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Ion Exchange in Geopolymers

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Abstract

Geopolymers have been widely used for construction and building materials. Nevertheless, some other applications have been found from their ability to be ion exchanged. An example is the encapsulation of heavy metals, but some others involve the ion exchange of the aluminosilicate structure to form photoactive particles or to link copper ions. In this chapter, we summarize some of the properties which make aluminosilicate inorganic polymer (geopolymers) ion exchangeable: the synthesized temperature, its effect over their porosity and their stoichiometric nature. Also, the effects of ion exchanging a geopolymer with an NH_4^+Cl, $(NH_4)_2TiO_2(C_2O_4)_2$ and $(CH_3)_4N^+Br$ are presented. The geopolymer was characterized by FT-IR, XRD, BET and MAS NMR, showing how a 100% of replacement was achieved for NH_4^+Cl. On the contrary, the efficiency was reduced in $(NH_4)_2TiO_2(C_2O_4)_2$ and $(CH_3)_4N^+Br$, effect ascribed to the fact of the molecular size that did not allow the counterions to reach the aluminum atoms in the geopolymer. Finally, the procedure followed to ion exchange a metakaolinite-based geopolymer is described, and the potential applications related are presented.

Keywords: geopolymer, ion exchange

1. Introduction

Since the origin of the term geopolymer to define those materials synthesized by the alkali activation of aluminosilicate monomers at ambient temperature, studies about geopolymers have been widely spread [1].

Examples include environmental alternatives for Portland cement [2], refractories [3] and ceramic precursor, for instance [4, 5].

Nevertheless, while these studies continue, others have explored new applications as immobilizations of waste, radioactive and toxic materials [6, 7], medicinal applications, catalytic materials [8, 9], catalytic materials for volatile organic degradation [9–11] and support material for optical applications like color holder, color pH indicator and photoluminescent material.

These new applications take advantage of the nonordered AlO_4-SiO_4 structure of geopolymers that results in a negative charged framework where alkali or alkaline earth cations (Na^+, K^+, Ca^{2+}, Li^+ and rarely Cs^+) need to be present to balance the charge of the geopolymer.

The chemical similarity of geopolymers to zeolites makes them an important former material to synthesize a wide variety of new ceramics through the ion exchange of the charge-balancing cation [8, 12].

To improve the studies and increase the amount of applications of geopolymers, it is necessary to understand clearly the core variables that determine a good ion exchange. Therefore, in this chapter, we review some of these core variables which make geopolymers ion exchangeable: the synthesis temperature was varied from 40 to 90°C to define a specific pore size distribution (PSD) within the samples, the removal of soluble species from the samples and the use of the right chemical compound according to the desired ion to be exchanged to avoid any change in the geopolymer structure after ion exchange. Finally, we describe the procedure followed to ion exchange a metakaolinite-based geopolymer and their potential applications.

2. Synthesis of geopolymers

Geopolymers are synthesized by the dissolution and polycondensation of an aluminosilicate powder in an alkaline silicate solution under hydrothermal conditions [13]. Even though there are different sources for solid aluminosilicate like slag, fly ash and mine tailing [2], the metakaolin is the preferred starting material chosen to synthesize geopolymers. This is mainly due to its high purity that results in a suitable geopolymer to be ion exchanged.

On the other hand, the available alkaline silicate solutions needed to synthesize a geopolymer are limited to solution in which cations are alkaline enough for synthesizing geopolymers (e.g. Na^+ or K^+) [14]. Therefore, the variety of geopolymers that can be synthesized is constrained to this issue.

The samples synthesized for this study were prepared by mechanically mixing stoichiometric amounts of metakaolin, sodium hydroxide, distilled water and sodium silicate (Na_2O/SiO_2 wt. ratio: 0.31) to follow the recommended molar ratios: SiO_2:Al_2O_3 = 2.89, NaO_2:SiO_2 = 0.29 and H_2O:Na_2O = 10.01 which gave geopolymers good mechanical properties (3.16, 0.34 and 16.2 for the SiO_2/Al_2O_3, K_2O/SiO_2 and H_2O/K_2O, respectively, in the case of potassium geopolymers) [15, 16].

To have a homogeneous slurry, a mechanical mixing followed by 15 min of vibration was done. Final samples were casted into plastic containers, and they were left under constant temperature at 40 and 90°C for 24 h [16–19]. After cooling, geopolymers were cut with a diamond disc to have samples of around 1 g weight.

