Carbonation-induced volume change in alkali-activated slag

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Abstract: In this work, the volume changes of alkali-activated slag (AAS) paste prepared using various types of activator were characterized at nitrogen and atmospheric conditions. The results show that atmospheric carbonation of AAS results in volumetric expansion and disintegration, which may be attributed to the generation of crystallization stress in restrained pore spaces. This study suggests that the carbonation-induced volume change in cementitious materials is a combined result of chemical reactions and physical characteristics, depending on hydrated phase assemblage, composition, and pore structure of cementitious solids. The potassium ions (K^+), compared to sodium ions (Na^+), can enter the interlayer space of calcium-alumina-silicate-hydrate (C-A-S-H), distort the C-A-S-H layers stacking, coarsen the pore structure, and make AAS more vulnerable to carbonation. It is suggested that the high alkali content in AAS systems contributes considerably to its poor volumetric stability under carbonation.

Keywords: Alkali-activated slag; Volume change mechanism; Crystal growth model; Alkaline; Calcium-alumina-silicate-hydrate

1. Introduction

Alkali-activated slag (AAS) binder is typically produced by chemical reaction between ground-granulated blast-furnace slag and an alkaline solution (e.g. sodium hydroxide or silicates) [1-3]. Since blast-furnace slag is a by-product of iron ore smelting, the production of AAS can improve the sustainability of concrete products by lowering the embodied energy and greenhouse gas emissions, as compared to ordinary portland cement (OPC) [4, 5]. Although AAS exhibits well-established environmental benefits and promising mechanical properties, its broader acceptance is hindered by concerns regarding its long-term durability [2, 5]. One major obstacle inhibiting the practical application of AAS is their poor volumetric stability at atmospheric condition [5]. Previous studies have shown that AAS exhibits large chemical, autogenous, and drying shrinkage [6-11], rapid carbonation [12, 13], and extensive micro-cracking [14], in comparison to OPC. However, the mechanisms of volumetric instability of AAS at atmospheric condition have not been fully understood.

When hardened cementitious materials are exposed to the atmosphere, drying and carbonation occur simultaneously. The low relative humidity (RH) in ambient drives water evaporation from the drying surfaces of cementitious solids, inducing flow of liquid and diffusion of vapor in the interior of materials [15, 16]. During drying process, the menisci are formed in the pores, which generate hydrostatic tensile stress (i.e. capillary stress) that pulls adjacent pore walls closer, resulting in drying shrinkage [16-18]. In the meantime, atmospheric CO₂ dissolves in the pore water and forms carbonic acid. The reaction of carbonic acid with the existing anion leads to the carbonation of pore solution, resulting in pH reduction and precipitation of alkali-containing carbonates [19]. The solid phases formed in AAS, including calcium-alumina-silicate-hydrate

(C-A-S-H) and other secondary products, may undergo dissolution, decomposition, or decalcification. The carbonation of solid phases can result in a volume change of bulk materials, which is typically referred to as carbonation shrinkage.

The explanation for the carbonation shrinkage of cementitious materials remains unclear because carbonation theoretically results in an increase in unit cell volume whether the product is calcite, aragonite, or vaterite. Several mechanisms for the carbonation shrinkage of OPC paste have been proposed. For example, Powers [20] attributed the carbonation shrinkage to the dissolution of portlandite crystals, which are under crystallization pressure. As such, carbonation shrinkage is the result of crystallization pressure reduction, while precipitation of calcite in the pores does not exert crystallization pressure on the solid skeleton. Based on the Power's theory, the carbonation shrinkage of AAS should be lower than that of OPC paste, due to the little amount of portlandite formation in AAS. By contrast, Chen et al. [21] argued that the proportion of carbonation shrinkage in OPC paste induced by portlandite dissolution is relatively small compared to that induced by decalcification of calcium-silicate-hydrate (C-S-H). They suggested that the decalcification shrinkage of cement paste is primarily due to the nanostructure changes of C-S-H, which eventually decomposes into silica gels. As also reported by Matsushita et al. [22], in C-S-H, the Ca ions dissolved from the Ca-O layer and the double-chain silicate anion structures were decomposed, shrunk and were polymerized to the silica-gel-like structure. In agreement with this reasoning, the C-A-S-H in AAS should exhibit greater decalcification shrinkage than the C-S-H in OPC paste due to its much lower Ca/Si ratio.

