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Study on the surface chemistry behavior of pyrochlore during froth flotation

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Graduate Program in Geology

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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Study on the surface chemistry behavior of pyrochlore during froth flotation

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by

Saeed Chehreh Chelgani

Graduate Program in Geology

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

Separation of pyrochlore from its associated minerals is typically accomplished by froth flotation. The surface chemistry of pyrochlore is similar to many of its associated non-value minerals. Therefore, understanding the surface chemical properties of the pyrochlore for selective pyrochlore flotation will potentially aid in the design of flotation strategies for optimized recovery. In this study, pyrochlore samples were collected from various points in the flotation scheme at the Niobec plant, Quebec, Canada. The SEM-EDX analysis revealed that pyrochlore from the Niobec deposit occurs as high and low iron varieties, and that recovery favours varieties with a lower Fe content. To understand a potential relationship between pyrochlore matrix composition and the related effect on collector adsorption, the surface of grains from the concentrate and tails were examined by TOF-SIMS. The surface analyses of different pyrochlore grains showed that species indicative of the cationic collector (Tallow diamine acetate) favour Fe poor pyrochlore relative to the Fe rich variety. XPS was used to analyse the surface of high Fe and low Fe pyrochlore in order to identify a potential relationship between pyrochlore matrix composition and surface chemistry. The XPS results verified a relationship between pyrochlore surface oxidation and Fe content in the mineral matrix; high Fe pyrochlore particles showed a greater proportion of surface oxidation species suggesting preferential oxidation in comparison with low Fe pyrochlore particles. SEM-EDX analyses revealed that many of the pyrochlore grains were compositionally zoned into regions of high and low Fe contents. TOF-SIMS and XPS analyses were used to analyze the surface of the compositionally zoned Fe pyrochlore grains, in order to link collector adsorption to Fe contents and identify potential mechanisms for the partitioning. Surface analyses of conditioned pyrochlore grains showing zones of high and low Fe content revealed that species indicative of the collector favour the regions with low iron. XPS analyses of similarly treated compositionally zoned pyrochlore grains showed that a greater proportion of surface oxidation species corresponded to the zones with high matrix Fe content. These results are in accord with the results identified for non-zoned pyrochlore grains of variable matrix Fe content and verifies the link between pyrochlore Fe composition, surface oxidation and, area selective collector loading.

Keywords: Pyrochlore, Flotation, SEM-EDX, TOF-SIMS, XPS.
Co-Authorship Statement

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Chapter 1

1 Introduction

Mineral separation by froth flotation is a physical and chemical process which depends on complex phenomena occurring at the surfaces of mineral particles and air bubbles in the flotation pulp. The basis of froth flotation is related to the difference in surface wet-abilities of the different minerals; those that are easily wettable by water are hydrophilic, those that are water-repellent are hydrophobic. Mineral flotation is a process that involves the collision between particles and their interaction with air bubbles in the pulp. When air is bubbled through a mixture of hydrophobic and hydrophilic particles suspended in water, the hydrophobic particles will tend to attach to the air bubbles and float to the surface. The froth layer on the surface of the flotation cell either overflows the lip of the cell or is removed by froth scraper. The hydrophilic particles which are less inclined to attach to air bubbles, remain in suspension and are ultimately removed from flotation cell the tails (Rao & Leja, 2004; Bulatovic, 2007; Wills, 2010).

Particles can either be naturally hydrophobic, or the hydrophobicity can be induced by chemical treatments. In order to induce hydrophobicity to selected minerals, reagents (e.g. chemical treatment; collectors, depressants, activators) are added to the pulp. Surface chemical modifiers designed to render a mineral surface hydrophobic (collectors) are reagents which are designed to selectively coat a specific particle (mineral) surface with a monolayer of a polar molecule. Chemicals are needed to control both the relative hydrophobicities of the particles, and to maintain the proper froth characteristics. Selective flotation is strongly dependent on the degree of collector adsorption on the mineral’s surface. Whether the collector adsorption is due to electrostatic attraction or chemisorption, is a function of the surface charge of the mineral and the type of collector. If electrostatic attraction is the major driving force, the adsorption process is characterised as physical; if however, the collector forms strong covalent or coordinate bonds with surface species, the process is characterized as chemisorption (Smith, 1987; Rao & Leja, 2004; Bulatovic, 2007; Wills, 2010).
Froth flotation is a highly versatile method for separating sulfide minerals. Various oxide minerals on the other hand are usually not as responsive to the froth flotation process. Hydrophobicity of oxides is believed to be influenced, to a large extent, by the electrochemical nature of the oxide–solution interface. The hydrogen and hydroxyl ions, when adsorbed on the oxide surface, together constitute a polarizable hydration layer with a hydrogen-bonded structure. The flotation behaviour of oxides and silicates is highly pH dependent, and because of their surface chemical similarities (Smith, 1987; Rao & Leja, 2004; Bulatovic, 2007; Wills, 2010) their flotation behaviour can be very similar. In most cases, the presence of metal ions in the pulp can be highly detrimental to the flotation of most oxide minerals. The adsorption of metallic cations on silicates and oxides impairs selectivity and separation of oxides and silicates or individual silicates themselves. It is believed that chemisorption of high molecular-weight collectors on oxide and silicate minerals is hindered where metal ions, present in aqueous solution, have hydrolyzed and precipitated as hydroxide complexes on the mineral surfaces.

Surface chemistry is the principal determinant for selective separation of the various mineral phases. With a rise in the complexity of the ores processed by flotation, understanding the reactivity of mineral surfaces in this context is becoming increasingly more important. Instrumental techniques such as X-ray photoelectron spectroscopy (XPS), and Time of flight secondary ion mass spectrometry (TOF-SIMS) are unique in that they have the capacity to analyze surfaces, and therefore, are powerful tools to help understand mineral surface properties, and their reactions during the flotation process.

This investigation evaluates factors affecting the recovery of pyrochlore, the primary Nb host, from the Niobec pyrochlore flotation plant. The Niobec underground mine is located twenty-five kilometres north of Ville de Saguenay (Chicoutimi), in the limits of the municipality of Saint-Honoré (Fig 1-1). The host rock is divided in three distinct litho-structural units. The first unit constitutes a gneiss complex. The second unit is represented by anorthosite and charnockite-mangerite batholiths (showing well preserved igneous structures and textures). The third unit is characterized by calc-alkaline intrusions that cross-cut the host rocks. The intrusive mass (i.e St-Honoré alkaline complex) is almost completely covered by Trenton limestone of Palaeozoic age. It consists of a series
of crescentic lenses of carbonatite with compositions that change progressively inwards from calcitite through dolomitite to ferrocarbonatite. Niobium minerals of bi-pyramidal form are disseminated throughout the carbonatite. The economic mineralization is found in ferrian and sodic pyrochlore, generally in association with geological units rich in magnetite and biotite. Open stoping has been the only mining method used since mine start-up. Stopes are planned and designed based on geological information obtained from diamond drilling.

Fig 1-1.Niobec mine, regional geology (Belzile, 2009).

Since 1974 Niobec has been extracting niobium from the Staint-Honoré carbonatite deposit. Niobec is the only North American pyrochlore source and one of the three major world producers of ferroniobium. In the St-Honoré carbonatite ore, pyrochlore represents about 1% of the total mass. The dominant minerals are carbonates (mainly dolomite and
calcite), silicates (biotite, chlorite and Na, K-feldspars) and to a lesser extent apatite. Other constituent minerals include magnetite, hematite, pyrite and zircon.

In almost all pyrochlore processing operations, after mining and comminution, the ore is subjected to desliming to remove particles finer than 10 µm. The deslimed mineral pulp is subjected to three stages of flotation. The first stage involves flotation of carbonates, which removes a significant proportion of feed without much loss of pyrochlore (niobium). The tail of carbonate flotation is then subjected to pyrochlore flotation. The froth at this stage not only contains pyrochlore but also some sulphides, such as pyrite and pyrrhotite, which are removed by reverse flotation in the next processing stage.

In order to increase selective separation, various reagents are used in Niobec plant (Table 1-1). A major difficulty in selective pyrochlore flotation results from the similar surface chemical characteristics of pyrochlore and its associated gangue (non-value) minerals (other oxides and silicates). Selectivity of the pyrochlore cannot be achieved solely by choosing a single collector. The base of this difficulty is related to the similarity in isoelectric points (IEP) of pyrochlore with main the gangue minerals. This similarity in surface charge partially limits pyrochlore flotation selectivity. Therefore, understanding the primary mechanisms of collector attachment along with the surface chemistry of pyrochlore is essential in order to modify the current reagent scheme or potentially develop new collectors towards increasing pyrochlore selectivity. Furthermore, details from the investigation can potentially provide information towards the reduction in reagent use and the development of a simpler circuit.

The main purpose of this study is to evaluate the factors affecting pyrochlore stream partitioning within the pyrochlore flotation circuit at Niobec. This thesis is organized in several chapters which follow the course of the study. In the first chapter, variability in the matrix composition of pyrochlore grains in relation to the froth flotation stream products is investigated. The second chapter of this study is intended to provide a comprehensive review of the TOF-SIMS applications in the mineral flotation context and how this technique has been applied to the various mineral processing applications. The third chapter discusses the TOF-SIMS surface chemical evaluation of pyrochlore grains.
from the flotation products. The chapter explores the possible factors affecting the collector (tallow diamine acetate) absorption on the high and low iron pyrochlore grains. Chapter four describes the chemical zoning of the Fe pyrochlore minerals. The main aim of this chapter is to link pyrochlore matrix composition to surface chemistry and its affect on collector attachment. The results are used to better understand the variability in collector loading along with gaining some information on the collector adsorption mechanism. In chapter five, XPS analyses are used to examine the variability in surface oxidation of compositionally zoned pyrochlore grains. The aim of the study is to link pyrochlore matrix composition to variability in surface oxidation in order to evaluate this relationship with the observed mineral recovery.

The final results of this investigation may provide some understanding regarding the loss of selected pyrochlore grains. The results will also be used towards the selection of potential alternative commercial reagents for optimizing selectivity and recovery, or to help design reagents particularly suited for pyrochlore in this flotation context.

Table 1-1. Reagents are used in Niobec flotation plant.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tallow diamine acetate</td>
<td>220 g/t</td>
</tr>
<tr>
<td>Sulphonate</td>
<td>30 g/t</td>
</tr>
<tr>
<td>Phosphate</td>
<td>25 g/t</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>25 g/t</td>
</tr>
<tr>
<td>Dowfroth 250C</td>
<td>20 g/t</td>
</tr>
<tr>
<td>H$_2$SiF$_6$</td>
<td>140 g/t</td>
</tr>
</tbody>
</table>

1.1. References


Chapter 2

2 Study of pyrochlore matrix composition effects on froth flotation by SEM–EDX

2.1. Introduction

Niobium is used as an alloying agent predominantly in the steel production industry. Niobium-containing super alloys are used in the construction of jet and rocket engines because of their temperature stability properties. Superconducting alloys containing Nb along with titanium and tin are widely used in MRI scanners. Other applications include welding, electronics, optics, numismatics and jewelry. The predominant niobium bearing minerals are pyrochlore and columbite (Tanabe, 2003; Belzile, 2009).

Pyrochlore deposits contain substantial amounts of carbonates, sulphides, and other gangue minerals such as biotite, apatite, and feldspar. In almost all pyrochlore processing operations, after mining and comminution, the ore body is subjected to desliming to remove particles finer than 10 µm. The deslimed mineral pulp is subjected to three stages of flotation. The first stage involves flotation of carbonates, which removes a significant proportion of the feed without much loss of pyrochlore. The tail of carbonate flotation is then subjected to pyrochlore flotation. The froth at this stage not only contains pyrochlore but also some sulphides, such as pyrite and pyrrhotite, which are removed by reverse flotation in the next processing stage (Burks, 1958; Shapolov and Polkin, 1958; Zakharov et al., 1967; Razvozzhaev and Nikiforov, 1972; Bogdanov et al., 1973; Abeidu, 1974; Raby and Desrochers, 1975; Wilson, 1979; Biss and Nadeau, 1982; Biss, 1985).

The largest pyrochlore deposit is the CBMM mine located south of Araxá, Minas Gerais, followed by the Catalão mine east of Catalão, Goiás, in Brazil. The third largest deposit of niobium ore is the Saint-Honoré mine west of Saint-Honoré near Chicoutimi, Quebec (Kouptsidis et al., 2008). Since 1974, Niobec has been extracting niobium from the Saint-Honoré carbonatite deposit. Niobec is the only operating Nb extraction facility in North American and one of the three major world producers of ferroniobium (Dufresne and Goyette, 2004; Belzile, 2009).
In the St-Honoré carbonatite ore, pyrochlore represents only about 1% of the total mineral mass. The dominant minerals are carbonates (mainly dolomite and calcite), silicates (biotite, chlorite and Na/K-feldspars) and to a lesser extent apatite. Other constituent minerals include magnetite, hematite, pyrite and zircon (Dufresne and Goyette, 2004).

With the aim of optimizing the flotation process for the Niobec ore, experiments were performed on the influence of collector, activator and type of water on Nb₂O₅ recovery and grade in the rougher and cleaner concentrates (Gomez et al., 1987; Rao et al., 1988). During process development it became evident that mild cationic collectors were preferable to anionic collectors because of their ability to collect less calcite and dolomite. Electro-kinetic measurements showed pyrochlore surfaces to be negatively charged in the desired pH flotation range. In light of this, tallow diamine acetate was selected for pyrochlore flotation; addition rates were 220 g/t (Dufresne and Goyette, 2004; Belzile, 2009).

Along with the pyrochlore, tallow diamine floats all of the silicates, iron oxides, apatite, sulfides and part of the dolomite, but by gradually reducing the pH, and by introducing silicate depressant all of these except pyrite are depressed (Dufresne and Goyette, 2004). A series of tests were performed at various lower flotation pHs to assess selectivity and recovery. However, no significant improvement in selectivity was observed when the pH was reduced and therefore the pH was maintained between 6.8 and 7.5 (Rao et al., 1988; Dufresne and Goyette, 2004; Belzile, 2009). A major difficulty of pyrochlore flotation results from the similar flotation characteristics (the same surface chemistry) of pyrochlore and its associated minerals (other oxides and silicates) (Gomez et al., 1987); selectivity cannot be achieved solely by choosing a single collector (Dufresne and Goyette, 2004). The basis of this difficulty is related to the similarity in the iso electric points (IEP) of pyrochlore and the main contaminant minerals (the IEP of charge for pyrochlore, biotite, pyrite and feldspar at potable water is 2.5, 2, 1.5 and 1.9, respectively (Gomez, 1987)) which limits selective flotation in response to electrostatic collector adsorption (Gomez et al., 1987; Rao et al., 1988).
There is significant evidence to support that surface chemical variability can be directly related to variability in matrix composition (Hu et al., 2003; Barros et al., 2008; Oelkers et al., 2009). In a paper looking at the surface chemistry of multi-oxide silicates, in particular the pyroxenes diopside and enstatite, Oelkers et al. (2009) identified (1) divalent metal loss was directly related to pH, highest in alkaline solutions and (2) the removal rate and amount of Mg was on the order of 2x greater in diopside relative to enstatite. In this instance the loss of divalent metals results in the creation of ‘‘internal’’ surface sites, some of which can become protonated. Furthermore, the loss of metal ions corresponds to a linear increase in protonation, the degree of which is a function of the mineral composition. The data indicates that, metal-proton exchange reactions play a major role in surface reactivity and that variability in surface reactivity is strongly linked to mineral composition. Given this example it would be reasonable to assume that similar relationships occur in compositionally variable pyrochlore grains where collector adsorption may be linked to variability in metal ion removal rates. Therefore, understanding collector attachment in relation to variable matrix chemistry and its expression on the pyrochlore surface will potentially aid in the development of collectors or reagent strategies towards, increasing selectivity, lowering reagent consumption, promoting improved Nb-recoveries, and finally leading to simpler circuits.

