Influence of Mn$^{2+}$ ion in reverse cationic flotation of iron ore

Abstract

This paper presents the study results of Mn$^{2+}$ ion influence on reverse cationic flotation of iron ore at pH 10.5. A small influence was observed on all response variables evaluated: mass recovery, Fe metallurgical recovery, grade of Fe and SiO$_2$ in obtained concentrates for dosages of MnCl$_2$ from 600 g/ton. The conditioning of pulp with ethylene diamine tetraacetic acid - EDTA complexing agent (720 g/ton) in presence of MnCl$_2$ (600 g/ton) at natural pH, before the addition and conditioning with corn starch (400 g/ton) and amine (50 g/ton) at pH 10.5, produced a concentrate with 63% Fe, 5.1% SiO$_2$, which is similar to results obtained in flotation test without manganese species present in pulp.

keywords: Iron ore; reverse cationic flotation, Mn$^{2+}$ ion, EDTA.

1. Introduction

The Brazilian iron ore reserves correspond to 13.6% of the total world reserves. The world production of iron ore in 2013 was estimated at 3 billion tons (similar to the previous year). The Brazilian production was of 386.3 Mt with an average content of 63.6% Fe (third largest world production) split into pebble ore (10.7 %) and fine products (pellet feed and sinter feed) (89.3 %). About 70 % of Brazilian production comes from Minas Gerais State (60 Mt in 2012) (DNPM, 2014).

It is a common practice in Iron Quadrangle – Minas Gerais State to concentrate the fraction fines of iron ore by gravimetric, magnetic separation and flotation methods. As well known, the method choice to concentrate a specific iron ore depends on several factors such as its physical and mineralogical properties, and the liberation fraction size of quartz (Araujo et al., 2003; Filippov et al., 2014).

The cationic reverse flotation at pH 10.5, using corn starch as iron minerals depressant and amine as silicate gangue collector, is the most successful route used to concentrate fines of iron ores (Filippov et al., 2014, Araujo et al., 2005). However, the particles in fraction size smaller than 4 μm hamper the selectivity of this process route. To solve this problem a previous desliming operation is used, which causes metal loss (Houot, 1983; Ma et al., 2011; Filippov et al., 2014).

Multivalent cations and its hydroxy-complexes formed in water can adsorb on the surface of minerals in pulp, modifying their surface charges and thus interfering in the action of flotation reagents, causing the loss of selectivity in the process. Therefore, it is necessary to treat the process water or to complex the multivalent metallic cations present in the pulp before addition of depressant and collector reagents (Pinheiro et al., 2012, Lelis, 2014).

Lelis (2014) studied the effect of Mn$^{2+}$ species on recoveries of hematite and quartz at pH 10.5 without and with previous complexation by EDTA. In this basic, study the researcher observed that the depression of quartz by manganese species was effective only for dosages from 100 mg/L. In this pH value the dominant manganese species is Mn(OH)$_{2,5}$, which settled on both mineral surfaces. The recoveries of both minerals studied were restored by previous complexation of manganese species by EDTA.

In this paper are presented the results of the effect of MnCl$_2$ on bench cationic reverse flotation carried out with an iron ore at pH10.5 and the use of EDTA as complexing agent of Mn$^{2+}$ ions in pulp.

2. Materials and methods

2.1 Materials

The iron ore from conventional flotation feed of industrial flow sheet of Samarco A. S. was used in bench flotation tests at pH 10.5. The $d_{80}$ of the ore was equal to 135μm. The mineral phases identified by X-ray diffractometry were quartz, hematite and goethite. The contents of Fe and SiO$_2$ were respectively 44.7% and 31.8% (Cruz, 2015).

In the flotation tests, the following reagents were used: commercial ethylenediamine acetate (Flotigam EDA) with 50% of neutralization degree (Clariant A.S.) as collector; MnCl$_2$,4H$_2$O (Mn$^{2+}$ ions source) and EDTA complexing (C$_{10}$H$_{12}$N$_2$O$_4$Na$_2$.2H$_2$O) of analytical purity provided by Sinth (Labsynth Products for laboratories LTDA), commercial corn starch (Unilever A.S) as depressant; NaOH and HCl of analytical purity (VETEC A.S.) as pH control.

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2.2 Methods

The bench flotation tests, using tap water, were performed using a CDC flotation cell, at 1200 rpm speed, pulp density of 45 %wt., using a vessel of volume 2L. All tests were carried out at pH 10.5, 400 g/ton of corn starch and 50 g/ton of amine, which was determined by Cruz (2015).

