

# A FUNDAMENTAL STUDY ON CHLORIDE DIFFUSIVITY OF HARDENED HIGH VOLUME POZZOLANS CEMENT PASTES

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## 1. Introduction

Recently, a research about the development of a low-alkaline cement using pozzolans for geological disposal of long-lived radioactive waste 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 [1].

Since these structures will be built and placed at considerable low depths, underground at 300m, where groundwater with its abundant hazardous chemicals is present, durability becomes a key concern. In order to raise 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.

The present extended study aims to contribute to a better understanding of the hydration characteristics and microstructures of these new type cement pastes while finding their relation to diffusivity of chloride ions through cement pastes.

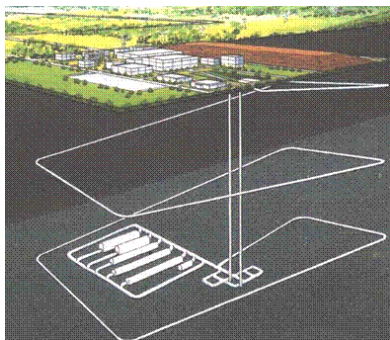


Fig. 1: Model of radioactive waste disposal site

## 2. Experiments

### 2.1. Materials

Six cement pastes were prepared according to the mixing proportions presented in Table 2. Ordinary Portland cement (density: 3.16 g/cm<sup>3</sup>, specific surface area by Blaine: 3260 cm<sup>2</sup>/g), Fly ash in accordance with JIS II class (from Coal burning power plant in Takasago city) and commercial Silica fume imported from overseas (Norway) were used.

Table I: Mix proportions of cement pastes

| Cement Type | W/C Ratio | OPC (%) | S.F (%) | F.A (%) | AE 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

The cement 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 5 min. The slurry was cast into PVC acrylic rings 5mm thick and 30mm internal diameter placed on glass plates, compacted and covered for one day to prevent dryness and evaporation. The cement pastes were then allowed to cure in Ca(OH)<sub>2</sub> saturated water solution for 7, 28 and 91 days at constant temperature and humidity conditions (20 °C; 50% R.H).

Diffusion cells as shown in Fig. 2 were prepared, containing 100ml solutions of NaCl (for all specimens) and CaCl<sub>2</sub> (OPC-0.30; HFSC424-0.30) with concentrations of 0.50mol/l and 0.25mol/l respectively in the tracer cell and 100ml of de-ionized water in the measurement cell, with the cement paste forming the partition between the two sides. After 24 hours, samples of 2ml were taken every 2 days interval from the measurement cell and replaced with the same volume amount of de-ionized water to keep the solution volume constant and the ion concentrations were measured through personal ion analyzer (PIA-1000).



Fig. 2: Diffusion cell apparatus



Fig. 3: Hardened cement paste specimen

**Keywords:** Long-lived radioactive waste, Low-alkaline cement, Cement pastes, Chloride diffusion, Pozzolans  
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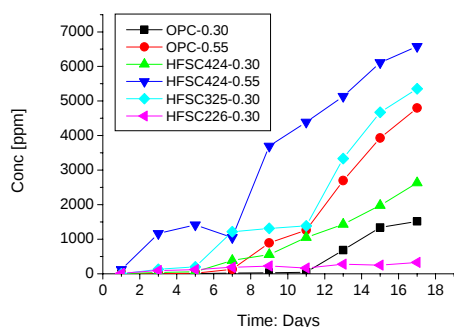


Fig.4: Diffusion of  $\text{Cl}^-$  from NaCl solution (Curing time: 7 days)

### 3. Results and Discussion

In this paper, results related to 7 and 28 days specimens are presented.

Figure 4 shows the anion  $\text{Cl}^-$  concentration change in the de-ionized water in the measurement cells of NaCl solutions for 7 days specimens. A good relation can be found between the W/C ratio and the diffusion gradients of same type cement specimens. Higher W/C ratios have shown quicker diffusion start times (1 day for HFSC424-0.55 and 5 days for OPC-0.55) and steeper diffusion gradients. High fly ash silica fume cements (HFSC) with the same W/C ratio revealed a complex behavior. HFSC226 with 60% of fly ash has the smallest diffusion coefficient, HFSC325 the highest, while HFSC424 with 40% fly ash has the medium value.

