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The Effect of Alkali Concentration and Sodium Silicate Modulus on the Properties of Alkali-Activated Slag Concrete

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Abstract

In this study, the effect of alkali concentration and sodium silicate modulus of the activator solution on workability, compressive strength, and drying shrinkage of alkali-activated slag (AAS) concrete was investigated experimentally. Twenty mixes were prepared with the ground granulated blast furnace slag (GGBFS) activated with the various alkali concentrations and sodium silicate modulus. The compressive strength at the ages of 7, 28 and 90 days was measured and the drying shrinkage of the concrete samples up to 400 days were measured. Based on the results, in most mixes, by increasing the sodium silicate modulus and the concentration of the alkali solution, the slump, compressive strength, and the rate of the drying shrinkage of the samples were increased, but the setting time was reduced. These results were contrary to those specimens cast with high alkalinity. The effect of the sodium silicate modulus was much higher than the concentration of the alkali solution on the drying shrinkage of the samples. In order to evaluate the effect of the alkali concentration and the silicate modulus on the microstructure and the reaction product of the AAS paste, x-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) images were examined.

1. Introduction

The use of industrial by-products as binders can be a good alternative to the ordinary Portland cement (OPC). Worldwide production of Portland cement has been 4.2 billion tons in 2017 (U. S. Geological Survey 2017). While the production of 1 ton cement releases about 0.9 ton of CO₂ (Gartner 2004; Taylor *et al.* 2006), and it can be reduced by the implementation of the current green technologies and energy efficiency measures (Gessa-Perera and González-Expósito 2017; Zuberi and Patel 2017), most of it is due to heating and decomposition of limestone, leading to the formation of calcio-silicate phases. The use of alkali-activated binders based on the high-calcium materials has been considered during the recent century, by utilizing GGBFS and other industrial by-products (Pacheco-Torgal *et al.* 2014).

The formation of the gel structure in the activation of slag depends on the activator and the properties of the raw materials (Duxson *et al.* 2007). The anions in the activator react with the Ca²⁺ from the slag particles, producing mainly calcium aluminosilicate hydrate that is more resistant to leaching and chemical attack than Ca(OH)₂ (Shi and Day 1996; Taylor 1997), which is generated in OPC hydration. However, the use of alkali-

activated slag (AAS) binders is limited due to the low workability, the high drying shrinkage, and high carbonation rates (Bakharev *et al.* 2001; Behfarnia and Rostami 2017a; Law *et al.* 2012; Rostami and Behfarnia 2017). In order to make the widespread use of AAS concrete in the construction industry, it is necessary to examine the effect of different factors on the properties of the AAS concrete.

The setting time is decreased with the increase in the silicate modulus and the sodium concentration of alkaline solution, but in the mixes with a high alkali concentration and for a silicate modulus greater than 1.2, the setting time should be increased (Atiş *et al.* 2009; Bakharev *et al.* 1999b).

Neto *et al.* (2008) showed that enhancing the amount of alkali in the AAS paste increased the rate and the total amount of the released heat, concluding that this factor could increase the degree of hydration (Neto *et al.* 2008). The use of sodium silicate activation results in the highest compressive strength and drying shrinkage, as compared to other common types of activators in the AAS concrete (Bakharev *et al.* 1999b), which can produce the highest compressive strength by using a silicate sodium solution with a silicate modulus of 0.6 to 1.5 (Gao *et al.* 2016; Krizan and Zivanovic 2002). Some researchers have also reported a loss in the compressive strength for the mixtures with a silicate modulus of more than 1 (Wang *et al.* 1994). The compressive strength is enhanced with increasing the alkali concentration, but high alkali concentrations can weaken the gel structure of the binder (Cheng and Chiu 2003; Shojaei *et al.* 2015; Wang *et al.* 2005).