Although a significant amount of work has been done on characterizing the carbonation characteristics of AAS, to the best of authors' knowledge, no one has ever investigated the volume changes of AAS during carbonation process. Previous research shows that AAS is more intensely and deeply carbonated than OPC [12, 13]. Due to the insufficient amount of portlandite in AAS, carbonation directly affects gels, causing decalcification, loss of cohesion and strength, and micro-cracking [12, 13, 19]. However, it is still unknown if the volumetric instability of AAS observed at atmospheric condition is a result of large carbonation shrinkage or drying shrinkage (due to the reduction of RH) or both. Distinguishing the volume change mechanism due to drying and carbonation is important since it provides the fundamental knowledge about the origins of poor volumetric stability of AAS.

To fill the aforementioned knowledge gaps, this study investigates the shrinkage performance of AAS prepared with various alkaline solutions at both nitrogen and atmospheric conditions. The goal of this research is to provide a better understanding of the mechanisms of volumetric instability of alkali-activated materials and potentially provide new insights on finding effective shrinkage cracking mitigation strategies.

2. Experimental procedure

2.1 Materials

A Grade 120 ground granulated blast-furnace slag with a specific gravity of 2.89 was used in this work. The slag composition as measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) method is listed in Table 1. The X-ray diffraction analysis indicates that

the slag contains primarily amorphous structure with a trace amount of gypsum and monoclinic alite. The broad and diffuse peak in the range $2\theta = 30^\circ$ to 31.6° (see Figure 1) is the result of the short range order of the aluminosilicate glass structure in slag [3, 11].

2.2 Specimen preparation

Four different types of alkaline solution were prepared in order to investigate the effects of type of alkali salts on the hydrated phases assemblage, pore structure, and shrinkage performance of AAS. To prepare activators, alkali salts pellets or powders, i.e. sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na_2CO_3), and potassium hydroxide (KOH), were dissolved in distilled water, to reach the targeted concentration and composition shown in Table 2. The main purpose of adding NaCl or Na_2CO_3 in the activator is to study the presence of other types of anion on the behaviors of AAS. The volumetric activator- to-slag ratio was kept constant at 1.45 for all four mixtures. The prepared activators were sealed in airtight containers to prevent carbonation and evaporation and shaken continuously to create a homogenous solution before mixing.

After mixing according to ASTM C305-12, a non-standardized mold was designed to cast “mini-bar” prism specimens of a dimension of $12.7\text{ mm} \times 12.7\text{ mm} \times 139.7\text{ mm}$ ($\frac{1}{2}\text{ inch} \times \frac{1}{2}\text{ inch} \times 5\frac{1}{2}\text{ inches}$). The small geometry enabled the specimens to reach equilibrium with environments in a much shorter time, in comparison to the conventional size. The specimens were further cured in a moist room (100%RH, $23 \pm 0.5^\circ\text{C}$) for 24h before demolding.

2.3 Length and weight changes

In order to investigate the effects of carbonation on volume change of AAS, samples were placed in two drying environments after demolding:

Nitrogen gas condition: A Vena VC-10 environmental chamber was programmed at 50% RH and $23\pm0.5^{\circ}\text{C}$. To prevent carbonation of AAS during experiments, dry nitrogen (N_2) was purged in chambers continuously and the concentration of CO_2 was periodically checked with a portable CO_2 analyzer to confirm consistent 0 ppm.

Atmospheric condition: A walk-in environmental chamber which was maintained at $50\pm4\%$ RH and $23\pm0.5^{\circ}\text{C}$ was used. The concentration of CO_2 in that room was measured to be 400 ppm.

The changes in length and weight of AAS paste specimens were recorded, utilizing a modified digital comparator with a measuring precision of 0.0001 inch and a balance with a measuring accuracy of 0.01g.

