J Mater Sci (2015) 50:6768–6778
DOI 10.1007/s10853-015-9232-5

Degree of reaction and phase content of silica-based one-part geopolymers investigated using chemical and NMR spectroscopic methods

P. Sturm[1] · **S. Greiser**[2] · **G. J. G. Gluth**[1] · **C. Jäger**[2] · **H. J. H. Brouwers**[3]

Received: 6 May 2015 / Accepted: 2 July 2015 / Published online: 15 July 2015

Abstract One-part geopolymers were synthesized from two different silica materials (a silica-rich residue from chlorosilane production and a commercial microsilica) and sodium aluminate at three different SiO_2/Al_2O_3 ratios and a nominal water/solids ratio of 0.5. The degree of reaction of the silica in the cured geopolymers (i.e. the fraction of silica dissolved to form aluminosilicates and minor products) was determined using two different methods: chemical attack with HCl to dissolve the reaction products and evaluation of peak areas of ^{29}Si MAS NMR spectra. It was found that the degree of reaction of the silica decreases with increasing the silica content of the starting mix, and that it is almost constant after 1 day of curing and almost independent from the kind of starting silica. From the results of the NMR-based method, the mean SiO_2/Al_2O_3 ratio of the reaction products (aluminosilicates and minor products) can be estimated to be ca. 2.0, nearly independent of the starting composition of the geopolymers. The dissolution method is biased, but of sufficient precision to be useful for following changes of the degree of reaction. Major crystalline phases in the cured geopolymers are zeolite A and/or hydrosodalite. Depending on the starting composition, the relative amounts of these zeolites vary; additionally, sodalite (only for the residue from chlorosilane production with >1 wt% Cl^-), faujasite, and zeolite EMT can appear in the geopolymers. The ^{29}Si and ^{27}Al MAS NMR results indicate mainly Si(4Al) and Al(4Si) sites, in line with the presence of zeolite A, hydrosodalite, sodalite, and geopolymeric gel of comparatively low SiO_2/Al_2O_3 ratio.

Introduction

Geopolymers are promising inorganic materials with a wide range of possible applications including heat-resistant coatings and adhesives [1–5] as well as repair mortars with high acid-resistance [6] and concretes with lower associated CO_2 emissions than conventional Portland cement-based concretes [7]. Because of this great potential, geopolymers have been extensively studied, in particular in terms of mechanical properties, microstructure, and thermal properties; these studies focused on conventional "two-part" geopolymer systems—i.e. geopolymers made from solid aluminosilicates and highly alkaline liquids, usually sodium silicate (waterglass) or sodium hydroxide solutions (see, e.g. [8, 9]).

A new approach is the so-called "one-part" mixes [10] which are produced by a different synthesis route. One-part geopolymers contain the activator in solid form and therefore only water has to be added to initiate hardening, i.e. mixing is performed in the same way as for conventional Portland cements. By applying this approach, it is not necessary to store and handle highly alkaline waterglass or sodium hydroxide solutions, which avoids problems with carbonation and ageing of these solutions as well as problems with health and safety issues. This can provide a higher social and economic acceptance of these new binder materials [10, 11].

✉ P. Sturm
patrick.sturm@bam.de

[1] Division 7.4 Technology of Construction Materials, BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

[2] Division 1.3 Structure Analysis, BAM Federal Institute for Materials Research and Testing, Berlin, Germany

[3] Department of the Built Environment, Eindhoven University of Technology, Eindhoven, The Netherlands

Different ways to synthesize one-part geopolymers have been described [10, 12–14], and microstructural, mechanical and rheological studies are reported [10, 12–20]. However, compared to conventional geopolymers, much less is known about their microstructure as well as the processes during geopolymerization and the factors influencing the latter. In a previous study [17], a one-part geopolymer based on a by-product silica and sodium aluminate has been investigated. The degree of reaction of the silica was measured to be about 50 %, proving that the composition of the reaction products differed considerably from the composition of the starting mix. In earlier studies on similar systems [10, 15], the SiO_2/Al_2O_3 and H_2O/Na_2O ratios of the starting composition were varied and microstructural differences of the hardened geopolymers were observed, while the fraction of reacted silica was not determined.

To obtain a more complete picture of the behaviour of this class of materials, in the present contribution, one-part geopolymers were made from two different silica materials and sodium aluminate at three different SiO_2/Al_2O_3 ratios. The phase content of the cured geopolymers was investigated by means of XRD, ^{29}Si and ^{27}Al MAS NMR, and the degree of reaction of the silica materials in the geopolymers was measured using two different methods: chemical attack with HCl to dissolve the reaction products and evaluation of peak areas of ^{29}Si MAS NMR spectra, using the fact that the intensity of each peak corresponds to the abundance of the Si-sites in the different compounds. The resulting degrees of reaction were compared and related to the phase content of the geopolymers, thus giving new insights into the behaviour of the silica and the composition of the hardened geopolymers.

Materials and methods

Starting materials

Two different silicas and a sodium aluminate (nominally $NaAlO_2$) were used as starting materials for geopolymer synthesis. The chemical composition of the materials is shown in Table 1.

Silica MS is a commercial microsilica, consisting of 95 wt% SiO_2; XRD indicated minor amounts of silicon carbide (PDF # 01-072-1625) as the only crystalline phase in the material (Fig. 1). The median of the particle size distribution of silica MS was determined by laser granulometry to be 0.20 μm.

Silica CR is an industrial by-product, produced in several steps in wastewater treatment of chlorosilane production [17]. It consists of 84 wt% SiO_2; the main part is amorphous SiO_2, but XRD analyses indicated also low amounts of quartz (PDF # 00-046-1045) as well as calcite (PDF # 01-086-0174) (Fig. 1). The loss on ignition of the CR silica was 5.08 wt%, of which 4.20 wt% were CO_2, due to the calcite content of the material. The median of the particle size distribution of silica CR was determined by laser granulometry to be 6.83 μm; as is indicated by SEM images of this silica material [17], the latter value represents the size of agglomerates consisting of primary particles with diameters of about 0.05–0.20 μm.

The sodium aluminate used had a nearly ideal Na/Al ratio of 0.98 mol/mol, and a loss on ignition of 1.73 wt%, of which 0.18 wt% were CO_2. In line with the latter values, XRD analyses showed, besides dry sodium aluminate (PDF # 00-033-1200), low amounts of sodium aluminate 5/4-hydrate (PDF # 01-083-0315) as well as natrite (PDF # 01-077-2082) in the material (Fig. 1).

Geopolymer synthesis

One-part geopolymers were synthesized by first mixing the solid precursors (silica MS or CR and sodium aluminate) in amounts to yield the desired SiO_2/Al_2O_3 ratios and subsequently adding water at a nominal water/solids ratio of 0.50. The resulting compositions and molar ratios of the pastes are shown in Table 2. In the following, the samples are referred to according to the silica used, their approximate SiO_2/Al_2O_3 ratio and, if applicable, their curing time (e.g. MS_2_3d for the paste made from silica MS with a SiO_2/Al_2O_3 ratio of 1.86, cured for 3 days).

