



SOLUBILITY OF PRECURSORS AND CARBONATION OF WATERGLASS-FREE GEOPOLYMERS

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Abstract—Geopolymers have the potential to function as an environmentally friendly substitute for ordinary Portland cement, with up to 80% less CO₂ emission during production. The effect is best utilized for geopolymers prepared with amorphous silica instead of waterglass (Na_{2x}Si_yO_{2y+x}) to adjust the Si:Al ratio. The reactivity of the precursors with the alkaline activator affects the final mineralogical properties of the binder. The purpose of the present study was to investigate the amount of different phases formed during geopolymerization and to understand the quantitative evolution of carbonation during geopolymer synthesis by determining the solubility of metakaolinite and amorphous SiO₂ in NaOH at various concentrations. The solubility was studied by ICP-OES measurements. X-ray diffraction was used for qualitative and quantitative phase analysis of the geopolymers. The solubility of the precursors increased with calcination temperature of metakaolinite, reaction time for amorphous SiO₂, and at higher NaOH concentrations. Partial dissolution resulted in free Na⁺, which is a source for the formation of carbonates in the geopolymers. Thermonatrite occurred prior to trona formation in all samples.

Keywords—Amorphous silica · Carbonation · Geopolymers · Metakaolinite

INTRODUCTION

Geopolymer binders are inorganic polymers with a 3-dimensional framework structure of oligomers with various ratios of Si, Al, O, and OH⁻. The negative charge created by Si/Al substitutions is balanced by the cation of the alkaline activator solution. As well as supplementary cementitious materials (SCM), geopolymer binders are potential substitutes for ordinary Portland cement (OPC), and emit up to 40–80% less CO₂ than OPC during their production (McLellan et al. 2011; Davidovits 2013). The lower emissions are mainly due to the fact that the raw materials contain no structural CO₂. In contrast to SCM, which replace only a certain amount of OPC, geopolymers are ideally OPC-free binders. OPC is a hydraulic binder, while geopolymers are alkaline-activated binders. High-Ca and low-Ca/Ca-free types of alkaline-activated binders differ from one another (Herrmann et al. 2018) in that geopolymers contain little or no Ca. Aluminosilicates (fly ash, furnace slag, silica fume, or calcined clays) function as precursors and are activated with a highly alkaline solution (waterglass and/or highly concentrated alkali brines), which leads to a geopolymerization reaction (Davidovits 1991). The polymerization takes place in three successive reactions: the dissolution of the precursors in the alkaline activator solution; the reorganization and diffusion of monomers; and, afterwards, the formation of the 3-dimensional network and hardening of the binder (Heah et al. 2013; Esaifan et al. 2015).

The mechanical properties of geopolymers are comparable to those of binders prepared with OPC (Oh et al. 2010; Gao et al. 2014; Djobo et al. 2016; Yaseri et al. 2017; Hájková 2018). When calcined clay minerals such as metakaolinite (Si:Al = 1:1) are used as a precursor, adjusting the Si:Al ratio may be necessary to optimize the mechanical performance of the geopolymers (Duxson et al. 2005; Ozer and Soyer-Uzun 2015; Yaseri et al. 2017). A Si:Al ratio of 3:1 is given as a suitable ratio (Davidovits 1982; Yaseri et al. 2017). For this purpose, commercial waterglass solutions are mostly used for the production of geopolymers. The term waterglass describes aqueous solutions of the glassy frozen melts of alkali silicates, mostly sodium silicates, with varying SiO₂:M₂O (M: Na, K, or Li) ratios (e.g. Na₂SiO₃). In the production of geopolymers, however, waterglass accounts for most of the CO₂ emissions. The environmental benefit is reduced by commercial waterglass, therefore, in comparison with OPC cements. The usage of alkaline brines (e.g. NaOH) can lead to a reduction in CO₂ emissions of up to 50% and the Si:Al ratio can be adjusted by alternative SiO₂ sources (Mellado et al. 2014). Microcrystalline or amorphous SiO₂ can be obtained by combustion of organic materials or by technical manufacturing (e.g. silica fume). Rice husk ash appeared to be suitable for producing an alkaline-activator solution in combination with NaOH (He et al. 2013; Tchakouté et al. 2016). Furthermore, waste glass and sugar cane bagasse ash performed well in terms of geopolymer production (Tchakouté et al. 2016, 2017). The solubility of any other alternative SiO₂ sources in NaOH was not considered here. The

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solubility of SiO₂ in alkaline solutions was investigated only up to a pH value of 12 (Alexander et al. 1954; Crundwell 2017).

