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Investigation of the interaction mechanism of depressants in the reverse cationic flotation of complex iron ores

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ABSTRACT

Iron ore mineral processing techniques are constantly challenged with the emergence of complex gangue minerals such as amphiboles, pyroxenes and others. Magnetic separation technique that achieves good results for some richer iron ores cannot guarantee the same results for such complex ores. The flotation route allows upgrading the concentrate grade but is also challenged because of the depression of Fe–Mg–Al-bearing silicates due to the presence of metal ions on the mineral surface, which can form strong chemical complexes with starch molecules used as depressant of iron oxides. The adsorption mechanism of the principal depressants used in oxide ore flotation was investigated on chamosite (chlorite group), diopside (pyroxene group) and epidote. Since the adsorption of reagents is related to the mineral surface charge in physical adsorption systems, the electrokinetic properties of these minerals were also investigated to develop a common approach for complex iron ores processing by flotation when the gangue is presented by complex Fe-Mg-Al bearing silicates.

1. Introduction

Iron corresponds to approximately 6% of earth's crust composition (McDonough and Sun, 1995). The iron-bearing minerals most commonly found in nature and economically exploited are magnetite [Fe_3O_4], hematite [Fe_2O_3], goethite [FeO(OH)] and siderite [$FeCO_3$] (Filippov et al., 2014). The hematite and magnetite containing iron ores constitute main source of primary iron for the world's iron and steel industries. Iron ore has been traditionally the second largest commodity market after crude oil and, despite the currently weaker demand, the expectation is an increase in the longer-term demand especially due to the intense urbanisation that has been taking place in many countries around the world. 98% of the iron mined around the world is processed into steel (USGS, 2017). Iron ores consumed in steel industry require a certain level of quality regarding iron and impurities content. According to the iron content, it can be used directly as direct-shipping ore or converted to briquettes, concentrates, metallized pellets, iron nuggets, pellets or sinter. The first one can supply directly blast furnaces without much effort needing a minimum physical processing and no beneficiation. However, this way does not apply to the others iron products, which need to be systematically processed to achieve the desired quality.

Magnetic separation is the most used technique to process iron ores due to the intrinsic properties of the iron oxides. However, with the increase in the production of low-grade iron ores often with a complex mineralogy, finer grinding is often necessary to achieve adequate mineral liberation. The magnetic force exerted on fine particles, most of the time, is not enough to pick them up adequately, generating a loss in quality on the final product (Arol and Aydogan, 2004). Therefore, joining the inability of magnetic separation to provide adequate products from some of the current exploited iron ores with the demand for fines with low silica content as pellet feed, flotation appears as a solution to produce concentrates with high levels of quality. Research on the potential use of flotation in the beneficiation of iron ores dates from 1931 (Crabtree and Vincent, 1962) and the first industrial application debuted in 1954 (Frommer, 1967). Direct anionic flotation seemed to be a good solution for a long time until the introduction of the concept of reverse cationic flotation, due to its better economic performance. Araujo et al., 2005, provides an excellent review of all reagents that are used in iron ore flotation. Reverse cationic flotation which was normally applied to simple systems composed by hematite/magnetite and quartz was found confronted with gangue minerals much more complex (Filippov et al., 2010). These minerals often have similar surface properties to iron oxides, rendering their separation complicated

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(Filippov et al., 2014, Severov et al., 2016). Corn starch is the most widely used depressant for iron oxide in the reverse cationic flotation of iron ores while the silicate minerals are floated using usually amine as collector. Kar et al (2013) tested the ability of four different starches: soluble starch (slightly dextrinized starch); corn starch; potato starch and rice starch, as depressant of hematite in the presence of dodecylamine (DDA) as cationic collector. As a result, all starches are effective in depressing hematite in the presence of quartz at a pH between 5 and 9. The experimental research on the adsorption mechanism conducted by Filippov and co-workers (Filippov et al., 2013) demonstrated that starch cannot be considered as a selective depressant for magnetite at a pH of approximately 10 in the process of the reverse cationic flotation of iron ores when the Fe–Mg–Al-bearing silicates as amphiboles are present in the flotation system. Several propositions of collectors and combinations of them have been suggested (Filippov et al., 2010) to achieve better flotation selectivity of iron ore with complexes silicate gangues when undesired adsorption of depressants onto gangue minerals may occur. Several studies on alternative depressants were conducted in the last years such as humic acid (dos Santos and Oliveira, 2007), carboxymetyl cellulose (CMC) and lignosulphonate and guar gum (GG) (Turrer and Peres, 2010). It has been shown that certain iron-containing minerals have a preferential affinity for humic acid as a depressant (dos Santos and Oliveira, 2007). Humic acids are organic macromolecules resulting from the degradation and polymerization of animal or plant biomass. They are insoluble in acidic region and soluble in alkaline medium. Their structure is composed of an internal nucleus surrounded by numerous branches to which are attached carboxyl and phenols that make possible the bond with the surface of the metals and confer a hydrophilicity to the molecule (Eyheraguibel et al., 2004). Indeed, the study conducted by dos Santos and Oliveira, 2007, showed that in the presence of humic acid the measured contact angle value on the quartz-water interface was lower than with starch. Although it is true that humic acid also has a depressing effect on quartz. In the presence of a cationic collector (DDA for example), hematite remains the most depressed mineral for humic acid concentration of 40 mg/L at a pH between 9.5 and 11.5. However, the hematite flotation was activated when the dodecylamine concentration was higher than 15 mg/L. Thus, the optimal ratio between collector and depressant was defined for an optimal separation.

