Pergamon

Cement and Concrete Research 31 (2001) 603–607

CEMENT AND CONCRETE RESEARCH

Validation of resistivity spectra from reinforced concrete corrosion by Kramers–Kronig transformations

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Received 31 May 2000; accepted 18 December 2000

Abstract

In order to determine the true corrosion conditions in reinforced concrete structures, the measured impedance data must be of high quality. This paper applies Kramers–Kronig transforms (KKT) to validate the resistivity spectra measured from corrosion of reinforcing steel bar in concrete. The resistivity spectra were measured using four-electrode Wenner array that was placed on the surface of a reinforced concrete specimen. Various levels of anodic corrosion rates were applied to the sample in order to induce corrosion. This paper shows that the KKT successfully assess the quality of the data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion; Kramers–Kronig transforms; Reinforced concrete

1. Introduction

Electrochemical impedance or resistivity spectra that are obtained from a corroding system by using a small AC electrical signal over a wide range of frequencies can determine fundamental parameters related to corrosion kinetics. While in data collection, errors can easily arise from instrumental artifacts, noise, or time-dependent phenomena. Therefore, it is essential that accuracy of the measured data be validated.

Currently, data consistency is assessed by direct observation or by regression models of electrical circuits (EC). The model often has to be modified to accommodate different circumstances, such as using inhibitors, coatings, or pitting corrosion. The selection of a model becomes difficult when the experimental data display complex characteristics, such as depressed and distorted semicircles and multiple loops in the Nyquist plot. It is even more difficult when the data exhibit a new or an unexpected feature. A common practice is to employ many adjusting coefficients, whose physical meanings are not clear [2]. In such cases, the EC models raise immediate concerns: Is the model appropriate? Are the model parameters adequate? Are the data valid?

To address these concerns, the discussion below applies the Kramers–Kronig transforms (KKT) to assess the validity of data. The Kramers–Kronig relations disclose the causal nature of the response of materials: the real and imaginary parts in a response spectrum are coupled if the system is causal, stable, and linear in nature. They are extensively used in the field of optics, acoustics, and dielectric phenomena [3–5]. Due to Bode's well-tabulated equations [1], since the 1980s [6,7], application of KKT has proved useful in the validating electrochemical impedance data from corrosion systems. Recently, KKT has been used to validate the impedance spectra of concrete in order to evaluate its microstructural stability [8]. In order to adequately determine the service life of a structure, an accurate evaluation of the corrosion of reinforcing steel bars (rebar) is critical. This paper presents validation of the measured resistivity spectra from the reinforced concrete using KKT.

2. Application of KKT

The impedance response of a corrosion system from a small AC voltage $V(j\omega)$ or current $I(j\omega)$ perturbation is a spectrum $Z(j\omega)$ with frequency ω as the independent vari-

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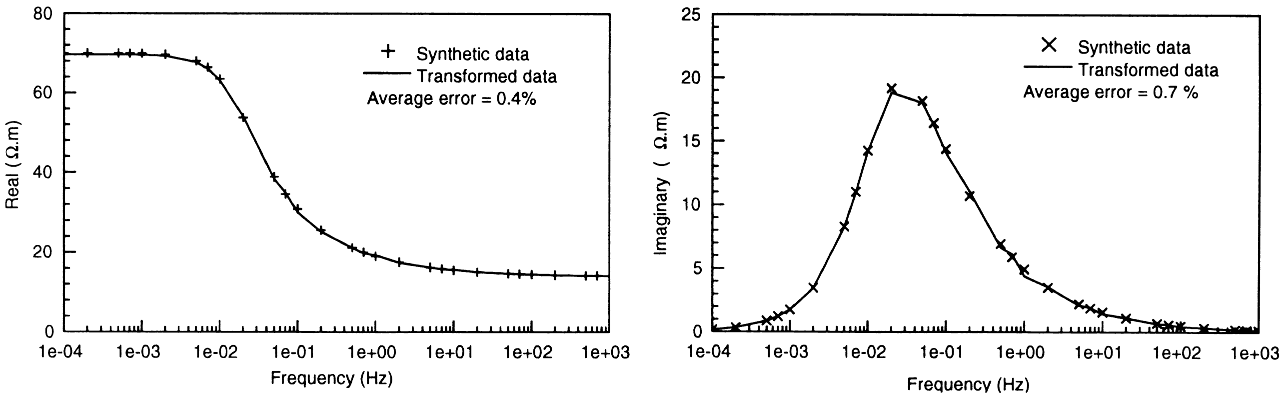
PII: S0008-8846(01)00451-3



(a) *Im*-to-*Re* (b) *Re*-to-*Im*

Fig. 1. The KKT on a synthetic spectrum.

able, which is used to quantify a corrosion state. Such a spectrum includes a real part, Re(ω), and an imaginary part, Im(ω),where $j = \sqrt{-1}$, as shown in Eq. (1).

$$Z(j\omega) = \mathrm{Re}(\omega) - jI(\omega). \quad (1)$$

The perturbation has to be small enough for the response to locate in a linear regime [9]. For a system satisfying four conditions, namely, linearity, causality, stability, and finite values in its transfer function, the real part and the imaginary part have the following Kramers–Kronig relations [Eqs. (2) and (3)], which were tabulated by Bode in the 1940s [1].

