Western Australian School of Mines
Department of Mining Engineering and Metallurgical Engineering

# Studying the Interactions of Mill Media and Recycled Process Water on Media Wear and Downstream Operations During Gold Ore Processing

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## DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: ……………………………………………

Date: 08/09/2017

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I dedicate this thesis to my wife, Nazanin Nourifard. Without your daily reassurance, I would never have had the confidence and endurance to finish this project. Thank you for giving me strength to chase my dream. I love and appreciate you so very much. I would also like to thank my parents for allowing me to realize my own potential. All the support they have provided me over the years was the greatest gift.

## List of Abbreviations and Acronyms

| | |
|---|---|
| AAS | (atomic absorption spectroscopy) |
| AR | (analytical reagent) |
| CuSO4 | (copper sulfate) |
| DO | (Dissolved Oxygen) |
| EDTA | (Ethylene Diamine Tetra Acetic disodium) |
| EDX | (Energy-dispersive X-ray spectroscopy) |
| HPLC | (High Performance Liquid Chromatography) |
| ICP | (induction coupled plasma) |
| KBGM | (Kanowna Belle Gold Mine) |
| NaCN | (sodium cyanide) |
| OCP | (Open Circuit Potential) |
| ORP | (Oxidation Reduction Potential) |
| PAX | (potassium amyl xanthate) |
| RPM | (Rotations Per Minute) |
| SAD | (Strong acid dissociable) |
| SEM | (Scanning Electron Microscopy) |
| SHE | (Standard Hydrogen Electrode) |
| VMS | (Volcanogenic massive sulfide) |
| WAD | (Weak Acid Dissociable) |
| XPS | (X-ray Photoelectron Spectroscopy) |

## Journal articles

The following publications have resulted from the research presented in this thesis:

1. Rabieh, A., Albijanic, B., Eksteen, J. J., 2016. A review of the effects of grinding media and chemical conditions on the flotation of pyrite in refractory gold operations. Minerals Engineering, 94, 21-28.

2. Rabieh, A., Albijanic, B., Eksteen, J. J., 2017. Influence of grinding media and water quality on flotation performance of gold bearing pyrite. Minerals Engineering, 112, 68-76.

3. Rabieh, A., Eksteen, J. J., Albijanic, B., 2017. Effect of grinding media on cyanide leaching of gold in the presence of pyrrhotite. Hydrometallurgy, 173, 115-124.

4. Rabieh, A., Eksteen, J. J., Albijanic, B., 2018. Galvanic interaction of grinding media with arsenopyrite and pyrite and its effect on gold cyanide leaching. Minerals Engineering, 116, 46-55.

5. Rabieh, A., Eksteen, J. J., Albijanic, B., 2018. Influence of grinding media, pyrite mineralogy and water chemistry on the galvanic interaction between grinding media and pyrite. Submitted to Minerals Engineering.

# ABSTRACT

The type of grinding media can affect downstream operations such as flotation and leaching. The main focus of this thesis was to better understand the influence of grinding media type on flotation of gold bearing pyrite and cyanide gold leaching in the presence of iron sulfide minerals.

In this Thesis, the influence of the grinding media (forged steel, 18% chromium and ceramic) on floatability of gold bearing pyrite and gold recovery were investigated in the tap water and the synthetic process water. $Cu^{2+}$ as an activator was added prior to grinding. The results showed that pyrite recovery and gold recovery was the highest when grinding was performed with the forged steel media. It is postulated that the improved pyrite recovery in the presence of the forged steel media is attributed to better activation of the pyrite surface with $Cu^{2+}$ under strong reducing conditions. The highest amount of iron hydroxide was observed when the forged media was used as confirmed experimentally by X-ray Photoelectron Spectroscopy (XPS) analysis and Ethylene Diamine Tetra Acetic disodium (EDTA) extraction technique. The dissolved ions in the synthetic process water increased the amount of EDTA extractable iron when the grinding was performed with the forged steel media which could be an indication of increased corrosion rates of the grinding media. Therefore, flotation recovery of valuable mineral and corrosion rate of grinding media are two important factors which should be considered for selection of grinding media.

This PhD also focused on the influence of grinding media (forged, 21% chromium, 30% chromium and ceramic) on cyanide gold leaching in the presence of pyrrhotite, arsenopyrite and pyrite. The synthetic ore was prepared by mixing different sulfide minerals (pyrrhotite, arsenopyrite and pyrite) with gravity gold concentrate, and quartz. Pyrrhotite was selected because this sulfide mineral is the highest cyanide- and oxygen- consuming iron sulfide and, contrary to pyrite, tends to behave as a reactive anode. For pyrrhotite, the results showed that when the grinding of the ore was performed using the ceramic media or the 30% chromium media, the gold extraction process was up to three times more efficient than that when the forged steel media was used. The reason is that the galvanic interactions between the forged steel media and pyrrhotite resulted in the formation of iron hydroxide; the formed iron hydroxide converted free cyanide to ferrocyanide that cannot dissolve gold (i.e. 75% of free cyanide was converted to ferrocyanide). Additionally, the galvanic interactions also significantly reduced the dissolved oxygen content and thus cyanide gold leaching was more difficult particularly during the first two hours of leaching because the dissolved oxygen is required to dissolve gold. By contrast, when grinding was performed with the ceramic media or the 30% chromium media, insignificant amount of free cyanide was decomposed (i.e. 1% of free cyanide was converted to ferrocyanide while 2.5% of that was converted to thiocyanate). For that reason, cyanide gold leaching is efficient when the 30% chromium media was used during the grinding of the ore. The 30% chromium media behaved more like the ceramic media than the 21% chromium media with regards to gold leaching performance. For arsenopyrite and pyrite, the results showed a similar trend as for pyrrhotite. However, the galvanic interactions between the grinding media and arsenopyrite and pyrite was lower than those when pyrrhotite was added. Therefore, gold extraction in the presence of arsenopyrite and pyrite was more efficient than that when pyrrhotite was added. A theoretical model was developed to describe the correlation between the galvanic currents and the grinding media oxidation product (i.e. iron hydroxide). A linear relationship between the galvanic currents and media oxidation was obtained. It was found that the higher the galvanic current, the higher the amount of iron hydroxide was produced.

This thesis demonstrated that the selection of grinding media is essential to maximize flotation and leaching performance. In addition to that, it can be concluded that both flotation and leaching tests can serve as a useful diagnostic to determine the extent of galvanic interactions between grinding media and sulfide minerals in grinding mills.

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# Chapter 1 Introduction

## 1.1 Background

Grinding media consumption, either in laboratory or plant, is usually caused by abrasion, impact and corrosion mechanisms. Abrasion and impact wear occur due to the mechanical forces on the grinding media. Corrosive wear occurs due to the galvanic interactions between grinding media and sulfide minerals in wet environments. Impact is not significant in laboratory mills unlike in industrial mills where larger fall heights are possible (Natarajan, 1996) which is the reason that ceramic media is not used in industrial ball mills, but rather in stirred mills for fine grinding of concentrates.

Another important issue is that the consumption of steel grinding media may affect the downstream processing (gold recovery and reagent consumption). Specifically, during grinding with forged steel grinding media, mineral particles become coated with different species of iron, changing the surface properties of minerals. For example, it was found that the higher the percentage of iron in grinding media, the lower the flotation response of sulfide minerals (Cullinan et al., 1999; Martin et al., 1991; Greet et al., 2004). The reason for this was proposed to be due to the presence of hydrophilic layer of oxidized species on the surface of sulfide minerals. Interestingly, Teague et al. (1999) found the improved flotation performance of free gold and gold bearing minerals when metallic iron was added prior to grinding with the ceramic mill media due to the improved stability of froth phase (which may be due to iron hydroxide slimes). Apart from the effect of mill media on froth flotation process, the grinding media may also affect leaching performance of gold. For example, it was found that when gold was in contact with the forged steel media, the dissolution rate of gold in cyanide solution decreased due to the formation of the passive film on gold particles and the galvanic interactions between gold and iron. During grinding due to the galvanic current between forged steel grinding media and sulfide minerals, electrons are transferred from the anode (i.e. grinding media) to the cathode (i.e. cathodic mineral), causing the change of the potential of both materials from their rest potential to the mixed potential due to the tendency to achieve the equilibrium potential (Adam et al., 1984; Martin et al., 1991). As a result, the corrosion of the less cathodic material (grinding media) increases and the corrosion of the more cathodic material (high rest potential) decreases (Fontana, 1987). Therefore, grinding media oxidation increases and more iron hydroxide is produced; iron hydroxide can consume a certain amount of free cyanide during leaching and hence reduce metal leaching recovery.

## 1.2 Problem statement

It has been widely demonstrated that the grinding chemistry has a pronounced effect on the flotation performance of sulfide minerals such as pyrite, chalcopyrite, galena, pyrrhotite and sphalerite (Peng et al., 2003a; Pozzo et al., 1988). Many researchers have investigated the influence of grinding chemistry (grinding media type, water chemistry and gas purging) on flotation performance of sulfide minerals (Adam et al., 1984; Ahn and Gebhardt, 1991; Greet et al., 2004; Huang and Grano, 2005; Huang and Grano, 2006; Huang et al., 2006; Kinal et al., 2009; Bruckard et al., 2011; Chen et al., 2013) . It was found that the selection of grinding media is very important to maximize flotation recovery. The grinding media type, ore mineralogy, and water chemistry is therefore expected to play an important part in flotation recovery.

However, the literature review does not provide any information about the influence of grinding media type and different chemical species in the process water during the grinding stage on the floatability of gold-bearing sulfide mineral as well as the effect on cyanide gold leaching. For that reason, the focus of this research was to investigate the influence of the type of grinding media and water quality on floatability of gold bearing pyrite ore and the effect of grinding media on cyanide gold leaching of the synthetic gold ore. The pyritic-gold ore was used for the flotation experiments; the ore was obtained from the KBGM (Kanowna Belle gold mine) which is located in Kalgoorlie in Western Australia. The flow sheet diagram of the KBGM plant is shown in Figure 1-1. This plant has the flotation and cyanide leaching circuit to recover pyrite (gold locked in pyrite) and the gravity circuit to recover free gold.

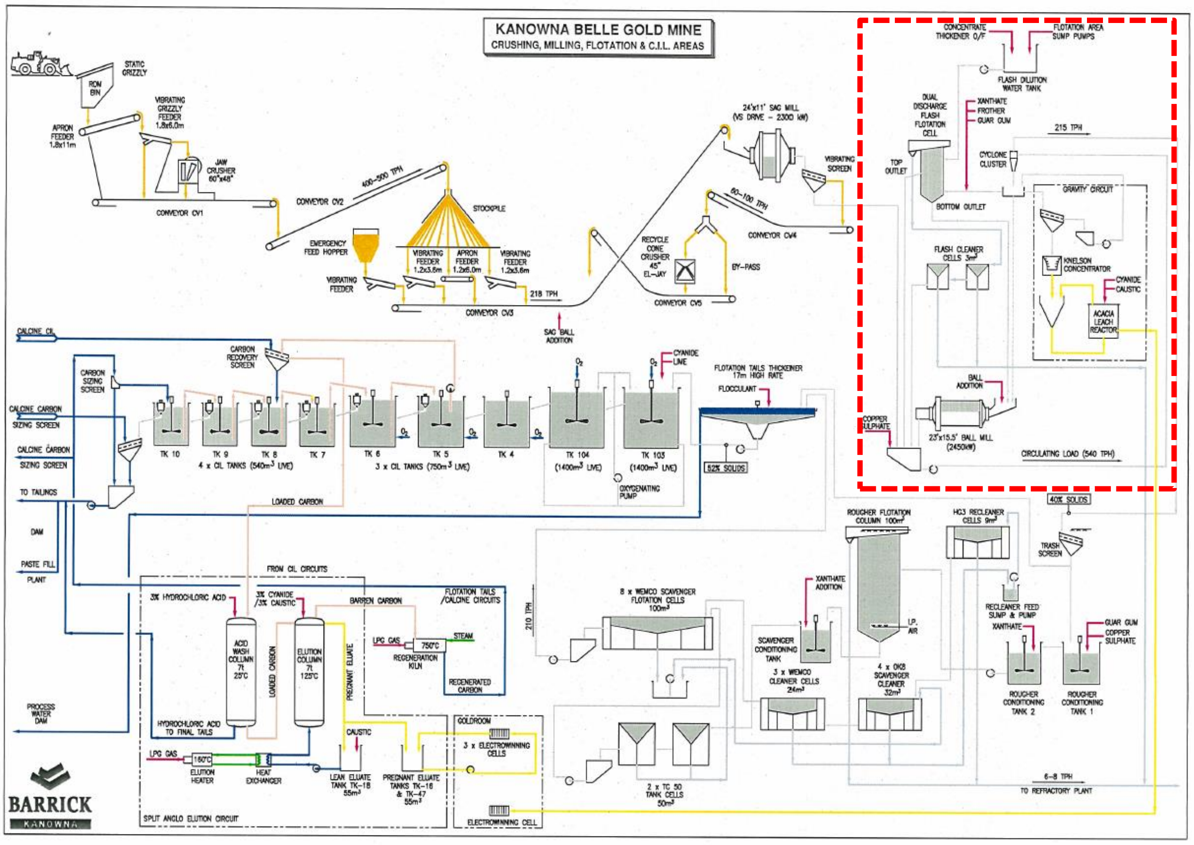


Figure 1-1. Kanowna Belle gold plant flowsheet (Newcombe et al., 2013)

With regards to the cyanide leaching experiments, synthetic gold ore was obtained by mixing clear gravity gold concentrate, iron sulfide mineral (pyrite, pyrrhotite or arsenopyrite) in a same concentrate (2% in the synthetic ore)and quartz. It should be noted that the main focus of the cyanidation experiments was to investigate the effect of different iron sulfide minerals on the galvanic interaction and subsequently on cyanidation, therefore, we have to make it synthetically to be sure about the concentration.

### 1.3 Objectives

The main research objective of this thesis is to better understand the influence of grinding media type on flotation of gold bearing pyrite and leaching performance of gold in the presence of iron sulfide minerals. The obtained results will benefit suppliers and operating companies to select the most appropriate grinding media for a given gold ore type, and benefit operating companies to understand the impact of the interaction of grinding media, process water and gold ore type on gold recovery during flotation and leaching. The objectives of the project can be summarised as follows:

(1) To characterize surface coatings on gold – bearing sulfide particles after grinding with different grinding media and in contact with the tap or synthetic process water;
(2) To investigate the influence of water quality and grinding media type on gold-bearing sulfide ore flotation, and conversely establish laboratory flotation experiments as a diagnostic for media wear;
(3) To investigate the influence of galvanic interaction between grinding media and sulfide minerals on gold cyanidation and leaching process.

### 1.4 Hypotheses

The following hypotheses were developed through the thesis:

- Different grinding media behave different during grinding of sulfide bearing gold ore and influence the downstream operation such as flotation and leaching, the reason is linked to the galvanic interaction between grinding media and sulphide minerals which can increase the corrosion of grinding media. This can leads to more iron hydroxide production and subsequently this iron hydroxide can affect the flotation and leaching performance.
- The most appropriate choice of grinding media depends on the nature of the sulfide minerals in the ore. Different sulphide minerals have different rest potential which can lead to generate different galvanic current during grinding and subsequently produce different amount of iron hydroxide.
- The optimal choice of grinding media depends on water chemistry. Optimality is not only linked to the consumption and cost of the grinding media, but also to the effect of grinding media on metal recovery in downstream operations.

### 1.5 Scope

A literature review has identified the knowledge gaps on the effects of grinding media type and water quality during grinding of different gold ores on downstream operations such as flotation and leaching. This is particularly true for studies investigating the effect of grinding media type on cyanide gold leaching. There is also not an understanding of the influence of grinding media type on gold-bearing sulfide ore flotation. For these reasons, the main scope of this thesis is to understand the influence of the grinding media on flotation of gold bearing pyrite as well as cyanide gold leaching of gold-bearing sulfide ores. Specifically, in the first part of the thesis, the material used for the experimental program was quartz and the gold pyritic ore supplied from the KBGM. While quartz was used to investigate the corrosion of the grinding media, the gold pyritic ore was used to study the flotation recovery of pyrite and gold. The grinding chemical conditions in the laboratory ball mill were controlled to produce the same grinding environment as that in the plant ball mill. The feed ore was prepared to a $P_{80}$ of 106 µm by wet grinding at 50% w/w solids in the laboratory ball mill. The experiments were performed using the tap water or the synthetic process water. Three types of grinding media were used in this work i.e. the forged steel, 18% chromium and ceramic media. EDTA extraction was used to quantify the corrosion of grinding media (i.e. the amount of oxidized iron species after grinding) while XPS analysis was used to study surface changes of ground particles.

In the second part of this thesis, the galvanic interactions between the grinding media (the forged, 15 % chromium, 21 % chromium or 30 % chromium media) and a pyrite electrode (pure pyrite or gold-bearing pyrite electrode) were investigated in the tap water or the synthetic process water. The galvanic interactions were quantified by measuring the galvanic currents using the polarization measurements. The morphological and chemical changes on the grinding media after conditioning with the tap water and the synthetic process water were investigated using SEM/EDX to establish the relationship between the surface changes of the grinding media and the galvanic interactions between the pyrite electrode and the grinding media.

In the third part of this thesis, the synthetic gold ores were used to investigate the effect of grinding media on gold cyanide leaching. The synthetic gold ores were obtained by mixing quartz, an iron sulfide mineral (pyrite, arsenopyrite or pyrrothite) and gold concentrate. Four types of grinding media were used in this work i.e. the forged steel, 21% chromium, 30% chromium and ceramic media. The grinding system is designed not only to replicate plant mill performance at a laboratory scale but also to quantify the galvanic interaction in-situ in the mill. The feed ore was prepared to a $P_{80}$ of 75 µm by wet grinding at 34% w/w solids in the grinding system. The ground slurries were collected for EDTA iron extraction and sulfur measurements. The galvanic interactions were quantified on the basis of electrochemical measurements in-situ of the mill. The rest potentials of both the grinding media and the sulfide minerals were measured in-situ of the mill to determine the galvanic currents.

### 1.6 Overview

This thesis is divided into eight chapters to systemically investigate the effect of grinding media and water quality during grinding of gold bearing sulfide ores on subsequent flotation and gold cyanide leaching process.

**Chapter 1** presents background, problem statement, hypotheses, objectives, and scope of this thesis. **Chapter 2** provides a literature review of the experimental work on studies investigating galvanic interactions between grinding media and sulfide minerals, and the effect of galvanic interactions on pulp chemical conditions during grinding of ores. The effect of grinding media type on flotation performance of gold bearing sulfide ore and cyanidation process are extensively discussed. The literature review provides an overall picture of the current status of studies in this area and pinpoints the gaps in knowledge and hypotheses for future research which are presented at the end of this Chapter. Some parts of Chapter 2 were published in Minerals Engineering (Rabieh, A., Albijanic, B., Eksteen, J. J., 2016. A review of the effects of grinding media and chemical conditions on the flotation of pyrite in refractory gold operations. Minerals Engineering, 94, 21-28.).

**Chapter 3** presents materials and experimental methods used in this thesis. The following experimental procedures were described: using of the Magotteaux mill and the flotation cell, the electrode preparation for voltammetry measurements, using of the modified grinding system, the cyanidation tests, and the EDTA iron extraction technique.

**Chapter 4** covers the experimental investigation of corrosion of different grinding media during grinding of silica in the tap water and the synthetic process water.

**Chapter 5** discusses the results about the influence of different grinding conditions (grinding media type and water quality) on floatability of gold bearing pyrite ore. The results of this work were published in Minerals Engineering (Rabieh, A., Albijanic, B., Eksteen, J. J., 2017. Influence of grinding media and water quality on flotation performance of gold bearing pyrite. Minerals Engineering, 112, 68-76.).

**Chapter 6** investigates the role of the grinding media type, the water chemistry and the pyrite mineralogy on the galvanic interactions between the grinding media and pyrite in the tap water and the synthetic process water.

**Chapter 7** discusses the influence of galvanic interactions between the grinding media and the iron sulfide minerals (pyrrhotite, pyrite or arsenopyrite) on gold cyanidation process. The results of this work were published in Hydrometallurgy and Minerals Engineering Journal:

i. Rabieh, A., Eksteen, J. J., Albijanic, B., 2017. Effect of grinding media on cyanide leaching of gold in the presence of pyrrhotite. Hydrometallurgy, 173, 115-124
ii. Rabieh, A., Eksteen, J. J., Albijanic, B., 2018. Galvanic interaction of grinding media with arsenopyrite and pyrite and its effect on gold cyanide leaching. Minerals Engineering, 116, 46-55.

The final chapter (**Chapter 8**) describes the conclusions drawn from this work and makes recommendation for further research and implementation.

# Chapter 2 Literature Review

A literature review was conducted based on the research objectives and research questions described in Chapter 1. This literature review covers the causes of grinding media consumption during grinding, the galvanic interaction between grinding media and sulfide minerals, the influence of galvanic coupling on pulp chemistry during grinding, and the effect of grinding media type and water quality on flotation and cyanide leaching process.

## 2.1 Grinding media consumption

Grinding media consumption is one of the major operating costs in mineral processing industry; it was found that the consumption of media in ball mills during grinding operation can be up to 50% of grinding operating cost (Aldrich, 2013). Due to these costs significant effort has been undertaken into developing a material to be more resistance for grinding media (Figure 2-1).

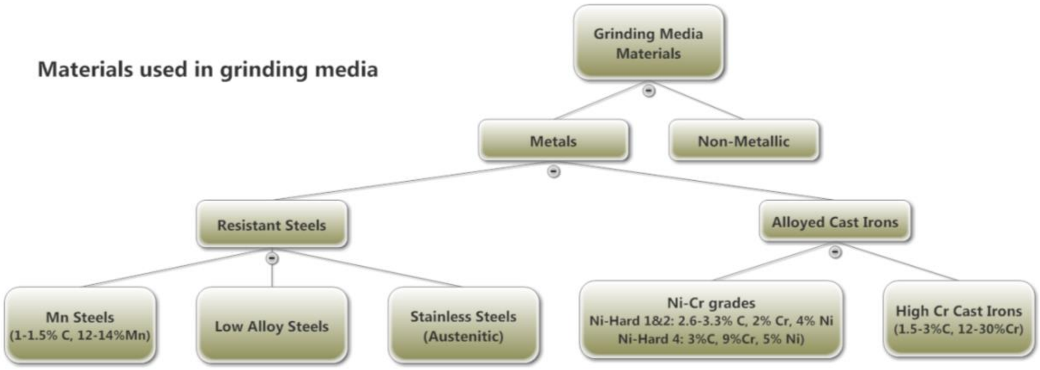


Figure 2-1. Materials used in grinding media (Aldrich, 2013).

Grinding media consumption is caused by impact, abrasion and corrosion. Abrasion and impact occur due to mechanical force, while electrochemical reactions between process water, grinding balls and mineral particles play a key role in the corrosion mechanism (Natarajan, 1996). Corrosive wear of steel grinding media is strongly associated with wet milling environments and has been studied by a number of investigators by use of electrochemical measurements. During wet milling of non-sulfide minerals or ores, Chenje (2003) reported that corrosive wear was usually less than 15% of the total wear during wet laboratory grinding. In particular, for low chromium media (17.8%), corrosion only results in less than 4% of the total metal loss. However, corrosion wear may play a predominant role in metal loss in acidic environments (Tao, 2005) and in the presence of sulfide minerals (Natarajan, 1996; Natarajan and Iwasaki, 1984; Pitt, 1988). In acidic environments, most metal oxides and hydroxides may not exist on grinding media surfaces. As a result, no passive film protects grinding media, causing their corrosion due to the chemical or electrochemical reactions within milling environments (Tao, 2005).

## 2.2 Galvanic interactions

### 2.2.1 Galvanic interaction between steel grinding media and sulfide minerals

Galvanic interactions, occurring between different materials, strongly depend on electrochemical activity of the materials (Rao, 2004). The measure of electrochemical activity of the material is the rest potential which represents the difference between the potential of the selected material and the potential of the reference electrode when the oxidation and reduction current are equal (Rao, 2004). According to McNaught and Wilkinson (1997), under the same chemical conditions, a lower rest potential indicates a higher electrochemical activity. Table 2.1 shows the rest potential of several sulfide minerals and forged steel grinding media. The forged steel has a significantly lower rest potential than all the minerals, suggesting that the forged steel is more electrochemically active than the sulfide minerals. Table, 2-2 presents the rest potential of various sulfide minerals at pH 4. As seen in Table 2-2, pyrite has the highest rest potential while molybdenyte and stibnite have the lowest rest potential. Table 2-3 shows the rest potential of various steels in a number of aqueous environments.

Table 2-1. Rest potentials of common sulfide minerals and grinding media at neutral pH (Cheng et al, 1993).

| **Mineral/media** | **Rest potential, V (SHE)** | | |
|---|---|---|---|
| | **N2** | **Air** | **O2** |
| Pyrite | 0.389 | 0.392 | 0.395 |
| Arsenopyrite | 0.277 | 0.303 | 0.323 |
| Pyrrhotite | 0.276 | 0.285 | 0.318 |
| Chalcopyrite | 0.290 | 0.355 | 0.371 |
| Cobaltite | 0.200 | 0.275 | 0.303 |
| Nickel arsenide | 0.173 | 0.175 | 0.201 |
| Galena | 0.142 | 0.172 | 0.218 |
| Forged steel | -0.515 | -0.335 | -0.175 |

Table 2-2. Rest potential (vs. SHE) of sulfide minerals at pH 4 (Rao, 2004)

| Minerals | E(V) |
|---|---|
| Molybdenite, $MoS_2$ | 0.11 |
| Stibnite, $Sb_2S_3$ | 0.12 |
| Argentite, $Ag_2S$ | 0.28 |
| Galena, PbS | 0.40 |
| Bornite, $Cu_5FeS_4$ | 0.42 |
| Covelite, CuS | 0.45 |
| Sphalerite, ZnS | 0.46 |
| Chalcopyrite, $CuFeS_2$ | 0.56 |
| Marcasite, (Zn,Fe)S | 0.63 |
| Pyrite, $FeS_2$ | 0.66 |

Table 2-3. Rest potentials (vs. SHE) of mild steel (M.S.), austenitic stainless steel (A.S.S), and martensitic stainless steels (M.S.S.) (Adam et al., 1984).

| Electrolyte | pH | $E_{A.S.S.}$ (V) | $E_{M.S.S.}$(V) | $E_{M.S.}$(V) |
|---|---|---|---|---|
| 0.5 M NaCl (air exposed) | 6.7 | 0.088 | -0.056 | -0.396 |
| Distilled water ($N_2$ bubbling) | 6.8 | 0.118 | -0.298 | -0.516 |
| Distilled water (air exposed) | 4.0 | 0.150 | -0.106 | -0.374 |
| | 6.8 | 0.206 | 0.098 | -0.336 |
| | 10.0 | 0.010 | -0.088 | -0.242 |
| Distilled water ($O_2$ exposed) | 6.6 | 0.027 | 0.066 | -0.176 |

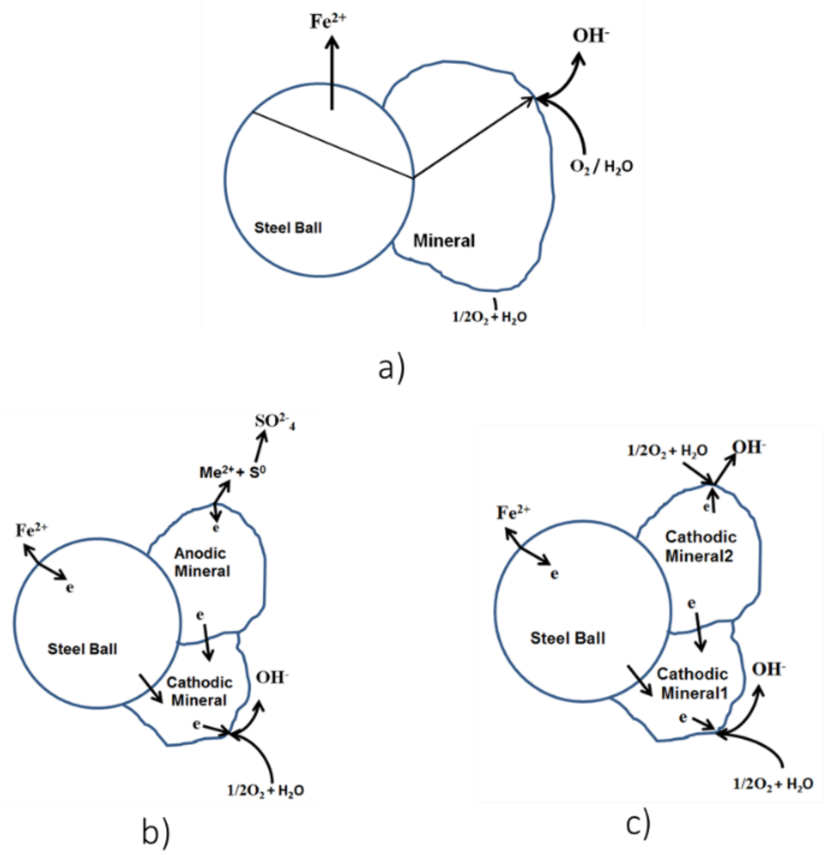
When the difference between the rest potential of the sulfide mineral and that of the grinding media is high, the galvanic interactions are more pronounced during the grinding stage due to the large galvanic current. Therefore, electrons are transferred from the anode (i.e. grinding media, less cathodic mineral) to the cathode (i.e. cathodic mineral), causing the change of the potential of both materials from their rest potential to the mixed potential due to the tendency to achieve the equilibrium potential (Adam et al., 1984; Martin et al., 1991). As a result, the corrosion of the less cathodic material (low rest potential) increases and the corrosion of the more cathodic material (high rest potential) decreases (Fontana, 1987). Given that pyrite has the highest rest potential, and thus it is the least electrochemically active sulfide mineral, grinding with forged steel grinding media causes the significant galvanic interactions due to the large difference between the rest potential of pyrite and that of the forged steel grinding media (see Tables 2-1, 2-2 and 2-3). Figure 2-2 shows the schematic representation of the galvanic interaction model for the following systems:

a) forged steel media-cathodic mineral,

b) forged steel media-anodic mineral-cathodic mineral,

c) forged steel media-cathodic mineral-cathodic mineral.

The electrochemical reactions which might occur during the galvanic interactions are explained in Section 2-3. It should be noted that a sulfide mineral with a moderate rest potential can act as a cathode or an anode depending on the thermodynamic and kinetic properties of two sulfide minerals and forged steel media (Pozzo et al., 1988).



a)

b)

c)

Figure 2-2. Galvanic interaction between a) forged steel media and cathodic mineral b) forged steel media-anodic mineral-cathodic mineral c) forged steel media-cathodic mineral-cathodic mineral.

### 2.2.2 Effect of galvanic interactions on pulp chemistry

Different electrochemical reactions occur during the galvanic interactions between sulfide minerals and forged steel media, giving rise to variations in the pulp chemistry variables (i.e $E_h$, pH, dissolved oxygen, oxygen demand, and surface chemistry). The main consequence of galvanic interactions is the oxidation of iron from grinding media (Rao, 2004). Figure 2-3 shows an $E_h$/pH diagram for the iron–water system. The ball mill discharge has low $E_h$ and neutral to slightly alkaline pH typically between 7 and 9 after the grinding of refractory gold ores (O'Connor and Mills, 1990). The corrosion of forged steel media might be explained with the following electrochemical reactions:

$Fe^0 + 2OH^- = Fe(OH)_2 + 2e^-$ (2-1)

$Fe(OH)_2 + OH^- = Fe(OH)_3 + e^-$ (2-2)

$Fe^{2+} + 3OH^- = Fe(OH)_3 + e^-$ (2-3)

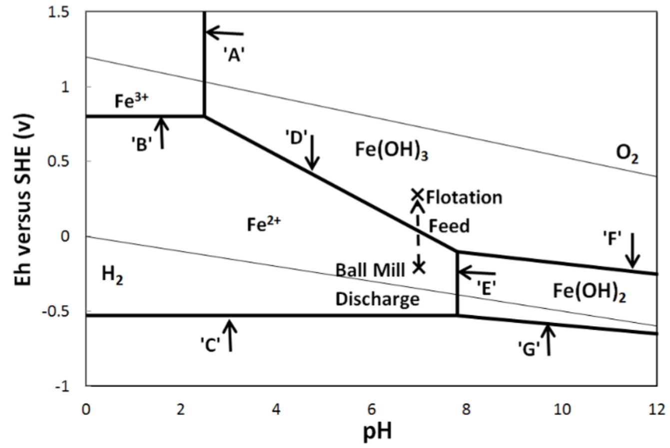


Figure 2-3. $E_h$-pH diagram for the iron–water system (O'Connor and Mills, 1990).

The released electrons in the electrochemical reactions (see Equations 2-1 to 2-3) are being transferred to the cathodic sulfide mineral, resulting in the cathodic reduction of oxygen:

$0.5O_2 + H_2O + 2e^- = 2OH^-$ (2-4)

If the ore contains two sulfide minerals, the one with the lower rest potential is the anodic mineral, and it is anticipated that elemental sulfur forms on its surface thereby improving the floatability of that mineral:

$MS + 2OH^- = M(OH)_2 + S + 2e^-$ (2-5)

Equation 2-5 shows forming of both a metal hydroxide and elemental sulfur during the reaction. The sulfur may undergo a further, but slower, oxidation to a range of anionic sulfur-oxygen compounds (thiosulfates, sulfites and sulfates).

The reactions, shown in Equations 2-1 to 2-5, can be used to explain the main effects of the galvanic interactions on pulp chemistry variables i.e. dissolved oxygen content, pulp potential, and coating of mineral surface. The influence of galvanic interactions on these variables is described below.

#### 2.2.2.1 Dissolved oxygen

The concentration of dissolved oxygen strongly depends on numerous factors such as grinding media, ore type, and pulp temperature (Bruckard et al., 2011). The corrosion of forged steel grinding media can reduce the dissolved oxygen concentration to well below 1 ppm (Kelebek and Yoruk, 2002) due to the corrosion of the grinding media, or by the reaction of the dissolved oxygen with reactive sulfides, or by the reactions with ions in solutions such as chlorides and cupric ions. It should be noted that the reduction of the dissolved oxygen content is particularly significant after the grinding of volcanogenic massive sulfide ores, which contain a large amount of pyrite (Greet et al., 2014). The decrease of the dissolved oxygen content also hinders the successful adsorption of xanthate on the surface of sulfide minerals (Fuerstenau et al., 2007), and thus retards the floatability of these minerals.

An increase in the pulp temperature reduces the dissolved oxygen content (Huang and Schmith, 2014) due to a decrease of the solubility of oxygen in the aqueous phase. The reduced dissolved oxygen content prevents the oxidation of pyrite surfaces, which is essential to improve the floatability of pyrite. It should also be noted that elevated temperature causes the decomposition of xanthate collector (Mustafa et al., 2004).

Apart from the measurements of dissolved oxygen content, it is also very useful to determine the oxygen demand rate constant which represents the oxygen consumption of system from the pulp phase (Grano, 2010). The oxygen demand rate constant depends particularly on ore mineralogy and specific surface area (Owusu et al., 2013). For example, Owusu et al. (2013) found that non-arsenian pyrite had 7.5 times higher the oxygen demand rate constant than arsenian pyrite (i.e. pyrite in which As is incorporated into pyrite crystals). The reason for the less activity of arsenian pyrite is probably that as an electron acceptor this mineral is less conductive (Owusu et al., 2013). Additionally, the decrease in the particle size of arsenian pyrite considerably increased the oxygen demand rate constant due to the presence of more reactive sites at pyrite surfaces (Owusu et al., 2013).

#### 2.2.2.2 Pulp potential

Pulp potential is particularly affected by the dissolved oxygen content. The dissolved oxygen content is low when grinding of sulfide ore is performed with forged steel grinding media. If there is not enough dissolved oxygen to consume the excess amount of electrons, being produced due to the corrosion processes (Equations 1 to 4), and the pulp potential decreases. The lowering of pulp potential can prevent the adsorption of collector at the cathodic mineral surface, reducing the floatability of the sulfide mineral which is more floatable in an oxidizing environment (Woods, 1976; He et al., 2005). It should be noted that pyrite is also floatable when the pulp potential is reducing and the dissolved oxygen content is low probably because the reduced dissolved oxygen content prevents the oxidation of pyrite, making pyrite more floatable. There is therefore a trade-off between the natural hydrophobicity of pyrite under reducing conditions and the need for slightly oxidizing conditions for improved collector adsorption. There is therefore a significant redox sensitivity that must be kept in mind and no one-directional argument can be made with regards to redox potential.

## 2.3 Influence of grinding media on mineral flotation

Grinding media can be made of different materials such as forged steel, high carbon steel, stainless steel, high chromium steel and ceramic media. However, due to the low manufacturing cost, forged steel is the most commonly used grinding media.

Different types of grinding media produce different amounts of iron oxidation species due to the electrochemical reactions occurring inside the grinding mill (Kocabag and Smith, 1985). Therefore, grinding media cause different pulp chemical conditions due to galvanic interactions between grinding media and sulfide minerals, affecting subsequent mineral flotation. The influence of grinding media on flotation is reviewed in this section.

### 2.3.1 Iron oxidation species

During wet grinding with steel grinding media, the electrochemical corrosion plays an important role in grinding media wear, producing iron oxidation species. Iron steel media can be oxidised through the reactions 2-6 and 2-7.

