DOI: 10.4408/IJEGE.2016-01.O-01

TEMPERATURE EFFECT ON MECHANICAL AND PHYSICAL PROPRIETIES OF Na OR K ALKALINE SILICATE ACTIVATED METAKAOLIN-BASED GEOPOLYMERS

Ahmed NMIRI(*), (**), Oumaya YAZOGHLI-MARZOUK(***), Myriam DUC(****),
Noureddine HAMDI(*) & Ezzeddine SRASRA(*)

(*)Centre National des Recherches en Sciences des Matériaux - Laboratoire de Physico Chimie des Matériaux Minéraux et leurs applications
Technopôle Borj Cedria, BP 73 - 8027 Soliman, Tunisia
(**)Faculté des Sciences de Tunis - Campus Universitaire - 2092 El Manar, Tunis, Tunisia
(***)CEREMA - Direction Départementale Centre-Est - Département Laboratoire Autun - BP 141 Boulevard Bernard Giberstein - 71404 Autun, France
(****)Université Paris Est, IFSTTAR, Département Géotechnique, Environnement, Risques Naturels et Sciences de la Terre, 14-20 boulevard Newton -
77447 Marne-la-Vallée cedex 2, Champs-sur-Marne, France. Corresponding author: myriam.duc@ifsttar.fr

EXTENDED ABSTRACT

Il cemento risulta un materiale edile di alta qualità, usato in tutto il mondo in molti progetti di costruzione. La produzione globale di cemento è stata stimata nel 2013 attorno a 4 miliardi di tonnellate all'anno. Tale valore è destinato a crescere tra il 2030 e il 2050 fino ai 5 miliardi di tonnallate; un esempio è la Tunisia dove, nel 2013, la produzione crescente raggiunge i 5.88 milioni di tonnellate all'anno. I processi di fabbricazione del cemento attuale comportano effetti dannosi sull'atmosfera, causando un riscaldamento globale dovuto all'emissione di grandi quantità di gas ad effetto serra. Il cemento geopolimerizzato, caratterizzato da proprietà meccaniche, ignifughe e isolanti, puo' essere utilizzato nell'industria edilizia come cemento ecologico e resistente al fuoco. Questo lavoro tratta della sintetizzazione di geopolimeri con soluzioni matacaoline (Mk) e alcaline (K_2SiO_3 or Na_2SiO_3 miste a KOH o NaOH rispettivamente). Le prestazioni tecniche dei geopolimeri di tipo (Na-) Mk e (K-) Mk sono state comparate esponendoli prima a trattamenti ad alte temperature. Test di laboratorio sono stati condottti per seguire le loro proprietà fisico-meccaniche e i cambiamenti microstrutturali dopo l'esposizione ad alte temperature per due ore (200, 400 o 600 °C). Le proprietà meccaniche dei campioni sono state studiate considerando la resistenza alla compressione che puo' essere vista come un indicatore della qualità del processo di geopolimerizzazione stesso. La resistenza alla compression dipende dal grado di dissoluzione dei materiali alluminosilicati (come la metacaolina) in soluzioni alcaline. Particelle non dissolte rimangono legate alla matrice, e impurità presenti nei materiali grezzi possono subire reazioni collaterali che possono influenzare la cinetica della geopolimerizzazione e quindi la resistenza meccanica del geopolimero ottenuto. La misura della resistenza alla compressione è stata eseguita su campioni ciclindrici preparati in maniera da avere un rapporto diametro/altezza uguale a 1/2. I campioni sono stati anche caratterizzati con diffrazione ai raggi X (XRD) e via spettrometria a infrarossi (FT-IR); per confermare l'avvenuto processo di formazione del geopolimero e per determinare le differenze mineralogiche fra i polimeri anche scansioni al microscopio elettronico (SEM) e porosimetria all'intrusione di mercurio (MIP) sono state eseguite prima e dopo il trattamento termico. I risultati hanno mostrato che i geopolimeri di tipo Na-Mk esibiscono resistenze alla compression maggiori di quelle dei polimeri di tipo K-Mk dopo la polimerizzazione a temperature ambiente. L'alta resistenza del polimero Na-Mk sembra essere associata alla mineralogia (con presenza di faujasite e alluminosilicate di sodio) combinata ad una bassa porosità, a pori di piccole dimensioni (osservati con immagini SEM e come dedotto dalla curva di distribuzione ottenuta con MIP). I geopolimeri di tipo Na-Mk sono caratterizzati da un più alto grado di condensazione rispetto al polimero di tipo K-Mk, grazie ad una maggiore dissoluzione del precursore alluminosilicato in presenza di cationi Na^+ rispetto ai cationi K^+. Cio' spiega la presenza di metacaolina inerte nei geopilimeri K-Mk, identificata via analisi termiche e con infrarossi. Questa fase è anche responsabile della diminuzione osservata della resistenza meccanica nei polimeri di tipo K-Mk. Inoltre, il maggior linear shrinkage cosi' come una perdita significativa di ignizione (essenzialmente acqua fisicamente assorbita e rilasciata a temperature <400°) osservati per i geopolimeri di tipo Na-Mk rispetto ai polimeri di tipo K-Mk, sembra comunque non governare il comportamento meccanico del polimero; nessuna microfrattura (potenzialmente osservabile via linear shrinkage) è stata osservata in microscopio a piccolo scala. I risultati ottenuti dopo la calcinazione messi a confronto con quelli ottenuti a temperature ambiente dimostrano che la porosità e la densità dei geopolimeri crescono lievemente o rimangono circa costanti cosi' come la resistenza a compressione. Tuttavia, la prestazione meccanica diminuisce a 600° (a causa di un aumento della taglia dei pori per effetti termici) sui polimeri di tipo K-Mk. Questo studio conclude che i geopolimeri di tipo Na-Mk (se comparati a quelli di tipo K-Mk) risultano i più appropriati per la produzione di cementi geopolimerizzati resistenti alle alte temperature. Questo risultato sembra essere in opposizione a quanto presentato in letteratura sui geopolimeri basati su ceneri volatili e fra i quali i geopolimeri di tipo K- presentano generalmente maggiori resistenze al fuoco. Questi tipi di polimeri hanno una grande quantità di piccoli pori che facilitano l'uscita dell'umidità quando il materiale viene riscaldato. Questa rete di pori permette la minimizzazione dei danni alla matrice del geopolimero. L'aumento di resistenza meccanica nei geopolimeri contenenti ceneri volatili viene parzialmente attribuito alle reazioni di sinterizzazione delle particelle di cenere. Nel caso dei geopolimeri di tipo Mk, la piccola quantità di pori nei geopolimeri di tipo Na-Mk sembra non abbassare la resistenza termica del materiale rispetto a quella del geopolimero K-Mk.

ABSTRACT

In this work geopolymeric materials were synthesized in order to reach the best thermal characteristics allowing the use of them as flame retardant natural stone. The mechanical strength (notably after high temperature exposure) as well as the microstructure were investigated on hardened specimens of geopolymer manufactured at ambient temperature with metakaolin and a mixture of alkali hydroxide solution (MOH) and alkali silicate solution (M_2SiO_3) with M = K or Na. Geopolymers were subjected to thermogravimetric analysis, scanning electron microscopy and mercury intrusion porosimetry tests and linear shrinkage, loss on ignition and compressive strength measurements. Results showed that Na-Mk geopolymer exhibits higher compressive strength at ambient temperature after the curing, du to a minor value of porosity compared to the value for the K-Mk geopolymer. Na-Mk geopolymer gave a geopolymer with a high degree of condensation compared to K-Mk geopolymer because the dissolution of aluminosilicate precursor is still greater in presence of Na^+ cations than in presence of K^+ cations. The strength of the Na or K-based geopolymer decreased after exposure to elevated temperatures (until 600°C). The conclusion of the study is that Na-Mk geopolymer is the most appropriate for using in the production of thermal resistant geopolymer cement than K-Mk based geopolymer.

