

Study on long-term leaching behavior of low alkaline cement

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ABSTRACT

Leaching procedure is studied on low alkaline cement (HFSC: Highly Fly-ash contained Silica fume Cement) in which pozzolanic reaction is used for decreasing pH of pore water of cement hydrate to avoid influence on rock and other materials. Leached depth of HFSC by the immersion examination with simulated groundwater in Horonobe URL was smaller than depth of ion-exchanged Water. water exchanging is smaller than that of Ordinary Portland Cement (OPC) with the same water binder ratio, since soluble Portlandite was not produced and dissoluble Calcium Silicate components were mainly produced. Although simulated groundwater in Horonobe URL was used for immersion examination, the low alkaline cement hydrates is more durable for leaching degradation than OPC. For all cements, groundwater showed tendency of accelerate leaching compared to ion exchanged water. This study shows that HFSC has higher durability for leaching degradation to groundwater than OPC.

Keywords. Low alkaline cement, Immersion examination, Durability, Calcium leaching

INTRODUCTION

For the high level radioactive waste repositories (HLW repository), concrete has been considered as a supporting which is necessary for the sedimentary rock in particular. To avoid influence on rock and other materials, the pH of the groundwater in contact with the concrete is required to be less than 11.0 (Japan Nuclear Cycle Development Institute, 2005). The use of high pozzolan containing low alkaline cement (HFSC: Highly Fly-ash contained Silica fume Cement) is examined. HFSC consist of Ordinary Portland Cement (OPC) and pozzolanic materials (Fly-ash and Silica-fume). In HFSC, pozzolanic materials react with portlandite, then Calcium Silicate Hydrates (following C-S-H) is produced and Portlandite is consumed. However, there is little information on the long-term durability of cement that

contains pozzolan with groundwater and its long-term performance of the repository environment. For example, about the property of C-S-H of OPC and Silica-fume mixture, short comment of Richardson in his reports was seen (Richardson, 2004). This paper describes the stability of HFSC using immersion examination of simulated groundwater of Horonobe, focusing on calcium leaching from cement paste specimens.

IMMERSION EXAMINATION IN HORONOBE GROUNDWATER

Employed Materials and Mix Proportion. Two kinds of cement, HFSC and OPC, were used for comparison. The specimens were made from cement paste of water-binder ratio (W/B) = 50%. **Table 1** shows the materials used. **Table 2** shows the mix proportions of each specimen. Fly-ash and silica-fume are abbreviated as FA and SF. For OPC, a low breeding agent was used to reduce bleeding. In addition, for HFSC, an anti-foaming agent was used to reduce air void with SF.

Table 1. Materials

Materials	Detail
Ordinary portland cement	For research type by Japan Cement Association (Density: 3.22g/cm ³)
Fly-ash	Product of Tomatou-Atsuma Power Plant (JIS II type, Density: 2.22g/cm ³)
Silica-fume	Density: 2.20g/cm ³ , Blaine's specific surface area: 200,000cm ² /g
Mixing water	Ion exchanged water
Low breeding agent / cellulosic	Cellulose type
Superplasticizer	Polycarboxylic ether compound

Table 2. Mix proportions

Cement type	W/B(%)	Quantity of material per unit volume (kg/m ³)					
		W	OPC	SF	FA	Low breeding agent	Super-plasticizer
OPC	50	614	1228	0	0	12	0
HFSC	50	557	446	251	446	0	22

Specimen Preparation. The test specimens were made by the following procedure. At first, the materials were mixed, and cast into cylindrical molds with 50mm in diameter and 100mm in height. They were cured in a constant temperature room at 20 degrees Celsius for 24 hours. The cylindrical test specimens were demolded at 24 hours and cured in water at 20 degrees Celsius for 28 days. Finally, they were processed into cubic test specimens with 10 mm thickness and all face except one side were sealed by epoxy resin.

Items and Methods of Examination. **Figure 1** shows the device used for the water exchange immersion examination (Hitomi, 2009). Nine specimens were put in immersion cell to give water/solid ratio of 5:1. The immersion water of the cell was exchanged every three days to accelerate calcium (Ca) elution from the specimen. As the immersion water, the simulated Horonobe groundwater (the following, SHG) and ion exchanged water (IEW)

were considered. The column was filled with argon gas to exclude carbon dioxide gas. In addition, the specimen which was no water exchanged was examined. This was immersed in ion exchanged water with sealed in a polyethylene container filled with argon gas stored at 20 degrees Celsius for the same age (Non water exchange : NWE). **Table 3** shows the ion components of the water of the Horonobe groundwater and SHG.

