



Binding and setting of kaolin based materials with natural organic acids



Céline Martias^a, Nicolas Villandier^b, Elsa Thune^a, Aurélien Glomot^b, Vincent Gloaguen^b, Agnès Smith^{a,*}

^a CNRS – Ecole Nationale Supérieure de Céramique Industrielle, Science des Procédés Céramiques et de Traitements de Surface (UMR 7315), 12 rue Atlantis, 87068 Limoges cedex, France

^b Laboratoire de Chimie des Substances Naturelles (LCSN), Université de Limoges, 123 avenue Albert Thomas, 87065 Limoges cedex, France

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ABSTRACT

In the present study, the correlation between adsorption experiments and the setting process of “geomimetic” materials prepared with humic-like solutions (HS) and a kaolin were investigated. Two HS were compared: a humic acid solution (HA, pH = 13) and a fulvic acid solution (FA, pH = 3). The adsorption experiments revealed a higher capacity of adsorption of the kaolin towards FA than HA, which could be attributed to the charge effects on the clay surface and to the organic molecule conformation depending on the pH. Materials elaborated, with high content of HA was consolidated after 4 days of curing whereas no setting was observed for materials prepared in the same conditions with FA. The hypothesis of inter/intra-molecular H-bonding between carboxylate groups of HA molecules, taken in evidence by FTIR analyses, and carboxylic or hydroxyl groups, was proposed to explain the material setting. Indeed, the characterization of HA revealed a highly aromatic structure favorable to mesomeric effects which led to the apparition of negative and/or positive charges and thus increased the reactivity of HA molecules. The structure of FA rather aliphatic was not favorable to mesomeric effect. Moreover, goethite was “mechanically” added in the kaolin powder because this iron phase was identified to be favorable to material setting. In this study, the addition of iron hydroxides, as powder, did not improve the material setting.

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1. Introduction

The EU has committed to cutting its CO₂ emissions to 20% below 1990 levels by the end of 2020 because of the global warming (“Notices from European Union institutions and bodies”, 2008). One CO₂ producer is the building and construction sector. The tile or brick production is concerned due to the firing step at high temperatures (around 1000 °C) in order to consolidate the materials. Alternative solutions need to be explored to strengthen materials at lower temperatures and to reduce the CO₂ footprint of such productions. One solution developed at the laboratory scale was inspired from the natural process of strengthening of soils. It consisted in introducing organic matter in clay materials to consolidate at relatively low temperature (Goure-Doubi et al., 2014). Indeed, it is known that the strengthening of soils is mainly due to the formation of an organic–clay complex through thousands of years and under specific conditions of temperature and humidity (Cornejo and Hermosin, 1996). In the present study, the organic matter was humic-like substances (noted HS) and especially the humic and fulvic fractions (noted HA and FA, respectively).

FA and HA consist in macromolecules; they present some similarities and also distinct characteristics. Compared to FA, the structure of HA is more aromatic and HA is only soluble at alkaline pH (Litvin

et al., 2012). The major functional groups of HS are phenolic, followed by carboxylic, carbonyl, hydroxyl, amine and amide groups. These different groups can bind strongly with the mineral matter. Peñaméndez and Havel (2005) describe humic-like substances as a polyaromatic core surrounded with aliphatic chains. Nevertheless, it is difficult to describe HS with a general formula because of their maturation over time, which leads to a polycondensation of HS and a modification of the structure. The adsorption of FA and HA was observed on kaolinite, smectite, vermiculite or on goethite and hematite (Elfarissi and Pefferkorn, 2000; Zhang et al., 2012) but not really correlated with various parameters which can influence the adsorption process such as pH (Bergaya and Lagaly, 2006), conformation of FA/HA polymers, modification of HS structure and chemical composition in the course of time or the number of reactive sites on these minerals. In previous studies, the presence of aluminum and iron particles in clays was revealed to increase the affinity between HS and minerals (Elfarissi and Pefferkorn, 2000; Tombác et al., 2004; Vreysen and Maes, 2008; Weng et al., 2005). Therefore, a first work was carried out with a lateritic clay rich in iron oxides (Goure-Doubi et al., 2014).

