

EFFECT OF SOME PREPARED SUPERPLASTICIZERS (ACETONE BASED) ON PHYSICO-CHEMICAL AND MECHANICAL PROPERTIES OF OIL WELL CEMENT PASTES

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Abstract

This study aims to prepare two different superplasticizers particularly acetone formaldehyde sulfanilate (AFS) and acetone glyoxylic sulfanilate (AGS); also, their effect on physico-chemical and mechanical properties of oil well cement was studied. The chemical structures were confirmed by FTIR technique. The prepared compounds were evaluated as superplasticizers for cement pastes. The cement pastes were prepared by the addition of the prepared admixtures; AFS or AGS, to cement by the ratios of 0, 0.25, 0.50, 0.75, and 1.00 as mass % of cement. The water of consistency, combined water content, the rate of hydration and compressive strength of the hardened pastes were determined at different time intervals. The phase composition and microstructure of the hardened pastes were studied by DSC and XRD techniques. The results revealed that as the admixture dose rate increases the demand water for consistency of the cement paste decreases. Also, as the admixture addition rate increases the chemically combined water content decreases, so the rate of hydration decreases; meanwhile compressive strength increases due to the low initial porosity of the sample.

1. Introduction

In the oil well cementing process, cement slurry is pumped through a steel casing to the bottom of the well and then up through the annulus between the casing and the surrounding rock. The two principle functions of the primary cementing process are to restrict fluid movement between formations (e.g., to isolate fluids such as water or gas in one zone from oil in another zone) and to bond and support the casing (Zhang et al., 2010). As cement descends into the well, the slurry is hydrating under elevated temperature, T, and pressure, P. The entire depth of a well is not cemented in a single operation, but even so, pumping can take several hours, and retarders and dispersants are widely employed to prevent premature hardening. The high temperature, high



pressure, and the additives involved make oil well cementing a challenging process. The rate of increase in viscosity is the most important property in the well cementing operation (Nelson *et al.*, 2006). When the viscosity of the slurry exceeds a few Pa.s, it becomes too difficult to pump, so it is essential that this limit not be reached before the cement paste fills the annulus. Setting transforms the paste from workable plastic slurry into a rigid material. Since setting occurs when the amount of product is sufficient to cause the particles to overlap, forming a continuous solid network, it can be regarded as a percolation process. Knowing the setting time of oil well cement is essential for scheduling the drilling operation. After the cement is pumped into place, the well is left shut for a sufficient time to allow the cement to harden before resuming drilling to a deeper horizon. To avoid damage of the pumping equipment used to place the cement slurry, the cement must remain in a fluid state for several hours while it is pumped into place; to avoid wasting valuable rig time, the cement should set shortly after being placed. Thus, to understand the hydration process and predict the setting time of oil well cement slurries are of considerable economic importance. Some factors that may affect setting time include water/cement ratio (W/C), the composition and particle size distribution of cement (Ramachandran *et al.*, 1998), presence of additives (mineral and chemical), temperature and pressure (Shahriar and Nehdi., 2012). A low W/C ratio, small size of cement particles, accelerators, high temperature and high pressure will reduce the setting time (Zhang *et al.*, 2010). It has been shown that the rate of increase of slurry viscosity over a range of temperature and pressure is described by an activation energy and activation volume (Scherer *et al.*, 2010); therefore, the viscosity can be predicted quantitatively during a variety of T and P. The American Petroleum Institute (API) has defined various classes of Portland cement, of which Class G and Class H are widely used in well cementing. In this paper, Class G cement was studied. Generally the improved fluidity of cement by adding the organic admixture is considered mainly to be caused by the dispersion of solid cement particles by the electrostatic repulsive force due to the increase of the surface potential caused by the admixture adsorbed to the surface of solid particles and by the steric repulsive force based on the interaction between the adsorption layers of admixture (Abo-El-Enein *et al.*, 2005; Aiad *et al.*, 2003; Aiad, I., 2005; 2006).

2. Experimental

2.1 Materials

2.1.1 Cement

A freshly produced sample of class G moderate sulfate resistant cement supplied by Schlumberger Company, Egypt was used. Its chemical composition was found to be: CaO, 60.4%; SiO₂, 20.2%; Al₂O₃, 2.2%; Fe₂O₃, 2.7%; MgO;



6.0%; SO₃, 3.0%; total alkali expressed as Na₂O, 0.75%; insoluble residue, 0.75% and loss on ignition, 3%. The specific surface area as determined by the Blaine air-permeability method was found to be 3800 cm²/g.

2.2 Synthesis of superplasticizers

2.2.1 Acetone formaldehyde sulfanilic acid sodium salt condensate

86.5 g of sulfanilic acid (0.5 mol) sodium salt, 116 g of acetone (2.00 mol) and 400 ml water were added to a reaction vessel equipped with a stirrer and 20% aqueous sodium hydroxide was added to adjust pH 9. Thereafter, the mixture was stirred and heated to the temperature of 60-65 °C, and 168 g of 37% aqueous formaldehyde was dropwise added into the reactor. After 3.5 hrs, the reaction mixture was cooled to room temperature and was adjusted the pH to 11.0 with 20 wt % aqueous sodium hydroxide. 1 hr later, the unreacted acetone and formaldehyde were separated by distillation.

