BEHAVIOR OF DELAYED ADDITION TIME OF SNF SUPERPLASTICIZER ON MICROSILICA-SULPHATE RESISTING CEMENTS

H. EL-DIDAMONY, #MOHAMED HEIKAL*, **, I. AIAD***, S. AL-MASRY

Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
** Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*
***Chemistry Department, College of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU),*
P.O. Box 90950, Riyadh, 11623, Saudi Arabia
**** Petrochemical Department, Egyptian Petroleum Research Institute, Cairo, Egypt*

#E-mail: ayaheikal@hotmail.com

Submitted January 8, 2013; accepted May 12, 2013

Keywords: Fluidity, Hydration kinetics, Mechanical properties, Superplasticizers, Delayed addition time

Most concrete produced today includes either chemical additions or chemical admixtures added to concrete, or both. These additives alter the properties of cementitious systems, including fluidity, hydration kinetics, microstructure and strength. Therefore, the development and use of the most suitable type, optimum dosage and delayed addition time (DAT) of superplasticiser in concrete technology have been of increasing importance. The present investigation aimed to evaluate the influence of DAT of sulfonated naphthalene formaldehyde (SNF) condensate on the hydration kinetics of sulfate resisting cement (SRC) pastes incorporating 10 mass % silica fume (SF). Superplasticized cement pastes were prepared using the required water of standard consistency with different dosages and DAT of SNF. The pastes were hydrated for 90 days under normal curing conditions. The results revealed that, the fluidity of cement pastes increases with SNF content and DAT up to 7.5 minutes, due to the electrostatic repulsion between cement particles and the decrease of anhydrous C_3A content that is minimized with hydration time. Also, the chemical and physico-mechanical characteristics improve with superplasticizer dosage up to 1.0 mass % and DAT up to 7.5 minutes, due to the improvement of superplasticizing effect, leading to increase the hydration of silicate phases (C_3S and β-C_2S) and formation of more CSH, CAH and CASH. These hydrates increase the gel/space ratio, modify the microstructure and consequently enhance the strength of cement paste. FTIR spectra are in a good agreement with those of chemical and physico–mechanical characteristics.

INTRODUCTION

As widely known, high strength cement paste, mortar and concrete, can be obtained by the incorporation of a well–designed combination of cement, filler, and superplasticizer (SP) [1-3]. Quite often, SF is applied as good filler, due to its high surface area and is a very reactive pozzolana because of its highly amorphous silica and its ability to react with free calcium hydroxide (CH), to the form hydrosilicates [4].

Cement containing SF exhibits higher strength than non–blended materials, therefore it is used to manufacture high-strength concrete [5, 6]. Moreover, SF acts not only as filler or pozzolanic material, but also to improve the cement paste–aggregate interface, which contributes to further improving concrete strength. Incorporation of SF, also affects fresh cement flowability, however, substantially raising the water demand, and its high early age hydration reactivity increases the heat of hydration and consequently intensifies total shrinkage [7-10].

The characteristics of transition zone between the aggregate particles and cement paste plays a significant role in the strength of cement–aggregate bond. SF addition decreases the thickness of transition phase and reduces the degree of orientation of CH crystals. Therefore, the mechanical properties are improved. Mechanism behind is not only connected to chemical formation of CSH at interface, but also to the microstructure modification [11]. The effect of SF in cement paste, mortar or concrete can be studied basically under three roles: i) pore size refinement and matrix densification, ii) reaction with the liberated lime during the hydration of Portland cement and iii) cement paste–aggregate interfacial refinement [11].

The development and use of admixtures have greatly accelerated in the last two decades. Today, the commonly used admixtures in concrete technology can contain set retarding or set accelerating chemicals, which obviously will directly impact kinetics. Most of concretes in developed countries also use a cement dispersing agents, commonly called water reducing or plasticizing admixtures. These water reducing admixtures exhibit a more powerful dispersing capability, are called high-range water reducing admixtures (HRWRA) or superplasticizers (SPs). These materials both increase workability and reduce the amount of agglomerated cement particles. These agglomerates can lead to low w/c regions, which limits cement hydration in those areas, while allowing other regions to be higher than nominal w/c. Thus, SP can often lead to improve the strength and permeability even at equal w/c. If a water reduction is also taken, more substantial improvements in both are achieved. SP compositions may also include materials that directly impact hydration kinetics beyond the dispersion effects. Such admixtures frequently contain some combination of set retarding and accelerating components [12].

Superplasticizers (SPs) are linear polymers with hydrophobic and ionizable hydrophilic polar groups. The nature of hydrophilic and hydrophobic groups should insure minimum surfactancy to avoid foaming and air entrainment by the admixtures. The addition of small amounts of superplacticizer enhances the workability, but they often associated with strong, undesired retardation phenomena of set cement paste. Superplasticizers are frequently used in concrete technology for three different purposes or a combination of these:

- to increase the workability without changing the mix composition to enhance placing characteristics of concrete,
- to reduce the required water of standard consistency in order to increase the strength of concrete [13, 14],
- to reduce both water and cement at a given workability in order to save cement and reduce creep, shrinkage and thermal strains caused by heat of cement hydration [15].

The fresh characteristics of concrete made with Portland cement (PC) can be modified and controlled with superplasticizers. Achieving the steepest decline in the water–cement ratio, greatest workability and decreasing the viscosity is, however, contingent upon the compatibility between the admixture chosen and the cement. The presence of fly ash (FA) and SF may positively affect the interaction between SP and cement components [16].

Superplasticizers improve the rheological performance of cement paste, due to the dispersion of agglomerated cement and hydrating particles [17]. Such agglomerates formed during the initial mixing of OPC with water; result from relatively large Van der Waals attractive forces, which operate at inter–particle distances in the range of 5 to 7 nm. Loosely entrapped quantities of water are associated with the agglomerated network of particles. Anionic polymers, such as SNF or SMF have the ability to overcome the Van der Waals forces by imparting a stronger repulsive force at the surface–liquid interface, freeing the entrapped water. The dispersing effect of superplasticizer was ascribed to the development of the electrostatic (negative) charge on the cement particles [18, 19]. This process was described by Spiratos *et al.,* to occur as follows [17]:

- the mixing actions break down the cement agglomerates and distribute the HRWRA agent, fully miscible in the high ionic strength pore water, through the cement slurry;
- an attractive force between SP, which usually bears a negative charge at the relatively high pH of the pore water, and the positively charged cement surfaces, causes fairly rapid adsorption of the SP onto the cement particles;
- the adsorbed compounds produce some combination of electrostatic and steric repulsive forces that prevent re-agglomeration of cement particles and liberate the water trapped within the flocculated structure.

This can be used to lower the viscosity of the cementitious mixture.

The dispersing effects of HRWRA, however, vary according to different factors such as, its type and dosage, the nature and amount of cement, aggregates, temperature and mixing procedure [20-23]. Regarding the effect of addition time, it was reported that, delayed addition of SP decreased slump values for the period from 5 to 50 minutes after mixing the cement with water [24]. The delayed addition of SP in cement based mixes enhances significantly the effectiveness of their dispersing power in comparison to the direct addition [25-28]. Also, delayed addition modifies the microstructure rather than simultaneous addition or vigorous mixing (rather than hand mixing) [12, 29].