In this chapter, matrix compositions of pyrochlore grains from Niobec froth flotation circuit were investigated. The study utilized scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDX) to measure concentrations of the main matrix elements in pyrochlore grains from the mill feed (MF), pyrochlore rougher feed (RF), pyrochlore rougher concentrate (RC), and pyrochlore rougher tail (T) (Fig. 2-1). The main aim of this study is to examine the pyrochlore matrix composition from various stream products with the potential to relate the matrix composition to variability in flotation recovery. This study is investigating the link between pyrochlore surface and matrix chemistry and their effects on collector adsorption.
Fig. 2-1. Simplified flowsheet of the Niobec process. The feed (mill feed: MF), after size reduction, is subjected to carbonate flotation; the tails from carbonate flotation, referred to as the rougher feed (RF), are pumped to a pyrochlore flotation bank; the rougher concentrate (RC) is then sent through five countercurrent stages of cleaning; the cleaner concentrate (CC) is subjected to sulfide flotation. The rejects from the pyrochlore rougher banks and the cleaner circuit are sent to tailings (T) 

(Dufresne and Goyette, 2004).

2.2. Experimental methodology

For the mineralogical investigation, pyrochlore grains were collected from various points in the flotation scheme at the Niobec plant. Approximately two hundred pyrochlore gains were analyzed from the mill feed (carbonate rougher feed), pyrochlore rougher feed (carbonate rougher tail), pyrochlore rougher concentrate, and pyrochlore rougher tail. The concentration of selected elements were measured in the pyrochlore grains with a LEO 440 SEM equipped with a Gresham light element detector and a Quartz XOne EDX
system. The instrument was operated at 20 keV, 400 pA. Samples were sputter-coated with Au/Pt in order to prevent charging during analyses.

2.3. Result and discussion

2.3.1. Pyrochlore structure

Pyrochlores (A$_2$B$_5$O$_7$) are complex oxides whose structures are made up of interconnected octahedra, consisting predominantly of Na, Ca, Fe and Sr in the A position and Nb, Ti, and Ta (B position). The various pyrochlore group end members are made by isomorphic substitution in the B position. Predictable variability in the proportion of A site ions results in minor compositional variability of the subgroups. Pyrochlore grains containing inclusions of Fe (presumably as an oxide) have also been identified (Hogarth, 1960, 1977; Petruk and Owens, 1975; Zurevinski and Mitchell, 2004).

The EDX analysis of pyrochlore grains from mill feed (MF), pyrochlore rougher feed (RF), pyrochlore rougher concentrate (RC), and pyrochlore rougher tail (T) are presented in Table 2-1. Analyses of pyrochlore grains from the RC and Tail samples show a relative decrease in matrix Na and Ca, along with a corresponding increase in Fe in grains from the tail (Fig. 2-2). These results suggest that the presence of iron in pyrochlore (either as an inclusion or structurally bound) may have an impact on its selectivity.

Given the observed relationship between Fe content and pyrochlore floatability, it was important to determine whether this relationship was due to Fe in the mineral matrix or related to potential inclusions within the mineral. In order to determine the nature of the Fe in the pyrochlore, statistical methods were performed on the analyses within the entire data set (MF, RF, RC, and T) in an attempt to distinguish matrix from inclusion iron. Inter-correlations between A site elements (Ca, Na, Fe, and Sr) indicate that higher Fe contents correspond to lower amounts of Ca, Na and Sr (Table 2-2). In addition, the linear and non-linear enter-remove regression methods shows that the Fe content in Niobec pyrochlore grains is predictable with other A position elements (Eqs. (2-1), and
where the difference between actual and non-linear predicted iron content for more than a hundred grains is less than %1 (Fig. 2-3).

Table 2-1. Results of EDX analysis of pyrochlore grains in mill feed (MF), pyrochlore rougher feed (RF), pyrochlore rougher concentrate (RC), and Tail (T) at.%. (*MDL = detection limits, elements may be present but are below for detection) (data was normalized based on appendix I).

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<th></th>
<th>MF (%)</th>
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<th>Std. Deviation</th>
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Fig 2-2. Comparison of Fe, Ca, and Na-Concentration (%) mass signals of pyrochlore grains.

Table 2-2. Inter correlation between A site pyrochlore ($A_2B_5O_7$) elements.

<table>
<thead>
<tr>
<th>Pearson correlation</th>
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<tr>
<td>Fe</td>
<td>1.000</td>
<td>-.590</td>
<td>-.246</td>
<td>-.518</td>
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Fe (%)=$20.629-1.517\text{Na}-0.942\text{Sr}-0.856\text{Ca} \quad R^2=0.73 \quad (2-1)$

Fe (%)=$31.957-5.621\text{Na}+0.953\text{Na}^2-0.056\text{Na}^3-3.965\text{Ca}+0.28\text{Ca}^2-0.007\text{Ca}^3-0.407\text{Sr} \quad R^2=0.88 \quad (2-2)$
Fig. 2-3. Distribution of difference between actual and estimated Fe concentration from Eq. (2-2).

Both statistical methods theoretically corroborate that the Fe in pyrochlore is indeed a matrix member. A significant contribution to the Fe content in pyrochlore grains by inclusions would have resulted in poor inter-correlation data and large differences between the actual and non-linear predicted Fe values. EDX mapping of several cross sectioned pyrochlore grains supports the statistical analysis. The Fe map of the pyrochlore grain in Fig. 2-4 shows a relatively homogenous distribution across the grain, supporting the statistical analysis that Fe in the Niobec pyrochlore grains is predominantly matrix bound. For comparison EDX maps of a pyrochlore containing Fe as inclusions is included. Note the localized Fe regions identifying the Fe inclusions (Fig. 2-5).
These analyses indicate that a higher concentration of matrix Fe in pyrochlore grains can potentially be linked to poor selectivity. Given these observations we have identified two potential explanations for the results (1) the higher proportion of Fe decreases the relative negative surface charge on pyrochlore, potentially preventing the adsorption of the cationic amine collector (Barros et al. (2008) reported higher concentrations of iron in apatites, rendering the surface of the apatites positive or less negative in the weakly alkaline pH range inhibiting collector attachment) and (2) higher surface iron content could promote a greater degree of surface oxidation thereby interfering with collector adsorption (poor flotation of iron pyrochlore is noted in the plant (Rao et al., 1988)). These 2 scenarios potentially explain the results from the SEM–EDX study. Ongoing
investigations linking pyrochlore surface reactivity to the variability in matrix Fe content using surface analytical tools are currently underway. The results will be applied to testing scenarios designed to improve flotation recovery.

Fig.2-5. EDX maps of a pyrochlore grain containing Fe as inclusions.

2.4. Conclusions

SEM–EDX analysis of pyrochlore grains has linked poor flotation performance to an increase in grain Fe content. Statistical analyses identified that the increase in Fe in the pyrochlore is not as a result of Fe rich inclusions, rather it has been identified as an increase matrix Fe content. Support for this conclusion is provided by EDX element
mapping where the Fe in cross sectioned pyrochlore grains appears evenly distributed. The results suggest that poor floatability is related to higher matrix Fe contents. Two possible explanations linking high Fe content to poor recovery have been suggested: (1) high Fe content resulting in change in surface charge, (2) high Fe content resulting in a variable degree and rate of surface oxidation. In progress studies linking pyrochlore surface reactivity using surface analytical tools are investigated. The results will be applied to testing scenarios designed to improve flotation selectivity.

2.5. References


Chapter 3

3 Studies on surface chemistry of minerals subjected to flotation separation by TOF-SIMS – A review

3.1. Introduction

Flotation is a complex process, partially governed by particle size and topography, the composition of the particle and the nature of the particle surface (edges and dislocations etc). Selective recovery however is driven by the chemistry of the top few monolayers of the mineral surface. The mineral particle-bubble attachment and its ensuing stability are governed by the balance of hydrophobic/hydrophilic species on the particle surface. Given that numerous species can coexist on the mineral surface simultaneously, shifts in this balance can have significant consequences on recovery. For example, the promotion of mineral surface hydrophobicity through the adsorption of hydrophobic collectors is easily and commonly hampered by the presence of oxidation products (oxy-S-species, oxy-hydroxides), precipitates, adsorbed ions, depressants and fine particles of other mineral phases (Trahar, 1976; Stowe et al., 1995; Crawford and Ralston, 1988; Boulton et al., 2003; Malysiak et al., 2004; Smart et al., 2007; Shackleton et al., 2007; Muganda et al., 2012, Smart et al, 2013).

In order to optimize mineral beneficiation by means of froth flotation, a detailed evaluation of the surface chemistry of both value and non-value minerals by phase and stream in a process is essential. Ideally the surface evaluation must be weighed in context of the flotation (grade and recovery) along with other significant contributors to the recovery process: solution chemistry and speciation along with mineral chemistry and liberation data. The approach to process improvement then becomes integrated, potentially identifying recovery controls by linking various contributing factors prior to looking at opportunities for improvement, for example in grinding, water quality, reagent control and dosage etc (Stowe et al., 1995; Piantadosi et al., 2000; Dimov & Chryssoulis, 2004a; Ralston et al., 2007, Gerson and Napier-Munn, 2013).
For the identification of the surface chemical control factors in a flotation process, it is necessary to measure statistically, differences in surface species by mineral phase within the flotation circuit (feed, conditioners, roughers, cleaners and tails) (Hart et al., 2006, Gerson et al., 2012). Due to the complexity of the flotation procedure, the characterization of mineral grain surfaces from this process is a significantly challenging task. There have however been great advancements in the application of various surface analytical tools to flotation in the last 2 decades. An excellent review on a wide range of innovative surface analytical techniques, applied to the fundamental understanding of the flotation process is given by Smart, 2013. The article provides a short description on the development and application of the most common tools along with case studies and some insights to new techniques for analyses.

There are numerous spectrometric and spectroscopic techniques that can be employed to study both mineral bulk and surface chemistry (Cormia et al., 1992; Marabini et al., 1993). Some of these techniques are more applicable for identifying and understanding interactions between minerals and various components within the hosting pulp. The most sensitive and reliable method for surface analysis is secondary ion mass spectrometry (SIMS) which collects and analyzes the secondary ions that are removed from the surface after bombardment with an ion beam. The process, referred to as sputtering, results in the removal of surface material through the generation of positive and negative ions along with neutral fragments. SIMS is divided into two categories, dynamic and static, depending on the energy and nature of the primary ionizing beam. In the dynamic mode (D-SIMS), the high energy direct current ion beam continuously removes surface material creating a depth profile through the sample being analysed. The technique is considered destructive and provides information regarding the matrix composition of the sample (typical analytical sample depths are on the order of several microns). In the static mode (SSIMS or more commonly TOF-SIMS) a pulsed low energy ion current removes surface material. In the time of analysis generally less than 0.1% of the samples atomic sites are involved in ion beam interaction. The ion interaction leads to a very low sputter rate, on the order of a fraction of a monolayer per hour and therefore the technique is considered non destructive. The SSIMS or TOF-SIMS technique is best suited for the analysis of surface materials, particularly organics, which may be present as thin over
layers. Chemical imaging has been well established for both DSIMS and TOF-SIMS (Brinen et al., 1993).

TOF-SIMS is widely used to conduct qualitative surface chemical analysis. Properly identified secondary ions on the mineral surfaces can be characteristic of hydrophobicity functionalities. In the flotation context, an excess of “hydrophobic fragments” or “hydrophilic fragments” can be applied to identify the predominant surface chemical species contributing to the concentration (floated) or rejection (tail) of a particular particles (Trahar, 1976; Stowe et al., 1995; Crawford and Ralston, 1988; Piantadosi et al., 2000; Boulton et al., 2003; Ralston et al., 2007). Moreover, the intensity of TOF-SIMS signals from these surface chemical species as a qualitative indication tool can be used to estimate surface wettability of a mineral (Boulton et al., 2003; Piantadosi et al., 2000; Khmeleva et al., 2005).

TOF-SIMS signal intensities can be affected by (1) the concentration of ion species on the mineral surfaces, (2) sputter yield of species, (3) matrix effects (e.g., ion yield), and (4) the beam conditions (Benninghoven, 1969; Vickerman and Briggs, 2001; Hagenhoff, 2000; Piantadosi et al., 2000). Numerous studies have shown that TOF-SIMS has the required level of sensitivity for detection and analysis of mineral surfaces from flotation products (Chryssoulis et al., 1995; Nagaraj and Brinen, 1996, 1997, 2001; Smart et al., 2008). However as the procedure is based on a comparative measurement of secondary ions generated from the surface of minerals (secondary ion yield, SIY), issues regarding matrix dependent variations in SIY, relative sensitivity factors (RSF) and surface component loading should be considered and incorporated into a separation method of minerals. For sulphides, comparative RSFs for various matrix components and several surface adsorbed reagents have been worked out (Hart et al., 2010). However for the various other value added minerals (for example rare earth element minerals), this task remains a work in progress.

It is the intent of this paper to provide a comprehensive review of the TOF-SIMS applications in the mineral flotation context. We hope to demonstrate how this technique has been applied to the various mineral processing applications including: the various
testing strategies, grinding, hydrophobicity, contact angle, flotation which can reveal elemental and molecular information from the surface of different minerals during flotation, and the surface chemistry of single particles present in a mixture of mineral grains.

3.2. TOF-SIMS analyses in the mineral flotation context

In the flotation context, the surface chemistry of grains representing samples from the various points in the process stream are analysed by TOF-SIMS. The spectra are obtained by bombarding the surface of the grains with a pulsed primary ion beam to desorb and ionize species from the sample surface. Damage to the uppermost monolayer is minimized by applying extremely low primary ion fluxes (Gerson et al., 2012). The process results in the production of sputtered neutrals as well as positive and negatively charged ions. The most versatile ion beam for analysis of mineral surfaces from flotation process samples is Bi\(^{+1}\) which can be clustered into 3, 5 and 7 ion clusters, retaining the same kinetic energy while reducing or, spreading out, the ionization impact. The true value of the Bi\(^{+1}\) ion gun is in its capacity for minimizing fragmentation of larger molecules (collectors) allowing for significantly improved identification. Older generation ion beams include Au, Ga\(^{+}\), Ar\(^{+}\), O\(^{-}\), Cs\(^{+}\), and SF\(_6\) however with the advent of the new generation ion guns these have been phased out except for special circumstances (for example, Cs\(^{+}\) depth profile sputtering, and Au cluster ions to enhance the sensitivity for molecular species).

As a result of the low primary ion current, the majority of the sputtered species are molecular in nature, both fragmented and parent, a feature which is exploited for reagent identification. The generated charged ions are separated according to mass in a time of flight (TOF) drift tube and detected by a sensitive dual channel plate analyser. By rastering the primary ion beam over a selected area on the sample, elemental and molecular distribution maps are obtained. From these maps, region-specific variability in atomic and molecular intensity can be established on a qualitative basis. Under the best conditions spectroscopic mapping at 0.2 micron spatial resolution is possible (Stowe et al., 1995).
All raw spectra are processed generally with instrument proprietary software (e.g., IONTOF or Wincadence-N). Peaks in the calibrated spectra are assigned to specific isotopes in accordance with their atomic mass. Peaks representative of specific materials (collectors) are defined based on spectral fingerprints which are generated by analysing a small portion of the collector mounted on a specific substrate. For surface species loading, comparative evaluation of the corrected ion intensity for each mass position, measured as the integrated area under each peak corrected for dead times, is calculated. In order to compare intensities between areas of different dimensions, corrected intensities are normalized to the total number of counts for the areas examined (Hart et al., 2006; Vizcarra et al., 2011).

Possibly one of the greatest challenges to studying the interactions between pulp and mineral surfaces in aqueous medium from flotation plants is sample collection. The key is to preserve the sample for analysis at a later date in a different facility. For this a method has been developed where surface reactions after collection are minimized by degassing the sample immediately after collection with de-oxygenated nitrogen and snap freezing with liquid nitrogen (Smart, 1991; Piantadosi and Smart, 2002; Hart et al., 2006, 2007). The sample must remain frozen during transport. In time delayed testing (when analysed within a 3 month period after collection) no difference in the surface characteristics in relation to the time of analyses have been identified.

