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Carderock Division Naval Surface Warfare Center

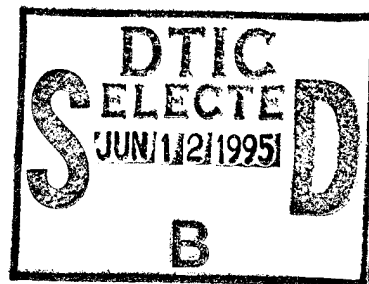
Bethesda, Md. 20084-5000

CARDIVNSWC-TR-61-94/44 April 1995

Survivability, Structures, and Materials Directorate
Technical Report

Atlas of Polarization Diagrams for Naval Materials in Seawater

by
Harvey P. Hack



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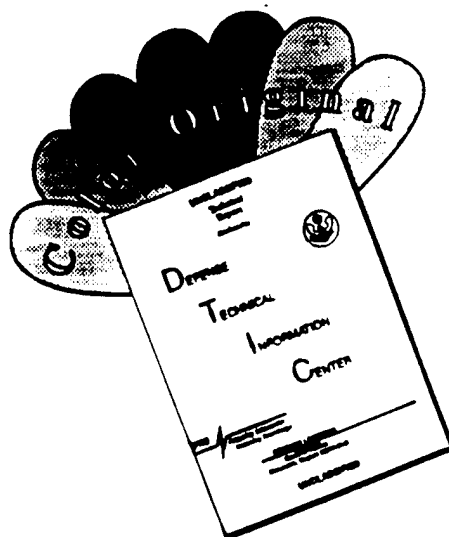
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CARDIVNSWC-TR-61-94/44 Atlas of Polarization Diagrams for Naval Materials in Seawater

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**Atlas of Polarization Diagrams for Naval Materials in
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ABSTRACT

Polarization curves were developed in seawater at low (quiescent) flow and at 2.4 m/s flow for nine structural alloys. Potentiostatically generated curves for up to 120 days are compared with potentiodynamically generated curves at four scan rates with freely corroding pre-exposures of 1 or 120 days. Smoothed curves successfully used in computer model predictions of cathodic protection current and potential distributions are also presented. These curves are compared with previously published data available for 800 days exposure and with cathodic protection current density design guidelines. Corrosion rate data as a function of potential after up to 120 days exposure are also presented.

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ADMINISTRATIVE INFORMATION

This project was funded under the Surface Ship Materials Technology Program sponsored by the Office of Naval Research (ONR) and managed by Mr. Ivan Caplan. The work was performed under program element 62761N, task area SF61541-591, work units 1-2803-162 and 1-2803-164. Work was conducted in the Marine Corrosion Branch under the direction of Mr. Robert J. Ferrara.

ACKNOWLEDGMENTS

I wish to particularly acknowledge the contributions of Dr. John R. Scully, who performed many of the experiments described herein. Also acknowledged is the staff at the LaQue Center for Corrosion Technology for help in the design and conduct of these experiments.

ABBREVIATIONS

ASTM	American Society for Testing and Materials
CARDEROCKDIV, NSWC	Carderock Division, Naval Surface Warfare Center
EG&G PAR	EG&G Princeton Applied Research
IR	Current $\times$ Resistance
rms	root mean square

INTRODUCTION

Predicting the amount of galvanic corrosion and the current demand for cathodic protection in seawater requires accurate polarization data for the materials involved. Computer models that predict the distribution of galvanic corrosion, stray current corrosion, and cathodic protection also require accurate polarization data.

Rates of galvanic corrosion are commonly predicted using tables of galvanic compatibility,¹ differences in corrosion potential between members of the galvanic couple where the corrosion potentials are obtained from a list or chart,² or by conducting relatively short-term exposures or electrochemical tests and extrapolating the results to apply to the item in service.^{3, 4} The first two methods are qualitative, providing only an indication of the tendency for corrosion damage in the galvanic couple. Unfortunately, polarization curves for most structural materials in seawater are exposure-time dependent and scan-rate dependent, making quantitative prediction from short-term exposures inaccurate.

Current densities for cathodic protection are frequently predicted from values found in standards.^{5, 6} These values, although based on long-term exposures, are not complete polarization curves and are, therefore, not adequate for use in computer modeling.

The need for a single source of polarization curves for commonly used materials in seawater and for a quantification of exposure time and scan rate effects led to this investigation. Although portions of these data have been presented elsewhere,⁷⁻¹² this document presents all of the data collected over the course of the investigation.

MATERIALS

Materials in this study were selected to be representative of the major classes of structural materials used by the Navy for seawater systems on ships. The following materials were studied:

- HY-80 steel (MIL-S-16216H*)
- 90-10 copper-nickel (C70600)
- 70-30 copper-nickel (C71500)
- Monel 400 (C92200)
- Nickel-aluminum bronze (C95800)
- Bronze composition M (C92200)
- Titanium grade 50 (R50400)
- Alloy 625 (N06625)
- Anode grade zinc (MIL-A-18001J**).

Nominal compositions of the alloys tested appear in the following table. Corrosion samples were prepared by rough cutting blanks from the supplied bars or plates, milling to

*"Steel Plate, Alloy, Structural, High Yield Strength (HY-80 and HY-100)."

**"Anodes, Sacrificial Zinc Alloy."

Table—Nominal composition of alloys tested.

Material	SAE/ ASTM UNS Number	Purchase Specification	Cu	Ni	Fe	C	Mn	P	S	Al	Zn	Ti	Sn	Pb	Mo	Si	Others
90-10 CuNi	C70600	MIL-C-15726E ^a	88.04	10.2	1.45	-	0.10	<0.02	<0.02	-	0.13	-	-	<0.2	-	-	-
Monel 400	N04400	QQ-N-281D ^b	31.43	65.55	1.63	0.11	1.08	-	0.006	0.020	-	-	-	-	-	0.17	-
Inconel 625	N06625	ASTM-B443 ^c	-	62.15	3.46	0.02	0.16	0.013	-	0.16	-	0.26	-	-	8.41	0.25	21.46 Cr 3.66 Cb & Ta
M- Bronze	C92200	MIL-B-16541 ^d	86.91	0.45	0.09	-	-	-	-	-	4.74	-	6.05	1.7	-	-	0.06
NiAl Bronze	C95800	MIL-B-21230A ^e	79.85	4.88	4.24	-	1.49	-	-	9.36	0.07	-	0.04	0.02	-	-	-
HY-80 Steel	-	MIL-S-16216H ^f	0.046	2.83	bal	0.15	0.23	0.012	0.020	-	-	0.001	-	-	0.47	0.27	<0.001 V 1.61 Cr
Tita- nium 50	R50400	MIL-T-79939	-	0.1	0.3	0.10	-	-	-	-	-	bal	-	-	-	-	0.250
70-30 CuNi	CA7150 0	-	68.02	30.34	0.60	<0.03	0.77	0.01	0.006	-	0.09	-	-	0.01	-	-	-
Anode Grade Zinc	-	MIL-STD-18001J	0.05 max	-	0.05 max	-	-	-	-	0.1 to 0.5	bal	-	-	0.06 max	-	0.125 max	0.025 Cd max

^aCopper-Nickel Alloy, Sheet Plate, Strip, Bar, Rod, and Wire."^bNickel-Copper Alloy Bar, Rod, Plate, Sheet, Strip, Wire, Forgings, and Structural and Special Shaped Sections" (QQ indicates a Federal specification).^cStandard Specification for Nickel-Chromium-Molybdenum-Columbium Alloy (UNS N06625) Plate, Sheet, and Strip."^dBronze, Valve Casting."^eBronze, Nickel Aluminum, and Manganese-Nickel Aluminum: Castings, Ship Propeller Application."^fSteel Plate, Alloy, Structural, High Yield Strength (HY-80 and HY-100)."^gTitanium, Sheet, Strip and Plate (Unalloyed)."

approximate dimensions, and grinding to final dimensions—yielding a 32-rms (approximately 120-grit) finish on all surfaces.

APPARATUS AND PROCEDURE

QUIESCENT FLOW, POTENTIOSTATIC TESTS

For the short-term exposures (5 min and 1 day), specimens were 12.7 mm square by 6.2 mm thick. Exposures were performed sequentially in beakers of fully oxygenated natural seawater heated to a constant 30 °C. For the long-term exposures, specimens were 25.4 mm square by 6.2 mm thick. Three specimens of identical material were exposed at the same potential for different lengths of time connected to the same potentiostat. In this way, all 30-, 60-, and 120-day exposures were conducted simultaneously. A series of individual exposure vessels was used to avoid ground loops or stray current effects (see Figure 1). One hundred eight 4-L vessels were fitted into two wooden boxes lined with thermal insulation. Heated, filtered natural seawater was drip-fed into each container to maintain oxygen levels in the bulk solution at saturation and temperatures at 30 °C. Quiescent flow was maintained via the low refreshment rate. Corrosion coupons were suspended in the exposure vessels by means of a threaded rod screwed into a hole tapped into the specimen edge. This rod was also used for electrical contact to the specimen (see Figure 2). Water was excluded from the electrical contact/mounting rod by means of a glass tube and Teflon gasket. Platinum-coated counter electrodes were placed adjacent to the specimen faces. Ag/AgCl reference electrodes were placed in the plane of the corrosion coupons, directly below the specimens. Some vessels contained three identical, freely corroding specimens of each material for sequential removal at 30, 60, and 120 days. These vessels also contained reference electrodes, but no counter electrodes.

