Rem: Revista Escola de Minas
ISSN: 0370-4467
editor@rem.com.br
Universidade Federal de Ouro Preto
Brasil

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Rem: Revista Escola de Minas, vol. 68, núm. 3, julio-septiembre, 2015, pp. 319-322
Universidade Federal de Ouro Preto
Ouro Preto, Brasil

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

http://dx.doi.org/10.1590/0370-44672015680051

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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 deslaming 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 complexion 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 $Mn(OH)_{2(s)}$, 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 etheramine acetate (Flotigam EDA) with 50% of neutralization degree (Clariant A.S.) as collector; $MnCl_2.4H_2O$ (Mn^{2+} ions source) and EDTA complexing ($C_{10}H_{14}N_2O_8Na_2.2H_2O$) 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.

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 Mn^{2+}, 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.

ix. Collecting of the flotation products, drying and weighing.

In the flotation tests, using EDTA as complexing agent of Mn^{2+} species, the $MnCl_2$ 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 $MnCl_2$ dosages. Figure 2 presents the Fe and SiO_2 grades in the obtained concentrates in function of $MnCl_2$ dosage.

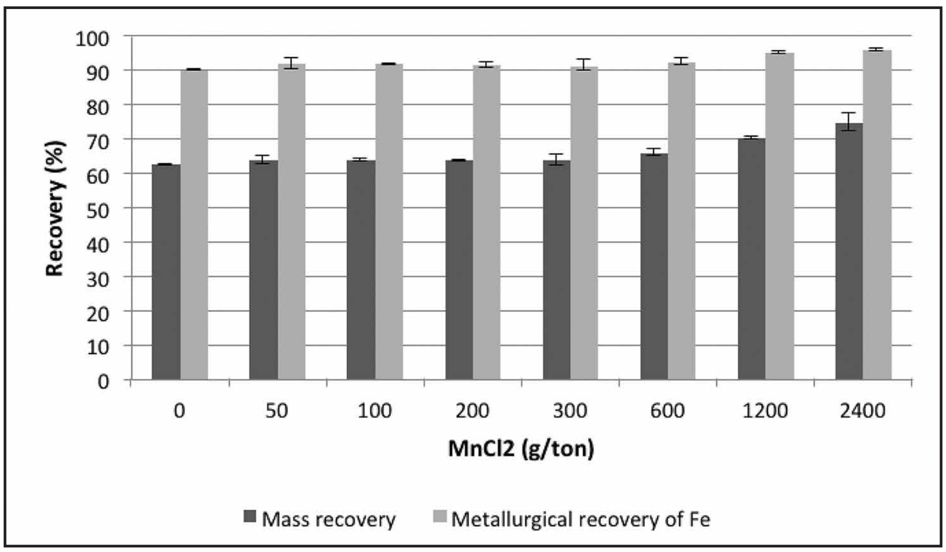

Figure 1
Mass recovery and Fe metallurgical recovery vs $MnCl_2$ dosages (400g/ton starch, 50g/ton amine, pH 10.5).

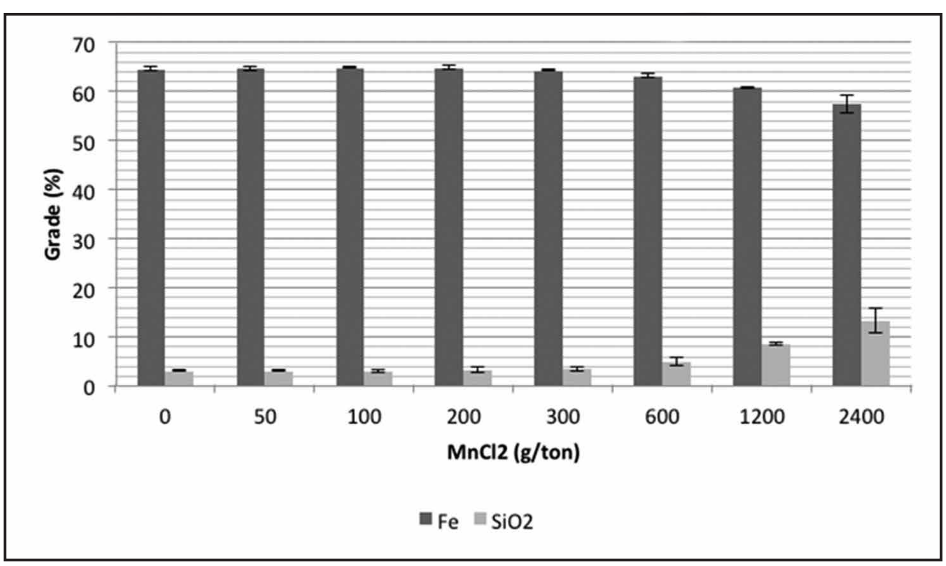

Figure 2
Fe and SiO_2 grades in the concentrates vs dosage of $MnCl_2$ (400g/ton starch, 50g/ton amine, pH 10.5).

The mass recovery reached value around 75 % for the dosage of 2,400g/ton $MnCl_2$. 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 Mn^{2+} 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 $MnCl_2$. 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 $MnCl_2$ dosage.

As can be observed in Figure 2, both Fe and SiO_2 grades have almost the same values up 300 g/ton $MnCl_2$. Only from 600 g/ton on, was there observed a decrease of Fe grades and increase in SiO_2 grades in obtained concentrates.

