Rheology and sedimentation velocity of alkaline suspensions of hematite particles at elevated temperature

Sadjia Khelifi, Denis Fünfschilling*, Huai-Zhi Li, François Lapicque

Laboratoire Réactions et Génie des Procédés, CNRS – Université de Lorraine, ENSIC, 1 rue Grandville, BP 20451, F-54001 Nancy, France

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ABSTRACT

This study aims to characterize the sedimentation velocity and the rheology of suspensions of hematite particles suspended in strongly alkaline media at 100 and 110 °C, as done for an alternative electrochemical process in development for iron production by direct electrode reduction of hematite. Considering the medium used in the process, i.e. 12% (v/v) suspension of hematite particles in 50% sodium hydroxide aqueous, the sedimentation velocity of hematite particle at 110 °C is 0.010 mm/s, which is very slow because the average size of the solid particles is around 10 μm and the significant collisions and interactions occuring between the particles in the concentrated suspension. Two geometries were used to characterize the rheological behavior of the apparent viscosity of the suspension of 12% (v/v) (i.e. 33 wt%) at 100 °C: a conventional Couette geometry and a helical ribbon mixer. The suspension was found shear thinning in the range of shear rate studied. The rheological behavior of the suspension can be described by a power-law model. The apparent viscosity of the hematite suspension estimated at a shear rate between 0.5 and 10 s^{-1} is between 100 and 20 mPa s for the two geometries. The apparent viscosity calculated from the terminal velocity of 10 μm particles is of the same order of magnitude of the results obtained with the two rheometer configurations. The effect of the particle concentration on the sedimentation velocity and viscosity of the hematite suspensions was also studied.

1. Introduction

Currently, iron is produced by the reduction of iron ore by charcoal in blast furnaces in a process that has been imagined and designed centuries ago. Improvement in the technology and the process could allow substantial reduction in energy consumption down to 4.5 MWh/ton. In addition to the above consumption, iron manufacturing results in CO_2 emissions, near 1.9 ton/ton iron in the most recent processes. Iron production alone is estimated to be responsible for 5% of the world's CO_2 emissions. In the current world where global warming pushes toward a reduction in emission of greenhouse gases, alternative processes producing less CO_2 and with lower energy consumption have to be investigated.

Amongst the various routes that can be considered [1], iron metal can be produced by electrolysis of iron ore particles in concentrated alkaline solutions [2–6]. Electrolysis of iron ore should not only be beneficial for the reduction of CO_2 produced, but should also be economical from an energy consumption viewpoint. A pilot setup with a 10 dm^2 cathode has been designed and constructed [7], and the results are very promising in terms of energy

consumption and yield of iron deposition. Contrary to most electrochemical conversion of solids, it could be demonstrated [3–5] that the reduction of the ore does not follow the usual pathway – dissolution in the liquid, transfer of dissolved ions, then electron transfer – but relies upon the direct contact of the little soluble ore (hematite) particles on the cathode surface, through a complex electrochemical pathway, still under investigation. In order to extrapolate to larger scale pilots or even to an industrial scale level, it is necessary to understand in details the physical processes involved in the process, in particular the hydrodynamic behavior of the ore particles transported in the suspension.

Previous works quoted above allowed operating conditions to be defined: the suspension was prepared from 12% (v/v) suspension of hematite particles in a solution of 50% sodium hydroxide aqueous. The working temperature in the electrolytic cell was 110 °C. The electrolyte bath flowed continuously between a flat, inclined cathode where hematite reduction takes place and the anode of a comb structure, the teeth of the comb facing the cathode. Oxygen bubbles generated on the anode complex structure, rise between the teeth of the anode before leaving the cell. The anode-to-cathode gap is 15 mm, and the mean velocity of the electrolytic two-phase medium is near 0.15 m/s.

In a first attempt to characterize the hydrodynamic behavior of the transported ore particles, the sedimentation velocity of the particles was measured for the operating conditions of the

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* Corresponding author. Tel.: +33 0383 17 53 46.
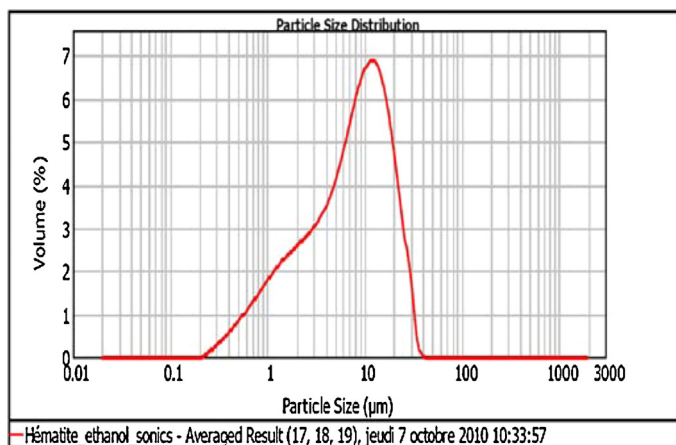*E-mail address:* denis.funfschilling@univ-lorraine.fr (D. Fünfschilling).