Concrete experiences chemical shrinkage, autogenous, drying, and carbonation shrinkage after casting. The drying shrinkage is due to a change in the volume of

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Table 1 Chemical composition (wt%) of the slag and cement.

oxide	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	alkalies
Slag (%)	35.5	9.5	36.0	0.5	9.5	0.8
Cement (%)	21.5	5.3	63.5	3.3	2.4	0.8

hydration products, consumption of the pore water during the hydration and also, the evaporation of the pore water to the outside of the concrete surface; it is usually measured in a hardened state. It is reported that the drying shrinkage of the AAS concrete is higher than that of the ordinary Portland cement (OPC) concrete (Collins and Sanjayan 1999; Douglas *et al.* 1992); this is such that the drying shrinkage has been measured to be 3.33 times higher than that of the OPC concrete. Therefore, understanding the factors affecting the shrinkage of the AAS concrete are necessary.

A large number of pores exists in the mesopore range for AAS binders, as compared with OPC (Collins and Sanjayan 2000b); capillary tensile forces and the absence of expansive phases such as ettringite and portlandite within the AAS binders are the reasons for the higher shrinkage of AAS binders, relative to OPC (Ye and Radlińska 2016a; Yuan *et al.* 2014). The viscous performance of AAS binders is due to the reorganization of C-A-S-H sheets under capillary stresses that influence the drying shrinkage, and drying shrinkage is not directly related to the amount of water loss, and the maximum of the drying shrinkage has occurred in AAS samples cured at the relative humidity of 50% (Ye and Radlińska 2016b). In addition, recent studies have shown that the creep coefficient of AAS concrete is more than that of OPC (Ma and Dehn 2017); the reason for the high drying shrinkage of AAS binders may be the visco-elastic / visco-plastic behavior of these binder (Ye 2015; Ye and Radlińska 2017b), and the type and dosage of activator, as well as the relative humidity of drying room in the microstructure rearrangement over time (Wardhono *et al.* 2015; Ye *et al.* 2017). The alkali concentration and silicate modulus could have a direct relationship with the drying shrinkage of AAS binders (Atiş *et al.* 2009; Bakharev *et al.* 1999b; Krizan and Zivanovic 2002), so that porosity reduction and pore refinement could be observed with increasing the alkalinity of the mixture. The highest amount of drying shrinkage has been obtained by using the silicate sodium solution with the silicate modulus of 1 (Bakharev *et al.* 1999b). Decreasing curing temperature to less than the normal temperature (Gu *et al.* 2015) and replacing the slag with a low calcium-based material (Chi and Huang 2013; Lee *et al.* 2014) can reduce the drying shrinkage and also retard the compressive strength. Curing at elevated temperatures and also curing in the wet conditions (Bakharev *et al.* 1999a; Collins and Sanjayan 2000a) can reduce the drying shrinkage.

A large number of studies have been carried out on the shrinkage of the conventional concrete, helping to provide the analytical models for the shrinkage prediction of the OPC concrete gathered in ACI 209.2R-08

(2008). Due to limited studies on the shrinkage of the AAS concrete, it is difficult to predict the shrinkage of this type of concrete.

In many publications the effect of activators on properties of AAS mixtures is studied; however, contradictory results have been reported because of type and amount of the activator used. In this study, twenty mixes were designed with a certain range of alkali concentration and silicate modulus. The hydration mechanism and products were investigated in order to evaluate the relationship between the workability, compressive strength and microstructure of AAS mixture with the drying shrinkage. Based on the results, the appropriate range of alkali concentration and sodium silicate modulus to prevent the loss of compressive strength, rapid setting and high shrinkage of AAS concrete is defined. In order to evaluate the workability of AAS concrete, the slump of fresh concrete and setting time were considered. The compressive strength of 7, 28 and 90 days was measured for the concrete specimens. The drying shrinkage was measured over 400 days and the differences and similarities between the microstructures and reaction products were investigated through XRD analysis and SEM images.

2. Experimental program

2.1 Materials

In this research, in order to cast AAS concrete specimens, the ground granulated blast furnace slag was activated by the combination of sodium hydroxide and sodium silicate. The slag used in this study was a product of Esfahan Steel Company, with a specific gravity of 2.85 gr/cm³ and a specific surface area of 400 m²/kg. The basicity coefficient $K_b = (CaO + MgO) / (SiO_2 + Al_2O_3)$ was 1.01. The OPC control mix was provided by Sepahan Cement Company. The chemical compositions of the slag and cement are shown in **Table 1**.

