

## **Influence of Steel Corrosion Products in Concrete on Crack Opening Weight Loss of Corrosion**

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### **Abstract**

Corrosion of reinforcing steel in concrete induces cracking in the cover concrete because the volume of the corrosion products is much greater than that of the original steel. Not only do these cracks result in acceleration of corrosion, but also deterioration of load-carrying capacity. For this reason, there have been many investigations of reinforcement corrosion in concrete. On the other hand, there has been much less study of the corrosion products themselves, with the mechanism of corrosion product formation in concrete remaining unclear. In this study, the influence of environment on the formation of different corrosion products is first investigated, and this is followed by a discussion of the influence of these various corrosion products on crack propagation.

*Keywords:* corrosion products, environment, volumetric expansion ratio, XRD

### **1. Introduction**

It is well known that a passive film generally protects reinforcing steel embedded in concrete. The steel starts to corrode, however, if the film is destroyed by chloride ions or through carbonation of the cover concrete. Since the corrosion products occupy a larger volume than the original steel, cracks are then induced in the cover concrete. Once cracking begins, corrosion factors such as water, oxygen, and chloride ions readily penetrate the concrete through the cracks, and as a result reinforcement corrosion accelerates. Ultimately, corrosion of the reinforcing steel may cause a deterioration in load-carrying capacity. For this reason, it can be said that evaluation of corrosion propagation is one of the important tasks facing a concrete engineer.

The most simple and economical method of evaluating corrosion propagation is to investigate crack width. Many past studies have looked at the relationship between weight loss of steel and crack width. No unified evaluation method has been developed, however, because various values have been reported as shown in **Table 1**. In particular, values obtained from electric corrosion tests seem to be smaller than those obtained in exposure tests or accelerated tests. It might be imagined that these differences are caused by differences in the corrosion products. More than 20 different corrosion products have been reported, each with its own density and expansion ratio, so it can be assumed that the types of corrosion products have a large influence on crack propagation. However, the formation and transformation processes of corrosion products in concrete remain unclear.

In this study, the first step is to investigate the influence of environment on the formation and transformation of various corrosion products. The influence of these different corrosion products on crack propagation is then discussed.

**Tab.1 Crack Opening Weight Loss Reported in Past Studies**

Researcher	Methods	Corrosion length (mm)	Cover thickness (mm)	Bar diameter (mm)	Weight Loss (mg/cm <sup>2</sup> )
Japanese Standard	Electric	Based on the results of past studies			10>
Tamori	Electric	200	25	φ19	2.22
Andres	Electric	C/L=0~2.0		φ21	12
Andrade	Electric	380	20,30	D16	16
Takewaka	Electric	100	40	φ13	5~10
					20
Uno	Electric	100	20	D13	31
				D19	31
				D29	48
Matsushima	Electric	450	25	D25	50~80
	Analysis		30~100	φ16,22	25~75
Hamada	Electric	50~1000	40	D19	80
Kutomi	Electric	400	30	D10,13	2~8
Nakagawa	Wet & Dry	100	15~40	D16	38~116
Sasaki	Salt Spray	200	20	D13	75.2
Horiguchi	Salt Spray	800	20	D13	138~576
Matsumura	Exposure	1200	15	φ19	150

## 2. Formation of Corrosion Products in Various Environments

### 2.1 Experiment

Four different corrosion tests were carried out as follows.

- (1) Wet and dry cycle tests on steel bars: steel bars were exposed to three cycles of 5 days in a wet environment (40°C, 95%RH) and 2 days in a dry environment (20°C, 40%RH).
- (2) Salt spray test on steel bars: steel bars were exposed to 20°C, 40%RH for three weeks and during this period 3% NaOH solution was sprayed on them twice a day.
- (3) Electric corrosion tests on steel bars: steel bars were immersed in 3% NaCl solution and a current (1.22mA/cm<sup>2</sup>) was provided by a DC power supply. A copper plate was used as the cathode.
- (4) Electric corrosion test on steel bars in concrete: concrete specimens were immersed in 3% NaCl solution and a current (1.22mA/cm<sup>2</sup>) was provided by a DC power supply. A copper plate was used as the cathode.