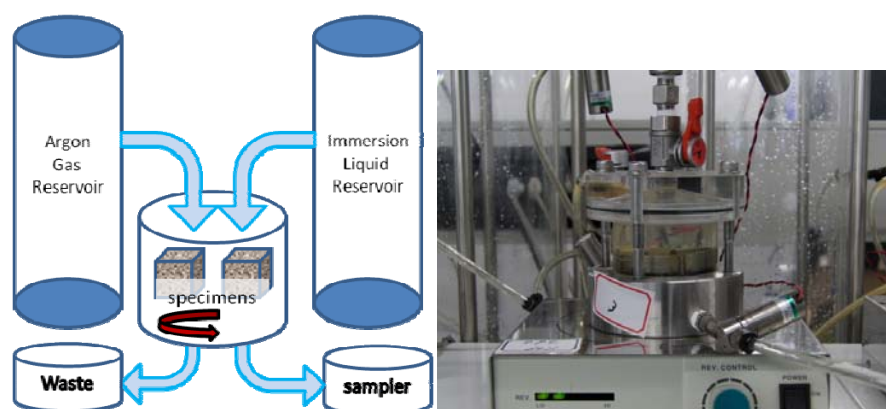


Figure 1. Diagram and Picture of Immersion Examination

Table 3. Ion components of water

	Concentration (mg/l)					pH
	Na ⁺	K ⁺	Ca ²⁺	NH ₄ ⁺	Cl ⁻	
Horonobe Groundwater	4110	106	302	150	7000	7.52
Simulated Groundwater (SHG)	3980	115	293	—	7170	7.0

After the immersion examination started, the exchanged immersion water of all specimens were sampled, and the exchanged water were analysed. The pH of immersion water was measured with the glass electrode method every three exchanging times of water. The atomic absorption spectrometry was used to determine the Ca quantities and absorptiometry was used to determine the Si quantities. Composition analyses were performed every ten times of water exchange. After 120 times of water exchange, one of each species was taken out. At the cross section of the sampled test specimen, the concentrations of elements were measured by electron probe micro analyser (EPMA). The measurements were carried out for six elements: Ca, Si, Na, K, Al and Cl. The observed areas were reed-shaped 2mm x10mm. For the test specimen with water-curing of the same age, observation in the domain of 2mm x 2mm was carried out. Since Ca elusion area was supposed smaller than immersion tests. For examinations with ion-exchanged water, observation was carried out for a domain of 3mm x 5mm. Because the ions of Na, K and Cl were included in ion exchanged water, the measurement elements were carried out for three elements: Ca, Si and Al.

EXAMINATION RESULTS-EXCHANGED WATER

pH Measurement. **Figure 2** shows the changes of pH with times of exchanged water. At the start, the pH of the immersion water of HFSC was 9.5 with the test specimen immersed in the groundwater, and showed 10.5 with the test specimen immersed in water. The

tendency of lowered pH was seen in SHG. With increase in the number of exchanges, the pH of the exchanged water of HFSC showed a decreasing tendency for both. At 120 times of water exchange, the pH showed 8.2 for SHG and 8.5 for IEW. The pH of the exchanged water showed a tendency of decreasing OPC, and the pH became 9.7 for groundwater and 11.3 for water. In comparison with OPC, a decreasing tendency was seen in the pH of the immersion water of HFSC. In addition, the change of pH decreased in HFSC and OPC when they were immersed in water.

