Aluminosilicate gels were synthesized by mixing metakaolin with potassium water glass solution. Mechanical strength values showed a strong increase between 25 and 100 h but decreased again above 200 h for aging at 25°C. A similar curve was observed during aging at 50°C but the maximum strength shifted to shorter time. Aging at 90°C and 130°C revealed only the decreasing wing in mechanical strength. The strengthening and weakening during aging at 25°C were further investigated by the molybdate method and infrared absorption spectroscopy. The results indicate basically that different time-dependent formations of two structural units dominate the mechanical properties: (i) A fast formation of longer (polymeric) silicate chains is enforced by the consumption of hydroxide in the solution of metakaolin up to about 25 h of aging. (ii) An aluminosilicate network grows slowly and encloses the chain-like units giving rise to an initial increase in strength within 100 h. During further aging the destruction of the polysilicate chains weakens the geopolymer. The destruction of the chain-like units is explained by the increasing amount of hydroxide produced during network condensation. The results imply that the same reactions occur for aging at a higher temperature but on faster time scales.

1. Introduction

There have been a lot of investigations concerning the structure, properties, and alteration mechanism during aging of aluminosilicate gels following two completely different aims, however. Historically, one aim has been the optimization for the crystallization of zeolites and later on for special material systems like mullite ceramics. The second aim concerns the optimization of the aluminosilicate gels for their use as building materials and for the term “geopolymer” was introduced. For an overview of the basic ideas and literature up to 2000 in this very special field, we may refer to the article of Davidovits.

The importance of a better understanding of the alteration of the micro- and nanostructures of the X-ray amorphous aluminosilicate gels for the interdependence of composition, structure, and properties has been reported in a number of papers including FTIR and MAS-NMR spectroscopic methods, e.g. MacKenzie and colleagues. Most of these studies, however, concern either the optimization of the chemical composition–mechanical strength relationship or focus on the spectroscopy of rather complex compositions and less on the question, of which nanostructural units are responsible for obtaining high strength or what underlying mechanisms are responsible for the often observed unfavorable weakening of certain geopolymer compositions during aging. Thus, it was our main aim to answer the question, as to what determines the properties of an aluminosilicate gel during aging and hardening, rather than to optimize its properties as suitable building materials. For this reason, we investigated the alkali activation of metakaolin as a very pure aluminosilicate source of Si/Al = 1 which could be observed as a model system for the processes that are involved during aging and hardening (“geopolymerization”). Using the combination of mechanical testing and infrared absorption spectroscopy together with investigations by the molybdate measurement—a method known to be sensitive to the characterization and quantification of monomer, dimer, and oligomer silicate units—a distinction between the silicate species responsible for the main variation in strength during aging could be achieved. Some preliminary results were recently presented in Conference contributions. Here, we describe our experiments and results concerning the aging of alkali-activated metakaolin of a special composition in more detail.

II. Experimental Procedure

The aluminosilicate (geopolymer) samples were prepared by stirring metakaolin (Metastar 501, Imerys, Cornwall, U.K.) in a solution of potassium water glass (KWG) (Silirit M60, Cognis Deutschland GmbH, Düsseldorf, Germany). The chemical composition of both raw materials is given in Table I. XRD pattern showed minor amounts (estimated <2% by weight) of impurity phases (Quartz, Muscovite) superimposed on the metakaolin-related broad diffraction peak in the range between 15° and 35° 2θ and centered at about 22° 2θ (CuKα-radiation). The minor phases do not change during alkali activation and aging.

The aging process was followed at 25°C between 0.5 and 750 h. The mass ratio of KWG to metakaolin was 15/9 according to a molar ratio of aluminum to potassium of about 1 and a Si/Al ratio of 2 as seen from Table II. The raw materials were mixed...
together manually for about 3 min forming a homogeneous slurry. The slurry was given in cylindric standard tiles for the mechanical testings (3 cm in length and 1.5 cm in diameter) and into cylindric PE-containers (2 cm in diameter and 1.2 cm in height), which were closed in order to hinder any evaporation of water during sample aging in a series of experiments repeated several times.

