

# Ambient temperature drying shrinkage and cracking in metakaolin-based geopolymers

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## ABSTRACT

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<sup>+</sup> vs K<sup>+</sup> cations) on the sensitivity to ambient temperature drying shrinkage is reported. The definition of “structural” water as being the minimum water content required to prevent 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:  $\text{AlO}_4^-$  pairs in the paste are the major factors affecting the sensitivity of pastes to ambient temperature drying shrinkage.

**Keywords:** geopolymer, metakaolin, drying, shrinkage, cracking

## 1. INTRODUCTION

Geopolymers, also often referred to as alkali activated cements, 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 20-90°C. During setting and hardening, the dissolved aluminate and silicate groups poly-condense 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].

The general trend seen in the literature with these materials is that MK based binders are referred to as “*geopolymers*” and fly ash or slag based binders as “*alkali activated cements*”. The latter two starting materials are industrial by products, whose effectiveness as alternative, Portland cement-free binders has been largely pioneered by the research groups at the Eduardo Torroja Institute in Madrid and the Glukhovsky Institute in Kiev [3-7].

Some advantages of specific geopolymer formulas over traditional Portland cements include: higher early compressive strengths [8], improved fire resistance [9], acid resistance [10, 11] and lower embodied CO<sub>2</sub> content [12, 13]. Such properties have also led to geopolymers being considered as possible matrices for hazardous/nuclear waste stabilisation and solidification applications [14-20].

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 plate-like 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<sub>4</sub> and AlO<sub>4</sub><sup>-</sup> groups [21, 22]. Such structures have a negative charge on the aluminium site which is balanced by Na<sup>+</sup> or K<sup>+</sup> cations from the alkali activation solution, forming N-A-S-H or K-A-S-H gel, depending on the counter ion present [23].

The chemistry of MK geopolymerisation has been extensively reported in the literature. The influence of the main experimental variables such as curing temperature, activation solution pH and Si:Al: cation ratio on the MK geopolymerisation process have previously been reported in

the literature [2, 24-30]. Only specific ranges of Si:Al, Na:Al and Na:H<sub>2</sub>O ratios give aluminosilicate geopolymer gel structures with desirable properties [31-33]. 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 to 2.15, developed higher Young's modulus values but that the opposite trend was noted with K based samples [34, 35].

Although resistance to thermal shrinkage of MK geopolymers exposed at temperatures above 700 °C is in many cases far superior to Portland cements [36-39], very little attention has been given to the wider issue of ambient temperature drying shrinkage [40]. The image in Figure 1 gives a typical example of what can happen 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 [41]. 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 [39]. Despite the lack of chemically bound water, it still plays an important role in structural stability and if excess water is not removed properly, extensive shrinkage cracking of specimens can occur [40].

A possible explanation for geopolymer drying cracking is the generation of high capillary pressures between wet and dry areas of the micro-pore network, which is reported to initiate crack propagation in the microstructure [41, 42]. Attempts to avoid drying shrinkage and crack

propagation have focussed on modifying the pore structure to minimise capillary porosity and on controlling water loss during curing [41, 42].

The Na/K:Al ratio in particular could be important if loss of  $\text{Na}^+$  or  $\text{K}^+$  spheres of hydration have an important role in drying shrinkage. Another important factor could be the relative number of  $\text{AlO}_4^-$  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.

## **2. MATERIALS AND METHODS**

### **2.1 Materials**

Commercially available metakaolin (Metastar 501, Imerys, UK) with a mean particle size of  $3.9\ \mu\text{m}$  was used. XRF analysis showed the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents to be 59.5% and 34.0% respectively. Alkaline activation solutions were prepared from sodium silicate solution (26%  $\text{SiO}_2$ /8%  $\text{Na}_2\text{O}$ , VWR International), sodium hydroxide pellets ( $\text{NaOH}$ , Fischer), and from potassium silicate solution (23.4%  $\text{SiO}_2$ /11.5% $\text{K}_2\text{O}$ , PQ Cooperation), potassium hydroxide pellets ( $\text{KOH}$ , Fischer) and deionised water.

## **2.2 MK geopolymer paste preparation**

MK geopolymer pastes were prepared with Al:Si:Na/K:H<sub>2</sub>O ratios as shown in Table 1. In the first set of samples (#1-4), the Al:Si:Na ratios were kept constant and the water content was varied. It should be noted that in order to maintain good workability across all samples, the minimum H<sub>2</sub>O molar ratio possible was 8, so the molar water range of 7.5 to 10.5 was chosen. In the second set of samples (#5-9) the Si:Al ratio was varied while 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 while keeping the Si:Al ratio and water content 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 hours to reach equilibrium. The activation solution was then mixed with metakaolin by hand for 3 minutes, and cast into plastic (ABS) moulds. A vibrating table was used during casting to remove air bubbles from samples which were then cured in sealed polyethylene bags at room temperature ( $22 \pm 3$  °C). Samples were de-moulded 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 (Rheometric Scientific STA 1500).

## **2.3 Drying procedure**

Samples cured for 56 days were subjected to a slow, incremental drying procedure. This involved storing the samples at ambient temperature and  $45 \pm 5\%$  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.

#### **2.4 Physical and mechanical tests on MK geopolymers pastes**

Total water content and heat stability were determined using differential scanning calorimetry and thermogravimetry (DSC/TGA, Rheometric Scientific STA 1500) at a heating rate of  $2\text{ }^{\circ}\text{C min}^{-1}$ .

Sample weight during drying was determined at various times to 0.0001 g accuracy. 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, UK), with the final value derived from the average of 5 measurements.

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

$$New_{mwr} = Original_{mwr} \times [(Total_{H2O} - Lost_{H2O}) / Total_{H2O}] \quad (1)$$

Where:

$Original_{mwr}$  = the mixture design molar water ratio (i.e. 7.5, 8, 8.5, 9.5 or 10.5).

$Total_{H2O}$  = the total  $H_2O$  content as determined by TGA analysis expressed as % of sample mass.

$Lost_{H2O}$  = the sample mass loss during the drying period expressed as % of sample mass.

