Pergamon

Cement and Concrete Research, Vol. 28, No. 5, pp. 655–664, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00025-8

EARLY AGE STRENGTH AND WORKABILITY OF SLAG PASTES ACTIVATED BY NaOH AND Na_2CO_3

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(Received January 16, 1998; in final form February 10, 1998)

ABSTRACT

This paper reports the results of an investigation on activation of blast furnace slag with the emphasis on achievement of equivalent one-day strength to Portland cement at normal curing temperatures and reasonable workability. The effects of varying dosages of activators NaOH and Na_2CO_3 are discussed in terms of strength of mini cylinders and also workability by the mini slump method. The results are mainly based on pastes, but comparisons are also made with mortar and concrete results. The effects of preblended gypsum dosage within the slag as well as the effect of ultrafine slag on workability are reported. The results of trials with various water- reducing admixtures and superplastisers and their effects on strength and workability are reported. *© 1998 Elsevier Science Ltd*

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Introduction

Alkali activated slag (AAS) concretes can yield high early strength (a characteristic currently not achieved by blends of slag + portland cement) while providing lower heat of hydration and better durability than the Portland cements. Talling and Brandstetr (1) provide a comprehensive state of the art summary of the subject.

The aim of this investigation was to evaluate the suitability of NaOH and Na_2CO_3 as activators for slag to yield equivalent or better one-day strength to ordinary Portland cement (OPC) at normal curing temperatures (23°C). Equivalent one-day strength to OPC has been achieved in the past using elevated temperature curing (2,3,4,5) and steam curing (6,7,8). However, these curing conditions necessitate specialised equipment and facilities and requires attendance by staff. This study therefore concentrated on the achievement of equivalent one-day strength at normal curing conditions. Hakkinen (9) reports one-day concrete strengths up to 28.3 MPa following normal moist curing. The concretes consisted of 5% NaOH plus F-admixture and had a water-to-cementitious ratio ranging from 0.25 to 0.30. However, the initial workability and the loss of workability with time are unreported. Shi (10) recorded significantly lower one-day strength of NaOH activated slag mortars.

Jolicoeur, et. al. (11) reports the combination of NaOH + Na_2CO_3 yields comparable one-day strength to Portland cement. Improved workability was reported with the addition of

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TABLE 1
Properties of cementitious materials.

Constituent/Property	Slag	UFS	OPC	GB 50/50
SiO_3 (%)	N/A	N/A	N/A	2.6
SiO_2 (%)	35.04	33.2	19.9	26.4
Al_2O_3 (%)	13.91	14.6	4.62	8.4
Fe_2O_3 (%)	0.29	0.4	3.97	2.4
MgO (%)	6.13	5.5	1.73	3.6
CaO (%)	39.43	42.4	64.27	53.8
Na_2O (%)	0.34	0.3		
TiO_2 (%)	0.42			
K_2O (%)	0.39	0.44	0.57	
P_2O_5 (%)	<0.1			
MnO (%)	0.43			
Total Sulphur as SO_3 (%)	2.43	0.2	2.56	
Sulphide Sulphur as S^{2-}	0.44			
Cl (p.p.m)	80			
Fineness (m^2/kg)	460	1496	342	
Loss on ignition (%)	1.45		2.9	1.9
Time to initial set (hours)	N/A	N/A	2.0	2.45
Strength				
(MPa)	N/A	N/A		
3 Days			32.7	22.2
7 Days			42.0	36.0
28 Days			54.1	59.1

sodium poly-naphthalene and sodium gluconate. The effect of these chemical admixtures on one-day strength was not investigated. Wang (12,13) recorded relatively low one-day strength for slag mortars activated by NaOH.

Experimental Programme

The chemical composition and properties of the cementitious binders are summarised in Table 1. The binders used are ground granulated blast furnace slag (Slag), ultra fine slag (UFS), Portland cement (OPC), and 50% ground granulated blast furnace slag + 50% Portland cement (GB50/50). The term water/binder (w/b) ratio is used instead of the conventional water/cement ratio, to include all the binders mentioned above. The slag is supplied with 2% gypsum, which is blended with the slag (although slag samples containing 0% gypsum were also investigated).

The activators and adjuncts investigated were liquid sodium hydroxide (60% solution) (NaOH) and sodium carbonate powder (decahydrate; i.e., $Na_2CO_3.0H_2O$).

The chemical admixtures which were investigated were as follows:

NLSNS: Normal-life superplasticiser based on naphthalene sulphonates, which complies with ASTM C-494 Type F.