2.2.2 Acetone glyoxylic sulfanilic acid sodium salt condensate

270 g of water and 244.1 g (1.649 mol) of 50% aqueous glyoxylic acid are introduced into a 1 L reaction vessel with a thermometer, stirrer, reflux condenser, pH equipment and dropping funnel. 123.4 g of 50% aqueous caustic soda is added while the contents of the vessel are stirred adjusted the pH to 4.0. The temperature was adjusted to 50 °C and 116 g of acetone (2.00 mol) was added with continued stirring. The contents of the vessel are stirred at 50 °C for a further 75 minutes until the original suspension has turned into a clear solution. The pH rises during this time to 5.9. While the solution is cooled, 88 g (0.509 mol) of sulfanilic acid and 48g of 20% caustic soda are added simultaneously, which causes the pH to drop to 5.2. The reaction mixture is then stirred at 50 °C until a final viscosity of 5.52 cSt (20 wt. % solution at 20 °C) is obtained. The pH is adjusted to 10.0 by adding 39.2 g of 50% caustic soda. The clear aqueous solution of polycondensation product has a solid content of 40.9 wt % cooled to 25 °C.

2.3 Methods of measurements

2.3.1 FT-IR analysis

The synthetic routes of novel superplasticizer were trappable by FT-IR spectroscopy. The FT-IR analysis was done in Egyptian Petroleum Research Institute using ATI Mattsonm Infinity SeriesTM, Bench top 961 controlled by Win FirstTM V2.01 Software.

2.3.2 Water of consistency and setting time

The standered water of consistency, initial and final setting times of cement pastes were determined using a Vicat apparatus according to **ASTM Designation., 2011& 2013.**

2.3.3 Moulding and curing



The various cement pastes were prepared by mixing the dry cement with the required water of consistency including different doses of superplasticizer using the water/cement (W/C) ratios as shown in Figs. 3 (a&b). The operation was completed by continuous and vigorous mixing for about three minutes. After complete mixing the resulting pastes were molded into cubic specimens by using stainless steel (2.54 x 2.54 x 2.54 cm³) cubic moulds. Compacting by vibration was carried out, and the leveling and smoothness of the top surface of the pastes was made by a thin edged towel (ASTM Designation., 2015). Immediately after moulding, the specimens with their moulds were cured at about 100 % relative humidity at room temperature for the first 24 hours in order to attain the final setting of the specimens. The hardened cement pastes were then removed from the moulds and cured under tap water for various time intervals of 3, 7, 28 and 90 days.

2.3.4 Compressive strength determination

At each time interval, compressive strength tests were performed on the hardened cement pastes using three cubic specimens at each hydration time and the average value was recorded as kg/cm². This test was performed using a Ton-industrial machine (West Germany) for maximum load of 60 tons.

2.3.5 Stopping of hydration

The stopping of hydration process was performed on the crushed cubic specimens after the compressive strength determination according to the method reported in an earlier investigation (El-Gamal et al., 2015).

2.3.6 Determination of chemically combined water content (W_n, %)

Two representative samples of the dried specimens, exactly about 1g each, were weighted in porcelain crucibles and ignited for one hour at 1000°C in an adjustable muffle furnace, cooled in a desiccator and then weighted. The chemically-combined water content (i.e., the amount of water retained after drying) was calculated as W_n (%) using the following equation:

$$W_n (\%) = [(W_1 - W_2) / W_2] \times 100 - L$$

W₁: is the weight of the dried sample before ignition (g) and

W₂: is the ignited weight of sample (g)

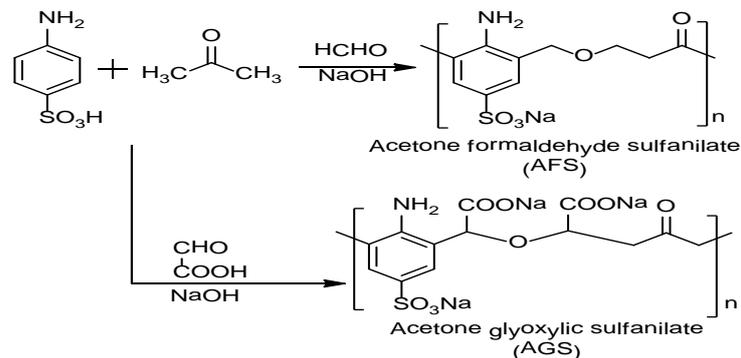
L : is ignition loss

3. Results and Discussion

3.1 IR Spectrophotometric analysis

The synthesized superplasticizers particularly acetone formaldehyde sulfanilate (AFS) and acetone glyoxylic sulfanilate (AGS) have common groups according to preparation methodology. The general process is the reaction of formaldehyde or glyoxylic acid with active methylene (-CH₂-) of acetone to form a methylol group. As the reaction progresses, the condensation takes place among methylol (-CH₂OH) groups leading to the formation of the ether linkage (-CH₂OCH₂-) of AFS or AGS products. Finally, the methylol group on the

terminal part reacts with sulfanilic acid to produce the AFS or AGS product (scheme 1).



Scheme 1: Synthetic route of AFS and AGS superplasticizer

IR spectra of these compounds are represented in Figs (1 and 2). This is attributed to the intermolecular hydrogen bonding in the solid materials as the result of the coiling structure of the polymer molecules. Spectra of the synthesized superplasticizers were indicated in Figs. (1 and 2), the characteristic absorption of the ether linkage (C-O-C) formed due to condensation of methylol groups is a strong band in the 1035-1178 cm^{-1} . S=O stretching frequency range is 1354 cm^{-1} , see also Table (1).

