EVALUATION OF
HIGH PERFORMANCE METAL ALLOYS
IN THE STS LAUNCH ENVIRONMENT USING
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

PREPARED BY:

ENGINEERING DEVELOPMENT DIRECTORATE
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TEST REPORT

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Environment Using Electrochemical Impedance Spectroscopy

ISSUED **BY**

National Aeronautics and Space Administration
Kennedy Space Center
Materials Testing Branch

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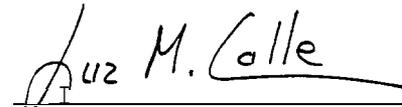
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ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) techniques using
AC impedance measurements were chosen to investigate the
corrosion resistance of 19 alloys under conditions similar to
the Space Transportation System (STS) launch environment.
The alloys were: Zirconium 702, Hastelloy C-22, Inconel 625,
Hastelloy C-276, Hastelloy C-4, Inconel 600, 7Mo + N,
Ferralium 255, Inco Alloy G-3, 20Cb-3, SS 904L, Inconel 825,
SS 304LN, SS 316L, SS 317L, ES 2205, SS 304L, Hastelloy B-2,
and Monel 400. AC impedance data were gathered for each
alloy after one hour immersion time in each of the following
three electrolyte solutions: 3.55% NaCl, 3.55% NaCl-0.1N
HCl, and 3.55% NaCl-1.0N HCl. The data were analyzed
qualitatively using the Nyquist plot and quantitatively using
the Bode plot. Polarization resistance, R_p, values were
obtained using the Bode plot. Zirconium 702 was the most
corrosion resistant alloy in the three electrolytes. The
ordering of the other alloys according to their resistance to
corrosion varied as the concentration of hydrochloric acid in
the electrolyte increased. The corrosion resistance of
Zirconium 702 and Ferralium 255 increased as the
concentration of hydrochloric acid in the electrolyte
increased. The corrosion resistance of the other 17 alloys
decreased as the concentration of the hydrochloric acid in
the electrolyte increased.

AC impedance data were gathered for 18 of the alloys at
various immersion times in 3.55% NaCl-0.1N HCl. Alloy SS
304LN was not included in this part of the investigation
because of its similarity to SS 304L and due to time
constraints.

Polarization resistance, R_p, values were obtained from the
Nyquist plots at each immersion time using the EQUIVALENT
CIRCUIT software package available with the 388
Electrochemical Impedance software. Hastelloy C-22 showed
the highest overall values for R_p while Monel 400 and Inconel
600 had the lowest overall values. There was good general
correlation found between the corrosion performance of the
alloys from the beach corrosion testing site and the
predicted rate of corrosion that was based on the R_p values
obtained in the laboratory. These data suggest that
Electrochemical Impedance Spectroscopy can be used to predict
the corrosion performance of metal alloys.

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1.0 INTRODUCTION

1.1 Flexible metal hoses are presently used as part of various supply lines that service the Orbiter at the launch pad. These convoluted flexible hoses were originally constructed of 304L stainless steel. The severely corrosive environment at the launch site caused pitting corrosion in many of these flex hoses. In the case of vacuum jacketed cryogenic lines, failure of a flex hose by pitting would cause a localized loss of vacuum and a subsequent localized loss of insulation in that part of the line.

1.2 The environment at the launch site is severely corrosive due to the high chloride content caused by the proximity of the Atlantic Ocean, and from the generation of concentrated hydrochloric acid (HCl) as a fuel combustion product from the Solid Rocket Boosters (SRB's) during launch. These corrosive conditions caused severe pitting on some of the commonly used stainless steel alloys.

1.3 An investigation was undertaken in 1987 to evaluate 19 metal alloys with the purpose of finding a more corrosion resistant replacement material for 304L stainless steel. Tests performed in that investigation were: electrochemical corrosion testing, accelerated corrosion testing in a salt fog chamber, long term exposure at the beach corrosion testing site, and pitting corrosion tests in ferric chloride solution. These tests led to the conclusion that the most corrosion resistant alloys were, in descending order, Hastelloy C-22, Inconel 625, Hastelloy C-276, Hastelloy C-4, and Inco Alloy G-3. Of these five alloys, the Hastelloy C-22 stood out as being the best of the alloys tested. The details of this investigation are found in report MTB-325-87A (1). Furthermore, when corrosion resistance was combined with weld and mechanical properties, Hastelloy C-22 was determined to be the best material for the fabrication of flex hoses used as part of the fuel lines servicing the Orbiter at the launch site.

1.4 The above electrochemical corrosion testing was based on the use of DC polarization techniques. In our present investigation, Electrochemical Impedance Spectroscopy (EIS) techniques using AC impedance measurements were utilized in order to study the corrosion of the same 19 alloys tested in 1987. During the first part of the investigation, the 19 alloys were tested after one hour immersion in three different electrolyte conditions: neutral

3.55% NaCl, 3.55% NaCl-0.1N HCl, and 3.55% NaCl-
1.0N HCl. The second part of the investigation
involved the study of 18 of the 19 alloys in 3.55%
NaCl-0.1N HCl at different immersion times. The
3.55% NaCl-0.1N HCl electrolyte provides an envi-
ronment similar to the conditions at the launch
pad.

2.0 MATERIALS AND EQUIPMENT

2.1 CANDIDATE ALLOYS

The 19 alloys tested and their nominal compositions
in weight percent are shown in Table 1. The choice
of these alloys for the investigation was based on
their advertised resistance to corrosion in chlo-
ride environments.

2.2 AC IMPEDANCE MEASUREMENTS

2.2.1 A Model 378 Electrochemical Impedance system
manufactured by EG&G Princeton Applied
Research Corporation (PARC) was used for all
EIS measurements. The system includes: (1)
the Model 273 Computer-Controlled
Potentiostat/Galvanostat; (2) the Model
5301A Computer-Controlled Lock-In Amplifier;
(3) the IBM XT Microcomputer with periph-
erals; and (4) the Model 378 Electrochemical
Impedance Software. An updated version of
the software (PARC version 2.7) including
circuit modeling routines was used for the
EIS measurements at different immersion
times.

2.2.2 Specimens were flat coupons 1.59 cm (5/8")
in diameter. The PARC flat specimen holder
in the electrochemical cell was designed
such that the exposed metal surface area is
1 cm^2.

TABLE 1   CANDIDATE ALLOYS AND THEIR
           NOMINAL COMPOSITIONS (WT%)

ALLOY	Ni	Fe	Cr	Mo	Mn*	Co*	Cu	C*	Si*	P*	S*	Other
HASTELLOY C-4	Bal.	3.0	18	17	1.0	2.0		0.01	0.08	0.02	0.01	Ti 0.7
HASTELLOY C-22	Bal.	3.0	22	13	0.5	2.5		0.01	0.08	0.02	0.01	V 0.3, W 3
HASTELLOY C-276	Bal.	7.0	17	17	1.0	2.5		0.01	0.08	0.02	0.01	0.3, W 4.5
HASTELLOY B-2	Bal.	2.0	1	28	1.0	1.0		0.01	0.1	0.02	0.01	
INCONEL 600	Bal.	8.0	16		1.0		0.5	0.15	0.5		0.01	
INCONEL 625	Bal.	5.0	23	10	0.5	1.0		0.10	0.5	0.01	0.01	Cb 4.1
INCONEL 825	Bal.	22.0	21	3	1.0		2.5	0.05	0.5		0.03	
INCO G-3	Bal.	20.0	22	7	1.0	5.0	2.0	0.02	1.0	0.04	0.03	Cb 0.5, W 1.5
MONEL 400	Bal.	2.5			2.0		31	0.30	0.5		0.02	
ZIRCONIUM 702												Zr 99.2, Hf 4.5
SS 304L	10	Bal.	19		2.0			0.03	1.0		0.03	
SS 304LN	10	Bal.	19		2.0			0.03	1.0	0.04	0.03	N 0.13
SS 316L	12	Bal.	17	2.5	2.0			0.03	1.0	0.04		
SS 317L	13	Bal.	19	3.5	2.0			0.03	1.0			
SS 904L	25	Bal.	21	4.5	2.0		1.5	0.02	1.0	0.04	0.03	
20 Cb-3	35	Bal.	20	2.5	2.0		3.5	0.07	1.0			
7Mo + N	4	Bal.	28	2	2.0			0.03	0.6	0.03	0.01	N 0.25
ES 2205	5	Bal.	22	3	2.0			0.03	1.0	0.03	0.02	N 0.14
FERRALIUM 255	5	Bal.	26	3	1.5		2.0	0.04	1.0	0.04	0.03	N 0.17

* Values are max.

2.2.3   The electrochemical cell included a satu-
         rated calomel reference electrode (SCE), 2
         graphite rod counter electrodes, a metal
         working electrode, and a bubbler/vent tube.
         Each alloy was studied in three different
         electrolyte conditions after one hour immer-
         sion and at different immersion times in
         aerated 3.55% NaCl-0.1N HCl. The electro-
         lyte conditions for the one hour immersion
         time were: aerated 3.55% neutral NaCl,
         aerated 3.55% NaCl-0.1N HCl (similar to the
         conditions at the launch site), and aerated
         3.55% NaCl-1.0N HCl (more aggressive than
         the conditions at the launch site). All
         solutions were prepared using deionized
         water.

3.0 <u>PROCEDURE FOR AC IMPEDANCE MEASUREMENTS</u>

  3.1 ONE HOUR IMMERSION IN THREE DIFFERENT ELECTROLYTES

3.1.1   The test specimens were polished with 600-
         grit paper, wiped with methyl-ethyl ketone,
         ultrasonically degreased for five minutes in
         a detergent solution, rinsed with deionized
         water, and dried. Each specimen was
         observed under the microscope and weighed
         before and after each experiment to monitor
         changes caused by corrosion on its
         appearance and weight.

3.1.2   The electrolyte solution was aerated with
         dry air for at least 15 minutes before
         immersion of the test specimen. Aeration
         continued throughout the test.

3.1.3   AC impedance measurements were performed
         under each of the three electrolyte con-
         ditions chosen. After immersion in the
         electrolyte, the sample was allowed to
         equilibrate for 3600 seconds before the
         instrument started acquiring data. It was
         determined previously that after 3600
         seconds, the corrosion potential had usually
         stabilized (2).

3.1.4   The AC impedance measurements were gathered
         in the frequency range from 100 kHz to
         0.1001 Hz to produce Electrochemical
         Impedance Spectra. A combination of two
         methods was employed in order to obtain data
         over the above range of frequencies: (1)
         phase-sensitive lock-in detection for

measurements from 5 Hz to 100 kHz; and (2)
the FFT (Fast Fourier Transform) technique
for measurements from 0.1001 Hz to 11 Hz.
The data from lock-in (single-sine) and FFT
(multi-sine) were automatically merged in
the IBM XT microcomputer by the M378
software.

3.1.5 The conditions for the lock-in experiments
were: initial frequency, 100 kHz; final
frequency, 5 Hz; points/decade, 5; AC
amplitude, 5 mV; DC potential, 0 volts (V)
vs OC (open circuit); condition time,
0 seconds; condition potential, 0 V vs OC;
open circuit delay, 3600 seconds. As a
backup, the open circuit potential was also
monitored with a high input impedance
voltmeter.

3.1.6 The conditions for the FFT experiments were:
base frequency, 0.1001 Hz; data cycles, 5;
AC amplitude, 10 mV; DC potential, 0 V vs
OC; open circuit delay, 0 seconds. The open
circuit potential was also monitored with a
high input impedance voltmeter.

3.1.7 The data for each experiment were plotted in
the Nyquist and Bode plot formats.

3.2 DIFFERENT IMMERSION TIMES IN 3.55% NaCl-0.1N HCl

3.2.1 The test specimens were prepared as
described in 3.1.1 and immersed in 3.55%
NaCl-0.1N HCl. Aeration continued through-
out the test. SS 304LN was excluded from
this part of the investigation due to its
similarity to SS 304L.

3.2.2 The EIS data were acquired at different
immersion times commencing with one hour
(zero hours for 304L and Inconel 625). Data
were gathered in the frequency range from
100 kHz to 0.001 Hz using the Auto Execute
selection of the EG&G PARC M378 Software
System version 2.70. Three experiments were
performed covering the following frequency
ranges: 100 kHz to 5 Hz, 10-0.1 Hz, and 0.1-
0.001 Hz. The data from these three experi-
ments were merged automatically. The AC
amplitude was 10 mV.

3.2.3 The data for each immersion time were
plotted in the Nyquist and Bode plot format.

4.0 <u>TEST RESULTS AND DISCUSSION</u>

4.1 THEORETICAL BACKGROUND

4.1.1   AC impedance techniques does offer some distinct advantages over DC techniques (3). First, the small excitation amplitudes, generally in the ranges of 5 to 10 mV peak-to-peak, would cause only minimal perturbations in the electrochemical system, thus reducing errors normally caused by the measuring technique itself. Second, the AC technique offers valuable information about the mechanisms and kinetics of electrochemical processes such as corrosion. Third, measurements can be made in low conductivity solutions where DC techniques are subject to serious potential-control errors.

4.1.2 Despite the advantages of the EIS techniques mentioned above, their application requires sophisticated methods in order to interpret the data and thereby extract meaningful results. The application of AC impedance measurements toward the study of corrosion has so far resulted in the publication of large amounts of experimental data without much interpretation. At the present time, the technique is in a transition from the data collection stage to the data analysis stage (4).

4.1.3 EIS is based on the presumption that an electrochemical system, such as those studied in this investigation, can be represented by an equivalent electrical circuit. The equivalent circuit for a simple electrochemical cell is shown in Figure 1 (5). The circuit elements R, R_p, and C_{dl} represent, respectively, the uncompensated resistance (resistance from the reference to the working electrode), the polarization resistance (resistance to electrochemical oxidation), and the capacitance close to the metal surface (at the double layer). There are several formats that could be used for the graphical representation of the AC impedance data (3,6,7). Each format offers specific advantages for revealing certain characteristics of a given test system. It was evident from the beginning that the most

suitable formats for plotting the AC
impedance data were the Nyquist and the Bode
plots.
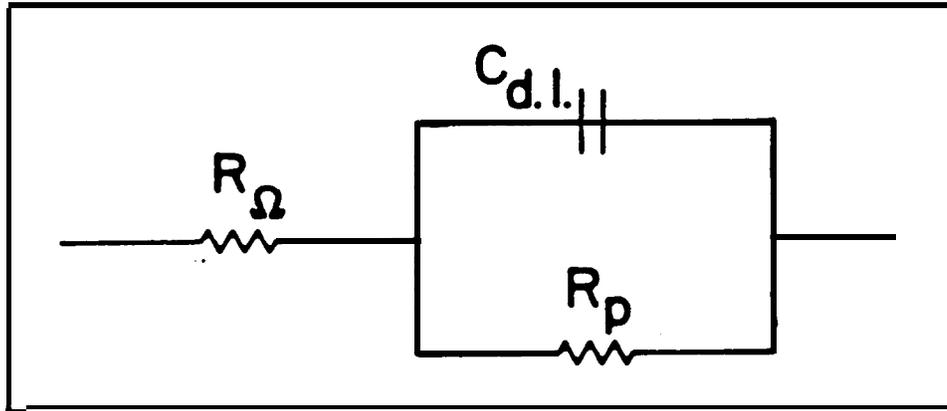
Figure 1. Equivalent circuit for a simple electrochemical cell.

4.1.4 The Nyquist plot is also known as a Cole-
      Cole plot or a complex impedance plane
      diagram. Figure 2 (5) shows the Nyquist
      plot for the equivalent circuit shown in
      Figure 1. The imaginary component of the
      impedance (Z") is plotted versus the real
      component of the impedance (Z') for each
      excitation frequency. As indicated in
      Figure 2, this plot can be used to calculate
      the values of R, R_p, and C_{dl}.
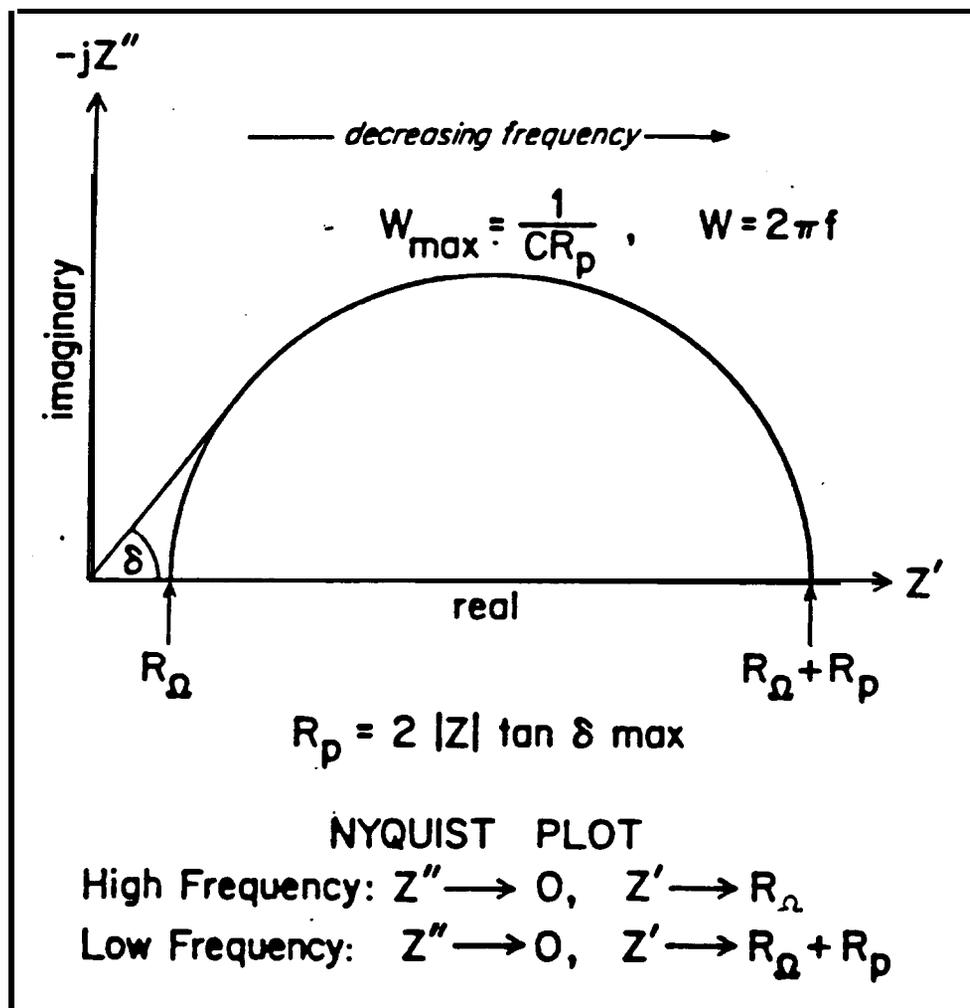
Figure 2. Nyquist plot for equivalent circuit in Figure 1.

4.1.5 The Bode plot for the equivalent circuit in
      Figure 1 is shown in Figure 3 (5). This
      graphical representation of the AC impedance
      data involves plotting both the phase angle
      ($\emptyset$) and the log of absolute impedance
      ($\log|Z|$) versus the log of the frequency (w
      = $2\pi f$). As indicated on the figure, values
      for R_Ω, R_p, and C_{dl} can also be obtained from
      the Bode plot. Of special interest for this
      research is the determination of the R_p
      values which can be used to calculate the
      corrosion rate of an electrode material in a
      given electrolyte (3,8).
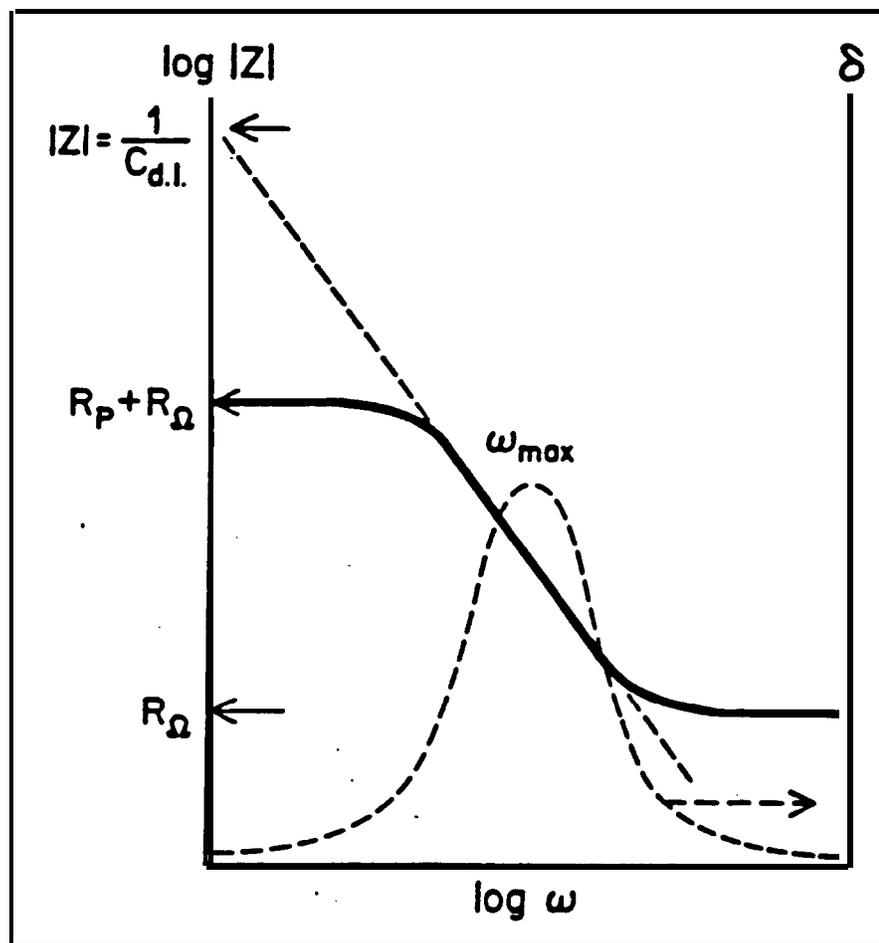
Figure 3. Bode plot for equivalent circuit in Figure 1.

