The Effect of Drying Rate on Shrinkage of Alkali-Activated Slag Cements

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ABSTRACT

The volumetric instability of alkali-activated slag (AAS) binders has raised concerns and impeded the acceptance of this Portland cement-free material. The objective of present work is to characterize the influence of drying rate on drying shrinkage behavior of alkali-activated slag mortars to better understand the mechanisms responsible for its large shrinkage deformation. A series of four AAS mortar mixtures with varying activator composition, as well as a reference Portland cement mortar was cast and dried at different relative humidities, i.e. 30%, 50%, 70% and 85% RH. Drying took place inside nitrogen purged environmental chambers, for the purpose of eliminating the contribution of carbonation to the total volumetric change of AAS. The shrinkage and corresponding mass loss of $1.27\text{cm} \times 1.27\text{cm} \times 12.7\text{cm}$ prisms were measured as a function of time. The results show that shrinkage of AAS varies largely depending on the drying rate, i.e. ambient RH. Interestingly, even though the drying mass loss increases with reducing the RH, the magnitude of shrinkage is the largest for samples stored at 50% and 70% RH, depending on the mixture type. Possible causes of these irregular behaviors are discussed. It is concluded that the drying rate has a much more significant influence on AAS than on OPC, which implies a more complicated shrinkage mechanism for AAS samples stored at various relative humidities.

1. INTRODUCTION

Ground-granulated blast furnace slag (GGBFS) is an amorphous by-product of the steel industry. It has a latent hydraulic reactivity, which can be catalyzed by proper activators to form cementitious materials. Alkali-activated slag (AAS) is one type of alkali-activated cement products which can offer superior properties over ordinary Portland cement (OPC) concrete, including high compressive strength at early age and excellent durability against chemical (acid, sulfate) attack (Shi et al., 2005). In addition, AAS has lower CO₂ emissions than OPC, and its eco-friendly advantage mainly originates from utilization of by-products (Jiang et al., 2014). However, some drawbacks of AAS still exist which hinder its broad acceptance and industry application. One of the main disadvantages for potential applications of AAS in construction industry is the volumetric instability, i.e. high shrinkage of AAS (Cartwright et al., 2013a, 2014; Shi et al., 2005).

Many researchers have reported that AAS exhibits significantly higher drying shrinkage

than that of OPC (Bakharev et al., 2000; Bakharev et al., 1999; Cartwright et al., 2013a, 2014; Cartwright et al., 2013b; Collins and Sanjayan, 2000; Melo Neto et al., 2008; Shi et al., 2005). For example, Cartwright et al. measured the drying shrinkage of AAS mortar of four mixtures under 50% RH, documenting that AAS has significantly higher drying shrinkage, finer pore structure, and lower stiffness than OPC (Cartwright et al., 2014). Collins et al. also observed the high shrinkage of AAS and related this phenomena to uniform pore size distribution in AAS (Collins and Sanjayan, 2000). Similar experimental results and conclusions were also reported by Neto et al., who evaluated the shrinkage of AAS with different amounts of dissolved silica from activators (Melo Neto et al., 2008). However, the scientific reasoning behind the high drying shrinkage behavior of AAS is still unknown. Some authors hypothesize that upon drying, a high capillary force forms in the materials of fine pore structure like AAS (Collins and Sanjayan, 2000; Melo Neto et al., 2008). This assumption has not been verified though, as drying shrinkage tests under a broad range of relative humidities (e.g. from 30% RH to 100% RH) have not yet been conducted. Additionally,

previous research merely observes the drying shrinkage of AAS under a constant relative humidity (50% RH in most cases). As such, this limited availability of experimental data prevents a more thorough understanding of the shrinkage behavior of AAS.

This paper presents the advanced drying shrinkage characterization of AAS mortar with various natures and dosages of activators. In particular, drying shrinkage of AAS is measured under two types of drying conditions, namely rapid drying and step-wise drying, as explained later. Both of these drying conditions cover a broad range of relative humidities from 30% to 85% RH. The objective of present work is to contribute to the better understanding of drying shrinkage behavior of AAS and its associated underlying mechanism. The outcomes of this research can provide fundamental information on the shrinkage mechanism of AAS, and provide further insights into possible shrinkage reduction and mitigations strategies.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

