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EFFECT OF GRINDING CHEMISTRY ON THE SULPHIDISATION AND FLOTATION PERFORMANCES OF TRANSITIONAL OXIDE-SULPHIDE COPPER ORE

By

Simon JACQUES

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ii. SUMMARY

The influence of pulp chemistry on the flotation performance of sulphide ores has been widely studied. It is well recognised that shifting from a reductive to an oxidative grinding environment affects the pulp chemistry and improves the flotation performances of sulphide ores. Today numerous operations use high chrome media in their communion circuits for this purpose. However, the role of pulp chemistry on the flotation response of mixed ore is poorly understood. Mixed ore consists of a variety of sulphide and oxide minerals, and forms a part of the supergene enrichment zone of sulphide ore bodies; zones which can be well developed and are of primary importance for the economics of the mining project. However, they present technical challenges during their beneficiation: oxide and sulphide minerals often require different extraction methods; the presence of partially oxidised (tarnished) sulphide minerals make the ore less amenable to flotation; there is a high proportion of hydrophobic gangue; increased slime generation, etc.

This study highlights the importance of pulp chemistry for mixed ore recovered by sulphidisation and flotation. Experimental work conducted in this thesis has demonstrated that when shifting the chemistry from reductive to oxidative conditions during grinding, the metallurgical performance of both the sulphide and oxide minerals were affected, demonstrating the importance of matching the right grinding environment for each stage of the flotation process.

To have a better understanding of the fundamental mechanisms, the system was simplified. Oxidised sulphide mineral and oxide mineral were studied separately in the first approach.

The oxidised sulphide ore was studied by artificially oxidising a copper sulphide ore to various states during 16 months. For each oxidation state, the effect of chemistry was studied through a series of grinding and flotation tests completed under various grinding environments. The results show that the grinding chemistry drives the flotation performances of the ore at each oxidation stage, however strong ore oxidation presents a lower difference in pulp chemistry and similar flotation response for all grinding media tested.

For the oxide ore, the system of sulphidisation and flotation are more complex with little to no references in the literature about the importance of pulp chemistry. As such, for this study a simplified system was used whereby two different synthetic oxide ores were studied. The fundamental mechanism of the sulphidisation process was reviewed and some aspects clarified. A new equation was proposed. On the chemistry side, the oxide systems showed that the type of grinding environment affected the pulp chemistry and the subsequent sulphidisation-flotation process. The experiments revealed that an intermediate grinding pulp chemistry (not too reducing nor too oxidising) gave the best flotation performances.

Finally, a mixed synthetic ore was tested. With help from the system thermodynamics, the optimum pulp chemistry was identified for each stage of the process. The data showed that while the sulphide flotation stage required oxidative pulp chemistry, the oxide sulphidisation-flotation stage was more efficient in more reductive conditions. Therefore, various solutions were tested to manipulate the pulp chemistry during the oxide sulphidisation-flotation stage to try and improve the oxide flotation performances while using optimum conditions for sulphide flotation.

Techniques such as continuous pulp chemistry measurements, size by size recovery, XPS analysis and capillary electrophoresis were used to understand the problem stated in this work.

RESUMÉ:

L'influence de la chimie de la pulpe sur les performances de flottation des minerais sulfurés est l'objet d'études et de documentations approfondies dans la littérature scientifique. Il est ainsi largement reconnu que modifier la chimie de broyage d'un environnement réducteur à un environnement oxydant améliore les performances de flottation des minerais sulfurés. Aujourd'hui de nombreuses opérations minières utilisent à cet effet des corps broyant à haut contenu en chrome dans leur circuit de broyage.

Cependant le rôle de la chimie de la pulpe sur les performances de flottation des minerais mixtes reste très peu connu. Ceux-ci sont formés par enrichissement supergène et sont constitués d'une variété de minéraux sulfurés et oxydés. Pour certains gisements, cette zone mixte est très importante et influence de manière non négligeable l'économie générale du projet minier en entraînent cependant des défis techniques importants lors de sa concentration: minerais constitués de minéraux oxydés et sulfurés requérant des méthodes de concentration généralement différentes, présence de minéraux sulfurés partiellement oxydés plus difficilement récupérables par flottation, proportion importante de gangue hydrophobique, augmentation de la génération de matière fine (slime), etc.

Cette étude met en évidence l'importance de la chimie de la pulpe sur la récupération des minerais mixtes traités par sulphidisation et flottation. Les travaux expérimentaux menés dans cette thèse ont permis de démontrer que, lorsque les conditions électrochimiques lors du broyage passaient d'un environnement réducteur à un environnement oxydant, les résultats métallurgiques de récupération des minéraux sulfurés et oxydés étaient affectés, démontrant en cela l'importance d'obtenir une chimie de broyage adéquate pour maximiser les performances de flottation des minerais mixtes.

Pour mieux comprendre les mécanismes fondamentaux, le système étudié a été simplifié: Les minéraux sulfurés partiellement oxydés et les minéraux oxydés ont été étudiés séparément dans une première approche.

Les minerais sulfurés oxydés ont été étudiés en oxydant artificiellement un minerai de sulfure de cuivre à différents degrés pendant 16 mois. Pour chaque état d'oxydation, l'effet de la chimie de la pulpe a été étudié à travers une série de tests de broyage et flottation réalisés à l'aide de différents corps broyant produisant à chaque fois des conditions chimiques différentes. Les résultats montrent que la chimie de broyage influence les performances de flottation du minerai à chaque état d'oxydation de celui-ci. Cependant lorsque le minerai est fortement oxydé, les résultats montrent peu de différences de chimie de la pulpe et un rendement de flottation similaire entre les différents types corps broyant testés.

ii. Summary

Quant à la récupération des minéraux oxydés par sulfuration et flottation - plus complexe - et l’influence de la chimie de la pulpe sur le processus de sulphidisation et de flottation, il est constaté qu'elles sont très peu documentées dans la littérature scientifique. Raison pour laquelle des systèmes simplifiés tels que des minerais synthétiques composés d’oxyde de cuivre ont été étudiés. Le mécanisme fondamental du processus de sulfuration a été revu et certains aspects ont été clarifiés. Une nouvelle équation a été proposée. Du point de vue chimique, les systèmes composés de minéraux oxydés ont montré qu’ils étaient affectés par le type corps broyant, affectant la chimie de la pulpe ainsi que le processus de sulfuration et de flottation. Les expériences ont révélé qu'une chimie de broyage intermédiaire (ni trop réductrice, ni trop oxydante) donnait les meilleures performances de flottation.

Finalement, un minerai synthétique mixte a été testé. Avec l'aide de la thermodynamique du système, la chimie de la pulpe optimale a été identifiée à chaque étape du processus. Les résultats montrent que l´étape de flottation des sulfures requiert une chimie de pulpe oxydante, alors que l’étape de sulfuration-flottation des oxydes est plus efficace dans des conditions plus réductrices. Par conséquent, différentes solutions ont été testées pour modifier la chimie de la pulpe au cours de la phase de sulfuration et flottation dans le but d'améliorer les performances de flottation des oxydes de cuivre tout en utilisant des conditions optimales (oxydantes) pour la flottation de sulfure.

Des techniques telles que des mesures continues de la chimie de la pulpe, la récupération par fraction granulométrique, l’analyse de surface XPS et l'électrophorèse capillaire ont été utilisées pour comprendre le problème énoncé dans ce travail.

ii. Summary

iii. CONCLUSIONS

The recovery of copper by sulphidisation and flotation from a mixed ore has been studied in detail in this thesis. Particular focus was given to the effect of pulp chemistry on the sulphidisation mechanism and subsequent flotation response of oxidised sulphide minerals, both of which are not prevalent in the literature.

An important experimental work was completed to study the problem during which the mixed system was simplified. The effect of pulp chemistry on oxidised copper sulphide minerals and copper oxide minerals were first studied separately before examining a mixed system.

The work completed on the oxidised sulphide mineral revealed that grinding pulp chemistry affects the flotation performance of the ore for each oxidation degree tested. For the majority of the oxidation states, oxidative pulp chemistry, delivered by electrochemically inert grinding media (such as high chrome media), resulted in better flotation performance and better selectivity of chalcopyrite against pyrite. At the start of the oxidation period, weak ore oxidation resulted in strong pyrite activation regardless of the pulp chemistry generated during grinding. At the end, when the ore was heavily oxidised (after 16 months of artificial oxidation), all grinding media tested generated similar pulp chemistry and flotation performances of the ore, suggesting that when sulphide minerals are strongly oxidised, less galvanic interactions occur during grinding.

The experiments conducted on two synthetic oxide ores (pure malachite and a mixture of malachite and quartz) demonstrated that while oxide minerals are not as electrochemically active as sulphide minerals, different electrochemically active grinding media still generated different pulp chemistry and flotation performances of the ore. It was hence suspected that changing pulp chemistry affected the sulphidisation mechanism of the malachite.

Looking in more detail at the sulphidisation mechanism fundamentals, a study of the thermodynamics of the process combined with a sensitivity analysis of the surface (XPS technique) revealed that redox reactions involving copper reduction and sulphide oxidation were taking place during the sulphidisation process. The complex and various roles of the sulphidising agent were determined. Optimal pulp chemistry conditions for adequate sulphidisation of the malachite were also identified. These showed that when too oxidative conditions were created during grinding, in addition to a higher oxidation rate of the sulphidising agent (a sulphide salt), the pulp chemical conditions were quickly moving out of the optimal Eh-pH range for the formation of copper sulphide species, not allowing the formation of a sufficient sulphide layer at the malachite surface, negatively impacting malachite recovery.

Finally, the experimental work conducted on the mixed synthetic ore indicated that the optimum pulp chemistry conditions were different for the recovery of the sulphide and oxide minerals. While oxidative conditions were required for optimum sulphide flotation, reductive conditions were more adequate for oxide minerals. This means that the optimal grinding media for sulphide and oxide flotation are different. Size by size recovery was used to highlight these differences. From these observations, it was clear that by combining the best of the of the sulphide and oxide systems, the overall flotation performance of the ore could be noticeably improved. Various techniques were tested to try to manipulate the pulp chemistry to improve the oxide flotation performance under oxidative conditions, suitable for the sulphide flotation stage. Some of these techniques showed promising results.

In all instances, this study has revealed the importance of delivering the right grinding chemistry conditions to obtain the best flotation performance of a mixed ore.

iii. Conclusions

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I. INTRODUCTION

While the influence of pulp chemistry, through modification of the grinding environment, on the flotation performances of sulphide ores has been largely studied (Adam *et al.*, 1984; Bruckward *et al.*, 2011; Gonçalves *et al.*, 2003; Greet *et al.*, 2004; Huang and Grano, 2005a and b; Ekmekçi *et al.*, 2005; Grano 2009), its role in the flotation of mixed (oxide and sulphide minerals) ores is poorly documented.

For some deposits, the mixed ores zone is substantial and can be of great economic importance for a mining project. However these ore zones often present technical challenges to beneficiation such as oxide recovery, treatment of tarnished sulphides, slimes generation, presence of hydrophobic gangue and presence of acid consuming gangue, to name a few.

Preliminary works, in the framework of a Master's Thesis in 2010 (Jacques, 2010), have highlighted the importance of grinding-flotation chemistry on the flotation response of both the sulphide and oxide fractions of different copper mixed ores. The key findings of these sighter tests indicate that going from a reductive to an oxidative chemical environment during grinding and flotation had the effect of noticeably improving the metallurgical response of the sulphide fraction. However this was not true for the oxide fraction, for which variable results were observed. These observations revealed the importance of having a better understanding of the mixed system, with particular focus on the impact of the chemistry and its effects on the flotation response of the ore: the objective of this thesis.

The scope of this thesis; the effect of the pulp chemistry on mixed ore, has been summarised in Figure 1. Mixed ores come from weathered ore bodies and are composed of oxide and sulphide minerals. The sulphides present in these types of ore are often (partially) tarnished, i.e. oxidised. There are only few references in the literature which focus on the impact of chemistry on oxidised sulphide ores. As for oxide minerals, they can be recovered by various techniques. In these works, the processes used were sulphidisation and flotation. Very few mentions of the impact of chemistry on sulphidisation-flotation (of oxide ore) can be found in the literature.

Mixed ores are complex systems for which their beneficiation requires different sulphide and oxide flotation stages, making their study complicated. Therefore, the approach used in this work has been to study, in the first instance, the impact of chemistry on the tarnished sulphide and the oxide minerals separately before looking at the entire system. Tarnished sulphides minerals were studied through artificial oxidation of a fresh sulphide ore to various degrees. As sulphidisation and flotation of oxide minerals is a more complex process, single mineral and simplified "synthetic ore" were used during this study. Firstly, a bulk malachite sample was used and the sulphidisation mechanism reviewed. A new interpretation of the mechanism has been proposed. Then, with a better understanding of the process, synthetic oxide ore (a mixture of quartz and malachite) and mixed ore (a mixture of quartz-malachite-chalcopyrite) were used and a particular focus was given to the impact of pulp chemistry, especially during the sulphidisation stage on the process. Finally the outcomes of those simplified systems should have been used to understand the impact of pulp chemistry on a real mixed ore. However, due to insufficient time in this thesis only a few experiments with real ores were conducted, and thus the remainder has been relegated to perspective studies.

As described in this introduction, the main objective of this work is to study "*the impact of chemistry*" on a mixed system. Studying "*the impact of chemistry*" means gradually shifting the pulp chemistry of the system from reductive to oxidative conditions and observing the impact on the metallurgical response. The aim was to find the most appropriate chemical conditions giving the best metallurgical response for both the sulphide and oxide parts of the ore. The method used in this work to modify the chemistry was to shift the grinding environment by substituting various types of grinding media. Forged steel, high chrome and ceramic media were used to progressively shift the chemistry from a more reducing to a more oxidising environment.

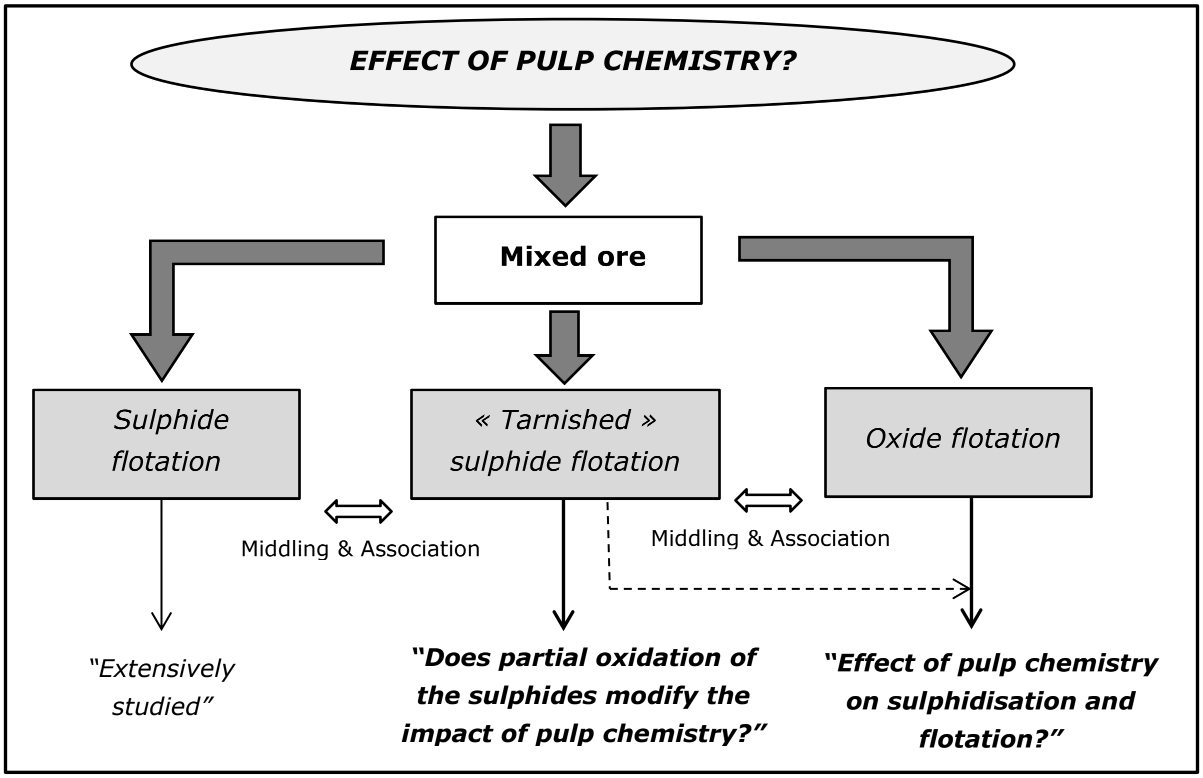

Figure 1: Scope of work.

II. GEOLOGY OF MIXED ORE DEPOSITS: TRANSITIONAL ORE

This chapter briefly introduces the context in which mixed ores are formed.

A mixed ore is part of the supergene enrichment zone of a sulphide orebody and is at the transition between the sulphide and the oxide zones (i.e. transitional ore). This enriched zone of economic importance usually overlies the primary hypogene mineralisation composed of primary sulphides; mainly chalcopyrite and pyrite. Their formation is briefly described hereafter. The principles involved in the supergene enrichment are illustrated in Figure 2. Detailed description can be found elsewhere in literature: Dold, 2003; Dold and Fontboté, 2001; Evans, 1993; Guilbert and Park, 1986; Garrels, 1954; Robb, 2005; Petruk, 2000; Sillitoe, 2005; Blain and Andrew, 1977.

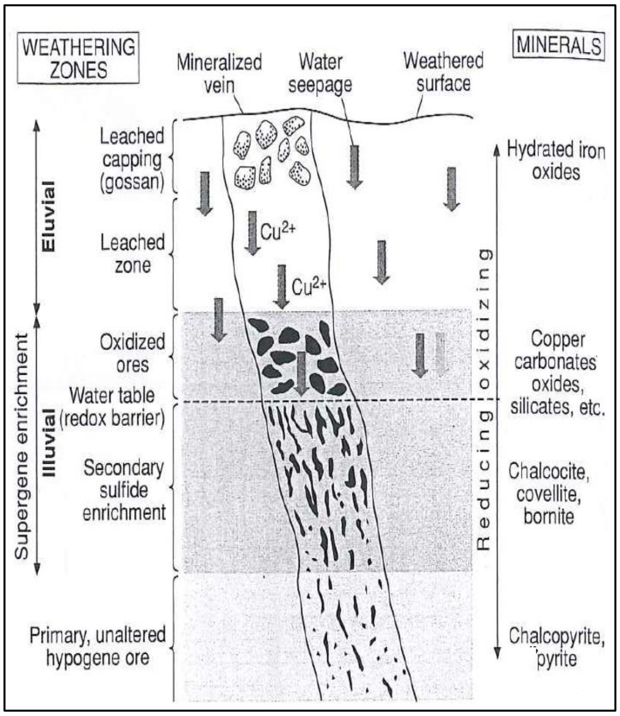

Figure 2: Schematic cross-section through a copper deposit showing typical patterns of supergene enrichment (Robb, 2005).

As oxidative weathering by the meteoric water of the upper part of the primary mineralisation takes place, the acidic waters generated by the dissolution of pyrite, an ubiquitous mineral of the sulphide deposits (Evans, 1993), leach the primary hypogene copper sulphide minerals, leaving a residual superficial zone enriched in iron (Gossan). The soluble copper ions percolate downwards and encounter progressively more reducing conditions. Either as a function of the neutralisation of acid solutions by the host rocks, or at water table level, copper ions precipitate as various secondary minerals. Their compositions reflect the ground water composition, the host rock nature, as well as the local Eh and pH conditions in the supergene zone (Robb 2005). The minerals formed are oxides such as cuprite, carbonates such as malachite and azurite, sulphates such as brochantite, chloride such as atacamite or silicates such as chrysocolla. In more reductive environments, copper ions can precipitate to form native copper or also replace the iron in pre-existing sulphide minerals (i.e. pyrite and chalcopyrite) to form a suite of Cu-enriched secondary sulphide minerals including chalcocite (Cu_2S), covellite (CuS), and bornite (Cu_5FeS_4) (Robb, 2005).

The role of bacteria in the supergene enrichment zone is not clearly defined but they most probably play a role in sulphide oxidation and may also contribute to the enrichment process (Sillitoe, 2005).

From a mineralogical point of view, various replacement textures of the primary sulphides by secondary sulphides are typical of these weathering processes (Bastin, 2010; Cailteux *et al.,* 2005; Guilbert and Park, 1986; Dold and Fontboté, 2001; Dold, 2003; Blain and Andrew, 1977). Figure 3 shows the complexities of such types of deposits.

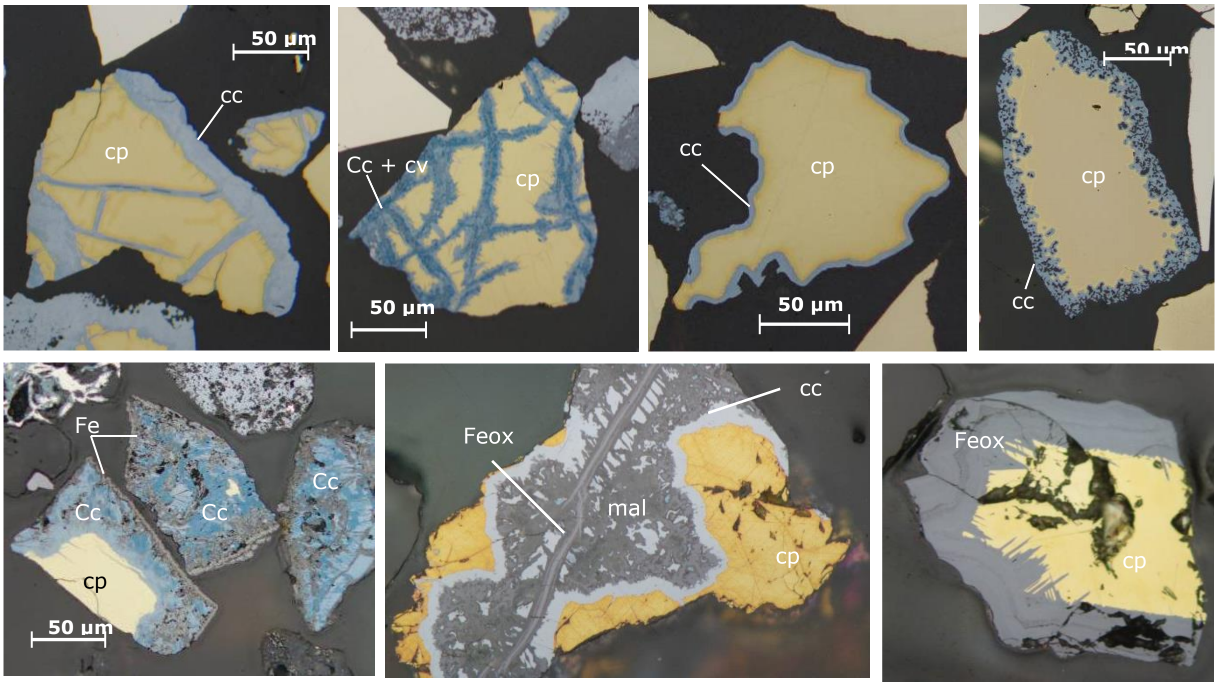

Figure 3 : Various replacement textures of chalcopyrite in Kansanshi mixed ores (a) partial replacement by chalcocite, (b) partial replacement by a fine intergrowth of chalcocite and covellite, (c) complete rimming with chalcocite, (d) replacement by porous chalcocite, (e and f) partial to total replacement by a complex association of chalcocite, malachite and goethite, (g) replacement by amorphous iron hydroxide (Bastin, 2010).

III. LITERATURE REVIEW

The 3 main phenomena studied in this thesis are reviewed in this section: the effect of chemistry on sulphide flotation, sulphide oxidation, and the sulphidisation mechanism.

3.1. Sulphide flotation

3.1.1. Effect of (grinding) chemistry on sulphide flotation: A brief review

The importance and dependency of sulphide flotation on pulp chemistry and its role in the selective flotation of sulphide minerals has been well established. Pulp chemical conditions and especially the electrochemistry, play an important role in mineral collector interaction and in the nature and composition of the species present at the mineral surface affecting the floatability of sulphide minerals (Tolley *et al.*, 1996; Woods, 2003 and 2010, Ekmekçi *et al.*, 2005).

Focussing more particularly on grinding chemistry, the electrochemical interactions between grinding media and sulphide minerals and their impacts on subsequent sulphide flotation performances have been widely studied by many authors (Bruckward *et al.*, 2011; Greet *et al.*, 2005; Iwasaki et al., 1983; Adam et al., 1984; Natarajan and Iwasaki, 1984; Rao et al., 1976; Rao and Finch, 1988; Yelloji Rao and Natarajan, 1989; Wang and Xie, 1990; Peng *et al.*, 2003; Peng and Grano, 2010 a and b). In their recent review, Bruckard *et al.* (2011) reported that the pulp chemical environment, ore composition, properties and type of the grinding media, pre-conditioning stages and reagent addition during grinding could influence the subsequent flotation process.

During grinding, the most commonly accepted mechanisms affecting sulphide flotation are galvanic interactions between the electrochemically active grinding media and sulphide minerals or between different sulphide minerals. Sulphide minerals are nobler than grinding media (i.e. they have a higher rest potential). When contact between the media and a sulphide (or between different sulphides) occurs, a galvanic couple appears; oxidising the media and increasing its rate of corrosion (Eqs. 1 and 2 or 4). The corrosion products can precipitate as iron oxy-hydroxide species onto the sulphide mineral surface (surface passivation or sulphide tarnishing) (Eqs. 3 or 5) as well as by combination with the various species present in the aqueous phase (Eq. 5). These interactions increase the presence of iron hydroxide species at the sulphide surface, lower the dissolved oxygen content of the pulp and decrease the pulp oxido-reductive potential (Bruckward *et al*., 2011; Greet *et al.*, 2004; Peng and Grano, 2010a). These limit the effectiveness of collector-sulphide interactions and hence can reduce mineral floatability.

<u>Medium-mineral interaction:</u>

$$Fe^0 + \frac{1}{2}O_2 + H_2O \xrightarrow{MeS} Fe^{2+} + 2OH^- \qquad (1)$$

$$2Fe^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^- \quad (2)$$

$$\begin{aligned} &Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \\ &Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \end{aligned} \quad (3)$$

Mineral (Me_1S)-Mineral (Me_2S) interaction

$$\begin{aligned} &Me_1S + \frac{1}{2}O_2 + H_2O \xrightarrow{Me_2S} Me_1^{2+} + S^0 + 2OH^- \\ &S^0 \rightarrow S_2O_5^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-} \end{aligned} \quad (4)$$

$$\begin{aligned} &Me_1^{2+} + 2OH^- \rightarrow Me_1(OH)_2 \\ &Me_1^{2+} + SO_4^{2-} \rightarrow Me_1SO_4 \\ &Me_1^{2+} + CO_3^{2-} \rightarrow Me_1CO_3 \end{aligned} \quad (5)$$

An additional mechanism can affect sulphide flotation; the direct interaction of the aqueous phase with the grinding media or with the sulphide minerals. The corrosion of grinding media in aqueous phase increases the quantity of iron ions in the solution and modifies the electrochemical conditions (chemistry) of the pulp. These oxidation products can be adsorbed or precipitated on the surface of both valuable and gangue minerals as hydrophilic iron hydroxides such as $Fe(OH)_2$, FeOOH and $Fe(OH)_3$ (Smart, 1991; Peng *et al.*, 2003). These surfaces modifications are less selective towards sulphides than in the case of grinding media-sulphides galvanic interactions.

The use of less electrochemically active grinding media (such as high chromium alloys) can counteract the deleterious effects of electrochemically active grinding media (such as forged steel media) on sulphide flotation. High chromium media can reduce the quantity of iron oxidation products generated, thus increasing the pulp electrochemical potential and oxygen content, thereby improving collector-sulphide mineral surface interactions.

3.1.2. Sulphide oxidation/tarnishing

Due to their electrochemical properties, sulphide minerals are very reactive and lead to the formation of various species at the surface, affecting their floatability. They start oxidising as soon as they are in contact with oxygen, water, solution species or due to electrochemical interactions that occur between sulphide minerals and/or grinding media (see Section 3.1.1.) (Ralston *et al.*, 2007; Peng *et al*., 2011; Owusu *et al.*, 2014). Various oxidation events can affect a sulphide ore, either during in situ weathering of an orebody or during the different extraction and processing stages (mining operations, stockpiling, milling and flotation) (Clark *et al.*, 2000).

Sulphide oxidation affects the flotation and separation of the valuable sulphide minerals since sulphide flotation depends on the proportion of hydrophobic and hydrophilic species covering its surface (Smart 1991; Guy and Trahar 1985). Copper sulphide surface oxidation leads, in the first instance, to dissolution of Cu and Fe ions from the mineral surface leaving a metal deficient layer enriched in sulphur, with some metal hydroxide present at the surface in alkaline conditions (Owusu *et al.*, 2014; Peng *et al.*, 2003; Peng and Zhao 2011). This has been supported by surface analysis studies by several authors (Smart 1991; Smart *et al.*, 1998; Vaughan *et al.*, 1995; Todd *et al.*, 2003; Buckley and Woods 1984). Since collectorless flotation is attributed to the presence of sulphur rich species such as polysulphide or elemental sulphide (Lutrell *et al.*, 1984 a and b; Yoon, 1981; McCarron *et al*., 1990; Barzyk *et al*., 1981; Walker *et al.*, 1986), slight surface oxidation may enhance the flotation performance of the sulphide mineral. However, the presence of dissolved Cu ions also promotes pyrite flotation through Cu adsorption on the surface (i.e. copper activation of pyrite) (Von Oertzen *et al.*, 2007; Chandra and Gerson, 2009; Lascelles and Finch, 2002), adversely affecting the selectivity of the flotation process.

Further oxidation leads to increased precipitation of iron hydroxides, covering the metal deficient sulphur rich surface and further decreasing the flotation response of the sulphide minerals. These hydrophilic metal hydroxides decrease the mineral’s hydrophobicity, inhibit collector adsorption and reduce selectivity against the various other sulphide minerals (Senior and Trahar, 1991; Clarke *et al.*, 1995).

3.2. Oxide sulphidisation

3.2.1. Sulphidisation technique

3.2.1.1. Overview

Sulphidisation is an aqueous chemical mechanism which converts a non-sulphide mineral surface into a sulphide surface by the addition of soluble sulphide salts (usually NaHS or Na_2S) and makes the mineral more easily floatable by traditional sulphide collectors such as xanthate. This technique is commonly used in the flotation of base metal oxide ores as well as to recover tarnished sulphide minerals (Newell *et al.*, 2007b).

Schwarz (1905) was the first to discover the application of using soluble sulphide species in flotation of oxide copper ores. The technique was initially commercially employed for the flotation of lead oxide ore in Australia (Crozier, 1992) and has been actively developed in the USA between 1920 and 1930 (Rey, 1954; Clark D.W. *et al*., 2000). Today this technique is employed for the concentration of oxide cobalt and copper ores (Kabombo and Witika, 2002; Banza and Kongolo, 2001; Kongolo *et al.*, 2003), as well as lead and zinc oxide ores (Pereira and Peres, 2004; Onal *et al.*, 2005; Herrera-Urbina *et al.*, 1999). Additionally, sulphidisation is used to recover tarnished or secondary sulphide ores (Orwe and Grano, 1997; Newell *et al.*, 2007a and b) and in the flotation of mixed (oxide and sulphide) ores (John *et al.*, 1991).

The sulphidisation process consists of the injection of soluble sulphide salts into the pulp, generating a reaction between the reagent and mineral particles which forms a sulphide layer at the surface. The dosage of the sulphide salt is critical; a too low quantity prevents the mechanism from taking place, a too high quantity depresses flotation. The nature of the reaction is not yet clearly understood. Nevertheless, numerous studies on sulphidised minerals tends to demonstrate that copper sulphides such as covellite or chalcocite are formed on the sulphidised mineral surfaces (Castro *et al.,* 1974a; Bustamente and Castro, 1975; Fuerstenau *et al.,* 1985; Wright and Prosser, 1965; Zhou and Chander, 1993; Raghavan *et al.,* 1984; Soto and Laskowski, 1973).

3.2.1.2. Sulphidisation reaction

- Oxide minerals:

In the literature, the sulphidisation reaction with oxide minerals is still not yet clearly understood there are several different mechanisms that are used to explain the process leading to the formation of a sulphide layer at the oxide surface. Some authors (Castro *et al.,* 1974a; Bustamente and Castro, 1975; Fuerstenau *et al.*, 1985; Bustamente and Shergold, 1983) attribute it to the strong adsorption of hydrosulphide ions onto the mineral surface followed by the formation of a sulphide surface through anionic exchange. Other authors think that the mechanism involves the precipitation of base metal sulphides onto the mineral surface (Wright and Prosser, 1965; Zhou and Chander 1993).

Bustamente and Castro (1975) were the first to propose a reaction mechanism for this reaction in the form of an anionic exchange mechanism between malachite and hydrosulphides:

$$CuCO_3Cu(OH)_2 + HS^- + OH^- \rightarrow Cu(OH)_2 + CuS + CO_3^{2-} + H_2O \tag{6}$$

They also noticed that substantial sulphide oxidation should take place but did not elucidate the chemical mechanism behind this (Bustamante and Castro, 1975; Castro et al., 1974a).