The flexural strength of samples (8 mm × 8 mm x 40 mm) was determined using a three-point bending test (Zwick/Roell Z2.5). 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) 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 °Cmin<sup>-1</sup>.

### **3. RESULTS**

#### **3.1 Effect of water content**

##### *3.1.1 Total water contents*

Representative DSC/TGA results for a geopolymer sample can be seen in Figure 2. The DSC signal shows an endothermic peak between 20 to 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., (2007) [41]. Total water contents of the samples were 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.



### *3.1.2. 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 Figures 3a and b. Figure 3a shows that higher initial mixing water contents allow a greater absolute quantity of water to be removed before shrinkage starts. Figure 3b represents the same data as Figure 3a, but with water losses normalised to calculate the effective molar water ratio remaining in each sample as drying progresses. Since the normalised 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 around 3 in the 1:2:1:x system, where  $7.5 \leq x \leq 10.5$ .

### *3.1.3. Resistance to flexural strength loss on drying*

The change in flexural strength of the geopolymer samples with decreasing water molar contents loss as during occurs is shown in Figure 4. Similar trends were noticed as in Figure 3b, with sudden changes in flexural strengths occurring in all samples as 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 Figures 3b and 4, a sudden increase in flexural strengths was noted at the onset of drying shrinkage, before samples lost all structural integrity. This unexpected behaviour could perhaps offer a clue to the shrinkage mechanism and will be discussed later.

### *3.1.4. Thermal shrinkage*

Thermal shrinkage up to 1000 °C of two samples with different water contents is shown in Figure 5, with the data regions spilt into 4 sections as per Duxson et al, 2007 [39]. 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 can perhaps be misleading in that it suggests that ambient temperature drying shrinkage is not an issue. In Figure 5, we see no appreciable shrinkage until a temperature of 150 °C, despite that fact that we have already shown 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 quick rates to be practical. The heating rate of 10 °C.min<sup>-1</sup> used here does not permit the free water to evaporate completely before a temperature of at least around 150 – 200 °C had been reached. 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 [36, 39].

The MK-geopolymers started to sinter at ~800 °C [39]. Sintering and densification provoked a significantly higher degree of shrinkage in the sample with an initial 10.5 molar water content than the sample with 8.5 molar water, consistent with the increased initial porosity that would be expected in the former's microstructure.

### **3.2 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 - 300°C and 300 - 600 °C respectively [39], we can see some clear differences in the response of samples with different Si:Al ratios in a dilatometry test shown in Figure 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 better resistance to ambient temperature drying shrinkage shown in Figure 6. However, this did 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 [39], it was observed that improved thermal shrinkage with increasing Si:Al ratio could perhaps be attributed to better Young's modulus values 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 Si:Al ratios of 1.15 and 1.65, which may not be relevant to our samples (Si:Al ratio of 1.6-2.4). Furthermore, we have not presented any Young's modulus data and so such an explanation would be purely speculative here.

### **3.3 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 has a strong effect on sensitivity to drying shrinkage over the range studied. Within the Na:Al molar range of 0.7 – 1.3, no optimum ratio was found. Instead, sensitivity to drying shrinkage decreased linearly with decreasing Na content.

Two batches of samples were repeated with K based activators instead of Na based ones. Although the data is limited, in Figure 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 behaviour measured by dilatometry of Na and K based geopolymers (of 1:1.8:1:8 composition) is shown in Figure 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 upon 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. (2006) [13], although perhaps the fact that their samples were cured at 40 °C for 20 hours whereas ours were cured at ambient temperature is important.

#### **4. 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 is affected differently by the respective ratios of Al/Si, Na/K and H<sub>2</sub>O in the mixture. A discussion of how changing the sample mix compositions may affect this characteristic minimum water content is presented here.

#### **4.1. Effect of changing molar water ratio**

##### *4.1.1. 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 Figure 3b). 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 Figure 3a). This suggests that the drying shrinkage mechanism is relatively independent of total sample porosity and gel density, since the initial molar water ratio significantly affects 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 here 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 around 5.5 as reported elsewhere [39], different effects would be noted due to much denser gel structures. However, in order 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 micro pore network. However, removing more than the free water provokes shrinkage.

#### *4.1.2. On the onset of flexural strength loss*

The data presented in Figures 4 very closely reflect the trends in Figures 3b, 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 strong shrinkage and causes the strength to decrease.

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

#### **4.2. 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. MK geopolymers with Si:Al ratios of  $\leq 1.4$  were shown by  $^{27}\text{Al}$  MAS NMR, to fail to incorporate all dissolved Al into the gel structure. However, at Si:Al ratios  $\geq 1.65$ , no unincorporated  $\text{AlO}_4^-$  was found [43]. In terms of mechanical properties, the ideal Si:Al ratio is generally regarded to be around 2.

To ensure that poor  $\text{AlO}_4^-$  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 Figure 6). In another study, it was shown that increasing the Si:Al ratio from 1.15 to 2.15 caused  $^2\text{H}$  MAS NMR spectra to broaden progressively, possibly indicating that the contents of “structural” water increase with increasing Si:Al ratio [43]. This would support the observations noted in this study.

Another way of interpreting this trend is to consider that the minimum “structural” water required to prevent shrinkage decreased as the relative Al content increased. The Al content is likely to affect the ion activity of the charge balancing  $\text{Na}^+$  cations, with lower activities expected at higher Al contents. This interpretation would imply that the spheres of hydration of  $\text{Na}^+$  cations could be a significant part of the “structural” water considered here.

### **4.3. Effect of changing the Na:Al molar ratio**

The original role of  $\text{Na}^+$  ions is to facilitate a highly alkaline medium in which the metakaolin can dissolve. It is widely accepted that these ions act as charge balancing cations on negatively charged tetrahedral  $\text{AlO}_4^-$  groups formed in the cementitious gel. These ions are not considered to be chemically bound, but can be leached out [19] 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  $\text{Na}^+$  ions in hardened pastes from a chemical point of view.

