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An atomic force microscopy study of the interaction between magnetite particles: The effect of Ca^{2+} ions and pH

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ABSTRACT

Force interactions between a microsize (m-s) magnetite probe and thin layers of synthesized magnetite particles as well as microsize (m-s) magnetite particles from magnetite concentrate were investigated using atomic force microscopy (AFM). Of special interest was the influence of Ca^{2+} ions and pH on the interaction between the probe and the two different magnetite particle surfaces. The probe and the magnetite surfaces were immersed in aqueous Ca^{2+} solutions (100, 10, and 1 mM) at various pH values (4, 6, and 10). The colloidal probe technique and a self-made computer program for automatic evaluation of adhesion forces were used. The analysis revealed an increase in adhesion force with increased calcium concentration at pH 6 for both the systems investigated. However, the adhesion behavior between the probe and the m-s and n-s magnetite particle surfaces is different at pH 10. The possible appearance of calcium carbonate precipitated onto the magnetite surfaces as well as the possible influence of already adsorbed silicate on magnetite particles from the concentrate is discussed. In addition to Ca, Cl and Na atoms, added to the working solutions, and the Fe and O detected signals, the SEM-EDS analysis also detected Si atoms on the surface of the m-s particles.

1. Introduction

Magnetite particles are of great interest in many different applications, such as targeted drug delivery, as a contrast agent for magnetic resonance imaging, in magnetoelectronic devices, and in steel production where pellets from agglomerated magnetite concentrate are used [1–4]. Their bulk and surface properties have therefore been thoroughly investigated but not usually with a focus on aggregation properties. The aggregation properties of magnetite particles are important in the pelletizing of iron ore, where pellet strength is the ultimate aim. The surface properties of magnetite particles are of primary importance in particle–particle interactions and the interaction is also strongly dependent on the particle size in addition to various surface modifications. Microsize (m-s) magnetite particles (sizes of 10–30 μm) are ferrimagnetic [5] and their magnetic properties depend on the number of magnetic domains and their orientation [6]. Magnetite particles with sizes smaller than 50 nm are superparamagnetic [7,8] and their average magnetization is zero in the absence of an applied external field. Microsize magnetite particles are usually obtained from an ore (natural particles), whereas magnetite particles of nanosize (n-s) are usually synthesized. Accordingly, natural and synthesized particles are produced in different ways, which expose their particle surfaces to quite different aqueous solutions. The former are exposed to process water, whilst the latter are produced using Milli-Q or distilled water. Natural particles usually contain mineral impurities such as apatite, calcite and silicates, which contribute to the appearance of various ions in the process water and on the particle surface. The process water contains various ions including Ca^{2+}, Cl^{-}, Na^{+}, K^{+}, NO^{3-}, Mg^{2+} [9]. The m-s magnetite particles obtained from the LKAB concentrating plant were first subjected to the process water. Among these ions are Ca^{2+}, which were shown to improve the sorption of other species onto the surface of synthetic particles, species such as soluble silicate, carbonate, and organic collector molecules [10,11]. Ca^{2+} ions are also expected to strongly affect the agglomeration and chemical properties of magnetite particles [10–12]. Since the properties of the magnetite surfaces are important for the agglomeration of magnetite concentrate, it was necessary to measure the interaction properties between natural particles and to compare these interaction forces with those between synthetic particles and natural particles.

The atomic force microscope (AFM), using the colloidal probe technique [13], is a suitable tool for sensitive measurements of particle–particle force interactions in-situ, under different conditions. The colloidal probe AFM technique allows measurement of the interaction forces between a particle attached to the AFM cantilever and the surface of interest. This technique has frequently been used with probes of well-defined geometry to measure and model forces between various

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surfaces [14–17]. However, it is less often used with particle probes of more complex surface structure, as in the case of natural magnetite.

Toikka *et al.* used a spherical magnetite particle as a probe to measure the force between magnetite and silica surfaces in a dilute electrolyte solution [18]. The adhesion energy was measured as a function of ionic strength and pH. It was found that the adhesion force in the pH range studied correlated with electrokinetic data and it was suggested that an electrostatic mechanism was dominant. The measured adhesion forces were compared with theoretical values and revealed significant differences. The differences were explained in terms of the surface roughness which was not taken into account by the model. The significant influence of surface roughness on the adhesion force measurements has been well established by other authors and new theoretical models for adhesion estimation have been proposed [19]. Although the roughness of the surfaces in this study may be even more complex than that encountered in the force measurements between a spherical magnetite particle and a silicon wafer [18], it was necessary and possible to investigate the direct interaction of magnetite particles with each other under varying conditions and non-spherical geometry. Since the geometry of the colloidal particles and the roughness of the contacting area [17] are important, the statistics and repeatability are the main parameters in order to obtain reliable results in our measurements. Although the surface structure is complex and measured values are very difficult to compare with values obtained by theoretical modeling, it might be possible to trace relative differences in magnetite particle force interaction and thus investigate the influence of pH and Ca^{2+} ions on the force between the particles.