In addition, unreacted metakaolinite remains following the production of geopolymers (Rowles and O'Connor 2003; Duxson et al. 2005; Heah et al. 2013; Esaifan et al. 2015; Faisal et al. 2015), but usually the amount of unreacted material and the range of the solubility of metakaolinite in the alkaline activator have not been investigated further. The solubility of clay minerals increases with the concentration of NaOH (Xu and Van Deventer 2003). In addition, geopolymers produced with more concentrated NaOH show greater compressive strengths (Heah et al. 2013). Research on clay-mineral solubility in alkaline environments is carried out mainly in the field of nuclear-waste storage. The highest concentration of alkaline solution used is 4 mol/L (Chermak 1992; Bauer and Berger 1998; Cuevas et al. 2006).

The solubility of metakaolinite and SiO₂ at pH = 14 and at high NaOH concentrations should be investigated with respect to the amount of unreacted material left after geopolymerization. Unreacted material must be considered because of its impact on the compressive strength and carbonation (formation of carbonates) of geopolymers. While unreacted material can act as a filler and increase mechanical strength (Xu and Van Deventer 2000; Moosberg-Bustnes et al. 2004), a non-stoichiometric conversion of precursors and activator will lead to unreacted Na⁺ and carbonation. Carbonation was observed in various geopolymers (e.g. Fletcher et al. 2005; Zaharaki et al. 2010; Nikolov et al. 2017), but a quantitative description was not given.

The present study investigated geopolymers prepared using metakaolinite and NaOH but without commercial waterglass. The Si:Al ratio was adjusted by amorphous SiO₂. The objective was first to determine quantitatively the solubility of metakaolinite and amorphous SiO₂ and second to study the carbonation of geopolymers prepared with the initial Si:Al:Na ratio ranging from 1:1:1 to 3:1:1 with the expected incomplete dissolution of the precursors.

MATERIALS AND METHODS

Raw Materials

The Bavarian kaolin KBE-1 (grain size ≤20 μm) from Amberger Kaolinwerke Eduard Kick GmbH & Co. KG (Hirschau, Bavaria, Germany) was used to produce metakaolin by calcination. The calcination of KBE-1 was carried out at 480, 555, 615, 700, and 900°C in a L9/12/B180 furnace from Nabetherm (Lilienthal, Germany). These temperature steps were selected based on the dehydroxylation of kaolinite (beginning at the onset of DHX and ending prior to recrystallization) determined by thermal analysis (see supplementary material, Fig. S1). Samples were heated at a rate of 10 K/min in air without forced recirculation. No holding time at maximum temperature was applied. The raw material contained 93% kaolinite and small amounts of accessory minerals (Table 1). The metakaolin consisted mainly of metakaolinite, therefore. This term will be used through the manuscript to describe the samples.

Table 1. Proportions (wt.%) of mineral phases present in KBE-1

Phase	Kaolinite	Muscovite/Illite	Quartz	Anatase
	93 ± 0.5	5.5 ± 0.5	1.0 ± 0.5	<0.5

Kaolinite of KBE1 consists of 46–47 mass% ordered kaolinite and 50–51 mass% disordered kaolinite. The disordered kaolinite is characterized by 93% B/7% BC stacking sequences. 88% of BB sequences have no additional *b*/3 stacking errors and, thus, the kaolinite is low *b*-axis error-ordered. The Hinckley index of KBE1_M2 was 1.63, characteristic of a well ordered kaolinite (Izadifar et al. 2020).

Amorphous silica (Amosil® from HPF – The Mineral Engineers, Frechen, Germany; grain size ≤ 12 μm; Table 2) was added to adjust the Si:Al ratio of the geopolymers.

Ultra-pure NaOH solutions (Carl Roth GmbH & Co.KG, Karlsruhe, Germany) with concentrations of 10.79 mol/L (32%), 7.96 mol/L (25%), 6.1 mol/L (20%), 5 mol/L (16.88%), and 4 mol/L (13.9%) were utilized. Solutions with concentrations of 1 mol/L (3.8%), 0.1 mol/L (0.38%), and 0.01 mol/L (0.038%) were also prepared.

Analytical Techniques

Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out using an Optima 8300DV instrument (Perkin Elmer, Waltham, Massachusetts, USA). The measuring range of Si and Al concentrations in solution was 30 mg/L. Liquid samples were, therefore, diluted by a factor of 200.

For X-ray diffraction (XRD), a Bruker D8 Advance A25 diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with a LYNXEYE XE Detector (2.94° opening angle) was used. Powdered samples (<32 μm) and solid geopolymer discs were analyzed between 5 and 80°2θ or between 2 and 60°2θ. The step size was 0.02°2θ and the scan rate was 2 s per step. An automatic slit (primary side), Soller collimators of 2.5° (primary and secondary sides), and an automatic knife edge were used. The CuKα radiation (1.54 Å) was generated at 40 kV and 35 mA. For quantitative analysis, the Rietveld software *Autoquan* (GE Inspection Technologies GmbH, Boston, Massachusetts USA) was used.

Investigations with a scanning electron microscope (SEM) were conducted using a VEGA3 instrument (TESCAN, Brno, Czech Republic). First, solid discs of geopolymer were used without polishing to study the sample surface. For further investigations, cross sections of the discs were embedded in epoxy resin (Epoxy2000 from Cloeren Technology GmbH, Wegberg, Germany) and polished. The tests were complemented by EDX analysis (measuring field of 250 μm × 250 μm).