Four steel bars were prepared for each corrosion test. One of these bars was analyzed by powder XRD within 2-3 hours of conclusion of the corrosion regime. The rest were analyzed after two weeks of exposure to one of three environments (ambient air, vacuum and dry), respectively, in order to investigate the influence of water and oxygen on the transformation of corrosion products.

### 2.2 Results and Discussion

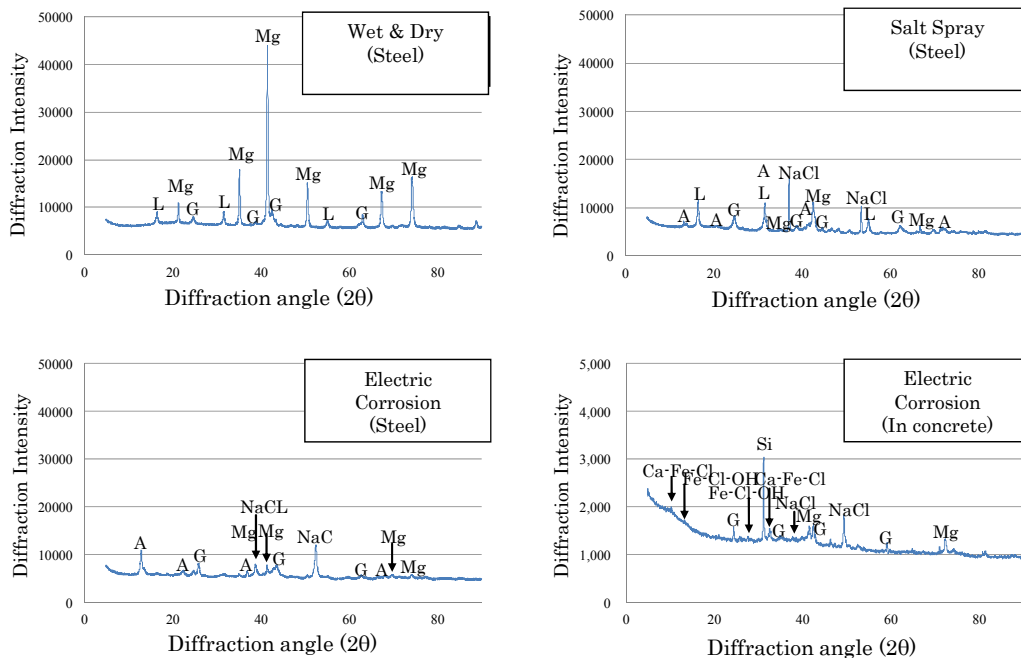
The corrosion products identified in each test are in **Table 2** and examples of XRD patterns are presented in **Fig. 1**. In the table, a ○ mark means that the corrosion product represented in that column was

observed, while a  $\triangle$  mark means that the diffraction intensity of the corrosion product was so small that its presence could not be verified. In the following section, the influence of environment on each of these corrosion products is discussed using the results of this experiment. Though a full quantitative analysis was not carried out, the discussion does include some quantitative investigations. This is possible because the sample sizes used in each analysis were almost the same (0.1 g) and it can be assumed that discussion of the quantity of corrosion products present is possible to some extent by comparison of diffraction intensity.

