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Full Length Research Paper

Effects of alkaline and alkaline-earth ions on the rheological behavior and zetametric study of two cement pastes (artificial cement portland-CEMI and cement resistant to the sulfates-CRS) with the polynaphthalene sulfonate (PNS)

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The use of admixtures which tends to be generalized in the formulation of self-compacting concrete (SCC), requires taking into account the chemical composition of cement, particularly its content of SO_3, which can inhibit or restrain the effect of these admixtures (superplasticizers). For more information of the compatibility problem of cement-superplasticizer, the rheological tests with a rheometer-AR2000 and measurements of zeta potential with a Zêtasiser-2000 were used in this study. In order to understand this phenomenon due to the presence of SO_3 in cement, we propose to evaluate the action of alkaline and alkaline-earth ions, incorporating different types of additions (K^+, Na^+, and Ca^{2+}) to the cement pastes. To achieve this, our work will concern the study of rheological properties and physical characteristics of the pastes obtained using two types of cement (C1: Cement Resistant to the Sulfates (CRS) and C2: CEMI). This experiment will focus on two reports: Water/Cement (W/C) = 0.30 for which the polynaphthalene sulfonate (PNS) is used as superplasticizer and W/C = 0.50 (without superplasticizer). The results show that the presence of sulfate leads to different rheological behaviors which are function of sulfates and the cements used.

Key words: Cement, rheology, superplasticizer, yield stress, plastic viscosity, self-compacting concrete, sulfates.

INTRODUCTION

Several authors proved that the most important mineral in cement, is the tricalcium aluminate (C_3A), which can be a very reactive component and onto which superplasticizers (SP) highly absorbs (Ramachandran et al., 1998). The C_3A has an important role in the presence of superplasticizers, particularly those which contain sulfonate groups (Ramachandran et al., 1998). Ramachandran et al. (1998) and Jiang et al. (1999) concluded that the reaction of C_3A is a phenomenon of chemical sorption of anions SO_3^{2-} on the active sites of interface of the C_3A. Brown et al. (1984) showed that C_3A hydration carried out in different solutions containing various amounts of sodium, calcium, hydroxide, and sulfate ions gives rise to at least two hydrated phases (ettringite and hydroxy-gypsum) precipitating in the same time, the proportions, and the rate of precipitation of each phase depends on the composition of the solution. These results are also in a good agreement with the work of Eitel (1957) showing hexagonal hydrate phases

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precipitating in direct contact with C_3A. More recently, the study made by Minard et al. (2007) confirmed the formation of ettringite and hydroxy-AFm phase at the early ages in C_3A-gypsum hydration and determined the quantity of hydro-aluminates precipitating by employing a method based on microcalorimetry in the stirred up diluted suspension.

Some studies showed that Na_2SO_4 addition has improved the rheological properties of cement phases (Jiang et al., 1999). Other authors also reported that the alkaline sulfate content was one of the major parameters controlling flowability and the loss of that property in cement pastes containing a polynaphthalene sulfonate (PNS) superplasticizer. According to their work, the optimum soluble alkaline content in terms of flowability is 0.4 to 0.6% Na_2Oe. The C_3A content has practically no effect on fluidity, with the optimum amount of soluble alkalis in cement found by these authors. Kim et al. (2000) found cements having a high PNS adsorption capacity to be incompatible with such superplasticizers. High adsorption capacity was the result of a dearth of soluble alkaline sulfates in the cement. Indeed, with the addition of Na_2SO_4 and the concomitant decline in the amount of PNS adsorbed, the slump area grew. The existence of such a link between high adsorption and incompatibility clashes with the generally accepted assumption that superplasticizer adsorption affects cement paste rheology positively by increasing the electrostatic forces that lead to repulsion between cement particles. According to these authors, the PNS molecules remaining in the solution might act as an additional repulsive barrier between cement particles, thereby contributing to greater paste flowability (Kim et al., 2000). The influence of sulphates on the rheological behavior of cement paste does not depend only on the amounts of sulphates present in the clinker, but also their nature, their rate of solubility, and diffusion rate of ions SO_4^{2-} and Ca^{2+} in solution in water mixing (Greenberg et al., 1963; Ish-Shalom and Greenberg, 1960). In the other works, Prince et al. (2003) maintained that ettringite and its modification in the presence of PNS was the determining factor in cement paste rheology. More specifically, they found that the growth of long ettringite needles that usually reduce paste flowability was retarded when PNS was added. Certain authors (Prince et al., 2003; Pourchet et al., 2009) stressed that the interaction of SP molecules with ettringite particles might also explain the high consumption of these molecules in the early stages of hydration. In fact, the amount of alkali sulfates from different influences on the early hydration of cement and the action of the latter differs from that of alkali in the phase's silicate and aluminate of cement (Collepardi et al., 1971; Uchikawa et al., 1992). Moreover, the formulation of modern concretes (SCC) that needs low W/C ratios requires the use of different superplasticizers. This brings us to the study of the interaction between cement and superplasticizer to try to clarify the problem of incompatibility between these two elements and thus avoid the problems of loss of fluidity in the implementation of concrete. For this, we first present the experiment, followed by results and discussions.

EXPERIMENTATION

The chemical and mineralogical composition of clinker used and the results of the action of different types of alkali sulphates on rheological behavior and initial hydration of cement paste are presented subsequently before being discussed. All tests are performed according to the standards (AFNOR) with a water/cement (W/C) = 0.50; however, in the presence of the superplasticizer, the W/C is reduced to 0.30.

Cements

Two cement types were used: the C1: Cement Resistant to the Sulfates (CRS) and C2: Artificial Cement Portland (CEMI). The C_3A content in the C1 and C2 are respectively of 2.33 and 8.83%. The alkali equivalent content of clinkers C1 and C2 are respectively 0.46 and 0.95%. Their content of SO_3, are respectively equal to 1.82 and 2.28%. In 1974, Oligonucleotide Separation Technology (OST) proposes a formula of the ionic composition of pore solution:

$Na_2Oeq. = Na_2O\ (\%) + 0.658\ K_2O\ (\%)$

In our case, we also considered the SO_3 from sulfates added. Cements with low alkali content tend to absorb more super-plasticizer (by electrostatic effect), but those who pose the most problems of incompatibility with polysulfonates which induce a decrease in workability (increased threshold) of suspensions (Kim et al., 2000; Griesser, 2002; Perche, 2004; Yamada et al., 2001) and cause friction between particles. The rate of solubility of sulphate is more important than the content of sulfates in cements (Prince et al., 2003).

Superplasticizer

The superplasticizer used was PNS which is a polymer that consists of the repetition of a single unit of formula: $[-CH_2-CH_5(SO_3Na)-]$. It has little effect on the hydration of clinker C_3A. Ramachadran et al. (1998) found that superplasticizers containing sulfonates are subject to an interaction preferably with the phases of C_3A. It is a chemical reaction in competition with that between the gypsum and C_3A. This reaction regulates the hydration of C_3A, otherwise, very fast (Ramachadran et al., 1998). The compositions of mixtures studied are given in the following Table 1.