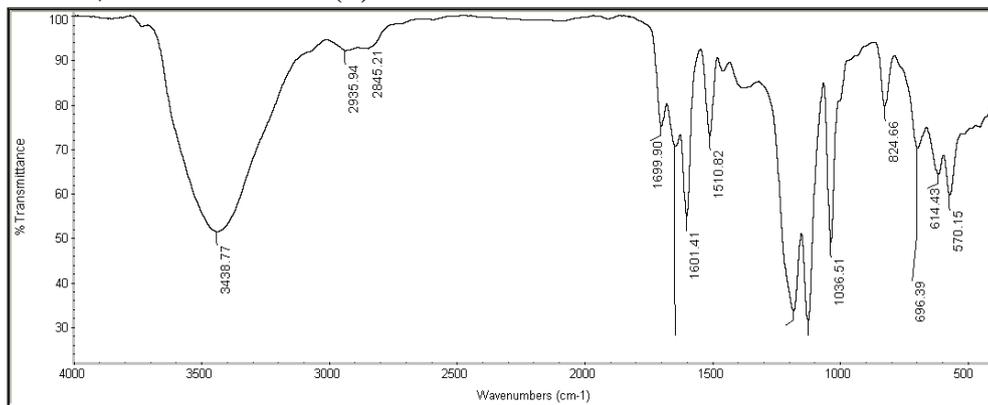


Fig. (1): FT-IR spectrum of AFS

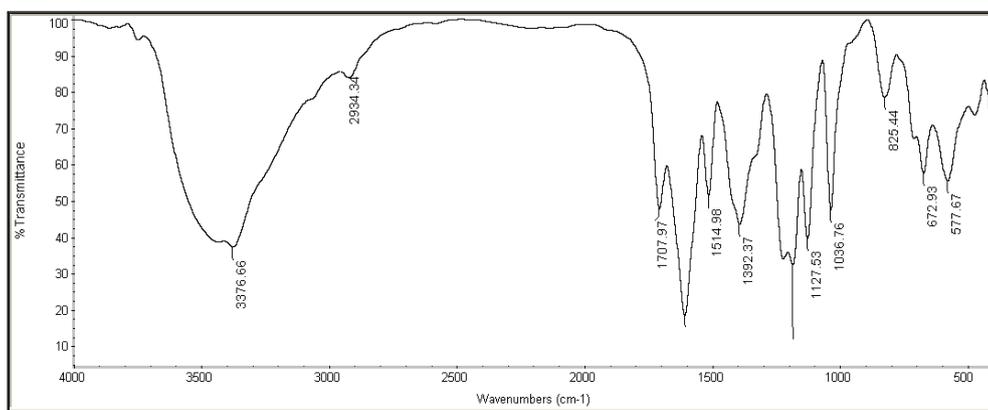


Fig. (2): FT-IR spectrum of AGS

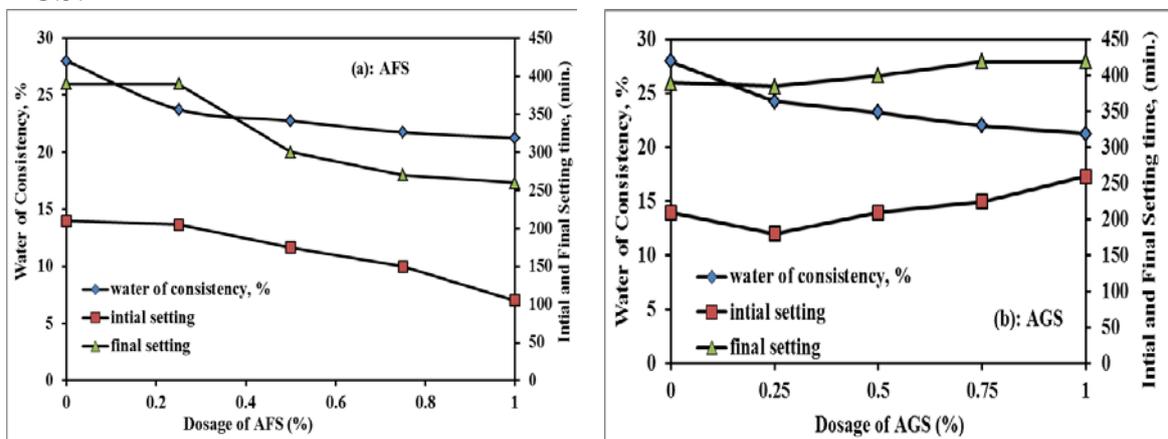
Table 1: IR Characteristic bands of the synthesized superplasticizers

Compounds. Band (cm ⁻¹)	AFS	AGS
NH ₂ stretching	3438	3376
C-O-C stretching	1036-1182	1036-1185
C=O stretching	1699	1707
C=C stretching	1510-1601	1514-1608
S=O stretching	1350	1392
C-H stretching aliphatic	2935	2934

3.2 Water of consistency and setting time

Cement reacts with water; calcium hydroxide is liberated during the hydration of Portland cement. Calcium hydroxide reacts with the colloidal acid hydrates to form hydrated calcium aluminates, silicates and hydrogarnets (Michalakis *et al.*, 2004; Qing *et al.*, 2007). The reactions of tricalcium aluminates solid-solution phases predominate at the early ages of hydration. The reaction of calcium silicate phases predominate from about the time of initial set (Heikal *et al.*, 2005). The setting and hardening of the cement pastes are due to several chemical reactions which begin as soon as water is in contact with cement.

The cement pastes were prepared by the addition of the admixtures, sulfanilic acid-acetone formaldehyde (AFS) and sulfanilic acid-acetone glyoxylic (AGS) to cement by the ratios of 0.0, 0.25, 0.50, 0.75, and 1.00 mass % of cement, respectively. The water of consistency, initial and final setting times of the different cement pastes made with various ratios of admixtures are shown in Figs. 3 (a and b). From the Figs. 3 (a & b), it is clear that the water demand for the standard water of consistency tends to decrease with the increase of the admixture dose. The reduction of mixing water at 0.25% admixture is 15% and 13% for AFS and AGS, respectively. On the other side, the reduction of mixing water at 1.00 % admixture is 24% for the two admixtures. Therefore, the water of consistency decreases with increasing admixture dosage for both AFS and AGS.



