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An investigation into the effects of pulp chemistry under wet and dry grinding on the flotation response of pyrite

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ABSTRACT

Considering the depletion of high-grade ore deposits, the mining industry is faced with the challenge of processing low grade and more complex ores in order to meet the growing demand for metals and metal products. Therefore, it is of paramount importance to have a fundamental understanding of minerals processing operations in order to improve the recoveries of valuable metals on an industrial scale. It has been acknowledged that the chemical conditions during grinding as well as pulp chemistry have a significant influence on the recovery and selectivity of most sulphide minerals in the flotation process. Floatability of ores is mostly determined by surface properties and the surface properties are essentially controlled by the grinding conditions. The flotation response of sulphide minerals is influenced by factors such as: collector-mineral interactions, mineral surface oxidation, deposition of iron hydroxides/oxides from grinding media and the attachment of inorganic ions on the surfaces of minerals. These factors are on the other hand affected by dissolved oxygen (DO), pH, ionic strength of process water and other pulp chemistry factors. With the highly instrumented Magotteaux Mill®, the effects of these variables may be investigated during grinding.

Several studies have shown that the grinding environment plays a vital role in the selectivity and recovery of sulphide minerals. During wet grinding, water allows the flow of electrons within the pulp (galvanic interactions between minerals themselves and minerals and grinding media). Pyrite is reactive and can easily oxidise when exposed to air or oxygen. Pyrite and most sulphide minerals are more inert than the electrochemically reactive grinding media. Therefore, during grinding, grinding media come into frequent contact with sulphide minerals and a galvanic couple is created between the grinding media and sulphides. Due to galvanic interactions, oxygen reduction occurs on the sulphide mineral surface and iron oxidation takes place on the steel media. The redox reaction results in the formation of iron oxy-hydroxides on the surface of sulphide minerals. The oxy-hydroxide species prevent the adsorption of collector onto the mineral surface, making the mineral less floatable. Dry grinding limits the galvanic interactions present during wet grinding, due to the absence of water. Studies have been conducted and it has been shown that dry grinding yielded significantly less media wear relative to wet grinding owing to the absence of corrosive abrasion in the form of electrochemical oxidation of media during grinding. Reduced grinding media wear may imply that lesser iron hydroxide precipitates build up on the surface of the mineral hence improving collector adsorption and subsequently mineral recovery. Therefore, this suggests that dry grinding could result in improved sulphide mineral recovery as compared to wet grinding. It is necessary to consider the fundamental aspects of both grinding and flotation in order to

improve concentrator performance as well as sulphide mineral recovery in the presence of non-sulphide minerals.

Previous studies have investigated the influence of the grinding pulp chemistry factors on the flotation response of pyrite and other pure sulphide minerals. The possible influence that the presence of a non-sulphide gangue mineral may have during grinding and flotation has been ignored. The non-sulphide gangue cleans the surface of the sulphide minerals. Studies have shown that presence of quartz influences the formation of layers of hydrophilic species on the surface of sulphide minerals. The metal hydroxides will preferably deposit on the surface of non-sulphide mineral such as quartz rather than sulphide minerals. These studies also did not investigate the combined effects of pulp chemistry factors under dry and wet grinding. It should be noted that it is not possible to control pulp chemistry during dry grinding, thus these variables are controlled in the flotation cell in order to understand their effect on mineral surface after dry milling on pyrite flotation recovery relative to how they change the minerals surface properties during grinding. Change in chemical, surface properties of sulphide minerals can take place during milling and froth flotation. Therefore, this study aims to investigate the effects of DO, pH and grinding media type (forged steel and ceramic media) during milling and flotation process on the flotation response of pyrite (sulphide mineral) in the presence of quartz (non-sulphide gangue material).

Wet milling was conducted in a Magotteaux Mill® while a Sala Batch grinding mill was used to carry out dry grinding. DO concentration and pH were controlled and measured in situ during wet grinding and were manipulated inside the flotation cell after dry grinding. The effects of the DO and pH, with changing grinding media type, on water and solids recovery, pyrite recovery and grade as well as flotation kinetic constants were studied. The EDTA extraction technique was employed to quantify the percentage of extractable oxidized iron leached from the mill product.

The findings of this study have shown that under both wet grinding and dry grinding, an increase in pH from 9 to 11 resulted in increased water and solids recovery due to an increase the total concentration of OH^- ions in the system which led to increased froth stability owing to the reduction in pulp bubble size, as well as reduced bubble coalescence. This shows that the control of pulp chemistry during milling and flotation affected flotation process in the same way. The study has further shown that the highest recovery of pyrite, 100%, was achieved with inert grinding media (ceramic) under dry grinding. This might be due to cleaner pyrite surfaces created during dry grinding, since the prevention of media corrosion may lead to improved recoveries. During wet grinding, iron hydroxide is generated and reduces the flotation response of pyrite. Dry grinding generally produces much faster pyrite flotation kinetics than wet grinding because of the generation

of particles with high surface energy and that leads to highly activated particles. It was therefore concluded that the grinding environment indeed has an effect on the flotation response of pyrite in the presence of gangue. This study has shown that careful manipulation of pulp chemistry, selection of grinding media and grinding environment may be used to manage pyrite recoveries within flotation.

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1SPW	Standard synthetic plant water
BMS	Base Metal Sulphides
C1	First Concentrate
C2	Second Concentrate
C3	Third Concentrate
C4	Fourth Concentrate
Ca^{2+}	Calcium ion
CMR	Centre for Minerals Research
CO_3^{2-}	Carbonate ion
Cu^{+}	Cuprous ion
Cu^{2+}	Cupric ion
°C	Degrees Celsius
DO	Dissolved oxygen
EDTA	EthyleneDiamineTetra-acetic Acid
Eh	Reduction/Oxidation Potential
g	Grams
g/t	Grams per tonne
kg	Kilograms
L	Litres
L/min	Litres per minute
MIBC	Methyl isobutyl carbinol
mins	Minutes
ml	Millilitres
µm	Microns
mm	Millimetres
mV	Millivolts
Na^{+}	Sodium ion
NO_3^{-}	Nitrate ion
ORP	Oxidation reduction potential
ppm	Parts per million
PGM	Platinum Group Minerals
PLC	Programmable logic control

rpm	Revolutions per minute
Sec	Seconds
SIBX	Sodium isobutyl xanthate
SO_4^{2-}	Sulphate ion
TDS	Total Dissolved Solids
UCT	University of Cape Town
UG2	Upper Group Chromite No. 2
X_2	Dixanthogen
X^-	Xanthate ions
XPS	X-ray photoelectron spectroscopy

1. CHAPTER ONE: Introduction

1.1. Background

The challenge in mining, metallurgy and materials processing is in the development of economic approaches for extracting metals from their ores (Mustafa et al., 2004). Due to advancements in technology, the demand for metals and metal products has significantly increased. Metals are processed from Platinum Group Minerals (PGMs), Base Metal Sulphides (BMSs), as well as Metal Oxides. Metals find their use in many economically important industries, for instance metallurgy, telecommunications, electronics, automotive industries, construction, jewellery and high technology devices. Considering the depletion of high-grade ore deposits, the mining industry is faced with the challenge of processing low grade and more complex ores in order to meet the growing demand for metals and metal products. Therefore, it is of paramount importance to have a fundamental understanding of minerals processing operations in order to improve recoveries of valuable minerals from low-grade ores.

Mineral processing involves two primary stages; comminution and separation (Craig and Vaughan, 1981). Comminution is essential in order to achieve the desired liberation of the valuable minerals from unwanted gangue material to effect good separation. The most common separation process is flotation. The key to an effective separation in mineral processing is the preparation of particles with sufficient liberation under optimal pulp chemical conditions. According to Fuerstenau (2005), currently close to 400 million tonnes per annum of sulphide ores are processed by flotation worldwide. The process of flotation has been explained by a number of different authors (Mustafa, et al., 2004; Kuopanportti, et al., 1997; Leja, 1982; Sutherland and Wark, 1955; King, 1982) as a separation process which utilizes the differences in the surface properties of the minerals to be separated. A targeted mineral attains a hydrophobic surface and is attracted to air bubbles which rise to a froth zone for collection, while unwanted minerals acquire a hydrophilic surface and remain in the pulp phase (Mustafa, et al., 2004).

During grinding several mechanochemical transformations of the particle take place, namely; surface activation, polymorphic transformation, chemical/electrochemical reactions and formation of amorphous phases (Feng and Aldrich, 2000). It has been acknowledged that the chemical conditions during grinding have a significant influence on the recovery and selectivity of most sulphide minerals such as pyrite, chalcopyrite, galena, pyrrhotite and sphalerite (Peng et al., 2003). Gonçalves et al. (2003) stated that floatability of ores is mostly determined by surface properties and the surface properties are essentially controlled by the grinding conditions. The flotation response of sulphide minerals is influenced by factors such as: collector-mineral interactions, mineral surface oxidation (Bozkurt et al., 1998), deposition of iron hydroxides/oxides from grinding media (Adam et al., 1984) and the attachment of inorganic ions on the surfaces of minerals. These factors are affected by dissolved oxygen (DO), pH, ionic strength of process water, Eh and temperature. With the highly instrumented Magotteaux Mill® and flotation cell, the effects of these variables may be investigated during grinding, conditioning and flotation stages. In this thesis, the effect of the conditions of grinding will be explored.

Based on previous studies, it is clear that the recovery of valuable minerals through separation methods such as flotation are significantly influenced by the grinding environment (Rey and Formanek, 1960; Cullinan et al., 1999; Pease et al., 2006b; Grano, 2009). Wet grinding is favoured over dry grinding due to higher energy efficiency in wet grinding as well as other downstream processing requirements (Feng and Aldrich, 2000). During wet grinding, the major reaction products result from chemical surface reactions of minerals, while oxidation of sulphides is a major factor in dry grinding.

Pyrite is reactive and can easily oxidise when exposed to air or oxygen. Most sulphide minerals are more inert than the electrochemically reactive grinding media. Therefore, during grinding, grinding media come into frequent contact with sulphide minerals and a galvanic couple is created between the grinding media and sulphides. Due to galvanic interactions, oxygen reduction occurs on the sulphide mineral surface and iron oxidation takes place on the steel media (Pease, et al., 2006). The redox reaction results in the formation of iron oxy-hydroxides on the surface of sulphide minerals. According to Johnson (2002) these iron oxy-hydroxides precipitate on mineral surfaces thereby affecting their flotation response. The oxy-hydroxide species prevent the adsorption of collectors onto the mineral surface, making the mineral less floatable (Rabieh, et al., 2017). Therefore, it is necessary to have a good understanding of fundamental aspects of both grinding and flotation in order to improve concentrator performance as well as sulphide mineral recovery in the presence of non-sulphide minerals.

Most studies have attempted to understand the individual effects of DO, pH and grinding media on the flotation response of sulphide minerals ground under a wet environment, however applying the findings from pure minerals to both real sulphide ores and industrial applications remains a challenge. The influence that a non-sulphide gangue mineral may have on these variables needs to be considered. Again, relatively little is understood regarding how grinding pulp chemistry factors influence flotation after dry grinding, when controlled inside a float cell. Therefore, in this study the effects of the grinding pulp chemistry factors on the flotation response of pyrite in the presence of quartz are investigated after dry grinding (inside float cell) and during wet grinding.

1.2. Problem Statement definition

Several studies of the individual effects of DO, pH and grinding media type on flotation response of selected pure sulphide minerals have been carried out. The influence that the presence of a non-sulphide gangue mineral may have on these effects needs to be determined under dry and wet grinding. There is still a challenge in the application of findings from pure mineral studies to both real sulphide ores and industrial applications. It is therefore of vital importance to have a good understanding of the fundamental aspects of the grinding environment and flotation system in order to improve concentrator performance as well as efficiency of sulphide mineral separation in the presence of non-sulphide minerals. Therefore, in this study, the effects of DO, pH and grinding media type during the grinding process on the flotation response of pyrite in the presence of gangue material (quartz) are investigated. The results can be used to get a better understanding of how a real ore may respond when ground and floated under the same milling and flotation conditions, as synthetic ore is prepared to mimic real ore which has 5 % sulphide mineral content

1.3. Scope of the project

The pulp chemistry in the mill during wet grinding was monitored using a highly-instrumented mill manufactured by Magotteaux. Dry grinding was conducted in a Sala Batch grinding mill manufactured by Polaris Mining Equipment (PTY) LTD. The flotation performance of the ground ore was assessed using the standard UCT batch flotation procedure in a bottom-driven Magotteaux Mill ® flotation cell. The tests were carried out at varying levels of DO and pH, while the comparative grinding media used were forged steel and ceramic. Froth flotation in this case was used as the diagnostic instrument for changes in grinding environment and pulp chemistry, therefore the physical and operational parameters of froth flotation were kept constant and not investigated in this study.

1.4. Aim and Objectives

The aim of this study is to assess whether it is possible to manage pyrite recovery by controlling the chemical conditions under which it is ground and floated. To achieve this, the following objectives were formulated:

- To investigate the influence of different chemical conditions on the flotation response of pyrite; in the presence of non-sulphide gangue minerals under wet and dry grinding, with emphasis on the effects of changes in DO concentration and pH.

- To assess how different media types (forged steel and ceramic) affect the floatability of pyrite in the presence of non-sulphide gangue minerals under wet and dry grinding.

2. CHAPTER TWO: Literature review

The main objective of the study is to investigate the effects of pulp chemistry under wet and dry grinding. This section of the report presents a review of literature related to the effects of different chemical grinding conditions on the froth flotation response of pyrite under dry and wet grinding. Articles related to the effects of DO and pH as well as the effects of different grinding media (forged steel and ceramic balls) are reviewed.

2.1. Wet vs dry grinding

Communition is utilized to accomplish the liberation of valuable minerals trapped inside gangue material of an ore. In order to produce adequately liberated valuable minerals, the ore should be ground finely enough to liberate the minerals. However, it is worth noting that extra fine grinding may lead to the production of very fine particles and separation of valuable minerals from their gangue minerals may therefore be made difficult or even impossible. Also, operating costs may be increased.Therefore, it is necessary to compromise between high grade concentrates, operating costs and losses of fine minerals to tailings (Wills, 1988).

Several studies have shown that the grinding environment plays a vital role in the selectivity and recovery of sulphide minerals. According to Wei and Sandenbergh (2007), grinding of sulphide minerals in an aqueous environment can cause dissolution of the media onto the mineral surface, as well as give rise to complex galvanic interactions within the pulp between the minerals (in a mixed-minerals system) and the grinding media and mineral surface. The galvanic interactions are influenced by water due to its conductivity. Dry grinding limits these galvanic interactions due to the absence of water. The dry grinding of hematite-magnetic ore yielded significantly less media wear relative to wet grinding due to the absence of electrochemical oxidation of the grinding media and consequent corrosive abrasion (Gunderwar et al., 1990). Reduced grinding media wear may imply that less iron hydroxide precipitates build up onto the surface of the mineral hence improving collector adsorption and subsequently the mineral recovery. Therefore, this suggests that dry grinding could result in improved sulphide mineral recovery as compared to wet grinding. However, Bruckard et al. (2011) found that excessive oxidation of sulphide minerals during dry grinding can lead to loss of recovery. The dry grinding of Merensky ore consisting of 1% sulphides produced higher solids recovery but lower sulphide grade when compared to wet grinding (Feng and Aldrich, 2000).

Seke (2005) also investigated the effects of dry and wet grinding on the pulp chemistry and flotation response of the Rosh Pinah ore. It was reported that the grinding environment can affect pulp potential and the targeted mineral surface properties. The observations made in that study are summarized below:

- Dry grinding produced more positive pulp potentials as compared to wet grinding
- Dry grinding resulted in better recoveries of sphalerite compared with wet grinding. However, the opposite was true for galena. In summary, Seke (2005) reported that the flotation selectivity between sphalerite and galena improved when the ore was milled in a wet environment.

A similar behaviour was observed when the effects of dry and wet grinding were investigated by Palm et al. (2010) on a base metal sulphide ore containing 52% sulphides. For a Platreef ore containing 2% sulphides, dry grinding resulted in lower PGM grade and recovery as compared to wet milling. However, dry grinding produced more positive pulp potentials.

The discrepancies in the findings and observations could possibly be due to the ore types used by different researchers.

2.1.1. Magotteaux Mill

In the past, laboratory studies have not used plant-operating conditions during testing as this was difficult to achieve. The Magotteaux mill® has since been developed to allow researchers the ability to generate a product on laboratory scale that has similar physical properties (particle size distribution) and pulp chemical properties (Eh, pH, DO and EDTA extractable iron) as a sample taken from the plant (Greet, 2008). This is a highly instrumented mill, allowing for the measurement of pulp chemical parameters; pH, Eh, dissolved oxygen (DO) and temperature, in situ during grinding. An appropriate sample is ground to achieve the particle size distribution of the flotation feed and the pulp chemistry is manipulated so that it matches the industrial grinding mill product. A schematic presentation of the Magotteaux mill® is given in Figure 2-1

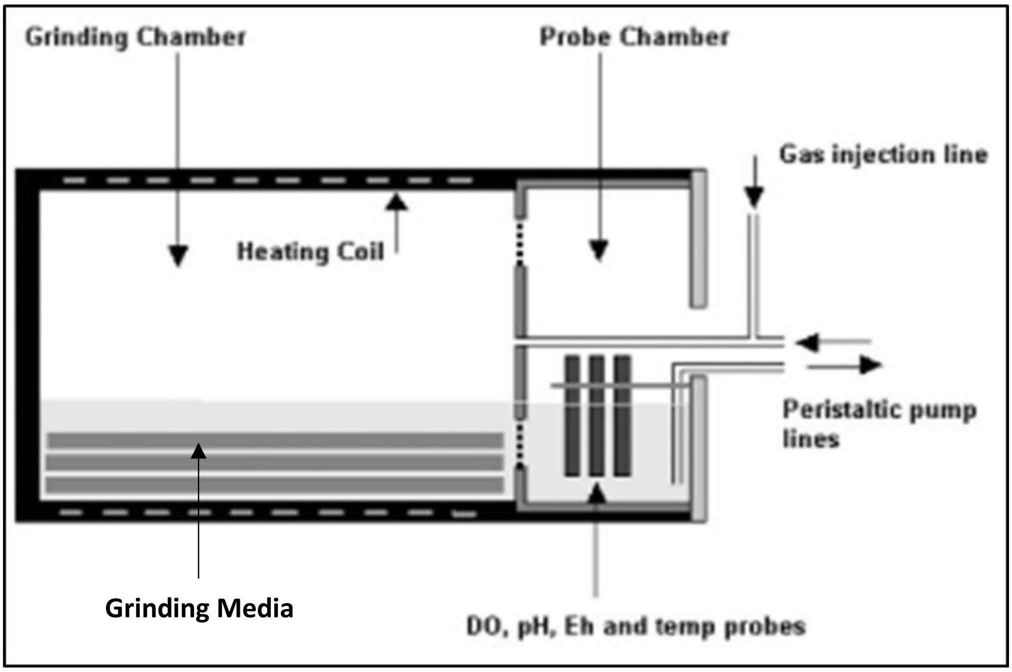


Figure 2-1: Schematic presentation of the Magotteaux Mill (Greet, 2008)

The Magotteaux Mill was designed in order to achieve the following objectives:

- To mimic the plant conditions so that the laboratory conditions are as similar as possible to those found in the industrial plant to allow a good comparison between the product from the laboratory with the sample from the industrial plant.
- To improve the recovery of sulphide minerals by controlling their surface properties, through the use of different types of grinding media and purging gases.
- To quantify the galvanic interactions between different grinding media and sulphide minerals by analyzing their electrochemical behaviour during grinding.

2.2. Electrochemistry of grinding

Huang and Grano (2005) suggested that electrochemistry may provide a method to quantify the degree of galvanic interaction between the grinding media and sulphide minerals. The extent of galvanic interaction resulting from the coupling may be affected by the following factors:

- Rest potential differences between grinding media and sulphide minerals
- Chemical conditions such as DO concentration and the pH in the slurry

A considerable volume of work exists in the literature examining the effect of galvanic interactions in the flotation response of sulphide minerals (Rao and Finch, (1991); Bozkurt et al., (1998); Junior et al., (2006); Rao and Finch, (1988); Urbano et al., (2008)). The following observations were made:

- The flotation response of the binary mixtures of sulphide minerals did not follow the behaviour predicted from the measure of the single minerals. This was due to the galvanic interactions between the two minerals and that can be explained by the mixed potential theory.

- Galvanic interactions are stronger in locked particles than in liberated particles.
- Oxygen is the most important factor for the galvanic interaction to occur.
- Oxidation products on the surface of sulphide minerals (which are generally metal hydroxide or oxy-hydroxide species) may obstruct the collector adsorption.
- The rate of oxidation on the surface of sulphide minerals in binary-mineral systems depends on the difference in the rest potentials of the two minerals.
- Density and viscosity of the slurry affects oxidation rate.

2.2.1. Rest potential

Generally, sulphide minerals are very reactive and are prone to oxidation. Therefore, when a sulphide mineral is immersed in water, it forms an electrode. Bradshaw et al. (2006) noted that sulphide minerals are semiconductors and can oxidize when in contact with oxygen and water through a coupled electrochemical reaction, whereby oxygen is reduced.

When the mineral electrode is connected to a second (reference) electrode via a voltmeter, a potential, termed the rest potential (Rao and Leja, 2004), can be recorded. The rest potential is believed to result from the following reaction at the sulphide mineral-water interface:

$$MS + H_2O \rightarrow M(H_2O)^{2+} + S^{-} + e^{-} \qquad \text{Eq } 2-1$$

From this reaction, the electrons produced are accepted by the second electrode and the rest potential values are quoted for various reference electrodes such as Standard Calomel Electrode (SCE), Standard Hydrogen Electrode (SHE) and silver-silver chloride (Ag/AgCl) (Rao and Leja, 2004). The value of the rest potential of a mineral is a measure of its susceptibility to oxidation. Generally, oxidation reactions occur on the mineral with lower rest potential while reduction reactions occur on the mineral with the highest rest potential. The rest potential values of minerals give insight into the impact of grinding media on mineral surfaces, sulphide minerals on one another, collectors on mineral surfaces and copper ions on mineral surfaces (Ekmekçi and Demirel, 1997, Bozkurt et al. 1998, Buswell et al., 2002; Ekmecki et al., 2005; Bradshaw et al., 2006).

The rest potentials for selected minerals (where SHE is a reference electrode) are given in Table 2-1

Table 2-1: Rest potentials of some sulphide minerals at pH 4 (Majima and Takeda, 1969)

Sulphide Mineral	Molecular formula	Rest Potential (V) vs SHE
Stibnite	Sb_2S_3	0.11
Argentite	Ag_2S	0.12
Galena	PbS	0.28
Bornite	Cu_5FeS_4	0.40
Covellite	CuS	0.42
Sphalerite	(Zn,Fe)S	0.45
Chalcopyrite	$CuFeS_2$	0.56
Marcasite	FeS_2	0.63
Pyrite	FeS_2	0.66

It can be seen from Table 2-1 that pyrite has the highest rest potential relative to the other minerals given in the table. Therefore, when they are in contact with pyrite, the surface of the other mineral may be oxidized (Payant et al., 2012). In simple terms, electrons flow from the surface of a mineral with lower rest potential to that of a higher rest potential, such as the pyrite, where oxygen reduction takes place. Metal hydroxide may be formed which precipitates on the surfaces of sulphide minerals.

In a mixed-mineral system, the galvanic interactions become more complex. When sulphide minerals come into contact with each other, a galvanic cell is formed. Goncalves et al. (2003) stated that when two sulphide minerals presenting large differences in their rest potential are milled or are in contact, the sulphide mineral with the lower rest potential will act as an anode and the other will act as a cathode. The mineral with the higher rest potential draws electrons from the one with the lower rest potential. The mechanism of galvanic interaction occurring between two minerals with different rest potentials is illustrated in Figure 2-2

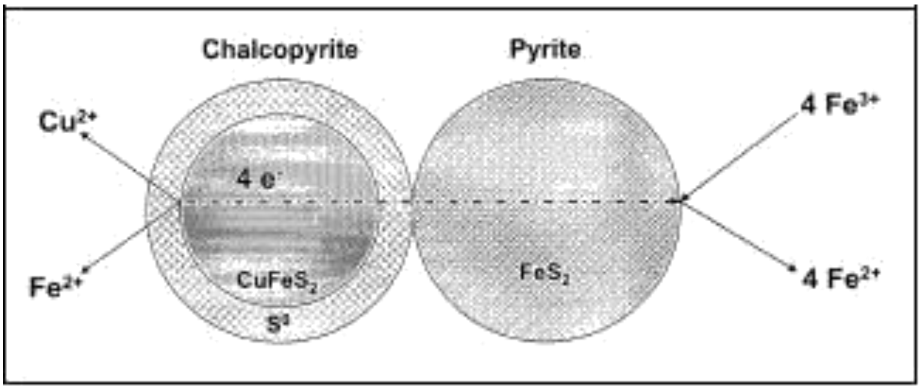


Figure 2-2: The mechanism of galvanic interaction occurring between Chalcopyrite and Pyrite (Darren, 2004)

The anodic sulphide mineral will exhibit improved flotation performance because a mineral surface in an oxidized state favours xanthate oxidation and adsorption. Xiang and Yen (1998) suggest that oxygen reduction takes place on the most inert sulphide mineral and its surface presents very low affinity towards xanthate because of its reduced state. The redox reactions occurring on the surfaces of the sulphide minerals are given by Equations 2 – 2 to 2 – 4:

$$MS \rightarrow M^{2+} + S^0 + 2e^- \qquad \text{Eq } 2-5$$

$$MS + H_2O \rightarrow M(OH)_2 + S^0 + 2H^+ + 2e^- \qquad \text{Eq } 2-6$$

$$X\ S^0 + yH_2O \rightarrow SxOy^{2-} + (2y\text{-}2)e^- \qquad \text{Eq } 2-7$$

2.2.2. Galvanic interaction between Mineral-Grinding Media Systems

Comminution is essential for the liberation of the sulphide minerals from non-sulphide minerals (gangue material). To accomplish effective liberation, steel media may be used. During milling, grinding media come into frequent contact with one another and a galvanic couple is created between the grinding media and sulphide minerals. In general, most sulphide minerals are more inert than the grinding media during grinding (Greet et al., 2004). Therefore, a galvanic couple between the media and sulphide minerals exists. Hu et al. (2009) showed that most sulphide minerals have a higher rest potential, more noble, than grinding media. Therefore, the sulphide mineral acts as a cathode and the media acts as an anode, due to their rest potential differences.

Figure 2-3 illustrates the mechanism of galvanic interaction occurring between the grinding media and a single sulphide mineral.

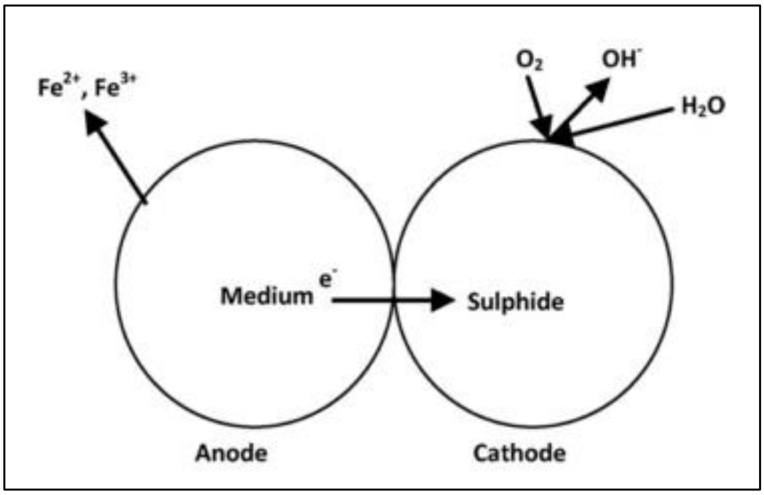


Figure 2-3: Galvanic interaction occurring between a single sulphide mineral and grinding media during grinding (Peng and Grano, 2010)

Due to galvanic interactions, oxygen reduction occurs on the sulphide mineral surface and iron oxidation takes place on the steel media. The redox reactions occurring are represented by Equations 2 – 5 to 2 – 7 (Wei and Sandenbergh, 2007):

$Fe \rightarrow\ Fe^{2+} + 2e^-$ (Anodic reaction) Eq 2 – 2

$\frac{1}{2}O_2 + 2H_2O + 2e^- \rightarrow 4OH^-$ (Cathodic reaction) Eq 2 – 3

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3$ (Precipitation) Eq 2 – 4

The redox reaction results in formation of iron oxy-hydroxides on the surface of sulphide minerals. According to Johnson (2002) these iron oxy-hydroxides precipitate on mineral surfaces thereby affecting their flotation response. Several researchers have reported that the recovery of most sulphide minerals is improved by changing from steel media (more active media) to electrochemically inert media (high chrome > Austenitic > stainless steel or ceramic) (Cullinan et al., 1999; Greet et al., 2004; Huang and Grano, 2005; Greet, 2008 Peng and Grano, 2010). This observation is attributed to the occurrence of a cleaner grinding environment, resulting in lower concentrations of oxidized iron species within the system.

2.2.3. Galvanic interaction between Mixed-Mineral-Grinding media systems

Pozzo et al. (1990) postulated that in a mixed-mineral system, the most cathodic mineral acts as the cathode, the grinding media serves as an anode, any other sulphide mineral acts as either an intermediate cathode or anode conditional on its rest potential as illustrated in Figure 2-4

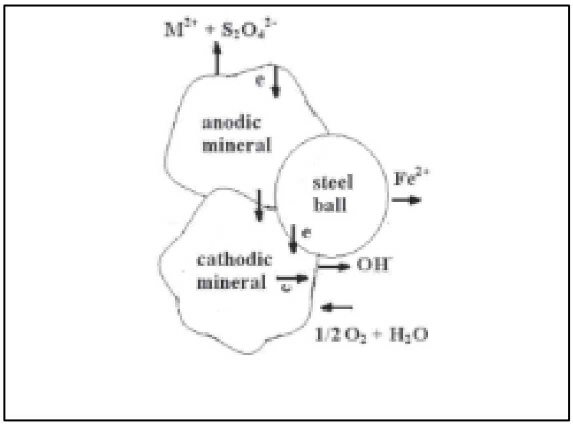


Figure 2-4: Galvanic interactions occurring between minerals and grinding media in a mixed-mineral system (Moslemi, Shamsi and Alimohammady, 2012)

The findings from previous studies have been questioned because of the conditions under which experiments were conducted (Greet et al, 2004). Most of these studies investigated the effect of grinding media on flotation performance by conditioning pure minerals in crucibles made of either steel, stainless steel or ceramic. These methods have been criticized as not being representative of true milling.

Peng et al. (2003) extended the studies on galvanic interactions between sulphide minerals and grinding media (mild steel and 30 wt.% chromium) to binary mixtures of pyrite and chalcopyrite. The study also investigated the effect of three types of purging gases (nitrogen, oxygen and air) on galvanic interactions. The results illustrated that chalcopyrite separation from pyrite was improved by the activation of pyrite. This could be due to the fact that, in the study, pyrite was mixed with chalcopyrite and Yelloji Rao and Natarajan (1989) suggested that galvanic interactions between an inert mineral and an active mineral significantly affect the floatability on the noble metal but has insignificant impact on the floatability of the active mineral; in this case, chalcopyrite is active relative to pyrite (Peng et al. 2003. The reducing grinding conditions generated by the mild steel media favoured the formation of a Cu^+ sulphide phase from Cu^{2+} which resulted in high pyrite activation by Cu^{2+} leached into the pulp from chalcopyrite. Hence, high chrome media produced better chalcopyrite selectivity against pyrite than the mild steel media (Peng, 2003). The flotation response of an active mineral increases after the addition of a comparatively noble mineral due to the fact that the change in surface properties are believed to occur mostly on the noble mineral.

Peng and Grano (2010) indicated that there is a linear relationship between the production of iron oxidation species and flotation recovery for both galena and chalcopyrite. Huang and Grano (2005) reported that the pulp DO and the Cu ion concentration had a marked effect on both the amount of EDTA extractable iron produced and the galvanic current measured; both indicators of galvanic activity

In order to measure the quantity of the metal oxidation products present in the slurry and on the surface of the minerals, ethylene diamine tetra acetic disodium salt (EDTA) extraction can be employed (He et al., 2005). Huang and Grano (2005) found that the EDTA extraction technique can show the relationship between oxidation of grinding media and sulphide minerals during grinding and galvanic density on media. It was also reported that the EDTA extractable iron originated from oxidation of both steel and pyrite. However, it was evident from the calculations performed that most of the iron extracted using EDTA solution originated from grinding media (steel).

The detailed method on how EDTA extractable iron was calculated in this study is shown in Chapter 3

2.2.4. Effect of grinding media type on the flotation response of pyrite

Peng et al. (2012) indicated that the grinding environment has a notable effect on the electrochemical potential at the mineral surface/solution interface because the presence or absence of iron in the mill during grinding has an influence on the reactions taking place. Grinding with an electrochemically reactive grinding media results in galvanic interactions between the sulphide minerals, such as pyrite and the grinding media. During grinding of pyrite with an active grinding media such as forged steel, reduction of oxygen occurs on its surface and hydroxyl ions are produced. The grinding media acts as an anode and iron is oxidized to form ferrous ions, which further oxidize to produce ferric ions. The ferric ions react with hydroxide to form an iron hydroxide precipitate on the surface of pyrite (Moslemi et al., 2012). The electrochemically reactive grinding media reduces the flotation response of pyrite due to the formation of hydrophilic iron hydroxide precipitate on its surface. This precipitate hinders xanthate from adsorbing on the surface of the mineral. Again, floatability of pyrite is lowered due to a decrease in the xanthate oxidation during flotation because grinding media consumes dissolved oxygen in the pulp during grinding. Chen et al. (2013) carried out a study on two pyrite samples with stainless steel and mild steel media, the study showed that stainless steel, being a less electrochemically active grinding media, yielded significantly higher pyrite recoveries than mild steel. The results of XPS analysis showed that grinding with mild steel resulted in an increased amount of oxidation species on the surface of pyrite. Peng et al. (2012) also found similar results using EDTA extraction method.

Cullinan (1999) also stated that a change in grinding media type had an influence on the pulp chemistry of the system and changed the flotation response of the sulphide minerals present. In the study, galena recovery increased significantly as the media type changed from forged steel to high chrome, to ceramic. This was due to the fact that the levels of oxidised iron decreased in the pulp as measured using an EDTA extraction technique.

Peng et al. (2003) studied the effects of chromium media, mild steel and DO during grinding on chalcopyrite flotation and chalcopyrite separation from pyrite. Peng et al. (2003) noted that mild steel reduces the floatability of chalcopyrite. That is, chromium resulted in higher chalcopyrite recovery than mild steel media. Grano (2009) conducted work to determine how ceramic and mild steel grinding media affect flotation recovery of a copper ore containing chalcopyrite (3.6%), pyrite (12.5%) and non-sulphide gangue. A similar observation to that of Peng et al. (2003) was made. The results obtained by both Peng et al. (2003) and Grano (2009) are shown in Figure 2-5 and Figure 2-6, respectively.

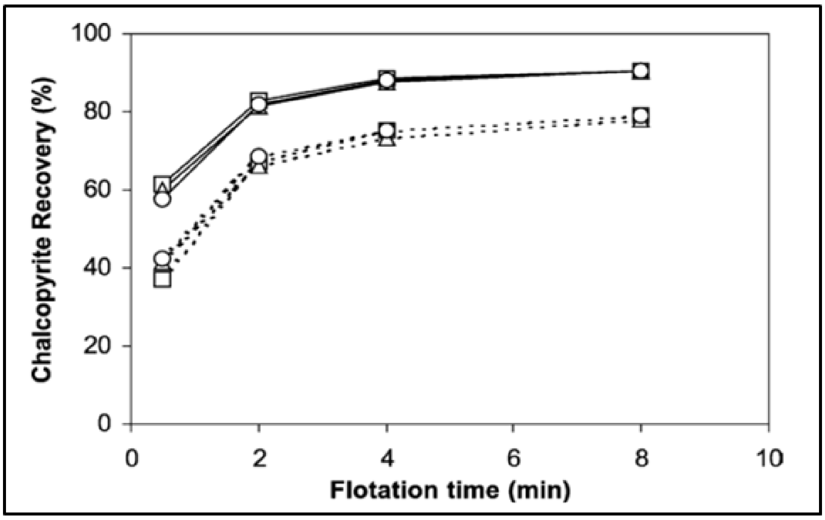


Figure 2-5: The effect of grinding media and purging gas on chalcopyrite recovery as a function flotation time: dashed lines (mild steel media); solid lines (30% chromium media); (Δ) Air purging; (□) Nitrogen purging; (○) Oxygen purging

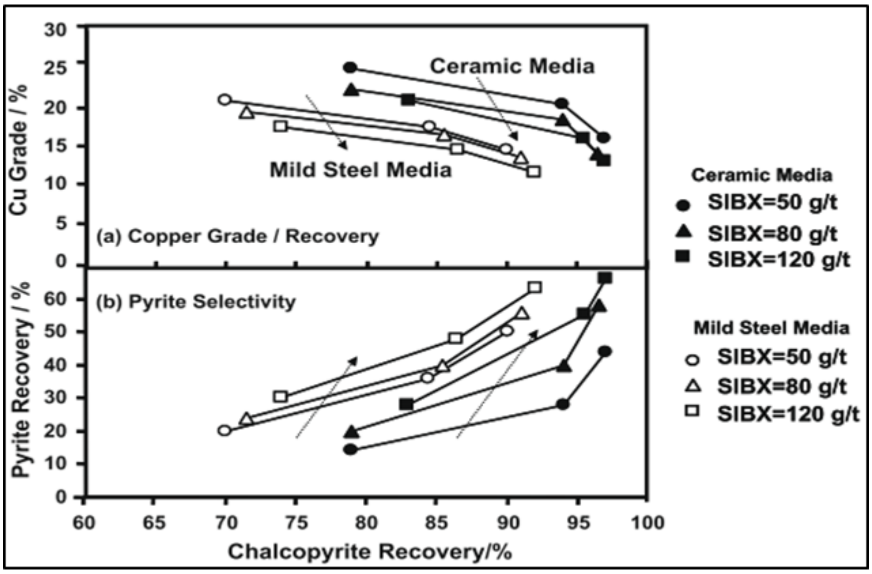


Figure 2-6: Copper grade as a function of copper recovery: (a) *pyrite recovery as a function of copper recovery, (b) for various collector additions and for the two grinding environments*

Gonçalves et al. (2003) studied sulphide copper ore ground with different mill types; rubber lined jar mill, unlined mill and ceramic mill as well as different media types; stainless steel, carbon steel balls and rods and ceramic media. They noted that ceramic media produced higher recoveries of copper sulphides than grinding with carbon steel media, a layer of metal sulphide deficient in the metal is believed to form on the surface of the minerals, enhancing the self-induced floatability of the copper minerals. On the other hand, carbon steel reduced floatability of copper minerals due to the presence of iron oxides and hydroxides precipitated on the surface of the mineral, inhibiting self-induced floatability of minerals. It is worth noting that Peng et al. (2003) stated that mild steel media produces higher pyrite recovery than 30% chromium media. This could be due to the fact that both mild steel and chromium are more active than pyrite. Therefore, ferric hydroxide forming on the surface of pyrite may be reduced to a more soluble iron species (mild steel results in more iron hydroxides than 30% chromium during grinding), consequently, increasing the floatability of pyrite.

