Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Evaluation method of degradation of anti-corrosion epoxy lining for concrete structures

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ABSTRACT

Evaluation study on lining materials under sulfuric acid condition for sewage and waste water plants has been conducted. Not only an accelerated test but also an actual long-term in-situ examination were performed using many kinds of commercial anti-corrosion resins, and a comparative test was also performed through weight and mechanical strength measurements to establish their corrosion degradation behaviour under sulfuric acid environment. Penetration of sulfuric acid into lining was experimentally monitored by S element analysis on specimen cross-section during sulfuric acid solution immersion test. The penetration depth was found to be proportional to root immersion time. The penetration rate was found to be a function of temperature and concentration of environment. A master curve was obtained and life-estimation of lining was discussed.

To confirm these results, immersion test under sulphur-oxidizing bacteria in controlled H_2S gas condition had been conducted for over seven years. The penetration data was measured and compared with above accelerated results and discussed. The penetration progressed close to the estimation during the initial period of immersion. Accelerating deviation from estimation was observed after over five years.

Keywords. Epoxy Lining, Sewerage, Sulfuric Acid, Anti-corrosion, Life Estimation

INTRODUCTION

Concrete corrosion under sulfuric acid condition is a serious problem in sewage and waste water plants (Nakamoto, 1993) which requires polymeric lining application for mitigation (Prian, 1999). Although acid resistant concrete has been developed, still two types of polymeric lining, *i.e.* sheet lining and resin lining are used as long-life and high reliable protection for concrete structure especially under severe corrosive environment. Since epoxy resin is known as its good adhesive property and chemical durability, it is widely applied as protection and repair applications for these concrete structures. However, it is also known to be quite permeable to sulfuric acid, when it is compare to other corrosion resistant polymers. Hence, evaluation of penetration rate and life estimation method for epoxy lining is strongly desired from maintain huge infrastructure point of view.

Network polymers (i.e. thermosets) are used for various corrosion protection applications because of their excellent corrosion resistance. The anti-corrosion resin is used further in various environments in the large field, because it is applied to a large variety of object. Though there are many resins such as epoxy resin, unsaturated polyester, vinyl ester resin, phenolic resin, polyurethane, and urea resin, *etc*. used for the anti-corrosion application, these characteristics is greatly different. However, there is no resin that resists any corrosive environment, and some resin is difficult to apply depending on the object. Therefore, when polymer is used as a corrosion-resistant application, it is necessary to understand the corrosion factor in the environment used in detail, to select the resin which has the sufficient ability, and to select an appropriate application method.

Though there are some reports of the degradation behaviour of polymer in the acid and the base and the penetration behaviour of an environmental liquid in these resins (Gu, 2001; Woytowich, 1991), the reports which focused on the corrosion behaviour in the sulfuric acid environment is few as for the resin used for the sewerage plant and piping. Under corroborative research with Tokyo Institute of Technology, Plastic Lining Association and Japan Sewage Works Agency for a decade, many results were obtained and reported (Masuda, 2007; Kubouchi, 2012). In this report, to conclude the results from this series of works, general findings from past studies were compared to experimental results of over seven years immersion test.

POLYMER CORROSION

The corrosion mechanism of polymeric materials is classified roughly into 2 groups: one is physical type such as swelling, while the other is chemical type, such as hydrolysis, oxidation reaction, *etc*. The changes of appearance, weight and mechanical properties were investigated for understanding these mechanisms of chemical deterioration (Amer, 1996; Sembokuya, 2001; Golovoy, 1988).

This chemical type degradation could still further be classified into 3 groups by classification of degradation form: (1) the surface reaction type; (2) the corroded layer-forming type, and (3) the penetration type (Hojo, 1991; Hojo, 1998). These three forms are concluded in the illustration shown in Figure 1.

