Rheological Properties of Rock-Based Geopolymer Slurries with Different Dispersant and Counterion Combinations

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ABSTRACT

The production of Ordinary Portland Cement is responsible for a significant part of global CO_2 emissions. A potential alternative to OPC is alkali-activated materials, which do not contain OPC and are not produced in processes to release CO_2. Thus, these materials have considerably lower CO_2 emissions during production. It is estimated that the CO_2 emissions from rock-based geopolymer concrete would be reduced by 70-80 % compared to standard OPC based concrete. Furthermore, the use of mine tailings in concrete will reduce the area needed for landfills, thereby lowering the impact on natural resources.

Dispersants, plasticizers or superplasticizers are important admixtures that increase the workability of fresh concrete, usually by lowering the yield stress or reducing the viscosity. The rheological properties of slurries with 7 different dispersants were tested in different ionic compositions. The dispersing effect seems to be highly dependent on the type of dispersant and the ionic composition of the slurry. Seven different types of dispersants were tested with varying dispersing effect in the different slurries. The chemical structure and its behaviour in the systems seems to be crucial for the dispersing effect.

INTRODUCTION

The production of Ordinary Portland Cement (OPC) is responsible for a significant part of global CO_2 emissions. A potential alternative to OPC is alkali-activated materials (AAM), which do not contain OPC and thus have considerably lower CO_2 emissions during production. AAM can be made from different types of precursor materials, typically waste materials such as blast furnace slag, fly ash and mine tailings[1]. AAMs made from low calcium containing precursors are often called "geopolymers"[2,3]. It is estimated that the CO_2 emissions from rock-based geopolymer concrete would be reduced by 70-80 % compared to conventional OPC based concrete. Furthermore, the use of mine tailings in concrete will reduce the area needed for landfills, thereby lowering the impact on natural resources.

Dispersants, plasticizers or superplasticizers are important additives to control the workability of fresh concrete, usually by lowering the yield stress or reducing the overall viscosity. These compounds are surface active molecules, where the particle dispersing effect is obtained by electrostatic repulsion and/or steric hindrance. In concrete industry the term plasticizer and superplasticizers are used to name first and second generation of these admixtures, respectively. Whereas the term "dispersants" are used for these compounds in well cementing and surface chemistry[4-6]. In this text the designation "dispersants" will be used to describe these admixtures. Numerous dispersants are commercially available for OPC mixtures.

However, effective dispersants for low calcium geopolymer concrete are currently less available. There are significant differences in surface chemistry and subsequent functionality of the dispersants used for OPC-based and geopolymer based slurries, which may explain why there are fewer suitable dispersant candidates for geopolymers. Consequently, several laboratory studies have investigated the use of dispersants in geopolymer slurries[7-9]. The aim of this paper is to study the suitability of different types of dispersants in some more depth.

Surface chemistry and dispersants

A particle can be stabilized in a solution by the adsorption of polymers on the particle surface. When sufficiently covered by the polymer the particle will behave as a polymer with infinitely high molecular weight in solution. It is crucial that the polymer is sufficiently adsorbed at the surface to obtain a dispersing effect[5]. The adsorption mechanism depends on the specific conditions of the dispersant and the particle surface. The driving forces of polymer surface adsorption can be:

- **Electrostatic interactions:** The driving force is an effective interaction between polymer segments and the surface. Such as the adsorption of a cationic polymer at an anionic surface. The introduction of a positively charged "bridging" ion might also result in electrostatic adsorption of a negatively charged polymer on a negatively charged surface.
- **Solubility:** Poor solubility of the polymer in the solution. The polymer will seek any opportunity to escape contact with the solvent and adsorb on almost any surface. High molecular weight polymers are less soluble and more prone to adsorb than low molecular weight polymers. Increased ionic strength in the solution might reduce the solubility of polymers.
- **Entropy:** When a polyelectrolyte adsorbs on a surface, the counterions from both the polymer and the surface are released into the bulk. Thus, increasing the entropy of the system and bringing the system into a lower free energy state. The entropic effect might be stronger in systems with a higher amount of counterions associated to the surface.
- **Chemical interaction**: In some cases, the dispersant can bond to the surface by covalent bonds, hydrogen bonds or van der Waals interactions[5, 6].