2.2.5. Effect of pH on the flotation response of pyrite

At higher pH levels (alkaline solutions) pyrite becomes less floatable (Peng et al., 2012). According to Moslemi et al. (2012), formation of iron hydroxides on the surface of pyrite during grinding increases in alkaline solutions as compared to acidic solutions. This is due to the fact that the intermediate products during pyrite oxidation are more stable in alkaline solutions than in acidic solutions. Therefore, production of iron oxides and hydroxides increase due to higher stability in the alkaline solutions. Furthermore, the formation of hydroxides increases in the alkaline solutions due to the fast reaction between steel and oxygen. At lower pH values, the difference in potential between the minerals and steel is higher than at high pH values, as shown in Figure 2-7. Therefore, corrosion of steel increases and the hydrophobic species are removed from the surface of sulphide minerals in the acidic solutions.

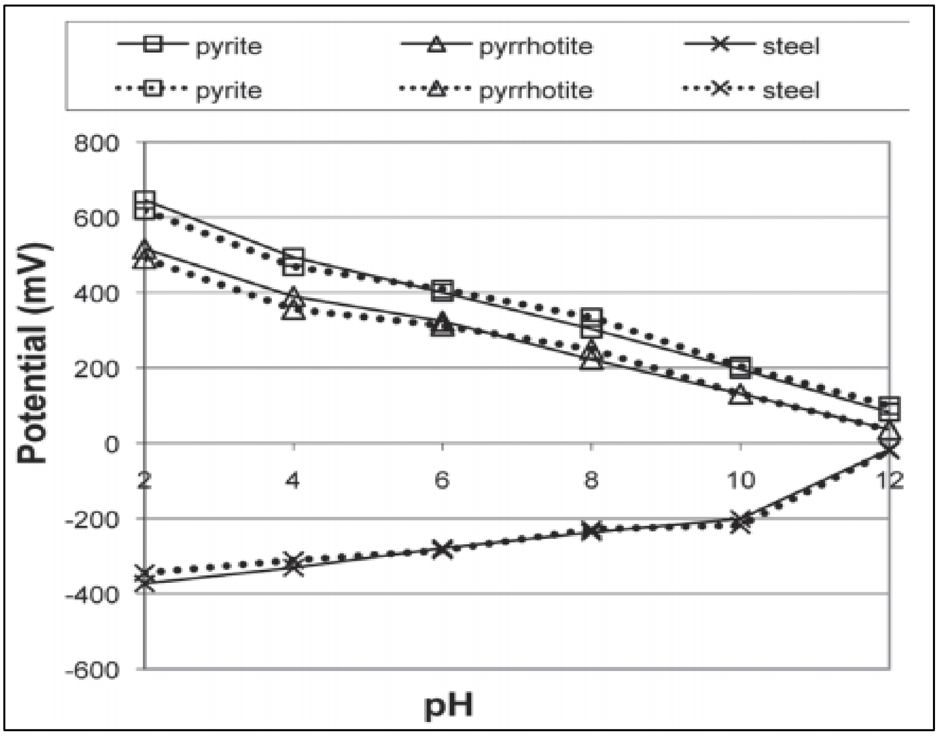


Figure 2-7: pH-potential relationships of pyrite, pyrrhotite and steel with respect to saturated calomel reference electrode (solid line) and gold reference electrode (dotted line) (Moslemi et al., 2012)

High pH results in adequate chalcopyrite recovery and selectivity from a high pyrite feed – because surface oxidation of pyrite assists depression of copper activated pyrite and promotes recovery of chalcopyrite (AIMM, 2010). According to Gardner and Woods, (1979), elemental sulphur may form on the surface of chalcopyrite under acidic conditions, making it more hydrophobic. Ackerman et al. (2000) noted that recovery of chalcopyrite decreased when pH was increased from 5 to 10.5. Corin et al. (2013) showed that at high pH values (from 9 to 11) chalcopyrite recovery is independent of the pH. The study showed that the recovery of sulphide minerals such as pentlandite and pyrrhotite drops at high pH values owing to their surface oxidation. Moreover, recovery of minerals decreased at high pH values owing to hydroxide ions forming in the pulp which may result in increased ferric hydroxide formation.

Apart from the floatabiltity of sulphides, changes in pH also has an impact on the froth stability. An increase in pH results in increased water recoveries (Sheni et al., 2018), indicating more stable froth. This is due to an increase in hydroxyl ions in the pulp, subsequently increasing the ionic strength of water.

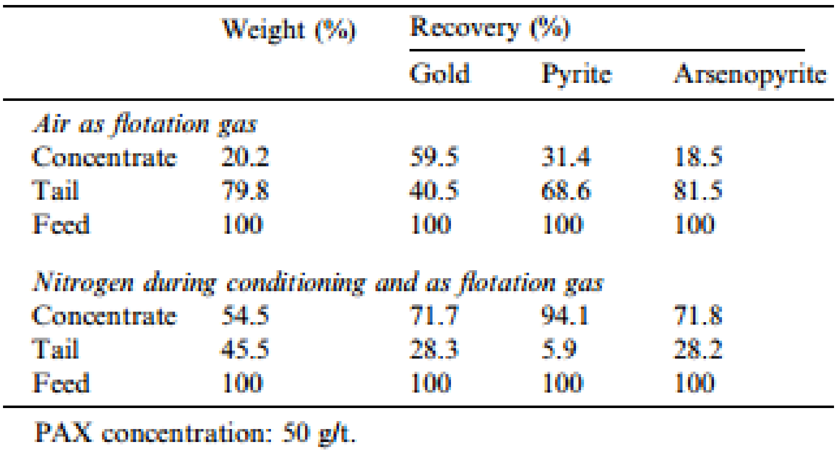
2.2.6. Effect of purging gas on the flotation response of pyrite

The degree of galvanic interactions occurring between two or more electrochemically reactive materials may be affected by a number factors, including the concentration of dissolved oxygen and ions in the pulp. Huang and Grano (2005) investigated the galvanic interactions of grinding media (mild steel) with pyrite and its effect on flotation. During the study, the galvanic interactions between mild steel and pyrite were quantified using a specialized grinding system which linked to the electrochemical analysis at different concentrations of DO during grinding. Huang and Grano (2005) found that DO had a significant influence on the floatability of sulphide minerals due to the fact that reduction of oxygen produced hydroxyl ions which formed metal hydroxide on the surface of the minerals depressing the flotation response of pyrite. Monte et al. (2002) showed that in order to improve the flotation response of minerals, the production of undesired or hydrophilic species may be avoided by using nitrogen gas (non-oxidizing gas) instead of oxygen.

Clark et al. (2000) also showed that DO influences flotation recovery of sulphide minerals such as chalcocite, chalcopyrite and bornite. Moslemi et al. (2012) also indicated that the partial pressure of oxygen in the mill during grinding had an influence on the grinding environment. It was further stated that oxygen purging results in a more oxidizing grinding environment, while the opposite is true for nitrogen purging.

It was found that the concentration of DO has an impact on the adsorption of xanthate on the surface of sulphide minerals. DO concentration also had an effect on the grinding environment. Monte et al. (2002) studied the influence of air and nitrogen, used in the pre-conditioning stage and as flotation gases, on the flotation response of free gold, pyrite and arsenopyrite, with potassium amyl xanthate (PAX) as a collector. The study showed that nitrogen gas resulted in low pulp potential, thus preventing formation of oxidation products. Therefore, the recoveries of free gold, pyrite and arsenopyrite were improved. The results obtained are summarized in Table 2-2.

Table 2-2: Sulphide and free gold recoveries using air and nitrogen in the pre-conditioning stage and as flotation gas (Monte et al., 2002)



	Weight (%)	Recovery (%)		
		Gold	Pyrite	Arsenopyrite
Air as flotation gas				
Concentrate	20.2	59.5	31.4	18.5
Tail	79.8	40.5	68.6	81.5
Feed	100	100	100	100
Nitrogen during conditioning and as flotation gas				
Concentrate	54.5	71.7	94.1	71.8
Tail	45.5	28.3	5.9	28.2
Feed	100	100	100	100

PAX concentration: 50 g/t.

2.3. Froth Flotation

Froth flotation has become the most vital process when recovering sulphide minerals from sulphide ores in the minerals industry. Discovered in the mid-18th century, the process employs the differences in the surface properties of materials in order to separate valuable minerals from undesired gangue (Tolley et al., 1995; Fuerstenau, 1976). Currently close to 400 million tonnes per annum of sulphide minerals are processed by flotation worldwide (Fuerstenau, 2005). There are two distinct zones in flotation, namely, the froth zone and the pulp zone (Goodall, 1992). Mineral recovery takes place in the pulp zone, and the concentrated valuable minerals are separated from the bulk in the froth phase. The valuable mineral is transported to the froth, while the gangue material is left in the pulp. A schematic of a typical flotation cell is shown in Figure 2-8

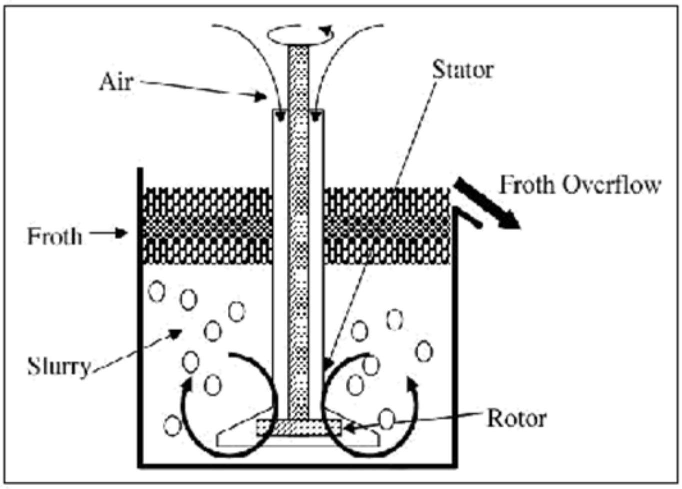


Figure 2-8: A simple schematic of a flotation cell (Kawatra, 2011)

All minerals can be classified into polar or non-polar types, based on their surface properties (Wills, 1988). The surfaces of the polar type of minerals have strong covalent or ionic bonds. The polar surfaces react strongly to water dipoles, therefore, the minerals are hydrophilic in nature. On the other hand, the surfaces of non-polar minerals have molecules which are bonded together by weak van der Waals forces. The surfaces cannot easily attach to water; therefore, the minerals are hydrophobic in nature.

During the froth flotation process, hydrophobic material attaches to air bubbles and moves up to the froth phase to be collected to the concentrate. The hydrophilic material stays in the pulp and reports to the tailings. The valuable minerals can be separated from gangue material by manipulating their surface properties. The froth transportation consists of two motions; horizontal motion and vertical motion (Chao, et al., 2016). During vertical motion, air bubbles flow up with particles from the pulp phase to form the froth phase. The vertical motion is driven by the superficial gas velocity. The horizontal motion is defined by the motion towards the overflow weir and it is driven by gravitational force, froth stability and the resistance of air bubbles to flow.

In order to determine floatability of a solid, it is of paramount importance to understand the concept of wettability. Wettability can be defined in terms of contact angle and it is characterized by the hydrophobicity of a material. The floatability of minerals increases with increasing contact angle; minerals with high contact angle have higher affinity to air bubbles than for water (Wills, 1988).

The froth flotation process is affected by various chemical and physical variables. While Klimpel (1984) divided the major parameters influencing flotation process into three groups as shown in Figure 2-9, this study focuses on the chemistry, specifically DO and pH.

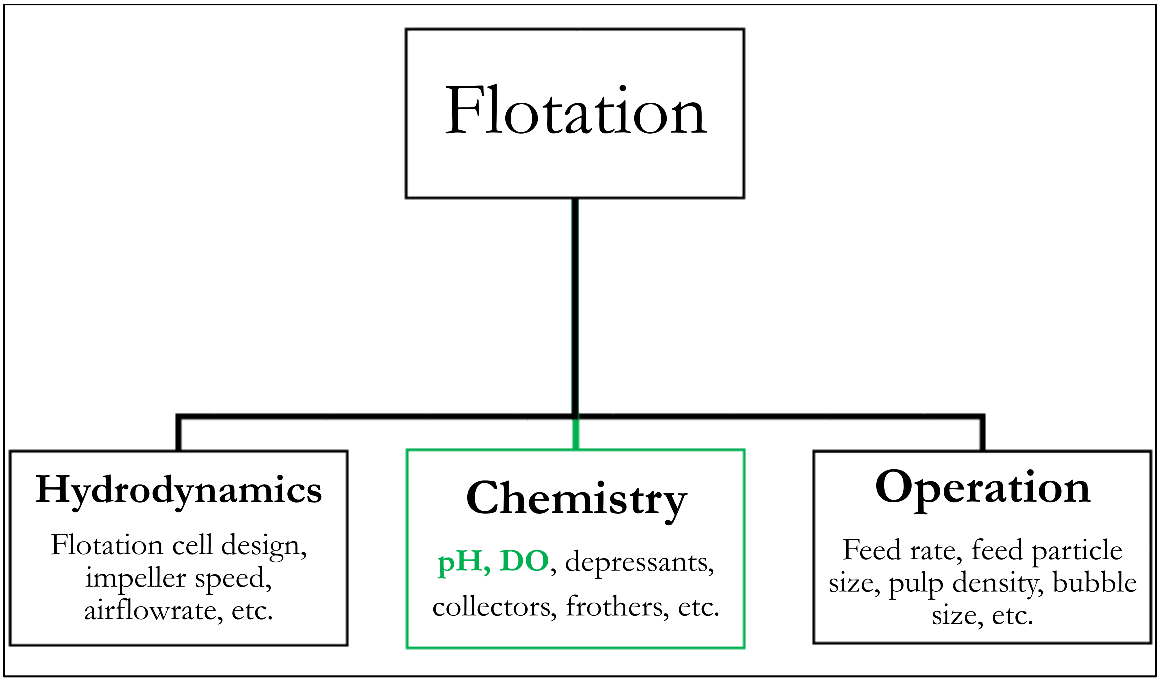


Figure 2-9: Summary of the variables influencing froth flotation (Klimpel, 1984)

Factors such as DO, pH and grinding media type affect surface properties of sulphide minerals, thereby their floatability. The flotation response and selective flotation of sulphide minerals is influenced by their surface properties. The surface properties are influenced by the level of surface oxidation of the minerals (Tayebi-Khorami et al., 2018)

According to Chehreh Chelgani and Hart (2014) the balance between hydrophobic and hydrophilic species on a mineral particle's surface determines the effectiveness of the mineral particle-bubble attachment. Metal hydroxides, collector species, oxy-sulphur, metal deficient sulphides, elemental sulphur and inorganic ions precipitates are responsible for the hydrophobic and hydrophilic nature of sulphide minerals (Greet et al, 2004).

2.4. Flotation reagents

Most minerals are not hydrophobic in nature; therefore, flotation reagents are added to the pulp to modify their surface properties. Flotation reagents have a significant influence on the flotation response of minerals, by changing the minerals surface properties such as, wettability (Dong and Lin, 2012). The reagents used in froth flotation are classified traditionally into collectors, depressants and regulators. These can change the flotation chemical environment by imparting of hydrophobicity and hydrophilicity to mineral surfaces and so the flotation performance of the minerals may be optimized. The aforementioned reagents are added to accomplish specific roles in order to manipulate the pulp chemistry and enhance the differences in mineral surface hydrophobicity and facilitate the froth phase. Frothers are also added in order to maintain reasonable froth stability. Wiese et al. (2006) found that pentlandite, pyrrhotite and chalcopyrite show different responses to various reagent combinations and collector addition points. In this study, the only flotation reagents used were collector and frother.

2.4.1. Collectors

Collectors are defined as hetero-polar chemical species comprising of a polar head group which is hydrophilic, and attaches to a mineral surface, and a non-polar hydrocarbon functional group, hydrophobic in nature, through which attachment to the bubbles can occur. The primary role of collectors is to render the targeted valuable minerals surface hydrophobic so that they can attach to the bubbles which move up to the froth (Bradshaw et al., 2005). Collectors can attach to the mineral surface through either physisorption or chemisorption. During physisorption, the collector is bonded to the mineral surface through physical forces such as weak Van der Waals forces. During chemisorption, the collector reacts with the mineral surface, resulting in a permanent change in mineral's surface chemistry. There are various classes of collectors; xanthates, dithiophosphates and dithiocarbamates being the most common. In this work, xanthate, specifically SIBX was used. The structure of SIBX is shown in Figure 2-10

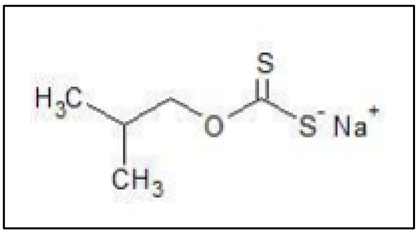


Figure 2-10: Chemical structure of sodium isobutyl xanthate (King, 1982)

2.4.1.1. Xanthates

Xanthates are commonly used collectors in sulphide mineral flotation (Wiese and Harris, 2012) because they are relatively cheap, powerful collectors, but are not as selective as other collectors (Wiese, et al., 2006; Chen, et al., 2013). Xanthate collectors bond onto the mineral surface through chemisorption. The reaction taking place on the surface of the mineral is considered to be an electrochemical reaction. Xanthate is oxidised to dixanthogen and reacts with the sulphide mineral to yield metal xanthate (Mu et al., 2016). Cathode reduction of oxygen takes place in water in order to preserve the charge balance for the oxidation reaction. This can be summarized in equations 2 – 8 to 2 – 11.

$X^- \rightarrow X_{ads} + e^-$ Eq 2 – 8

$2X^- \leftrightarrow X_2 + 2e^-$ Eq 2 – 9

$MS + 2X^- \rightarrow MX_2 + S + 2e^-$ Eq 2 – 10

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ Eq 2 – 11

Where $X^-, X_{ads}, X_2, MS, MX_2$ and S represent xanthate ions, adsorbed xanthate, dixanthogen, sulphide mineral, metal xanthate and elemental sulphur, respectively.

2.4.1.2. Collector adsorption theory

The adsorption of collectors onto the surface of sulphide minerals is electrochemical in nature owing to their semiconducting properties and is affected by the redox potential, dissolved oxygen, and pH (Tolley, et al., 1996; Kuopanportti et al., 2000). Normally, the adsorption of xanthate collector has been found to be a very fast process and usually occurs in the first few minutes after the addition of the collector. The xanthates render the sulphide minerals (including pyrite) surface hydrophobic through oxidation of xanthate to dixanthogen (which is hydrophobic in nature) and their reaction on the surface. The adsorption of xanthate collectors on the surface of pyrite takes place through the following main steps:

- Pyrite surface oxidation.
- Xanthate ions adsorption on the surface of pyrite and formation of ferric xanthates
- Xanthate ions oxidation and dixanthogen formation
- Dixanthagen adsorption on pyrite through ferric xanthates presents on the surface

The appropriate site such as ferric xanthate should be formed on the surface of pyrite for dixanthogen to be efficiently adsorbed (Moslemi and Gharabaghi, 2017).

2.4.1.3. Effect of pyrite surface oxidation products on collector adsorption

Matveeva et al. (2013) indicated that the oxidation products on the surface of pyrite are very important in the adsorption of xanthate. It was found that a severely oxidized pyrite sample resulted in decreased adsorption of xanthate due to iron oxidation species on its surface. In contrast, adsorption of xanthate on the pyrite surface significantly improved in slightly oxidizing or reducing environments. This may be due to an appropriate transfer of electrons between the slightly oxidized pyrite surface and the solution.

2.4.1.4. Effect of pH on collector adsorption

The adsorption of collector on the surface of sulphide minerals affected by the oxidizing and reducing agents in the pulp. Factors such as pH and oxygen content have an impact on the adsorption of collector on the surface of sulphide minerals. It has been reported that the dominant electrochemical reactions at lower pH levels are oxygen reduction and oxidation of xanthate. Therefore, the pyrite surface becomes hydrophobic due to adsorption of dixanthogen (Janetski, et al., 1977). At higher pH levels, the main electrochemical reactions taking place in the flotation pulp include oxygen reduction and oxidation of the pyrite surface. The surface of pyrite will remain hydrophilic because at higher pH levels the rate at which xanthate is oxidized decreases.

Jiang et al. (1998) reported that at low pH, the adsorption of xanthate is due to chemisorption of xanthate ions, dixanthogen and ferric xanthate compounds. On the other hand, at high pH levels, the adsorption of xanthate is attributed to the physical adsorption of dixanthogen, formed in equation 2 – 9 and xanthate ions.

2.4.1.5. Effect of oxygen content on collector adsorption

The effect of concentration of dissolved oxygen on xanthate adsorption has extensively been studied. Kuopanportti et al. (1997) found that the pulp potential is the driving force for adsorption of collector. The pulp potential may be manipulated by changing the concentration of dissolved oxygen, and this ultimately affects floatability of the sulphide minerals. This is because increased oxygen content in the pulp results in increased oxidation of xanthate to dixanthogen (Moslemi and Gharabaghi, 2017). It has also been found that adsorption of xanthate on the surface of pyrite takes place simultaneously with ferric hydroxide reduction to ferrous ions. This is schematically shown in Figure 2-11

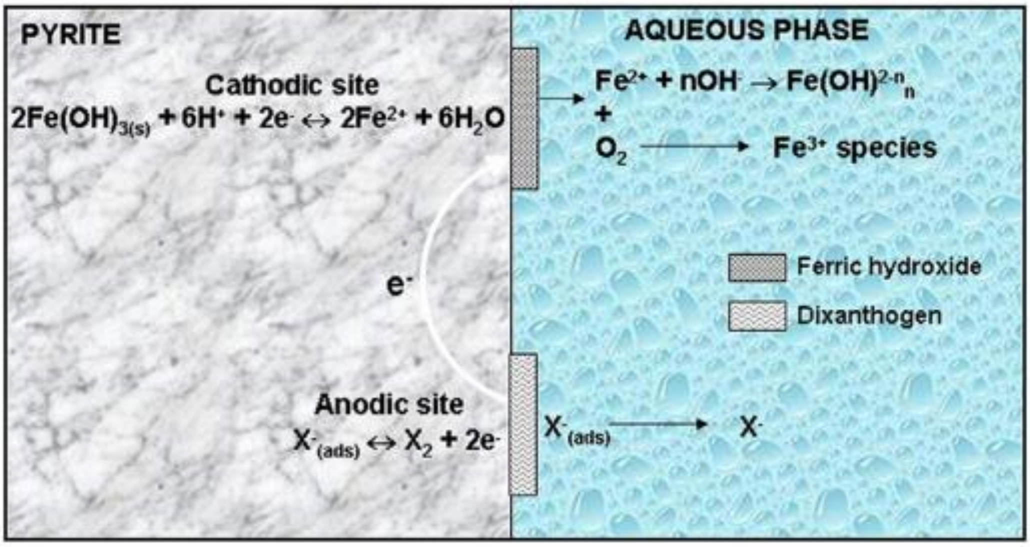


Figure 2-11: Schematic illustration of formation of ferric hydroxide and dixanthogen (Moslemi and Gharabaghi, 2017)

Monte et al., (2002) has shown that the flotation response of pyrite can be improved by using nitrogen gas during flotation instead of oxygen. The study has shown that when nitrogen is used as flotation gas, the pulp potential is lower and that makes it difficult for hydrophilic compounds to be formed. Therefore, oxidation rate of xanthate to dixanthogen increases. Furthermore, lack of oxygen in the pulp phase results in the reduction of compounds on the surface of pyrite, hence adsorption of xanthate on the surface of pyrite is enabled.

2.4.2. Frothers

The stability of the froth is enhanced by adding surfactants called frothers. Their main role in the flotation process is to provide a large air-water interface of sufficient stability to ensure that the air bubbles will stay intact for long enough to allow attachment of valuable minerals and flow upwards to the froth phase such that the valuable minerals will not fall back into the flotation pulp before they can be removed from the flotation cell as concentrate. Frothers decrease the surface tension (through bubble-size reduction) because they are preferentially adsorbed at the water-gas interface (Drzymala, 2007). Frothers decrease bubble coalescence because upon their addition, they result in the formation of a thin film of water around air bubbles which prevents rapid leaking of water from the inter-bubble space. The frothers also speed up the flotation process (Klimpel and Isherwood, 1991; Klimpel, 1984) by diminishing the time needed by a hydrophobic particle to bond itself to a bubble and to eliminate the water film between bubble and particle.

2.5. Synthetic ore

The present study involved the use of synthetic ore consisting of pyrite, quartz and talc. Synthetic ore allows for the isolation of distinct sulphide mineral behaviour and the use of synthetic ore allows the influence of the variables investigated on the flotation response of pyrite to be applicable to a real ore.

2.5.1. Pyrite

Pyrite (FeS_2) is the most common sulphide mineral in the earth's crust and it is commonly associated with other sulphide minerals, gold and coal (Moslemi and Gharabaghi, 2017; Tu et al., 2017). Pyrite is brass-yellow in colour. It is very hard and it cannot be scratched with a nail. This sulphide mineral is reactive and can be easily oxidized. It tarnishes to a dull grey-green colour when it has been milled down to finer particles. Apart from that, pyrite can lead to reduced grade if it is present in valuable mineral concentrates and an increase in iron and sulphur contamination can result in high smelting costs. (Tao et al., 1994) stated that burning pyrite-containing coal can lead to the emission of sulphur oxides into the atmosphere and subsequently result in acid rain. Therefore, it is important to separate pyrite from valuable minerals at early mineral processing stages. Pyrite is normally rejected through flotation processes with xanthate used as a collector (Jiang et al., 1998).

When pyrite is exposed to O_2 and moisture, its oxidation is driven by Equations 1 (Carlito, et al., 2017) and 2 (Fairthone et al., 1997). Equation 2 – 12 represents complete oxidation of pyrite. However, experiments have shown that pyrite does not oxidize completely, instead, elemental sulphur, ferrous iron and sulphate ions are also produced. Ferrous ions further react to form ferric hydroxide precipitates. This occurs according to reactions 2 – 12 to 2 – 15 (Tayebi-Khorami et al., 2018):

$FeS_2 + O_2 + H_2O \rightarrow Fe^{2+} (aq) + 2H^+ (aq) + 2SO_4^{2-} (aq)$ Eq 2 – 12

$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O$ Eq 2 – 13

$FeS_2 + 2.9\ O_2 + 0.6\ H_2O \rightarrow Fe^{2+} (aq) + 1.2\ H^+ (aq) + 1.6\ SO_4^{2-} (aq) + 0.4\ S^0$ Eq 2 – 14

$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+$ Eq 2 – 15

The regions of thermodynamic stability of different species of iron and sulphur are shown in Figure 2-12 with respect to pH and Eh.

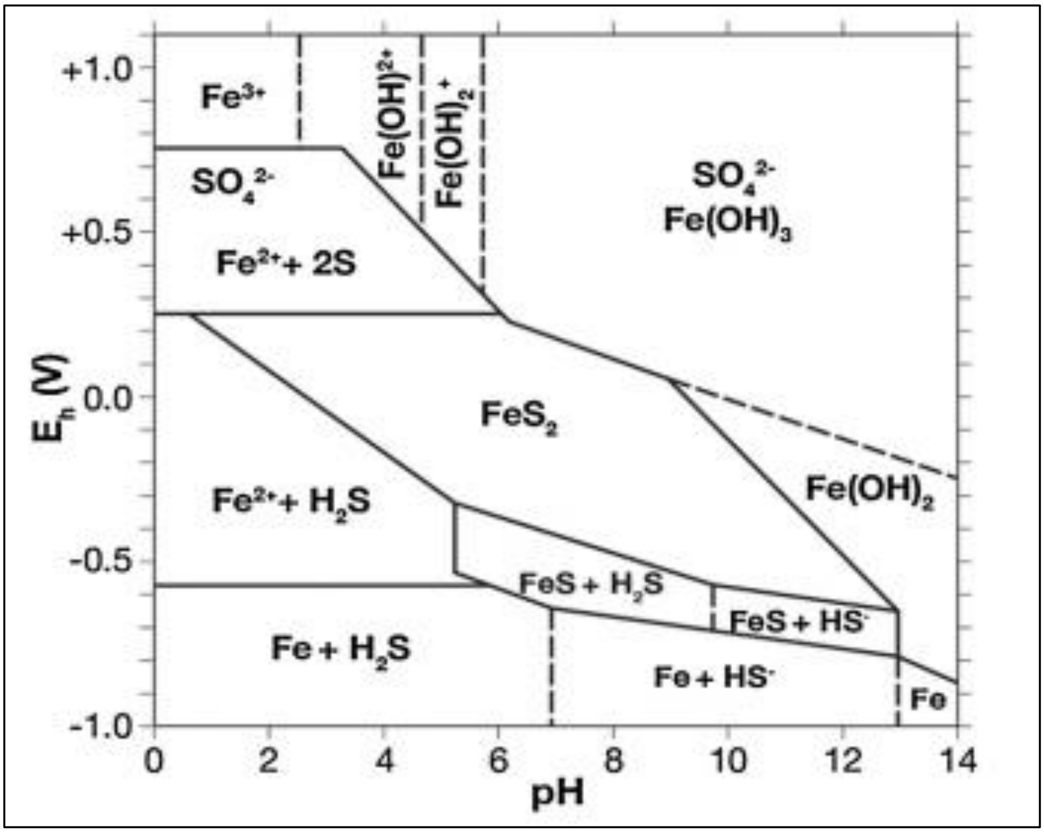


Figure 2-12: Eh-pH diagram for FeS_2-H_2O system at 298K and 10^{-5} dissolved species (Kocabag, et al., 1990)

According to Yong-Jun et al. (2005), most of the sulphide minerals are natural semiconductors, their surface oxidation has often been described as an electrochemical oxidation. Tu et al. (2017)

reported that pyrite oxidation results in the formation of $Fe(OH)_3$, Fe_2O_3, FeO and S_8. These species accumulate on the surface of pyrite.

2.5.1.1. Effect of oxidation on pyrite floatability

Several investigations have been conducted in order to evaluate the species formed during pyrite oxidation. Pyrite is considered to be naturally floatable, however, it is only naturally floatable under certain condition. It has been reported that slight changes in the surface chemistry of pyrite can lead to substantial impact on its floatability. Tao et al. (1994) mentioned that iron polysulfide ($FeS_n, n > 2$) and metal deficient sulphides ($Fe_{1-x}S_2, x < 1$) are the sulphur oxidation species that are produced during the initial oxidation of pyrite at electrochemical potentials slightly higher than the stable potential or potential at which pyrite is not oxidized or reduced. The formation of these species increases the flotation response of pyrite.

2.5.1.2. Effect of oxidation on pyrite depression

Certain species such as $SO_3^{2-}, S_2O_3^{2-}, SO_4^{2-}$ and iron hydroxides produced during oxidation of pyrite may render it less floatable or non-floatable. The depression of pyrite by sulphur-oxy species is very complex and studies have been conducted to investigate it. Yamamoto (1980) and Misra et al. (1985) showed that sulphoxyl species lead to decomposition of xanthate. Furthermore, sulphide species can react with the hydrophobic species such as elemental sulphur producing thiosulphate which may further oxidize to form sulphate, resulting in a reduction in surface hydrophobicity of pyrite (Li et al., 1995; Khmeleva et al., 2005; Khmeleva et al., 2006; Dávila-Pulido et al., 2011). It has been reported that a decrease in flotation response of pyrite may also be due to the formation of hydrophilic compounds such as iron hydroxide precipitates at high potentials on the mineral surface (Bruckard et al., 2011). Güler et al. (2013) also indicated that at highly oxidizing potentials, ferrous ions formed are oxidized to the ferric oxy-hydroxide species. The ferric oxy-hydroxide species lead to depression of pyrite because they are hydrophilic in nature. Furthermore, high potentials result in less floatable pyrite due to oxidation of elemental sulphur into hydrophilic species such as sulphates. He et al. (2005) also showed that the percentage of oxidation species was higher than sulphur species at positive (highly oxidizing) potentials while the opposite was true for the negative potentials.

2.5.2. Quartz

Quartz (SiO_2) is one of the most common non-floatable gangue materials. Though, quartz is a gangue mineral, it has a number of uses; foundry sand, abrasives and it can be used as a filter media in the production of glass, silicon carbide and silicon metal. High purity quartz concentrates are required in the production of electronic and solar grade silicon. Flotation is a good method to be applied in the production of high purity quartz concentrates due to the fact that most contaminants can be floated with the appropriate collectors leaving the purified quartz behind in the sink fraction due to its hydrophilic nature (Larsen and Kleiv, 2015; Kowalczuk, 2015). Amine concentration and pH of a solution significantly influence the value of the contact angle of quartz (Laskowski and Kitchener, 1969). Larsen and Kleiv, (2015) found that the low molecular weight frothers such as DOW 200 and MIBC failed to float quartz. Jin et al. (2016) indicated that the quartz surface can be activated by metal ions produced during grinding and flotation. One of the most common ions is Fe^{3+} which can be released from minerals or grinding media. Furthermore, Fuerstenau et al. (1963) found that under an acidic environment, Fe^{3+} can activate quartz. This results in an increased adsorption of collector on quartz surfaces, subsequently increasing the flotation response of quartz.

2.5.3. Talc

Talc ($Mg_3Si_{10}O_{10}(OH)_2$) is a common naturally floatable gangue mineral (Parolis et al., 2008). It is a layered silicate mineral comprising of octahedral magnesium hydroxide structures sandwiched between sheets of siliconoxygen tetrahedral, as shown in Figure 2-13. The sheets are bonded together by weak Van der Waals forces. Talc is of secondary origin; it forms through alteration of magnesium silicate such as chrysolite, enstatite, pyroxene, amphibole, etc. (Hurlbut, 1941).

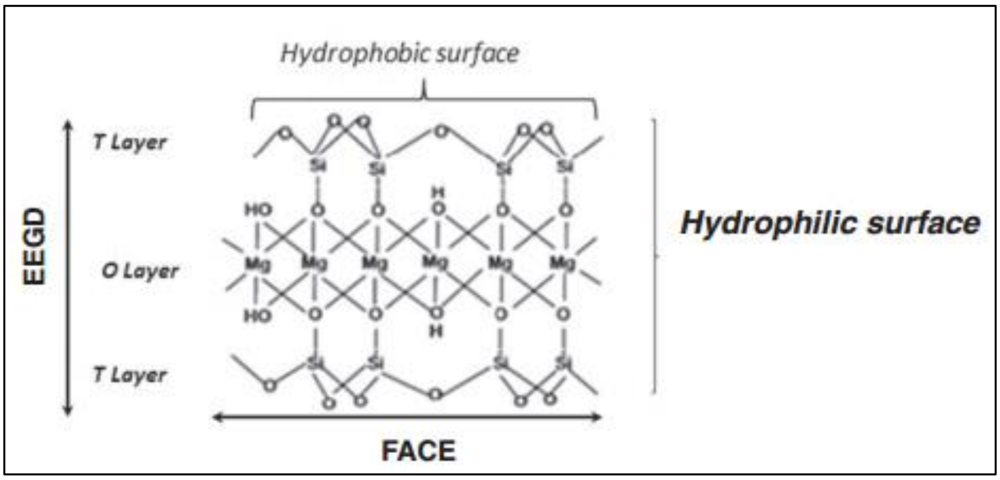


Figure 2-13: Schematic of the structure of talc (Farrokhpay et al., 2018)

Talc results in a stable froth phase due to its hydrophobicity which makes it a naturally floatable gangue mineral (Parolis et al., 2008; Farrokhpay et al., 2018). Talc is present in relatively small amounts in the Bushveld Igneous Complex, however it known to have a disproportionate effect on flotation performance by enhancing froth stability and increasing entrainment of other gangue material (Martinovic et al., 2005).

