A STUDY ON THE REACTION MECHANISM OF HARDENED CEMENT CHEMICALLY DAMAGED BY MIXED ACIDS

Shintaro Miyamoto[1] , Hiroshi Minagawa[1], Makoto Hisada[1]

[1] *Tohoku University, Department of Civil Engineering, Sendai, Japan*
980-8579 Miyagi, Sendai, Aoba-ku, Aramaki, Aoba, 6-6-06,s-miyamoto@civil.tohoku.ac.jp
same as above,minagawa@civil.tohoku.ac.jp
same as above,hisada@civil.tohoku.ac.jp

ABSTRACT

It is well known that the concrete under acidic environment is deteriorated due to a chemical attack. For example, acid rain cause concrete unexpectedly short service life due to the damages for concrete cover.

For these background, the purpose of this study are (1) to clarify the relation between sulfuric acid mol fraction of mixed acids and mass decrease rate of hardened cement deteriorated by mixed acids and (2) these relations are arranged with physical chemistry theories.

From the experimental results, in the case of sulfuric acid mol fraction of mixed acids are larger than about 0.40, mass decrease rate are at the same as deteriorated by sulfuric acid. On the other hand, in the case of sulfuric acid mol fraction of this are smaller than about 0.40, mass decrease rate increase liner and finally mass decrease rate are at the same as deteriorated by nitric acid or hydrochloric acid.

Keywords. sulfuric acid, hydrochloric acid, nitric acid, molar fraction, chemical kinetics.

1. INTRODUCTION

It is well known that the concrete under acidic environment is deteriorated due to a chemical attack. For example, acid rain and acid river cause concrete structures unexpectedly short service life due to the damages for concrete cover. Therefore, relevant researches on this deterioration are done in many countries of this world (JSCE, 2003, J. Monteny, 2001, Z. Changa, 2001, I. Kurashige, 2002, W. Sand and E. Bock, 1984, Beddoe Robin E, 2005.). In one result on these researches, deterioration mechanisms are varied with kind of acid acting to concrete.

In actual environment, condition of acid acting to concrete is often mixed acid not only one kind of acid. For example, focus on contained materials of acid rain and acid river, it's

contains sulfuric acid, nitric acid and hydrochloric acid. Moreover, molar fractions of contained materials are different according to the environment.

Researches which deteriorated of concrete with action of acid range from fields that chemical kinetics, diffusion of ions and product of chemical reactions as previously explained. In those result, deterioration factors (i.e. chemical kinetics, diffusion of ions, and product of chemical reactions) are influenced with each other. Accordingly, it is difficult to predict concrete deterioration with action of acid. Especially, long-term deterioration prediction is almost impossible as it stands now. The cause of this problem is cannot clarified each deterioration factor. For example, chemical reaction speed of hardened cement and acid is reaction- controlled in the early days of chemical reaction. But, chemical reaction is advancing at some level, product with chemical reaction deposited on surface layer of hardened cement and chemical reaction speed is diffusion- controlled under influence of this product. Furthermore, chemical reaction is advancing with further progression; product is removed on surface layer of hardened cement. That is to say, this means that chemical reaction speed is reaction-controlled again. In addition to this problem, when acid acting to concrete is different, diffusion coefficient that ions penetrate in product is different. Because, when acid acting to concrete is different, product is different.

In this study, this problem, focused on condition of formation of products (i.e. calcium chloride, calcium nitrate and gypsum). More specifically, this study focused on the relationship of molar fraction of sulfuric acid and product of chemical reaction. And the objective of this study was (1) to clarify experimentally the relation between molar fraction of contained material at mixed acids and mass decrease rate of hardened cement deteriorated by mixed acids and (2) these relations are arranged with physical chemistry theories.

