Carbonation-induced volume change in alkali-activated slag

Hailong Ye *, Aleksandra Radlińska

Department of Civil and Environmental Engineering, The Pennsylvania State University, 3127 Research Drive, State College, PA 16801, United States

HIGHLIGHTS

- Crystal growth model explains the carbonation-induced volume change in AAS.
- The effect of different types of cation and anion in activator on AAS is studied.
- New insights on the mechanisms of volumetric instability of AAS are provided.

ARTICLE INFO

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.

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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 CO_2 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,

* Corresponding author.
  E-mail address: huy131@psu.edu (H. Ye).

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 $2\theta = 30°$–$31.6°$ (see Fig. 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 mm × 12.7 mm × 139.7 mm (½ inch × ½ inch × 5½ 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 ± 0.5 °C) for 24 h 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 ± 0.5 °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 ± 4% RH and 23 ± 0.5 °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 0.01 g.

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 ± 0.5 °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 28 d.

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 114 d, while for atmospheric condition it was 55 d), 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

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