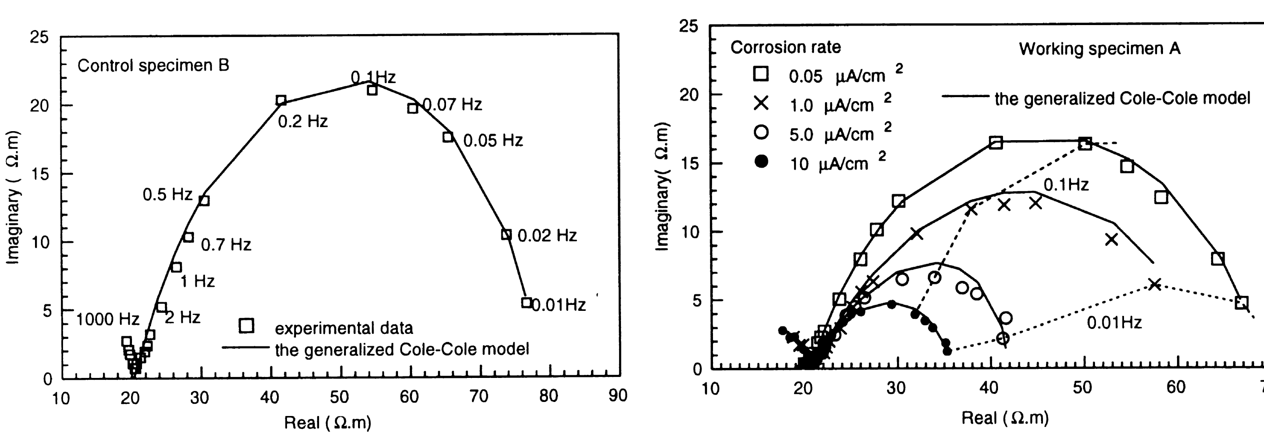
$$\mathrm{Im}(\omega) = \left(\frac{2\omega}{\pi}\right) \int_0^{\infty} \frac{\mathrm{Re}(x) - \mathrm{Re}(\omega)}{x^2 - \omega^2} \mathrm{d}x \quad (2)$$

$$\mathrm{Re}(\omega) = \mathrm{Re}(\infty) + \left(\frac{2}{\pi}\right) \int_0^{\infty} \frac{x\mathrm{Im}(x) - \omega\mathrm{Im}(\omega)}{x^2 - \omega^2} \mathrm{d}x \quad (3)$$

In theory, the real and imaginary parts, which are measured independently in experiment, can be calculated from one another prescribed over the complete frequency spectrum. If not, it can be concluded that not all of the four conditions listed above are fulfilled in the measured system, which produces inconsistent data.

In practice, experiments are always performed over a finite frequency range, thereby causing a major obstacle to the application of KKT. Therefore, the numerical integrals in Eqs. (2) and (3) of the transforms have to be carried out with discrete experimental data over a limited frequency range, instead of the theoretically required infinity one. Unfortunately, the limited frequency range produces an inherent inaccuracy beyond the numerical algorithm during conduction of the transforms. The transforms can be evaluated by comparing the transformed data Z_{KKT}, which can be either the real or the imaginary part, with the experimental data Z_{ex}, using a statistical formula given by Urquidi-Macdonald et al. [6] to calculate an average error (AE) by Eq. (4).

$$\mathrm{AE} = \frac{100 \times \sum_{\omega} |Z_{\mathrm{ex}}(\omega) - Z_{\mathrm{KKT}}(\omega)|}{NZ_{\mathrm{ex,max}}} \quad (4)$$



(a) (b)

Fig. 2. The measured resistivity spectra: (a) specimen B, (b) specimen A.

