# Magnetite-Clay Composites: Morphology and Magnetic Properties

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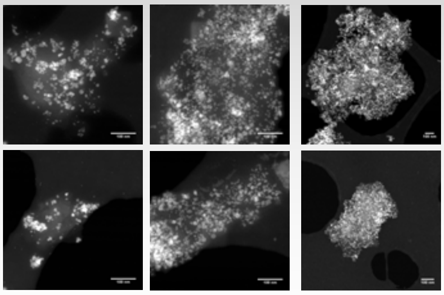
## Introduction

Our research is based mainly on the development of a novel magnetic fluid composed by composite particles of magnetite nanoparticles and micron-size clay particles (sodium montmorillonite). In previous works we have analyzed the optimal adhesion conditions, the sedimentation behavior of the particles in diluted and concentrated aqueous suspensions and the interaction energy between the particles dispersed in water. In this work we use some TEM techniques to analyze the size and shape of the particles, the distribution of the magnetite particles on the surface of the clay particles and the magnetic properties of the composites particles. In addition, the magnetic properties are obtained by means of magnetic hysteresis and low field susceptibility measurements. The results obtained allow us to tackle a complete analysis of the magnetorheological behavior of the suspensions in future work.

## Materials

Magnetite particles were synthesized using the technique of Massart [1]. Sodium montmorillonite particles were obtained by homoionization of a natural bentonite from Almeria (Spain) [2]. The clay-magnetite suspensions were prepared by means of a controlled pH procedure in order to ensure the adhesion of the magnetite nanoparticles on the faces of the montmorillonite [3]. This work analyzes three samples with ratios between the magnetite volume fraction and clay volume fraction ($\phi_M/\phi_C$) of 0.33, 1, and 3 (samples 1:3, 1:1, and 3:1 respectively).



Sample 1:3 Sample 1:1 Sample 3:1

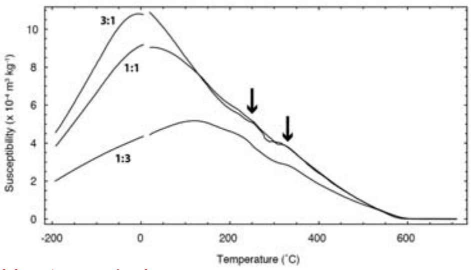
TEM pictures of the three samples.

Magnetite particles cover the face of the montmorillonite particles.

The mean diameter of the magnetite particles from the size distribution for each sample is:
Sample 1:3: (10.8 ± 3.6) nm
Sample 1:1: (11.1 ± 3.2) nm
Sample 3:1: (13.2 ± 3.2) nm

## Magnetic Susceptibility

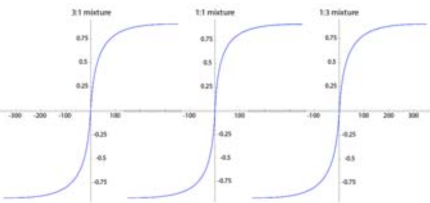
Magnetic susceptibility as a function of temperature for the three samples measured using an AGICO MFK1-FA Kappabridge instrument (University of Cambridge)




Peaks correspond to the superparamagnetic blocking temperature of the magnetite grains.
Below the blocking temperature: magnetite particles behave as an assemblage of interacting single domain particles.
Above the blocking temperature : superparamagnetic behavior.

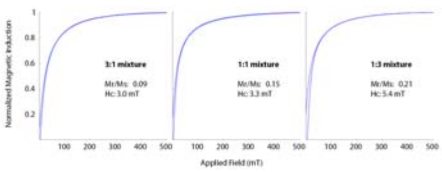
## Hysteresis loops

Normalized hysteresis loops at room temperature




Classic superparamagnetic behavior: loops are perfectly reversible and show no magnetic remanence

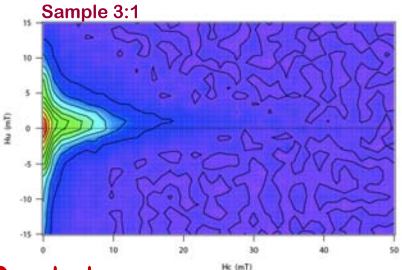
Normalized hysteresis loops at -194°C




Some magnetite grains pass through their superparamagnetic blocking temperatures and behave as single domain grains. There is magnetic remanence.