WRSRL: Water-reducing and set-retarding admixture based on lignosulphonates, which complies with ASTM C 494 Types B and D.
WRSRSP: Water-reducing and set-retarding admixture based on calcium- complexing sugar-based material which was primarily sodium gluconate, which complies with ASTM C 494 Type D.

In the case of mortars, the sand:cementitious binder ratio was 3:1. The sand was a locally produced river sand from Lynhurst.

The size of the paste cylinders for compressive strength testing were 35 mm in diameter and 70 mm in length. The water to binder (w/b) ratio was fixed to 0.5 to enable reasonable paste workability. A total of 6 cylinders were tested for each data set. This phase of testing also enabled the qualitative assessment of paste workability. Activated slag pastes that appeared to be considerably "stiffer" than an OPC equivalent were therefore rejected for further assessment (regardless of the one-day strength).

Workability was assessed by the mini-slump test, as reported by Kantro (14). The dimensions of the mini slump cone mould are: top diameter 19 mm, bottom diameter 38 mm, and height 57 mm. The mould is placed firmly on a plastic sheet and filled with paste. The paste is tamped down with a spatula to ensure compaction. When the mould is full, the top surface is levelled and the excess paste is removed. The mould is removed vertically, ensuring no lateral disturbance, and the sample is left to harden over 24 h. The outline of the slump sample is traced onto the underlying plastic sheet with indelible ink and the area of the base is measured using a planimeter. Each data point shown on the attached figures is the average of 3 test results, with the exception of the OPC controls which were the average of 6 test results.

The base area of the paste measured 24 h after conducting the test is a better indicator of workability than the height measurements (14). Perrenchio (15) has established a linear relationship between the base area of the mini-slump paste and the base area of concrete; therefore the test lends itself to the estimation of likely concrete workability.

Strength Results

One-day Strength

The range of NaOH and Na_2CO_3 dosages that was investigated are summarised in Table 2. The results are compared with the control OPC with w/b of 0.5. As indicated in Table 2, the range of NaOH dosages, without any addition of Na_2CO_3, were 3%, 4%, and 5% (% weight of slag). The test results indicate that at all NaOH dosages (with 0% Na_2CO_3) the one-day strength is less than OPC. The worst one-day strength was at the 4% dosage. All of the mixes with 0% Na_2CO_3 were observed to be stiffer than OPC at the same w/b.

With the addition of Na_2CO_3, the results indicate the one-day strength is generally greater than OPC at the higher dosage levels of NaOH and Na_2CO_3, and there is a trend of increasing strength with increasing Na_2CO_3 dose. The paste was quite stiff at the 1% Na_2CO_3 dose for all mixes, and workability improved with increasing Na_2CO_3 dosage. Based on one-day strength and (observed) workability, the following activator combinations were considered for further assessment: (a) 3% NaOH + 4% Na_2CO_3; (b) 5% NaOH + 4% Na_2CO_3; (c) 6% NaOH + 4% Na_2CO_3. Further mixes were manufactured to assess the strength development with time. The mixes also include three batches of OPC and one batch of 50% slag blended

TABLE 2
One-day strength of activated slag pastes (MPa).

NaOH Dosage (% Slag)	Na_2CO_3 Dosage (% Slag)				
	0%	1%	2%	3%	4%
2%			4.37		
3%	4.37	3.54	6.68	7.23	6.52
4%	2.72		6.22		
5%	3.71	6.23	6.62	8.64	8.47
6%		5.92	7.62	7.34	8.67
7%			6.78		

Portland Cement Paste = 4.96

cement for comparison with the activated slag pastes. All the mixes were manufactured with w/b ratio of 0.5. Six cylinders from each batch were tested at 1, 3, 7, and 28 days. The results are summarised in Figure 1.

The results indicate:

1. The 28-day strength of NaOH + Na_2CO_3 activated slags is similar regardless of NaOH concentration. This observation is supported by Anderson and Gram (6).
2. Although the one-day strength of NaOH activated slags is similar to OPC, no strength gain has been observed after 7 days compared to OPC, which doubled its strength from 7 to 28 days.

The 5% NaOH + 4% Na_2CO_3 had the best combination of 1- to 7-day strength development and workability.

