



Research paper

Alkali activation behaviour of un-calcined montmorillonite and illite clay minerals

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ABSTRACT

Using alkali activation, un-calcined soils have potential as precursors for low carbon, low cost, geopolymer-stabilised construction materials. This technology has been recently promoted as a lower impact alternative to cement stabilisation for walling materials in construction around the world. There is a lack of fundamental understanding around the alkali activation of un-calcined montmorillonite and illite, which, along with kaolinite, are clay minerals commonly found in soils. Kaolinite, as a 1:1 clay mineral, has been shown to form crystalline hydrosodalite when alkali-activated, but 2:1 montmorillonite and illite could form stronger geopolymer structures due to the higher Si:Al ratio in the precursor mineral. The lack of understanding of the underlying mechanisms at work with 2:1 clay minerals is a barrier to knowing how viable un-calcined geopolymer stabilised soil materials are for the range of soil types found in nature. In this study, montmorillonite and illite precursors were activated with a range of sodium hydroxide concentrations, compacted, and then cured at 80 °C for 24 h. The cured samples were characterised using a variety of advanced analytical techniques, including powder XRD, SEM, TGA, ²⁷Al and ²⁹Si-MAS-NMR, and FTIR. For the first time it was confirmed that alkali activation of uncalcined montmorillonite forms a NASH or (N,C)ASH geopolymer as the major product phase, which increases in quantity with increasing Na:Al molar ratio of the system. Although it has a similar Si:Al ratio, alkali activation of illite seems to result in structural alteration and increased porosity for Na:Al ≥ 0.5. The behaviour of these individual clay minerals suggests that the alkali activation of un-calcined 2:1 clay minerals is complex. Although alkali activation of montmorillonite can form a geopolymer, alkali activation of soils containing illite may lead to poor quality materials. This research has shown that the focus of future development work should be around montmorillonite-based clays.

1. Introduction

Alkali activation of aluminosilicates for construction materials has been the focus of extensive research in recent years, due to the potential of lower energy and carbon costs compared to conventional materials such as Portland cement based concrete (Provis, 2014). Alongside industrial by-products such as fly ash (Fernández-Jiménez et al., 2006; van Jaarsveld et al., 2002) and rice husk ash (Zhang, 2013), alkali activation of clays and soils has been investigated, due to their abundance and low cost (Diop and Grutzeck, 2008; MacKenzie, 2009). Clays can be used not only as supplementary cementitious materials (Fernandez et al., 2011; Garg and Skibsted, 2014; Hollanders et al., 2016; Tironi et al., 2013), but also as primary aluminosilicate precursors in alkali activation. While a few studies have been done on montmorillonitic and illitic soils, studies of clay minerals in isolation

have been dominated by kaolinite and metakaolin (Liew et al., 2016). At the same time, a wide range of soils found around the world contain montmorillonite and/or illite (Nickovic et al., 2012). An improved fundamental understanding of the alkali activation behaviour of these two clay minerals in isolation is required. This is in order to develop a better understanding of how mixed mineral soils will behave, and therefore which soils might be suitable or unsuitable for alkali activation.

In the specific application being considered, the goal of alkali activation is to convert clay minerals into strong, durable and water resistant product phases which will allow the manufacture of concrete block replacements, or similar products. A sufficiently reactive aluminosilicate system with a Si:Al molar ratio of 1.5–2.5 is expected to form a geopolymer in the presence of a sufficiently concentrated alkaline activating solution (Duxson et al., 2007b). The amount of geopolymer

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phase formed depends on both the extent of dissolution of the aluminosilicate precursor (i.e. the clay mineral) in the alkaline activating solution (Duxson et al., 2007a), as well as the total amount of metal cation in the system, as required for charge balancing (Barbosa et al., 2000).

Both, montmorillonite and illite are dioctahedral 2:1 clay minerals having layers consisting of one octahedral sheet between two tetrahedral sheets. Montmorillonite is a member of the smectite family; illite, the mica family (Brindley and Brown, 1980). For their crystal structure, montmorillonite has a triclinic lattice, with a P space group (Gualtieri et al., 2001; Viani et al., 2002) while illite has a monoclinic lattice, with a C2/c or C2/m space group for the 1 M and 2 M1 polytypes respectively (Gualtieri, 2000; Gualtieri et al., 2008). In chemical composition, both minerals have formula ranges rather than fixed stoichiometry, due to substitutions. For montmorillonite, there is substitution of Mg^{2+} for Al^{3+} in the octahedral sheet; for illite there is Al^{3+} substitution for Si^{4+} in the tetrahedral sheet, and possible Mg^{2+} or Fe^{2+} substitution for Al^{3+} in the octahedral sheet (Brigatti et al., 2013; Brindley and Brown, 1980).

To balance the negative layer charges resulting from these substitutions, both minerals have interlayer cations. Montmorillonite can host a range of different interlayer cations including Ca^{2+} , Na^+ , Mg^{2+} , K^+ and Sr^{2+} , whereas illite has only K^+ . Illite has a much lower cation exchange capacity than montmorillonite (Kahr and Madsen, 1995). This is due to its small interlayer space and the 'fixed' nature of the small potassium ions in the ditrigonal cavities on the surfaces of the tetrahedral sheet (Bergaya et al., 2013; Verburg and Baveye, 1994). The hydration of the interlayer cations and subsequent osmotic behaviour of their diffuse double layers in montmorillonites results in swelling behaviour, whereas the positioning of the K^+ interlayer cations in illite results in non-swelling behaviour (Van Olphen, 1963).