2. MATERIALS AND EXPERIMENTAL PROGRAM

The objective of this study was to (1) to clarify experimentally the relation between molar fraction of contained material at mixed acids and mass decrease rate of hardened cement deteriorated by mixed acids and (2) these relations are arranged with physical chemistry theories. To achieve this objective, "immersion test in 120 minutes" carried out on hardened cement paste and cement mortar by mixed acids which changed molar fractions of contained acids.

2.1 MATERIALS AND MIX PROPORTIONS. Ordinary Portland cement (density: 3.16 g/cm³, specific surface area by Blaine method: 3290 cm²/g), Japanese normal siliceous sand (density: 2.60 g/cm³, water absorption: 2.64%, fineness modulus: 2.71) from Tsurusu, Miyagi Prefecture, were used. Since, in general, siliceous sand is difficult to be deteriorated due to acid, the mineralogical influence of aggregate reaction was neglected in this study. Actually, no reaction can be seen in this investigation.

Table 1 shows the mix proportions of cement paste and mortar used in this study. To investigate the influence of the water-cement ratio (W/C) and the volume of fine aggregate (S/C) on the degradation process, the specimens were prepared at only W/C=55 % and two S/C ratios (S/C=0.0 is cement paste and S/C=2.5 is cement mortar). And in this study's mix proportion may easily cause material segregation because of high W/C, alkyl aryl sulfonate and alkyl ammonium salt based thickening agent, which is usually used in self-compacting concrete, was used to prevent the material segregation.

Table 1. Mix Proportions

name	water-cement ratio W/C (%)	sand-cement ratio S/C	Air (%)	unit content (kg/m^3)			
				water W	cement C	sand S	thickening agent
55P	65	0	5	607	1150	0	25
55M	55	2.5	5	290	550	1374	12

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 ϕ50 x 100 mm cylinder mold form. Test pieces were kept in a moist room, then, they were deformed 24 hours after casting. After the deformation, the test pieces were cured under temperature controlled water at 20°C for up to 28 days. After curing, the test pieces were cut and shaped in a ϕ50 x 10 mm discoid shape using a diamond disk cutter. The cut test pieces were kept in tapped water at 20°C for five days to eliminate the water absorption of test pieces caused by drying at the beginning of the immersion test.

2.3 METHOD OF IMMERSION TEST. A plastic container, which is not affected by acid solutions, was used for immersion test. The test pieces were placed in the containers, and filled with enough solution to immerse the exposure faces completely. The solutions used were about 15 litters for each container, and the ratio of the test piece and solution were prepared about 150 by volume. The ambient temperature of the immersion test was determined at 20°C. The test duration was limited to 120 minutes and scrub surface of test pieces for the immersion test period at the frEquency once every 20 minutes, 40 minutes, 60 minutes and 120 minutes were adopted as the exposure conditions. Details are shown in Figure 1.
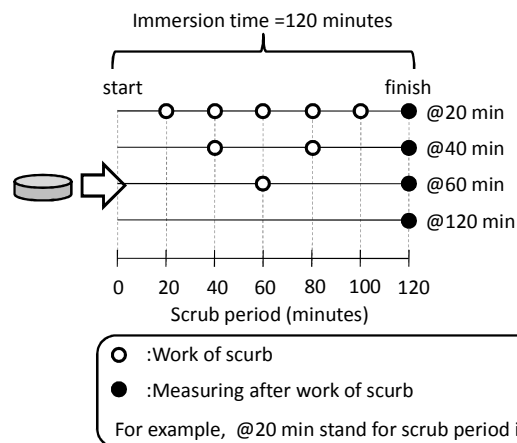
Figure 1. Details of immersion test with scrub

2.4 TYPES OF SOLUTION. A sulfuric acid solution was used to simulate the various acidic environments while a hydrochloric acid – sulfuric acid and nitric acid – sulfuric acid mixed with aqueous solution. In this study, solution contained hydrochloride acid and sulfuric acid named by [CS] and solution contained nitric acid and sulfuric acid named by [NS]. And, this study's position as the accelerated test, pH of solutions unified 0.30(i.e. [H+] =0.50 mol/L).

