

EFFECTS OF ANION ON THE CORROSION BEHAVIORS OF CARBON STEEL UNDER ARTIFICIAL RAIN FALL TEST

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Abstract

Rain is one of the main importance issues for atmospheric corrosion problem. Effects of rainfall on corrosion behaviors of carbon steels were investigated using artificial rainfall equipment. Three types of Atmospheric Corrosion Monitoring (ACM) sensors, which consist of Fe-Ag, Zn-Ag, and Al-Ag galvanic couples, were used to illustrate the correlation between the sensors output, Corrosion Rate (CR), and chemical concentration in the rain. The effects of ionic species on the corrosion behaviors were observed by using NaCl, KCl, Na₂SO₄, NaNO₃, and KNO₃ as rainfall solutions. The result revealed that the rainfall rate was insensitive to ACM sensors outputs and CRs. In contrast, the chemical species and their concentrations in the rainfall solution significantly affected the ACM outputs and CRs. The corrosivity of the cations (Na⁺ and K⁺) is negligible compared to the anions (Cl⁻, SO₄²⁻, NO₃⁻). For a given number of molar concentration, the CRs resulted from the corrosivity of SO₄²⁻ anions were higher than that of Cl⁻ and NO₃⁻ anions, respectively. According to the empirical data, the CRs is increased and then reach a steady state as the molar concentration is continuously increased. This research also indicates that the ACM sensors outputs of Fe-Ag and Zn-Ag couples are capable of estimating corrosivity of the atmosphere, while the ACM sensor of Al-Ag couple can be used to determine not only the time of wetness but also the type of chemical species in the environment. The research methods discussed in this paper proves that the CRs are dependent on the atmospheric composition and can be forecasted through ACM sensors.

Keywords: Corrosion Rate (CR), Atmospheric Corrosion, Air Pollution, Atmospheric Corrosion Monitoring (ACM) Sensor, Sodium Chloride (NaCl), Sodium Sulfate (Na₂SO₄), Sodium Nitrate (NaNO₃), Potassium Chloride (KCl), Potassium Nitrate (KNO₃).

1. INTRODUCTION

An environmental effect, such as corrosion attack, is the most important factor for the design of metallic structure like infrastructures, automotive, and other equipment, which usually exposed to an outdoor environment. Atmospheric corrosion is a very complicated process that causes deterioration of metallic materials by chemical or electrochemical reaction between the metal and its environment. The Relative Humidity (RH), time of wetness and numerous pollutant substances which involve species deposited from atmosphere and species from the metal resulting from corrosion itself affect to the atmospheric corrosion [1]. The atmospheric corrosions are often classified into several qualitative zones, based on subjective assessments of pollution factors, namely Rural, Urban, Industrial, and Marine atmosphere [1-6]. Generally, the rural area is low corrosivity while Urban, Industrial, and Marine atmosphere are, respectively, higher corrosivity due to the existence of higher chemical contain in the atmosphere [3,4]. The corrosive of marine area relates to the existence of high Cl⁻ concentrations in the atmosphere. Other chemical species that can be found in the Urban and Industrial atmospheres are SO₂, CO₂, and NO₂, that product by gas emission from the combustion engine [6-8]. Further

oxidation of SO₂, usually in the presence of a catalyst such as NO₂, forms H₂SO₄, and thus, acid rain could initiate [8].

Atmospheric corrosion, depends mainly on air pollution, is commonly initiates and develops under the thin water films, the film which is considered as surface electrolyte layer, formed by fog, dew, or raindrop. For a given time of wetness (time during which the wet film exists), the greater the pollution value, the greater the corrosivity formation. To know and elucidate the effect of the pollution on the corrosion behaviors, it is necessary to identify the pollutant substances, and likewise, the time of wetness should be taken into account. In this research, the corrosion behaviors of carbon steel affected by several types of ionic species were investigated by simulating artificial rainfall test. Three type of ACM sensors were used to create the empirical data for estimating the relation between sensor outputs and CRs. The chemical species and its concentration in the rainfall solution were taken as the main parameters of corrosion.

