HYDRATION AND PORE STRUCTURE CHARACTERISTICS OF SUPERPLASTICIZED HARDENED SLAG CEMENT PASTES

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The effect of addition of superplasticizers on the hydration and pore structure characteristics of the hardened slag cement pastes was studied. Superplasticizers include some water soluble poly-condensates; these are Na-styrene sulphonate, Na-β-naphthol sulphonate formaldehyde and Na-phenol sulphonate formaldehyde condensates. The pastes were prepared using an initial water/cement ratio of 0.25 with poly-condensate content of 0.25 % by weight of the slag cement. The improvement of the mechanical properties of the superplasticized hardened slag cement pastes were presented and related as much as possible to the pore structure of the hardened pastes.

INTRODUCTION

Earlier studies on superplasticized concrete that contained blast-furnace slag have been reported by several investigators [1-3]. Previous papers have been published that dealt with superplasticizers and their effect on the mechanical and physicochemical properties of cement paste, mortar and concrete [4-10]. Several papers were presented regarding cement hydration and mechanism of interaction with superplasticizers [11-15]. The role of steric handerance in the performance of superplasticizers in concrete was discussed in the work of Yoshioka et al., [16]. Hanafi et al. [17] studied methanol adsorption to evaluate the effect of superplasticizers on the surface texture of various blended cement pastes. Three review articles were also reported in Japan on various formulation and usage of superplasticizers [18-20].

The present study deals with the effect of some superplasticizers on the hydration and pore structural characteristics of hardened neat and superplasticized slag cement pastes.

EXPERIMENTAL

The chemical oxide composition of slag cement used in this study was found to be (wt.%): 35.94 SiO_2, 13.56 Al_2O_3, 0.72 Fe_2O_3, 46.02 CaO, 3.48 MgO and 0.3 insoluble residue. The Blaine surface area was 3100 cm^2/g.

The various superplasticizers, namely, Na-styrene sulphonate, Na-β-naphthol sulphonate formaldehyde and Na-phenol sulphonate formaldehyde poly condensates, were prepared according to the methods reported in an earlier publication [10], and these are designated as Na-SS, Na-β-NSF and Na-Ph SF, respectively.

The neat and superplasticized slag cement pastes were prepared by using an initial water/slag cement ratio of 0.25 by weight. The dose of admixture was 0.25 % by the weight of cement. The cement pastes were moulded into cubes of one inch dimensions, demoulded after curing at 100 % relative humidity for one day and then cured under water for different time intervals of 3, 7, 28 and 90 days. After each time interval, a fraction of hardened specimen was first ground and the hydration reaction of the hardened cement pastes was stopped using methanol-acetone mixture (1:1 by volume) according to the method reported in earlier studies [21], then the samples were dried and kept in a dessicator until the desired times of testing were reached.

Chemically combined water content W_n (%) of hardened pastes were determined on an ignited weight basis at different times of hydration, namely, 0.02, 0.08, 0.25, 1, 3, 7, 28 and 90 days by using the following equation:

$$W_n\,(\%) = \frac{W_d - W}{W} \cdot 100$$

Where W_d is the weight of the dried sample before ignition and W is the weight of the sample after ignition at 1000°C for one hour.

The results of the combined water content were used to calculate the gel/space ratio of the hardened pastes according to the following equation [22]:

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

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

$$\alpha = \frac{W_n}{W_n^{\infty}}$$

where: W_n^{∞} 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).

The values of compressive strength of hardened specimens (on three cubic samples) were measured at various ages of hydration of 1, 3, 7, 28 and 90 days.

Surface and pore structure characteristics of the selected hardened pastes, after being dried, were measured volumetrically from the adsorption of the nitrogen gas at the liquid nitrogen temperature (- 195.8°C) using a volumetric apparatus of the conventional type.

