

The mineralogy of pyrrhotite from the Sudbury CCN and Phoenix nickel ores and its effect on flotation performance

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The non-stoichiometric sulfide pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), common to many nickel ores, occurs in a variety of crystallographic forms and compositions. In order to manipulate its performance in nickel processing operations either to target the recovery or rejection of pyrrhotite, one needs an understanding of pyrrhotite mineralogy, reactivity and the effect this may have on its flotation performance. In this study, a non-magnetic Fe_9S_{10} pyrrhotite from Sudbury CCN in Canada and a magnetic Fe_7S_8 pyrrhotite from Phoenix in Botswana were selected to explore the relationship between mineralogy, reactivity and microflotation. Non-magnetic Sudbury pyrrhotite was less reactive in terms of its oxygen uptake and showed the best collectorless flotation recovery. Magnetic Phoenix pyrrhotite was more reactive and showed poor collectorless flotation, which was significantly improved with the addition of xanthate and copper activation. These differences in reactivity and flotation performance are interpreted to

be a result of the pyrrhotite mineralogy, the implications of which may aid in the manipulation of flotation performance.

Keywords: pyrrhotite, mineralogy, oxidation, reactivity and sulfide flotation

INTRODUCTION

Pyrrhotite $\text{Fe}_{(1-x)}\text{S}$ is one of the most commonly occurring metal sulfide minerals and is recognised in a variety of ore deposits including nickel-copper, lead-zinc, and platinum group element. Since the principal nickel ore mineral, pentlandite, almost ubiquitously occurs coexisting with pyrrhotite, the understanding of the behaviour of pyrrhotite during flotation is of fundamental interest. For many nickel processing operations, pyrrhotite is rejected to the tailings in order to control circuit throughput and concentrate grade and thereby reduce excess sulfur dioxide smelter emissions, e.g. Sudbury [1]. However, for some nickel processing operations, pyrrhotite recovery is targeted due to the abundant fine grained pentlandite locked in pyrrhotite, e.g. Phoenix pyrrhotite at Tati Nickel Mine. Therefore, the ability to manipulate pyrrhotite performance in flotation is of great importance. It can be best achieved if the mineralogical characteristics of the pyrrhotite being processed can be measured and the relationship between mineralogy and flotation performance is understood.

The pyrrhotite mineral group is non-stoichiometric and has the generic formula of $\text{Fe}_{(1-x)}\text{S}$ where $0 \leq x < 0.125$. Pyrrhotite is based on the nickeline (NiAs) structure and is comprised of several superstructures owing to the presence and ordering of vacancies within its structure. Numerous pyrrhotite superstructures have been recognised in the literature, but only three of them are naturally occurring at ambient conditions [2, 3]. This includes the stoichiometric FeS known as troilite which is generally found in extraterrestrial localities, but on occasion, has also been recognised in some nickel deposits. The commonly occurring magnetic pyrrhotite is correctly known as 4C pyrrhotite, has an ideal composition Fe_7S_8 and monoclinic crystallography [4]. Non-magnetic pyrrhotite is formally described as NC pyrrhotite where N is an integer between 5 and 11 [5]. Non-magnetic NC pyrrhotite has a range of ideal compositions varying from Fe_9S_{10} , $\text{Fe}_{10}\text{S}_{11}$ to the least iron deficient composition of $\text{Fe}_{11}\text{S}_{12}$. Although NC pyrrhotite is generally known as “hexagonal pyrrhotite”, it has been argued to be pseudo-hexagonal and may actually be monoclinic or orthorhombic [5-8]. On the basis of this discrepancy in pyrrhotite crystallography, the terminology magnetic and non-magnetic pyrrhotite is preferentially used in this study.

Pyrrhotite is known to be a reactive mineral which is highly prone to oxidation [9, 10] and which can be detrimental to flotation [11]. During flotation, the propensity of pyrrhotite for oxidation may sometimes be reflected by near zero dissolved oxygen concentrations within the pulp phase [12, 13]. In general, there appears to be a lack of consensus in the literature as to whether magnetic or non-magnetic pyrrhotite is more reactive, although magnetic monoclinic pyrrhotite is more frequently attributed to be the more reactive phase towards oxidation [14-16]. Accounts in the literature with respect to the flotation behaviour of magnetic and non-magnetic pyrrhotite are similarly somewhat contradictory. According to Iwasaki [17] it was noted by Harada [18] that samples of freshly ground monoclinic pyrrhotite were more floatable than “hexagonal” pyrrhotite, although the reverse occurred on more oxidised samples. Although Alekseeva [19] showed an increase in surface oxidation with decreasing Fe/S ratio, the depression of pyrrhotite was unaffected. Kalahdoozan [20] showed that synthetic “hexagonal” pyrrhotite exhibited better xanthate adsorption and flotation recovery at a higher pH (≥ 10), whereas at a lower pH (7 - 8.5) monoclinic pyrrhotite was more floatable. Using pyrrhotite samples derived from the Mengzi lead zinc ore deposit, He *et al.* [21] also showed that monoclinic pyrrhotite was more floatable than “hexagonal” pyrrhotite. Others such as Lawson *et al.* [22] and Wiese *et al.* [23] have demonstrated that differences in flotation performance between different pyrrhotite types exist. Lawson *et al.* [22] showed a difference in pyrrhotite recovery between non-magnetic and magnetic circuits of the Sudbury ore where pyrrhotite depression was targeted. Similarly, results of batch flotation tests performed on Bushveld Merensky Reef ores by Wiese *et al.* [23] have shown that the recovery of pyrrhotite from Merensky Reef ore from one location was greatly increased when copper sulfate was used as an activator during flotation, whereas for ore from another location the effect of copper sulfate addition on pyrrhotite recovery was minor. It is probable that these differences in recovery may have been due to the differences in pyrrhotite mineralogy.

