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# The effect of nano-size additives on the electrical conductivity of matrix suspension and properties of self-flowing low-cement high alumina refractory castables

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## Abstract

Influence of two nano-size additives on electrical properties of suspension matrix of self-flowing low-cement high alumina refractory castable is investigated. For this purpose, castament FS 10 and FS 20 on the basis of polycarboxylate ether were considered. The self-flow value, workability and mechanical strength of the castable are evaluated and their relations with electrical conductivity are determined. Using these relations, the type and optimum amount of proper additive for these refractory castables are determined. It was shown that if the electrical conductivity of matrix suspension is less than 0.71 mS/cm, high alumina low-cement self-flowing refractory castable can be obtained. The best self-flow, sufficient working time and adequate mechanical strength in the castables are obtained with 0.08 wt.% FS 20.

*Keywords:* A. Suspensions; C. Electrical conductivity; E. Refractories; Castable

## 1. Introduction

Self-flowing refractory castables are characterized by their consistency after mixing, which allows them to flow and de-air without the application of external energy (i.e. vibration) [1]. These types of refractory castables will flow under their own weight and easily fills intricate forms and shapes without any external force. This makes the installation operation easier and fewer depending on the skill and awareness of the workers [1–4]. The first sequence in setting of a self-flowing refractory castable is loss of flow, i.e. it becomes impossible to place in the mold. Hence, initial setting time or working time is the time after mixing when vibration is needed for the installation [1,5].

Controlling the working time has always been one of the most important and challenging aspects of refractory castable technology [1,4,5]. Working time tests of self-flowing refractory castables are usually performed using the Vicat apparatus. In this method, the flow of a refractory castable is measured as a function of time and working time is determined [1,6]. In order to fully understand the setting time of refractory castables, the dissolution mechanism of calcium aluminate cement (CAC) is considered. When the CAC grains come into contact with water, three distinct reactions can be identified: (1) dissolution, (2) nucleation and (3) precipitation. During the first period, dissolution of the cement particles brings $Ca^{2+}$ and $Al(OH)_4^-$ ions into the solution. As the result of increased number of ions, electrical conductivity is increased. A small amount of hydrates forms at this stage. Therefore, very slight variations of the electrical conductivity are detected. The dissolution continues with a consequent increase in the concentration of $Ca^{2+}$and $Al(OH)_4^-$ ions until a saturation point is reached. After the dissolution reaction completed, the nuclei are formed and grown to a critical size and quantity. In the rapid precipitation of hydrates that follows, the electrical conductivity decreases instantly, consuming ions from the solution. This causes a drop in solution concentration, and accelerated dissolution of the anhydrous CAC is detected. Consequently, electrical conductivity increases [7–10].

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Table 1
Raw materials and composition of self-flowing low-cement high alumina refractory castable studied.

| Raw materials | | Source (type) | wt.% |
|---|---|---|---|
| Tabular alumina | 2–5 mm<br>1–2 mm<br>0.5–1 mm<br>0–0.5 mm<br>≤45 μm | Alcoa Chemicals, T-60 | 80 |
| Microsilica | | Elkem, 971U | 5 |
| Reactive alumina | | Alcoa Chemicals, CTC-20 | 10 |
| Calcium aluminate cement | | Lafarge, Secar-71 | 5 |

Hydration mechanism of CAC is a process that involves the passage of ions into solution. Therefore, the study of hydration is possible by investigating the quantity of ions in the solution at a given time. A developed technique to study the hydration is based on measuring the electrical conductivity of the suspensions containing CAC. Using this technique, a mixture of water and CAC with different concentrations is prepared and time variations of electrical conductivity are continuously measured. The conductivity of a solution is directly proportional to the number of ions in the solution; i.e. the higher the quantity of ions, the higher the conductivity. The measured data are collected electronically and presented in graphs [9,11]. In practice, the initial setting time or working time of refractory castables can be controlled by additives such as: accelerator or retarding agent. In addition, the additives such as deflocculants absorb the ions in the suspension [12–14]. Therefore, electrical conductivity reduces and the setting time of castable varies [9,11,12]. In this paper, the effect of additives such as deflocculants on the electrical conductivity of suspension matrix and other properties of self-flowing low-cement high alumina refractory castable are investigated. For this purpose, two nano-size industrial deflocculants on the basis of polycarboxylate ether are used. Castable properties such as self-flow value, working time and mechanical strength are evaluated and their correlations with electrical conductivity of suspension matrix are determined.