For the mechanical testing measurements were carried out for series of samples aged at 25°C, 50°C, 90°C, and 130°C, respectively. For characterization of the physical properties the relative flexural bending force, the 3 cm × 1.5 cm cylindrical aluminosilicate pieces have been measured on a universal testing machine (MEGA 2-3000-100 D, FORM+TEST Seidner and Co. GmbH, Riedlingen, Germany), by a specifically designed device for the measurement of small test pieces.

The molybdate method24–27 was used for the characterization of the condensation of silicate species in the aluminosilicate solid. The yellowish silico–molybdic acid complex was due to the reaction of silicate monomers and molybdic acid. Its rate of solidification - condensed fraction increased between 13 and 25 h from 18% to 39%, which can also be directly deduced from Fig. 3. Thus, the polymeric silicate fraction monotonously increased to 99% at 525 h curing. It is important to note that the amount of molybdate active species during aging showed a renewed increase up to about 39% of polysilicate units at 700 h. The molybdate active silicate fraction could be further subdivided into oligomeric silicate molecules and monomeric plus dimeric units. This shows (Fig. 3) that the oligomeric fraction slightly decreases during aging from 13 h (59%) to 25 h (57%). During further aging up to 525 h, the

### Table I. Composition of Raw Materials for Preparation of Aluminosilicates

<table>
<thead>
<tr>
<th>Source</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>H₂O</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water glass</td>
<td>19.3</td>
<td>24.5</td>
<td>56.2</td>
<td>0.7</td>
<td>1.52</td>
</tr>
<tr>
<td>Metakaolin</td>
<td>61.5</td>
<td>37.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Composition of the 15/9 Aluminosilicate Mixture of Water Glass and Metakaolin

<table>
<thead>
<tr>
<th>Mixture</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/9</td>
<td>843.0</td>
<td>340.2</td>
<td>367.5</td>
<td>849.3</td>
</tr>
<tr>
<td>Total mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar</td>
<td>4.2</td>
<td>1</td>
<td>1.2</td>
<td>14.2</td>
</tr>
</tbody>
</table>

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**Fig. 1.** The flexural force measurement of alkali-activated metakaolin cured at 25°C, 50°C, 90°C, 130°C, respectively.

**Fig. 2.** The compressive force measurement of alkali-activated metakaolin cured at 25°C, 50°C, 90°C, 130°C, respectively.
The molar ratio of aluminosilicate glasses follows a linear relationship on the Al DOSPM, density of states peak maximum, in the following) for which the peak position (called Ruesser, E. Mielcarek, J. Wongpa, C. Jaturapitakkul, F. Jirasit and W. Lutz, unpublished data) that the peak position of the asymmetric Si–O vibration observed in aluminosilicates depending on the Si/Al ratio. It has been proposed and shown in further systematic investigations (C. H. Ruescher, E. Mielcarek, J. Wongpa, C. Jaturapitakkul, F. Jirasit and L. Lohaus, unpublished data) (C. H. Ruescher, E. Mielcarek, J. Wongpa, C. Jaturapitakkul, F. Jirasit and W. Lutz, unpublished data). In the following, we shall concentrate on the development in DOSPM. Although the kinetics of at least two parallel reactions control the development of the mechanical properties.