The field of process mineralogy aims to assist in addressing problems in metallurgy with the use of applied mineralogy, thereby using an interdisciplinary approach from the traditionally discrete fields of geology and metallurgy. Various authors [24-27] have shown the benefit achieved on a range of operations when a complete geological and mineralogical characterisation of the ore was undertaken in conjunction with experimental tests to determine its metallurgical performance. This suggests that in order to be able to successfully

optimise the behaviour of an ore during flotation, a comprehensive understanding of its mineralogy and relationship to flotation behaviour is needed. It is probable that the lack of agreement in studies comparing the effects of pyrrhotite mineralogy and reactivity on flotation performance have been due to the fact that only limited aspects of the pyrrhotite mineralogy were examined.

The objective of this paper is therefore to characterise the mineralogy of the pyrrhotite samples, determine their oxygen demand and flotation performance and explore the relationship between these three areas in order to show how the use of an integrated approach can assist in understanding the effect of mineralogy on flotation performance. Some final implications towards processing routes of magnetic and non-magnetic pyrrhotite types will also be given.

EXPERIMENTAL DETAILS

Pyrrhotite samples in this study were sourced from the 100 ore body at the Sudbury Copper Cliff North (CCN) mine in Canada by Vale INCO personnel and by handpicking pyrrhotite from the massive sulfide veins in the open pit at the Tati Phoenix mine in Botswana. A summary of the key mineralogical characteristics of the pyrrhotite samples used in this study is given in table 1. A standard optical microscopy examination of the pyrrhotite samples was performed with the use of the magnetic colloid method described in Craig and Vaughan (1981) in order to differentiate between magnetic and non-magnetic pyrrhotite. Pyrrhotite compositions were analysed on a Jeol JXA 8100 Superprobe housed at the University of Cape Town and further details of the analysis conditions used are given in Becker *et al.* [28]. Quantitative determination of the proportions of the different mineral phases present in the microflotation feed samples was obtained using MLA for which the results are given in table 2. MLA analyses were performed by Vale INCO Technical services in Toronto on a JEOL 6400 SEM fitted with two energy dispersive EDAX Si(Li) spectrometers with digital pulse processors. Measurements were run using the GXMAP routine at 0.77 μm pixel spacing so that the liberation characteristics of pyrrhotite could also be investigated.

Experimental tests were carried out using pyrrhotite which was ground with a ring mill and then dry screened to the desired size fraction of 53 to 106 μm . Pyrrhotite samples were split and then stored in a freezer until needed for the test work programme. BET surface area measurements of pyrrhotite samples were obtained on a Micrometrics Tristar 3000 unit with nitrogen adsorption to ensure that the surface area of all the pyrrhotite samples was less than 0.35 $\text{m}^2\cdot\text{g}^{-1}$. Oxygen uptake measurements were quantified by the Reactivity Number (RN), using the Linde/Afrox OSCAR device. A schematic of the experimental set up is illustrated in figure 1. A slurry of pyrrhotite was oxygenated with pure oxygen for 10s according to the specifications in table 3, and the decay of dissolved oxygen (DO) then measured. The reactivity number calculated by OSCAR is derived from the first order rate constant of an exponential curve fitted to a graph of dissolved oxygen concentration versus time [29]. Microflotation tests were conducted using the UCT microfloat cell as developed and described by Bradshaw and O'Connor [30] using the procedure given in table 4. Reagent concentrations for both sets of test work were adjusted accordingly to account for the sulfide content of the feed sample as given in table 2. Sodium n-propyl xanthate (SNPX) collector

was supplied by SENMIN, Sty 504 guar from Chemquest and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from Merck. Mineral concentrates were collected after 2, 5, 10 and 15 minutes of flotation, filtered and dried for further analysis. Although iron, nickel and sulfur assays were obtained using atomic absorption spectroscopy and a Leco sulfur analyser, final mass recovery was determined to be the best measure of pyrrhotite recovery from the microflotation test due to the fact that some concentrate masses were too small for assay, and sometimes anomalous calculated pyrrhotite recoveries were obtained (since no allowance for nickel hosted by pyrrhotite could be made).

RESULTS

Pyrrhotite Characterisation

Both the Sudbury CCN and Phoenix pyrrhotite samples examined in this study were derived from sulfide ores at operating nickel mines (Table 1). Therefore, it is not only of interest to examine the mineralogy of pyrrhotite, but also to determine the relationship between pyrrhotite and pentlandite (Figure 2). Based on calculations of the average metal to sulfur ratio determined from electron microprobe analyses, the composition of the Sudbury CCN pyrrhotite was determined to be close to Fe_9S_{10} , and the Phoenix pyrrhotite to be close to Fe_7S_8 (Table 1). This corresponds with the classification of Sudbury CCN pyrrhotite as non-magnetic NC pyrrhotite and Phoenix as magnetic 4C pyrrhotite [8, 31].

In general, pyrrhotite occurs as large (up to 2 mm), well developed grains that form a matrix which hosts other sulfide minerals, primarily pentlandite and chalcopyrite (Figure 2 a-d). Application of the magnetic colloid onto the pyrrhotite samples revealed that the Sudbury CCN pyrrhotite was non-magnetic (Figure 2b) in agreement with the mineral chemistry determination. On occasion, very fine grained magnetic pyrrhotite occurs as rims surrounding pentlandite grains, an exsolution feature related to the monosulfide solid solution from which pyrrhotite and pentlandite form [32]. The presence of magnetic pyrrhotite is by no means volumetrically abundant and constituted less than 1% of the sample. It should be noted that this is a particular characteristic of pyrrhotite derived from the 100 ore body at Copper Cliff North, since magnetic pyrrhotite is generally common in the Sudbury ore [33]. Application of the magnetic colloid onto the Phoenix pyrrhotite sample showed that it was entirely magnetic (Figure 2d), in agreement with the mineral chemistry determination. No non-magnetic pyrrhotite was noted in the Phoenix pyrrhotite sample.

