

A STUDY ON THE SODIUM AND IODINE DIFFUSIVITY OF HARDENED HIGH VOLUME POZZOLANIC CEMENT PASTES

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1. Introduction

As part of an ongoing study on the mass transport behavior in hardened cement pastes with higher rate of pozzolans and low-alkaline content, sodium iodine solution has been considered for ion diffusion cell test.

The decision to research the diffusivity of this electrolyte was motivated primarily by the fact that iodine ion is known to be only weakly bind to cementitious hydration products. Therefore, the diffusion would not, itself, be affected by other ongoing processes then, allowing for a better understanding of each cement pastes' behavior.

To accomplish the research's objectives, the following tasks have been determined:

- Investigate the iodine and sodium ion diffusivity of hardened cement pastes according to cement mix, water cement ratio (30% and 55%), curing time (7, 28 and 91 days) and electrolyte source (NaI), using "Through Diffusion Technique".
- Characterize the pore structure through Mercury Intrusion Porosimetry (MIP) measurements.

The present extended study aimed to contribute to a better understanding of microstructures, while finding their relationship to diffusivity of iodine and sodium ions through these new type cement pastes.

2. Experiments

2.1. Materials

Six cement pastes were prepared according to the mixing proportions presented in Table 1. Ordinary Portland cement Type I, Fly ash in accordance with JIS A6201 Class II (from Hekinan Electric Power Station) and commercial Silica fume from Elkem Materials, Norway (Microsilica 940U) were used.

Table I: Mix proportions of cement pastes

Cement Type	W/C Ratio	OPC (%)	S.F (%)	F.A (%)	Sup.Plant *
OPC	0.30	100	0	0	0.30%
	0.55				0
HFSC424	0.30	40	20	40	1.50%
	0.55				0.70%
HFSC325	0.30	30	20	50	1.60%
HFSC226	0.30	20	20	60	1.60%

*Cement weight (%)

2.2. Methods

Before the paste's preparation, the cement and pozzolanic materials were thoroughly mixed in plastic bags. Then pastes were prepared by mixing batches of 200g of corresponding composition and the required quantity of water and super-plasticizer in a mechanical mixer, for approximately 5 minutes. The slurry was cast into PVC acrylic rings 5mm thick and 30mm internal diameter placed on glass plates, manually compacted and covered for one day to prevent dryness and evaporation. The cement pastes were then allowed to cure in Ca(OH)_2 saturated water solution for 7 days, 28 days and 91 days, under room temperature of 20 °C and 50% R.H.

Diffusion cells were prepared, containing 100ml solutions of NaI with concentration of 0.50mol/l in the tracer cell and 100ml of de-ionized water in the measurement cell.

After the first 24 hours and every following 2 days interval, samples of 2ml were taken from the measurement cell after stirring well and replaced with the same volume amount of de-ionized water to keep the solution volume constant. Before the concentration measurements, the extracted solution was first diluted and thoroughly mixed in a glass volumetric flask. The ion concentrations were measured with a personal ion analyzer (Shimadzu, PIA-1000).

3. Results, Discussion and Conclusions

3.1. Diffusion Starting Time (DST)

In this study, DST refers to the first day the anion (I^-) was detected in the measurement cell. The ion analyzer used during the research has a precision of 0.01 ppm.

Fig. 1 shows the DST of iodine ion, which increased with time for all types of cement. However, it's worth note that, once started, the diffusion of I^- was faster than that of Cl^- . As we will see later, binding of I^- is almost negligible and then, once started, diffusion tends to occur "freely". This assertion is also supported by the comparably more regular diffusion profiles, without disruption of continuity and steadiness, particularly in the younger ages.

