STUDY ON LONG TERM CONCRETE DETERIORATION DUE TO SULFURIC ACID

Yutaka OOKAME[1], Yuji HATANO[2] and Kenji KAWAI[3]

[1,2,3]*Hiroshima University, Japan*
[*1,*2,*3] *1-3-2 Kagamiyama Higashi-Hiroshima, Hiroshima 739-8511 Japan ,*
[*1]*d135636@hiroshima-u.ac.jp*
[*2]*m126849@hiroshima-u.ac.jp*
[*3] *kkawai@hiroshima-u.ac.jp*

ABSTRACT

Recently, the deterioration of concrete caused by sulfuric acid attacks in sewage and waste water treatment plants has been reported. In this study, prismatic concrete (W/B=0.55) specimens in which a part of cement was replaced with blast furnace slag, fly ash and silica fume were prepared. There were coated with acid-resistant epoxy-acrylic resin and immersed in flowing (0.7~0.9 m/s) sulfuric acid solution of concentrations 2 mol/L, 1 mol/L, 0.09 mol/L and 0.006 mol/L, and the effects of the flow of solution as well as the use of mineral admixtures were investigated. The results showed that there was a linear relationship between the CaO and both the duration before the beginning of peeling of concrete as well as the erosion rate.

Keywords. Sulfuric acid, Blast furnace slag, Fly ash, Silica fume, Deterioration

INTRODUCTIONS

Recently the deterioration of concrete caused by sulfuric acid attacks in sewage and waste water treatment plants has been reported. The deterioration of concrete by sulfuric acid attacks can be characterized by the erosion of concrete due to sulfuric acid and erosion caused by the expansion of products due to the reaction of the calcium compounds in concrete with sulfuric acid. As a countermeasure to this deterioration, the development of acid resistant cementitious material using multiple mineral admixtures for the purpose of inhibiting the production of calcium hydroxide is performed. It has been confirmed that the multiple use of mineral admixtures can significantly reduce the erosion due to sulfuric acid attacks (SOEDA 1991), but investigations on the performance of such materials have not been carried out enough. It is thought that both the understanding of the performance of acid resistant cementitious material, and the evaluation of the resistance to sulfuric acid for these types of materials can lead to the development of much higher-quality acid resistant cementitious materials. On the other hand, it is thought that the flow of sewage materials accelerates the deterioration of concrete caused by sulfuric acid. This study aimed at clarifying the effect of the flow of fluid on concrete deterioration caused by sulfuric acid attack, together the effect of the use of mineral admixtures.

Table 1. The material properties

Names		sign	Type/property
Cement		NC	Ordinary Portland cement / Density: 3.16 g/cm^3 / Specific surface area: 3,360 cm^2/g
Fine aggregate		S	Crushed quartz / Surface-dry density: 2.60 g/cm^3 / Absorption:1.06 %
Coarse aggregate		G	Crushed gravel (Sandstone) / Surface-dry density: 2.62 g/cm^3 / Absorption: 0.69%
Mineral admixture	Blast furnace slug	B	Blast furnace slug / Density: 2.91 g/cm^3 / Specific surface area: 4,520 cm^2/g
	Fly ash	F	Fly ash / Density: 2.34 g/cm^3 / Specific surface area: 3,820 cm^2/g
	Silica fume	S	Silica fume / Density: 2.25 g/cm^3 / Specific surface area: 16.5 m^2/g
Chemical admixtures			

Table 2. Major chemical components of cementitious material

Component parts (%)	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$
Ordinary Portland cement	20.7	5.6	3.1	63.3	2.1	2.3
Blast furnace slug	33.8	14.7	0.3	42.5	6.2	0.07
Fly ash	55.7	26.1	5.5	6.4	1.4	1.5
Silica fume	94.1	-	-	0.3	0.6	0.5

EXPERIMENTAL OVERVIEW

Preparation of specimens and curing conditions. Table 1 shows the material properties. Normal Portland cement, blast furnace slag, fly ash and silica fume were used for the binding material. The major chemical components are shown in Table 2. Table 3 shows the mixture proportions of Prismatic concrete specimens of sizes 100×100×400 mm (W/B=0.55) were prepared and demolded for 24 hours, and thereafter were cured in water of 20 degrees for 28 days. At the age of 28 days, each piece was cut into three equal pieces and the sides were coated with acid-resistant epoxy-acrylic resin as shown in Figure 1. Table 4 shows the replacement ratios of the mineral admixtures. The abbreviations BFS denotes blast furnace slug, FA represents fly ash, and SF represents silica fumes.