In the meantime, the same batch of AAS paste was cast in a series of sealed vials (stored in a moist room with 100%RH and $23\pm0.5^{\circ}\text{C}$) to investigate the effects of alkali salts on the hydrated phase assemblage and pore structure of AAS. X-ray diffraction (XRD) was used to investigate the hydrated phase assemblage evolution of AAS paste at 1d, 7d, and 28d. Scanning electron microscopy equipped with X-ray microanalysis (SEM/EDS) and mercury intrusion porosimetry (MIP) were used to investigate the composition, hydrated phase assemblage, and pore structure of AAS paste at 28d.

In order to investigate the effects of carbonation on the phase assemblage and microstructure of AAS paste, at the end of shrinkage measurements (for nitrogen gas condition it was at the age of 114d, while for atmospheric condition it was 55d), the samples were collected for XRD and field emission scanning electron microscope (FESEM) analysis. Given the fact that the level of carbonation may be inhomogeneous across the cross section of specimens, the entire ‘mini-bar’ specimens were implemented. However, based on the experimental results, it is believed that the carbonation of specimens was almost complete. The detailed description of the implemented techniques is included in the Sections 2.4-2.7. Prior to testing, the solvent-exchange method (i.e. immersion in isopropyl alcohol for two weeks and then vacuum drying for one week) was adopted to preserve the phases and microstructure of samples.

2.4 X-ray diffraction (XRD)

The AAS paste samples were crushed and milled for about 15 minutes, and further front-filled into a zero-background plate. XRD data was collected using a PANalytical Empyrean diffractometer in a conventional Bragg-Brentano θ - 2θ configuration. CuK α X-ray ($\lambda=1.5418$ Å) was generated using 40 mA and 45 kV operating conditions. A beta-filter Nickle was used to remove the β diffraction spectrums. Incident beam Soller slits of 0.04 radians were used, and the incident divergence and anti-scatter slits were fixed at 0.25° and 0.5°, respectively. The samples were scanned continuously between 5° and 45° 2θ under these conditions.

2.5 Scanning electron microscopy with X-ray microanalysis (SEM/EDS)

FEI Quanta 200 equipped with X-ray microanalysis was used to investigate the composition of hydrated phases in AAS. The samples were first impregnated with a low viscosity epoxy in

desiccators, and the surface epoxy was polished off and the specimens were polished down to 1 μm . More than 50 EDS microanalysis data points were collected randomly across the hydrated matrix for each specimen.

2.6 Mercury intrusion porosimetry (MIP)

Micromeritics AutoPore V Model 9620, which is capable of measuring pore diameters ranging from 360 to 0.003 μm , was implemented to characterize the pore structure (e.g. pore entry size distribution, porosity) of AAS paste samples.

2.7 Field emission scanning electron microscope (FESEM)

FEI NanoSEM 630 equipped with secondary electron detector was adopted to investigate the microstructure and morphology of hydrated products in AAS. Fractured samples were directly loaded under detector after carbon coating.

3 Results and Discussion

3.1 Phase assemblage

Figure 1 shows the XRD patterns of slag and AAS paste cured for 1d, 7d, and 28d. It can be seen that the main identified crystalline phases in AAS are C-S-H (I), portlandite, hydrotalcite-like (Mg-Al) phase, and sodium calcium alumina sulfate hydrate, regardless of the activator type [11, 23]. In comparison to NH mixture, the addition of chloride in NL mixture results in the Friedel's salt formation. For potassium-activated slag, the interlayer thickness and the peak shape of C-S-H (I) are larger and more diffusive, in comparison to those in sodium-activated slag mixtures. It

indicates that the binding mechanisms of Na^+ and K^+ on the hydrated phases of AAS are different. It seems that the K^+ can extensively enter the interlayer space [24], which may distort the stacking regulation of C-A-S-H layers. In addition, cordierite and dipotassium sulfate were exclusively detected in potassium-activated slag. For NC mixture, the peak intensities of phases, especially C-S-H (I) and Mg-Al phases, seem to be slightly stronger, which may be attributed to the additional activation effect of sodium carbonate.