2.5 MEASUREMENTS. Measurements of the mass decrease rate and ratio of mass decrease rate of test pieces were carried out after the immersion test. a) and b) are detailed of mass decrease rate (Eq.1) and ratio and mass decrease rate (Eq.2).

$$R = \frac{W_0 - W_1}{W_0} \times 100 \tag{1}$$

Here, R is mass decease rate. W_0 is mass of test piece before it is deteriorated. W_1 is mass of test piece after it is deteriorated. Additionally, if mass decrease rate of sulfuric acid acting hardened cement, it is written $R_{sulfuric\ acid}$ and mass decrease rate of CS1 acting to hardened cement is expressed, it is written R_{CS1}.

$$r_{mixed\ acid} = \frac{R_{mixed\ acid}}{R_{sulfuric\ acid}} \tag{2}$$

Here, r is ratio of mass decrease rate. $R_{mixed\ acid}$ is mass decrease rate of test piece that immersed in mixed acid [i.e. sulfuric acid, hydrochloric acid, nitric acid, CS, NS]. Therefore, if $R_{mixed\ acid}$ is $R_{sulfuric\ acid}$, $r_{mixed\ acid}$ is named $r_{sulfuric\ acid}$ and $r_{sulfuric\ acid} = 1.0$.

3. HARDENED CEMENT DETERIORATED BY ONE ACID

3.1 EXPERIMENTAL RESULT. Figure 2 shows relationship between kind of acid and mass decrease rate. At first, mass decrease rate of test piece that immersed in hydrochloric acid or nitric acid is larger than mass decrease rate of test piece that immersed in sulfuric acid. Secondly, when same acid is used by immersion, the shorter scrub period is, the larger mass decrease rate is. The reason of these phenomena is kind of product of chemical reaction and amount of product.
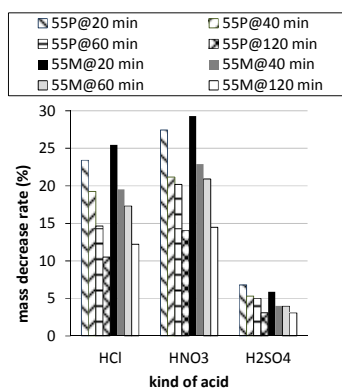
Figure 2. Relationship between kind of acid and mass decrease rate

3.2 THEORETICAL DISCUSSION. Here, sulfuric acid, hydrochloric acid or nitric acid reacts with hardened cement, gypsum, calcium chloride or calcium nitrate is produced respectively to showing Eq.3, Eq.4 and Eq.5.

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 \cdot 2H_2O \tag{3}$$

$$Ca(OH)_2 + HCl = CaCl_2 + 2H_2O \tag{4}$$

$$Ca(OH)_2 + HNO_3 = Ca(NO_3)_2 + 2H_2O \tag{5}$$

When product of chemical reaction is calcium chloride or calcium nitrate, these products are fusibility. Therefore, speed of mass decrease is high because products don't deposit on surface layer of hardened cement. Conversely, product of chemical reaction is gypsum, this is difficult solubility. Therefore, speed of mass decrease is low because product deposit on surface layer of hardened cement. This discussion of solubility or not is explained by change in Gibbs free energy. For example, Eq.6 is calculation result of change in free energy of fusibility of Eq.3's product. And, Eq.7 and Eq.8 is calculation result of change in Gibbs free energy of fusibility of Eq.4's product and fusibility of Eq.5's product respectively. And the value of Gibbs free energy referred to chemical handbook [The Chemical Society of Japan, 2004.].

