Behaviour of ilmenite as a gangue mineral in the benzohydroxamic flotation of a complex pyrochlore-bearing ore

C.E. Gibson, R. Hansuld, S. Kelebek, M. Aghamirian

A R T I C L E   I N F O

Article history:
Received 25 October 2016
Revised 14 February 2017
Accepted 21 February 2017

Keywords:
Flotation
Benzohydroxamic acid
Ilmenite
Pyrochlore
Titanium
Niobium
Sodium hexametaphosphate

A B S T R A C T

One challenge identified in the flotation of niobium bearing minerals with hydroxamates is the recovery of gangue minerals which can result in concentrate grade dilution. Micro-flotation of single and mixed minerals and bench scale flotation tests on a low-grade complex pyrochlore-bearing ore were conducted to assess the flotation behavior of ilmenite as a gangue mineral in the flotation of pyrochlore using benzohydroxamic acid (BHA) as a collector and sodium hexametaphosphate (SHMP) as a dispersant/depressant. In micro-flotation, high dosages of BHA resulted in high pyrochlore recovery and low ilmenite recovery at pH 8. It was observed that the order of addition of SHMP in relation to BHA had a strong effect on pyrochlore recovery, with high recovery maintained only when SHMP was added after BHA. When ilmenite and pyrochlore were floated in the same system, it was found that reagent addition order played an important role in selective flotation of pyrochlore. Flotation of pyrochlore was more selective over ilmenite when SHMP was added before BHA, similar to a cleaner flotation stage in real-ore flotation. Contrary to micro-flotation results titanium recovery was high (more than 60% TiO₂ recovery in most cases) under similar pulp conditions in bench scale flotation, an indication that to some extent titanium minerals were recovered by a mechanism other than genuine flotation. Similarly, in mixed mineral micro-flotation, the recovery of ilmenite increased in the presence of pyrochlore. Two possible scenarios, one physical and the other chemical in nature, have been proposed to explain this observed phenomenon. First, it is possible that moderately floatable titanium mineral particles were recovered in the froth by association with highly floatable pyrochlore, particularly at starvation levels of a dispersant (SHMP) through the hydraulic entrainment of fines. The second possibility is that titanium minerals experienced inadvertent activation in multi-mineral systems, perhaps with metal-hydroxamates as the activating species, forming hydroxamate complexes involving ferric and/or niobium species. This research area is under further investigation.

1. Introduction

Pyrochlore (Na,Ca)₂Nb₂O₆(OH,F) is the most economically important niobium-bearing mineral and is typically upgraded by flotation using an amine-based collector. The pulp pH is maintained between 5.5 and 7 in the rougher circuit and is gradually dropped to as low as pH 2 in the final cleaner stage (Gibson et al., 2015a; Bulatovic, 2010; Guimares and Weiss, 2003; Filho et al., 2002; Oliveira et al., 2001; Gendron et al., 1981). This beneficia-
of beneficiation process that can tolerate slimes and selectively recover fine grained pyrochlore from associated gangue minerals.

Flotation using hydroxamic acids (chelating reagents) as collectors has been demonstrated as an effective means to upgrade ultra fine grained material (Pradip and Fuerstenau, 1988). Although hydroxamates have historically not been widely used in industry in western countries due to lack of commercial availability, an alkyl hydroxamic acid product named ‘IM-50’ is reported to have been in commercial use in Russia (former Soviet Union) since the 1960s and China since the 1970s (Nagaraj, 1987). Hydroxamic acids are now commercially available worldwide (from reagent manufacturers such as Cytec), warranting more testwork on real ore systems.

Hydroxamates can form complexes with nearly all transition metals, although stability is stronger with iron, copper and highly charged cations than with other transition metals (niobium, tantalum, titanium etc.) (Nagaraj, 1987). As a result, selective flotation of transition metals from one another using hydroxamic acids is challenging and tends to vary depending on the type of hydroxamic acid used. Factors affecting collector selectivity include both mineral and chelate solubility; chelate solubility being primarily affected by the stability constant (Nagaraj, 1987).

The application of alkyl hydroxamic acid as a collector in flotation of pyrochlore-bearing ores at the laboratory scale has been well documented (Ni and Liu, 2012a; Gorlovskii et al., 1968). Other hydroxamic acid types such as benzohydroxamic acid have shown to be effective for pyrochlore recovery through single mineral micro-flotation studies by Espinosa Gomez et al. (1987) and on real ore systems by Gibson et al. (2015a). Independent of the type of hydroxamic acid, a major issue identified in the flotation of niobium-bearing minerals with hydroxamates is the recovery of other transition metal gangue minerals, such as magnetite, hematite, pyrite, ilmenite and rutile (Ni, 2013) which result in concentrate grade dilution.

The present work aims to investigate the flotation of behavior of ilmenite as a gangue mineral in the flotation of pyrochlore using benzohydroxamic acid as a collector.