The excess  $\text{Na}^+$  ions have a clearly negative effect on resistance to ambient temperature drying shrinkage as shown in Figure 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. Extrapolation of the trendline in Figure 8 indicates that an increase in Na:Al molar ratio of 1.0 would increase the “structural” water content by 6.0 moles, perhaps being linked with the typical sphere of hydration of hydrated  $\text{Na}^+$  cations which contains 6 molecules of  $\text{H}_2\text{O}$  per  $\text{Na}^+$  ion [44].

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, again the data implies that a significant 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.

#### **4.4. Effect of changing the cation from Na to K**

The principal difference between Na and K ions is that the larger  $\text{K}^+$  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  $\text{Na}^+$  ion. This is supported by the lower free energy of hydration for  $\text{K}^+$  ions ( $\sim 75\text{kcal/mol}$ ) than for Na ( $\sim 95\text{kcal/mol}$ ) [45].

It is debatable whether the  $\text{K}^+$  ion represents advantages over the  $\text{Na}^+$  ion in terms of being able to better stabilise the  $\text{AlO}_4^-$  charge. However, compelling  $^{39}\text{K}$  MAS NMR evidence has shown

that in a mixed K/Na system,  $K^+$  is preferentially absorbed at  $AlO_4^-$  sites than  $Na^+$  [46]. At the macrostructural level, there are some clear differences noted by replacing Na with K on compressive strength and Young's modulus [35].

Careful analysis of XRD data from K-based MK geopolymers heated at various temperatures using a pair distribution function method showed that there is a relocation of the  $K^+$  ion in the paste structure following heating beyond 300 °C [47]. An interesting idea for further work would be to repeat such a study but with Na and Cs based samples and compare the relative relocations following heating or ambient temperature drying shrinkage.

In terms of resistance to ambient temperature drying shrinkage, Figure 9 clearly shows that the replacement of Na by K significantly reduces the critical minimum molar water ratio required to prevent drying shrinkage. The better 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 above, it appears that “structural” water content is strongly related to the total hydration sphere water requirements of the alkali cations. To stabilise 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.

#### **4. CONCLUSIONS**

The very common but little reported phenomenon of ambient temperature drying shrinkage of MK geopolymers has been investigated in this work. The authors coin the term “structural” water to identify the critical minimum water contents, normalised 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. From the results presented, the following conclusions can be drawn:

- 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 correlated very well with drying shrinkage.
- Increasing the Si content or decreasing the Al content, increased the quantity of “structural” water required to prevent shrinkage (within Si:Al ratios of 1.6-2.4).
- Increasing the Na content dramatically increased the quantity of “structural” water required to prevent shrinkage. Implying that the hydration spheres of Na<sup>+</sup> cations play a highly significant role in maintaining the structural stability of pastes.
- Replacing the Na<sup>+</sup> ions with K<sup>+</sup> ions decreased the minimum required “structural” water. Consistent with the previous conclusion since the hydration water requirement of K<sup>+</sup> ions is less than Na<sup>+</sup> ions to provide a given ionic charge density and that the cation:AlO<sub>4</sub><sup>-</sup> pair is more stable with K<sup>+</sup>.

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:  $\text{AlO}_4^-$  pairs in the paste are the major factors affecting the sensitivity of paste samples to ambient temperature drying shrinkage.

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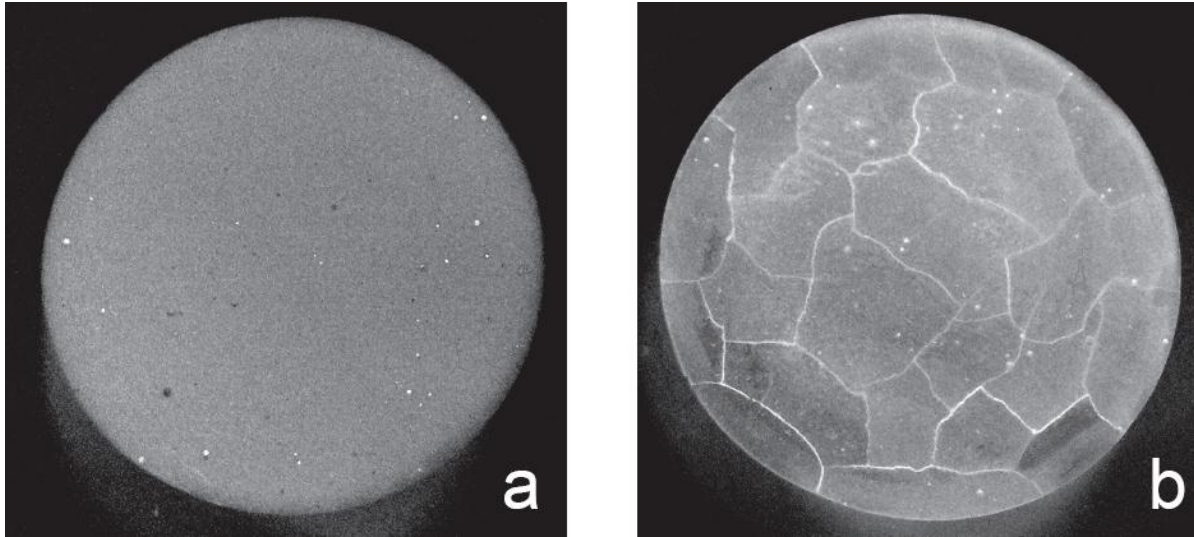
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## REFERENCES

