

## Atmospheric corrosion of carbon steel in acid rain by accelerated weathering test

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**Abstract**—In this work, the accelerated weathering test of immersion-wet-dry combined cycles was carried out. The artificial acid rain of  $\text{NaHSO}_3\text{-(NH}_4\text{)}_2\text{SO}_4\text{-H}_2\text{SO}_4$  solution system was selected as immersion solution. Acidity of artificial acid rain affected corrosion weight loss of carbon steel, and pH 4.1 was found to be a critical point. Anodic reaction resistance of the samples during accelerated weathering test increased with exposed time by electrochemical measurement.

**Keywords:** acid rain; atmospheric corrosion; carbon steel; weathering test.

### INTRODUCTION

Acid rain is one of ten great dangers in the world, and a research on it becomes very important. Materials are easily corroded in acid rain areas in which carbon steel is the most evident fact. It is very difficult to find real mechanism of corrosion in acid rain for outdoor exposure test because of the great number of climatic variables influencing corrosion processes and the test periods are identified too long. In contrast, accelerated weathering test in laboratory bears the excellent characteristics of being fast and capable of identifying the real mechanism of corrosion caused by individual factor.

The accelerated weathering test of immersion-wet-dry combined cycles was employed for the simulation of raining, foggy and sunny processes in natural environment. Atmospheric corrosion of carbon steel was discussed in artificial acid rain in various pH of  $\text{NaHSO}_3\text{-(NH}_4\text{)}_2\text{SO}_4\text{-H}_2\text{SO}_4$  solution system and electrochemical behaviors of rust film formed in the accelerated weathering test were determined by electrochemical measurement.

### EXPERIMENTS

#### *Accelerated weathering test*

Samples were polished by mechanical device and cut to the sizes of  $100 \times 50 \times 2.5 \text{ mm}^3$ , then washed by acetone for removing oil on surface. After drying, samples were weighed and were

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taken into special equipment for accelerated weathering test. The test conditions were shown in Table 1.

Table 1 Parameters of accelerated test

State	Temperature, °C	Time, min.
Immersion	40	2
Wet	40	2
Dry	50	11

NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solution system was selected for immersion in order that high pH value corresponded to low concentration of the solution system. One group of samples (consisting of three samples) were carried out on designed times in alternation immersion test and taken out, then rust was removed with HCl-urotropine and samples were weighed for calculation of weight loss, which was calibrated by base samples.

#### *Electrochemical experiment*

Immersion potential was determined during immersion of cycle test in immersion solution of accelerated weathering test mentioned above. A saturated calomel electrode was used as reference electrode. The exposed area of the sample was only 1 cm<sup>2</sup> and the rest was covered by resin.

Measurement of polarized curve was done in 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> solution bubbling 99.99% N<sub>2</sub> gas. The cell consists of a platinum counter electrode and a saturated calomel reference electrode through a salt bridge of a Luggin capillary. The samples were taken into electrolyte and free corrosion potential was recorded for 30 minutes. Then sample was polarized 10 minutes at -1000 mV and current-potential curves can be recorded potentiokinetically in the positive direction at the scanning rate of 100 mV/min. Here the sample was ones undergoing alternation immersion mentioned above, which exposed area was also 1 cm<sup>2</sup>.

The surface composition and structure of samples having been tested were analyzed by X-ray diffraction.

## RESULTS AND DISCUSSION

#### *Accelerated weathering tests*

In NaHSO<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solution system, concentrations were changed to get four kinds of different pH value solution (pH were 2.8±0.1, 3.4±0.1, 4.1±0.1, and 5.0±0.4 respectively) which could correspond to severe, middle and light acid rain pollution caused mainly by SO<sub>2</sub> and NH<sub>3</sub>. And distilled water was used as alternation immersion solution for representing free acid rain pollution. The accelerated weathering test results showed that weight loss increase with the exposed times and acidity, as shown in Fig. 1.

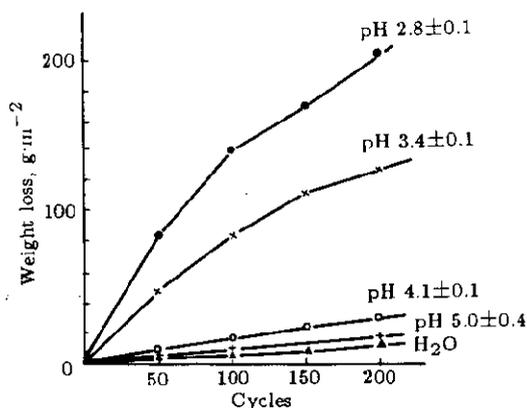


Fig. 1 Plot of corrosion weight loss vs. alternation immersion times

If the concentration of  $\text{NH}_4^+$  was constant and pH value of solution was controlled at pH  $4.1 \pm 0.1$ , the influence of  $\text{HSO}_3^-$  concentration on weight loss of carbon steel was shown in Fig. 2, in which high  $\text{HSO}_3^-$  concentration resulted in severe corrosion of carbon steel.

