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Influence of cement and superplasticizers type and dosage on the fluidity of cement mortars—Part I

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Abstract

Concrete quality is controlled by the flow behavior of cement paste, which is related to the dispersion of cement particles. Superplasticizers (SPs) provide the possibility of a better dispersion of cement particles, thereby producing paste of higher fluidity. With the development of high strength, high performance concrete, SPs are becoming indispensable. SPs are adsorbed on the cement particles. This adsorption is uneven and depends upon the clinker composition of cement and the type of SP used. This work is focused on the study of the influence of lignosulfonic acid (LS)- and melamine sulfonic acid (SMF)-based SPs on the fluidity of mortars made with ordinary Portland (OPC), low alkali (LAC) and white cement (WC) at different water to cement ratio. It is shown that LS are more effective than SMF in providing better fluidity. Further WC has given the highest fluidity among the cements used. It is attributed to the lower C_3A+C_4AF and alkali content, and higher SO_3 content.

Keywords: Adsorption; Clinker mineral; Workability; Cement paste; High-range water reducers

1. Introduction

The properties of concrete are governed by its flow behavior, which is controlled by the dispersion of cement particles. It is widely known that better fluidity is achieved by the addition of superplasticizers (SPs). The role of SPs in concrete has therefore become increasingly important. For instance, the contribution of SP in the development of high strength concrete is remarkably larger than that of cement. The SPs are adsorbed on the cement particles, which deflocculate and separate, releasing trapped water from cement flocks. A variety of SPs have been developed and are available in the market. These belong to different basic groups, such as lignosulfonic acid (LS), melamine formaldehyde sulfonic acid (SMF), naphthalene formaldehyde sulfonic acid (SNF) and polycarboxylic acid (CE). Apart from the SPs of different basic groups, there can also be differences in SPs from the same group depending upon their synthesis, which influences upon the molecular weight and chemical configuration. The problem, which is encountered in the interpretation of results, very often is the non-availability of data, especially the molecular weight of SPs. Cements, on the other hand, vary in composition and fineness, which influence upon the hydration process and thereby on the flow behavior of cement paste. In this work, influence of different dosage of lignosulfonate and sulfonated melamine formaldehyde SPs, on the fluidity of mortars made with ordinary Portland cement (OPC), low alkali cement (LAC) and white cement (WC) has been studied. Possible mechanism of interaction is discussed.

2. Materials and methods

2.1. Cements

Three types of cements were used. OPC and LAC were supplied by Cementa, Sweden. WC was supplied by Aalborg Portland Cement, Denmark. The properties are shown in Table 1.

2.2. SPs

LS, Cementa P40, was supplied by Cementa.
SMF, Cementa Flyt 92M, was supplied by Cementa.

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Table 1
Composition and properties of the cements used: OPC, LAC, WC

	OPC	LAC	WC
C_2S, %	13	22.8	25
C_3S, %	64	55.7	63
C_3A, %	5	2.1	4
C_4AF, %	10	13.1	1
K_2O+Na_2O, %	1.6	0.5	0.3
SO_3, %	3.2	2.4	3–5
Specific surface area, m^2/kg	337	304	410
Density, kg/m^3	3200	3210	3150

* Data presented were supplied by the manufacturers.

Standard grade sands 1, 2 and 3 was used. The mortars were made with 1:3 cement to sand ratio, where equal part of each sand grade was mixed. Mortars were mixed in a Hobart mixer. Fluidity was measured on the cement mortars made with different types of cements and SPs at different water to cement ratios. The dosage of SP mentioned in this study was calculated to the weight of cement. Flow was measured at 20 °C by pull out spread of the mortar from a cone of top diameter 70 mm, bottom diameter 100 mm and height 60 mm. The spread was the average of two perpendicularly crossing diameters. From the spread (F), relative flow area ($\tilde{A}$) was calculated by Eq. (1) [1].

$$\tilde{A} = (F/r_0)^2 - 1 \quad (1)$$

where $r_0 = 50$ mm, bottom cone radius.

