



## Comparison of collector performance for a South African and a Brazilian iron ore considering mineralogical characteristics



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### ABSTRACT

The behaviour of cationic amine collectors used in the reverse cationic flotation of quartz from iron oxide minerals appears to change from one mineral system to the other, deviating from theoretical predictions based on the reagent chemistry. The performance of five amine collectors in the flotation of a South African iron ore and a Brazilian iron ore, each with different textural characteristics was investigated using reverse flotation techniques from Brazil. Furthermore, the overall collection efficacy of the five collectors in iron ore reverse flotation was analysed. Batch flotation tests and a mineralogical characterisation of the ore using QEMSCAN was conducted. Mineral liberation heavily influenced the flotation behaviour of the two ores. A well liberated Brazilian iron ore was amenable to reverse cationic flotation, whereas, the texturally complex South African iron ore did not respond well to reverse cationic flotation. Alkyl ether amines proved to be superior to quaternary amine compounds in the flotation of quartz from hematite.

### 1. Introduction

As the excessive extraction of high grade iron ore reserves has led to the rapid depletion of these ore bodies, there is a growing need to extract and upgrade low grade iron ores into more economically viable products. The beneficiation of low grade iron ores through the reverse cationic flotation procedure is gradually gaining popularity as a possible processing route for the future of South Africa's iron industry. Reverse cationic flotation employs a reagent suite consisting of an amine compound which functions as a quartz collector in addition to providing the frothing effect in the flotation system, and hydrolysed starch, which serves to depress hematite during flotation.

#### 1.1. Amine chemistry and collector efficacy

The most commonly employed cationic collectors fall within the class of alkyl ether amines namely, alkyl ether diamines and alkyl ether monoamines. Alkyl ether monoamines are the product of a reaction between alcohols and acrylonitrile acid. The general molecular formula of alkyl ether monoamines is  $R-O-(CH_2)_3-NH_2$ . The presence of the  $-NH_2$  group allows the ether amine compounds to adsorb on the mineral surface through hydrogen bonding, in addition to electrostatic bonding via  $NH_3^+$  cations present when the ether amines associate with protons in aqueous solutions. The  $O-(CH_2)_3$  group enhances solubility and adsorption at the liquid-gas interface and it enhances the elasticity

of the liquid film around bubbles (Araujo et al., 2005).

A secondary reaction between the alcohol and acrylonitrile acid forms an alkyl ether diamine. Alkyl ether diamines are characterised by the formula  $R-O-(CH_2)_3-NH-(CH_2)_3-NH_2$ , where R is the alkyl chain. The distinct difference between the monoamines and diamines is the presence of the extra  $NH-$  group which possesses an extra lone pair of electrons. The extra pair of electrons enhances the probability of hydrogen bond formations with the mineral surface as the electrons are readily available for hydrogen bonding.

Quaternary ammonium salts have also been employed in reverse cationic flotation due to their high selectivity in the separation of quartz from hematite. These compounds are synthesized from the reaction between a tertiary amine and a halocarbon compound (Svensson et al., 2003). Adsorption of quaternary ammonium salts on a mineral surface is due to physisorption i.e. electrostatic interactions with a negatively charged mineral surface since the compound is fully dissociated in solution at all pH values and possesses a positive charge (Yuhua and Jianwei, 2005).

Imidazoline quaternary compounds are products of the reaction between fatty acids and diethylenetriamine (DETA). Reacting the imidazoline ring with a dimethyl sulphate produces the quaternary ammonium salt of the imidazoline (Bajpai & Tyagi, 2006; Tyagi et al., 2007). Imidazolines are strongly cationic, thus, they can adsorb on negatively charged mineral surfaces inducing hydrophobic properties in the mineral. The positive charge on the molecule is unaffected by

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changes in pH, hence, adsorption occurs in both alkaline and acidic conditions. Imidazoline compounds have traditionally been used in the flotation of dolomite, an impurity in phosphate ores (Sis and Chander, 2003).

Extensive research into the flotation of quartz using alkyl ether amines has shown that some ores respond to flotation using ether monoamines whilst other ores respond well to flotation using ether diamines. Papini et al. (2001) reported that iron concentrates with lower silica contents were achieved using alkyl ether monoamines in comparison to alkyl ether diamines, suggesting that alkyl ether amines were superior in quartz flotation for the ore under investigation. Quast et al. (2014) also reported higher solids recoveries when using alkyl ether monoamine collectors compared to alkyl ether diamines. However, the aforementioned results contradict molecular chemistry which predicts that alkyl ether diamines would perform better as quartz collectors since they possess an extra N–H site for hydrogen bonding with quartz silanol sites.

Vieira and Peres (2007) observed that the collector performance was also dependent on the particle sizes of the quartz mineral. In their studies on pure quartz flotation, fine quartz responded well to flotation using an alkyl ether monoamine, Flotigam EDA, whereas, medium and coarse sized particles were better floated when using the alkyl ether diamine collector Flotigam 2835, for all pH conditions that were investigated.

