Key Engineering Materials
ISSN: 1662-9795, Vol. 803, pp 262-266
doi:10.4028/www.scientific.net/KEM.803.262

Submitted: 2019-01-27
Accepted: 2019-02-13
Online: 2019-05-20

A Review of Alkali-Activated Slag as Cement Replacement

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Keywords: alkali activated slag, carbonation, shrinkage, rheology, alkaline activator, compressive strength.

Abstract. Alkali activated slag (AAS) offers opportunities to the construction industry as an alternative to ordinary Portland cement (OPC). The production of OPC and its use contributes significantly to release of CO_2 into the atmosphere while AAS is an industrial by-product that contributes much less to the environmental footprint that needs to be recycled if not landfilled. This paper outlines some of the key properties, merits and demerits of AAS when used as alternative to OPC. Competitive compressive strength of AAS concrete is amongst of the advantages of replacing cement with AAS while high shrinkage and carbonation levels are potential disadvantages.

Introduction

Replacement of OPC with alumnisilicates activated with alkalis is gaining popularity in research and industry, a movement that is motivated by the desire to reduce the emmission of CO_2 associated with the production of OPC. The International Engery Agency (IEA) [1] estimates that cement industry is responsbile for 7% of the global CO_2 emission. Cement industry is also the third largest industrial enery consumer. Popular aluminusilicates studied or used in industry include ground granulated blast furnace slag (GGBS), fly ash, and metakoaline. It is possible to enhance compressive strength, impermeatiliby, and chloride penetration resistane of AAS concrete by partial replacement of slag with silica fume [2]. Slag is activated using various compounds such as sodium hydroxide (NaOH), potassium hydroxide, sodium carbonate, sodium silicate, or certain combinations of these alkalis.

Slag Alkaline Activators

A variety of alkaline activators were used in AAS concrete that were studied by researchers including but not limited to sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium silicates. Brough and Atkinson [3] reported that potassium hydroxide (KOH) alkaline activator produced more rapid reaction but less homogeneous microstructure, and lower strength compared to AAS mixes activated using sodium silicates. The authors reported that activation of AAS with KOH produced higher strength only after one day of curing, but not in the long term. NaOH alkaline activator solution may be prepared by adding water to sodium oxide (Na_2O) according to the reaction $Na_2O + H_2O \rightarrow 2NaOH$.

In order to assess the effect of curing method on performance of AAS concrete, El-Hassan et al. [4] activated slag using grade N soldium silicate, also known as water glass (GW), combined with sodium hydroxide (NaOH) solution. Sodium silicate solution solution consists of 26.3% SiO_2, 10.3% Na_2O, and 63.4% H_2O by mass. NaOH was prepared to a molar concentration of 14 M by dissolving 97%-98% pure NaOH pellets in tap water. The ratio of sodium silicate solution to sodium hydroxide solution was 2.5. The alkali-activator solution to slag ratio ranged from 0.45 to 0.55 by weight. In preparing the activator mix, NaOH solution was prepared 48 hours prior to casting and was added to the sodium silicate solution 24 hours after mixing. This allow the heat released from the two reactions to dissipate prior to beginning the concrete mixing protocol.

In order to understand the rheological properties of AAS concrete, Puertas et al. [5] prepared two activator solutions: 1) 10 M NaOH solution prepared by dissolving in water 5% Na_2O by mass of slag and 2) sodium silicate hydrate solution. Sodium silicate hydrate solution was prepared using sodium

silicate solution consisting of 27 wt% SiO_2, 8 wt% Na_2O; and 65 wt% H_2O. The modulus (Ms = SiO_2/Na_2O) of the sodium silicate solution was adjusted using NaOH solution (5% Na_2O by slag mass).

Shi et al. [6] investigated alkali-silica reaction (ASR) of AAS mortars activated used NaOH. AAS mortar specimens were prepared with one part of slag activated by NaOH and 2.25 parts of graded sand by mass at w/b ratio of 0.47. NaOH activator solutions was prepared using 4, 6 and 8 wt.% Na_2O by mass of slag. The activator was pre-dissolved in a fraction of the mixing water before mixing.

