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# Ambient Temperature Drying Shrinkage and Cracking in Metakaolin-Based Geopolymers

Carsten Kuenzel,[‡,§] Luc J. Vandeperre,[§,*] Shane Donatello,[¶] Aldo R. Boccaccini,[§,‖,*] and Chris Cheeseman[‡,†]

[‡]Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

[§]Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

[¶]Eduardo Torroja Institute of Construction Science (CSIC), C/Serrrano Galvache, 4, Madrid 28033, Spain

[‖]Institute of Biomaterials, University of Erlangen-Nuremberg, Cauerstrasse 6, Erlangen 91058, Germany

**Ambient temperature drying shrinkage in metakaolin-based geopolymer pastes exposed to low relative humidity environments has been investigated. The effect of varying the geopolymer composition (water content, Si:Al ratio, Na:Al ratio, and $Na^+$ or $K^+$ cations) on the sensitivity to ambient temperature drying shrinkage is reported. The definition of "structural" water as being the minimum water content required that prevents contractions in the gel structure, and thus drying shrinkage from occurring, is introduced. From the results presented, it is clear that the ionic charge density of cations, the total quantity of cations, and the relative quantities and stabilities of cation: $AlO_4^-$ pairs in the paste are major factors affecting the sensitivity of pastes to ambient temperature drying shrinkage.**

## I. Introduction

GEOPOLYMERS have been the subject of a great deal of research interest, particularly during the last decade. Aluminosilicate materials such as metakaolin (MK), coal fly ash, and blast furnace slag, react to form a cementitious gel via a two-stage reaction in which poorly ordered and XRD amorphous aluminosilicates present in the material are dissolved in a highly alkaline medium and the paste cured at temperatures ranging from 20°C to 90°C. During setting and hardening, the dissolved aluminate and silicate groups polycondense into short-range ordered and cross-linked chains to form a cementitious gel that is responsible for the binding properties of these materials.[1,2]

Some advantages of specific geopolymer formulas over traditional Portland cements include the following: higher early compressive strengths,[3] improved fire resistance,[4] acid resistance,[5–7] and lower embodied $CO_2$ content.[8,9] Such properties have also led to geopolymers being considered as possible matrices for hazardous/nuclear waste stabilization and solidification applications.[10–16]

Despite the improved chemical consistency of MK as a starting material compared to fly ash and slag, MK geopolymers have not been seriously considered as alternative binders for mainstream construction products because it is inherently more expensive than industrial by-products and because the platelike structure, high specific surface area, and high electrostatic charge density of MK particles mean that excessive mixing water and/or high shear mixing are required to form flowable pastes. However, in nuclear and hazardous waste encapsulation applications, the higher cost of MK is not a major issue and chemical consistency of the product is of paramount importance.

Unlike calcium silicate hydrate (C–S–H) type gel formed during Portland cement hydration, MK-based geopolymers contain an alumino-silicate network consisting of tetrahedral coordinated $SiO_4$ and $AlO_4^-$ groups.[17,18] Such structures have a negative charge on the aluminum site which is balanced by $Na^+$ or $K^+$ cations from the alkali activation solution, forming N–A–S–H or K–A–S–H gel, depending on the counter ion present.[19]

The chemistry of MK geopolymerization has been extensively reported in the literature. The influence of the main experimental variables such as curing temperature, activation solution pH, and molar Si:Al:cation ratios on the MK geopolymerization process have previously been reported in the literature.[2,20–29] Only specific ranges of Si:Al, Na:Al, and Na:$H_2O$ ratios give alumino-silicate geopolymer gel structures desirable properties.[30] The role of the charge balancing cations is also very important. For example, it was found that Na-based MK geopolymers with higher Si:Al molar ratios within the range of 1.15–2.15, developed higher Young's modulus values but that the opposite trend was noted with K-based samples.[31,32]

Although resistance to thermal shrinkage of MK geopolymers exposed at temperatures above 700°C is in many cases far superior to Portland cements,[33–36] very little attention has been given to the wider issue of ambient temperature drying shrinkage.[37] The image in Fig. 1 shows a typical example of what can occur with many MK pastes subject to ambient temperature drying at low relative humidity.

Unlike Portland cement, water is not incorporated directly into the geopolymer gel product. Only a small percentage of the mixing water remains as interstitial water in the geopolymer gel.[38] This fact, combined with the high water requirement to mix MK-geopolymer pastes, means that there is a large excess of unbound or free water, which can evaporate from the hardened paste under low relative humidity conditions at ambient temperature.[36] Despite the lack of chemically bound water, it still plays an important role in structural stability. Excessive water loss under relatively normal environmental conditions can result in extensive shrinkage cracking of specimens.[37]
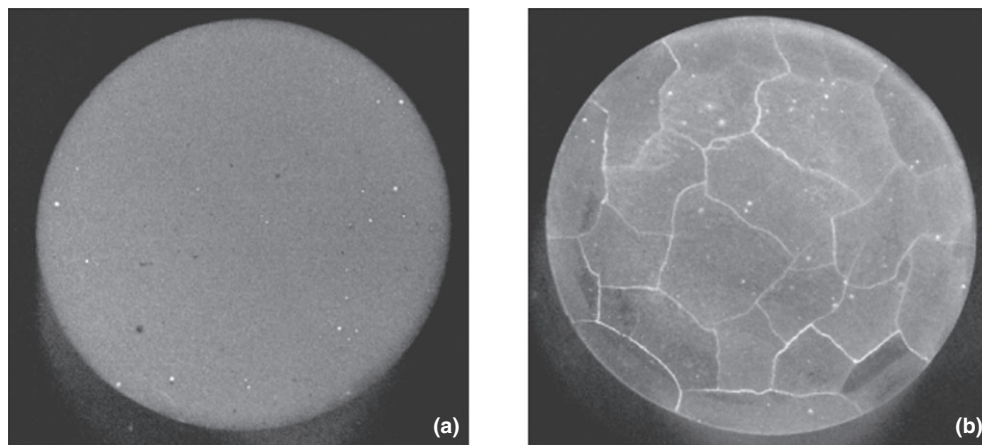
**Fig. 1.** Negative picture of cracking due to ambient temperature drying in a 30 mm diameter MK-geopolymer sample prepared with a molar ratio Al:Si:Na:H$_2$O of 1:2:1:8.5: (a) before drying and (b) after drying.