Table 2. Composition of amorphous silica – Amosil® (wt.%)

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO + MgO	Na ₂ O + K ₂ O
	99	0.3	0.03	0.03	0.03

Table 3. Composition of blends

Geopolymer sample	Si:Al ratio	NaOH concentration (mol/L)	s/l	l/s	Metakaolinite (g)	Amorphous silica (g)	NaOH (g)
GP1	1:1	10.79	0.89	1.13	5	—	5.63
GP2	2:1	6.1	0.86	1.17	3.25	1.76	5.85
GP3	2:1	7.96	1.07	0.94	3.25	1.76	4.68
GP4	3:1	4	0.8	1.24	2.45	2.65	6.34
GP5	3:1	5	0.98	1.03	2.45	2.65	5.23
GP6	3:1	6.1	1.16	0.86	2.45	2.65	4.41
GP7	3:1	7.96	1.44	0.69	2.45	2.65	3.53

EXPERIMENTAL PROCEDURE

Determination of Dissolution Characteristics

0.1 g of either raw KBE-1, metakaolinite, or amorphous SiO₂ was mixed with 5 g of NaOH solution, which is equal to a solid/liquid (s/l) ratio of 0.02. The NaOH solutions reflected a pH value ranging between 12 and 14. The samples were left on a shaking table for 24 h or 7 days. Afterward the samples were centrifuged for 25 min at 4347×g. 0.5 mL of supernatant was diluted in each case for ICP-OES measurement.

Geopolymer Production

The geopolymers were manufactured with the metakaolinite calcined at 700°C, to ensure fully dehydroxylated material (see supplementary material, Fig. S1). After calcination, the metakaolinite was ground manually and gently to destroy small aggregates which were formed during calcination. Metakaolinite has a natural Si:Al ratio of 1:1. The Si:Al ratio was increased to the supposed optimum of 3:1 by adding amorphous silica as a solid powder in various amounts (Table 3). The Na:Al ratio was fixed at 1:1 and, thus, the s/l ratio varied (Table 3). In preliminary tests, s/l ratios of between 0.8 and 2 yielded sufficient hardening and good workability. S/l ratios of <0.8 led to mixtures with very low viscosity and insufficient hardening. If the NaOH concentration was too high, its volume in the formulation was too low (s/l > 2) and workability was lost.

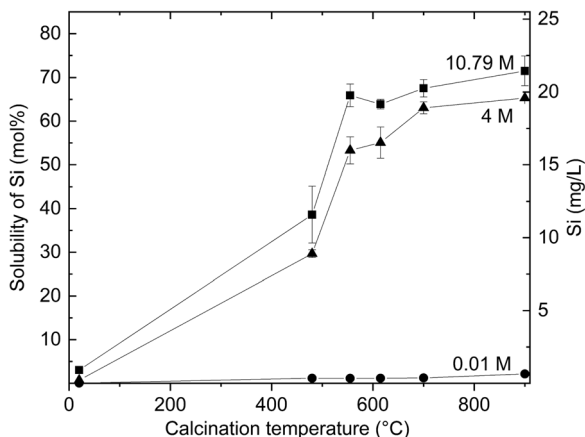


Fig. 1 Solubility of KBE-1 in NaOH (10.79 mol/L, 4 mol/L, 1 mol/L) as a function of calcination temperature (reaction time 24 h)

The solids were mixed with the NaOH solutions for several minutes at 10,000 rpm using a Roti-Speed-Stirrer (Xenox MHX/E from Proxxon, Wecker, Luxembourg) operated at 40 W. Next, the stirred material was placed on a vibration table (Vortex Genie 2 from Scientific Industries Inc., Bohemia, New York, USA) for several more minutes to avoid trapped air in the hardening samples. The hardening took place in open PE cylinders (from Kulzer GmbH, Hanau, Germany) with 30 mm diameter under ambient conditions (~21°C, ~50% relative humidity). Three days after preparation, the geopolymer discs were subjected to XRD for qualitative phase analysis. For quantitative analysis, powdered samples were prepared from a second set of geopolymer discs prepared in parallel. They were crushed after 1 day of hardening and ground gently after the second day. After 3 days, the samples were ground again and sieved (<32 μm). As an internal standard, 10 wt.% ZnO was added. XRD analysis of the powdered samples also started at a sample age of 3 days.

