

# Effect of alkali cation type on the plasticizing effect of lignosulfonate in alkali-activated systems

V Iliushchenko<sup>1</sup>, V Bilek Jr.<sup>1</sup>, L Kalina<sup>1</sup>, P Hruby<sup>1</sup>, T Opravil<sup>1</sup> and J Bojanovsky<sup>2</sup>

<sup>1</sup> Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno, Czech Republic

<sup>2</sup> Brno University of Technology, Faculty of Mechanical Engineering, Technická 2896/2, 616 69 Brno, Czech Republic

Email: xciliushchenko@vutbr.cz

**Abstract.** The rheological properties of alkali-activated systems are significantly affected by the nature of the alkaline activator. Hydroxide-activated systems' workability is typically lower than that of alkali-activated systems but can be improved by lignosulfonate plasticizer. However, the lignosulfonate plasticizer's effectivity depends on the dosage of lignosulfonate, the nature of hydroxide and pH of their solutions. Therefore, in this study, the effectiveness of lignosulfonate plasticizer with respect to alkali ion type ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ) in alkali hydroxide-activated systems based on ground granulated blast furnace slag was evaluated. The concentration of the alkaline activator ( $\text{NaOH}$ ,  $\text{KOH}$  and  $\text{LiOH}$ ) was the same in all cases of 4M. The superplasticizer dosage was 0%, 0.5% and 1.0% of dry matter of lignosulfonate plasticizer to the slag weight. Rheological properties were determined using a rotational rheometer equipped with vane in-cup geometry working in oscillation amplitude sweep mode, from which critical strain and corresponding viscoelastic variables were obtained.

## 1. Introduction

Over time, humankind has become more trying to protect the planet against global warming and is looking for innovative ways to reduce the negative impact of the rapidly industrializing world. Ordinary Portland cement (OPC) with regard to the scale of its production around the world (annual production is around 3Gt) is considered as the dominant construction binder. One of the crucial problems with the use of OPC is the relatively high  $\text{CO}_2$  footprint related to the production of its main component - Portland clinker. Approximately one tonne of  $\text{CO}_2$  is formed per tonne of produce Portland clinker. Given the current position in relation to the ecological and economic situation, alternative solutions are being sought to replace (completely or partially) the high-emission binder. Aluminosiliceous by-products are gaining attention as the viable alternative to OPC. The reaction processes, which are taking part during the setting and hardening of the alkali-activated systems (AAS), are quite well-described and understood [1–4]. Meanwhile, there are only a few publications that clarify the rheological aspect of AAS.

An appropriate design of AAS could be leading the attainment of earlier compressive strength, better chemical resistance, lower permeability over the OPC. Although it cannot be expected that AAS will replace OPC on wide scale, these advantages can be used in some applications [1]. Nevertheless, the corresponding rheological behaviour of AAS is indispensable for its utilization. The rheological models used to interpret the behaviour of cement-based systems such as the Bingham model, modified



Bingham model as well as Hershel-Bulkley are also applied to characterize AAS [5]. Puertas et al. [6] found out that the nature and the dosage of the alkaline activator has a significant influence on the rheological behaviour of AAS. Behaviour of AAS activated by NaOH followed Bingham model, while AAS activated with sodium silicate rather fits Herschel-Bulkley model [6].

The rheological behaviour of cement-based binders are well controlled by using organic admixtures like superplasticizers, which greatly improve their workability by reducing yield stress and plastic viscosity. The mechanism of the efficiency of superplasticizers in cement-based systems is well known, where due to the adsorption on the cement particles, the electrostatic or steric forces arise, resulting in to the repulsive effect of these particles. However, not all superplasticizers are in AAS as effective as in cement-based binders [7]. Palacios et.al. [8] found that polycarboxylate or polyacrylated-based superplasticizers are non-stable in highly alkaline environment ( $\text{pH} > 13$ ). Lukkonen et al. [9] reported that among the tested superplasticizers, lignosulfonates showed the best efficiency due to their steric repulsion effect, but it was emphasized that type and concentration of the activator strongly affect the plasticizer suitability. Significant efficiency of lignosulfonate plasticizer in NaOH-activated slag in contrast to analogous AAS pastes with  $\text{Na}_2\text{CO}_3$ , and sodium silicate was proven in our previous study [10].