Flowability and slump test

Samples were tested for flowability immediately after mixing, and 30, 60, 90, and 120 min later. The slump was measured at 20°C, using a mini-cone with a top diameter of 70 mm, a 100 mm bottom diameter and a height of 60 mm (EFNARC, 2002).

Rheological test

These tests are performed on several series of samples with a W/C = 0.30 in the presence of superplasticizer. The superplasticizer dosage is determined by testing the saturation point. Rheology tests were performed at 20°C using a rheometer AR2000 equipped with a valve rotor speed imposed according to the following:

Table 1. Characteristics of mixtures.

Mixtures	**wt%**						**DS**
	C_3A	**SO_3**	**Na_2Oeq**	**Na_2O**	**K_2O**	**SO_3***	
C1 without addition	2.33	1.82	0.46	0.09	0.56	0.00	3.07
C1-GY (5 wt% Gypsum)	2.33	1.82	0.46	0.09	0.56	2.06	6.55
C1-Na (5 wt% Na_2SO_4)	2.33	1.82	0.46	0.09	0.56	2.81	7.82
C1-K (5 wt% (K_2SO_4)	2.33	1.82	0.46	0.09	0.56	2.70	7.63
C2 without addition	8.83	2.28	0.95	0.41	0.82	0.00	1.85
C2-GY (5 wt% Gypsum)	8.83	2.28	0.95	0.41	0.82	2.06	3.53
C2-Na (5 wt% Na_2SO_4)	8.83	2.28	0.95	0.41	0.82	2.81	4.14
C2-K (5 wt% K_2SO_4)	8.83	2.28	0.95	0.41	0.82	2.70	4.05

SO_3*: from sulfates added.

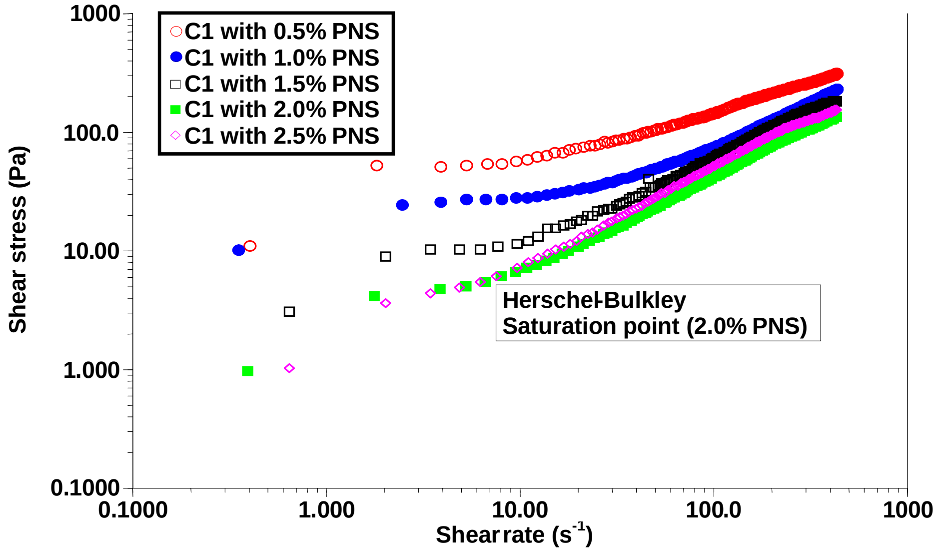

Figure 1. Shear stress as a function of shear rate of paste C1 (0.5, 1, 1.5, 2, and 2.5% of PNS) with W/C = 0.30.

presheared to 50 s^{-1} for 60 s followed by a rest period of 30 s, then a linear ramp increasing rate of 0 to 435 s^{-1} is applied through the rheometer. The flow curves were analyzed and modeled by the software, Rheology Advantage Data Analysis (Version-V4.021/TA-Instrument).

Electrokinetic potential test

The effect of different dosages of superplasticizer on the zeta potential of cement pastes was determined on a Malvern Instruments ZETASIZER 2000 particle sizer. The measuring principle consisted of forcing the particles to be studied across an electric field using laser light scattering techniques. After the bombardments of the particles, the refracted laser will be collected using a correlator in order to transform it into measurement data with the potential of the particle's electric double-layer. One centimetre cube of the cementitious suspension was diluted in 30 cm^3 of distilled water, after which 5 ml of this suspension was injected into the analyser.

RESULTS AND DISCUSSION

Saturation point of superplasticizer by rheometer

The saturation point is the dosage beyond which the superplasticizer has no effect on the rheological properties of the slurry of cement paste or concrete. It is determined, using the rheometer AR 2000. The saturation point of superplasticizer with a W/C ratio of 0.30 was first determined for the C1 and C2 alone (without sulfates). The results are as shown in Figures 1 to 6.

From these curves, we note that the saturation point in PNS is 2% for the C1 and 2.5% for the C2. This is due to the

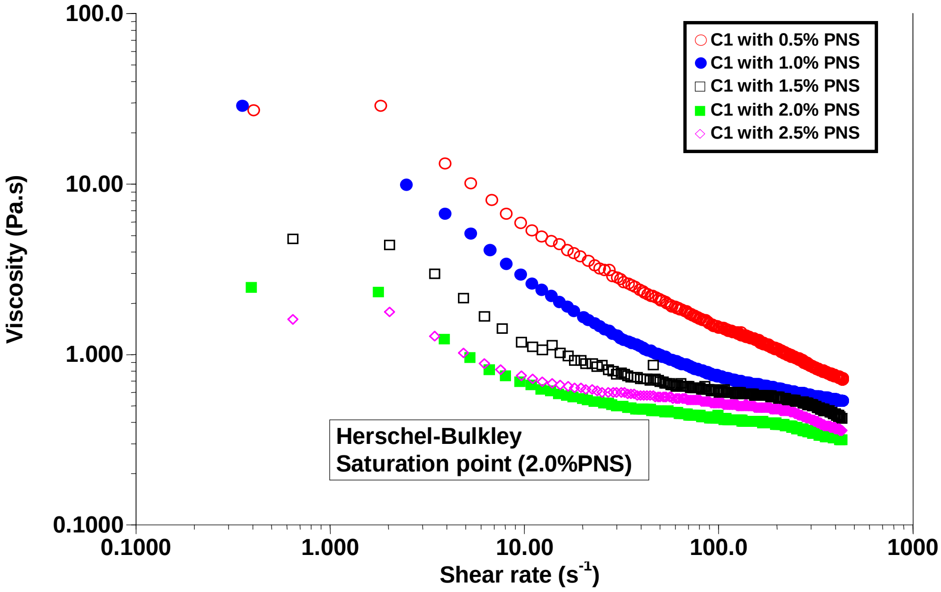

Figure 2. Plastic viscosity as a function of shear rate of paste C1 (0.5, 1, 1.5, 2, and 2.5% of PNS) with W/C = 0.30.