Table 1
Simulation parameters from different corrosion rates

Corrosion rate ($\mu A/cm^2$)	R_0 (Ω m)	m	τ (s)	c	a
Free corrosion	78.24	0.74	1.77	0.89	0.77
0.05	68.86	0.70	1.29	0.81	0.89
1	62.52	0.67	4.05	0.78	0.72
5	41.60	0.52	2.69	1.06	0.44
10	35.71	0.44	1.34	0.85	0.57
Precision required	±0.01	±0.001	±0.001	±0.001	±0.001

Table 2
Values of AE in transforming the experimental data and synthetic data

		AE					
		Im-to-Re			Re-to-Im		
Specimen	Corrosion rate ($\mu A/cm^2$)	E^* (%)	S^* (%)	$\|E-S\|^*$ (%)	E^* (%)	S^* (%)	$\|E-S\|^*$ (%)
B		1.65	0.33	1.25	3.51	2.49	1.02
A	0.05	1.86	0.94	0.92	2.26	2.67	0.41
A	1	2.13	1.12	1.01	4.16	4.34	0.18
A	5	2.72	0.69	2.03	4.59	2.15	2.44
A	10	1.92	0.51	1.41	7.43	2.35	5.08

E^*, experimental data; S^*, simulations by the generalized Cole–Cole model; $|E-S|^*$, the absolute difference between E^* and S^*.

where N is the number of datum used and $Z_{ex,max}$ is the one with the maximum value among Z_{ex}.

3. Validation of experimental data

3.1. Algorithm assessment

It is necessary to assess the quality of the numerical stability of the KKT algorithm before being applied to experimental data. Therefore, a synthetic resistivity spectrum, Z, produced from a generalized Cole–Cole relaxation model [Eq. (5)], was tested in order to evaluate the algorithm used.

$$Z = R_0\left(1 - m\left(1 - \frac{1}{(1 + (j\omega\tau)^c)^a}\right)\right) \tag{5}$$

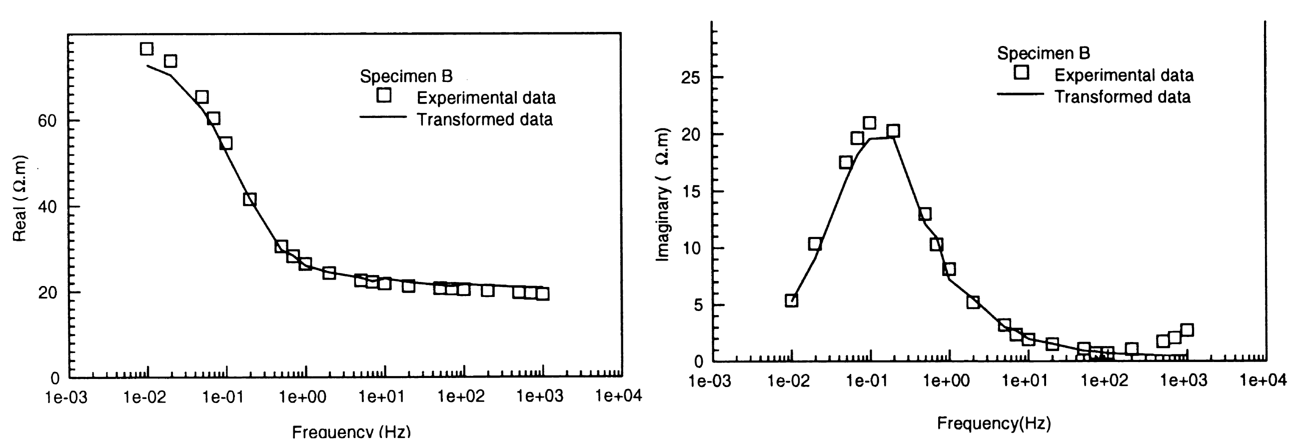
where $R_0 = 70$ Ω m, $m = 0.8$, $\tau = 10$ s, $c = 1.0$, $a = 0.5$, $j = \sqrt{-1}$, $\omega = 2\pi f$, and f is the frequency in a wide seven-decade range from 10^{-4} to 10^3 Hz.

As shown in Fig. 1, the transformed spectrum is in excellent agreement with the synthetic spectrum, with an AE of 0.7% in real-to-imaginary transform (Re-to-Im) and an AE of 0.4% in imaginary-to-real transform (Im-to-Re). The algorithm itself conducts satisfactory transforms over a wide frequency range.