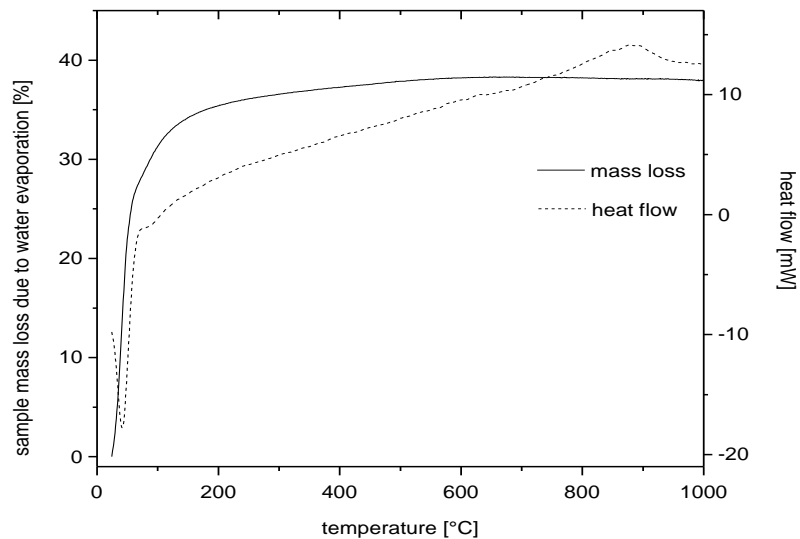
1. Provis, J.L. and J.S.J. van Deventer, *Direct measurement of the kinetics of geopolymerisation by in-situ energy dispersive X-ray diffractometry*. Journal of Materials Science, 2007. **42**(9): p. 2974-2981.
2. Duxson, P., et al., *Geopolymer technology: the current state of the art*. Journal of Materials Science, 2007. **42**(9): p. 2917-2933.
3. Glukhovskiy, V.D., *Soil silicates. Their properties, technology and manufacturing and fields of application*. 1965, Kiev Civil Engineering Institute: Kiev, Ukraine.
4. Krivenko, P.V., *Synthesis of binders with required properties in the system  $\text{R}_2\text{O}-\text{RO}-\text{R}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$*  1986, Polytechnique Institute Kiev, Ukraine.
5. Fernández-Jiménez, A. and F. Puertas, *Alkali-activated slag cements: Kinetic studies*. Cement and Concrete Research, 1997. **27**(3): p. 1323-1329.
6. Palomo, A., M.W. Grutzeck, and M.T. Blanco, *Alkali-activated fly ashes - A cement for the future*. Cement and Concrete Research, 1999. **29**: p. 1323-1329.
7. Palomo, A., S. Alonso, and A. Fernandez-Jimenez, *Alkaline Activation of Fly Ashes: NMR Study of the Reaction Products*. Journal of the American Ceramic Society, 2004. **87**: p. 1141-1145.
8. Fernández-Jiménez, A. and A. Palomo, *Factors affecting early compressive strength of alkali activated fly ash (AAFA) concrete*. Materiales de Construcción, 2007. **57,287**: p. 7-22.
9. Lyon, R.E., et al., *Fire resistant aluminosilicate composites*. Fire and Materials, 1997: p. 67-73.
10. Bakharev, T., *Resistance of geopolymer materials to acid attack*. Cement and Concrete Research, 2005. **35**(4): p. 658-670.
11. Fernández-Jiménez, A., I. García-Lodeiro, and A. Palomo, *Durability of alkali-activated fly ash cementitious materials*. Journal of Materials Science, 2007. **42**: p. 3055-3065.
12. Davidovits, J., *Properties of Geopolymer Cements*, in *First International Conference on Alkaline Cements and Concretes*. 1994: Kiev, Ukraine.
13. Duxson, P., et al., *The role of inorganic polymer technology in the development of 'green concrete'*. Cement and Concrete Research, 2007. **37**(12): p. 1590-1597.

14. van Jaarsveld, J.G.S., J.S.J. van Deventer, and L. Lorenzen, *The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and Applications*. Minerals Engineering, 1997. **10**(7): p. 659-669.
15. Zosin, A.P., T.I. Priimak, and K.B. Avsaragov, *Geopolymer materials based on magnesia-iron slags for normalization and storage of radioactive wastes*. Atomic Energy, 1998. **85**(1): p. 510-514.
16. van Jaarsveld, J.G.S., J.S.J. van Deventer, and A. Schwartzman, *The potential use of geopolymeric materials to immobilise toxic metals: Part II. Materials and Leaching characteristics*. Minerals Engineering, 1999. **12**(1): p. 75-91.
17. Palomo, A. and M. Palacios, *Alkali activated cementitious materials: Alternative matrices for the immobilisation of hazardous wastes. Part II. Stabilisation of Chromium and Lead*. Cement and Concrete Research, 2003. **33**(2): p. 289-295.
18. Fernández-Jiménez, A., et al., *Fixing Arsenic in alkali activated cementitious matrices*. Journal of the American Ceramic Society, 2005. **88**(5): p. 1122-1126.
19. Aly, Z., et al., *Aqueous leachability of metakaolin-based geopolymers with molar ratios of Si/Al=1.5-4*. Journal of Nuclear Materials, 2008. **378**(2): p. 172-179.
20. Donatello, S., A. Fernández-Jiménez, and A. Palomo, *An assessment of Mercury immobilisation in alkali activated fly ash (AAFA) cements*. Journal of Hazardous Materials, 2012. **in press**.
21. Fernández-Jiménez, A., et al., *The role played by the reactive alumina content in the alkaline activation of fly ashes*. Microporous and Mesoporous Materials, 2006. **91**(1-3): p. 111-119.
22. Provis, J.L. and J.S.J. van Deventer, *Geopolymerisation kinetics. 1. In situ energy-dispersive X-ray diffractometry*. Chemical Engineering Science, 2007. **62**: p. 2309-2317.
23. García-Lodeiro, I., et al., *Effect of Calcium additions on N-A-S-H cementitious gels*. Journal of the American Ceramic Society, 2010. **93**(7): p. 1934-1940.
24. Cioffi, R., L. Maffucci, and L. Santoro, *Optimization of geopolymer synthesis by calcination and polycondensation of a kaolinitic residue*. Resources, Conservation and Recycling, 2003. **40**(1): p. 27-38.
25. Phair, J.W. and J.S.J. van Deventer, *Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers*. Minerals Engineering, 2001. **14**(3): p. 289-304.
26. Phair, J.W. and J.S.J. van Deventer, *Effect of the silicate activator pH on the microstructural characteristics of waste-based geopolymers*. International Journal Mineral Processing, 2002. **66**(1): p. 121-143.
27. Rahier, H., et al., *Low-temperature synthesized aluminosilicate glasses Part III Influence of the composition of the silicate solution on production, structure and properties*. Journal of Materials Science, 1997. **32**(9): p. 2237-2247.
28. Wang, H., H. Li, and F. Yan, *Synthesis and mechanical properties of metakaolinite-based geopolymer*. Colloids and Surfaces. A, Physicochemical and Engineering Aspects, 2005. **268**(1-3): p. 1-6.
29. Sagoe-Crentsil, K. and L. Weng, *Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part II. High Si/Al ratio systems*. Journal of Materials Science, 2007. **42**(9): p. 3007-3014.
30. Weng, L. and K. Sagoe-Crentsil, *Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part I—Low Si /Al ratio systems*. Journal of Materials Science, 2007. **42**(9): p. 2997-3006.
31. Barbosa, V.F.F., K.J.D. MacKenzie, and C. Thaumaturgo, *Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers*. International Journal of Inorganic materials, 2000. **2**(4): p. 309-317.

