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Influence of Some Synthesized Chemical Admixtures on the Rheological Behavior of Oil Well Cement Pastes

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Abstract

Two superplasticizers namely: cyclohexanone-formaldehyde-sulfanilate (CFS) and acetone-formaldehyde-sulfanilate (AFS) were synthesized and characterized utilizing FT-IR. The synthesized superplasticizers were examined like added ingredient to enhance the rheological characteristics of oil well cement. The impact of temperature (25°, 45° and 65°C) and superplasticizer dosages (0.25, 0.5, 0.75 and 1%) were assigned on the apparent viscosity, plastic viscosity and yield stress. The outcomes indicating that the synthesized superplasticizers, CFS and AFS decrease all such criteria and can work like delayers and dispersant in support of oil well cement. The two synthesized superplasticizers displayed good improvement on the rheological characteristics which imply with the purpose of utilizing in the application of oil cementing.

Keywords: *Admixtures; Rheological properties; Apparent viscosity; Plastic viscosity; Yield stress.*

1. Introduction

Oil well cement (OWC) carries out many capacities, comprising ensuring and reinforcing the packaging, forestalling well watered motion exterior of the packaging, and prevents surrendered well areas (zonal separation) [1].

There are fifth phases of the quenching of OWC - initial hydrolysis, induction, acceleration, deceleration, and steady period. Cement admixtures containing accelerator operator, retarder, and dispersant and so forth are utilized to enhance the overall performance of cement paste [2-4]. Oil well cement slurry's great flowability considers the main operator to effectively abuse petroleum and gas reserve in support of cementing activities.

In essential added ingredients in cement, the dispersant (named admixtures) consider a basic segment in support of keeping the particles of cement in a big distance of aggregation also diminishing the viscosity of cement paste that altogether enhances the workability and streaming of cement slurry [5].

To show signs of improvement mixability and workability of fresh cement particles, an appropriate comprehension of cement rheology is the key. Rheology characteristic of OWC paste assumes a major job toward guarantee a fruitful cementing work. Concrete paste shows shear shinning conduct [6]. The rheological characteristics of OWC slurry are affected by numerous variables, for example, water/cement proportions.

A sufficient rheological portrayal is expected to explore the streaming beside shift proficiency of cement paste [7]. Also, cement based products display distinctive rheological practices as for expansion of admixture, chemical structure of the cement, testing method, and so on [8-9]. At the point when the admixture is included into cementitious materials, the added substance greatly affects the rheological property of fresh cement paste, because of the collaboration among added substance and the cement particles.

Msinjili [10] called attention to what the expansion of dispersants led to an underlying enhancement of flowability like affirmed through minimizing of the yield stress. Altable [11] detected what the advancement of the rheological criteria (yield stress and apparent viscosity) chiefly relied upon the states of the superplasticizer planning, particularly the dose of dispersants. Qian [12] suggested that the dispersant with various molecular structures influenced the diminishing examples of energetic yield stress, that has been firmly identified with the adsorption and dispersing technique of all such various sorts of dispersants.

This examination means to get ready two superplasticizers, CFS and AFS considering their effect on the rheological characteristics of the oil well cement pastes. Additionally, the plastic viscosity and yield stress has been resolved.

2. Materials

2.1. Cement

A newly created model of type G mild sulfate resistant oil well cement provided by Schlumberger Company, Egypt was utilized. It consists of: CaO, 60.4%; SiO_2, 20.2%; Al_2O_3, 2.2%; Fe_2O_3, 2.7%; MgO; 6.0%; SO_3, 3.0%; total alkali communicated as Na_2O, 0.75%; insoluble residue, 0.75% and loss on ignition, 3%. The specific surface area as controlled by the Blaine air-permeability technique was seen as 3000 cm^2/g.

2.2. Preparation of admixtures

2.2.1. Cyclohexanone formaldehyde sulphanilate (CFS)

96 g of sulfanilic acid, 98 g of cyclohexanone and 400 mL water were inserted to a reaction container furnished with a stirrer and 20% aqueous sodium hydroxide was inserted to change pH at 9. From that point, the blend was mixed and warmed to the temperature of 90°C and 168 g of 37% aqueous formaldehyde was drop-wisely included inside the container. The blend was cooled to the room temperature after 3.5 hr. of the reaction then controlled to pH 11 with 20 wt %, aqueous sodium hydroxide. After one hour, the untreated cyclohexanone and formaldehyde were isolated by refining [13-14].

