Suitability of commercial superplasticizers for one-part alkali-activated blast-furnace slag mortar

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Alkali-activated materials are a low-CO$_2$ alternative for Portland cement in construction. However, one major issue in their use is the poor or varying functionality of the currently available commercial superplasticizers. Especially for one-part (“just add water”) alkali-activated materials, the number of studies is limited. In this study, one-part alkali-activated mortar was prepared from blast furnace slag by using solid sodium hydroxide as an activator and microsilica as an additional silica source. Comparison of commonly used superplasticizer types revealed that lignosulfonate, melamine, and naphthalene-based superplasticizers are more efficient than the currently most used polyacrylate and polycarboxylate-superplasticizers. Lignosulfonate-based superplasticizer was overall best-performing: it improved significantly the workability (+41% spread, -51% yield stress, -27% viscosity), setting time (+70%), and compressive strength (+19%) at a 0.5 wt% dose. When the amount of water and superplasticizer were optimized, compressive strength of mortar could be doubled (from 19 to 38 MPa at 28 d).

Keywords: admixture; geopolymer; lignosulfonate; rheology; superplasticizer; workability

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Introduction

Alkali-activated materials (AAMs) are becoming universally accepted alternative low-CO$_2$ binders for which several industrial by-products can be used as precursors [1]. Although they are not likely to replace ordinary Portland cement (OPC) completely, they can become important environmentally friendly substitutes in locations where suitable raw materials are readily available [2]. However, one major issue in their use is the...
frequently reported poor or contradictory functionality of commercially available superplasticizers [3]. Superplasticizers have a significant role in the modern construction industry as they allow improving concrete workability, strength, and durability, shrinkage, and cement consumption [4]. For example, they are a prerequisite for self-compacting concrete formulations (i.e., casting without external vibration) and construction of extremely high structures. In addition, the use of superplasticizers is a means of increasing concrete sustainability [5]. Therefore, it is of paramount importance to develop superplasticizers for AAMs, as well.

The currently used third-generation superplasticizers consist of polyacrylate, polycarboxylate, or polyethylene-based copolymers in a comb-like structure [6]. The earlier first- and second-generation superplasticizers contained modified lignosulfonates (LSs), sulfonated melamine-formaldehyde, or naphthalene-formaldehyde condensates, and they are still in use to some extent [7]. Superplasticizers function by adsorption on the cement particles, which causes blocking of reactive sites and electrostatic and/or steric repulsion (the exact mechanism depends on the superplasticizer type) [6]. As a result, the dispersion of cement particles increases [8] and the surface tension of the surrounding water decreases [9], which affect the rate of hydration (the exact effect depends again on the superplasticizer type) and fluidity [10]. The specifications of superplasticizers (or high-range water-reducing admixtures) in terms of resulting concrete properties (e.g., water demand, setting time, or compressive and flexural strength) are listed in the standard ASTM C494/C494M [11].

The current commercially available superplasticizers have been developed for OPC-based concrete, and, thus, they do not work similarly with AAMs [12]. Differences of AAMs in comparison to OPC include typically higher pH, which can cause the decomposition of superplasticizers [13], but also different reaction
mechanisms and products [14]. Recently, there has been a pronounced interest in one-part (“just add water”) AAMs (in which both the aluminosilicate precursor and activator are in solid form) [15]. Although several studies have aimed to use commercial superplasticizers in both low [16-20] and high calcium [21-24] conventional two-part AAMs, very few studies exist for one-part systems. For instance, Ye et al. [25] used an LS-based superplasticizer in a one-part red mud-based geopolymer paste to reduce the water/solid ratio from 0.55 to 0.45. Also, Kovtun et al. [26] used LS superplasticizer to improve workability of one-part alkali-activated blast-furnace slag. Another example is the study by Yang et al. [27], in which a polycarboxylate-based superplasticizer was used in one-part alkali-activated blast-furnace slag. However, no systematic comparison of commercially used superplasticizer types exists for one-part AAMs.