The pastes were mixed in a contact-free planetary centrifugal mixer for 3 min at a rotation speed of 1750 rpm to form homogenous binder pastes. Subsequently, the pastes were cast into 20 mm × 20 mm × 20 mm cube moulds and cured in the open moulds at 80 °C and $\geq$80 % r.H. in an oven with climate conditioning for 1, 3, or 7 days.

XRD and NMR analyses

X-ray diffractograms were recorded on a Rigaku Ultima IV diffractometer under the following conditions: Bragg–Brentano geometry; Cu Kα radiation ($\lambda = 1.5419$ Å); divergence slit: 10 mm; scanning range: 3°–63° 2θ; sampling interval: 0.02° 2θ; scan rate: 1.0° 2θ min^{-1} (silica starting materials and insoluble residues: sampling interval: 0.01° 2θ; scan rate: 0.2° 2θ min^{-1}).

^{29}Si MAS NMR experiments were performed on a Bruker DMX 400 spectrometer with a wide bore magnet (9.4 T) using a 7-mm triple-resonance probe with a sample spinning frequency of 6.5 kHz. The spectra were recorded at room temperature with a 90° pulse of 7.7 μs and at least 144 scans were accumulated. The recycle delay was 400 s for the silica and the geopolymer with the lowest SiO_2/Al_2O_3 ratio; a recycle delay of 1200 s was used for the

Table 1 Chemical composition of the starting materials

Component	Silica MS (wt%)	Silica CR (wt%)	Sodium aluminate (wt%)
SiO_2	95.16	84.23	0.61
Al_2O_3	0.17	4.18	60.85
Fe_2O_3	0.04	0.43	0.06
TiO_2	<0.01	0.06	0.00
CaO	1.71	2.97	0.26
MgO	0.28	0.17	0.02
Na_2O	0.19	0.22	36.07
K_2O	0.65	0.03	0.03
SO_3	0.25	0.16	0.16
Cl^-		1.36	
LOI	1.12	5.08	1.73

LOI loss on ignition

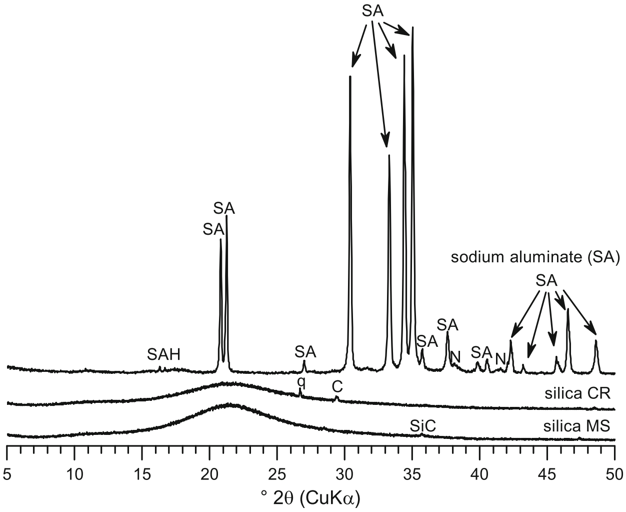

Fig. 1 X-ray diffractograms of the starting materials (*SAH* sodium aluminate 5/4-hydrate, *SA* sodium aluminate, *N* natrite, *q* quartz, *C* calcite)

other geopolymers because of long relaxation times of Q^4 species (see "Results" section). The ^{29}Si MAS NMR shift was referenced using kaolinite as secondary chemical shift standard with −91.5 ppm for the upfield peak. Two-pulse phase modulation sequence [21] was used for high-power proton decoupling.

The results of the ^{29}Si MAS NMR measurements of the cured samples were compared to the spectrum of the silica MS starting material. The signal intensities of the different species in these spectra are directly related to the number of the respective nuclei and therefore the spectra can be used for the quantification of the silica reaction degree. Spectra, accumulated with a sufficiently long recycle delay, were fitted using the fitting tool of the "Dmfit" software [22].

^{27}Al MAS NMR experiments were performed on a Bruker AVANCE 600 spectrometer with a wide bore magnet (14.1 T) using a 4-mm triple-resonance probe with a sample spinning frequency of 12.5 kHz. Spectra were recorded at room temperature with a selective (strong quadrupole interaction) 90° pulse of 7.7 µs, which was calibrated using the AlO_4 signal of yttrium aluminium garnet (YAG), and were accumulated at least 256 times. The ^{27}Al MAS NMR shift was referenced to YAG with 0.6 ppm for its AlO_6 peak. High-power proton decoupling was applied analogously to the ^{29}Si MAS NMR experiments.

Table 2 Oxide composition and resulting molar oxide ratios of the geopolymer pastes

Paste	Na_2O (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)	H_2O (wt%)	Na_2O/Al_2O_3 (mol/mol)	SiO_2/Al_2O_3 (mol/mol)	H_2O/Al_2O_3 (mol/mol)
CR_2	13.40	23.74	25.01	34.17	0.93	1.79	8.15
CR_3.5	9.85	18.12	33.37	34.10	0.89	3.13	10.65
CR_6	6.61	13.00	40.97	34.04	0.84	5.35	14.82
MS_2	14.17	23.86	26.20	34.25	0.98	1.86	8.12
MS_3.5	10.63	17.88	35.58	34.21	0.98	3.38	10.83
MS_6	8.03	13.47	42.49	34.17	0.98	5.35	14.36

Determination of the degree of reaction of the silica (dissolution method)

The procedure for the chemical determination of the degree of reaction of the silica sources was adopted from Fernández-Jiménez et al. [23], who introduced it for the determination of the degree of reaction of fly ash in conventional fly ash-based geopolymers. During the procedure, all geopolymerization products including zeolites are almost completely dissolved, while the silicate starting material (fly ash or silica) remains largely unaffected.

For the procedure, the hardened geopolymer specimens were crushed and ground in a disc mill for 18 s. The resulting powders were dried in a vacuum chamber at $p = 40$ mbar until a constant mass (defined as $\Delta m < 0.2$ wt% within 24 h) was reached. The powders thus prepared completely passed a 63 µm-width-sieve.

Powder masses of (1.0000 ± 0.0005) g were stirred with 250 ml HCl (1:20) at ambient temperatures for 3 h using a magnetic stirrer at a rotation speed of 750 rpm. After 3 h the suspensions were filtered through ash-free “red ribbon” filter paper. The insoluble residue together with the filter paper was burned with a Bunsen burner using platinum crucibles as sampling holders. The samples were then put into a pre-heated oven at 1000 °C for at least 5 h. After cooling down to ambient temperature in a desiccator, the samples were weighed again; the percentage insoluble residue was calculated from the latter value and the initial sample weight. For each geopolymer, the procedure was repeated on three samples and the results averaged. The standard deviation of the percentage insoluble residue, IR, thus determined was lower than 0.2 wt% in most cases and never greater than 0.55 wt%.

The procedure was also applied to the both silica starting materials (MS and CR) and a sample of zeolite A. The silica materials differed in their dissolution behaviour during the acid attack: while (2.6 ± 0.2) wt% of MS were dissolved during the procedure; (13.6 ± 0.3) wt% of CR were dissolved. This is readily explained by the lower amount of SiO_2 and the higher amount of impurities in CR (Table 1). The zeolite A was virtually completely (99.7 ± 0.1 wt%) dissolved during the acid treatment, indicating that also similarly composed amorphous geopolymer gel would be almost completely dissolved.