For application as masonry blocks, alkali-activated soil materials must be able to be manufactured at block scale and placed in a wall at which point dimensional stability is required. Given their swelling behaviour, montmorillonitic soils have usually been avoided in earth construction, even when using chemical stabilisation such as cement or lime (Jagadish, 2007). It remains to be seen whether alkali activation can be used to transform the montmorillonite into a strong and durable stabilising phase, which ensures that any unreacted clay fraction is constrained in its ability to have a detrimental effect on overall properties. The viability of an alkali-activated soil material, especially if containing a swelling clay such as a montmorillonite, therefore depends not only on the ability to form a geopolymer phase, but also how much geopolymer phase is formed and how that geopolymer phase interacts with any unreacted minerals. To be compatible with extrusion processing, an established process used in brickmaking, the consistency of the wet mix needs to be approximately at the plastic limit (Maskell et al., 2013). Practical constraints such as these are not often considered in studies on alkali-activated materials, but are vital to the feasibility of any new material.

In previous studies in this field, a popular processing technique is to heat a clay (or soil containing clay minerals) above its dehydroxylation temperature in order to increase its reactivity (Liew et al., 2016; Tchadjie and Ekolu, 2018). Unlike the dehydroxylation of kaolinite, dioctahedral 2:1 clays retain their layer structure (Heller-Kallai, 2013) but still undergo a reduction in Al coordination in the octahedral layer (Heller-Kallai, 2013; Muller et al., 2000). However, these coordination changes are reversible as dehydroxylated 2:1 clays can undergo varying degrees of rehydroxylation, even under ambient conditions (Emmerich, 2000; Muller et al., 2000). Given that the dehydroxylation temperatures for montmorillonite and illite are in the ranges of 620–780 °C and 520–650 °C respectively (Földvári, 1991), there is a significant energy investment required for this. Since the main driver for alkali activated materials is a lower energy footprint (MacKenzie, 2009), it is desirable to know under which conditions these two clay minerals might be sufficiently reactive in their uncalcined state.

The behaviour of montmorillonite in alkali solutions is the subject of ongoing research for the application of barrier materials for radioactive waste storage (Dohrmann et al., 2013; Fernández et al., 2014; Nakayama et al., 2004). For example, the transformation of montmorillonite to illite in the presence of K-rich groundwater is of concern, as this leads to loss of swelling capacity (Kaufhold and Dohrmann, 2010; Lee et al., 2010). The transferability of such knowledge is limited for the present application for several reasons: alkaline concentrations are lower ($[OH] < 1 M$); timescales are longer; liquid:solid ratios are much higher, and alkali solutions used are often complex mixtures of metal hydroxides designed to mimic the composition of Portland cement pore fluids. In contrast, there are few previous studies on alkali activation of montmorillonite for the intentional production of alkali aluminosilicate phases. In early studies, Willoughby et al. (1968) and Ingles (1970) activated uncalcined montmorillonite with a range of alkali hydroxides, showing a loss of strength when sodium hydroxide was used with room temperature curing. Belviso et al. (2017) showed that a 700 °C calcined Ca-montmorillonite precursor formed a geopolymer by hydrothermal alkali activation, but formed zeolites when an additional NaOH pre-fusion step was used. Seiffarth et al. (2013) thermally pre-treated a smectite clay sample (550–950 °C), and mixed it with a sodium silicate solution. Geopolymerisation was inferred from the increased strength of the alkali activated samples, but detailed phase characterisation was not performed. The causal link between geopolymerisation and higher strength is not straightforward since sodium silicate itself is an adhesive, used to strengthen materials such as cardboard (Fawer et al., 1999).

More studies have been done on illite alkali activation, but most of them have focussed on calcined precursors. Seiffarth et al. (2013) thermally pre-treated illite clay between 550 and 950 °C, and mixed it with a sodium silicate solution. Again, geopolymerisation was inferred from increased strength, but without detailed phase characterisation. El Hafid and Hajjaji (2015) calcined an illite-kaolinite clay sample at 700 °C and mixed it with NaOH solutions, producing the zeolites chabazite and natrolite. It was unclear what role the kaolinite and the illite played in the development of these product phases. Sperberga et al. (2011) mixed a calcined (700–900 °C) illite deposit with KOH solution, Sedmale et al. (2013) mixed the same illite deposit with KOH solution, but without calcination. In both cases, although improved compressive strength was noted, proof of geopolymer phase production was not definitive. In contrast to their results for montmorillonite, Belviso et al. (2017) showed that a calcined illite precursor underwent no obvious changes by hydrothermal alkali activation, but did form zeolites when an additional NaOH pre-fusion step was used.

Although the existing range of studies provides some insight, there is still a knowledge gap in the direct comparison of the alkali activation of non-calcined montmorillonite and illite. A recurring obstacle to developing a fuller fundamental understanding of precursor influence on alkali activation behaviour is that given the numbers of variables involved, comparison between studies is difficult. In order to develop a fundamental understanding of the processes at work, this study is a systematic investigation and comparison of the alkali activation behaviour of un-calcined montmorillonite and illite. The aim is to understand phase formation behaviour, in order to determine which conditions might be suitable for producing stabilised soil materials.

2. Experimental

2.1. Materials

K10 montmorillonite (Sigma-Aldrich, product no. 69866-1KG) and Clay Minerals Society IMt-2 (Silver Hill) illite were used as the aluminosilicate precursors. Chemical compositions were determined by energy dispersive X-rays (EDX) in a scanning electron microscope (JEOL SEM6480LV with Oxford INCA X-Act SDD X-ray detector) and using 4 scan areas per sample.

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