Intensification of the Reverse Cationic Flotation of Hematite Ores with Optimization of Process and Hydrodynamic Parameters of Flotation Cell

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Abstract. The demand of high grade iron ore concentrates is a major issue due to the depletion of rich iron-bearing ores and high competitiveness in the iron ore market. Iron ore production is forced out to upgrade flowsheets to decrease the silica content in the pelettes. Different types of ore have different mineral composition and texture-structural features which require different mineral processing methods and technologies. The paper presents a comparative study of the cationic and anionic flotation routes to process a fine-grain oxidized iron ore. The modified carboxymethyl cellulose was found as the most efficient depressant in reverse cationic flotation. The results of flotation optimization of hematite ores using matrix of second-order center rotatable uniform design allowed to define the collector concentration, impeller rotation speed and air flowrate as the main flotation parameters impacting on the iron ore concentrate quality and iron recovery in a laboratory flotation machine. These parameters have been selected as independent during the experiments.

1. Introduction
Currently the mining industry faces the challenge of rebellious iron ore processing. Flotation is one of the most used and efficient methods to treat oxidized ferruginous quartzite when it comes to low-grade iron ore (less than 40%) and it can produce high grade concentrates. Specialists of SP ZAO IVS has developed and patented a hematite ore flotation technology [1]. Hematite ores are different by mineral composition of host rocks and texture-structural features, which thus requires a thorough selection of flotation reagents. Consequently, the processing conditions of hematite ores are dictated by their composition and mineral dissemination, and the selective efficiency of reagents applied.

2. Collector selectivity in reverse cationic and anionic flotation routes.
The quartz and carbonate minerals (dolomite, calcite and siderite) cause iron concentrate dilution. The majority of minerals, that can be referred to as oxides and silicates, have strong flotation properties in the presence of anionic (fatty acid, etc.) and cationic type collectors. However, the floatability of minerals using anionic collectors depends on the type and quantity of compounds present on the mineral surface which can vary widely from one mineral to the other. As a result, these minerals are
characteristic of a strong dependence of their floatability on mineral composition and preparation for flotation separation [2].

Oxides and silicates can be divided into two different sub-classes for the interaction of their surface with anionic collectors [3].

The minerals in the first sub-class have a large amount of active surface species to interact with anionic collectors and can be floated without activators. Elimination of polyvalent metal compounds from their surface can improve the adsorption of anionic collectors (hematite, magnetite, goethite and others);

The minerals in the second sub-class include quartz, calcite, dolomite and others. The presence of polyvalent metal compounds (cations, hydroxides, oxides, etc.) on their surface can activate their floatability.

To sum up, the flotation performance of each mineral in an ore depends on the type and quantity of polyvalent metal compounds present at the mineral surface which can passivate (first sub-class) or activate (second sub-class) flotation [4].

Flotation comparative experiments have been conducted using different collectors for iron ore flotation such as monoetheramine and modified fatty acids. In both cases, hydrolyzed starch has been applied for iron depression and polyalkylene glycol as a froth control agent. The metallurgical results for iron concentrates obtained as non-floated (cell) products as well as the full material balance for both flotation routes are presented in Table 1. The Fe recovery is high by 9.3% with cationic route while the anionic flotation with modified fatty acids as collector leads to very low silica content of 0.88 % in the iron concentrate.

Table 1 – Impact of collector type on waste rock minerals reverse flotation performance; monoamine ether and modified fatty acids are used in the cationic and anionic reverse flotations, respectively.

| Collector             | Product  | Yield | Grade, % | Recovery, % |
|-----------------------|----------|-------|----------|-------------|
|                       |          |       | Fe<sub>total</sub> | SiO<sub>2</sub> | Fe<sub>total</sub> | SiO<sub>2</sub> |
| Monoamine ether       | Tailings | 50.80 | 15.62    | 75.01       | 19.45        | 95.63       |
|                       | Fe concentrate | 49.20 | 66.80    | 3.54        | 80.55        | 4.37        |
|                       | Ore      | 100.00 | 40.80    | 39.85       | 100.00      | 100.00      |
| Modified fatty acids  | Tailings | 57.77 | 20.12    | 67.88       | 28.75       | 99.06       |
|                       | Fe concentrate | 42.23 | 68.20    | 0.88        | 71.25       | 0.94        |
|                       | Ore      | 100.00 | 40.42    | 39.59       | 100.00      | 100.00      |