**Tab.2 Corrosion Products Obtained from Each Tests**

Corrosion products		Test Condition		Steel												Steel in Concrete			
				Wet & Dry				Salt Spray				Electric				Electric			
				J	A	V	D	J	A	V	D	J	A	V	D	J	A	V	D
Goethite	$\alpha$ -FeOOH	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○		
Akaganeite	$\beta$ -FeOOH					○	○	○	○	○	○		○		$\triangle$	$\triangle$	$\triangle$		
Lepidocrocite	$\gamma$ -FeOOH	○	○	○	○	○	○	○	○	$\triangle$	○	○	○		○				
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	⊙	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○		
Calcium Iron Oxide (III) Chloride	CaFeO <sub>2</sub> Cl													○	○	○	○		
Iron Chloride Hydroxide	Fe <sub>6</sub> Cl <sub>2-x</sub> (OH) <sub>12+x</sub>													○	○	○	○		

J; analyzed just after corrosion test  
 A; analyzed after air exposure  
 V; analyzed after vacuum exposure  
 D; analyzed after dry exposure



G: Goethite, A: Akaganeite, L: Lepidocrocite, Mg: Magnetite, Ca-Fe-Cl: Calcium iron Oxide (III) Chloride, Fe-Cl-OH: Iron Chloride Hydroxide, Si: Quartz

**Fig.1 Examples of XRD patterns**

The corrosion products  $\alpha$ -FeOOH and  $\text{Fe}_3\text{O}_4$  were observed in all test samples; these corrosion products seem to be formed in various environments. From **Fig. 1**, it can be said that  $\text{Fe}_3\text{O}_4$  is particularly readily formed in a wet and dry cycle environment.

It is well known that chloride ions are necessary for  $\beta$ -FeOOH formation, and indeed  $\beta$ -FeOOH was observed in the salt spray test and the electric corrosion test of steel bars. On the other hand, no  $\beta$ -FeOOH was observed in the electric corrosion test on steel bars in concrete. This may be because  $\beta$ -FeOOH is not stable in a  $\text{pH}>8$  environment.

The corrosion product  $\gamma$ -FeOOH was also observed in almost all test cases. Only in the case of the electric corrosion test on steel bars in concrete was it not observed. This is because  $\gamma$ -FeOOH readily transforms into  $\alpha$ -FeOOH and  $\text{Fe}_3\text{O}_4$  in a  $\text{pH}>8$  environment.

Formation of the corrosion products  $\text{CaFeClO}_2$  (calcium iron (III) chloride oxide) and  $\text{Fe}_6\text{Cl}_{2-x}(\text{OH})_{12+x}$  was observed only in the case of the electric corrosion test on steel bars in concrete. In this test, specimens were immersed in NaCl solution, so pores were saturated with a solution of NaCl and  $\text{Ca}(\text{OH})_2$ . And in this case, the dissolution rate of steel is high, whereas following oxidation rate is low because oxygen is lacking in concrete. For these reasons, it can be thought that dissolved  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  in the pore solution were easily taken into the crystal structure in the process of oxidation.

### **3. Corrosion Products Formed in Electric Corrosion Tests and Their Volumetric Expansion Ratio**

As already seen in **Table 1**, the crack opening weight loss obtained from electric corrosion tests is much less than that obtained from accelerated or exposure tests. Further, in this study, it has been made clear that  $\text{CaFeClO}_2$ , which is not normally formed in concrete, is formed in the case of electric corrosion tests for steel in concrete. Considering these findings, there is a possibility that the volumetric expansion ratio of this unique corrosion product is different from that of other corrosion products. Then, in this study, the volumetric expansion ratio of the corrosion products formed in electric corrosion tests for steel in concrete was measured and the influence of these volumetric expansion ratios on weight loss as derived from crack opening was investigated.

#### **3.1 Experiment**

Electric corrosion tests were implemented using almost the same method as explained in section **2.1**. In previous studies, it has been reported that when the current density is lower than  $0.2\text{mA}/\text{cm}^2$  the crack opening weight loss is greater than at higher current densities. Therefore, in this study, two variants of the corrosion test were carried out: a low current corrosion test ( $0.168\text{mA}/\text{cm}^2$ ) and a high current corrosion test ( $1.68\text{mA}/\text{cm}^2$ ). And because it was expected that corrosion products would be different before crack opening and after crack opening, the influence of crack width on the formation of corrosion products was also taken into consideration. Two specimens were prepared for each test case. One was used for analysis of corrosion products by XRD and measurement of corrosion weight loss, while the other was used for measurement of volumetric expansion ratio.