2. Materials and methods

2.1. Mineral sample preparation

A high purity sample of pyrochlore flotation concentrate was obtained from laboratory and pilot plant flotation testwork conducted at SGS in Lakefield, Ontario as this mineral was not available at sufficiently high purity from other sources. In order to ensure de-activation/purification of the pyrochlore concentrate, it was leached with hydrochloric acid at a concentration of 20 g/L at 20% solids concentration for 4 h at a temperature of 50 °C. The leach residue was then filtered and washed five times with de-ionized water. The dried leach residue was then heated to 200 °C for 45 min to further ensure destruction of any remaining organics on the mineral surface. The purified mineral sample contained ~86% pyrochlore assaying 42.8% Nb determined through semi-quantitative XRD and X-ray Fluorescence, respectively. The ilmenite sample was from mineral storage at the Mining Department at Queen's University. It indicated 35.6% Ti. Subsequent XRD analysis indicated rutile and pseudorutile as minor impurities. In preparation for testing, the ilmenite was de-slimed after repeated ultrasonic treatment and decantation/washing at each particle size of interest. The XRF results for the pyrochlore concentrate and ilmenite samples are presented in Table 1.

Table 1

| XRF Analysis of pyrochlore and ilmenite used in micro-flotation tests. |
|---|---|---|
| XRF results | Assay (%) | Pyrochlore | Ilmenite |
| Nb | 42.8 | - | - |
| NbO2 | 61.2 | - | - |
| SiO2 | 4.80 | 0.95 | |
| Al2O3 | 0.63 | 1.01 | |
| Fe2O3 | 3.11 | 31.5 | |
| MgO | 0.07 | 0.26 | |
| CaO | 9.95 | 0.14 | |
| Na2O | 2.78 | 0.12 | |
| K2O | 0.34 | 0.05 | |
| TiO2 | 3.39 | 61.5 | |
| F2O5 | 0.19 | 0.01 | |
| MnO | 0.06 | 1.48 | |
| LOI | 3.68 | 2.06 | |

Samples were ground using a porcelain mortar and pestle and required microsieves.

2.2. Micro-flotation

Micro-flotation tests were carried out in a 70 mL modified Halilimond tube (Partridge and Smith, 1971). The shaft of the micro-flotation cell was approximately 250 mm long and opened into a rounded concentrate launder. A medium porosity piece of fritted glass was located approximately 10 mm above the gas inlet. A schematic of the micro-flotation cell together with a photo showing the cell in action is illustrated in Fig. 1. A Teflon magnetic stirring bar from Fisher Scientific was used to suspend mineral particles in the cell during testing. For all tests, the magnetic stir bar was rotated at a rate of 1000 rpm.

The image in Fig. 1 (right) shows the separation of pyrochlore (brownish froth) from ilmenite (black particles at the bottom remaining mostly unfloatable). It is important to note the presence of practically barren bubbles in the collection zone separating the concentrate product and tails after about 30 s into flotation (pH: 8.1, BHA: 1.04 × 10⁻³ M, MIBC: 60 ppm).

For all tests the cell was filled with approximately 40 mL of de-ionized water. The pH in the cell was measured and then adjusted using sodium hydroxide to reach alkaline conditions. The sample was conditioned at pH 8 for two minutes. Benzohydroxamic acid collector with 99% purity from Alfa Aesar (BHA at 2% by wt.) was then added and the sample was conditioned for an additional three minutes. The BHA dosage ranged from 1 kg/tonne (1.04 × 10⁻⁴ M) to 20 kg/tonne, based on weight of the mineral added (1 g). The sodium hexametaphosphate (or SHMP (NaPO₃)₆ purchased as ‘Calgon’), dosage ranged from 0.5 kg/tonne (1.17 × 10⁻⁵ M) to 5 kg/tonne. The conditioning period was exactly the same whether the SHMP was added before or after the collector. MIBC was added as a frother in the last minute of conditioning at a rate of 60 mg/L (provided by a tiny drop of pure MIBC from a syringe). After conditioning, the air was turned on and adjusted to a flowrate of 36 mL/min. Concentrate was collected from the overflow launder for 1 min while water (de-ionized) was added at the top of the cell (~70 mL/min) to facilitate a continuous overflow of the concentrate slurry into the launder. Washing water was added only to the launder and was not used to change the cell level during concentrate collection. In the tests involving sodium hexametaphosphate (SHMP), its addition was made directly into the cell in powder form.

2.3. Bench scale flotation

A Box-Behnken experimental design was conducted on a low-grade, niobium-bearing carbonatite gravity tailings product to...
examine the main and interaction effects of benzohydroxamic acid (BHA) dosage, pulp temperature, and SHMP dosage. A detailed procedure for this set of tests including head assay and ore sample characteristics, experimental run orders, as well as coded and uncoded variable level selection for the experimental design are outlined by Gibson et al. (2015b). For the convenience of the reader, the flotation feed head assay and experimental conditions for the Box-Behnken bench scale flotation tests have been reproduced in Tables 2 and 3, respectively.