4.2 AC IMPEDANCE MEASUREMENTS AFTER ONE HOUR IMMERSION
    IN THREE DIFFERENT ELECTROLYTES

        4.2.1 The Bode plots included in this report
              appear in the form of two separate graphs:
              $\log|Z|$ versus log Frequency (Hz) and O
              versus log Frequency (Hz). Nyquist (at the
              top) and Bode plots (at the bottom) for the
              19 alloys used in this investigation are
              shown in Appendix A. None of the Nyquist
              plots obtained in this investigation
              exhibited the ideal semicircle shown in
              Figure 2. Experimentally, it was observed

that deviations from the results predicted
using simple equivalent circuits did occur
with real, corroding systems (6,9). Some of
the deviations that have been observed for
real systems are: a semicircle with its
center depressed below the real axis, a
partial semicircle, and a partial semicircle
that changes shape at the low frequency end.
EIS data that result in a Nyquist plot in
the form of a depressed or partial semi-
circle could still be used to calculate R_p
values. Several authors have described
computer modeling of electrochemical imped-
ance (10,11). The usual approach is to
curve-fit the semicircle that results from a
single time constant capacitive response.
This approach allows an estimate to be made
of the low frequency intersection of the
semicircle response with the real axis.
This procedure is especially important when
the response still offers a large imaginary
contribution at low frequency resulting in a
partial semicircle. Deviations that result
in a Nyquist plot with the shape of a
partial semicircle that changes at the low
frequency end would require a more complex
computer program with more circuit elements.
The time constraint of completing this
research project prevented the use of the
above methods in analyzing the Nyquist plots
for the 19 alloys.

4.2.2   Valuable qualitative information could be
extracted by comparing the Nyquist plots
shown in Appendix A. Each Figure shows the
change in the Nyquist plot for a one hour
immersion time of the alloy in the three
different electrolytes: (X) 3.55% NaCl, (□)
3.55% NaCl-0.1N HCl and (o) 3.55% NaCl-1.0N
HCl. The change in the corrosion rate,
which is inversely proportional to R_p, could
be estimated qualitatively by looking at the
change in the Nyquist plot.

4.2.3   Zirconium 702 (Figure A-1a) stands out as
being the most corrosion resistant alloy
under the conditions used in this study.
Its R_p was not only the highest but it also
showed the least change upon increasing the
concentration of the hydrochloric acid from
0.0N to 0.1N to 1.0N. That is, Zirconium
702 became more corrosion resistant as the
concentration of hydrochloric acid
increased. This finding agrees with the

known fact that Zirconium is resistant to hydrochloric acid at all concentrations up to boiling temperatures. However, there are indications that the metal is vulnerable to pitting in sea water (12).

4.2.4 Ferralium 255 (Figure A-1b) also became more corrosion resistant upon increasing concentrations of the acid. Its R_p values were similar in all three electrolytes but lower than those for Zirconium 702. The change in R_p for the other 17 alloys was in the opposite direction to that observed for Zirconium 702 and Ferralium 255: they became less resistant to corrosion as the concentration of the acid increased. Hastelloy C-22 (Figure A-2a), Inco Alloy G-3 (Figure A-2b), Hastelloy C-4 (Figure A-3a), Inconel 625 (Figure A-3b), Hastelloy C-276 (Figure A-4a), and Hastelloy B-2 (Figure A-4b) have similar Nyquist plots showing a decrease in R_p as the concentration of the acid increases. Monel 400 (Figure A-5a) shows partial semicircles with a slight decrease in R_p when increasing the acid concentration. The semicircle obtained in 3.55% NaCl-0.1N HCl has a feature at the end (a straight line with a positive slope) that has been associated with a Warburg impedance (13). This behavior has been compensated by an extra impedance term in the equivalent circuit that is associated with diffusion controlled processes. 20Cb-3, ES 2205, and 7Mo + N (Figures A-5b, A-6a, A-6b) showed patterns in the Nyquist plot where there was no drastic change in the R_p values when the concentration of hydrochloric acid was increased from 0.0N to 0.1N (as indicated by the two parallel lines). However, a significant change in the Nyquist plot became evident when the concentration of the acid was increased to 1.0N that resulted in a considerable decrease in R_p. The turn at the low frequency end of the curve is probably an indication of a diffusion process taking place. SS 304L (Figure A-7a) exhibited a Nyquist plot that is different from all the others. It should be pointed out that one of the experiments involving SS 304L resulted in a partial breakdown of the surface of the metal sample. Data from that experiment was subsequently discarded. The complex Nyquist plot obtained for SS 304L in 3.55% NaCl-1.0N HCl is similar to the

Nyquist plot obtained for a pin-holed coal
tar epoxy coating on mild steel (13). SS
304LN (Figure A-7b) showed good resistance
to corrosion in neutral 3.55% NaCl but low
resistance to corrosion (low R_p values) in
3.55% NaCl-0.1N HCl and 3.55% NaCl-1.0N HCl.
Inconel 600 (Figure A-8a) showed a similar
behavior. Inconel 825, SS 317L, SS 904L,
and SS 316L (Figures A-8b, A-9a, A-9b,
A-10a) show a similar behavior indicating
good resistance to corrosion in 3.55% NaCl
and 3.55% NaCl-0.1N HCl and a considerably
lower resistance to corrosion in 3.55% NaCl-
1.0N HCl.

4.2.5 Since the Nyquist plots obtained in this
investigation did not resemble the ideal
Nyquist plot shown in Figure 2, calculation
of R_p values from those plots was not
pursued. The Bode plot presented a more
straightforward means of calculating R_p. In
a Bode plot, the impedance of a "perfect
capacitance" can be represented as a
straight line with a slope of -1 and a phase
angle of $-90°·$ A "resistor" will plot as a
horizontal line for the $\log|Z|$ with a phase
angle of $0°·$ A Warburg impedance is a
straight line with a slope of -1/2 and a
phase angle of $-45°$ (14). The data gathered
for the 19 alloys, when plotted in the Bode
format (lower plot in Figures A-1 to A-10),
was interpreted as shown in Figure 3. The
value of Z at the lowest frequency (0.1001
Hz) is the sum of R_p and R while the value
of Z at the highest frequency (100.020 kHz)
is R. The values for R_p obtained from the
Bode plot data after one hour immersion in
the three different electrolytes are given
in Tables 2-4. These values indicate that
Zirconium 702 is the most corrosion resis-
tant alloy under the conditions used in this
study. The ranking of the other 18 alloys
differs for the three electrolytes. In
general, it can be concluded that for all
the alloys, with the exception of Zirconium
702 and Ferralium 255, the R_p values
decrease as the concentration of hydro-
chloric acid increases in the electrolyte.
The changes in R_p can thus be followed
qualitatively by examining the data in the
Nyquist plot format and quantitatively by
using the Bode plot format.

TABLE 2

POLARIZATION RESISTANCE IN 3.55% NACL

MATERIAL NAME	Rp (ohms)
ZIRCONIUM 702	60884
HASTELLOY C-22	23146
INCONEL 625	18338
HASTELLOY C-276	17121
HASTELLOY C-4	15797
INCONEL 600	15426
7M0 + N	15394
FERRALIUM 255	15057
INCO ALLOY G-3	14787
20CB-3	14660
ss 904L	14449
INCONEL 825	14237
SS 304N	13103
SS 316L	12598
SS 317L	12290
ES-2205	11913
SS 304L	11383
HASTELLOY B-2	3779
MONEL 400	652

TABLE 3

POLARIZATION RESISTANCE IN 3.55% NACL-O.1N HCL

MATERIAL NAME	Rp (ohms)
ZIRCONIUM 702	59937
FERRALIUM 255	15675
20CB-3	1 5 3 6 9
SS 317L	14745
SS 316L	14290
INCONEL 625	13798
INCONEL 825	13281
ES-2205	13227
SS 904L	12786
INCO ALLOY G-3	12716
7M0 + N	12502
HASTELLOY C-4	11723
HASTELLOY C-276	10947
HASTELLOY C-22	9758
HASTELLOY B-2	1806
ss 304L	778
MONEL 400	586
SS 304LN	531
INCONEL 600	498

TABLE 4

POLARIZATION RESISTANCE IN 3.55% NACL-1.ON HCL

MATERIAL NAME	Rp (ohms)
ZIRCONIUM 702	57081
FERRALIUM 255	15133
.INCONEL 625	12213 .
INCO ALLOY G-3	11665
HASTELLOY C-4	8698
HASTELLOY C-276	5201
HASTELLOY C-22	6800
HASTELLOY B-2	1487
MONEL 400	538
INCONEL 825	490
INCONEL 600	481
SS 304LN	431
20CB-3	422
ss 304L	325
ss 904L	300
SS 317L	203
SS 3 1 6 L	158
ES-2205	101
7M0 + N	49

4.2.6 The one hour immersion data revealed the
need to vary the immersion time for each
metal alloy and to expand the frequency
range of the measurements to 0.001 Hz. The
implementation of these changes resulted in
a considerable increase in time required to
obtain measurements. The time to collect
the data changed from one hour and ten
minutes to three and a half hours. Section
4.6 below deals with AC impedance measure-
ments in 3.55% NaCl-0.1N HCl at different
immersion times.

4.3 COMPARISON WITH DC POLARIZATION RESULTS

A comparison of R_p values obtained in this investi-
gation with R_p values obtained by DC polarization
techniques for the same alloys in 3.55% NaCl-0.1N
HCl (ref. 2, Table 3) and for 10 of the alloys in
3.55% NaCl-1.0N HCl (ref. 2, Table 9) have shown
that there was no similarity found between their
respective values of R_p. However, there was good
correlation between the two methods when the alloys
are rated according to their resistance to corro-
sion even though ranking does not match exactly.
The fact that AC impedance techniques use signals
that do not disturb the electrode properties to be
measured have added validity to the R_p values
obtained by this technique.

4.4 COMPARISON WITH BEACH CORROSION DATA

A comparison of R_p values obtained from AC imped-
ance measurements with beach corrosion data for all
the alloys in 3.55% NaCl-1.0N HCl (ref. 2, Figure
9) showed that there was, in general, a good corre-
lation even though the ranking of the metals did
not match exactly. For example, Hastelloy C-22 was
the most resistant alloy when tested at the beach
corrosion site while it ranked only seventh accord-
ding to the R_p value in this study. It should be
pointed out that, as a group, there was good
correlation found between the alloys that performed
at the top (Zirconium 702, Ferralium 255, Inconel
625, Inco Alloy G-3, Hastelloy C-4, Hastelloy
C-276, and Hastelloy C-22) in both investigations.
A tentative conclusion that could be drawn from
this comparison is that the AC impedance technique
could be used to choose candidate materials for
possible long-term corrosion testing at the beach
testing site. The lack of a close correlation
between the AC impedance data and the beach
corrosion data may be from the fact that the AC

impedance measurements were obtained after one hour
immersion in the aerated electrolytes at room
temperature. The conditions at the beach testing
site are obviously different (ref. 1, p. 8) and
more similar to conditions in the STS launch
environment. The results from the present investi-
gation may be more appropriate for testing the
corrosion resistance of alloys that are likely to
be in contact with liquid electrolytes such as the
ones used here.

4.5 AC IMPEDANCE MEASUREMENTS AT DIFFERENT IMMERSION
    TIMES IN 3.55% NACL-0.1N HCL

   4.5.1 The data for this part of the investigation
         were plotted in the Nyquist and Bode plot
         format. A close examination of both types
         of plots revealed that the Nyquist plot
         provided more information for the 18 alloys
         at each immersion time and are, therefore,
         shown in Appendix B. The Bode plots were
         all very similar in shape and were not
         included in this report for the sake of
         brevity.

   4.5.2 R_p values for the 18 alloys at different
         immersion times in 3.55% NaCl-0.1N HCl were
         calculated using the Find Circle option of
         the Data Cruncher pre-analysis part of the
         EQUIVALENT CIRCUIT software package avail-
         able with the Model 388 Electrochemical
         Impedance Software package. Due to the time
         constraints imposed on this part of the
         investigation, a more thorough analysis of
         the data was not undertaken at this time.
         The R_p values shown on Table 5 are prelim-
         inary and it is anticipated that they will
         be refined within the near future.

TABLE 5

MERSION TIME, POLAR. RESISTANCE (Rp), AND CORR. POTENTIAL (Ecorr)

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ALLOY NAME	TIME (hrs)	Rp (ohms)	Ecorr (volts)
HASTELLOY C-4	1	1.9E+05	-0.075
	75	8.2E+05	0.020
	168	1.8E+06	0.178
HASTELLOY C-22	1	2.4E+05	-0.037
	4	4.9E+05	-0.003
	28	3.3E+05	0.080
	122	1.4E+06	0.149
	145	4.9E+05	0.272
	170	3.9E+06	0.224
	192	6.3E+06	0.212
	262	3.5E+07	0.177
	286/312	6.3E+07	0.159
		2.0E+07	
	336	1.4E+08	
	360	2.1E+06	
	476	2.1E+06	
	696	8.9E+05	
HASTELLOY C-276	1	2.0E+05	
	24	8.0E+05	
	144	2.3E+06	
	168		
HASTELLOY B-2		1.7E+03	-0.134
	32	1.3E+03	
	120	1.6E+03	
	192	1.6E+03	-0.124
INCONEL 600	1	4.5E+02	
	28	8.8E+02	
	72	6.3E+02	-0.221
	224	7.6E+02	
	268	6.0E+02	
INCONEL 625	0	1.8E+05	
	5	5.0E+05	0.138
	31	4.0E+05	0.363
	100	2.5E+05	0.450
	291	1.7E+05	0.451
	395	1.4E+05	0.150

TABLE 5 (cont.)

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ALLOY NAME	TIME (hrs)	Rp (ohms)	Ecorr (volts)
INCONEL 825	1	6.2E+05	-0.081
	28	4.9E+05	-0.090
	72	3.2E+06	-0.050
	168	6.5E+05	-0.052
INCO G-3	1	4.5E+05	-0.060
	40	9.4E+05	0.216
	61	1.0E+06	0.242
	88	2.8E+06	0.249
	161	3.3E+06	0.253
	188	3.7E+06	0.254
	331	6.4E+06	0.238
	505	9.6E+06	0.233
MONEL 400	1	9.7E+02	-0.146
	48	6.5E+02	-0.132
	120	5.7E+02	-0.129
	192	6.8E+02	-0.115
ZIRCONIUM 702 SAMPLE 1	1	1.7E+05	-0.060
	24	4.3E+02	-0.049
	48	1.0E+03	0.090
	72	1.1E+01	0.157
SAMPLE 3	3	5.9E+05	-0.110
	20	7.4E+05	0.136
	43	7.7E+01	0.158
	67	5.9E+01	-0.017
	91	7.6E+01	0.168
	163	3.3E+01	0.152
SS 304L	0	3.8E+02	-0.311
	7	6.5E+02	-0.315
	24	7.8E+02	-0.323
	31	6.2E+02	-0.322
	54	5.0E+05	-0.127
	100	1.3E+05	-0.161
	192	1.4E+05	-0.165
	243	2.3E+05	-0.151

TABLE 5 (cont.)

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ALLOT NAME	TIME (hrs)	Rp (ohms)	Ecorr (volts)
SS 316L	1	2.6E+05	-0.117
	48	9.5E+05	-0.077
	120	6.4E+05	-0.140
	192	5.1E+05	-0.120
ss 317L	24	1.4E+06	-0.030
	128	2.1E+06	-0.102
	168	6.5E+06	-0.007
ss 904L	1	6.3E+05	-0.033
	44	4.2E+06	0.032
	120	9.1E+06	0.158
	168	1.6E+06	0.239
20 CB-3	1	3.4E+05	-0.091
	2s	2.9E+06	0.000
	96	8.8E+05	-0.020
	168	1.4E+06	0.019
7 MO + N	1	5.3E+05	-0.122
	25	3.1E+06	-0.020
	90	2.3E+06	-0.112
	115	4.6E+05	-0.176
	137	1.5E+06	-0.211
	161	1.5E+06	-0.130
ES-2205	1	3.0E+05	-0.101
	26	2.0E+06	0.015
	73	9.8E+05	-0.057
	166	7.2E+05	-0.120
FERRALIUM 255	1	4.3E+05	-0.115
	24	7.1E+05	-0.068
	48	2.1E+06	0.003
	120	3.0E+05	-0.209
	124	2.9E+05	-0.209
	151	1.1E+07	-0.002
	175	2.3E+07	0.043
	200	3.7E+07	0.057
	223	8.3E+06	0.071
	393	2.0E+06	0.100
	317	7.4E+02	0.113
	343	5.1E+02	0.126
	367	8.6E+05	0.140
	551	1.3E+07	0.249
	634	1.8E+07	0.247

4.5.3 Examination of R_p values for different immersion times revealed that R_p changes differently with time for each alloy. This means that alloys differ significantly in terms of how their rates of corrosion change with immersion time.

4.5.4 Hastelloy C-22 showed the highest overall values of R_p while Monel 400 and Inconel 600 had the lowest overall values. Zirconium 702 showed a variation in R_p from 10^5 to 10^1. Data collection for this sample was very difficult because the instrument would cease to gather data when dark spots, indicative of pitting, appeared on the exposed surface of the sample. This is the reason for having used two samples of this material. It should be noted that Zirconium 702 was found to be the most corrosion resistant alloy in the one-hour immersion time/ /different electrolyte investigation. The drastic change in the rate of corrosion for this material at different immersion times indicated the importance of performing AC impedance measurements at different immersion times. Other alloys that showed significant changes in the magnitude of R_p with varying immersion times are Ferralium 255 and SS 304L. SS 304L has R_p values indicative of a rate of corrosion that is high at first (low R_p) and then slows down (higher R_p). All the other alloys exhibited R_p values that were on the order of 10^5 to 10^6.

4.6 COMPARISON WITH BEACH CORROSION DATA

4.6.1 A comparison of R_p values obtained in this part of the investigation with beach corrosion data for all the alloys given in Figure 9 of reference 2 indicated that AC impedance measurements could discriminate between the best (Hastelloy C-22) and the worst (Monel 400) performing materials at the beach. There was also good correlation found among the best performing materials as a group (those with the highest R_p values in our study) and the poorest performers (those with the lowest R_p values).

4.6.2 There was a discrepancy found between the AC impedance results for 20Cb-3 and its actual performance at the beach corrosion test

site. While its R_p values would predict a
low rate of corrosion, this material
exhibited one of the two highest rates of
corrosion at the beach. A possible explana-
tion for this discrepancy could be obtained
by examining the one-hour immersion time
data in three different electrolytes (Figure
A-5b). The Nyquist plots on this Figure
clearly showed the effect on the R_p value
caused by increasing the concentration of
HCl. While R_p is high for one hour immer-
sion in neutral 3.55% NaCl and in 3.55%
NaCl-0.1N HCl, a considerable decrease is
observed when the concentration of HCl is
increased to 1.0N. It should be noted that
the samples at the beach test site were
periodically sprayed with 10% HCl which is a
higher concentration than the 0.1N used in
this part of the investigation.

5.0 CONCLUSIONS

5.1 ONE HOUR IMMERSION TIME IN THREE DIFFERENT ELECTROLYTES

5.1.1 AC impedance techniques, when used for
corrosion testing, provided useful quali-
tative (Nyquist plot) and quantitative
information (R_p values) that could be used
to screen alloys to be subjected to long-
term corrosion testing.