3.3. Principle Component Analysis (PCA)

A major challenge associated with the application of TOF-SIMS analyses on the mineral flotation stream products is mineral phase recognition due to the composition complexity of minerals within multiphase ores and their surface chemistry. Principal component analysis (PCA) is a common technique applied to analyze multivariate data and has been applied in various disciplines (Jolliffe, 1986). PCA is generally utilized to reveal underlying information in the data (patterns and relationships among variables) and to decrease the dimension of data. Linear combinations of the original variables based on the covariance and correlation matrix are derived PCs. The test data of various analyses and the model of PC coefficients for different correlation matrixes can be compared.
based on the inter-correlations. The maximum possible variation in the database can be presented by the first principal component (PC1) data with the maximum variation in the uncorrelated data with PC1 represented by the second principal component (PC2). In this interactive fashion all the variations in the database are represented by PCs derived.

The first few PCs will represent the most variation in the database if the original variables show inter-correlation. In a two dimension plan, PC1 and PC2 are geometrically applied to indicate the structure of variables on PC1 x PC2 bi-plot and the observation patterns on a PC1 x PC2 scatter-plot. For more information, the interested reader is referred to the original work for a detailed description of this technique (Jolliffe, 1986).

One of the main beneficiations of PCA pattern is that this method can be applied for “the systematic examination and interpretation of the model outputs” (Kourti & MacGregor, 1995). It allows for classification of the ore into several phases, using all elements present (Smeink et al., 2005) and also reduces the number of secondary ions that would be useful to understand the variation of reactions without missing essential data (Abreu et al., 2010).

Hart et al. (2005) have shown that for TOF-SIMS data analysis of flotation products, PCA is capable of providing useful information towards phase recognition and particle selection. They have demonstrated that in a complex multi-phase ore, mineral identification using PCA is a more reliable approach compared with elemental imaging and manual particle selection; as it can provide a clearer definition of particle boundaries using multi-variable recognition (Biesinger et al., 2004; Hart et al., 2005; Hart et al., 2006). In particular, it allows for detection of different mineral phases and their surface species rather than manually focussing on one mineral for statistical analysis. This methodology is the subject of a patent (Smart et al., 2008).

PLS_Toolbox 2.1 from Eigenvector Research Ltd. (Manson, WA, USA) running on Matlab 6.0 (or 7.0) was the software used for PCA analysis. In processing TOF-SIMS images, PCA selects these correlations from the mass spectra recorded at each of 256 x 256 pixels in a selected area of particles (Hart et al., 2005). For each set of data as many significant mass peaks as possible were added to the peak list for analysis. Also included
in the peak selection is the total remaining ion image (sum of ion intensity not selected as a specific peak) shown at mass zero in the loadings. Data was either “mean centred” or “auto scaled” prior to PCA (Hart et al., 2006). Mean centring is done by subtracting the column mean from each column, thus forming a matrix where each column has a mean of zero. For the “auto scaled” data, the data is first mean centred and each mean centred variable is then divided by its standard deviation resulting in variables with unit variance. This procedure puts all variables on an equal basis in the analysis. Thus, the less intense but more chemically significant higher mass peaks receive the same level of consideration in the analysis as the intense, low mass peaks (Hart et al., 2005, Gerson et al., 2012).

In the image mode, PCA has proved to be an applicable method of selecting particles by mineral phase with clearer definition of particle boundaries due to multi-variable recognition. Hart et al. (2005) have shown that intensities between the sphalerite and pyrite/chalcopyrite phases are clearly separated by statistical difference in copper (Fig.3-1). The experimental results validate the selective transfer of Cu from chalcopyrite to sphalerite.

In another investigation, Hart et al. (2006) applied the PCA method on concentrate and tails samples collected from the Inco Matte Concentrator. The results indicate that the transfer of Cu and Ni between chalcocite and heazelwoodite results in the inadvertent activation of heazelwoodite and depression of the chalcocite. The data also provided evidence that the collectordiphenyl guanidine (DPG) may be selectively attaching to hydroxylated Cu sites. The data revealed that there is a considerably higher CuOH signal on both Cc and Hz particles in the concentrate relative to the tails and higher CuO intensities on Cc and Hz particles from the tails. This finding is supported by the statistical analyses of all TOF-SIMS variables where Pearson product moment inter-correlations between CuOH and DPG (119) for Hz in the concentrate is 0.70 and for Cc in concentrate 0.96 where as for the tail samples, the inter-correlation for Cc in tails is significantly lower; 0.3, presumably due to the high surface concentrations of Ni ions.
Fig. 3-1. TOF-SIMS total ion image of particles in pyrite, sphalerite, and chalcopyrite mixture (a), reconstructed image (b) and Mass loadings (c) and for PC2 selected area (a) (Hart et al., 2005).

Abreu and Skinner (2011a) also used the PCA for TOF-SIMS images to examine the potential impact of surface chemistry on mineral recovery at constant hydrodynamic conditions. Results indicate that PCA can be applied on TOF-SIMS signals to differentiate chalcopyrite grains in the concentrate and tail, and on the quantified particle responses to the flotation process. Abreu et al. (2010) also applied PCA on TOF-SIMS outputs as a database to predict the contact angle of chalcopyrite particles according to their surface chemistry analyses.
They used principal components to classify the surface species (secondary ions) into hydrophobic or hydrophilic categories. They have stated that “this approach is capable of determining the surface chemistry contribution to the contact angle of individual mineral particles and the distribution of contact angles within a large ensemble of particles” (Abreu et al., 2010; Aberu & Skinner, 2011a).

Gerson et al. (2012) applied PCA on TOF-SIMS analyses in order to examine the surface species on both concentrates and tails samples from the Bingham Canyon porphyry copper deposit. The source of the ore, is geologically complex (Triffett and Bradshaw 2008) but can be simplified into limestone skarn (LSN) ore, containing economic concentrations of Cu sulfide minerals, and monzonite (MZ) ore, containing economic concentrations of both Mo and Cu sulfide minerals. It had been proposed, as a result of plant-based flotation observations that blending of these two ore types would lead to ‘poisoning’ of the flotation response. The TOF-SIMS PCA analyses indicate that copper-containing components within both the MZ and LSN ores showed significant surface contamination so that, on blending, their flotation response was not significantly affected. However, the surface of the molybdenite component of the MZ ore was largely clean. On blending, partial transfer of the hydrophilic load in the LSN ore took place on to the MZ molybdenite resulting in apparent ‘poisoning’ of the flotation response of this component (Smart et al 2013).

3.4. Grinding

Flotation separation of galena from pyrite was significantly affected by the oxidation of metal species on the surface of galena and pyrite throughout grinding. Iron hydroxide species on the surface of both minerals depressed their flotation, whereas lead hydroxide species can activate the pyrite surfaces with negligible impact on galena flotation. To optimize selective separation of galena from pyrite by flotation, grinding conditions should allow for the control of lead and iron oxidation (Peng et al., 2003; Chandra and Gerson, 2009).
Peng et al. (2003) used a specific type of mill which allowed for controlling the pH during grinding. It was utilized to study the impact of grinding conditions on selective flotation of galena from pyrite. Two types of iron media were investigated: mild steel and 30 wt. % chromium (with ≈ 70wt. % iron). They used TOF-SIMS to identify differences in surface species occurring as a result of the different media and test parameters. The TOF-SIMS results revealed the highest percentage of oxygen and iron species on the surface of galena was observed during grinding with mild steel and oxygen purging. In flotation testing, these results correlated with the poor galena recovery.

In the same investigation, TOF-SIMS analyses of pyrite surfaces also identified that the highest concentration of FeOH was observed during grinding with mild steel and oxygen purging. The percentage of lead and lead hydroxide species on the pyrite surfaces also had a positive correlation with low recovery of pyrite. Comparative analyses between EDTA extraction analyses and TOF-SIMS results suggest that on the surface of galena and pyrite, lead hydroxide could be covered by iron hydroxide. This explains the reduction of lead oxidation species in the presence of iron oxidation species, independent of whether lead oxidation species depressed galena flotation or activated pyrite flotation (Peng et al., 2003).

In another investigation on flotation of galena and chalcopyrite, by using a similar experimental procedure, it was shown that flotation of fine particles, in the order of ~10 µm, strongly depended on grinding conditions (Peng & Grano, 2010). Two hypotheses were suggested: 1. Fe contamination depressed flotation of particles; 2. various percentages of iron hydroxide species could be present on the surface of fine and intermediate size grains. These possibilities were examined by TOF-SIMS, using two types of grinding media: the tapered cylinder mild steel grinding medium (~100wt. % iron, supplied from Pasminco Mining Co., Elura, Australia) and the spherical chromium grinding medium (30 wt.% chromium, supplied from Magotteaux, Australia) (Peng & Grano, 2010).

The normalized intensities of selected ions on the surface of treated galena for various sizes under different conditions were shown in Fig. 3-2. TOF-SIMS analyses indicated
that the surfaces of treated fine particles under grinding with mild steel medium and oxygen purging showed much stronger intensities of O, Fe and Fe(OH) compared with intermediate particles (Fig. 3-2a). The higher adsorption of iron hydroxide species on the surface of fine grains is consistent with the lower recovery of those particles. Also, the same intensities of O, Fe and Fe(OH) on the surface of both fine and intermediate grains were observed when grinding was done with 30 wt. % chromium medium with nitrogen purging (Fig. 3-2b). The same recoveries under this condition for different particle sizes were achieved (Peng & Grano, 2010).

Fig. 3-2. TOF-SIMS normalized intensities of oxygen and iron on chalcopyrite particles: (a) mild steel medium with oxygen purging (b) chromium medium with nitrogen purging (Peng & Grano, 2010).
The same procedure was conducted on the surface of chalcopyrite particles under different grinding conditions. Greater intensities of O, Fe and Fe(OH) were detected on the surface of fine particles compared with intermediate ones after grinding with mild steel medium and oxygen purging (Fig. 3-3a). These results explained the low recovery of fine chalcopyrite particles even when minimizing iron contamination from grinding conditions. The normalized intensities of O, Fe and Fe(OH) on the surface of fine grains for samples ground with 30 wt. % chromium medium with nitrogen purging show a relative decrease on O, Fe and OH loading relative to the mild steel with oxygen purge.
test. The later test conditions resulted in higher particle depression during flotation. These results demonstrated that mild steel medium and oxygen purging mostly showed an increase in iron hydroxide species on the fine particle surfaces (comparing Fig. 3-2a with b and Fig. 3-3a with b). From the distribution of the FeOH species, it is apparent that the finer particles have a greater proportion of Fe oxidative species, certainly in response to galvanic interactions and/or as a result of surface precipitation. In summary, the TOF-SIMS results identified that poor recovery of fine particles of both pyrite and chalcopyrite ground in conventional mills is partially linked to the presence of surface Fe-oxidation species. Therefore, minimizing iron contamination in the grinding condition when fine particles are targeted would be beneficial (Peng & Grano, 2010).

A similar study was conducted by Hyde et al (2009) using TOF-SIMS analyses to investigate the preferential surface oxidation, and also copper activation (by pure chalcopyrite) of pyrite versus arsenopyrite during milling with mild steel, stainless steel, 18% and 30% Cr steel grinding media. For pyrite, the development of surface oxidation products was greatest when using stainless steel and decreased when using mild steel, reflecting the preferential oxidation of the mild steel grinding media over pyrite. The more inert characteristic of stainless steel hinders Fe oxidation in the grinding media, preferentially promoting oxidation of the pyrite grains.

The TOF-SIMS data (FeO, FeOH and AsO) for arsenopyrite ground with 18% Cr and 30% Cr steel grinding media shows higher levels of all three species on grains ground with 18% Cr steel. The data agree well with those of Huang et al. (2006) who suggests that the increase is related to the more electrochemically active grinding media and a resulting transfer and precipitation of oxide species on the arsenopyrite surfaces. The investigation by Hyde et al 2009 however also identified an increase in the proportion of As oxides on the surface of the arsenopyrite in the test with 18% Cr steel grinding medium. The implication here is that the surface oxidation products potentially also represent those developed in-situ as opposed to solely transferred and precipitated species from the oxidation of the grinding medium.
Chapman et al., 2011 studied the effect of crushing by High Pressure Grinding Rollers (HPGR) in combination with rod milling (wet and dry) on the batch flotation test of Platinum-Group Minerals (PGMs). Results indicated a decrease in the recovery and grade of PGMs when HPGR-dry milling was used. TOF-SIMS was used to understand the mechanism of this reduction. The TOF-SIMS results demonstrated that the concentrate samples of both wet and dry grinding showed an increase in xanthate and dithiophosphate along with slightly lower levels of hydrophilic passivating species (calcium, magnesium, silicon and aluminium) when compared to the feed and tails samples. (Chapman et al., 2011).

3.5. Contact angle

In mineral flotation, hydrophobicity is commonly determined by measuring the contact angle among the mineral surface and a bubble at the air/water/mineral three-phase system. There is no easy and reliable technique to measure the contact angle of a particular mineral in an ore. Capillary penetration is the recommended method to determine the contact angle of particles, using a powdered packed bed (e.g., the Washburn method). It is reported that this method provides the most accurate contact-angle values for a real mineral. Real minerals are non-ideal rough surfaces, with irregular size and shape, and can be chemically heterogeneous. As a result, a wide range of contact angles can be obtained due to the complexity of mineral surfaces and the variety of minerals measured in the PPB (Chau, 2009).

Duan et al. (2003) studied the possible correlation between the contact angle of chalcopyrite minerals and their surface analyses by TOF-SIMS. Also in 2008, Priest and his co-workers examined TOF-SIMS as a potential technique to predict surface wettability. They identified a correlation between the surface wettability and the relative intensity of secondary ions. These results suggested that TOF-SIMS analysis can be utilized as a predictive method for both advancing and receding contact angles on the surface of minerals (Priest et al., 2008).
Abreu et al. (2010) used TOF-SIMS signals obtained from flotation experiments on a single-mineral, chalcopyrite (CuFeS$_2$), and found the correlation with their average contact angle, as measured by the Washburn method. In this study, PCA identified a set of seven secondary ions (Cu, O, S, C$_7$H$_7$O, FeO, FeOOH, and S$_2$) which describes the main variation in the chalcopyrite surface chemistry. The correlation between these secondary ions (SIs) and the contact angle of particles were examined and the intensity of total oxygen, total sulfur, and the collector fragment (C$_7$H$_7$O) were shown having a strong correlation with the contact angle. Using a multi-variable regression, a multi-variable linear equation of SIs was generated to estimate the contact angle:

$$\theta = 45.74 - 1.208I_o + 3.065I_S + 15.82I_{C_7H_7O}$$

(3-1)

Abreu et al.’s results demonstrated that the presented model has several benefits over the conventional techniques such as the prediction of contact angles for different particle surfaces (small amount of samples) regardless of the particle size. Therefore, no pre-sizing of minerals is involved, and various mineral sizes/regions can be studied at the same time (Abreu et al., 2010; Abreu & Skinner, 2011b). Muganda et al. (2011) also found a good correlation between the advancing contact angle values predicted by TOF-SIMS and those determined from direct contact angle measurement on the 53–75 µm size fraction of chalcopyrite.

3.6. Hydrophobicity

In sulfide flotation, recovery and selectivity are fundamentally dependent on the relative rate constants of various mineral phases (Boulton et al., 2003). Therefore, an evaluation of the hydrophobicity balance by mineral particles requires accurate selection of the mineral phase. The hydrophobic-hydrophilic (hydrophobicity) balance by mineral phases and the relative statistical average require determination of the main species contributing to each category in surface layers. This determination is not a simple procedure in a flotation pulp containing diverse mineral phases, various mineral sizes, adsorption of various reagents, different products oxidation, precipitations (often colloidal), and
polysulfide $S_n^{2-}$ species (resulting from loss of metal ions, usually $Fe^{2+}$) on mineral surfaces (Smart et al. 2003a; 2003b, Smart et al., 2007).

Numerous studies have been conducted to evaluate the hydrophobic-hydrophilic (hydrophobicity) balance by mineral phases (Vickers et al., 1999; Piantadosi et al., 2000; Piantadosi & Smart, 2002; Duan et al. 2003). For adsorption studies in mineral flotation, quantification of surface species by TOF-SIMS and simply using the peak intensities of adsorbed and substrate signals are unsuitable (It does not take into account many of the matrix effects of mineral phases) (Piantadosi et al., 2000). To generalize, in the case of adsorption, the ion ratio of interest can be expressed as:

$$RPI = \frac{I_{ads}}{I_{ads} + I_{sub}}$$

(3-2)

Where RPI is the relative peak intensity, $I_{ads}$ is the integrated peak area of the ion fragment characteristic of the adsorbed molecule, and $I_{sub}$ is the integrated peak area of the ion fragment characteristic of the substrate. In principle, RPI is the relative peak intensity measured by TOF-SIMS (or RPI is the ideal parameter for adsorption studies since it has the character of $\theta$), the traditional measurement of uptake ($I_{ads}$) function of monolayer capacity ($I_{ads} + I_{sub}$), and $I_{sub}$ might be expected to vary regularly with the extent of coverage of the substrate adsorbent by the adsorption (Vickers et al., 1999).