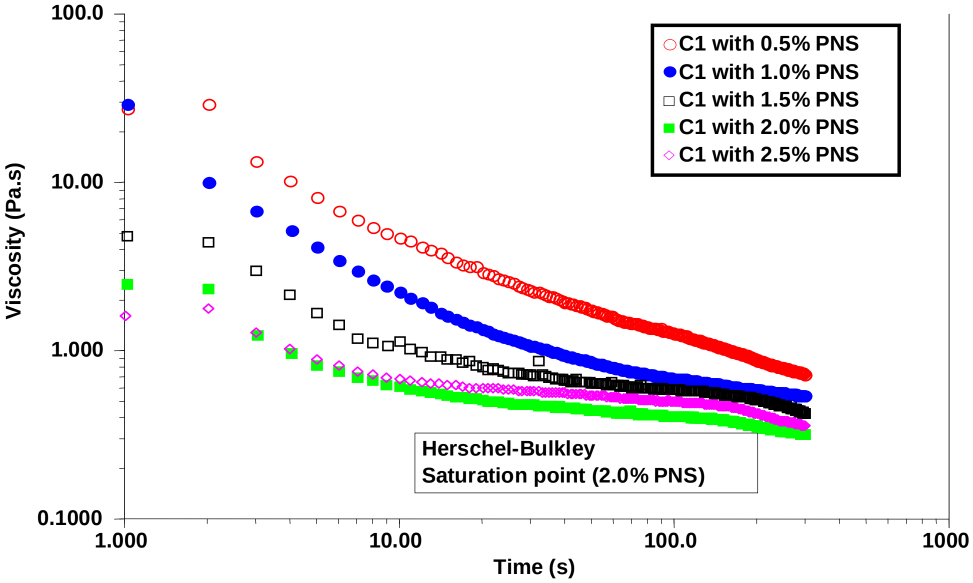

Figure 3. Time dependent behavior of paste C1 (0.5, 1, 1.5, 2, and 2.5% of PNS).

fact that both cements have different mineralogical and chemical compositions. However, the C2 cement has a higher content of C_3A and SO_3 which are more reactive sites (Figures 1 and 4).

At 2% of PNS, the cementitious pastes (C1) become more fluid with a constant viscosity (Figure 3). However, in the cement paste (C2), the flow becomes Newtonian at 2.5% dosage of PNS (Figure 6).

Physical properties of cement pastes (normal consistency and setting time)

From Figure 7, we can see that the PNS superplasticizer always plays the role of water reducer, but in a different way, depending on the type of cement and with the content and nature of sulfate, therefore normal consistency depends of dosage of PNS.

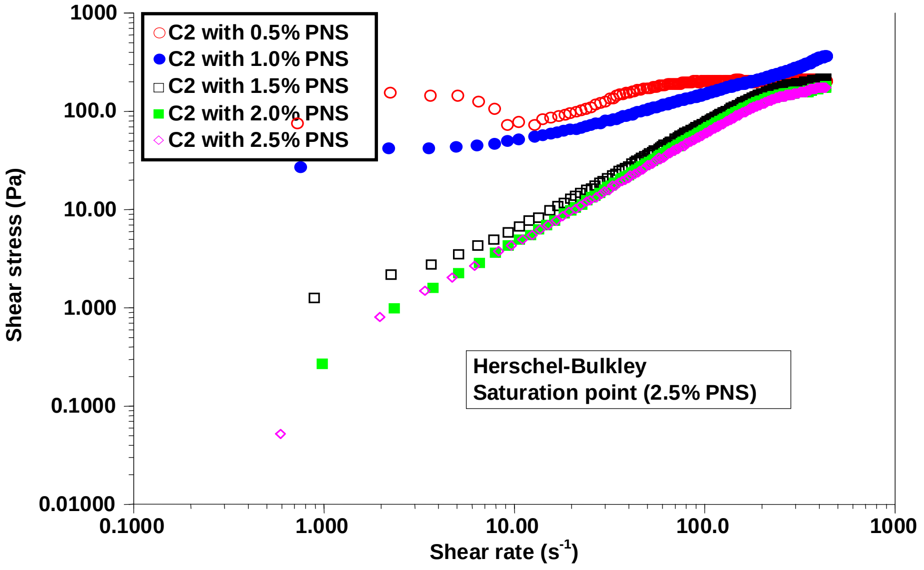

Figure 4. Shear stress as a function of shear rate of paste C2 (0.5, 1, 1.5, 2, and 2.5% of PNS) with W/C = 0.30.

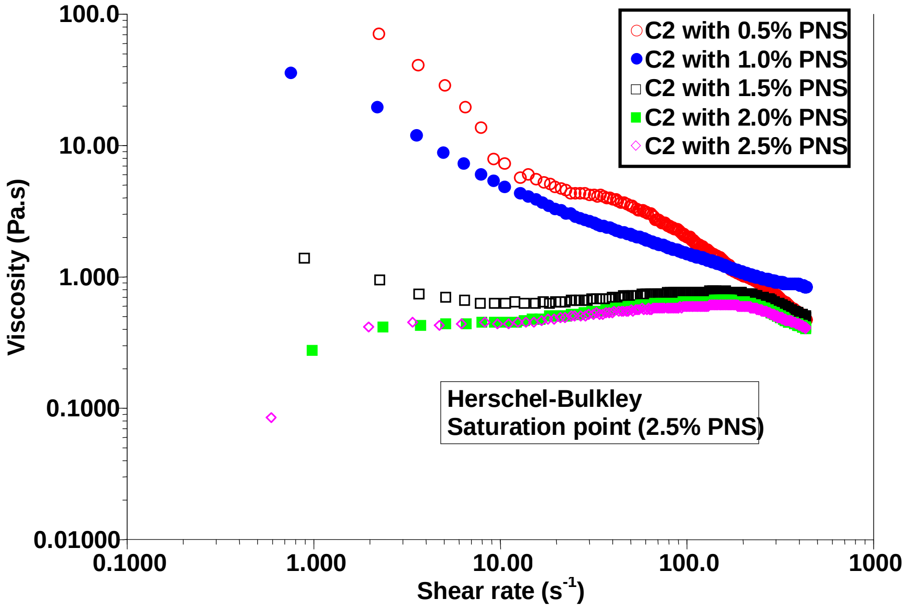

Figure 5. Plastic viscosity as a function of shear rate of paste C2 (0.5, 1, 1.5, 2, and 2.5% of PNS) with W/C = 0.30.

Generally, the water demand decreases with the increase of PNS dosage.