Most likely, more than one type of interaction will be present in the systems.

The presented dispersants are lignosulphonates (LS), acrylic polymer (AP), carboxylic acid copolymer (CAC) and commercial OPC concrete superplasticizers (CSP). The exact structures of the dispersants are proprietary information known only to the supplier, which were unfortunately not shared. However, it is reasonable to assume they are polyelectrolytes e.g., polymers with many charged groups. The charged groups can be ionizable groups like carboxylate, sulphate groups and ammonium ions. These are highly pH dependent and the degree of expansion of the polyelectrolyte increases with the degree of ionization[5]. Lignosulphonates are by-products from sulphite pulping of wood and are used in many different applications. However, the most common use is as dispersants. Anionic functional groups, like sulfonate and carboxylic groups ensure water solubility. The chemical structure of lignosulphonates comes in a wide variety, the structure is branched and three dimensional. The number and type of functional groups can vary significantly. In addition, the molecules can have

a wide range of molecular weight distributions (in the range of 1000-400 000 g/mol). Hence, the surface properties and three-dimensional structure can vary significantly. In this study, four different types of Lignosulphonates have been tested[10]. Acrylic polymers and carboxylic acid copolymer are synthetic polymers often used and designed as dispersants for pigments[6]. Both the AP and CAC used in this study are anionic dispersants.

Influence of ion composition and surface charge

An important property of a charged surface in aqueous solution is its zeta potential, which is the electric potential at the surface. It should be noted that the zeta potential is not the actual surface potential, which is not possible to measure experimentally: the zeta potential it is the potential at the so-called Stern layer, which is outside the layer of adsorbed counter-ions (i.e. oppositely charged ions)[11]. The zeta potential is therefore significantly affected by the ion concentration and especially the type of counter-ions, where di-valent ions affect the zeta potential considerably more than monovalent ions.

The major components of the mine tailings used in this study is SiO_2 or similar structures (e.g. aluminates). The isoelectric point of silica is around pH 2, depending on the type of structure[12]. However, at pH 14 it is reasonable to assume that a great quantity of the silanol groups on the surface are deprotonated (figure 1a). Consequently, the mine tailing surface will be covered with negatively charged silicic groups. All dispersants have been tested in both NaOH activated slurry (Na-slurry) and KOH activated slurry (K-slurry). The potassium ions (K^+) are less hydrated than the sodium ions (Na^+) in solution. Consequently, the K^+ ions are more likely to adsorb on the particle surface in a greater quantity than Na^+ ions[12].