2.2.2. Acetone formaldehyde sulphanilate (AFS)

96 g of sulfanilic acid, 116 g of acetone and 400 mL water were inserted to a reaction container furnished with a stirrer and 20% aqueous sodium hydroxide was inserted to change pH at 9. From that point, the blend was mixed and warmed to the temperature of 60-65°C, and 168 g of 37% aqueous formaldehyde was drop-wisely included inside the container. The blend was cooled to the room temperature after 3.5 hr. of the reaction then adjusted to pH 11 with 20 wt %, aqueous sodium hydroxide. After one hour, the untreated acetone and formaldehyde were isolated by refining [15].

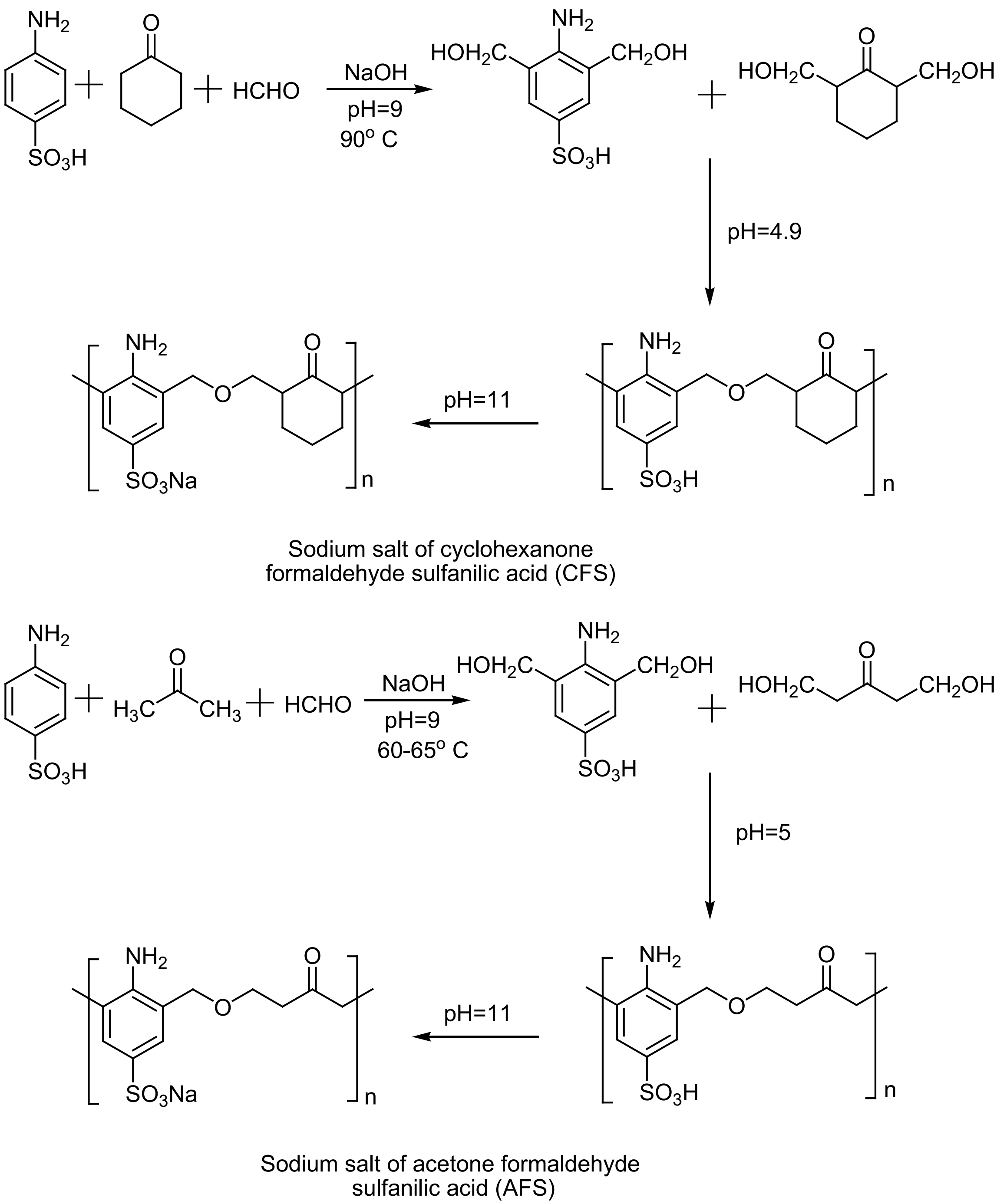
2.3. Mixing and preparing cement slurry

The liquidizer style blender had utilized toward arranged cement pastes as per the accompanying system. The necessary water and the amount of fluid superplasticizer had filled the liquidizer. At a moderate rate the blending began over a time of 15 sec headed for disperse the chemical superplasticizers careful the liquid.

The cement was introduced to the combined fluids over a time of 15 sec. by an elastic spatula, hand blending was proceeded for 15 sec to guarantee identity of objects adhering to the blending vessel surface. At long last, over additional time of 35 sec the blending continued at fast. All such cement pastes the blending method was carefully observed. The whole blending was directed at an adjusted surrounding room temperature of 23±1°C. The complete period among the start of blending and the beginning of the rheological trials had been preserved to prevent the external impact factors on the outcomes. The rheometer arrangement had been likewise kept up stable in support of the whole pastes. The homocentric chamber trial geometry had been reserved on the examined temperature toward evade abrupt warm stun of the slurry.