3. Geopolymer structure

As all geopolymers, the sample synthesis takes place in local coordination environment like zeolites. The silicate and aluminate units that form the geopolymer are completely disordered on length scales longer than 10 Å and are connected to form a disordered network
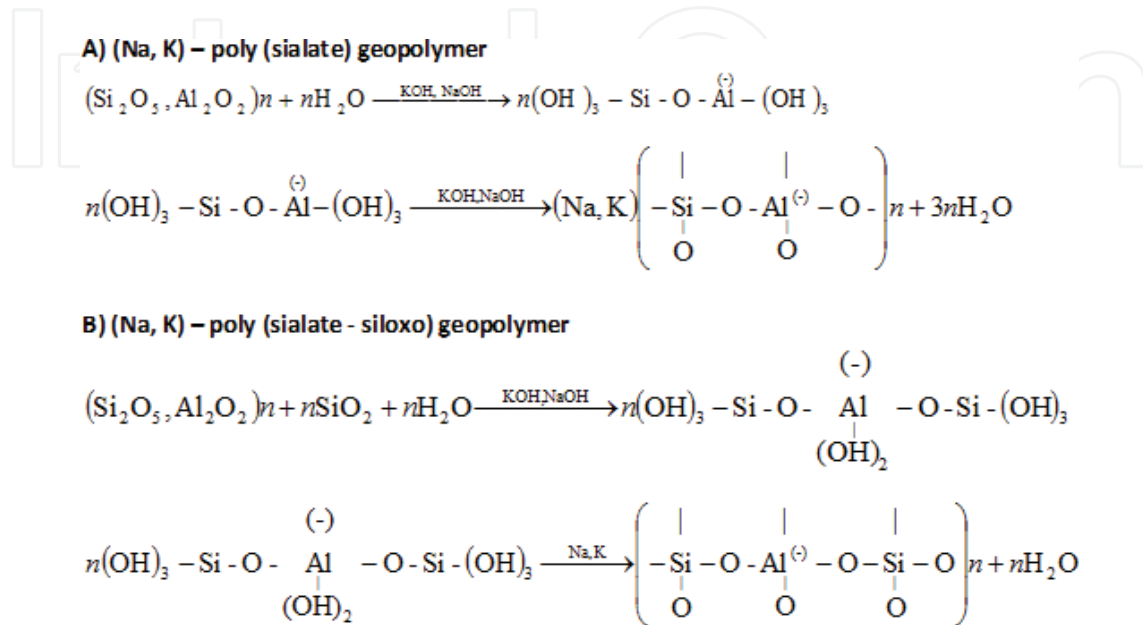
A) (Na, K) – poly (sialate) geopolymer

$$(Si_2O_5, Al_2O_2)n + nH_2O \xrightarrow{KOH, NaOH} n(OH)_3 - Si - O - \overset{(-)}{Al} - (OH)_3$$

$$n(OH)_3 - Si - O - \overset{(-)}{Al} - (OH)_3 \xrightarrow{KOH, NaOH} (Na, K) \left(\begin{array}{cc} | & | \\ -Si - O - Al^{(-)} - O - \\ | & | \\ O & O \end{array} \right) n + 3nH_2O$$

B) (Na, K) – poly (sialate - siloxo) geopolymer

$$(Si_2O_5, Al_2O_2)n + nSiO_2 + nH_2O \xrightarrow{KOH, NaOH} n(OH)_3 - Si - O - \underset{(OH)_2}{\overset{(-)}{Al}} - O - Si - (OH)_3$$

$$n(OH)_3 - Si - O - \underset{(OH)_2}{\overset{(-)}{Al}} - O - Si - (OH)_3 \xrightarrow{Na, K} \left(\begin{array}{ccc} | & | & | \\ -Si - O - Al^{(-)} - O - Si - O \\ | & | & | \\ O & O & O \end{array} \right) n + nH_2O$$

Figure 1. Formation of geopolymers: (A) poly(sialate) and (B) poly(sialate-siloxo).

Si:Al ratio	Potential applications	Si:Al ratio	Potential applications
Si-O-Si-O-Si-O-Si-O-Si-O- O -Al- O Si-O-Si-O-Si-O-Si-O-Si-O- 20:1 < Si:Al < 35:1	Fire resistant materials	(-Si-O-Al-O-Si-O) Si:Al 2:1	Cementitious material. Toxic waste encapsulation.
(Si-O-Al-O-Si-O- O -Si- O (F, SiO₂)) Si:Al >3:1	Thermal insulation material (200 to 600 °C). Tooling for SPF aluminium.	(-Si-O-Al-O) Si:Al 1:1	Fire protection construction Materials. Building bricks.
(Si-O-Al-O-Si-O- O -Si- O) Si:Al 3:1	Thermal insulation material (200 a 1000 °C). Tooling for titanium processing.		

Figure 2. Potential applications of geopolymers according to the Si:Al ratio.

with the alkali cations in irregular sites [14]. These cations are present inside the geopolymer framework, and they are needed to balance the negative charge of Al_3^+ in $[AlO_4]^{-1}$ [20].