## 2. Materials and methods

### 2.1. Raw materials and compositions

The raw materials and compositions used for the self-flowing low-cement high alumina refractory castable are listed in Table 1.

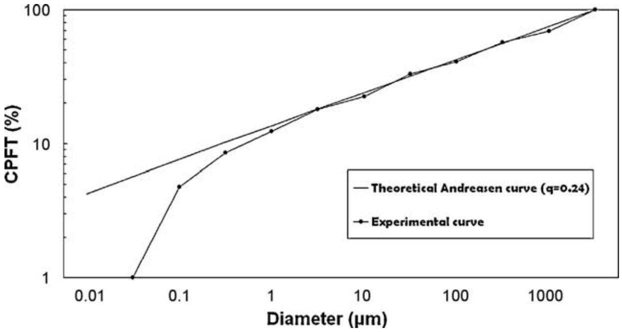

Fig. 1. Theoretical and experimental particle size distribution of self-flowing castable.

The particle size distribution of the castable was adjusted to a theoretical self-flowing continuous curve based on the Andreassen model as Eq. (1) [2]:

$$\mathrm{CPFT} = 100 \times \left(\frac{d}{D}\right)^{q} \tag{1}$$

where CPFT, $d$, $D$, and $q$ indicate the cumulative percentage finer than, particle size, the largest particle size (5000 μm) and the distribution modulus, respectively. In order to achieve self-flowing, the $q$ values should be in the range of 0.21–0.26 [1–3]. In this study, $q$ is chosen to be 0.24. Fig. 1 shows particle size distribution of the castable with $q = 0.24$.

Particles, with a small mean diameter (<100 μm) and a large specific surface area (>1 $m^2/g$) play a major role in the flow ability, setting and hardening time of the castable. These particles constitute the castable matrix [4,12,15]. The purity and physical characteristics of the raw materials in the matrix are shown in Table 2. The content of raw materials and solid loadings used to prepare the matrix representative suspensions

Table 2
Purity and physical characteristics of matrix particles.

| Raw materials | Characteristic | | | |
|---|---|---|---|---|
| | Purity (wt.%) | Specific surface area ($m^2/g$) | Density ($g/cm^3$) | Particle size $D_{50}$ (μm) |
| Tabular alumina | >99 | 0.83 | 3.83 | 7.70 |
| Reactive alumina | >99.7 | 2.10 | 3.91 | 1.90 |
| Microsilica | >97.1 | 17.12 | 2.27 | 0.25 |
| Cement | ($Al_2O_3$) > 70 | 1.00 | 2.93 | 3.03 |

Table 3
Content of raw materials and solids loading used to prepare the matrix representative suspensions.

| Raw materials | wt.% |
|---|---|
| Tabular alumina | 31.04 |
| Reactive alumina | 34.49 |
| Microsilica | 17.24 |
| Calcium aluminate Cement | 17.24 |
| Solid content | 83.45 |

are presented in Table 3. Two types of polycarboxylate ether based on polycarboxylic acid with comb-like structure were used as deflocculant. The structure of these deflocculants consists of a negatively charged backbone (main chain) and additional (non-ionic) side chains. Polycarboxylate ethers have different length and molecular weight. Their characteristics are listed in Table 4.

### 2.2. Self-flow and working time measurements

Self-flow tests were carried out, based on the ASTM C-1446-99 standard, to provide an index of castable flow ability [6]. The same mass ratio (water/solid loading) as in the case of matrix representative suspensions was used to prepare the castable mix. This resulted in a fixed water content of 4.8 wt.% based on dried solids. After dry mixing the batch for 30 s in a planetary mixer (Hobart), the distilled water was added within 10 s while the mixer was running. The wet mixing was conducted for 5 min at a slow speed (Hobart, speed 1). After the mixing, the castable was transferred to a sealed container, while special attention was paid to keep the moisture content. Ten minutes after, the mixed castable was poured into a standard cone with a base diameter of 100 mm (ASTM C-230). The cone was then elevated to allow the mix to flow for 60 s and the patty diameter was measured. The percentage increase in spreading diameter after 60 s is taken as the self-flow value (SFV) according to the following equation [6]:

$$\mathrm{SFV}\ (\%) = (D_f - D_i) \times \frac{100}{D_i} \qquad (2)$$

where $D_f$ is the final average diameter after removal of mold and $D_i$ denotes the initial diameter (100 mm). During the SFV evaluation, the ambient temperature was controlled to be in the range of 20–24 °C. The castable is considered self-flow able when the above value lies within the range of 80–110% of the base diameter [16]. In addition, working time was measured as the point at which the castable shows no movement under its own weight (SFV < 80%).