RESULTS AND DISCUSSION

Solubility of Metakaolinite and Amorphous Silica

Kaolinite and metakaolinite showed a congruent solubility of Si and Al (for solubility of Al see supplementary material, Fig. S2). Non-congruent solubility would lead to an excess or a

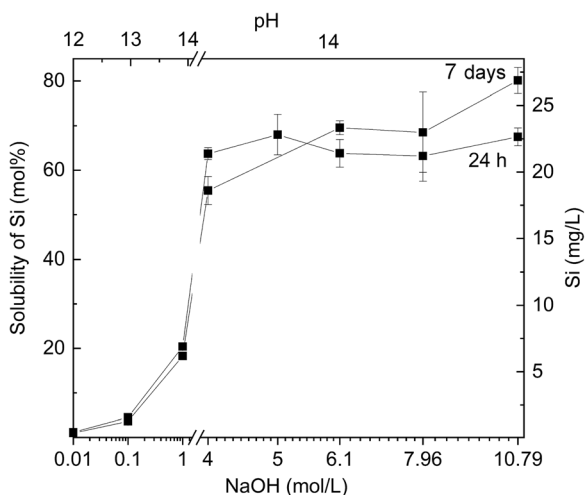


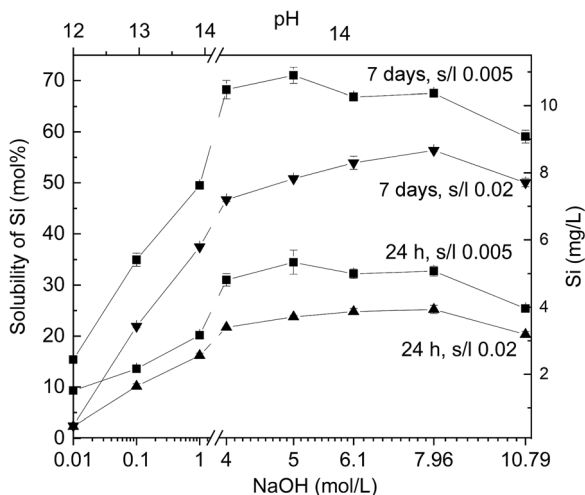
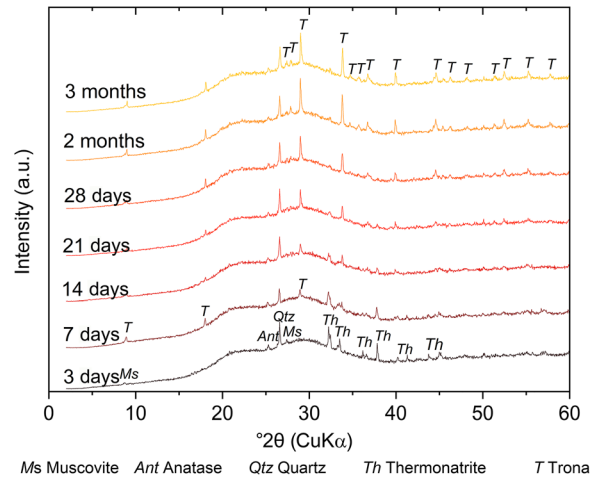
Fig. 2 Solubility of metakaolinite (KBE-1 calcined at 700°C) at various NaOH concentrations (reaction time 24 h and 7 days)

Table 4. Estimated amounts of free Na⁺ and thermonatrite

Geopolymer sample	Surplus Na ⁺ (mol)	Thermonatrite (wt.%)
GP1	0.015	11.2
GP2	0.010	8.2
GP3	0.011	8.5
GP4	0.008	7
GP5	0.007	6.4
GP6	0.008	7.5
GP7	0.008	7.9

deficit of Al in the geopolymer matrix. The samples that were not calcined presented the lowest solubility (<5%, Fig. 1). The solubility increased by >20% after the calcination temperature was increased from 480 to 555°C. At calcination temperatures of >555°C the increase in solubility declined (≤10%). The maximum solubility (e.g. 65% in 4 mol/L and 71.5% in 10.79 mol/L NaOH) was reached in sample KBE-1 calcined at 900°C (Fig. 1). This trend was observed in all NaOH concentrations. The solubility of samples calcined at 700 and 900°C differed only slightly (0–5%). Calcination to 700°C is sufficient, therefore, for geopolymer production.

The solubility of metakaolinite calcined at 700°C increased with the concentration of NaOH (Fig. 2). In 0.01 and 0.1 mol/L, solubilities of <5% were reached even after 7 days. The greatest solubility for the same metakaolinite was reached in 10.79 mol/L NaOH after 7 days (80%, Fig. 2). Note that none of the samples reached a solubility of 100%. At the beginning of geopolymer formation, the incomplete dissolution of metakaolinite in NaOH led to an excess of unreacted Na⁺ in the mixture. This unreacted Na⁺ formed carbonates (thermonatrite at first) from reaction with airborne CO₂. Theoretical amounts of free Na⁺ and thermonatrite (Table 4) were estimated based on the solubility of metakaolinite after 24 h (Fig. 2) and the assumption that the solubility of metakaolinite

