Understanding the strengthening of a lateritic "geomimetic" material

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HIGHLIGHTS

- Lime-based and soda-based materials exhibit similar compressive strength.
- Lime-based products present the lowest thermal conductivity and the highest durability.
- Geopolymerisation-like interactions are promoted when using NaOH.
- The yield stress and consistency are gradually increased during the aging period.
- Binding phases occur after 4 days while a solid-like behaviour prevails after 7 days of aging at 60 °C.

GRAPHICAL ABSTRACT

"Geomimetic" materials consolidation involves an acidic and alkaline reaction steps and a curing period at 60 °C for 18 days under water saturated atmosphere. The use of lime ($Ca(OH)_2$) or soda (NaOH) gives rise to consolidated products exhibiting similar compressive strengths. Soda-based products appear to be less resistant within water solution. The lime-based materials are good thermal insulators and their strengthening can be represented graphically as shown below.
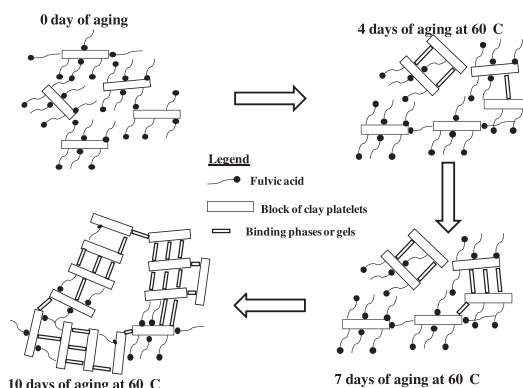
ARTICLE INFO

ABSTRACT

The present work aimed to investigate the interactions that control the strengthening of "geomimetic" materials. The raw lateritic clay used mainly contained kaolinite, goethite, quartz and hematite. The processing involved a 24 h-reaction with fulvic acid followed by neutralization with lime or with NaOH prior to the curing at 60 °C for 18 days under water saturated atmosphere. The compressive strength and thermal conductivity after consolidation were respectively 0.7 MPa and 0.19 W m^{-1} K^{-1} for lime-based products, and 0.78 MPa and 0.3 W m^{-1} K^{-1} for soda-based products. The latter exhibited low durability in water. Such differences could be related to the high degradation of kaolinite particles when using NaOH, leading to the formation of sodalite, cancrinite and nontronite, which phases did not act as binder. Cementitious CAH and CSH phases were obtained when using lime. Rheological measurements performed on lime-based samples indicated that a shear-thinning behavior prevails up to the 7th day of curing. Above this period, the samples reached a determinant step whereby a solid-like behavior became predominant. The occurrence of binding precursors during the first 7 days of curing conducted to a progressive increase of the yield stress and consistency from 1 to 53 Pa and from 0.2 to 2.3 Pa s, respectively.

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1. Introduction

Low energy demand materials are in constant evolution regarding formulation and processing. Sustainability is a key factor for the development of such environmental conscious materials. Among available raw materials, clays appear as interesting naturally occurring and environmentally friendly starting materials. Clays are mainly constituted of finely sized (submicron) clay mineral platelets which are layered alumino-silicates. Depending on their compositions, these layered minerals exhibit a high reactivity degree towards acidic and/or alkaline media [1–5]. These interactions can be promoted and used for the processing of original low energy consuming products with a view to wide use. From this perspective a processing for "geomimetic" materials has been developed in a previous study [6], derived from the formation of lateritic concretions within some iron-rich soils. The term "geomimetic" was adopted in reference to mimicking the consolidation observed with naturally occurring lateritic concretions in soils ("geo"). The "geomimetic" material processing implies the use of a lateritic clay together with fulvic acid and lime. The consolidated products are obtained after a curing period of 18 days at 60 °C under water saturated atmosphere. These as-obtained products present interesting properties with respect to a potential use as building materials, namely: a compressive strength of 12 MPa, and a good durability when immersed in water. Since such an elaboration route is quite new, the interactions and mechanisms that govern the strengthening are not clearly understood. A physical evolution of the system is noted from a slurry state at the beginning to a solid at the end of the curing period. The present study is therefore aiming to investigate the strengthening of such products, with the scope to further elucidate the key interaction stages involved in the strengthening of the "geomimetic" materials.

2. Materials and methods

X-ray diffraction (XRD) diagrams were obtained on powdered samples with a Bruker-AXS D5000 powder diffractometer using K_1 radiation of Cu and a graphite back-monochromator. XRD experiments were achieved in step-scan mode from 3° to 45° (2θ) with a counting time of 10.1 s per 0.02° step. Crystalline phases were identified by comparison with PDF standards (Powder Diffraction Files) from ICDD (the International Center for Diffraction Data).

Scanning electron microscopy (SEM) observations were performed using a field emission gun (FEGSEM) microscope JEOL 7400 FEGSEM (JEOL, Tokyo, Japan) equipped with an Energy Dispersive Spectroscopy (EDS) analyzer. Samples were submitted to metallisation with platinum prior to their observation under an accelerating voltage of 2 kV.

The Atomic Force Microscopy (AFM) platform used in this study was a Pico Scan from Agilent [7]. All AFM probes were for tapping mode applications and consisted in N-type Si bar-shape cantilevers (radius <10 nm and height ≈14–16 µm). These AFM probes were purchased to Scientec (Les Ulis, France) and exhibit a nominal frequency in the range 200–400 kHz and a spring constant in the range 25–75 N/m, respectively. Topography images obtained were analysed using SPIP software in order to have the surface roughness and particle size profile.