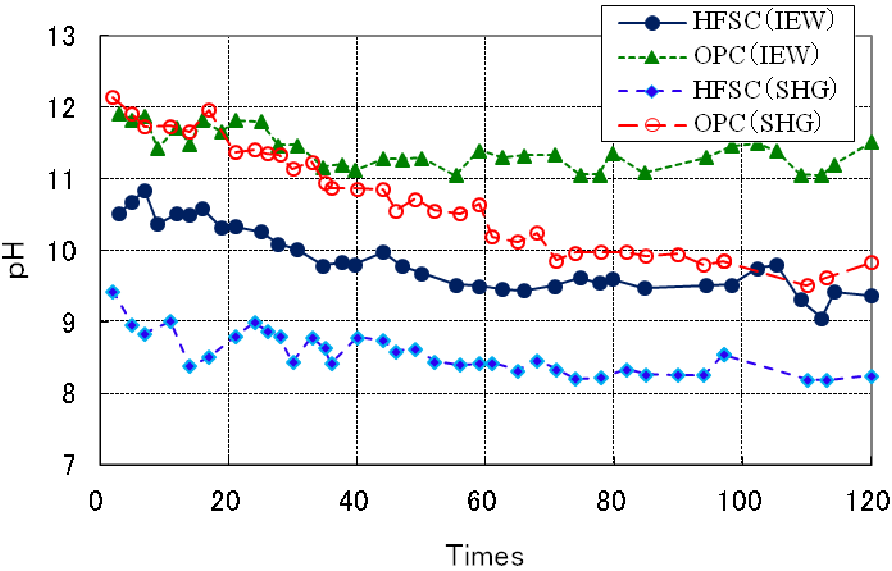


Figure 2. pH of immersed water

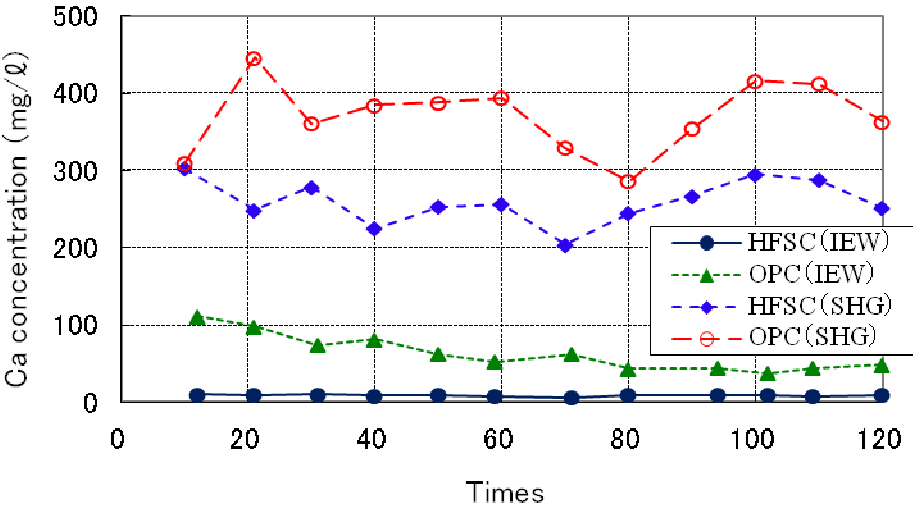


Figure 3. Ca concentration of immersed water

Elemental Concentration Measurement. Figure 3 shows the Ca concentration in the immersion water, which vary with immersion water. This results from difference between the original Ca contents of the groundwater and ion-exchanged water. The concentration of Ca in HFSC was smaller than OPC. Any results show Ca contents are decreasing with the times of exchange. For groundwater immersion of HFSC, the concentrations of Ca were under 300mg/l, there was a tendency for HFSC absorption of Ca.

Figure 4 show Si concentrations in the immersion water, which were all very small compared to the Ca concentrations. In the beginning of examination, Si quantities of HFSC showed bigger than OPC with its Si content. For 120 times of exchange water, all values were around 2mg/l. Thus, all of the cements eluted only small amounts of Si ion.