Consequently, this paper deals with the efficiency of different dosages of lignosulfonate (0, 0.5, and 1.0%) in AAS with various alkali hydroxides (NaOH, KOH, LiOH) and its comparison to water- and cement-based pastes. In contrast to commonly used rotational tests, non-traditional approach based on oscillatory rheology in terms of the strain sweep tests was used in this study. Such test enables the determination of viscoelastic parameters of the arising paste's structure including stress needed to its destruction.

## 2. Experimental Procedure

### 2.1. Raw materials

**2.1.1. Blast furnace slag (BFS).** In this study, the slag was obtained from Kotouč Štramberk, s.r.o. (Blaine specific surface area is  $400 \text{ m}^2 \cdot \text{kg}^{-1}$ ) was used as an aluminosilicate precursor. Its density was determined by pycnometer method and makes  $2.88 \text{ g} \cdot \text{cm}^{-3}$ . The phase composition was determined by using X-ray diffraction analysis (XRD, on an Empyrea X-ray diffractometer from Panalytical with Bragg-Brentano goniometer; Cu anode, with parameters 40 kV and 30 mA), Rietveld method, where the amorphous part was about 84% whilst the rest was in crystalline forms (akermanite – 9.5%, calcite – 2.3%, merwinite – 2.3% and quartz – 0.5%).

**2.1.2. Ordinary Portland cement (OPC).** Then, ordinary Portland cement (OPC) CEM I 42.5 R from Mokrý-Českomoravský cement, a.s. Heidelberg Cement, Mokrý-Horákov, Czech Republic with the specific surface area  $377 \text{ m}^2 \cdot \text{kg}^{-1}$ . The chemical compositions of BFS and OPC (XRF, using Olympus Delta professional) are presented in table 1.

**Table 1.** Chemical composition of BFS and OPC.

Blast Furnace Slag											
CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SrO	ZrO <sub>2</sub>	BaO
37.35	39.80	8.64	8.15	1.37	0.30	1.19	0.89	0.74	0.06	0.02	0.12
Ordinary Portland Cement CEM I 42.5 R											
CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>				
65.0	19.0	1.0	4.0	3.0	0.77	0.17	3.0				

*2.1.3. Alkaline activators.* The BFS was activated by three different alkaline activators, more precisely sodium hydroxide, potassium hydroxide (from Vodní sklo a.s.), lithium hydroxide (from Schem a.s.), and also mixed only with water. The suspension of OPC with water was used as well. The stock activating solutions were prepared somewhat more concentrated ( $4.23 \text{ mol}\cdot\text{dm}^{-3}$ ) than target concentrations of  $4.00 \text{ mol}\cdot\text{dm}^{-3}$  due to the dilution by addition of plasticizer and water to simultaneously reach slag volume fraction in the final suspension of 0.50. The same volume fraction was set for the paste of slag in water as well as for OPC paste to ensure the comparability of all mixtures.

Suspensions were modified by the commercial plasticizer, namely lignosulfonate (LS). Three different doses of LS were tested, more specifically, 0%, 0.5% and 1.0% of the dry matter to the weight of slag.

*2.1.4. Rheological experiment.* The measurement was performed on hybride rheometer Discovery HR-2 from TA-Instruments, using the vane-cup geometry. The experiment itself was started from the preparation of the suspension using the polypropylene beaker and hand mixer. The whole duration of the mixing process was 3.0 minutes, of which during the first minute the mixture was mixing at the slow rate, for the following 30 s the speed was increased to the maximum, while the following 30 s the mixture was stirred manually using spatula and the stick residuals were homogenized with the suspension. In the last minute, the suspension was mixed using the maximum rate.