For a polyelectrolyte to be adsorbed due to electrostatic interactions on a negatively charged surface, there are two alternatives. The first is the adsorption of a positively charged polymer directly on the surface. This is difficult to obtain since there are, to our knowledge, a limited number of commercially available cationic dispersants. The second alternative is a negatively charged polymer adsorbed to a negatively charged surface with a layer of cationic counterions ("ion bridge"). K^+ would be a better "bridging ion" than Na^+ due to the previously discussed hydration of Na^+. However, divalent cations have been known to perform better as bridging ions than monovalent ions[5]. Unfortunately, most divalent cations precipitate as hydroxides at high pH. However, calcium have some solubility at high pH (K_{sp} of $Ca(OH)_2$ is ~2,2 x 10^{-6})[13]. In this study, Ca^{2+} is added to the slurries to investigate the effect as a potential "bridging ion" (Figure 1b). Blast furnace slag (BFS) is sometimes used as co-binder in rock-based geopolymer slurries to improve strength development[2, 14], which ensures available Ca^{2+} ions in solution.
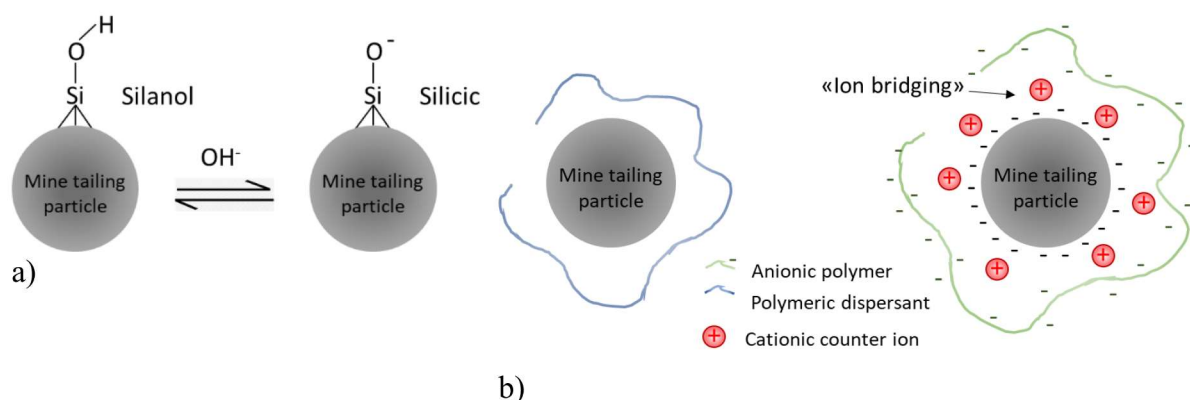
FIGURE 1: Illustration of a) the simplified surface chemistry of SiO2 on the particle surface in high pH[15] b) The simplified adsorption mechanism of polymeric dispersants with and without "bridging ions." The illustrations are not to scale.

EXPERIMENTAL PROCEDURE

Materials

The experiments were conducted using norite mine tailings from the Titania mine in the southern part of Norway, details of this mine tailing have been described previously.[14] The norite was milled down using a pilot scale vertical roller mill. The norite powder had a D10 of 2,4 μm, D50 of 12,0 μm and a D90 of 34,0 μm. The chemical composition of the norite powder is presented in table 1. The dominant minerals in the norite were plagioclase, pyroxene and ilmenite. The different dispersants used, and their abbreviation are presented in table 2.

TABLE 1: The chemical composition of the norite powder used in the experiments.

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na2O
			%			
43,7	16,5	14,4	8,8	6,2	6,1	3,5

Zeta potential measurements

The surface charge of the particles was determined with the zeta potential using a Malvern Panalytical Zetasizer instrument. The upper pH limit of the instrument is 12, consequently the zeta potential measurements were performed at pH 12. The measurements were performed three times per sample in deionized (DI) water, NaOH, KOH and with a combination of NaOH/KOH and 5,5 g/L $CaCl_2$.

Mixing procedure and testing

The recipes of the different mixes are presented in table 2. The solids were 100% norite in all samples. The molarity of the activator in the slurries were 10 M and the dispersant concentration were 2 % of the solid weight. Calcium ions (Ca^{2+}) were added to obtain a saturated solution. Due to high viscosity, the slurries with sodium hydroxide (NaOH) were tested with a higher water/solid ratio (0,4) than the KOH slurries (0,35). The samples with $CaCl_2$ are denoted with "Ca" at the end of the Mix ID. All samples were mixed in a Kenwood Titan mixer. The slurry was mixed for 3 minutes at speed 3 until it was homogenous. The dispersant was then added to the slurry and mixed at speed 3 for 5 minutes. The slurry was then tested in a Orcada Model 900 Viscometer 5 minutes after the mixing was completed.

TABLE 2: The mix ID and recipies of the different mixtures. The samples with $CaCl_2$ are denoted with "Ca" at the end of the Mix ID.

