Evaluation of Corrosion Behavior of Carbon Steel for Containment Liner Plate According to Environmental Factors

Won-Jun Choi [a], Chi Bum Bahn [a*]

[a] Department of Mechanical Engineering School of Mechanical Engineering,
Pusan National University, Busan 46241, South Korea,
[*]Corresponding author: bahn@pusan.ac.kr

1. Introduction

Containment Liner Plate (CLP) of nuclear power plant containment building is made of carbon steels and plays an important role for the safety of nuclear power plants. It behaves as a concrete mold during construction and as a barrier during operation in order to prevent the leakage of radioactive materials in case of accidents. However, since early 2000s, the corrosion occurring at the interface between CLP and concrete has been reported worldwide [1]. The CLP corrosion was also detected in Korean nuclear power plants recently. The CLP corrosion may be affected by various environment factors, such as pH, chloride ion concentration, oxygen concentration and humidity [2]. However, the environmental effects on carbon steel corrosion have not been studied systematically. Therefore, the corrosion behavior of carbon steel in saturated $Ca(OH)_2$ solution was studied by various experimental methods. The polarization curves of carbon steels were acquired under various environments. The corrosion rates were estimated from the polarization tests. The immersion test was also conducted to determine the morphology of oxide films formed in each environment.

2. Experimental Methods

2.1 Material and electrolytic solution

The material of the CLP of the containment building is carbon steel (SA516-60) and its chemical composition is shown in Table 1.

Table I: Composition of Carbon Steel (SA516-60)

Fe (%)	C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)
Bal.	0.152	0.264	1.075	0.011	0.003	0.022
Ni (%)	B (ppm)	Cu (%)	Mo (%)	Ti (%)	V (%)	
0.009	2	0.022	0.002	0.001	0.002	

The experimental specimen for a working electrode was machined from a plate and fitted into a specimen holder to be exposed only $1cm^2$ area. The working area of the specimen was ground with 400-grit, 1200-grit waterproof abrasive paper and polished with 9μm, 3μm diamond polishing film, and then cleaned with alcohol and distilled water.

The electrolytic solution was consisted of saturated $Ca(OH)_2$ with different concentrations of sodium chloride added. The pH of the saturated $Ca(OH)_2$ solution was adjusted with hydrochloric acid (HCl). The reference electrode was a mercury-oxide mercury electrode, connected with the electrolyte solution through a salt bridge positioned close to the working electrode surface. The counter electrode was platinum electrode. In the deaerated state experiment, Ar gas was purged at a rate of $1cm^3$/min for 30 minutes, and the temperature was controlled by a heating mantle. Figure 1 shows the in-use experimental equipment.

Fig. 1. In-use experimental equipment.

2.2 Electrochemical measurements

Potentiodynamic polarization tests were performed to evaluate the corrosion behavior of carbon steel. Before polarization tests, the working electrode was immersed in the test solution for 1h until a steady state was reached, and the open-circuit potential (OCP) was obtained. Potentiodynamic polarization curves were measured from −0.5 V to 1.0 V with respect to the open circuit potential with a scan rate of 1 mV/s. The corrosion rates were estimated from the polarization tests by Tafel extrapolation.

2.3 Immersion test

The carbon steel plate (SA516-60) was cut into coupons of 60mm x 15mm x 1mm and then cleaned by

Clarke solution to remove corrosion product. The test was conducted in aerated saturated Ca(OH)$_2$ with different chloride ion concentrations. Then, the surface analysis was conducted to determine the morphology of oxide films formed though scanning electron microscopy.

3. Results and Discussion

3.1 Effect of Cl$^-$ concentration and temperature

The results of potentiodynamic polarization curves obtained from aerated saturated Ca(OH)$_2$ with different chloride ion concentrations and different temperature are shown in Fig.2. In Fig.2 and other figures that following, '0,1 ppm' means that chloride ion was not added at all. Comparing the overall tendency, it was found that the corrosion rate is proportional to the chloride ion concentration and temperature, respectively. However, when the concentration of chloride ion was 0 ppm, the corrosion rate did not follow the general tendency at 27°C and 45°C. This is not a big difference considering that the difference in corrosion rate is only 0.004 mm/yr. In addition, it was confirmed that the corrosion rate was within the range of the annual average corrosion rate (0.1 ~ 0.5 mm/yr) estimated from the actual CLP when the chloride ion concentration was 1000 ppm. In addition, it was also confirmed that at the temperature of 60°C, the only 10 ppm contents of chloride ion is enough to be within the actual CLP corrosion rate range.
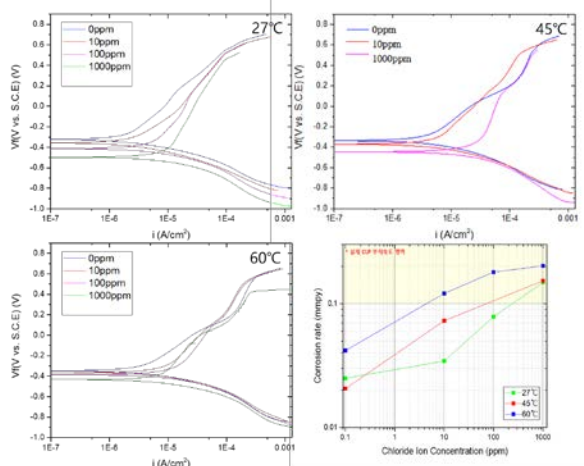

Fig. 2. Polarization curves and corrosion rates of Carbon Steel according to chloride ion concentration and temperature.

