



Research paper

Tailored montmorillonite nanoparticles and their behaviour in the alkaline cement environment

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ABSTRACT

This is the first time an analytical protocol is proposed to investigate and live-monitor the behaviour of montmorillonite nanoparticles, of different natures, in alkaline cement environment (pH of 12–13). In this study inorganic and organomodified montmorillonite nanoparticles were characterised via TEM, XRD, SEM-EDX and TGA. The inorganic montmorillonite used consisted of a purified montmorillonite commercially available as HPS-clay, and an organomodified montmorillonite, namely XDB-organoclay, consisted of purified montmorillonite modified with Noramonium MB2HT salt. Both montmorillonite nanoparticles were tailored to increase their compatibility with the hydrating cement environment. This gave rise to three different slurries: (i) reference-slurry, (ii) inorganic-slurry, and (iii) organic-slurry. The slurries were characterised and investigated through UV/vis, to measure suspension quality in terms of physical stability and rheological properties, and by AFM and FTIR to determine the chemical stability. The results indicated that the organic-slurry can offer a good stability, preventing aggregation of the clay particles at the targeted pH (13). The inorganic-slurry showed a reduction in surface charge and increased double layer repulsion. At pH 13 it was possible to obtain dispersion of the reference slurry although it underwent gelation and became viscous. The research findings informed that the inorganic slurry favours miscibility of the montmorillonite nanoparticles with cement particles and offers additional nucleation sites for CSH. Therefore it can be considered an alternative to organomodified montmorillonite as an addition in cement based materials.

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1. Introduction

Montmorillonite (Mt) is a clay mineral of significant commercial importance. This naturally occurring hydrous aluminium silicate exists as an octahedral sheet between two tetrahedral sheets, producing plate-like layers that can be up to a micron or more in diameter and about 1 nm thick. This high aspect ratio platelet structure can confer enhanced physical and mechanical properties when incorporated in cement matrices (Chang et al., 2007). The main focus to-date on Mt use has been as clay polymer nanocomposites (CPN) to confer enhanced mechanical properties and increased functionality (Ataefard and Moradian, 2011). By nature, Mt particles are inorganic, hence, hydrophilic and can readily disperse in water due to the hydration of the basal surfaces, swelling and exfoliating the clay (Birgisson and Dham, 2011; Nehdi, 2014). Generally, dispersion of hydrophilic Mt particles within a CPN is not feasible due to thermodynamic incompatibility of the mineral and organic phases. In which case, surface modification of the particles using an

organic agent is necessary to provide compatibility with the polymeric matrix. The organomodification primarily takes place through cation exchange, replacing metal ions with organic cations such as alkylammonium. As well as conferring compatibility of the clay for the polymeric matrix, the adsorption of fatty surfactant molecules in the interlayer region of platy minerals allows separation of the layers which promotes intercalation of polymer chains into the interlayer space during CPN preparation; the greater the intercalation distance, the easier it is for attractive van der Waals forces to be overcome and full exfoliation into discrete nanoparticles to be achieved (Ouellet-Plamondon et al., 2012). Good particle dispersion is critical in realising the 'nano-effect' provided by the clay addition for optimum performance. Regarding the cement paste environment, in the one hand organomodification of Mt renders it thermodynamically incompatible with the aqueous environment of cement and concrete formulations (Kuo et al., 2006). Nonetheless organomodified Mt (OMt) is expected to enhance water penetration resistance (the hydrophobic Mt does not allow water to enter the interlayer region) and strength development until day 28 in OMt nanoparticles-enhanced cement pastes (Brinkienė et al., 2015). Chloride permeability reduction of OMt nanoparticles-enhanced

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cement mortars can be observed through electrochemical impedance spectroscopy and field emission scanning electron microscopy tests shown an increase in the ionic transport resistance and denser microstructure respectively (He and Shi, 2008). Moreover, water penetration resistance, electrical resistivity and splitting tensile strength can also be improved until day 56 in OMt enhanced concrete (Hosseini et al., 2015). However, further findings suggest that OMt nanoparticles are particularly sensitive to the functional group of modifier used with respect to microstructure and strength development of cement paste-OMt nanoparticle formulations (Kalpokaitė-Dičkuvienė et al., 2015). Exfoliated OMt nanoparticles are preferred in cement pastes and according to Xi exhibits a greater d_{001} -value (Xi, 2006). However, OMt nanoparticles with larger d_{001} -value has been found to increase capillary porosity in hardened cement (Kalpokaitė-Dičkuvienė et al., 2015). Dispersing agents can be used in order to improve compatibility of the hydrophilic environment of the cement paste with the hydrophobic OMt nanoparticles. The water-soluble polyacrylates in addition to the electrostatic stabilising effect, provide steric stabilisation of the clay particles through a combination of elastic and osmotic interactions. The result is an increase in the concentration of particles in suspension. On the other hand there is evidence in recent research that the enhancement of the pozzolanic reaction, of the flexural strength and of the microstructure of composite cement pastes can be more pronounced when inorganic Mt is added in cement pastes rather than OMt slurries with different dispersants (Papatzani and Paine, 2015). In which case, there is good reason to use the unmodified Mt nanoparticles (or inorganically modified Mt with Na^+ ions to produce purified sodium Mt) in cement and concrete formulations. In aqueous environment clay platelets will readily disperse, with an element of stability afforded to the dispersed particles due to the predominantly negative charge that result from isomorphous substitution of ions within the crystal structure. The negative charges act to stabilise the particles by repulsive interaction that can, in favourable solvent environments, overcome the attractive van der Waals interactions, as described by DLVO theory (Derjaguin et al., 1987). However it is important to mention that hydrophilic Mt nanoparticles may affect durability of cement and concrete due to the presence of alkali metal ions present in the interlayer regions of the un-modified clay that can contribute to destructive alkali-aggregate reactions (West, 1996). Given the significant effect organomodifier and surfactants have on the structure of Mt nanoparticles, the protocol and set of analytical tools proposed in this study was paramount in obtaining information of the tailored Mt nanoparticles behaviour in the alkaline cement environment. In this paper, inorganic (HPS) and organomodified (XDB) Mt nanoparticles in powder form were first characterised via TEM, XRD, SEM-EDX and TGA. Furthermore, the Mt nanoparticles were tailored to cement environment in which three different Mt nanoparticles systems of aqueous dispersions (slurries) were derived. (i) Reference-slurry, (ii) Inorganic-slurry (iii) Organic-slurry. Their behaviour was investigated at various pH environments through atomic force spectroscopy (AFS), Fourier transform infrared (FTIR) spectroscopy, rheology, and spectrophotometry.