Mix ID	Activator	W/S	Dispersant	
Na-0,4-LS1	NaOH	0,4	LS1	
K-0,35-LS1	KOH	0,35		Lignosulphonate
Na-0,4-LS2	NaOH	0,4	LS2	
K-0,35-LS2	KOH	0,35		
Na-0,4-LS3	NaOH	0,4	LS3	
K-0,35-LS3	KOH	0,35		
Na-0,4-LS4	NaOH	0,4	LS4	
K-0,35-LS4	KOH	0,35		
Na-0,4-AP	NaOH	0,4	AP	Acrylic polymer (coatings dispersant)
K-0,35-AP	KOH	0,35		
Na-0,4-CAC	NaOH	0,4	CAC	Carboxylic acid polymer (coatings dispersant)
K-0,35-CAC	KOH	0,35		
Na-0,4-CSP	NaOH	0,4	CSP	Commercial concrete superplasticizer
K-0,35-CSP	KOH	0,35		

RESULTS AND DISCUSSION

Zeta potential measurements of the surface of mine tailing particles were performed in different ionic conditions at pH 7 and 12. The results are presented in figure 2. The zeta potential of the particle surface was negative in DI water and NaOH and KOH solutions. The absolute negative value was higher at high pH, most likely due to deprotonation of the particle surface (Figure 1a). However, the zeta potential of the particle surface was positive when small amounts of Ca^{2+} were added. This would facilitate "ion bridging" and adsorption of negatively charged polyelectrolytes. The adsorption of anionic polymers is strongly dependent on the pH and the dissociation of the functional groups (carboxylic acid, sulphonate, alcohol etc.) The dissociation of the groups will increase the negative charge on the polymer[6]. At very high pH (10 M hydroxide) the polyelectrolytes are assumed to have a high degree of dissociation and consequently a higher negative charge[5].

The flow curves of NaOH-activated (Na-slurry) and KOH-activates (K-slurry) slurries are presented in figure 2.
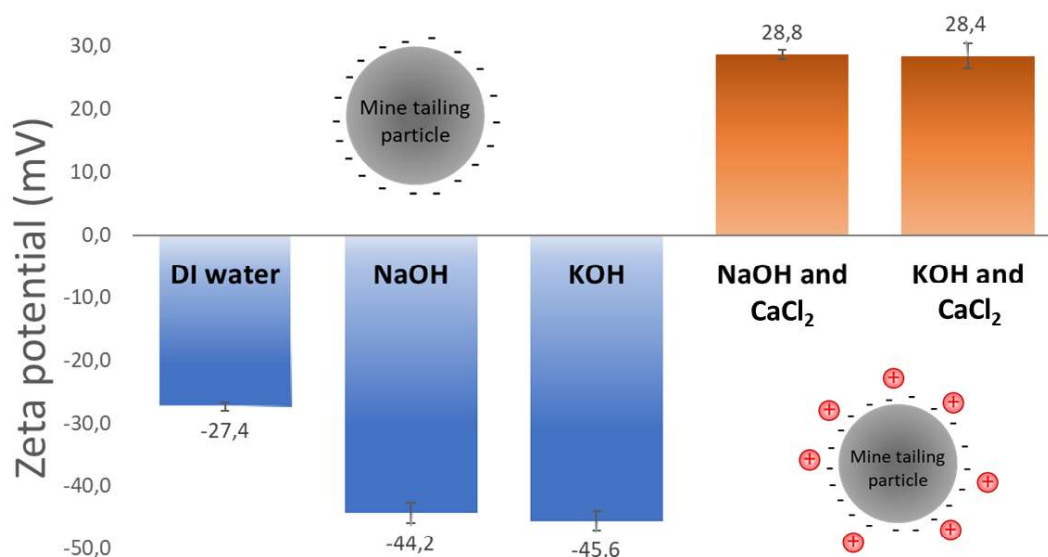
FIGURE 2: The zeta potential of the surface in different solutions: DI water, KOH and NaOH (pH 12) with and without $CaCl_2$ (5,5 g/L).