RESULTS AND DISCUSSION

Hydration characteristics

Hydration kinetics of the neat and superplasticized slag cement pastes were studied by determining the values of chemically combined water content W_n at various ages of hydration; the results are shown in figure 1. Obviously a fast rate of hydration reaction takes place from the time of mixing up to 0.02 day of hydration, as the result of the initial contact of water with slag cement grains; this represents the "pre-dormant period". The initially formed hydration products, due to their highly amorphous character, warp the slag cement grains with the formation of an almost impervious coating leading to a slower stage in the hydration process up to 0.25 day; this stage represents the "dormant period". This stag is followed by a relatively fast step with a marked increase in the chemically combined water content W_n is observed during the hydration period 0.25-7 days as representing the acceleration period. After 7 days of hydration, a gradual increase in the W_n - content is observed up to the longest duration of hydration studied (90 days). The results of W_n - contents of superplasticized slag cement pastes show almost the same general trend of hydration as those of the neat slag cement pastes with a slight increase in the W_n - values at all ages of hydration.

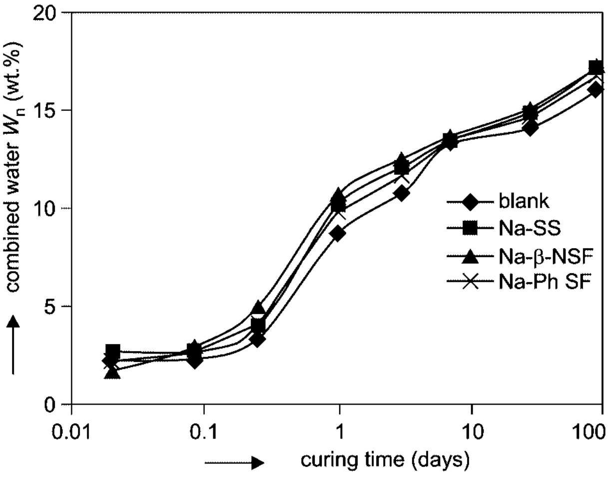

Figure 1. Combined water results of the hardened neat and superplasticized slag cement pastes versus curing time.

The results of figure 2 indicated that the compressive strength values of the neat and superplasticized slag cement pastes increased markedly up to 7 days of the hydration. This is followed by gradual increase in the compressive strength values up to 28 days of hydration. Evidently, after 28 days, the compressive strength increases slightly up to the longest duration studied for the hydration process. The addition of superplasticizers results in an improvement of the plastic and hardening properties of the slag cement pastes leading to higher compressive strength values. From the results in figure 2 it is obvious that the addition of Na-β-NSF poly-condensate causes the highest improvement in compressive strength. It is evident form the results of this investigation that the degree of improvement in compressive strength values of the superplasticized slag cement pastes is mainly dependent on the pore structure of the hardened pastes which consists mainly of micropores leading to a more denser structure as indicated from the results of surface area and pore structure of the hardened pastes presented later in this paper.

It is more convenient to relate the results of compressive strength to the gel/space ratio (the ratio of the volume of cement hydrates to the sum of the volumes of cement hydrates and capillary pores). The use of gel space ratio reduces the number of variables in comparing the compressive strength values. The compressive strength results versus the gel/space ratios of the hardened pastes are presented in figure 3 at different curing ages. The results of figure 3 indicate that the higher values of the compressive strength of the superplasticized slag cement pastes are mainly due to the relatively higher values of gel/space ratio than those of the neat slag cement pastes.

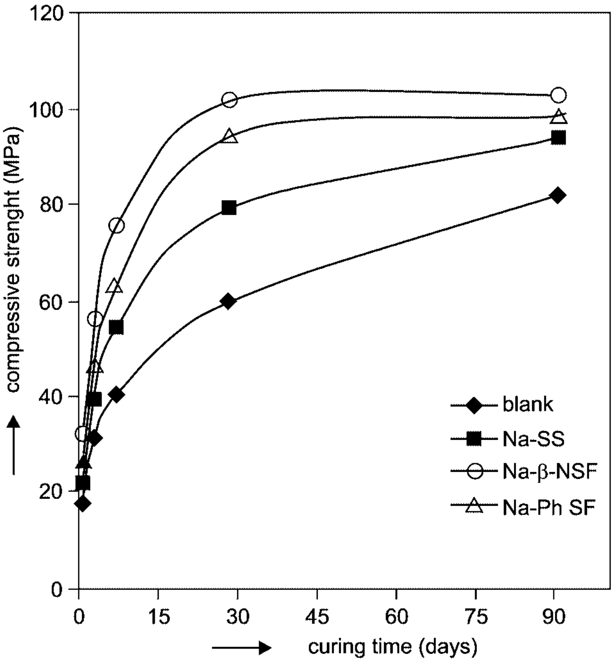

Figure 2. Compressive strength results of the hardened neat and superplasticized slag cement pastes versus curing time.