A possible explanation for geopolymer drying shrinkage and cracking is the generation of high capillary pressures between wet and dry areas of the micropore network, which has been reported to initiate crack propagation in the microstructure.[39] Attempts to avoid drying shrinkage and crack propagation have focused on modifying the pore structure to minimize capillary porosity, and controlling water loss during curing.[38,40]

The Na/K:Al ratio in particular could be important if loss of Na$^+$ or K$^+$ spheres of hydration has an important role in drying shrinkage. Another important factor could be the relative number of AlO$_4^-$ sites in the gel structure, which would be a direct function of the Si:Al ratio. Therefore, the aim of this work was to evaluate the effect of MK-geopolymer composition on drying shrinkage and cracking at ambient temperature.

## II. Materials and Methods

### (1) Materials

Commercially available metakaolin (Metastar 501; Imerys Minerals, Par, UK) with a mean particle size of 3.9 μm was used. XRF analysis showed the SiO$_2$ and Al$_2$O$_3$ contents to be 59.5% and 34.0%, respectively. Alkaline activation solutions were prepared from sodium silicate solution (26% SiO$_2$/8% Na$_2$O; VWR International, Radnor, PA), sodium hydroxide pellets (NaOH; Fischer Scientific, Hampton, NH), and from potassium silicate solution (23.4% SiO$_2$/11.5% K$_2$O; PQ Cooperation, Malvern, PA), potassium hydroxide pellets (KOH; Fischer Scientific), and deionized water.

### (2) MK-Geopolymer Paste Preparation

MK-geopolymer pastes were prepared with Al:Si:Na/K:H$_2$O ratios as shown in Table I. In the first set of samples (#1–4), the Al:Si:Na ratios was kept constant and the water content varied. It should be noted that to maintain good workability across all samples, the minimum H$_2$O molar ratio possible was 8, so the molar water range of 7.5–10.5 was chosen. In the second set of samples (#5–9) the Si:Al ratio was varied whereas the Al:Na ratio and water content were kept constant. In the third set of samples (#10–13) the Al to Na ratio was varied whereas the Si:Al ratio and water content were kept constant. In the final set (#14–17) the influence of the cation type (Na or K) was investigated.

Activation solutions were prepared by mixing appropriate quantities of silicate solution with water and either NaOH or KOH, and stirring for 24 h to reach equilibrium. The activation solution was then mixed with metakaolin by hand for 3 min, and cast into plastic (ABS) molds. A vibrating table was used during casting to remove air bubbles from samples,

**Table I. Molar Compositions of Samples**

| Sample | Al | Si | Na | K | H$_2$O |
|---|---|---|---|---|---|
| 1 | 1 | 2 | 1 | — | 7.5 |
| 2 | 1 | 2 | 1 | — | 8.5 |
| 3 | 1 | 2 | 1 | — | 9.5 |
| 4 | 1 | 2 | 1 | — | 10.5 |
| 5 | 1 | 1.6 | 1 | — | 8 |
| 6 | 1 | 1.8 | 1 | — | 8 |
| 7 | 1 | 2 | 1 | — | 8 |
| 8 | 1 | 2.2 | 1 | — | 8 |
| 9 | 1 | 2.4 | 1 | — | 8 |
| 10 | 1 | 2 | 0.7 | — | 8 |
| 11 | 1 | 2 | 0.85 | — | 8 |
| 12 | 1 | 2 | 1.15 | — | 8 |
| 13 | 1 | 2 | 1.3 | — | 8 |
| 14 | 1 | 1.8 | 1 | — | 8 |
| 15 | 1 | 2.2 | 1 | — | 8 |
| 16 | 1 | 1.8 | — | 1 | 8 |
| 17 | 1 | 2.2 | — | 1 | 8 |

which were then cured in sealed polyethylene bags at room temperature (22 ± 3°C). Samples were de-molded after curing for 2 days and allowed to continue curing within sealed plastic bags, for a total of 56 days. The total water content of the 56-day cured samples was determined by simultaneous TGA/DTA (STA 1500; Rheometric Scientific, Piscataway, NJ).

### (3) Drying Procedure

Samples cured for 56 days were subjected to a slow, incremental drying procedure. This involved storing the samples at ambient temperature and 45 ± 5% relative humidity, and then placing them in a fume cupboard for up to 2 days. When no further weight loss was recorded the samples were placed in a sealed desiccator containing silica gel. During the drying procedure the sample weight loss, shrinkage, and flexural strength were measured.

### (4) Physical and Mechanical Tests on MK-Geopolymer Pastes

Total water content and heat stability were determined using differential scanning calorimetry and thermogravimetry (TGA/DTA, STA 1500; Rheometric Scientific) at a heating rate of 2°C/min

Sample weights were measured at various times during the drying procedure. Drying shrinkage was determined by

measuring the change in length of 30 mm-long cylindrical samples of 15 mm diameter using a manual extensometer (Instron, High Wycombe, UK), with the final value derived from the average of five measurements.