From the measurements, the degree of reaction of the silica (MS or CR) in the geopolymers was calculated as follows: The insoluble residue of the dried geopolymer sample is defined as

$$\mathrm{IR} = \frac{m_{\mathrm{IR}}}{m}, \tag{1}$$

where IR is the insoluble residue of the dried powder, m is the initial weight of the sample and m_{IR} is the sample weight after acid treatment and ignition at 1000 °C. An analogous definition applies to the silica starting materials. The remaining silica after drying (but before acid treatment) in the sample is then

$$\mathrm{RS} = \frac{1}{\mathrm{IR}_{\mathrm{silica}}} \times \mathrm{IR}_{\mathrm{geopolymer}}, \tag{2}$$

where RS is the remaining silica, $\mathrm{IR}_{\mathrm{silica}}$ is the insoluble residue of the silica used (97.4 wt% for MS; 86.4 wt% for CR) and $\mathrm{IR}_{\mathrm{geopolymer}}$ is the insoluble residue of the dried geopolymer sample under investigation.

From the mix-design of the pastes and the water content of the vacuum dried powders (measured as LOI or calculated from the mass loss during hardening and drying), the total amount of silica (reacted and unreacted) in the dried powders can be calculated as

$$c_{\mathrm{silica,dried}} = c_{\mathrm{silica,paste}} \times \frac{1 - w_{\mathrm{dried}}}{1 - w_{\mathrm{paste}}}, \tag{3}$$

where $c_{\mathrm{silica,dried}}$ is the total amount of silica in the dried powder, $c_{\mathrm{silica,paste}}$ is the amount of silica in the paste (Table 1), w_{dried} is the water content of the dried powder and w_{paste} is the water content of the paste (Table 1). Using *RS* and $c_{\mathrm{silica,dried}}$, the degree of reaction of the silica in the geopolymer under investigation can then be calculated as follows:

$$\alpha[\mathrm{HCl}] = 1 - \frac{\mathrm{RS}}{c_{\mathrm{silica,dried}}}, \tag{4}$$

where α[HCl] is the degree of reaction of the silica, based on the dissolution method.

Results

XRD of the cured geopolymers

Figure 2 shows the diffractograms of the geopolymers cured for 1 day. Diffractograms for the other curing times were very similar. As shown in Fig. 3 for the example of MS_3.5, the only difference was a very slight increase of the intensities of the reflections of the crystalline compounds in general; a somewhat more pronounced increase of the amount of sodalite (see below) with time was observed in the CR_2 samples.

In the MS-based geopolymers, the major crystalline phases after curing were hydrated zeolite A (PDF # 00-039-0222) and a hydrosodalite of intermediate water content, $Na_6(AlSiO_4)_6{\cdot}4H_2O$ (PDF # 00-042-0216). This hydrosodalite was also identified by Hajimohammadi et al. [13] and Zhang et al. [24] in geopolymers (one-part and metakaolin-based, respectively) of comparatively low starting SiO_2/Al_2O_3 ratio. The latter authors determined the

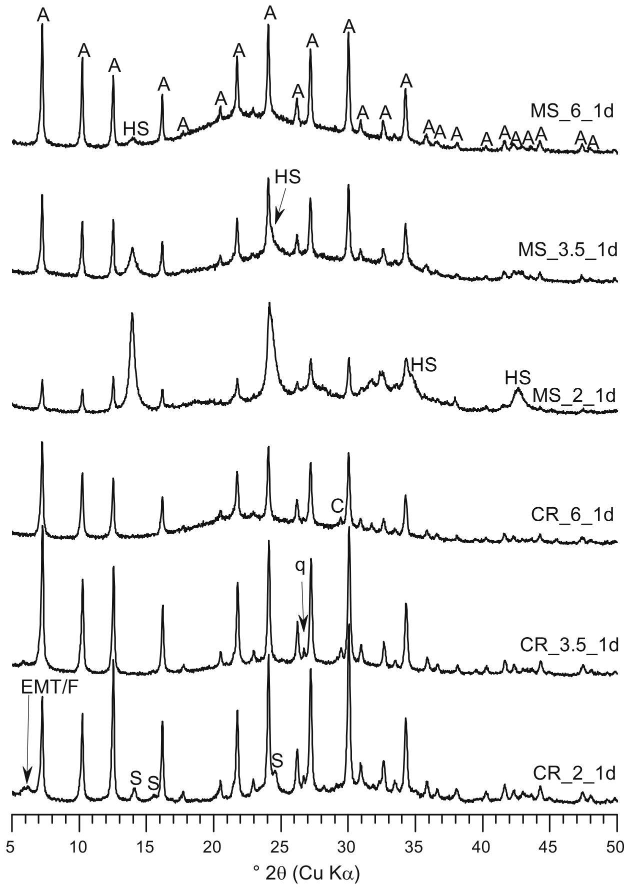

Fig. 2 X-ray diffractograms of the geopolymers cured for 1 day (*A* zeolite A, *HS* hydrosodalite, *C* calcite, *q* quartz, *EMT* zeolite EMT, *F* faujasite, *S* sodalite)

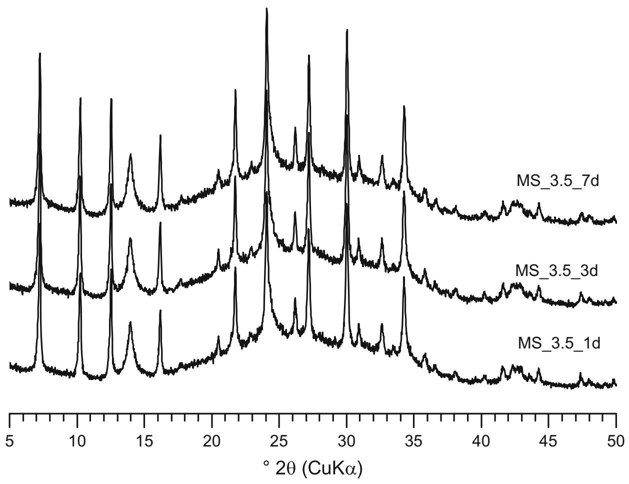

Fig. 3 X-ray diffractograms of the MS_3.5 geopolymers cured for different curing times (1 day, 3 and 7 days)

average size of the hydrosodalite crystallites in their samples to be ca. 21 nm; also in the present study, the broad reflections of this zeolite indicate either a small crystallite size or a considerable degree of disorder. The relative amount of hydrosodalite versus the amount of zeolite A increased with decreasing silica content in the starting mix.

In the CR-based geopolymers, zeolite A was the dominant crystalline phase for all starting SiO_2/Al_2O_3 ratios. All CR-based specimens also incorporated small amounts of calcite (PDF # 01-083-1762) and quartz (PDF # 00-046-1045) as remainders from the silica feedstock. At low silica content (CR_2), sodalite (sensu stricto, i.e. containing Cl^- in the cavities of the aluminosilicate framework; PDF # 01-072-0029) occurred; chloride for its formation is supplied by the CR silica (*cf.* Table 1). In addition, these specimens contained small amounts of faujasite (PDF # 00-038-0239) and zeolite EMT (PDF # 00-046-0566). The structure of zeolite EMT is related to that of faujasite and these zeolites tend to form intergrowths under non-hydrothermal conditions [25], which makes the presence of both zeolites plausible.