Based on data of the mineralogical analysis of iron concentrate (Table 2) obtained using optical microscopy (Nikon, reflected light, parallel Nicol prism), the content in hematite is practically the same in the concentrate, 68.5 and 69.0 %, respectively for the reverse cationic and anionic flotation. The magnetite grade in the iron concentrate of the anionic flotation is increased up to 26.0% while the grade of non-metallic minerals is decreased to 1.2%.

Hematite and magnetite liberation in both flotation tails is almost similar and equals 70% and 60%, respectively. The grain size of particles in the ore and those of the non-metallic minerals in flotation tails does not exceed 40 µm. The main mineral aggregates consist of magnetite and hematite and hematite particles form aggregates with non-metallic minerals.
Table 2 Mineral composition of the iron concentrates generated by reverse cationic and anionic flotation routes using optical microscopy (using reflected light and Nicol prism //)

| Cationic route | Anionic route |
|----------------|---------------|
| $\text{Fe}_{\text{total}} = 66.8\%$, $\text{SiO}_2 = 3.54\%$, $\text{CaO} = 0.4\%$ | $\text{Fe}_{\text{total}} = 68.2\%$, $\text{SiO}_2 = 0.88\%$, $\text{CaO} = 0.2\%$ |
| Hematite = 68.5% | Hematite = 69.0% |
| Magnetite = 22.8% | Magnetite = 26.0% |
| Goethite = 3.0% | Goethite = 3.8% |
| Carbonates = 0.8% | Carbonates = 0.2% |
| Non-metallic minerals = 4.9% | Non-metallic minerals = 1.2% |

Figure 1 shows comparative diffractograms of iron ore concentrates. It is clearly seen that flotation cell product do not contain reflexes of carbonate minerals as calcite and dolomite for anionic route. For the carbonate minerals, siderite ($\text{FeCO}_3$) is present in the concentrate obtained using the cationic route but almost absent in the concentrate of the anionic flotation. Also, there is practically no quartz in the concentrate obtained with the anionic route.

Therefore, an iron content of up to 68.2% in the non-floated product, which is iron concentrate, using the anionic route is obtained by removing the non-metallic minerals within the froth product. In the other hand a redistribution of hematite and magnetite content in the iron concentrate (cell product) was produced by increasing the latter, and redirecting siderite to froth product (tailings) (Figure 1).

However, the magnetite proportion is less in the concentrate obtained by reverse cationic flotation. Moreover, the amounts of quartz and non-metallic minerals are significantly higher, 3.5 and 4.9 %, respectively with the reverse cationic flotation, which limits the use of this concentrate for further processing in electrometallurgy. Thus, we suggest that the reduced flotation performances using the reverse cationic flotation are related to the less efficient depression of magnetite and the poor flotation behavior of the Fe-containing silicates minerals such as amphiboles in the presence of starch as
depressant [9]. Among the iron containing silicates the actinolite from the family of amphibole was detected by the optical microscopy. Thus, a new depressant was studied in this work to achieve the requirements for iron concentrate by reducing the SiO$_2$ content below 2% with the reverse cationic flotation route.

3. Study of hematite alternative depressants

Reverse cationic flotation of waste rock is associated to iron oxide depression. The depressant efficiency and property have been studied for several decades. Liu et al. (2000) have investigated the polysaccharide adsorption mechanism on mineral surface. Polysaccharides (such as starch, dextrin, guar gum and other) are simple sugars used as depressants of iron oxides and, in particular, hematite [5-7].

