

INVESTIGATION ON THE ACTIVATING EFFECT OF Na_2CO_3 AND NaOH ON SLAG

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Abstract

This study aims to investigate the activating effect of Na_2CO_3 and NaOH on the workability and mechanic strength of slag-based alkali activated materials with different alkali contents and water to binder ratios. The heat release during the reaction process of slag activated with sodium carbonate and sodium hydroxide were monitored respectively to analyze the hydration process. Meanwhile, the workability and compressive strength were also tested with two types of activators (Na_2CO_3 and NaOH), two different dosages (5% and 7% of equivalent Na_2O by slag weight) and three different water to binder (W/B) ratios (0.37, 0.45 and 0.5). The results show that the reaction process of slag activated with sodium carbonate is much slower than that of sodium hydroxide activated one, and its reaction phase happens approximately 40 h after the dissolution phase, and in all cases, sodium carbonate gives the higher fluidity and compressive strength with the same Na_2O content and W/B ratio.

Keywords: Sodium carbonate, Sodium hydroxide, Hydration heat, Workability, Compressive strength

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1. INTRODUCTION

Due to the serious environment issues occurring worldwide in recent years, many efforts have been contributed to reduce the usage of conventional cement based materials and to recycle industrial wastes. It is generally accepted that alkali activated materials (AAM) is considered to be the most potential product in replacing currently widely used traditional cement in terms of mechanical properties and durabilities e.g. fire resistance [1,2] and heavy metal immobilization [3–7]. Slag has been considered as the most potential raw material in AAM system, and the relevant properties and influential factors of slag-based AAM have been extensively studied from the early stage [8,9]. The alkali activation of slag involves the dissolution of calcium and participation of Al to form a C-(A)-S-H type gel [8,9], promoting the development of high mechanical strength and durability in AAM systems [10–12].

As a matter of fact, the influence of different alkali activators, different concentrations and compound alkali activators on the mechanical properties of AAMs has been extensively studied. Wang [13] investigated the effect of the type of alkaline activator, dosage of alkali, the type and fineness of slag, $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the strength of slag-based AAM, and concluded that waterglass is the best activator in all cases and the best alkali dosage is within the range of 3.0-5.5% Na_2O by mass of slag. Similar results was obtained by [14], who used sodium silicate, sodium hydroxide, sodium carbonate, sodium phosphate and combinations of these activators to study the influence of activators on the compressive strengths of Australian slag-based AAM. They concluded that liquid sodium silicate gave the highest mechanical strengths followed by sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) and recommended the

optimum proportion of sodium silicate solution with a module ratios of 0.75, and 4% Na based on the workability and compressive strength.

Even though the activating effect of different types of alkali activator with different concentrations and W/B ratios have been widely researched, however, only the reaction process of sodium silicate with slag was systematically studied, while that of sodium carbonate, in most cases, only behaves as a reference showing the superiority of sodium silicate. As a result, actually few researches have been conducted on the differences of reaction process of sodium carbonate with the raw material slag compared to other alkali activators. In this study, the hydration heat of slag activated by sodium carbonate and sodium hydroxide respectively with the same related parameters were detected by a calorimeter instrument to analyze the reaction differences of these two alkali activators and compare to general AAM and conventional cement as well. And then, two types of activators (Na_2CO_3 and NaOH), two different dosages (5% and 7% of equivalent Na_2O by slag weight) and three water to binder ratios (W/B) (0.37, 0.45 and 0.5) were selected to investigate their influences on the workability and compressive strength of slag based AAM.

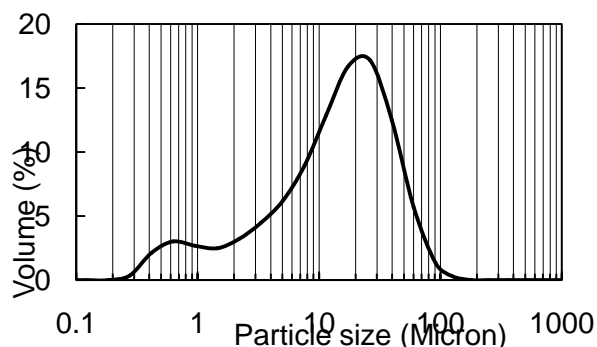
2. MATERIALS

2.1 Ground Granulated Blast Furnace Slag

The ground granulated blast furnace slag (GGBS) used in this study was provided by ENCI B.V, the Netherlands, with the specific surface area of 2998 cm^2/g . Table 1 presents the chemical composition of the GGBS determined by X-ray Fluorescence (XRF) and the particle size distribution is shown in Fig. 1.