A grade 120 (according to ASTM C989/C989M-13) ground granulated blast-furnace slag with a density of 2.89 g/cm³ and a Type I Portland cement (according to ASTM C150/C150M-12) with a density of 3.14 g/cm³ were used in present study. Table 1 shows the oxide composition of the aforementioned materials. When preparing the activating solutions, sodium hydroxide, sodium silicate solution, and distilled water were used. The sodium silicate solution (Na₂O(SiO₂)_{1.6}(H₂O)₁₀) had a specific gravity of 1.60 and pH of 13.7 at 20°C. The NaOH pellets had a specific gravity of 2.13. To prepare the activating solutions, reagent NaOH pellets were dissolved in water and covered in closed beaker to avoid the loss of moisture and ingress of external CO₂. The solution was then shaken for 5 minutes and set aside for approximately two hours to allow for heat dissipation. In addition, a small dosage of water-reducing admixture (WRA) was added to AAS systems to ensure adequate workability. A natural river sand (according to ASTM C33/C33M-13) was also used for each mixture. The sand had a fineness modulus of 2.60, oven dry specific gravity of 2.52, and absorption capacity of 2.0%.

2.2 Sample preparation

Four AAS mortars and a control OPC mortar were designed using a constant volumetric liquid (water+activator) to solid (slag or cement) ratio of 1.30. This resulted in an initial binder porosity of 56.5% in all five mixtures. For the control OPC mixture, the mass-based w/c was 0.414. For the AAS mixtures, the mass-based liquid to solid ratio was in the range 0.489 to 0.510, depending on the concentration and density of the activating solutions. The details of mixture proportions are shown in Table 2 and Table 3. In particular, mortars AAS1 (lower silica concentration) and AAS2 (higher silica concentration) were activated using an alkaline solution which contained a combination of dissolved sodium hydroxide (NaOH) pellets, aqueous sodium silicate (Na₂O(SiO₂)_{1.6}·10H₂O) (waterglass), and water. Mortars AAS3 and AAS4 were activated solely by NaOH in water (either 2M or 4M). It should be mentioned here that the amount of water reported in Table 2 accounts for the absorption of oven-dried sand.

Table 1. Oxide compositions of slag and Portland cement (mass %)

	C	S	A	M	S	F	N	K	LOI
Slag	47.5	30.8	11.45	3.65	3.03	1.81	0.17	0.38	1.17
Cement	62.5	19.9	5.44	2.31	4.93	2.26	0.30	0.89	0.86

Notes: Following abbreviated symbols are used above
C=CaO, S=SiO₂, A= Al₂O₃, M=MgO, F= Fe₂O₃, S=SO₃,
H=H₂O, N=Na₂O, K=K₂O.

Table 2. Mortar mixture proportions (in grams per liter of mortar)

Mix ID	NaOH	Na ₂ O(SiO ₂) _n	Water*	Cement	Slag	Sand
OPC	0	0	296.8	657	0	1,247
AAS1	23.77	35.70	263.6	0	604	1,247
AAS2	5.94	95.49	234.6	0	604	1,247
AAS3	23.77	0	285.9	0	604	1,247
AAS4	47.54	0	274.8	0	604	1,247

*Note: Water content accounts for sand absorption

Table 3. Activating solution properties for AAS mixtures

Mix ID	SiO ₂ /Na ₂ O	pH	Density (g/cc)	WRA (cc/kg)
AAS1	0.41	14.31	1.09	5.00
AAS2	1.22	13.78	1.13	2.00
AAS3	0	14.30	1.04	4.15
AAS4	0	14.60	1.09	8.00

To evaluate shrinkage deformation, a series of “mini-bar” prism samples ($1.27 \times 1.27 \times 12.7$ cm) was cast in this study. The smaller dimension of the samples allowed the systems to reach equilibrium in a relatively short period of time. A PVC mold with a gage length of four inches was used in samples preparation. All samples were dried in nitrogen purged Vena VC-10 environmental chambers.

2.3 Testing procedure

In order to evaluate the effect of drying rate on shrinkage behavior of AAS, two types of experimental procedures were utilized, namely rapid drying and step-wise drying. Rapid drying involved measuring shrinkage at constant RH until equilibrium was reached, while step-wise drying measured shrinkage across a broad range of RH. In particular, environmental chambers were programmed for four different humidities (85%, 70%, 50%, and 30% RH) at constant temperature ($23 \pm 0.5^\circ\text{C}$). The rapid drying shrinkage was measured for all five mixtures (four samples per mixture) at each constant relative humidity under dry nitrogen (N_2) purge, after seven days of moist curing (100% RH, $23 \pm 0.5^\circ\text{C}$). The concentration of CO_2 in environmental chambers was periodically measured with a portable CO_2 analyzer and was found to be 0ppm. In case of step-wise drying procedure, the specimens were dried initially at 85% RH until they reached equilibrium, at which point the humidity was dropped to 70%. Subsequent RH reductions to 50% and 30% RH occurred after specimens came to equilibrium at each RH step. Length measurements were taken via a modified digital comparator with an invar reference bar. The accuracy of length measurements was 0.0001 inch. Simultaneous mass measurements were taken using a high precision balance with an accuracy of 0.01g.