Figs. 3(a, b): Water of consistency and setting time of admixed OWC pastes with AFS and AGS superplasticizers.

Evidently, the initial and final setting times of cement pastes admixed by AFS are accelerated due to the reduction of mixing water with increasing dose of admixture (Fig.3a); It can be concluded that the prepared AFS superplasticizer is water reducer and accelerating admixture. Fig. (3b) shows the initial and final setting times of the hardened cement pastes admixed by AGS. The results show that the initial setting time is retarded by the addition of this admixture. As the dose of admixture increases the initial setting time increases. Therefore, it can be concluded that the AGS acts as water reducer and retarder.

The mechanism of this operation is based on the adsorption of the prepared compound on surface of cement particles; this could decrease flocculation. The prepared compounds increase the zeta-potential of cement particles which carry a surface charge of the same sign (negative charge); therefore, the cement particles will repel each other and disperse. Basically, there are two types of dispersion mechanisms: electrostatic repulsion and steric hindrance. The relatively high negative zeta-potentials obtained when superplasticizers with a sulfonic group, were used to suggest that the dispersion mechanism of cement particles is mainly controlled by electrostatic repulsion between negatively charged particles. This proves that the mechanism by which cement particles are dispersed is not attributed to electrostatic repulsion. Dispersion of cement particles in this case must be due to steric effects as reported by Aiad, (2006).

3.3 Chemically combined water content (W_n, %)

The values of the chemically combined water contents (W_n, %) of the different cement pastes admixed with different dosages of AFS and AGS (0.25, 0.5, 0.75 and 1.0% by weight of the cement) as well as the control cement paste are graphically represented in Figs. (4) and (5), respectively.

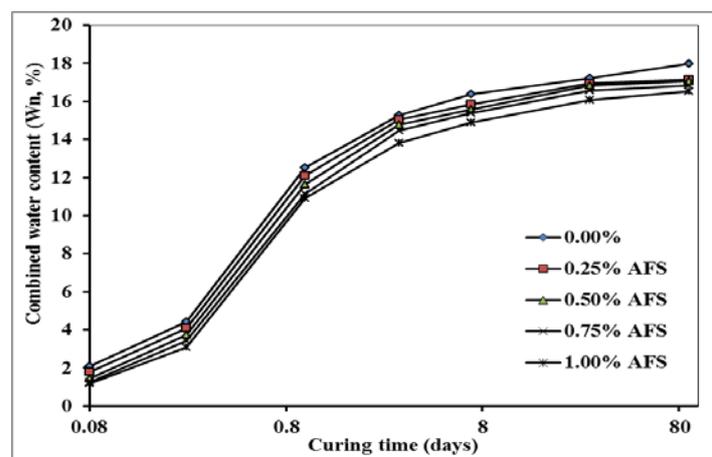


Fig. (4): Chemically combined water contents of cement pastes having different dosages of AFS at various ages of hydration.

During the hydration of the cement pastes admixed with AFS or AGS, two stages of hydration could be distinguished; the first stage is dependent on the dosage of admixture, while the second stage is dependent on the initially formed hydration products. The rate of hydration of AFS or AGS admixed cement pastes is lower than that of the control. As the time interval increases from 2hrs. to 90 days, the combined water content increases from 2%, 1.77%, 1.45%, 1.26% and 1.19% to 17.99%, 17.15% , 17.05%, 16.85% and 16.54%, which corresponding to 0, 0.25, 0.5, 0.75 and 1.00% dosages by weight of the cement. On the other hand, the combined water value decreases with increasing the AFS dosages as shown in Fig. (4).

The values of the chemically combined water content of the cement pastes admixed with acetone glyoxylic sulfanilate (AGS) additive are shown in Fig. (5).

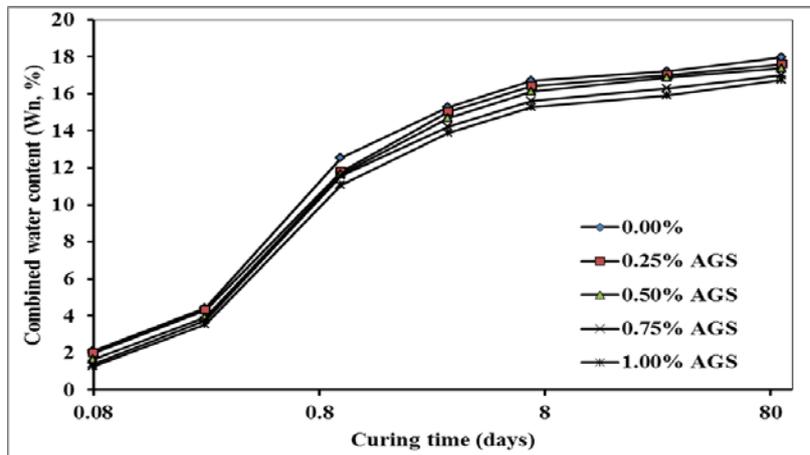


Fig. (5): Chemically combined water contents of cement pastes admixed with different dosages of AGS at various ages of hydration.

3.4 Degree of Hydration (α)

The extent to which the cement has hydrated can be expressed by the degree of hydration α , which is defined as the weight fraction of original cement which has become fully hydrated ($0 \leq \alpha \leq 1$) as shown in equation (1).

$$\alpha = \frac{W_n}{W_\infty} \dots\dots\dots (1)$$

Where: W_n is the combined water content (%) at a given curing time.