As it can be seen in **Figure 1** where geopolymers are classified according to the ratio of aluminates and silicates, the geopolymer synthesized was poly(sialate) geopolymers which are mainly used as cementitious and toxic waste encapsulation material (**Figure 2**).

According to their structure, the applications of geopolymer may be summarized in **Figure 2**.

4. Background of ion exchange

Ion exchange is a chemical reaction where an ion carrier material (ion exchanger) exchanges their own ions with others disposed in solution (counterions). Even though the ion exchanger is not dissolved, the ion exchanger must have an open network structure to let ions be dissolved in the aqueous solution [21].

The ion exchangers can be cationic, anionic or amphoteric in accordance with the charge of the balancing ion, and the number of ions exchanged should be equal to the proportion of free counterions in solution in agreement with the stoichiometric ratio of exchange.

In the case of geopolymers, which are X-ray amorphous materials formed by non-localized but well-distributed negative tetrahedral silicate and aluminate units [1, 15], they can be considered as cationic exchangers. Their negatively charged structure, balanced by alkali metals such as Na^+ or K^+ (**Figure 3**), can be completely hydrated and mobilized [3, 22]. This gives a lower bonding strength in comparison with zeolites [20] and an ease to be ion exchanged when they are in contact with solutions of chloride or nitrate of a desired cation.

The geopolymer structure is made up by silicon and aluminium atoms linked by oxygen (**Figure 3**), and it is not modified when the sodium atom, the exchangeable ion linked to the aluminum atom, is replaced with another cation. The maximum number of possible exchangeable cations, known as theoretical ion exchange capacity (TEC), is equal to the negative charge of the geopolymer network and can be measured by elemental analysis of aluminum. Nevertheless, it is not always possible to ion exchange the total amount of available exchangeable cations (TEC value), and a real exchange capacity (REC value) should be determined by an ion-exchange method [23, 24].

The general procedure of ion exchange can be formulated by Eq. (1). When the geopolymer, represented as Na^+G^- (ion exchanger), is ionized in an aqueous solution, the released cation (Na^+ or K^+) diffuses inside the material, transfers through the interphase boundary and finally arrives to the solution. If a salt MY is also dissolved in the solution (M^+ and Y^- ions), the Na^+ in geopolymer is replaced by an equivalent amount of counterion M^+ due to the electroneutrality requirement:

$$Na^+ G^- + M^+ Y^- \; \rightarrow \; M^+ G^- + Na^+ + Y^- \tag{1}$$
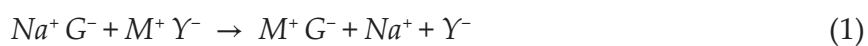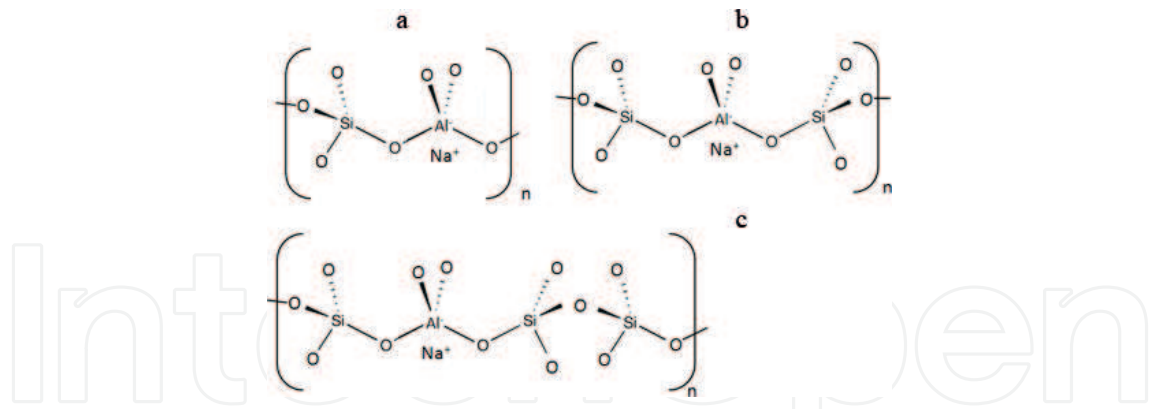
Figure 3. Position of the cation in the (a) sialate geopolymer, (b) sialate-siloxo geopolymer and (c) sialate-disiloxo geopolymer.

5. Procedure of ion exchange in geopolymers

Before an ion exchange is done, some soluble species from the samples must be removed. In this case, we followed a procedure described by Skorina [18]. The samples were rinsed several times with deionized water and a sequence of wash cycles, followed by a final treatment with a solution of KNO_3 until neutral "pH" was reached.