2. Materials and methodology

Two types of Mt (raw material) in powder form were used, both of which were supplied by *Laviosa Chimica Mineraria S.p.A*, Italy, and dried before use to remove any residual moisture:

- a purified sodium Mt Named as “HPS-clay” hereafter.
- an organically modified Mt by exchange of basal metal cations with methylbenzyl di-hydrogenated tallow ammonium chloride (Noramonium MB2HT). Named as “XDB-organoclay” hereafter.

Aqueous Mt nanoparticle dispersions were prepared using dispersing agents which were selected based on the nature of the Mt nanoparticle surface:

- (i) Sodium polyacrylate (NaPA) with average molar mass 5100 and used as received (supplied by Sigma Aldrich) was used to aid the dispersion of HPS-clay in aqueous environment.
- (ii) Synperonic 10/6, a non-ionic fatty alcohol/polyethoxy surfactant and used as received (supplied by Croda Chemicals Europe) was employed to disperse XDB-organoclay in aqueous environment. The methodology employed comprised of three steps: characterisation of Mt (raw material); stability of the tailored Mt nanoparticle slurries; and behaviour of the tailored Mt nanoparticles at different pH environments.

2.1. Characterisation of the Mt nanoparticles (raw materials)

Both Mt types, namely HPS-clay and XDB-organoclay, were characterised through the following test regimes:

2.1.1. Transmission Electron Microscopy (TEM)

Aqueous dispersions at 10 ng/mL were prepared from the Mt nanoparticles (HPS-clay and XDB-organoclay). These were then deposited onto hydrophilised formvar/carbon films on Copper supports and analysed in a Jeol JEM 1200 mkII. Images were recorded on a Gatan Dual View camera.

2.1.2. X-ray diffraction (XRD)

Measurements were performed using a D8 ADVANCE X-ray diffractometer with $\text{CuK}\alpha$ radiation. Spectra were obtained in the range $4^\circ < 2\theta < 60^\circ$. Analysis of reflections and d -value were calculated using EVA software, following Bragg's law ($n\lambda = 2d\sin\theta$) (Ramachandran and Beaudoin, 2001).

2.1.3. Scanning electron microscopy/X-ray energy dispersive spectroscopy (SEM/EDX)

For SEM/EDX. Sample preparation was carried out in two steps. First dispersions of the HPS-clay and XDB-organoclay were prepared (same as for the TEM sample preparation) In the second step HPS-clay and XDB-organoclay dispersions were vacuum dried for three days at a pressure of 10–2 mbar (100 Pa). After that HPS-clay and XDB-organoclay powders were placed on a sheet of molybdenum, an element absent from both Mt types. The equipment used was a Jeol 6480LV.

2.1.4. Thermogravimetric analyses (TGA)

These analyses were carried out using a Setaram TGA92 instrument. Approximately 20 mg of each Mt were placed in an alumina crucible and heated at a rate of 10 °C/min from 20 °C to 1000 °C under 100 mL/min flow of inert nitrogen gas. Mass change, differential mass change and heat flow measurements were recorded and analysed using the built-in software. The differential thermogravimetric curve (dTG) was derived from the TG curve. The first derivative curve was obtained for the various Mt samples and was used for comparisons, instead of the mass loss curve, as it yields sharp distinctive reflections.

2.2. Stability of the tailored Mt nanoparticle slurries

Mt were tailored to remain as discrete nanoparticles within the hydrating cement paste. This is of paramount importance if Mt nanoparticles are to be added to cement based materials to act as nucleation agent for promoting hydration. Three aqueous dispersions were prepared, two of which were aided with the surfactants described in Section 2. The three tailored Mt dispersions' preparation methods can be described as follows: (i) Reference-slurry: HPS-clay aqueous dispersion at 15% mass was prepared by ultrasonication using a Herman dynamic 2000CV 20 kHz ultrasonic processor fitted with a 10 mm diameter sonotrode operating at 100% voltage. This dispersion was water based only, without addition of surfactants

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