

THERMAL AND PORE STRUCTURAL CHARACTERISTICS OF POLYMER-IMPREGNATED AND SUPERPLASTICIZED CEMENT PASTES

*K. Kh. Al-Noaimi*¹, *F. I. El-Hosiny*² and *S. A. Abo-El-Enein*^{2*}

¹Faculty of Science, Qatar University, Doha, Qatar

²Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

(Received August 24, 1999; in revised form December 23, 1999)

Abstract

Two sets of hardened cement pastes were prepared by (a) impregnation with polymethyl methacrylate and polystyrene or (b) admixing with water-soluble condensates (superplasticizers) such as Na-phenol sulphonate formaldehyde, Na-polystyrene sulphonate and Na- β -naphthol sulphonate formaldehyde. The pastes were hydrated for 180 days. The results of nitrogen adsorption indicated that polymer impregnation strongly affected the specific surface areas and the total pore volumes of the hardened cement pastes. XRD analysis, DTA and TG demonstrated (a) the formation of new phases as a result of the interactions involving the polymer within the pore system of the hydrated products of the impregnated cement pastes, and (b) no change in the phase composition of the hydrated products of the cement pastes admixed with superplasticizers.

Keywords: cement pastes, polymer-impregnated and superplasticized pastes, thermal properties and pore structure

Introduction

Previous studies on polymer-impregnated concrete have been reported by several investigators [1–5]. Various reviews have also been published regarding the utilization of superplasticizers and their effects on concrete [6–9]. The most comprehensive studies that dealt with superplasticizers were those of Malhotra [10], Singh [11], Bramkam [12], Idemistu *et al.* [13], Mather [14] and Tagnit *et al.* [15]. The addition of superplasticizers was found to affect the surface texture of the hardened cement pastes [16] and to improve the fire-resistance of concrete [17].

El-Hosiny *et al.* [18] recently studied the effects of certain superplasticizers on the mechanical and physicochemical properties of blended cement pastes. The present study deals with the effects of polymer impregnation and superplasticizers on the phases formed from the hydration of cement pastes.

* Author to whom all correspondence should be addressed.

Experimental

The chemical composition of the ordinary portland cement used in this study was found to be SiO₂ 20.40%, Al₂O₃ 6.12%, Fe₂O₃ 3.051%, CaO 63.16%, MgO 2.32%, SO₃ 2.40%, free CaO 1.41%, insoluble residue 0.62% and ignition loss 2.00%.

The cement was ground to a Blaine surface area of 3000 cm² g⁻¹. The water/cement ratio used was 0.25 by mass for all pastes investigated. The pastes were moulded in cylindrical moulds 2 cm in diameter and 2 cm in height. For polymer impregnation, the neat cement pastes were first cured under water for 180 days, and the hardened pastes were then impregnated with the monomer, using either methyl methacrylate (MMA) or styrene (S), followed by polymerization at 60°C for 3 h using benzoyl peroxide as initiator. The polymer-impregnated samples are designated MMA and S for the pastes impregnated with MMA and S, respectively.

Superplasticized cement pastes were prepared by using three types of superplasticizers: Na-phenol sulphonate formaldehyde (PhSF), Na-polystyrene sulphonate (PSS) and Na-β-naphthol sulphonate formaldehyde (β-NSF) condensates. The condensate content of the cement was 0.25% by mass. The prepared pastes were cured under water for 180 days.

The specific surface areas and total pore volumes of the hardened pastes were measured volumetrically via the adsorption of nitrogen gas at liquid nitrogen temperature (-195.8°C). The phase compositions of the hydration products formed were identified by using X-ray diffraction analysis (XRD), differential thermal analysis (DTA) and thermogravimetric analysis (TG).

Results and discussion

Surface properties and pore structure

A typical adsorption-desorption isotherm is shown in Fig. 1; this can be regarded as representative of all of the hardened cement pastes investigated. All the isotherms obtained are similar in shape to type II of Brunauer's classification [19], with an ill-defined knee. The samples display hysteresis with loops closing at some intermediate pressures, a phenomenon characteristic of capillary condensation.

The specific surface areas, S_{BET} (m² g⁻¹), were evaluated by applying the BET-equation [20] and using the molecular area of nitrogen of 16.2 Å² [21]. The total pore volumes, V_p (ml g⁻¹), were taken as the saturation values of the isotherms.

The main surface characteristics are given in Table 1 for all of the hardened neat, impregnated and superplasticized cement pastes.

Table 1 reveals that the polymer impregnation technique strongly affects the specific surface areas and the total pore volumes of the hardened cement pastes, to different extents. These effects are more obvious for the pastes impregnated with styrene, leading to decrease in the total surface areas and total volumes of the impregnated samples.

