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# Mechano-chemically and thermally activated montmorillonite clays as precursors for alkali-activated cements production

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## EXTENDED ABSTRACT

### INTRODUCTION

In the search for reliable sources of cementitious precursors in the U.K. to supplement the uncertain supply of fly ash and blast furnace slag, there is growing attention paid to common clays. Common clays provide many opportunities to manufacture alkali-activated cements, but challenges arise from the variation in their mineralogy [1]. Many common clays in the European region contain substantial proportions of 2:1 clay minerals, and these are typically much less reactive than kaolinite once calcined [2]. Amongst the 2:1 clay minerals, montmorillonite is a commonly occurring 2:1 clay mineral in sub-soils. Understanding the activation of montmorillonite is, therefore, an important step for getting the best value from clay-based resources. Mechano-chemical activation is an alternative processing route to thermal activation, which involves intense grinding. This approach is gaining attention, especially for the activation of 2:1 clay minerals [3]. In order to improve our understanding of this important clay mineral in isolation, this study investigated the use of thermal and mechano-chemical activation routes for high purity Na-montmorillonite to produce alkali-activated cements.

### MATERIALS AND METHODS

A Na-montmorillonitic clay (subsequently abbreviated as Na-mont) was sourced from Southern Clay Products, U.S.A. The chemical oxide composition of the clay is given in Table 1. The  $d_{50}$  value and the specific surface area of the clay (measured via the B.E.T.  $N_2$  sorption method) were  $10.3 \mu m$  and  $20.6 m^2 g^{-1}$ , respectively. The primary phase present in the clay was Na-montmorillonite ( $\approx 70\%$ ), with quartz and feldspar as the minor phases. For thermal activation, the clay was calcined in a static furnace at  $830^\circ C$  with a soaking time of 1 hour (T1 C60). For mechanochemical activation, 10g of the clay was milled in a planetary ball mill for 1 hour with 250g of stainless-steel grinding balls (T1 M60).

**Table 1.** Chemical oxide composition in wt.% of both clays, determined by XRF. Loss on ignition (L.O.I) was determined at  $1000^\circ C$ .

Clay sample	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	SiO <sub>2</sub>	SO <sub>3</sub>	TiO <sub>2</sub>	Other (<0.1wt.%)	L.O.I.	Total
Na-mont	15.1	1.9	3.1	0.5	1.4	2.6	63.8	0.6	0.1	0.3	10.6	100.0

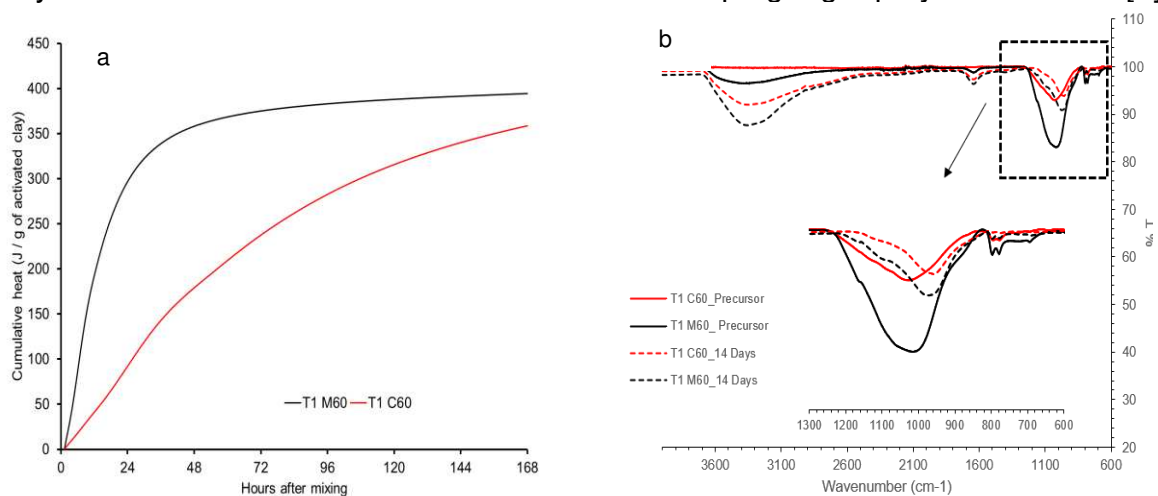
The activating solution was prepared by dissolving 222g of NaOH pellets in 500 ml of deionized water. The mix designs used for preparing the alkali activated cements are given in Table 2. Samples were mixed using a high-shear mixer for 5 minutes, then sealed in plastic vials and cured at 40°C until testing. The samples were ground in a mortar pestle before analyses. No other pretreatments were done on the samples. The phase assemblages of the hardened pastes were analyzed by X-ray diffraction after curing for 14 days using a Bruker D8 Advance diffractometer from 3° to 60° degrees, with an average scan time of 30 minutes per sample. FTIR studies were conducted on a Perkin Elmer ATR-FTIR on the 14 days samples to monitor the nano structural evolution in the geopolymer systems.