This method of quantification yields a clearer illustration of the differences between concentrates and tails (Piantadosi & Smart, 2002). It is required to use eq.2 for each index (Vickers et al., 1999). Piantadosi et al. (2000) investigated the coverage of potassium isobutyl xanthate (IBX) and sodium diisobutylidithiophosphinate (DBPhos) adsorbed on the surface of galena by TOF-SIMS. They developed models which fully described both hydrophilic and hydrophobic indices of recovery of particles by flotation. An example of an initial development is described below:

$$Hydrophobic = \frac{DBPhos}{S} \left(ie \frac{I_{ads}}{I_{substrate}}\right)$$

(3-3)
Development of a more extensive hydrophobic/hydrophilic index may involve the ratios of a number of these indices, as shown above. For instance, the DBPhos/SO$_3$ indices may be chosen as a first attempt at a hydrophobic/hydrophilic ratio. An alternative hydrophobic/hydrophilic ratio has been chosen to form a more direct overall index ($I$), using the $I_{\text{ad}}/I_{\text{sub}}$ ratios.

\[
I = \frac{\text{DBPhos}}{S} \cdot \frac{\text{Pb}}{\text{PbOH}}
\]

Piantadosi and smart (2002) demonstrated that statistically, particles in the concentrate are more hydrophobic and separable than particles in the tail when both hydrophobic (collectors) and hydrophilic (oxidation products) species are combined (Piantadosi and smart, 2002). Piantadosi et al. (2002) continued their surface analysis by TOF-SIMS with the aim of investigation on the particle-by-particle statistics of hydrophilic and hydrophobic species on the surfaces of mixed samples (galena and pyrite) under flotation-related conditions. Using a similar procedure, they found that in the concentrate the surface of galena have less Ca/Pb, PbOH/Pb and oxy-sulphur species (SO$_3$/S) compared to articles in the tail. In other words, they were less hydrophilic. These differences are statistically considerable. Statistical results obtained for other species, such as Mg/Pb species, did not show any significant difference. This technique identified the effective species that correlate with flotation. Using a similar method, Duan et al. (2003) predicted an advancing contact angle of 71±2 (degrees) for the chalcopyrite particles in the Mount Isa Mines ore using the DTP/SO$_3$ ratio as measured by TOF-SIMS.

3.7. Detection of reactions on mineral surfaces during flotation

3.7.1. Platinum group metals (PGM)

Numerous studies have been conducted on flotation separation of minerals from the Merensky reef ore (Bushveld Igneous Complex, South Africa), containing platinum
group metals (PGM), and also metal sulphides which mostly include pentlandite, chalcopyrite and pyrrhotite. The main gangue phases of the ore are pyroxene and feldspar as well as minor quantities of talc, chlorite and chromite. Bulk PGM and sulphide flotation are the main treatment methods to optimize the recovery of valuable particles and remove gangue minerals. Surface chemistry analyses have been used to understand the mechanism of maximizing the concentration of valuable minerals (PGM and sulphide minerals), and also minimizing the recovery of gangue phases (pyroxene, feldspar, talc and chlorite) in concentrates to reduce their adverse effects on smelting (Malysiak et al. 2002, 2004; Shackleton et al., 2003; Lotter et al., 2008; Jasieniak and Smart, 2009, 2010).

Malysiak et al. (2002) utilized TOF-SIMS in their study of potential interactions between collector (sodium isobutyl xanthate), andionic activation (Ca ions) to demonstrate their effects on mineral surfaces in a pentlandite–feldspar flotation system. Analyses of the surface of feldspar particles indicated that the coverage of Cu species were lower in the presence of Ca ions compared with the presence of the collector ions. They revealed that the surface coverage of pentlandite by Cu species is hardly affected by the addition of Ca ions, and a higher proportion of Cu was detected on the surface of pentlandite particles compared with the feldspars. Also, TOF-SIMS data demonstrated that there is a positive correlation between the collector adsorption (xanthate) and the intensity of Cu species on the feldspar surfaces; xanthate ions were not observed on the feldspar surface in the absence of Cu. At pH 9, however copper and xanthate were both identified on feldspar surface indicating inadvertent Cu-xanthate activation. In summary, results indicated that in at low copper concentrations, limit inadvertent Cu feldspar activation potentially improving the concentrate grade (Malysiak et al., 2002).

The effect of the chelating agents (diethylenetriamine (DETA), ethylenediamine (EDA), triethylenetetramine (TETA), and ethylenediaminetetraacetic acid (EDTA)), to control inadvertent activation of Cu and Ni ions in the flotation separation of pentlandite from pyroxene was studied by Shackleton et al. (2003). TOF-SIMS results identified the presence of both Cu and Ni ions on pyroxene and pentlandite surfaces. Surface analyses of the same minerals in tests with the addition of EDA revealed a decrease in both Cu and
Ni from the mineral surfaces however the decrease appeared to be more significant for pyroxene.

Malysiak et al. (2004) used TOF-SIMS to evaluate mineral surface changes from a series of microflotation tests performed to maximize the flotation of pentlandite while simultaneously minimizing the proportion of pyroxene reporting to the concentrate. The results revealed that inadvertent activation of pyroxene by Cu and Ni ions can be minimized by the addition DETA. It was proposed that the decrease in these surface species is related to the development of soluble stable chelates and their removal from the mineral surface to the pulp.

Lotter et al. (2008) discussed the undesirable flotation behaviour of orthopyroxene showing talc rims in the processing of Bushveld Merensky deposits. TOF-SIMS surface chemical analyses of the grains with the talc rims did not show the activating Cu or Ni species on the surface, while Cu and Ni ions were identified associated with the non-talc rimed coarse liberated orthopyroxene grains. The data reveal that the orthopyroxene is reporting to the concentrate either by the natural floatability of the talc rim or inadvertent activation by Cu or Ni.

Jasieniak and Smart (2009) compared the surface chemistry of pyroxene reporting into the concentrate and into the tail to understand parameters that affect floatability of Merensky ores. TOF-SIMS results did not indicate an essential variation in copper-collector activation species on the surface of pyroxene particles from concentrate and tail. The essential difference on the particle surfaces was observed in the concentration of Mg and Si. Although these intensities may only be associated with clean surfaces of pyroxene, it is worth to mention that pyroxene inherently is a hydrophilic mineral, and would not be expected to float. Therefore the inadvertent flotation of pyroxene particles can be explained by the increase of hydrophobicity as a result of coverage their surfaces with talc particles (Jasieniak and Smart, 2009).

In 2010, Jasieniak et al used TOF-SIMS to detect species that could possibly activate and effect on the surface of coarse chromite in the flotation process of Bushveld complex. The main purpose of the investigation was a comparison between the surface chemical
properties of coarse chromite grains reporting to the concentrate and to the tail. TOF-SIMS images indicate a high intensity of magnesium and silicon-rich patches on the surface of recovered coarse chromite grains in the concentrate. The analyses reveal patches of altered magnesium silicate hydrophobic species of patches present on the mineral grains. A silicon to chromium intensity ratio from TOF-SIMS data identifies a discriminating floatability parameter for chromite in these samples (Jasieniak & Smart, 2010).

3.7.2. Sulfides

In 1992, Brinen et al. studied the reaction of a series of homologous collectors (dialkyldithiophosphinates) with the surface of natural galena using TOF-SIMS. The non-uniform distribution of the dithiophosphinate adsorption on the surface of various grains was demonstrated by TOF-SIMS images. Results revealed a possible correlation with the non-uniform adsorption and oxygen rich areas on sample surfaces. Also TOF-SIMS analyses showed an approximate relationship between flotation data as a function of pH and the relative amounts of the collector on the surface of galena crystals (Brinen et al., 1993).

TOF-SIMS mapping was used by Stowe et al. (1995) to discriminate sulphite phases (sphalerite, pyrrhotite, and pyrite), characterize the surface composition of the sulfide minerals, in particular amyl xanthate and di-isoamylidithiophosphate on the surface of sphalerite and galena from the mineral processing plant at the Geco Cu-Zn mine (Ontario, Canada). Using the relevant TOF-SIMS information, they could successfully distinguished reagents on the surface of mineral phases. More importantly, the intensity differences for activators and xanthate correlate and show that the relative difference in surface loading is related to recovery. The results also revealed that collector adsorption on the sulphide mineral grains were localized and non-uniform (Stowe et al. 1995).

Boulton et al. (2003), using TOF-SIMS surface analyses to examine factors controlling the recovery of sphalerite, reported that the intensity of FeOH on the surface of sphalerite reporting to the concentrate is less than that on their surface of sphalerite particles
reporting to the tail. They also reported that poor pyrite recovery is linked a significant proportion of surface FeOH, limiting Cu activation and xanthate adsorption.

TOF-SIMS has been used to identify the surface interaction mechanisms between sodium bisulphite (an effective depressant) ions and copper-activated sphalerite in the collectorless flotation. The results suggested that there is a significant change in the nature of the various sulphur species on the surface of grains which would partially account for the collector less flotation (Khmeleva et al., 2005). This study was continued using TOF-SIMS to examine the interaction between sulphite ions, the collector (isobutyl xanthate) and the sphalerite surface. Analyses showed that sodium bisulphite interacts with the surface of Cu activated sphalerite regardless of the collector. The postulated mechanism is that sodium bisulphite results in oxidation of the polysulphide species on the sphalerite surface, rendering it more hydrophilic and less floatable. In addition a greater proportion of ZnOH was observed on the surface of the sphalerite grains after sodium bisulphite addition (Khmeleva et al., 2006).

In a similar study by Olsen et al 2012, both the TOF-SIMS and XPS analyses were used to identify the effect of ZnSO$_4$ and NaSO$_3$ on the inadvertent activation of sphalerite in a poly metallic ore. The data revealed that addition of sulfite ions through NaSO$_3$ dissociation adsorb to hydrophobic Cu coordinated S (polysulphide) generated as a result of Cu substitution for Zn. The sulfite ion decomposition of the polysulphides, generates thiosulfate, which is subsequently oxidized to sulfate. The effect is to remove the hydrophobic polysulphide while rendering the Cu ineffective for collector attachment.

In 2006, (Goh et al., 2006) designed experiments to examine the ability of TOF-SIMS analyses to distinguished monolayer from multilayer species arising from the interaction between thiol collectors and metal sulfides. Results revealed that the analysis can provide valuable data complementary to that obtained by XPS, and for all the systems studied, they were able to differentiate monolayer from multilayer coverage. According to these results, Goh et al. (2008) attempted to understand the undiminished floatability of sulfide minerals observed for collector (Cu and Ag thiolate multilayers) coverage exceeding a monolayer. TOF-SIMS results provided valuable information on the formation of
multilayer patches or islands on top of a chemisorbed monolayer and hence continued exposure of the monolayer in the presence of the multilayer. According to the results, it can be concluded that undiminished floatability of sulfides with multilayer collector coverage can probably be attributed to the patch-wise nature of the multilayer (Goh et al., 2008).

Zanin et al. (2009) applied TOF-SIMS to survey the surface chemistry of molybdenite in the concentrate from the bulk copper-molybdenum flotation circuit at Kennecott Utah Copper. Grains with the +150 µm were subject for the TOF-SIMS analysis. To understand the possible relationship between differences in surface composition of particles with their floatability, the surface of fast and slow floating particles was studied. The surface chemistry analysis indicated higher concentrations of Ca, Fe, Mg and K on the surface of slow floating molybdenite minerals compared to the fast floating grains. The flotation response and surface chemistry can be correlated to the presence of specific gangue phases present in the typical limestone skarn (LSN) ore. This investigation was continued by Gerson et al. (2012), who analyzed the surface chemistry of flotation stream samples to understand whether hydrophilic poisoning did actually occur on the chalcopyrite or molybdenite surfaces during the processing of monzonite ore (MZ) blended with LSN, as opposed to simply a pro-rata effect of the individual ore types. TOF-SIMS data suggested that blending had little effect on chalcopyrite flotation, since both minerals already had similar levels of surface contamination within the two ore types. However, as a result of blending, the formerly relatively clean molybdenite surfaces from the MZ ore were contaminated, and the flotation response was dramatically reduced.

In flotation of galena by xanthate, the recovery of chalcopyrite can be depressed (selective depression) with chitosan (a natural polymer extracted from crustacean shells). TOF-SIMS studies indicated that with presence of both minerals in the separation process, chitosan is selectively adsorbed on chalcopyrite, and the adsorption on galena was negligible (Fig. 3-4) (Huang et al., 2012a).
Further studies were done to understand the mechanism of selective interactions of chitosan on chalcopyrite compared with galena. The dominant stable species of CuNH$_3$ was found by TOF-SIMS on the surface of chalcopyrite as a result of reaction with chitosan. The TOF-SIMS data suggest that the main mechanism of selective adsorption of chitosan on the surface of chalcopyrite is the chemical interaction between the surface copper atoms with the protonated amine and (to a lesser degree) the hydroxyl groups on the structure of chitosan; the identification of species indicative of this chemical interaction was not observed on the surface of galena) (Huang et al., 2012b).

3.7.3. Other minerals

**Talc:** Talc, a common gangue phase in Ni sulphide deposits, is naturally hydrophobic and highly floatable. To reduce the floatability of talc, carboxymethyl cellulose (CMC) has been typically used as a depressant. TOF-SIMS was used to examine the characteristics CMC adsorption on the basal planes of New York talc. Surface analyses demonstrated that increased Ca in the pulp resulted in a more homogenous coverage of CMC and suggested that there was a link between surface Ca adsorption and CMC attachment (Parolis et al., 2007).
Studies have shown that even at low concentrations of Ca in an electrolyte solution at pH 9, CaOH\(^+\) can adsorb on the surface of talc. In tests with CMC, negligible adsorption of divalent Ca\(^{2+}\) ions was observed on the talc surface in the absence of CMC, however in the presence of CMC, Ca\(^{2+}\) uptake increased significantly. This information indicated that the main mechanism in the adsorption of CMC macromolecules on the surface of samples was the interaction between acid and metal hydroxyl species. TOF-SIMS data identified a positive correlation between CaOH\(^+\) intensity and the rate of CMC adsorption indicating surface adsorption of CMC is facilitated by hydroxylated Ca ions (Burdukova et al., 2010).

**Sylvinite (KCL):** The flotation recovery of coarse KCl particles with an amine collector (Armac HT) from the TaquariVassouras mine (Companhia Vale do Rio Doce; CVRD, Aracaju, Brazil) is affected by several mechanisms. Several years of experience has shown that an increase in carnallite (KCl.Ca(Mg)Cl\(_2\).6H\(_2\)O) content in the feed ore decreases the recovery of coarse KCl grains.

TOF-SIMS analysis was used to study the surface properties of coarse KCl particles from a series of flotation tests to understand the how the recovery of KCl is affected by the presence of high concentrations of carnallite. Analyses of laboratory tests indicated that an increase in solution Mg\(^{2+}\) concentration resulted in the nucleation and precipitation of fine NaCl (mostly) and KCl salt crystals on the surface of the coarse KCl grains. Their precipitation resulted in a diminished number of sites for collector adsorption and causing depression of the coarse KCl (Fig.3-5). The recovery data linked the increase in Mg content to the increase of carnallite in the feed and explained the reduction in coarse KCl hydrophobicity and flotation recovery (Weedon et al., 2007a, 2007b).

