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DEVELOPMENT OF AC IMPEDANCE
METHODS FOR EVALUATING
CORRODING METAL SURFACES
AND COATINGS

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ABSTRACT

In an effort to investigate metal surface corrosion and
the breakdown of metal protective coatings the AC
Impedance Method was applied to zinc chromate primer
coated 2219-T87 aluminum. The Model 368-1 AC Impedance
Measurement System recently acquired by the MSFC Corrosion
Research Branch was used to monitor changing properties of
coated aluminum disks immersed in 3.5% NaCl buffered at pH
5.5 over three to four weeks. DC polarization resistance
runs were performed on the same samples.

The corrosion system can be represented by an electronic
analog called an equivalent circuit that consists of
resistors and capacitors in specific arrangements. This
equivalent circuit parallels the impedance behavior of the
corrosion system during a frequency scan. Values for
resistances and capacitances that can be assigned in the
equivalent circuit following a least squares analysis of
the data describe changes that occur on the corroding
metal surface and in the protective coating.

A suitable equivalent circuit has been determined that
predicts the correct Bode phase and magnitude for the
experimental sample. DC corrosion current density data
are related to equivalent circuit element parameters.

ACKNOWLEDGEMENTS

Again I express my deep appreciation to the many persons
enabling my second participation in the summer program.
Special thanks go to Dr. Merlin Danford, my research
colleague in EH24 whose patience and insights kept the
project moving along. I will remember also with gratitude
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programs. Mike's personal interest in each participant is
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scientific contributions in seminar discussions provided
mature viewpoints; it was a treat to have him around.

To my many NASA friends who welcomed me unhestatingly as a
friend, I say Thanks!

INTRODUCTION

Electrochemical methods for estimating corrosion rates of bare and painted metal surfaces serve as effective accelerated approaches to scientific techniques of corrosion studies. For at least fifteen years direct current (DC) methods, particularly polarization resistance, have permitted quick determination (30 to 60 minutes) of corrosion currents that translate into mils per year of metal surface corroding.

Within the past six to eight years alternating current (AC) methods, particularly AC impedance scans of metals in corrosive solution environments have resulted in studying the corrosion system in more detail. The several data from a typical AC impedance scan can indicate change in corrosion rate, progressive deterioration of metal coatings, changes in metal surface, and reaction mechanisms. Moreover, changes in coating condition can be detected by AC experiments before DC methods show an increase in metal corrosion current.

However, the AC impedance study of corroding metals is in its infancy. A few dozen papers describe AC corrosion studies, but clear interpretation of the data is rare and stated conclusions are sometimes unsupported or untrue. A review of the field is needed to sort out the complex data obtained and to indicate what conclusions are justified. A standard treatment of the most useful data from the typical AC impedance experiment needs to be indicated. So the researcher in this field has to be ready to blaze trails with thoughtfulness, imagination, and patience.

Nevertheless, the reader should consider two papers that do provide useful background (Mansfeld, 1981, 1982). Anyone interested in the field should begin with AC studies of bare metal surfaces that produce data more easily analyzed and understood. Coated surfaces yield data much more complex and challenging to unravel.
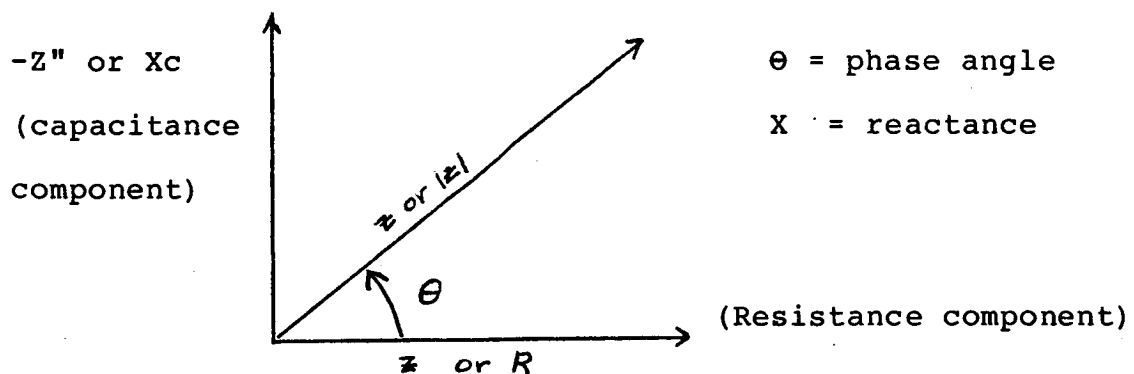
OBJECTIVES

The objectives of this work were to:

(1)   Perform AC Impedance experiments on primer coated aluminum samples.

(2)   Correlate AC Impedance data with DC corrosion current density data from the same samples.

(3)   Determine a suitable equivalent circuit that represents the AC impedance behavior of the primer coated aluminum sample immersed in 3.5% NaCl.

(4)   Assign values to the various elements in the equivalent circuit that represent specific parts of the corroding coated aluminum disk.

(5)   Determine specific circuit elements that signal an onset of significant corrosion rate.

THEORY

Basics.   In AC Ohm's Law has the form E = IZ, where Z is
impedance in ohms and E and I are waveform amplitudes of
voltage and current, respectively. Impedance, the
resistance within an AC circuit to electron movement, is
caused by circuit elements such as resistors, capacitors,
and inductors.

Impedance can affect not only the current waveform at a
fixed voltage, but also can alter time-dependent
characteristics of the current or voltage waveform with
respect to each other. The separation of voltage and
current waves that can occur in reactive circuits is called
phase or phase shift and is expressed in degrees. Phase
depends on circuit elements, their arrangement and the AC
frequency. In fact, a phase versus frequency plot is
characteristic of a given circuit. No phase shift occurs
with only resistances in an AC circuit, but the presence of
a capacitor can cause the voltage to log the current wave
by as much as ninety degrees.

The total impedance Z or |Z| at a given frequency depends
on resistive and capacitive contributions. Total impedance
can be represented by a vector, Z, with a resistive
component, Z', and a capacitive component, -Z".