Compared to the diffractograms of the silica starting materials (Fig. 1), the maximum of the "amorphous" hump in the diffractograms of the cured geopolymers is broadened and shifted to higher 2θ, reaching up to ca. 25°–35° 2θ (Figs. 2 and 3; *cf.* also Fig. 6), which indicates the formation of amorphous geopolymeric gel, possibly containing nanometer-sized crystalline zeolites [26].

Degree of reaction (dissolution method)

For both, the MS-based and the CR-based geopolymers, the degree of reaction of the silica, α[HCl], increased with decreasing silica content in the starting mix but generally did not change significantly with curing time (Fig. 4; Table 4). The low-silica samples (MS_2 and CR_2) exhibited nearly 100 % reacted silica. Medium-silica (MS_3.5 and CR_3.5) and high-silica (MS_6 and CR_6) samples exhibited considerably lower reaction degrees of ~45 and ~20 %, respectively.

The differences in reaction degree are also reflected in the XRD results: the more unreacted silica remained in the geopolymer samples the less pronounced is the shift to higher 2θ values in the diffractograms (Fig. 2).

Insoluble residues, obtained after the dissolution procedure (HCl + 1000 °C), were investigated by XRD to analyse the processes during the procedure. For the low-silica samples not enough sample mass could be obtained (α[HCl] ≈ 100 %). All investigated samples exhibited similar diffractograms after the dissolution procedure (Fig. 5). In particular, the maximum of the amorphous hump shifted back to a lower 2θ value, in line with the maximum of the hump in the diffractograms of the silica sources; Fig. 6 shows the example of CR_6_1d (cured geopolymer measured at the same conditions, i.e. sampling interval: 0.01° 2θ; scan rate: 0.2° 2θ min^{-1}). The only

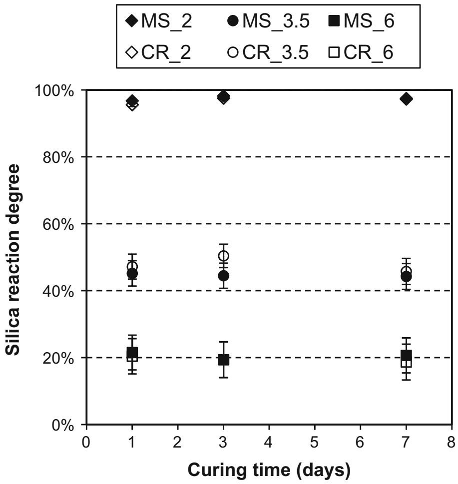

Fig. 4 Degree of reaction of the silica in the cured geopolymers, determined by the dissolution method. *Error bars* represent the estimated uncertainties, expressed as one standard deviation in each direction

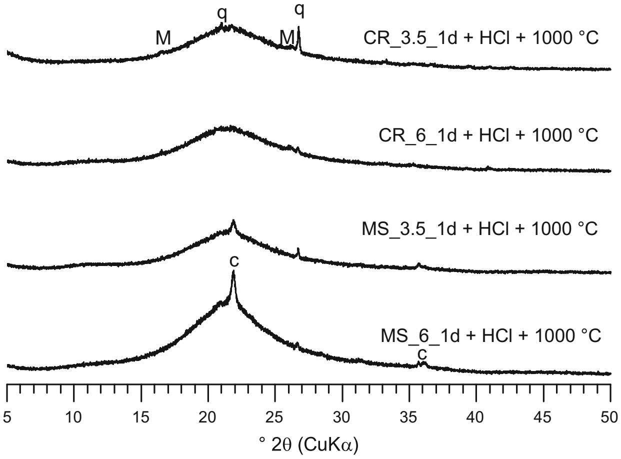

Fig. 5 X-ray diffractograms of the insoluble residues (HCl + 1000 °C) of the geopolymers with $SiO_2/Al_2O_3 \approx 3.5$ and $SiO_2/Al_2O_3 \approx 6$, cured for 1 day (*M* mullite, *q* quartz, *c* cristobalite)

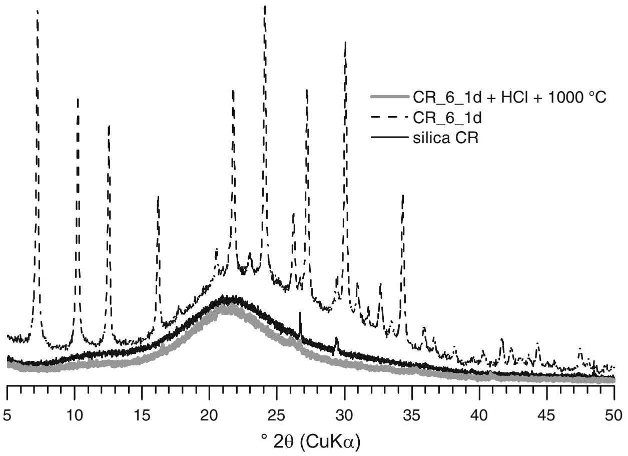

Fig. 6 X-ray diffractograms of the silica CR, the CR-based geopolymer with $SiO_2/Al_2O_3 \approx 6$ cured for 1 day and the insoluble residue (HCl + 1000 °C) of the same geopolymer

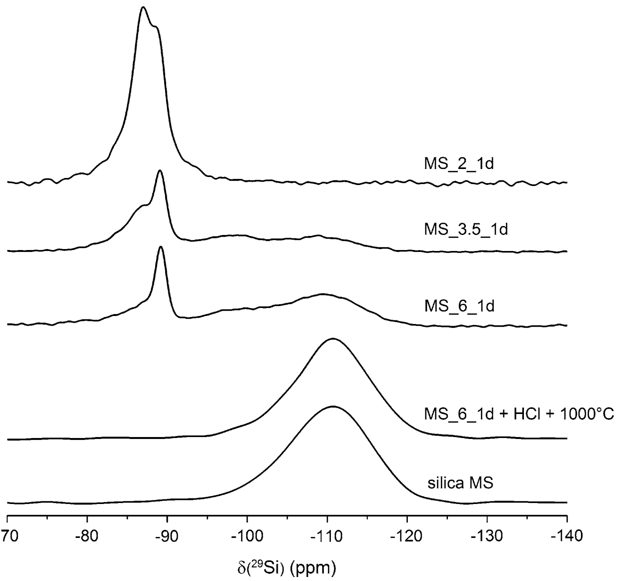

Fig. 7 ^{29}Si MAS NMR spectra of the silica MS, the MS-based geopolymers cured for 1 day and the insoluble residue (HCl + 1000 °C) of the MS-based geopolymer with a starting ratio $SiO_2/Al_2O_3 \approx 6$ cured for 1 day

detectable crystalline phases were cristobalite (PDF # 01-076-0941) for MS-based geopolymer residues, and cristobalite as well as synthetic quartz (PDF # 00-046-1045) and low amounts of mullite (PDF # 01-073-1389) in the CR-based samples. Apparently, the quartz is a residue from the silica CR (*cf*. Figs. 1, 2). The presence of mullite can be explained by low amounts of Al_2O_3 remaining in the system after dissolution in HCl (see discussion below) and the subsequent high-temperature treatment at 1000 °C.

