How fine particles on haematite mineral ultimately define the mineral surface charge and the overall floatability behaviour

by S. Montes*, G. Montes Atenas†, and E. Valero*

Synopsis

Mineral floatability is strongly connected with mineral structure and composition. The complexity of mineral surfaces has meant that few attempts have been made to understand the effect of impurities (trace elements) on the flotation process. Zeta potential technique has been extensively used to evaluate the surface charge of mineral particles. Nevertheless, those measurements consider only an average of mineral particles surface charge. The presence of fine particles and inclusions covering a mineral may influence the local reagent adsorption process, which will ultimately be reflected in the subsequent global response of the mineral froth flotation efficiency. The current work assesses the iron oxide mineral, haematite (Fe$_2$O$_3$). Zeta potential and streaming potential techniques were used to determine the surface charge of fine and coarser particles of haematite. Further analysis was performed to determine the point of zero charge (PZC) of the mineral. In addition, adsorption isotherms of alkylammonium chloride reagents with different lengths of carbon chains were carried out. It was found haematite floatability depends strongly on the isoelectric point (IEP) value, which is affected by other mineral species present at the mineral surface. Haematite floatability became significant only at relatively high tetradecyl ammonium chloride collector concentrations (concen-

tration greater than 4 x 10^-4 M), which does not happen with other oxides such as quartz. Unlike quartz, haematite develops a low surface charge over a wide range of pH, disabling all long-range attractive interactions between the mineral and the collector. Therefore, hydrophobic chain interaction is probably the most likely mechanism acting to promote collector adsorption and enhance further floatability. Diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to suggest a possible mechanism to understand the sequence of collector adsorption and the effect of trace species on it.

Keywords: floatability, haematite, adsorption, electrochemistry, zeta potential.

Introduction

The connection between the electrochemistry of minerals and their flotation behaviour has been widely studied during the last decade1–3. Insoluble mineral oxides produce a surface charge at the solid-solution interface, which depends on mineral surface structure, solution pH, electrolyte nature, etc.4. Besides those variables, there is a striking relationship between trace elements within minerals and their effect over the different processes taking part at mineral enrichment procedures. It is well known that the flotation behaviour of iron ore, particularly haematite, is dependent on the ore’s chemical composition5–6. For example, Kulkarni et al. determined an isoelectric point (IEP) equal to 3.0 and a point of zero charge (PZC) equal to 7.1 for the same natural haematite7. Often these two concepts are assumed to be similar but their definition proves otherwise8. Earlier, Stumm proposed that these two zero charge conditions could be equal only when strong adsorption of electrolyte ions by a charged colloid does not occur. Usually the PZC is defined as the pH value where one of the following surface charge conditions equals to zero:

- structural charge derived from the mineral composition and disorder,
- charge due to adsorption/desorption of protons or hydroxyl groups, and
- any charge coming from any external ions included in the solution in contact with the mineral surface.

The experimental condition under which the latter mathematical constraint can be achieved involves keeping all thermodynamic variables constant (temperature, pressure, etc.). New models tend to focus on the construction of more realistic molecular description of the mineral surface, and if it is possible, to indicate the relationship between mineral surface structure and intrinsic reactivity towards reagent adsorption. Scientific reports have demonstrated that electrostatic interactions between haematite and alkylammonium ions constitute a key factor in its floatability8,9. Once collector is adsorbed, the mineral surface charge can
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maintain similar values (such as the isoelectric point of quartz at low alkylammonium concentrations) or change its value to the opposite sign or become zero (such as the case of hydrolysable surfactants)\textsuperscript{10,11}. Hydrolysable surfactants make the electrical double layer much more complex since not only charged species can be adsorbed at the mineral surface but also neutral molecular structures, which may be weakly adsorbed or blocked at the double layer through steric effects.

Concerning the mineral hydrophobicity concept, most scientific reports\textsuperscript{12–14} indicated that regardless of the mineral chemical composition and surface structure, the ore requires, at some point, a certain hydrophobicity to make possible its floatability. Hydrophobic property is classically studied in terms of the fraction of solid surface covered by surfactant or alternatively by determining the minimum equivalent monolayer required to enhance the floatation to relatively significant levels. Nevertheless, when the mineral surface is composed of several mineralogical phases, the surfactant monolayer concept is still poorly understood.

