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Effect of addition of Sikament-R superplasticizer on the hydration characteristics of portland cement pastes

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Abstract The effect of addition of Sikament-R superplasticizer (modified lignosulphonate base) on the hydration characteristics of hardened Portland cement pastes were studied at different curing conditions. Four mixtures were prepared using 0, 0.2, 0.4 and 0.6 wt% addition of Sikament-R superplasticizer (SR) of cement. These pastes were hydrated under two different conditions; (i) normal curing at room temperature; 25 °C up to 90 days periods and (ii) hydrothermal curing at a pressure of 8 atm. of saturated steam up to 24 h. The compressive strength, combined water content, free lime content, gel/space ratio and microstructure of hardened cement pastes were studied. The results revealed that addition of SR superplasticizer promote the dispersion of cement particles and interacts with Ca(OH)₂. The addition of SR superplasticizer exhibits Portland cement better workability during the preparation of pastes. In addition, amore compact structure were obtained leading to higher values of compressive strength for all the hardened hydrated pastes under both normal and hydrothermal curing. The results indicated that the addition of SR superplasticizer to Portland cement does not alter the types of hydration products formed during normal or hydrothermal conditions; only it caused a decrease in the degree of the porosity of the formed pastes.

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Introduction

The improvement mechanical and physicochemical properties of cement has been continuously undertaken since the inven-

tion of cement technology. Many ways can be used to improve cement properties, the most important one is to use cement admixtures as well as hydration under hydrothermal condition. Well known examples of admixtures are superplasticizers. Superplasticizers are usually chemical compounds such as sulphonated melamine formaldehyde (SMF), sulphonated naphthalene formaldehyde (SNF), modified lignosulphonates (MLS) and polycarboxylate derivatives [1,2]. Superplasticizers work on dispersing mechanism. The main polymers chains (sulphonate groups $-\text{SO}_3^{(-)}$) adsorb onto the surface of cement particles; the cement particles become negatively charged. Consequently, electrostatic repulsion occurs between the cement particles [3–9]. The cement particle arrangement in a

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paste matrix offsets the inter-particle attractive forces [10]. The interaction between superplasticizers and cement is still under investigation. Major aspects are whether superplasticizers adsorb evenly on the surface of a hydrating cement grain, and whether superplasticizers are not only adsorbed, but also absorbed. Cement grains show a mosaic surface resulting from the different clinker phases. Previous studies of superplasticizer adsorption on the pure cement clinker phases C_3S , C_2S , C_3A and C_4AF revealed that much higher adsorption occurs on the aluminate and ferrite than on the silicate phases [11]. Hence, superplasticizers may also adsorb onto C-S-H. Autoclaving adds highly preferred features to building materials. Especially the possibility to produce lightweight materials with high strength and low thermal conductivity and the significant low shrinkage are features related to autoclaved products. This applies in particular for autoclaved aerated concrete (AAC) and calcium silicate boards. In fiber cement the air cured and autoclave process are common. Both processes have their benefits [12]. Autoclaving or air curing is also related to the tradition and the climates in various countries. Whilst Europe was long time focusing on air cured products, USA and Australia have always preferred autoclaved sheets [12–14]. The type of curing and consequently the type of calcium silicate hydrate produced has significant influences on the properties of the building material [15]. Saturated steam under pressure (autoclaving) does not only accelerate the hardening of cement or concrete but forms different types of calcium silicate hydrate. The structure of the calcium silicate hydrate formed at ambient temperatures is amorphous or poorly crystallized where as autoclaved calcium silicate hydrate however is mostly well crystallized. The degree of crystallization depends on the raw materials, autoclaving conditions and other factors. It is generally agreed that crystallization decreases drying shrinkage and improves resistance to chemical attack [16].

The effect of high temperatures up to 900 °C on normal strength, normal and autoclave curing high strength mortars were studied [17]. Mechanical properties such as, compressive strength, flexural strength, modulus of elasticity, and weight loss of the specimens were determined. The effect of polypropylene (PP) and steel fibers incorporation on high temperature behavior of high strength mortars were also investigated. Test results indicated that compressive strength of all mixtures increased with temperature up to 300 °C. However, above 300 °C all specimens showed explosive disintegration except normal strength mortars, and high strength mortars with PP fibers.