2. EXPERIMENTAL PROCEDURE

2.1 Chemical Composition in Rainfall Solution

Chemical properties, pH values, and electrical conductivities of actual rain at National Institute for Material Science

(NIMS), Tsukuba, Japan, were analyzed. The measurement results show that the highest chemical concentration is HCO_3^- and follow by NO_3^- , SO_4^- , and Cl^- (as seen in Table (1)). The pH value and electrical conductivities are about 4.8 ~5.7 and 10~43 $\mu\text{s}/\text{cm}$ respectively. In general, SO_4^- , Cl^- , and NO_3^- are the most aggressive ionic species for corrosion acceleration [1, 2]. In this experiment, NaCl, KCl, Na_2SO_4 , NaNO_3 , and KNO_3 species, which are the major contain in the actual rain, were mixed with Deionized water and used as artificial rainfall solution.

2.2 Artificial Rainfall Equipment

The artificial rainfall equipment, as seen in Fig. 1, composed of a chamber, a water reservoir, an air-compressor-mixer, ACM sensors which are connected to a Data logger, and a nozzle spray which is installed on the top of the chamber. The rainfall distribution is considerably uniform, and it can be adjusted to get a wide range of rainfall rate: 0.5 mm/h to 10 mm/h. However, the results of this experiment show that the rainfall rate, H (mm/h), is insensitive to the CRs and ACM sensors outputs. Hence, H= 1 mm/h was used for all cases.

Table-1: Chemical properties in actual rainwater [9]

Date	06-Jun	07-Jul	25-Jul	
			Beginning	Main
pH (24 C)	5.5	4.8	5.2	5.7
Conductivity ($\mu\text{s}/\text{cm}$)	10	26	43	11
Concentration (mg/L)				
Cl^-	0.7	0.6	2.4	0.7
SO_4^{2-}	2.0	3.7	5.3	1.3
NO_3^-	1.2	3.5	7.5	1.4
Na^+	0.3	0.5	2.0	0.4
K^+	0.3	0.7	2.3	0.7
Ca^{2+}	<0.1	0.2	0.2	<0.1
Mg^{2+}	<0.1	<0.1	<0.1	<0.1
HCO_3^-	<5.0	<5.0	<5.0	<5.0

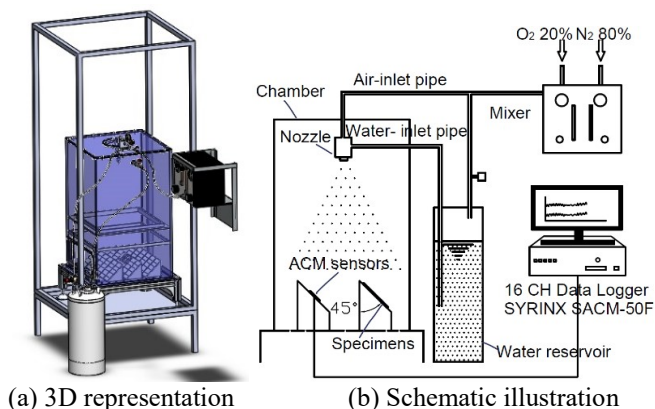


Fig-1: Artificial rainfall equipment

2.3 Atmospheric Corrosion Monitoring (ACM) Sensor

Sensor

It has been known that galvanic couple sensing probe was used for dew detector [10] time-of-wetness meter [11], or moisture sensor [12]. Further integrations and applications of this type of sensor, which is called Atmospheric Corrosion Monitoring (ACM) sensor, has been used to predict the behaviors of corrosion under atmospheric condition [13]. The schematic illustration of ACM sensor, which consists of the Fe-Ag couple, is presented in the Fig. 2. The signal output, which can be called galvanic current, range between nanoampere to milliampere, depends mainly on the electrical conductivity of aqueous film formed by dew or raindrop on the striped surface of the sensor, as seen in Fig. 2 (b). And the signal outputs of the sensors are recorded and collected every minute by 16 CH Data logger SYRINX SAXM-50F. In this research, three types ACM sensors, Fe-Ag, Zn-Ag, and Al-Ag, were used to investigate the phenomenon of corrosion through the signal output of ACM sensors.