Figure 1. Rapid drying shrinkage under nitrogen purge for all mortar mixtures (a) AAS1; (b) AAS2; (c) AAS3; (d) AAS4; (e) OPC (after 7 days moist curing)

3. EXPERIMENTAL RESULTS

3.1 Rapid drying shrinkage of AAS

Figure 1 shows the results of the measured rapid drying shrinkage of all five mortar mixtures during the first 30 days of testing. All AAS mixtures show higher drying shrinkage strains than the control OPC mixture at all relative humidities, except for AAS3 at 30% RH.

OPC shows increasing shrinkage with a decreasing relative humidity, which is consistent with the findings of other authors (Baroghel-Bouny et al., 2006; Hansen, 1987). On the contrary, the AAS mixtures show more complicated drying shrinkage behavior, where the largest ultimate drying shrinkage of AAS3 and AAS4 is observed at 70% RH. Similarly, AAS1 and AAS2 shrink the most at 50% RH, even though all mixtures were also dried to 30% RH.

Figure 2 presents the mass loss data for the four AAS and the control OPC mixtures. It can be seen that for all mixtures, a lower RH promotes higher moisture loss. Furthermore, moisture loss of each AAS mixture is larger than that for OPC. This contradicts the findings of Collins and Sanjayan, who measured lower mass loss upon drying for AAS than OPC (Collins and Sanjayan, 2000). At each relative humidity, AAS3 showed the highest mass loss. This is likely due to the coarse porosity of the paste in AAS3. The moisture loss for the other three AAS mixtures was measured to be similar.

Figure 2. Mass loss under rapid drying (nitrogen purged) for all mortar mixtures: (a) AAS1; (b) AAS2; (c) AAS3; (d) AAS4; (e) OPC (after 7 days moist curing)

3.2 Step-wise drying shrinkage

The second series of experiments involved drying samples to equilibrium and then gradually dropping the RH. Figure 3 and Figure 4 display the step-wise drying shrinkage and mass loss results of all five mortar mixtures. Similar to rapid drying, the control OPC showed the lowest drying shrinkage and mass loss among all mixtures evaluated. It can be seen that when dried gradually, the relationship between shrinkage and relative humidity for AAS materials differs significantly from that observed under rapid drying. Generally, drying shrinkage of all AAS samples exposed to step-wise procedure showed relatively higher values than those measured in the case of rapid drying. It should be noted here, that ultimately all samples were dried until they reached equilibrium at 30% RH. Comparing rapid and step-wise drying of AAS3, it can be seen that when dried gradually to a relative humidity of 50%, AAS3 shows 77% higher shrinkage deformations that when dried rapidly to the same RH. Similar tendencies are observed for the other AAS mixtures. All mixtures had slightly lower mass loss during the step-wise drying compared to the direct drying process. As such, it can be concluded that drying shrinkage behavior of AAS materials is highly dependent on the rate of drying.

Figure 3. Step-wise drying shrinkage results for all five mortar mixtures.

Figure 4. Step-wise drying moisture loss results for all five mortar mixtures.

4. DISCUSSION

According to Mackenzie-Bentz equation (Bentz et al., 1998), one can calculate the ultimate paste shrinkage due to capillary stresses (P_{cap}) induced by drying:

$$\varepsilon_p = \frac{S}{3} P_{cap} \left[\frac{1}{K} - \frac{1}{K_s} \right] \quad \text{Eq.1}$$

Where S corresponds to the volumetric degree of saturation, K is the bulk elastic modulus of the paste (as shown in Table 4), and K_s is the bulk modulus of the solid skeleton (e.g., C-S-H or unreacted solids). It can be seen that the material parameters controlling the calculated strain include the degree of saturation, effective bulk modulus and skeleton modulus (Bentz et al., 1998; Cartwright et al., 2014). Capillary pressure is similar at the same RH according to Kelvin equation (Eq. 2).

$$P_{cap} = -\rho_l \frac{RT}{M_l} \ln(RH) \quad \text{Eq.2}$$

Where P_{cap} is the capillary pressure, ρ_l is density of liquid, M_l is molecular mass and assumed to be same with pure water, $R=8.314$ [J/(mol K)] is the universal gas constant, T is temperature [K]. Additionally, a recent study also showed that the skeleton stiffness (K_s) of AAS is similar to that of OPC (Gebregziabihir and Peethamparan, 2013).

