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Research paper

Ion exchange in amorphous alkali-activated aluminosilicates: Potassium based geopolymers

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ABSTRACT

Ion exchange properties of *pure* potassium-based geopolymer (*pure* K-GP) formulated with Si/Al = 2.1 and K/Al = 1.0 ± 0.02 atomic ratios have been studied. For *pure* K-GP, the maximum ion-exchange level of K^+ with respect to Na^+ and Cs^+ is 77 and 61%, respectively, as determined by exhausted exchange with 1 M solutions of appropriate nitrates at 22 ± 2 °C. The geopolymer shows a slight preference for K^+ over Cs^+ as indicated by the normalized Cs/K-GP isotherm obtained under noncompetitive exchange. Parent geopolymer yields a *pure* geopolymer when it is extensively washed with deionized water until neutral pH is obtained and equilibrated with aqueous solution of KNO_3 resulting in changing in composition and textural properties. As calculated from N_2 sorption–desorption isotherms, surface specific area and cumulative pore volume for parent K-GP are 5.5 $m^2\ g^{-1}$ and 0.01 $cm^3\ g^{-1}$, respectively, whereas for *pure* K-GP surface specific area and cumulative pore volume are 270 $m^2\ g^{-1}$ and 0.4 $cm^3\ g^{-1}$, respectively.

1. Introduction

"Geopolymer" is a name suggested for alkali-activated aluminosilicate binders capable of hardening at ambient conditions due to the formation of AlO_4^-–SiO_4 tetrahedral framework (Davidovits, 1991). In the framework formation, alkali or alkaline earth cations (Na^+, K^+, Ca^{2+} and in fewer cases Cs^+) act as charge balancing species (O'Connor et al., 2010; Provis et al., 2005a,b). Although the possibility of preparing binding materials by the reaction of natural aluminosilicates with alkaline solutions goes back to the 1950s (Glukhovsky, 1957), some aspects of the polycondensation mechanism are still the subjects of debate. The structure of geopolymers synthesized at temperatures below 100 °C is defined as X-Ray amorphous; however, some authors mention the coexistence of nanometer-sized zeolitic crystals with long- and medium-range disordered aluminosilicate gel (Bell et al., 2008; Palomo et al., 1999; Provis et al., 2005a,b). During the last 30 years geopolymers have been considered for a variety of applications, including an environmental friendly alternative to Portland cement (Duxson et al., 2007; Hardjito et al., 2004; Palomo et al., 1999), as refractories (V. Barbosa and MacKenzie, 2003; V.F.F. Barbosa and MacKenzie; Davidovits, 1991), ceramic precursors (Bell et al., 2009; He et al., 2010; Ikeda et al., 2001), and matrices for immobilization of radioactive wastes (Van Jaarsveld et al., 1998; Zosin et al., 1998), and as catalytic materials (O'Connor et al., 2010; Sazama et al., 2011). Geopolymers can be also viewed as amorphous analogs of zeolites, capable of cation exchange and possessing catalytic properties when incorporated with Pt, Fe, Cu and Co (Bortnovsky et al., 2008; Sazama et al., 2011). Although zeolitic ion exchangers already hold a good portion of sorbent markets due to their relatively low cost, cation exchange properties of geopolymers have not been extensively studied: a comprehensive set of data has been reported only for Na-based geopolymers (O'Connor et al., 2010).

Natural zeolites usually contain impurities, which do not take part in ion exchange; therefore the theoretical ion exchange capacity (TEC) of natural zeolites expresses the number of possible exchangeable cations. For pure zeolites, TEC measured by elemental analysis is equal to the negative charge of the aluminosilicate framework. Real exchange capacity (REC) refers to the amount of actual exchangeable cations of zeolite measured by ion-exchange methods (Inglezkis, 2005; Lehto and Harjula, 1995). For some zeolites, TEC can be higher than REC for certain pairs of cations e.g. for Cs^+–Na^+ exchange in zeolite Y. Sodium ions located in small cages of zeolite Y framework cannot be replaced by the Cs^+ ion which has a larger ionic radius, therefore this ion exchange isotherm terminates at a point less than 100% (Sherry, 1966).