Flatt and Houst [30] proposed that, SP forms organomineral phases by intercalation, cooprecipitation, or micellization around the cement particles. It either adsorbed by hydrated phases or incorporated into organomineral phases and it is expected to provide no dispersing effect.

HRWRA are broadly classified into four groups, sulfonated melamine-formaldehyde condensates (SMF), sulfonated naphthalene-formaldehyde condensates (SNF), modified lignosulfonates (MLS), and polycarboxylate derivatives (PCEs) [31]. SNF and MLS polymers are still widely used in China today. SNF dispersing agent was the first synthetic admixture [32]. Its dispersing ability has been shown to vary with cement composition [33-36]. The uptake of SNF and PCEs with aluminate phases has been verified by XRD, elemental analysis, IR spectroscopy and TEM. Fernon et al [37] confirmed the formation of intercalated organo-mineral phases during the preparation of calcium aluminate hydrates with SNF. FTIR spectroscopy corroborates the assumption that sulfonate groups are chemically bound to the principal layers, which represents the driving force for intercalation [37-39].

Uchikawa et al [26] confirmed that, SNF polymer is more particularly adsorbed on hydrated C_3A, when the immediate addition procedure is adopted. The superplasticizer effect is improved with SNF delayed addition because of the lower adsorption of the polymer on the hydrated C_3A. Also, the fluidity of fresh cement paste prepared by later addition is improved due to that water fixed in the spaces inside the flocks of cement particles is decreased from its uniform dispersion, and thereby water film which has relatively uniform thickness is formed on the surface of cement particles. Setting of cement is further delayed by later addition of SNF that, the superplasticizer still remaining in the mixing water after the initial setting consumes some of calcium ions (Ca^{2+}) and decreases its concentration in the freshly prepared cement paste, and then the final setting time is elongated.

The influence of the addition time on the effect of SP has been ascribed to the different capabilities of SMF or SNF polymer molecules to be adsorbed on anhydrous or hydrated cement particles [12, 40, 41]. This effect seems to be related to the production of an ettringite coating film on the surface of cement particles during the preliminary water treatment. Consequently, the adsorption of SMF or SNF polymer molecules on the prehydrated cement surface is reduced and the subsequent dispersing action appears to be much more effective than that recorded in the absence of the preliminary water treatment.

The hydration mechanism of ordinary Portland cement (OPC) with SP and the effect of a polycarboxylate superplasticizer on the mechanical, mineralogical, microstructural, and rheological behavior of OPC pastes were studied [42-45]. The results indicated that, at very early ages an initial retardation of cement hydration is produced. This effect is more pronounced at higher doses of SP, due its interaction with the reactive species. The organic admixtures affect the hydration kinetics and consequently hydrated phase diffusion, nucleation and growth, therefore process. The effects of water dispersible polymers on the properties of hardened cement pastes, mortar, and concrete were investigated. The hydration and microstructure characteristics of superplasticized OPC pastes were studied [46-50]. It was concluded that, the addition of acrylate-polyethylene glycol to OPC pastes blended with 5 and 7.5 mass % SF improves the mechanical properties during all stages of hydration [51]. The interaction between SF implemented as partial cement replacement and SNF superplasticiser consists of two effects: i) a dilution effect, leading to a decrease in SNF dosage and ii) a surface area effect, leading to an increase in SNF dosage. The combination of both effects leads to an optimal cement replacement level with regard to the workability of cement paste, mortar or concrete. The effect of intergrinding different percentages of a naphthalene-based superplasticizer with Portland cement clinker and gypsum on the fineness of the product, the water requirement and the compressive strength of superplasticized cement mortars was studied [10, 52]. The effect of lignosulfonate (SLS) and SNF on the microstructure and hydration characteristics of hardened OPC pastes was studied [53]. The efficiency of SNF in reducing the w/c ratios is higher than that of SLS. Therefore, OPC pastes made with SNF have higher improvement mechanical properties than those with SLS. XRD and SEM indicate that, the addition of SLS or SNF to OPC pastes does not alter the types of hydration products, but it affects only the degree of crystallinity of the hydrates, which leads to highly amorphous hydration products.

The present study is concerned with the behavior of delayed addition time of SNF condensate on the hydration kinetics and mechanical properties of microsilica SRC pastes to evaluate the individual relative effectiveness of the dosage and delaying addition time of SNF.

EXPERIMENTAL

The materials used in this work were Egyptian sulfate resisting cement (SRC) provided from El–Masria Cement Company, (Suez) and microsilica (SF) derived from ferrosilicon alloys Company, (Edfo, Aswan). The chemical composition of these materials is shown in Table 1.

The specific surface area of SRC and microsilica determined by the Blaine air permeability method was found to be 3300 and 22400 $cm^2\ g^{-1}$. Water-soluble SNF condensate, was used and its structure was confirmed by Mattson gensis, FTIR spectrometer in the range 400 - 4000 cm^{-1} and shown in Figure 1.The main band characterizing the condensation process is the CH_2 linkage, which appears as stretching vibration band at 2922.39 cm^{-1} and bending (scissors) vibration band at 1499.33 cm^{-1}. Also, IR spectrum contains aromatic C–H stretching band at 3053.73 cm^{-1}, aromatic ring modes at 1625.29 and 1596 cm^{-1} as well as sulfonate group bands at 1190, and 1031.55 cm^{-1}. The other bands show: S=O stretching vibration band at 1347.09 cm^{-1}, S–O group at 677.06 cm^{-1}, C=C aromatic groups at 2366.02 cm^{-1}.

SRC and SF were blended together in the ratio SRC/SF, (90/10) mass % in a porcelain ball mill with four balls for two hours using a mechanical roller to attain complete homogeneity. Different mixes were prepared with the required water of standard consistency according to ASTM Designation: C187-92, 2008 [54]. The initial and final setting times of each mix were determined using Vicat Apparatus [55]. The polymer dosage was chosen as 0.0, 0.5, 1.0, 1.5 and 2.0, mass %. The fluidity of cement paste (mini-slump) was carried out on small amounts of cement pastes at constant w/c ratio of 0.55 Only 75 mass % of mixing water was initially

Table 1. Chemical composition of starting materials, (mass %).

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	L.O.I	Total
SRC	21.40	3.67	5.05	64.73	1.50	2.05	0.30	0.22	2.60	99.70
SF	94.81	0.16	0.84	0.89	0.49	0.08	0.20	0.05	2.43	99.95

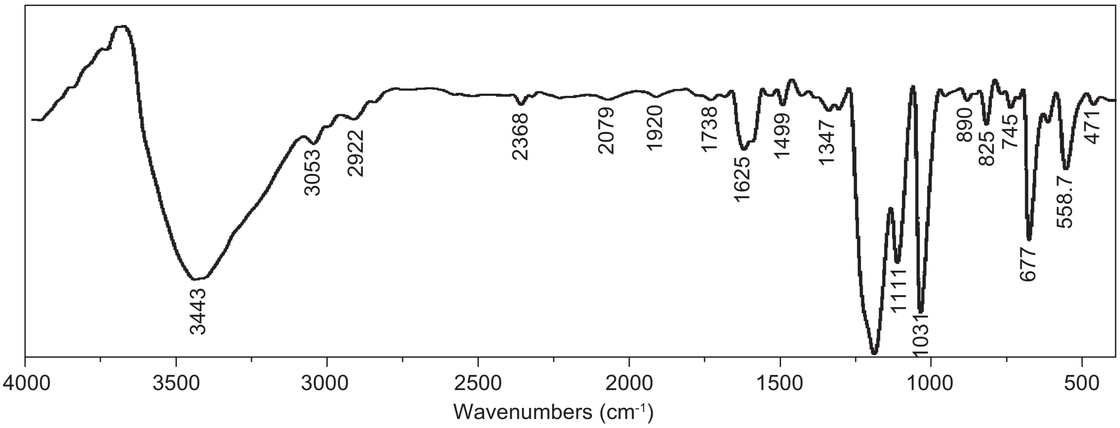


Figure 1. FTIR spectra of SNF.

