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Concrete mixtures incorporating synthesized sulfonated acetophenone–formaldehyde resin as superplasticizer

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ABSTRACT

Polymers in concrete have received considerable attention over the past 25 years. Water-soluble sulfonated acetophenone–formaldehyde (SAF) resin was produced in the laboratory from the reaction between acetophenone–formaldehyde, and sodium bisulfite. Its performance as a concrete admixture was evaluated through its effect on the (w/c) ratio, air content, setting time, compressive strength at different ages, water absorption and permeable pores. Also, the performance of the concrete when subjected to acidic environment using sulfuric acid (pH = 4), and sulphate attack using magnesium sulphate (pH = 6.5) were investigated. SAF resin could be classified as a high-range water reducer with retarding effect (Type F and G according to ASTM C494). It was found that concrete mixtures incorporating SAF resin-based admixture yielded higher compressive strength results compared with the control concrete mixtures, as well as they are more resistant to aggressive environments investigated due to the higher resistance to water movement.

1. Introduction

The amount of admixture used in high performance concrete has increased; therefore, the cost of admixture is sometimes comparable to that of cement in such mixtures. New admixtures play an important role in concrete [1]. The superplasticizers are organic polyelectrolytes that are polymeric dispersants. They are classified according to their chemical compositions as sulfonated synthetic polymers, carboxylated synthetic polymers, and synthetic polymers with mixed functionality [2]. Water-soluble polymers such as sulfonated phenolic resin (SPF), water-soluble acrylate/sulfonate copolymer and sulfonated acetone formaldehyde (SAF) have also been used successfully in concrete [3–8]. One of the main areas of application of water-soluble polymers is its use in the production of self-compacting concrete [9,10].

The effect of melamine and naphthalene-formaldehydes condensates on concrete properties were studied [3]. Results showed that the naphthalene-based superplasticizer provided better workability (i.e. slump values) compared with melamine superplasticizers, and both improved compressive strength. The preparation of Na-sulfanilate phenol–formaldehyde condensate (SSPF) and its performance in concrete was investigated [11]. It was noticed that the synthesized (SSPF) is more suitable to be used in pumping and self-compacting concretes. Through the use of superplasticizers, the minimum amount of water needed to hydrate all cement particles now serves not only to hydrate the cement, but also to ensure adequate workability and the desired slump. This is just one of the recent, major technological developments that have contributed significantly to the significant increase in the compressive strength of concrete [12].

The use of the first generation of superplasticizers for example, sulfonated naphthalene formaldehyde (SNF) and modified lignosulfonates (LSs) resulted in improvements in the properties of fresh concrete, and they are still widely used. However, increasing demands for better flowability, extended working time, and a reduction in concrete porosity have created a need for superplasticizers with improved performance [13,14].

In some locations, the cost of superplasticizer can be a major issue in the concrete production since most of the admixtures are imported. In this study locally synthesized water-soluble sulfonated acetophenone–formaldehyde (SAF) resin is investigated and reported. Also, the potential of using the produced resin SAF resin as concrete admixture is evaluated for both fresh and hardened concrete. For fresh concrete, the effect of the SAF resin on

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the water demand, air content and setting time of the concrete mixture is assessed for different dosages of the resin (0.5%, 1.0%, 2% and 2.5% by weight of cement). For hardened concrete, the effect of using different dosages on compressive strength at different ages is measured. Also, the water transport through concrete is evaluated by measuring the water absorption % and permeable pores at 28 days of age. The performance of the concrete mixtures exposed to aggressive environments mainly acidic solution (sulfuric acid with pH = 4), and sulfate attack by magnesium sulphate solution (pH = 6.5) was examined as well.

2. Experimental work

2.1. Concrete materials

All concrete mixtures were made using ordinary Portland cement. The aggregates used were natural siliceous gravel and sand with the grading as per the ASTM C494. The concrete mixture composition was according to ASTM C494. The cement content was 310 kg/m^3, the water content for the control mix was adjusted to obtain a slump value of 90 ± 15 mm. The water content for the concrete mixtures containing the admixture with different dosage was varied in order to obtain the same slump.