-Z" or Xc θ = phase angle

(capacitance   X = reactance

component)

                                             (Resistance component)

z or R

From the Figure $Z = \sqrt{R^2 + X_c^2} = \sqrt{(Z')^2 + (Z'')^2}$

and $\tan \theta = \dfrac{X_c}{R} = \dfrac{-Z''}{Z'}$

Since, $X_c = \dfrac{1}{WC} = \dfrac{1}{2\pi fc}$, $Z = \sqrt{R^2 + (\dfrac{1}{2\pi fc})^2}$
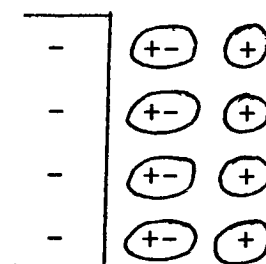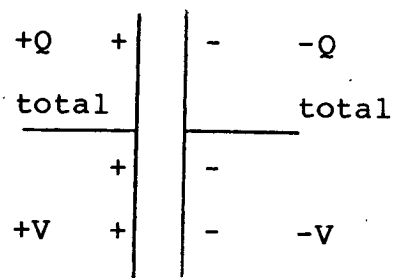
C = Capacitance in farads
W = frequency in radians per second
f = frequecny in Hertz

At sufficiently high frequencies capacitors contribute
little to the total impedance in an AC circuit. A plot of
-Z" (often called imaginary impedance) versus Z' (often
called real impedance) is termed a "complex plane plot" or
Nyquist plot. In a Nyquist plot from a corroding metal
surface the highest frequency points begin on the
horizontal Z' axis at a distance from the -Z" axis
proportional to the combined solution and coating layer (if
present) resistances.

Capacitors. A capacitor is a simple device capable of
storing electric charges at some potential difference.
Often a capacitor (or condenser) consists of two solid
metal surfaces separated by a dielectric, but a single
charged metal surface dipping in a polar solvent (like
water) functions as capacitor because a "double layer"
forms.

```
+Q    +|    |-     -Q                -  | (+-)  (+)
                                        |
 total  |    |   total               -  | (+-)  (+)
                                        |
      +|    |-                       -  | (+-)  (+)
                                        |
+V    +|    |-     -V                 -  | (+-)  (+)
```

Parallel plate capacitor   Electric double layer

        (ppc)   Charged electrode capacitor

The double layer consists of excess electrons near the metal surface separated from a rigid layer of hydrated cations by a monolayer of polar water molecules. The electron layer and the cation layer also is labeled Helmholtz Double Layer; it is strictly analogous to the PPC. If the electrode is charged positive, the orientation of water molecules reverses and the counter ion monolayer is anions.

The capacitance C in farads equals the charge build-up Q, in colombs per volt of potential difference, V, or $C = Q/V$. The capacitance of a PPC is increased by a factor K if an insulator with dielectric constant K is placed between the plates. $K = 1$ for a vacuum; for a completely oriented monolayer of water molecules on an electrode surface $K = 6$ (Reference 3).

A protective coating can take on capacitive properties in an electrolyte solution if it becomes porous to permit water and charge build-up on either side of its surface. A conductive coating like zinc chromate would not show capicatance like that of an organic polymer, although if a conductive coating absorbs water it would increase in capacitance. Porous metal oxide coatings should also show capacitance although this has not been clearly demonstrated.

The charging or discharging of a capacitor in an AC circuit is driven by the applied voltage and its polarity. The charging time for a capacitor in series with a resistor depends on its capacitance, C, in farads and the resistance R in ohms of the resistor. R x C is called the time constant; in five time constants such a capacitor is over 99 percent charged. Obviously if the AC frequency is greater than five time constants, a circuit capacitor cannot fully charge or discharge.

The Equivalent Circuit Concept. The basis of the AC impedance method is the modeling of the corrosion cell in terms of a purely electronic circuit model. This model consists of one or more resistors and capacitors in a suitable arrangement. The equivalent circuit is designed to mirror the electronic behavior of the corrosion cell in the most accurate manner possible.

A corroding bare metal surface in aqueous solution shows resistance R to electron flow and its electrical double layer shows capacitance C. If the solution has resistance Rs, then the equivalent circuit can be represented as
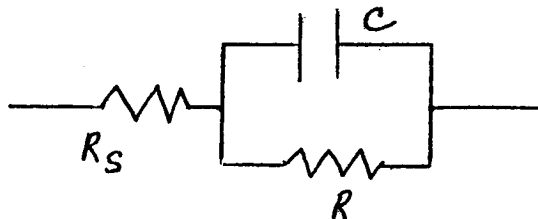
A suitable equivalent circuit should reasonably reproduce experimental plots obtained from the corrosion cell when experimentally determined parameters are used. These plots include the Bode phase (degrees versus log W), complex plane or Nyquist plot ($-Z''$ or $|Z|$ versus log W).

Equivalent circuits for coated metal surfaces involve additional capacitor-resistor combinations. Such a circuit labeled RC9 (The 9th resistor-capacitor model designed) that seems to fit corroding zinc chromated aluminum is shown in Figure 3. It also must display similar Bode and Nyquist plots that resemble the experimental data plots. Figure 1 shows these idealized plots for bare and chromated aluminum after salt water immersion for about one day. It should be pointed out that these plots can vary between similarly prepared samples and can change as corrosion and coating deterioration progresses.

AC Data Analysis

The goals of analyzing AC impedance data are threefold:
(1) Determine the equivalent circuit that most accurately
describes the corrosion cell, and (2) Assign the best
possible values to resistors and capacitors in the
equivalent circuit for that particular experiment.
Experiments should be run every 3-4 days for 3-4 weeks or
until the corrosion rate stabilizes or the coating visibly
deteriorates. (3) Discover the best parameters in the
equivalent circuit to describe the corrosion rate. As
sample immersion continues all of the model parameters
change, some more than others.