2.6. Gaps in literature

It is widely known that pure and perfect minerals do not exist in nature. Minerals are found mixed with undesired material (gangue material). Therefore, in this study, the effects of DO, pH and grinding media type were investigated focusing on pyrite, in the presence of quartz.

Several studies have been conducted in order to investigate and understand the influence of the aforementioned factors on the flotation response of pyrite. However, the studies do not investigate the effects of these factors combined together under dry and wet grinding. It should be noted that it is impossible to control DO concentration and pH during dry grinding, therefore these variables are controlled in the flotation cell. Most previous studies focused on the effects of the aforementioned factors on pure sulphide minerals. The possible influence that the presence of a non-sulphide gangue mineral can have on the effect of these variables needs to be determined. The non-sulphide gangue cleans the surface of the sulphide minerals. The presence of quartz influences the formation of layers of hydrophilic species on the surface of sulphide minerals (Clarke et al., 1995; Ekmecki and Demirel, 1997). The metal hydroxides will deposit on the surface of quartz rather than on sulphide minerals. Again, there is still a challenge in the application of findings from pure minerals to both real sulphide ores and industrial applications. Therefore, in this study, the effects of DO, pH and grinding media type under dry and wet grinding on the flotation response of pyrite in the presence of gangue material (quartz) will be investigated.

2.7. Key questions

Based on the literature review, the following key questions were formulated for this study:

- How does DO during grinding affect the flotation response of pyrite in the presence of quartz
- How does pH during grinding affect the flotation response of pyrite in the presence of quartz
- How do different grinding media types affect the floatability of pyrite in the presence of quartz?
- How does flotation pulp chemistry affect recovery of pyrite following dry grinding?

2.8. Hypotheses

The hypotheses tested in this research project are:

Hypothesis 1

DO 8 and pH 11 during grinding are expected to result in reduced subsequent flotation response of pyrite due to increased formation of iron oxides and iron hydroxides on the surface of pyrite. The formation of precipitates on pyrite also leads to lower adsorption of xanthate.

Hypothesis 2

Dry grinding with ceramic media is expected to yield high recoveries of pyrite relative to other grinding and flotation conditions when pyrite is floated at DO 0 and pH 9 due cleaner surfaces of pyrite resulting from grinding and reduced production of FeOOH in the subsequent flotation process.

Hypothesis 3

Lower flotation recoveries of pyrite are expected when the synthetic ore is milled in the presence of water at high concentration of DO (DO 8) and pH 11 because of increased formation of iron hydroxide precipitates (which are hydrophilic in nature) on the surface of pyrite and reduced adsorption of xanthate.

Hypothesis 4

Lower grades of pyrite and higher recoveries of quartz are expected under wet grinding with forged steel because metal ions such as Fe^{3+} which can be released from minerals or grinding media during grinding and flotation can activate quartz, leading to increased adsorption of collector on quartz surfaces, subsequently increasing the flotation response of quartz.

3. CHAPTER THREE: Experimental methods

The materials and apparatus used, the experimental approach which was followed in order to collect data, test the stated hypotheses and answer the key questions are described in this section. The test work to perform grinding tests on synthetic ore involved using a laboratory scale Magotteaux Mill® and a Sala Batch Grinding Mill. After grinding, the flotation process was performed using a 4.5 litre Magotteaux flotation cell. The tests were conducted in order to understand the influence of chemical conditions on the flotation response of pyrite in the presence of quartz under dry and wet grinding.

3.1. Ore preparation

Synthetic ore was prepared to mimic a real ore which has a 5 % sulphide mineral content; in this case pyrite was mixed with quartz. This allows for the isolation of distinct sulphide mineral behaviour.

The initial tests were conducted using pyrite and quartz only with forged steel media under wet grinding and proved unmanageable and gave results of solids and water recovered which were not reproducible. It was suggested that this was owing to the make-up of the synthetic ore in which no amount of froth stabilizing gangue had been incorporated (Feng et al., 2012). Thus, 1% talc obtained from Wards Natural Science Establishment, New York was added to all further tests. The results are shown in Figure 3-1. As can be seen from Figure 3-1, considering the two tests conducted under DO 8, the difference in water recovery from pH 9 is almost 10 times larger under pH 11.

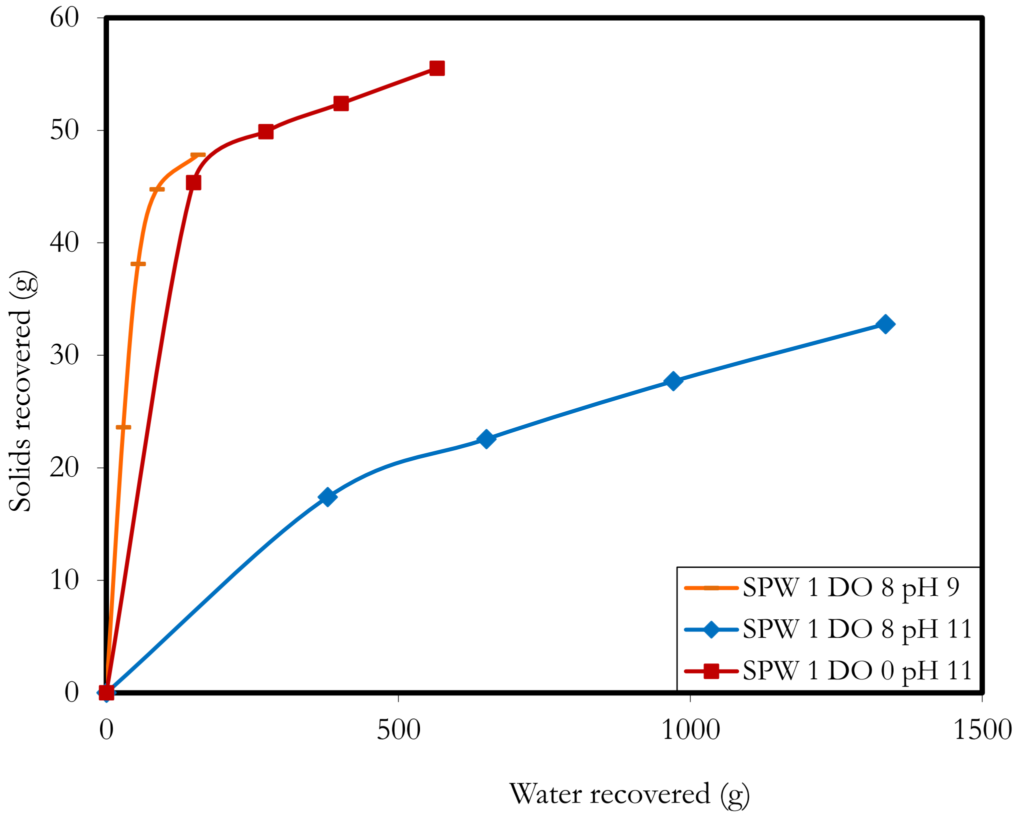


Figure 3-1: Solids vs Water recoveries for forged steel media without addition of talc under wet grinding

The quartz obtained from Consol Glass (Pty) Ltd was screened to a top size of 2 mm. The screened quartz was riffled and split to obtain 2 kg subsamples using a rotary splitter manufactured by Dickie and Stockler to obtain well-blended representative samples (Wiese, 2009).

The sulphide mineral; pyrite, was obtained as a pure sample in chunk form from Wards Natural Science Establishment, New York. The sample was crushed using a hammer. The crushed mineral was screened to a top size of 2 mm with the larger retained particles being crushed again to obtain the required size. The crushed samples were split and packed in zip lock plastic bags, purged with nitrogen and stored in a freezer at -18°C in order to minimize oxidation.

3.1.1. Particle size distribution

100 g and 50 g samples of quartz and pyrite feed material, respectively, were screened using the following screen sizes to obtain a full particle size distribution (PSD): 1700, 1180, 850, 600, 425, 300, 212, 150, 106, 75, 53, 38 and 25 µm. The PSD curves for the quartz and pyrite feed material are given in Figure 3-2

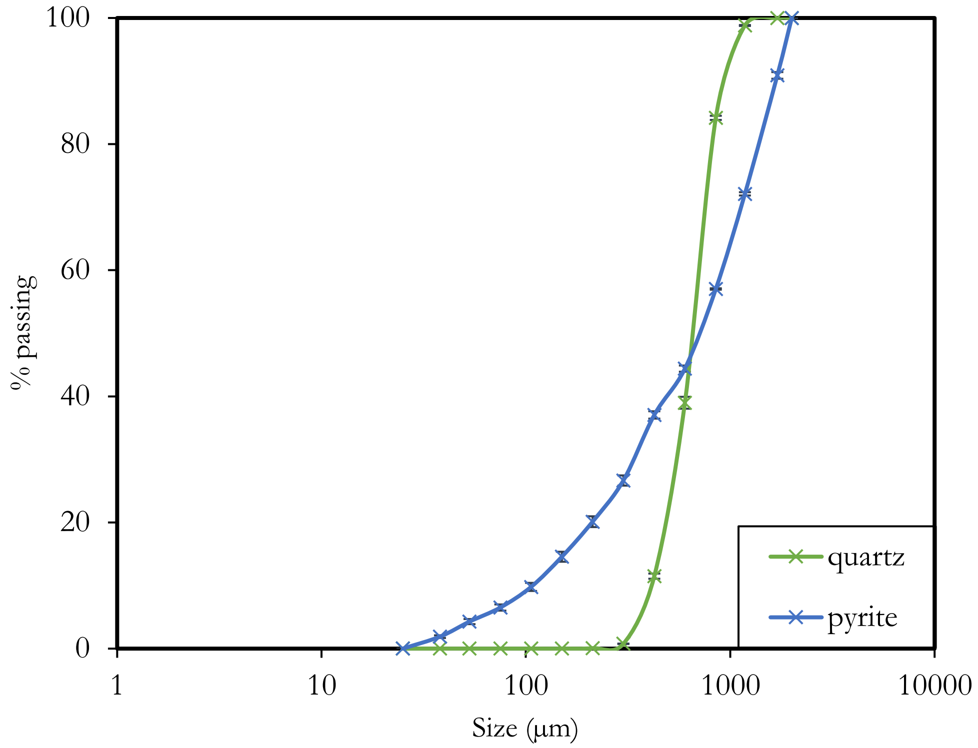


Figure 3-2: Particle Size Distribution curves for quartz and pyrite feed

3.2. Synthetic Plant Water

Synthetic plant water was used to conduct all wet grinding and batch flotation tests (Wiese, 2009). The synthetic plant water was prepared in the Centre for Minerals Research (CMR) laboratory by adding various salts supplied by Merck in powder form, to distilled water. This was done to achieve a dissolved solids concentration similar to that found in real concentrators. The salts were added in sequential order to produce standard synthetic plant water (SPW) containing the ions shown in Table 3-1.

Table 3-1: Composition of synthetic plant water used in all wet grinding and batch flotation tests

Ion	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**Cl^{-}**	**SO_4^{2-}**	**NO_3^{-}**	**CO_3^{2-}**	**TDS**
Concentration (ppm)	80	70	153	287	240	176	17	1023

3.3. Wet grinding

3.3.1. Milling

Wet milling was conducted in a Magotteaux Mill® (Magotteaux, 2009) supplied by Magotteaux Australia (PTY) Ltd. Figure 3-3 shows a photograph of the Magotteaux mill®. This is a highly instrumented mill, allowing for the measurement of pulp chemical parameters; pH, Eh, dissolved oxygen (DO) and temperature, in situ during grinding. The mill is composed of a grinding chamber and a measuring chamber, separated by a separating plate containing mesh ports (400 µm sieves), through which slurry can continuously flow and pulp chemistry can be monitored. The mill is fitted with recirculation pumps which allow for the slurry in the measuring chamber to be pumped back into the grinding chamber to ensure a fresh sample in the measuring chamber at all times. The pH and reagent dosing pumps give the operator control over the pulp chemistry throughout the grinding.

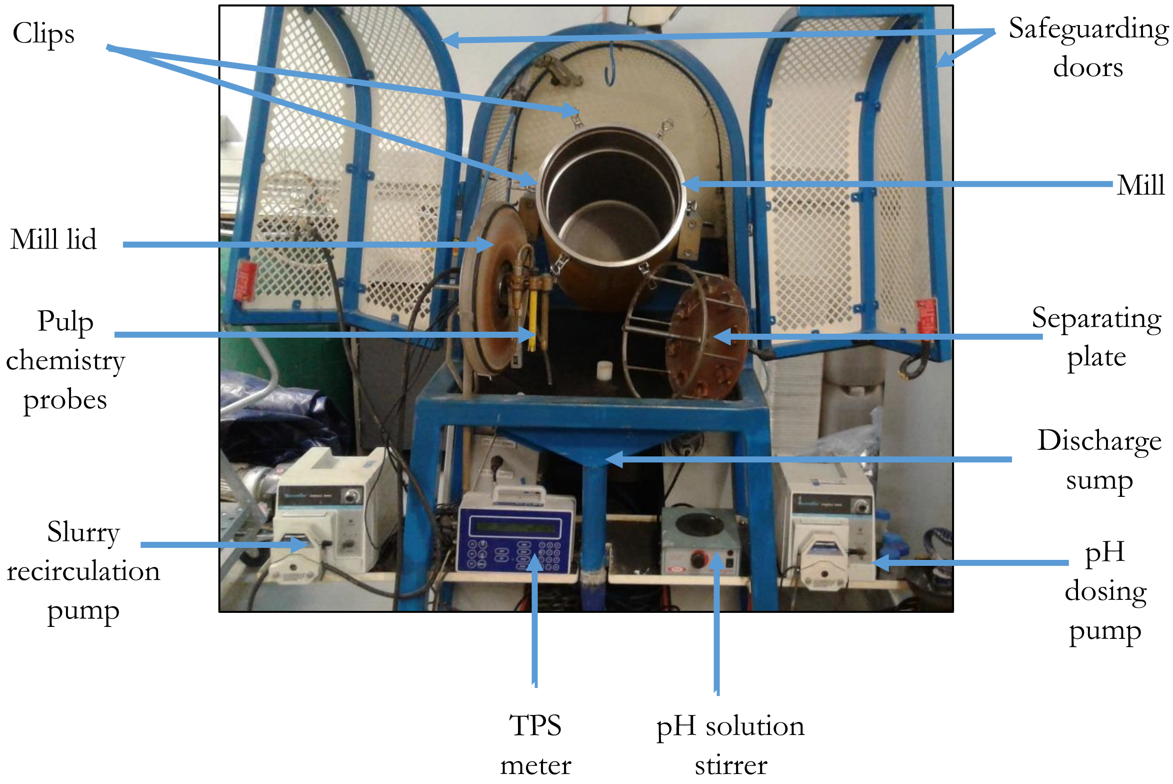


Figure 3-3: Magotteaux Mill®

For the determination of the milling curve, the mill was charged with either ceramic or forged steel media (20 kg of grinding media of 30-35 mm in size), 2 kg of quartz and 1.5 L of SPW. The mill was closed and adjusted to a horizontal position for milling. The grind was completed at a fixed speed (60 rpm) at three different time intervals using three different quartz samples. Prior to actual grinding, the contents of the mill were mixed for 3 minutes at a speed of 10 rpm. After milling, the wet mill discharge was filtered and dried in an oven at a temperature of 100°C. The dried sample was split using a rotary splitter to obtain 100 g subsamples. 100 g subsample was screened using 75 µm. Three different milling times were used to generate a milling curve, Figure 3-4. From the curve, the time required to achieve the desired grind of 60% passing 75 µm was determined.

Figure 3-4 shows the milling curves for quartz ground with ceramic and forged steel media under wet grinding.

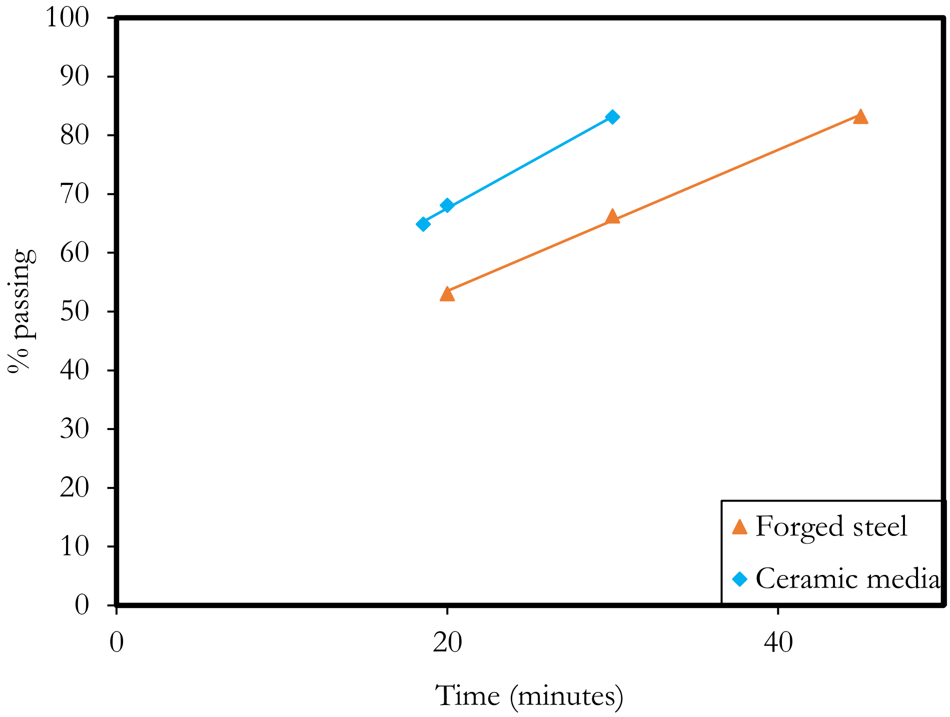


Figure 3-4: Milling curve for quartz ground with ceramic and forged steel media under wet grinding

Table 3-2: Milling periods under wet grinding

Media Type	Milling period
Ceramic	15 min 14 sec
Forged Steel	25 min 41sec

To conduct the actual grinding tests, the procedure outlined below was followed for wet grinding;

1. Preparation of media

Ceramic media was cleaned by washing it with distilled water. The forged steel media was prone to oxidation forming an iron oxide layer on its surface. The corrosion layer was removed prior to grinding by placing the media in the Magotteaux Mill® and grinding 2 kg of crushed quartz in 1.5 litres of distilled water for 10 minutes. The cleaned media was stored in a bucket containing water and lime to minimise media oxidation prior to the actual grinding tests. The lime was washed off the forged steel balls before mill loading (described in step 3) to prevent change in pH.

2. Calibration of probes

All probes were calibrated every day before commencing any test work to ensure the accuracy of the results. The probes used to monitor pulp chemistry were, DO, pH and Eh.

- **Dissolved oxygen probe**
  To calibrate the DO probe, the probe was connected to a TPS meter, which is a field meter and logger used for pulp chemistry measurements. The probe was placed into sodium sulphite solution (oxygen free solution), which was prepared by dissolving 2 g of sodium sulphite powder in 100 ml of distilled water. The reading on the TPS meter was then allowed to stabilize at zero ppm before the probe was calibrated for zero ppm. After calibration, the probe was rinsed with distilled water and blotted dry. The probe was then calibrated in air by allowing the tip of the probe to hang downwards in air. The reading was again allowed to stabilize ~ 8 ppm before calibration.

  After use, the DO probe was stored by placing the tip of the probe in a small storage bottle containing water and a sponge.

- **pH probe**
  The pH probe was connected to the TPS meter and the pH range of 7 to 10 was selected. The probe was placed into a pH 7 buffer solution. The pH reading on the TPS meter was allowed to stabilize and the probe was calibrated. The probe was rinsed with distilled water before being placed in a pH 10 buffer solution and the calibration process was repeated.

  After use, the probe was placed in a small storage bottle filled with water.

- **Eh probe**
  Before use, the Eh probe was checked for accuracy. This was done by connecting the probe to the TPS meter and immersing it in a 250 mV ORP reference solution. It was ensured that the reading on the TPS meter was 250 mV. After use, the Eh probe was stored in a small storage bottle filled with water.

3. Mill loading

After calibration of all the probes, the mill was tilted to an upright position (as shown in Figure 3-5) using a locking pin. The mill was then loaded with 20 kg of clean grinding media, 2 kg of synthetic sulphide ore (1% of talc, 2.5% of Pyrite and 96.5% of Quartz) and 1.5 litres of synthetic plant water. After loading the mill, the separator plate was placed into the mill and pushed firmly into position. The mill lid was secured using clips. The locking pin was once again used to position the drum to a horizontal operating position.

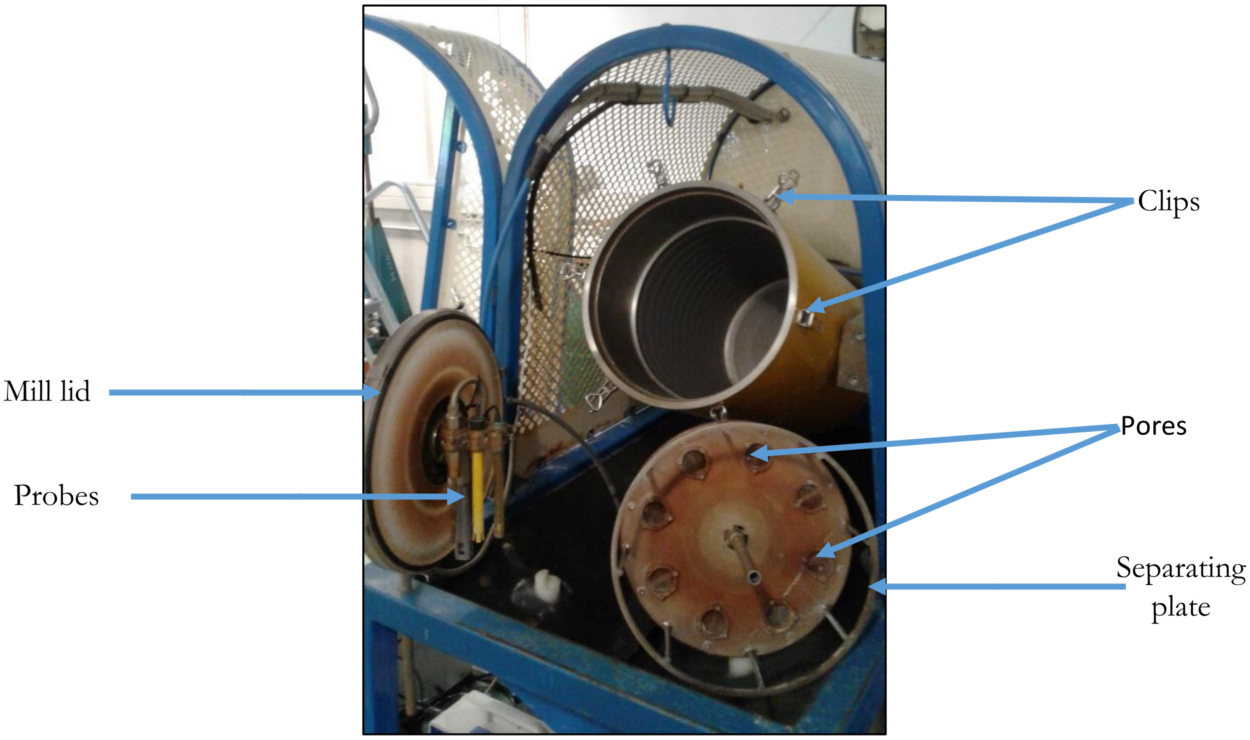


Figure 3-5: Magotteaux Mill® in upright position

4. Mill start-up

The slurry recirculation piping was connected, the Magotteaux Mill® safeguarding doors were closed and a clean bucket was placed under the mill discharge sump. Thereafter the safety rest button on the mill instrument panel was pressed.

5. Control system operation

The mill connects to the laptop computer (Magotteaux Mill® control system). In order to ensure a continuous connection, the laptop was connected to the mill PLC using a cable. The mill can operate in four different modes, namely, local automatic operation, remote automatic operation, remote manual operation and local manual. The mill was operated in the remote automatic mode throughout the tests involving wet grinding. After logging into the laptop, the following procedure was followed to operate the mill in remote automatic mode (Magotteaux, 2009):

- At the bottom of the screen, click **Formulate Recipe**, and the screen that contains all the important input items to execute a **batch** appears. A batch consists of three stages, which are; conditioning, mixing and grinding (Figure 3-6).

Figure 3-6: Batch stages

During the conditioning stage, the mill does not move and the pulp chemistry parameters are adjusted to a point similar to an operating mill. When the mill was operated under 0 ppm of dissolved oxygen, all the oxygen dissolved in the mill was purged out for 7 minutes at 10 l/min using nitrogen gas.

- After entering all the required information into the input boxes, the batch was started. At the end of the batch, the mill stopped and a pop-up window appeared and the file was saved by pressing **Confirm**.

In the mixing stage, the mill was rotated for 3 minutes at 10 rpm. During this stage, synthetic sulphide ore and plant water with a newly adjusted mill environment are mixed together. After the mixing stage, the mill grinds the ore for the period of time (as was predetermined using the milling curves described in section 3.3) at an increased speed of 60 rpm.

6. Mill loading

After saving the file, the **Drum Jog** button was pressed to rotate the mill drum to a horizontal position so that the drum tilt handle could enter its sockets. Then, safeguarding doors were opened and the recirculation tubes were taken out and flushed with water. After cleaning the tubes, the drum was raised to an upright position. The mill lid and separator plate were removed and cleaned with water to wash off the slurry. The balls were removed from the mill by hand and washed free of slurry. After removing the balls, the mill drum was tilted slowly to the unloading position so that the slurry could run out of the mill. Finally, the mill was rinsed and the slurry was washed from the mill discharge sump into the bucket. The mill product was then transferred to a flotation cell.

3.1.1.1. pH controlled grinding

One of the objectives of this study was to investigate the influence of pH during grinding on the flotation response of pyrite in the presence of quartz. Therefore, grinding was performed at different slurry pH values. Tests were conducted under the natural pH (whereby pH was not controlled at all, but merely monitored, ~ pH 9) and at pH 11, where pH was controlled using a sodium hydroxide (NaOH) solution and the dosage was dependant on control within the mill.

Before commencing the test work, it was ensured that there was sufficient NaOH solution which was constantly agitated using a magnetic stirrer.

3.1.1.2. Dissolved oxygen controlled grinding

The wet grinding was performed under natural conditions (whereby dissolved oxygen was not controlled) and under inert grinding condition (air inside the mill was purged out using nitrogen). The concentration of dissolved oxygen is affected by a number of factors such as temperature, atmospheric pressure and salinity. The concentration of dissolved oxygen at atmospheric room temperature and pressure is 8 ppm. Therefore, the presence of oxygen during tests without DO control was assumed to be 8 ppm and the absence of DO as 0 ppm.

3.3.2. Flotation

Sodium isobutyl xanthate (SIBX) with a purity of 90%, supplied in powder form by Senmin was used as a collector. A 1% fresh solution of SIBX was prepared daily using distilled water. DOW 200 with specific gravity 0.973, supplied by Betachem was used in concentrated form as a frother in all the flotation tests. Table 3-3 shows the dosages and conditioning times which were used for frother and collector for all the experimental tests.

Table 3-3: Summary of the reagent dosages used

Reagent	Name	Dosage (g/t)	Conditioning time (mins)
Collector	SIBX	100	2
Frother	DOW 200	50	1

The flotation tests were carried out in a Magotteaux bottom driven flotation cell with a capacity of 4.5 litres shown in Figure 3-7.

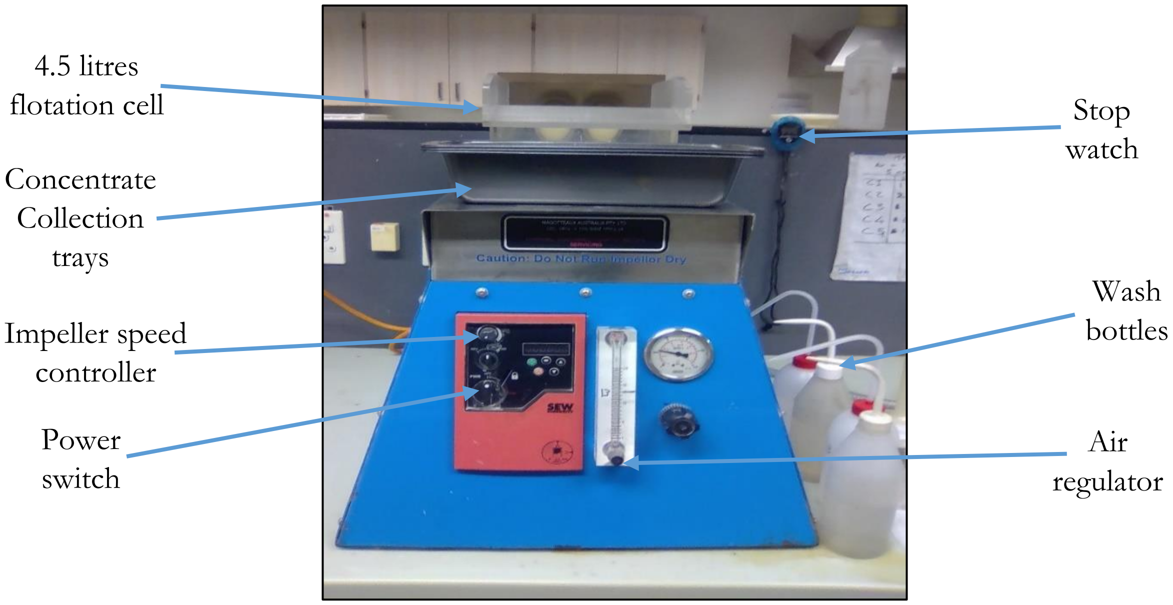


Figure 3-7: 4.5 litre Magotteaux flotation cell

The flotation cell is fitted with a stainless steel impeller and an air flow meter. The impeller speed can be regulated between 0 and 2100 rpm, while flotation gas supply into the flotation cell can be controlled between 0 and 20 L/min.

Post milling, the mill product was immediately transferred into the flotation cell and the standard UCT batch flotation procedure was followed. After wet grinding, the milling conditions were not maintained, there was no further control. The volume was set to 4.5 litres using SPW. The impeller speed was adjusted to 1200 rpm before extracting two samples of the flotation feed sample using syringes. The required amount of collector and frother were added and conditioned for periods shown in Table 3-3. After the conditioning of the reagents, the air was turned on at a flowrate of 13 L/min and the froth was allowed to accumulate. A froth height of 2 cm was kept constant throughout the tests by the manual addition of SPW.

Four concentrates were collected over a period of 20 minutes by scraping the froth into a collecting pan at 15 seconds intervals for 2, 4, 6 and 8 minutes respectively. The water recovered with each of the four concentrate samples was measured and recorded. Two tailings samples were taken at the end of the flotation test using syringes.

Concentrate, feed and tailings samples were filtered using a Buchner Funnel connected to a vacuum pump. The filtered concentrate samples were dried overnight in an oven at 80 °C, while feeds and tailings samples were dried at 100°C after which the dry samples were weighed.

A summary of the flotation procedure followed is given in Table 3-4

Table 3-4: Summary of flotation procedure

	Time (minutes)
Collector addition	2
Frother addition	1
Concentrate 1 collection	2
Concentrate 2 collection	4
Concentrate 3 collection	6
Concentrate 2 collection	8

3.4. Dry grinding

3.4.1. Milling

Dry grinding was conducted in a Sala Batch grinding mill manufactured by Polaris Mining Equipment (PTY) LTD, Figure 3-9. This is a stainless steel tumbling mill with a diameter of 300 mm. For the determination of the milling curve, the mill was charged with either ceramic or forged steel media (20 kg of grinding media of 30-35 mm in size) and 2 kg of quartz. The mill was closed and adjusted to a horizontal position for milling. The grind was completed at 75% critical speed equal to 56.4 rpm at three different time intervals using three different quartz samples. After grinding, the grinding media was removed from the mill by hand. The mill drum was then tilted slowly to the unloading position using an adjustment lever (shown in Figure 3-9) so that the dry product could be collected in a tray. The dry sample was split using a rotary splitter to obtain 100 g subsamples. The milling curve was obtained as described in section 3.3.1

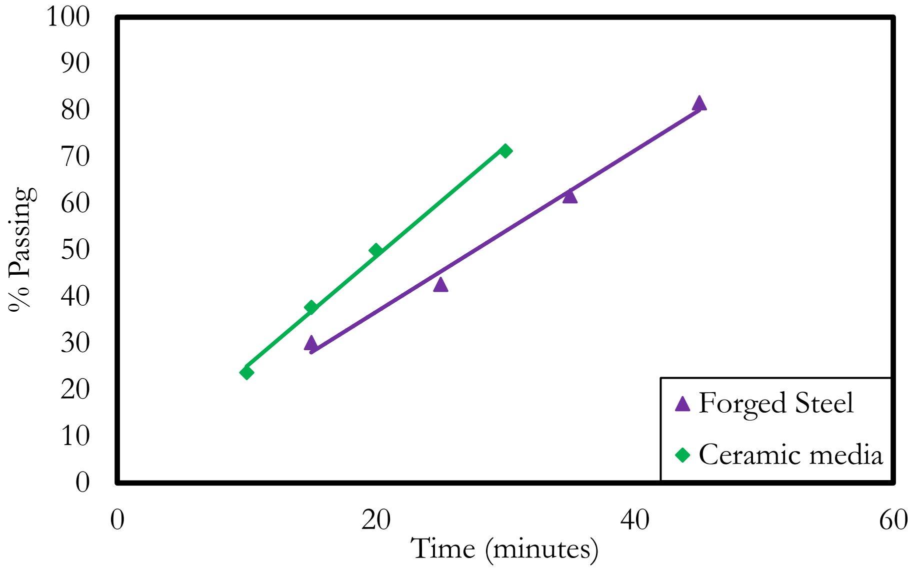


Figure 3-8: Milling curve for quartz ground with forged steel and ceramic media under dry grinding

Table 3-5: Milling periods under dry grinding

Media Type	Milling period
Ceramic media	24 min 84 sec
Forged steel media	33 min 45 sec

To conduct the actual grinding tests, the mill was tilted to an upright position using an adjustment lever. It was charged with 20 kg of either forged steel or ceramic media and 2 kg of synthetic ore (1% of talc, 2.5% of pyrite and 96.5% of quartz). After loading the mill, the mill was closed. The adjustment lever was once again used to position the drum to a horizontal operating position. The grind was completed at 75% critical speed which was equal to 56.4 rpm. After the grinding was completed, the dry mill product was washed from the mill into a bucket using standard synthetic plant water. It is clearly not possible to monitor or control the chemistry within the mill when dry grinding, thus in this case, the chemistry was considered only in the flotation cell.

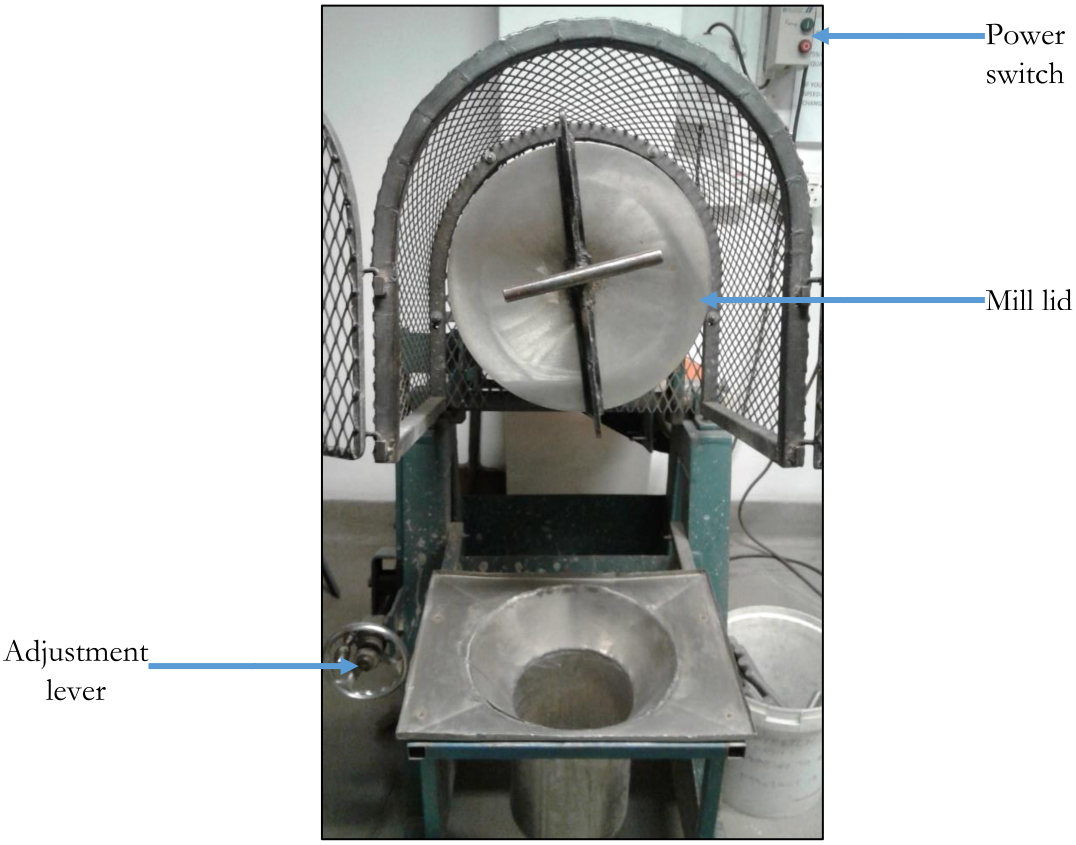


Figure 3-9: Sala Batch Grinding Mill

3.4.2. Flotation

For the dry grinding tests the same reagents, dosages and flotation procedure described in section 3.3.2 was followed. However, the pulp chemistry was controlled inside the flotation cell. All the tests were carried out under the following conditions:

Table 3-6: Grinding chemical conditions

Condition	Low	High
DO	0 ppm	8 ppm
pH	9	11

Tests were conducted under the natural pH (whereby pH was not controlled at all, but merely monitored, ~ pH 9) and at pH 11, where pH was controlled using a sodium hydroxide (NaOH) solution

The concentration of DO was controlled at 0 ppm by conducting flotation tests while purging the system with nitrogen. At 8 ppm, air was purged through the cell. The flotation process described in section 3.3.2 was followed.