For both the Sudbury CCN and Phoenix pyrrhotite samples, pentlandite typically occurs in three textural relationships consisting of domains of granular pentlandite with well developed cleavage, granular pentlandite veins or as fine grained flame-like exsolution lamellae. The relative proportion of the various pentlandite types is quite different for the two samples, Sudbury CCN pyrrhotite is dominated by granular pentlandite with rare flame pentlandite, whereas flame pentlandite is far more predominant in the Phoenix pyrrhotite sample. Figure

2a and b illustrate an example of non-magnetic Sudbury CCN pyrrhotite cross cut by granular pentlandite veins. Figure 2c and d illustrate the abundance of the very fine grained, crystallographically controlled flame-like lamellae of pentlandite hosted by magnetic pyrrhotite in the Phoenix samples.

In addition to the ubiquitous presence of nickel hosted by pentlandite in the pyrrhotite samples examined in this study, nickel is also hosted by the pyrrhotite crystal structure as solid solution nickel, i.e. Ni substitution for Fe in the pyrrhotite crystal structure. As shown by Table 1, the average nickel content of the Phoenix magnetic pyrrhotite samples was greater (1.06 wt %) than the non-magnetic Sudbury CCN pyrrhotite (0.75 wt %).

Pyrrhotite samples were then prepared for oxygen uptake and microflotation experiments, and the feed samples were analysed by MLA to determine their purity and pyrrhotite liberation. It is evident from table 2 that the pyrrhotite content for both samples was greater than 75 wt %. The pyrrhotite content of the Phoenix magnetic pyrrhotite (81.8 wt %) was slightly greater than the Sudbury CCN pyrrhotite sample (75.4 wt %). The concentration of pentlandite in the flotation feed samples varied between 7.9 wt % (Sudbury CCN) and 16.9 wt % (Phoenix). The chalcopyrite (< 0.7 wt %) was very low for both pyrrhotite samples. The pyrite content of the Phoenix pyrrhotite samples was 0.5 wt %. No pyrite was detected in the Sudbury CCN pyrrhotite sample. The total base metal sulfide content of the Sudbury CCN pyrrhotite sample was slightly lower (84 wt %) than the Phoenix pyrrhotite sample (99 wt %) due to the presence of some silicate gangue minerals (plagioclase, amphibole, quartz).

Pyrrhotite was over 90 % liberated in the Sudbury CCN pyrrhotite samples (Figure 3), whereas the liberation of Phoenix pyrrhotite was considerably lower (50.7 % liberated). This was due to a significant proportion of binary particles consisting of locked flame pentlandite hosted by pyrrhotite (46.3% out of the 50.3% binary particles; Figure 3). The lower degree of pyrrhotite liberation of the Phoenix sample was not unexpected given the abundance of locked flame pentlandite (Figure 2c, d) in contrast to the Sudbury CCN pyrrhotite.

Reactivity Results

The Reactivity Numbers (RN) shown in figure 4 are a representation of the propensity of the pyrrhotite sample for oxidation such that the faster the decrease of dissolved oxygen in solution through pyrrhotite oxidation, the higher the Reactivity Number. It is clearly evident that the Reactivity Numbers were significantly different for the two pyrrhotite samples and were dependent on both pH and reagent addition (SNPX alone or SNPX with copper activation). The Reactivity Numbers were significantly higher for the magnetic Phoenix pyrrhotite sample (e.g. 110 at pH 10 for collectorless test) relative to the non-magnetic Sudbury CCN pyrrhotite sample (e.g. 8 at pH 10 for collectorless test) indicating that the magnetic pyrrhotite was more reactive towards oxidation. It is also evident that the Reactivity Numbers were significantly higher at pH 10 than pH 7, due to the increase in reaction rates at the greater OH⁻ concentration. The addition of reagents to the slurry containing the Sudbury CCN non-magnetic pyrrhotite appeared to have little effect on the Reactivity Number at both pH 7 and 10 due to the relatively unreactive nature of this non-magnetic pyrrhotite. In contrast, the addition of reagents to the slurry containing the Phoenix magnetic pyrrhotite caused a distinct decrease in the Reactivity Number from 110 (pH 10, collectorless test) to 28 (pH 10, SNPX with copper test). This decrease in Reactivity Number of the magnetic pyrrhotite with reagent addition can be attributed to formation of a superficial chemical layer that effectively protected the surface of pyrrhotite from further oxidation. These results are in agreement with those of the XPS and ToF-SIMS study of [16] on pyrrhotite which showed that magnetic pyrrhotite was more reactive than non-magnetic pyrrhotite and that copper activation of pyrrhotite effectively stabilised the pyrrhotite surface from further oxidation.

Microflotation Results

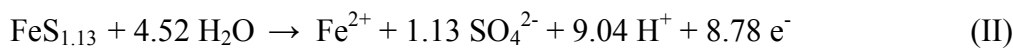
In order to compare the differences in floatability between the pyrrhotite samples, the final mass recovery from the different test conditions is shown for comparison in figure 5. Although the feed composition of the pyrrhotite samples was variably contaminated with additional sulfide minerals such as pentlandite, their contribution to the overall mass recovery was determined not to be significant based on the analysis of the nickel grades (< 0.5 wt % Ni).

Non-magnetic Sudbury CCN pyrrhotite showed significantly greater natural floatability or collectorless flotation at pH 7 (36 % recovery) than the magnetic Phoenix pyrrhotite (6 % recovery; Figure 5). With the addition of SNPX collector at pH 7, the floatability of both pyrrhotite samples showed a marked increase (e.g. up to 52 % recovery for Phoenix pyrrhotite). With the addition of copper at pH 7 for copper activation, the floatability of both pyrrhotite samples showed a further increase (e.g. up to 70 % recovery for Phoenix pyrrhotite).

