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Preliminary study on combined-alkali–slag paste materials

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Abstract

This article mainly describes a study on combined-alkali-activated slag paste materials. Without any coarse and fine aggregates, the effect of several factors, such as the kind of alkali, additives, as well as curing conditions on the strength and other properties of the paste materials, has been investigated. The activation of sodium hydroxide shows a better early strength developing than sodium carbonate. However, by using both NaOH and Na_2CO_3 together at the same dosage, the strength developing shows even better. The most severe problem of the cured paste materials is the shrinkage cracking, which causes the decrease of both flexural and compressive strengths apparently. The effect of several factors is considered and discussed in this paper, hoping to gain a better understanding of the processing of alkali-activated slag solid paste materials. It was shown that there is a good effect of some suitable additives and curing forms on the properties of hardened slag paste materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Granulated blast-furnace slag; Alkali-activated cement

1. Introduction

It is well known that granulated blast-furnace slag can be used as cement replacement and cementitious material in concrete. In recent years, with the development of energy conservation and environment protection, many research works have been conducted on this field [1–3].

However, most of the previously available data from the literature relates to the results of the concrete properties obtained with slag, waterglass solution as activator and coarse and fine aggregates. Concrete with very high compressive strength, good chemical resistance and superior durability were obtained in previous works [4–7]. In this paper, the experiment results of combined-alkali-activated slag with different powder additives were revealed. The effect of a solid combined-alkali activator and the different curing forms are also reported. This kind of paste would be suitable for self-leveling floor materials or other destination uses.

2. Experimental

2.1. Experimental materials

For a preliminary study, the reactivity of commercial blast-furnace slag (mark S) activated with two kinds of alkali Na_2CO_3 (mark T) and NaOH (mark N), and its combination were tested. Various kinds of the mineral powders as additives were added to compare the change in the strength and other properties. Special attention was paid to the effect of a solid combined-alkali activator and some additives.

All of the mixtures have had sufficient workability during the mixing and the moulding. The flexural and compressive strengths were investigated. For some se-

Table 1
Physical properties and chemical analysis of slag (S) (%)

Chemical analysis	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	SO_3	Total
Content (%)	31.30	36.82	10.80	9.39	0.36	4.05	92.72
Basicity coefficient		$M_0 = (CaO + MgO) / (SiO_2 + Al_2O_3) = 1.098$					
Property			Basicity				
Fineness			5000 cm^2/g				

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Table 2
Chemical analysis of fly ash (A) (%)

Chemical analysis	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	SO_3	Loss on ignition	Total
Content (%)	52.4	6.95	4.33	26.37	1.13	0.51	4.79	96.48

lected samples, the shrinkage, impermeability and the durability by freeze and thaw cycles were investigated. The additives included were a fly ash (mark A), an inflation agent UEA (mark U), a composite inflation agent (mark V), a zeolite (mark K), a fluorgypsum (mark F) and a kieselgur (mark G). They were either alone or combined as additives added in different amounts to the mixtures.

Tables 1–4 show some physical properties and chemical analysis of these raw materials.

2.2. Experimental methods and sample preparation

Granulated blast-furnace slag and the selected additives were mixed and the alkaline solutions with different consistency were used as activator. The mixes were stirred uniformly to keep the initial fluidity of the paste between 14 and 16 cm according to Chinese standard GB 8076-92. The paste was cast into a steel mould, sealed and cured at 20 ± 2°C in air or immersed in water until the required ages. The samples' strength was tested both in compress and flexural mode according to Chinese standard GB177-85. The shrinkage determination and the freeze–thaw cycle test were referenced to Chinese standard GBJ82-85, but the size of the specimens was $40 \times 40 \times 160$ mm.

Most of the samples were sealed with plastic film at room temperature, 20 ± 2°C and some of them were immersed in 20°C water for curing. *L*/*B* means the quantity ratio of the liquid solution to the solid binder mixtures.

