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Effect of type and dosage of alkaline activators on the mechanical properties of alkali-activated slag concrete complied with ASTM C150

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Portland cement (PC) is the most widely used material in the world. Cement production is one of the leading industries that cause pollution and emission of greenhouse gases. Alkali-activated cement concrete (AACC) has received particular attention as a suitable alternative to Portland cement concrete due to its acceptable properties and environmental impact. In this research, the type and amount of alkaline activator on the mechanical properties and workability of alkali-activated slag concretes are investigated. For this purpose, two types of sodium hydroxide and powdered sodium silicate activators were used in amounts of 2, 6, 10, and 14 weight percent of slag. The flexural and compressive strength of the concretes, were measured after 3, 7, 28, and 90 days of curing in water at a temperature of 20±2°C. X-ray fluorescence (XRF) and X-ray diffraction (XRD) were used for Chemical and phase analysis of slag. The flexural and compressive strength of the samples were measured according to ISO 679 and the results were compared with ASTM C150 requirements.

The results showed that the highest strength was obtained in the sample with 10% sodium hydroxide and 6% sodium silicate.The 90-day compressive strength was 58.38 MPa and 66.52 MPa for the sample with 10 (wt%) of sodium hydroxide and 6 (wt%) sodium silicate, respectively. This value was 47.38 for Portland cement concrete. The results of comparing the mechanical properties of the samples with PC, disclosed that AASC could be a suitable alternative to Portland cement. [DOI: 10.22034/ASAS.2022.163111]

Keywords: Alkali-Activated slag cement, Green concrete, Mechanical properties

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Introduction

The consumption of Portland cement (PC), the most commonly used martial in construction, is increasing promptly. The production of the PC industry has high energy consumption and sources greenhouse gases emission and consequently air pollution and environmental problems. Among the alternatives to PC, alkali-activated slag cement (AASC), due to the reduction of environmental pollutants, is an appropriate option. [1-4]. The AASC production emits 50-80% fewer greenhouse gases than Portland cement production [5,6]. Furthermore, in the production of AASC, slag, the main ingredient, is a by-product of pig iron. Consequently, AASC production reduces the waste material. The utilization of alkali-activated slag cement has a lot of technological benefits, too. Compared with PC, AASC presents some elevated mechanical and chemical properties. The higher mechanical strength [7-10], lower hydration heat [11,12], higher resistance to chemical attacks [13-15], and carbon diffusion [16] are the reported advantages of AASC compared with PC. On the other hand, rapid setting and so lower workability [17-23], higher shrinkage, and consequent cracking [24-26], are challengeable concerns that should be considered before application.

Water to slag ratio, mixing protocol, curing conditions (temperature and humidity), dosage and type of activator, various admixtures, and slag composition are the most important factors that affect the properties of alkali-activated slag cement and so needed to optimize according to the favorite properties [19-23, 27-29]

Industrial production of alkali-activated slag cement (AASC) originated in Ukraine in 1960-1964 [11]. Although the AASCC is old technology, it has been the issue of many studies in the latest decades. There are several researches that investigate the dosage and types of activators on the mechanical properties of ASCC. However, lack of dedicated standard for specification of this kind of concretes is challengeable. In this article the obtained results are compared with mechanical properties of Portland cement concrete according to the DIN EN196-1 to clear the performance the AASCC. So, the objective of this paper is to investigate the effects of type and dosage of alkaline activators on mechanical performance of AASCC

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in comparison with PC according to related standards.

Experimental Procedure

Materials and sample preparation

In this study, Granulated Blast Furnace Slag (GBFS), which was provided by Esfahan Steel Company, Iran, and commercial Portland cement type 1-425, which complies with the requirements of ASTM C150, were used as binders. The chemical composition of binders is summarized in table 1. The PC concretes were prepared as references sample to compare the obtained results. To investigate the effect of the amount and type of activator on the properties of alkali-activated slag concrete, industrial grade sodium hydroxide and commercial sodium silicate were used.