Table: 1 Chemical composition of GGBS determined by XRF

Chemical	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	S-total	MgO	TiO ₂	Cl
Component (wt.%)	38.6	35.5	13.6	0.48	0.48	0.35	1.27	10.2	1.01	0.011

**Fig. 1** Particle size distribution of GGBS

2.2 Alkali Activator

The investigated alkali activators were sodium carbonate and sodium hydroxide (both are in powder form, chemical analysis level). The powder of alkali activator firstly was dissolved in water in a 2000 ml glass beaker and then was put in a sink containing water to cool down for half an hour. The content of alkali activator and amount of water was determined by different materials design as shown in Table 2, while basically the mass of sodium carbonate versus that of sodium hydroxide equals with the equivalent sodium oxide (Na₂O).

Table: 2 Mix proportions of slag based AAM paste and related design parameters

Mixture no.	Activators	W/B ratio	Content of activator (Na ₂ O %)	Weight of materials /g		
				Slag	Water	Activator
1	NaOH	0.37	5%	1200	440	70.99
2		0.45	7%		540	108.38
3		0.45	5%		540	77.44
4		0.5	7%		600	108.38
5	Na ₂ CO ₃	0.37	5%		440	102.6
6		0.45	5%		540	102.6
7		0.45	7%			143.65
8		0.5	5%			600

The content of activator: equivalent Na₂O content of activator by mass of slag.

3. EXPERIMENT

Table 2 listed the various mixes that were made considering the different content of alkali activators and water to binder ratios (W/B). Two types of alkali activator (Na₂CO₃ and NaOH), two different dosages (5% and 7% of equivalent Na₂O content by mass of binder) and three different W/B ratios (0.5, 0.45 and 0.4 respectively), were applied to compare the relevant materials properties of slag activated by different alkali activators.

3.1 Heat Release

The heat released from the slag reacted with different types and content of alkali activators was detected by a calorimetry instrument (TAM AIR Calorimeter). For hydration heat experiment, the materials were first mixed in a container and then poured into a glass of bottle which is then measured in the calorimeter instrument. As a result, the first procedure of this experiment would generally takes 4~5 minutes before measuring the hydration heat of samples.

3.2 Flowability

Following Nematollahi [15] and according to EN 1015-3, the fresh paste was poured into a Hägermann cone (top diameter = 70 mm, bottom diameter = 100 mm, height = 50 mm). Subsequently the top surface of the cone was leveled and the extra paste was removed. After about 15 seconds the Hägermann cone was lifted vertically and diameter of the paste spread was measured along two perpendicular directions. The relative slump value was derived from the following equation:

$$\Gamma_p = \left(\frac{d}{d_0}\right)^2 - 1 \quad \text{with} \quad d = \frac{d_1 + d_2}{2} \quad (1)$$

where Γ_p is relative slump, d is the average of two measured diameters of the paste spread and d_0 is bottom diameter of the conical cone, equals to 100 mm.

3.3 Compressive Strength

To measure the compressive strength of the paste, 8 groups of specimens (40×40×160 mm³) were casted in plastic moulds respectively. To prevent the moisture loss the molded specimens were sealed with a plastic foil. The specimens were cured at ambient temperature for 1 day and then removed from the moulds and cured in water at room temperature until the age of testing. While in the case of slag activated by sodium carbonate the specimens could not be demoulded after 24 h curing because of the slow reaction rate based on the hydration results. As a result, the specimens of slag activated with sodium carbonate were removed from moulds after 3 days of casting. 7-days compression strengths after casting were measured using a compression machine at a load rate of 2400 KN/min.

4. RESULTS AND DISCUSSION

4.1 Effect of Activator on the Hydration

The heat release experimental results are shown in Fig. 2. As can be seen, the reaction process of slag activated by sodium carbonate and sodium hydroxide is quite different from each other. According to the conceptual model for reaction

processes involved in geopolymerisation suggested by Provis and Deventer [16,17], the first reaction procedure is the dissolution (first peak) of raw materials in the alkali solution followed by the oligomerisation/gelation (second peak), which are also confirmed by the experiment. The hydration curve of slag activated with sodium carbonate indicates that the reaction of the specimens started about 40 hours (second peak) later than the dissolution (first peak), while the slag activated with sodium hydroxide started just after the dissolution part at around 30 minutes. This phenomenon is confirmed by the compressive strength results. The products of slag activated with sodium carbonate cannot be demoulded and remains soft after nearly 2 days curing, while that of sodium hydroxide can be demoulded after 2 hours casting, which are correspondence with the heat release process.