The mechanism proposed by Zhou and Chander (1993) differs. Based on thermodynamics as well as observations of the presence of metal colloidal sulphides during sulphidisation (also observed by Fuerstenau *et al*., 1985); they considered the formation of a primary sulphide layer through direct precipitation of copper sulphides with diffusion of copper ion through the primary sulphide layer. This is followed by the precipitation of the “liberated” copper ions as a “secondary” copper sulphide layer:

$$CuCO_3Cu(OH)_2 + HS^- \rightarrow CuS + Cu^{2+} + 2OH^- + HCO^{3-} \tag{7}$$

As for the first model, the mechanism proposed by Zhou and Chander (1993) also involves oxidation of the sulphides present. Soto and Laskowski (1973) considered that a catalytic mechanism of sulphide oxidation was taking place during sulphidisation. This oxidation process is necessary to remove the excess sulphides, but has a depressive effect during the sulphide flotation (Castro *et al.*, 1974b; Soto and Laskowski, 1973). While pulp aeration is normally used to remove the excess sulphides, air oxidation of sulphide species is a very slow process, except in the presence of catalytic reactions (see Section 3.2.1.3.). In addition, this oxidation step was suspected to have subsequently oxidised the freshly formed copper sulphide layer, again reducing the efficiency of the process. Although these authors had glimpsed the electrochemical character of the sulphidisation mechanism, none of them have highlighted the reaction behind that. For example, studies of the crystallographic structure of the copper sulphides indicate that the oxidation state of copper in any sulphide species (Goh *et al.*, 2006; Pattrick *et al.*, 1997) is Cu (1+) while the oxidation state of copper in malachite is Cu (2+). Therefore malachite sulphidisation should involve a reduction of the copper, which has not been discussed in the literature. Those observations have led to a review and new interpretation of the sulphidisation mechanism at the start of the current experimental work.

The above reactions show the importance of the availability of metal sites on the mineral surface and reveal the importance of the mineral solubility for sulphidisation. This is why sulphidisation of chrysocolla was found to be more effective in acidic conditions (Wright and Prosser, 1965; Zhou and Chander, 1993; Laskowski et al., 1985). On the contrary, the very high solubility of lead minerals leads to a high consumption of hydrosulphides by the aqueous lead ions present in the pulp.

In terms of sulphide coverage, Castro *et al.* (1974 a and b) estimated the presence of approximately 10 monolayers of sulphides at the oxide surface. Zhou and Chander (1993) observed that the malachite was coated with loosely adherent precipitates, ripped off under strong agitation.

The kinetics of the sulphidisation mechanism is considered to be very fast (Malghan, 1985; Castro *et al.,* 1974b). Based on their reactions, Zhou and Chander (1993) tried to establish a model of the consumption rate of Na_2S as a function of time. The results show that there was a rapid drop of Na_2S concentration within the first seconds of the process followed by a period of slower uptake. Rey *et al.* (1954) showed that the initial sulphide concentration played a role in the kinetics of the reaction: the higher the initial sulphide concentration, the faster the reaction. The nature and property of the mineral (solubility, porosity, etc.) also affects the rate and consumption of the sulphidising agent (Castro *et al.,* 1974b; Wright and Prosser, 1965; Laskowski *et al.,* 1985). The pH of the reaction also has a strong influence because of its role in the decomposition of the sulphidising agent (Section 3.2.1.3) and in the solubility of the mineral (Zhou and Chander, 1993; Raghavan *et al.*, 1984; Castro *et al.*, 1974b; Soto and Laskowski, 1973; Wright and Prosser, 1965).

- Tarnished sulphides

Practical applications in industry have shown the opportunity of using this technique for the treatment of primary or secondary tarnished/oxidised sulphide minerals such as chalcopyrite (Bulatovic and Wyslouzil, 1985; John *et al.*, 1991; Rey *et al.*, 1979), pentlandite (Barker *et al.*, 1982), digenite (Orwe *et al.*, 1998) and bornite (Freeman *et al.*, 2000). While the feasibility of sulphidising these minerals has been demonstrated by different authors (Newell *et al.,* 2007b; Bulatovic and Wyslouzil, 1985; Malghan S.G., 1985); the sulphidisation mechanisms of oxidised sulphide minerals are less well documented.

Prior to formation of a sulphide coating itself, the addition of sulphide salts seems to restore the sulphide surface of the tarnished minerals by removing oxidation products from the surface (Luttrel and Yoon, 1984b; McCarron *et al.*, 1990; Orwe *et al*., 1998). Orwe *et al.* (1997) invokes the precipitation of metal hydroxides as insoluble metal sulphides to restore the sulphide surface. Subsequently, the addition of sodium sulphide forms a copper sulphide phase with a higher sulphur to copper ratio (McCarron *et al.*, 1990; Walker et al., 1986; Luttrel and Yoon, 1984b). The presence of elemental sulphur, restoring the mineral hydrophobicity, has been observed by Walker *et al.* (1986) for pyrite and gold, and for chalcopyrite at low sulphide concentration only by Luttrell and Yoon (1984a).

Newell *et al.* (2007a) identified three different mechanisms to describe the process, driven principally by the nature of the sulphide minerals: electrochemical reactions, anionic exchange and precipitation. For example, it seems that the sulphidisation of chalcopyrite shows high similitude to the mechanism proposed by Busamente and Castro (1975) for malachite.

XPS analysis has revealed the presence of copper sulphide species on all the sulphidised surfaces as well as the presence of either polysulphide or elemental sulphur, both contributing to sulphide flotation (McCarron *et al.*, 1990; Luttrel and Yoon, 1984a)

The sulphidisation of tarnished sulphide minerals, by restoring the sulphide surface, often allows the collector consumption to be significantly reduced, usually high in the case of tarnished sulphides (Orwe *et al.,* 1998).

3.2.1.3. Effect of chemistry

- pH

Apart from its role in the solubility of mineral surfaces, the pH level is responsible for the nature of the active soluble sulphide salt used during sulphidisation. Indeed, the dissociation of hydrosulphides such as NaHS or Na_2S (the most common reagents used for sulphidisation) is a function of pH according to the following reaction:

$$H_2S \leftrightarrow HS^- + H^+ (\mathrm{p}K_1=7.04) \quad (8)$$

$$HS^- \leftrightarrow S^{2-} + H^+ (\mathrm{p}K_2=12.92) \quad (9)$$

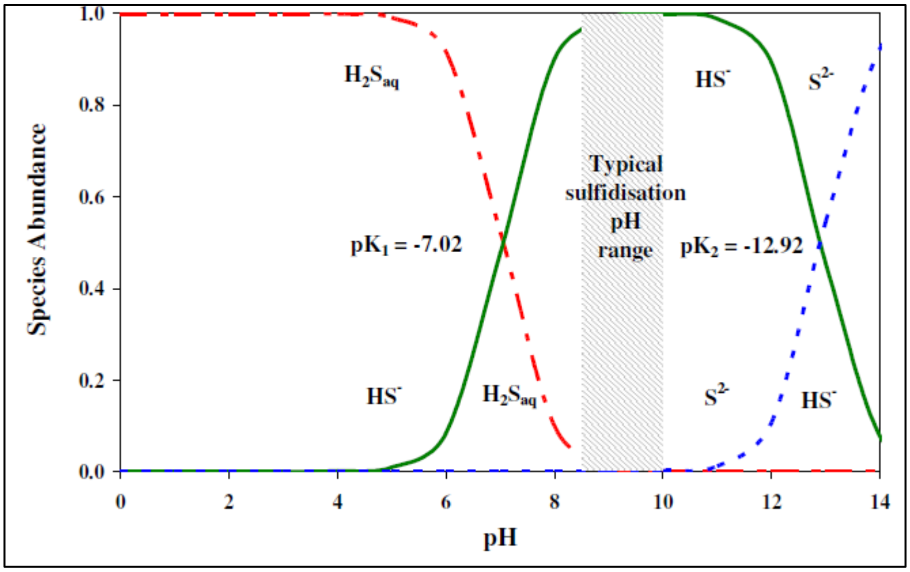

Figure 4: Sulphur speciation as a function of pH(Newell, 2007c (modified from Crozier, 1992)).

The speciation of the soluble sulphides as a function of pH is represented in Figure 4. The values of the two equilibrium constants are those found in Crozier, 1992. As the sulphidisation pH is often between 9 and 10, the dominant species is always HS^-. Indeed, the hydrolysis of NaHS or Na_2S in water liberates OH^- ions and the pH naturally increases to between 9 and 10, depending of the quantity of the sulphide salt added. Therefore, usually no pH adjustments are needed prior to sulphidisation.

- Electrochemical potential (Eh):

While the description of the sulphidisation mechanism in the literature does not really reflect the electrochemical property of the reactions taking place, the electrochemical potential, or more particularly the Eh-pH conditions, these are of primary importance for the thermodynamics of the reactions.

Eh-pH equilibrium diagrams give the stability regions of the species present for a given system (i.e. the thermodynamically most stable specie for any Eh-pH condition). For example, in this case, the stability domain of the copper species formed during sulphidisation can be studied by looking at the Cu-S-H_2O Pourbaix diagram. However, it is important to keep in mind that such diagrams do not take into account the limitation of the kinetics of the reaction as well as the development of metastable phases.

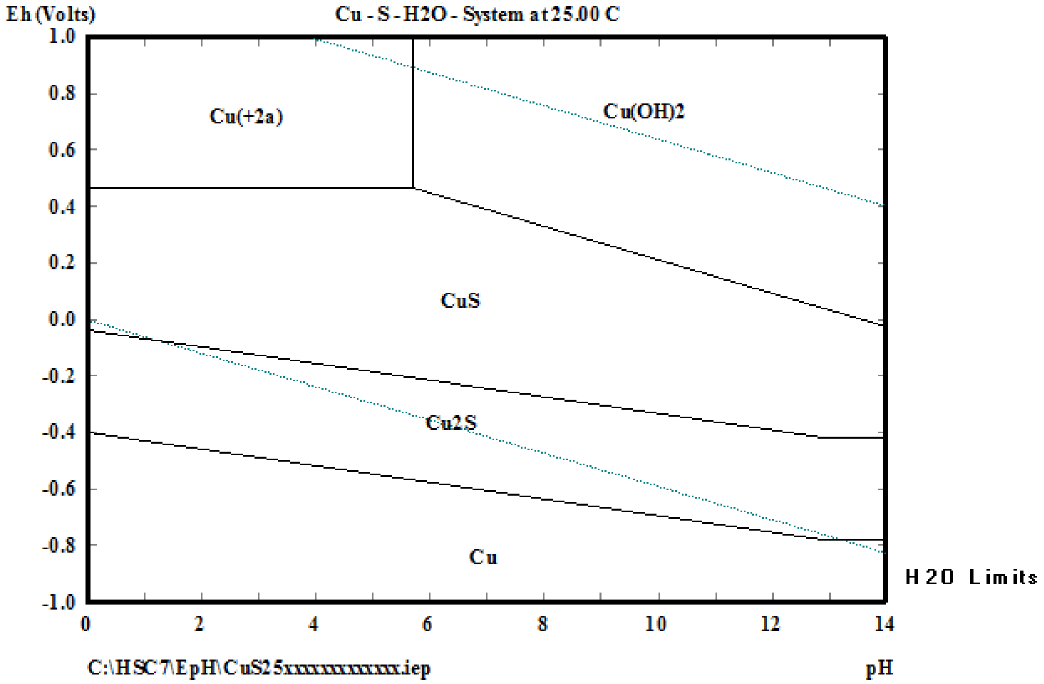

Figure 5: Eh-pH diagram for the Cu-S-H_2O system. [Cu] and [S]=10 E-6. Sulphur oxidation state: -II (generated by HSC Chemistry®).

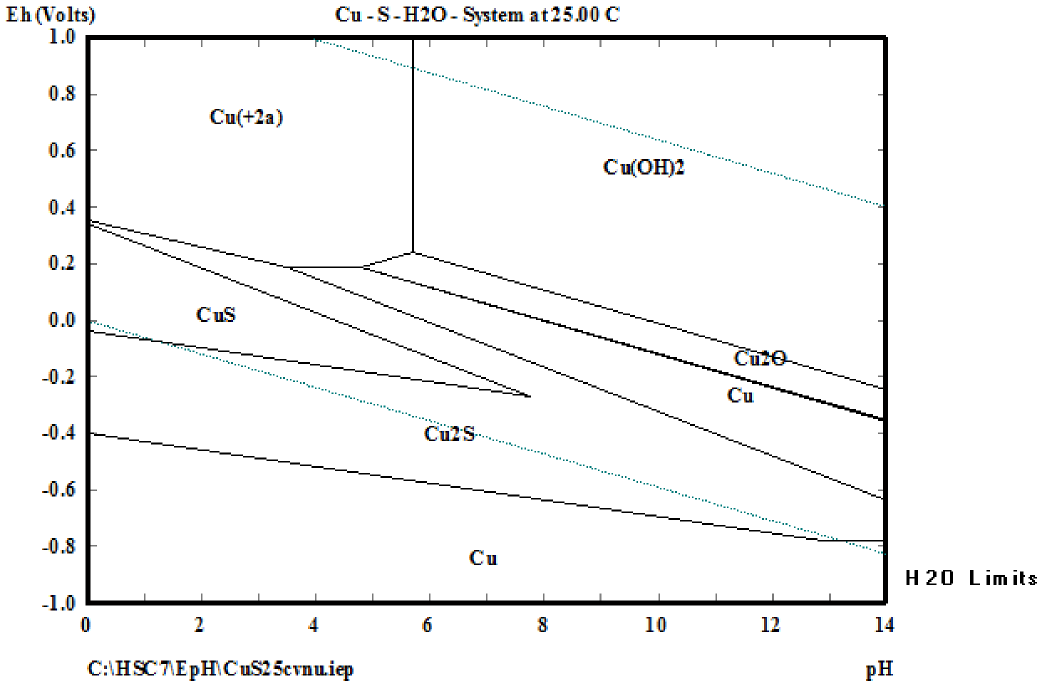

Figure 6: Eh-pH diagram for the Cu-S-H_2O system. [Cu] and [S]=10 E-6M. Sulphur oxidation state: -II to +VI (generated by HSC Chemistry®).

Investigations conducted by Woods *et al.* (1987) on the Cu-S-H_2O system have shown that the stability region of the copper sulphides was dependent on the copper to sulphide ratio (and hence is different for each copper sulphide species) as well as the presence of metastable sulphur species, increasing the stability region of the copper sulphides species through high electrochemical potential. Sulphidisation is expected to take place in the CuS or Cu_2s domains; Zhang (1994) noted that in all of the diagrams, the combination of the CuS and Cu_2S domains was the same at the same copper concentration: the CuS domain growing and Cu_2S domain shrinking as the sulphur concentration increases. He concluded that the construction of a simple Cu-S-H_2O diagram with the correct sulphur concentration, independent of mineral type, could be sufficient to help design sulphidisation experiments.

Those observations indicate that when drawing a Cu-S-H_2O diagram for sulphidisation, in addition to the copper concentration, the sulphur concentration was important to delimitate the CuS-Cu_2S stability domain. The oxidation of sulphides and the apparition of their different valence states also modifies the stability region of the copper sulphide species. Indeed, when considering the oxidation of sulphides from sulphide (-II) to sulphate (+VI), the stability region of the copper sulphides evolved from Figure 5 to Figure 6 respectively; the CuS and Cu_2S domains shrinking with the apparition of oxidised sulphide species. Note that according to Woods *et al.* (1987), sulphide oxidation leads to the apparition of metastable sulphide species which can extend the stability region of the copper sulphides in the high Eh domain.

The diagrams presented in Figure 5 and Figure 6 were made by using the HSC Chemistry® software developed by Royne (2011). The thermodynamic data used to build those diagrams are presented in Appendix 5.4.4.

- Dissolved Oxygen

The oxygen content of the pulp plays an important role in the oxidation reaction of most of the species present in the pulp as well as the soluble sulphide salt (NaHS, Na_2S) used for the sulphidisation mechanism. Indeed, oxygen reduction couples most oxidation reactions such as sulphide oxidation.

In an aqueous sulphur-oxygen system, sulphides represent the lowest oxidation state (-II) and can be progressively oxidised to any higher level (0, +II, +IV) to reach the highest oxidation state (+VI) and form sulphates, dependent on the thermodynamic conditions. The various oxidation states of sulphur in aqueous media are represented in Figure 7 (Kuhn *et al.*, 1983). Sulphide oxidation by oxygen is well documented. It is clear from the literature that sulphide oxidation by oxygen alone is very slow but that in the presence of species in solution (Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+} cations for example) a catalytic effect takes place, accelerating the sulphide oxidation (Dohnalek and Fitzpatrick, 1983; Chen and Morris, 1972; Malghan, 1985). Hecker *et al*, (1985) reported evidences of catalytic oxidation of sulphides by malachite and chrysocolla and confirm that sulphide oxidation was taking place during sulphidisation.

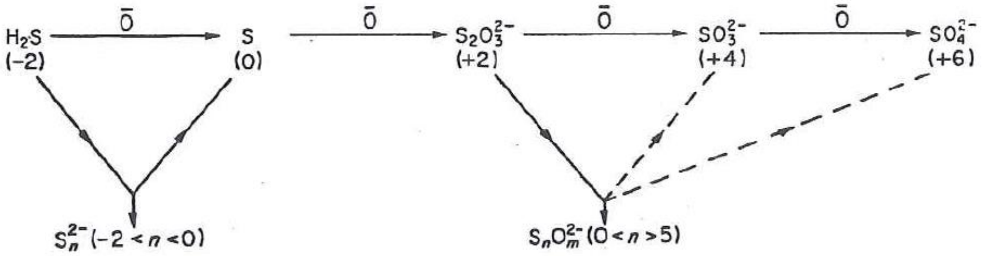

Figure 7: Schematic representation of the various valence states of sulphur in aqueous solution, Khun *et al.,* 1983.

Due to the effect on sulphide oxidation, the oxygen content of the pulp is important during two stages of the sulphidisation process:

- During the addition of the soluble sulphide salt;
- At the end of the sulphidisation process.

When the sulphide salt is added, a low oxygen concentration of the pulp is optimal. Reducing the oxygen content will reduce the consumption of the sulphides by limiting their oxidation and increasing their availability for the sulphidisation reaction. This has been observed by Clark *et al.*, 2000; Soto and Laskowski, 1973; and Hecker *et al.*, 1985.

On the contrary, at the end of the sulphidisation process, a high oxygen concentration is required to remove the excess sulphides and their undesirable depressing effect from the pulp. This has been observed by many authors who have noticed that an aeration step was required between the sulphidisation and the flotation stages (Woods *et al.,* 1989; Castro *et al.*, 1974b; Soto and Laskowski, 1973; Gebhardt and Kotlyar, 1991). Indeed, after sulphidisation, the remaining sulphur species in solution are in competition with the sulphides on the mineral surface for collector interaction (Gebhardt and Kotlyar, 1991; Woods *et al.*, 1989). Moreover, they shift the pulp potential to reducing conditions which is not optimum for sulphide flotation and mineral-collector attachment (dixanthogen formation for example) (Woods *et al.*, 1989; Woods, 2003 and 2010; Guy and Trahar, 1985; Chander and Fuerstenau, 1983).

3.2.1.4. Practical application

The sulphidisation technique consists of the injection of an appropriate dosage of soluble sulphide salts into the pulp to react with the minerals present.

Various types of soluble sulphide salts can be used in the process: NaHS, Na_2S; $(NH_4)_2S$. NaHS is one of the most commonly used reagents because of the low price and minimal impact on pH due to its hydrolysis in water (Crozier 1992). Therefore, it is the sulphide salt used in this work.

The critical step of the process is the reagent dosage: a too weak quantity prevents the mechanism from taking place while a too high quantity depresses flotation (Section 3.2.1.3.). To overcome the sensitive reagent addition and its undesired effects, a Controlled Potential Sulphidisation (CPS) technique is often used to control the reagent dosage (Jones and Woodcock, 1978 a and b and 1979; John *et al.,* 1991; Nagaraj and Gorken, 1991). This technique has been developed by Jones and Woodcock (1978b) and enables constant and optimum sulphidisation conditions. During CPS, the sulphide ion concentration of the pulp is continuously measured by an appropriate ion selective electrode Ag/Ag_2S and the control of the reagent addition is achieved by maintaining the electrode potential (E_s) at a fixed value (Figure 8). The choice of the correct E_s is of critical importance. E_s governs the quantity of sulphide present in the pulp as well as the E_h potential of the pulp. An E_s potential of around -500 to -600 mV is usually required to sulphidise correctly the oxide base metal minerals while a less reductive potential of around -350 mV should be sufficient to remove the oxidation products of tarnished sulphide minerals (Jones and Woodcock, 1978a; John *et al.,* 1991; Nagaraj and Groken, 1991).

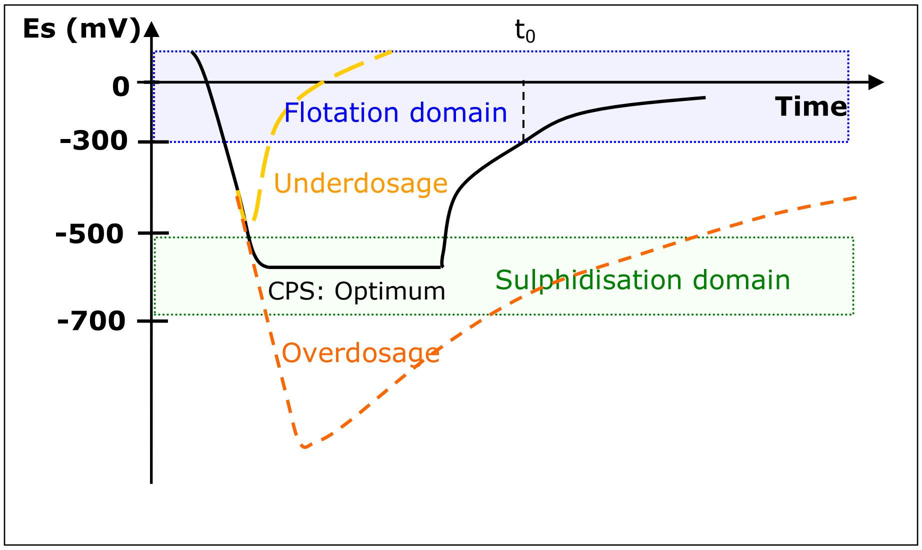

Figure 8: **Es variation during the sulphidisation process. Optimum sulphidisation domain of oxide mineral is often below -500 mV (Es) while the flotation domain is above -300mV (Es).**

Another advantage of the CPS technique is that it naturally overcomes the variation of ore feed grade, very common in processing plants. Figure 8 also shows the importance of removing the excess sulphide species after sulphidisation to remove their undesired effect and reach a potential suitable for flotation.

The sulphidisation time required should be small because of the fast kinetics of the reaction. Jones and Woodcock (1979) found that a conditioning time of several minutes, typically 3, was optimum although longer conditioning time may be required with some ore types. A two minute conditioning period is generally used at the University of Liège (Ulg), Belgium, and has proven to be sufficient in most of the cases (Bastin D., 2013). In terms of reagent consumption, during CPS usually up to 50 percent of the reagent is consumed within the first several seconds of the process.

Jones and Woodcock (1978a) have compared different sulphidisation techniques (slug addition, simultaneous CPS and flotation, and CPS followed by flotation) and found that a multi-stage (4 stages) CPS-flotation gave the best recoveries at lowest reagent consumption. Multi-stage sulphidisation-flotation has also been found to be the most effective technique in practice by Bastin and Frenay (2003) to recover copper-cobalt oxide ores from the Democratic Republic of Congo.

IV. EXPERIMENTAL

4.1. Sample description

4.1.1. Sulphide ore

A sample of approximately 600 kilograms of copper sulphide ore was sourced from the plant feed conveyor from an Australian copper mine. Mineralogical analysis of the ore revealed that copper was present as chalcopyrite only. Pyrite was the main iron sulphide mineral with small amount of pyrrhotite. The sample was dispatched to the Ulg laboratory in Belgium. The ore was received as a mixture of coarse and fine material.

4.1.2. Synthetic ore

Synthetic ores were made by mixing pure mineral in various proportions. Pure quartz was used to simulate the non-sulphide gangue. Lumps of pure malachite and chalcopyrite were used as the source of oxide and sulphide minerals, respectively. Three types of synthetic ore were made by mixing the minerals as below :

- Bulk malachite sample: 100 percent malachite;
- Synthetic oxide ore: a mixture of malachite and quartz;
- Synthetic mixed ore: a mixture of malachite, quartz and chalcopyrite.

4.2. Sample preparation

When received in Belgium, all samples were crushed to 100 percent passing 2 millimetres. They were then thoroughly mixed and split into lots. Each sub-sample was placed in a plastic bag, sealed under vacuum and stored in a freezer prior to use to minimise oxidation. The charge weights used during the tests were chosen to achieve the desired percent solids for the rougher flotation.

4.3. Assays

Flotation test products were assayed at the Bureau Veritas Limited laboratory in Adelaide. The solid samples were assayed for:

- Sulphide ore: Cu, Fe, S
- Oxide synthetic ore: Cu
- Mixed synthetic ore: Cu, AsCu, S, Fe

Iron sulphide (for sulphide ore only) and non-sulphide gangue assays were calculated from the elemental assays. For these calculations, assumptions for mineral composition were used and are detailed in Appendix 1.1.

For the mixed synthetic ore, distinction of the mineralogical copper deportment was done through diagnostic and sequential leaching. Copper dissolved in sulphuric acid is traditionally referred to as Acid Soluble Copper (ASCu) and the copper remaining in the leached residue as Acid Insoluble Copper (AICu). When performed under the optimum conditions (granulometry, pH, temperature, agitation and leach time) a sulphuric acid digestion will dissolve 100% of the copper contained in malachite. Hence, ASCu assays refer to the oxide fraction and the AICu fraction, calculated by subtracting AsCu from Cu, corresponds to the sulphide fraction.

$$AICu = Cu - ASCu \tag{10}$$

The EDTA extraction solutions were all assayed for Cu and Fe at the University of Liège.

4.4. Water

University of Liège tap water was used for all experiments.

4.5. Laboratory testing

4.5.1. Grinding calibration

Grinding was completed in the Magotteaux Mill® which is described in Appendix 1.2. An ore charge was added to the mill, along with 2000 millilitres of Ulg tap water and the desired weight of 30 millimetre balls. The lid was placed on the mill, and the mill rotated for the desired length of time at the desired speed. If necessary, nitrogen gas or air was purged into the mill during grinding to modify the Eh and dissolved oxygen concentration. The temperature was controlled through the use of the heating coil installed in the mill shell. The pulp chemistry parameters were automatically controlled by the Magotteaux Mill® process control system.

Initially, the grinding calibration was completed using forged steel grinding media to establish the time and amount of grinding media required to achieve the desired P_{80}. With these parameters established, the calibration procedure continued using forged steel to determine an appropriate gas purging regime such that the desired pulp chemistry was obtained. With the grinding time, media configuration and gas purging procedure established, test grinds were completed using a range of high chrome and ceramic grinding media to determine if the same size distribution was achieved using these alloys. If the size distribution did not match, the mill speed was adjusted until a match was obtained.

4.5.2. Flotation procedure

Flotation tests were completed using the Magotteaux Flotation Machine described in Appendix 1.3.

After grinding, the pulp was transferred into the flotation cell and mixed for two minutes to homogenise the pulp. For each series of tests conducted, a detailed explanation and a flow sheet of the flotation procedure used is explained in the results section (Section V).

For all flotation tests:

- Each concentrate was collected by hand scraping the froth from the surface of the pulp once every 10 seconds
- The pulp chemistry (Es, Eh, pH, dissolved oxygen, and temperature) was monitored throughout.
- Tap water was added during flotation to maintain the pulp level in the flotation cell.
- The wet weights of all concentrate and tailing products were recorded to enable the water recovery to be calculated. These samples were subsequently filtered and dried. The dry samples were weighed and submitted for assay.
- Tests were completed in duplicate or triplicate to ensure good confidence in the data produced. The reproducibility was examined for each condition and some tests repeated if necessary.

4.5.3. Flotation kinetic parameters

The mineral recovery response measured in a laboratory batch flotation experiment can be used to calculate the ore floatability parameter, a number which represents the rate and extent to which a mineral floats. These numbers are used as a means of comparison of different batch test experiments (Runge, 2010).

Flotation can be considered as a first order kinetics process:

$$R_t = R_{\max}(1 - e^{-kt}) \tag{12}$$

Where, R_t = recovery at time *t,* R_{max} is the maximum recovery at infinite time and *k* is the first order rate constant (min^{-1}). The parameters were estimated by using Excel's Solver to minimise the sum of squares (SS) of the differences between the observed recovery values: R_{obs} (experimental results) and those predicted by the fitted model (R_{pred}, Eq. 12):

$$SS = \sum_{i=1}^{n} (R_{i\,Obs} - R_{i\,pred})^2 \tag{13}$$

i= number of concentrates

From these two kinetic parameters, two additional parameters can be calculated and used for results comparison: the modified rate constant K_M and the copper/iron sulphide selectivity index ($SI_{Cu/IS}$) (Xu, 1998).

$$K_M = R_{\max} \cdot k \tag{14}$$

$$SI_{Cu/SI} = \frac{K_M Cu}{K_M IS} \tag{15}$$

4.5.4. Student's t-test

The t-test (two-sample assuming equal variance) method is used to compare the averages of two sets of data; specifically, the difference in the average parameters or performance values between the two periods.

Detailed explanation of the t-test methodology can be found in Napier-Munn (2014). Simply, when statistically comparing the means of two sets of data through a t-test, two pieces of information can be obtained:

1) The difference in means, with a 2-sided (say 90 percent) confidence interval. Simply the subtraction of the two means, with the interval in which we are 90 percent confident the difference lies.
2) Confidence level of the difference. Common practice considers that a minimum confidence of 90 percent is required to affirm that the means are statistically different.

4.6. Chemistry measurements

4.6.1. E_h, pH, DO, T° data collection

The pH, Eh (i.e. *pulp oxido-reductive potential* (Pt-Ag/AgCl electrode, +199mV vs SHE)), dissolved oxygen (DO), and pulp temperature data were recorded through grinding and flotation using a TPS 90-FLMV data logger. All potentials reported in this thesis have been converted to the standard hydrogen electrode (SHE) scale.

The pH probe was calibrated using pH buffer solutions 7 and 10. The Eh probe was checked using Zobell solution (1:1 solution of Part A and B = 231 mV), and the dissolved oxygen probe was calibrated in a 0.2 g/L solution of sodium sulphite for the zero calibration, and air.

4.6.2. E_s data collection

When necessary, Es, i.e. *the sulphide ion potential*, was also recorded with a combination Ion Specific Electrode (ISE-Ag/Ag_2S).

The potential measured by this electrode is a direct measurement of the S^{2-} concentration of the pulp:

$$2Ag^0 + S^{2-} \Leftrightarrow Ag_2S + 2e^- \qquad (16)$$

Following the Nernst equation:

$$E_s = E_0 + \frac{0.0592}{2}\ln(\frac{1}{S^{2-}}) \qquad (17)$$

This electrode was used to control the NaHS addition during the Controlled Potential Sulphidisation steps (CPS). The probe slope was checked daily with standard solutions.

4.6.3. EDTA extractable metal ions

EDTA (Ethylenediaminetetraacetic acid) is a chelating agent, leaching any oxidation products from the surfaces of the minerals and holding them in solution. Assaying the filtered solution is a way of measuring the extent of oxidation of the sulphide minerals. EDTA extractions were completed prior to flotation by taking a 25 ml sample of pulp with a syringe from the flotation cell.

The EDTA extraction process is as follows:

- Inject the contents of the syringe into a 400 millilitre beaker containing 250 millilitres of three percent (by weight) EDTA solution, pH modified to 7.5 with sodium hydroxide and previously purged for 5 minutes with 4 litre/min N_2.
- Thoroughly mix the slurry and EDTA solution using a magnetic stirrer, for five minutes while purging with N_2
- Filter the EDTA/slurry mixture using a 0.2 micron Millipore filter.
- Submit the filtered EDTA solution and solids sample for Cu and Fe assay.

The percentage of copper and iron extracted by EDTA are then calculated as a ratio of the EDTA soluble copper or iron to the total amount of copper or iron present in the solid sample (Rumball and Richmond, 1996).

4.6.4. Oxygen demand

Oxygen demand is a measure of how quickly the pulp consumes oxygen. The majority of oxygen is consumed by redox reactions in the pulp; therefore a high oxygen demand indicates that the pulp is highly reactive with a high number of redox reactions taking place. A low oxygen demand indicates the pulp is in a stable oxidation state with low levels of redox reactions taking place.

The oxygen demand of a plant process stream is determined by measuring the dissolved oxygen decay of the pulp. The dissolved oxygen concentration is recorded every 5 seconds over a two minute period to establish an oxygen decay curve.

The oxygen decay curves are plotted in Microsoft Excel and fitted to the first order rate equation (Equation 18):

$$DO = DO_0.e^{-kt} \tag{18}$$

Where DO is the dissolved oxygen concentration at time, t; DO_0 is the dissolved oxygen concentration at time zero; and k is the oxygen demand rate constant. Comparing the rate constants of different sample points allows a comparison of the reactivity at those points.