Figure 2 shows the EDS atomic relationship in the solid hydrated phases of AAS paste at 28d. The Mg/Ca ratio versus Al/Ca ratio plot suggests the presence of Mg-Al and AFm phases. The slope of Mg/Ca versus Al/Ca obtained by least square regression analysis provides the estimation of Mg/Al ratio of Mg-Al phase, which is about 2.04 for NH mixture, 1.55 and 1.60 for NC and KH mixture, and 1.1 for NL mixture. In addition, the strong linear correlation between Al/Ca ratio versus Si/Ca ratio indicates the structural substitution of Al^{3+} for Si^{4+} in the tetrahedral silicate chain of C-A-S-H [25, 26]. Based on the regression analysis, the type of cation (e.g. Na^+ , K^+) does not substantially affect the incorporation of Al^{3+} in C-A-S-H. On the other hand, the strong correlation between $(\text{Na}+\text{K})/\text{Ca}$ versus Si/Ca for sodium-activated slag implies the alkali binding on the hydrated phases [27]. This binding mechanism may be a result of structural incorporation of alkalis into the silicate structure, or a physical adsorption at the surface of C-A-S-H [28]. At the same Ca/Si ratio, the amount of bound sodium in NL and NC mixtures tends to be higher than that of NH mixture, which is likely due to the initial higher sodium concentration in the pore solution. By contrast, for potassium-activated slag, the retention of alkalis is substantially higher than that of sodium-activated slag, and no correlation between $(\text{Na}+\text{K})/\text{Ca}$ and Si/Ca can be clearly observed. It may be attributed to the presence of potassium-rich crystals

in potassium-activated slag as detected in XRD. Furthermore, it is likely that the K^+ , unlike Na^+ , can access to larger surface areas or sites in C-A-S-H, and enter the interlayer space in addition to the external surface adsorption and structural incorporation [24].

3.2 Pore structure

Figure 3 shows the MIP pore size distribution of all AAS mixtures at 28d. It can be seen that the addition of chloride does not dramatically change the pore size distribution of NH mixture, while carbonate seems to slightly refine pore structure, although the effect is marginal. However, potassium-activated slag has a substantially coarser pore structure and larger porosity than sodium-activated slag.

3.3 Length and weight changes

Figure 4 (a), (b) shows the length and weight changes of AAS mixtures dried at nitrogen and atmospheric conditions. At nitrogen condition, potassium-activated slag loses relatively more weight and shrinks less than sodium-activated slag mixture. It may be attributed to its coarser pore structure, which retains less moisture and builds lower *effective capillary stress* (defined as the capillary stress multiplied by the degree of saturation [18]) on the solid skeleton. Similarly, for sodium-activated slag, the addition of chloride and carbonate reduces the weight loss but increases the magnitude of drying shrinkage. This observation simply confirms the previous findings that the dominant shrinkage driving force for AAS at 50% RH is capillary stress due to meniscus formation in pores [9, 10, 16]. According to the capillary pressure theory, the radius of the meniscus formed in capillary pores is primarily controlled by the ambient RH, surface tension, and water activity of pore solution [16, 29]. Therefore, at the same RH under

equilibrium condition, the amount of water retained in the material is a function of pore solution properties and pore structure [16]. Considering that the pore size distributions of sodium-activated slag are similar as obtained by MIP, the lower moisture loss in NL and NC mixtures indicates lower water activities in the pore solution due to higher ionic concentrations, in comparison to NH mixture.

It can be seen, from Figure 4 (a), that NL and NC mixtures show slower shrinkage kinetics, in comparison to NH mixture. As evidenced from the correlation of length and weight changes for AAS mixtures at nitrogen condition (see Figure 4 (c)), all mixture exhibits a visco-elastic/visco-plastic shrinkage characteristic, in which the shrinkage magnitude continues to increase while the moisture loss amount almost constant. The mechanisms of visco-elastic/visco-plastic shrinkage characteristics in AAS have been extensively studied in our previous studies [9, 10, 16, 30]. This shrinkage characteristic was mainly attributed to the high alkalinity in AAS, and OPC paste containing alkalis shows similar performances [27, 31]. As such, the relatively higher magnitude of shrinkage and delayed shrinkage kinetics in NC and NL mixtures, as compared to NH mixture, can also be attributed to the higher amount of alkalis incorporated in C-A-S-H.