added and mixed for 3 minutes, then the rest water added after delayed addition times of 0, 7.5, 10, and 15 minutes. The cement pastes were stirred mechanically for three minutes, rest for one minute and restirred two minutes with the same speed, then poured into a stainless steel cone with similar geometry as Abram's cone for regular slump tests, but with reduced dimensions (height of 40 mm, top diameter of 20 mm and bottom diameter of 40 mm). The minicone is put on vibrated table, vertically removed and the diameter of the spread area of the cement paste is measured [56].

Freshly prepared cement pastes were placed in one inch cubic moulds into two approximately equal layers manually compacted and pressed until a homogeneous specimen was obtained. The moulds were vibrated for a 3 minutes to remove any air bubbles to give a better compaction, cured in a humidity chamber at 100 % RH at constant temperature of 25 ± 1°C for 1 day, then demolded and immersed under tap water until the time of testing (1, 3, 7, 28 and 90 days). A set of three cubes was used for the determination of compressive strength of cement paste as described by ASTM Specifications [57]. The measurements were done on a compressive strength machine of Seidner, Riedinger, Germany, with maximum capacity of 600 KN force.

The bulk density was carried out before the pastes subjected to compressive strength determination through weighing the hardened pastes suspended in water and in air (saturated surface dry). Each measurement was conducted on at least three similar cubes of the same age [58]. The following equation was used for calculating the bulk density:

$$\text{Bulk density (dp)} = \frac{\text{saturated weight}}{\text{volume of sample}} \quad \text{g cm}^{-3}$$

$$\text{Volume of sample} = \frac{\text{saturated + suspended weight}}{\text{density of liquid (water)}}$$

$$\text{Bulk density (dp)} = \frac{\text{saturated weight}}{\text{saturated + suspended weight}} \times 1$$

The total porosity was determined from the evaporable (We), total water (Wt) contents and bulk density (dp) of the hardened cement specimen using the following equation [59]:

$$\varepsilon = \frac{0.99W_e \times dp}{1 + W_t} \times 100$$

The free lime (CH) content of cement paste was thermally measured. Exactly 0.5 g of the hardened cement was placed in a porcelain crucible and introduced in a cold muffle furnace. The temperature was increased up to 390, then to 550°C at heating rate of 5°C/min. The weight loss occurred between 390 - 550°C with soaking time of 15 min is equal to the weight of water of CH. Consequently, the free lime can be calculated.

The combined water content (Wn, %) is considered as the percentage of ignition loss of the dried sample (on the ignited weight basis). 2 g of dried sample, was gradually ignited up to 1000°C for 1hr. The Wn was corrected from the water of free CH present in each sample [60].

FTIR spectroscopic analysis was carried out to investigate the hydration products. The samples were prepared using alkali halide pressed disk technique as it gives a further reduction in scattering. Exactly 2.0 mg of the sample was interground with 198 mg of potassium bromide (KBr) in agate mortar to produce a homogeneous mixture. The formed mixture was pressed under vacuum to give a transparent disk of 1cm in diameter. FTIR data was recorded from KBr disks using Mattson Gensis IR spectrometer in the range from 400 up to 4000 cm^{-1}.

RESULTS AND DISCUSSION

The variations of required water of standard consistency, water reduction and setting times of cement pastes with different dosages of SNF are graphically represented in Figure 2. The results show that the required water of standard consistency decreases, whereas water reduction increases with SNF dosage. This is due to the effectiveness of SNF in breaking and dispersing the cement particle networks minimizing the amount of water required to suspend particles and renders the mix workable. SNF is anionic SP and adsorbed on cement particles, forming a good ionic repulsion raised from the negative charge of sulfonate groups, and consequently increasing the cement paste fluidity. The initial setting time shortened, whereas the final setting time elongated with SNF content. Also, SRC shows slow hydration rate, due to its lower C_3A content, which causes rapid setting and hydration.

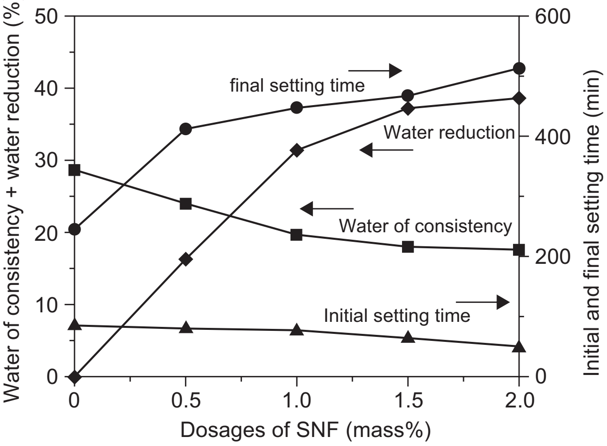
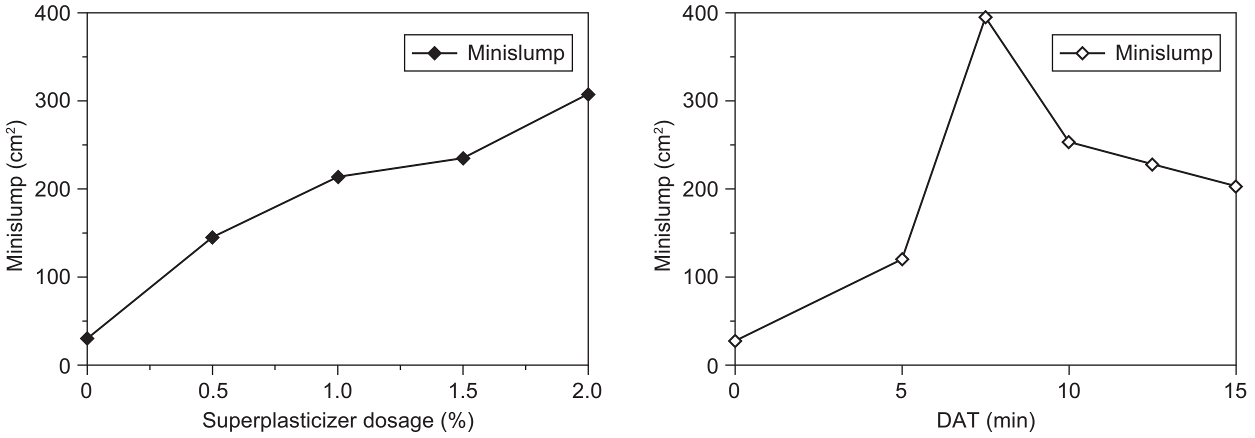


Figure 2. Water of consistency, water reduction, initial and final setting times of cement pastes at different dosages of SNF.