Interpretation of the Nyquist (Complex Plane) Plot

The starting point in deciphering the experimental results
is the Nyquist or complex plane plot. Points on this plot
correspond to changing $-Z''$, Z' values as the signal
frequency changes during a typical scan from 10^{-2} to 10^5
hertz. Usually the Nyquist plot consists of one semicircle
for a corroding bare metal and two semicircles (often one
and one-half) for a coated metal. Theoretical origin of
the data points that approximate a semicircle is discussed
in Reference 1 (Mansfeld, 1981). From each semicircle is
obtained two resistances and one capacitance.

A typical semicircle is shown below:
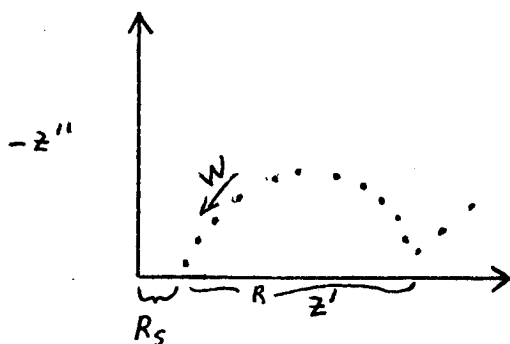
R_S = ohmic resistance from solution

R = resistance to charge transfer

W_{max} = frequency at top of semicircle

This simple plot is obtained for a corroding bare metal surface which has the equivalent circuit given in earlier. Reading Z' from the plot at frequency W_{max} enables calculation of C. R_s and R are estimated by linear measurement along the Z' axis. In practice a least squares computer calculation for these equivalent circuit parameters gives the best values. Input values are from linear measurements of Nyquist semicircles. Actual output values for bare metals are in Table 1. Similarly a second semicircle which lies to the right of the first in the Nyquist plot for a coated metal surface yields two more resistance and one more capacitor parameters.

At this point in the research of primer coated aluminum corroding in salt water, the equivalent circuit that best fits the experimental data is the one shown in Figure 3. A complex least squares program developed by Dr. Merlin Danford, EH24, MSFC, NASA gives the best values for RC9 equivalent circuit. Input parameters include four resistances and two capacitances from a least squares fitting of the two semicircles from the experiment. The eight RC9 model results are shown in Table 2. The physical model that RC9 model equivalent circuit represents is shown in Figure 2.

Impedance Change Interpretation

Figures 6 and 7 give a picture of changes in the eight least squares output values over the time of the experiment. All the resistances show a general decrease with the solution resistance the most regular. This is not surprising as corrosion rate increases. Not enough is known regarding the system and its interactions to comment on the rather extreme variability of the capacitances. An oscillation of resistance and capacitance is noted in Reference 2.

Of interest with Disk 2 is a maximum in the charge transfer impedance (at 1000 Hz) that coincides with a charge increase in corrosion rate. Dr. Danford suggests this change transfer impedance increase coincides with a thickening of the amorphous Al_2O_3 layer between the primer and the aluminum metal surface. This increased corrosion rate is accomplished by H_2 evolution as usual. This large increase in impedance is taking place with the large drop in R , primer resistance (in series).

Calculations of impedance for the two units of the overall model (metal-primer unit), solution primer unit) for the two disks or samples are given in Table 3. With both disks the solution-primer unit impedance value shows a regular steady decrease as the coating progressively deteriorates.

Since the coating destruction permits penetration of the solution to the primer-metal interface, changes in these impedances occur. Particularly noted is the increase in metal-primer impedance with both disks that occurs after 11-12 days. As mentioned before the growth of amorphorus layer on the metal could account for this apparent increase.

Bode Phase Interpretations. A plot of the phase versus log (frequency) is a Bode Phase Plot. Phase depends on the relative values and arrangements of the various resistors and capacitors in the equivalent circuit. Capacitors are particularly important because

(1) Phase depends on the imaginary impedance contribution from the capacitors as well as the real contribution from the resistors.

(2)   A capacitor in parallel with other circuit elements
controls the current in those elements in an AC circuit.
(A very high capacitance functions as a direct short in an
AC circuit).

Bare aluminum in 3.5% NaCl (pH 5.5, 8.2) displays a
single phase, maximum mid-frequency. Zinc chromated
aluminum shortly after immersion in similar media usually
gives similar results. It has been observed that
chromated samples initially showing one maximum are
slower to corrode than those giving maxima.

Excellent confirmation of the RC 9 model is provided by
the Bode plot. At the high frequency limit (100 KHz) of
the Bode plot the phase shows a sharp increase
(Figure   5). If RC 9 model parameters outputs are used
to calculate total impedance which in turn is graphed
versus log frequency, a similar phase is observed at high
frequency. This agreement of the RC 9 model output with
the experimental Bode phase supports the contention that
this model is an accurate representation.

CONCLUSIONS

1.   The AC impedance method is a means of obtaining significantly more information about corroding surfaces, coated and uncoated, compared to DC polarization resistance.

2.   The double layer capacitances of bare 4130 steel and bare 2219 aluminum in corrosive environments differ significantly.

3.   The equivalent circuit that best describes a zinc chromated 2219 aluminum surface in 3.5% NaCl consists of four resistor-capacitor pairs and is given in Figure 3.

4.   In order to determine the response of a particular part of the physical model of a corrosion system, the total impedance for the RC combination representing that part should be calculated.

5.   Experimental and calculated Bode phase and magnitude curves can be compared to verify a particular equivalent circuit for the corrosion system.

RECOMMENDATIONS

1.   AC impedance studies of corroding surfaces should be continued by NASA.

2.   To maximize data correspondence AC and DC runs should be made on the same sample in close time proximity.

3.   Parameters and/or circuit elements should be isolated that best relate to sample corrosion current.

4.   The AC impedance responses of various coatings on various metals in various corrosive environments be determined by experiment.

5.   The effect of chelating agents on bare metal corrosion parameters be determined.

References

1.   Mansfeld, F., "Recording and Analysis of AC Impedance Data for Corrosion Studies", Part I, Corrosion-NACE, 36, 301-307 (1981).