In the present work, haematite’s electrochemical behaviour was connected to the mineral surface area covered by surfactant. The surface charge studies were performed by using the appropriate laboratory technique to measure it, depending on the range of particle size. The way in which trace mineralogical phases influence the collector adsorption was studied. Analysis of the variables to be taken into account to obtain good haematite floatability was proposed. Furthermore, by using the tools presented, the floatability results previously reported\textsuperscript{12} were also explained.

Materials and methods

A high grade natural mineral haematite from Vallenar (III region), Chile, was used to perform the study. The mineral was found to have a mhaematite structure ($\gamma – Fe_2O_3$), dispensing magnetic properties to the ore. The parasite ferromagnetism observed is classically associated with the transference of ferric to ferrous ions, producing an alteration of the ore magnetic moments. The mineral was ground and two fractions were separately analysed: the fine particles (< 10 µm diameter) and the coarser particles (> 10 µm). The original haematite has a particle size ranging between 100 and 200 µm exhibiting 5% of the coarser particles, > 10 µm). The original haematite has a particle size ranging between 100 and 200 µm exhibits 5% of fines with a particle size lower than 10 µm of which 20% is below 1 µm (Figure 1). The mineral composition of the original ore is presented in Table I.

The specific surface area was estimated through a continuous volumetric technique using argon adsorption at low pressures (BET method). Previous to the specific surface measurements, the sample was degassed at 110 °C and 3 mPa. For fine particles, the specific surface was found to be 7.7 m\textsuperscript{2}g\textsuperscript{-1} with an energy constant, $C$, equal to 65 (normally strong affinity shows values of the order 100 and higher), which indicated a low gas-solid affinity. The identical procedure was carried out with the original deslimed mineral obtaining a specific surface equal to 1.88 m\textsuperscript{2}g\textsuperscript{-1}. Fine particle crystallographic analysis allowed the identification of haematite and goethite as major phases, the latter present in greater quantity in the original deslimed haematite\textsuperscript{12}. It was observed that an intensified desliming did not fully eliminate the fine particles (< 10 µm), a fact, described later in this paper, that affects the electrochemical behaviour of the original mineral. The experiments performed to evaluate zeta potential with fine particles were conducted using either electrophoresis (Zeemeter Model 501, mineral particle sizes < 2 µm immersed in diluted KCl solution at ambient temperature) or streaming potential technique (cylindrical Pyrex cell 60 mm long, 12 mm diameter, two platinum electrodes, measured at ambient temperature) depending on the particle sizes distribution being assessed. The first technique was used for fine particles while the second for coarser particles. The adsorption isotherms were obtained by means of UV-visible spectrophotometry following the method described by Cases et al.\textsuperscript{13}. All measurements were made in duplicate and averages are presented.

Continuous automatic potentiometric titration technique was utilized to determine the number of equivalent monomolecular sites present in the deslimed haematite sample. The technique comprised placing 5 g of mineral in 100 ml of KCl solution, for 15 h. Separate assays using concentrations of $10^{-1}$, $10^{-2}$ and $10^{-3}$ M were conducted. The solution was brought from the initial pH of 5.2 to pH 9.7 by progressively adding a solution of 0.1M KOH. Similarly, to construct the acid branch of titration, a solution of 0.1M HCl was used. All reagents used throughout the measurements were of high purity.

Results and discussion

Mineral surface charge: electrophoresis vs. streaming potential techniques

Figure 2 shows the results obtained from the electrophoresis technique for fine particles of iron (III) oxides at two ionic strengths. The ionic strength was modified using different concentrations of KCl salt.