$Fe \rightarrow Fe^{2+} + 2e^-$ (2-6)

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (2-7)

The iron ions hydrolyse through reactions 2-8 and 2-9:

$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$ (2-8)

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$ (2-9)

It was found that the iron hydroxide species at alkaline conditions, precipitate onto the surface of the sulfide minerals and therefore affecting their floatability. In general, the forged steel (electrochemically active grinding media) produces much more iron oxidation species than stainless steel (electrochemically inactive grinding media). Iron oxidation species are hydrophilic and thus can depress the flotation of most sulfide minerals (Natarajan and Iwasaki, 1984; Peng et al., 2003a; Peng et al., 2003b; Greet et al., 2004).

Numerous mechanisms have been suggested to describe the effect of iron hydroxide on mineral flotation. For example, Rey and Formanek (1960) proposed that the consumption of xanthate collector by grinding media oxidation products as a possible mechanism for the decreased sulfide mineral recovery with electrochemically active steel grinding media. However, subsequent studies showed that it was not possible for the thiol collectors to react with iron oxidation products. A possible explanation was related to the presence of the iron hydroxide layer on particle surfaces, preventing collector adsorption on particle surfaces. Grano et al. (1997a) and Grano et al. (1997b) revealed that the decrease in the adsorption of the thiol collectors onto chalcopyrite was the dominant mechanism responsible for the reduced chalcopyrite flotation in the presence of ferric hydroxides in the pH range of 6–8.

As discussed in section 2.2, galvanic interactions occur between steel grinding media and sulfide minerals, increasing the oxidation of grinding media (Martin et al., 1991; Huang and Grano, 2005) and hence producing of more iron oxidation species. Adam and Iwasaki (1984) and Pozzo et al., (1988) suggested that when the grinding media is more electrochemically active and the grinding time is longer, the galvanic current is higher, reducing the floatability of pyrrhotite due to the formation of iron hydroxide on the pyrrhotite surfaces. Other researchers have seen similar results from grinding of other sulfide minerals (Rao and Natarajan, 1988; Ahn and Gebhardt, 1991; Huang and Grano, 2005). It should be noted that fine particles are more sensitive to the iron contamination, which suggests that the control of grinding media oxidation may be more important during regrinding (Huang et al., 2005).

Minimizing the galvanic interaction during grinding is useful for sulfide mineral flotation due to the generation of lower amount of iron hydroxides (Huang and Grano, 2006). Galvanic interactions can be reduced by using electrochemically inactive grinding media (e.g. stainless steel, ceramic media and high chromium) or by purging inert gas (e.g. nitrogen) into the grinding mill to reduce the dissolved oxygen content.

### 2.3.2 Effect of grinding media on separation of different sulfide minerals

Numerous researchers have also investigated the effect of grinding media on flotation separation of different minerals. It is well known that the various sulfide minerals have different electrochemical properties and thus can respond differently to the iron contamination and pulp chemistry generated by the grinding media. As a result, selective separation between these minerals has been observed.

Wang and Xie (1990) investigated the separation of chalcopyrite, galena and sphalerite from pyrite when the ore was ground in the stainless steel mill. With ceramic or stainless steel media, the more electrochemically active sulfide mineral (i.e. chalcopyrite, galena or sphalerite) was oxidized first to form a sulfur rich surface and thus exhibiting good flotation response. By contrast, the least electrochemically active sulfide mineral (i.e. pyrite) is less oxidized, reducing the xanthate collector adsorption and hence flotation response. Similarly, Peng et al. (2003a) observed that grinding with the 30 wt% chromium grinding media (i.e. oxidizing environment) produced higher chalcopyrite and lower pyrite flotation recovery than grinding with the forged steel media (i.e. reducing environment); it means that grinding with the 30% chromium media improved flotation selectivity for the chalcopyrite-pyrite system. Peng et al. (2003b) also studied the effect of grinding media on the separation of galena from pyrite. They found that grinding with the 30 wt% chromium media during oxygen purging produced an amount of iron oxidation species which depressed pyrite flotation significantly but depressed galena flotation only slightly, resulting in the highest galena selectivity against pyrite. A similar conclusion was also obtained by Huang et al., (2005) who used the copper–lead–zinc sulfide ore from Newmont Golden Grove Operation. It was found that the enhanced selectivity of chalcopyrite against sulfide gangue minerals was achieved by using the high chromium grinding media while the mild steel grinding media depressed the flotation of all the sulfide minerals due to the generation of the high amount of iron oxidation species.

The electrochemically inactive grinding media such as stainless steel media does not always produce better flotation response than the forged steel media. Precisely, the mineral selectivity can be reduced when the minerals were ground in an oxidizing environment produced by stainless steel or ceramic media; the opposite was true after grinding in a reducing environment generated by the forged steel media (Van Deventer et al., 1990; Yuan et al., 1996b; Leppinen et al., 1990). Kinal et al. (2009) investigated the effect of grinding media on lead-zinc flotation in a lead cleaner circuit. Interestingly, the use of high chromium media was potentially detrimental to lead cleaner flotation due to the difficulty in depressing sphalerite. It was also found that a 1% chrome alloy produced the desired pulp chemistry to yield an increase in lead grade through the rejection of sphalerite. This study indicates that the selection of grinding media should depend on the specific ore properties and operation conditions, and the composition of grinding media can be adjusted to provide the most suitable grinding chemistry for the subsequent mineral flotation.

The effect of grinding media on the separation of different minerals has also been found to be highly dependent on the flotation conditions such as gas purging during flotation. For example, Yuan et al. (1996a) investigated the copper-zinc selectivity after grinding with either the stainless steel media or the mild steel media, and various gases were used in subsequent flotation. It was found that the stainless steel media improved copper flotation regardless of the flotation conditions. However, Cu/Zn selectivity showed a strong dependence on the flotation gases after grinding with the mild steel media. Similar results were also found in the case of the copper-iron ore (Yuan et al., 1996b).

Overall, past studies have demonstrated that grinding media can influence subsequent mineral flotation and separation of different minerals through the production of iron contamination species and the generation of different pulp chemistry. After regrinding, as most of the particles are fine or ultra-fine fraction, it is more difficult to separate the valuable minerals from gangue minerals, and the loss of fine particles into flotation tailings is becoming one of the biggest challenges in many mineral processing plants. The galvanic interactions between the grinding media and the fine particles may become stronger due to the larger particle surface area. Therefore, the selection of grinding media is particularly important to modify the regrinding chemistry and thus achieve the best metallurgical performance.

### 2.3.3 Effect of grinding media on flotation performance of gold ore

The effect of grinding media on flotation performance of sulfide minerals have been studied by a number of researchers (Adam el al., 1984; Learmont and Iwasaki, 1984; Martin et al., 1991; Rao and Finch, 1988). For example, it was found that the higher the percentage of iron in grinding media, the lower the flotation response of sulfide minerals (Cullinan et al., 1999; Martin et al., 1991). In terms of the effect of grinding media on gold ore flotation, Teague et al. (1999) studied the effect of grinding media on flotation behaviour of free gold and gold locked in the iron sulfide minerals. The ore samples were ground with a ceramic grinding media and the forged steel environment was simulated by adding different amounts of metallic iron powder to the ore before grinding. The flotation response of the ground product was compared in the presence of three different collectors i.e. potassium amyl xanthate (PAX), trithiocarbonate or combination of the two collectors. Table 2-4 shows flotation results for PAX, a trithiocarbonate and the combination of PAX and GX.

Table 2-4. Flotation results using PAX, GX and a combination of PAX and GX (Teague et al., 1999).

| Conditions | Recovery (%) | | |
|---|---|---|---|
| | Free gold | Refractory | Total gold |
| PAX without Fe | 70.3 | 45.5 | 61.8 |
| PAX with 300g Fe/t | 68.3 | 69.5 | 68.6 |
| PAX with 5kg Fe/t | 63.9 | 74.2 | 71.7 |
| GX without Fe | 70.6 | 41.2 | 63.7 |
| GX with 300g Fe/t | 79.7 | 50 | 70.2 |
| GX with 5kg Fe/t | 76.8 | 63.5 | 74.9 |
| PAX + GX without Fe | 73 | 65.2 | 66.1 |
| PAX + GX with 300g Fe/t | 69.3 | 61.5 | 68.2 |
| PAX + GX with 5kg Fe/t | 76.5 | 59.1 | 71.5 |

The results show that the gold recovery increased when more iron was added to the ore before grinding. However, the literature review revealed the lack of knowledge of the effect of grinding media type (forged steel, different chromium media) on flotation of gold bearing sulfide ore. In addition, the galvanic interactions between grinding media, sulfide minerals and gold and the effect on flotation performance of gold bearing sulfide ore has not yet been systematically evaluated.

## 2.4 Influence of grinding media and sulfide minerals on gold cyanide leaching

### 2.4.1 Gold dissolution

Gold dissolution in alkaline cyanide solution is an electrochemical process which can be described by oxidation of gold by oxygen and reduction of oxygen to hydroxide as follows:

Anodic reaction at pH 10:

$Au + 2CN^- = Au(CN)^-_2 + e^-$ (2-10)

Cathodic reaction:

$O_2 + 2H_2O + 4\ e^- = 4OH^-$ (2-11)

Therefore, by combining the two half reactions, the equations can be shown as follows, which known as Elsner' equation (Marsden and House 2009):

$4Au + 8CN^- + O2 + 2H_2O = 4Au(CN)_2^- + 4OH^-$ (2-12)

### 2.4.2 Galvanic effect between gold and sulfide minerals on gold dissolution

Galvanic interactions occur between sulfide minerals which are in direct contact with gold during leaching. This galvanic interaction can affect the gold leaching rate. It was found that the galvanic interaction can increase the gold leaching rate when gold is in contact with galena. However, when gold is in contact with chalcopyrite, the galvanic interaction decreases the gold dissolution, while chalcocite stops the gold dissolution completely (Van Deventer et al., 1990; Lorenzen and Van Deventer, 1992; Aghamirian and Yen, 2005).

### 2.4.3 Behaviour of minerals in alkaline cyanide solutions

Gold ore often associates with sulfide minerals. While gold-bearing sulfide ore cyanidation is generally problematic, there is a great variation in the extent to which sulfide minerals affect the leaching process. Moreover, the effect of sulfide minerals on gold cyanidation is governed by other factors, such as their concentration in the ore, solubility, and reactivity (Deschenes et al., 2007). The effects of sulfide minerals and their dissolved ions on the gold leaching process have been investigated (Ntemi et al., 2013). It should be noted that apart from gold, other minerals might also decompose in alkaline cyanide solutions. The decomposition of some minerals can consume free cyanide and oxygen, as well as generate a mixture of solution species which can affect the efficiency of gold extraction. Most of the sulfides minerals decompose in aerated alkaline cyanide solution to generate metal ions, metal oxides, or metal cyanide complexes and various sulfur-containing species (i.e. thiocyanate, sulfide, and thiosulfate ions). The common reaction for a sulfide mineral dissolution in alkaline cyanide solution is given as follows (Marsden and House, 2009):

$$2MS + 2(x + 1)CN^- + O_2 + 2H_2O = 2M(CN)_x^{(x-2)-} + 2SCN^- + 4OH^- \qquad (2\text{-}13)$$

Apart from sulfide minerals, non-sulfide minerals (oxides, carbonates and sulfates) can also dissolve in alkaline cyanide solutions. However, non-sulfide minerals consume lower amount of cyanide and oxygen than sulfides, because in the presence of non-sufide minerals, the anions produced in solutions do not react with free cyanide. Therefore, the presence of non-sulfide minerals rarely have an impact on gold dissolution (Marsden and House, 2009).

### 1. Copper Minerals

Some gold ores contain copper. In some cases, most of free cyanide, consumed by copper, cause the treatment of gold ore by cyanidation uneconomical (Marsden and House 2009). Table 2-5 showed the relative solubilities of copper minerals ground to $P_{100}$ <150 µm in 0.1 % sodium cyanide solution over a period of 24 hours (Flatt and Woods, 2000).

Table 2-5. Copper mineral's solubility in 0.1% NaCN solutions (Flatt and Woods, 2000).

| **Mineral** | | **Total copper dissolved (%)** | |
|---|---|---|---|
| | | **23°C** | **45°C** |
| Azurite | $2CuCO_3·Cu(OH)_2$ | 94.5 | 100.0 |
| Malachite | $CuCO_3·Cu(OH)_2$ | 90.2 | 100.0 |
| Chalcocite | $Cu_2S$ | 90.2 | 100.0 |
| Copper metal | Cu | 90.0 | 100.0 |
| Cuprite | $Cu_2O$ | 85.5 | 100.0 |
| Bornite | $Cu_5FeS_4$ | 70.0 | 100.0 |
| Enargite | $Cu_3AsS_4$ | 65.8 | 75.1 |
| Tetrahedrite | $4Cu_2S·Sb_2S_3$ | 21.9 | 43.7 |
| Chrysocolla | $CuSiO_3$ | 11.8 | 15.7 |
| Chalcopyrite | $CuFeS_2$ | 5.6 | 8.2 |

Copper minerals dissolve in cyanide solutions to form a variety of Cu(I) cyanide complexes, $Cu(CN)_2^{-}$, $Cu(CN)_3^{2}$, $Cu(CN)_4^{3-}$, as shown by the Eh–pH diagrams for the Cu–CN–$H_2O$ system (Figure 2-4), and for the Cu–S–CN–$H_2O$ system (Figure 2-5). The formation of $Cu(CN)_3^{2-}$ shows the area in Figures 2-4 and 2-5 at which gold dissolution occurs.

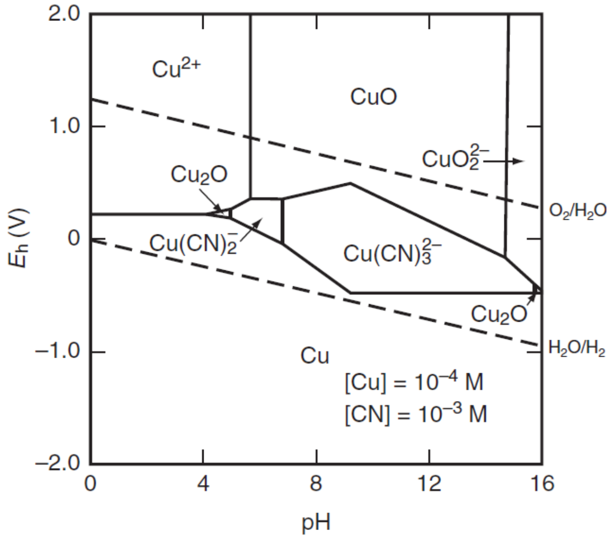


Figure 2-4 $E_h$-pH diagram of Cu-CN-$H_2O$ system at 25°C (Osseo-Asare et al., 1984).

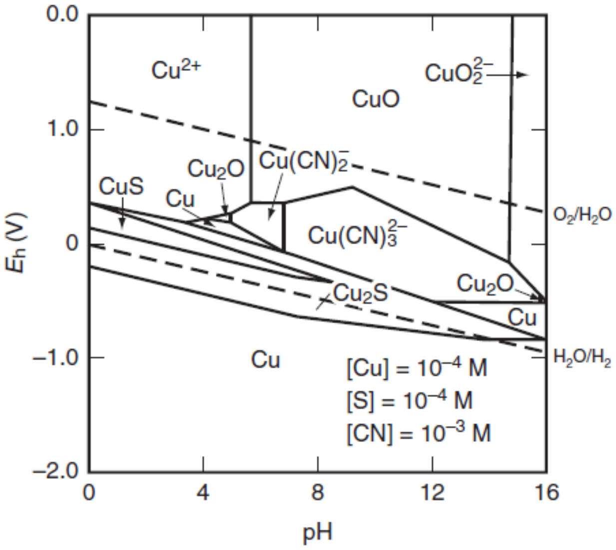


Figure 2-5. $E_h$-pH diagram of Cu-S-CN-$H_2O$ system at 25°C (Osseo-Asare et al., 1984).

Apart from the effect on gold leaching, the presence of copper cyanide ions in leach solutions can make the free cyanide titration with silver nitrate complicated. The reason for this is because during titration with silver nitrate, a part of the copper cyanide makes complexes with silver nitrate (Marsden and House, 2009). This provides a false sign of free cyanide concentration available for gold dissolution.

**2. Iron minerals**

Hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), goethite ($FeO{\cdot}OH$), siderite ($FeCO_3$), and iron silicates are insoluble in alkaline cyanide solutions (Marsden and House, 2009). Similarly, metallic iron (used for grinding media or process equipment) oxidised very slowly, and the cyanide consumption is insignificant in most leaching systems (Marsden and House, 2009).

The common iron-bearing sulfide minerals that are usually associated with gold are pyrite, arsenopyrite, marcasite, and pyrrhotite. The $E_h$–pH diagram for the Fe–S–CN–$H_2O$ system at 25°C is given in Figure 2-6. Pyrrhotite is the most reactive iron sulfide in alkaline cyanide solution (Marsden and House, 2009). Pyrrhotite releases one sulfur atom and reacts with cyanide as follows:

$$Fe_7S_8 + CN^- = 7FeS + CNS^- \qquad (2\text{-}14)$$

Further reaction produces ferrocyanide and various dissolved sulfur species:

$$2FeS + 12CN^- + 5O_2 + 2H_2O = 2Fe(CN)_6^{4-} + 2SO_4^{2-} + 4OH^- \qquad (2\text{-}15)$$

The order of decomposition rate of the most iron sulfide minerals in alkaline cyanide solutions is considered to be as follows (Marsden and House, 2009):

pyrrhotite >>> marcasite > arsenopyrite > pyrite

Other factors such as the presence of some ions in the mineral crystal structure, the association of the mineral with other reactive and/or conductive minerals may affect the decomposition rate of the minerals in alkaline cyanide solutions.

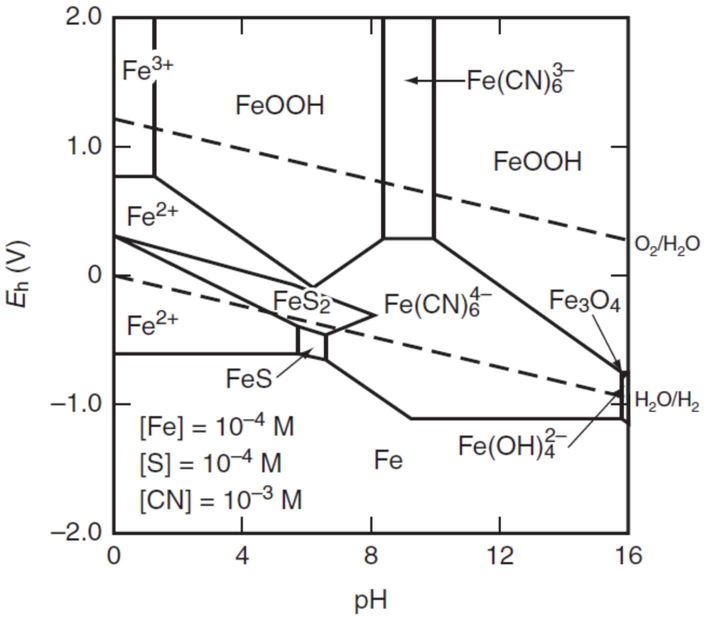


Figure 2-6. Eh–pH diagram for the Fe–S–CN–H2O system at 25°C (Osseo-Asare et al., 1984).

### 2.4.4 Grinding media effect on gold cyanidation

Apart from the effect of grinding media on the flotation process, grinding media may also affect the gold dissolution in cyanide. For example, it was found that when gold particles were in contact with forged steel, the dissolution rate of gold in the cyanide solution decreased due to the formation of a passive film on the gold particles and galvanic interaction between the gold and iron particles (Van Deventer et al., 1990). However, the effect of galvanic interaction between grinding media and sulfide minerals during grinding on gold dissolution in cyanide has not yet been systematically evaluated. One of the objectives of this thesis has been to study the influence of the grinding media (forged steel, low and high chromium, and ceramic media) on cyanide gold leaching in the presence of the most common iron sulfide minerlas such as pyrrhotite, pyrite and arsenopyrite.

## 2.5 Influence of water quality on gold leaching and flotation

Process water of the gold plant practically contains different cyanide species (cyanate, thiocyanate, and weak acid dissociable and strong acid dissociable cyanide), chloride ion and different salts. These species might have an effect on leaching and flotation performance which is discussed in this section. It is important to mention this work, did not look at the effect of salts from saline water and hyper-saline water.

### 2.5.1 Influence of metal-cyanide complexes on gold leaching

The behaviour of metal-cyanide complexes on gold leaching were evaluated by Rees and Van Deventer (1999). It was found that in the absence of free cyanide, some metal-cyanide complexes such as copper cyanide, zinc cyanide, nickel cyanide, silver cyanide and ferrous cyanide can release the free cyanide and dissolve gold. The reason for that is because metal-cyanide reacts with gold, leading to the formation of free cyanide and thus the dissolution of gold (Rees and Van Deventer, 1999). The reactions between gold and metal-cyanide complexes are given below:

$2Au + 4Cu(CN)_4^{3-} + ½O_2 + H_2O = 2Au(CN)^{2-}+2OH^- + 4Cu(CN)_3^{2-}$ (2-16)

$2Au + 4Cu(CN)_3^{2-} + ½O_2 + H_2O = 2Au(CN)^{2-}+2OH^- + 4Cu(CN)^{2-}$ (2-17)

$2Au + Ni(CN)_4^{2-} + ½O_2 + H_2O = 2Au(CN)^{2-} + 2OH^- + Ni^{2+}$ (2-18)

$2Au + 2Ag(CN)^{2-} + ½O_2 + H_2O = 2Au(CN)^{2-} + 2OH^- + 2Ag$ (2-19)

$2Au + 4Ag(CN)^{2-} + ½O_2 + H_2O = 2Au(CN)^{2-} + 2OH^- + 4AgCN$ (2-20)

Reactions 2-16 to 2-20 are expected to occur, followed by the formation of metal (copper, iron and nickel) hydroxide or in the case of silver, solid silver or AgCN. These gold leaching reactions happened due to the high stability of the gold cyanide species. Table 2-6 shows the stability constants for various metal cyanide species.

Table 2-6. Stability constants for metal cyanide species (Rees and Van Deventer, 1999).

| **Species** | **Stability (log Ɓ )** | **Species** | **Stability (log Ɓ)** |
|---|---|---|---|
| $Au(CN)_2^-$ | 39.3 | $Fe(CN)_6^{4-}$ | 35.4 |
| $Ag(CN)_2^-$ | 20.48 | $Fe(CN)_6^{3-}$ | 43.6 |
| $Cu(CN)_2^-$ | 16.26 | $Ni(CN)_4^{2-}$ | 30.22 |
| $Cu(CN)_3^{-2}$ | 21.66 | $Zn(CN)_4^{2-}$ | 19.62 |
| $Cu(CN)_4^{-3}$ | 23.1 | | |

### 2.5.2 Influence of cyanide complexes on flotation

Selective depression of sulfide minerals such as pyrite, pyrrhotite, sphalerite, marcasite can occur when cyanide or ferrocyanates are added during flotation. Cyanide depression of sufide minerals has been the subject of many investigations. Some researchers have proposed that the depressing effect of cyanide is due to the competition between cyanide and xanthate ions for the mineral surface (Marsden and House, 2009). Yannopoulos (1991) suggested that the depressing action of cyanide is due to removal of adsorbed copper ions from the mineral surface into solution. In the case of pyrite, the suggested mechanism of depression is the formation of a reaction product between the ferric ion and the pyrite surface and cyanide (ferrocyanide) ions (Yannopoulos, 1991).

It should be noted that cyanide in solutions can form various complexes with metals, organic compounds (collectors) and other reagents present in the pulp. Considering these facts, the action of cyanides in mineral pulp is highly complex. Each of the cyanide compounds may in one way or another affect flotation (i.e. depression or activation) of particular minerals (Bulatovic, 2007). It can be concluded that although cyanide is a widely used depressant, depressing action is highly complex and dependent on the nature of the mineral used, the composition of the pulp, pulp pH and the type of collector used.

### 2.5.3 Corrosive effects of chloride ion on metals and flotation performance

Corrosion is an electrochemical oxidation-reduction process, which occurs on the surface of metals in the presence of the electrolyte.

Anodic reactions: $Fe = Fe^{2+} + 2e^-$ (dissolution of iron) (2-21)

Cathodic reaction: $\frac{1}{2} O_2 + H_2O + 2e^- = 2(OH)^-$ (2-22)

According to Silva (2013), in the presence of chloride ion, the following reactions might occur:

$2FeCl_2 + 3H_2O + ½ O_2 \rightarrow 2FeOOH + 4HCl$ (2-23)

$2Fe + 4HCl + O_2 \rightarrow 2FeCl_2 + 2H_2O$ (2-24)

Equations 2-23 and 2-24 are known as acid regeneration reactions because the hydrochloric acid is produced (Equation 2-23), consumed (Equation 2-24) and generated again (Jegdić et al., 2011). This cycle shows that chloride ions play an important role in the corrosion process.

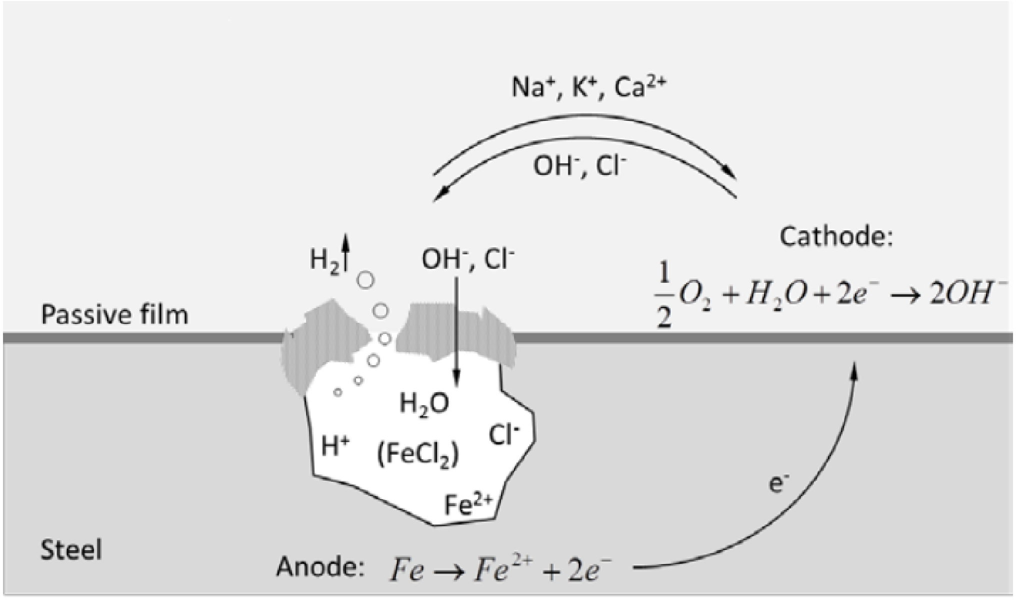


Figure 2-7. Schematic diagram of chlorine effect on corrosion (Silva, 2013).

Figure 2-7 shows the effect of chloride ions on corrosion of iron. It is known that in the presence of chloride ions, the corrosion rate of iron increases due to the formation of a soluble compound ($FeCl_2$) and difficulty to form a passive film on the iron (Selwyn et al., 1999). Therefore, in the presence of process water which contains large amount of chloride ions, iron hydroxide is produced. The formed iron hydroxide has a negative effect on flotation performance of some sulfide minerals (Peng and Grano, 2010).

## 2.6 Summary

The literature review has highlighted several significant areas requiring the investigations in order to understand the influence of grinding media on flotation and leaching performance of gold bearing sulfide ores. The key questions for considerations are:

- What are the effects of using different grinding media type on flotation performance of gold bearing sulfide ore?
- What are the effects of using different water quality (tap and process water) on flotation performance of gold bearing sulfide ore?
- What are the effects of using different grinding media type on cyanide leaching performance of gold in the presence of pyrrhotite, arsenopyrite and pyrite?
- What are the effects of grinding media, water quality and sulfide minerals on the galvanic interactions between grinding media and sulfide minerals during grinding?
- Are surface analysis techniques (SEM-EDX and XPS) sensitive enough to identify the chemical differences in particles collected during grinding with various grinding media?

Based on the literature review, the objectives of this study are:

(1) To characterize surface coatings on gold – bearing sulfide particles after grinding with different grinding media in tap water or synthetic process water;
(2) To investigate the influence of water quality and grinding media type on gold-bearing sulfide ore flotation performance;
(3) To investigate the influence of galvanic interaction between grinding media and sulfide minerals during grinding on gold cyanidation process.

# Chapter 3 Experimental Methods

The literature has highlighted a lack of understanding of the behaviour of different grinding media and water chemistry on downstream operations of gold ore processing such as flotation and leaching especially when the ore contains sulfide minerals. The proposed flotation and leaching tests will define the effect of grinding media and water quality on flotation and leaching performance of gold in the presence of low (pyrite) and high reactive (pyrrhotite and arsenopyrite) sulfide minerals.

## 3.1 Material

### 3.1.1 Kanowna Belle gold samples

The only valuable mineral in the ore is gold-rich pyrite (2.0%), while major non-valuable minerals are quartz (29.6%), albite (22.9%), muscovite (22.5%) and dolomite (11.6%). The concentration of gold in the ore is 5 g/tonne.

### 3.1.2 Minerals

Pure pyrite and arsenopyrite samples were obtained from Willyama Earth History Supplies, NSW, Australia. Pyrrhotite samples were obtained from Dalnegorsk, Primorskij Kraj, Russia. Silica was purchased from Bergie's Soils in Kalgoorlie (Western Australia). The purity of these minerals was above 99% as analysed with XRD.

### 3.1.3 Gold concentrate

Gravity gold concentrate from Serra Grande gold operation in Brazil was used for synthetic ore preparation (6% gold in Knelson gold concentrate). Table 3-1 shows the XRD analysis of the Sara Grande gold concentrate. It should be noted that pyrite is the only sulfide mineral contaminant and is present at very low levels compared to the amount of sulfide minerals in the ore used (or prepared synthetic ore).

Table 3-1 XRD analysis of the Sara Grande gold concentrate

| Mineral | Mass % |
|---|---|
| Clinochlore | 6 |
| Annite - biotite - phlogopite | 27 |
| Muscovite - sericite | 25 |
| Clinopyroxene | 3 |
| Albite | 3 |
| Alpha quartz | 26 |
| Dolomite - ankerite | 4 |
| Pyrite | 1 |
| Magnetite | 3 |

### 3.1.4 Synthetic ore

Pyrrhotite, arsenopyrite and pyrite samples, gravity gold concentrate and crushed silicate (P100 of 2 mm) were used to prepare the synthetic ore samples (see Table 3-2, 3-3 and 3-4) for grinding and leaching tests.

Table 3-2. Gold –pyrrhotite synthetic ore

| Gold-pyrrhotite Synthetic ore | Source | Weight (g) | Percentage |
|---|---|---|---|
| Pyrrhotite | 99% Pyrrhotite from Dalnegorsk, Russia | 12 | 2% |
| Gold | 6% Au Knelson gold concentrate | 0.5 | 50 ppm |
| Quarts | 99% Si and P100 < 2 mm | 587.5 | 98% |
| Total | | 600 | 100% |

Table 3-3. Gold –arsenopyrite synthetic ore

| Gold-arsenopyrite Synthetic ore | Source | Weight (g) | Percentage |
|---|---|---|---|
| Arsenopyrite | 98.5% Arsenopyrite | 12 | 2% |
| Gold | 6% Au Knelson gold concentrate | 0.5 | 50 ppm |
| Quarts | 99% Si and P100 < 2 mm | 587.5 | 98% |
| Total | | 600 | 100% |

Table3-4. Gold –pyrite synthetic ore

| Gold-pyrite Synthetic ore | Source | Weight (g) | Percentage |
|---|---|---|---|
| Pyrite | 98.5% pyrite | 12 | 2% |
| Gold | 6% Au Knelson gold concentrate | 0.5 | 50 ppm |
| Quarts | 99% Si and P100 < 2 mm | 587.5 | 98% |
| Total | | 600 | 100% |

### 3.1.5 Water compositions

The synthetic process water and the tap water were used during wet grinding and flotation experiments. The composition of the synthetic process water was based on the chemical analysis of the plant process water from the plant ball mill discharge (see Table 3-5). It should be noted that HPLC was used to determine the concentration of $SCN^-$, $OCN^-$and $SO_4^{2-}$ ions while ICP-OES was used to measure the concentration of $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$ ions. The chemical analysis of Adelaide tap water is given in Table 3-6.

Table 3-5. Chemical analysis of the process water from the ball mill discharge

| Species | Concentration (mg/L) |
|---|---|
| $Ca^{2+}$ | 2100 |
| $Mg^{2+}$ | 2800 |
| $Cl^-$ | 100000 |
| $SO_4^{2-}$ | 4340 |
| $SCN^-$ | 80 |
| $Fe(CN)_6^{4-}$ | 7.38 |

Table 3-6. Chemical analysis of Adelaide tap water

| Species | Concentration (mg/L) |
|---|---|
| Manganese | 0.0013 |
| Iron | 0.0104 |
| Chloride | 0.3 |
| Fluoride | 0.85 |
| Total dissolved solids | 187 |

## 3.2 Magotteaux mill and flotation system

### 3.2.1 Magotteaux mill

Grinding of the Kanowna belle gold ore was performed in a specially designed laboratory ball mill manufactured by Magotteaux which allows better simulations of plant chemical conditions by controlling pH, pulp potential and dissolved oxygen (DO) during grinding. The feed ore was prepared to a $P_{80}$ of 106 µm by wet grinding at 50% w/w solids in the ball mill. This ball mill allows better control of Eh, pH and DO (dissolved oxygen) content by regulating the duration of air and nitrogen purging during grinding of ores (Greet et al., 2004). The three different grinding media used were:

- Forged steel media,
- Chromium media (18% Chromium) and
- Ceramic media.

Given that grinding of ores in the Kanowna Belle plant ball mill is conducted with chromium media in the presence of the plant process water and 60 g/t of $CuSO_4$ as an activator, the calibration of the Magotteaux mill was also performed with the same grinding media in the presence of the synthetic process water and 60 g/t of $CuSO_4$. The Magotteaux mill was calibrated to match pulp chemical variables of the plant ball mill discharge (pH=8.0 ± 0.2; Eh = -60 ± 24 mV (SHE); DO = 2.1±0.5 ppm; T = 31°C) by adjusting the time required for nitrogen and air purging during grinding. The duration of nitrogen and air purging was kept constant in all experiments, and 60 g/t of $CuSO_4$ was added prior to grinding stage.

### 3.2.2 Flotation Experiments

The ground pulp was transferred to a 5 L flotation cell, and the required amount of water was added to the system. The impeller speed was set at 900 rpm. The mixing pulp was conditioned with 60 g/t of the guar gum depressant, 45 g/t of the potassium amyl xanthate collector and 20 g/t of the frother Dowfroth 400. It should be noted that all flotation chemicals were used as supplied from the Kanowna Belle mine site. Once conditioning of flotation pulp was completed, 10 L/min of air was introduced at the bottom of the flotation cell, and the flotation took place. A manual scraper was used to collect the froth into launders every 10 s. The concentrates were collected after cumulative time of 0.5 min, 1.5 min, 3 min and 5 min. It should be noted that all the grinding and flotation experiments were repeated two times. The obtained flotation data were used to calculate the flotation rate constants using a first order model:

$$R = R_{\infty}(1-\exp(-kt)) \tag{1}$$

Where k is the rate constant and $R_{\infty}$ is the ultimate recovery. The first order model was selected since this model gives a good prediction of pyrite recovery under a wide range of pulp chemical conditions (Albijanic et al., 2015).

### 3.3 Modified grinding system

The modified grinding system was designed not only to replicate plant mill performance at a laboratory scale but also for conducting the in situ electrochemistry measurements. To match this performance it is necessary to operate the mill for producing the desired particle size distribution. It is also important to calibrate the mill for each grinding media type being used to ensure the same size distribution is produced in each experiment. The schematic diagram of this modified grinding system, the mechanical parts and the grinding system are shown in Figures 3-1 to 3-3, respectively.

In Chapter 7 of this project, the feed ore was prepared to a P80 of 75 µm by wet grinding at 34% w/w solids in the modified grinding system as seen in Figures 3-3. The four different grinding media were used: forged steel, 21% chromium, 30% chromium, and ceramic media. The surface area of the grinding chamber is 0.2 $m^2$. Table 3- 7 shows the dimension, surface area, and chemical properties of different grinding media types used in this project.

The grinding system (see Figure 3-3) was built not only to grind the ore but also to monitor the chemical conditions (pH, Eh, and dissolved oxygen) during grinding of the ore samples. The changes of chemical conditions during grinding of the ore were recorded every minute by the controller system. In addition, every 20 minutes around 35 mL of the slurry was collected (from the peristaltic pump tube) for the EDTA iron extraction and sulfur measurements.

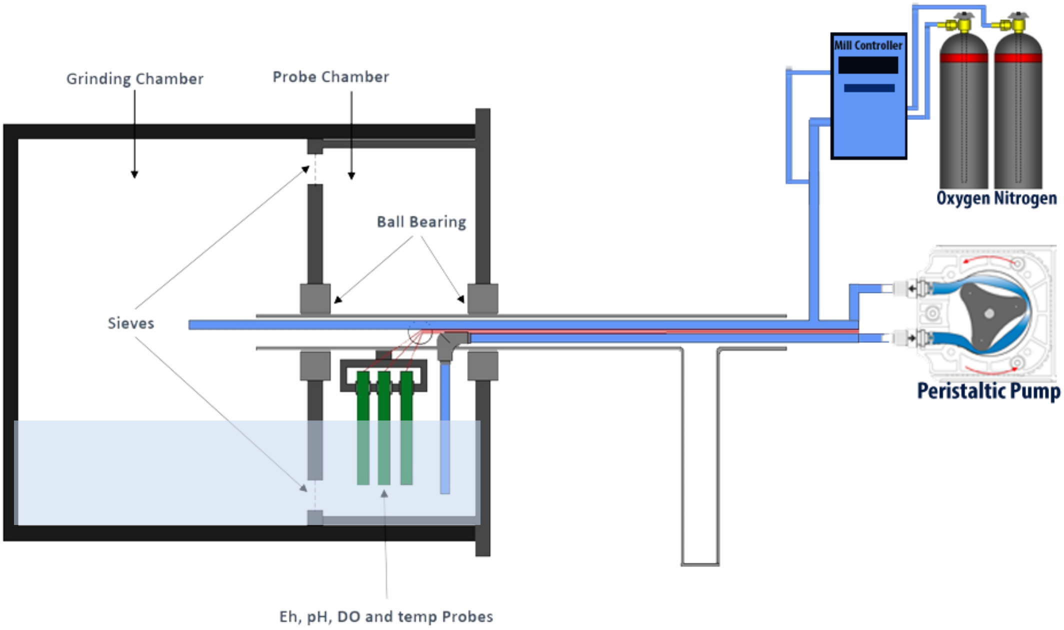


Figure 3-1. Schematic diagram of the modified grinding system (Rabieh et al., 2017b).