Keywords: *metakaolin, alkaline solution, geopolymer*

INTRODUCTION

Portland cement concretes (PCC), subjected to high temperatures such as 800°C or 1000°C, are damaged by dehydration phenomena. CSH hydrates (and some other crystalline compounds) are deteriorated and that causes a significant decreasing of the compressive strength down to about 70% (Singh *et alii*, 2015). Thermal treatment or fire involves strong temperature gradients which are at the origin of catastrophic concrete spalling (Neville, 2011). Geopolymers characterized by a low shrinkage during the setting, a low permeability, as well as a good durability under acid attack offer a good alternative to PCC. Geopolymer cement is incombustible and contains no volatile chemical compounds, which are at the origin of harmful fumes. It doesn't release toxic compounds at high temperatures because of its composition that consists mainly of silica mixed at ambient conditions with alkaline solutions.

The effect of thermal treatment (or fire conditions) on mechanical and physical proprieties of geopolymer depends on several parameters conducting to a more or less important decrease of the mechanical strength. Each parameter impacting on the metakaolin-based behavior at ambient temperature may impact also after thermal treatment. Parameters such as the aluminosilicate sources (metakaolin, fly ash, blast furnace slag…), the Si/Al ratio, the solid/liquid ratio (S/L) (or the water content) and the chemical composition of the geopolymer (the concentration and Na or K metal cations in alkaline solutions used as activator) were highlighted in the follow for their effect on its thermal properties and linear shrinkage curves (Mohd Salahuddin *et alii*, 2015).

(1) The aluminosilicate source: the metakaolin-based geopolymers (Mk geopolymers) are the most widespread geopolymer. Metakaolin is obtained after kaolin calcination at temperatures above 550°C. Kaolin contains in majority kaolinite ($Al_2Si_2O_5(OH)_4$) that is widely used in ceramic for its low expansion/shrinkage under temperature. The mechanical strength of Mk geopolymers usually depends on the rate of kaolinite amorphization varying with the temperature and the duration of calcination. Above 550°C, Kong *et alii* (2008) showed that the calcinating temperature between 650 and 800°C of kaolin have a little influence on the performance of Mk geopolymers at elevated temperature. If geopolymers containing metakaolin showed good mechanical properties at room temperature, these binders are prone to a large degree of drying shrinkage and cracking conducting to the degradation of their mechanical strength when exposed to high temperatures (Bernal *et alii*, 2011). Fly ash generally proved to be much more effective to produce thermal resistant geopolymer.

(2) The SiO_2/Al_2O_3 ratio (as well as the Na_2O/Al_2O_3) may change with the type of raw material used as source of aluminosilicate (Van Jaarsveld *et alii*, 2003) and then impact on geopolymers properties (Komnitsas & Zaharaki, 2007). The physical properties of Mk geopolymer are improved when SiO_2 are added to the mixture (Davidovits, 2013). De Silva & Sagoe-Crentsil (2008) demonstrated that the setting time of Mk-geopolymer (based on a calcined commercial kaolin at 750°C) is mainly controlled by Al_2O_3 content and it increases with increasing SiO_2/Al_2O_3 ratio of initial mixture (when Al_2O_3 decreases). At the same time, the increase of SiO_2/Al_2O_3 molar ratios up to 3.4-3.8 leads to high compressive strength development. The increase in Al_2O_3 (low SiO_2/Al_2O_3) leads to products of low strengths, accompanied by microstructural change in Na-Al-Si matrix. The best resistances (at ambient temperature) are obtained when the molar ratio SiO_2/Al_2O_3 is between 3 and 3.8 and the molar ratio Na_2O/Al_2O_3 is about 1 (Silva *et alii*, 2007; Bernal *et alii*, 2011). Kong & Sanjayan (2008) stated also that alkaline solution selection and concentration ratio are critical parameters necessary to optimize the performance of Mk geopolymer (at ambient or at elevated temperature). SiO_2/Al_2O_3 ratio has a significant influence on elevated temperature exposure deterioration and lesser strength loss due to elevated temperature exposures were observed in geopolymer with high SiO_2/Al_2O_3 ratios (>3).

(3) The solid-liquid ratio (S/L): water in alkaline solution is the third component of the mixture that impacts the geopolymer synthesis. During geopolymerization, water acts as a way

of ion transport. Furthermore, water is essential for good fluidity of fresh geopolymer cement paste (Yunsheng *et alii*, 2010). Moreover, the compressive strength of Mk geopolymer may vary when similar S/L ratios are imposed but the amount of sodium silicate is changed (Gao *et alii*, 2013). The compressive strength is high when the S/L ratio is 1.03 and the amount of sodium silicate is close to 1% of the total solid weight. A S/L ratio higher than 1.03 generates an improvement of the compressive strength because of the good contact between the activating solution and the reactive raw materials but for the highest S/L ratio (close to 1.19), the dissolution of aluminosilicate raw material is limited and the geopolymer paste hardens quickly while some particles of raw materials remain unreacted. The uncompleted dissolution produces a low level of polycondensation generating the decrease of the compressive strength of geopolymer. When the ratio S/L is low (around 0.97), the contact between activating solution and raw material is limited due to the large volume of liquid which weakens the compressive strength of geopolymer. The compressive strength follows the same trend before or after thermal treatment (Kong & Sanjayan, 2008). The replacement of metakaolin by fly ash allows to have a high solid/liquid ratio in the starting mixture and then less water has to diffuse and evaporate when the temperature rises during fire. Less moisture by adding more fly ash in geopolymer improves the fire resistance (Kong *et alii*, 2007; Zhang *et alii*, 2014). This property is in relation with the water demand of the reacting mixes (Provis *et alii*, 2010) and Mk is usually characterized by a high water demand.

(4) The nature of the alkali metal cation in alkaline solution usually a mixture of M_2SiO_3 and MOH with M = Na or K plays also a role. In presence of sodium, the Na_2SiO_3/NaOH alkali activation of metakaolin is known to give material with better mechanical properties compared to the activated geopolymers with only NaOH (Komnitsas & Zaharaki, 2007). Sindhunata *et alii* (2006) studied also the effect of the silicate ratio of the activating solutions (SiO_2/M_2O, with M = Na or K) as well as the effect of curing temperature on fly-ash-based geopolymer. Very high silicate ratios (SiO_2/M_2O) are believed to slow the reactions and the pore structure of K-based geopolymer is more susceptible to change in temperature than the one associated to Na-based geopolymer (an increase in the total pore volume and the surface area when the cure temperature increases was observed). It could explain Cheng & Chiu (2003)'s results showing that KOH gives better results in terms of fire resistance as confirmed also by (Kong *et alii*, 2008). Cheng & Chiu (2003) showed that when a geopolymer panel of 10 mm of thickness is exposed to a flame of 1100°C, the temperature on the opposite face of the panel decreases depending on the initial concentration of KOH (the temperature reached 250°C-300°C after 15 minutes). Jaarsveld & Deventer (1999) showed also on fly ash-based geopolymer that alkali metal cations play a determining role in the raw material dissolution, and in the nucleation process which leads to a 3-dimensional structure. The size of the cations affects the crystal morphology: K^+ produces a geopolymer with a high degree of condensation compared to Na^+ in the same conditions whilst the dissolution of alumina and silica oligomers is greater in presence of Na^+ cations than in the presence of K^+ cations. The densification and the weight loss of Na-geopolymer for $1.15 \leq$ Si/Al ≤ 2.15 ($2.3 \leq SiO_2/Al_2O_3 \leq 4.3$) were observed by Duxson *et alii* (2007) when hardened paste is heated at 1000°C. Despite the great differences in shrinkage and densification with temperature, the weight losses of Na-geopolymer for different Si/Al ratios are similar. These differences are to be linked to the geopolymer gel structure (van Jaarsveld *et alii*, 1997).