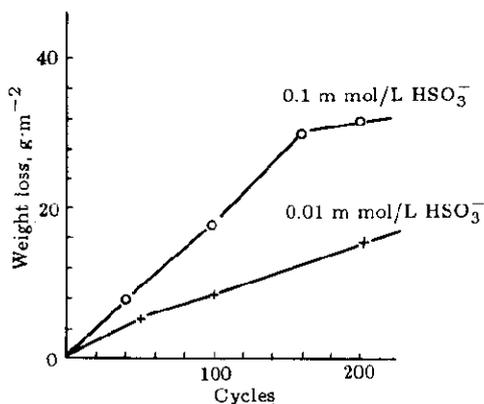
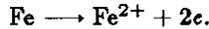
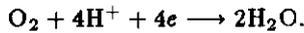


Fig. 2 Influence of  $\text{HSO}_3^-$  concentration on carbon steel corrosion

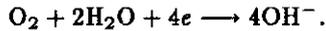
In general, atmospheric corrosion includes three processes: dry, wet and damp. Metal surface may adsorb a thin layer of water in damp atmosphere. When the layer of water gets to some thickness about 20—30 molecular layers, electrolyte film will be formed which is necessary for electrochemical corrosion. So the corrosion process in atmosphere is a kind of electrochemical corrosion in thin film electrolyte. Corrosion occurs in anodic electrode:



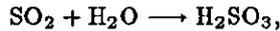
In the same time, cathodic reaction mainly is depolarization reaction of oxygen because that oxygen moves easily to cathodic surface. Beneath acidic solution film, cathodic reaction occurs:



However, the cathodic reaction occurs in neutral solution film:



In the case of pollution of high  $\text{SO}_2$  concentration,  $\text{H}_2\text{SO}_3$  was easily formed in water as depolarizer:



and in acidic solution, reaction occurs:



Therefore, the acidity and  $\text{SO}_2$  concentration are high and corrosion occurs very easily.

The relationship between corrosion weight loss and acidity of simulated rain was presented in Fig. 3. The influence of acidity of simulated rain on corrosion weight loss can be fallen into two regions, as shown in Fig. 3.

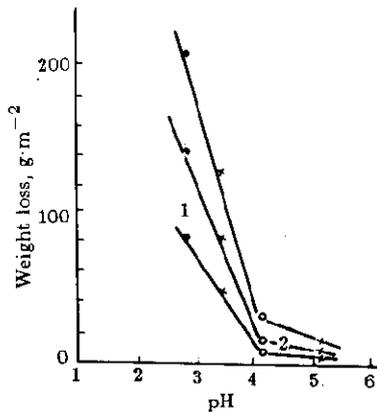


Fig. 3 Influence of pH value on weight loss

In region I ( $\text{pH} < 4.1$ ), weight loss increased very quickly with the decrease of pH value, however weight loss increased very slowly with the decrease of pH value in region II ( $\text{pH} > 4.1$ ). The weight loss of carbon steel at pH 2.8 was seven times higher than at pH 4.1, which agrees well to the result obtained by Haagenrud from accelerated test for 4-weeks in laboratory (Haagenrud, 1982).

All data were treated mathematically and we found the relationship between weight loss

( $W$ ,  $\text{g.m}^{-2}$ ) and the pH value of simulated acid rain as follows:

$$\log W = 3.79 - 0.53\text{pH} \quad r = 0.98 \quad (\text{for 200 cycles}),$$

that is  $W = 6.17 \times 10^3 [\text{H}^+]^{0.53}$  where  $r$  is the relative constant.

Also, it is identified that weight loss is directly proportional to power series of  $\text{H}^+$  ionic concentrations, and we can get empiric equation:

$$W = A[\text{H}^+]^B,$$

where  $A$  and  $B$  could be considered as the parameters which are affected by cycle times and other factors.

That empiric equation is useful for explation of influence of rain acidity on corrosion weight loss in practice.

The corrosion products formed in accelerated weathering test were in brown-yellow, specially the color of samples in immersion solution with pH 2.8 is more black. The X-ray diffraction analysis were presented in Fig. 4 for the samples which were tested in immersion solution with  $\text{pH } 4.1 \pm 0.1$  for 200 cycle times. The main products were  $\gamma\text{-FeOOH}$  and  $\text{Fe}_3\text{O}_4$  that is similar to outdoor exposure.

