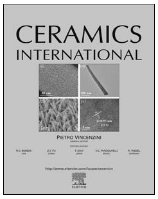
ARTICLE IN PRESS

Ceramics International xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Differentiation of the solid-state NMR signals of gel, zeolite phases and water species in geopolymer-zeolite composites

Sebastian Greiser[a], Patrick Sturm[b], Gregor J.G. Gluth[b,*], Michael Hunger[c], Christian Jäger[a]

[a] *Bundesanstalt für Materialforschung und -prüfung (BAM), Division 1.3 Structure Analysis, Richard-Willstätter-Straße 11, 12489 Berlin, Germany*
[b] *Bundesanstalt für Materialforschung und -prüfung (BAM), Division 7.4 Technology of Construction Materials, Unter den Eichen 87, 12205 Berlin, Germany*
[c] *University of Stuttgart, Institute of Chemical Technology, Pfaffenwaldring 55, 70550 Stuttgart, Germany*

ARTICLE INFO

Keywords:
A. Drying
B. Composites
B. Spectroscopy
B. Porosity
Aluminosilicate inorganic polymers
Zeolite Na-A

ABSTRACT

Geopolymer-zeolite composites were synthesized using a silica-rich industrial byproduct from chlorosilane production and sodium aluminate. Pastes were cured at 80 °C and 80% RH, and subsequently dried in two different climates: at 23 °C and 50% RH, and under vacuum. ^{1}H MAS, ^{23}Na MAS and ^{29}Si MAS NMR and XRD measurements were performed after the drying procedures as well as after subsequent aging. Zeolite Na-A was found beside traces of faujasite-type zeolite and zeolite EMT as major crystalline phases in the cured composites; the fraction of geopolymeric gel in the reaction products was determined to be ~18% on a molar basis. Various water species could be distinguished using ^{1}H MAS and ^{1}H-^{29}Si CP MAS NMR, applying rotor-synchronized echo experiments. The largest fraction of the pore water resides in the α-cages of the zeolite Na-A and in the geopolymeric gel; in addition, water exists in the β-cages of the zeolites and adsorbed at sodium ions. The water species in α-cages and in the pores of the geopolymeric gel exhibit slightly different chemical shifts of 4.7 ppm and 4.9 ppm, respectively, in the ^{1}H MAS NMR spectra. Changes of the water content in the geopolymer pores of differently dried samples were observed and led to slightly varied chemical shifts in the ^{29}Si MAS NMR spectra too. Measurements after more than 500 days revealed no significant aging effects of the composites, which confirm their chemical stability.

1. Introduction

Aluminosilicate inorganic polymers, often referred to as geopolymers, are promising materials for various applications, *e.g.* as alternative to conventional Portland cement-based binders [1,2], as heat-resistant coatings and adhesives [1,3–6], or as cost-efficient precursors for ceramics [7–10]. The properties of geopolymers have been extensively studied [11], but certain aspects are still poorly understood. This includes the state of water in these materials as well as their aging. The state of water and its gradual loss on drying is particularly relevant for the heat insulating characteristics as well as drying shrinkage and associated cracking during heating [12], which is an issue also for the production of ceramics from geopolymers [9]. Aging is a potential problem of all binder materials, but is not often considered in the context of geopolymer technology. However, some studies [13–16] highlighted that aging is a potential issue also for geopolymers, leading *e.g.* to microstructural changes and a substantial decrease of mechanical strength.

Conventionally, geopolymers are produced by adding an alkali silicate solution ('activator') to a solid aluminosilicate precursor powder. Another approach is to incorporate the activator in solid form into the precursor powder and adding just water to initiate the geopolymerization reactions, so as to avoid the stocking and handling of the alkaline activator solution; this is advantageous in real-world applications on site and may lead to a higher commercial acceptance of these materials [17]. Geopolymers produced by this route have been termed one-part geopolymers [17–22].