**Pyrochlore:** Recent investigations on the mineralogy of samples from the rougher circuit at the Niobec plant (Quebec, Canada) have shown that high iron content pyrochlore grains appear to be less recoverable than those with a lower iron content (Chehreh chelgani et al., 2012a). TOF-SIMS was used to study the relationship between the matrix and surface properties of different pyrochlore grains, and their impact on collector (diamine) adsorption. Analyses revealed that the species indicative of the
diamine molecules, favour the surface of low iron pyrochlore more than the iron rich samples. TOF-SIMS along with XPS analyses showed that higher surface oxidation in high iron grains reduces diamine attachment and yield low recovery (Chehreh chelgani et al., 2012b).

Fig. 3-5. TOF-SIMS images of mixed salt precipitates (produced from the addition of 5 wt.% Mg$^{2+}$ to saturated brine) (Wooden et al., 2007).

**Free gold:** TOF-SIMS was applied to identify factors controlling collector loading on gold particles towards optimizing the flotation scheme and improving gold recovery. TOF-SIMS analyses indicated that the collector loading (di-isobutyl dithiophosphate, DIBDTP) is sensitive to changes in surface silver. Results indicated that silver would activate flotation of gold and there is a strong relation between concentration of silver on the surface of gold and the loading of certain collectors (Dimov & Chryssoulis, 2004a, 2004b).

### 3.8. Summary

Mineral separation by flotation is a complex procedure. Establishing a chemical evaluation of a particular process requires a detailed, integrated examination of the flotation data in the context of the mineralogical, liberation, solution and mineral surface data from the various stream products. Given that the top few monolayers of mineral surfaces play the critical role in selective flotation, a detailed evaluation of the surface
chemistry of both value and non-value minerals in the process, is essential. The Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) technique is uniquely suited for mineral surface evaluation. Numerous studies have shown that TOF-SIMS has the required level of sensitivity for detection and analysis of mineral surfaces from the flotation process and, with the development and application of the modern day instruments, TOF-SIMS analyses is becoming more accessible and routine. The literature review indicates that TOF-SIMS analysis has a positive track record for evaluating factors effecting mineral recovery both in the laboratory and from industrial flotation systems.

The objective of this review was to examine and identify the various applications of the TOF-SIMS technique in the mineral processing context. There is significant information to indicate that a mineral surface from a flotation process is a patch work of different species, all of which can affect selective recovery. Examples of chemical transfer from one mineral phase to another affecting the flotation outcome have been reported by numerous TOF-SIMS analyses. Copper has been commonly identified by TOF-SIMS as an inadvertent activator of various sulphides. Similarly, surface analyses of recovered gangue silicate phases from a flotation process showed a positive correlation between the collector adsorption and the concentration of Cu and Ni species on gangue surfaces. Both Cu and Ni are implicated as factors controlling inadvertent collector attachment and flotation.

TOF-SIMS studies on the flotation of sulfide minerals also revealed a correlation between the non-uniform adsorption of collectors and oxygen rich areas on sample surfaces. The surface analyses also showed a difference in the ratio of collector to oxygen rich areas between the coarse and finer grains. The fine and intermediate sized grains had a higher proportion of oxygen rich areas identifying their greater potential for surface oxidation, likely in response to residence time in the grinding process. The technique in combination with other analytical tools has been used to understand the operative process in response to various reagents added to promote flotation or depression. In the flotation of galena by xanthate, chalcopyrite can selectively depressed with chitosan. The stable species of CuNH3 was identified on the surface of copper sulphide as a result of reaction.
with chitosan. Clearly mineral surface analysis by TOF-SIMS has the capacity to identify surface chemical factors controlling the partitioning of minerals to stream products.

Preferential oxidation of mineral surfaces during grinding and its relation to galvanic interaction has been well established for many years. TOF-SIMS has been used to validate and identify different reactions occurring on the surface of mineral phases during the grinding process. TOF-SIMS surface analyses of sulphides from a poly metallic ore ground with mild steel showed that iron hydroxide covered lead hydroxide on the surface of both pyrite and galena. This explained a reduction in recovery for both pyrite and galena when grinding in mild steel environments. In a similar study, TOF-SIMS analyses of pyrite and arsenopyrite grains ground with stainless steel balls and those of various Cr contents identified selectivity in the degree of mineral surface oxidation in relation to ball composition. The surface analysis by TOF-SIMS validated the previously identified relationship between mineral recovery and the electrochemical activity of both the minerals and grinding media.

TOF-SIMS investigations have also been conducted to evaluate the possible correlation between surface contact angle and surface chemistry. These studies suggested that TOF-SIMS analysis can be utilized as a predictive method for performing a hydrophobicity evaluation on the surface of minerals. A predication of contact angle based on ion species intensities has several benefits over the conventional techniques as the estimation can be carried out concurrently for different particle surfaces regardless of the particle size. Direct evaluation of the hydrophobic-hydrophilic balance based on a statistical evaluation of ion intensity on the mineral surfaces indicated that when both hydrophobic (collectors) and hydrophilic (oxidation products) species are combined, particles in the concentrate are more hydrophobic than those in the tail. The TOF-SIMS examination was able to clearly link contact angle to surface chemistry a thereby provide a recovery prediction evaluation.

Although the quantity of research carried out in this field is limited, the reports that have been published to date provide compelling evidence of successful applications of TOF-
SIMS within the flotation context. The review identifies the capacity of the TOF-SIMS technique to provide reliable surface chemical data for evaluating factors controlling stream partitioning in various mineral flotation processes. Furthermore TOF-SIMS data can potentially be used to select the most suitable commercially available reagents to optimize selectivity and recovery, or to help design reagents particularly suited to the mineral in flotation process. Ultimately, as part of an integrated approach, TOF-SIMS surface chemical analyses may become indispensable for evaluating and/or designing flotation processes.

3.9. References


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Chapter 4

4 Study of pyrochlore surface chemistry effects on collector adsorption by TOF-SIMS

4.1. Introduction

Pyrochlore, the most abundant niobium containing mineral (Perrault and Manker, 1981) is economically recovered in Brazil, China, and Canada (Kouptsidis et al., 2008). Flotation is the preferred and most cost-effective method for pyrochlore recovery (Burks, 1958; Shapolov and Polkin, 1958; Zakharov et al., 1967; Razvozzhaev and Nikiforov, 1972; Bogdanov et al., 1973; Abeidu, 1974; Raby and Desrochers, 1975; Wilson, 1979; Biss and Nadeau, 1982; Biss, 1985). The Saint-Honoré mine (west of Saint-Honoré near Chicoutimi, Quebec) is the largest deposit of pyrochlore in North America. Economic recovery of pyrochlore by Niobec Inc. has continued since 1974 (Kouptsidis et al., 2008).

Numerous experiments were performed on the influence of surfactants and type of water to optimize pyrochlore recovery and grade during flotation (Gomez et al., 1987; Rao et al., 1988; Dufresne and Goyette, 2004; Belzile, 2009). These investigations showed that the pyrochlore surfaces in the desired pH (6–7) flotation range were negatively charged and therefore flotation of the pyrochlore was accomplished by the mild cationic collector, tallow diamine acetate (Dufresne and Goyette, 2004; Belzile, 2009).

Recent mineralogical investigations on samples from the rougher banks at the Niobec plant have shown that pyrochlore grains with high Fe content appear to be less recoverable than those with a lower Fe content. The analysis identified that the flotation response is related to matrix (structural) Fe rather than Fe occurring as inclusions within the pyrochlore and suggested that poor floatability is linked to matrix composition (Chehreh Chelgani et al., 2012).

Surface chemistry is the principal determinant for selective separation of the various mineral phases. With a rise in the complexity of the ores processed by flotation, understanding the reactivity of mineral surfaces in this context is becoming increasingly
more important. Advanced surface analytical tools are unique in that they have the capacity to link mineral surface characteristics, to process parameters in order to better understand a flotation response (Hart et al., 2006; Biesinger et al., 2007). Several studies have shown that Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) has the capacity for measuring the relative loading characteristics of surface species, mapping their distribution between phases and streams, and therefore can be utilised as a diagnostic tool for process optimization (Chryssoulis et al., 1995; Nagaraj and Brinen, 1996, 1997, 2001; Smart et al., 2000, 2006; Piantadosi et al., 2000; Piantadosi and Smart, 2002; Hart et al., 2006).

The purpose of this chapter is to investigate the surface chemical factors affecting the adsorption of the cationic collector tallow diamine on both high iron (Fe-pyrochlore) and low iron pyrochlore (pyrochlore). The investigation is a follow-up to previous work where flotation recovery was linked to matrix Fe content. TOF-SIMS was used to explore the possible factors affecting reagent absorption on the pyrochlorides. These investigations will potentially aid in modeling molecular interactions of the collector and the pyrochlore surface under specific conditions. The results may be used to select the most suitable commercial reagents to optimize selectivity and recovery, or help to design reagents particularly suited to the mineral in this flotation context.

4.2. Experimental methodology

Samples (Fe-pyrochlore and pyrochlore) were obtained from the Niobec mine. In order to evaluate collector adsorption variability and potential causes for identified differences, samples of both high and low Fe pyrochlore were freshly fractured and conditioned with tallow diamine at plant operating conditions. Test conditions were as follows; agitation of the minerals for 10 min in 227 ml deionized water (DIW) (pH 6.2) mixed with 0.05 ml tallow diamine. After 10 min the samples were removed, repeatedly rinsed with DIW (pH 6.2) then immediately transferred to the instrument for analysis.

The instrument used in this work is an ION-TOF, TOF SIMS IV secondary ion mass spectrometer. This technique allows for the analysis of the outermost atomic layers of a
surface by mass spectrometry. An isotopically enriched $^{209}$Bi$^+$ (Bismuth) primary ion beam is rastered across an area of interest on the sample surface.

The raster size used was ~300 µm with an acquisition time of 100 scans. The bombardment of the surface with the bismuth primary ion beam induces the emission of positively and negatively charged secondary ions from the sample surface. These secondary ions are extracted from the sample surface and mass analyzed using a time-of-flight mass spectrometer. A plot of secondary ion intensity versus mass results in a traditional first order mass spectrum, with a resolution of 10,000 above 200 atomic mass units (amu). TOF-SIMS can detect species with concentrations in the ppm range. The data were recorded with full mass spectra in 256 × 256 pixels using a hybrid focused bunched mode $^{209}$Bi$_3^+$ cluster ion beam with the following beam conditions for spatial resolution:

- Ion source: 25 keV Bi$^+$.
- Current: ~0.3 pA.
- Pulse: 1 ns.
- Beam spot size: ~1 µm.
- Raster area: generally 300 × 300 lm (variable).
- Mass range: 1–850 amu.
- Mass resolution: 10,000 amu.

Sample charging was neutralized with an electron flood gun.

4.2.1. Data treatment

Prior to analysis of the test samples, TOF-SIMS mass spectra of unconditioned freshly fractured high and low Fe pyrochlore grains, and tallow diamine were obtained. All raw spectra were processed using the IONTOF software. Peaks in the calibrated spectra were assigned to specific isotopes in accordance with their atomic mass unit (amu) and similarly peaks reflecting molecular species of the collector were assigned mass positions. The corrected ion intensity for each mass position, measured as the integrated
area under each peak corrected for dead times can be related to abundance of the particular specie. In order to compare intensities between areas of different dimensions, corrected intensities were normalized to the total number of counts for the areas examined (appendix II).

The analytical approach was to conduct comparative surface analyses of the different pyrochlore grains in order to determine statistically significant differences in the surface composition of species particularly related to collector adsorption and potential factors affecting adsorption. The analysis provides a comprehensive survey of the surface species on the mineral grains.

4.3. Results

The elemental composition of the samples, determined with energy dispersive X-ray spectroscopy (EDX) is shown in Table 4-1.

**Table 4-1. EDX analysis of high iron content (Fe-pyrochlore) and low iron content (pyrochlore) pyrochlore grains. The concentration data is expressed in weight %.

<table>
<thead>
<tr>
<th>Fe-Pyrochlore</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. Deviation</th>
<th>Pyrochlore</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>31.65</td>
<td>41.12</td>
<td>36.06</td>
<td>3.89</td>
<td>Oxygen</td>
<td>36.12</td>
<td>47.06</td>
<td>41.00</td>
<td>5.37</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.76</td>
<td>1.21</td>
<td>0.93</td>
<td>0.2</td>
<td>Sodium</td>
<td>2.88</td>
<td>5.91</td>
<td>3.93</td>
<td>1.35</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.44</td>
<td>0.59</td>
<td>0.51</td>
<td>0.06</td>
<td>Magnesium</td>
<td>*MDL</td>
<td>0.73</td>
<td>0.37</td>
<td>0.30</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.47</td>
<td>1.03</td>
<td>0.72</td>
<td>0.23</td>
<td>Calcium</td>
<td>6.62</td>
<td>12.82</td>
<td>9.49</td>
<td>2.73</td>
</tr>
<tr>
<td>Titanium</td>
<td>2</td>
<td>3</td>
<td>2.63</td>
<td>0.28</td>
<td>Titanium</td>
<td>2</td>
<td>3</td>
<td>2.27</td>
<td>0.43</td>
</tr>
<tr>
<td>Iron</td>
<td>14.28</td>
<td>20.30</td>
<td>16.63</td>
<td>2.58</td>
<td>Iron</td>
<td>*MDL</td>
<td>1.72</td>
<td>0.81</td>
<td>0.7</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.26</td>
<td>1.94</td>
<td>1.53</td>
<td>0.29</td>
<td>Strontium</td>
<td>1.15</td>
<td>5.62</td>
<td>3.82</td>
<td>1.96</td>
</tr>
<tr>
<td>Niobium</td>
<td>35.28</td>
<td>39.22</td>
<td>37.97</td>
<td>1.83</td>
<td>Niobium</td>
<td>28.79</td>
<td>37.25</td>
<td>33.33</td>
<td>3.54</td>
</tr>
<tr>
<td>Fluorine</td>
<td>*MDL</td>
<td>*MDL</td>
<td>*MDL</td>
<td>*MDL</td>
<td>Fluorine</td>
<td>2.92</td>
<td>5.59</td>
<td>4.57</td>
<td>1.17</td>
</tr>
</tbody>
</table>

* MDL = method detection limits, elements may be present but are below detection.
TOF-SIMS spectra in the specified mass position representative of the collector, pyrochlore and Fe-pyrochlore, without conditioning, and after conditioning with tallow diamine are given in Fig. 4-1. Spectral mass positions representative of tallow diamine occur at mass 327 amu (TDM-1), 351 amu (TDM-2), and 369 amu (TDM-3). None of the diamine representative peaks were identified in the spectra of the untreated pyrochlore samples. The overlain spectra illustrate that the intensity of the collector appears to be stronger on the surface of the pyrochlore grains relative to the Fe-pyrochlore grains (Fig. 4-1).

Fig.4-1. Positive ion ToF-SIMS spectrum for tallow diamine (collector), high and low iron content pyrochlore (pyrochlore, and Fe-pyrochlore) with and without treatment. (a: Collector, b: Fe-Pyrochlore without conditioning, c: Pyrochlore without conditioning, d: Fe-pyrochlore after conditioning, e: Pyrochlore after conditioning).

The correlation between two variables reflects the degree to which the variables are related. The most common measure of correlation is the Pearson Product Moment
Correlation (called Pearson’s correlation). The value for a Pearson’s correlation can fall between 0 (no correlation) and 1 (perfect correlation). In order to evaluate the relationship between species identified on the surface of pyrochlore grains Pearson correlations were performed on the species intensity data. Inter-correlations between selected ions on the surface of treated pyrochlore and Fe-pyrochlore grains are given in Table 4-2. These results indicate that there is no significant linear correlation between Fe and the collector species TDM-1, TDM-2, and TDM-3.

Table 4-2. Pearson correlation (r) between the average normalized mass intensities for selected species measured on the surface of both high and low iron content pyrochlore gains.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Nb</th>
<th>Na</th>
<th>Ca</th>
<th>Fe</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.954</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.929</td>
<td>0.932</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>-0.111</td>
<td>-0.244</td>
<td>-0.250</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.718</td>
<td>0.792</td>
<td>0.869</td>
<td>-0.186</td>
<td>1.000</td>
</tr>
<tr>
<td>*TDM-1</td>
<td>0.709</td>
<td>0.674</td>
<td>0.486</td>
<td>0.032</td>
<td>0.259</td>
</tr>
<tr>
<td>*TDM-2</td>
<td>0.532</td>
<td>0.585</td>
<td>0.379</td>
<td>0.027</td>
<td>0.276</td>
</tr>
<tr>
<td>*TDM-3</td>
<td>0.495</td>
<td>0.631</td>
<td>0.437</td>
<td>0.118</td>
<td>0.373</td>
</tr>
</tbody>
</table>

*TDM-1, TDM-2, TDM-3 peaks for tallow diamine molecular ion at mass 327, 351, and 369, respectively.