As showed for the nature of alkali metal cation in geopolymer, a better understanding of geopolymer microstructure can explain its thermal behavior. Villaquirán-caicedo *et alii* (2015) showed clearly that the thermal properties of geopolymer (specific heat diffusivity and thermal conductivity) are connected tightly to the pore volume, the water content and the microstructure of geopolymer which are parameters influencing the heat flow within the material. Geopolymer concretes (with fly ash or fiber for reinforcement) clearly show a better resistance against the spalling effect because of the presence of temperature gradients much lower between the surface and the heart of the material (compared to what happens in Portland concrete). This characteristic limits the cracking surface and conduct to a decreasing of the spalling phenomena (Sarker *et alii*, 2014). Moreover, Duxson *et alii* (2007) explain that geopolymers are highly resistant to fire because of the existence of nano-pores allowing the physically and chemically bounded water to migrate and evaporate without damaging the alumino-silicate geopolymer network. Singh *et alii* (2015) and Mohd Salahuddin *et alii* (2015) described also the steps occurring in fly ash-based geopolymers when exposed to fire: it occurs dehydration of free water with minimal shrinkage, collapse of pores with constant shrinkage accompanied by dehydroxylation (OH departure from the structure), a step of densification (550-650°C) followed by crystallization and sintering of unreacted particles (600-800°C) which probably contributes to the strengthening of the geopolymer subjected to high temperatures. The densification is due to geopolymerization and to sintering of fly ash particles under temperature (Sarker *et alii*, 2014; Kong *et alii*, 2007, 2008). The geopolymerization exclusively involves the amorphous parts of ashes (Fernandez & Scrivener, 2011) and other crystallized particles undergo sintering and densification during fire exposure which significantly increases the strength at high temperatures. In the case of Mk geopolymer, the same phenomenon may happen if much of metakaolinite particle is not involved in geopolymerization reactions (Schmücker & MacKenzie, 2005). In this case, just a fraction of the raw material is dissolved, producing free SiO_2 and Al_2O_3 amounts. If all the

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	P_2O_5	LOI
Kaolin	58.7	26.7	1.3	0.1	0.3	0.1	0.96	1.4	0.2	0.2	9.9
Metakaolin	63.7	30.9	1.4	0.1	0.3	0.1	0.88	1.6	0.10	0.1	0.6

Tab. 1 - Chemical composition of kaolin and metakaolin (LOI: Loss on ignition at 1100°C)

Compositions (%)	H_2O	SiO_2	Na_2O	K_2O
Na_2SiO_3	93.55	4.3	2.15	-
NaOH	76.46	-	23.54	-
K_2SiO_3	92.08	5.65	-	2.27
KOH	65.95	-	-	34.05

Tab. 2 - Chemical composition of alkaline solutions used as activators

amorphous Mk material reacts by geopolymerization, no densification is then possible during a fire exposure (Zhang *et alii*, 2014).

The purpose of this paper is to synthesize geopolymer materials from mixtures of metakaolin and alkaline solution in order to reach the best thermal characteristics to use the material as flame retardant natural stone. (Na-) and (K-) Mk geopolymers are compared and their performance when exposed to high temperatures are determined by following their physico-mechanical properties and their microstructural change after spending two hours at high temperature (200, 400 and 600°C).

MATERIALS AND METHODS

Materials

Natural kaolin from a quarry in Tabarka region (in Tunisia) was used as the primary aluminosilicate source for geopolymerization (its chemical composition is given in Tab. 1). After a crushing in a Retsch RMO mortar lab grinder (with agate mortar) until the full passage through 106 µm sieve, the kaolin was calcined at 700°C for 2 hours (previous tests evidenced that this temperature allows to reach the best mechanical properties of geopolymer).

Sodium hydroxide powder (NaOH, 99%) and potassium hydroxide powder (KOH, 99%), both from Sigma-Aldrich were used as well as sodium silicate solution Na_2SiO_3 ($SiO_2/Na_2O = 2$) supplied by Fisher Chemicals. Potassium silicate solution ($SiO_2/K_2O = 2.5$) was supplied by Alfa Aesar. The alkali metal hydroxide MOH solutions (M: K or Na) were obtained by dissolving the dry powders in distilled water. After the cooling down to ambient temperature (around 25°C), solutions at 10 mol/L were kept safe from air. Afterwards, NaOH and KOH solutions were mixed with the alkali silicate Na_2SiO_3 and K_2SiO_3 solutions respectively. Mixture, using a mechanical mixer, took place just 24 h before the geopolymer manufacture to ensure that the activator component was mixed uniformly. The chemical composition of activators used to make geopolymer cement is listed in Tab. 2.

Preparation of geopolymers

Two types of geopolymer were synthesized and studied:

Geopolymer G1 (K-geopolymer obtained from metakaolin

It was obtained making the following mixture: Metakaolin + KOH (10M; d=1.46 d=1.39) + K_2SiO_3 (0,55M; d=1.07) with mass ratio K_2SiO_3 (solution)/KOH (solution) (g/g) = 0.14

Geopolymer G2 (Na-geopolymer obtained from metakaolin)

It was obtained making the following mixture: Metakaolin + NaOH (10M; d=1.34 d=1.330) + Na_2SiO_3 (0,55M; d=1.04) with mass ratio Na_2SiO_3 (solution)/NaOH (solution) (g/g) = 0.14

Each solutions of alkali metal hydroxide mixed with alkali silicate was added on metakaolin powder and further manually mixed for 3 to 5 minutes. The quantities of each components added follow the weight ratios given in Tab. 3. After mixing, the fresh geopolymer paste is rapidly poured into cylindrical PVC molds with a 1:2 diameter-to-length ratio (Latella *et alii*, 2008; van Jaarsveld & van Deventer, 1999; Bernal *et alii*, 2011). All samples were vibrated for 2 min on a vibration table to remove trapped air bubbles.

Methods of solid characterization

The temperature effects on the physical properties of geopolymer were tested using linear shrinkage and loss on ignition as well as compressive strength testing. Linear shrinkage and loss on ignition were measured on hardened geopolymer specimens after heat treatment during 2 hours at 200, 400 or 600°C in a programmable furnace (Nabertherm B180). A thermal increase of 2°C/min was imposed to reach each final temperature in order to avoid the cracking of material (van Jaarsveld *et alii*, 2002).

The linear shrinkage was determined using a calliper by measuring the variations in length of the samples before and after heating, both after previous 28 days of curing at ambient temperature. Linear shrinkage (Ls) was calculated for each specimen according to equation 1:

$$Ls = \frac{L_0 - L}{L_0} \times 100 \qquad \text{Eq. 1}$$

where, L_0 and L are the lengths of specimen before and after calcination, respectively.

Formulation G1			Formulation G2		
ratios	g/g	mol/mol	ratios	g/g	mol/mol
L/S	1.16	-	L/S	1.11	-
SiO_2/Al_2O_3	2.09	3.54	SiO_2/Al_2O_3	2.08	3.54
SiO_2/K_2O	1.8	2.82	SiO_2/Na_2O	2.78	2.87
Al_2O_3/K_2O	0.86	0.8	Al_2O_3/Na_2O	1.33	0.8
H_2O/K_2O	2.26	11.84	H_2O/Na_2O	3.79	13.05

Tab. 3 - Weight and molar ratios calculated for G1 and G2 geopolymer mixtures. L/S is the liquid upon solid ratio

Loss on ignition (Li) was calculated for each specimen according to equation 2, where m_1 and m_2 are the masses of the specimen before and after calcination, respectively (both after previous 28 days of curing at ambient temperature).

$$L_i = \frac{m_1 - m_2}{m_1} \times 100 \qquad \text{Eq. 2}$$

Compressive strength testing was performed using cylinders with a 1:2 diameter-to-length ratio (Van Jaarsveld & Van Deventer, 1999). Three cylinders of each geopolymer sample were tested to calculate average experimental values. All the samples were tested after 28 days of curing under ambient laboratory atmosphere. A Zwick/Roell compressive strength testing apparatus was used, with a constant and controlled displacement rate (5 mm per min) for all the tests (Al Bakri *et alii*, 2013). Compressive strength was measured at 20°C on the 200, 400 or 600°C heated geopolymers.