**Fig. 3** Solubility of amorphous silica at various NaOH concentrations (reaction times of 24 h and 7 days)**Fig. 4** Qualitative phase analysis of GP7 over a period of 3 months

is not influenced by the dissolution of amorphous SiO₂ in geopolymer formulation. Excess Na⁺ is determined by the amount of metakaolinite (s/l) and its solubility in the specific NaOH in the geopolymer formulation. As solubility of metakaolinite in NaOH with a concentration of ≥ 4 mol/L varies only slightly, the samples with higher s/l (with the same amount of metakaolinite) must contain a larger amount of thermonatrite. GP2 has a calculated amount of thermonatrite of 8.17 wt.% (s/l 0.86) while that of GP3 is slightly larger with 8.50 wt.% (s/l 1.07). The same goes for GP4–7 (s/l 0.80–1.44). The slightly smaller amount of thermonatrite calculated for GP5 compared to GP4 is a result of the greater solubility of metakaolinite measured at 5 mol/L NaOH. The largest amount of thermonatrite at the beginning of the geopolymerization was found in GP1.

The solubility of amorphous silica was between 20 and 25% after 24 h and up to 55% after 7 days at a s/l ratio of 0.02 (Fig. 3). The solubility in 10.79 mol/L NaOH was slightly less than in 7.96 mol/L NaOH. By lowering the s/l to 0.005, the

Table 5. Si:Al ratios for GP, calculated by solubilities of metakaolinite and amorphous SiO₂

Geopolymer	Dissolved Si ≈ Al (metakaolinite) ¹ (mol)	Dissolved Si (amorphous SiO ₂) ^{1,2} (mol)	Total Si in GP ³ (after 24 h) (mol)	Si:Al in GP
GP1	0.675	–	0.675	1:1
GP2	0.638	0.25	0.888	1.39:1
GP3	0.632	0.25	0.882	1.4:1
GP4	0.637	0.5	1.137	1.79:1
GP5	0.680	0.5	1.18	1.74:1
GP6	0.638	0.5	1.138	1.78:1
GP7	0.632	0.5	1.132	1.79:1

¹ normalized solubility of metakaolinite² 0.25y Si (y = 1 or 2)³ x Si + 0.25y Si (x: normalized solubility of metakaolinite)

Table 6. First appearance of carbonates in geopolymer discs (determined by XRD)

	GP1	GP2	GP3	GP4	GP5	GP6	GP7
Occurrence of carbonates (determined by XRD) (days)							
Thermonatrite	3	7	3	7	7	7	3
Trona	14	14	7	14	7	14	7

solubility had already increased after 24 h. At 7 days, a maximum of 70% was reached in 5 mol/L NaOH (Fig. 3). Because the solubility of amorphous silica at a *s/l* ratio of 0.02 was only 20–25% in NaOH of 4–7.96 mol/L after 24 h, even less SiO₂ dissolution after 24 h could be assumed during geopolymer production with a much higher *s/l* ratio of 0.8–1.44. To estimate the resulting Si:Al of the geopolymer matrix after 24 h, however, a solubility of 25% was considered (Table 5).

Phase Composition of Geopolymers

All the geopolymers described in this study hardened, and those prepared with NaOH concentrations of >5 mol/L showed compressive strengths of a few MPa. Further study and the optimization of mechanical properties were not the aim of the present study, however.

The formation of carbonates during the early stages of hardening was evident from the appearance of white

efflorescence at the surface of the geopolymer discs and confirmed by XRD (Fig. 4). First, thermonatrite (Na₂CO₃·H₂O) and, shortly afterward, trona (Na₃(HCO₃)(CO₃)·2H₂O) were formed. For GP1, GP3, and GP7 the carbonation started after 3 days; for the other GP samples, carbonates first appeared at a sample age of 7 days (Table 6). While the amount of trona increased for up to 3 months, thermonatrite disappeared with time; after 28 days, thermonatrite could no longer be detected (Fig. 4).

In the powdered samples, small amounts of trona (1.13–3.59 wt.%) could be observed after 3 days in all geopolymers (Table 7). The reduction of thermonatrite over time, which was already detected in the discs, was confirmed with the powders. The largest amount of thermonatrite at the beginning of geopolymerization was calculated and observed in GP1 (theoretical amount = 11.19 wt.%; measured amount = 22.11 wt.%). The large deviation between the theoretical and measured amounts of thermonatrite for GP1 was explained by the larger *s/l* ratio in the geopolymer and, therefore, a larger surplus of Na⁺ than estimated. The measured amounts of thermonatrite in GP2 to GP6 were within the range of estimation and measurement error. The increasing amount of thermonatrite with increasing *s/l* could be confirmed at least for GP4 to GP6. The amount of thermonatrite measured in GP7 (5.28 wt.%) was less than the estimated amount (7.9 wt.%). The largest *s/l* ratio in GP7 of all samples could result in a denser fabric with trapping of free Na⁺ and hindered air exposure and, thus, reduced carbonation.