A bank of 70 potentiostats constructed for this experiment was located in an adjacent temperature-controlled room and was connected to the test cells through insulated electrical leads. Potential and current readings were taken by a computerized data acquisition system. For the potentiostats employed, a plus or minus 5-mV variation in set potential was maintained. A thermal instability coefficient of about 1 mV/°C air temperature and IR (Current $\times$ Resistance) drop through the cabling was identified as the source of these variations. Electrical leads from the specimen groups of three were connected in series to 1-ohm resistors for current measurement as potential drop.

Fifteen to seventeen potentials were chosen for each material in potentiostatic polarization experiments. Exposures were conducted in several runs, each run consisting of simultaneous testing of all materials over the 120-day period. Currents, potentials, and temperatures were recorded once a minute for the first day of exposure, every 10 minutes for the first week, and three times daily thereafter.

ASTM-recommended procedures for cleaning, drying, and massing were followed for mass loss determinations.¹³ Special care was taken to ensure that the threaded hole was dry prior to massing. Massing was performed to the nearest 0.1 mg.

QUIESCENT FLOW, POTENTIODYNAMIC TESTS

Exposure vessels and coupon mounting were the same as the potentiostatic exposures. Specimens were 12.7 mm square by 6.2 mm thick. Platinum-coated counter

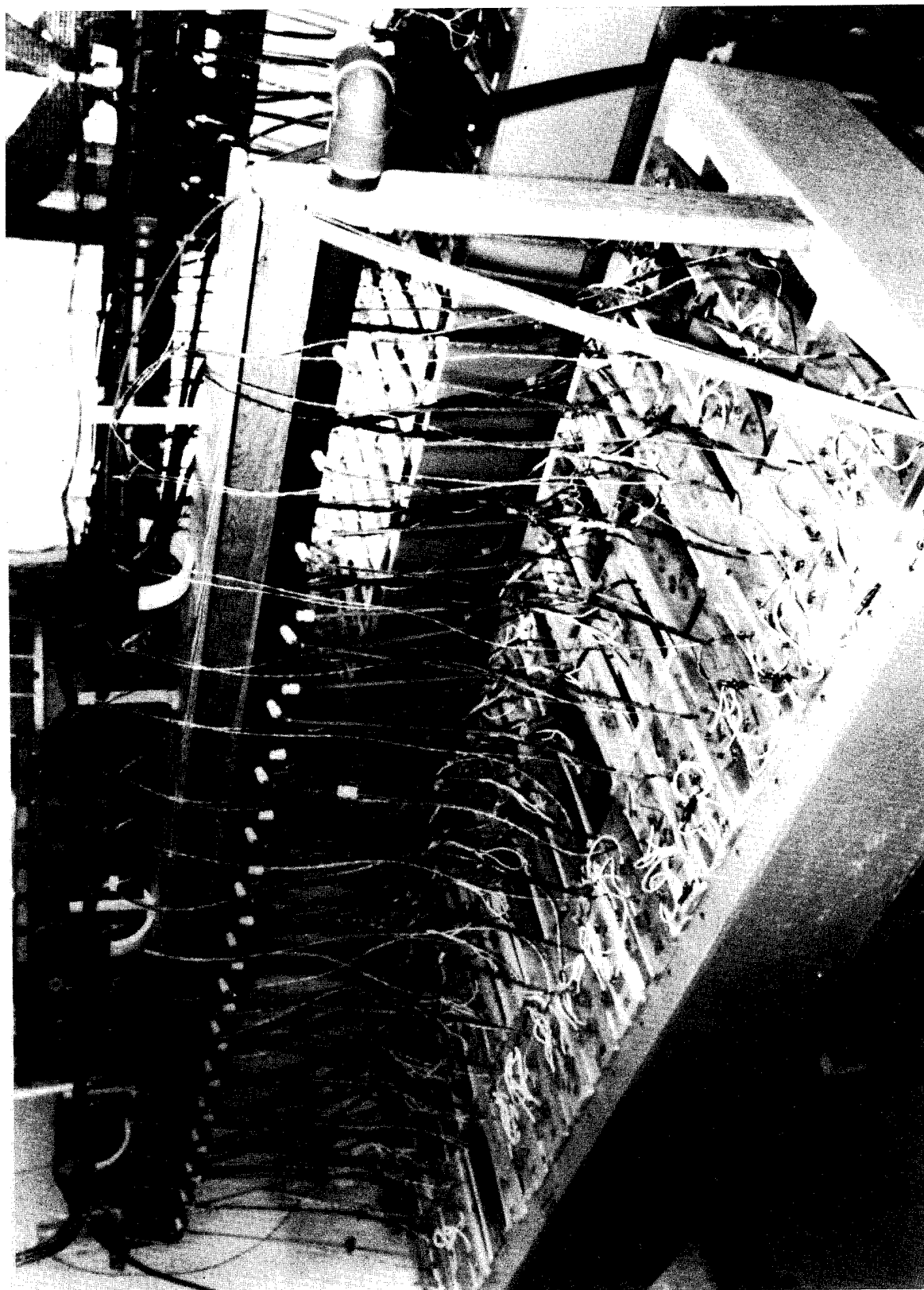


Figure 1. Exposure vessels for quiescent tests.

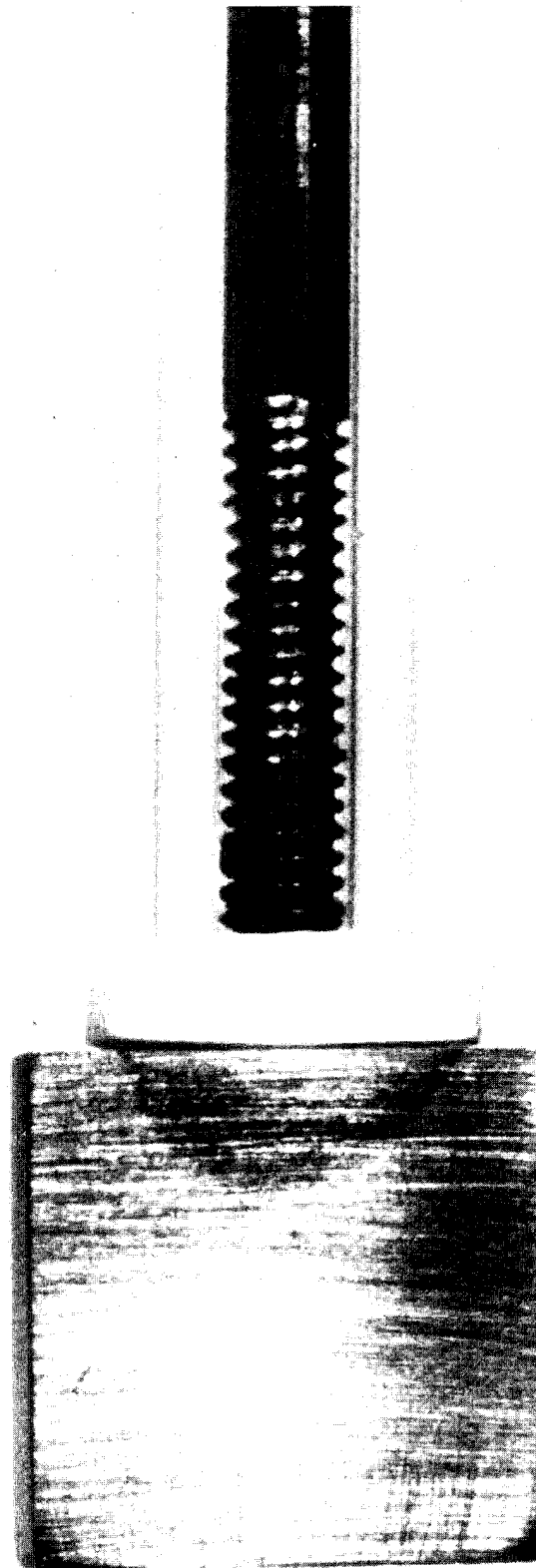


Figure 2. Specimen mounting for quiescent tests.

electrodes and a saturated calomel reference electrode with Luggin probe were used. Instrumentation consisted of an EG&G PAR (Princeton Applied Research) model 173 potentiostat with a log current converter and a model 175 programmer. An Apple computer was used for analog-to-digital conversions and for data storage and retrieval.