Solid sodium hydroxide with the purity of 98% was used to make an alkali solution; at least two hours before concrete casting, sodium hydroxide was mixed with a certain amount of water to complete the chemical reactions and achieve some water-temperature equilibrium. Liquid Sodium silicate (water glass) with $M_s = SiO_2/Na_2O$ modulus was 2.32, with 52% water; it was mixed with sodium hydroxide solution and used as an activator in the AAS mixture to provide a solution with the M_s modulus being in the range of 0.35 to 1.05, and n ($Na_2O/slag$) in the range of 3.5 to 7.5%. River sand with the fineness modulus of 3.06 was selected according to ASTM C33/C33M-18 (2018) as the fine aggregate, and crushed gravel with the maximum aggregate size of 12.5 mm was employed as the coarse aggregate.

Table 2 Mix proportions of the AAS concrete.

Mix	n (Na ₂ O ^a /Slag)	M _s (SiO ₂ ^b /Na ₂ O ^a)	Water glass ^c (kg/m ³)	NaOH (kg/m ³)	W _{add} ^d (kg/m ³)	Binder ^e (kg/m ³)	Water content ^f (kg/m ³)
N35M45	0.035	0.45	18.78	14.56	172.37	423.57	182.14
N45M45	0.045		24.15	18.72	172.47	430.31	185.03
N55M45	0.055		29.52	22.88	172.58	437.04	187.93
N65M45	0.065		34.88	27.03	172.69	443.78	190.82
N75M45	0.075		40.25	31.19	172.79	450.51	193.72
N35M65	0.035	0.65	27.13	13.00	169.08	426.02	183.19
N45M65	0.045		34.88	16.71	168.25	433.46	186.39
N55M65	0.055		42.63	20.43	167.41	440.89	189.58
N65M65	0.065		50.38	24.14	166.58	448.33	192.78
N75M65	0.075		58.14	27.86	165.75	455.76	195.98
N35M85	0.035	0.85	35.48	11.44	165.79	428.47	184.24
N45M85	0.045		45.61	14.71	164.02	436.61	187.74
N55M85	0.055		55.75	17.98	162.25	444.74	191.24
N65M85	0.065		65.89	21.25	160.48	452.88	194.74
N75M85	0.075		76.02	24.52	158.70	461.01	198.24
N35M105	0.035	1.05	43.83	9.89	162.51	430.92	185.30
N45M105	0.045		56.35	12.71	159.80	439.76	189.10
N55M105	0.055		68.87	15.54	157.08	448.59	192.89
N65M105	0.065		81.39	18.36	154.37	457.43	196.69
N75M105	0.075		93.91	21.18	151.66	466.26	200.49
OPC	C=436 kg/m ³ w/c=0.43						

w/b = 0.43, Slag content = 400 kg/m³

^aNa₂O = Na₂O (within water glass) + Na₂O (obtained from NaOH: equal to 1.29NaOH as following reaction)

2NaOH (1.29 gram) → Na₂O (1 gram) + H₂O (0.29 gram)

^bSiO₂ = SiO₂ (within water glass)

^cWater glass = water (0.52%) + SiO₂ (0.34%) + Na₂O (0.14%)

^dW_{add}: Additional water

^eBinder = slag content + NaOH + solid part of water glass

^fWater content = water part of water glass + W_{add}

2.2 Mixture proportions

The minimum concentration of alkali (n) was 3.5% for slag activation. Also, to achieve suitable workability and prevent rapid setting and get the optimum concrete strength, the maximum n content was 7.5% and the silicate modulus (M_s) was selected in the range of 0.45 to 1.05 (Chi and Huang 2013; Marjanović *et al.* 2015; Wang *et al.* 1994). In this study, the alkali concentration, n, was 3.5, 4.5, 5.5, 6.5 and 7.5%; also, M_s, the silicate modulus, was 0.45, 0.65, 0.85 and 1.05.