Experimental methodology. After curing for 28 days, the specimens were soaked in acetone to stop hydration reaction. They then de-aerated using a vacuum deaerator and thereafter pulverized until fine consistency. The amount of calcium hydroxide was measured

Table 3. Mixture proportion of concrete specimens

Maximum size of coarse aggregate	Slump (cm)	Air content (%)	W/B	Unit content （kg/m^3）			
				Water	Binding material	Fine aggregate	Coarse aggregate
20	10	5.0	0.55	174	316	830	998

Table 4. Concrete specimen name and replacement rate of each mineral admixture

Names	OPC	B	F	S
NC	100	-	-	-
B30	70	30	-	-
F30	70	-	30	-
S20	80	-	-	20
B30F30	40	30	30	-
B30S20	50	30	-	20
F30S20	50	-	30	20
B30F30S20	20	30	30	20

100mm
100mm
400mm
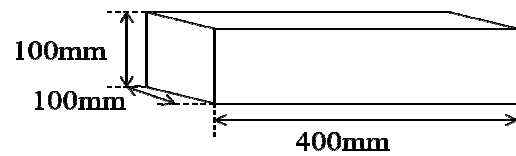
Coated with acid resistant epoxy-acrylic resin
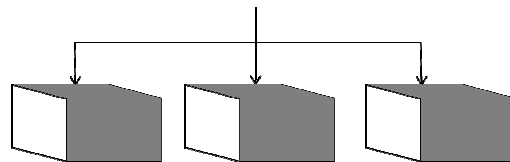
Figure 1. Outline of the specimens

using TG-DTA, and the pore volume of the fine pulverized specimens was measured using Mercury Intrusion Porosimetry. After the specimens were coated with acid-resistant epoxy-acrylic resin, they were immersed in flowing (0.7 ~ 0.9 m/s) sulfuric acid solutions of concentrations 2 mol/L, 1 mol/L, 0.09 mol/L and 0.006 mol/L, and for comparison purposes, some specimens were immersed in non-flowing sulfuric acid solution. The erosion depth and neutralization depth of each specimen were measured using a vernier caliper with a minimum graduation of 0.05 mm, while the mass loss was measured using a mass meter of minimum graduation of 0.1 g at fixed durations. Erosion depth here is defined as the difference between the original length of the specimen and the length measured after erosion. In the case where the deterioration products remained attached to the concrete specimen's surface at the time of measurement, they were considered as a part of the concrete specimens and were not removed. Result of the measurement was used average results of each measurement point. Then neutralization length was measured using phenolphthalein.
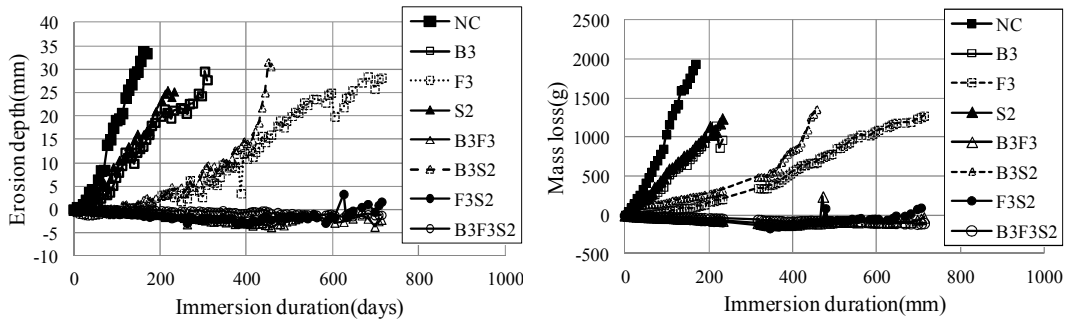
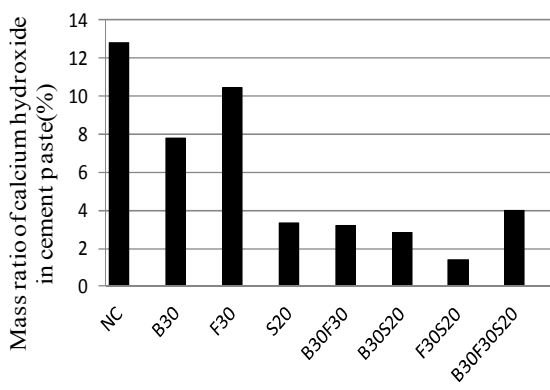**Figure 2. Erosion depth and mass loss in the non-flowing sulfuric acid solution of concentration 2 mol/L**
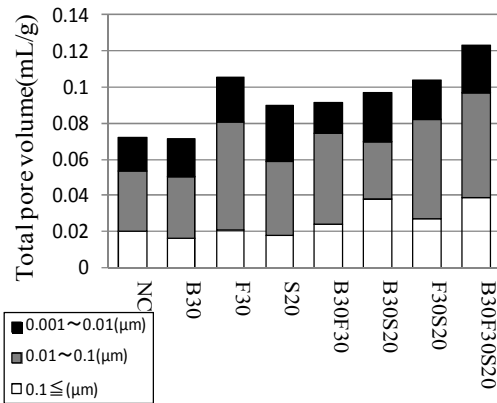