The C_3A content of cement: more cement is rich in C_3A, superplasticizer is less efficient because a certain amount of PNS adsorbed on the C_3A and no longer contributes, to the dispersion of cement grains. The addition of PNS to CRS and CPA gave the same consistency. Therefore, determining the saturation point was accurate.

The alkaline sulfate content of cement and nature of the sulfate used is a competitive adsorption between superplasticizer and sulfate ions on the C_3A. If the concentration of sulfate ion in cement suspension is increased, then the amount of PNS adsorbed on the surface of cement grains will be lower (Figure 7). The

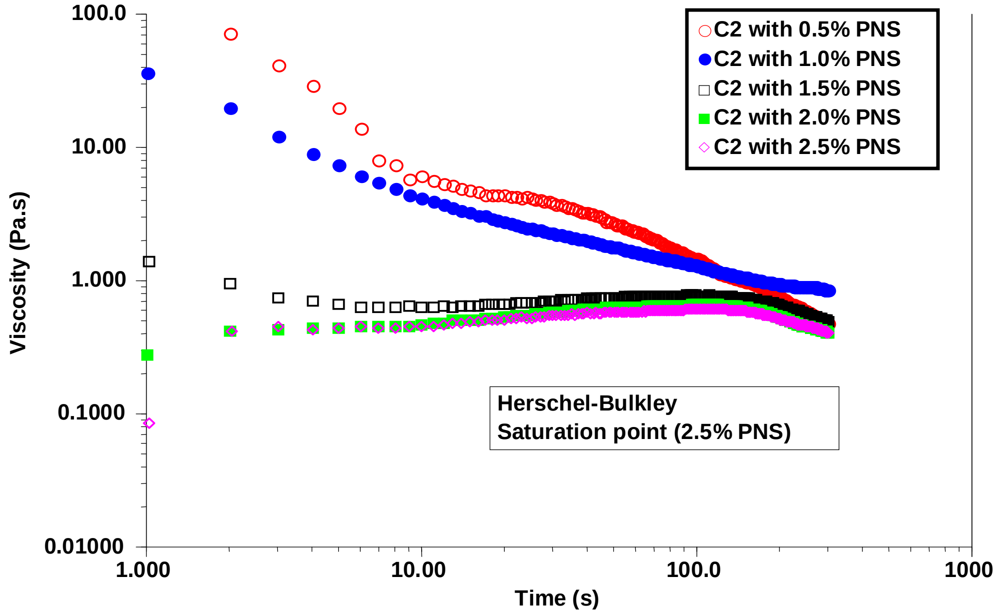

Figure 6. Time dependent behavior of paste C2 (0.5, 1, 1.5, 2, and 2.5% of PNS).

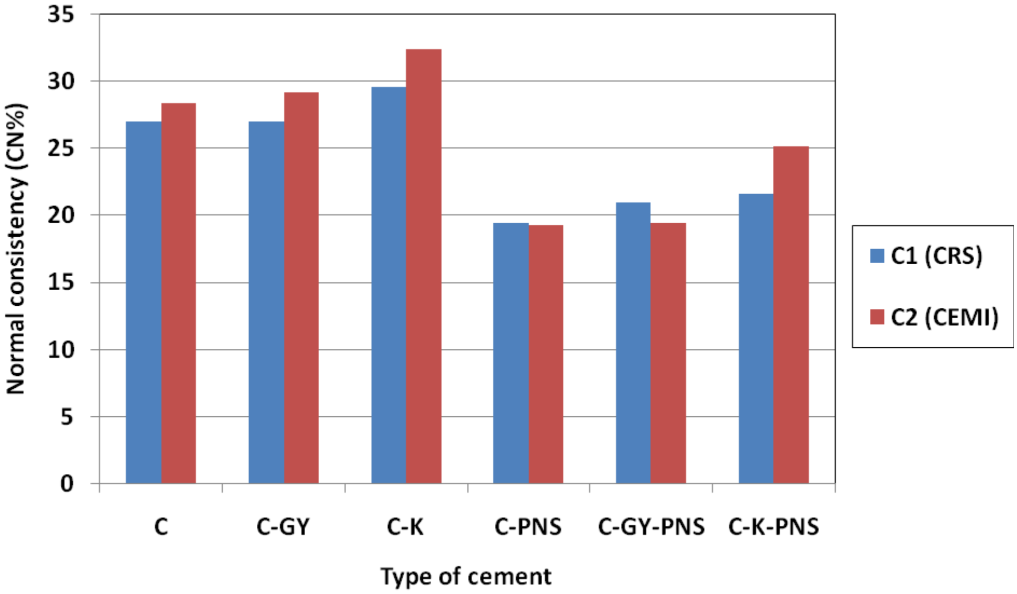

Figure 7. Effect of various alkaline and alkaline-earth ions on the normal consistency cement pastes (C1 and C2) with and without PNS superplasticizer.

types mixing C1-GY, C1-K, C2-GY, and C2-K with the PNS have greater consistency in relation to cement control (C1 and C2). Therefore, the presence of alkali tends to reduce the effectiveness of the superplasticizer. With the presence of alkali and a high concentration of alkali sulfate, the sulfate adsorb faster on the active sites of C_3A.

The nature of calcium sulfate used in the cement gypsum additions: the nature of calcium sulfate occurs mainly by its speed of dissolution, the normal consistency generally decreases with the solubility.

The specific surface cement: the more the specific surface increases, the more the normal consistency increases. The setting time of cement C2 is higher

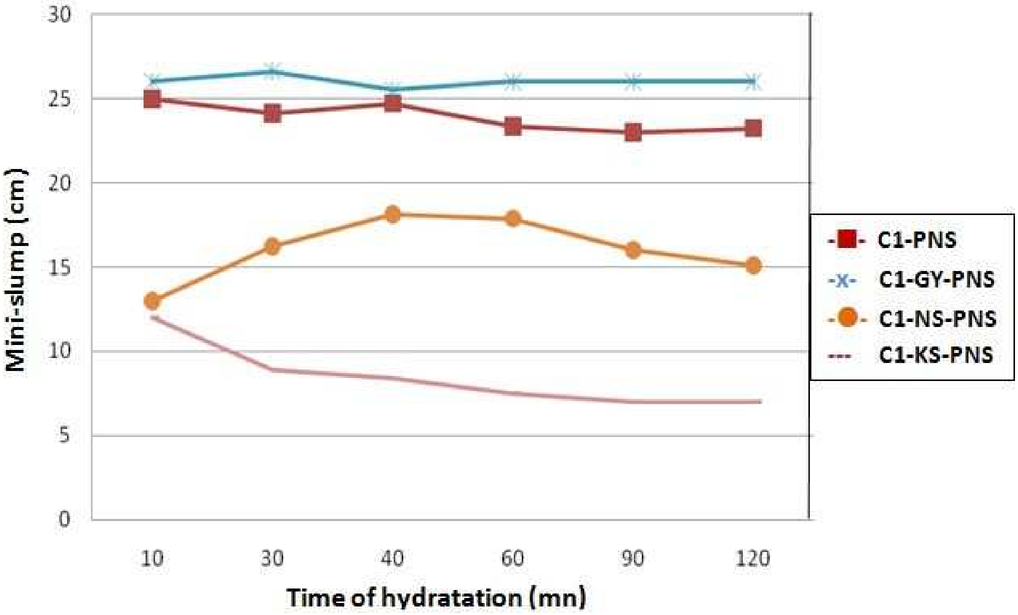

Figure 8. Fluidity and mini-slump tests as a function of hydration time of cement paste C1 (C1-Ca^{2+}, C1-Na^+ and C1-K^+) for a W/C = 0.30, with 2% of PNS.