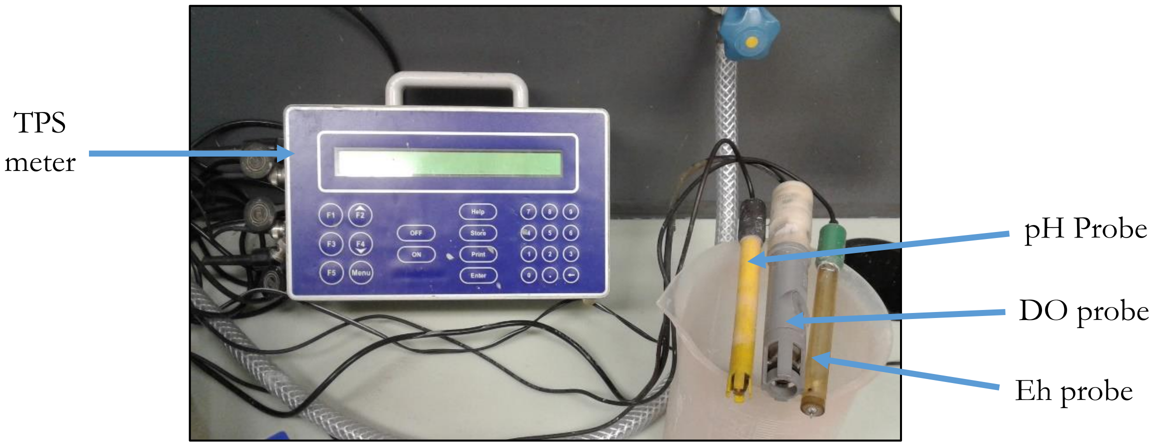


Figure 3-10: TPS meter and pH, DO and Eh probes

It should be noted that all the tests were conducted in duplicate and Eh was monitored but not controlled.

3.5. Analytical techniques performed

The analytical techniques listed in Table 3-7 were employed to assess both flotation performance and grinding chemistry, at difference tests conditions.

Table 3-7: Analytical techniques employed

Analysis	Property analysed	Equipment/technique
Particle size distribution	Feed particle size analysis	Dry screening
EDTA extraction	Extractable metal ion content on slurry	ICP-AES
Sulphide recovery	Sulphur	LECO

3.5.1. Flotation performance analysis

To assess the flotation performance, dry feed, tailings and concentrate samples were analysed for sulphur. Sulphur analysis was conducted using a Laboratory Equipment Corporation (LECO) sulphur analyser. During LECO analysis for sulphur, an ore sample is heated to a sufficiently high temperature to induce combustion in oxygen. The sulphur in the ore is oxidised to Sulphur dioxide (SO_2), and measured using Infrared detectors. The results obtained were used to calculate sulphide mineral recovery and grade at various tests conditions.

3.5.2. EDTA Extraction technique

An EDTA extraction technique was employed to quantify the percentage of extractable oxidized iron on the mill product. A 3 wt.% solution of ethylene diamine-tetra acetic acid (EDTA) was prepared using deionized water and the pH was adjusted to 7.5 by the addition of NaOH pellets. A weighed feed sample (25 ml) was transferred to a stirred vessel together with 250 ml of EDTA solution in order to leach the oxidized iron species from this sample while stirring for 10 minutes. During stirring, it was ensured that air did not become incorporated into the solution through the formation of a vortex in the beaker. After stirring, the slurry was filtered through a 0.22 µm Millipore membrane. The filtrate was transferred to a 100 ml plastic container and sent for iron assay using ICP-AES. ICP-AES analysis is a technique that is used to determine the concentrations of trace to major elements in the periodic table and can detect most elements (LI, 2017)

The percentage of extractable iron was calculated as the ratio of the amount of iron in the filtrate to the amount of iron in the sample. The percentage was calculated through the following steps:

- calculate the dry weight of the syringed sample:

$$Dry\ wt. = net\ wt. \times percent\ solids$$

- Using the dry weight of the sample, along with the assay, calculate the metal units in solids:

$$Metal\ units\ in\ solids = dry\ wt.\ \times Assay\ (\%)$$

- The metal units in solution is calculated from the solution assays:

$$Metal\ units\ in\ soln = \frac{Soln\ Assay\ \times (EDTA\ volume\ + water\ volume\ in\ syringe)}{1000}$$

- The percentage of EDTA extractable ion is calculated from:

$$EDTA\ extractable = \frac{Metal\ units\ in\ solution}{Metal\ units\ in\ solids} \times 100\%$$

4. CHAPTER FOUR: Results

4.1. Introduction

The objective of this study was to investigate the influence of different pulp chemical conditions on the froth flotation response of a pyrite containing synthetic ore ground under dry and wet conditions with forged steel and ceramic media. The pulp chemical conditions were controlled in the Magotteaux Mill® during wet grinding and in the flotation cell during dry grinding. This chapter discusses and presents all the key results and findings from both wet and dry grinding as well as the results from the batch flotation experiments conducted.

This chapter is divided into nine sections. Section 4.2 shows the reproducibility tests that examine the reliability of flotation and pulp chemistry results. Sections 4.3 and 4.4 show the flotation results obtained under wet and dry grinding, respectively. Under these sections, the solids and water recoveries are represented. Section 4.5 presents the effects of grinding media under wet and dry grinding on the solids and water recoveries. Sections 4.6 and 4.7 show the pyrite recovery and the effects of grinding media on pyrite recovery and grade for wet and dry grinding. EDTA extracted iron results are presented in section 4.8. The last section (section 4.9) shows the overall solids and pyrite flotation rate constants.

4.2. Reproducibility

According to Mahmood et al. (2018), reproducibility is defined as the ability of a study to recompile the same scientific or experimental data, analyses and experimental procedures for validation. Reproducibility was conducted to investigate the reliability of the equipment and procedure followed to collect data. In this test work, the grinding and batch flotation tests were conducted in duplicate for all the conditions tested to minimize the error associated with experimental results. The water recovery, solids recovery and pyrite recovery were used as the key variables to determine reproducibility.

4.2.1. Milling

To investigate the reliability of the Magotteaux Mill and Sala Batch Grinding Mill, milling curves were prepared for each mill by grinding 2 kg of only quartz feed with forged steel media. For each mill, the experiment was repeated twice. Figure 4-1 shows the results obtained. From the figure, it is clear that the milling method was reproducible.

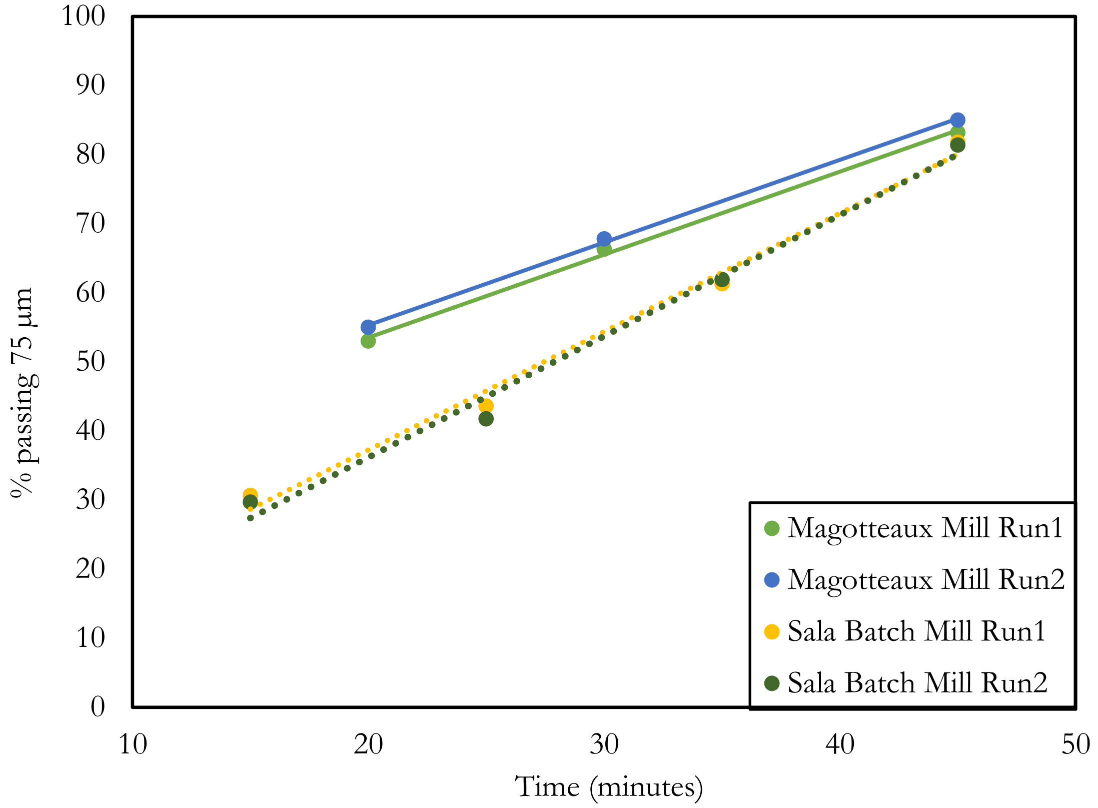


Figure 4-1: Percentage passing 75 µm for both mills using forged steel media

4.2.2. Batch flotation

For the purpose of investigating the reliability of the Magotteaux flotation cell and operator technique, pyrite mixed with quartz and talc was milled using the Magotteaux Mill under DO 8 and pH 9 using ceramic balls as the grinding media. The Magotteaux flotation cell was then used to determine the recovery by flotation of pyrite. The experiment was repeated. The results obtained are shown in Figure 4-2.

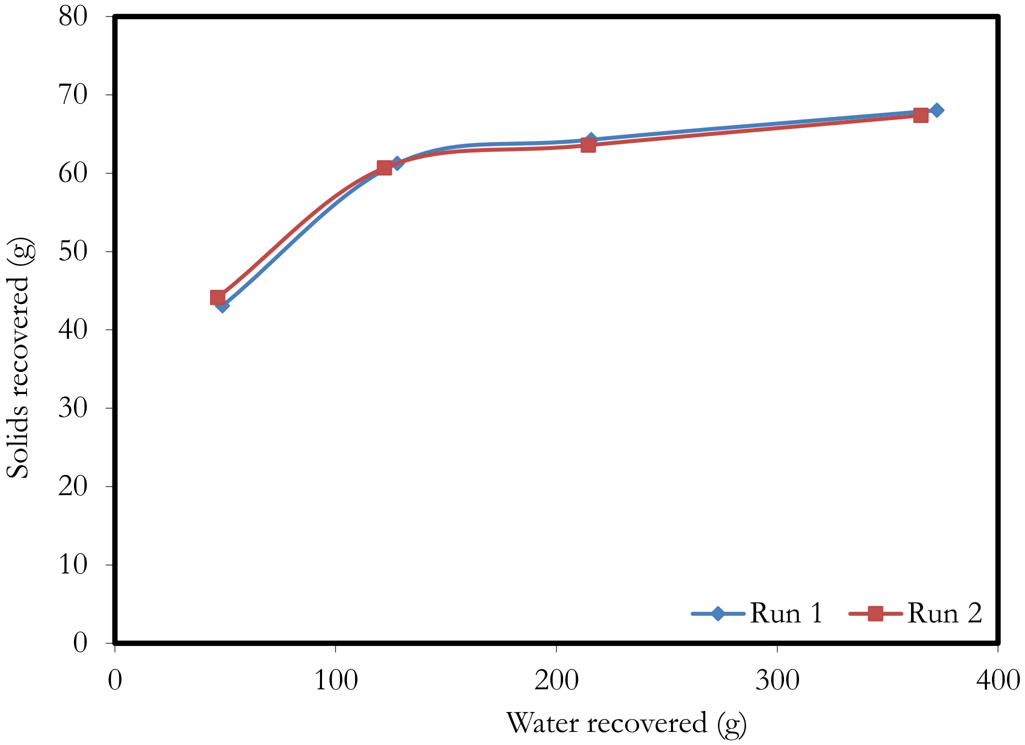


Figure 4-2: Solids recovery versus water recovery for ceramic media under wet grinding at DO 8 and pH 9

It is clear from Figure 4-2 that the technique was reproducible.

NB: All figures contain error bars (representing standard error), but in a number of cases may not be visible on the figure as they are very small.

4.3. Wet grinding

4.3.1. Water and solids recovery

4.3.1.1. Forged steel media

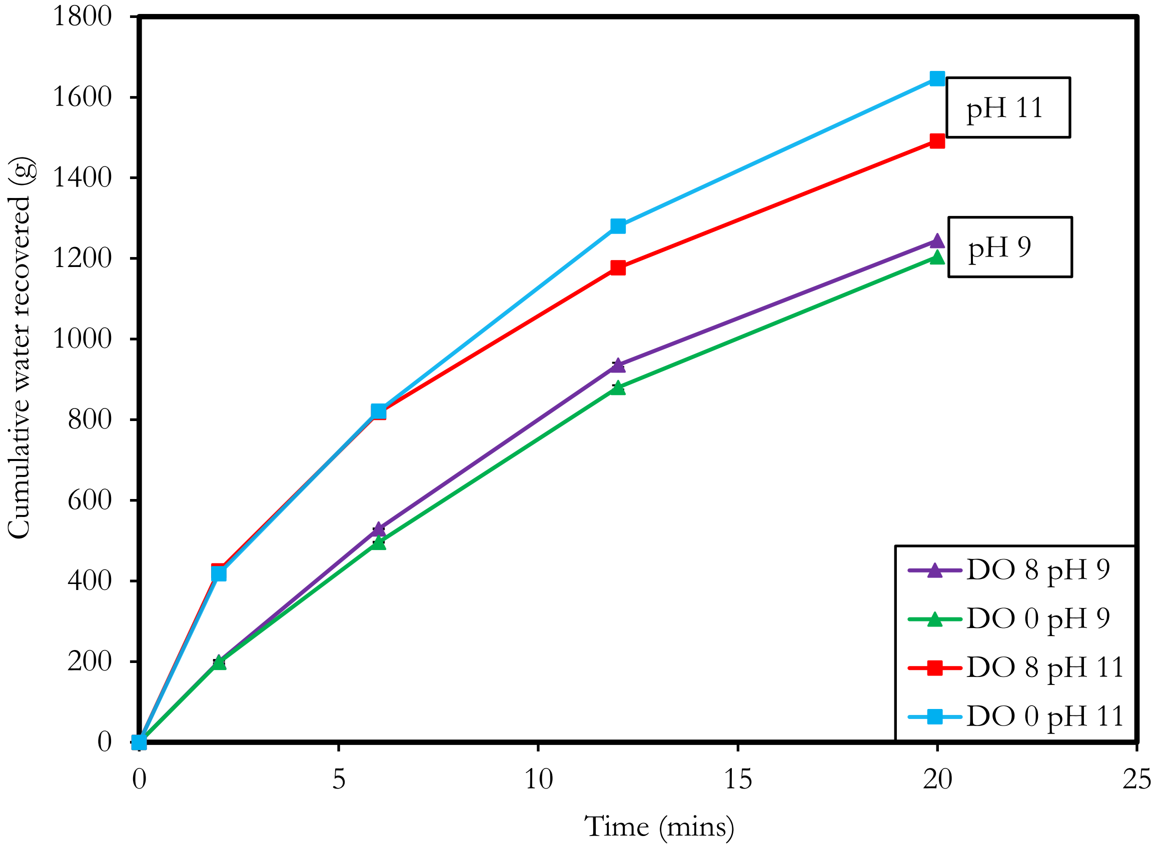


Figure 4-3: Cumulative water recovered versus time for forged steel under wet grinding.

Figure 4-3 shows the water recovery versus time for the test conditions under wet grinding with forged steel and therefore indicates the rate at which water was recovered. Water recovery was strongly dependent on the pH of the system. It is evident that after the first 7 minutes of flotation, the rate of water recovery did not depend upon DO. However, for the last 13 minutes of flotation, a substantial effect of DO on the rate of water recovery was recorded, more so for pH 11, than pH 9. The highest rate of water recovery was obtained at DO 0/pH 11. DO 0/pH 9 resulted in the lowest rate of water recovery. The rate of water recovery increased with an increase in the pH of the system.

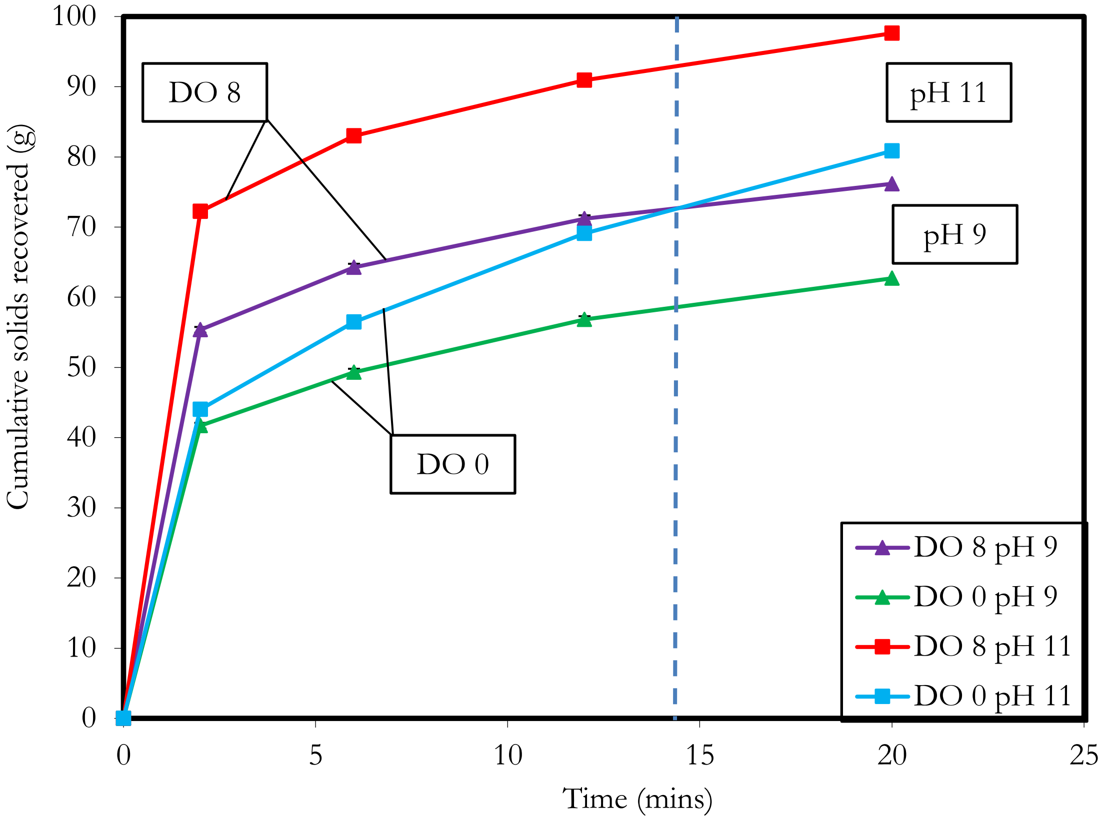


Figure 4-4: Cumulative solids recovered versus time for forged steel media under wet grinding

Figure 4-4 shows solids recovery versus time for forged steel media under wet grinding for the conditions tested. Figure 4-4 illustrates that the highest rate of solids recovery was obtained at DO 8/pH 11 and DO 0/pH 9 yielded the lowest rate of solids recovery. The initial rate of solids recovery was lower under conditions of DO 0/pH 11 than at DO 8/pH 9. This figure also indicates that removal of oxygen during grinding led to a decrease in the rate of solids recovery. The rate of solids recovery increased with increasing pH. This can clearly be seen after 15 minutes of flotation.

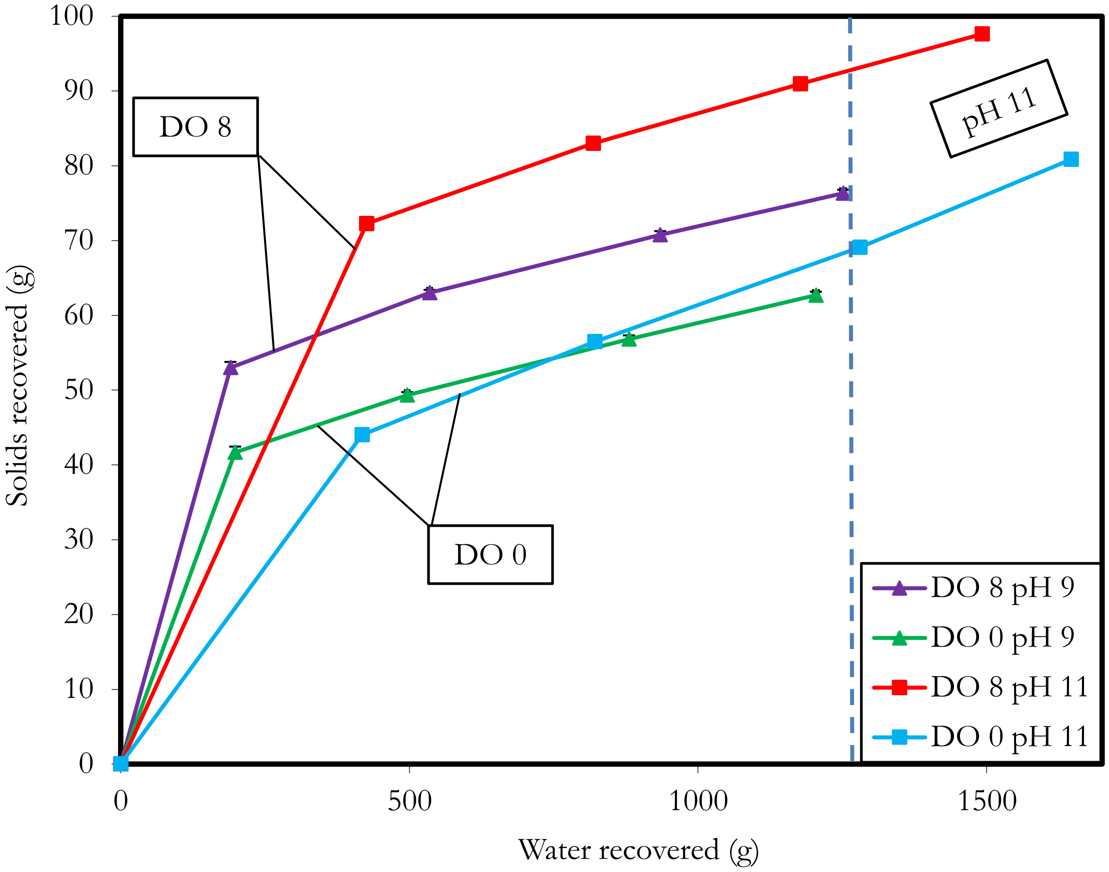


Figure 4-5: Solids versus water recoveries for forged steel media under wet grinding

Figure 4-5 shows the solids versus water recoveries for all the tests conducted using forged steel media under wet grinding. It is clear from Figure 4-5 that the solids recovery is strongly dependent upon the pulp chemistry of the system. DO 8 produced much higher solids recoveries than DO 0. The rate of water and solids recoveries increased when the synthetic ore was ground in the presence of oxygen. pH had a greater influence on the water recovery than DO with pH 11 yielding higher water recoveries than pH 9. A slightly higher water recovery was obtained under conditions of DO 0/pH 11 than all other conditions. Removal of oxygen during grinding resulted in a decrease in solids recovery.

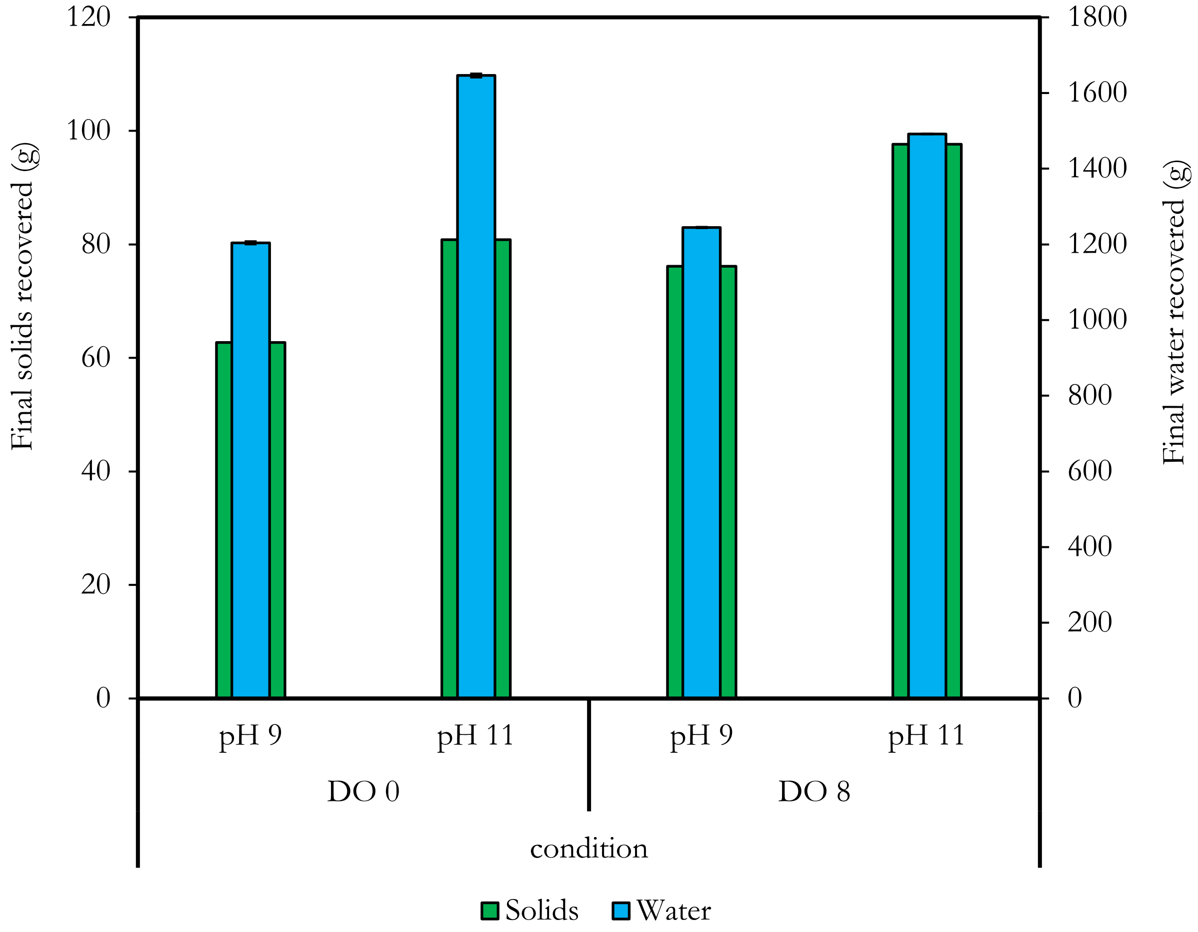


Figure 4-6: Final water and solids recovered for forged steel media under wet grinding conditions

Figure 4-6 shows the total solids and water recovered while grinding the synthetic ore with forged steel media under wet grinding. It can be construed from the figure that the highest solids recovery was achieved at DO 8/pH 11 while the lowest amount of solids was recovered at DO 0/pH 9. Overall, the solids recovery increase is commensurate with pH while removal of oxygen (DO 0) inside the Magotteaux Mill® during grinding yielded a reduction in the total solids recovery.

Furthermore, in this figure, it can be clearly seen that DO 0 and pH 11, resulted in the highest water recoveries. pH 9 and DO 0 yielded the lowest water recovery. It can also be seen that, on varying DO concentration during grinding (keeping pH constant), water recovery remains the same at pH 9 and as slight change at pH 11. A significant increase in water recovery was recorded upon increasing pH of the system during grinding.

4.3.1.2. Ceramic media

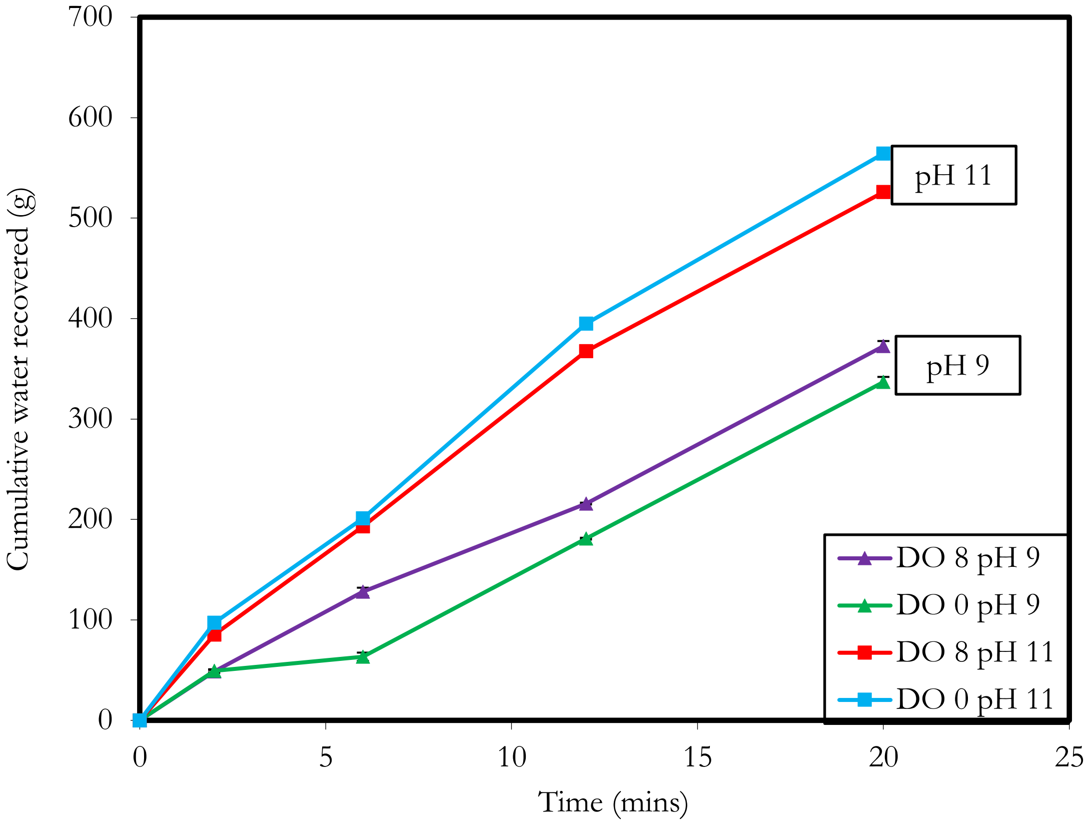


Figure 4-7: Cumulative water recovered versus time for ceramic media under wet grinding

Figure 4-7 shows the water recovery versus time for ceramic media under wet grinding for the conditions tested. The highest rate of water recovery was achieved for tests conducted at DO 0/pH 11. The figure shows that DO 0/pH 9 yielded the lowest rate of water recovery. It can also be seen from this figure that the rate of water recovery is slightly affected by a change in DO concentration while pH has a sharp impact on the rate at which water was recovered under wet grinding when ceramic balls were used as grinding media.

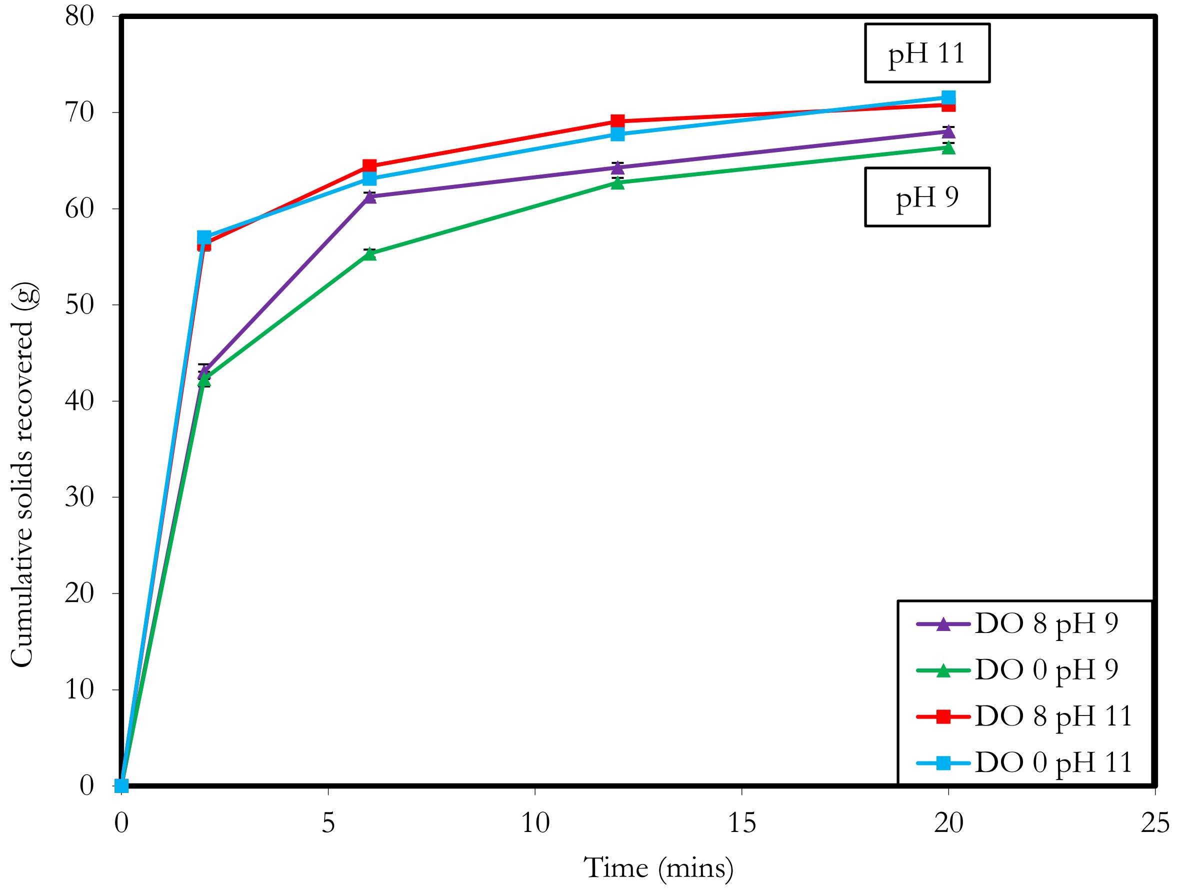


Figure 4-8: Cumulative solids recovered versus time for ceramic media under wet grinding

Figure 4-8 shows solids recovery versus time for ceramic media under wet grinding for all the conditions tested and therefore indicates the rate of solids recovery. As seen from Figure 4-8, pH 11 produced the higher rate of solids recovery compared to pH 9, while at each pH, there was little difference in the rate of solids recovery recorded by altering DO concentration during grinding.