3.2 Effect of O$_2$ concentration

The results of potentiodynamic polarization curves obtained from various chloride ion concentrations in the deaerated state are shown in Fig. 3. In general, it was confirmed that the corrosion rate decreases in the deaerated state. However, when the concentration of chloride ion is 1000 ppm or more in the deaerated state,

the corrosion rate becomes close to the actual CLP corrosion rate region. I It is confirmed that chloride ion has a great influence on the corrosion rate regardless of the oxygen concentration.
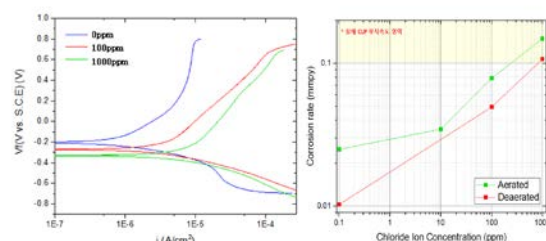

Fig. 3. Polarization curves and corrosion rates of Carbon Steel according to O2 concentration

3.3 Effect of pH

As the solution pH is decreased from 12.5, which is the pH of saturated Ca(OH)$_2$, the corrosion rate is increased as shown in Fig. 4. Since the concentration of chloride ion increased by the addition of hydrochloric acid is only 10 ppm or less, the addition of chloride ion itself does not seem to affect the corrosion rate. If pH of the concrete pore solution is reduced slightly (pH<10) due to the influx of foreign substances during construction, the corrosion rate can belong to the range of the actual CLP corrosion rate.
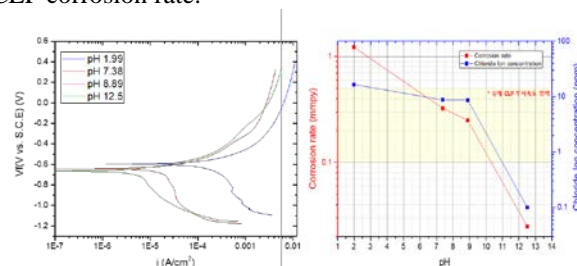

Fig. 4. Polarization curves and corrosion rates of Carbon Steel according to pH

3.4 Immersion test

Carbon steels were immersed in the saturated Ca(OH)$_2$ solution with different chloride ion concentrations for 50 days, and the surface of carbon steels specimens were analyzed using an scanning electron microscope. Figure 5 shows cross-sectional morphologies of the specimens. It was not certain that the relationship between the oxide film thickness formed on the surface and the concentration of chloride ion. However, in the saturated Ca(OH)$_2$ solution with 1000 ppm chloride ion concentration, it was confirmed that a calcium carbonate layer was formed, which appears as a white region on the SEM-EDS image in Fig. 6.
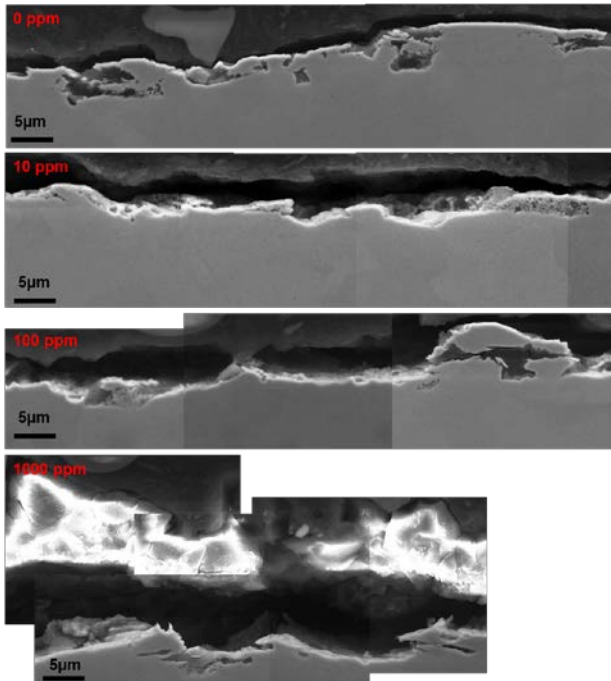
Fig. 5. The cross-sectional morphologies during 50 days with various chloride ion concentrations
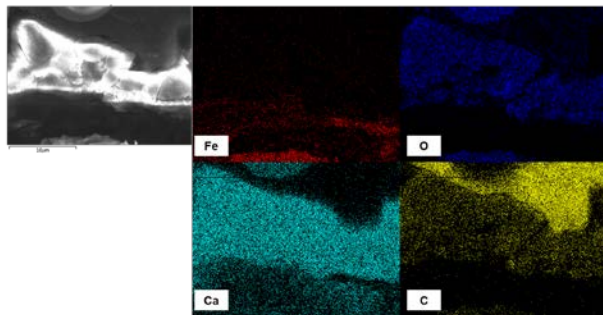

Fig. 6. The cross-sectional SEM-EDS images during 50 days with the chloride ion concentration of 1000 ppm

4. Conclusions and Future Work

The polarization curves of carbon steels were acquired under various environments. The corrosion rates estimated from the polarization tests by Tafel extrapolation. These results showed that the corrosion rate of carbon steels in saturated $Ca(OH)_2$ solution increases with increasing the chloride ion concentration, temperature and oxygen concentration. As the solution pH is decreased from 12.5, which is the pH of saturated $Ca(OH)_2$ solution, the corrosion rate increases rapidly. In order to estimate more accurate corrosion rate, it is planned to conduct electrochemical impedance spectroscopy. The surface analysis was conducted to determine the morphology of oxide films formed in each environment using SEM-EDS. X-ray diffraction (XRD) analysis is also planned to identify corrosion products. The results of this study are expected to be used as basic data for understanding the CLP corrosion and developing a maintenance strategy.

REFERENCES

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