Role of Zeta Potential on Rheology of One-part Geopolymer Slurries – Influence of Superplasticizers

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ABSTRACT

One-part geopolymers have great potential as an alternative cementitious material to replace ordinary Portland cement (OPC). They are more convenient to be utilized in cast-in-situ applications than the conventional two-part geopolymers as well. Superplasticizers are admixtures that plasticize and fluidize the cementitious slurry through steric and electrostatic mechanisms that apply repulsion forces between the slurry particles. They are commonly used to improve the workability of cement and conventional geopolymer slurries. However, the most developed superplasticizers are suitable for Ordinary Portland cement. Zeta potential measurements of geopolymer slurries can be used in the evaluation of superplasticizers. Therefore, the effect of zeta potential on rheological properties of one-part geopolymer slurries due to the influence of three different superplasticizers is presented. The results show that lignosulfonate-based material could be an effective superplasticizer for Just Add Water geopolymer slurries. It gave the lowest yield stress and API gel strength while having the highest absolute zeta potential value.

Introduction

Superplasticizers are admixtures which plasticize and fluidize cement slurries by means of electrostatic and steric repulsion mechanisms that apply repulsion forces between the slurry particles. They are commonly used to improve the workability of cement and geopolymer pastes. They are used to control the flow properties and allow the possibility of reducing the water to solid ratio without affecting their workability to achieve high mechanical strength and long-term durability. These admixtures have several chemical bases such as lignosulfonates, naphthalene, melamine, polycarboxylates, etc [1-5].

Lignosulphonates were used not only as superplasticizers but also as retarders to enhance the viscosity and pumpability of OPC. Naphthalenes and melamines are superplasticizers that influence dispersing of cementitious particles through electrostatic repulsion mechanisms. Polycarboxylates are other types of superplasticizers that have electrostatic repulsion mechanisms like naphthalenes and melamines, in addition to applying the steric repulsion mechanism due to the long lateral chains of ether on the molecules [1-4].

Davidovits et al. [6] introduced the geopolymers with chemical designation as polysialates, where sialate is the silicon-oxygen-aluminate network [-Si-O-Al-O-]. This network is a tetrahedra SiO4 and AlO4 structure linked by sharing all oxygens. Hence, positive ions such as alkali metal cations (e.g., potassium ion K^+ and sodium ion Na^+) have to be presented within the structure cavities for balancing negative charges of Al3+ in the IV-fold coordination. Geopolymers have generally low calcium content [6-8]. Therefore, the available superplasticizers for OPC may not influence them properly [5].

Although several articles focus on controlling the reaction, setting time and strength development of geopolymer mixes [6-13], few studied the effect of superplasticisers on one-part geopolymer slurries. Several variables affect the geopolymeric structure such as particle size and shape, and solid phase volume fraction besides surface effects such as electrostatic forces and adsorption of ions between the particles [3-9]. Hence, Superplasticisers as surfactants may be more suitable candidates for enhancing the rheology of the geopolymeric slurries, due to their structures' compatibility with the geopolymer structures.

A study conducted by Palacios et al. [10] shows that the pH of the slurry significantly impacts the performance of the superplasticizers. At pH values below 11.7, most of the superplasticizers perform better on alkali-activated-based materials. However, at higher pH values, especially above 13.6, most of the superplasticizers get unstable and do not perform properly. One should note that naphthalene-based admixtures are stable in high pH environments. The reader should distinguish between alkali-activated-based materials and geopolymers whereas geopolymers are a sub-group of alkali-activated materials. Thus, geopolymer properties like pH of the slurry and size and surface potential of the geopolymer particles have a significant role in controlling the adsorption rate of the superplasticizers [10].

This work aims to present the effect of utilization of three different superplasticizers by utilization of the electrokinetic potential of the slurries. In addition, it will discuss their zeta potential role in the rheology of geopolymer slurries, especially on viscosity and yield stress of one-part rock-based geopolymer recipe at varying shear rates for well construction in the petroleum industry.

Experimental Materials

This research is based on selecting one of the top candidate one-part geopolymer recipes from Omran & Khalifeh[11], "W1Pb-Z6" or so-called in this paper "OP-Z" as the neat recipe. The solid phase includes a precursor, a solid activator, and a superplasticiser. The liquid phase includes distilled water. The chemical composition and mineralogy of the powder mix have been thoroughly studied [11-14].