Cement slurries utilized right now arranged utilizing mild sulfate-resistant style G oil well cement in the company of a particular gravity of 3.15. The Distilled water was utilized for the blending, and its temperature was kept up at 23±1°C utilizing an isothermal holder.

Various customary synthetic admixtures alongside new-age superplasticizers were utilized and their impacts on the rheological characteristics of cement pastes on various temperatures were assessed. These two engineered superplasticizers Cyclohexanone Formaldehyde Sulfanilate (CFS) and Acetone Formaldehyde Sulfanilate (AFS) (Scheme 1) were utilized through various unique measurements 0.25%, 0.50%, 0.75% and 1% of weight of cement.



Scheme 1.

3. Results and discussion

3.1. Chemical structure

The chemical structure of the synthesized admixtures was affirmed by FTIR spectra.

3.1.1. FTIR spectra

The FTIR spectra of the prepared superplasticizers as appeared in Figs. (1, 2) [14-15] indicated the accompanying absorption bands as appeared in Table 1. IR spectra are spoken to in Fig. (1, 2) indicating the intermolecular hydrogen relation in the rigid products since a result of the polymer particles' coiling form. Within totally engineered admixtures spectra, the typical absorption of the ether bonding (C-O-C) created because of condensation of methylol groups. The FTIR spectra affirmed the anticipated functional groups in the prepared admixtures.

