Effect of Composition on Structure and Mechanical Properties of Metakaolin Based PSS-Geopolymer

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Abstract

Geopolymer is a type of cross linked long-chain inorganic compound, built in three-dimensional structures and has different attractive properties (thermal, mechanical, chemical, etc). This study elucidated the structure and mechanical properties of PSS type geopolymer obtained by alkaline attack of metakaolin. A systematic investigation was conducted to comprehend the effect of molar ratios Si/Al and Na/Al on the properties of this geopolymer by using $^{29}$Si and $^{27}$Al magnetic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, X-Ray diffraction and mechanical measurements. The results indicate that an increase of Si/Al ratio improves the geopolymer mechanical properties due probably to the formation of Si-O-Si bond in the geopolymer at the expense of Si-O-Al one. It was also shown that an introduction of NaOH in the geopolymer composition enhances the mechanical properties until a molar ratio Na/Al=1. Beyond this value, the excess of Na$^+$ cation causes fragility of the geopolymer structure confirmed by a decrease of the mechanical strength.

Keywords:
Geopolymer; Metakaolin; Structure Evolution; $^{29}$Si; $^{27}$Al NMR; XRD Resolution; Alkali Activation

Introduction

“Geopolymers”, ill-organized polymeric aluminosilicate materials obtained by alkaline or alkaline-earth activation of aluminosilicates, were introduced into the inorganic cementious by Davidovits in 1970 (Komnitsas & Zaharaki 2007). According to the molecular structure; geopolymeric binder can be expressed by the following empirical formula $M^n\{SiO_2\}_z\{AlO_2\}_w\cdot w\cdot H_2O$ where M is a cation such as potassium (K) or sodium (Na); n the degree of polycondensation; z is 1, 2 or 3, then geopolymer is termed as PS; PSS or PSDS respectively; w is binding water amount. These structures consist of a polymeric Si–O–Al framework, similar to that found in zeolites. The main difference with zeolitic structures is that geopolymers are amorphous to X-rays diffraction.

Geopolymers are currently of large interest, due to their good thermal, chemical and mechanical properties and their potential as “green” cementitious binder (Duxson, Fernandez-Jimenez, Provis, Lukey, Palomo & Van Deventer). Geopolymerization involves an exothermic reaction between an alumino-silicate pre-cursor, such as metakaolin for instance, and a high alkalinity silicate solution (Davidovits 1994). Xu and Van Deventer (2002) considered that the basic steps of geopolymerization are the dissolution of the solid alumino-silicate oxide in the MOH solution (M: alkali metal), the diffusion of dissolved Al and Si complexes from the particle surface to the inter-particle space, the formation of a gel phase resulting from the polymerization between the silicate solution and Al and Si complexes, and finally, the hardening of the gel phase.

Many materials composed of silica and alumina can be used in order to synthesize geopolymers. Indeed, many investigations have used metakaolin, Kaolinitic clays, fly ashes sand blast furnace slags as raw materials (Pacheco-Torgal, Castro-Gomesb, & Jalali 2008). It was demonstrated that the reactivity of these materials is higher when its amorphous content is higher.

The most used alkaline activators are mixture of sodium or potassium hydroxide with sodium or potassium waterglass.

In addition to water content, Divya and Rubina (2007) reported that parameters of geochemistry reaction for geopolymer system include the molar ratios $M_2O/SiO_2$ and Si/Al and the concentration of MOH (where M is Na or K element).

The objective of this paper was to study the effect of Si/Al and Na/Al ratios on a PSS metakaolin based...
geopolymer structure. XRD, MAS-NMR and DTA, TGA techniques have been applied to analyze the structure of the synthesized geopolymers. The correlation between mechanical strength and geopolymer structure has also been considered.

### Materials and Experimental Techniques

#### Materials

Different raw materials are used in this work:
- Metakaolin: used as aluminosilicate raw material and obtained by calcining kaolin (supplied by CHEMI–PHARMA Company) at 700°C for 5 h.
- Analytical reagents NaOH pelled (purity = 99.5%) and sodium silicate solution (Si/Na=1.5, ρ=1.39g/cm³) used as alkaline reagents.
- Distilled water

#### Geopolymer Synthesis

Geopolymer samples were prepared by:
- mixing sodium silicate and NaOH pellets together 24h before use;
- adding metakaolin to the alkaline solution and mixing until the paste is homogenous;
- All the mixtures are prepared with a constant Solide/Liquide ratio equal to 1.8.
- after mixing, paste specimens were poured in 32 mm diameter plastic containers and then cured at ambient temperature for 7 days.