Figure 3. Mass ratio of calcium hydroxide

Figure 4. Total pore volume (of mortar)

EXPERIMENTAL RESULTS

The effects of using mineral admixtures. Figure 2 indicates both the results of all the composition's erosion depth and the mass loss of concrete specimens immersed in the non-flowing sulfuric acid solution of concentration 2 mol/L. According to Figure 2, the beginning of the peeling of concrete with the mineral admixture begins at later ages compared to NC. Figure 3 indicates calcium hydroxide ratio of mass in the cement paste while Figure 4 indicates total pore volume at the age of 28 days for all the mixture proportions. According to Figure 3 and Figure 4, the mass ratio of calcium hydroxide decreases and the amount of total pore volume increases in the case where mineral admixtures were used. Based on these, the results in Figure 2 can be explained by the decrease in expansion caused by reaction of CaO and sulfuric acid and the presence of large pore volumes in the specimens with mineral admixtures. Figure 5 and Figure 6 indicates the neutralization depths of concrete specimens immersed for 28 days in non-flowing sulfuric acid solutions of concentrations 0.09 mol/L and 2 mol/L. According to Figure 5, the neutralization depth of concrete specimens immersed in the sulfuric acid solution of concentration 0.09 mol/L was large in the case where the mineral admixtures were used. According to Figure 4, the total pore volume was also large in the case where mineral admixtures especially Fly ash or Silica fume were used, compared to NC. This implies that
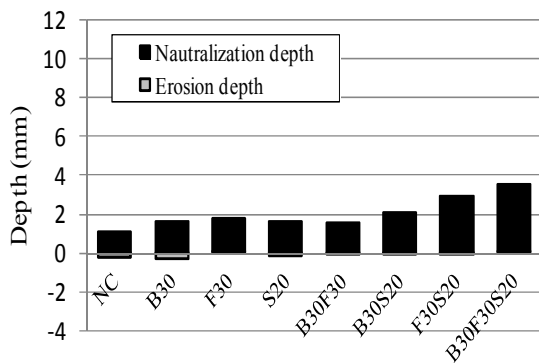
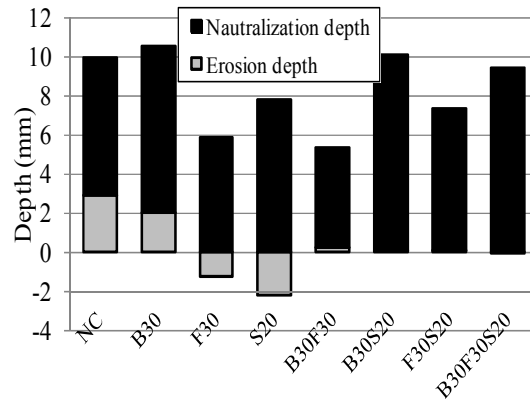**Figure 5. Neutralization depth (0.09mol/L)**