5.1.2 The R_p values obtained for the 19 alloys
under three different electrolyte conditions
could be used to rank the alloys according
to their resistance to corrosion since R_p is
inversely proportional to the rate of
corrosion.

5.1.3 Zirconium 702 was found to be the most
corrosion resistant alloy under the
conditions used in this investigation.

5.1.4 There was a good general agreement between
the results obtained using DC and AC tech-
niques even though the actual R_p values were
found to be different. It is believed that
the R_p values obtained by the AC technique
are more accurate.

5.2 VARIOUS IMMERSION TIMES IN 3.55% NACL-0.1N HCL

   5.2.1 AC impedance measurements in 3.55% NaCl-0.1N
         HCl at different immersion times revealed
         that the rate of corrosion, as indicated by
         the R_p values obtained, varies with time for
         the 18 alloys included in this part of the
         investigation.

   5.2.2 An examination of the overall R_p values for
         each alloy over a range of different
         immersion times enabled the prediction of
         the long-term performance of the alloys
         under similar conditions.

   5.2.3 AC impedance measurements could be used to
         rank high performance metal alloys according
         to their rate of corrosion in order to
         distinguish between those materials expected
         to have a low rate of corrosion (high R_p)
         and those expected to have a high rate of
         corrosion (low R_p).

   5.2.4 AC impedance measurements, like those
         reported in this investigation, did not
         provide the information necessary to
         discriminate the corrosion rates of the
         different metal alloys in a way that allows
         for ranking them exactly according to their
         rate of corrosion.

   5.2.5 This part of the investigation revealed the
         importance of performing AC impedance meas-
         urements at different immersion times in
         order to predict the long-term performance
         of the metal alloys under similar
         conditions.

6.0 RECOMMENDATIONS

   6.1 A further analysis of the data using the full
       capabilities of the EQUIVALENT CIRCUIT software
       package.

   6.2 Include testing of alloys after exposure to
       conditions that are as similar to the STS launch
       environment as possible.

   6.3 Study the effect of protective coatings on the rate
       of corrosion on the 19 alloys.

   6.4 Modify the electrolyte conditions to include other
       chemicals normally found at the STS launch
       environment.

6.5 Study the effect of changes in temperature, similar to the seasonal changes that occur at the STS launch environment, on the rate of corrosion.