W_∞ is the total combined water content after complete hydration ≈ 0.23

The factor of 0.23 in equation (1) represents the non-evaporable water content per gram of cement in the mixture for complete hydration. It is an estimated value calculated based on the Bogue composition of cement (Bentz et al., 2005). Tables (2 and 3) show the values of the degree of hydration of the hardened cement pastes made with AFS and AGS respectively, at the various ages of hydration. It is evident that the degree of hydration is depending on the initial W/C ratio. Thus, all of the values of the degree of hydration of hardened

cement pastes mixed with admixtures are lower than those of the control samples. In addition, as the dosage of admixtures increases the degree of hydration decreases.

Table (2): The degree of hydration (α) of the hardened cement pastes made by different dosages of AFS at various ages of hydration

Curing Time	Degree of Hydration (α)				
	Doses				
	0%	0.25%	0.50%	0.75%	1.00%
2 hrs.	0.091	0.077	0.063	0.055	0.052
6 hrs.	0.193	0.177	0.162	0.149	0.134
1 day	0.545	0.526	0.506	0.485	0.474
3 days	0.664	0.653	0.643	0.630	0.601
7 days	0.711	0.689	0.677	0.669	0.647
28 days	0.748	0.737	0.732	0.720	0.699
90 days	0.782	0.746	0.741	0.733	0.719

Table (3): The degree of hydration (α) of the hardened cement pastes made by different dosages of AGS at various ages of hydration

Curing Time	Degree of Hydration (α)				
	Doses				
	0%	0.25%	0.50%	0.75%	1.00%
2 hrs.	0.091	0.087	0.071	0.061	0.055
6 hrs.	0.193	0.186	0.170	0.163	0.153
1 day	0.545	0.513	0.508	0.503	0.481
3 days	0.664	0.654	0.639	0.618	0.603
7 days	0.711	0.714	0.701	0.679	0.664
28 days	0.748	0.740	0.733	0.708	0.693
90 days	0.782	0.765	0.755	0.740	0.729

3.5 Gel/Space ratio

The gel/space ratio represents the ratio of the volume of cement hydrates to the volume available to accumulate these hydrates; the latter volume consists of the volume of hydration products plus the volume of the residual pores (capillary pores). The use of gel/space ratio results in a reduction in the number of variables as it represents a combined effect of the degree of hydration and the initial porosity as controlled by the initial W/C ratio. The gel/space ratio is given by the following equation:

$$X = \frac{0.646 \alpha}{0.319 \alpha + W_o/C} \dots\dots\dots (2)$$

Where: α is the fraction of the hydrated cement (degree of hydration).

C is the weight of the cement.

W_o is the volume of mixing water.

W_o/C is the initial water/cement ratio (by weight).

The values of the gel/space ratio for the hardened cement pastes made with different doses of admixtures as well as the control paste (free of admixture) at different curing time intervals are graphically represented in Figs. (6 and 7).

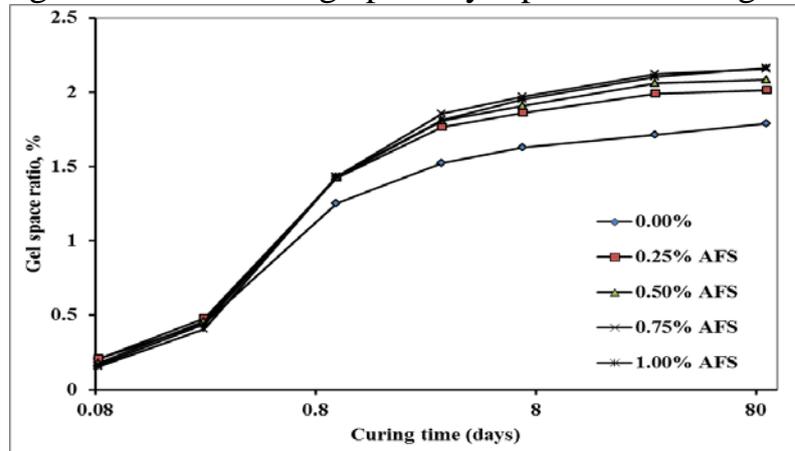


Fig. (6): Variation of gel/space ratio values of the various hardened cement pastes made by different dosages of AFS with age of hydration.

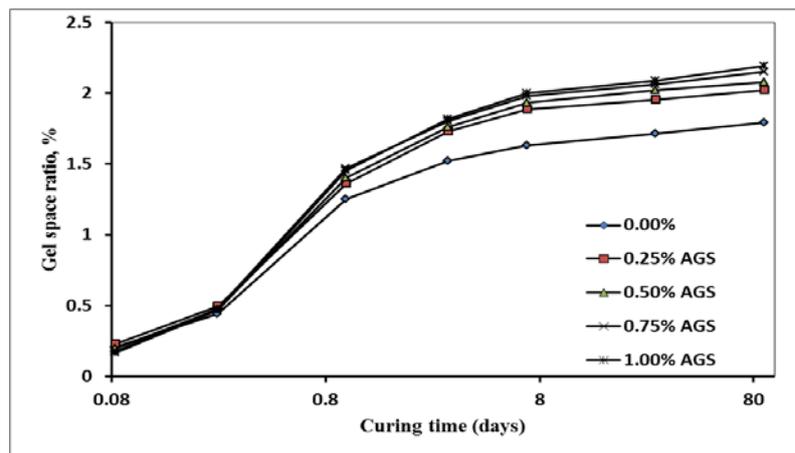


Figure (7): Gel/Space ratio values of the various hardened cement pastes made by different dosages of AGS at various ages of hydration.