Therefore, the purpose of the present paper is to study the suitability of different superplasticizers for one-part alkali-activated blast-furnace slag (BFS) mortar. The mix design is based on the previous work by authors [28] and it was selected due to relatively long setting time, which allows easier study of workability and rheological properties. One problem with commercial superplasticizers is the lack of the technical data (molecular weight, chemical structure, additives, etc.) which makes interpretation of results more difficult. However, superplasticizers were selected to include all three generations (i.e., LS, naphthalene, melamine, polycarboxylate, and polyacrylate-based chemicals). First, the superplasticizers were screened using a constant dose and mix design for workability, setting time, compressive strength, viscosity, and yield stress. Then, the most effective superplasticizer was selected for dose and water amount optimization together with further rheology characterization.
Materials and methods

Materials

Ground-granulated BFS was obtained from Finnsementti (Finland), microsilica (tradename Parmix-silika) from Fescon (Finland), and sodium hydroxide powder (≥ 97% purity, Honeywell) from VWR (Finland). GGBFS had a $d_{50}$ value and density of 10.8 μm and 2.93 g/cm$^3$, respectively. Microsilica was supplied as loosely granulated particles (d ≈ 1 mm) with the following specifications: SiO$_2$ > 85%, Cl < 0.10%, Na$_2$O equivalent < 3.0%, and specific surface area 15–35 m$^2$/g. Aggregate was standard sand (Normensand, Germany) according to standard EN 196-1 [29]. Each material was used as received. The main components of GGBFS are (reported as oxides, w/w) CaO 38.51 %, SiO$_2$ 32.33 %, MgO 10.24 %, Al$_2$O$_3$ 9.58 %, SO$_3$ 4.00 %, TiO$_2$ 2.21 %, and Fe$_2$O$_3$ 1.23 %. Microsilica consists mainly of SiO$_2$ (94.25 %). More detailed analyses of these materials are available in [28].

Commercial superplasticizers employed in the study were obtained from Finnish retailers (Semtu and Sakret). Their general structures are presented in Fig. 1 and properties, as reported by the manufacturers, in Table 1. SMF 2, SMF 3, and SNF were solid powders, whereas others were supplied as aqueous solutions. The addition method (see Table 1) was selected based on the superplasticizer instructions. Molecular weight of the best-performing superplasticizer, LS, was 3000 g/mol [30]. For other superplasticizers, molecular weight information was not available.
Preparation of alkali-activated GGBFS mortar

The mix design was based on an earlier study [28]: the binder consisted of GGBFS, microsilica, and sodium hydroxide at 95.6, 2.0, and 2.4 wt%, respectively. The amount of aggregate was 200% of the binder. The water-to-binder ratio was 0.35 in the initial experiments, but it was reduced to 0.30 in the experiments with the most efficient superplasticizer. The binder had the following calculated molar ratios (assuming 100% reactivity of the binder materials): SiO$_2$/Al$_2$O$_3$ = 6.07, Na$_2$O/SiO$_2$ = 0.07, Na$_2$O/Al$_2$O$_3$ = 0.43, CaO/SiO$_2$ = 1.20, H$_2$O/Na$_2$O = 50.21, and H$_2$O/Al$_2$O$_3$ = 21.53.

Mortar was prepared by mixing dry solids for 3 min, tap water (hardness ≈ 0.85 mmol/L) was added, and mixing was continued for an additional 3 min. The mixture was cast in a prismatic mold with dimensions of 40 × 40 × 160 mm and compacted using a jolting table (2 × 60 shocks, 1 shock/s). The mold was placed in a curing chamber (22 °C and 100% relative humidity) for approximately 24 h, demolded, and placed back in the curing chamber until the testing day.
Superplasticizers were either mixed with water or added after water, according to the manufacturer specifications (see Table 1). The amount of superplasticizer was fixed at 0.5 wt% of the binder weight in the initial experiments, as this value is in the low end of the suggested dosing range of all superplasticizers (Table 1).