In the present study, the investigations were principally carried out on kaolin, characterized by a low content of iron oxides, and results were compared with a lateritic clay similar to the one used in our previous work (Goure-Doubi et al., 2014). Adsorption experiments using the batch method were realized to provide essential information about the affinity between FA/HA and kaolin in alkaline and acid medium, which are the conditions of preparation of materials. At the same time, different formulations of materials, including FA or HA solutions, kaolin and

* Corresponding author.

E-mail addresses: celine.martias@unilim.fr (C. Martias), nicolas.villandier@unilim.fr (N. Villandier), elsa.thune@unilim.fr (E. Thune), aurelien.glomot@unilim.fr (A. Glomot), vincent.gloaguen@unilim.fr (V. Gloaguen), agnes.smith@unilim.fr (A. Smith).

lime, were prepared. The effects of various parameters on the setting of materials were studied: the amount of iron oxides in clay, the quantity of HS used and the nature of HS. To examine the effect of iron phases, the kaolin was enriched with goethite identified as the most reactive iron phase involving in the setting of materials (Lecomte-Nana et al., 2012). Thus, the combination of adsorption experiments with the observation of the setting of materials will provide a better understanding of the mechanism of interaction between HS and kaolin. The originality of that work is precisely the simultaneous investigations on the formulation of materials and on adsorption experiments.

2. Materials and methods

2.1. Clay minerals

The kaolin used in this work was purchased from the company Kaolin de Beauvoir. It came from the region of Auvergne (France), and was designated with its commercial name BIO. The kaolin was compared to a lateritic clay (noted LAT) from Cameroon. Mineral materials were sieved to 100 μm . The chemical compositions of clays were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and their mineralogical compositions were established from XRD and DTA-TGA analyses (Table 1).

2.2. Organic matters

FA solution was provided by the Bois Valor Company located in Albi, France. FA was extracted from poplar wood chips according to a patented process (Morard et al., 2008). It was delivered in the form of a solution concentrated at 5 mass% and at pH = 3 but, as it was said in the introduction, FA is also soluble in alkaline medium. To be compared to HA solution (alkaline pH), some experiments were carried out with the commercial FA solution with pH adjusted to 13 with a 3 M NaOH solution. This alkaline FA solution was noted FA*.

HA was extracted from a manure compost according to the method described below and then dissolved in a 3 M NaOH solution and concentrated at 5 mass%. The pH of HA solution was 13.

2.2.1. Extraction

Manure compost was purchased in a garden center, Jardiland, located in Limoges, France. It was a mixture of poultry manure, horse manure and seaweed from the Vendée coast. The compost was frozen at $-18\text{ }^{\circ}\text{C}$ and lyophilized during three days. Then, the sample was grinded with a mortar and sift to 2 mm. Humic acid fraction was obtained following the International Humic Substances Society (IHSS) procedure (Celierier et al., 2009). Free lipids were extracted at $80\text{ }^{\circ}\text{C}$ by Soxhlet Extractor using a mixture dichloromethane/methanol (2/1, v/v, $12.5\text{ mL}\cdot\text{g}^{-1}$) for 3 days. The solvent was changed every 24 h. The residue was treated with a 1 M HCl solution ($10\text{ mL}\cdot\text{g}^{-1}$) to remove part of the fulvic acids and minerals such as carbonates. Humic and remaining fulvic acids were then extracted with a 0.1 M NaOH solution ($10\text{ mL}\cdot\text{g}^{-1}$) under a nitrogen atmosphere during 12 h. Five successive extractions were carried out. The different basic phases were combined and the humic acids were separated from fulvic acids by precipitation at pH = 1 after dropwise addition of a 12 M HCl solution and centrifugation (20 min,

8000 rpm). Finally, humic acids were dialysed (Spectra/Por MWCO 1000 Da) for 2 days and lyophilized. The extraction process is presented on Fig. 1.

