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Effect of Sulfonated Acetone Formaldehyde (SAF) on the Firing Resistance and Aggressive Attack of SRC-SF Composite Cement Pastes

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Abstract: This work aimed to study the effect of the dosage of laboratory synthesized Sulfonated Acetone Formaldehyde (SAF) on the physical-mechanical characteristics and durability of SF-SRC cement pastes immersed in 4% MgCl₂ or 4% MgSO₄ solutions or at elevated temperatures up to 800°C. The compressive strength of thermally treatment cement pastes with 1.5% SAF increases up to 600°C, then decreases up to 800°C. Presence of 2.0% SAF works to produce a compact cementing structure, which decreases the accessibility of the penetration of chloride as well as sulphate ion penetration and enhances the durability, hence the total chloride and sulphate contents diminished.

Keywords: Accelerator, Firing Resistance, Aggressive Attack, SAF

Introduction

The durability of cementing materials has been a major concern of civil engineering professionals over the last few decades (Chen and Wu, 2013; Sánchez et al., 2011). Cements with low C₃A as well Ca(OH)₂ contents generally, exhibit good performance in sulphate environment. It is possible to produce, durable concrete with long-term strength by partial replacement of cement with Supplementary Cementitious Materials (SCMs), such as Fly Ash (FA), Silica Fume (SF) and Granulated Blast-Furnace Slag (GBFS) (Irassar et al., 2000; Shanahan and Zayed, 2007; Montes et al., 2012).

The superior performance of pozzolanic cements containing SCMs over plain cements in minimizing sulphate and chloride attack is mainly due to the following: (i) The pozzolanic reaction of SCMs, which reduces gypsum formation; (ii) low C₃A content, dilution effect; (iii) the reduction of pH value therefore, the ettringite becomes less expansive; (iv) the formation of additional amounts of C-S-H, which produces a coating film on the alumina-rich and other reactive phases, thereby hindering the formation of secondary and lastly ettringite; and (v) the formation of secondary C-S-H also results in pore size refinement, which reduces the permeability as well as the ingress of aggressive ions (Wong and Poole, 1988; Al-Dulaijian, 2007; Aye and Oguchi, 2011; Thomas et al., 2012).

The aggressive attack of sulphate and chloride ions is one of the factors responsible for damage to concrete. The corrosive action of chlorides is due to the formation of chloroaluminate hydrate, C₃A.CaCl₂.10H₂O, commonly known as Friedel’s salt, which causes softening of concrete. The formed CaCl₂ from the reaction of MgCl₂ with the liberated lime increases the solubility of Ca(OH)₂ that permits leaching. Thus, brucite (MgOH)₂ dissociates C-S-H and produces Ca(OH)₂ and silica gel. The later may react with Mg(OH)₂ to form Magnesium Silicate Hydrates (M-S-H), which has no binding properties. Also, sulphate ions can enter into chemical reactions with certain constituents of concrete, producing sulphoaluminate hydrates, C₄A₆S₄H₁₂ (ettringite), gypsum and M-S-H which has little binding properties (Page and Page, 2007). All of these reactions are accompanied by decrease in strength.

The production of Sulphate Resisting Cement (SRC) is expected to increase, due to its high durability against the aggressive attack of sulphates in soils and ground water. Therefore, it could be argued that, it is theoretically ideal cement for massive structures exposed to seawater or ground water (Howlett, 2004).

Durability of concrete with Sulfonated-Acetone Formaldehyde (SAF) condensate superplasticizer was studied using sulfuric acid at pH = 4.0 and magnesium sulphate at pH = 6.5 after 6 months of immersion. The use of SAF improved the resistance of concrete to the solutions which is a direct result of reducing the water absorption and the permeable pores of concrete. It was concluded that, the aggressive solutions did not have...
significant damage effect on the concrete mixtures incorporating SAF resin compared to the control mix (Pei et al., 2004). It was found that, the effectiveness of superplasticizers on concrete was strongly related to the adsorption behavior of the admixtures on cement particles, as well as the degree of hydration (Hsu et al., 1999).

The effect of temperature on the properties of cement pastes can be studied up to 800°C. The change in the phase composition of the thermally treated cement pastes can be investigated by the XRD and SEM techniques. The elevated temperature reduces the cement paste-aggregate bonds, progressive breakdown of cement gel structure, loss in concrete load-bearing capacity, reduces durability and increases tendency of structural cracking. This deterioration can often reach a level at which the structure may have to be thoroughly renovated or completely replaced, depending on various factors such as: Humidity, rate of heating, temperature level, heating time, cooling mode after heating, applied load, type of mineral admixture and inclusion levels (Yazıcı et al., 2012; Handoo et al., 2002; Aydın and Baradan, 2007; Lau and Anson, 2006).