Furthermore, 1 wt.% solid powder of three different superplasticizers (two naphthalene-based and a Na-based lignosulfonate superplasticizer) are used separately to enhance the rheology of one-part rock-based OP-Z neat geopolymer mix design. The chemical structure of the superplasticizers is given in Figure 1. The selection of the superplasticizers is based on selecting the most stable superplasticizers that can be utilized and worked effectively for rheology enhancement in high pH environments.

a) b)

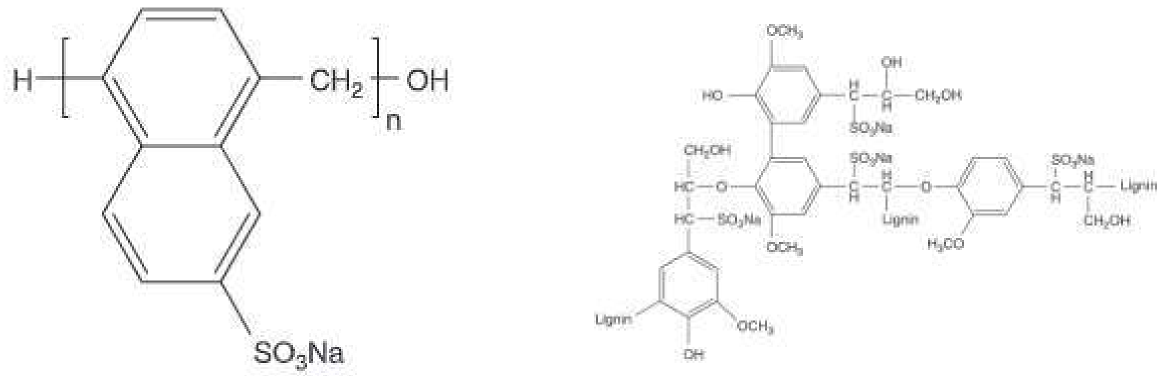

FIGURE 1: Chemical structure of the superplasticizers: a) naphthalene derivate, b) lignosulfonate molecule [15].

Experimental Methods

All the experiments and preparation of the slurries were conducted according to the international standard [16]. A high-shear cement blender, the OFITE Model 20 Constant Speed Blender, was used for mixing all the components to form the slurry in each experiment.

An atmospheric consistometer, OFITE Model 60, was employed for conditioning all the given slurries in ambient conditions. A non-pressurized rotational viscometer, OFITE 900, was used for the viscosity measurement. Shear stresses of the slurries were recorded in $lb_f/100\ ft^2$.

The zeta potential of the geopolymer slurries was examined at ambient temperature (25°C) by Electrophoretic Light Scattering (ELS) using a Zetasizer Nano ZS (Malvern) equipped with a laser source (wavelength 633 nm) at a scattered angle of 13°.

Results

The shear stress and viscosity of the slurries were studied to investigate the impact of the superplasticizers on the neat geopolymer slurry OP-Z (see Figures 2-4). The pH of the neat slurry after conditioning was measured to be 13.94.

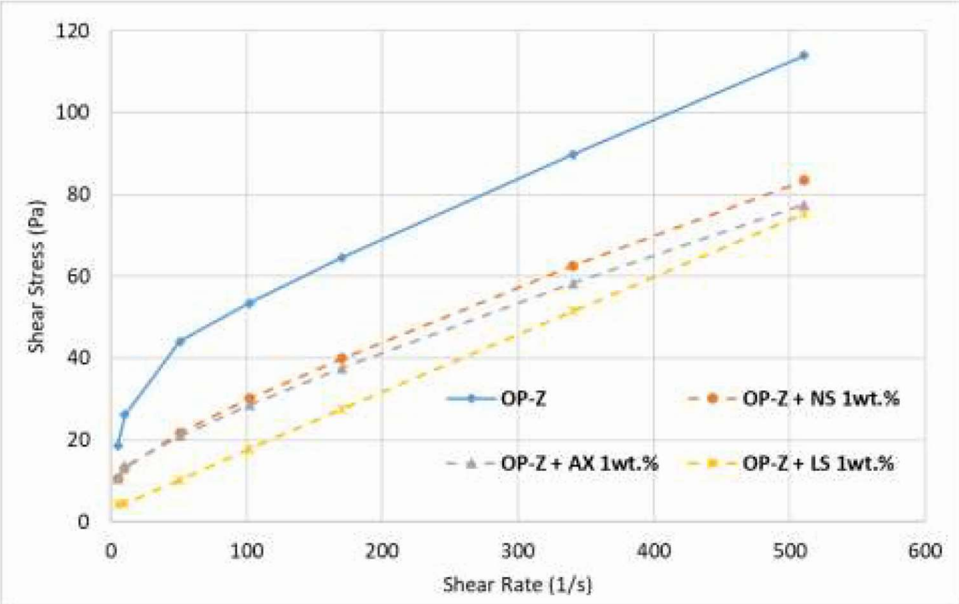

FIGURE 2: Shear stress - Shear rate curves of neat slurry with 1 wt.% superplasticizer in solid form.