Flow area and fresh density of mortars with OPC, LAC and WC with different dosage of LS (P40) and SMF (Cementa Flyt 92M) were measured at different water to cement ratios. Air content was calculated. Flow area and

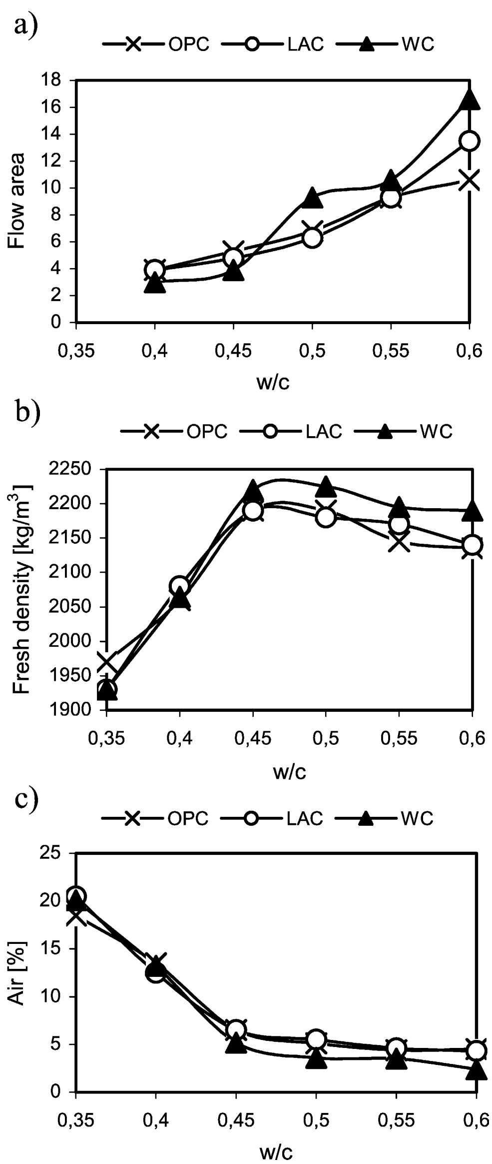

Fig. 1. Relation between flow area (a), fresh density (b) and air content (c) for OPC, LAC and WC at different water to cement ratio.

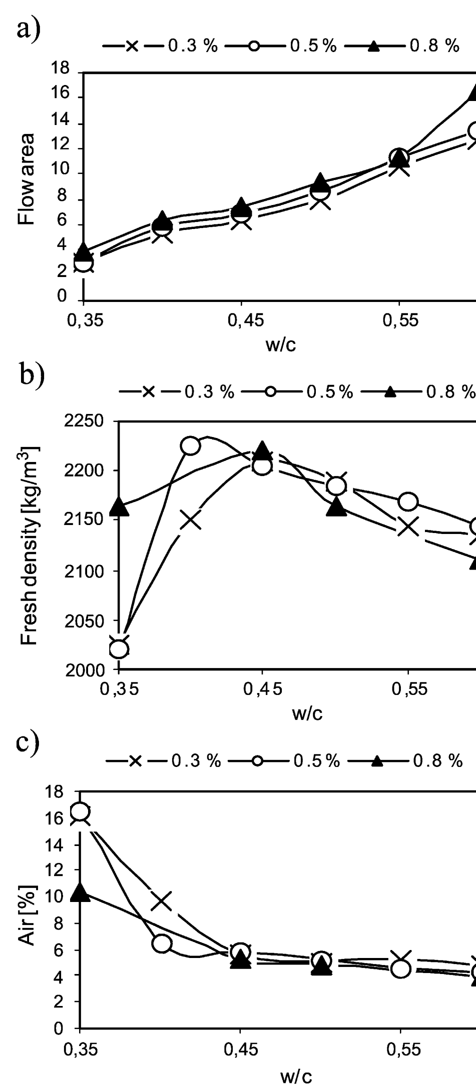

Fig. 2. Flow area (a), fresh density (b) and air content (c) with respect to water to cement ratio at different dosage of lignosulfonate SP, P40. For OPC.