#### Experimental Techniques

The raw material and geopolymers mineral phases are identified by X-ray diffraction (XRD) using a «BRUKER-AXS-D8-Advance. The XRD patterns are obtained with a scanning rate of 1° min⁻¹ from 5° to 60° (2θ). The wavelength is selected as 15.40562nm (Cu).

The characterisation of these materials is also performed by:
- Simultaneous DTA and TGA measurements using(Set Soft 2000). Experiments are carried out between 25°C and 1200°C at a heating and cooling rates of 10°C/min with a helium gas purge.
- ²⁷Al and ²⁹Si MAS NMR using a Bruker ASX500 (7T magnetic field) spectrometer, operating at 15 KHz for ²⁷Al and 8 KHz for ²⁹Si.
- Brazilian test on geopolymer samples (6mm height and 32 mm diameter) in order to assess the mechanical properties. At least six samples of each formula were tested. The average value is served as the ultimate compressive strength. The loading is displacement controlled at a constant rate of 0.5mm min⁻¹ for all the compression tests. All samples were tested after 7 days of curing.

### Results and Discussions

#### Characterization of Kaolin

The chemical composition of kaolin (Table 1) shows that, in addition to silica and alumina, the sample contains Fe₂O₃, CaO, K₂O and MgO.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>CaO</th>
<th>K₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mass %)</td>
<td>44.7</td>
<td>36.55</td>
<td>1.69</td>
<td>0.27</td>
<td>1.83</td>
<td>1.81</td>
<td>0.73</td>
<td>12</td>
</tr>
</tbody>
</table>

XRD analysis (Fig. 1) of the kaolin before and after calcination shows that the used clay contains, in addition to kaolinite, some illite and quartz. The calcination of kaolin, transforms kaolinite to an amorphous material confirmed by the presence of a halo between 20° and 30° (2θ), while quartz and illite remain unchanged.

![FIG. 1 X-RAY DIFFRACTION PATTERNS OF KAOLIN BEFORE AND AFTER CALCINATION](image)

Kaolin burned

![FIG. 2 DTA-TG THERMOGRAMS OF KAOLIN: (a) ATG, (b) ATD](image)

The DTA/TG curves of this kaolin are presented in Fig. 2. The main changes pointed out during the heating...
are the following:
- T<100°C: endothermic release of the free water,
- 430-620°C: endothermic dehydroxylation of kaolinite and formation of metakaolinite,
- ~970°C: exothermic reorganization of the metakaolinite structure (recrystallization).

Was minded that the amorphous state is obtained when the clay is heated at a temperature between the end of dehydroxylation and the beginning of recrystallization. Consequently the chosen calcination temperature for the present study is 700°C.

**Effect of Si/Al Ratio**

In order to understand the effect of Si/Al molar ratio on the structures and mechanical properties of geopolymer, different mixtures were prepared with Si/Al molar ratios varying from 1.8 to 2.33 as shown in Table 2, by introducing different amounts of sodium silicate.

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>Si/Al (molar ratio)</th>
<th>Na/Al (molar ratio)</th>
<th>Compressive Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geop a</td>
<td>1.80</td>
<td>0.531</td>
<td>2.1</td>
</tr>
<tr>
<td>Geop b</td>
<td>1.96</td>
<td>0.638</td>
<td>3.6</td>
</tr>
<tr>
<td>Geop c</td>
<td>2.19</td>
<td>0.793</td>
<td>4.9</td>
</tr>
<tr>
<td>Geop d</td>
<td>2.33</td>
<td>0.886</td>
<td>5.5</td>
</tr>
</tbody>
</table>

This domain is selected in order to obtain PSS geopolymer type. The used amount of NaOH introduced is constant in all mixtures (amount of NaOH = 0.35 g).

It is interesting to notice that the adjunction of sodium silicate in order to increase Si/Al ratio induces inevitably an increase of Na/Al ratio too.

The results of mechanical characterization of the obtained samples are presented in Table 2 and Fig. 3.

**TABLE 2 COMPOSITIONS AND MECHANICAL STRENGTHS OF GEOPOLYMER SAMPLES PREPARED AT DIFFERENT MOLAR SI/AL RATIOS (AMOUNT OF NaOH = 0.35g)**

It was noticed that the geopolymer compressive strength increases with increasing Si/Al ratio. In fact, the mechanical strength value of geopolymer with Si/Al = 2.33 is almost three times that of geopolymer with Si/Al = 1.8. This behavior can be mainly attributed to the formation of stronger Si-O-Si bonds at the expense of Si-O-Al ones (Duxson, Provis & Lukey 2005). It is interesting to note that the increase of the mechanical properties is not only related to Si/Al ratio but also to that of Na/Al.

1) **X-ray Diffraction Analyses**

In order to elucidate in a microscopic scale the evolution of the compressive strength for different synthesized geopolymers, XRD technique was employed to characterize the structure of these geopolymers.

