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Relationship between degradation characteristics of organic coating on internal bottom plate of oil storage tank and constant-phase element parameter values

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ABSTRACT

A quantitative evaluation method is proposed based on electrical impedance measurements for predicting the residual lifetime of a high-performance anticorrosion organic coating on the internal bottom plates of oil storage tanks. The field data obtained from an actual oil storage tank suggest that the impedance characteristics of the degradation of the coating were elucidated by three equivalent circuit models including two CPEs (constant-phase elements) in parallel. It was revealed that these CPEs indicate the intact and the deteriorating coatings. In addition, the degradation process of the coating with age can be monitored quantitatively by using scatter diagrams of CPE parameters.

1. Introduction

The internal bottom plates of oil storage tanks are constantly exposed to a corrosive electrolyte solution called drain water, as summarized in Table 1. From Table 1, it is found that the drain water is a neutral solution, which contains chloride ions (Cl^-) and oxygen (O_2) that are enough to cause corrosion. Since the sulfite ion ($SO_4{}^{2-}$) concentration is smaller than that of sea water in the range of 800–3400 ppm [1], it is supposed that the occurrence of hydrogen sulfide (H_2S) resulting from the reduction reaction of $SO_4{}^{2-}$ by sulfate-reducing bacterium (SRB) [2] is almost negligible. Furthermore, it is reported that the originally containing H_2S concentration in drain water is very low, even if the H_2S concentration in a gas phase is very high (e.g., when the H_2S concentration in the gas phase was 8000 ppm, while that of the drain water was 10 ppm) [3].

With the goal to isolate the steel substrate from the corrosive electrolyte solution, the steel plates are generally coated with an organic coating. Recently, a vinyl ester resin organic coating containing glass flakes has become one of the high-performance anticorrosion coatings used for aggressive environments [4,5], and so has been adopted in many tanks. It is thought that the application of this coating prevents the corrosion of the steel, because no fatal oil leak accidents have happened for over 20 years in our experience. However, the gradual deterioration of the anticorrosion performance of the coating with age cannot be avoided. Therefore, it is important to accurately measure the residual lifetime of the coating to prevent serious oil leak accidents.

For the inspection of oil storage tanks, a periodic internal inspection is conducted according to the corresponding regulations in Japan. Detecting the physical failure of the coating is often done by a visual appearance inspection. Any visually detected defects of the coating, such as flaws, delamination and blisters, are repaired. In particular, blisters are regarded as a frequently critical defect, because the cause of blisters is attributed to the insufficient protection of coatings accompanied by a corrosion reaction at a metal substrate [6,7]. Although a visual appearance inspection is simple, the evaluation performance is dependent on the inspector's skill and the decrease of barrier properties of coatings cannot be detected by a visual observation. In addition, it is necessary to evaluate the anti-corrosion performances of the non-defective coatings, because visually defective coatings are less than several percentages of the whole area of the bottom surfaces.

Impedance measurements are a non-destructive and quantitative evaluation method that is able to clarify the characteristics

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Table 1
The typical composition of the electrolyte solution in contact with an internal bottom plate of oil storage tank.[a]

pH	Dissolved oxygen (ppm)	Chloride ion concentration (ppm)	Sulfate ion concentration (ppm)
6.7–7.3	0.1–4.5	2485–15760	2.0–83.0

[a] Results of the monthly composition analysis over 1 year.

Table 2
The periodical inspection results of the coating on the internal bottom plate of the oil storage tank.

Inspection number	Period in oil (Months)	Percentage of the defect area by visual observation[a] (%)
1	37	0.02
2	97	0
3	171	0.02
4	266	0.04

[a] Percentage of defects are detected at each inspection. The defects include flaws and blisters.

of organic coatings in detail [8–10]. Therefore, they have attracted much attention as a method for quantitative evaluation of the coating of the internal bottom plates of oil storage tanks. However, impedance measurements are not utilized as the residual lifetime evaluation method for the coating, because impedance at a limited frequency is used only as the indicator of the degradation of the coating, presently. As the first step for the accurate prediction of the residual lifetime of the coating, it is important to clarify the degradation mechanism by the sufficient interpretation of the electrical properties of the coating.

In this study, a field survey using impedance measurements was conducted on an actual oil storage tank. The degradation mechanism of the coating used for a long period was investigated.