Zhu et al. [7] studied the effect of $Ca(OH)_2$ on shrinkage characteristics and microstructures of alkali-activated slag concrete. AAS was activated using sodium silicates (water glass). Na_2O equals to 5% by mass of slag was used to create NaOH solution and added to the sodium silicate solution to adjust the modulus (Ms = SiO_2/Na_2O = 1.2) of water glass.

Ye and Radlinska [8] studied carbonation of AAS mortars using alkali activator solutions prepared using four different compounds including sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na_2CO_3), and potassium hyroxide (KOH). To prepare activator solutions, alkali salts pellets or powders of sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na_2CO3), or potassium hydroxide (KOH), were dissolved in distilled water. 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.

Fresh Properties, Rheology, and Hardened Properties

Puertas et al. [5] studied the effect of activator type used for AAS on the rheology and compressive strength of concrete. The effects of two activator solutions were examined, NaOH solution and sodium silicate solution (water glass). OPC concrete samples and AAS samples were prepared at the same water-to-binder ratio of 0.5. Rheology of concrete is adversely affected by longer mixing time when the binder used is OPC or slag activated with NaOH. However, longer mixing time improved both the rheology and mechanical properties of concrete when the binder is slag activated using water glass (WG). Compared to control mixes prepared using OPC, AAS mixes had larger slump regardless of the activator type used. Specimens tested for compressive strength were 100 mm cubes demolded after 24 hours of casting and cured for 7-days and 28-days. The authors noted that the highest compressive strength after 7- and 28-days of curing was obtained when commercial waterglass activator was used to activate AAS concrete, compared to OPC or to mixes that used NaOH as activator.

Similar to traditional OPC concrete, curing method affects compressive strength development of AAS concrete. El-Hassan and Shehab [4] noted that intermitted curing of AAS concrete produced higher compressive strength after 28-days of curing compared to air curing and continuous curing under water. In intermittment water curing regime, the authors cured AAS concrete under water for 7 days, then in air for 21 days. On the other hand curing of AAS concrete under water was shown to produce higher compressive strength compared to curing under plastic cover [2].

Volume Change Due to Alkali-silica Reaction

In ordinary Portland cement (OPC) mortar and concrete, alkali–silica reaction (ASR) takes place between potentially reactive aggregates and the alkalis present in cements (Na_2O+K_2O) and $Ca(OH)_2$ under favorable humidity conditions. ASR can result in significat reduction in concrete compressive strength in the long term [9].

Fernandez-Jimenez and Puertas [10] studied Alkali-aggregate reaction in mortar mixes using AAS as binder and compared the results to OPC samples. The aggregate used in making these samples contained 21% reactive silica. The mixes were prepared using slag activated with calcium hydroxide NaOH solution prepared using Na_2O equals to 4% by weight of slag. They concluded that ASR expansion occurs in AAS specimens but at a slower rate compared to OPC mortar specimens. The

authors observed expansion of samples due to the formation of sodium and calcium silicate hydrate reaction products with rosette-type morphology. After 140 days, AAS mortar specimens immersed in water showed very little expansion compared to OPC samples. Similarly, AAS mortar samples showed less expansion compared to OPC mortar samples immersed in NaOH solution.

Shi et al. [6] investigated alkali-silica reaction (ASR) of mortars prepared using slag activated using 4%, 6%, and 8% wt Na_2O by mass of slag. Accelerated ASR test was conducted by submerging mortar samples in 1 mol/L of NaOH solution and ASR expansion of mortar samples was measured up to 28 days. Before adding the NaOH solution, the alkalinity of the pore solution was higher in AAS mortars compared to Portland cement mortars. However, 28-days after adding the NaOH solution, the alkalinity of the pore solution of the mortars was higher in Portland cement mortars than in AAS mortars. As a result, ASR expansion was lower in AAS mortars compared to the Portland cement mortars.