The evaporable water is lost at 100-110°C, whereas the interlayer CSH water and some of combined water from the CSH and sulfoaluminate hydrates lost at about 300°C. Further decomposition of CH begins at about 400-550°C. On cooling, the CaO is rehydrated to Ca(OH)₂ with a volume expansion of 97% and formation of cracks. Tobermorite gel (CSH) is decomposed at 900°C (El-Didamony et al., 2012).

Use of SCMs can reduce the thermal deterioration of cement paste, mortar and concrete which can react with the liberated CH forming excess CSH, which more powerful and thermally stable than CH. Therefore, pozzolanic cement blends are less affected to high temperature (Yazıcı et al., 2012; Handoo et al., 2002; Aydın and Baradan, 2007; Lau and Anson, 2006; El-Didamony et al., 2012; Shui et al., 2010).

The aim of the present investigation is to evaluate the effectiveness of laboratory synthesized SAF condensate on the durability of SRC pastes incorporating 10% SF immersed in 4% MgSO₄ or 4% MgCl₂ corrosive solutions up to one year as well as subjected to elevated temperatures up to 800°C.

Materials and Methods

Starting Materials

The materials used in this investigation were Sulphate Resisting Cement (SRC) provided from El-masria Cement Company and condensed Silica Fume (SF) from Ferrosilicon Alloys Company, (Edfo and Aswan, Egypt). The chemical composition of starting materials is shown in Table 1. The surface area of SRC determined by the Blaine air permeability method, was found to be 3488 cm²/g whereas that of silica fume is about 20 m²/g.

The mineralogical composition of silica fume and preparation of Sulfonated Acetone-Formaldehyde (SAF) Resin are found in previous study by Osman and Al-Masry (2014).

Preparation of Cement Pastes

Preparation of Dry Mixes

The ingredients of each mix of Sulphate Resisting Cement (SRC) and 10 wt% silica fume were mixed for one hour with four balls using a mechanical roller to assure complete homogeneity. The samples were kept in airtight container.

Mixing of Cement Paste

The required amount of each dry mix was placed on a smooth, non-absorbent surface and a crater was formed in the center. The required amounts of mixing water as water of consistency containing the admixture with different dosages (0.0, 0.5, 1.0, 1.5 and 2.0% of the water-admixture) were poured into the crater and the cement on the outer edges was turned into the crater by the aid of a trowel. The dry cement around the outside of the crater was slightly toweled over the mixture to absorb the water for about one minute. The mixing operation was then completed by continuous vigorous mixing for about three minutes by means of gauging trowel.

Moulding

Stainless steel ½ inch cubic moulds were used to prepare the cement pastes. Freshly prepared cement paste was placed in the moulds into two approximately equal layers. Each layer was compacted and manually pressed until homogeneous specimen was obtained. After the top of the layer was compacted, the moulds were then vibrated for a few minutes to remove any air bubbles to get a better compaction of the prepared pastes. The surface of the paste was smoothed by the aid of thin edged trowel.

Curing

Immediately after moulding, the moulds were cured in humidity chamber at about 100% relative humidity at room temperature 23±1°C for 24 h then demoulded and cured under tap water up to the time of testing. In the present study, all mixes were moulded and divided into three sets which used in the following curing modes:

Curing Under Tap Water

One set of all cement pastes was cured under tap water immediately after demoulding to study the hydration characteristics after one, 3, 7, 28, 90 days (Osman and Al-Masry, 2014).
Table 1. Chemical analysis of starting materials, (wt%)

| Oxides Material   | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O | I.L | Total |
|-------------------|------|-------|-------|-----|-----|-----|------|-----|----|-------|
| SRC               | 21.40| 3.67  | 5.05  | 64.73| 1.50| 2.05| 0.30 | 0.22| 2.60| 99.70 |
| Silica fume       | 94.81| 0.16  | 0.84  | 0.89 | 0.49| 0.08| 0.20 | 0.0| 5.24| 99.95 |

Curing Under 4% MgSO₄·7H₂O or MgCl₂·6H₂O Solution

Another set of all cement pastes was cured under tap water for 28 days (zero time) then cured under 4% MgSO₄·7H₂O or 4% MgCl₂·6H₂O to investigate their resistance to these aggressive media at the desired testing times 1, 3, 6, 9 and 12 months respectively. The aggressive solution was renewed monthly to maintain constant concentration.