Fig. 1. Hematite particles size distribution measured on the Malvern Mastersizer 2000.

electrolytic process, then the rheological properties of the suspension were determined.

Literature on the viscosity of concentrated solutions of hematite is rather scarce. The few studies in this field show that aqueous suspensions of iron oxide particles exhibit a shear thinning or Bingham behavior depending on the shear rate range investigated [8–10], as with other metal oxide particles [11]. However, the case of high concentrations of sodium hydroxide in the continuous phase was never investigated.

2. Materials and methods

2.1. Chemicals

Hematite particles (Fe(III) Oxide Anhydrous, Technical) have been purchased from VWR (West Chester, PA, USA) and have been used as is. The density of hematite is ρ_s = 5260 kg/m^3. The size distribution of the particles dispersed in ethanol through sonication was measured by using a Malvern Mastersizer 2000 (Malvern Instruments Ltd Worcestershire, United Kingdom). This size distribution given in Fig. 1 shows that the solid mainly consists of 3–20 μm particles, but an appreciable fraction is formed by far smaller particles, with diameter below 1 μm. The average size of particles by weight, expressed by D[4, 3] is near 10 μm. The shape of the particles is far from regular spheres as it can be seen by SEM (scanning electron microscope) photos, as illustrated by Fig. 2. The aspect ratio is usually less than 2. In spite of the non-even size distribution and the irregular shape, hematite particles were considered as regular spheres in a first approximation, in particular for use of Stokes law (Section 3).

The sodium hydroxide solution 50% in H$_2$O comes from Sigma Aldrich (St. Louis, MO, USA) and its density is ρ_f = 1525 kg/m^3 at 20 °C.

2.2. Experimental tools

Viscosities were measured using an ARG2 rheometer (TA Instruments, Delaware, USA). The ARG2 is a shear stress imposed rheometer of high precision. Two geometries have been used: a Taylor–Couette geometry and a helical ribbon. The first geometry has often been preferred over rotating impellers for rheological measurements with suspension of oxides and ores [12–14]. The two systems above of very different geometries have been designed and built by the mechanical workshop of our lab in 316L stainless steel because of the corrosive character of the solution.

For the Taylor–Couette geometry, the mixing chamber being 70 mm deep has a diameter of 31.7 mm; the cylindrical rotor has a diameter of 27.7 mm and was 30 mm high. The gap between the cup and the rotor is 2 mm, which is more than a hundred times the average size of the particles: particle flow can therefore be considered as not affected by the solid walls.

The helical ribbon was used in a specific mixing chamber being 48 mm in diameter and 70 mm deep. The helical ribbon itself has a diameter of 42.5 mm and a height of 54 mm; the width of the swirling ribbon was 8 mm.

2.3. Experimental procedures

For the viscosity measurements, in order to limit the evaporation extent and the production of highly corrosive vapors from concentrated sodium hydroxide solutions, the temperature was reduced to 100 °C instead of 110 °C in the electrolysis pilot. For the sake of reproducible measurements, it was necessary to develop a very strict experimental protocol, as detailed below:

1. Prepare the 50 wt% NaOH solution with distilled water, then add hematite particles at the desired concentration,
2. Mix the suspension vigorously,
3. Heat the suspension to 80 °C under continuous agitation,
4. Fill the 100 °C pre-heated rheometer cup with a syringe,
5. Before viscosity measurements begin, the suspension is pre-sheared to homogenize the solution and avoid aggregation of the hematite solutions.

Sedimentation was measured in 100 cm^3 glass test tubes with an inner diameter of 29 mm and a height of 290 mm. Test tubes were maintained at the desired temperature with the RTE-7D thermostated bath (Thermo Fisher Scientific, USA) in a double envelope vessel. The height of the sedimentation front in the graduated tube was measured in function of time in a solution consisting of 50% sodium hydroxide, 50% distilled water and various amounts of hematite particles. The density of the 50% sodium hydroxide solution was measured at 1462 kg/m^3 at 110 °C. The prepared suspensions were energetically shaken after reaching the desired temperature to ensure uniformity of the suspension before settling was initiated. The experiments were carried out at 110 °C. All experiments have been repeated at least once. An additional experiment has been carried out at 100 °C with 12% (v/v) hematite in the alkaline solution.

3. Sedimentation of hematite particles

The sedimentation of hematite particles in a 50 wt% NaOH solution at 110 °C was measured with different concentrations of solids (see Fig. 3). The height H of the settling front of the suspension was measured in function of time. The movement of the sedimentation front consisted in three phases as often observed in settling operations: first, the front moved regularly with the time at a constant velocity, corresponding to the settling zone; the solid sedimentation enters the transition settling, with a decreasing sedimentation velocity. Finally the compression sedimentation takes place, with very low velocity of the solid front. Experiments were continued until no visible change in the front location was observed in the tube (final stage) (see Fig. 3). The sedimentation velocity could be deduced from the linear decreasing part of the curve. This velocity was shown to be a decreasing function of the particle concentration (Table 1). Other characteristics of the sedimentation process were summarized in Table 1.

After all ore particles have settled, the deposit occupies a fraction Φ_d of the initial volume which is defined as the ratio between the