$$\Delta G(CaSO_4 \cdot 2H_2O) = \{-553.6+ (-744.5)\} - (-1321.86) = 24.7 \text{ kJ mol}^{-1} \tag{6}$$

$$\Delta G(CaCl_2) = \{-553.6+(-131.2)\} - (-748.1) = -67.9 \text{ kJ mol}^{-1} \tag{7}$$

$$\Delta G(Ca(NO_3)_2) = \{-553.6+(-108.7)\} - (-748.1) = -27.8 \text{ kJ mol}^{-1} \tag{8}$$
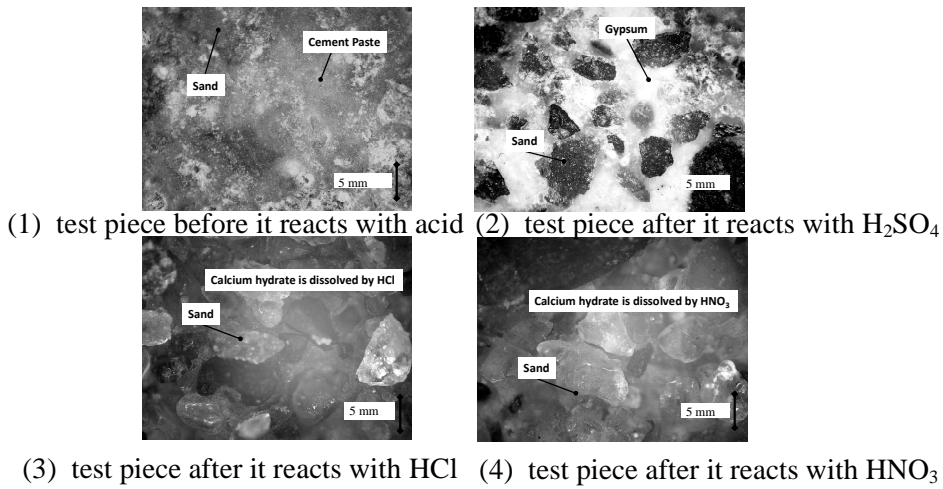
Here, ΔG is change in Gibbs free energy.

If change in Gibbs free energy is minus, its chemical reactions advance automatically. Conversely, change in Gibbs free energy is plus, its chemical reactions cannot advance automatically.

Figure 3 shows photograph of the surface of hardened cement after deterioration by some acid taken by the microscope. Actually, can be confirmed calcium chloride and calcium nitrate are dissolve and gypsum is not dissolve by the visual contact.

In the next place, discuss about scrub period. If scrub period is short, amount of product on the surface layer of hardened cement is light. And if amount of product on the surface layer of hardened cement is light, the influence of diffusion of acid into product becomes small. It means that this phenomenon is nearly reaction-controlled, not diffusion-controlled. As a result, when scrub period is short, speed of mass decrease is high.

Summarize the results, effect of fusibility and amount of product on hardened cement deteriorate by one acid is very large and hardened cement deteriorate by one acid can be predict by organizing this effect.

(1) test piece before it reacts with acid (2) test piece after it reacts with H_2SO_4

(3) test piece after it reacts with HCl (4) test piece after it reacts with HNO_3