#### **3.2 Results and Discussions**

The measured average crack widths of specimen ① and specimen ② were almost the same, and it was thought that differences in corrosion products between the two specimens were very small.

The measured corrosion weight loss in the high rate tests tended to be larger than in the low rate tests. In the high current tests, rust was observed to flow out through the cracks and it can be assumed that this is

the reason crack propagation was associated with a higher corrosion weight loss in the case of the high current test.

XRD analysis showed that in all cases  $\alpha$ -FeOOH, Fe<sub>3</sub>O<sub>4</sub>, CaFeClO<sub>2</sub> and Fe<sub>6</sub>Cl<sub>2-x</sub>(OH)<sub>12+x</sub> were formed, and there were no detectable differences between the cases.

Volumetric expansion ratio was calculated geometrically using cross section loss and rust thickness by the following equation:

$$\gamma = \frac{(r' + \Delta r)^2 - r'^2}{r^2 - r'^2} \quad (1)$$

**Table 5** shows the calculated volumetric expansion ratios. Volumetric expansion is less in the high current tests than in the low current tests. In both cases, the volumetric expansion ratio tended to be lower as the crack width increased. This result demonstrates that the amount of rust flowing out through the cracks increased as the cracks widened. In general, the volumetric expansion ratio is said to be about 2.5. In the case of the low current corrosion tests, in which corrosion products seemed to crystallize well, the volumetric expansion ratio was found to be larger than this generally stated value. In order to investigate the cause of this difference, an attempt was made to calculate the volumetric expansion ratio of each corrosion product from its density and atomic mass using the following equation:

$$\gamma = \frac{\rho_{Fe} \cdot \sum u_i n_i}{u_{Fe} \cdot n_{Fe} \cdot \rho} \quad (2)$$

where,  $\gamma$ : volumetric expansion ratio,  $\rho$ : density of corrosion product,  $\rho_{Fe}$ : density of iron,  $u_i$ : atomic mass of each atom (such as Fe, H, O), and  $n_i$ : number of atoms in a molecule of the corrosion product.

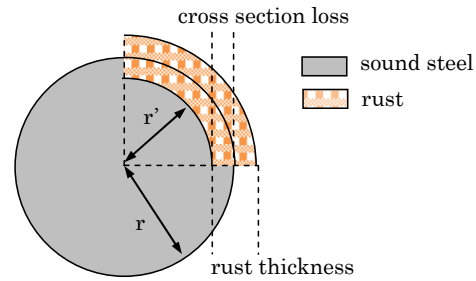
The result of this calculation is shown in **Table 6**. The density of these corrosion products is still unknown and various values have been reported. In this study, densities reported by Conell et al. were used in the main. The volumetric expansion ratios

**Tab.3 Crack Width**

Case	Expected Crack Width (mm)	Average Crack Width (mm)	
		Specimen①	Specimen②
L0	0	0.00	0.00
L5	0.05	0.04	0.07
L10	0.1	0.09	0.11
L30	0.3	0.24	0.37
L50	0.5	0.46	0.51
H0	0	0.00	0.00
H5	0.05	0.04	0.09
H10	0.1	0.12	0.14
H30	0.3	0.38	0.29
H50	0.5	0.49	0.45

**Tab.4 Corrosion Weight Loss**

Case	Accumulated Current (A · h)	Weight Loss(mg/cm <sup>2</sup> )	
		Calculated	Measured
L0	7.8	46	13
L5	10.8	63	30
L10	15.2	88	50
L30	25.3	147	87
L50	30.8	179	104
H0	7.8	45	34
H5	9.6	56	44
H10	14.1	82	71
H30	23.7	138	105
H50	27.0	157	133