Firing at 200-800°C

Last set of cement pastes was cured under tap water for 28 days, dried at 105°C for 24 h and fired at 200-800°C in intervals of 100°C to investigate their firing resistance. The firing program is carried out in a muffle furnace with a rate of 10°C/min for 2 h at each temperature and cooled to room temperature in the furnace.

Methods of Investigation

Fire Resistance Determination

The fire resistance of cement pastes was studied at 250, 450, 600 and 800°C in a muffle furnace with soaking time for 2 h. The cement pastes were kept to cool in the furnace then, the fire resistance was measured (ignition loss), bulk density, total porosity and compressive strength of each cement paste at a definite temperature.

A set of three cubes for each mix fired at an appropriate temperature were immersed in kerosene for 24 h. Specimens were then weighed (weight of saturated sample) and reweighed suspended in kerosene (weight of suspended sample). Specimens were dried at 105°C for 24 h and weighed in air (dried weight).

The bulk density and total porosity were calculated as in case of water but using the density of kerosene (0.8 g/cm³). The Ignition loss illustrates the behavior of cement pastes after fire exposure and was assessed as the difference between the weights before and after ignition divided by ignited weight:

\[
\text{Ignition loss, } \% = \frac{\text{Weight before ignition} - \text{Weight after ignition}}{\text{Weight after ignition}} \times 100
\]

The compressive strength measurements were done on a compressive strength machine of SEIDNER, Riedinger, Germany, with maximum capacity of 600 KN forces (ASTM, 2007).

Determination of Total Sulphate

The total sulphate content was gravimetrically estimated by using one g of powdered sample dissolved in 5 mL of concentrated HCl, 100 mL of distilled water was added, then boiled for 5 min, then filtered and washed several times with distilled water. Ten milliliters of 10% BaCl₂ was added to the filtrate, which was digested, filtered and ignited at 1000°C for 30 min. The total sulphate content was calculated as:

\[
\text{SO}_3, \% = \frac{\text{Weight of ppt}}{M} \times 34.3
\]

where, M is the weight of sample in grams.

Determination of Total Chloride

Total chloride content was determined in the hardened pastes by weighing 2 g sample into a stopper conical flask. The specimen was dispersed with 25 mL water and then added with 10 mL of nitric acid (sp. gr. 1.42). Fifty milliliters of hot water was added, heated to near boiling and kept warm for 10 to 15 min. If the supernatant liquid is turbid, it was filtered through a rapid paper (41 filter paper) and washed with hot water and then cooled to room temperature. An excess of standard 0.1 N AgNO₃ (16.98 g pure dry AgNO₃, in liter) was added and 2-3 mL of nitrobenzene to stopple the flask, then vigorously shaken to coagulate the precipitate, then 1 mL ammonium ferric alum as indicator and titrate against standard 0.1 N ammonium thiocyanate.

Results and Discussion

Effect of Treatment Temperature

The effect of temperature on the properties of cement pastes admixed with various dosages of SAF can be studied by the determination of the weight loss, bulk density, total porosity and compressive strength of hardened cement pastes treated up to 800°C.

Weight Loss

The weight loss of cement pastes admixed with various dosages of SAF as a function of treatment temperature up to 800°C is represented in Fig. 1. The weight loss increases with treatment temperature. This is mainly due to the decomposition of some hydration products (Cook and Hover, 1999). The free water is removed at 105°C, a partial decomposition of calcium silicate hydrate and sulfoaluminate hydrates occurred around 200°C. Moreover, the decomposition of
Bulk Density

The bulk density of cement pastes admixed with various dosages of SAF as a function of treatment temperature is graphically plotted in Fig. 2. The results indicate that the bulk density of cement pastes decreases with the treatment temperature up to 250°C. This is related to the removal of the free as well as some of bound water leaving pores that leads to decrease the density.

Generally, the bulk density for all cement pastes increases up to 600°C due to the reaction of silica fume with the decomposed lime forming more cementitious materials that fill some of the open pores. As the temperature increases up to 800°C the bulk density sharply increases due to the activation of hydration with the treatment temperature forming extra cementitious materials. On the other side, as the amount of SAF increases up to 1.5 wt% the bulk density increases due to the acceleration of hydration. The bulk density decreases at 2.0 wt% SAF due to the retardation effect that decreases the hydration effect that decreases the hydration products and then the bulk density.