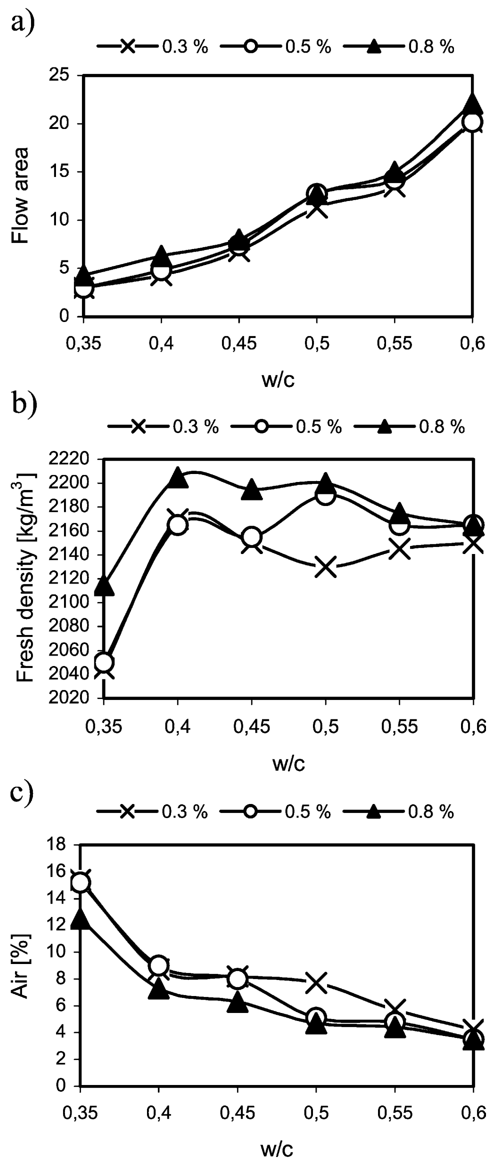

Fig. 3. Flow area (a), fresh density (b) and air content (c) with respect to water to cement ratio at different dosage of lignosulfonate SP, P40. For LAC.

fresh density data presented are based on triplicate measurements. The average standard deviation in determining flow area is 1.12 and for the fresh density determinations 5.88. The results are shown in Figs. 1–7.

3. Results and discussions

The results of the tests performed with three cements without SP are shown in Fig. 1a–c. It is seen here that there is no significant difference on the fluidity of mortars up to 0.45 water to cement ratio. At 0.50 water to cement ratio, the fluidity of WC increased compared to the other cements, whereas the cement OPC and LAC have shown the same fluidity. High fluidity was marked at 0.60 water to cement ratio. Similar trends were observed with the fresh density up to 0.45 water to cement ratio. At 0.50 water to cement ratio, the fresh density of WC was slightly higher, while the air content was slightly lower than for the other two cements. This was due to better compaction of the mortar because of enhanced fluidity.

Fig. 2 shows the results of mortars made with OPC and 0.3, 0.5 and 0.8 wt.% of lignosulfonate (P40) SP. It is seen from Fig. 2a–c that the addition of P40 has increased the flow. However, an increase in the dosage from 0.3% to 0.5% did not result in a significant increase on the flow, marginal changes are, however, noted. At 0.8% P40, the flow was also similar to 0.3% and 0.5%, but has significantly increased at 0.6 water to cement ratio. Substantial differences on fresh density were observed up to 0.45 water to cement ratio, exceeding, which no appreciable difference in the fresh density could be noticed. At 0.35 water to cement ratio, the density of mortars with 0.3% and 0.5% P40 are

