



## Research paper

# Valorization of mussel and oyster shells toward metakaolin-based alkaline activated material

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## ABSTRACT

The valorization of oyster or mussel shells toward metakaolin-based geomaterials was investigated. The aim is to better understand the feasibility and the reaction involved during the incorporation of shells (natural or calcined) into a metakaolin-based alkaline solution for potential building or contaminants sorbents applications. Mixtures are realized by (i) the substitution of metakaolin (MK) source by shells raw material (from 0 to 100% mass) or (ii) addition up to 50% mass. Substitution of MK by shells was conducted without material structure loss up to 40% and 30% addition, whether the type and treatment of shells used. In each addition or substitution, the results highlight the duality between both reactions i.e. polycondensation versus hydration. (i) using natural shells, only polycondensation reaction occurs due to the unreactivity of shells (interaction of shells with matrix by surface binding: role of aggregates or fillers); (ii) using calcined shells, coexistence of polycondensation in first followed (or stopped) by hydration reaction: presence of portlandite and C(A)SH. Then the results traduce the role of MK (Al and Si source) reactivity and calcium form (carbonate versus lime; reactivity) in MK-based alkali activated materials. The geochemical leaching approach can be used as a sensitive probe of the structural network.

## 1. Introduction

Shells of various mollusks such as oyster and mussel are quite available abundantly all around the world. For example, France accounts for almost all European production in oyster culture and ranks 4th in the world, behind China, Japan and Korea. Thus, 60 million dozen of oysters are consumed in France between Christmas and New Year's i.e. 6.3 million tons of oysters and mussels. For example, in Indonesia, the production of pearl oysters and green mussels in 2007 was 64,641 tons and 420 tons, respectively (Olivia et al., 2015). According to this production, the oyster industry has to face with a new problem, the shellfish waste management. Knowing that in a conventional treatment process, the treatment of this type of waste induces relatively high cost. For this reason, the disposal of oysters and mussels waste led to serious environmental problems. From the last decade, such recovery techniques have been developed and shellfish are currently used for various applications such as embankment material, soil amendment (Lee et al., 2005), or also in more varied sectors such as cosmetics industry (Neefe, 1984). Recent studies are interested in the

adsorbent properties of shells or in the possibility of substituting limestone by shells in fertilizers (Lee et al., 2008) or toward a high-tech product as biodegradable filaments for 3D printers based on oyster shells (Allameh, 2015). However, the volumes used for these applications are relatively low. Recent works are focus onto the potential shells by-product use as green concrete construction (Prusty et al., 2016), reef restoration (Graham et al., 2017), aggregates (Eo and Yi, 2015) and so on. One of the most innovative applications for shells waste management is their use as inexpensive raw materials in the synthesis of metakaolin-based alkali activated materials (AAM) or geopolymers. Indeed, there has been increasing interest in producing eco-friendly geomaterials from natural and inexpensive materials (e.g. Xu and van Deventer, 2003) or by-product/waste recycling (Ahmari and Zhang, 2012; Gharzouni et al., 2016). Metakaolin-based geomaterials are new materials obtained through the activation of aluminosilicates and alumina- and silica-rich materials such as calcined clays which are used as precursors (Davidovits, 2015; Selmani et al., 2017). Moreover, it is current to modify raw material properties in the way to increase their reactivity in mixture from thermal treatment or grinding (Kuenzel

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et al., 2013; San Nicolas et al., 2013). The metakaolin (noted MK) is one of the more reactive components in mixture, as well as being the main source of alumina. The purity of MK, the treatment involved (flash- or rotative-treated), and the nature of primary kaolinite ore are the main parameters that controls their reactivity toward alkaline treatment (e.g. Kuenzel et al., 2013). In the case of geopolymer materials, the basic step of geopolymerization is the dissolution of the aluminosilicate phases in an alkaline media (NaOH or KOH) to form free  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral units then in which the aluminum atoms crosslink chains of  $\text{SiO}_4$  tetrahedral. Their properties and the interest of these materials are no longer to be dismantled. So, it appears to be a promising alternative for conventional cementitious materials due to their thermal stability and acidic resistance as well as their promising mechanical and thermal properties. Recently, geopolymer based material are also used as stabilization/solidification or adsorption of contaminants (e.g. Zhang et al., 2015; El-Eswed et al., 2017; Kara et al., 2018). Due to their interesting properties, it seems to be an alternative for shells reuse (in term of shells quality and as expected quantity) as fillers or directly as reactive compounds. Shells are essentially composed by carbonates (i.e. calcium phase such as calcite and/or aragonite; Chiou et al., 2014) which can be considered as impurities in geopolymer science. The presence of calcium in the system can induce dramatical effect onto geopolymer material inducing the nucleation of calcium silicate hydrate (CSH; e.g. Granizo et al., 2004). The potential use of carbonate mineral as aggregate in the MK-based geopolymer has been investigated by Yip et al. (2008) and they have evidenced a positive effect of addition of carbonates mineral (calcite or dolomite raw material) up to 20% additive improving working properties (mechanical properties). Since shells waste are abundant and inexpensive around the world, the aim of this paper is to study the feasibility to use and valorize oyster or mussel shells toward a MK-based geomaterials (i) by substitute MK aluminosilicate source by a reactive secondary raw material or (ii) by addition. The work investigates the effect of shells and their activation (calcined or natural) on a MK-based alkali activated formulation by XRD, FTIR and SEM, in order to evidence and understand the different reactions involved.