2.   Mansfeld, F., Kendig, M.W., Tsai, S., "Recording and Analysis of AC Impedance Data for Corrosion Studies", Part II, Corrosion-NACE, 38, 570-580 (1982).

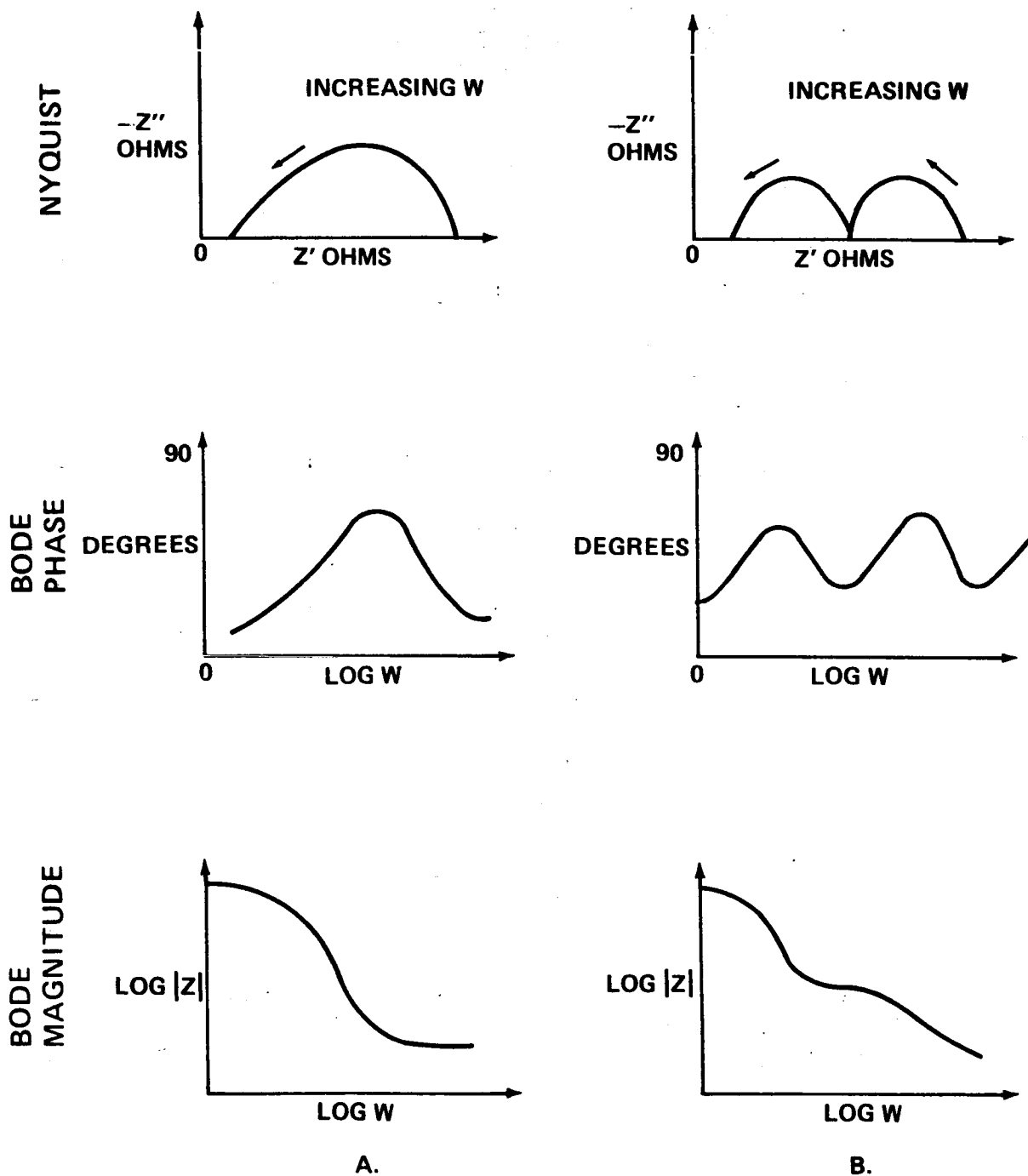3.   Bockris, J. O'M. and Reddy, A.K.N., Modern Electrochemistry, p. 760, Plenum Press, New York (1970).
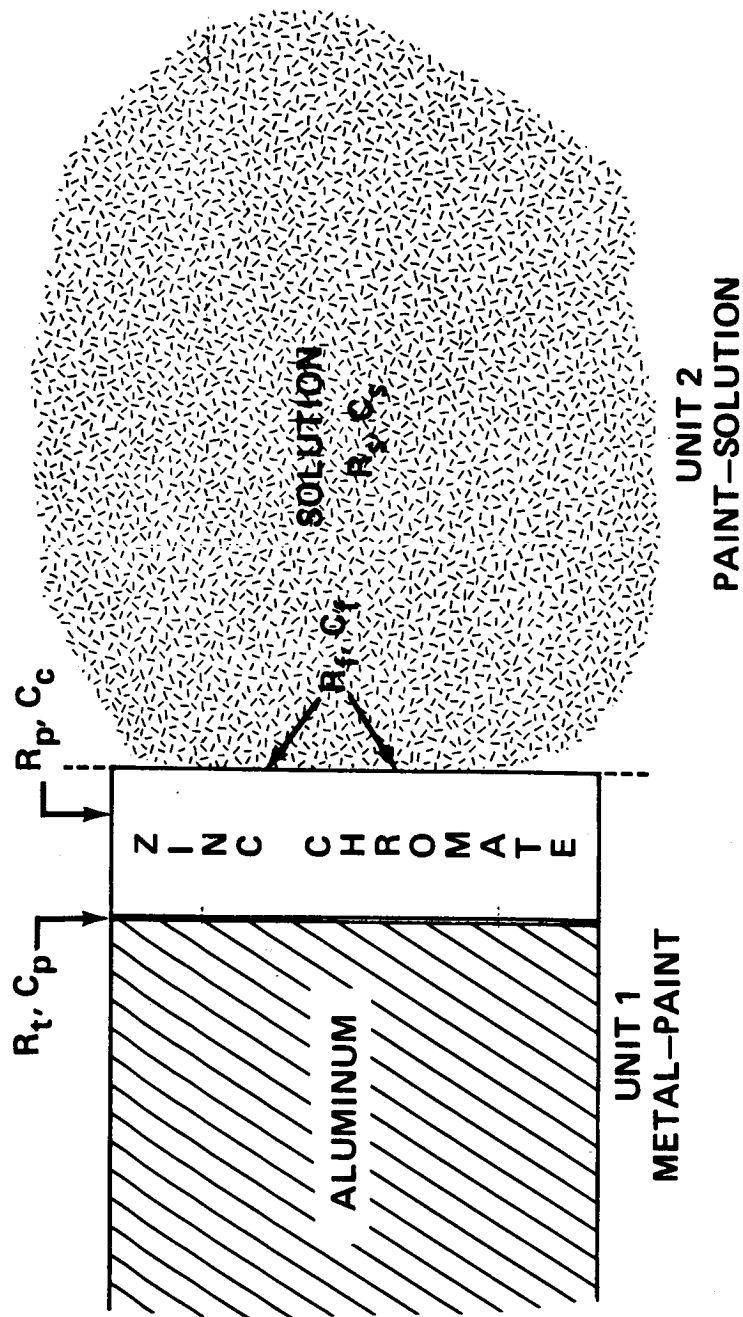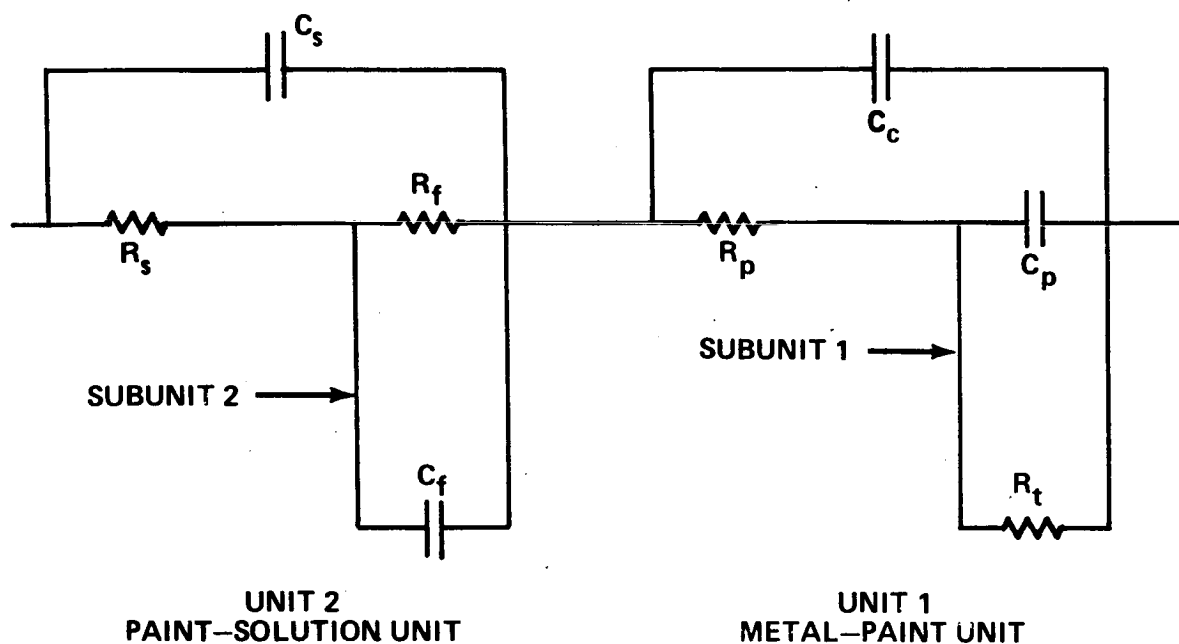
FIGURE 1   IDEALIZED NYQUIST AND BODE PLOTS FOR A. BARE
ALUMINUM B. COATED ALUMINUM FOLLOWING
IMMERSION IN 3.5% NaCl FOR APPROX. 1 DAY.
W = FREQUENCY, - Z" IMAGINARY IMPEDANCE,
Z' REAL IMPEDANCE