According to the desired ion to be exchanged with, the geopolymer was kept in contact for 12 h with solutions of NH_4Cl, $(NH_4)_2TiO_2(C_2O_4)_2$ and $(CH_3)_4NBr$ in concentration of 0.1 M with the aim of having a larger proportion of free counterions in solution and to guarantee a complete ion exchange. Finally, the samples were removed from the solution, rinsed several times with deionized water and dried for 1 week at ambient temperature.

6. Test performed over geopolymers

The pore diameter and surface area of samples were done under water desorped samples (120° C for 24 h) by nitrogen adsorption on a NOVA 2000e Quantachrome instruments employing the Barrett–Joyner–Halenda method of analysis.

The geopolymer external surface was observed with a Philips XL-30 ESEM scanning electron microscope coupled with an EDAX energy-dispersive X-ray microanalyzer. The extent of ion exchange was determined by calculating the ratio of sodium with aluminum in the geopolymer as it was described by O'Connor [14].

The modification to the geopolymer structure was followed with a RIGAKU Ultima IV X-ray diffractometer using Cu irradiation ($\lambda = 1.5406$ Å), and the chemical composition was analyzed with a Perkin Elmer Spectrum Two using the IR-KBr technique.

Finally, ^{27}Al and ^{29}Si MAS NMR was performed to distinguish the atoms surrounding the aluminum atom with a Bruker Avance III HD 400 MHZ MAS NMR. This equipment was operated at 15 KHz for ^{27}Al and 8 KHz for ^{29}Si.
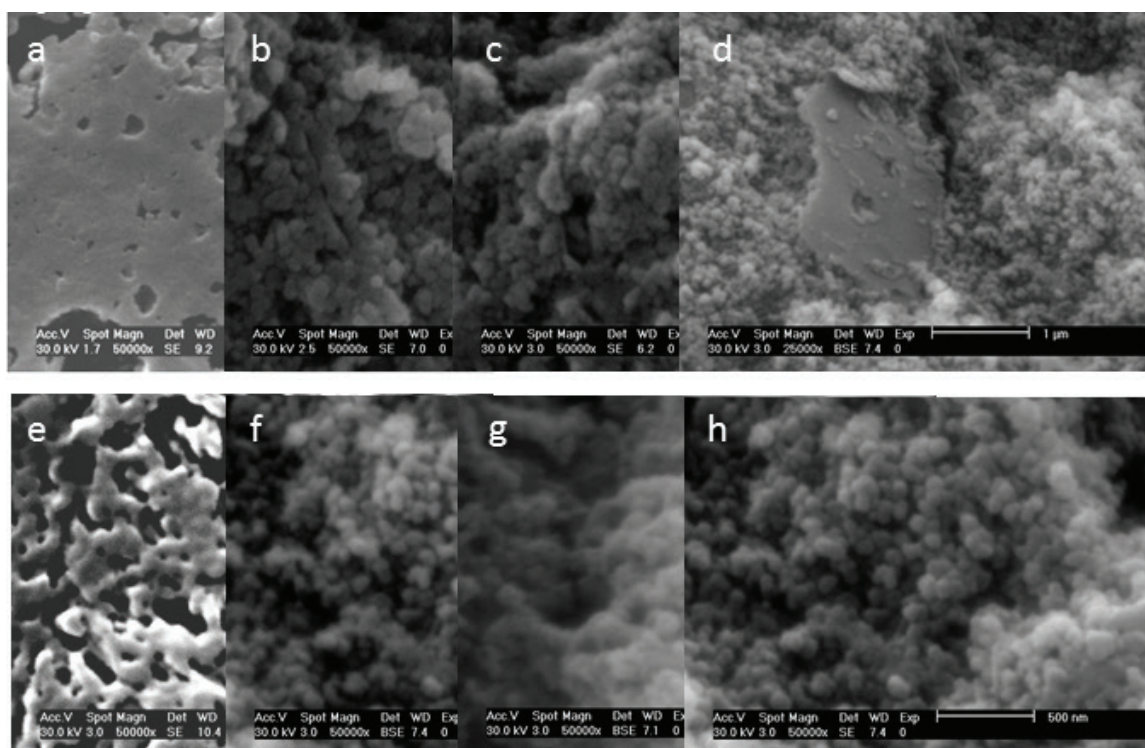
7. Effect of ion exchange over geopolymers

The total surface area and pore diameter of geopolymers synthesized at 40 and 90°C are summarized in **Table 1**. As it can be observed, the main factor that modified these parameters was the temperature synthesis. In addition, a reduction in pore width and the increase in specific surface were observed in all samples when the geopolymer was ion exchanged.

Modifications on the geopolymer surface were also observed in **Figure 4**. The ion exchanged samples were settled of small particles that occupied the void sites of the former geopolymer but leaving unchanged the geopolymer structure.