4.7. Capillary electrophoresis

Capillary electrophoresis (CE) is a commonly used method to determine the speciation of sulphur ions species, particularly for environmental or food industry application where the type and quantity of sulphur ion species is of great importance. The CE analyses were performed at the University of Liège using indirect UV detection method.

4.8. Sulphide tarnishing/oxidation

A sulphide ore was artificially oxidised to various lengths by percolating a small quantity of acidic ferric sulphate solution inoculated with a mixed bacterial culture through packed columns. Bacteria were not only used to maintain the solution in oxidative conditions through their role in conversion of ferrous into ferric ions but also because of their possible direct implication in sulphide oxidation (Watling, 2006; Boon, 2001).

A schematic of the experimental apparatus used is presented in Figure 9, with photos displayed in Appendix 1.4. The solution used was made of the nutriment medium called the Lundgren-Silveramn 9K, to maintain the bacteria growth. The composition can be found in Appendix 1.4 Table 1. Daily, 70 ml of fresh 9K solution at pH 1.8 and containing 9 g/l $FeSO_4$ were pumped into the fermenter where the bacteria (*Acidithiobacillus ferrooxidans*) were cultured. In the fermenter, ferrous ions were oxidised to ferric ion by the bacteria metabolism. From the fermenter, 70 ml of the inoculated solution was pumped (daily) to the top of the packed column containing the sulphide ore (around 35kg of ore per column) from which it percolated down and oxidised the ore. Holes were drilled at the bottom of each column to allow excess solution to escape. The excess solution was regularly assayed to control the quantity of iron and copper that was being leached into the solution. The temperature of the entire equipment was maintained at 35 °C in a closed room. Initially the columns were moistened by hosing the top of the column with water until water escaped from the bottom of the column.

A total of 7 representative samples were prepared for the experiment. One (T0) was kept aside as the baseline, while the other six were packed in the columns and artificially oxidised for various lengths of time (15 days, 1, 2, 4, 8, 16 months). The sample identification and oxidation time are presented in
Table 1.

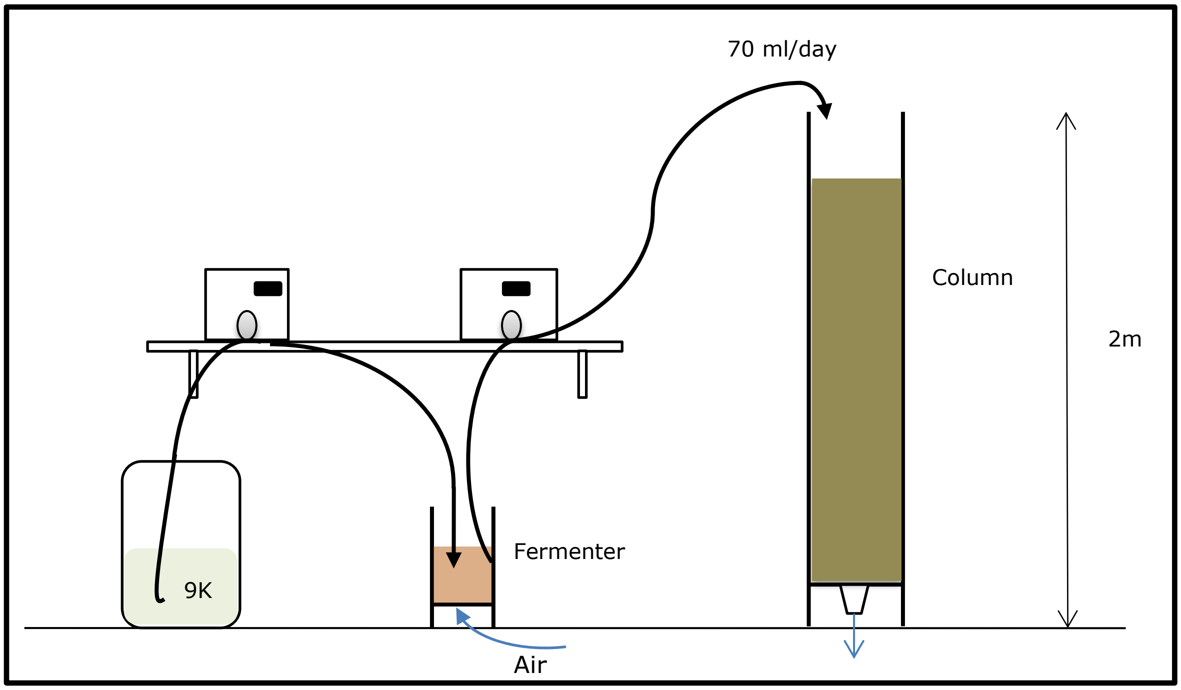

Figure 9: Sulphide oxidation through packed column: apparatus scheme.

Table 1: Sample name and oxidation time for the oxidised sulphide ore.

Sample ID	Oxidation time
T0	0
T1	15 days
T2	1 month
T3	2 months
T4	4 months
T5	8 months
T6	16 months

4.9. Surface characterisation technique: XPS

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive analysis technique that uses the photoelectric effect to identify and quantify elements on the surface of materials. The significance of the technique is that it provides not only the composition of the species present at the surface but also their chemical state.

Sample preparation:

The slurry samples collected for XPS surface analysis were placed in a plastic tube, frozen in liquid nitrogen and stored in a freezer until immediately prior to surface analysis. The slurry samples were placed onto carbon tape and transferred into the X-ray spectrometer. No sample cooling stage was performed prior to the introduction of the sample into the XPS chamber.

XPS measurements:

All XPS analyses were carried out at the Ian Wark Research Institute, South Australia. The XPS instrument used was a Kratos Axis Ultra with DLD. The x-ray was a monochromatic aluminium x-ray running at 225 W with a characteristic energy of 1486.6 eV. The area of analysis (iris aperture) was a 0.3 mm x 0.7 mm slot and the analysis depth was approximately 15 nm into the surface of the sample. The analysis vacuum was $4x10^{-9}$ Torr. The electron take off angle was normal to the sample surface. Two spectral regimes were recorded during the analysis: survey spectrum (using pass energy of 160 eV) and high resolution spectra (pass energy of 20 eV). Spectra were interpreted using the software package CasaXPS. The spectra were calibrated to the adventitious carbon C 1s peak set to a binding energy of 284.4 eV. The Shirley background was fitted to the spectra. Gaussian-Lorentzian (GL(30)) profiles as defined in CasaXPS were used to fit each component.

V. RESULTS

5.1. Flotation of oxidised sulphide mineral

In this section, the influence of grinding chemistry on the oxidised sulphide has been studied by completing a series of grinding-flotation tests with different grinding media on a copper sulphide ore artificially oxidised to various degrees.

5.1.1. Analysis of the percolating solution

The solution escaping the columns was assayed regularly to control the level of copper and iron content into the solution. The data are plotted in Figure 10 in function of the oxidation time.

Overall the results show a very low level of copper leached into solution with values lower than 1 ppm through the most of the oxidation time. The exception to this was during the first month of oxidation. At the start of the oxidation process, the data shows a peak of copper into the solution higher than 5 ppm. This period most probably corresponds to chalcopyrite surface oxidation (rapidly stopped by surface passivation) or to surface cleaning where the acidic solution is removing the unstable copper oxidised product from the chalcopyrite surface. Dissolution of other copper soluble minerals present in trace amounts in the ore could also be responsible for the high quantity of copper leached at the start of the oxidation period.

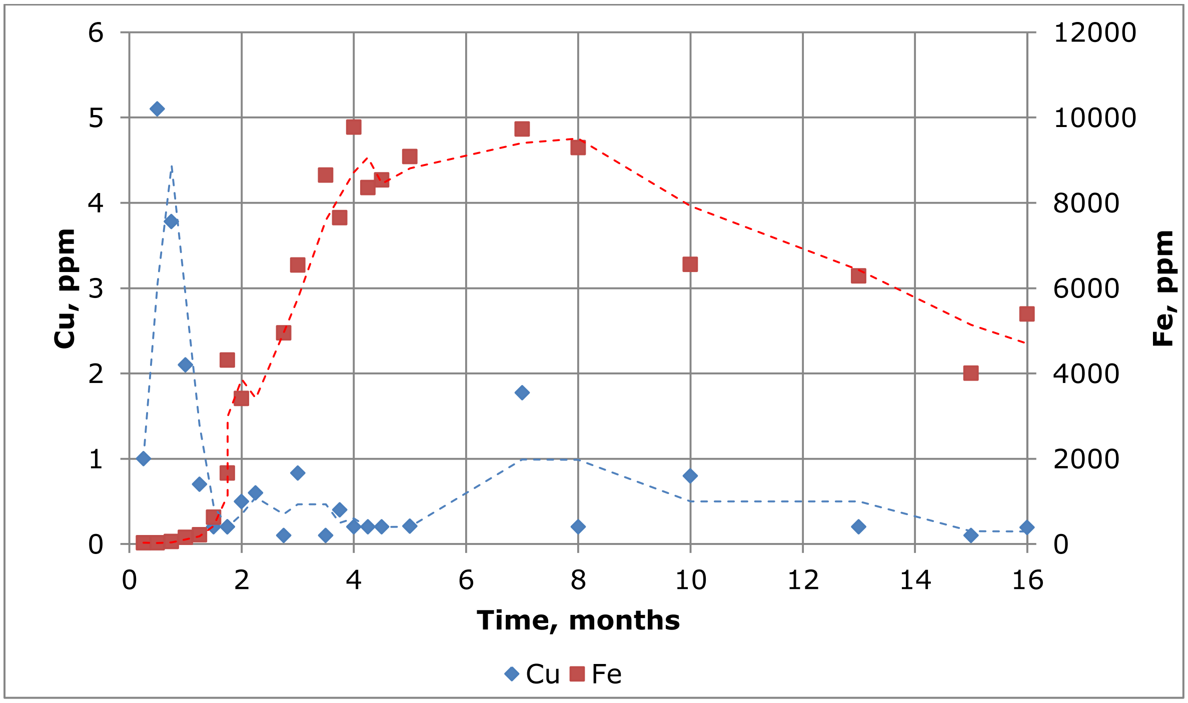

Figure 10: Copper and iron content in the solution escaping the columns versus oxidation time.

Concerning iron, the first 4 months are characterised by iron precipitation within the column, probably through acid neutralisation by the gangue. After complete neutralisation, the maximum iron content in the solution is reached at around 9 grams per litre (the concentration of the solution injected) after 7 months. The next period is then characterised by a decrease of iron in the solution.

5.1.2. Head assay

The head assays of the copper samples after each oxidation period are displayed in Table 2. The fresh sample (T0) contains 0.47 percent copper and 3.1 percent pyrite. The data indicates that oxidation time has little effect on the copper head grade with only small variation of the copper content among time. The data also indicates that there is a slight decrease of iron sulphide with oxidation time (confirmed by the Fe assays).

Table 2: Head assay at each oxidation time for the copper sulphide ore samples

Sample ID	Cu, %	Fe, %	S, %	IS, %	NSG, %
T0	0.47	11.56	2.14	3.13	95.5
T1	0.48	11.22	2.10	3.02	95.6
T2	0.46	11.20	2.06	2.98	95.6
T3	0.47	11.30	2.04	2.93	95.7
T4	0.47	11.47	2.01	2.88	95.7
T5	0.45	10.80	1.97	2.83	95.8
T6	0.48	10.75	2.04	2.92	95.7

Those observations indicate that the ore samples are consistent and that the oxidation process did not leach the copper from the ore (which was not the goal). Hence the results obtained for each ore can be compared with the others.

5.1.3. Grinding-flotation conditions

5.1.3.1. Mill calibration

The standard procedure adopted for the grinding process was to add 2200 g of ore with 2 litres of tap water and 10 kg of grinding media. The ore sample was ground for 20 minutes and the pH was adjusted to 9.4 during grinding. The Magotteaux Mill® discharge particle size and pulp chemistry targets for the mill calibration are listed in Table 3. The T0 sample ground with forged steel media was used as reference media for the pulp chemistry calibration. The pulp chemistry recipe generated from that test was then used for the seven ores and all media tested.

The mill speed was readjusted for the seven ores tested and for each alloy. The P_{80} and particle size distributions obtained are given in Appendix 2.1. The targeted P_{80} of 187 µm was reasonably achieved for all ores and alloys tested. In terms of chemistry, the dissolved oxygen pH and temperature (Table 3 in Appendix 2.1) were able to be matched to the targets (Table 3 for T0 ore sample ground with forged steel media).

Table 3: Mill discharge parameters and tolerances targeted during the calibration of the Magotteaux Mill®.

Parameter	Target	Tolerance
P_{80}, µm	187	± 5
Eh, mV vs SHE	natural	-
pH	9.4	± 0.2
DO, ppm	1.4	± 0.5
Temperature, °C	32.0	± 2

5.1.3.2. Flotation procedure

After grinding, the pulp was transferred into a 5 litre flotation cell and homogenised during two minutes. The pH of the homogenised ground slurry was first adjusted to pH10.3. Then the pulp was conditioned for 2 minutes with 10g/t of Aero3418A collector and 5 drops of MIBC frother was added 1 minute after the collector. Following conditioning, four timed copper rougher concentrates were collected for 0.5, 1.5, 3 and 5 minutes, for a total flotation time of 10 minutes.

The flotation flow sheet used for the flotation tests is represented in Figure 11. The locations of the chemistry measurements are indicated.

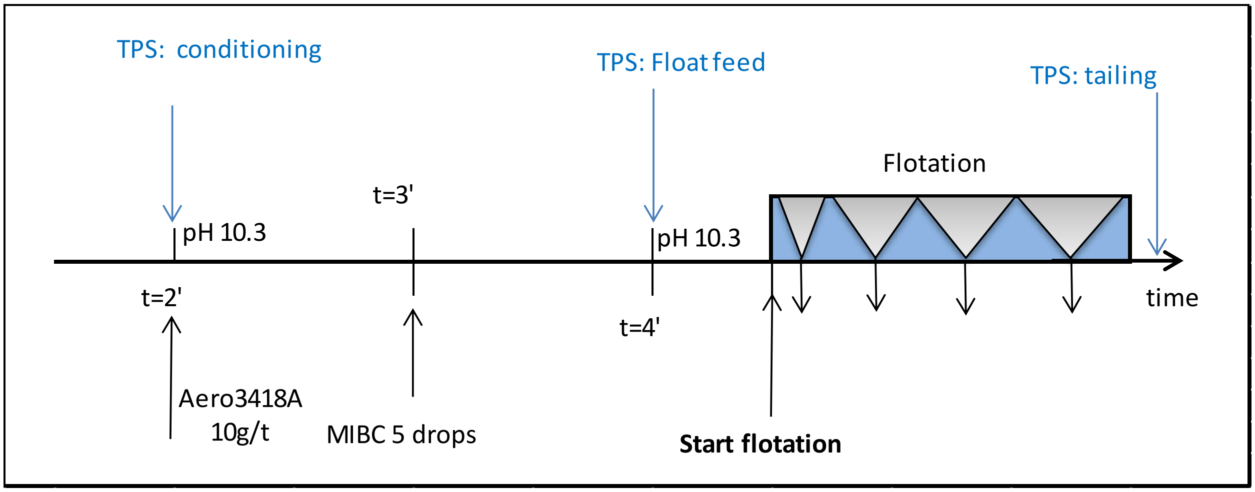

Figure 11: Flotation flow sheet used for the oxidised sulphide ore

5.1.4. Pulp chemistry

5.1.4.1. Grinding & flotation chemistry

- <u>Grinding</u>

The ball mill discharge pulp chemistry data for all media and ores tested are on display in Table 3 in Appendix 2.1. The mill discharge Eh and DO profiles versus oxidation time are plotted in Figure 12 and Figure 13, respectively. The pH and temperature profiles can be found in Appendix 2.1.

An observation of the data indicates that at each oxidation time, the high chrome and ceramic media produced more oxidising pulp chemistries with higher levels of pulp potential (Eh) and dissolved oxygen content (DO) than forged steel media. The pH was kept constant at 9.3 and the temperature was similar in all instances (Table 3 in Appendix 2.1.).

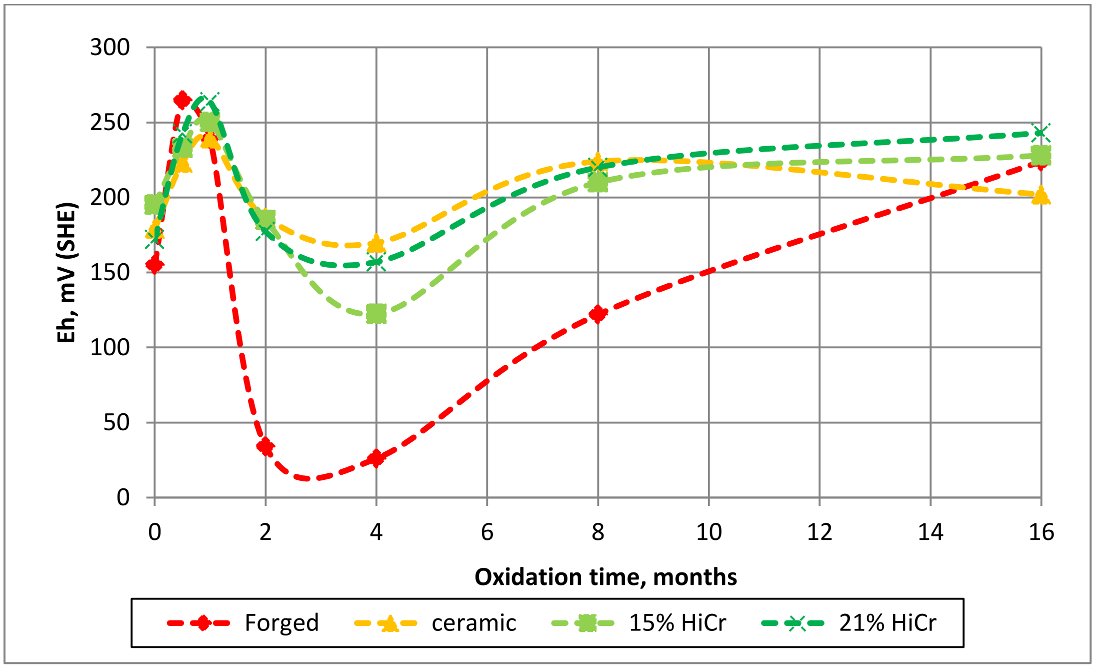

Figure 12: Mill discharge Eh values against oxidation time (i.e. for each ore tested) for all media.

Looking into more detail in Figure 12 (Eh) and Figure 13 (DO), indicates that during the first month of oxidation, the pulp moves into more oxidising conditions (higher Eh and DO) for all media tested. Then, as oxidation progresses, at the point of complete gangue neutralisation (T2), the Eh markedly dropped. Examining the pulp electrochemical potential (Eh) and dissolved oxygen (DO) values obtained for all grinding environments reveals that the magnitude of the changes are more pronounced with forged steel than high chrome and ceramic media; the inert media delivering a more stable pulp chemistry independent of the oxidative processes that are taking place in the columns during the 16 months of the experiment. Whilst during the first month of oxidation (T1 and T2), the differences between forged steel and high chrome and ceramic grinding environments are small, the difference in Eh and DO between forged and high chrome or ceramic becomes more accentuated with increased oxidation time (T3, T4 and to a lesser extent T5 samples). At the end of the oxidative process when the ore is heavily oxidised (T6), the chemistry conditions again become similar for all media tested.

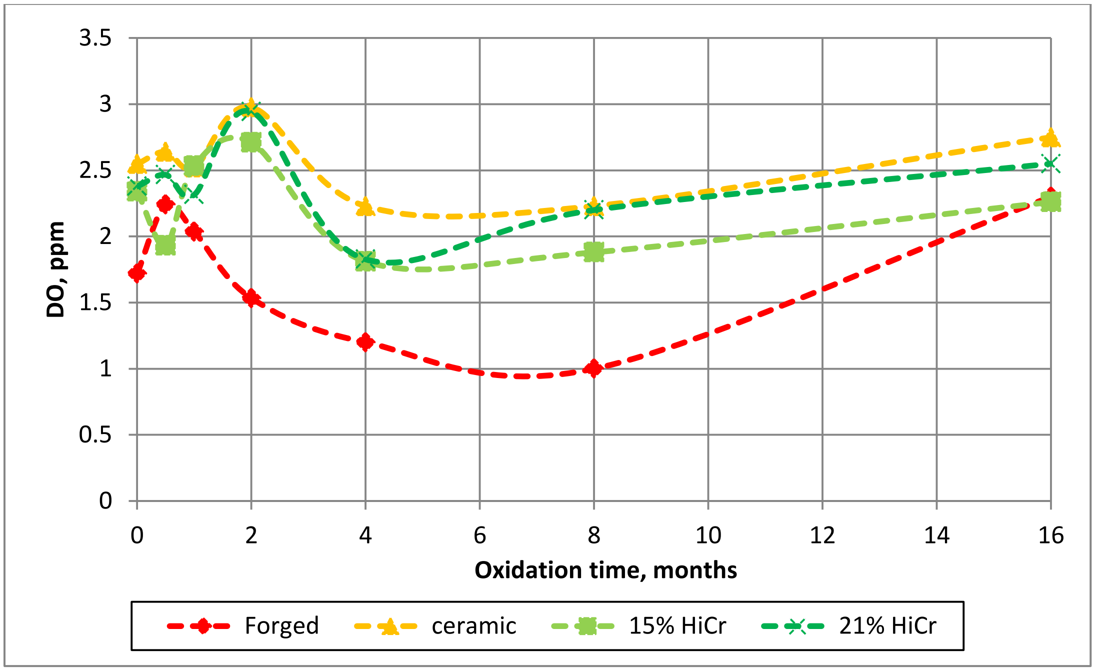

Figure 13: Mill discharge DO values against oxidation time (i.e. for each ore tested) for all media.

- <u>Flotation</u>

The flotation feed Eh and dissolved oxygen (DO) against oxidation time for all media tested are plotted in Figure 14 and Figure 15 respectively. The pH and temperature profiles as well as the flotation feed chemistry can be found in Appendix 2.2. The Eh-pH profiles during the flotation tests for all ore ground with forged steel media are presented in Figure 16.

The data indicates that overall, the pulp chemistry conditions became more oxidising with increased oxidation time (higher Eh and DO). When comparing the different grinding media tested, the data shows that high chrome and ceramic media have similar Eh and DO values after each oxidation time. During the first month of oxidation (until T2), the chemistry difference between forged and high chrome or ceramic media is minimised due to a shift to more oxidative conditions (higher DO and Eh) of the ore ground with forged steel media. With time, as ore oxidation progresses, the Eh and DO increase similarly for all media and similar Eh levels are reached by the end of the experimental period (T6).

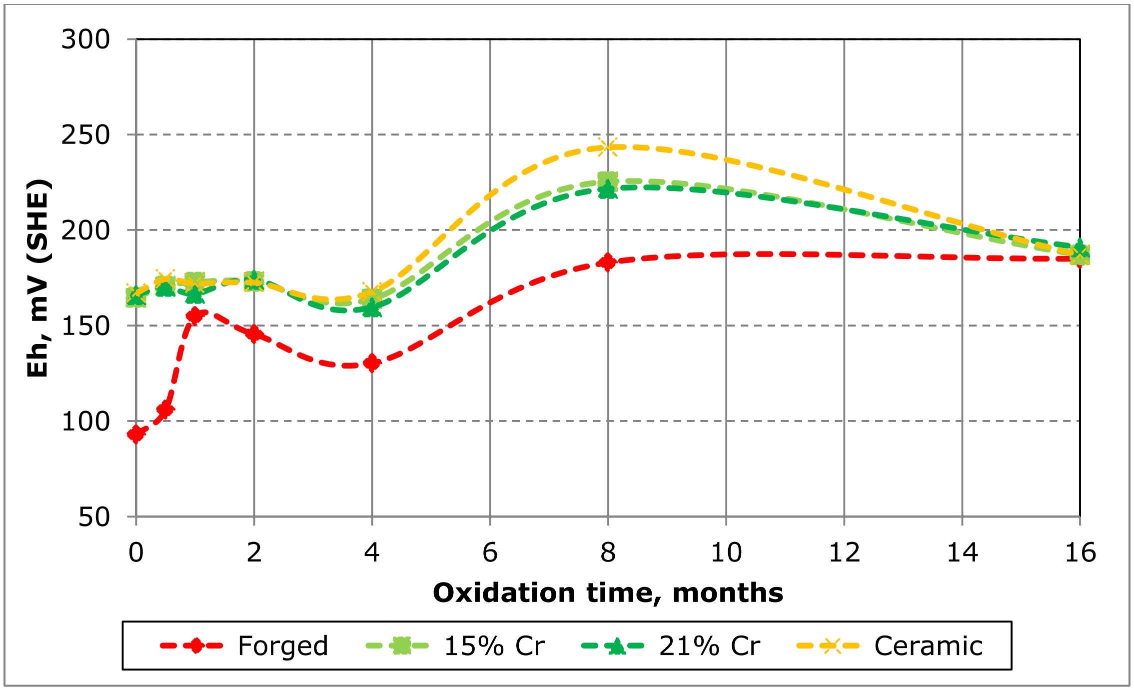

Figure 14: Flotation feed Eh values (vs SHE) against oxidation time (i.e. for each ore tested) for all media.

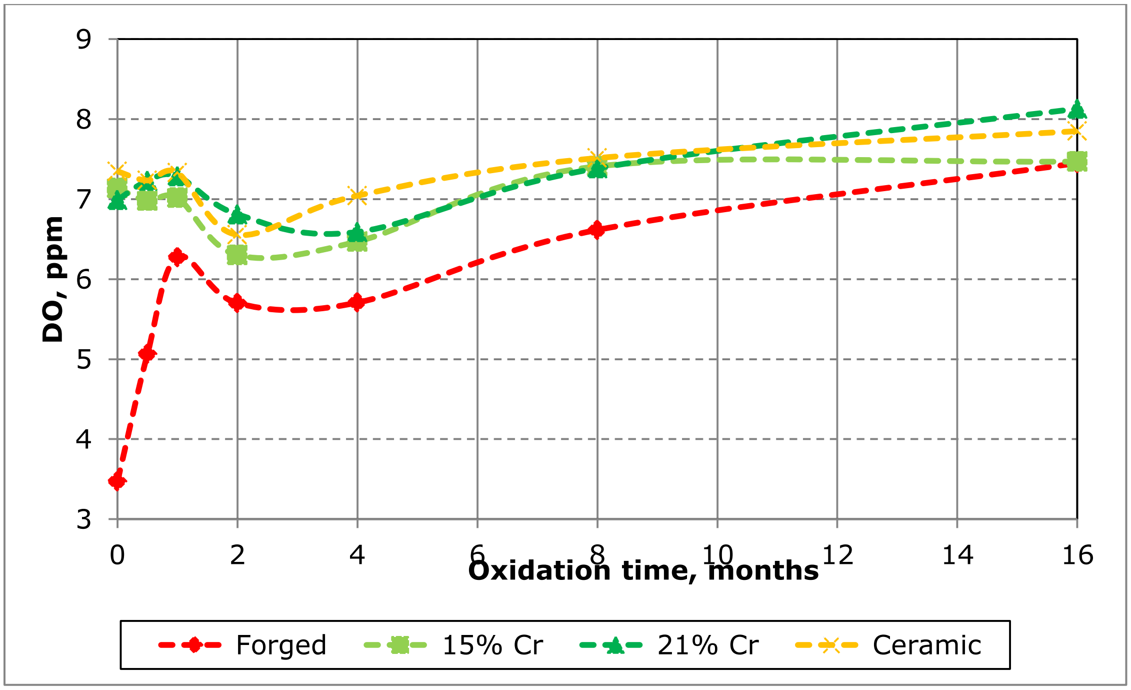

Figure 15: Flotation feed DO values against oxidation time (i.e. for each ore tested) for all media.

Interestingly, the Eh-pH diagram for forged steel media shows 3 distinct behaviours of the ore. From T0 to T2, the profiles are quite parallel to the water stability lines indicating that little redox reactions are occurring. Then, from T3 to T5, as oxidation progresses, the trends become more perpendicular to the water stability lines showing that more redox reactions are occurring, particularly between the grinding and flotation feed stages. Finally, when the ore is strongly oxidised (T6), the data suggests that the ore becomes much less reactive.

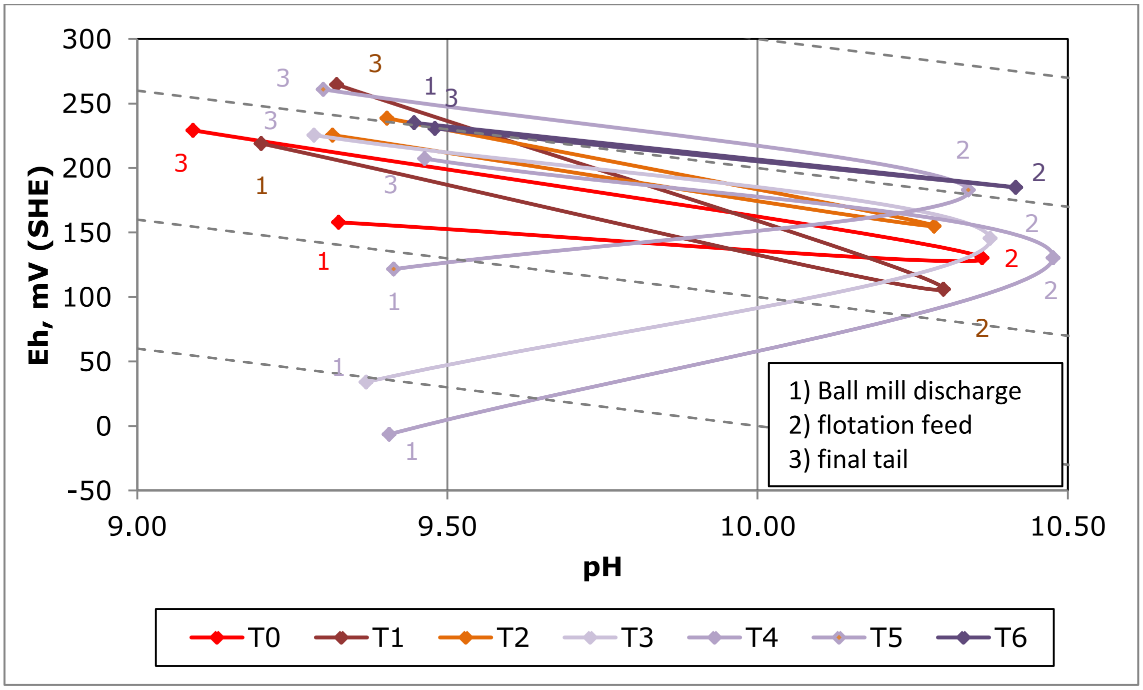

Figure 16: Eh-pH diagram during the flotation test of ore ground with forged steel media comparing all ores tested.

5.1.4.2. EDTA

The level of iron and copper extracted by EDTA versus oxidation time for all media tested are plotted in Figure 17 and Figure 18 respectively.

Interestingly, the EDTA copper data (Figure 17) shows a quite constant level of copper extracted by EDTA for the different oxidation times (except with T6 samples which show a strong increase of Cu EDTA extracted with high chrome and ceramic media); with forged steel media showing slightly lower percentages of EDTA copper than the high chrome and ceramic media. Slightly higher Cu EDTA extractable values at the beginning of the experiments (particularly marked in the high chrome and ceramic media tests) could be related to partial adsorption of the Cu leached during the first month.

The EDTA extractable iron shows a different behaviour (Figure 18): while high chrome and ceramic grinding media have similar concentrations of just below 0.1%, the forged steel data shows much higher values at the start of the oxidation process (0.4% at T0), then decreases as the oxidation time increases to reach 0.2% at T6. This could be attributed to the formation of more stable iron oxide species with oxidation time (less soluble in EDTA) or to a decrease in the quantity of the galvanic interactions taking place between the media and the partially oxidised sulphide minerals.

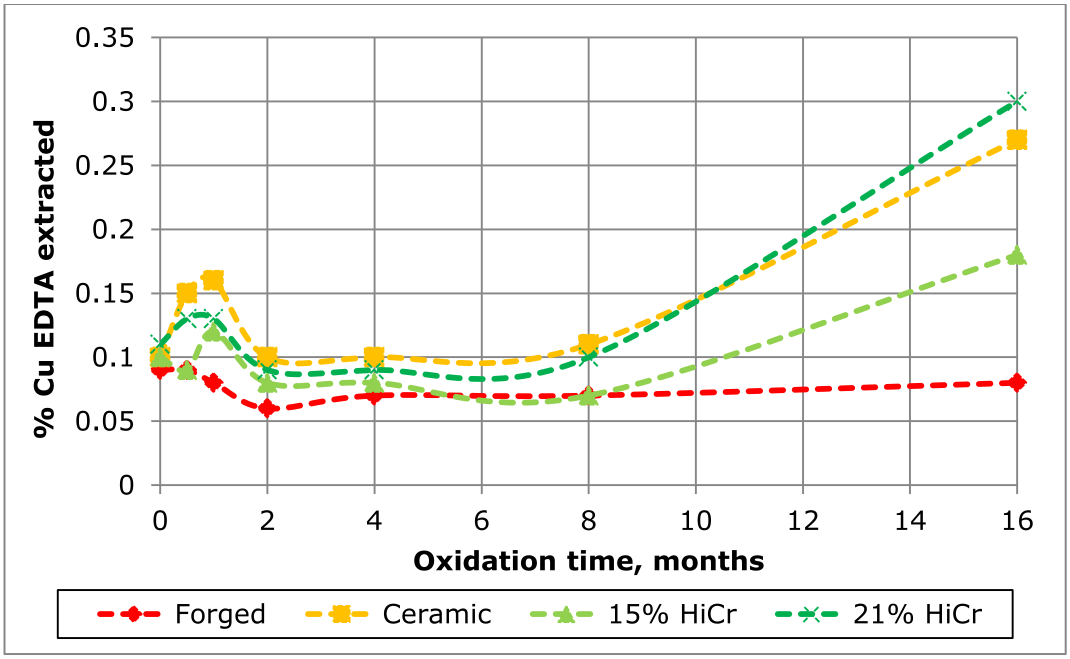

Figure 17: Copper EDTA extracted against oxidation time (i.e. for all ores tested) for all media.

