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# AN EFFECTIVE APPROACH TO IMPROVE THE PERFORMANCE OF PC-BASED SUPERPLASTICIZER IN ALKALI-ACTIVATED SLAG

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ABSTRACT: The lack of workability has hindered the industriallisation of alkali-activated slag (AAS) - a novel, low carbon cementitious building material. In order to address this main barrier, adding superplasticiser (SP) is essential. The main reason causing the dysfunction of current commercial SP in AAS has been identified as competitive adsorption between the SPs and the activators. The separate SP addition methods (adding SP and activator separately) offers the potentials to tackle the above issue. In this paper, the effects of separate addition methods of

lignosulfonate superplasticiser (LS) in AAS activated by NaOH were investigated. The adsorption between the LS and the slag was examined to understand the interaction between the SP and the slag. The workability and rheological properties of fresh NaOH-activated slag and the compressive strength of hardened NaOH-activated slag were also investigated. The results indicated that the separate addition methods reduced the competitive adsorption between the SPs and the NaOH activator, leading to a higher adsorption of the SPs on the slag. Consequently, the workability and rheological properties of NaOH-activated slag was enhanced by separate addition methods without reducing the compressive strength of hardened NaOH-activated slag.
Keywords: Superplasticiser, Alkali-activated slag, Separate addition, Adsorption, Rheological Properties.

## INTRODUCTION

Superplasticisers (SPs), also known as high-range water reducer, is one of the most important chemical mixtures employed either to improve workability or to reduce mixing water [1]. Although extensive research have been conducted on the SPs in Portland cement-based (PC-based) system, its research and application in various novel cement systems is still limited in the literature [2] . This is particularly the case for alkali-activated slag (AAS) systems, a novel, low carbon cementitious system mainly composing with ground granulated blast-furnace slag (GGBS, short for slag hereafter) and alkaline activator [3].

Based from the limited information available in literature, the competitive adsorption between negatively charged alkaline activator and superplasticisers with negatively charged anchor groups has been identified as one of the main reason cause the dysfunction of the SPs in AAS. Using proper mixing procedure is a convenient route to functionalise the PC-based SPs in AAS. It has been proved that adding SP in different mixing stage could improve the performance of SPs in Portland cement [4]. Therefore, separately adding the SP and the alkaline activator can provides a potential to reduce the competitive adsorption, and then, enhance the performance of current superplasticisers in AAS. Previous work reported by the authors indicated that adding PC-based lignosulfonate derivation superplasticiser (LS) and waterglass activator at different mixing stage can improve the workability of AAS [5]. However, the effect of addition method of LS on AAS activated by NaOH has still not been explored, yet.

The aim of this study is, therefore, to investigate the effects of different addition methods of LS on some fresh properties and hardened properties of NaOH–activated slag paste. To understand the mechanism, the adsorption of LS in NaOH-activate slag suspension was investigated. The effects of different addition methods of LS on the workability (in terms of minislump) and rheological properties (yield stress and plastic viscosity) were examined. Meantime, its effects on the compressive strength of NaOH-activated slag pastes were also investigated.

## EXPERIMENTAL METHODS

### Materials

Slag is supplied by Hanson Heidelberg Cement Group, U.K., the chemical composition of which is shown in Table 1. The raw NaOH was obtained from Tennants Distribution. Lignosulfonate derivation superplasticiser was supplied by Tianjin Jiangong Special Material Co. Ltd.

**Table 1.** *Chemical composition of slag*

| CaO | $SiO_2$ | $Al_2O_3$ | MgO | $SO_3$ | $TiO_2$ | MnO | $Na_2O$ | $Fe_2O_3$ | $K_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|
| 39.03% | 35.79% | 12.28% | 7.75% | 1.66% | 0.74% | 0.71% | 0.34% | 0.30% | 0.59% | 0.39% |
| The fineness: 518 $m^2$/kg; Specific gravity: 2900 kg.$m^3$ | | | | | | | | | | |

### Mixing Procedure

The water to slag ratio for all the mixes was fixed at 0.48. The dosage of L for the tests of workability and rheology was fixed as 0, 0.500, 0.750, and 1.000% (by the mass of slag) and for adsorption was controlled as 0, 0.125, 0.250, 0.500, 0.750 and 1.000%. NaOH solution was used as the activator and its content was controlled at 4 % (counted as $Na_2O$ equivalent) by the mass of slag. Both the activator and LS were dissolved in water. Three different addition methods were studied, namely: 1) *simultaneous addition (**SA**)*: mixing slag with both LS and activator together; 2) *prior addition (**PA**)*: mixing slag with LS first, then adding activator at 3 min interval; and 3) *delayed addition (**DA**)*: mixing slag with activator first, then adding LS at 3 min interval.