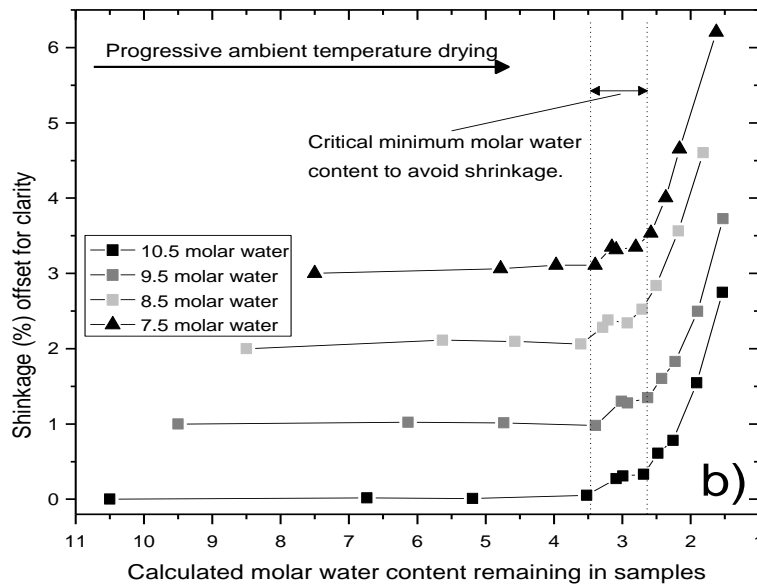
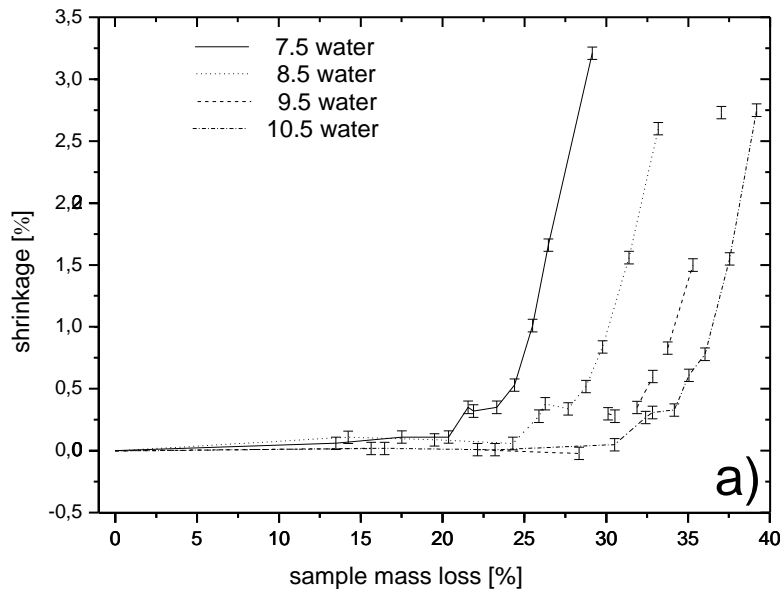
32. Cheng, T.W. and J.P. Chiu, *Fire-resistant geopolymer produced by granulated blast furnace slag*. Minerals Engineering, 2003. **16**(3): p. 205-210.
33. Palomo, A., et al., *Chemical stability of cementitious materials based on metakaolin*. Cement and Concrete Research, 1999. **29**: p. 997-1004.
34. Duxson, P., et al., *Understanding the relationship between geopolymer composition, microstructure and mechanical properties*. Colloids and Surfaces. A, Physicochemical and Engineering Aspects, 2005. **269**(1-3): p. 47-58.
35. Duxson, P., et al., *The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers*. Colloids and Surfaces. A, Physicochemical and Engineering Aspects, 2007. **292**(1): p. 8-20.
36. Rahier, H., B. van Mele, and J. Wastiels, *Low-temperature synthesized aluminosilicate glasses Part II Rheological transformations during low-temperature cure and high-temperature properties of a mode/compound*. Journal of Materials Science, 1996. **31**(1): p. 80-85.
37. Barbosa, V.F.F. and K.J.D. MacKenzie, *Synthesis and thermal behaviour of potassium silicate geopolymers*. Materials Letters, 2003. **57**(9-10): p. 1477-1482.
38. Barbosa, V.F.F. and K.J.D. MacKenzie, *Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate*. Materials Research Bulletin, 2003. **38**(2): p. 319-331.
39. Duxson, P., G.C. Lukey, and J.S.J. van Deventer, *Physical evolution of Na-geopolymer derived from metakaolin up to 1000 °C*. Journal of Materials Science, 2007. **42**(9): p. 3044-3054.
40. Zuhua, Z., et al., *Role of water in the synthesis of calcined kaolin-based geopolymer*. Applied Clay Science, 2009. **43**(2): p. 218-223.
41. Perera, D.S., et al., *Influence of curing schedule on the integrity of geopolymers*. Journal of Materials Science, 2007. **42**(9): p. 3099-3106.
42. Bell, J.L. and W.M. Kriven. *Preparations of ceramic foams from metakaolin-based geopolymer gels. In: Developments in Strategic Materials, Ceramic Engineering and Science Proceedings*. 2008.
43. Duxson, P., et al., *Effect of Alkali Cations on Aluminum Incorporation in Geopolymeric Gels*. Industrial & Engineering Chemistry Research, 2005. **44**: p. 832-839.
44. Waizumi, K., H. Masuda, and N. Fukushima, *Structural rigidity of first hydration spheres of Na<sup>+</sup> and Ca<sup>2+</sup> in cluster models. Full geometry optimizations of [M(H<sub>2</sub>O)<sub>6</sub>]<sup>n+</sup>, [M(H<sub>2</sub>O)<sub>6</sub>···H<sub>2</sub>O]<sup>n+</sup> and [M(H<sub>2</sub>O)<sub>6</sub>···Cl]<sup>(n-1)+</sup> (M = Na and Ca, n = 1 for Na and 2 for Ca) by density functional calculations*. Inorganica Chimica Acta, 1993. **209**(2): p. 207-211.
45. Migliore, M., et al., *Monte Carlo study of free energy of hydration for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, F<sup>-</sup>, and Cl<sup>-</sup> with ab initio potentials* The Journal of Chemical Physics, 1988. **88**(12): p. 7766-7771.
46. Duxson, P., et al., *39K NMR of free potassium in geopolymers*. Industrial & Engineering Chemistry Research, 2006. **45**: p. 9208-9210.
47. Bell, J.L., et al., *X-ray pair distribution function analysis of a metakaolin-based, KAlSi<sub>2</sub>O<sub>6</sub>·5H<sub>2</sub>O inorganic polymer (geopolymer)*. Journal of Materials Chemistry, 2008. **18**: p. 5974-5981.