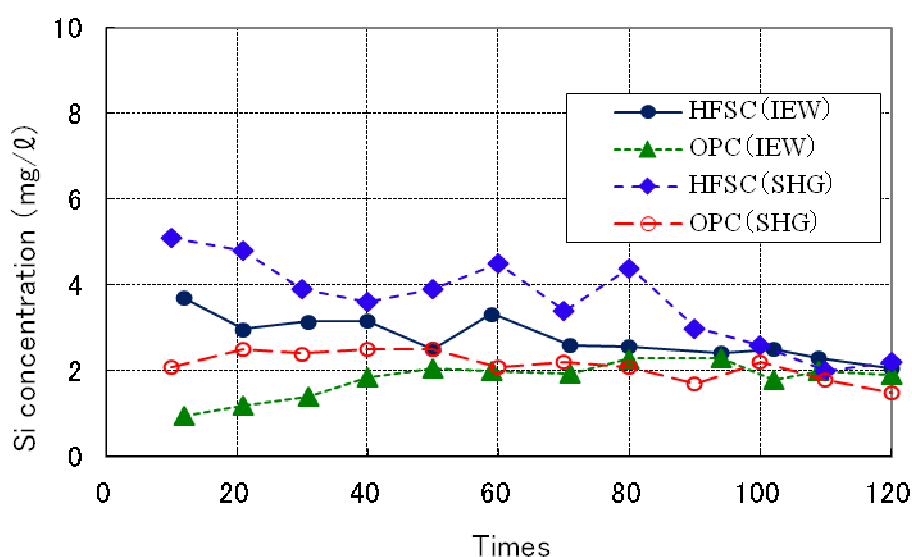


Figure 4. Si concentration of immersed water

EXAMINATION RESULTS-SOLID PHASE

EPMA Surface Analysis. Figure 5 shows the concentrations of elements from surface of HFSC measured by EPMA. Figure 6 shows the concentrations of elements of OPC. The upper section shows a result of non water exchange, and the middle section shows a result of SHG immersion, and the lower section shows the result of IEW immersion. The top surface of the specimen in the figure is in contact with the water. Ca leaching from this surface was seen in both HFSC and OPC of the immersion examination. Comparing CaO/SiO₂ ratio of HFSC to OPC, the ratio of HFSC is smaller than of OPC. This result is supposed to attribute from Portlandite consumption of HFSC. From the results, the lengths of Ca elusion, thus, Ca leaching depth were calculated. Table 4 shows the leaching depth of Ca. In SHG, the leaching depth of Ca ion of OPC in comparison with HFSC became around 3.4 times. It was recognized that HFSC had high Ca elution resistance. Also, SHG has tendency of accelerate Ca ion elusion in comparison with ion exchanged water and became around 3 times in a Ca ion decreasing area.

Si is also decreasing same area in all specimens. There was The result for each cement show that groundwater accelerates the elution of Ca. In particular, the leaching range Ca of OPC

was about 10 mm. The amount of Ca from HFSC was much less than that from OPC in any immersion water. In HFSC, Cl was observed in the domain where the concentration of Ca was decreased. In OPC, Cl was observed over the whole range.

Table 4. Leaching depth of Ca

	Immersion water	Leaching depth of Ca (mm)
HFSC	SHG	2.83
	IEW	1.19
OPC	SHG	9.75
	IEW	3.11