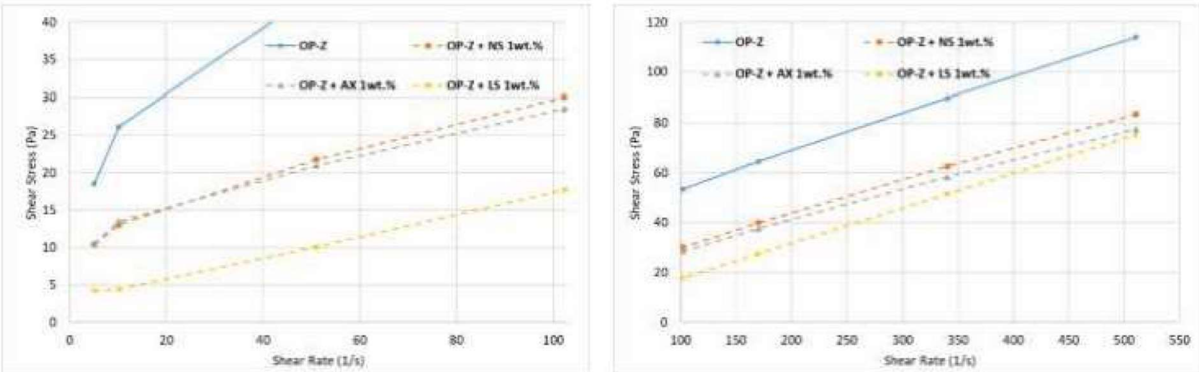

FIGURE 3: Shear stress - Shear rate curves of neat slurry with 1 wt.% superplasticizer in solid form; Left) shear rates below 100 1/s, and Right) shear rates above 100 1/s.

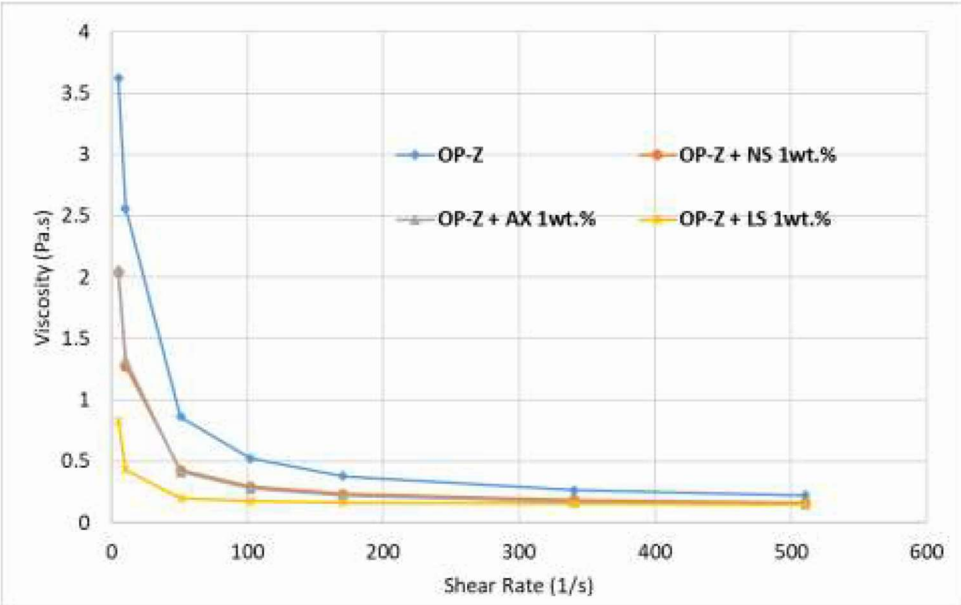

FIGURE 4: Viscosity profiles of neat slurry with 1 wt.% superplasticizer in solid form.

Hershel-Bulkley model was used to estimate yield stress for all geopolymer mixtures as linear scaling regression analysis between 5.11 to 10.2 1/s shear rates as given in Table 1. This model could fit the given shear stress vs shear rate profiles in Figure 1. The power-law index (flow index, n) was measured to indicate the changes in viscosity with shear rate. It was equivalated as the slope of the log-log shear stress to shear rate curve.

Table 1: Yield stress and API Gel-strength results

Recipes	*Superplasticizer*	*10 sec API Gel-strength [Pa]*	*10 min API Gel- strength [Pa]*	*Estimated Yield Stress [Pa]*	*Flow Index*
OP-Z	Non	18.5	19.1	15.4	0.37
OP-Z + NS 1wt.%	Naphthalene-SP	10.5	10.6	8.5	0.44
OP-Z + AX 1wt.%	Auxilchem NS181	10.4	11.3	8.5	0.42
OP-Z + LS 1wt.%	Lignosulfonate-SP	5.6	6.9	4.1	0.64

All given geopolymer recipes were examined for their zeta potential, which includes slurries with and without superplasticizers (see Table 2).