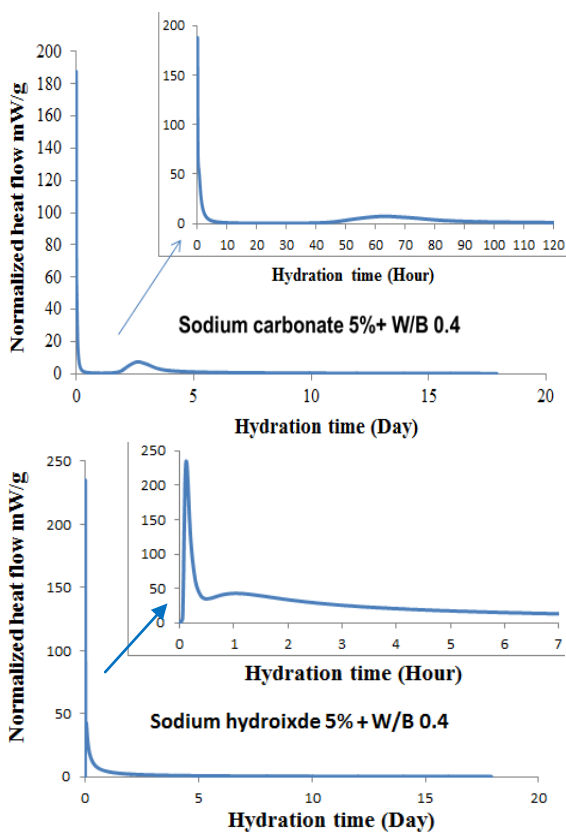


Fig 2 Effect of different types of alkali activators with the equivalent content of Na₂O to the binder on the hydration heat of specimens at 20 °C

As a matter of fact, the hydration tendency of both slag activated by sodium carbonate and sodium hydroxide are different from that of cement based materials. As shown in Fig. 3, the hydration heat evaluation rate of different replacement levels of cement by slag were investigated by Han [18]. The hydration tendency of cement-slag binder is similar to that of slag activated with sodium hydroxide but the period of reaction hump (second hump) of former one (around 100 hours) is much longer than that of the later one (about 10 hours). Similarly, the delayed setting of slag based AAM was reported by other authors [14].

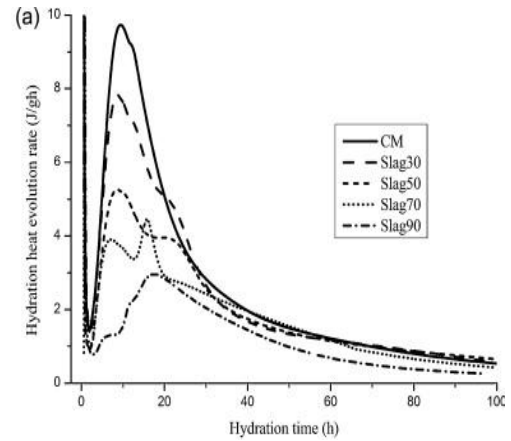


Fig 3 Hydration heat evolution rate of cement (CM) replacing with different contents of slag at 25 °C [18]

3.2 Flowability

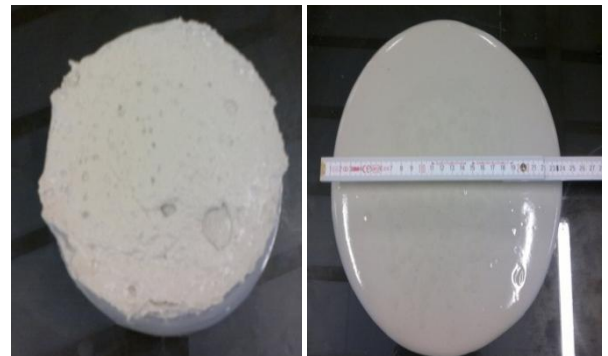


Fig 4. Examples of flow of slag activated by: (Left) Sodium hydroxide (W/B 0.37 and 5% equivalent Na₂O by mass to the binder/slag), (Right) Sodium carbonate (W/B 0.45 and 7% equivalent Na₂O by mass to the binder/slag)

The relative slump of slag activated with sodium carbonate and sodium hydroxide is shown in Table 2. As can be seen, in general, the higher the water content (W/B ratio) the higher the relative slump will be, which is similar to that of cement based materials without using superplasticizer. On the other hand, the higher the alkali content to the binder is, the lower the relative slump will be. Meanwhile, under the same equivalent content of Na₂O by mass to the binder and same W/B ratio, the fresh paste of slag activated by sodium carbonate shows better fluidity than that of sodium hydroxide. Fig. 4 shows two examples of slump of slag based AAM paste with different proportions, and the one of slag activated by sodium carbonate with W/B of 0.45 and 7 % equivalent Na₂O by mass to the binder, while the other one with 5 % equivalent Na₂O and W/B of 0.45 hardly shows any slump.