2.4 Exposure Test and Measurement

Low-carbon steel sheets, SPCC, were used as specimens and exposed to the artificial rainfall by a limited and single face. The backside, cut edge, and fringe of the specimens were covered by polyethylene sheetin order to avoid undesired corrosion occurs, as seen in Fig. 3. The ACM sensors and specimens were installed at the bottom of the chamber and incline 45° with a vertical plan. Each test was conducted 16 hours with two times repeated. The CRs were computed based on weight loss method; the samples were immersed in the Hydrochloric Acid (HCl) to remove the corrosion products or rust layer, then weight-loss was measured (ISO/DIS 8403.3 [14]).

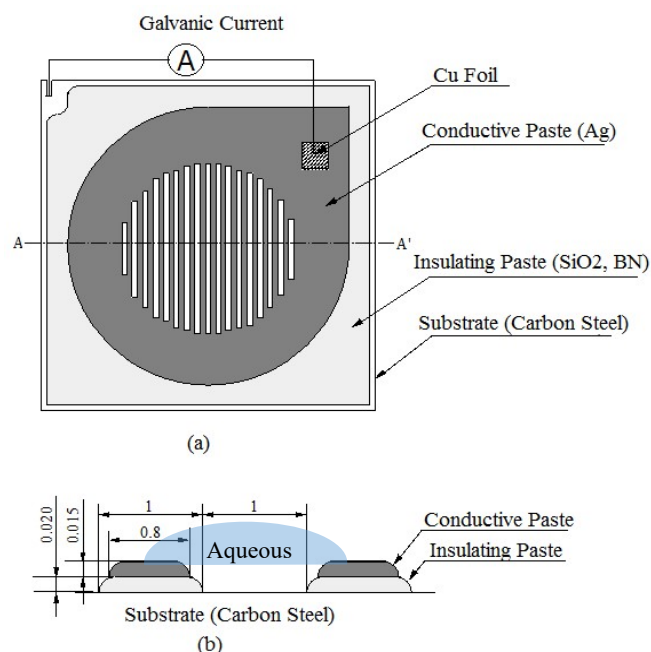


Fig-2: Schematic illustration of Fe-Ag ACM sensor, (a) overall view, (b) section view [13].

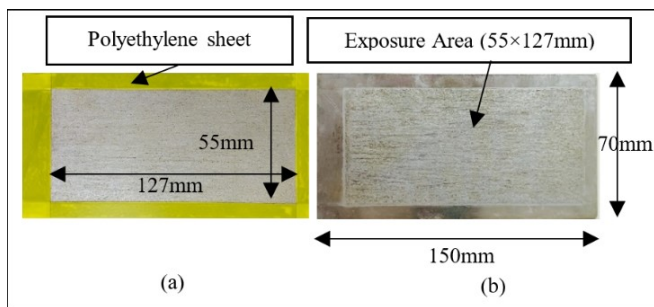


Fig-3: Carbon steel sheet specimens, (a) Preparation of the specimen before exposure test, (b) After removing corrosion product.

3. RESULTS

3.1 Molarity and Electrical Conductivity

The electric conductivity, σ ($\mu\text{s}/\text{cm}$), of all solutions linearly increase with the increasing of molarity, c (mol/L), (Fig. 4). In addition, Na_2SO_4 solutions present the highest electrical conductivity while NaCl and NaNO_3 solutions are considerably similar trend line. It should be noted that the relation between σ and c follow a general formula:

$$\sigma = \beta \cdot c + D \tag{1}$$

Where β is the electricity coefficient and D is electrical conductivity of deionize-water, in this experiment $D \approx 0.9$ to $1.5 \mu\text{s}/\text{cm}$.