The rheological parameters were studied with the stainless-steel vane (diameter 20.3 mm and length 19.5 mm) in cup (diameter 30.4 mm) geometry. The rheological experiment started 4.5 minutes after the mixing with the 30 s pre-shear at the shear rate of  $100 \text{ s}^{-1}$ , followed by 30 s rest before the amplitude sweep measurement. The angular frequency was set to 10 rad/s, while the strain was logarithmically increased from the  $5\cdot 10^{-4}\%$  to 500%.

The domain of linear viscoelastic (LVE) behaviour of the samples was obtained from the graphical dependency of storage modulus  $G'$  on oscillation strain. According to the literature, the critical strain of LVE is usually evaluated as the deviation of about 5–10% from the linear part of the curve [11]. In this study, the smaller deviation of 2% was selected, especially due to the evolution of viscoelastic parameters in time. The stress corresponding to the critical strain (yield point) as well as the stress corresponding to the destruction of the pastes' structure shown as a sharp drop of viscoelastic moduli (flow point) was evaluated.

### 3. Results and discussion

One representative rheological response of each paste is given in figure 1 as the evolution of complex modulus plotted depending on the oscillation stress. In most cases, there is an increase in the complex modulus for low stresses corresponding to LVE region due to the simultaneous structural build-up. At certain stress, the complex modulus starts to decrease. Further increase in the oscillation stress results in a drop of complex modulus by 2–3 orders of magnitude. In this region, the paste starts to flow, which is indicated by higher loss modulus than storage modulus (not shown here). As was already mentioned, the stress needed to start breaking of the evolved structure was termed as the yield point (green on the graph), while the latter as the flow point (purple on the graph). Their clearer comparison depending on the activator type and LS dose is given in figure 2.

Firstly, the influence of the type of alkaline activator on the rheological behaviour of BFS is commented. The complex modulus provides the information about rigidity of the paste, whereas the yield and flow points characterize the solidity.

Generally, in some literature [12, 13] it is shown that suspensions activated by NaOH usually exhibit higher yield stress than the suspensions containing KOH. The reason why it can be performed is that  $\text{K}^+$  has lower charge density, which causes lower ion-dipole forces. Zeta potential of slags activated by KOH is higher than NaOH-based suspensions due to the lower absorption of  $\text{Na}^+$  on the BFS grains surface. Higher adsorption of  $\text{K}^+$  on the particles leads to the increasing of repulsive force of double-layer between these particles, which contributes to the decreasing of the yield point. In contrast with  $\text{Na}^+$