The results of X-ray diffraction analysis of metakaolin and geopolymer synthesized at different Si/Al ratios are shown in Fig. 4 revealing a halo diffraction pattern from almost 15° to 35° (2θ) for all geopolymers, showing that these materials are amorphous,(Derrien 2004).

Some peaks related to crystallized phases were also detected, which is attributed to quartz and illite initially present in the kaolin and which has not contributed to the polymerization.

In addition, it was noted that the intensity of the peaks relative to illite decreases when the Si/Al ratio increases (Na/Al increases also). This evolution indicates that with high amount of sodium silicate, illite is probably dissolved and contributes to the geopolymerisation.

The diffractogram of the geopolymer with Si/Al=1.8 shows some peaks which are not present in the others geopolymer spectra indicating more orderly phases in this material. This is probably due to the local formation of crystalline phase zeolite which is consistent with the results of Duxson, Fernandez-
2) **MAS-NMR Analysis**

The geopolymer structures are also studied using MAS-NMR analysis.

$^{29}\text{Si}$ MAS NMR spectra of metakaolin and geopolymers synthesized with different Si/Al ratios are shown in Fig. 5. The evolution of $^{29}\text{Si}$ NMR chemical shifts (ppm) with Si/Al ratios is presented in Table 3.

![FIG. 5 $^{29}\text{Si}$ MAS-NMR SPECTRA OF METAKAOLIN AND GEOPOLYMERS SYNTHESIZED AT DIFFERENT Si/Al RATIOS](image)

**TABLE 3 THE EVOLUTION OF $^{29}\text{Si}$ NMR CHEMICAL SHIFTS WITH Si/Al RATIOS (ppm)**

<table>
<thead>
<tr>
<th>Si/Al</th>
<th>1.8</th>
<th>1.96</th>
<th>2.19</th>
<th>2.33</th>
<th>Metakaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ (ppm)</td>
<td>-100.6</td>
<td>-86</td>
<td>-89.52</td>
<td>-90.89</td>
<td>-99.56</td>
</tr>
</tbody>
</table>

These results show the presence of a broad peak assigned to $Q^3$, whose intensity increases with Si/Al ratio and whose position evolves from -92 ppm for Si/Al=2.33 to -86 ppm for Si/Al=1.8. This is related, according to Zibouche, Kerdjoudj & Van Damme (2009), to the replacement of Al as the first neighbor for Si $Q^3$ nucleus by the other Si nuclei. The resonance at -100.6 ppm observed only for Si/Al=1.8 is assigned Si $Q^3$ (1Al) and may be due to the residual metakaolin (Yao, Zhang, Zhua & Chena 2009).

![FIG. 6 $^{27}\text{Al}$ MAS NMR SPECTRA OF METAKAOLIN AND GEOPOLYMER SYNTHESIZED AT DIFFERENT Si/Al RATIO](image)

3) **Thermal Analysis**

The DTA thermograms of Na-Geopolymers obtained at different Si/Al ratios are presented in Fig. 7. The results show an endothermic peak spreads from ambient temperature until 200°C, accompanied by a weight loss, for all specimens (Fig. 8) which can be attributed to the elimination of free pore water in geopolymer.

![FIG. 7 DTA THERMOGRAMS OF Na-GEOPOLYMERS OBTEINED AT DIFFERENT Si/Al RATIOS: a:Si/Al=1.8, b:Si/Al=1.96, c:Si/Al=2.19](image)

It seems that the amount of free water in the geopolymer increases when the Si/Al increases (geopolymer (c) with Si/Al = 2.19). This water is then related to the polycondensation reaction (Zuhua, Xiao, Huajun & Yue 2009).

The geopolymers continue to lose weight at about 600°C but with a much slower rate (Fig. 8). This weight loss is probably due to the elimination of...
water caused by the condensation of silanol or aluminol groups (dehydroxylation) on the surface of geopolymer.

According to the results presented in Fig. 9, the compressive strength of geopolymer samples increases with Si/Al ratio to reach maximum when Si/Al=1.96 corresponding to Na/Al=0.965≈1. This behaviour is the same as that observed previously and explained by the formation of Si-O-Si bonds at the expense of Si-O-Al ones. For higher Si/Al ratio, the compressive strength decreases due probably to the structure fragilisation of geopolymer by the excess of Na⁺ cation in the mixture comparatively to the amount of Al³⁺.

It is well known that the Na⁺ cations are needed in geopolymerisation to compensate the negative charge imbalance created when Al forms tetrahedra in geopolymer structure. This means that the number of needed Na⁺ cations must be equal to that of the transformed Al tetrahedra (Na/Al=1) in the geopolymer.