GBFS was firstly crushed in a jaw crusher to pass through a 2 mm diameter sieve, then passed through a magnet to remove any contamination of iron melt, then ground in a steel ball mill to reach adequate finesse. Concrete samples were prepared with different alkaline activators and according to the ISO 679, entitled "Methods of testing cement – Determination of strength." Separate mixes were prepared from GBFS and PC, as shown in Table 2. To prepare concrete samples, standard sand was used according to DIN En196-1. The water to binder ratio (w/b) and the binder to sand ratio (b/s) were 0.5 and 0.3, respectively. These ratios were kept constant in all samples to make the results comparable. The amount of alkaline activator was 2, 6,10, and 14 weight percent of slag. After mixing the starting materials, the mortars were poured into steel molds with dimensions of 160 x 40 x 40 mm. Material within the mold is kept in a controlled condition for 24 h at a temperature of 20 ± 2 °C and a humidity of 90%. After demolding, the specimens were placed in a curing tank for 3, 7, 28, and 90 days. Subsequently, a specified period of curing, the strength test of the specimens was conducted shortly after taking those out from storage water.

Characterization techniques

X-ray fluorescence (XRF, Spectro xepos) and X-ray diffraction (Siemens-D500) were used to determine the chemical and phase composition of powdered slag and cement respectively. Flexural and compressive strength of concrete samples were measured with Toni Technik apparatus.

The finesse of the slag and cement used was measured by the Blain method according to the ASTM C204-07, 2008: Standard Test Methods for Fineness of Hydraulic Cement by Air Permeability Apparatus. The setting time of the samples with different dosages of alkaline activators was determined according to ASTM C191: 2019, "Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle "and compared with the PC sample.

Results and discussion

The physical properties of the binders

Figure 1 illustrates the XRD of GBFS. The GBFS is entirely vitreous with an amorphous structure. Further-

Table 1- The chemical composition of binders

Oxide (٪)	SiO_2	Al_2O_3	CaO	MgO	Na_2O	Fe_2O_3	K_2O	SO_3	MnO	TiO_2	L.O.I
Slag	35.13	14.04	39.72	5.87	0.37	0.25	0.34	2.55	0.34	0.39	1.03
PC	21.3	5.6	62.1	1.8	0.36	3.59	0.68	2.57	-	-	2.01

Table 2- The mix plans of prepared samples.

Mix. code	Portland cement(g)	Powdered slag(g)	NaOH(wt%)	Na_2SiO_3(wt%)
OPC	450	-	-	-
SH-2	0	450	2	-
SH-6	0	450	6	-
SH-10	-	450	10	-
SH-14	-	450	14	-
SS-2	-	450	-	2
SS-6	-	450	-	6
SS-10	-	450	-	10
SS-14	-	450	-	14

more, the specific surface area of slag and cement measured by the Blain method was 3480.76 and 3310.51 cm^2/g, respectively. With a comparison these values it can be concluded that the softness of both starting binders is approximately the same.

Setting time

The setting time is considered the boundary between the fresh and hardened state of concrete. Knowing the setting time gives valuable information about the workability of concrete. The subsequent strength and durability of concrete can be significantly influenced by the chemical reactions and microstructure during the setting. Therefore, the setting behavior of concrete and cementitious materials is very essential in the performance of fresh and hardened concrete. The setting time is the time that starts from the moment of adding water to cement materials and continues until the mixture reaches a degree of hardness that is measured by a specific method such as Vicat's needle. To achieve the initial setting time, a suitable and certain amount of C-S-H is needed to connect the different components of concrete and form a microstructure resistant to the penetration of the setting time measuring device. By increasing the hydration and after the initial setting, more hydration of calcium silicate (especially C3S) produces more C-S-H gel, which causes more hardness of the mixture and finally reaches the final setting. Table 3 summarizes the setting time measured by the Vicat needle method for the samples.

It can be seen from the results in the table, alkali-active slag mortars have a shorter setting time than Portland cement.

This issue depends on the type of activator more than its amount. In the NaOH activator, the initial setting is 50%, and the final setting is 34% shorter than Portland cement. The sodium silicate activator, showed a lower setting time than the sodium hydroxide activator, so it reduced the initial setting time by 65% and the final setting time by 62%.

