Effectiveness of common water-reducing admixtures in alkali-activated slag pastes with different types of activator

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Abstract. Rheology of alkali-activated slag (AAS) is a very complex issue, where the activator nature as well as its dose play an important role. Moreover, the use of water-reducing admixtures in these systems is an issue, as they often do not work properly. This could be attributed to the high pH as well as to the surface chemistry of AAS. Therefore, lignosulfonate-, polynaphthalene- and polycarboxylate-based superplasticizers were used to modify AAS pastes with sodium waterglass, hydroxide and carbonate activator. These pastes were tested using a rotational rheometer in an oscillatory shear mode of increasing shear strain to observe the evolution of viscoelastic moduli and to determine the oscillatory stress corresponding to the linear viscoelastic region limit ("yield point") and to the crossover point, where the storage modulus equals the loss modulus ("flow point"). In most cases, the used plasticizers did not improve the rheological properties; the only exception was the lignosulfonate one in sodium hydroxide-activated slag.

1. Introduction

Rheological parameters are the key characteristics of any binder system and strongly affect its further performance. They have to allow appropriate mixing, transport, casting, and compacting of the mixture. Simultaneously, the water content should be as low as possible to achieve higher mechanical properties, lower porosity and higher durability. For this purpose, plenty of water-reducing admixtures or superplasticizers (SPs) have been developed and their increasingly sophisticated development continues in an unprecedented way. Thanks to them, high-performance or even ultra-high-performance concretes can be designed and used.

However, the above-mentioned stands for the Portland cement-based concretes, while the use of conventional SPs and other organic admixtures in alkali-activated materials often fails. This is most often attributed to their decreased stability due to very high pH [1–3], but the surface chemistry and presence of dissolved species are also very important aspects [4, 5].

Usually, the rheological properties of alkali-activated slag (AAS) pastes are determined using rotational tests across a given range of shear rates and fitting the obtained data by rheological models for yield stress fluids [3, 6–8]. However, rheological investigations can also be carried out by oscillatory tests that, unlike rotational tests, enable the testing of the material in a non-destructed state close to the rest via sufficiently low amplitudes facilitating deformations within the so-called viscoelastic region (LVR).

Based on the above, comprehensive research on the relationships between surface chemistry, the composition of activating solution and the behaviour of organic additives in alkali-activated

materials is the main topic of the implemented project GA20-26896S. The presented paper is only a small output of the corresponding research and combines its aims with oscillatory measurements that are only rarely used in AAS.

2. Experimental part

2.1. Materials and composition of the pastes

Granulated blast furnace slag ground to Blaine fineness of 400 m^2/kg was used in this study. The slag consisted of about 70% of an amorphous phase, 20% of akermanite, and lower amounts of calcite, quartz, and merwinite. Density of the slag was determined to be 2.88 g/cm^3 using the pycnometer method. The slag was activated by three different activating solutions, namely sodium hydroxide (SH), sodium waterglass (SWG) with silicate modulus adjusted to 1.5, and sodium carbonate (SC). The concentration of Na^+ in all activating solutions was 4.0 mol/dm^3. Their dose was adjusted to keep the volume fraction of slag in the resulting suspension constant at the value of 0.50 to ensure their comparativeness from the rheological point of view. In this case, the described activator dosing corresponds to 4.3% Na_2O with respect to the slag weight regardless of the activator type and water to slag ratio to 0.36, 0.33, and 0.34 for SWG-activated slag (SWGAS), SH-activated slag (SHAS) and SC-activated slag (SCAS), respectively.

These pastes were modified by three different types of commercially available SPs as follows: lignosulfonate-based (LS), polynaphthalene sulfonate-based (PNS), and polycarboxylate ether-based (PCE) one. Their doses were 0.3% of their dry matter to the slag weight regardless of the SP type. They were added to the activating solution and homogenized just prior to the paste's preparation. Volume of the SP was subtracted from the volume of activating solution to keep the total volume of liquid components constant and thus keep the slag volume fraction in the resulting paste of 0.50. The dilution of the activating solution with SP was taken into account for the design of the pastes' composition.