<table>
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<th>Table I</th>
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<td>Mineral composition of fine and coarser particles</td>
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<td>Sample</td>
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<td>Fine particles</td>
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The isoelectric point (IEP) was found to be 3.3, which is rather low in comparison to the value determined by streaming potential for coarser particles, equal to 6.0 (Figure 3). These results are in agreement with the fine particles' chemical composition in Table I where oxide species such as quartz will reduce the IEP value. Analysis revealed that magnetite and goethite are mainly associated with the original haematite structure. It is important to highlight those zeta potential values, due to particle size effect, at pH values ranging between 5 and 7 that are relatively negative in comparison with the results obtained with the original mineral at the same ionic strength.12

Determination of haematite monomolecular surface sites by potentiometric titration

Figure 4 shows the haematite surface charge during potentiometric titration as a function of pH at two ionic strengths. The mineral was previously deslimed with acid solution and washed with distilled water, following the procedure previously mentioned. This resulted in a PZC of pH 8.8. The PZC obtained for deslimed haematite produced after being washed only with doubly distilled water was pH 7.8, and it is shown by an arrow (Figure 5).

Therefore, the following ideas can be extracted from Figure 4:

➤ The H+ ion consumption by the mineral surface previously activated at pH 5 to 9 is very small, which indicates that the mineral surface is mainly neutral at that pH range. Therefore, a mediocre floatability would be expected, which is in agreement with results already published12 (see Figure 2 of the reference).

➤ The number of adsorption sites per nm² at pH 5 can be estimated to be 0.3, assuming that each proton occupies one monovalent site. This value is lower than that obtained by Shergold et al.14 of 1 site per nm² at pH 8. Even though it is not exactly the same ionic strength, it can be considered close. This result is in agreement with the low charge value measured at the mineral surface, which remains almost unaffected throughout the range of pH considered. The calculation is reported in Appendix A.
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- The surface charge density at pH 4 is 1.33 x 10^4 µEq/cm^2 (Appendix B); the value is lower than the one reported by Atkinson et al. (1967) of 4.9 x 10^4 µEq/cm^2 in the presence of a solution of 1M KCl.
- If the ore is deslimed by washing with doubly distilled water only, the surface charge density at pH 5 decreases to a fifth of the value previously mentioned (2.8 x 10^4 µEq/cm^2) and the PZC decreases to pH 7.8. This result can be explained by the presence of fine particles of goethite agglomerated over haematite particles.

Then, it could be hypothesized that acidic washing of the ore generates a double effect: (i) desliming and (ii) activation of iron surface oxide. Consequently, the diversity of values reported are not just the result of the chemical composition, morphology and structure of iron oxides in ore, but also its surface reactivity.

Indeed, the surface reactivity will produce an outspread of possible behaviours of the ore facing flotation processes.

Studies on collector adsorption isotherms

Figure 5 shows the adsorption isotherms for different alkylammonium chloride chain sizes at natural pH (7.5 ± 0.2). Haematite immersed in aqueous neutral solution generates an alkaline media, which demonstrates its high surface activity in comparison to other oxides, such as quartz, which essentially does not have any effect upon the pH of distilled water.

At similar sizes of alkyl chains, the adsorbed quantities of collector over haematite per unit area are significantly lower than those reported for quartz. This fact can be justified by the concurrence of the natural pH value and the ore IEP. The larger the alkyl chain size, the greater the shift towards lower surfactant equilibrium concentrations. The tendency is also confirmed by the results shown in a previous publication about the C14 adsorption over the same haematite mineral. The main argument to explain this effect is the increase of hydrophobic interactions between alkyl chains. A similar effect has also been reported for quartz ore. Nevertheless, the adsorption controlled by the chains’ interaction involves quite weak adsorption energies, which render the formation of surfactant multilayers unlikely. The latter explains the reason why a high concentration of surfactant is required to reach a pseudo-monolayer state or its equivalent. However, the concentration observed to produce this effect is still below the corresponding surfactant critical micelle concentration (CMC) of 4.0 x 10^-3 M. It has been demonstrated that, unlike with quartz, the pH increase does not favour the formation of a monolayer, which was explained by the absence of significant changes in the zeta potential of nearby haematite IEP.

Electrostatic adsorption energy arising between collector and mineral is lower with other cases such as quartz. This fact is confirmed by the low number of adsorption sites determined for haematite. Although it can be considered possible to modify the zeta potential at a not high tetradecylammonium chloride concentration, this situation will not necessarily lead to a higher floatability response. Indeed, floatability assays and adsorption isotherm measurements encompass considerable changes in hydrodynamic conditions and, therefore, extrapolation cannot be performed.