<table>
<thead>
<tr>
<th>Identifier and active component</th>
<th>Trade name</th>
<th>Solid content [% weight-%]</th>
<th>pH</th>
<th>Effect on setting</th>
<th>Recommended dosing [% of binder]</th>
<th>Addition method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE 1</td>
<td>Dynamon NRG-600</td>
<td>27</td>
<td>6.0</td>
<td>Accelerating</td>
<td>0.3–2.0</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>CAE 2</td>
<td>Dynamon SX-23</td>
<td>17</td>
<td>6.5</td>
<td>Retarding</td>
<td>0.4–2.0</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>CAE 3</td>
<td>Dynamon SX-23</td>
<td>23</td>
<td>6.0</td>
<td>Retarding</td>
<td>0.3–2.0</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>LS</td>
<td>WRDA 90D</td>
<td>30</td>
<td>5.0</td>
<td>Retarding</td>
<td>0.2–1.0</td>
<td>Added after water</td>
</tr>
<tr>
<td>PCE 1</td>
<td>Structuro 200</td>
<td>22</td>
<td>6.0</td>
<td>n.r.</td>
<td>0.3–1.3</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>PCE 2</td>
<td>Sem Flow MC 21 a</td>
<td>22</td>
<td>7.0</td>
<td>Retarding</td>
<td>0.25–2.5</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>PCE 3</td>
<td>Sem Flow ELE 20</td>
<td>26 a</td>
<td>7.0</td>
<td>n.r.</td>
<td>0.4–2.0</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>PCE 4</td>
<td>Sem Flow ELE-S 19 a</td>
<td>49</td>
<td>4</td>
<td>n.r.</td>
<td>0.3–0.9</td>
<td>Mixed with water</td>
</tr>
<tr>
<td>SMF 1</td>
<td>Daracem F</td>
<td>35</td>
<td>9.0</td>
<td>Accelerating</td>
<td>0.5–3.0</td>
<td>Added after water</td>
</tr>
<tr>
<td>SMF 2</td>
<td>Peramin SMF 93.5 10</td>
<td>8.5 b</td>
<td>8.5</td>
<td>No effect</td>
<td>0.2–2.0</td>
<td>Mixed with dry binder</td>
</tr>
<tr>
<td>SMF 3</td>
<td>Melment F 10 ≥ 96.0</td>
<td>9.0–11.4 c</td>
<td>9.0–11.4</td>
<td>n.r.</td>
<td>0.2–2.0</td>
<td>Mixed with dry binder</td>
</tr>
<tr>
<td>SNF</td>
<td>Mighty 100</td>
<td>92</td>
<td>7</td>
<td>n.r.</td>
<td>n.r.</td>
<td>Mixed with dry binder</td>
</tr>
</tbody>
</table>

SMF = sulfonated melamine-formaldehyde; SNF = sulfonated naphthalene-formaldehyde; LS = lignosulfonate; PCE = polycarboxylate ester; CAE = copolymer of carboxylic acrylic acid with acrylic ester; n.r. = not reported; a = estimated by evaporating water at 100 °C; b = aqueous 5 % solution; c = aqueous 20 % solution

The experiments for optimizing the superplasticizer and water amount employed a statistical design of the experiments: a face-centered central composite design
prepared with MODDE 11 Pro software (Umetrics). The experiments involved three levels for factors: 30.0 (-1), 32.5 (0), and 35.0 wt% (-1) for water and 0.20 (-1), 1.10 (0), and 2.00 wt% (-1) for the superplasticizer (% of binder). Multiple linear regression was used to fit a quadratic model, and the significance of the model was tested with analysis of variance using a 95 % confidence level. Details of the model fitting are presented in the supplementary material.

**Fresh and hardened properties and chemical characterization**

The initial and final setting times were determined with a Vicat apparatus (Vicatronic Matest) according to the standard EN 196-3 [31]. Workability was evaluated using the flow table test according to standard SFS-EN 12350-5 [32].

The yield stress and viscosity of the pastes were studied with a Discovery HR-1 rheometer (TA Instruments) with a set-up which consisted of a four bladed vane (box shaped blades without openings with a height of 42 mm and diameter of 28 mm) and a serrated, grooved cup (with an inner diameter of 30.35 mm). A sample of 100 g of each paste were loaded into the cup after it was prepared by mixing with a high shear mixer (IKA T25 Ultra Turrax) for 3 min at 500 l/min. The experimental protocol was started after 15 min from the start of the mixing. The experimental protocol was performed at constant 20 °C and consisted of a 1 min pre-shearing period (200 l/s), 1 min equilibrium period, and 2 min shear rate ramp from 0.01 to 200 l/s. The yield stress was recorded from the point at which viscosity was at its maximum value and the viscosity value was recorded at the shear rate of 20 l/s. The paste behavior was described according to the Hershel-Buckley model. Measurements were repeated three times for each sample, and the average of measurements was recorded. In addition, paste with
and without LS superplasticizer was studied with longer rheological measurements: the shear rate ramp protocol explained above was repeated 8 times with a 2 min pause between each shear rate ramp. This experimental protocol was started 10 min after the start of mixing. The purpose of the longer experiment was to see the rheological behavior of the best-performing superplasticizer as a function of time.