The infrared absorption spectrum of the raw material metakaolin, KWG solution and KWG solution polycondensed by the addition of hydrochloric acid is shown in Fig. 4, together with the series of samples aged between 1 and 700 h at 25°C. Metakaolin shows the peak maximum of the asymmetric Si–O stretching frequency of the SiO2 units at about 1070 cm⁻¹, which could be related to polymeric sheet fragments from the SiO2 sheets in kaolinite. The KWG solution as used for alkali activation of metakaolin and the water glass solution polycondensed by acid treatment (PWG) show the peak maximum of the asymmetric Si–O stretching frequency at 1002 and 1044 cm⁻¹, respectively. For KWG, the position of the peak maximum can be related to a majority of monomeric/dimeric Q0/Q1 silicate units (Qn denotes Si–O–Si bonds of fourfold coordinated silicons, where n counts the number of bridging oxygen. Q4(nAl) denotes units with n bridging oxygen to Al and 4-n Si, as used below). For PWG, the peak maximum corresponds to a mixture of mainly chain-type Q2 units together with some higher condensed Q3 units. Therefore, it can be seen that the peak position of the asymmetric Si–O stretching mode of pure silicate systems largely vary depending on the distribution of Q0 (monomeric) to Q4 (fully polymerized) units. We may suggest an analogy to the peak position of the asymmetric Si–O vibration observed in aluminosilicates depending on the Si/Al ratio. It has been proposed and shown in further systematic investigations (C. H. Ruescher, E. Mielcarek, J. Wongpa, C. Jaturapitakkul, F. Jirasit and L. Lohaus, unpublished data) that the peak position (called DOSPM, density of states peak maximum, in the following) for aluminosilicate glasses follow a linear relationship on the Al molar ratio (x = 1/(1+Si/Al)) according to (Fig. 4)

\[ \text{DOSPM} = -257x + 1105 \ (\text{cm}^{-1}) \]  

Equation (1) was obtained by a linear regression to the DOSPM of pure SiO2 glass (Glass.1) glasses containing Si/Al ratios 12.1 (Glass.2), 4 (Glass.3), and 2.8 (Glass.4) (C. H. Ruescher, E. Mielcarek, J. Wongpa, C. Jaturapitakkul, F. Jirasit and L. Lohaus, unpublished data). This relation becomes remarkably close to that obtained by Fichtner-Schmittler et al. for faujasite-type zeolites covering a wide range of Si/Al ratios. Thus we can claim a close equivalence in DOSPM between Q4(4Al), Q4(3Al), Q4(2Al), and Q0, Q1, Q2 for the aluminosilicates and silicates, respectively.

The peak doublet around 1400 cm⁻¹ indicates the formation of hydrogen–carbonate species, which occurs most intensively in samples aged 1–13 h due to the reaction of hydroxide ions with CO2 when opened for their further investigation. Some amount is already observed in the water glass, which disappears during precipitation with HCl (Fig. 4). A significant increase in peak intensity at about 1640 cm⁻¹ (H2O bending) relative to a decrease at 560 cm⁻¹ (Si–OH) was observed during aging between 25 and 100 h, which has been related to the effect of strong network condensation. This observation and development of the peaks in the range between 550 and 800 cm⁻¹ are discussed in more detail elsewhere (C. H. Ruescher, E. Mielcarek, J. Wongpa, F. Jirasit and W. Lutz, unpublished data). In the following, we shall concentrate on the development in DOSPM. Although a strong superimposition of the various silicate and aluminosilicate units in the DOSPM occurs during aging, the following interpretation may be extracted in a straightforward manner. After stirring of the metakaolin with diluted water glass solution
and taking a spectrum after 1 and 5 h, the DOSPM was observed to have a maximum at about 1025 and 1010 cm\(^{-1}\), respectively (Fig. 4). This trend still continues to 13 h, which is indicated by the DOSPM at about 1007 cm\(^{-1}\). The shift to smaller wavenumbers can be related to the rapid dissolution of the metakaolin. However this process consumes hydroxide solution taken from the KWG. According to this fact, the water glass solution invariably polymerizes. This effect leads to the shift in the DOSPM up to about 1025 cm\(^{-1}\) observed for aging at 25 h. The increase in concentration of polymeric silicate units is observed in the molybdate activity (Fig. 3). Above 25 h, a systematic shift in the DOSPM occurs to 1020 cm\(^{-1}\) after 48 h, and further to 1016 cm\(^{-1}\) after 72 h. Further aging leaves the DOSPM largely invariant (Fig. 4). The DOSPM of 1016 cm\(^{-1}\) suggests a Si/Al ratio of about 1.9 using Eq. (1) (compare with Fig. 5), which closely corresponds to the Si/Al ratio as given by the mixture of the water glass solution with metakaolin. However, the increasing molybdate activity indicates structural changes that decrease the amount of polycondensed silicate units continuously during aging from 25 h to 525 h (Fig. 1). Therefore, the DOSPM, although stable at 1016 cm\(^{-1}\) for aging above 100 h, covers such structural changes. A support that the constant DOSPM during further aging above 100 h contains changing contents of silicate and aluminosilicate units can be further given by further acid-leaching experiments. A minimum shift in the DOSPM for acid-leached samples is observed for samples aged around 500 h (Fig. 6). This observation is in line with the results obtained by the molybdate method, although observing the highest contribution of molybdate activity was observed at 525 h aging. It may be noted that acid treatment within the molybdate method is followed by complexity of all silicate forming monomers, which leads to the characteristic yellow color. On the contrary, in conducting the acid leaching for the infrared absorption experiment it is the degree of polymerization of silicate units that leads to the shift in the DOSPM. Any meaningful changes in the DOSPM can only be observed in kinetically controlled leaching experiments interrupted at short times. In the limit, at longer time acid treatment it was observed that the DOSPM always tends to 1080 cm\(^{-1}\) for all samples, irrespective of aging time. Therefore, a minimum shift in the DOSPM for acid-treated samples indicates here the highest stability against acid, which can be assumed for a most suitable protection of Al–O–Si bonds within an aluminosilicate network. For comparison in the crystalline counterparts, zeolite X with Si/Al\(_{5}\) immediately becomes decomposed during acid treatment whereas zeolite Y with Si/Al\(_{2.5}\) withstands acid attack reasonably longer, which is a direct consequence of the increased amount of Si–O–Si bonds.\(^{32}\)