As summarized in the previous work, the flotation tests were conducted on 2 kg flotation charges in a Denver flotation at a natural pH of 8 (Gibson et al., 2015b). No pulp pH adjustments were made through conditioning/flotation and the ore was not deslimed prior to flotation and the feed particle size distribution was 80% passing 59.3 μm. Four rougher flotation stages were performed, each for four minutes in length. Reagents were added in equal quantities in each flotation stage; therefore the results could be analysed in each cumulative rougher stage as it was conducted before by Nanthakumar and Kelebek (2007).

3. Results and discussion

3.1. Micro-flotation

The mass recovery of pyrochlore and ilmenite (−150/+53 μm) flotation with benzohydroxamic acid at two different concentrations is plotted as a function of pH in Fig. 2. It was expected that pyrochlore and ilmenite flotation recovery with benzohydroxamic acid would be highest between pH 8 and pH 9, near the dissociation constant (pK_a) of the reagent, which is given as 8.8 (Bonnitcha et al., 2012). Optimal flotation recovery near the pK_a of hydroxamic acid has been attributed to co-adsorption of both collector ions and neutral molecules at the mineral surface. The reaction of meta-hydroxyl complexes at the surface in the presence hydrolyzing metal ions may also increase flotation recovery (Nagaraj, 1987). Based on Fig. 2, pyrochlore demonstrated high floatability between pH 7 and 8.5, while pyrochlore recovery dropped at pH 9, particularly at low collector dosages. Xu et al. (2016) investigated the flotation of ilmenite with collector 2-ethyl-2-hexenoic hydroxamic acid (EHHHA) and discovered that at the single mineral scale, ilmenite recovery was the highest in the range of pH 8–10. Recovery was significantly lower outside of this pH range. In the current case, pyrochlore floatability appears to be more sensitive to alkalinity, as recovery dropped significantly between pH 8.5 and 10. Ilmenite recoveries were low regardless of pH although they reached a maximum around pH 9 at a high collector dosage. Under highly alkaline conditions surface reactivity of these minerals towards OH^− increases, which progressively inhibits collector action (Liu et al., 2006). It was noted that at an extreme pH 12.3; there was no flotation activity for both minerals and the solution developed a light brownish color, particularly in the case of ilmenite possible indicative of the precipitation of iron

![Fig. 1. Schematic of micro-flotation cell (left) and a photo showing its use during flotation.](image)

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nb₂O₅</td>
</tr>
<tr>
<td>Flotation Feed</td>
<td>0.25</td>
</tr>
</tbody>
</table>
hydroxamates. This alkaline reactivity is the basis for extractive decomposition of ilmenite using KOH solutions (Liu et al., 2006). Flotation tests were performed and repeated three times on ilmenite and pyrochlore at pH 8, for high and low collector concentrations (5 kg/tonne and 20 kg/tonne BHA). Results for the repeated tests are presented in Table 4.

At a collector concentration of 5 kg/t ilmenite recovery was between 9% and 13.5% and pyrochlore recovery was between 87% and 91%. At a collector concentration of 20 kg/t ilmenite recovery was between 11% and 23% and pyrochlore recovery was between 92% and 96%.

Further testing with benzohydroxamic acid was conducted at pH 8 due to the high flotation recovery of pyrochlore compared to ilmenite regardless of collector dosage and proximity to the pKₐ. Further, the natural pH of the flotation pulp in bench scale testing rested at around pH 8 and flotation under these conditions eliminated the need to modify pH prior to flotation.

Fig. 3 shows the relationship between mass recovery of pyrochlore and ilmenite as a function of benzohydroxamic acid concentration at pH 8. For this study the particle size range was –150 µm/+53 µm. Pyrochlore recovery was approximately 80% when the benzohydroxamic acid addition rate was 5 kg/t. Recovery did not increase significantly when the collector dosage was increased beyond 5 kg/t. The recovery of ilmenite reached a plateau at an addition rate of 2 kg/t BHA and did not increase significantly thereafter.

Lower recovery of pyrochlore observed at high BHA concentrations in micro-flotation was due in part to mechanical reasons. It was observed that bubbles were sticking to the walls of the cell, which kept some hydrophobic particles from floating (fixed at the walls), preventing them from reporting to the concentrate (Fig. 4).

It is hypothesized that this phenomenon might be related to pre-adsorption of active BHA-bearing species on the glass (with or without prior adsorption of some species from pyrochlore), as the occurrence was not observed when no collector was added to the system. The observed agglomeration and armouring of tiny bubbles by the pyrochlore particles is also important to comment on. This occurred not only in the concentrate but also in the tails fraction during transfer into a beaker for quantification. Particle agglomeration and armouring of tiny bubbles also occurred within the tails. This is indicative of the hydrophobicity of the tailings, although perhaps at a slightly lower level than in the concentrate. These particles possibly remain in the tails fraction because of mechanical conditions.