Counterion	Geopolymers at 40°C				Geopolymers at 90°C			
	Before ion exchange		After ion exchange		Before ion exchange		After ion exchange	
	S (m² g⁻¹)	D (nm)	S (m² g⁻¹)	D (nm)	S (m² g⁻¹)	D (nm)	S (m² g⁻¹)	D (nm)
NH$_4$Cl	45.88	19.56	123.84	2.19	27.21	30.52	491.33	2.45
(NH$_4$)$_2$TiO$_2$(C$_2$O$_4$)$_2$	45.88	19.56	526.54	2.19	27.21	30.52	195.99	2.19
(CH$_3$)$_4$NBr	45.88	19.56	150.14	2.19	27.21	30.52	450.17	2.7

Table 1. Surface area and pore diameter of geopolymers at 40 and 90°C, before and after ion exchange.

Figure 4. Effect of the ion exchange over the geopolymer surface. (a) Geopolymer at 40°C, (b) geopolymer at 40°C ion exchanged with NH$_4$Cl, (c) geopolymer at 40°C ion exchanged with (NH$_4$)$_2$TiO$_2$(C$_2$O$_4$)$_2$, (d) geopolymer at 40°C ion exchanged with (CH$_3$)$_4$NBr, (e) geopolymer at 90°C, (f) geopolymer at 90°C ion exchanged with NH$_4$Cl, (g) geopolymer at 90°C ion exchanged with (NH$_4$)$_2$TiO$_2$(C$_2$O$_4$)$_2$ and (h) geopolymer at 90°C ion exchanged with (CH$_3$)$_4$NBr.

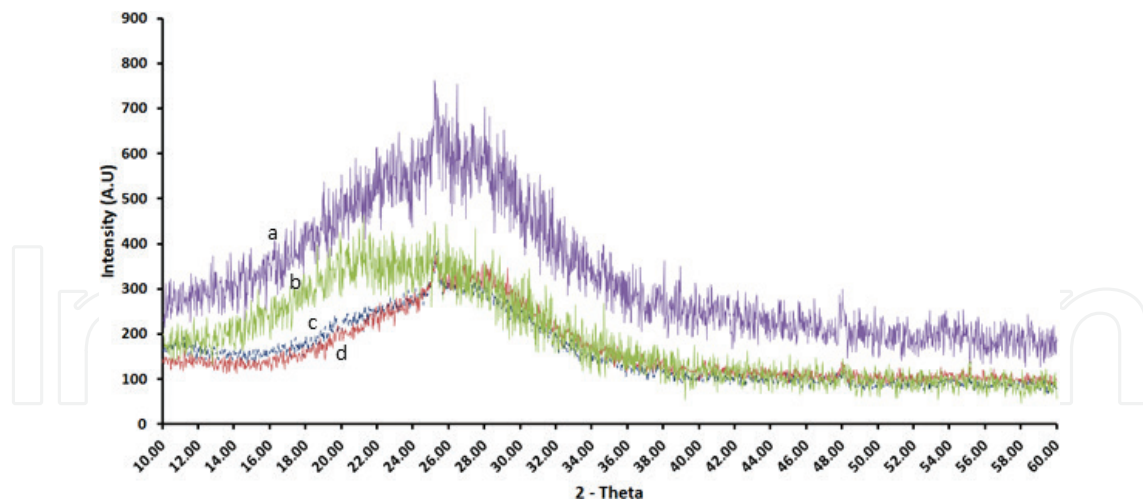**Figure 5.** XRD pattern of (a) former geopolymer, (b) geopolymer ion exchanged with $(NH_4)_2TiO_2(C_2O_4)_2$, (c) geopolymer ion exchanged with NH_4Cl and (d) geopolymer ion exchanged with $(CH_3)_4NBr$.

This observation was supported by results obtained by XRD (**Figure 5**), where the amorphous structure of the geopolymer, represented by a hump at $2\Theta = 28°$, remained after ion exchange.

