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INVESTIGATING ALUMINIUM CO-ORDINATION IN A THERMALLY ACTIVATED IRON RICH KAOLINITIC CLAY BY STEM-EELS

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Introduction

Iron-rich kaolinitic clay deposits provide opportunities for supplementary cementitious material production due to their widespread occurrence in several regions, but they also provide challenges around characterisation. In particular, high iron contents preclude the use of solid state nuclear magnetic resonance (NMR) spectroscopy to assess changes in Al coordination state after calcination. Chemical treatments to remove crystalline Fe compounds from clays [1] cannot be guaranteed to have no effect on the clay minerals themselves, and so there is value in exploring alternative techniques to measure Al coordination which are compatible with high Fe contents. Electron energy loss spectroscopy (EELS) is a microscope-based analytical technique that has been widely used to measure coordination states for a range of minerals [2]. In this study an iron-rich clay was thermally activated, and subjected to a range of conventional/bulk solid-state characterisation techniques, and then results were augmented with Scanning Transmission Electron Microscopy (STEM) with Energy Dispersive X-ray Spectroscopy (EDX) and EELS.

Materials and Methods

A pre-ground iron-rich lithomarge from the interbasaltic formation in Country Antrim, UK, was thermally activated by calcination for 1 hour at 750°C in a laboratory static furnace. Quantitative powder X-ray Diffraction (XRD) analysis was carried out via the full pattern reference intensity ratio method [3]. TEM samples were prepared by diluting suspensions of the clays in ethanol and drop casting onto holey amorphous carbon Cu grids. A FEI Titan^3 Themis G2 S/TEM operating at 300 kV was used with an FEI Super-X energy dispersive X-ray (EDX) system, a monochromator with an energy spread of ca. 0.4 eV, a Gatan Quantum 965 ER energy filter for dual EELS and a Gatan OneView CCD. Spectra were acquired by continuously scanning the focussed probe over a 30 mrad collection angle, at < 180*k* times to ensure minimal damage per pixel dwell occurred at the kaolinite plates (as per the method described in Freeman et al. [4]. Collected spectra were energy calibrated and background subtracted (power law) in 'Gatan Microscopy Suite' software (version 3.0.1).

Results and Discussion

XRD results showed that thermal treatment resulted in the complete dehydroxylation of kaolinite to form metakaolinite, alongside transformation of goethite surface particles to hematite (Table 1).

Table 1: Quantitative breakdown of phases, in wt.%. Mineral abbreviations: Qz = Quartz; Ant = Anatase; Gth = Goethite; Hem = Hematite; Mag = Magnetite; Gbs = Gibbsite; Kln = Kaolinite.

Sample ID	*Qz*	*Ant*	*Gth*	*Hem*	*Mag*	*Gbs*	*Kln*	*Amorphous-I*	*TOTAL*
Raw	1.1	0.3	29	2.7	2.6	1.6	62.7	0	100
Calcined	1.6	1.1	1.1	24.2	0	0	0	72	100

In the uncalcined clay, TEM images show regularly spaced kaolinite sheets with nanoscale particles of goethite adsorbed to their surfaces (Figure 1a,b). After calcination, there is some evidence of delamination of the metakaolin plates, along with transformation of goethite to larger, hematite particles on the clay plates' surface (see arrow, Figure 1c). In the uncalcined clay, STEM-EEL spectra of kaolinite plates' Al *K*-edge suggests 100% Al^{VI} co-ordination [5] (Figure 2a). After calcination, the Al *K*-edge profile suggests a transformation to Al^{IV} co-ordination, associated with metakaolin formation [5, 6] (Figure 2b).

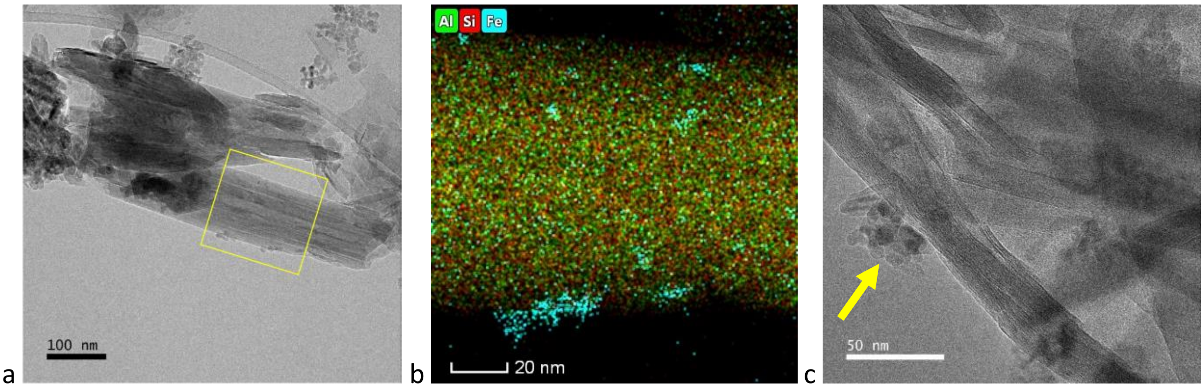

Figure 1: Bright field TEM images of kaolinite plates pre-calcination (a) with Fe-rich surface nanoparticles shown by STEM-EDX elemental maps from the yellow boxed inset (b; Al – green; Si- red; Fe blue), and post-calcination (c).

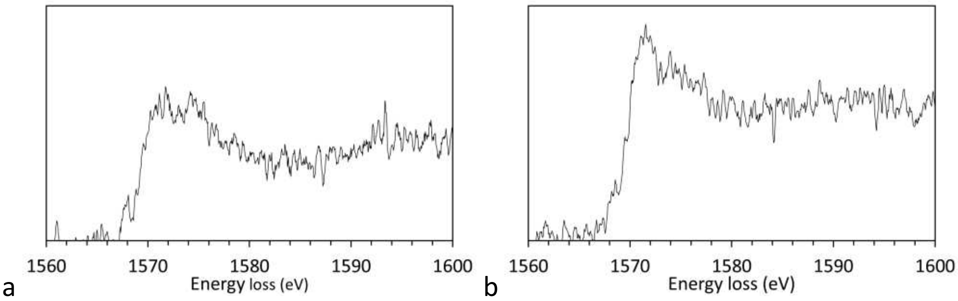

Figure 2: EEL Al K-edge spectra pre-calcination (a) and post-calcination (b).

Conclusions

STEM-EELS shows potential for assessing Al co-ordination in kaolinite and metakaolin particles present in a mixed phase clay, in a spatially resolved manner not achievable with NMR. There is further potential to investigate the changes in iron hydroxide/oxide minerals adsorbed on clay minerals both pre- and post-calcination, and their role in affecting reactivity and early age hydration in blended cementitious systems. STEM-EELS will not be a routine characterisation technique, but does offer potential insight to the local degree of kaolinite transformation. The sensitivity to Al coordination changes will be quantified by fitting of experimental data by reference spectra from pre- and post-calcined china clay standards.

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Keywords: Transmission electron microscopy; electron energy loss spectroscopy; metakaolin.

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