Figure 6. Neutralization depth (2mol/L)

the diffusion of sulphate ion was quickened by use of mineral admixtures, and hence neutralization depth was large. However, compared to the neutralization depths of the concrete specimens immersed in high concentrations of sulfuric acid solution, a different trend was observed. According to Figure 6 contrary to what was observed in Figure 3, there was no observable relationship between total pore volume and neutralization depth. This could be due to the peeling of concrete from specimens which resulted in the diffusion of sulphate ions for longer distances than in the specimens where peeling of concrete did not take place. These results show that the neutralization caused by sulfuric acid was reduced by use of mineral admixtures, especially where the specimens were exposed to high concentrations of sulfuric acid.

The effects of concentration of sulfuric acid. Figure 7 indicates both the erosion depth and the mass loss of concrete specimens immersed in the non-flowing sulfuric acid solution of concentration 0.09 mol/L while Figure 8 indicates both the erosion depth and the mass loss of concrete specimens immersed in the non-flowing sulfuric acid solution of concentration 0.006 mol/L. According to Figure 7, deterioration was observed to decrease in the case where mineral admixtures were used, which is similar to the trend observed in Figure 2. However, mass loss in NC specimens was not observed until around 1000 days, and thereafter repeated deterioration occurred for a while. From Figure 8, there was no observable deterioration in the specimens, however, these results show the average values of all the specimens. Figure 9 indicates both the results of erosion depth and mass loss for all B30 specimens immersed in the non-flowing sulfuric acid solution of concentration 0.006 mol/L. From this Figure, in the first stages, the reaction between sulfuric acid and CaO is taking place therefore there was no observable mass loss, but at around the age of 750 days, the mass of specimens began to decrease At present, the mass of one of the three specimens is smaller than the initial value. It was also observed that concrete surface immediately after peeling became yellowish-brown in colour, therefore ~~so~~ it is thought that peeling was occurring at the border between the coloured and the unaffected region, which represents neutrality. In conditions of low concentration of sulfuric acid, the peeled concrete at a time was thick. It is estimated that a gypsum layer thickens through the reaction of sulfuric acid with CaO and that the layer peels due to its own dead weight.
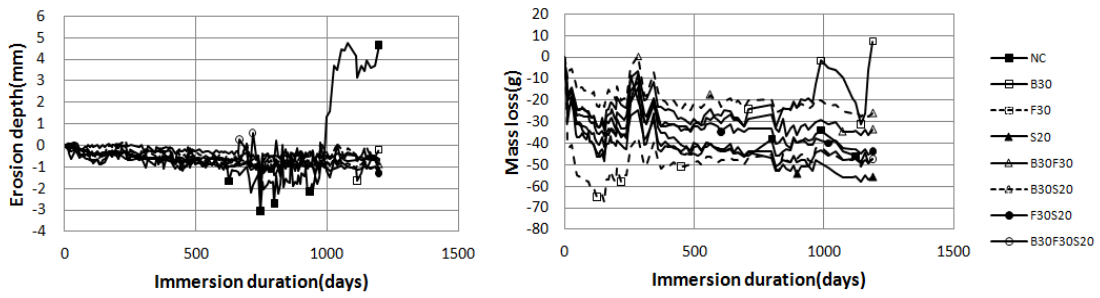
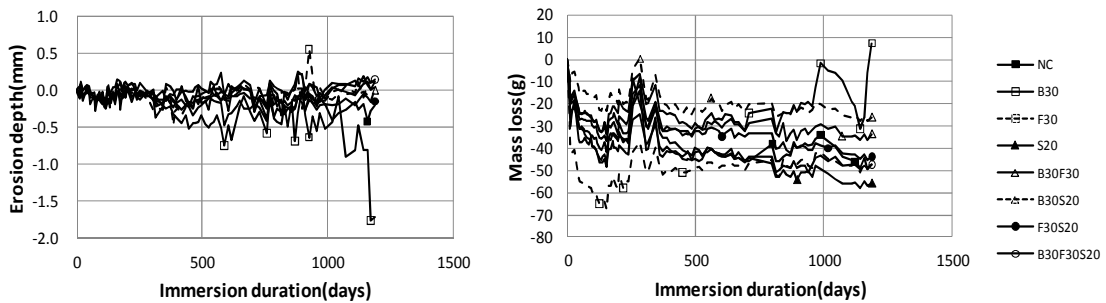**Figure 7. Erosion depth and the mass loss (0.09 mol/L non-flowing)**