NMR results

^{29}Si MAS NMR measurements were performed on the MS silica and the MS-based geopolymers (Fig. 7). The silica exhibited a broad main resonance around −110 ppm originating from Q^4 units (fully condensed SiO_4 tetrahedra) and a shoulder downfield, which indicates a small amount (6 %) of Q^3 units (SiO_4 unit linked to three SiO_4 tetrahedra and a non-bridging oxygen atom) [27].

In the spectra of the hardened geopolymers three main resonances appear: Q^3 at around −98 ppm and Q^4 at around −110 ppm from the silica, and overlapping signals at chemical shifts from ca. −80 to −92 ppm. The latter originate from Si(4Al) units, i.e. SiO_4 tetrahedra linked to four AlO_4, which are structural units of zeolites [27, 28] as well as of geopolymers with comparatively low SiO_2/Al_2O_3 ratio [15, 24, 29]. Smaller amounts of Si(3Al) units (SiO_4 tetrahedra having bridging oxygens to three AlO_4 and one SiO_4 unit), possibly present in the amorphous geopolymeric gel, may also contribute to the signals from −80 to −92 ppm. The main resonance of zeolite A at −89.2 ppm [28] can be distinguished as peak on top these overlapping signals for samples MS_6 and MS_3.5, and as a shoulder for sample MS_2. At −87.0 ppm a shoulder is present for MS_6 and MS_3.5, while this signal occurs as main peak for MS_2. The relative heights of the peaks/shoulders at −89.2 and −87.0 ppm parallel the differing amounts of zeolite A and hydrosodalite in the geopolymers of different composition as observed by XRD (Fig. 2), thus the signal at −87.0 ppm can be assigned to the hydrosodalite. This assignment is in agreement with results by Engelhardt et al. [30], who reported ^{29}Si MAS NMR chemical shifts for hydrosodalites of different water contents and for hydrated hydroxysodalite. According to their results, hydrosodalite of intermediate water content, as found in the geopolymers under study, exhibits a signal at −86.5 ppm, while the higher and lower water state would cause signals at ca. −82.5 and −90.5 ppm, respectively.

In the spectrum of sample MS_2 no Q^3 and Q^4 resonances, but only signals from the reaction products (i.e. between −80 and −92 ppm) can be observed, i.e. all SiO_2 had reacted in this geopolymer. The reaction degrees of the silica, α[NMR], in the other geopolymers were calculated from fitted peak areas using an additional resonance (referred to as peak "5"), centred at ca. −85 ppm; Fig. 8 shows the example of MS_3.5_1d. Peak 5 may originate from more highly hydrated hydrosodalite-like species (*cf.* the chemical shifts given above) and/or less complete polymerized SiO_4 species in the geopolymeric gel. Due to long longitudinal relaxation times T_1 of the hydrosodalite and of the Q^4 resonances (Fig. 9), the spectra of samples MS_3.5 and MS_6 were acquired with a recycle delay of 1200 s. A repetition time of 400 s was sufficient for the fully reacted sample MS_2 (α[NMR] ≈ 100 %) and the silica MS (α[NMR] ≈ 0 %), because no detailed reaction degree was calculated. The results are shown in Table 3.

Table 3 also shows that in the cured samples with remaining silica (MS_3.5 and MS_6) the relative amount of Q^3 sites is considerably increased and the amount of Q^4 sites decreased, compared to the starting silica. These changes are most likely related to the alteration of the silica surface during dissolution. This interpretation is in line with previous studies [31, 32] in which it was observed that dissolution of microsilica in alkaline (Ca-dominated) media led to the formation of Q^3 species. These were assigned fully [31] or in large part [32] to the silica; in the latter study, it was shown by ^{1}H–^{29}Si CP MAS NMR that these species can be assigned to a hydrated layer on the surface of the microsilica. Another study [33] found that formation of a significant amount of Q^3 species took place also during dissolution of microsilica in 1 M NaOH solution, but no unequivocal assignment was given.

^{27}Al MAS NMR spectra of the hardened MS-based samples are shown in Fig. 10. In accord with the identification of Si(4Al) units in the ^{29}Si MAS NMR spectra, all ^{27}Al MAS NMR spectra exhibit a large signal with its maximum at ca. 58–59 ppm (59.1 ppm for MS_2_1d, 58.4 ppm for MS_3.5_1d and MS_6_1d) that originates from Al(4Si) units, i.e. AlO_4 tetrahedra linked to four SiO_4 tetrahedra [34, 35]. Again, this observation agrees with the occurrence of zeolite A, hydrosodalite and geopolymeric gel in the samples.

In addition to the signal at 58–59 ppm, a small, broad signal centred at around 8 ppm occurred, which is related to aluminium in octahedral coordination. The relative

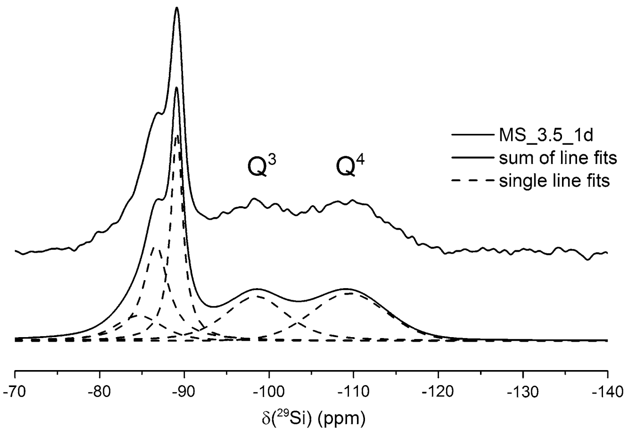

Fig. 8 Fit (*grey line*) of the measured ^{29}Si MAS NMR spectrum (*full black line*) of sample MS_3.5_1d, recycle delay 1200 s. *Dashed lines* represent the fitted resonances

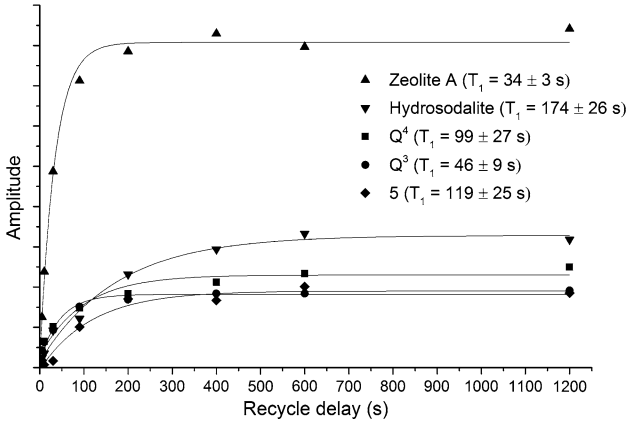

Fig. 9 ^{29}Si MAS NMR signal intensities of the various species of sample MS_3.5_1d for different recycle delays. Hydrosodalite, resonance "5" and Q^4 exhibit the longest relaxation times T_1

