EFFECT OF COMPOSITION OF PRECURSOR AND SOLID CONTENT ON RHEOLOGICAL BEHAVIOUR OF ALKALI ACTIVATED BINDERS

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Introduction

Global cement production in 2017 was around 4100 million metric tons[1] and contributes to ~8% of global anthropogenic CO_2 emissions.[2] To curb these emissions, there is an utmost need to look for alternative materials which can replace and perform similar to or better than Ordinary Portland Cement (OPC). Alkali-activated materials (AAMs) are one such alternative binders to OPC which can reduce carbon emissions. AAMs use a precursor (mostly a by-product) and an alkaline activator that produces a binder having cementitious properties.[3] However, these materials have a few drawbacks which limit their usage in large scale application, one of the most important being the rapid setting which inhibits the workability of the material. As is prevalent in OPC binder, workability can be improved either by chemical or mechanical means. However, before making efforts to make these binders more workable, it is essential to understand the workability and various factors that influence it. Slump tests are considered to be an equivalent *in-situ* test to predict the yield stress of the material.[4] In this study, the workability is measured in terms of the spread diameter using a minislump test. The effect of parameters such as oxide composition of precursors, water to binder (w/b) ratio, molar modulus and activator dosage (% of Na_2O (by weight of binder)) on the spread diameter are studied.

Experimental Methods

The experiments were conducted using slags obtained from a steel industry and fly ash obtained from a thermal power station located near Mumbai, India. These materials were sieved through 150 µm sieve. The total oxide composition of slag and fly ash as determined by ICP-AES is presented in Table 1.

Table 1: Oxide Composition (wt%) of slag and fly ash

Precursor	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O
Slag	35.4	40.8	14.5	1.2	7.1	0.5	0.4
Fly ash	3.4	55.4	25.1	11.8	1.3	0.6	1.0

Alkali activated slag/fly ash binders were prepared by activating precursors with an activator solution. The activator solutions of required molar modulus and percentage Na_2O were prepared by mixing sodium silicate and 14 M NaOH solution in appropriate proportions. 125 different alkali-activated slag/fly ash binders were designed for investigation of the following parameters: composition of binder (slag was volumetrically replaced with fly ash at 25, 50, 75 and 100%), water to binder ratio (0.40, 0.45 and 0.50), molar modulus (1.0, 1.5 and 2.0) and % of Na_2O (4, 6 and 8%).

A frustum (minislump cone) with a bottom diameter of 38 mm, a top diameter of 19 mm and height 54 mm was selected for this study.[5] Pastes were prepared by weighing the appropriate quantities of slag, fly ash, NaOH, sodium silicate and distilled water. Dry mixing of precursors was done (priorly) for 2 minutes. The mixing regime as given in ASTM C 305[6] was followed. After mixing for 2 min 30 s, the paste was poured in mini-slump cone. The paste was left undisturbed for a minute in frustum. The paste was allowed to spread and the diameter of spread was measured in four directions and their average was considered as the spread diameter.

Since the amorphous oxides are reactive and their amount governs the kinetics of the reaction, the amorphous oxide composition was considered in this study and is obtained by subtracting the crystalline content (as determined with QXRD) from the total oxide composition and observed that slag and fly ash have 98% and 50% amorphous content respectively. On the replacement of slag with fly ash, maximum variation was obtained in CaO content and hereby the percentage of replacement is said in terms of the ratio of CaO to SiO_2 (C/S) (Table 2).

Table 2: Amorphous oxide Composition (wt%) of slag and fly ash combinations

Material	CaO	SiO_2	Al_2O_3		$\frac{CaO}{SiO_2}$
Slag (0)	34.9	39.2	14.5		0.89
25%	27.0	36.2	12.6		0.74
50%	19.1	33.2	10.8		0.57
75%	11.3	30.2	8.9		0.37
Fly ash(100)	3.4	27.3	7.1		0.12

Results and Discussion

The variation of spread diameter with reactive oxide composition of precursor, w/b ratio, molar modulus and % of Na_2O is given in Figure 1A-H. The main effects plot of fitted means for the diameter of spread is given in Figure 2. A decrease in spread diameter is observed with an increase in C/S ratio and is significant at 4% of Na_2O. A significant variation in spread diameter is not observed at low C/S ratios. The

dissolution of precursor increases with an increase in Ca^{2+} ion and results in the formation of C-S-H which gives rigidity to the system. In this study, a significant reduction in spread diameter is observed with CaO content above 20%. Increase in spread diameter is observed with an increase in w/b ratio and % of Na_2O. Increase in spread diameter is observed with increase in molar modulus up to 1.5 and decreased with further increment in molar modulus to 2.0. Kashani *et al.*[7] reported a similar trend in alkali-activated slag pastes. At higher concentrations, the ions in order to reduce their free energy occupy the positions between neighbouring particles and results in flocculation which in turn increases the yield stress even with negative zeta potential values.[8]