Whereas the linear correlation data suggests that there is no relationship between collectors and Fe intensity, the relationship is clearly illustrated graphically where intensities of various species on the surface of the pyrochlore grain are compared. A comparison of the normalized intensities of NH4, TDM-1, TDM-2, and TDM-3 mass positions (representative of the tallow diamine) for treated samples reveals a preference for these species on the surface of the pyrochlore relative to the Fe-pyrochlore (Fig. 4-2). Discrimination in surface species in favour of Fe rich pyrochlore grains was also noted.
for Fe, O, OH and FeOH (Fig. 4-3). Discrimination in favour of Fe poor pyrochlore grain surfaces was noted for fluorine (without conditioning samples) (Fig. 4-4).

**Fig.4-2.** Box and whisker plots illustrating the relative intensity of cationic collector mass species on the surface of the conditioned Fe-pyrochlore (high iron) and pyrochlore (low iron) grains.
Fig.4-3. Box and whisker plots illustrating the relative intensity of oxygen and hydroxide on the surface of conditioned pyrochlore particles.

Fig.4-4. Negative mass spectra on the surface of untreated particles.
4.4. Discussion

The data suggest that Fe-pyrochlore grains had, on average, less tallow diamine on their surfaces when compared to the low iron content pyrochlore. Moreover, Fe-pyrochlore grains have more Fe along with FeOH, OH and O on their surface, potentially indicative of preferential oxidation or at the very least, a greater proportion of surface oxidation species. Observations by Abeidu (1974) and Chehreh Chelgani et al. (2012), that indicate pyrochlore grains with high Fe content appear to be less recoverable, can possibly be related to preferential surface oxidation of the Fe rich pyrochlore rendering the surface unsuitable for collector attachment. Previous investigations have also suggested that a higher proportion of Fe possibly decreases the negative surface charge on grains, potentially preventing the adsorption of the cationic amine collectors (Barros et al., 2008; Chehreh Chelgani et al., 2012).

From this study, it is evident that the surface of Fe-pyrochlore grains contains a greater intensity of species indicative of oxidation relative to the low Fe pyrochlore. In oxide minerals, the magnitude of the negative surface charge is determined by the density of the structural (matrix compound) or adsorbed potential-determining negative ions (i.e. N-, F-, Cl-, etc.) (Somasundaran and Agar, 1967; Somasundaran, 1968; Elimelech et al., 1994). According to the previous studies on Niobec samples, the surface of pyrochlore was negatively charged in the 6–7 pH range (Dufresne and Goyette, 2004; Gomez, 1987; Rao et al., 1988; Belzile, 2009). Although there was little discussion on surface charge in relation to matrix chemistry, the exhibited negative surface charge may be related to the presence of negative ions in the matrix or attached to the surface. According to the results in this study (Fig. 4-4), the average normalized intensity of fluorine on the surface of pyrochlore is greater than that on the surface of Fe-pyrochlore particles. Higher fluorine contents in the low iron pyrochlore grains were also detected in the EDX analysis (Table 4-1), suggesting that the F surface expression may be related to the matrix composition.

From these analyses better flotation performance by the low Fe pyrochlore grains is likely in response to the greater proportion of cationic collectors attached to their surface. Their preference for attachment may be related to a higher proportion of near surface
negatively charged matrix ions effectively increasing the negative surface charge. Poor collector attachment to the Fe-pyrochlore grain surface may be related to the presence of oxidative species (Fig. 4-3). As the mineral surface becomes increasingly covered with metal oxide/hydroxide species, the surface becomes increasingly less negative and can even become positively charged (Fornasiero et al., 1992, 1994; Witika and Dobias, 1993; Fairthorne et al., 1997; Fullston et al., 1999; Barnes et al., 2009). From this data, it appears that surface oxidation negatively affects collector attachment and, that an increase in surface oxidation is linked to higher proportions of matrix Fe in the pyrochlore structure.

4.5. Conclusion

Surface composition controls the surface reactivity and consequently plays an important role in determining flotation behaviour of minerals. Surface analysis techniques such as TOF-SIMS allow for a direct ex situ determination of the degree of collector adsorption on the surfaces of minerals. The present study utilises the TOF-SIMS technique to investigate the adsorption of the cationic collector, tallow diamine, on the surface of different types of pyrochlore (high iron and low iron content). The TOF-SIMS results verify a relationship between pyrochlore surface reactivity and Fe content in the mineral matrix. It was demonstrated that the intensity of the oxidative species O, OH and FeOH was greater on the surfaces of high Fe pyrochlore particles in comparison with low Fe pyrochlore particles. Furthermore, the intensity of collector species was significantly higher on the surface of the Fe poor pyrochlore. The link between surface and matrix chemistry is identified. The results from these tests at least partially explain the flotation selectivity of low Fe pyrochlore grains relative to high Fe pyrochlore grains, where preferential surface oxidation favours the high Fe pyrochlores resulting in diminished collector attachment and poor recovery.

4.6. References


Chapter 5

5 Study the relationship between the compositional zoning of high iron content

5.1. Introduction

In North America, Niobec is the only operating Nb extraction facility which has recovered pyrochlore \((\text{Na, Ca})_2\text{Nb}_2\text{O}_6(\text{OH, F})\), the most abundant niobium containing mineral, from the St-Honoré carbonatite deposit by froth flotation. In the Niobec plant, the pyrochlore surfaces in the desired pH (6–7) flotation range were negatively charged and therefore flotation of the pyrochlore was accomplished by the cationic collector, tallow diamine acetate (Dufresne and Goyette, 2004; Belzile, 2009).

Poor flotation of high iron pyrochlore is noted in the plant (Rao et al., 1988, Chehreh Chelgani et al., 2012a). Investigations indicated that the Fe increase in the pyrochlore is not a result of Fe rich inclusions, but rather it has been identified as an increase in matrix Fe content, this also suggests that poor floatability is linked to higher matrix Fe content (Chehreh Chelgani et al., 2012a). Surface chemical analyses of high and low iron pyrochlores by TOF-SIMS verified a relationship between pyrochlore surface reactivity and Fe content in the mineral matrix, and demonstrated that the intensity of collector species was significantly higher on the surface of the Fe poor pyrochlore. Surface analyses revealed that the flotation selectivity of low Fe pyrochlore grains relative to high Fe pyrochlore grains, was in response to surface oxidation of the high Fe pyrochlore, resulting in diminished collector attachment and poor recovery (Chehreh Chelgani et al., 2012b).

Zonation in pyrochlore \((\text{A}_2\text{B}_2\text{O}_7)\) mineral groups is well recognized but less well understood. This is due, in part, from failure to recognize secondary alteration (replacement) phenomena and to distinguish them from primary (growth) features (Sharygin et al., 2009). Lumpkin & Ewing (1995 & 1996) described alteration trends in pyrochlore from a range of parageneses and weathering environments. They identified three trends relating to alteration: “primary”, “transitional”, and “secondary”. The
distinction is compositionally related, using triangular diagrams with apices corresponding to divalent A-site cations (Zurevinski & Mitchell, 2004).

In this chapter, the relationship between compositional zoning and surface chemistry of high iron pyrochlore grains from the Niobec deposit were investigated. To the authors' knowledge, it is the first record of compositional zoning in Fe pyrochlore for the Saint-Honoré deposit. This work describes zoning and chemistry of the Fe pyrochlore mineral, which is the main source of Nb. The study utilized energy dispersive X-ray spectroscopy (EDX) to measure concentrations of the main matrix elements in zoned areas of Fe pyrochlore grains, which ultimately will affect the surface chemistry and factors controlling collector attachment. Time of flight secondary ion mass spectroscopy (TOF-SIMS) analyses were performed to examine the surface chemistry of Fe pyrochlore grains from the various areas in order to identify variability in reagent adsorption along with possible factors affecting the absorption. The main aim of this chapter is to link pyrochlore matrix composition to surface chemistry in an attempt to relate the noted variability in flotation recovery to compositional zoning. The results will be used to better understand the effect of compositional zoning on collector loading, the collector adsorption mechanism, and selective flotation.

5.2. Experimental

The concentration of matrix elements were measured in the Fe pyrochlore grains with a LEO 440 SEM equipped with a Gresham light element detector and a Quartz XOne EDX system. The instrument was operated at 20 keV, 400 pA. Samples were sputter-coated with carbon in order to prevent charging during analyses.

In order to evaluate collector adsorption variability and potential causes for identified differences, samples of Fe pyrochlore (6 large pyrochlore grains (3-6 mm)) were freshly fractured, polished and conditioned with tallow diamine at plant operating conditions. Test conditions were as follows; agitation of the minerals for 10 min in 227 ml deionized water (DIW) (pH 6.2) mixed with 0.05 ml tallow diamine. After 10 min the samples were
removed, repeatedly rinsed with DIW (pH 6.2) then immediately transferred to the instrument for analysis.

In order to analyze the outer-most layer of samples, an ION-TOF, TOF SIMS IV secondary ion mass spectrometer was used in this study. An isotopically enriched 209Bi+ (Bismuth) primary ion beam was rastered across an area of interest on the sample surface. The raster size used was ~300 µm with an acquisition pattern comprised of 100 scan lines. In order to examine the surface chemistry of compositional zones and also to identify variability in reagent adsorption in different zones, the surfaces of fresh and conditioned samples were analysed and then compared. Spectral mass positions representative of tallow diamine occur at mass 207amu (TDM-1), and 327amu (TDM-2) (S. Chehrehchelgani et al., 2012b, 2013).

5.3. Results and discussion

5.3.1. EDX

In general, alteration of pyrochlore (A$_2$B$_2$O$_7$) involves loss of F, Na, and Ca driving the altered Fe pyrochlore composition toward the A$^{2+}$ cation-vacancy (Lumpkin & Ewing, 1996). At Saint-Honoré, pyrochlore formed throughout magmatic crystallization (Fournier, 1993). Pyrochlore minerals at Saint-Honoré have A sites commonly occupied by Ca, Na, Sr and Fe. Their B sites are commonly occupied by Nb, and Ti. In Fe pyrochlores, the grains exhibit compositional zonation, reflecting changes in the fluid composition during crystal growth. Optical microscope and back-scattered electron images, along with semi-quantitative elemental analyses of selected areas on a Fe pyrochlore grain are given in Fig 5-1. X-ray concentration maps for the same pyrochlore grain are given in Fig. 5-2. All images reveal structure and compositional zoning in the Fe pyrochlore samples. Denomme et al. (1982) considered that ferro pyrochlores having zonation formed from pyrochlore by addition of iron.
5.3.2. TOF-SIMS

The dominant peak positions for the cationic collector (tallow diamine acetate) examined and the parent and mass fragment positions (207 and 327 amu) were used to identify the presence of the reagent and assess variations in loading between different compositional zones of the samples investigated.

The relationship between collectors and Fe intensity is clearly illustrated graphically where intensities of various species on the surfaces of different compositional zones of the Fe pyrochlore grains are compared. A comparison of the normalized intensities of 207 amu, and 327 amu mass positions for treated samples reveals a preference for these species for the surface of the low Fe areas relative to the high Fe areas (Fig. 5-3).

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>F</th>
<th>Na</th>
<th>Al</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Sr</th>
<th>Nb</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area 1</td>
<td>35.89</td>
<td>*MDL</td>
<td>0.65</td>
<td>0.42</td>
<td>0.77</td>
<td>3.19</td>
<td>15.22</td>
<td>1.52</td>
<td>41.65</td>
<td>0.7</td>
</tr>
<tr>
<td>Area 2</td>
<td>36.3</td>
<td>2.35</td>
<td>4.63</td>
<td>0.44</td>
<td>12.93</td>
<td>2.54</td>
<td>0.43</td>
<td>2.14</td>
<td>37.7</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*MDL: Method detection limits, elements may be present but are below for detection.

Fig.5-1. Optical microscopic (right) and BSE images (left), and EDX analysis of a Fe pyrochlore grain at wt%.
Discrimination for surface species Fe, O, and OH in favour of Fe rich areas was also observed (Fig. 5-3).

Fig.5-2. Elemental maps for a zoned crystal of Fe- pyrochlore form Saint-Honoré deposit.
Fig. 5-3. Box and wisker plots illustrating the relative intensity of oxygen, hydroxide and cationic collector mass species on the surfaces of the conditioned high and low iron compositional zones of Fe pyrochlores. The horizontal bars in the boxes represent the median (mean of the data).
The data indicate that high iron zones have, on average, less tallow diamine on their surfaces when compared to the low iron content zones. Moreover, high Fe parts have more Fe along with OH and O on their surface, potentially indicative of preferential oxidation or at the very least, a greater proportion of surface oxidation species.

The link between diminished collector loading and a greater presence of oxidized species suggests that attachment is not favoured where oxidation occurs. Moreover, these areas are consistently higher in Fe content suggesting that areas of preferential oxidation and poor collector loading are linked to mineral matrix composition. These results are in agreement with previous studies by Rao et al. (1988) and Chehreh Chelgani et al. (2012a), who noted poor flotation of iron pyrochlore in the plant. The results here reveal that pyrochlore grains with outer Fe rims may not be easily recovered in the current flotation process.

5.4. Conclusion

SEM–EDX analysis of Fe pyrochlore has identified that the high iron content pyrochlores are compositionally zoned. The TOF-SIMS results verify a relationship between pyrochlore compositional zoning and collector loading. The surface analysis demonstrated that the intensity of the oxidized species O and OH was greater in zones corresponding to high matrix Fe content. The surface analysis also revealed that collector loading favours zones with low matrix Fe content, indicating that oxidation particular to the Fe zones inhibits collector attachment. This study identifies the link between collector attachment and compositional zoning in Fe pyrochlores.

5.5. References


Chapter 6

6 Pyrochlore surface oxidation in relation to matrix Fe composition: a study by X-ray photoelectron spectroscopy

6.1. Introduction

The separation of pyrochlore, which is the main source of niobium, from the remainder of the gangue phases in the Saint-Honoré Carbonatite Nb deposit (Niobec) is accomplished by froth flotation. The overall Nb recovery at Niobec is less than 60%. Investigations directed towards understanding the factors leading to poor recovery include: Gomez et al., 1987a, b who studied the influence of surfactants and type of water to optimize pyrochlore recovery and grade during flotation and showed plant recycle water decreased selectivity and increased reagent consumption; Rao et al., 1988 who noted poor flotation of iron pyrochlore in the plant; Dufresne, and Goyette, 2004; Belzile, E., 2009; Ni et al., 2012 reported that the pyrochlore surfaces in the desired pH (6–7) flotation range were negatively charged and therefore flotation of the pyrochlore was accomplished by the cationic collector, tallow diamine acetate.

Recent work by Chehreh Chelgani, et al. (2012a) using SEM-EDX analyses revealed that the Niobec deposit contains pyrochlore grains of both high (Fe-pyrochlore) and low iron (pyrochlore) contents. The study also revealed that high Fe pyrochlore grains appear to be less recoverable than those with a lower Fe content, suggesting that pyrochlore flotation is at least partially linked to mineral composition.

Further work by the same group using TOF-SIMS analysis identified a potential relationship between pyrochlore matrix composition and collector adsorption (Chehreh Chelgani, et al., 2012b). The study showed that species indicative of the cationic collector (identify the collector) favour the surface of Fe poor pyrochlore relative to the Fe rich variety. The TOF-SIMS analyses also revealed a negative relationship between collector loading and the presence of Fe and related oxidation species. These results suggested a potential scenario where higher surface iron content could promote preferential oxidation.
or at the very least, is linked to a greater proportion of surface oxidation species thereby interfering with collector adsorption.