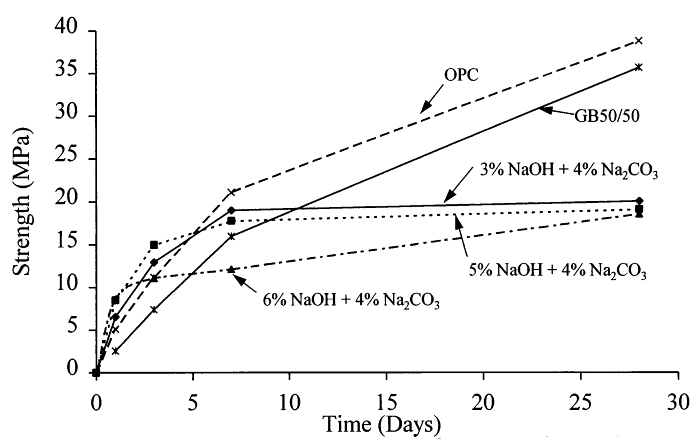

FIG. 1.
Strength Development of Slag Pastes; w/b = 0.5.

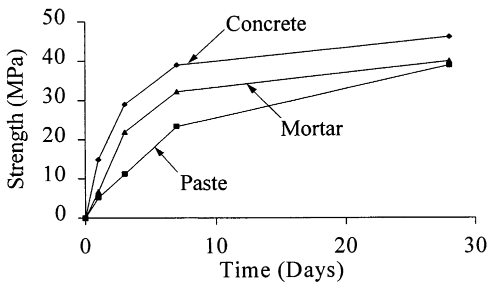

FIG. 2.
OPC Strength versus Time; w/b = 0.5.

Strength Development of Mortars

The strength-vs.-time graphs of pastes do not truly mimic the strength-vs.-time relationship for concrete, as shown in Figures 2 and 3. The concrete strength test data is reported separately (16).

Further testing of mini cylinders has been conducted with mortars. The mixes consisted of:

1. OPC, w/b = 0.5, 3 separate batches, 6 cylinders tested at 1, 3, 7 and 28 days;
2. Slag activated by 5%NaOH + 4%Na_2CO_3, w/b = 0.5, 6 cylinders tested at 1, 3, 7 and 28 days.

Figures 2 and 3 indicate the mortars mimic the concrete strength development curves well. This indicates the paste samples are very sensitive to local defects acting as stress concentrations. Also, the sand acts as nucleation points for cement hydration (and bond strength development), which also affects the measured strength. Nevertheless, the paste strength test results are good indicators of likely strength development trends.

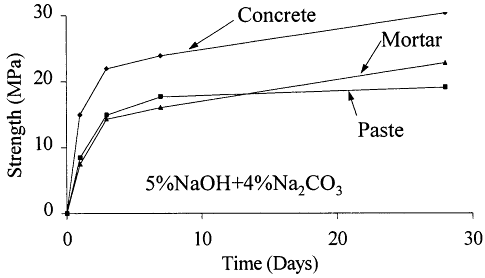

FIG. 3.
Activated Slag Strength vs Time; w/b = 0.5.

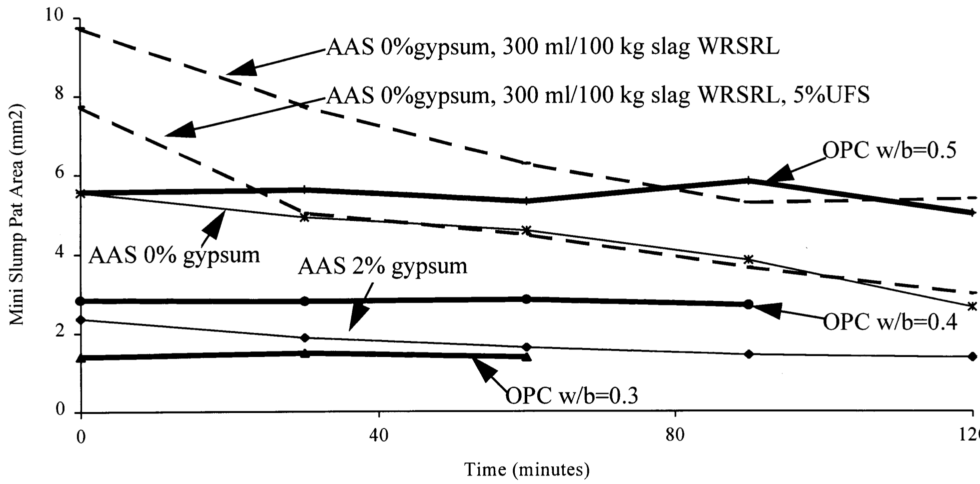

FIG. 4.
Workability of Pastes (w/b = 0.5 except where indicated otherwise).