a)

b)
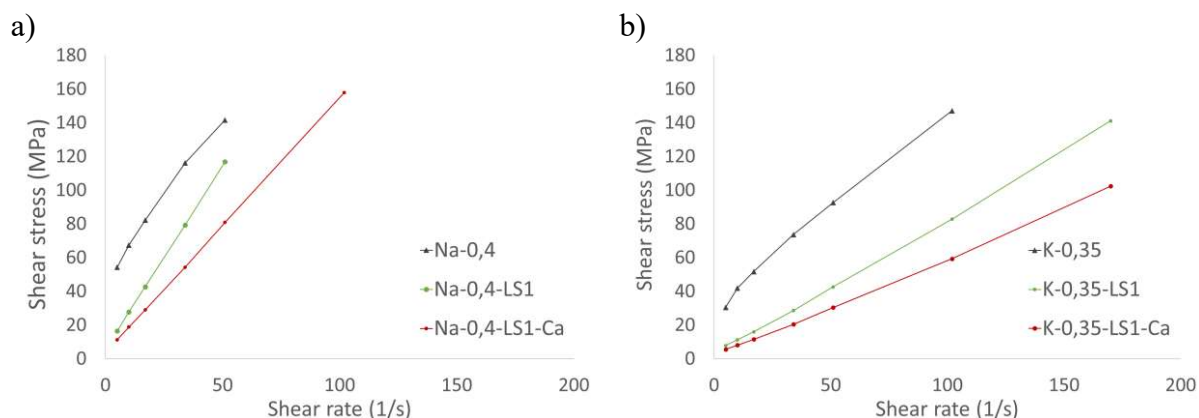
FIGURE 3: The flow curves of the Na-slurry (a) and the K-slurry (b) with LS1

The addition of LS1 in the K-slurry decreased the viscosity and the addition of Ca^{2+} further decreased the viscosity at all measured shear rates as shown in figure 3. This indicates a "bridging ion" effect of Ca^{2+} on the adsorbtion of the polymer in the particle surface. However, the effect of additon of LS1 in the Na-slurry was minor. The yield stress appeared to be reduced by the addition of LS1 in both slurry systems (Figure 3).

a)

b)
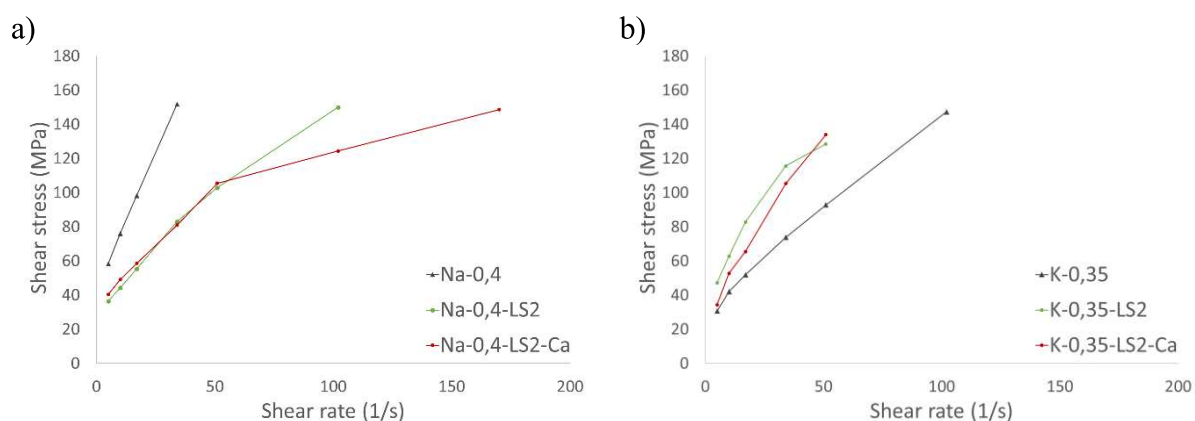
FIGURE 4: The flow curves of the Na-slurry (a) and the K-slurry (b) with LS2