FIGURE 2 ALUMINUM – PRIMER – SOLUTION MODEL SHOWING
RESISTOR AND CAPACITOR LOCATIONS

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C_S	SOLUTION CAPACITANCE
R_S	SOLUTION RESISTANCE
C_f	FARADAIC CAPACITANCE (COATING/SOLUTION)
R_f	FARADAIC RESISTANCE
C_c	COATING CAPACITANCE
R_p	COATING RESISTANCE
C_p	METAL/COATING INTERFACE CAPACITANCE
R_t	CHARGE TRANSFER RESISTANCE

FIGURE 3   RC 9 MODEL EQUIVALENT CIRCUIT

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PRIMER COATED 2219–T87AI
DISK 2, 7/31/86
BODE MAGNITUDE

LOG 1Z1, OHMS

LOG w

—— CALCULATED
● OBSERVED
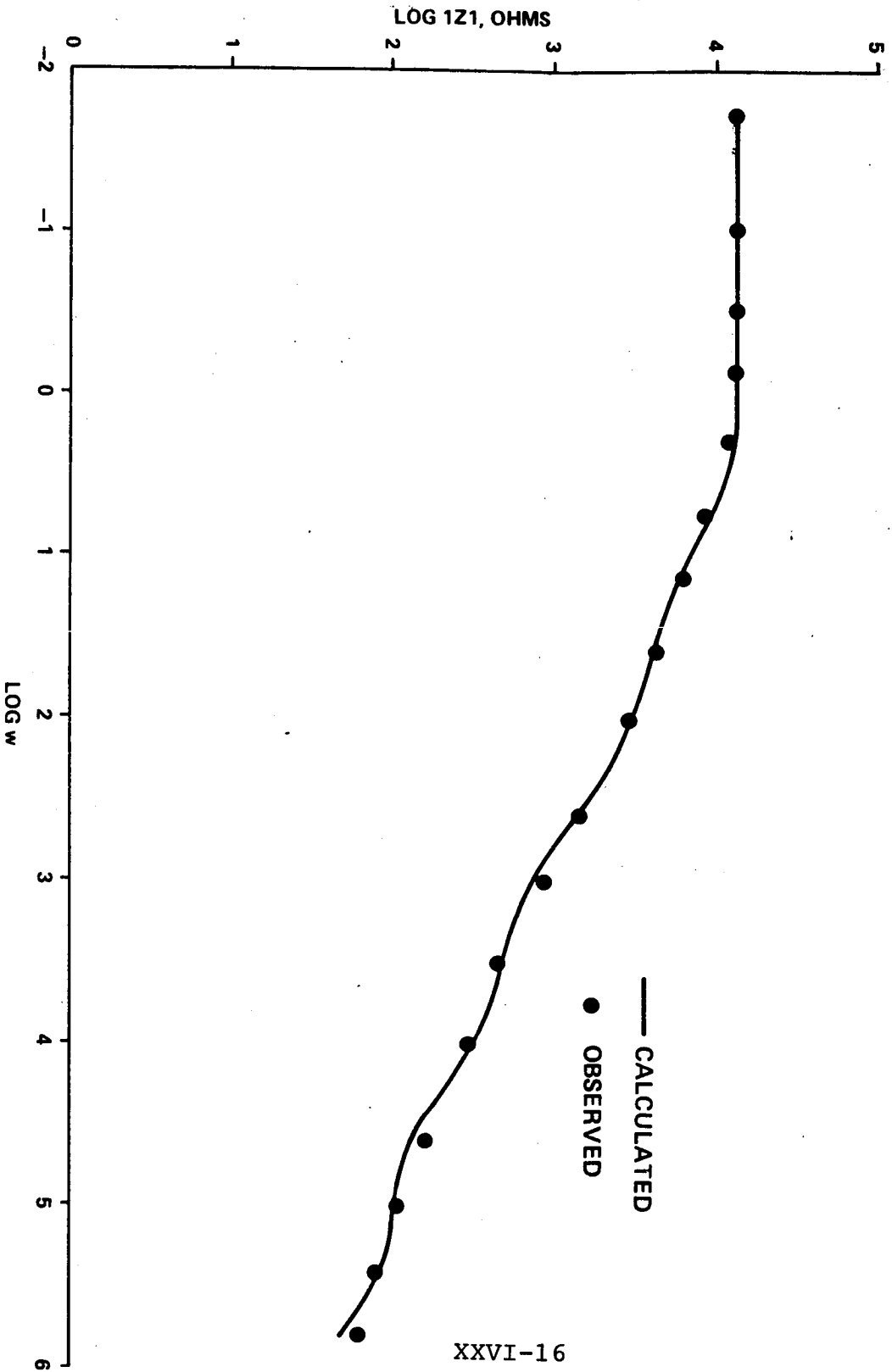
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FIGURE 4