than C1, because the setting depends on the fineness of cement, W/C ratio, temperature, and type of cement. In our case, mineralogical composition of cement is the most important factor. C1 has a high content of C_3S giving a setting time shorter. In the presence of superplasticizer (PNS), it is making a slight acceleration of setting time of cement due to better dispersion, the grain distribution of cement and water-reducing effect.

The presence of PNS in solution leads for sure to a slight increase in the solubility of sulfate in the saturated solution. However, this affects the dosages of superplasticizer and makes the setting time of cement to move faster (Platel, 2005).

Cements with low alkali content tend to absorb more superplasticizer (for electrostatic effect), but those who pose the greatest problems of incompatibility with polysulfonates, which induce a decrease in workability (increased threshold) suspensions (Kim et al., 2000), and cause friction between particles. The rate of solubility of sulphate is a parameter more important than the sulfate content in cement (Prince et al., 2003) and the setting time decreases in general in the presence of sulfates, especially with potassium sulfate (Comparet, 2004).

In the case of the addition of gypsum, the setting is accelerated with the C2, but reversed with the C1, for the content of C_3A in the C1 is low. Therefore, the gypsum is in excess and inhibits the hydration of C_3A. It is obvious that the nature of sulfate affects the setting time of cement paste. This effect also depends on the temperature, the type of clinker, the amount of SO_3, and W/C. The adsorption of polymers on the surface of cement particles would prevent the dissolution of the clinker phases in contact with water.

Rheology of cement paste

Spreading (mini slump flow test)

The mini slump flow test is typically used to study the evolution of the workability of the grout by measuring the spread diameter of the slurry on the plate at different time intervals (10.20, 30.40, 60, 90, and 120 min) (Figures 8 and 9).

All cements were tested for W/C = 0.30 in the presence of superplasticizer. The superplasticizer dosage is determined by testing the saturation point.

Usually, after mixing, the concentrations of Ca^{2+}, K^+, Na^+, OH^-, and SO_4^{2-} are rapidly reaching high values. These alkalis (Na_2O and K_2O) are initially present in the main phases of clinker or sulfated form [Na_2SO_4, K_2SO_4, $K_2Ca(SO_4)2H_2O$, $K_2Ca_5(SO_4)6H_2O$, $K_2Ca_2\ (SO_4)_3$]. The presence of these salts (Na^+, K^+) in the pore water, particularly, induces a decrease in the relative fluidity (Perche, 2004; Nehdi and Rahmam, 2004). These alkalis also have effect on the hydration of cement phases, and they cause an activation form.

Rheological behavior of cement pastes

Evolution of shear stress: from these graphs, cements behave as viscoplastic suspensions. However, exception is noted for cements which are added the Arcanite or sodium sulfate.

The threshold shear: in practice, the cement grout has a yield point and shear-thinning behavior. In the presence of superplasticizers, the threshold flow becomes very low

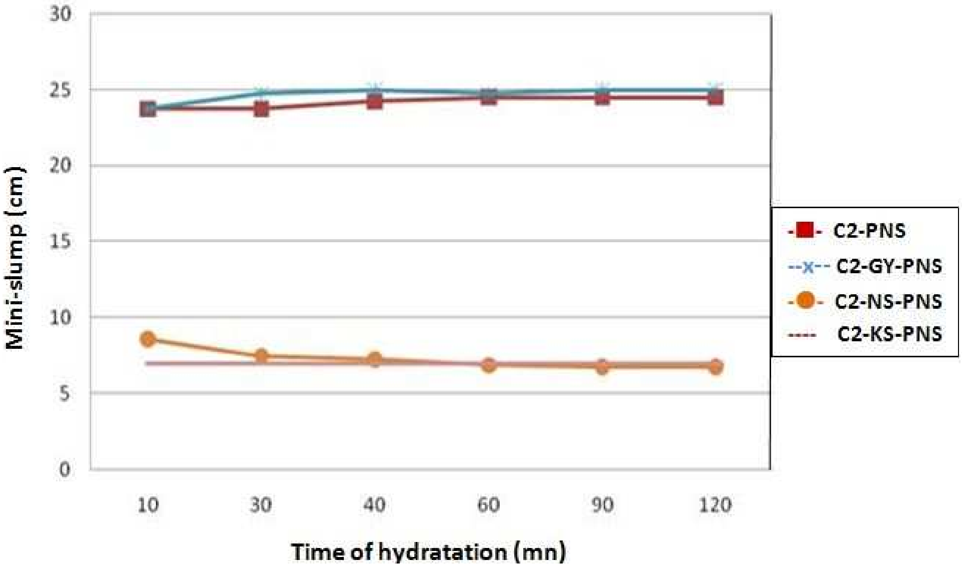

Figure 9. Fluidity and mini-slump tests as a function of hydration time of cement paste C2 (C2-Ca^{2+}, C2-Na^+ and C2-K^+) for a W/C = 0.30, with 2.5% of PNS.

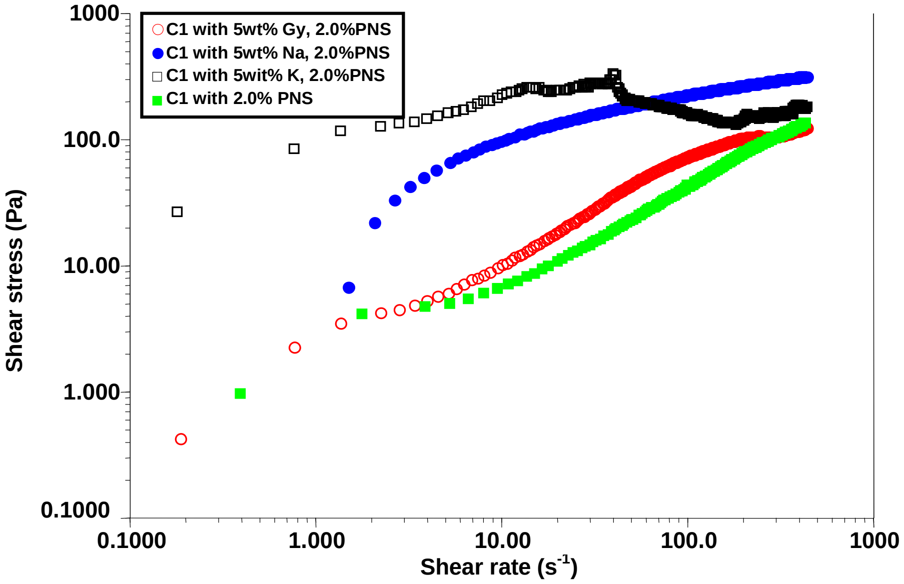

Figure 10. Shear stress as a function of shear rate of cement pastes (C1, C1-Ca^{2+}, C1-Na^+ and C1-K^+) after 12 min of hydration W/C=0.3, with PNS.