The structural characteristics of geopolymers (morphology and particles arrangement) have been studied and compared on fresh fractured surface before and after calcination from both G1 and G2 geopolymer specimens using environmental scanning electron microscopy (FEI Quanta 400).

Thermal analysis (DTA–TGA) using a STA-409 E apparatus from NETZSCH was performed under air sweeping on 180 mg of ground geopolymers (at 80 µm). It allows to identify the chemical reactions or the phase changes that may occur in the sample under heating. Indeed, the powder was placed in a platinum crucible and was heated at a temperature ranging from 20 to 1250°C with a heating rate of 10°C/min. In DTA, alumina is used as a reference (inert substance) that shows no thermal change in the explored temperature interval.

The functional groups of ground synthesized geopolymers were identified by FT infrared spectroscopy (from 4000 to 450 cm^{-1}) using a Perkin Elmer spectrometer 180. Mineralogical qualitative analyses were realized by X-ray diffraction (XRD) using a D8 Advance from Bruker with a cobalt anode (λ Cokα1 = 1.79 Å). The XRD patterns were measured from 5° to 80° 2θ at a scan rate of 0.01°2θ/1s. The porosity was carried out on freeze-dried samples using a mercury porosimeter Autopore IV from Micrometritics. The freeze drying is a technique that remove most of the water contained in the specimen by water sublimation at low-temperature and low-pressure and that prevents microstructure change during usual drying.

EXPERIMENTAL RESULTS

STRUCTURAL AND MINERALOGY OF SYNTHESISED GEOPOLYMERS

X-ray diffraction (XRD)

XRD patterns of raw kaolin (Kb), metakaolin (Mk) (calcined kaolinite Kb) and geopolymers G1 and G2 are shown in Fig. 1. XRD patterns were performed on geopolymers fragments after mechanical measurements applied after 28 days of curing at ambient temperature.

Each diffractograms show the presence of characteristic peaks of quartz (d=3.34 Å close to 31°2θ), anatase (TiO_2) usually associated to kaolin and illitic clay (d=10Å near 10°2θ). These minerals were present initially in raw kaolin before heating and are not modified by calcination at 700°C. They are not involved in the synthesis of geopolymer (Burciaga-Diaz *et alii*, 2012). Compared to Kb pattern, XRD pattern of metakaolin shows the disappearance of peaks of kaolinite phase after calcination (the main peak is positioned at d= 7Å around 14°2θ) and the presence of a larger peak with weak amplitude between 20° and 33°2θ. It reveals the amorphous character of metakaolin. This wide peak shifts to 28°- 40° 2θ range on G1 and G2 XRD patterns which is characteristic of geopolymer systems (Van Jaarsveld & Van Deventer, 1999).

In the case of Na-geopolymer G2 contrary to K-geopolymer G1, it appears new peaks representative of sodium aluminosilicate (d= 6.35 Å and d= 3.65 Å close to 16.23°2θ and 28.4°2θ respectively) and faujasite ($Na_2Al_2Si2.4O_{8.8}.6.7\ H_2O$) (d=14.3 Å near 7.17°2θ and d=8.84 Å near 11.67°2θ.) (Zibouche *et alii*, 2009).

FTIR analysis

FTIR curves obtained on metakaolin (Mk) and geopolymers G1 and G2 are shown in Fig. 2. The absorption broadband at about 3440 cm-1 and 1640 cm^{-1} are the stretching and bending vibration frequencies of OH groups associated to water, respectively (Zheng *et alii*, 2009).

The absorption peak at about 2350 cm^{-1} on Mk spectrum is due to adsorptive CO_2 vibration on clay particle surface. Two bands located at 1093 cm^{-1} and 994 cm^{-1} are characteristic of Si-O and Si-O-Si stretching vibrations respectively (Duxson, 2006). Compared to Mk spectrum, IR spectra collected on G1 and G2

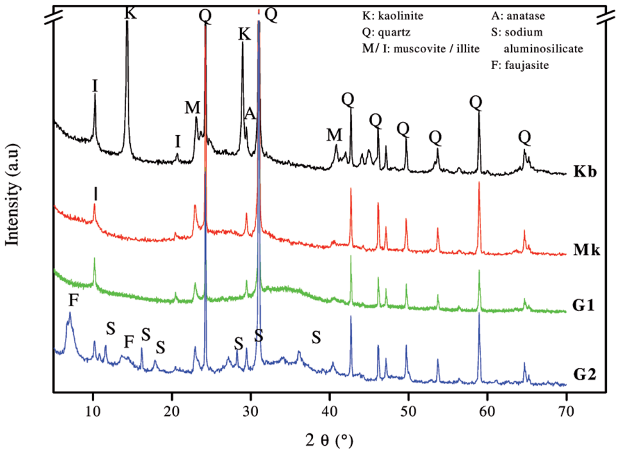

Fig. 1 - X-ray diffraction patterns on raw kaolin Kb, metakaolin Mk, K-geopolymer G1 and Na-geopolymer G2

geopolymers show the appearance of a new absorption band at about 1437 cm^{-1} which is assigned to the C-O stretching vibration of carbonate (experiments are done under air). In addition, the vibration frequency at 798 cm^{-1} on metakaolin spectrum, linked to Al-O stretching vibration, was reduced after geopolymerization. It corresponds to the change of aluminum coordination from VI to IV, the coordination number IV characterizing the geopolymer structure (YUNSHENG *et alii*, 2010). This band is still present on spectrum associated to geopolymer G1, indicating that the geopolymer structure contains more unreacted metakaolin than the geopolymer G2. The absorption bands at about 797 and 724 cm^{-1} on both G1 and G2 spectra are respectively attributed to asymmetric and symmetric vibrations of Si-O and Si-Al-O-Si bonds that provide the cohesion between AlO_4 and SiO_4 tetrahedrons in geopolymeric structure (RATTANASAK & CHINDAPRASIRT, 2009). Finally, the band at approximately 470 cm^{-1} is attributed to O-Si-O bending mode.

DTA–TGA thermal analysis and loss on ignition

Endothermic reactions corresponding to successive release of physically absorbed, interlayer and crystalline water are identified by thermal analyses. Exothermic reactions (identified by peaks pointing up on DTA curve as at 977°C on Fig. 3) may correspond to new compounds formation or organic matter calcinations.

Thermal behavior of kaolin Kb is shown in Fig. 3. The total weight loss is 6.06% at 1150°C. The first loss (0.86%) between room temperature and 320°C corresponds to the release of moisture (physically and partially chemically adsorbed water). In DTA curve the broad endothermic peak at around 565°C (with intense loss weight on TGA curve corresponding to 5.10 %) is attributed to dehydroxylation of kaolinite and metakaolin formation (SHVARZMAN *et alii*, 2003) according to the following reaction given by KAKALI *et alii* (2001):

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_5(OH)xO2\text{-}x + (2\text{-}x/2)H_2O \qquad \text{Eq. 3}$$

with values much lower than x (x depends on the time and temperature of calcination).