In the atmosphere, a distinctive shrinkage performance is observed for all AAS mixtures while the weight change trends remain similar, in comparison to those in nitrogen condition. The measurements were terminated at about 55d because all air-dried samples were disintegrated with extensive micro-cracking. The length change plot (see Figure 4 (a)) shows that the AAS mixtures undergo subsequent expansion after initial shrinkage. The shrinkage at early ages is undoubtedly attributed to the drying, while the subsequent expansion is due to the carbonation.

However, the magnitude of shrinkage at early ages is still smaller than that at nitrogen condition, indicating that the effect of carbonation on volume change begins at a very early age. Therefore, it is argued that carbonation does not contribute to the large shrinkage of AAS, as it actually reduces it.

Figure 4 (a) also displays that potassium-activated slag starts to expand after drying for 14d, NH and NC show expansion at 35d, and NL shows expansion after 54d. Considering that sodium-activated slags have similar hydrated phase assemblage and pore structure, the relatively delayed expansion in NL mixture may be related to protection from the slow carbonation kinetics of Friedel's salt [32]. From Figure 4 (c), it can be seen that there exists an intersection point for each mixture dried at nitrogen and air condition. Before that intersection point, the correlation between shrinkage and moisture loss are similar for AAS dried at nitrogen and air, while after that point, the samples dried at air show expansion.

3.4 Carbonation-induced phase and microstructural changes

Figure 5 shows the comparison of XRD patterns of AAS dried at nitrogen and atmospheric conditions. The peaks corresponding to Mg-Al phase, Friedel's salt, portlandite, and C-S-H (I) are significantly lower or completely gone due to carbonation, resulting in extensive formation of calcite and vaterite. The significant reduction of Mg-Al phase at air confirms that it is vulnerable to carbonation and may postpone the carbonation of C-A-S-H [33], although it is clear that the carbonation of Mg-Al phase and C-S-H (I) occurs simultaneously. The main carbonation product of Mg-Al phase, which is believed to be carbonate-containing hydrotalcite [33], is however not unambiguously detected in XRD. For potassium-activated slag, the extent of carbonation seems

to be larger than that of sodium activated slag, as evidenced by the complete decomposition of hydrated phases, which agrees with the earliest appearance of volume expansion of this mixture. It indicates that the potassium makes AAS more vulnerable to carbonation, probably due to the higher bound alkali content and more amorphous structure of C-A-S-H.

Figure 6 shows the secondary electron images of AAS dried at nitrogen condition for 114d. It can be seen that various crystals can be observed in AAS, with the exact sizes and shapes depending on the activator types. A distinctive morphology of C-A-S-H formed at NC mixture is observed, as compared to others. As shown in Figure 7 (a), (b), it seems that convergent needle-like C-A-S-H phase forms in the non-carbonate mixture (i.e. NH, NL, and KH), while a compacted foil-like C-A-S-H phase forms in NC mixture. Additionally, the morphological changes are observed for AAS samples undergoing carbonation in air, as shown in Figure 7 (c), (d). It clearly shows the clusters of amorphous particles (mainly calcite) depositing at the surface of C-A-S-H, which is intimately mixed with or completely embed with C-A-S-H. The carbonation of C-A-S-H may be responsible for the transformation from needle-like to foil-like morphology. Furthermore, crystalline phases with varying shapes, sizes and morphologies, as shown in Figure 7(e), (f) can be observed in air-dried samples. The sizes of these crystals observed in carbonated samples are generally larger than that in non-carbonated samples shown in Figure 6. The formation of these large crystals due to carbonation is believed to cause the expansion and volumetric disintegration in AAS as explained in the Section 3.5.