Changes in effective molar water ratios remaining in samples during the drying process offered a useful way of normalizing data and identifying the critical point at which samples undergo ambient temperature drying shrinkage. Changes in the effective sample molar water ratio were calculated using the following equation:

$$New_{mwr} = Original_{mwr} x[(Total_{H_2O} - Lost_{H_2O})/Total_{H_2O}] \quad (1)$$

where $Original_{mwr}$ is the mixture design molar water ratio (i.e., 7.5, 8, 8.5, 9.5 or 10.5), $Total_{H_2O}$ is the total $H_2O$ content as determined by TGA analysis expressed as percentage of sample mass, and $Lost_{H_2O}$ is the sample mass loss during the drying period expressed as percentage of sample mass.

The flexural strength of samples (8 mm × 8 mm ×40 mm) was determined using a three-point bending test (Zwick/Roell Z2.5; Ulm, Germany). The distance of the major span was 30 mm and the crosshead speed during loading was 0.2 mm/min.

Dilatometry was used to measure the total dimensional changes (Netzsch 402 E; Selb, Germany) of a series of 8 mm cubic samples, which were prepared and heated to 1000°C in a He atmosphere at a heating rate of 10°C/min.

## III. Results

### (1) Effect of Water Content

*(A) Total Water Contents:* Representative DSC/TGA results for a geopolymer sample can be seen in Fig. 2. The DSC signal shows an endothermic peak between 20°C and 100°C, due to extensive water evaporation and a small exothermic hump at ~850°C due to sample sintering. The sample mass loss represented by the TGA data increases sharply up to ~35% at 150°C due to loss of free water and then only gradually up to ~37% at 600°C due to loss of interstitial water, in general agreement with the observations of Perera *et al.*[38] Total water contents of the samples was estimated by taking data for mass loss at 600°C. The total water contents for samples containing molar water ratios of 7.5, 8.5, 9.5 and 10.5 were 37.2%, 42.2%, 44.1%, and 45.9% of initial sample masses, respectively.

*(B) Resistance to Drying Shrinkage:* The effect of drying on 56 day old samples of 30 mm high, 15 mm diameter wide cylinders as a function of mix water molar ratio is shown in Figs. 3(a) and (b). Fig 3(a) shows that higher initial mixing water content allows for a greater absolute quantity of water to be removed before shrinkage starts. Fig 3(b)
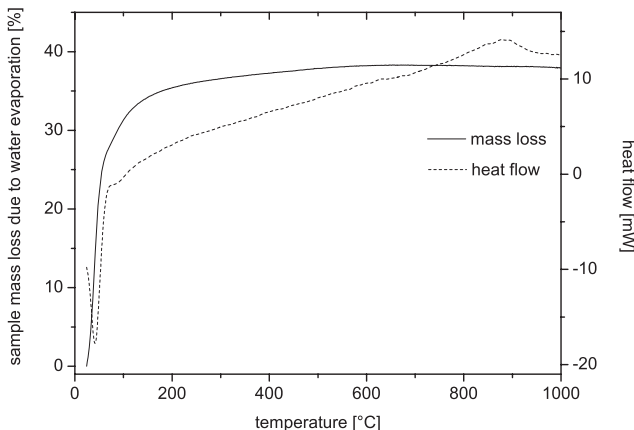


**Fig. 2.** DSC/TGA result for MK geopolymer paste with a molar ratio Al:Si:Na:$H_2O$ of 1:2:1:8. Note that total water contents were calculated by taking sample mass loss at 600°C.
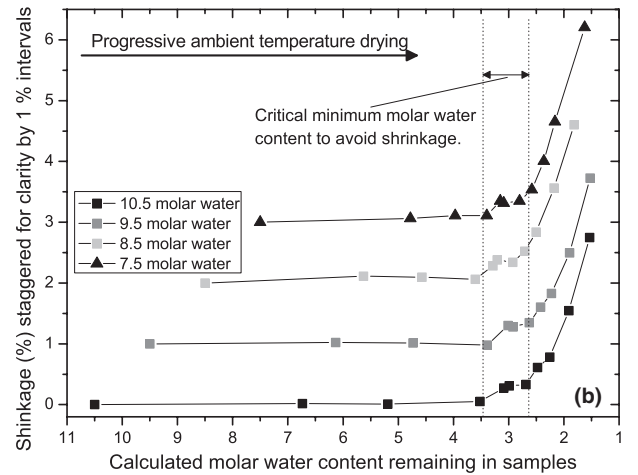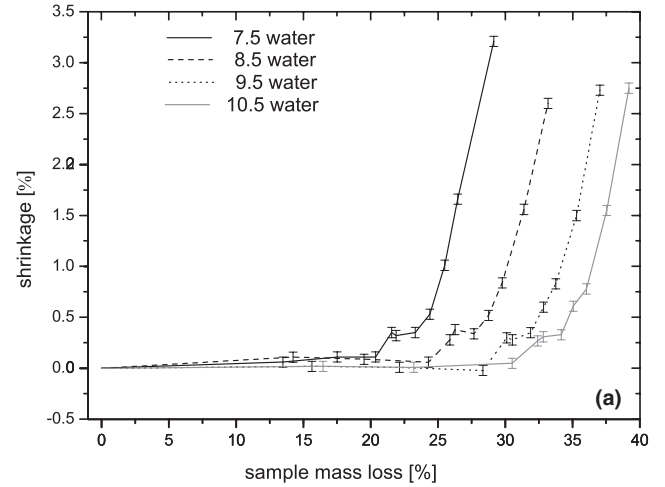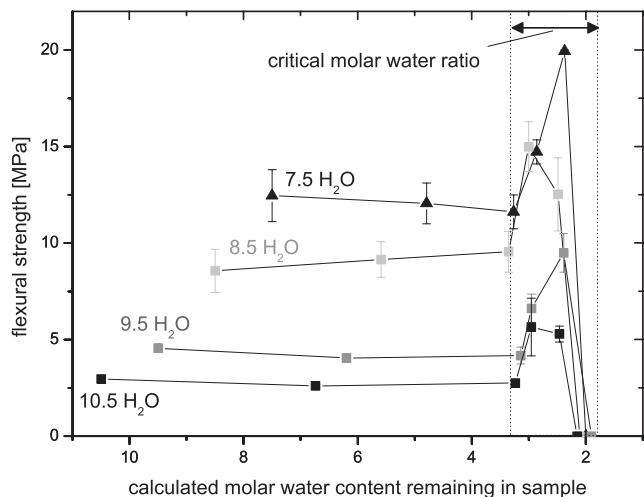