Turrer and Peres (2010) showed that most of the depressants tested for iron ore also acted as depressants for quartz, thereby increasing the amount of silicate in the concentrate. In their studies only one carboxymethylcellulose (with high degree of substitution), guar gum and starch made it possible to obtain a concentrate with 2.5% silicates and an acceptable iron recovery rate.

The current study has been carried out to obtain a better understanding about the adsorption behaviour of some depressants not well investigated in iron ore flotation practice such as humic acid, CMC and dextrin (low-molecular-weight polysaccharide) when the gangue minerals to be floated are presented by complexes Fe bearing silicates. The investigation of the adsorption of corn starch on the surface of complex silicates found in some iron ores deposits was also carried out in the current study.

2. Experimental

2.1. Materials

The pure minerals used for adsorption tests and electrophoretic mobility measurements were crushed and sieved during sample preparation. The size fraction below 38 μm was used to perform adsorption tests and the size fraction below 5 μm, achieved by sedimentation, was used for the electrophoretic mobility measurements. The diopside sample was purchased from Crystal Magick and comes from a deposit in Brazil, chamosite was supplied from the original deposit called Chamoson in Switzerland and epidote was purchased from Wards Science and comes from Madagascar. Chemical analyses obtained by XRF (X-ray fluorescence) shown in Table 1, confirmed the high purity level of the minerals.

Table 1
Chemical analyses of pure mineral samples.

Sample	Elemental analysis (% of oxides)						
	FeO	SiO_2	Al_2O_3	CaO	MgO	TiO_2	LOI
Chamosite	30.60	21.40	11.60	1.15	1.95	0.64	10.25
Diopside	4.03	55.20	0.70	20.30	15.95	0.02	1.90
Epidote	0.35	37.80	22.40	22.50	0.14	0.09	1.09

Chamosite is a phyllosilicate (mica) containing sheets of six-Membered Rings belonging to the chlorite group. Its theoretical composition would be represented by a formula like $[(Fe^{2+}, Mg, Fe^{3+})_5 Al (AlSi_3 O_{10}) (OH)_8]$. It is important to realise that this type of silicates is generally platy and prone to generate very fine particles (clay like). It is also important to point out that both oxidation degrees of Fe cations are present in this mineral and that among the iron-bearing silicates in this ore, chamosite is the one with the highest Fe content. Diopside is an inosilicate that can be classified as a clinopyroxene. Its theoretical composition would be represented by a formula like $[CaMgSi_2O_6]$. It forms a series with hedenbergite which is Fe-bearing $[CaFe^{2+}Si_2O_6]$. As seen in Table 1, the pure diopside sample used in the current work is likely an intermediate member of this series. Epidote is a sorosilicate and it has a theoretical chemical formula as follows: $[Ca_2 (Fe^{3+}, Al) Al_2 (SiO_4) (Si_2O_7) O (OH)]$. Epidote is the name for a group of minerals and also the name of an individual mineral species, belonging to the Clinozoisite subgroup.

The ore sample used to perform the flotation tests is a magnetic concentrate from one of the largest iron ore deposit in Mexico. The chemical composition of the sample was also obtained by XRF and shows high silica content and is presented in Table 2.

2.2. Reagents

Unmodified regular corn starch (73% amylopectin and 27% amylose), dextrin from corn, humic acid sodium salt (technical grade) and the sodium carboxymethyl cellulose (Mw ~ 250.000 with degree of substation of 0.96) were purchased from Sigma Aldrich. Corn starch preparation was carried out with its gelatinisation by adding NaOH at a 4:1 ratio and deionised water and the other depressants were diluted with deionised water. A stock solution of each depressant was prepared daily, to avoid degradation of the compounds as discussed by Iwasaki et al. (1969). For the adsorption tests a stock solution at 1000 ppm was prepared for each depressant. For the flotation tests a stock solution at 1 g/L was also prepared for CMC and a stock solution at 4 g/L for the other depressants. Sulphide collectors used were Hostaflot LIB and potassium amyl xanthate (KAX) at a 1:1 ratio, both provided by Clariant. Silicate collector used was Flotigam EDA provided by Clariant. Analytical grade HCl and NaOH were used as pH modifiers.

2.3. BET measurements

The specific surface area (area per unit mass or volume) of the samples was measured by a multi-point BET method with N_2

Table 2
Chemical analyses of the magnetic concentrate.

Elemental analysis (%)				
Fe	SiO_2	Al_2O_3	S	P
66.9	4.02	1.23	0.11	0.010