



Service Life Prediction of Concrete Structures Exposed to a Sulfuric Acid Environment

Joong-Kyu Jeon^{1)*}, Han-Young Moon²⁾, Chan-Ki Jeon³⁾, and Jong-Hwa Song¹⁾

¹⁾Kolon E&C R&D Institute, Yongin 449-815, Korea

²⁾Dept. of Civil Engineering, Hanyang University, Seoul 133-791, Korea

³⁾Dept. of Civil Engineering, Incheon City College, Incheon 402-750, Korea

Abstract : In this study, it was investigated the resistance of OPC, 60% GGBS, 20% PFA and 10% SF mortar specimens against sulfuric acid corrosion. As an index for degree of acid corrosion, the corrosion depth was evaluated. Then, it was found that an increase in the duration of immersion and a decrease in the pH, as expected, resulted in a more severe corrosion irrespective of binders; 60% GGBS mortar specimen was the most resistant to sulfuric acid corrosion. From the laboratory testing of sulfuric acid corrosion, an empirical prediction model was suggested as a power function of time and the pH of sulfuric acid, and was applied to an assessment of concrete structures exposed to an acidic environment. It was found that the empirical model gave a more precise prediction of sulfuric acid deterioration of concrete rather than a conventional model, mostly used for predicting carbonation of concrete.

Keywords : sulfuric acid corrosion, deterioration, pH, empirical model, corrosion depth

1. Introduction

The durability of concrete structures subjected to waste treatment, hot spring, or chemical industry is susceptible to chemical corrosion. It was previously reported that acid corrosion of concrete structures, of chemical attack, depends on free water/cement ratio¹⁾ and type of acid.²⁾ In the course of an acid corrosion a layer of corrosive products develops on the surface of cement matrix. Properties of the layer, such as porosity and bulk density, depend on the type of attacking acid, concentration and pH value of acid solution, composition of cement and other factors.³⁾

It is well known that in particular, concrete exposed to a sewer system may be subjected to sulfuric acid corrosion^{4,5)}, which is induced from sulfate-reducing bacteria, generating hydrogen sulfide⁶⁾ then to from sulfuric acid on the surface of concrete structures.^{6,7)}

In predicting acid corrosion of concrete structures exposed to acidic environment, the Fick's 1st law has been preferred due to its simple, convenient application.^{8,9)} However, acid corrosion destroys the concrete pore structure, properties and changes the state of concrete surface, unlike carbonation which does not significantly affect the concrete properties in spite of a chemical reaction between external gases and cement matrix.¹⁰⁾ Moreover, the complexity of acid corrosion may not make it less possible to theoretically model the propagation of acidic deterioration of a concrete structures.

In this study, the sulfuric acid corrosion of ordinary portland cement (OPC), 60% ground granulated blast slag (GGBS), 20% pulverised fuel ash (PFA) and 10% silica fume (SF) mortars was examined to assess the acid deterioration of cement matrix. Then, based on the data from the laboratory experiments, an empirical prediction model was made using an equation in the form of a power function of the time of exposure and the pH of acid. This equation was subsequently applied to acid corrosion of concrete structures exposed to a low pH environment, such as sewer boxes and covered creek concrete structures, in order to predict the residual life of the structures.

2. Experimental work

2.1 Materials and preparation

As binders, OPC, 60% GGBS, 20% PFA and 10% SF were used to manufacture mortar specimens. Their oxide composition is given in Table 1. The mix proportion for binder: water: sand was 1.00 : 0.45 : 2.00. After 28 days curing in tap water at 20±1°C, the specimens were immersed in a sulfuric acid solution for up to 250 days, whose pH ranged 0.5, 1.0, 2.0 and 3.0. The concentration and pH of the sulfuric acid solution were controlled using distilled water, and the solution was calibrated every 2 weeks to maintain the pH of solution.