Figure 3. Photograph of the surface of hardened cement after deterioration

4. HARDENED CEMENT DETERIORATED BY MIXED ACID

4.1 EXPERIMENTAL RESULT. In actual environment, condition of acid acting to hardened cement is often mixed acid. In this chapter, mixed acid made to react to hardened cement, and deterioration mechanism is organized by experimentally. Figure 4 shows relation between x_{H2SO4} and ratio of mass decrease rate (r). It can be observed that sulfuric acid strongly influences deteriorates by mixed acid from Figure 4. Therefore influence of sulfuric acid is not influenced amount of product on surface layer of hardened cement.
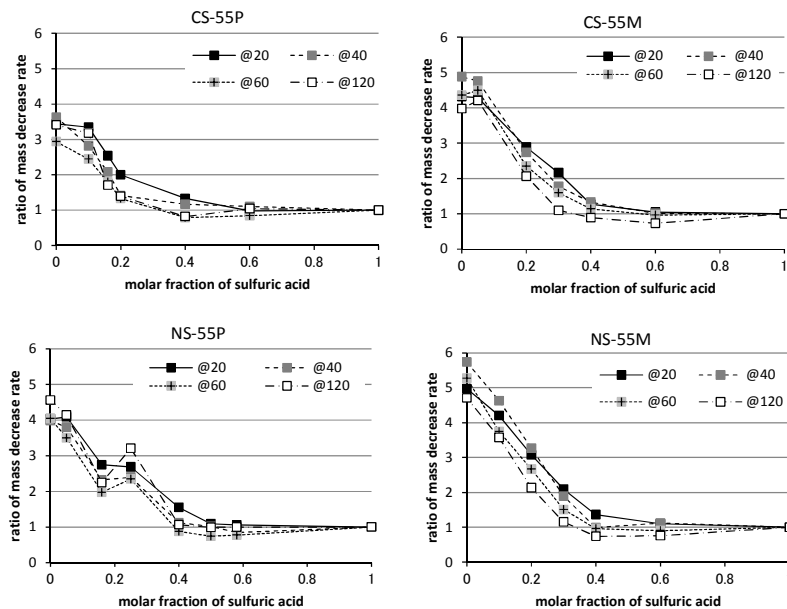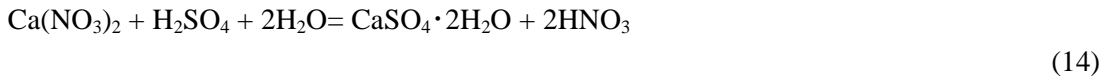

Figure 4. Relation between mole fraction of sulfuric acid and ratio of mass decrease rate

4.2 THEORITICAL DISCUSSION. In this section, deterioration mechanism of hardened cement chemically damaged by mixed acids is organized by change of Gibbs free energy and chemical kinetics. At first, CS or NS made to react to hardened cement, the following chemical reactions shown by Eq.9-Eq.11 or Eq.12-Eq.14 are advanced respectively based on change of Gibbs free energy.

i) In the case of CS made to react to hardened cement

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 \cdot 2H_2O \qquad (9)$$

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O \qquad (10)$$

$$CaCl_2 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + 2HCl \qquad (11)$$

ii) In the case of NS made to react to hardened cement

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 \cdot 2H_2O \qquad (12)$$

$$Ca(OH)_2 + HNO_3 = Ca(NO_3)_2 + 2H_2O \qquad (13)$$

$$Ca(NO_3)_2 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + 2HNO_3$$

$$(14)$$

Thus, gypsum is produced by priority in each chemical reaction. Therefore, sulfuric acid strongly influences hardened cement deteriorates by reaction with mixed acid.

In the next place, discuss about increase of r. r increases when x_{H2SO4} becomes small less than about 0.40 from Fig.5. This phenomenon is discussed by chemical kinetics. The outline of chemical kinetics is shown below. For example, if AB is produced as A reacts with B shown by Eq.15. This reaction velocity of produce AB is expressed by chemical kinetics, shown by Eq.16 [Shigeo Shibata, 2004.].

$$\alpha A + \beta B = \gamma AB$$

$$(15)$$

$$\frac{\partial [AB]}{\partial t} = \frac{1}{\gamma} k [A]^{\alpha} [B]^{\beta}$$

$$(16)$$

Here, [A] is an activity of A. [B] is an activity of B. [AB] is an activity of AB. α is a chemical amount of A. β is a chemical amount of B. γ is a chemical amount of C. k is a kinetic constant.

And here, CS made to react to hardened cement based on chemical kinetics. If Eq.10-Eq.11 follow Eq.16, it is possible to express Eq.17-Eq.18 by chemical kinetics.

$$\frac{\partial [CaCl_2]}{\partial t} = k_{CaCl2} [Ca(OH)_2] \, x_{HCl}^2$$

$$(17)$$

$$\frac{\partial[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]}{\partial t} = k_{\text{CaSO4·2H2O}}[\text{CaCl}_2] \, x_{\text{H2SO4}} \tag{18}$$

Here, $[\text{CaCl}_2]$ is an activity of CaCl_2. $[\text{Ca(OH)}_2]$ is an activity of Ca(OH)_2. $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$ is an activity of CaSO_4. xHCl is a mole fraction of HCl. x_{H2SO4} is a molar fraction of H_2SO_4. k_{CaCl2} is a kinetic constant of Eq.17. $k_{\text{CaSO4·2H2O}}$ is a kinetic constant of Eq.18.