Figure 3a represents the mini-slump of cement pastes as a function of SNF dosage up to 2.0 mass %. The effect of DAT of 1.0 % SNF up to 15 min on the mini-slump values are graphically represented in Figure 3b. It can be seen that, the mini-slump increases with SNF dosage, due to the increase of cement paste fluidity with SP content. As SP was added to cement paste, the rapid adsorption of SP molecules on cement particles causes strong dispersion, thus generating high fluidity of cement paste [61]. The fluidity of cement pastes prepared with 1.0 mass % SNF increases with DAT at 7.5 min and then decreases for 15 min. DAT enhances the fluidity of cement pastes, attributed to the decrease of anhydrous C_3A content within the first few minutes of hydration and SP adsorption on anhydrous C_3A and C_3S is higher than that on the hydrated phases [21]. The positive sites of C_3A are responsible for consuming large amount of SP, which reduced with DAT. It has showed that 7.5 min seems to be the suitable DAT for SNF. It gives relatively higher mini-slump of cement pastes containing 1.0 mass % SNF in comparison to the other used DATs. Above 7.5 min the fluidity of cement pastes decreases with DAT, due to the increase of hydration products and as such a great part of SNF is adsorbed on the formed hydrates, so that the dispersing effect of SNF is greatly reduced.

The degree of hydration of cement paste is measured from the combined water (Wn) and free lime (FL) contents. Figure 4a shows the effect DAT of 1.0 mass % SNF up to 15 min on (Wn) of cement pastes hydrated up to 90 days. It is apparent that Wn % increases with curing time for all cement pastes. This mainly due to the continuous hydration of cement phases as well as the pozzolanic reaction of microsilica with the liberated lime [62], leading to the formation and accumulation of more hydration products (CSH, CSA and CASH). It is also obvious that Wn % increases with DAT up to 7.5 min, then decreases .This is attributed to the improved superplasticizing effect with DAT, especially at 7.5 minutes. Consequently, the hydration of cement phases increases with DAT in addition to the pozzolanic reaction of SF with the liberated $Ca(OH)_2$. Increse of DATs more than 12.5 minutes, Wn % decreases, due to the retardation effect of SP. SNF molecules form a complex with Ca^{2+} on the surface of CSH gel or CH crystals, i.e. SP inhibits the growth of hydrates [56].

The Wn % of cement pastes up to 90 days with SNF dosage at DAT 7.5 min is graphically plotted in Figure 4b. It decreases with polymer dosage up to 2.0 mass, due



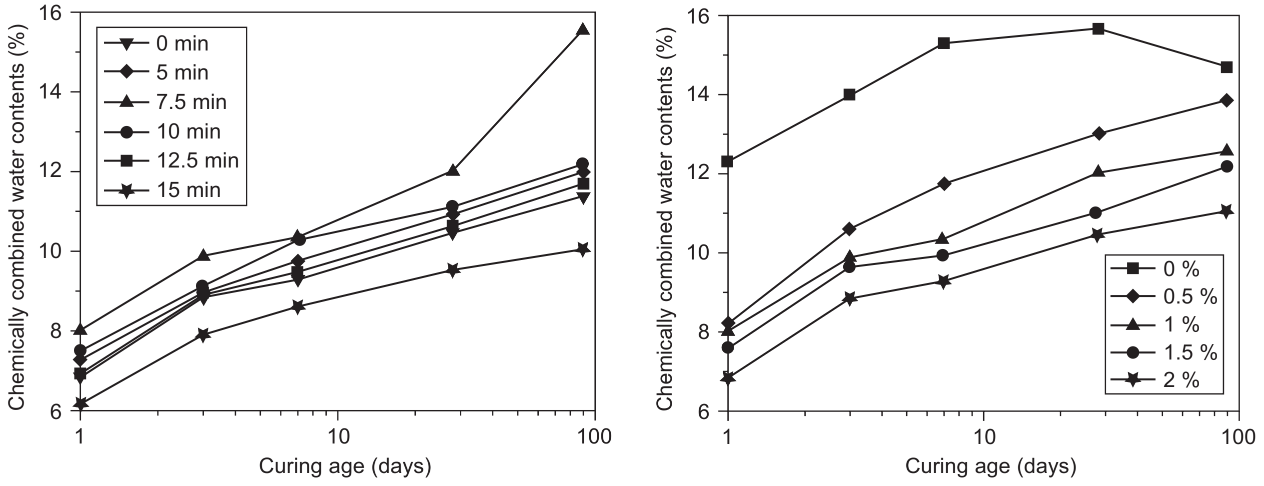
a) b)

Figure 3. Minislump of cement pastes: a) Effect of different dosages of SNF, b) effect of delaying addition time of 1.00 % SNF up to 15 min.

to the water reduction and retardation effect of SNF with SNF polymer dosage. These two factors work together and adversely affect the hydration rate of cement phases. The free lime contents (FL %) of superplasticized cement pastes with 1.0 % SNF up to 90 days as a function of DAT are depicted in Figure 5A. It is indicated that FL % increases with DAT, due to the improvement of superplasticizing effect of SNF, because of the lower adsorption of SNF molecules on the hydrated C_3A, and more SNF molecules are left for dispersion of C_3S and β–C_2S. Therefore, their dispersion and hydration rates increase with DAT, leading to increase FL, %. Also, FL contents at 7.5 minutes are lower than those at 0, 5, 10, 12.5 and 15 minutes. This may be due to the highest retardation effect of SNF at 7.5 minutes comparing with those at the other DATs.

FL of cement pastes cured up to 90 days with SNF dosage at DAT 7.5 minutes is graphically represented in Figure 5b. Generally, it is shown that, F.L, % decreases with SNF content. This may be attributed to two factors; the first is the retardation effect of SNF which reacts with Ca^{2+} ions and hold their action via complex formation [21]. The chelating capacity of SNF to Ca^{2+} increases with polymer content; the second is the increase of SF pozzolanic activity with SNF dosage.

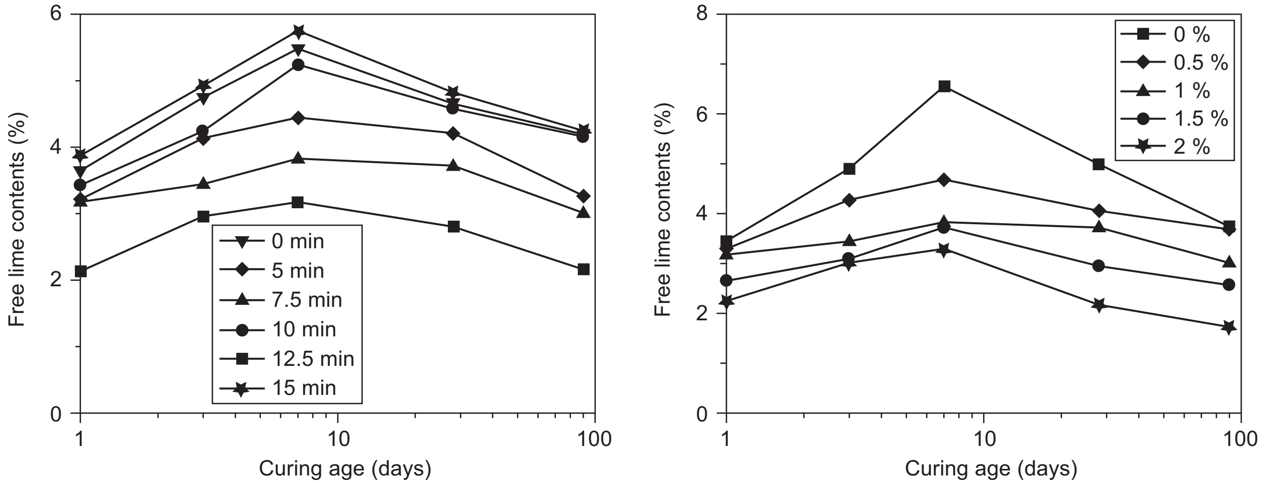
The effect of DAT of 1.0 mass % SNF for 15 min on the compressive strength of cement pastes hydrated up to 90 days is graphically plotted in Figure 6a. It can be seen that the compressive strength increases with curing time for all cement pastes, due to the formation of additional hydration products with time, especially tobermorite gel (the main source of strength). These