**Fig. 3.** Effect of water evaporation via ambient temperature drying on shrinkage of different MK geopolymers containing different initial molar water ratios: (a) absolute water losses and (b) water loss normalized to a remaining molar water ratio. Data points were averages of three results.

represents the same data as Fig. 3(a), but with water losses normalized to calculate the effective molar water ratio remaining in each sample as drying progresses. As the normalized data for each of the four pastes coincided so strongly, it was necessary to offset each of the data series by 1% shrinkage on the *y*-axis. In all samples, no or negligible shrinkage is noted until water content falls below a common minimum molar water ratio of ~3 in the 1:2:1:*x* system, where $7.5 \leq x \leq 10.5$.
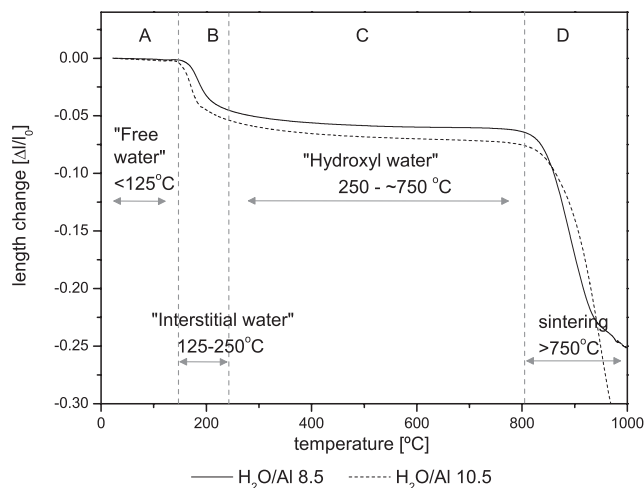
*(C) Resistance to Flexural Strength Loss on Drying:* The change in flexural strength of the geopolymer samples as water content decreases during drying is shown in Fig. 4. The trend in Fig. 4 was similar to that of Fig. 3(b), where sudden changes in flexural strengths occured in all samples as the effective molar water ratio approached 3, independent of the starting water content. It was expected that flexural strengths would decrease in line with the degree of shrinkage observed in samples. However, comparing the trends in Figs. 3(b) and 4 (a) sudden increase in flexural strengths was noted at the onset of drying shrinkage, before samples lost all structural intergrity. This unexpected behavior will be further discussed later.

*(D) Thermal Shrinkage:* Thermal shrinkage up to 1000°C for two samples with different water contents is shown in Fig. 5, with the data regions split into four sections as in Duxson *et al.*[36] Although thermal shrinkage is a useful test and an important property of many materials, we wish to point out that in the case of MK geopolymers, such data
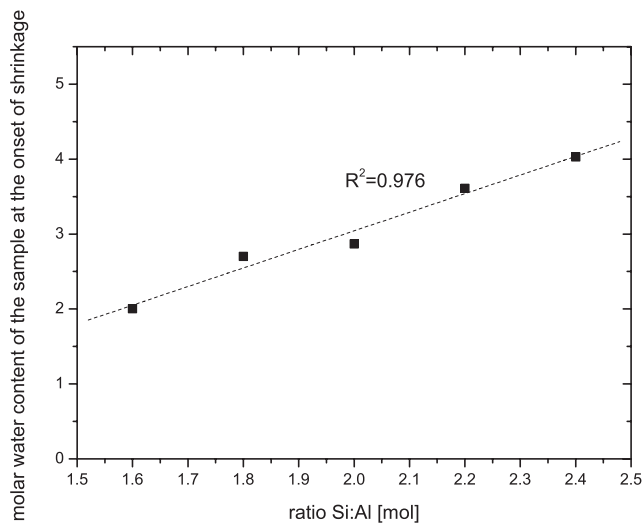
**Fig. 4.** Effect of water evaporation via ambient temperature drying on flexural strengths of 8 mm × 8 mm × 40 mm prismatic MK geopolymers containing different initial molar water ratios. Water losses were normalized to calculate the effective remaining molar water ratio. Data points were averages of five results.
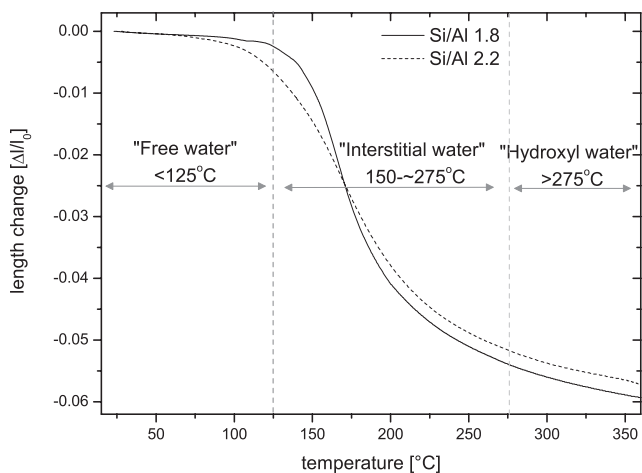


**Fig. 6.** Effect of molar Si to Al ratio on the minimum required molar water ratio to prevent the onset of ambient temperature drying shrinkage in an Al:Si:Na:$H_2O$ system of 1:$x$:1:8 composition where $x$ was varied from 1.6–2.4. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of three measurements.