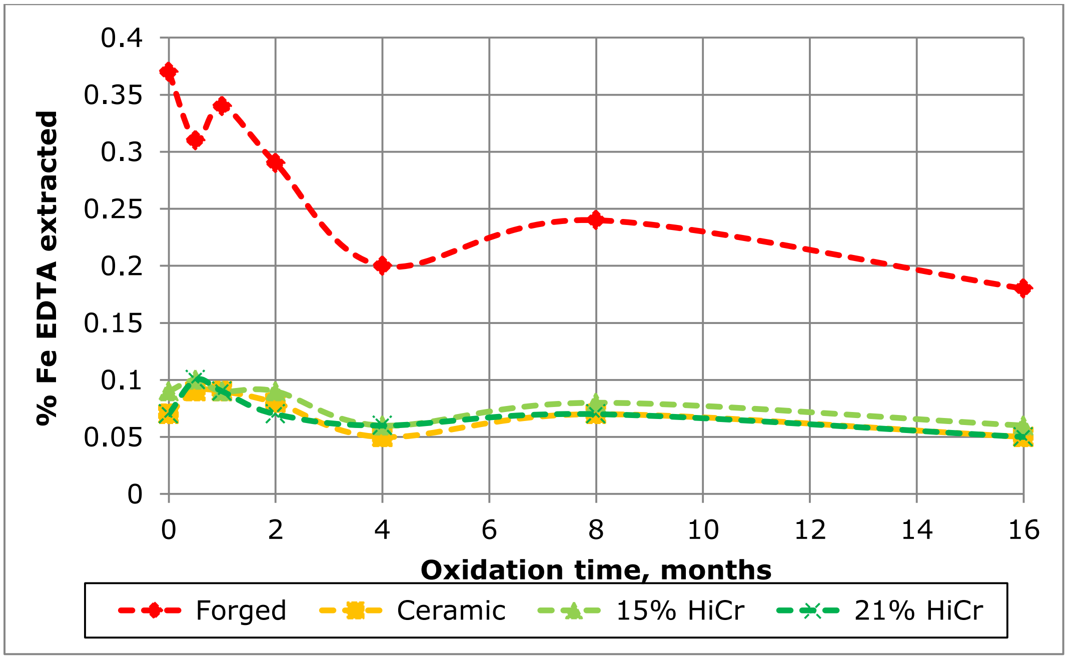

Figure 18: Iron EDTA extracted against oxidation time (i.e. for all ores tested) for all media.

5.1.4.3. Oxygen demand

The oxygen demand values (after 1 minute of aeration) against oxidation time are plotted in Figure 19. The oxygen demand profiles for each ore sample tested are presented in Appendix 2.3.

Overall, the general trend indicates a decrease in the oxygen demand with oxidation time for all media tested suggesting that the reactivity of the ore deceases with higher oxidation states. Comparing the 4 media tested, the forged steel shows a higher oxygen demand than the high chrome and ceramic media. It also appears that the difference in oxygen demand between the various alloys stays quite constant against oxidation time.

At the start (T0), the data indicates that the reactivity of the ore increases with the increased reactivity of the grinding media: Ceramic < 21% HiCr < 12% HiCr < forged steel. Then, as oxidation progresses, the oxygen demand of the high chrome and ceramic media become similar (T5) while the values obtained for forged steel media stay separate at a higher rate.

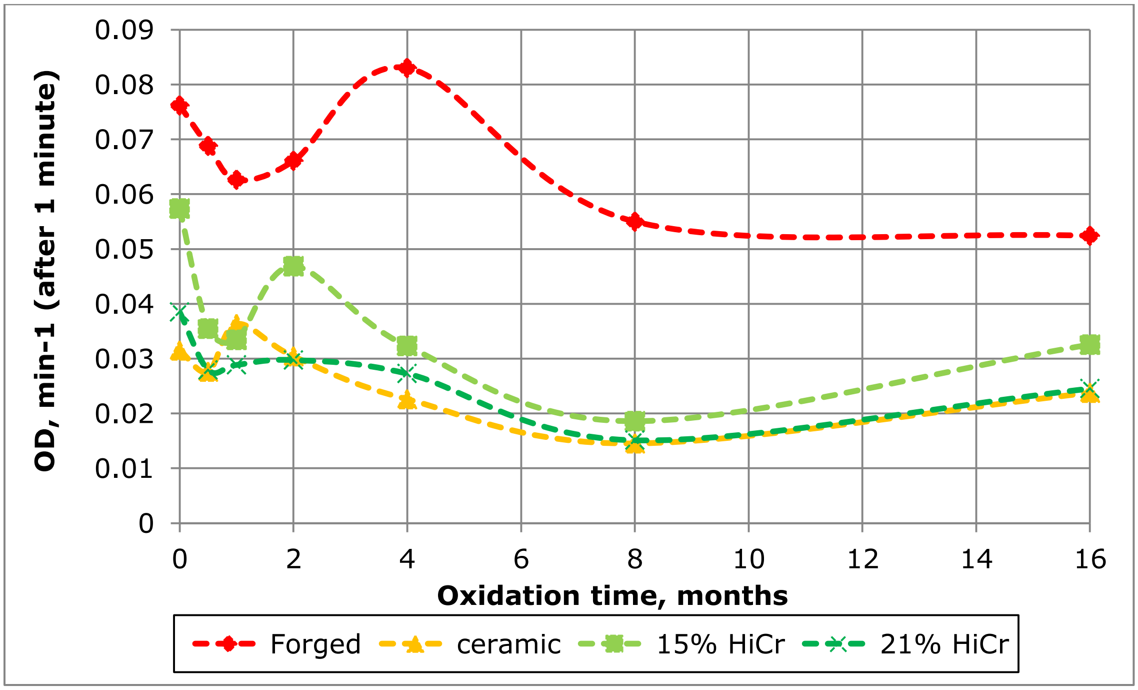

Figure 19: Oxygen demand after 1 minute of aeration against oxidation time (i.e. for each ore tested) for all media.

The individual profiles in Appendix 2.3 show a typical oxygen demand for each ore tested with decreased oxygen demand values with aeration time for forged steel media. Ceramic media show the lowest oxygen demand, constant with increased aeration time. In most of the cases, high chrome media have similar profiles to that of ceramic media but with slightly higher values.

5.1.5. Flotation response

5.1.5.1. *Reproducibility*

All the tests were completed in triplicate to give confidence in the data produced. The reproducibility was examined for each condition and some tests discarded or repeated if necessary. The triplicate tests completed with forged media for all ore tested are on display in Appendix 2.4.1. For most of the ores, it is evident that the triplicate tests are in close agreement, suggesting that the reproducibility of the experiment is good.

In order to make the analysis simpler, in subsequent sections only the average results will be used.

5.1.5.2. Rougher flotation

The copper grade recovery curves as well as the copper selectivity curves against iron sulphide and non-sulphide gangue for each ore tested and all media types are plotted in Appendix 2.4.2. Table 4 tabulates the copper and iron sulphide maximum recovery and flotation rate constant. The copper and iron sulphide modified rate constant are plotted in Figure 20 and Figure 21 respectively. Finally, the selectivity index profiles are display in Figure 22.

Overall, the data in Table 4 indicates that as expected, ore oxidation adversely affected the copper metallurgy, with the maximum copper recovery decreasing from around 90 percent with the T0 sample down to 65 percent after 16 months of oxidation (T6). Comparing the four grinding environments, the data indicates that 21% high chrome media produced better maximum copper recovery and flotation rate constants at each oxidation time except with the most heavily oxidised sample (T6) where all media show similar results except 15% high chrome media which show better copper and iron sulphide maximum recovery but lower flotation kinetics. Interestingly, ceramic media show an intermediate behaviour between forged steel and high chrome media and does not seems to respond as well as high chrome media to ore oxidation. An observation of the non-sulphide gangue data in Appendix 2.4.2 indicates that there is little variation of the non-sulphide gangue flotation behaviour in all instances.

Looking more deeply at the results and the copper and iron sulphide modified rate constants in Figure 20 and Figure 21 respectively; it appears that 3 different periods can be distinguished. They correspond to *weak*, *medium* and *strong* mineral oxidation. At the start (T0), the trends in Figure 20 and Figure 21 show much higher copper and iron sulphide modified rate constants with high chrome and ceramic media than forged steel media. While with the more inert grinding media (HiCr and ceramic media) the copper modified rate constant was much higher than that of iron sulphide (± 400 vs 40), with forged steel media they are much closer (100 vs 30), indicating a lower selectivity between chalcopyrite and pyrite. During the initial period of oxidation (*weak* oxidation: T1 and T2), it appears that the pyrite was strongly activated with the iron sulphide modified rate constant reaching its maximum at T2 with all media tested. While with high chrome and ceramic media the Cu modified rate constant was poorly affected, it peaked at T2 with forged steel media. During the second period (*medium* oxidation: T3, T4 and T5), the ore oxidation progressed, pyrite activation decreased and chalcopyrite flotation became more adversely affected. That is, the iron sulphide and copper modified rate constant deceased for all media tested. Finally, the third period corresponds to *stron*g ore oxidation (T6). The metallurgical performances of the ore ground with the various media tested became closer, with Figure 20 showing similar copper modified rate constants for all media.

Table 4 Copper and iron sulphide maximum recovery and flotation rate constant versus oxidation time for all media tested.

Cu								
Time, months	**Forged**		**15% HiCr**		**21% HiCr**		**Ceramic**	
	R_{max}, %	**k, min^{-1}**	**R_{max}, %**	**k, min^{-1}**	**R_{max}, %**	**k, min^{-1}**	**R_{max}, %**	**K, min^{-1}**
0 (T0)	88.8	1.0	91.1	4.1	92.4	4.3	92.2	4.4
0.5 (T1)	83.8	0.6	90.6	3.9	89.7	4.0	88.8	3.9
1 (T2)	84.2	1.9	88.6	3.9	89.4	4.2	88.8	3.9
2 (T3)	84.7	0.8	88.5	4.1	88.8	4.2	89.3	4.2
4 (T4)	81.9	1.1	86.3	3.0	86.1	3.2	84.3	3.0
8 (T5)	73.4	1.0	81.6	3.2	82.4	3.2	78.3	2.7
16 (T6)	65.2	2.1	69.8	1.6	65.4	2.2	64.4	2.0
IS								
Time, months	**Forged**		**15% HiCr**		**21% HiCr**		**Ceramic**	
	R_{max}, %	**k, min^{-1}**	**R_{max}, %**	**k, min^{-1}**	**R_{max}, %**	**k, min^{-1}**	**R_{max}, %**	**K, min^{-1}**
0 (T0)	26.8	0.6	32.1	1.3	31.6	1.3	30.3	1.2
0.5 (T1)	39.3	1.0	48.2	1.6	45.5	1.6	43.1	1.3
1 (T2)	43.7	1.2	50.7	1.8	47.7	1.7	44.9	1.3
2 (T3)	38.3	1.1	41.5	1.9	43.0	1.7	38.9	1.5
4 (T4)	38.1	0.7	40.5	1.0	42.4	1.1	36.1	1.0
8 (T5)	35.6	0.7	40.4	1.2	36.8	1.0	34.0	0.8
16 (T6)	26.8	0.9	29.9	1.1	24.3	0.9	27.0	0.8

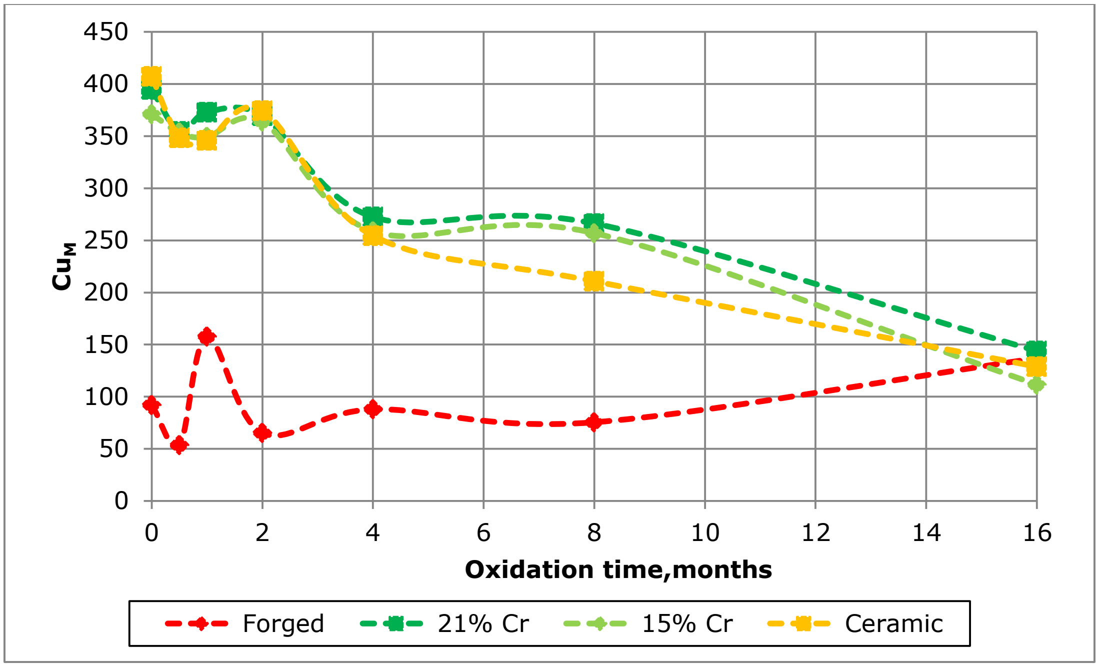

Figure 20: Copper (K_M Cu) modified rate constant versus oxidation for all media tested.

Now considering the $SI_{Cu/IS}$ trends in Figure 22, these show that overall, ceramic and high chrome media produced superior selectivity indexes than forged steel media except at the end of the oxidation process where 21% HiCr media had the best selectivity index and 15% HiCr media the lowest.

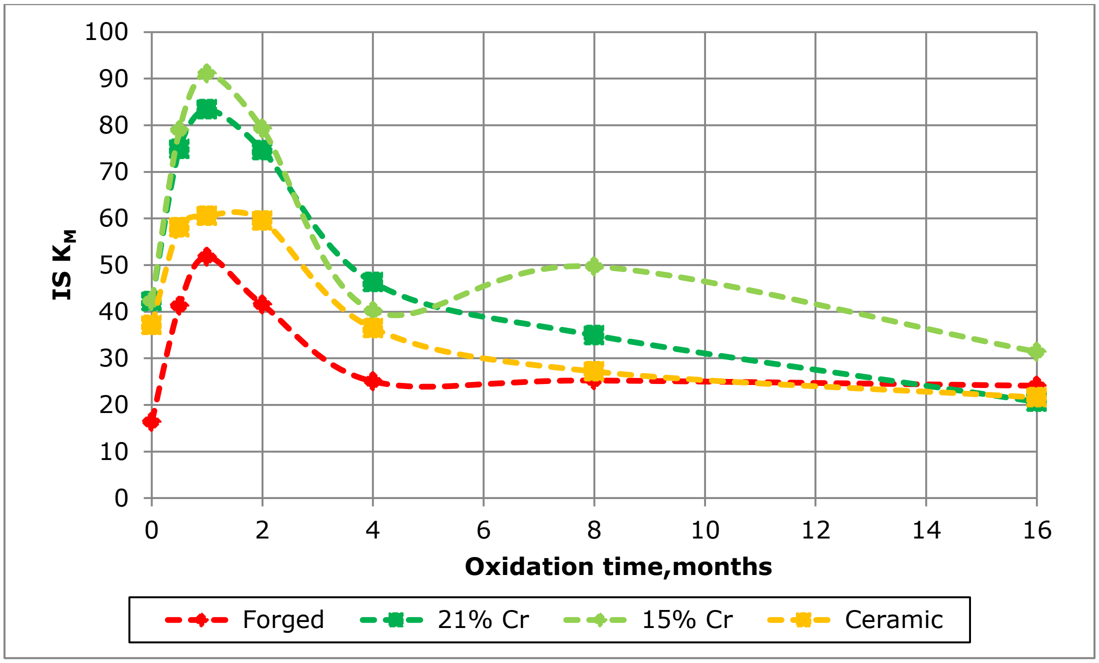

Figure 21: Iron sulphide (K_M IS) modified rate constant versus oxidation for all media tested.

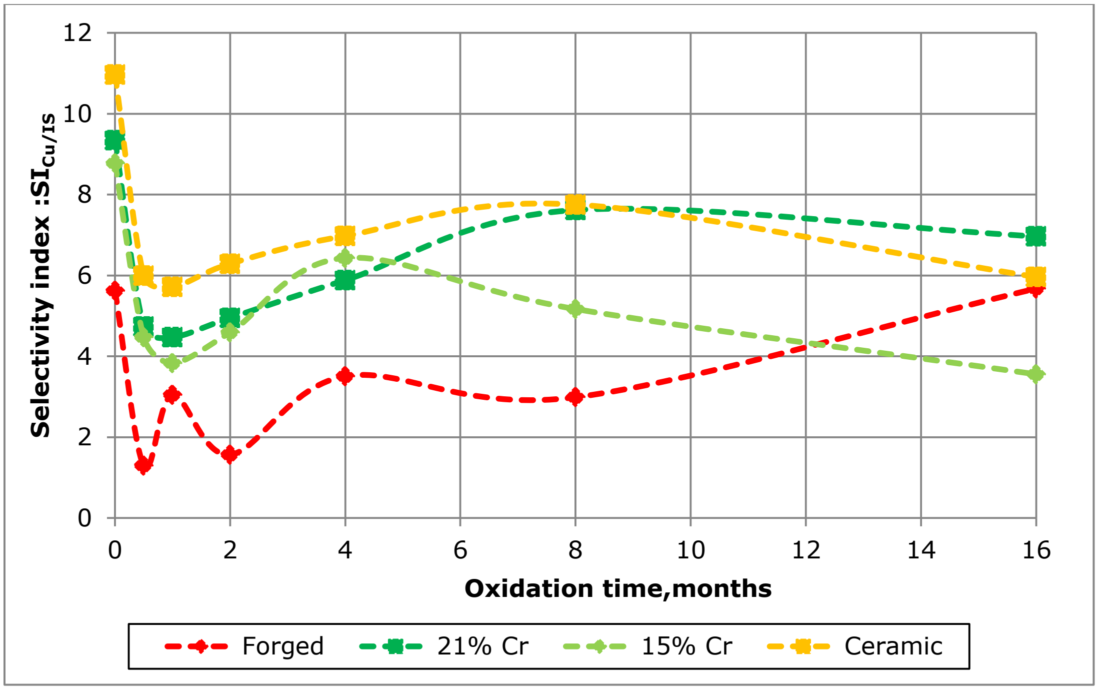

Figure 22: $SI_{Cu/IS}$ selectivity index versus oxidation time for all media tested.

Pyrite activation is clearly marked with a strong decrease in the selectivity index during the first month of oxidation with all media tested. As oxidation progresses, pyrite seems more affected than chalcopyrite, resulting in an increase in selectivity with accentuated differences between forged steel and the more inert media (21% HiCr and ceramic). Finally, at the end of the oxidation period, the data shows that the selectivity of chalcopyrite against iron sulphide is better with 21% high chrome media but to a lesser extent to that observed initially when compared to forged steel media. Interestingly, the selectivity index of the 15% chromium media started to deteriorate strongly from 8 months of oxidation to become worse than forged steel at the end of the oxidation process.

5.1.5.3. Recovery by size

The flotation products of selected experiments were sized and assayed to allow recovery by size calculation. The size by size recovery and flotation rate constant for T0, T1 and T6 samples comparing forged steel and 21% high chrome media are presented in Figure 23 and Figure 24 for copper and in Figure 25 and Figure 26 for iron sulphide. The copper and iron sulphide size by size feed distribution can be found in Appendix 2.4.3 for comparison purposes.

The feed distribution data in the appendix indicates that all media show similar copper and iron sulphide feed distribution with most of the copper and iron sulphides present in the intermediate fractions and small amounts (<10%) at both end of the size spectrum.

The recovery versus size curves (Figure 23 and Figure 25) show typical behaviour, with high recoveries for the intermediate (-75/+10 micron) size fractions and decreases in the fine (-10 micron) and coarse (+75 micron) ends of the size spectrum. The kinetics by size data (Figure 24 and Figure 26) show similar profiles with faster flotation kinetics for the intermediate size fractions with decreased rate constants for both end of the size spectrum; more pronounced for the fines.

An examination of the copper data (Figure 23) shows that at T0 forged steel produced slightly higher recoveries of fines compared to high chrome, but lower coarse particle recoveries. The initial oxidation step (T1) resulted in significant losses in both the fine and coarse particle recoveries for both alloys, with the forged steel case showing higher fine particle recoveries but lower coarse particle recoveries compared to the high chrome test. By the end of the oxidation period (T6) the recoveries of the +10 micron size fractions had dramatically deteriorated, with forged steel fairing marginally better than the high chrome case. However, it was interesting to note that the recovery of -10 micron particles markedly increased. In this instance, the ore ground with high chrome grinding media had produced a significant increase in recovery over that ground with forged steel.

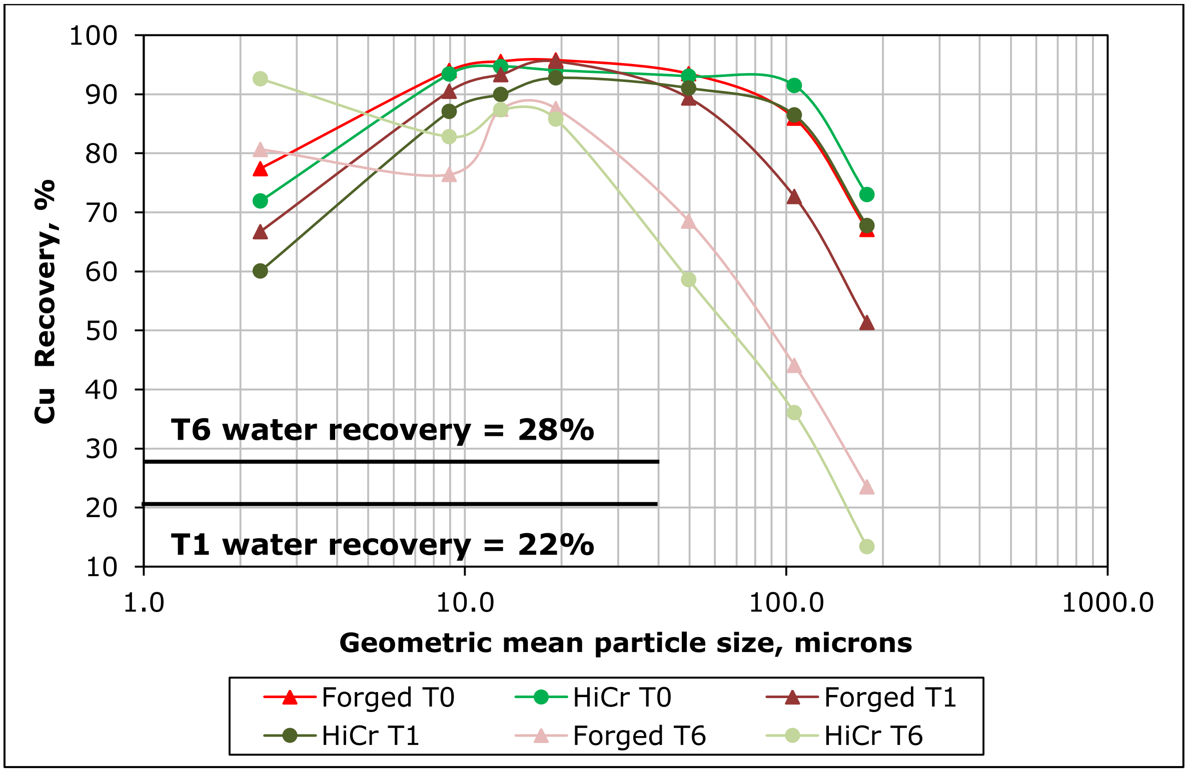

Figure 23: Copper size by size recovery for T1, T2 and T6 samples ground with forged steel and 21% HiCr media.

In terms of flotation kinetics by size, similar observations can be made. Initially, the data in Figure 24 show much higher flotation rate constants with high chrome than forged steel media; the difference in kinetics increasing with particle size. Then, the initial oxidation step (T1) resulted in a decrease of flotation kinetics for both media across all particle ranges. Finally, at the end of the oxidation period, both media show similar flotation kinetics rate constant with values slightly higher than that obtained with forged steel media and the fresh sample (T0).

Looking at the pyrite flotation response, the data in Figure 25 exhibited the same characteristic curve as the copper data. In this case the strongest recoveries occurred in the -20/+8 micron (intermediate) size fractions, then decreased either side of this in the fine (-8 micron) and coarse (+20 micron) size fractions. At T0 the test performed with high chrome grinding media produced higher iron sulphide recoveries across all size fractions compared with the forged steel case. At the beginning of oxidation (T1) the iron sulphide recoveries were increased considerably across all size fractions compared to the T0 tests, suggesting that the iron sulphides were inadvertently activated. The difference between the two media types was predominantly in the coarse size fractions where the recovery of coarse pyrite was enhanced when grinding with high chrome grinding media. At the end of the oxidation period (T6) the iron sulphide recoveries across most size fractions had dropped back to levels for forged steel at T0. In this case, the forged steel data showed marginally higher iron sulphide recoveries of coarse particles when compared to the high chrome case. However, the high chrome data showed a marked increase in iron sulphide recoveries in the fine fractions.

In terms of the pyrite flotation rate constant, at the start (T0), Figure 26 indicates that faster flotation kinetics occurs in the -100/+10 micron particle range with much faster flotation kinetics observed for high chrome media over the entire size spectrum at the start (T0). The pyrite activation occurring during the first part of the oxidation period is strongly marked with much faster pyrite flotation observed at T1 for both media. Finally, as observed previously for copper, at the end of the oxidation process (T6), the ore shows similar flotation rate constants between both media tested, with an intermediate profile between those of the forged steel and high chrome media obtained with the fresh sample (T0).

It should be noted that the recovery of -50 micron iron sulphide particles for both media types, and all three oxidation conditions, was greater than water recovery (22% for T0 and 28% for T6). This suggests that the dominant mechanism by which these particles were recovered was by genuine flotation, and not entrainment.

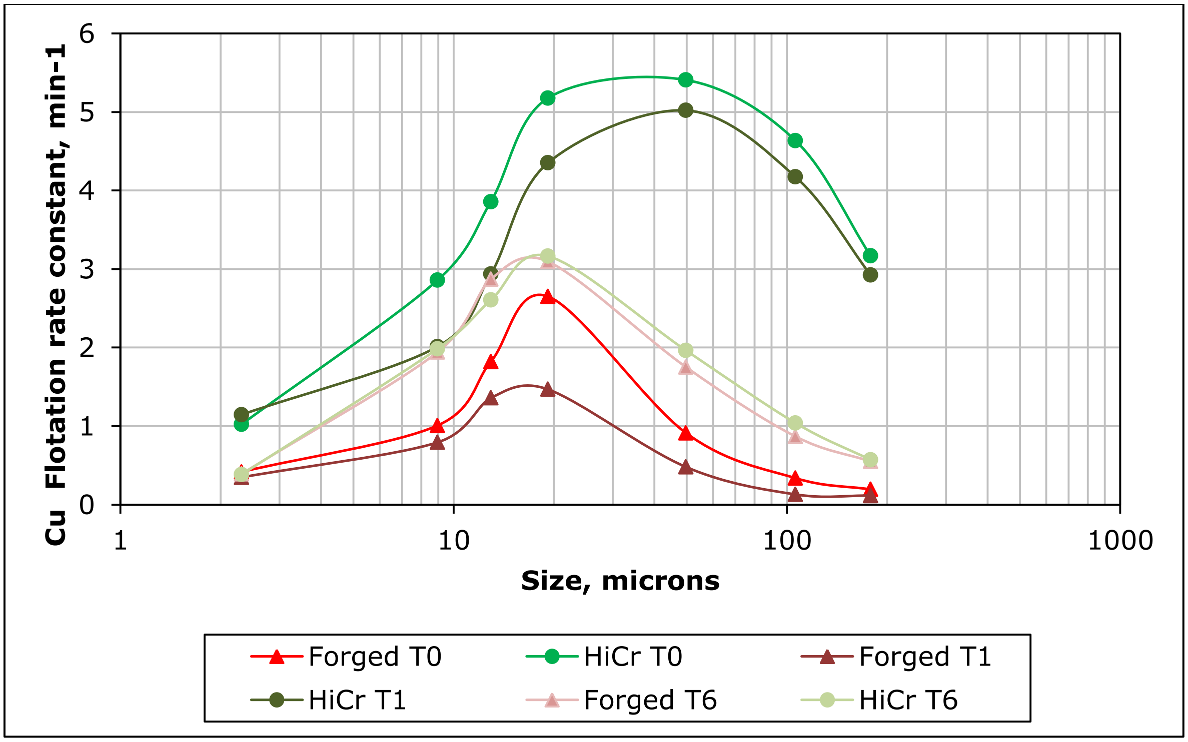

Figure 24: Copper size by size flotation rate constant for T0, T1 and T6 samples ground with forged steel and 21% HiCr media.

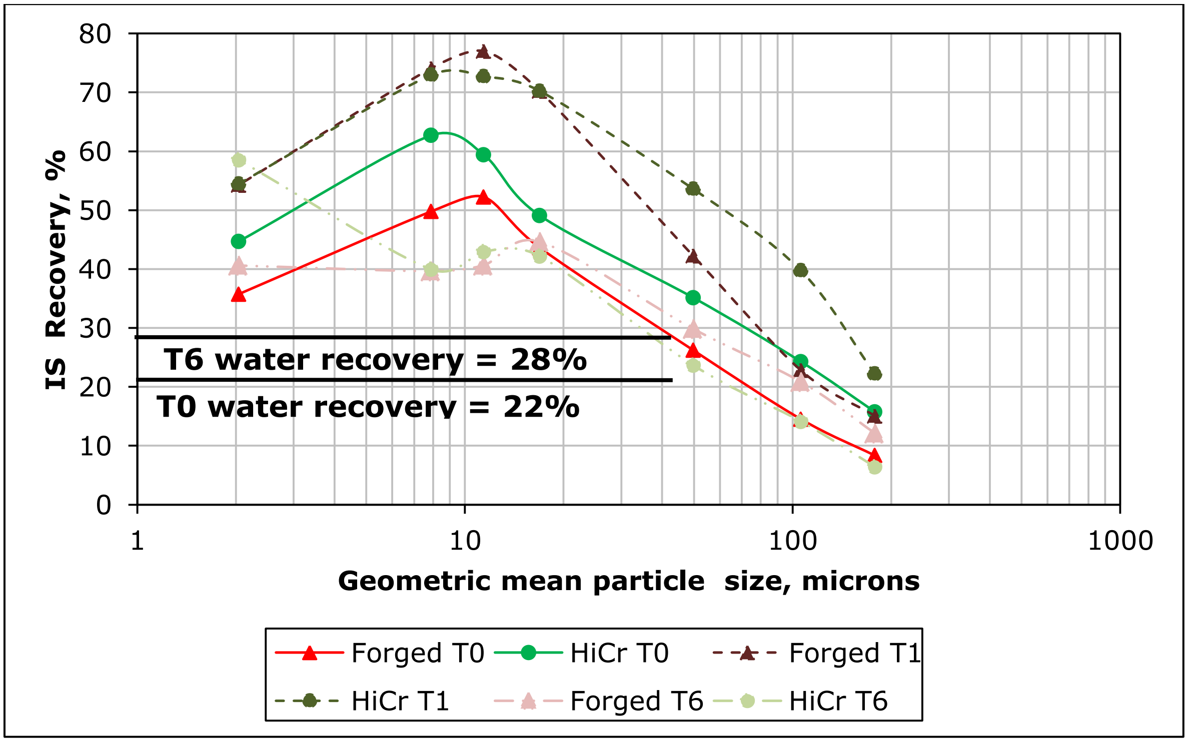

Figure 25: Iron sulphide size by size recovery for T0, T1 and T6 samples ground with forged steel and 21% HiCr media.