Mixture proportions of the specimens in the experiment are shown in **Table 2**. The water-to-binder ratio of all mixtures was 0.43 to provide the proper workability. The amount of water was the sum of water contained in the sodium silicate solution and the water added to the mixture. Also, the binder included slag, sodium hydroxide, and the solid part of the water glass.

The slag content in the concrete mixture was 400 kg/m³. The weight ratio of aggregates to the concrete mixture was 0.75, and the weight ratio of the coarse aggregates to the total aggregates was 0.575. The coarse and the fine aggregate contents were 1035 kg/m³ and 765 kg/m³, respectively. OPC concrete samples were also made to be compared with the AAS concrete. The cement content of the OPC mix was 436 kg/m³, which was equal to the solid content of the N45M85 mix.

In the process of mixing the components of the AAS

concrete, aggregates and slag were mixed together for 2 minutes; then the activator solution was added to the mixture and mixing was continued for 5 minutes.

2.3 Test method

The slump test was carried out according to ASTM C143/C143M-08 (2008) to determine the fluidity of fresh concrete. Measurement of the setting time was tested by following the modified ASTM C191-04 (2004). For this purpose, the paste was poured into the mold with a ratio of water to binder being 0.43, and the initial and final times of the setting were calculated as the elapsed time between the addition of mixing water to the mixture and the time when the penetration of the vicat needle was 25 mm and 1 mm, respectively.

In order to measure the compressive strength, a triplicate set of 100 × 100 × 100 mm cubes specimens was prepared for each test in accordance with BS 1881-116 (1983). Specimens were demolded after 24 hours of storage at (23 ± 2°C) and subjected to bath curing until the time of testing; also, the compressive strength tests were performed at the ages of 7, 28 and 90 days.

In this research, prismatic specimens with the dimensions of 75 × 75 × 285 mm were used to measure the drying shrinkage according to ASTM C157/C157M-08 (2008). In each mixture, 3 prism samples were used to measure the sample length variation. As shown in **Fig. 1**,

strain measurements of the specimens were performed using a DEMEC strain gauge with points fixed on both sides of the specimen with an accuracy of 8 microstrain. This was less than the maximum error of 10 microstrain, as recommended in ASTM C157. The shrinkage was measured along the longitudinal axis of the specimens according to ASTM C157; however, the results of the present study were based on surface measurements. It should be noted after a period of time, differences between internal and surface strain could be reduced (ACI 209.2R-08 2008); it is assumed that shrinkage in a specimen could occur uniformly through the cross section. The concrete was placed in the mold in two layers and each layer was compacted by a vibrating table for all specimens to be compared. The specimens were covered with a plastic cover after molding; after 24 hours, they were removed from the mold and the first reading was performed. The specimens were stored in the drying room at a temperature of $23 \pm 2^\circ\text{C}$ and the relative humidity of 50%. Measuring the length change of the samples was done up to 400 days after the first reading.

In order to perform the XRD test, parts of the hardened paste were removed after a compressive strength test at 100 days. The samples were cast and cured in a manner similar to that of the shrinkage test. For XRD analysis, the specimens were dried at a temperature of 60°C for 24 hours; then they were ground and passed

through a 100# sieve. Characteristics of the ground powder were considered with an XRD device (PHILIPS PW1800 machine) in the range of (2θ) 10 to 100° , with a step size of 0.05° ; the time step of scanning was 1s $\text{CuK}\alpha$ ($1.542 \text{ \AA}$).

The morphology of the surface of the specimens was also analyzed with a Philips XL30 scanning electron microscopy at 20 KeV.

3. Results and discussion

3.1 Slump

Figure 2 shows the amount of slump for AAS concrete samples. In most of the mixtures, slump was enhanced with increasing the alkali concentration of the AAS concrete. Similar results have also been observed in the previous works (Collins and Sanjayan 1999; Wang *et al.* 2015).

According to the results obtained by the researchers, the mixes with a high alkali concentration have a rapid loss in workability and slump over time (Bakharev *et al.* 2000; Collins and Sanjayan 1999). Increasing the amount of silicate modulus and alkali concentration could increase the hydration rate and reduce the setting time. It is, therefore, necessary to maintain the concrete workability in a desirable condition until concreting.

