- Technical Paper -

COMPARISON OF CI⁻ AND I⁻ ION DIFFUSIVITY THROUGH HARDENED POZZOLANIC CEMENT PASTES

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ABSTRACT

Mass transport behavior of hardened pozzolanic cement pastes was investigated through diffusion cell test. Four different pastes composed of mixtures ranging from entirely ordinary Portland cement (OPC) to combinations of 20% silica fume and 40% fly ash (HFSC), water cement ratio of 30% and 55%, curing times of 7 days, 28 days and 91 days and electrolyte sources of NaCl and NaI have been considered. Iodine (Γ) ion revealed a stronger diffusivity and a smaller chemical binding capacity than chloride ($C\Gamma$) ion.

Keywords: High volume pozzolanic cement, diffusion cell test, chloride, iodine, binding capacity

1. INTRODUCTION

Actually Japan is under extensive research for the development of long-lived radioactive waste geological disposal methods and the development of a low-alkaline cement using pozzolans for that purpose has been successfully done. These cements composed by mixes of ordinary Portland cement, silica fume and high proportions of fly ash have shown satisfactory results not only for low-alkaline content but also for self-compaction. Higher alkalinity (PH>11) is undesirable since under such conditions, bentonite, one of the common buffer and filler materials, is susceptible to undergo dissolution-precipitation reactions, which are considered to affect its performance, such as, degradation in swelling characteristics [1].

Since these structures and, according to the Japanese law, have to be built and placed at considerable deep depths, underground over 300m, where groundwater with its abundant hazardous chemicals are present, durability becomes a key concern. In order to assure the safety of disposal sites to a greater extent, the mass transport behavior in the hardened cement paste was investigated to determine which of the newly developed cement type material was suitable for the geological disposal.

The ionic diffusivity of concrete is a function of its microstructure, which is largely controlled by the initial concrete mixture proportions and the ultimate curing conditions [2]. Although it is found in the literature resourceful information regarding ordinary Portland cement, very little research has considered the ionic diffusivity of a wide range of pozzolanic material's combination with that of OPC pastes, which is the core subject of this study.

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

- Investigate the chloride/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 (NaCl and NaI).
- Through X-ray Diffraction and Differential Scanning Calorimetry analysis, characterize the type of hydration products of the cement pastes and it's role in the ion diffusion process. Particular aspect was also the evaluation of the chloride and iodine binding capacities of these cement pastes.

The present extended study aims to contribute to a better understanding of the hydration characteristics and microstructures while finding their relationship to the diffusivity of chloride/iodine and sodium ions through these new type cement pastes [3].

2. EXPERIMENTS

2.1 Materials

Ordinary Portland cement, fly ash in accordance with JIS A6201 class II (from Hekinan Electric Power Station) and silica fume from Elkem Materials, Norway (Microsilica 940U) were used. The chemical compositions of these materials are shown in Table 1.

Table 1 Chemical compositions of OPC, fly ash (FA) and silica fume (SF)												
Materials	Density	Blaine	Chemical Composition (Wt%)									
	g/cm ³	Specific	Ig.	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	TiO ₂	SO_3	Na ₂ O	K_2O
	-	Surface	Loss					-				
		g/cm ²	(%)									
OPC	3.17	3,410	2.1	20.4	5.6	67.5	3.3	N/D	N/D	1.9	0.9	0.4
FA	2.26	2,430	1.6	63.9	25.6	2.6	4.6	0.9	0.9	0.4	N/D	1.1
SF	2.21	213,450*	1.4	95.9	2.4	0.3	0.2	0.4	N/D	0.1	N/D	0.8
*BET specific surface												

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Table 2 Mixture proportions of cement pastes

<u> </u>	W/C	Portland	Silica	Fly	Super				
Cement	Ratio	Cement	Fume	Ash	Plasticizer				
Туре	(%)	(%)	(%)	(%)	(%)*				
ODC	30	100	0	0	0.30				
OPC	55	100	0	0	0				
LIESC424	30	40	20	40	1.50				
HFSC424	55	40	20	40	0.70				
*Cement weight (%)									

Four cement pastes were prepared according to the mixing proportions indicated in Table 2.

2.2 Preparation of Testing Samples

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 [4]. The photograph of specimen cast into a PVC acrylic ring is shown in Fig. 1.