## 2. Materials & methods

### 2.1. Raw materials

The oysters' and mussels' shells used in this study have been collected from Leucate (Occitanie, France). In order to run comparable study, the shells have been washed, dried and crushed using a roller crusher SiebTechnik GMBHT100A. The obtained sample is then sifted at 125  $\mu\text{m}$  to obtain a homogenous particle size distribution. A part of the shells (sifted at 125  $\mu\text{m}$ ) has been calcined at 850  $^\circ\text{C}$  for 4 h at a heating rate of 10  $^\circ\text{C}/\text{min}$  in a Nabertherm B150 oven. In the way to simplify, the following nomenclature will be used: M, O, Mc and Oc for untreated mussel i.e. natural, untreated oyster, calcined mussel and oyster respectively.

To prepare the pure alkaline activated materials, several raw materials have been used: (i) the sodium silicate solution from Woellner giving a Si/Na ratio = 1.65 was mixed with NaOH pellets (99% purity; Merck), (ii) MK supplied by Imerys.

### 2.2. Sample synthesis

To highlight the potential reuse of shells onto alkaline activated material, the consolidated materials were prepared by dissolving sodium hydroxide pellets (NaOH) in the sodium silicate solution to obtain the activating solution. MK is added as a source of aluminosilicate and mixed with the activating solution. The mixture was thoroughly homogenized in a teflon mold with a magnetic stirrer and kept in a closed mold during 7 days at 20  $^\circ\text{C}$ . The synthesized material is a classical-based geopolymer (Autef et al., 2013) so without the presence of

shells (0% shells). Then, shells-based materials were also realized (i) from several substitutions of MK by shells (oyster or mussel, calcined or not). The substitutions were realized from 0 to 100% (0%, 25%, 40%, 50%, 75% and 100%); and (ii) from several shell additions (i.e. 15%, 30% and 50%) from the classical based geopolymer formulation (i.e. 0%, see before). Finally, a total of 32 formulations were prepared.

The nomenclature used for the different mixtures is  $\text{XY}_z$  with X corresponding to O, O<sub>c</sub>, M, M<sub>c</sub>; Y to the percentage of MK substituted by the shells or to the percentage of shell added to the conventional formulation and z corresponding to 's' or 'a' for substitution and addition, respectively. For example, M<sub>c</sub>25s means that 25% of the MK is substituted by calcined mussels' shells, whereas M<sub>c</sub>15a the addition of 15% of calcined mussels shells from the classical based geopolymer formulation.

### 2.3. Sample characterization

The different raw materials and resulting materials were characterized by various physical, chemical and physical-chemical methods.

Total chemical analysis of raw materials (MK and shells) are achieved after total microwave-assisted acid digestions and measured by MP-AES (Microwave Plasma-Atomic Emission Spectroscopy) Agilent MP 4100. X-Ray diffraction (XRD) measurements and scanning electron microscopy (SEM) were performed on the CarMaLim platform (University of Limoges, France). The XRD analysis of raw material and alkali-activated material was obtained thanks to a Bruker D8 advance diffractometer on powder materials with a  $\text{CuK}\alpha$  radiation ( $\lambda_{\text{K}\alpha} = 0.154186 \text{ nm}$ ), between 5 and 50  $^\circ 2\theta$  with a 0.04  $^\circ 2\theta$  step for 2 s. The XRD patterns obtained were processed using EVA software (Bruker). Quantification of crystalline phases was investigated by Rietveld method using Topaz software (Bruker). The micro structural observations were carried out using a XL30 Philips SEM in secondary electron mode. Chemical analyzes were performed at 15 kV with a 4  $\mu\text{m}$  spot size using an INCA Oxford EDX. Observations were conducted after metallization by Au-Pd.

The Fourier transform infrared (FTIR) spectroscopy was achieved on powders of raw materials and alkali activated materials using a Perkin Elmer FT-IR/NIR Frontier Spectrometer device operating in ATR mode in the mid infrared (600–4000  $\text{cm}^{-1}$ ). For each spectrum, 8 scans were performed and then summed. The theoretical resolution of the device was 1  $\text{cm}^{-1}$ . The results were then analyzed using Spectrum software.

### 2.4. Leaching experiments

The EN 12457-2 leaching tests were performed onto selected samples. Briefly, the crushed samples were brought into contact with water under agitation for 24 h with a solid/liquid ratio of 1/10 (AFNOR, 2002). The leaching solution was then filtered at 0.45  $\mu\text{m}$  from cellulose acetate filter and the eluate analyzed. All analysis were run in duplicate. Double deionized water (18.2  $\text{M}\Omega\text{cm}^{-1}$ ) was used for all experiments. The chemical analyses of leaching experiments (Si, Al, Ca) were performed with an MP-AES (Microwave Plasma-Atomic Emission Spectroscopy) Agilent MP 4100 (measurements parameters of analysis are reported in the Supplementary Table S1). All reagents were of analytical grade or higher purity.

## 3. Results and discussion

### 3.1. Raw materials characterization

#### 3.1.1. Metakaolin

The chemical and mineralogical composition of raw material (MK, oysters and mussels) are presented in Table 1 and in supplementary information file (Fig. S1). The main oxides in the MK, used as aluminosilicate source, are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  with a Si/Al ratio of about 1.17. This ratio value is higher than the theoretical value ratio of pure MK

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