The aim of this work is to investigate the effect of addition of SR superplasticizer on the hydration characteristics of OPC pastes hydrated under normal and autoclaving conditions.

Experimental

Materials

The materials used in this study were ordinary Portland cement (OPC; Type I) with Blaine specific surface area of 3200 cm²/g and has chemical oxide composition given in

Table 2 The percentage addition of SR superplasticizer and values of standard water of consistency of different mixes and their designations.

Mixes	W/S	SR (wt.%)
Ao	0.280	–
A1	0.277	0.20
A2	0.264	0.40
A3	0.250	0.60
Bo	0.280	–
B1	0.277	0.20
B2	0.264	0.40
B3	0.250	0.60

Table 1 and Sikament-R superplasticizer; SR (modified lignosulphonate base) obtained from Sika Egypt for Construction Chemicals, EL-Abour City, Cairo, Egypt. Table 2 shows the varies ratios of SR superplasticizer, required W/S ratios to give standard consistency and the designations of the different mixes.

Preparation of the hardened cement pastes

Different cement pastes were prepared using the values of standard water of consistency and different Wt.% addition of SR superplasticizer Table 2. Each paste was prepared by mixing the dry cement with the required amount of water for about three minutes. After complete mixing, the resultant paste was molded into one inch cubic moulds. Then cured in 100% relative humidity for 24 h. For normal curing the cubic specimens were removed from the moulds after 24 h and cured under water for 1, 3,7,28 and 90 days .While for autoclaving the cubic specimens were removed from the moulds then dried for 24 h at 105 °C, and kept in a desiccator until the desired time of autoclaving. The specimens of each paste were cured under hydrothermal conditions in an autoclave at a pressure of 8 atmosphere of saturated steam for 0.5, 2, 6, 12 and 24 h.

Techniques

The compressive strength

A set of three specimens representing the same Mix, and age as well as having a certain W/C ratio were tested for the determination of the compressive strength of the hardened cement paste. The compressive strength test machine used for strength measurements is Controlap Machine and having a maximum load of 1000 KN, the average of the three results was considered and expressed in kg/cm².

Chemically combined water

The content of chemically combined water, W_n (%), was determined as follows. An exact weight of the dried cement paste was gradually ignited in a silica crucible for 2 h in a

Table 1 Chemical oxides composition of ordinary portland cement.

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	Cl ⁻	Ignition loss
Weight (%)	20.63	5.53	3.54	64.29	1.72	2.77	0.02	0.29	0.03	1.18

muffle furnace at 1000 °C (with the rate of 20 °C/min.). The crucible was cooled in a desiccator then weighed at room temperature. Duplicate measurements were carried out for each sample and the mean value was recorded:

$$W_n(\%) = [(W_o - W_i)/W_i] \times 100$$

where W_o is the weight of the dried sample before ignition, and W_i is the weight of sample after ignition.

The results of the combined water content were used to calculate the gel/space ratio of the hardened pastes according to the following equation [18]:

$$\chi = \frac{0.647\alpha}{0.319\alpha + W_o/C}$$

where α is the fraction of the cement that has been hydrated (degree of hydration) as calculated from the following equation:

$$\frac{w_o}{w_o^\infty}$$

where w_o^∞ is the chemically combined water content after complete hydration, C is the weight of cement and W_o is the volume of mixing water (i.e. W_o/C represents the initial water/cement ratio).

Free-Lime Content

The free lime content, (CaO%), was determined by the method reported by Kondo et al. [19]. A certain weight of the sample (0.5 g) was dispersed in 40 ml of a glycerol-ethanol mixture (1:5 ratio by volume); together with a small amount of anhydrous barium chloride (about 0.5 g) as a catalyst and phenolphthalein as an indicator. The mixture was kept boiling in a conical flask, fitted with an air reflux, on a hot plate for 3 min (the color becomes pink). All the contents of the flask were then titrated using a standard ammonium acetate solution till the pink color just disappeared. The mixture was repeatedly heated and titrated until no further appearance of pink color occurs. The free, CaO%, is calculated as gram free CaO per 100 grams ignited sample.