2. Theory

To interpret the physical and chemical properties of electrochemical systems, three simple elements are generally used: resistance (R), capacitance (C) and inductance (L). However, impedance characteristics deviate from the ideal behavior represented by these simple elements because the physical and chemical properties in many cases cannot be regarded as a homogeneous system [11].

A constant-phase element (CPE) is a useful circuit element to express the non-ideal behavior of electrochemical systems. Impedance spectra can be well-fitted by using a CPE instead of simple elements in the equivalent circuit. The CPE impedance is defined according to Eq. (1).

$$Z = \frac{1}{T(j\omega)^n} \tag{1}$$

where Z = impedance of the CPE ($Z = Z' + jZ''$); j = imaginary number ($j^2 = -1$); ω = angular frequency (rad/s); n = CPE-power ($-1 \le n \le 1$); T = CPE-constant ($s^n\ \Omega^{-1}$).

Since the CPE-constant T includes the ohm^{-1} dimension, its numerical value is related to the electrical conductivity of the measured systems. Then, the value of CPE-power n can be expressed in terms of a constant phase angle θ, as denoted in Eq. (2).

$$n = \frac{\theta}{-90^\circ} \tag{2}$$

For $n = 1$ the CPE shows an ideal capacitor, for $n = 0$ an ideal resistor is obtained, and for $n = 0.5$ the Warburg impedance is defined [12].

Although the physical origins of the CPE are still unclear, it is generally agreed that the CPE behavior arises from the distribution of time constants. The result comes from the distributions of physical properties of inhomogeneous electrochemical systems, such as electrode surface roughness, electrode porosity and current, and/or potential distribution [13]. Some recent research [14,15] suggests that the CPE behavior of coatings appears due to the distribution of time constants as the results from the inhomogeneous electrolyte uptake in the coating. It is important to confirm the CPE behavior of the coating applied to actual oil storage tanks.

3. Experimental

3.1. Specification for the crude oil storage tank and the inspection data

The investigation crude oil storage tank has a capacity of 110,000 kl. It had stored crude oil over 266 months. The internal bottom plates of the tank are coated with a vinyl ester resin organic coating containing glass flakes. The coating is composed of three layers: primer, middle coat and top coat. A base coating solution contains vinyl ester resins (novolac based and/or bis-phenol based), pigments, additives and a thinner (styrene monomer), and is mixed according to a manufacture's specification. Typical hardener is a methyl ethyl ketone peroxide. The mixing ratio of the base coating solution and the hardener is 100:0.5 to 3.0 by weight. The ratio is adjusted according to the condition of the application such as ambient temperature. The middle and top coat include glass flakes in the range from 18 wt.% to 27 wt.%. This range is determined in the corresponding regulations in Japan. Prior to the application of the coating, internal bottom plates are sandblasted until a surface finish of type ISO-Sa 2 1/2. The primer is coated using a brush or a roller, and then the middle and top coat is applied by an airless spray. Each layer is fully cured taking enough time.

Table 2 shows the periodical inspection results. Since the defects were repaired at every inspection to comply with the regulation, "the percentage of the defect area by visual observation" indicates the defects (flaws and blisters) detected at each inspection. As shown in Table 2, the percentage of the defect area detected by visual observation indicates almost no defect occurrences during each oil storage period. Although the coating almost keeps its integrity visually, it is supposed that the visually undetected degradation with age progresses because the coating was used for a long period.

3.2. Impedance measurements and analysis

Fig. 1(a) shows the top view of the internal bottom plate of the oil storage tank. The shaded regions in the figure represent 10 steel

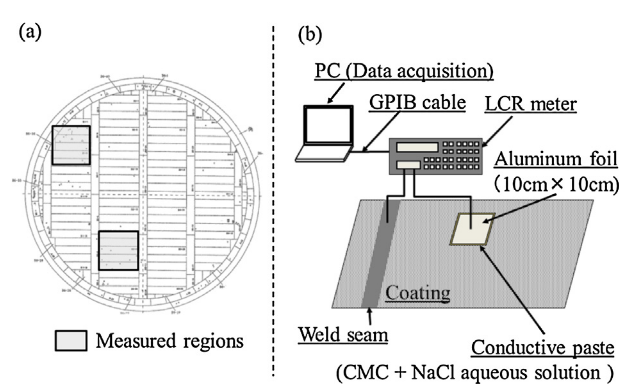

Fig. 1. (a) Ten measured regions of the internal bottom plate of the oil storage tank and (b) schematic diagram of impedance measurements by using LCR meter.