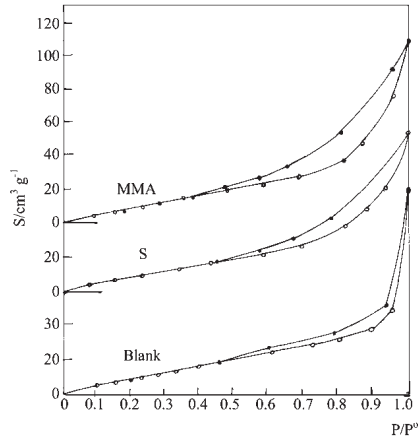


Fig. 1 Adsorption-desorption isotherms of nitrogen gas on neat and polymer-impregnated cement pastes

Polymer impregnation is mainly associated with the partial filling and/or fractionation of the pore system of the hardened cement pastes. This effect results in pore narrowing due to the fractionation of the mesopores by the polymers, and the adsorption of nitrogen molecules becomes more hindered, leading to decrease in the total surface areas and the pore volumes of the impregnated specimens.

Table 1 Surface characteristics of the neat, impregnated and superplasticized cement pastes, from nitrogen gas adsorption

Sample	BET constant C	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$S/\text{m}^2 \text{g}^{-1}$	$V_p/\text{ml g}^{-1}$
Blank (neat)	4	51.3	52.4	0.1841
S	4	44.0	47.8	0.1439
MMA	4	49.7	55.9	0.1625
PhSF	4	50.3	46.2	0.1825
PSS	4	52.3	49.2	0.1913
β -NSF	5	42.4	43.8	0.1548

The results in Table 1 also indicate that β -NSF strongly affects the specific surface areas and the total pore volumes of the hardened cement pastes. This leads to decrease in the total surface areas and total pore volumes of the specimens containing β -NSF, a result which is mainly associated with partial filling of the pore system (pore narrowing), leading to a denser structure of the hardened cement pastes, with a decreased accessibility of nitrogen towards the pore system.

The V_1 vs. t plots were constructed by using the t values suggested by Mikhail *et al.* [22]; Fig. 2 is representative of all the pastes investigated.

The initial straight line which passes through the origin in the V_1 vs. t plots could be used as a measure of the total surface area reported as S_t ($\text{m}^2 \text{g}^{-1}$) (Table 1).

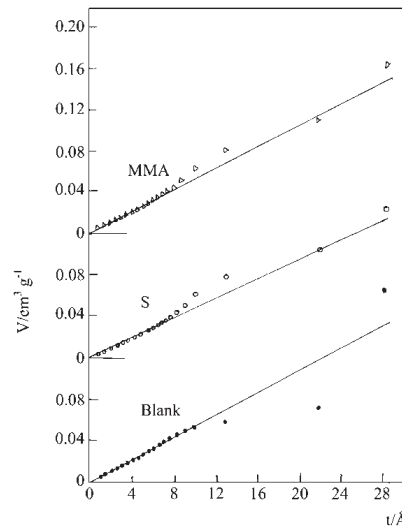


Fig. 2 V_1 vs. t plots of nitrogen gas adsorption on neat and polymer-impregnated cement pastes

The upward deviations in the V_1 vs. t plots (Fig. 2) for the various hardened cement pastes indicate that the pore system consists mainly of mesopores of limited size and number.

Phase compositions of the formed hydrates

DTA curves of the neat cement paste (Blank) and the polymer-impregnated pastes (S and MMA) are shown in Fig. 3. The curves reveal the characteristic endothermic peaks of calcium silicate hydrates and calcium hydroxide as the dominant hydration phases; small amounts of calcium carbonate are also detected. The characteristic endothermic peaks of hydrated calcium silicates lie in the temperature range 130–170°C. The curves also indicate the endothermic peak characteristic of calcium hydroxide, at 500–520°C; a relatively small peak is also observed at 740–780°C, reflecting the decomposition of calcium carbonates. In addition, an exothermic peak at 340–350°C is observed in the DTA curves of the polymer-impregnated pastes (S and MMA), which characterizes the combustion of the polymer formed within the pore system of the hardened paste.

The DTA results for the neat (Blank) and superplasticized (PhSF PSS and β -NSF) cement pastes (Fig. 4) display the common characteristics, with the appearance of three thermal dehydration stages in the temperature ranges 120–200, 465–520 and 720–790°C. Figure 5 also shows that the effect of addition of the superplasticizers is restricted only to the production of a more packed and denser structure of the cement paste.