Microstructure

Morphology and microstructure of some selected dried samples were studied using Scanning Electron Microscopy (SEM). Jeol-Jsm-6360 LV, MP 165087 Scanning Electron Microscopy, was used in this investigation.

Results and discussion

Compressive Strength

The results of compressive strength for hardened OPC paste as well as SR superplasticized OPC pastes, (Mixes A0, A1, A2 and A3) with 0, 0.2, 0.4 and 0.6 wt% SR of cement, respectively, and hydrated under normal and hydrothermal curing condition are given in Figs. 1 and 2 respectively. The values of compressive strength obtained for the OPC paste (blank, A0) show a continuous increase with curing time up to 90 days. The results of compressive strength of OPC superplasticized pastes (Mixes A1–A3) show the same trend as in case of blank

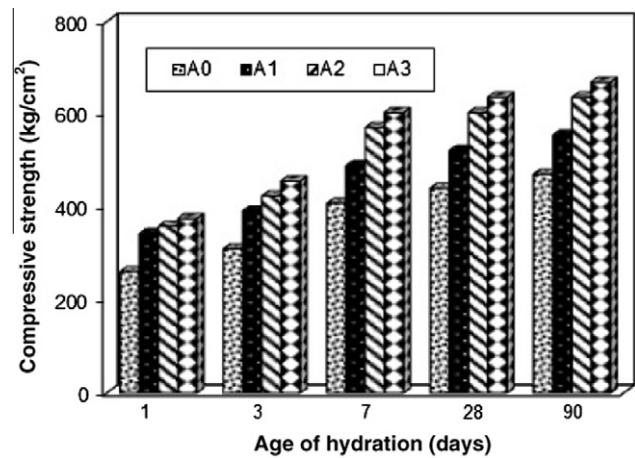


Fig. 1 Variation of compressive strength for normally cured neat OPC and SR superplasticized OPC pastes with curing time.

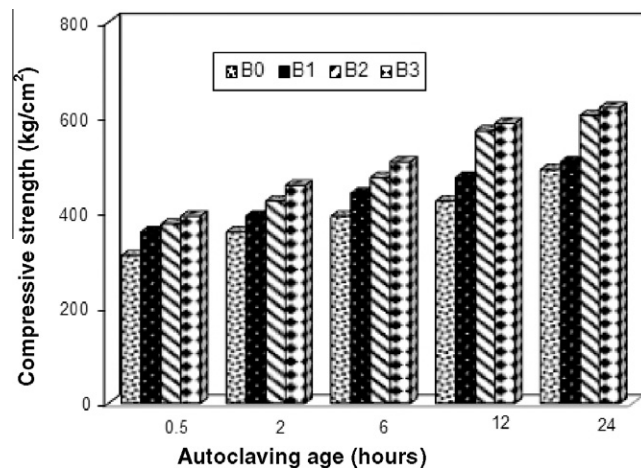


Fig. 2 Variation of compressive strength for hydrothermally cured neat OPC and SR superplasticized OPC pastes with autoclaving time.

(A0), but with higher values of strength Fig. 1. The results of compressive strength for OPC paste cured at hydrothermal condition (blank, B0) show a continuous increase with increasing time of autoclaving from (0.5 to 24 h) Fig. 2. The compressive strength for Mixes B1, B2 and B3 give nearly the same behavior as in case of blank (B0) but with higher strength values. The previous results are attributed to the hydration of OPC and formation the hydration products (mainly calcium silicate hydrates) having a relatively high hydraulic properties. The increase in the values of compressive strength which occurred by SR addition in both hydration conditions attributed to the decrease in the values of standard water of consistency that occurred by SR addition which leads to a decrease in the total porosity of the hardened cement pastes. Comparing the results of Figs. 1 and 2 indicate that there is no great difference in the results of compressive strength, instead the results of compressive strength of the normally cured mixes showed a relatively high values specially at later ages. This can be attributed to the well crystallized of the obtained CSH. Hence, the compressive strength decreases.

