Effect of Some Superplasticizers on the Mechanical and Physicochemical Properties of Blended Cement Pastes

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SYNOPSIS

Blended cement pastes made of Portland cement and fine sand (known in Egypt as El-Karnak cement) were made using a water–cement ratio of 0.25 by weight. Three pastes containing admixture (water-soluble condensates) were also prepared using a water–cement ratio of 0.25 and condensate (superplasticizer) content of 0.25% by the weight of cement; the superplasticizers used are Na-phenol sulfonate formaldehyde, Na-polystyrene sulfonate, and Na-β-naphthol sulfonate formaldehyde condensates. All pastes were cured for various time intervals within the range of 0.02–90 days. Compressive strength tests, hydration kinetics, X-ray diffraction analysis, thermal analysis, and surface properties were studied and related as much as possible to the pore structure of the hardened pastes. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Superplasticizers are water reducing admixtures which have an effective property in dispersing cement. This dispersing action increases the workability of concrete. The resulting concrete can be placed with little or no compaction and is not subjected to excessive bleeding or segregation. The second use of superplasticizers is in the production of concrete of normal workability but with an extremely high strength owing to a very substantial reduction in the water–cement ratio. Various reviews have been published that dealt with superplasticizers and their effect on concrete.[1–4] The most comprehensive papers that dealt with superplasticizers were those of Malhotra,[5] Makizuma et al.,[6] Bromkam,[7] Idmitsu et al.,[8] and Mather.[9]

Mikhail et al.[10] analyzed various hardened cement pastes using surface area and pore structure analysis techniques to achieve a consistent interpretation of results. Butt et al.[11] studied the influence of cement paste using mercury porosimetry. The pore structure of hydrated cement pastes was also studied by water sorption.[12]

EXPERIMENTAL

The chemical composition of blended cement pastes made of Portland cement and fine sand, known as El-Karnak cement, used in this study was found to be total SiO_2, 30.4%; Al_2O_3, 4.93%; Fe_2O_3, 2.00%; CaO, 54.08%; MgO, 2.47%; SO_3, 2.50%; ignition loss, 1.18%; free lime 0.4%, and Blaine surface area 2450, cm^2g^{-1}.

Three types of superplasticizers were prepared: Na-phenol sulfonate formaldehyde condensate, Na-polystyrene sulfonate condensate, and Na-β-naphthol sulfonate formaldehyde condensate. Na-phenol sulfonate formaldehyde condensate was prepared as follows: 40 g of phenol were mixed with an equal amount of concentrated H_2SO_4. The reactants were refluxed for 2 h; the temperature must not exceed 160°C; and 50 mL of formaline (37%) were added. The mixture was refluxed for an additional 2 h during which the condensation process takes place. The average molecular weight of the formed Na-phenol sulfonate formaldehyde condensate was found to be about 2500.

Na-polystyrene sulfonate was prepared as follows: 10 g of polystyrene pellets (average mol. wt. = 2.8×10^5), 0.2 g Ag_2SO_4 as a catalyst, and 200 mL of concentrated H_2SO_4 were refluxed in a water bath until the polystyrene was completely dissolved. The

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product is washed with water several times, then neutralized using a NaOH solution. The degree of sulfonation was found to be 89.88%.

Na-β-naphthol sulfonate formaldehyde condensate was prepared as follows: 46 g of β-naphthol was sulfonated using 0.3 mol concentrated H_2SO_4. Then NaOH was added to adjust pH at 3; 0.3 mol of formaline (37%) was added, and the mixture was refluxed for 2 h. The average molecular weight was about 2950.

The neat and superplasticized blended cement pastes were prepared by using an initial water–cement ratio of 0.25 by weight. The condensate content was 0.25% by weight of cement. Each paste was cured for various time intervals of 0.02, 0.08, 0.25, 1, 3, 7, 28, and 90 days.

The values of compressive strength of hardened specimens (one cubic inch each) were determined at various ages of hydration (1, 3, 7, 28, and 90 days). The compressive strength test machine used was APEX (Hydraulic press; model A 14; manufactured by APEX construction LTD); which gives a maximum load of 15 tons.

Chemically combined water of various hardened blended cement pastes were determined at different ages of hydration, namely at 0.02, 0.08, 0.25, 1, 3, 7, 28, and 90 days. An accurate dried sample was placed in a platinum crucible and introduced into a cold muffle furnace. The temperature was increased gradually from room temperature up to 1000°C with a heating rate of 10°C/min and then kept for 2 h soaking time. The chemically combined water, W_n, was determined as the percentage of the loss in respect to the ignited weight basis.