Rheological measurements were performed in flow mode using a controlled-stress rheometer AR1500ex from TA® Instruments. Parallel plate geometry (40 mm steel upper plate and Peltier lower plate) was mounted on the rheometer for all rheological experiments, with a gap of 1 mm in order to fulfil optimized conditions regarding particle size evolution (gap more than ten times larger than the largest particle size). The temperature was maintained in all cases at 22 °C. For most samples, the shear stress was increased from 0 to 50 Pa for 90 s, then held for 30 s at the maximal shear stress, and finally the shear stress was decreased to 0 Pa for 90 s. When required, in some cases, the maximal yield stress was 100 Pa, nevertheless the duration of experiment was maintained as described above (90 s for the testing ramp and 30 s for the dwell at 100 Pa.). Herschel Bulkley law (Eq. (1)) has been used to determine the rheological parameters.

$$\tau = \tau_o + (k \cdot (\dot{\gamma})^n) \qquad (1)$$

where τ and τ_0 are respectively the shear stress and the yield stress, K the consistency (viscosity in the case of a Newtonian or Bingham fluid), $\dot{\gamma}$ refers to the shear rate, and n is the power law exponent (rate index). By using this law, a fluid can be well-characterized regarding its fluidity through the value of the consistency

(K) and its resistance towards increasing shear stress through the rate index (n) [8–10]. A shear-thinning or a shear-thickening behavior can be observed when $n < 1$ or $n > 1$, respectively.

The compressive strength of final products was carried on samples previously rectified to obtain a cylindrical shape with a ratio height/diameter = 2. A LLYOD EZ20 device, equipped with compressive, tensile and bending test units, has been used. The samples are subjected to an increasing load until failure, the applied testing rate was 0.1 mm/min. All values of the maximum compressive strength reported in this study are mean values over five tests under the same conditions. Before characterizations, samples were kept sealed in a shrink-wrap bag.

The raw material used in the present work (labeled Lat) is a naturally occurring iron-rich clay from Yaoundé in Cameroon.

Additional reagents were fulvic acid [11–13] (a fulvic acid is an organic macro-molecule having several functional groups Fig. 1) purchased to Bois Valor in France, NaOH from Merck and lime (99.9 mass% of $Ca(OH)_2$) provided by Aldrich.

The processing of "geomimetic" materials (Fig. 2) was performed as follow:

- prior to elaboration, the raw clay (Lat sample) was ground and sieved under 100 micrometers;
- the acidic solutions were prepared by an homogeneous mixing during 5 min of fulvic acid (V_{AF}) and deionized water (V_W) to obtain a final pH value of 2 (this acid solution is noted AF);
- the Lat sample (mass of lat clay noted m_{Lat}) was added and mixed for 24 h with AF;
- finally, lime (noted CH) or sodium hydroxide (labeled S) was added and the mixture (mass of lime noted m_{CH}) was left to cure at 60 °C for 18 days.

The solid part,, represented 80 mass% of Lat clay (Lat) and 20 mass% of lime (CH) or NaOH (S). The quantities were calculated in order to obtain a final mass ratio, water over solid, equal to 0.29. For example, when using m_{Lat} = 50 g of Lat clay, it was required to introduce 115.5 mL of acidic solution AF (volume of fulvic acid, V_{AF} = 97.5 mL and volume of water, V_W = 18 mL) and $m_{CH(orS)}$ = 13 g of lime (or sodium hydroxide).

With respect to the elaboration flowchart, the following notation is used:

- 24 h after the addition of Lat clay slurry in AF solution, sample labeled LatAF;
- after the addition of lime and during the subsequent ageing at 60 °C under water saturated atmosphere, samples were labeled LatAFCHi, where "i" represents the ith curing day;
- after the addition of NaOH and during the subsequent ageing at 60 °C under water saturated atmosphere, samples were labeled LatAFSi, where "i" represents the ith curing day.

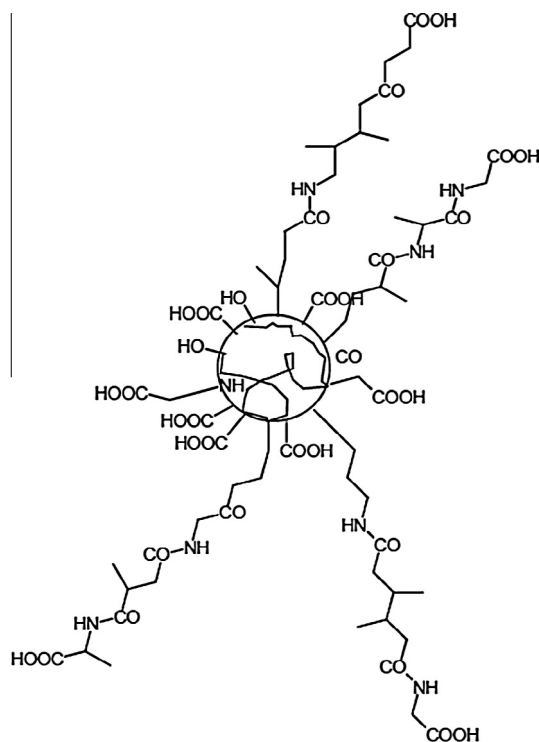Fig. 1. Basic structural model of a fulvic acid [Schnitzer and Kodama, 1975].