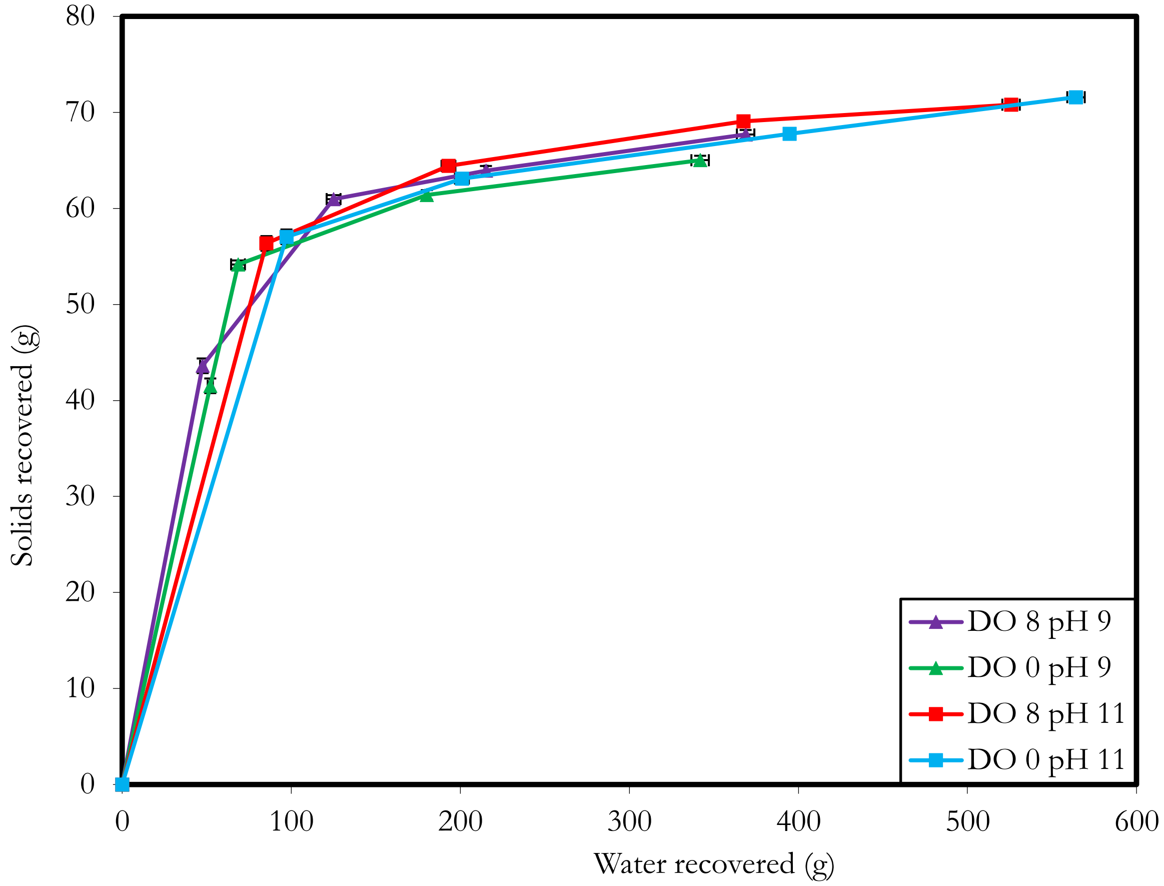


Figure 4-9: Solids versus water recoveries for ceramic media under wet grinding

Figure 4-9 illustrates the influence of pulp chemistry of the system during wet grinding on the amount of solids and water recovered when synthetic ore was ground with ceramic media. When monitoring grinding with inert ceramic media, the total solids recovery is not dependent upon the pulp chemistry of the system. There is no obvious effect of DO shown under ceramic media in Figure 4-9, however the total water recovery is again higher with pH 11 than with pH 9.

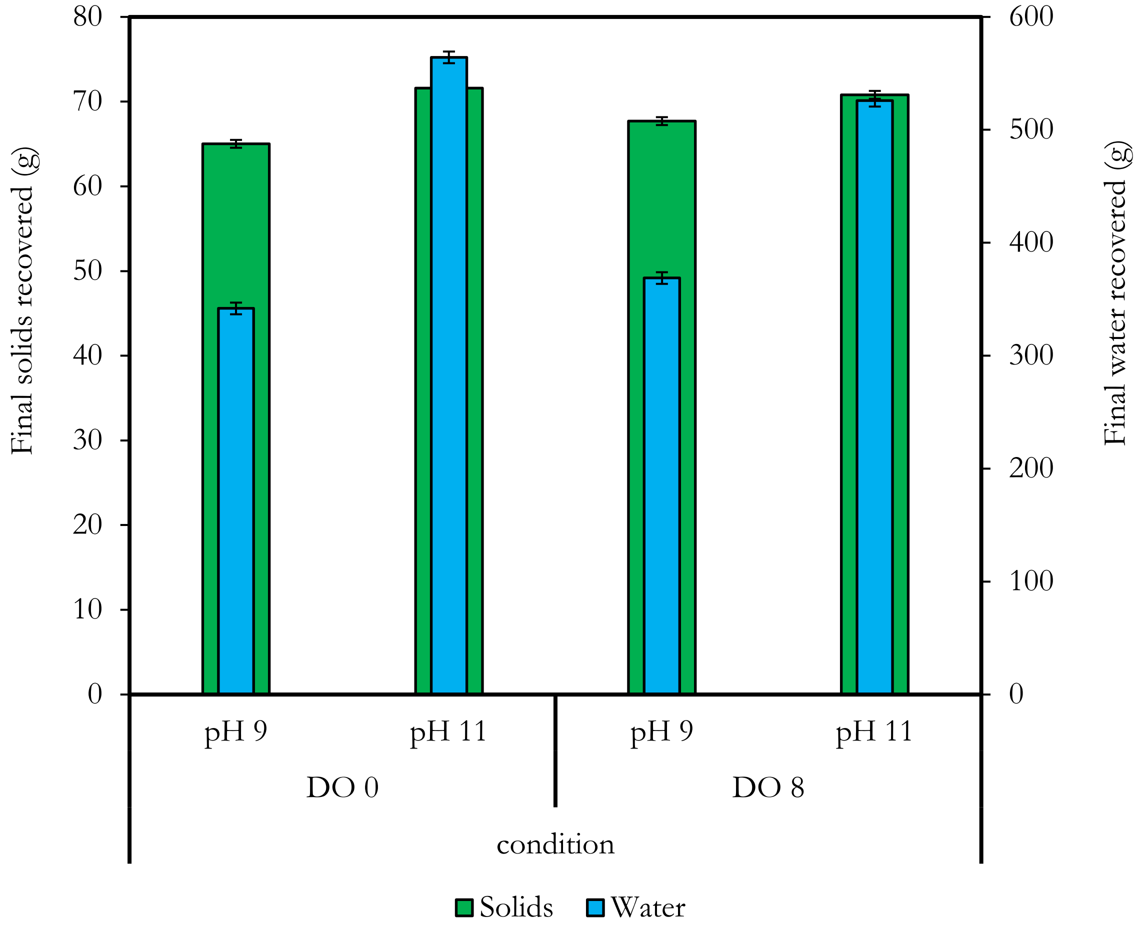


Figure 4-10: Final water and solids recovered for ceramic media under wet grinding for all the conditions

The final solids and water recoveries for all the conditions tested when ceramic media was used to grind under wet conditions are shown in Figure 4-10. The highest amount of water was recovered at DO 0/pH 11. The lowest water recoveries were obtained at DO 0/pH 9. The amount of water recovered increased with increasing pH of the system during milling. The marginal differences in water recoveries were observed at constant pH when DO concentration was changed under wet grinding with ceramic media. It can also be seen that DO 0/pH 11 resulted in the highest solids recovery while DO 0/pH 9 produced the lowest solids recovery.

4.4. Dry grinding

(It should be noted that under dry grinding the pulp chemistry was controlled inside the float cell post grinding).

4.4.1. Water and solids recovery

4.4.1.1. Forged Steel media

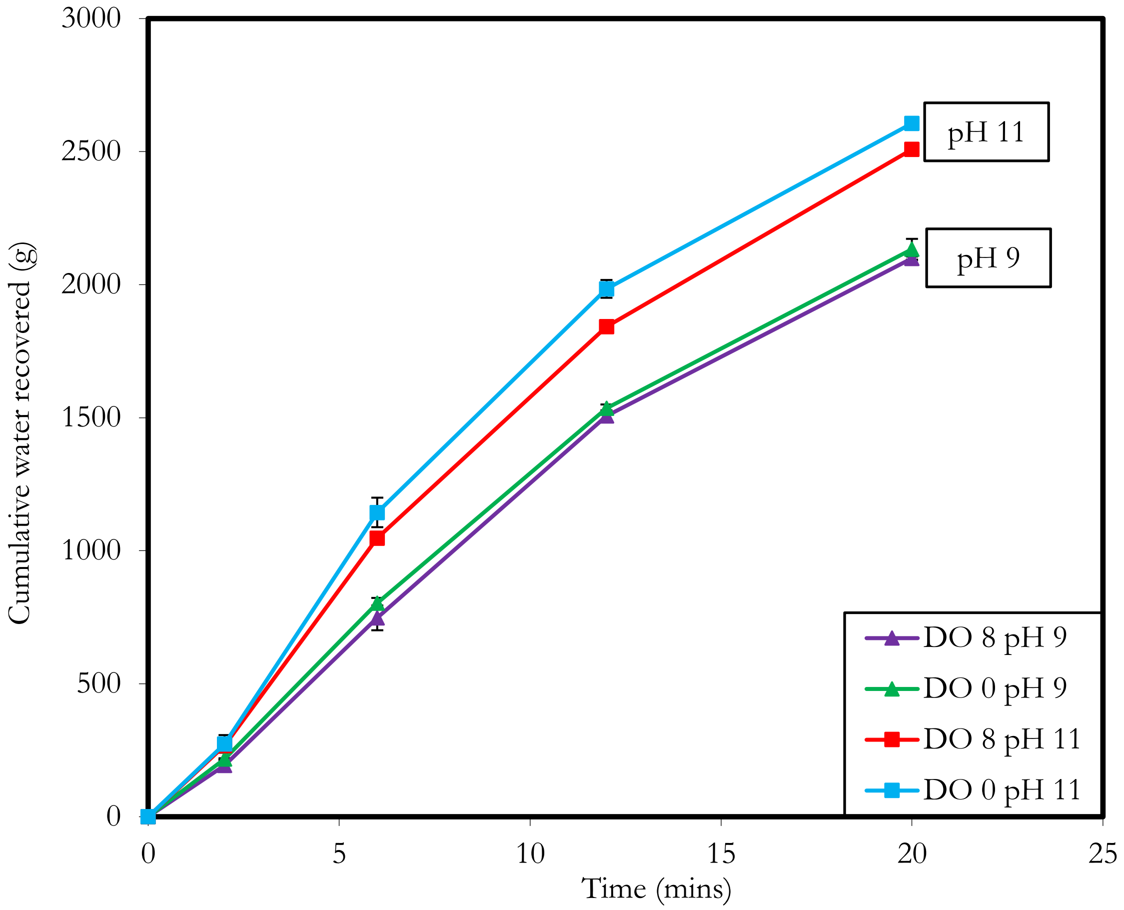


Figure 4-11: Cumulative water recovered versus time for forged steel media under dry grinding

Figure 4-11 shows water recovery versus time and thus indicates the rate of water recovery under dry grinding with forged steel media for the conditions tested. The highest rate of water recovery was achieved at DO 0/pH 11 while pH 9 yielded the lowest rate of water recovery. It can be seen that there were significant changes in the rate of water recovery when pH was changed from 9 to 11. Figure 4-11 shows that at pH 11, removing oxygen from the system (DO 0) resulted in an increase in the rate of water recovery. At pH 9, water recovery does not appear to be dependent upon DO concentration in the system during flotation.

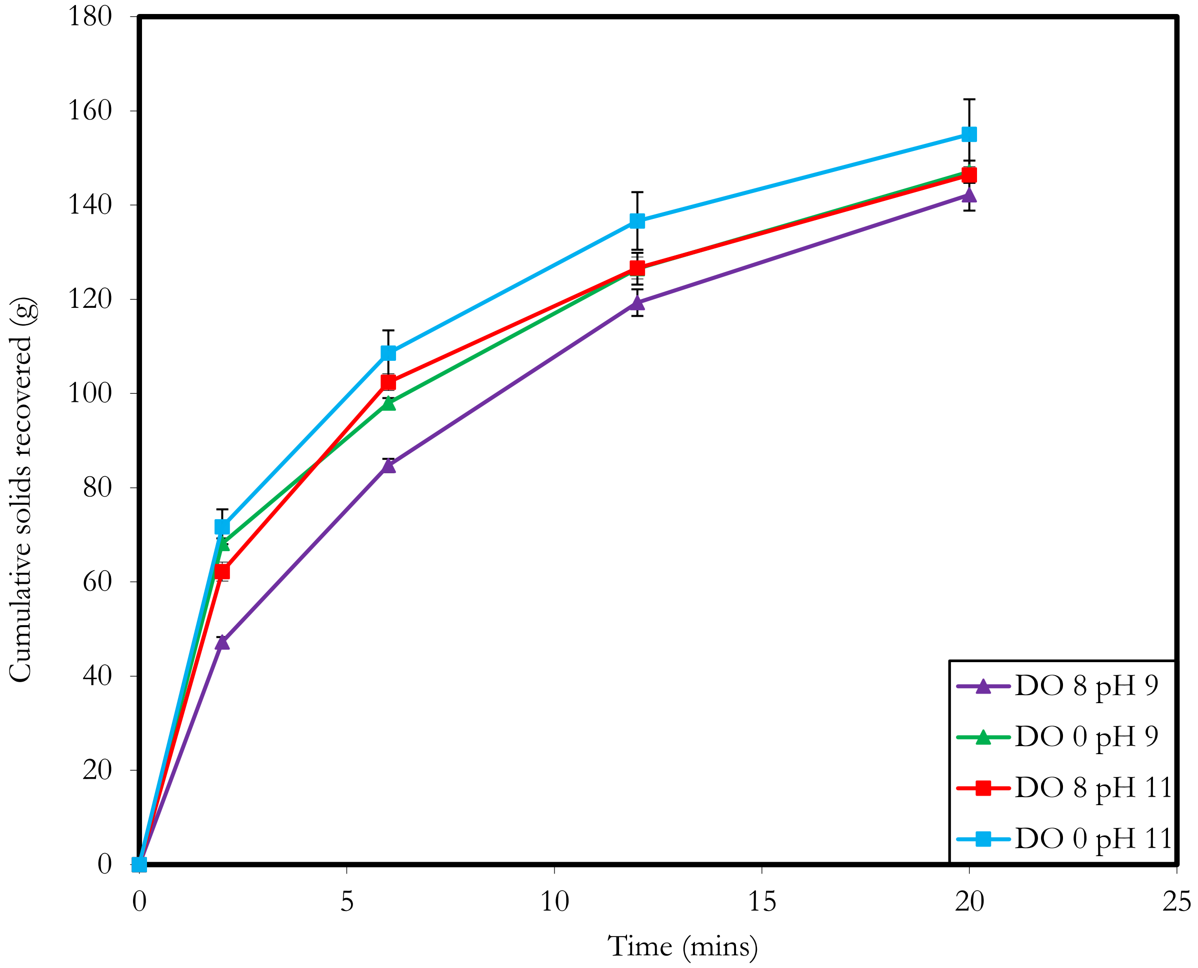


Figure 4-12: Cumulative solids recovered versus time for forged steel under dry grinding

Figure 4-12 shows solids versus time for forged steel media under dry grinding for all the conditions tested. It can be seen that DO 8/pH 9 yielded the lowest rate of solids recovery. The highest rate of solids recovery was obtained at DO/pH 11. DO 0/pH 9 resulted in similar solids recovery rates to that obtained at DO 8/pH 11.

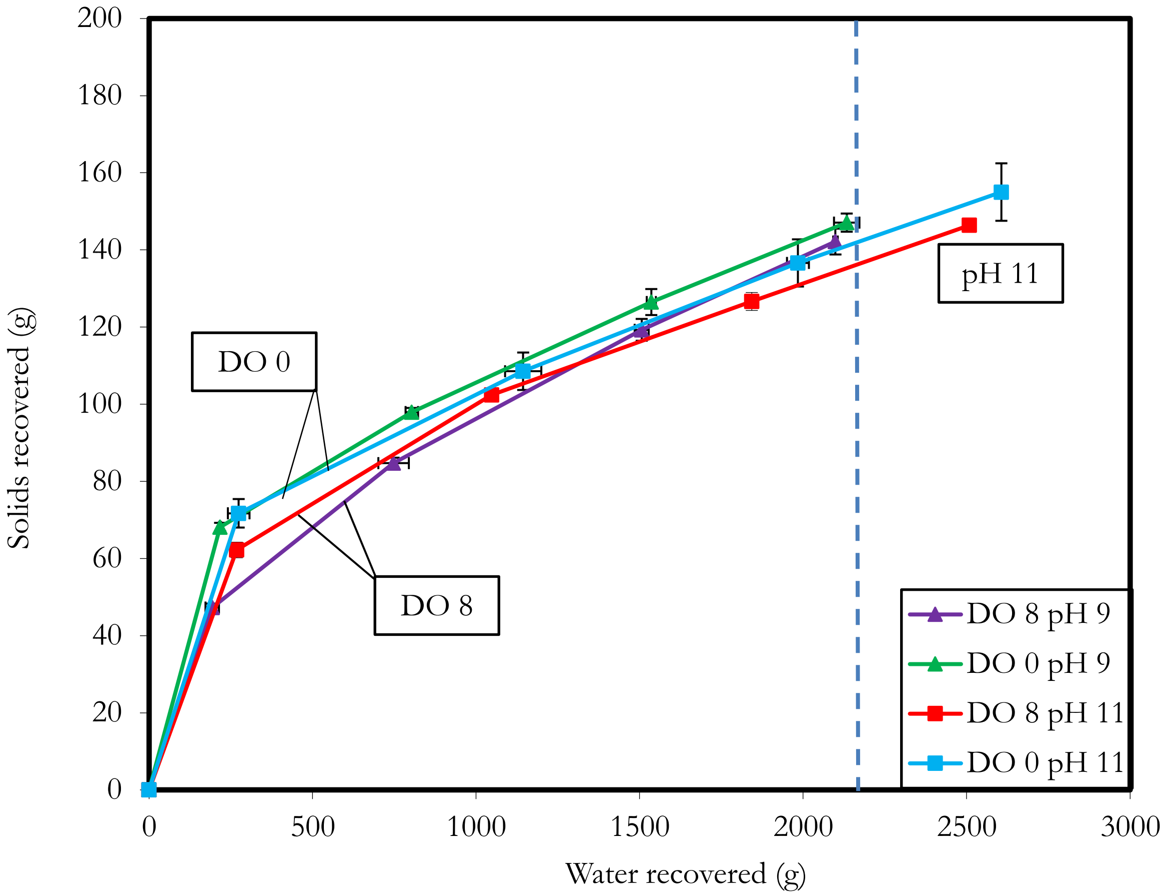


Figure 4-13: Solids versus Water recoveries for forged steel media under dry grinding

Figure 4-13 illustrates the influence of chemistry in the pulp phase during flotation on the amount of solids and water recovered for forged steel media under dry grinding for the conditions tested. Figure 4-13 shows that pH influenced the amount of water recovered; there was a substantial increase in the amount of water recovered when the pH was increased from 9 to 11. The figure also shows that at each pH, DO 0 initially resulted in higher solids recovery as compared to DO 8.

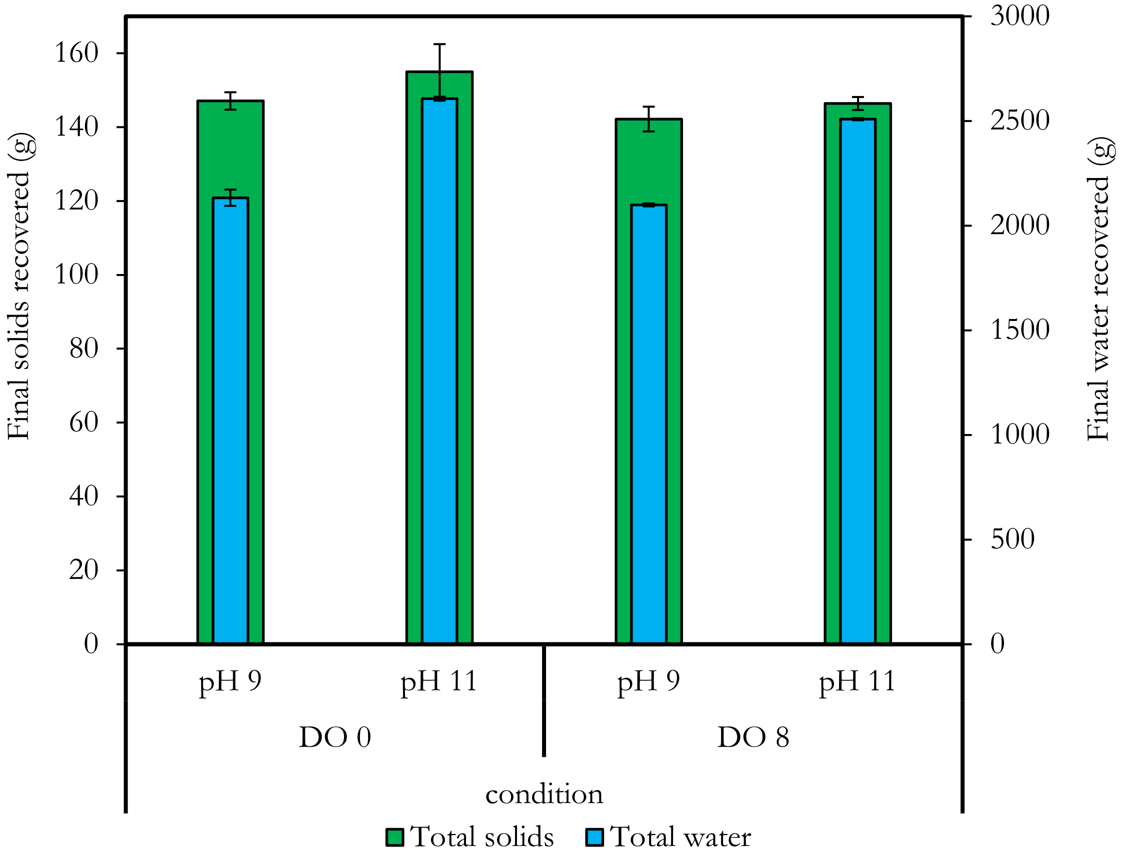


Figure 4-14: Final water and solids recovered for forged steel media under dry grinding for the conditions

Figure 4-14 shows the total water and solids recovered under different conditions tested during dry grinding with forged steel media. Figure 4-14 shows that the highest amounts of water and solids were recovered at pH 11 while pH 9 resulted in the lowest water recoveries. It can be seen from the figure that the total amount of water and solids recovered increased when the slurry was sparged with nitrogen gas. The water recovery also increased with increasing pH of the system during grinding.

4.4.1.2. Ceramic media

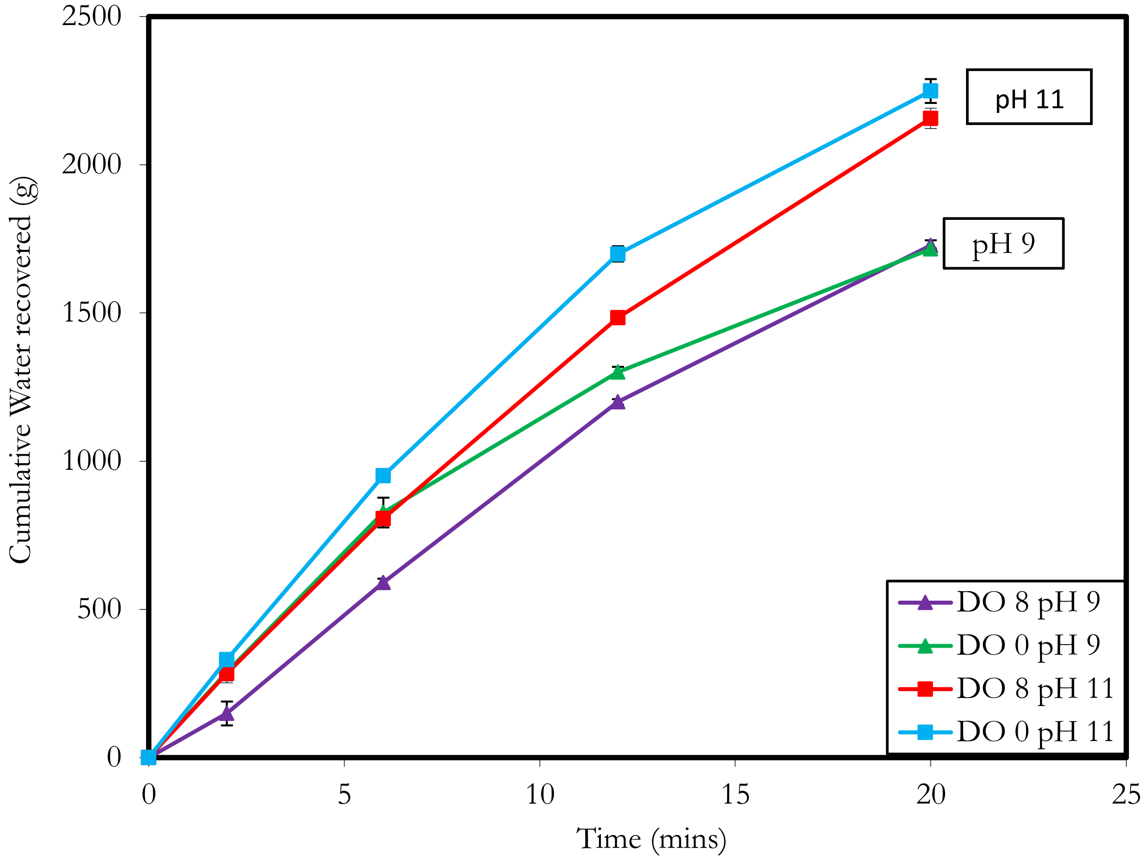


Figure 4-15: Cumulative water recovered versus time for ceramic media under dry grinding

Figure 4-15 indicates the rate of water recovery under dry grinding with ceramic media for all conditions tested. The figure shows that DO 0/pH 11 resulted in the highest rate of water recovery. The lowest rate of water recovery was obtained at DO 8/pH 9. At pH 11, the rate of water recovery increased when the slurry was sparged with nitrogen gas. Figure 4-15 also shows that at pH 9, the rate of water recovery was considerably lower at DO 8 than the rate of recovery that was recorded at DO 0. However, the final amount of water recovered was in a similar range.

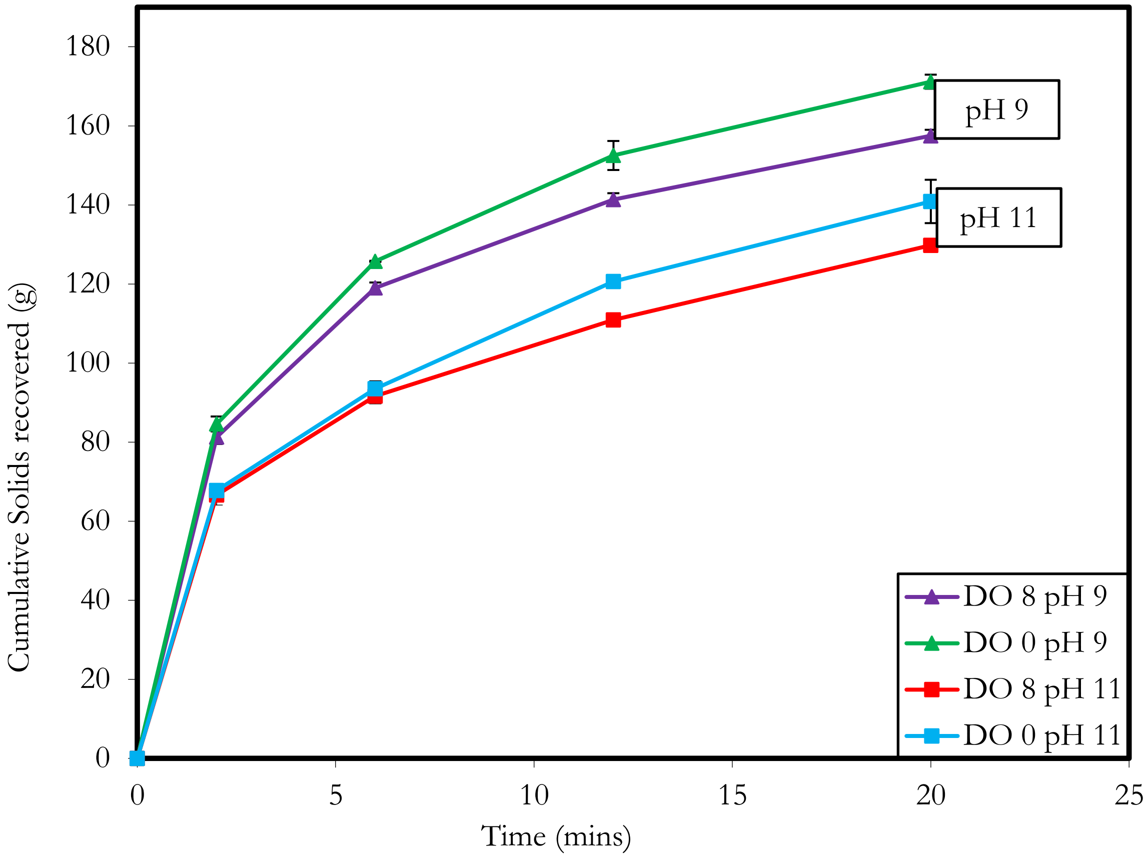


Figure 4-16: Cumulative solids recovered versus time for ceramic media under dry grinding

Figure 4-16 shows solids recovery versus time and therefore indicates the rate of solids recovery for ceramic under dry grinding for conditions tested. The figure shows that DO 0/pH 9 yielded the highest rate of solids recovery while DO 8/pH 11 resulted in the lowest solids recovery. It can be clearly seen that an increase in pH resulted in a reduction in the rate of solids recovery. For all the conditions tested, the removal of oxygen from the system resulted in a decrease in the rate at which solids were recovered.

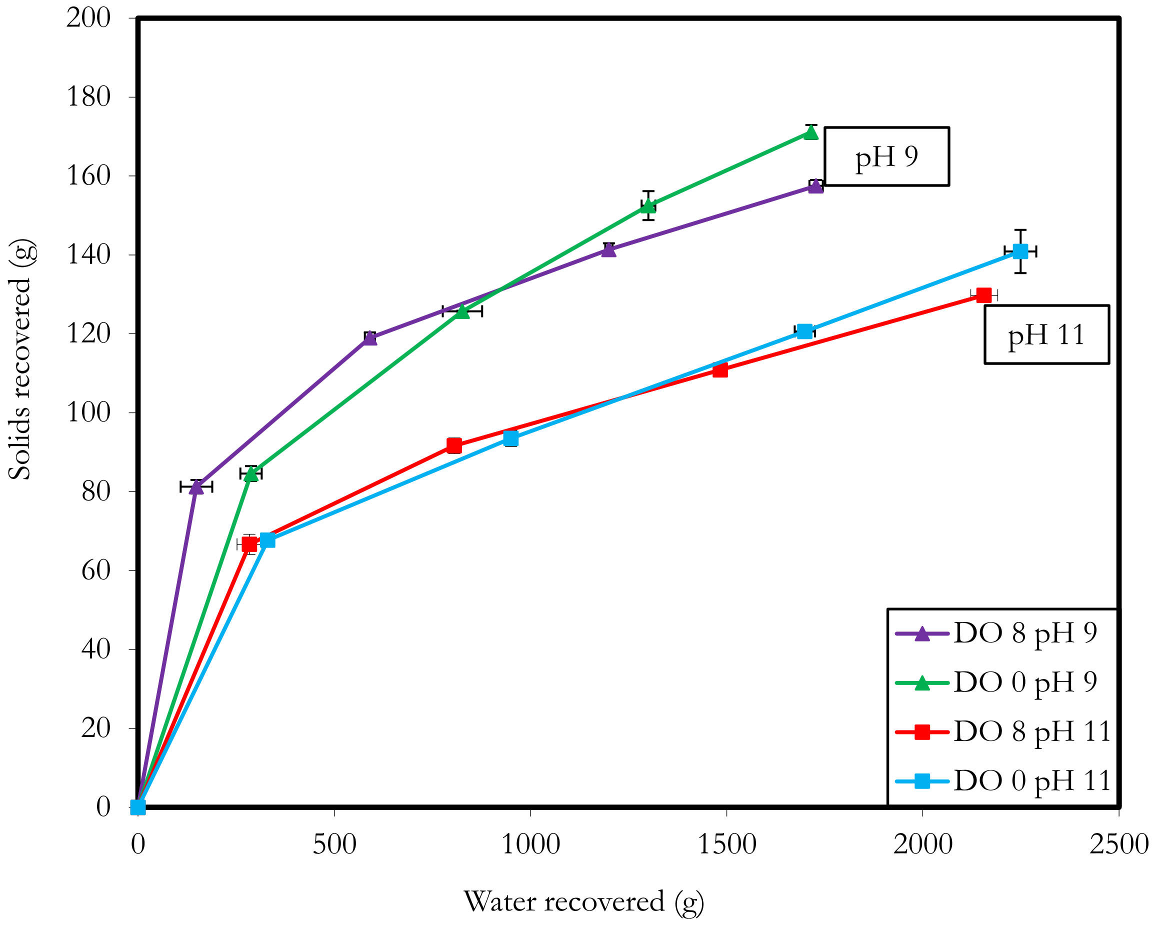


Figure 4-17: Solids versus water recoveries for ceramic media under dry grinding

Figure 4-17 shows the effects of pH and the concentration of DO in the pulp phase during flotation on the solids and water recovered for ceramic media under dry grinding. It can be noted that both water and solids recovery are influenced by pulp chemistry in the flotation cell. It can be seen that the highest water recoveries were obtained at pH 11. On the other hand, the amount of solids recovered increased with decreasing pH. DO 0 yielded lower water and solids recoveries at the beginning of the flotation test and higher recoveries towards the end of the test.

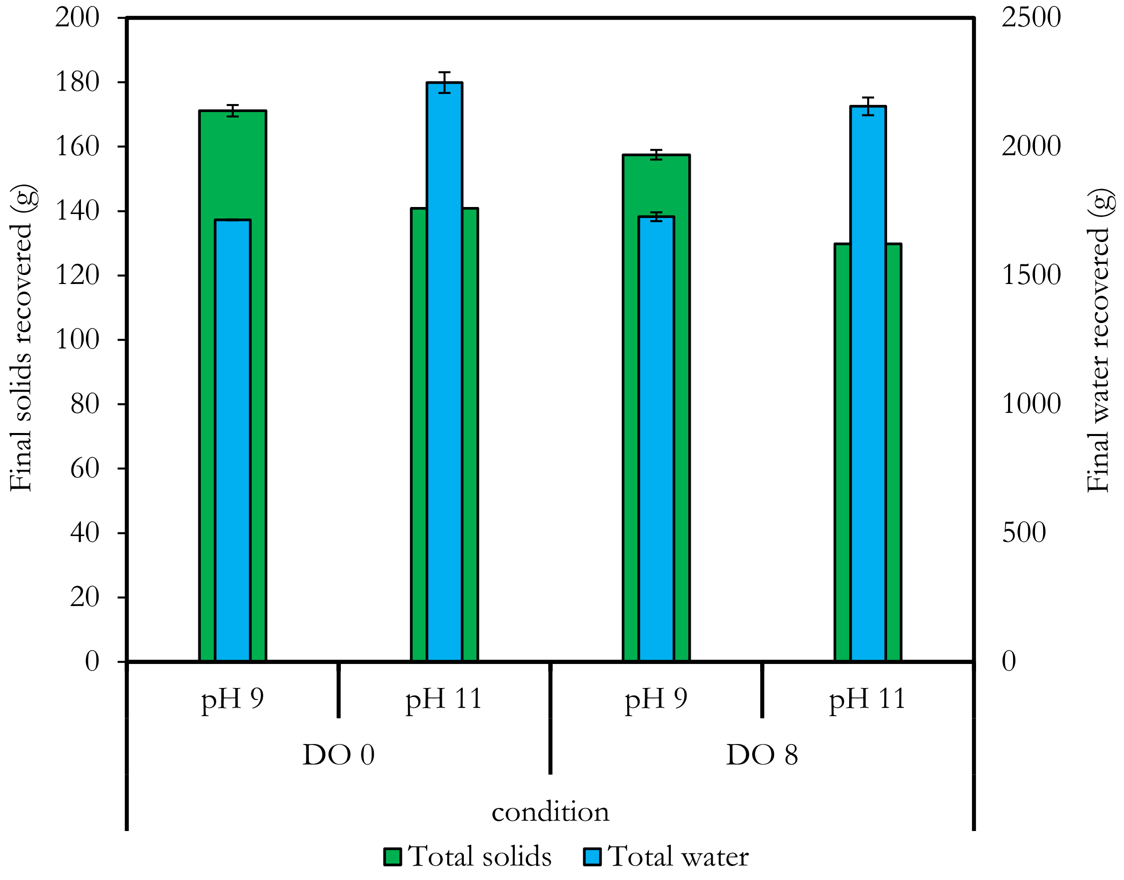


Figure 4-18: Final water and solids recovered for ceramic media under dry grinding for all the conditions

Figure 4-18 shows the total solids and water recovered for ceramic media under dry grinding for all the conditions tested. The figure shows that the highest amount of water was recovered at pH 11. The lowest water recoveries were obtained at pH 9. It can also be observed that the recovery of water significantly depends on pH; but only slightly changes upon changing DO concentration.

It is also clear from Figure 4-18 that the highest amount of solids was recovered at DO 0/pH 9. DO 8/pH 11 produced the lowest solids recovery. The amount of solids recovered generally decreased with increasing pH. It can also be noted that the amount of solids increased upon removal of DO from the system.

