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Ceramics International 38 (2012) 5061–5067

CERAMICS INTERNATIONAL

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Degree of reactivity of two kaolinitic minerals in alkali solution using zeolitic tuff or silica sand filler

Rushdi I. Yousef [a,*], Bassam El-Eswed [b], Mazen Alshaaer [c], Fawwaz Khalili [d], Hubert Rahier [e]

[a] Chemistry Department, College of Science, Preparatory Year Deanship, King Faisal University, P.O. Box 380, Al-Ahsaa 31982, Saudi Arabia
[b] Zarka University College, Al-Balqa Applied University, P.O. Box 313, Zarka, Jordan
[c] Materials Research Laboratory, University of Jordan, Amman 11942, Jordan
[d] Department of Chemistry, Faculty of Sciences, University of Jordan, Amman 11942, Jordan
[e] Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

Received 25 December 2011; received in revised form 23 February 2012; accepted 2 March 2012
Available online 10 March 2012

Abstract

Four geopolymers were synthesized by NaOH-activation of a mixture of kaolinite (Jordanian kaolinite or Ukrainian kaolinite) and a filler (zeolitic tuff or silica sand). X-ray powder diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), and solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) were employed to monitor the extent of reaction and to characterize the phases in the geopolymer. Remaining kaolinite in all produced geopolymer specimens unambiguously indicated an incomplete reaction. The ^{29}Si MAS-NMR spectra of the geopolymers revealed the presence of tetrahedral-SiO_4 whereas the ^{27}Al MAS-NMR spectra revealed the presence of both tetrahedral-AlO_4 and octahedral-AlO_6. The XRD patterns of geopolymers showed the formation of a new feldspar mineral. Replacing silica sand filler by zeolitic tuff enhanced markedly the specific surface area of the corresponding geopolymers.

Keywords: Geopolymers; Inorganic polymers; Kaolinite; Zeolitic tuff

1. Introduction

Geopolymers are a class of mostly X-ray amorphous aluminosilicate materials, generally synthesized at ambient or slightly elevated temperature by reaction of a solid aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution [1–6]. Due to the fact that aluminosilicates are the compounds most abundant in the earth's crust, there exist a large number of raw material sources rich in alumina and silicon with the potential for producing geopolymers. Among the materials with which have been used for procuring geopolymers predominates flying ash [7,8] and include calcined clays [9], tailings [10], kaolin [11,12], and puzzolans [13]. These works have shown that geopolymerization with calcined materials promote quick dissolution and gelation and at the same time develop high mechanical strength in short time [14]. In this work kaolinite and zeolitic tuff will be used without a thermal treatment. In doing so less energy is needed for the production of this material, helping in reducing the amount of CO_2 emitted. A drawback is the lower reactivity and hence lower reaction rate at room temperature. As such, pure NaOH or KOH solutions have to be used to alkali activate the kaolinite and heating to about 60–80 °C is necessary to reduce the curing time [15].

The effects of high pH on the stability of clay minerals have been extensively studied on clay rocks [16–19]. Some of the earlier investigations focused on the stability of the kaolinites under highly alkaline conditions [20]. Numerous investigations have been carried out to understand the interaction between high pH alkaline solutions and natural clay barriers [21–24].

Abbreviations: JK, Jordanian kaolinite; RK, reference kaolinite; Z, Jordanian zeolitic tuff; S, Jordanian silica sand; RKS, geopolymer prepared from reference kaolinite and silica sand; RKZ, geopolymer prepared from reference kaolinite and zeolitic tuff; JKS, geopolymer prepared from Jordanian kaolinite and silica sand; JKZ, geopolymer prepared from Jordanian kaolinite and zeolitic tuff; MB, methylene blue; *C*, equilibrium concentration of MB (mmol/L); *Q*, amount of MB adsorbed (mmol/g adsorbent); Q_m, monolayer adsorption capacity of MB (mmol/g adsorbent); *K*, affinity constant of MB (L/mmol MB); *SSA*, specific surface area (m^2/g); *CSA*, cross sectional area occupied by one molecule (Å^2); *N*, Avogadro's number (mol^{-1}).

* Corresponding author. Fax: +966 35886437.
E-mail addresses: rushdiy@hotmail.com (R.I. Yousef), bassameleswed@yahoo.com (B. El-Eswed), mazen72@yahoo.com (M. Alshaaer), hrahier@vub.ac.be (H. Rahier).

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doi:10.1016/j.ceramint.2012.03.008

Geopolymers can be considered amorphous equivalents of certain synthetic zeolites. The polymerization reaction route can be classified as an inorganic polycondensation reaction and can be compared with zeolite formation. Most zeolite syntheses are carried out under basic conditions by using OH^- as a mineralizing agent. According to Van Jaarsveld [25] an alkaline metal is necessary for silicon and aluminum dissolution to occur. This is also true for catalyzing the condensation reaction [26]. Geopolymers are formed by individual co-polymerization of the aluminum and silicate species, which in turn are formed from silicon and aluminum dissolution contained in materials with high pH in the presence of soluble silicates [27].