Surface and pore structure characteristics

Adsorption-desorption isotherms of nitrogen gas at liquid nitrogen temperature were measured volumetrically on the hardened pastes after hydration for 90 days figure 4. All the isotherms obtained were of type II of Brunauer's classification [23] and exhibited narrow hysteresis loops; these loops are closed at some intermediate pressures characteristic for capillary condensation. The neat slag cement specimen exhibited a wider hysteresis loop relative to those of superplasticized cement specimens, thereby emphasizing the presence of a relatively wider pore system in the neat cement paste.

The specific surface areas of the samples A_{BET} (m^2/g) were estimated through the application of the BET - equation [24] over its normal range of applicability and adopting a value of 16.2 Ĺ for the molecular cross-sectional area of nitrogen molecule. The BET surface areas A_{BET} as well as the total pore volume V_p (ml/g) are summarized in table 1. Obviously, the surface areas measured by nitrogen adsorption for all of the hardened specimens increase when these specimens were admixed by various superplasticizers especially with Na-PhSF. Apparently, addition of superplasticizers to slag cement pastes is, therefore, associated with a definite change in the pore system of the specimens; the total pore volumes for all superplasticized specimens decreased. The main observation derived from the results of surface areas and pore volumes is that, the addition of superplasticizers is mainly associated with a partial fractionation of the pore system of the hardened

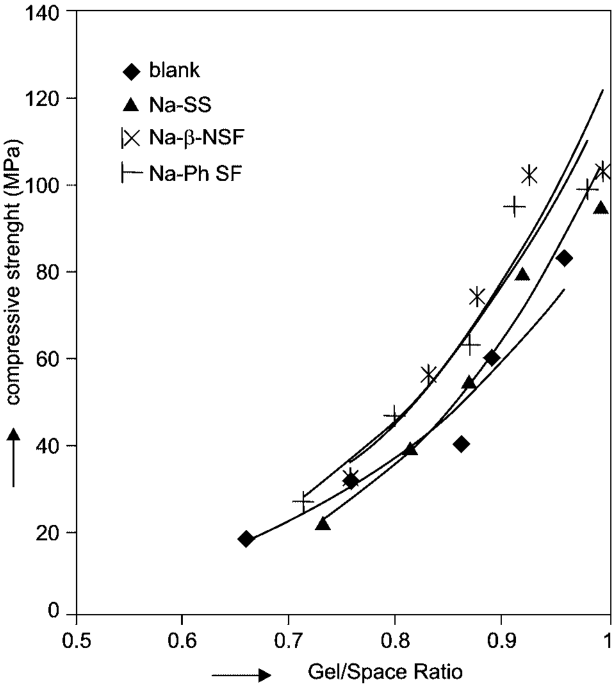

Figure 3. Variation of compressive strength of the hardened superplasticized slag cement pastes versus gel/space ratio.