3.2. Transforms on experimental data

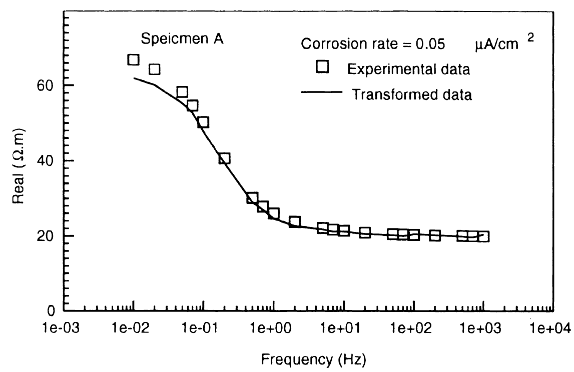
The resistivity spectra were measured on the prismatic $8.9 \times 11.4 \times 40.6$ cm reinforced concrete samples. The concrete over the rebar was 3.81 cm. The rebars used were ASTM A 615 Grade 60 steel, with a nominal diameter of 1.27 cm. Control specimen B, which was stored in the saturated $Ca(OH)_2$ solution, provided the passive condition for the rebar. In working (or corroding) specimen A, an anodic current was impressed to the rebar to induce corrosion, and the anodic current density for each measurement was 0.05, 1, 5, or 10 $\mu A/cm^2$, respectively. A more detailed description can be found in the Zhang et al. [10]. The measured resistivity spectra are shown by the discrete symbols shown in Fig. 2, where the solid lines are the simulations using the generalized Cole–Cole model (Eq. (5)), with the parameters shown in Table 1.

The KKT were conducted on both the experimental and simulated spectra, with the same frequencies and the same amount of the datum. If no limitations arise from the frequency range, discrete datum, and the algorithm, the simulated spectra will be transformed with the AE equal to

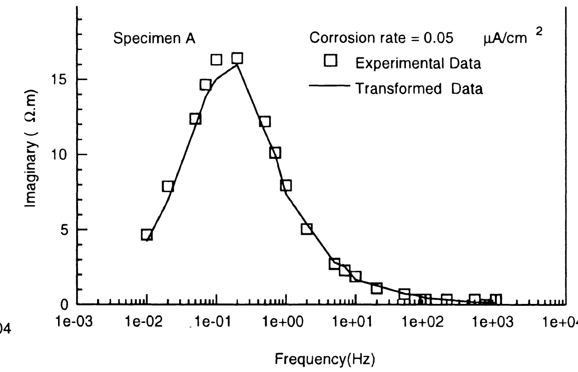


(a) *Im*-to-*Re* (b) *Re*-to-*Im*

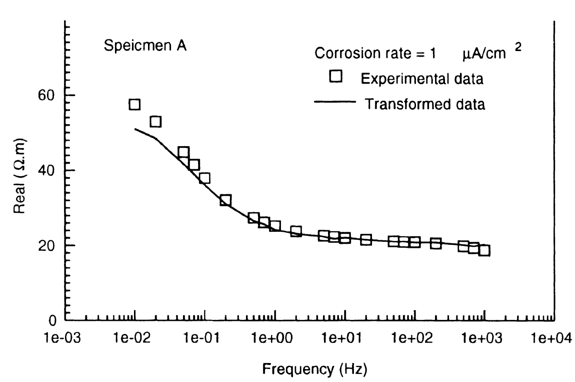
Fig. 3. The KKT on the spectrum in Fig. 2(a).