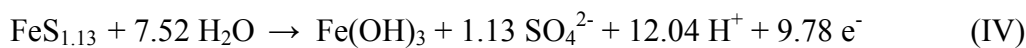
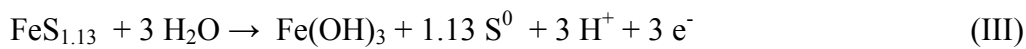
At pH 10, the natural or collectorless flotation of both pyrrhotite samples was slightly lower. The Sudbury CCN non-magnetic pyrrhotite showed a decrease in collectorless flotation from 36 % recovery to 27 % recovery with the increase in pH. The collectorless flotation recovery of the magnetic Phoenix pyrrhotite was almost negligible at pH 10 (3 % recovery). The addition of SNPX alone caused a significant increase in the recovery of the non-magnetic Sudbury CCN pyrrhotite (up to 39 % recovery), whereas only with copper activation was the floatability of the magnetic Phoenix pyrrhotite significantly improved (up to 43 % recovery). The improvement in flotation performance of the Sudbury CCN pyrrhotite with copper activation was not nearly as dramatic (from 39 to 54 % recovery).

DISCUSSION

Prior to the interpretation of the effect of mineralogy on flotation performance, some understanding of the electrochemical reactions taking place on the surface of pyrrhotite during oxidation and flotation is required. In order to promote the collectorless flotation of pyrrhotite, some mild oxidation is required such as that given in equations I and II, from Hamilton and Woods [34].



Given that ferric iron is likely to be a stable reaction product at alkaline conditions, the reactions can be represented as given in equations III and IV:



A variety of sulfur species have been proposed to provide the necessary hydrophobicity for the collectorless flotation of pyrrhotite (e.g. elemental sulfur, polysulfides, metal deficient sulfides, stable $\text{Fe}(\text{OH})\text{S}_2$ intermediate species; [34-38]. However, extensive oxidation is well known to be detrimental to the flotation performance of pyrrhotite due to the formation of hydrophilic ferric hydroxides species [11, 39]. Although ferric hydroxide species were not actively identified on the surface of pyrrhotite during the flotation tests in this study, their presence is assumed as the reason for poor pyrrhotite flotation. Therefore, the interpretation of the flotation results needs to be based on the relative reactivity of the different pyrrhotite samples for oxidation.

The results of the collectorless tests from the Reactivity Numbers studies at both pH 7 and 10 clearly showed that the magnetic Phoenix pyrrhotite was significantly more prone to oxidation than the non-magnetic Sudbury CCN pyrrhotite (Figure 4). Therefore, due to the very reactive character of the magnetic Phoenix pyrrhotite, it was extensively oxidised prior to flotation resulting in the formation of hydrophilic ferric hydroxide surface species that prevented the natural flotation of the Phoenix pyrrhotite (Figure 5). In contrast, due to the relatively unreactive nature of the Sudbury CCN pyrrhotite for extensive oxidation, only mild oxidation occurred resulting in the formation of hydrophobic surface species and collectorless flotation of the Sudbury CCN pyrrhotite.

The floatability of all the pyrrhotite samples was significantly improved with the addition of xanthate collector due to collector adsorption and formation of the dixanthogen species (MX_2) which is known to render pyrrhotite its hydrophobicity during flotation [40-42]. Kelebek [11] suggested that mild oxidation of the pyrrhotite surface promoted the amount of surface sites available for xanthate adsorption, the production of elemental sulfur and the oxidation of xanthate to dixanthogen. Extensive oxidation however, would have shifted the balance so that the layer of hydrophilic ferric hydroxides covering the surface of the pyrrhotite would not have allowed for sufficient xanthate adsorption.

The results of the microflotation studies showed that with collector addition, the floatability of the Sudbury CCN pyrrhotite was good at both pH 7 and 10, due to its relatively unreactive response to oxidation that allowed effective collector adsorption. For the more reactive Phoenix pyrrhotite however, this only occurred at pH 7. Due to the increase in electrochemical reaction rates at pH 10, the reactivity of the Phoenix pyrrhotite was much greater causing surface oxidation that prevented collector adsorption. The addition of copper at pH 10 however, stabilised the surface of the Phoenix pyrrhotite from further oxidation and so resulted in effective copper activation during flotation (Figure 5).

It can therefore be argued that the differences in the reactivity and flotation performance of the two pyrrhotite samples examined in this study are a function of their crystallography, composition and mineral association, which is by definition, their *mineralogy* [43]. The effect

of *crystal structure* on reactivity and flotation performance is considered to be due to the presence of vacancies. Since vacancies have been argued to be the most reactive sites for oxygen reduction [44], the presence of vacancies would therefore facilitate electron transfer as well as the diffusion of iron through the crystal lattice to the surface, thereby assisting the oxidation reaction. Since the magnetic pyrrhotite structure has more vacancies (1/8 vacant sites in Fe_7S_8) relative to non-magnetic pyrrhotite (1/10 vacant sites in Fe_9S_{10}), the greater abundance of vacancies is considered to accelerate the oxidation process for magnetic pyrrhotite relative to non-magnetic pyrrhotite. The effect of *mineral composition* on reactivity and flotation performance is considered to be due to the presence of ferric iron as well as trace element impurities (e.g. Ni). Ferric iron was noted by Janzen *et al.* [45] to be a much stronger oxidising agent than oxygen. On the basis that magnetic pyrrhotite ($\text{Fe}^{3+}_2\text{Fe}^{2+}_5\text{S}^{2-}_8$ for Fe_7S_8) has proportionally more ferric iron [44, 46, 47] in its structure than non-magnetic pyrrhotite ($\text{Fe}^{3+}_2\text{Fe}^{2+}_7\text{S}^{2-}_{10}$ for Fe_9S_{10}), it would be expected that magnetic pyrrhotite is more prone to oxidation, especially since the most reactive sites for oxidation are associated with the ferric iron – sulfur bonds [44]. The effect of *mineral association* on reactivity and flotation performance is considered to be due to the association of pentlandite with pyrrhotite. The presence of unliberated pentlandite occurring as composite pyrrhotite pentlandite particles may result in galvanic interactions between these phases affecting the reactivity, as well as improved pyrrhotite flotation since pentlandite is known to be more floatable than pyrrhotite [48-51]. This could account for the good flotation performance of the poorly liberated magnetic Phoenix pyrrhotite in the presence of collector. Clearly though, a larger pyrrhotite data set is needed to positively identify the extent to which mineral association affects the reactivity and flotation of pyrrhotite.

