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The Effect of Alkaline Activator on Workability and Compressive Strength of Alkali-Activated Slag Concrete

K. Behfarnia*, H. Taghvayi Yazeli, M. B. Khalili Khasraghi

Department of Civil Engineering, Isfahan University of Technology, Isfahan, Iran

ABSTRACT: In this study, experimental results on alkali activated slag (AAS) concrete was assessed to achieve the optimum strength and workability. The alkali contents of Na_2O to activate slag in concrete were equal to 3.5, 4.5, 5.5, 6.5 and 7.5 % by mass of slag and silicate moduli of alkali solution varied from 0.45, 0.65, 0.85 and 1.05. The compressive strength test of concrete specimens over 7, 28 and 90 days was measured. To evaluate the concrete workability, the slump of fresh concrete and the setting time of paste were also examined. The results showed that in the proposed range of activation, by increasing the amount of alkali concentration as well as silicate modulus in activator solutions, the workability and compressive strength increased but the setting time of paste reduced. Optimum values for the preparation of AAS mixtures with suitable compressive strength and desirable workability are suggested based on the results.

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1- Introduction

Cement and concrete have an important role in the manufacturing industry and the budgets allocated to this industry in the world. A large part of the cost is relative to manufacturing materials. World production of cement was about 2.9 billion tons in 2008, and it was reported that cement has become the largest product in the entire world [1, 2]. This high volume production is associated with the serious losses to the environment that is accompanied by the release of almost 0.9 ton of CO_2 for the production of one ton of Portland cement. Most of the CO_2 is released by heating limestone to form calcium silicate or aluminate phase [3, 4].

During the last century, development and the use of alkali-activated binders have taken place on the basis of containing high calcium material such as blast furnace slag and other industrial by-products. But interest in learning about the binder microstructures has grown over the past few decades to introduce scientific methods for the optimum activation to lead to the high-performance concrete [5]. The structure of binder gel that is formed in activation of slag is dependent on various factors that affect the chemical reaction process, development of mechanical strength and the performance over time. These factors are examined in two aspects. One of them is directly dependent on the activator and the other is associated with properties of related raw materials [6]. However, the application of AAS is limited because of its low workability, high drying shrinkage and high rate of carbonation [7-11]. Additionally, similar to any other cementitious binders, durability issues such as resistance to freeze and thaw cycles, the possibility of AAR and ASR reactions must be considered in the use of alkali activated slag concrete. In order to widespread use of AAS concrete in the manufacturing industry, it deems necessary that the effects of various factors on the properties of the AAS concrete should be well studied. Workability and strength are the properties that have a great impact on the placement and durability of concrete, however, there is limited research to obtain an optimum mix design to satisfy all of these properties related to experimental data.

Neto et al. [7] showed an increase in alkalinity of cement paste causing an accelerated rate and increased amount of heat evolution, and they concluded that this factor can increase the degree of hydration. Bakharev et al. [12] observed that for low sodium content, setting time decreases by increasing the alkaline modulus, but in high alkalinity, an increase of setting time was observed after modulus of 1.2.

Generally, the samples had the highest long-term strength in modulus of 1.25 and a strength loss was observed for a higher-modulus activator. Atiş et al. [13] studied the alkali activated slag mortar and observed that by increasing the sodium concentration and also modulus of alkaline solutions, drying shrinkage increased while setting time decreased. They observed that the sodium concentration increases the compressive strength of the mortar, but cannot be a definite statement about the relationship between compressive strength and modulus of an alkaline solution. Krizan and Zivanovic [8] have shown that the compressive strength and shrinkage of AAS mortar is significantly higher than Ordinary Portland Cement (OPC) and these properties

Corresponding author, E-mail: kia@cc.iut.ac.ir

straightforwardly are affected by alkali concentration and silicate modulus. Marjanović et al. [14] examined the alkali activated mortar and paste containing slag and fly ash. Mortar samples containing slag had a compressive and flexural strength greater than fly ash, and mainly after 7 % Na_2O, the reduction of strength was observed in slag samples. They also showed that the replacement of slag with fly ash increased the setting time and unlike the fly ash samples, an increase in the concentration of alkali reduces the setting time. Bakharev et al. investigated the effect of thermal curing on properties of alkali-activated slag concrete. Thermal curing also increases the early strength, but has a negative influence on the long-term strength. Also, heat treated AAS concrete unlike OPC caused an open microstructure near the slag grains [15, 16].