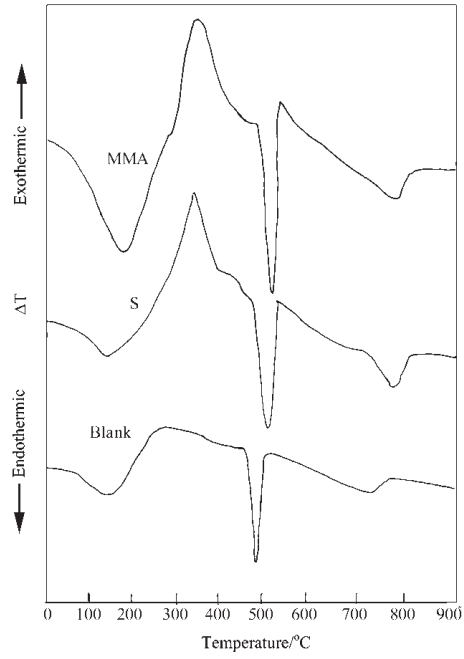


Fig. 3 DTA curves for neat and polymer-impregnated cement pastes

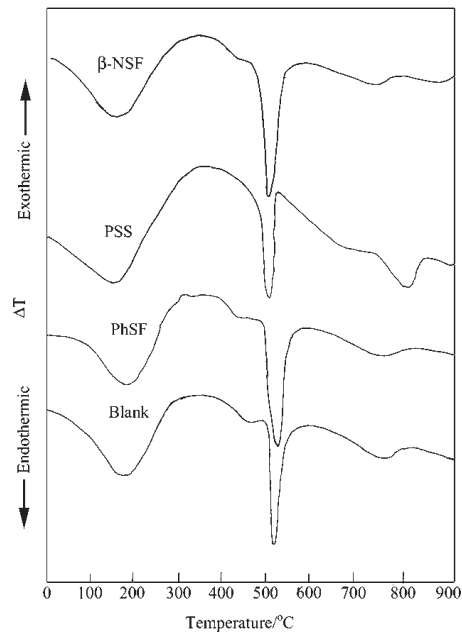


Fig. 4 DTA curves for neat and superplasticized cement pastes

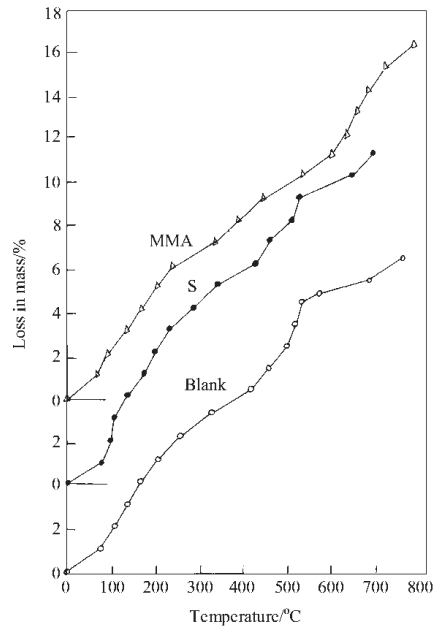


Fig. 5 TG curves for neat and polymer-impregnated cement pastes

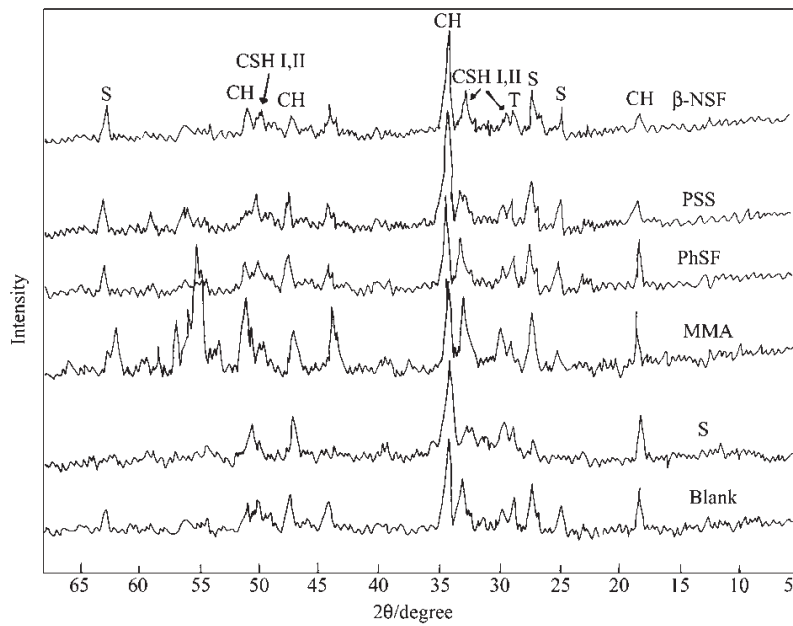


Fig. 6 XRD patterns for neat, impregnated and superplasticized cement pastes. CH, calcium hydroxide; S, silica; CSH(I) and (II), calcium silicate hydrates(I) and (II); T, tobermorite