On the other hand, the FT-IR results of geopolymers at 40°C and 90°C before and after being ion exchanged are shown in **Figures 6** and **7**. As it can be observed in all spectra, the vibration modes corresponding to amorphous sodium aluminosilicate (1645.44, 878.56 cm^{-1}), symmetric stretching of Si-O-Al, Si-O-Si (706.9 cm^{-1}) and flexion of Si-O-Si and O-Si-O (571.73 cm^{-1})
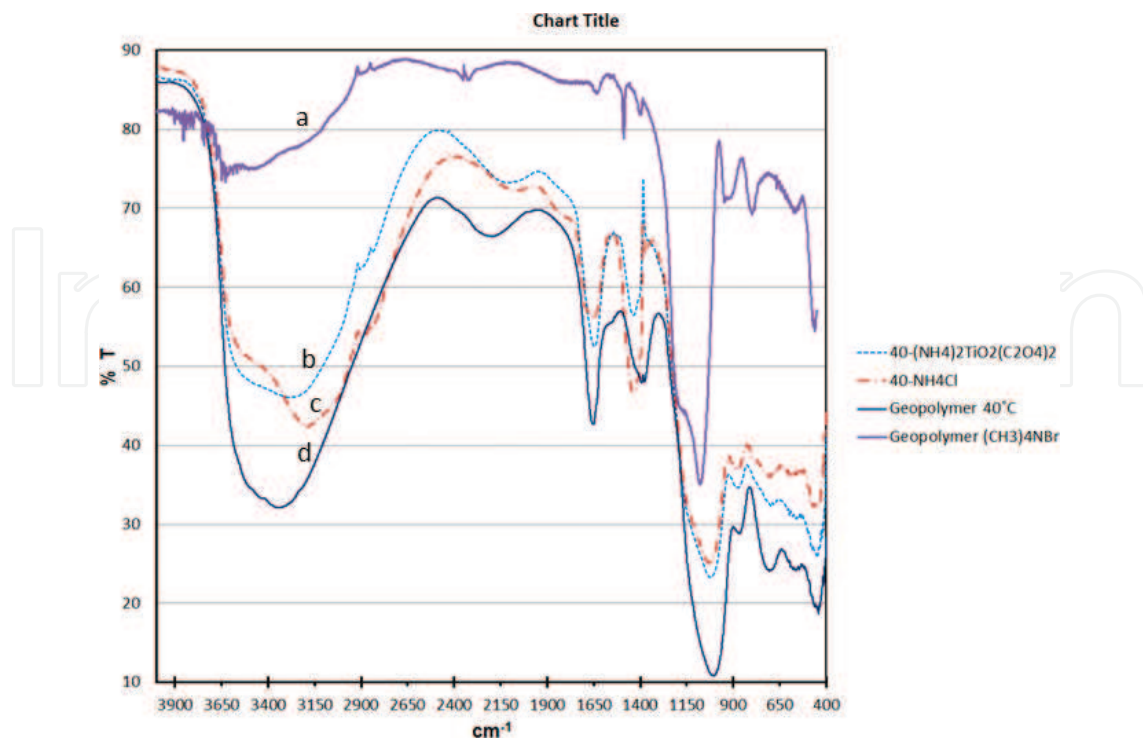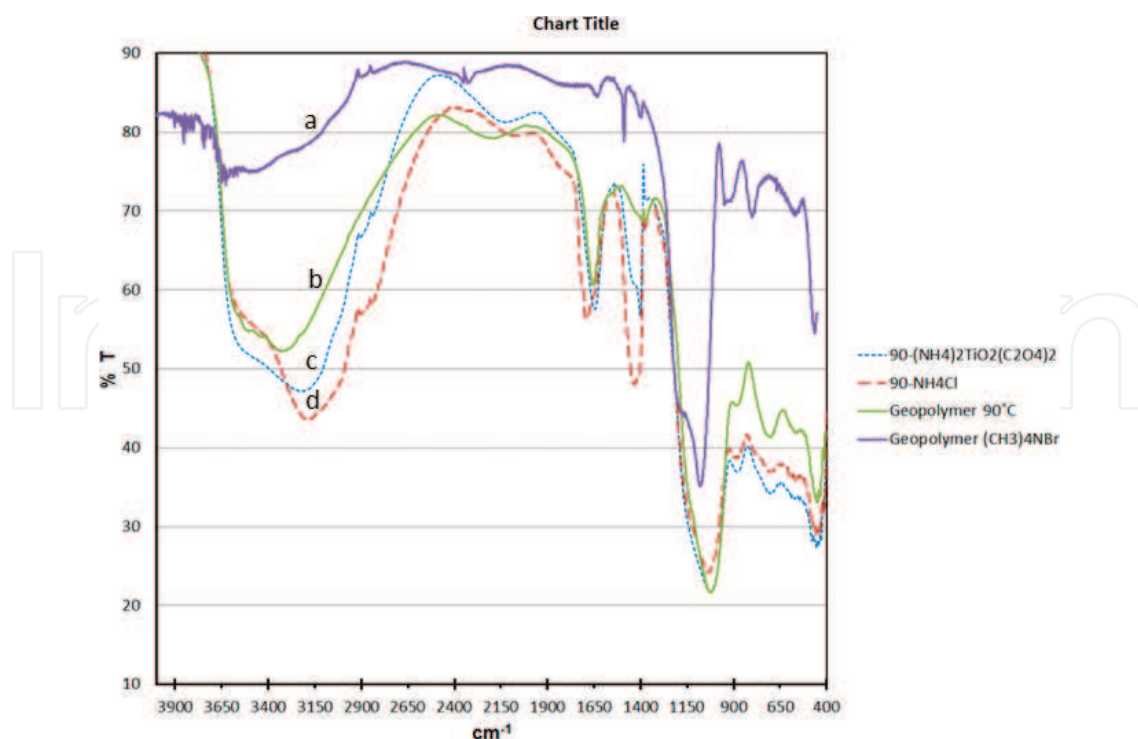