**Fig.2 Cross Section of Corroded Steel**

**Tab.5 Volumetric Expansion Ratio**

Case	Cross Section Loss (mm)	Rust Thickness (mm)	Volumetric Expansion Ratio
L0	-	-	-
L5	0.017	0.087	5.12
L10	0.021	0.143	6.81
L30	0.048	0.281	5.85
L50	0.062	0.265	4.27
H0	-	-	-
H5	0.021	0.050	2.38
H10	0.037	0.064	1.73
H30	0.076	0.109	1.43
H50	0.105	0.133	1.27

given in the table are the values under free expansion, and although the average values for goethite and magnetite formed in normal environments are generally stated as 2.5, the values in the table are reasonably close and are thought to be valid to some extent. On the other hand, the volumetric expansion ratio of  $\text{CaFeClO}_2$  is much larger than that of other corrosion products. Hence, it can be thought that the cause of the large volumetric expansion ratio obtained in electric corrosion tests for steel in concrete is the existence of  $\text{CaFeClO}_2$ . Considering that the volumetric expansion ratio of this corrosion product as obtained in this experiment was larger than 5.0, there is a possibility that it is the main corrosion product in electric corrosion tests.

**Tab.6 Volumetric Expansion Ratio of Each Corrosion Product**

Corrosion product		Density (mg/cm <sup>3</sup> )	Volumetric Expansion ratio
Goethite	$\alpha\text{-FeOOH}$	4.3	2.9
Akaganeite	$\beta\text{-FeOOH}$	3.6	3.5
Lepidocrocite	$\gamma\text{-FeOOH}$	4.1	3.1
Magnetite	$\text{Fe}_3\text{O}_4$	5.2	2.1
Calcium Iron Oxide (III) Chloride	$\text{CaFeO}_2\text{Cl}$	3.4	6.9

#### 4. Crack Opening Weight Loss under Various Corrosion Environments

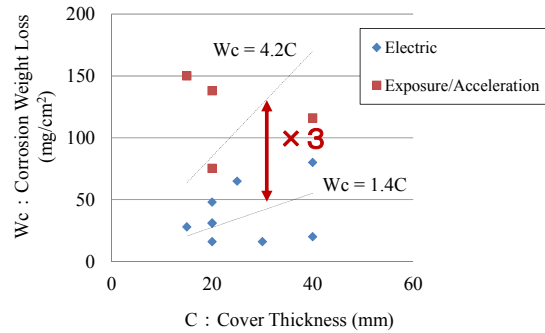
Figure 3 shows the relationship between cover thickness and crack opening weight loss obtained from past studies. In the figure, the crack opening weight loss obtained from exposure tests or accelerated tests is 3.0 times greater than in electric corrosion tests.

Considering that volumetric expansion ratio is determined by cross sectional loss and rust thickness, the relationship between volumetric expansion ratio and crack opening weight loss can be expressed by the following equation:

$$\frac{W_c}{W_c'} = \frac{\gamma' - 1}{\gamma - 1}$$

where,  $W_c$ ,  $W_c'$ : crack opening weight loss (mg/cm<sup>2</sup>),  $\gamma$ ,  $\gamma'$ : volumetric expansion ratio.

Under the assumption that the volumetric expansion ratio of corrosion products obtained from electric corrosion tests is 5.12 (the value obtained in this experiment) and the volumetric expansion ratio from exposure/accelerated tests is 2.5, the calculated value of crack opening weight loss in exposure/accelerated tests is 2.7 times that of electric corrosion tests. This value is almost the same as the value of 3.0 shown in Fig. 3, so this result implies that the difference in corrosion products is the main cause of difference in crack opening weight loss between electric corrosion tests and exposure/acceleration.



**Fig.3 Relationship between Cover Thickness and Crack Opening Weight Loss Obtained from Past Studies**

(3)