

Condensation of aluminosilicate gels—model system for geopolymer binders

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ABSTRACT

The reaction of geopolymer binders can be subdivided into two more or less parallel reactions, (1) the dissolution of reactable silicate and aluminate monomers from the reactive solid material and (2) the condensation to an aluminosilicate gel. Due to the wide range of possible raw materials, the question arises whether the Si/Al ratio of the hardened aluminosilicate network is predominated by the Si/Al ratio of the raw materials, or a gel with preferred Si/Al ratio wants to condense. Therefore, aluminosilicate gels were synthesized with pure alkali silicate and alkali aluminate solutions. Two measurement series were started to investigate the influence of hydroxide concentration as well as the influence of Si/Al in the model system. The gels were characterized by chemical analysis, FT-IR spectroscopy, X-ray diffraction as well as ²⁹Si and ²⁷Al MAS NMR spectroscopy.

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1. Introduction

The term “geopolymer” as used by Davidovits [1] was originally connected to the reaction of metakaolin with alkaline solutions forming amorphous to semi-crystalline three-dimensional aluminosilicate networks by polycondensation [2].

Nowadays geopolymer binders are generally understood as alkaline activated aluminosilicates or an inorganic 2-component system, consisting of the following:

- (1) a *reactive solid* component that contains SiO₂ and Al₂O₃ in sufficient amounts and in reactive form (e.g., ashes, active clays, pozzolana, slags etc.) and
- (2) an *alkaline activation solution* that contains (apart from water) individual alkali hydroxides, silicates, aluminates, carbonates, and sulphates or combinations thereof.

When the solid and the activator components come into contact with each other, hardening results due to the formation of an *aluminosilicate network* ranging from amorphous to partial crystalline aluminosilicate, which is water-resistant [3,4]. Therefore, geopolymers can also be interpreted as amorphous precursors of zeolites [5].

At the beginning of the geopolymerization, the alkaline solution comes into contact with the aluminosilicate solid material. The dissolution step starts. Therefore, the solution's chemistry is dominated

by a high alkalinity and pH value, respectively (e.g., by NaOH). The silicate and aluminate concentration in the pore solution increases with the ongoing dissolution reaction. If attaining a certain concentration, the condensation step starts.

The Si/Al ratio of geopolymer binders has a main influence on its properties. This is related to several aspects:

- (1) Different raw materials are characterized by a broad variation of Si/Al ratios within their reactive phase. Therefore, the resulting Si/Al ratio in the pore solution varies [6]. How different Si/Al ratios affect the strength and other properties of the hardened binder is difficult to estimate, unless using one and the same material with different Si/Al ratios but the same extent and kinetic of dissolution. Therefore, model investigations of aluminosilicate gels were done occasionally [7–10].
- (2) A blend of raw materials changes the Si/Al ratio in summary. The overall Si/Al ratio may vary locally and with time.
- (3) The Si/Al ratio might be varied by the addition of a silicate solution that usually increases the strength of the hardened geopolymer. This is mostly caused by micro-structural changes of the geopolymer matrix [11,12].

Occasional investigations on aluminosilicate gels prepared via sodium aluminate and sodium silicate solution are done to optimize the crystallization of zeolites from aluminosilicate gel precursors [13,14]. Basic knowledge about the interdependence of batch concentrations and the condensates was generated by Krznarič et al. [15], the Si/Al ratio [16] and the alkali hydroxide concentration [17] were discussed as main influences. It has to be mentioned that the hydroxide concentration was not kept constant in their investigations. Because the focus was set only on the influence on the gel composition, no structural investigation was done. Harvey and Glasser [14] as well as Lechert [18]

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pointed out the enormous importance of the pH on the formed aluminosilicate gel and the crystalline structure of the zeolites formed.

NMR spectroscopic investigations on aluminosilicate gels were published, for instance, by Wang et al. [13] and Phair et al. [7,19]. It could be shown that the amorphous aluminosilicate precursors of zeolites already consists of the 3 dimensionally connected Q_4 units.

The kinetic of condensation of (alumino-)silicates out of alkaline solutions in terms of geopolymer formation is dominated by the available aluminium as shown by Wenig, Sagoe-Crentsil, and Weng [20–22] by applying the partial charge model. The gel formation time of aluminosilicate gels for the zeolite syntheses was wide discussed by Harvey and Glasser [14]; therein it became obvious that aluminosilicate gels with highly polymerized silicate solutions showed a significant higher gel forming time than same compositions with lower polymerized silicate solutions. These solutions were depolymerized with the excess alkalinity before combining silicate and aluminate solution.