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APPENDIX A
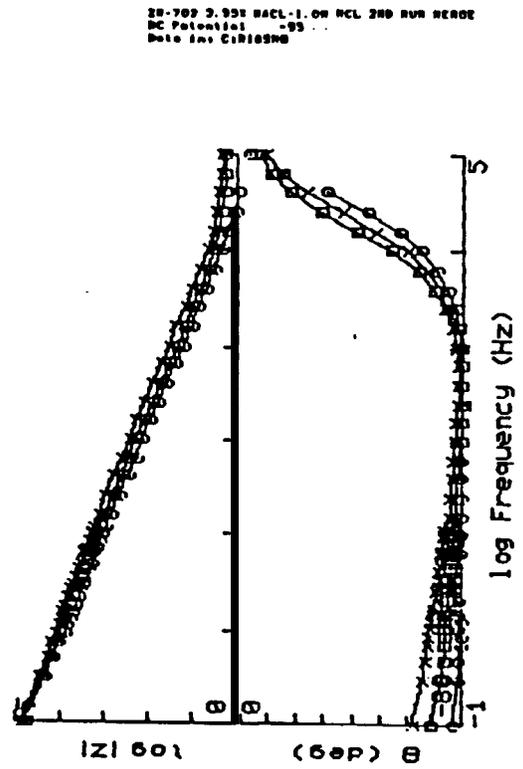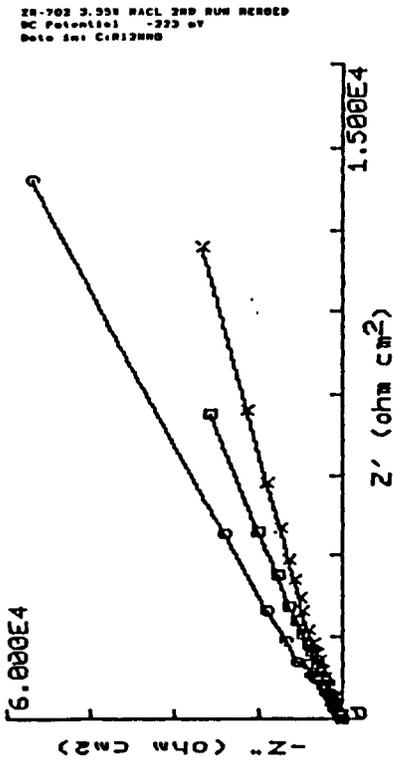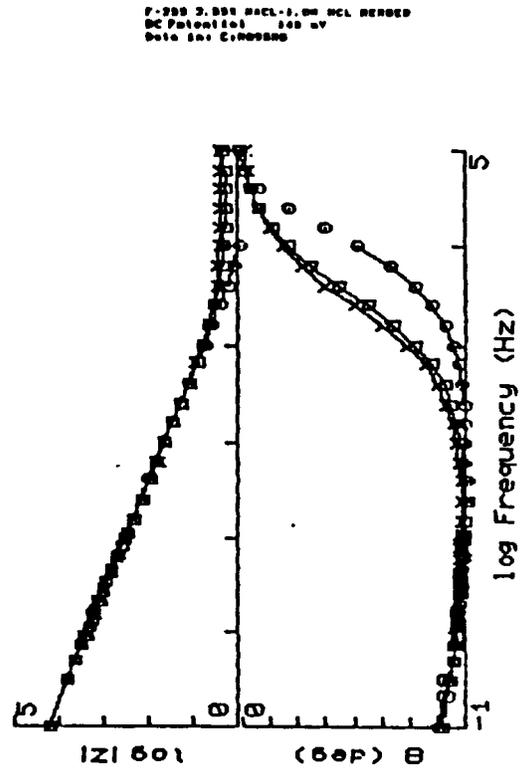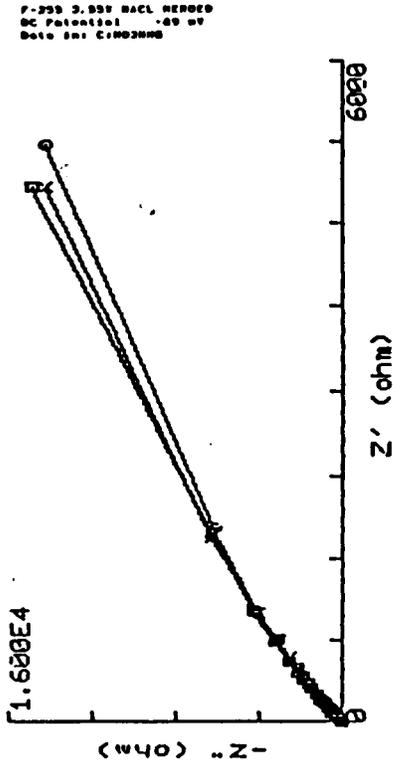
Figure A-1   Nyquist and Bode Plots for Zirconium 702 (a,c) and Ferralium 255 (b,d)
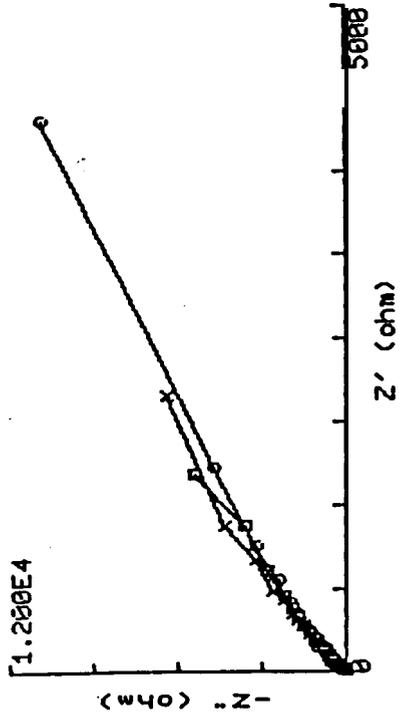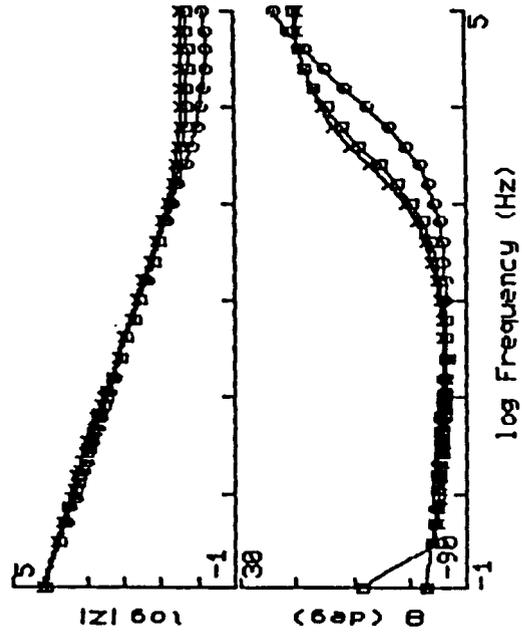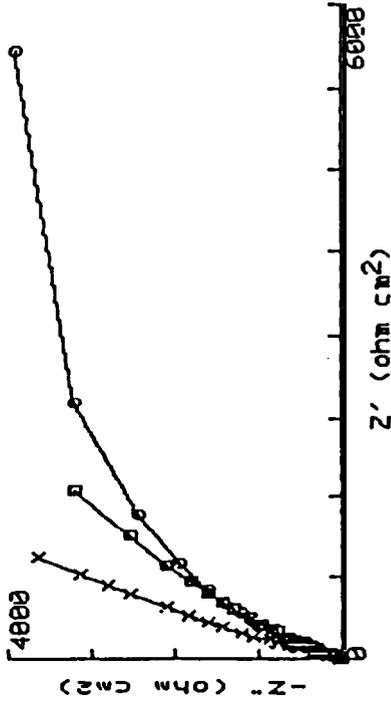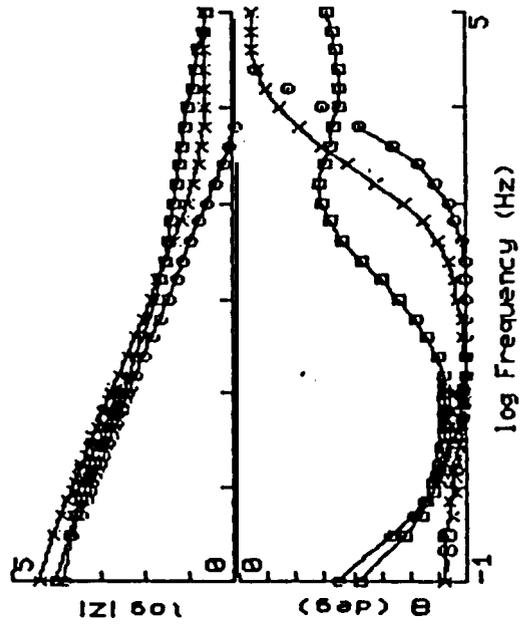
Figure A-2   Nyquist and Bode Plots for Hastelloy C-22 (a,c) and Inco Alloy G-3 (b,d)
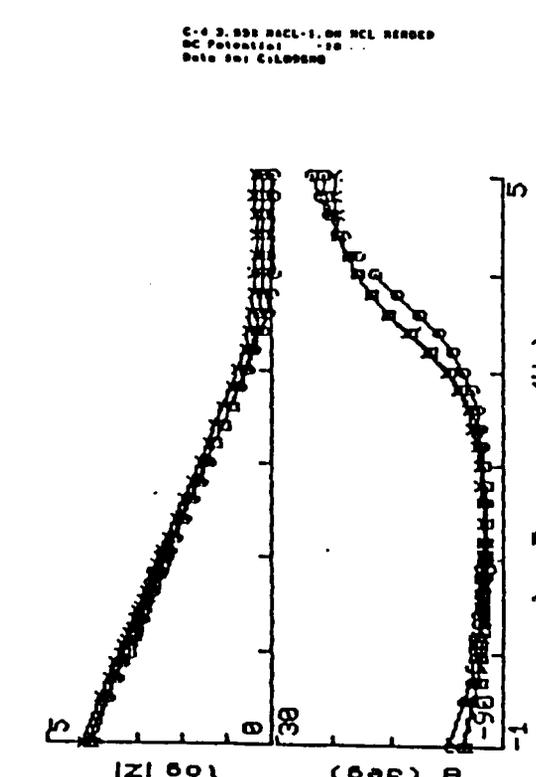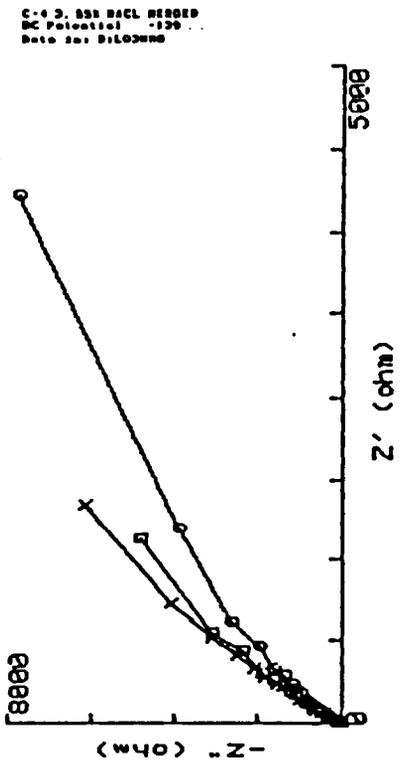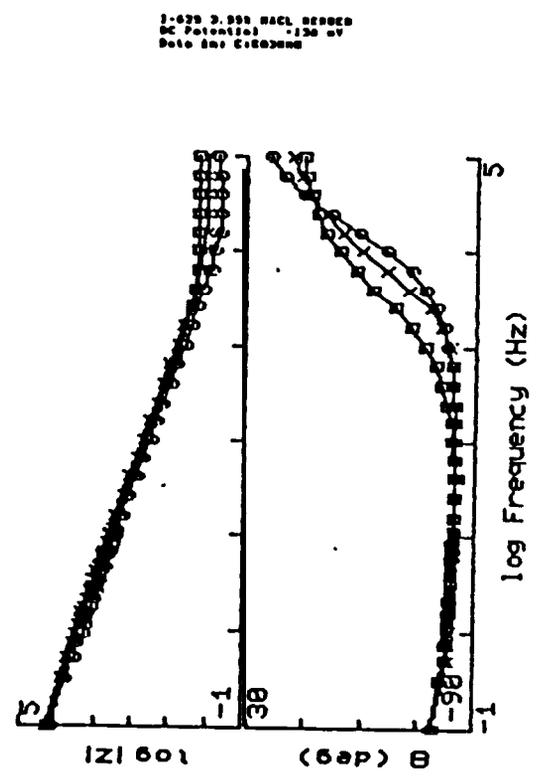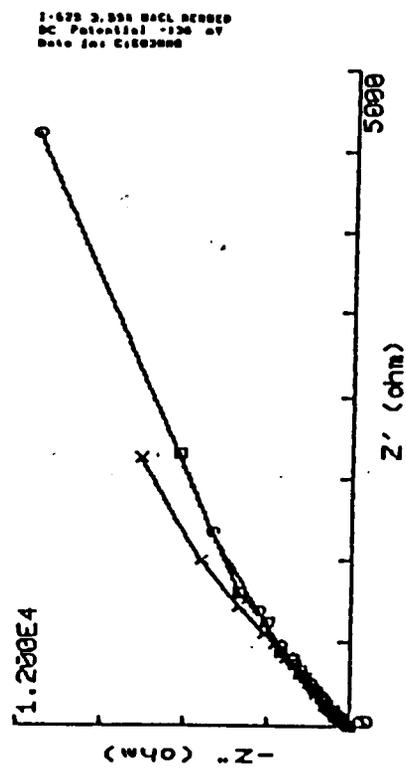
Figure A-3   Nyquist and Bode Plots for Hastelloy C-4 (a,c) and Inconel 625 (b,d)
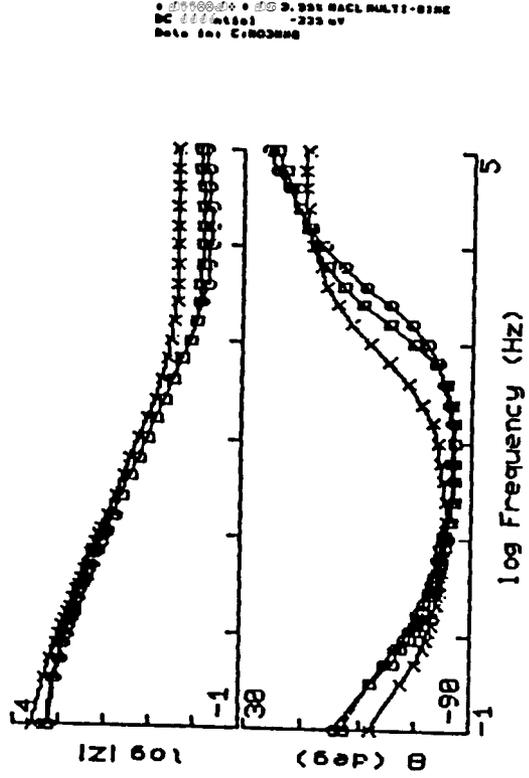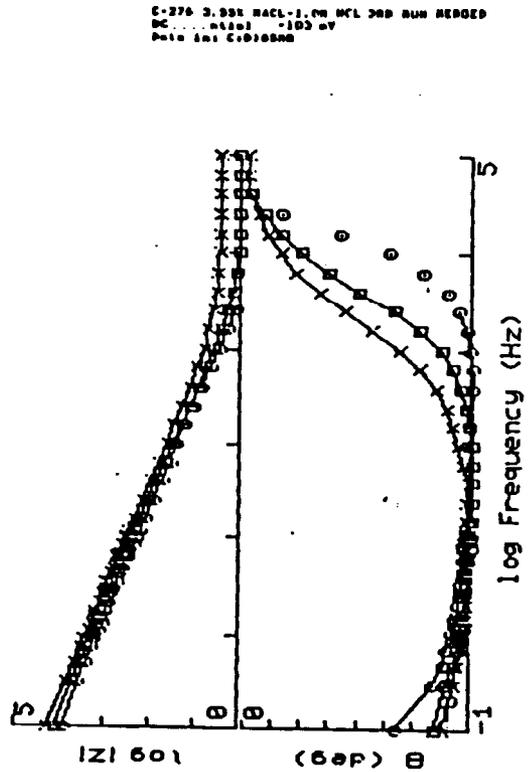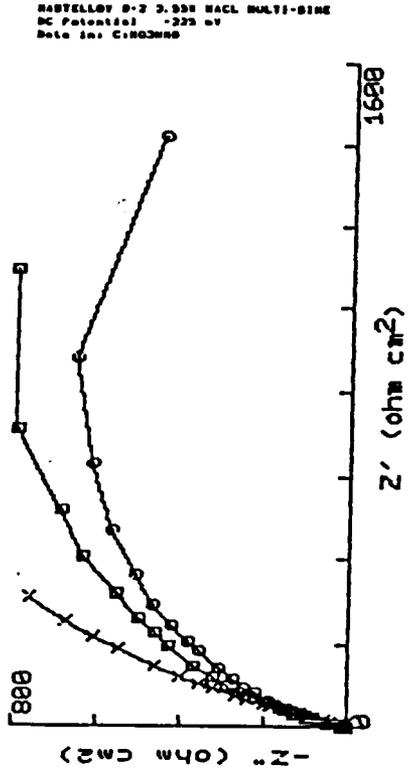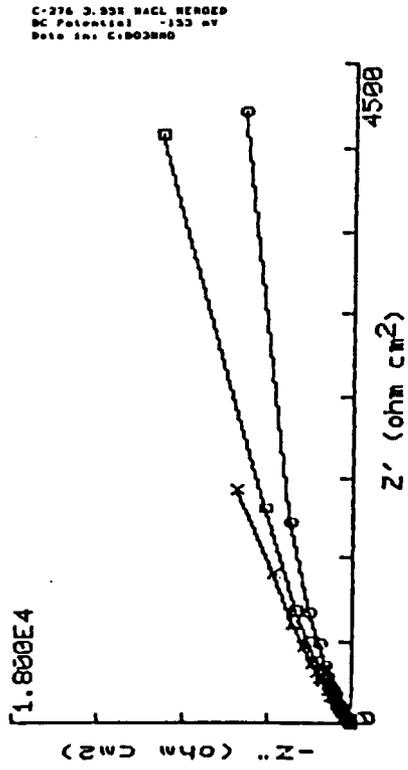
Figure A-4   Nyquist and Bode Plots for Hastelloy C-276 (a,c) and Hastelloy B-2 (b,[a]
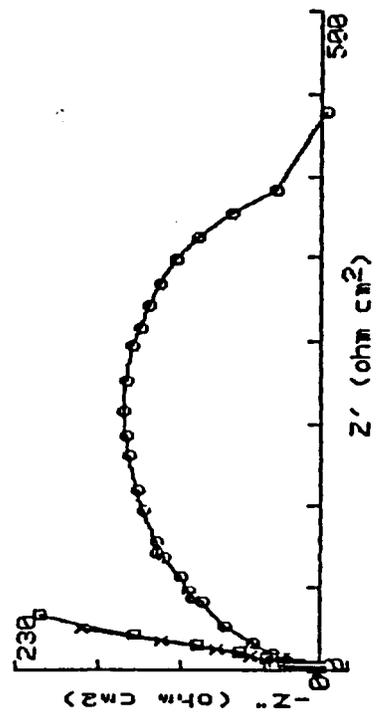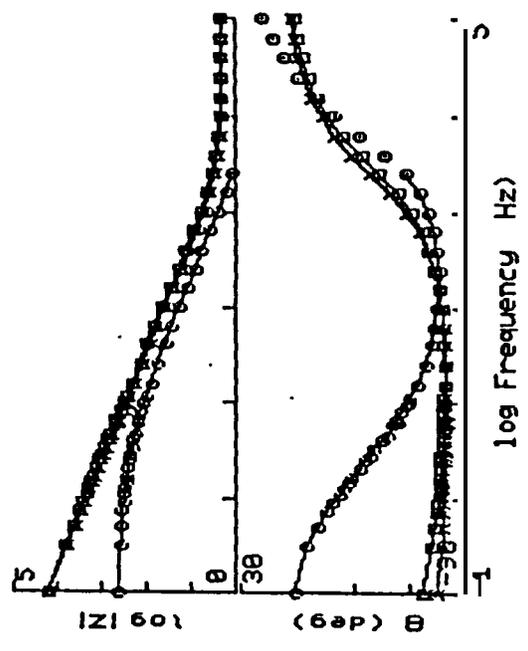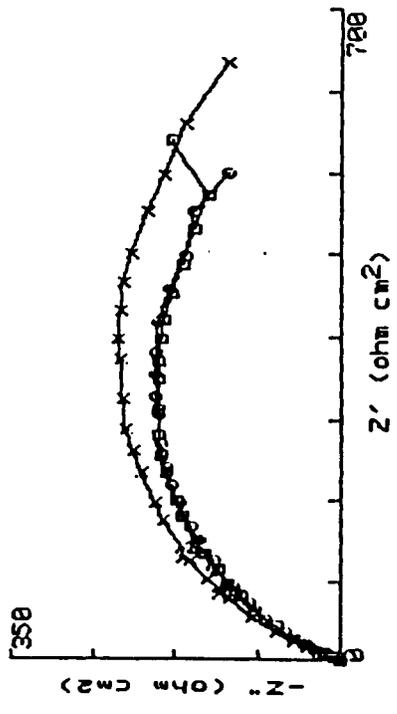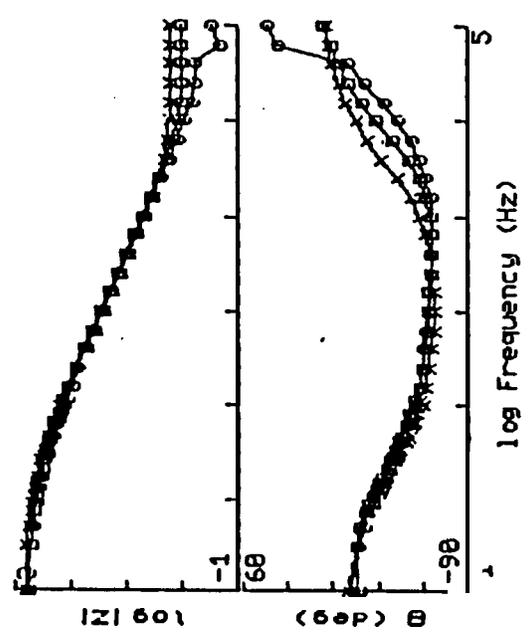
Figure A-5   Nyquist and Bode Plots for Monel 400 (a,c) and 20Cb-3 (b,a)
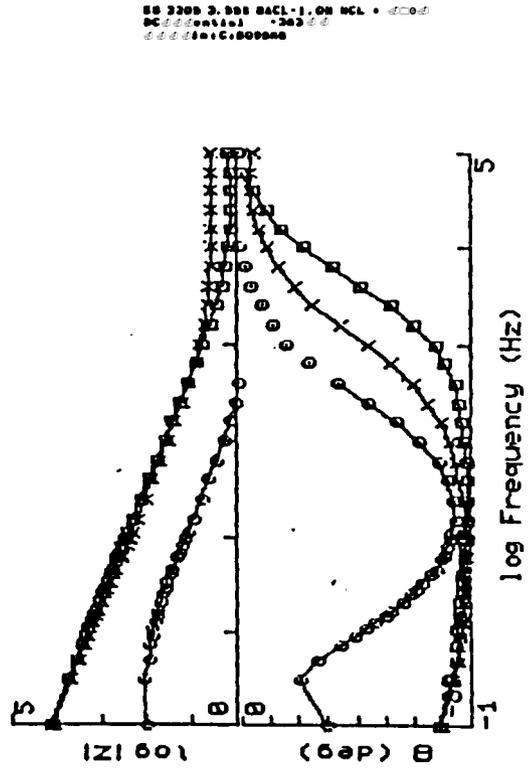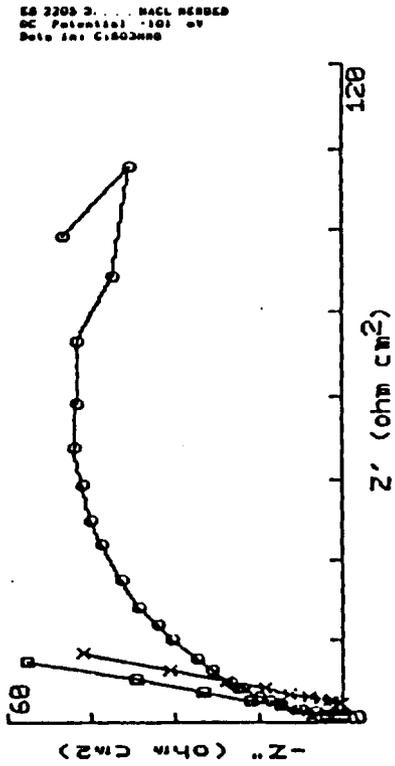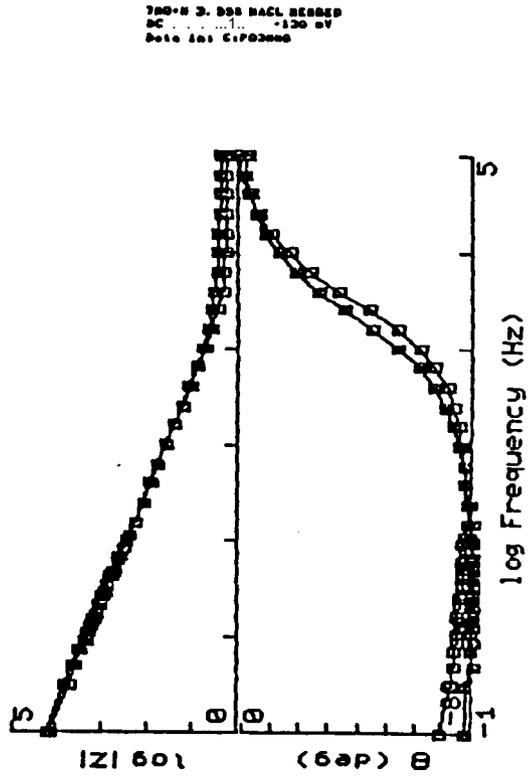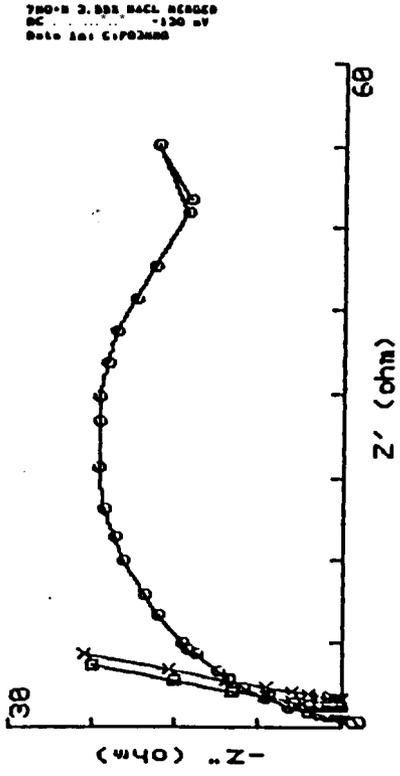
Figure A-6   Nyquist and Bode Plots for ₩S 2205 (a,c) and 7Mo + N (b,d)
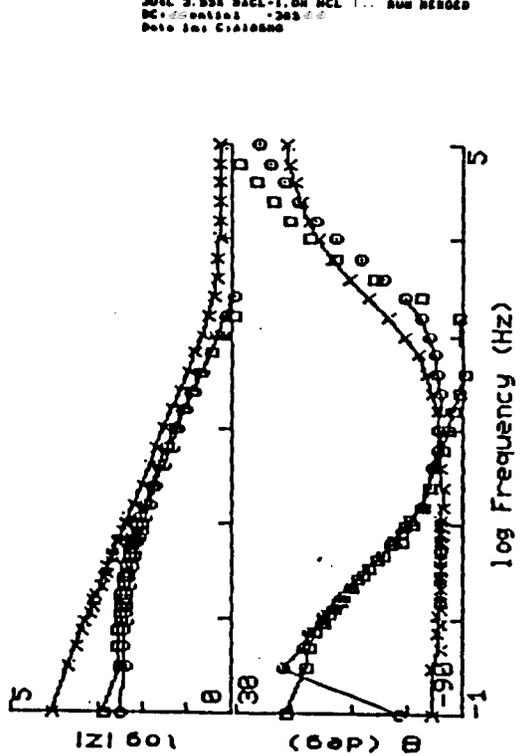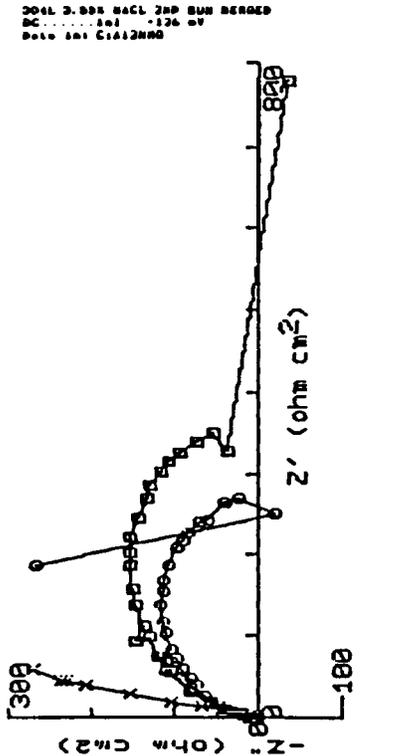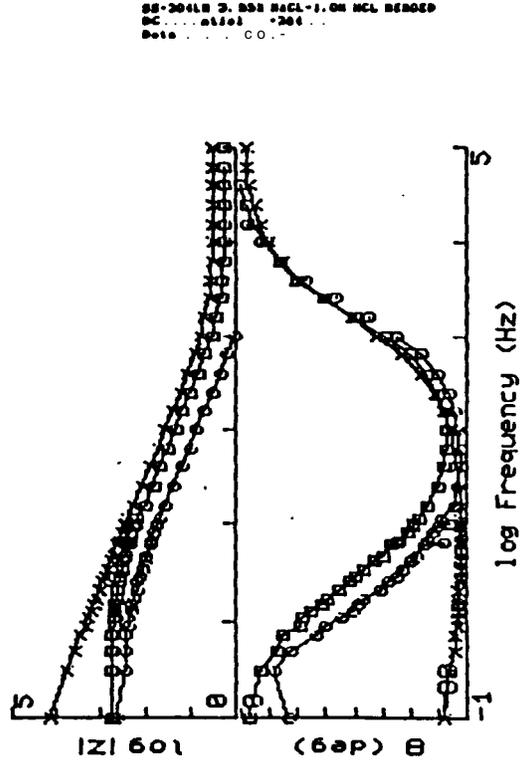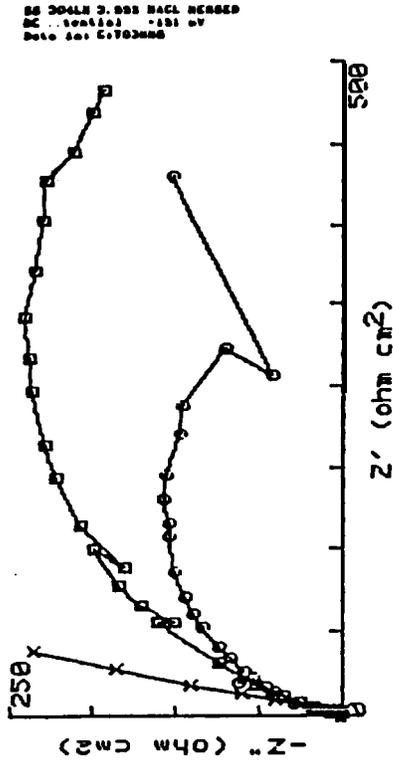
Figure A-7   Nyquist and Bode Plots for SS 304L (a,c) and SS 304LN (b,d)
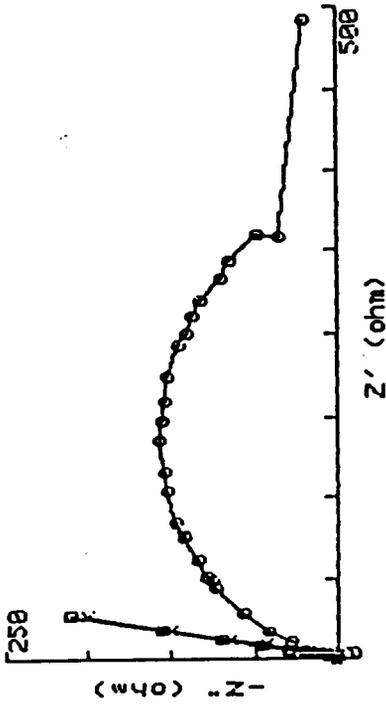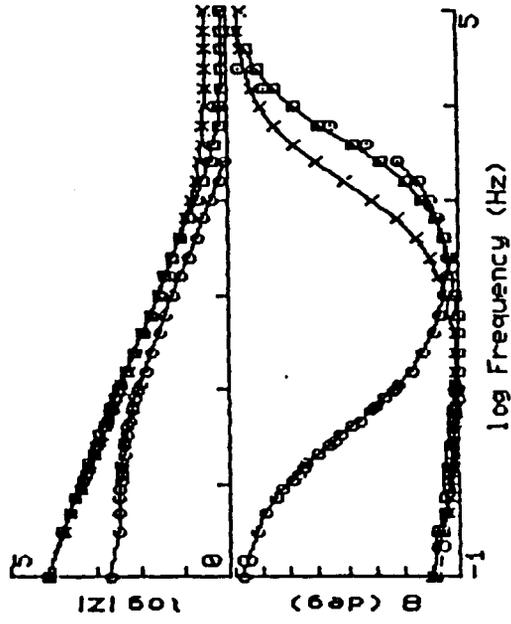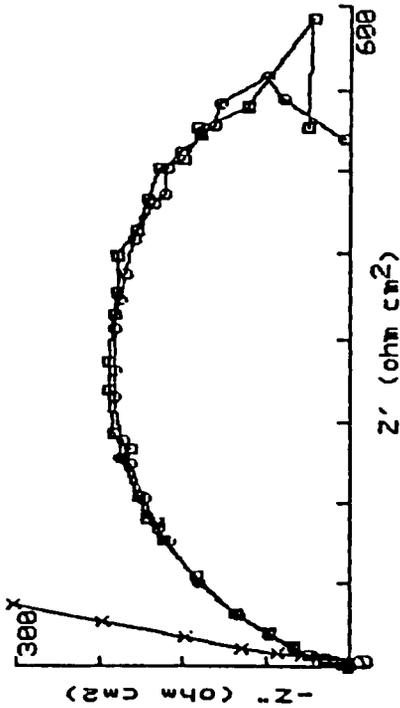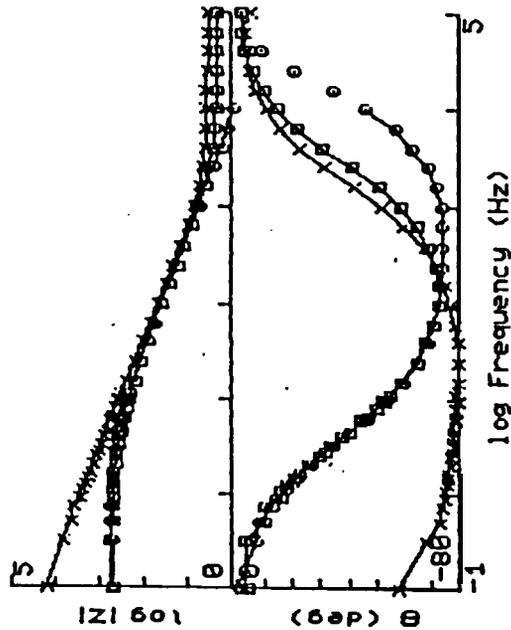
Figure A-8   Nyquist and Bode Plots for Inconel 600 (a,c) and Inconel 825 (b,d)
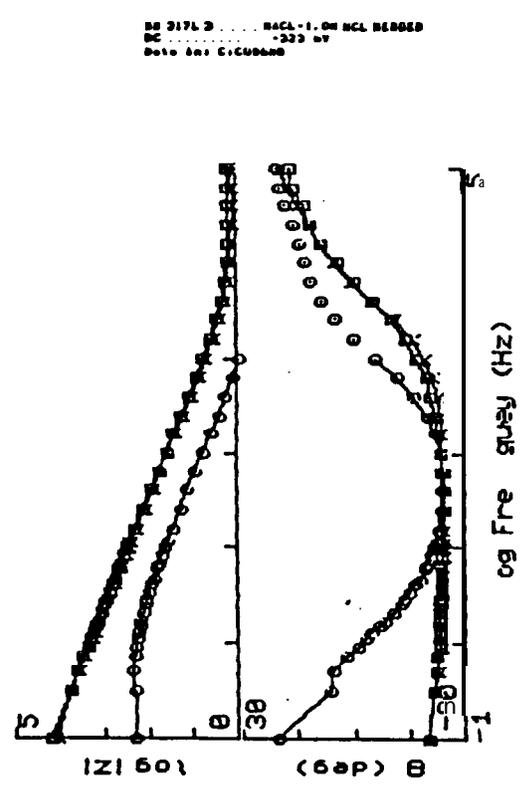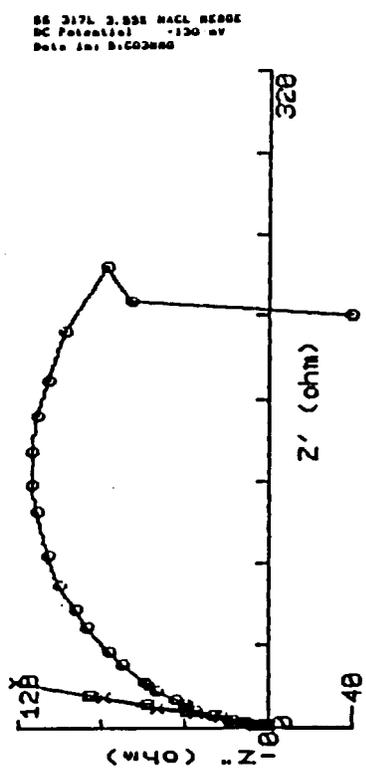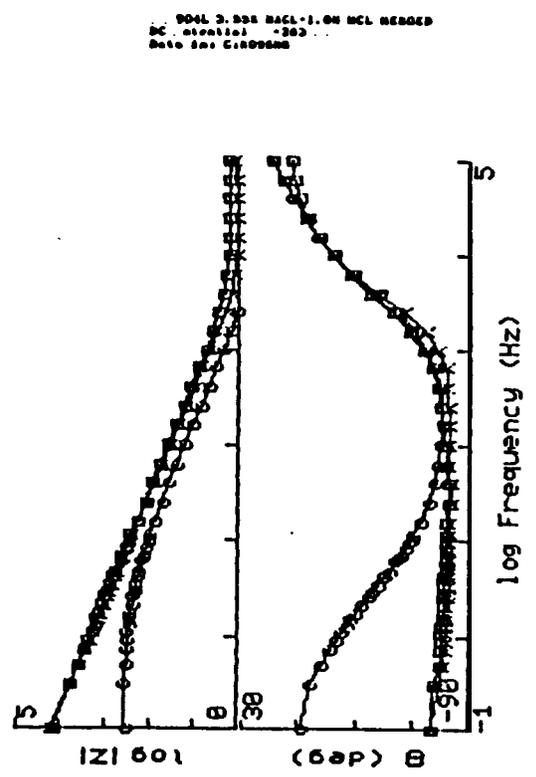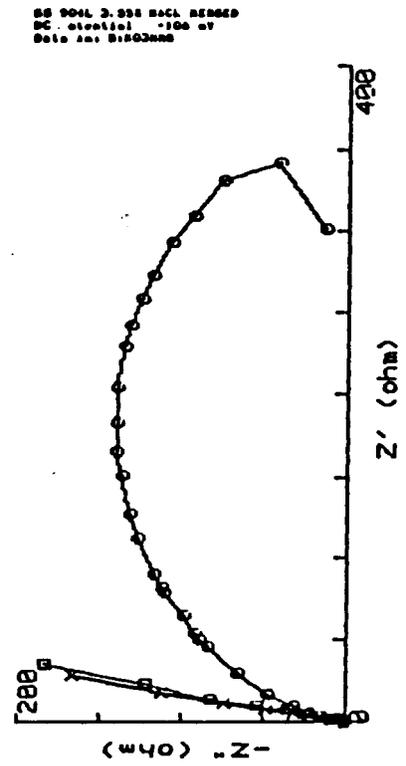
Figure A-9   Nyquist and Bode Plots for SS 317L (a,c) and SS 904L (b,d)
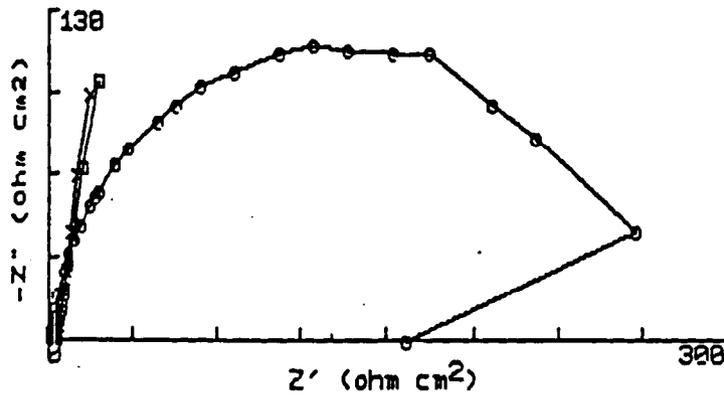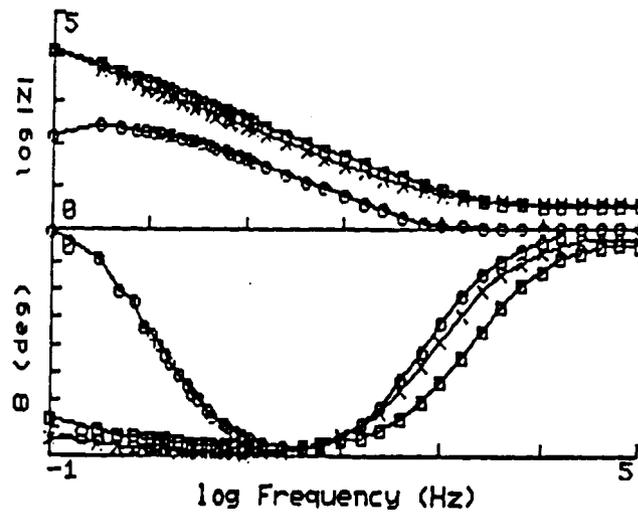
Figure A-10 Nyquist and Bode Plots for SS 316L (a,b)