Both X-ray differaction and differential thermal analysis were used to investigate the phase composition of the formed hydration products. X-ray differaction analysis was carried out using a stabilized X-ray generator fitted with a copper target X-ray tube, Geiger Muller tube. The setting used were tube run at 30 kV, 15 μA; divergance, receiving, and scatter slites, 1, 1, and 1 cm, respectively; and chart speed 100 cps. Differential thermal analysis was carried out using Shimadzu DT-30 H apparatus by using α-Al_2O_3 as reference material and a Pt-Pt/Rh thermocouple. The heating rate was $10°C\ min^{-1}$ over the temperature range from ambient to 800°C.

Specific surface areas and total pore volumes of the selected pastes were measured volumetrically from the absorption of nitrogen gas at liquid nitrogen temperature (−195.8°C).

The neat cement pastes made without admixtures are designated B and the superplasticized cement pastes with Na-phenol sulfonate formaldehyde, Na-polystyrene sulfonate, and Na-β-naphthol sulfonate formaldehyde condensates are designated PhSF, PSS, and β-NSF, respectively.

RESULTS AND DISCUSSION

Compressive Strength

It is obvious from the results of Figure 1 that the compressive strength of the various hardened blended pastes increases with increasing age of hydration. As hydration proceeds, with increasing age of hydration, the amount of hydration products increases and therefore the total porosity of the hardened paste decreases. The increase in the amount of hydration products results in an increase in the total content of the binding centers between the remaining unhydrated parts of the cement grains. Similar results were also reported in earlier publications.[13–15]

The results of Figure 1 also indicate that the strength values of the hardened blended cement pastes containing superplasticizers are less than those of neat cement pastes during early stages of hydration (after one day of hydration). This is due to the fact that the superplasticizers improve the cement dispersability and accordingly, the consistency of the fresh cement paste leading to a reduction in the strength development during the initial stages of hydration. At the latter stages (3–90 days) of hydration, however, all superplasticizers improve the plastic and hardening characteristics of the blended cement pastes leading to higher compressive strength values.

From the results of Figure 1, it is obvious that the highest improvement of compressive strength was obtained with the pastes containing Na-β-naphthol sulfonate formaldehyde condensate; a result which is mainly associated with partial filling of the pore system leading to a more dense structure of the hardened cement pastes.

Hydration Kinetics

Hydration kinetics of hardened blended cement pastes were studied by determining the chemically combined (nonevaporable) water content at various ages of hydration.

The results of chemically combined water (W_n%) shown in Figure 2 indicate that a fast rate of hydration reaction takes place from the time of mixing up to 0.02 day of hydration, this is, the "predormant period." The initially formed hydration products shield the cement grains leading to a slower hydration stage up to 0.25 day of hydration. After 0.25

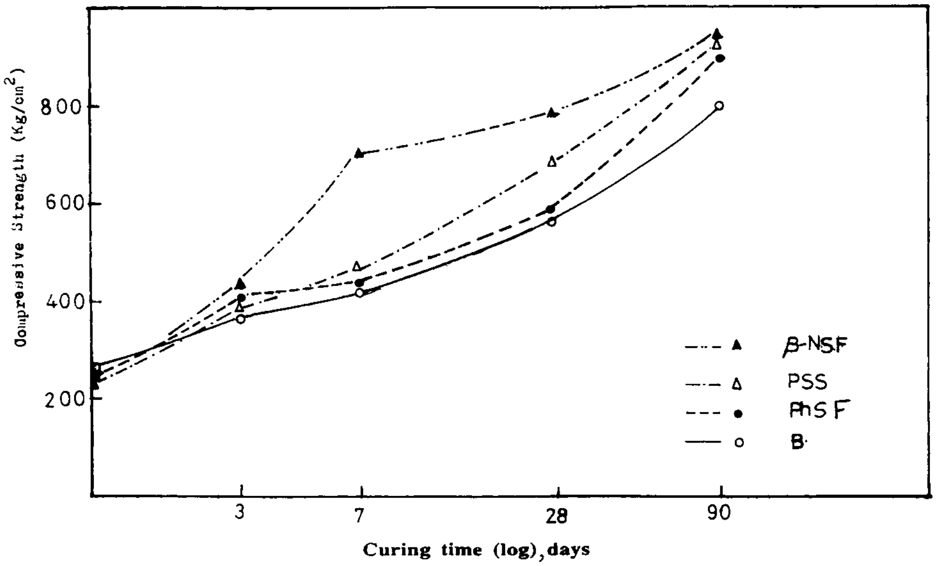

Figure 1 Variation of the compressive strength with curing time for the hardened blended cement pastes made with and without superplasticizers.