The obtained results show the different effects of the studied activators on the setting time and workability of AAS cement mixtures depending on their type and dosage. Obviously, the type and dosage of the activator are essential factors that affect the properties of alkali-activated slag mortars. This result is due to the fact that the type and dosage of activators play an essential role in determining the hydration and structure development of AAS cement and, thus, their setting and workability as characteristics that indicate its hardening process.

The obtained results show that the activators used can significantly accelerate the setting of AAS cement. This acceleration effect was shown more in sodium silicate compared to sodium hydroxide activator. Based on this, it seems that the effects of sodium silicate in the initial phase of hydration of AAS cements are more significant than the sodium hydroxide. Other researchers obtained similar results. For example, Bakharev et al. reported that AAS cement with sodium hydroxide

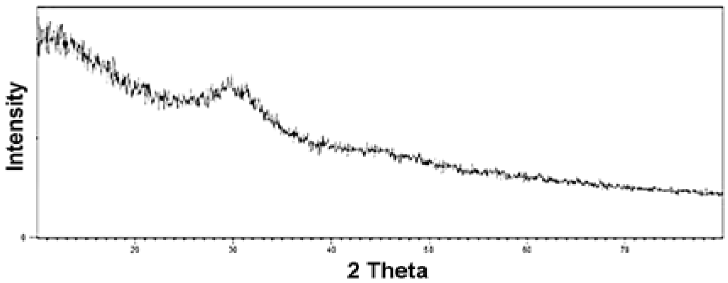

Figure 1- XRD pattern of slag powder

Table 3- The setting time measured by the Vicat needle method.

Sample code	Initial setting (min)	Final setting (min)	Change of initial setting compared to PC	Change of final setting compared to PC
OPC	140	210	1	1
SH-2	70	140	0.5	0.66
SH-6	70	140	0.5	0.66
SH-10	70	140	0.5	0.66
SH-14	70	140	0.5	0.66
SS-2	50	80	0.35	0.38
SS-6	50	80	0.35	0.38
SS-10	50	80	0.35	0.38
SS-14	50	80	0.35	0.38

showed better workability than AAS cements with sodium silicate [30, 31].

Mechanical properties of concretes

The flexural and compressive strength of the samples were evaluated at different ages of 3, 7, 28, and 90-das. Activators were added to the slag in 2, 6, 10, and 14% by weight. Also, a control sample was made with Portland cement to compare the results.

The flexural and compressive strength of each sample code was obtained from the average of three and six samples, respectively.

Figures 2 and 3 display the flexural and compressive strength of slag concretes activated with different amounts of sodium hydroxide and sodium silicate activators and at 3, 7, 28, and 90-day curing times, correspondingly. It should be noted that the SS-14 sample was destroyed during demolding due to not having enough strength.

According to the figures, it can be seen that in all the samples, with each weight percentage of activator, the bending and compressive strength of concrete increases with the increase of curing time. This issue is attributed to the progress of hydration reactions and, as a result, the development of the hydrated calcium silicate (CSH) phase, which has the most significant effect on concrete strength.

Additionally, it can be seen that the amount of alkaline activator has a significant effect on the compressive and bending strength of concrete. By increasing the amount of sodium hydroxide activator up to 10% by weight, the flexural and compressive strength increased, still, in higher amounts, a reduction in the mechanical properties can be observed. In the case of slag activated with sodium silicate, according to figure 3, the flexural and compressive strength reaches its highest value at 6% by weight of slag.

It can be concluded that the amount of activator has an optimal value on concrete properties. Lower values of alkali activators will delay the activation process. On the other hand, higher amounts can lead to scaling and brittleness (along with other factors such as the type of slag, the type of the activator, and the curing temperature). In addition, a high concentration of activators is not recommended from an economic point of view.

The results obtained in this research are in accordance with the results of other researchers. Recommended concentration values are between 3 and 5% Na_2O by slag weight.

In alkali-activated slag cement, C-S-H gel is the main product of hydration reaction but with less Ca/Si ratio compared with Portland cement.