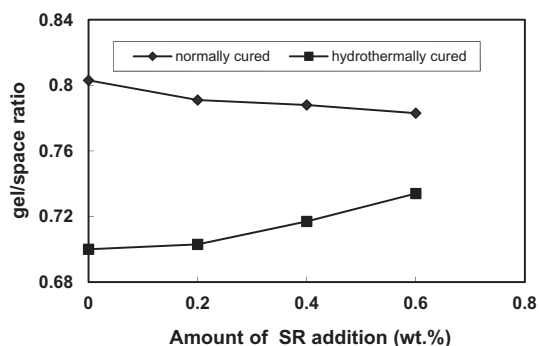


Fig. 3 Gel/space ratio of normally and hydrothermally cured neat SR superplasticized OPC.

Fig. 3 illustrate the values percentages of gel/space ratios for normally and hydrothermally cured -OPC hardened pastes with different% of SR superplasticizer additions. As shown in the figure the values of gel/space ratios for normally cured pastes are higher than those cured hydrothermally. This is the main reason for the high compressive strength values obtained for normally cured hardened cement pastes.

Chemically-combined water content

The results of combined water for OPC and SR superplasticized OPC pastes hydrated under water and hydrothermally cured are given in Figs. 4 and 5. The values of chemically-combined water of the normally cured hardened OPC paste shows sharp increase during the early ages of hydration up to 7 days; followed by a continuous and gradual increase up to the final stage of hydration (90 days) Fig. 4. Addition of SR superplasticizer to OPC pastes give nearly the same behavior as blank specimens but with lower values. The values of combined water obtained for autoclaved OPC pastes indicates a high rate of hydration during the early age of autoclaving (0.5 h), followed by a very slight increase up to the final stage of autoclaving (24 h) Fig. 5. The addition of SR superplasticizer to the OPC gives a nearly similar behavior as that of the OPC hydration but also with lower values. The decrease of the values of combined water of superplasticized cement pastes is mainly attributed to the decrease of the water consistency which affects the rate of hydration, i.e. as the mixing water decreases the combined water content diminishes [16].

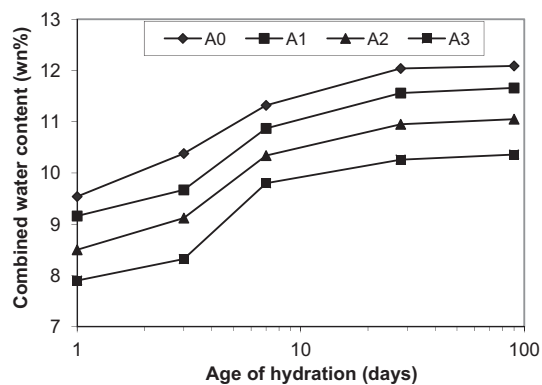


Fig. 4 Combined water content for neat OPC and SR superplasticized OPC pastes hydrated under normal curing.

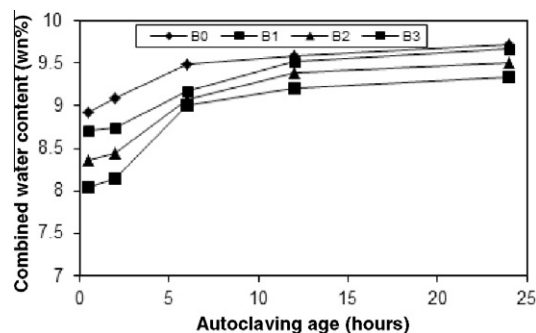


Fig. 5 Combined water content for neat OPC and SR superplasticized OPC pastes hydrated under hydrothermal curing.

Free lime content

The results of the free lime content of the hardened OPC and SR superplasticized OPC pastes, cured under water and in autoclave are given in Figs. 6 and 7 respectively. Fig. 6 indicates a continuous and gradual increase in the free lime values obtained from hydration of both OPC and SR-OPC superplasticized pastes up to final ages of hydration (90 days). The decrease in the free lime values that occurred by addition of SR to OPC pastes is explained in term of the low degree of hydration, as well as interaction of SR with $\text{Ca}(\text{OH})_2$ as well as the decrease of mixing water which affects the rate of hydration [16]. Since SR contains sulfonate groups it expected to be capable of interacting with $\text{Ca}(\text{OH})_2$ which librated from hydration of OPC. As a result morphology or microstructure of the resulting pastes would be altered and the mechanical properties or other properties of the pastes would also be affected [20,21]. Similar behavior was obtained for the autoclaved OPC and SR superplasticized OPC pastes Fig. 7. As shown in Fig. 7, the results of free lime show that also a very high rate of hydration of OPC pastes, since the values of free lime give a marked high values during all ages of hydration.

