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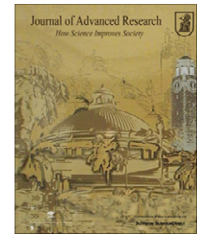

ORIGINAL ARTICLE

Effect of superplasticizers on the hydration kinetic and mechanical properties of Portland cement pastes

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Abstract Hydration of ordinary Portland cement in the presence of two different types of superplasticizers namely sodium lignosulfonate (LS) and naphthalene sulfonate-formaldehyde condensate (NSF) was studied using different experimental techniques. Superplasticized ordinary Portland cement pastes were prepared using the values of standard water of consistency with different additions of each types of superplasticizers used. Pastes were hydrated for different time intervals under normal curing conditions. The results reveal that both of superplasticizers increase the workability and reduce the standard water of consistency. This results in an improvement in the mechanical properties of superplasticized cement pastes at all ages of the hydration–hardening process. Naphthalene sulfonate-formaldehyde condensate was found to has the higher efficiency in improving the mechanical properties of the hardened pastes than that of sodium lignosulfonate superplasticizer.

Introduction

Various studies have been published that deal with the effect of addition of superplasticizer on the physicochemical properties of ordinary Portland cement pastes [1–7]. Superplasticizers are linear polymers containing sulfonic acid groups attached to the polymer backbone at regular intervals. Superplasticizers are broadly classified into four groups, sulfonated melamine-formaldehyde condensates (SMF), sulfonated naphthalene-formaldehyde condensates (SNF), modified lignosulfonates (MLS), and polycarboxylate derivatives [8]. Many papers presented investigated hydration of ordinary Portland cement and mechanism of interaction with superplasticizer [9–12]. The effect of a polycarboxylate (PC) superplasticizer admixture on the mechanical, mineralogical, microstructural, and rheological behavior of Portland cement pastes was studied [13]. The results obtained that at very early ages an initial retardation of cement hydration is produced. This effect is more pronounced at higher doses of superplasticizer in its interactions with the reactive species, the organic admixture affects hydrated phase diffusion, nucleation and growth and therefore the hydration process. The effects of water dispersible polymers on the

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properties of hardened cement pastes, mortar, and concrete were investigated [14,15]. The hydration and microstructure characteristics of superplasticized ordinary Portland cement pastes were studied in many papers [16–18], the results indicated that, at high dosages, superplasticizers not only had a significant effect on the early cement hydration process, but on later microstructure development as well. At the same W/C ratio, the microstructure of pastes containing superplasticizers developed at much slower rate than in the control paste. The effect of acrylate-polyethylene glycol superplasticizer on the mechanical and physico-chemical properties of ordinary Portland cement (OPC) blended with condensed silica fume (CSF) was investigated [19]. The results indicated that addition of superplasticizer to OPC pastes blended with 5% and 7.5% of CSF improves the mechanical properties during all stages of hydration; this result from the reduction of the total porosity and the improvement of the workability of the fresh cement pastes. The effect of intergrinding different percentages of a naphthalene-based superplasticizer (SP) with Portland cement clinker and gypsum on the fineness of the product, the water requirement and the compressive strength of the mortars made with the superplasticized cement was studied [20]. The results showed that the water requirement of the mortars made with the superplasticized cements was similar to that of the mortars made with the control Portland cements when the same amount of the SP was added at the mortar mixer. The mortars made with the superplasticized cements had shorter setting times and higher compressive strengths than those made with the control Portland cements. This was primarily due to the lower water-to-cement ratio of the mortars made with the superplasticized cements. The hydration of white Portland cement in the presence of two different types of superplasticizers, namely Melment and Lomar-D, one melamine based and the other naphthalene sulfonic acid based was investigated [21]. The results indicated that both of the superplasticizers increase the workability and reduce the water content. Initial and final setting time increased with the increase of superplasticizer concentration. In the presence of Melment the pore size is decreased, whereas in the presence of Lomar-D it is increased. Adsorption of Lomar-D over hydrated cement is much higher compared to Melment and that is why it acts as a strong retarder. The present study is concerned with the effect of addition of sodium lignosulfonate and polynaphthalene sulfonate superplasticizers on the microstructure and hydration characteristics of hardened Portland cement pastes. These two types of superplasticizers were selected because they used as a highly effective water reducing agent, used for the production of high quality concrete in hot climate and having dual action, since they promote accelerated hardening with highly early and ultimate strength. The effect of different percentage addition of each superplasticizer on the hydration characteristics and mechanical properties of hardened pastes was also studied to investigate the most effective percentage addition.