PRIMER COATED 2219-T87 AI
DISK 2, 7/31/86
PHASE

— CALCULATED
● OBSERVED

PHASE, DEGREES

LOG W
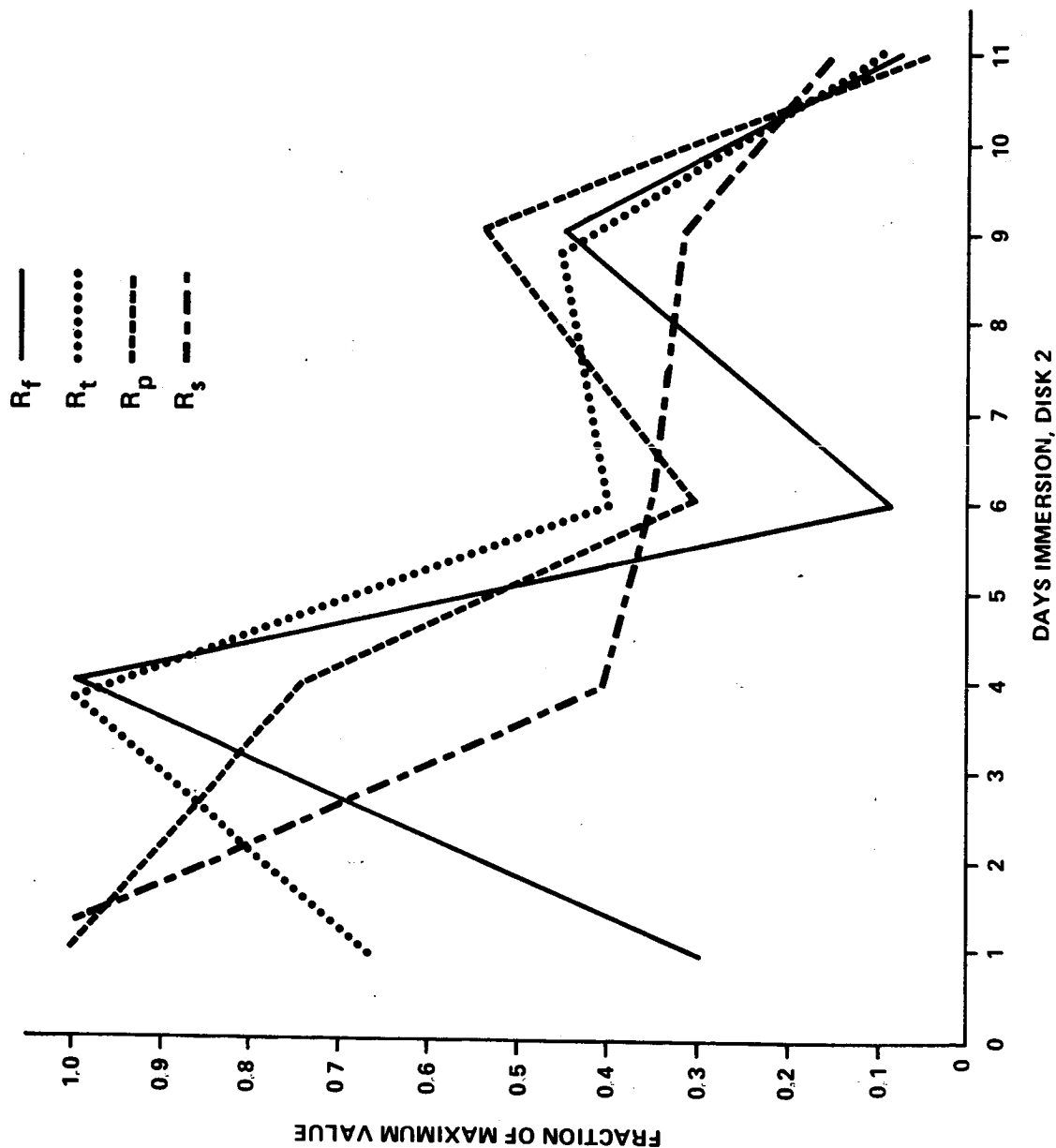FIGURE 5
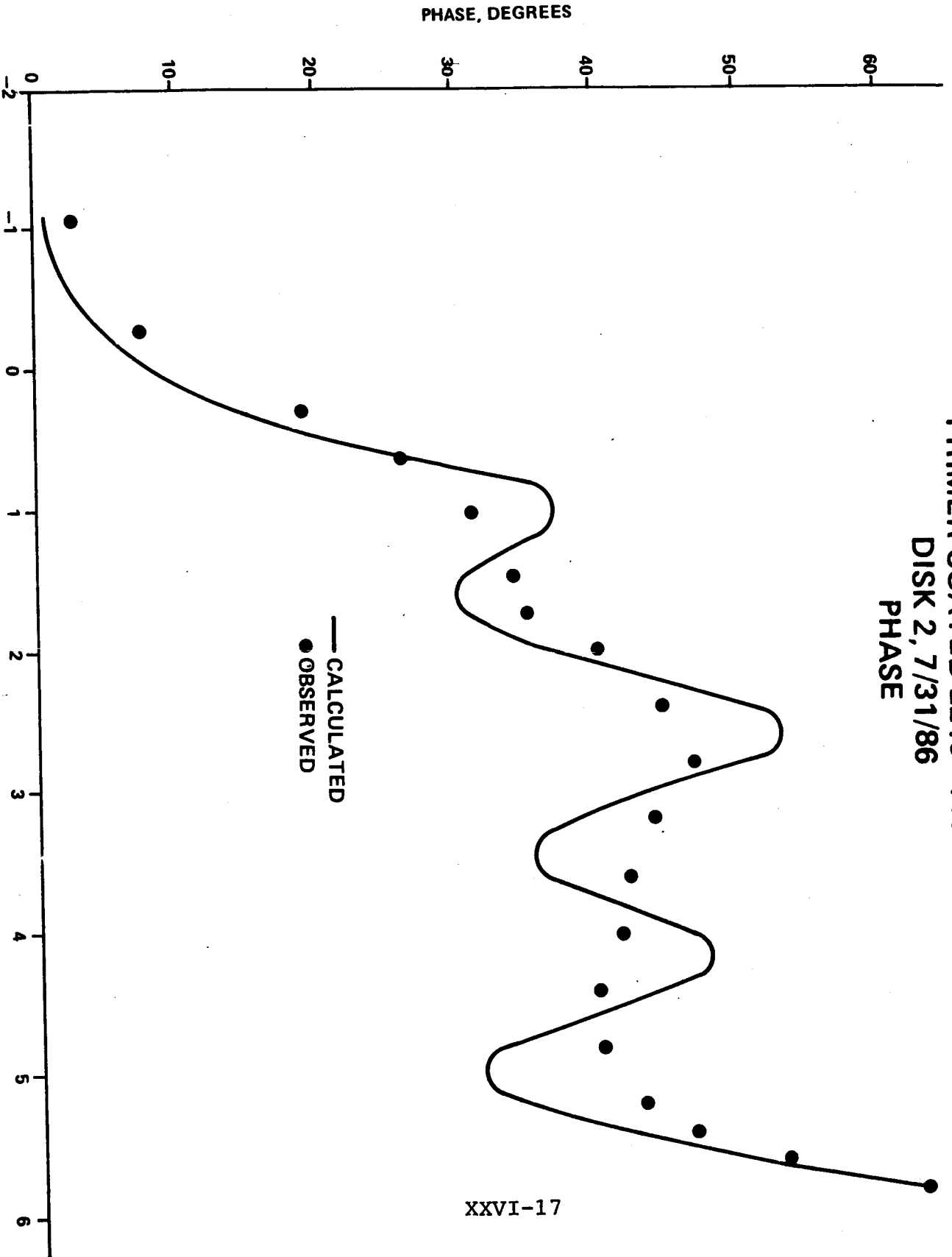