4.5. The effects of grinding media on solids and water recoveries under dry and wet grinding

4.5.1. Water recovery

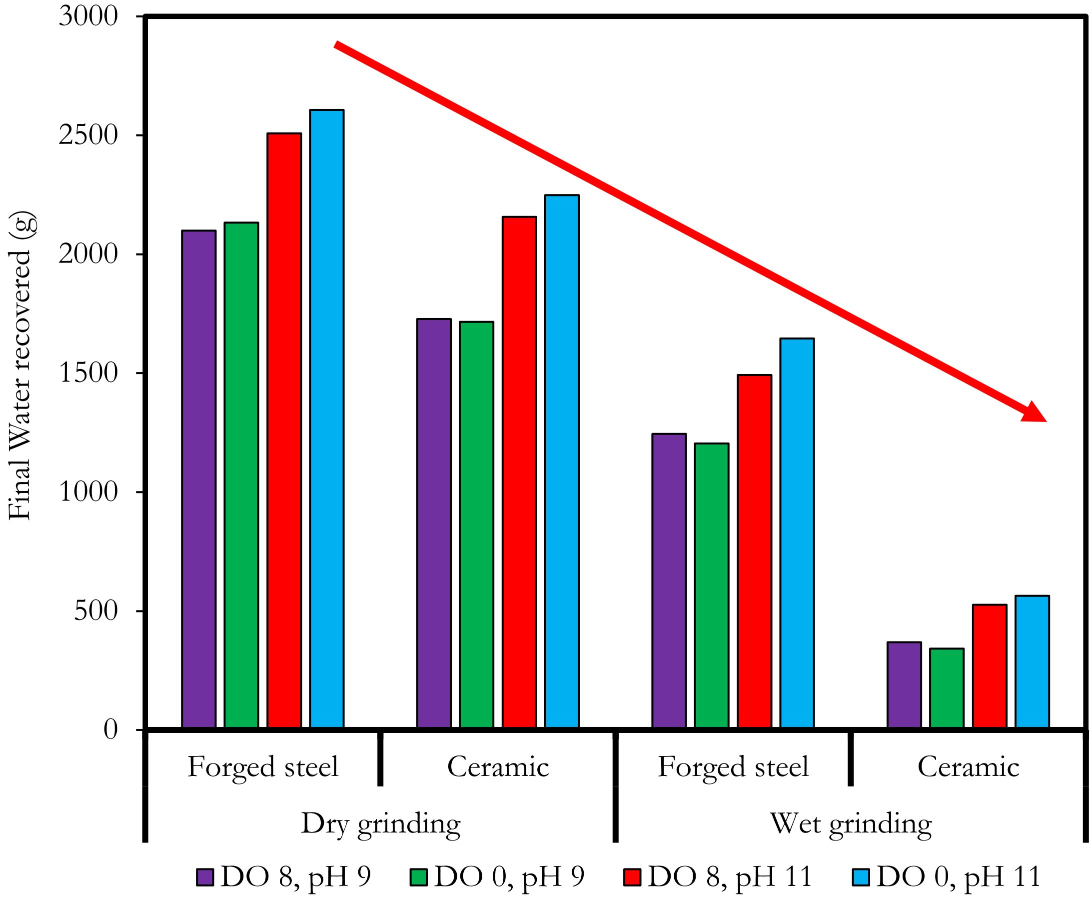


Figure 4-19: Final water recovered for forged steel and ceramic media under dry and wet grinding for all conditions

Figure 4-19 shows the results for the final amount of water recovered for both forged steel and ceramic media under wet and dry grinding for all the conditions tested. The highest amount of water was recovered at DO 0/pH 11 under dry grinding with forged steel. The lowest water recoveries were obtained at DO 0/pH 9 under wet grinding with ceramic media. For all conditions tested, water recovery increased with increasing pH. Overall, wet grinding yielded lower water recoveries relative to dry grinding. Furthermore, forged steel media resulted in higher water recoveries compared to ceramic media, under both dry grinding and wet grinding.

4.5.2. Solids recovery

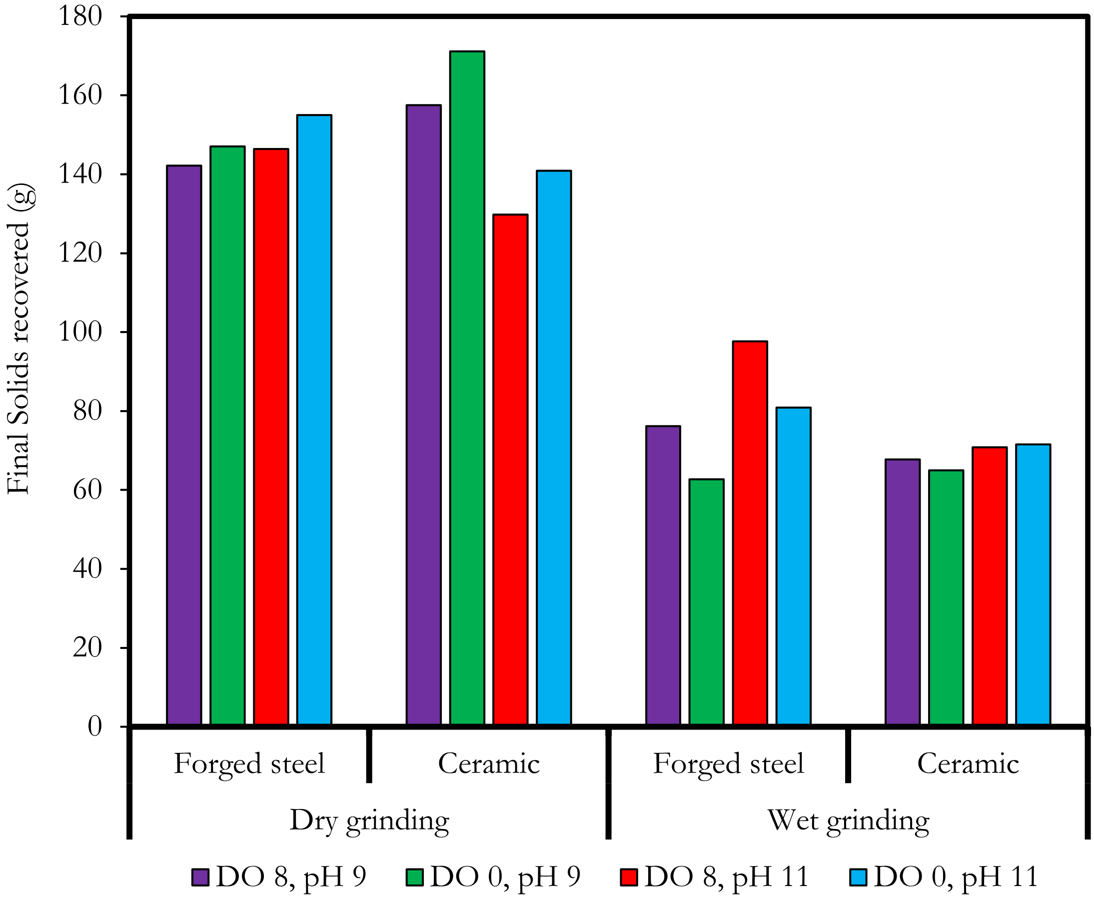


Figure 4-20: Final Solids recovered for forged steel and ceramic media under dry and wet grinding for all conditions

Figure 4-20 shows the total solids recovered for forged steel and ceramic media under dry and wet grinding for all conditions tested. Figure 4-20 shows that the highest amount of solids was recovered at DO 0/pH 9 during dry grinding with ceramic media. This is followed by DO 8/pH 9 under dry grinding with ceramic media. The lowest solids recovery was produced at DO 0/pH 9 during wet grinding with forged steel media. In general, wet grinding for all the conditions tested resulted in lower solids recovered compared to dry grinding.

Upon observation of both Figure 4-19 and Figure 4-20, it can be seen that when water recoveries were high they were accompanied by high solids recoveries.

4.6. Pyrite recovery

It should be noted that for all the tests conducted, the synthetic ore contained 50 g of pyrite, which is 2.5 % of the mill feed.

4.6.1. Wet grinding

4.6.1.1. Forged Steel

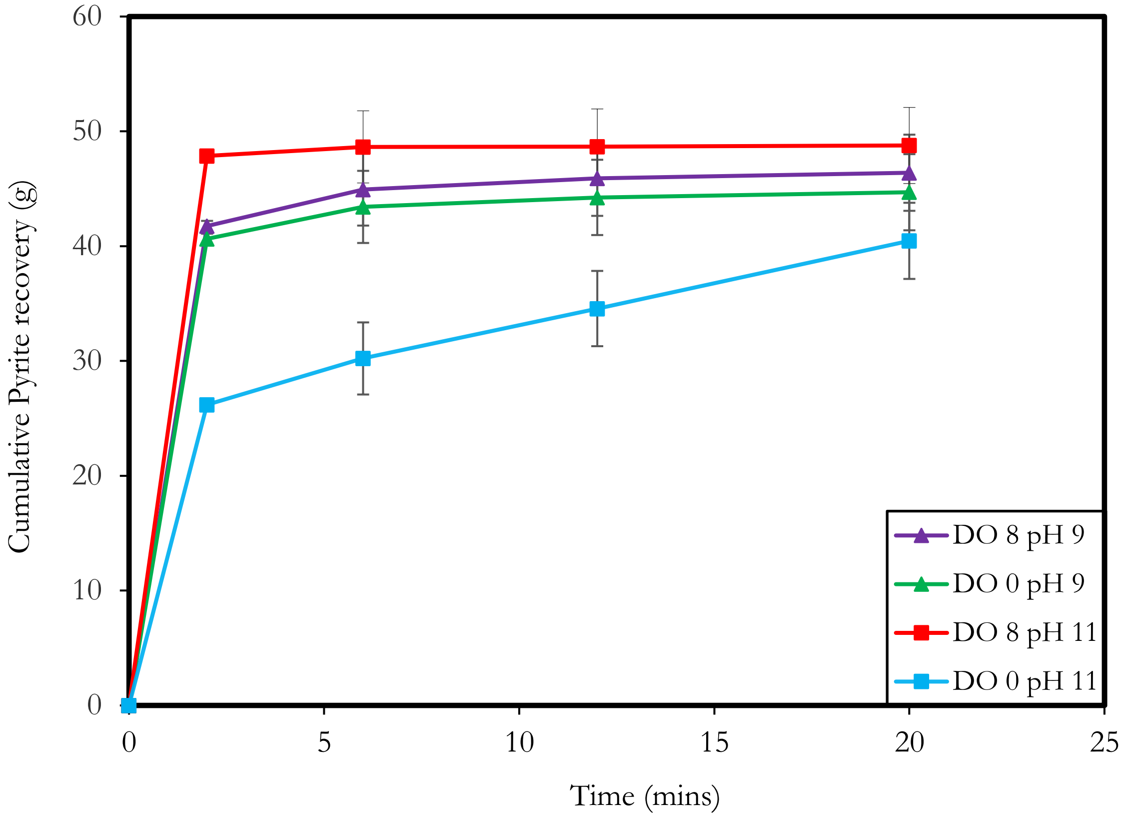


Figure 4-21: Cumulative pyrite recovery versus time for forged steel under wet grinding

Figure 4-21 shows pyrite recovery versus for the conditions tested under wet grinding with forged steel. It can be seen that DO 0/pH 11 resulted in the lowest rate of pyrite recovery. The highest rate of pyrite recovery was obtained at DO 8/pH 11. It can also be seen that at pH 9, the concentration of DO inside the mill during grinding did not have a significant influence on pyrite recoveries, however the opposite appears to be true for pH 11.

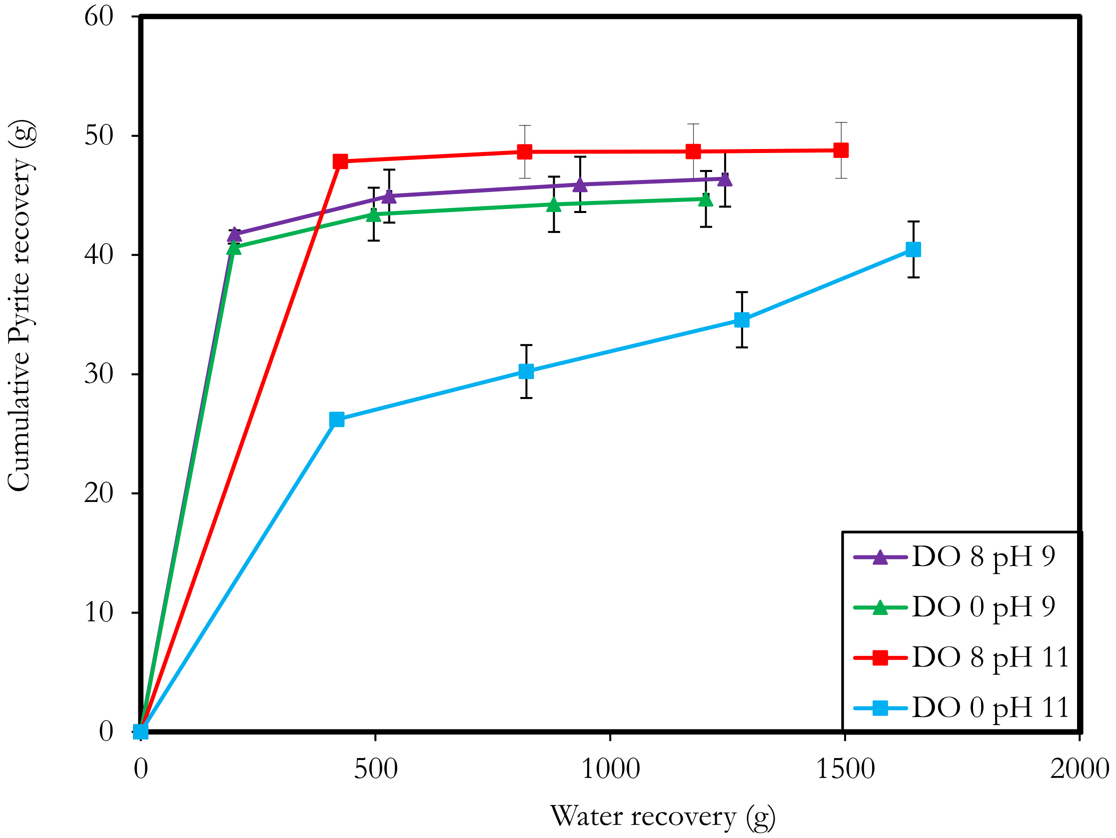


Figure 4-22: Cumulative pyrite recovery versus water recovery for forged steel under wet grinding for all conditions

Figure 4-22 shows the amount of pyrite recovered versus water when forged steel was used as a grinding media under wet grinding for all the conditions tested. These results show that the lowest pyrite recoveries were achieved at DO 0/pH 11 while the highest pyrite recoveries were observed at DO 8/pH 11. The effects of DO concentration at pH 9 on the pyrite recovery were marginal.

4.6.1.2. Ceramic Media

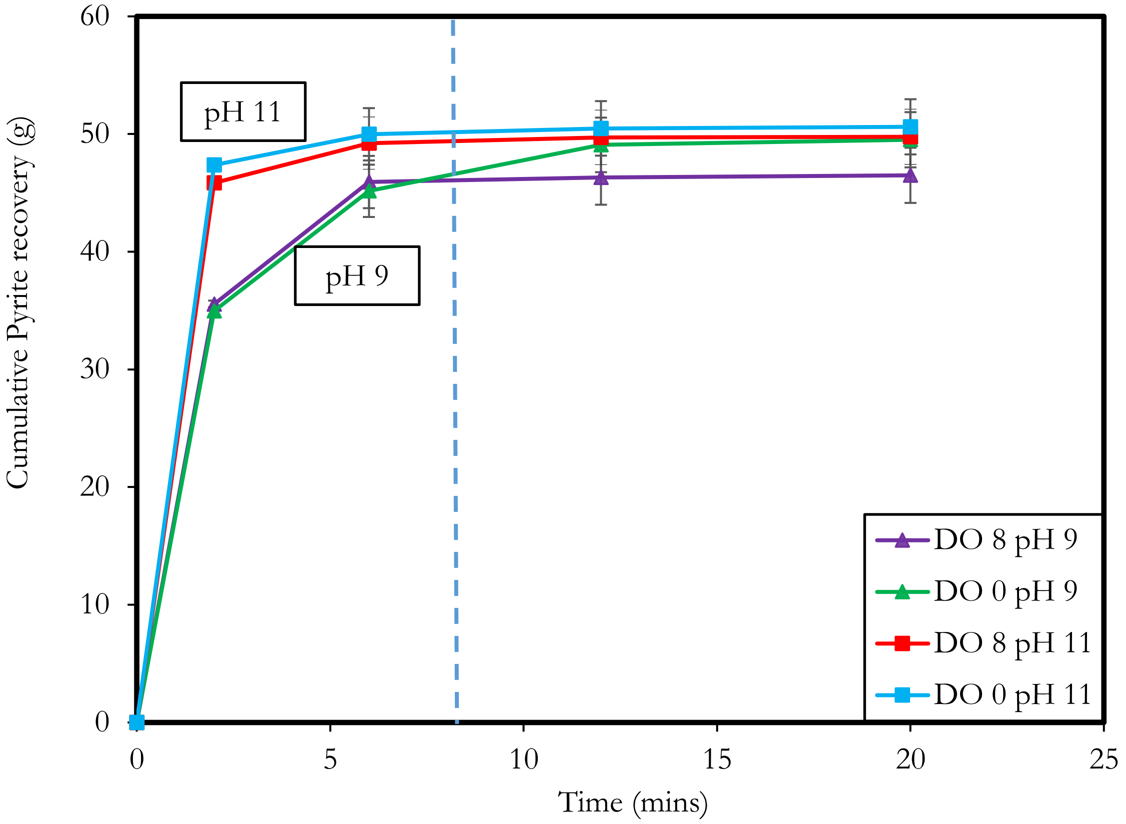


Figure 4-23: Cumulative pyrite recovery versus time for ceramic media under wet grinding for all the conditions

The results for pyrite recovery versus time are shown in Figure 4-23. The results indicate that after the first 8 minutes of flotation, higher pyrite recoveries were obtained at pH 11 compared to pH 9 while pyrite recoveries were independent of DO concentration. However, the final recoveries were within the same range for all conditions.

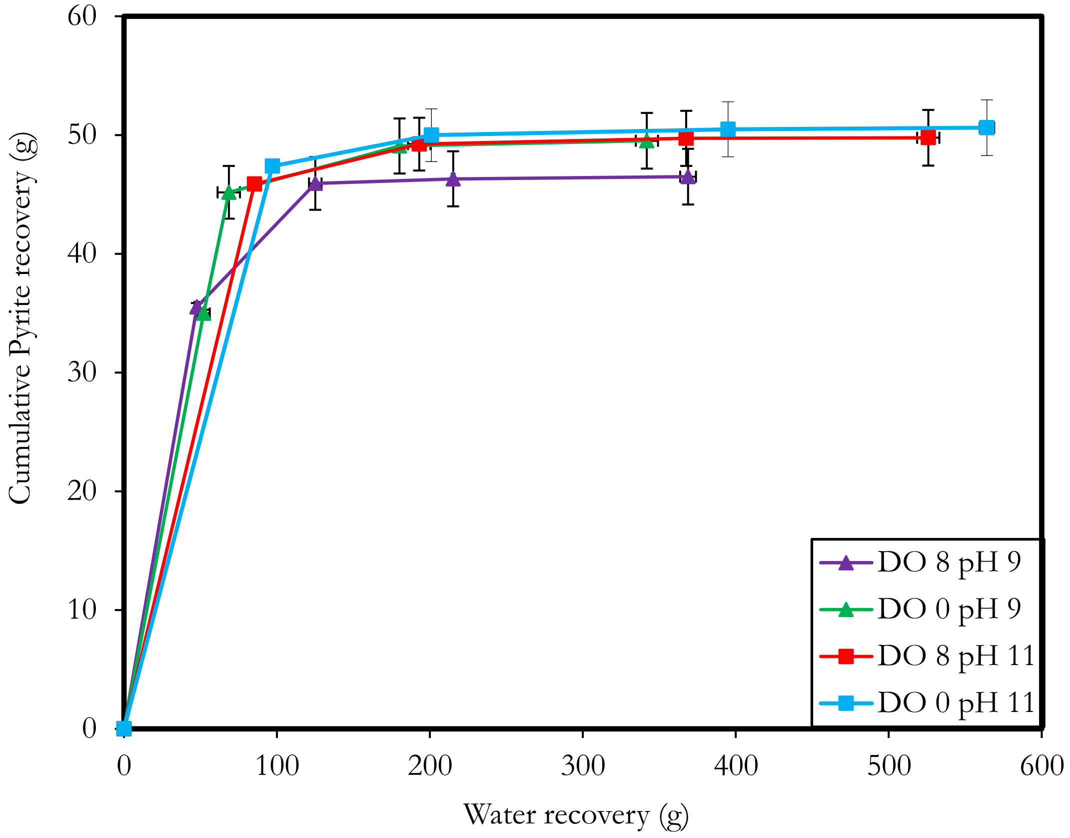


Figure 4-24: Cumulative pyrite recovery versus water recovery for ceramic media under wet grinding for all the conditions

Figure 4-24 shows pyrite recovery versus water recovery for ceramic media under wet grinding for all the conditions tested. From these results it is observed that the lowest pyrite recoveries were obtained at DO 8/pH 9. At pH 11, pyrite recovery did not depend on DO concentration inside the mill. It can also be observed that pyrite recovery increased upon removal of DO inside the mill during grinding at pH 9.

4.6.2. Dry grinding

4.6.2.1. Forged Steel

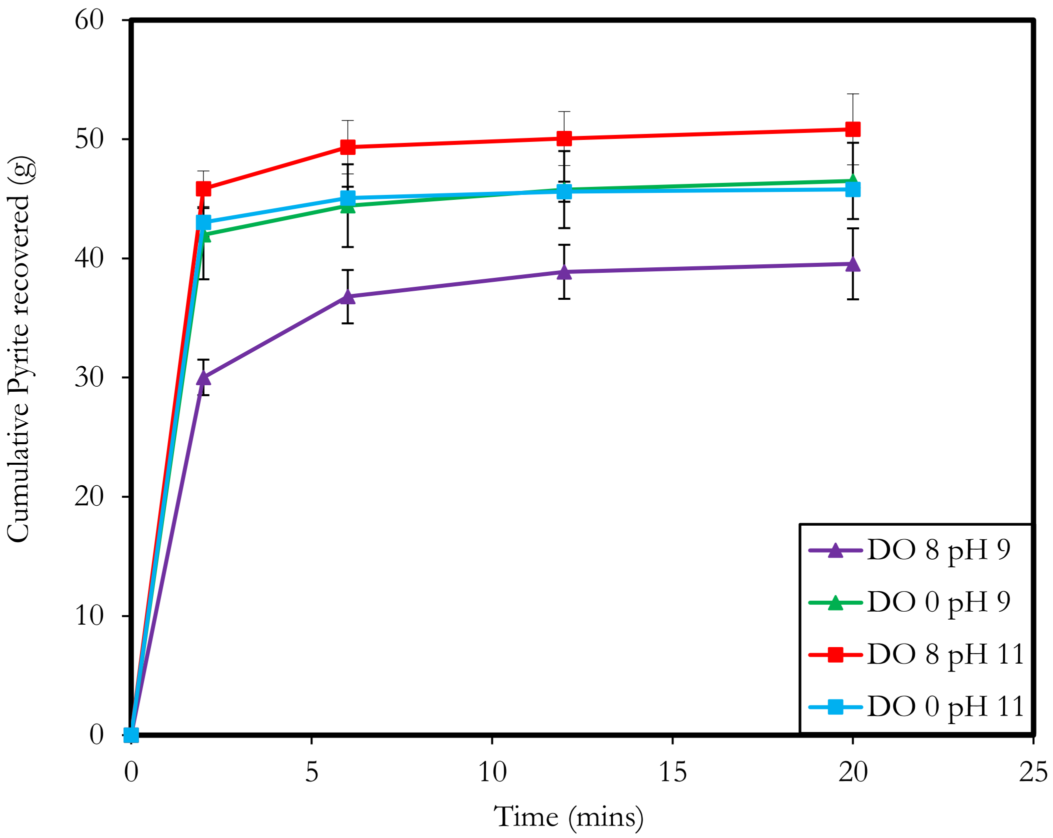


Figure 4-25: Cumulative pyrite recovery versus time for forged steel under dry grinding for all the conditions

Figure 4-25 shows the rate at which pyrite was recovered under dry grinding with forged steel. It can clearly be seen that the lowest rate of pyrite recovery was achieved at DO 8/pH 9. DO 8/pH 11 yielded the highest rate of pyrite recovery. At DO 0, the rate of pyrite recovery did not change upon change in pH during flotation.

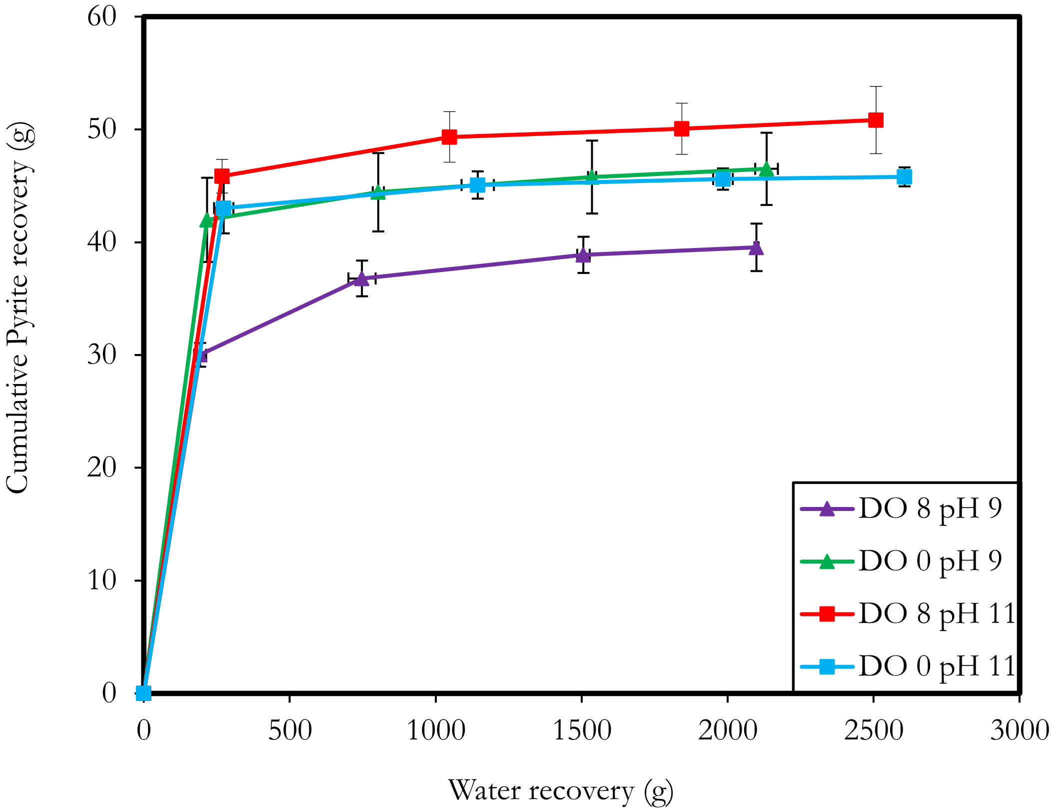


Figure 4-26: Cumulative pyrite recovery versus water recovery for forged steel under dry grinding for all the conditions

The results for pyrite recovery versus water recovery under dry grinding with forged steel for all the conditions tested are shown in Figure 4-26. It can be observed that DO 8/pH 9 resulted in the lowest pyrite recovery. The highest amount of pyrite was recovered at DO 8/pH 11. It is evident from this figure that pyrite recovery did not depend on the change in pH at DO 0.

4.6.2.2. Ceramic Media

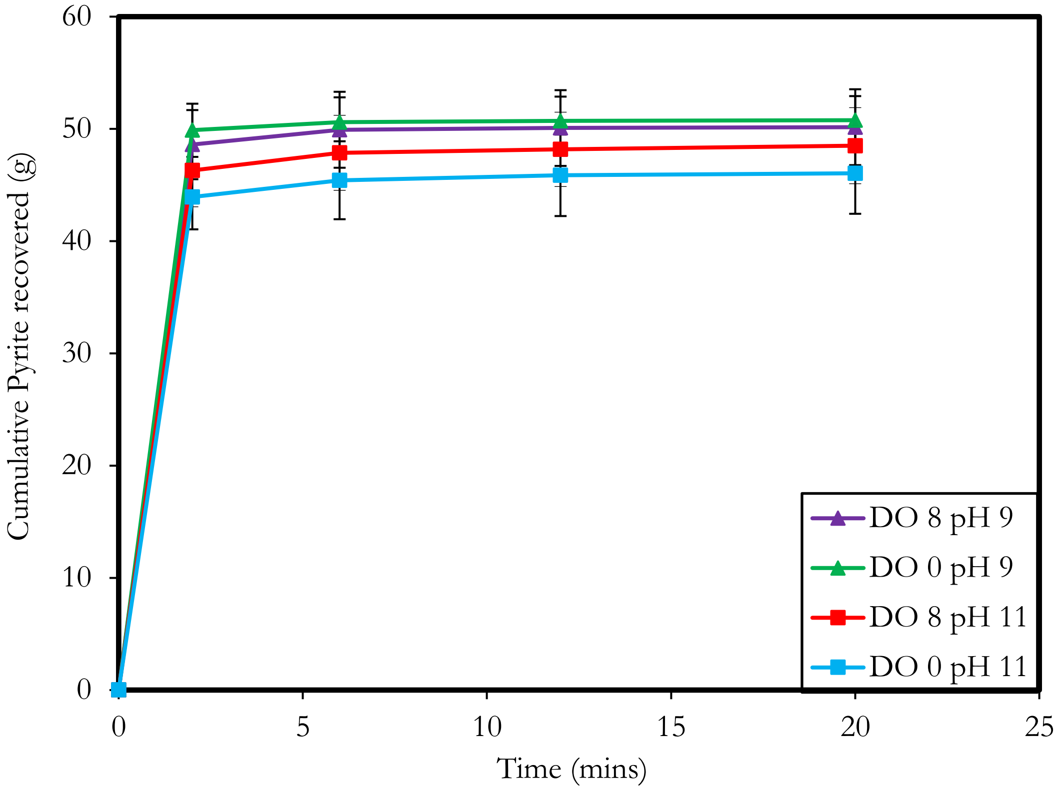


Figure 4-27: Cumulative pyrite recovery versus time for ceramic media under dry grinding for all the conditions

Figure 4-27 shows pyrite recovery versus time for ceramic media under dry grinding for all the conditions tested. The lowest rate of pyrite recovery was obtained at DO 0/pH 11, while the highest rate of recovery was observed at DO 0/pH 9. It can also be seen that at pH 9, the rate of pyrite recovery was slightly affected by the concentration of DO during flotation. It is also evident that at pH 11, the rate of pyrite recovery decreased upon removal of DO inside the flotation cell.

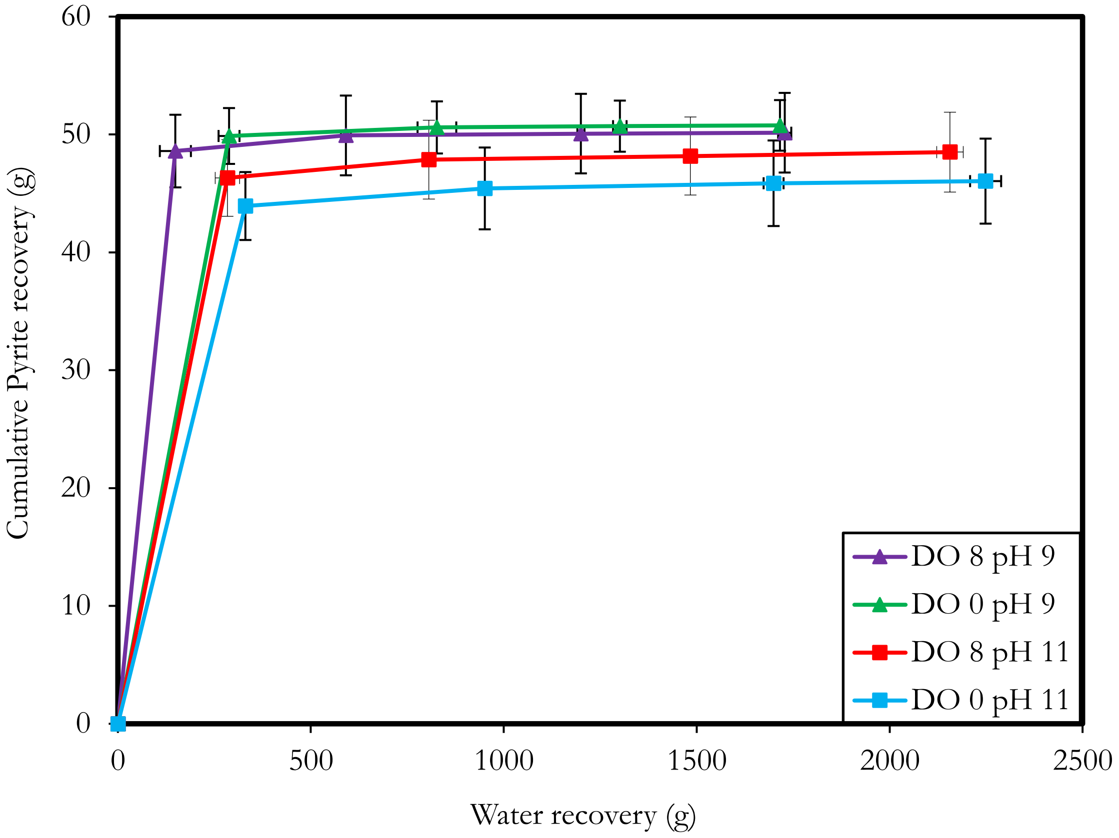


Figure 4-28: Cumulative pyrite recovery versus water recovery for ceramic media under dry grinding for all the conditions

The results for pyrite recovery versus water recovery during dry grinding with ceramic media for all the conditions tested are shown in Figure 4-28. It can clearly be seen that lowest pyrite recoveries were obtained at pH 11. It can also be seen that the pyrite recovery at pH 9 was independent of DO concentration. On the other hand, pyrite recovery decreased at pH 11 when oxygen was purged from the flotation cell using nitrogen.

4.7. The effects of grinding media on pyrite recovery and grade under wet and dry grinding

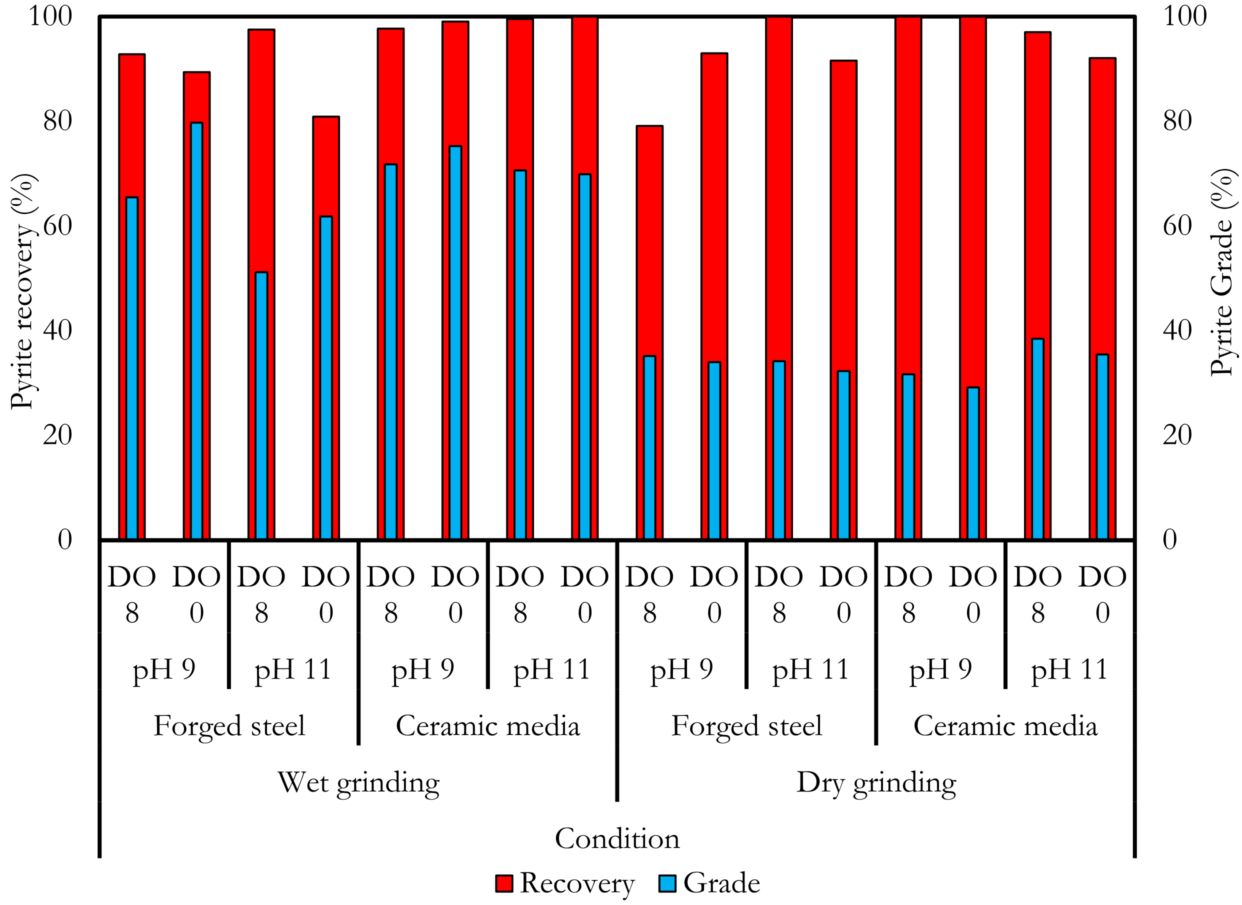


Figure 4-29: Final pyrite recovery and grade forged steel and ceramic media under wet and dry grinding for all conditions

The results for the final pyrite recovery and grade obtained for all tests are shown in Figure 4-29. The results indicate that the highest recoveries of pyrite were achieved with inert grinding media (ceramic media) under wet grinding. The maximum recoveries obtained were around 100%. Overall, the lowest recoveries were obtained with forged steel under dry grinding. Pyrite recovery was generally constant at DO 0/pH 11 under dry grinding with the two different grinding media. On the other hand, pyrite recovery showed a dramatic increase at DO 0/pH 11 under wet grinding when the grinding media was changed from active to inert. Furthermore, it can be observed that pyrite recovery decreased upon removal of DO during wet grinding with forged steel, while DO removal resulted in marginal differences in pyrite recovery when ceramic media was used in a wet system. Pyrite grade was generally constant for the two grinding media used under dry grinding. The results show that under wet grinding, ceramic media generally yielded better pyrite grade as compared to forged steel. Dry grinding resulted in lowest pyrite grade while wet grinding produced higher grades.