## First Order Reversal Curves (FORC)

Sample 3:1



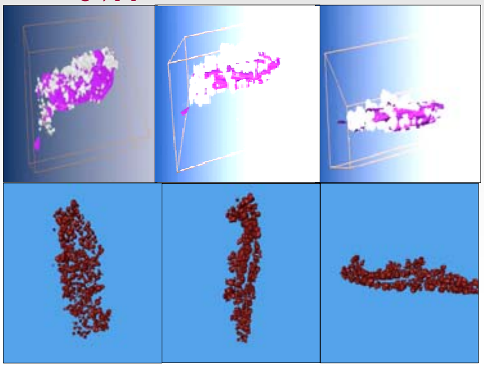

Portions of the sample are behaving as single domain grains with coercivities ranging from 2.5 to 25 mT. A fraction of the sample is still behaving superparamagnetically as shown by the portion of the FORC distribution that extends along the Hu axis near the origin.

## Conclusions

- TEM pictures and electron tomography measurements provide whole information about the morphology of the magnetite covered montmorillonite particles.
- Electron holography and magnetic measurements give complete data about the magnetic properties of the composite particles
-- The knowledge of the morphology and magnetic properties of the particles supplies the needed information in order to understand the structures formed between the composite particles in aqueous suspensions when an external magnetic field is applied and the behavior of these structures in the presence of a magnetic field and under shear flow (magnetorheological behavior).

## Electron Tomography

Tomographic reconstructions of the sample 3:1 created from a series of ultra-high-tilt high angle annular dark field (HAADF) using a Tecnai F20 FEG TEM (University of Cambridge) [4].

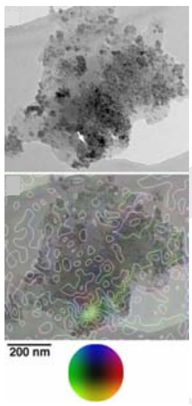


Magnetite particles are adhered mainly to the faces of the montmorillonite particles due to their opposite surface charges.

- Mean diameter of magnetite particles: (9.8 ± 4.5) nm (This agrees within error with the diameter obtained from TEM pictures).
- Mean distance between each magnetite particle and its neighbors: 16.3 nm.
- Mean coordination number: 6.33 nm.

## Electron Holography

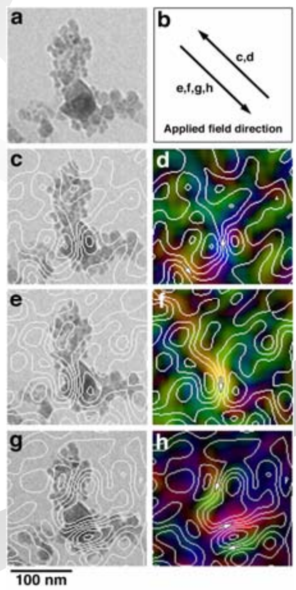
Electron holography is a TEM technique that allows the phase shift of an electron wave to be recorded. The phase shift is sensitive to electrostatic and magnetic fields in a sample, and can be used to obtain information about these fields at the nanometer scale [5].




The measurements for samples 1:3 and 3:1 were made using a Philips CM300-ST FEG TEM (University of Cambridge) at -181°C.

BF image and contour map of magnetite particles adhered to a montmorillonite platelet in sample 1:3.
There is a homogeneous distribution of magnetite particles except for two bigger particles of diameters 47 and 48 nm (arrow in the picture). These particles give a dipole-like magnetic signal with a measured magnetization of 0.53 T (420 A/m²).
The smaller particles do not show any significant magnetic features (no remanent magnetization).

Magnetic materials with unaxial anisotropy such as elongated particles and nanoparticles chains often display perfectly reversed magnetic remanent states when magnetized using equal and opposite fields.
Occasionally agglomerates of magnetic particles do not exhibit this reversibility, as it can be observed in the picture to the right. Magnetic remanent structures in the biggest particles (37 and 43 nm) in the images (c)(d) and (e)(f) are similar but reversed, but those in the images (e)(f) and (g)(h) are different.




Stray fields from a large particles often follow path marked by smaller magnetite particles in the agglomerate, which in isolation would be paramagnetic, as it is observed in pictures (c) and (d). In pictures (g) and (h) the return fluxes of the large particles follow the distribution of magnetic nanoparticles. Such structures can explain the little magnetic remanence in the hysteresis loops.

### References

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