day of hydration, the degree of roughness of initial hydrates is increased which facilitates the penetration of water through the hydrated layers into the unhydrated cement grains; this is, the "first acceleration period," which begins at 0.25 day and ends at 3 days of hydration. After 3 days, a slight increase in W_n content is observed up to 7 days. Later, the hydration of hardened cement pastes is again accelerated after 7 days up to the final stage of hydration (90 days) indicating a "second acceleration period." During this period, other hydrated layers located deeper in the cement grains are formed. The results of the combined water contents of the blended cement pastes mixed with superplasticizers show the same trend of hydration as those of the neat blended cement pastes.

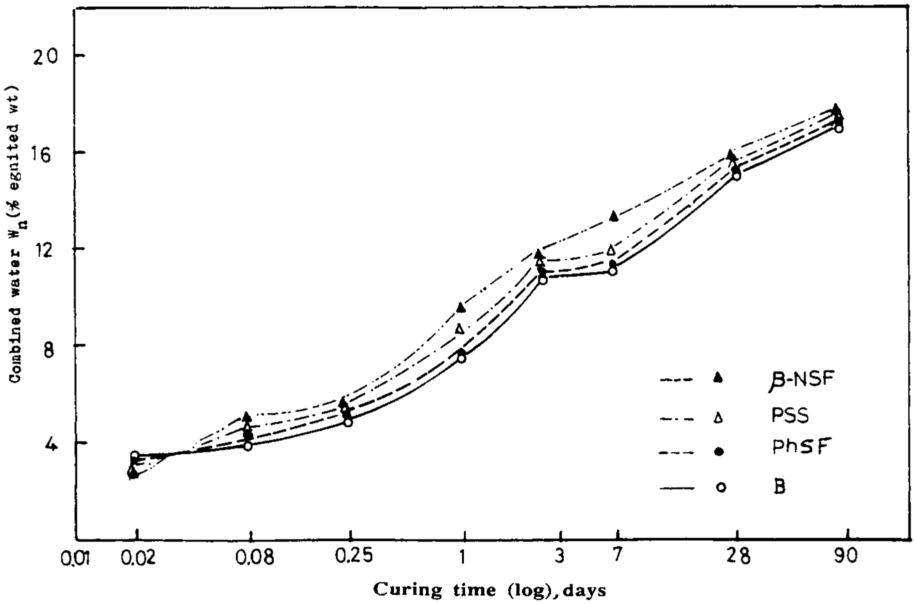

Figure 2 Variation of combined water (W_n%) with curing time for the hardened blended cement pastes made with and without superplasticizers.

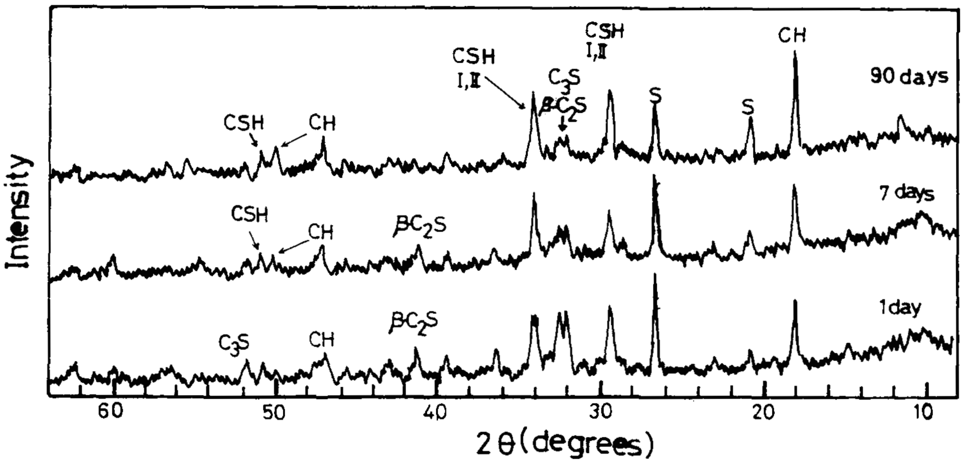

Figure 3 X-ray diffraction patterns for the hardened blended cement pastes without superplasticizers. CH, calcium hydroxide; S, silica; C_3S, tricalcium silicate; β-C_2S, β-dicalcium silicate; C_3A, tricalcium aluminate; CSH (I) and (II), calcium silicate hydrates (I) and (II).