Recently, the presence of amphiboles in iron ores have been highlighted as one of the main issues in the flotation of oxidized ferruginous quartzite [8, 9]. Fillipov et al. (2013) suggested a starch adsorption mechanism on the Fe-Mg amphiboles surface by mean of hydrogen bonds and followed by formation of complex compounds on minerals surface [10]. Recent studies on the relationships between crystallographic properties of calcic amphiboles (greenschist facies) and flotation properties support the fact that floatability of ferruginous silicates is considerably decreased in the presence of amine used as a collector and starch [11]. As was demonstrated by Severov et al [11] the floatability of amphiboles at a given pH is related to the ratio tetrahedral Si$^{4+}$/Σoctahedral cations, substitutions between Al$^{3+}$ cations and Si$^{4+}$ in tetrahedral coordination and Mg$^{2+}$ ions contents. As a results the floatability drops in the presence of starch for those amphiboles which have more Mg ions in their crystal structures. Moreover, starch adsorption on the surface of ferruginous silicates (including amphiboles) can be explained by layering where the ferruginous cations come out on the surface, and adsorb the starch. This means that the task is to minimize the depressant impact on Fe containing silicates to obtain a high quality iron concentrate with low silica content. It has been shown that an increase of depressant concentration increases iron yield, but in turn, it decreases iron in the concentrate as starch is adsorbed on the surface of ferruginous silicates. It should be noted that starch, used for iron depression, has amylopectin that tends to form agglomerates with ferruginous silicates, and as a result, low grade concentrate (Figure 2) [10-12].

![Figure 2 - Iron ore concentrate obtained using hydrolyzed potato starch depressant](image-url)
Several studies have been focused on the search of more selective depressants than starch [14]. As part of this study, the following depressants have been tested: guar gum, modified carboxyl methyl cellulose (CMC) and caustic potato starch.

The experimental flotation results shown in Figure 3 indicate that at 58% Fe recovery the best Fe grades have been obtained using the modified CMC (DLM XP) followed by starch, CMC and guar gum.

![Figure 3 - Iron recovery into concentrate for different types of depressants](image)

4. **Intensifying the reverse cationic flotation of hematite ores using an optimization of process and hydrodynamic parameters of flotation cell**

The main aim of this second part of the study is to optimise the operational flotation conditions in the cell and the concentrations of collector and depressant for maximum flotation performances. A second order design of experiment matrix [15] has been used to investigate the effects of multiple factors such as ore properties—laboratory flotation cell operating parameters – standard deviations of iron and silicon dioxide separation. Factorial experimental design approach to optimize the flotation performance is not very often seen as worth mentioning to explain this approach in [16].

Optimization of oxidized ferruginous quartzite flotation has been studied using a laboratory pneumatic mechanical flotation cell designed by RIVS that allows an independent variation of impeller rotation speed and air flowrate.

Three independent factors or variables have been selected in this study: impeller rotation speed, air flowrate and monoetheramine concentration (X1, X2 and X3). Table 3 presents the experiment design conditions according where factors are varied within a lower limit of -1.633 and an upper limit of +1.633, and a principal factor of 0.

**Table 3 – Independent variables domain (X) and its values**

| Factor          | Value                  | Unit  | -1.633 | -1  | 0   | +1  | +1.633 |
|-----------------|------------------------|-------|--------|-----|-----|-----|-------|
| X1              | Impeller rotary speed  | rpm   | 800    | 1033| 1400| 1767| 2000  |
| X2              | Air flowrate           | l/min | 3      | 4.36| 6.5 | 8.64| 10    |
| X3              | Monoetheramine         | %     | 0.5    | 1.27| 2.5 | 3.73| 4.5   |
The results of flotation tests using center composite design can be seen in Table 4. Under the experiment design conditions, 20 tests have been conducted including eight points of two-level variability interval, six limiting points and six center of design points. All limiting points have factor central value, except factors that have variable domain as \( \pm \epsilon \) where \( \epsilon \) means difference between difference between the principal factor of 0 and the lower/upper limit of factor.