Figs. (6 and 7) indicate that the curves of the cement pastes containing admixtures are shifted to higher values of gel/space ratio and higher values of compressive strength at each time of hydration. In other words, as the gel/space ratio increases the compressive strength increases (**Heikal et al., 2001**). This can be explained by the fact that as the curing time increases, the rate of hydration reaction increases and leads to increase the hydration products (gel products), which can fill the limited pores existing in the pastes leading to high compressive strength values.

3.6 Compressive Strength

The compressive strength values of the hardened cement pastes made with different dosages of AFS or AGS admixtures are graphically represented in

Figs. (8) and (9), respectively. The values of compressive strength show a sharp increase during the early ages of hydration up to 3 days, followed by a gradual increase up to 28 days; then a very slight increase up to the later age of hydration (90 days). The previous results are attributed to the hydration of Portland cement and formation of hydration products, mainly as calcium silicate hydrates (C-S-H) having good hydraulic characteristics and act as strong binding centers between the cement grains. Evidently, the chemical structure and the dosages of the admixtures are essential factors affecting the improvement of mechanical characteristics of the hardened cement pastes.

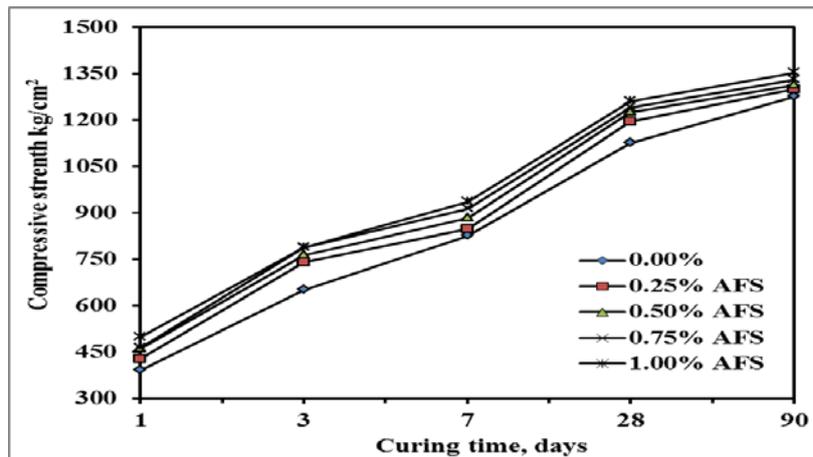


Figure (8): Variations of compressive strength of the various cement pastes having different dosages of AFS with age of hydration.

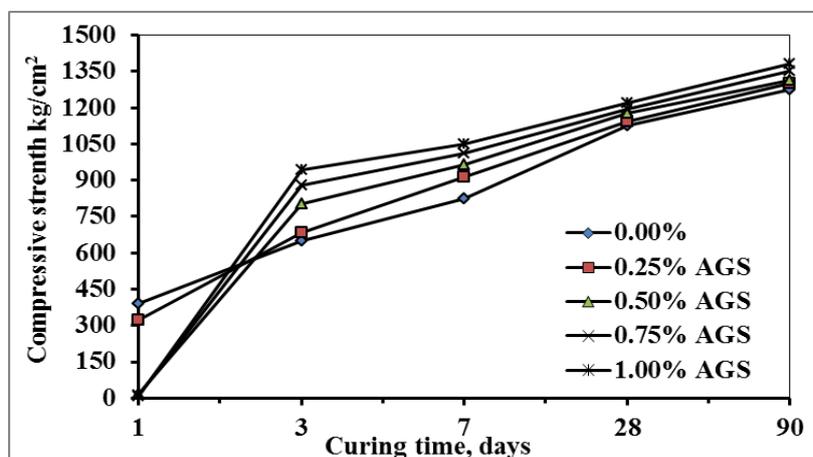


Figure (9): Variations of compressive strength of the various cement pastes having different dosages of AGS with age of hydration.

For all the admixed cement pastes, as the dosage increases the compressive strength increases. Evidently, there are some inter-related parameters; namely, W/C ratio, admixture dosage and degree of hydration that affect the main hydration characteristics of the fresh and hardened cement pastes. By comparing the effect of admixture dosages on the combined water content and compressive strength, it is evident that as the dosage of these admixtures



increases, the combined water content decreases and the strength improvement enhances. By another meaning, this result is mainly attributed to the more dense structure of the hardened admixed cement pastes affected by the strong water reduction caused by the addition of each admixture (Ming et al., 2015). The stronger the water reduction caused by any admixture, the lower the initial porosity and the increase in the values of both gel/space ratio and compressive strength of the admixed cement paste. The strength results seem to be dependent on the nature and the physical state of the hydration products formed within the pore system of the hardened admixed cement pastes.

4. Phase composition of the formed hydrates of the admixed hardened OWC pastes

The phase composition of the formed hydrates obtained for some selected admixed hardened OWC pastes were identified using X-ray diffraction (XRD) analysis and differential scanning calorimetry (DSC).

