Magnetic Study of Fe$_3$O$_4$ Particles for Implementation as Magnetic Fluids

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Abstract. In this work, iron oxide was synthesized by mechanical alloy vibratory disc method. The dependence of magnetic properties on both natural and commercial iron oxide has been studied by using hysteresis loops performed by a vibrating sample magnetometer. The natural oxide phases were determined via X-ray diffraction technique. Magnetic fluid samples were produced by using oleic acid as surfactant and oil as carrier liquid. The viscosity of selected samples was studied at room temperature through rotational viscometer. The results show dependence between the syntheses processes in which the samples were obtained, although experimental results are within those reported in the literature.

1. Introduction

Iron oxide (Fe$_3$O$_4$) or magnetite has interesting optical, electric, and magnetic properties for technological applications due to its composition, spinel structure, and ferrimagnetic behaviour. In colloids science, Fe$_3$O$_4$ is important in the fabrication of magnetic fluids because the rheological properties can be controlled for application in engineering [1,2] and biomedical [3,4] areas.

These magnetic fluids must have a Newtonian behaviour in the absence of an external magnetic field; high stability against aggregation processes and gravitational sedimentation is achieved by stabilizing the suspension from the particles controlling the densities between the particles and liquid carrier. This can be achieved through steric repulsion (surfactant) [3,4] or by changing the surface chemistry of the particles to obtain electrostatic repulsion between them (peptized) [4,5].

2. Experimental

The natural oxide was obtained from the Hobo – Huila region in Colombia and it was milled in a vibrating disc mill (sample m1). A commercial oxide was acquired from Carbones Andinos (sample m2). These oxides were selected by size and labelled T5, T2 and ST with regards to sift 500, between 200-230 mesh and without sift, respectively. Particle size was determined via optical microscopy.
using Leica digital equipment (DVM200) to measure the smallest diameter of a minimum of 800 particles and adjusted to a lognormal distribution. Qualitative determination of the phases was performed through X-ray diffraction (XRD) using XPERT-PRO PANalytical equipment and magnetic hysteresis loops by vibrating sample magnetometer (VSM) in a VersaLab at selected temperatures of 300 K and 320 K. Fluid preparation was performed with 20, 30, and 50% of magnetite surfactant oil prepared by mechanical agitation for 2 h at 24 °C and 43 rpm. The viscosities of magnetic fluids were analysed in a rotational viscometer (DV-E1, BROOKFIELD) with a spindle of 0.3 without magnetic field.

3. Results and discussions

We found that the T5 and T2 samples were in the 15 – 22 µm and 42 – 47 µm ranges, respectively. For the m1T5 sample, the XDR and size results are shown in Figure 1.

The irregular particle shape complicates the theoretical study of the magnetic interaction between particles of magnetic fluid, in which a calculation is necessary for the magnetization of the particle in statistical or random manner [6]. With respect to the crystal structure of the m1 sample, the XRD patterns were associated to the stoichiometric phase of magnetite (82%), followed by hematite (17%) and some silica impurities (1%).

The results of magnetic measurements for the ST, T2 and T5 samples showed that saturation magnetization values are different, revealing magnetization dependence on particle size and temperature, respectively (Figure 2).
The dependence on temperature shows the system is in a thermodynamic phase transition associated to dipole moments disorder, which is that thermal energy tends to exceed the energy coupling of the magnetic dipole moments, thus, decreasing the oxide saturation magnetization.

When coercivity increases grain size decreases due to the anisotropy of the particle surface; otherwise, its value would decrease as in the case of nanoparticles [7,8]. The saturation magnetization and coercive field values are shown in Table 1 for the m1 and m2 samples because the micrometric size of the particles present multidomain parameters.

| Sample | T (K) | Ms (emu/mol) | Hc (Oe) |
|--------|-------|--------------|---------|
|        |       | m1           | m2      | m1           | m2      |
| ST     | 300   | 78.42        | 84.42   | 142.5        | 51.55   |
|        | 320   | 77.55        | 81.5    | 142.5        | 51.02   |
| T2     | 300   | 81.59        | 83.95   | 132.2        | 53.07   |
|        | 320   | 80.7         | 83.07   | 133.4        | 48.5    |
| T5     | 300   | 77.53        | 84.34   | 144.62       | 71.05   |
|        | 320   | 76.45        | 83.72   | 147          | 69.27   |

Table 1 shows that saturation magnetization for m1 is lower than for the m2 sample, respectively, due to the presence of the hematite and silica phase. This decrease in saturation magnetization is not significant to affect the magnetic response of the sample since their values are within the ranges reported in the literature [6-8]. The difference between the m1 and m2 samples is notable in terms of the coercive field obtained, attributed to the percentage of hematite m1 present in the sample. In this case, the m2 sample can be a better candidate to study rheological or structural properties (Figure 4) of magnetic fluid under the action of a small external field.