2.3. Characterization of minerals

2.3.1. Chemical analyses

The chemical composition of the clay minerals used was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Prior to analysis, the dried sample powders were dissolved at $180\text{ }^{\circ}\text{C}$ using a microwave (A CEM MARS 5) under acidic (fluorhydric and nitric acids) and high pressure conditions (3 MPa).

2.3.2. Specific surface area and Scanning Electron Microscopy

The Brunauer Emmett and Teller (Brunauer et al., 1938) method was used to determine the specific surface area of clay minerals, using a TriStar II equipment from Micromeritics. Measurements were carried out after a 16 hour degassing step at $150\text{ }^{\circ}\text{C}$ and on dried samples previously crushed and sieved to 100 μm . Scanning Electron Microscopy (SEM, Cambridge Instrument, S290) was used for microstructure observation under an accelerating voltage of 15 kV. Prior to their observation, the samples were coated with a 10 nm thick layer of platinum onto the sample surface.

2.3.3. X-ray diffraction

X-ray diffractograms were obtained on powdered samples with a Bruker-AXS D5000 powder diffractometer using $\text{K}\alpha 1$ radiation of Cu ($\lambda = 1.5406\text{ \AA}$) and a graphite back monochromator. XRD experiments were achieved in step-scan mode in the range $2.02^{\circ} \leq 2\theta \leq 60^{\circ}$ with a counting time of 10.1 s per 0.02° step and a slit width of 0.1 mm. The scan speed was $0.002^{\circ}\text{s}^{-1}$.

2.4. Characterization of organic matters

2.4.1. Specific UV absorbance (SUVA_{254})

SUVA_{254} is defined as the ratio of the UV absorbance at 254 nm to the dissolved organic carbon concentration (DOC) of a given solution. It is expressed in $\text{L}\cdot\text{mg}\text{C}^{-1}\cdot\text{m}^{-1}$. UV spectroscopy analyses were conducted with a UV spectrometer lambda 40 (Perkin Elmer) equipped with a quartz cuvette of 1 cm path length. DOC analyses were performed by a TOC-L analyzer (Shimadzu, Japan, precision $\pm 50\text{ }\mu\text{g}\text{C/L}$). Each sample was measured three times and a standard deviation was calculated. SUVA_{254} was shown to be strongly correlated with the percentage of aromaticity as determined by ^{13}C NMR for organic matter extracted from aquatic systems or from soils (Weishaar et al., 2003). In the work by Weishaar et al. (2003) the ^{13}C NMR spectra were measured on solutions of approximately $100\text{ mg}\cdot\text{mL}^{-1}$ of the sodium salt of each isolate dissolved in $\text{H}_2\text{O}-\text{D}_2\text{O}$ (1:1), adjusted to pH 7, in 10 mm tubes on a Varian spectrometer (Model 300) at 75.429 MHz using inverse gated-decoupling with an 8-s delay. SUVA_{254} increases with the molecule aromaticity.

2.4.2. Total acidity

The total acidity of FA or HA was measured using the barium hydroxide method described by Stevenson (1994). The principle is that FA or

Table 1
Chemical and mineralogical compositions of BIO and LAT.

		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Loss on ignition at $1000\text{ }^{\circ}\text{C}$
Chemical composition (mass%)	BIO	46.60	36.50	1.20	<0.10	0.20	<0.10	1.85	<0.05	1.28	13
	LAT	40.48	23.89	20.54	0.91	0.02	0.21	0.17	1.65	1.70	10.43
Mineralogical composition (mass%)	BIO	Kaolinite; mica; quartz = 1.5									
	LAT	Kaolinite = 51; quartz = 19.1; goethite = 23.6; hematite = 1.4; ferrihydrite (traces)									

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