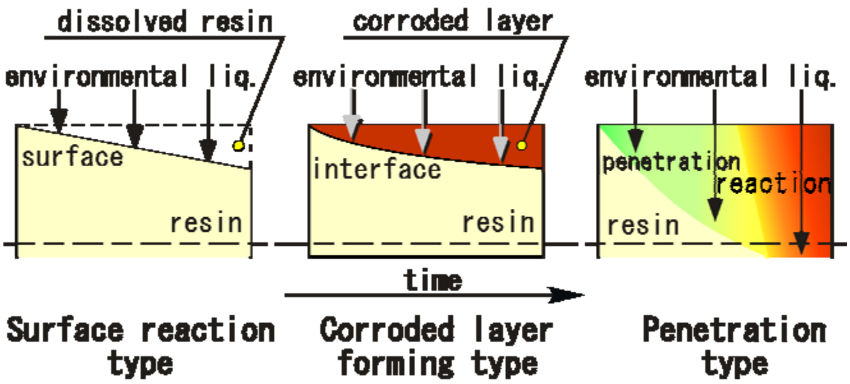

Figure 1. Three forms of polymer corrosion

In the case of amine cured epoxy resin immersed in sulfuric acid environment, it shows "penetration type" as the corrosion type shown in Figure 1. In this corrosion type, initially an environmental solution penetrates into the resin in full area, and its degradation (chemical scission of polymer chain) occurred after a long moment. Therefore, it may happen that the sulfuric acid reaches the concrete substrate before the resin breaks. Thus, to discuss the service life of the epoxy linings, it is need to consider not only the degradation time of epoxy resin itself, but also the penetration time of sulfuric acid through the linings.

EXPERIMENTAL

Test Materials. To evaluate corrosion resistance, several types of epoxy resin are selected. Combinations of the epoxy resin and hardener used are listed in Table 1. In this report nine amine cured epoxy samples were selected as main materials.

Table 1. Materials

Sample	Epoxy resin	Hardener
EP1	Bisphenol A type	Aliphatic polyamine (Mannich)
EP2	Bisphenol F type	Aliphatic polyamine (Mannich)
EP3	Bisphenol F type	Aromatic polyamine
EP4	Bisphenol A type	Modified-aromatic polyamine
EP5	Bisphenol A type	Modified-meta-xylene-diamine
EP6	Bisphenol A type	Modified-aliphatic polyamine
EP7	Bisphenol A type	Modified-aliphatic polyamine
EP8	Bisphenol F type	Menthanediamine
EP9	Bisphenol A type	Aliphatic diamine

Immersion Test. To conduct accelerated immersion test, 25x60x2mm samples were immersed in sulfuric acid solution in beaker. Temperature of these immersion vessels are kept by water bath. Periodically samples are picked up and weighed a mass, measured strength and analysed sulfuric acid penetration by EDS (X-lay element analysis). Immersion test was conducted at a range of environmental temperature from 40 to 80 degree C and in a rage of sulphuric acid concentration from1 to 30 mass%.

Permeation Test. Permeation test was conducted with the set-up of special glass vessels shown in Figure 2. Thin film form specimen is put between the vessel one side contains pure-water and the other side contains sulfuric acid. The pH of the water is measured.

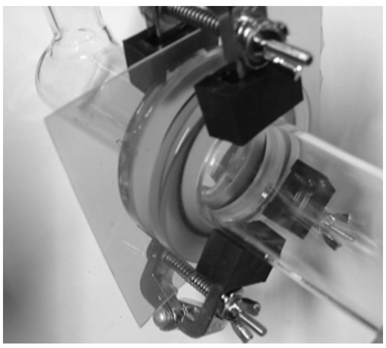

Figure 2. Permeation test set-up

Stress Corrosion Test. To obtain the effect of stress on sulfuric acid penetration rate, creep type tensile test is conducted. Dumbbell shape tensile specimen (straight pert length is 60mm, width is 10mm and thickness is 4mm) is set as shown in Figure 3. Sulfuric acid is kept in the glass vessel and temperature is controlled by heater surround the vessel.