(virtually zero). However, viscosity approximately depends on the applied stress and it decreases with increasing shear rate. We note that cements C1, C1-GY, C2, and C2-GY have the same yield stress (8 Pa., approximately), while the cement-Na C1, C1-K, Na-PCA, and PCA-K have higher levels of shear (Westerholm, 2006; Plank and Hirsch, 2003).

Cements series of C2 (C2, C2-GY, PCA-Na, and C2-K) have a low yield stress as compared to cement series of C1 (C1, C1-GY, C1-Na, and C1-K): the C1 has more C_3A which ensures more adsorption of superplasticizer, that is, high fluidity and low viscosity. All grout showed a similar rheological model of Herschel Bulkley.

Viscosity: the evolution of plastic viscosity as a function of shear rate is identical to the C1 series cements and C2, with and without additions of sulfates (in the presence of PNS superplasticizer) (Figures 9 to 11). The highest plastic viscosity (C1-C2-K and K) can result in the

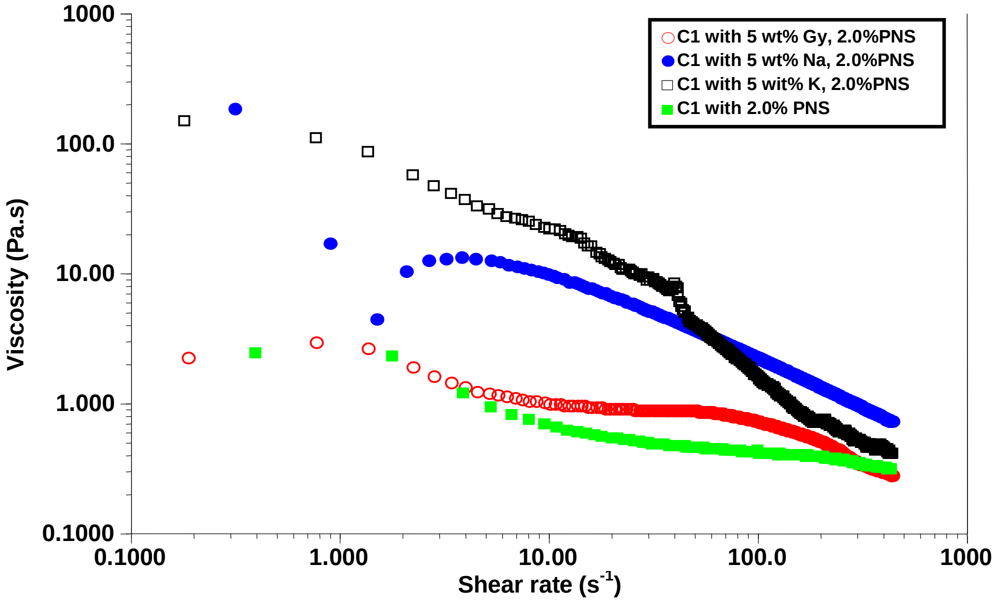

Figure 11. Apparent Viscosity as a function of shear rate of cement pastes (C1, C1-Ca^{2+}, C1-Na^{+} and C1-K^{+}) after 12 min of hydration W/C=0.3, with PNS.

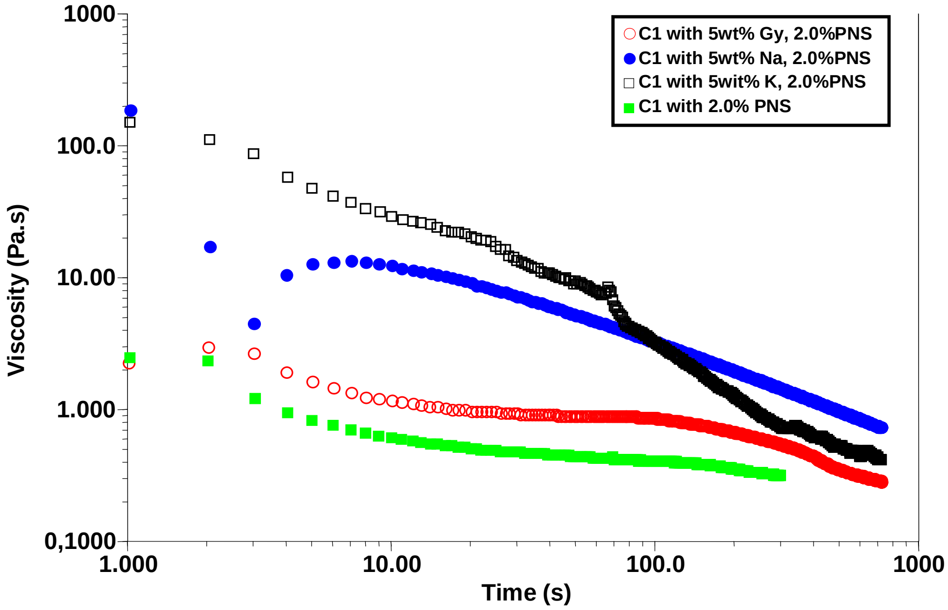

Figure 12. Time dependent behavior of paste C1 (C1, C1-Ca^{2+}, C1-Na^{+} and C1-K^{+}).

formation of syngenite ($CaSO_4.K_2SO_4.2H_2O$) from the Arcanite. This training requires a lot of water, and in addition there will be an increase in the kinetics of hydration of cement phases (especially C_3A) by the alkali ions from the Arcanite. The negative effect of the Arcanite aphtitalite and the fluidity is enhanced by the presence of superplasticizer (Collepardi, 1971; Uchikawa et al., 1992). It seems that the dispersing effect of superplasticizer accelerates the hydration reaction (Prince, 2002; Pourchet et al., 2009). The analysis shows that increasing the amount of alkali in cements (mostly cement with Arcanite) significantly increases the loss-spreading grout corresponding (Figures 10 to 12). This loss spreading is associated with a high viscosity