DRIFT analysis

Figure 6 shows the spectrum between 3500 and 2500 cm^-1. Significant changes were observed in the spectra collected for the minerals before and after adsorption of tetradecylammonium ions. At θ = 0.00 condition (coverage factor equal to zero which is the initial state of mineral surface) there is a strong and broad band in the region, classically assigned to hydroxyl groups. The shoulder located at around 3600 cm^-1 and related to isolated hydroxyl groups (free surface OH vibrations) is not well resolved; possibly due to the fact that the ore samples are not pure and other species with hydroxyl groups may overlap the bands, agreeing with previous reported outcomes. When the haematite surface is 30% covered with collector (θ = 0.3) the shoulder is completely overlapped, indicating that these sites are initially replaced by ammonium groups. The overlap occurs mainly near 3400 cm^-1, a range that has been associated with strong hydrogen bonding OH groups in the surface of micropores. After collector adsorption, there is a band at 3405 cm^-1, responsible for the overlap and linked to ammonium vibrations. Presumably this mechanism might be driven through Lewis acidic sites. Although most of the published results are based on haematite produced by thermal decomposition of goethite, it has been stated that the Lewis sites are not a product of how haematite is obtained; consequently, it may be expected as an overall behaviour. At greater covered surfaces, equivalent to 116% and 189% of a monolayer (θ = 1.16 and θ = 1.89, respectively), the shape of the shoulder follows continuous changes, which can be mainly connected to further chain interactions. This fact corroborates that adsorption process cannot continue since micropores become unreachable to further molecules. Similar analysis has been confirmed studying pyridine adsorption. Furthermore, the...
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The value of a specific surface area measured for haematite (1.88 m²/g) may confirm the small amount of tetracylammonium ions that can be adsorbed. However, at low mineral surface coverage isolated OH groups are not the only active sites for adsorption. At earlier stages of the adsorption process (θ = 0.3) other sites are also active (bands at 2924 and 2853 cm⁻¹). If the equivalent mineral covered surface goes from 116% to 189%, the bands’ intensities stay approximately constant, which proves that further adsorption and hydrophobic interactions arising between alkane chains, producing more tetracylammonium ions at the haematite surface, do not occur. The latter is in agreement with the low adsorption obtained in the previous section.

It is important to highlight that other bands located at 3360, 3260 and 3170 cm⁻¹ relate to νₐsNH, ν₁NH and 2δNH₃ respectively, were not discussed due to the overlap with the strong broad band.

Figure 7 shows the DRIFT pattern obtained at wavenumbers ranging between 2000 and 500 cm⁻¹. There are three bands at 1780, 1662 and 1519 cm⁻¹ that correspond to the mineral structure. There are also bands below 1000 cm⁻¹, particularly at 849 and 630 cm⁻¹ linked to Fe-O and Fe-OH bond stretching. After tetracylammonium ion adsorption, the bands at 1662 and 1519 cm⁻¹ change significantly in both shape and intensity. In fact, both bands appear to be connected and form one massive broad peak at early stages of adsorption. The peak at 1662 cm⁻¹ might be related to the metal-amine complex formation. This band position has been confirmed as δNH₃ molecularly chemisorbed ammonia since there are also reports that indicate that this band is characteristic of NH bending vibration. However, according to Rochester, the latter band at 1519 cm⁻¹ should be correlated to bands located at 1225 and 1180 cm⁻¹, which are not significantly apparent in the pattern. No effect on Fe-O and Fe-OH bonds appears to happen before and after adsorption.

The broadening of some peaks has been suggested to be linked to particles’ shape and size distribution.

Recently, Ivenson showed that for a mineral constituted mainly of haematite and goethite, the contact angle (defined as the angle between solid and liquid phases) increased with haematite content. The higher the haematite content in the ore, the higher the hydrophobicity of the sample. However, highly hydrophilic surfaces found in pores due to the presence of quartz and the positive surface charge provided by goethite (this situation in particular has been described by the adsorption of cetyltrimethylammonium bromide, which at concentrations above 10⁻⁴ M leaves all goethite surfaces charged positively) make the whole mineral resistant to gain in hydrophobicity. Moreover, considering the tetracylammonium chloride concentration assessed, the goethite governs the overall behaviour since to obtain negative surface charge values will involve going to pH higher than 9.