Implications of this study

Nickel processing operations treating pyrrhotite need to manipulate pyrrhotite performance so as to recover pyrrhotite due to the presence of abundant locked fine grained flame pentlandite (e.g. Phoenix ore, Tati Nickel, Botswana), or reject pyrrhotite in order to control circuit throughput and concentrate grade and thereby reduce excess sulfur dioxide smelter emissions (e.g. Sudbury, Canada). On the basis of the results from the two pyrrhotite samples analysed in this study, some generic implications for pyrrhotite processing can be explored. It should be noted however, that many operations treating pyrrhotite process both magnetic and non-

magnetic pyrrhotite. This may involve a magnetic separation step up stream, and then independently processing a magnetic (high sulfur) and a non-magnetic (low sulfur) pyrrhotite stream [22].

The results of this study have shown that the non-magnetic Sudbury CCN pyrrhotite was relatively unreactive towards oxidation and consequently showed good floatability. This suggests that the recovery of non-magnetic pyrrhotite similar in character to Sudbury CCN, should not be problematic for processing operations targeting pyrrhotite recovery. The recovery of the more reactive Phoenix magnetic pyrrhotite however, was not as good as non-magnetic pyrrhotite due to its propensity for oxidation. Consequently, the recovery of magnetic pyrrhotite similar in character to Phoenix pyrrhotite may be more problematic for operations targeting pyrrhotite recovery, and a better understanding of the relationship between surface oxidation and efficient copper activation, as well as how to prevent surface oxidation, is needed.

For nickel processing operations targeting pyrrhotite rejection during flotation, the role of oxidation is of particular interest. Although the use of oxygen as a pyrrhotite depressant has previously been evaluated [11] and has in the past been used in some Pb-Zn flotation operations (e.g. Actifloat O₂ at Elura Mine in Australia), it does not appear to have been implemented in nickel flotation operations [22]. Given the relatively unreactive nature of non-magnetic pyrrhotite this would not be advised. The results from this study however, suggest that it should not be too difficult to actively oxidise very reactive magnetic pyrrhotite, and perhaps the use of oxidation should be re-evaluated as an economically viable, environmentally friendly or “green” depressant for pyrrhotite in nickel processing operations.

Since pyrrhotite flotation performance is influenced by the presence of locked flame pentlandite (mineral association), a change in the grind size and liberation characteristics of pyrrhotite and pentlandite should be evaluated as a mechanism to assist in manipulating pyrrhotite flotation performance.

Finally, the importance of process mineralogy as a whole is to be able to better understand and optimise metallurgical performance, of which the flotation performance was investigated in this study. Important factors in accomplishing this goal are the availability of mineralogical and metallurgical information and most importantly, dialogue between mineralogists and metallurgists.

CONCLUSIONS

Pyrrhotite from the Sudbury CCN nickel mine in Canada is non-magnetic with a composition close to Fe_9S_{10} pyrrhotite, whereas pyrrhotite from the Tati Phoenix nickel mine in Botswana is magnetic with a composition close to Fe_7S_8 pyrrhotite. Granular pentlandite is common in the Sudbury CCN pyrrhotite, whereas pentlandite predominantly occurs as very fine grained flame lamellae in Phoenix pyrrhotite. Upon grinding, these flame lamellae in the Phoenix pyrrhotite are unliberated and account for one of the reasons why pyrrhotite recovery is targeted at the Phoenix mine in comparison to Sudbury CCN where pyrrhotite is rejected.

Oxygen uptake studies showed that the slurry of the magnetic Phoenix pyrrhotite was very reactive, whereas the slurry of the non-magnetic Sudbury pyrrhotite was relatively unreactive. The addition of flotation reagents caused a decrease in the Reactivity Number of the pyrrhotite slurry samples due to the adsorption of the reagents which prevented the pyrrhotite surface from further oxidation. Microflotation studies showed that the collectorless flotation recovery of non-magnetic Sudbury CCN pyrrhotite was much greater than the magnetic Phoenix pyrrhotite. Only with the addition of collector at pH 7, was the floatability of the Phoenix pyrrhotite similar to the Sudbury CCN pyrrhotite. At pH 10 however, copper activation was needed to improve the floatability of the magnetic Phoenix pyrrhotite so that it was similar to the Sudbury CCN pyrrhotite.

Differences in the floatability of the two pyrrhotite samples were linked to their propensity for oxidation and formation of hydrophilic ferric hydroxides which are detrimental to flotation. Due to the relatively unreactive nature of the non-magnetic Sudbury CCN pyrrhotite for oxidation, its floatability was good. In contrast, the propensity of the magnetic Phoenix pyrrhotite for oxidation and formation of hydrophilic ferric hydroxides was detrimental to its natural floatability, although this could be restored with the addition of flotation reagents.

This study has clearly shown that the flotation performance of magnetic Phoenix and non-magnetic Sudbury CCN pyrrhotite is different and is influenced by the reactivity of the

pyrrhotite for oxidation, which is attributed to differences in mineralogy (crystallography, composition and mineral association) of the pyrrhotite samples. This implies that if the mineralogy of pyrrhotite is known, the performance of pyrrhotite in processing operations can be manipulated to exploit specific attributes of the different pyrrhotite types. This study has also shown the usefulness of process mineralogy as a field of research in aiding the understanding of pyrrhotite flotation performance.

