \exp(b + aT_r) + \frac{T - T_r}{\Theta} \right] \times \frac{1 + a\Theta \exp(b + aT)}{1 + a\Theta \exp(b + aT_r)} + \Delta S_n^o(T_r) + \alpha \ln \frac{T}{T_r} + \beta (T - T_r) + \frac{\gamma}{2} (T^2 - T_r^2) \]  
\( (II. 8) \)

The general expression for the dissociation constant of dissociational reactions as a function of temperature resulting from this analysis is cumbersome and unpractical. However, \( \log K_T \) (diss.) for many complexes below 210°C can be closely approximated by assuming that:

\[ \frac{\Delta S_e^o(T)}{\Delta S_e^o(T_r)} \approx \frac{\Delta S_n^o(T)}{\Delta S_n^o(T_r)} \]  
\( (II. 9) \)

which is consistent with the statement that:

\[ \frac{\Delta C_{p,e}^o(diss.)}{\Delta C_{p,e}^o(T)} = \text{constant} \]  
\( (II. 10) \)

The effectiveness of this approximation is partly due to the insensitivity of \( \log K_T \) (diss.) to substantial departures from the above constant ratio, and partly to the similar behavior of the non-electrostatic power function of temperature and the electrostatic exponential function at low temperatures.

The assumption that \( \Delta C_{p,e}^o(diss.) \) is proportional to \( \Delta C_{p,e}^o(diss.) \) leads to:
\[
\log K_T(\text{diss.}) = \left[ T - \frac{\Theta}{\omega} \left[ 1 - \exp[b + aT + \frac{T - T_T}{\Theta}] \right] \right] \times \frac{\Delta S^o_T(T_R)}{RT \ln 10} + \frac{\Delta H^o_T(T_R)}{RT \ln 10} \quad (\text{II. 11})
\]

where
\[
\omega = 1 + a \Theta \exp(a + b T_T) = 1.00322 \quad (\text{II. 12})
\]

Only when the entropy and enthalpy of dissociation at 25°C are both negative, close approximations of \(\log K_T(\text{diss.})\) (or \(\Delta G^o_T(\text{diss.})\)) to about 210°C can be made assuming \(\Delta C^o_{p,T}(\text{diss.})/\Delta C^o_{p,e}(\text{diss.})\) is constant. The negative entropy value reflects the major contribution of solvent interaction to complex stability. On the contrary, if the heat capacity of dissociation and/or \(\Delta S^o_T(T_R)\) and \(\Delta H^o_T(T_R)\) are positive, the non-electrostatic contribution to \(\Delta C^o_{p,T}(\text{diss.})\) is considerable and an approximation to \(\log K_T(\text{diss.})\) (or \(\Delta G^o_T(\text{diss.})\)) using equation (II-11) is not warranted. In the bordering case, i.e. negative entropy and large positive enthalpy of dissociation (e.g. the water equilibrium), the approximation of equation (II.10) also holds. In such case the effectiveness of equation (II.11) is primarily due to the fact that \(\log K_T(\text{diss.})\) is dominated by the enthalpy term.

Since:
\[
\Delta G^o_T(\text{diss.}) = -RT \ln K_T(\text{diss.}) = -RT \ln 10 \log K_T(\text{diss.}) \quad (\text{II. 13})
\]

it follows that:
\[
\Delta G^o_T(\text{diss.}) = \left[ T - \frac{\Theta}{\omega} \left[ 1 - \exp[b + aT + \frac{T - T_T}{\Theta}] \right] \right] \times \Delta S^o_T(T_R) + \Delta H^o_T(T_R) \quad (\text{II. 14})
\]

Hence, the free energy of formation of the neutral complex is calculated using the following equation:
\[
\Delta G^o_{f,T}(\text{diss.})(\text{complex}) = \Sigma \Delta G^o_{f,T}(\text{ions}) - \Delta G^o_T(\text{diss.}) \quad (\text{II. 15})
\]