Thus, the aim of the present work was to investigate force interactions between microsize-microsize and microsize-nanosize magnetite particles in Ca^{2+} solution and to examine the effect of calcium concentration and pH on their mutual interaction. Investigation of adhesion force behavior under different experimental conditions was one of the main goals, which may be relevant to magnetite aggregation properties. To perform this study it was necessary to develop a reliable experimental setup and automatic evaluation of the array of force curves.

2. Materials and methods

2.1. Magnetite particles and reagents

Magnetite nanoparticles with an average diameter of 10 nm, were synthesized using the precipitation technique described previously [20,21]. Microsize magnetite particles were supplied from the LKAB, Malmberget, Sweden with about 97% purity [21]. Calcium chloride ($CaCl_2$*$2H_2O$, 95%, Riedel-de Haen) was used to prepare aqueous Ca^{2+} solutions. Analytical grades of NaOH and HCl were used to adjust pH. Degased Milli-Q water was used for solution preparation and as a reference liquid for the force measurements. Water was degased using the vacuum degasification method. To remove organic impurities from the substrate surfaces, the glass slides were kept in 0.1 M aqueous HNO_3 solution for 1 h and afterwards washed with acetone, methanol and Milli-Q water before magnetite particle deposition.

2.2. Particle deposition and preparation of probes

The dip-coating technique (using a Nima dip coater, Nima Technology Ltd.) was used for the deposition of n-s magnetite particles on the glass slides. The deposition was performed as described in reference [22]. The dipping speed was set to 8 mm/min for immersing and raising of the glass substrate. The waiting time at the bottom of each cycle was 300 s and the total number of cycles used to obtain one coated substrate was 15. Samples with microsize magnetite particles were prepared by spraying the particles onto a glass slide covered by a thin layer of epoxy glue. They were then allowed to cure for 24 h. Optical microscopy and AFM were used to image the surface of microparticles on the glass substrates for the absence of glue. AFM colloidal probes were prepared by gluing the microsize magnetite particles to the end of 200 μm long V-shaped, contact-mode Si_3N_4 cantilevers (NP-S, Digital Instruments/Bruker, Santa Barbara, CA). The spring constant of the cantilevers was determined using the thermal tune method [23], with a custom device setup based on a PCI-6110 data acquisition board (National Instruments, United States), and was close to 0.12 N/m for all cantilevers. Magnetite particles with diameters between 10 and 30 μm were glued onto NP-S cantilevers using a small amount of epoxy glue. Particles were manipulated with the AFM piezo-stage mechanism in order to precisely place them at the end of the cantilever. This process was controlled through the optical microscope and by monitoring the deflection signal. The homogeneity and the surface roughness of the magnetite nano-particle layer on the glass slide and the microsize magnetite probe were characterized by AFM in TappingMode using a standard NSG-01 probe (NT-MDT, Moscow) of tetrahedral total tip shape with curvature radius less than 10 nm.

2.3. XRD and EDS measurements

Characterization of natural and synthesized magnetite particles was performed using X-ray diffraction (D5000 X-ray diffractometer, Siemens) confirming the magnetite crystallographic structure. After each experiment the magnetite probe particles were dried and characterized by SEM-EDS (energy dispersive spectroscopy) (Jeol, JSM-6460LV) to detect sorbed species on the magnetite surface.

2.4. Force measurements and AFM data analysis

Force measurements were performed with an NTEGRA AFM (NT-MDT). A liquid cell (MP6LCNTF), a scanning measuring head for liquid operation (SFC100LNTF), a fully closed-loop AFM setup and the 100 μm sample scanner (NT-MDT Z50251CLPI) equipped with capacitive sensors were used. AFM force curves were acquired between the m-s magnetite probe and either the n-s magnetite layer or m-s magnetite particles on a glass surface. The force measurements between m-s magnetite particles required either the use of a non-magnetic sample scanner or a head scanner (NT-MDT) to prevent magnetization of the m-s particles on the substrate, because the 100 μm sample scanner is equipped with a weak magnet. It was observed that the latter causes a significant magnetic interaction between m-s magnetite particles which had to be avoided. The aqueous media were 1, 10 and 100 mM Ca^{2+} solutions at nominal pH 6, which is close to magnetite PZC (point of zero charge) [21] and at nominal pH 10 and 4. The ionic strength of the solutions was calculated to be 0.003, 0.03 and 0.3 M. The time to reach the equilibrium state in the liquid cell was 15 min for each change of concentration and pH of the solution [11]. The pH value of the solution was measured with a pH meter (744 pH Meter, Metrohm AG, Herisau, Switzerland). All pH values are nominal and hereafter denoted pH 4, 6 and 10. Force curves were collected at the same approaching speed (around 70 nm/s) and the curve time for all measurements was 2 s. The deflection signals were transformed into force values using the equation:

$$F_{adhesion} = \kappa \cdot \Delta_{deflection},$$

where κ is the cantilever spring constant and $\Delta_{\mathrm{deflection}}$ is the cantilever displacement on the force curve. The adhesion force was calculated as the height displacement between the virtual level, which is the extrapolation of the lever zero force, and the minimum of the force step.

Because of the complex geometry of the microsize particles the force curves were collected on the same surface spot to eliminate effects from particle geometry imperfections. Also, it was important