Experimental

Materials

The material used in this investigation is ordinary Portland cement (OPC) with Blaine area 3200 cm^2/g and its chemical oxide composition is given in Table 1. Two types of superplasticizers named sodium lignosulfonate (LS) and naphthalene sulfonate-formaldehyde condensate (NSF), were supplied by Sika Egypt for construction chemicals.

Preparation of pastes

The superplasticized cement pastes were prepared from OPC using the water/solid (W/C) ratios of standard water of consistency with various additions of 0.15%, 0.3%, and 0.5% of LS and NSF by weight of cement. The values of standard water of consistency for each paste are given in Table 2. The pastes were molded in 1 inch cubic molds, cured at 100% relative humidity up to 24 h, then cured under water for different time intervals of 3, 7, 28, 90, and 180 days. The hydration reaction of hardened cement pastes was stopped at each time interval according to the method reported in an earlier investigation [22]. Samples then were dried at 90 °C for three hours, and kept in a desiccator until the time of testing was reached.

Techniques

The physicochemical and mechanical properties were studied by determination of the compressive strength using the fresh hardened cement pastes, while the free lime content, and the combined water content were determined using the dried samples at the various hydration times, the phase composition of some selected dried samples were studied using X-ray diffraction analysis (XRD). The instrument is PHILIPS model PW1710 diffractometer with Mo target and 0.71073 angstrom wavelength. The samples were finally ground to pass a 200 mesh sieve so as to minimize the effect of absorption and extinction of the X-ray beam. 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 obtained for hardened neat OPC paste as well as LS-OPC and NSF-OPC superplasticized cement pastes, made using the values of standard water of consistency, with 0.15%, 0.3%, and 0.5% additions of LS and NFS (by weight of cement) are given in Figs. 1 and 2, respectively. The result of compressive strength obtained for hardened OPC pastes showed a continuous gradual increase during all ages of hydration, Fig. 1. This result is mainly due to hydration of OPC and formation of hydration products (mainly as calcium silicate hydrates) having strong mechanical properties. In case of OPC-LS and OPC-NSF superplasticized pastes, the role of LS or NSF is the negative segment of LS or NSF polymers coating the surfaces of cement particles, causing their mutual repulsion, leading to high degree of dispersion and break up flocks causing release of the trapped water and therefore the workability increases at lower values of standard water of consistency. Figs. 1 and 2 indicate that addition of LS or NSF to OPC improved the mechanical properties of the hardened superplasticized cement pastes at various addition of LS or NSF during all stages of hydration. This result is mainly associated with the reduction in the values of standard

Table 1 Chemical analysis of OPC.

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl^-	Ignition loss
Weight (%)	20.63	5.53	3.54	64.29	1.72	2.77	0.02	0.29	0.03	1.18

Table 2 The values of standard water of consistency for PPC with LS and NSF superplasticizer.

Superplasticizer concentration (wt/wt.%)	W/C ratios	
	LS superplasticizer	NFS superplasticizer
0	0.259	0.259
0.15	0.256	0.254
0.30	0.251	0.250
0.50	0.247	0.246

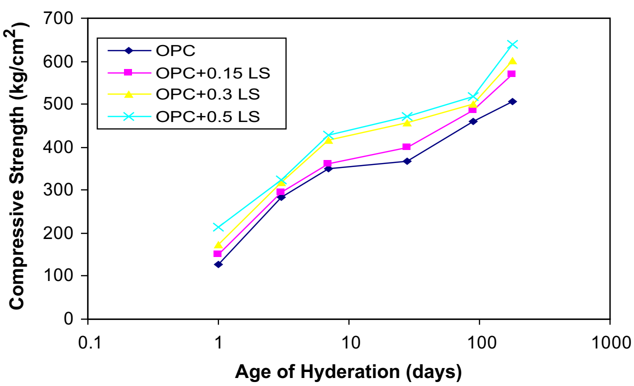

Fig. 1 Compressive strength versus different ages of hydration for various LS superplasticized ordinary Portland cement pastes.