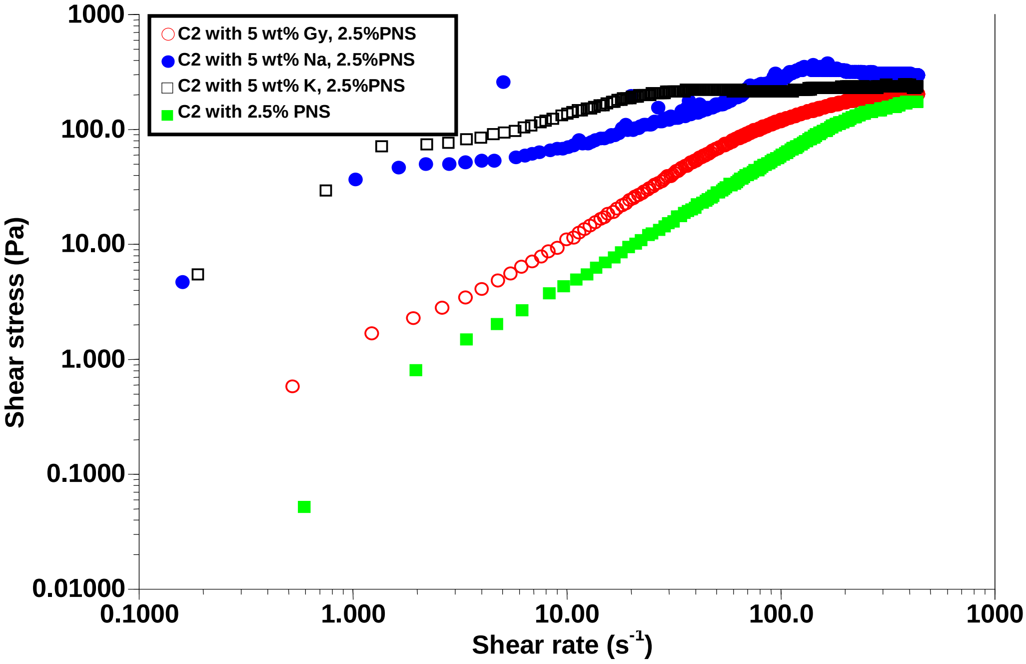

Figure 13. Shear stress as a function of shear rate of cement pastes (C2, $C2\text{-}Ca^{2+}$, $C2\text{-}Na^{+}$ and $C2\text{-}K^{+}$) after 12 min of hydration W/C=0.3, with PNS.

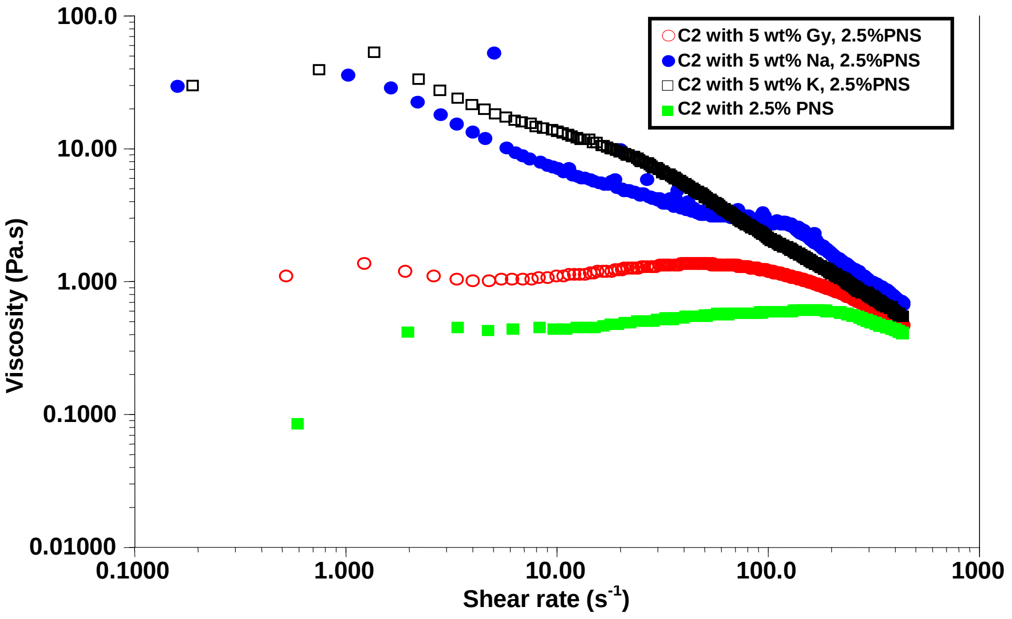

Figure 14. Apparent Viscosity as a function of shear rate of cement pastes (C2, $C2\text{-}Ca^{2+}$, $C2\text{-}Na^{+}$ and $C2\text{-}K^{+}$) after 12 min of hydration W/C=0.3, with PNS.

(Figures 13 to 15). At ratios W/C = 0.30, despite the presence of superplasticizer, grouts based cements Arcanite are too steep to be kneaded. We conclude that the substitution of the Arcanite (or aphtitalite) with gypsum, could improve the fluidity of cement, which provides a better initial hydration.

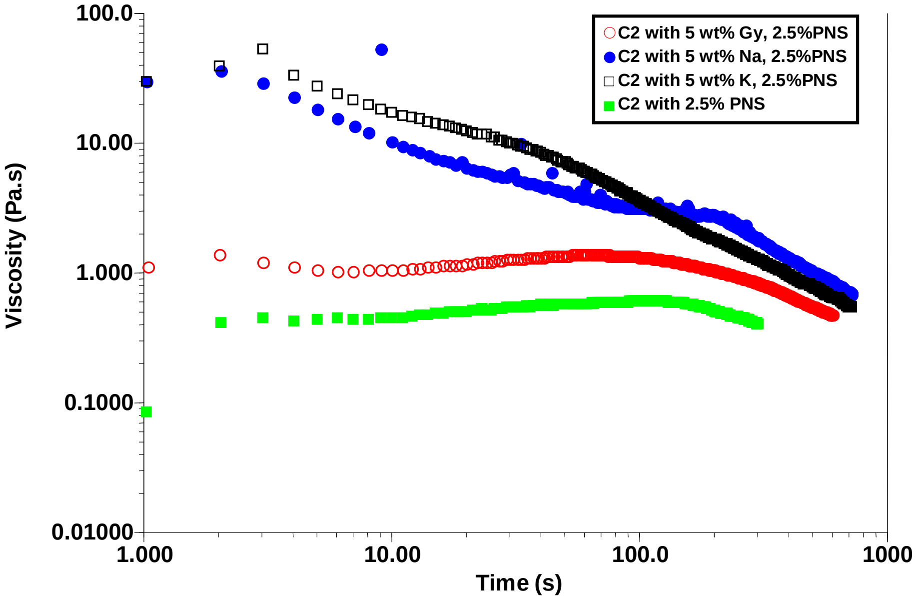

Figure 15. Time dependent behavior of paste C2 (C2, C2-Ca^{2+}, C2-Na^{+} and C2-K^{+}).