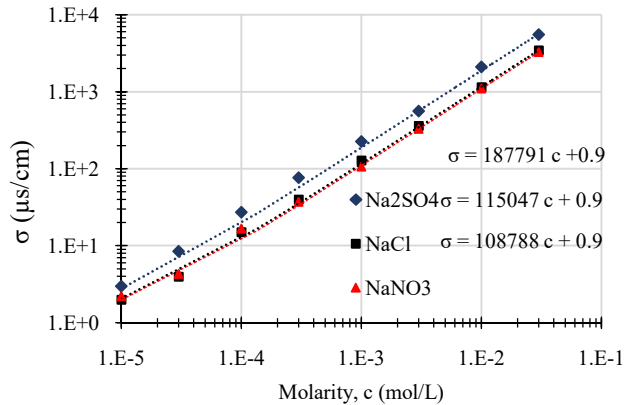


Fig-4: The electrical conductivity of Na_2SO_4 , NaCl , and NaNO_3 solutions in function of molar concentration

3.2 Corrosion Rate Calculation

After removing corrosion product, or rust layer, from the surface of the samples, weight loss was measured and converted to thickness loss. The thickness loss per year is called Corrosion Rate, CR (mm/y). The CR of the exposure sample can be calculated according to the following equation:

$$\text{CR}(\text{mm}/\text{y}) = \frac{10 W_y}{\rho A} \tag{2}$$

Where W_y is weight loss per year (g/y), ρ is the density of carbon steel ($7.86\text{g}/\text{cm}^3$), and A is the exposed area ($12.7 \times 5.5\text{cm}^2$).

3.3 Effect of Rainfall Rate

The rainfall rates were insensitive to CRs and ACM sensors outputs as seen in Fig. 5. It can be explained by the fact that the CR can approach maximum when the electrolytes surface film covering the metal become very thin, below $56 \mu\text{m}$ [1,9,15-17]. For the larger thickness of the film, especially under the rainfall with homogenous concentration, the CRs will stabilize at a constant value.

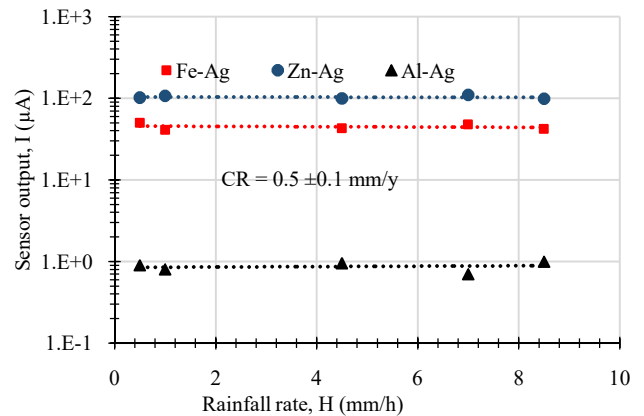
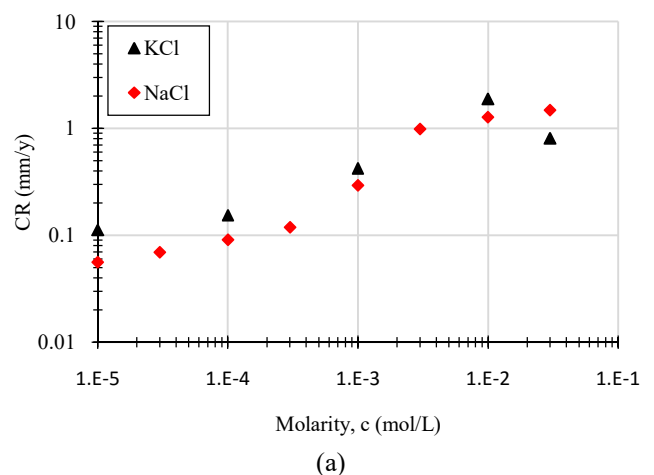
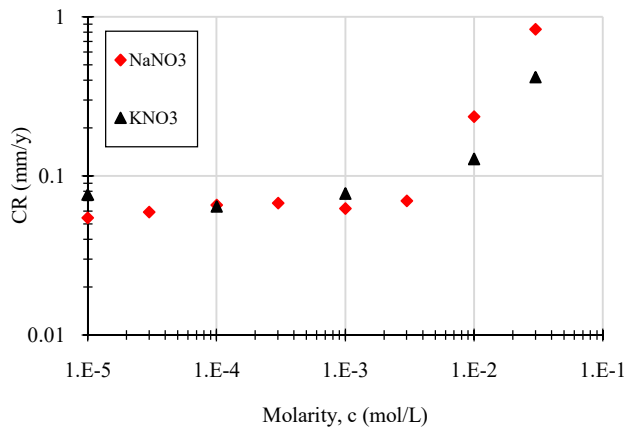