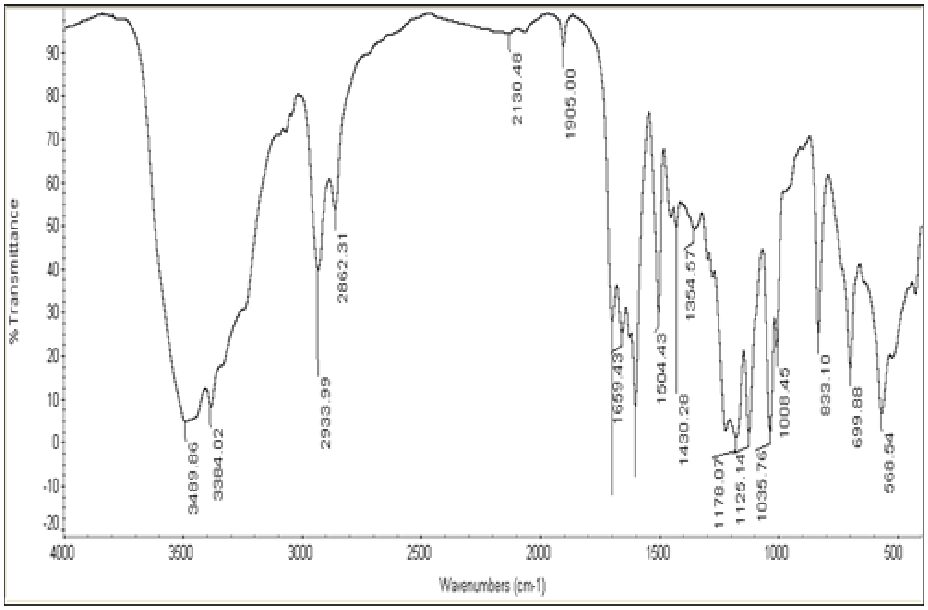


Figure 1. The FT-IR spectrum of CFS

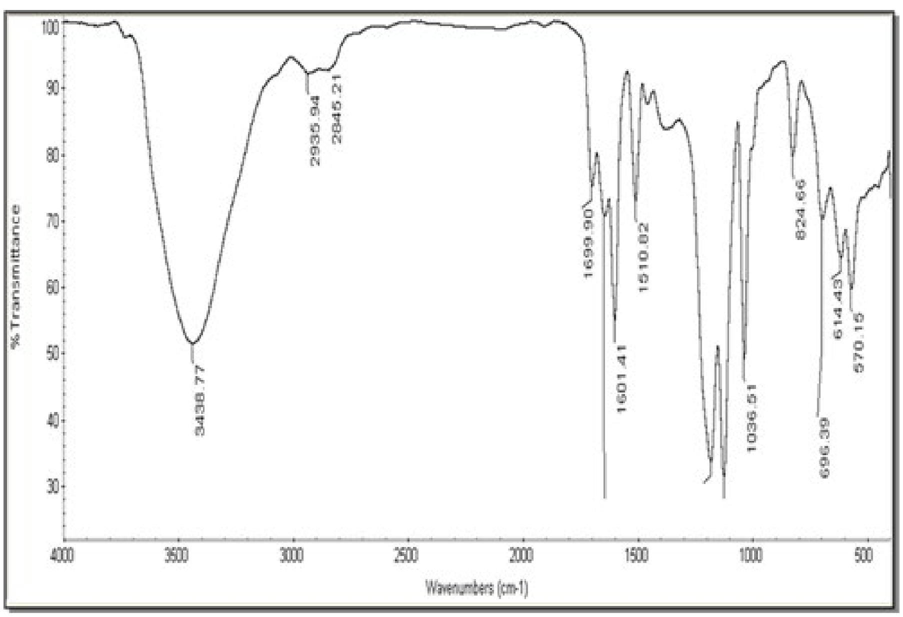


Figure 2. The FT-IR spectrum of AFS

Table 1. IR Characteristic bands of the synthesized superplasticizers

Compounds	CFS Band (cm^{-1})	AFS Band (cm^{-1})
NH2 stretching	3384	3438
C-O-C stretching	1035-1178	1036-1182
C=O stretching	1699	1699
C=C stretching	1504- 1602	1510-1601
S=O stretching	1354	1350
Stretching aliphatic	2862	2845
C-H asymmetric Stretching aliphatic	2933	2935

3.2. Impact of temperature and engineered superplasticizers on apparent viscosity

The outcomes of the apparent viscosity belong to OWC pastes on fixed shear rate equal to $31s^{-1}$. A fixed shear rate 31 s^{-1} had been selected as this shear rate considers the average one that utilized in the investigational course [16].

As appeared in Figs (3, 4) the apparent viscosity increased gradually with increasing the dosage of CFS and AFS admixtures up to 0.25% after that there is a gradually decrease in the apparent viscosity with maximize the dosage of the two admixtures from 0.25% to 1%. Also the apparent viscosity increases with increasing the temperature from 25°C to 65°C. It seems that the two admixtures CFS and AFS works as accelerator at low dosages and as retarder at higher dosages because at lower dosages the adsorbed layer of admixture on the cement grains and hydration products probably won't be adequately viable to go about as a hindrance to forestall touching of liquid and cement particles, which advances the growing speed of hydration responses. While, at higher doses the superplasticizer hinder touching of cement particles with the liquid throughout the hydration process and thereby delay it. Moreover, their acceleration action when rising the temperature from 25°C to 65°C can be explained on the basis that heat breaks down the layer formed around the cement grains and the hydration products by the admixture throughout the hydration process that prevent them to contact with water, the effect that promotes the acceleration of the hydration reactions.