Total Porosity

The total porosity of cement pastes admixed with various dosages of SAF as a function of treatment temperature is plotted in Fig. 3.

The total porosity decreases with the treatment temperature up to 250°C. This is attributed to that the treatment temperature enhances the hydration of cement clinker phases as well as the reaction of silica fume with CH liberated from the hydration of Portland cement to form additional hydration products that fill more pores (Radwan et al., 2011; Komonen and Penttala, 2003). Therefore, the total porosity decreases.

Obviously, the total porosity increases sharply from 250°C up to 800°C for all cement pastes as a result of the formation of microcracks which result from the dehydration of CH crystals, the decomposition of calcium carbonate, increase vapor pressure of steam and crystal transformation of pozzolana as well as increase of crystallinity of the formed hydrates leading to a sort of opening of the pore system of cement paste (Komonen and Penttala, 2003). On the other hand, as the amount of SAF increases up to 2.0 wt% the total porosity increases due to the retardation effect.

Compressive Strength

Figure 4 shows the compressive strength of thermally treated cement pastes admixed with SAF up to 2.0 mass% cured up to 28 days, then subjected to elevated temperature up to 800°C.

The compressive strength of cement pastes increases as a result of enhancing the hydration of unhydrated cement clinker (Walters and Jones, 1991) as well as the improvement of pozzolanic reaction of silica fume with free lime to form extra CSH that has low Ca/Si ratio with high strength (Walters and Jones, 1991).

This is also occurred by the internal autoclaving effect that builds up as a result of flow of steam produced from elimination of capillary, physically adsorbed and combined water at high temperature that increases the pressure which accelerates the hydration (Chan and Anson, 1999; Mohammed et al., 2014a; Piasta et al., 1984).

The compressive strength increases with the treatment temperature up to 600°C due to the pozzolanic reaction of silica fume with the decomposed CaO to produce more C-S-H which deposits in the pore system and forms more dense structure. However, the decrease of the compressive strength at 800°C may be ascribed to the decomposition of cementitious materials as well as the CaCO$_3$.

On the other side, as the amount of SAF increases up to 1.5 wt% the compressive strength increases due to the acceleration of hydration. This leads to increase the hydration products. The compressive strength decreases at 2.0 wt% SAF due to the retardation effect which leads to decrease the hydration products.

Aggressive Attack on Cement Pastes

The presence of sulphate or chloride ions in water leads to an aggressive behavior towards concrete because some constituents of the cement can enter into deleterious chemical reactions with these ions. Sulphates of various bases attack hardened cements very markedly. Magnesium, sodium, potassium, ammonium and various other sulphates react with both free calcium hydroxide in set cement to form calcium sulphate and with its hydrated calcium aluminates to form the more insoluble calcium sulphoaluminate hydrates. The reactions with sodium sulphate, for example, can be formulated as:

$$\text{Ca(OH)}_2 + 3\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} + 2\text{NaOH} + 8\text{H}_2\text{O}$$

$$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{H}_2\text{O} + 3(\text{CaSO}_4\cdot 2\text{H}_2\text{O}) + 13\text{H}_2\text{O} \rightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$$
The alkali sulphates do not attack hydrated calcium silicates to any appreciable extent, they are more insoluble than the calcium sulphate and alkali silicates which would result.
Fig. 3. The total porosity of cement pastes in presence of different dosages of SAF as a function of treatment temperature.

Fig. 4. The compressive strength of cement pastes in presence of different dosages of SAF as a function of treatment temperature.
Magnesium sulphate has a more far-reaching action that other sulphates and decomposes the hydrated calcium silicates in addition to reacting with the aluminates and calcium hydroxide. If tri- or β-dicalcium silicate is placed in a magnesium sulphate solution, formation of gypsum crystals occurs rapidly. The hydrated calcium silicates react in the following general manner:

\[
3\text{CaO}.2\text{SiO}_2.3\text{H}_2\text{O} + 3(\text{MgSO}_4\cdot7\text{H}_2\text{O}) \rightarrow \\
3\text{CaSO}_4\cdot2\text{H}_2\text{O} + 3\text{Mg(OH)}_2 + 2\text{SiO}_2\text{gel}
\]

The reason why this reaction proceeds completely, while with sodium sulphate does not occur, is to be found in the low solubility of magnesium hydroxide and resulting low pH value of its saturated solution (Greene, 1962; Mohammed et al., 2014b; Radwan et al., 2012a; Yeon et al., 2013; Radwan et al., 2012b; Fiertak and Stryzewska, 2013). The hydrated magnesium silicate appears to have no binding power, in contrast to calcium silicate hydrate and its formation represents therefore a final stage in the deterioration of concrete attacked by magnesium sulphate solution.