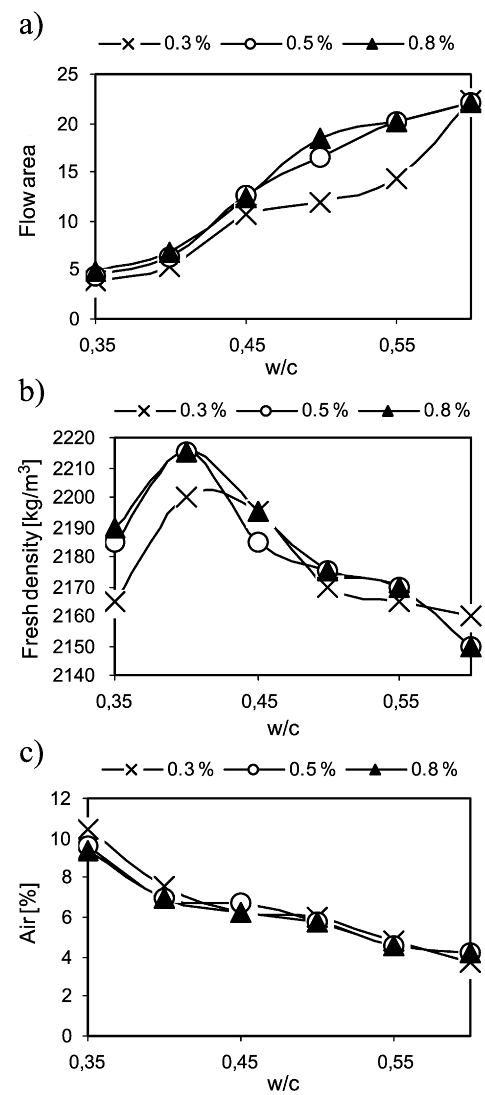

Fig. 4. Flow area (a), fresh density (b) and air content (c) with respect to water to cement ratio at different dosage of lignosulfonate SP, P40. For WC.

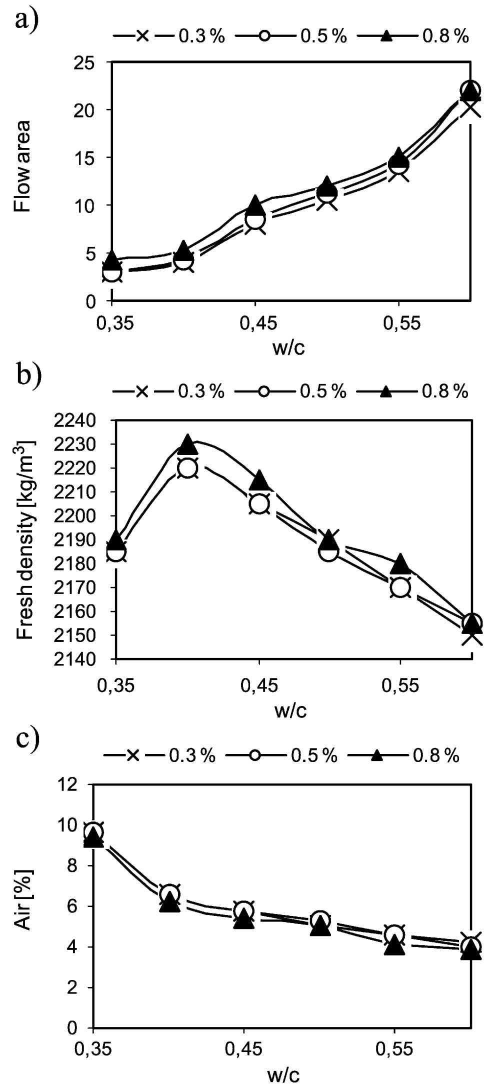

Fig. 5. Flow area (a), fresh density (b) and air content (c) with respect to water to cement ratio at different dosage of SMF SP, Flyt 92M. For OPC.

similar and lower than that obtained with 0.8% P40. This is in agreement with the air content, which is higher for 0.3% and 0.5% and lower for 0.8% P40. Increase in the density at 0.45 water to cement ratio follows with lower air content. At 0.35 water to cement ratio, the lower density and consequently higher air content is due to inadequate packing of the mortar in the pot during weighing for density determination. With increase in the water to cement ratio to 0.50 wettability increases, which provides better compaction, thereby density increases and air content decreases compared to with 0.35 water to cement ratio. With further increase in the water to cement ratio, flowability increased but there is not so much decrease in the density as the mass was very cohesive and there was no bleeding. Because of this the air content is low and stable.