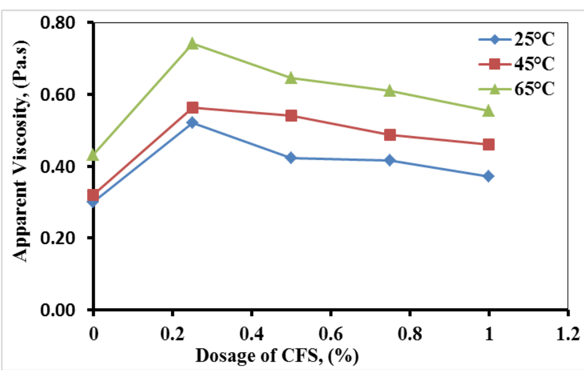


Figure 3. The apparent viscosity of oil well cement slurries at various temperatures and different dosages of admixtures of CFS (w/c = 0.40)

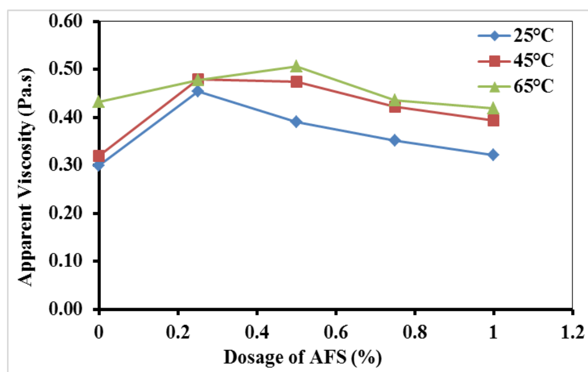


Figure 4. The apparent viscosity of oil well cement slurries at various temperatures and different dosages of admixtures of AFS (w/c = 0.40)

3.3. Impact of temperature and engineered superplasticizers on yield stress

There is an increase of the yield stress with increasing the dosage of the two admixtures up to 0.25 % as shown in Figs (5, 6) i.e. the admixtures work as accelerator due at minor dosages the formed superplasticizer film probably won't be adequately beneficial to function as a boundary to stop touching of liquid and cement particles, that stimulates the speeding up of hydration responses; a behaviour also observed elsewhere [17-18]. But by maximizing the dose of the admixture from 0.25% to 1% they work as retarders, a slight decrease in the yield stress is observed because the concentration of the admixture is enough to a little bit delay the hydration process. Also as the temperature rising from 25°C to 65 °C, the rate of hydration increased i.e. the two admixtures work as accelerator.

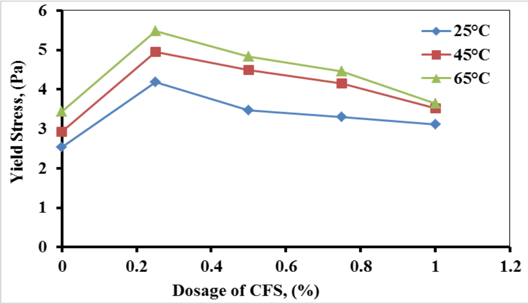


Figure 5. The yield stress of oil well cement slurries at various temperatures and different dosages of CFS admixture (w/c = 0.40)

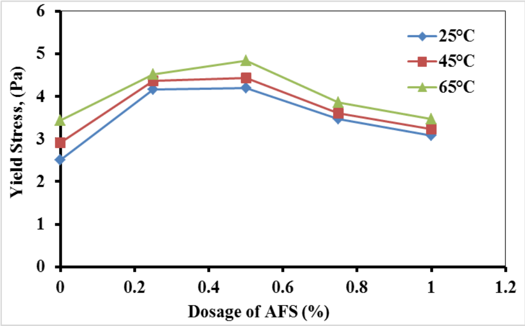


Figure 6. The yield stress of oil well cement slurries at various temperatures and different dosages of AFS admixture (w/c = 0.40)

3.4. Impact of temperature and engineered superplasticizers on plastic viscosity

The plastic viscosity on various temperatures of OWC pastes including various doses of different superplasticizers was resolved in the slope of the shear stress - shear strain down curve. The estimated plastic viscosity doesn't in every case really speak to the material appropriately and occasionally may possibly be misguiding a result in big fault associated with the fitting curve to the Bingham model [19]. Be that as it may, plastic viscosity was estimated and introduced right now it is extremely hard to make automatic patterns in support of the distortion manners of cement paste utilizing the apparent viscosity on a piece shear rate point [20].