a)

b)

Figure 4. Chemically combined water contents of cement pastes: a) effect of delaying addition time at 1.0 % SNF up to 15 min b) effect of SNF dosage at delayed addition time at 7.5 min.



a)

b)

Figure 5. Free lime contents of cement pastes: a) effect of delaying addition time of 1.0 % SNF up to 15 min, b) effect of SNF dosage at DAT 7.5 min.

products accumulate in the open pores to form a more compact body [60]. Also, the results illustrate that, the compressive strength increases with DAT up to 12.5 min, then decreases at 15 min. There is sharp increase of compressive strength at 7.5 min.

The increase of compressive strength with DAT up to 12.5 may be due to the improvement of superplasticizing effect with DAT. The hydration of C_3S and β–C_2S increases sharply with DAT of SNF at 7.5 min, then smoothly up to 12.5 min. At 15 min, the compressive strength decreases, due to the retardation effect of SNF condensate. SNF acts as complexing agent and can react with the liberated Ca^{2+} forming chelate. The chelating action of SNF on Ca^{2+} increases with DAT.

Figure 6b shows the effect of SNF dosage at DAT 7.5 minutes on the compressive strength of cement pastes up to 90 days. It is clear that all superplasticized give higher compressive strength than the control mix (0.0 % SNF). The compressive strength increases with SNF content to reach its maximum at 1.0 %, then decreases up 2.0 % SNF. The increase of compressive strength with SNF dosage is mainly attributed to three factors, the first is the superplasticizing effect which negatively affect the total porosity and bulk density leading to the improvement of microstructure [61]; the second is the enhancement of pozzolanic activity of SF portion with SNF content to react with liberated $Ca(OH)_2$, therefore the hydration products increase and accumulate in water filled pores forming of more dense compact structure; and the third factor is the decrease of mixing water with SNF dosage. It is well known that, the compressive strength is in a good agreement with the degree of water reduction, a high degree of water reduction gives a higher strength enhancement [62, 63]. These factors enhance the degree of pastes compaction which positively reflected on the compressive strength. On the other side, the decrease of compressive strength is due to its retardation effect on the hydration of C_3S and β–C_2S. Therefore, the amounts of hydrated silicates decrease with SNF content.

The variations of bulk density and total porosity of cement pastes containing 1.0 % SNF and hydrated up to 90 days with DAT up to 15 min are represented in Figure 7. The results indicate that the bulk density increases and total porosity decreases with curing time for all cement pastes, due to the continuous hydration of cement phases, leading to the formation and accumulation of additional hydrated silicates and aluminosilicates which tend to decrease the total porosity and increase the gel/space ratio as well as the bulk density [60, 64]. As DAT increases, the bulk density increases to reach its maximum at 7.5 minutes, then decreases at 10 min, but still more than the control mix (zero DAT). This is attributed to the higher efficiency of SNF with delayed than simultaneous addition. Delayed addition decreases the adsorption capacity of SNF on the hydrated C_3A. So, large amounts of SNF are left for dispersion of silicate

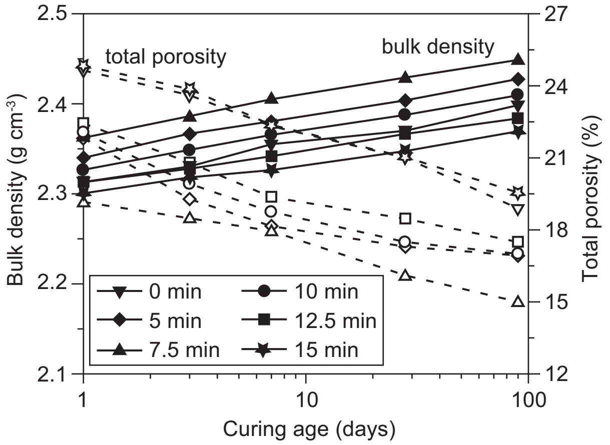
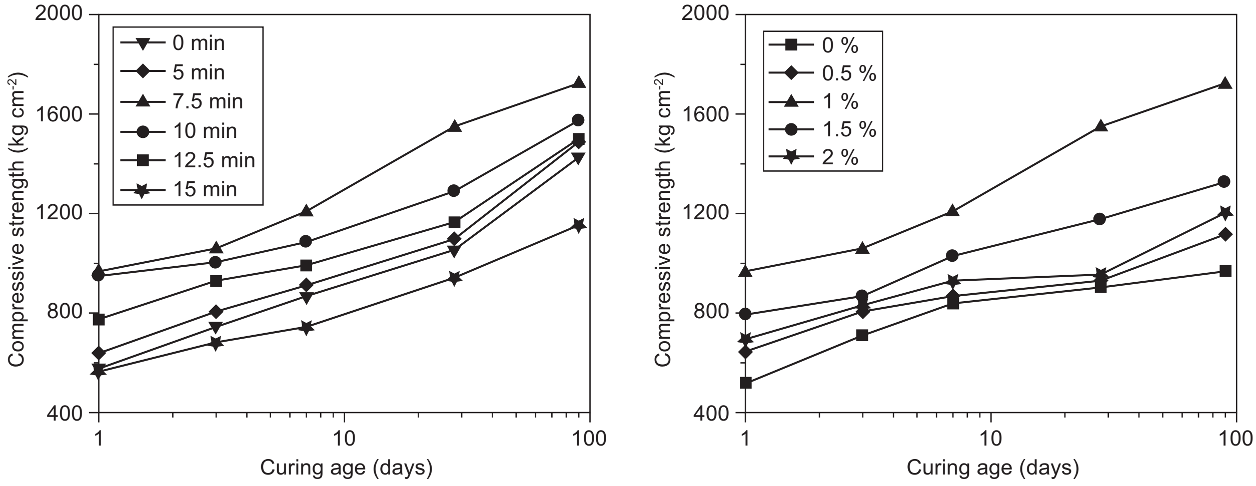


Figure 7. Bulk density and total porosity of cement pastes at delaying addition 7.5 min with 1.00 % SNF.



a) b)

Figure 6. Compressive strength of cement pastes: a) effect of delaying addition time of 1.0 % SNF up to 15 min, b) effect of SNF dosage of DAT at 7.5 min.

phases and enhancing their hydration, leading to the production of additional amounts of hydro-silicates which is the main source of strength. At delaying time more than 10 min, bulk density decreases to become lower than that of the control mix due to the retardation effect of SNF superplasticizer. SP molecules react with Ca^{2+} forming chelate on the surface of C–S–H gel or CH crystals; the interweaved net structure consists of ion bonded large molecular system bridged by means of $Ca(OH)_2$ [65]. The chelating capacity of SP to Ca^{2+} increases with DAT leading to more retardation effect of the cementitious system .