**Figure 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<sub>2</sub>O of 1:2:1:8.5: (a) before drying and (b) after drying.

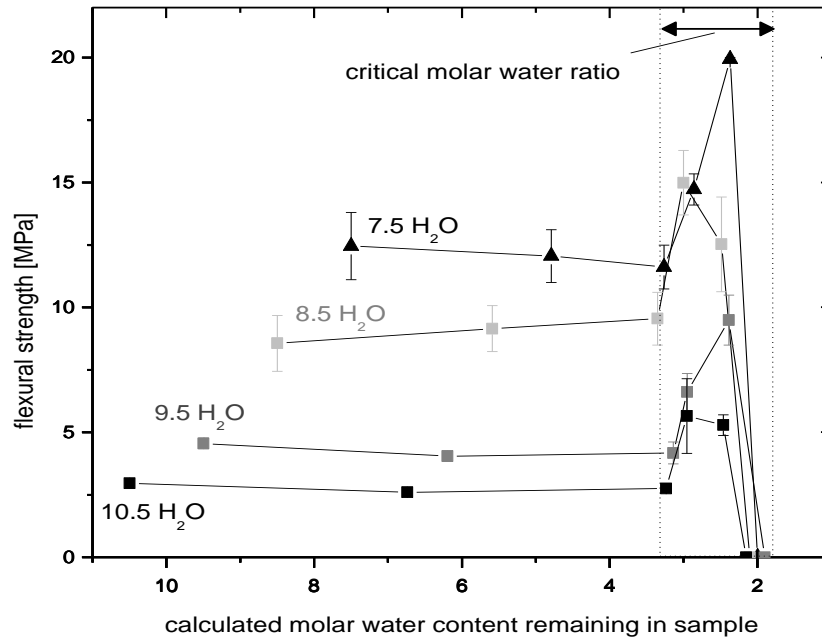


**Figure 2:** DSC/TGA result for MK geopolymer paste with a molar ratio Al:Si:Na:H<sub>2</sub>O of 1:2:1:8. Note that total water contents were calculated by taking sample mass loss at 600 °C.

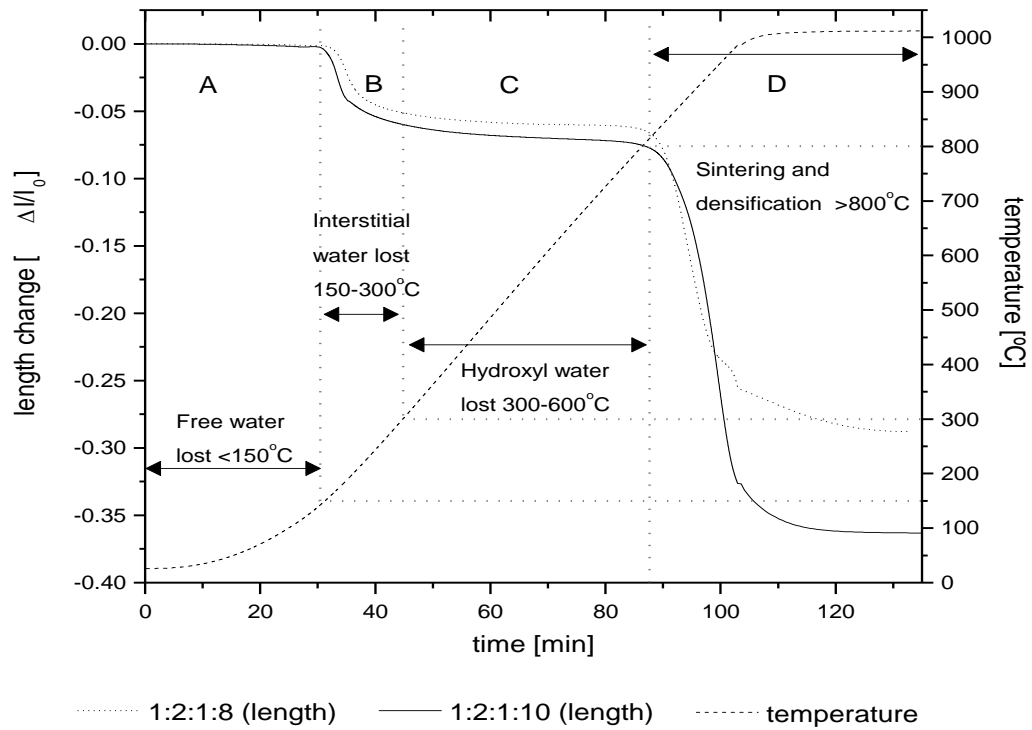


**Figure 3:** Effect of water evaporation via ambient temperature drying on shrinkage of different MK geopolymers containing different initial molar water ratios: a) absolute water losses and b) water loss normalised to a remaining molar water ratio. Data points were averages of 3 results.