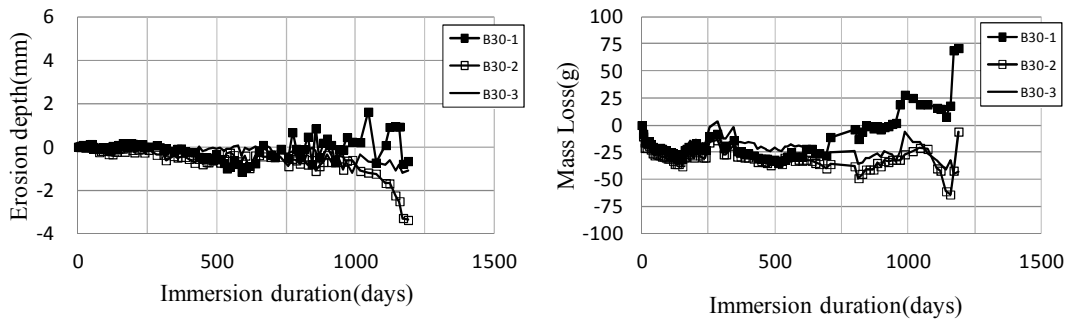**Figure 8. Erosion depth and the mass loss (0.006 mol/L non-flowing)**

Figure 9. Erosion depth and the mass loss of B30 (0.006 mol/L non-flowing)

Compared to these, the trend observed in Figure 2 is thought to have been due to the reaction of CaO in concrete with sulfuric acid. Based on these, the results of the accelerated deterioration tests did not show the same phenomenon as would be observed in real conditions, however, the resistance of deterioration by using mineral admixtures is similar in both high and low concentrations of sulfuric acid. There was no observable deterioration in the other specimens, and for this reason continued observation is necessary.
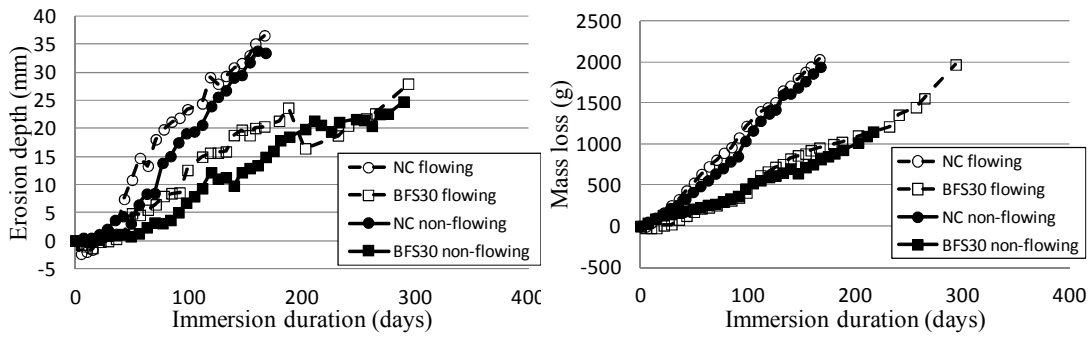
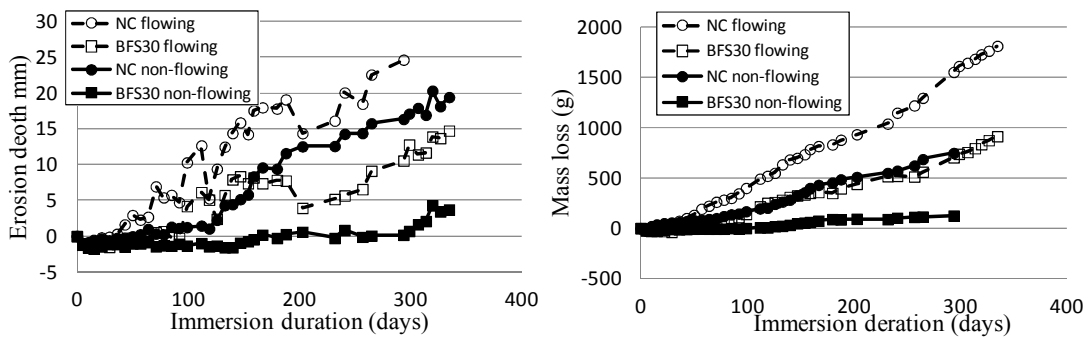**Figure 10. Erosion depth and the mass loss of NC and B30 (2 mol/L)**