Fig -5: The effect of rainfall rate to the sensor output in Na_2SO_4 solution with the concentration of $3 \times 10^{-4} \text{mol}/\text{L}$

3.4 Effect of Anions on Corrosion Rate

In water, NaCl for instance, the molecules will separate into ions: Na^+ (cation), and Cl^- (anion). And likewise for KCl , NaNO_3 , and KNO_3 : K^+ , Cl^- , Na^+ , NO_3^- . The negative charge, called anion, is the most corrosive ion because it has much more tendency to catch electron from the metal surface. Consequently, the metal will oxidize by transferring the electron to the anion and liberating metal ion from metal the surface. Fig. 6 show CRs resulting from the effect of the anion and the variation of molarity. Evidently, Fig. 6 (a) and (b) indicate corrosion tendency depend on Cl^- and NO_3^- respectively, while the effect of K^+ and Na^+ is negligible. This Phenomenon does not mean for all cation, especially H^+ that has natural tendency to accept the electron from metallic-solution interface.





(b)

Fig-6: Effect of anion on corrosion rate, (a) the effect of Cl⁻, (b) the effect of NO₃⁻

3.5 Relation between Corrosion Rate and Molarity

Fig. 7 shows the logarithmic scale representation of CR in function of molar concentration. Each data point is the CR mean value of two-time repeated tests with three samples. As it can be seen, SO₄²⁻ is the most aggressiveness anion, and follow by Cl⁻ and NO₃⁻, respectively. According to the empirical data, the CR of Na₂SO₄ and NaCl indicate the transition from corrosion acceleration to deceleration and tend to reach a steady state when molarity is continuously increased. In particular, the CR of NaNO₃ is considerably constant, CR ≈ 0.05 mm/y, for c < 3.10⁻³ mol/L, elsewhere, c > 3.10⁻³, the CR rapidly raises up. For the smaller concentration, c < 3.10⁻⁵ mol/L, all the CRs are approximately similar and remain steady.