Zeta potential: according to the literature, the zeta potential of cement without superplasticizer is positive in the range from 2 to 5 mV and cement with superplasticizer has a negative potential from -8 to -28.4 mV (Plank and Hirsch, 2003; Bassioni, 2006).

The two cement pastes exhibited a value of potential (+2.02 mV for C1 cement and -7.14 mV for C2 cement) before superplasticizer was added, but the most high value of zeta potential recorded is approximately -22.30 mV (Figure 16). Indeed, the cement particle is positively charged and will be neutralized by adsorption of the superplasticizer on the surface of cement grains of side COO^{--} group, which gives a negative zeta potential. This is explained by the fact that adsorption of superplasticizer increases gradually. Thus, the double layer becomes thicker which helps increase the potential zeta. The zeta potential measurements showed that C2 (CEMI) has values higher than those presented by C1 (CRS). This can be explained by the mineralogical composition of the two cements and also the reports C_3S/C_2S and C_3A/C_4AF. Moreover, a greater amount of polymer adsorbed increases the value of zeta potential (Perche, 2004).

The reason of the positive value of zeta potential of the cement paste with C1 is that the zeta potential of this cement depended on their C_3A content. During hydration, cements with higher C_3A and sulphate contents form larger amounts of ettringite, a phase with a positive zeta potential (Prince et al., 2003; Pourchet et al., 2009). However, the cement pastes with C2 (0% PNS), present values of the negative potential. That is explained by the presence of the ions sulphates coming from the electrolytes (NS, KS and GY), which increased the thickness of the diffused layer of the cement particles (Andersen, 1986; Kim, 2000).

The zeta potential remained essentially unaffected in both types of pastes when a 0.5% dose of PNS was added. The absolute value of the zeta potential clearly increased with rising dosages of PNS. In the C2 suspensions, the potential increased from 0.5, a 2.5% PNS. The pastes containing 0.5 or 2.5% PNS exhibited nearly identical zeta potentials. The explanation for this observation is the difference between the mechanisms governing the action of the superplasticizer (PNS) in presence the different sulphates (Pourchet et al., 2009).

Conclusion

The influence of sulphates on the rheological behavior of cement paste depends not only on the quantities present in the clinker, but the natures of sulfates that are present. The presence of a high amount of alkali in alkali sulphates has a negative effect on fluidity.

The effect of calcium sulfate is twofold. It starts by reducing the amount of alkali in replacing them, but also brings Ca^{2+} in the solution, which allows slow hydration phases of cement. Adding a large amount of gypsum is needed with the clinkers rich Arcanite and/or aphtitalite. Arcanite cements with and/or have an application aphtitalite superplasticizer higher than cements with syngenite and/or calcium langbeinite. A large presence of sulfates or hemihydrate in cement can cause crystallization of syngenite or gypsum which may decrease the fluidity. The optimization of the quantity and nature of sulfate in the cement remains a delicate

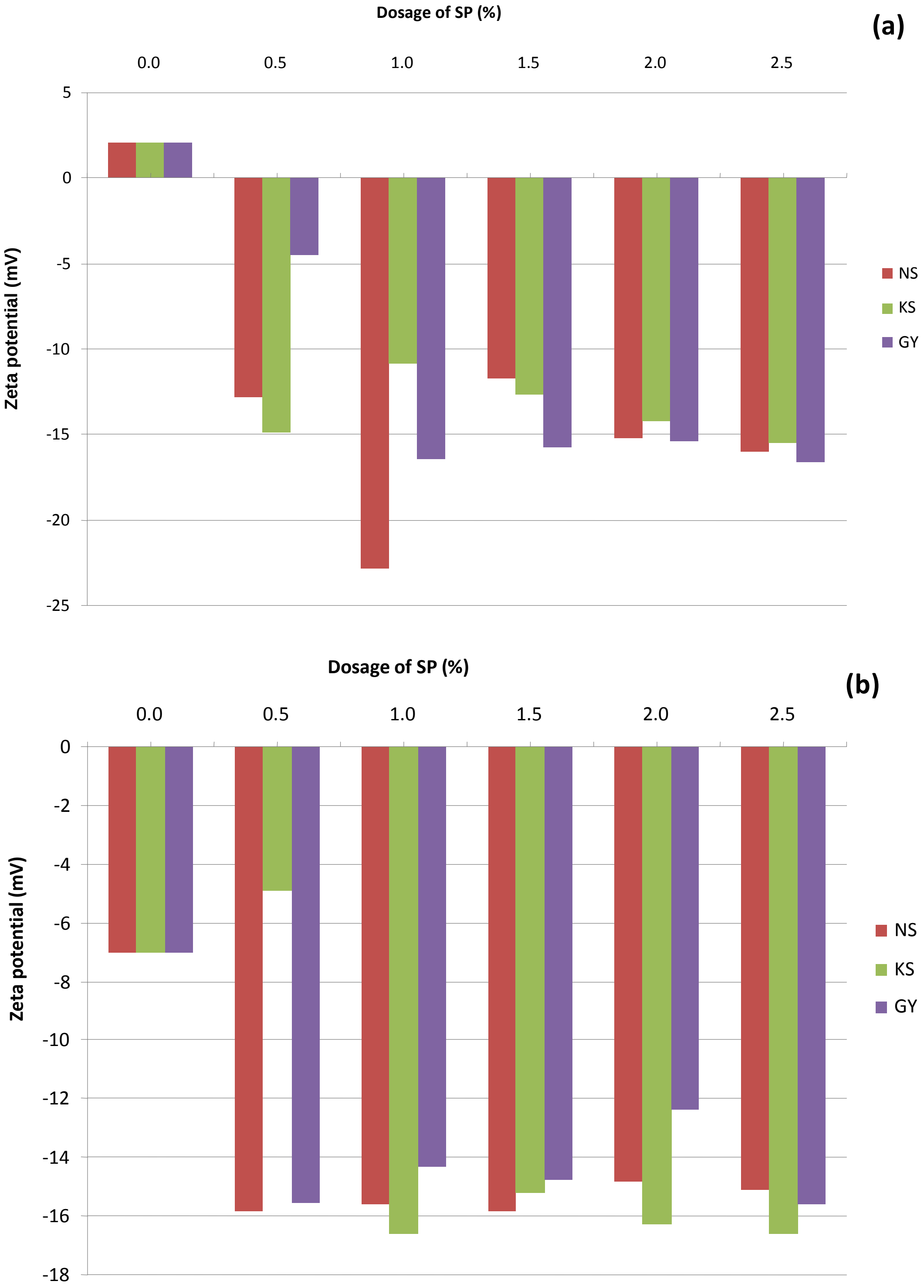

Figure 16. Variation of zeta potential in cement pastes with increase of PNS; (a) C1 (b) C2.

experimental procedure. The hydration reactions are governed by the texture hydrates spontaneously products and their formation is generally a function of the composition of the solutions. The complexity of these reactions, as well as the variation of phases and types of sulfates in cement, forms a system difficult to control.

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