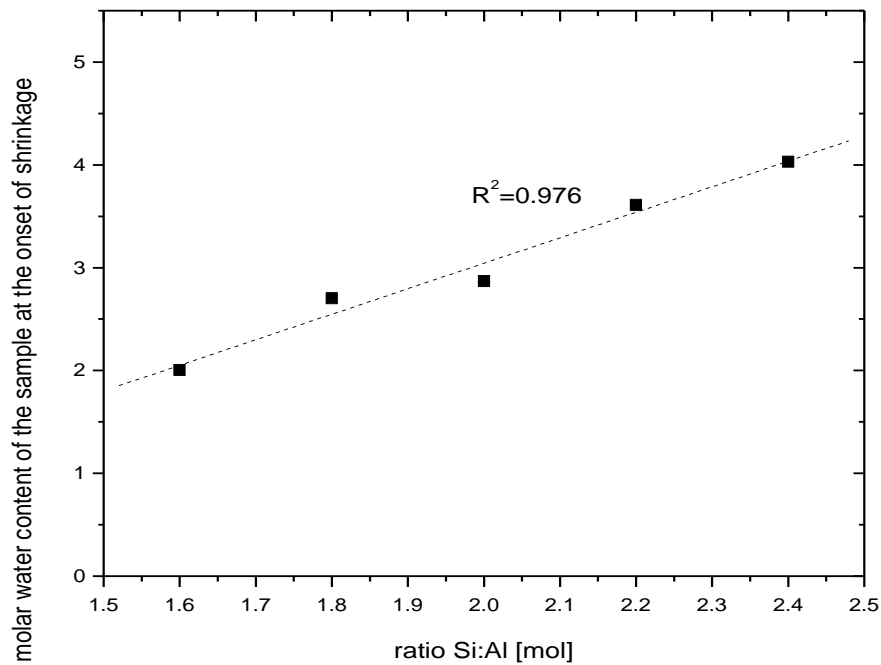




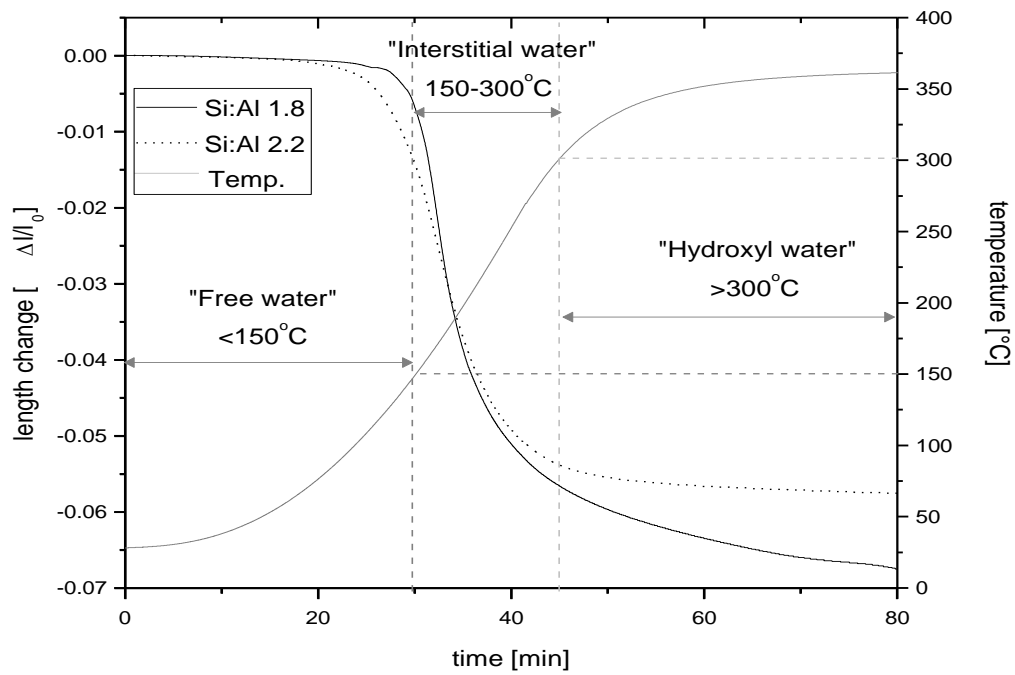
**Figure 4:** Effect of water evaporation via ambient temperature drying on flexural strengths of 8 x 8 x 40 mm prismatic MK geopolymers containing different initial molar water ratios. Water losses were normalised to calculate the effective remaining molar water ratio. Final point data for all samples was 0 MPa (points and lines not included for clarity). Data points were averages of 5 results.



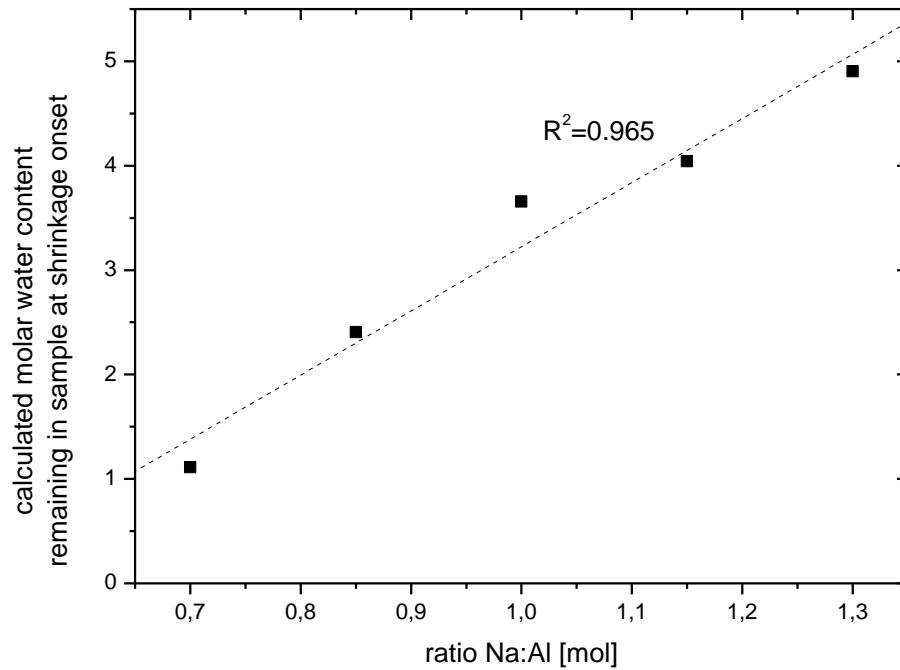
**Figure 5:** Dilatometric analysis up to 1000°C (10°C/min, He gas) of two MK pastes containing different mixing water molar ratios.