Fig. 3 shows the influence of P40 on LAC. It is seen from the figure that the flow of mortars with 0.3%, 0.5% and 0.8% P40 were similar. The density and air content have, however, some differences when the dosage increased to 0.8% compared to 0.3% and 0.5%. It is attributed to the increase in cohesiveness of mortar with increased dose of P40.

Fig. 4 shows the influence of P40 on WC. It is seen from Fig. 4a that there is no significant difference in the fluidity up to 0.40 water to cement ratio for different doses of P40. At 0.45 water to cement ratio, there is a substantial difference in fluidity between 0.3% and 0.5%. Whereas between 0.5% and 0.8%, there is practically no difference. There was no substantial difference in the densities and air content for the three dosages of P40 at all the water to cement ratios (Fig. 4b,c). It is, however, observed that, at 0.35 water to cement ratio, the density was low and the air content was high. It is because of the inadequate fluidity and thereby bad compaction of the mass in the density measurements. At 0.40 water to cement ratio, the density increased for the three dosages. With higher water to cement ratios,

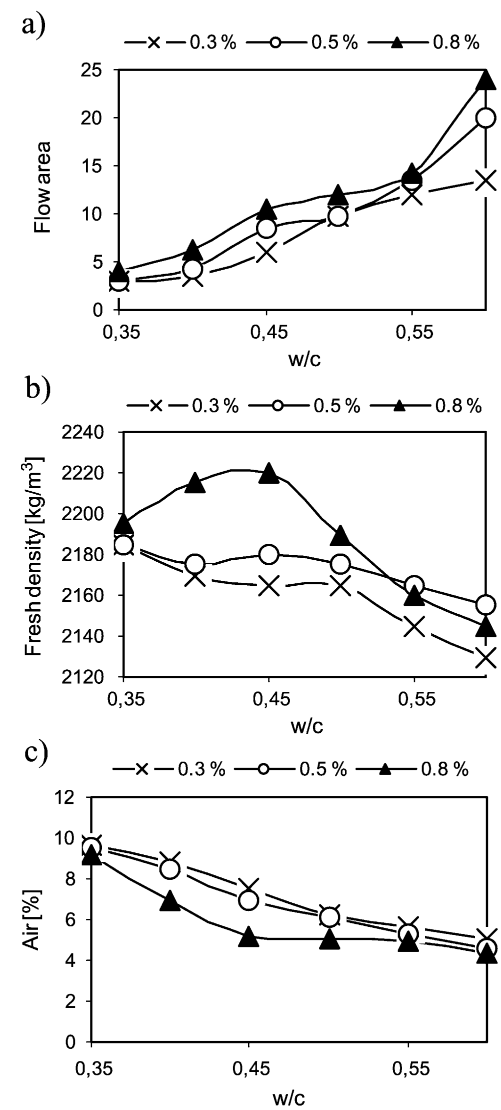

Fig. 6. Flow area (a), fresh density (b) and air content (c) with respect to water to cement ratio at different dosage of SMF SP, Flyt 92M. For LAC.