**Fig. 5.** Dilatometric analysis up to 1000°C (10°C/min, He gas) of two MK pastes containing different mixing water molar ratios.



**Fig. 7.** Dilatometer results of MK geopolymers heated up to 360°C where the Si:Al ratio was altered in a 1:$x$:1:8 mix composition. Measured after 56 days curing.

can perhaps be misleading in that it suggests that ambient temperature drying shrinkage is not an issue. In Fig. 5, there is no appreciable shrinkage until a temperature of 150°C, despite that fact that these same samples lose all structural integrity by sufficient drying at ambient temperature. However, this is simply due to the nature of the thermal shrinkage tests, which require samples to be heated at relatively rapid rates to be practical. The heating rate of 10°C/min used here does not permit the free water to evaporate completely before a temperature of between 150°C and 200°C had been reached. In future work, perhaps it would be more appropriate to conduct dilatometry tests at a constant temperature when examining the first shrinkage event. At this point, the first of two shrinkage events occurred. This first event has been attributed to capillary strains in the sample following the loss of free water.[33,36]

The MK geopolymers started to sinter at ~800°C.[36] Sintering and densification provoked a significantly higher degree of shrinkage in the sample with an initial 10.5$M$ water content than the sample with 8.5$M$ water, consistent with the increased initial porosity that would be expected in the higher water content paste.

### (2) Effect of Si/Al Ratio on Drying Shrinkage

Figure 6 shows the influence of Si:Al ratio on the critical amount of water that can be removed before the onset of ambient temperature drying shrinkage. In contrast to the effect of the initial water content, altering the Si:Al ratio does change the minimum water molar ratio required in pastes to prevent shrinkage.

Applying arbitrary distinctions of "free water," "interstitial water," and "hydroxyl water" as water lost at <150°C, 150°C–300°C, and 300°C–600°C, respectively,[36] there are some clear differences in the response of samples with different Si:Al ratios in the dilatometry results shown in Fig. 7. The data show that the lower Si:Al ratio sample was more resistant to shrinkage following the loss of "free water" in agreement with the improved resistance to ambient temperature drying shrinkage shown in Fig. 6. However, this does not translate to better resistance to thermal shrinkage following the loss of "interstitial and some hydroxyl water," where the opposite effect of Si:Al ratio was noted.

In a study by Duxson *et al.*[36] it was observed that improved thermal shrinkage with increasing Si:Al ratio could possibly be

**Fig. 8.** Effect of molar Na to Al ratio on the critical minimum molar water content needed to prevent the onset of ambient temperature drying shrinkage in an Al:Si:Na:H₂O system of 1:2:x:8 composition. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of three measurements.
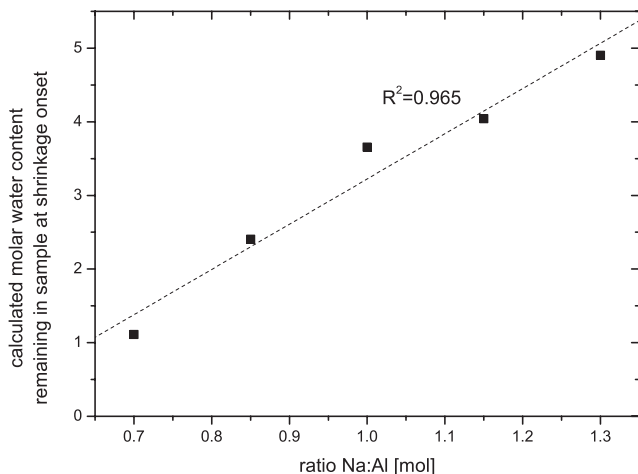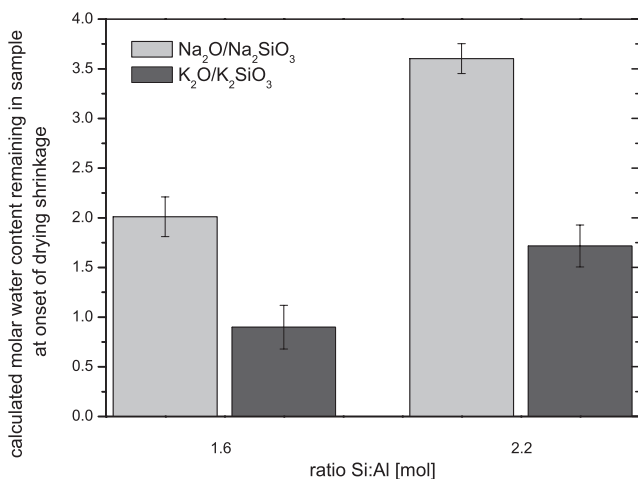


**Fig. 9.** Effect of Na versus K on the critical minimum molar water ratios required to prevent the onset of ambient temperature drying shrinkage of samples at two different Al:Si ratios. Samples were cured for 56 days in sealed plastic bags in an Al:Si:Na/K:H₂O system of composition 1:x:1:8. Data points are averages of three measurements.

attributed to higher Young's modulus for the higher silica content samples, meaning that they would be better able to resist a given capillary strain. However, the authors only offered this explanation for changes between molar Si:Al ratios of 1.15 and 1.65, which may not be relevant to these samples (molar Si:Al ratio of 1.6–2.4). Despite this, experimental data in the literature suggest that Young's modulus would increase as the molar Si:Al ratio increased up to a molar Si:Al ratio of 2.15.[31] At ratios above 2.15 a decrease of the Young's modulus has been measured.[41] However, since Young's modulus data are not presented for our samples, such an explanation would be speculative.