Compressive and flexural strengths were determined using a Zwick/Roell Z100 testing machine (with a load cell of 100 kN). The prismatic beams were first assessed under the flexural loading, and then the broken half-specimens were used to evaluate the compressive strength. Loading rates were 50 N/s and 2.4 kN/s during the flexural and compressive strength tests, respectively, according to the standard [29].

Zeta potential was measured using Malvern Zetasizer Nano ZS. The measurements were conducted by adding 8.82 g of BFS and 0.18 g of finely ground microsilica to 300 mL of distilled water and mixing. Measurements were conducted using 0, 0.2, 1.1, and 2.1 % of LS superplasticizer. The zeta potential instrument titrated pH from approximately 3 to 11. Unfortunately, higher pH could not be used with the instrument.

A field emission scanning electron microscope with an energy dispersive spectroscope (SEM-EDS, Zeiss Ultra Plus; Zeiss) was used to take micrographs of hardened mortar intersections and to provide semi-quantitative information about the chemical composition. Analyses were conducted using a backscatter electron detector with 15 kV acceleration voltage and 8.5 mm working distance. The samples were prepared by casting specimens in epoxy resin (Buehler) and were polished with P120, P240, and P1200 abrasive grinding paper and ethanol flushing to reveal cross-sections. The samples were coated with carbon prior to measurement.
Results and discussion

Screening of efficient superplasticizers

The most efficient superplasticizer was LS when judging the overall effect on spread value, initial and final setting times, compressive strength, viscosity, and yield stress (Fig. 2). LS-based admixtures have functioned well also in some other AAM studies [24,26] but they have also been deemed to be unsuitable for certain AAM compositions [33,34]. Moreover, LSs are environmentally friendly chemicals, as they can be prepared from the by-products of pulp manufacturing [35], and they are generally the least expensive of available superplasticizers [36].

The workability (i.e., “the ease with which concrete can be deformed by an applied stress” [36]) was measured by means of a spread value from a flow table test. All superplasticizers improved the spread value of mortar up to 41%, with the highest increase observed with SNF and the LS type of superplasticizers. None of the studied superplasticizers caused segregation on the flow table. All superplasticizers decreased both yield stress and viscosity up to 60%.

In terms of setting time, only the LS superplasticizer was capable of efficient retarding, while most of the other superplasticizers significantly accelerated both initial and final setting time. SMF2 and SNF were able to increase initial setting time slightly (≈ 10 %) but final setting time was shorter than without superplasticizer. One-part alkali-activated slag mortars (and also other one-part AAMs) frequently have too short setting time due to the heat generation from solid activators upon water addition [28,37]. Thus, the retarding effect of superplasticizer is beneficial in many cases. The
setting time can also be prolonged, in general, by the delayed addition of superplasticizer (not directly with water) [38].

First- and second-generation superplasticizers (SMF, SNF, and LS) clearly had a higher positive effect on compressive strength, compared to the third-generation (PCE and CAE). The best was SMF 2, with an approximate increase of 32% for both 7 and 28 d compressive strength, compared to the control without superplasticizer. LS, which was selected for further testing, increased compressive strength by approximately 18%.

Figure 2. Superplasticizer screening results: (A) spread, (B) initial and final setting times, (C) 7 and 28 d compressive strength, and (D) viscosity and yield stress in...
comparison to control (without superplasticizer). The superplasticizer dose was constant 0.5 wt% of the binder in every case.