The free energies of formation of the ions are calculated by the method of Criss and Cobble [iii, iv] as previously described.
The reactions treated according to the simplified Helgeson equation are:

\[
\text{HAsO}_2 \rightarrow \text{H}^+ + \text{AsO}_2^- \quad \text{(II. 16)}
\]

\[
\text{H}_3\text{AsO}_3 \rightarrow \text{H}^+ + \text{H}_2\text{AsO}_3^- \quad \text{(II. 17)}
\]

\[
\text{H}_3\text{AsO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{AsO}_4^- \quad \text{(II. 18)}
\]

Reference


APPENDIX III

COMPOSITION OF PYRITE AND ORPIMENT SPECIMENS

Table III-1 Composition of the pyrite samples in different screen sizes (from IPL)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size mesh</th>
<th>Fe %</th>
<th>Cu %</th>
<th>S° %</th>
<th>S²⁻ %</th>
<th>S_{tot} %</th>
<th>A.I.* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>-100+140</td>
<td>46.94</td>
<td>0.028</td>
<td>&lt;0.01</td>
<td>52.00</td>
<td>52.24</td>
<td>0.23</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-140+200</td>
<td>47.45</td>
<td>0.034</td>
<td>&lt;0.01</td>
<td>51.85</td>
<td>52.00</td>
<td>0.32</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-200+270</td>
<td>47.25</td>
<td>0.044</td>
<td>&lt;0.01</td>
<td>51.86</td>
<td>51.93</td>
<td>0.30</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-270+325</td>
<td>46.19</td>
<td>0.075</td>
<td>&lt;0.01</td>
<td>50.18</td>
<td>50.69</td>
<td>0.52</td>
</tr>
</tbody>
</table>

* A.I. - Acid insoluble content, indicative of siliceous gangue.

Table III-2 Composition of the pyrite samples in different screen sizes (from CMC)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size mesh</th>
<th>Fe %</th>
<th>Cu %</th>
<th>S° %</th>
<th>S²⁻ %</th>
<th>S_{tot} %</th>
<th>A.I.* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>-100+140</td>
<td>47.8</td>
<td>0.032</td>
<td>&lt;0.01</td>
<td>51.0</td>
<td>51.2</td>
<td>0.24</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-140+200</td>
<td>47.8</td>
<td>0.040</td>
<td>&lt;0.01</td>
<td>50.2</td>
<td>50.4</td>
<td>0.28</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-200+270</td>
<td>47.8</td>
<td>0.052</td>
<td>&lt;0.01</td>
<td>50.4</td>
<td>50.6</td>
<td>0.26</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-270+325</td>
<td>46.2</td>
<td>0.082</td>
<td>&lt;0.01</td>
<td>49.0</td>
<td>49.5</td>
<td>0.40</td>
</tr>
</tbody>
</table>

* A.I. - Acid insoluble content, indicative of siliceous gangue.

Table III-3 Composition of the orpiment samples in different screen sizes (from IPL)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size mesh</th>
<th>As %</th>
<th>Fe %</th>
<th>Cu %</th>
<th>S° %</th>
<th>S²⁻ %</th>
<th>A.I.* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orpiment</td>
<td>-100+140</td>
<td>53.34</td>
<td>0.27</td>
<td>0.006</td>
<td>0.27</td>
<td>33.38</td>
<td>4.55</td>
</tr>
<tr>
<td>Orpiment</td>
<td>-140+200</td>
<td>53.11</td>
<td>0.29</td>
<td>0.005</td>
<td>0.35</td>
<td>33.07</td>
<td>4.34</td>
</tr>
<tr>
<td>Orpiment</td>
<td>-200+270</td>
<td>52.25</td>
<td>0.38</td>
<td>0.006</td>
<td>0.31</td>
<td>33.31</td>
<td>3.98</td>
</tr>
<tr>
<td>Orpiment</td>
<td>-270+325</td>
<td>54.55</td>
<td>0.47</td>
<td>0.018</td>
<td>0.37</td>
<td>32.61</td>
<td>3.36</td>
</tr>
</tbody>
</table>