2.2. Rheological experiments

Slag was homogenized with liquid components in a beaker using a hand mixer. Total mixing time took three minutes and comprised of the following stages: During the first 60 s, a low mixing rate was set, after which the highest possible mixing rate was applied for 30 s. During the next 30 s, the paste was homogenized by a spatula and in the last 60 s again at the highest rate. After that, the paste was transferred into the rheometer (DHR-2, TA Instruments).

Crosshatched parallel plate geometry was used for the rheological investigations. The measuring gap of 1 mm was used. Each measurement started five minutes from the first contact of slag with a mixture of liquids. The first step was preshear at the shear rate of 5 s^{-1} for 10 s and after 10 s of rest, the amplitude sweep measurement at the frequency of 10 rad/s started. The strain was logarithmically increased from 10^{-4}% to 500%, 20 points per decade were measured, 2 cycles for each point. At least four measurements of each paste composition were carried out.

2.3. Evaluation of rheological experiments

Linear viscoelasticity region (LVR) was obtained from the storage modulus G′ plotted against the oscillation stress as is shown in Figure 1. Usually, LVR is determined via the decrease of G′ by 5 or 10% [9]. As the rheological parameters evolve in time, G′ is not constant within the range of LVR, but increases during the measurement, which complicates the determination of LVR. Moreover, LVR of these suspensions is very short and therefore close to the limits of the instrument, which can lead to scattering of the results within the LVR. Therefore, several points at the top of the flat region of the observed "peak" were averaged and the last point higher than 95% of the averaged value was considered as the LVR limit. The corresponding oscillation stress was termed as the "yield point" in accordance with [9]. The values of other parameters, namely loss modulus G″, complex modulus G*, loss factor (tanδ) as well as strain at the yield point, were obtained.

Besides the yield point, also the oscillation stress corresponding to the modulus crossover, where $G' = G''$ was determined and in accordance with [9] termed as the "flow point", i.e. the stress after which the rheological behaviour changes from rather viscoelastic solid-like to rather viscoelastic liquid-like.
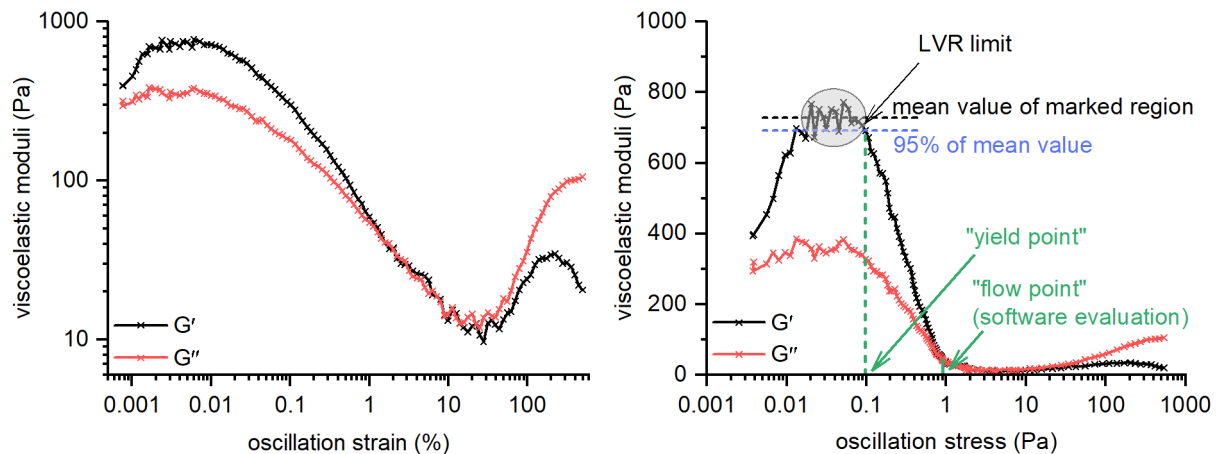

Figure 1. Typical outcome of the amplitude sweep measurement, where viscoelastic moduli are plotted against oscillation strain (left) and the procedure to evaluate important points on the same measurement with moduli plotted against oscillation stress (right).

3. Results and discussion

The average results for all tested combinations of activator and superplasticizer obtained using the procedure described in Section 2.3 are given in Figure 2 and Figure 3 for the yield point and flow point, respectively. The fact that $G' > G''$ at low or intermediate strains indicates that AAS pastes have cross-linked structure originating from attractive forces acting between the pastes' components.

