



# Deterioration rate of hardened cement caused by high concentrated mixed acid attack



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## HIGHLIGHTS

- Deterioration of hardened cement caused by pure strong acid attack was clarified.
- Deterioration of hardened cement caused by mixed strong acid attack was clarified.
- Dissolution of  $\text{Ca}(\text{OH})_2$  model of deteriorated by mixed acid is constructed.

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## ABSTRACT

The purposes of this study are to clarify the deterioration mechanism of hardened cement caused by high concentrated acid attack. As the result, In the case of high concentrated pure acid, deterioration rate varies greatly according to the kind of product of the attack of acid. This behavior can be explained by solubility of product. Next, in the case of which mixed acids containing  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  or  $\text{HNO}_3$  is attacking on hardened cement, the deterioration rate begins to increase when  $\text{H}_2\text{SO}_4$  molar fraction decreases from between about 0.7 and 0.4–0.0. This behavior can be explained by chemical kinetics.

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## 1. Introduction

It is well known that concrete structures deteriorate due to chemical attack under acidic environments. Acidic environments consist of a wide variety of conditions such as acid rain, acid river, sewerage, chemical facility or hot spring area. In these environments, the kind of acid that acts toward concrete structure is different from one environment to another. For example, acid rain and acid river cause concrete structures to unexpectedly fall short on their service life due to damages at concrete cover. Therefore, relevant researches on this deterioration had been done in many countries [1–9]. One result from these studies is, deterioration mechanisms are varied from kind of acid that attacking on concrete [10,11].

In actual environment, the acid attacking on concrete is not a pure acid but often a type of mixed acid. For example, for materials contained in acid rain or acid river, the acid attacking on concrete contains mixture of sulfuric acid, nitric acid and hydrochloric acid. Moreover, molar fractions of contained materials are different from one environment to another.

Studies on acid deterioration of concrete are examined with theories such as chemical kinetics, diffusion of ions and product of chemical reactions as previously explained. As results, deterioration factors (*i.e.* chemical kinetics, mass transport of ions, and product of chemical reactions) are influenced with each other. Therefore, it is difficult to predict concrete deterioration caused by acid attack with a high degree of accuracy. The cause of the difficulty is that each deterioration factor cannot be clarified. For example, chemical reaction rate of hardened cement reacting with acid is reaction-controlled in the early days of the reaction. However, as the chemical reaction processes, the product from the reaction is being deposited to the surface layer of hardened cement. Here, the chemical reaction rate becomes diffusion-controlled due to the deposited layer of chemical product. Furthermore, chemical reaction later advances to with further progression. After sometime, when product is removed on surface layer of hardened cement, chemical reaction rate returns to reaction-controlled again. In addition of which, when the kind of acid attacking on concrete is different, diffusion coefficient of which ions permeate through product are different since different products are product.

In this study, focused on condition of product formation (*i.e.* calcium chloride and gypsum), the relationship  $\text{H}_2\text{SO}_4$  molar fraction of mixed acids, product produced from reaction and deterioration

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rate of hardened cement by acid attack is clarified. Moreover, these relationships are discussed from a chemical theories.

## 2. Materials and experimental procedure

The purposes of this study are (1) to clarify experimentally the relationship between the molar fraction of contained material in mixed acids and the deterioration rate of hardened cement by mixed acids attack and, (2) to discuss on these relations from chemical perspective. In order to achieve these purposes, "immersion test in 120 min" had been carried out on hardened cement paste and cement mortar.

### 2.1. Materials and mix proportions

Ordinary Portland cement that conforms to Japanese Industrial Standards R 5201 (density: 3.16 g/cm<sup>3</sup>, specific surface area by Blaine method: 3290 cm<sup>2</sup>/g), Japanese normal siliceous sand (density: 2.60 g/cm<sup>3</sup>, water absorption: 2.64%, fineness modulus: 2.71) from Tsurusu, Miyagi Prefecture, were used. Since, in general, siliceous sand is known for its high resistance to acid deterioration, the mineralogical influence of aggregate reaction was neglected in this study. Actually, no aggregate reaction can be seen during the investigation.