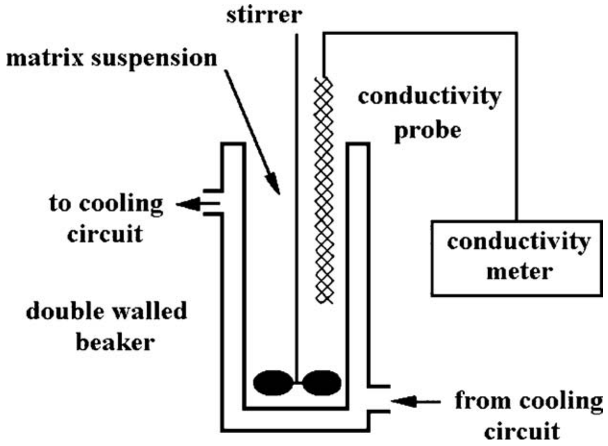

Fig. 2. Experimental set-up for the conductivity measurements.

### 2.3. Electrical conductivity measurements

The electrical conductivity of matrix suspension was measured by conductimetric cell that was comprised of a double walled beaker connected to a water circuit to maintain a constant temperature (20–24 °C). A schematic of the experimental set-up is shown in Fig. 2. After inserting a conductivity probe along with a stirring device, 80 g of distilled water was added to the beaker and the solution stirred continuously until a constant temperature was reached. Then, 16 g of matrix powder was placed into the cell and the measurement started. Electrical conductivity was measured in milli-siemens/cm in 5-min intervals [8,9].

### 2.4. Castable preparation

The dry constituents of the castable were mixed for 4 min in a planetary mixer (Hobart), water was added, and the whole composition was wet-mixed for an additional 4 min. Then, the castable was cast into standard mold without vibration. After curing at 20 °C and 90% relative humidity for 24 h, the specimens were taken out of the mold and dried for 24 h at 110 °C. After that, the cold crushing strength (C.C.S) and cold modulus of rupture (C.MOR) of the specimens was measured. Cold crushing strength and cold modulus of rupture (3-point bend test) were performed in accordance with ASTM C 133-97 [17]. Mechanical strength data presented in this article correspond to an average of five specimens for each composition.

## 3. Results and discussion

The effect of various types of deflocculating agent and its weight percentage on the SFV of the low-cement castable is

Table 4
Characteristics of used additives.

| Additive | Molecular weight (g/mol) | Molecular structure | Molecular length (nm) | Source |
|---|---|---|---|---|
| Polycarboxylate ether (FS 10) | 10,000 | Comb | 3.0 × 3.2 | S.K.W. Polymers |
| Polycarboxylate ether (FS 20) | 8000 | Comb | 24.0 × 0.5 | S.K.W. Polymers |

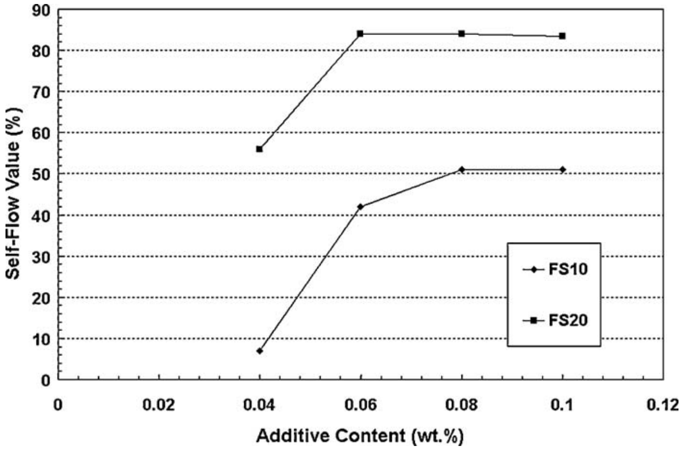

Fig. 3. The effect of additives content on SFV of castable.