### (3)   Effect of Na/Al Ratio and Na/K Ions on Drying Shrinkage

Figure 8 illustrates the effect of changing the Na:Al molar ratio on the minimum molar water ratios required to prevent the onset of ambient temperature drying shrinkage. It is clear that the Na:Al ratio has a strong effect on sensitivity to drying shrinkage over the range studied. Within the Na:Al molar ratio range of 0.7–1.3, no optimum ratio was found.
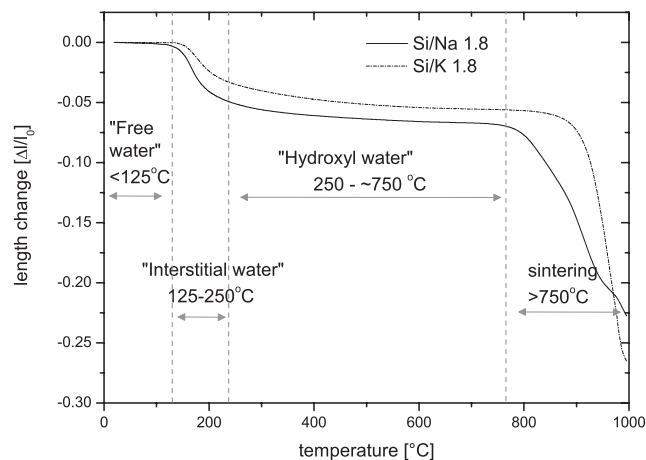


**Fig. 10.** Dilatometer results of geopolymers with an Si:Al ratio of 1.8:1 using Na or K ions to balance the negative aluminate charge. Samples were cured for 56 days in sealed plastic bags prior to measurement.

Instead, sensitivity to drying shrinkage decreased linearly with decreasing Na content.

Two batches of samples were repeated using K- instead of Na-based activator. Although the data are limited, in Fig. 9 it appears that the K cations allow for significantly lower molar water ratios to be accommodated prior to the onset of ambient temperature drying shrinkage, all other factors being equal.

A comparison of the thermal shrinkage behavior measured using dilatometry of Na- and K-based geopolymers (of 1:1.8:1:8 composition) is shown in Fig. 10. The data show that the K-based sample exhibited a significantly smaller degree of shrinkage following the loss of "free water," "interstitial water," and "hydroxyl water." Sintering and densification began at a higher temperature with the K-based sample, but on continued heating, provoked a larger overall shrinkage, indicating that the K sample had a more porous microstructure. This final observation is in contrast to that reported by Duxson *et al.*[42] although the fact that the samples were cured at 40°C for 20 h whereas the samples in the present work were cured at ambient temperature may be important.

### IV.   Discussion

The evidence presented here provides a strong case for arguing that the onset of drying shrinkage occurs only when the sample moisture content falls below a characteristic minimum content. The characteristic minimum water content required to prevent shrinkage was affected differently by variations in the respective Al:Si, Na:K ratios and Na/Si/Al:H₂O ratios. A discussion, of how changing the sample mix compositions may affect this characteristic minimum water requirement is presented.

### (1)   Effect of Changing Molar Water Ratio

*(A)   On the Onset of Drying Shrinkage:*   Changing the starting water molar ratio did not appreciably change the critical minimum water content required to prevent drying shrinkage [see Fig. 3(b)]. The main difference was that, in samples with higher initial water contents, more water had to be removed prior to reaching the critical minimum water content [see Fig. 3(a)]. This suggests that the drying shrinkage mechanism is relatively independent of total sample porosity and gel density, since the initial molar water ratio would significantly affect these properties. It also suggests that a fixed amount of what could tentatively be termed "structural" water is present in all samples and it is the loss of this water which brings about the onset of shrinkage. The

precise quantity of this "structural" water required is more likely to be a function of gel structure, which in turn is affected directly by the Si:Al and Na:Al molar ratios.

It is worth noting that all the sample molar water ratios were somewhat higher than the bare minimum possible to produce a workable paste. Perhaps with significantly lower molar water ratios of ~5.5 as reported elsewhere,[36] different effects would be noted due to much denser gel structures. However, to apply the wide range of Si:Al and Na:Al ratios used in this study, it was necessary to have a minimum water content that could be adapted to all sample mixes. The minimum molar water ratio that could be applied to all samples with straightforward mixing and casting was 8 and the range studied in this section was varied around that number (from 7.5 to 10.5).

The water lost before drying shrinkage occurs is arbitrarily referred to as "free water." Since this water is not chemically bound, it can simply be removed from the open macro-pore network without creating any capillary pressure in the micropore network. However, when the free water content reaches zero, further water loss provokes shrinkage.

*(B)   On the Onset of Flexural Strength Loss:*   The data presented in Fig. 4 very closely reflect the trends in Fig. 3(b), implying a strong correlation between drying shrinkage and changes in mechanical properties. One point of interest is that in the drying shrinkage results, there is a step immediately after the onset of drying shrinkage which suggests that the microstructure is partially resisting further shrinkage. The point at which this step occurs in drying shrinkage correlates to a sudden increase in flexural strength. One possible explanation for these observations is that the shrinkage mechanism causes a uniform physical contraction in the gel microstructure which, albeit only briefly, brings about an increase in flexural strength. Further drying then induces more shrinkage and then the sample loses its structural integrity.