4.1 X-ray diffraction (XRD) analysis

The X-ray diffractograms obtained for the hardened OWC pastes admixed with 0.25 and 0.75% of AFS and AGS admixtures after 7 and 90 days of hydration are shown in Figs. (10) and (11) respectively. The results of Figs. (10 and 11) indicated that the distinct phases identified at various ages of hydration are for both, (i) unhydrated phases; alite (C_3S) have been identified by its characteristic basal reflections. (ii) hydrated phases; the formation of calcium hydroxide ($Ca(OH)_2$), as a result of hydration of tricalcium silicates (C_3S) could be distinguished. Calcium silicate hydrates, C-S-H (I) and (II), could also be distinguished, as main hydration products. In conclusion, the results of Figs. (10) and (11) shows that the intensities of the peaks characterizing C_3S decrease with increasing age of hydration; meanwhile, the intensities of the peaks characterizing the hydration products, namely calcium silicate hydrates (CSH) and (CH), increase with increasing age of hydration up to a final age of hydration (90 days).

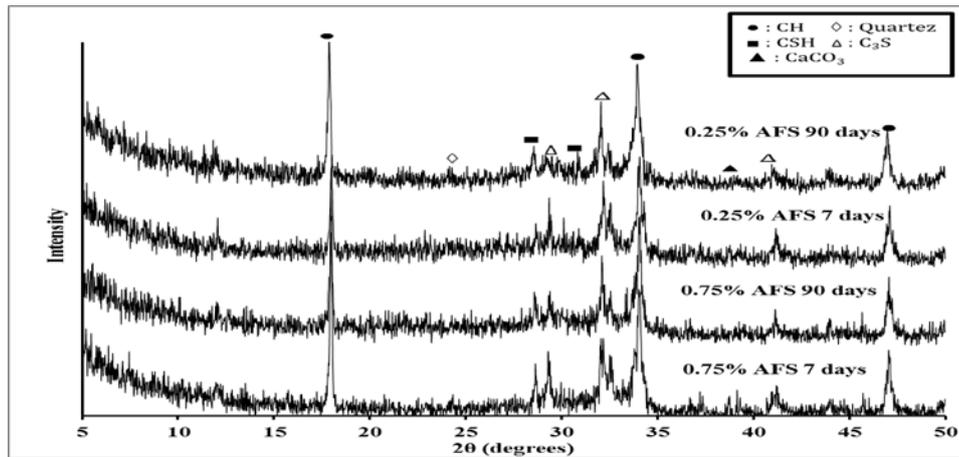


Fig. (10): XRD patterns of the admixed hardened paste by 0.25% and 0.75% AFS polymer after different ages of hydration.

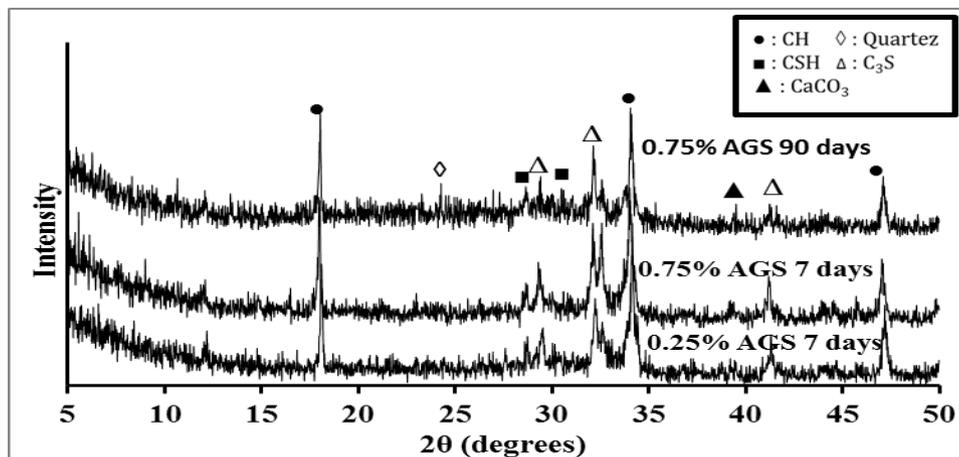


Fig. (11): XRD patterns of the admixed hardened paste by 0.25% and 0.75% AGS polymer after different ages of hydration.

4.2 Differential scanning calorimetry (DSC)

The thermograms of the hardened of OWC pastes admixed with 0.25% and 1.00% of AFS and AGS and hydrated for 3 days and 28 days are shown in Figs. (12) and (13), respectively. The thermograms indicate three endothermic peaks at 90-105, 490 – 510 and 718 – 750°C. The first endotherm located at 90 – 105°C is mainly due to the removal for free water and the dehydration of the amorphous part of calcium silicate hydrates (CSH), (Amin et al., 2012). The second endotherm located at 490-510 °C, represents the major weight loss, is mainly related to the decomposition of portlandite (CH), (Amin et al., 2013). The intensity of this endotherm increases with increasing age of hydration for 3 and 28 days of hydration respectively; this increase is attributed to increase in the amount of liberated free lime. Finally the third endotherm located at 718 – 750°C is due to the decomposition of calcium carbonate.

