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Adsorption and electroreduction of hematite particles on steel in strong alkaline media

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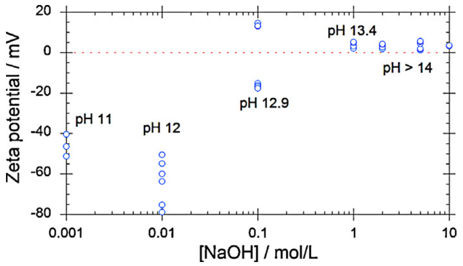
HIGHLIGHTS

- Adsorption of hematite onto steel is observed in strong alkaline solutions.
- Zeta potential of hematite in NaOH solutions up to 10 M was measured.
- A charge reversal of zeta potential occurs for $[Na^+] > 0.1$ M.
- No electrostatic repulsion is expected between particles and electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to use various electrokinetic measurement techniques, from which zeta potential values were obtained, in order to investigate the behavior of the surface charge of hematite particles in highly concentrated electrolytes (up to 10 M) and to correlate these results with the electrochemical reduction of hematite in a strong alkaline media at 110 °C. Electrochemistry experiments showed that adsorption of hematite onto steel in this strong media was possible although weak, thus the electroreduction of hematite into elemental iron was observed. At alkaline pH, zeta potential measurements by electrophoresis in diluted media yielded coherent results, and in high concentration electrolytes, electroacoustic measurements allowed proving that over a concentration in $[Na^+]$ of 0.1 M, a charge reversal occurs. Zeta potential then remains slightly positive in the range of 0.1–10 M.

1. Introduction

Several new processes to produce iron from ores with high environmental efficiency are currently under investigation within the European project ULCOS (Ultra-Low CO_2 in Steelmaking) lead by ArcelorMittal [1]. Amongst them, the electrochemical reduction of hematite from a suspension in concentrated sodium hydroxide solution at 110 °C has yielded promising preliminary results [2]. Previous investigations [3] concluded that the overall process consists of two individual steps, the first being the adsorption of hematite particles onto the steel and the second being the electrochemical reduction of hematite into elemental iron. Thus, it can be expected that the efficiency of the reduction step is correlated with the interaction between the hematite particles and the electrode surface. The interaction phenomena between two solids through an electrolytic media has been studied for decades, following the DLVO theory [4] where the total interaction force is considered as the sum of the electrostatic forces and the Van der Waals forces. In most cases, electrostatic forces have been shown to be predominant [5,6], which makes the characterization of the surface potential a major issue to understand and model these interactions. In order to optimize the hematite adsorption step, it is necessary to determine the surface potential of hematite particles in physico-conditions as close as possible to those found in the electrochemical device.

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The usual methods to determine surface potential are based on electrophoresis, which involves measuring the speed and direction of particles in an electrical field. However, these methods suffer from limitations both in the concentration of the particles in suspension and in the concentration of the electrolyte (usually $\leq 10^{-1}$ M). Since the industrial process requires a temperature of 110 °C and a concentration of NaOH in the electrolyte of 50% weight, the electrophoretic cannot be used. In this work, we use an electroacoustic method that permits the measurement of the zeta potential in highly concentrated suspensions, as well as highly concentrated electrolytes (more than 1 M).

In the present work, we present results about electrochemical reduction of hematite particles in a strong alkaline media are shown, supporting the two-step reaction. Then, calculated zeta potential values of hematite obtained from electrokinetic measurements are given. At last, the role of sodium ions on zeta potential is discussed, along with the correlation between zeta potential and particles adhesion.

2. Experimental

2.1. Materials

The iron oxide (hematite) was of 99.9% purity and was supplied by NOAH Technologies. Suspensions of hematite into various electrolyte solutions were prepared a day before the experiments. As observed by scanning electron microscopy, the size of individual particles ranged from 100 nm to 500 nm, but an average value of 800 nm with a standard deviation of 0.3 was used for all electrokinetic experiments and following calculations. This value reflects the agglomeration of the particles in solution and was verified by granulometry measurements (not shown herein). Sodium hydroxide (VWR) was of AnalaR Normapur quality. Sodium nitrate (Alfa Aesar) was of 98%+ purity. Purified water (Millipore system, resistivity 18.2 MΩ) was used.