The effect of 4% MgSO\(_4\) and 4% MgCl\(_2\) on cement pastes admixed with various dosages of Sulfonated Acetone Formaldehyde (SAF) up to one year has been studied. The cubes of cement pastes were immersed in distilled water for 28 days (Zero time), then immersed under the aggressive medium up to one year. The solutions were renewed every month to keep the concentration nearly constant. The relative resistance of hardened cement pastes against the aggressive solutions was assessed by determining compressive strength, bulk density, total porosity, total sulphate and total chloride contents of the attacked cement pastes.

**Magnesium Sulphate Solution**

**Bulk Density**

Bulk density of the cement pastes admixed with various dosages of Sulfonated Acetone Formaldehyde (SAF) immersed under 4% MgSO\(_4\) solution up to one year are graphically represented in Fig. 5. The results show that bulk density of different cement pastes increases up to 1 month and then decreases up to one year. The increase of bulk density for all cement pastes is due to activation action of sulphate solution and formation of additional hydration products which increases the amount of hydration products especially MgSO\(_4\). These two reactions lead to decrease bulk density of the hardened cement pastes. As the amount of the SAF increases up to 2.0 wt% the bulk density increases due to the filling effect and the acceleration of hydration; more hydration products are formed and then the pores decreases between the cement particles to produce more compact structure.

**Total Porosity**

The results of total porosity of cement pastes admixed with various dosages of SAF immersed under 4% MgSO\(_4\) solution up to one year are shown Fig. 6. It is clear that the total porosity of different cement pastes decreases up to 1 month and then increases up to one year. The decrease of total porosity for all cement pastes is due to the precipitation of the hydration products in the open pores that lead to decrease the total porosity. The increase of total porosity after 1 month may be due to the formation of gypsum and ettringite which are formed due to the action of sulphate solution. The ettringite gives expansion and then the total porosity increases. Consequently there is no disruption, but only increase in total porosity. On the other side, as the amount of SAF increases up to 2.0 wt% the corresponding total porosity decreases. This is due to the acceleration of hydration which forming more hydration products precipitated in the open pores of the cement pastes.

**Compressive Strength**

The compressive strength values of hardened cement pastes admixed with various dosages of SAF immersed under 4% MgSO\(_4\) solution up to one year are shown Fig. 7. It is clear that the compressive strength of different cement pastes increases up to 1 month and then decreases up to one year. The increase of compressive strength is regarded to the progress of hydration as well as sulfate ions activate the hydration of cement pastes and formation of ettringite which fill some of pores and then the compressive strength increases (Chindaprasirt et al., 2014; Binici et al., 2012). The decrease of compressive strength after 1 month may be due to that the sulfate ions migrate from the aggressive medium to the interior of the hardened cement pastes and react with calcium aluminate hydrate and ferrite forming ettringite and/or monosulfate hydrate which expands at later ages causing cracks and deterioration of cement paste. Also MgSO\(_4\) reacts with CSH to produce gypsum, silica gel and brucite (Ye et al., 2014). Gypsum reacts at later ages with C\(_2\)AH\(_6\) to form additional amounts of ettringite and/or monosulfate hydrate whereas brucite attacks CSH to form CH and MSH which has no binding properties. As the amount of SAF increases up to 2.0 wt% the compressive strength increases. This is mainly due to the acceleration of hydration which increases the amount of hydration products especially
tobermorite-like gel (CSH). Generally, as the amount of accelerator increases the hydration of cement paste enhances and then the pozzolanic reaction between SF and CH increases. Therefore, the bulk density and compressive strength increases as well as the total porosity of the cement paste decreases.