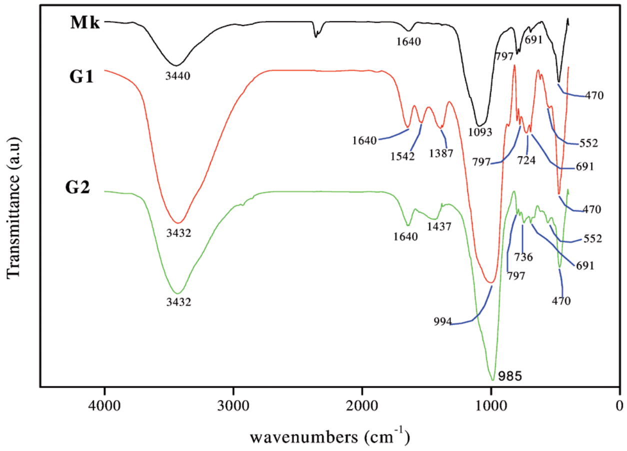

Fig. 2 - FTIR spectra of metakaolin Mk, K-geopolymer G1 and Na-geopolymer G2

In our case, the heating at 700°C during two hours allows to make disappear almost all OH from kaolinite but the OH from illite remains. Such OH remains until 900°C but above 800°C, metakaolin may be transformed into crystallized form. The small exothermic peak on DTA curve at 977.7°C, with negligible loss of weight on the TGA, indicates such crystallization into crystalline aluminosilicate such as spinelle ($Al_4Si_3O_{12}$). The exothermic peak at 1203.1°C corresponds to transformation of spinelle to another crystalline form such as mullite ($Al_6Si_2O_{13}$) (SHVARZMAN *et alii*, 2003; KAKALI *et alii*, 2001). These new crystallized phases decrease the reactivity of metakaolin and then the mechanical properties of synthesized geopolymer. The TGA and DTA curves of metakaolin is not given as they correspond to the state of kaolin after heating at 700°C (the total weight loss of metakaolin is almost zero with just the presence of the DTA peak at 977°C). The temperature resistance of geopolymers is partially explained by thermal analysis. The TGA curve of K-geopolymer G1 on Fig. 4a shows several losses which gives a total weight loss of 12%. The first weight loss of 9.7% (that represents almost 81% of the total loss) characterized by an endothermic DTA peak at 157.1°C corresponds to evaporation of physically absorbed water.

Then, there is a small loss of 2.22% at 800°C that corresponds to the release of crystalline water from illite and other components. The exothermic peak at 1020.9°C may correspond to a recrystallization of residual metakaolin to spinelle (KAKALI *et alii*, 2001). The exothermic peak at 1226.2°C corresponds to the mullite appearance from spinelle formed from unpolymerised metakaolin (SCHMÜCKER & MACKENZIE, 2005). Thermal analysis of Na-geopolymer G2 on Fig. 4(b) shows a higher total weight loss of 14.99%. The first weight loss (until 400°C) of 12.86% characterized by a DTA peak at 139.6°C corresponds as previously to evaporated superficial moisture (the water content is higher than 9.7% lost by G1 in similar condition). Then, there is a loss of remaining water (2.12% close to 2.22% lost by G1) until 635°C. The exothermic peak at 864°C may be attributed to illite deshydroxylation (although this phenomenon is not visible on geopolymer G1). G2 curve does not show an exothermic peak at temperature above 1200°C, which may be explained by the polymerization of all aluminosilicate when NaOH and Na_2SiO_3 are used as activator. Such observation validates the fact that the dissolution of aluminum and silicon precursor is greater in the presence of Na+ cations that in the presence of K+ cations. It contributes to explain why Na-geopolymer G2 is steadier than K-geopolymer G1. Finally, both G1 and G2 geopolymers appear stable under heating: the main loss of mass comes from superficially adsorbed water and no exo- or endo-thermal reaction (except in presence of side mineral phases in raw material) seems to

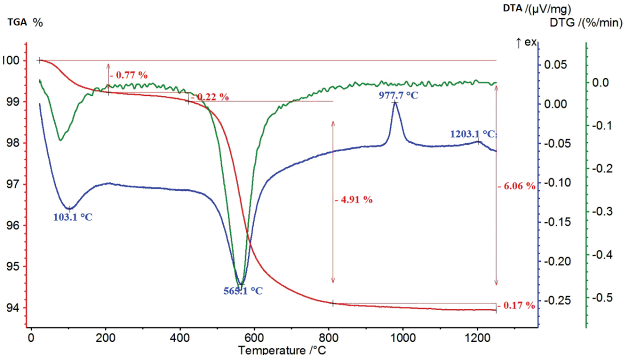

Fig. 3 - Thermal analysis on kaolin Kb (TGA curve in red, DTG curve derived from TGA in green and DTA curve in blue)

occur between 400 and 1000°C.

In parallel to thermal analysis, the loss on ignition of geopolymers (a macroscopic and simple measure compared to TGA-DTA) was measured as a function of temperature. Measures shown in Fig. 5 are in accordance with previous thermogravimetric data on Fig. 4. We observe that both geopolymers G1 and G2 reached a maximum loss at 600°C: 11.42% in G1 and 13.42% in G2. The higher the temperature of calcination is, the greatest the loss on ignition appears (with systematic larger amount of released water for Na-geopolymer G2).

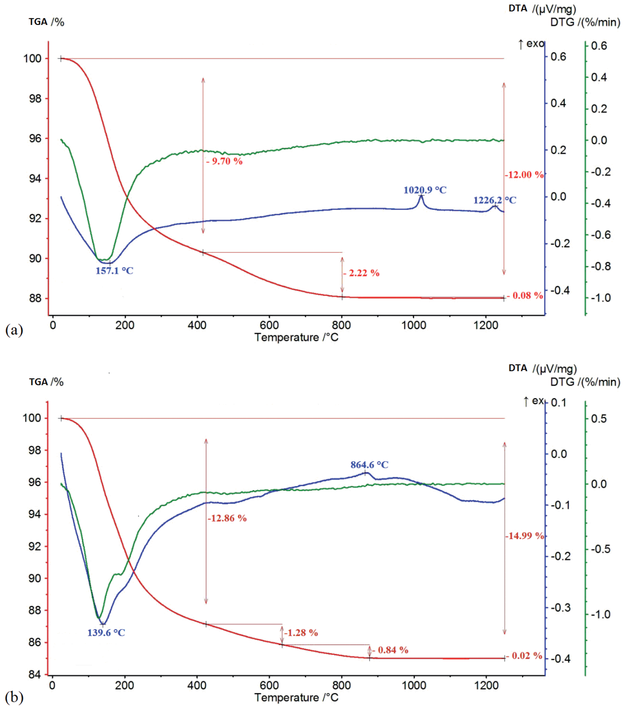

Fig. 4 - Thermal analysis on geopolymers G1 (a) and G2 (b) (TGA curve in red, DTG curve derived from TGA in green and DTA curve in blue)

TEMPERATURE EFFECT ON THE PHYSICAL PROPERTIES OF GEOPOLYMER

Compressive strength

The compressive strength measured on geopolymer specimens G1 and G2 after calcination at various temperatures are shown in Fig. 6 (average values calculated from 3 replicates on each geopolymer tested for each temperature). A slight increase of the compressive strength is observed at temperatures ranging between 25 and 400°C in both geopolymer formulations due to acceleration of the geopolymerization reaction which is not yet completed at 25°C after the 28 days of curing. A calcination of G1 and G2 at higher temperature leads to a decrease in mechanical properties with a compressive strength that drops to 12.74 MPa in G1 and 18.47 MPa in G2. It is correlated to the vaporization of the remaining water linked to the presence of illite (and other components) not affected by geopolymerization as shown on XRD patterns, and the creation of micro cracks in specimens. If geopolymers G1 and G2 behave similarly with the temperature of calcination, they are clearly differentiated on Fig. 6. The new crystalline phases detected by XRD on Fig. 1 on geopolymer G2 (compared to G1) are probably at the origin of the improved mechanical properties of G2 (compressive strength for G1: 14 MPa and G2: 20.64 MPa without calcination and 12.74 MPa for G1 and 20.64 MPa for G2 after calcination at 600°C).