If reaction velocity of CaCl_2 shown by Eq.17 is faster than reaction velocity of $\text{CaSO}_4.2\text{H}_2\text{O}$ shown by Eq.18, a part of finished products becomes CaCl_2. As I have described previously, CaCl_2 is fusibility. So CaCl_2 easily melts to solution and becomes calcium ion (Ca^{2+}). It is thought that rCS increases because of this reason. Therefore, Eq.18 is subtracted from Eq.17, and it is defined as amount of Ca^{2+} in finished products, shown by Eq.19.

$$\frac{\partial[\text{Ca}^{2+}]}{\partial t} = k_{\text{CaCl2}}[\text{Ca(OH)}_2] \, x_{\text{HCl}}^2 - k_{\text{CaSO4·2H2O}}[\text{CaCl}_2] \, x_{\text{H2SO4}} \tag{19}$$

Here, Ca(OH)_2 and CaCl_2 are solids. Therefore, in this study, activity of Ca(OH)_2 and CaCl_2 [i.e. $[\text{Ca(OH)}_2]$ and $[\text{CaCl}_2]$] hypothecated 1.0.And Eq.10 and Eq.11 are neutralization that react promptly. Therefore, in this study, it was hypothecated $k\text{CaCl}_2$ Equal $k_{\text{CaSO4·2H2O}}$. If these hypotheses are reflected in Eq.19, it becomes Eq.20.

$$\frac{\partial[\text{Ca}^{2+}]}{\partial t} = k \, x_{\text{HCl}}^2 - k \, x_{\text{H2SO4}} \tag{20}$$

And to show Eq.20 in the ratio, it divides by Eq.20 in the case of $x_{\text{HCl}} = 1.0$. When this is calculated, it becomes Eq.21.

$$\frac{\partial[\text{Ca}^{2+}]}{\partial t} = x_{\text{HCl}}^2 - x_{\text{H2SO4}} \tag{21}$$

Moreover, because the relation of Eq.22 is approved for molar fractions, Eq.23 is approved.

$$x_{\text{HCl}} + x_{\text{H2SO4}} = 1.0 \tag{22}$$

$$S_{\text{CS}} = x_{\text{H2SO4}}^2 - 3x_{\text{H2SO4}} + 1 \tag{23}$$

Here, S_{CS} is ratio of dissolution speed of CaCl_2.

Eq.23 shows ratio of dissolution speed of CaCl_2. In the case of NS made to react to hardened cement, the similar to case of CS is possible. Therefore, in the case of NS made to react to hardened cement, dissolution speed of $\text{Ca(NO}_3)_2$ can be defined by Eq.24.

$$S_{\text{NS}} = x_{\text{H2SO4}}^2 - 3x_{\text{H2SO4}} + 1 \tag{24}$$

Here, S_{NS} is ratio of dissolution speed of $\text{Ca(NO}_3)_2$.