Fig. 5. Bulk density of cement pastes in presence of different dosages of SAF immersed under 4% MgSO₄ solution up to one year

Fig. 6. Total porosity of cement pastes in presence of different dosages of SAF immersed under 4% MgSO₄ solution up to one year
Total Sulphates

The total sulphate of cement pastes admixed with various dosages of SAF immersed under 4% MgSO$_4$ solution up to one year are given in Fig. 8. It is clear that the total sulphate content increases with immersing time up to one year. This is mainly due to the migration of the sulphate ions from the aggressive medium (MgSO$_4$ solution) to the cement pastes which reacts with C$_3$A and Ca(OH)$_2$ forming ettringite and/or calcium monosulphoaluminate hydrate. Also, MgSO$_4$ reacts with calcium silicate hydrate to produce gypsum, silica gel and Mg(OH)$_2$. Gypsum produced reacts furtherly with 3CaO.Al$_2$O$_3$.6H$_2$O to form calcium sulphaaluminate hydrate (ettringite) and/or monosulphate hydrate. As the amount of the SAF increases up to 2.0 wt% the total sulphate content decreases due to the acceleration of hydration; more hydration products are formed and then the pores decreases between the cement particles to produce more compact structure. This is confirmed from the bulk density, total porosity and compressive strength.

Magnesium Chloride Solution

Bulk Density

The results of bulk density of cement pastes admixed with various dosages of SAF immersed under 4% MgCl$_2$ solution up to one year are graphically plotted in Fig. 9. It is clear that bulk density of all cement pastes increases up to 6 months and then decreases up to one year. The increase of bulk density up to 6 months is due to the accelerating action of chloride to the hydration of calcium silicate or calcium aluminate hydrates. So, these hydration products will precipitate into the pores of the paste which lead to increase the bulk density. The decrease of bulk density after 6 months up to one year for all cement pastes is mainly due to the formation of hydration products such as chloroaluminate hydrate which decreases the bulk density. As the amount of the SAF increases up to 2.0 wt% the bulk density increases due to the filling effect and the acceleration of hydration; more hydration products are formed and then the pores decrease between the cement particles to produce more compact structure.

Total Porosity

Total porosity of cement pastes admixed with various dosages of SAF immersed under 4% MgCl$_2$ solution up to one year are given and graphically plotted in Fig. 10. The results show that total porosity of different cement pastes decreases up to 6 months and then increases up to one year. The decrease of total porosity for all cement pastes up to 6 months is due to the accumulation of the hydrated products which fill a part of the originally filled spaces. The increase of total porosity after 6 months up to one year is due to the formation of calcium chloroaluminate hydrate which makes softening, therefore, total porosity increases. This is also due to the formation of Mg(OH)$_2$ as a gelatinous material that
increases the total porosity. On the other side, as the amount of SAF increases up to 2.0 wt% the corresponding total porosity decreases. This is due to the acceleration of hydration which forming more hydration products precipitated in the open pores of the cement pastes.

**Compressive Strength**

The compressive strength of cement pastes admixed with various dosages of SAF immersed under 4% MgCl₂ solution up to one year are given in Fig. 11. It is clear that the compressive strength of all cement pastes increases up to 6 months and then decreases up to one year. The increase of compressive strength is attributed to that chloride ions activate the hydration of cement. Hence formed hydration products fill some of pores then the total porosity decreases and compressive strength enhances. The increase of compressive strength at early ages may be also due to the adsorption and incorporation of a part of Mg²⁺ ions in to the CSH particles which enhance the crystallization of CSH as well as the strength of cement paste. The compressive strength decreases for all cement pastes due to the combination of MgCl₂ with CH forming CaCl₂ and Mg(OH)₂. CaCl₂ reacts with C₃A to form chloroaluminate hydrates. While Mg(OH)₂ dissociates CSH to form MSH and CH. Both of chloroaluminate hydrates and MSH possess no binding properties and are accompanied by softening and loss of strength, consequently, the strength of hardened cement pastes decrease. The values of bulk density and total porosity are in a good agreement with those of compressive strength at all ages of immersion. The amount of diffused MgCl₂ increases with curing time and as a result, deterioration of cement paste enhanced. As the amount of SAF increases up to 2.0 wt% the compressive strength increases. This is mainly due to the acceleration of hydration which increases the amount of hydration products especially tobermorite-like gel (CSH).

**Total Chloride**

The total chloride contents of cement pastes admixed with various dosages of SAF immersed under 4% MgCl₂ solution up to one year are plotted in Fig. 12. The chloride content gradually increases with time up to one year for all cement pastes. This is due to the chemical reactions between chloride ions and the hydrated components, such as calcium aluminate ferrite and Ca(OH)₂. The diffusion process of chloride ions in cement pastes is influenced by the cement composition and total porosity. As the amount of the SAF increases up to 2.0 wt% the total chloride content decreases due to the acceleration of hydration; more hydration products are formed and then the pores decreases between the cement particles to produce more compact structure. This is confirmed from the bulk density, total porosity and compressive strength. The reaction of Cl⁻ ions goes with high rate at early ages due to the decrease of its radius. Therefore the Cl⁻ content is sharply increases at early ages.