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FIGURE 6 RC9 MODEL RESISTANCE CHANGES
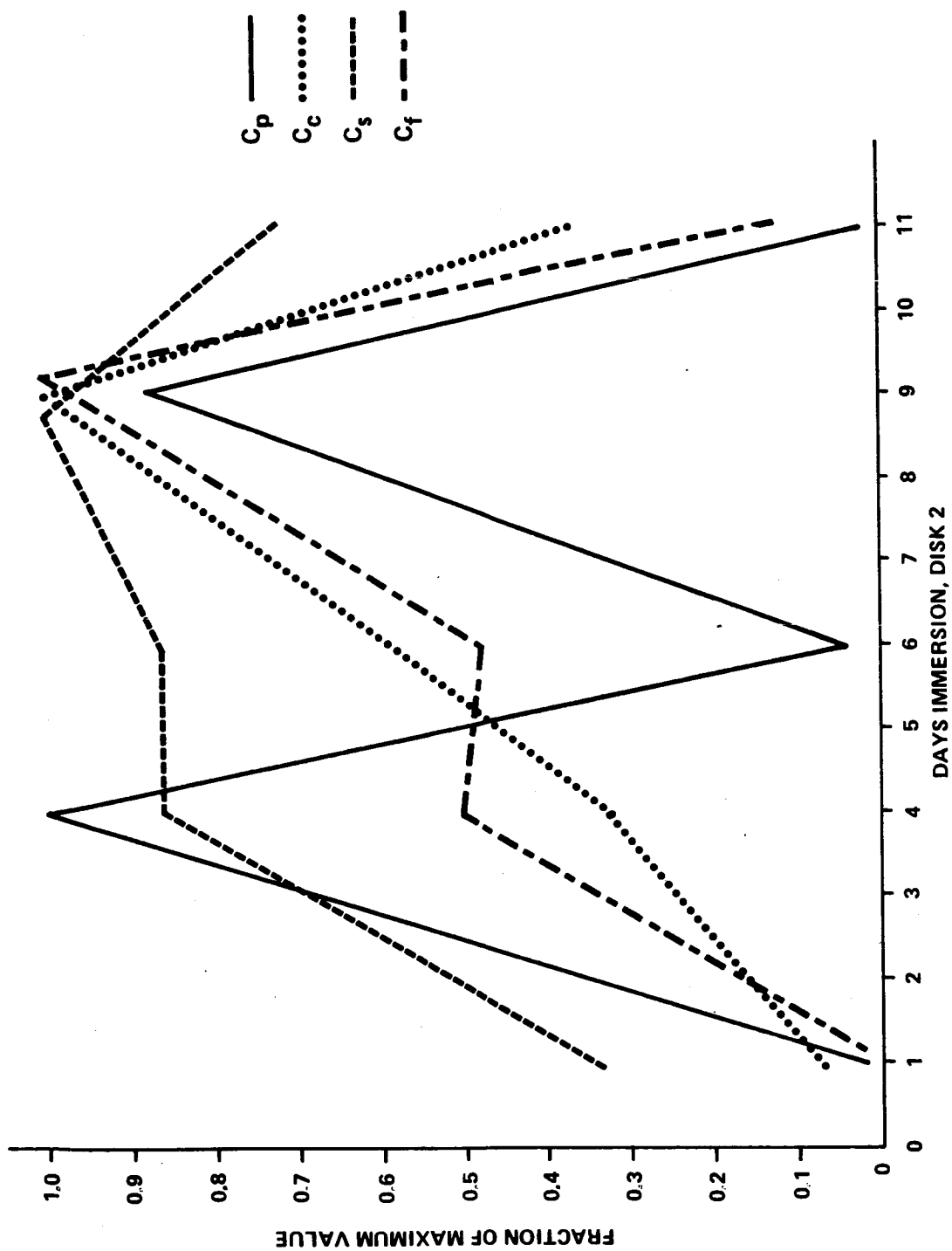CHROMATED ALUMINUM IN 3.5% NaCl, pH 5.5