Cationic selectivity of an ion exchanger is generally determined by measuring of an equilibrium uptake of ingoing cations from a solution. Visual inspection of the ion exchange isotherms allows making conclusions as to the preference of an ion exchanger for the ingoing or outgoing cation. The full description of the analysis of ion exchange data can be found in the literature (Dyer, 1988; Sherry, 1966). Ionic radius, hydration energy, and locations of cations (small cages or super cages) are the main factors determining the preference of zeolite for a cation over the other one. In zeolites, the mechanism of cation attachment to the aluminosilicate framework also affects selectivity of ion exchange. Hydrated and mobile cations act in a different way than partially bare cations coordinated to oxygen atoms (Sherry, 1968). It appears that in the amorphous structure of geopolymers, negative charge is not localized, and it is more or less uniformly distributed in the

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framework (Duxson et al., 2007). Therefore, charge-balancing cations can act as fully hydrated and mobile or as unhydrated (coordinated to oxygen atoms by analogy with aluminosilicate glasses). For Na-based geopolymer, it has been demonstrated by 23-Na NMR that the cations are hydrated and they do not form part of the tetrahedral framework. However, the 23-Na spectra shows that the Na environment is sensitive to dehydration: heating of Na-based geopolymer up to 1100–1300 °C causes changes of typically hydrated sites to sites more typical of unhydrated glasses (V. Barbosa and MacKenzie, 2003; V.F.F. Barbosa and MacKenzie).

The main objective of this work has been to characterize K-based geopolymer as an ion exchanger by determining the maximum cation exchange level and ion exchange selectivity, taking into account structural and composition alteration associated with applied aqueous treatment.

2. Experimental

2.1. Synthesis of parent geopolymer

Parent potassium geopolymer samples (K-GP) were made by dissolving potassium hydroxide (Sigma Aldrich, 85%) in deionized water followed by addition of a proportional amount of fumed silica (CAB-O-SIL® EH-5, Cabot Corporation) along with metakaolin powder. Metakaolin powder was obtained by calcination of kaolinite ($Al_2Si_2O_7 \cdot 2H_2O$ Alfa Aesar, >97% purity) at 800 °C. This mixture was stirred vigorously for about 10 min, and then cast into a plastic container. The parent geopolymer was formulated with the following mole ratios: $Si/Al = 2.8$, $K/Al = 3$, $H_2O/Al = 10$. Polycondensation was performed in a closed vessel in laboratory oven at 60 °C for 24 h. After aging for more than 1 week, the geopolymer samples were ground in an agate mortar with subsequent separation of the fraction 1.2–1.6 mm.

2.2. Preparation of pure geopolymeric ion exchangers

Before the study of ion exchange properties, geopolymers, by analogy with zeolites, should have a good cation balance, i.e. the atomic ratio of charge-balancing cations to aluminum is to be equal to 1 (Sherry, 1968). In this regard, it is extremely important to remove all soluble species from parent geopolymer avoiding overwashing (replacement of charge balancing ions by H_3O^+). Geopolymeric ion exchanger that met these requirements (*pure* K-GP) was prepared as follows. About 1 g of the ground K-GP was placed into 50 cm^3 centrifuge tube and repeatedly washed with deionized water until neutral pH is obtained (usually 5–7 cycles). After the final decantation, the tube containing pure geopolymer was refilled with 50 cm^3 of 1 M KNO_3. The sample was treated under stirring (700 rpm) for 24 h at 22 ° C followed by 5 cycles of washing with 1 M solution and 5 cycles with 10^{-3} M solution of the same salt, then briefly washed with deionized water and dried at 60 °C to the constant weight.

2.3. Preparation of maximally exchanged geopolymers

The samples of K-GP maximally exchanged with Na^+ and Cs^+ (labeled Na–K-GP and Cs–K-GP, respectively) were prepared by exhaustively exchanging of 1 g aliquots of *pure* K-GP with 50 cm^3 of 1 M solution of the appropriate nitrate in a centrifuge tube fitted with a stirrer. The system was stirred for 24 h and then allowed to equilibrate for 48 h at which point the geopolymer phase was separated by centrifuging, briefly washed with deionized water, and dried at 60 °C to the constant weight.