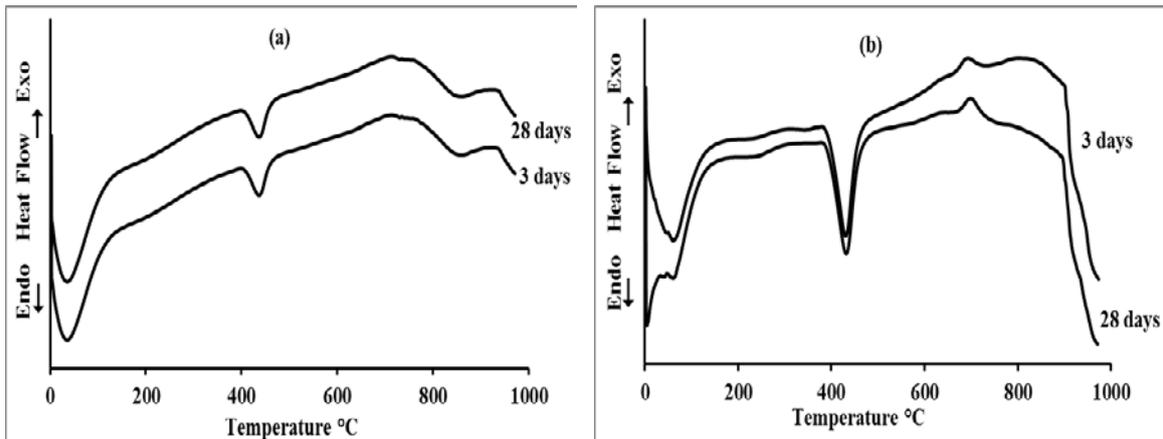


Fig. (12): DSC patterns of the admixed hardened OWC paste with:
(a) 0.25% AFS after 3 and 28 days of hydration.
(b) 1.00% AFS after 3 and 28 days of hydration.

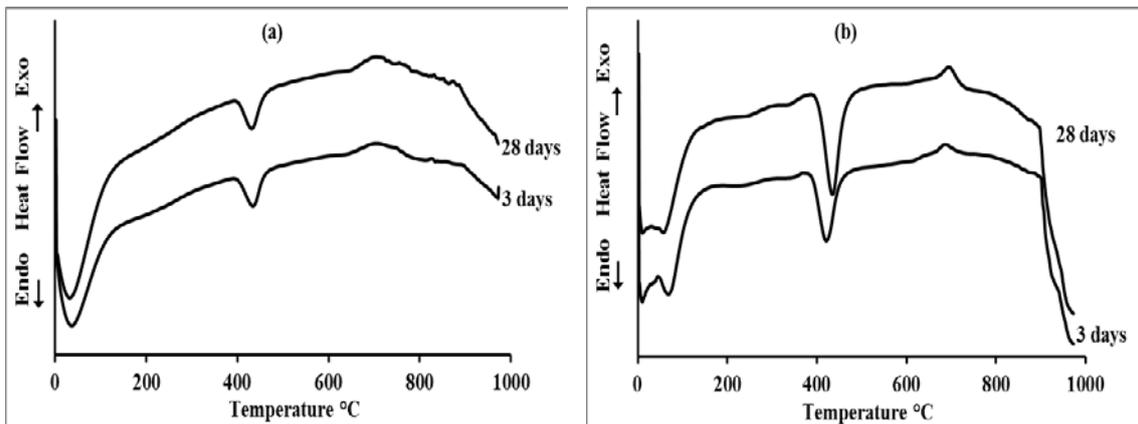


Fig. (13): DSC patterns of the admixed hardened OWC paste with:
(a) 0.25% AGS after 3 and 28 days of hydration.
(b) 1.00% AGS after 3 and 28 days of hydration.

Conclusion:

From the obtained results, the following conclusion can be drawn:

- 1- AFS or AGS superplasticizers have significant reduction in the water of consistency reached to 24%. AFS accelerates the initial setting time due to the reduction of mixing water. On the other hand, the final setting time is accelerated by the increase of the admixture. As the dose of AGS increases the initial and final setting times increase. Meanwhile, as the admixture dosage increases the compressive strength increases for all hardened cement pastes investigated.
- 2- By comparing the effect of admixture dosages on the combined water content and the compressive strength, it is evident that as the dosage of



these admixtures increases, the combined water content decreases and the strength improvement enhances.

The results of phase composition of the formed hydrates for some selected samples of the admixed OWC pastes obtained by X-ray diffraction (XRD) analysis are in agreement with those obtained by differential scanning calorimetry (DSC).

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تأثير بعض ملدنات الأسيتون المحضرة على الخواص الفيزيوكيميائية والميكانيكية لعجائن أسمنت آبار البترول

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تهدف هذه الدراسة إلى تحضير اثنين من الملدنات المختلفة وهي الأسيتون سلفانيات الفورمالديهايد (AFS) والأسيتون سلفانيات الجليوكسيليك (AGS) ومن ثم دراسة تأثير هذه الملدنات على الخواص الفيزيوكيميائية والميكانيكية لأسمنت آبار البترول. تم إثبات التركيب الكيميائي عن طريق تقنية (FT-IR). وكذا تم دراسة تأثير المركبات المحضرة كخلطات كيميائية لمعاجين الإسمنت وكانت الإضافة من AFS أو AGS كالتالي ٠، ٠.٢٥، ٠.٥٠، ٠.٧٥، و ١٪ من كتلة الاسمنت. تم تحديد نسبة الماء القياسية وكان لكل من المركبين تأثير على انخفاض ماء الخلط القياسي ليصل إلى ٢٤.١٪ عند إضافة ١٪ من إحدى المركبين. كما تم دراسة زمن الشك الابتدائي والنهائي وكان لكل من المركبين تأثير مغاير على زمن الشك الابتدائي أو النهائي. تم دراسة الماء المتحد كيميائيا وقوة تحمل الضغط على عجائن الأسمنت المتصلبة في مختلف الأوقات الفاصلة من يوم واحد إلى ٩٠ يوما، تم اثبات التركيب الصنفي لنواتج التآدرت للعجائن الصلبة بواسطة DSC و XRD. وأوضحت النتائج أنه كلما زادت جرعة الملدنات المحضرة انخفضت نسبة مياه الخلط المطلوبة لعجائن الأسمنت ومن ثم انخفاض كمية الماء المتحد كيميائيا وزيادة قيمة قوة التحمل للضغط الهيدروليكي نظرا لانخفاض نسبة المسامية الأولية للعينات.