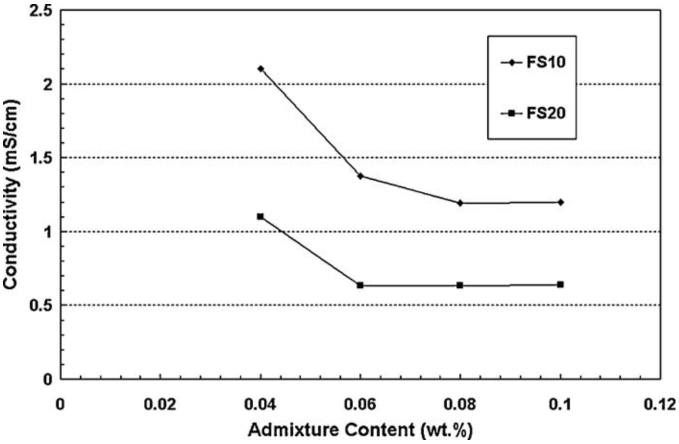

Fig. 4. The effect of additives content on electrical conductivity of matrix suspension.

graphically shown in Fig. 3. It is clearly seen that the best flow values are obtained with FS 20. Moreover, the optimum deflocculant content for maximum SFV is seen to be 0.06 wt.% for FS 20. From Fig. 3, one can see that the SFV of the high alumina low-cement refractory castable with FS 20 is about 84%, in agreement with the definition of self-flowing castables (80% < SFV < 110%).

At the beginning of water contact with grains of cement, dissolution reaction take place and ions such as $Ca^{2+}$ and $Al^{3+}$ starts to leach from alumina cement into the solution. Therefore, agglomerates of CAC and microsilica particles are formed due to their opposite surface charge. Thus, the refractory castable mix is in flocculation state, showing a thixotropic flow. Therefore, the dispersion of particles in the castable is an essential requirement to obtain castable associating high flow ability with low water content. Furthermore, particles dispersion inhibits the formation of agglomerates that can hinder optimum particle packing and affect the castable final mechanical strength. Deflocculants or dispersants are absorbed on the surface of the cement and other grains, increasing the zeta potential and promoting good dispersion due to the repulsion between positively charged grains. They are able to break up the agglomerates of the cement and microsilica particles; therefore a high-strength dense refractory castable will be obtained, with well dispersed fine-particles portions including alumina cement. As indicated by the manufacturer, comb structure of FS 10 results in a small molecule ($\approx$3.0 nm × 3.2 nm) composed of a highly charged main chain and a set of lateral uncharged chains that display a steric lubricating barrier. Therefore, FS 10 combines the advantages of high molecular weight polyelectrolyte (steric barrier and high charge density) with the superior mobility of short chain additives. On the other hand, FS 20 presents non-symmetrical comb-type molecule ($\approx$24.0 nm × 0.5 nm—as indicated by the manufacturer). According to the supplier instruction, FS 20 is a suitable dispersant for microsilica containing compositions which has been confirmed through the results of this study [13,14]. Based on these results, the length and shape of deflocculant molecule have a great effect on the dispersion mechanism. The higher length of FS 20 molecule and its non-symmetrical comb-type structure increases its dispersion efficiency in comparison with FS 10. Therefore, FS 20 displays a high potential for modern placing techniques such as self-flowing. The effect of additives used on the electrical conductivity of matrix suspension is shown in Fig. 4. Because of the time variation of conductivity in the castable containing calcium aluminate cement, electrical conductivity was measured 10 min after water addition. This 10-min interval exactly equals the time lapse in self-flowing evaluations.

It is seen that suspensions containing different additives show similar behavior with increasing additives content. It is further evident that the use of FS 20 gives the lowest values of electrical conductivity. In addition, the optimum additive content for minimum conductivity is seen to be 0.06 wt.% for FS 20. By comparing Figs. 3 and 4, one can immediately see the correlation between SFV and the electrical conductivity for the different deflocculants. Therefore, the variation of SFV can directly be represented as a function of the electrical conductivity of the castable matrix. This, indeed, is represented in Fig. 5, for different amounts of additives. It is evident that the electrical conductivity must be less than 0.71 mS/cm for our system to be self-flowable.

The effect of additives used on the electrical conductivity–time curves of matrix suspension up to 45 min is shown in

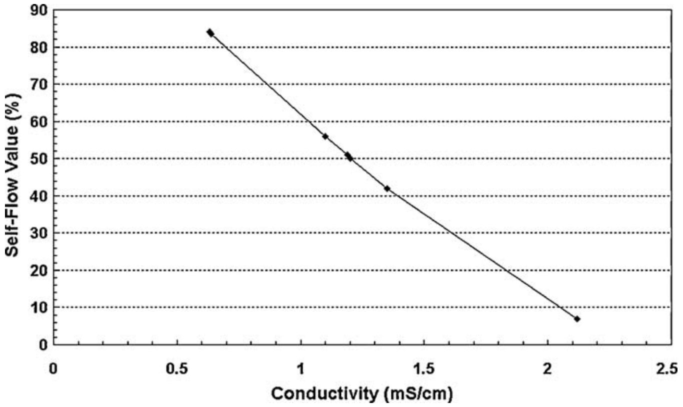

Fig. 5. SFV of castable vs. electrical conductivity of matrix suspension containing different amounts of additives.