Workability Results

Slump Loss with Time; w/b = 0.5

Slump loss versus time for OPC pastes at various w/b's is shown in Figure 4. Figure 4 also shows loss of workability with time of activated slags. The slag activated by 5% NaOH + 4% Na_2CO_3 (2% gypsum) displays less workability than OPC at the time of mixing and displays a mini slump equal to OPC with w/b = 0.4. Significant false set (i.e., the stiffened paste could be made workable by remixing) is demonstrated with this activator at ages beyond 30 min. Additions of a lignosulphonate significantly improve workability (to OPC equivalent w/b = 0.5) at the time of mixing, but slump loss is still evidenced.

Effect of Gypsum

Without gypsum, NaOH + Na_2CO_3 activated slag shows a significant increase in workability, as shown in Figure 4. Nevertheless, false set was still evidenced, even with the addition of the lignosulphonate-based set retarder (WRSRL). The one-day strength of the paste was virtually equal to the samples which contained gypsum. Therefore, for this activator, slag without gypsum was adopted for the lower w/b studies.

NaOH + Na_2CO_3—Chemical Admixture Sensitivity

At the time of mixing, activated slag with w/b ratio of 0.5 shows almost identical workability to OPC (Fig. 4). However, slump loss occurred with time and became significant beyond 60 min. The addition of a lignosulphonate based set retarder (WRSRL) showed significant dispersion at the time of mixing, but showed rapid loss of workability at 30 min. and beyond.

Figure 5 shows the effect of various dosages of water-reducing and set-retarding admixture

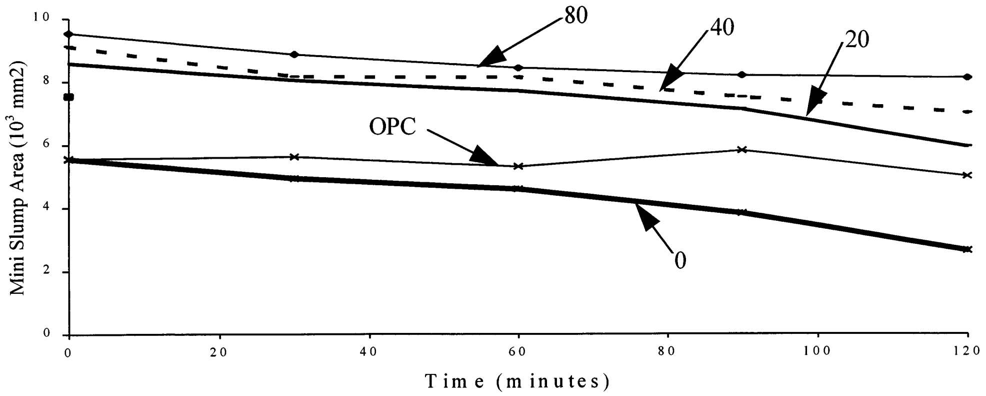

FIG. 5.
Effects Calcium Complexing Retarder (WRSRSP) on Workability (Dosages indicated in ml/100 kg Slag; 5% NaOH + 4% Na_2CO_3; w/b = 0.5).

based on calcium-complexing sugar-based material that was primarily sodium gluconate (WRSRSP) on mini slump over a 2-h period for w/b = 0.5. With increasing dosage, the dispersion at the time of mixing increases significantly. Workability diminishes with time, but, at 120 min. the workability is better than OPC. All pastes displayed a high buildup of bleed water on the top surface (which increased with increasing dosages). The surface few millimeters of hardened paste were soft and could be easily scraped away. The bulk mass of the sample was hardened, indicating that the bleed water contains retarder that is prolonging setting of the surface concrete and reducing the surface strength. The one-day strength of mortars containing various additions of retarder is shown in Table 3. All dosages show a significantly lower one-day strength than OPC.

For w/b = 0.4, Table 4 shows less workability of the activated slag at the time of mixing than the OPC control. The paste demonstrated good workability with additions of normal life naphthalene sulphonate based superplasticiser (NLSNS).

The workability loss over a 2-h period is shown in Figure 6. At 30 min. the paste rapidly loses workability and, despite the combination of lignosulphonate based set retarder (WRSRL) and normal-life naphthalene sulphonate-based superplasticiser (NLSNS), the false setting phenomenon is apparent. The false setting effect was reduced by utilising a set retarder based on a water-reducing and set-retarding admixture based on calcium-complexing

TABLE 3
One-day strength of mortars (w/b = 0.5) effects of calcium complexing retarder.

OPC	Slag Activated by 5% NaOH + 4% Na_2CO_3 (MPa)					
MPa	Dosages of Retarder WRSRSP (mL/100 kg Slag)					
	0	20	40	80	130	250
6.73	7.51	3.65	3.46	2.84	2.50	2.13

TABLE 4
Mini slump area at time of mixing (mm^2) (w/b = 0.4).