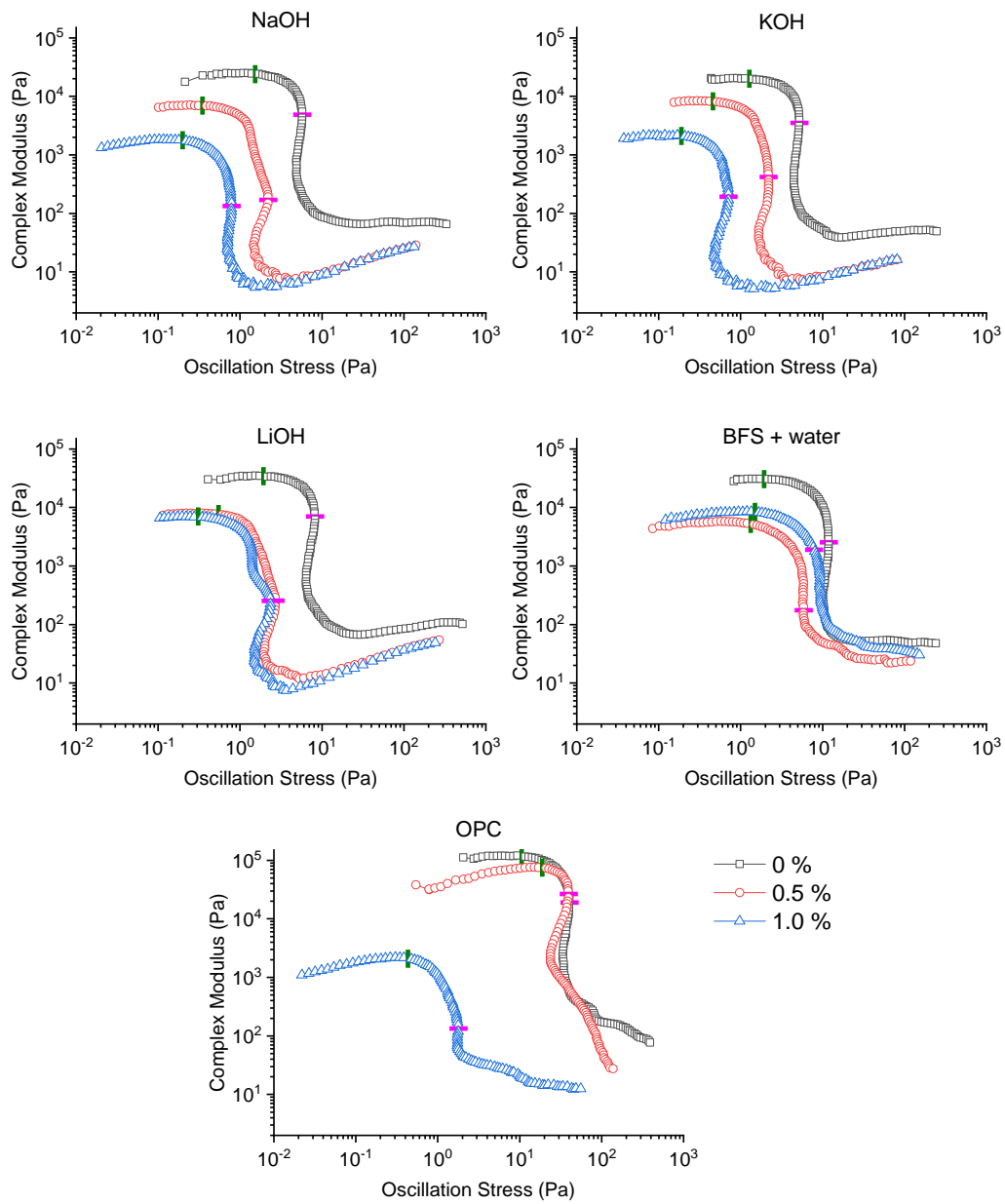
cations have bigger solvation shell. Related to the better adsorption ability of KOH on the particles, negatively charged lignosulfonates groups can have higher affinity to bond with them [13–15].

The yield point was evaluated from the LVE area on graphical dependence of complex modulus on oscillation stress. In the case of NaOH and KOH-based activated systems, it can be observed that with the increasing dosage of LS, the oscillation stress gradually decreases. The course of the suspensions responding to the LS adding is similar, and it can be assumed that even 1% of LS is still effective. For the clear arrangement, the yield point was plotted to the graph with the LS dosage. From figure 2, it can be seen that the addition of LS (0.5 and 1%) in BFS activated by KOH leads to the lower values of yield point (about 1.20 and 1.05 times respectively), with regard to the fact that reference values (0% of LS) of KOH-activated systems were higher than NaOH-activated (1.08 times). On the other hand, these differences can be accepted with regard to the standard deviation. In any case, with the adding LS, the smooth decrease of yield point can be observed.