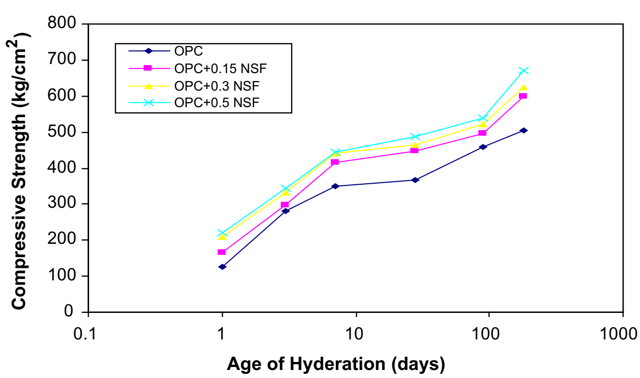

Fig. 2 Compressive strength versus different ages of hydration for various NSF superplasticized ordinary Portland cement pastes.

water of consistency from 0.259 to 0.256, 0.251, and 0.247 and from 0.259 to 0.254, 0.250, and 0.246 by addition of 0.15%, 0.3%, and 0.5% addition of LS and NSF (by weight of cement) respectively. This results in the formation of hardened cement pastes with lower porosity from initial stage of hydration. This is due to the increase of fluidity of the fresh cement pastes as a result of addition of superplasticizers leading to a marked reduction in the initial water/cement (W/C) ratio; therefore the hardened cement pastes produced possess high hydraulic characters.

Therefore, a more dense structure is obtained with relatively high mechanical properties. The results of Fig. 1, Fig. 2 indicate that the efficiency of NSF in improving the mechanical properties of the hardened OPC pastes is higher than that of LS; this is due to the efficiency of NSF in reducing the standard water of consistency to lower values than that of LS which may attribute to the lower in molecular weight of NSF than LS superplasticizer. The smallest molecular weight polymer is the most adsorbed one [23].

Hydration kinetics

Hydration kinetics of the neat OPC and superplasticized OPC pastes were studied by determining the values of chemically-combined water ($W_{n,}$ %) and the free lime (CaO, %) contents at various ages of hydration. The results of combined water obtained for OPC and superplasticized OPC-LS and OPC-NSF pastes are given in Tables 3 and 4. As indicated in the Tables 3 and 4 the values of combined water for hardened OPC and superplasticized OPC pastes show a gradual increase up to the final ages of hydration (180 days) this due to hydration of OPC pastes The results of W_n – content obtained for LS and NSF superplasticized PPC pastes show almost the same general trend of hydration as those obtained for the neat OPC paste (without admixture), with a slight decrease in the W_n – values at all ages of hydration. This effect is due to the decrease of W/C of standard water of consistency by LS and NSF addition to OPC. Tables 3 and 4 indicate also that the values of W_n – content obtained for NSF-OPC superplasticized pastes are lower than those obtained for LS-OPC superplasticized pastes. The results of free lime contents obtained for OPC and superplasticized OPC-LS and OPC-NSF pastes are given in Tables 5 and 6, respectively. The free lime content of hardened OPC pastes shows a continuous gradual increase up to the final age of hydration, due to cement hydration. The results of free lime content of LS and NFS superplasticized OPC pastes show almost the same general trend of hydration as those obtained for the neat OPC paste (without admixture), with slight

Table 3 Combined water contents obtained for OPC and OPC-LS superplasticized pastes at various ages of hydration .

Age of hydration (days)	LS concentration (wt/wt)			
	0	0.1	0.3	0.5
0.0833	1.84	1.42	1.35	1.04
0.25	3.78	3.50	3.36	2.88
1	10.01	9.73	9.46	9.44
3	12.43	12.18	11.99	11.79
7	13.58	12.98	12.91	12.73
28	15.12	14.82	14.46	14.33
90	17.51	16.84	16.37	16.15
180	21.72	20.58	20.12	19.91

Table 4 Combined water contents obtained for OPC and OPC-NSF superplasticized pastes at various ages of hydration.