* A.I. - Acid insoluble content, indicative of siliceous gangue.
Table III-4  Composition of the orpiment samples in different screen sizes (from CMC)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size mesh</th>
<th>As %</th>
<th>Fe %</th>
<th>Cu %</th>
<th>$S^\circ$ %</th>
<th>$S^{2-}$ %</th>
<th>A.I. * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orpiment</td>
<td>-100+140</td>
<td>56.00</td>
<td>0.231</td>
<td>0.008</td>
<td>0.20</td>
<td>35.1</td>
<td>4.52</td>
</tr>
<tr>
<td>Orpiment</td>
<td>-140+200</td>
<td>54.40</td>
<td>0.280</td>
<td>0.008</td>
<td>0.27</td>
<td>34.6</td>
<td>4.34</td>
</tr>
<tr>
<td>Orpiment</td>
<td>-200+270</td>
<td>57.60</td>
<td>0.353</td>
<td>0.012</td>
<td>0.26</td>
<td>34.2</td>
<td>3.84</td>
</tr>
<tr>
<td>Orpiment</td>
<td>-270+325</td>
<td>57.60</td>
<td>0.458</td>
<td>0.024</td>
<td>0.34</td>
<td>33.7</td>
<td>3.08</td>
</tr>
</tbody>
</table>

* A.I. - Acid insoluble content, indicative of siliceous gangue.
APPENDIX IV

X-RAY DIFFRACTION PATTERNS
Figure IV-1 X-ray diffraction pattern for pure pyrite sample
Figure IV-2 X-ray diffraction pattern for pure orpiment sample
Figure IV-3  X-ray diffraction pattern for the residue obtained from orpiment oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and 20 gram orpiment in 0.1 M H₂SO₄
Figure IV-4  X-ray diffraction pattern for the residue obtained from pyrite oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and 20 gram pyrite in 0.5 M H₂SO₄.
Figure IV-5  X-ray diffraction pattern for the residue obtained from pyrite oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and 20 gram pyrite in 0.1 M H₂SO₄
Figure IV-6 X-ray diffraction pattern for the residue obtained from pyrite oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and 168 gram pyrite in 0.1 M H₂SO₄.
Figure IV-7  X-ray diffraction pattern for the residue obtained from orpiment oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and 168 gram orpiment in 0.1 M H₂SO₄
Figure IV-8  X-ray diffraction pattern for the residue obtained from the mixture of pyrite and orpiment oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and Fe/As=0.5 in 0.1 M H₂SO₄.
Figure IV-9  X-ray diffraction pattern for the residue obtained from the mixture of pyrite and orpiment oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and Fe/As=1 in 0.1 M H₂SO₄
Figure IV-10  X-ray diffraction pattern for the residue obtained from the mixture of pyrite and orpiment oxidation at the conditions of 210°C, 100 psi, 800 rpm, -140+200 mesh, 2 hours, and Fe/As=2 in 0.1 M H₂SO₄.
APPENDIX V

SEM MICROGRAPHS

Figure V. 1 SEM micrograph of pyrite specimen (-200+270 mesh)
Figure V. 2 SEM micrograph of reacted pyrite sample (-200+270 mesh)
APPENDIX VI

STANDARD TITRIMETRIC METHOD

FOR THE DETERMINATION OF Fe(II) AND As(III) USING

CERIUM (IV) SULFATE

Fe(II) and As(III) were determined by using cerium (IV) sulfate titrimetric method. Ce(IV) is a powerful oxidizing agent capable of oxidizing both ferrous and arsenite ions in acidic solutions. The reactions are shown as follows:

\[
\begin{align*}
\text{Ce}^{4+} + \text{Fe}^{2+} & = \text{Ce}^{3+} + \text{Fe}^{3+} \\
2 \text{Ce}^{4+} + \text{As}^{3+} & = 2 \text{Ce}^{3+} + \text{As}^{5+}
\end{align*}
\]