2.2. Synthesis of sulfonated acetophenone–formaldehyde (SAF) resin

Acetophenone is a crystalline ketone that is used as a solvent for cellulose ethers and esters in the manufacture of alcohol-soluble resins. Commercial acetophenone can be obtained from benzene with acetic anhydride or acetyl chloride by Friedel–Crafts process. It can also be obtained by air oxidation of ethyl benzene, as a by-product of cumene or from acrylonitrile. It is used as a polymerization catalyst for the manufacture of olefins. The following chemical reaction, shown in Fig. 1, represents the main method of preparing acetophenone. Table 1 gives the physical properties of the used acetophenone.

The dimmer of acetophenone (dypnone) is used as a plasticizer. Acetophenone and its derivatives, among which its polymers, having additionally substituted saturated alkyls, oxygenated alkyl groups, thio groups, additional aromatic groups, unsaturated aliphatic side chains, and other functional groups which in turn, affect on the performance of these polymers as concrete admixtures.

Sodium bisulfite was dissolved in water in a jacketed reactor flask equipped with a baffle stirrer and a reflex condenser at 50 °C. The temperature of the solution was maintained at 50 °C before the solution becomes clear. As soon as the solution became clear, the temperature was decreased to 40 °C and acetophenone was added. The sulfonated acetophenone–formaldehyde (SAF) resin was synthesized by mixing (0.1) mole of acetophenone with (0.2) mole of formaldehyde and the mixture was heated for 4 h under reflux at 80 °C. The resin formed was triturated with petroleum ether for several times to get rid of the solid un-reacted materials. The produced pale yellow moderately viscous resin has pH value above 10. At the beginning of the reaction, acetophenone reacts with formaldehyde in keto-form and then polymerization was achieved through the enol-form of acetophenone. The expected molecular structure of the produced SAF resin is as shown in Fig. 2. The physical properties of the produced SAF resin are given in Table 2.

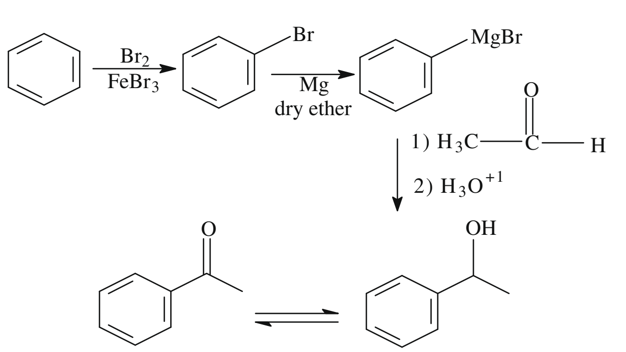

Fig. 1. Chemical reaction representing the main method of preparing acetophenone.

Table 1
Physical properties of used acetophenone.

Synonyms	Phenyl methyl ketone; hypnone; acetylbenzene
Molecular weight (mol/gm)	120.15
Density (gm/cm^3)	1.0281
Flash point	82.2 °C
Boiling point	202 °C
Freezing point	19.7 °C
Solubility	Slightly soluble in water, freely soluble in alcohol, chloroform, ether, fatty oils, and glycerol
Description	Combustible, colorless liquid, with sweet, pungent odor, and taste.
Molecular structure	$C_6H_5COCH_3$

2.2.1. NMR spectroscopy

The postulated molecular structure of the synthesized resin was established by Nuclear Magnetic Resonance spectroscopy (NMR). NMR spectroscopy is an analytical chemistry technique used for determining the content and purity of a sample as well as its molecular structure. For example, NMR can quantitatively analyze mixtures containing known compounds. For unknown compounds, NMR can either be used to match against spectral libraries or to infer the basic structure directly. In order to achieve the desired results, a variety of NMR techniques was used.

The ^{1}H (proton) NMR experiment is the most common NMR experiment. The proton (^{1}Hydrogen nucleus) is the most sensitive nucleus (apart from tritium) and usually yields sharp signals. Even though its chemical shift range is narrow, its sharp signals make proton NMR very useful. The produced proton NMR chart of the

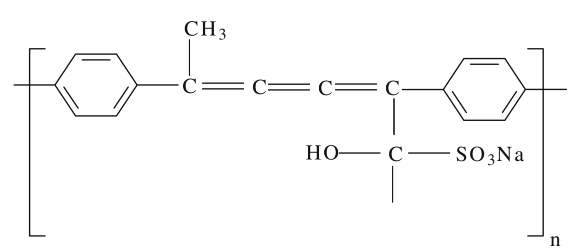

Fig. 2. The expected molecular structure of SAF resin.