Volume Change Due Shrinkage of AAS Concrete and Mortar

Shrinkage of concrete may lead to cracking and allow aggressive substances to penetrate concrete and increases risk of corrosion of reinforcement in structures. Some investigators reported that AAS concrete showed about 3 times higher drying shrinkage than PC concrete and the greater proportion of mesopores (1.25 to 25 nanometers in radius) in AAS concrete was believed to be one main reason for the increasing drying shrinkages.

The capillary pores include mesopores and macropores (25 to 5000 nanometers in radius) and represent the space between binder grains that will be filled by mixing water. Micropores (less than 1.25 nanometers in radius) constitute part of the calcium silicate hydrate gel component. Shrinkage under typical circumstances occurs due to loss of water from the mesopores, therefore, the size of the macropores determines how easily water may be lost from the mesopores. In the case of alkali-activated slag, the proportion of pores in the micropore size range tend to be higher than OPC.

Analysis of the incremental pore size distribution data shows that AAS concrete has a much higher proportion of pore sizes within the mesopore range than OPC cement. The proportion of pores within the mesopore classification ranges from 74.0% to 82.0% for AAS concrete compared with 24.7 - 36.4% for OPC concrete [11]. Similarly, macropores in AAS concrete ranged from 12.5% to 16.6% compared to a range of 56.7% to 69% for OPC concrete.

Zhu et al. [7] studied the effect of adding $Ca(OH)_2$ to AAS concrete to assess the effect on shrinkage characteristics. The authors investigated plastic shrinkage, autogenous shrinkage, and drying shrinkage. 5% and 10% of the slag content was replaced with $Ca(OH)_2$ which resulted in increased plastic shrinkage but reduced autogenous and drying shrinkage. $Ca(OH)_2$ increased hydration at early age, up to 120 hours, which contributed to increased plastic shrinkage. Mesopores which are typically linked to autogenous and drying shrinkage, decreased by adding $Ca(OH)_2$ to mixes that contained water-to-binder ratio (w/b) of 0.45. Decreased mesopores which contributed to reduction to reduction in autogenous and drying shrinkage. The Ca/Si ratio in C-S-H gel of samples containing $Ca(OH)_2$ increased to 1.4 in 28 days, which the authors believe contributed to decrease of autogenous and drying shrinkage.

Collins and Sanjayan [11], studied pore size distribution and drying shrinkage in AAS concrete in comparison to equivalent OPC concrete samples. The water-to-binder (w/b) ratio for concrete studied was maintained at 0.5 They concluded that drying shrinkage is much higher in AAS paste compared to equivalent OPC paste. This higher drying shrinkage is associated with higher percentage of mesopores (2 to 50 nanometers) in AAS paste compared to OPC. The authors attribute the higher drying shrinkage to capillary tensile forces during rather, not the moisture content. The activator solution was prepared from powdered sodium metasilicates and hydrated lime ($Ca(OH)_2$).

The authors also noted that weight loss during drying was higher in OPC samples compared to AAS samples, yet drying shrinkage was higher in AAS samples compared to OPC samples. Therefore, the

authors concluded that drying shrinkage is not entirely due to weight loss of weight from concrete. After 365 days, the difference between drying shrinkage of AAS and OPC becomes constant.

Carbonation Alkali Activated Slag

Carbonation of the pore solution in concrete and mortar results in reduction of alkalinity, which increases susceptibility of reinforcing steel bars to corrosion. Reduction in alkalinity may also lead to decalcification in calcium bearing phases such as C-(A)-S-H phase, katoite (C_3AH6) and/or strätlingite (C_2ASH8) formed in alkali-activated slag mortars or concretes. Therefore, unlike in OPC concrete, carbonation of alkali-activated slag paste occurs directly in the C–A–S–H gel because of the lack of portlandite ($Ca(OH)_2$), leaving an alumina-containing remnant siliceous gel in addition to $CaCO_3$ [[12].