Within the investigation presented, the focus was set on the formation of aluminosilicate gels prepared by silicate and aluminate solutions. The investigation setup was strongly influenced by the background of geopolymer syntheses. The focus was set on two directions, the pH value and the Si/Al ratio of the starting solution and their influence on the gel composition formed within 24 h and the crystallization products after heating/drying the gels. Further on several links will be drawn between gel formation and its relevance for the geopolymer formation in real binders.

2. Experimental

2.1. Gel preparation

Series A spans the ratio Na/(Si + Al) from 3.3 to 15 at a fixed Si/Al ratio of 1 to allow for the increasing amount of silicate and aluminate in the pore solution.

Series B spans the Si/Al from 0.1 to 10 at a fixed Na/(Si + Al) of 6.

Two starting solutions (solution I: 3 M Na; 0.5 M Si and solution II: 3 M Na; 0.5 M Al) were used for the gel preparation. A lower NaOH content than 6 M was realized by diluting a sodium silicate solution with water and dissolving the necessary amount of NaOH. A higher NaOH content than 6 M was realized by solving NaOH pellets within the silicate starting solution I.

After mixing the silicate and aluminate solutions, the mixed solution was stirred for 5 min and kept closed for 24 h. Afterwards the gel was washed 3 times, centrifuged and decanted. All the clear solution was collected and filled up to a defined volume. The gel was dried at 80 °C for 5 days (1 day in closed, 4 days in opened boxes) and characterized afterwards (chemical composition, structure by NMR, XRD and FT-IR).

2.2. Chemical composition

The chemical composition (Si, Al, Na) of the remnant solution was analyzed by ICP-OES using a Perkin-Elmer Optimas 3000. The gel composition was calculated by using the starting content and the content in the remnant solution. Selected gels were analyzed as well for control.

2.3. X-ray diffraction

To determine the X-ray diffraction pattern, the hardened and dried material was ground under addition of iso-Propanol in a bar mill (McCrone-Micronizer, McCrone Ltd., UK) for about 1 min. This mill was used to avoid preferred orientation (texture) and the introduction of stress. X-ray diffraction patterns were collected using a Seiffarth X-ray powder diffractometer (Model TT3000) equipped with a Cu K α source ($\lambda = 0.1540598$ nm). A single crystal monochromator

in the diffracted beam path was used to acquire XRD patterns in Bragg–Brentano geometry, over a 2 Theta range of 4–70° with a step size of 0.03° (stepscan 3 s) by measuring a constant sample area at every angle. X-ray patterns were subsequently analysed using the software Analyze™.

2.4. FT-IR spectroscopy

A Biorad FTS 175 C spectrometer was used for infrared investigations in the measurement range 400–4000 cm^{-1} . The dried and ground samples were measured in a Diamond Micro-ATR cell with KRS5 crystal. Afterwards the spectra were ATR corrected using standard software.

2.5. NMR spectroscopy

Solid-state NMR experiments were performed with a Bruker Avance 300 spectrometer (magnetic field strength 7.0455 T, resonance frequency of ^{29}Si and ^{27}Al is 59.63 and 78.20 MHz, respectively). For the ^{29}Si MAS NMR spectra, the samples were packed in 7 mm zirconia rotors and spun at 5 kHz under an angle of 54°44'. The chemical shifts were recorded relative to external tetramethylsilane (TMS). Single pulse technique was applied with a pulse width of 4 μs . The repetition time was 30 s, and a typical number of scans were 1000. For the ^{27}Al MAS NMR spectra, the samples were packed in 4 mm zirconia rotors and spun at 15 kHz under an angle of 54°44'. The chemical shifts were recorded relative to external $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Single pulse technique was used with a pulse width of 3 μs . The repetition time was 2 s, and the number of scans was 1000. The signal patterns of the spectra were deconvoluted with the seasolve PeakFit™ software using a Gaussian–Lorentzian sum with about 90% Gaussian shape. The peaks were set to fixed widths in calculation.

3. Results and discussion

3.1. Influence of NaOH concentration (series A)

Fig. 1 summarizes the results of the solution chemistry at the start and within the remnant solution. For comparison purpose, the (diluted) remnant solution was recalculated on the volume of the starting solution. The yield as precipitated as aluminosilicate gel is shown in addition (above part of Fig. 1). It can be seen that the yield of aluminosilicate gel is very low at high NaOH concentration of 7.5 mol/l. The silicate and