2.2 Fundamental properties

After immersion of the specimens in the sulfuric acid solutions for 7, 28, 56, 91, 180 and 250 days, the specimens were split and then 1% phenolphthalein solution was sprayed to detect the

*Corresponding author E-mail : jkjeon31@kolon.com
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Table 1 Oxide composition of OPC, GGBS, PFA and SF used in this study

Oxide	OPC	GGBS	PFA	SF
CaO (%)	63.3	41.7	3.4	0.7
SiO ₂ (%)	20.2	31.7	57.6	91.2
Al ₂ O ₃ (%)	5.8	14.5	25.5	1.3
Fe ₂ O ₃ (%)	3.0	0.7	6.1	0.8
MgO (%)	3.4	5.4	0.9	0.3
SO ₃ (%)	2.1	2.1	-	-
Specific gravity	3.15	2.92	2.39	2.20
Fineness (cm ² /g)	3,120	4,450	3,590	204,700

corrosion depth. The corrosion depth could be visually determined by whether or not colour was changed by the indicator. Four measurements were carried out across the section of a specimen and the average value of these measurements was reported in the present study.

3. Prediction model

3.1 Conventional model

Sulfuric acid corrosion of concrete structure exposed to acidic environments has been investigated to predict the corrosion depth and thus the deterioration of structure^{8,9)} For the deterioration chemistry of concrete by ion penetration altogether with its chemical damage to structure, for example carbonation of concrete and sulfuric acid corrosion, diffusion has been considered as a dominant transport mechanism of aggressive ions into concrete¹¹⁾. The Fick's 1st law is preferred to analyse the ionic diffusion as follows:

$$m = -DA \frac{C_1 - C_2}{x} t \quad (1)$$

where m is the amount of ions, D the diffusion coefficient, A the cross-sectional area of media, C_1 the external concentration of ions C_2 the concentration of ions in the media, t the time of exposure and x the depth of penetration. The amount of ions m can be determined by mass flux theory as follows:

$$m = aAx \quad (2)$$

where a is the amount of ions in a unit volume. Hence, the eq. (2) is replaced for the amount of ions m in the eq. (1).

$$aAx = -DA \frac{C_1 - C_2}{x} t \quad (3)$$

Then, the penetration depth x can be calculated and usually expressed in a simpler form.

$$x = \sqrt{\frac{2}{a} D(C_1 - C_2) \times \sqrt{t}} \quad (4)$$

$$x = C\sqrt{t} \quad (5)$$

where the constant C equates $\sqrt{\frac{2}{a} D(C_1 - C_2)}$. This equation is usually used for predicting the carbonation of concrete. However, in the same way, the prediction model of sulfuric acid corrosion of concrete has been suggested and standardized⁹⁾. The diffusivity

of ions within concrete is usually dependent on pore structure and concrete properties: for pore structure, the distribution of pores, their connectivity and tortuosity, and for concrete properties, concrete mix design, mineral admixture and hydration degree. As carbonation, a chemical reaction with hydration products, does not significantly affect pore structure, the square root time dependent model would well accord with the experimental results. In contrast, acid corrosion or/and sulfuric acid corrosion distorts the concrete pore structure and dissolves the cement hydration products.¹²⁾ Moreover, the corroded part of concrete can be taken away and thus the exposed area to an sulfuric acid is changeable with degree of corrosion. Thus it is very difficult to theoretically model an sulfuric acid corrosion of concrete, considering all these factors.

3.2 Empirical model

The present study suggests an empirical model of sulfuric acid corrosion of concrete, based on the data sets for OPC, 60% GGBS, 20% PFA and 10% SF mortars, obtained from 250 days immersion testing in four levels of sulfuric acid concentration. The corrosion depth can be expressed as a power function of time and the concentration of sulfuric acid.

$$d = k \cdot t^n \cdot p^m \quad (6)$$

where d is the corrosion depth, k a constant, t the immersed duration, p the concentration of sulfuric acid (i.e. pH), n the coefficient for the immersed duration, m the coefficient for the sulfuric acid concentration.

Fig. 1 gives the best fit to the results from OPC mortar exposed to an acidic environment of 0.5 in the pH for 250 days, in the power time-dependent model (i.e. empirical model, eq. (6)) and in the square root time-dependent model (i.e. conventional model, eq. (5)). The fit equation and determination coefficient are also given. It is seen that the power time-dependent model more accurately describes the corrosion depth than the square root time-dependent model.