Table 3 Intensities of Q^3 and Q^4 peak areas and resulting degrees of reaction of the silica

Geopolymer	Curing time (d)	Recycle delay (s)	Q^3 (%)	Q^4 (%)	α[NMR] (%)
MS_2	1	400			~100
MS_3.5	1	1200	17.1 ± 0.3	27.1 ± 0.5	55.8 ± 1.4
MS_3.5	7	1200	16.8 ± 0.3	26.8 ± 0.5	56.4 ± 1.4
MS_6	1	1200	13.9 ± 0.3	51.1 ± 1.0	35.0 ± 1.7
Silica MS		400	6.0 ± 0.2	94.0 ± 1.9	~0

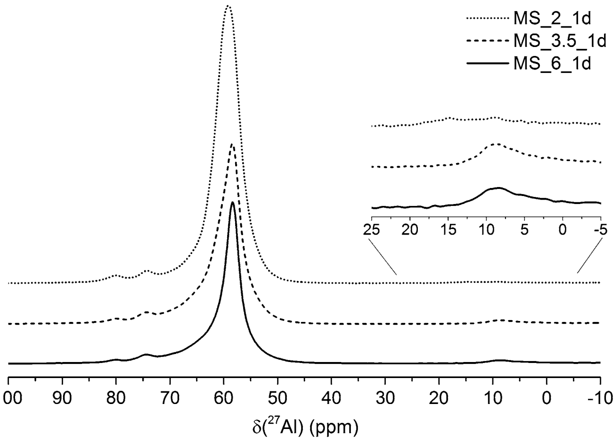

Fig. 10 ^{27}Al MAS NMR spectra of the MS-based geopolymers cured for 1 day. The *inset* shows the signals from aluminium in octahedral coordination

amount of this octahedral aluminium in the cured geopolymers was significantly higher in the samples with a starting SiO_2/Al_2O_3 ratio of ca. 3.5 or 6 (MS_3.5 and MS_6) than in the sample with $SiO_2/Al_2O_3 \approx 2$, as shown by the corresponding peak areas (Fig. 10, inset). The nature of the octahedral aluminium giving rise to these signals is discussed below.

The low-silica sample (MS_2) exhibited another small broad signal around 15 ppm (Fig. 10, inset), which presumably is related to remaining sodium aluminate or impurities of the sodium aluminate [15]. Very low amounts of remaining sodium aluminate in that sample can be tentatively identified as very weak peaks in the XRD results too (which, due to their low intensity, are not distinguishable in Figs. 2 and 3).

Discussion

Degree of reaction of the silica

Deviations exist between the results of the two applied methods for the measurement of the degree of reaction of the silica in the geopolymers (dissolution in HCl and ^{29}Si MAS NMR, respectively). In all cases, the reaction degree as determined by NMR spectra curve fitting is larger than the results based on the dissolution method, the deviations increasing with decreasing reaction degree (Table 4).

A possible reason for the observed deviations between the results of the two methods is incomplete dissolution of the reaction products during the HCl treatment (*cf.* Refs. [36, 37]). While ^{29}Si MAS NMR measures only silicon atoms in the samples, the results of the dissolution method are based on the accuracy of the measurements of the insoluble residue, and the assumption that the insoluble residue contains only remaining silica but no reaction products. However, ^{27}Al MAS NMR spectra of samples MS_3.5_1d and MS_6_1d after dissolution in HCl and heating to 1000 °C (not shown) reveal that a significant amount of aluminium (1–2 at.%), i.e. considerably more than in the starting MS silica (*cf.* Table 1), remained in the samples. Although no aluminium-bearing phases could be detected in the XRD traces of these samples (Figs. 5, 6), the corresponding CR-based geopolymers were shown by XRD to contain some mullite ($2Al_2O_3 \cdot SiO_2$; PDF # 01-073-1389) after the dissolution treatment and ignition (Fig. 5). These observations indicate that the chemical attack with HCl on the reaction products was not complete, and hence, the calculated silica reaction degrees α[HCl] are too low. This explanation, however, cannot fully account for the observed differences between the methods: allowing for 1–2 at.% of aluminium in the samples after the dissolution procedure results in reaction degrees, α[HCl], that are only 1–3 % (abs.) higher than the values shown in Table 4.

Despite the bias of the dissolution method, its results can serve to identify the changes of the degree of reaction of the silica, e.g. with curing time and/or temperature. In the present context, it is important to note that under the employed curing conditions, the dissolution of the silica did not proceed significantly after a curing time of 1 day (Fig. 4). In line with this, only very minor changes of the diffractograms of the geopolymers could be observed after this curing time.

Composition of the reaction products

The degree of reaction of the silica was nearly 100 % in the geopolymers with starting $SiO_2/Al_2O_3 \approx 2$ (low-silica), but considerably lower in the medium- and high-silica

Table 4 Comparison of silica reaction degrees as determined by ^{29}Si MAS NMR and by the dissolution method

Geopolymer	Curing time (d)	α[NMR] (%)	α[HCl] (%)	Δ abs. (%)
MS_2	1	~100	96.7 ± 0.3	~3.3
MS_3.5	1	55.8 ± 1.4	45.2 ± 3.8	10.6
MS_3.5	7	56.4 ± 1.4	44.3 ± 3.9	12.1
MS_6	1	35.0 ± 1.7	21.5 ± 5.2	13.5

geopolymers (Fig. 4; Table 4). In contrast to the paste SiO_2/Al_2O_3 ratio, the source of the silica starting material was of minor importance for its degree of reaction in the geopolymer systems under investigation.

From the degrees of reaction of the silica MS as determined by NMR (Table 4), the composition of the silica materials (Table 1) and the starting composition of the geopolymers (Table 2), the mean SiO_2/Al_2O_3 ratio of the reaction products can be estimated. For the calculations it is assumed that the sodium aluminate has been dissolved completely, which is close to the actual behaviour, as XRD and NMR indicated only minor amounts of sodium aluminate in the reaction products. The SiO_2/Al_2O_3 ratios of the reaction products thus obtained are slightly below 2 mol/mol (i.e. ~1.9 mol/mol) for all starting MS contents.

It can be assumed that the error made in the determination of the degree of reaction of the silica CR by the chemical method is similar to the error for the MS-based samples. From this assumption and the almost identical reaction degrees (Fig. 4), it follows that also for all CR-based geopolymers the SiO_2/Al_2O_3 ratio of the reaction products is close to 2. Thus, it appears that under the employed synthesis conditions the silica material is dissolved only to an extent that the reaction products achieve a SiO_2/Al_2O_3 ratio of ~2 mol/mol; afterwards dissolution of the silica ceases.

This observation warrants a reevaluation of the results of the aforementioned previous investigation on a one-part geopolymer [17]. In this latter study, the reaction degree of the silica was determined with the dissolution method to be ca. 50 %, which resulted in a calculated SiO_2/Al_2O_3 ratio of the reaction products of ca. 1.8. Since the present study showed that dissolution method is biased (underestimates the degree of reaction), it is likely that the actual degree of reaction of the silica in the previous study was higher and thus also in these geopolymers the SiO_2/Al_2O_3 ratio of the reaction products was closer to 2.