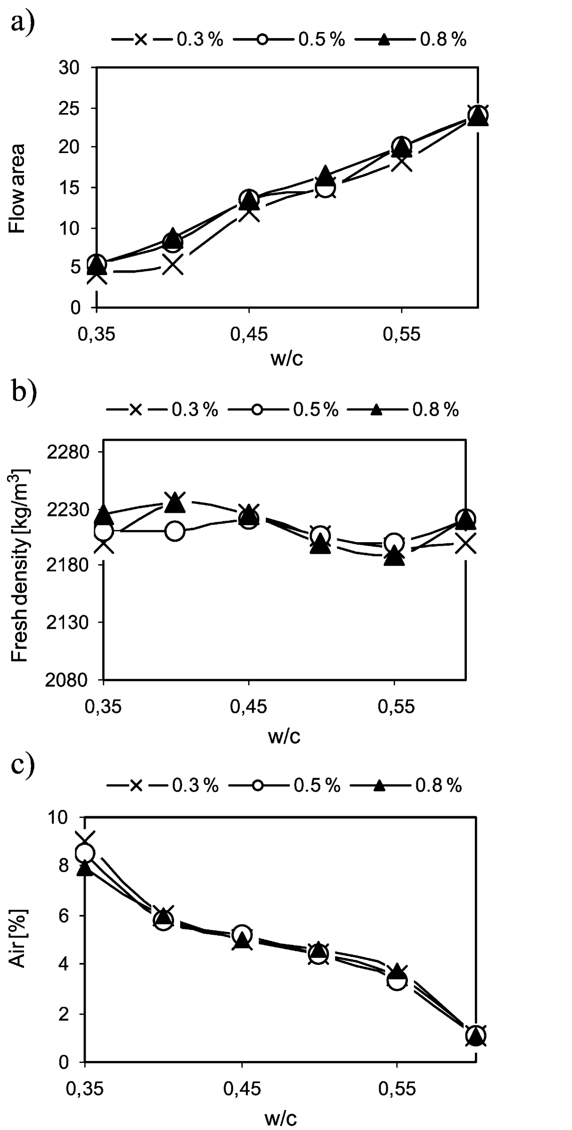

Fig. 7. Flow area (a), fresh density (b) and air content (c) with respect to water to cement ratio at different dosage of SMF SP, Flyt 92M. For WC.

the density decreased, as the fluidity increased. The air content decreased simultaneously. It was noted that the cohesiveness of the mixture increased with the increase in the P40 dosages.

Identical tests were performed with SMF (Flyt 92M) and three cements OPC, LAC and WC. Fig. 5 shows the influence of SMF on OPC. It is seen here that, with OPC, there is no difference in the flow, density and air content with increase in the dosages of SP (Fig. 5a–c). Increase in the water to cement ratio increased the fluidity equally.

Fig. 6 shows the influence of SMF on LAC. It is seen from Fig. 6a that, with LAC, the fluidity increased with the increase in the water to cement ratio. It was higher for 0.8% compared to 0.3% and 0.5%. At 0.55 and 0.60 water to cement ratio, the fluidity increased more for 0.5% and 0.8% compared to 0.3% (Fig. 6a). The density was lower for 0.3%. For 0.5%, it was almost constant up to 0.55 water to cement ratio and then decreased at 0.60 water to cement ratio. At 0.8% SMF, there is a slight increase in the density at 0.4 and 0.45 water to cement ratio and then a decrease. This decrease in density is due to the increase in the fluidity (Fig. 6b). The air content for 0.3% and 0.5% SMF was the same at all the water to cement ratios. It, however, decreased with 0.8% water to cement ratio up to 0.50, beyond which it became constant (Fig. 6c).

Fig. 7 shows the influence of SMF on WC. It is seen here that there is no appreciable difference on fluidity, density and air content with increasing dosage. The fluidity increased with increase in water to cement ratio (Fig. 7a). But there was practically no difference in the density (Fig. 7b). The air content decreased with the increase in the fluidity and exceeding 0.55 water to cement ratio, there was practically no air in the mixture (Fig. 7c). It shows that the increase in the dose of SMF does not increase the fluidity, 0.3% can be translated as the optimum dose. WC cement has shown the highest fluidity compared to the other cements.

3.1. Compatibility of cements with LS and SMF

The fluidity of a cement paste is related to the hydration of the cement, which, in its turn, is connected with the cement composition and fineness. Cement particles contain several mineral phases of different reactivity, as well as a variety of chemical and structural defects. Their initial hydration will likely generate a surface with important variation in the surface charge density, both in size and magnitude. These localized surface charges promote flocculation of hydrating cement particles, but they can be effectively neutralized and separated by the anionic charge of the SP molecules.