Microstructure of the formed hydrates

The microstructure of hardened OPC pastes containing 0.2 and 0.6% of SR superplasticizer by weight of OPC and

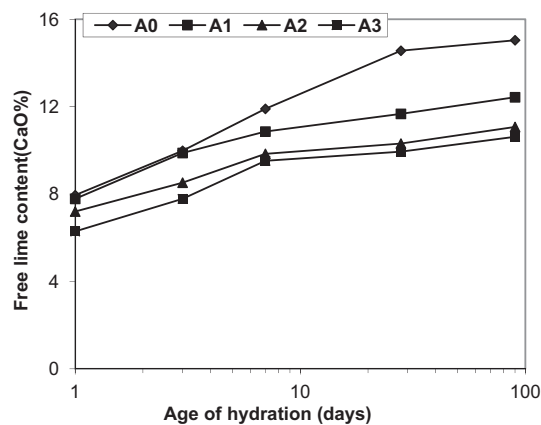


Fig. 6 Free lime content for neat OPC and SR superplasticized OPC pastes hydrated under normal curing.

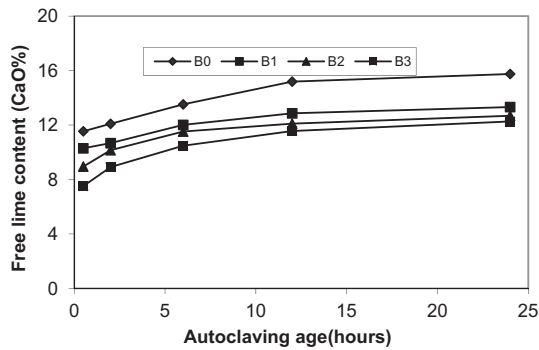


Fig. 7 Free lime content for neat OPC and SR superplasticized OPC pastes after hydrothermal condition.

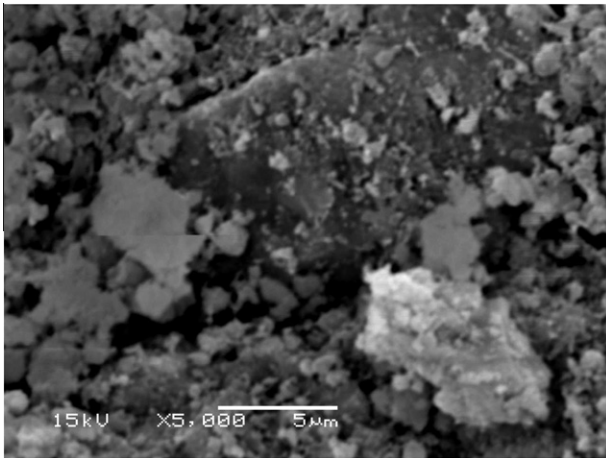


Fig. 8 SEM Micrographs of A1 specimens after 28 days of normal hydration.

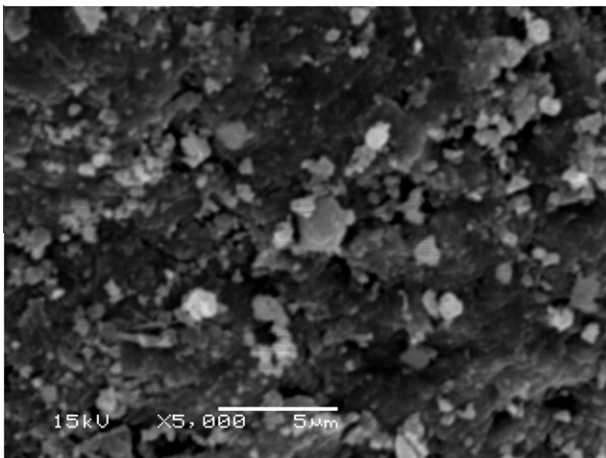


Fig. 9 SEM micrographs of A3 specimens after 28 days of normal hydration.