Phase Composition of the Formed Hydrates

The phase composition of the formed hydration products could be distinguished by means of X-ray diffraction analysis (XRD) and differential thermal analysis (DTA).

The results of XRD analysis of hardened blended pastes at various ages of hydration shown in Figure 3 indicated the formation of different hydrates beside the unhydrous constituents (alite, belite, and aluminate phases) and silica additions. The main hydration products identified at various hydration ages are the tricalcium aluminate trisulfate hydrate, known as ettringite, calcium silicate hydrates (CSH I and II), and calcium hydroxide. With increasing age of hydration, the intensities of X-ray peaks characteristic for the unhydrate blended cement constituents are decreased while those of the hydration products are increased. Figure 4 shows the X-ray diffraction analysis of the neat and super-

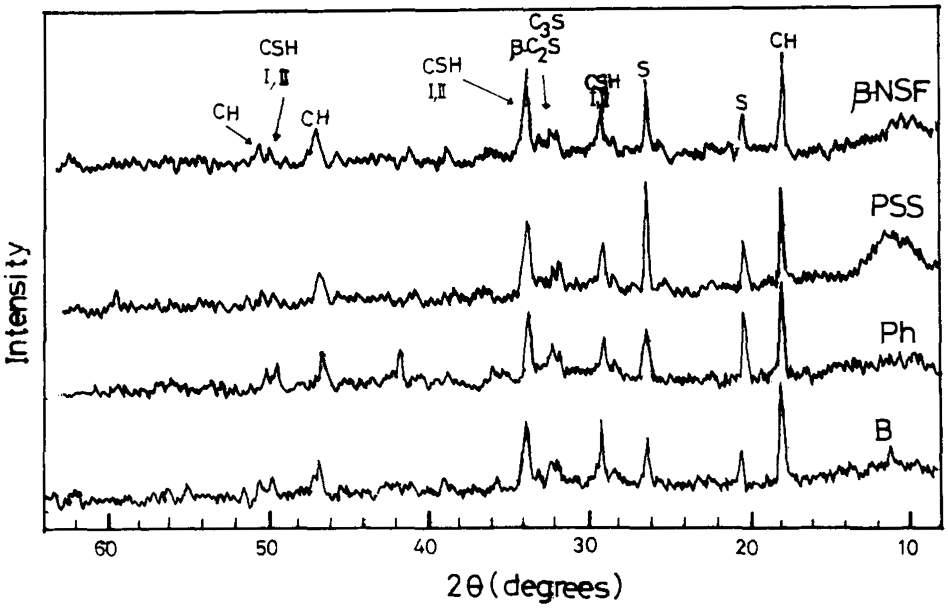

Figure 4 X-ray diffraction patterns for the hardened blended cement pastes made with and without superplasticiers at 90 days of hydration.

plasticized blended cement pastes cured for 90 days. It was found that the addition of superplasticizers does not alter the phase composition of the blended cement hydration products; those superplasticizers affect only the physical state and the degree of crystallinity of the formed hydrates.

The results of DTA are shown in Figure 5. The DTA thermograms obtained for the neat and superplasticized blended cement hydrated for 90 days show common characteristics with the appearance of three thermal dehydration stages at temperature ranges of 120–200°C, 465–520°C, and 720–790°C. The endotherms located at the temperature range 120–200°C represent the decomposition of ettringite and calcium silicate hydrates (CSH). The endothermic peak observed at the temperature range of 465–520°C is due to thermal decomposition of the free calcium hydroxide released as a result of cement hydration. The double endothermic peaks at 720–790°C are due to the decomposition of calcium carbonate, which is formed during preparation and curing of the samples as a result of the contamination with atmospheric carbon dioxide. Evidently the addition of superplasticizers does not affect the phase composition of the blended cement hydration products (Fig. 5).