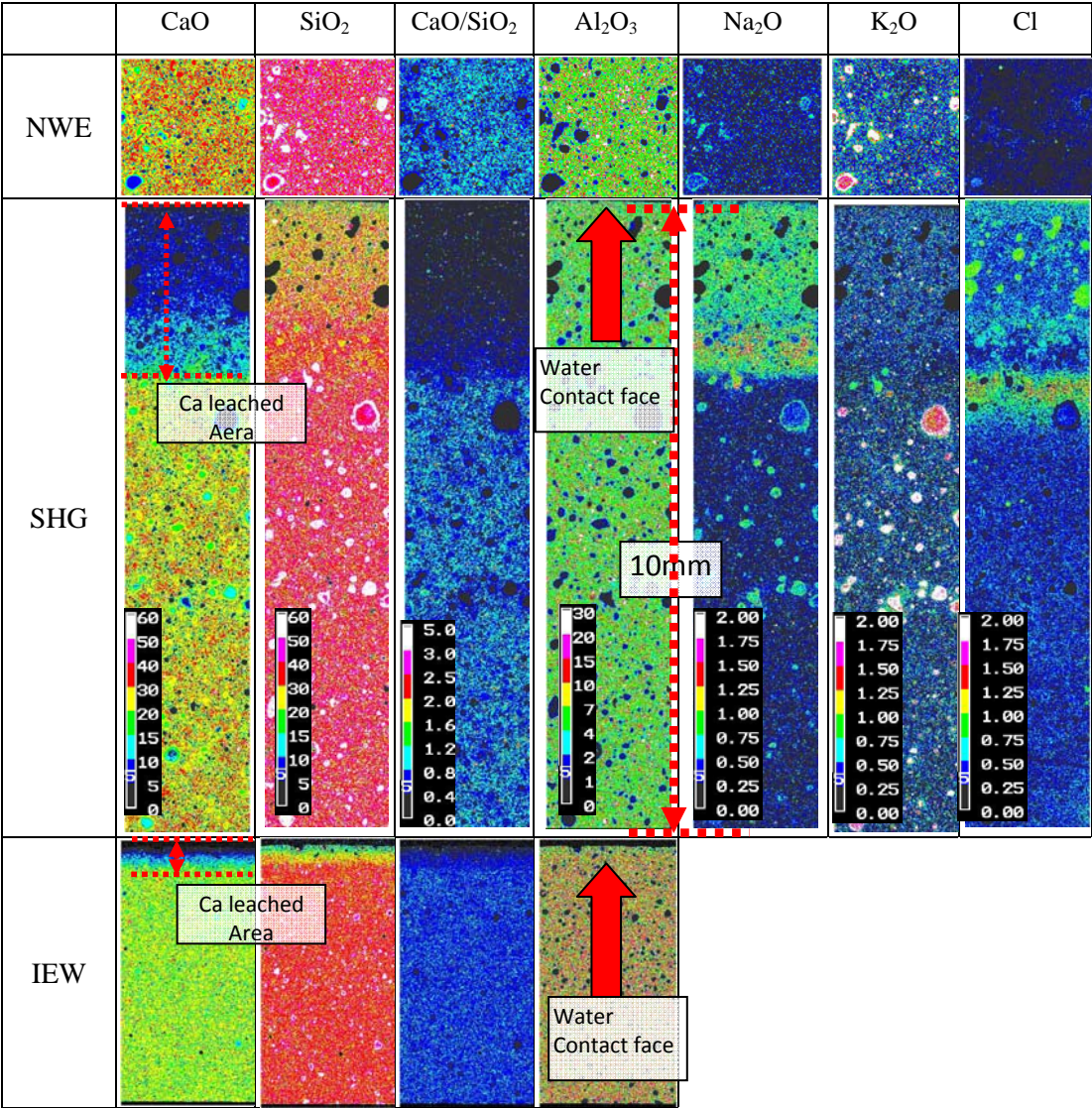


Figure 5. Element distributions of HFSC

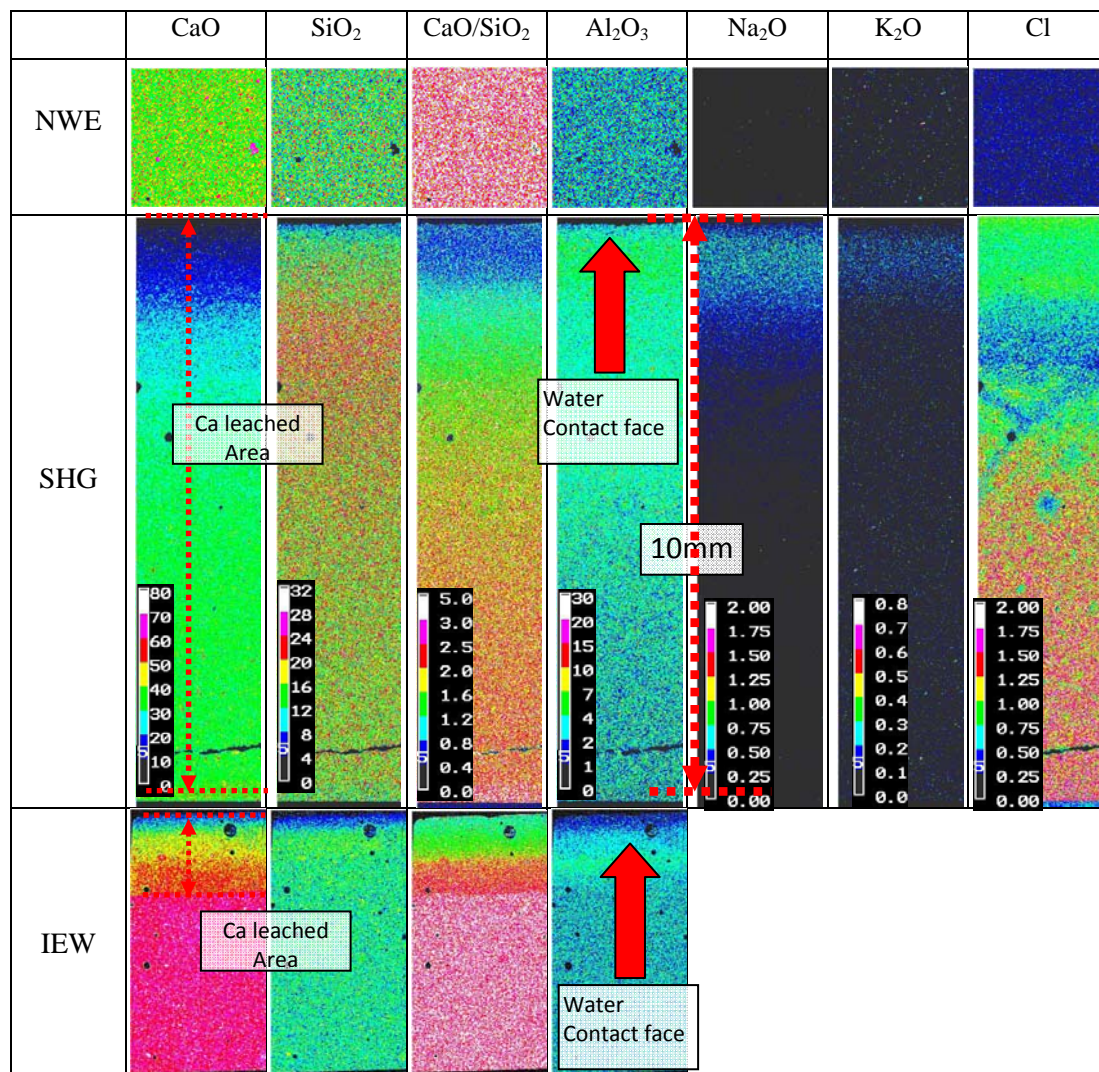


Figure 6. Element distributions of OPC

CONSIDERATION

Immersion Examination. SHG were used in an immersion examination, a remarkable tendency was found in the pH. The pH of immersion groundwater showed less than 10.0 at the beginning in HFSC. Iriya and Hitomi predicted the time, when the pH of the immersion water was less than 11.0, is 18.8 years based on the result of ion exchanged water immersion examination with no exchange (Iriya, 2007, Hitomi, 2010).

Ueda obtained a similar result (Ueda, 2008). Ueda carried out seawater immersion examination of HFSC, and reported that the pH of seawater immersion was less than that of ion exchanged water. They considered that this resulted from the buffering effect of pH due to the existence of ions such as Na and Cl included in the simulated groundwater. Because SHG is near to the diluted seawater, it is estimated that a similar tendency was shown. The Ca concentration in exchanged water of SHG from OPC was bigger than SHG. However the result of HFSC, the Ca concentration in exchanged water of SHG showed same or lower as

that of SHG. Ueda found difficulty in measuring the Ca concentration of the simulated seawater immersion examination. About the Si concentrations of exchanged water, they were less than 10 mg/l both immersion water after an immersion start. As an immersion period advances, the Si concentration showed a tendency of the decrease. It is thought that the Si in specimen showed the tendency because of hard to be lost.