Slag hydration is a multi-step process that includes the initial destruction of slag particles and condensation of

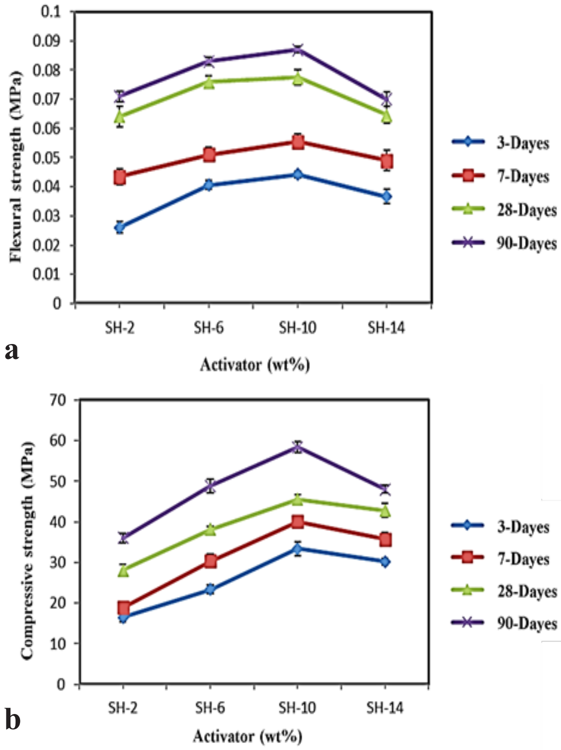

Figure 2- a) flexural strength and b) compressive strength of slag concrete activated with sodium hydroxide.

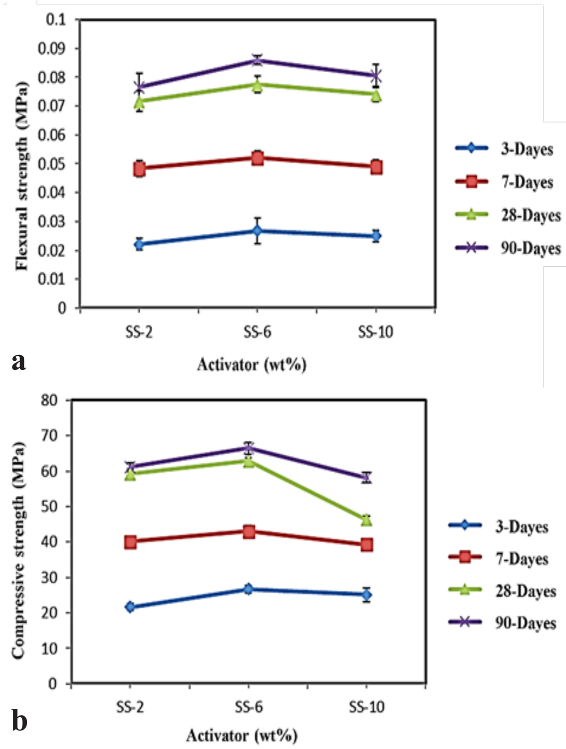

Figure 3- a) flexural strength and b) compressive strength of slag concrete activated with sodium silicate.

hydration products. Hydration of slag starts with ion exchange of H^+ in water for Ca^{+2} or Na^+. Al-O-Si bonds are hydrolyzed, and then the depolymerized slag network is broken. Therefore, Si and Al are released in the form of $Al(OH)^{-4}$ and (H_3SiO_4)- and $(H_2SiO_4)^{-2}$ ions in water, and finally, with increasing concentration, they precipitate on the surface of slag particles [32]. During the hydration of alkali-activated slag, dissolution and precipitation is the dominant mechanism in the initial stages of the reaction that continues with the solid-state mechanism. With high amounts of activators and a constant part of water, the concentration of activators during the hydration process around the slag grains is high. As a result, the rate of hydration is higher, and more reaction products precipitated on the surface of the slag grains at a constant time compared to the sample with less concentration of activators. Therefore, more precipitation of the product slows down the diffusion of water towards the slag grains. This factor reduces the development of hydration and the formation of C-S-H gel.

In Figure 4, the flexural and compressive strength of concrete activated with hydroxide and sodium silicate, are compared with Portland cement.