The estimated SiO_2/Al_2O_3 of the reaction products in the present study is in line with zeolite A, hydrosodalite and sodalite (all have $SiO_2/Al_2O_3 = 2.0$) as the main crystalline reaction products in the geopolymers. However, depending on the starting silica material used and the composition of the paste, the relative abundance of these zeolites varied (Fig. 2). In addition, CR_2 contained small amounts of faujasite and zeolite EMT, whose SiO_2/Al_2O_3 ratios are 4.8 and 6.6, respectively.

The observed differences in the amount of remaining (non-reacted) silica and in the phase assemblage of the cured geopolymers affect their properties. A previous investigation [19] showed that the compressive strength of MS-based one-part geopolymers (water/solids ratio 0.60) increased consistently with increasing starting SiO_2/Al_2O_3 ratio; the highest strength was obtained at $SiO_2/Al_2O_3 = 6$ (Fig. 11). The strength results for the MS-based pastes studied here (i.e. with a nominal water/solids ratio of 0.50) exhibited an analogous trend, but larger scatter (probably because of the less good workability, caused by the lower water content). This increase of strength with increasing SiO_2/Al_2O_3 ratio can be attributed, at least partly, to the remaining silica particles, which may act as micro-aggregates, and/or differences in porosity and pore sizes of the cured geopolymers. As pointed out by Oh et al. [38], also the relative amounts of different kinds of zeolites (and/or the similarity of the geopolymeric gel to these zeolites) can significantly impact on the mechanical properties of the cured geopolymers. However, the latter authors reported only on the bulk modulus of hydroxysodalite (basic hydrosodalite), while the major crystalline phases in the present MS-based geopolymers were zeolite A at high starting SiO_2/Al_2O_3 ratio and (non-basic) hydrosodalite at low starting SiO_2/Al_2O_3 ratio. It should also be noted that

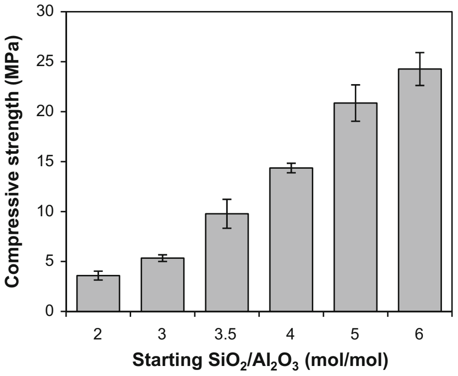

Fig. 11 Compressive strength of MS-based one-part geopolymers (water/solids ratio = 0.60) cured for 7 days, depending on starting SiO_2/Al_2O_3 ratio. *Error bars* represent one standard deviation in each direction. Data from Ref. [19]

the occurrence of differing amounts of hydrosodalite in these geopolymers is of importance in the context of high-temperature applications, as the volume of this zeolite increases significantly on dehydration [39].

In the medium- and high-silica geopolymers a minor but significant fraction of the aluminium in the products was found to be in octahedral coordination, leading to a broad resonance centred at ca. 8 ppm (Fig. 10, inset). This octahedral aluminium is possibly contained in amorphous or semi-crystalline $Al(OH)_3$ as proposed by Brew and MacKenzie [15]. These authors found indications of a poorly ordered gibbsite-like phase in the XRD traces of geopolymers made from silica fume and sodium aluminate solution, and suggested that the minor amounts of octahedral aluminium in these samples can be assigned to that phase. This assignment would also be in line with previous $^{27}Al\{^{1}H\}$ and $^{27}Al\{^{29}Si\}$ REDOR NMR measurements on CR-based one-part geopolymers [18], which indicate that the octahedral aluminium in the products (resonance at 5–10 ppm) has protons, but no or little silicon in spatial proximity.

Conclusions

One-part geopolymers, synthesized from silica and sodium aluminate, yield zeolite A and hydrosodalite as major crystalline reaction products, as well as geopolymeric gel. The relative amounts of the zeolites depend on the initial SiO_2/Al_2O_3 ratio, higher SiO_2/Al_2O_3 ratios generally leading to a higher fraction of zeolite A.

The degree of reaction of the silica in the geopolymers can be estimated using a chemical method (dissolution in HCl) and by evaluation of ^{29}Si MAS NMR peak areas. Judging from the NMR analyses, the results of the dissolution method are biased, in particular at low reaction degrees. However, both methods clearly disclosed the same trends for changes of the degree of reaction depending on geopolymer formulation and curing time, making the dissolution method at least useful to follow these trends.

Both methods showed that in all formulations, the degree of reaction of the silica did not change significantly after 1 day of curing, indicating that longer curing times are of no use for these materials. The kind of silica (MS or CR) had no significant influence on the degree of reaction, while the degree of reaction was strongly dependent on paste SiO_2/Al_2O_3 ratio. In the geopolymers with a SiO_2/Al_2O_3 ratio of ~ 2 the silica reacted virtually completely. For higher starting SiO_2/Al_2O_3 ratios (higher starting silica contents) the degree of reaction of the silica was considerably lower. The NMR-based results disclosed that in these geopolymers the silica dissolved only to an extent that the composition of the reaction products was close to $SiO_2/Al_2O_3 = 2$ too.

Differences in the mechanical properties of the geopolymers were related to the observed differences in the amount of remaining (non-reacted) silica and the phase assemblage. In addition, the occurrence in the reaction products of differing amounts of hydrosodalite, with its unusual behaviour of volume increase on dehydration, is considered to be of importance for high-temperature applications. Further studies will analyse the influence of these variations on the mechanical, chemical and thermal properties of the investigated one-part geopolymers in more detail.

References

1. Herr R (2004) Geopolymere - eine neue mineralische Baustoff-Generation für den Brandschutz von Ingenieurbauwerken. IEMB Info 2004/7. Institut für Erhaltung und Modernisierung von Bauwerken e.V., Berlin
2. Bell J, Gordon M, Kriven W (2005) Use of geopolymeric cements as a refractory adhesive for metal and ceramic joins. Ceram Eng Sci Proc 26(3):407–413
3. Krivenko PV, Kovalchuk GY (2007) Directed synthesis of alkaline aluminosilicate minerals in a geocement matrix. J Mater Sci 42:2944–2952. doi:10.1007/s10853-006-0528-3
4. Krivenko PV, Pushkavera YK, Sukhanevich MV, Guziy SG (2009) Fireproof coatings on the basis of alkaline aluminum silicate systems. Ceram Eng Sci Proc 29(10):129–142
5. Temuujin J, Minjigmaa A, Rickard W, Lee M, Williams I, van Riessen A (2010) Fly ash based geopolymer thin coatings on metal substrates and its thermal evaluation. J Hazard Mater 180:748–752
6. Montes C, Allouche EN (2012) Evaluation of the potential of geopolymer mortar in the rehabilitation of buried infrastructure. Struct Infrastruct Eng 8:89–98
7. Duxson P, Provis JL, Lukey GC, van Deventer JSJ (2007) The role of inorganic polymer technology in the development of 'green concrete'. Cem Concr Res 37:1590–1597
8. Duxson P, Fernández-Jiménez A, Provis JL, Lukey GC, Palomo A, van Deventer JSJ (2007) Geopolymer technology: the current state of the art. J Mater Sci 42:2917–2933. doi:10.1007/s10853-006-0637-z
9. Provis JL, van Deventer JSJ (eds) (2014) Alkali activated materials: state-of-the-art-report, RILEM TC 224-AAM. Springer, Dordrecht
10. Hajimohammadi A, Provis JL, van Deventer JSJ (2008) One-part geopolymer mixes from geothermal silica and sodium aluminate. Ind Eng Chem Res 47:9396–9405
11. Duxson P, Provis JL (2008) Designing precursors for geopolymer cements. J Am Ceram Soc 91:3864–3869
12. Koloušek D, Brus J, Urbanova M, Andertova J, Hulinsky V, Vorel J (2007) Preparation, structure and hydrothermal stability of alternative (sodium silicate-free) geopolymers. J Mater Sci 42:9267–9275. doi:10.1007/s10853-007-1910-5
13. Hajimohammadi A, Provis JL, van Deventer JSJ (2010) Effect of alumina release rate on the mechanism of geopolymer gel formation. Chem Mater 22:5199–5208