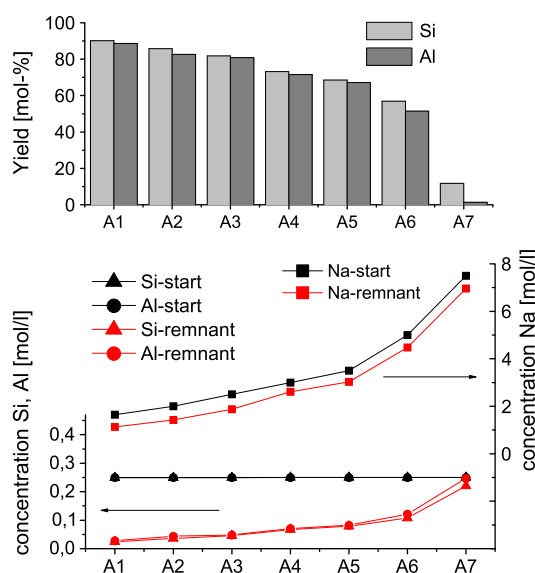


Fig. 1. Series A, concentration of starting and remnant solution as well as yield.

Table 1
Series A—chemical characteristics via solution chemistry.

No.	Starting solution			Within the aluminosilicate gel	
	$\frac{Si}{Al}$	$\frac{Na}{(Si + Al)_t}$	c_{NaOH} [mol/l]	$\frac{Si}{Al}$	$\frac{Na}{Al_G}$
A1	1	3.3	1.65	1.01	2.3
A2	1	4	2.0	1.04	2.8
A3	1	5	2.5	1.01	3.1
A4	1	6	3.0	1.02	2.2
A5	1	7	3.5	1.02	2.8
A6	1	10	5.0	1.11	4.0
A7	1	15	7.5	8	150

aluminate monomers remain stabilized within the solution instead of precipitating. Below a NaOH concentration of 5 mol/l the yield increases and reaches about 90 mol%. The Si/Al ratio in the precipitate (see Table 1) is almost 1.0 and thus identical to the Si/Al ratio of the starting solution. The gel A6 has a slightly higher Si/Al ratio of 1.1. This is seen more strongly for gel A7. Obviously the high pH stabilizes the aluminate monomers stronger than the silicate monomers. It has to be mentioned that due to the small difference between the concentrations of the starting solutions and the remnant solution, a small measurement fault will influence the calculated gel composition extremely strong (Table 1). Therefore, the composition of gel A7 has to be taken as indication (therefore, in italic style).

The dried gels were highly crystalline. The X-ray patterns are given in Fig. 2 for the low angle range $4^\circ \leq 2\theta \leq 20^\circ$. At this identical Si/Al ratio of 1.0 of the starting solutions – that resulted in gels with almost identical Si/Al ratio – different zeolites crystallized out of the gel depending on the pH of the starting solutions. At high NaOH concentration Sodalite (SOD) is preferred to build at this Si/Al ratio. If the NaOH concentration is lower than the Zeolite A (LTA) appears and again a lower NaOH concentration produces Zeolite X (Faujasite-type FAU).

All three zeolites (sodalite, faujasie, and zeolite A) are built from a sodalite cage (SOD-cage) formed by connected single four and six rings (SBU: S4R, S6R). The difference between them is the connection of the sodalite cages (see Fig. 3). In faujasite structure zeolites (zeolite X, Y, and natural faujasite), the SOD-cage is connected to four nearest neighboring SOD-cages through double T6-rings (D6R). In LTA, each SOD-cage is connected to six nearest neighboring SOD-cages through double T4-rings (D4R). In sodalite each SOD-cage is connected to six nearest neighboring SOD-cages through common T4-rings [23].

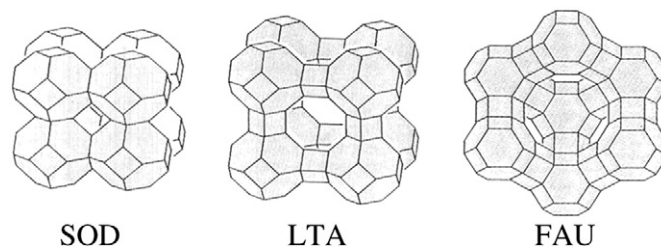


Fig. 3. Structure of zeolites SOD, LTA, FAU.

All these structural changes can also be followed by FT-IR spectroscopy (see Fig. 4). Significant bands are observed at $950\text{--}960\text{ cm}^{-1}$, which correspond to the T–O asymmetric stretching (Si–O and Al–O) of the (alumo-) silicate tetrahedra, and $450\text{--}460\text{ cm}^{-1}$, which correspond to the inner T–O bending vibration [24]. The wave number of these inner-tetrahedral vibrations is identical for the gel of series A as expected due to the identical Si/Al ratio that influences these bands.