Table 1 shows the mix proportions of hardened cement used in this study. In this study, two types of test pieces were fabricated. One type is just using water and cement paste. The other type is cement mortar. All test pieces have water–cement ratio of 0.55 or 0.65. For identification, test pieces with only cement paste is named 55P or 65P, and cement mortar is named 55M or 65M. In this study, cement paste and mortar mix may easily undergo material segregation due to the high W/C. Therefore, alkyl aryl sulfonate and alkyl ammonium salt based thickening agent, which is usually used in self-compacting concrete, was used to prevent material segregation.

### 2.2. Specimen preparation

Mixing of cement paste and cement mortar was carried out in accordance with ISO 679 (i.e. JIS A 5201). Mixed cement paste and cement mortar was placed in a  $\phi$  50 × 100 mm cylinder mold form. Test pieces were kept in a moist room. After 24 ± 2 h after casting, the test pieces were demolded. Then, the test pieces were cured under temperature controlled water at 20 ± 2 °C for up to 28 days. After curing, test pieces were cut and shaped in a  $\phi$  50 × 10 mm discoid shape using a diamond disk cutter. The cut test pieces were immersed in water at 20 ± 2 °C for 5 days to eliminate the water advection. This advection of water was caused by drying at the beginning of the immersion test.

### 2.3. Method of immersion test

A clean acid-free plastic container was used for the immersion test. The test pieces were placed in the containers. Then, enough solution was filled into the plastic container to immerse the exposed surfaces completely. There were about 15 L solution used in each container, and the ratio of the test piece and solution were prepared at about 1 to 150 by volume. The ambient temperature of the immersion



Fig. 1. Details on method of scrub.

test was set at 20 ± 2 °C. The test duration was limited to 120 min. As the exposure condition, the surfaces of test pieces were scrubbed at every 20, 40, 60 and 120 min during the immersion test as shown in Table 2. About method of scrub, test pieces are scrubbing with the brush made of stainless steel as shown in Fig. 1.

### 2.4. Types of solution

In this study, there are two experiment, namely, the pure strong acid (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) and the mixed acid (i.e. HCl + H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) are used for the immersion test. In this study, mixed acid contained HCl and H<sub>2</sub>SO<sub>4</sub> is named CS and mixed acid contained HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> is named NS were used. Moreover, in the both of tests, pH of the acid is set to be 0.30 (i.e. [H<sup>+</sup>] = 0.5 mol/L). Table 3 is shown in the ratios in which the acids were mixed.

### 2.5. Measurements

After the immersion test, mass decrease rate of test species and their ratio of mass decrease rate compared to the original mass were measured. Calculation of the mass decrease rate (Eq. (1)) and ratio of mass decrease rate (Eq. (2)) is shown below.

$$R = \frac{W_0 - W_1}{W_0} \times \frac{1}{t} \quad (1)$$

where  $R$  is the mass decrease rate per hour (h<sup>-1</sup>),  $W_0$  is the original mass of test piece before acid deterioration,  $W_1$  is the mass of test piece after acid deterioration, and  $t$  is the immersion time (hour). In addition, mass decrease rate due to different acid is

Table 1  
Cement paste and mortar mix in this study.

Name	W/C (%)	Sand–cement ratio S/C	Air (%)	Unit content (kg/m <sup>3</sup> )			
				Water	Cement	Sand	Thickening agent
				W	C	S	
55P	55	0	5	607	1150	0	25
55M	55	2.5	5	290	550	1374	12
65P	65	0	5	642	1029	0	27
65M	65	2.5	5	318	509	1271	13

Table 2  
Scrubbing interval of test pieces during immersion test.

Immersion time	Scrub interval			
	Scrub@20 min	Scrub@40 min	Scrub@60 min	Scrub@120 min
20	○	–	–	–
40	○	○	–	–
60	○	–	○	–
80	○	○	–	–
100	○	–	–	–
120 (finish)	○	○	○	○
Total times of scrub	6	3	2	1

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