Fig. 2 gives the best fit in the form of $d = k_1 \cdot t^n$ to the

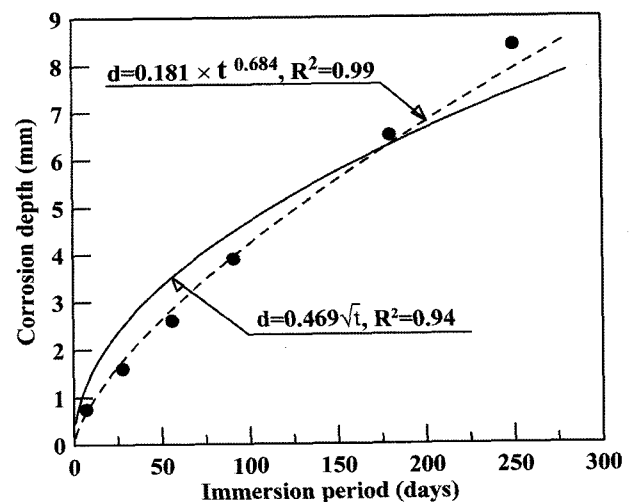


Fig. 1 Corrosion depth of OPC mortar exposed to an sulfuric acid solution of 0.5 in the pH and its best fit in the forms of $d = k \cdot t^n$ and $d = C\sqrt{t}$

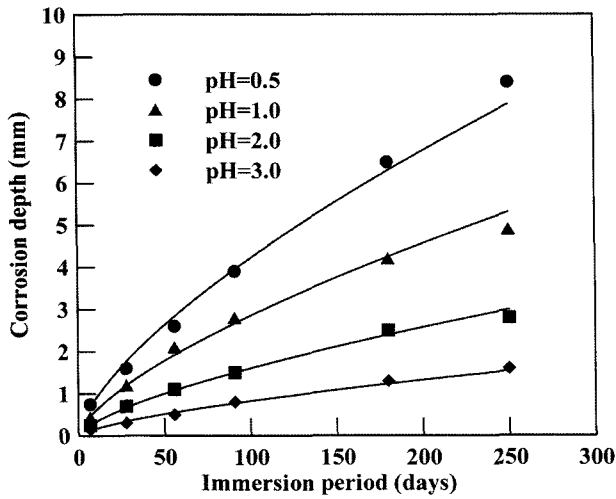


Fig. 2 Corrosion depth of OPC mortar exposed to an sulfuric acid solution of 0.5, 1.0, 2.0 and 3.0 in the pH and its best fit in the form of $d = k_1 \cdot t^n$

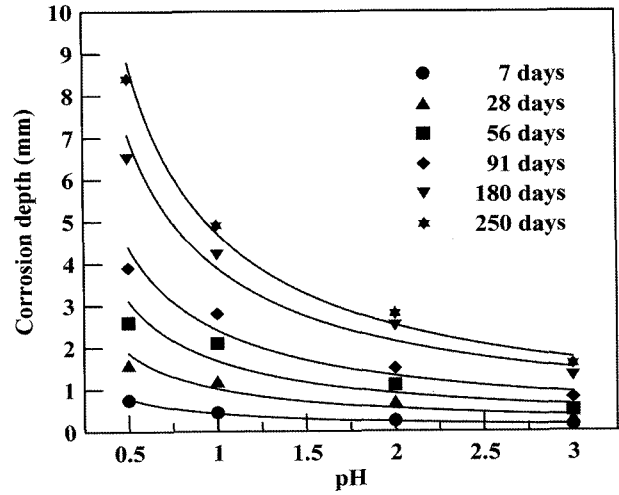


Fig. 3 Corrosion depth of OPC mortar as a function of the pH of an sulfuric acid solution at 7~250 days and its best fit in the form of $d = k_2 \cdot p^m$

corrosion depth of OPC mortar exposed to acidic environment, of which pH range 0.5, 1.0, 2.0 and 3.0.

Table 2 gives the prediction model for the corrosion depth of concrete exposed to acidic environments, of which pH range 0.5, 1.0, 2.0 and 3.0 for OPC, 60% GGBS, 20% PFA and 10% SF mortars. The average of the constant value of n for the immersed duration was calculated for all acidic environments.

Fig. 3 gives the best fits in the form of $d = k_2 \cdot p^m$ to the corrosion depth of OPC mortar exposed to acidic environment, depending on the immersed duration ranging from 7 to 250 days.