In accordance with manganese diagram species (Fuerstenau, 1985), at pH 10.5, the concentrations of Mn^{2+} and $MnOH^+$ are very low. The predominant specie is $Mn(OH)_{2(s)}$. At the maximum dosage of $MnCl_2$ (2,400g/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 $Mn(OH)_{2(s)}$ and $MnO(OH)_{2(s)}$ 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 SiO_2 grades in the obtained concentrates in function of EDTA dosage at fixed dosage of 600 g/ton $MnCl_2$.

As can be observed in Figures 3 and 4, the metallurgical recoveries and grades of Fe were around 90% and 63%, respectively. The SiO_2 grades in obtained concentrates remained in the range of 5% independent of EDTA dosage (in the absence of EDTA, the SiO_2 grade was 7.5%). Such grades are within the range of commercial specifications required for sinter feed (~63.5% Fe, 4-6% SiO_2) (Lima, 1997).

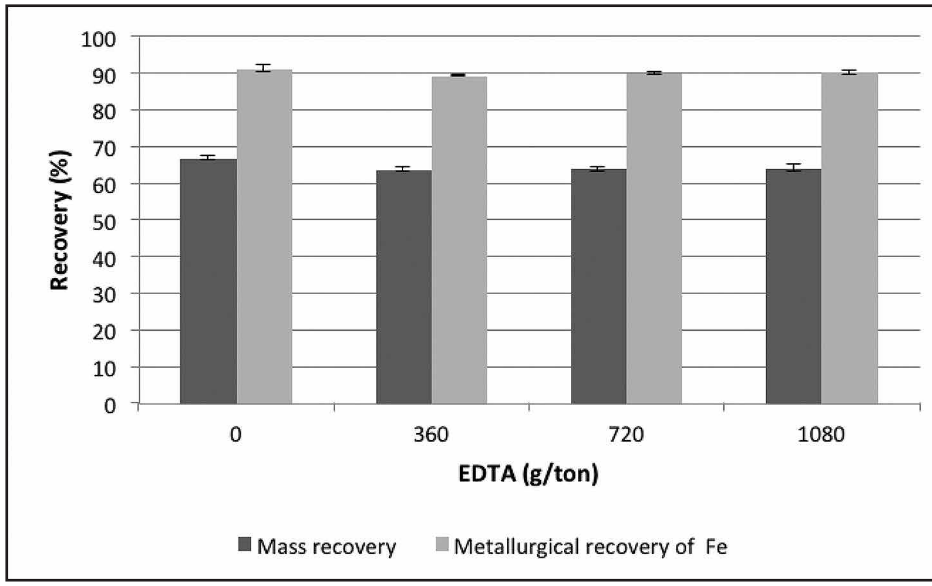

Figure 3
Mass recovery and Fe metallurgical recovery vs EDTA dosages ($MnCl_2$ 600 g/ton, 400g/ton starch, 50g/ton amine, pH 10.5).

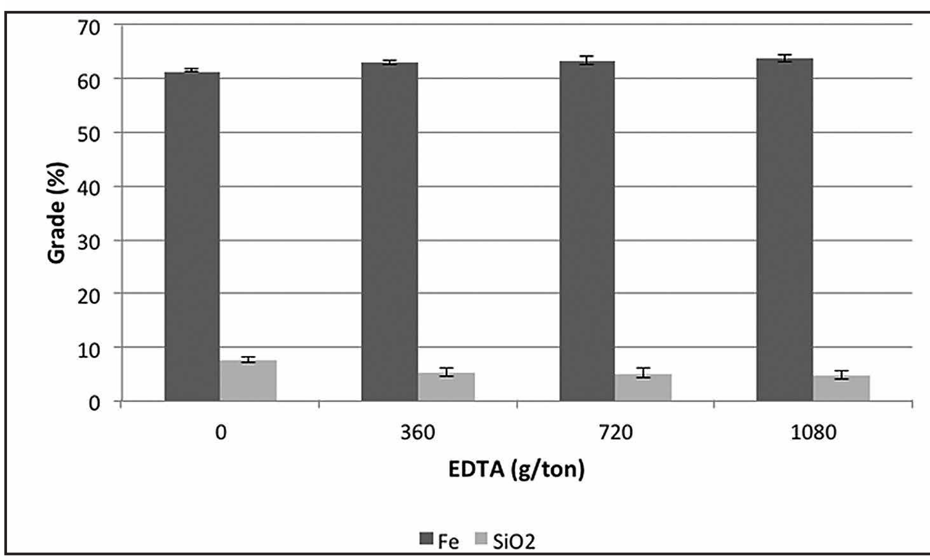

Figure 4
Fe and SiO_2 grades in the concentrates vs dosage of EDTA ($MnCl_2$ 600 g/ton, 400g/ton starch, 50g/ton amine, pH 10.5).

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 Mn^{2+} increased the mass recoveries, Fe metallurgical recoveries, SiO_2 grades and decreased the Fe grades in obtained concentrate only from 600 g/ton $MnCl_2$. With addition of EDTA at 600 g/ton $MnCl_2$ before addition and conditioning with corn starch and amine, concentrates with greater Fe grade (~63.5%) and lower SiO_2 grade (~5%) were obtained, which are close to the commercial specifications of pellet feed, generally lower than 5% SiO_2 and higher than 60% Fe.

5. Acknowledgments

The authors would like to thank CNPq by financial support and a scholarship for one of the authors, CAPES for a scholarship for one of the authors, Samarco A.S. by iron ore sample supply, Clariant A. S. by amine reagent supply and DEGEO/UFOP by chemical and mineralogical analysis.

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Received: 23 March 2015 - Accepted: 15 May 2015.