The exact chemical mechanisms responsible for the dissolution and gel formation reactions in geopolymeric systems are still unknown. However, it is apparent that in many cases where materials such as fly ash and clays are used, the dissolution of the starting materials is not completed before the final hardened structure is formed [28].

The alkali activation of Jordanian kaolinite has already been described [29]. The maximum compression strength of kaolinite/NaOH samples was obtained for a mixture of 100kaolinite/16NaOH/22H_2O (wt%). The amount of water used is close to the plasticity limit of the kaolinite. The alkali activation of kaolinite with NaOH leads to the formation of a mainly amorphous matrix with some sodium zeolite phases and feldspathoids. At the composition used, not all of the kaolinite is reacted, so remaining flakes of unreacted kaolinite can be retrieved after the hardening.

A selection of multiple source materials may also be used to manipulate the geopolymeric reaction by exploiting their respective structural and surface properties and elemental compositions [30]. Using a low cost mineral, namely zeolitic tuff, in combination with kaolinite has been reported by our group [31–33]. In an attempt to shed some light on the reaction mechanism of the geopolymer formation under the employed conditions, in this work the X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), solid-state magic angle spinning nuclear magnetic resonance (^{27}Al and ^{29}Si MAS-NMR), and the surface area for the synthesized geopolymers and their raw materials were investigated.

2. Materials and methods

2.1. Materials

Jordanian Kaolinite (*JK*) with a purity of 60 wt%, and about 40 wt% of α-quartz [31] was obtained from El-Hiswa deposit, which is located in the south of Jordan about 45 km to the east of Al-Quweira town. Preparation of the Jordanian kaolinite samples involved crushing (using Jaw crusher RETCH-BB1A) of an oven dried clay (at 105 °C) to a grain size less than 425 μm. *Reference Kaolinite* (*RK*) from Ukraine (purchased from Jordan International Modern Trade Company) with a purity of 95 wt% was used as a reference mineral. *Jordanian Zeolitic Tuff* (*Z*) was obtained from North–East Jordan deposits (Aritayn area) located around 50 km to the east from Amman, which belongs to the phillipsite type of zeolites ($(Ca,Na_2,K_2)_3Al_6Si_{10}O_{32}\cdot 12H_2O$) [34–36]. *Jordanian Silica Sand* (*S*) of high quality was processed by washing with distilled water and sieved at 100 micron and 400 micron to satisfy the needs of using it as a filler material [37]. *Sodium hydroxide* pellets (96 wt%) were purchased from GCC (Gainland Chemical Company, UK).

2.2. Geopolymers synthesis

Four geopolymers (RKS, RKZ, JKS, and JKZ) with different compositions were prepared from kaolinite (Jordanian kaolinite JK, reference kaolinite RK), filler (zeolitic tuff Z, silica sand S), and sodium hydroxide solution similar to our previous work [31], Table 1. The weighed filler (S or Z) and kaolinite (JK or RK) were mixed first and then sodium hydroxide solution was added. After mixing, the paste was molded in a stainless steel cylinder at a pressure of 15 MPa and cured at 80 °C for 24 h. The specimens were aged for around one month at room temperature before subjected to different characterization techniques.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

The X-ray diffraction (XRD) measurements were carried out with an X-ray diffractometer-6000, Shimadzu, on powdered samples of geopolymers RKS, RKZ, JKS, and JKZ and their starting materials, i.e. zeolitic tuff (Z), kaolinite (JK and RK) to identify the dominant crystalline phases. The XRD patterns were measured from 5° to 80° 2θ at a scan rate of 2°/min. The crystalline phases were identified by analyzing the positions of the peaks using the software package supplied with the instrument.

2.3.2. Fourier-transform infrared spectrometry (FTIR)

The FTIR spectra for geopolymers RKS, RKZ, JKS, and JKZ as well as zeolitic tuff (Z), kaolinite (JK, RK), and silica sand (S) were collected using a Nexus 870 FTIR spectrophotometer in transmittance mode from 400 to 4000 cm^{-1}

Table 1
Composition (wt%) of geopolymers used in this work [31].

Geopolymer	Jordanian kaolinite (JK)	Reference kaolinite (RK)	Zeolitic tuff (Z)	Silica sand (S)	NaOH	Water
JKS	29.8	–	–	59.5	4.2	6.5
JKZ	41.7	–	41.7	–	5.8	10.8
RKS	–	28.1	–	56.2	5.1	10.7
RKZ	–	48.3	24.2	–	8.7	18.8