Ye and Radlinska [8] studied volume changes in mortars prepared using AAS activated using different activators. Mortar samples tested for carbonation were prepared from four alkali activator types, namely, sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na_2CO_3), and potassium hydroxide (KOH). The mortar samples were subject to either atmospheric conditions or nitrogen environment. The investigators noted that AAS samples undergo expansion and disintegration under atmospheric conditions. Potassium ions (K^{++}) can enter the interlayer space of calcium-alumina-silicate-hydrate (C-A-S-H) and make AAS vulnerable to carbonation. The authors argue that the high alkali content in AAS systems contribute to poor volumetric stability associated with carbonation.

Shi et al. [13] studied carbonation of mortar samples prepared used AAS activated using 6 wt% and 8 wt% Na_20 by mass of slag. Samples prepared with AAS activated with alkaline solutions having different moduli were stored in carbonation chamber for 56 days. They noted that Alkali-activated slag mortars are more susceptible to carbonation under accelerated carbonation condition compared to the Portland cement mortar. However, it may exhibit higher carbonation resistance under natural conditions, especially when AAS is activated with water glass having high modulus as shown in Fig. 1. AAS mortars with high alkali content and high silicate modulus have reduced total porosity and average pore size. The results in increased carbonation resistance and compressive strength. The carbonation depth of AAS mortars made with 8% Na_2O was lower than AAS mortars made with 6% Na_2O

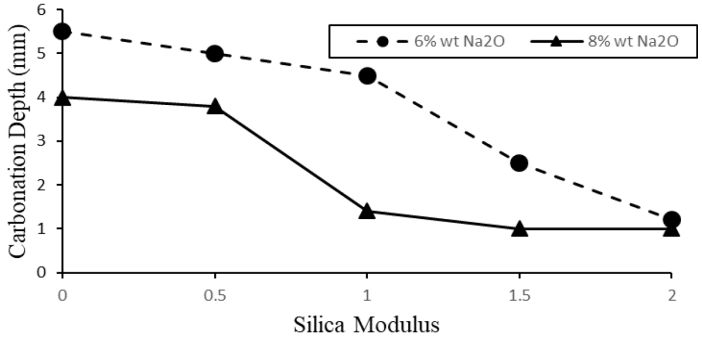

Figure 1. Carbonation Depth Variation with Silica Modulus for 6% and 8% Na_2O

The authors argue that carbonation of C-(A)-S-H phase leads to reduction in the molar volume of solids, which explains the increase of the total porosity and average pore size, subsequently reduction in compressive strength. However, Carbonation of C_3AH_6 phase leads to increase of the molar volume of solids, which explains the reduction in total porosity and average pore size of the NaOH activated slag mortars, and explains the increase of compressive strength as well.

It is important to note that currently implemented carbonation testing methods are accelerated under elevated CO_2 levels. This is done in order to make the naturally slow carbonation process observable in the laboratory. These accelerated tests are extremely aggressively and unlikely represent

realistic service conditions. As a result current accelerated carbonation tests may overestimate the risk of carbonation under realistic service conditions [12]. Furthermore, Under natural CO_2 exposure conditions, the excess alkalis present in the pore solution of an alkali-activated binder may potentially maintain the internal pH at a level which is sufficiently high to protect steel in a passive state

Summary

Compressive strength of concrete prepared using AAS activated with commercial sodium silicate activator is higher than equivalent concrete prepared using sodium hydroxide as activator or using ordinarily Portland cement. AAS concrete is susceptible to high levels of volume change to shrinkage, carbonation, and alkali-silica reaction. However, response of concrete depends on activator type and modulus. Concrete with AAS activated using water glass with high alkali content (8%) and high modulus (up to 2.0) exhibited higher resistance to carbonation and higher compressive strength compared to lower alkali content and lower modulus. It is possible to decrease autogenous and draying shrinkage by adding $Ca(OH)_2$ to AAS concrete, but this leads to increase in plastic shrinkage.

Acknowledgment

The authors appreciate the financial support of the Abu Dhabi Department of Education and Knowledge (ADEK) provided under the ADEK Award for Research Excellence (AARE) 2017 program.

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