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Long-term monitoring of atmospheric corrosion at weathering steel bridges by an electrochemical impedance method

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ABSTRACT

Weathering steel corrosion was monitored for one to two years under natural atmosphere by an electrochemical impedance technique. Two identical comb-shape weathering steel sheets embedded in epoxy resin were used as monitoring probe electrodes at two different bridges in Japan. Impedances at 10 kHz (Z_{10kHz}) and 10 mHz (Z_{10mHz}) were automatically measured every hour. Coupons ($50 \times 50 \times 2$ mm^3) prepared from the same steel sheets were exposed together to measure the corrosion mass loss. The average $(Z_{10mHz})^{-1}$ value for half to one year exposure correlated well with the average corrosion rate determined from the corrosion mass loss.

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1. Introduction

Weathering steels are increasingly used as bridge materials owing to their environmental and economic benefits. Protective rusts formed on their surface at early stages reduce further rusting. Therefore, these steels can be used without painting or after rust stabilizing surface treatment. Being applicable to relatively mild environments such as rural and urban setting, these steels encounter difficulties in coastal areas because airborne salt deposits may generate porous and non-adhesive rusts on their surface. Advanced weathering steels containing a small amount of nickel have been developed and applied to bridges exposed to relatively high airborne salt concentrations. Rust growth strongly depends on environmental factors such as rainfall, temperature, relative humidity, and airborne salts. Thus, determining the appropriate environmental conditions for these weathering steels as bridge materials is important.

Weathering steels have been investigated via long-term exposure tests in various rural, urban, marine, and industrial atmospheres. Corrosion resistance was evaluated using corrosion mass loss measurements after the long-term exposure test [1–5]. Characterization of the rusts by X-ray diffraction (XRD) [1], Raman spectroscopy [2], electron probe microanalysis (EPMA) [3], Mossbauer spectroscopy [2,4], and Synchrotron radiation [5] indicated that the rusts comprised a magnetite (Fe$_3$O$_4$) inner layer and an oxyhydroxide (FeOOH) outer layer. Four distinct types of FeOOH are often observed in rust: goethite (α), akaganeite (β), lepidocrocite (γ), and amorphous. β-FeOOH is known to form in chloride-rich environments. γ-FeOOH, which is often observed at initial stages of exposure to various environments, turns into α-FeOOH and amorphous FeOOH in relatively mild environments and serves as a protective rust layer for weathering steel. Its formation strongly depends on environmental factors such as amount of airborne salt, relative humidity, and temperature. Both regional and local environment should be considered prudently when selecting bridge materials between weathering steels, painted steel, and concrete. The local environment may vary at different parts of the same bridge. For instance, less airborne salt may accumulate on the exterior than on the interior webbing of a bridge because the exterior webbing surface may be frequently washed by rainfall. In general, the corrosion rate of steels is much higher in sheltered parts of steel structures close to a coastal line. Corrosion mass loss data are not sufficient to determine the protective rust formation process. A better understanding of this process requires a monitoring system that records corrosion rates in addition to environmental factors such as temperature, relative humidity, rainfall, airborne salt concentration and nature, and "time of wetness (TOW)."

The atmospheric corrosion of metals has typically been monitored using a galvanic-cell type atmospheric corrosion monitor (ACM) sensor [6–12]. Most recently, Shinohara et al. have monitored steel constructions under various atmospheres using the ACM sensor [11]. This sensor measured the galvanic current through a thin water film between Ag–Zn or Ag–Fe couple, acting

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as an environmental sensor for factors such as TOW. Mansfeld et al. attempted to monitor instantaneous atmospheric metal corrosion rates by measuring the polarization resistance using an atmospheric corrosion rate monitor (ACRM) and correlated this resistance with the corrosion mass loss [12].

The atmospheric corrosion of carbon and weathering steels [13–16], as well as galvanized [17–22], stainless [23–25], and painted steels [26] has been studied under wet and dry cyclic conditions in a laboratory chamber. In these studies, a technique based on electrochemical impedance theory was successfully applied to corrosion process monitoring. In natural atmospheric environments, the corrosion of nickel-containing steels was recorded via continuous impedance measurements at 10 mHz (Z_{10mHz}) on open exposure test racks [27,28]. Z_{10mHz} responded according to changes in environmental factors, such as rainfall and relative humidity, but was not correlated to actual corrosion rates in atmospheric environments. Under immersion conditions in bulk aqueous solutions, the frequency impedance at 10 kHz (Z_{10kHz}) corresponds to the solution resistance, and the difference ($Z_{10mHz} - Z_{10kHz}$) represents the polarization resistance R_p [29]. Moreover, the reciprocal of R_p is proportional to the corrosion current I_{corr}. However, determining R_p for ultrathin electrolyte films under atmospheric conditions R_p is expected to be challenging [13,16].

In this study, the atmospheric corrosion of weathering steels was monitored at two different bridges in Japan using the same type of probe electrodes as that used in a previous study [27,28]. The steels in partially and fully sheltered sites were examined for one to two years and the recorded data was correlated with the corrosion-induced mass loss.