Within the particle size range tested, results showed that for a given concentration of benzohydroxamic acid, pyrochlore was more readily floated than ilmenite. For ilmenite and pyrochlore, it is expected that benzohydroxamic acid participates in a complexation surface reaction with active metal sites (e.g., Nb, Fe, Ti) at the mineral surface. The tendency of metals to form chelates with hydroxamates follows the following order (Nagaraj, 1987):

### Table 3
Operating conditions for Box-Behnken bench scale flotation tests (Gibson et al., 2015b).

<table>
<thead>
<tr>
<th>Order</th>
<th>Std. Order</th>
<th>Run Order</th>
<th>Collector (±1)</th>
<th>Dispersant (±2)</th>
<th>Pulp Temp (±3)</th>
<th>Actual variable level (uncoded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BB11</td>
<td>BB1</td>
<td>–1</td>
<td>–1</td>
<td>0</td>
<td>200 (g/t) 0 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>2</td>
<td>BB4</td>
<td>BB3</td>
<td>1</td>
<td>–1</td>
<td>0</td>
<td>1300 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>3</td>
<td>BB12</td>
<td>BB2</td>
<td>–1</td>
<td>1</td>
<td>0</td>
<td>200 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>4</td>
<td>BB9</td>
<td>BB1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1300 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>5</td>
<td>BB7</td>
<td>BB10</td>
<td>–1</td>
<td>0</td>
<td>–1</td>
<td>200 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>6</td>
<td>BB14</td>
<td>BB12</td>
<td>1</td>
<td>0</td>
<td>–1</td>
<td>1300 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>7</td>
<td>BB5</td>
<td>BB11</td>
<td>–1</td>
<td>0</td>
<td>1</td>
<td>200 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>8</td>
<td>BB1</td>
<td>BB8</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1300 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>9</td>
<td>BB8</td>
<td>BB10</td>
<td>0</td>
<td>–1</td>
<td>–1</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>10</td>
<td>BB2</td>
<td>BB13</td>
<td>0</td>
<td>1</td>
<td>–1</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>11</td>
<td>BB10</td>
<td>BB6</td>
<td>0</td>
<td>–1</td>
<td>1</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>12</td>
<td>BB3</td>
<td>BB15</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>13</td>
<td>BB6</td>
<td>BB12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>14</td>
<td>BB13</td>
<td>BB8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
<tr>
<td>15</td>
<td>BB15</td>
<td>BB10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>750 (g/t) 400 (g/t) 40 (°C)</td>
</tr>
</tbody>
</table>

* Dosage per rougher (4 roughers total).

### Table 4
Statistics of repeatability tests for flotation of ilmenite and pyrochlore with BHA.

<table>
<thead>
<tr>
<th></th>
<th>Ilmenite</th>
<th></th>
<th>Pyrochlore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 kg/t BHA</td>
<td>5 kg/t BHA</td>
<td>20 kg/t BHA</td>
</tr>
<tr>
<td>Mean:</td>
<td>16.7</td>
<td>11.8</td>
<td>94.0</td>
</tr>
<tr>
<td>Max:</td>
<td>23.0</td>
<td>13.5</td>
<td>96.0</td>
</tr>
<tr>
<td>Min:</td>
<td>11.0</td>
<td>9.0</td>
<td>92.0</td>
</tr>
<tr>
<td>St Dev:</td>
<td>6.0</td>
<td>2.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Fig. 2. Recovery of pyrochlore and ilmenite (–150/+53 µm) with BHA as a function of pH.
Fe, Cu, highly charged cations (i.e. Nb$^{5+}$, Ta$^{5+}$) 

Rare earths and Al 

Transition metals, Nb, Ti, V, Mn, Zr, Hf, Ta 

Alkaline earth metals

More recently, Parker et al. (2012) experimentally compared chemical interactions of n-octyl hydroxamate with various copper sulphides such as bornite (Cu$_3$FeS$_4$) and chalcopyrite (CuFeS$_2$), as well as pyrite as pH 9.5 and above. Formation of multilayer copper hydroxamate was observed on these minerals. Strong chemical interaction was evident especially following pre-oxidation and the hydroxamate was found to be adsorbed on Fe sites of these copper sulphide minerals. Co-adsorbed hydroxamic acid and ferric hydroxamate were also observed. Pyrite interacted poorly with the hydroxamate unless it was pre-oxidized. In addition, Yang et al. (2016) conducted a study on the flotation of wolframite with benzohydroxamic acid that concluded the adsorption of benzohydroxamic acid on high iron wolframite surfaces was higher, as was the flotation recovery. This was attributed to the formation of a new ferric product generated from the reaction between benzohydroxamic acid and iron on the mineral surface.

In reference to the current work, the adsorption of BHA through interaction with iron sites rather than titanium on the surface of ilmenite particles is likely a stronger reaction and will result in increased flotation recovery. Finer grinding may result in increased surface exposure of iron (ilmenite) and niobium (pyrochlore), and therefore increased flotation recovery. These results are in agreement with recent investigations which showed the role of iron in pyrochlore flotation (Chelgani et al. (2014, 2013, 2012a, 2012b), Ni and Liu (2012b)).