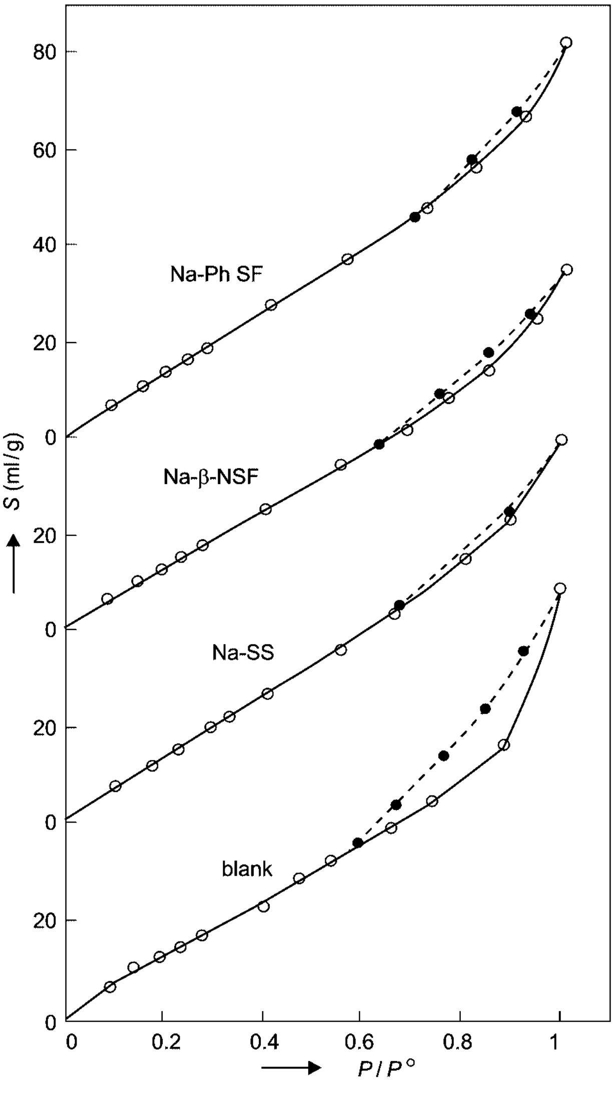

Figure 4. Adsorption-desorption isotherms of nitrogen gas on the hardened superplasticized slag cement pastes at 90 days of hydration.

Table 1. Some pore surface characteristics of neat and superplasticized slag cement pastes from nitrogen gas adsorption.

admixture	BET C-constant	A_{BET} (m^2/g)	A_t (m^2/g)	V_p (ml/g)	average r (Ĺ)	A_w (m^2/g)	A_n (m^2/g)	V_n (ml/g)	V_w (ml/g)	V_n/V_p	A_n/A_{BET}
blank	4	87.37	86.11	0.1404	16.30	30.95	56.42	0.0440	0.0960	0.3133	0.6458
Na-SS	4	101.30	100.23	0.1263	12.47	18.04	82.19	0.0800	0.0463	0.6334	0.8114
Na-β-NSF	4	97.08	96.27	0.1186	12.21	15.33	80.94	0.0760	0.0426	0.6408	0.8337
Na-Ph SF	4	105.05	102.91	0.1279	12.17	18.89	84.04	0.0780	0.0499	0.6098	0.7998

cement pastes. This effect result in a sort of pore narrowing (average hydraulic radius of 12 Ĺ) due to the fractionation of mesopores by addition the superplasticizer. The accessibility of nitrogen molecules towards the pore system decreases leading to a decrease in the total pore volumes of superplasticized specimens; in addition, micropores posses a lower volume/surface ratio than mesopores.

The average pore radius r (Ĺ) of the total pore system accessible to nitrogen molecules was calculated as $r = V_p/A_{BET}$.

The results indicated that the addition of various superplasticizers leads to a decrease in the r - values; this is mainly attributed to the fractionation of some mesopores into micropores. The V_l - 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. [25] depending on the values of the BET - C constant. The V_l - t plots are shown in figure 5 for the various hardened pastes cured for 90 days. The initial straight line which passes through the origin in the V_l - t plots could be used as a measure of the total surface area, known as A_t (m^2/g); and these values are also summarized in table 1. The close agreement between the surface areas derived from the V_l - t plots A_t and the BET - surface areas A_{BET} is a good evidence for the correctness of the t - values used in this investigation.