Table 7. Amounts of minerals present in powdered geopolymers (wt.% after 3 days, 28 days, and 3 months; measured by XRD and calculated using *Autoquan*)

	GP1	GP2	GP3	GP4	GP5	GP6	GP7
3 days							
Thermonatrite	22	8	7	5	7.5	8	5
Trona	3.5	2	3	1	1	2	1.5
Quartz	1.5	1	1	0.5	0.5	0.8	1
Anatase	1	0.5	0.2	0.1	0.1	0.1	0.1
Muscovite	1.5	1	3	2	2	2	2.5
Amorphous phase	71	87.5	85	92	89	87	90
28 days							
Thermonatrite	15	0	0	0	0	0	0.5
Trona	2	2	2	1	3	2	2
Quartz	1	1	1	0.5	1	1	1
Anatase	0.5	0.1	0.1	0.1	0.1	0.1	0.1
Muscovite	2.5	1	1	1	1	2	2
Amorphous phase	78	96	96	98	95	95	94
3 months							
Thermonatrite	0	0	0	0	0	0	0
Trona	2	2	2	1	3	2	2
Quartz	1	1	1	0.5	1	1	1
Anatase	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Muscovite	1	1	1	1	1	2	2
Amorphous phase	95	96	96	98	95	95	94

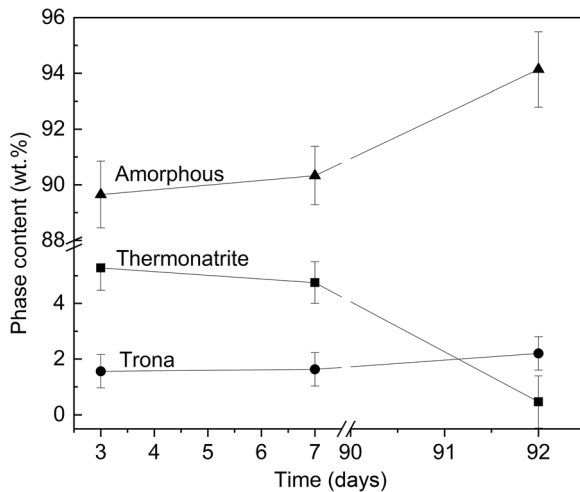


Fig. 5 Time-dependent change in mineralogical content of GP7 (from 3 days to 3 months)

While the quantity of thermonatrite decreased over time, the amorphous content increased (Fig. 5). The amount of trona remained approximately the same (variation of <1%). The decrease in the amount of thermonatrite and a nearly constant, small amount of trona in the powder samples, combined with the increase in amorphous phase, indicated that geopolymerization took place for far longer than 24 h. The continuing dissolution of metakaolinite led to the subsequent binding of free Na^+ and, therefore, a reduction of thermonatrite. After 28 days, GP1 still contained 15.13 wt.% thermonatrite, GP7 contained <0.5 wt.%. After 3 months, thermonatrite could be detected in none of the powder samples. After 28 days, the increase in the amorphous phase was marginal for GP2–7, but GP1 showed a significant increase until 3 months. Geopolymerization in the discs could have been inhibited by the fast hardening, but, in the solid samples, thermonatrite also disappeared and the amount of amorphous material increased over time.

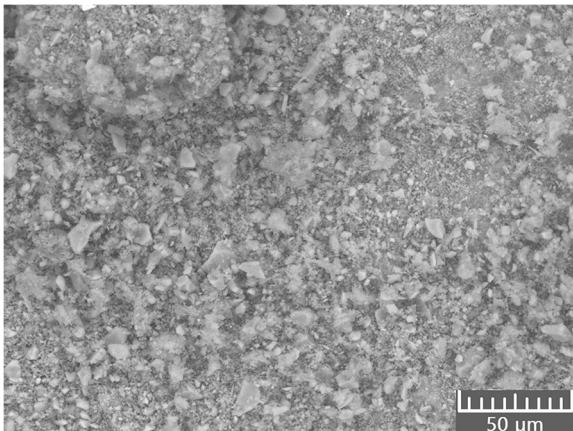


Fig. 6 SEM image of an air-exposed surface of GP4

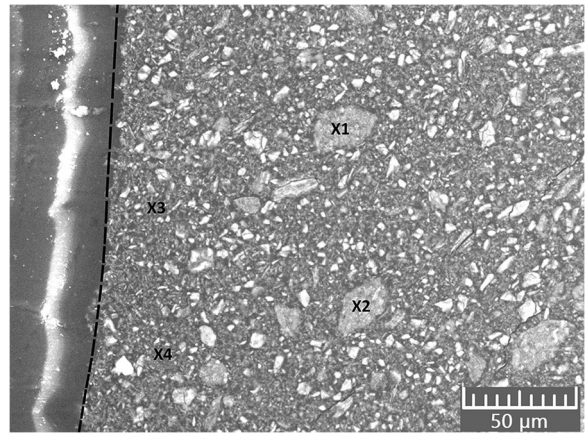


Fig. 7 SEM image of a polished section of GP4 (the dashed line marks the edge of the sample)

Microstructural Properties of Geopolymers

The unpolished samples showed a rough surface (e.g. GP4; 4 months; Fig. 6). The element ratios reflected the components added at geopolymer production (Na:Al 1:1 and Si:Al 3:1), but spots with a surplus of Na were observed up to Na:Al ratios of 2.25:1, indicating remaining trona deposits at the surface.