Figure 4-30 to Figure 4-33 makes these results even more clear by showing how pyrite grade changes with its recovery.

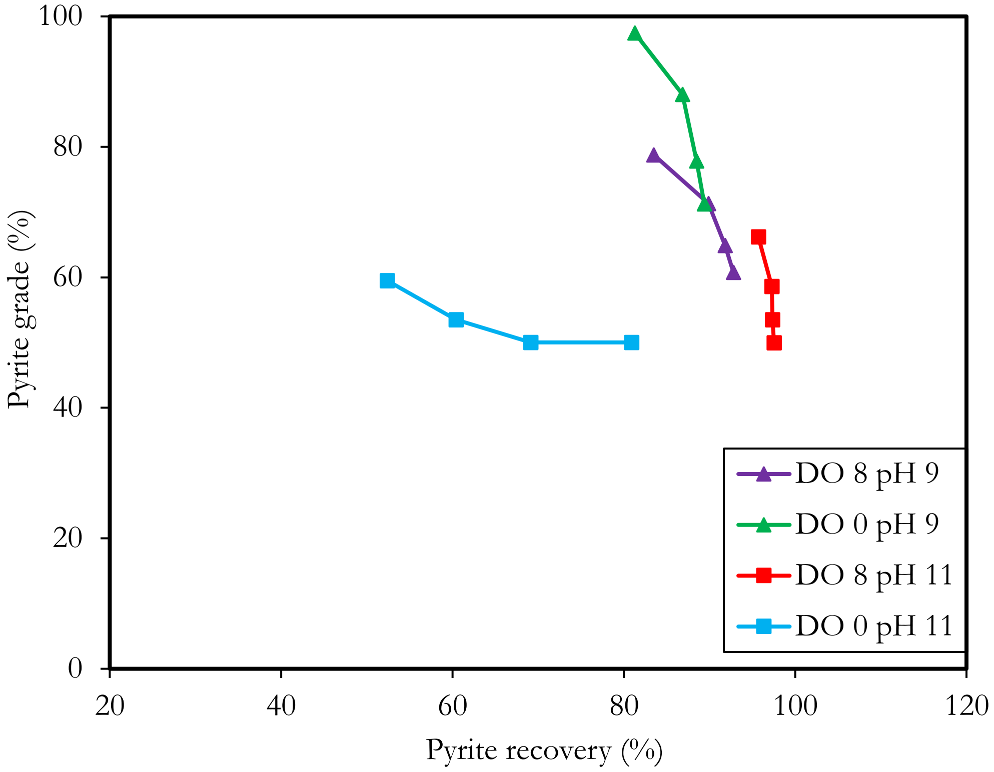


Figure 4-30: Pyrite grade versus pyrite recovery for forged steel under wet grinding

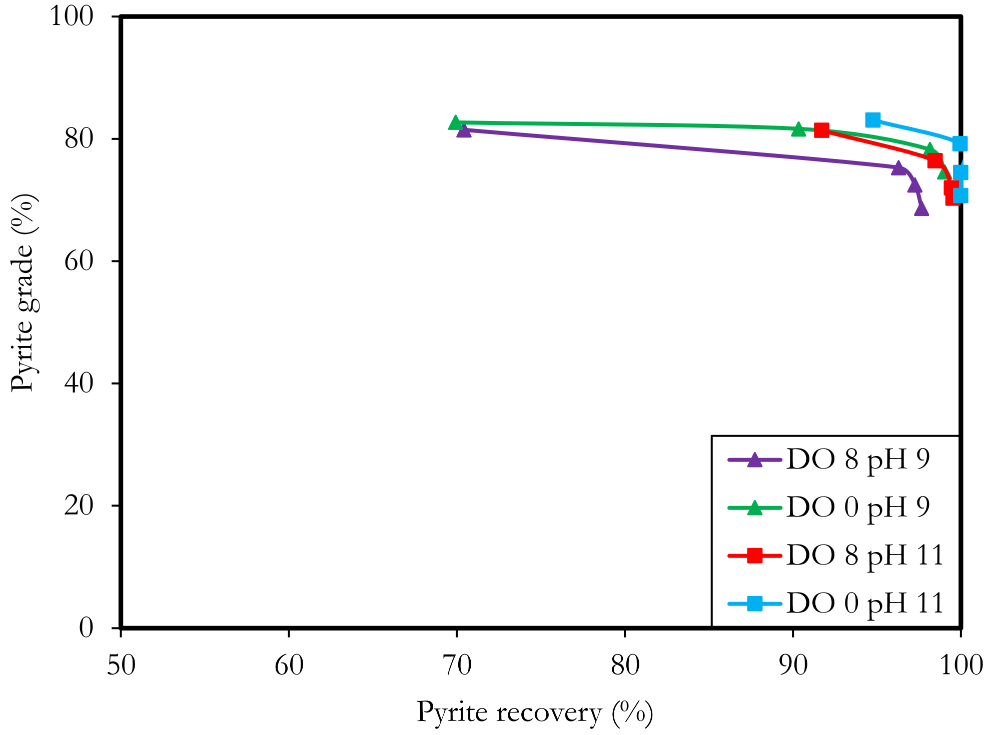


Figure 4-31: Pyrite grade versus pyrite recovery for ceramic media under wet grinding

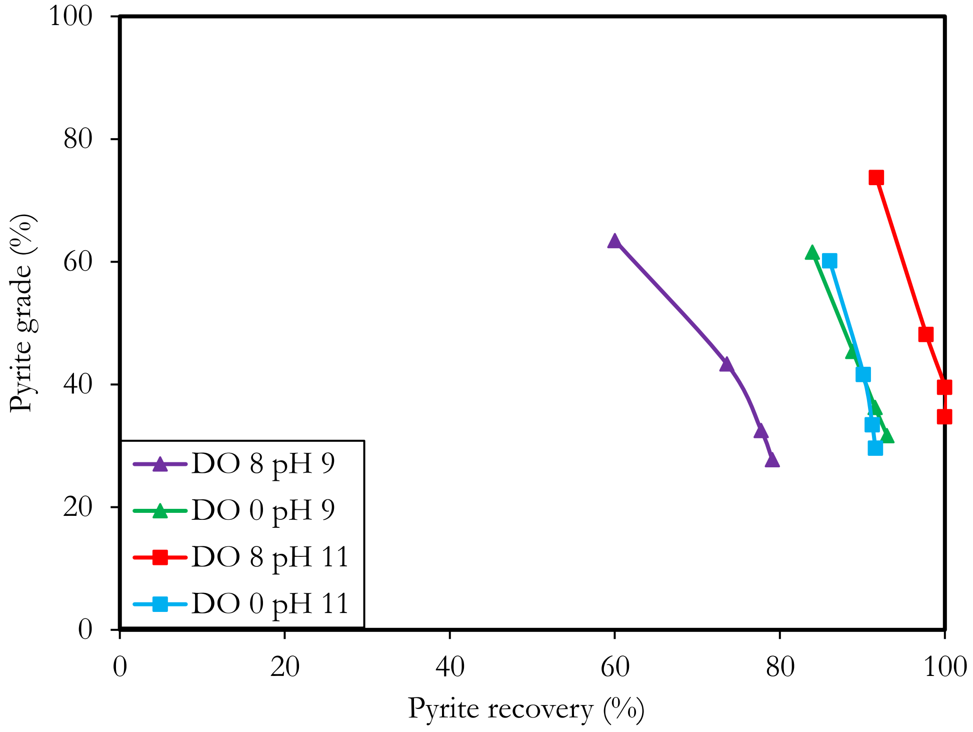


Figure 4-32: Pyrite grade versus pyrite recovery for forged steel under dry grinding

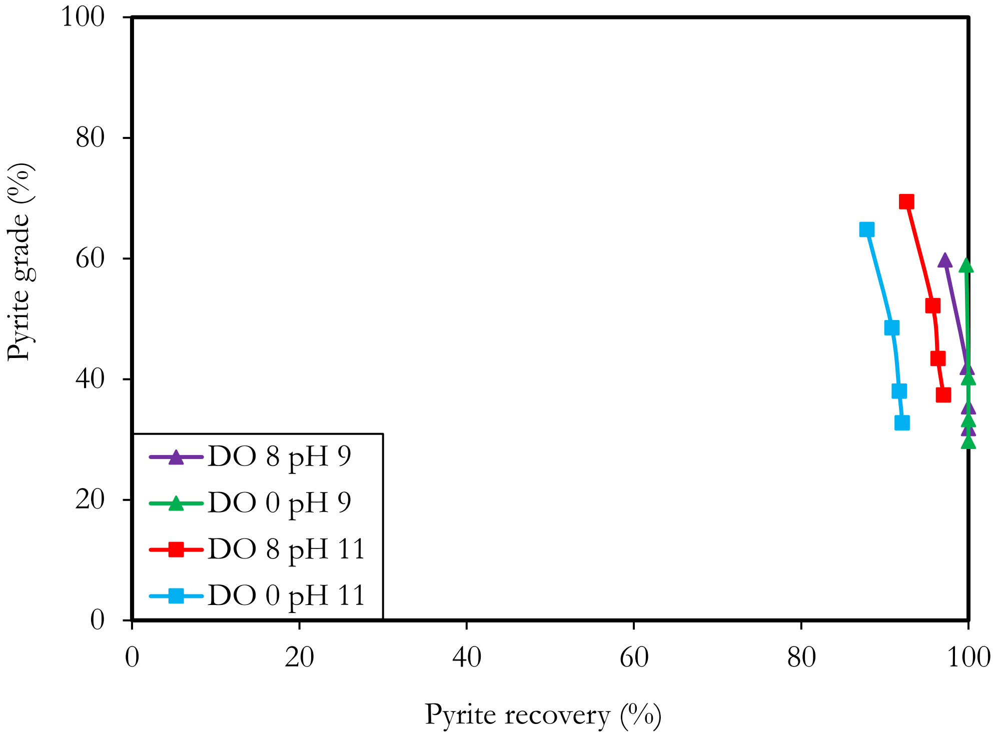


Figure 4-33: Pyrite grade versus pyrite recovery for ceramic media under dry grinding

4.8. EDTA extraction

The EDTA extraction measurements were performed with the samples extracted from the mill discharge under wet grinding and from the flotation cell feed under dry grinding. The percentage of the EDTA extractable iron at different grinding conditions is shown in Figure 4-34.

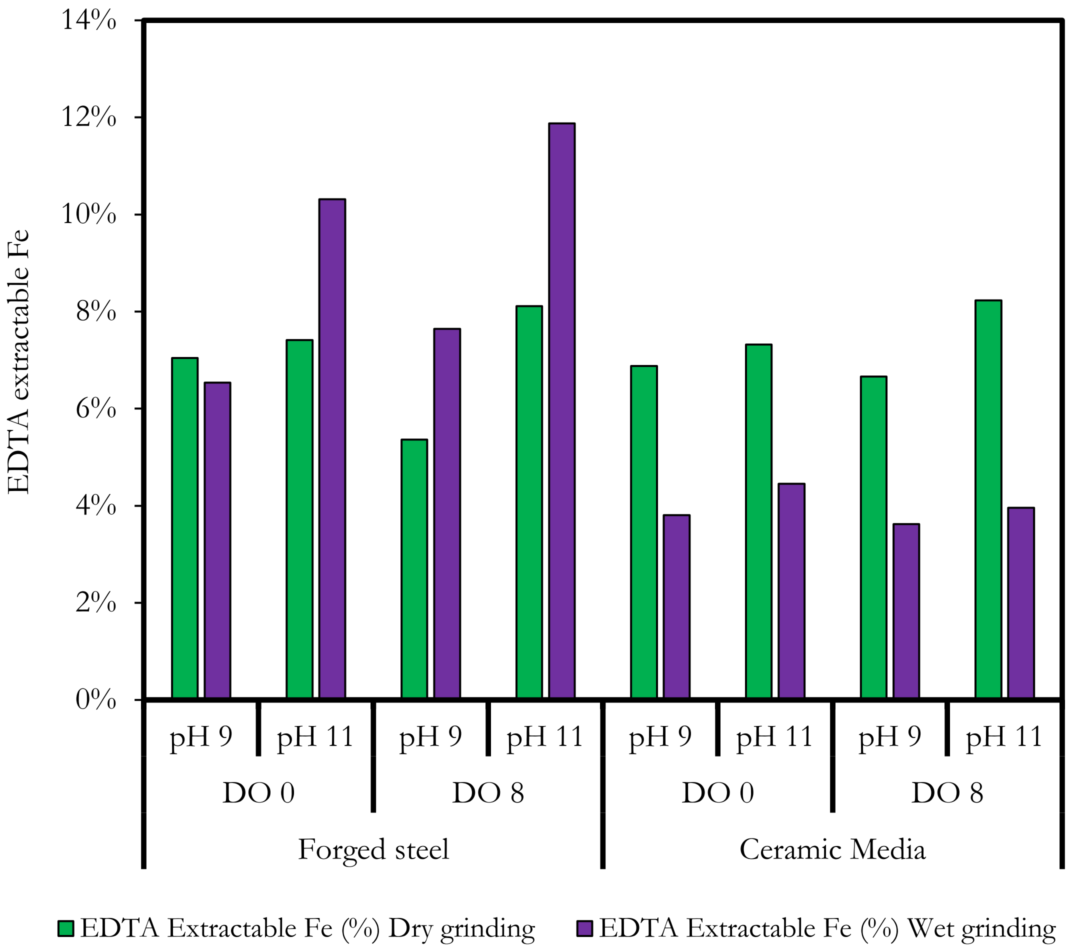


Figure 4-34: EDTA extractable iron under different grinding conditions for dry and wet grinding

Forged steel generally led to higher amounts of iron oxidation products than ceramic media under wet grinding. In addition to this, forged steel produced the highest amount of iron oxidation products during wet grinding at DO 8/pH 11 than any other conditions, while the amount was lowest when milling was conducted with ceramic media at DO 0/pH 9 under wet grinding environment. As seen from Figure 4-34, an increase in pH resulted in more iron being extracted. The figure also shows that for both ceramic media and forged steel, DO 8 produced more EDTA extractable iron than DO 0 at pH 11.

4.9. Flotation rate constants

The flotation recovery rate constants for overall solids and pyrite recoveries were modelled using a classical first-order model (Xiangning *et al.*, 2017);

$$R = R_{max}(1 - e^{kt}) \qquad \text{Eq } 4-1$$

Where R is the calculated recovery, R_{max} is the theoretical maximum recovery, k is the flotation first-order rate constant and t is time. Using this model k was determined using the Excel solver function.

Table 4-1: Overall solids first order flotation constants for all the test constants

Solids recovery		***Forged steel***				***Ceramic Media***			
		DO 0		DO 8		DO 0		DO 8	
		pH 9	pH 11	pH 9	pH 11	pH 9	pH 11	pH 9	pH 11
First order rate constants, k (min^{-1})	***Dry grinding***	**0.249**	**0.264**	**0.155**	**0.241**	**0.306**	**0.262**	**0.336**	**0.321**
	Wet grinding	**0.597**	**0.358**	**0.649**	**0.760**	**0.518**	**0.910**	**0.538**	**0.856**

Table 4-2: First order pyrite flotation constants for all the conditions tested

Pyrite recovery		***Forged steel***				***Ceramic Media***			
		DO 0		DO 8		DO 0		DO 8	
		pH 9	pH 11	pH 9	pH 11	pH 9	pH 11	pH 9	pH 11
First order rate constants, k (min^{-1})	***Dry grinding***	**1.26**	**1.46**	**0.739**	**1.27**	**2.99**	**1.60**	**1.79**	**1.62**
	Wet grinding	**1.26**	**0.597**	**1.21**	**2.03**	**0.620**	**1.48**	**0.725**	**1.29**

The results shown in Table 4-1 and Table 4-2. Table 4-1 indicate that dry grinding resulted in slower kinetics of floating of solids than wet grinding. It can also be established from the same table that ceramic media resulted in relatively faster floating of solids under both wet and dry grinding than forged steel media. Again, it is clear from Table 4-1 that an increase in pH resulted in faster floating of solids under dry grinding with forged steel, while the opposite is true for ceramic media. This finding is consistent with the solids recovery results presented in section 4.3

Table 4-2 shows the results obtained in the kinetic analysis of the pyrite flotation results obtained at different pH values and DO concentrations. It can be seen that ceramic media resulted in faster floating of pyrite under dry grinding than wet grinding. It can also be observed that under dry grinding with ceramic media, an increase in pH resulted in slower floating of pyrite. The opposite is true for wet grinding. It can also be established from the same table that at DO 8, an increase in pH led to faster recovering of pyrite when forged steel was used as a grinding media, under both dry and wet grinding. Again, it can be seen that forged steel resulted in faster floating of pyrite under wet grinding than dry grinding. Under DO 0, it is not clear as to how both pH and grinding environment affect kinetics pyrite recovery.

5. CHAPTER FIVE: Discussion

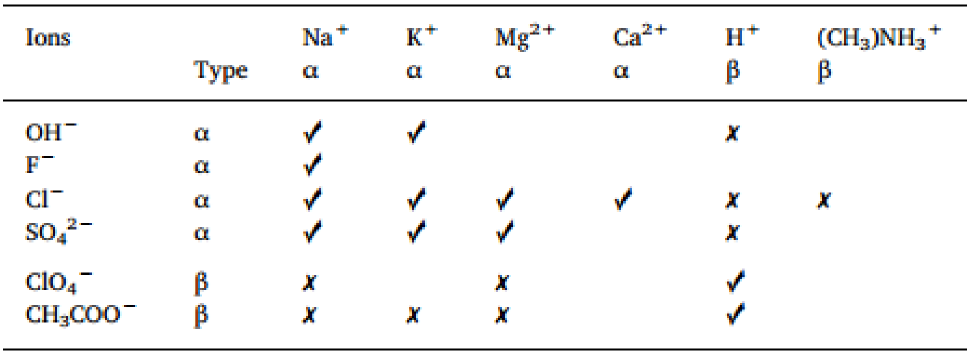
The objective of this study was to investigate and understand the effects of chemical conditions, specifically DO and pH during grinding and flotation, on the flotation response of a pyrite containing synthetic ore milled under dry and wet grinding environments. The results obtained in the study are discussed in relation to the answers to the key questions formulated in Chapter 2:

- How does DO during grinding affect solids and water recovery, as well as the flotation response of pyrite in the presence of quartz?
- How does pH during grinding affect solids and water recovery, as well as the flotation response of pyrite in the presence of quartz?
- How do different grinding media types affect the floatability of pyrite in the presence of quartz?
- How does flotation pulp chemistry affect recovery of pyrite following dry grinding?

This chapter begins with a discussion of the effect of pulp chemistry on solids and water recovery under wet and dry grinding environments, followed by the effects of grinding media type. The effect of pulp chemistry on the recovery of pyrite is then considered.

5.1. The effect of pulp chemistry on solids and water recovery

The effects of pulp chemistry on solids and water recovery are considered in sections 4.3 and 4.4. Figure 4-5 and Figure 4-9 show that increased pH resulted in an increase in water recovery for all wet grinding conditions. This increased water recovery may be linked to increased froth stability. Froth stability is influenced by factors such as concentration of frother, water quality (including pH), and the properties of solids suspended in the flotation cell (Schwarz and Grano, 2005). The increased water recovery at high pH level could be due to a higher number of hydroxyl ions present in the mill from the NaOH used as a pH modifier in this study. Addition of OH^- ions to the system led to an increase in the total concentration of ions, and therefore in the ionic strength of the system. An increase in the ionic strength led to increased froth stability due to the reduction in pulp bubble size, as well as reduced bubble coalescence. Bubble coalescence occurs when a liquid film between bubbles drains and ruptures, it can be minimized by reduced surface tension between the air bubbles (Ata, 2012; Pugh, 1996; Michaux et al., 2018). According to Craig (2004), the combining rule illustrated in Table 5-1 can be used to determine the pairs of ions that prevent or promote bubbles coalescence. The αα and ββ pairs inhibit the coalescence, while αβ and βα do not.



Ions		Na^+	K^+	Mg^{2+}	Ca^{2+}	H^+	$(CH_3)NH_3^+$
	Type	α	α	α	α	β	β
OH^-	α	✓	✓			✗	
F^-	α	✓					
Cl^-	α	✓	✓	✓	✓	✗	✗
SO_4^{2-}	α	✓	✓	✓		✗	
ClO_4^-	β	✗		✗		✓	
CH_3COO^-	β	✗	✗	✗		✓	

Table 5-1: Classification of ions according to their adsorption behaviour on the air-water interface (Craig, 2004)

From Table 5-1 it can be seen that the combination of Na^+ and OH^- prevents the coalescence of bubbles. This may explain the high water recovery which was recorded at high pH.

Farrokhpay and Zanin (2012) used a zinc sulphide-rich ore to study the influence of pH on froth stability by studying pulp viscosity and zeta potential as functions of pH. Zeta potential indicates the surface charge of the particles and gives insight into the degree of repulsion between particles with similar charges in the slurry. They found that zeta potential increased with increasing pH, while viscosity decreased with increasing pH; and that froth stability decreased with increasing pH. It was concluded, therefore, that this was due to low pulp viscosity and possible particle aggregation. The present study suggests that froth stability increases with increasing pH; these results are not in agreement with those of Farrokhpay and Zanin, (2012) and this may be attributed to differences in ore type or ion type within the synthetic plant water used. Sheni et al. (2018) also found that an increase in pH resulted in increased water recoveries. The increased water recovery was linked to an increase in hydroxyl ions which led to an increase in ionic strength. Ions dissolved in water can decrease or increase viscosity (Desnoyers and Perron, 1972). Gurney (1953) classified ions into structure-making ions (increasing viscosity) and structure-breaking ions (decreasing viscosity) based on how the ions affect the pure water structure. Small inorganic ions with high surface charge density such as Na^+, Mg^{2+}, Ca^{2+}, Li^+, OH^-, etc., are strongly hydrated and tend to increase water viscosity, while large inorganic ions of low surface charge density (e.g., CH_4^+, Cs^+, K^+, I^- etc.) are weakly hydrated and are capable of decreasing viscosity of water (Weissenborn and Pugh, 1996; Michaux et al., 2018; Peng and Nguyen, 2018). Cations such as Na^+, Ca^{2+} and Mg^{2+}, which tend to increase the viscosity of water were present in the synthetic plant water which was used in the current study. Thus, increasing water recovery.

It was observed from Figure 4-6 and Figure 4-10 that high pH resulted in increased solids recovery, possibly due to entrained gangue particles proceeding to the concentrate owing to the increased water recovery. It is important to emphasize that pyrite grade decreased when pH was increased from 9 to 11, therefore increased solids recovery at high pH can be linked to the increased entrainment of gangue minerals. It has been shown in previous studies that entrainment of particles is strongly linked to the recovery of water (Engelbrecht and Woodburn, 1975; Warren, 1985). Farrokhpay and Zanin (2012) reported that the more stable the froth, the higher the possibility that particles will be recovered to the concentrates. According to Ata (2003), the entrained gangue minerals decrease the rate of bubble coalescence by increasing the viscosity of slurry between the bubbles, thereby preventing drainage.

After wet grinding with forged steel, Figure 4-4 illustrates that during the first 7 minutes of flotation the rate of water recovery did not depend upon grinding DO concentration, although a substantial effect of DO was recorded for the last 13 minutes of flotation, more so for pH 11, than pH 9. At pH 11, water recovery increased after grinding had been conducted in the absence of oxygen. This suggests the formation of hydrophobic species with metal deficient sulphur rich surfaces such as elemental sulphur, when nitrogen was used as a purging gas; nitrogen purging causes the grinding environment to be more reducing; reduced pyrite is believed to be more hydrophobic than pyrite (Peng et al., 2003; Moslemi, et al., 2012; Mu et al., 2016; Moslemi and Gharabaghi, 2017). These species have possibly affected froth stability, owing to their hydrophobic nature and hence the increased recovery of water. The study conducted by Peng et al., (2003) on chalcopyrite showed that nitrogen purging resulted in more metal deficient sulfide species compared to oxygen. Elemental sulphur has been reported to be an important factor in the collector-less flotation of pyrite. It can be produced by oxidation of HS^- ions as shown in Eq 5 – 1, which may be formed by reduction of oxidation products on pyrite surface (Moslemi and Gharabaghi, 2017)

$$HS^{-} \rightarrow S^{0} + H^{+} + 2e^{-} \qquad \text{Eq 5 – 1}$$

These ions are believed to be produced in neutral or alkaline solutions. Farrokhpay (2011) has reported that moderately hydrophobic species can stabilize the froth phase by forming a layer of fine particles around air bubbles, thus inhibiting coalescence and subsequently more water is recovered.

The removal of dissolved oxygen during wet grinding with forged steel facilitated the recovery of increased solids. This could have been a result of the presence of the aforementioned hydrophobic species, such as elemental sulphur, metal-deficient or sulfur-rich species possibly formed during grinding in the absence of oxygen. Several studies (Dippenaar, 1982a; Johansson and Pugh, 1992; Aveyard et al., 1994; Ata et al., 2003) have attempted to identify the effect that the hydrophobicity of particles has on froth stability. Dippenaar (1982a) studied how different hydrophobic particles interact with a thin film. He found that spherical, strongly hydrophobic particles (with contact angles greater than 90º) lessen the stability of the froth phase due to the thinning of the inter-bubble liquid bridged by the particle, while particles which are irregular in shape with contact angles even less than 90º could rupture the films. Johansson and Pugh (1992) investigated the effect of various degrees of hydrophobicity of quartz particles on froth stability. They found that there is an optimum degree of hydrophobicity (contact angle ~ 65ºC) that promotes froth stability. They also determined that weakly hydrophobic particles do not have an impact on froth stability, because they stream out of the bubble lamella. They concluded that particles with intermediate hydrophobicity are able to increase the rigidity of the froth by forming stable bridges across the film. In the present study, however, when grinding with forged steel under wet conditions, froth stability was found to increase when grinding was conducted under an inert environment, and it can thus be postulated that intermediately hydrophobic particles were created under these conditions.

Furthermore, during wet grinding with ceramic media, it was found that an increase in pH level produced similar results to those produced by forged steel, in terms of water and solids recovery. The results are presented in Figure 4-9. The oxidation products which are formed when forged steel was used as grinding media are prevented by simply using an inert media. However, with an increased pH, similar species were created on the surface of particles as forged steel media due to addition of the OH- ions to the system. During grinding with ceramic media, the pyrite surface is oxidized, releasing ferrous ions, whereas with forged steel, the ferrous ions could also originate from the grinding media. At high pH values, the released ferrous ions react with hydroxyl ions to produce ferrous hydroxide. Ferrous hydroxide is oxidized to ferric hydroxide, which deposits on the pyrite surface as a precipitate. It was also found that with ceramic media, DO concentration resulted in minimal differences in the rate of solids recovery. This could have been due to the fact that DO does not influence the production of oxidation products (iron hydroxides) owing to the inert nature of the ceramic media.

It is clear that grinding chemistry could not be controlled during dry grinding: in this case the chemistry was only controlled in the flotation cell. It should also be noted that with dry grinding, the process is not influenced by the galvanic interactions between grinding media and pyrite due to the absence of water. There was a notable increase observed in the rate of water recovery when pH was changed from 9 to 11 with both forged steel and ceramic media. This could have been due to an increase in electrolytes (ionic strength) when the pH level was changed from 9 to 11. An increase in electrolytes (OH^- ions) present in the flotation cell therefore resulted in lower surface tension between the bubbles; which led to more stable froth, just like under wet grinding. Figure 4-11 shows that removing oxygen from the system (DO 0) resulted in an increase in the rate of water recovery, while at pH 9, water recovery did not appear to be dependent upon DO concentration in the system during flotation. This indicates that, at pH 11, an increase in water recovery was caused by the combination of DO concentration and pH. The water recovery might have decreased at DO 8/pH 11 because of a strongly-oxidised system during flotation which may have resulted in a lower attachment of particles to bubbles during flotation (Hu et al., 2009). It is known that both oxygen and high pH accelerate the oxidation of sulphide minerals to hydrophilic species such as iron oxides/hydroxides and sulfates. This could therefore lead to reduced solids particles in the froth, and that may have resulted in reduced effective viscosity of froth and lower froth stability.

5.2. The effect of grinding media type under dry and wet conditions

Figure 4-19 shows that forged steel media produced higher water recoveries when compared with that of ceramic media, under both dry and wet grinding. Wiese et al. (2006) stated that water recovery is strongly related to froth stability. It can therefore be said that grinding with forged steel resulted in a more stable froth. Under wet grinding with forged steel, an increase in water recovery could have been due to the fact that the oxidation products (iron hydroxide) formed during grinding had resulted in a more stable froth. Ceramic media results in cleaner milled sulphide mineral (pyrite) particles, which are more hydrophobic relative to those produced when forged steel is used as a grinding media. Formation of such species was inhibited, or minimal, when ceramic was used as grinding medium because it is electrochemically inert. It should be noted that this is all within the context of low pH (pH 9). Dippenaar et al. (1978) suggested that strongly hydrophobic particles destabilize the froth by rupturing the liquid films between the gas bubbles of the froth. Increased water recovery was observed during dry grinding with forged steel. Again, it is more likely that the ore was more easily oxidised in the flow of air through the mill due to lower volume filling by forged steel compared to ceramic media. Furthermore, forged steel might have worn off and the debris oxidised when the milled product was mixed with water inside the flotation cell. The oxidised debris might have led to a more stable froth, and consequently higher water recovery. Cullinan (1999) conducted a study on galena and it was found that the galena recovery increased significantly as the media type varied between forged steel, high chrome and ceramic. It was postulated, therefore, that debris from forged steel media would affect the flotation response of galena and other sulphide minerals. In the present study, even though forged steel produced higher water recovery under both wet and dry grinding, it was observed that wet grinding produced higher variation in water recovery than did dry grinding.

Figures 4-19 and 4-20 show that dry grinding produced higher solids and water recovery than wet grinding for both forged steel and ceramic media. This indicates that dry grinding created particles with particular characteristics which may have enhanced the froth stability. This observation agrees with results found by Feng and Aldrich, (2000). In their study, wet grinding resulted in a relatively unstable froth, and the froth layer had low solids loading. A possible explanation is the increased adsorption rate of reagent and attachment of particles to bubbles, subsequently stabilising the froth. It was also stated that the particle surfaces are activated during dry grinding because dry grinding results in rough particle surfaces, and a large number of fine particles can adsorb themselves to such surfaces. In addition to this, particles in dry grinding tend to conserve more energy because of lattice strain, reduction in crystallite size, and formation of amorphous phases, leading to increased reagent (collector) adsorption. Some of the energy conserved in dry grinding is in the form of defects and these defects help in reagent adsorption during flotation (Feng and Aldrich, 2000). Hence, recovery of solids increases. By contrast, wet grinding produces smooth and cleaner particle surfaces, resulting in only a few fine particles attaching to the surface.

5.3. The effect of pulp chemistry on pyrite recovery under dry and wet grinding

Figure 4-21 shows that, at pH 9, the concentration of DO inside the mill did not have a significant influence on pyrite recovery during wet grinding with forged steel; however, the recovery of pyrite decreased upon removal of DO during milling at pH 11. Floatability of pyrite can be affected by either the grinding environment or flotation conditions. Based on EDTA extraction results, pH and DO concentration during wet grinding influenced the formation of oxidation products. However, the flotation response of pyrite at pH 9 was not affected by DO concentration which indicates that adsorption of xanthate during flotation might not have been affected by the oxidation products on the surface of pyrite which were formed at pH 9. The lowest pyrite recovery was achieved at pH 11/DO 0, which implies that these grinding conditions resulted in fewer floatable particles, or as previously stated, highly hydrophobic surface species. The lack of oxygen in the system changes the redox formulae, or prevents them from taking place.

Ceramic media produced a higher rate of pyrite recovery at pH 11 than at pH 9, while pyrite recovery was independent of DO concentration. However, the final recoveries were within the same range for all conditions. This suggests that pulp chemistry affects pyrite recovery slightly under wet grinding with ceramic media. This could be due to the fact that ceramic is inert, so the presence or absence of oxygen during grinding would not have affected the formation of electrochemical reaction products which are normally produced in redox reactions between the sulphide mineral and the electrochemically - active grinding media.

It can also be seen from Figure 4-29 that, under wet grinding, pyrite recovery generally increased when the grinding media was changed from forged steel to ceramic. It is evident from EDTA extraction results that forged steel led to higher amounts of iron oxidation products than ceramic media under wet grinding. This could have been due to the reactivity of the forged steel. The EDTA extractable iron content of the pulp could be a product of oxidation of grinding media and/or pyrite. (Bruckard et al., 2011; Rabieh et al., 2017). Huang and Grano (2005) proposed that oxidation of pyrite during grinding happens through Equation 5 – 2 and 5 – 3

$$FeS_2 + 3H_2O \rightarrow Fe(OH)_3 + 2S + 3H^+ + 3e^- \qquad \text{Eq 5 – 2}$$

$$FeS_2 + 11H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 11H^+ + 15e^- \qquad \text{Eq 5 – 3}$$

In the case of ceramic media, therefore, oxidation products might have originated from the oxidation of pyrite only. As a result, more oxidation products were formed during wet grinding with forged steel, which might have precipitated on the pyrite surface, hindering adsorption of xanthate which would subsequently have had a deleterious effect on the flotation response. The accumulation of oxidation products on the surface of pyrite could also decrease its recovery by preventing pyrite particles from being naturally floatable (Mu et al., 2016).

During pyrite grinding with an electrochemically reactive grinding medium, oxygen reduction takes place on the surface of the pyrite, while oxidation occurs on the surface of the grinding media (Wei and Sandenbergh, 2007). During grinding, forged steel comes into direct contact with pyrite; oxidation of forged steel increases because it is more electrochemically active than pyrite. It is concluded, therefore, that oxidation of pyrite during grinding with a strong electrochemically - reactive medium such as forged steel may be ignored for the purpose of the study. The EDTA extraction of dissolved species is a good indication of grinding medium corrosion (Huang and

Grano, 2005; Rabieh et al., 2017). In the case of ceramic media, therefore, oxidation products could have originated from pyrite only, due to the lack of galvanic interaction between the grinding media and pyrite.

In the present study, it was observed that forged steel resulted in the highest amount of iron oxidation products during wet grinding at DO 8/pH 11 than under any other condition. This could be due to increased formation of oxy-hydroxide species in the system owing to the presence of both oxygen and hydroxyl ions. Formation of iron oxides or hydroxide is therefore accelerated in an alkaline system; which is borne out by EDTA extraction results. Furthermore, it was found that an increase in pH resulted in an enhanced iron extraction. This could be due to the fact that, at pH 11, more hydroxide (OH^-) ions were introduced into the system, and oxidation of the forged steel and the pyrite surface increased, doubtless, due to the presence of oxygen. Moslemi et al. (2012) reported that the formation of iron hydroxide during grinding on the surface of pyrite increases in alkaline solutions although not in acid solutions, due to the fact that the intermediate products during pyrite oxidation are more stable in alkaline solutions than they are in acidic solutions.

Figure 4-25 shows the rate at which pyrite was recovered under dry grinding with forged steel. It may be observed that the lowest rate of pyrite recovery was achieved at DO 8/pH 9. DO 8/pH 11 yielded the highest rate of pyrite recovery. Göktepe (2002) investigated the effects of pH on the pulp potential and flotation response of sulphide minerals such as pyrite. They mentioned that the recovery of pyrite at pH values less than or equal to 5 is enhanced due to rapid oxidation of xanthate to dixanthogen; dixanthogen renders the pyrite surface more hydrophobic. At high pH, the pyrite surface is more easily oxidized than xanthate. As a result, dixanthogen is not formed and the pyrite surface remains hydrophilic due to its surface oxidation. The present study results are in disagreement to those reported by Göktepe (2002). It is worth noting that his study used a pH of 5 as a limit, whereas in the present study, all the tests were conducted at pH values above 5. At DO 0, the rate of pyrite recovery did not vary upon change in pH during flotation.

Figure 4-27 shows pyrite recovery as a function of time for ceramic media under dry grinding for all conditions tested. The lowest rate of pyrite recovery was obtained at DO 0/pH 11, while the highest rate was observed at DO 0/pH 9. The reason for high pyrite recovery at DO 0/pH 9 could be the reduced formation of oxidation products. The figure also shows that, at pH 9, the rate of pyrite recovery was slightly affected by the concentration of DO during flotation. It is also evident that, at pH 11, the rate of pyrite recovery decreased upon removal of DO inside the flotation cell.