In this study, the percentage of Na_2O and module of the activator solution was investigated as some of the most important factors affecting the compressive strength and workability of AAS concrete.

2- Properties of Materials

2- 1- Slag

Blast furnace slag is the main binder ingredient in AAS concrete. In this study, blast furnace slag from Isfahan Zob-Ahan Company was used for the production of AAS concrete samples and ground in Madaen cement plants to the specific surface of 4000 cm^2/gr and basicity coefficient ($CaO+MgO/SiO_2+Al_2O_3$) of 1.02. The chemical composition and slag properties are shown in Table 1.

Table 1. Chemical composition (by mass %) of slag.

oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	alkalis
slag (%)	35.5	9.5	36	0.5	9.5	0.8

2- 2- Activators

The activators which were liquid sodium silicate (prepared from Silicate-Gostar company with a silicate module SiO_2/Na_2O = 2.32 contained 52% water) and solid sodium hydroxide (prepared from Niro-Chlor company with a purity of 98%) were used to make an alkaline solution. Liquid sodium silicate and sodium hydroxide were mixed together and the solution modulus, M_s, (molar ratio of SiO_2/Na_2O) equal to 0.35 to 1.05 and Na_2O %, n, (Na_2O weight ratio of the slag) of 3.5 to 7.5 % was made.

2- 3- Mix Design

Considering recent studies, at least 3.5 % alkali concentration, n, was selected for activation of the alkaline solution and according to previous studies [14, 17, 18] to achieve workability, avoiding fast setting and optimal strength of concrete, maximum Na_2O ratio was selected equal to 7.5 % and modulus of silicate selected between 0.45 and 1.05. In this paper, alkali concentration, n, for the range of 3.5 %, 4.5 %, 5.5 %, 6.5% and 7.5% and silicate modulus, M_s, equal to 0.45, 0.65, 0.85 and 1.05 were used.

Mixed compositions of AAS concrete are shown in Table 2. Water to binder ratio to achieve suitable workability was maintained at 0.43. The amount of water is the sum of water in water glass solution and water added to the mix and the binder includes slag, sodium hydroxide and solid part of water glass solution. Maximum aggregate size equal to 12.5 mm, weight ratio of aggregates to the concrete mix was 0.75 and the weight ratio of the gravel to sand was 0.575. For the production of sodium hydroxide solution, at least two hours before pouring it into the mixer, solid sodium hydroxide was mixed with the fixed amount of water to reach thermal equilibrium with the environment. In the processes of mixing concrete ingredients together, sand, gravel, and slag were mixed for two minutes and then activation solution was added to the blend and mixing was continued for five minutes.

Table 2. Mix proportions of AAS concrete.

No	n= Na_2O/slag	Ms= SiO_2/Na_2O	Water glass (kg/m³)	NaOH (kg/m³)	W_{add}^a (kg/m³)
1	0.035		18.78	14.56	172.37
2	0.045		24.15	18.72	172.47
3	0.055	0.45	29.52	22.88	172.58
4	0.065		34.88	27.03	172.69
5	0.075		40.25	31.19	172.79
6	0.035		27.13	13.00	169.08
7	0.045		34.88	16.71	168.25
8	0.055	0.65	42.63	20.43	167.41
9	0.065		50.38	24.14	166.58
10	0.075		58.14	27.86	165.75
11	0.035		35.48	11.44	165.79
12	0.045		45.61	14.71	164.02
13	0.055	0.85	55.75	17.98	162.25
14	0.065		65.89	21.25	160.48
15	0.075		76.02	24.52	158.70
16	0.035		43.83	9.89	162.51
17	0.045		56.35	12.71	159.80
18	0.055	1.05	68.87	15.54	157.08
19	0.065		81.39	18.36	154.37
20	0.075		93.91	21.18	151.66

Slag=400kg/m³

Coarse aggregate=1035 kg/m³

Fine aggregate=765 kg/m³

[a]W_{add}: Additional water.