Age of hydration (days)	NFS concentration (wt/wt)			
	0	0.15	0.3	0.5
0.0833	1.84	1.23	1.19	0.99
0.25	3.78	2.41	2.11	1.96
1	10.01	9.43	9.33	9.21
3	12.43	12.01	11.84	11.48
7	13.58	12.94	12.75	12.65
28	15.12	14.47	14.10	14.04
90	17.51	16.52	16.17	16.00
180	21.72	19.82	19.39	19.22

Table 5 Free lime contents obtained for OPC and OPC-LS superplasticized pastes at various ages of hydration.

Age of hydration (days)	LS concentration (wt/wt)			
	0	0.15	0.3	0.5
0.0833	0.45	0.39	0.35	0.33
0.25	1.53	1.17	1.14	1.12
1	2.65	2.32	2.06	1.89
3	4.71	4.45	4.16	4.11
7	5.55	5.12	4.85	4.63
28	6.45	6.06	5.77	5.74
90	6.82	6.44	6.10	6.04
180	7.93	7.35	7.02	7.00

Table 6 Free lime contents obtained for OPC and OPC-NSF superplasticized pastes at various ages of hydration.

Age of hydration (days)	NFS concentration (wt/wt)			
	0	0.15	0.3	0.5
0.0833	0.45	0.33	0.30	0.28
0.25	1.53	0.96	0.95	0.92
1	2.65	2.08	2.06	1.73
3	4.71	4.24	4.15	4.09
7	5.55	5.05	4.83	4.60
28	6.45	5.99	5.74	5.71
90	6.82	6.28	6.09	6.03
180	7.93	7.11	7.02	6.96

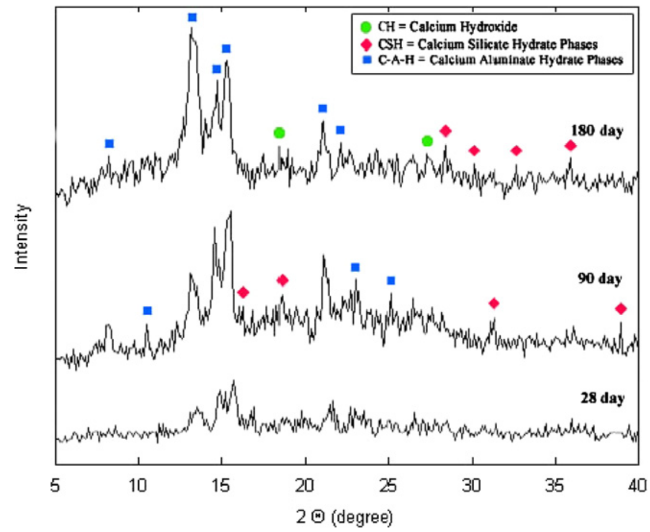

Fig. 3 X-ray diffraction patterns of hydrated ordinary Portland cement specimens.

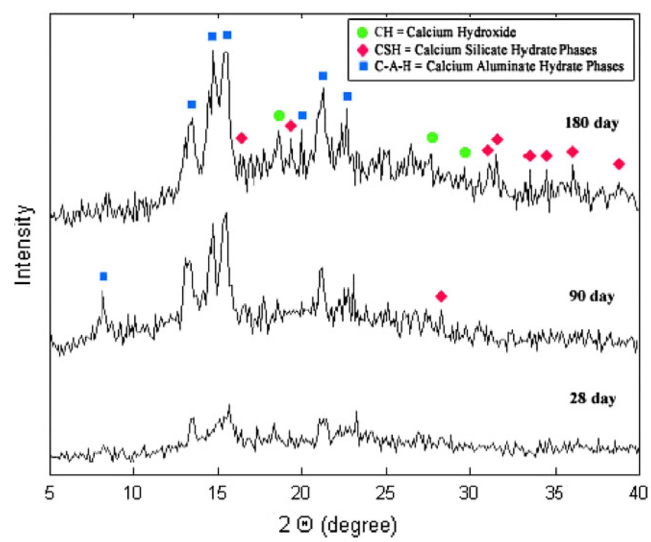

Fig. 4 X-ray diffraction patterns of the hydrated OPC-LS superplasticized cement pastes (containing 0.3% LS).

decrease in the values of free lime (due to the decrease in the values of standard water of consistency by LS and NFS addition. Results of both combined water and free lime contents of hardened pastes indicate that addition of LS or NSF superplasticizer to OPC does not alter the hydration product formed; thus, superplasticizers affect only the microstructure and degree of crystallinity of the formed hydrates.