Table 2
Properties of synthesized SAF resin.

Color	Pale yellow
Specific gravity	1.10
pH value	10–11
Molecular weight (mol/gm)[a]	5000
Polymer solid content	40%
Chloride content	Nil
Free sulphate content	0.04%

[a] According to gel permeation chromatography (GPC) technique.

synthesized resin is given in Fig. 3. Carbon-13 NMR is the application of nuclear magnetic resonance in spectroscopy with respect to carbon. It is analogous to proton NMR and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such carbon NMR is an important tool in structure elucidation in organic chemistry. The produced carbon NMR chart of the synthesized resin is as shown in Fig. 4.

2.2.2. GPC technique

The molecular weight of resin, Table 2, was determined with GPC measurements. Various detectors are used to sense when the polymers finally emerge (or "elute") from the porous material column. Tetrahydrofuran (THF) was used as a solvent and monodispersed polystyrene sulfonates of different molecular weights were used as calibration standards.

2.2.3. IR analysis

The IR spectrum of the SAF resin sample was recorded over a wave number range of 4000–400 cm^{-1} on a Nicolet spectrophotometer; as shown in Fig. 5, the sample was prepared as a standard KBr pellet (4% of the sample).

The infrared of all aromatic systems are characterized by many needle-like sharp peaks. This is due to the rigid structure of these molecules, which excludes the formation of rotational conformers. The aromatic character is apparent from sharp peaks above 3000 cm^{-1}, sharp peaks at about 1500 cm^{-1} and strong peak below 900 cm^{-1}. Allenes like other cumulative double bond systems do not show normal double bond absorption. Instead, typical for all allenes is the antisymmetrical stretching, which absorbs at a rather high frequency [2000–1900] cm^{-1}. The carbon–sulfur single bond is of very limited value in infrared, [715–620] cm^{-1}. The sulfonate group is represented in the spectrum by strong peaks at about 1200 cm^{-1}, which may be attributed to vibrations of the (OSO_2) entity. The hydroxyl groups give rise to a broad peak in the [3100–2500] cm^{-1} region arising from (O–H) stretching vibrations.

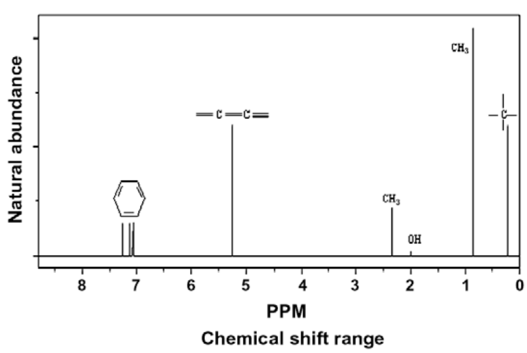

Fig. 3. Produced proton NMR chart of the synthesized SAF resin.

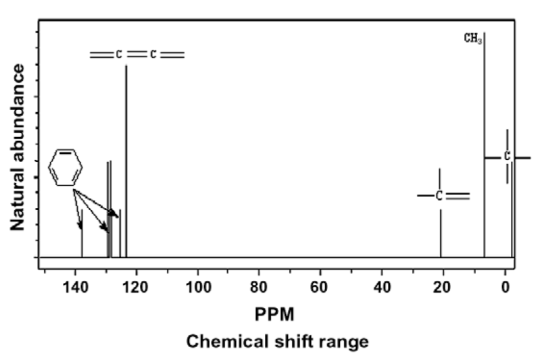

Fig. 4. Produced carbon NMR chart of the synthesized SAF resin.

2.2.4. Elemental analysis

The results of elemental analysis are in good agreement with calculated values of %C, %H, and %S, as shown in Table 3, and also are in good agreement with the molecular structure represented in Fig. 2, as well as the NMR and IR analysis.

2.3. Mixing, casting and curing

The prepared admixture is dissolved in the mixing water and then added to the concrete ingredients in a rotating drum type mixer. Specimens were de-molded after 24 h from casting. All specimens were cured by immersion in water until test date.

2.4. Testing

Setting time was measured according to ASTM C403 using proctor needle on mortar wet sieved from the concrete mixture. Air content of fresh concrete was carried out using pressure method according to ASTM C23.