3- Experimental Program

3- 1- Compressive Strength

To evaluate the compressive strength according to BS 1881 [19] guidelines, 100x100x100 mm cubes were used. Ten cubes were cast for each mixture and after demoulding, at least a triplicate set of specimens were prepared for the evaluation of compressive strength at 7, 28 and 90 days. Samples were extracted from the mold 24 hours after concrete placement and then emerged in lime-saturated water solution at 23 ± 2 °C temperature until the test time. BS standard recommends that the loading devices be placed so that the load exerted perpendicular to the sample in the form of concrete placement. Then specimen was loaded at a controlled rate of 0.25 MPa/s until failure, and maximum load was reported.

3- 2- Slump

From a practical point of view, workability is one of the most important aspects of concrete characteristics. Slump test somehow shows this feature of concrete. Slump test was performed according to AStM C143 [20].

3- 3- Setting Time

Determination of setting time according to the modified AStM C191 [21] and penetration of vicat needle into the paste samples was carried out. For this purpose, the paste with water to binder ratio of 0.43 was poured into the mold. After making the paste, durations that the needle penetration reach to 25 mm and 2 mm depths were recorded as the initial and final setting time, respectively.

4- Discussion and Results

4- 1- Compressive Strength

Figure 1 shows the effect of alkali concentration and silicate modulus on 7, 28 and 90 days compressive strength of AAS concrete. It can be seen from the results that in many cases of the proposed range, compressive strength and the rate of early strength development were increased when alkaline concentration and also silicate modulus were increased. Based on the results, presented in Figure 1, by increasing the alkali concentration greater than 6.5%, 7-day compressive strength increased but 28-day and 90-day strengths decreased. This phenomenon is also reported by Marjanović, N., et al. [14]. (This is especially evident in solutions with high modules.

Strength loss in the high alkalinity can be explained by hydration reaction of slag with an alkaline solution. During the alkaline reaction, a thin layer of $Ca(OH)_2$ is formed on slag particles due to the reaction of Ca^{2+} from slag with OH- of activator solution [22]. When the OH- concentration is high, the Ca^{2+} moves hard so Ca^{2+} is less capable of reacting with aluminum and silica ions and forming the C-A-S-H gel [23]. Some researchers observed the strength loss for Na_2O concentration higher than 7 % [14].

Compressive strength results for the blends with a modulus of 0.85 and 1.05 were seen close together and even a reduction in 90-day compressive strength was seen in mixtures with M_s=1.05 and alkali concentration equal to 6.5 and 7.5% compared to the mixtures at the same concentration with M_s=0.85. In another study, a reduction in the compressive strengths was also seen for the blends with modules greater than M_s=1 and results between moduli of 0.75 and 1 were close to each other [13].

Activation with a high modulus of solutions prevents the formation of C-A-S-H gel because silica increases in composition and other effective ions remain constant, particularly the aluminum content.

Recent studies have shown that the ratio of Al/Si in C-S-H gel has a maximum value of 0.2 [24, 25] and when slag samples (made with slag) were replaced with a source containing high aluminum content like fly ash and activated with high silicate modulus solutions and Na_2O, strength developed while in slag samples the strength loss was observed [14, 26].

Table 3 presents 7, 28 and 90-day compressive strength values. From the results shown in Table 1, it can be deduced that, by increasing the alkali concentration, both the ratio of 7-day to 28-day compressive strength and the rate of strength development increases and by increasing the modulus of activator solution in alkali concentrations from 6.5 and 7.5%, the ratio of 90-day to 28-day strength decreases.