Interestingly, the effect of LS2 displayed a very different effect in the K and Na-slurry. In the Na-slurry, the addition of LS2 decreased the viscosity at all shear rates as shown in Figure 4. The addition of Ca^{2+} changed the flow curve from being a linear curve in shear rates to a curve with two branches and a cusp. The yield stress decreased sligthly with the addition of LS2. This indicates a "bridging" ion resulting in adsorption of the polymer on the particle surfaces (figure 1b). Suprisingly, the effect of adding LS2 to the K-slurry resulted in a sligthly higher viscosity both with and without Ca^{2+}. There was also a small increase in yield stress. The driving force of polymer adsorption in this system is unknown, but most likely not electrostatic.
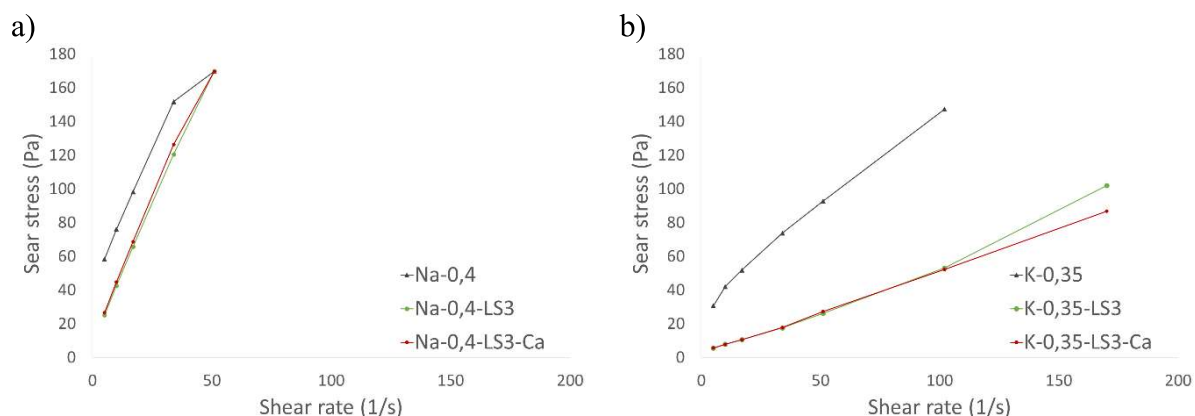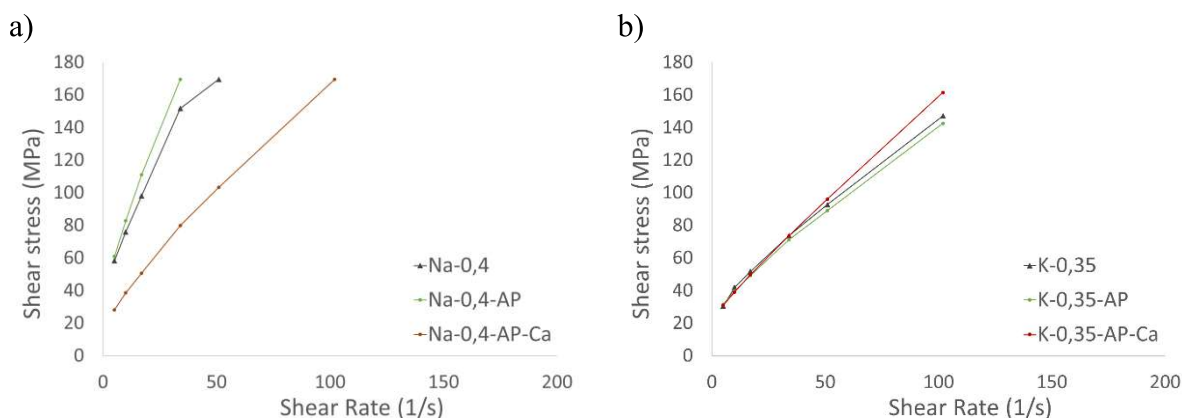
FIGURE 5: The flow curves of the Na-slurry (a) and the K-slurry (b) with LS3