The vibration in the range between 500 and 800 cm^{-1} are believed to give structural information about the secondary building units (SBU) in the zeolite [24,25]. It is obvious from Fig. 3 that gel precipitated in higher pH environment shows no vibration at 560 cm^{-1} , whereas the other bands tend to be identical ($665, 700, 735\text{ cm}^{-1}$). This band at 560 cm^{-1} corresponds to the vibration of double rings [24] (D6R and D4R) as existent in the faujasite and the zeolite A structure. The gel A3 ($Na/(Si + Al) = 5$) shows only little crystalline FAU structure (Fig. 2) but a clear double ring vibration band at 560 cm^{-1} coming from zeolite A.

3.2. Influence of Si/Al ratio on sol-gel reaction (series B)

Fig. 5 summarizes the results of the solution chemistry at the start and within the remnant solution. For comparison purpose, the (diluted) remnant solution was recalculated on the volume of the starting solution. The yield precipitated as aluminosilicate gel is shown in addition (above part of Fig. 5). The NaOH concentration remains almost identical in the starting and remnant solution. The concentration of silicate and aluminate changes depending on the Si/Al ratio of the starting solution. The gel B1, which starting solution is characterized by an oversupply of aluminate, only part of it reacts resulting in a yield of about 10 mol% Al. The yield of aluminate increases with decreasing aluminate concentration up to solution B3 (80 mol% Al) and decreases again to 40 mol% in solution B7. The yield

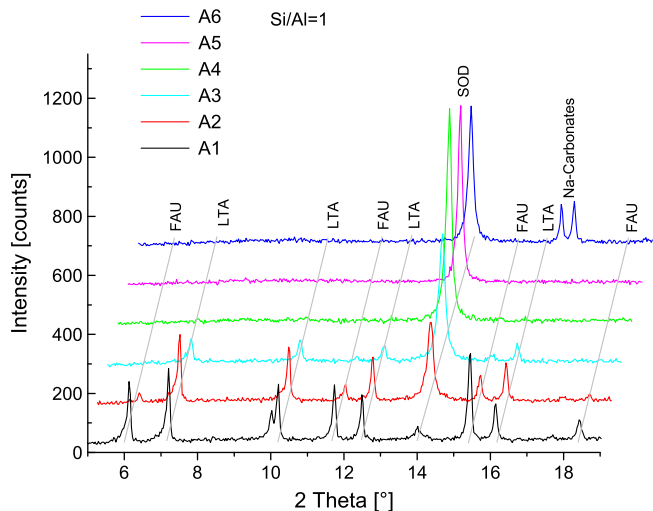


Fig. 2. X-ray diffraction pattern of gels with different NaOH content (Si/Al = 1).

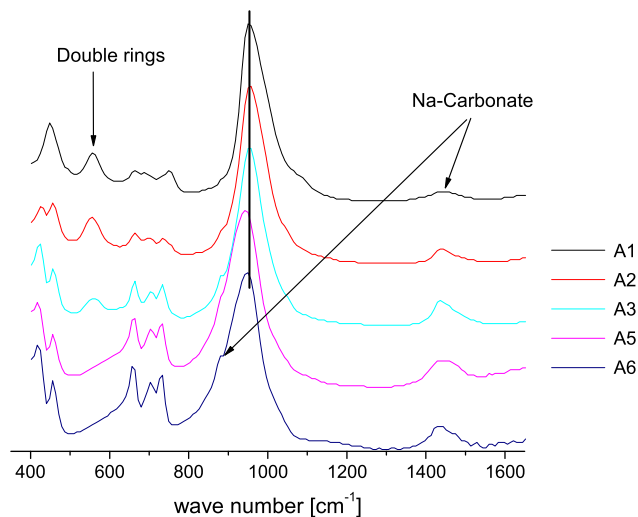


Fig. 4. FT-IR spectra of gels with different NaOH content (Si/Al = 1).

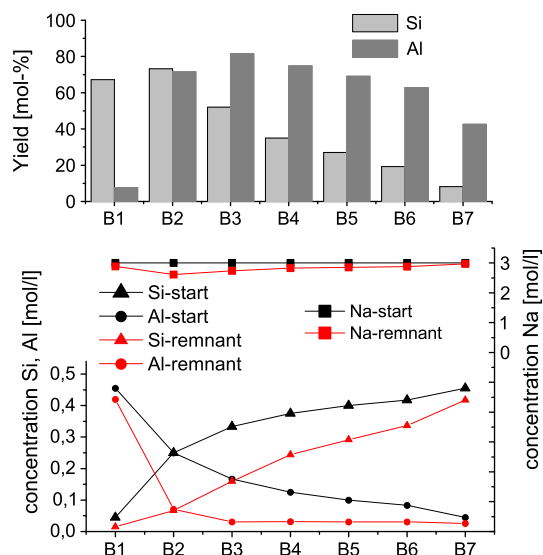


Fig. 5. Series B, concentration of starting and remnant solution as well as yield.

of silicate has its maximum at B2 (about 70 mol%) and decreases with increasing silicate content in the starting solution. The reason can be seen by looking at the aluminate concentration. The Al concentration in the remnant solutions B3–B7 appears to be identical. Obviously it is the maximal Al concentration remaining stable without no gel formation under these conditions. All aluminate above this concentration can be used for condensation. The other extreme is the remnant solution B1 therein the silicate concentration is rather low, dominating the amount of aluminosilicate gel that can precipitate.