3.5 Volume change mechanisms

The volume expansion, micro-cracking, and disintegration of AAS dried in the air can be attributed to the localized expansion in microstructure as a result of crystals growth. As carbon dioxide is progressively dissolved in the pore solution, the growth of calcites (or aragonite, or vaterite) nucleus begins when it is supersaturated with respect to Ca^{2+} , carbonate acids, and probably other ions (e.g. Na^+). Assume that the calcite crystals is spherical with a radius of r_c , and the interfacial free energy between carbonates crystals and pore solution is γ_{CL} , then the amount of pressure that would have to be imposed to inhibit the growth of crystals can be estimated as [34]:

$$p = -\frac{2\gamma_{CL} \cos \theta_{CL}}{r_c} \quad (1)$$

In which θ_{CL} denotes the contact angle between the crystal-pore solution interface and the pore wall. It can be seen that p increases for decreasing r_c . Because of the presence of pressure p on the surface of the crystal, the solubility of crystal, Q_c , shifts from the bulk solubility, K , depending on the crystal curvature [35]:

$$p = \frac{RT}{V_c} \ln \left(\frac{Q_c}{K} \right) \quad (2)$$

In which K is the equilibrium solubility for a macroscopic crystal; Q_c is the solubility products of crystals with a curvature of $1/r_c$; R is the gas constant, T is the absolute temperature, and V_c is the molar volume of the crystal. Eq. (2) implies that a small crystal is in equilibrium with a higher concentration of solution than a macroscopic crystal.

When the growth of crystal has not been restrained by the pore walls (i.e., $r_c \leq r_p$, where r_p is the radius of pore with a cylindrical shape), as illustrated in Figure 8 (a), the crystal continues to

grow as far as the solubility product, Q_E , of the pore solution adjacent to the crystal is larger than Q_C . Since the growth crystal has not been restrained by the pore wall, there is no crystallization pressure exert on the solid skeleton. At a critical point (see Figure 8 (b)), in which the crystal has just contacted with the pore walls in an equilibrium state, i.e., $r_C=r_p$, the products solubility, Q_S , must be equal to Q_C . However, when crystal has contacted with the pore wall (see Figure 8 (c)), and the liquid surrounding the unrestrained surface of crystals has a solubility product, Q_E , larger than that Q_S , the pore wall must apply pressure to block the growth of crystals. In other words, a confined crystal can only exert stress if it is in contact with a pore solution that is supersaturated with respect to the unloaded face of the crystal [36]. In return, the crystallization pressure, p_w , that crystal exerts on the pore wall is [37]:

$$p_w = \frac{RT}{V_C} \ln \left(\frac{Q_E}{Q_S} \right), \text{ where, } Q_S = K \cdot \exp \left(-\frac{V_C}{RT} \cdot \frac{2\gamma_{CL} \cos \theta_{CL}}{r_p} \right) \quad (3)$$

It should be noted that Q_S is dependent on the pore radius r_p . According to Eq. (3), a higher crystallization pressure in porous materials can originate from either smaller pore sizes or higher product solubility Q_E (i.e. higher level of supersaturation). This argument is based on the assumption that the type of crystals and the interfacial free energy between crystals and pore solution are similar among various systems.

In comparison to OPC paste, AAS has been reported to have a finer pore structure (i.e., smaller r_p) based on MIP data [8, 9]; therefore, the precipitation of calcite in the restrained small pore space of AAS can generate large crystallization stress, resulting in expansion and cracking. It indicates that the apparent carbonation-induced volume change in cementitious materials is not

merely related to the chemical reactions, but also the physical characteristics (e.g. pore structure) of cementitious microstructure. On the other hand, the presence of alkalis in the pore solution may promote the formation of alkali-rich carbonates, with a relatively high Q_E . It should be mentioned here that a recent study shows that atmospheric carbonation can induce expansion in OPC paste containing alkalis [27]. In addition, previous studies show that the addition of alkalis promotes the carbonation of C-S-H, by modifying its chemical composition and structure [38, 39]. The increased concentration of alkalis in pore solution decreases the Ca/Si ratio of C(-A)-S-H, due to the competition effects between Ca^{2+} and alkali cations on compensating the negative charge of deprotonated silicate chains [28]. Therefore, it is reasonable to deduce that the C-A-S-H formed in AAS, which has higher alkali content and lower Ca/Si ratio, is more thermodynamically vulnerable to carbonation, compared with that the C-S-H in OPC. It is suggested here that the high content of alkalis in AAS systems contributes considerably to the expansion and micro-cracking during carbonation.