3.1.1. Mixed mineral micro-flotation tests

A series of micro-flotation tests was conducted using 1:1 mixtures of pyrochlore and ilmenite at high and low BHA concentrations. Two different mixtures were tested:

1. Coarse pyrochlore (−150 μm/+53 μm) and fine ilmenite (−53 μm/+20 μm)
2. Fine pyrochlore (−53 μm/+20 μm) and coarse ilmenite (−150 μm/+53 μm)

The objective of these tests was to understand how particle size affects flotation recovery of the different minerals and how the minerals compete for collector adsorption in flotation as well as the effect of SHMP on the floatability of single minerals. The results are presented in Figs. 5 and 6; the flotation recoveries of pyrochlore and ilmenite in single mineral flotation tests have been included for comparison purposes. Note that in the mineral mixture tests, recovery of individual minerals was calculated as a function of the initial mass of that mineral following screening of the products at 270 mesh (53 μm).

Fig. 5 shows that fine ilmenite had an adverse effect on the flotation of coarse pyrochlore when floated in the same environment. At low collector concentration, fine ilmenite out-competed coarse pyrochlore for collector. At high collector concentrations, a negative effect on coarse pyrochlore by the presence of fine ilmenite recovery was less significant. These observations highlight the need for a careful control of collector dosage to starve ilmenite fines to non-floatability to allow selective recovery of coarse pyrochlore. In single mineral pyrochlore flotation with 5 kg/t BHA, the concentration level for starvation of ilmenite was likely met. However when fine ilmenite was present in the flotation system and competed with pyrochlore for collector adsorption, there

![Fig. 3. Recovery of pyrochlore and ilmenite as a function of BHA dosage at pH 8.](image3)

![Fig. 4. Incomplete pyrochlore recovery with BHA due to hydrophobic particles sticking to the side of the flotation cell.](image4)

![Fig. 5. Flotation of coarse pyrochlore-fine ilmenite mixture using BHA.](image5)
was no longer sufficient collector available to recover both ilmenite and the coarse pyrochlore. At a collector concentration of 20 kg/t, it is feasible that there was sufficient collector available to recover coarse pyrochlore even in the presence of fine ilmenite. Decreased pyrochlore recovery observed in the mixture test compared to the single mineral test at 20 kg/t BHA is likely within the range of experimental variability.

The case for behaviour of coarse ilmenite mixed with fine pyrochlore is given in Fig. 6. Ilmenite recovery was greater when floated together with the fine pyrochlore at both low and high collector dosage levels. The recovery of fine ilmenite was higher when floated together with pyrochlore than when floated as a single mineral for three of four conditions tested. This indicated the possibility of inadvertent activation of ilmenite by pyrochlore. It is suggested that the high flotation recovery of ilmenite observed in bench scale flotation (as will be discussed in subsequent sections) may be partly related to the same phenomenon of inadvertent activation. Of course, it is also possible that small amounts of fine ilmenite were recovered through entrainment with the highly floatable pyrochlore particles.

It appears that the possibility of inadvertent activation is statistically significant rather than attributing the trend in these results to merely experimental error. The percentage of difference in some cases is greater than that observed in repeatability tests (Table 4). In bench scale testing, the ore sample in its entirety (i.e. pyrochlore and all gangue minerals) is processed together and there are numerous mineral-mineral interactions not only during conditioning/flotation, but also during grinding which enable evolution and transfer of active species from mineral to mineral as well as through the grinding media. The aqueous phase should play a role as a medium in the transfer of activating species considering the use of high collector dosage levels (3–20 kg/tonne) and possibly through complexation reactions.

3.1.2. Effect of SHMP in micro-flotation: Single mineral and mixed mineral cases

The impact of SHMP was tested on flotation recovery of pyrochlore and ilmenite as single minerals and as 1 to 1 mixtures. Fig. 7 shows the single mineral recoveries as a function of SHMP dosage for both minerals, with respect to the order of its addition in relation to BHA. In both cases, pyrochlore recovery decreased with an increase in SHMP dosage. Recovery of ilmenite, which was much lower than that of pyrochlore, also decreased with SHMP dosage but the reduction was not as significant as in the case of pyrochlore. This may be because the level of ilmenite recovery was already low and any further decrease was marginal due to physical constraints related to the small-scale of testing. From a fundamental perspective, the difference in function of BHA and SHMP is mainly related to their adsorption mechanism. Sodium hexametaphosphate is a source of polyanionic species (Bulatovic, 2007). As such, it can act as a dispersant in aqueous processing systems through adsorption of its polyanions. It can also act as a depressant for gangue minerals associated with pyrochlore. In general, such interactions are typical of weak adsorption, eventually leading to formation of relatively soluble surface complexes (Hatch and Rice, 1939; Ni and Liu, 2013). According to the current results, SHMP can act as a pyrochlore depressant in flotation with BHA. This suggests that the dosage of SHMP needs to be closely controlled in flotation circuits.

A striking feature of the results presented in Fig. 7 is the effect of reagent addition order. When SHMP was added before BHA, the depression effect on pyrochlore was quite severe compared to when it was added after BHA. The same effect of the addition order was also visible on ilmenite, but to a lesser extent due mainly to the fact that recovery level was already low. It can be hypothesized that when SHMP is adsorbed on the surface of such minerals, it stabilizes the hydrophilicity of that surface through hydrogen bonding. Since it is a large molecule with 18 oxygen atoms ((NaPO₃)₆), it is capable of forming multiple hydrogen bonds with water. Therefore the barrier between the mineral surface and collector species of BHA is thicker and denser. When BHA is used before SHMP, the hydrogen bonding capability of the surface is considerably blocked and the depressing action of SHMP is limited.