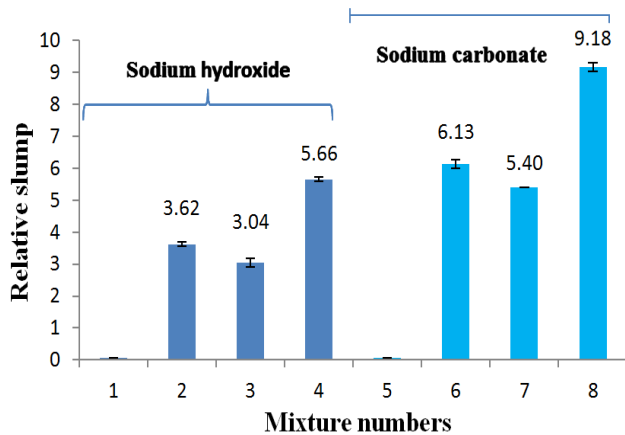


Fig 5. Effect of alkali types and contents (Na_2O wt.%) and W/B ratios on the relative slump of slag based AAM paste (the mixture numbers correlate with Table 2)

3.3 Compressive Strength

Fig. 6 indicates an overview of the influence of alkali types, alkali content and W/B ratios on the compressive strength of slag based AAM paste. As can be seen, in general, with an equivalent content of alkali activator and same W/B ratio, the slag activated with sodium carbonate shows much better compressive strength than that of slag reacted with sodium hydroxide, which is in line with other authors [14]. The compressive strength of specimens increases with the decreasing content of water in this alkali activating system, which is similar to that of cement-based materials. On the other hand, the compressive strength increases with the increasing content of alkali activator to the binder, which are also confirmed others experimental results.

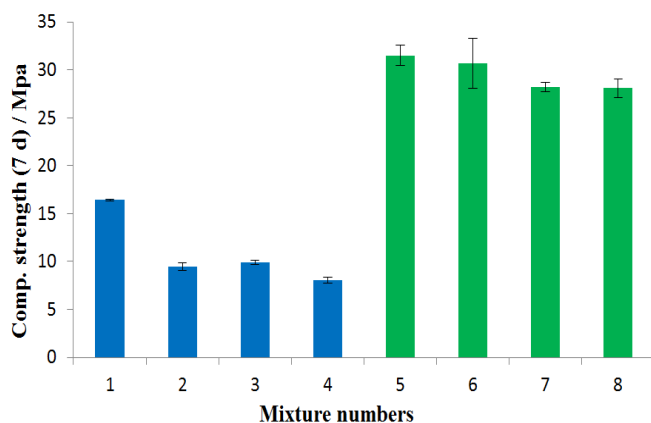


Fig 6. Effect of alkali types and contents (Na_2O wt.%) and W/B ratios on the 7-day compressive strength of slag based AAM paste

As shown in Fig. 6, the strength tendency of specimens generally fits with the rules described above. Nevertheless, the mixture proportions of mixture No.5 (M5) have lower water content than that of M6 with same Na_2O content, while the strength of M5 is nearly the same as M6. On the other hand, under an equal W/B ratio, M6 shows a better compressive strength than that of M7 but with a lower alkali content. The possible reasons for this phenomenon may lay on two aspects: 1, water content. A low water content will

cause a poor flowability (Fig. 4), which means air cannot escape easily from the matrix leading to high porosity. 2, a high alkali content may increase the viscosity of fresh reaction product and reduce the workability as well (Fig. 5), inducing a poor strength.

4. CONCLUSIONS

To conclude, from the perspective of hydration process, it is apparent that slag activated by sodium carbonate is much slower than that of sodium hydroxide and conventional cement-based materials, and slag activated by sodium silicate [16,17].

1. The reaction process of slag activated with sodium carbonate is slower than that of those activated with sodium hydroxide/silicate, and its reaction phase happens approximately 40 h after the dissolution phase, indicated by the hydration heat experiment;
2. The slags activated with sodium carbonate shows better workability than those activated with sodium hydroxide with the same W/B ratio and Na_2O content;
3. The compressive strength of slag activated with sodium carbonate is much better than that of sodium hydroxide activated ones;
4. In general, the higher the alkali activator content and the lower the W/B ratio is, the higher the compressive strength would be.

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