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Table 1: Summary of the mineralogical characteristics of pyrrhotite samples in this study. The average pyrrhotite nickel content is also given and excludes nickel associated with pentlandite. Full details of the pyrrhotite mineralogy are given in [28].

| Pyrrhotite Sample | Origin | Type | Ideal Composition | Ave Ni (wt %) |
|----------------------------------|---------------|-----------------|----------------------------|---------------------------------------|
| Sudbury Copper Cliff North (CCN) | Canada | Non-magnetic Po | Fe_9S_{10} | 0.75 ($2\sigma = 0.67$, n=203) |
| Tati Phoenix | Botswana | Magnetic Po | Fe_7S_8 | 1.06 ($2\sigma = 0.19$, n = 201) |

Table 2: Composition of pyrrhotite samples used in microflotation tests as determined by MLA, n.d. = not detected.

| Mineral (wt %) | Sudbury CCN | Phoenix |
|------------------|-----------------|-------------|
| | Non-magnetic Po | Magnetic Po |
| Pyrrhotite | 75.4 | 81.8 |
| Pentlandite | 7.9 | 16.9 |
| Chalcopyrite | 0.7 | 0.2 |
| Pyrite | <0.01 | 0.5 |
| Olivine | 0.4 | 0.1 |
| Orthopyroxene | 0.4 | <0.01 |
| Clinopyroxene | n.d. | <0.01 |
| Amphibole | 3.4 | 0.1 |
| Chlorite | 0.2 | <0.1 |
| Biotite | 1.6 | <0.01 |
| Plagioclase | 6.4 | n.d. |
| Quartz | 2.3 | <0.1 |
| Calcite | <0.01 | n.d. |
| Magnetite | 1.1 | 0.2 |
| Other oxides | 0.3 | <0.1 |
| Other | <0.1 | 0.1 |
| | | |
| Total BMS | 84 | 99 |
| Total | 100 | 100 |

Table 3: Summary of the procedure used for Reactivity Number tests. * Reagent dosages are given for a sample with 100% base metal sulfides. DO represents dissolved oxygen.

| Activity | Conditions | Time (min) |
|----------------------------------|---|-------------------|
| Retrieval of sample from freezer | ~ 80g pyrrhotite sample (53-106 μm) | - |
| Ultrasonification | 400 ml Distilled Water | 5 |
| Wet screening | Synthetic water @ desired pH, 10^{-2}M ionic strength Ca^{2+} | - |
| Transferral into beaker | Stirring of slurry (~ 20% solids) at point of depressant addition | - |
| Depressant addition | Sty 504 @ 10ppm | 5 |
| Activator addition* | CuSO_4 @ $1.6 \times 10^{-4}\text{M}$ | 2 |
| Collector addition* | SNPX @ $4.0 \times 10^{-4}\text{M}$ | 2 |
| pH modification | NaOH | - |
| DO measurement | - | - |
| O_2 Introduction | O_2 sparging at $1.15 \text{ L}\cdot\text{min}^{-1}$ | 10 sec |
| DO measurement | - | 3 |

Table 4: Summary of the procedure used for microflotation tests. * Reagent dosages are given for a sample with 100% base metal sulfides.

| Activity | Conditions | Time (min) |
|----------------------------------|---|-------------------|
| Sample weighing | 2g pyrrhotite sample (53-106 μm) | - |
| Ultrasonification | 80 ml Distilled Water | 5 |
| Wet screening | Synthetic water @ desired pH, 10^{-2} ionic strength Ca^{2+} | - |
| Transferral into beaker | Sample stirring at point of depressant addition | - |
| Depressant addition | Sty 504 @ 10ppm | 5 |
| Activator addition* | CuSO_4 @ $0.4 \times 10^{-5}\text{M}$ | 2 |
| Collector addition* | SNPX @ $1.0 \times 10^{-5}\text{M}$ | 2 |
| pH modification | NaOH or HNO_3 | - |
| Transferral into microfloat cell | 100 rpm pump speed, $7\text{ml}\cdot\text{min}^{-1}$ synthetic air flow | - |
| Conc 1 Collection | - | 2 |
| Conc 2 Collection | - | 3 |
| Conc 3 Collection | - | 5 |
| Conc 4 Collection | - | 5 |

Figure 1: Diagram of the apparatus used for Reactivity Number measurements.