Specimens were studied under two conditions: 1-hr or 120-day pre-exposure at open circuit potential in natural seawater. In general, test procedures followed ASTM Standard G5.¹⁴ Separate specimens were independently polarized anodically and cathodically starting at the corrosion potential. Duplicate specimens were tested at most scan rates. The following four scan rates were used:

1. 0.5 V/hr (0.14 mV/s)
2. 5 V/hr (1.4 mV/s)
3. 50 V/hr (14 mV/s)
4. 100 V/hr (28 mV/s).

FLOWING TESTS

The test cell design for flowing seawater exposures is shown in Figures 3 to 5. The direction of flow was parallel to the specimen length through a rectangular channel 2.54 cm high by 0.635 cm wide. Eight 1-cm square working electrodes and eight platinum counter electrodes were mounted flush against the interior wall of the rectangular cross section facing each other across opposite walls (see Figure 3). An insulated electrical lead was attached to the dry back face of both counter and working electrodes. The same arrangement was used for potentiostatic and potentiodynamic testing. Reference electrode ports were drilled through the top interior wall of all parallel plate cell positions (see Figure 3). Hydrostatic pressure forced seawater through a vinyl tube containing microelectrodes. A 0.42-cm diameter Ag/AgCl microreference electrode was positioned above the reference electrode port. A valve was positioned between the port and the reference electrode to allow air bubble removal.

Figure 4 shows a single flow-through cell test loop. Heated natural seawater was pumped from a 70-L (17-gal) holding tank through the test cell and back to the tank. Filtered (8 μ m) natural seawater for refreshment was fed from a common 200-L (50-gal) preheated makeup tank at a rate of 5 L/min to each holding tank in each loop, where it was heated to 30 °C plus or minus 3 °C, and the excess allowed to overflow. The flow velocity in the test cells was 2.4 m/s. Four flow-through cells were used (see Figure 5). Concern for electrodeposition on a specimen "downstream" of metal lost from a specimen "upstream" led to careful consideration of specimen placement within each cell and between the four test loops. Aluminum gutters were also placed in each holding tank. Flow in this test setup was determined to be turbulent by Reynolds number analysis. Wall shear stress was calculated to be 17.4 to 18.7 N/m².

Six to nine potentials were chosen for each material in the potentiostatic tests. Only single 120-day potentiostatic specimens were exposed. Anodically and cathodically polarized potentiodynamic specimens, pre-exposed for 120 days, were exposed in separate cells. One-hour, pre-exposed potentiodynamic specimens were exposed in individual flow-through cells. Potentiodynamic scans were conducted at two scan rates: 0.5 and 5 V/hr (0.14 and 1.4 mV/s, respectively).

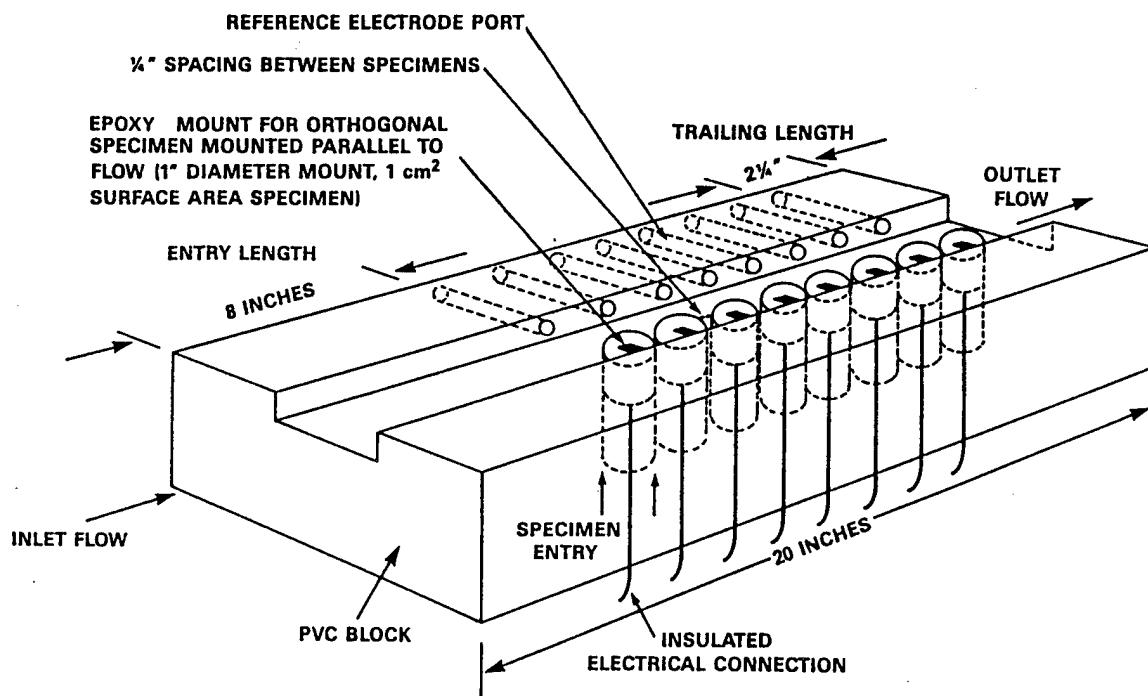


Figure 3. Flowing test cell design.

DATA ANALYSIS TECHNIQUES

Potential variability was plus or minus 10 mV. Where the actual potential deviated significantly from the set potential, the actual potential value was used at the time period being analyzed. Current resolution was better than 1 percent of the reported values for 5-min exposures, better than 1 $\mu\text{A}/\text{cm}^2$ for 1-day exposures, and better than 0.1 to 0.6 $\mu\text{A}/\text{cm}^2$ for longer exposures, depending on the number of specimens in test. In some cases, data averaging or curve fitting was used to reduce the quantity of data handled. To obtain current densities, the current vs. time plots were hand-fitted with smooth curves and values picked off at the appropriate exposure times, normalizing for the number of specimens remaining in test at that time. Where duplicate specimen data were available, a composite curve was constructed. In some cases, due to rapid fluctuations, current was numerically integrated over the exposure period of interest to get an average value. Depth of attack measurements made on some specimens after the test duration were linearly ex-

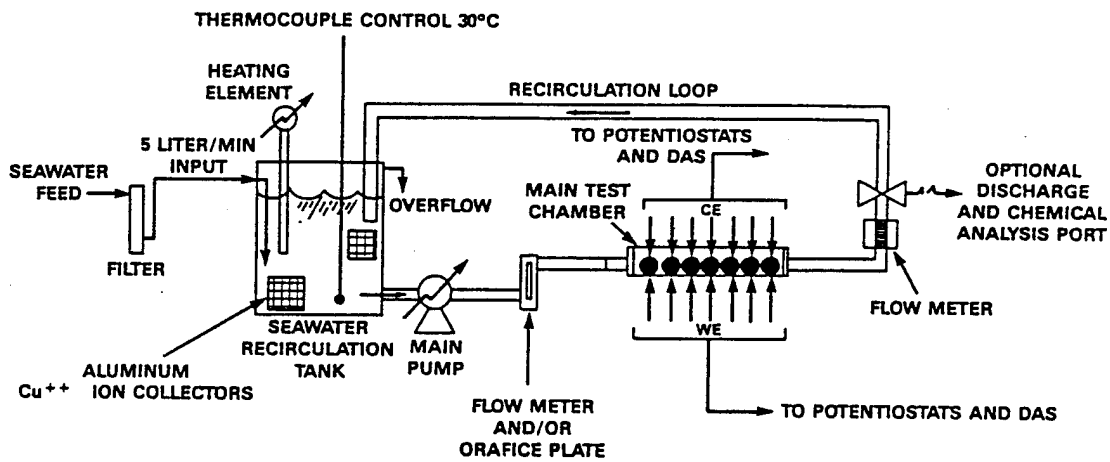


Figure 4. One flowing cell test loop.