4. Conclusions

In this paper, the hydrated phase assemblage, microstructure, and pore structure of AAS activated by four different types of activator were characterized and their shrinkage performance at two gaseous conditions (i.e. nitrogen and air) were studied. Following conclusions can be drawn based on this study:

(1) Carbonation shrinkage does not significantly contribute to the large shrinkage deformation of AAS. In fact, carbonation of AAS in the atmosphere results in volumetric expansion and subsequent disintegration.

(2) The origin of carbonation-induced volumetric expansion and disintegration of AAS may be attributed to the crystals precipitation in refined pore space.

(3) Carbonation-induced volume change in cementitious materials is a combined result of the chemical reactions and physical characteristics. For AAS, due to its refined pore structure, the growth of carbonates can generate high crystallization stress due to restriction from pore walls.

(4) Carbonation of AAS results in the dissolution and decomposition of Mg-Al phase, Friedel's salt, portlandite, and C-S-H (I), forming amorphous and crystalline calcite and vaterite.

(5) The binding mechanisms of Na^+ and K^+ in hardened AAS are different; K^+ seem to enter the interlayer space, distort the stacking ordering of C-A-S-H layers, and adsorbs in a larger amount in AAS than Na^+ .

(6) Potassium-activated slag shows coarser pore structure, larger moisture loss, and slightly lower shrinkage, in comparison to sodium-activated slag.

(7) It is suggested that the high alkali content in AAS systems contributes considerably to its poor volumetric stability under carbonation.

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Table 1 Chemical composition (by mass %) of slag

	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	S ²⁻	Fe ₂ O ₃	Na ₂ O	K ₂ O	P ₂ O ₅	MnO	LOI
Slag	43.83	30.04	12.74	4.79	3.11	0.85	1.16	0.24	0.40	0.08	0.22	2.56

Table 2 Mix proportion for AAS paste with various alkalis

Mixture ID	Composition of activator	Volumetric activator-to-slag ratio
S_NH	4M NaOH	
S_NL	4M NaOH+1M NaCl	
S_NC	4M NaOH+0.5M Na ₂ CO ₃	1.45
S_KH	4M KOH	

Note: In the Mixture ID, N and K represent sodium and potassium, while H, L, and C represent hydroxide, chloride, and carbonates.

Figure 1 XRD patterns of AAS prepared with various alkaline solutions at 1d, 7d and 28d, which shows the evolution of hydrated phase assemblage in AAS as a function of age and type of activator. The mixture description is elaborated in Table 2.

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(a)

(b)

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(c)

Figure 2 The atomic relationship in the solid hydrated phases of AAS (a) Mg/Ca ratio versus Al/Ca ratio; (b) Si/Ca ratio versus Al/Ca ratio; (c) (Na+K)/Ca ratio versus Si/Ca ratio

Figure 3 Pore size distribution of AAS paste cured for 28d, which shows that potassium-activated slag has a substantially coarser pore structure than sodium-activated slag.

(a)

(b)

(c)

Figure 4 (a) Time-dependent shrinkage of AAS, which shows that drying at atmospheric condition results in an initial shrinkage but subsequent expansion; (b) Time-dependent moisture loss of AAS, which shows the similar trends when dried at nitrogen and atmospheric conditions; (c) Correlation of shrinkage and moisture loss of AAS, which shows the presence of intersection points.

Figure 5 XRD patterns of AAS dried at nitrogen and atmospheric conditions

Figure 6 Secondary electron images of AAS paste dried at nitrogen condition for 114d (a) S_NH; (b) S_NL; (c) S_NC; (d) S_KH

(a)

(b)

(c)

(d)

Figure 7 (a) S_NH mixture dried at nitrogen for 114d, magnification 80000x; (b) S_NC mixture dried at nitrogen for 114d, 80000x; (c) S_NH mixture dried at air for 55d, 30000x; (d) S_NH mixture dried at air for 55d, 80000x; (e) S_NC mixture dried at air for 55d, 30000x; (f) S_KH mixture dried at air for 55d, 10000x

Figure 8 Illustration of crystal growing in a cylindrical pore

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