APPENDIX B
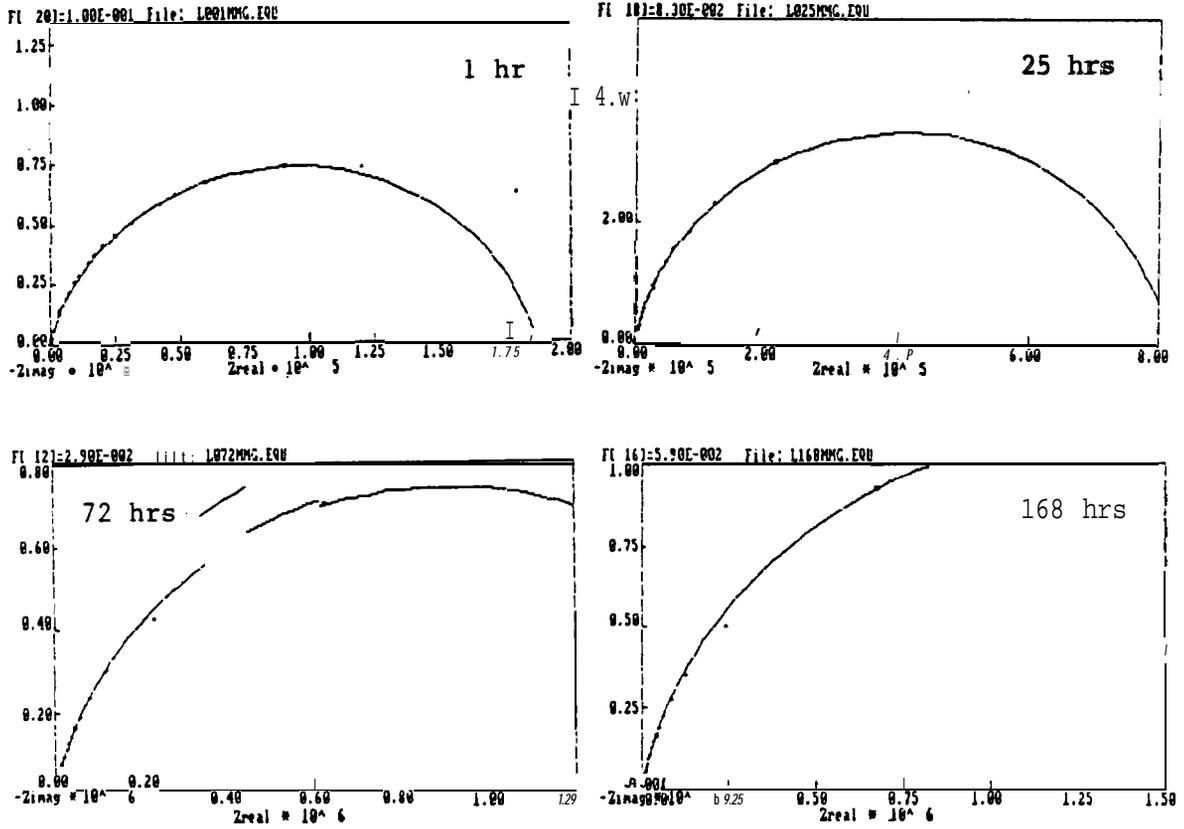
Figure B-1   Nyquist Plots for Hastelloy C-4 in 3.55% **NaCl-0.1N HCl** at Various Immersion Times
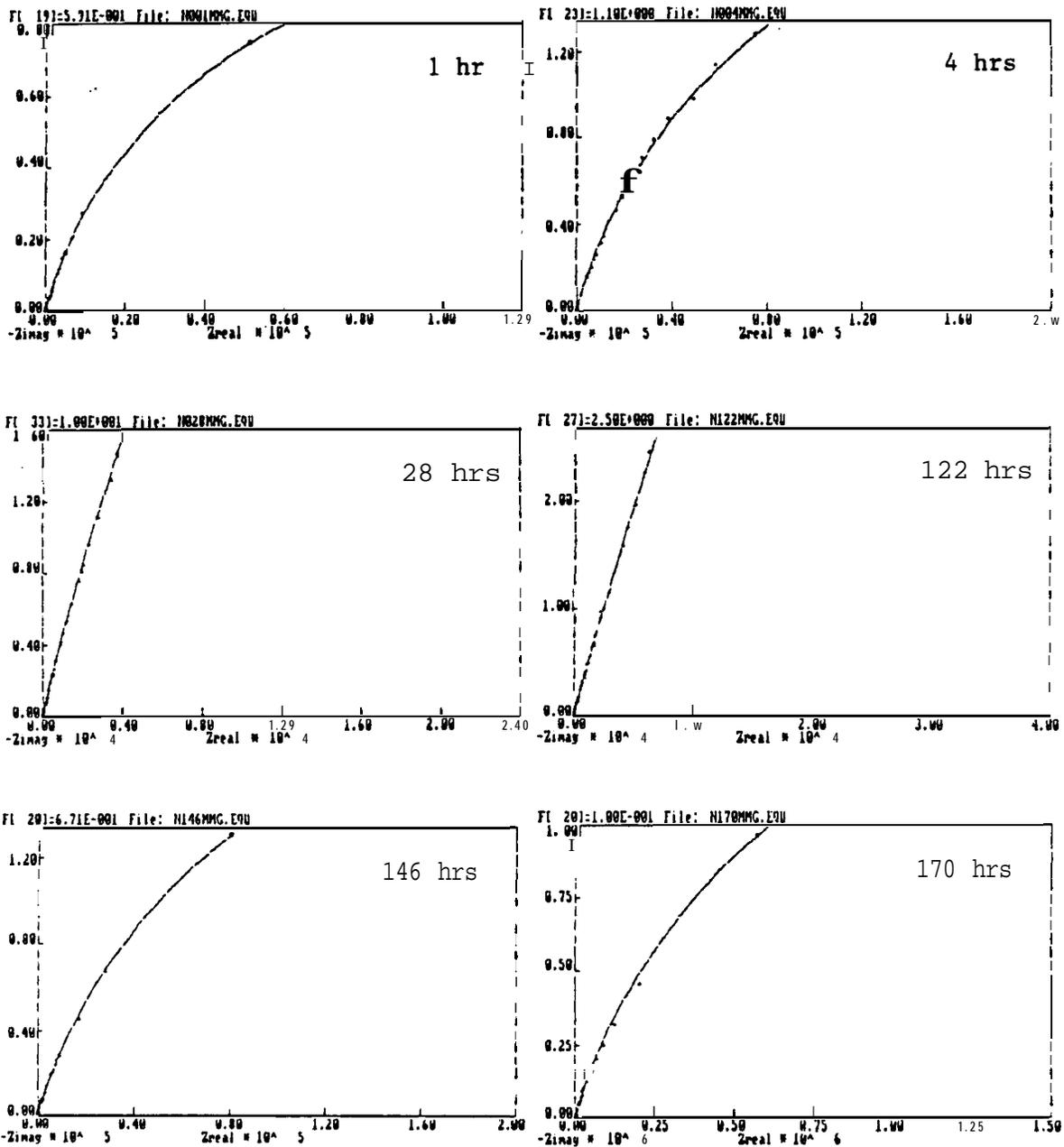
Figure B-2   Nyquist Plots for Hastelloy C-22 in 3.55% **NaCl-0.lN HCl** at
           Various Immersion Times

Figure B-2   (Cont)

F[29]:1.13E+001 File: N476MMG.EVU

476 hrs

6.00
4.00
2.00
0.00
        0.00   2.00   4.00   6.00   8.00   10.00
-Zimag * 10^ 4   Zreal * 10^ 4