Linear shrinkage

The slight increase in resistance after calcination on Fig. 6 is accompanied by a slight increase of weight loss on Fig. 5 due to evaporation of superficial water adsorbed on external surface and of gravity and capillary water in pores. Such phenomenon causes also partial shrinkage of porous material (after release of water) resulting in a linear shrinkage presented on Fig. 7. Linear shrinkage may come also from the development of microcracks under heating. Results show that the linear shrinkage increases with the temperature of calcination. The lower linear shrinkage

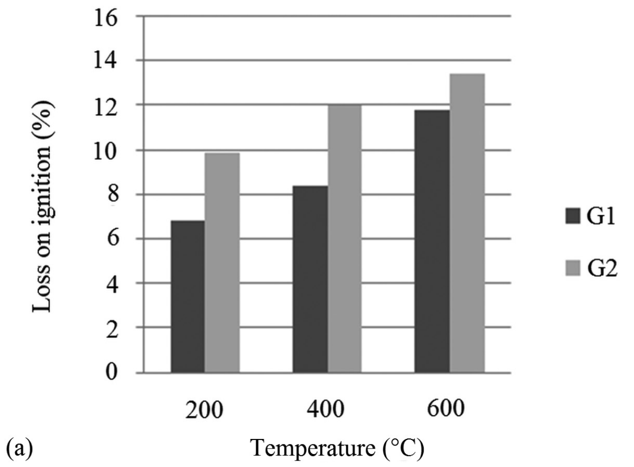

Fig. 5 - Loss on ignition of G1 and G2 heated at different temperatures

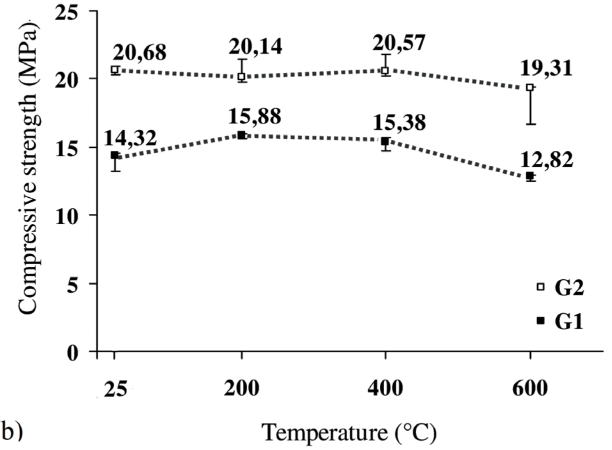

Fig. 6 - Compressive strength of G1 and G2 geopolymers heated at different temperatures

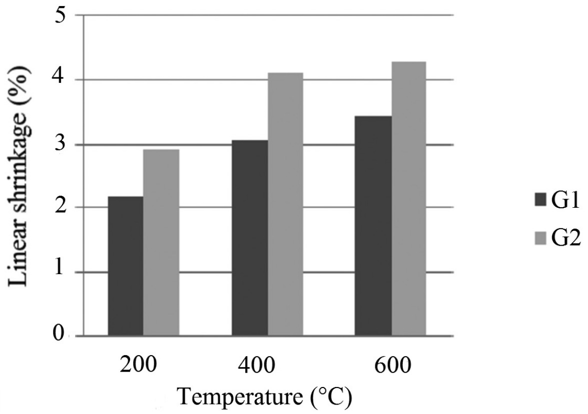

Fig. 7 - Linear shrinkage of G1 and G2 heated at different temperatures

values (2.18% and 2.93%) are obtained respectively for G1 and G2 treated at 200°C. The greatest values (3.46% and 4.27%) correspond to G1 and G2 treated at 600°C.

Furthermore correlated to the loss on ignition, K-geopolymer G1 has the lowest linear shrinkage compared to Na-geopolymer G2. Surprisingly, G1 has the lowest mechanical strength while G2 has the greatest (the geopolymer with strong water release and with the highest linear shrinkage in favor of microcracks, is expected to be the weakest mechanically). Such behavior should be linked to the mineralogical difference observed on G1 and G2 geopolymers. The presence of faujasite and sodium aluminosilicate probably strengthen the Na-geopolymer G2 (more rigid structure) but such structure may shrink with heating without or with a few microcracks.

MIP analysis

The mercury intrusion porosimetry (MIP) on hardened geopolymers paste after 28 days of curing and heating at different temperature gives complementary information on the presence of microcracks and on pore distribution. As the pore diameter is a function of the mercury pressure, the volume of mercury entering into the sample (per unit mass of the material - mL/g) gives the pore volume for each pore size and the total porosity (%) may be calculated. Results are given in Tab. 4.

Before heating, Na-geopolymer G2 is less porous than K-geopolymer G1with a porosity equal to 24.3% and 30.1% respectively. Such observation is consistent with the higher mechanical resistance of geopolymer G2. When heat treatment is applied with increasing temperature of calcination, porosity remains quite constant for G1, but it increases in geopolymer G2 which reaches 33.2% at 400°C and then decreases at 600°C. The microcracks or porosity seems to increase with temperature for Na-geopolymer G2 (while it remains stable until 400°C for K-geopolymer G1) and then falls at 600°C for both geopolymers. However, G2 is more resistant than G1. The apparent density of both geopolymers follows the same trend: it increases with calcination temperature and then decreases after a 600°C calcination. It's correlated to the decrease of the compressive strength at 600°C for both geopolymers and to the variation of pore size under the thermal effect.

Parallel to the quantity of pore, the mercury intrusion curves on Fig. 8 allow to observe the pore family and their evolution under heating. Results show clearly that G1 and G2 pore family characteristics are different. Before heat treatment, they are characteristic of unimodal and bimodal systems for G2 and G1 respectively. The average pore diameters range from 50 to 200 nm in G2 and from 150 to 500 nm in G1 (the two pore families in G1 are close, centered on 400 nm for the main pores and to 350 for the second ones). The literature indicated that pores larger than 200 nm in geopolymer pastes were probably associated with

Samples	G1	G1 (200°C)	G1 (400°C)	G1 (600°C)	G2	G2 (200°C)	G2 (400°C)	G2 (600°C)
Total intrusion Volume (mL/g)	0.20	0.17	0.19	0.19	0.16	0.20	0.21	0.19
Total porosity (%)	30.1	28.3	30.8	29.8	24.3	30.7	33.2	30.2
Calculated apparent particle density (g/cm^3)	2.20	2.28	2.36	2.21	2.00	2.23	2.37	2.30
Calculated median pore diameter (nm)	300.0	276.8	256.4	289.9	137.7	143.6	152.6	147.0

Tab. 4 - Mercury intrusion porosimetry of geopolymers before and after heating interfacial spaces between partially reacted or unreacted raw material and the geopolymer gel (Gao *et alii*, 2013). The presence of such pores in K-geopolymer G1, indicating the presence of unreacted metakaolin, agrees with previous TGA-DTA and FTIR results.

Na-geopolymer G2 has not only quantitatively a lower porosity than G1, but also smaller pores, which contributes to its highest mechanical resistance. After a 2 hours heat treatment at 200, 400 and 600°C, mercury intrusion curves on K-geopolymer G2 demonstrated the pore family changes with the appearance of a bimodal system (the pore sizes of the two families are positioned around 160 nm and 300 nm). For G1, after the decrease of the mean size of the two pore families (close to each other) until 400°C, the calcination at 600°C induces the increase of pores size with clearly two families with average diameters about 300 nm and 450 nm.

Environmental scanning electron microscopy observations

The environmental SEM images of geopolymers G1 and G2 (Fig. 9 and Fig. 10) show matrices containing particles with a certain porosity which directly influences the resistance of geopolymer.