The bulk density and total porosity of cement pastes admixed with different dosages of SNF up to 2.0 mass % at DAT of 7.5 minutes cured for 90 days are graphically plotted in Figure 8. The total porosity decreases and bulk density increases with curing time. This is due to the increase of the hydration products, especially tobermorite-like gel with high binding properties which improves the microstructure of cement paste [60]. Also, the total porosity values of superplasticized cement pastes are lower and bulk densities are higher than those of the control mix (0.0 % SNF). As the polymer dosage increases, the bulk density increases up to 1.0 mass %. This is due to the effect of SP, which reduces the mixing water then decreases the total porosity and increase the gel/space ratio and the degree of cement paste compaction.

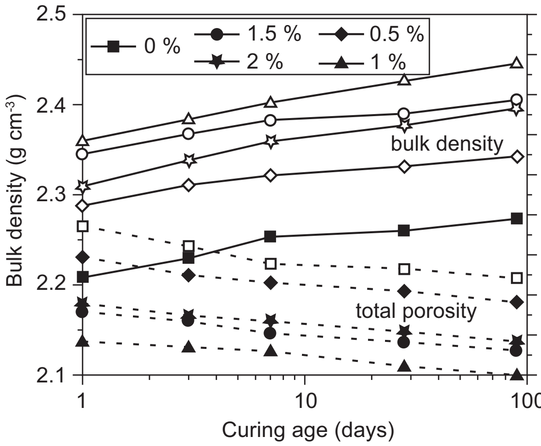


Figure 8. Bulk density and total porosity of cement pastes of different dosages of SNF delayed addition time at 7.5 min.

FTIR spectra of some selected samples were recorded using Fourier transformation infrared Mattson Genesis-IR spectrometer. Spectra were collected in the mid-infrared region (400-4000 cm^{-1}) at 2 cm^{-1} resolution. FTIR spectra of cement pastes in presence of different SNF dosages at DAT 7.5 min at 7 days is shown in Figure 9. The small band at 3637-3641 cm^{-1} is attributed to the –OH group of $Ca(OH)_2$. This band is very useful for diagnosis of the initiation of hydration process [66] and follow up the hydration kinetics. Therefore, the intensity of that band decreases with the pozzolanic reaction, which increases with the SP dosage. The broad band around 3400 cm^{-1} and that observed at 1640 - 1650 cm^{-1} are assigned to the stretching and bending vibration of water bound in the hydration products. Their widths decrease and their intensities increase with SP content, because the increase of SP enhances the pozzolanic reaction of SF with free CH forming successive amounts of hydrated products. It was reported that [67], the phases of nonordered structures increase the band width and those of strictly ordered structures give sharp needle bands with high intensities. The band at the range 950 - 980 cm^{-1} is due to the formation of calcium silicate hydrate (CSH) and its intensity increases with SNF content. This band is shifted towards higher frequencies with polymer dosage, because the pozzolanic reaction of SF with free lime is enhanced with SNF dosage, giving additional amounts of CSH. The band at 1490 cm^{-1} is indicated to C–O bond stretching of CO_3^{2-}, which results from the carbonation of hydration products. Exposure of the hydrated cement pastes to CO_2 results very quick carbonation [68]. The intensity of that peak decreases with SNF content. The observed band at 450 - 492 cm^{-1} is due to bending vibration of Si–O bond in SiO_4^{2-} tetrahedral [69]. Its intensity increases with SNF dosage. This is due to the increase of pozzolanic reaction and formation of large amounts of CSH.

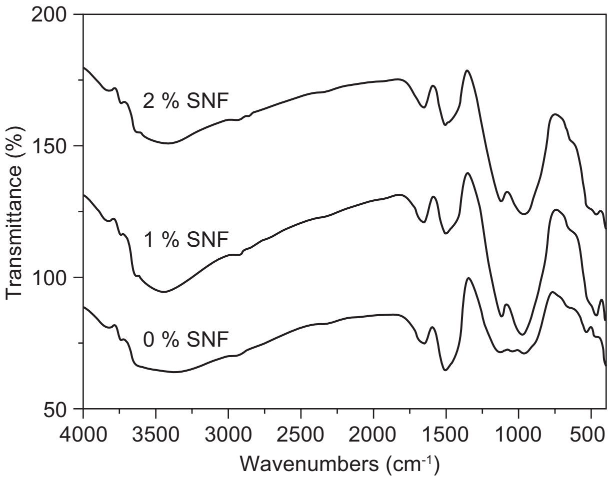


Figure 9. IR spectra of cement pastes with NFS at 7.5 min up to 7 days.

FTIR spectra of cement pastes in presence of two different dosages (1.0 and 2.0 %) of SNF at DAT 7.5 minutes and hydrated for 90 days are graphically represented in Figure 10. The small band located at 3637 - 3641 cm^{-1} is attributed to the –OH band from hydrated lime (CH). Its intensity decreases with SNF dosage, due to two factors, the first is the retardation effect of SP, which acts as chelating agent and reacts with Ca^{2+}, holding their action via chelation process [26]; the second factor is the increase of pozzolanic activity of SF in the presence of SNF. The band at 3400 cm^{-1} as well as at the range 1640 - 1650 cm^{-1} are assigned to stretching and bending vibration of H_2O bound in the hydration products, their intensities increase with SNF. The band at the range from 950 to 980 cm^{-1} is assigned to the formation of CSH. Its intensity increases with SNF content. The band around 1475 cm^{-1} is attributed to C–O bond stretching of CO_3^{2-}. The intensity of that band decreases with SNF dosage, due to the increase of SF pozzolanic activity towards free $Ca(OH)_2$, then the lime consumption increases with polymer content. The band located at the range from 450 to 492 cm^{-1} is attributed to bending vibration of Si–O bond in SiO_4^{2-}. The intensity of that band increases with SNF dosage, due to the above mentioned reason.

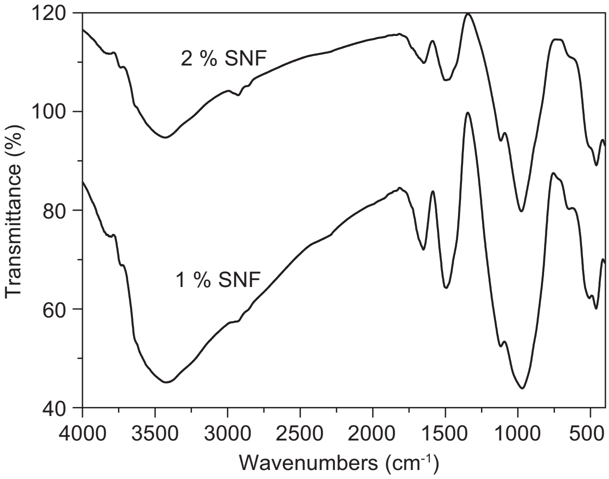


Figure 10. FTIR spectra of cement pastes with 1.00 and 2.00 % NFS at 7.5 min hydrated at 90 days.