Mechanical properties of the concrete mixtures was evaluated by the compressive strength, which was carried out on cube specimens (100 × 100 × 100 mm) at age (1, 3, 7, 28, and 90) days. Water transport through concrete has become of increasing concern especially in relation to the durability and the ultimate performance of concrete particularly when exposed to aggressive environment. Therefore, several researchers concluded that water transport through concrete and permeable pores are the key to all durability problems, and could be used as durability indices of the concrete [15,16]. The water absorption and permeable pores were measured according to ASTM C642. Replicates were used for each test date and the average value is recorded and used in the discussion.

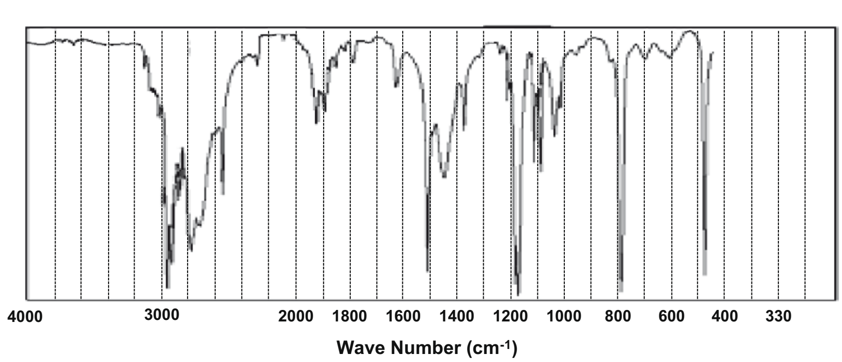

Fig. 5. IR Spectra for SAF resin.

Table 3
Elemental analysis of the synthesized SAF resin.

Element	%C	%H	%S
Calculated	65.38	3.84	10.25
Measured	65.57	3.81	10.41

The performance of the concrete incorporating the synthesized admixture SAF resin in aggressive environments was investigated by exposing the concrete to acidic environment (sulfuric acid pH = 4), and sulphate solution (magnesium sulfate pH = 6.5). Concrete cubes (with dimensions $100 \times 100 \times 100$ mm) were immersed in the solutions at 28 days of age. The temperature was maintained at (25 ± 3) °C over the entire immersion period (6 months). The compressive strength after the immersion in the solutions for 6 months was measured and compared to that of the corresponding mix not exposed to the aggressive environment.

3. Results and discussion

3.1. Fresh concrete

The effect of using SAF resin as admixture with different dosages on the water content of the concrete mixture to obtain a constant slump value (90 ± 15 mm) was examined. Fig. 6 shows the effect of different SAF resin dosages on the water content reduction percent with respect to the control mixture. Sulfonated acetophenone–formaldehyde (SAF) resin considerably reduces the water content from 12% to 19%. Based on ASTM C494, SAF resin acts as a high-range water reducer (Type F). Also, it can be noticed that 2% of the SAF resin yields the highest reduction in water content, and it is considered that the sulphonic groups are responsible for neutralizing the surface charges on the cement particles and causing dispersion, thus releasing the water tied up in the cement particles agglomerations and thereafter reducing the viscosity of the paste and concrete. These anions are attracted to the surface of cement grains and, at normal levels of admixture usage, are adsorbed in sufficient numbers to form complete monolayer around cement particles. The combination of electrostatic repulsion and large ionic size (which provide physical separation) brings about a rapid dispersion of the individual cement grains. In doing so, water trapped within the original flocks is released and can then contribute to the mobility of the cement paste and hence to the workability of the concrete mixture.

Fig. 7 shows the penetration resistance of fresh concrete versus time by using proctor needle, for concrete mixtures incorporating different dosages of SAF resin. Table 4 gives the initial and final setting times for all concrete mixtures. It is known that, under moderate weather conditions, the slump loss represent no real problems because in practice, the concrete remains workable for enough time to allow its handling without any appreciable difficulties. However, under hot weather conditions, this may not be the case, because the associated slump loss is increased, and the initial and final setting times are both decreased with the rise in temperature. In general, retarding admixtures slow down the hydration of cement and thereby delays its setting. It is to be expected, therefore, that the corresponding slump loss in such a mixture at the time considered will be smaller than in a mixture made without a retarder. As shown in Fig. 7, the presence of SAF resin causes a retardation effect and the retardation increase when increasing the percentage of the admixture used. Therefore, it can be concluded that, the presence of SAF resin molecules at the cement particles surface acts as a barrier to the diffusion of hydration products created which in turn increases the dormancy period. Based on ASTM C494 criteria, SAF resin could be classified as Type F and G.