The gels formed can be characterized by a slightly increasing Si/Al ratio in the gel with increasing Si/Al ratio in the starting solution. But the possible range seems to be limited. Table 2 summarizes the Si/Al ratios of the starting solution and the precipitated gel as calculated by the concentration of the starting and remnant solution. The Si/Al ratios of the aluminosilicate gel precipitated are in the range between 0.9 and 1.9. If the Si/Al ratio in the starting solution is close to one, the gel will precipitate in the same Si/Al ratio. Higher content of silicate in the solution increases the Si/Al ratio in the gel precipitated.

Gels with a low Si/Al ratio below 1.5 were obtained in crystalline state after drying at 80 °C. Higher Si/Al ratio does not lead to crystalline phase formation under the preparation conditions (Fig. 6). The results of X-ray diffraction presented in Fig. 6 show the formation of sodalite only for a Si/Al ratio of one. Higher Si/Al ratios prefer the formation of faujasite structure.

This can also be seen in the FT-IR spectrum presented in Fig. 7. The starting solution B1 (Si/Al=1) results in sodalite formation—no double ring vibration is seen at 560 cm⁻¹. The solutions B3 and B4 (Si/Al of solution: 2 and 3, respectively) show the significant vibration at

Table 2
Series B—chemical characteristics via solution chemistry.

No.	Starting solution			Within the aluminosilicate gel	
	$\frac{Si}{Al}$	$\frac{Na}{(Si+Al)_L}$	$\frac{Si}{Al}$	$\frac{Na}{(Si+Al)_L}$	$\frac{Si}{Al}$
B1	0.1	6	3.0	0.87	3.2
B2	1	6	3.0	1.02	2.2
B3	2	6	3.0	1.28	2.0
B4	3	6	3.0	1.40	1.8
B5	4	6	3.0	1.57	2.2
B6	5	6	3.0	1.52	2.3
B7	10	6	3.0	1.92	1.8

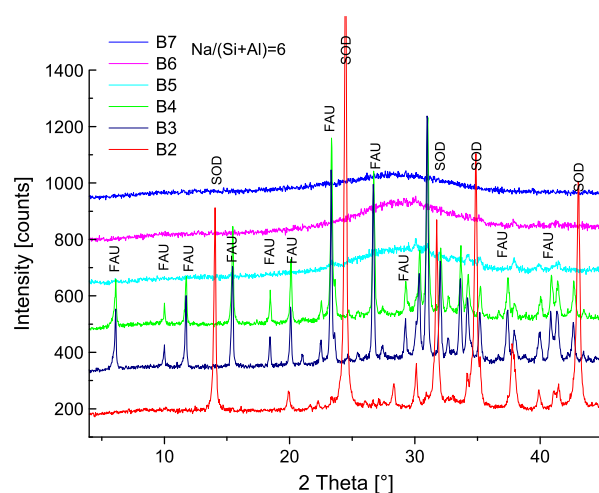


Fig. 6. X-ray diffraction pattern of gels with different Si/Al ratio ($Na/(Si + Al) = 6$).

560 cm⁻¹. The other FT-IR spectra show weaker bands typically for non-crystalline material. Therefore, it is difficult to say whether the double ring vibration is existent or not. The very weak but detectable band between 550 and 620 cm⁻¹ favors the evidence of the existence of few double ring structures with strongly distorted structure instead of the absence of them as Shigemoto pointed out [26].

The structural-insensitive bands of inter-tetrahedral vibration (asymmetric stretching around 960 cm⁻¹, symmetric stretching at 700 cm⁻¹, and bending between 420 and 460 cm⁻¹) are clearly visible in all spectra and do not change in size and position with lower crystallinity [24]. The Si/Al ratio influences the position of the asymmetric stretching band [24].

Further information on the short-range order of the silicate and aluminate tetrahedra is given by the NMR spectroscopy. Results of the ²⁹Si MAS NMR spectroscopy of four gels B2–B5 are shown in Fig. 8. The spectrum of sample B2 seems to consist of one main signal at a chemical shift of -85 ppm as typical for sodalite; two small peaks can be seen by chemical shifts of about -78 ppm and -89 ppm. The ²⁹Si NMR spectra of B3 and B4 look almost identical showing four peaks of different silicon environments. These peaks can be assigned to Q₄(1–4Al), whereas the Q₄(4Al) unit has a chemical shift of -84 ppm that is typical for the faujasite structure. The spectrum of gel B5 has a very low ordering as typical for amorphous gels.