It can be seen that the 3-day flexural strength of the sample activated with 10% sodium hydroxide (optimal sample using this activator) is 0.044 MPa, compared to the sample with 6% sodium silicate activator (0.026 MPa) is higher. The compressive strength after three days of curing, is 33.36 MPa and 26.7 MPa in the sample with 10% NaOH and 6% sodium silicate respectively. But this trend reverses after 28 and 90 days of curing. The 28 and 90-day compressive strength of the sample with 10 (wt%) of sodium hydroxide is 45.59 and 58.38 MPa, respectively. While those are 62.88 and 66.52 MPa for the sample with 6 (wt%) sodium silicate.

Hydration reaction rate is related to the amount of alkaline in the activator [33]. In this research, the activators were first dissolved in water, and then added to the slag. Using sodium hydroxide, the pH of the water and activator solution was about 14 and using sodium silicate was approximately 11. At higher pH, the rate of hydration reaction was more elevated and, therefore, the strength is higher in the initial days of curing. However, with the time and the precipitation of hydration products around the slag particles, the diffusion barriers increase, and the rate of hydration reaction decreases.

Comparing the results obtained for the compressive and flexural strength of alkali-activated slag concrete with Portland cement concrete, demonstrates that AASCC illustrates higher strength in almost all samples except for 14% by weight of sodium silicate and 2% sodium hydroxide. As a result, it can be claimed that alkali-activated slag cement can be a suitable substitution for Portland cement, especially in typical applications.

Using AASC is an appropriate way to reduce cement production and air pollution. As a result, the development of the AASC market solved the environmental problem of disposing of slag as waste material.

Conclusion

• By increasing the curing time, the flexural and compressive strength of alkali-activated slag samples increases.

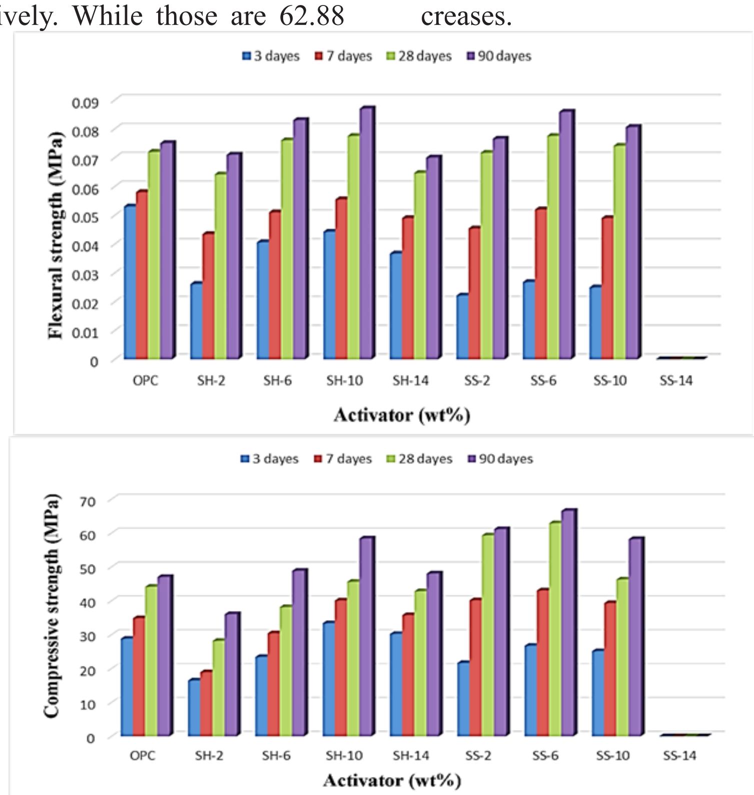

Figure 4- Comparison between a) flexural strength and b) compressive strength of slag concrete with different activators and Portland cement.

• Mortars activated with sodium silicate have a shorter setting time than samples activated with sodium hydroxide and Portland cement.
• Using a sodium hydroxide activator, the highest flexural and compressive strength are obtained in the amount of 10 wt% of the activator.
• Using a sodium silicate activator, the highest flexural and compressive strength are obtained in the amount of 6 wt% of the activator.
• Samples activated with sodium silicate show higher compressive and bending strength than samples activated with sodium hydroxide.
• The results of measuring flexural and compressive strength and comparing them with the strength values of PCC showed that AASC is a suitable alternative to PC.

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