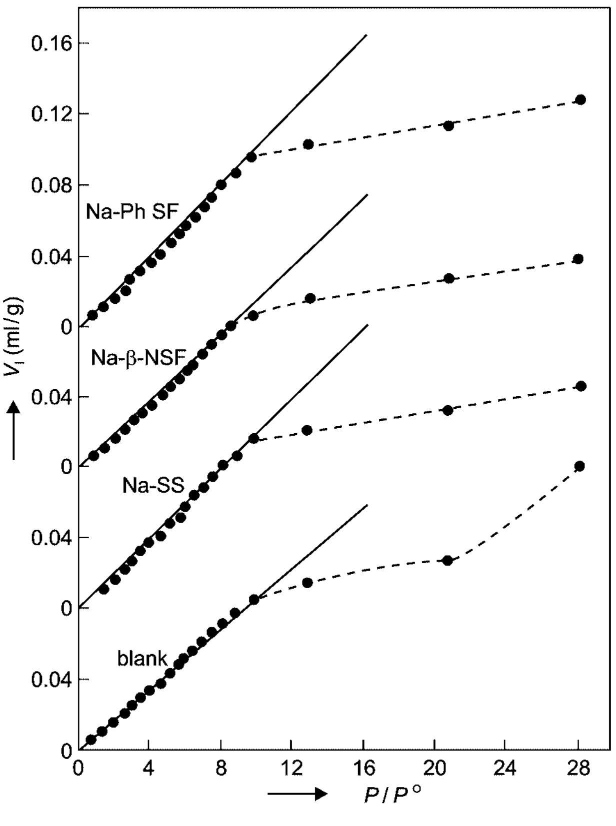

Figure 5. V_l - t plots for adsorption of nitrogen gas on the hardened superplasticized slag cement pastes at 90 days of hydration.

From the V_l - t plots, the area of the wider pores (mesopores) A_w (m^2/g), can be determined from the slope of the straight line at the higher region of relative pressures where the points of the V_l - t plot begin to deviate upwards above this straight line; at this particular relative vapour pressure the micropores are all filled and the difference between the total specific area A_t and the area of mesopores A_w represents the area of micropores, known as A_n (m^2/g). In addition, the volume of micropores, V_n (ml/g), can be evaluated by extrapolation of the last straight line according extrapolation method suggested by Sing et al., [26].

The volume of mesopores V_w (ml/g), can be evaluated from the difference between the total pore volume V_p and the volume of micropores. All these pore structure characteristics are given in table 1 for the adsorption of nitrogen gas on the neat and superplasticized slag cement pastes. Obviously, the results given in table 1 indicate that the addition of various superplasticizers (Na-SS, Na-β-NSF & Na-Ph SF) affects strongly the area and volume of micropores.

In conclusion, addition of superplasticizers leads to a more dense structure of the hardened slag cement pastes; this reflects the predominance of micropores. Therefore, the total pore system consists mainly of micropores leading to relatively higher strength values of the hardened slag cement pastes made with superplasticizers.

CONCLUSIONS

The neat and superplasticized slag cement pastes were prepared using an initial water/cement ratio of 0.25 with a poly condensate content of 0.25% by weight of the slag cement. The various superplasticizers used were Na-styrene sulphonate, Na-β-naphathol sulphonate formaldehyde and Na-phenol sulphonate formaldehyde poly condensates. The cement pastes were cured under water for different time intervals of 1, 3, 7, 28 and 90 days. The hydration and pore structure characteristics of hardened slag cement pastes were studied. The specific surface area of hardened slag cement increases by addition of superplasticizers while the total pore volume decreases; this effect is mainly attributed to a sort of pore narrowing through the fractionation of some mesopores into narrower pores within the hardened pastes. This effect leads to a more dense structure of the superplasticized slag cement pastes; such a structure gives a paste with relatively high hydraulic properties.

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HYDRATACE A STRUKTURA PÓRŮ PLASTIFIKOVANÝCH ZTUHLÝCH STRUSKO-CEMENTOVÝCH KAŠÍ

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Byl studován účinek přídavku plastifikátorů na hydrataci a strukturu pórů ztuhlých strusko-cementových kaší. Plastifikátory obsahují některé ve vodě rozpustné polykondenzáty, např. styrensulfonát sodný případně polykondenzát formaldehydu a fenolsulfonátu nebo b-naftolsulfonátu sodného. Cementové kaše byly připraveny při poměru voda/cement 0,25 a obsahovaly 0,25 hmotn.% polykondenzátu. Zjištěné zlepšení mechanických vlastností je diskutováno s ohledem na strukturu pórů ztuhlých cementových kaší.