In the present contribution we investigate geopolymer-zeolite composites produced by the one-part route from a waste silica and sodium aluminate. These materials contain a comparatively large fraction of zeolites, while conventional geopolymers are amorphous to X-rays and usually contain only minor amounts of crystalline byproducts. The presence of significant amounts of zeolites in the materials is thought to be an advantage for heat insulating applications (e.g. coatings) due to their release of zeolitic water on heating [23]; in addition, the geopolymer-zeolite composites may be utilized as precursors for the production of nepheline-type ceramics [10,24,25]. Regarding the former application, the presence of high amounts of

---

[*] Corresponding author.
E-mail addresses: gregor.gluth@bam.de (G.J.G. Gluth), christian.jaeger@bam.de (C. Jäger).

http://dx.doi.org/10.1016/j.ceramint.2016.11.004
Received 20 September 2016; Received in revised form 27 October 2016; Accepted 1 November 2016
Available online xxxx

Please cite this article as: Greiser, S., Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.11.004

Table 1
Composition of silica CR (in wt%).

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	Cl^-	LOI
84.23	4.18	0.43	0.06	2.97	0.17	0.22	0.03	0.16	1.36	5.08

LOI: loss on ignition (1000 °C).

zeolites may raise questions about the long-term stability of the materials, as these abundant crystallites may aid nucleation of the geopolymeric gel to form additional zeolites, while for both, the former and the latter application, knowledge of the phase assemblage and the state of water in the composites is crucial. Therefore, differentiation of geopolymer gel and zeolites as well as various water species in these materials was conducted, and structural changes after aging for more than 500 days were analyzed, using XRD, ^1H, ^{23}Na, and ^{29}Si MAS NMR.

2. Experimental

2.1. Materials

One-part geopolymer-zeolite composites were produced from a silica-rich residue from chlorosilane production [26] (hereafter referred to as ‘silica CR’) and sodium aluminate, nominally $NaAlO_2$. The chemical composition of CR is given in Table 1; the silica was almost completely amorphous (Fig. 2). SEM showed the average size of the primary silica particles to be in the range ca. 50–200 nm. The sodium aluminate had a nearly stoichiometric Na/Al ratio of 0.98 mol/mol and only very minor impurities (natrite and sodium aluminate 5/4-hydrate), as seen by XRD; its loss on ignition was 1.73 wt%.

Silica CR and sodium aluminate were mixed in proportions to yield a molar SiO_2/Al_2O_3 ratio of 3.5 mol/mol (sample designation ‘CR_3.5’). Subsequently water was added to yield a nominal water/solids ratio (w/s) of 0.50; the resulting H_2O/Al_2O_3 ratio was 10.8 mol/mol. The pastes were mixed in a contact free planetary centrifugal mixer (1750 rpm; 2 min), poured into 20 mm×20 mm×20 mm moulds and cured in the open moulds at 80 °C and 80% RH for 1, 3 or 7 days (denoted ‘1d’, ‘3d’ and ‘7d’, respectively). The silica CR in the materials thus produced has been shown to exhibit a degree of reaction (*i.e.* fraction dissolved) of ca. 50 ± 10%, leading to a mean Si:Al ratio of the reaction products of approximately 1 mol/mol ($SiO_2/Al_2O_3 \approx 2$ mol/mol) [21,26].

After curing, the samples were allowed to cool down to ambient temperatures naturally; after that the samples were removed from the moulds and ground in a disc mill for 15 s. The resulting powders were mildly dried in a climate chamber (denoted ‘CC’; 50% RH, T=23 °C) or harshly dried under vacuum (denoted ‘VA’; p=40 mbar, T=23 °C) for a period of 75 ± 4 days. In the following, sample designations are complemented with the curing time and drying regime, e.g., CR_3.5_1d_CC is the composite cured for 1 day at 80 °C and 80% RH, and subsequently dried in the climate chamber for 75 ± 4 days.

In addition to the geopolymer-zeolite composites, a zeolite Na-A sample (Henkel KGaA, Düsseldorf, Germany) was measured as reference. The phase purity of the zeolite was checked by means of XRD; the sample contained very minor amounts of hydrosodalite and possibly faujasite-type zeolite as crystalline impurities. A partition of the Na-A sample was dried under the same vacuum conditions (VA) as the geopolymers.

2.2. XRD and NMR measurements

Powder XRD measurements in Bragg-Brentano geometry were done on a Rigaku Ultima IV device under the following conditions: CuKα radiation λ=1.5419 Å; increment 0.02° 2θ; scan rate 1° 2θ min^{-1}.