3.2 Setting time

The results of the initial and final setting time are shown in Fig. 3. The activation of slag with the combination of sodium hydroxide and sodium silicate has the same heat release curve as OPC cement. The pastes maintain their flowability for a certain duration depending on the type and amount of the activators. The paste hardened over the time, due to the precipitation of the hydration products. Until the final setting time, there was no bleeding or segregation and the composition retained its homogeneous form.

In most cases, with increasing M_s and n , setting time was decreased, indicating an increase in the rate of precipitation of cementitious materials (Altan and Erdoğan 2012; Bernal *et al.* 2011; Shi and Day 1995). Increasing the alkali concentration up to 5.5% reduced the setting time. This was due to the release of more hydroxide ions and accelerated slag dissolution and consequently more precipitation of the C-A-S-H gel. However, an increase in alkali concentration from 5.5% to 6.5 and 7.5% would have little effect on reduction of the setting time, and even setting time slightly increased in some mixes. Reduction of the calcium solubility (Yip and Van Deventer 2003) and precipitation a large amount of C-S-H gel in the early age (Fernández-Jiménez *et al.* 1999) were reported as the reasons for the difficulty of the hydration reaction at high alkali concentrations. Increasing the silicate modulus supply the soluble silicon in the mixture (Marjanović *et al.* 2015) and can accelerate the hydration reaction and reduce setting time.

Fig. 1 Measuring the length variation of drying shrinkage samples.

Fig. 2 The effect of alkali solution parameters on the slump of the AAS concrete.

3.3 Compressive strength

Figure 4 shows the effect of the alkali concentration and the silicate modulus on the compressive strength of 7, 28 and 90 days in AAS and OPC concrete samples. In most cases, the compressive strength was increased when n and M_s were enhanced; this was consistent with the results obtained for increasing the degree of hydration and producing the C-S-H gel (Chang 2003; Song *et al.* 2000). With regard to Fig. 4a, in the mixes, with an increase in the alkali concentration to above 6.5%, the 7, 28 and 90-day compressive strength was changed slightly (Figs. 4b and 4c), and a slight decrease in the compressive strength was observed in some mixes. The reason for the reduction of the compressive strength in high alkali concentrations was due to the formation of $\text{Ca}(\text{OH})_2$ around the slag surface (Yip *et al.* 2005), preventing the slag hydration and reducing the required calcium to form the C-S-H gel. Some researchers have observed strength loss in the mixtures with Na_2O concentrations of more than 7% (Marjanović *et al.* 2015), thereby indicating a decrease in the hydration of slag particles. However, the coexistence of calcium hydroxide to the C-S-H gel is unlikely in the long term, and additional reactions are expected to increase the amount of Ca/Si in the C-S-H gel (Wang *et al.* 1995). Also, some researchers have reported that a large amount of hydration products in the short term, which would fill the required space for the development of the

hydration reaction, could cause the formation of heterogeneous composition (Caijun and Yinyu 1989).

Figure 5 shows the compressive strength of concrete specimens at 7, 28 and 90 days. The compressive strength results were close for the mixes with the silicate moduli of 0.85 and 1.05; also, even in the alkali concentrations of 6.5 and 7.5%, the 90 days compressive strength in the mixes with the silicate modulus of 1.05 was lower than that of the mixes with the silicate modulus of 0.85. The reason could be the reduction of slag hydration and the porosity increase in the AAS paste so that in another study, an increase in porosity was observed in the mixes with high M_s by addition of silicate modulus (Aydın and Baradan 2014). In another study, the loss of compressive strength was observed in the mixtures with a silicate modulus (M_s) greater than 1, and the compressive strength of the specimens from mixtures with M_s was between 0.75 and 1, which was

Fig. 3 The effect of alkali solution parameters on the setting time of the AAS paste: (a) initial setting time, and (b) final setting time.