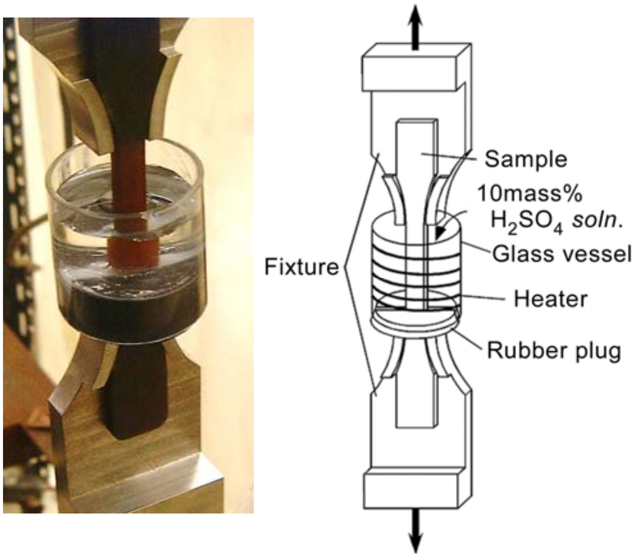

Figure 3. Permeation test set-up

AGETRON Exposure Test. Immersion test under sulphur-oxidizing bacteria in controlled H_2S gas condition was also conducted and compared with the former results. This test had been conducted by the "AGETORON" machine shown in Figure 4, which developed and installed in Japan Sewage Works Agency. Rectangular shape test sample are fixed by Teflon tube to keep separate each other. To evaluate the penetration depth of sulfuric acid EDS analysis on specimen cross-section of for S element was conducted.

Figure 4. Photographs of AGETRON machine

RESULTS AND DISCUSSION

Immersion Test. It was experimentally observed by EDS analysis on specimen cross-section that sulfuric acid penetrates into epoxy lining as forming an uniform layer. Figure 5 shows penetration depth plotted to root immersion time. Although for a long time immersion, penetration depth is proportional to root immersion time. From this result, slope in this straight line is defined as penetration rate; λ. Besides the step like distribution of penetrant, since mechanical strength of specimen after dried remained near the initial one, sulfuric acid makes kind of salt without chain scission.

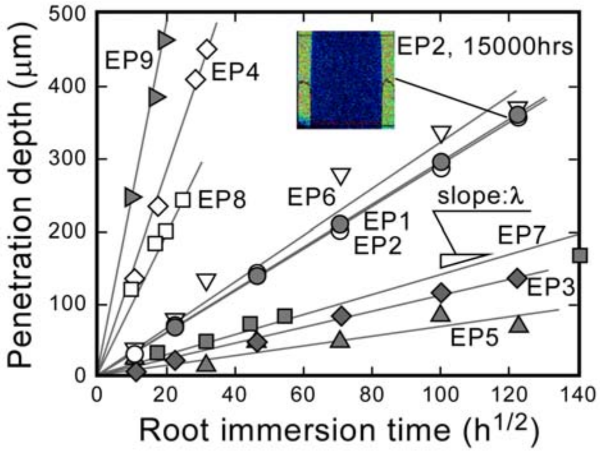

Figure 5. Results of S element penetration depth measurements for several epoxy samples (40 deg. C, 10 mass% sulphuric acid)

The study on the effects of temperature and concentration of environment were conducted. These results show that penetration depth is proportional to root immersion time at all conditions. Then, the penetration rates; λ defined by the slope in Figure 5 were recognized as a function of temperature and concentration. Penetration rates depend on temperature follows Arrhenius low. On the other hand, measured rates at different environment concentrations are plotted in Figure 6. The rates are proportional to root sulfuric acid concentration for dilute concentration area. (Masuda, 2007; Kubouchi, 2012) Here, since penetration rate shows saturation or maximum value at 10 to 30 mass%, for the accelerated test condition too high concentration is no meaning.