In contrast to addition of LS1 and LS2, addition of LS3 in the slurries resulted in a far greater effect on viscosity in the K-slurry than in the Na-slurry. In both slurries, as shown in Figure 5 the addition of Ca^{2+} does not seen to have an effect. This might be an indication that the adsorption mechanism of LS3 is not primarily an electrostatic effect. The effect could come from poor solubility in the K-slurry. Hence, the polymer seeks any opportunity to escape the bulk solution. However, the entropic effect might also be a contributing factor. It is likely that the entropic effect is higher in a K-slurry than the Na-slurry due to the hydration of Na^+. The hydration of Na^+ would result in a higher fraction of the Na^+ in the bulk solution rather than on the particle surface. The K^+ is not as hydrated and would adsorb more easily on the particle surface. Hence, an entropic effect would be expected when a polymer adsorbs, with another mechanism than electrostatic interactions, and counterions are released into the bulk phase[12].
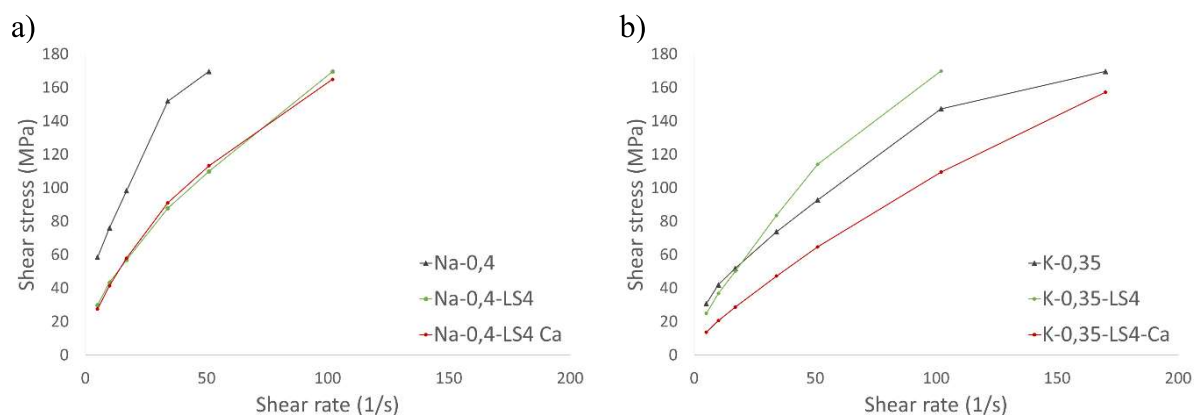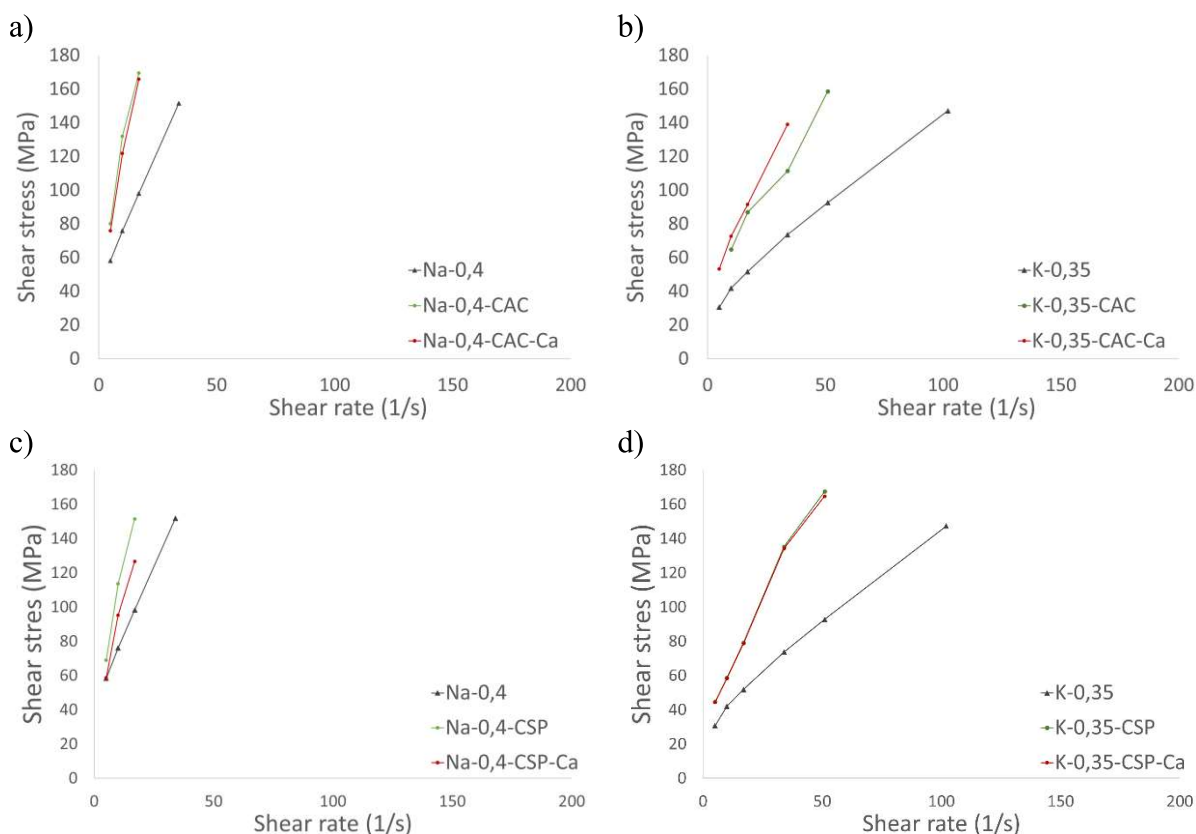