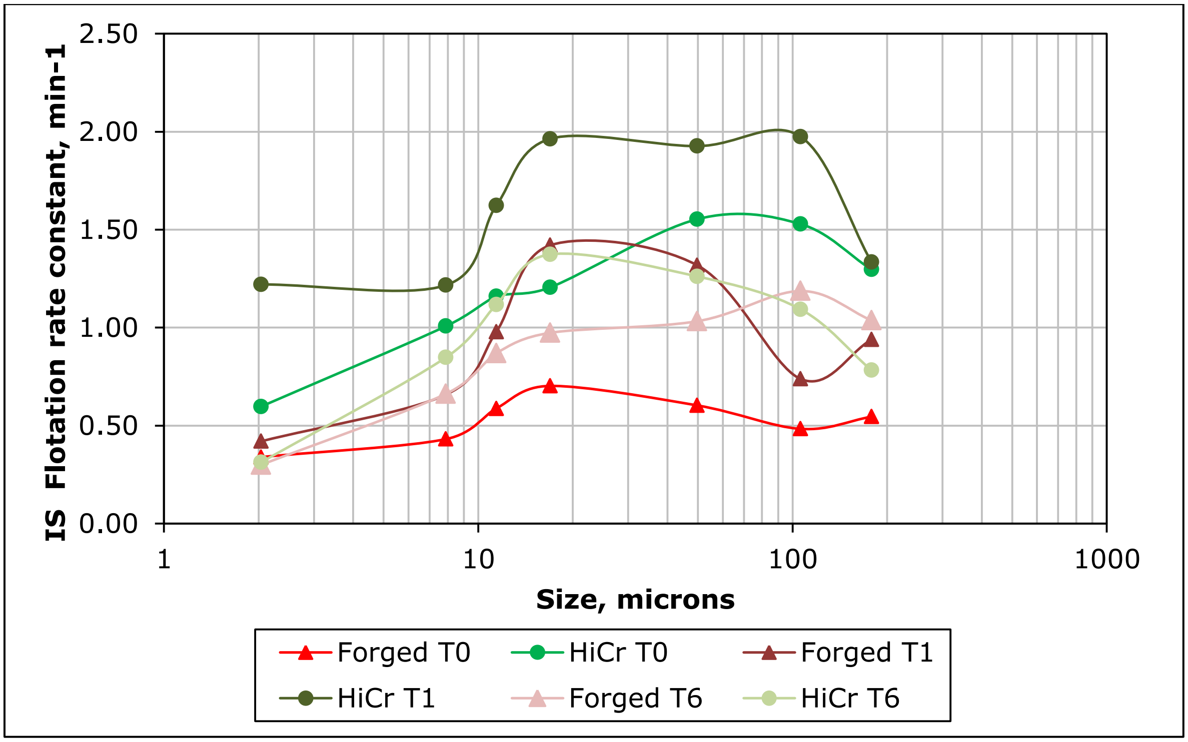

Figure 26: Iron sulphide size by size flotation rate constant for T0, T1 and T6 samples ground with forged steel and 21% HiCr media.

5.1.5.4. Discussion

The results have shown that the type of grinding environment and the resulting pulp chemistry drive the flotation performances of the ore for each oxidation degree tested. At each oxidation step, high chrome or ceramic media produced more oxidative pulp chemistry (at both the ball mill discharge and the flotation feed) with lower levels of iron extracted by EDTA, and better flotation performances than that obtained with forged steel media regardless of the phenomena taking place in the percolation column.

It is most likely that the pyrite activation during the initial month of oxidation (T1 and T2) was due to copper activation as it corresponds to the peak of copper leached in the percolating solution which was then adsorbed on the pyrite surface, activating it. The size by size data showed that pyrite activation improved pyrite flotation regardless of the size fraction for all grinding environments. After two months of oxidative treatment, the acid neutralisation by the gangue was completed (Figure 1), the pulp potential markedly dropped (Table 2), and the flotation kinetics for copper halved for the forged steel media. As the oxidation of the ore progressed (T3, T4 and T5), the metallurgical performances deteriorated for all media tested. The metallurgy is likely to have been impaired by a shift of grinding chemistry to more reducing conditions. In addition, the decrease of EDTA Fe extracted with forged steel media most probably indicates a decrease in the number galvanic interactions taking place between the partially oxidised sulphides and the grinding media, reducing the number of iron ions released through media corrosion.

Finally, by the end of the oxidation process when the ore was heavily oxidised and the copper flotation strongly deteriorated, the pulp chemistry was found to be similar for all grinding media, with similar flotation performances observed. In terms of pyrite selectivity, the selectivity index was still showing better selectivity of chalcopyrite against pyrite with 21% HiCr media but to a lesser extent than that obtained with the less oxidised samples. This tends to suggest that when sulphide minerals become heavily oxidised, fewer galvanic interactions between the sulphide minerals and grinding media occurs, both media generate similar pulp chemistry and hence similar flotation performances of the ore are seen.

5.1.5.5. Conclusions

Most of the experimental works reported in the literature study separate the influence of the type of grinding media and ore weathering on sulphides flotation. In this section, it was intended to understand the combined effects of these two parameters.

The results have shown that the grinding pulp chemistry affects the flotation performance of the ore at each oxidation stage. During most of the oxidation period, high chrome and ceramic media resulted in better copper flotation and better selectivity of chalcopyrite for pyrite through generation of more optimal pulp chemistry than that obtained with forged steel media. Regardless of the phenomena taking place in the percolation column during the entire time of the experiments, high chrome and ceramic media delivered more stable pulp chemistry, not only at the ball mill discharge but also at the flotation feed. This can be of importance for controlling continuous operations at plant scale.

At the start of the oxidation period, it was observed that weak ore oxidation resulted in strong pyrite activation through adsorption of soluble copper released in the percolating solution. At the end of the experimental period (after 16 months of artificial ore oxidation), all grinding media tested generated similar pulp chemistry and flotation performances of the ore, suggesting that when sulphide minerals are strongly oxidised less galvanic interactions occur during grinding.

In all instances, this study revealed the importance of delivering the right grinding chemistry to obtain the best ore flotation performances.

5.2. Flotation of oxide and mixed synthetic ores by sulphidisation

In this section, various series of grinding-flotation tests under different grinding chemistry have been completed to study the influence of the pulp chemistry on the sulphidisation process and its effect on the oxide mineral recovery by flotation. The first “ore” tested made of malachite only was very simple and used to obtain a good understanding of the fundamentals of the mechanisms taking part during the sulphidisation process. Then, two more complex ores were tested: a synthetic oxide ore and a synthetic mixed oxide-sulphide ore. For all systems, particular focus was given to the relation between the pulp chemistry, especially during the sulphidisation stage, and the oxide flotation response of the ore.

5.2.1. Bulk malachite ore

5.2.1.1. Ore sample

Samples of 400 g of pure malachite mineral were used.

5.2.1.2. Grinding-flotation conditions

5.2.1.2.1. Mill calibration

The standard procedure adopted for the grinding process was to add 400 g of ore with 2 litres of tap water and 10 kg of grinding media. The ore was ground for 10 minutes. The Magotteaux Mill® discharge particle size distribution and pulp chemistry targets for the mill calibration are listed in Table 5. Forged steel media were used as reference media during the pulp chemistry calibration.

The target $P_{65\mu m}$ of 65 percent was reasonably achieved for all alloys. The particle size distributions obtained for the four media types is given in Appendix 3.1. In terms of chemistry, the dissolved oxygen and temperature were able to be matched to the targets (Table 6).

Table 5: Mill discharge parameters and tolerances targeted during the calibration of the Magotteaux Mill®.

Parameter	Target	Tolerance
$P_{65\mu m}$, %	65	± 5
Eh, mV vs SHE	natural	-
pH	natural	-
DO, ppm	1.4	± 0.5
Temperature, °C	32.0	± 2

5.2.1.2.2. Flotation procedure

After grinding, the ground pulp was transferred to a 2.5 litre flotation cell and homogenised during 2 minutes ("conditioning"). The homogenised ground slurry was then conditioned for 2 minutes ("sulphidisation") with sodium hydrosulphide (NaHS) and 3125 grams per tonne of potassium ethyl xanthate (PAX) collector was added 15 seconds after the NaHS. Five drops of frother were added after 1 minute of NaHS conditioning. Following conditioning, four timed copper rougher concentrates were collected for 0.5, 1.5, 2 and 2 minutes, for a total flotation time of 6 minutes.

Two NaHS dosages were used. The first series of tests was carried out with a NaHS dosage of 3750 grams per tonne (equivalent to two minutes' CPS conditioning with forged media at an Es of -500 mV). A second series of tests was undertaken at a lower NaHS dosage of 2500 grams per tonne to study the variation of the chemistry on a system not sulphidised under optimum conditions.

The flotation flow sheet used for the flotation tests is represented in Figure 27. The locations of the chemistry measurement are indicated.

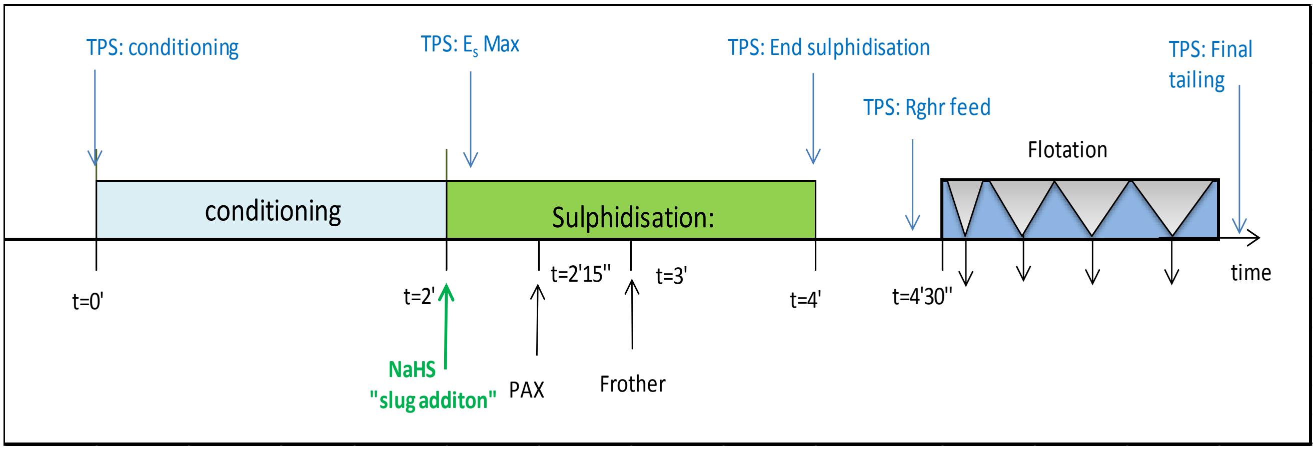

Figure 27: flotation flow sheet used for the single malachite test work.

5.2.1.3. Pulp chemistry

5.2.1.3.1. Grinding & flotation chemistry

- Grinding

Table 6 summarises the grinding chemistry observed at the ball mill discharge. The Eh, pH, dissolved oxygen and temperature profiles are on display in Appendix 3.2.

Table 6: Mill discharge pulp chemistry for each alloy tested

Parameter	pH	Eh, mV (SHE)	DO, ppm	Temp, °C
Forged	8.24	392	1.77	32.1
12%Cr	8.28	382	1.93	33.9
21%Cr	8.06	408	2.07	34.4
Ceramic	8.08	395	2.06	33.4

Table 6 shows that there are only subtle variations of pulp chemistry between the different alloys used. The different behaviours of the various alloys tested in water due to their differences in electrochemical properties most probably explain the small variation in chemistry observed. Moreover, malachite, as a carbonate oxide ore, is not a semi-conductor mineral and thus no galvanic couple with the grinding media (affecting the chemistry) should occur during grinding.

- Flotation

The Eh and Es profiles during sulphidisation (i.e. NaHS conditioning) and flotation are charted in Figure 28 and Figure 29 respectively, while Table 7 reports the pulp chemistry at the end of the NaHS conditioning. The dissolved oxygen (DO) and Eh-pH diagrams can be found in Appendix 3.3.

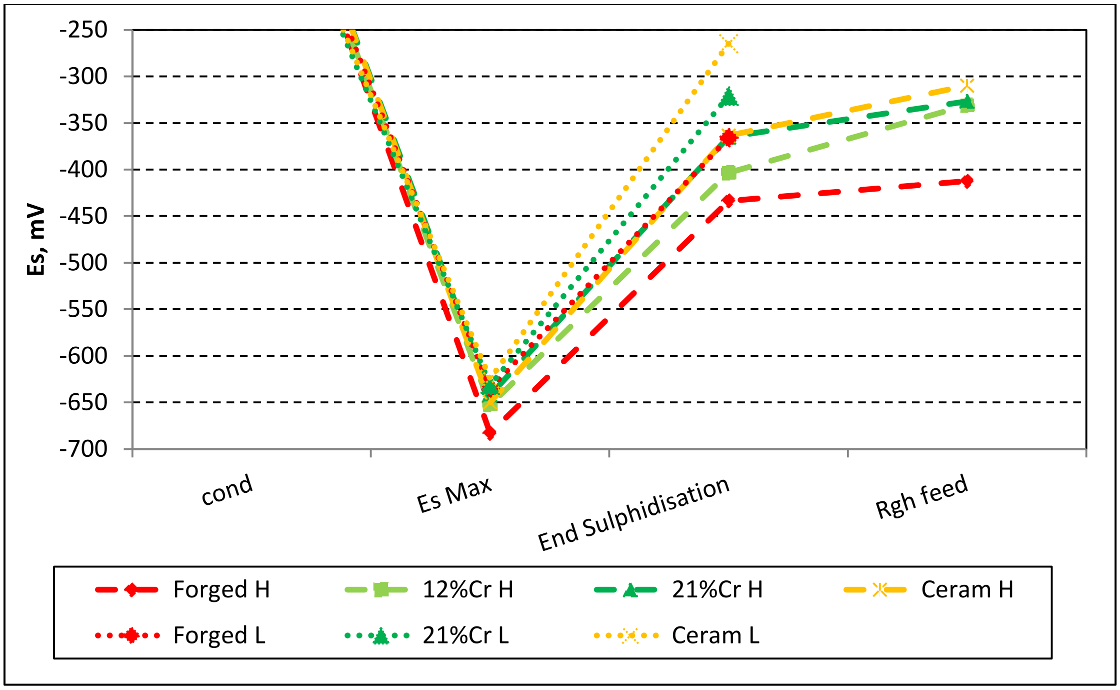

Figure 28: Es profiles during NaHS conditioning. L= low NaHS addition, H= High NaHS dosage, bulk ore.

The Es profiles (zoomed in to focus on the sulphidisation step) in Figure 28 show that the Es reaches a minimum within the first few seconds after the introduction of NaHS, then it starts increasing as the sulphides species are consumed though sulphidisation and oxidation. It is interesting to note that after two minutes of conditioning ("*End sulphidisation*") and at the "*rougher feed*", the Es has different values for each media tested and for both NaHS dosages (Table 7): Forged steel media showing the lowest Es values (-433 mV) and ceramic media the highest (-363 mV) at high dosage. Moreover, with forged steel and 12% HiCr media, the Es value after 2 minutes of NaHS conditioning (sulphidisation) was too low to allow correct flotation and the conditioning time was extended until reaching an Es value of -360 mV (required for correct flotation). Those observations indicate that the NaHS consumption was different for each media type; forged steel media presenting the slowest consumption and ceramic media the highest.

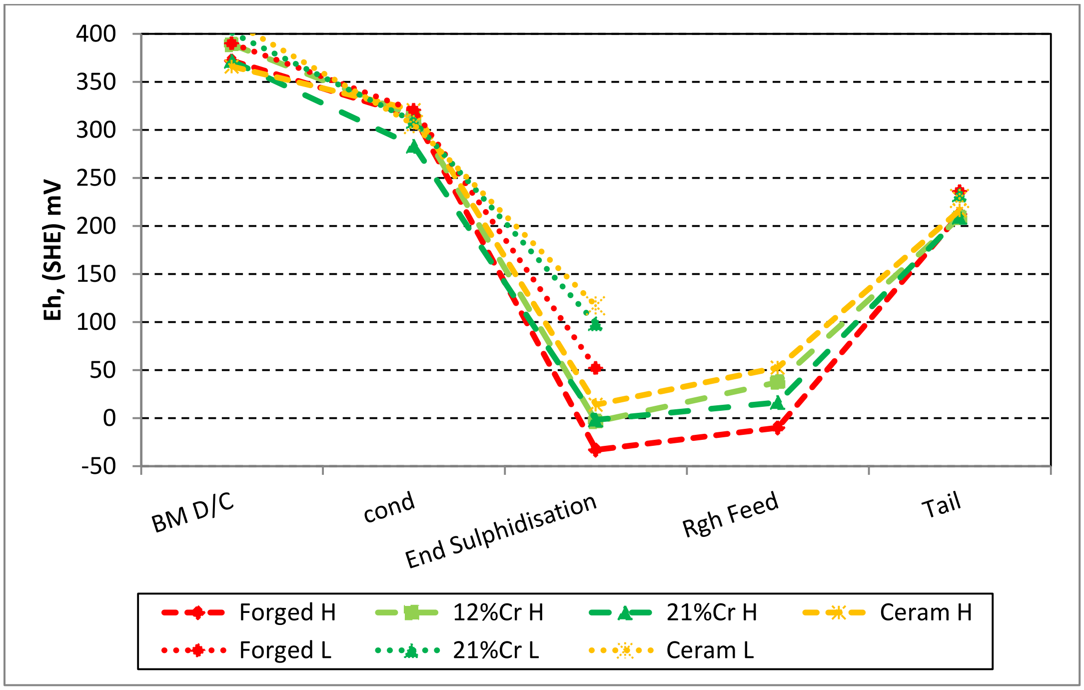

Figure 29: Eh profiles through NaHS conditioning and flotation. L = low NaHS addition, H = High NaHS dosage, bulk ore.

Table 7: Pulp chemistry at the end of NaHS conditioning, bulk ore.

Parameter	pH	Eh, mV (SHE)	Es, mV	DO, ppm	Temp, °C
Forged H	10.60	-31	-433	0.31	29
12%Cr H	10.70	-1	-403	0.52	29
21%Cr H	10.66	1	-365	0.7	29
Ceramic H	10.62	17	-363	0.48	30
Forged L	10.75	54	-366	1.22	28
21%Cr L	10.70	101	-321	2.02	28
Ceramic L	10.73	119	-265	2.15	28

An observation of the Eh profiles (Figure 29) shows that the Eh decreases from the ball mill discharge to the end of NaHS conditioning. Dotted lines were used in Figure 29 as during the NaHS conditioning, Eh profiles should show similar profiles to that observed for Es and mark a minimum within the first few seconds after the NaHS addition (Figure 28). However, this has not been recorded in this first set of experiments. Nevertheless, as for the Es profiles, the Eh profiles show differences between the media; forged steel resulting in the most reductive Eh and ceramic the highest. It also seems that the Eh difference between forged steel and the other media was higher at low NaHS dosage compared to that observed at high NaHS dosage (Table 7). That is: a 30 mV difference between forged steel and 21 HiCr media was observed at high NaHS dosage while a 50 mV difference was observed at low NaHS dosage, at the end of the NaHS conditioning. Table 7 also indicates that the DO was lower with forged steel than high chrome and ceramic media while little differences were observed for pH.

It is assumed that these variations in pulp chemistry conditions should affect the sulphidisation mechanism and could impact the recovery of the malachite.

5.2.1.3.2. EDTA

The level of iron and copper extracted by EDTA are presented in Table 8. No iron was detected in the EDTA solution for any media. This was expected due to the soft grinding conditions and the poor abrasiveness of the malachite, not wearing the media during grinding.

High percentages of copper have been extracted by EDTA, most probably due to the high solubility of the malachite. Table 8 indicates that the percent copper extracted by EDTA increased from forged steel to ceramic media as the conditions became more oxidative.

Table 8: EDTA extractable iron and copper for each alloy tested, bulk ore.

Parameter	EDTA Cu, %	EDTA Fe, %
Forged	6.5	-
12%Cr	6.7	-
21%Cr	7.6	-
Ceramic	8.1	-

5.2.1.4. Flotation response

5.2.1.4.1. Reproducibility

All the tests at high NaHS dosage were completed in triplicate and the tests at low NaHS dosage in duplicate to give confidence in the data produced. The reproducibility was examined for each condition and some tests repeated if necessary. The triplicate tests completed with forged media at high dosage are on display in Appendix 3.4. It is evident that the triplicate tests are in close agreement, suggesting that the reproducibility of the experiment is good.

In order to make the analysis simpler, in subsequent sections only the average results will be used.

5.2.1.4.2. Rougher flotation

The average copper recovery versus time curves for tests completed at high and low NaHS dosage with each media are presented in Figure 30 and the kinetics parameters are given Table 9. A test without sulphidisation has been carried out to demonstrate that without sulphidisation almost no copper is recovered.

Overall, Figure 30 and Table 9 show that the copper recovery does not reach 50 percent under any conditions. This is low and most probably due to a high fraction of very coarse material in the feed, too coarse to be recovered by traditional flotation (Figure 55 in Appendix 3.4). Comparing the different conditions, at high NaHS dosage there is only subtle variation of recovery and flotation kinetics between the media. However, at low NaHS dosage the data show significant differences: the maximum recovery and flotation kinetic for forged media higher than those obtained with high chrome and ceramic media.

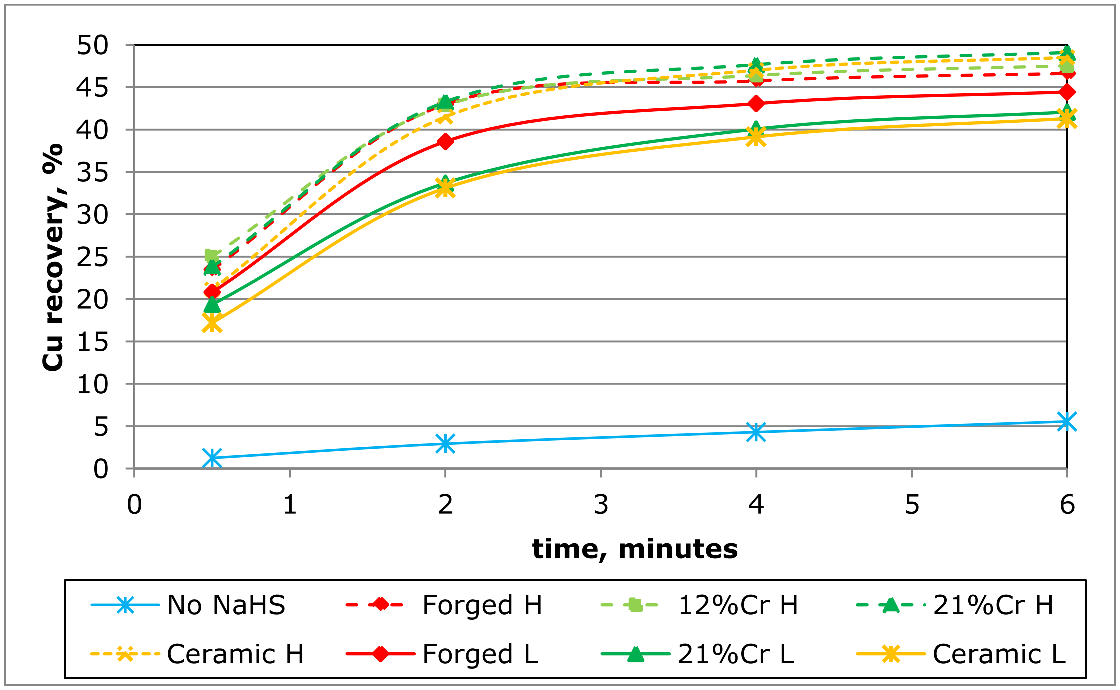

Figure 30: Copper recovery vs time for each alloy tested. L = low NaHS addition, H = High NaHS dosage, bulk ore.

Those results suggest that at high NaHS dosage where only slight variation of pulp chemistry were observed between the media, only subtle differences of metallurgical response were noticed. However, when sulphidisation is not performed under optimum conditions at low NaHS addition, pulp chemistry variations are bigger and thus a variation of flotation response can be seen: forged steel media showing the most reductive chemical conditions and the better flotation results.

Table 9: Copper maximum recovery and flotation kinetics, bulk ore.

Parameter	Cu_{Rmax}, %	K, min^{-1}
Forged H	46.1	1.4
12%Cr H	46.5	1.5
21%Cr H	46.5	1.3
Ceramic H	47.7	1.2
Forged L	43.5	1.2
21%Cr L	40.5	1.1
Ceramic L	40.2	1.0

5.2.1.5. Discussion

This first set of experiments has been completed on a very simple system made of malachite only. These have demonstrated that in some conditions (low NaHS dosage), the shift from an electrochemically active to a less electrochemically active grinding media resulted in variations of pulp chemistry during the sulphidisation process which subsequently affected malachite flotation. It is most likely that the more oxidative conditions obtained with ceramic media had negatively impacted on the sulphidisation process, resulting in lower malachite recovery when compared to the results obtained with forged steel media.

One of the biggest chemistry changes noticed was the Es at the end of the sulphidisation stage which was much higher with ceramic than forged steel media. This is an indication that the NaHS was consumed more quickly in the ceramic conditions or more probably more quickly oxidised because of the more oxidative pulp chemical conditions generated, i.e. higher Eh and DO levels. This most probably affected the sulphide coverage of the malachite and thus its floatability.

These observations are hypotheses only and it is clear that a deeper understanding of the sulphidisation mechanism is required to be able to understand the impact of the chemistry changes on the sulphidisation process. An XPS study of the malachite surface was also completed to help understanding the mechanism.

5.2.2. Review of the sulphidisation mechanism

The literature review has shown that the mechanisms leading to the formation of copper sulphide species onto the malachite surface are not clearly understood. No author has clearly identified which type of reaction led to the formation of copper species. The reasoning conducted in this work has led to the review of the mechanism occurring during sulphidisation. This would involve 3 steps, namely:

1) Adsorption,
2) Oxido-reduction reaction (Redox reactions), and
3) Precipitation

It is most likely that the adsorption of the HS^- species, liberated in solution through NaHS decomposition in water, is the first step of the reaction. It has been reported by several authors that following the introduction of the sulphide species, the zeta potential measured at the malachite surface decreased.

The second step involves an oxidation-reduction reaction. Although the electrochemical nature of some of the reactions occurring during sulphidisation have been proposed by several authors, they have not been clearly exposed. Most of them speak about the need of an aeration step to oxidise the excess sulphides from the solution. However, a look at some recent studies of the oxidation state of copper in sulphide mineral systems (Goh *et al.,* 2006; Pattrick *et al.,* 1997; Skinner, 2014) reveals that in any copper sulphide species, all of the copper present is Cu(I) (valence +1). The crystallographic structure of the malachite (Klein *et al.*, 1993) indicates that all copper is present at valence +2 (Cu(II)). Therefore, any copper present at the malachite surface must be reduced from Cu(II) to Cu(I) prior to the formation of Cu(I) sulphide species on the malachite surface. In this work, the proposed coupled oxidation reduction is the oxidation of the sulphide species in solution coupled with the reduction of copper:

Reduction:

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (E^0=150\ \text{mV}) \tag{11}$$

Oxidation:

$$HS^- \rightarrow S^0 + H^+ + 2e^- \quad (E^0= -70\ \text{mV}) \tag{12}$$

$$HS^- + O_2 \rightarrow S_xO_y^{2-} + ne^- \tag{13}$$

It is most likely that sulphide oxidation does not (only) produce elemental sulphur (12) but continues further (as per Eq 13) until the sulphur has the highest oxidation state (+VI). In fact, in this mechanism, malachite would play a catalytic role in sulphide oxidation, which would be very slow in the presence of oxygen only (Section 3.2.1.3). This can be observed experimentally when looking at the E_s potential while introducing NaHS into water. With water only, the sulphide oxidation is very slow and the E_s measurement stable. However, as soon as some malachite is introduced into the solution, the E_s starts increasing, revealing that the proportion of S^{2-} in solution is decreasing. This observation also highlights the Eh-pH dependency of the sulphidisation mechanism as some oxidation-reduction reactions are taking place. Eh-pH diagram of a Cu-S-H_2O system are presented in Section 3.2.1.2. Reductive conditions are necessary for the formation of CuS or Cu_2S species. It is also important to consider the dynamic nature of the stability window shown in the Pourbaux diagram: with the oxidation state of the sulphur species changing, the CuS and Cu_2S stability regions vary as well. This has not been highlighted in the literature, as in Zhang, 1994, for example). At the start of the reaction, the CuS and Cu_2S stability region is wide (Figure 5) with the sulphides at valence –II only (i.e. S^{2-}). However, as soon as the sulphides start oxidising (as per eq. 13), the CuS and Cu_2S domains start shrinking to reach the profile presented in Figure 6 when all sulphides species have reached their highest oxidation state (+VI).

Finally, the third step of the sulphidisation process corresponds to the precipitation of copper sulphides as per the next equation:

$$Cu^{+} + HS^{-} \rightarrow CuS + H^{+} \qquad (14)$$

The exact nature of the copper species formed at the malachite surface is probably difficult to determine. Indeed, the nature of the Cu-S system is extremely complex with a high number of stable, metastable, and intermediate compositions and structures occurring between the two common sulphides end-members: CuS and Cu_2S (Pattrick *et al.,* 1997).

A schematic summarising the mechanism is presented in Figure 31. The proposed equation is as follows (Eq. 15):

$$2Cu_{mal}^{\ 2+} + 3HS_{ad}^{\ -} \rightarrow 2CuS + S^{0} + 3H^{+} \qquad (15)$$

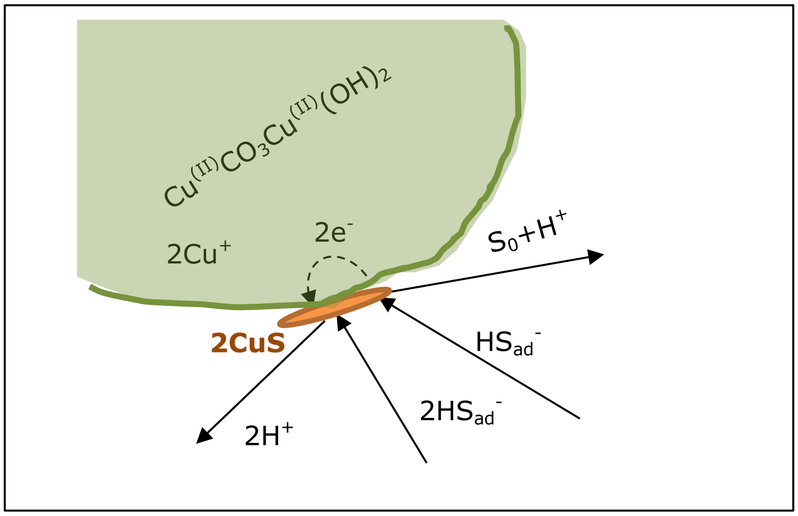

Figure 31: Schematic of the sulphidisation reaction.

In this mechanism, the role of the HS^- species is complex as they take part in two distinct reactions:

1) Coupled oxidation reaction to reduce Cu(II) to Cu(I); and
2) Precipitation of copper sulphides through the combination of Cu(I) and HS^-.

It is most likely that these two reactions are in competition for the use of the HS^-, illustrating the complexity of the mechanism and the importance of having an appropriate sulphide dosage for the sulphidisation reaction.

Given the better understanding of the sulphidisation mechanism, the possible effects of varying the pulp chemistry of the system could be:

- A shift of Eh-pH conditions out of the stability region of the copper sulphides could prevent their formation and favour the appearance of copper oxide for example;
- Higher dissolved oxygen contents could accelerate the oxidation of the sulphide species dissolved in the pulp (HS^-) and prevent the formation of a copper sulphide layer at the malachite surface by lack of HS^- species available for copper reduction and/or copper sulphide precipitation;
- On the other hand, a higher level of dissolved oxygen at the end of the sulphidisation reaction should be beneficial by accelerating the oxidation of the remaining sulphides species dissolved in the pulp and not suitable at that stage for subsequent flotation;.
- In addition, higher levels of pulp dissolved oxygen and higher Eh should favour xanthate adsorption (chemisorption);
- A high level of EDTA extractable copper (produced due to the oxidative conditions from the use of HiCr and ceramic media) should favour the sulphidisation mechanism though higher levels of copper sites available for the sulphidisation reaction at the malachite surface;
- The presence of various quantities of iron ions produced by the different grinding media (especially with forged steel media) could affect the process through:
    - Presence of iron hydroxide species at the malachite surface
    - Precipitation of iron sulphide species (i.e. HS^- consumption) either as colloids in solution or at the malachite surface.
    - Oxidation of HS^- through reduction of iron ions.

5.2.3. XPS study of sulphidised malachite

Surface characterisation of sulphidised malachite has been undertaken through XPS analysis to validate the mechanism described above. Samples were collected before and after the sulphidisation stage to allow the identification of the transformations occurring during sulphidisation at the malachite surface. General spectrum and high resolution spectra of Cu, S, Fe, O and C were carried out. Note that no iron was detected at the surface of any sample. The surface composition of the malachite before and after sulphidisation is tabulated in Table 10. Spectral fitting parameters for Cu2$p_{3/2}$, O 1s and S2$p_{3/2}$ are on display in Table 11 to Table 13 respectively. All spectra are displayed in Appendix 3.5.

Table 10 reveals that before sulphidisation, copper, oxygen and carbon are present at the malachite surface with oxygen being the most abundant species covering around 50 percent of the surface, following by copper (around 25 percent) and carbon (around 20 percent). The introduction of NaHS during the sulphidisation stage led to the apparition of a small quantity of sulphur on the surface (around 5%). Very small amounts of sodium (from NaHS) and calcium (as impurities?) were also detected.