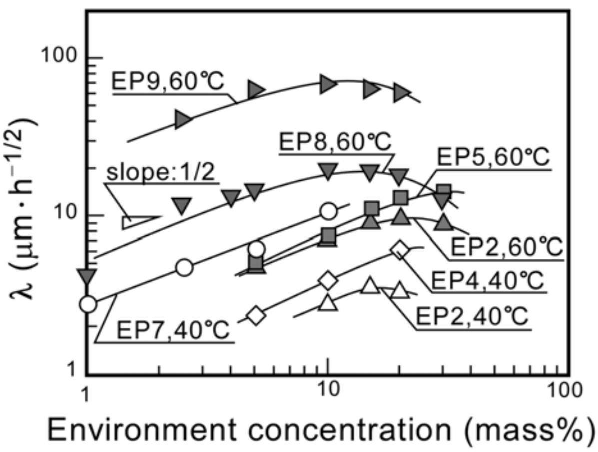

Figure 6. Effect of environment concentration on penetration rate

From these results, penetration rate; λ is shown as the equation below,

$$\lambda = AC^{1/2}\exp(-E/RT) \qquad (1)$$

where, C is concentration, T is temperature E is activation energy, R is gas constant and A is proportional constant, respectively. The master curve calculated by this equation for EP2 sample at different conditions is shown in Figure 7. From this figure equation (1) agree well with experimental results.

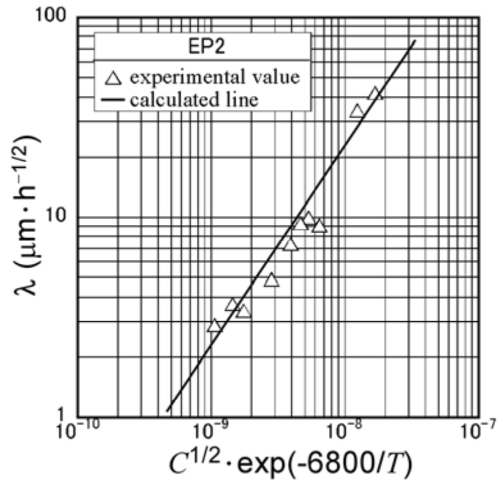

Figure 7. Master curve of surfer penetration for EP2 sample

Permeation Test. From above discussion, permeation of sulfuric acid into epoxy film was confirmed, however strength is remained. Then, most concerned matter is whether penetrated acid act as corrosive environment or not after it reached to the interface of lining and the base material. To answer this question experimentally, permeation test was conducted. When about 200 μm thick EP4 film was evaluated, pH and SO_4^{2-} ion concentration change are shown in Figure 8. (Kubouchi, 2004)

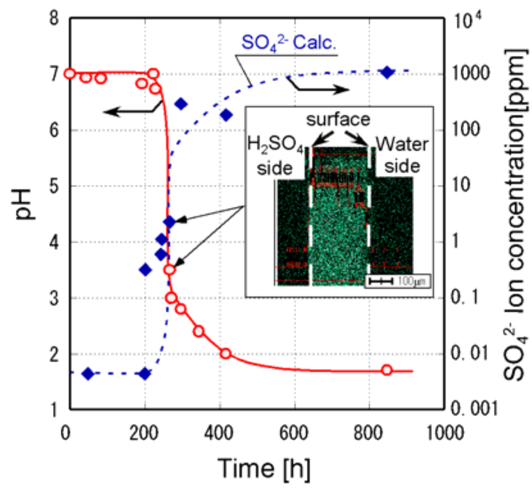

Figure 8. Results of penetration test

At 240 hours of immersion time, pH drops immediately and ion concentration symmetrically increases in pure water side. The S element mapping result by EDS for 240 hours immersion sample is inserted in same figure. This analytical data shows this time is the just sulfuric acid reached to the water side surface. This 240 h corresponds to the penetration time of EP4 sulphur reaches 200μm shown in Figure 5. From these results, penetrated sulfuric acid appreciated that it attacks the base material as corrosive environment when it reaches to the interface. This means penetration time to reach interface should be considered as lining life.