The case for the binary mixture of pyrochlore and ilmenite is given in Fig. 8, where the effect of SHMP at 5 kg/tonne is compared for two levels of BHA dosage at 5 kg/tonne and 20 kg/tonne. It was observed that the order of reagent addition had the same effect on flotation behavior in the pyrochlore-ilmenite mixed mineral system. However, recovery levels were somewhat different in the mixed mineral system compared to the single mineral system. Pyrochlore recovery in the absence of SHMP was similar at about 80% and was reduced to 17% following SHMP addition ahead of BHA. When the SHMP was added after BHA, the recovery of pyrochlore did not drop to the same extent. When the dosage of BHA was increased to 20 kg/tonne, the depressing action of SHMP on pyrochlore was less significant as the collector/depressant ratio was more favourable. The relative effect of SHMP on the flotation behaviour of ilmenite is similar. Table 5 shows the variation of the pyrochlore/ilmenite ratio in the concentrate with respect to use of SHMP. The ratios were consistently higher for a larger BHA/SHMP ratio (high BHA dosage, with SHMP dosage held constant) regardless of the order of addition, indicating that pyrochlore selectivity is favoured by the relative dosage of BHA. It is also clear that the pyrochlore/ilmenite ratio is highest when SHMP is added after BHA. The practice of adding a modifier (such as SHMP) after collector addition in flotation corresponds to a “cleaners” stage, where...
an upgraded stream originating from a primary flotation stage has already been treated with collector. Thus, these results have relevance to relative effects of reagents in flotation practice (e.g. selectivity function in the cleaners).

3.2. Bench scale flotation

Grade-recovery curves and assessment of the interaction effects of the parameters tested in the Box-Behnken experiment have been detailed for niobium by Gibson et al. (2015b) and for various gangue components by Gibson et al. (2015c).

A plot of titanium dioxide recovery as a function of niobium pentoxide recovery is presented in Fig. 9. A ‘Line of No Selectivity’ has been included in the plot to clearly illustrate that the selective flotation of niobium over titanium is minimal. In fact, for most tests conducted there is a near perfect linear correlation between niobium recovery and titanium recovery. While it is known that pyrochlores are complex oxides and can contain titanium in their crystal structure (Chelgani et al. (2012a), XRD analysis of the flotation concentrate (Section 3.2.1) shows the presence of ilmenite as a distinct mineral phase. Therefore it is unlikely that the linear trend observed Fig. 9 can be wholly attributed to the presence of titanium within the pyrochlore structure.

Fig. 9 suggests that niobium and titanium minerals have a nearly equal affinity for, and therefore equal flotation response, to the collector. However, small scale flotation testing of ilmenite at pH 8 has revealed that this is not the case, leaving two possibilities for the co-dependent recovery of niobium and titanium. As previously mentioned, the first possibility is that titanium minerals (mainly ilmenite in this ore) are subject to inadvertent activation in real ore flotation where the flotation pulp can act as a medium to transfer soluble species (such as iron species) which may contribute to the increased recovery of titanium oxides. Investigations by Parker et al. (2012) indicated multiple species on copper sulphides forming hydrophobic layers, which included not only copper hydroxamate and hydroxamic acid, but also ferric hydroxamatate. Jordens et al. (2014) reported that adsorption of ferrous and ferric iron species caused positive shifts in the zeta potential of allanite (a rare earth oxide mineral) providing active sites for stronger interactions with benzohydroxamic acid. Considering that there are multiple sources of iron species in process streams including the grinding mill and media, they are often an integral part of process chemistry. It is possible that activating species for gangue minerals such as ilmenite in the present case are in the form of metal-hydroxamates, which may have formed hydroxamate complexes involving ferric and possibly niobium species (a research area under further investigation). Assuming that the mechanism does not significantly involve locked particle recovery, the second possibility is that titanium minerals, which exhibit some floatability as has been noted in earlier research on flotation (Gaudin, 1957; Klassen and Mokrousov, 1963), are also recovered by physical association among strongly hydrophobized pyrochlore particles and bubbles forming clusters, a phenomena given recent attention by Ata and Jameson (2005). Another possibility of course is hydraulic entrainment mechanism, which may contribute to recovery of gangue in the fines particle size range.

### Table 5

<table>
<thead>
<tr>
<th>Reagent conditions</th>
<th>Pyrophylite to ilmenite ratio in concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 kg/tonne BHA</td>
</tr>
<tr>
<td>BHA, No SHMP</td>
<td>3.7</td>
</tr>
<tr>
<td>SHMP before BHA</td>
<td>1.7</td>
</tr>
<tr>
<td>SHMP after BHA</td>
<td>5.0</td>
</tr>
</tbody>
</table>

3.2.1. Mineral balance

Flotation products from test BB6 (Fig. 9), one of the three centre point runs (in terms of coded variables: BHA = 0 level, SHMP = 0...
Sturges and Harrison (1989). Comparing the high recovery presented in Fig. 10. The error bar (±25%) is a conservative representation of relative accuracy of the semi-quantitative XRD results based on XRD accuracy studies conducted by Brime (1985) and Sturges and Harrison (1989). Comparing the high recovery (~90%) of ilmenite to the overall elemental TiO₂ recovery of 72.7% (after 4 stages) in BB6 in Fig. 9, it is evident that titanium must be present in another mineral, which is not being recovered to the concentrate.