F[27]:2.51E+001 File: N696MMG.EVU

696 hrs

3.00
2.00
1.00
0.00
        0.00   1.00   2.00   3.00   4.00   5.00
-Zimag * 10^ 4   Zreal * 10^ 4
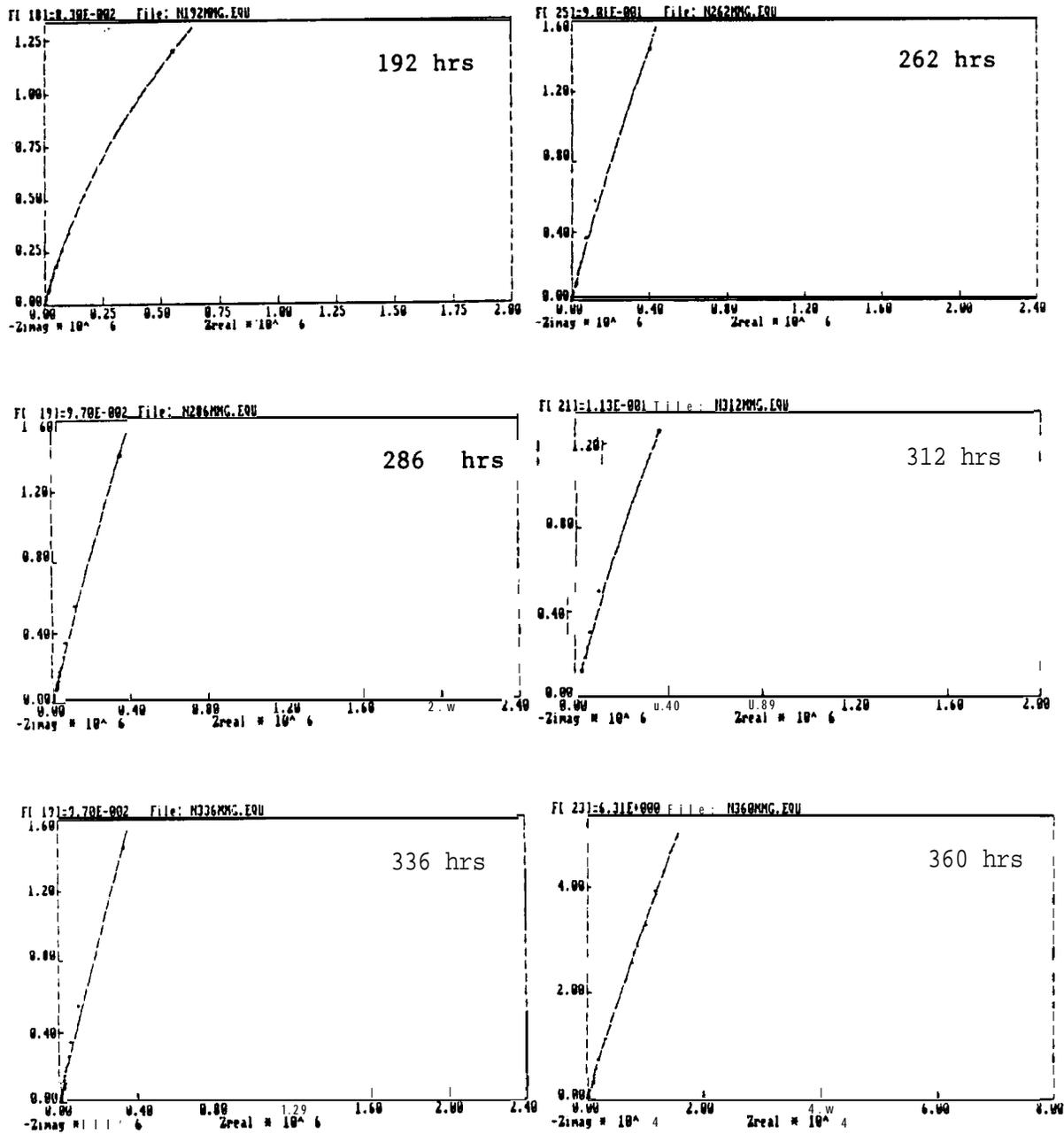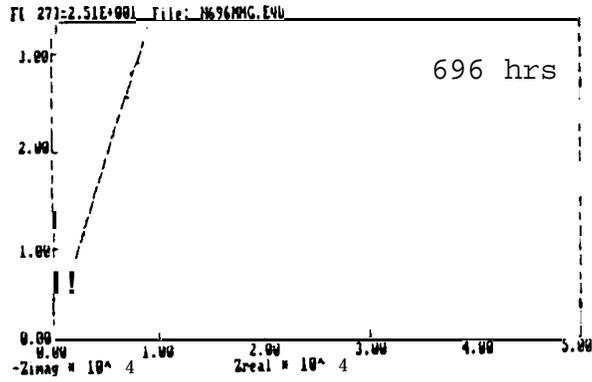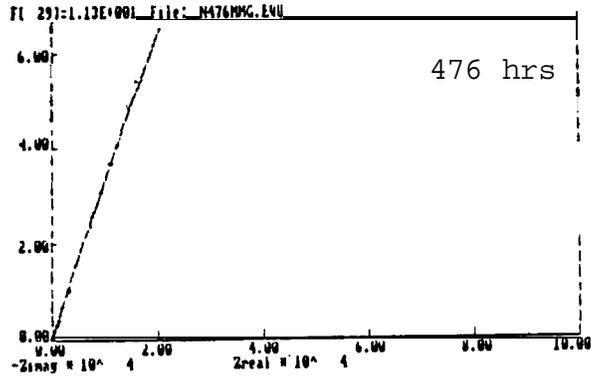
Figure B-2   (Cont)
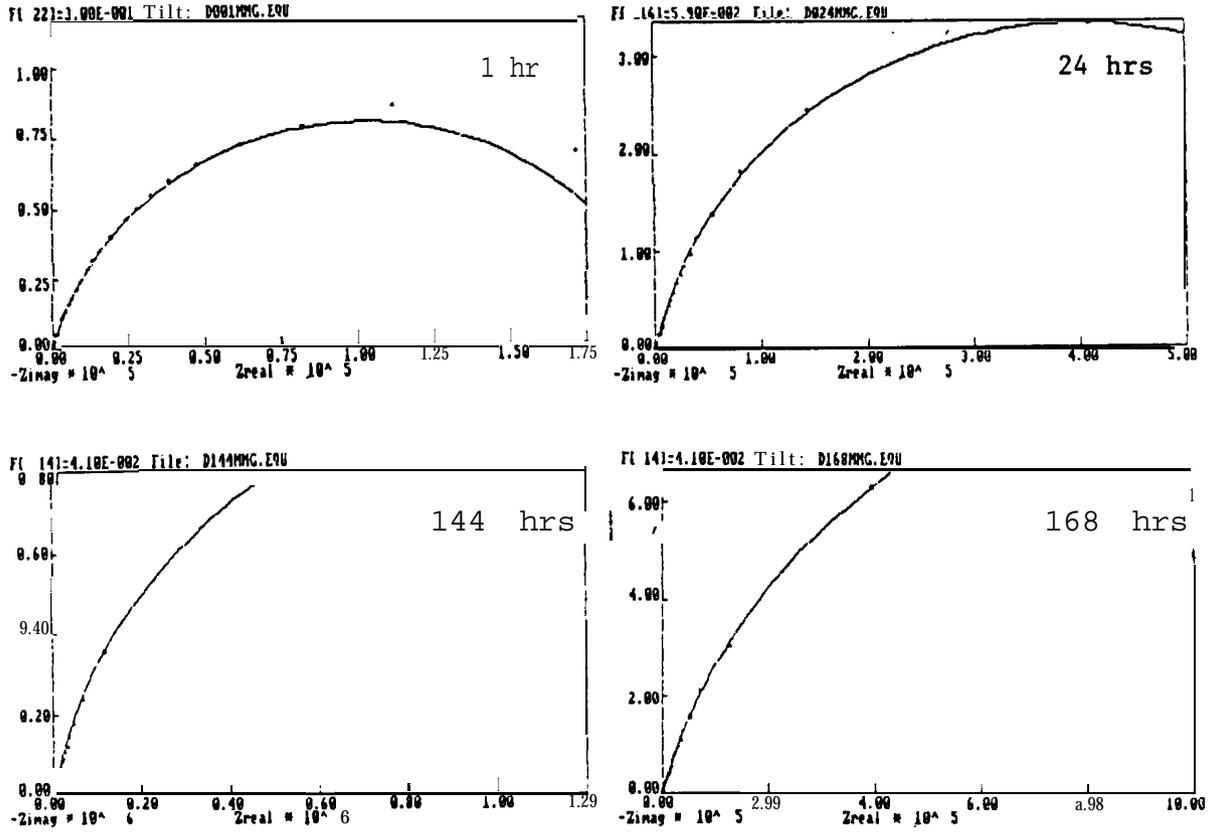
Figure B-3   Niquist Plots for Hastelloy C-276 in 3.55% **NaCl-0.1N HCl** at
            Various Immersion Times
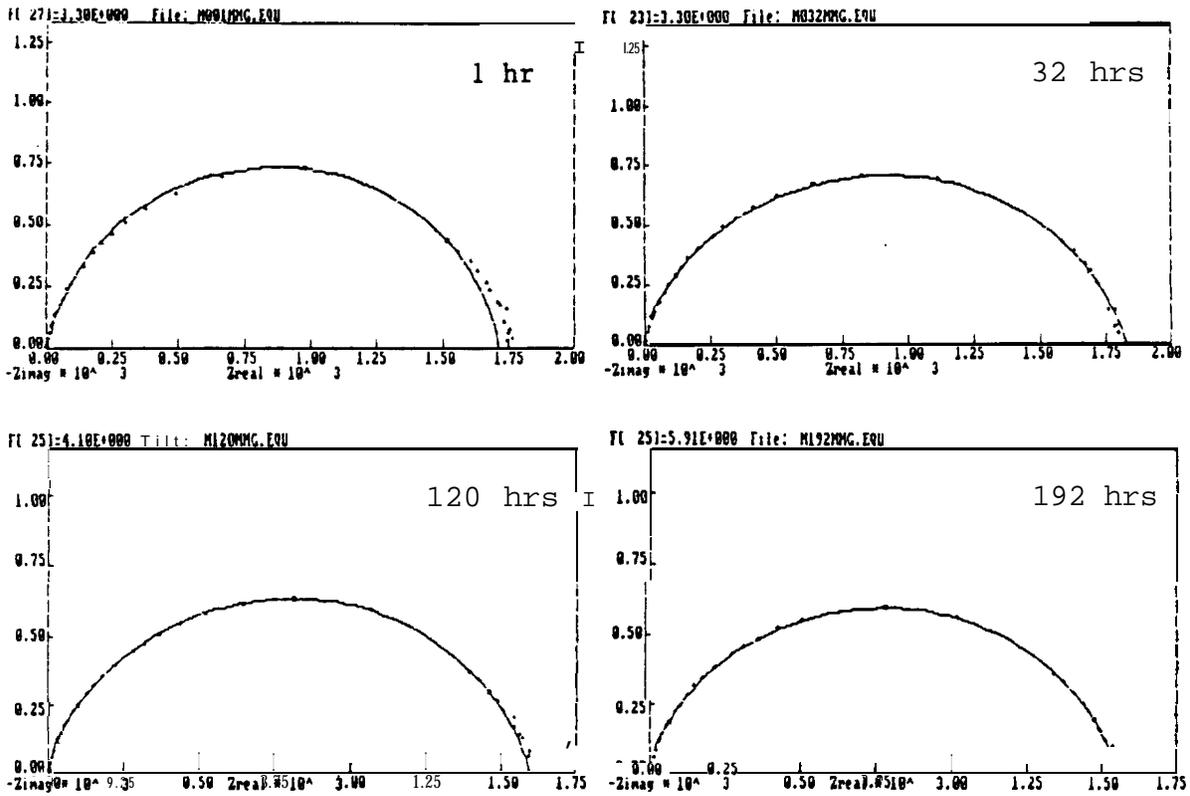
Figure B-4   Nyquist Plots for Hastelloy B-2 in 3.55% **NaCl-0.1N HCl** at
Various Immersion Times
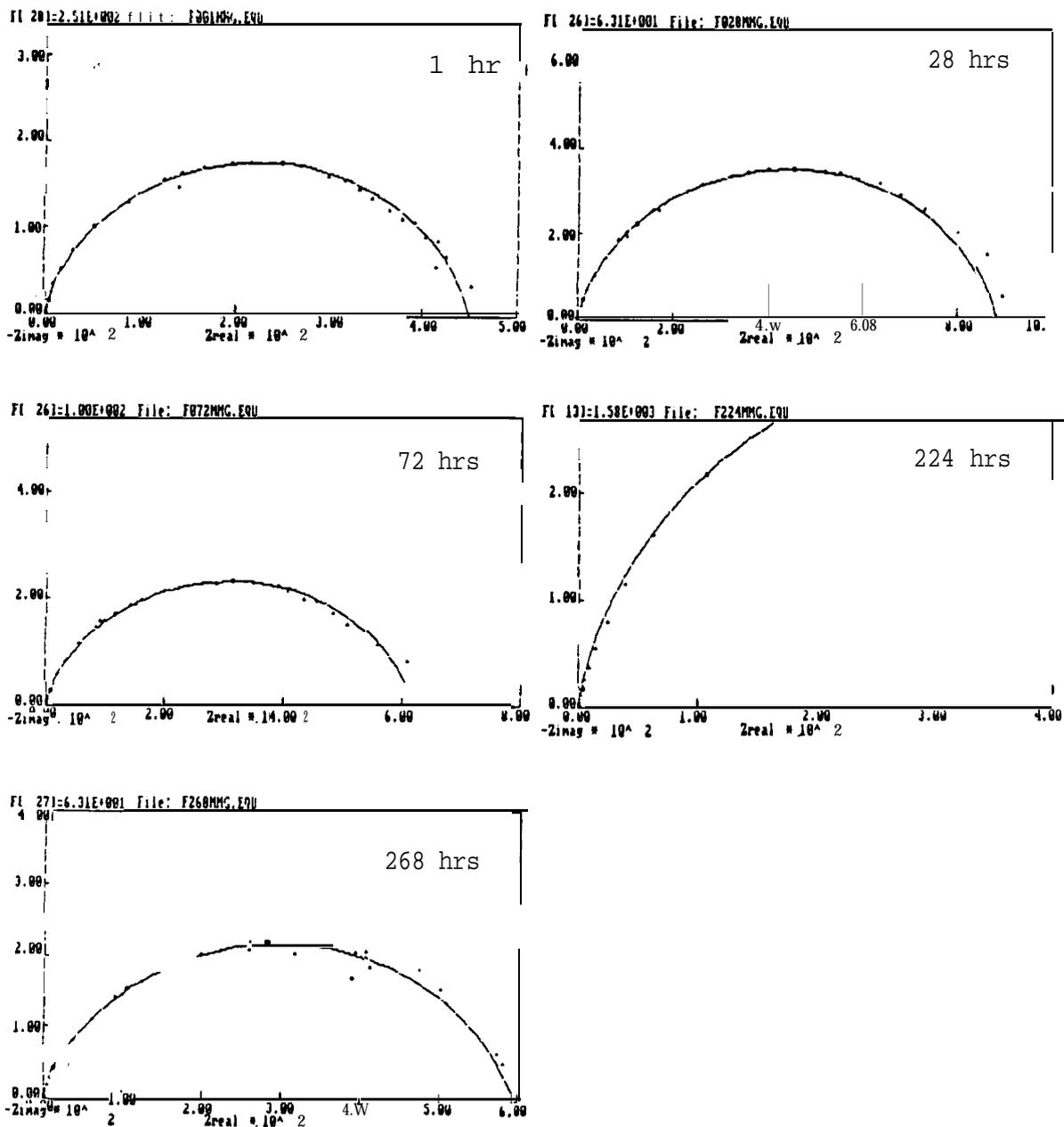
Figure B-5   Nyquist Plots for Inconel 600 in 3.55% NaCl-0.1N HCl at
             Various Immersion Times
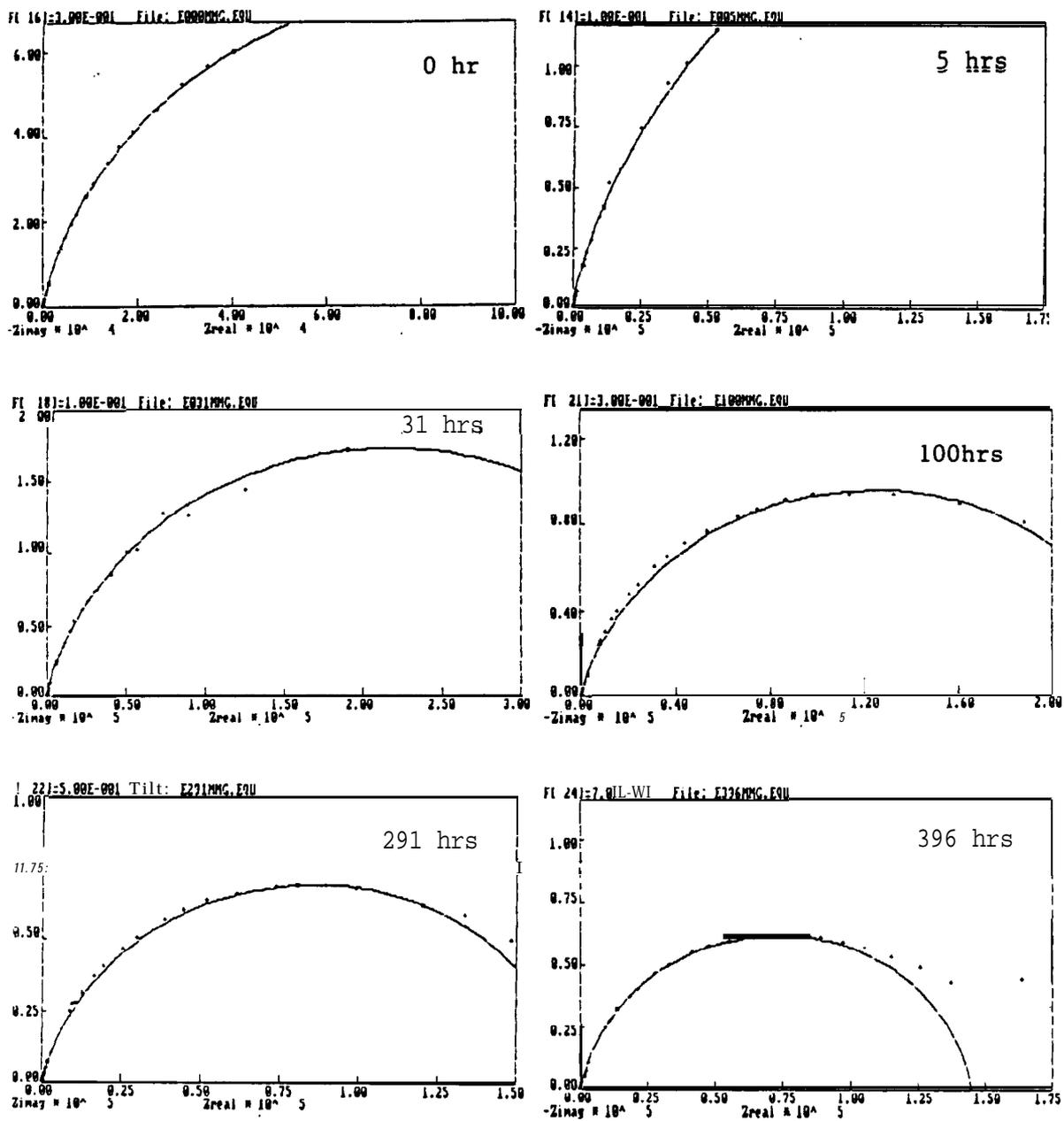
Figure B-6   Nyquist Plots for Inconel 625 in 3.55% **NaCl-0.1N HCl** at
              Various Immersion Times
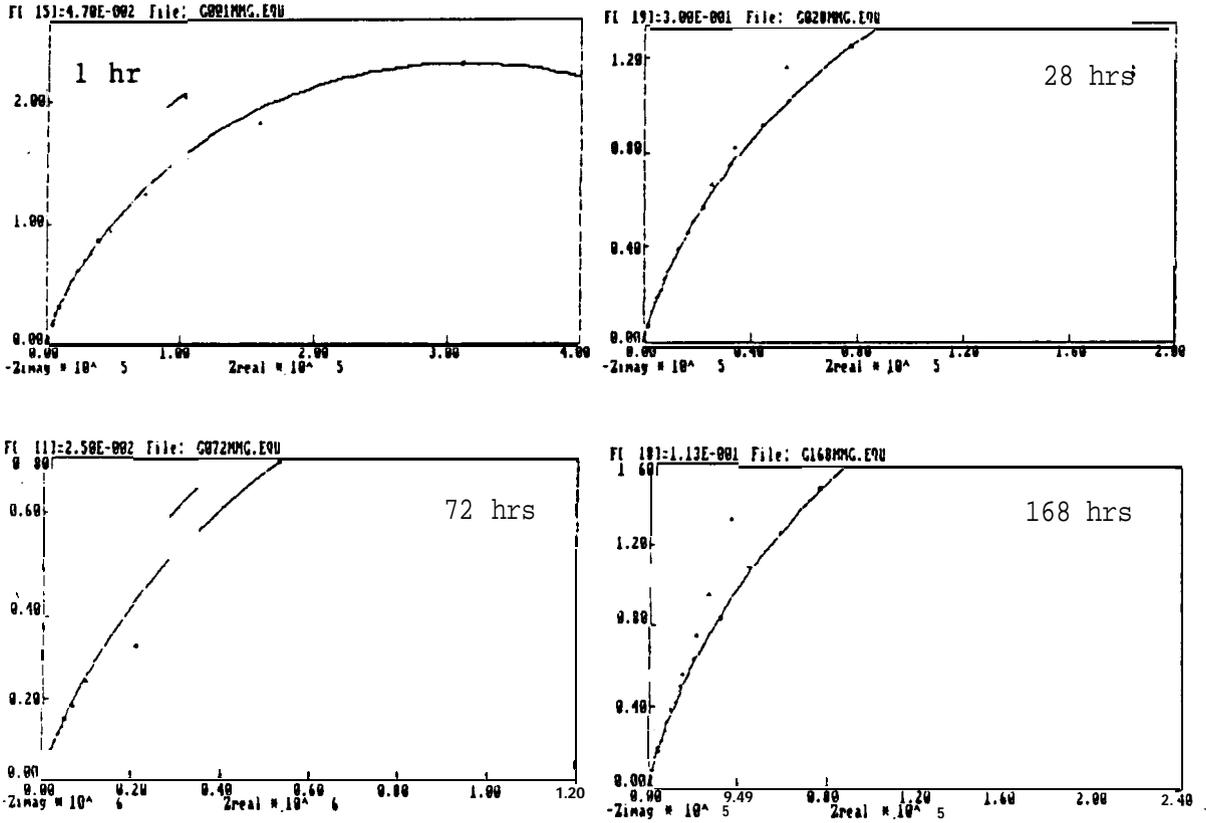
Figure B-7   Nyquist Plots for Inconel 825 in 3.55% **NaCl-0.1N HCl** at
             Various Immersion Times
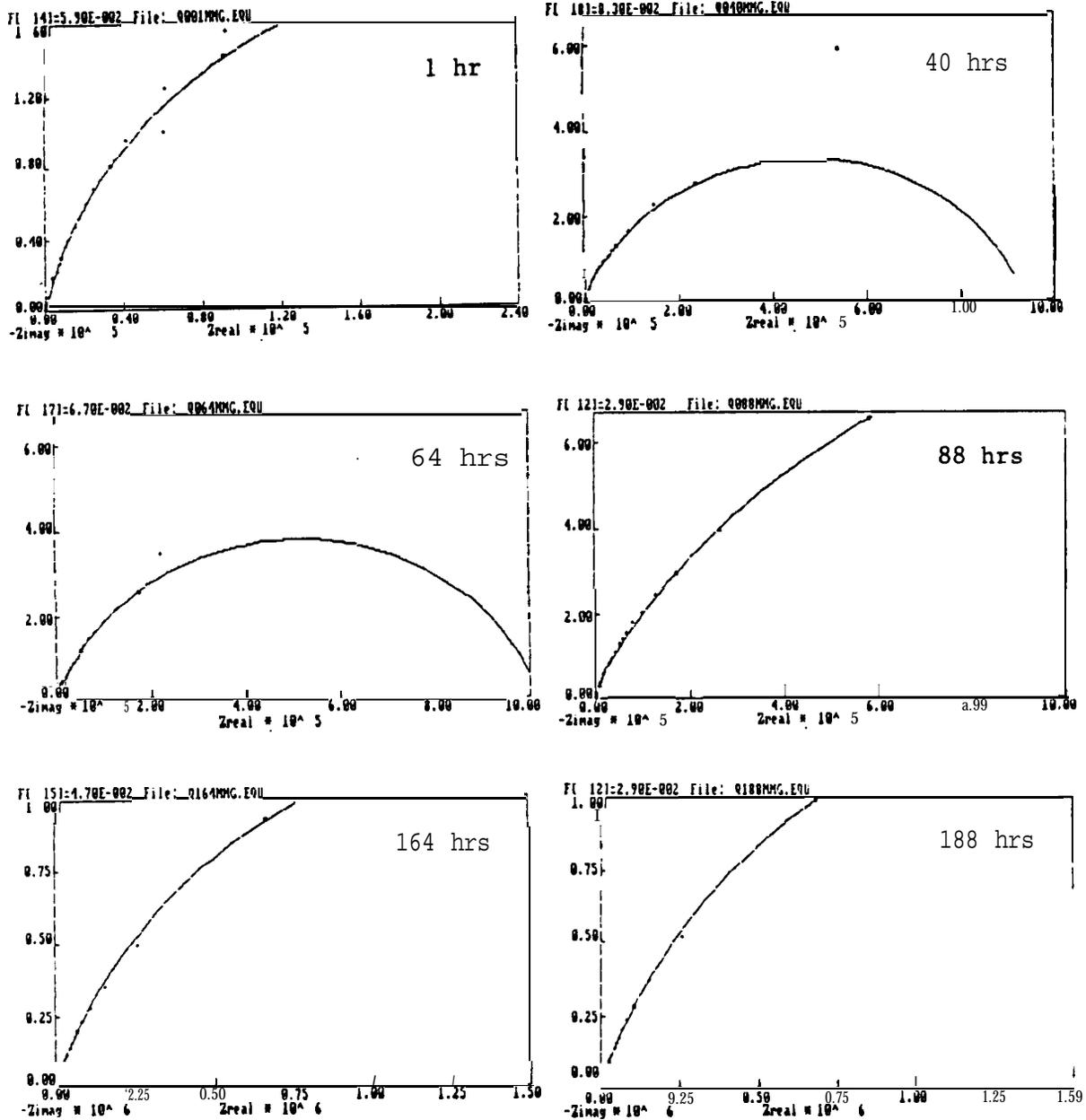
Figure B-8   Nyquist Plots for **Inco** G-3 in 3.55% **NaCl-0.1N HCl** at Various
Immersion Times

F[13]=3.30E-002 File: 4337MMG.EQU

337 hrs .