2.2. Electrochemistry measurements

Two polytetrafluoroethylene (PTFE) beakers (500 mL capacity) embedded in heating silicone mats and placed on heating plates were used. The temperature was controlled with an electronic thermostat and maintained at 110 °C. The electrolyte used is a solution of NaOH at 50 wt.% and was prepared by dissolving 300 g of NaOH pellets in 300 g of water in each beaker. The beaker #1 contained the hematite suspension in the same electrolyte. The suspension was prepared by adding 90 g of hematite powder in the electrolyte. As a result, the total concentration of hematite used was 13 wt.% versus the total weight (electrolyte + hematite). The suspension was always stirred. The beaker #2 was used as the electrochemical cell, and contained the electrolyte and electrodes. The cathode that served as the working electrode consisted of a cylinder of steel embedded in Teflon. The reference electrode (Hg/HgO) was equipped with a glass extension containing a solution of NaOH 1 M. The pure electrolyte was stirred between two experiments.

The adsorption step of hematite onto steel was conducted by immersing the working electrode into the hematite suspension (beaker #1) for 3 min. The electrode was then transferred to the electrochemical cell (beaker #2), and the potential sweep (from −1.05 to −1.3 V vs Hg/HgO) was applied after a delay herein called “immersion time”. This delay allows the suspension remaining on the electrode due to capillarity forces to be dispersed in the beaker solution.

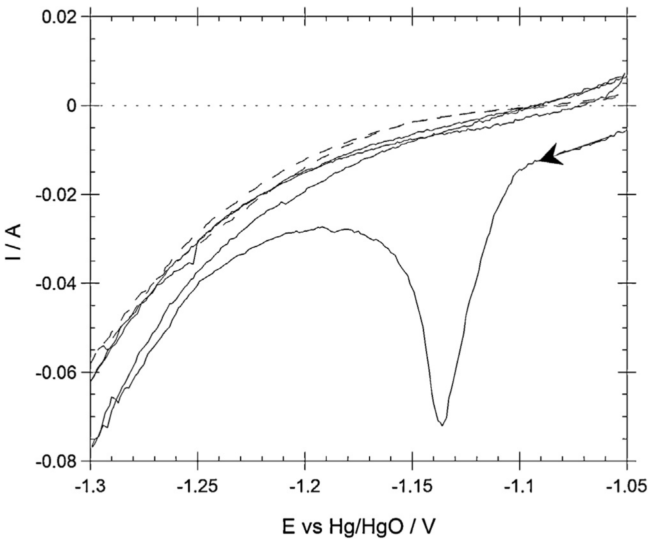

Fig. 1. Voltammogram using a steel electrode in electrolyte without adsorption step (dotted line), or after adsorption step in a hematite suspension (full line).

2.3. Zeta potential measurements

Zeta potential measurements through electrophoresis were achieved with a Nano-ZS instrument from Malvern. The concentration of hematite used was 0.5 g L^{-1}. pH was adjusted with HNO_3 and NaOH solutions.

A DT-300 system from Quantachrome/Dispersion Technology was used for the electroacoustic experiments. This instrument uses a specifically designed probe which converts a radio frequency pulse into an acoustic pulse. The acoustic pulse, sent into the suspension through a piezoelectric transducer, creates a perturbation on the immediate environment of the particles, which in turn causes the apparition of a dipole moment. Thus, an electric field is created and the colloid vibration current (CVI) can be measured. The zeta potential is then calculated from the CVI thanks to the electroacoustic theory [7]. Before each new measurement, a calibration of the probe is done in a particle-free solution, and the background current is automatically subtracted from the suspension measurements. Moreover, ultrasounds are applied for 3 min in the suspensions before any experiment using a sonotrode (UP100H model from Hielscher). Each sample used had a volume of 100 mL and the concentration of hematite particles in the samples was 20 g L^{-1}. The suspensions were always prepared 1 day before the experiments.

In experiments requiring highly concentrated NaOH electrolytes, pH was not measured in order to avoid any so-called alkaline error due to the presence of Na^+ ions. Values given hereafter were obtained from the literature [8].

3. Results and discussion

3.1. Electrochemical experiments

A typical cyclic voltammogram of hematite is presented in Fig. 1, in comparison with a blank (i.e. the voltammogram of the electrolyte only). A peak is observed at −1.13 V and was previously assigned to reduction of hematite in iron [2,3], as confirmed by the absence of signal in the blank sample (without hematite particles). After the first cycle (from −1.05 V to −1.30 V, and back to −1.05 V), a second cycle was carried out, but no peak was visible, indicating that all hematite had been reduced during the first cycle. Thanks to potentiostatic coulometry measurements, the amount of adsorbed hematite has been evaluated around 0.1 mg/cm^2. In the