

## 1.6.P04

## Nanocrystalline iron oxides from thermal oxidation of iron disulphide

E. ENEROTH

Geological Institute, Lund University, SWEDEN  
(erik.eneroth@geol.lu.se)

Iron oxides formed during thermal oxidation of pyrite (cubic  $\text{FeS}_2$ ), and marcasite (orthorhombic  $\text{FeS}_2$ ) have been investigated with XRD peak profiling,  $\text{N}_2$ -BET-adsorption, TEM, Mössbauer spectroscopy in the temperature range 10 K - RT, and a variety of magnetic measurements at room- and cryogenic temperatures. The heating was made in air for 1 h at temperatures from 200 to 650°C, and comparisons were made between residues from the two polymorphs and two different grain size fractions (125-250  $\mu\text{m}$  versus 710-1000  $\mu\text{m}$ ). The oxidation followed a chain of reactions with  $\gamma\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  as main products, and it was shown that due to the poorly crystalline nature, bulk magnetic measurements were necessary to monitor the alteration of iron oxides with temperature. In particular, a quantitative view of the inversion of the mostly superparamagnetic  $\gamma\text{-Fe}_2\text{O}_3$  could only be achieved with saturation magnetisation measurements, showing  $\gamma\text{-Fe}_2\text{O}_3$  contents of up to c. 25 % at 500°C and less than c. 0.5 % at 650°C. MCD values from XRD-peak profiles lie in the range 15-20 nm for the  $\alpha\text{-Fe}_2\text{O}_3$  at 500 °C, but at 650°C platy crystallites were indicated with  $25 < \text{MCD}_c < 35$  and  $45 < \text{MCD}_a < 60$  [1]. There was an overall consensus between all applied methods that the small grain size fraction (125-250  $\mu\text{m}$ ) favoured  $\gamma\text{-Fe}_2\text{O}_3$  formation as well as smaller crystallites of both  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$ . The latter had a minimum in crystallite size around 550°C as indicated by RT frequency sweeps of susceptibility, as well as by thermal demagnetisation of SIRM and hysteresis loops versus temperature starting from a uniaxial SSD state at 20 K. Magnetic and Mössbauer results were affected by inter-crystallite interactions giving rise to decreased relaxation in  $\alpha\text{-Fe}_2\text{O}_3$  as indicated by Mössbauer spectroscopy and increased relaxation in  $\gamma\text{-Fe}_2\text{O}_3$  as indicated by magnetisation measurements. Thermal oxidation of iron disulphide occurs in a variety of industrial processes. However, investigations of the oxidation products have been sparse due to the previous focussing on reaction kinetics and thermodynamics. Here it is argued that the properties of the poorly crystalline iron oxides that form upon thermal iron disulphide oxidation might influence both the long-term geochemical behaviour of industrial wastes, as well as our understanding of these reactions in general [2].

### References

- [1] Eneroth E. and Bender Koch C. (2003) *Min. Eng.* **16**, 1257-1267.  
[2] Lin Z. and Qvarfort U. (1996) *Waste Man.* **16**, 871-681.

## 1.6.P05

## Large-scale MD simulations for studying the interlayer structure in cationic and anionic clays and nanocomposite materials

P.V. COVENEY AND H.C. GREENWELL

Centre for Computational Science, Department of Chemistry,  
University College London, 20 Gordon Street, London,  
WC1H 0AJ, United Kingdom (h.greenwell@ucl.ac.uk)

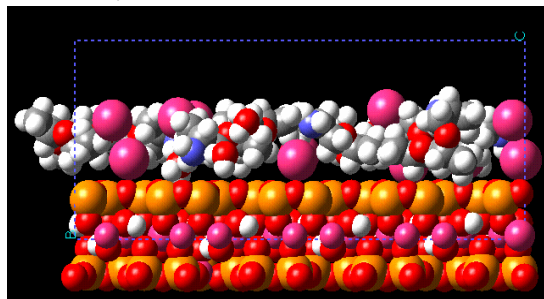
### Introduction

At the Centre for Computational Science at UCL we are interested in the use of highly scalable computer algorithms for simulating condensed matter systems over a wide range of length and time scales.

Here we present very large-scale molecular dynamics (MD) simulations of clay minerals intercalated with organic molecules. Organo-clay materials have diverse applications, which include catalysts, adsorbents, and pharmaceuticals, and are also of interest for use as novel nanocomposite materials with improved structural and fire-retardant properties.

### Techniques

For our large scale MD simulations we use the Large Atomic/Molecular Massively Parallel Simulator (LAMMPS) code.[1] This code has been used to simulate clay systems with up to 250,000 atoms. Illustrated below is a smaller model showing a clay-polymer nanocomposite system, such as simulated by us.



### Results

Simulated clay interlayer spacing show good agreement with experiment using similar loadings of organic molecules. Insight is gained into interlayer structure not obtainable by experiment.[2] Large-scale simulations give better statistics with these systems, especially where long-chain organic molecules are intercalated.

### References

- [1] Plimpton S. J. (1995) *J. Comp. Physics* **117**,1.  
[2] Boulet P.B., Bowden A.A., Coveney P.V., and Whiting A. (2003) *J. Mater. Chem.* **13**, 2540.