Figure 6. FT-IR of (a) geopolymer at 40°C ion exchanged with $(CH_3)_4NBr$, (b) geopolymer at 40°C ion exchanged with $(NH_4)_2TiO_2(C_2O_4)_2$, (c) geopolymer at 40°C ion exchanged with NH_4Cl and (d) geopolymer at 40°C.
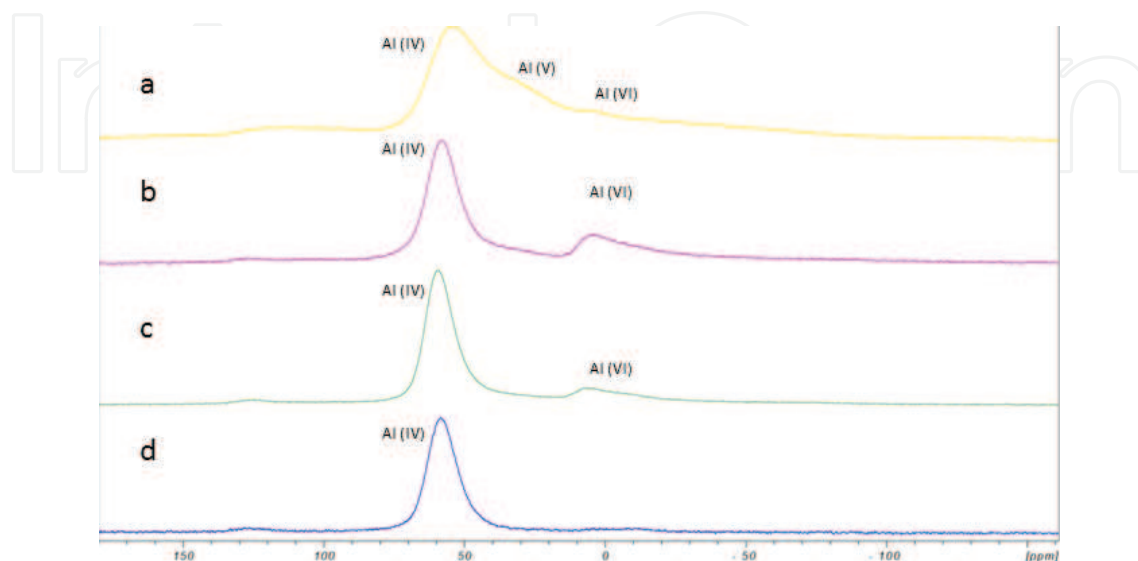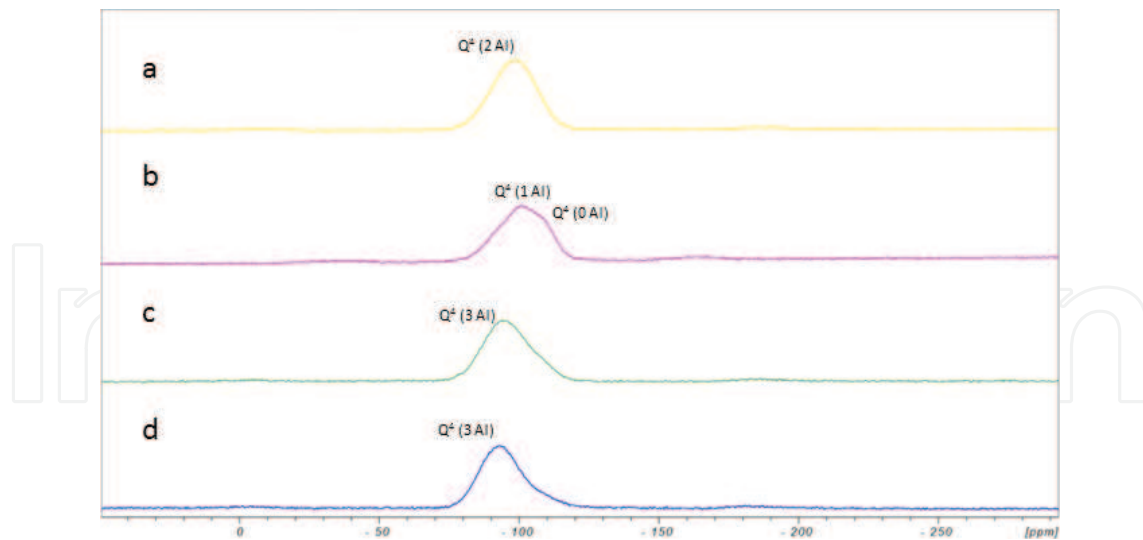
Figure 7. FT-IR of (a) geopolymer at 90°C ion exchanged with $(CH_3)_4NBr$, (b) geopolymer at 90°C, (c) geopolymer at 90°C ion exchanged with $(NH_4)_2TiO_2(C_2O_4)_2$ and (d) geopolymer at 90°C ion exchanged with NH_4Cl.