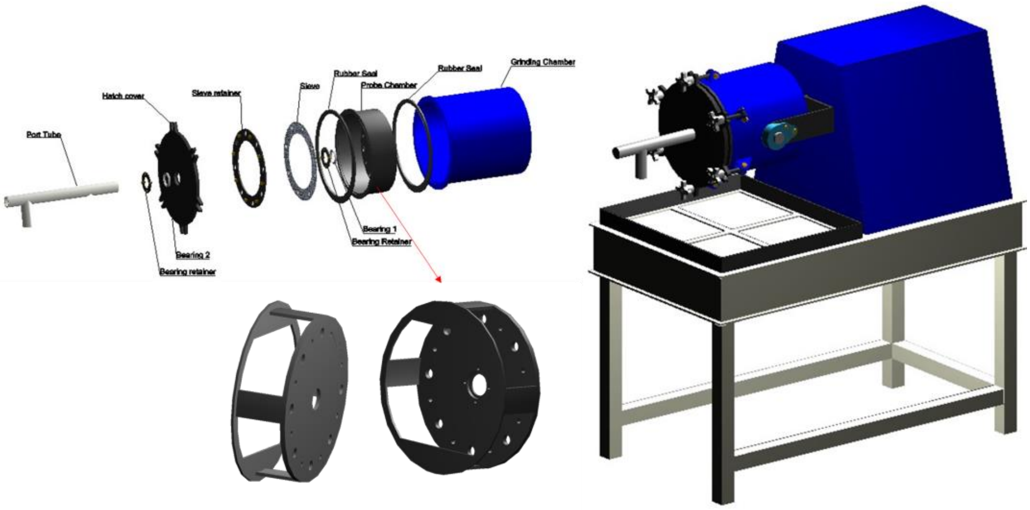


Figure 3-2. Schematic diagram of the mechanical parts of the grinding system (Rabieh et al., 2017b).

Figure 3-3. Modified laboratory mill (Rabieh et al., 2017b).

Table 3-7. Properties of grinding media

| Media | Diameter (mm) | Weight (kg) | Surface area (m$^2$) | Chemical Composition of Media |
|---|---|---|---|---|
| Forged steel | 25 | 6 | 0.3 | 98% Fe; 0.8% C; 0.3% Cr; 0.2% Si and 0.7% Mn |
| 21%chromium | 25 | 6 | 0.3 | 75% Fe; 2.8% C; 21% Cr; 0.45% Si and 0.75% Mn |
| 30% chromium | 25 | 6 | 0.3 | 67% Fe; 2.3% C; 30% Cr; 0.45% Si; and 0.45% Mn |
| Ceramic | 20 | 6 | 0.4 | 97% $ZrO_2$; 3% MgO; 0.3% $SiO_2$; 0.2% $Fe_2O_3$; 0.3% CaO; 0.2% $TiO_2$; 0.2% $Al_2O_3$ |

### 3.4 Cyanide leaching test procedure

After grinding, the mill discharge was transferred into the 3L glass reactor (Figure 3-4), mechanically agitated along with a sufficient quantity of Perth tap water to generate slurry samples at 22% (w/w) solid ratio. Around 12 mL of caustic soda solution (1 M NaOH) was added to maintain pulp pH of approximately 10.5 and then mixed for another five minutes; after that, the solid sodium cyanide was added to the slurry in order to keep cyanide solution strength at 500ppm. During the leaching process, approximately 20ml of slurry samples were collected after 2, 4, and 24 hours. These samples were filtered to analyse the solution for gold content by atomic absorption technique, cyanide speciation by high performance liquid chromatography (HPLC), and solution cyanide strength by silver nitrate titration.

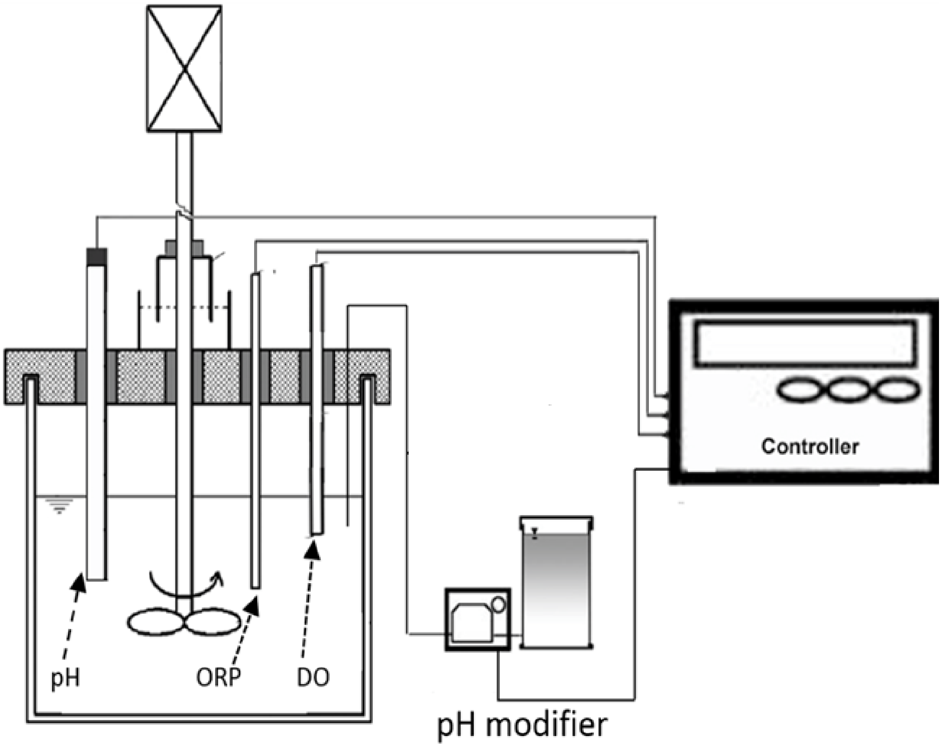


Figure 3-4. Schematic view of the leaching apparatus.

### 3.5 Determination of iron hydroxide content by EDTA

Ethylene diamine tetra acetic disodium salt (EDTA) extraction followed by induction coupled plasma (ICP) analysis technique was employed to measure the percentage of extractable iron oxide/hydroxide from minerals or grinding media at the mineral particle surfaces. A volume of 250 mL of a 3 wt. % solution of AR grade EDTA solution was prepared. The solution was then placed into the Magotteaux EDTA extraction vessel. The solution was stirred slowly with a magnetic stirrer and purged with nitrogen gas at 4 L/min for 5 minutes to remove any dissolved oxygen and then approximately 25 mL of slurry was collected from the flotation cell and injected into the EDTA solution. The stirrer speed was adjusted to ensure suspension of solids. The EDTA/slurry mixture was stirred for 5 minutes while continuing to purge with nitrogen at 4 L/min. The EDTA/slurry mixture was then filtered by using a 0.2 microns millipore filter membrane and the solutions was analysed by ICP for iron content.

### 3.6 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive analysis technique which uses the photoelectric effect to identify and quantify elements on the surface of materials (Chen et al., 2013). The instrument focuses an X-ray beam at the target material; photoelectrons are ejected from the atoms of the material with a specific kinetic energy depending on the presence of different atoms in the studied material. By measuring this kinetic energy, the identity of the atom is found. The number of electrons measured at that energy provides information about the amount of this element on the surface of the material. Two spectral regimes can be produced by XPS, survey spectra and high resolution spectra (Chen et al., 2013). The survey spectra allow the identification and quantification of the elements on the surface, while the high resolution spectra allow the identification and quantification of the bonding associated with an element.

The XPS instrument used in this study was a Kratos Axis Ultra with DLD. The X-ray was a monochromatic aluminium X-ray running at 225 W with a characteristic energy of 1486.6 eV. The area of analysis (Iris aperture) was a 0.3 mm x 0.7 mm slot; the analysis depth was approximately 15 nm into the surface of the sample. The analysis vacuum was $4 \times 10^{-9}$ Torr. The electron take off angle was normal to the sample surface. Spectra were interpreted using the software package CasaXPS.

### 3.7 SEM/EDX analysis

The Scanning Electron Microscope (SEM) is a type of electron microscope, which produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with the atoms in the sample, producing three signals (secondary electrons, backscattered electrons and X-rays) that contain information about the sample surface, topography and composition. Secondary electrons are emitted from the top surface atoms and produce an image of the surface. Backscattered electrons are primary beam electrons that are 'reflected' from atoms in the solid. The contrast in the images is determined by the atomic number of the elements in the sample. The image will, therefore, show the distribution of different chemical phases in the sample.

The interaction of the primary beam with atoms in the sample causes shell transitions that result in the emission of an X-ray. The emitted X-ray has an energy characteristic of the parent element. Detection and measurement of the energy permit elemental analysis (Energy Dispersive X-ray Spectroscopy, or EDX). EDX analysis can provide rapid qualitative or, with adequate standards, quantitative analysis of elemental composition with a sampling depth of 1–2 µm. X-rays may also be used to form maps or line profiles, showing the elemental distribution in a sample surface (Velásquez et al., 2000; Azizi, 2015).

The SEM/EDX instrument used in this study is a ZEISS NEON 40EsB FIBSEM. The NEON is a dual beam focussed ion beam scanning electron microscope (FIBSEM) equipped with a field emission gun and a liquid metal $Ga^+$ ion source. This instrument combines high-resolution imaging with a precision ion beam with the capabilities of high-resolution imaging using Secondary Electrons (SE), Back Scattered Electrons (BSE) and in-lens detectors (the resolution is 1.1 nm at 20 kV to 2.5 nm at 1 kV), as well as elemental composition analysis of the samples with Energy Dispersive X-ray Spectroscopy (EDX).

## 3.8 Electrodes preparation and voltammetry apparatus

### 3.8.1 Grinding media electrodes preparation

Four types of grinding media were used to make the working electrodes. A grinding media sample was cut to the size of 15 x 15 x 3 mm to fill a Teflon tube. The electrode was connected to a screw by a conductive epoxy resin, and non-conductive epoxy was used to fill between the Teflon tube and electrodes for isolation. Before each experiment, the electrode surface was gently polished by a set of polishing discs and alumina slurries (grain size of 0.3 and 0.05 µm) for around 10 minute. The surface of the polished electrodes, analysed by SEM, was flat with small holes. Some scratch lines can be seen diagonally across the microphotograph (see Figure 3-5). Figure 3-6 shows the quantitative EDX analysis of the polished grinding media electrodes.  The results obtained by quantitative SEM/EDX analysis are in agreement with the chemical composition data (Table 3-8) provided by the supplier, Magotteaux Company.

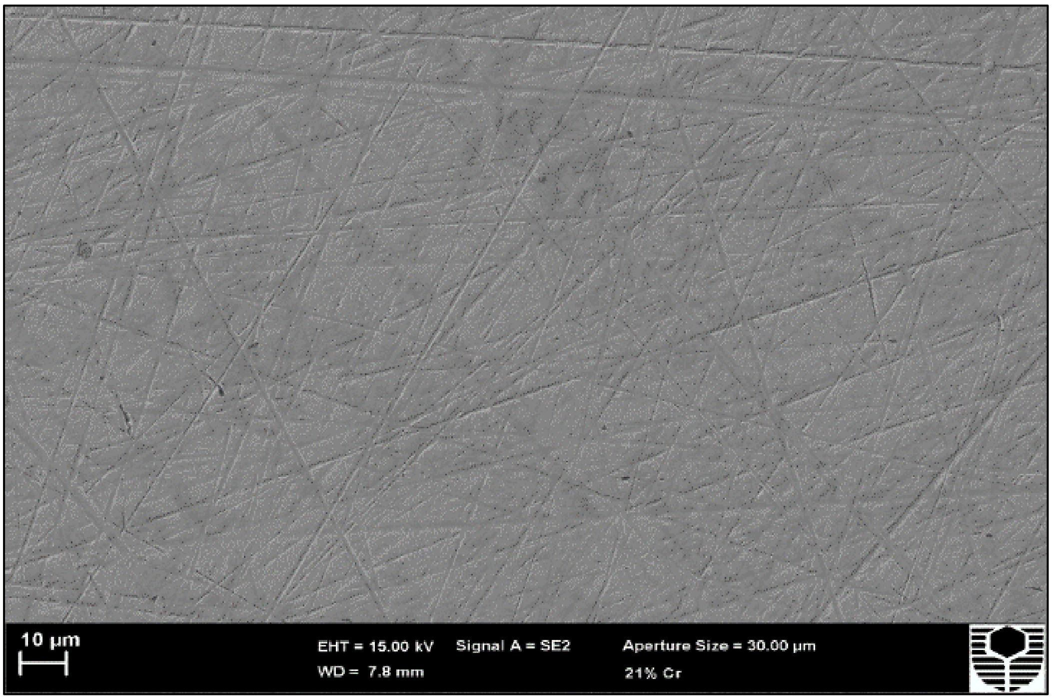
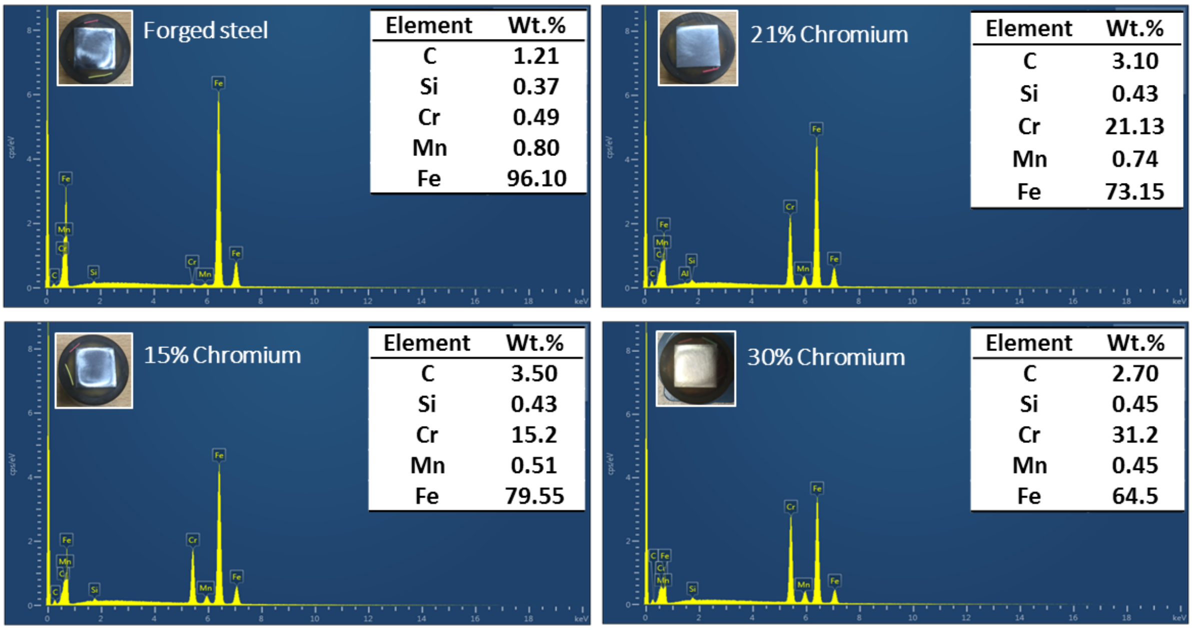


Figure 3-5. Secondary electron image of 21% chromium grinding media electrode



Forged steel

| Element | Wt.% |
|---|---|
| C | 1.21 |
| Si | 0.37 |
| Cr | 0.49 |
| Mn | 0.80 |
| Fe | 96.10 |

21% Chromium

| Element | Wt.% |
|---|---|
| C | 3.10 |
| Si | 0.43 |
| Cr | 21.13 |
| Mn | 0.74 |
| Fe | 73.15 |

15% Chromium

| Element | Wt.% |
|---|---|
| C | 3.50 |
| Si | 0.43 |
| Cr | 15.2 |
| Mn | 0.51 |
| Fe | 79.55 |

30% Chromium

| Element | Wt.% |
|---|---|
| C | 2.70 |
| Si | 0.45 |
| Cr | 31.2 |
| Mn | 0.45 |
| Fe | 64.5 |

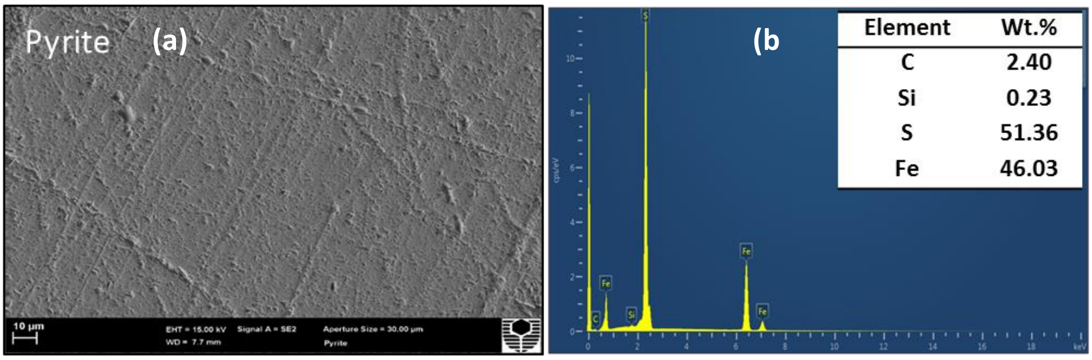
Figure 3-6. Quantitative EDX analysis of grinding media electrodes (polished electrodes)

Table 3-8. Chemical composition of grinding media types

| Media | Elements present (Wt. %) | | | | | |
|---|---|---|---|---|---|---|
| | C | Mn | Cr | Si | S | P |
| Forged steel | 0.8 | 0.8 | 0.3 | 0.2 | 0.05 | 0.05 |
| 15% Chromium (15% Cr) | 3.2 | 0.45 | 15 | 0.45 | <0.09 | <0.09 |
| 21% Chromium (21% Cr) | 2.8 | 0.75 | 21 | 0.45 | - | - |
| 30% Chromium (30% Cr) | 2.3 | 0.45 | 30 | 0.45 | 0.06 | 0.06 |

### 3.8.2 Mineral electrode preparation

Four types of carbon paste-mineral electrodes (pyrite, arsenopyrite, pyrrhotite and, gold-bearing pyrite electrode) were prepared. The crystal mineral electrodes consisted of ground pure pyrite, arsenopyrite and pyrrhotite particles. The gold-bearing pyrite electrode had a sized fraction of (+38-53 µm) the concentrate obtained by flotation of the Kanowna Belle gold ore and contained 94 % of gold-bearing pyrite particles. The carbon paste-mineral electrode was prepared by thoroughly mixing 4 g of graphite powder with 3 g of pure sulfide minerals or gold-bearing pyrite and 3 g of paraffin oil. The carbon paste-mineral was packed into the hole of the electrode's body and smoothed on clean paper until it had a shiny surface. Figure 3-7 shows the SEM and quantitative EDX analysis of the pure pyrite.



| Element | Wt.% |
|---|---|
| C | 2.40 |
| Si | 0.23 |
| S | 51.36 |
| Fe | 46.03 |

Figure 3-7. Secondary electron image (a) and quantitative EDX analysis (b) of pure pyrite

### 3.8.3 Voltammetry apparatus

All linear sweep voltammetry measurements were performed using a WaveNow Potentiostat/Galvanostat system (Model number: AFTP1) provided by Pine Research Instrumentation (Figure 3-8). The three-electrode setup consisted of the grinding media electrode or carbon paste-mineral electrode as the working electrode, an Ag/AgCl in 3 mol/L KCl as a reference electrode and platinum wire as a counter electrode.

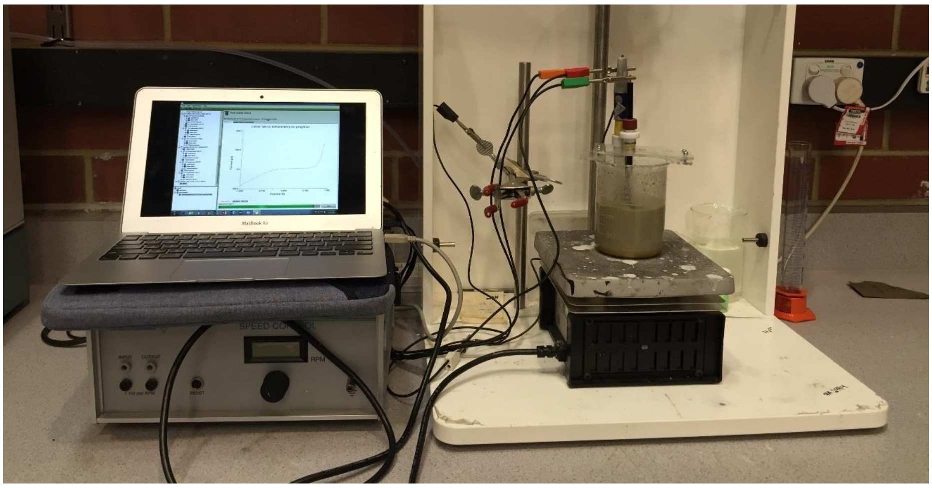


Figure 3-8. Voltammetry apparatus

### 3.8.4 In situ mill voltammetry

All in situ mill electrochemistry measurements were performed using a WaveNow Potentiostat/Galvanostat system where the Potentiostat’s electrodes were placed inside the mill. The three-electrode setup consisted of the grinding media electrode or carbon paste-mineral electrode as the working electrode, Ag/AgCl in 3 mol/L KCl as a reference electrode and platinum wire as a counter electrode.

# Chapter 4 Investigation of corrosion process of grinding media in the absence of sulfide minerals

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## 4.1 Introduction

Consumption of grinding media during wet grinding of ores can be up to 50% of the overall grinding cost (Aldrich, 2013). There are three different mechanisms that can cause the consumption of grinding media: abrasion, impact and corrosion. Although abrasion and impact take place due to the mechanical force only, the corrosion process is more complex as it depends on numerous factors such as grinding media, water composition and ore mineralogy (Rabieh et al., 2016). Therefore, understanding of corrosion process is essential to reduce the consumption of grinding media. More importantly, it has been reported that during corrosion process, the dissolution of the grinding media leads to the formation of iron hydroxide species, which can significantly influence flotation recovery of pyrite (Greet et al., 2004) and sulfide minerals (Rabieh et al., 2017a).

Corrosion of grinding media can be investigated by analysing the surface properties of particles using numerous experimental techniques such as conventional X-ray photoelectron spectroscopy (XPS), synchrotron XPS and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS). However, the conventional XPS technique has been widely used since this technique has the required level of sensitivity for quantitative analysis of mineral surfaces (Nagaraj and Brinen, 2001; Smart et al., 2000).

Apart from XPS analysis, ethylene diamine tetra acetic disodium salt (EDTA) extraction technique is also extensively used to quantify the degree of corrosion of grinding media. For example, Peng and Grano (2010) used EDTA extraction technique and found that grinding of pure pyrite with the forged steel media produced 30% more iron oxidising species than grinding of pyrite with the chromium media.

Although some authors have investigated the corrosion of grinding media during grinding of sulfide ores, the literature does not provide any information about corrosion process of grinding media during grinding of electrochemically inert minerals (i.e. there are no galvanic interactions between grinding media and mineral particles). For that reason, the main objective of this work is to contribute to better understanding of this matter. In this study, pure quartz particles were selected as an electrochemically inert mineral. Different grinding media (forged, 18% chromium and ceramic media) and different types of water (the tap water and the synthetic process water) were used to alter grinding conditions. XPS and EDTA extraction technique were performed to analyse quartz surfaces after grinding. This provides the baseline or background effect in the absence of sulfide minerals. It should be noted that the presence of sulfide minerals in ores may lead to formation of various products (i.e. iron hydroxide species) due to galvanic interactions between sulfide minerals and grinding media.

## 4.2 Results and Discussion

### 4.2.1 Pulp chemistry during grinding

The sample was prepared to a P80 of 106 µm by wet grinding at 50% w/w solids in the specially designed laboratory ball mill (Magotteaux, Belgium) which can simulate plant conditions by controlling pH and pulp potential during grinding process (Greet et al., 2004). Three different grinding media were employed: chromium media (18% Cr), ceramic media and forged steel media.

The calibration of the laboratory ball mill was performed with the chromium media in the presence of synthetic process water to match pulp chemical conditions of the plant ball mill discharge (pH=8.0 ± 0.2; Eh (SHE) =-60 ± 24 mV; DO=2.1±0.5 ppm; T=31°C). The results of the calibration of this mill showed that the time for nitrogen purging was 13 min while that for air purging was 8 min. The duration of nitrogen and air purging was kept constant in all experiments.

The pulp potential and dissolved oxygen measurements during grinding of quartz are given in Figure 4-1. As seen in Figure 4-1, when grinding of quartz was performed in the presence of synthetic process water, changes from forged steel media to chromium and ceramic media shifted the grinding conditions from strongly reducing to mildly oxidising. Although the similar trend was also observed during grinding of quartz in tap water, the difference between grinding media was much less pronounced.

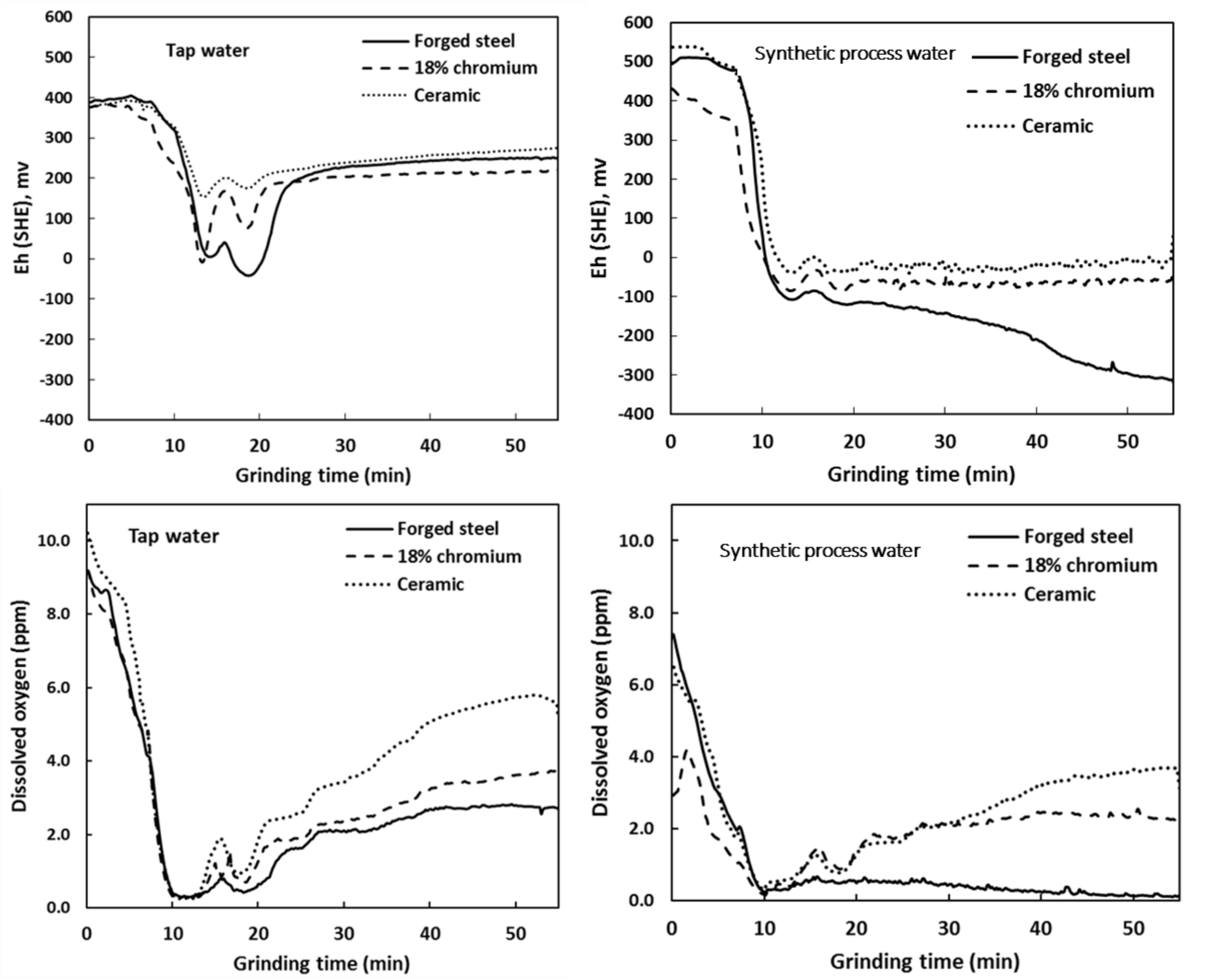


Figure 4-1. Pulp potential and dissolved oxygen measurements during grinding in tap and synthetic process water.

The significant reduction of pulp potential during grinding of quartz in the synthetic process water is probably due to a large amount of chloride ions, causing the corrosion of grinding media (Fontana, 1987). According to Silva (2013) in the presence of chloride ions, the corrosion of iron is accelerated because the oxide layer is partially solubilised as ferrous chloride.

### 4.2.2 EDTA measurements

The samples from mill discharge were analysed by EDTA extraction technique. The EDTA extracted iron originated from the oxidation of grinding media since the grinding sample did not contain any sulfide minerals, and thus galvanic interactions between mineral particles and grinding media do not exist. For that reason, the amount of EDTA extractable iron is an indicator for the corrosion rate of the grinding media.

The percentage of extractable iron at different grinding conditions is shown in Figure 4-2. As seen in Figure 4-2, grinding of quartz with the forged media (electrochemically active media) produced the highest amount of EDTA extracted iron, while the opposite is true in the case of grinding with the ceramic media (electrochemically inert media). Additionally, grinding of quartz with the synthetic process water slightly accelerated the corrosion of grinding media due to the chloride ions presence in the synthetic process water which can accelerate the corrosion rate of iron (Fontana, 1987).

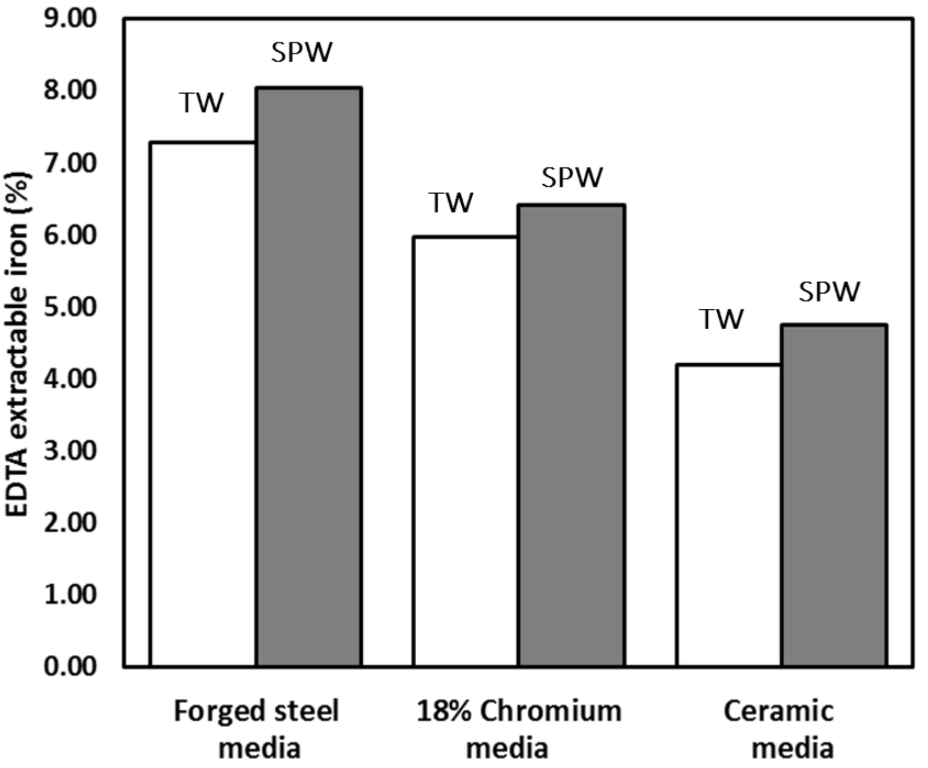


Figure 4-2. EDTA extractable iron under different grinding conditions.

### 4.2.3 XPS spectrum

XPS analysis was performed to study surface composition of quartz particles collected after grinding with different grinding media in the presence of the synthetic process water or the tap water. The XPS analysis involved the survey spectrum (i.e. identifications and quantifications the elements on the surface of samples) as well as the high resolution spectra showing the oxidation state of Fe.

Table 4-1. Concentration of the elements measured by XPS on the surface of samples.

| Grinding conditions | Elemental concentration (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | O | C | Na | Fe | Si | Cl | Ca | Al | Mg |
| Forged + TW | 60.06 | 14.89 | 0.50 | 1.25 | 21.45 | - | 0.21 | 0.65 | 0.85 |
| 18% Cr + TW | 60.64 | 14.79 | 0.49 | 1.22 | 20.79 | - | 0.26 | 0.55 | 0.67 |
| Ceramic + TW | 61.95 | 13.39 | 0.82 | 0.88 | 21.32 | - | 0.19 | 0.39 | 0.49 |
| Forged + SPW | 57.52 | 15.32 | 1.53 | 2.13 | 19.07 | 0.91 | 0.32 | 0.65 | 1.68 |
| 18% Cr + SPW | 57.90 | 17.17 | 1.31 | 1.72 | 18.68 | 0.61 | 0.61 | 0.68 | 0.33 |
| Ceramic + SPW | 57.05 | 16.52 | 1.61 | 1.25 | 19.14 | 0.73 | 0.36 | 1.07 | 1.40 |

TW-tap water; SPW-Synthetic process water

Table 4-1 shows the percentage of elements on the surface of quartz particles. The percentage of Fe on the surface of the samples was the highest when grinding was performed with the forged steel media due to the corrosion process of this media. This correlates well with the EDTA extraction results. Table 4-1 also shows that the surface of quartz samples contained higher amount of Na, Mg and Cl when experiments were performed in the presence of the synthetic process water than that in the tap water. This is attributed due to the addition of NaCl, $MgSO_4$ and KSCN in the tap water during the preparation of the synthetic process water to simulate the chemistry of the process plant water. It should be noted that when the ceramic media was used, iron was detected due to the corrosion of the mill liner in the tap and synthetic process water; this gives the background iron for all the tests.

Figure 4-3 shows the high resolution spectrum of Fe. The table in each graph shows the position and percentage of each species in the survey spectrum of the samples. Iron was detected on the surface of all samples and the $Fe_{2p}$ spectra indicate that iron oxide and hydroxide was present on quartz surfaces. This is shown by the band in the $Fe_{2p}$ spectrum at 711 eV and 713 eV for iron oxide and hydroxide species, respectively (Buckley and Woods, 1984).

This study showed that XPS and EDTA technique are sensitive enough to study the corrosion process of grinding media. This is particularly useful to understand the influence of grinding media on flotation recovery of valuable minerals.