Keywords: High pozzolanic cement, Diffusion cell, Low-alkaline cement, Cement pastes, Iodine diffusion, Pozzolans
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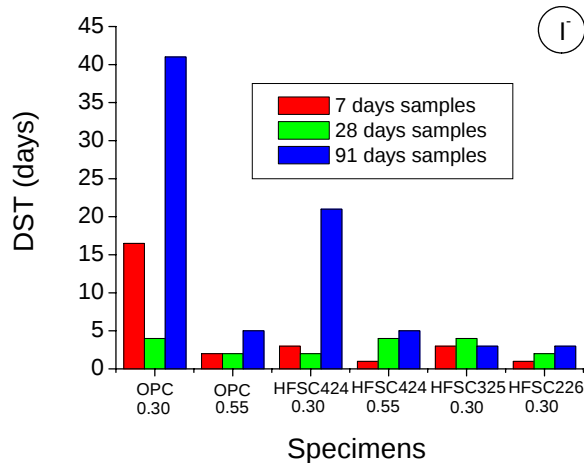
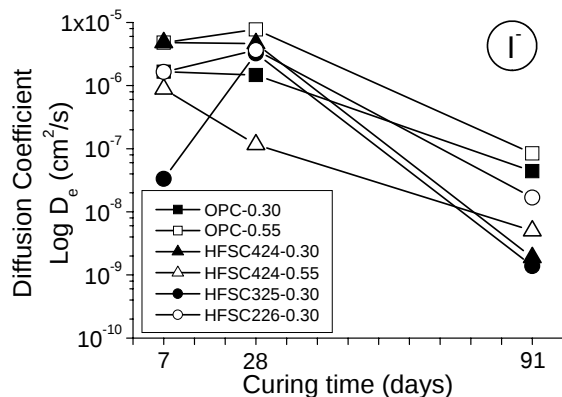
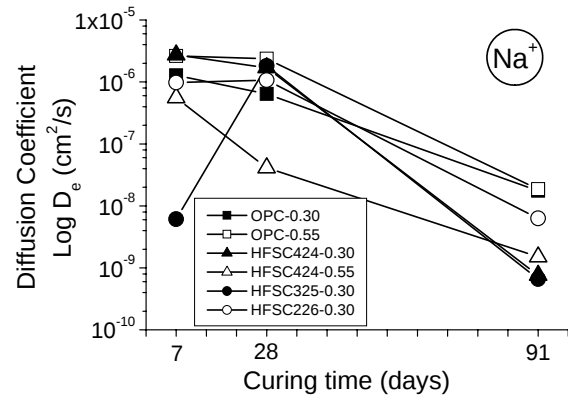


Fig.1 DST of NaI solution test

However, the physical properties of this halogen, specially the large iodine atomic radii, may affect significantly the DST due to ongoing hydration process, decreasing of porosity and development of thinner and discontinuous pore structure.

3.2. Diffusion Coefficients (D_e)

The effective diffusion coefficients (D_e) of iodine and sodium ions regarding NaI solution and calculated from Fick's 2nd Law are indicated in Figs. 2 and 3, respectively. Though some exceptions and unlike the Cl^- case, diffusion coefficients tended to remain constant within the first month (7 and 28 days curing time) and then decreased for the rest of the research period, the only exception being the HFSC424-0.55 and HFSC325 samples. This can be in part explained by the poorer binding capacity of I^- ion and little or even nil interference of its diffusion with the cement pastes' hydration process in the younger ages. A good directly proportional relationship between D_e and W/C ratio was observed in OPC samples and HFSC424 samples with higher

Fig.2 Diffusion of I^- in NaI solution testFig.3 Diffusion of Na^+ in NaI solution test

W/C ratio revealed a smaller D_e , for most of the research period. The sodium (Na^+) diffusion also followed the same pattern of the corresponding I^- anion for all samples and, as observed previously, D_e were a little bit smaller but almost comparable, with the same magnitude order.

The overall results' evaluation suggests that HFSC424 has a better diffusion resistance than OPC as observed in the NaCl solution study.

3.3. Mercury Intrusion Porosimetry (MIP)

Mercury intrusion porosity test was conducted for 28 days samples, before and after the diffusion test, as shown in Fig. 4. It was noted that porosity of HFSC significantly decreased, while for OPC samples, no much difference was observed. This fact can be explained through the ongoing hydration process of HFSC, since the diffusion test last almost one month after the proposed curing time (28 days) and set up of diffusion cells. During this period, the hydration of entire OPC specimens is almost complete and because of that, not much difference in the pore structure is observed.

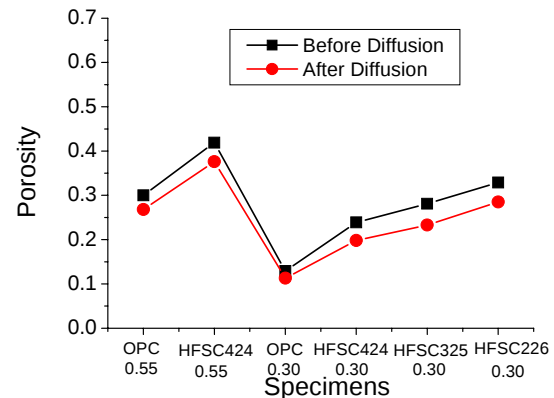


Fig. 4 Porosity of specimens in NaI solution test