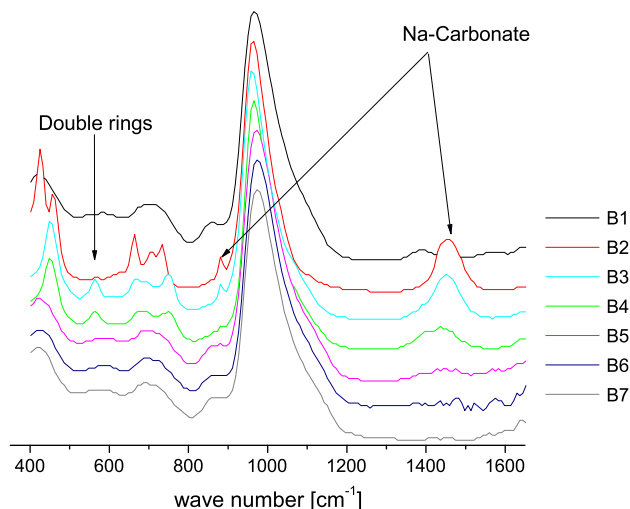


Fig. 7. FT-IR spectra of gels with different Si/Al ratio ($Na/(Si + Al) = 6$).

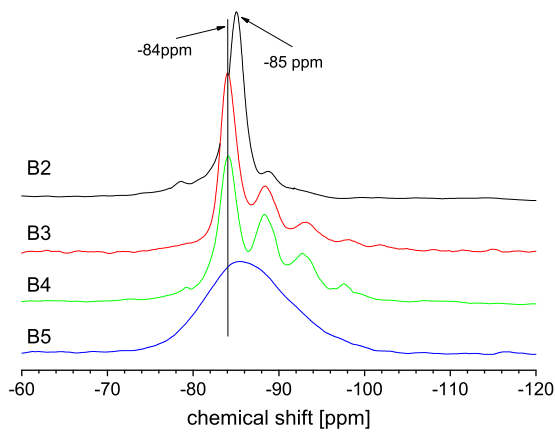


Fig. 8. ^{29}Si MAS NMR spectra of gels with different Si/Al ratio ($\text{Na}/(\text{Si} + \text{Al}) = 6$).

The ^{27}Al MAS NMR spectra of these four samples (B2–B5) are given in Fig. 9. All spectra consist of one single peak around 60 ppm showing the incorporation of tetrahedral aluminium in a silicate network surrounded by four silicate tetrahedra. The peak width increases with increasing Si/Al ratio, whereas the peak position decreases. Gel B2 (with a Si/Al = 1) has its peak at 63 ppm and Gel B4 at about 56 ppm. This is in good agreement with statements in literature that “the chemical shift should decrease if the number of Al atoms in the neighborhood of the central Al atom decreases” [27].

A deconvolution of the ^{29}Si NMR spectra was done in order to calculate the Si/Al ratio of the gel. The deconvolution result of gel B4 is shown in Fig. 10. The fit was done using the same peak shape and widths of the four Q_4 environments.

The results of gel B2 are shown in Fig. 11. Therein a different deconvolution method has to be used based on the known information from XRD measurements. The peak positions of the gel B4 were used for the faujasite structured gel. These peaks were fitted with identical peak shape and width. Additionally a peak for the sodalite was inserted as well as a peak for the signal at -78 ppm assigned to be a $Q_1(1\text{Al})$ unit. This dimer ($[\text{Al}(\text{OH})_3\text{OSi}(\text{OH})_3]^-$) is often described as preferred starting species for the condensation [18]. Both peaks were fitted with independent peak widths.

The deconvolution of Gel B5 that contained only one broad hump was deconvoluted with the known peak positions of gel B4 again using fixed calculated peak widths. The Si/Al ratio was calculated

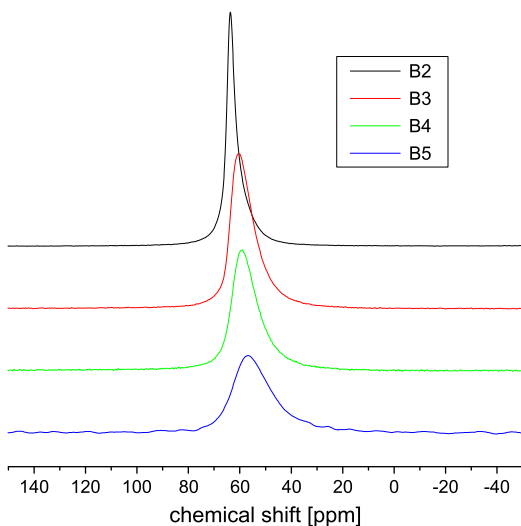


Fig. 9. ^{27}Al MAS NMR spectra of gels with different Si/Al ratio ($\text{Na}/(\text{Si} + \text{Al}) = 6$).