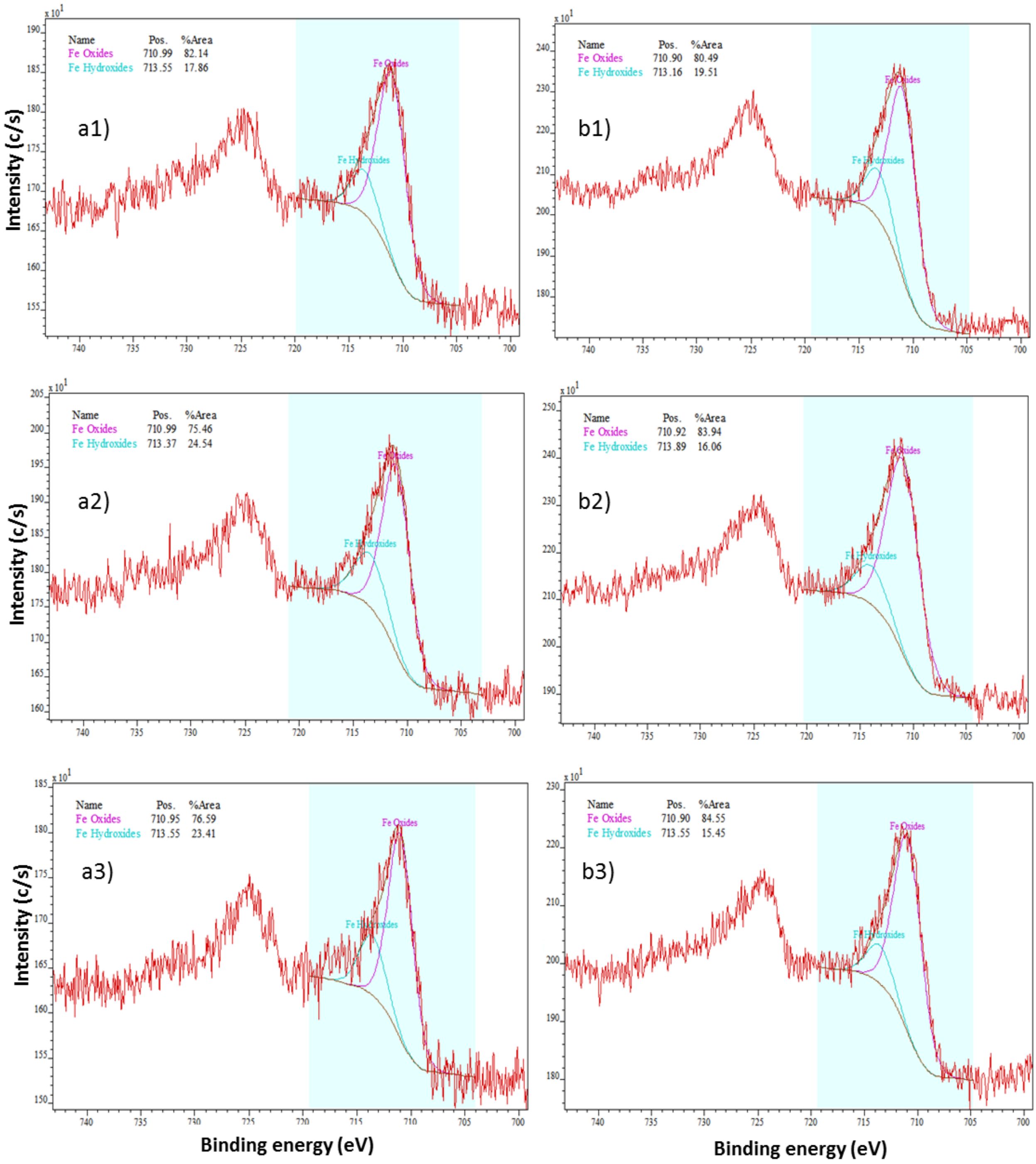


Figure 4-3. The iron high resolution spectrum of mill discharge obtained under different grinding conditions: forged steel media with a1) tap water and b1) synthetic process water; 18% chromium media with a2) tap water and b2) synthetic process water; ceramic media with a3) tap water and b3) synthetic process water.

### 4.3 Summary

In this work, XPS and EDTA extraction technique were conducted to study the influence of different grinding media and composition of water on corrosion of grinding media during grinding of quartz. Both techniques demonstrated higher corrosion rate of the forged media. The synthetic process water also accelerated the corrosion process of the grinding media probably due to a significant amount of chloride ions. When the ceramic media was used, iron was detected due to the corrosion of the mill liner in the tap and synthetic process water; this gives the background iron for all the tests. This research demonstrated the importance of XPS and EDTA extraction technique to study the corrosion process of grinding media. Further work is required to establish the relationships between the corrosion of grinding media and downstream processing.

# Chapter 5 Influence of grinding media and water quality on flotation performance of gold bearing pyrite

## 5.1 Introduction

Flotation is used to recover gold-bearing pyrite, and is based on the differences between the surface properties of pyrite and non-sulfide minerals. The surface properties of pyrite strongly depend on the grinding environment which might improve, aggravate or have no effect on pyrite floatability (Rabieh et al., 2016).

The grinding environment can be changed by the presence of some chemical species in the process water. For example, in the gold mining industry, free cyanide is added during leaching to dissolve gold locked in pyrite. Although a significant amount of free cyanide (and its metal complexes and derivatives) might be destroyed following the leaching process (Adams, 2013), the recycled process water commonly contains some residual cyanide, cyanide derivatives such as cyanate and thiocyanate and metal cyanide complexes such as copper and iron cyano-complexes, which are known to depress pyrite flotation. Additionally, if a small amount of free cyanide is present in the process water, floatability of liberated gold is reduced due to the formation of the stable and soluble ion $Au(CN)_2^-$ (Rees and Van Deventer, 1999; Yin et al., 2011).

Apart from chemical species dissolved in the process water, the grinding media might also affect the grinding environment and thus the floatability of pyrite. The selection of media for grinding of pyrite ores may be dependent on whether or not $Cu^{2+}$ (activator) is added prior to the grinding stage (Peng and Grano, 2010; Chen et al., 2013). Peng and Grano (2010) found that if $Cu^{2+}$ was not added during grinding of pure pyrite, the floatability of this mineral was enhanced when the grinding was conducted with the high chromium media compared to that with the mild steel media. This was probably due to the contamination of pyrite surfaces with hydrophilic iron hydroxide species during the grinding with the mild steel media, which prevented the adsorption of collector on the pyrite surface, rendering this mineral less floatable. Greet et al. (2004) also found a beneficial effect of chromium media on the floatability of pyrite from its ores when the grinding was performed in the absence of $Cu^{2+}$ ion.

On the other hand, if $Cu^{2+}$ was added before the grinding of pure pyrite, the floatability of this mineral was higher when the grinding was performed with the mild steel media than with the chromium media (Peng and Grano, 2010; Chen et al., 2013). The reason for this behaviour can be attributed to the less oxidizing environment (200 mV (SHE)) produced during the grinding with the mild steel media, which provides an environment for the activation of the pyrite surfaces through the reduction of $Cu^{2+}$ to $Cu^{+}$. This observation was experimentally confirmed using conventional XPS (Peng et al, 2003a). More precisely, it was found that the percentage of adsorbed $Cu^{+}$ on pyrite surfaces was 1.5 times higher when grinding of this mineral was performed with the mild steel media than that with the 18% chromium media. In the case of grinding of pure pyrite with the chromium media, Richardson et al. (1996) showed that the oxidising environment (330 mV (SHE)) produced during grinding with this media diminished the adsorption of copper ions on pyrite surfaces and thus significantly reduced the floatability of pyrite.

A literature review has identified the following knowledge gaps: 1) There is no study investigating the influence of the grinding environment on floatability of pyrite from its ores when $Cu^{2+}$ is added during grinding; 2) The influence of water quality on flotation performance of pyrite from its ore is rarely available; 3) There is limited information about using of XPS analysis and EDTA extraction method to explain the flotation behaviour of valuable minerals from its ore. For that reason, the objective of this work was to investigate the effect of the type of grinding media (i.e. 18% chromium, ceramic and forged media) and water quality (tap water and synthetic process water) on floatability of gold bearing pyrite and gold recovery using XPS analysis and EDTA extraction technique. The gold ore used in this work was obtained from Kanowna Belle gold mine (Kalgoorlie, Western Australia). This plant has a flotation circuit to recover gold-bearing pyrite and a gravity circuit to recover free gold. Therefore, the flotation feed contained gold locked in pyrite and free gold.

## 5.2 Results and Discussion

### 5.2.1 Pulp chemistry

The pulp chemical measurements of the mill discharge are given in Table 5-1. As seen in Table 5-1, changes from forged steel media to chromium and ceramic media shifted the grinding conditions from strongly reducing to moderately oxidising. The cause for the decrease of pulp potential during grinding with forged media is due to the galvanic interactions between forged media and pyrite. For more details about galvanic interactions, the readers are referred to the relevant literature (Bruckard et al., 2011). The pulp variables after conditioning are given in Table 5-2. As seen in Table 5-2 and Table 5-3, DO content generally increased after conditioning, resulting in an increase in the pulp potential.

Table 5-1. Chemical measurements of mill discharge. (SPW is the synthetic process water and TW is the tap water.)

| Water | Media | Mill discharge | | | |
|---|---|---|---|---|---|
| | | DO (ppm) | pH | Eh, SHE (mV) | Temp (°C) |
| TW | Forged steel | 0.10 | 9.10 | -241 | 31.20 |
| SPW | Forged steel | 0.30 | 8.00 | -310 | 32.00 |
| TW | 18% Chromium | 0.50 | 9.00 | 187 | 32.00 |
| SPW | 18% Chromium | 0.40 | 8.10 | -70 | 31.60 |
| TW | Ceramic | 0.90 | 9.20 | 247 | 30.80 |
| SPW | Ceramic | 0.70 | 8.00 | 169 | 33.10 |

Table 5-2. Chemical measurements of flotation pulp after conditioning.

| Water | Media | Flotation pulp after conditioning | | | |
|---|---|---|---|---|---|
| | | DO (ppm) | pH | Eh, SHE (mV) | Temp (°C) |
| TW | Forged steel | 0.57 | 8.94 | 155 | 24.30 |
| SPW | Forged steel | 0.05 | 8.03 | -8 | 25.90 |
| TW | 18% Chromium | 4.55 | 8.97 | 221 | 25.20 |
| SPW | 18% Chromium | 0.51 | 8.22 | 208 | 24.80 |
| TW | Ceramic | 6.06 | 9.01 | 246 | 23.90 |
| SPW | Ceramic | 1.93 | 8.14 | 259 | 27.10 |

Table 5-3. Chemical measurements of flotation tailings.

| Water | Media | Tailings | | | |
|---|---|---|---|---|---|
| | | DO (ppm) | pH | Eh, SHE (mV) | Temp ($^{o}$C) |
| TW | Forged steel | 7.81 | 8.75 | 225 | 24.20 |
| SPW | Forged steel | 5.96 | 7.95 | 195 | 26.00 |
| TW | 18% Chromium | 8.06 | 8.76 | 246 | 25.10 |
| SPW | 18% Chromium | 7.48 | 8.11 | 681 | 25.20 |
| TW | Ceramic | 8.65 | 8.77 | 270 | 23.70 |
| SPW | Ceramic | 6.48 | 8.03 | 281 | 27.30 |

### 5.2.2 Flotation results

#### 1. Influence of grinding media

The influence of three types of grinding media (forged steel, 18% chromium and ceramic media) on pyrite recovery is given in Figure 5-1. It should be noted that all the flotation experiments were conducted in duplicates. As seen in Figure 5-1, the pyrite recovery slightly decreases in the following order: forged steel media (electrochemically strongly active)>18% chromium media (electrochemically slightly active)>ceramic media (electrochemically inert). The values for the flotation rate constant, shown in Table 6, indicated the same trend since flotation recovery is directly related to rate constant. With synthetic process water this decrease was even les defined

Flotation recovery results are in agreement with the results obtained by Peng and Grano (2010). However, it is important to highlight that Peng and Grano (2010) found that the recovery of pure pyrite was up to three times higher when grinding was conducted with the mild steel media than that with the chromium media, while our results showed that there is a slight increase in pyrite recovery after using the forged steel media. The discrepancy between our results and the results obtained by Peng and Grano (2010) is due to the difference between pulp potential in our work and that obtained by Peng and Grano (2010). It should be also noted that Peng and Grano (2010) conducted experiments with pure pyrite while, in this study, the ore contained a very small amount of pyrite (i.e. 2.0%) which is comparable with the amount of pyrite in Western Australian gold ores of the orogenic geological type.

The reason for the slightly improved the pyrite recovery when grinding was performed with the forged steel media is probably because the grinding environment was strongly reducing (see Table 5-1), which is required to activate pyrite surfaces (i.e. the reduction of $Cu^{2+}$ to $Cu^{+}$). Furthermore, the zeta potential measurements showed that the electrostatic repulsion between copper-activated pyrite and iron hydroxide species from the mild steel media prevented the precipitation of iron hydroxide species on pyrite surfaces (Peng and Grano, 2010).

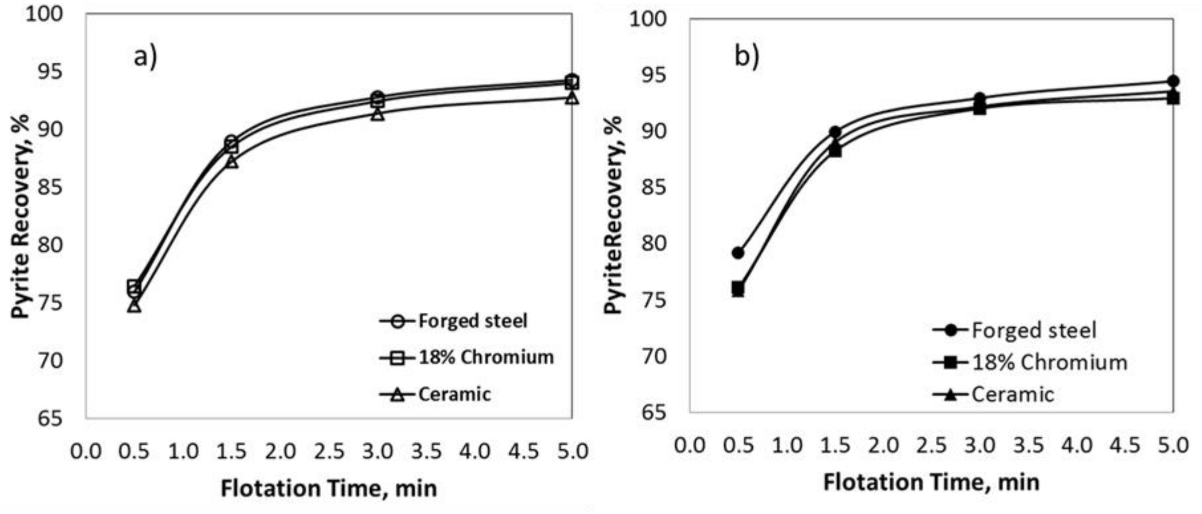


Figure 5-1. Pyrite recovery as a function of grinding media when grinding was performed in a) tap water and in b) synthetic process water.

Table 5-4. Influence of grinding media and water quality on flotation rate constant.

| Water | Media | k($min^{-1}$) |
|---|---|---|
| TW | Forged | 3.52 |
| SPW | Forged | 3.87 |
| TW | 18% Chromium | 3.46 |
| SPW | 18% Chromium | 3.67 |
| TW | Ceramic | 3.32 |
| SPW | Ceramic | 3.40 |

Grinding media choice affects gold recovery as seen in Figure 5-2. These results reveal that the gold recovery was the highest when the forged steel media was used, and was the lowest with the ceramic media. The positive effect of the forged media was more pronounced on the gold recovery than on the pyrite recovery. It means that the gold recovery followed the same trend as the pyrite recovery since a significant amount of gold is locked in pyrite. Flotation feed also contains free (gravity recoverable) gold which is highly floatable in the presence of xanthate collector (McGrath et al., 2013, 2015). The determination of the amount of free gold in flotation feed was beyond the scope of this study. It should be noted that a flotation rate constant was not calculated for gold since locked gold in pyrite is recovered by flotation of pyrite.

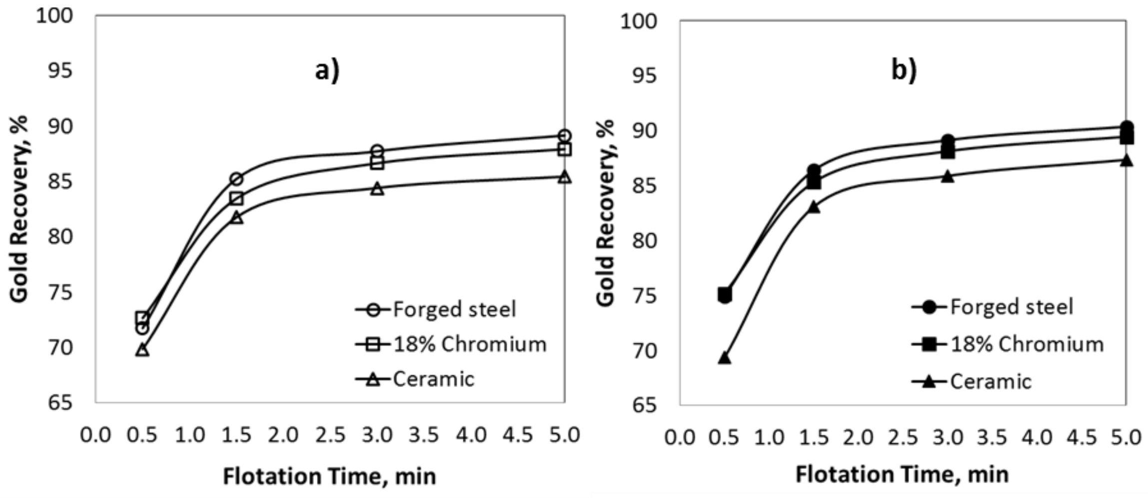


Figure 5-2. Gold recovery as a function of grinding media when grinding was performed in a) tap water and in b) synthetic process water.

## 2. Influence of water quality

The influence of two types of water (i.e. the tap water and the synthetic process water) on the floatability of pyrite is shown in Figure 5-3. As seen in Figure 5-5, the synthetic process water slightly improved pyrite recovery, due to the presence of $Ca^{2+}$ (2100 mg/L). The activation of pyrite surfaces with $Ca^{2+}$ occurs due to the catalytic effect of this ion on the formation of dixanthogen (Zhang et al., 1997). It is not expected that a very small amount of $SCN^-$ (80 mg/L) depressed pyrite surface since $SCN^-$ has a minor depressing effect on this mineral (Adams, 2013). In the case of grinding with the chromium media, the results showed a slightly positive effect of synthetic process water. Further work is required to find the minimum concentration of different chemical species (e.g. $Ca^{2+}$, $SCN^-$) needed to improve or reduce floatability of pyrite from its ores.

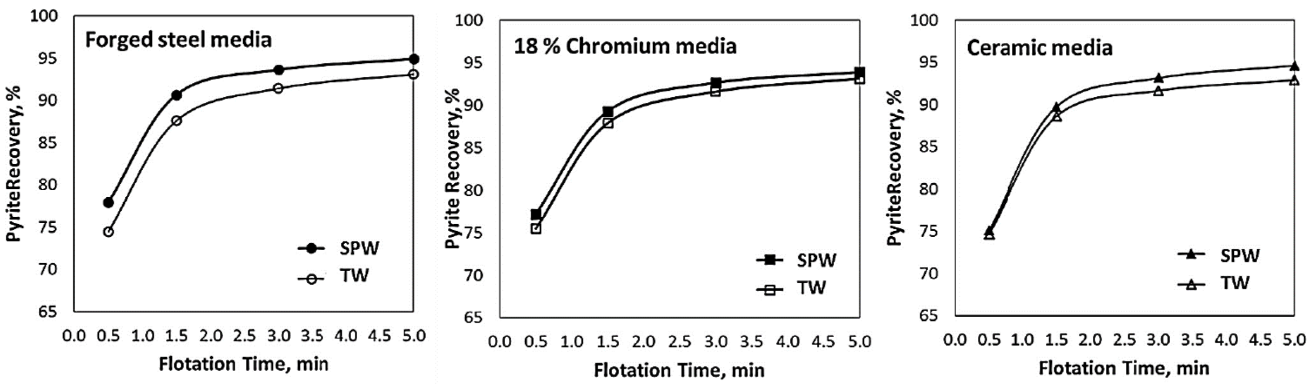


Figure 5-3. Pyrite recovery as a function of water quality.

Water quality influences gold recovery as shown in Figure 5-4. It is very important to emphasize that the difference between the pyrite recovery and the gold recovery results might be attributed to the presence of free gold particles in flotation feed.

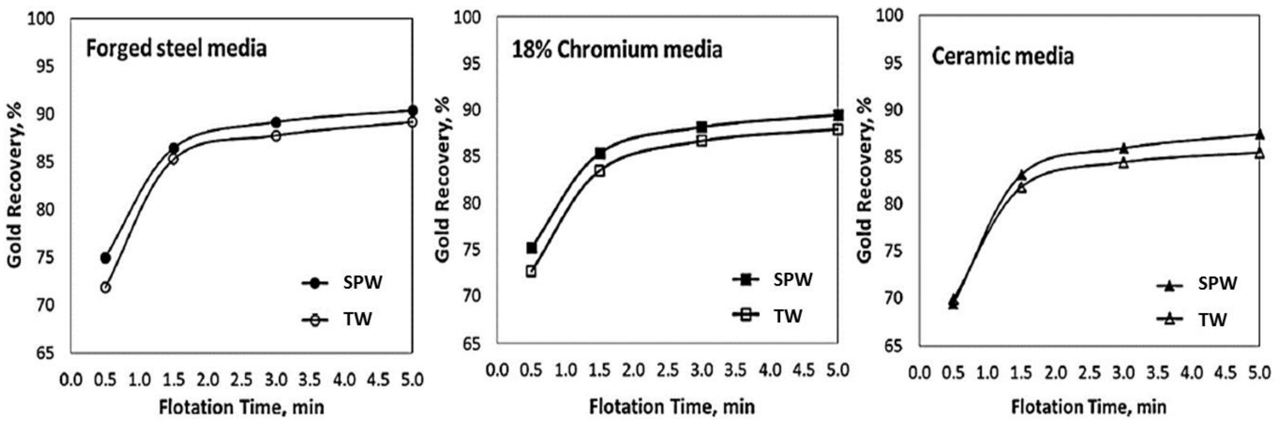


Figure 5-4. Gold recovery as a function of water quality.

### 5.2.3 EDTA Extraction

EDTA measurements were performed with the samples taken from the mill discharge. The percentage of extracted iron at different grinding conditions is shown in Figure 5-5. As seen in Figure 5-5, the percentage of EDTA extracted iron was the highest when grinding was performed with the forged media, while that was the lowest when grinding was conducted with the ceramic media. The effect of water quality on EDTA extracted iron is not significant.

The origin of EDTA extracted iron can be due to the oxidation of pyrite and grinding media. However, when pyrite and the forged media are in direct contact, the oxidation rate of pyrite (electrochemically less active material) decreases, while the opposite is true for the oxidation rate of the forged media (electrochemically more active material) (Fontana, 1978). Given that pyrite is electrochemically less active material, the oxidation of pyrite can be neglected. Therefore, the amount of EDTA extracted iron is an indicator for the corrosion rate of the grinding media.

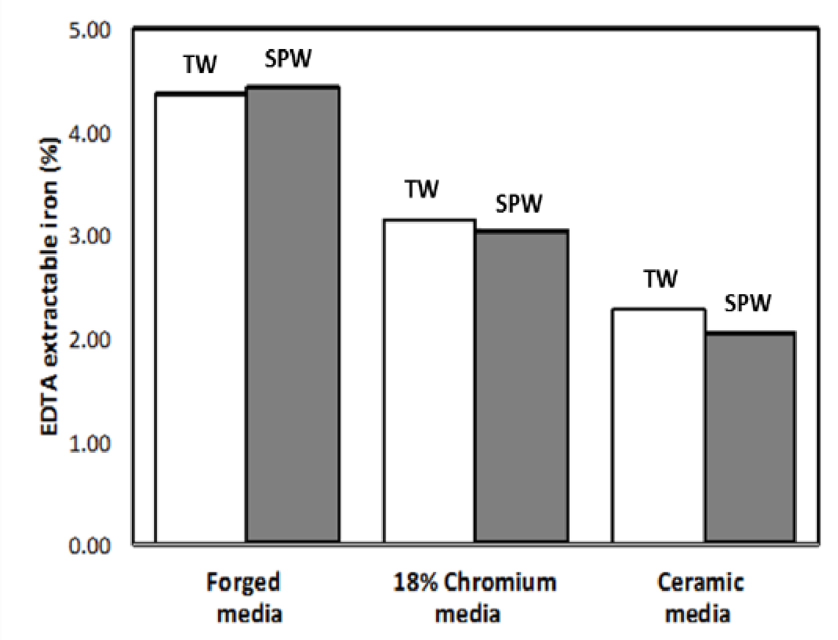


Figure 5-5. Influence of grinding conditions on the percentage of EDTA extractable iron from the samples taken from the mill discharge.

### 5.2.4 XPS analysis

XPS analysis involved the survey spectrum and the high resolution spectra of the following elements: Fe, O and S. The survey spectrum was used to identify and quantify the elements on the surface of the samples, while the high resolution spectra provided the information about the oxidation state and chemical bonding of these elements. The percentage of elements on the surface of samples are shown in Table 5-5. The percentage of Fe on the surface of the samples was the highest when grinding of ore was performed with the forged media due to the corrosion process of this media.

The percentage of Si, O and K was higher in the tap water than that in the synthetic process water. It is not clear whether it occurred due to the improved entrainment of silicates since the determination of the amount of entrained particles was beyond the scope of this study. It should be noted that the tap water contained higher amount of dissolved oxygen content than the synthetic process water (see Tables 5-1 to 5-3).

Table 5-5 also showed that the surface of samples contained higher amount of Na, Cl, Mg, and S when experiments were performed in the presence of the synthetic process water than that in the tap water. This is attributed due to the addition of NaCl, $MgSO_4$ and KSCN in the tap water during the preparation of the synthetic process water.

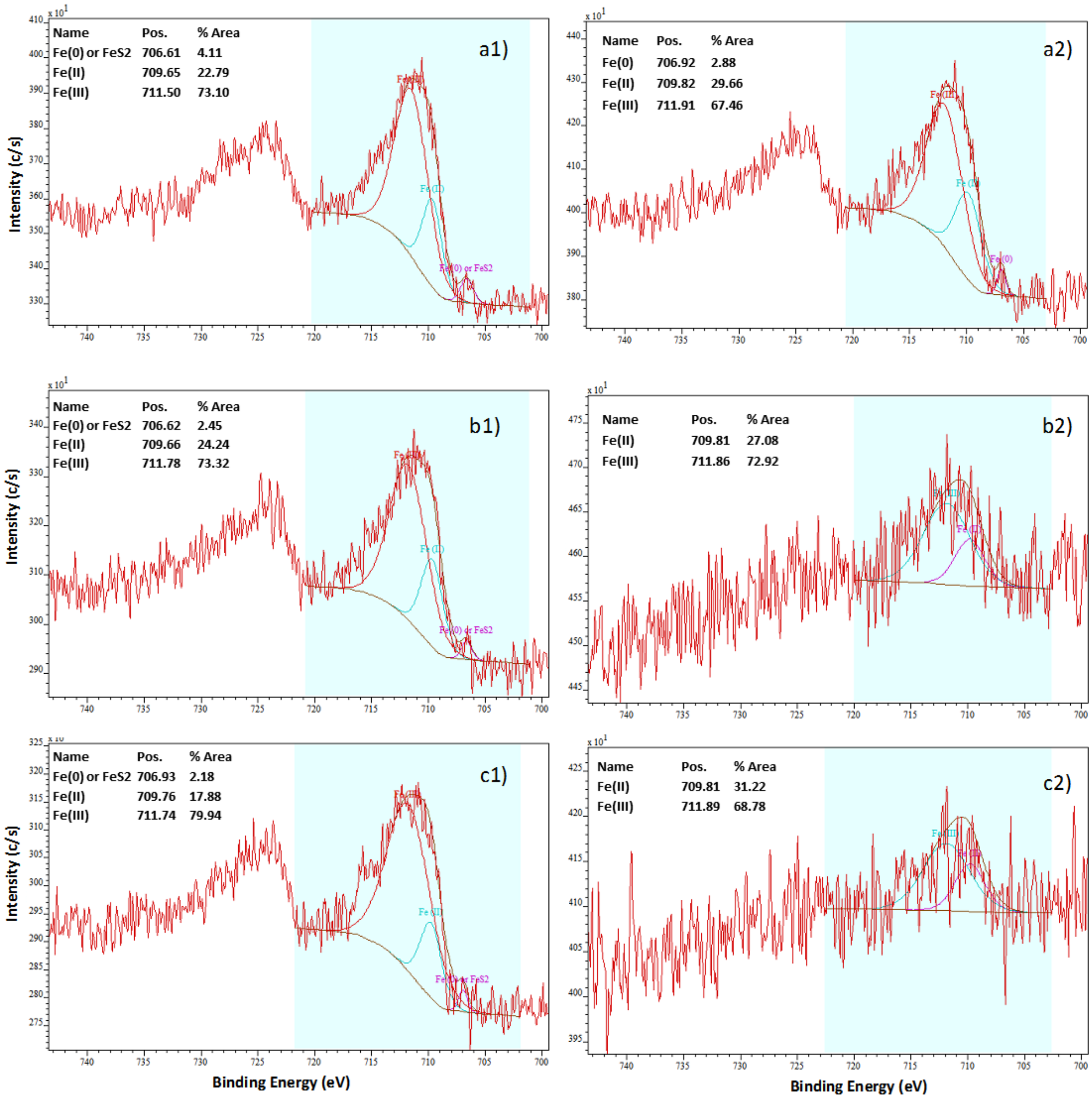
Table 5-5. Concentration of the elements measured by XPS on the surface of samples.

| Grinding Condition | Surface elemental compositions (atomic %) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (Water; Media) | O | Na | Ca | Cl | Si | K | S | Fe | Mg |
| TW; Forged | 74.58 | 2.75 | 2.56 | 0.77 | 14.91 | 1.50 | 0.45 | 1.32 | 1.16 |
| TW; 18% Chromium | 75.59 | 2.62 | 2.29 | 0.48 | 14.84 | 1.63 | 0.24 | 1.04 | 1.26 |
| TW; Ceramic | 75.35 | 2.35 | 2.15 | 0.88 | 15.48 | 1.73 | 0.16 | 0.63 | 1.27 |
| SPW; Forged | 65.64 | 9.10 | 2.29 | 6.42 | 12.07 | 1.19 | 1.80 | 1.09 | 1.88 |
| SPW; 18% Chromium | 45.19 | 19.34 | 2.47 | 22.93 | 5.09 | 0.24 | 1.70 | 0.40 | 2.95 |
| SPW; Ceramic | 47.87 | 18.56 | 2.45 | 20.30 | 5.61 | 0.35 | 1.66 | 0.37 | 2.82 |

### 1. High Resolution Spectrum of Fe

Figure 5-6 shows the high resolution spectrum of Fe. The table in each graph indicates the position and percentage of each species in the survey spectrum of the samples. Iron was detected on the surface of all samples and the $Fe_{2p}$ spectra indicates that an iron oxy-hydroxide layer is present on the mineral surface. This is shown by a band in the $Fe_{2p}$ spectrum near 711 eV for Fe (III) and Fe (II) species while the iron associated with sulfur ($FeS_2$) or Fe (0) occurs at 708 eV (Buckley and Woods, 1984). Therefore, Fe (0) and $FeS_2$ occur at the same binding energy and cannot be individually identified. The two remaining iron species had the oxidation state Fe (II) and Fe (III). In all samples, Fe (II) and Fe (III) can be identified most likely from oxides and hydroxide or sulphate.

As regards the effect of different grinding media, the percentage of the iron hydroxide on the surface of the samples is the highest when the forged steel media was used. This correlates well with the EDTA extraction results.



a1)

| Name | Pos. | % Area |
|---|---|---|
| Fe(0) or FeS2 | 706.61 | 4.11 |
| Fe(II) | 709.65 | 22.79 |
| Fe(III) | 711.50 | 73.10 |

a2)

| Name | Pos. | % Area |
|---|---|---|
| Fe(0) | 706.92 | 2.88 |
| Fe(II) | 709.82 | 29.66 |
| Fe(III) | 711.91 | 67.46 |

b1)

| Name | Pos. | % Area |
|---|---|---|
| Fe(0) or FeS2 | 706.62 | 2.45 |
| Fe(II) | 709.66 | 24.24 |
| Fe(III) | 711.78 | 73.32 |

b2)

| Name | Pos. | % Area |
|---|---|---|
| Fe(II) | 709.81 | 27.08 |
| Fe(III) | 711.86 | 72.92 |

c1)

| Name | Pos. | % Area |
|---|---|---|
| Fe(0) or FeS2 | 706.93 | 2.18 |
| Fe(II) | 709.76 | 17.88 |
| Fe(III) | 711.74 | 79.94 |

c2)

| Name | Pos. | % Area |
|---|---|---|
| Fe(II) | 709.81 | 31.22 |
| Fe(III) | 711.89 | 68.78 |

Figure 5-6. The iron high resolution spectrum of flotation concentrates under different grinding conditions: forged steel media with a1) tap water and a2) synthetic process water; 18% chromium media with b1) tap water and b2) synthetic process water; ceramic media with c1) tap water and c2) synthetic process water.

## 2. High Resolution Spectrum of S

The $S_{2p}$ high resolution spectrum of the surface of particles taken from flotation concentrate are shown in Figure 5-7. These spectra were fitted using the $2p_{1/2}$ and $2p_{3/2}$ doublet with a fixed 1:2 intensity ratio. The doublet with the S $2p_{3/2}$ binding energy at the range of 161.4 to 162.8 eV is an indicator for the mono sulfide $S^{2-}$ and the doublet at 162.0-163.4 eV is from disulfide $S_2^{2-}$. The peak at about 169 eV indicated the presence of the sulphate $SO_4^{2-}$.The table in each graph shows the position and percentage of the sulfur species given in the survey spectrum.

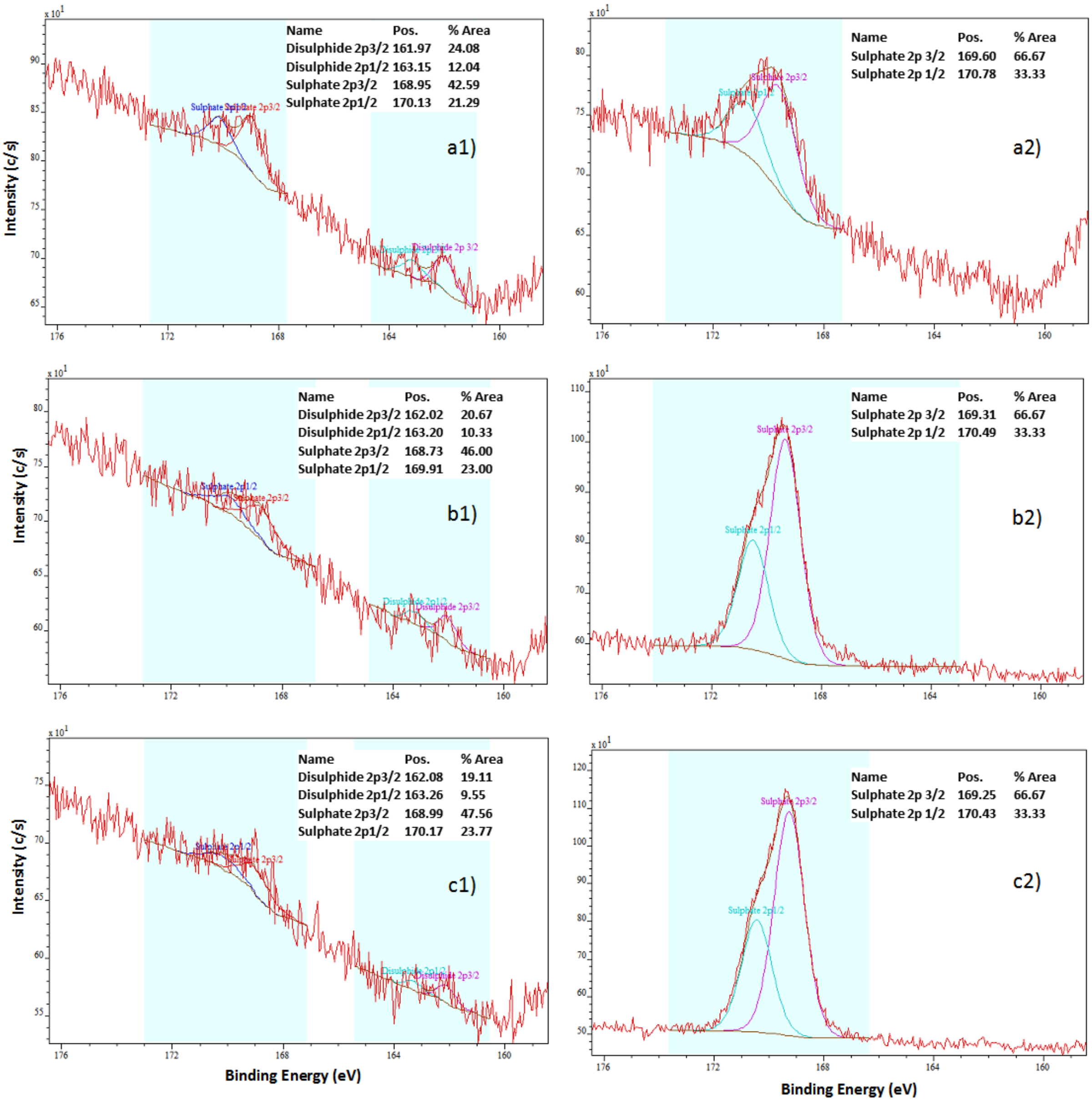


Figure 5-7. The sulfur high resolution spectrum of flotation concentrates under different grinding conditions: forged steel media with a1) tap water and a2) synthetic process water; 18% chromium media with b1) tap water and b2) synthetic process water; ceramic media with c1) tap water and c2) synthetic process water.

As seen in Figure 5-7, when grinding was performed in the presence of tap water regardless of the type of grinding media, the sulfur high resolution spectra showed the presence of disulfide ($2p_{1/2}$ and $2p_{3/2}$) and sulphate ($2p_{3/2}$ and $2p_{1/2}$). When the synthetic process water was used, the sulphate level on the surface of samples significantly increased due to the presence of sulphate in the synthetic process water.

### 3. High Resolution Spectrum of Oxygen

Figure 5-8 shows the oxygen high resolution spectrum of the samples. The binding energy at the range of 530.2 eV is an indicator for the oxides while that of 531 eV showed the presence of carbonates. The binding energy of 531.5 eV was attributed to the hydroxides. The peak at 532.35 eV represents the sulphates and 533.5 eV indicates the bond between oxygen and carbon. The oxygen high resolution spectrum showed that that the percentage of adsorbed sulphates in the tap water slightly decreased in the following order: forged media>18% chromium media>ceramic media. The reason for the formation of sulphate in the tap water is due to the oxidation of pyrite surface which is to certain degree required to facilitate the adsorption of xanthate collector (Rabieh et al., 2016). It should be noted that when experiments were performed in the presence of the synthetic process water, the same conclusion cannot be applied.