The end points can be detected by means of a ferroin (1,10 phenanthroline-ferrous complex solution) redox indicator. The reaction of Ce(IV) with As(III) is, however, extremely slow at room temperature, and requires the addition of a catalyst in the form of osmium tetroxide. The As(III) concentration can then be calculated using following equation

\[ V_{\text{As(III)}} = V_{\text{As(III)}+\text{Fe(II)}} - V_{\text{Fe(II)}} \]

V.1. Reagents

V.1.1 Cerium (IV) Sulfate Solution (0.05 M)

Standard cerium (IV) sulfate solution is available from the majority of chemical supplies.

V.1.2 Spekker Acid Solution

1. Measure out 1600 ml distilled water in 5 L beaker and agitate.

2. Slowly and carefully add 600 ml concentrated (98%) sulfuric acid and then 600 ml concentrated (85%) phosphoric acid.

3. Allow to cool before transferring to storage bottle.

V.1.3 Osmium Tetroxide Solution (~0.01 M)

1. Quantitatively transfer 1 g of osmium tetroxide, OsO₄ from the glass ampoule into a 500 ml beaker, using distilled water (to be carried out in fume cupboard).
2. Add 250 ml distilled water and 20 ml 1 M H₂SO₄ solution and agitate until the OsO₄ crystals have dissolved.

3. Make up to 400 ml with distilled water and store in a glass bottle with a glass stopper.

V.1.4 Indicator

Ferroin (1,10 phenothroline-ferrous complex solution), which is available from the majority of chemical supplies.

V.2. Procedures

V.2.1 For Fe(II)

1. Pipette the required aliquot of solution into a 50 ml-100 ml conical flask.

2. Add 10 ml spekker acid solution and 1-2 drops of ferroin indicator solution.

3. Titrate with the standard cerium (IV) sulfate solution until the first permanent color change from orange/red to colorless/blue is obtained.

The calculation of ferrous concentration is shown as follow:

\[
\text{Fe(II) (g/l)} = \frac{C_{ce} \times V_T \times 55.84}{V_{sol}}
\]

where:
- \(C_{ce}\) = concentration of Ce (IV) sulfate solution (M)
- \(V_T\) = titration volume (ml)
- \(V_{sol}\) = volume of solution aliquot (ml)

V.2.2 For As(III)

1. Pipette the required aliquot of solution into a 50 ml-100 ml conical flask.

2. Add 10 ml spekker acid solution, 3 drops of osmium tetroxide solution and 1-2 drops of ferroin indicator solution.

3. Titrate with the standard cerium (IV) sulfate solution until the first permanent color change from orange/red to colorless/blue is obtained.

The calculation of arsenic concentration is shown as follow:

\[
\text{As(III) (g/l)} = \frac{C_{ce} \times 74.92 \times (V_T - V_{Fe})}{V_{sol} \times 2}
\]
where: $C_{Ce} =$ concentration of Ce (IV) sulfate solution (M)
$V_T =$ total titration volume (ml) ($V_{Ce+Fe}$)
$V_{Fe} =$ volume which was titrated for Fe(II) (if not Fe(II) in the solution, it is zero)
$V_{sol} =$ volume of solution aliquot (ml)

V.3 Hazards and Safety Procedures

1. Both arsenic and osmium tetroxide are toxic whilst the sulfuric and phosphoric acids are corrosive. The following safety precautions must be followed.

2. Operators must make sure they are familiar with the hazards of, and safety procedures for, arsenic, osmium tetroxide and the acids.

3. Due to the volative nature of osmium tetroxide, the preparation of the solution and all As(III) titrations must be carried out in a fume cupboard. All precautions must be taken to avoid exposure to osmium tetroxide vapors and it is therefore recommended that the solution is maintained permanently in the fume cupboard.

4. Gloves and a lab coat must be worn at all times.