Table 10: Surface composition of the malachite before and after sulphidisation determined by XPS (general spectrum).

Specie	Position: BE (eV)		FWHM (eV)		% Surface coverage	
	Before	After	Before	After	Before	After
S (2p)	-	161.76	-	3.36	-	5.10
C (1s)	284.91	284.26	3.37	3.13	18.06	20.50
O (1s)	531.14	530.76	3.43	2.66	56.14	49.82
Cu ($2p_{3/2}$)	935.14	934.26	5.37	5.21	25.8	23.97
Na (1s)	-	1071.26	-	2.90	-	0.40
Ca (2p)	-	349.76	-	3.31	-	0.23

Table 11: Spectral fitting parameters for Cu $2p_{3/2}$ species before and after sulphidisation of malachite.

Compound	Position: BE (eV)		FWHM (eV)		% Surface coverage	
	Before	After	Before	After	Before	After
Cu(I) sulphides	-	931.99	-	1.086	-	16.31
Cu(I) oxide	-	932.23	-	2.10	-	11.32
Cu(II) Oxide	934.10	933.12	2.97	2.35	40.80	19.27
Cu(II) hydroxide	935.40	934.48	2.89	1.86	42.20	37.67
Cu(II) carbonate	936.92	935.77	2.5	2.03	17.03	15.43

Looking at the higher resolution spectra for copper, Figure 60 and 61 in Appendix 3.5 show the presence of a well formed shake-up satellite peak indicator of the presence of copper at valence +II (Cu(II)) (Biesinger *et al.,* 2007 and 2010; Bassel, 2012; Grosvenor *et al.,* 2006; Biesinger, 2014), as expected for malachite. In Table 11, it can be seen that a model with 3 components was fitted to the Cu $2p_{3/2}$ spectrum of the malachite including copper oxide, hydroxide and carbonate components with copper only present at valence (II). From the literature, the component with the lowest binding energy was attributed to Cu(II) oxide, following by hydroxides and carbonates. The binding energy values fitted in that model are close to those found in literature (Naumkin *et al.,* 2012; Biesinger *et al.,* 2010; Folmer and Jellinek, 1980; Perry and Taylor, 1986; Biesinger, 2014) giving confidence in the model produced. In the sulphidised Cu $2p_{3/2}$ spectrum, two additional components were added on the lower energy side (Figure 61 in Appendix 3.5) revealing the presence of Cu(I) components, namely Cu(I) sulphide and Cu(I) oxide. The presence of the copper sulphide component corroborates the hypothesis that Cu(II) was reduced during sulphidisation to Cu(I) to allow the formation of copper sulphide species, only possible with the presence of copper at valence +1 (Skinner, 2014; Goh *et al.*, 2006; Patrick *et al.*, 1997). Based on the literature, the peak with the lowest biding energy was attributed to Cu(I) sulphide, followed by Cu(I) oxide and the 3 components defined for the fresh sample. The binding energy (BE) and full width at half maximum parameters (FWHM) were found to be close to those found in Naumkin *et al.,* 2012; Biesinger *et al.,* 2010; Folmer and Jellinek, 1980; Perry and Taylor, 1986; and Biesinger, 2014. In addtition, it is apparent from Table 11 that after sulphidisation, the amount of Cu(II) oxide was reduced from 40 to 20 percent and that around 16 percent of the Cu(I) was associated with sulphur and 10 percent with oxygen.

Table 12: Spectral fitting parameters for O 1s species before and after sulphidisation of malachite.

Compound	Position: BE (eV)		FWHM (eV)		% Surface coverage	
	Before	After	Before	After	Before	After
Cu (I and II) oxide	530.17	530.49	1.25	1.79	5.95	15.87
Cu(II) hydroxide	530.91	531.09	1.66	1.51	32.57	38.25
Cu(II) carbonate	531.53	532.29	1.23	1.81	44.33	37.57
Sulphates	532.45	-	1.26	-	11.17	-
Water	533.33	533.72	1.36	2.05	5.98	8.31

Looking at the O 1S data in Table 12, it can be seen that 4 components were fitted to the oxygen spectra of the non-sulphidised malachite and one additional after sulphidisation (sulphates). The four peaks were attributed to copper oxide (without distinction of the valence state of copper as both peaks overlap each other and have very similar binding energy (Bassell, 2012), hydroxide, carbonate and water (always present (Bassell, 2012)). As for copper, the peak attribution was according to the values found in the literature (Naumkin *et al.,* 2012; Beisinger *et al.*, 2010).

Table 13: Spectral fitting parameters for S $2p_{3/2}$ species after sulphidisation of malachite.

Compound	Position: BE (eV)	FWHM (eV)	% Surface coverage
Sulphide S^{2-}	161.05	0.91	15.49
Di-sulphide S_2^{2-}	161.82	0.87	36.96
Polysulphide S_n^{2-}	162.66	1.10	24.1
S_0/ Sulphites	164.28	1.97	18.36
Sulphates	167.18	1.97	5.1

Finally, the S $2p_{3/2}$ spectrum was examined. Sulphur 2p peaks occur as doublets (S 2p3/2 and S 2p1/2) as result of spin orbit splitting. Therefore, components were fitted with doublet 2p3/2 – 2p1/2: the two components having an intensity ratio of 2:1; a separation of 1.18 eV through higher energy for the 2p1/2 peak and the same FWHM (Bassell, 2012; Pattrick *et al.,* 1997; Harmer *et al.,* 2004; Acres *et al.,* 2010). In addition to the 3 components usually attributed to sulphur minerals (sulphide, di-sulphide and polysuphide) the presence of a tail on the high energy side of the $2p_{3/2}$ spectrum (Figure 64 in Appendix 3.5) reveals the presence of oxidised sulphur species. Therefore, two additonal components were added which correpond to sulphites and sulphates. The binding energy and full width at half maximum parameters (FWHM) presented in Table 13 are close to the values found in literature (Bassel, 2013; Naumkin *et al.,* 2012; Pattrick *et al.,* 1997; Harmer *et al.,* 2004 and 2006; Acres *et al.,* 2010; Smart *et al.,* 1999).

The XPS study of the malachite surface clearly identifies the changes occuring at the surface during the sulphidisation process and corroborates the mechanism described in the previous section. Changes in the valance state of copper, presence of copper sulphide species as well as various oxidation states of the sulphide species, all predicited by the sulphidisation mechanism, were detected in this study.

5.2.4. Oxide synthetic ore

5.2.4.1. Ore sample

Samples of oxide synthetic ore were made by mixing 1500 g of pure quartz and 40 g of pure malachite to obtain 1540 g of an ore sample totalling 1.35 percent copper.

5.2.4.2. Grinding-flotation conditions

5.2.4.2.1. Mill calibration

The standard procedure adopted for the grinding process was to grind the ore sample with 2 litres of tap water and 20 kg of grinding media during 20 minutes. The Magotteaux Mill® discharge particle size distribution and pulp chemistry targets for the mill calibration are listed in Table 14. As per previously, forged steel media were used as the reference media during the pulp chemistry calibration.

The target P_{80} of 150 microns was reasonably achieved for all alloys. The particle size distributions obtained for the four media types is given in Appendix 4.1. In terms of chemistry, the dissolved oxygen and temperature were able to be matched to the targets (Table 16).

Table 14: Mill discharge parameters and tolerances targeted during the calibration of the Magotteaux Mill®, oxide synthetic ore.

Parameter	Target	Tolerance
P_{80}, µm	150	± 5
Eh, mV vs SHE	natural	-
pH	natural	-
DO, ppm	1.4	± 0.5
Temperature, ^{o}C	32.0	± 2

5.2.4.2.2. Flotation procedure

After grinding, the ground pulp was transferred to a 5 litre flotation cell and homogenised during 2 minutes ("conditioning"). The homogenised ground slurry was then conditioned for 2 minutes with sodium hydrosulphide (NaHS) ("Sulphidisation: CPS -500mV") and an extra 2 minutes with 40 grams per ton of potassium ethyl xanthate (PAX) collector. Five drops of Aero68 frother were added 1 minute after the collector. Following conditioning, four timed copper rougher concentrates were collected for 0.5, 1.5, 2 and 4 minutes, for a total flotation time of 8 minutes.

The NaHS addition was completed through "controlled potential sulphidisation" (CPS) at an E_s of -500 mV; i.e., by adding the NaHS to maintain the Es at -500 mV during two minutes. On the contrary to the single mineral tests for which the dosage was fixed and adapted to the forged steel chemistry, this technique allows the adaption of the NaHS dosage to the pulp chemistry of each system and therefore should be optimum for all media tested. The different NaHS dosages recorded for the various grinding media tested are presented in Table 15.

The flotation flow sheet used for the flotation tests is represented in Figure 32, with the locations of the chemistry measurement indicated.

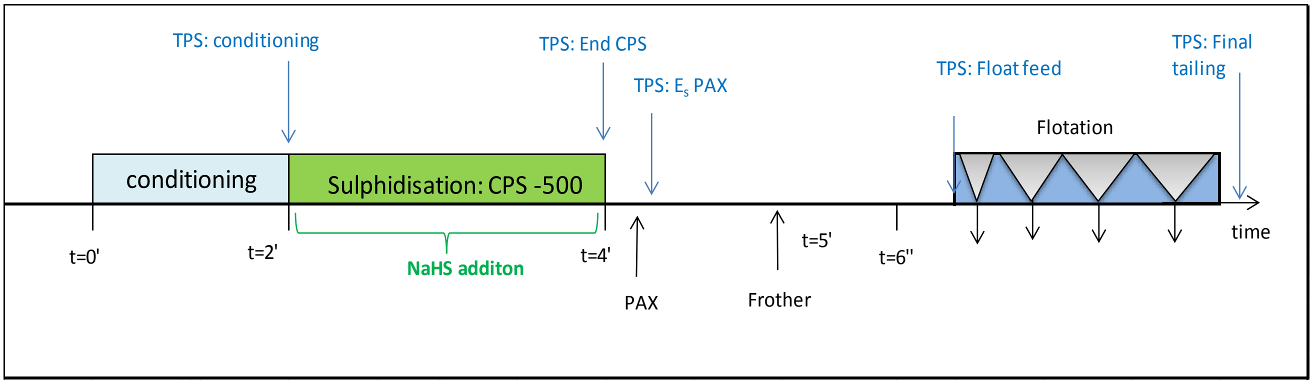

Figure 32: Flotation flow sheet, oxide synthetic ore.

Table 15: NaHS consumption during CPS with various grinding media, oxide synthetic ore.

Media	NaHS, ml (2.5% w/w)	NaHS g/t
Forged	11	178
12% HiCr	11.8	191
21% HiCr	12.2	198
Ceramic	14.7	238

5.2.4.3. Pulp chemistry

5.2.4.3.1. Grinding & flotation chemistry

- *Grinding*

Table 16 summarises the grinding chemistry observed at the ball mill discharge. The Eh, pH, dissolved oxygen (DO) and temperature profiles are on display in Appendix 4.2.

Table 16 indicates that, as with the sulphide minerals, grinding an oxide ore with different electrochemically active grinding media produces different grinding pulp chemistry. The level of oxygen, adjusted at 1.2 ppm with forged steel media, increased with high chrome and ceramic media. In terms of pulp electrochemical potential, the forged steel media produced the more reductive Eh than high chrome and ceramic media. It interesting to note that when looking at the Eh profiles during grinding (Figure 67, Appendix 4.2), for each alloy tested, the Eh very slightly decreases from the start to the end of the grinding stage. This is different from the Eh profiles usually observed for sulphide minerals for which the Eh decreases more strongly during grinding because of the galvanic couple created by the contact between the mineral and media. As no galvanic couple between the non-electrochemically active oxide minerals and the grinding media should occur in this case, the variations of pulp chemistry observed are most probably due to the difference in reactivity of the various media tested in water (highlighting their different electrochemical properties). In terms of pH and temperature, the data shows similar values for all media tested.

Table 16: Ball mill discharge pulp chemistry for an oxide synthetic ore ground with various grinding media.

Media	pH	Eh, mV (SHE)	DO, ppm	T°C
Forged	7.77	260	1.21	30.8
12% HiCr	7.95	326	1.64	31.4
21% HiCr	7.99	343	2.29	30.9
Ceramic	7.99	404	2.50	30.4

- *Flotation*

The DO, Eh, pH and Eh-pH pulp chemistry profiles during conditioning and flotation are presented in Appendix 4.3. Figure 33 charts the E_s profiles for the various media tested during conditioning. The pulp chemistry at the flotation feed is presented in Table 17.

Identically to the observation made at the ball mill discharge, after the 2 minutes conditioning, the data plotted in Appendix 4.3 indicates that the homogenised ground slurry has a higher Eh and DO when moving from forged steel to ceramic media. It is most likely that the more oxidative conditions observed with high chrome and ceramic media at the start of the sulphidisation process are responsible for the highest NaHS consumption observed with those media during the CPS stage (Table 15).

Turing to the E_s profile, Figure 33 shows that despite the higher NaHS dosage used with ceramic media, the consumption of sulphides was faster with high chrome and ceramic media. Indeed, ceramic media showed higher E_s values through all of the conditioning stages. For high chrome media, Table 17 shows higher E_s values at the flotation feed (end of PAX conditioning) (faster E_s increase = faster S^{2-} consumption). Note that the drop of E_s observed in Figure 33 when the PAX was introduced was due to the S^{2-} present in the PAX molecule.

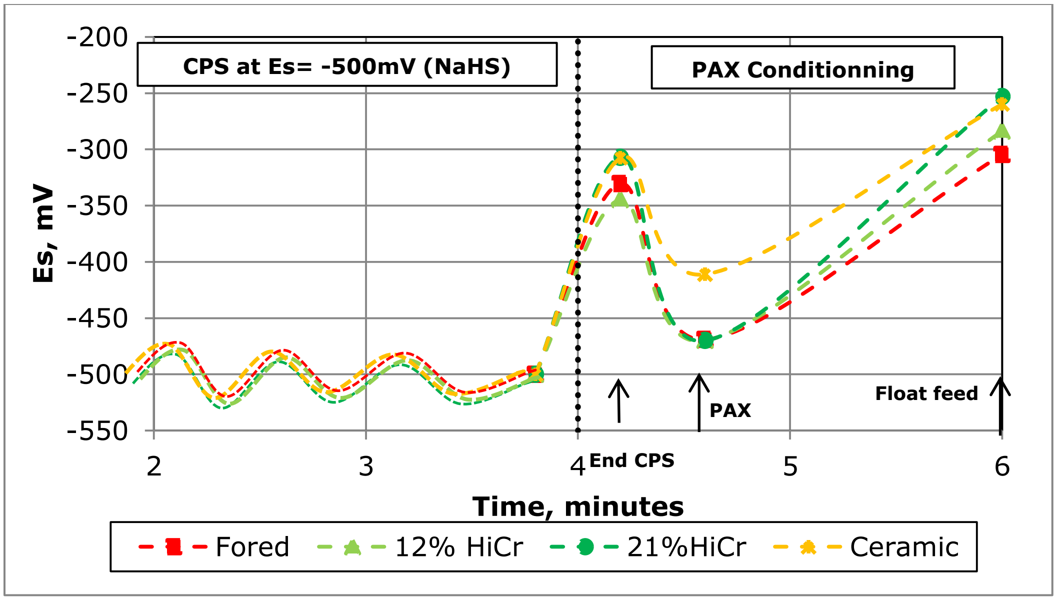

Figure 33: Es profiles during NaHS and PAX conditioning.

Table 17 (and Figure 71 in Appendix 4.3) also reveals that apart from the E_s, the flotation feed Eh was also more oxidative with ceramic and high chrome media than that observed with forged steel. Dissolved oxygen and pH showed similar values.

Table 17: Pulp chemistry at the flotation feed, oxide synthetic ore.

Parameter	pH	Eh, mV (SHE)	Es, mV	DO, ppm	Temp, °C
Forged	8.98	129	-300	7.56	27.8
12% HiCr	9.0	162	-283	7.53	28.2
21% HiCr	9.02	246	-253	7.43	27.8
Ceramic	9.16	234	-259	7.54	27.4

Although the NaHS dosage was able to be adapted to each chemistry system by the use of the CPS technique and more NaHS was used for high chrome and ceramic media than with forged steel media, differences in sulphides consumption and Eh conditions were still apparent at the end of the sulphidisation stage and at the flotation feed. It is most likely that these variations in NaHS consumption and pulp chemistry conditions will affect malachite flotation as observed in the previous set of experiments (Section 5.2.1).

5.2.4.3.2. EDTA

The level of iron and copper extracted by EDTA are presented in Table 18.

High percentages of copper have been extracted by EDTA, most probably due to the high solubility of the malachite. As noticed for the single mineral system, Table 18 indicates that the percent copper extracted by EDTA increases from forged to ceramic media as the media is becoming less electrochemically active.

In terms of iron, as no iron was present in the ore sample, it is not possible to calculate the percentage of iron extracted by EDTA as was done for copper. Therefore iron is reported in terms of mg/l of iron present in the solution (direct assay results). All iron found in the EDTA solution should come from media oxidation. The results show, as expected, that forged steel media releases a higher quantity of iron into the solution than ceramic media. This should adversely affect the copper metallurgy though the precipitation of iron hydroxide species on the particle surfaces.

Table 18: Iron in solution and EDTA extractable copper after milling with different grinding media.

Media	EDTA Cu,%	Fe, mg/l
Forged	15.72	7.70
12% HiCr	17.08	4.70
21% HiCr	16.81	2.15
Ceramic	18.25	1.35

5.2.4.3.3. Oxygen demand

The oxygen demand is presented in Appendix 4.3 Figure 74 for the forged steel media. The data shows a flat profile, indicating that the pulp has low reactivity. This is not unexpected as there should not be any galvanic couple between the non-electrochemically active oxide minerals and the grinding media (oxygen consumer) in this case.

5.2.4.4. Flotation response

5.2.4.4.1. Reproducibility

All the tests were completed in triplicates to give confidence in the data produced. The reproducibility was examined for each condition and some test discarded or repeated if necessary. The triplicate tests completed with forged steel media are on display in Appendix 4.4.1. It is evident that the triplicate tests are in close agreement, suggesting that the reproducibility of the experiment is good.

In order to make the analysis simpler, in subsequent sections only the average results will be used.

5.2.4.4.2. Rougher flotation

The average copper grade recovery curves for each alloy tested are presented in Figure 34 and the first ordered maximum recoveries and flotation rate constant in Table 19. The selectivity curves against non-sulphide gangue and the non-ulphide gangue versus water recovery are presented in Appendix 4.4.2.

The data (Figure 34,Table 19) shows that while 12% high chrome media gave the best copper maximum recovery (95.6%) and kinetics (4.1 min^{-1}), ceramic media gave the lowest (90.9% Cu recovery and k of 3.2 min^{-1}), despite the highest NaHS dosage used. It is most likely that with ceramic media, the pulp chemistry was too oxidising, consuming the NaHS too fast (most probably through sulphide oxidation and not oxide sulphidisation) to properly sulphidise the malachite surface. The better recovery obtained with high chrome media compared to forged steel is an indication that there is an optimum chemistry condition between the highly reducing forged steel and the very oxidising ceramic systems, which is ideal for the sulphidisation stage and produces the best copper recovery. In terms of grade, the selectivity curves in the appendix show that both high chrome and ceramic media were more selective against non-sulphide gangue than forged steel media.

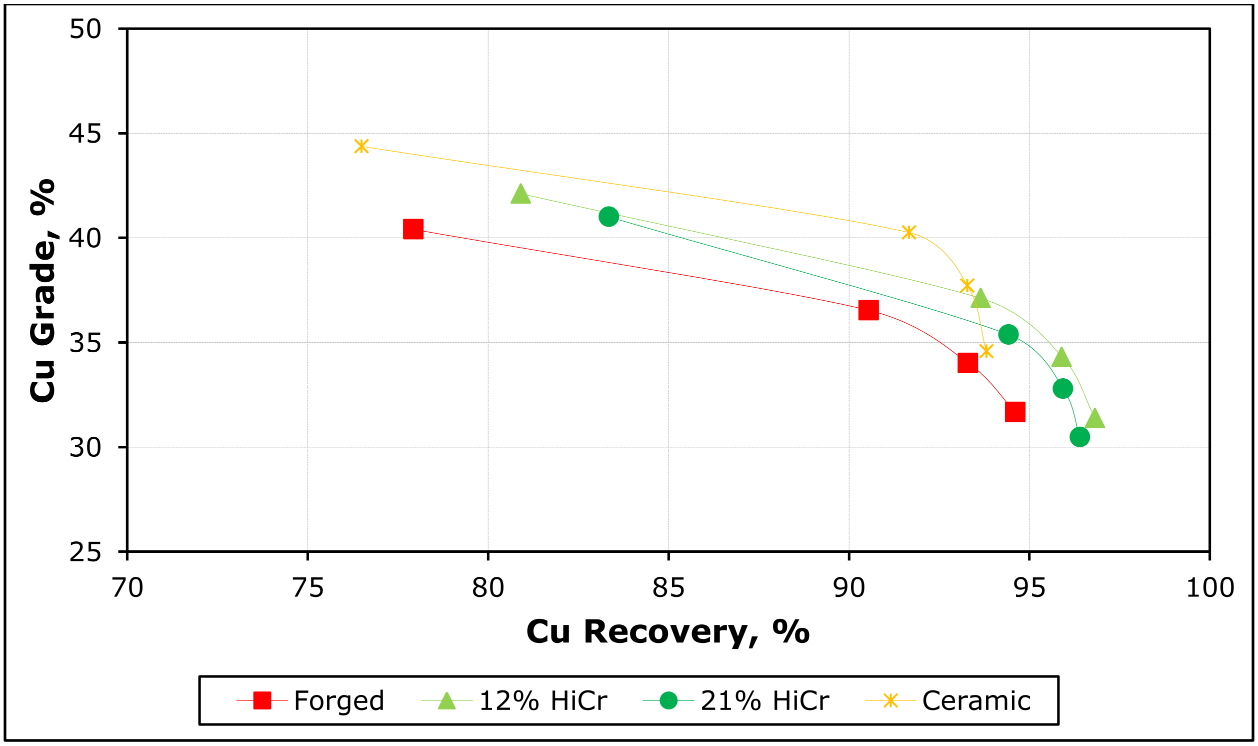

Figure 34: Copper grade recovery curve for the oxide mineral ground with several grinding media.

Table 19: Copper maximum recovery for the sulphide flotation with various grinding media, mixed synthetic ore.

Media	Cu R_{max}, %	K, min^{-2}
Forged	92.8	3.65
12% HiCr	95.4	3.77
21% HiCr	95.6	4.11
Ceramic	90.9	3.18

5.2.4.4.3. Recovery by size

The cumulative copper recovery by size after the first concentrate and total (after four concentrates) are represented in Figure 35. The particle size distributions for each media tested are plotted in Appendix 4.4.3 for comparison.

The feed distribution data in Appendix 4.4.3 indicates that all media show a similar copper distribution. The data also suggests that the copper is well distributed through the size spectrum.

A first look at the recovery versus size curves shows typical behaviour, with higher recoveries for the intermediate size fraction (-100/+10 microns), slightly decreasing for the fine ends (-10 micron) and a stronger decrease at the coarser end (>10 microns) of the size spectrum.

Comparing the different profiles, the data reveals that ceramic media produces slightly faster (first concentrate (C1) curve) and higher recovery of fines compared to forged steel media but the contrary for the particles at the coarse end of the spectrum. The data also shows that the difference between the several media tested was stronger after the first concentrate than overall. Interestingly, high chrome media which produced the best recoveries, showed an intermediate profile between forged steel and ceramic.

The lower recovery of the fine particles with forged steel (and high chrome) media can be attributed to their higher specific surface and thus their higher affinity for iron hydroxide products (more abundant with forged steel) than coarse particles. Iron hydroxides are most probably in competition with the HS^- species at the mineral surface during sulphidisation, preventing the formation of an optimum copper sulphide layer, decreasing the mineral floatability of the fine particles.

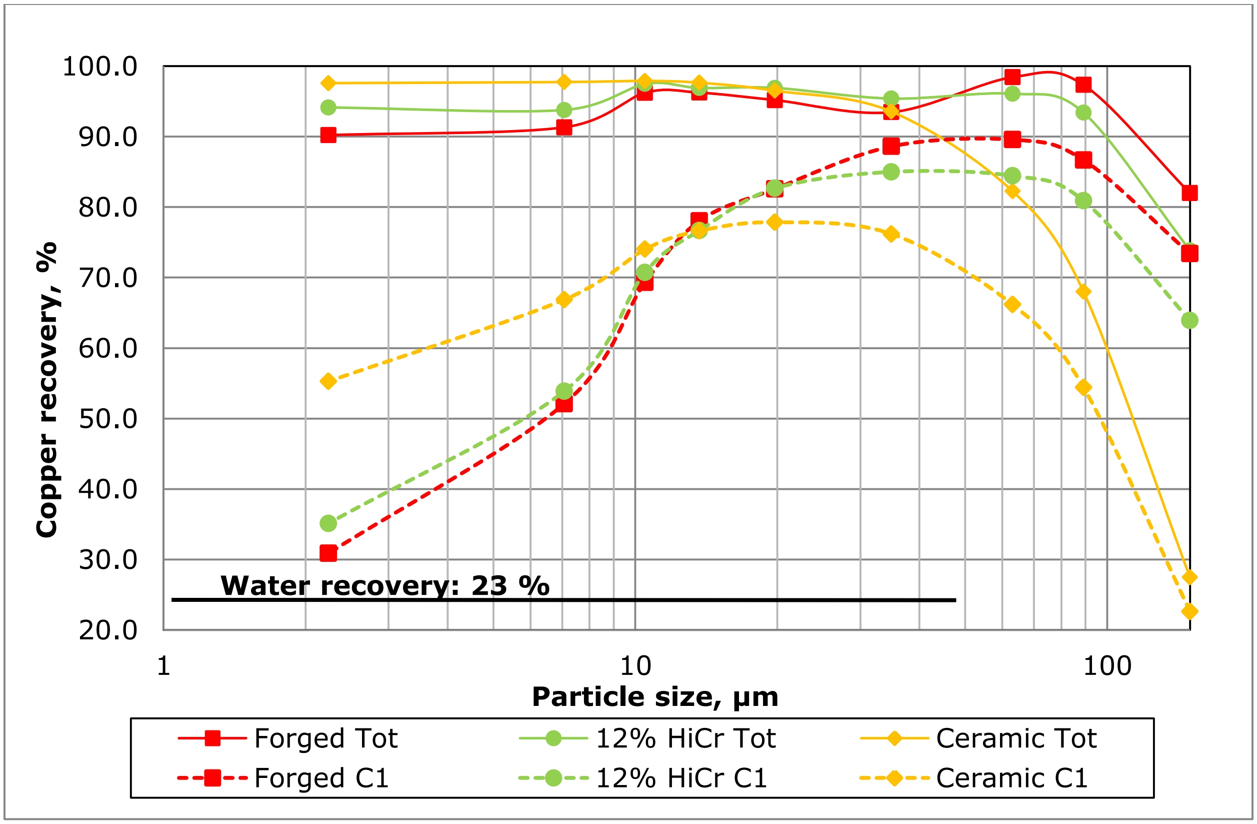

Figure 35: Cumulative copper size by size recovery after the first concentrate (C1) and total (tot) with various grinding media.

For the coarse particles, the lower recoveries observed with ceramic media could be explained by a lack of sulphide coverage of the particles due to insufficient sulphides species (HS^-) present in the pulp to form a sufficient copper sulphide layer on the coarse particle surfaces. Two reasons could be responsible for this:

- The oxidative conditions created with ceramic media, oxidising the HS^- species. This would suggest that the higher NaHS dosage used with those media was mainly lost through HS- oxidation and not used for the formation of copper sulphide at the malachite surface.
- A higher consumption by the fine particles of the HS^- species because of the cleaner surfaces obtained with ceramic media (less hydroxide species, and hence less competition between HS^- and $Fe(OH)_x$).

It should be noted that the recovery of the -50 micron particles was greater than water recovery in all instances, indicating that the dominant mechanism by which these particles were recovered was genuine flotation and not entrainment.

5.2.4.5. Discussion

The study of the flotation results has shown that when shifting from forged steel to high chrome and ceramic media, differences in the flotation response appear. This was confirmed by size by size recovery data which showed that the fines and coarse particles have different flotation behaviour with the different media tested.

These differences were attributed to a variation of pulp chemistry observed for each media tested, affecting the sulphidisation mechanism and subsequent copper flotation. Indeed it is most likely that there is a relation between the level of oxidation of the pulp and the level of NaHS consumption; the most oxidising chemistry, the greater the NaHS uptake during sulphidisation. However, the flotation results demonstrated that the additional NaHS used does not necessarily improve the flotation results, indicating that the extra NaHS used is most probably oxidised and not available to take part in the sulphidisation process. Since it is clear that the sulphidisation mechanism is Eh-pH dependent because of the redox reduction taking place to reduce the copper from the malachite and for the precipitation of the copper sulphide, it is most probable that in addition to the appropriate NaHS dosage, optimum Eh-pH conditions are required to make good use of the NaHS and to allow the formation of a copper sulphide layer on the malachite surface.

In these particular experiments, the optimum pulp chemistry was obtained with 12% high chrome media. Ceramic conditions were probably too oxidative (NaHS oxidation, CuO formation instead of CuS or oxidation of the freshly formed copper sulphide layer) and forged steel media too reductive (high quantity of $Fe(OH)_x$ at the malachite surface, presence of excessive sulphide species at the end of the sulphidisation due to the reducing conditions).

This clearly indicates that there is a need to understand the Eh-pH conditions during the sulphidisation process and not only before and after as they were recorded during this series of experiments (Figure 73 in Appendix 4.3). Therefore, in the next series of experiments, the Eh-pH conditions will be recorded continuously during the entire sulphidisation process to ensure that they match the Eh-pH conditions suitable for sulphidisation (Section 3.2.1.3) under all conditions.

5.2.5. Mixed synthetic ore

5.2.5.1. Ore samples

Samples of mixed synthetic ore were made by mixing 1500 g of pure quartz, 40 g of pure malachite and 70 g of pure chalcopyrite to obtain ore charges averaging 2.6 percent copper. The proportion of malachite and chalcopyrite were adjusted to obtain a copper repartition of 50% between the two minerals as shown in Table 20 summarising the sample head grade.

Table 20: Head grade of the mixed synthetic ore

TCu, %	AsCu, %	AiCu, %	Fe, %	S, %	SiO_2, %
2.57	1.26	1.32	1.73	1.35	94.0

5.2.5.2. Grinding-flotation conditions

5.2.5.2.1. Mill calibration

The grinding parameters and recipe were the same than that used for the oxide ore in Section 5.2.4.2.1). In terms of particle size distribution, the mill speed was readjusted (compared to the oxide synthetic ore) to match the targeted P_{80} of 150 microns. The particle size distributions obtained for the four media types are given in Appendix 5.1.

5.2.5.2.2. Flotation procedure

The ground samples were floated through a sequential sulphide and oxide sulphidisation flotation scheme.

For the sulphide flotation stage, the pulp was conditioned during 2 minutes with 5 g/t of SIBX as the collector and 6 drops of F501 as the frother. Sulphide concentrates were recovered after 0.5, 0.5, 1 and 1 minutes for a total flotation time of 3 minutes.

Following sulphide flotation, the oxide sulphidisation-flotation stage was completed. The flow sheet used is represented in Figure 36. The NaHS (2.5% w/w solution) was added first (as a slug addition), then 15 seconds after, 40g/t of PAX was introduced and another 45 seconds later, 2 drops of F501 frother was added. Once the E_s was above -360 mV, the conditioning period was stopped and flotation started. To accurately measure the variation in pulp chemistry and NaHS consumption with the different media tested, the pulp chemistry parameters (Eh, DO, pH, T° and E_s) where continuously recorded every 5 seconds with a TPS meter during the entire conditioning stage. The "increased time" necessary for the E_s probe to go back to -360 mV (E_s potential corresponding to a mineralised froth ready to be recovered) was also recorded for each test and was used as an indication of the NaHS consumption kinetics.

In terms of NaHS dosage, a fixed quantity of 10 ml of NaHS (2.5% w/w solution) was added. The fixed dosage was chosen for all media to accentuate the differences of pulp chemistry and flotation performances between all media tested.

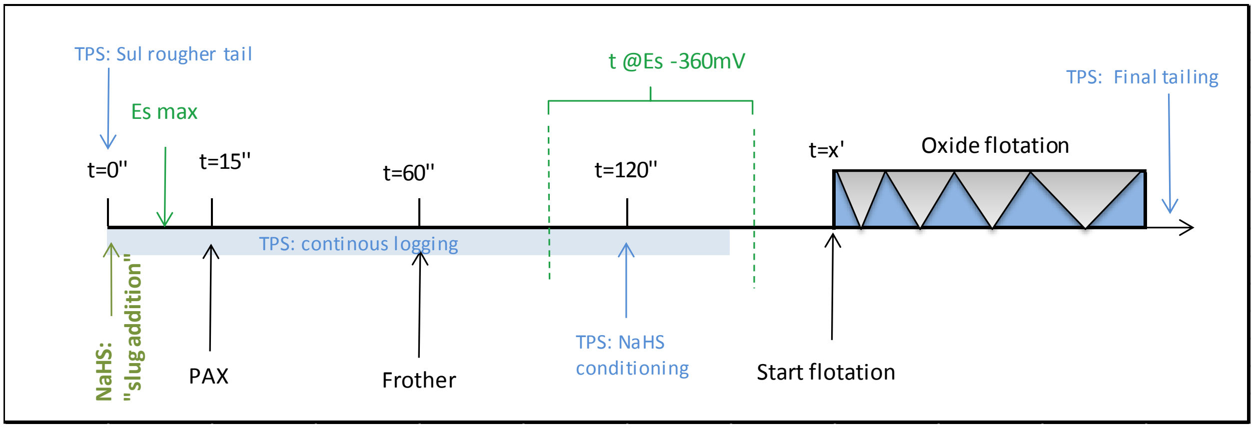

Figure 36: Oxide sulphidisation-flotation flow sheet, mixed synthetic ore.