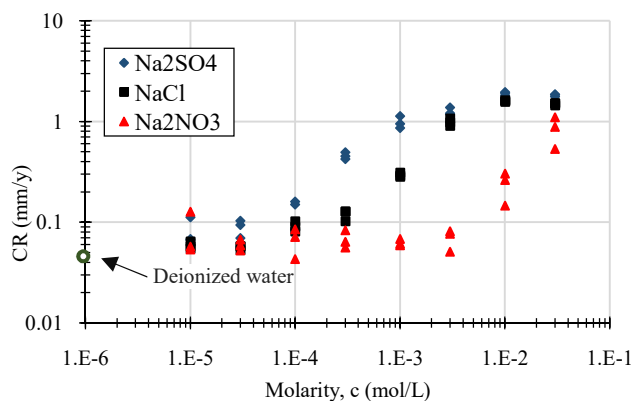
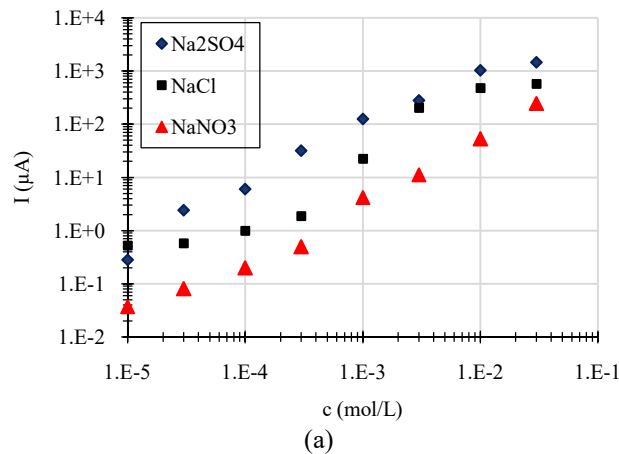


Fig-7: Corrosivity of carbon steel sheet corroded by Na₂SO₄, NaCl, and NaNO₃ solutions

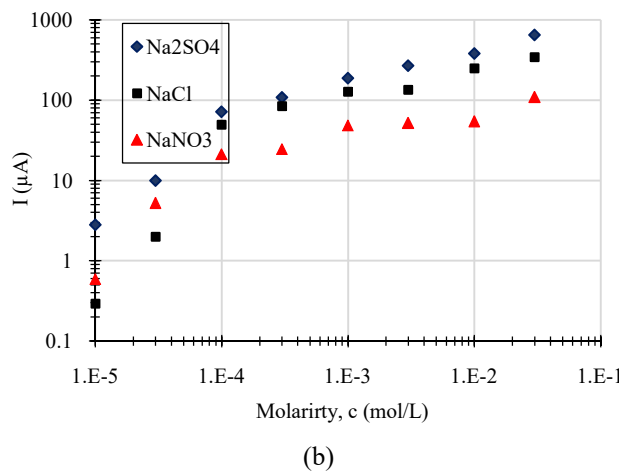
3.6 Relation between Sensor Outputs and Molar Concentration

Fig. 8 shows the relation between sensor outputs in function of molar concentrations. The galvanic currents of the three sensors increase with the increasing of molar concentrations, except Al-Ag galvanic current in NaNO₃ solution (see Fig 8 (c)) that considerably unchangeable when c > 10⁻⁴ mol/L. For

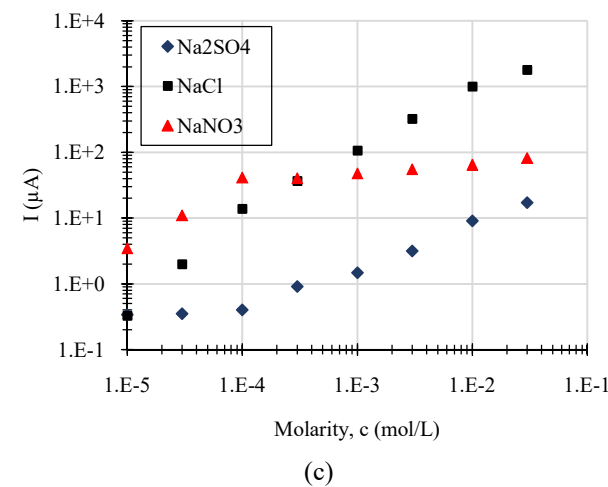
Fe-Ag and Zn-Ag sensor, the galvanic currents in the Na₂SO₄ solutions are higher than those in NaCl and NaNO₃ solutions, respectively (see Fig. 8 (a) and (b)). On the contrary, the Al-Ag galvanic currents in Na₂SO₄ solutions are lower than those in NaNO₃ and NaCl solution (see Fig. 8 (c)).