Viscosity measurements for the m1 and m2 samples are given in Figure 3. The different curves correspond to the fast sedimentation in sample m2 and stability in sample m1.

The rheological behaviour of fluids changes in the presence of an applied external magnetic field, reaching threshold stress and high viscosity. The particles align their magnetic dipole moments with the magnetic field direction and form different structures in this direction, which increases flow resistance [9]. Figure 4 shows the structures produced for different magnetic field orientations. We see in the images that a portion of iron oxide particles were condensed, forming chains or columns, depending on the direction of the applied magnetic fields. These phenomena can bring up the feasibility of electro-optical devices by using homogeneous ferrofluid films [10].
When magnetic field ceases, the magnetic fluid tends to its original disordered state with a quasi-reversible process appearing, having a tendency for paramagnetic behaviour, which is due to the presence of the surfactant coating that covers the particle with a film, moderating the molecular interaction through steric repulsion.

4. Conclusions

The magnetic properties of Fe$_3$O$_4$ show dependence on the synthesis process, particle size, and temperature. These oxides were dispersed in carrier liquid with magnetorheological properties. The structures formed in the medium depend on the direction of the magnetic field and obtained fibrous or cylindrical structures. This behaviour with the magnetic field enables their rheological control for applications in engineering.

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5. References

[1] Donado F., Mendoza, C.Y., Valencia, R., Santiago García, J.A., 2007. Estudio experimental de la viscosidad de un fluido magneto-reológico a base de magnetita mineral, Rev. Mex. Fis. E 53 31 – 40.
[2] Friák M., Schindlmayr A., Scheffler M., 2007. Ab initio study of the half-metal to metal transition in strained magnetite, New. J. Phys. 9 1 – 15
[3] Shokrollahi H., 2013. Contrast agents for MRI, Mater. Sci. Eng. C 33 4485 – 4497
[4] Qu J., Liu G., Wang Y., Hong R., 2010. Preparation of Fe3O4-chitosan nanoparticles used for hyperthermia, Adv. Powder Technol. 21 461 – 467.
[5] Betancourt R., Saldívar R., Rodríguez Fernández O., 2004. Preparación de látices magnéticos, Rev. Mex. Fis. 50 33 – 36.
[6] Shaw D. J., 1970. Introducción a la química de superficies y coloides (Madrid:Al ham bra Ch1
[7] Blanco-Mantecón M., O’Grady K., 2006. Interaction and size effects in magnetic nanoparticles, J. Mag. Magn. Mater. 296 124 – 133.
[8] Özdemir Ö., Dunlop D. J., Moskowitz B. M., 2002. Changes in remanence, coercivity and domain state at low temperature in magnetite, Earth planet. sci. Lett. 194 343 – 358.
[9] Bronstein L. M., Huang X., Retrum J., Schmucker A., Pink M., Stein B. D., Dragnea B., 2007. Influence of iron oleate complex structure on iron oxide nanoparticle formation, Chem. Mater. 19 3624 – 3632.
[10] Yang S. Y., Horng H. E., Hong C. Y., Yang H. C., 2002. Structures, Optical Properties and Potentially Electro-Optical Applications of Magnetic Fluid Films, J. Sci. Eng. 5 85-93
Erratum: Magnetic Study of Fe$_3$O$_4$ Particles for Implementation as Magnetic Fluids

Figures 1 and 3 were incorrectly reproduced in the original PDF, the correct figures are given below.

**Figure 1.** Morphology, particle size distribution and XRD for the m1T5 sample

**Figure 3.** Viscosity of magnetic fluids elaborated from the m1 and m2 samples, as a function of revolutions per minute