**Table 2.** Mix designs for the alkali-activated cement pastes. Solids is the sum of clay and sodium hydroxide used to prepare the paste.

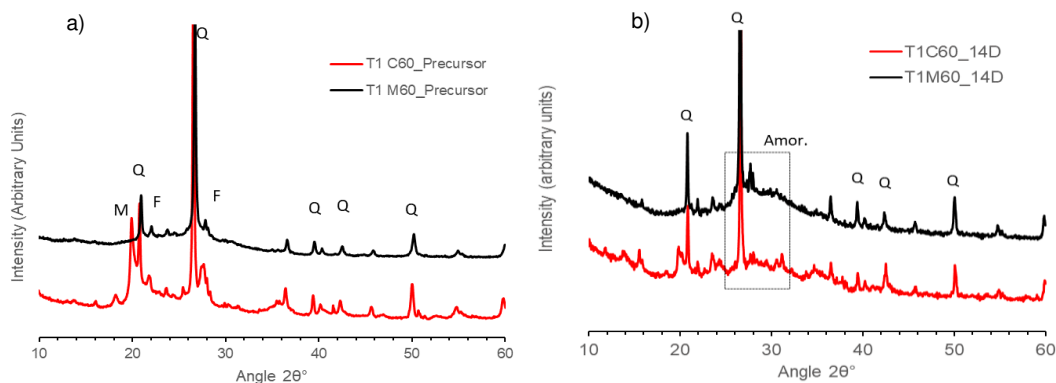
Sample ID	Clay mass (g)	Water mass (g)	NaOH mass (g)	Water: solids ratio
T1 M60	50	16.7	13.3	0.26
T1 C60	50	16.7	13.3	0.26

## RESULTS AND DISCUSSIONS

The R3 test [4] was used to estimate the reactivity of the activated clays (Figure 1 Left) which indicates that mechano-chemically activated clay is more reactive than thermally activated clay. The diffractograms of the alkali-activated cement systems (Figure 2) show a clear amorphous band centered around 29° angle in both thermally and mechano-chemically activated clays indicating the formation of sodium aluminosilicate hydrate (N-A-S-H) type gel [5]. The FTIR spectra of the precursors and alkali activated clays are shown in Figure 1 (Right). A clear shift in the T-O-T band from around 1035 cm<sup>-1</sup> in the clays to lower wavenumber centered around 965 cm<sup>-1</sup> in alkali-activated clays was observed. This indicates formation of N-A-S-H gel in both systems. This shift has been attributed to the asymmetric stretch of Si-O-Al bonds in the developing a geopolymer network [6].



**Figure 1.** (a) The R3 calorimetry curves for the activated clays (b) The FTIR spectra for the precursor and alkali activated clay samples



**Figure 2.** XRD patterns (a) Precursor clays (b) Alkali-activated clays. Q – Quartz (01-070-3755), M – Montmorillonite (00-029-1499), F – Feldspar (00-010-0393)

## Conclusions

The results from the present study indicate that mechano-chemical activation of 2:1 clays appear to offer significant promise as an alternative activation route to thermal activation for producing alkali-activated cements. The R3 test indicate that mechano-chemically activated clays are more reactive than thermally activated clays. An in-dept study (which is presently in progress) is required to obtain a greater understanding of the similarities and differences in the different activation routes for 2:1 clays.

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