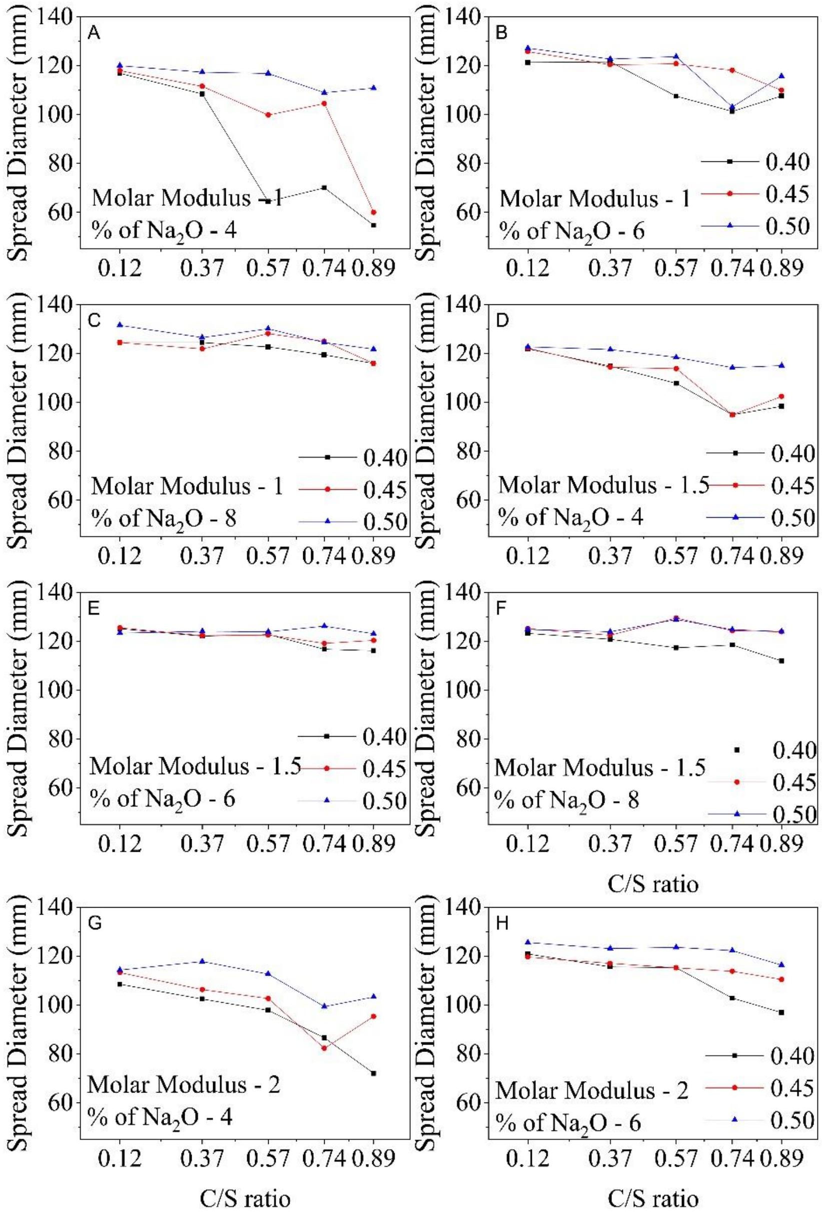

Figure 1: Variation in spread diameter (mm) with C/S ratio, w/b ratio, molar modulus and % of Na_2O

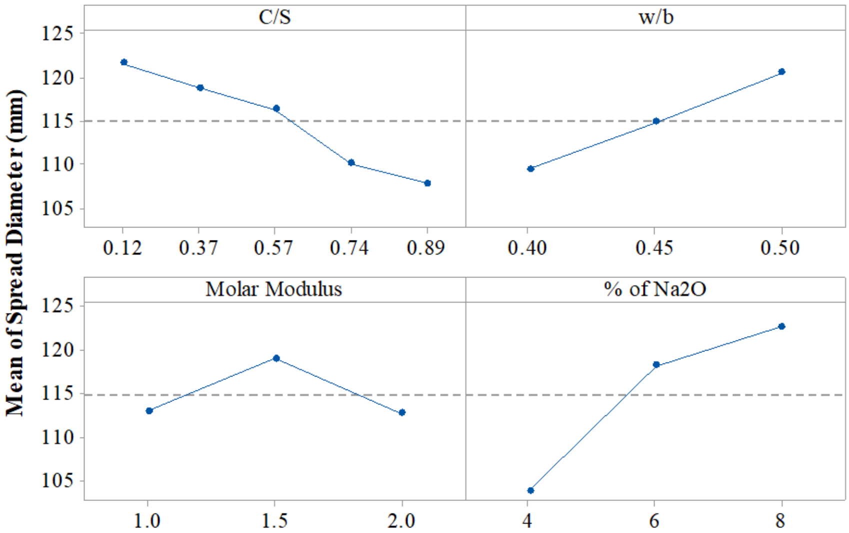

Figure 2: Main effects plot (fitted mean) for the spread diameter (mm)

Conclusions

The spread diameter as representative of the rheological behaviour was found to be dependent on the amount of oxide composition, w/b ratio, molar modulus and activator dosage (% of Na_2O) for alkali activated slag/fly ash binders. The spread diameter increased with an increase in w/b ratio and % of Na_2O. Increase in spread diameter was observed with increase in molar modulus up to 1.5 and decreased with a further increment of molar modulus to 2.0. The amount of CaO content (more than 20%) was found to have a significant effect on the spread diameter of alkali-activated slag/fly ash binders.

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