EPMA Analysis. The leaching depth of the Ca were focused, HFSC becomes lower than one-third than OPC. It was supposed that HFSC have higher Ca leaching resistance than OPC. This result shows that the SHG, which is similar to diluted seawater, has a higher tendency to elute Ca ion from the cement hardenings than IEW.

SHG accelerates Ca elution in comparison with ion exchanged water because the C-S-H of the cement hydrates causes exchange with Ca ion and Na ion, and it is considered that C-S-H changes into a highly soluble material. As for the exchange with Ca ion and Na ion in C-S-H, the mechanism has been confirmed by Sugiyama (Sugiyama, 2004). Because there is little free Ca ions in HFSC, Cl ions are not combined, and Friedel's salt is not produced. However, in the area of Ca and Na exchange in C-S-H, Cl combines with free Ca and Friedel's salt is produced. This is thought that distribution of Ca and Na exist in a replaceable form in the whole specimen for this exchange mechanism.

CONCLUSION

Immersion examinations of HFSC and OPC were performed with Horonobe simulated groundwater and ion exchanged water. A study for one year gave the following results : (1) The pH of the immersion water of HFSC was less than 11.0 from the beginning. (2) The pH of the immersion water of HFSC decreased with the progress of the examination and became around 9.0. (3) In the immersion in Horonobe simulated groundwater, the leaching depth of Ca ion of OPC in comparison with HFSC became around 3.4 times. It was recognized that HFSC had high Ca elution resistance. (4) The Horonobe simulated groundwater tended to accelerate Ca ion elution in comparison with ion exchanged water and became around 3 times in a Ca ion decreasing area. 5) It was supposed that a Ca ion was easy to be lost in Horonobe simulated groundwater because of Ca and Na exchange mechanism in C-S-H worked.

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