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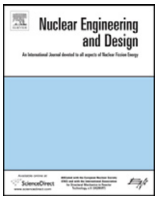

Effect of calcium leaching on the pore structure, strength, and chloride penetration resistance in concrete specimens

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HIGHLIGHTS

- The volume of pores with diameters ranging from 50 nm to 500 nm is increased.
- The Pores larger than 200 nm in size increase in number during the initial time.
- The residual strength of the leached part with OPC ranges from 35% to 60%.
- The residual strength of the mineral admixture replacement ranges from 23% to 50%.
- The chloride diffusion coefficient of leached concrete is increased 2–5 times.

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ABSTRACT

In radioactive waste repositories constructed underground and on shorelines, concrete members can remain in contact with groundwater for a long period. However, even pure water creates concentration gradients which lead to the diffusion of Ca ions from the pore water and the degradation of the underground concrete. Therefore, the purposes of this study are to investigate not only the alteration of the pore structure and the loss of compressive strength associated with dissolution but also the characteristics of chloride penetration after leaching-related degradation.

The results show that as the leaching period increases, the volume of pores with diameters ranging from 50 nm to 500 nm is greatly increased. Also, pores larger than 200 nm in size rapidly increase in number during the initial leaching time, while those smaller than 200 nm increase in number only gradually. Furthermore, the residual strength of the leached part with OPC ranges from 35% to 60%. In addition, those of the mineral admixture replacement ranged from 23% to 50%. The chloride diffusion coefficient measured by the chloride profile increased two-to-five-times with the leaching duration.

1. Introduction

The radioactive waste repositories are scheduled to be constructed deep underground and on shorelines in South Korea. Also, these facilities require long-term durability of the concrete, as the concrete members will likely be in contact with groundwater for a long period (Faucon et al., 1997). However, pure water creates concentration gradients which lead to the diffusion of Ca ions from the pore water and the subsequent degradation of underground concrete. Therefore, the main degradation factors are the gradual leaching of cement hydrate in pore water and chloride attack by sea water. This causes the concrete's porosity to increase and its strength to decrease (Haga et al., 2005; Yang and Choi, 2011; Carde and François, 1999). In addition, the chloride diffusion coefficient will increased due to the change in the pore size distribution (Yang, 2006). Therefore, it is important to investigate the degradation factors related to the leaching of cement hydrate. These include the pore structure and strength as well as the chloride diffusion coefficient.

Many studies have investigated the leaching of cement constituents from cement hydrate. Atkinson and Guppy (Atkinson et al., 1987; Atkinson and Guppy, 1987) as well as Berner (1998) developed cement paste dissolution models to evaluate long-term changes in the compositions of liquid phase. Faucon et al. (1997) studied the alteration of hardened cement paste by dissolution and indicated that hydrate phases and the structures of hydrates change with the progress of dissolution. Meanwhile, Buil (1992) and Carde et al. (1997) considered diffusion as the transport mechanism of leached constituents in their experiments. Haga et al. (2005) also studied the effects of the pore volume in hardened cement paste on dissolution phenomena, and Saito et al. (Saito and Nakane, 1999; Saito and Deguchi, 2000) developed a new acceleration test method for the leaching degradation of cement hydrate.

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Table 1
Concrete mix proportion.

W/B (%)	S/a (%)	Unit weight (kg/m^3)					
		Water	Cement	Sand	Gravel	Fly ash	Blast furnace slag
40	43	170	425	721	934	–	–
50	45	173	345	782	933	–	–
	45	173	311	776	927	35	–
	45	173	242	778	929	–	104

As mentioned in the previous paragraphs, these studies focused on modeling cement paste alterations and structural changes of hardened cement paste as associated with dissolution. Also, the mortar specimen size for the leaching test was small. Above all, the material used in radioactive waste disposal facilities is concrete, and the concrete used is not homogeneous in comparison with the mortar. Specifically, concrete has many interfacial transition zone (ITZ) between the aggregates and the cement paste. Most concrete properties are affected by the ITZ characteristics. In ordinary concrete, the ITZ has less crack resistance than either hydrate cement or the mortar, and so fractures occur preferentially in the ITZ. Even before any load has been applied, a large number of micro-cracks exist in the ITZ of sound concrete. Moreover, calcium-leaching may occurs mainly in the ITZ because there is a higher proportion of portlnadite and ettringite compared to bulk paste (Mindess, 2003). Therefore, it is desirable to evaluate the degree of degradation using a leached concrete specimen, directly.