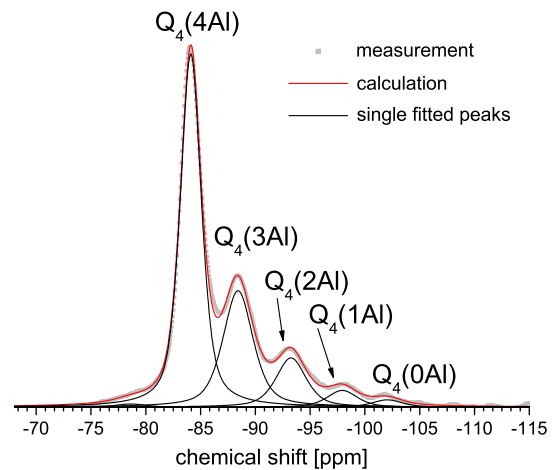


Fig. 10. Deconvolution of the ^{29}Si MAS NMR spectra of gel B4.

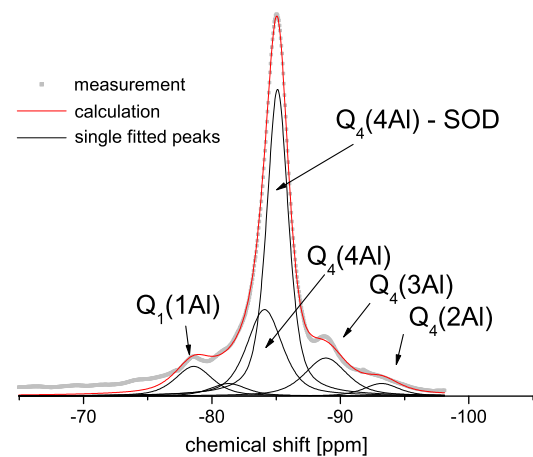


Fig. 11. Deconvolution of the ^{29}Si MAS NMR spectra of gel B2.

using the following formula according to the work of Engelhardt and Michel [28]:

$$\frac{\text{Si}}{\text{Al}} = \frac{\sum I_{Q_4(n\text{Al})} + I_{Q_1(1\text{Al})}}{\sum \frac{n}{4} I_{Q_4(n\text{Al})} + I_{Q_1(1\text{Al})}}$$

The calculated Si/Al values from NMR measurement and from chemical analysis of the gels are summarized in Table 3.

It can be clearly seen from Table 3 that the Si/Al ratio of the gel increases with increasing Si/Al ratio of the starting solution. Nevertheless, the calculated Si/Al ratios from the concentration measurement of the remnant solution seem to be not precise enough since there is a difference to the directly measured Si/Al ratio by dissolving the gel. The values from the chemical analysis of the gel are almost identical to the

Table 3
Series B–Si/Al ratio measured and calculated by different methods.

No.	Starting solution	Within the aluminosilicate gel		
		Calculated from remnant solution	Chemical analysis of the gel	NMR
B1	0.1	0.87	1.04	
B2	1	1.02	1.04	1.08
B3	2	1.28	1.24	1.21
B4	3	1.40	1.30	1.25
B5	4	1.57	1.37	1.25
B6	5	1.52	1.33	
B7	10	1.92	1.32	

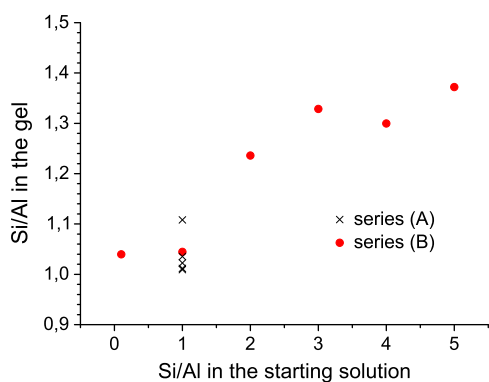


Fig. 12. Influence of Si/Al batch concentration and reaction time on the Si/Al ratio of the precipitated gel.

NMR result except of gel B5, which is difficult to deconvolute due to the shapelessness of the curve. Therefore, this value cannot be taken seriously and is therefore formatted in *Italic style*.