![Fig. 8. Total sulphate content of cement pastes in presence of different dosages of SAF immersed under 4% MgSO₄ solution up to one year](image)
Fig. 9. Bulk density of cement pastes in presence of different dosages of SAF immersed under 4% MgCl₂ solution up to one year

Fig. 10. Total porosity of cement pastes in presence of different dosages of SAF immersed under 4% MgCl₂ solution up to one year
Fig. 11. Compressive strength of cement pastes in presence of different dosages of SAF immersed under 4% MgCl₂ solution up to one year

Fig. 12. Total chloride of cement pastes in presence of different dosages of SAF immersed under 4% MgCl₂ solution up to one year
Conclusion

Based on the results of experimental study concerning the effectiveness of laboratory prepared SAF superplasticizer dosage up to 2 mass% on the hydration kinetics, total porosity, bulk density, compressive strength and durability of SRC pastes containing 10% SF cured in salt solutions (immersed in 4% MgSO\textsubscript{4} or 4% MgCl\textsubscript{2}) and at elevated temperatures up to 800°C. Several recommendations and conclusions can be derived and presented as follows:

- The total chloride and sulphate contents decrease with SAF content up to 2.0%, due to the pozzolanic reaction of SF with CH forming additional calcium silicate hydrate to fills some open pores, thereby inhibiting the chloride and sulphate ions penetration.
- The compressive strength of thermally treated cement pastes admixed with 1.5% SAF increases up to 600°C and then decreases up to 800°C. The increase of compressive strength up to 600°C may be due to the acceleration of the hydration of pozzolanic reaction. The decrease at 800°C is due to the decomposition of cementitious materials and the coarsening of pore size distribution, which drastically increases the total porosity and decreases the bulk density.
- SRC-SF composite admixed with 1.5% of SAF is more durable against fire up to 800°C and 4% MgSO\textsubscript{4} or 4% MgCl\textsubscript{2} solutions.

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Author’s Contributions

All authors equally contributed in this work.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

References

Al-Dulaijan, S.U., 2007. Sulfate resistance of plain and blended cements exposed to magnesium sulfate solutions. Construct. Build. Mater., 21: 1792-802. DOI: 10.1016/j.conbuildmat.2006.05.017

ASTM, 2007. Standard test method for compressive strength of hydraulic cement mortars. ASTM Standards.

Aydın, S. and B. Baradan, 2007. Effect of pumice and fly ash incorporation on high temperature resistance of cement based mortars. Cement Concrete Res., 37: 988-995. DOI: 10.1016/j.cemconres.2007.02.005

Aye, T. and C.T. Oguchi, 2011. Resistance of plain and blended cement mortars exposed to severe sulfate attacks. Construct. Build. Mater., 25: 2988-2996. DOI: 10.1016/j.conbuildmat.2010.11.106

Binici, H., S. Kapur, J. Arocena and H. Kaplan, 2012. The sulfate resistance of cements containing red brick dust and ground basaltic pumice with sub-microscopic evidence of intra-pore gypsum and ettringite as strengtheners. Cement Concrete Compos., 34: 279-287. DOI: 10.1016/j.cemconcomp.2011.10.001

Chan, S.Y.N. and G.F. Anson, 1999. Residual strength and pore structure of high-strength concrete and normal strength concrete after exposure to high temperatures. Cement Concrete Compos., 21: 1-23. DOI: 10.1016/S0958-9465(98)00034-1

Chen, X. and S. Wu, 2013. Influence of water-to-cement ratio and curing period on pore structure of cement mortar. Construct. Build. Mater., 38: 804-812. DOI: 10.1016/j.conbuildmat.2012.09.058

Chindaprasirt, P., P. Paisitsrisawat and U. Rattanasak, 2014. Strength and resistance to sulfate and sulfuric acid of ground fluidized bed combustion fly ash-silica fume alkali-activated composite. Adv. Powder Technol., 25: 1087-1093. DOI: 10.1016/j.apt.2014.02.007

Cook, R.A. and K.C. Hover, 1999. Mercury porosimetry of hardened cement pastes. Cement Concrete Res., 29: 933-943. DOI: 10.1016/S0008-8846(99)00083-6

El-Didamony, H., E.A. El-Rahman and R.M. Osman, 2012. Fire resistance of fired clay bricks-fly ash composite cement pastes. Ceram. Int., 38: 201-209. DOI: 10.1016/j.ceramint.2011.06.050

Fiertak, M. and T. Stryszewska, 2013. Resistance of three-component cement binders in highly chemically corrosive environments. Procedia Eng., 57: 278-286. DOI: 10.1016/j.proeng.2013.04.038

Greene, K.T., 1962. Early hydration reactions of portland cement. Proceedings of the 4th International Symposium on the Chemistry of Cement, (SCC’ 62), Washington, pp: 359-374.