The procedure adopted for bench flotation tests was (Cruz, 2015):

i. Preparation of a pulp with 45 %wt. density (1800 mL of water at pH 10.5 and 1500g of ore).

ii. Setting speed cell at 1200rpm.

iii. Addition of the appropriate solution volume with ions Mn²⁺, corresponding to the established dosage for each test, and conditioning for 6 minutes.

iv. Addition of starch solution (1 %wt), corresponding to 400g/ton dosage.

v. Pulp pH setting to 10.5 and conditioning for 5 minutes.

vi. Addition of amine solution (1 %wt.), corresponding to the dosage of 50g/ton.

vii. pH correction, if necessary, and conditioning for 3 more minutes.

viii. Opening of the air injection valve and flotation for 3 minutes.

The bench flotation tests, using EDTA as complexing agent of Mn²⁺ species, the MnCl₂ dosage was fixed at 600g/ton and the conditioning was performed in the pulp natural pH (~7.5). Then, EDTA was added, which lowered the pulp pH for approximately 4.0 (depending on dosage added), and it was conditioned for 6 minutes. Subsequently, starch (400g/ton) and amine (50g/ton) were added, following the standard procedure, steps from iv to ix described previously.

3 Results and discussion

Figure 1 presents the mass recoveries and Fe metallurgical recoveries of flotation tests in function of MnCl₂ dosages. Figure 2 presents the Fe and SiO₂ grades in the obtained concentrates in function of MnCl₂ dosage.

The mass recovery reached value around 75 % for the dosage of 2,400g/ton MnCl₂. The Fe metallurgical recovery reached value of 96 %. It means an increase of little more than 10% for mass recovery and 6% for Fe metallurgical recovery compared to the test performed without Mn²⁺ ion (mass recovery = 62.6 %, Fe metallurgical recovery = 90.4 %). The increase in both mass recovery and Fe metallurgical recovery was more evident from 600 g/ton MnCl₂. See Figure 1. These
results are coherent with Lelis (2014), which verified decrease in recoveries in micro-flotation tests of hematite and quartz, carried out at pH 10.5 and 5 mg/L amine, with increase of MnCl₂ dosage.

As can be observed in Figure 2, both Fe and SiO₂ grades have almost the same values up 300 g/ton MnCl₂. Only from 600 g/ton on, was there observed a decrease of Fe grades and increase in SiO₂ grades in obtained concentrates.

In accordance with manganese diagram species (Fuerstenau, 1985), at pH 10.5, the concentrations of Mn²⁺ and MnOH⁺ are very low. The predominant specie is Mn(OH)₂. At the maximum dosage of MnCl₂ (2,400 g/ton), a dark aspect of the pulp was observed. Duarte (2012) and Lelis (2014) also highlighted the formation of a brown precipitate, due to the Mn(OH)₂ and MnO(OH)₂ precipitation on the mineral surfaces, which was responsible for the decrease in their floatabilities, due the “slime coating” phenomenon. Thus, the increased mass recovery, observed in Figure 1 is related mainly to precipitation of the specie Mn(OH)₂ on surfaces of quartz and iron minerals.

Figure 3 presents the mass recovery and Fe metallurgical recovery in function of EDTA dosage and Figure 4 presents the Fe and SiO₂ grades in the obtained concentrates in function of EDTA dosage at fixed dosage of 600 g/ton MnCl₂.

As can be observed in Figures 3 and 4, the metallurgical recoveries and grades of Fe were around 90% and 63%, respectively. The SiO₂ grades in obtained concentrates remained in the range of 5% independent of EDTA dosage (in the absence of EDTA, the SiO₂ grade was 7.5%). Such grades are within the range of commercial specifications required for sinter feed (~63.5% Fe, 4-6% SiO₂) (Lima, 1997).

![Figure 3](image1.png)

Figure 3
Mass recovery and Fe metallurgical recovery vs EDTA dosages (MnCl₂ 600 g/ton, 400g/ton starch, 50g/ton amine, pH 10.5).

![Figure 4](image2.png)

Figure 4
Fe and SiO₂ grades in the concentrates vs dosage of EDTA (MnCl₂ 600 g/ton, 400g/ton starch, 50g/ton amine, pH 10.5).

4 Conclusions

Based on results of cationic reverse flotation tests at pH 10.5, performed with an iron ore sample in the presence of manganese species, it is concluded that the presence of ions Mn²⁺ increased the mass recoveries, Fe metallurgical recoveries, SiO₂ grades and decreased the Fe grades in obtained concentrate only from 600 g/ton MnCl₂. With addition of EDTA at 600 g/ton MnCl₂ before addition and conditioning with corn starch and amine, concentrates with greater Fe grade (~63.5%) and lower SiO₂ grade (~5%) were obtained, which are close to the commercial specifications of pellet feed, generally lower than 5% SiO₂ and higher than 60% Fe.
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6. References


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