The TG results of (Fig. 5) on the neat (Blank) and polymer-impregnated (S and MMA) cement pastes indicate two stages of water loss for the neat cement paste, at 100–200 and 450–520°C, corresponding to the decomposition of calcium silicate hydrates and calcium hydroxides, respectively. For the polymer-impregnated specimens, the TG curves demonstrate exactly the low-temperature decomposition range (100–200°C) characterizing the dehydration of calcium silicate hydrates, while the high-temperature decomposition range is not clearly distinct, extending gradually to cover a wider temperature range. This result confirms the fact that calcium hydroxide interacts with the polymer in the impregnated specimens and results in the difficulty of dehydration of the new phases formed and the remaining free calcium hydroxide.

The XRD results are shown in Fig. 6 for neat (Blank), impregnated (S and MMA) and superplasticized (PhSF, PSS and β -NSF) cement pastes. The XRD patterns obtained for the neat cement paste indicate the formation of calcium hydroxide and calcium silicate hydrates with varying degrees of crystallinity, mainly as C–S–H(I), C–S–H(II) and tobermorite gel (nearly amorphous calcium silicate hydrates). In the impregnated pastes, however, the results of X-ray diffraction studies indicate the formation of other new phases as a result of the interactions between the polymer (especially with MMA), during its formation within the pore system, and the hydration products of the cement components; these phases are detected in addition to the hydration products described above. The most active phase of the hydrated cement pastes which reacts with the polymer is the free calcium hydroxide.

It was found that the addition of superplasticizers does not affect the phase composition of the cement hydration products to a noticeable extent, but only the physical state and the decreased degree of crystallinity of the hydrates formed.

References

- 1 A. Auskern and W. Horn, BNL-17572, Jan., 1973.
- 2 J. Gebaur and R. W. Coughlin, *Cement and Concrete Research*, 1 (1971) 387.
- 3 V. S. Ramachandran and P. J. Sereda, *Thermochim. Acta*, 5 (1973) 443.
- 4 D. J. Cook, D. R. Morgan, V. Siriviatnanon and R. P. Chaplin, *Cement and Concrete Research*, 6 (1976) 757.
- 5 J. W. Vanderhoff, J. D. Hofman and J. A. Manson, *J. Am. Germ. Soc.*, 56 (1973) 206.
- 6 H. H. Chen and T'u Mu Shui Li, 4 (1978) 731.
- 7 R. L. Munn, Proc. 8th Bienn. Conf. Concr. Inst. Australia, Brisbane 1977.
- 8 M. R. Rixon, Proc. Workshop on Use of Chemical Admixture for Concrete Unisearch Ltd. Kensington, N.S.W., Austria, 1975, p. 149–175.
- 9 V. M. Malhotra, E. E. Berry and T. A. Wheat, Eds., *Superplasticizers in Concrete*, Proc. Int. Sym., Ottawa, May, Vol. I (1978), Vol. II (1987), (CANMET, Ottawa 1978) 38.
- 10 V. M. Malhotra, *Modern Concr.*, 42 (1978) 38.
- 11 N. B. Singh and S. P. Singh, *J. Sci., Ind. Res.*, 52 (1993) 661.
- 12 S. B. Bramkam, *Natl. Conf. Publ. Inst. Eng. Abstr.*, 77–78 (1977) 77.
- 13 T. Idemistu, S. Takayama and Y. Emoto, *Cem. Assoc., Jpn. (Eng. Abstr.)* 31 (1977) 108.
- 14 B. Mather, Army Engr. Waterways Expt. Sth., Vicks-burg Miss., Final Report, (1978) 28.

- 15 A. Tagnit-Hamouard and P. C. Aitcin, *World Cement*, 24 (1993) 42.
- 16 S. Hanafi, E. E. Hekal, T. M. Salem and S. A. Abo-El-Enein, *TIZ (Tonindustrie-zeitung)* 133 (1989) 822.
- 17 V. Kumar, B. N. Roy and A. S. R. Sai, *Indian Conc. J.*, 63 (1989) 350.
- 18 F. I. El-Hosiny and E. A. Gad, *J. Applied Polymer Science*, 56 (1995) 153.
- 19 S. Brunauer, *The Adsorption of gases and vapours*, Oxford University Press, Princeton 1945, p. 150.
- 20 S. Brunauer, P. H. Emmett and T. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
- 21 B. C. Lippens and G. H. De-Boer, *J. Catalysis*, 3 (1964) 32.
- 22 R. Sh. Mikhail, N. M. Guindy and S. Hanafi, *J. Chem. Egypt*, 16 (1973) 53.