As showed up in Figs (7, 8) the plastic viscosity expanded bit by bit with expanding the dosages of CFS and AFS admixtures up to 0.25% then there is a bit by bit decline in the plastic viscosity with amplify the dose of the two admixtures from 0.25% to 1%. Additionally, the plastic viscosity increments with expand the temperature from 25°C to 65°C. The admixtures go about as accelerators at low portion may explain because minor volume of water diminishes the gap among cement grains. Henceforth, hydration items are able to without much of a stretch approach in touch among one another, resulting into quicker pace of hydration processes as well as prior solidifying. It would also potentially even be an explanation how come synthesized superplasticizers have been applied to a particular dosage as activators. While, at higher portions they function as deactivators because of their concentration is adequately enough to condense to the core of hydration items as well as be able to stop the advance hydration, yet by rising the temperature, this layer collapses and the rate of hydration is accelerated.

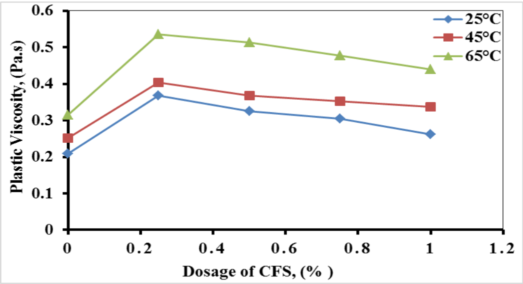


Figure 7. The plastic viscosity of oil well cement slurries at various temperatures and different dosages of CFS admixture (w/c = 0.40)

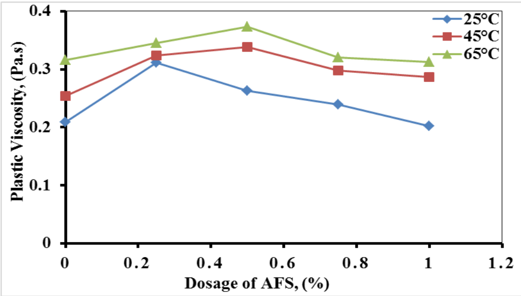


Figure 8. The plastic viscosity of oil well cement slurries at various temperatures and different dosages of AFS admixture (w/c = 0.40)

As referenced before, the rheology of OWC slurries rely on various components, for example, cement hydration thermodynamics, fluid rheology backing, interparticulate powers, and strong volume division [21].

The rheological characteristics of OWC pastes designed for appropriate position into sharp plus thin oil well annulus were altered by utilizing various chemical admixtures, for example, the admixtures/ water lowering (dispersants), delayers, measurement operators, risers. Mainly water lowering superplasticizers hinder the cement hydration pace notwithstanding going about as a deflocculant because of electrostatic repulsion, steric repulsion, or both [22].

In addition, the performance of synthetic admixtures likewise relies upon different components involving the sort of cement and the fine quality of it, the composition and calculation of calcium sulfate and dissolvable alkali sulfate, the amount of C3A and the circulation of aluminum and silicate stages outside cement particles, the reactions of cement stages, period, power blending and blending technique, liquid, heat, w/c ratio, and so on.

4. Conclusion

The superplasticizer amount makes a noticeable impact taking place the rheology of the paste, the minor amounts of CFS and AFS work as accelerators and the rate of hydration was retarded with increasing the admixture doses.

The rheological properties of OWC slurries are profoundly temperature dependent; they for the most part expanded nonlinearly through expanding the heat, mostly because of the reliance of the development of hydration items on heat. Like predicted, OWC pastes viscosity diminished altogether by increment the w/c proportion.

The rheological characteristics of OWC pastes rely on the sort of the utilized superplasticizer, slurries incorporating CFS and AFS need further power to start their stream given that the yield stress enlarged on the entire examined doses.

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