2.4. Construction of ion exchange isotherms

All isotherms were constructed at 22 °C, at the constant ionic strength (total exchange solution concentration of 100 $mmol \cdot dm^{-3}$). Isotherm points were obtained by contacting 0.5-g aliquots of dried and ground *pure* K-GP with 50-cm^3 aqueous solutions containing nitrates of the in-going cation (Cs^+ or Na^+) and the indigenous cation (K^+). The exchange solutions contained varying proportions of in-going and indigenous ions in the range from 10 to 100 $mmol \cdot dm^{-3}$. The system was stirred at 22 °C for 24 h and subsequently equilibrated for 48 h. Solid and liquid phases were separated, and the content of the aqueous phase entrained in the solid was determined after equilibration. Both exchanging phases, the solid geopolymer and the exchanging solution, were analyzed by PIXE and ICP–MS (Thermo Scientific, USA). The isotherms are expressed as $A_g = f(A_s)$ at the constant total ion concentration of the solution (N_t, $mmol \cdot dm^{-3}$), where A_g and A_s are the equivalent fractions of ion A in the geopolymer and solution. The subscript "s" refers to the solution and subscript "g" refers to geopolymer.

The equivalent fractions of the exchanging cation in solution and in geopolymer are given as

$$A_s = [A]/(N_t)$$

$$A_g = [m_A]/M_t,$$

where [A] and m_A are the equilibrium concentrations of ion A in solution ($mmol \cdot dm^{-3}$) and in the geopolymer ($mmol \cdot kg^{-1}$) respectively, and M_t is the theoretical ion exchange capacity of the geopolymer sample determined by elemental analysis ($mmol \cdot kg^{-1}$).

The silica- and charge-balancing cations to aluminum mole ratios were determined (Table 1). Elemental analysis of the solid phase was performed by Proton Induced X-ray Emission (PIXE) using 1.7 MV Tandetron Accelerator (General Ionex Corp). Proton beams were accelerated at 1.8 MeV. The proton beam crosses a 7 μm kapton foil window before entering the chamber containing the sample. Samples were kept at 200 mTorr pressure for the measurement. The PIXE detector (Si(Li)-type) signals were processed with the Windows GUPIX software package.

2.5. Materials characterization

X-Ray powder diffraction (XRPD) patterns were recorded in PANalytical X'Pert Pro Multipurpose Diffractometer with CuKα radiation and X'Celerator position sensitive detector. The generator tension and current were set at 45 kV and 40 mA, respectively. Samples were scanned over 2θ angles in the range 15–65. The step size and scan speed were set at 0.017° and 0.014°/s, respectively. Data acquisition was performed using the X'Pert Data Collector program, and the XRD patterns were processed by the PANalytical X'Pert HighScore Plus software (V3.0.5).

Nitrogen sorption isotherms were collected at a Micrometric ASAP 2020 Surface area and Porosity Analyzer at 77 K. Samples were degassed under vacuum at 150 °C for ~8 h. For surface specific area calculation, the Braunauer–Emmett–Teller (BET) model has been applied to the desorption branch. For pore size distribution, the Barrett–Joyner–Halenda (BJH) model was applied to the desorption branch with the Halsey thickness curve (Halsey, 1948) for non-uniform surfaces and Faas correction (Faas, 1981) to account for multilayer desorption in adsorbed layer thickness estimation. Total pore volume was

Table 1
Chemical composition of geopolymeric ion exchangers determined by PIXE.

Sample	Atomic ratios				X_{max}, (%)[a]
	Si/Al	K/Al	Na/Al	Cs/Al	
Pure K-GP	2.11	1.02	0	0	0
Cs–K-GP	2.20	0.39	0	0.61	61
Na–K-GP	2.23	0.23	0.77	0	77

[a] The maximum exchanged level of the indigenous ion.