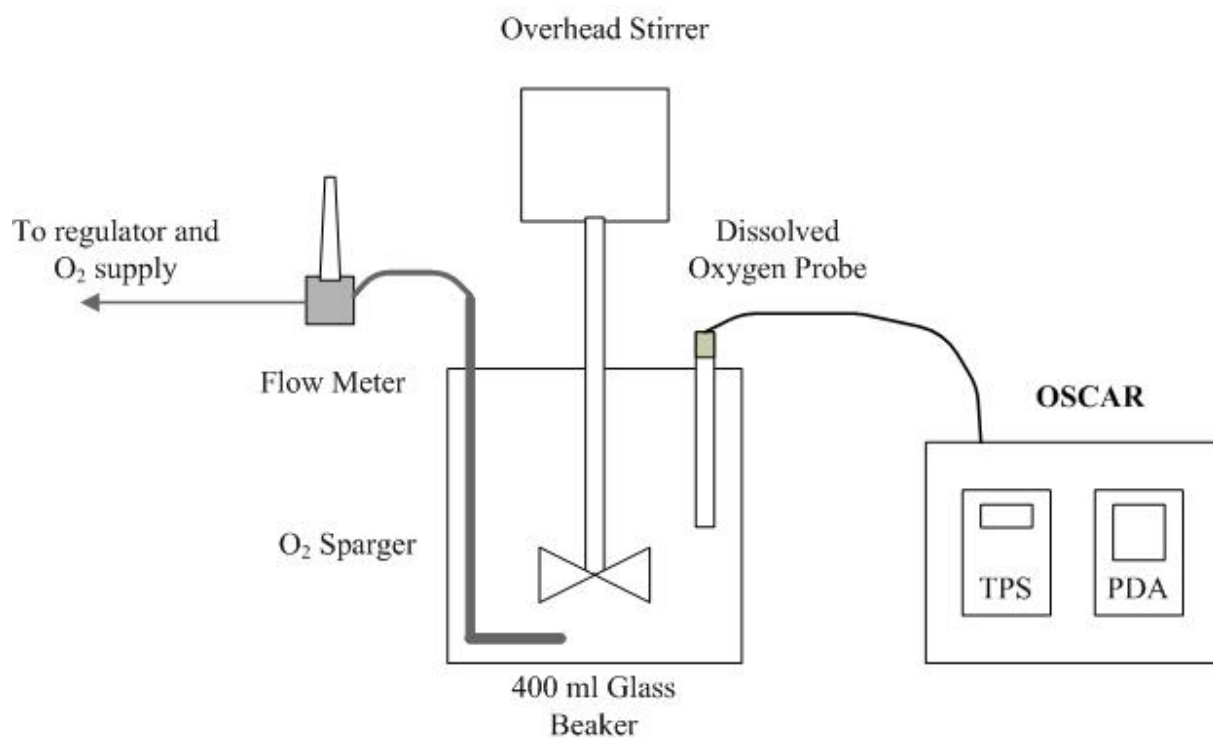


Figure 2: Photomicrographs of pyrrhotite samples shown in reflected polarised light (a-d) and treated with the magnetic colloid (b, d) that is used to highlight the presence of magnetic pyrrhotite. (a) Sudbury CCN non-magnetic pyrrhotite cross cut by a granular pentlandite vein. (b) Sudbury CCN non-magnetic pyrrhotite with pentlandite veins rimmed by very fine grained magnetic pyrrhotite in a host of non-magnetic pyrrhotite. (c) Phoenix magnetic pyrrhotite with exsolution of very fine grained pentlandite flames and cross cut by a pyrite vein (d) Phoenix magnetic pyrrhotite with exsolution of very fine grained pentlandite flames along fractures hosted by a magnetic pyrrhotite matrix. Scale bar represents 200 μm for all photomicrographs. Mag-po = magnetic pyrrhotite, non-mag po = non-magnetic pyrrhotite, pent = pentlandite, py = pyrite.

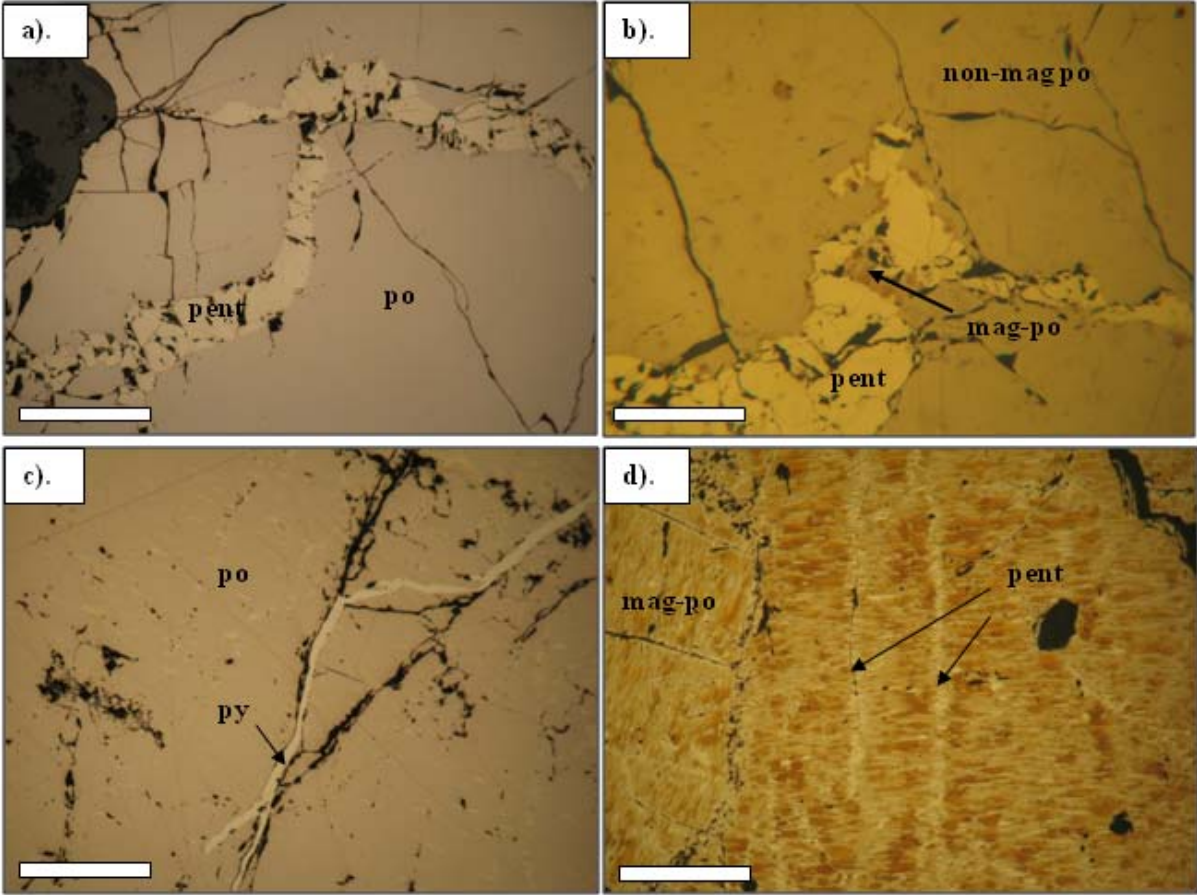


Figure 3: Proportion of pyrrhotite particles in microflotation feed samples as liberated (> 95% area), binary or ternary particles.