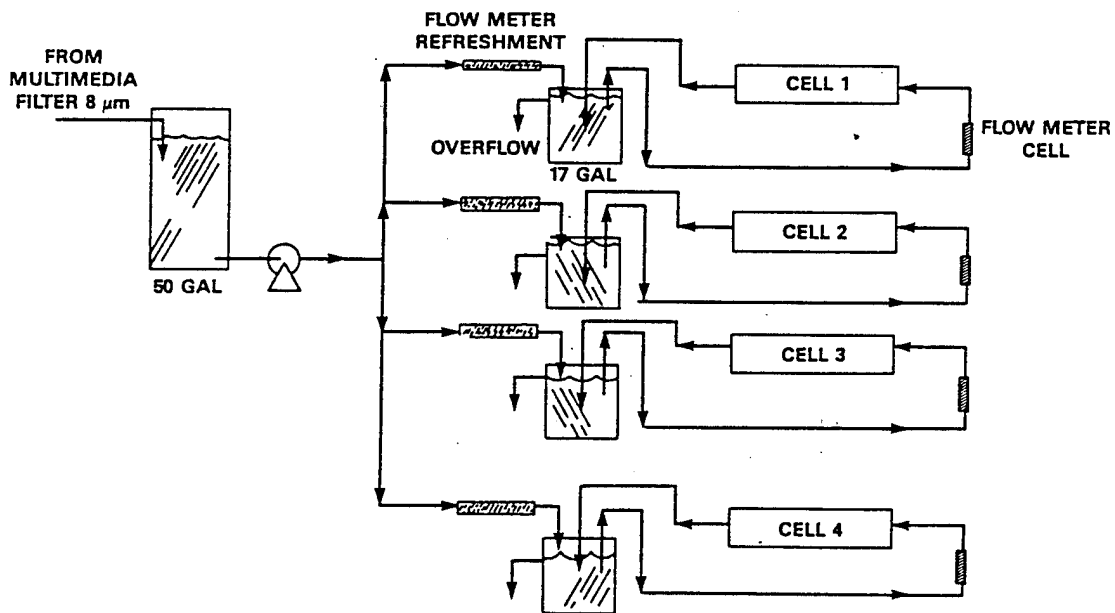


Figure 5. Four flowing cell test loops.

trapolated to estimate attack depths after 1 yr. Corrosion rates reported are based on metal loss and surface area and, therefore, do not reflect localization of corrosion.

RESULTS AND DISCUSSION

The results of this investigation are contained in the polarization curves in Appendixes A through I. Detailed descriptions of the behavior of each material, flow, type of polarization, exposure duration, scan rate, etc., would be too lengthy to state here. Some general results are that scan rate and pre-exposure time have a significant effect on potentiodynamic polarization behavior. Exposure time has a large effect on potentiostatic polarization behavior. The polarization current usually levels out after 30 days under quiescent conditions, except at the most negative potentials where the assumed buildup of calcareous deposits allows for continued current decay, even up to 120 days. Under quiescent conditions, the cathodic behavior of all materials is roughly the same, with a constant current density of about $10 \mu\text{A}/\text{cm}^2$ at potentials well below the corrosion potential and above approximately -900 mV . Flowing potentiostatic data have too much scatter to make many conclusions other than that current densities are typically significantly higher than under quiescent conditions. None of the potentiodynamic curves, even those after a 120-day pre-exposure, resemble the long-term potentiostatic curves sufficiently to be used for accurate prediction of galvanic or cathodic protection behavior.

Appendix J contains curves showing corrosion rate from mass loss, normalized to 1 yr, of each material except Ti-50 and Alloy 625, which had no measurable mass loss under quiescent flow conditions as a function of exposure time and potential.

Appendix K contains the smoothed 120-day potentiostatic polarization curves used as boundary conditions for a boundary element model of a 16-m-long, cathodically protected barge in seawater.¹⁵ In that paper, the potential and current distributions predicted by the boundary element model accurately matched those measured on a real barge. This means that the curves used in the model were representative of the long-term performance of the materials on the barge.

Another study was performed on many of the same materials as this study by Foster and Moores at the Defence Research Establishment Pacific in Canada.¹⁶ Their study was conducted in water at 9°C for time periods up to 2,000 days exposure, although only data up to 800 days were reported. Potentials used were as low as $-1,100 \text{ mV}$ vs. Ag/AgCl . Only average current densities over the entire test were reported. These are replotted in a format consistent with the data generated in this study in Appendix L. Foster and Moores' data are very similar to the long-term potentiostatic data generated here, but their $-1,100\text{-mV}$ specimens usually had significantly higher current densities than the $-1,100\text{-mV}$ specimens from the current study reported in Appendixes A through I.

Comparison of HY-80 steel data from these studies to actual cathodic protection design current density and potential ranges for steel is instructive. Design data from NACE International,⁵ technical guidance from the Naval Sea Systems Command,⁶ and several Norwegian and United Kingdom design guidelines, as reported by Wyatt,¹⁷ are shown in Appendix M. While all design guidelines recommend protection to -800 mV vs. Ag/AgCl , the design current densities used range over more than an order of magnitude, centered roughly around the $10\text{-}\mu\text{A}/\text{cm}^2$ value from the steel data in Appendix A. The data in Appendix A are, therefore, consistent with design practice.

CONCLUSIONS

None of the potentiodynamic curves resembles the long-term potentiostatic curves sufficiently to be used for accurate prediction of galvanic or cathodic protection behavior. Adequate prediction requires the use of long-term, potentiostatically derived polarization curves. Data are presented that have been successfully used to predict cathodic protection current and potential distribution on a large structure. Data from this study are in agreement with data from other investigators and with cathodic protection current density design guidelines from several countries.

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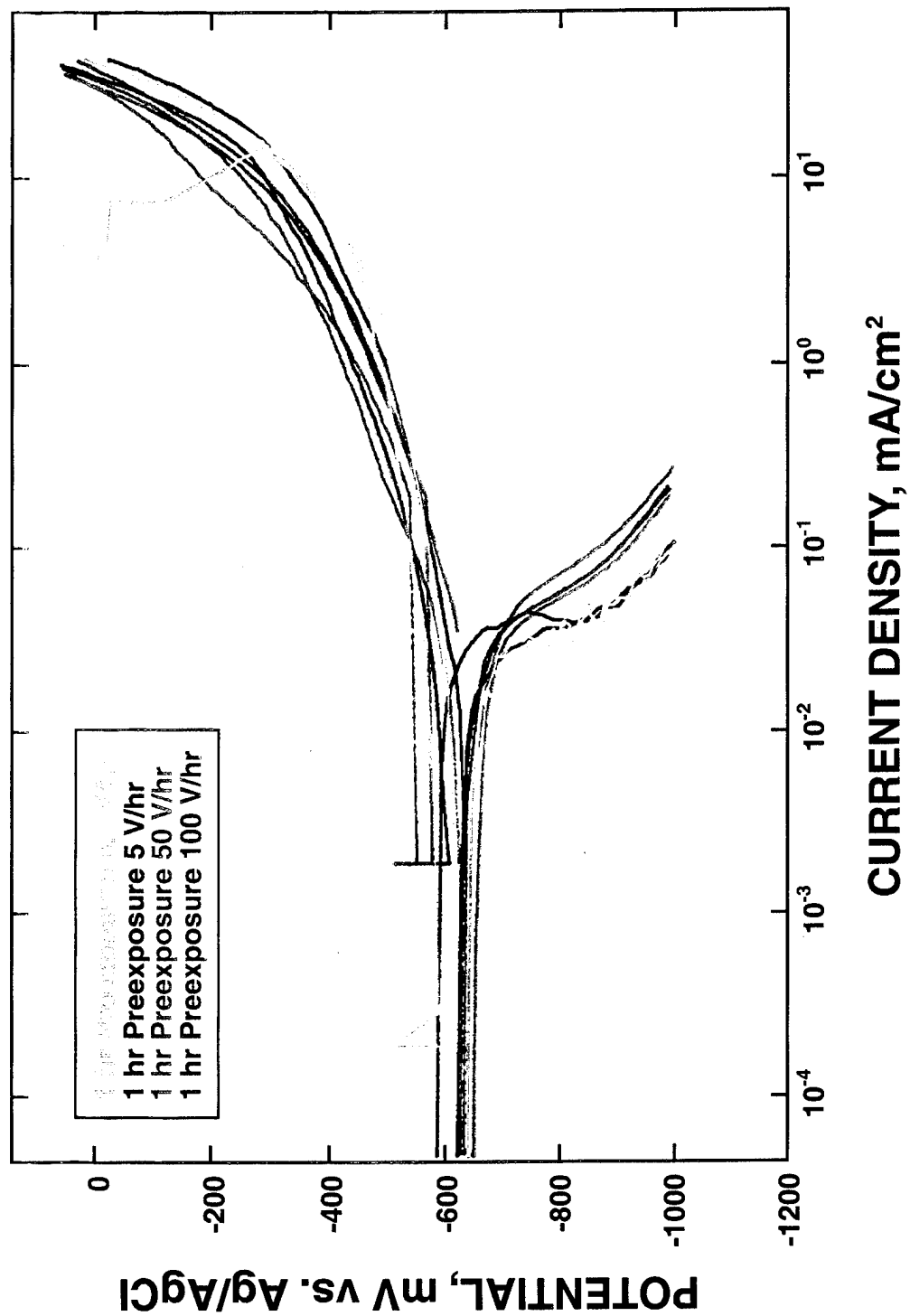
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APPENDIX A
POLARIZATION CURVES FROM THIS STUDY FOR HY-80 STEEL