	Slag Activated by 5% NaOH + 4% Na_2CO_3; 0% gypsum;					
	Dosages of Superplasticiser NLSNS (mL/100 kg Slag)					
OPC	0	300	600	900	1200	1500
2845	2340	2293	4327	5437	6253	7050

sugar-based material that was primarily sodium gluconate (WRSRSP) together with normal-life naphthalene sulphonate-based superplasticiser (NLSNS). This is also shown in Figure 6. However, the effect of this type of retarder is to significantly reduce the one-day strength and it was no longer used in this investigation.

Effect of Ultrafine Slag

For the slag activated by NaOH + Na_2CO_3, Figure 5 shows the replacement of 5% of the slag by ultrafine slag caused a significant increase in workability at the time of mixing. Slump loss did occur over a period of 2 h, but the workability was significantly better at 2 h than binders not containing ultrafine slag. Further work has been reported separately (17).

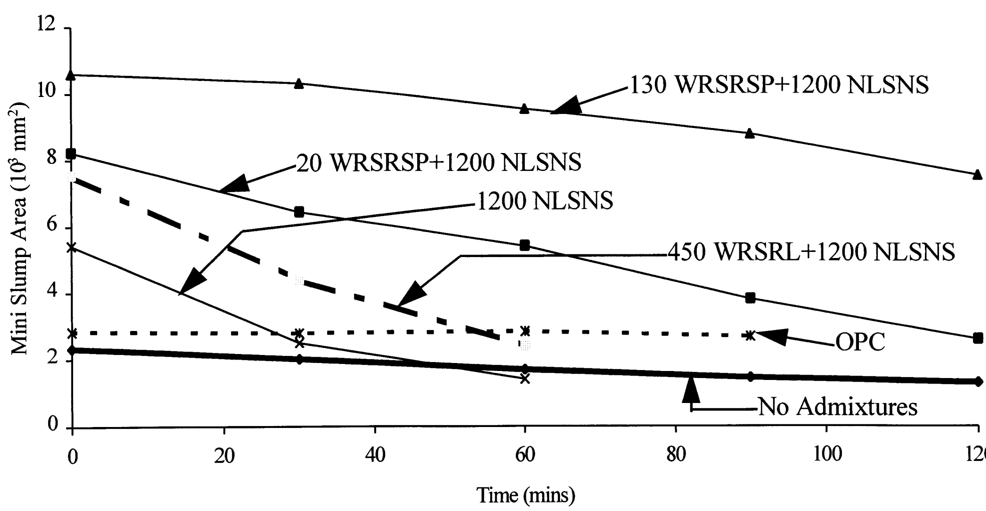

FIG. 6.
Effects of Calcium Complexing Retarder (WRSRSP), Water Reducing Set Retarder (WRSRL) and Superplasticiser (NLSNS) (Dosages indicated in ml/100 kg Slag) 5% NaOH + 4% Na_2CO_3; w/b = 0.4.

Conclusions

The results of this initial investigation indicate:

1. Equivalent one-day compressive strength to OPC is achievable with 100% alkali-activated slag.
2. The activation of slag with NaOH yielded lower one-day strength than OPC, but NaOH in combination with Na_2CO_3 produced equivalent one-day strength. Workability improved with increasing dosages of Na_2CO_3. Although early age strength growth was rapid, the 28-day strength was significantly lower than OPC. Regardless of NaOH dosage, the 28-day strength was similar. The optimum combination for strength and workability was 5% NaOH + 4% Na_2CO_3.
3. The slag was supplied pre-blended with 2% gypsum. Without gypsum, the slag activated by NaOH + Na_2CO_3 showed significantly better workability than activated slag containing gypsum. The one-day strength was identical regardless of gypsum content.
4. Slag activated by NaOH + Na_2CO_3 demonstrates false setting. Response to retarders was reasonable for 30 min., but loss of workability beyond 30 min. was significant. The best results were achieved by use of a calcium-complexing retarder, but at the expense of one-day strength (even at minor dosages). Response to conventional superplasticiser was good.
5. Replacement of the slag by ultrafine slag did not reduce workability (at the 5% and 10% replacement levels).

Acknowledgments

The financial support for this project is jointly provided by Independent Cement and Lime Pty Ltd, Blue Circle Southern Cement Ltd and Australian Steel Mill Services. The authors thank the sponsors especially Alan Dow, Tom Wauer, and Dr. Ihor Hinczak for the guidance and support. The efforts and assistance with the laboratory work provided by Soo Lim, Eric Tang, Jeff Doddrell, Roger Doulis, and Peter Dunbar are also gratefully acknowledged.

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