It is plausible that a portion of titanium is present in the form of other minerals such as rutile, which would account for some of the discrepancy between titanium mineral and elemental recovery to the niobium concentrate. Since semi-quantitative XRD analysis has a significant inherent error in the analysis of minor components it is probable that ilmenite recovery was even lower. Similarly, pyrochlore recovery in Fig. 10 was reported to be about 60% after two rougher flotation stages, while more reliable elemental analysis by XRF puts niobium recovery closer to 90% after two rougher flotation stages. This discrepancy is also likely in part due to the lack of accuracy of semi-quantitative XRD analysis in complex mineralogical systems.

3.2.2. Significant factors (niobium and titanium Recovery)

Table 6 outlines the statistically significant factors that affected the recovery of niobium and titanium minerals.

At the 95% confidence interval, temperature (°C) showed no statistically significant effect on either niobium or titanium recovery. The probable reason for this was attributed to the fact that the required concentration of BHA to show its overall collecting power through its predominant chemisorption mechanism in this flotation system was attainable within its solubility limit at ambient temperature (Gibson et al., 2015b). The interaction term 'AB' shows the positive interaction effect of collector and SHMP on the recovery of both titanium and niobium. The 'A²' term defines the curvature of the surface plots presented in Fig. 11.

3.2.3. Titanium recovery (Rougher 1)

Surface plots for titanium recovery after the first stage of rougher flotation are presented in Fig. 11. Beginning in the first stage of rougher flotation the significant factors from Table 6 (including the positive effect of collector, the negative interactive effect of collector and SHMP, and the negative exponential effect for the collector dosage which defines the curvature of the surface plots) are the same for both niobium and titanium. Moreover, the surface plots for titanium recovery in Fig. 11 after one rougher flotation stage are nearly identical in terms of shape and curvature to those reported earlier for pyrochlore (Gibson et al., 2015b). However, from a quantitative point of view, some differences are noticeable. One difference is the relative drop in recovery with decreasing dosage of BHA with respect to temperature, which was greater for ilmenite (Fig. 11B). The other difference is related to the sensitivity of ilmenite recovery to the dosage of SHMP (referred to as Calgon in figures). The relative drop in ilmenite recovery with increasing dosage of this dispersant/depressant is somewhat greater at higher temperature. Both of these quantitative effects make sense in view of intended functionality of these reagents for ilmenite as a gangue mineral.

The fact that the statistically significant factors are exactly the same for both niobium and titanium (Table 6) and flotation of the latter is nearly complete suggests that the recovery mechanism of both minerals have common features. As discussed previously, this can be a manifestation of association between the two minerals, or their somewhat similar surface chemistry due to inadvertent activation or both aspects acting together. According to results of single mineral experiments representing a fully liberated case, one can conclude that the flotation response of ilmenite in mixtures is limited due to a genuine lack of surface chemical activity. More detailed research is required in this area combining the liberation analysis and surface chemical responses.

3.2.4. Titanium recovery (Rougher 1–2)

Surface plots for titanium recovery after the first stage of rougher flotation are presented in Fig. 12. After two rougher flotation stages, increased addition of SHMP had a statistically significant negative effect on titanium recovery, but not on niobium recovery. The negative effect of SHMP addition rate on titanium recovery is clearly visible in comparison with the first stage (Fig. 11C). This simply points to the increased dispersion/depressant effects on titanium minerals with higher addition rates of SHMP. Considering that these results represent cumulative recoveries, it can be concluded that onset of the selective negative impact of SHMP on ilmenite recovery occurred in the individual second stage. Thus, this technique of stage wise analysis of flotation by statistical design of experiments (Nanthakumar and Kelebek, 2007) is a helpful diagnostic statistical approach characterizing the evolution of reagent effects from a kinetics point of view.

It is worth noting that SHMP is a multifunctional reagent and it can act differently depending on the flotation system in which it is

![Mineral Recovery (%)](image_url)

**Fig. 10.** Mineral recovery in centre point run BB6 (A = 0; B = 0; C = 0 level) for pyrochlore, ilmenite and calcite after Gibson et al. (2015c).