Before heating, G1 and G2 present various morphology and particle size even if raw material used to synthesized them are similar., The fresh-fractured surface observed on geopolymer G2 shows globally a denser matrix (Fig. 10d) with very fine particles. Local area show also the presence of gathered hexagonal platelets (Fig. 10c) that could be identified as unreacted metakaolinite particles, even if such particles are expected in geopolymer G1 as demonstrated by previous FTIR and TGA-DTA analysis. Geopolymer G1 shows a more heterogeneous matrix with large amount of particles with lumpy texture. The more compact structure observed on polymer G2 contribute to explain the increase in compressive strength, but no significant porosity differences in both geopolymers had been recorded because observations are somewhat subjective and remain local.

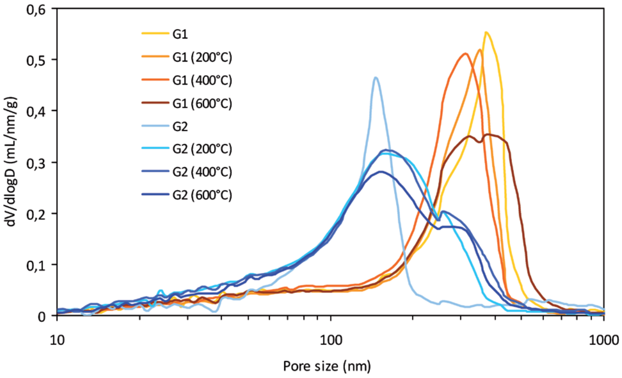

Fig. 8 - MIP curves from G1 and G2 geopolymers heated at different temperatures

CONCLUSION

As a conclusion, Na-geopolymer (G2) obtained from metakaolin is mechanically more resistant than geopolymer K-geopolymer (G1) obtained also from metakaolin. The high resistance of geopolymer G2 seems to be linked to the mineralogy (with the presence of faujasite and sodium aluminosilicate) combined to a lower porosity with small-sized pores (demonstrated by SEM images and MIP analysis). Metakaolin and Na alkaline silicate give a geopolymer with high degree of condensation relative to metakaolin and K alkaline silicate. The probable presence of unreacted metakaolinite in K–geopolymer G1 identified by thermal or infrared analyses contributes also to decrease the mechanical strength of G1 (it agrees with literature that mentions that sodic activators compared to potassic promote the dissolution of aluminosilicate precursor). Furthermore, the

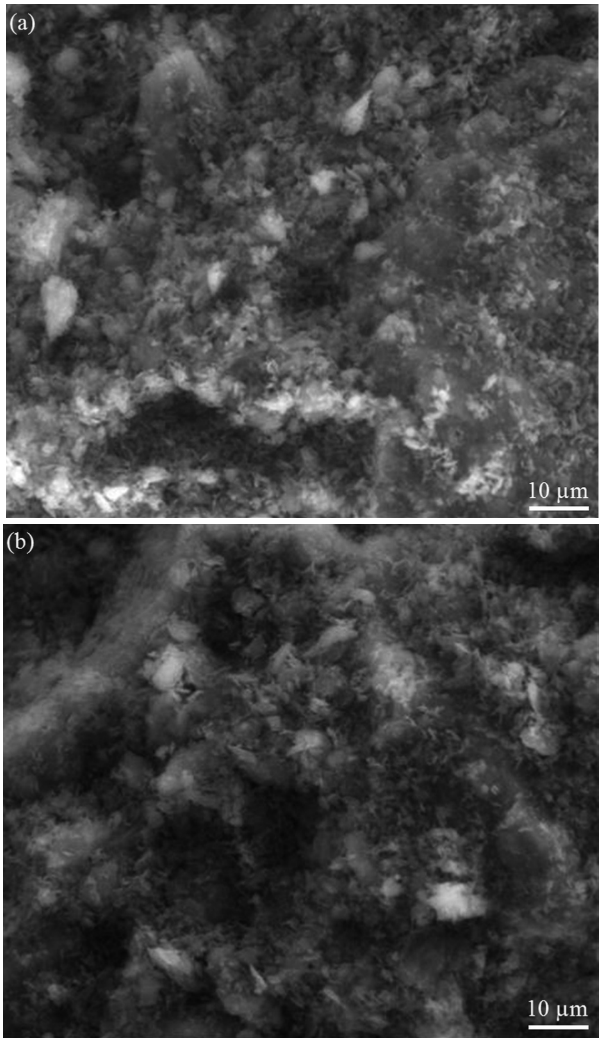

Fig. 9 - Environmental SEM images of fresh fractured geopolymers (a) G1 and (b) G1 after heating at 600°C

greater linear shrinkage of Na-geopolymer G2 (compared to G1) as well as its significant loss on ignition (essentially physically adsorbed water released at temperature < 400°C) seems not to govern the mechanical behavior of geopolymer. No microcracks that could appear with high linear shrinkage were observed by microscopy at small scale. After calcination, the porosity and density of geopolymer slightly increases or remains quite constant as well as the compressive strength, but at 600°C, they decreased (due to the increase of pore size under the thermal effect for G1). To conclude, the Na-metakaolin based geopolymer compared to K-metakaolin based one is the most appropriate to produce heat resistant geopolymer cement. This material, with a light color after calcination, could be used in the construction industry as new ecological cement (for flooring, artificial stone wall, pedestrian roads…) or applied instead of asbestos as thermal insulator in electric oven.

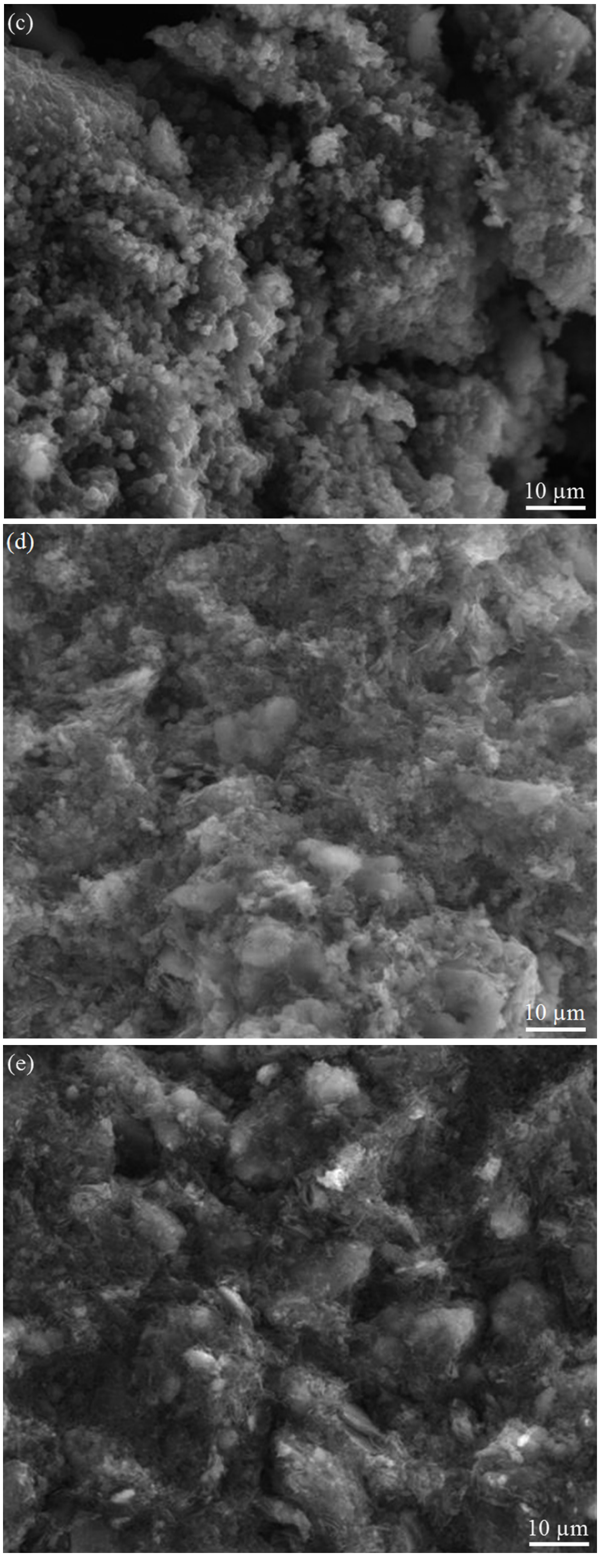

Fig. 10 - Environmental SEM images of fresh fractured geopolymers (c)-(d) G2 and (e) G2 after heating at 600°C

REFERENCES

Al Bakri A.M.M., Kamarudin H., Bnhussain M., Liyana J. & Ruzaidi Ghazali C.M. (2013) - *Nano geopolymer for sustainable concrete using fly ash synthesized by high energy ball milling.* Appl. Mech. Mater., **313-314**: 169-173.