F[11]=2.50E-002 File: 0585MMG.EQU

505 hrs
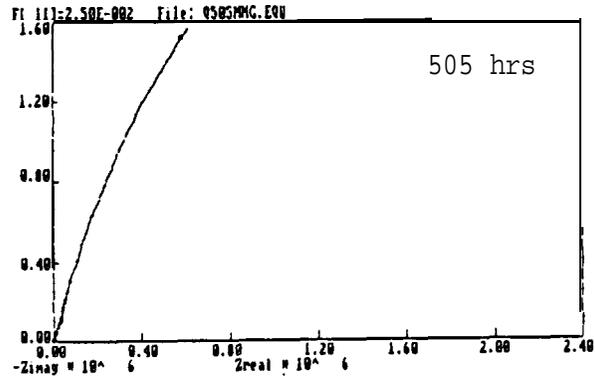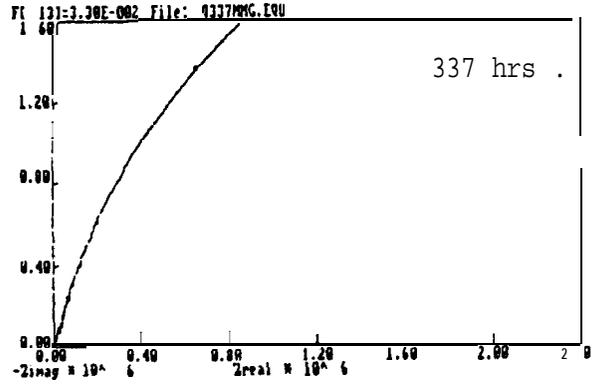
Figure B-8   (Cont)
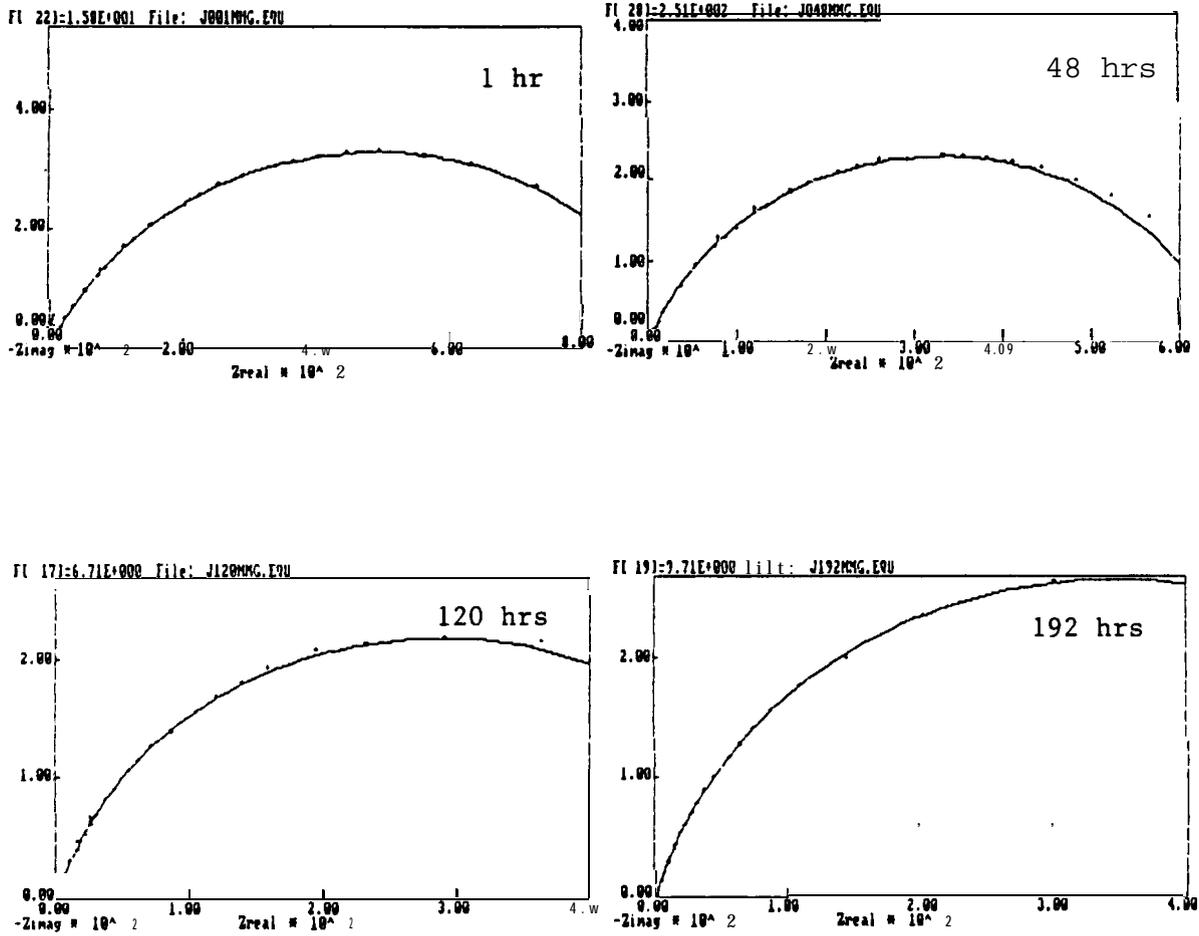
Figure B-9   Nyquist Plots for Monel 400 in 3.55% **NaCl-0.1N HCl** at Various
             Immersion Times
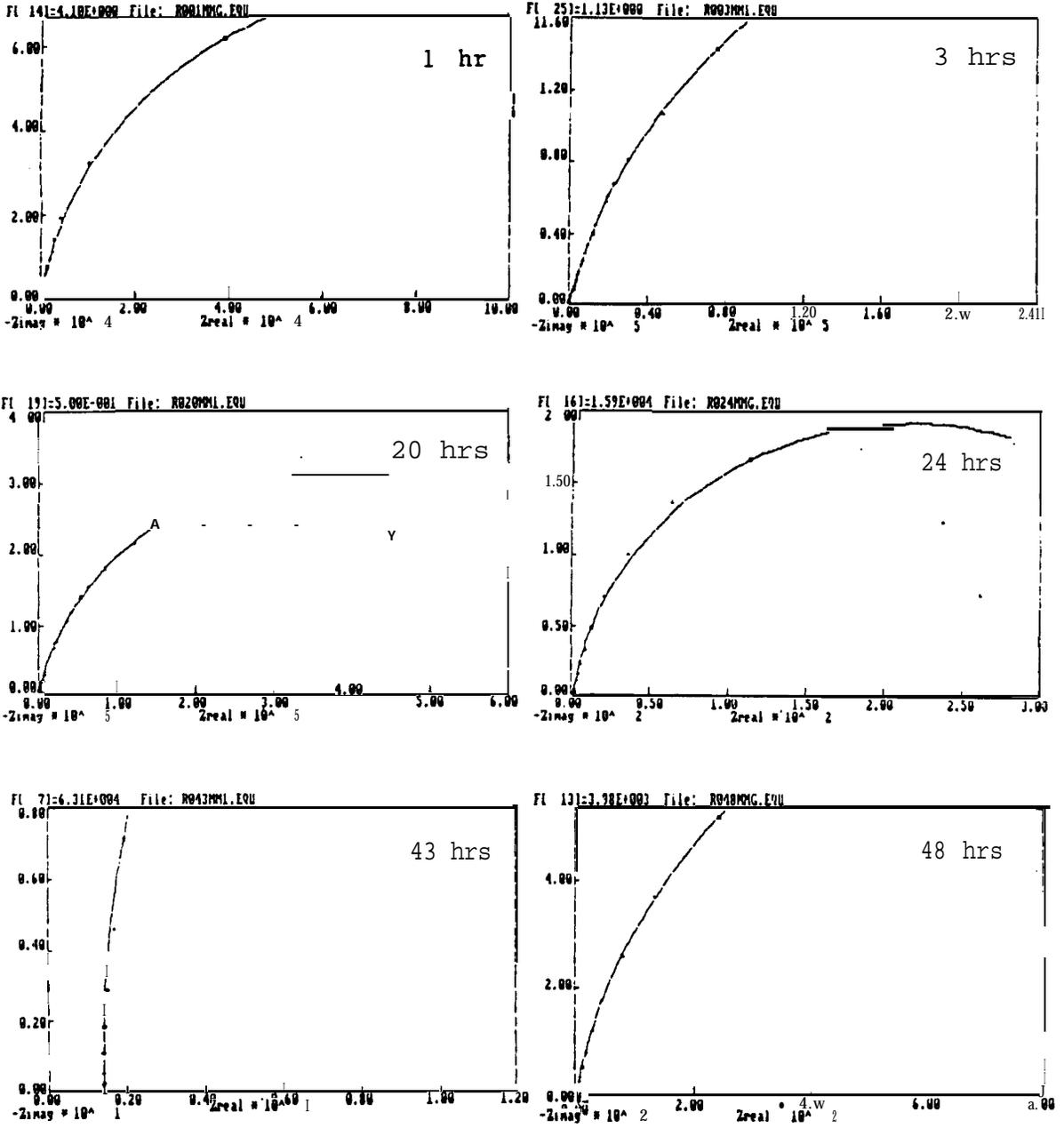
Figure B-10 Nyquist Plots for Zirconium 702 in 3.55% **NaCl-0.1N HCl** in
Various Immersion Times
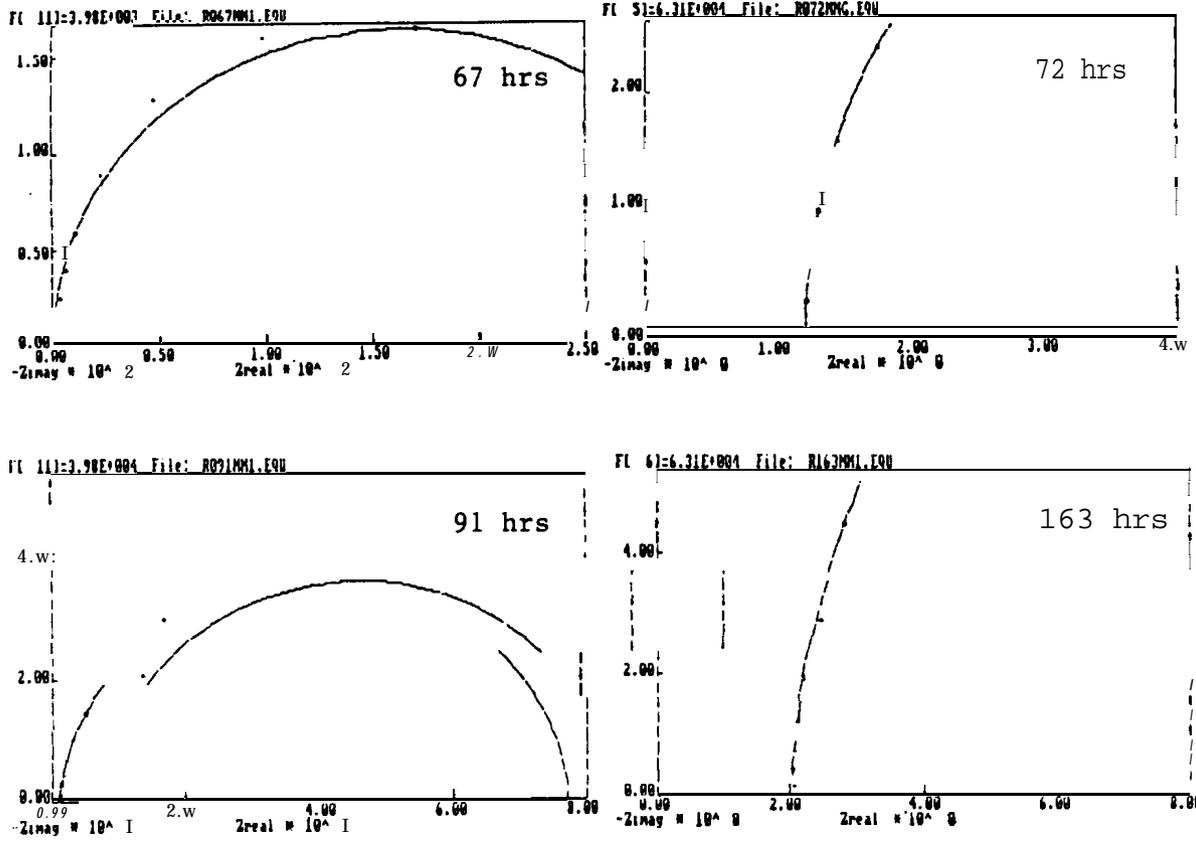
Figure B-10 (Cont)
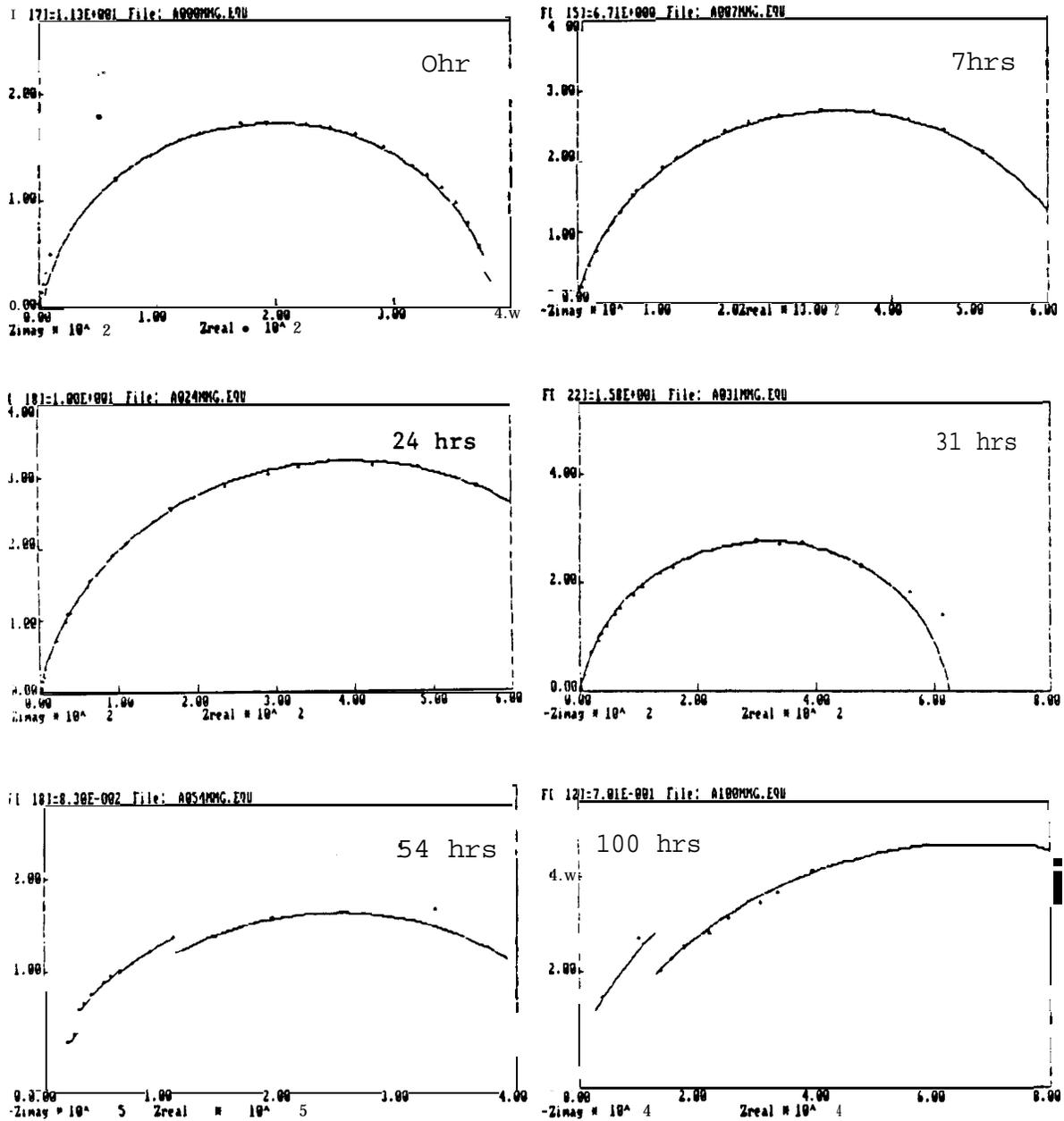
Figure B-11   Nyquist Plots for SS 304L in 3.55% NaCl-0.1N HCl at Various
             Immersion Times
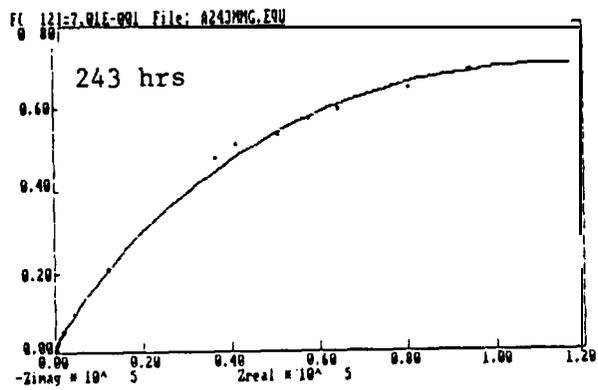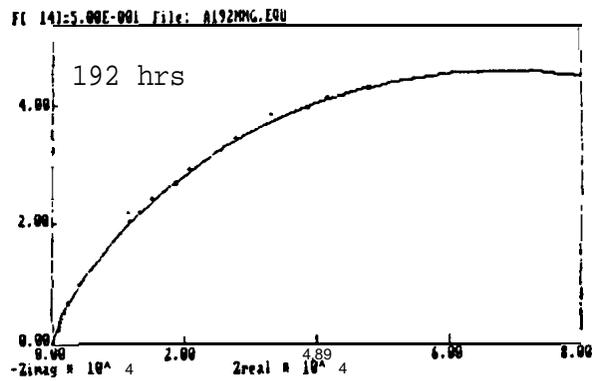
F(14)=5.00E-001 File: A192MMG.EQU

192 hrs

4.00

2.00

0.00
0.00   2.00   4.89   6.00   8.00
-Zimag ⨯ 10^ 4   Zreal ⨯ 10^ 4

F(12)=7.01E-001 File: A243MMG.EQU
0.80

243 hrs

0.60

0.40

0.20

0.00
0.00   0.20   0.40   0.60   0.80   1.00   1.20
-Zimag ⨯ 10^ 5   Zreal ⨯ 10^ 5

Figure B-11 **(Cont)**
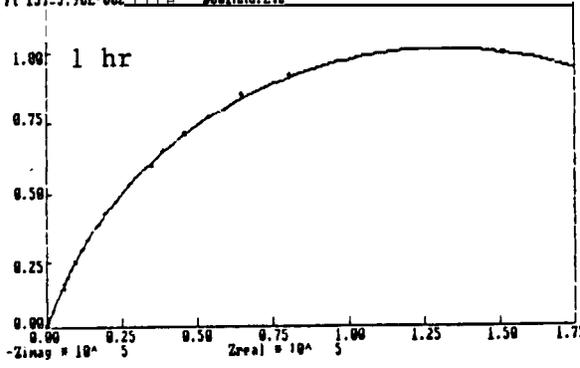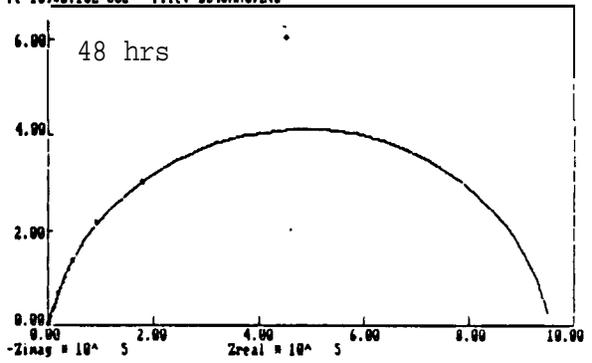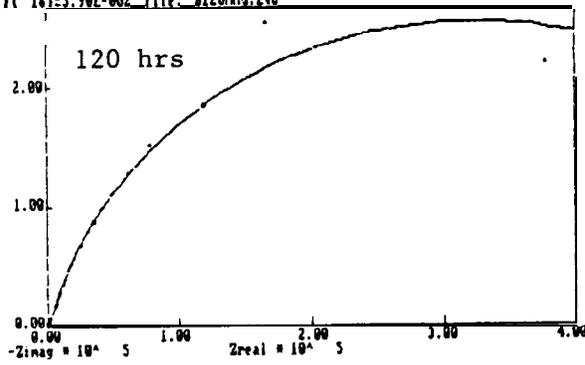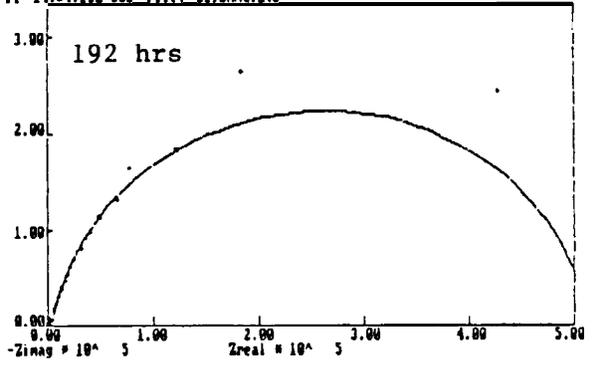
Figure B-12 Nyquist Plots for SS 316L in 3.55% **NaCl-0.1N HCl** at Various Immersion Times

FI 13]= 30E-002 File: C024MMG.EQU

24 hrs

0.75

0.50

0.25

0.00
0.00   0.25   0.50   0.75   1.00   1.25   1.50
-Zimag ¤ 10^ 6   Zreal ¤ 10^ 6