**Optimizing superplasticizer dose and water amount**

As previously noted, the overall best-performing superplasticizer was LS; therefore, it was selected for subsequent dose and water amount optimization (Fig. 3). The details of the optimization model fitting are presented in the supplementary material. In terms of spread value (i.e., workability), the optimum LS superplasticizer dose is 1–1.7% with a water amount of 35%. When using larger LS doses than this, the spread value clearly decreased. Also, with 4 and 5% doses, segregation occurred on the flow table. The effects of the LS-based superplasticizer overdose for alkali-activated BFS have been poorly documented in scientific literature earlier. However, the overdose of LS-based superplasticizer (up to 5%) does not cause any detrimental effect in OPC mortar [39]. In terms of compressive strength, increasing the superplasticizer dose and decreasing the water amount results in higher compressive strength. The 28 d compressive strength increased up to 100% (from 19 to 38 MPa) when the water amounts of the superplastic were optimized, compared to mortar without superplasticizer. For setting time, the highest values were obtained by increasing both the superplasticizer and the water amounts.

[Type here]
Figure 3. Optimization of water and superplasticizer amount in terms of (A) spread, (B) initial setting time, (C) final setting time, (D) compressive strength (7 d), and (E) compressive strength (28 d).

Viscosity and yield stress

LS superplasticizer decreased yield stress of the paste consistently around 60% up to 40 min, compared to the reference sample (Fig. 4). The same behavior occurred with the viscosities of the pastes (Fig. 4). Yield stress increased as a function time for both pastes in reference to the gel formation reactions taking place and the formation of more interactions between BFS and microsilica particles. After 10 min from the start of mixing, the difference in yield stress was 61%, and, after 40 min, the difference was slightly decreased to 56%. This same behavior applied also for viscosity. Therefore, LS was shown to retard reactions consistently.

The alkali-activated pastes studied here had a different behavior compared to the study by Puertas et al. [40] (in their study alkali-activators were in liquid form) who found that the yield stresses of NaOH or NaOH/Na₂CO₃-activated BFS did not increase at all during the measurement (up to 27 min). However, when they used sodium silicate as an alkali activation solution, yield stress increased first strongly and then subsequently dropped [40]. Authors explained this to happen due to the formation and destruction of primary C-S-H gel [40]. The yield stress development is governed by several factors such as the type of alkali activator, viscosity of alkali activator, type of aluminosilicate precursor, and water content. However, in the present study, yield stress was observed to increase linearly without a drop, which might indicate a fundamental difference between one and two-part systems.

[Type here]
Figure 4. (A) Yield stress and (B) viscosity of pastes as a function of time. LS was used at a 0.5 wt% dose in these experiments.

**Microstructure**

Micrographs of mortars without superplasticizer; with 0.5% of LS (water/binder = 0.35); and with 2.0% of LS (water/binder = 0.30) are shown in Fig. 5. Those samples correspond to 28 d compressive strength of approximately 19, 23, and 40 MPa, respectively. All mortars contained three phases: aggregates (dark grey large particles), unreacted BFS particles (light grey particles with a diameter of less than 50 μm), and matrix (material inbetween). Unreacted BFS particles act as microfillers in the system. The morphology of three mortars appears to be rather similar in terms of porosity, aggregate-mortar interface, and the amount of unreacted BFS. However, the semiquantitative X-ray microanalyses of the matrix phase (shown in Fig. 5B, C, and F) reveal that the relative amounts of Na and Si decrease and the ratio of Ca/Si increases as LS is introduced to the mortar. These observations could be explained by the complexation of Ca$^{2+}$ by lignosulfonate [41], which facilitates the dissolution of BFS (i.e., increases the amount of available calcium), even though the amount of activator is constant. The improved dissolution of BFS has likely contributed to the increased compressive strength. The ratio of Na/Al is < 1 with LS-containing mortars, which indicates that some of the Ca$^{2+}$ or Mg$^{2+}$ are acting as charge balancing cations.
Figure 5. Microstructures of mortars: (A,B) without superplasticizer (reference); (C,D) with 0.5% of LS (water/binder ¼ 0.35); and (E,F) with 2.0% of LS (water/binder ¼ 0.30).