Table 4 – Independent factor matrix to implement optimum second order rotatable design

| Test n° | Factor 1 | Factor 2 | Factor 3 | Response 1 | Response 2 |
|---------|----------|----------|----------|------------|------------|
|         | X₁       | X₂       | X₃       | Y₁         | Y₂         |
|         | rpm      | l/min    | %        | %          | %          |
| 1       | 1033     | 4.36     | 3.73     | 57.8       | 77.45      |
| 2       | 1767     | 4.36     | 1.27     | 57.1       | 74.93      |
| 3       | 1033     | 8.64     | 1.27     | 56.2       | 75.34      |
| 4       | 1767     | 8.64     | 3.73     | 58.9       | 80.55      |
| 5       | 1400     | 6.5      | 2.5      | 58.8       | 78.71      |
| 6       | 1400     | 6.5      | 2.5      | 57.8       | 77.77      |
| 7       | 1033     | 4.36     | 1.27     | 58.6       | 79.46      |
| 8       | 1767     | 4.36     | 3.73     | 57.2       | 76.56      |
| 9       | 1033     | 8.64     | 3.73     | 57.5       | 79.28      |
| 10      | 1767     | 8.64     | 1.27     | 61.3       | 87.52      |
| 11      | 1400     | 6.5      | 2.5      | 57.9       | 80.96      |
| 12      | 1400     | 6.5      | 2.5      | 59.2       | 83.06      |
| 13      | 800      | 6.5      | 2.5      | 49.9       | 52.71      |
| 14      | 2000     | 6.5      | 2.5      | 58.6       | 81.05      |
| 15      | 1400     | 3        | 2.5      | 60.3       | 84.14      |
| 16      | 1400     | 10       | 2.5      | 59.2       | 82.6       |
| 17      | 1400     | 6.5      | 0.5      | 56.4       | 73.65      |
| 18      | 1400     | 6.5      | 4.5      | 62.3       | 87.39      |
| 19      | 1400     | 6.5      | 2.5      | 59.2       | 82.54      |
| 20      | 1400     | 6.5      | 2.5      | 60.2       | 83.96      |

Second power polynomials for each response function are the following:

\[
Y₁ = 58.82 + 1.40X₁ + 0.59X₃ + 1.07X₁X₂ - 1.63X₁² + 0.44X₂²
\]

\[
Y₂ = 81.01 + 4.07X₁ + 1.43X₃ - 4.78X₃² + 2.36X₁X₂ + 1.40X₁²
\]

When considering the influence of the three factors \( X₁, X₂ \) and \( X₃ \) on the separation efficiency of oxidized ferruginous quartzite (iron and silicon dioxide) using reverse cationic flotation, the following separation criterion has been revealed: a maximum recovery of silicon dioxide into the froth product is obtained at maximum iron content in concentrate. Figure 5 shows that both impeller rotation speed and monoetheramine concentration have simultaneous impact on the reverse flotation of oxidized ferruginous quartzite.

Study of standard deviations dependency on impeller rotation speed has shown that optimum indexes (as iron grade in concentrate of 59% and silicon dioxide recovery into froth product of 81%) are achieved at a rotation speed of 1600 rpm and that a speed decrease or increase results in sharp decline of qualitative-quantitative values.
Low concentration of monoetheramine produces low silicon dioxide recovery and as a consequence, low grade of iron ore in the concentrate (Figure 4).

![Figure 4](image)

**Figure 4** – Impact of monotheramine concentration on iron content in concentrate and silicon dioxide recovery into froth product

Based on the studies performed, regression models have been built for iron content in concentrate ($Y_1$) and for silicon dioxide recovery into froth product ($Y_2$) (Figures 5).

Two-factor interaction of impeller rotary speed and monoetheramine concentration results in a decrease of the parameter standard deviation at small values, and an increase at large values.

![Figure 5](image)

**Figure 5** – Impact of impeller rotational speed ($n_i$) and monoetheramine concentration ($C_{col}$) on iron content in concentrate (a) and silicon dioxide recovery into froth product (b)
Therefore, the optimization of the flotation parameters, impeller rotation speed and monoetheramine concentration, provides maximum separation of iron and silicon dioxide.

5. Conclusions
After a large amount of research performed, several factors have been identified to improve the reverse cationic flotation of hematite ores:

- selective collectors based on modified fatty acids produce an efficient flotation of ferruginous amphiboles from fine-disseminated hematite ores and minimum iron losses;
- modified CMC used for hematite depression produces a concentrate iron grade over 68%;
- both impeller rotation speed and monoetheramine concentration influence the reverse cationic flotation of oxidized ferruginous quartzite.

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