However, it should be added that these trends were noted with small, 8 mm × 8 mm × 40 mm samples. Flexural strength tests during the drying procedure were repeated with larger specimens (25 mm × 25 × 80 mm—data not included) and no such increase in flexural strength or step in drying shrinkage was observed. Therefore, these effects must be attributed to sample size specific effects, allowing for an initial uniform, crack-free, shrinkage event in small samples, but not in larger ones.

### (2)   Effect of Changing the Si:Al Molar Ratio

The Si:Al ratio is a crucial factor in the formation of MK-geopolymer gels from the very initial moments of dissolution. In terms of mechanical properties, the ideal molar Si:Al ratio is generally regarded to be around 2. To increase the molar Si:Al ratio in MK generally means increasing the sodium silicate content in the activator solution at the expense of NaOH. In a recent geopolymerization simulation study by White *et al.*[43] the presence of soluble silica was determined not only to decrease the degree of reaction with MK particles, but to produce a more homogeneous microstructure.[43,44] Up to a certain point this appears to be beneficial on mechanical properties, but beyond that point, further soluble silica has a detrimental effect. Decreasing the molar Si:Al ratio to ≤ 1.4 was shown by ^{27}Al NMR, to lead to a reduction in Al incorporation into the gel structure. However, at Si:Al ratios ≥ 1.65, no unincorporated $AlO_4^-$ was found.[45]

To ensure that poor $AlO_4^-$ incorporation into the gel would not be a major issue, the Si:Al ratio was only varied between 1.6 and 2.4 in this study. Increasing the relative content of Si relative to Al in MK pastes within this range caused samples to become less resistant to drying shrinkage. More specifically, the critical minimum water content, or "structural" water, necessary to prevent drying shrinkage, increases linearly with increasing Si content (see Fig. 6).

The higher sensitivity to drying shrinkage of pastes that are expected to be denser (according to the literature higher molar Si:Al ratios in this range tend to form denser gels) is perhaps somewhat contradictory. However, it was shown that increasing the Si:Al ratio from 1.15 to 2.15 caused ^{2}H MAS NMR spectra to broaden progressively, possibly indicating that the content of "structural" water increases with increasing Si:Al ratio.[45] This would support the observations noted in this study. The increased gel formation expected at higher molar Si:Al ratios and the associated denser microstructure may also cause an increase in the total volume of capillary-sized porosity, which in turn may be responsible for the higher sensitivity to drying shrinkage.

Another way of interpreting this trend is to consider that the minimum "structural" water, required to prevent shrinkage, decreases as the relative Al content increases. The Al content is likely to affect the gel structure and the distribution of aluminate groups in the aluminosilicate gel polymer. An increase in aluminate group density in gel structures could perhaps result in more restricted environments where the hydration water of $Na^+$ ions is not permitted as illustrated in Fig. 11. Such an interpretation implies that the spheres of hydration of $Na^+$ cations could be a significant part of the "structural" water considered here.

### (3)   Effect of Changing the Na:Al Molar Ratio

The original role of $Na^+$ ions is to facilitate a highly alkaline medium in which the metakoalin can dissolve. It is widely



Increase of molar Si:Al ratio

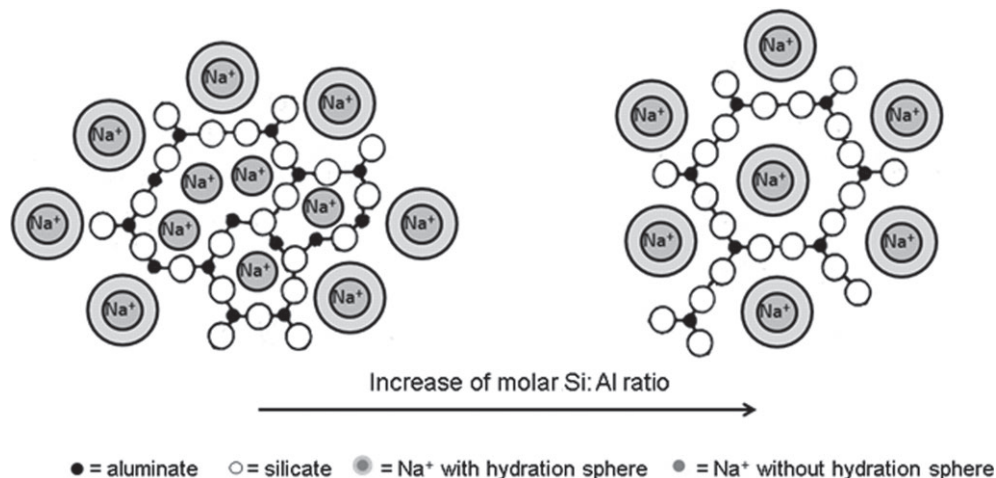● = aluminate    ○ = silicate    ◉ = Na⁺ with hydration sphere    • = Na⁺ without hydration sphere

**Fig. 11.**   Schematic structure of geopolymers with a molar Si:Al ratio lower 2 (left) and a molar Si:Al ratio higher than 2 (right).

accepted that these ions act as charge balancing cations to negatively charged tetrahedral $AlO_4^-$ groups formed in the cementitious gel. These ions are not considered to be chemically bound, but can be leached out[15] and potentially replaced by other ions.

Stoichiometrically and experimentally, a Na:Al molar ratio of 1 is generally considered to be ideal. An excess of Na, when added as NaOH, as was the case in these experiments to maintain a constant Si:Al ratio, would increase the alkalinity of the paste, which is important for the initial dissolution stage. However, with Na:Al ratios > 1, theoretically there is little obvious benefit to the presence of excess $Na^+$ ions in hardened pastes from a chemical point of view.