Then validity of this theory is calculated by using Eq.23. Figure 5 shows relationship between calculation value and experimental value in the case of CS made to react to hardened cement paste with scrub period is 20 minutes. And average of correlation coefficient equal to 0.97 is obtained as a result of confirming the correlation of calculation value and experimental value.
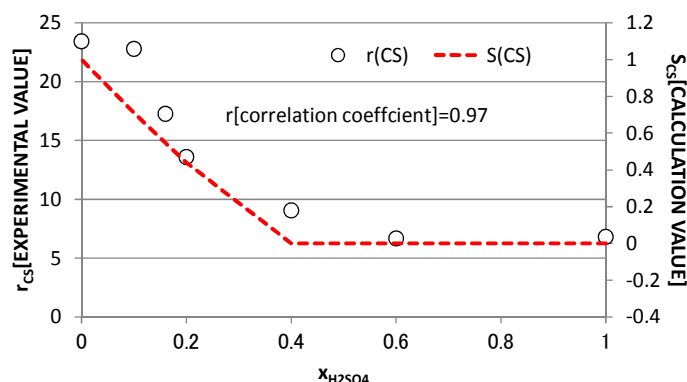
Figure 5. Relationship between S_{CS} [calculation value] and r_{CS} [experimental value] about CS – 55P - @20 min

5. CONCLUSIONS

In this study, objective of study was (1) to clarify experimentally the relation between molar fraction of contained material at mixed acids and mass decrease rate of hardened cement deteriorated by mixed acids and (2) these relations are arranged with physical chemistry theories.

In the result, some of the following were clarified.

1.   In the case of H_2SO_4 react to hardened cement, calcium sulfate is produced with the chemical reaction. Here, calcium sulfate is difficult solubility compound. Therefore speed of mass decrease is low, because culcium sulfate deposit on the surface layer of hardened cement.

2.   In the case of HCl react to hardened cement, calcium chloride is produced with the chemical reaction. Here, calcium chloride is fusibility compound. Therefore speed of mass decrease is high, because calcium chloride does not deposit on the surface layer of hardened cement.

3.   In the case of HNO_3 made to react to hardened cement, calcium nitrate is produced with the chemical reaction. Here, calcium nitrate is fusibility compound. Therefore speed of mass decrease is high, because calcium nitrate does not deposit on the surface layer of hardened cement.

4.   In the case of CS or NS made to react to hardened cement, ratio of mass decrease rate (r_{CS} or r_{NS}) are depended in a large part on sulfuric acid when value of mole fraction of sulfuric acid is between about 0.4 and 1.0 and in the case of CS or NS

made to react to hardened cement, ratio of mass decrease rate increases compared with in the case of sulfuric acid made to react when value of molar fraction of sulfuric acid is between 0.0 and about 0.4.

5.   In the case of CS or NS react to hardened cement, ratio of mass decrease rate (r_{CS} or r_{NS}) can be estimated by change in Gibbs free energy and chemical kinetics.

6.ACKNOWLEDGEMENT

7. REFERENCES

Current Status of Research on Chemical Corrosion and Leaching of Concrete, Concrete Technology Series, Japan Society of Civil Engineering, No. 53, pp. 3-12, 2003 (In Japanese).

J. Monteny, N. De Belie, E. Vincke, W. Verstraete and L. Taerwe: Chemical and microbiological tests to simulate sulfuric acid corrosion of polymer-modified concrete, Cement and Concrete Research, Vol. 31, No. 9, pp. 1359-1365, 2001.

Z. Changa, X. Song, R. Munn and M. Marosszeky: Using limestone aggregates and different cements for enhancing resistance of concrete to sulfuric acid attack, Cement and Concrete Research, Vol. 35, No. 8, pp. 1486-1494, 2005.

I. Kurashige: Concrete Deterioration Mechanism due to Sulfuric Acid and its Prediction Method, University of Tokyo Doctoral Thesis, 2002 (In Japanese).

W. Sand and E. Bock: Concrete Corrosion in the Hamburg Sewer System, Environmental Technology Letters, No. 5, pp. 517-528, 1984.

Beddoe Robin E, Dorner Horst W: Modelling acid attack on concrete: Part 1 the essential mechanisms, Cement and Concrete Research, Vol. 35, No. 12, pp. 2333-2339, 2005.

The Chemical Society of Japan: Chemical Handbook basic edition Part 2 fifth edition, pp.291-314, 2004.

Shigeo Shibata: Basis of physical chemistry, KYORITSU SUPPAN CO, LTD, 2004