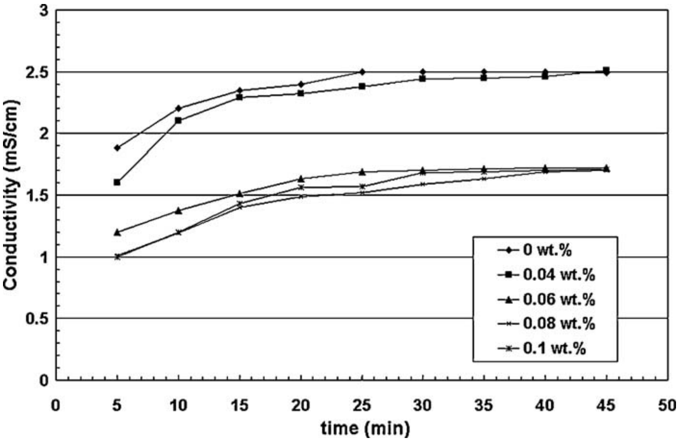

Fig. 6. The effect of FS 10 content (wt.%) on the electrical conductivity of matrix suspension as a function of time.

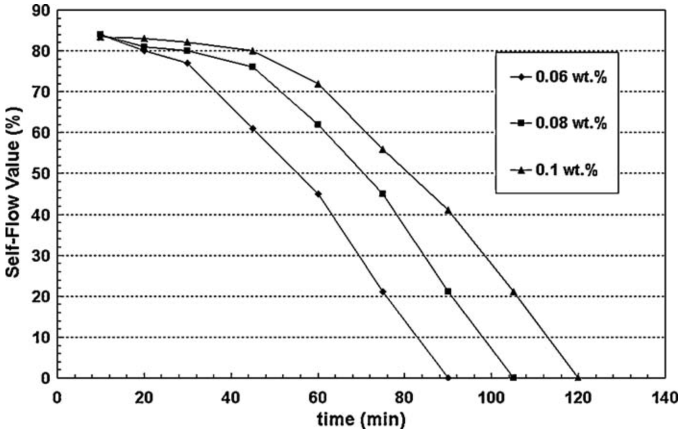

Fig. 8. SFV of castables containing different amount of FS 20 (wt.%) as a function of time.

Figs. 6 and 7. According to these results, one can see that the electrical conductivity of matrix suspension increases with time. Furthermore, the type and amount of used additives can affect these curves.

The conductivity of the matrix suspension without additives increases rapidly with dissolution of the anhydrous CAC in the presence of water. Therefore, Ca$^{2+}$ and Al(OH)$_4^-$ ions are introduced into the solution. These ions act as charge carriers, leading to a rapid increase in the conductivity. The results show that addition of these additives introduces a delay in the increasing rate of conductivity at the first period which, FS 20 has higher effect. In terms of ions in solution, this means that saturation or super saturation is reached later. This is due to the fact that FS 20 can adsorb part of the Ca-ions in the solution and inhibits the growth of hydrates; this is due to the shifting and broadening of the peaks of electrical conductivity to a longer hydration time. The effect of various amount of FS 20 on the SFV of castable as a function of time is shown in Fig. 8.

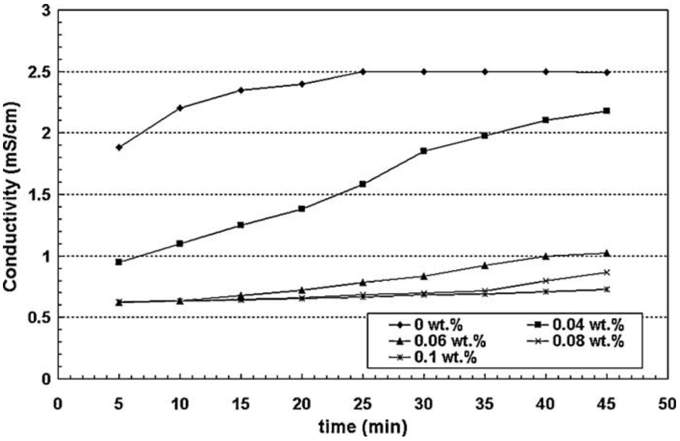

Fig. 7. The effect of FS 20 content (wt.%) on the electrical conductivity of matrix suspension as a function of time.