All of the samples were expressed in such a way that the character mark indicated the kind of the activator and the additives. The number after the activators was the solution concentration, but the number after the additives was the adding amount expressed in weight percent of the slag. The end number was for the *L*/*B*.

For example, SN5T5K5F5-0.37 means slag was activated with the combined alkali solution of 5% sodium hydroxide and 5% sodium carbonate. The additives was zeolite (5 wt.% of slag) and fluorgypsum (5 wt.% of slag).

Table 3
Chemical analysis of zeolite (K) (%)

Chemical analysis	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	K_2O	Loss on ignition	Total
Content (%)	67.02	0.67	2.81	11.11	0.93	2.76	4.79	98.25

Table 4
Chemical analysis of UEA (U) (%)

Chemical analysis	SiO_2	Fe_2O_3	CaO	Al_2O_3	MgO	SO_3	K_2O	Loss on ignition
Content (%)	36.95	1.38	16.99	9.18	1.16	28.72	2.13	4.79

The *L*/*B* was 0.37 and the sample was cured in air, but sealed in a plastic pocket.

3. Results and discussion

3.1. Alkali activation

Some preliminary experiments with S + 3%, 5%, 10% $NaHCO_3$; S + 2%, 5%, 10% NaOH; S + 2%, 5%, 10% Na_2CO_3; S + 5% Na_2CO_3 and 3%, 5%, 10% NaOH as well as S + 10% Na_2CO_3 + 5% NaOH were conducted. The experiments showed that $NaHCO_3$ could not be used as the activator for this system, because both the flexural and the compressive strength of the samples were too low to test it. When Na_2CO_3 and NaOH were used individually or combined as the activator, the results of the experiments were demonstrated in Table 5 and Fig. 1. Both compounds were suitable activators for the slag system.

It can be seen that NaOH has more active effect than Na_2CO_3, especially for the strength at the early stage. The combined effect of T and N is better than when individually used, especially at late ages. In fact, one of the characteristics of the present work is to use a combined alkali as the activator.

3.2. Additives effect

The properties of the alkali-activated slag materials can be improved by adding various mineral powders. Douglas et al. [7] have carried out an investigation using additives, such as fly ash, silica fume and lime. It showed that partial substitution of silica fume and fly ash may result in an

Table 5
Take alkali solution T and N individually as activator of slag

Properties						
	Flexural strength (MPa)			Compressive strength (MPa)		
Samples	3 days	7 days	28 days	3 days	7 days	28 days
ST2-0.34	0	1.7	3.2	0	19.9	35.9
ST5-0.36	0	1.7	2.2	0	29.8	56.1
ST10-0.38	0	2.7	4.7	0	34.1	60.0
SN2-0.37	1.9	4.7	1.4	7.4	24.6	31.6
SN5-0.37	3.1	3.6	5.9	16.9	28.9	46.5
SN10-0.37	6.9	7.6	5.1	33.0	50.3	63.1

Note: (1) The strength was tested according to GB177-85;
(2) Samples were cured in 20 ± 2°C air, sealed in a plastic pocket.

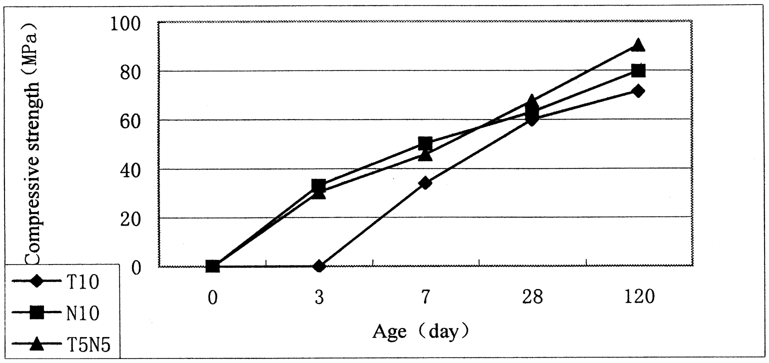

Fig.1. The effect of TN combined-alkali solution as the activator of slag.

increase in strength, however, when the substitution is in higher proportions, the strength would reduce noticeably. Several kinds of additives have been added to improve some special properties of slag paste materials. The results of our experiments showed that some of them could improve compressive strength of the samples, but the flexural strength reduces according the curing ages. The reason is likely due to the cracking development. Actually, the more important role of the additives was the effect in the avoiding of crack initiation, because there would be a severe cracking tendency when only slag and alkali exist. Some experiment results were shown in Table 6. All of these samples were maintained at room temperature and covered with a plastic film until the required ages.