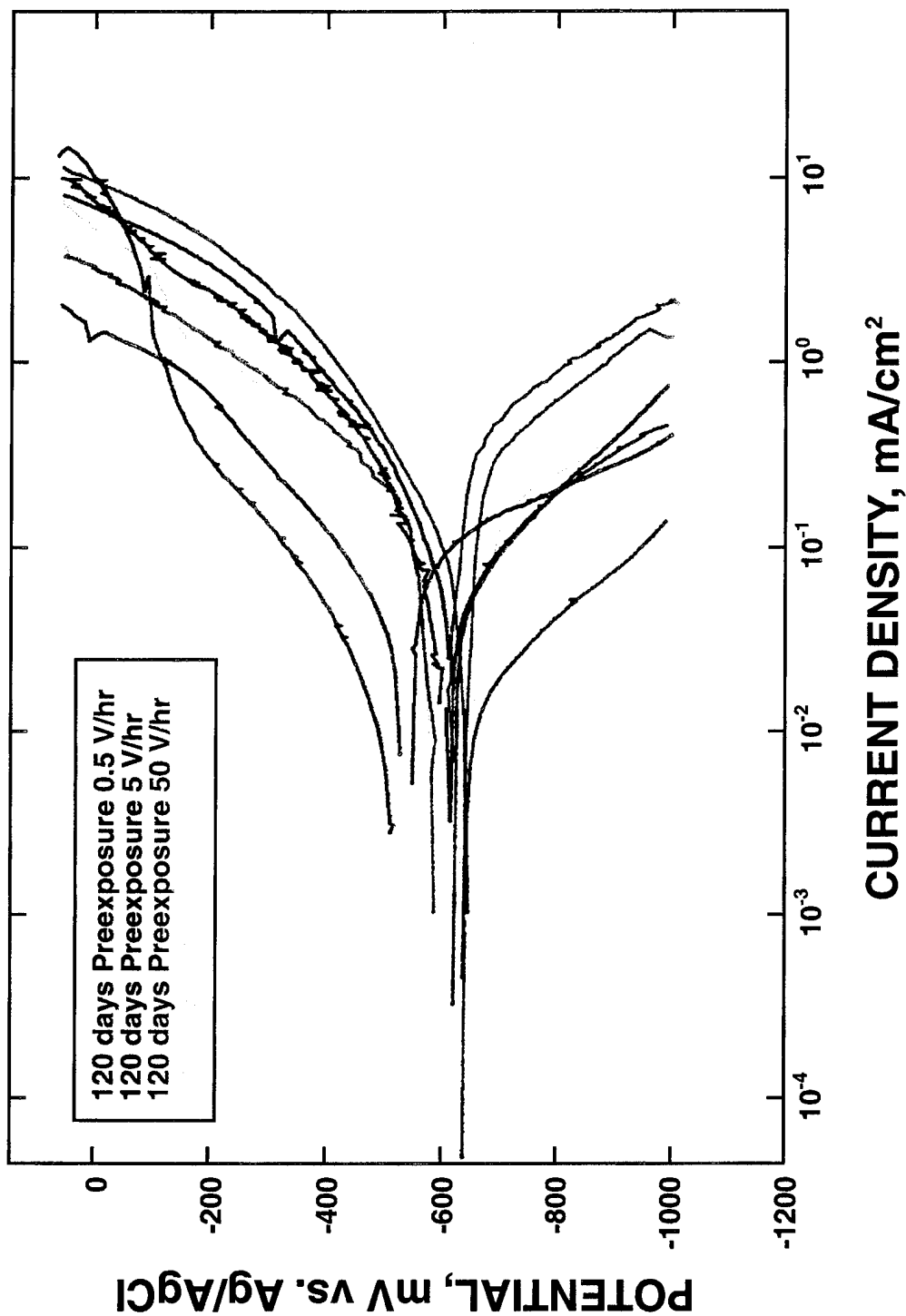
(Potentiodynamic)

HY - 80 STEEL Quiescent Flow



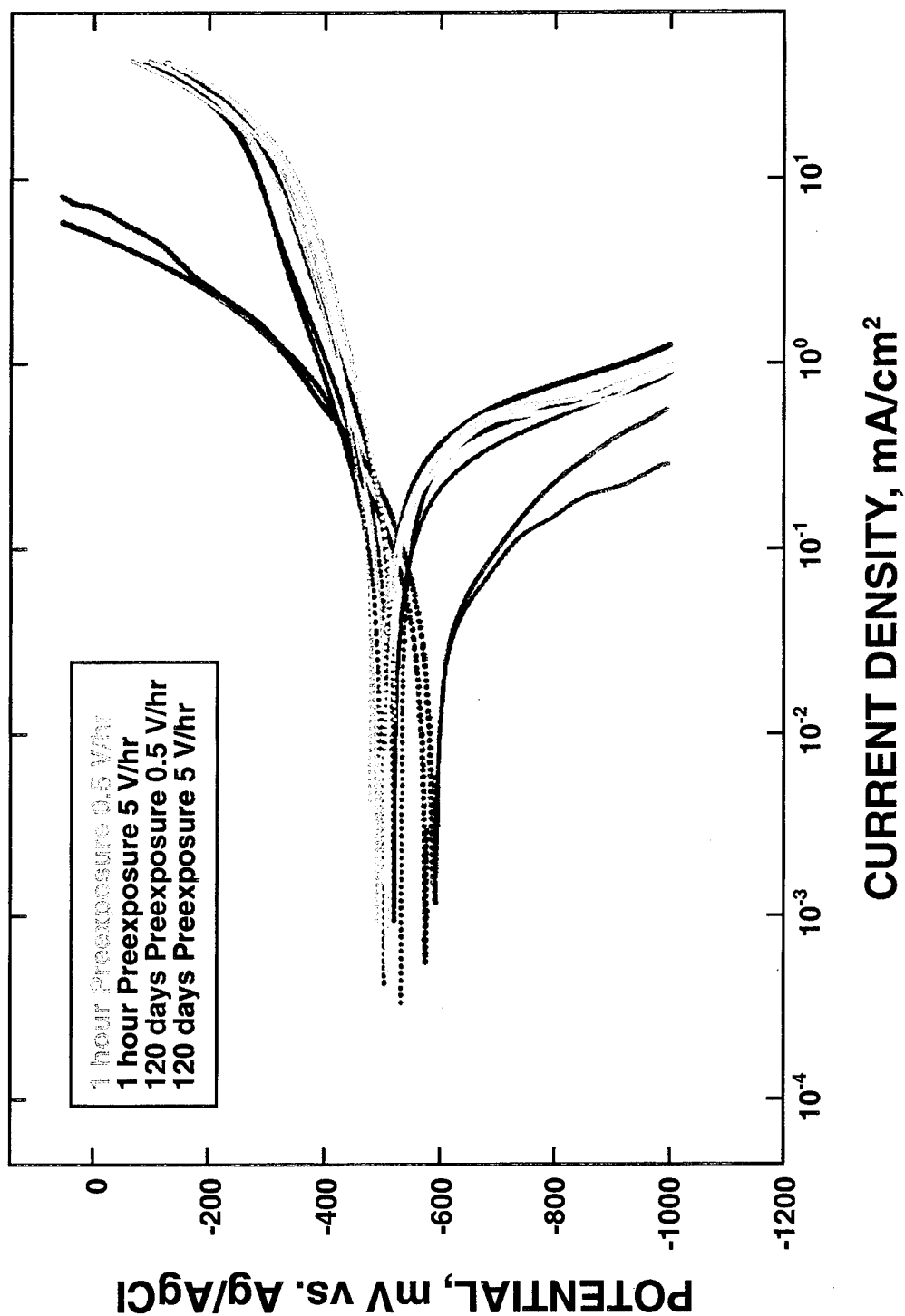
(Potentiodynamic)

HY - 80 STEEL Quiescent Flow



(Potentiodynamic)