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FIGURE 7 RC9 MODEL CAPACITOR CHANGES
CHROMATED ALUMINUM IN 3.5% NaCl, pH 5.5

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TABLE 1 MODEL RC 1 PARAMETERS FOR BARE METALS

RESISTANCE IN KILO OHMS
CAPACITANCE IN MICROFARADS
I_{CORR} IN MICROAMPS

ALUMINUM, 2219—T87 IN 3.5% NaCl

	I_{CORR}	R_s	R	C
pH 5.5	0.32	.0085	14.5	13.1
pH 8.2	0.44	.0503	9.2	25.5

STEEL 4130 IN CORROSIVE WATER, pH 8.2

I_{CORR}	R_s	R	C
0.81	0.130	5.40	1630.
1.30	0.218	2.01	2701.
4.67*	0.260	1.85	404.
30.3*	0.196	2.32	260.

* CHELATING AGENT PRESENT, EDTA

TABLE 2 MODEL RC9 PARAMETERS FOR ZINC CHROMATE 0.5 MIL ON 2219-T87 ALUMINUM 3.5% NaCl, PH 5.5

R IN KILO OHMS
C IN MICRO-FARADS
Δt DAYS IMMERSION
I_{CORR} IN MICROAMPS

DISK 1

Δt	I_{CORR}	R_p	C_p	C_C	R_t	R_S	C_S	C_f	R_f
1	.017	6.98	1.9	.19	3666.	1.87	.0052	.90	120.0
5	.062	9.59	31.7	.78	438.	.35	.030	3.94	125.0
8	.018	.57	8.5	.29	22.1	.17	.024	3.3	3.3
10	.068	.94	16.3	.57	268.1	.18	.028	5.0	12.9
12	.157	.49	4.0	.41	3.2	.13	.025	11.4	84.2

DISK 2

Δt	I_{CORR}	R_p	C_p	C_C	R_t	R_S	C_S	C_f	R_f
1	.056	4.46	4.7	.065	63.8	.66	.013	.26	14.9
4	.242	3.27	913.	.318	95.4	.26	.033	9.6	49.9
6	.221	1.43	30.2	.589	29.8	.23	.033	8.7	4.5
9	.083	2.59	806.	.990	41.8	.22	.038	18.2	20.7
11	2.072	.40	19.8	.363	9.8	.10	.028	2.3	3.0

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TABLE 3 CALCULATED IMPEDANCES (IN OHMS) FROM MODEL RC 9 OUTPUT VALUES. Δt – DAYS IMMERSION, 3.5% NaCl, PH 5.5 2219–T87 ALUMINUM COATED WITH 0.5 MIL ZINC CHROMATE

DISK 1 Δt	METAL-PRIMER UNIT	SOLUTION-PRIMER UNIT	TOTAL
1	854	1996	2850
5	205	389	594
8	402	230	632
10	268	220	488
12	392	144	536

DISK 2 Δt	METAL-PRIMER UNIT	SOLUTION-PRIMER UNIT	TOTAL
1	2152	1095	3247
4	495	270	765
6	266	250	516
9	197	220	417
11	296	170	466

C-8