Zonation in pyrochlore \((A_2B_2O_7)\) mineral groups is well recognized but less well understood. This is due, in part, to difficulties in recognizing and distinguishing secondary alteration (replacement) phenomena from primary (growth) features \((\text{Sharygin et al., 2009})\). Recent work by \text{Chehreh chelgani et al., (2013)} identified compositional zoning in the structure of Fe-pyrochlore grains from Niobec; two distinct zones were observed, high iron and low iron zones. TOF-SIMS analyses of pyrochlore grains conditioned with the reagent (tallow diamine acetate) identified that the mass species indicative of the collector favour the regions of low iron content. Furthermore the low iron areas also show a lower relative proportion of species indicative of oxidation. The results identified the link between Fe pyrochlore compositional zoning, and area selective collector loading \((\text{S. Chehreh Chelgani, 2013})\).

Surface sensitive techniques, scanning Auger microscopy (SAM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), SEM and X-ray photoelectron spectroscopy (XPS) along with the more indirect methodologies like zeta potential, and cyclic voltammetry \((\text{Smart, 1991; O’ Connor et al., 1992; Laajalehto et al., 1993; Hochela, 1995; Kim et al., 1995; Peng et al., 2012})\) have been used for more than 20 years in a variety of studies related to the mechanisms of oxidation in mineral flotation. Among these techniques, XPS is the most suitable for identifying surface oxidation products and has probably contributed more understanding on the mechanisms of surface chemical actions in flotation than any other surface analytical technique \((\text{Buckley and Woods, 1985a, b, 1987, 1991; Smart, 1991; Smart et al., 1999, 2000, 2003a, 2003b, 2007; Jones et al., 1992; Fornasiero et al., 1994; Prestidge et al., 1995; Descostes et al., 2000; Hart et al., 2006; Fredriksson & Holmgren, 2007; Gerson & Jasieniak, 2008; Olson et al., 2012})\). It is well established that metal sulfide minerals exhibit oxide and hydroxide species on their surface after exposure to air or aqueous solution during mineral processing. However, information regarding the surface chemistry and changes in response to variability in pulp conditions both experimental and from plant environments is limited \((\text{Kim et al., 1995; Smart et al., 1998})\).
In this chapter XPS analyses were performed to examine the variability in surface oxidation of compositional zoning in pyrochlore grains with different Fe content. The aim of the study is to link pyrochlore matrix composition to variability in surface oxidation in order to evaluate this relationship to the observed mineral recovery. The results will provide some understanding regarding the loss of selected pyrochlore grains. The results will also be used towards the selection of potential alternative commercial reagents for optimizing selectivity and recovery, or to help design reagents particularly suited for pyrochlore in this flotation context.

6.2. Experimental

Pyrochlore grains (6 grains) were collected from the Saint-Honoré carbonatite deposit, Niobec, Quebec, Canada. The concentration of matrix elements were measured in pyrochlore grains with a LEO 440 SEM equipped with a Gresham light element detector and a Quartz XOne EDX system. The instrument was operated at 20 keV, 400 pA. Samples were sputter-coated with carbon in order to prevent charging during analyses. X-ray concentration maps for a Fe-pyrochlore grain is given in Fig.6-1. The EDX analysis of Fe-pyrochlores is presented in Table 6-1.

The XPS analyses were carried out with a Kratos Axis Nova spectrometer using a monochromatic Al Ka source (15 mA, 14 keV). The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f7/2 line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p3/2 line of metallic copper. Binding energy accuracy is ±0.025 eV. The Kratos charge neutralizer system was used on all specimens. Survey spectra were collected with a pass energy of 160 eV from an analysis area of ~300 X 700 µm. High-resolution spectra were obtained using either a 20 eV or 40 eV pass energy and an analysis area of ~300 X 700 µm. Spectra were analysed using Casa XPS software (version 2.2.107)(Fairley, 1999–2005).

In order to develop a baseline for comparative analyses between high and low Fe zones, selected grains were mounted in epoxy and polished to a 0.3 micron finish. The grains
were then sputtered in vacuum (4 days to sputter surfaces of all 6 grains) in order to
generate fresh surfaces for analyses then were subsequently analysed. To examine
differences in surface species in relation to oxidation, the fresh samples (subsequent to
sputtering) were removed from the instrument and placed in oxygen saturated deionised
water (pH 6.2) for 30 min. After reaction the samples were removed, and placed
immediately into the instrument and analysed.

Fig.6-1. Optical microscopic image, BSE image, and elemental maps for zoned crystal of
a Fe-pyrochlore for St- Honoré deposit.
Table 6-1. EDX analysis of different zones in Fe-pyrochlore grains from Niobec. The concentration data is expressed in weight %.*MDL = method detection limits, elements may be present but are below detection.

<table>
<thead>
<tr>
<th>Fe zone</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. Deviation</th>
<th>Low Fe zone</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>35.89</td>
<td>36.89</td>
<td>36.48</td>
<td>.52</td>
<td>Oxygen</td>
<td>33.65</td>
<td>37.78</td>
<td>35.91</td>
<td>2.09</td>
</tr>
<tr>
<td>Florin</td>
<td>*MDL</td>
<td>*MDL</td>
<td>*MDL</td>
<td>*MDL</td>
<td>Florin</td>
<td>2.35</td>
<td>3.45</td>
<td>2.83</td>
<td>.56</td>
</tr>
<tr>
<td>Sodium</td>
<td>.57</td>
<td>.90</td>
<td>.71</td>
<td>.17</td>
<td>Sodium</td>
<td>4.63</td>
<td>6.08</td>
<td>5.15</td>
<td>.81</td>
</tr>
<tr>
<td>Aluminum</td>
<td>.32</td>
<td>.49</td>
<td>.41</td>
<td>.085</td>
<td>Aluminum</td>
<td>.31</td>
<td>.45</td>
<td>.40</td>
<td>.08</td>
</tr>
<tr>
<td>Calcium</td>
<td>.70</td>
<td>1.09</td>
<td>.85</td>
<td>.21</td>
<td>Calcium</td>
<td>11.23</td>
<td>12.93</td>
<td>11.80</td>
<td>.98</td>
</tr>
<tr>
<td>Titanium</td>
<td>2.50</td>
<td>3.19</td>
<td>2.74</td>
<td>.39</td>
<td>Titanium</td>
<td>1.80</td>
<td>2.74</td>
<td>2.36</td>
<td>.49</td>
</tr>
<tr>
<td>Iron</td>
<td>11.81</td>
<td>15.22</td>
<td>13.73</td>
<td>1.74</td>
<td>Iron</td>
<td>*MDL</td>
<td>.94</td>
<td>.46</td>
<td>.47</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.52</td>
<td>1.69</td>
<td>1.58</td>
<td>.093</td>
<td>Strontium</td>
<td>1.16</td>
<td>2.14</td>
<td>1.71</td>
<td>.50</td>
</tr>
<tr>
<td>Niobium</td>
<td>41.48</td>
<td>43.69</td>
<td>42.27</td>
<td>1.23</td>
<td>Niobium</td>
<td>36.30</td>
<td>37.85</td>
<td>37.28</td>
<td>.85</td>
</tr>
</tbody>
</table>

6.3. Results

6.3.1. XPS survey spectra and high resolution Nb3d5/2

The various Nb species were assigned based on the binding energy data provided by the NIST data base, these are: Nb₂O₅: 207.4 eV, NbO₂: 206.2 eV, and NbO: 203.7 eV (Naumkin et al., 2000; Cooley & Sibener, 2007).

Fig. 6-2 shows the binding energies of the Nb 3d5/2 electrons from the analysis of a high Fe pyrochlore before and after treatment. Comparison of the sputtered pyrochlore surface with that after conditioning shows a significant change in the relative proportion of Nb species. The doublet at binding energy 207 eV representing Nb(V) shows a significant increase in the conditioned sample relative to those at 204 and 206 eV representing Nb(II) and Nb(IV) respectively (Fig. 6-3). The data indicates an increase in the proportion of oxidized Nb species present on the surface of grains after conditioning. A comparison between the high and low Fe zones revealed that the actual amount of Nb(V) was the same on both grains before conditioning. After conditioning, the surface proportion of
Nb(V) increased on both high and low Fe zones, however the average surface proportion of Nb(V) on low Fe zones is on the order of 2% lower than the high Fe zones (Fig. 6-4).

**Fig. 6-2.** Niobium states on the surface of a sputtered and conditioned sample.
Fig. 6-3. Relative proportion of Niobium species measured on the surface of the sputtered (S), and conditioned (C) grains.

Fig. 6-4. Concentration of Nb(V) on the surface of high and low iron zones.
6.3.2. XPS survey spectra and high resolution Fe 2p3/2

Compared to the other transition metal species, the complex multiple species fitting of Fe is the most problematic. Pratt et al. (1994) used a series of multiplet peaks to curve fit oxidized iron sulfide (pyrrhotite) surfaces. Biesinger et al. (2011) presented a summary of full fitting parameters for Fe including the multiplet and satellite structure. The paper clearly stated that, materials with numerous possible species showing overlapping binding energies can result in erroneous interpretations. They further went on to indicate that two distinct species can likely be fitted accurately, fitting three is difficult fitting four very problematic and must only be looked at as indicative. Given that, from a comparative analytical perspective, XPS Fe data in this study is of value in that it can provide information related to the process based on the relative changes in the proportion of species identified on the surface of the mineral phases. For species identification we have used the Fe 2p3/2 peak fitting parameters identified in Biesinger et al (2011) (appendix III).

The pyrochlore family is complex. The general mineral formula can be given by: \( A_{2-m}B_{2+6}(O,OH,F)_{1-n}pH_{20} \) where \( A = \) Na, Ca, K, Sr, Ba, Mn, Fe \(^{2+} \), Mg, Sn, Pb, Bi, Cs, Sb \(^{3+} \), Th, U, Y, Ce, Nd, La and \( B = \) Nb, Ta, Ti, Zr, Fe \(^{3+} \), Al (Vlasov, 1966; Hogarth, 1977; Fleischer, 1987). Since the assignment of Fe can either occur in the A or B positions, the correct position of Fe and therefore its valence state in the structure of pyrochlore from Niobec is generally unknown. Investigations by Zurevinski and Mitchell, (2004) mentioned that it would not be surprising if Fe\(^{2+}\) is present at the A sites, where the cation exchange reactions occur more easily. Recent studies (S. Chehreh Chelgani et al., 2012a) using statistical analyses of EDX data from Niobec pyrochlore grains indicated that the Fe in the matrix is likely located at the A position.

Unfortunately, the concentration of Fe in the low Fe pyrochlore grains did not allow for the collection of spectra amenable to reasonable interpretation. Hence a direct comparison between the development of Fe species on grains with very low Fe contents was not possible. What follows is a comparison between grains considered as high Fe pyrochlore grains with differing Fe contents. The objective is to determine if there are
reasonable, measurable chemical state differences similar to those observed in the TOF-SIMS analyses which can be potentially linked to the observed flotation response. Representative XPS spectra of iron on the surface of sputtered and conditioned high Fe pyrochlore zones are show in Fig.6-5.

Fig.6-5. Iron states on the surface of a sputtered and conditioned pyrochlore grain.
Fig. 6-6. Comparison of the high resolution XPS spectra between grains with different Fe content after conditioning. Included for each grain examined is the weight % Fe, as determined by EDX, along with the relative proportion of surface Fe (At %) from the XPS broad scan data and the proportion of Fe metal (At %) as determined in the high resolution XPS scans. Fe(XPS ZV) refers to the Fe metal in the spectra.
The sputtering process results in the removal of Fe-oxides and the reduction of Fe giving rise to the zero valent Fe peak (Fe metal) at a BE of 706 on the sample. The conditioning process resulted in the development of significant Fe oxide on the surface of the pyrochlore. Evaluation of the spectra reveals that the process resulted in the generation of Fe$^{2+}$, identified as FeO, along with minor and varying proportions of Fe$^{3+}$ as Fe$_2$O$_3$. A positive identification of FeOOH was not accomplished due to the complicated nature of the spectrum, however its presence is indeed possible. Comparison of the spectra from pyrochlore grains with relatively high and lower Fe contents after conditioning reveals several significant differences: i) surface Fe content is significantly higher in the high matrix Fe content sample, ii) the proportion of zero valent Fe (Fe-metal) is higher on the surface of the low Fe pyrochlore sample and iii) there is a greater proportion of Fe-O species on the surface of the high Fe pyrochlore grains (Fig. 6-6).

![Box and whisker plots illustrating the relative intensity of oxygen on the surface of the sputtered and conditioned high and low iron compositional zones of Fe pyrochlores.](image)

Fig.6-7. Box and whisker plots illustrating the relative intensity of oxygen on the surface of the sputtered and conditioned high and low iron compositional zones of Fe pyrochlores.
6.3.3. Oxygen

The XPS instrument was used to examine the development of surface oxidation species in relationship to pyrochlore matrix compositional zones. XPS spectra were collected from low Fe and high Fe compositional zones after sputtering, and after conditioning (Fig. 6-7). The data from the sputtered samples reveals no difference in the surface oxygen content between the high and low Fe content zones. After conditioning however the high iron content zones showed overall higher oxygen content (~5%) as compared to the low Fe zones.

6.4. Discussion

Observations by Abeidu, (1974) showed that pyrochlores with high Fe content appear to be less recoverable than those of low Fe content. He speculated that the flotation selectivity can possibly be related to preferential surface oxidation of the Fe rich mineral rendering the surface unsuitable for collector attachment. Investigations on the effects of surface oxidation and/or the precipitation of oxidative species indicated that, as the mineral surface becomes increasingly covered with metal oxide/hydroxide species the surface becomes increasingly less negative and can even become positively charged (Fornasiero et al., 1992, 1994; Witika and Dobias, 1993; Fairthorne et al., 1997; Fullston et al., 1999; Barnes et al., 2009). The data gathered from the surface evaluation of pyrochlore grains from the Niobec operation by Chehreh Chelgani et al., (2012a) indicate that differential cationic collector attachment efficiency is linked to Fe content in the pyrochlore grains. Given this observation, a potential scenario for flotation selectivity in relation to matrix Fe content is put forward: inhibition of collector attachment due to preferential oxidation of the high Fe pyrochlore grains or regions in zoned pyrochlore grains during the recovery process.

Previous investigations at Niobec have shown that a higher concentration of matrix Fe in pyrochlore grains can potentially be linked to poor selectivity (Rao et al., 1988; Chehreh Chelgani et al., 2012a). Surface analyses by TOF-SIMS demonstrated that the intensity of
oxidative species O, OH and FeOH was greater on the surface of high Fe pyrochlore grains in comparison with low Fe pyrochlore grains (Chehreh Chelgani et al., 2012b). Although the XPS analyses were not able to fully differentiate the types of Fe oxidation species on the surface of the pyrochlore grains, variations in the relative proportions of oxidation products demonstrate a number of factors in support of the contention that collector attachment is linked to preferential surface oxidation of Fe rich grains or regions. A significant line of support comes from the oxygen data, which shows an overall higher O content on the surface conditioned Fe rich pyrochlore grains or zones relative to the low Fe pyrochlore particles or zones (Fig.6-6). This is in agreement with the TOF-SIMS data which linked higher O contents to Fe rich pyrochlore grains and zones with diminished collector presence (Chehreh Chelgani et al., 2012b). There is also a curious overall greater proportion of oxidised Nb on the surface of the high Fe grains accompanied with a greater proportion of more reduced Nb species on the low Fe grains or regions (Table 6-2). While it is not clear if the degree of Nb oxidation and the resulting proportional difference of oxidised Nb species is facilitated by matrix Fe content, it is clear that in zones or grains with higher Fe content, there is a greater proportion of both Nb and Fe oxidation products.

**Table 6-2. High resolution XPS data for Nb as measured on the surface of conditioned high and low Fe grains and zones. All data in relative %.