The results show that addition of FS 20 increases the working time of castable composition. One may simply state that more FS 20 in the castable composition seems to have a retarding effect. Generally, the primary role of these additives in deflocculated castable system is to provide sufficient flow for placing at low water additions, necessary to conserve a compact structure. However, their impact is also on the hydration of calcium aluminate cement, often retarding the precipitation reactions. This is particularly true in the case of highly efficient dispersing additives, necessary for high flow or prolonged workability, which utilizes electrosteric dispersion. FS 20 at a low level of 0.06% addition generally produced very high flow. However, the castable composition suffers from low working time. Addition of 0.08% FS 20 and higher amounts of this additive generally produced very high flow and sufficient workability over time. Therefore, FS 20 proved to be the most effective setting retarding without any addition of the retarding agent. The polycarboxylate ether molecules are absorbed on the fine particles; such as cement particles and inhibited the reaction of cement and microsilica that can hinder setting time of castable. Therefore, the working time of castable can be increased. As seen from Figs. 7 and 8, conductivity–time curves have good relation with working time of self-flowing castable. As a result, the increase of conductivity higher than 0.71 mS/cm corresponds to loss of SFV below 80% where workability finishes. So with respect to conductivity–time curve, the working time of castable can be recognized. In these experiments, conductivity of castable containing 0.06 wt.% FS 20 begins to increase higher than 0.71 mS/cm after 20 min. Hence, SFV of refractory castable decreases and become less than 80% which, corresponds to working time of this castable. In addition, in the castable containing 0.08 wt.% FS 20, conductivity begins to increase after 35 min and therefore, working time of this castable corresponds to 35 min. In practice, 30 min up to 100 min can provide working time long enough for appropriate placement of refractory castables. Therefore, castables containing higher than 0.08 wt.% FS 20 will have adequate working time and can be installed properly. The results of C.C.S and C.MOR of refractory castable containing different amount of FS 20 after drying at 110 °C are shown in Fig. 9. It is found that higher contents of these used additives have a disadvantage in the strength development. If the FS 20 contents in the high alumina low-cement self-flowing castables are increased up to 0.1%, its flow remains stable up to 45 min but the green strength after 24 h is reduced. This

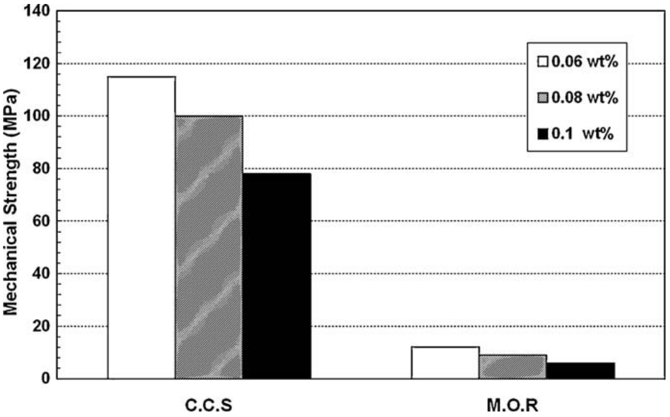

Fig. 9. C.C.S and C.MOR of castable after drying at 110 °C as a function of different amounts of FS 20.

phenomenon is possibly related to the absorption of polycarboxylate ether molecules on cement particles and decreases their bonding action.

In practice, the higher the cold crushing strength, the higher is the erosion resistance and more life time. Hence, the high alumina self-flowing castables must have cold crushing strength and modulus of rupture values above 80 and 10 MPa at 110 °C, respectively. Therefore, if the FS 20 content in castable composition be used lower than 0.1 wt.%, the high alumina self-flowing castable with adequate mechanical strength and working time will be obtained.

## 4. Conclusion

The effect of two different nano-size deflocculants on the electrical conductivity of suspension matrix and other properties of self-flowing low-cement high alumina castable is investigated. By the use of relations between self-flow and electrical conductivity–time, the proper deflocculants and its optimum content for these refractory castables are determined. Also, working time of castable containing different deflocculants is determined. It was found that electrical conductivity of matrix suspension should be lowered to values near 0.71 mS/cm in order to achieve self-flowability. FS 20 on the basis of polycarboxylate ether is proved to be the most effective in reducing the conductivity of this refractory castable matrix. The best results are obtained with 0.08 wt.% FS 20 which generally defines the self-flowing castable with sufficient working time and adequate mechanical strength.

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