FIGURE 6: The flow curves of the Na-slurry (a) and the K-slurry (b) with LS4

As shown in Figure 6, the effect of adding LS4 results in a decrease in viscosity in the Na-slurry at all shear rates, both with and without adding Ca^{2+}. In the Na-slurry the addition of Ca^{2+} does not seem to have an effect on the viscosity, indicating an adsorbtion mechanism other than electrostatic interaction. However, the yield stress was decreased by the addition of LS4 for the Na-slurry. For the K-slurry the addition of LS4 seem to increase the viscosity at higher shear rates. Conversely, the addition of Ca^{2+} in the K-slurry decreased the viscosity, indicating an "ion bridging" effect of Ca^{2+}. There might be an entropic effect on the adsobtion of polymer on the surface in the K-slurry related to the affinity of the K^+ ions on the surface. The yield stress was also reduced by the addition of Ca^{2+}.

FIGURE 7: The flow curves of the Na-slurry (a) and the K-slurry (b) with AP

The addition of AP resulted in no notable change in viscosity in either the K-slurry or the Na-slurry. Addition of Ca^{2+} had no effect in the K-slurry. However, as shown in Figure 7, in the Na-slurry there was a decrease in viscosity at all shear rates in the sample with both Ca^{2+} and AP.

FIGURE 8: The flow curves of the Na-slurry (a) and the K-slurry (b) with CAC. And the Na-slurry (c) and K-slurry (d) with CSP.

As shown in Figure 8, the addition of CAC resulted in increased viscosity at all measured shear rates in both the K and Na-slurries. Further addition of Ca^{2+} did not alter the viscosity. The increase in viscosity could be a chelating or flocculating effect. Similarly, the addition of CSP increased the viscosity at all shear rates in the K-slurries with and without Ca^{2+}. However, there was no significant change in the viscosity or yield stress in the Na-slurry.

CONCLUSION

Zeta potential measurements of the surface of mine tailing particles revealed a shift in charge from negative to positive by the addition of a small amount of Ca^{2+} into the solution. A positive zeta potential would favour electrostatic adsorption of negatively charged dispersants. And consequently, result in a better dispersion effect. The rheological properties of slurries with 7 different dispersants were tested in different ionic compositions. The dispersing effect seems to be highly dependent on the type of dispersant and the ionic composition of the slurry. Four different types of lignosulphonates were tested with varying dispersing effect in the different slurries. The chemical structure and its behaviour in the systems seems to be crucial for the dispersing effect.

Acknowledgement

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