Fig. 4 Compressive strength of the AAS concrete based on M_s and n : (a) 7 days; (b) 28 days, and (c) 90 days.

very close (Atiş *et al.* 2009); this indicated that due to the accumulation of reaction products around the slag particles, the slag hydration in the mixtures with high M_s was prevented (Fernández-Jiménez and Puertas 1997; Fernandez-Jimenez *et al.* 1998).

According to the results, the mixtures with high n and M_s had higher strength development than those with the low ones. For example, the ratios of the compressive strength of 7 and 28 days to that of 90 days for the mix (with the lowest amount of n and M_s) were 0.55 and 0.75, respectively, while for the N75M105 mix (with the highest amount of n and M_s), these ratios were 0.77 and 0.96, respectively. The reason for the higher strength development in the N75M105 mix rather than N35M45 could be the difference in the rate of hydration, which could be consistent with the results obtained in Section 3.2.

3.4 Drying shrinkage

Figures 6 and 7 show the measured drying shrinkage of concrete samples over 400 days. The drying shrinkage of AAS concrete samples was measured between 1300 and 2200 microstrain after 400 days, while this amount was 915 microstrain for the OPC concrete.

As can be observed in Fig. 6a, the prediction model (ACI 209.2R-08 2008) was in a good agreement with OPC concrete results; however, the drying shrinkage of the AAS concrete was 1.5 to 2.5 times higher than that of the OPC concrete.

The shrinkage rate was initially enhanced by an increase in the alkali concentration and the activator modulus, so that half of the 400 day drying shrinkage in the N35M45 mix ($n = 3.5\%$, $M_s = 0.45$), which had the lowest n and M_s , approximately occurred within 32 days; for the N75M105 mix ($n = 7.5\%$, $M_s = 1.05$), with

Fig. 5 Compressive strength of AAS concrete at 7, 28 and 90 days: a) $n=3.5\%$ b) $n=4.5\%$, c) $n=5.5\%$, d) $n=6.5\%$, and e) $n=7.5\%$.

the highest activation parameters among the mixes, it occurred within 5 days.

The shrinkage rate could be correlated with the rate of hydration and the formation of the C-A-S-H gel. The results were consistent with other studies addressing the setting time and the calorimetric study, indicating that increasing the modulus of M_s and the alkali concentration of n could shorten the setting time of AAS pastes; this could show an increase in the rate of the dissolution of slag particles and products precipitation (Altan and Erdoğan 2012; Bernal *et al.* 2011; Shi and Day 1995). However, as shown in **Fig. 7d**, in the mixes with the silicate modulus of 1.05, there was no direct correlation

between the shrinkage rate and the alkali concentration, and the rate of shrinkage in all mixtures was very close.

As shown in **Fig. 7**, the final value of the drying shrinkage was highly dependent on the solution modulus M_s , while in the mixtures with the same M_s , the alkali concentration had no significant effect on the final value of the drying shrinkage. The reason for the effect of silicate modulus on the drying shrinkage could lie in the relationship between the drying shrinkage and the size of pores (Collins and Sanjayan 2000b). Since the activation with water glass caused small porosity and a fine pore size relative to the sodium hydroxide activator (Shi 1996), and the increase of the solution

Fig. 6 Drying Shrinkage of AAS concrete: a) $n=3.5\%$, b) $n=4.5\%$, c) $n=5.5\%$, d) $n=6.5\%$, and e) $n=7.5\%$.

modulus could result in smaller pore sizes (Aydın and Baradan 2014), this could also increase the tensile stresses of capillary pores and consequently, enhance the drying shrinkage (Mehta 1986; Slowik *et al.* 2008).

As can be seen in **Figs. 7c** and **7d**, in the mixtures with the alkali concentrations of 6.5 and 7.5%, the drying shrinkage values were close for the silicate moduli of 0.85 and 1.05; even in the silicate modulus of 1.05, the final drying shrinkage for the mixtures with the alkali concentrations of 6.5 and 7.5% was lower than that of 4.5 and 5.5% (see **Fig. 7d**).