**Mechanism**

The main molecular-level mechanisms of concrete superplasticizers are adsorption on the cement particles (or BFS and microsilica in this case) and subsequent improved dispersion due to steric or electric repulsion [42]. To observe the effects of LS addition on the surface charge of BFS and microsilica particles, zeta potential measurements were conducted as a function of LS dose (Fig. 6). The surface charge of BFS is negative due to silanol groups (-Si-OH), which can fully deprotonate at high pH [43], which
causes the strongly negative charge at the LS dose of 0 %. The negative surface charge is balanced by cations, such as Na\(^+\) and Ca\(^{2+}\) (i.e., there is an electrical double layer on the surface of slag), which can interact with the sulfonic acid groups (-SO\(_3^-\)) of LS [43]. When LS is added to the system, zeta potential increases slightly up to a dose of approximately 1 % of binder and then decreases again. Interestingly, this behavior coincides closely with the observed optimum dosing range in terms of workability (i.e., the spread value decreased with LS doses higher than 1 % of binder). However, lower zeta potential values indicate less electrostatic repulsion between particles and thus the observed behavior does not explain the mechanism of the plasticizing effect. Therefore, these observations point out that the mechanism of the LS superplasticizer in the studied system is not based on electrostatic repulsion but rather on steric repulsion as illustrated in Fig. 7.

Regarding the retarding effect of LS superplasticizer, it is likely related to chelation of Ca\(^{2+}\) by lignosulfonate, which increases strongly at high pH [41]. As already mentioned earlier, this chelating effect has likely contributed also to the improved compressive strength.

The poor functionality of the polycarboxylate or polyacrylate-based superplasticizers has been explained in earlier research by instability at high pH (> 13) of alkali-activated systems [44]. However, in the present study, they (CAE 1–3 and PCE 1–5) provided some plasticizing effect (although not as effectively as LS). This could be due to lower pH (≈ 12 [28]) in the studied one-part system.
Figure 6. Zeta potential of BFS and microsilica in water (pH ≈ 10) as a function of LS dose.

Figure 7. Schematic presentation of possible lignosulfonate adsorption: negatively charged silanol (-Si-O⁻) groups attract a layer of cations (Na⁺ and Ca²⁺) on which lignosulfonate adsorbs. Lignin chains (green lines) cause steric repulsion between particles.
**Comparison of obtained results to the literature**

Most of the earlier published studies (Table 2) of superplasticizers with high calcium AAMs have identified the first- or second-generation superplasticizers (i.e., LSs or naphthalene-based ones) as the most functional [13,21,24,45,46]. This is in agreement with the present study. However, in some cases, also PCE-based superplasticizers have been reported to function well [22,23]. Nevertheless, a systematic comparison of all superplasticizer types has been conducted rarely. In all cases, the workability (either using flow table spread or slump tests) increased as a result of superplasticizer dose (reported range 1–5 % of binder) [13,21-24,45,46]. The effect on setting time and compressive or flexural strength, however, has been either positive or negative. This has reportedly depended on the type and concentration of the alkali-activator [13,24]. Therefore, it appears that the results obtained in each superplasticizer study apply only for that specific AAM mix design.
Table 2. Overview of published studies in which superplasticizers have been used for high calcium alkali-activated materials.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Activator a</th>
<th>pH of AA M</th>
<th>SP b</th>
<th>Dose [% of binder]</th>
<th>Workability</th>
<th>Setting time</th>
<th>Strength</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS</td>
<td>NaOH, microsilica c</td>
<td>12.5 – 12.8</td>
<td>LS</td>
<td>1</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>This study</td>
</tr>
<tr>
<td>BFS</td>
<td>NaCO₃, calcined hydrotalcite</td>
<td>n.r.</td>
<td>LS</td>
<td>0.6</td>
<td>+</td>
<td>n.r.</td>
<td>n.e.</td>
<td>[45]</td>
</tr>
<tr>
<td>BFS, class F fly ash</td>
<td>NaOH, (Na₂SiO₃)ₙO</td>
<td>n.r.</td>
<td>PCE</td>
<td>4</td>
<td>+</td>
<td>+</td>
<td>n.r.</td>
<td>[23]</td>
</tr>
<tr>
<td>BFS, class F fly ash</td>
<td>NaOH</td>
<td>n.r.</td>
<td>PCE</td>
<td>1.5</td>
<td>+</td>
<td>n.r.</td>
<td>n.r.</td>
<td>[22]</td>
</tr>
<tr>
<td>High Ca fly ash</td>
<td>NaOH, (Na₂SiO₃)ₙO</td>
<td>n.r.</td>
<td>LS</td>
<td>5</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>BFS, class F fly ash, glass powder</td>
<td>NaOH</td>
<td>n.r.</td>
<td>SNF</td>
<td>n.r.</td>
<td>+</td>
<td>n.r.</td>
<td>n.r.</td>
<td>[21]</td>
</tr>
<tr>
<td>BFS</td>
<td>NaOH or (Na₂SiO₃)ₙO</td>
<td>12.4 – 13.6</td>
<td>SNF</td>
<td>1</td>
<td>+</td>
<td>+/-</td>
<td>+/-</td>
<td>[13]</td>
</tr>
<tr>
<td>BFS</td>
<td>(Na₂SiO₃)ₙO or NaOH and Na₂CO₃</td>
<td>n.r.</td>
<td>LS</td>
<td>n.r. e</td>
<td>+</td>
<td>+</td>
<td>+/-</td>
<td>[24]</td>
</tr>
</tbody>
</table>