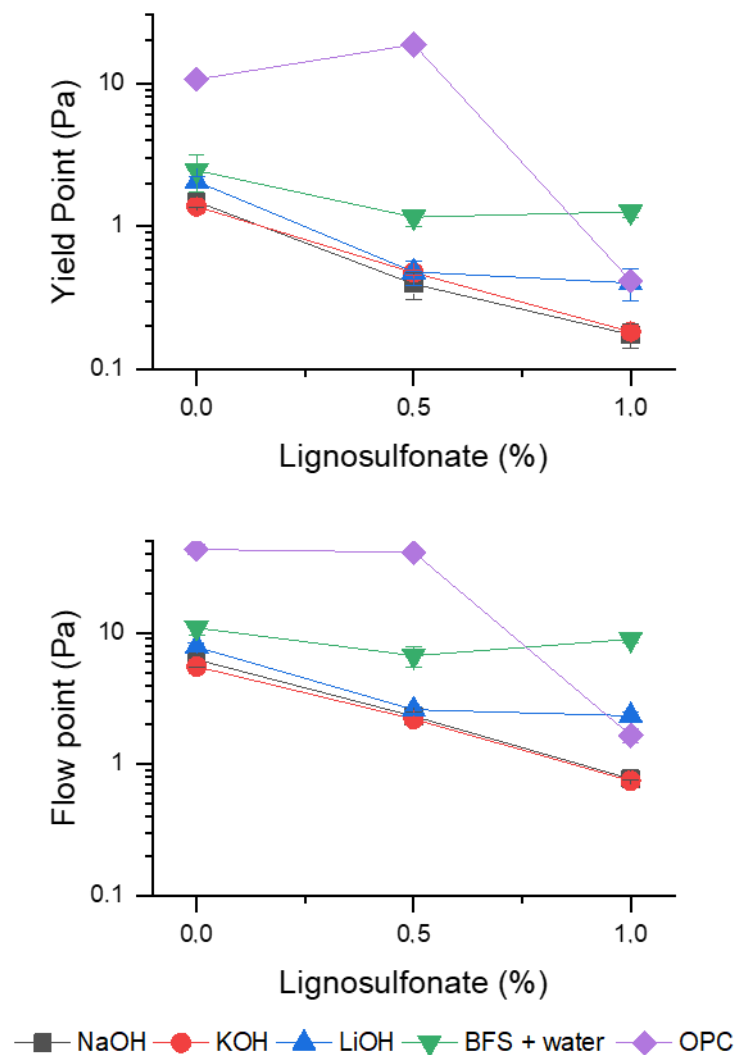
Different rheological behaviour with respect to the LS dose can be observed in the case of LiOH and BFS-water-based systems. From figure 2, it can be observed that the 0.5 and 1.0% of LS contribute to the similar yield point decreasing. This kind of behaviour can indicate that the limit value of the LS, which is effective in LiOH and water-based systems, is between 0 and 0.5%.

The behaviour of BFS was compared with the rheological response of the traditional binder on LS adding. The rheological behaviour of OPC is noticeably different from the BFS-activated materials. In OPC pastes, 0.5% of LS had only limited effect on yield point and flow point, while they both were greatly decreased by 1% of LS and the same stands for complex modulus. It should be noted that the results of the paste with 0.50% of LS is affected by the rate of its structural build-up prior to reaching the yield point as the evolution complex modulus starts from much lower values compared to the reference paste without LS. Therefore, it can be expected that if the structure is destroyed (e.g. by mixing), the flowability of the paste with 0.5% LS will be much better than that of the reference paste. Hence the effectiveness of LS at intermediate dose is time and shear dependent.

The flow point in all cases was evaluated from the loss factor, where the destruction of substantial amount of bonds is performed, and the suspension loses its properties. The rheological behaviour of tradition binder is remarkable different from the measured alternative binders. In OPC, the flow point is 42 times decreased by 1.0% LS, whereas its use in AAS offers about six times reduction at most (for NaOH).



**Figure 1.** Complex modulus on oscillation stress of BFS activated by various activators, different dosages of LS, with the increasing strain from  $5 \cdot 10^{-4}$  to 500% (yield point marked by olive green colour, flow point by pink colour).



**Figure 2.** Yield/flow point on the dosage of LS in various pastes.

#### 4. Conclusion

Within this paper, the effectiveness of the plasticizing effect of lignosulfonate on the type of alkali cation in alkali-activated systems was investigated from the rheological point of view. The gained results have shown that the response of alkali-activated systems depends not only on the kind of alkaline activator but on the dosage of admixture (LS) as well. Sodium and potassium hydroxide demonstrated the similar behaviour in terms of gradual weakening of the paste with increasing LS. In contrast, when the lithium hydroxide or water was used, a higher dosage than 0.5% of LS was not accompanied with improvement of workability, so the limit dosage of LS, which can be still effective, is between 0 and 0.5%. Plasticizing efficiency of LS in OPC paste was by order of magnitude higher than that in AAS, as illustrated by flow point reduction by 42 and 6 times, respectively.