(a)



(b)



(c)

Fig-8: Relation between molar concentration and sensor outputs, (a) Fe-Ag galvanic couple, (b) Zn-Ag Galvanic couple, and (c) Al-Ag galvanic couple.

3.7 Relation between CR and Sensor Output

Recall that; the sensor output is a current of the galvanic couple that highly depend on ionic species in the aqueous film formed on the surface of ACM sensor. Fig. 9 (a), (b), and (c) present the outputs of the three sensors, Fe-Ag, Zn-Ag, and Al-Ag in function of CR. With Na₂SO₄, NaCl, and NaNO₃ solutions, the sensor outputs of Fe-Ag and Zn-Ag couple are relatively similar and congregated as a curve, as seen in Fig. 9 (a) and (b). Conversely, the outputs of Al-Ag sensor are completely deviated by chemical species (Fig. 9 (c)). Additionally, Na₂SO₄ solution is less sensitive to the Al-Ag sensor output, while it is sensible to the Fe-Ag and Zn-Ag.

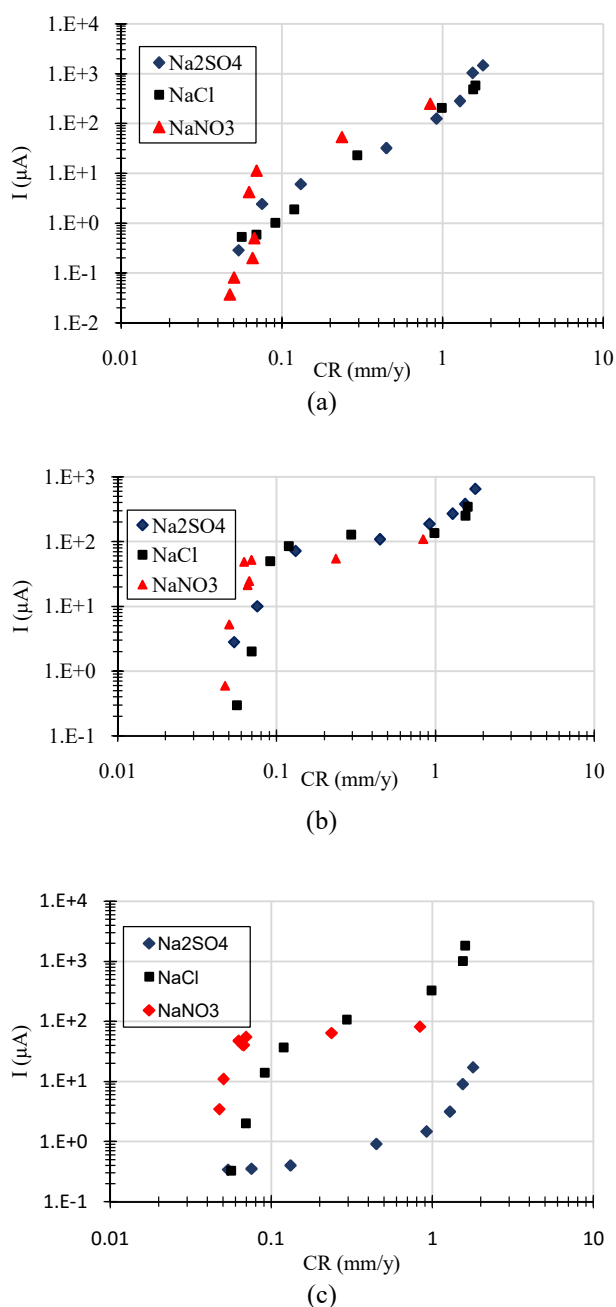


Fig -9: Relation between sensor output and CR, (a) Fe-Ag, (b) Zn-Ag, and (c) Al-Ag galvanic couple