[25, 26] remained as a former geopolymer. The only modifications observed between spectra were those ascribed to vibration modes representative of their counterions.

Whenever a geopolymer is synthesized, the three-coordinated aluminum in metakaolin, Al (IV), Al (V) and Al (VI) (chemical shift: 49–80, 35–40 and −5–15 ppm, respectively), are transformed into Al (IV) to form the geopolymer structure [27]. As it can be observed in **Figure 8**, this structure remained in all ion exchanged samples, and in some occasions, Al (V) and AI (VI) arose at 30 ppm and 2 ppm as in the case of $(CH_3)_4NBr$ because of the size of the counterion mainly.

Figure 8. ^{27}Al MAS NMR of (a) geopolymer ion exchanged with $(CH_3)_4NBr$, (b) geopolymer ion exchanged with NH_4Cl, (c) geopolymer ion exchanged with $(NH_4)_2TiO_2(C_2O_4)_2$ and (d) former geopolymer.

Figure 9. ^{29}Si MAS NMR of (a) geopolymer ion exchanged with $(CH_3)_4NBr$, (b) geopolymer ion exchanged with NH_4Cl, (c) geopolymer ion exchanged with $(NH_4)_2TiO_2(C_2O_4)_2$ and (d) former geopolymer.

Counterion	Real exchange capacity (%)
NH_4^+	100
$(NH_4)_2TiO_2(C_2O_4)_2$	80
$(CH_3)_4N^+$	85
Li^+	82
Cd^+	78
Mg^{2+}	57

Table 2. Real exchange capacity of geopolymers.

In the case of the ^{29}Si MAS NMR, all the geopolymer spectra presented a resonance peak between -90 and -100 ppm which were ascribed to tetrahedral silicon surrounded by two aluminum atoms [28] (**Figure 9**).

Finally, the real exchange capacity of samples is summarized in **Table 2**. A total replacement of sodium cation by NH_4^+ and a reduction on samples ion exchanged with $(NH_4)_2TiO_2(C_2O_4)_2$ and $(CH_3)_4N^+$ were determined. Results reported by O'Connor for Li^+, Cd^+ or Mg^{2+} are summarized, as a comparative, in **Table 2** [14].

8. Conclusions

In this chapter, the effects of ion exchanging a geopolymer with NH_4^+Cl, $(NH_4)_2TiO_2(C_2O_4)_2$ and $(CH_3)_4N^+Br$ were analyzed. Results were compared with the ion exchange with Li^+, Cd^+ and Mg^{2+} reported by O'Connor. A 100% of replacement was achieved for NH_4^+Cl. Nevertheless, the efficiency was reduced in $(NH_4)_2TiO_2(C_2O_4)_2$ and $(CH_3)_4N^+Br$ probably due to their molecular size that inhibited the counterions to reach the aluminum atom.

As it was observed by FT-IR, the ion exchange procedure did not modify the amorphous structure of geopolymers and the vibration modes ascribed to the symmetric stretching of Si-O-Al and Si-O-S, and the flexion energy of Si-O-Si and O-Si-O remained unmodified after the process. This can be explained if it is considered that the exchanged atom, Na^+, does not take part of the rigid structure of the geopolymer.

A similar conclusion was obtained from the XRD pattern, where the characteristic hump of amorphous geopolymer remained in all samples. Same results were observed in geopolymers synthesized at 40 and 90°C. The only observable change in this case was the superficial morphology which was measured by BET. Results gave a more porous material for samples synthesized at 40°C, but the extent of ion exchange was not affected by this parameter as it was summarized in **Table 2**.

In addition, the ^{27}Al and ^{29}Si MAS NMR spectra exposed the presence of Al (IV) and tetrahedral silicon, respectively, as an indicative of a structural order. In some cases, Al (V) and Al (VI) arose as it was reported by O'Connor for Mg^{2+}, Pb^{2+} and Cd^{2+} ions.

Finally, because the variety of geopolymers that can be produced by direct synthesis is limited to the selection of Na^+ or K^+ cations, the aim to find new application for geopolymer should lead research to find more exchange counterions.

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