Stress Corrosion Test. To consider stress effect, stress corrosion test was conducted as loading tensile creep load with environmental immersion. Penetration depth increases with the creep load as shown in Figure 9. From the relation between penetration depth and root immersion time, λ also increases with creep load. When material is pulled, molecular distance is separated and penetration is accelerated. This effect is also found in epoxy under sulphuric acid. (Masuda, 2008)

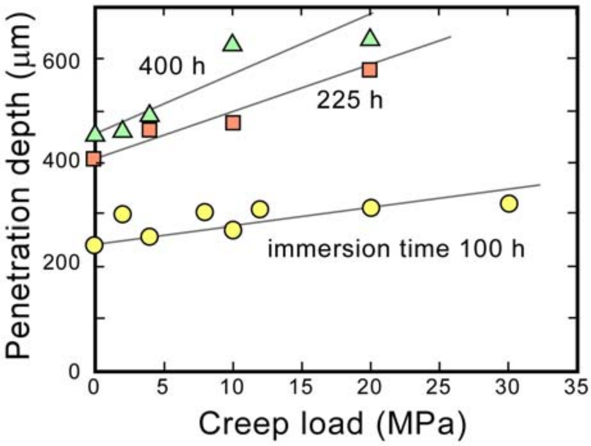

Figure 9. Agetron experimental results

AGETRON Exposure Test. To confirm the master curve results mentioned above, immersion test under sulphur-oxidizing bacteria in controlled H_2S gas condition by the "**AGETRON**" machine had been conducted for over seven years, shown in Figure 10. Although large scattering is recognized, the penetration data also detected.

Then Penetration rate is calculated by equation (1) for this test. The environment in this apparatus is evaluated as temperature is 30 deg. C and concentration is nearly 0.05 mass%. Then, these values are substitute into the equation and penetration rate is calculated as λ = 0.096 $\mu m \cdot h^{-1/2}$. This absolute value, correspond to the line in figure 10, is close to the experimental values obtained by AGETRON exposure test. However accelerated deviation tendency from the estimation was observed after over five years.

Life Estimation. From the master curve for arbitrary material as shown in Figure 7, actual field penetration ratio will be evaluated as function of temperature and concentration. The rate is strongly depends on material, then material selection should be important. For example, in Figure 5, when EP4 is selected and 2mm thickness is assumed, 20000 hours are estimated as life time, however, EP3 is calculated over 100 years.

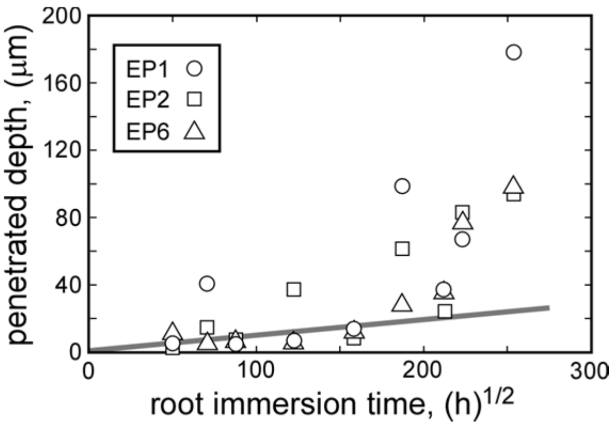

Figure 10. AGETRON experimental results

CONCLUSION

The penetration of sulfuric acid into epoxy lining film was studied by immersion tests and life time estimation was discussed. From these results, penetration model was obtained and the model was compared with the AGETRON test results which represents real bio-induced degradation condition.

Beside of temperature and concentration, still many factors, such as stress, may affect on the penetration rate. Organic acid or organic solvent will also have strong effect on the penetration behaviour (Hiramoto, 2003).

ACKNOWLEDGMENTS

The author with to acknowledge the assistance of Messrs Y. Suga, M. Mochida, M. Sasaki of JSWA and Y. Uno and K. Nomaguchi of PLA, and the cooperation of Messrs A. Yashiro, H. Asaki, Y. Masuda and Y. Nakamura of students in Tokyo Institute of Technology.

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