5.2.5.3. Pulp chemistry

5.2.5.3.1. Grinding & flotation chemistry

Grinding

The ball mill discharge pulp chemistry is given in Table 21 and the Eh, dissolved oxygen (DO), pH and T° profiles through the entire grinding stage are charted in Appendix 5.2.

Table 21: Ball mill discharge pulp chemistry for the synthetic mixed ore ground with different grinding media.

Media	pH	Eh, mV (SHE)	DO, ppm	T°C
Forged	7.9	134	0.7	30.2
12% HiCr	8.0	179	1.1	30.4
15% HiCr	8.0	197	1.2	30.1
Ceramic	8.1	303	1.9	29.7

The data indicates that as previously observed for the bulk malachite and synthetic oxide ores, there was a difference of chemistry between the various alloys tested. Contrary to that observed with the two samples tested previously, the differences were more pronounced in this case. That is, the Eh was found to significantly decrease from ceramic (303 mV) to forged steel media (134 mV) (Table 21). Looking in more detail at the Eh profiles during grinding in Appendix 5.2 (Figure 81), the data shows that the Eh drops strongly with forged steel and high chrome media, probably because of the galvanic interactions taking place between the sulphide minerals and media while it stays quite constant with the more inert ceramic media. In terms of DO, higher levels of DO were recorded with the ceramic media (1.9 ppm) when compared to forged steel (0.75 ppm) and high chrome media (1.2 ppm)

(Table 21). The Eh and DO profiles obtained in Appendix 5.2 are quite similar to those observed for the sulphide ore. This indicates that, while differences in pulp chemistry were observed when grinding an oxide mineral only, most of the differences in pulp chemistry observed in a mixed system are due to the presence of the sulphide minerals in the ore and the galvanic interactions taking place between the sulphide minerals and the media.. Table 21 also indicates that the pH and temperature were similar in all instances.

Sulphide flotation

The dissolved oxygen (DO), Eh and pH profiles through the sulphide and oxide flotation stages are shown in Appendix 5.3. Table 22 presents the pulp chemistry data for the sulphide flotation feed.

Table 22 indicates that as for the ball mill discharge, the pulp conditions became gradually more oxidative from forged steel to ceramic media. That is, the Eh went from 273 mV with Forged steel to up to 300mV with ceramic media. Identically, the dissolved oxygen content increased from 7.5 to 8 ppm while the pH and temperature were similar for all media.

Table 22: Sulphide flotation feed chemistry for a synthetic mixed ore ground with different grinding media.

Media	pH	Eh, mV (SHE)	DO, ppm	T°C
Forged	8.4	273	7.5	28.3
12% HiCr	8.1	281	7.3	28.4
15% HiCr	8.0	293	7.5	28.2
Ceramic	8.0	303	8.0	27.8

Oxide flotation

During the NaHS and PAX conditioning stages, the Eh, DO, pH and E_s profiles were recorded continuously and are presented in Appendix 5.3 (Figure 87 to Figure 89 for DO, Eh and pH respectively) and in Figure 37 for E_s. The pulp chemistry at the oxide flotation feed is presented in Table 24.

At the sulphide rougher tailing, i.e. at the start of the sulphidisation stage, the data in Appendix 5.3 shows quite similar chemistry between the various media tested. However, during the sulphidisation stage, differences appeared. The E_s profiles give an indication of the NaHS consumption during sulphidisation, showing (Figure 37) that the kinetics of NaHS consumption varied between the media tested: ceramic media resulted in the fastest NaHS consumption; high chrome media gave intermediate values and forged steel media the slowest consumption. This is also highlighted in Table 23 where the time required for the E_s potential to return to an E_s of -360 mV has been measured: it decreases from forged steel (105 s) to ceramic media (65 s). The DO and Eh profiles also display differences (Figure 87 and Figure 88 in Appendix 5.3), particularly between ceramic and forged steel media. At the end of the conditioning stage (i.e. oxide flotation feed), Table 24 shows that the differences in terms of Eh and DO was important. That is, the Eh increases from 118 mV with forged steel to 208 mV with ceramic media and the DO from 7.5 to 8 ppm. This tends to suggest that the variation in chemistry observed during grinding continues to impact the sulphidation stage, and thus even after sulphide flotation, affecting the NaHS consumption and hence most probably the subsequent oxide flotation.

Table 23: E_s kinetics: time at E_s= -360 mV (mineralised froth) with various grinding media.

Media	Time at E_s=-360 mV, seconds
Forged	105
12% HiCr	100
15% HiCr	85
Ceramic	65

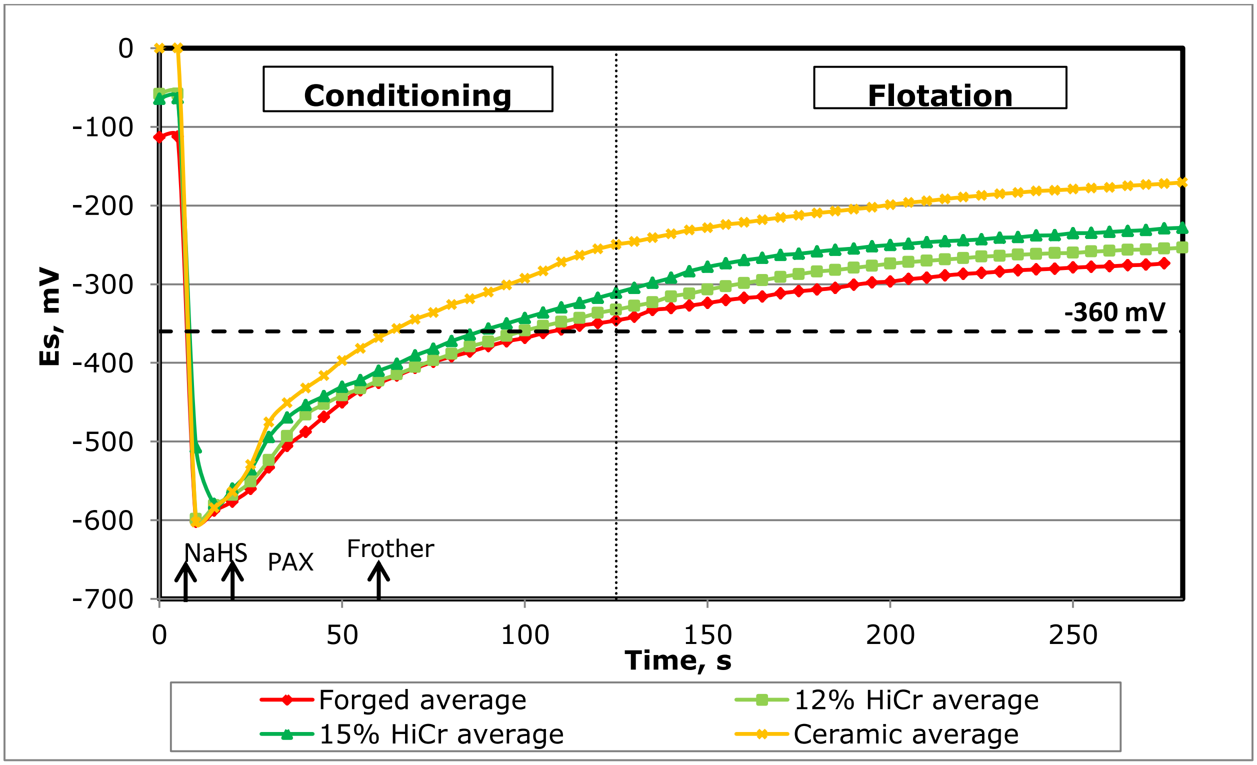

Figure 37: E_s during conditioning (slug addition) and copper flotation. Black dashed line represent E_s= -360mV.

Table 24: Oxide flotation feed chemistry for a synthetic mixed ore ground with different grinding media.

Media	pH	Eh, mV (SHE)	DO, ppm	T°C
Forged	9.2	118	7.5	28.3
12% HiCr	9.1	132	7.3	28.4
15% HiCr	9.1	145	7.4	28.3
Ceramic	9.2	208	8.1	28.0

5.2.5.3.2. EDTA

The iron and copper extracted by EDTA are presented in Table 25.

The level of copper extracted by EDTA give an indication of the oxidation degree of the copper minerals. Similarly to that observed with the oxide ore, Table 25 indicates that the copper minerals are more oxidised when the ore was ground with ceramic and 15% chromium media compared to the ore ground with forged steel and 12% chromium media. The higher level of EDTA copper may be an indication that more copper sites are available with high these media at the malachite surface and hence could favour the sulphidisation reaction.

In terms of iron, as previously observed, the percentage of iron extracted by EDTA decreases from forged steel to ceramic media as the media becomes less electrochemically active. The cleaner system obtained with high chrome and ceramic media should be beneficial for the sulphide and oxide flotation.

Table 25: EDTA extractable iron and copper after milling with different grinding media, mixed synthetic ore.

Media	Cu,%	Fe,%
Forged	11.9	4.5
12% HiCr	11.0	2.9
15% HiCr	12.3	2.9
Ceramic	13.2	1.0

5.2.5.3.3. Oxygen demand

The oxygen demand profiles are presented in Figure 38 for both the sulphide and oxide flotation feeds for all media tested.

A look at the oxygen demand profiles at the sulphide flotation feed shows that the pulp presents the highest reactivity with forged steel media, intermediate with high chrome and the lowest with ceramic media. This is typically observed with sulphide minerals. That is, the oxygen demand decreases as the media becomes less electrochemically active and as the number of redox reactions between the media and the ore deceases.

Turning to the oxygen demand obtained at the oxide flotation feed, the data indicates that the ore has reached a stable oxidation state with all media tested (flat curves). This was expected as oxide minerals are not electrochemically active (see Section 5.2.4.3.3).

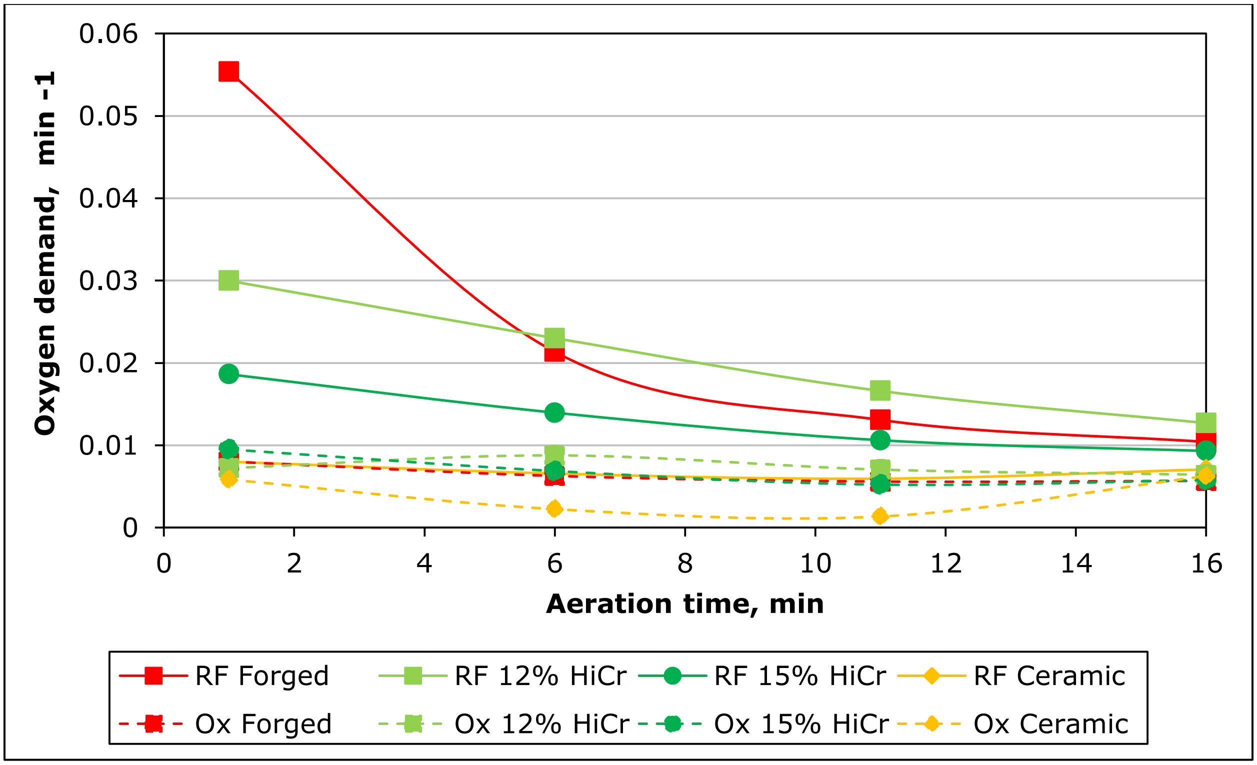

Figure 38: Oxygen demand at the sulphide flotation feed (RF) and before the NaHS conditioning (Ox) at the sulphide flotation tailing.

5.2.5.4. Flotation response

5.2.5.4.1. Reproducibility

All the tests were completed in triplicate under standard conditions and duplicate when other conditions were tested, to give confidence in the data produced. The reproducibility was examined for each condition and some tests discarded or repeated if necessary. The triplicate tests completed with forged are on display in Appendix 5.4.1 for both sulphide and oxide flotation. It is evident that the triplicate tests are in close agreement, suggesting that the reproducibility of the experiment is good.

In order to make the analysis simpler, in subsequent sections only the average results will be used.

5.2.5.4.2. *Standard rougher flotation*

Sulphide flotation

The average copper and acid insoluble copper grade recovery curves for each alloy tested are presented in Appendix 5.4.2. The first order maximum recoveries and flotation rate constants are tabulated in Table 26. The acid insoluble copper selectivity curves against acid soluble copper are shown in Figure 39 while the selectivity curves against non-sulphide gangue and the non-sulphide gangue versus water recovery are presented in Appendix 5.4.2 (Figure 94 and Figure 95 respectively).

Table 26: Copper kinetics and copper and silica maximum recovery for the sulphide flotation stage with various grinding media, mixed synthetic ore.

Media	Cu		AiCu		AsCu		SiO_2
	R_{max}, %	K,min^{-1}	R_{max}, %	K,min^{-1}	R_{max}, %	K,min^{-1}	R_{max}, %
Forged	49.0	3.8	89.8	4.0	5.1	1.3	1.6
12% HiCr	48.7	3.7	92.6	4.0	5.8	1.2	1.6
15% HiCr	49.4	3.9	90.8	4.2	6.3	1.2	1.6
Ceramic	50.2	3.6	89.4	3.9	9.3	1.4	1.9

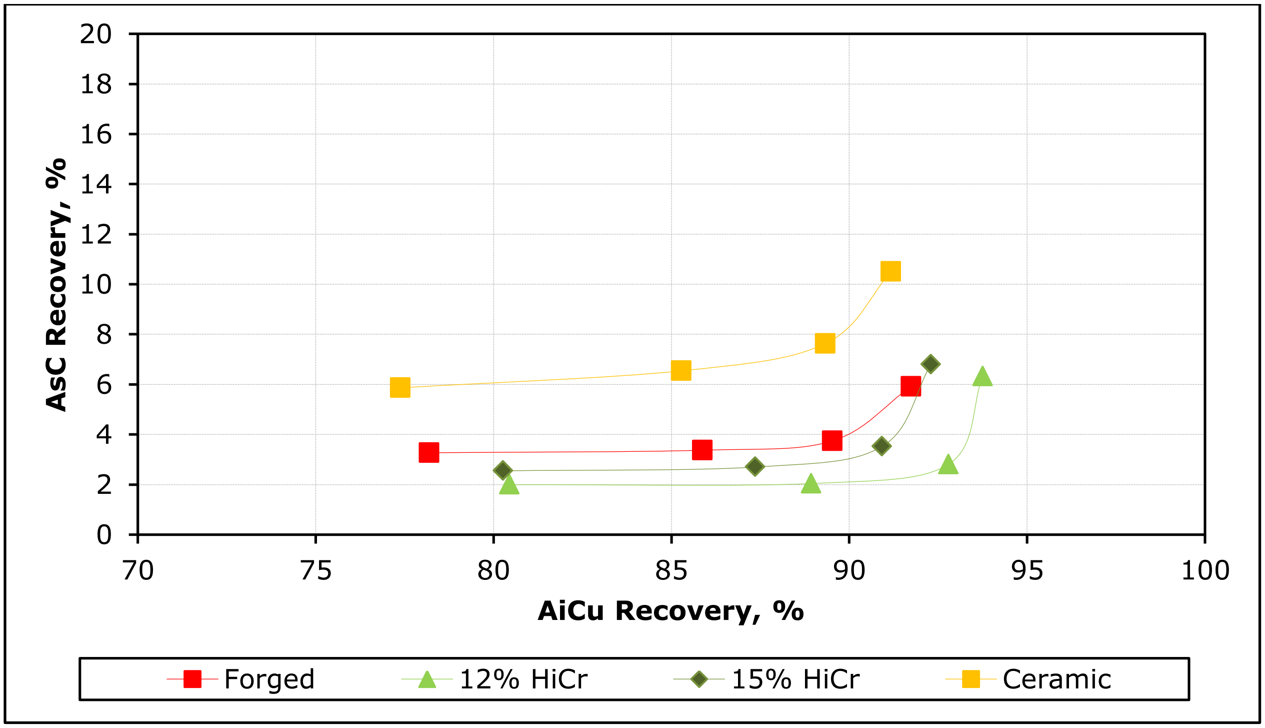

Figure 39: Acid soluble copper selectivity curves against insoluble copper for the sulphide flotation stage of the synthetic mixed ore ground with several media.

In terms of sulphide flotation, the insoluble copper grade recovery graph in Appendix 5.4.2 shows typical sulphide grade recovery profiles with 12% high chrome media giving the best results and ceramic media the lowest. This is confirmed by the data presented in Table 26, where 12% high chrome media shows the best maximum recovery (92.6%) and kinetics (4 min$^{-1)}$. In terms of total copper, the contrary is seen. That is, Table 26 shows that ceramic media gives the highest recovery at 50.2 percent and 12% high chrome media the lowest at 48.7 percent. Indeed, looking at the oxide selectivity against sulphides curves in Figure 39, the data shows that more oxide minerals were recovered with ceramic media compared to high chrome and forged steel media, explaining the highest total copper recovery obtained with that media type. In addition, ceramic media entrains more non-sulphide gangue but it does not seem to be due to a higher water recovery (Figure 95, Appendix 5.4.2), so is most probably to the cleaner system obtained with that media. Considering the pulp chemistry, it seems that the optimum chemistry conditions for the sulphide flotation stage was obtained with high chrome media; forged steel chemistry being too reductive and ceramic media most probably too oxidative.

Oxide flotation

Turning to oxide flotation, the oxide flotation feed grades are presented in Table 8 in Appendix 5.4.2. The flotation first order kinetics and maximum recoveries can be found in Table 27. The acid soluble copper grade recovery curves are plotted in Figure 40 for all media tested. The total copper grade recovery curves as well as the acid soluble copper selectivity curve against acid insoluble copper and the non-sulphide gangue versus water recovery can be found in Appendix 5.4.2 (Figure 96 to Figure 98, respectively). Finally, the final recovery is tabulated in Table 28.

Firstly, a check of the feed grade (Table 8 in Appendix 5.4.2) reveals that the total copper head grades are similar for all media tested while there is slight variation of acid soluble and insoluble copper. This was due to the differences in metallurgical results observed during the sulphide flotation stage between the different media tested.

The oxide flotation results in Figure 40 and Table 27 show that the best oxide recovery and flotation kinetics were obtained with forged steel (92.6%) media while ceramic media show the lowest results (90.3%). Overall (i.e. Cu), Table 27 and Figure 96 in Appendix 5.4.2 show that forged steel and 15% high chrome media have similar maximum copper recoveries but with lower flotation kinetics and with a higher grade for 15% high chrome media. The oxides selectivity against sulphides graph (Figure 97 in Appendix 5.4.2) show that ceramic media presents the lowest selectivity against sulphides minerals. That is, most of the sulphides not recovered during the sulphide stage were able to be recovered with ceramic media during the oxide stage. Looking at the gangue mineral, Table 27 and Figure 98 in Appendix 5.4.2 indicate similar non-sulphide gangue and water recoveries with all media tested.

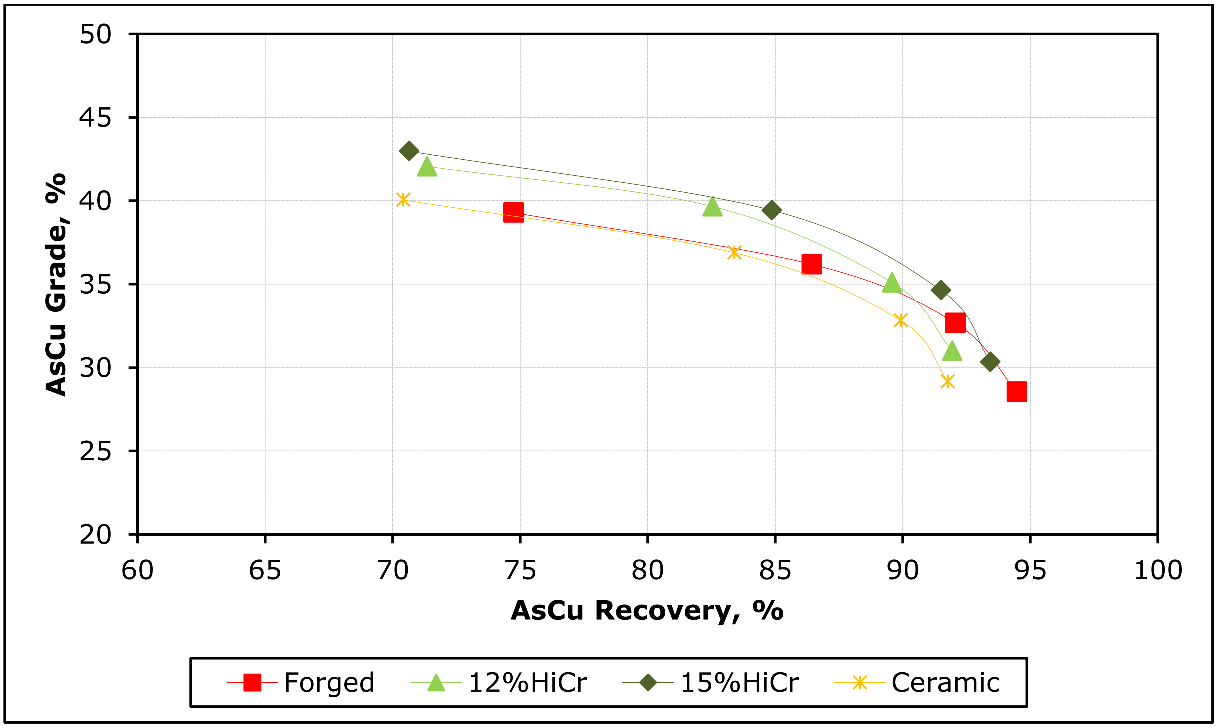

Figure 40 AsCu grade-recovery curve for the oxide flotation stage with respect to oxide flotation feed for a synthetic ore ground with several grinding media.

Table 27: Oxide flotation maximum recovery and flotation rate constant with respect to oxide flotation feed for the various grinding media tested.

Media	Cu		AiCu		AsCu		SiO2,
	R_{max},%	K,min^{-1}	R_{max},%	K,min^{-1}	R_{max},%	K,min^{-1}	R_{max}%
Forged	89.9	2.95	71.9	0.8	92.6	3.2	1.7
12% HiCr	87.1	2.81	63.4	0.26	89.9	3.0	1.6
15% HiCr	89.8	2.63	79.9	0.63	92.0	2.8	1.6
Ceramic	88.7	2.81	75.6	1.67	90.3	2.9	1.6

Now, considering the entire flotation results (sulphide + oxide stages), the data in Table 28 indicates that the best total copper recovery was obtained with forged steel media at 96.4 percent and the lowest with 12% high chrome media at 95.1 percent. The better results obtained with forged steel media are mainly due to the highest recovery of oxide minerals (94.8 percent) as the sulphide final recovery was one of the lowest (97.6 percent).

The difference of optimum media type for the sulphide and oxide flotation stages has been highlighted by statistically comparing the forged steel and 15% high chrome media with the *Student's t-test method* (t-test). The results are displayed in Table 29. These indicate that while there is no statistical difference for the overall copper recovery (Cu) between the two media types, there was a statistically confident difference in the sulphide mineral recovery (AiCu), which was 0.5% higher for the 15% high chrome media, and the oxide mineral recovery (AsCu) which was 0.9% lower, compared with forged steel media.

Once again, the results obtained in these experiments can be explained by the difference in chemistry observed previously (Section 5.2.5.3). The results suggest that when a mixed ore is recovered by flotation, the optimum alloy producing the most adequate chemistry and the best flotation response is different for both the sulphide (high chrome) and the oxide (forged steel) flotation stage.

Table 28: Final recovery (sulphide+oxide stages) with various grinding media.

Media	Cu, %	AiCu, %	AsCu, %	SiO2,%
Forged	96.4	97.9	94.8	3.4
12% HiCr	95.1	97.7	92.5	3.2
15% HiCr	96.2	98.4	93.9	3.2
Ceramic	95.6	98.4	92.6	3.5

Table 29: t-test analysis comparing the overall flotation performances of forged steel and 15% high chrome media.

Parameters	Forged	15% HiCr
Cu recovery, % Number of Samples	96.4 4	96.2 3
Mean difference (forged - 15% HiCr), % Confidence level of the difference (1 sided), %	+0.2 30%	
AiCu recovery, % Number of Samples	97.9 4	98.4 3
Mean difference (forged - 15% HiCr), % Confidence level of the difference (1 sided), %	-0.5 92%	
AsCu recovery, % Number of Samples	94.8 4	93.9 3
Mean difference (forged - 15% HiCr), % Confidence level of the difference (1 sided), %	+0.9 97%	

5.2.5.4.3. Recovery by size

The three cumulative recovery versus size curves after the sulphide, oxide flotation first concentrate (oxide C1), and oxide flotation fourth concentrate (oxide C4) stages are represented in Figure 41 for the acid soluble copper (oxide minerals) and in Appendix 5.4.3 for acid insoluble copper as well as total copper. The particle size distributions for each media tested are also plotted in Appendix 5.4.3 for comparison purposes.

The feed distribution data in Appendix 5.4.3 indicates that all media show similar copper distribution. It is also evident that the sulphide and oxide copper distribution are similar with around 60 percent of the copper present in the size fractions above 40 microns.

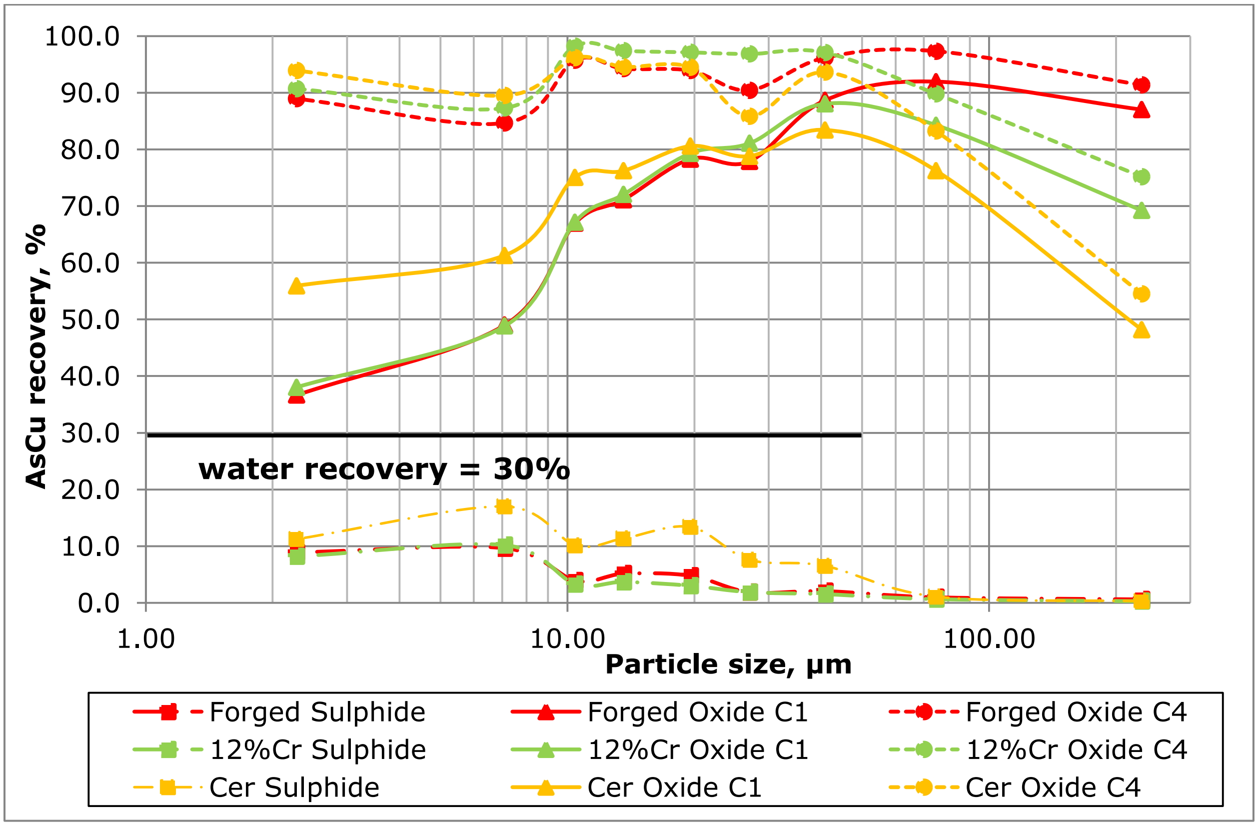

Figure 41 Cumulative acid soluble copper by size recovery after the sulphide flotation stage, showing the first and the fourth (i.e. total) concentrate of the oxide flotation, mixed ore. The oxide flotation total water recovery is also indicated.

The recovery versus size curves show typical behaviour, with higher recoveries for the intermediate (-40/+10 micron) size fractions and decreases for the fine (-10 micron) and coarse (+40 micron) ends of the size spectrum. The data in Figure 41 shows that during the sulphide flotation stage, higher oxide recoveries were observed with ceramic media through most of the size spectrum, except for the particles coarser than 70 microns. During the oxide stage, similar observations to that made for the oxide ore (Section 5.2.4.4.3) can be made. That is, the fine particles (<10 microns) show better recoveries with ceramic media and the coarse particles (>40 microns) had higher recoveries with forged steel media.

These differences are particularly marked after the first oxide concentrate while overall (after C4), the differences subsist principally on the coarser end of the size spectrum. As explained for the oxide synthetic ore (Section 5.2.4.4.3), this clearly indicates differences of sulphidisation intensity between the various media tested.

Similar observations can be made for insoluble and total copper in Figure 102 and Figure 103 in Appendix 5.4.3. However the intensity of the differences observed between the various media tested at both ends of the size spectrum are different. For the sulphide fraction (AiCu), to the contrary of the oxide profile, the most accentuated difference between the media is found in the fine end of the spectrum (<10 micron) with ceramic media showing the best results, while on the coarser end (>40 micron), the differences are minor. Overall (Cu), the sulphide and oxide fractions compensate each other, so the differences still exist but are less pronounced, with ceramic media producing the highest recovery in the fine end size of the spectrum and forged steel media in the coarser end.

The analysis by size of the mixed ore flotation revealed that different media produced better flotation performances in different areas of the size spectrum (fine end for ceramic and coarse end for forged steel). This indicates that if it was possible to combine the best of both systems (by manipulating the chemistry), it should be possible to improve the overall flotation performances of the mixed ore.

5.2.5.5. Discussion

Once again with the mixed system, differences in flotation response of the ore have been observed with the different grinding media tested. These are attributed to variations in pulp chemistry through the entire grinding and flotation process, affecting both the sulphide and oxide flotation stages.