The infrared spectra of cement pastes admixed with 1.0 mass % of SNF at DAT of 7.5 min at 7 and 90 days is shown in Figure 11. The band at the range from 3637 to 3641 cm^{-1} is attributed to the –OH band from calcium hydroxide. Its intensity decreases from 7 to 90 days, due to the pozzolanic reaction of SF with the liberated lime. The bands centered at about 3400 cm^{-1} and that around 1640 - 1650 cm^{-1} are due to stretching and bending vibration of chemically bonded water in the hydration products [69]. The widths of those bands decrease and their intensities increase with curing time, due to the continuous hydration of cement phases in addition to the pozzolanic reaction of SF with the liberated lime, leading to the formation of additional hydration products. The band at 1475 cm^{-1} is assigned to C–O bond stretching of CO_3^{2-}. Its intensity decreases with curing time due to the increase of the pozzolanic reaction between SF and $Ca(OH)_2$, which is the main phase for carbonation. The detected band at 950-980 cm^{-1} is attributed to the formation of CSH, which its intensity increases and its position is shifted towards higher frequencies with hydration time. This is due to the increase of both hydration reaction of cement phases and the pozzolanic reaction of SF with free lime forming additional amounts of hydro-silicates. The band at the range 450 - 492 cm^{-1} is assigned to the bending vibration of Si–O bond in SiO_4^{2-}, which increases with curing time due to the pozzolanic reaction and formation of additional hydrated silicates.

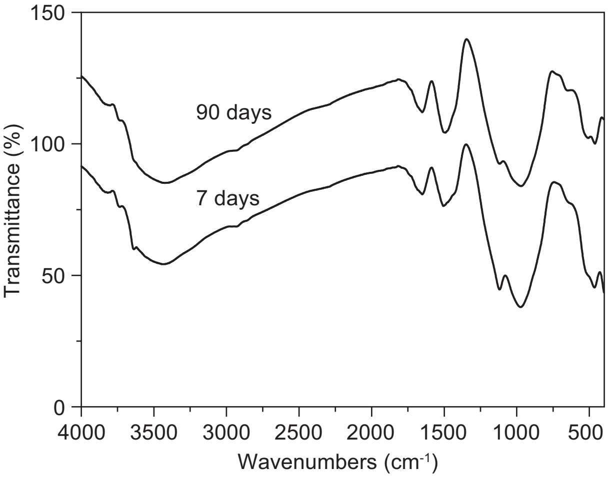


Figure 11. FTIR spectra of cement pastes with 1.0 % NFS at delaying addition time 7.5 min up to 90 days.

CONCLUSIONS

The behavior of DAT of SNF on the hydration and mechanical properties of SRC pastes incorporating 10 mass % SF to evaluate the effectiveness of both SNF dosage and its DAT was studied individually. The following conclusions can be drawn from the present study:

- The water of standard consistency decreases, whereas water reduction and fluidity increase, due to its effectiveness in breaking and dispersing the cement particle networks minimizing the amount of water required for suspending particles and renders the mix workable.
- Fluidity increases with DAT up to 7.5 minutes, then decreases up to 15 minutes. With delayed addition, SNF is not incorporated within the hydrated products. Therefore, it remains almost completely, thus a large fraction of SNF is available for dispersion of cement particles, which increases of cement paste flowability.
- The compressive strength, combined water and bulk density increase, whereas total porosity decreases with curing time for all cement pastes, due to the formation of additional hydration products with time, especially tobermorite gel. These products accumulate in some open pores to form a homogeneous compact closed microstructure.
- Compressive strength and bulk density of superplasticized cement pastes with SNF are higher than those without SNF, due to its superplasticizing effect which

increases the reduction of mixing water, improves the microstructure and consequently enhances the mechanical properties.

- The strength properties and bulk density of cement pastes admixed with SNF at DAT 7.5 minutes increase with SNF content to reach its maximum at 1.0 %, and then decrease at 2.0 % SNF.
- At 1.0 mass % SNF, the strength, bulk density and combined water increase and those of total porosity decrease with DAT up to 12.5 min, then decrease at 15 min.
- The results of FTIR spectra are in a good agreement with those of chemical and physico-mechanical properties of the investigated pastes.
- Cement pastes prepared using 1.0 mass % SNF at DAT 7.5 minutes have higher improvement of hydration kinetics and mechanical properties than those prepared with higher doses and DAT. Therefore, it is suggested that, the most suitable DAT of SNF is 7.5 min and its optimum dosage is 1.0 wt %.
- High performance cement paste, mortar and concrete can be obtained by incorporation of a well-designed combination of SRC, SF, and SNF superplasticizer.

Acknowledgement

The authors would like to thank Prof. Dr. Mohamed Heikal, Professor of Inorganic Chemistry and Building Materials, Chemistry Department, College of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), for his great help thougrouth the interpretation of the results of this article.