Figure 11. Erosion depth and the mass loss of NC and B30 (1 mol/L)
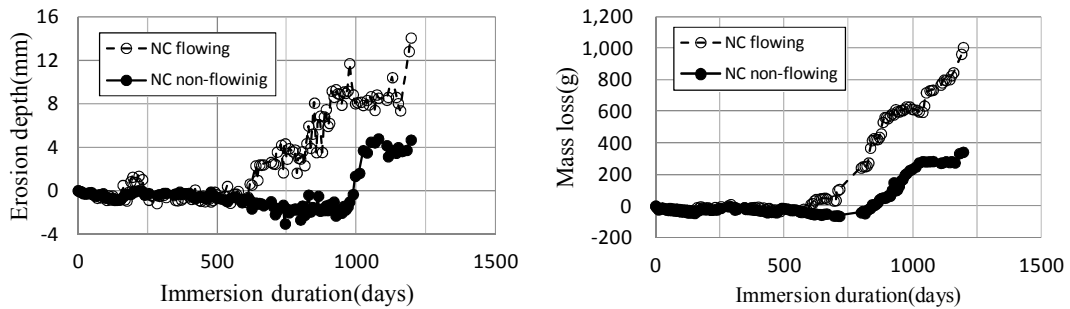

Figure 12. Erosion depth and the mass loss of NC (0.09 mol/L)

Effects of a flowing solution. Figure 10 indicates the erosion depth and mass loss of the NC and BFS30 concretes immersed in both the non-flowing sulfuric acid solution and in the flowing sulfuric acid solution of concentration 2 mol/L. Figure 11 indicates the results of a concentration of 1 mol/L. According to Figure 10, there were no observable erosion differences between
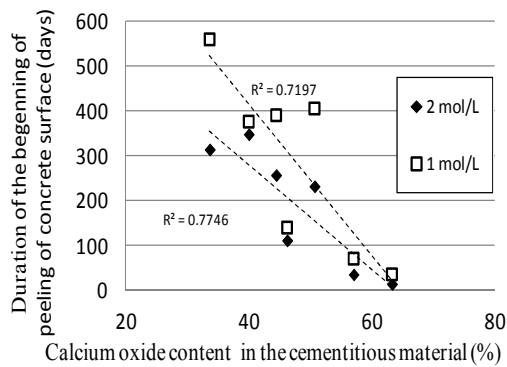
Figure 13. Relationship between CaO content and duration before peeling
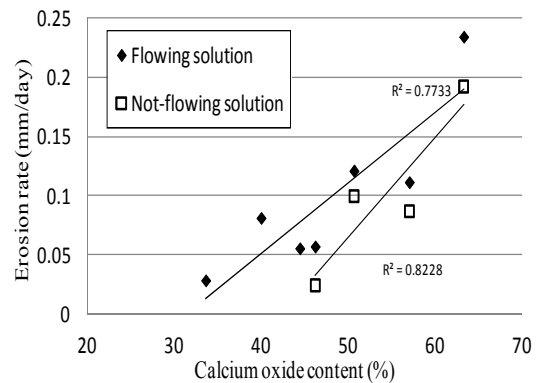