The need of recording accurately the Eh-pH conditions during the sulphidisation process has been mentioned previously. For these experiments, the parameters were recorded and are plotted in Figure 42. This shows the Eh-pH conditions as a function of time during the NaHS+PAX conditioning with the different media tested. The data indicates that the Eh drops more slowly with forged steel media than any other media. This is probably an indication of the slower oxidation rate of the sulphide species. Another main difference is the higher Eh observed with ceramic media at the end of NaHS conditioning. When putting these data in parallel with the Eh-pH diagram for sulphidisation (the parameters used to build the diagram can be found in Appendix 5.4.4), Figure 104 in Appendix 5.4.4 and Figure 43 show interesting information. As explained in the literature review, this is a dynamic system and the boundaries of the Cu-S-H_20 system evolve as the oxidation state of the sulphide species increases. At the start of the sulphidisation process, the sulphides oxidation state (from NaHS) is –II only and the stability region of the system should be close to that of Figure 104 in Appendix 5.4.4. When superimposing the Eh-pH data recorded during sulphidisation on that chart, the data (green circle) shows that the Eh-pH conditions are suitable for the formation of a copper sulphide on the malachite surface. However, as the oxidation state of the sulphide species increase, the boundaries of the Eh-pH diagram evolved to reach the profile presented in Figure 43 when all sulphide have reached their highest oxidation state. In Figure 43, it can be seen that the Eh-pH conditions recorded during sulphidisation are not suitable anymore for the formation of a copper sulphide but tend to produce copper oxide species.

Therefore, one of the hypotheses made to explain why oxidative conditions (with ceramic media) give lower oxide flotation response than that obtained with forged steel media (for which the conditions are more reductive) is that the Cu-S-H_20 system evolved more quickly from Figure 104 in Appendix 5.4.4 to Figure 43, preventing the formation of a sufficient copper sulphide layer on the malachite surface.

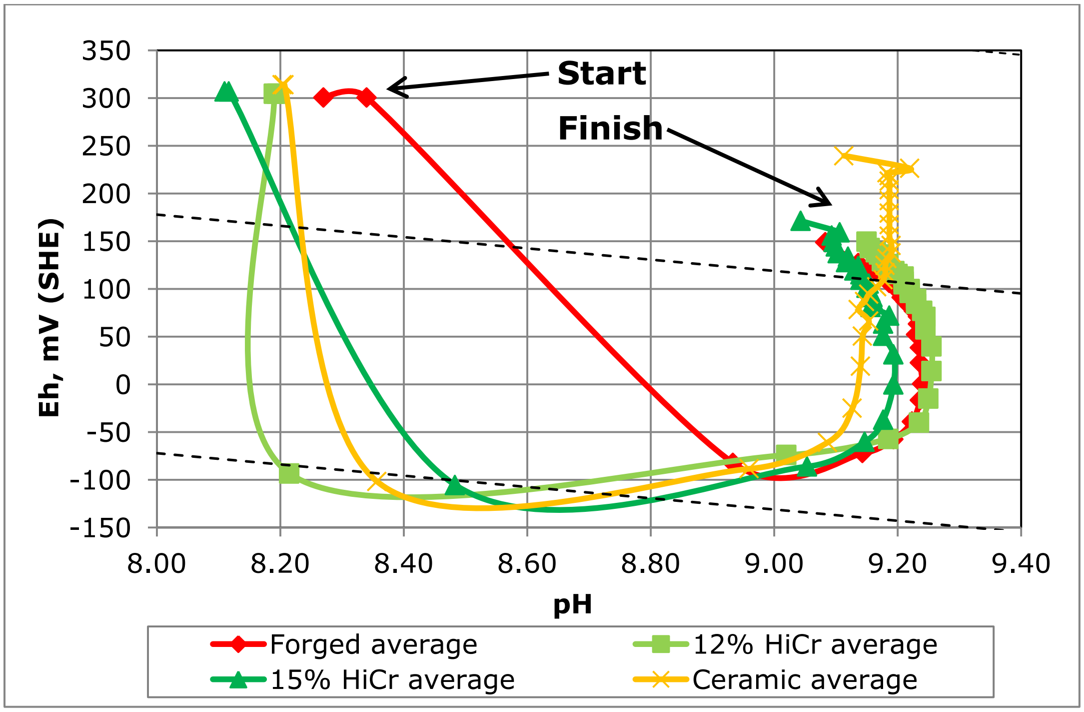

Figure 42: Eh-pH diagram during NaHS conditioning (slug addition) as a function of time (5 seconds between each point recorded).

To validate this hypothesis, an analysis of the sulphide chemistry in the liquid phase of the pulp after NaHS conditioning (at en E_s of -360 mV) has been performed by capillary electrophoresis. This technique allows the detection of the presence of sulphates and thiosulphates in the liquid phase. A detailed explanation of the results can be found in Appendix 5.4.5. The results are presented in Table 30**Error! Reference source not found.**. They show that when the conditions are more oxidative (with ceramic media), a higher quantity of SO_4^{2-} and $S_2O_3^{2-}$ are formed at equivalent E_s which suggests that sulphides oxidation is quicker in such systems and that the Cu-S-H_2O system evolved more quickly from Figure 104 in Appendix 5.4.4 to Figure 43, preventing good sulphidisation of the malachite (demonstrated by the lower flotation of coarse malachite particles with ceramic media).

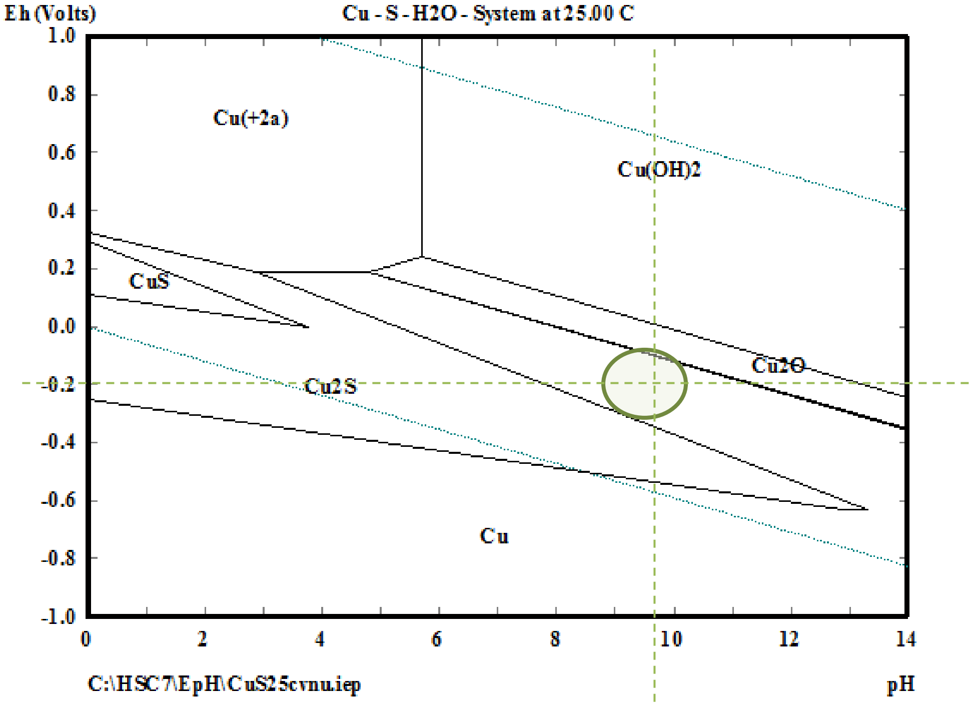

Figure 43: Eh-pH diagram for the Cu-S-H_2O system. [Cu]=10^{-6} M and [S]=10 E^{-11} M. Sulphur oxidation state: -II to +VI. Green circle corresponds to the Eh-pH window measured during the sulphidisation stage. Blue lines correspond to water dissociation limits (HSC chemistry 2013).

Table 30: sulphates and thiosulphates concentration in the pulp determine by capillary electrophoresis.

Media	SO_4^{2-}, mg/l	$S_2O_3^{2-}$, peak area**
Water	3.2	-
Forged	7.3	109
Ceramic	8.4	146

**for $S_2O_3^{2-}$, only the comparison of the peak areas is possible as the device was not calibrated to give exact quantification of that specie.

It is important to note that to a certain extent, rapidly oxidising the sulphide species can be beneficial for oxide flotation by removing more quickly the excess sulphide species (detrimental for flotation) present in the pulp at the end of the sulphidisation stage. This is why it is most probable that an optimum chemistry exists between the very reductive forged steel system and the very oxidative ceramic system (perhaps being high chrome media) which should provide the best flotation response of the oxide minerals.

5.2.6. Improving oxide flotation

The flotation experiments and more particularly the size by size recovery data suggest that by combining the best of the ceramic and the forged steel results, it should be possible to increase the overall copper recovery. In this section, several attempts were made to try to improve the mixed flotation results by manipulating the chemistry of the pulp by various means. These are presented here after.

5.2.6.1. Extra NaHS

The first method tested was to increase the NaHS addition with high chrome and ceramic media to counteract NaHS oxidation in the more oxidative conditions. Two NaHS dosages were tested for 12% high chrome and ceramic media. A summary of the dosages used and the corresponding time required for the E_s to go back to -360 mV are presented in Table 31.

The data indicate that a small increase of NaHS dosage does not have an impact on the Es kinetics while a larger NaHS increase (+20% with 12% high chrome and +50% with ceramic media) slow down the Es increase. The effect of higher NaHS dosage is also clear in the chemistry data (E_s, Eh, DO, pH, Eh-pH) presented in Appendix 5.4.6. These show that adding more NaHS produces more reductive conditions which most probably slows down sulphide oxidation and keep the Eh-pH conditions in a suitable Eh-pH window for the formation of copper sulphides for longer.

Table 31: NaHS dosage and E_s kinetics (time required for the pulp to reach an E_s= -360 mV (mineralised froth)) with 12% HiCr and ceramic media.

Media	NaHS, ml	Time (seconds)
Forged	10	105
12% HiCr	**10**	**100**
	10.8	95
	12	110
Ceramic	**10**	**65**
	13.4	65
	15	85

In terms of flotation, the first ordered maximum recoveries and flotation rate constant in Table 32 and the acid soluble copper grade-recovery curves in Figure 44 show that when increasing the NaHS dosage, the metallurgical performance increases. That is, with ceramic media, the maximum AsCu recoveries increases from 90 percent at normal dosage (10 ml,

Table 27 in Section 5.2.5.4.2) to 90.5 percent with the stronger NaHS dosage, and the flotation kinetics also increase from 2.9 to 3.8 min^{-1}.

This indicates that it is possible to increase the oxide flotation with high chrome and ceramic media by adding extra NaHS.

Table 32: Effect of higher NaHS dosages on oxide flotation maximum recovery and flotation rate constant with respect to oxide flotation feed for the various grinding media tested, synthetic mixed ore.

Media	NaHS, ml	Cu		AiCu		AsCu		SiO2,
		R_{max},%	K,min^{-1}	R_{max},%	K,min^{-1}	R_{max},%	K,min^{-1}	R_{max}%
12%Cr	10.8	88.1	3.8	62.1	2.7	90.4	3.7	1.2
12%Cr	12	91.3	4.1	64.5	2.3	93.4	4.2	1.7
Ceramic	13.4	92.0	3.5	79.6	2.6	90.0	3.5	1.6
Ceramic	15	91.7	3.7	80.4	2.8	90.5	3.8	1.7

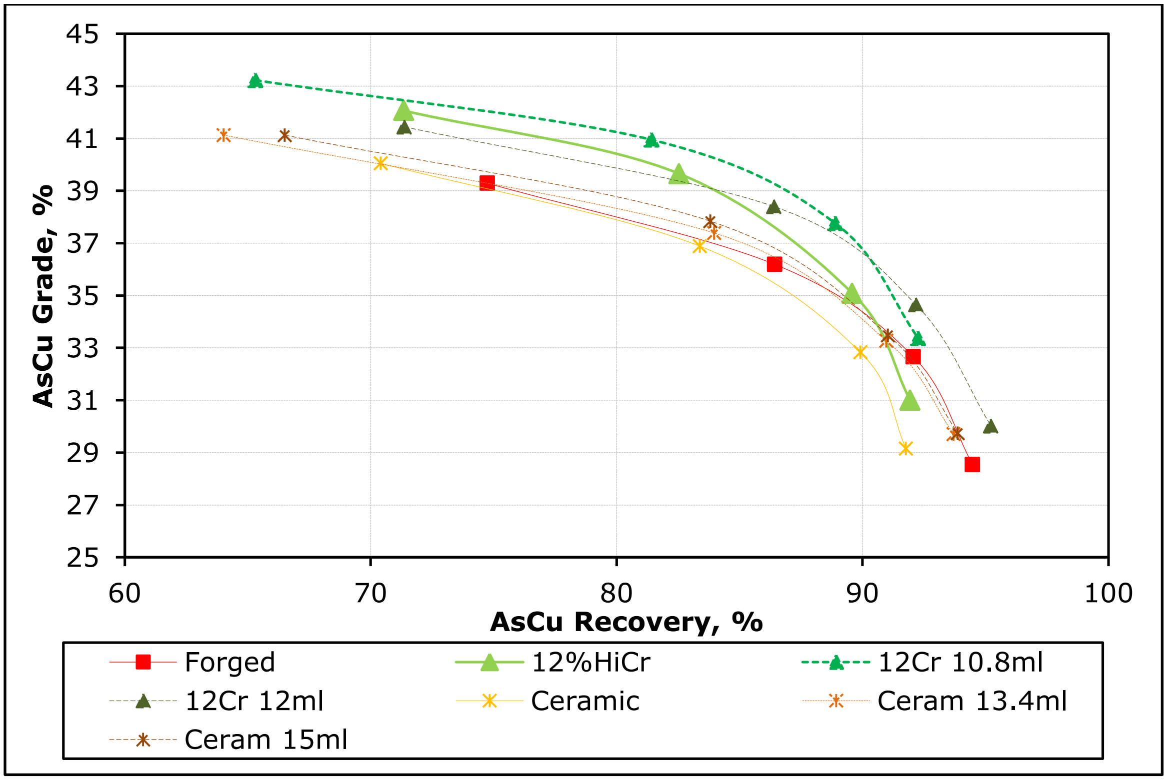

Figure 44: Effect of various NaHS addition on the AsCu grade-recovery curves for the oxide flotation stage with respect to oxide flotation feed for a synthetic ore ground with several grinding media. Different flotation times were used for the first concentrate (C1): 30’’ for standard conditions and 20’’.at higher NaHS dosages. The flotation time of the second concentrate was adjusted to maintain the cumulative flotation time equal for all conditions.

5.2.6.2. *Effect of ferrous iron sulphate*

The influence of ferrous iron sulphate, a reducing agent, was tested to try to extend the time during which the pulp chemistry matches the Eh-pH window suitable for sulphidisation. It was expected that the addition of iron sulphate should consume the dissolved oxygen in the pulp and decrease the pulp potential. In addition to this, the presence of ferrous iron in solution could lead to the precipitation of iron sulphides and possibly increase the sulphide coverage of the malachite. Two $FeSO_4$ dosages were tested: 0.14 g and 0.014 g, which correspond to an iron molar concentration of 10^{-4} and 10^{-5} M in the pulp, respectively. The tests were carried out with forged steel and ceramic media. The NaHS dosage was kept similar to the baseline.

The pulp chemistry profiles (E_s, Eh, DO and Eh-pH) during NaHS conditioning (i.e. sulphidisation) are presented in Appendix 5.4.7. The pulp chemistry at the oxide flotation feed (at the end of the conditioning stage) is on display in Table 33.

Table 33: Effect of $FeSO_4$ addition on pulp chemistry at the oxide flotation feed for a synthetic mixed ore ground with different grinding media.

Media	$FeSO_4$, g	pH	Eh, mV (SHE)	DO, ppm	T°C
Forged	0	9.2	118	7.4	28.2
Forged	0.014	9.4	100	7.4	25.5
Forged	0.14	9.2	94	7.3	26.2
Ceramic	0	9.2	213	7.8	28.0
Ceramic	0.014	9.5	187	7.5	26.0
Ceramic	0.14	9.2	150	7.5	26.4

The data in Appendix 5.4.7 and Table 33 show that the conditions are more reductive when ferrous iron sulphate was added. That this, Table 33 shows lower Eh and lower DO content of the pulp at the end of the NaHS conditioning. For the DO, the profiles in Figure 114 in Appendix 5.4.7 clearly show lower DO values through the NaHS conditioning stage when $FeSO_4$ was added.

In terms of flotation results, the first order kinetics data in Table 34 and the acid soluble copper grade recovery curve in Figure 45 reveal that extra oxide recovery can be obtained with the addition of ferrous iron sulphates, especially at high dosage with ceramic media. That is, the oxide modelled maximum recovery increased from 90 percent (baseline, no iron sulphate, Table 27 in Section 5.2.5.4.2) to 93 percent when 0.14 g of iron sulphate was added with ceramic media. However Figure 45 show that despite this, it was not possible to improve upon the oxide recovery obtained with forged steel media.

Table 34: Effect of $FeSO_4$ addition on oxide flotation maximum recovery and flotation rate constant with respect to oxide flotation feed for the various grinding media tested, synthetic mixed ore.

Media	$FeSO_4$, g	Cu		AiCu		AsCu		SiO_2,
		R_{max},%	K,min^{-1}	R_{max},%	K,min^{-1}	R_{max},%	K,min^{-1}	R_{max}%
Forged	0.014	90.8	3.7	66.1	2.2	92.8	3.8	2.1
Forged	0.14	90.9	3.7	62.6	1.9	92.4	3.8	1.9
Ceramic	0.014	88.4	4.0	64.2	2.0	89.2	4.1	1.9
Ceramic	0.14	90.1	4.0	77.4	2.8	93.0	4.0	1.8

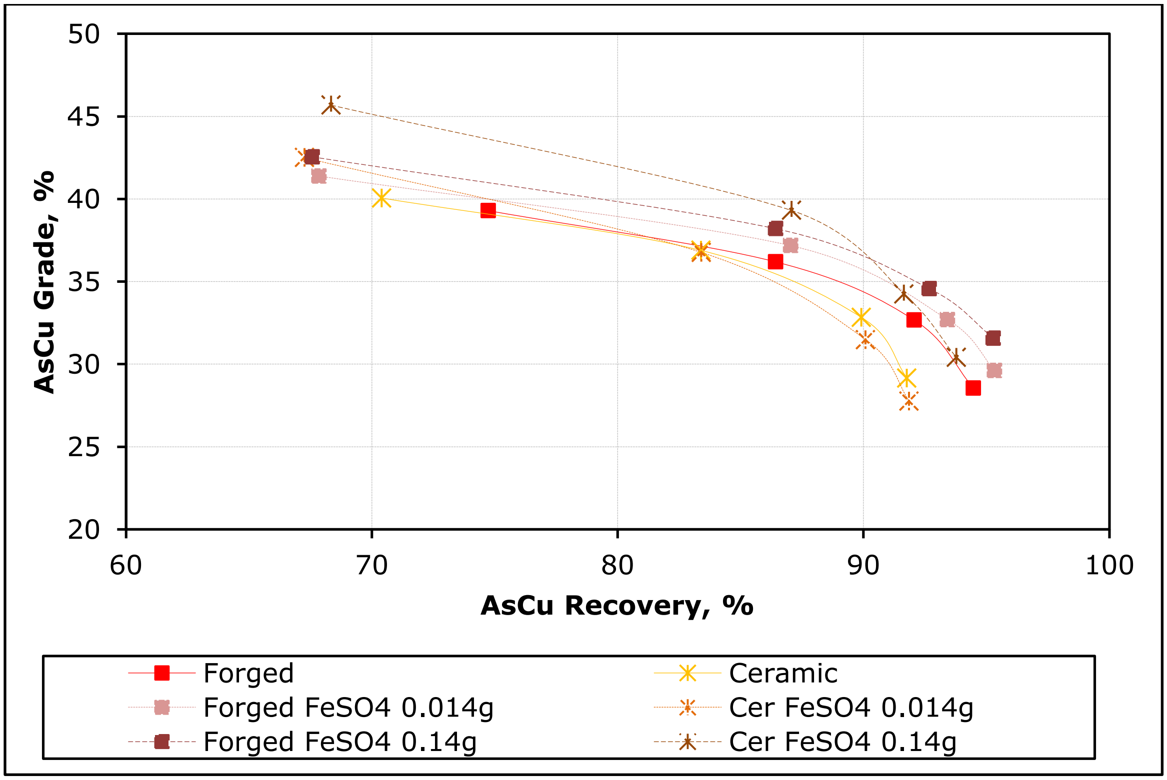

Figure 45 Effect of $FeSO_4$ addition on the AsCu grade-recovery curve for the oxide flotation stage (with respect to oxide flotation feed) for a synthetic ore ground with several grinding media. Different flotation times were used for the first concentrate (C1): 30'' at standard conditions and 20'' at higher NaHS dosages. The flotation time of the second concentrate was adjusted to maintain the cumulative flotation time equal for all conditions.

5.2.6.3. N_2 purging

Another way that was tested to try to limit the NaHS oxidation and keep the Eh-pH conditions as long as possible in a suitable window for sulphidisation was to purge the pulp with nitrogen prior to NaHS addition. Two dissolved oxygen values were targeted. Therefore the pulp was purged with nitrogen prior to NaHS addition to reach dissolved oxygen values of either 5.5 ppm or 2.5 ppm while using ceramic media.

The E_s, Eh, DO and Eh-pH profiles are presented in Appendix 5.4.8. The chemistry data reveals that there was no significant impact of N_2 purging on the E_s kinetics (Figure 116 in Appendix 5.4.8.). Figure 118 in Appendix 5.4.8 shows that the level of dissolved oxygen in the pulp during the NaHS conditioning stage was much lower at the start of conditioning when N_2 was added but increased quickly, probably because of pulp agitation and air ingression, to come back to a similar level to that obtained without nitrogen purging. This could be beneficial for the sulphidisation mechanism by having low and very reductive conditions when the NaHS is first added and more oxidative conditions at the end to oxidise the remaining excess sulphide species present.

The oxide flotation results are presented in Figure 46 and the first order kinetics data in Table 35. Figure 46 shows superior grade-recovery curves for ceramic media when the ore was purged with nitrogen prior to flotation. That is the maximum AsCu recovery increased from 90.3 for the baseline (Table 27 in Section 5.2.5.4.2) to 91 percent with nitrogen purging. However, despite the increase, it was not possible to reach the recovery obtained with forged steel media.

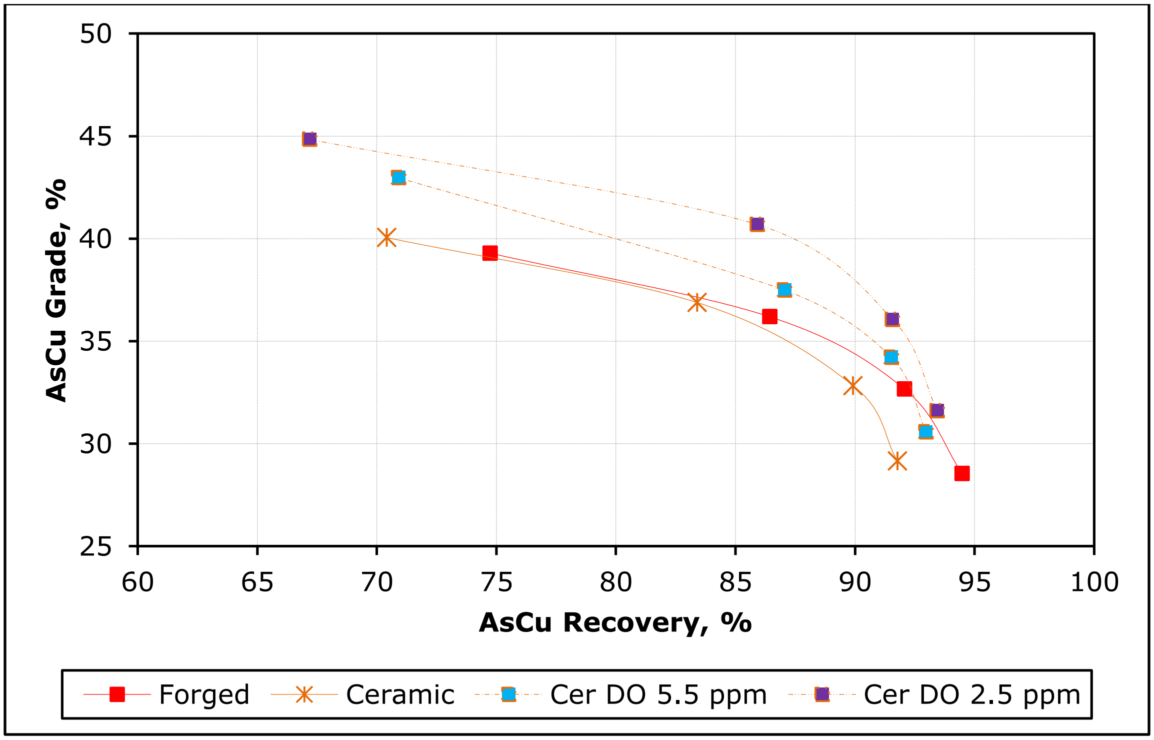

Figure 46: Effect of N_2 purging on the AsCu grade-recovery curve for the oxide flotation stage (with respect to oxide flotation feed) of the synthetic mixed ore ground with ceramic media. Different flotation times were used for the first concentrate (C1): 30'' for standard conditions and 20'' at higher NaHS dosages. The flotation time of the second concentrate was adjusted to maintain the cumulative flotation equal for all conditions.

Table 35: Effect of N_2 purging on oxide flotation maximum recovery and flotation rate constant with respect to oxide flotation feed of the synthetic ore ground with ceramic media.

Media	**N_2 purging to, ppm**	**Cu**		**AiCu**		**AsCu**		**SiO_2, R_{max}%**
		R_{max},%	**K,min^{-1}**	**R_{max},%**	**K,min^{-1}**	**R_{max},%**	**K,min^{-1}**	
Ceramic	5.5	89.5	4.4	60.7	3.2	91.0	4.5	1.8
	2.5	89.4	3.9	55.5	1.9	91.1	3.9	1.5

5.2.6.4. Discussion

These experiments showed that with the methods tested (extra NaHS, addition of ferrous iron sulphate and nitrogen purging), it was possible to manipulate the pulp chemistry to various degrees. A study of the flotation results indicates that when the pulp chemistry was shifted strongly enough to more reducing conditions, the sulphidisation mechanism was most probably improved and malachite flotation better.

The key seems to be to limit the oxidation of the NaHS during the sulphidisation stage, thus adding more NaHS created more reductive conditions and gave more sulphide species available for the sulphidisation reaction. This resulted in superior flotation performance of the high chrome media compared with that obtained with forged steel media.. The two other solutions tested involved introducing a reducing agent into the pulp prior to sulphidisation to reduce the Eh, and to scavenge the dissolved oxygen from the pulp prior to NaHS introduction. Both methods seem encouraging and show improvement of the oxide copper recovery but were not able to reach the results obtained with forged steel media. It is clear that more testing is required to evaluate more accurately the potential of each method tested and encounter the optimal condition.

5.2.7. Conclusions

In this section, 3 series of tests on 3 different synthetic ore samples, gradually more complex, has have demonstrated that in each case, the type of grinding media and the resulting pulp chemistry affects the sulphidisation and flotation process of both the oxide and sulphide minerals. This occured even when the chemistry differences recorded were small.

It was quickly clear that some clarification and a better understanding of the sulphidisation mechanism was necessary. With the help of surface analysis (XPS), it has been demonstrated that redox reactions involving copper reduction (most probably) coupled with sulphide oxidation were taking place during the sulphidisation mechanism. The complex and various roles of the sulphides were also approached. Another interesting finding of the XPS surface analysis was the very little quantity of sulphur present at the malachite surface after sulphidisation with less than 5 percent of the malachite surface coved by sulphur.

The requirement for accurate and continuous pulp chemistry monitoring was found to be necessary to highlight the chemistry differences between the various media tested during the sulphidisation process. Therefore between the first set of tests on bulk malachite ore, and the last one on the mixed synthetic ore, the pulp chemistry methodology and measurement was improved and parameters such as the kinetics of E_s increase back to -360 mV were measured, to highlight the variation of NaHS consumption with the variations of pulp chemistry.

With the help of thermodynamics, the dynamics of the system were taken into account and the evolution over time of the stability region of the copper sulphide in the Eh-pH diagram as the sulphide species become more oxidised (something not exposed in the literature), was determined. Then, it was demonstrated that the too oxidative environment created by the ceramic media was accelerating sulphide oxidation, thereby quickly shifting the pulp chemistry conditions out of the stability region suitable for copper sulphide formation, preventing optimum sulphidisation of the malachite. Capillary electrophoresis confirmed this hypothesis by measuring higher quantity of sulphate and thiosulphate ions present in the case of ceramic media. This theory was used to explain why oxide recovery was lower in the case of ceramic than forged steel media.

Finally, the study of the mixed system revealed that the optimum chemistry conditions were not the same for the recovery of the sulphide and oxide minerals. While the chemistry produced by high chrome media was optimum for sulphide flotation, the sulphidisation and oxide flotation stage required more reductive conditions such as that generated with forged steel media. Size by size recovery was used to highlight the difference in flotation behaviour between the sulphide and oxide flotation stages with the various grinding media tested. It was clear from this study that by combining the best results of each flotation stage, the overall flotation performances should be able to be improved. To that end, extra tests were carried out to modify the oxidative pulp chemistry obtained with high chrome media (which produced the best sulphide flotation performance) to try to improve the sulphidisation process and subsequent oxide flotation. Some of the techniques tested show promising results. However, more tests are required to evaluate more accurately the potential of each method evaluated and encounter the optimal condition.

VI. CONCLUSIONS

The recovery of copper by sulphidisation and flotation from a mixed ore has been studied in detail in this thesis. Particular focus was given to the effect of pulp chemistry on the sulphidisation mechanism and subsequent flotation response of oxidised sulphide minerals, both of which are not prevalent in the literature.

An important experimental work was completed to study the problem during which the mixed system was simplified. The effect of pulp chemistry on oxidised copper sulphide minerals and copper oxide minerals were first studied separately before examining a mixed system.

The work completed on the oxidised sulphide mineral revealed that grinding pulp chemistry affects the flotation performance of the ore for each oxidation degree tested. For the majority of the oxidation states, oxidative pulp chemistry, delivered by electrochemically inert grinding media (such as high chrome media), resulted in better flotation performance and better selectivity of chalcopyrite against pyrite. At the start of the oxidation period, weak ore oxidation resulted in strong pyrite activation regardless of the pulp chemistry generated during grinding. At the end, when the ore was heavily oxidised (after 16 months of artificial oxidation), all grinding media tested generated similar pulp chemistry and flotation performances of the ore, suggesting that when sulphide minerals are strongly oxidised, less galvanic interactions occur during grinding.

The experiments conducted on two synthetic oxide ores (pure malachite and a mixture of malachite and quartz) demonstrated that while oxide minerals are not as electrochemically active as sulphide minerals, different electrochemically active grinding media still generated different pulp chemistry and flotation performances of the ore. It was hence suspected that changing pulp chemistry affected the sulphidisation mechanism of the malachite.

Looking in more detail at the sulphidisation mechanism fundamentals, a study of the thermodynamics of the process combined with a sensitivity analysis of the surface (XPS technique) revealed that redox reactions involving copper reduction and sulphide oxidation were taking place during the sulphidisation process. The complex and various roles of the sulphidising agent were determined. Optimal pulp chemistry conditions for adequate sulphidisation of the malachite were also identified. These showed that when too oxidative conditions were created during grinding, in addition to a higher oxidation rate of the sulphidising agent (a sulphide salt), the pulp chemical conditions were quickly moving out of the optimal Eh-pH range for the formation of copper sulphide species, not allowing the formation of a sufficient sulphide layer at the malachite surface, negatively impacting malachite recovery.

Finally, the experimental work conducted on the mixed synthetic ore indicated that the optimum pulp chemistry conditions were different for the recovery of the sulphide and oxide minerals. While oxidative conditions were required for optimum sulphide flotation, reductive conditions were more adequate for oxide minerals. This means that the optimal grinding media for sulphide and oxide flotation are different. Size by size recovery was used to highlight these differences. From these observations, it was clear that by combining the best of the of the sulphide and oxide systems, the overall flotation performance of the ore could be noticeably improved. Various techniques were tested to try to manipulate the pulp chemistry to improve the oxide flotation performance under oxidative conditions, suitable for the sulphide flotation stage. Some of these techniques showed promising results.

In all instances, this study has revealed the importance of delivering the right grinding chemistry conditions to obtain the best flotation performance of a mixed ore.

VII. PERSPECTIVES AND FUTURE WORK

An important number of experimental works have been completed in this thesis. All experiments were completed on a simplified system: oxidised sulphide minerals were artificially oxidised, and the oxide and mixed ores were artificially created by mixing various proportions of chalcopyrite, malachite and quartz. It is clear that experiments on a real mixed ore should be conducted. To that end, a sampling campaign of various mixed ore was completed at the Kanasanshi mine in Zambia at the start of the thesis. However, insufficient time did not allow the testing of these ores as part of this thesis. Industrial validation of the theories developed in this thesis would be a plus.

Artificial oxidation of the sulphide minerals proved to be efficient with a strong decrease in copper flotation performance with oxidation time. However the phenomena taking place in the column has not been studied, nor was a characterisation of the oxidised sulphide minerals undertaken. This should also be completed. It is important to note that some XPS surface analyses of the oxidised sulphide minerals were conducted to that aim. Unfortunately, for some reason, the spectra produced were not usable and no interpretation could be made.

Finally, various techniques were used to try to manipulate the oxidative pulp chemistry produced by high chrome and ceramic media to improve oxide sulphidisation and flotation under those conditions. The results are promising but more tests are required to find and develop the most appropriate technique giving the best flotation performance of the ore.

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