Table 3 gives the prediction model for the corrosion depth of OPC, 60% GGBS, 20% PFA and 10% SF mortars and coefficients of m for the constant of the pH. The value of m was chosen as an average value for the durations of immersion in the sulfuric acid solution.

For binder, the order of resistance of sulfuric acid corrosion was OPC < 10% SF < 20% PFA < 60% GGBS.

Then, the results obtained from Tables 2 and 3 are combined to meet the eq. (6) and the all constants for the equation are given in Table 4. The coefficient of determination was always greater than 0.94 for all cases and the average was 0.98~0.99.

Table 4 Prediction model of sulfuric acid corrosion of mortars as a function of the immersed duration and the pH of sulfuric acid solution altogether with determination coefficients to the results on corrosion depth obtained from mortars experiment (governing equation : $d = k \cdot t^n \cdot p^m$)

Binder	$d = k \cdot t^n \cdot p^m$	R ²
OPC	$d = 0.109 \cdot t^{0.683} \cdot p^{-0.880}$	0.98
60% GGBS	$d = 0.107 \cdot t^{0.637} \cdot p^{-0.905}$	0.98
20% PFA	$d = 0.108 \cdot t^{0.654} \cdot p^{-0.890}$	0.99
10% SF	$d = 0.102 \cdot t^{0.675} \cdot p^{-0.900}$	0.98

Table 2 Prediction model of sulfuric acid corrosion of mortars as a function of the immersed duration at 0.5, 1.0, 2.0 and 3.0 in the pH (governing equation : $d = k_1 \cdot t^n$)

Binder	pH				Average
	0.5	1.0	2.0	3.0	
OPC	$d = 0.181 \cdot t^{0.684}$	$d = 0.123 \cdot t^{0.681}$	$d = 0.069 \cdot t^{0.684}$	$d = 0.035 \cdot t^{0.683}$	$d = k_1 \cdot t^{0.683}$
60% GGBS	$d = 0.183 \cdot t^{0.638}$	$d = 0.119 \cdot t^{0.637}$	$d = 0.061 \cdot t^{0.638}$	$d = 0.036 \cdot t^{0.636}$	$d = k_1 \cdot t^{0.637}$
20% PFA	$d = 0.188 \cdot t^{0.653}$	$d = 0.116 \cdot t^{0.656}$	$d = 0.065 \cdot t^{0.653}$	$d = 0.036 \cdot t^{0.654}$	$d = k_1 \cdot t^{0.654}$
10% SF	$d = 0.173 \cdot t^{0.674}$	$d = 0.113 \cdot t^{0.674}$	$d = 0.065 \cdot t^{0.672}$	$d = 0.032 \cdot t^{0.679}$	$d = k_1 \cdot t^{0.675}$

Table 3 Prediction model of sulfuric acid corrosion of mortars as a function of the pH of an sulfuric acid solution at 7~250 days (governing equation : $d = k_2 \cdot p^m$)

Binder	Immersion period (days)					Average
	7	28	56	91	250	
OPC	$d = 0.427 \cdot p^{-0.882}$	$d = 1.015 \cdot p^{-0.882}$	$d = 1.681 \cdot p^{-0.889}$	$d = 2.413 \cdot p^{-0.865}$	$d = 4.717 \cdot p^{-0.899}$	$d = k_2 \cdot p^{-0.880}$
60% GGBS	$d = 0.381 \cdot p^{-0.901}$	$d = 0.834 \cdot p^{-0.907}$	$d = 1.353 \cdot p^{-0.909}$	$d = 1.999 \cdot p^{-0.902}$	$d = 3.573 \cdot p^{-0.903}$	$d = k_2 \cdot p^{-0.905}$
20% PFA	$d = 0.388 \cdot p^{-0.894}$	$d = 0.936 \cdot p^{-0.896}$	$d = 1.495 \cdot p^{-0.894}$	$d = 2.136 \cdot p^{-0.899}$	$d = 3.957 \cdot p^{-0.894}$	$d = k_2 \cdot p^{-0.890}$
10% SF	$d = 0.405 \cdot p^{-0.894}$	$d = 0.891 \cdot p^{-0.915}$	$d = 1.476 \cdot p^{-0.905}$	$d = 2.139 \cdot p^{-0.892}$	$d = 4.323 \cdot p^{-0.892}$	$d = k_2 \cdot p^{-0.900}$