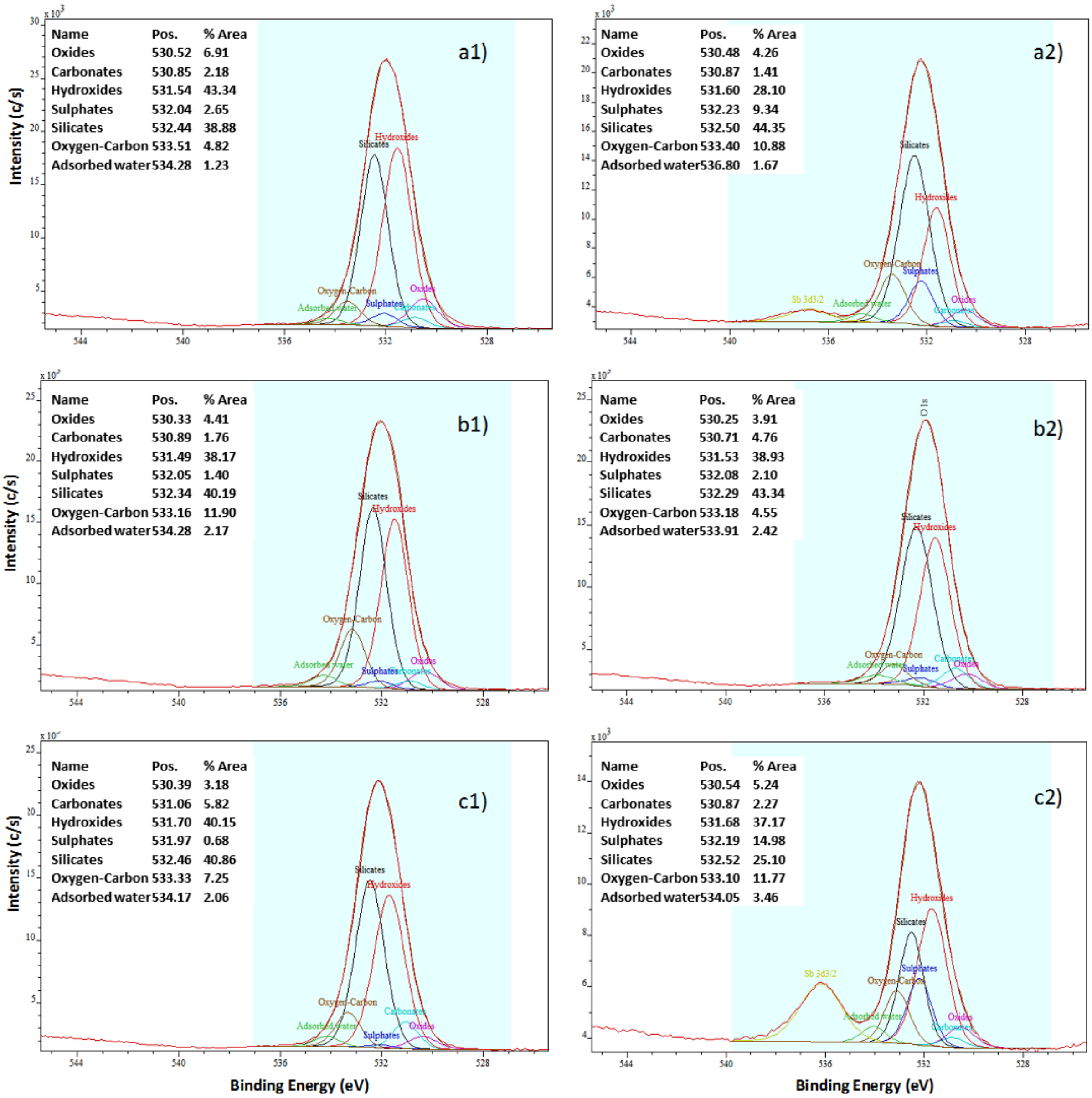


Figure 5-8. The oxygen high resolution spectrum of flotation concentrates obtained under different grinding conditions: forged steel media with a1) tap water and a2) synthetic process water; 18% chromium media with b1) tap water and b2) synthetic process water; ceramic media with c1) tap water and c2) synthetic process water.

## 4. Limitation of XPS Spectrum

The XPS analysis could not detect the adsorbed copper species on the investigated samples probably because the samples had about 5% of pyrite and a small amount of $Cu^{2+}$ (60 g/ton) was sufficient to activate pyrite surfaces. Quite opposite to our observations, Peng el al.

(2003a) detected the adsorbed $Cu^+$ species on pyrite surfaces by using XPS analysis. The reason for that is probably because these authors collected the samples after grinding of pure pyrite in the presence of a large amount of $Cu^{2+}$ (4220 g/t). This paper also demonstrated that XPS analysis can be used to study the influence of water quality on properties of particle surfaces, even though flotation recovery results showed a negligible influence of water quality on flotation performance of pyrite. However, XPS analysis was unsuccessful to explain the influence of different grinding media on particle surfaces, probably due to the insensitivity of XPS analysis to detect the low amount of adsorbed copper species on the surface of samples. It should be noted that Tof-SIMS technique might be able to detect the presence of copper species on the investigated samples. However, this requires a significant amount of further work.

### 5.3 Summary

In this project, the influence of the grinding media (forged, 18% chromium and ceramic) and the water quality (the synthetic process water and the tap water) on flotation perfomance of pyrite and gold recovery was studied using XPS and EDTA extraction technique. The water quality did not significantly affect the floatability of pyrite. The flotation tests confirmed a minor improvement in the pyrite recovery when the grinding was performed with the forged media due to the better activation of pyrite surfaces with $Cu^{2+}$ under the reducing conditions produced during the grinding with this media. XPS and EDTA extraction technique demonstrated that the forged steel media produced more iron hydroxide species than the 18% chromium or ceramic media, indicating the high corrosion rate of the forged media. The results also revealed that XPS technique can be used to study the influence of water quality on changes of particle surfaces, although the flotation recovery results showed a negligible influence of the water quality on the flotation performance of pyrite.

# Chapter 6 Influence of grinding media, pyrite mineralogy and water chemistry on the galvanic interaction between grinding media and pyrite: an electrochemical study

## 6.1 Introduction

During wet grinding of sulfide ores, electrons can transfer between sulfide minerals and grinding media, causing galvanic interactions (Huang and Grano, 2005). This galvanic interaction changes the surface properties of sulfide minerals and thus affects downstream processing such as flotation and leaching (Pozzo et al., 1988; Grano et al., 1990; Rao et al., 1990; Van Deventer et al., 1993; Cheng et al., 1999; Teague et al., 1999; Huang et al., 2006; Li et al., 2006).

Numerous factors such as grinding media type, ore mineralogy, grinding environment (i.e. pulp pH, pulp rheology, pulp potential, gas atmosphere during grinding, pulp temperature, etc.) can affect the galvanic interactions between sulfide minerals and grinding media in a wet grinding environment (Azizi et al., 2013a; Rabieh et al., 2016). This galvanic interaction occurs due to rest potential differences between grinding media and sulfide minerals. To the author's knowledge, there has not been any prior research that has compared the galvanic interaction between grinding media and different pyrite mineralogies (i.e. pure pyrite and gold-rich pyrite). In addition, the effect of water chemistry (specifically, anions $Cl^-$ and $SO_4^{2-}$, and cations $Ca^{2+}$, $Mg^{2+}$ and $Fe^{3+}$) on the galvanic interactions between pyrite and the grinding media has not been reported. Therefore, in this study, the effect of water chemistry and two types of pyrite mineralogy on the galvanic interactions between pyrite and the grinding media were investigated. It should be noted that in the previous flotation testwork, the influence of grinding media and water quality on flotation performance of gold bearing pyrite was investigated. The results showed that the forged steel grinding media produced more iron oxide-hydroxide species than the 18% chromium, indicating a comparatively high corrosion rate of the forged media (Rabieh et al., 2017a).

Given that electrochemical studies do not show morphological or chemical composition alterations on the surface of the electrodes, other analytical techniques such as Scanning Electron Microscopy (SEM), quantitative or qualitative Energy-dispersive X-ray spectroscopy

(EDX) and X-ray Photoelectron Spectroscopy (XPS) can be used to provide information about the nature of the electrode surface after electrochemical interactions (Velásquez et al., 2000; Azizi, 2015). The limitation for using XPS technique is gassing from the resin of the electrode holder during analysis. Therefore, SEM/EDX analysis has been employed for the morphological and chemical composition studies. The aim of the current work is to study the galvanic interactions between a given grinding media (forged, 15 % chromium, 21 % chromium or 30 % chromium) and a pyrite electrode (pure pyrite or gold-bearing pyrite electrode) in the tap or synthetic process water. The galvanic interactions were investigated by measuring the galvanic current using polarization measurements. Additionally, the morphological and chemical changes on the grinding media after conditioning with the tap and synthetic process water also were investigated using SEM/EDX to establish the relationship between the surface changes of the grinding media and the galvanic interactions between the pyrite electrode and the grinding media.

## 6.2 Results and Discussion

### 6.2.1 Polarization measurement

The reproducibility of the electrode surface was examined under the same conditions at different days. The results in Figure 6-1 show that the polarization curves of the forged steel and KBGM (i.e. gold bearing pyrite) electrodes at different times did not change significantly.

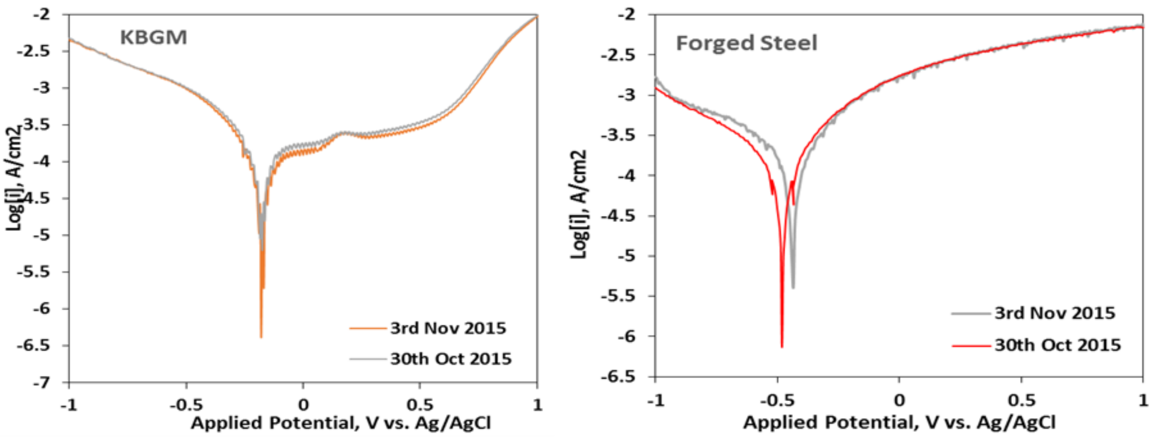


Figure 6-1. Reproducibility polarization experiments for forged steel media and KBGM electrodes.

### 6.2.2 Galvanic interaction between grinding media and pyrite

#### 1. Tap water - KBGM electrode

Figure 6-2 shows an example of how the galvanic current between the grinding media electrode and the pyrite electrode of the Kanowna Belle gold mine sample is calculated based on polarisation curves. The current in the polarisation curves represents the rate of all electron exchange reactions at the surface of the electrode. These results indicated that pyrite with a higher rest potential acts as the cathode while the grinding media with a lower rest potential acts as the anode which is in agreement with the results obtained by Azizi et al. (2013b). Table 6-1 showed that the galvanic current of the pyrite-grinding media couple increased with the electrochemical activity of the grinding media. It means that the galvanic currents of the couples decreased in the following order:

Forged - pyrite > 15 %Cr- pyrite > 21 %Cr- pyrite > 30 %Cr- pyrite

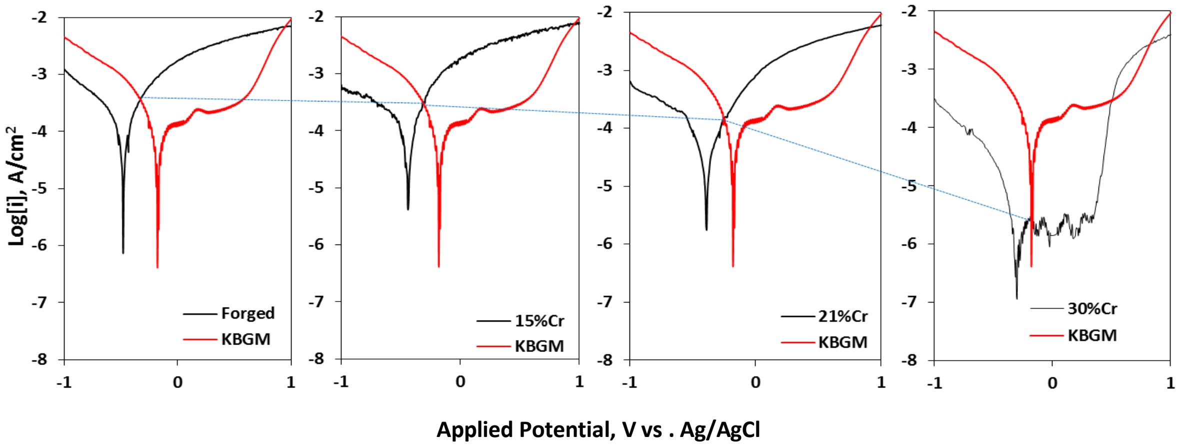


Figure 6-2. Polarization curves of the grinding media and gold-bearing pyrite electrode in the tap water.

Table 6-1. The measured galvanic current densities (μA/cm2) and combination potential (mV, SHE).

| Media | Galvanic current for the gold-bearing pyrite-grinding media couple, (μA/cm$^2$) | Combination potential for the gold-bearing pyrite and grinding media couple (mV, SHE) |
|---|---|---|
| 30% Cr | 3.5 | 18.1 |
| 21% Cr | 180.2 | -60.68 |
| 15%Cr | 436.6 | -106.1 |
| Forged steel | 482.9 | -141.8 |

**Forged steel** **15 %Cr** **21 %Cr** **30 %Cr**

Figure 6-3. Grinding media electrode surface after 20 min.

### 2. Tap water-pure pyrite electrode

Figure 6-4 shows the galvanic current between the grinding media and the pure pyrite electrode. The electrochemical activity order for the grinding media-pure pyrite couple was the same as that for the grinding media-gold-bearing pyrite couple; however, the only difference is that the galvanic current between the gold-bearing pyrite electrode and the grinding media electrode was greater than that between the pure pyrite electrode and the grinding media electrode. It means that the gold-bearing pyrite electrode is more electrochemically active than the pure pyrite electrode (cf. Tables 6-1 and 6-2).

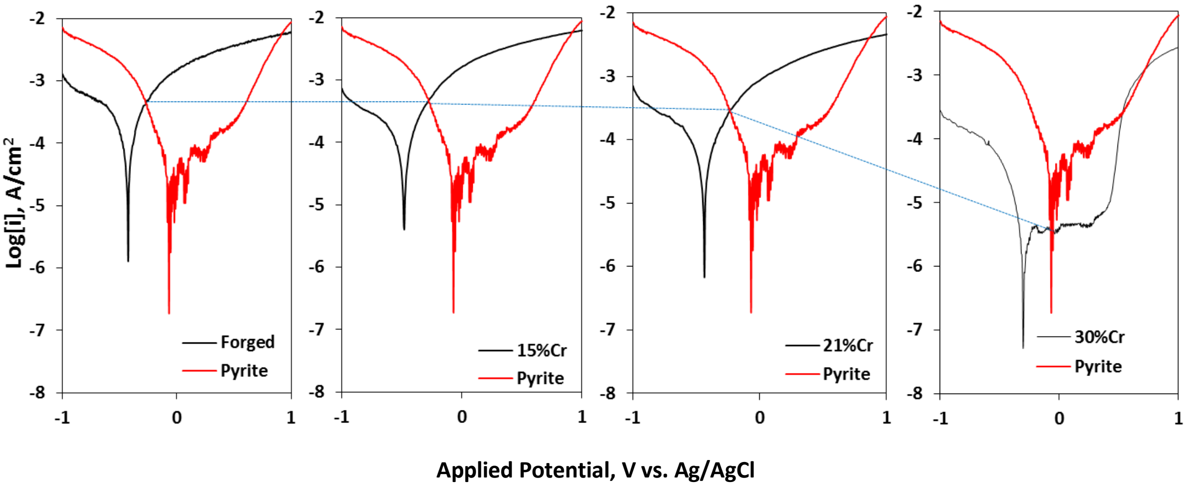


Figure 6-4. Polarization curves of grinding media and pure pyrite electrode.

Table 6-2. Measured galvanic current densities (μA/cm2) and combination potential (mv, SHE).

| Media | Galvanic current density of the pure pyrite-grinding media couple, (μA/cm$^2$) | Combination potential of the pure pyrite grinding media couple, (mV, SHE) |
|---|---|---|
| 30% Cr | 2.5 | 183.3 |
| 21% Cr | 170.2 | -44.5 |
| 15%Cr | 340.9 | -80.2 |
| Forged steel | 360.4 | -80.3 |

## 3. Synthetic process water – pure pyrite electrode

The influence of the synthetic process water on the galvanic current between the pure pyrite electrode and different grinding media electrode is shown in Figure 6-5. As can be seen in Figure 6-5, when the water contains a certain amount of $Cl^-$, $Mg^{2+}$, $Ca^{2+}$, $SO_4^{2-}$ and $SCN^-$ species, the galvanic current between the pure pyrite electrode and the forged steel grinding media electrode was lower than that in the tap water(Figure 6-2). Similar conclusions were also observed when the low-chromium media (15 % Cr and 21 % Cr) was used instead of the forged steel media. However, when the high-chromium media electrode (30 % Cr) was used, the galvanic current was higher in the synthetic process water than that in the tap water (Table 6-3).

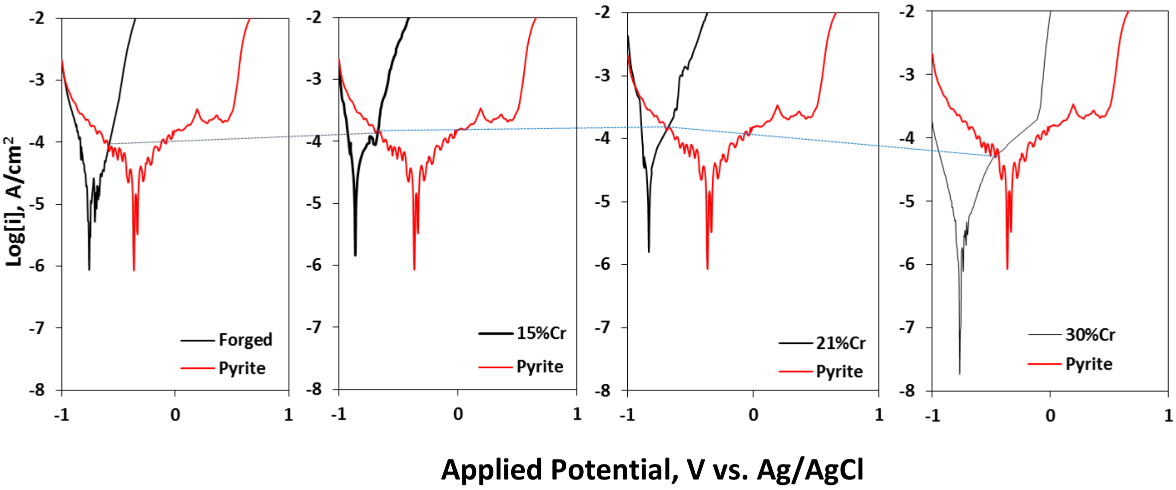
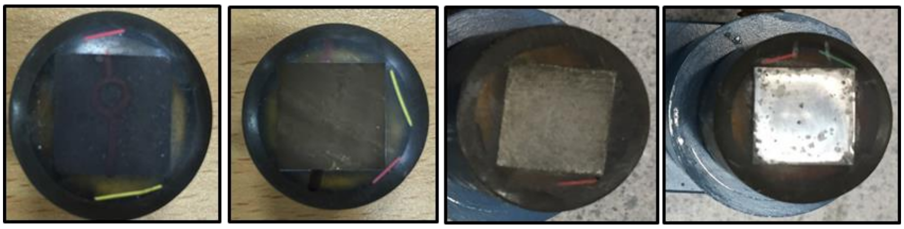


Figure 6-5. Polarization curves of grinding media and pure pyrite electrode.

The reason for this observation is related to the presence of more iron oxide and hydroxide on the surface of the grinding media electrodes in the synthetic process water (Figure 6-6) compared to that in the tap water (Figure 6-3), which might be the reason for the decreased galvanic current in the synthetic process water. This behaviour is due to the presence of $Cl^-$ and $SO_4^{2-}$ species in the synthetic process water which increased the corrosion rate of the grinding media (Fontana, 1987). The iron oxide and hydroxide species passivated the forged steel media surface and decreased the galvanic current. However, with increasing the chromium content of the grinding media, the oxidation mechanism changed. More precisely, when the 30 % chromium media electrode was used, no iron oxide or hydroxide were observed on the surface of the electrode. Therefore, that is the reason for the increased in the galvanic current when the 30% chromium was used.

Table 6-3. Measured galvanic current (μA/cm2) and combination potential (mV, SHE).

| Media | Galvanic current of the pure pyrite-grinding media couple, (μA/cm$^2$) | Combination potential of the pure pyrite-grinding media couple, (mV, SHE) |
|---|---|---|
| 30% Cr | 52.6 | -260 |
| 21% Cr | 72.3 | -400 |
| 15%Cr | 73.5 | -405 |
| Forged steel | 72.2 | -402 |



**Forged steel** **15 %Cr** **21 %Cr** **30 %Cr**

Figure 6-6. Grinding media electrode surface after 20 min.

### 6.2.3 SEM/EDX analysis

#### 1. Tap water

Understanding the electrochemical interactions alone will not show the morphological or chemical composition alterations on the surface of the electrodes during voltammetry studies. Therefore, other analytical techniques such as SEM/EDX can be used to give complementary information about the nature of electrode surfaces. EDX is a standard procedure for identifying and quantifying elemental composition of sample areas as small as a few square micrometres (Velásquez et al., 2000; Azizi, 2015).

The surface of the forged steel electrode after electrochemical interaction in the tap water condition was studied by SEM/EDX (Figures 6-7 and 6-8). Figure 6-7 shows a backscattered electron image of the electrochemistry product on the electrode surface after voltammetry studies. Figure 6-8 shows the EDX analysis of the different spectra for the area in the backscattered electron image. The results indicated that, in the tap water condition when the forged steel electrode was used, oxygen is detected on the surface of the electrode. This confirmed the presence of oxide species on the surface of the forged steel electrode in the tap water condition. However, the amount of oxygen on the surface of the low-chromium electrode (Figures 6-8 and 6-9), decreased compared to that for the forged steel electrode.

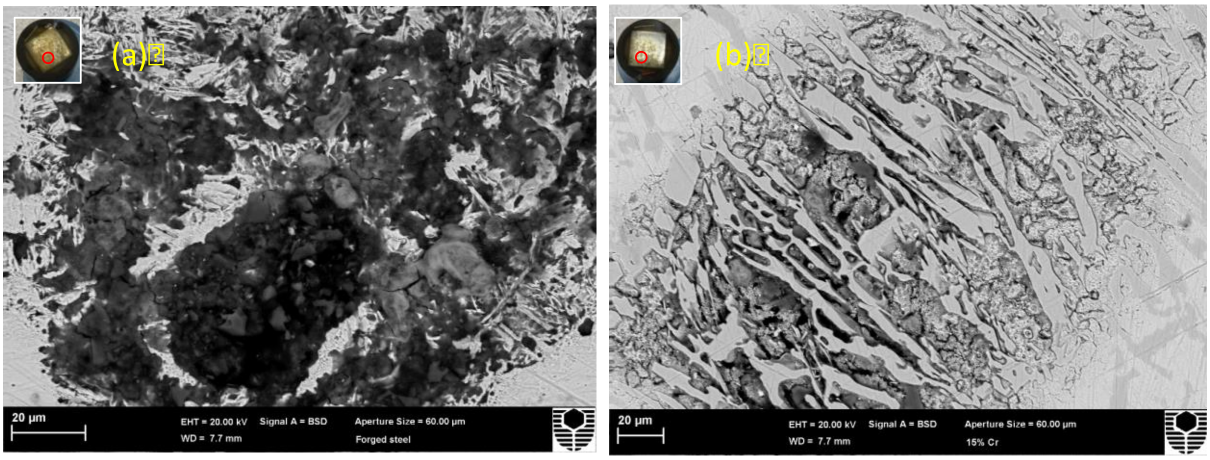


Figure 6-7. Backscattered electrons image of (a) forged steel and (b) 15% Cr electrode exposed to the tap water.

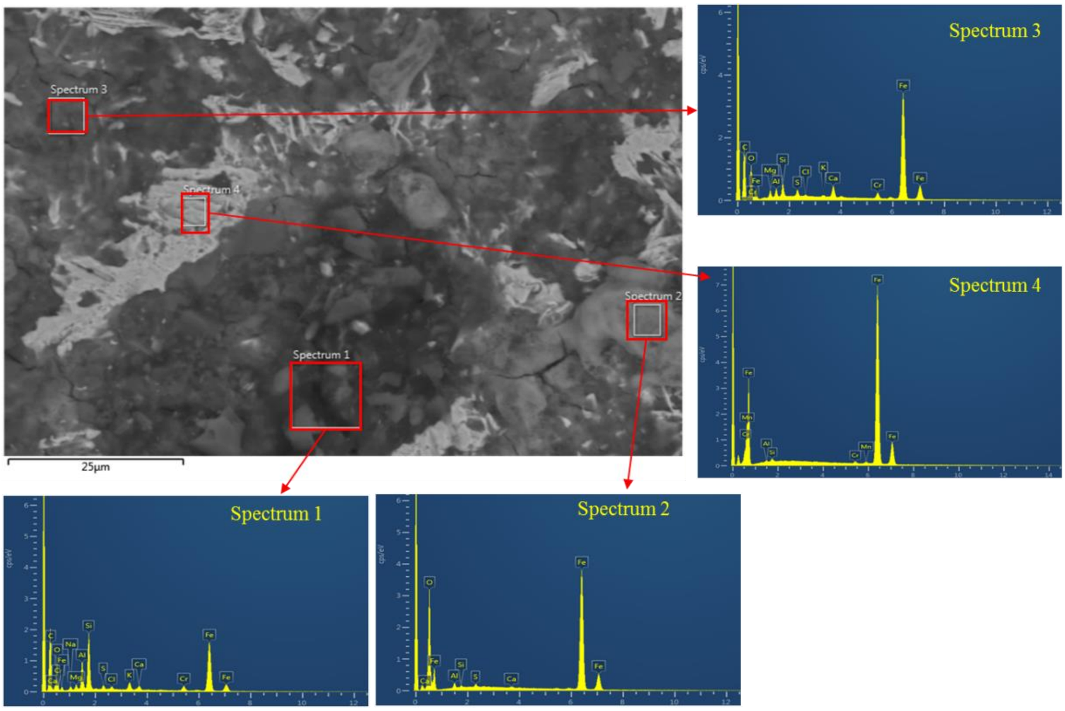


Figure 6-8. EDX analysis of forged steel electrode exposed to the tap water.

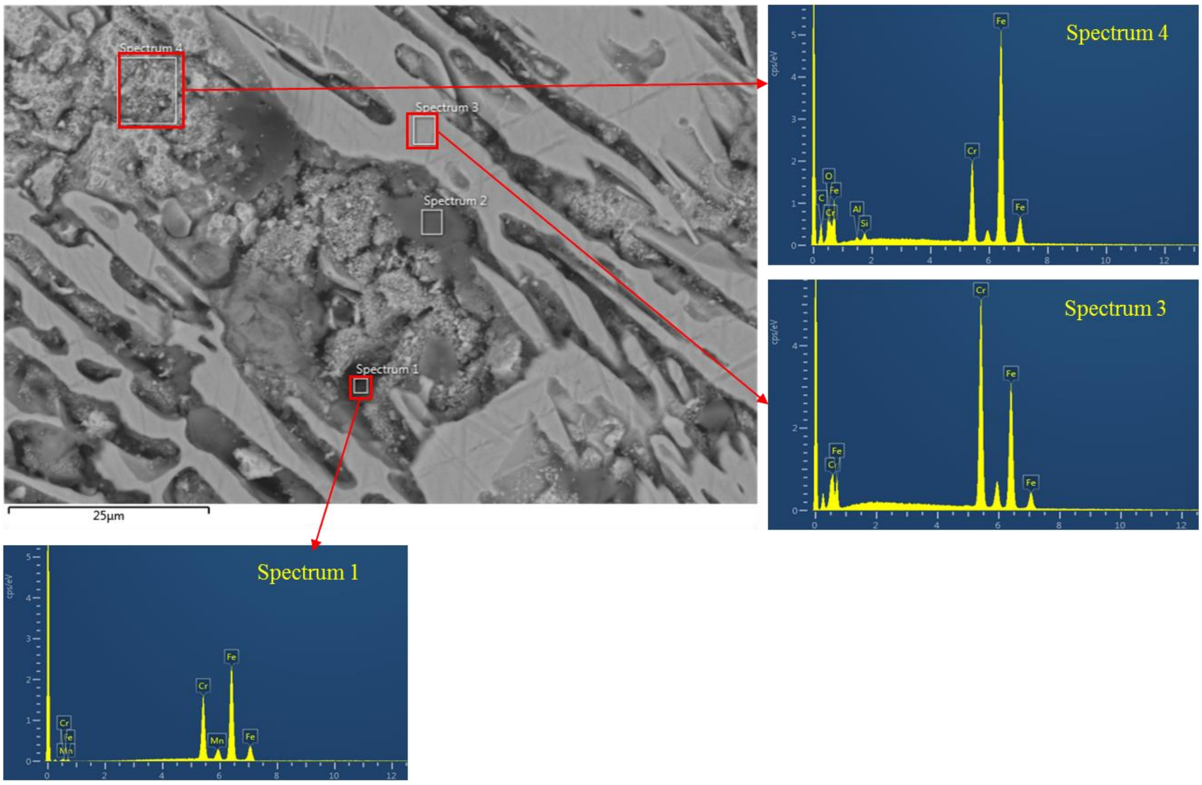


Figure 6-9. EDX analysis of the 15% chromium electrode exposed to the tap water.

## 2. Synthetic process water

In the synthetic process water condition, more dark spots were seen on the surface of the forged steel and low-chromium electrode than those in the tap water. Figure 6-10 shows the backscattered electron image of the electrochemistry product on the electrodes surface after voltammetry studies in the synthetic process water. Analysis of the forged steel surface by SEM/EDX (Figure 6-11) confirmed the presence of elements such as Ca, Mg, Na, K, S and Cl from the synthetic process water. The presence of oxygen was seen in all spectra, which confirms oxidation of the electrode surface in the synthetic process water. When the chromium content in the grinding media increased, the grinding media was less oxidized. Moreover, no oxygen was detected for the 30 % chromium in any spectra (Figures 6-12 to 6-14).

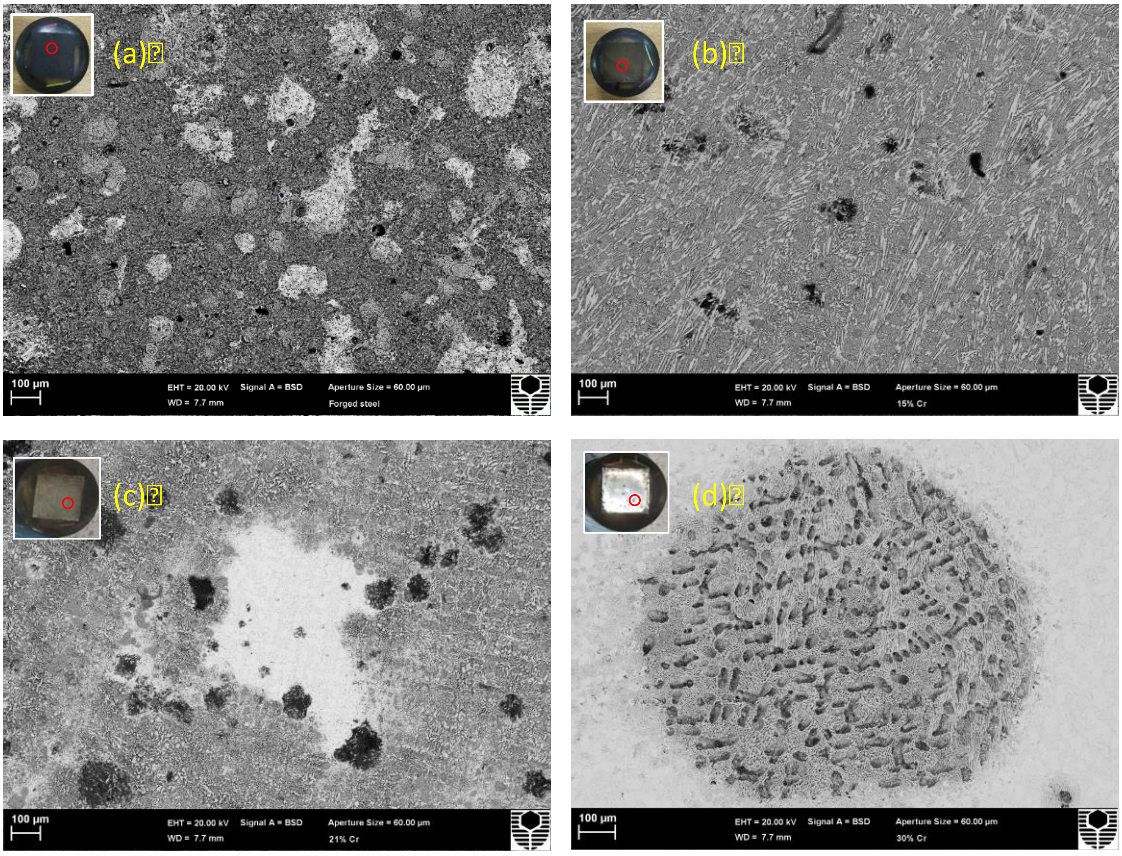


Figure 6-10. Backscattered electrons image of (a) forged steel (b) 15% Cr (c) 21% Cr and (d) 30% Cr electrode exposed to the synthetic process water.

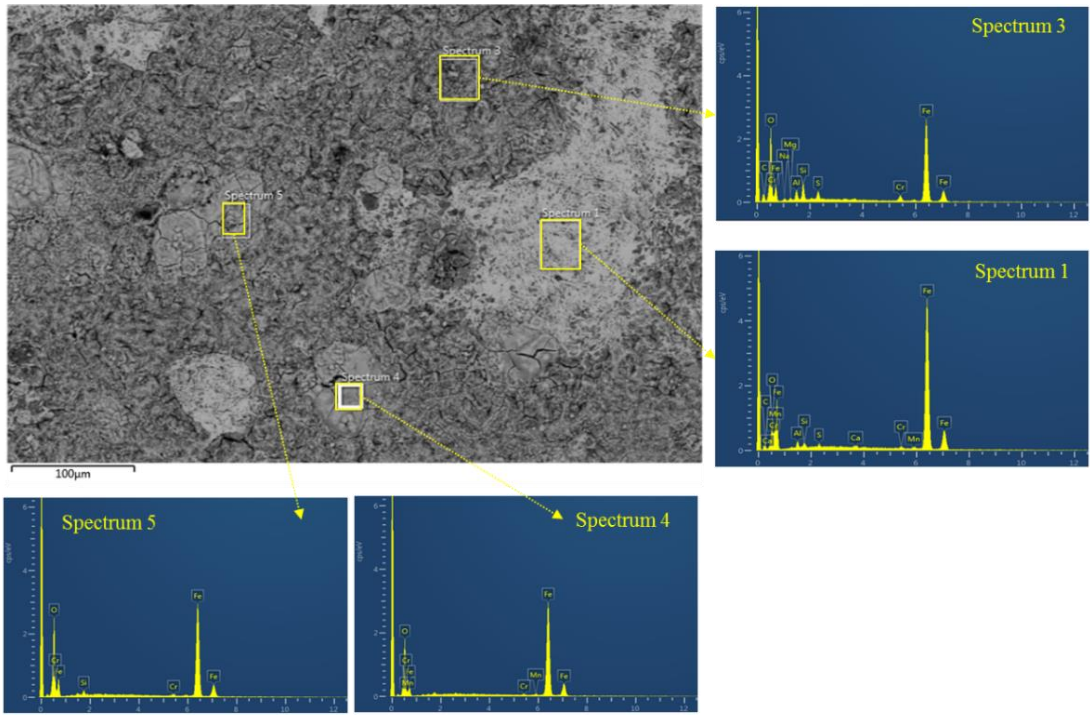


Figure 6-11. EDX analysis of forged steel electrode exposed to the synthetic process water.