### Table 6

<table>
<thead>
<tr>
<th>Significant factors</th>
<th>Recovery (%) Nb₂O₅</th>
<th>Recovery (%) TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rougher 1</td>
<td>A, AB, BHA, A²</td>
<td>A, AB, BHA, A²</td>
</tr>
<tr>
<td>Rougher 1–2</td>
<td>A, AB, BHA, A²</td>
<td>A, AB, BHA, A²</td>
</tr>
<tr>
<td>Rougher 1–3</td>
<td>A, AB, BHA, A²</td>
<td>A, AB, BHA, A²</td>
</tr>
<tr>
<td>Rougher 1–4</td>
<td>A, AB, BHA, A²</td>
<td>A, AB, BHA, A²</td>
</tr>
</tbody>
</table>

A = BHA dosage, B = Calgon dosage, C = Pulp temperature.
used. A study conducted by Ding et al. (2007) demonstrated that SHMP acted as an effective apatite depressant in the flotation of rutile by selectively dissolving Ca²⁺ on the surface of apatite, reducing surface cation points and lessening zeta potential; flotation of rutile as a titanium oxide as a single mineral was not affected by SHMP addition in the presence of an alkyl-amino-bismethylene phosphoric acid as a collector. Ni and Liu (2013) investigated the adsorption of SHMP on the surface of calcite. The authors found that SHMP formed a complex with calcium on the surface of calcite, preventing the adsorption of an alkyl hydroxamic acid. In the present batch flotation system, the mechanism of the observed ilmenite depression is not clear. It may involve an adsorption based passivation of the ilmenite surface by SHMP. However, an indirect mechanism involving other types of gangue minerals such as calcite interlocked with ilmenite (in the form of middlings) cannot be ruled out.

These aspects require a specific surface chemical investigation focusing on details of ilmenite-SHMP interactions under the influence of relevant collectors. The negative contribution of SHMP continued to have a significant effect on titanium recovery through the remaining stages of rougher flotation. It was not until the final two stages of rougher flotation that niobium recovery experienced a similar negative SHMP effect. This effect has been attributed to the depression of middlings particles by a similar mechanism as proposed above by Gibson et al. (2015b).

4. Summary and conclusions

Micro-flotation on single and mixed minerals and bench scale flotation tests on a low-grade complex pyrochlore-bearing ore were conducted with the objective to assess the flotation behavior of ilmenite as a gangue mineral in the flotation of pyrochlore with benzohydroxamic acid as a collector and sodium hexametaphosphate as a dispersant/depressant.

Considering the poor floatability of ilmenite observed in micro-flotation tests under similar pulp conditions to those tested in the Box-Behnken design bench scale flotation tests, it appears that in real ore systems, titanium minerals were recovered at least in part by a mechanism other than genuine flotation. One possible scenario is that moderately floatable titanium mineral particles were recovered in the froth by physical association with highly floatable pyrochlore, particularly when starvations levels of a dispersant (SHMP) were added to the system. Another possibility for recovery of ilmenite is an inadvertent activation by metal ions (e.g., involving iron and niobium) or their hydroxamate complexes.

In micro-flotation of single minerals it was observed that the order of addition of SHMP in relation to BHA had a strong effect on pyrochlore recovery. High pyrochlore recovery was achieved only when a high dosage of SHMP was added after BHA. The impact of SHMP addition on ilmenite recovery was less notable mainly due to the fact that ilmenite recovery was already quite low. In a

![Fig. 11. Interaction effects of variables on TiO₂ recovery after a single rougher flotation stages. For each surface plot, the third variable is held constant at the zero level (coded).](image-url)
mixed pyrochlore-ilmenite micro-flotation system, it was found that reagent addition order played an important role in the selective flotation of pyrochlore over ilmenite. Improved selectivity was observed when SHMP was added before BHA, similar to a cleaner flotation stage in real-ore flotation.

In bench scale flotation, as SHMP levels were increased titanium recovery decreased, showing that increased dispersion may help minimize entrainment. In addition, high dosages of SHMP may have contributed to the depression of titanium-calcite middlings particles, also explaining the significant negative effect of SHMP addition rate on titanium recovery. These results suggest that while SHMP can improve selective flotation of pyrochlore over ilmenite, it can also act as a pyrochlore depressant in flotation with BHA and that the dosage of SHMP needs to be closely controlled in flotation circuits.

In most cases, mixed-mineral micro-flotation tests showed that ilmenite recovery increased in the presence of pyrochlore. This observation may also be the result of ilmenite entrainment with highly floatable pyrochlore; however it also raises the possibility that titanium minerals experience inadvertent activation in the presence of pyrochlore and in the real ore system, potentially with metal-hydroxamates as the activating species which may have formed hydroxamate complexes involving ferric and/or niobium species. Further surface characterization of ilmenite is required to determine if inadvertent activation is occurring and if so, the mechanism of activation. Thorough understanding of the means by which titanium minerals are recovered to the niobium concentrate in flotation with benzohydroxamic acid will assist in rejection of unwanted gangue components.

Acknowledgements

The authors would like to acknowledge SGS Canada (Lakefield) for their ongoing support of this research. The authors would also like to acknowledge funding for C.E. Gibson from SGS Canada, the Robert M. Buchan Department of Mining, and Ontario Graduate Scholarships (OGS).

References

Fig. 12. Interaction effects of variables on TiO$_2$ recovery after two rougher flotation stages. For each surface plot, the third variable is held constant at the zero level (coded).


Butterworths, London.