In the first approach, the fly ash amount in the mix, cannot alone explain the diffusion process. In other hand, comparing the results of NaCl and  $\text{CaCl}_2$ , for the same type of specimens, the former have shown diffusion coefficients slightly higher, which conforms with results from previous studies.

The unusual pattern of diffusion profile (disruption of continuity and steadiness) in the earlier stages can be an indication that, while diffusion of  $\text{Cl}^-$  is occurring, part of it is also reacting with the hydration products.

For 28 days specimens, the diffusion starting times are much quicker (1 to 2 days) in the NaCl solution case and almost the same for  $\text{CaCl}_2$  solution if compared to the 7 days results. Due to the degree of hydration and reduction of porosity, the diffusion gradients are less pronounced.

The effective diffusion coefficients for 7 and 28 days specimens, calculated from Fick's 1st law are indicated in Figs. 5 and 6 respectively. In both cases, there is a good correspondence between the Na and  $\text{Cl}^-$  diffusion coefficients. However,  $\text{Cl}^-$  coefficients are slightly higher in the 7 days specimens case and this tends to be inverted in the 28 days samples case.

In terms of electrolyte source, NaCl solution

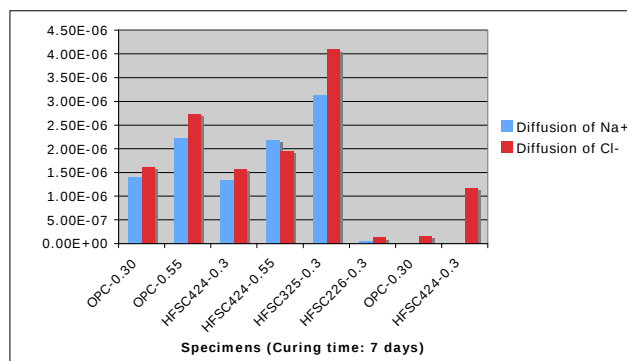


Fig.5: Diffusion coefficients of  $\text{Cl}^-$  and  $\text{Na}^+$  - (7 days)

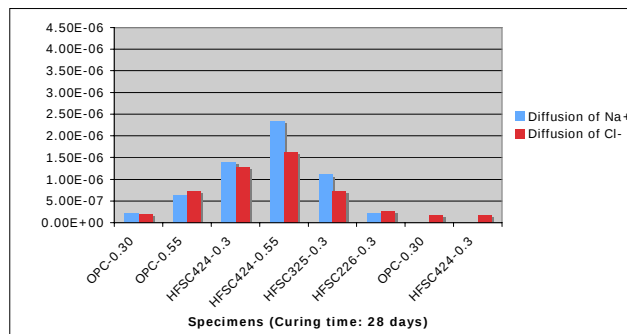


Fig.6: Diffusion coefficients of  $\text{Cl}^-$  and  $\text{Na}^+$  - (28 days)

revealed higher diffusion coefficients than those of  $\text{CaCl}_2$  solution, following the same behavior of 7 days specimens.

From the extensive X-ray diffraction analysis, it became clear that OPC samples are rich in  $\text{Ca}(\text{OH})_2$ . In other hand, HFSC samples tend to run out of  $\text{Ca}(\text{OH})_2$  with time. This can be explained with the fact that the pozzolanic reaction speed of fly ashes is low. Also, the ettringite amount in HFSC pastes almost double the one of OPC. It is known that, if  $\text{Ca}(\text{OH})_2$  is leached out of a thin plate of paste by water (a slow process), the paste will not disintegrate, although it becomes weak and porous. The direct implication is that the presence of  $\text{Ca}(\text{OH})_2$  might have influence in the diffusion of  $\text{Cl}^-$ . HFSC pastes with smaller amounts of  $\text{Ca}(\text{OH})_2$  revealed smaller diffusion coefficients. Although the C-S-H is a very insoluble material, its microporous 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 of pozzolanic material used.

### References

- [1] Mihara, M., Iriya, K., Torii, K., "Development of Low-Alkaline Cement using Pozzolans for Geological Disposal of Long-lived Radioactive waste", 2007, Japan.