hydrated under normal condition for 28 days are given in Figs. 8 and 9 respectively. The microstructure of hydrates is composed of calcium silicate hydrates, which represent the main hydration products, hexagonal $\text{Ca}(\text{OH})_2$ and hexagonal calcium aluminate hydrates. Increasing the wt.% addition of

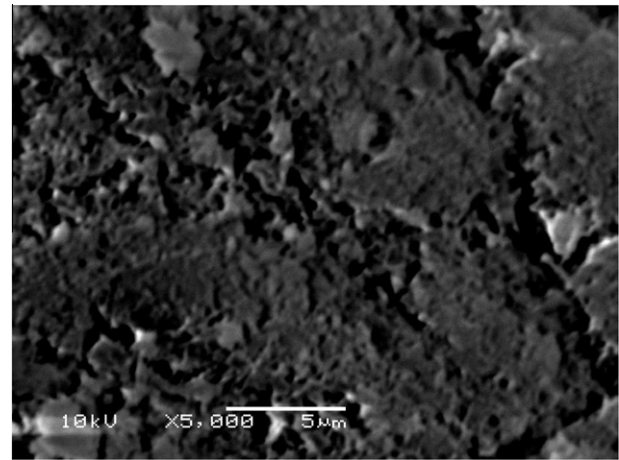


Fig. 10 SEM Micrograph for B1 pastes hydrothermally cured for 24 h.

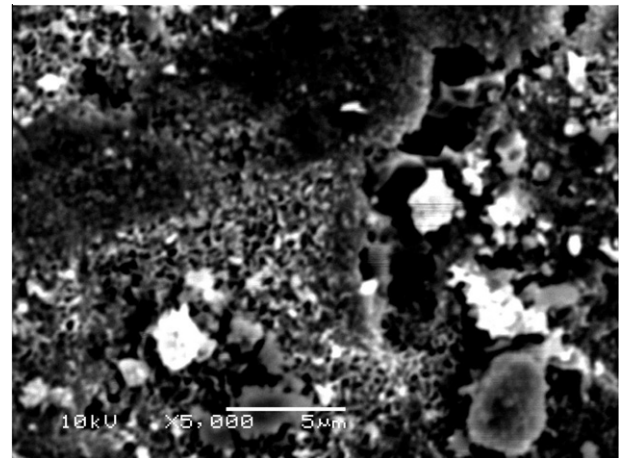


Fig. 11 SEM Micrograph for B3 pastes hydrothermally hydrated for 24 h.

SR to OPC from 0.2 to 0.6 results in a reduction of the degree of crystallinity of hydration products; leading to a dense structure of the calcium hydroxide and nearly amorphous calcium silicate hydrates blocking almost all of the pore system Fig. 9. The microstructure of hardened OPC pastes with 0.2 and 0.6 wt.% SR superplasticizer and hydrothermally hydrated for 24 days are given in Figs. 10 and 11 respectively. The microstructures of the autoclaved specimens display a dense and closely packed structure. The same phases are obtained as in case of normal curing with higher degree of crystallinity.

Conclusion

From the previous results it can be conclude that:

1. Addition of SR superplasticizer to OPC causes increases the values of compressive strength for all hydrated cement pastes and with the dose of SR.
2. The values of combined water of the hardened cement pastes decreased with the wt% addition of SR superplasticizer.

3. Addition of SR superplasticizer to OPC decreases the values of free lime contents, proving interaction of superplasticizer and lime liberated from cement hydration.
4. The combined water contents for hydrothermally (autoclaved) hydrated OPC and superplasticized OPC pastes indicates stabilization of the formed hydration products during various autoclaving periods.
5. Microstructure of pastes hydrated under normal and hydrothermal curing conditions display the same phases, proving that the presence of superplasticizer did not affect the mechanism of hydration, or the types of hydration products formed. It only affects the microstructure of the formed hydrates.

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