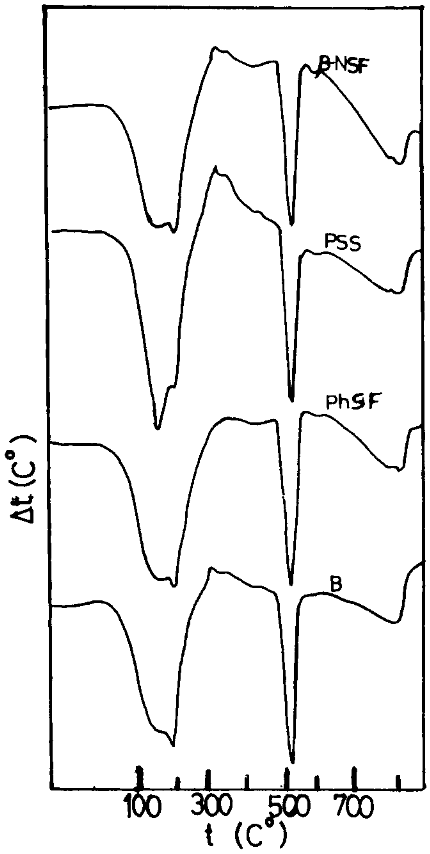

Figure 5 Differential thermal analysis curves for the hardened blended cement pastes made with and without superplasticizers at 90 days of hydration.

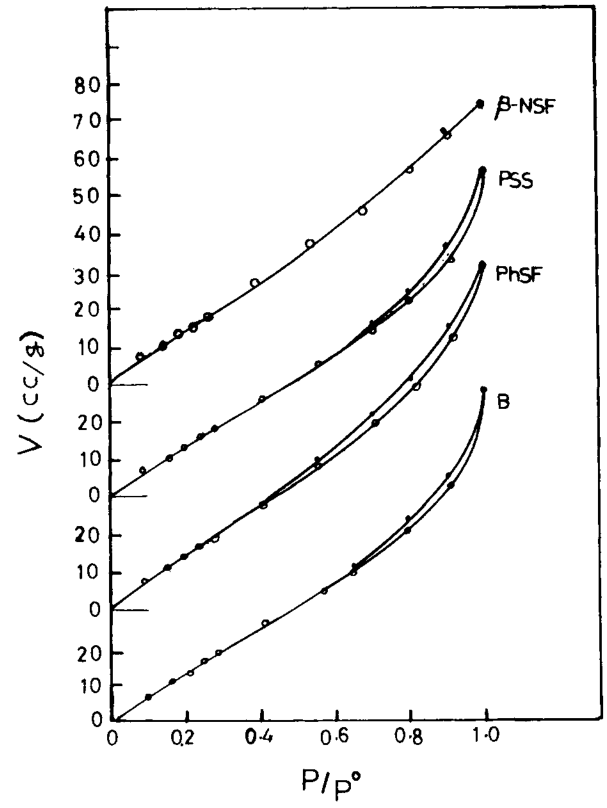

Figure 6 Adsorption–desorption isotherms of nitrogen gas on the hardened blended cement pastes made with and without superplasticizers at 90 days of hydration.

Surface Properties and Pore Structure

The adsorption isotherms of nitrogen on the various hardened blended cement pastes cured for 90 days are shown in Figure 6.

All isotherms show common characteristics and are similar in shape to type II of Brunauer's classification[16]: consisting of an initial sigmoid part representing the formation of the first adsorbed layer, an almost linear middle part representing multilayer formation, and finally an almost steep part representing capillary condensation. The adsorption-desorption isotherms indicate the existance of closed hysteresis loops in the high pressure end of the isotherms. The existance of such hysteresis loops is mainly explained in terms of capillary condensation in mesopores. The specific surface areas

(S_{BET}) could be evaluated by applying the BET equation.[17] The BET equation can be written in the linear form as follows:

$$\frac{P/P^0}{V(1-P/P^0)}=\frac{1}{V_mC}+\frac{C-1}{V_mC}P/P^0$$

where P is the measured equilibrium vapor pressure within the system, V is the total amount of gas adsorbed in cubic centimeters per gram of dried sample, V_m is the amount of gas forming a monomolecular adsorbed layer on the surface (monolayer capacity), P^0 is the saturated vapor pressure of the adsorbate at the temperature of the isotherm, and C is a constant related to the heat of adsorption in the first adsorbed layer. From the monolayer capacities, V_m, the specific surface areas S_{BET} (meters squared per gram) could be evaluated using the molecular area of nitrogen of 16.2 Å^2.[18]

The total pore volumes, V_p, were taken as the saturation values of the isotherms, and these are expressed in milliliters of liquid adsorbate (nitrogen) per one gram of the adsorbent (V_p, mL/g). The BET-C constants, the specific surface areas, S_{BET} (m^2/g), the total pore volumes, V_p (ml/g), as well as the mean hydraulic radii of the total pore systems, mean r_h (Å) are all given in Table I for the various hardened cement pastes cured for 90 days.