2. Experimental

A two-electrode cell was used for atmospheric corrosion monitoring [27,28]. Electrodes were prepared from ordinary weathering steel (WS) and nickel-containing weathering steel (NWS) plates. The chemical compositions are shown in Table 1. They were cut into comb shapes using a wire electric discharge machine. A pair of identical comb-like electrodes was embedded approximately 120 μm apart in epoxy resin, as illustrated in Fig. 1. The surface area of each electrode was approximately 1 cm². Steel coupons (50 × 50 × 2 mm³) were also prepared from the same steel plates to evaluate the corrosion mass loss.

Weathering steel bridges located in Niigata (Bridge A) and Hiroshima prefectures (Bridge B) in Japan were selected as exposure sites. Bridge A is approximately 10 m long and spans a farm ditch. It is located about 7 km south east of the Sea of Japan coastal line. In this part of Japan, the north wind usually carries a relatively large amount of airborne salts from the sea in winter. Bridge B is approximately 500 m long and is located about 0.5 km north from the Seto Inland Sea. The amount of airborne salts is expected to be small along this calm inland sea coast. Although its service duration was shorter, the weathering steel of Bridge A appeared more corroded than that of Bridge B, particularly in sheltered parts.

After rust removal of bridges, probes and coupons were fixed on the weathering steel bridges using double-sided adhesive tape. The corrosion of Bridge A was monitored over two time periods: from December 2, 2008 to December 2, 2009 and from June 05, 2011 to June 5, 2013. During the first period, the probes and coupons of WS
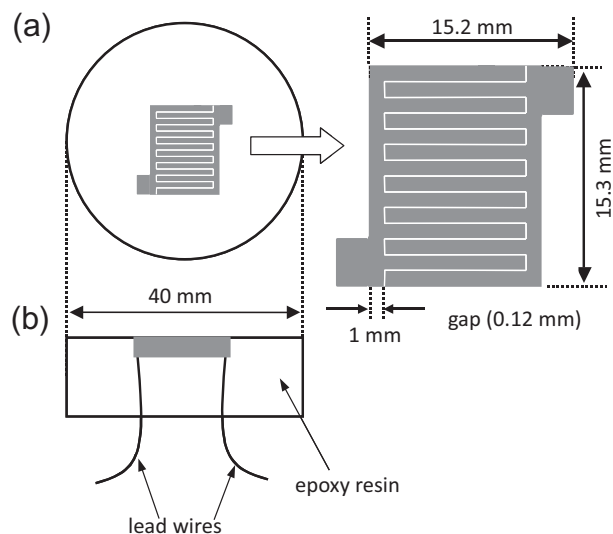

Fig. 1. Schematic diagram of a probe electrode for atmospheric corrosion monitoring (a) top view and (b) side view.

and NWS were horizontally placed skyward (#A-1) and earthward (#A-2) on both sides of the lower flange of wide flange beams. During the second period, WS probes and coupons were vertically set outside (#A-3) and inside the sea-side webbing (#A-4), as well as inside (#A-5) and outside the land-side webbing (#A-6). The Bridge A structure and positions #A-1–6 are illustrated in Fig. 2. Positions #A-3 and #A-6 were exposed to heavy rain, whereas the others were completely sheltered.

On Bridge B, the probes and coupons of WS and NWS were vertically placed outside the webbing (#B-1) and on an inside flange (#B-2). Airborne salts accumulated on #B-1 would be washed out by heavy rain. Position #B-2 was not directly exposed to rain, thus, allowing airborne salts to accumulate on material surfaces. The monitoring period lasted a year, starting from December 25, 2008.

Impedances at high (10 kHz) and low (10 mHz) frequency points were automatically measured using a corrosion monitor (Syrinx Inc.). In sheltered sites that were not directly exposed to rain, $Z_{10 kHz}$ always exceeded the maximum limit of the monitor by 10^4 kΩ. Therefore, the reciprocal of $Z_{10 mHz}$ was employed as the corrosion rate index without solution resistance compensation. The applied voltage amplitude between two electrodes equaled 10 or 50 mV. The obtained data were stored in an SD memory card. Temperature and relative humidity (RH) were measured every hour by sensors positioned close to the probes and coupons. The corrosion monitor was powered by a lead storage battery connected with a solar battery because AC power supply was not available on the bridges.

Coupons were removed from exposure sites after a half or one year and corrosion mass losses were measured after rust removal. Rusts were carefully removed by 3–5 min immersion in a 1 L solution containing HCl (18.5 g), hexamethylenetetramine (3.5 g), and an organic inhibitor (3 mL). At most, five coupons were treated in a batch at a time. A fresh solution was used for each batch because dissolved Fe^{3+} ions could possibly enhance the dissolution of the substrate steel. It was confirmed by as-polished samples that dissolution from the substrate steel was negligibly small. Average corrosion thickness loss was calculated from corrosion mass loss.

Before rust removal, rust thickness on coupons was also evaluated using an electromagnetic coating thickness tester. The measurement was taken at six randomly-selected points on the coupon surface, and average values were calculated.

Table 1
Chemical compositions of WS and NWS (mass%).

	C	Si	Mn	P	S	Cu	Ni	Cr
WS	0.10	0.19	0.71	0.017	0.005	0.32	0.22	0.50
NWS	0.02	0.24	0.33	0.006	0.004	0.32	2.61	0.04