FI 13]=3.30E-002 File: C128MMG.EQU

0.75

128 hrs

0.50

0.25

0.00
0.00   0.25   0.50   0.75   1.00   1.2s
-Zimag ¤ 10^ 6   Zreal ¤ 10^ 6

FI 15]=4.70E-002 File: C168MMG.EQU

1.00

168 hrs

0.75

0.50

0.25

0.00
0.00   0.25   0.50   9.75   1.00   1.25   1.59   1.75
-Zimag ¤ 10^ 6   Zreal ¤ 10^ 6
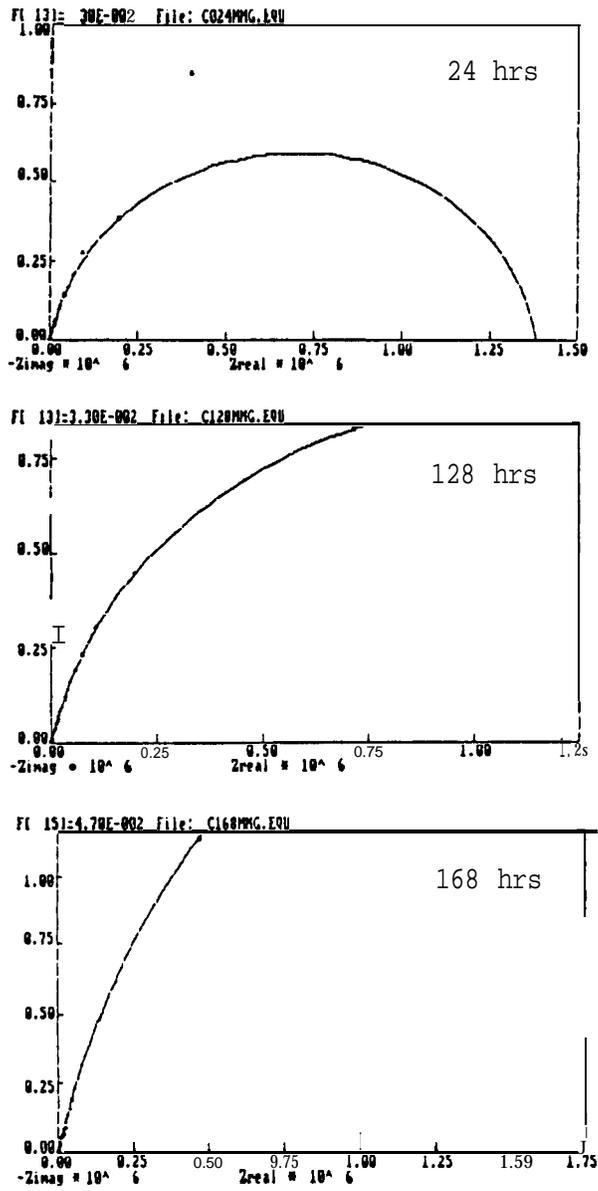
Figure B-13 Nyquist Plots for SS 317L in 3.55% **NaCl-0.1N HCl** at Various
         Immersion Times
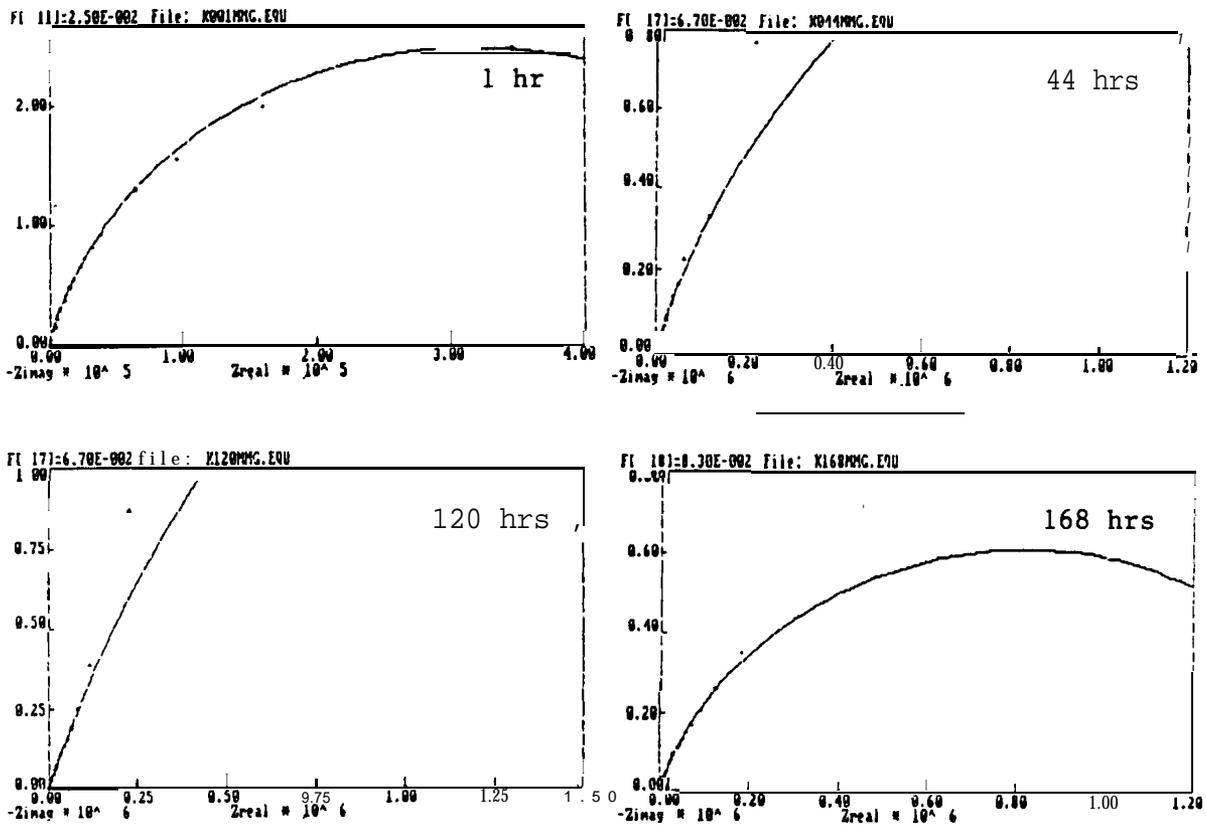
Figure B-14 Nyquist Plots for SS **904L** in 3.55% **NaCl-0.1N HCl** at Various
Immersion Times
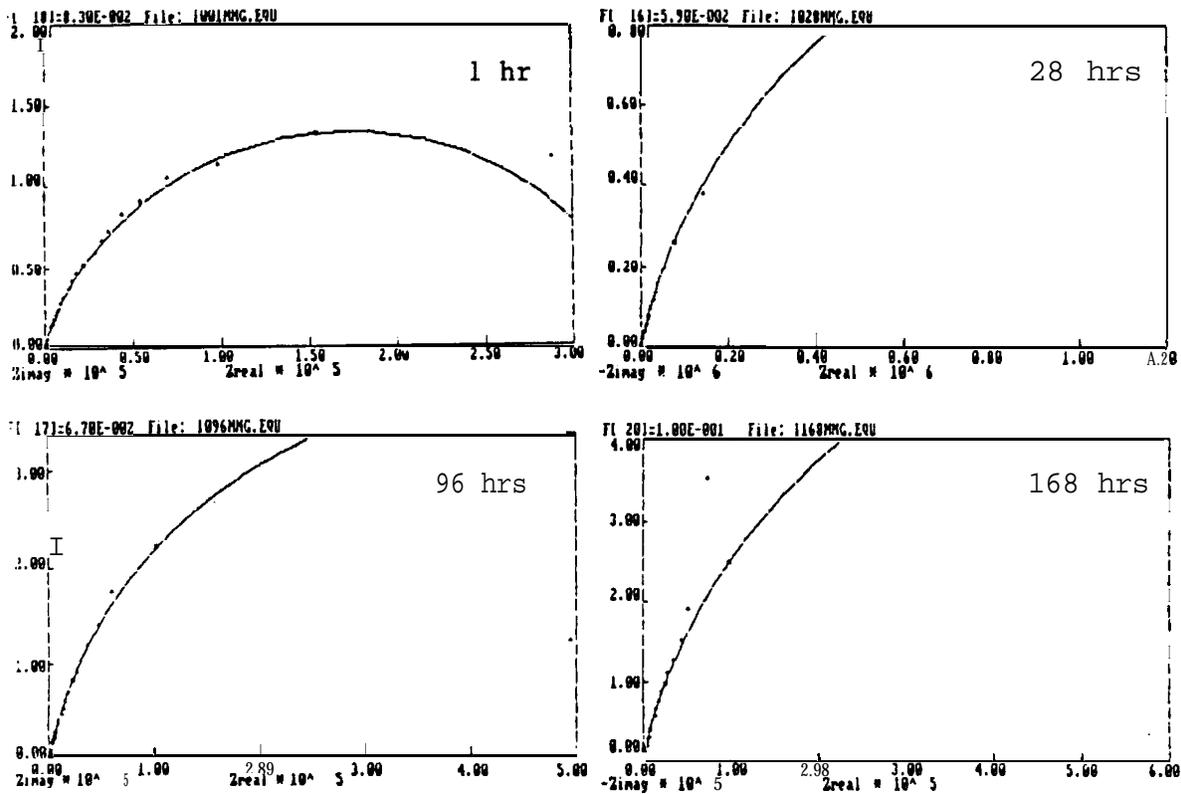
Figure B-15 Nyquist Plots for 20 Cb-3 in 3.55% **NaCl-0.1N HCl** in Various
Immersion Times
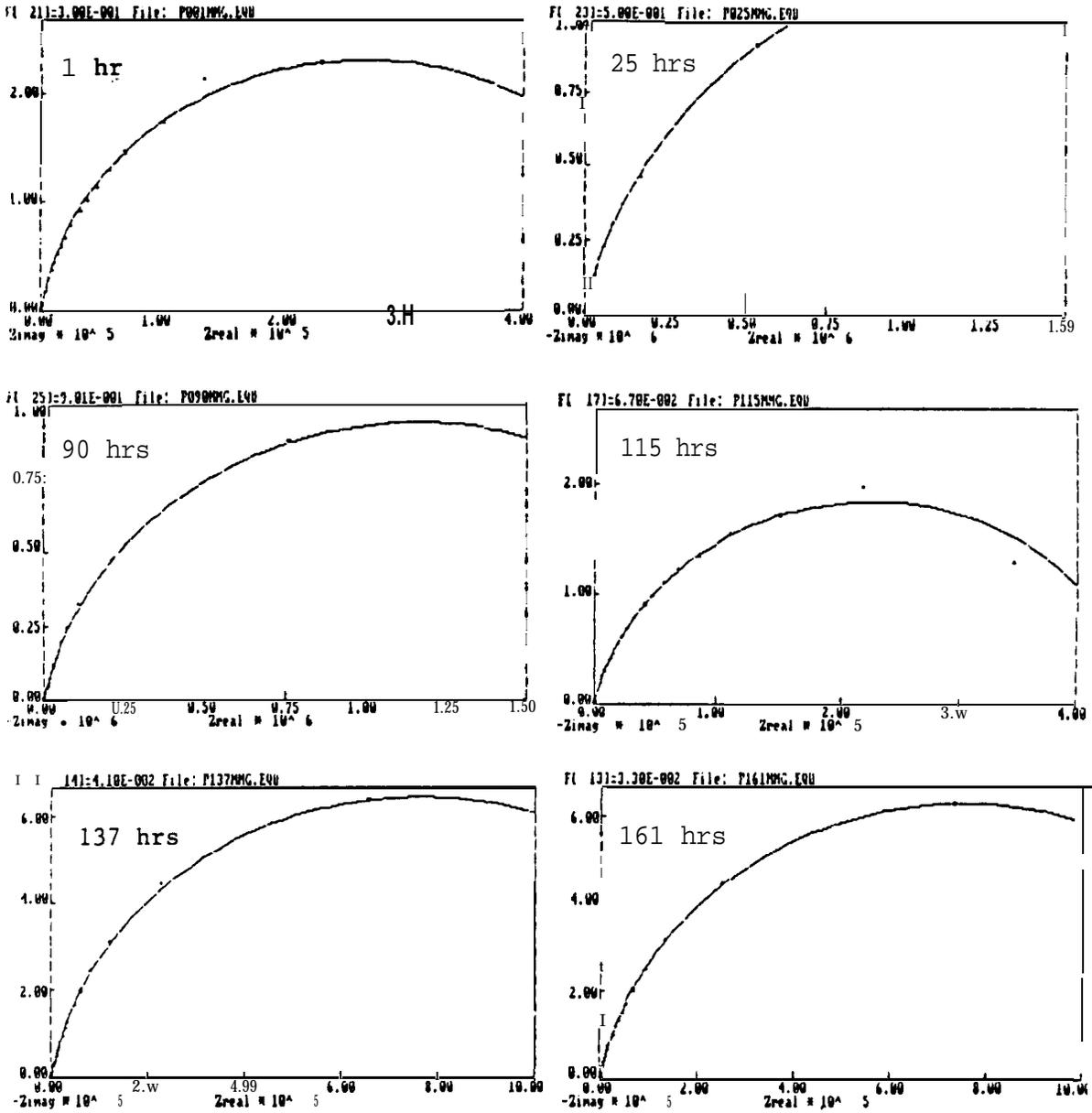
Figure B-16 Nyquist Plots for 7 Mo + N in 3.55% **NaCl-0.1N HCl** at Various Immersion Times
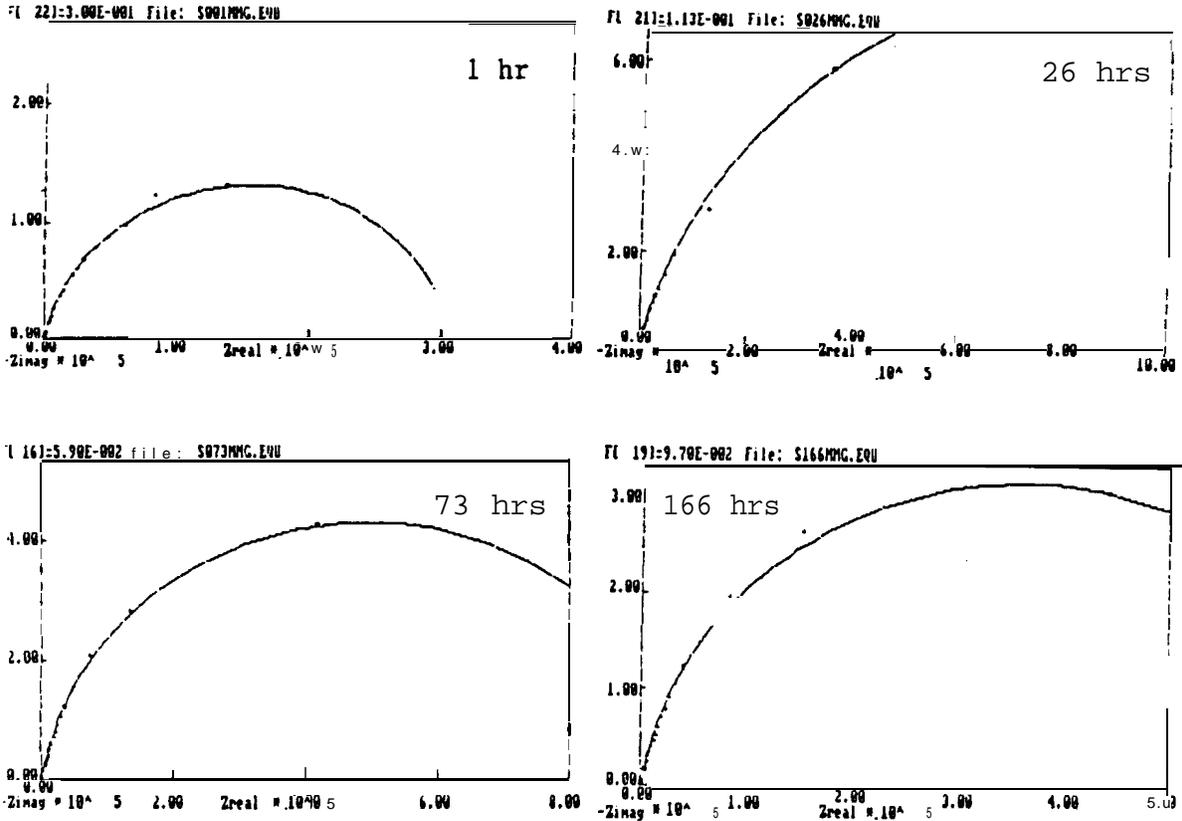
Figure B-17 Nyquist Plots for ES-2205 in 3.55% **NaCl-0.1N HCl** at Various
Immersion Times
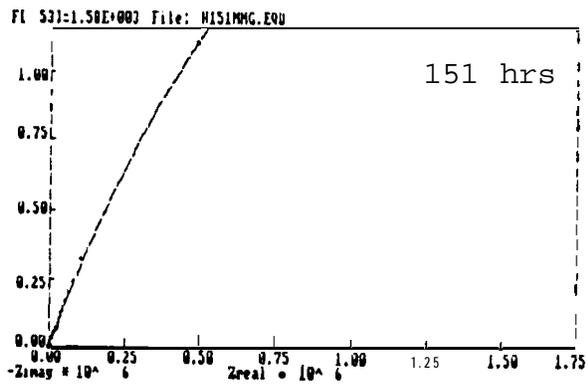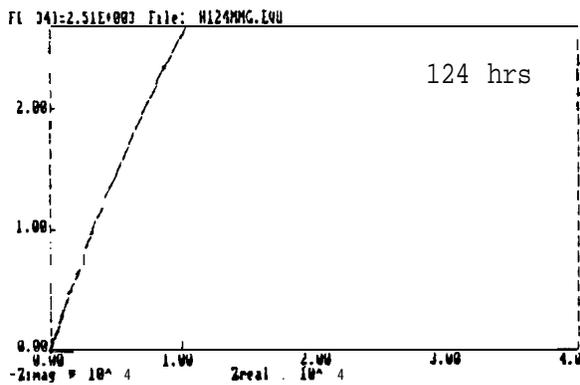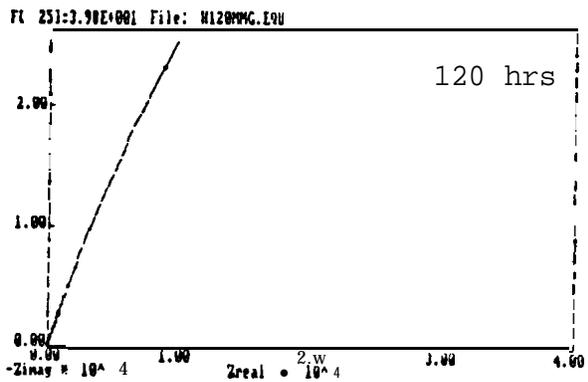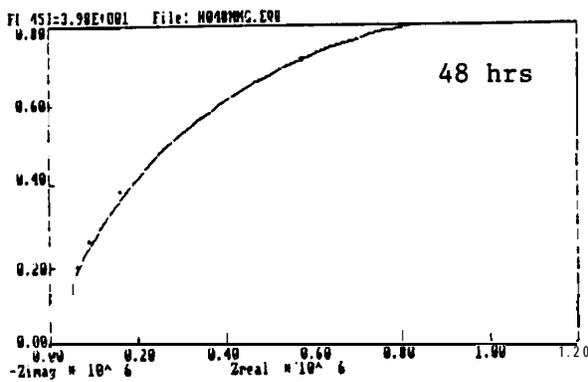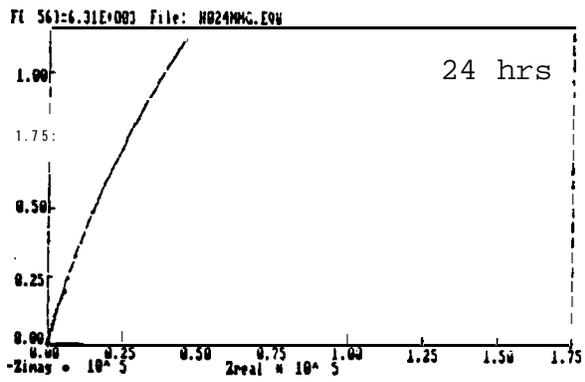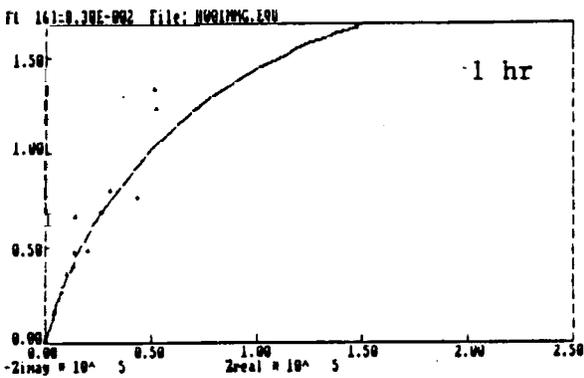
Figure B-18 Nyquist Plots for Ferralium 255 in 3.55% **NaCl-0.1N HCl** in Various Immersion Times

175 hrs

200 hrs

223 hrs

293 hrs

317 hrs

343 hrs

Figure B-18 **(Cont)**

FI 22]:6.31E+000 File: N367MMG.EQU

367 hrs

4.W:

2.00

0.00
0.00   2.00   4.W   6.00   8.00
-2imag * 10^ 4   2real * 10^ 4

FI 20]:1.00E-001 File: N551MMG.EQU

551 hrs

1.60

1.20

0.80

0.40

0.00
0.00   0.80   1.20   1.60   2.00   2.40
-2imag * 10^ 6   2real * 10^ 6

FI 17]:6.70E-002 File: H654MMG.EQU

654 hrs

1.50

1.00

0.50

0.00
0.00   0.50   1.00   1.50   2.00   2.50
-2imag * 10^ 6   2real * 10^ 6

Figure B-18   (Cont)