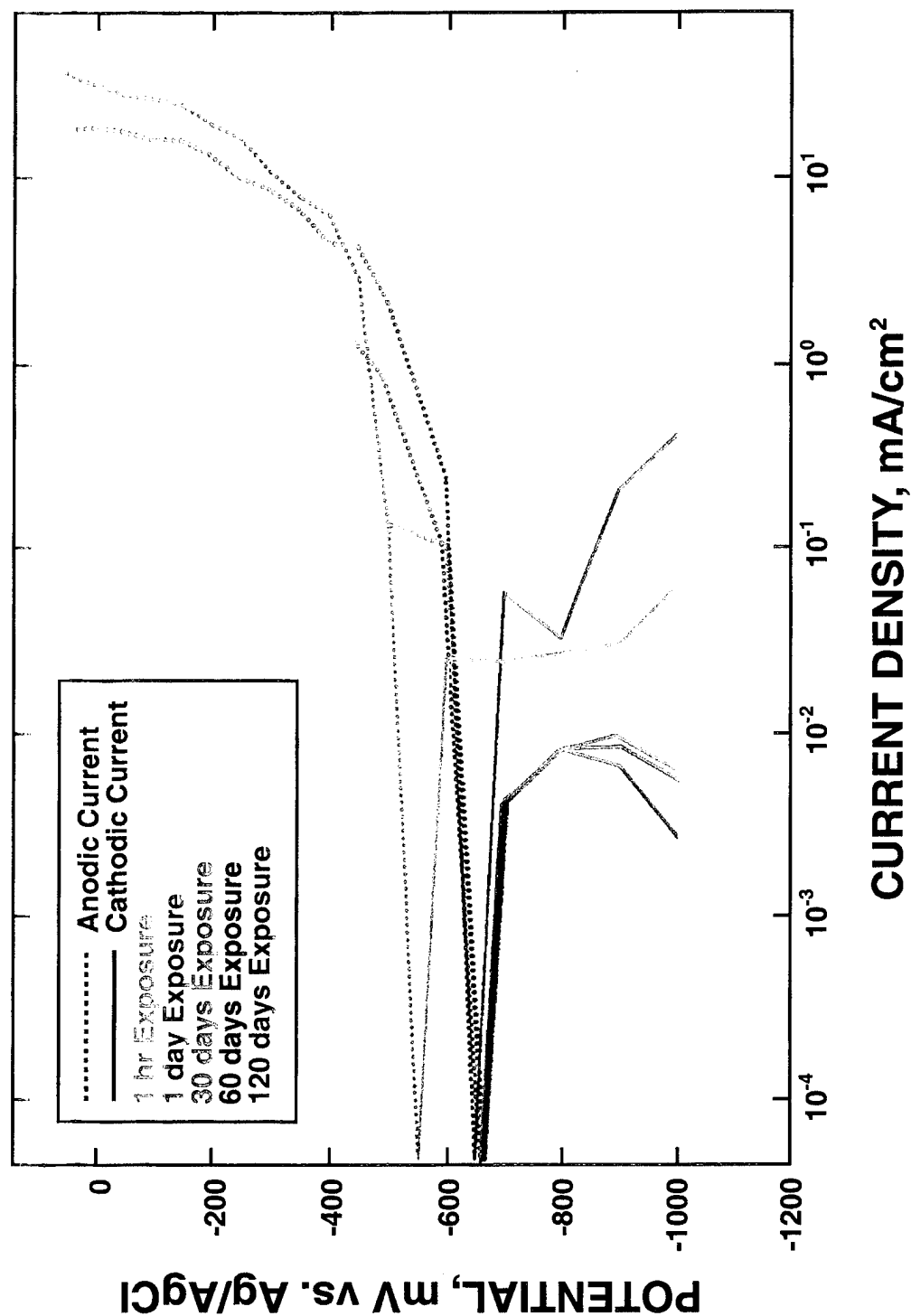
HY - 80 STEEL Flowing at 8.0 ft/s



(Potentiostatic)

HY - 80 STEEL

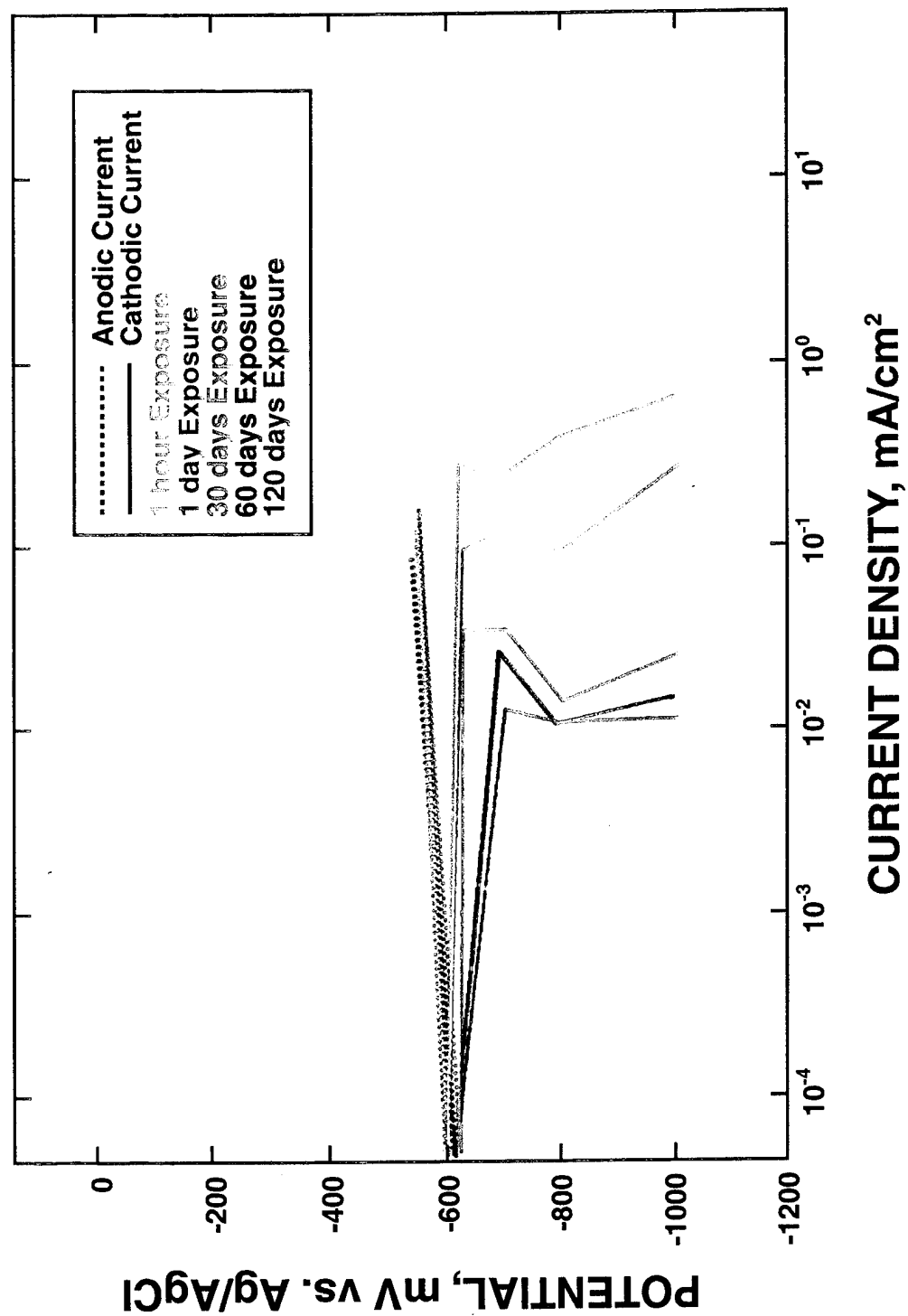
Quiescent Flow



(Potentiostatic)