Quast et al. (2014) established that imidazoline salts were poor collectors with poor quartz recoveries in comparison to alkyl ether amines. The observed results were attributed to the ability of ether amines to enhance adsorption on the quartz surface through co-adsorption of their neutral molecular amine and cationic species. They adsorbed on the quartz surface through hydrogen bonding and electrostatic interactions whereas the imidazoline cations only adsorbed on the quartz surface through electrostatic interactions

The necessity of a neutral molecular species in an iron ore flotation system has been emphasized in literature. Co-adsorption of neutral molecular species with amine cations results in a reduction in the electrostatic repulsion between cations subsequently leading to the formation of a densely packed layer of collector on the mineral surface, rendering the surface more hydrophobic (Vidyadhar et al., 2002; Filippov et al., 2010; Liu et al., 2015). Chernyshova et al. (2001) and Vidyadhar et al. (2002) reported on synergistic collector adsorption of alkyl amine cations in the presence of neutral alcohols as well as in the neutral (undissociated) alkyl amine molecules. Vieira and Peres (2007) observed that at pH 9.5 and pH 10, higher quartz recoveries were more prevalent than at pH 9, thereby, suggesting that pH 9.5 and pH 10 provided the ideal chemical conditions for the co-existence of the neutral amine molecule and its cationic species resulting in the high quartz recovery.

## 1.2. Ore mineralogy

In addition to the molecular chemistry of reagents used in flotation, the mineralogy of the ore under investigation plays a significant role in flotation performance. The constraints in the beneficiation of BHQ (banded hematite quartz) and BHJ (banded hematite jaspers), arise from the complex interlocking nature of quartz and hematite at both coarse and fine particle size ranges. The inclusion of finely disseminated quartz grains in hematite and vice versa at fine sizes, also results in difficulties in attaining good liberation, making beneficiation difficult. This necessitates the design of more advanced flotation circuits that incorporate finer grinding (Das et al., 2010; Nayak, 2013). The finer the grind size, the higher the liberation, which increases chances of valuable mineral recovery. However, a detrimental effect of slimes (ultra-fines) generated through fine grinding, is the inevitable deportment of ultra-fine hematite particles to the froth product through entrainment, thus reducing the recovery of hematite in the pulp product.

Araujo et al. (2003) reported that significant amounts of iron ore

mined in Brazil do not present any textural complexities. When the ore is extracted it presents high degrees of liberation possibly due to extensive weathering patterns exerted on the ore. Grinding and milling are therefore mainly aimed at size reduction instead of liberation. On the contrary, low grade South African banded hematite iron ore with an iron content of between 20% and 47% is finely grained (Taylort et al., 1988). The finely disseminated grains make liberation difficult and fine grinding is, therefore, necessary if separation of quartz from hematite is to be attained.

South Africa hosts 1000 Mt (million tonnes) of unprocessed iron ore with an iron content of 650 Mt (Holmes and Lu, 2015). Currently no iron ore mining operation in South Africa employs reverse flotation to upgrade iron ores. Traditionally iron ore mined at mining sites has been of a high grade and no beneficiation is employed. Only Sishen mine conducts some beneficiation work i.e. dense media separation and jigging, in order to meet their customers' specifications.

Outside China, Brazil is the world's largest producer of iron ore. Iron ore reserves in Brazil are situated in the Amazon basin particularly in the state of Para and in the "Iron Quadrangle" in the state of Minas Gerais (Prior, 2015). High grade iron ore extracted in the Minas Gerais state typically has an iron content of around 65% to 66% Fe. However, in some sections of the state, itabirite (banded hematite-quartz (BHQ)) with an iron content between 30% and 35% is present. The low grade iron ore is upgraded in order to meet shipping grade ore quality. Most beneficiation is conducted through magnetic separation, flotation or gravity concentration (Clout and Manuel, 2015).

With the increased mining activities, the depletion of high grade ores has necessitated the extraction and upgrading of low grade ores if South Africa is to remain a significant producer of iron ore on the world market. It is against this background that this project was conducted on the use of the collectors to ascertain whether the reverse flotation of a South African iron ore is viable. Brazilian iron ores bear mineralogical similarities to South African iron ores. The similarity lies in that, both ores are composed of hematite and quartz due to their similar genesis through supergene enrichment of banded iron formations (BIFs) (Prior, 2015). A Brazilian iron ore was, therefore, used for comparison of flotation performance.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Feed ore

The South African iron ore used in this study was first crushed and screened in order to separate fine material from coarse material. The crushed ore with top size of 3 mm, was then blended, riffled and split into 1 kg portions in order to acquire representative ore samples for flotation tests. The splitting procedure was achieved using a rotary sample splitter manufactured by Dickie and Stockler (Allen, 1990). The aforementioned technique minimises the variation in composition between replicate tests, as the spinning riffler reduces the group and segregation error, given that the topsize of the particle size distribution has been matched to the Gy's safety Line (Gy, 1979; Lotter and Fragomeni, 2009). This reduces the standard deviation of the sample mean paymetal grade. The Brazilian iron ore employed in the study was received from Vale Mineral Resources, as a milled sample with a grind size of 80% passing 150 µm. The ore was also blended, riffled and split into 1 kg portions. "Pure Industrial quartz" (94 wt% SiO<sub>2</sub>) used in scoping studies was blended and split into 1 kg bags before use in flotation tests. The flotation feed ores were characterised using XRF (X-ray fluorescence) and QEMSCAN (Quantitative Evaluation of Minerals by Scanning electron microscopy).

#### 2.1.2. Equipment

Rod mill: A 1 kg rod mill charged with six (285 mm × 16 mm) rods, eight (285 mm × 20 mm) rods and six (285 mm × 25 mm) rods was

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