First, it is worth comparing the rheological properties of AAS pastes with respect to the activator type and without the added plasticizer. Figure 2 shows that the rheology of SWGAS paste was noticeably different to that of SH and SC pastes. Its yield point was about 1.5 orders of magnitude lower and the viscoelastic moduli even about two times lower compared to the SHAS and SCAS pastes. Loss factor (tanδ) of SWG paste was determined to be 0.5, which is somewhat higher compared to the SH and SC pastes having a loss factor around 0.35 in both cases. The values of tanδ below 1 indicate that all pastes behave rather as viscoelastic solids with quite narrow LVR, which was determined to be 0.005–0.010%.

If larger amplitudes are applied and therefore the oscillation stress increases, the bonds between particles in the paste start to break, which is manifested by a decrease in viscoelastic moduli and an increase in loss factor, which means that the storage modulus decreases faster than the loss modulus. One example of this situation is given in Figure 1. After reaching a certain strain (or stress, i.e. flow point), for which $G' = G''$, the paste is just in between the viscoelastic solid and viscoelastic liquid behaviour. The corresponding rheological parameters are given in Figure 3. Similarly to the yield point, the flow point is about two orders of magnitude lower for SWG compared to that of SHAS and SCAS, while G' and G'' by "only" one order of magnitude. Unlike the critical strains at the yield point, which were slightly higher for SWG and SC than for SH, the flow point of SWGAS paste was reached at much lower strains (1.5 orders of magnitude) compared to SHAS and SCAS pastes.
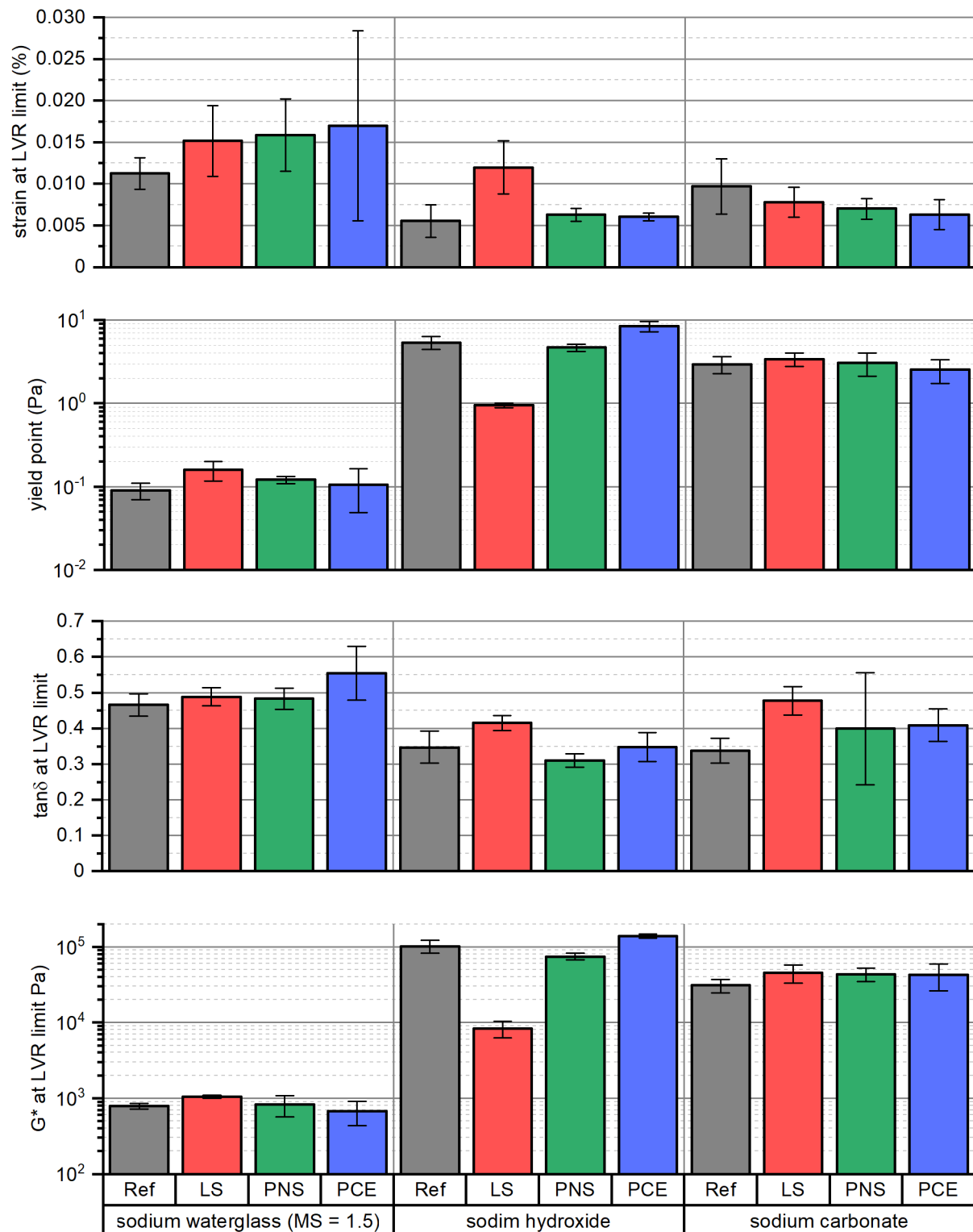
Figure 2. Viscoelastic parameters of alkali-activated slag pastes corresponding to the modulus crossover depending on the nature of the activator and superplasticizer type.
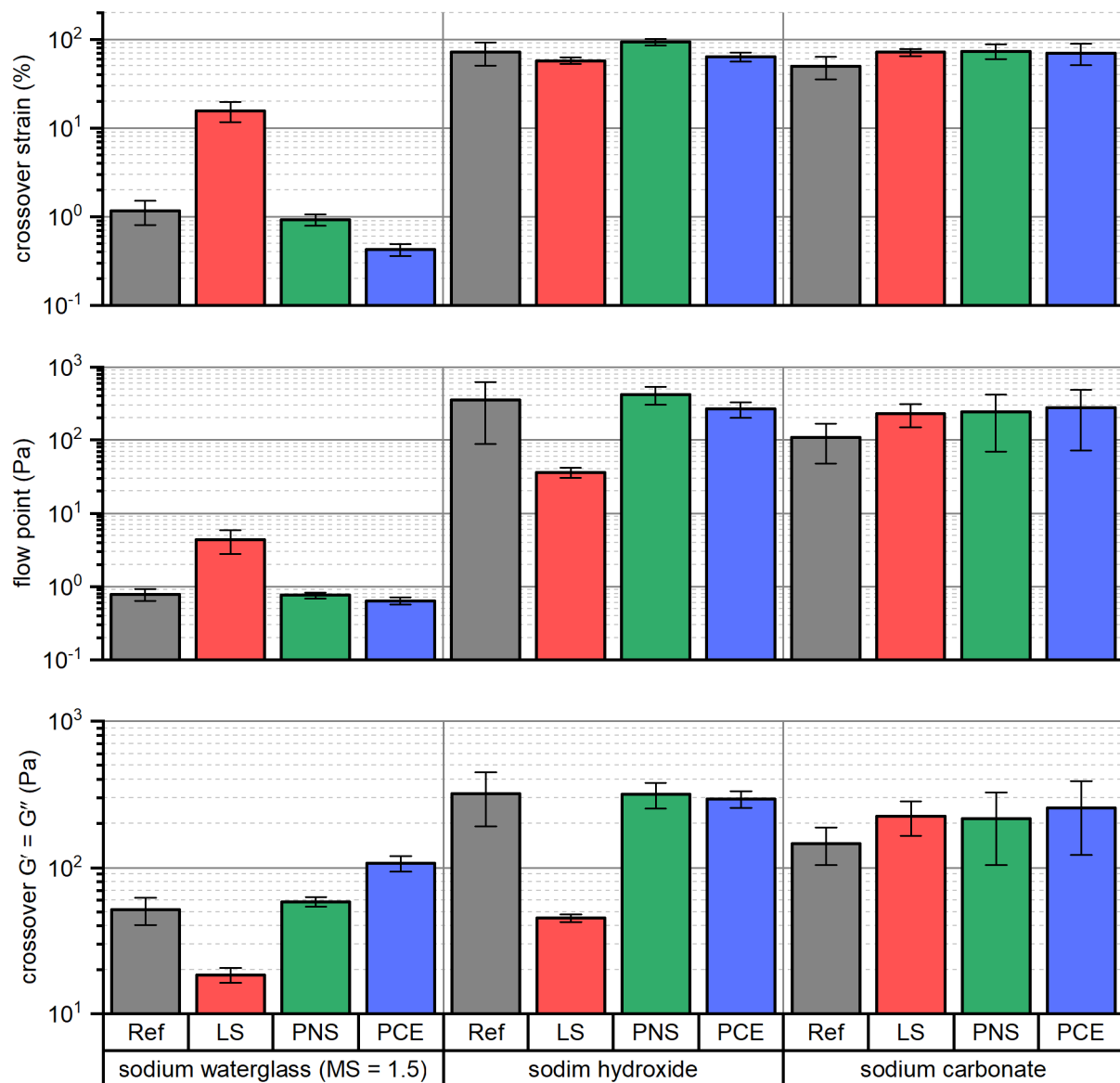
Figure 3. Viscoelastic parameters of alkali-activated slag pastes corresponding to the modulus crossover depending on the nature of the activator and superplasticizer type.