Bernal S.A., Rodríguez E.D., Mejía De Gutiérrez R., Gordillo M & Provis J.L. (2011) - *Mechanical and thermal characterisation of geopolymers based on silicate-activated metakaolin/slag blends*. J. Mater. Sci, **46**(16): 5477-5486.

Burciaga-Diaz O., Escalante-Garcia J.I. & Gorokhovsky A. (2012) - *Geopolymers based on a coarse low-purity kaolin mineral: mechanical strength as a function of the chemical composition and temperature.* Cem. Concr. Compos., **34**(1) : 18-24.

Cheng T.W. & Chiu J.P. (2003) - *Fire-resistant geopolymer produced by granulated blast furnace slag.* Miner. Eng. **16**(3): 205-210.

Davidovits J. (2013, Eds) - *Geopolymer cement 1–11,* Saint-Quentin, France.

De Silva P. & Sagoe-Crentsil K. (2008) - *The effect of Al_2O_3 and SiO_2 on setting and hardening of Na_2O-Al_2O_3-SiO_2-H_2O geopolymer systems.* J. Australia Ceram. Soc., **44**(1): 39-46.

Duxson P. (2006) - *The structure and thermal evolution of metakaolin geopolymers.* Ph.D. thesis, Department of Chemical & Biomolecular Engineering, The University of Melbourne.

Duxson P., Lukey G.C. & Van Deventer J.S.J. (2007) - *Physical evolution of Na-geopolymer derived from metakaolin up to 1000°C.* J. Mater. Sci., **42**: 3044-3054.

Fernandez R. & Scrivener K. (2011) - *Des argiles calcinées comme substitut au ciment.* Bull. Tech. la Suisse Rom., **137**: 11-14.

Gao K., Lin K., Wang D., Shiu H. & Hwang C. (2013) - *Effects of nano-SiO_2 on setting time and compressive strength of alkali-activated metakaolin-based geopolymer.* The Open Civil Engineering Journal, **7**: 84-92.

Kakali G., Perraki T., Tsivilis S. & Badogiannis E. (2001) - *Thermal* *treatment of kaolin: the effect of mineralogy on the pozzolanic activity.* Appl. Clay Sci., **20**: 73-80.

Komnitsas K. & Zaharaki D. (2007) - *Geopolymerisation: a review and prospects for the minerals industry.* Miner. Eng., **20**(14): 1261-1277.

Kong D.L.Y. & Sanjayan J.G. (2008) - *Damage behavior of geopolymer composites exposed to elevated temperatures.* Cem. Concr. Compos., **30**(10): 986-991.

Kong D.L.Y., Sanjayan J.G. & Sagoe-Crentsil K. (2008) - *Factors affecting the performance of metakaolin geopolymers exposed to elevated temperatures.* J. Mater. Sci., **43**(3): 824-831.

Kong D.L.Y., Sanjayan J.G. & Sagoe-Crentsil K. (2007) - *Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures.* Cem. Concr. Res., **37**(12): 1583-1589.

Latella B.A., Perera D.S., Durce D., Mehrtens E.G. & Davis J. (2008) - *Mechanical properties of metakaolin-based geopolymers with molar ratios of Si/Al ≈ 2 and Na/Al ≈ 1.* J. Mater. Sci., **43**(8): 2693-2699.

Mohd Salahuddin M.B., Norkhairunnisa M. & Mustapha F. (2015) - *A review on thermophysical evaluation of alkali-activated geopolymers.* Ceram. Int., **41**(3): 4273-4281.

Neville A. (2011, Eds) - *Properties of concrete.* 597-602.

Provis J.L., Duxson P. & Van Deventer J.S.J. (2010) - *The role of particle technology in developing sustainable construction materials.* Adv. Powder Technol., **21**(1): 2-7.

Rattanasak U. & Chindaprasirt P. (2009) - *Influence of NaOH solution on the synthesis of fly ash geopolymer.* Miner. Eng., **22**(12): 1073-1078.

Sarker P.K., Kelly S. & Yao Z. (2014) - *Effect of fire exposure on cracking, spalling and residual strength of fly ash geopolymer concrete.* Mater. Des., **63**: 584-592.

Schmücker M. & Mackenzie K.J.D. (2005) - *Microstructure of sodium polysialate siloxo geopolymer.* Ceram. Int. **31**(3): 433-437.

Shvarzman A., Kovler K., Grader G.S. & Shter G.E. (2003) - *The effect of dehydroxylation / amorphization degree on pozzolanic activity of kaolinite.* Cem. Concr. Res., **33**: 405-416.

Silva P. De, Sagoe-Crentsil K. & Sirivivatnanon V. (2007) - *Kinetics of geopolymerization: role of Al_2O_3 and SiO_2.* Cem. Concr. Res., **37**(4): 512-518.

Sindhunata, Van Deventer J.S.J., Lukey G.C. & Xu H. (2006) - *Effect of curing temperature and silicate concentration on fly-ash-based geopolymerization.* Ind. Eng. Chem. Res., **45**(10): 3559-3568.

Singh B., Ishwarya G., Gupta M. & Bhattacharyya S.K. (2015) - *Geopolymer concrete: a review of some recent developments.* Constr. Build. Mater., **85**: 78-90.

Van Jaarsveld J.G.S. & Van Deventer J.S.J. (1999) - *Effect of the alkali metal activator on the properties of fly ash based geopolymers*. Ind. Eng. Chem. Res. 38 (10): 3932-3941.

Van Jaarsveld J.G., Van Deventer J.S. & Lukey G. (2002) - *The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers.* Chem. Eng. J., **89**(1-3): 63-73.

Van Jaarsveld J.G.S., Van Deventer J.S.J. & Lorenzen L. (1997) - *Potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and applications.* Miner. Eng., **10**(7): 659-669.

Van Jaarsveld J.G.S., Van Deventer J.S.J. & Lukey G.C. (2003) - *The characterisation of source materials in fly ash-based geopolymers*. Mater. Lett., **57**(7): 1272-1280.

Villaquirán-Caicedo M.A., Mejía De Gutiérrez R., Sulekar S., Davis C. & Nino J.C. (2015) - *Thermal properties of novel binary geopolymers based on metakaolin and alternative silica sources.* Appl. Clay Sci., **118**: 276-282.

Yunsheng Z., Wei S. & Zongjin L. (2010) - *Composition design and microstructural characterization of calcined kaolin-based geopolymer cement.* Appl. Clay Sci., **47**(3-4): 271-275.

Zhang H.Y., Kodur V., Qi S.L., Cao L. & Wu B. (2014) - *Development of metakaolin-fly ash based geopolymers for fire resistance applications.* Constr. Build. Mater., **55**: 38-45.

Zheng G., Cui X., Zhang W. & Tong Z. (2009) - *Preparation of geopolymer precursors by sol–gel method and their characterization.* J. Mater. Sci. **44**(15): 3991-3996.

Zibouche F., Kerdjoudj H., De Lacaillerie J.-B., D'Espinose & Van Damme H. (2009) - *Geopolymers from Algerian metakaolin. Influence of secondary minerals.* Appl. Clay Sci., **43**(3-4): 453-458.

Received February 2016 - Accepted April 2016