2.3 Diffusion Measurements

Diffusion cells, as shown in Fig. 2, were prepared, containing 100ml solutions of NaCl or NaI with concentrations 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) [4].



Fig.1 Hardened cement paste cast into a PVC acrylic ring



Fig.2 Diffusion cell test apparatus

3. FICK'S LAWS FOR THE STUDY OF IONIC DIFFUSIVITY THROUGH CEMENT PASTES

3.1 Fick's 1st Law

Fick's first Law is used in the steady state diffusion, i.e., when the concentration within the diffusion volume does not change with respect to time. Although the law have been applied in the present study, regarding NaCl solution, it's assumptions are not entirely true, since sorption into the hardened cement paste and ion diffusion into the sampling cell reduces the concentration in the tracer cell. However, in most cases, as observed in this study, the concentration C_t in the tracer cell is considerable larger if compared to the concentration C_s in the sampling cell during the experiment period, that we can assume that the difference $\Delta C = C_t - C_s$ is almost negligible.

The effective diffusion coefficient is given by Eq.

$$D_e = \frac{QL}{\chi \Delta C} \tag{1}$$

where,

1:

 D_e : effective diffusion coefficient

Q : diffusion gradient

 ΔC : concentration difference

 χ : cross-sectional area

L : paste thickness

Diffusion gradients were obtained from the steady state sections of the diffusion profiles. Points were selected in order to get higher correlation factors (R^2 superior than 0.90). The results by this method were very similar to those obtained by fitting functions based on Fick's 2nd Law.

3.2 Fick's 2nd Law

Fick's second law is used in non-steady or continually changing state diffusion, i.e., when the concentration within the diffusion volume changes with respect to time. This was the case observed when NaI was the diffusing solution, so Fick's second law was used to calculate the diffusion coefficients. The mathematical formulation is given by Eq. 2:

$$\frac{\partial C_{(x,t)}}{\partial t} = \frac{\partial^2_{(x,t)}}{\partial x^2}$$
where:
 x : position
 t : time
 C : concentration (mass. length⁻³)
 D : diffusion coefficient (length².time⁻¹)

Zhang et al, in the study of time-dependent concentration change in the tracer cell and sampling (measurement) cell for stones and rocks, proposed the theoretical solution which is obtained from Fick's second law of diffusion for the computation of D_e . In this case, also the sorption capacity α can be computed simultaneously. The distance from the tracer cell to the hardened cement paste contact surface is designated as x [L]. At the distance x, the Cl⁻ concentration in the pore water solution of the hardened cement paste in elapsed time t [T] is considered C (x, t) [M/L³] and, with the initial and the boundary conditions, the theoretical solution obtained for solving the diffusion equation is shown below:

$$\alpha \frac{\partial C_{(x,t)}}{\partial t} = D_e \frac{\partial^2_{(x,t)}}{\partial x^2}$$
(3)

Initial conditions are stated as follows:

$$C_{(0,0)} = C_{(t)}$$

$$C_{(x,0)} = 0 \quad 0 < x \le L$$
(4)

And boundary conditions:

$$V_{t} \frac{\partial C_{(0,t)}}{\partial t} = \chi D_{e} \frac{\partial C_{(0,t)}}{\partial_{t}}$$
(5)

$$V_s \frac{\partial C_{(L,t)}}{\partial t} = \chi D_e \frac{\partial C_{(L,t)}}{\partial_t}$$

where, *V_t*: volume in the tracer cell *V_s*: volume in the sampling cell

With δ and γ in Eq. 6 and ϕ_m in Eq. 7, it's possible to express C(x, t) as shown in Eq. 8:

$$\delta = \alpha \frac{\chi L}{V_t} \qquad \gamma = \frac{V_s}{V_t} \tag{6}$$



Fig.3 Diffusion profiles and determination of DST of OPC-0.55 samples (NaCl solution)

$$\tan \phi_m = \frac{\delta(\gamma+1)\phi_m}{\gamma \phi_m^2 - \delta^2}$$

$$\pi \left(m - \frac{1}{2}\right) < \phi_m \le \pi \left(m + \frac{1}{2}\right)$$
(7)

Therefore, there is a solution for ϕ_m in Eq 7. The concentration of the sampling cell is equal to the Cl⁻ concentration of pore water solution in the hardened cement paste when x=L.