### IV. Summary and Conclusion

Alkali activation of metakaolin, for the mixtures used here and at 25°C, leads to the formation of an aluminosilicate network in a continuous reaction during aging between 25 and 525 h. The forming aluminosilicate network probably includes monomeric (Q4(4Al)) and dimeric (Q4(3Al)) aluminosilicate units, which were formed within the first 25 h and which comprise about 20% of the total silicate units. A further 20% of polycondensed silicate units are formed during aging between 13 and 25 h. These units originate necessarily from the water glass. The polycondensation of the water glass units can be observed by
the rapid shift in the DOSPM from 1007 to 1025 cm$^{-1}$ (Fig. 7) for aging between 13 and 25 h. On the other hand, the steep increase in strength coincides with the shift in the DOSPM from 1025 to 1016 cm$^{-1}$ which is dominated by the slowly growing aluminosilicate and probably crosslinking network covering the polysilicate chains. The weakening upon aging above 200 h is related to the decreasing fraction of polycondensed silicate. Therefore, the coexistence of two different structural units, i.e. the aluminosilicate network and silicate chains, in the right proportion and spatial distribution maximizes the mechanical strength. The destruction of the polymeric silicate chains can be understood as a consequence of network formation producing hydroxide solution. It can be suggested that all the oligomeric units become part of the aluminosilicate network during aging up to about 525 h (Fig. 3), which is supported by details in the infrared absorption behavior (Fig. 6). The driving force for the further reaction can be related to the fact that the aluminosilicate should tend to a Si/Al ratio of 1, thus leading to a disproportionation.

The observation of different trends in the DOSPM and in the molybdate activity could be achieved in the series of samples aged at 25°C within 96 h. From the change in strength behavior, it might be realized that any further separation of the various structural units by molybdate measurements and infrared absorption spectroscopy may be impossible. Therefore, we did not try any further investigation for the series of samples aged at 50°, 70°, and 130°C. However, we may suggest that the mechanical weakening is due to the breakdown of polymeric silicate chains as obtained for the series aged at 25°C. Our results show that sialate linking Al–O–Si$^{10}$ is responsible for the increase in strength but cannot hold strength on a high level invariably for long time. On the contrary it is the formation and long-term conservation of silicate chains that is crucial.

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References