Galvanic processes vs Adsorption

It has been shown experimentally, when electrochemical interactions are driven by galvanic interactions, the lowest surface potentials are observed as free potential measurements. In this case, impurities inhibit collector adsorption. The biggest negative surface charge is given by the alumina and quartz within the ore; however, most of those impurities are included in microporous sites, unreachable by large collector molecules. Goethite exhibits the biggest positive surface charge, producing areas over the mineral that are hard to be correctly hydrophobized through the adsorption of positive charges. On the other hand, haematite does not develop an important surface charge, which could favour the collector adsorption.

Figure 8 sketches a simple model of how charges are developed at the haematite surface. A more detailed distribution of different phases can be clearly observed in the SEM microphotograph already published. Goethite sites are presumably well covered by the collector, leading to an

Figure 7—DRIFT spectra of haematite powder at various mineral surface areas covered by tetracylammonium collector in the wavelength range 2000–500 cm⁻¹

Figure 8—Simplified sketch of surface charges developed by different mineralogical species within the ore and their connection with achievable adsorption sites on natural haematite using alkyl-ammonium salt collector
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overall positive surface charge \((\partial + 1)\). The magnetite might lead to positive surface charge \((\partial + 3)\) at neutral and alkaline conditions, which acts against collector adsorption. Besides, quartz is represented by a negative surface charge \((\partial - 1)\); however, collector adsorption is difficult due to quartz presence in micropores. The aluminium oxide, even though it appears as a very low percentage, is represented as a positive or negative \((\partial +/- 4)\). This is because the PZC is close to 9, and at the range of pH considered the charge developed may have any value though small.

Effects on floatability results

Figure 9 shows the floatability results. The volcano-shape of floatability curves with pH12 agree with the low mineral charge surface density at pH ranging from 6 to 9. Fine particles adsorbed over coarser particles of haematite (size > 100 \(\mu\)m) have a significant influence on mineral floatability. Haematite exhibits a sharp decrease of surface charge when it is immersed in aqueous solution, which is the main drawback to froth flotation process. Therefore the reagents must be chosen to offset this effect.

Conclusions

The floatability of natural haematite strongly depends on its IEP which is mainly determined by normal electrostatic interactions to the mineral surface. Superficial heterogeneity in composition and the presence of fine particles do not favour the stable adsorption over the mineral surface. Chemical impurities such as goethite and silicon oxide do not contribute to floatability due to the hydrophilic character they provide. This is particularly valid in the mineral assessed where fine particles enriched in silica are found in pores. Relatively high covered fractions of surface area are required to obtain good haematite flotation behaviour. It was proved experimentally that haematite adsorption comes in two stages which may apparently happen on a sequential basis. Firstly, there is a mechanism where mainly isolated hydroxyl groups are responsible for adsorption (up to a surface coverage near to 50%). Secondly, pore sites arise as the major mechanism to achieve collector adsorption (after achieving 50% surface coverage by the collector and thereafter). The latter mechanism in this work was not seen significantly due to the low porosity of the sample.

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Appendix A

The excess of positive charge between high and low ionic strengths is near to 1 \(\mu\)M/g. Taking into account that the specific surface obtained was 1.88 \(m^2/g\), the numbers of sites per \(nm^2\) can be calculated as follows:

\[
\phi' = \frac{1}{g} \times \frac{1}{1.88 \times 10^{-10} \, nm^2} \times 10^{-6} \times 0.02 \times 0.3 = \frac{2.5 \times 10^{-2} \, \mu\text{mol/g}}{1g \times 1.88 \times 10^{-10} \, cm^2} = 1.33 \times 10^{-4} \, \mu\text{mol/cm}^2
\]

Taking into account that 1 \(\mu\)Moles = 1 \(\mu\)Eqiv H+, the final adsorption per unit area is obtained.

References

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