14. Feng D, Provis JL, van Deventer JSJ (2012) Thermal activation of albite for the synthesis of one-part mix geopolymers. J Am Ceram Soc 95:565–572
15. Brew DRM, MacKenzie KJD (2007) Geopolymer synthesis using silica fume and sodium aluminate. J Mater Sci 42:3990–3993. doi:10.1007/s10853-006-0376-1
16. Hajimohammadi A, Provis JL, van Deventer JSJ (2011) The effect of silica availability on the mechanism of geopolymerisation. Cem Concr Res 41:210–216
17. Gluth GJG, Lehmann C, Rübner K, Kühne H-C (2013) Geopolymerization of a silica residue from waste treatment of chlorosilane production. Mater Struct 46:1291–1298
18. Greiser S, Gluth GJG, Sturm P, Brouwers HJH, Jäger C (2014) ^{27}Al-^{1}H and ^{27}Al-^{29}Si double resonance NMR of one-part geopolymers. In: Non-Traditional Cement & Concrete V—Proceedings of the International Conference, Brno, Czech Republic, pp 91–94
19. Sturm P, Gluth GJG, Schmidt W, Astorg A, Kühne H-C, Brouwers HJH (2014) Rheological properties of microsilica and sodium aluminate based one-part geopolymers compared to ordinary Portland cement. In: Non-Traditional Cement & Concrete V—Proceedings of the International Conference, Brno, Czech Republic, pp 241–244
20. Sturm P, Gluth GJG, Lindemann M, Greiser S, Jäger C, Brouwers HJH (2014) Structural investigations on one-part geopolymers after different drying regimes. In: Proceedings of the 34th Annual Cement and Concrete Science Conference, and Workshop on Waste Cementation, Sheffield, United Kingdom, pp 37–40
21. Bennett AE, Rienstra CM, Auger M, Lakshmi KV, Griffin RG (1995) Heteronuclear decoupling in rotating solids. J Chem Phys 103:6951–6958
22. Massiot D, Fayon F, Capron M, King I, Le Calvé S, Alonso B, Durand J-O, Bujoli B, Gan Z, Hoatson G (2002) Modelling one- and two-dimensional solid-state NMR spectra. Magn Reson Chem 40:70–76
23. Fernández-Jiménez A, de la Torre AG, Palomo A, López-Olmo G, Alonso MM, Aranda MAG (2006) Quantitative determination of phases in the alkaline activation of fly ash. Part II: degree of reaction. Fuel 85:1960–1969
24. Zhang B, MacKenzie KJD, Brown IWM (2009) Crystalline phase formation in metakaolinite geopolymers activated with NaOH and sodium silicate. J Mater Sci 44:4668–4676. doi:10.1007/s10853-009-3715-1
25. Weitkamp J, Schumacher R, Weiß U (1992) Hydrothermalsynthese und Charakterisierung von Zeolith EMT. Chem Ing Tech 64:1109–1112
26. Provis JL, Lukey GC, van Deventer JSJ (2005) Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results. Chem Mater 17:3075–3085
27. Engelhardt G, Michel D (1987) High-resolution solid-state NMR of silicates and zeolites. Wiley, Chichester
28. Lippmaa E, Mägi M, Samoson A, Tarmak M, Engelhardt G (1981) Investigation of the structure of zeolites by solid-state high-resolution ^{29}Si NMR spectroscopy. J Am Chem Soc 103:4992–4996
29. Fletcher RA, MacKenzie KJD, Nicholson CL, Shimada S (2005) The composition range of aluminosilicate geopolymers. J Eur Ceram Soc 25:1471–1477
30. Engelhardt G, Felsche J, Sieger P (1992) The hydrosodalite system $Na_{6+x}[SiAlO_4]_6(OH)_x \bullet nH_2O$: formation, phase composition, and de- and rehydration studied by ^{1}H, ^{23}Na, and ^{29}Si MAS–NMR spectroscopy in tandem with thermal analysis, X-ray diffraction, and IR spectroscopy. J Am Chem Soc 114:1173–1182
31. Brough AR, Dobson CM, Richardson IG, Groves GW (1995) A study of the pozzolanic reaction by solid-state ^{29}Si nuclear magnetic resonance using selective isotopic enrichment. J Mater Sci 30:1671–1678. doi:10.1007/BF00351595
32. Sun G, Brough AR, Young JF (1999) ^{29}Si NMR study of the hydration of Ca_3SiO_5 and β-Ca_2SiO_4 in the presence of silica fume. J Am Ceram Soc 82:3225–3230
33. Leemann A, Le Saout G, Winnefeld F, Rentsch D, Lothenbach B (2011) Alkali-silica reaction: the influence of calcium on silica dissolution and the formation of reaction products. J Am Ceram Soc 94:1243–1249
34. Fyfe CA, Gobbi GC, Hartman JS, Klinowski J, Thomas JM (1982) Solid-state magic-angle spinning aluminum-27 nuclear magnetic resonance studies of zeolites using a 400-MHz high-resolution spectrometer. J Phys Chem 86:1247–1250
35. Lippmaa E, Samoson A, Mägi M (1986) High-resolution ^{27}Al NMR of aluminosilicates. J Am Chem Soc 108:1730–1735
36. Hartman RL, Fogler HS (2005) Reaction kinetics and mechanisms of zeolite dissolution in hydrochloric acid. Ind Eng Chem Res 44:7738–7745
37. Hartman RL, Fogler HS (2007) Understanding the dissolution of zeolites. Langmuir 23:5477–5484
38. Oh JE, Moon J, Mancio M, Clark SM, Monteiro PJM (2011) Bulk modulus of basic hydrosodalite, $Na_8[AlSiO_4]_6(OH)_2 \cdot 2H_2O$, a possible zeolitic precursor in coal-fly-ash-based geopolymers. Cem Concr Res 41:107–112
39. Felsche J, Luger S (1987) Phases and thermal decomposition characteristics of hydro-sodalites $Na_{6+x}[AlSiO_4]_6(OH)_x \cdot nH_2O$. Thermochim Acta 118:35–55