A higher shrinkage of AAS may originate from a higher degree of saturation and lower bulk modulus. As shown in Fig. 5, the measured degree of saturation for OPC is slightly higher

than that of OPC for each RH at equilibrium. The effective capillary stress (i.e. $S \cdot P_{cap}$) can be calculated and shown in Fig. 6. It should be noted that the capillary stress theory is primarily valid for $RH > 60\%$ (approximately) as a liquid-vapor meniscus cannot form in pores smaller than those that correspond to $RH < 60\%$. It can be seen in Fig. 6 that the effective capillary stress of OPC is slightly higher than that of AAS. This would eliminate a higher degree of saturation as a primary cause of higher shrinkage of AAS. Thus, the larger drying shrinkage of AAS could result from a lower stiffness. As shown in Table 4, AAS3 and AAS4 mortars have approximately 33% lower stiffness, but the stiffness values of AAS1 and AAS2 are similar, or even higher to that of OPC. Therefore, the value of stiffness itself may partially explain the higher shrinkage of AAS3 and AAS4, but cannot properly explain the high shrinkage performance of AAS1 and AAS2. Therefore, the capillary pressure theory, at least for AAS1 and AAS2, cannot explain the high shrinkage performance of AAS by itself and its strong dependence on drying rate.

Table 4. Bulk modulus of Elasticity K of mortars at 28 days

Mix ID	Bulk Modulus (GPa)
AAS1	11.34
AAS2	10.63
AAS3	6.96
AAS4	7.42
OPC	9.44

Note: each data point is an average of 2 duplicate cylindrical specimens)

On the other hand, Eq. 1 assumes a linear elastic behavior and does not account, for example, for creep. Creep is a phenomenon that results in the gradual increase in deformation under a constant stress. As shown in Fig. 1 and Fig. 2, the mass loss of AAS plateaus much faster than that of shrinkage. This means that AAS mixtures continue to shrink even though they are not losing any more water. This may suggest significant creep deformation in AAS. While for OPC, the shrinkage practically ceases when moisture loss reaches equilibrium. This is strong evidence that creep plays a significant role in drying shrinkage of AAS.

The correlation between relative humidity and drying shrinkage for all five mortar mixtures subjected to rapid drying procedure has been shown in Fig. 7. It can be seen that the OPC mixture shows a bi-linear relationship, while AAS

mixtures show a parabolic relationship between ultimate shrinkage and relative humidity. Particularly, AAS1 and AAS2 showed the highest shrinkage at 70% RH, while AAS3 and AAS4 showed the highest shrinkage at 50% RH. This unique phenomenon notably demonstrates the influence of drying rate on shrinkage behaviors of AAS.

Interestingly, when dried under the step-wise process, the shrinkage behavior of AAS was found to differ significantly compared to rapid drying, where the highest drying shrinkage deformations were observed at the lowest relative humidity. This may be due to the formation of permanent shrinkage strains (e.g. creep) during the gradual drying process.

Figure 5. The correlation between relative humidity and degree of saturation at equilibrium for all five mortar mixtures

Figure 6. The correlation between relative humidity and drying shrinkage for all five mortar mixtures

Figure 7. The correlation between relative humidity and drying shrinkage for all five mortar mixtures

It is possible other shrinkage driving forces, (e.g. Gibbs-Bangham strain) play an important role in shrinkage behavior of AAS, since the notably dependent shrinkage behavior of AAS on drying rate cannot be completely explained in present studies. The investigation of the shrinkage mechanisms of AAS is currently a main research focus at Penn State.

CONCLUSIONS

In this paper, the influence of drying rate on shrinkage characteristics of AAS was studied. In particular, four AAS mortar mixtures and one control OPC mortar were exposed to different drying procedures, namely rapid drying and step-wise drying. For rapid drying, four different relative humidities (i.e. 30%, 50%, 70% and 85% RHs) were utilized to investigate the shrinkage behavior of AAS. In step-wise drying scenario, a gradual change of RH from 85% to 30% RH was applied.

The following conclusions can be drawn according to the experimental results and analysis:

- (1) AAS mixtures have a unique parabolic relationship between relative humidity and ultimate drying shrinkage that differs significantly from the bi-linear correlation found in OPC mixtures.
- (2) Drying rate significantly affects the drying shrinkage behavior of AAS mortars.
- (3) Creep deformation seems to contribute significantly to drying shrinkage of AAS.
- (4) Effective capillary stress ($S \cdot P_{cap}$) was estimated to be slightly higher for OPC than

AAS and cannot explain the high shrinkage of AAS

- (5) The stiffness of mixtures activated by NaOH is smaller than that of OPC and contributes to their high shrinkage deformations.

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