REFERENCES

1. APC. *L'emploi, des fluidifiants dans les bétons à hautes performances. Les Bétons à Hautes Performances*, Chapitre 3, p. 45–64, Presses de l'Ecole Nationale des Ponts et Chaussées, Paris, 1992.
2. Dodson V.H. in: *Concrete admixtures.* Structural engineering series, Ed. Van Nostrand Reinhold, New York, 1990.
3. Hanna E., Luka K., A PC. in: *Rheological behaviour of Portland cement in presence of a superplasticizer and other chemical admixtures in concrete*, In: Proceedings of the 3rd international meeting, CANMET/ACI, Ottawa, Canada, 1989.
4. Kadri El-Hadj, Duval R.: Constr. Build. Mater. *23* 3388 (2009).
5. Toutanji H.A., El-Korchi T.: Cem .Concr. Res. *25*, 1591 (1995).
6. Rao G.A.: Cem. Concr .Res. *31*, 443 (2001).
7. Mazloom M., Ramezanianpour A.A., Brooks J.J.: Cem. Concr. Compos. *26*, 347 (2004).
8. Al-Amoudi O.S.B., Abiola T.O., Maslehuddin M.: Constr. Build. Mater. *20*, 642 (2006).
9. Jo B., Kim. C., Tae G., Park J.: Constr. Build. Mater. *21*, 1351 (2007).
10. Kadri E., Aggoun S., Schutter G.: Constr. Build. Mater. *23*, 3124 (2009).
11. Khan M.I., Siddique R.: Resources Conservation and Recycling *57*, 30 (2011).
12. Cheung J., Jeknavorian A., Roberts L., Silva D.: Cem. Concr. Res. *41*, 1289 (2011).
13. Aiad I.: J. Appl. Polym. Sci. *98*, 2212 (2005).
14. Aiad I., Hafiz A.: J. Appl. polym. Sci. *90* 482 (2003).
15. Collepardi M. in: *Concrete Admixtures Handbook. Properties, Science and Technology*, p.286-396, ed. Ramachandran V. S., Noyes Publications, Park Ridge, New Jersey, USA, 1995.
16. Montes O.B., Palacios M., Rivilla P., Puertas F.: Constr. Build. Mater. *31*, 300 (2012).
17. Spiratos N., Pagé M., Mailavaganam N.P., Malhotra V.M., Jolicoeur C.: Superplasticizers for concrete: fundamentals, technology and practice, AGMV Marquis, Quebec, 2003.
18. Malhotra V.M., Ramachandran, V.S. in: *Superplasticizers in Concrete Admixtures Handbook, Properties, Science and Technology*, p. 410-506, ed. Ramachandran V. S., Noyes Publications, Park Ridge, New Jersey, USA, 1995.
19. Collepardi M., Ramachandran, V.S. in: Proceedings of the 9th International Congress on the Chemistry of Cement, p. 529-570, New Delhi. India., Vol.1, ThemeIIID, 1992.
20. Lei L., Plank J.: Cem. Concr. Res. *24*, 118 (2012).
21. Uchikawa H., Hanehara S., Shirasaka T., Sawaki D.: Cem. Concr. Res., 22, 1115 (1992).
22. Simard M. A., Nkinamubanzi P.C., Jolicoeur C., Perraton D., Aitcin P.C.: Cem. Concr. Res. *23*, 939 (1993).
23. Ramachandran V.S.: *Concrete Admixtures Handbook: Properties, Science and Technology*, p. 412–3. Noyes Publications, Park Ridge, NJ, 1984.
24. Kung-Chung Hsu, Jih-Jen Chiu, Sheng-Da Chen, Yuan-Cheng Tseng: Cement & Concrete Composites *21*, 425 (1999).
25. Chiocchio G., Paolini A.E.: Cem. Concr. Res. *15*, 901 (1985).
26. Uchikawa H., Sawaki D. Hanehara S.: Cem. Concr. Res. *25*, 353 (1995).
27. Aiad I., El-Aleem S.A., El-Didamony H.: Cem. Concr. Res. *32*, 1839 (2002).
28. Aiad I.: Cem. Concr. Res. *33*, 1229 (2003).
29. Chen T., Struble L.J.: ACI Mater. J. *106*, 503 (2009).
30. Flatt R.J., Y.F.Houst: Cem. Concr. Res. *31*, 1169 (2001).
31. Chandra S., Björnström J.: Cem. Concr. Res. *32*, 1605 (2002).
32. Ramachandran V.S.: *Superplasticizers: Properties and Applications in Concrete*. Canada Centre for Mineral and Energy Technology, Ottawa, Canada, (1997).
33. Sandberg P. J., Roberts L. R.: J. ASTM Int. *2*, 219 (2005).
34. Khalil S.M., Ward M.A .: Mag. Concr. Res. *32*, 28 (1980).
35. Nawa T., Eguchi H., Fukaya Y. in*: Superplasticizers and Other Chemical Admixtures in Concrete*, p. 405 –24, Third International Conference Proceedings, Ed. Malhotra V.M., American Concrete Institute, Detroit, MI, 1989.
36. Yoshioka K., Tazawa E.I., Kawai K., Enohata T.: Cem. Concr. Res. *32*, 1507 (2002).
37. Fernon V., Vichot A., Le Goanvic N., Colomber P., Corazza F., Costa U.: *Interaction between Portland cement hydrates and polynaphthalene sulfonates*, Fifth CANMET/ACI conference on superplasticizers in concrete, p. 225–248, ACI, 1997.

38. Plank J., Dai Z., Andres P.R.: Mater. Lett. *60*, 3614 (2006).
39. Plank J., Zhimin D., Keller H., Hossle F., Seidl W.: Cem. Concr. Res. *40*, 45 (2010).
40. Biagini, S., Collepardi M.: *Hydraulic cement improved by superplasticizers and plasticizers*. Eur. Pat. Appl., EP 290, 394, Nov. 9, 1988; Chem Abstr., 110 43946 (1989).
41. Collepardi M.: Cem. Concr. Comp. *20*, 103 (1998).
42. Chandra S., Björnström J.: Cement Concrete Res. *32*, 1613 (2002).
43. Hsu K.C., Chiu J.J., Chen S.D., Tseng Y.C.: Cem. Concr. Compos. *21*, 425 (1999).
44. Krstulovic´ R., Zˇ Mikic´ A., Dabic´ P.: Cement Concrete Res. *24*, 948 (1994).
45. Puertas F., Santos H., Palacios M., Martı´nez Ramı´rez S.: Adv. Cement Res. *17*, 77 (2005).
46. Colak A.: Cem. Concr. Res. *33*, 585 (2003).
47. Colak A.: Cem. Concr. Res. *35*, 1510 (2005).
48. Gu P., Xie P., Beaudoin J.J., Jolicoeur C.: Cement Concrete Res. *24*, 433 (1994).
49. Sakai E., Kasuga T., Sugiyama T., Asaga K., Daimon M.: Cement Concrete Res. *36*, 2049 (2006).
50. Yousuf M., Mollah A., Palta P., Hess T.R., Vempati R.K., Cocke D.L.: Cement Concrete Res. *25*, 671 (1995).
51. El Gamal S.M.A.: Silic. Ind. *70*, 19 (2005).
52. Bouzoubaa N., Zhang M.H., Malhotra V.M.: Cem. Concr. Res. *28*, 1783 (1998).
53. El-Gamal S.M.A., Al- Nowaiser F.M., Al-Baity A.O.: Journal of Advanced Research *3*, 119 (2012).
54. ASTM standards, standard test method for normal consistency of hydraulic cement, ASTM C187-92, p.195, 2008.
55. ASTM standards, standard test method for time of setting of hydraulic cement, Vicat needle, ASTM, designation C191-82, p.208, 1983.
56. Heikal M., Aiad I.: Ceramics-Silikaty *52*, 8 (2008).
57. ASTM Designation: C-150, (2007).
58. Heikal M., Abd-El.Aziz M.A.: Adv. Cem. Res. *21*, 91 (2009).
59. El-Didamony H., Heikal M., Al-Masry S.: in press (2012).
60. Abd El.Aziz M., Abd El Aleem S., Heikal M., Didamony H. El.: Sil. Ind. *69*, 73 (2004).
61. Sahu S., Badger S., Thaulow N., Lee R.J.: Cem. Concr. Compos. *26*, 987 (2004).
62. Pereira P., Evanglista L., de Brito J.: Constr. Build. Mater. *28*, 722 (2012).
63. Xinping O., Xinyuan J., Xueqing Q., Dongjie Y., Yuxia P.: Cem. Concr. Res. *39*, 283 (2009).
64. Heikal M., Aiad I., Shoaib M.M., El-Didamony H.: Materials Chemistry and Physics *71*, 76 (2001).
65. Heikal M., Morsy M.S., Aiad I.: L’industrial Italian del Cemento (iiC) *802*, 772 (2004).
66. Bensted J.: paper delivered at the Construction Materials Group and Institute of Materials Meeting on Techniques for Characterization of cement hydration, London Society of Chemical Industry, 1994.
67. Delgado A.H., Paroli R.M., Beaudoin J.J.: Applied Spectroscopy *50*, 970 (1996).
68. Lee: Chemistry of cement and concert, Arnold Ltd (2007), London.
69. Gao X.F., Lo Y., Tam C. M., Chung C.Y.: Cem. Concr. Res. *29*, 805 (1999).