### Test

Adsorption test was conducted to determine the interaction between the slag and the LS. The amount of LS remained in NaOH-activated slag was determined by a UV-spectrophotometer (Camspec M550) at a wave length of 260 nm. The amount of LS adsorbed on the slag was then calculated from the difference in concentration of LS before and after it contacted with the slag. The minislump test, which was conducted with a PVC plate and a cone with a lower inner diameter of 38.1 mm, an upper inner diameter of 19 mm, and a height of 52.7 mm, was used to determine the workability of NaOH-activated slag. The diameters at two perpendicular directions were measured and the average diameter was reported as the workability. The rheological properties were measured by using a modified Rheomat 115 viscometer. The initial measurements of both the minislump and the rheological property were conducted at 7 minutes after mixing. NaOH-activated slag paste specimens with size of 25×25×25 mm were prepared, and then cured at 20±2℃ under 100% relative humidity in sealed plastic bags with wet hessian. The compressive strengths of the specimens were determined after curing for 1, 7, 28, and 56 days.

## RESULTS AND DISCUSSIONS

### Adsorption

The effects of LS under different addition methods on the adsorption of NaOH-activated slag are shown in Fig. 1. It is clear that the adsorption of LS follows the trend of Langmuir isothermal adsorption, with forming a monolayer of adsorbed SP [6]. Compared to the adsorption on pure slag, the adsorption of both types of SPs was significantly reduced in the presence of the NaOH activator. This could be due to that, large amounts of $OH^-$ are introduced into the NaOH-activated slag system, which increases the ionic strength in the solution significantly, leading to a reduction of the adsorption [7]. However, under the separate addition methods, increased adsorption was observed in both the *DA* and *PA*, which indicates that adding SP and activator separately can reduce the competitive adsorption in the NaOH-activated slag. Based on the Langmuir isothermal adsorption [8], quantitative analysis of the adsorption behaviour of LS was conducted and the results are summarised in Table 2. The results suggested that when the SP and the NaOH were added separately, higher electrostatic attractive forces formed between the negatively charged LS and the positively charged slag, and therefore, more LS were adsorbed on the surface of slag.

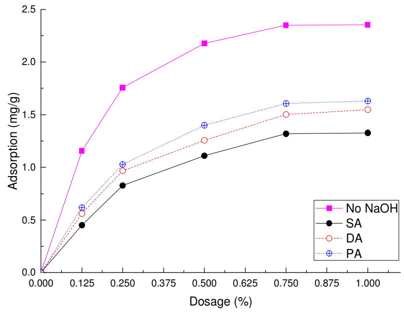


**Fig. 1:** *Effects of different addition methods of LS on adsorption behaviour of NaOH-activated slag suspension.*

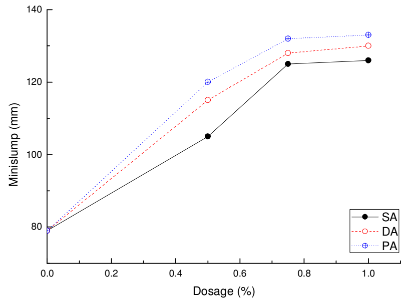


**Fig. 2:** *Effects of different addition methods of LS on initial minislump(at 7 minutes) of NaOH-activated slag paste:*

**Table 2.** *Parameters in Langmuir equation for LS in NaOH-activated slag*

| Activator | Addition method | $R^2$ | Intercept | Slope | k/ L·g$^{-1}$ | As/mg·g$^{-1}$ | $\Delta G_{ads}$/kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $H_2O$ | | 0.9973 | 379.7 | 90.5 | 4.194 | 2.634 | -3.658 |
| | SA | 0.9708 | 635.9 | 241.4 | 2.634 | 1.573 | -2.882 |
| NaOH | DA | 0.9677 | 555.8 | 195.5 | 2.842 | 1.799 | -3.632 |
| | PA | 0.9821 | 548.3 | 137.8 | 3.978 | 1.824 | -3.692 |

## Workability

The initial minislump of NaOH-activated slag under the different addition methods of LS are illustrated in Fig. 2. The addition of LS increased the minislump of NaOH-activated slag paste, which indicates that adding LS can improve the workability of NaOH-activated slag. Compared to *SA*, a further improvement of minislump can be observed by separate addition. The spread diameter of the minislump obtained from both *PA* and *DA* was at least 10 mm greater than that of the *SA* (approximately 10% improvement), with *PA* higher than *DA* in all the cases. The results correlated well with the adsorption results, which suggested that when adding LS and NaOH separately, due to the reduced competition, more LS can be adsorbed on the slag surface, further disperses the slag grains, and thus improves the workability of NaOH-activated slag.