The hydration of interstitial phases is affected by the concentration of Ca^{2+}, OH^- and SO_4^{2-} ions in the mixing water. The concentration of those ions depends upon the amounts of alkali sulfate, gypsum and free lime in the cement just after mixing with water, after that, it depends upon the hydration reaction of C_3S, alite. The hydration of interstitial phases is affected in particular by the lime–saturation ratio. Since small crystals of ettringite, which are produced in high concentration conditions, cover the unreacted interstitial phase, the hydration reaction rate slows down. On the contrary, in low ion concentration conditions, large amounts of ettringite are produced in the shape of large needles. In this case, the hydration of the interstitial phase continues to produce large amounts of ettringite, which causes the stiffness and pseudo-setting [2,3].

A few points relevant in the interaction of SP with cements, which are sometimes overlooked, are worth mentioning [4].

First, the relative sizes of the particles in a cementitious system of SP molecules differ typically by two or three orders of magnitude; the average diameter of cement particles are typically of 10 μm, whereas the size of the SP molecules is of the order of a few nanometers.

Second, since the initial surface hydration of cement particles is extremely rapid ($t^{1/2} < 1$ min), the action of SP molecules will mainly occur on the surface of the hydrated particles.

Third, as complex chemical entities, SP molecules can themselves participate in chemical processes.

3.2. Depletion effect

As the hydration reaction proceeds, the amount of free water decreases, and so does the distance between the hydration surfaces of the neighboring cement (hydrate) particles. As the interparticle volume becomes smaller, the concentration of SP molecules becomes higher, the concentration of SP molecules confined in this volume may create a substantial osmotic pressure effect. The latter would either tend to expel the SP molecules from the confined interparticle volume or create a water flow to dilute the polymer molecules in that region. The first effect would lead to induce a particle–particle attraction, while the latter would induce additional particle–particle repulsion.

The variation in lime saturation ratio with different water to cement ratio varies with the cement type used. The variation of the lime saturation ratio when using a lignin sulfonic acid based admixture is smaller than the variation observed when using no admixture or SMF. The reason is that lignin sulfonic acid based admixture binds up the Ca^{2+}, and the concentration of Ca^{2+} in the pore solution is therefore lowered. It is seen from the experiments that at up to 0.55 water to cement ratio there was not significant increase in the fluidity, but exceeding this, the fluidity increased substantially. It seems that, up to the water to cement ratio of 0.55, the Ca^{2+} were blocked by the LS, indicating the formation of an interlayer complex [5]. With an increase in the water to cement ratio, more alite hydrates and thereby more Ca^{2+} ions are produced. Lime saturation in the pore solution increases, poisoning the hydration process. Subsequently the fluidity increases.

The admixture is not evenly adsorbed on cement particles. It adsorbs more readily on C_3A, C_4AF than on C_3S and C_2S [6]. Comparisons of SMF and LS have shown that SMF is even more unevenly adsorbed on the clinker minerals than LS is.

The more even the adsorption of SMF, the higher the fluidity. The admixture is so unevenly adsorbed on cement containing much $C_3A + C_4AF$ that the amount of admixture adsorbed on alite and belite is relatively decreased, thereby lowering the fluidity of the paste. The more even the adsorption of admixture on cement minerals, the higher the fluidity of the paste will be. Thus, the amount of the admixture adsorbed on the cement sometimes fluctuates greatly, as it depends on the mineral composition of the clinker.