Fig. 10 shows the variation of geopolymer compressive strength with Si/Al molar ratio at different amounts of NaOH. It is clear that until Si/Al=2, compressive strength increases with Si/Al ratio independently of the NaOH amount.

For higher Si/Al ratio, if Na/Al molar ratio is lower than 1 (case of geopolymers with 0.35 g NaOH), compressive strength continues to increase, if not compressive strength decreases (case of geopolymer with 0.7 g NaOH) then the amount of alkaline solution must be well calculated before preparing geopolymer.

In order to explain the difference between the compressive strengths measured on geopolymers containing different amounts of NaOH, ²⁹Si NMR analyses were performed on samples with Si/Al ratio 2.33.

<table>
<thead>
<tr>
<th>Na/Al</th>
<th>0.886 (0.35 g NaOH)</th>
<th>1.214 (0.7 g NaOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MPa)</td>
<td>5.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Si δ (ppm)</td>
<td>-92.16</td>
<td>-89</td>
</tr>
<tr>
<td>Al δ (ppm)</td>
<td>55.4</td>
<td>56.38</td>
</tr>
</tbody>
</table>

In order to study the effect of the alkaline solution (NaOH) amount on the properties of geopolymer, we have prepared the same geopolymers but in the presence of 0.7 g NaOH. The composition and the properties of these geopolymers are shown in Table 4.

**TABLE 4 COMPOSITIONS AND COMPRESSIVE STRENGTHS OF GEOPOLYMER SAMPLES PREPARED WITH 0.7 g NaOH**

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geop a'</td>
<td>1.8</td>
<td>0.859</td>
<td>2.8</td>
</tr>
<tr>
<td>Geop b'</td>
<td>1.96</td>
<td>0.965</td>
<td>4.0</td>
</tr>
<tr>
<td>Geop c'</td>
<td>2.19</td>
<td>1.12</td>
<td>3.6</td>
</tr>
<tr>
<td>Geop d'</td>
<td>2.33</td>
<td>1.214</td>
<td>2.8</td>
</tr>
</tbody>
</table>
equal to 2.33 containing 0.35 and 0.7 g NaOH. The obtained results are presented in Table 5.

It was noticed that the increase of Na/Al to a value higher than 1, induces a decrease of the mechanical strength and a shift of $^{29}$Si NMR signal to lower values, which is probably a sign of structure fragility and that $^{27}$Al NMR signal is not very sensitive to the Na/Al ratio variation.

Although the increase in the amount of NaOH has promoted geopolymerization reaction, it hasn’t a significant influence on X-ray diffractograms of geopolymers (Fig. 11).

![Diffraction of geopolymers](image)

**FIG. 11 DIFFRACTOGRAMS OF METAKAOLIN AND GEOPOLYMERS SYNTHESIZED AT DIFFERENT Si/Al RATIO WITH 0.7g NaOH**

Indeed, it was noticed that when the Si/Al increases, the position of the diffuse halo moves to the highest angles whatever the amount of NaOH, but the phenomenon is more marked in the presence of 0.7g of NaOH (Fig. 12).

![Variation of the center position of the halo](image)

**FIG. 12. VARIATION OF THE CENTER POSITION OF THE HALO FOR GEOPOLYMERS HAVING DIFFERENT Si/Al RATIOS AT DIFFERENT AMOUNTS OF NaOH**

### Conclusion

The objective of this work has focused primarily on the synthesis of Polysiloxosialate geopolymer (PSS) from kaolin calcined at 700°C for 5 h, and to study the effect of a number of experimental parameters on the properties of geopolymer.

The increase of Si/Al ratio induces:
- the improvement of the geopolymer mechanical strengths,
- the formation of amorphous geopolymers regardless of the Si/Al ratios except for Si/Al=1.8, we have seen the formation of local zeolitic crystallized structure,
- the increase of weight loss (detected by thermogravimetric analysis) between ambient temperature and 200°C attributed to the elimination of free pore water, and between 200 and 600°C related to condensation of silanol and aluminol groups
- the shift of the broad peak in $^{29}$Si NMR spectra from -92 ppm for Si/Al = 2.33 to -86ppm for Si/Al = 1.8,
- the contribution of illite to the geopolymerisation.

Increasing the amount of NaOH during geopolymer synthesis leads to:
- an overall increase in mechanical strength due to an easier dissolution step, but beyond a Si/Al =1.96 mechanical strength decreases due to the fragility of the structure of geopolymer by the excess of Na+ cation comparatively to Al3+.
- the existence of an amorphous state for the prepared geopolymers (detected by XRD) and a shift of the angle 2θ corresponding to the center of the halo indicating the geopolymerization evolution.

### REFERENCES


Duxson, Peter., Provis John L. and Lukey Grant C., “Understanding the relationship between geopolymer