From the time-dependent concentration change obtained in the tracer cell of the "Through Diffusion test", the fitting of $C_{(L, t)}$ in Eq. 8 leads to the calculation of D_e and α [5].

4. RESULTS AND DISCUSSION

4.1 Diffusion Starting Time (DST) of Ions

Because the sodium ion (Na⁺) leaks from the pore solution and it's presence can be detected in the measurement cell just one day after the diffusion cell setup, which may in fact, mislead the determination of DST, the chloride (Cl⁻) and iodine (I⁻) ions were considered during the determination of diffusion starting time (DST). Therefore, in this study, DST refers to the first day the anion (Cl⁻ or I⁻) was detected in the measurement cell. The ion analyzer used during the research has a precision of 0.01 ppm. Fig. 3 shows an example of determination of DST.

In Figs. 4 and 5, the DST of chloride and iodine ions from the NaCl and NaI solutions are presented respectively. Although some discrepancies can be found, a clear trend has been identified. For NaCl solution and OPC samples with same W/C ratio, DST tend to remain

$$C_{(x,t)} = \frac{C_t}{\delta + \gamma + 1} - 2C_t \sum_{m=0}^{\infty} \left[\frac{\delta \cos\left(\phi_m \frac{L - x}{L}\right) - \gamma \phi_m \sin\left(\phi_m \frac{L - x}{L}\right)}{\left[\sqrt{\gamma \phi_m^2 - \delta(\delta + \gamma + 1)}\right] \cos(\phi_m) + \left[\delta \gamma + \delta + 2\gamma \phi_m\right] \sin(\phi_m)} \exp\left(-\frac{\phi_m^2}{L^2} \frac{D_e}{\alpha} t\right) \right] (8)$$



Fig.5 DST of Nal solution test

constant in the long range. However, for HFSC it is clear that the DST increases proportionally with curing time. This fact can be attributable to the almost complete hydration reaction in OPC samples up to one month period, while for HFSC this process keeps ongoing further, in some cases even exceeding one year. This hydration leads to thinner, discontinuous pore structure and lower porosity, making diffusion more difficult to occur. Regardless of cement type, DST was reversely proportional do W/C ratio. As for NaI solution, DST 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. However, the differences in physical properties between these two ions, 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. Considering these aspects, it's reasonable to refer that in terms of electrolyte source, NaI was more diffusive than NaCl, due to steeper diffusion gradients and relatively higher De (mainly in the younger ages) as



Fig.6 Diffusion of Cl⁻ in NaCl solution test



Fig.7 Diffusion of Na⁺ in NaCl solution test

we will see in the next section.

4.2 Diffusion Coefficients of lons

The effective diffusion coefficients D_e of chloride and sodium ions for all 7 days, 28 days and 91 days specimens regarding NaCl solution and calculated from Fick's 1st Law are indicated in Figs. 6 and 7 respectively.

Strong key trends have been found out. The first one is referent to the relation between the diffusion coefficients and W/C ratio. Regardless of cement type, a directly proportional relation was observed. Secondly, OPC samples revealed the decreasing of D_e in the first 28 days and then, they remained almost unalterable for the rest of the research period. Another fact is the direct relation between De and W/C ratio. However, HFSC424 samples tended to show little variation within the first month but a clearly sharp decrease of De in the following period was observed. In this case, samples with higher W/C ratio revealed smaller D_e . The Na⁺ cation diffusion followed the same pattern of the corresponding anion Cl⁻ for all samples and, although a little bit smaller, D_e were almost comparable in both cases.

Due to a continually changing diffusion state, Fick's second law was used to calculate the diffusion



Fig.8 Diffusion of I⁻ in Nal solution test



Fig.9 Diffusion of Na⁺ in Nal solution test

coefficients concerning NaI solution. The effective diffusion coefficients (D_e) of iodine and sodium ions are indicated in Figs. 8 and 9, respectively. 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. This can be in part explained by the poorer binding capacity of I ion and little or even nil interference of it's diffusion with the cement pastes' hydration process in the younger ages. A good directly proportional relationship between De and W/C ratio was observed in OPC samples and HFSC424 samples with higher W/C ratio revealed a smaller D_e throughout most of the research term, except in the later stages. However, in this case, De of HFSC424 samples with 30% and 55% W/C ratio were very approximate, with the magnitude order. The Na⁺ cation diffusion also followed the same pattern of the corresponding I anion for all samples and, as observed previously, De were a little bit smaller but almost comparable, also with the same magnitude order.