Table 2: Zeta potential measurements of the geopolymer slurries with and without superplasticizers.

Recipes	*ZP (mV)*	*Standard Deviation*
OP-Z	-25.4	± 0.29
OP-Z + NS 1wt.%	-27.9	± 1.32
OP-Z + AX 1wt.%	-31.7	± 0.65
OP-Z + LS 1wt.%	-33.1	± 0.66

Discussion

One-part geopolymeric slurries are non-Newtonian fluids in which the shear viscosity is no longer a material constant, as the viscosity is changing with changing shear rate and also with shearing time. Figure 2 shows shear-thinning behaviour for the examined one-part geopolymer recipes with and without adding superplasticizers. In addition, the flow indexes of the given slurries were 0.37 to 0.64, which were less than 1 ($n < 1$) for shear-thinning materials. It is observable that the absolute value of zeta potential for the slurries with superplasticizer can directly be correlated to the initial viscosity of the slurry, especially at 5 and 10 1/s shear rates as shown in Figures 2-4, below 100 s^{-1} shear rates.

From Figure 3, above 100 s^{-1} shear rates, zeta potential values might not be correlated with the viscous behaviour of the investigated geopolymer slurries anymore, especially at higher shear rates. The resistance of the formed particles network is weakened at which the shear rates increase and give rise to weaken the colloidal flocculent interactions [5, 13].

One-part rock-based geopolymers can be considered as being constructed by long-lasting time-dependent interactions and flow properties due to complex ongoing geopolymerization (i.e., dissolution and oligomerization) reactions. These interactions are replaced by a strong molecular network to form a gel structure [5-8].

Kashani et al. [17] have shown that when alkali silicate-based hardener is mixed with precursors, a negative zeta potential value is expected while for activators consisting of alkali solutions, the zeta potential value approaches positive values. In other words, when alkali silicate-based hardener is mixed with precursors, deflocculation of slag particulate suspensions occurs due to deflocculation and plasticizing effects of silicate anions, which is a result of repulsive forces. However, when alkali solution is used as an activator, the hydroxyl groups sit on precursors and create flocculation. Adsorption of the superplasticizer on the particles increases the magnitude of double-layer repulsive forces and subsequently reduces the yield stress of the slurry. Others presented the utilization of naphthalene-based superplasticizers for conventional geopolymer slurries had a great effect on lowering the yield stress and gel strength with the highest absolute zeta potential values [9-10, 17-20].

In this study, a lignosulfonate-based superplasticizer has been also investigated besides the two naphthalene-based superplasticizers. The results of these three superplasticisers show stable and effective plasticising behaviour to the given high pH rock-based OP-Z geopolymer recipe. Lignosulfonate-based superplasticizer gave the best effect on lowering the yield stress and gel strength with the highest absolute zeta potential value. It lowered the initial viscosity from 3.6 Pa.s for the neat recipe down to 0.8 Pa.s for OP-Z + LS 1wt.% mix design. It also lowered the yield stress and API gel strength by 73% and 70% respectively when it is compared with OP-Z neat recipe. The higher the absolute value of zeta potential, the better the colloidal effectiveness on the geopolymer slurry initially in static conditions. Hence, zeta potential measurements might be correlated to the initial rheological properties such as yield stress, without any considerable effect at high shear rates.

The observations show the presence of shear-thinning - thixotropic flow behaviour for the given one-part rock-based geopolymer recipe with naphthalene-based superplasticizers as time-dependent slurries. However, the Lignosulfonate-based superplasticizer gave Bingham Plastic behaviour. The investigated superplasticisers can be also applicable to be used for two-part geopolymer slurries, especially the lignosulfonate-based superplasticizer.

The recommended dosage of the superplasticizers is typically 0-1 wt.%, while below 0.5 wt.% is more of interest due to techno-economic reasons. Thus, a further investigation will be needed to study the effect of the weight content of these superplasticisers below 1 wt.% on the one-part geopolymer system. In addition, it would be useful to further correlate these observations with interactive forces between geopolymer materials and these three superplasticizers.

Conclusion

From the experimental results, Naphthalene-based superplasticizers are good candidates for lowering yield stress, API gel-strength and viscous behaviour of one-part rock-based geopolymers as they work effectively with the conventional two-part geopolymer systems. However, the lignosulfonate-based superplasticizer gave the best effect on lowering the yield stress and gel strength with the highest absolute zeta potential values due to their particle's dispersion with the highest absolute zeta potential value. Both Na-based lignosulfonate and Naphthalene-based superplasticizers might be the most effective superplasticizers for one- and two-part rock-based geopolymer systems. Zeta potential measurements might be correlated to the initial rheological properties such as yield stress, without any considerable effect at high shear rates.

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