The constant values of n and m for the immersed duration and pH may reflect the resistance of binders to a pH reduction of cement matrix. For example, the constant value of n for OPC and 60% GGBS mortars were 0.683 and 0.637 respectively, which implies that 60% GGBS mortar more strongly resists to acidic corrosion by about 6.73%, compared to OPC. In the same way, the constant value of m were -0.880 and -0.905 for OPC and 60% GGBS mortars respectively, which means 2.84% greater resistance of GGBS matrix to acid corrosion.

It was also found that 60% GGBS mortar specimen is likely to be the most resistant to penetration of acid at all pH values, whereas OPC is the least.

4. Corrosion of structures

To predict the residual life of concrete structures exposed to acidic environments, in this study, sulfuric acid corrosion of sewer boxes and covered creek structures in Seoul, Korea were examined in terms of the analysis of gas composition within the structures and the sulfuric acid corrosion depth. Fig. 4 shows a corroded sewer box and covered creek concrete structure.

It was seen that sulfuric acid corrosion took away mortar or/and cement paste on the surface of a sewer box and the embedded steel was exposed. Also, sulfuric acid corrosion of a covered creek concrete structure was visually observed. For the gas analysis, NH_3 , H_2S , CH_4 and CO_2 were measured using absorption spectrophotometer and gas chromatography. The moisture bubbles on the wall of structures were collected then to measure the pH. The corrosion depth of structures was measured by an indicator as previously referred in this study.

As a result, Table 5 gives the concentration of gases and the

pH of moisture bubbles on the structures. The concentration of NH_3 , H_2S and CH_4 ranged from 661 to 778 ppm, from 1.85 to 2.59 ppm and from 331 to 7,300 ppm respectively, while these gases were negligibly detected in the atmosphere. The concentration of CO_2 within the sewer boxes and covered creeks was at least doubled of that from the atmosphere, ranging from 785 to 1,700 ppm, which implies that the structures are exposed to a high risk of carbonation of concrete. The pH of the moisture bubbles ranged 4.62~5.09, as being acidic, while the pH of moisture in the atmosphere accounted for 6.40.

From the data on the pH, duration of exposure to acidic environments and the corrosion depth, the constant values for the eq. (6) (i.e. n , m , k) were calculated. As only OPC was used for the structures, the following equation and constants (see Table 4) were used to predict the residual life, which is the time of sulfuric acid corrosion reaching the depth of the steel.

$$d = 0.109 \cdot t^{0.683} \cdot p^{-0.880} \quad (7)$$

Table 6 gives the corrosion rate and the calculated residual life of structures, compared to the life calculated by a conventional prediction using the square root time-dependent model (i.e. $d = C\sqrt{t}$).

It is seen that the corrosion depth varied with types of structure, and the exposure environments (see Table 5). As expected, the corrosion depth was strongly dependent on the pH of moisture bubble on the structures, i.e. the pH on the covered creek concretes was slightly lower than for the sewer boxes, ranging from 4.62 to 4.99, while the pH on sewer boxes ranged from 5.06 to 5.09. Thus, the corrosion rate for covered creeks was more rapid, ranging from 0.52 to 1.48 mm/yr. However, the corrosion rate was bit lower than previously reported in a survey,