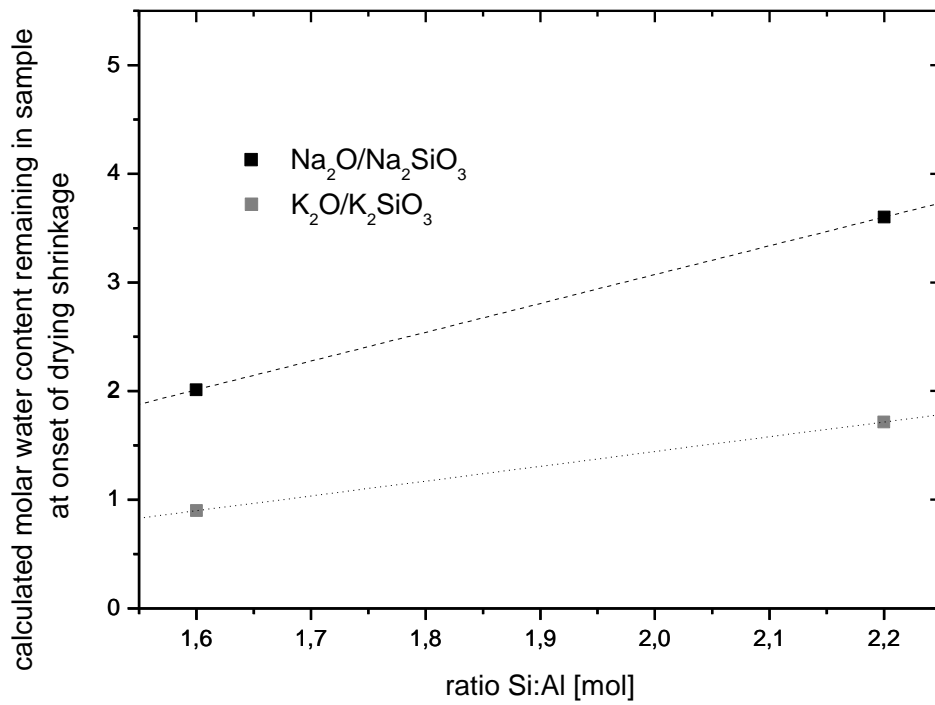
**Figure 6:** Effect of molar Si to Al ratio on the minimum required molar water ratio to prevent the onset of ambient temperature drying shrinkage in an Al:Si:Na:H<sub>2</sub>O system of 1:x:1:8 composition where x was varied from 1.6-2.4. Samples were cured for 56 days in sealed bags before being subject to a sequential drying procedure. Data points are averages of 3 measurements.



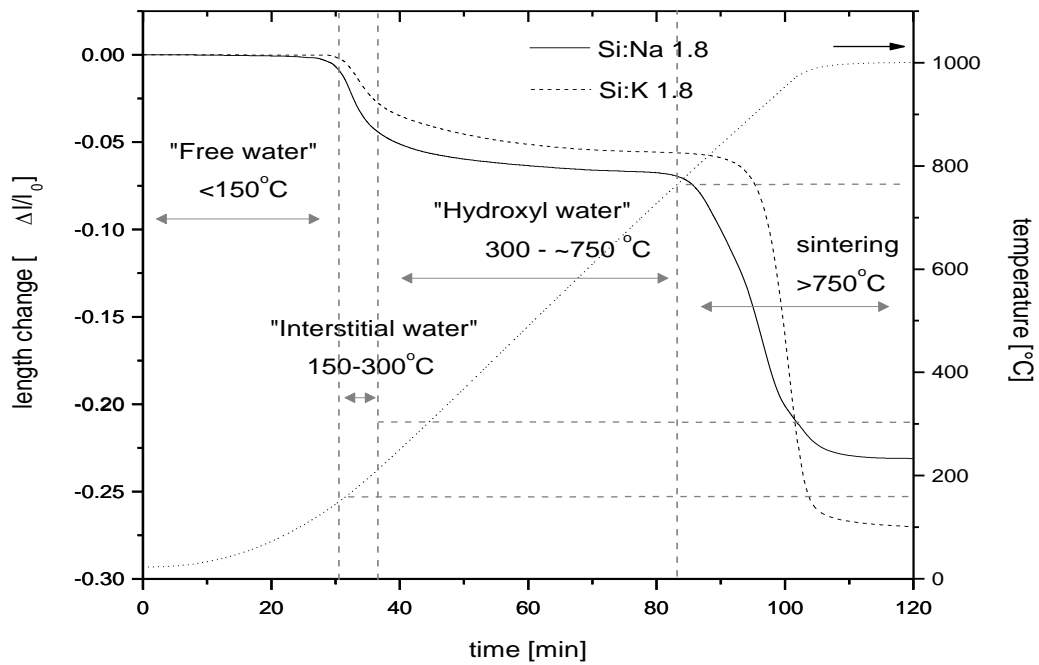
**Figure 7:** Dilatometer results of MK geopolymers heated up to 360°C where the Si:Al ratio was altered in a 1:x:1:8 mix composition. Measured after 56 days curing.



**Figure 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:H<sub>2</sub>O 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 3 measurements.



**Figure 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:H<sub>2</sub>O system of composition 1:x:1:8. Data points are averages of 3 measurements.



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