Handoo, S.K., S. Agarwal and S.K. Agarwal, 2002. Physicochemical, mineralogical and morphological characteristics of concrete exposed to elevated temperatures. Cement Concrete Res., 32: 1009-1018. DOI: 10.1016/S0008-8846(01)00736-0

Hewlett, P.C., 2004. Lea's Chemistry of Cement and Concrete. 4th Edn., Butterworth-Heinemann, Oxford ISBN-10: 0080535410, pp: 1092.
Hsu, K.C., J.J. Chiu, S.D. Chen and Y.C. Tseng, 1999. Effect of addition time of a superplasticizer on cement adsorption and on concrete workability. Cement Concrete Compos., 21: 425-430. DOI: 10.1016/S0958-9465(99)00030-X

Irassar, E.F., M.A. González and V.F. Rahhal, 2000. Sulphate resistance of type V cements with limestone filler and natural pozzolana. Cement Concrete Compos., 22: 361-368. DOI: 10.1016/S0958-9465(00)00019-6

Komenen, J. and V. Penttala, 2003. Effects of High Temperature on the pore structure and strength of plain and polypropylene fiber reinforced cement pastes. Fire Technol., 39: 23-34. DOI: 10.1007/A1021723126005

Lau, A. and M. Anson, 2006. Effect of high temperatures on high performance steel fiber reinforced concrete. Cement Concrete Res., 36: 1698-1700. DOI: 10.1016/j.cemconres.2006.03.024

Mohammed, M.S., A.E.S.I. Ahmed and R.M. Osman, 2014a. Microcrystalline cellulose as a reinforcement agent to cement pastes. Pigment Resin Technol., 43: 104-110. DOI: 10.1108/PRT-05-2013-0038

Montes, O.B., M. Palacios, P. Rivilla and F. Puertas, 2012. Compatibility between superplasticizer admixtures and cements with mineral additions. Construct. Build. Mater., 31: 300-309. DOI: 10.1016/j.conbuildmat.2011.12.092

Osman, R.M. and S. Al-Masry, 2014. Impact of Sulfonated Acetone Formaldehyde (SAF) on the durability of SRC-SF composite cement pastes. Int. J. Adv. Scientific Tech. Res., 6: 426-443.

Page, C.L. and M.M. Page, 2007. Durability of Concrete and Cement Composites. 1st Edn., Woodhead and Maney on behalf of Institute of Materials, Cambridge, ISBN-10: 1855739402, pp: 404.

Pei, M., Y. Yang, X. Zhang, J. Zhang and J. Dong et al., 2004. Synthesis and the effects of water-soluble sulfonated acetone-formaldehyde resin on the properties of concrete. Cement Concrete Res., 34: 1417-1420. DOI: 10.1016/j.cemconres.2004.01.012

Piasta, J., Z. Sawicz and L. Rudzinski, 1984. Changes in structure of hardened cement pastes due to the high temperature. ACI Mater Constr., 17: 291-296. DOI: 10.1007/BF02479085

Radwan, A.M., E.A. El-Alfi and R.M. Othman, 2012a. Influence of substitution of ordinary portland cement by silica fume in the durability of slag portland cement pastes in sea water. ARPN J. Eng. Applied Sci., 7: 283-291.

Radwan, A.M., E.A. El-Alfi and R.M. Osman, 2012b. Characteristics of portland cement pastes with high replacement of slag. J. Eng. Applied Sci., 7: 338-344.

Shanahan, N. and A. Zayed, 2007. Cement composition and sulfate attack: Part I. Cement Concrete Res., 37: 618-623. DOI: 10.1016/j.cemconres.2006.12.004

Shui, Z.H., R. Zhang, W. Chen and D.X. Xuan, 2010. Effects of mineral admixtures on the thermal expansion properties of hardened cement paste. Construct. Build. Mater., 24: 1761-1767. DOI: 10.1016/j.conbuildmat.2010.02.012

Yazıcı, S., G.I. Sezer and H. Şengül, 2012. The effect of high temperature on the compressive strength of mortars. Construct. Build. Mater., 35: 941-947.