Lower yield point, flow point and viscoelastic moduli, as well as higher tanδ of SWG pastes compared to those activated by SH and SC are related to weaker structure and higher fluidity of SWG pastes. This correlates with the findings in the literature [5, 10, 11]. Beneficial effect of silicates is attributed to their adsorption onto the slag particles, which leads to lower values of zeta potential and increase in the magnitude of repulsive electrical double layer (EDL) forces [5]. The rheological behaviour of SCAS is between SWGAS and SHAS, but closer to SHAS, which suggests that carbonate anions are not able to increase repulsive EDL forces or increase the range of their action enough to noticeably reduce the mechanical properties of the SCAS or in other words increase its fluidity.

The nature of anionic group of activators, the ionic strength of the activating solution and related surface chemistry seems the key aspect affecting the effectiveness of superplasticizers in AAS. Figure 2 and Figure 3 show that PNS and PCE superplasticizers did not significantly affect the rheological behaviour of AAS pastes regardless of the activator nature. In most cases, the obtained values are equal to those of the reference paste without activator or even slightly higher, which indicates that these SPs

do not work in AAS. The increase in rheological parameters in the presence of SPs could be related to their undesired interactions with AAS such as bridging forces [4].

The only SP, which showed the great effect on rheology in the present study, was LS in SHAS. In this case, the yield point was reduced more than five times and the corresponding viscoelastic moduli even by an order of magnitude. LS also slightly increased the loss factor, which again points to its effectiveness in SHAS, and a greatly beneficial effect can be also seen in terms of flow point and crossover modulus. The beneficial effect of LS in SHAS corresponds to the findings in the literature [11]. The reason LS did not reduce the yield point, the corresponding moduli and tanδ in SWG and SC pastes is likely that the negatively charged silicate or carbonate anions adsorbed on the surface of the slag grains hinder the LS adsorption. It is interesting that, unlike in SCAS, LS greatly decreased the crossover modulus of SWGAS, while increased crossover strain and flow point. These results suggest that despite the LS is not adsorbed onto the slag grains enough, the presence of its molecules in solution makes the paste's structure less rigid but more deformable prior to flow and therefore interacts with the dissolved species in solution. Nevertheless, this will be a subject of further study.

4. Conclusions

In this paper, the effect of common SPs on AAS rheology depending on the activator type was investigated by means of oscillatory amplitude sweep measurements that are unconventional for these materials so far. The results confirmed that AAS rheology is driven by the nature of both the activator and SP and that the workability improvement of AAS by SPs is a big issue. PNS- and PCE-based SPs showed incompatibility with slag activated by sodium hydroxide, waterglass as well as carbonate. For the last two activators, LS was inefficient too, while it showed considerable potential if sodium hydroxide is used as an activator. This is likely related mainly to the surface chemistry of AAS.

Besides, the paper briefly introduced a novel approach of expressing the activator dose based on the molar concentration of alkali in the activating solution and slag volume fraction in the whole suspension. Further research will be devoted to a wider establishment of this approach, to use oscillatory measurements for the characterisation of alkali-activated materials as well as to their interactions with organic substances.

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