^1H MAS NMR was performed on a BRUKER AVANCE 600 spectrometer with a wide-bore magnet at 14.1 T and a 2.5 mm probe applying a spinning frequency of 27.5 kHz. 32 scans with a recycle delay of 2 s and a 90° pulse length of 1.9 µs were accumulated. The same set-up was used for ^1H rotor-synchronized echo experiments with a corresponding 180° pulse length of 3.8 µs. An empty rotor was measured under the same conditions to subtract ^1H rotor and probe backgrounds for both experiments. Adamantane served as secondary field standard with 1.78 ppm.

^{23}Na MAS NMR measurements were accumulated in the same spectrometer with 64 scans, a 1 s recycle delay, a 3 µs pulse length and an external calibration to the NaCl (solid) signal at 7.2 ppm.

^{29}Si MAS NMR and ^1H-^{29}Si CP MAS (cross polarization) NMR measurements were carried out using a BRUKER DMX 400 spectrometer and a wide-bore magnet at 9.4 T. The 7 mm triple resonance probe was set to a spinning speed of 6.0 kHz. A ^1H Two-Pulse Phase Modulation (TPPM) decoupling was applied during data acquisition [27]. All spectra were externally calibrated to kaolinite's upfield peak at −91.5 ppm. ^{29}Si MAS NMR experiments were acquired with an accumulation number of 128, a recycle delay of 90 s and a 90° pulse length of 7.5 µs.

The deconvolution of a ^{29}Si MAS spectra was done for a measurement with a recycle delay of 1200 s, which is an appropriate delay according to previous results [21]. The fitting was conducted using the fitting tool SOLA in Bruker's Topspin 3.1 software. Chemical shift position (δ), full width at half-height (*fwhh*) and line shape form between Lorentzian and Gaussian ($x \cdot G/(1-x) \cdot L$) was adjusted in the beginning and released to the fitting process of the software. The procedure ended with 40% Lorentzian and 60% Gaussian line shape forms for zeolite and geopolymeric gel. The Q^3 and Q^4 sites were fitted with 100% Gaussian ones. The deconvolution of single resonances were highly reproducible and reliable due to their good separation.

Two different ^{29}Si CP MAS NMR experiments were performed to investigate the state of water in the geopolymers. All experiments were done with a recycle delay of 2 s and a ^1H-^{29}Si Hartmann-Hahn contact pulse length of 2 ms; the latter condition corresponds to the findings of Rowles et al. [28], which show this contact pulse length balances the signal intensity of the zeolites and the geopolymeric gel. The first CP MAS experiment was done with a usual ^1H 90° pulse excitation (of 6.5 µs) prior the CP contact pulse. For the second experiment, the ^1H 90° pulse was replaced by a ^1H rotor-synchronized echo pulse sequence (Fig. 1). The first experiment was accumulated with 20,480 scans and the second with 16,000. The resulting spectra were normalized to the same accumulation numbers by dividing the intensity of usual ^{29}Si CP MAS NMR measurement by 1.28.

For aging investigations, the powdered specimens (3 curing times, 2

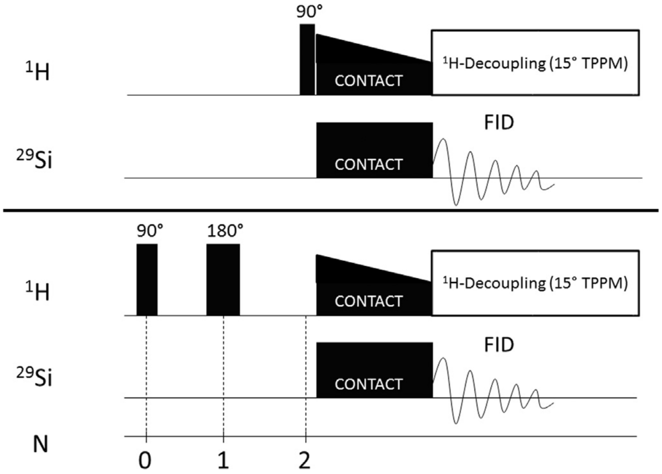


Fig. 1. ^1H-^{29}Si cross polarization (CP) pulse sequence with the usual ^1H 90° excitation (top), and with a ^1H rotor-synchronized echo excitation (bottom). N is the number of rotor periods.