The excess $Na^+$ ions clearly have a negative effect on resistance to ambient temperature drying shrinkage as shown in Fig. 8. Perhaps unexpectedly, there is no optimum resistance to drying shrinkage around Na:Al ratio of 1. Instead, a directly proportional relationship exists between the Na:Al ratio and the minimum molar water ratio permitted in pastes to avoid drying shrinkage over the range of 0.7–1.3 studied.

The fact that this relationship is linear, despite the myriad differences to samples that could be caused by more or less alkaline mix compositions, suggests that the total Na content is a highly significant factor in determining the important "structural" water content. Again, by "structural" water, we mean the minimum molar water ratio required to prevent drying shrinkage. Following this argument, the data imply that a fraction of this calculated "structural" water could be due to spheres of hydration for alkali cations to maintain low ionic charge densities in the pore network solutions.

### (4) Effect of Changing the Cation from Na to K

The principal difference between Na and K ions is that the larger $K^+$ ion presents a relatively lower charge density and thus, in an aqueous environment, creates a sphere(s) of polar water molecules around the ion that are comparatively easier to remove than with a $Na^+$ ion. This is supported by the lower free energy of hydration for $K^+$ ions ($\sim 75$ kcal/mol) than for Na ($\sim 95$ kcal/mol).[46]

Although it is debatable whether or not the $K^+$ ion represents advantages over the $Na^+$ ion in terms of being able to better stabilize the $AlO_4^-$ charge, the more weakly bound hydration sphere water in $K^+_{(aq)}$ ions should allow for the ion to more closely approach the $AlO_4^-$ site. Compelling $^{39}K$ MAS NMR evidence has shown that in a mixed K/Na system, $K^+$ is preferentially absorbed at $AlO_4^-$ sites than $Na^+$.[47] At the macro structural level, there are some clear differences noted by replacing Na with K on compressive strength and Young's modulus.[32]

Careful analysis of XRD data from K-based MK geopolymers heated at various temperatures using the pair distribution function method showed that there is a small relocation of the $K^+$ ions in the paste structure following heating beyond 300°C.[48] An interesting idea for further work would be to repeat such a study, but with Na- and Cs- based samples and to compare the relative relocations following heating or ambient temperature drying shrinkage. Differences in dislocations following the removal water, but prior to sintering, could reveal differences in the intimacy of cation:$AlO_4^-$ ion pairs.

In terms of resistance to ambient temperature drying shrinkage, Fig. 9 clearly shows that the replacement of Na by K significantly reduces the critical minimum molar water ratio required to prevent drying shrinkage. The improved resilience of K-based geopolymers in the 1:2:1:8 mix compositions may be directly or indirectly related to the improved stability of the $K^+$:$AlO_4^-$ pair. As with the Na:Al ratio comments mentioned above, it appears that "structural" water content is strongly related to the total hydration sphere water requirements of the alkali cations. To stabilize the ionic

charge density of a $K^+$ ion to a given level, would require less hydration sphere water than an equivalent $Na^+$ ion. Following this trend, it would be expected that Cs-based geopolymers would present even better resilience to ambient temperature drying shrinkage.

### V. Conclusions

The very common, but little reported phenomenon of ambient temperature drying shrinkage of MK geopolymers has been investigated in this work. The authors use the term "structural" water to identify the critical minimum water contents, normalized as molar water ratios, required to prevent the onset of shrinkage. The principal aim of the work was to determine the effect of geopolymer mix composition on the sensitivity to such drying shrinkage and, therefore, on the "structural" water content.

The initial molar water ratio in a 1:2:1:$x$ system where $x$ was varied from 7.5 to 10.5 did not affect the critical minimum "structural" water required to prevent shrinkage.

Flexural strengths generally correlated very well with drying shrinkage, although in the small samples used in this study (8 mm × 8 mm × 40 mm) an initial uniform shrinkage can occur which is associated with an initial increase in flexural strength. Further drying beyond this point led to more shrinkage and a complete loss of flexural strength, as expected. In tests repeated with larger samples (25 mm × 25 mm × 80 mm) no such intermediate increase in flexural strength was noted.

Increasing the molar Si:Al ratio of the geopolymers system increased the quantity of "structural" water required to prevent shrinkage (within Si:Al ratios of 1.6–2.4). According to the literature, an increase in molar Si:Al ratio in this region is expected to increase the degree of MK dissolution, gel formation, and the density of the resultant gel microstructure. However, such changes only increased the sensitivity of pastes to drying shrinkage. Possible reasons to explain this increase are the increased structural water due to higher gel quantities, the possible increase in capillary porosity with increased gel formation, and/or changes in the $Na^+$:$AlO_4^-$ ion pairs caused by changes in the distribution of aluminate groups in the gel structure.

Increasing the Na content dramatically increased the quantity of "structural" water required to prevent shrinkage. This implies that the hydration spheres of $Na^+$ cations play a significant role in maintaining the structural stability of pastes.

Replacing $Na^+$ ions with $K^+$ ions decreased the minimum required "structural" water. We believe the improvement associated with $K^+$ ions is due to its lower charge density and thus more weakly bound hydration sphere water (relative to $Na^+$) that result in the cation:$AlO_4^-$ pair being more stable with $K^+$.

Overall, the work presents strong evidence that the hydration sphere water of cations and consequently the ionic charge density of cations, the total quantity of cations, and the stability of cation: $AlO_4^-$ pairs in the paste are the major factors affecting the sensitivity of paste samples to ambient temperature drying shrinkage.

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