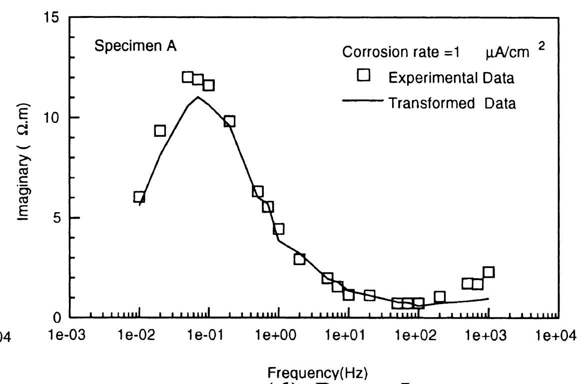
(a) *Im*-to-*Re*



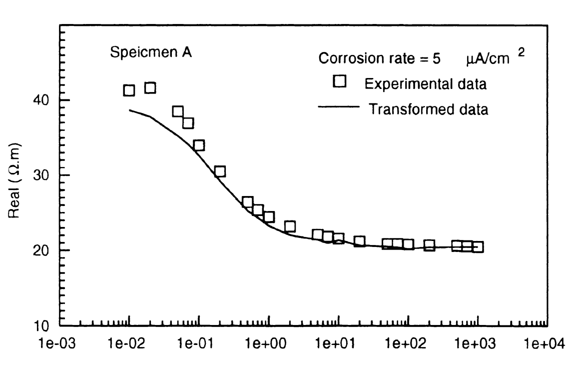
(b) *Re*-to-*Im*



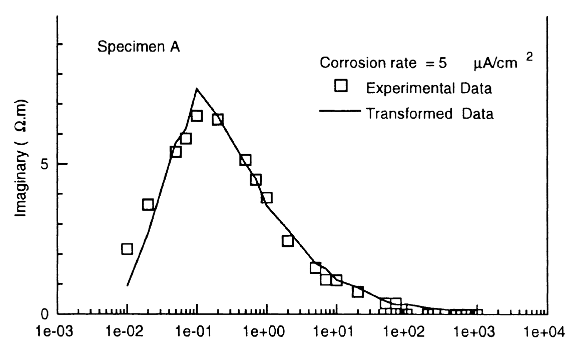
(c) *Im*-to-*Re*



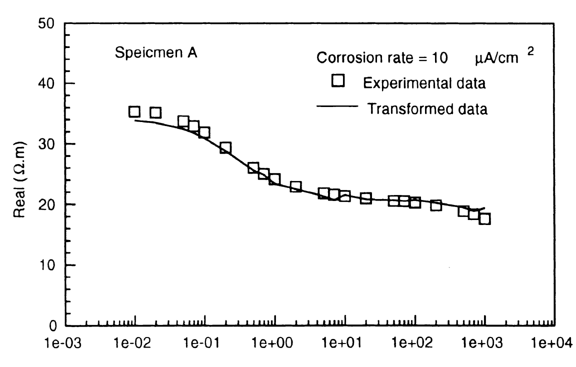
(d) *Re*-to-*Im*



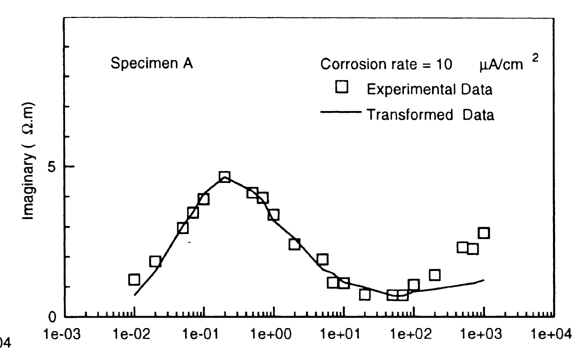
(e) *Im*-to-*Re*



(f) *Re*-to-*Im*



(g) *Im*-to-*Re*



(h) *Re*-to-*Im*

Fig. 4. The KKT on the spectra in Fig. 3(b).

zero. In other words, the nonzero AE from the simulated spectra reflects these limitations. Compared to these Cole–Cole model-simulated spectra, the experimentally obtained spectra are then subjected to both those limitations and the possible errors during data collection. Therefore, by comparing the difference between AE from the simulated data and AE from the experimental data, the quality of the experimental data can be assessed. Table 2 clearly shows that most of the differences are small (e.g., less than 2%), indicating that the experimental spectra comprise good data quality.

The transforms on the experimental data from specimen B (Fig. 2(a)) and specimen A (Fig. 2(b)) are shown in Figs. 3 and 4, respectively. The values in the transformed real part are slightly smaller than the experimental data in the low frequency range; there is a small deviation between the transformed imaginary part and the experimental data near the peak frequency, resulting from the limited frequency range used in the transforms [7].

The KKT on the experimental spectrum obtained at the impressed anodic current 10 $\mu m/cm^2$ indicate its poor quality, as shown in Table 2. This spectrum (Fig. 4(h)) will be reexamined in more detail. It is assumed that at the frequencies from 100 to 1000 Hz, the noise level, which was from inductive or capacitive pickup in the wiring of the instrument [10], made the data obtained in this frequency range susceptible. To confirm this suspicion, the KKT were repeated on this spectrum, but with the susceptible data from 100 to 1000 Hz truncated. If these truncated data are valid, the AE will accordingly become bigger due to the shortened frequency range. The values of AE before and after truncation are 7.43% and 6.61%, respectively. Note that AE becomes smaller from transforms conducted on a shorter frequency range, indicating that those truncated data from frequency 100 to 1000 Hz are of low quality. This shows the capability of the KKT to assess the presence of noise in the measurements.

4. Conclusions

(1) The method of KKT is a useful tool for evaluating resistivity spectrum quality measured from reinforcing steel bar corrosion in concrete in order to derive the correct corrosion information.

(2) The method of the KKT has validated most of the experimental spectra. This method also has detected the error data due to the instrumental pickup noise in the frequency range from 100 to 1000 Hz.

Acknowledgments

The authors wish to acknowledge the financial support given by NSF and the Federal Highway Administration (Award CMS-9812757).

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