In this work, the highest fluidity was observed with WC both for LS and SMF, followed by the cements LAC and OPC. The reason is the low $C_3A + C_4AF$ and low alkali content of the WC. This agrees with the results reported by Hanna et al. [7]. However, a comparison with the fineness shows a contradiction. The fineness of WC is the highest, yet it has shown the highest fluidity. This may be due to the fact that $C_3A + C_4AF$ and the alkali are very low and the sulfate content is high. Because of the competitive adsorption between SP and SO_3, most of the SP remained in the solution, poisoning the hydration process so much that the fineness became insignificant. It has been reported that the extent of adsorption is influenced more by the sulfate content than by the fineness. In high sulfate content cement, adsorption of SP is less than in low sulfate content cement [8]. Similar results have been reported by Simard et al. [9].

3.3. Influence of alkali content

In the absence of SP, cements containing high levels of alkali (e.g., Na_2SO_4 or K_2SO_4) will usually exhibit poorer rheological behaviors than cements having low alkali contents, other conditions being the same. Also, the water reduction with admixtures will be more readily achieved with LAC [7,10]. Several effects may be promoted by the alkalis, namely: flocculation of cement (or other) fine particles induced by the electrolytes, formation of new hydrates containing alkali ions (e.g., syngenite) or increase in the reactivity of mineral phases (particularly C_3A). WC has shown the highest fluidity followed by LAC and OPC. One of the reasons for this is due to its low alkali content.

In the presence of SP, it was found that the addition of alkali sulfates (Na_2SO_4) can lead to improvements in the rheological properties of cement paste [11,12]. While the results shown may not be generalized, they are consistent with the concepts of SO_4^{2-}/SP competition. The presence of SO_4^{2-} ions leads to a decreased absorption of the SP, leaving more of the latter available on the solution phase for paste fluidification; the fluidity of the paste increases, accordingly, with the amount of Na_2SO_4 added. In another study Andersson et al. [12] further reported that the adsorption of SP was reverted by addition of potassium hydroxide (KOH).

3.4. Influence of water to cement ratio

The water to cement ratio controls the concentration of ions in the pore solution. At low water to cement ratio, the surface of interstitial phases especially of C_3A and C_4AF is adsorbing the SP; thus, very little SP is in the pore solution. But with an increase in the water to cement ratio, more alite hydrates and thereby more Ca^{2+} ions are produced. Lime saturation in the pore solution increases, poisoning the hydration process. Subsequently, the fluidity increases.

It has been observed in the experiments that, up to a water to cement ratio of 0.45, there was no significant increase in the fluidity, but when it exceeded 0.45, there was substantial increase in the fluidity.

3.5. Fresh density and air content

Fresh density is a measure of compactness. Generally, it is low at 0.35 water to cement ratio, while the air content is high. It is due to the bad compaction because of inadequate fluidity. At 0.40–0.45 water to cement ratio, the fluidity increases, thereby the density increases due to better compaction. But, at higher water to cement ratios, the density decreases gradually. The air content also decreases gradually with the increase in fluidity. The decrease in density is due to decrease in the solid content in the mass as the water to cement ratio is increased, a dilution effect. Sometimes, the density is high observed at high water to cement ratios, it is due to mortar segregation.

4. Conclusions

The addition of a LS-based SP resulted in higher fluidity of the mortar compared to when a SMF-based SP was used. This is because the variation of lime saturation rate in the case of LS is smaller than that in the case of SMF. Further SMF is much more unevenly adsorbed than LS on the clinker minerals of cement. Higher fluidity was observed with WC for both LS and SMF than in the case of LAC and OPC cements. This is attributed to the lower C_3A+C_4AF and alkali content and higher sulfate content in WC compared to the LAC and OPC. WC has a particle size distribution with a large amount of fine material. This should have given a low fluidity in the mortar but the observations showed the opposite. The reason may be that the C_3A+C_4AF and alkali content was so low and sulfate content so high that much of the SP remained in the solution. When it adsorbed on alite and belite, it poisoned the hydration process so much that the fineness did not play a significant role.

Many factors are influencing the fluidity and hydration process of the cement paste some of these factors may also have synergistic effects. This makes a theory based on one parameter irrelevant, and it makes it difficult to point out one parameter, which is responsible to produce a particular property.

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