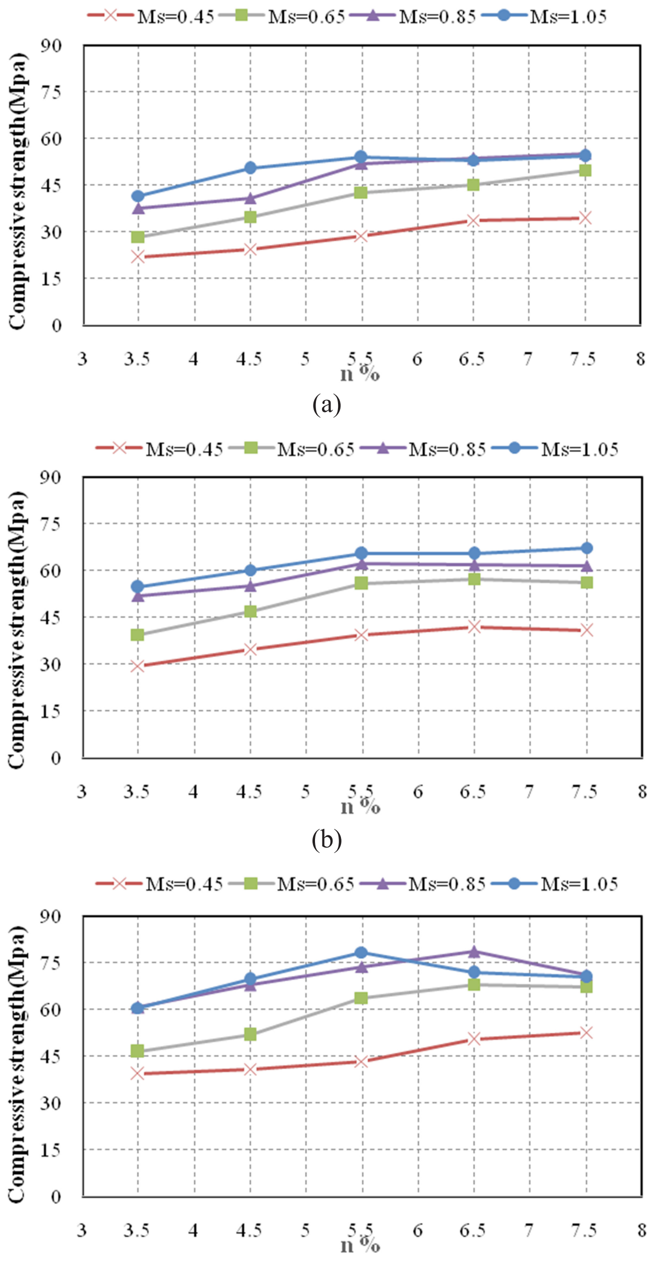


Fig. 1. Compressive strength of AAS concrete based on activator modulus and activator concentration: (a) 7- day; (b) 28-day and (c) 90-day compressive strength.

4- 2- Slump

Figure 3 shows the slump values for AAS concrete mixes. In most mixes, with the increase of the alkali concentration, the slump of AAS concrete increased which is in agreement with the result obtained in [27]. However, the increase of modulus and alkali concentration will increase the rate of hydration and reduce the setting time. It was recognized that the slump value will decline over time [28] and it is required that the concrete workability be kept suitable until concrete pouring.

4- 3- Setting Time

Setting time results are shown in Figure 3. As can be seen, in most cases the slope of the curves with alkali concentrations of 4.5 to 5.5 is increasing, which represents the increase

Table 3. compressive strength of AAS mixtures and strength ratios.

		(f_{c7}/f_{c28})	f_{c28} (MPa)	$((f_{c90}/f_{c28}))$									
						M_s							
			0.45			0.65			0.85			1.05	
$Na_2O\%$	3.5	(0.74)	29.3	((1.34))	(0.72)	39.4	((1.17))	(0.72)	51.8	((1.17))	(0.76)	54.6	((1.11))
	4.5	(0.71)	34.6	((1.18))	(0.74)	46.9	((1.10))	(0.74)	55.0	((1.23))	(0.83)	60.1	((1.16))
	5.5	(0.72)	39.4	((1.10))	(0.76)	55.7	((1.14))	(0.83)	62.2	((1.18))	(0.83)	65.2	((1.20))
	6.5	(0.81)	41.7	((1.21))	(0.79)	57.2	((1.19))	(0.87)	61.7	((1.27))	(0.81)	65.3	((1.10))
	7.5	(0.84)	40.6	((1.29))	(0.88)	56.2	((1.19))	(0.90)	61.4	((1.16))	(0.80)	67.3	((1.04))