It should be noted that all of these samples were made up of slag, alkali activators and some powder additives, without any fine and coarse aggregates. It is useful for some purposes to meet the special requisition. Some compressive strength at 28 days was even higher than 60 MPa. It can be seen that fly ash, inflation agent UEA, zeolite, kieselgur, etc., benefit the strength development. But a severe problem was the crack tendency in some samples. This caused the decrease in flexural strength immediately. It can be seen from Table 6 that kieselgur (10%), fluorgypsum (15%) and fly ash (20%) show rather good effect to avoid cracking.

Table 6
The effect of additives to the flexural and compressive strengths

Properties	Flexural strength (MPa)			Compressive strength (MPa)		
Samples	3 days	7 days	28 days	3 days	7 days	28 days
SN5G5-0.40	2.8	3.6	3.2	21.1	28.2	44.0
SN5G10-0.43	2.6	2.4	6.3	16.9	24.5	37.7
SN5G20-0.47	1.9	2.1	3.5	14.2	22.5	32.7
SN5F5-0.37	2.0	3.0	2.9	6.4	18.3	26.8
SN5F10-0.35	1.8	2.7	3.7	5.1	20.8	29.6
SN5F15-0.39	1.9	5.0	5.6	6.1	28.3	42.8
SN5F5K5-0.37	2.4	2.4	3.3	9.1	21	30.4
SN5F5K10-0.39	2.0	3.2	3.0	11.5	26.0	30.5
SN5F5K20-0.41	1.5	2.4	2.1	13.2	22	36.5
SN5T5A5-0.46	6.4	2.5	2.1	27.0	42.6	62.0
SN5T5A10-0.44	6.1	1.9	2.9	33.4	41.9	60.2
SN5T5A20-0.46	4.5	5.7	6.1	27.0	38.3	55.8
SN5T5A50-0.51	2.1	4.1	5.0	15.6	29.5	49.2
SN5T5U5-0.40	5.1	3.8	2.7	34.3	48.5	68.4
SN5T5U10-0.39	7.1	7.3	4.8	25.7	40.4	59.2
SN5T5U20-0.40	0	2.1	3.9	0	16.2	41.8
SN5T5G5K20V5-0.45	5.8	6.9	1.5	25.8	31.2	44.8
SN5T5G5K20V10-0.47	5.2	7.0	2.7	16.2	22.6	29.8
SN5T5G5A10U5-0.43	5.4	6.4	2.5	30.5	42.3	57.8
SN5T5G5A10V5-0.49	5.6	6.2	2.4	30.9	40.8	50.2

3.3. Effect of the curing forms

In fact, one of the important purpose of selecting additives was to inhibit the shrinkage and the crack developing, but it was difficult to achieve this target only by selection of the additives. Another important fact to avoid cracking was the curing form. When the samples were cured in water, the flexural strength developing was much better than in air, and the cracking tendency of the samples was decreased to a minimum. Table 7 showed the results of strength developing both in air and in water.