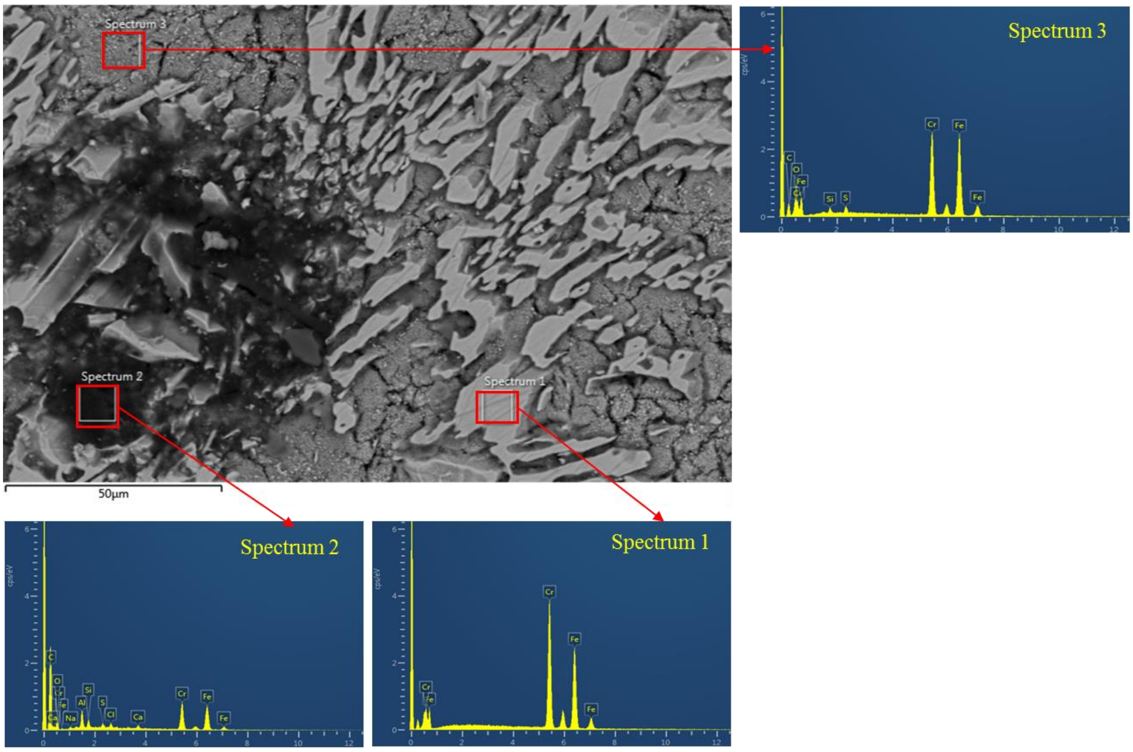


Figure 6-12. EDX analysis of 15% chromium electrode exposed to the synthetic process water.

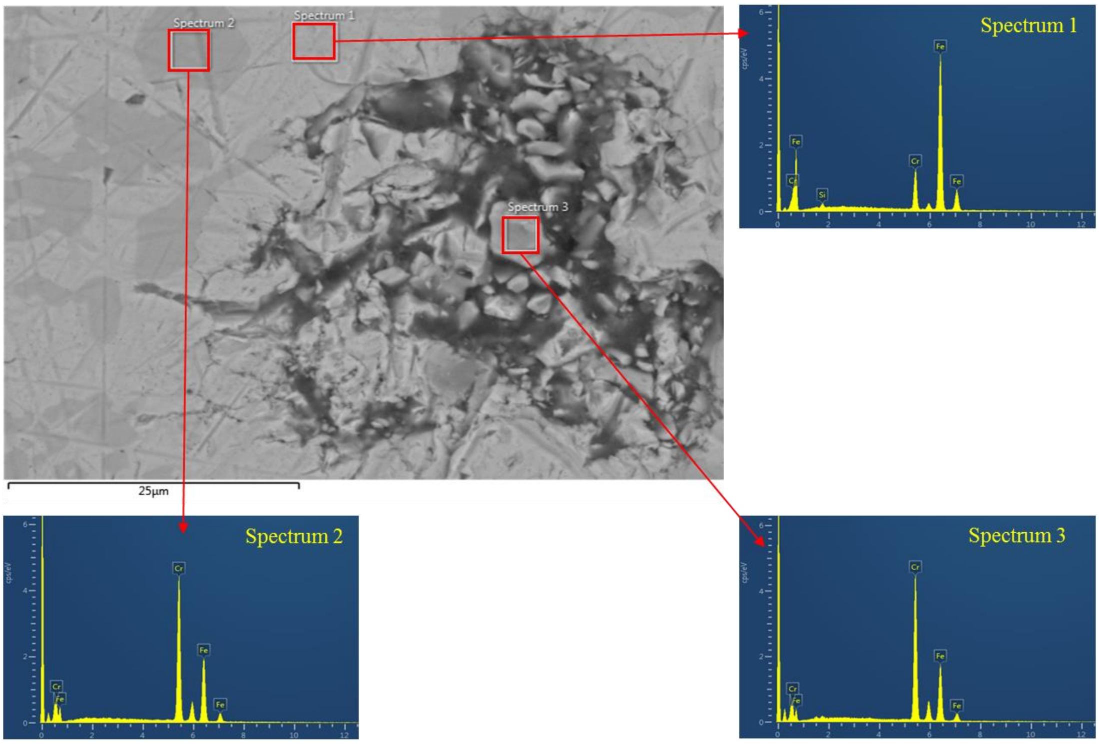


Figure 6-13. EDX analysis of 21% chromium electrode exposed to the synthetic process water.

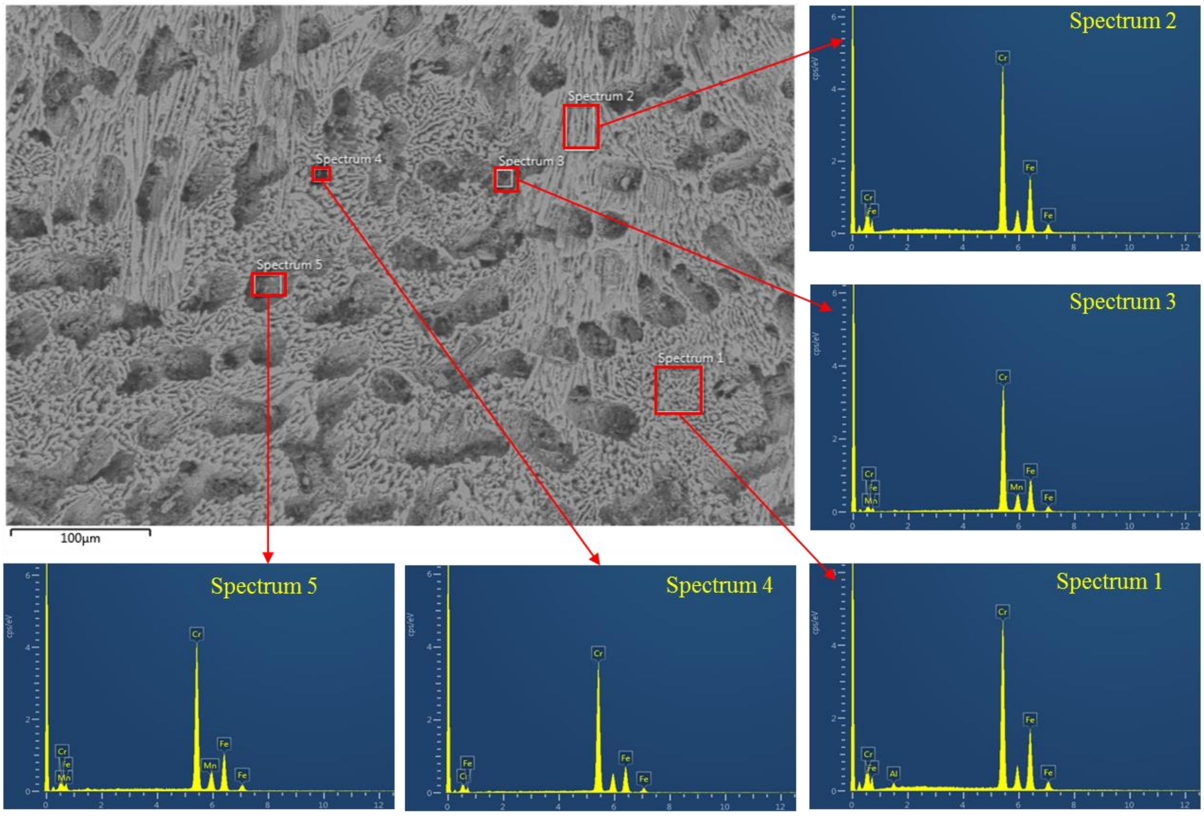


Figure 6-14. EDX analysis of 30% chromium electrode exposed to the synthetic process water.

### 6.3 Summary

This work established the relationship between the measured chemical changes on the grinding media surfaces and the galvanic current during voltammetry studies. The surface changes identified by SEM/EDX were related to the changes in the electrochemical variables obtained during voltammetry. The results indicated that changing from the forged steel grinding media to the high-chromium grinding media (30 % Cr) strongly reduced the galvanic current between pyrite and the grinding media electrodes (and therefore all associated reactions and their reaction products). In addition, the following results can be found.

(I) In all the polarisation curves, the galvanic current between pyrite and the forged steel grinding media electrode was higher than that between pyrite and the chromium media; the following order of the galvanic current can be seen:
Forged - pyrite > 15%Cr- pyrite > 21%Cr- pyrite > 30%Cr- pyrite.

(II) Pyrite mineralogy had an influence on the galvanic current. When the pure pyrite electrode was used, the galvanic current decreased compared to the gold-bearing pyrite electrode.

(III) Water chemistry was another important factor that influenced the galvanic interaction. For example, the 30% chromium grinding media electrode in the synthetic process water generated a higher galvanic current compared to the same electrode in the tap water, due to the salts present.

(IV) SEM/EDX analysis confirmed the chemical composition of the grinding media electrodes. The results demonstrated that in both the tap and synthetic process water conditions, oxide species were present on the surface of the forged steel and low-chromium electrodes. However, no oxygen was detected on the surface of the 30 % chromium grinding media in both the tap water and the synthetic process water. Therefore, virtually no oxidation occurred on the surface of the 30 % chromium grinding media electrode.

# Chapter 7 Effect of grinding media on cyanide leaching of gold in the presence of pyrrhotite, pyrite and arsenopyrite

## 7.1 Introduction

It is well known that grinding media type might affect downstream operations such as flotation and leaching (Adam et al., 1984; Martin et al., 1991; Cullinan et al., 1999; Greet et al., 2004; Huang and Grano, 2005; Huang and Grano, 2006; Huang et al., 2006; Kinal et al., 2009; Chen et al., 2013). Specifically, during grinding with steel grinding media, mineral particles become coated with different species of iron, changing the surface properties of the minerals. For example, it was found that the higher the percentage of iron in grinding media, the lower the flotation response of sulfide minerals (Martin et al., 1991; Cullinan et al., 1999). The reason for the decrease in flotation response is due to the presence of a hydrophilic layer of oxidised iron species on the surface of sulfide minerals.

Grinding media type may also affect cyanide gold leaching. For example, it was found that when gold particles were in contact with mild steel, the dissolution rate of gold in a cyanide solution decreased due to the formation of a passive film on the gold particles; the passive film was formed as a result of galvanic interaction between the gold and iron particles (Van Deventer et al., 1990).

During grinding of ores due to the galvanic current between forged steel grinding media and sulfide minerals, electrons are transferred from the anode (i.e. grinding media) to the cathode (i.e. cathodic mineral), causing the change of the potential of both materials from their rest potential to the mixed potential due to the tendency to achieve the equilibrium potential (Adam et al., 1984; Martin et al., 1991). As a result, the corrosion of the less cathodic material (grinding media) increases and the corrosion of the more cathodic material (high rest potential) decreases (Fontana, 1987). Therefore, grinding media oxidation increases. As a result, more iron hydroxide is produced which can consume the free cyanide during leaching.

While gold-bearing sulfide ore cyanidation can be challenging there is a great variation in the extent to which sulfide minerals affect the leaching process. Deschenes et al. (2003)

suggested that all sulfide minerals could be divided into three groups depending on their effect on gold leaching:

- a group that reduces gold leaching (stibnite>orpiment>pyrrhotite>chalcocite>arsenopyrite>chalcopyrite);
- a group has little impact on gold leaching (pyrite and sphalerite);
- And a group that improves gold leaching (galena).

The effect of sulfide minerals on gold cyanide leaching is governed by amount of sulfide in the ore, as well as solubility and reactivity of sulfide minerals (Deschenes et al., 2007). Although the effects of sulfide minerals and their dissolved ions on the gold leaching process have been investigated (Ntemi et al., 2013), the influence of galvanic interactions occurring between grinding media and sulfide minerals on gold cyanide leaching has not yet been systematically evaluated. For that reason, the objective of this part of the project was to investigate the influence of the sulfide mineral and the type of grinding media on cyanide gold leaching. Sulfide minerals with different rest potential such as pyrrhotite, arsenopyrite and pyrite were selected. Pyrrhotite was chosen because this sulfide mineral is the highest cyanide- and oxygen-consuming iron sulphide. By contrast, pyrite is significantly less active than arsenopyrite and pyrrhotite. Therefore, these sulfide minerals can be representative of behaviour of different sulfide minerals. With regards to grinding media type, forged steel, 21% chromium, 30% chromium, and ceramic media were used in this study.

## 7.2 Results and Discussion

The main focus of this part of project was to investigate the influence of different sulfide mineral (pyrrhotite, arsenopyrite and pyrite with a same concentrate in the synthetic ore) and the type of grinding media on cyanide gold leaching. The results first showed the influence of pyrrhotite then arsenopyrite and finally pyrite.

### 7.2.1 Pyrrhotite

#### 7.2.1.1 Grinding

**1. Pulp chemical environment**

The pulp chemical measurements during grinding of the gold-pyrrhotite synthetic ore with four different grinding media are given in Figure 7-1. As seen in Figure 7-1, changes from the forged steel grinding media to the 30% chromium and ceramic grinding media shifted the grinding conditions from a moderately reducing to a more oxidising environment. The reason for the decrease of the pulp potential during grinding with the forged steel grinding media is due to the galvanic interactions between the forged steel media and pyrrhotite, causing the increase in the hydroxide ion production as shown in Equation 7-1. Thus, the pulp potential decreased while the pulp pH increased. Furthermore, according to Marsden and House (2009), in neutral and alkaline solutions, and in the presence of dissolved oxygen, pyrrhotite can be oxidised by the reaction presented in Equation 7-6. The pyrrhotite oxidation consumed the oxygen in the slurry, resulting in a drop of the dissolved oxygen content.

On the surface of a sulfide mineral:

$$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2\,(OH)^- \qquad (7\text{-}1)$$

Steel media oxidation:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (7\text{-}2)$$

$$Fe \rightarrow Fe^{3+} + 3e^- \qquad (7\text{-}3)$$

Hydrolysis:

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ \qquad (7\text{-}4)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (7\text{-}5)$$

Pyrrhotite oxidation:

$$4Fe_7S_8 + 69\,O_2 + 74\,H_2O \rightarrow 28\,Fe\,(OH)_3 + 32\,SO_4^{2-} + 64\,H^+ \qquad (7\text{-}6)$$

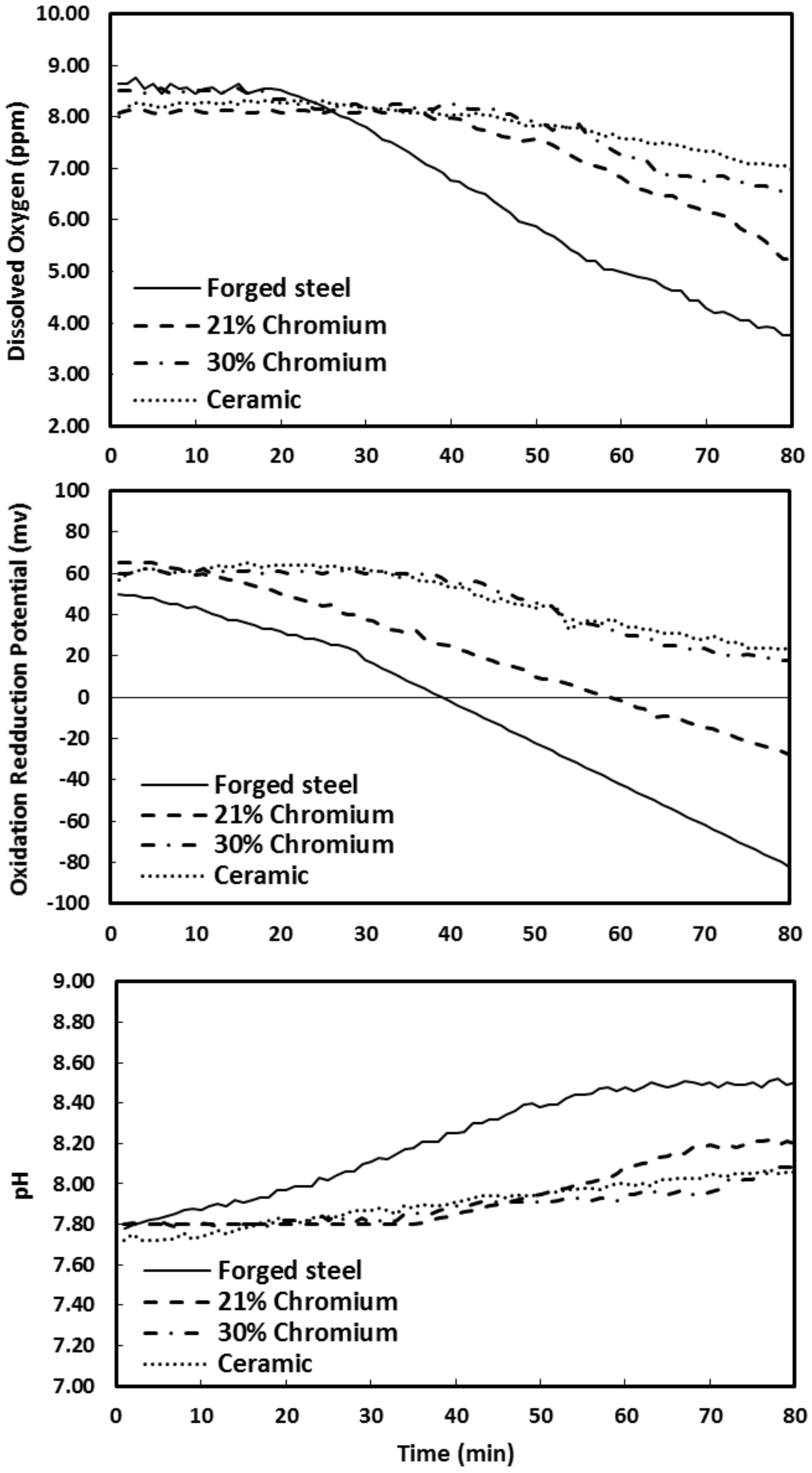


Figure 7-1. Pulp chemical conditions as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

**2. EDTA and dissolved sulfur measurements during grinding**

The EDTA iron extraction technique was performed on the samples collected every 20 min during grinding with different grinding media. EDTA-extracted iron can originate from the oxidation of grinding media and pyrrhotite. So, the amount of EDTA iron extraction can be shown as:

$Q_{\text{EDTA for Iron}} = Q_{\text{Fe from media oxidation}} + Q_{\text{Fe from pyrrhotite}}$ (7-7)

It is hypothesised that pyrrhotite was oxidised by the reactions shown in Equation 7-6. The equation shows that the amount of dissolved sulfur is 8/7 that of EDTA-extractable iron formed from pyrrhotite oxidation (Equation 7-6). Therefore, the oxidation amount of forged steel is given by the following equation:

$Q_{\text{Fe from pyrrhotite oxidation}} = 7/8\ Q_{SO4}$ (7-8)

$Q_{\text{Fe from media oxidation}} = Q_{\text{EDTA for Iron}} - 7/8\ Q_{SO4}$ (7-9)

Figures 7-2 and 7-3 show the amount of iron hydroxide and dissolved sulfur in the slurry as a function of grinding time and grinding media.

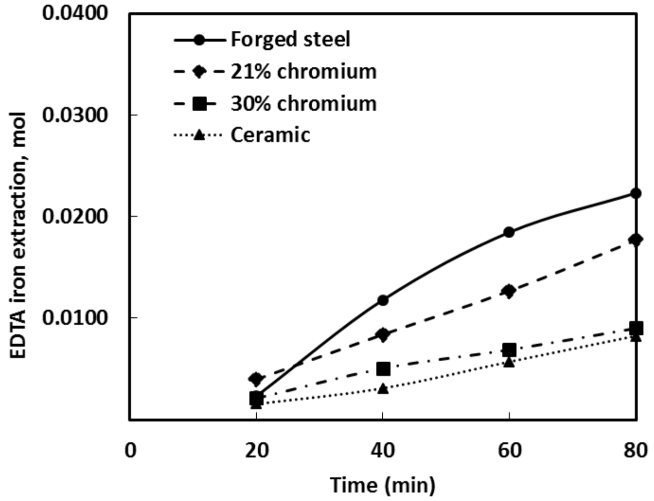


Figure 7-2. The amount of EDTA extractable iron as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

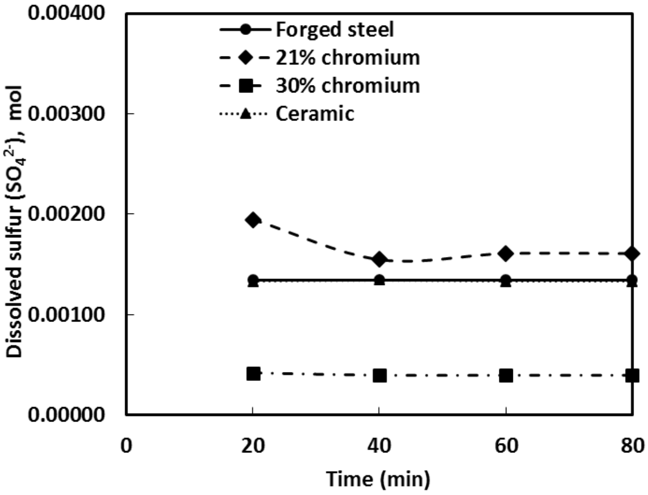


Figure 7-3. The amount of dissolved sulfur in slurry as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

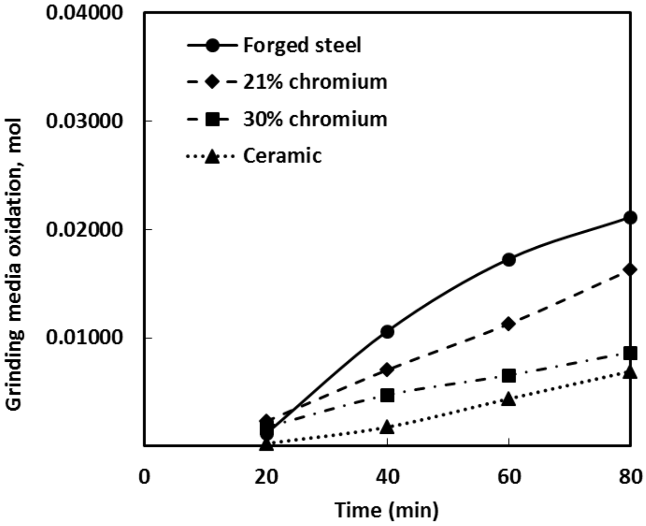


Figure 7-4. The amount of iron oxidised from media as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

Figure 7-4 presents the calculated amount of iron due to the oxidation of the grinding media. The forged steel media produced the highest amount of iron in comparison with the 30% chromium and ceramic media. The results show that most of the EDTA-extractable iron in the system originated from the grinding media oxidation. It is very important to highlight that in the case of the ceramic media, the grinding media oxidation apparently occurred even though the ceramic media is non-conductive material. The reason for that is probably because the inner wall of the mill was made of steel and thus there were the galvanic interactions between the inner wall of the mill and pyrrhotite particles.

#### 7.2.1.2 Cyanide gold leaching

**1. Pulp chemical environment during the cyanide gold leaching**

Although free cyanide was added to dissolve gold only (see Equation 7-10), free cyanide also reacts with pyrrhotite (Equations 7-11, 7-12 and 7-13) and iron hydroxide as presented in Equation 7-14 (Marsden and House, 2009). It should be noted that the presence of iron hydroxide can be explained by Equations 7-5, 7-6 and 7-13.

$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^-$ (7-10)

$Fe_7S_8 + CN^- \rightarrow 7FeS + SCN^-$ (7-11)

$2FeS + 12CN^- + 5O_2 + 2H_2O + 4e^- \rightarrow 2Fe(CN)_6^{4-} + 2SO_4^{2-} + 4OH^-$ (7-12)

$FeS + CN^- + 0.75O_2 + 1.5H_2O \rightarrow Fe(OH)_3 + SCN^-$ (7-13)

$Fe(OH)_3 + 6CN^- + e^- \rightarrow Fe(CN)_6^{4-} + 3OH^-$ (7-14)

Figure 7-5 shows $E_h$–pH diagram for the Fe–S–CN–$H_2O$ system at 25°C. As seen in Figure 7-5, the most dominant ion at conditions occurring during the cyanide gold leaching (i.e. pH=10.5, $E_h$= 0.3 to -1 V vs SHE) is ferrocyanide. The formation of ferrocyanide can be explained by Equations 7-12 and 7-14. It should be noted that other factors can also affect the consumption of free cyanide significantly, including the presence of impurities, foreign ion inclusions, lattice dislocations in the mineral crystal structure, and the interaction of the mineral with other reactive or conductive minerals and metals that can result in galvanic interactions (Marsden and House, 2009).

Figure 7-6 shows the changes of pulp chemical variables (pH, DO and $E_h$) during the cyanide gold leaching process. The amount of iron hydroxide was higher when the forged steel or 21% chromium grinding media were employed than that when the ceramic media was used. For that reason, using of the forged steel or 21% chromium media resulted in the production of a strong reducing environment during the first two hours of leaching probably due to the reaction between iron hydroxide and free cyanide (see Equation 7-14). Dissolved oxygen was consumed by the reaction of free cyanide with pyrrhotite (Equations 7-11 to 7-13). For that reason, the gold-bearing pyrrhotite ore is a problematic ore for the cyanidation process because dissolved oxygen is used not only for cyanide gold leaching (Equation 10) but also for the pyrrhotite oxidation (Equations 7-6, 7-12 and 7-13). Therefore, there is a competition for dissolved oxygen between pyrrhotite and gold. It is important to highlight that free cyanide was also consumed by iron hydroxide which is especially important when the forged steel or 21% chromium media were used (Equation 7-14). Additionally, when the forged steel or 21% chromium grinding media are employed in the first two hours of leaching, hydroxide ion is produced; therefore, the pulp pH increased to 11.4 until the free cyanide or iron hydroxide were consumed.

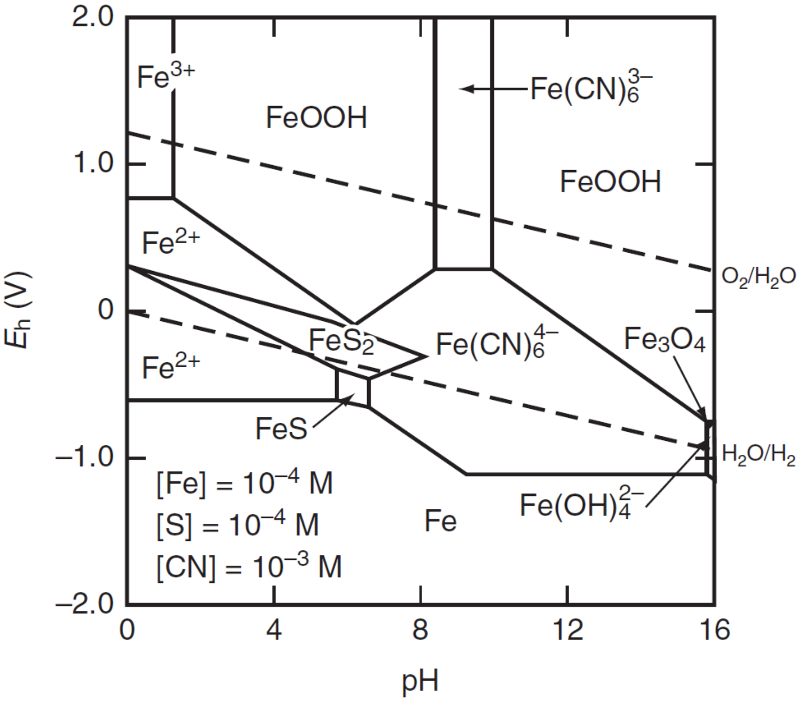


Figure 7-5. Eh–pH diagram for the Fe–S–CN–H2O system at 25°C (Marsden and House, 2009).

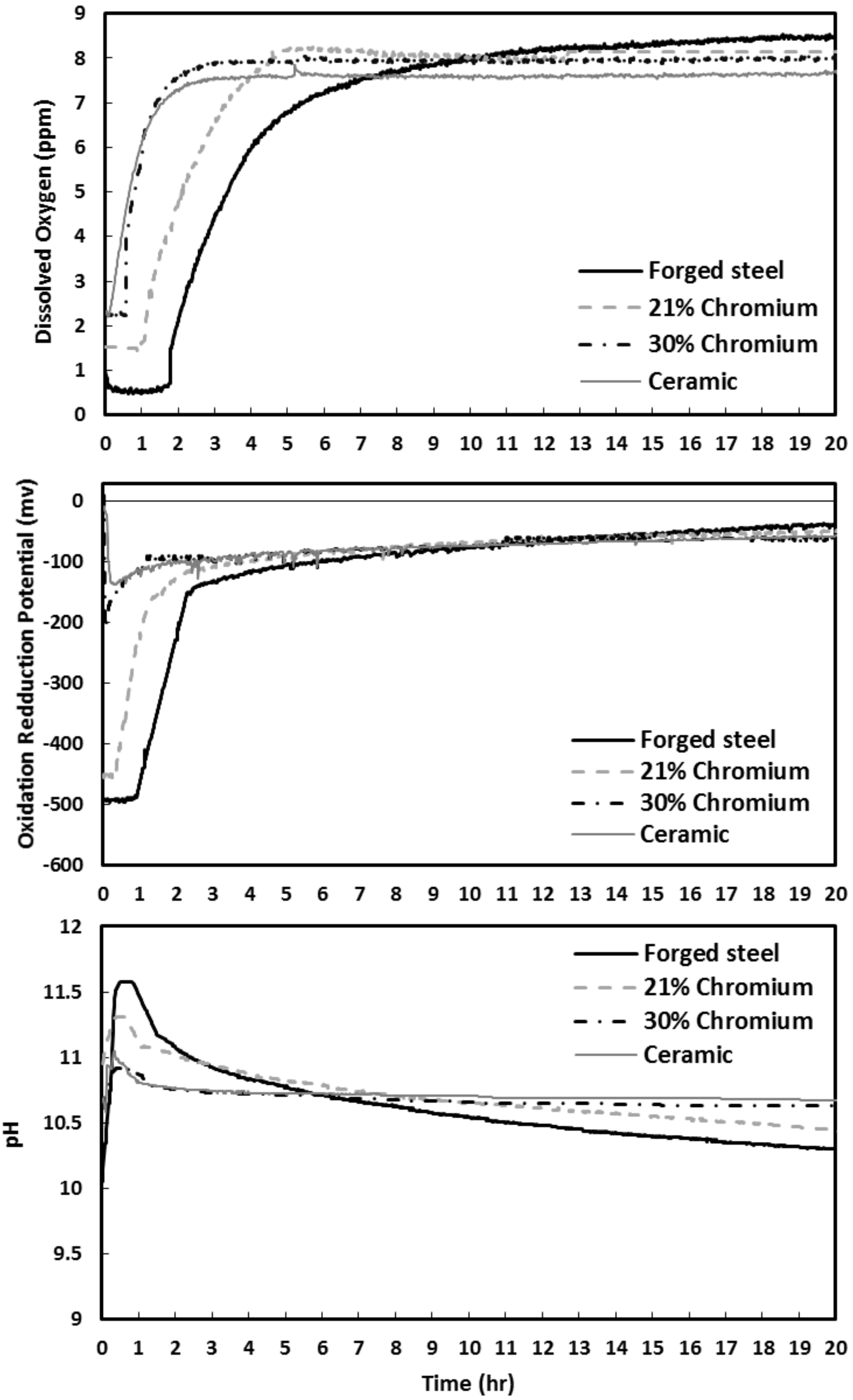


Figure 7-6. Pulp chemical conditions during cyanide leaching as a function of leaching time.

**2. Cyanide gold leaching performance**

Figure 7-7 shows the influence of grinding media on cyanide gold leaching. As seen in Figure 7-7, when the ceramic media was employed, gold dissolution in the presence of cyanide was the highest due to the lowest galvanic interaction. On the contrary, when the forged steel grinding media was used, the gold dissolution decreased dramatically due to the significant galvanic interactions between pyrrhotite and the forged steel media. More precisely, when the forged media was used, a significant amount of free cyanide was converted to ferrocyanide (see Equation 7-14) which cannot dissolve gold.

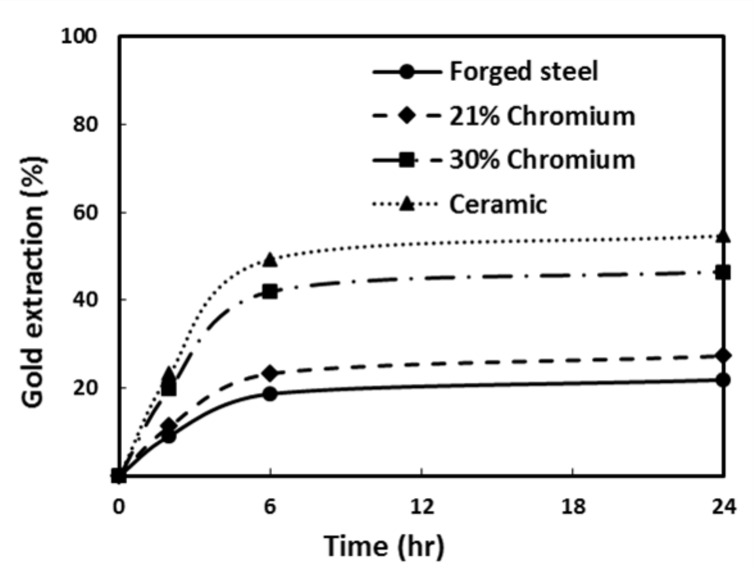


Figure 7-7. Effect of grinding media on gold-leaching in the presence of pyrrhotite: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

**3. Cyanide speciation during gold leaching**

Cyanide speciation was performed on the solution samples collected during leaching (at 2, 4, and 24 hours) to show how the grinding media can affect the cyanide speciation. As can be seen in Figure 7-8, when the forged steel or 21% chromium media were used, around 75% and 44% of the free cyanide was consumed by iron hydroxide and pyrrhotite to form ferrocyanide respectively (see Equation 7-14). For that reason, gold cyanide leaching was less efficient when the forged steel or 21% chromium media were used. It should be noted that a small amount (around 1%) of free cyanide was converted to thiocyanate as seen in Figure 7-9. By contrast, when the ceramic media was used, only 1% of free cyanide was converted to ferrocyanide because the amount of produced iron hydroxide during grinding with the ceramic media was insignificant. The amount of converted free cyanide to thiocyanate is also negligible. As a result, when the 30% chromium or ceramic media was used, the free cyanide almost did not decompose and thus gold leaching of cyanide was more efficient than that when grinding was performed with the forged steel grinding media or 21% chromium media.