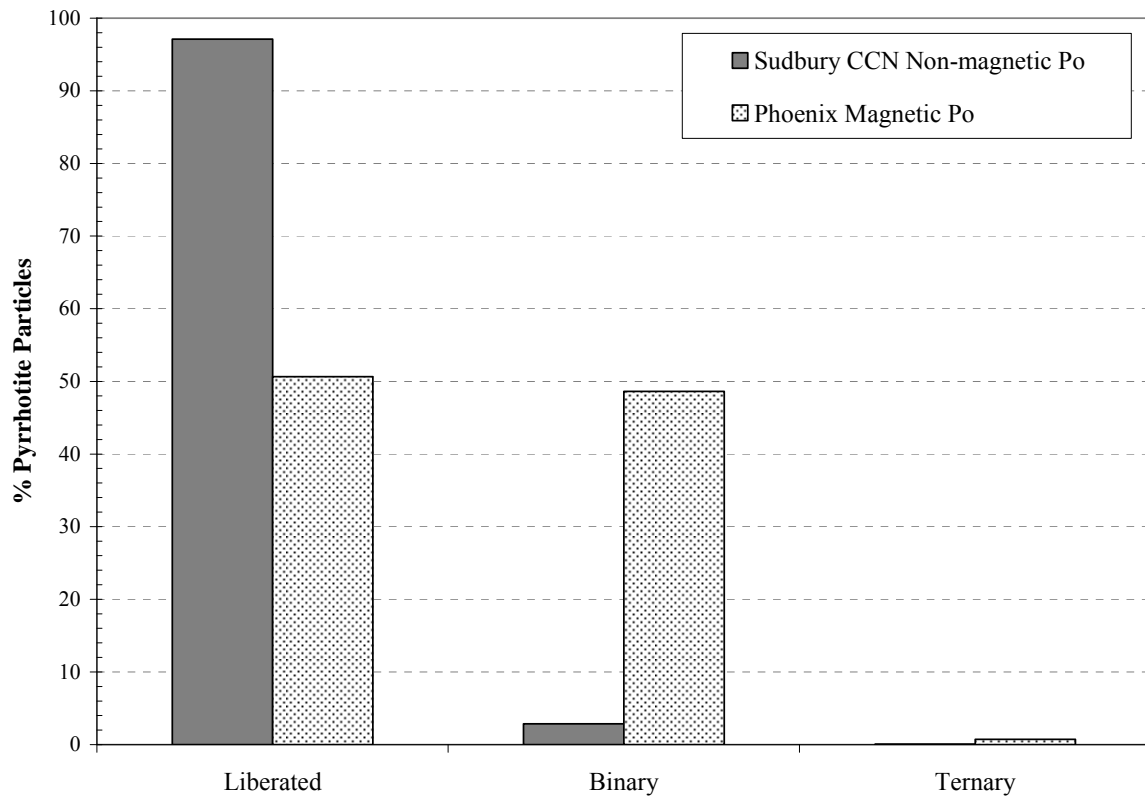


Figure 4: Comparison of the Reactivity Numbers for pyrrhotite samples at pH 7 and 10.

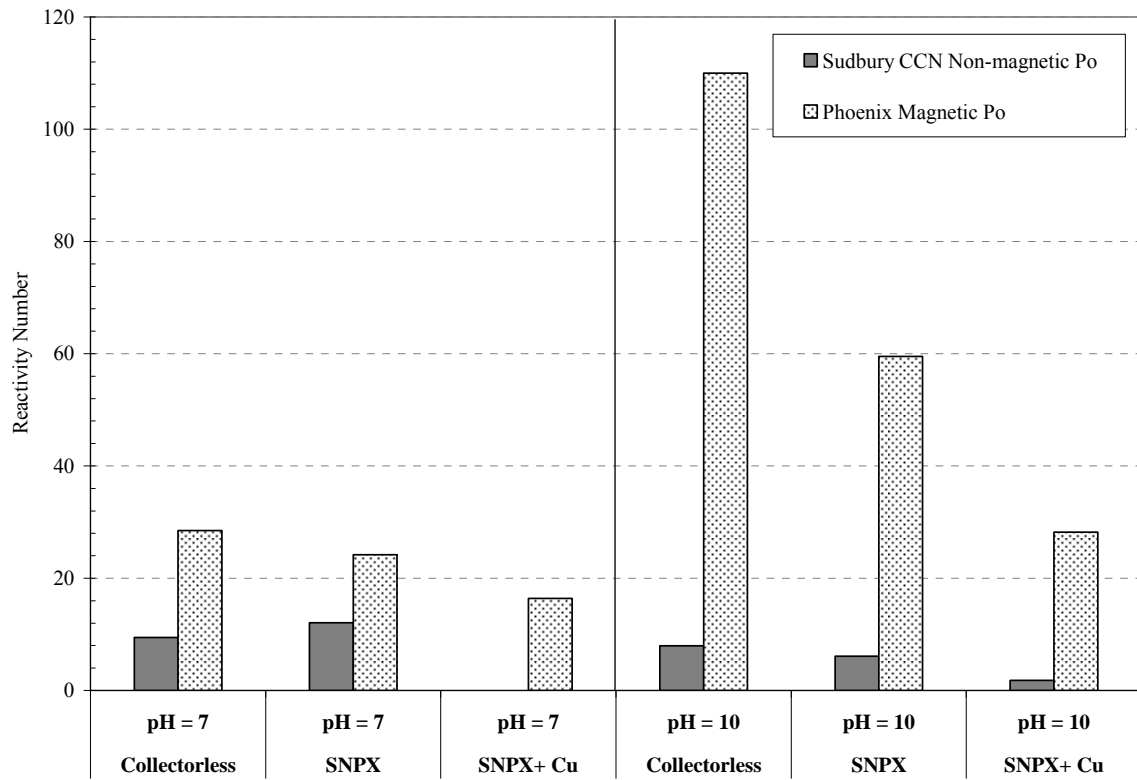


Figure 5: Comparison of the final flotation mass recovery for pyrrhotite samples at pH 7 and 10. The 2σ standard deviation is also shown.