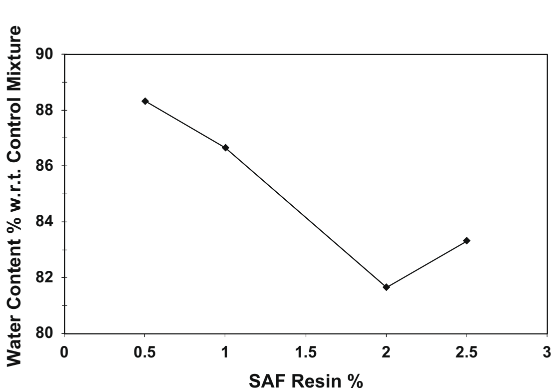

Fig. 6. Effect of SAF resin dosage on water content with respect to control mixture.

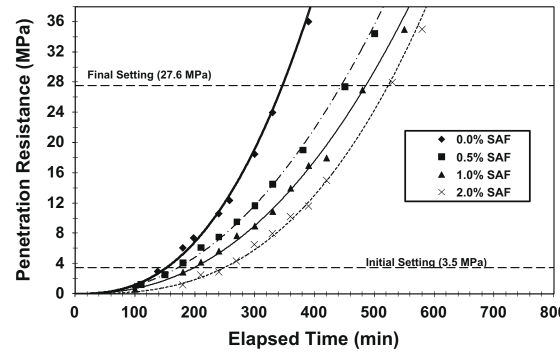

Fig. 7. Effect of SAF resin dosage on penetration resistance of fresh concrete.

Table 4
Initial and final setting time of different concrete mixtures.

SAF resin dosage (% by weight)[a]	Setting time (min)	
	Initial setting	Final setting
0	140	350
0.5	175	430
1.0	200	485
2.0	230	520

[a] % by weight of the cement mass in the mix.

Fig. 8 shows the air content of concrete mixtures with various percentages of SAF resin. The results clearly show that by increasing SAF resin percentage the air content decreases up to 1.9% at 2% of the admixture, and then the air content increases to 2.2% at 2.5% of the admixture but still lower than the control mixture. This could be attributed to the adsorption of more than one layer of the admixture molecules on the surface of the hydrates preventing the diffusion of the hydration products, thus increasing the porosity of the concrete. Due to the reduction in the air content when SAF resin is used, it should be noted that the compatibility of such admixture with air-entraining admixtures needs investigation. Previous studies indicated that in some cases the dosage of the air-entraining agent should be adjusted when used in conjunction with superplasticizers because the latter could increase the spacing factor or even reduce the entrained air [13].

3.2. Hardened concrete

The compressive strength of the concrete mixtures incorporating various dosages of the SAF resin is given in Fig. 9. Table 5 gives

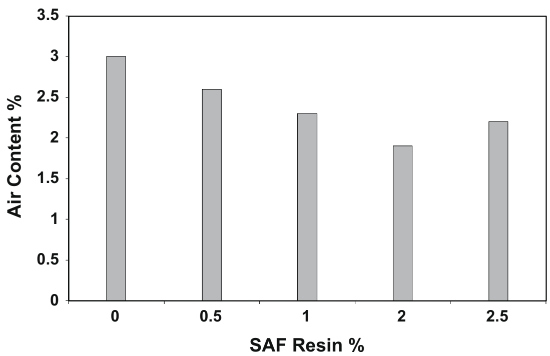

Fig. 8. Air content of fresh concrete with different dosages of SAF resin.

the standard deviation of the compressive strength test results at different test age and for various SAF resin dosage. As shown from the data, all concrete mixtures incorporating SAF resin yielded higher strength than the control mixture at all tested ages. Using a dosage of 2% of the SAF resin represents the highest compressive strength results compared with those mixtures incorporating smaller dosages which are still higher than the control mixture. This result coincides with the results of water reduction and air content values of fresh concrete mixtures.

From the results of water content reduction and air content of the fresh concrete, and the compressive strength, it could be concluded that the applicable dosage range for using SAF resin ranges from 0.5% to 2% by weight of cement mass.