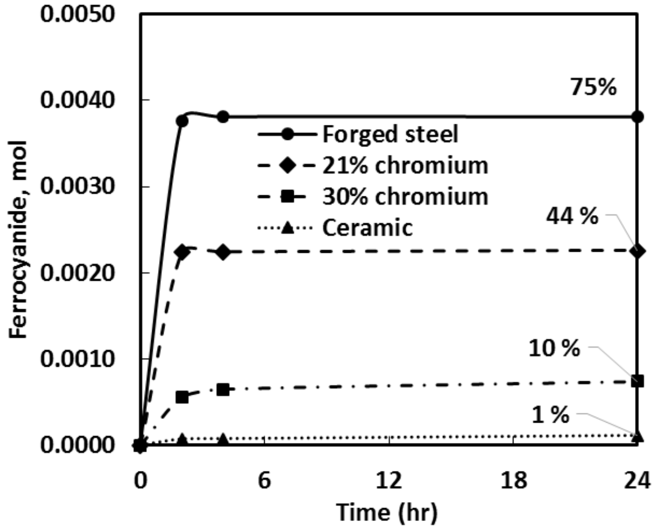


Figure 7-8. The amount of ferrocyanide in slurry as a function of leaching time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

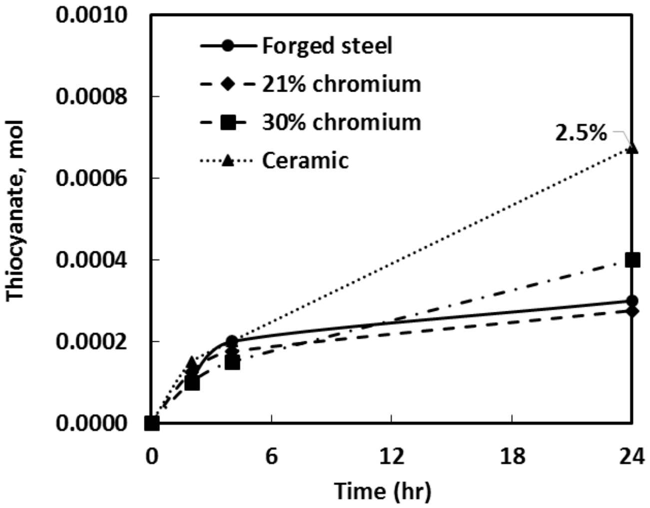


Figure 7-9. The amount of thiocyanate in slurry as a function of leaching time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

### 7.2.2 Arsenopyrite

#### 7.2.2.1 Grinding

**1. Pulp chemical environment during the grinding of the ore**

Figure 7-10 shows the pulp chemical properties during grinding of the gold-arsenopyrite synthetic ore with four different grinding media. Similar to grinding of the gold-pyrrhotite ore, changes from the 30% chromium and ceramic to the forged steel grinding media resulted in the drop in the pulp potential. The reason is the galvanic interactions between the forged steel media and arsenopyrite which cause the increase in the hydroxide ion production as shown in Equation 7-1. Thus, the pulp potential decreased while the pulp pH increased. Furthermore, according to Marsden and House (2009), in neutral and alkaline solutions, and in the presence of dissolved oxygen, arsenopyrite can be oxidised by the reaction presented in Equation 7-15.

$$2FeAsS + 7O_2 + 8H_2O = 2Fe(OH)_3 + 2H_3AsO_4 + 4H^+ + 2SO_4^{2-} \qquad (15)$$

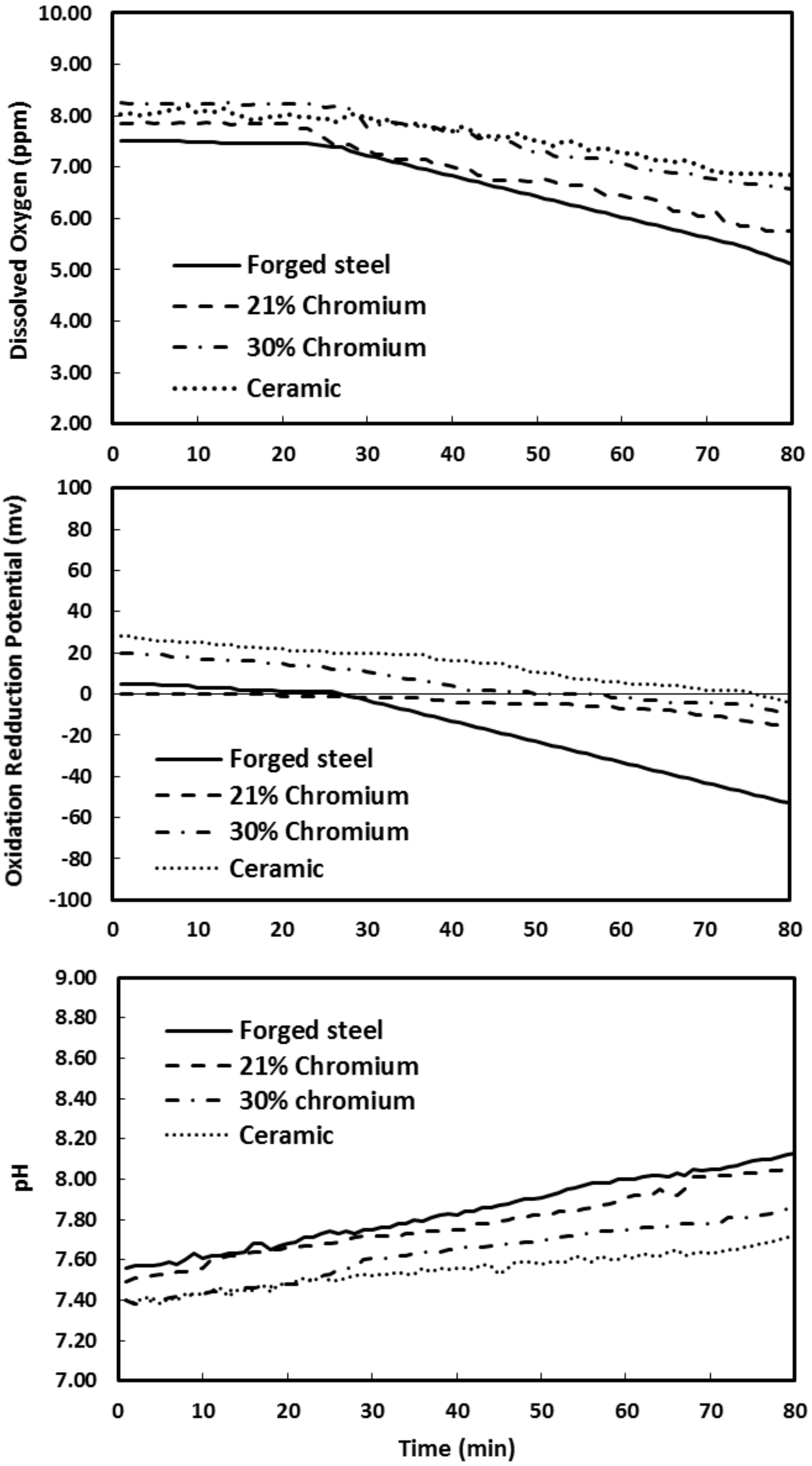


Figure 7-10. Pulp chemical conditions as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

**2. EDTA and dissolved sulfur measurements during grinding**

The samples collected every 20 minutes during grinding of the gold-arsenopyrite synthetic ore with four different grinding media were analysed by EDTA iron extraction technique. It should be noted that the EDTA-extracted iron originate from the oxidation of grinding media and arsenopyrite. Therefore, the amount of EDTA iron extraction can be shown as:

$$Q_{\text{EDTA for Iron}} = Q_{\text{Fe from media oxidation}} + Q_{\text{Fe from arsenopyrite}} \qquad (7\text{-}16)$$

It is hypothesised that arsenopyrite was oxidised by the reactions shown in Equation 15. The equation shows that the amount of dissolved sulfur is equal that of EDTA-extractable iron formed from arsenopyrite oxidation (Equation 7-15). Therefore, the oxidation amount of forged steel is given by the following equation:

$$Q_{\text{Fe from arsenopyrite oxidation}} = Q_{SO4} \qquad (7\text{-}17)$$

$$Q_{\text{Fe from media oxidation}} = Q_{\text{EDTA for Iron}} - Q_{SO4} \qquad (7\text{-}18)$$

Figures 7-11 and 7-12 show the amount of iron hydroxide and dissolved sulfur in the slurry as a function of grinding time and grinding media.

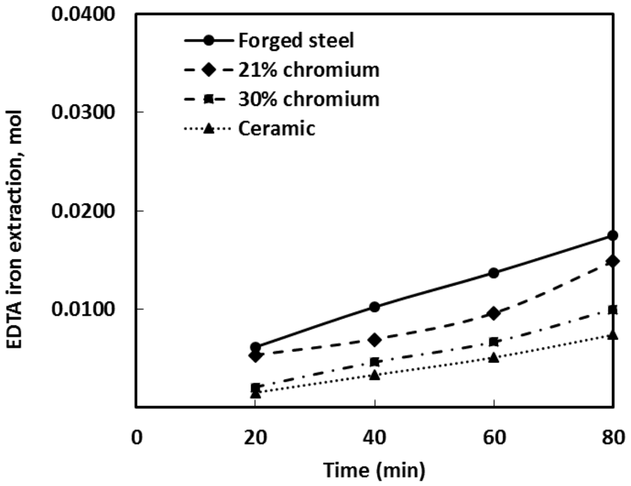


Figure 7-11. The amount of EDTA extractable iron as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

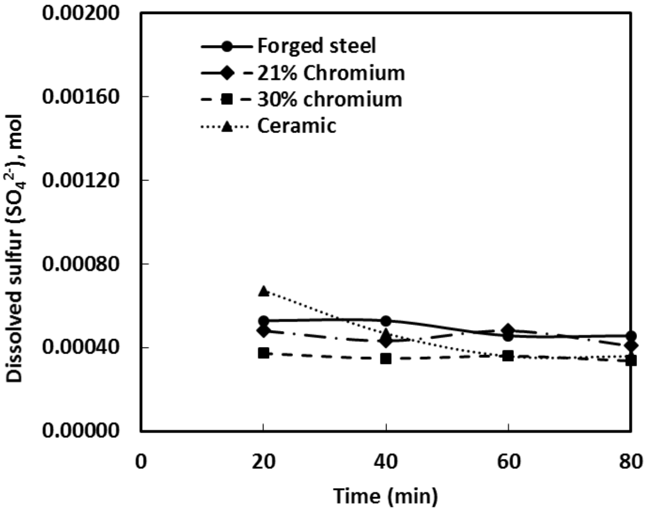


Figure 7-12. The amount of dissolved sulfur in slurry as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

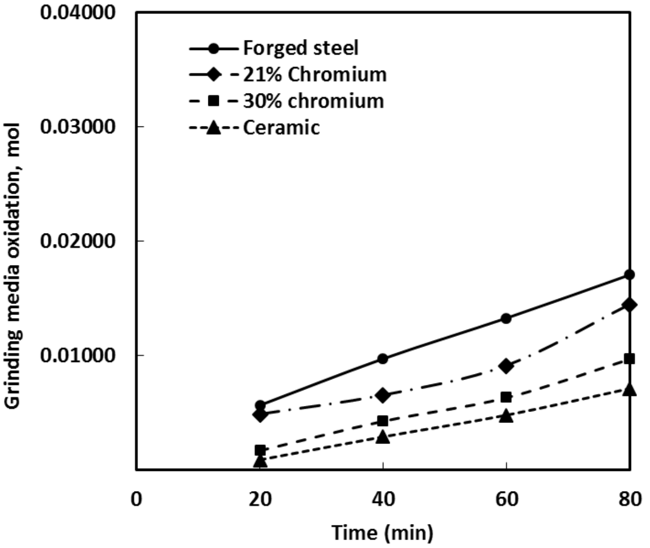


Figure 7-13. The amount of iron oxidised from media as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

Figure 7-13 presents the calculated amount of iron due to the oxidation of grinding media. The forged steel media produced the highest amount of iron in comparison with the 30%

chromium and ceramic media. The results show that most of the EDTA-extractable iron in the system originated from grinding media oxidation.

#### 7.2.2.2 Cyanide gold leaching

**1. Pulp chemical environment during the cyanide gold leaching**

Free cyanide was added to dissolve gold. However, free cyanide reacts with other species available in the mill discharge. More precisely, the free cyanide is consumed by iron hydroxide as presented in Equation 14 (Marsden and House, 2009). The free cyanide also reacts with arsenopyrite according to Equation 7-19 (Yannopoulos, 1991):

$$4FeAsS + 28CN^{-} + 5O_2 + 2H_2O \rightarrow AsO_3^{3-} + 4Fe(CN)_6^{4-} + 4SCN^{-} + 4H^{+} \qquad (7\text{-}19)$$

It should be noted that the presence of iron hydroxide can be explained by Equations 7-5 and 7-6. Figure 7-14 shows that the $E_h$-pH diagram for the Fe-S-As-CN-$H_2O$ system at 25°C (Marsden and House, 2009). The diagram was obtained for dissolved iron, arsenic, and sulfur species of $10^{-4}$ M and a free cyanide concentration of $10^{-3}$ M. Given that the pulp pH was between 10.5 and 11.5 as well as the pulp $E_h$ was between 0.3 and -1 V vs SHE during the leaching experiments in this work, ferrocyanide ($Fe(CN)_6^{4-}$) was the most dominant ion. The formation of ferrocyanide can be explained by Equations 7-19.

Figure 7-15 shows the changes of pulp chemical variables (pH, DO and $E_h$) during the cyanide gold leaching process. The amount of iron hydroxide was higher when the forged steel or 21% chromium grinding media were used than that when the ceramic or 30% chromium grinding media were used. For that reason, using of the forged steel or 21% chromium media resulted in the production of a strong reducing environment during the first hours of leaching probably due to the reaction between iron hydroxide and free cyanide (see Equation 7-14). It is important to highlight that free cyanide was consumed by iron hydroxide which is especially important when the forged steel or 21% chromium media were used (Equation 7-14). Additionally, when the forged steel or 21% chromium grinding media are employed in the first hours of leaching, hydroxide ion is produced; therefore, the pulp pH increased to 11.4 until the free cyanide or iron hydroxide were consumed.

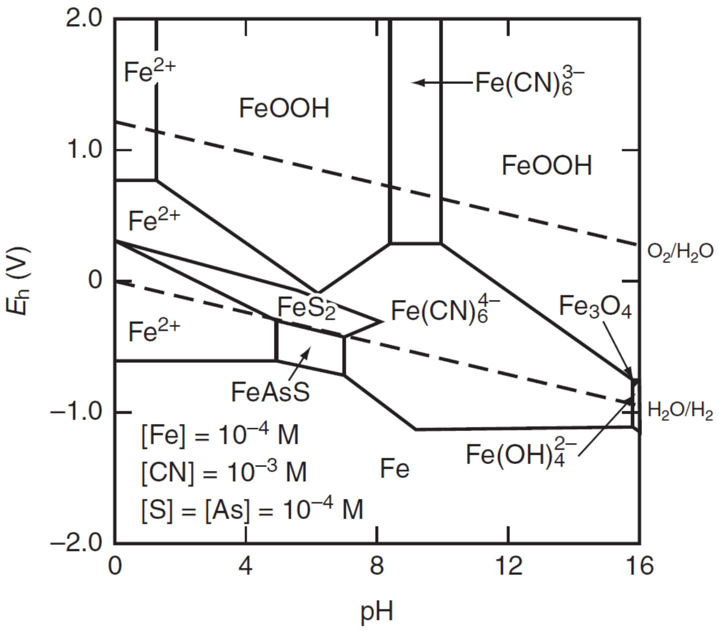


Figure 7-14. Eh–pH diagram for the Fe–S–As-CN–H2O system at 25°C (Marsden and House, 2009).

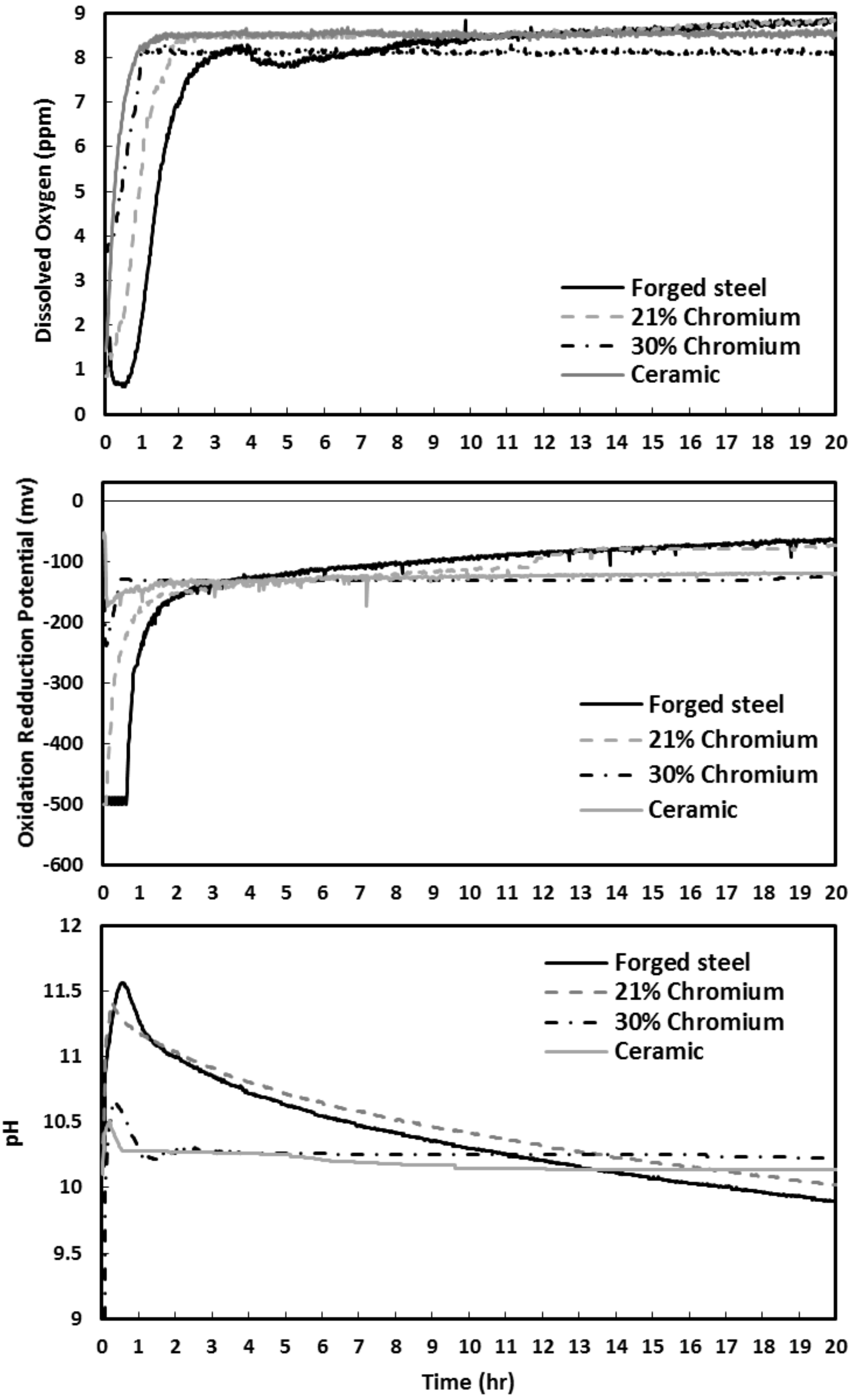


Figure 7-15. Pulp chemical conditions during cyanide leaching as a function of leaching time.

### 2. Cyanide gold leaching performance

The influence of grinding media on cyanide gold leaching in the presence of arsenopyrite is shown in Figure 7-16. Similar to the pyrrhotite ore, when the ceramic media or 30% chromium media was employed, gold dissolution in the presence of cyanide was the highest due to the lowest galvanic interaction. On the contrary, when the forged steel grinding media was used, the gold dissolution decreased due to the significant galvanic interactions between arsenopyrite and the forged steel media. It means that when the forged media was used, a significant amount of free cyanide was converted to ferrocyanide (see Equation 7-14) which cannot dissolve gold. In the case of the 30% chromium media, the formation of a highly refractory and dense $Cr_2O_3$ / $FeCr_2O_4$ layer makes the surface of the high chromium media behave similar to a ceramic surface.

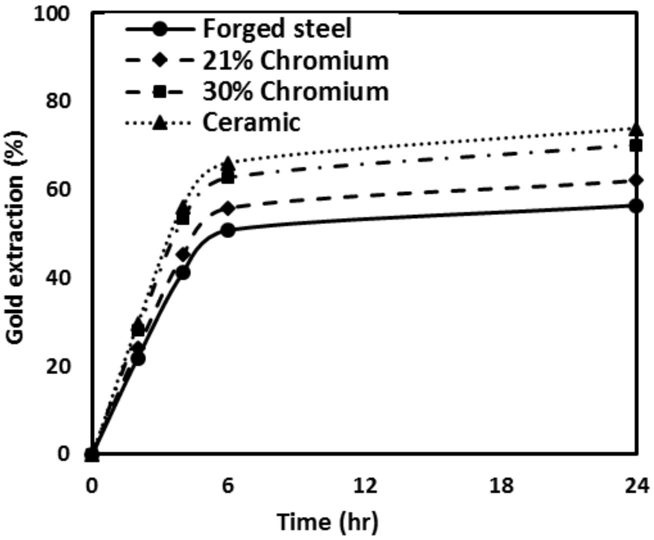


Figure 7-16. Effect of grinding media on gold-leaching in the presence of arsenopyrite: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

### 3. Cyanide speciation during gold leaching

The solution samples collected during leaching (at 2, 4, 6 and 24 hours) were analysed by HPLC for cyanide speciation to show how the grinding media can affect the cyanide speciation. As can be seen in Figure 7-17, when the forged steel or 21% chromium media were used, around 60% of the free cyanide was consumed to form ferrocyanide (see Equation 14). For that reason, gold cyanide leaching was less efficient when the forged steel or 21%

chromium media were used. It should be noted that a small amount (around 3%) of free cyanide was converted to thiocyanate due to the reaction of arsenopyrite with free cyanide (see Figure 7-18). By contrast, when the ceramic media and 30% chromium was used, only 5.5% of free cyanide was converted to ferrocyanide because the amount of produced iron hydroxide during grinding with the ceramic media was insignificant. The amount of converted free cyanide to thiocyanate is also negligible. As a result, when the ceramic media was used, the free cyanide almost did not decompose and thus gold leaching of cyanide was more efficient than that when grinding was performed with the forged media or 21% chromium media. It is important to highlight that the 30% high chromium media behaved similar to the ceramic media whereas the 21% chromium media showed more similarity to the forged steel media.

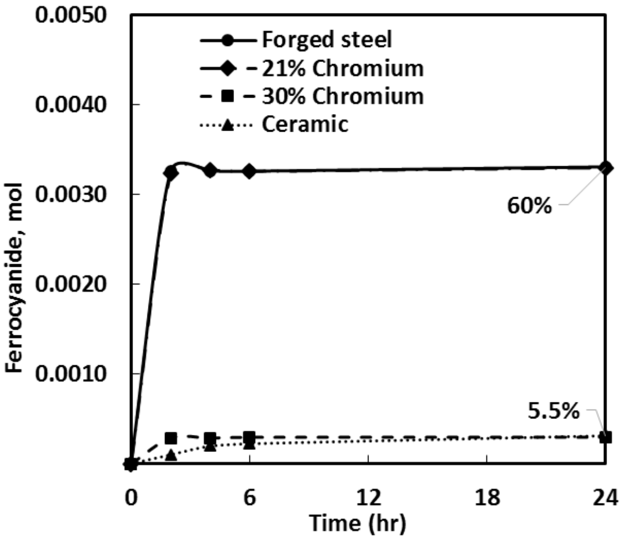


Figure 7-17. The amount of ferrocyanide in slurry as a function of leaching time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

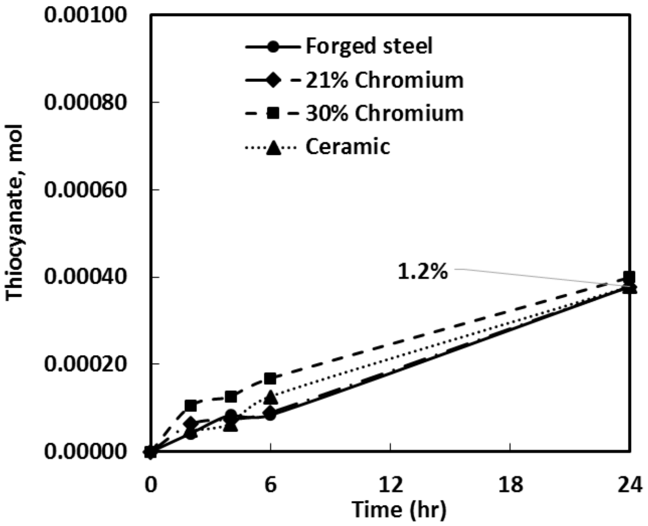


Figure 7-18. The amount of thiocyanate in slurry as a function of leaching time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

### 7.2.3 Pyrite

#### 7.2.3.1 Grinding

**1. Pulp chemical environment during the grinding of the ore**

The pulp chemical properties during grinding of the gold-pyrite synthetic ore with four different grinding media are given in Figure 7-19. As seen in Figure 7-19, changes from the forged steel grinding media to the 30% chromium and ceramic grinding media had a little impact on grinding conditions. The drop in the pulp potential was particularly pronounced during grinding with the forged steel grinding media due to the galvanic current between the forged steel grinding media and pyrite.

According to Marsden and House (2009), in neutral and alkaline solutions, and in the presence of dissolved oxygen, pyrite can be slightly oxidised (see Equation 7-20). It means that pyrite consumed very low amount of the oxygen in the slurry and thus the dissolved oxygen content slightly decreased.

Pyrite oxidation:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-} \qquad (7\text{-}20)$$

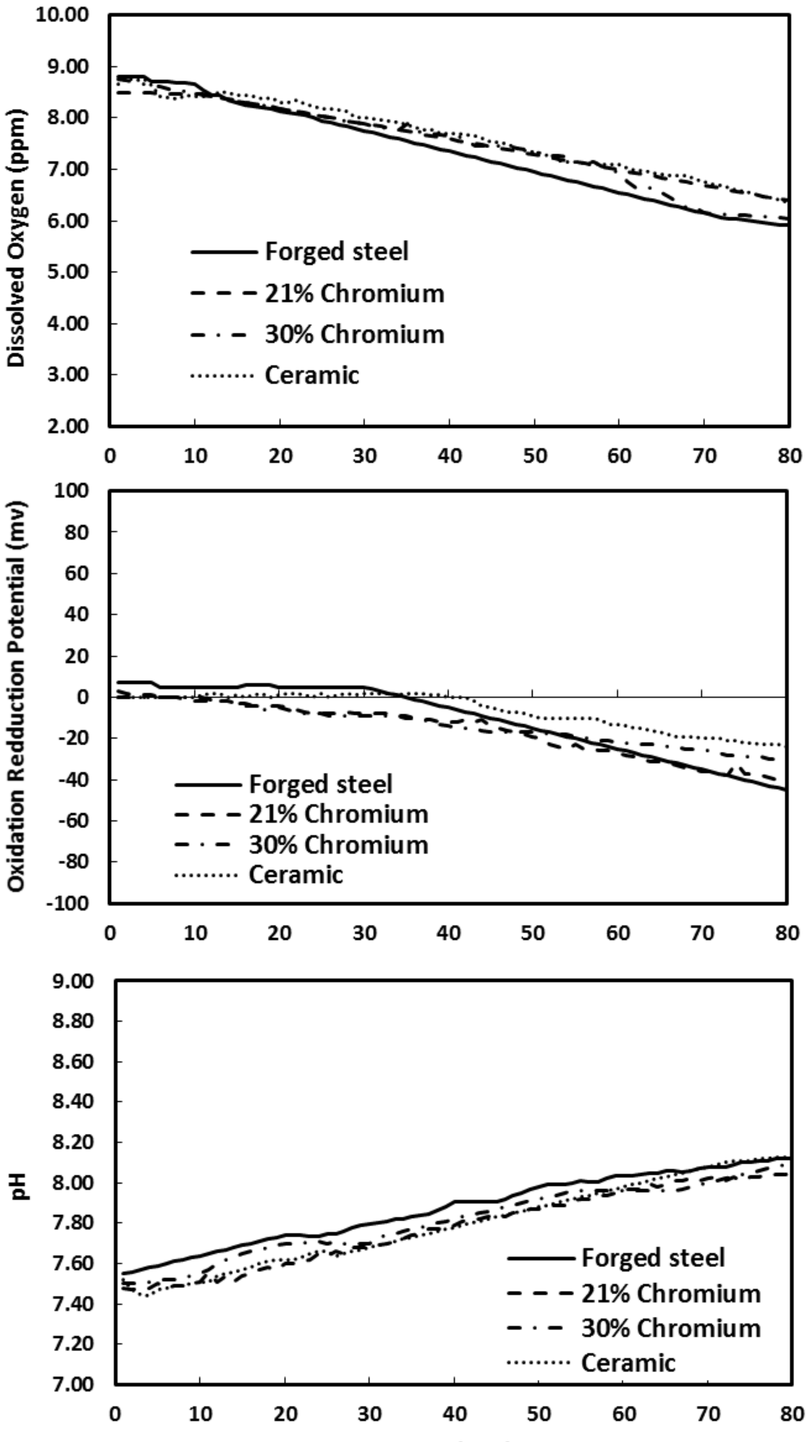


Figure 7-19. Pulp chemical conditions as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

**2. EDTA and dissolved sulfur measurements during grinding**

The EDTA iron extraction technique was performed on the samples collected every 20 min during grinding with four different grinding media. EDTA-extracted iron can originate from the oxidation of grinding media and pyrite. So, the amount of EDTA iron extraction can be shown as:

$$Q_{\text{EDTA for Iron}} = Q_{\text{Fe from media oxidation}} + Q_{\text{Fe from pyrite}} \tag{7-21}$$

It is hypothesised that pyrite was oxidised by the reactions shown in Equation 20. The equation shows that the amount of the dissolved sulfur is twice that of EDTA-extractable iron formed from pyrite oxidation (Equation 7-20). Therefore, the oxidation amount of forged steel is given by the following equation:

$$Q_{\text{Fe from pyrite oxidation}} = 1/2\ Q_{\text{SO4}} \tag{7-22}$$

$$Q_{\text{Fe from media oxidation}} = Q_{\text{EDTA for Iron}} - 1/2\ Q_{\text{SO4}} \tag{7-23}$$

Figures 7-20 and 7-21 show the amount of iron hydroxide and dissolved sulfur in the slurry as a function of grinding time and grinding media.

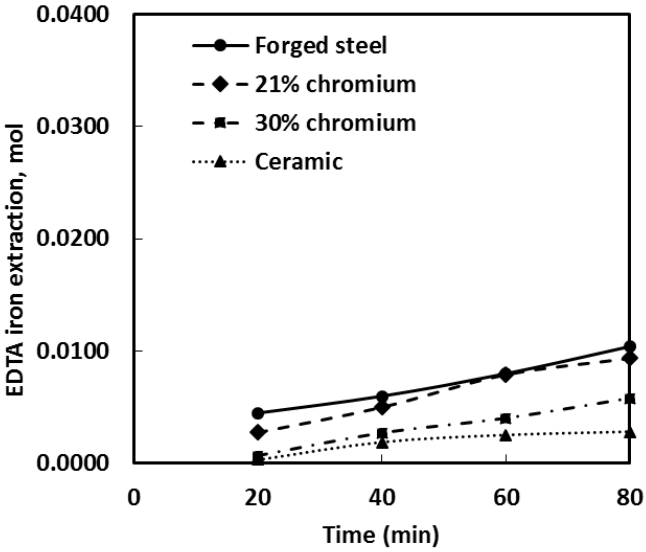


Figure 7-20. The amount of EDTA extractable iron as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

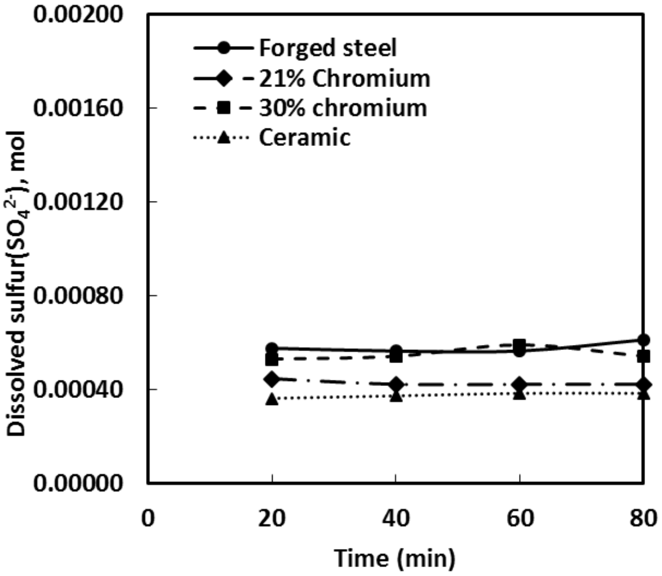


Figure 7-21. The amount of dissolved sulfur in slurry as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

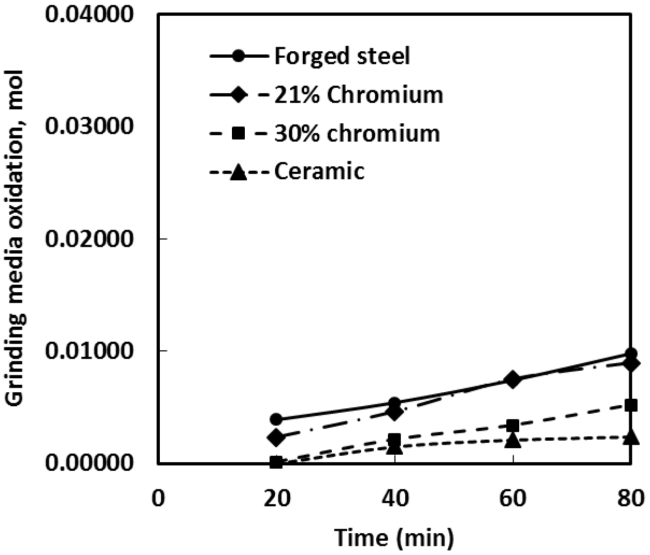


Figure 7-22. The amount of iron oxidised from media as a function of grinding time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

Figure 7-22 presents the calculated amount of iron due to the oxidation of grinding media. Forged steel produced the highest amount of iron in comparison with the 30% chromium and ceramic media. The results show that most of the EDTA-extractable iron in the system originated from the media oxidation.

### 7.2.3.2 Cyanide gold leaching

**1. Pulp chemical environment during the cyanide gold leaching**

Free cyanide was added to dissolve gold (see Equation 7-10). However, free cyanide reacts with iron hydroxide as presented in Equation 7-14 (Marsden and House, 2009) and pyrite (Equations 7-24 and 7-25). In addition, in the presence of free cyanide, pyrite may decompose at low rate according to the following reaction (Yannopoulos, 1991):

$$2FeS_2 + 9\ CN^- + 1/2\ O_2 + H_2O \rightarrow FeS + Fe(CN)_6^{4-} + 3SCN^- + 2OH^- \qquad (7\text{-}24)$$

$$2FeS + 2CN^- + 3/2\ O_2 + 3H_2O \rightarrow 2SCN^- + 2Fe(OH)_3 \qquad (7\text{-}25)$$

The presence of iron hydroxide can be explained by Equations 7-5, 7-6 and 7-25. The formed iron hydroxide reacts with free cyanide, resulting in the formation of ferrocyanide (see Equation 7-14). Figure 7-23 shows the changes of pulp chemical variables (pH, DO and $E_h$) during the cyanide gold leaching process. The amount of iron hydroxide was higher when the forged steel or 21% chromium grinding media were employed than that when the ceramic media was used. For that reason, using of the forged steel or 21% chromium media resulted in the production of a reducing environment during the first hours of leaching probably due to the reaction between iron hydroxide and free cyanide (see Equation 7-14). It is important to highlight that free cyanide was consumed by iron hydroxide which is especially important when the forged steel or 21% chromium media were used (Equation 7-14).

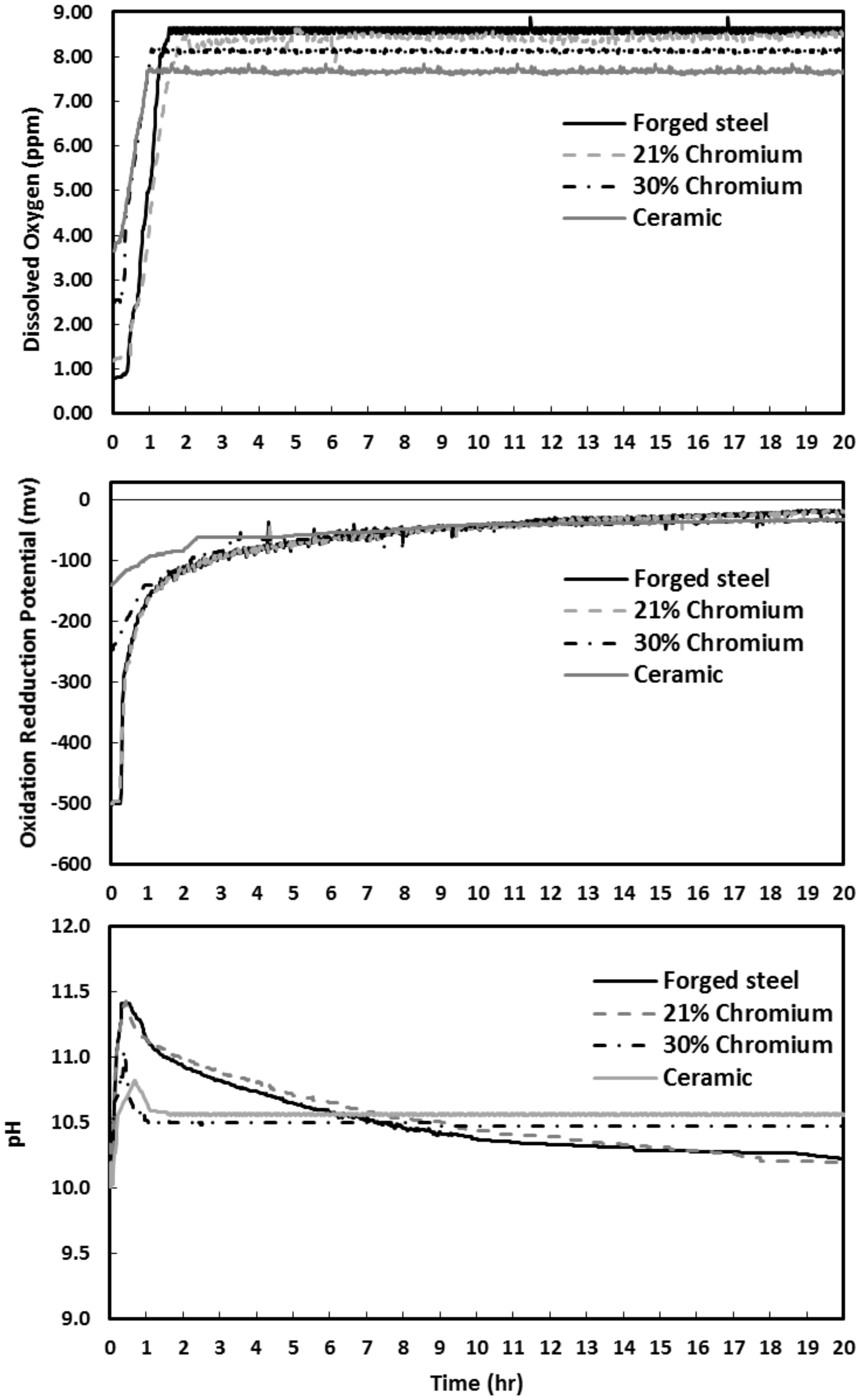


Figure 7-23. Pulp chemical conditions during cyanide leaching as a function of leaching time.

### 2. Cyanide gold leaching performance

Figure 7-24 shows the influence of grinding media on cyanide gold leaching in the presence of pyrite. As seen in Figure 7-24, when the ceramic media was employed, gold dissolution in the presence of cyanide was the highest due to the lowest galvanic interaction. On the contrary, when the forged steel grinding media was used, the gold dissolution decreased due to the galvanic interactions between pyrite and the forged steel media. However, due to the lower galvanic current between pyrite and grinding media, the amount of iron hydroxide was lower and thus more free cyanide was available for gold extraction. It means that more gold was extracted in the presence of pyrite than that in the presence of pyrrhotite. More precisely, when the 21% chromium grinding media was used, 65% of gold was extracted in the presence of pyrite while 25% of gold was extracted in the presence of pyrrhotite.