The micrographs of the polished cross sections revealed that the geopolymers consisted of a fine-grained matrix with a homogeneous distribution of bigger particles throughout the entire sample thickness. No reaction front of carbonates was detected at the surface of the samples (Fig. 7), by which the penetration depth of the carbonates within the geopolymer could be examined. The Si:Al ratio was ~1.5:1 for the bigger particles (X1 and X2, Fig. 7) and ~2.5:1 for the matrix (X3 and X4, Fig. 7). Both the particles and the matrix showed a Na:Al ratio of only 0.5:1, however. A few spots with Si:Al ratios up to 7:1 were found, which indicate agglomerated, unreacted SiO_2 attached to the geopolymer matrix. Aggregates of unreacted SiO_2 , together with a geopolymer matrix of about stoichiometric composition, showed that the raw materials were not converted completely into geopolymers.

SUMMARY AND CONCLUSION

Incomplete and/or delayed dissolution of metakaolinite in NaOH resulted in a surplus of reactive Na^+ of stoichiometrically mixed educts. Na^+ reacted with airborne CO_2 to form thermonatrite during the early stage of hardening. Ongoing exposure to the atmosphere of the freshly prepared geopolymer caused an increase in CO_2 incorporation during consumption of thermonatrite and the formation of trona. The progressive dissolution of the metakaolinite and geopolymerization reduced the formation of trona. Further studies are needed to show the influence of carbonation on mechanical strength and durability of geopolymers as well as on the pH value of geopolymers and its impact on steel corrosion. Furthermore, the s/l ratio at the same metakaolinite content had an impact on carbonation. The coupled influence on workability, extent of

thermonatrite formation, and mechanical strength also require study.

The incomplete dissolution of the amorphous silica added resulted in smaller Si:Al ratios within the geopolymers in relation to the initial stoichiometric calculations with no influence on carbonation but with a possible influence on mechanical strength. While a reduced Si:Al ratio reduces the mechanical strengths of geopolymers, amorphous SiO₂ fillers could increase the mechanical strength of construction materials by increasing bulk density and decreasing porosity. The combined influence needs to be studied in detail for practical applications. The presolution of amorphous SiO₂ in NaOH, e.g. at moderate temperatures, prior to mixing with metakaolinite should be considered.

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Compliance with Ethical Statements

Conflict of Interest

The authors declare that they have no conflict of interest.