a = activators are solutions unless stated otherwise, b = the best-performing superplasticizer, c = solid activator, d = dependent on activator type, e = dose was 6–10 mL/kg slag, + = increased the property, - = decreased the property, n.r. = not reported, n.e. = no effect, LS = lignosulfonate, PCE = polycarboxylate ester, SNF = sulfonated naphthalene-formaldehyde, VC = vinyl copolymer, PC = polyacrylate copolymer, (Na₂SiO₃)ₙO = general formula of sodium silicate.

Conclusions

The lack of reliably functioning superplasticizers has been identified as a major shortcoming of AAMs. In the present study, one-part alkali-activated mortar was prepared from BFS by using solid sodium hydroxide as an activator and microsilica as an additional silica source. First-, second-, and third-generation superplasticizer types were compared for their effects on workability (flow table spread), compressive strength (7 and 28 d), setting time, yield stress, and viscosity. Unexpectedly, all the studied superplasticizers worked to some extent: they were able to improve workability and compressive strength. However, the overall best-performing superplasticizer was [Type here]
based on LS: it was able to retard setting, which is beneficial with one-part AAMs that often set too rapidly. LS dose and mortar water content optimization revealed an unexpected effect of overdosing: workability clearly decreased at a dose > 1.8% (of the binder). The 28 d compressive strength could be increased from 19 MPa (no superplasticizer) to 38 MPa (optimum water and superplasticizer amount). The improved compressive strength might have been a result of Ca\(^{2+}\) chelation by lignosulfonate, whereas the increased workability was likely due to steric repulsion effect as indicated by zeta potential measurements. The present study demonstrated that commercially available superplasticizers are suitable for one-part NaOH-activated BFS. However, analysis of the literature indicates that the type and concentration of the activator strongly affect the suitability.

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Disclosure statement

No potential conflict of interest was reported by the authors.

References


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Table 1. Properties of studied superplasticizers as reported by manufacturers. Properties of WRDA 90D (LS) are from [30].

Table 2. Overview of published studies in which superplasticizers have been used for high calcium alkali-activated materials.

Figure 1. Generalized structures of studied superplasticizer types.

Figure 2. Superplasticizer screening results: A) spread, B) initial and final setting times, C) 7 and 28 d compressive strength, and D) viscosity and yield stress in comparison to control (without superplasticizer). The superplasticizer dose was constant 0.5 wt% of the binder in every case.

Figure 3. Optimization of water and superplasticizer amount in terms of A) spread, B) initial setting time, C) final setting time, D) compressive strength (7 d), and E) compressive strength (28 d).

Figure 4. A) Yield stress and B) viscosity of pastes as a function of time. LS was used at a 0.5 wt% dose in these experiments.

Figure 5. Microstructures of mortars: A-B) without superplasticizer (reference); C-D) with 0.5% of LS (water/binder = 0.35); and E-F) with 2.0% of LS (water/binder = 0.30).

Figure 6. Zeta potential of BFS and microsilica in water (pH ≈ 10) as a function of LS dose.

Figure 7. Schematic presentation of lignosulfonate adsorption: negatively charged silanol (−Si−O−) groups attract a layer of cations (Na⁺ and Ca²⁺) on which lignosulfonate adsorbs. Lignin chains (green lines) cause steric repulsion between particles.