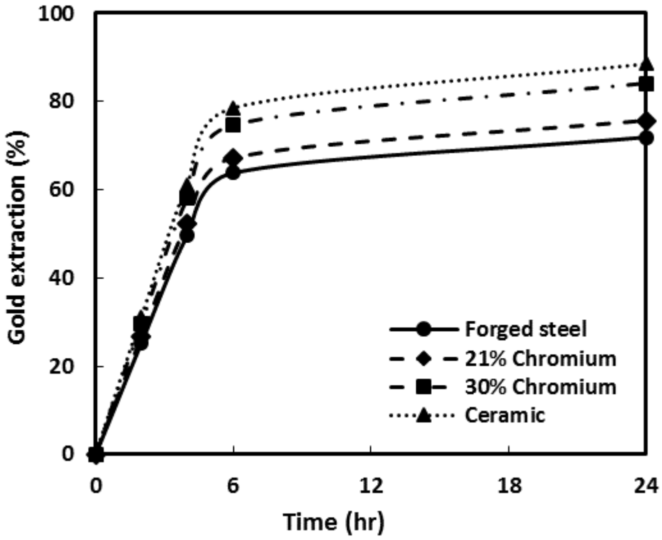


Figure 7-24. Effect of grinding media on gold-leaching in the presence of pyrite: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

### 3. Cyanide speciation during gold leaching

Cyanide speciation was performed on the solution samples collected during leaching (at 2, 4, 6 and 24 hours) to show how the grinding media can affect the cyanide speciation. As can be seen in Figure 7-25, when the forged steel and 21% chromium media were used, around 45% and 38% of the free cyanide was consumed by iron hydroxide to form ferrocyanide, respectively (see Equation 14). For that reason, gold cyanide leaching was less efficient when the forged steel or 21% chromium media were used. It should be noted that a small amount (around 0.5%) of free cyanide was converted to thiocyanate as seen in Figure 7-26. By contrast, when the ceramic media and 30% chromium was used, only 1% of free cyanide was converted to ferrocyanide because the amount of produced iron hydroxide during grinding with ceramic media was insignificant. The amount of converted free cyanide to thiocyanate is also negligible. As a result, when the ceramic media was used, the free cyanide almost did not decompose and thus gold leaching of cyanide was more efficient than that when grinding was performed with the forged media or the 21% chromium media.

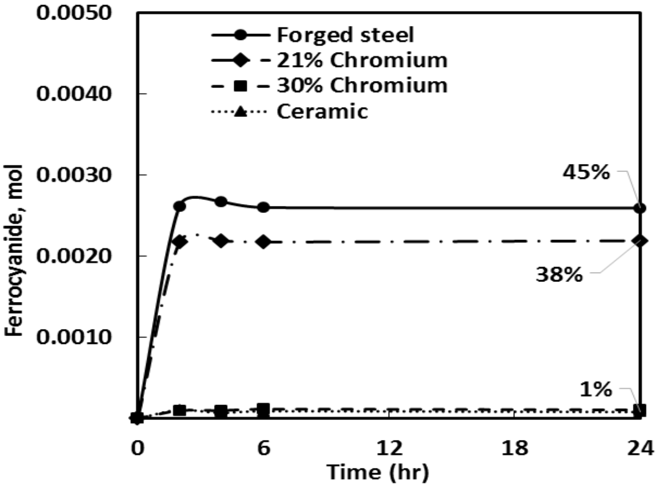


Figure 7-25. The amount of ferrocyanide in slurry as a function of leaching time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

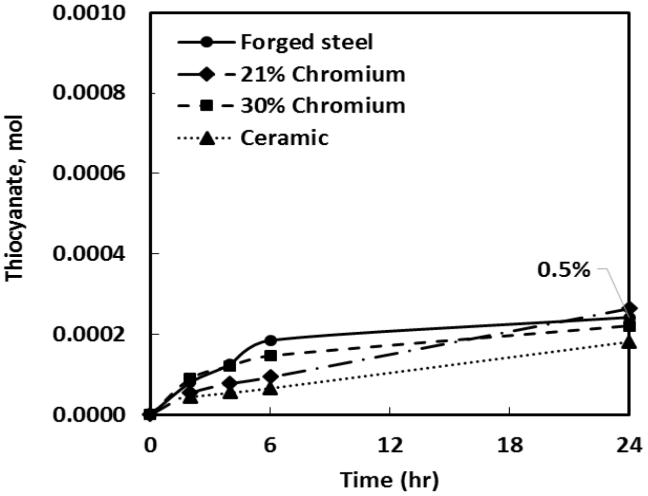


Figure 7-26. The amount of thiocyanate in slurry as a function of leaching time: (solid line) forged steel media; (dash line) 21% chromium media; (dash dot) 30% chromium; (dot line) ceramic media.

### 7.2.4 Electrochemical properties of grinding media and sulfide minerals

#### 7.2.4.1 Open circuit potentials (OCP)

The open circuit potential is one of the important electrochemical properties which determine the role of grinding media and sulfide minerals in the galvanic couple when exposed to the same environment. The open circuit potential of the grinding media (i.e. forged steel or 30% chromium grinding media) and the sulfide mineral (pyrrhotite, arsenopyrite or pyrite) electrodes were measured in situ of the mill. Figure 7-27 shows the open circuit potentials of the forged steel, 30% chromium grinding media and sulfide minerals electrodes during grinding of the gold-pyrrhotite, gold-arsenopyrite and gold -pyrite synthetic ore.

During grinding of the gold-pyrrhotite ore, the forged steel grinding media electrode showed much lower potentials than the pyrrhotite electrode, demonstrating that the forged steel media behaved as anode with regards to pyrrhotite. A similar observation was seen in the case of the 30% chromium grinding media electrode. However, the 30% chromium grinding media electrode had slightly higher potentials than the forged steel grinding media electrode. In the case of the arsenopyrite and pyrite electrodes, similar results were obtained; the only difference was that the arsenopyrite and pyrite electrodes had higher potential in comparison with the pyrrhotite electrode. As can be seen in Figure 7-27, the potentials of grinding media and minerals electrodes decreased in the following order:

Forged steel > 30% chromium > pyrrhotite > arsenopyrite > pyrite.

It means that pyrite is the least electrochemically active mineral while the opposite is true in the case of pyrrhotite. As a result, grinding of pyrite resulted in the lowest galvanic current and thus a small amount of produced iron hydroxide. By contrast, grinding of pyrrhotite lead to the highest galvanic current and hence a high amount of produced iron hydroxide.

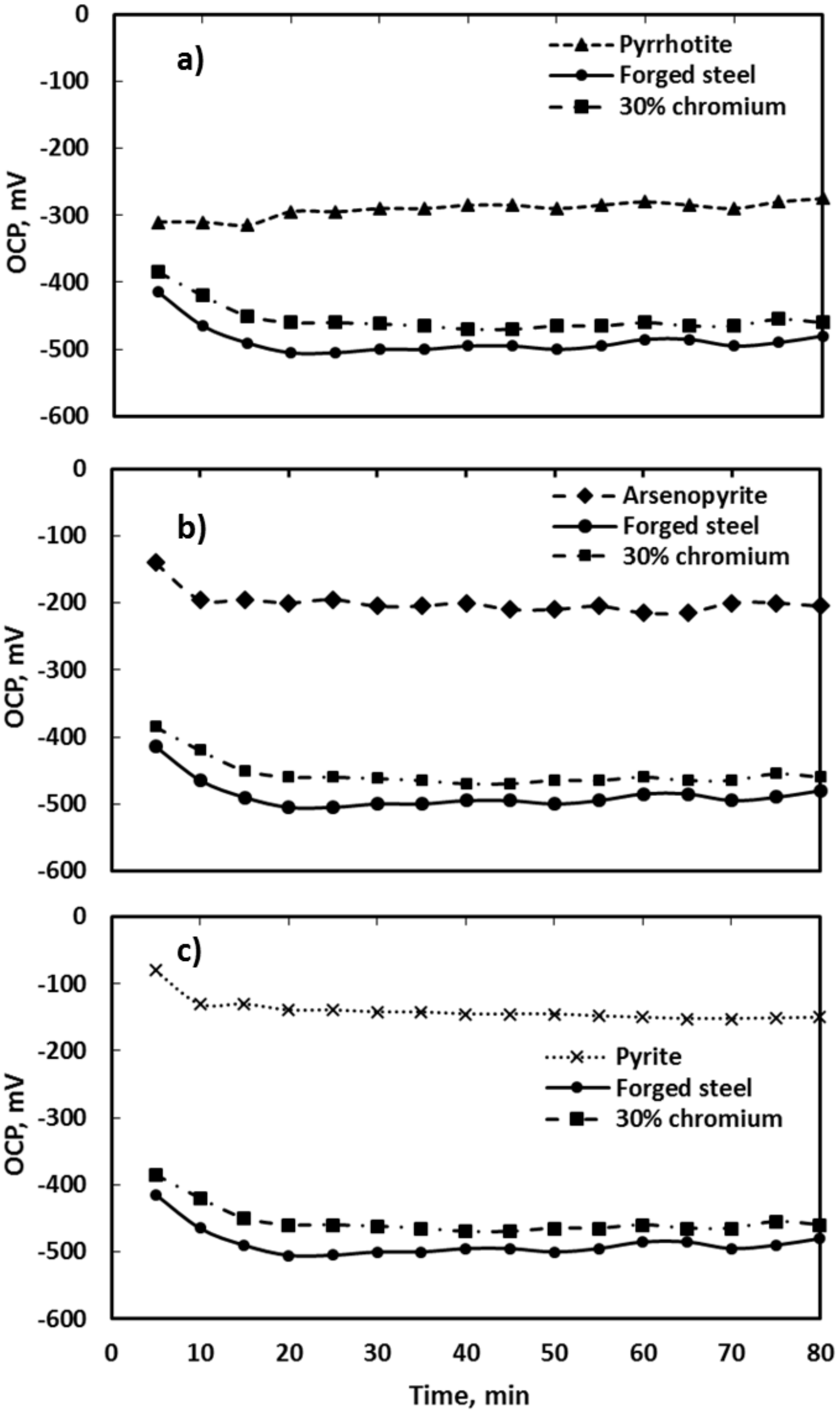


Figure 7-27. Rest potentials of forged steel, 30% chromium, pyrite, arsenopyrite and pyrrhotite electrodes during grinding of a) gold-pyrrhotite, b) gold-arsenopyrite and c) gold-pyrite synthetic ores as a function of time.

#### 7.2.4.2 Polarization measurements

Due to the difference in open circuit potentials of grinding media and sulfide minerals, a galvanic interaction occur during grinding. In this study, the galvanic current between grinding media and sulfide minerals was determined from polarization curves of the electrodes. Polarization curves of the grinding media (forged steel or 30% chromium) and the sulfide mineral electrode (pyrrhotite, arsenopyrite or pyrite) during grinding of the gold-pyrrhotite, gold-arsenopyrite or gold-pyrite synthetic ores with the forged steel and 30% chromium media are shown in Figures 7-28, 7-29 and 7-30, respectively. Figures show how to determine the galvanic current from the polarization curves of the forged steel and 30% chromium media during grinding. The dash line shows the galvanic current through sulfide minerals couple with different grinding media. The forged steel media has a significantly higher galvanic current with gold-pyrrhotite ore than the 30% chromium; the presence of chromium in the grinding media reduced the galvanic current between the grinding media and pyrrhotite. Similar observation was seen during grinding of the gold-arsenopyrite and gold-pyrite synthetic ores. However, in general, the galvanic current with the arsenopyrite and pyrite electrodes decreased in comparison with the pyrrhotite electrode. Comparison of the galvanic currents of the couples, the following order may be given:

Forged steel-pyrrhotite > forged steel-arsenopyrite > forged steel-pyrite> 30% chromium-pyrrhotite > 30% chromium-arsenopyrite > 30% chromium-pyrite

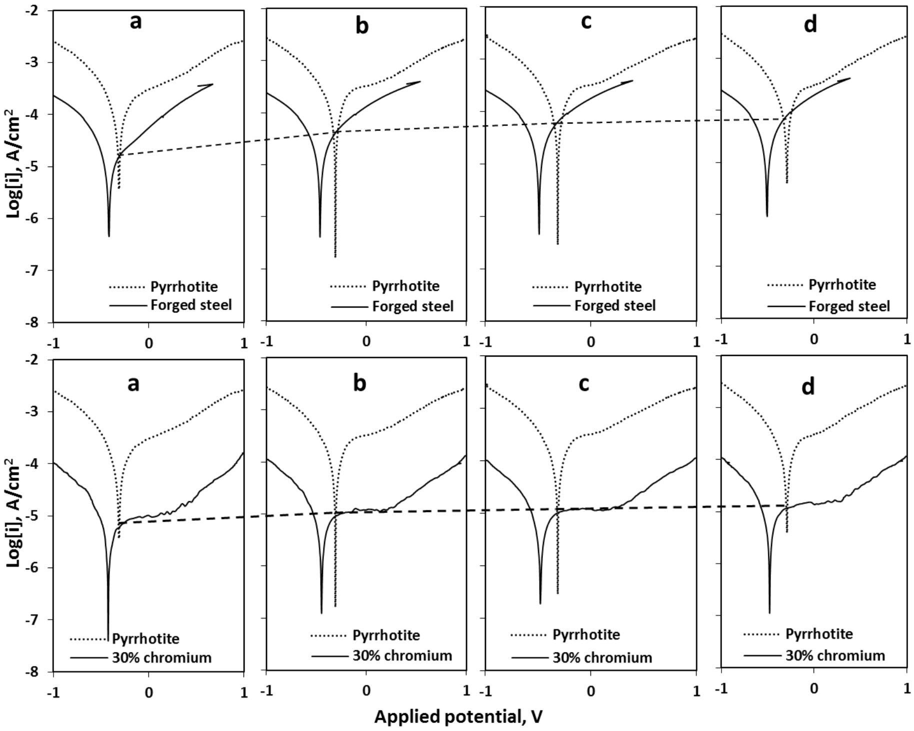


Figure 7-28. Polarization curve of forged steel, 30% chromium and pyrrhotite at different times. Measured times at (a) 20 min; (b) 40 min; (c) 60 min; (d) 80 min.

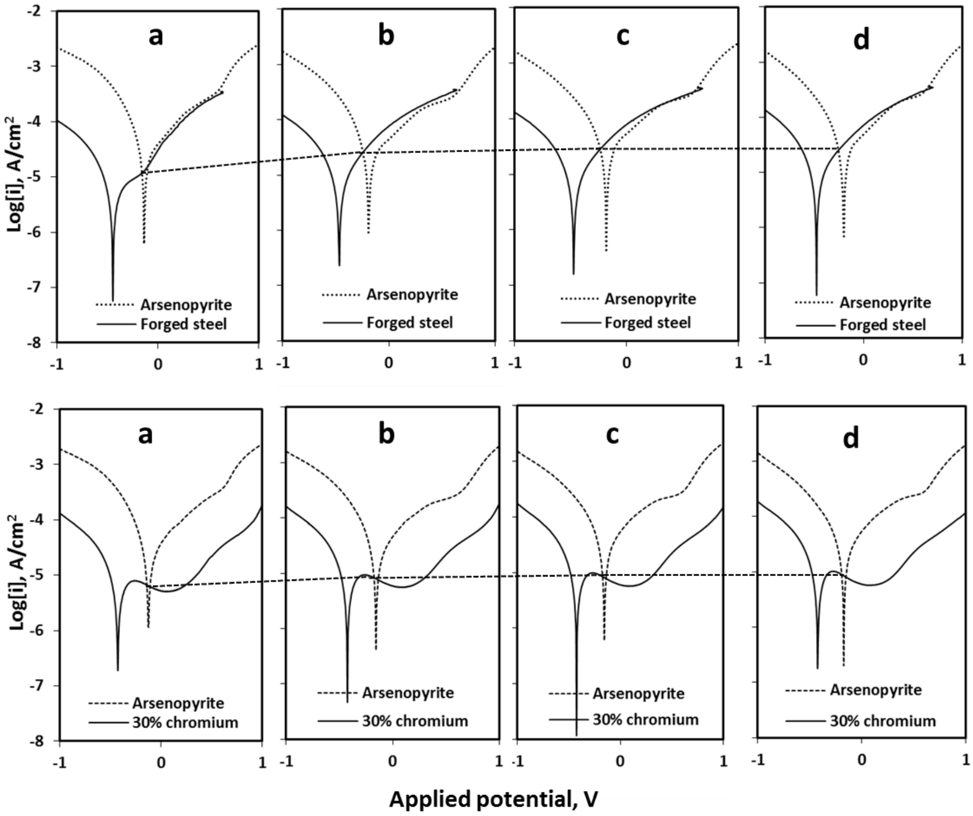


Figure 7-29. Polarization curve of grinding media and arsenopyrite at different grinding times. Measured times at (a) 20 min; (b) 40 min; (c) 60 min; (d) 80 min

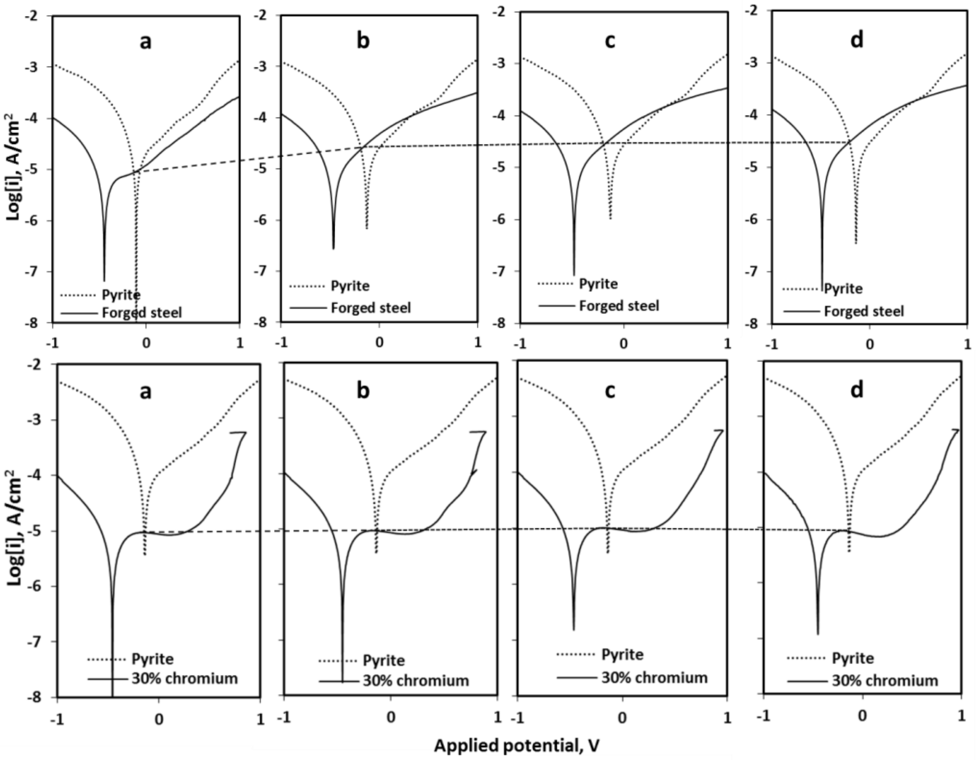


Figure 7-30. Polarization curve of grinding media and pyrite at different grinding times. Measured times at (a) 20 min; (b) 40 min; (c) 60 min; (d) 80 min

### 7.2.5 Correlation between oxidized iron and galvanic currents

#### 7.2.5.1 Theoretical model

It is well known that the galvanic interactions between sulfide minerals and the steel grinding media during grinding increase the corrosion rate of grinding media (Adam et al., 1984; Martin et al., 1991; Cullinan et al., 1999; Greet et al., 2004; Huang and Grano, 2005; Huang and Grano, 2006; Huang et al., 2006; Kinal et al., 2009; Chen et al., 2013; Rabieh et al., 2016; Rabieh et al., 2017a). The higher the corrosion rate of grinding media, the more hydroxide iron species in the mill discharge are produced.

Huang and Grano (2006) developed a model to describe the correlation between the galvanic current between grinding media and sulfide minerals and the iron hydroxide (i.e. the EDTA extractable iron). According to this model, in a grinding system, the amount of EDTA extractable iron ($Q_{Fe}(t)$) in the slurry is produced from the grinding media and the sulfide mineral. Additionally, $Q_0$ is also included in the model; $Q_0$ represents iron hydroxide identified on the surface of grinding media and the mineral samples before grinding of the ore. The total amount of oxidised iron ($Q_{Fe}(t)$), for a given time t, represents the sum of the oxidation amount of grinding media and the mineral, and is expressed by:

$$Q_{Fe}(t) = Q_0 + \frac{A_{Md}}{n_1F}\int_0^t I_{g,Md}(t)dt + \frac{1}{n_2F}\int_0^t A_{0,Mn}I_{0,Mn}(t)dt + \frac{A_{Md}}{n_1F}\int_0^t i_{c,Md}(t)dt + \frac{1}{n_2F}\int_0^t A_{g,Mn}i_{a,Mn}(t)dt \qquad (7\text{-}26)$$

where $I_{g,\,Md}$ (t) is the galvanic current of grinding media, $A_{g,\,Mn}$ is the contacted surface area of a sulfide mineral, $A_{Md}$ and $A_{0,Mn}$ are the surface area of grinding media and the particles, respectively. $I_{0,Mn}(t)$ is the exchange current density on the mineral surface. $i_{c,Md}$ (t) is the cathodic current on the grinding media surface while $i_{a,Mn}(t)$ is the anodic current on the mineral surface; $n_1$ and $n_2$ are the number of moles of electrons transferred per mole of iron and pyrrhotite oxidation, respectively. F is the Faraday constant i.e. 96500 C/mol.

Huang and Grano (2006) suggested that during grinding, the oxidation rate of the sulfide mineral due to galvanic interaction with grinding media and the cathodic current (the last two terms in the equation 7-26) are very low and can be neglected. Therefore, Equation 7-26 becomes:

$$Q_{Fe}(t) = Q_0 + \frac{A_{Md}}{n_1F}\int_0^t I_{g,Md}(t)dt + \frac{1}{n_2F}\int_0^t A_{0,Mn}I_{0,Mn}(t)dt \qquad (7\text{-}27)$$

Moreover, the average amount of EDTA extractable iron ($Q_{Fe}(t)$) during grinding can be measured from the average galvanic current ($\overline{IgA_{Md}}$), the average exchange current density of the mineral ($\overline{IA_{0,Mn}}$) and the grinding time ($t_{grind}$).

$$Q_{Fe}(t) = Q_0/t_{grind} + \frac{A_{Md}}{n_1F}\,\overline{Ig\,A_{Md}} + \frac{A_{0,Mn}}{n_2F}\overline{IA_{0,Mn}} \qquad (7\text{-}28)$$

The dissolved sulfur measurements during grinding reveal that the amount of iron oxide and hydroxide production due to sulfide minerals oxidation was very low in comparison with the grinding media oxidation. Therefore, the amount of oxidised iron due to the current density on the mineral surface can be neglected. As a result, the amount of oxidised iron is linear with the galvanic current as seen in Equation 7-29:

$$Q_{Fe}(t) = Q_0/t_{grind} + \frac{A_{Md}}{n_1 F} \overline{Ig\, A_{Md}} \tag{7-29}$$

### 7.2.5.2. Empirical correlation between iron oxidation and galvanic current

The theoretical model (see Equation 7-29) was used to explain the correlation between iron oxidation and the galvanic current. Figure 7-31, 7-32 and 7-33 show how the galvanic current influences the oxidation of grinding media (i.e. forged steel and 30% chromium grinding media).

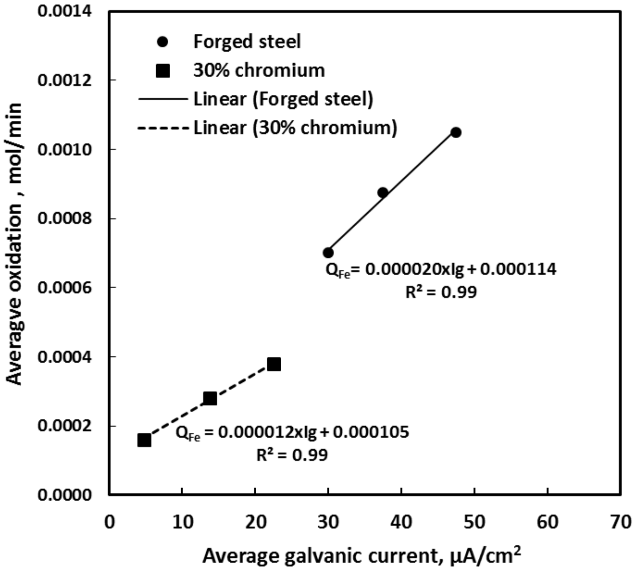


Figure 7-31. Correlation between the oxidation of grinding media and galvanic current between pyrrhotite and grinding media.

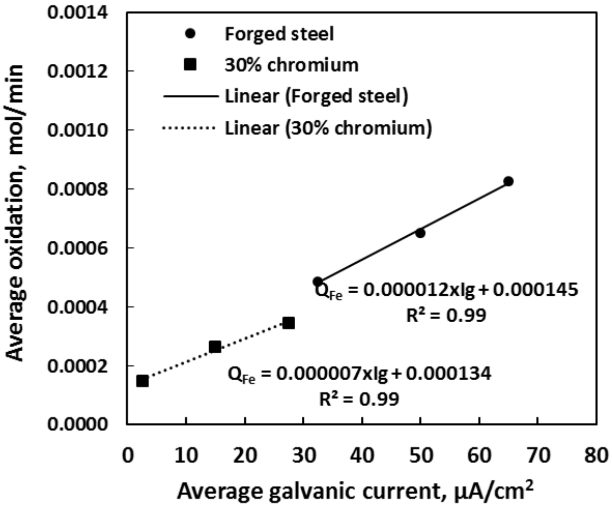


Figure 7-32. Correlation between the oxidation of grinding media and galvanic current between arsenopyrite and grinding media.

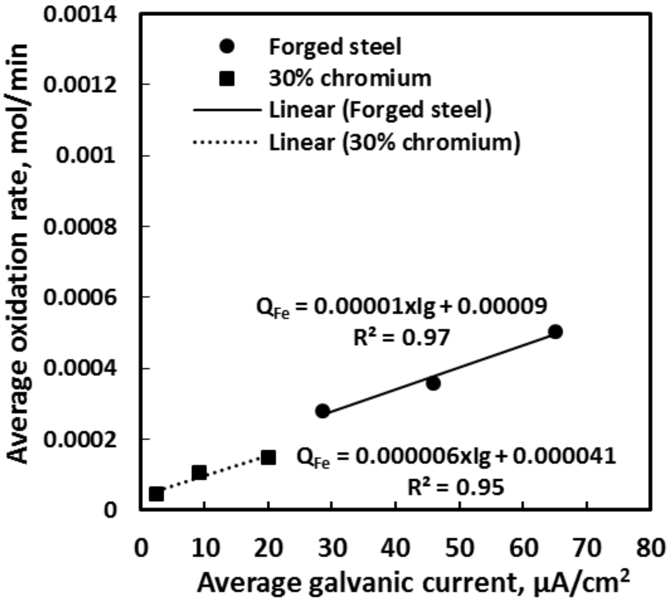


Figure 7-33. Correlation between the oxidation of grinding media and galvanic current between pyrite and grinding media.

Furthermore, Figures 7-31, 7-32 and 7-33 show the linear relationship between the galvanic currents and the amount of iron oxidation in the mill discharge during grinding of pyrrhotite, arsenopyrite and pyrite ores. It means that the higher the galvanic current between the grinding media and sulfide minerals, the greater the degree of oxidation of the grinding media (i.e. the amount of EDTA extractable iron produced). In general, the coefficient of galvanic current with the forged steel grinding media is around two times higher than that with the 30% chromium grinding media. The reason is probably due to the different physico-chemical properties of the grinding media.

## 7.3 Summary

In this work, the influence of the grinding media on cyanide gold leaching in the presence of different iron sulfide minerals (pyrrhotite, pyrite or arsenopyrite) was investigated. The oxidation of grinding media was quantified using EDTA extraction method and dissolved sulfur measurements while cyanide species was determined using high-performance liquid chromatography (HPLC). The following results have been observed:

i. Pulp chemistry data revealed that grinding with the forged steel grinding media resulted in a greater reducing environment in comparison with the 30% chromium and ceramic grinding media due to the galvanic interactions between the forged steel media and sulfide minerals. The degree of oxidation of the forged steel media was the highest while the opposite is true in the case of the ceramic grinding media as confirmed with the EDTA extraction and dissolved sulfur measurements. The degree of oxidation of grinding media also depends on the type of the ore. Specifically, when grinding was performed with the same grinding media, the amount of produced iron hydroxide decreased in the following order: pyrrhotite ore>arsenopyrite ore >pyrite ore. The reason is that pyrite is the least electrochemically active mineral while pyrrhotite is the most electrochemically active mineral.

ii. The gold extraction data showed that when the ceramic or 30% chromium grinding media were used, cyanide gold leaching was very efficient because the free cyanide almost did not decompose. In contrast, when the forged media was used, the cyanide gold leaching was the lowest.

iii. Cyanide speciation showed that when the forged steel or 21% chromium media were used, generated iron hydroxide reacts with free cyanide, resulting in the decomposition of the free cyanide; the free cyanide was converted to ferrocyanide which cannot dissolve gold. When the grinding was conducted in the presence of the forged media, the decomposition of the free cyanide decreased in the following order: pyrrhotite ore>arsenopyrite ore >pyrite ore.

iv. In many ways, the 30% chromium media behaved more like the ceramic media than like the 21% chromium media with regards to the downstream impacts on leaching.

# Chapter 8 Conclusions and recommendations

The conclusions of this thesis are summarized in this chapter as well as recommendations for future work.

## 8.1 Conclusions

The first phase of the project involved the experimental investigation of corrosion of different grinding media (i.e. forged, 18% chromium and ceramic media) during grinding of quartz in the tap water and the synthetic process water. Pure quartz was selected to prevent the galvanic interactions between the grinding media and mineral particles and thus it was possible to understand the corrosion of different grinding media in the absence of electrochemically active minerals. XPS analysis and EDTA extraction technique were performed to analyse quartz surfaces after grinding. Both techniques demonstrated that the forged steel media produced more iron species than the 18% chromium or ceramic media, indicating higher corrosion rate of the forged media. The synthetic process water accelerated the corrosion process of grinding media probably due to a large amount of chloride ions in the synthetic process water.

Secondly, the grinding media and the synthetic process water, mentioned in the first phase of the project, also were used during grinding of a refractory gold ore (Kanowna Belle gold mine) to study the influence of different grinding conditions on floatability of pyrite. The results showed that pyrite recovery and gold recovery was the highest when grinding was performed with the forged steel media. The improved pyrite recovery in the presence of the forged steel media may be attributed to better activation of the pyrite surface with $Cu^{2+}$ under strong reducing conditions. The results show that the changes in grinding conditions affect the pyrite recovery more than the gold recovery. Additionally, it was found that XPS technique failed to explain the influence of different grinding media on the floatability of pyrite from its ore probably due to the insensitivity of the technique to detect the presence of a low amount of copper species on the surface of samples collected by flotation.

In the third phase of the project, the role of grinding media type, water chemistry and pyrite mineralogy on the galvanic interaction between grinding media and pyrite were investigated. All these factors strongly affect the galvanic current between minerals and grinding media. The galvanic currents between pyrite and grinding media decreased as a function of increasing chromium content in the grinding media. Furthermore, changing the pyrite-based electrode from pure pyrite to a gold-bearing pyrite electrode increased the galvanic currents between the pyrite electrode and the grinding media electrode; therefore, the gold-bearing pyrite electrode was more electrochemically active than the pure pyrite one. In addition, using the synthetic process water instead of the tap water increased the galvanic currents between pyrite and the high-chromium grinding media electrode (30 % chromium). However, when the forged steel electrode or the low-chromium grinding media electrode were used, the galvanic currents were lower in the case of the synthetic process water compared to the tap water condition. In addition, the results obtained from SEM-EDX analysis showed that in both the tap and synthetic process water conditions, oxide species were identified on the surface of the forged steel electrode and the low chromium electrode. However, no oxygen species were detected on the surface of the 30 % chromium electrode.

Due to the importance of galvanic interactions occurring between grinding media and sulfide minerals on gold cyanide leaching performance and a limited number of studies conducted in this research area, the focus of the final phase of the project was to study the influence of the grinding media (forged steel, 21% chromium, 30% chromium, and ceramic media) on cyanide gold leaching in the presence of pyrrhotite, pyrite and arsenopyrite. Pyrrhotite was selected because this sulfide mineral is the highest cyanide- and oxygen-consuming iron sulfide (Marsden and House, 2009) and, contrary to pyrite, tends to behave as a reactive anode. All selected grinding media have different behaviour in the wet environments. More precisely, the forged steel media significantly corroded during wet grinding while the opposite is true in the case of the ceramic media. The high-chromium media slightly corroded during the wet grinding.

In the case of pyrrhotite, the results showed that when the grinding of the ore was performed using the ceramic media, the gold extraction process was up to three times more efficient than that when the forged steel media was used. The reason is that the galvanic interactions between the forged steel media and the sulfide mineral resulted in the formation of iron hydroxide; the formed iron hydroxide converted free cyanide to ferrocyanide that cannot dissolve gold (i.e. in case of pyrrhotite around 65% of free cyanide was converted to ferrocyanide). Additionally, the galvanic interactions also significantly reduced the dissolved oxygen content and thus cyanide gold leaching was more difficult particularly during the first two hours of leaching because the dissolved oxygen is required to dissolve gold. By contrast, when grinding was performed with the ceramic media, insignificant amount of free cyanide was decomposed (i.e. 2.8% of free cyanide was converted to ferrocyanide while 2.9% of that was converted to thiocyanate). For that reason, cyanide gold leaching was very efficient when the ceramic media was used during the grinding of the ore.

When pyrite or arsenopyrite were added, the results showed that the degree of oxidation of the grinding media also depends on the type of the ore. Specifically, when grinding was performed with the same grinding media, the amount of produced iron hydroxide decreased in the following order: pyrrhotite ore>arsenopyrite ore >pyrite ore. The reason is that pyrite is the least electrochemically active mineral while pyrrhotite is the most electrochemically active mineral. In addition, when the grinding was conducted in the presence of the forged media, the decomposition of the free cyanide decreased in the following order: pyrrhotite ore>arsenopyrite ore >pyrite ore.

Furthermore, a theoretical model was developed to describe the correlation between the galvanic currents and the grinding media oxidation, as measured by using EDTA extraction technique and dissolved sulfur analysis. The electrochemical data were correlated with the amount of grinding media oxidation during grinding with different grinding media. A linear relationship between the galvanic current and the grinding media oxidation was obtained. It was found that the higher the galvanic current, the higher the amount of hydroxide iron was produced by grinding media oxidation.

Finally, it is noted that, depending on the processing step directly after grinding (e.g. flotation versus leaching), even for the same ore, one may prefer to choose different media. Thus, where forged steel media marginally enhanced flotation recovery of gold-bearing pyrite, the same grinding media performed the worst when grinding is a direct precursor before leaching.

For leaching, grinding with high (30%) chromium media appears to be beneficial. Grinding with ceramic media is not suitable for ore grinding, but is very often used in concentrate grinding in stirred mills. The sulfide concentration in the flotation concentrates is much more than that in sulfide ores, and thus the effects of grinding media are probably much more dominant during grinding of the flotation concentrates than during sulfide ore grinding.

It is therefore clear that the selection of grinding media requires a scientific approach with a clear understanding of what is to be achieved in the downstream processing.

## 8.2 Recommendations

Future research should address the following areas:

- The literature review revealed that the gold-bearing sulfide ore in orogenic or sedimentary deposits will behave differently to sulfide minerals from volcanic massive sulfide, or from iron-oxide-copper-gold or gold bearing copper porphyry deposits. Greet et al. (2014) found that as the sulfide content of the ore increased, the pulp potential of the mill discharge became more reducing, the oxygen content of the pulp decreased, the oxygen demand increased and the EDTA extractable iron (corrosion rate) increased. This can be concluded that with increasing the sulfide content, the ore becomes more reactive. In the future, it is recommended to study the influence of grinding media type on flotation behaviour of gold bearing sulfide ore from different ore types such volcanic massive sulfide, iron-oxide-copper-gold or copper porphyry deposits.
- The grinding chemistry can influence mineral floatability. However, most of the research was focused on primary grinding and rougher flotation rather than the regrinding and cleaner flotation. Therefore, it is recommended to investigate the effect of regrinding chemistry on mineral floatability.
- It is important to mention that in this project we didn't look at the effect of salts from saline water and hyper-saline water on grinding chemistry. Therefore, it is recommended to investigate the effect of saline water and hyper-saline water on grinding chemistry and subsequently flotation and leaching.
- The relationships between the amount of hydroxide iron and the galvanic currents between grinding media and sulfide minerals during grinding were established only in the single mineral system (see Chapter 7). It is recommended to conduct similar research for a mixture of sulfide minerals and ore systems to predict and optimize the cyanide leaching process on the basis of electrochemical measurements during grinding.
- The theoretical model shows that the galvanic current is determined by oxidation-reduction behaviour of interacted materials (grinding media and sulfide minerals), as well as their surface areas. It is recommended to develop the method to remove the precipitated species from the surface of the electrodes during grinding to reduce the effect of precipitated species on polarization behaviour.

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