It can be seen that although there was no increase in the compressive strength of the samples cured in water, the flexural strength could develop with reaction time without decrease by this condition. It was found also that increasing curing temperature from 20°C to 80°C in water caused a rather large increase in compressive strength in 12 h. But

Table 7
Effect of curing form to the strengths

Properties	Flexural strength (MPa)			Compressive strength (MPa)		
Samples	3 days	7 days	28 days	3 days	7 days	28 days
SN5T5K10G5-0.42	2.8	4.2	3.1	32.8	41.2	44.8
SN5T5K10G5-0.42w	4.4	4.7	6.4	26.9	35.5	54.5
SN5T5K20G5-0.42	2.2	4.1	2.3	23.4	40.6	48.8
SN5T5K20G5-0.42w	3.5	4.3	7.9	26.3	38.0	51.2
SN5T5K30G5-0.46	2.2	3.3	3.0	20.4	37.2	49.6
SN5T5K30G5-0.46w	3.1	4.3	7.2	19.9	32.8	48.0

Note: The samples which end with "w" were cured in 20°C water until request ages. The other samples were cured in a sealed plastic pocket, kept in 20°C air until the request ages.

Table 8
Some results of the shrinkage determination

Samples	Change in lengths (mm/m) after days curing (in air/in water)				
	3 days	7 days	14 days	28 days	60 days
SN5T5G5-0.39	−0.7587/−0.0619	−0.8237/−0.1050	−0.9150/−0.1269	−9638/−0.4494	−2.7866/−0.6543
SN5T5G5K10-42	−1.3231/−0.0878	−1.3944/−0.0934	−1.5369/−0.3925	−1.7494/−0.4303	−3.5943/−0.5379
SN5T5G5K20-42	−0.4006/−0.0119	−1.0137/−0.0163	−1.6531/−0.0350	−2.0644/−0.1934	−4.0681/−0.3654
SN5T5G5K30-46	−0.9769/−0.0050	−2.3962/−0.0081	−2.4338/−0.0119	−2.6237/−0.1581	−3.6774/−0.2621
SN5T5A5G5-0.46	−0.8713/0.0713	−1.6813/0.0747	−1.6938/0.0141	−2.3294/−0.0569	−4.2144/−0.2469
SN5T5A10G5-0.44	−0.7800/0.0544	−1.0500/0.1141	−1.2862/0.1459	−1.8813/0.0516	−4.0065/0.0066
SN5T5A20G5-0.46	−0.7081/0.0478	−1.1087/0.0972	−1.4756/0.1562	−1.7494/−0.0612	−3.7697/−0.3084
SN5T5A10G5U5-0.43	−0.2281/−0.0144	−1.0081/0.0144	−1.1537/−0.0181	−1.6819/−0.0666	−2.0053/−0.1567
SN5T5A10G5V5-0.49	−0.4356/0.0091	−0.7862/0.0431	−1.1512/0.1709	−1.9250/0.2556	−2.3854/0.0038

Note: "−" means shrinkage, but without "−" means expansion.

afterwards when the samples were set in air, serious cracking was developing in a few days. It appears that the cracking of the sample relates directly to the shrinkage extent. There are obvious differences in shrinkage by different curing forms. The shrinkage determination results of some samples both cured in air and in water were shown in Table 8.

It can be seen that almost all of the samples have a great shrinkage when cured in air, even when the samples were sealed in a plastic pocket. The experiment results showed that cracking would develop on the surface of the samples when the value of the length change is about 2 mm/m. The reason for decrease in the flexural strength should be the rather large value of the shrinkage. There was no cracking and strength decreasing in the samples which was cured in water. However, the results of 50 cycles of freeze and thaw from −15°C to 20°C experiment showed that the samples, which were cured in air, were more stable than those cured in water. There is no decrease in the compressive strength of any of the samples, which were cured in air, but the was a 15–18% decrease in the samples cured in water. This would be because of little more free water in the samples.

4. Conclusions

1. Combined-alkali-activated slag could be used as high compressive strength cementitious materials. It was possible to get stable solid with this material without any fine and coarse aggregates.
2. Various mineral powders such as fly ash, zeolite, kieselgur, fluorgypsum and some inflation agent could be used as additives to the alkali-activated slag system to increase the strength and decrease the shrinkage of the samples, but there was a suitable scope for each kind of the additives.
3. There was a big effect about the strength developing and the shrinkage in the sample length by different curing forms. Specimens which cured in 20°C water had higher flexural strength and reduced shrinkage.

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