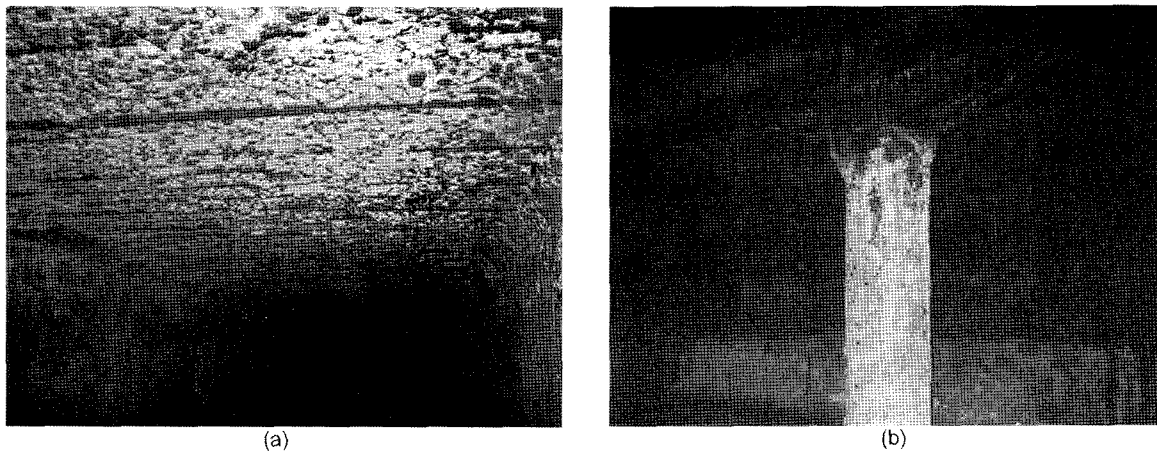


Fig. 4 Removal of cement paste and steel corrosion by sulfuric acid corrosion of concrete taking place (a) a sewer box, (b) chemical sulfuric acid corrosion of covered creek structure

Table 5 The concentration of gas within covered creek concrete structures and a sewer box and the pH of moisture on the structures

	In use (years)	NH_2 (ppm)	H_2S (ppm)	CH_4 (ppm)	CO_2 (ppm)	pH
Sewer box A	31	764	2.59	389	893	5.06
Sewer box B	34	778	2.48	422	994	5.09
Covered creek A	27	-	-	7300	1700	4.62
Covered creek B	21	661	1.85	331	785	4.99

Table 6 Prediction of residual sulfuric acid corrosion-free life at the depth the embedded steel and the corrosion rate using the square root time dependent model and power time dependent model (empirically fitted)

Structures		In use (years)	Corrosion depth (mm)	Concrete cover (mm)	Corrosion rate (mm/yr)	Residual life (years)	
						Model I*	Model II**
Sewer box A	Slab	31	25	30	0.81	9.5	13.6
	Wall		14	45	0.46	140.3	289.3
Sewer box B	Slab	34	35	21	1.03	***	
	Wall		17	50	0.50	131.0	260.1
Covered creek A	Column	27	27	48	1.00	35.7	58.3
	Slab		14	15	0.52	2.9	4.0
	Wall		40	52	1.48	12.6	18.6
Covered creek B	Column	21	30	48	1.42	20.8	32.8
	Slab		27	30	1.29	3.5	4.9
	Wall		16	30	0.76	90.4	184.1

* $d = k \cdot t^{0.683} \cdot p^{-0.880}$, ** $d = C\sqrt{t}$

*** Sulfuric acid corrosion took place beyond the depth of the steel

ranging from 3.1 to 4.7 mm/yr.⁴⁾

The residual life of structure was assessed using the empirical power time-dependent model (eq. (6)) and the square root time-dependent model (eq. (5)). As a result, for all cases, the residual service life of structure was much longer when the square root time-dependent model was applied than when the power time-dependent model was used. It is suggested that the conventional prediction model may underestimate the risk of sulfuric acid corrosion of concrete structures exposed to a low pH or/and acidic environment.

5. Conclusion

The present study investigated the resistance of OPC, 60% GGBS, 20% PFA, 10% SF mortar specimens against sulfuric acid corrosion, when immersed in sulfuric acid solutions. As an index for degree of sulfuric acid corrosion, the corrosion depth was evaluated.

- 1) As increase in the immersed duration and a decrease in the pH resulted in a significant increase in the sulfuric acid corrosion of specimens. For binders, the order of resistance of sulfuric acid corrosion was OPC < 10% SF < 20% PFA < 60% GGBS.
- 2) It was found that the environment within sewer boxes and covered creek structures was able to deteriorate structures by a low level of pH of the moisture bubbles on the concrete surface as well as other aggressive gases and ions.
- 3) The power time-dependent prediction model described more precisely the behaviour of sulfuric acid corrosion of concrete structures. whereas the conventional model using the square root time-dependent model is less appropriate due to underestimation of the sulfuric acid corrosion risk.

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