It is evident from the results of Table I that Na-β-naphthol sulfonate formaldehyde condensate (β-NSF) affects strongly the specific surface area as well as the total pore volumes of the hardened blended cement paste. This effect leads to a decrease in the total surface area and total pore volume of specimens containing β-NSF; a result which is mainly associated with partial filling and/or fractionation of the pore system leading to a more dense structure of hardened cement pastes. This effect results in a sort of pore narrowing by β-NSF with decreasing the accessibility of nitrogen toward the pore system.

The values of the mean hydraulic radii of the total pore system accessible to nitrogen molecules for various hardened blended cement pastes are found to be within the range of 13.64–13.88 Å. This indicates that nitrogen is only accessible to measure a certain fraction of mesopores having a definite size characteristic for the pastes.

The V_1-t plots were constructed on the basis of the adsorption branches of the nitrogen isotherms for each of the samples investigated at liquid nitrogen temperature. The t values used are those suggested by Mikhail et al.[19] depending on the values of the BET-C constant. The V_1-t plots are shown in Figure 7 for various hardened cement pastes cured for 90 days.

The initial straight line which passes through the origin in the V_1-t plots could be used as a measure of the total surface area, known as S_t (meters squared per gram); and these values are also summarized in Table I for the various hardened pastes cured for 90 days. The close agreement between the surface areas derived from V_1-t plots (S_t) and BET surface areas (S_{BET}) is good evidence for the correctness of the t values used in this investigation.

The V_1-t plots of the nitrogen adsorption on the various hardened cement pastes cured for 90 days indicate that the pore system consists mainly of mesopores with limited sizes. The indication is due to the linear V_1-t plots with slight upward deviations.

CONCLUSIONS

1. The addition of Na-β-naphthole sulfonate formaldehyde condensate (β-NSF) to the blended cement pastes causes a decrease in the specific surface area and total pore volume values, leading to a considerable improvement in compressive strength results.
2. The addition of superplasticizers in this study does not affect the phase composition of the blended cement hydration products.

Table I Surface Characteristics of Various Hardened Cement Pastes Cured for 90 Days

Admixture	BET C-Constant	S_{BET} (m^2/g)	S_t (m^2/g)	V_p (mL/g)	Mean r_h (Å)
B	4	100.48	91.12	0.1370	13.64
PhSF	4	98.66	90.57	0.1358	13.77
PSS	4	102.49	96.27	0.1424	13.88
B-NSF	5	83.13	85.72	0.1152	13.86

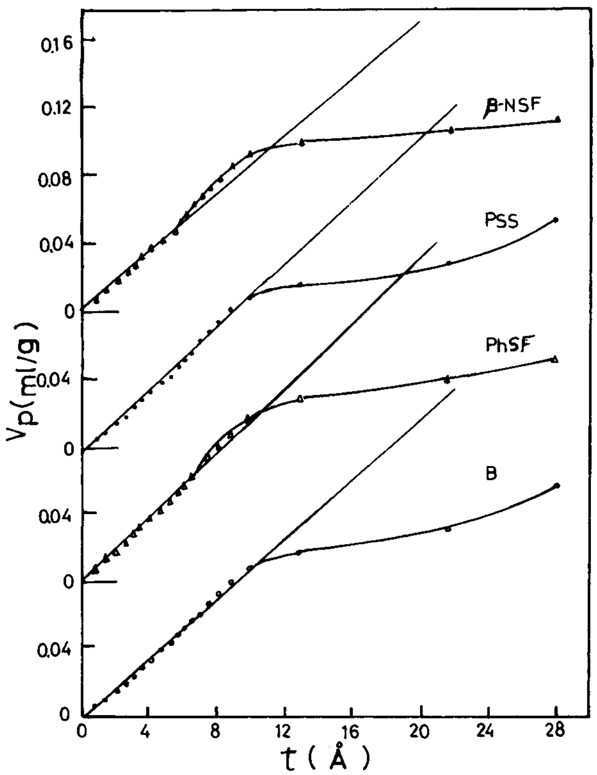

Figure 7 V_1-t plots for adsorption of nitrogen gas on the hardened blended cement pastes made with and without superplasticizers at 90 days of hydration.

3. The pore system of the various hardened cement pastes cured for 90 days consist mainly of mesopores with limited size and number.

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