Figure 14. Relationship between CaO content and erosion rate

specimens either in the flowing solution or in the non-flowing solution. However, according to Figure 11, the specimens immersed in the flowing solution were more eroded than those in the non-flowing solution. As mentioned above, changes in the amount of erosion were observed in the lower concentration 1 mol/L, as opposed to the higher concentration 2 mol/L. This difference is thought to have been as a result of shearing in the flowing solution of the concentration of 1 mol/L. The erosion depths of the specimens of the other concretes could not be observed, and for this reason, measurements in the future should be carried out for a longer period of time. Figure 12 indicates the results of erosion depth and mass loss of the NC immersed in the flowing sulfuric acid solution of concentration of 0.09 mol/L. According to Figure 12, the specimens immersed in the flowing solution were more eroded than those in the non-flowing solution. These results were similar to the results of concerning the erosion depth and the mass loss of specimens immersed in the sulfuric acid solution of concentration 0.09 mol/L. In addition, the beginning of the peeling of concrete from the specimens immersed in the flowing solution was quicker than those immersed in the non-flowing solution.

Quantitative estimation of concrete using mineral admixtures. In this study, the deterioration of concrete caused by sulfuric acid attacks was considered to consist of two parts. One was the duration of the expansion, which indicates both the period of diffusion of sulfuric acid ions into the concrete specimens and the reaction of sulfuric acid ions with calcium oxide. The product of this reaction has a larger volume than the reactants. This part is also defined as the duration before the beginning of the peeling of the concrete from the specimens' surface. The second part was the duration of the erosion. As a consideration of these durations, Figure 9 indicates the relationship between the duration before the beginning of the peeling of the concrete specimens surface immersed in the flowing sulfuric acid solution concentration of 2 mol/L and 1 mol/L and the calcium oxide content-in the cementitious materials and Figure 10 indicates the relationship between the erosion rate and the calcium oxide content in the cementitious materials. In this case, since the deterioration

of the concrete specimens was at an advanced stage, the erosion rate was calculated by a linear approximation as provided in JSCE (2010). According to Figure 9, it is observed that the beginning of the peeling of the concrete from the specimens started at later ages in the cases where mineral admixtures were used, and erosion was reduced with increases in the amount of mineral admixtures in the case of the concentration of 1 mol/L. According to Figure 10, the erosion rate was observed to decrease with increases in mineral admixtures, and this was more effective in the case of the non-flowing solution compared to the flowing solution. This was due to the lesser amount of calcium oxide in the concrete specimens with mineral admixtures. According to Figure 9 and Figure 10, it is found that the evaluation of the beginning of the erosion of the concrete specimens due to sulfuric acid is possible if the amount of calcium oxide present in the concrete is known.

CONCLUSIONS

- The deterioration of concrete caused by sulfuric acid was reduced by the use of mineral admixtures.

- The flowing effect of a solution promoted the deterioration of concrete.

- The peeling of gypsum from the surface of specimens started at later ages in the cases where mineral admixtures were used, and erosion was reduced with increases in the amount of mineral admixtures.

- The erosion rate decrease with increases in mineral admixtures, and better relationship was observed in the case of the non-flowing solution compared to the flowing solution.

- This study shows the existence of a linear relationship between CaO and both the duration before the beginning of peeling of concrete as well as the erosion rate.

REFERENCES

SOEDA, M., YAMATO, T., and EMOTO, Y. (1991). "INFLUENCE OF CONBINED ADMIXTURE ON THE CHEMICAL RESISTANCE OF CONCRETE." *Cement Science and Concrete Technology,* No.45: 228-233