Comparing the measured Si/Al values as shown in Fig. 12 with data from literature [14–17], an influence of the contact time of the aluminate and silicate reactants as well as of the pH value on the Si/Al ratio in the precipitate becomes obvious.

In contrast to the investigation described there, in this investigation, the reaction was stopped after 24 h and a further incorporation of silicate species into the gel was not possible. Therefore, the results of this model investigation symbolize the beginning of a geopolymerization reaction and not the whole process. That corresponds with phenomena described in literature: Fernandez-Jimenez et al. [29] described the transformation of an aluminosilicate gel that was initially rich in Al (Si/Al~1) to an aluminosilicate gel with higher Si/Al during the alkaline activation of fly ashes. The formation of crystalline sodalite in the early reaction state was confirmed as well, the ^{29}Si NMR results therein underlay the formation of sodalite and zeolite A with signals at -86 and -88 ppm with an Si/Al ratio of about 1. Therefore, a very high NaOH concentration was probably existent in this phase of reaction promoting the sodalite formation followed by the formation of zeolite A. A longer reaction time led to the formation of gels with higher Si/Al ratios [29,30]. Fernandez-Jimenez et al. [29] concluded that aluminate-rich gel 1 was formed quickly and further connected by silicates forming a silicate richer gel 2 later on.

4. Conclusions

The investigation shows the variability of aluminosilicate gels formed from solutions with a different batch composition. Two series were investigated. Series A symbolizes the influence of NaOH concentration on the precipitation of aluminosilicate gel by a fixed Si/Al ratio of one. Series B investigated the influence of the Si/Al ratio of the starting solution on the aluminosilicate gel formation.

It can be concluded that both factors, the Si/Al ratio in the solution and the NaOH concentration, play an important role. The results of series A show clearly the preference of the NaOH concentration. Most of the series investigations were done at relatively high pH. All samples had the same Si/Al ratio of 1. The results show that the formation of sodalite is preferred only for very high NaOH concentration. Lower concentrations favor the formation of zeolite A or faujasite (zeolite X). Therefore the co-existence of all phases is possible, as described also for the syntheses route for zeolite X [31].

The results of series B show clearly the preference of the Si/Al ratio. An increase of the Si/Al ratio in the starting solution will result in an increase of the Si/Al ratio in the gel. The used conditions,

- the short contact time of 24 h as well as
- the usage of the same Na concentration in the Si and Al starting solution

resulted in relatively low Si/Al ratios of the condensed gels. The crystallization tendency decreased with increasing Si/Al ratio. Si/Al ratios a little higher than one favor the formation of faujasite structure. A longer contact time as well as the utilization of non-depolymerized silicate sources will provide higher Si/Al ratios in aluminosilicate gels [14].

Translating these results to a geopolymerization process the following conclusion can be drawn:

- Within the geopolymerization, the OH^- concentration will decrease due to the OH^- utilization in the dissolution process. But this decreasing NaOH concentration will result in different crystalline phases being formed. In the case of the reaction of metakaolin with NaOH zeolite X, A and sodalite might co-exist as often detected in hardened geopolymers based on metakaolin and NaOH [6].
- Different Si/Al ratios and concentrations are present in the pore solution during the geopolymerization depending on the composition of the reactive phase and the activator composition. Imaging the simple case of a reaction with NaOH the following scenario might be plausible: the Si and Al concentration in the pore solution increases by time. They might either have the same Si/Al ratio over time (in case of congruent dissolution of a single reactive phase) or changing (in case of incongruent dissolution or existence of different reactive phases with different dissolution kinetic). Upon a certain concentration level, an aluminosilicate gel will be formed, favorable with a low Si/Al ratio. Over time its Si/Al ratio will increase by incorporation of further silicate monomers. If the activator contains silicate solution, it will have an important effect on the Si/Al in the pore solution over time. At begin of the reaction a high concentration of silicate will be present. Typically these silicates are higher polymerized and will catch every aluminate monomer that is released into solution. Depending on the pH, the condensation time can be enlarged [14].
- If the different structures (e.g., double ring structures) are formed only during crystallization (long range order) or if they already exist in the aluminosilicate gel (short range order), that cannot be distinguished by the results presented. Nevertheless, the zeolite formation (crystallization) will be the thermodynamic end state of these aluminosilicate gels. Therefore, geopolymers will undergo structural changes to a thermodynamically end state as long a certain humidity is present in the hardened binder [32].

The solution composition in aluminosilicate systems strongly influences the amount, composition, and structure of precipitated aluminosilicate gels. All parameters investigated change during an alkaline activation/geopolymerization reaction. Therefore, the actual solution composition as provided by the dissolution of the reactive material in the alkaline activator mainly influences the geopolymerization.

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