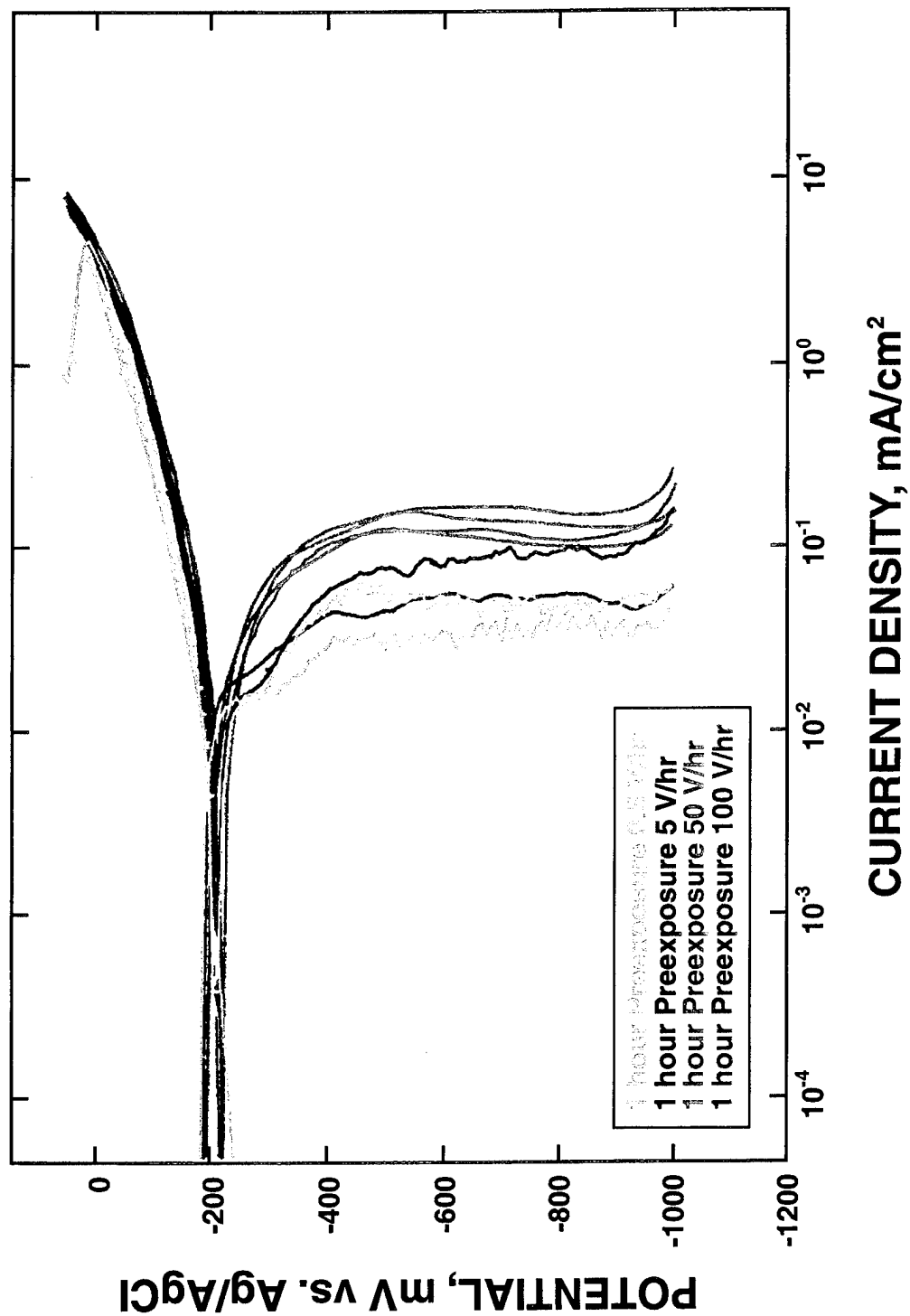
HY - 80 STEEL

Flowing at 8.0 ft/s



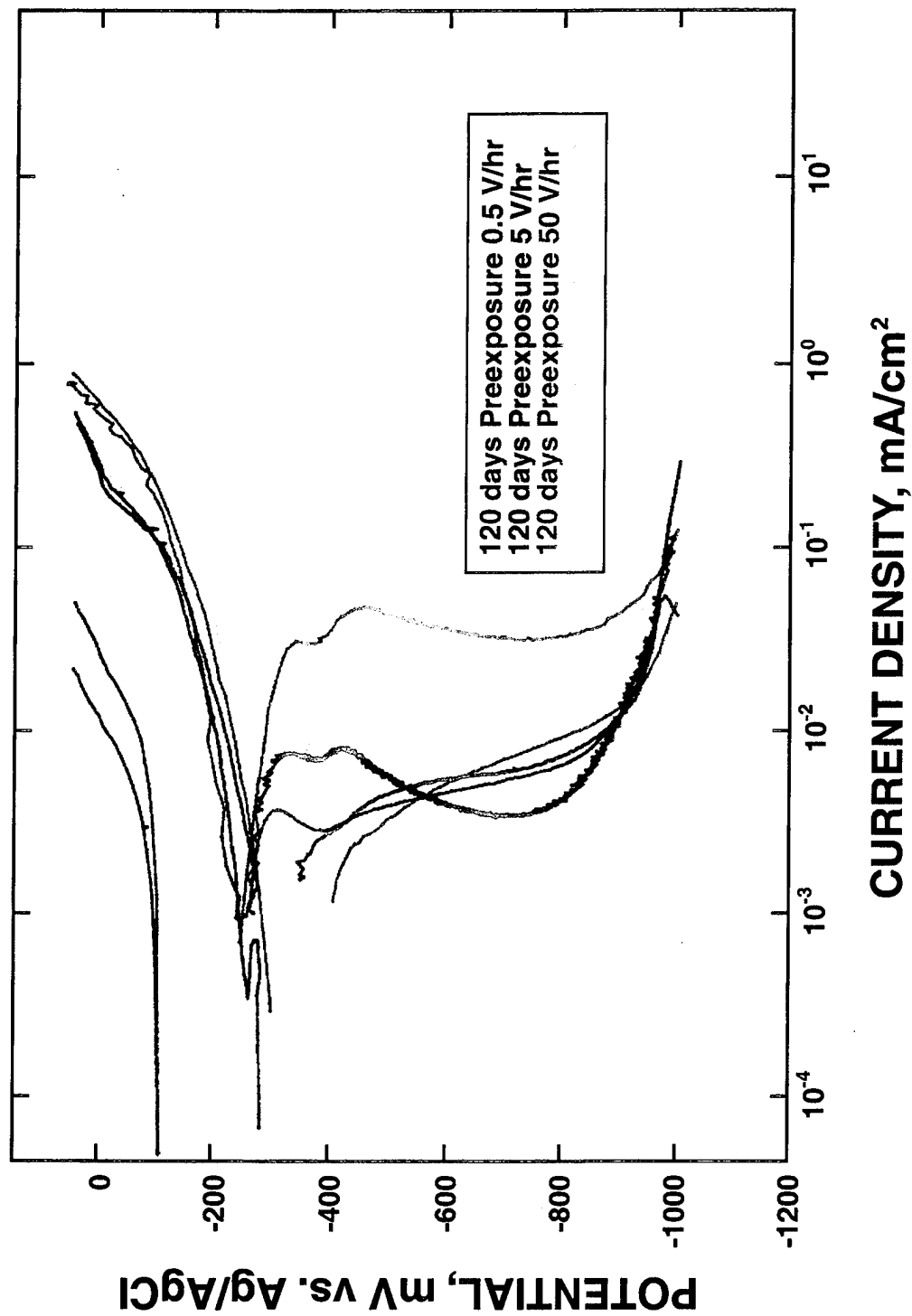
APPENDIX B
POLARIZATION CURVES FROM THIS STUDY FOR 90-10 COPPER-NICKEL

90 - 10 COPPER - NICKEL (Potentiodynamic) Quiescent Flow



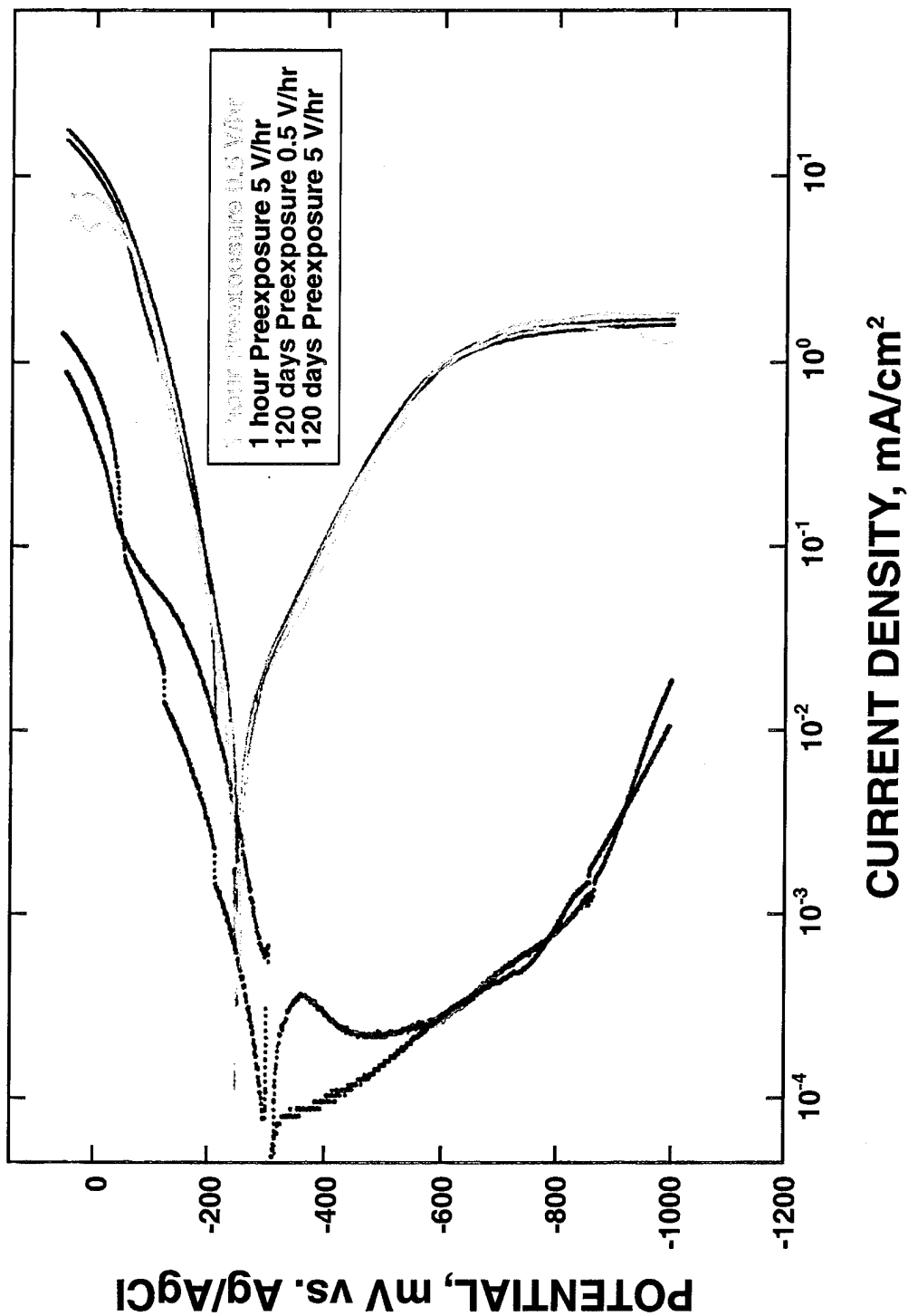
(Potentiodynamic)