Fig. 10, shows the compressive strength at different ages (7 and 28 days) for the concrete mixture incorporating 1.0% and 2.0% SAF resin compared to the compressive strength of another concrete mixture incorporating 1.5% traditional melamine formaldehyde sulphonate condensate (MFS) [2]. It should be noted, that the concrete mixture using the MFS condensate has a cement content of 400 kg/m^3, compared to the 310 kg/m^3 cement content used with the SAF resin mix, yet the compressive strength at 28 days of the mix using 1.0% SAF resin is close to that incorporating MFS condensate, and the strength of the mix including 2.0% SAF resin is higher than that incorporating MFS condensate. The strength at 7 days for the mixes including SAF resin is close to that of the MFS condensate mix, taking into consideration the higher cement content of the mix using MFS condensate and the early test age.

Fig. 11 gives the water absorption % and permeable pores % at 28 days of age for the different mixtures. It can be noticed that water absorption and permeable porosity decreases with increasing the SAF resin dosage. This could be attributed to the reduction in (w/c). It is not quite clear how the addition of SAF resin affect the pore size distribution and needs further investigation. The standard deviation of the water absorption % test values ranges between 0.18% and 0.22%, and that for the permeable pores % test values between 0.64% and 0.88%.

Table 5
Standard deviation (in MPa) for compressive strength test results.

Test age (days)	SAF resin dosage (% by weight)[a]			
	0 (%)	0.5 (%)	1.0 (%)	2 (%)
1	0.70	0.65	0.78	0.74
3	1.10	1.05	1.10	1.25
7	1.37	1.29	1.44	1.70
28	1.10	1.35	1.27	1.33
90	1.95	2.05	2.90	2.25

[a] % by weight of the cement mass in the mix.

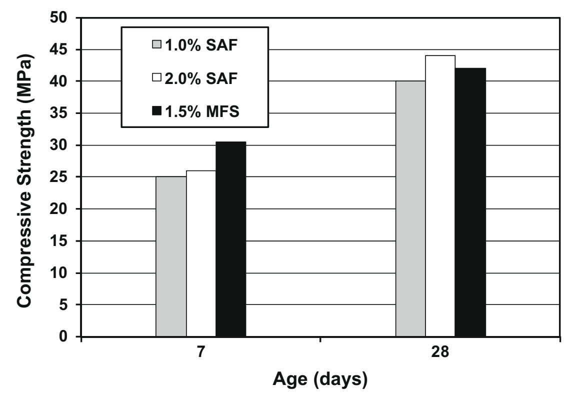

Fig. 10. Compressive strength of concrete mixtures incorporating synthesized SAF resin and traditional melamine formaldehyde sulphonate condensate (MFS).

Table 6 gives the compressive strength results for the concrete mixtures incorporating SAF resin with different dosages when subjected to acid attack using sulfuric acid (pH = 4), and sulphate attack using magnesium sulphate (pH = 6.5) after 6 months of immersion in the solutions, as well as the compressive strength of the control mixture exposed to the same environments. The use of SAF resin improved the resistance of the concrete mixtures to the aggressive solutions which is a direct result of reducing the water absorption and the permeable pores of the concrete. Fig. 12 shows the reduction in the compressive strength after exposure to the solutions. It was noted that the aggressive solutions did not have significant damage effect on the concrete mixtures incorporating SAF resin compared to that occurring to the control mix.

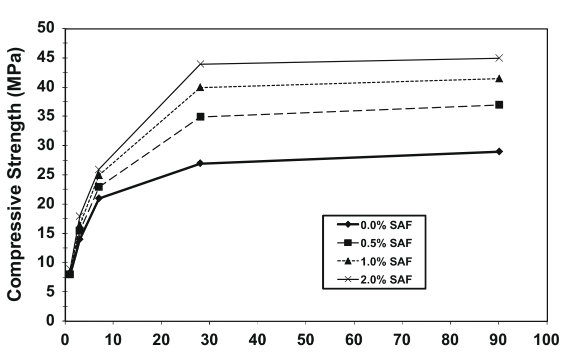

Fig. 9. Compressive strength with age for concrete mixtures incorporating different dosages of SAF resin.