Results for final pyrite recovery obtained for all tests are shown in Figure 4-29. The results indicate that the highest recovery of pyrite was achieved with inert grinding media (ceramic media) under wet grinding. The maximum recovery obtained was 100%. Pyrite recovery was generally constant at DO 0/pH 11 under dry grinding with the two different grinding media. This could be due to the absence of galvanic interactions during grinding since there is no water present during dry grinding. On the other hand, pyrite recovery showed a dramatic increase at DO 0/pH 11 under wet grinding when the grinding medium was changed from active to inert. This shows that the grinding environment had an effect on the flotation response of pyrite. Since forged steel is electrochemically active, there were galvanic interactions between pyrite and forged steel and that consequently led to the formation of oxidation species. Furthermore, it can be observed that pyrite recovery decreased upon removal of DO during wet grinding with forged steel, while DO removal resulted in marginal differences in pyrite recovery when ceramic media were used in a wet system. This indicates that when grinding with forged steel (being an active media) oxygen plays a major role in the formation of species which affect the flotation response of pyrite.

It was noted that dry grinding resulted in enhanced recovery of pyrite when compared with wet grinding. This might be due to clean pyrite surfaces created during dry grinding, since prevention of corrosion may lead to improved recovery (Wei and Sandenbergh, 2007). That might therefore have allowed adequate adsorption of xanthate on the surface of pyrite as soon as a collector was added to the float cell, thereby increasing the recovery. Feng and Aldrich (2000) reported that, during dry grinding, the surfaces of the particles are activated, thereby facilitating easy adsorption of the collector. The activation of particles under dry grinding may also explain higher EDTA extractable Fe in dry grinding with ceramic media compared to wet grinding with the same grinding media. Apart from better pyrite recoveries, dry grinding generally presented much faster pyrite flotation kinetics than wet grinding. During dry grinding, more energy is conserved than in wet grinding. Therefore, dry grinding results in particles with high surface energy and that leads to highly activated particles and consequently greater rates of recovery.

In overall, presence of non-sulphide gangue mineral did not have much impact on the recovery of pyrite. However, it led to lower grades of pyrite at higher pH.

6. CHAPTER SIX: Conclusions

The main objective of this study was to investigate the effects of pulp chemistry (with an emphasis on dissolved oxygen and pH) and media type on the flotation response of pyrite in the presence of quartz under dry and wet grinding. The study also aimed to understand the influence of the grinding pulp chemistry factors on water and overall solids recoveries under both dry and wet grinding. The following conclusions are presented as the answers to the key questions formulated in this study.

How does pH during grinding affect solids and water recovery, as well as the flotation response of pyrite in the presence of quartz?

This study has shown that upon increasing pH from 9 to 11 during grinding with both ceramic media and forged steel, water recovery increased. The increased water recovery at high pH is attributed to an increase in froth stability. Addition of pH modifier (NaOH) led to an increase in the total concentration of OH^- ions in the system. An increase in ionic strength led to increased froth stability due to the reduction in pulp bubble size, as well as reduced bubble coalescence. In addition to this, the combination of Na^+ and OH^- prevents the coalescence of bubbles (Craig, 2004).

The findings of this study have clearly shown that an increase in pH (from pH 9 to 11) resulted in increased solids recovery. It has been concluded that increased solids recovery at pH 11 can possibly be due to the increased entrainment of gangue minerals, since a decrease in pyrite grade was recorded when pH was increased from 9 to 11 (Manono,2012). The entrainment of particles is linked to the recovery of water, as the more stable the froth, the higher the possibility that particles will be recovered to the concentrate via the mechanism of entrainment.

The EDTA extraction results showed that oxidation products formed during grinding may be influenced by both pH and DO concentration. However, it has been found that the flotation response of pyrite at pH 9 was not affected by DO concentration. Therefore, it has been suggested that the adsorption of xanthate during flotation may not have been affected by oxidation products formed on the surface of pyrite at pH 9.

How does DO during grinding affect solids and water recovery, as well as the flotation response of pyrite in the presence of quartz?

This study has confirmed that in the absence of oxygen after wet grinding with forged steel at pH 11, water and solids recovery increased. This is attributed to the formation of hydrophobic species with metal deficient sulphur rich surfaces when nitrogen was used as a purging gas; nitrogen purging results in grinding environment which is more reducing (Moslemi et al. , 2012). Reduced pyrite is more hydrophobic than unreduced pyrite. The presence of species with metal deficient sulphur rich surfaces affected froth stability, resulting in increased water recovery. Particles with intermediate hydrophobicity are able to increase the stability of the froth by forming stable bridges across the bubble film (Johansson and Pugh, 1992). Based on this study, it has been postulated that intermediately hydrophobic particles were created when grinding with forged steel under wet conditions in the absence of oxygen. This study has also shown that with ceramic media, changes in DO concentration resulted in minimal differences in the rate of solids recovery. This could have been due to the fact that DO does not influence the production of oxidation products (iron hydroxides) owing to the inert nature of the ceramic media. The findings suggest that the effect of DO concentration under wet grinding depends mainly on the type of grinding media used.

This study also showed that pulp chemistry affected pyrite recovery slightly under wet grinding with ceramic media. This may have been due to the fact that ceramic media is inert and the presence or absence of oxygen during grinding would not have affected the formation of electrochemical reaction products which are normally produced in redox reactions between the sulphide mineral and the electrochemically - active grinding media.

How does different grinding media type affect the floatability of pyrite in the presence of quartz?

The study has shown that forged steel media produced higher water recoveries when compared with that of ceramic media, under both dry and wet grinding. Under wet grinding with forged steel, an increase in water recovery could have been due the fact that the oxidation products (iron hydroxide) formed during grinding resulted in a more stable froth. The use of electrochemically inert ceramic media resulted in sulphide mineral (pyrite) particles with cleaner surfaces, which are more hydrophobic relative to those produced when forged steel is used as a grinding media.

It was found that during wet grinding with ceramic media, an increase in pH produced similar results to those produced by forged steel, in terms of water and solids recovery. The oxidation products which were formed when forged steel was used as grinding media are prevented by simply using an inert media. However, at increased pH, similar species were formed on the surface of particles as with forged steel media due to the addition of OH- ions to the system.

Pyrite recovery increased when grinding media was changed from forged steel to ceramic. The EDTA extraction results showed that forged steel led to higher amounts of iron oxidation products than ceramic media under wet grinding. This is due to that fact that more oxidation products were formed during wet grinding with forged steel, which might have precipitated on the pyrite surface, hindering adsorption of xanthate which would subsequently have had a deleterious effect on the flotation response.

How does flotation pulp chemistry affect the recovery of pyrite following dry grinding?

A notable increase in the rate of water recovery was observed when the pH was changed from 9 to 11 with both forged steel and ceramic media. This could have been due to an increase in electrolytes when the pH level was changed from 9 to 11. An increase in electrolytes (OH^- ions) present in the flotation cell therefore resulted in lower surface tension between the bubbles; which may have led to a more stable froth, similar to wet grinding. Thus, the study has shown that even after dry grinding, an increase in pH from 9 to 11 during the flotation process resulted in increased water and solids recovery.

The study has also shown that after dry grinding at pH 11, water recovery increased when oxygen was removed from the system, while at pH 9, water recovery did not depend on DO concentration during flotation suggesting that water recovery was influenced by a combination of DO concentration and pH. The decreased water recovery recorded at DO 8 and pH 11 was due to a strongly-oxidised system during flotation which may have led to decreased attachment of particles to bubbles.

The findings of the study have confirmed that dry grinding produced higher solids and water recovery than wet grinding for both forged steel and ceramic media. This phenomenon is attributed to the particle surfaces that are activated during dry grinding because dry grinding results in rough particle surfaces onto which large numbers of ultra-fine particles can attach. In addition to this, particles in dry grinding tend to conserve more energy because of lattice strain, reduction in crystallite size and formation of amorphous phases, leading to increased reagent (collector) adsorption. Hence, recovery of solids increases. By contrast, wet grinding produces smooth particles with cleaner surfaces.

Overall, the highest recovery of pyrite was achieved with inert grinding media (ceramic media) under wet grinding.

7. CHAPTER SEVEN: Recommendations

Based on the findings and conclusions in this study, the following recommendations are made:

- Other sulphide minerals should be investigated in order to gain a better understanding of how the parameters investigated in this study affect the flotation response of various sulphide minerals and not just pyrite.
- Further work is required to investigate the effects of individual ions in the synthetic plant water used in the current study.
- Mixed-mineral systems should be investigated to determine whether it is possible to separate sulphide minerals from one another by controlling pulp chemistry during the grinding and flotation processes. Such studies would also allow for mineral-mineral galvanic interactions to be considered.

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9. APPENDICES

9.1. Milling curves data

9.1.1. Dry grinding

Ceramic media

Time (minutes)	Total Mass (g)		Mass passing (g)		% passing
	1	2	1	2	
10	199.94	201.81	47.52	47.61	23.68
15	198.46	203.60	74.97	76.66	37.71
20	200.46	200.33	100.26	99.94	49.95
30	198.65	199.94	141.49	142.57	71.27

Forged steel

Time (minutes)	Total Mass (g)		Mass passing (g)		% passing
	1	2	1	2	
15	199	198.47	61.04	58.93	30.18
25	201.09	199.97	87.68	83.49	42.68
35	199.51	200.98	122.36	124.49	61.63
45	198.08	203.19	162.09	165.43	81.62

9.1.2. Wet grinding

Ceramic media

Time (minutes)	Total Mass (g)	Mass passing + PAN (g)	PAN (g)	Mass passing (g)	% passing
18.55	100	302.29	237.42	64.87	64.87
20	100	305.52	237.42	68.1	68.1
30	100	320.56	237.42	83.14	83.14

Forged steel media

Time (minutes)	Total Mass (g)	Mass passing + PAN (g)	PAN (g)	Mass passing (g)	% passing
20	100	290.45	237.42	53.03	53.03
30	100	303.73	237.42	66.31	66.31
45	100	320.63	237.42	83.21	83.21

9.2. Batch Flotation Data

9.2.1. Dry grinding

Ceramic media

Run no.	Reagents			Sample	Time, min	Mass Pull, g	Water Rec, g	Cum Mass, g	Cum Water, g	Ave cum Mass, g	% solids	Ave cum w Rec, g	Sulphur %	Sample Mass	Mass pyrite	Cum pyrite Mass	Ave Cum pyrite Mass	pyrite Grade %	Pyrite Rec %	Ave pyrite grade %	Ave pyrite rec %	mass gangue	Ave mass gangue
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
1	***IS***	***SPW 1***	***SPW***	C1	2	80.02	177.45	80.02	177.45	81.24	0.04	148.97	0.30	0.17	45.51	45.51	48.59	56.9	91.0	59.8	95.51	34.51	32.64
	DO	***DO 8***		C2	4	37.99	422.53	118.01	599.98	118.99	0.06	590.90	0.01	0.17	1.02	46.53	49.92	39.4	93.1	41.9	96.53	71.48	69.07
	pH	***pH 9***		C3	6	22.19	593.48	140.20	1193.46	141.34	0.07	1200.01	0.00	0.18	0.17	46.70	50.07	33.3	93.4	35.4	100.00	93.50	91.27
	Media	***Ceramic media***		C4	8	16.23	522.52	156.43	1715.98	157.49	0.08	1728.06	0.00	0.17	0.07	46.77	50.15	29.9	93.5	31.8	100.00	109.66	107.34
	SIBX	***100***	***g/ton***	F		190.91									50.00					31.7			
	DOW200	***50***	***g/ton***	T		0.00					4.06												
				T2		16.66					5.95												
				T3		17.82					7.07												
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
2	***IS***	***SPW 1***	***SPW***	C1	2	82.45	120.48	82.45	120.48				0.34	0.17	51.68	51.68		62.7	100.0			30.77	
	DO	***DO 8***		C2	4	37.51	461.33	119.96	581.81				0.02	0.17	1.63	53.30		44.4	100.0			66.66	
	pH	***pH 9***		C3	6	22.52	624.74	142.48	1206.55				0.00	0.17	0.15	53.45		37.5	100.0			89.03	
	Media	***Ceramic media***		C4	8	16.07	533.58	158.55	1740.13				0.00	0.17	0.08	53.53		33.8	100.0			105.02	
	SIBX	***100***	***g/ton***	F		192.54									50.00								
	DOW200	***50***	***g/ton***	T		0.00																	
				T2		17.45																	
				T3		16.54																	
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00
3	***IS***	***SPW 1***	***SPW***	C1	2	64.83	261.48	64.83	261.48	66.64	0.03	283.82	0.36	0.18	43.06	43.06	46.31	66.42	86.1	69.4	92.62	21.77	20.33
	DO	***DO 8***		C2	4	25.40	533.21	90.23	794.69	91.63	0.05	806.03	0.03	0.17	1.46	44.52	47.87	49.34	89.0	52.2	94.52	45.71	43.76
	pH	***pH 11***		C3	6	20.48	679.46	110.71	1474.15	110.90	0.06	1483.85	0.01	0.17	0.34	44.86	48.17	40.52	89.7	43.4	94.86	65.85	62.72
	Media	***Ceramic media***		C4	8	19.16	658.02	129.87	2132.17	129.79	0.06	2156.46	0.01	0.16	0.25	45.11	48.50	34.74	90.2	37.4	95.11	84.76	81.28
	SIBX	***100***	***g/ton***	F		164.91									50.00					38.5			
	DOW200	***50***	***g/ton***	T		0.00					3.33												
				T2		17.69					4.58												
				T3		17.35					5.54												
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00
4	***IS***	***SPW 1***	***SPW***	C1	2	68.45	306.15	68.45	306.15				0.39	0.17	49.56	49.56		72.40	99.1			18.89	
	DO	***DO 8***		C2	4	24.58	511.22	93.03	817.37				0.04	0.17	1.65	51.21		55.05	100.0			41.82	
	pH	***pH 11***		C3	6	18.05	676.17	111.08	1493.54				0.01	0.17	0.28	51.49		46.35	100.0			59.59	
	Media	***Ceramic media***		C4	8	18.62	687.21	129.70	2180.75				0.01	0.17	0.40	51.89		40.01	100.0			77.81	
	SIBX	***100***	***g/ton***	F		165.03									50.00								
	DOW200	***50***	***g/ton***	T		0.00																	
				T2		17.73																	
				T3		17.60																	

Ceramic media

					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00
5	***IS***	***SPW 1***	***SPW***	C1	2	83.25	268.83	83.25	268.83	84.59	0.04	288.03	0.31	0.18	47.50	47.50	49.87	57.06	95.0	58.9	97.50	35.75	34.71
	DO	***DO 0***		C2	4	42.57	593.42	125.82	862.25	125.72	0.06	826.78	0.01	0.17	0.88	48.39	50.60	38.46	96.8	40.2	100.00	77.43	75.12
	pH	***pH 9***		C3	6	29.27	450.92	155.09	1313.17	152.50	0.08	1300.80	0.00	0.19	0.15	48.54	50.71	31.30	97.1	33.3	100.00	106.55	101.79
	Media	***Ceramic media***		C4	8	17.32	401.61	172.41	1714.78	171.15	0.09	1715.94	0.00	0.17	0.09	48.63	50.77	28.20	97.3	29.7	100.00	123.78	120.38
	SIBX	***100***	***g/ton***	F		206.73									50.00					29.2			
	DOW200	***50***	***g/ton***	T		0.00					4.23												
				T2		17.54					6.29												
				T3		16.78					7.62												
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00
4	***IS***	***SPW 1***	***SPW***	C1	2	85.92	307.22	85.92	307.22				0.33	0.17	52.24	52.24	49.53	60.80	100.0			33.68	
	DO	***DO 0***		C2	4	39.70	484.09	125.62	791.31				0.01	0.17	0.57	52.81	50.85	42.04	100.0			72.81	
	pH	***pH 9***		C3	6	24.28	497.12	149.90	1288.43				0.00	0.17	0.07	52.88	51.18	35.27	100.0			97.02	
	Media	***Ceramic media***		C4	8	19.99	428.67	169.89	1717.10				0.00	0.17	0.04	52.92	51.28	31.15	100.0			116.97	
	SIBX	***100***	***g/ton***	F		204.15									50.00								
	DOW200	***50***	***g/ton***	T		0.00																	
				T2		17.73																	
				T3		16.53																	
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00
	IS	***SPW 1***	***SPW***	C1	2	68.55	328.87	68.55	328.87	67.72	0.03	330.63	0.37	0.18	46.81	46.81	43.93	68.29	93.6	64.8	87.86	21.74	23.79
	DO	***DO 0***		C2	4	26.27	612.94	94.82	941.81	93.50	0.05	950.74	0.04	0.17	2.08	48.89	45.42	51.57	97.8	48.5	90.85	45.93	48.07
	pH	***pH 11***		C3	6	26.82	739.22	121.64	1681.03	120.62	0.06	1699.31	0.01	0.17	0.60	49.49	45.86	40.69	99.0	38.0	91.72	72.15	74.75
	Media	***Ceramic media***		C4	8	15.35	539.33	136.99	2220.36	140.87	0.07	2248.81	0.01	0.17	0.16	49.65	46.04	36.24	99.3	32.8	92.08	87.34	94.82
	SIBX	***100***	***g/ton***	F		174.40									50.00					35.5			
	DOW200	***50***	***g/ton***	T		0.00					3.39												
				T2		18.31					4.67												
				T3		19.10					6.03												
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.00	0.00	0.00
	IS	***SPW 1***	***SPW***	C1	2	66.89	332.38	66.89	332.38				0.33	0.17	41.05	41.05		61.37	82.1			25.84	
	DO	***DO 0***		C2	4	25.28	627.29	92.17	959.67				0.02	0.17	0.90	41.95		45.51	83.9			50.22	
	pH	***pH 11***		C3	6	27.42	757.91	119.59	1717.58				0.01	0.17	0.28	42.23		35.31	84.5			77.36	
	Media	***Ceramic media***		C4	8	25.15	559.68	144.74	2277.26				0.00	0.17	0.20	42.44		29.32	84.9			102.30	
	SIBX	***100***	***g/ton***	F		181.91										50.00							
	DOW200	***50***	***g/ton***	T		0.00																	
				T2		18.63																	
				T3		18.54																	

Forged steel

Run no.	Reagents			Sample	Time, min		Mass Pull, g	Water Rec, g	Cum Mass, g	Cum Water, g	Ave cum Mass, g	% rec	Ave cum w Rec, g	Sulphur %	Sample Mass	Mass pyrite	Cum pyrite Mass	Ave Cum pyrite Mass	pyrite Grade %	Pyrite Rec %	Ave pyrite grade %	Ave pyrite rec %	mass gangue	Ave gangue
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
1	***IS***	***SPW 1***	***SPW***	C1	2.00	2.00	46.55	178.38	46.55	178.38	47.28	2.36	192.96	0.31	0.17	27.26	27.26	30.02	58.6	54.5	63.4	60.0	19.29	17.26
	DO	***DO 8***		C2	4.00	6.00	37.18	536.22	83.73	714.60	84.73	4.24	747.59	0.03	0.17	1.83	29.09	36.79	34.7	58.2	43.3	73.6	54.64	47.93
	pH	***pH 9***		C3	6.00	12.00	33.56	776.47	117.29	1491.07	119.29	5.96	1506.22	0.01	0.17	0.40	29.49	38.88	25.1	59.0	32.5	77.8	87.80	80.41
	Media	***Forged steel***		C4	8.00	20.00	22.52	602.89	139.81	2093.96	142.18	7.11	2098.88	0.01	0.17	0.54	30.03	39.55	21.5	60.1	27.7	79.1	109.78	102.63
	SIBX	***100***	***g/ton***	F			175.70									50.00					35.2			
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			18.33																	
				T3			17.56																	
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
2	***IS***	***SPW 1***	***SPW***	C1	2.00	2.00	48.00	207.53	48.00	207.53				0.37	0.17	32.78	32.78		68.3	65.6			15.22	
	DO	***DO 8***		C2	4.00	6.00	37.72	573.04	85.72	780.57				0.17	0.17	11.71	44.49		51.9	89.0			41.23	
	pH	***pH 9***		C3	6.00	12.00	35.57	740.80	121.29	1521.37				0.06	0.17	3.78	48.27		39.8	96.5			73.02	
	Media	***Forged steel***		C4	8.00	20.00	23.26	582.43	144.55	2103.80				0.02	0.17	0.79	49.06		33.9	98.1			95.49	
	SIBX	***100***	***g/ton***	F			178.24									50.00								
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			16.37																	
				T3			17.32																	
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
3	***IS***	***SPW 1***	***SPW***	C1	2.00	2.00	63.63	274.17	63.63	274.17	62.20	3.11	268.21	0.39	0.17	46.90	46.90	45.85	73.7	93.8	73.7	91.7	16.73	16.35
	DO	***DO 8***		C2	4.00	6.00	40.04	774.42	103.67	1048.59	102.42	5.12	1047.16	0.05	0.18	4.02	50.92	49.33	49.1	100.0	48.2	97.7	52.75	53.08
	pH	***pH 11***		C3	6.00	12.00	24.62	798.56	128.29	1847.15	126.65	6.33	1842.88	0.02	0.19	0.74	51.66	50.06	40.3	100.0	39.5	100.0	76.63	76.59
	Media	***Forged steel***		C4	8.00	20.00	19.34	664.71	147.63	2511.86	146.39	7.32	2508.36	0.04	0.17	1.28	52.94	50.83	35.9	100.0	34.7	100.0	94.69	95.55
	SIBX	***100***	***g/ton***	F			183.03									50.00					34.2			
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			17.82																	
				T3			17.58																	
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
4	***IS***	***SPW 1***	***SPW***	C1	2.00	2.00	60.77	262.24	60.77	262.24				0.39	0.17	44.80	44.80		73.7	89.6			15.97	
	DO	***DO 8***		C2	4.00	6.00	40.39	783.49	101.16	1045.73				0.04	0.17	2.95	47.75		47.2	95.5			53.41	
	pH	***pH 11***		C3	6.00	12.00	23.84	792.87	125.00	1838.60				0.02	0.17	0.70	48.45		38.8	96.9			76.55	
	Media	***Forged steel***		C4	8.00	20.00	20.14	666.25	145.14	2504.85				0.01	0.17	0.27	48.73		33.6	97.5			96.41	
	SIBX	***100***	***g/ton***	F			180.35									50.00								
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			17.91																	
				T3			17.30																	

Forged steel

					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
5	***IS***	***SPW 1***	***SPW***	C1	2.00	2.00	67.40	214.91	67.40	214.91	68.17	3.41	217.00	0.31	0.18	39.34	39.34	41.98	58.4	78.7	61.6	84.0	28.06	26.18
	DO	***DO 0***		C2	4.00	6.00	31.32	574.95	98.72	789.86	97.97	4.90	803.38	0.04	0.17	2.63	41.97	44.43	42.5	83.9	45.4	88.9	56.75	53.54
	pH	***pH 9***		C3	6.00	12.00	30.16	755.70	128.88	1545.56	126.50	6.32	1535.70	0.03	0.17	1.52	43.49	45.78	33.7	87.0	36.2	91.6	85.39	80.72
	Media	***Forged steel***		C4	8.00	20.00	19.87	615.21	148.75	2160.77	147.09	7.35	2133.28	0.02	0.17	0.75	44.24	46.51	29.7	88.5	31.6	93.0	104.51	100.58
	SIBX	***100***	***g/ton***	F			184.96									50.00					34.0			
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			17.45																	
				T3			18.76																	
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
4	***IS***	***SPW 1***	***SPW***	C1	2.00	2.00	68.93	219.09	68.93	219.09				0.35	0.17	44.62	44.62		64.7	89.2			24.31	
	DO	***DO 0***		C2	4.00	6.00	28.28	597.81	97.21	816.90				0.04	0.17	2.26	46.88		48.2	93.8			50.33	
	pH	***pH 9***		C3	6.00	12.00	26.90	708.93	124.11	1525.83				0.02	0.17	1.18	48.06		38.7	96.1			76.05	
	Media	***Forged steel***		C4	8.00	20.00	21.31	579.95	145.42	2105.78				0.02	0.17	0.71	48.77		33.5	97.5			96.65	
	SIBX	***100***	***g/ton***	F			181.51									50.00								
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			18.43																	
				T3			17.66																	
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
	IS	***SPW 1***	***SPW***	C1	2.00	2.00	74.33	250.47	74.33	250.47	71.72	3.59	273.89	0.30	0.17	41.44	41.44	43.02	55.8	82.9	60.1	86.0	32.89	28.69
	DO	***DO 0***		C2	4.00	6.00	37.65	854.25	111.98	1104.72	108.55	5.43	1143.91	0.04	0.19	2.78	44.22	45.07	39.5	88.4	41.6	90.1	67.76	63.47
	pH	***pH 11***		C3	6.00	12.00	28.98	855.70	140.96	1960.42	136.64	6.83	1984.13	0.01	0.17	0.72	44.93	45.60	31.9	89.9	33.4	91.2	96.03	91.04
	Media	***Forged steel***		C4	8.00	20.00	19.32	639.27	160.28	2599.69	155.01	7.75	2606.22	0.01	0.17	0.27	45.20	45.79	28.2	90.4	29.6	91.6	115.08	109.22
	SIBX	***100***	***g/ton***	F			196.42									50.00					32.3			
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			17.47																	
				T3			18.67																	
					0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
	IS	***SPW 1***	***SPW***	C1	2.00	2.00	69.10	297.30	69.10	297.30				0.35	0.17	44.60	44.60		64.5	89.2			24.50	
	DO	***DO 0***		C2	4.00	6.00	36.01	885.80	105.11	1183.10				0.02	0.17	1.33	45.93		43.7	91.9			59.18	
	pH	***pH 11***		C3	6.00	12.00	27.20	824.73	132.31	2007.83				0.01	0.17	0.34	46.27		35.0	92.5			86.04	
	Media	***Forged steel***		C4	8.00	20.00	17.43	604.91	149.74	2612.74				0.00	0.17	0.12	46.39		31.0	92.8			103.35	
	SIBX	***100***	***g/ton***	F			183.82									50.00								
	DOW200	***50***	***g/ton***	T			0.00																	
				T2			17.42																	
				T3			16.66																	

9.2.2. Wet grinding

Ceramic media

Run no.	Reagents			Sample	Time, min	Mass Pull, g	Water Rec, g	Cum Mass, g	Cum Water, g	Ave cum Mass, g	% rec	Ave cum Water, g	Ave cum w Rec, g	Sulphur %	Sample Mass	Mass pyrite	Cum pyrite Mass	Ave Cum pyrite Mass	pyrite Grade %	Pyrite Rec %	Ave pyrite gra %	Ave pyrite rec %	mass gangue	Ave mass gangue
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
1	***IS***	***SPW 1***	***SPW***	C1	2	43.07	48.70	43.07	48.70	43.61	2.18	47.62	47.62	0.44	0.18	35.21	35.21	35.53	81.8	70.4	81.5	71.1	7.86	8.08
	DO	***DO 8***		C2	4	18.19	79.25	61.26	127.95	60.97	3.05	125.05	125.05	0.38	0.16	12.93	48.15	45.92	78.6	96.3	75.3	91.8	13.11	15.05
	pH	***pH 9***		C3	6	3.01	87.86	64.27	215.81	63.92	3.20	215.18	215.18	0.09	0.17	0.49	48.63	46.31	75.7	97.3	72.4	92.6	15.64	17.61
	Media	***Ceramic media***		C4	8	3.76	156.62	68.03	372.43	67.70	3.39	368.78	368.78	0.03	0.24	0.21	48.84	46.49	71.8	97.7	68.7	93.0	19.19	21.21
	SIBX	***100***	***g/ton***	F		102.35										50.00			71.8					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		17.55								0.00	0.40	0.02								
				T3		16.77								0.00	0.40	0.00								
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
2	***IS***	***SPW 1***	***SPW***	C1	2	44.15	46.54	44.15	46.54					0.43	0.15	35.85	35.85		81.2	71.7			8.30	
	DO	***DO 8***		C2	4	16.53	75.61	60.68	122.15					0.25	0.16	7.86	43.70		72.0	87.4			16.98	
	pH	***pH 9***		C3	6	2.89	92.39	63.57	214.54					0.05	0.18	0.29	43.99		69.2	88.0			19.58	
	Media	***Ceramic media***		C4	8	3.80	150.59	67.37	365.13					0.02	0.22	0.15	44.15		65.5	88.3			23.22	
	SIBX	***100***	***g/ton***	F		102.07										50.00								
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		17.71								0.00	0.40	0.01								
				T3		16.99								0.00	0.40	0.00								
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
3	***IS***	***SPW 1***	***SPW***	C1	2	42.29	49.31	42.29	49.31	41.53	2.08	52.11	52.11	0.44	0.20	34.97	34.97	34.97	82.7	69.9			7.32	
	DO	***DO 0***		C2	4	13.05	14.02	55.34	63.33	54.17	2.71	68.52	68.52	0.42	0.18	10.21	45.18	45.18	81.6	90.4			10.16	
	pH	***pH 9***		C3	6	7.37	117.55	62.71	180.88	61.41	3.07	180.21	180.21	0.28	0.17	3.90	49.08	49.08	78.3	98.2			13.63	
	Media	***Ceramic media***		C4	8	3.66	155.85	66.37	336.73	65.02	3.25	341.87	341.87	0.06	0.26	0.44	49.52	49.52	74.6	99.0			16.85	
	SIBX	***100***	***g/ton***	F		100.63										50.00			75.3					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		17.59								0.00	0.40	0.02								
				T3		16.67								0.00	0.40	0.00								
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
4	***IS***	***SPW 1***	***SPW***	C1	2	40.76	54.91	40.76	54.91															
	DO	***DO 0***		C2	4	12.24	18.79	53.00	73.70															
	pH	***pH 9***		C3	6	7.10	105.83	60.10	179.53															
	Media	***Ceramic media***		C4	8	3.56	167.47	63.66	347.00															
	SIBX	***100***	***g/ton***	F		98.62																		
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		17.38																		
				T3		17.58																		

Ceramic media

					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
6	***IS***	***SPW1***	***SPW***	C1	2	56.35	85.33	56.35	85.33	71.19	2.82		91.24	0.44	0.19	45.86	45.86		81.4	91.7			10.49	
	DO	***DO 8***		C2	4	8.08	107.67	64.43	193.00	85.39	3.22		196.98	0.22	0.15	3.37	49.23		76.4	98.5			15.20	
	pH	***pH 11***		C3	6	4.65	174.59	69.08	367.59	121.17	3.45		381.21	0.06	0.16	0.49	49.72		72.0	99.4			19.36	
	Media	***ceramic media***		C4	8	1.72	158.21	70.80	525.80	114.90	3.54		545.00	0.02	0.26	0.05	49.77		70.3	99.5			21.03	
	SIBX	***100***	***g/ton***	F		105.09										50.00			70.6					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		16.83								0.00	0.40	0.01								
				T3		17.46								0.00	0.40	0.01								
					0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.0	0.00	0.00
7	***IS***	***SPW1***		C1	2	57.04	97.15	57.04	97.15		2.85			0.44	0.22	47.38	47.38		83.1	94.8			7.86	
	DO	***DO 0***		C2	4	6.07	103.80	63.11	200.95		3.16			0.23	0.17	2.60	49.98		79.2	100.0			13.11	
	pH	***pH 11***		C3	6	4.64	193.87	67.75	394.82		3.39			0.06	0.17	0.50	50.48		74.5	100.0			15.64	
	Media	***ceramic media***		C4	8	3.83	169.38	71.58	564.20		3.58			0.02	0.17	0.13	50.62		70.7	100.0			19.19	
	SIBX	***100***	***g/ton***	F		105.28										50.00			69.9					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		17.42								0.00	0.40	0.01								
				T3		16.28								0.00	0.40	0.01								

Forged steel

Run no.	Reagents			Sample	Time, min	Mass Pull, g	Water Rec, g	Cum Mass, g	% Solid rec	Cum Water, g	Ave cum Mass, g	Ave cum Water, g	Ave cum w Rec, g	Sulphur %	Sample Mass	Mass pyrite	Cum pyrite Mass	Ave Cum Pyrite Mass	pyrite Grade %	Pyrite Rec %	Ave pyrite gra %	Ave pyrite rec %	mass gangue	Ave Mass gangue
					0	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
1	***IS***	***SPW 1***	***SPW***	C1	2	53.01	190.00	53.01	2.65	190.00	55.36	199.93	199.93	42.10%	0.1301	41.75	41.75	41.75	78.8	83.5	78.8		11.26	
	DO	***DO 8***		C2	4	10.00	345.01	63.01	3.15	535.01	64.28	529.39	529.39	17.00%	0.1298	3.18	44.93	44.93	71.3	89.9	71.3		18.08	
	pH	***pH 9***		C3	6	7.76	399.50	70.77	3.54	934.51	71.20	936.16	936.16	6.79%	0.1868	0.99	45.92	45.92	64.9	91.8	64.9		24.85	
	Media	***Forged steel***		C4	8	5.56	316.86	76.33	3.82	1251.37	76.17	1244.64	1244.64	4.57%	0.2179	0.48	46.39	46.39	60.8	92.8	60.8		29.94	
	SIBX	***100***	***g/ton***	F		113.60										50.00			65.5					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		18.39								0.06%	0.3992									
				T3		18.88								0.06%	0.4072									
					0	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
2	***IS***	***SPW 1***	***SPW***	C1	2	57.71	209.85	57.71	2.89	209.85														
	DO	***DO 8***		C2	4	7.84	313.91	65.55	3.28	523.76														
	pH	***pH 9***		C3	6	6.08	414.04	71.63	3.58	937.80														
	Media	***Forged steel***		C4	8	4.38	300.10	76.01	3.80	1237.90														
	SIBX	***100***	***g/ton***	F		112.54																		
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		18.28																		
				T3		18.25																		
					0	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
3	***IS***	***SPW 1***	***SPW***	C1	2	72.25	425.77	72.25	3.61	425.77	36.13	212.89	212.89	35.40%	0.17	47.85	47.85	47.85	66.2	95.7			24.40	
	DO	***DO 8***		C2	4	10.75	392.57	83.00	4.15	818.34	41.50	409.17	409.17	3.96%	0.18	0.80	48.65	48.65	58.6	97.3			34.35	
	pH	***pH 11***		C3	6	7.94	358.77	90.94	4.55	1177.11	45.47	588.56	588.56	0.17%	0.18	0.03	48.67	48.67	53.5	97.3			42.27	
	Media	***Forged steel***		C4	8	6.68	314.87	97.62	4.88	1491.98	48.81	745.99	745.99	0.79%	0.17	0.10	48.77	48.77	50.0	97.5			48.85	
	SIBX	***100***	***g/ton***	F		132.80								1.72%	0.17	50.00			51.2					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		18.03								0.01%	0.26									
				T3		17.15								0.01%	0.26									

Forged steel

					0	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
4	***IS***	***SPW 1***	***SPW***	C1	2	41.69	198.19	41.69	2.08	198.19	20.85	99.10	99.10	52.10%	0.18	40.64	40.64	40.64	97.5	81.3			1.05	
	DO	***DO 0***		C2	4	7.63	298.01	49.32	2.47	496.20	24.66	248.10	248.10	19.50%	0.18	2.78	43.42	43.42	88.0	86.8			5.90	
	pH	***pH 9***		C3	6	7.51	384.14	56.83	2.84	880.34	28.42	440.17	440.17	5.89%	0.17	0.83	44.25	44.25	77.9	88.5			12.58	
	Media	***Forged steel***		C4	8	5.87	323.81	62.70	3.14	1204.15	31.35	602.08	602.08	4.10%	0.18	0.45	44.70	44.70	71.3	89.4			18.00	
	SIBX	***100***	***g/ton***	F		98.51										50.00			79.7					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		18.04																		
				T3		17.77																		
					0	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00
5	***IS***	***SPW 1***	***SPW***	C1	2	44.03	418.08	44.03	2.20	418.08	22.02	209.04	209.04	31.80%	0.18	26.20	26.20	26.20	59.5	52.4			17.83	
	DO	***DO 0***		C2	4	12.44	403.29	56.47	2.82	821.37	28.24	410.69	410.69	17.30%	0.18	4.03	30.22	30.22	53.5	60.4			26.25	
	pH	***pH 11***		C3	6	12.62	459.13	69.09	3.45	1280.50	34.55	640.25	640.25	18.40%	0.19	4.34	34.57	34.57	50.0	69.1			34.52	
	Media	***Forged steel***		C4	8	11.76	365.73	80.85	4.04	1646.23	40.43	823.12	823.12	26.80%	0.17	5.90	40.46	40.46	50.0	80.9			40.39	
	SIBX	***100***	***g/ton***	F		116.67								1.60%	0.23	50.00			61.8					
	DOW200	***50***	***g/ton***	T		0.00																		
				T2		17.92								0.25%	0.21									
				T3		17.90								0.23%	0.24									

9.3. EDTA extraction

		Forged steel				***Ceramic Media***			
		DO 0		DO 8		DO 0		DO 8	
		pH 9	pH 11	pH 9	pH 11	pH 9	pH 11	pH 9	pH 11
EDTA Extractable Fe (%)	***Dry grinding***	**7.04%**	**7.41%**	**5.36%**	**8.11%**	**6.88%**	**7.32%**	**6.66%**	**8.23%**
	Wet grinding	**6.54%**	**10.3%**	**7.65%**	**11.88%**	**3.81%**	**4.45%**	**3.62%**	**3.96%**