However, literature data (Nguyen et al., 2007; Sellier et al., 2011; Marinoni et al., 2008) pertaining to the calcium leaching of concrete are not enough. Thus, in this study, a strongly concentrated ammonium nitrate solution was used to assess the leaching of cement hydrate in concrete. The pore-size distribution and compressive strength of the degraded parts were then measured and the deteriorations of resistance against chloride penetration were compared. And effect of calcium leaching on the pore structure, strength, and chloride penetration resistance in concrete was discussed.

2. Experiments

2.1. Materials and concrete mix proportions

Table 1 show the mix proportions of the concrete specimens. Ordinary Portland cement (OPC) (ASTM Type I) was used in all of the mixtures. The Crushed gravel was used as a coarse aggregate with a maximum aggregate size $G_{\max}$ of 20 mm. The Specific gravity and absorption ratio of the coarse aggregate were 2.54 and 0.63%, respectively. The specific gravity, absorption ratio, and the fineness modulus (FM) of the fine aggregate were 2.59, 1.07%, and 2.65, correspondingly.

In addition, to investigate the effect of mineral admixtures on leaching damage, part of the cement mixture was replaced by mineral admixtures at a water/binder (W/B) ratio of 0.5. The replacement ratios were 30% for blast-furnace slag (BFS) and 10% for fly Ash (FA). The physical and chemical compositions of the cement and mineral admixtures are shown in Table 2. After the removal of the mold, all specimens were cured for 28 days in saturated limewater at a temperature of 20 ± 3 °C.

2.2. Leaching acceleration tests

In this test, instead of slow leaching kinetics obtained by means of de-ionized water or an electrochemical method, an ammonium nitrate solution was used to degrade the concrete specimens. The ammonium nitrate (NH_4NO_3) reacts initially with the calcium hydroxide ($Ca(OH)_2$) in the cement hydrates, leading to the appearance of a very soluble calcium nitrate ($Ca(NO_3)_2$) and the emanation of gaseous ammoniac NH_3 (Carde et al., 1996). Unfortunately, these phenomena do not occur under natural conditions. Under natural conditions, there is a chemical equivalence between the $Ca(OH)_2$, C—S—H, and each ion component in the pore solution from the viewpoint of phase equilibrium. If the Ca^{2+} concentration in the pore water decreases, the $Ca(OH)_2$ dissolves, thus supplying additional $Ca(OH)_2$ ions from the cement hydrates to maintain the chemical equivalence. After the portlandite is completely dissolved, the Ca^{2+} ions supplemented from C—S—H start to dissolve and C—S—H finally degrades to SiO_2 gel. Nevertheless, these differences between the artificial condition and the natural condition do not change the mechanism of calcium leaching from the concrete (Carde et al., 1997).

For the leaching acceleration test, a 6 mole concentration of an ammonium nitrate solution was used and the concrete specimens were totally immersed for a predetermined period (15, 30, 60, 90, 180 and 365 days). Also, the leaching acceleration tests were performed in a thermostatic chamber at 20 °C (Gawin et al., 2009). After a specified period, the specimens were cut and shaped into cubes of 10 × 10 × 10 mm in size (a surface part 0 mm to 10 mm) using a diamond cutter for using in the MIP test. Also, the other sample pieces were used for calcium amounts.

To investigate the amount of leached calcium, the relative calcium amounts were measured by means of atomic absorption spectroscopy for leached specimens and for reference specimens cured during same periods in limewater.

Meanwhile, the depth of degradation thickness was measured optically by the phenol-phthalein test (total thickness of specimen: 100 mm). This substance turns red-pink if applied onto a material whose pH is higher than 10. Thus, the color of phenol-phthalein applied to a degraded zone would not turn red.

2.3. Main test items and test procedure

To investigate the long-term mechanical properties and durability as a function of the leaching kinetics, the experiments in this study are divided into two groups. For the evaluation of the long-term properties, pore size distribution, bulk density, porosity, and compressive strength tests were conducted. For durability, the rapid chloride permeability test (RCPT) (ASTM C 1202, 1997;

Table 2
Physical and chemical composition of materials.

Properties	Material		
	OPC	FA	BFS
Physical			
Specific gravity	3.15	2.25	2.89
Blaine (cm^2/g)	3200	3400	4300
Chemical (%)			
SiO_2	21.36	49.89	33.54
Al_2O_3	5.03	29.99	15.22
Fe_2O_3	3.31	7.42	0.51
CaO	63.18	5.01	43.88
MgO	2.89	0.98	2.62
SO_3	2.30	–	2.54
LOI	1.40	4.31	0.01