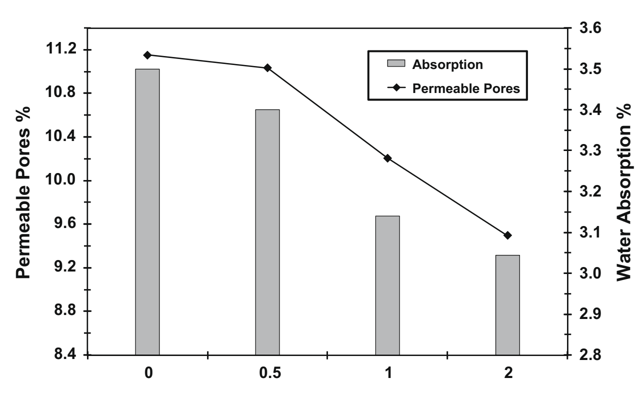

Fig. 11. Water absorption and permeable pores % for concrete mixture incorporating different dosages of SAF resin.

Table 6
Compressive strength for different mixtures immersed for 6 months in aggressive solutions.

SAF resin dosage (% by weight)[a]	28 days compressive strength (MPa)[b]	Compressive strength after immersion in aggressive solutions (MPa)[b]	
		Acid attack	Sulphate attack
0 (control)	27(1.10)	18(1.25)	22(1.35)
0.5	35(1.35)	24.5(1.77)	30(1.90)
1.0	40(1.27)	31.5(2.47)	37(2.30)
2.0	44(1.33)	37(2.34)	41(2.45)

[a] % by weight of the cement mass in the mix.
[b] Values between parenthesis is the standard deviation (in MPa).

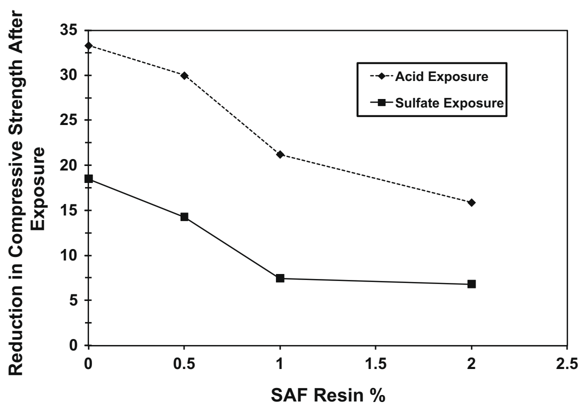

Fig. 12. Reduction in compressive strength of different mixtures after immersion for 6 months in aggressive solutions with respect to control mixture.

As indicated in another study [13], during the acid attack, it is believed that the protons enter the concrete and dissolve solid hydration products as they penetrate inside the concrete and this is controlled by the concrete's pore system (i.e. permeable pores). Hydroxyl ions contained in the hydration products are, in effect, neutralized by the protons. Calcium, iron, aluminum as well as sulphate ions diffuse toward the concrete surface. A highly porous corroded layer develops consisting essentially of hydrated silicates. The growth rate of the layer is determined by; (a) acid diffusion through the affected concrete layer and (b) reaction rate of the acid with the undamaged concrete controlled by the concrete's permeable pores. This is in agreement with obtained test results indicating lower permeable pores for concrete mixtures incorporating SAF resin which in turn results in a smaller affected depth and lower reduction of the concrete strength.

4. Conclusions

Water-soluble sulfonated acetophenone–formaldehyde (SAF) resin was locally synthesized by the reaction between acetophenone, formaldehyde, and sodium bisulfite. The synthesized SAF resin could be used as a high-range water reducer admixture for concrete mixtures. Its effect on the rheology of different concrete mixtures will be further investigated. Using SAF resin improved the compressive strength of concrete mix with lower cement content as compared with concrete mix incorporating traditional melamine formaldehyde sulphonate condensate (MFS) with higher cement content. Also, the use of SAF resin decreases the water absorption and permeable pores and significantly improved the durability of the concrete in aggressive solutions (magnesium sulfate and sulfuric acid). Based on the results of fresh concrete and hardened concrete, the applicable dosage of the admixture ranges from 0.5% to 2.0% by weight of the cement mass. SAF resin has the potential to be used as a concrete admixture conforming to ASTM Types F and G.

The use of SAF resin resulted in reduction of the air content of the concrete mixtures. Therefore, its compatibility with air-entraining agents must be checked before combining them in one mixture. Also, the effect of different cement types and supplementary cementing materials needs further investigation.

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