4. DISCUSSION

Atmospheric corrosion is an electrochemical process which can only proceed in the presence of an electrolyte film. It is, therefore, to be considered as discontinuous process, where the total corrosion loss, COR, in a given time or period is determined by the time of wetness, t_{wn} , and the average of corrosion rate, CR, during the each period, n, of condensation[1]:

$$\text{COR} = \sum_n t_{\text{wn}} \cdot \text{CR}_n \quad (3)$$

The calculation the time of wetness based on meteorological data (by taking $\text{RH} \geq 80\%$ and $T \geq 0^\circ\text{C}$) might not achieve the exact time that makes corrosion possible. Thus, the technical measurement method using ACM sensor exposure to the actual environment is more preferable. Virtually, Fe-Ag and/or Zn-Ag galvanic couples enable to estimate the time of wetness, t_{wn} , and corrosion rate, CR_n , through the empirical data (see Fig. 9 (a) and (b)). Al-Ag couple, however, is unable to forecast the CR in the unknown pollution species, especially the mixed species in the atmosphere, due to the inconsistent relation of I-CR in different solutions (Fig 9 (c)). Nonetheless, the Al-Ag enables to estimate the time of wetness based on the great lifetime service. And also, it allows predicting the chemical species in the environment. For instance, if the CR is high, and the Al-Ag sensor output is low, the SO_4^{2-} ions is assumed as the major contain in the solution or the environment. It has to be noted that the service-life of Fe-Ag galvanic sensor is much lower than those of Zn-Ag and Al-Ag, respectively. The rust layer could be visually detected on the striped surface of the Fe-Ag sensor after about 64 hours rain (see Fig. 10), and it results to the increasing of the sensor output and decreasing the sensibility of the sensor. Thus, it is recommended to change the sensor frequently during the exposure test.

5. CONCLUSION

The experimental analysis of the corrosion behaviors under the artificial rainfall investigation allows to conclude as below:

- The rainfall rates were insensitive to ACM sensors outputs and CRs. In contrast, the chemical species and their concentrations in the rainfall solution significantly affected the ACM outputs and the CRs.
- The corrosivity of cations is negligible compared to anions. For a certain of molar concentration, the most aggressiveness ions are SO_4^- , Cl^- , and NO_3^- , respectively.
- For further increasing molar concentration, the CR tends to reach a steady state at the maximum value of $\text{CR} = 2\text{mm/y}$.
- The ACM sensors are capable of estimating the time of wetness and aggressivity of atmosphere, and thus the total corrosion loss could be estimated.
- The lifetime of Fe-Ag galvanic sensor is much shorter than those of Zn-Ag, and Al-Ag respectively since the rust layer visually appears after 64 hours rain; thus the sensibility of the sensor would not perform well.

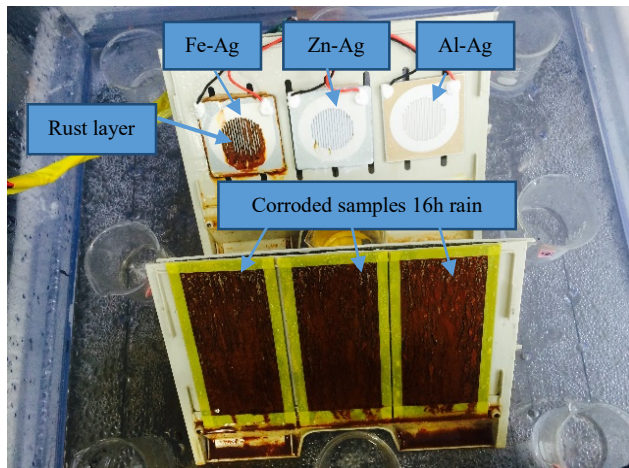


Fig-10: Overview of corroded sample after 16 hours rain with $\text{NaCl } 10^{-2} \text{ mol/L}$, and ACM sensor after 80 hours rain

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