## Rheology properties

The effects of different addition methods of LS dosages on the initial yield stress and the initial plastic viscosity based on Bingham model are presented by following the vectorised-rheograph approach as shown in Fig. 3 [9]. It should be noted that negative yield stress, which has no physical meaning, was identified, the circumstance of which could be mainly due to the adoption of linear Bingham model to fit the non-linear shear-thickening flow curve [10]. However, to simplify the complexity caused by application of rheology models, the commonly accepted Bingham model with an attempt only to show the difference in the yield stress when different addition methods and superplasticisers were used. With the increase of the LS dosage under all the addition methods, both initial yield stress and initial plastic viscosity of NaOH-activated slag paste moved toward the lower value, which results in the relocation of the data points to the bottom left of the rheograph. When the separate addition methods were applied, both of the initial yield stress and the initial plastic viscosity have been further reduced compared with the *SA*. A lower plastic viscosity was observed from the *PA*, and a lower yield stress was obtained also from the *PA,* except at 1.000% dosage. It was widely accepted that better workability is achieved with lower yield stress [11, 12]. Compared with that of the reference mixes, the yield stresses of NaOH-activated slag paste with SPs were significantly reduced, and the yield stress was also reduced when adding SP and activator separately (both *PA* and *DA*), which corresponded well to the minislump results. The plastic viscosity depends largely on the volume fraction of the solid particles and the packed density which could somehow reflect the flocculation state in the paste and the resistance of the flow [13]. Similar to the effects on the yield stress, the separate addition of SP further reduced the plastic viscosity of NaOH-activated slag, which indicated less flocculation existed and better flow was achieved.

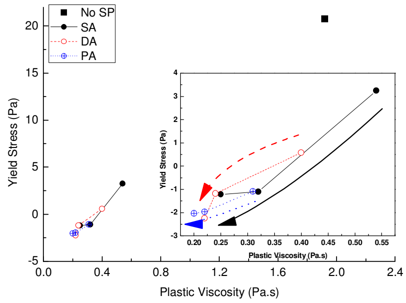


**Fig. 3:** *Rheograph of NaOH activated slag with LS at 7 minute (The direction of arrow indicates the increase of SP dosage: (a) LS*

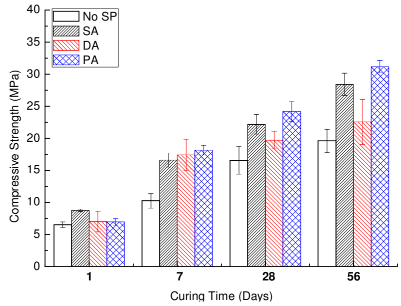


**Fig. 4:** *Effects of different addition methods of LS with dosage of 1.000% on compressive strength of NaOH-activated slag paste*

**Compressive strength**

The effects of LS on the compressive strength of NaOH-activated slag under different addition methods are shown in Fig. 4. It is clear that the compressive strengths of NaOH-activated slag pastes at all curing ages were increased with the addition of LS at all three SP addition methods. Comparing different addition methods, it was found that the trend of effects of addition methods is not obvious at early ages (e.g. 1 day and 7 days). However, with the development of compressive strength, *DA* showed the lowest compressive strength, while *PA* provided the highest compressive strength.

## CONCLUSION

Based on the results obtained, the following conclusion could be drawn:

1. The adsorption behaviour of LS can be characterised by Langmuir isothermal adsorption. The separate addition methods increased the adsorption of LS by avoiding the competitive adsorption between the LS and the NaOH activator, with a higher adsorbed amount in *PA*.
2. The initial minislump obtained by the separate addition methods was higher than that by *SA*, with *PA* better than *DA*.
3. The effects of different addition methods of LS on initial rheological properties of NaOH-activated slag were analysed on a rheograph. Both the yield stress and the plastic viscosity of NaOH-activated slag pastes were further reduced by adding the LS and the NaOH separately.
4. The addition of LS increased the compressive strengths of NaOH-activated slag (at fixed w/c ratio) at all ages except 1 day. The *PA* produced the highest compressive strength among different

addition methods.

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