Phase composition and microstructure

The results of X-ray diffraction analysis (XRD) obtained for the OPC paste and superplasticized OPC-LS and OPC-NSF pastes, having 0.30% of LS or NSF, hydrated for 28, 90, and 180 days are given in Figs. 3–5. The main phases identified are tobermorite-like calcium silicate hydrates (CSH), calcium aluminate hydrates (mainly as C_4AH_9) and calcium hydroxide (portlandite). Fig. 3, indicate that the intensity of the peaks characterized for calcium silicate hydrates (CSH) phases shows a slight increase with increasing age of hydration from 28 to 180 days. This is attributed to the ill-crystallized and nearly amorphous character of calcium silicate hydrates (CSH) product; the formation and later accumulation of amorphous CSH results in a minor effect on the intensities of the peaks characteristic for these hydrates. The peaks characterized for calcium aluminate hydrates shows a marked increase with increase in hydration period from 28 to 180 days, indicating a notable increase in both amount and degree of crystallinity of the calcium aluminate hydrates phase formed from hydration of OPC with increasing hydration time. Finally the peak characterized for calcium hydroxide (portlandite) phase was also observed, and its intensity increase with increase in the age of hydration due to the hydration of OPC. Addition of LS or

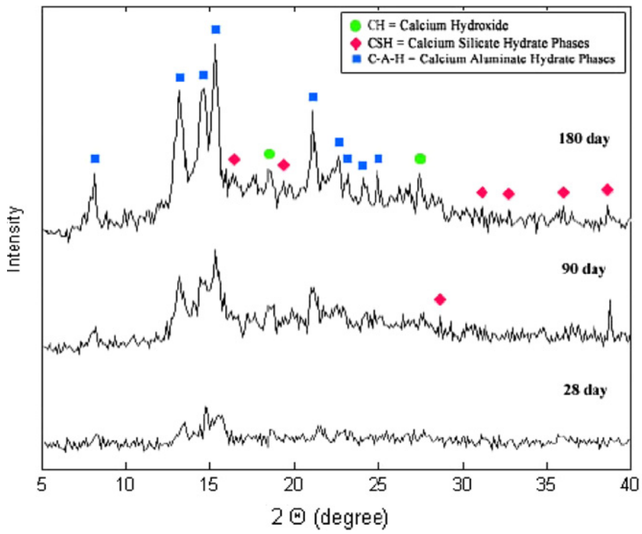

Fig. 5 X-ray diffraction patterns of the hydrated OPC-NSF superplasticized cement pastes (containing 0.3% NFS).

NSF superplasticizer (0.3 wt.%) to OPC display the same phases and same behavior as in case of OPC paste Figs. 6 and 7, but the intensities of the peaks characterized for calcium silicate hydrates and calcium aluminte hydrate phases are less. This reveals that addition of LS or NSF superplasticizer to OPC does not alter the formed hydration products, it only causes reduction in the degree of crystallinity of the formed hydrates, with a highly amorphous character.