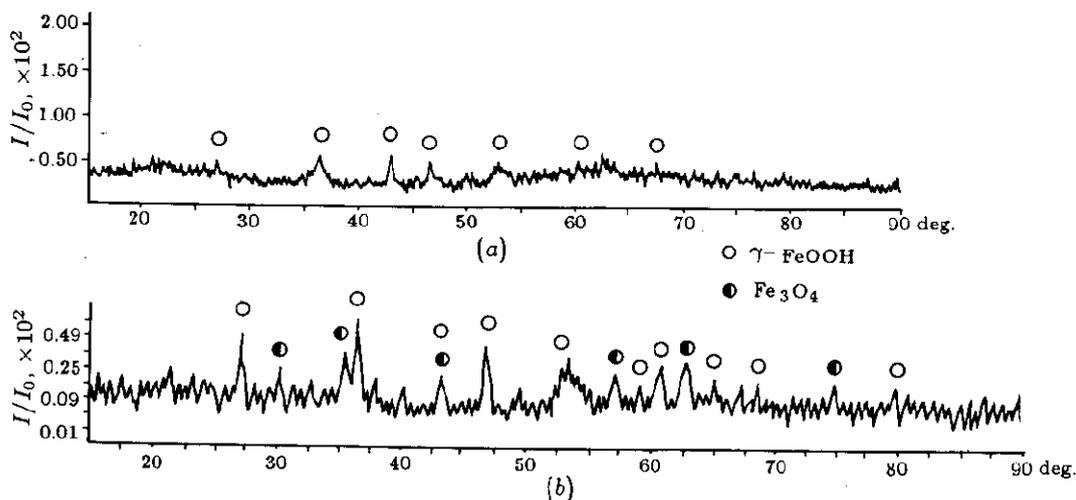


Fig. 4 X-ray diffraction analysis

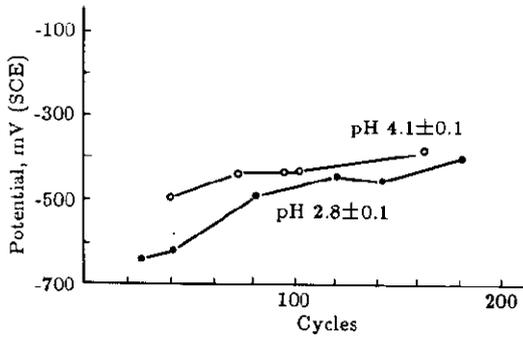
(a) The sample formed in outdoor exposure for one year;

(b) The sample formed in accelerated weathering test for 200 cycles.

#### Electrochemical experiment

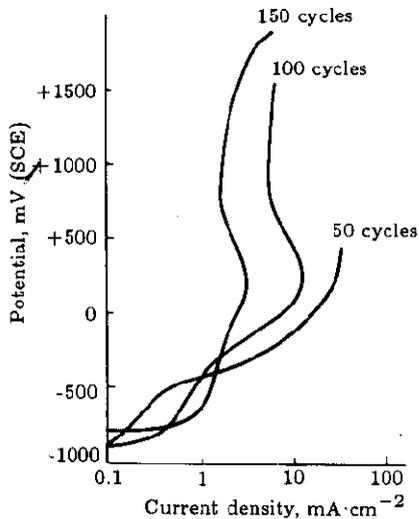
The electrode potential was measured during the immersion period of accelerated weathering test and increased as the increment of immersion times as shown in Fig. 5. These results

showed that rust film was formed continuously on the sample surface and developed to a stable phase in thermodynamics.



**Fig. 5** Effect of cycle times on emersion potential during accelerated weathering test

Fig. 6 showed the polarized curve of sample treated in test mentioned above for 50,100,150 times of cycle respectively. The results showed that more the test times were, more passive the samples became and anodic reactive could be resisted much easily, which was the same as that of Shliafirner (Shliafirner, 1975).



**Fig. 6** Anodic polarization curves for carbon steel in 0.1 mol/L  $\text{Na}_2\text{SO}_4$  solution  
(1) 50 cycles (2) 100 cycles (3) 150 cycles

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### CONCLUSION

Corrosion weight loss of carbon steel increases with acidity and bisulphite concentration. In fact, the influence of pH value on weight loss can be classified into two regions: high speed region of corrosion ( $\text{pH} < 4.1$ ) and slowly corrosion region ( $\text{pH} > 4.1$ ).

The accelerated weathering test in this research can obtain the similar results in short time than other accelerated tests.

The rust films formed in accelerated weathering test bore anodic reaction resistant, which became stronger as increment of time.

### REFERENCES

- Haagenrud, S., Atmospheric corrosion (Ed. by Ailor, W. H.), New York: John Wiley and Sons, 1982: 669  
Shliafirner, A. M., Zashita Metallov, 1975, 11:200