These results indicate that the nature of alkali cation and paste composition in general affect the plasticizer efficiency. It can be expected that it is related to the different surface chemistry of slag and plasticizer performance in various environments, but further study is needed to shed more light on this issue.

**Acknowledgement:**

This outcome was obtained thanks to the contribution of the following projects: GA20-26896S “Towards the organic admixtures tailoring for alkali-activated slag-based systems” founded by the Czech science foundation, and the project FCH/FSI-J-21-7387.

**References**

- [1] Provis J L and van Deventer S J J 2014 Alkali Activated Materials: State-of-the-Art Report RILEM TC 224-AAM (Brooklyn Publishing)
- [2] Nedeljković M, Zhenming L and Guang Y 2020 Setting, Strength, and Autogenous Shrinkage of Alkali-Activated Fly Ash and Slag Pastes: Effect of Slag Content *Materials* **11** pp 1–20
- [3] Hewlett P C 2004 *Lea's Chemistry of Cement and Concrete* (Butterworth-Heinemann: Elsevier Science & Technology Books)
- [4] Fernández-Jiménez A et al 2020 Structure of Calcium Silicate Hydrates Formed in Alkaline-Activated Slag: Influence of the Type of Alkaline Activator *Journal of the American Ceramic Society* **86** pp 1389–1394
- [5] Li L, Lu J-X, Zhang B and Poon C-S 2020 Rheology behavior of one-part alkali activated slag/glass powder (AASG) pastes *Construction and Building Materials* **258** pp 1–13
- [6] Puertas F, Varga C and Alonso M M 2014 Rheology of alkali-activated slag pastes. Effect of the nature and concentration of the activating solution *Cement and Concrete Composites* **53** pp 279–288
- [7] Lu C, Zhang Z, Shi C, Li N, Jiao D and Yuan Q 2021 Rheology of alkali-activated materials: A review. *Cement and Concrete Composites* **121** pp 40–48
- [8] Palacios M, Banfill P F G and Puertas F 2008. Rheology and setting of alkali-activated slag pastes and mortars: Effect of organic admixture *ACI Materials Journal* **105(2)** pp 140–148
- [9] Luukkonen T, Abdollahnejad Z, Ohenoja K, Kinnunen P and Illikainen M 2019 Suitability of commercial superplasticizers for one-part alkali-activated blast-furnace slag mortar *Journal of Sustainable Cement-Based Materials* **8** pp 244–257
- [10] Bilek V Jr, Iliushchenko V, Hruby P and Kalina L Effectiveness of common water-reducing admixtures in alkali-activated slag pastes with different types of activator (article submitted to same volume of IOP Conf. Ser.: Mater. Sci. Eng.)
- [11] Mezger T G 2014 *Applied Rheology: With Joe Flow on Rheology Road* (Anton Paar GmbH)
- [12] Vance K, Dakhane A, Sant G and Neithalath 2014 Observations on the rheological response of alkali activated fly ash suspensions: the role of activator type and concentration *Rheologica Acta* **53** pp 843–855
- [13] Kashani A, Provis J L, Qiao G G and van Deventer J S J 2014 The interrelationship between surface chemistry and rheology in alkali activated slag paste *Construction and Building Materials* **65** pp 583–591
- [14] Poulesquen A, Frizon F and Lambertin D 2011 Rheological behavior of alkali-activated metakaolin during geopolymerization *Journal of Non-Crystalline Solids* **357** pp 3565–3571
- [15] Ngele E and Schneider U 1989 The zeta-potential of blast furnace slag and fly ash, *Cement Concr. Res.* **19** pp 811–820