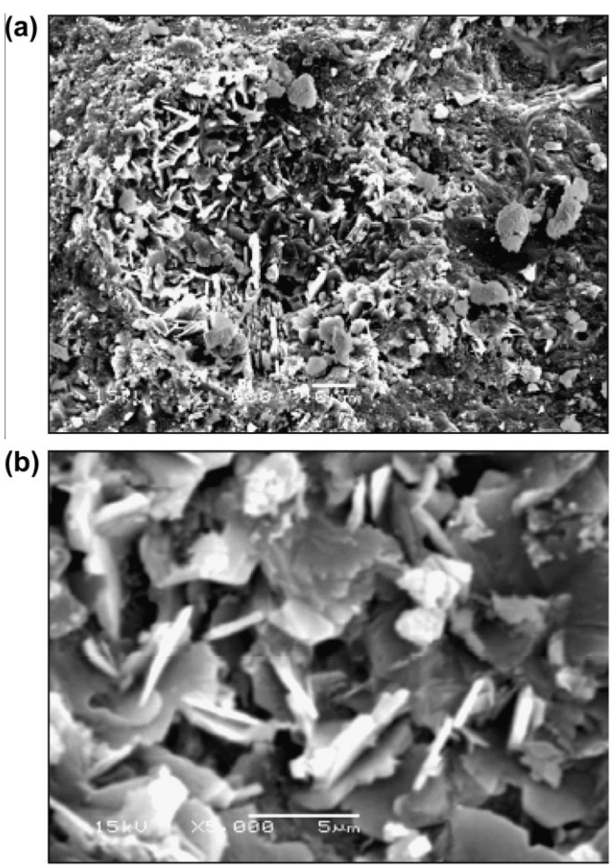

Fig. 6 SEM micrographs for the hydrated OPC-LS superplasticized cement pastes (containing 0.3% LS).

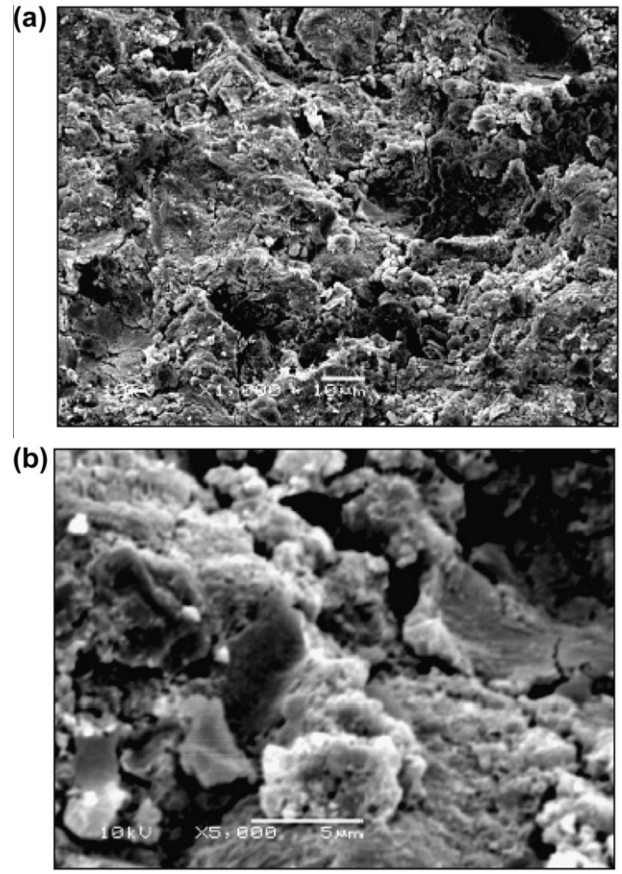

Fig. 7 SEM micrographs for the hydrated OPC-NSF superplasticized cement pastes (containing 0.3% NFS).

The results of scanning electron microscopy (SEM) examination for superplasticized OPC-LS and OPC-NSF pastes, having 0.3% of LS or NSF, hydrated for 180 days are given in Figs. 6 and 7, respectively. The microstructure of LS and NFS superplasticized OPC pastes (with 0.3% addition) hydrated for 180 days, composed closely packed structure consists of ill crystalline and nearly amorphous calcium silicate hydrates (CSH) which represent the main hydration product, also hexagonal crystals of calcium aluminate hydrates (CAH) and calcium hydroxide (CH), this highly dense structure Figs. 6a,b and 7a,b give hardened pastes with good mechanical characteristics.

Conclusion

Addition of LS or NSF to OPC pastes causes a notable improvement in the mechanical properties of the hardened pastes during all stages of hydration. Addition of LS or NSF to OPC pastes causes a slight decrease in both the values of combined water and free lime contents at all ages of hydration; this is due to the decrease in the values of W/C ratios of standard water of consistency by addition of LS or NSF to PPC. The results XRD analysis and SEM indicates that addition of LS or NSF to OPC pastes does not alter the types of formed hydration products, it affects only the degree of crystallinity of the formed hydrates, which leads to highly amorphous hydrates. The efficiency of NSF superplasticizer in reducing the values of W/C ratios of standard water of consistency is higher than that of LS superplasticizer. So OPC pastes prepared using NSF superplasticizer have higher improvement in their mechanical properties than those prepared using LS superplasticizer.

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