<table>
<thead>
<tr>
<th>Zones</th>
<th>Nb(O)</th>
<th>Nb(II)</th>
<th>Nb(IV)</th>
<th>Nb(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Fe</td>
<td>0.9</td>
<td>2.6</td>
<td>10.1</td>
<td>86.4</td>
</tr>
<tr>
<td>Low Fe</td>
<td>0.8</td>
<td>2.6</td>
<td>9.4</td>
<td>87.2</td>
</tr>
<tr>
<td>High Fe</td>
<td>0.0</td>
<td>2.7</td>
<td>9.7</td>
<td>87.7</td>
</tr>
<tr>
<td>Low Fe</td>
<td>1.9</td>
<td>8.1</td>
<td>15.1</td>
<td>74.9</td>
</tr>
<tr>
<td>High Fe</td>
<td>1.2</td>
<td>9.9</td>
<td>16.0</td>
<td>72.8</td>
</tr>
<tr>
<td>Low Fe</td>
<td>2.7</td>
<td>12.3</td>
<td>16.2</td>
<td>68.8</td>
</tr>
</tbody>
</table>

Although the argument can be made that the greater proportion of these species on the surface of the Fe rich pyrochlores could be related to a precipitation phenomenon, we
believe that the data for pyrochlores with variable Fe contents provides evidence that the process is related to preferential surface oxidation. The XPS data clearly shows that the proportion of surface oxidation products increases proportionally to the matrix Fe content of the grain; a similar link is highly unlikely to be shown by a precipitation mechanism. Thus, the established link between poor pyrochlore recovery and matrix Fe content from the previous SEM-EDX and TOF-SIMS studies (Chehreh Chelgani et al., 2012a, b; 2013) is related to a greater degree of both Fe and to some degree Nb oxidation, which results in zones or grains that preferentially inhibit collector attachment and therefore show poor recovery.

6.5. Conclusions

Previous chapters have linked poor flotation performance to an increase of Fe content in the matrix of grains. One possible explanation linking high Fe content to poor recovery suggested that high Fe content resulted in a variable degree and rate of surface oxidation. Surface analysis techniques such as XPS allow for a direct ex situ determination of the degree of oxidation on the surface of minerals. The present study utilises the XPS technique to investigate the oxidation states on the surface pyrochlore of different Fe content and grains that are compositional zoned pyrochlores (areas of high and low iron content). Bench testing and XPS analyses of variable Fe content pyrochlore grains verify a relationship between pyrochlore surface oxidation and Fe content in the mineral matrix. It was demonstrated that on the surface of conditioned samples, a greater proportion of oxygen was identified in high Fe zones in comparison to those with low Fe contents. Furthermore, the analyses revealed that there was a greater proportion of higher valence state Fe and Nb species developed on the surface of the high Fe pyrochlore zones during the conditioning tests. These data provide evidence that the previously identified link between matrix Fe content and collector attachment is likely in response to selective oxidation on the surface of Fe rich pyrochlore grains or zones within the pyrochlore grains. The data may be of significant value as they can be applied to testing scenarios designed in order to evaluate flotation improvement strategies.
6.6. References


Chapter 7

7 « Conclusion and future work»

7.1. Conclusion

A statistical evaluation of pyrochlore compositional analyses indicates that the Saint-Honoré deposit potentially contains two types of pyrochlore grains, high iron and low iron pyrochlores. SEM–EDX analysis of pyrochlore grains from the flotation circuit has linked poor flotation performance to an increase in grain Fe content. Statistical analyses identified that the increase in Fe in the pyrochlore is not a result of Fe rich inclusions; rather it has been identified as an increased matrix Fe content. The analyses suggest that poor pyrochlore floatability is related to higher matrix Fe contents. Two possible explanations linking high Fe content to poor recovery have been suggested: (1) high Fe content results in a variable degree and rate of surface oxidation, (2) high Fe content results in a change in surface charge. The current study evaluated the relationship between mineral chemistry, surface chemistry and flotation stream partitioning.

Surface chemistry controls surface reactivity and consequently plays a significant role in determining flotation behavior of minerals. Surface analysis techniques such as TOF-SIMS and XPS allow for direct ex situ examination of mineral surfaces and can provide relevant information on factors potentially controlling collector adsorption and hence flotation selectivity and recovery. In order to investigate the adsorption of tallow diamine (collector) on the surface of compositionally different pyrochlore grains (high iron and low iron content) the TOF-SIMS and XPS techniques were used.

The TOF-SIMS results verify a relationship between pyrochlore surface reactivity and mineral matrix Fe content. The intensity of collector species was significantly higher on the surface of the Fe poor pyrochlore. Also, it was demonstrated that the intensity of the oxidative species O, OH and FeOH was greater on the surface of high Fe pyrochlore grains in comparison with low Fe pyrochlore grains. The link between surface and matrix chemistry is identified. The results from these tests at least partially explain the flotation
selectivity of low Fe pyrochlore grains relative to high Fe pyrochlore grains. The data suggest that preferential surface oxidation favours the high Fe pyrochlores resulting in diminished collector attachment and poor recovery.

SEM–EDX analysis of Fe pyrochlore has identified that the high iron content pyrochlores are compositionally zoned into high iron and low iron zones. TOF-SIMS results from the analyses of zoned pyrochlore grains verified a relationship between pyrochlore compositional zoning and collector loading. The surface analysis demonstrated that the intensity of species indicative of oxidation O and OH were greater in zones corresponding to high matrix Fe content. The surface analysis also revealed that collector loading favours zones with low matrix Fe content, indicating that oxidation, particular to the Fe zones, inhibits collector attachment. This study identifies the link between collector attachment and compositional zoning in Fe pyrochlores.

The possible explanation, which suggested that high Fe content resulted in a variable degree and rate of surface oxidation, was examined by XPS. Surface analysis techniques such as XPS allow for a direct ex situ determination of the degree of oxidation on the surface of minerals. The present study utilises the XPS technique to investigate pyrochlore grains of different Fe content and those that are compositional zoned (areas of high and low iron content). Bench conditioning tests and XPS analyses of variable Fe content pyrochlore grains verify a relationship between pyrochlore surface oxidation and Fe content in the mineral matrix. It was demonstrated that on the surface of conditioned samples, a greater proportion of oxygen was identified in high Fe zones in comparison to those with low Fe contents. Furthermore, the analyses revealed that there was a greater proportion of higher valence state Fe and Nb species developed on the surface of the high Fe pyrochlore zones during the conditioning tests. These data provide evidence that the previously identified link between matrix Fe content and collector attachment is likely in response to selective oxidation on the surface of Fe rich pyrochlore grains or zones within the pyrochlore grains (Fig. 7-1). The data may be of significant value as they can be applied to testing scenarios designed in order to evaluate flotation improvement strategies.
Fig. 7-1. Optical microscopic images of polished surfaces of epoxy mounted high (Fe-pyrochlore) and low Fe pyrochlore (Pyrochlore) grains. Note the orange oxidation surface on the Fe pyrochlore grain which is not visible on the pyrochlore grains. The mounts were left on the lab bench at ambient conditions for +60 days.

7.2. Future work

The focus of this study was to understand the factors affecting the adsorption of the current cationic collector, tallow diamine acetate, used to recover the mineral pyrochlore in the Niobec flotation operation. Results indicate that the pyrochlore grains at Niobec are of variable Fe content. Those with high Fe contents are not recovered as collector attachment is inhibited by changes in surface chemistry. The identification that recovery can be linked to mineral chemistry is significant in that selective separation or improved recovery may not be possible within the current flotation scheme. Furthermore, in order to enhance separation a number of other reagents, for example oxalic acid and hydrofluorosilic acid, are added to the process however their function is not fully understood.

In regards to the current collector, investigations using hydroxamic acid collectors (Gomez et al., 1987; Ni et al, 2012, Huang et. al, 2013) for the selective separation of pyrochlore grains have shown that they have a high potential for adsorption, regardless of
grain compositional variability. Hydroxamates are the most commonly used flotation collectors for rare earth minerals and have been extensively used to produce concentrates of these minerals in Chinese plants since the 1960s. Recently, commercially produced hydroxamate collectors have been implemented in other flotation schemes and, given the results of this study, it is certainly worth investigating their potential in the current flotation scheme or their application toward the development of a new separation scheme.

In regards to the other reagents, it is of significant value to determine their actual role. This is particularly significant as the cost of reagents is ever increasing. A complete understanding of their function will allow for the evaluation of cheaper alternatives. Moreover, the current reagents may well have an impact on the selection of alternative reagents or collectors. For example, testing has established the significance of oxalic acid however its specific role in the Niobec flotation flow sheet is not well understood. In the flotation of REE minerals it is reportedly acting both a depressant and collector. In the Niobec flotation plant, the use of oxalic acid is critical to the operation. Pulp pH reduction trials with alternative acids have not shown the same effect on the pyrochlore recovery or the depression of gangue phases. Therefore, within the context of the current flow sheet, it is indeed worth investigating the roles of these reagents. A clear understanding of their functionality may, through changes in dosing or points of addition, result in improved selectivity and recovery. Furthermore, definition of their role may allow for the selection of alternatives to perform a similar function or aide in the selection of alternative collectors for the process.

7.3. References


Appendix I

**Corrected concentration calculation in EDX**

The calculation of the concentration of an element in a sample must take account of the differences in composition between the sample and the standard. A ZAF factor can be calculated that takes account of the stopping power, backscattering coefficient, absorption and fluorescence effects.

\[ C_{\text{smpl}} = K \cdot C_{\text{std}} \cdot ZA\text{F}_{\text{smpl}} / ZA\text{F}_{\text{std}} \]

The ZAF factor for the standard can be calculated from its composition, which is known, but the composition of the sample needs to be known before the ZAF factor can be calculated. As the composition of the sample is not known, an iterative technique is used, with an initial composition calculated from the measured K ratio. The ZAF factor for this composition is calculated and the composition of the sample is recalculated, and the process repeated until there is no change in the calculated composition.

For elements which display spectral overlaps, iterative calculations of K and L lines are used to best estimate the concentration element of interest. It should be noted however that where overlaps are significant the final estimated concentration of the element in question can have significant error.

Appendix II

**TOF-SIMS methodology**

Six regions of the each sample mounted on In foil were analyzed. A minimum of 6 grains per region were examined. The analysis provides a comprehensive survey of the surface species on the mineral grains in the various samples. The analytical approach was to conduct comparative surface analyses of the provided samples in order to determine statistically significant differences in the surface composition of species particularly related to potential depression or precipitation of the examined mineral phases.
All TOF-SIMS data presented (counts) are normalized by the total ion intensity (counts of the recorded total mass spectrum) for the region of interest (the procedure for normalization was defined by Piantadosi et. al., 2000 and further refined by in Hart et al., 2006). The normalized intensity data are plotted in vertical box plots and illustrate relative changes in surface specie abundance for the mineral grain examined in the sample. The discussion refers to a relative increase or decrease in measured specie intensity between grains in the samples. Relative differences are based on the median values indicated in the figures. Both positive and negative ions are collected in the time of analysis. The negative ions are most effective for identifying organic and oxidative species whereas positive ions commonly identify single element variability, along with specifically defined organic mass fragments particularly related to the reagents used.

Appendix III

XPS Fe peak fitting

The XPS Fe spectral fitting was performed according to the method defined by Dr. Mark Biesinger. The following is from the XPS blog post at:


Note the information in the blog and in the various cited articles were used as guidelines for spectral fitting.

For the analysis of photoelectron spectra of relatively pure iron oxides, one can use peak shape and peak binding energy comparisons to standard compounds to derive oxide composition. McIntyre and Zetaruk’s [1] paper is widely cited and is still an excellent starting point for qualitative iron oxide determination. Pratt et al. [2] used a series of multiplet peaks to curve fit oxidized iron sulfide (pyrrhotite) surfaces.

splittings and weightings are presented. An analysis of satellite to main peak separation is also given. All Fe(II) (high spin only as low spin Fe(II) does not exhibit multiplet splitting) and Fe(III) species can be fitted with Gupta and Sen multiplet structure. Variation in peak spacing and intensity occur for different ligands. Broad satellite peaks of varying intensities at binding energies above the main Fe 2p3/2 structure are present in the spectra for all high spin compounds. However, paper [3] only presents the main multiplet lines, excluding the details needed to fit the broader higher binding energy satellite structures.

Table 1 [5] presents full fitting parameters including the multiplet and satellite structure. FWHM values are reported for 10 eV pass energy only. To accommodate lower resolution settings slightly broader peaks would be necessary for best fit values. For these fits a Shirley background encompassing only the 2p3/2 portion of the spectrum is used. Also included in this Table are new spectral fitting parameters for FeCr2O4 and NiFe2O4, species that are important for the examination of oxide films on Fe-Cr-Ni alloys, as well as data for new analyses of α-Fe2O3 and γ-Fe2O3[5]. Fitting parameters for FeCO3, which has been noted in certain corrosion products, are also presented in Table 1. These analyses were collected from a mineral sample of siderite (cleaved in vacuum). Carbon 1s binding energy for FeCO3 is at 290.1 eV. The many spectra are best viewed in the original papers. References [3] and [5] are available here.

While these values [5] and reference spectra [1, 3, 5] will be useful for identification of pure oxide or oxy-hydroxide species, curve fitting of mixed systems quickly becomes complicated due to spectral overlaps. For example, it can be seen that various Fe(III) compounds have a similar range of Fe 2p binding energies and vary mostly in peak shape and satellite intensities. Any attempt at fitting two or more Fe(III) species to a spectrum will consequently contain an inherent degree of error. As well, overlap of the Fe(III) satellite structure with the Fe(0) and Fe(II) Fe 2p1/2 portion of the spectrum will result in setting the higher binding energy background endpoint placement at a point that will not cover the satellite structure of the Fe(III) species. This will require any fitting of mixed chemical state systems containing Fe(III) species to omit the higher binding energy Fe(III) satellite from the envelope of peaks. This will again increase the error associated
with the curve fitting. The fitting of a spectrum from pure Fe3O4 will also need to omit
the higher binding Fe(III) energy satellite contribution as is reflected in the values
presented in Table 1. Finally, determination of the Fe species present, especially in a mix
of Fe(III) species, should include corroborating evidence from O 1s analysis and even
other analytical techniques such as Raman spectroscopy or, for thin crystalline films,
grazing angle XRD. Some examples of fittings in mixed species samples are presented in
[5].

Table 1. Fe 2p3/2 spectral fitting parameters: binding energy (eV), percentage of
total area, FWHM value (eV) and spectral component separation (eV) [5].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak 1 (eV)</th>
<th>FWHM -10 eV</th>
<th>Peak 2 (eV)</th>
<th>Δ Peak2 - Peak1 (eV)</th>
<th>Peak 3 (eV)</th>
<th>FWHM -10 eV</th>
<th>Peak 4 (eV)</th>
<th>Δ Peak4 - Peak3 (eV)</th>
<th>Peak 5 (eV)</th>
<th>FWHM -10 eV</th>
<th>Peak 6 (eV)</th>
<th>Δ Peak6 - Peak5 (eV)</th>
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<td>α-Fe2O3</td>
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</table>

a) Binding energies are significant to 0.1 eV but an additional figure is added because energy splittings are much more accurate than the absolute binding energies.
b) Asymmetric pseudo-peak and FWHM defined by standard iron metal sample (La(2+), 2.4, 8.3))
c) Satellite structure for 3+ though likely present will be buried under Fe 2+ Fe 2p1/2 portion of spectrum

d) Sum of 2+ and 3+ areas is 100

e) Taken with a 20° pass energy

Compared to the other transition metal species, the complex multiple species fitting of Fe
is the most problematic. With so many possible species having overlapping binding
energies erroneous interpretation can result. A sample with two distinct species can likely
be fitted accurately, three species much less so, while four or more species must be
looked at as indicative but unreliable. It is worth again stating that corroborating evidence
is desirable for this type of Fe surface chemical state speciation.
References

Curriculum Vitae

Name: Saeed Chehreh Chelgani

Post-secondary Education and Degrees:
The University of Western Ontario, London, Ontario, Canada 2010-2013 Ph.D.

Honours and Awards:
The Ontario Graduate Scholarship (OGS), Canada 2013
The Outstanding Research Contributions Scholarship, Canada 2013
Robert & Ruth Lumsdon graduate fellowship, Canada 2012& 2013
The NSERC engage grant, Canada 2011

Related Work: Teaching& Researching Assistant
Experience: The University of Western Ontario 2010-2013

Publications:

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2. An Investigation on the Surface Chemistry of Some Rare Earth Minerals During Flotation by TOF-SIMS, SME, 2013, Denver, US.

3. An investigation on the surface chemistry of some rare earth minerals during flotation by TOF-SIMS, CIM, 2012, Niagara fall, Canada.


5. Rare earth minerals short course, University of western, London, March 2011.