The overall results' evaluation suggests that HFSC424 has a better diffusion resistance than OPC in both cases of NaCl and NaI solutions. As per electrolyte source, NaI was highly diffusive in the first stages, but in the long term, this tendency was clearly diminished. This may be a hint that iodine diffusivity is more affected by microstructure formation than chloride ion.



Fig.10 Ca(OH)₂ peaks in NaCl solution test



Fig.11 Ca(OH)₂ peaks in Nal solution test

4.3 X-ray Diffraction Analysis

Extensive X-ray diffraction analysis of specimens after the diffusion test of Cl⁻ and l⁻ were conducted in accordance with ASTM C 1365 method. The results revealed that OPC samples are richer in Ca(OH)₂ and HFSC samples tend to run out of Ca(OH)₂ with time, as shown in Figs. 10 and 11. This can be explained with the fact that the pozzolanic reaction speed of fly ashes is low at the beginning. It is known that, if Ca(OH)₂ is leached out of a thin plate of paste by water in a slow process, the paste will not disintegrate, although it becomes weak and porous [6]. The direct implication is that the presence of $Ca(OH)_2$ might have influence in the diffusion of Cl⁻. HFSC424-0.55 pastes with smaller amounts of Ca(OH)₂ revealed smaller diffusion coefficients. Although the C-S-H is a very insoluble material, its micropore structure is another factor that may take a roll in the diffusion process of these hardened pozzolanic cement pastes, since differences in terms of pore diameter, continuity and pattern may emerge due to the type and proportions of pozzolanic material used. In both cases, the X-ray intensity of Ca(OH)₂ were very similar in samples subjected to NaCl and NaI solutions.

The binding capacity was evaluated from the view point of Fridel's salt formation, as shown in the Fig. 12, for the NaCl solution case:



Fig.12 Friedel's Salt peaks in specimens from NaCl solution test

Because the chloride binding capacity is dominated by the aluminate and ferrite phases present in the OPC, these specimens revealed higher binding properties. Regardless of cement type, binding capacity was also proportional to W/C ratio. A clear trend of decreasing binding capacity was observed in the long term for specimens subjected to NaCl solution.

Binding of I⁻ from NaI solution was negligible at all, which suggests that this ion hardly forms compounds with cementitious materials.

5. CONCLUSIONS

- (1) Regarding NaCl solution, and while for OPC the D_e was directly proportional to W/C ratio and decreased within the first 28 days to remain almost stationary afterwards, HFSC samples had almost negligible D_e variation in the first stages due to slower pozzolanic reaction and dropped sharply after one month period. Furthermore, no direct relation was found out between D_e and W/C ratio for these specimens.
- (2) As for NaI solution, D_e tended to remain constant within the first month (7 and 28 days curing times) and then decreased for the rest of the research period.
- (3) The Na^{$\overline{+}$} cation diffusion followed the same pattern of the corresponding anion Cl⁻ or l⁻ for all samples and D_e were a little bit smaller but almost comparable, with same magnitude order.
- (4) In both cases, the pozzolanic combination (HFSC) and further progress of the hydration process led to thinner pore structure formation and smaller D_e than those of entirely OPC samples.
- (5) Because the chloride binding is governed by the aluminate and ferrite phases, OPC revealed higher binding capacity than HFSC. Binding was directly proportional to W/C ratio, regardless of cement type. A clear trend of decreasing binding capacity was also observed in the long term for specimens subjected to NaCl solution. Binding of I⁻ from NaI

solution was negligible at all, which suggests that this ion hardly forms compounds with cementitious materials.

- (6) As for the electrolyte source effect, NaI was highly diffusive in the first stages, but in the long term, this tendency was clearly diminished. The physical properties' differences between these two halogens, specially the large iodine atomic radii, may affect significantly the DST and D_e due to ongoing hydration process, decreasing of porosity and development of thinner and discontinuous pore structure.
- (7) From the outcome of the research, we can assure with confidence that HFSC424 revealed better diffusion resistance than corresponding OPC samples and can therefore, be considered for the purpose of radioactive waste disposal facility application, concerning the mass transport behavior properties.

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