This can be explained by the fact that high alkali concentrations in mixtures could cause the prevention of the slag hydration and the production of the C-S-H gel. During the alkali reaction of the slag, a thin layer of $\text{Ca}(\text{OH})_2$ was formed around the slag particles, which was caused by the reaction of Ca^{2+} from the slag with OH^- from the activator solution (Shi and Day 1996). When OH^- concentration was high, $\text{Ca}(\text{OH})_2$ thickness around the slag particles was increased and Ca^{2+} moved hard, resulting in less Ca^{2+} reaction with aluminum and silicon ions, as well as the less formation of the C-A-S-H gel (Burciaga-Díaz and Escalante-García 2013; Yip and Van Deventer 2003; Yip *et al.* 2005).

3.5 Microstructure

(1) X-ray diffraction

To investigate the effect of the alkali concentration and

the silicate modulus of the activator solution on the existing phases of the AAS paste, XRD analysis was used for the samples with the alkali concentrations of $n = 3.5\%$ and 7.5% and silicate moduli equal to $M_s = 0.45$ and 1.05.

Figure 8 shows the XRD patterns of AAS pastes made with different alkali concentrations and silicate moduli. In all XRD patterns, gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4(\text{H}_2\text{O})$), calcite (CaCO_3), quartz (SiO_2) and C-S-H phases were identified, which had also been detected in other studies (Behfarnia and Rostami 2017b; Bernal *et al.* 2011; Zhang *et al.* 2008). In the N75M45 mix with a low-modulus solution and a high alkali concentration, there was a slight peak at 11.6° and $23.4^\circ 2\theta$, indicating a hydrotalcite phase ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$). This phase has been detected more obviously in mixtures with high contents of MgO in the slag (Haha *et al.* 2011b) and the activator with sodium hydroxide (Haha *et al.* 2011a; Wang and Scrivener 1995). However, Energy Dispersion Spectroscopy analysis could demonstrate the presence of the hydrotalcite phase that had not been detected in XRD analysis (Haha *et al.* 2011a, 2012).

The most intense calcite phase occurred in the N35M105 mix. The high M_s and low n (NaOH content) in this mix could induce a greater calcite phase. Studies by other researchers have shown that AAS mixtures activated with sodium silicate are more susceptible to

Fig. 7 Drying shrinkage of the AAS concrete of: a) $M_s = 0.45$, b) $M_s = 0.65$, c) $M_s = 0.85$, and d) $M_s = 1.05$.

penetration and reactivity with atmospheric CO_2 than activation with NaOH, which could be due to more surface cracks caused by shrinkage and the lower internal adhesion in these mixtures (Puertas *et al.* 2006).

The intensity of the silico-aluminous phase of gismondine was also decreased in this mixture, which could be due to the calcification of this phase and the formation of calcite. In another study, a reduction in the C-S-H gel and hydrotalcite peaks and an increase in calcite were observed in the samples exposed to atmospheric conditions, as compared to those exposed to nitrogen (Ye and Radlińska 2017a). Due to the lower volume of the calcite than reactive substances, the formation of the calcite phase could lead to shrinkage (Newmann and Choo 2003).

The highest amount of quartz was observed in the N35M45 mix, such that this mix showed more intensity than other mixes at 26.7° and $20.8^\circ 2\theta$, due to the low n and M_s of the activator solution; these could be insufficient for the full dissolution and hydration of the slag grains. It can be argued that the greater amount of quartz means the further reduction in the production of the C-A-S-H gel. According to the results obtained in Section 3.3, regarding the low compressive strength of the N35M45 mix, as well as previous studies that demonstrate reduction of alkali concentration (Neto *et al.* 2008) and sodium silicate modulus (Aydın and Baradan 2014) cause porosity increase of the microstructure and reduce the capillary forces that would decrease the drying shrinkage.

(2) Microstructure of AAS paste

SEM images were used to compare the microstructures of AAS pastes cast with different n and M_s . SEM images were provided for the samples with alkali concentrations of 3.5 and 7.5% and silicate moduli of 0.45 and 1.05 upon 100 days of age.