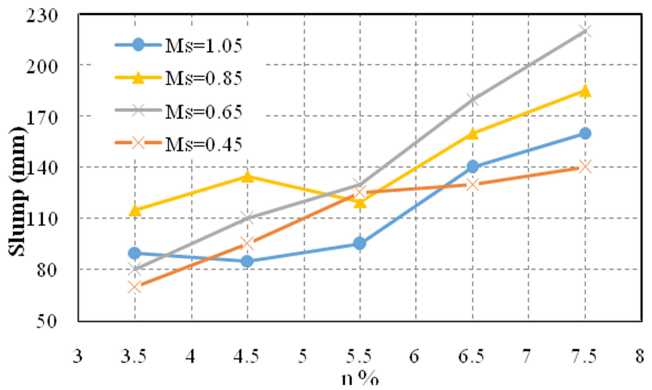
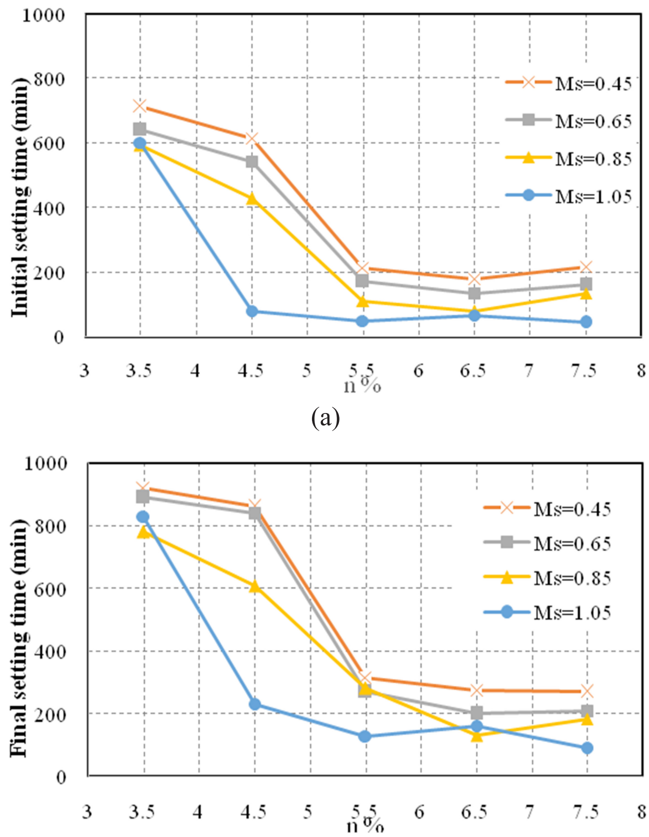


Fig. 2. The effect of alkali solution parameters on slump of AAS concrete.



(a)

(b)

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

of the hydration rate in this range. Despite the good initial workability in the pouring of concrete with Na_2O % and silicate moduli greater than 6.5 % and 0.85 respectively, shortly slump value dropped and concrete workability was not suitable for long-term. Increasing the amount of alkali concentration higher than 6.5% has been increased the setting time in mixtures with modulus equal to or less than 0.85 which is associated with a reduction in C-S-H gel precipitation [14]. In the mixed design with 1.05 module and at alkali concentration of 6.5%, setting time increased. This result is in agreement with other studies [12] in which setting time increased in mixtures at 8% concentration of Na_2O by increasing solution module greater than M_s=1. Curve slope in this range is also low due to a decrease in the rate of hydration and formation of C-A-S-H gel.

5- Conclusion

In this study, the effect of activation solution parameters on the properties of AAS concrete was investigated. A total of 20 mix designs in a range of concentration and module of alkaline solution were built. Compression strength of concrete samples, the slump of fresh concrete and setting time of paste were measured. The following conclusions are drawn:

1. Increasing the alkali concentration greater than 6.5% showed no positive effect on increasing compressive strength due to the formation of a thick layer of $Ca(OH)_2$ on slag particles that prevents slag hydration.
2. In the solutions with modulus more than 0.85, the amount of gel production reduced because other ingredients, especially aluminum held constant while silica increased.
3. Increasing concentrations of alkaline solution positively affected the slump of fresh concrete, but the setting time reduced.
4. Setting time of pastes with high alkali concentration and solution modulus did not show significant changes which means the hydration rate of slag is reduced.
5. According to the results of this research, the range of Na_2O between 4.5 and 6.5% by slag mass and modulus of silicate between 0.65 and 0.85 are proposed in making AAS mixtures for desirable compressive strength and workability.

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