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REFERENCES

- Alexander, G. B., Heston, W., & Iler, R. K. (1954). The solubility of amorphous silica in water. *The Journal of Physical Chemistry*, 58, 453–455.
- Bauer, A., & Berger, G. (1998). Kaolinite and smectite dissolution rate in high molar KOH solutions at 35 and 80°C. *Applied Geochemistry*, 13, 905–916.
- Chermak, J. (1992). Low temperature experimental investigation of the effect of high pH NaOH solutions on the Opalinus Shale, Switzerland. *Clays and Clay Minerals*, 40, 650–658.
- Crundwell, F. K. (2017). On the mechanism of the dissolution of quartz and silica in aqueous solutions. *ACS Omega*, 2, 1116–1127.
- Cuevas, J., De La Villa, R. V., Ramírez, S., Sánchez, L., Fernández, R., & Leguey, S. (2006). The alkaline reaction of FEBEX bentonite: a contribution to the study of the performance of bentonite/concrete engineered barrier systems. *Journal of Iberian Geology*, 32, 151–174.
- Davidovits, J. (1982). *U.S. Patent No. 4,349,386*. Washington, DC: U.S. Patent and Trademark Office.
- Davidovits, J. (1991). Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis and Calorimetry*, 37, 1633–1656.
- Davidovits, J. (2013). Geopolymer cement. *Geopolymer Science and Technics*, Technical Paper #21, Geopolymer Institute Library, France.
- Djobo, J. N. Y., Elimbi, A., Tchakouté, H. K., & Kumar, S. (2016). Mechanical activation of volcanic ash for geopolymer synthesis: effect on reaction kinetics, gel characteristics, physical and mechanical properties. *RSC Advances*, 6, 39106–39117.
- Duxson, P., Provis, J. L., Lukey, G. C., Mallicoat, S. W., Kriven, W. M., & Van Deventer, J. S. (2005). Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 269, 47–58.
- Esaifan, M., Rahier, H., Barhoum, A., Khoury, H., Hourani, M., & Wastiels, J. (2015). Development of inorganic polymer by alkali-activation of untreated kaolinitic clay: Reaction stoichiometry, strength and dimensional stability. *Construction and Building Materials*, 91, 251–259.
- Faisal, M., Muhammad, K., & Amin, W. (2015). Geopolymerization with bagasse bottom ash and china clay, effect of calcination temperature and silica to alumina ratio. *RSC Advances*, 5, 67814–67819.
- Fletcher, R. A., MacKenzie, K. J., Nicholson, C. L., & Shimada, S. (2005). The composition range of aluminosilicate geopolymers. *Journal of the European Ceramic Society*, 25, 1471–1477.
- Gao, X., Joussein, E., Michaud, P., & Rossignol, S. (2014). Role of the synthesis method on the microstructure and mechanical properties of metakaolin-based potassium geopolymers. *Ceramics-Silikáty*, 58, 215–222.
- Hájková, P. (2018). Kaolinite claystone-based geopolymer materials: Effect of chemical composition and curing conditions. *Minerals*, 8, 444.
- He, J., Jie, Y., Zhang, J., Yu, Y., & Zhang, G. (2013). Synthesis and characterization of red mud and rice husk ash-based geopolymer composites. *Cement and Concrete Composites*, 37, 108–118.
- Heah, C. Y., Kamarudin, H., Mustafa Al Bakri, A. M., Bnhussain, M., Luqman, M., Khairul Nizar, I., et al. (2013). Kaolin-based geopolymers with various NaOH concentrations. *International Journal of Minerals, Metallurgy, and Materials*, 20, 313–322.
- Herrmann, A., Koenig, A., & Dehn, F. (2018). Structural concrete based on alkali-activated binders: Terminology, reaction mechanisms, mix designs and performance. *Structural Concrete*, 19(3), 918–929.
- Izadifar, M., Thissen, P., Steudel, A., Kleeberg, R., Kauffhold, S., Kaltenbach, J., Schuhmann, R., Dehn, F., & Emmerich, K. (2020). Comprehensive examination of dehydroxylation of kaolinite, disordered kaolinite, and dickite: Experimental studies and Density Functional Theory. *Clays and Clay Minerals*, 68. <https://doi.org/10.1007/s42860-020-00082-w>.
- McLellan, B. C., Williams, R. P., Lay, J., van Riessen, A., & Corder, G. D. (2011). Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. *Journal of Cleaner Production*, 19, 1080–1090.
- Mellado, A., Catalán, C., Bouzón, N., Borrachero, M., Monzó, J., & Payá, J. (2014). Carbon footprint of geopolymeric mortar: study of the contribution of the alkaline activating solution and assessment of an alternative route. *RSC Advances*, 4, 23846–23852.
- Moosberg-Bustnes, H., Lagerblad, B., & Forssberg, E. (2004). The function of fillers in concrete. *Materials and Structures*, 37, 74.

- Nikolov, A., Rostovsky, I., & Nugteren, H. (2017). Geopolymer materials based on natural zeolite. *Case Studies in Construction Materials*, 6, 198–205.
- Oh, J. E., Monteiro, P. J. M., Jun, S. S., Choi, S., & Clark, S. M. (2010). The evolution of strength and crystalline phases for alkali-activated ground blast furnace slag and fly ash-based geopolymers. *Cement and Concrete Research*, 40, 189–196.
- Ozer, I., & Soyer-Uzun, S. (2015). Relations between the structural characteristics and compressive strength in metakaolin based geopolymers with different molar Si/Al ratios. *Ceramics International*, 418, 10192–10198.
- Rowles, M., & O'Connor, B. (2003). Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite. *Journal of Materials Chemistry*, 13, 1161–1165.
- Tchakouté, H. K., Rüscher, C. H., Kong, S., Kamseu, E., & Leonelli, C. (2016). Geopolymer binders from metakaolin using sodium waterglass from waste glass and rice husk ash as alternative activators: a comparative study. *Construction and Building Materials*, 114, 276–289.
- Tchakouté, H. K., Rüscher, C. H., Hirsch, M., Djobo, J. N. Y., Kamseu, E., & Leonelli, C. (2017). Utilization of sodium waterglass from sugar cane bagasse ash as a new alternative hardener for producing metakaolin-based geopolymer cement. *Geochemistry*, 77(2), 257–266.
- Xu, H., & Van Deventer, J. S. J. (2000). The geopolymerisation of alumino-silicate minerals. *International Journal of Mineral Processing*, 59, 247–266.
- Xu, H., & van Deventer, J. S. J. (2003). The effect of alkali metals on the formation of geopolymeric gels from alkali-feldspars. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 216, 27–44.
- Yaseri, S., Hajiaghahi, G., Mohammadi, F., Mahdikhani, M., & Farokhzad, R. (2017). The role of synthesis parameters on the workability, setting and strength properties of binary binder based geopolymer paste. *Construction and Building Materials*, 157, 534–545.
- Zaharaki, D., Komnitsas, K., & Perdikatsis, V. (2010). Use of analytical techniques for identification of inorganic polymer gel composition. *Journal of Materials Science*, 45, 2715–2724.

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