The curing conditions of the samples were similar to those of the drying shrinkage. In the mixes with a denser microstructure, as indicated by SEM image in

Fig. 9, the improvement of the compressive strength was observed, in accordance with the results of Sec 3-3. Increasing n and M_s caused the structure of the paste to be denser and the compressive strength was increased too (Wang *et al.* 1994). As shown in **Figs. 9a** and **9b**, in the mixtures with M_s of 0.45, with the increase of n from 3.5 to 7.5%, the microstructures of the AAS paste were densified and the free space between the hydration products was reduced. Some researchers believe that the tensile stress could be increased in the capillary pores by the condensation of the binder matrix and the reduction of the pores size, which would cause the increase of the capillary pressure in the wall of the capillary pores and the shrinkage of concrete (Berenjian 1988; Thomas *et al.* 2017). In comparison with **Figs. 9a** and **9c**, the increase in the solution modulus also enhanced the production of the C-A-S-H gel and caused void spaces between the particles to be filled.

As shown in **Fig. 9d**, in the N75M105 mix with a heterogenous microstructure of hydration products fewer void spaces were formed, as compared to the N35M45 mix; as shown in **Fig. 9a**. The loss of the 90 days compressive strength in the M75N105 mix, in relative to M55N105, M65N105 and M75N85 mixes, could be attributed to the presence of a less condensed microstructure (As shown in **Fig. 9d**). It was observed in another study that when mercury intrusion porosimetry analysis complemented SEM images, although activation with water glass reduced the size of the pores, the increase in the silicate modulus after a certain level enhanced the amount of macropores and mesopores (Aydın and Baradan 2014). Increasing the pore size in the mesopores region decreases the pressure on the capillary wall and could decrease the shrinkage (Fang *et al.* 2018; Kumarappa *et al.* 2018; Li and Li 2014), so that in the mixes with alkali concentrations of 6.5 and 7.5%, increasing the sodium silicate modulus from 0.85 to 1.05 had a slight effect on shrinkage (as shown in **Figs. 6c** and **6d**).

Fig. 8 XRD patterns of AAS samples prepared with various activator solutions.

Fig. 9 Microstructure of AAS pastes, sample-scale: 10 and 2 μ m. (a) $M_s=0.45$, $n=3.5\%$, (b) $M_s=0.45$, $n=7.5\%$, (c) $M_s=1.05$, $n=3.5\%$, and (d) $M_s=1.05$, $n=7.5\%$.

6. Conclusion

In this study, the effects of the alkali concentration and the silicate modulus of the activator solution on the slump, setting time, compressive strength, and drying shrinkage of the AAS concrete were investigated. The following conclusions could be drawn:

(1) Increasing the alkali concentration in most mixes enhanced the slump, but increasing the alkali con-

centration and silicate modulus could enhance the hydration rate and reduce the setting time. Increasing the alkali concentration up to 5.5% had a significant effect on the reduction of the setting time, but higher alkali concentrations had less effect on reducing the setting time.

(2) Increasing n and M_s up to 6.5% and 0.85, respectively, could increase the compressive strength of the specimens. However, in most of the mixes, higher n

and M_s had no positive effect on the increase of the compressive strength.

- (3) In the mixes made with low M_s and n , low early strength was found, but their strength development was higher than the strength of those cast with high M_s and n .
- (4) The final drying shrinkage of the AAS concrete was 1.5 to 2.5 times higher than that of the OPC concrete.
- (5) Increasing the silicate modulus and the alkali concentration resulted in a high shrinkage rate in the short term, but the silicate modulus had a more significant effect on the final amount of shrinkage, as compared to the alkali concentration.
- (6) High silicate modulus and low alkali concentrations tended to form calcite, which reduced the intensity of the gismondine phase, leading to further shrinkage of the AAS concrete.
- (7) Increasing n and M_s beyond a certain level adversely affected the compressive strength and lead to a less compact paste microstructure with reduction in the rate and the final amount of drying shrinkage.
- (8) According to the rheology and mechanical properties of AAS concrete, the alkali concentration range less than 5.5% and the sodium silicate modulus less than 0.85 were appropriate in order to prevent from rapid setting, loss of compressive strength and high drying shrinkage.

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