90 - 10 COPPER - NICKEL Quiescent Flow



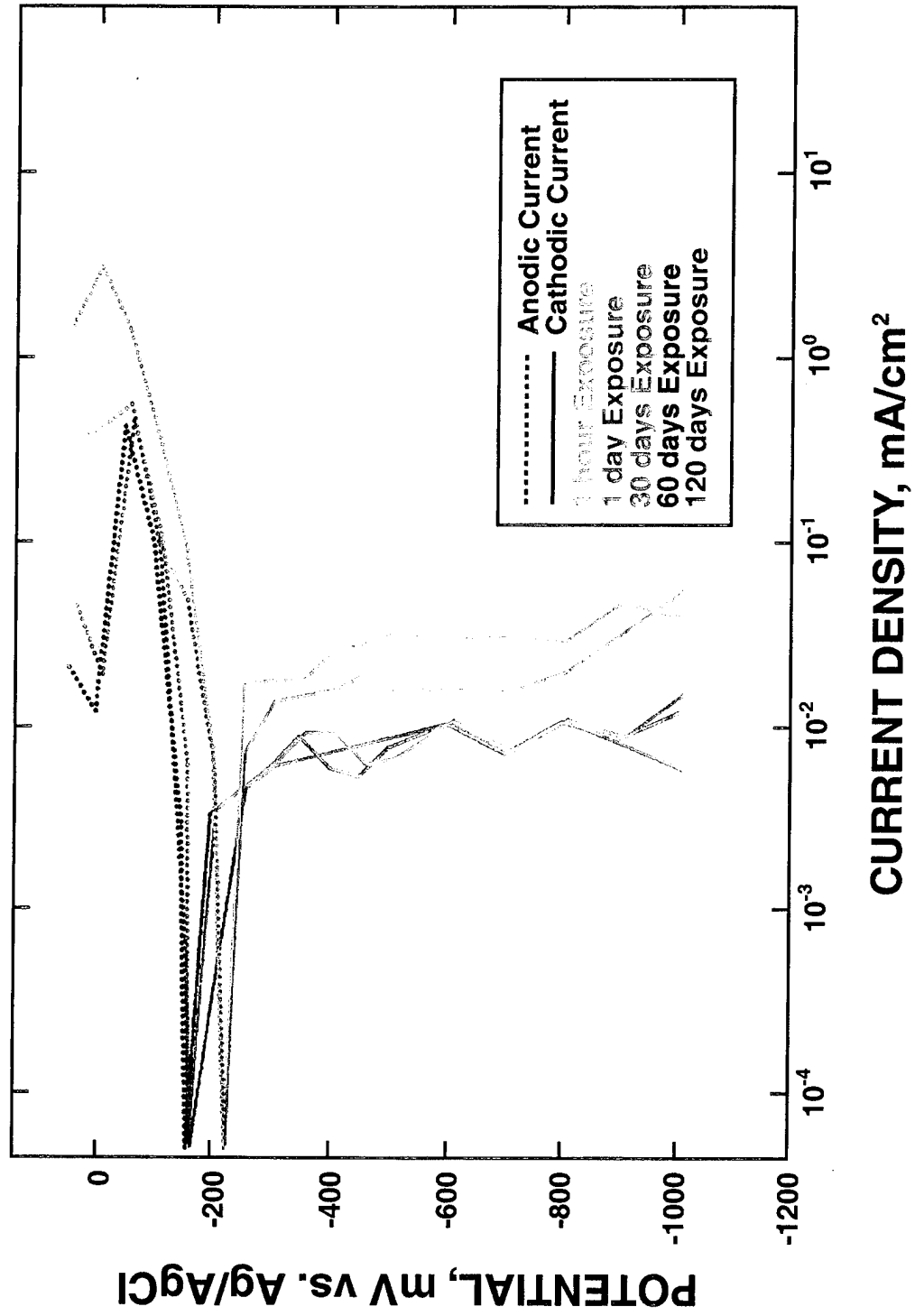
(Potentiodynamic)

90 - 10 COPPER - NICKEL Flowing at 8.0 ft/s



(Potentiostatic)

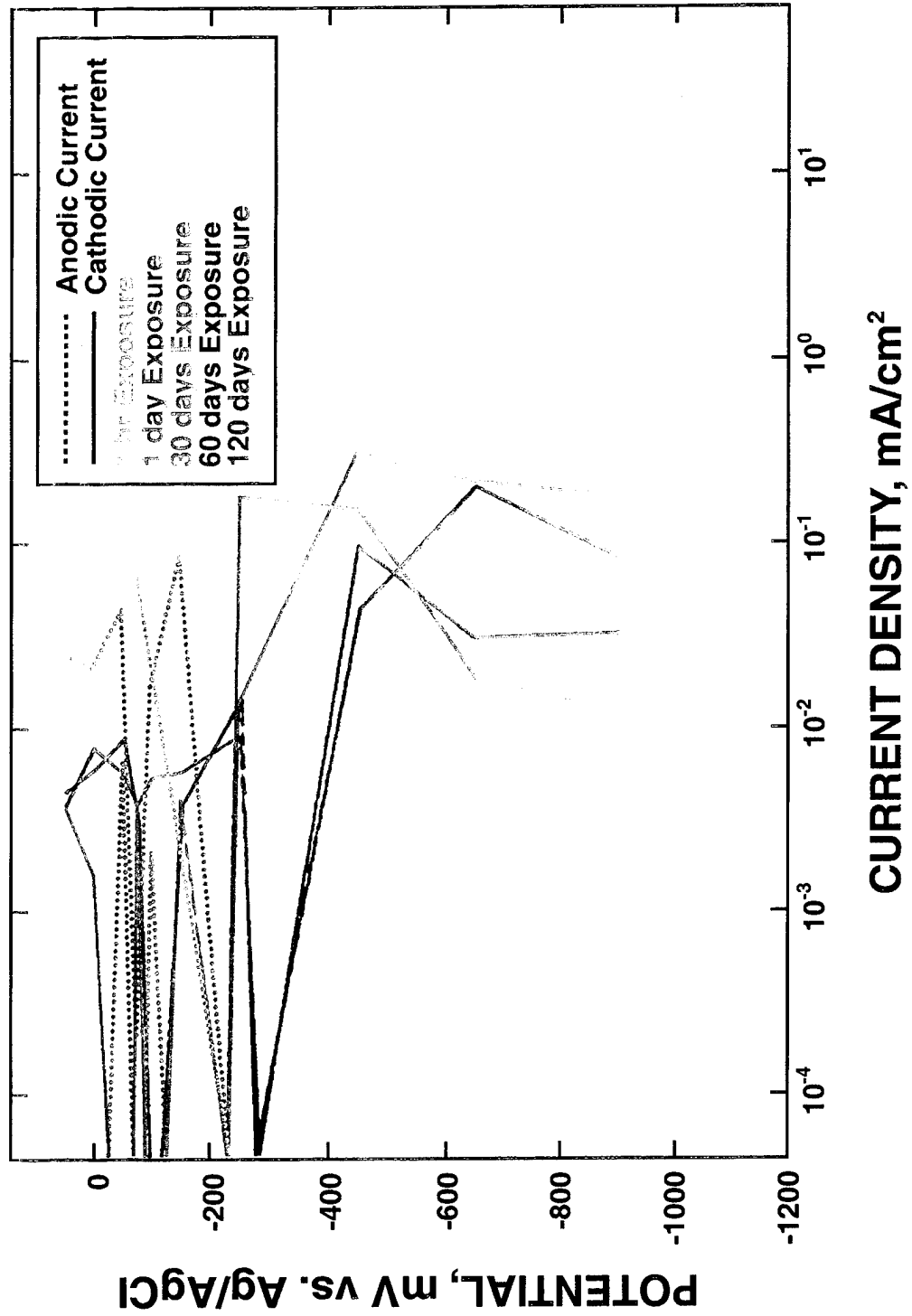
90 - 10 COPPER - NICKEL Quiescent Flow



(Potentiostatic)

90 - 10 COPPER - NICKEL

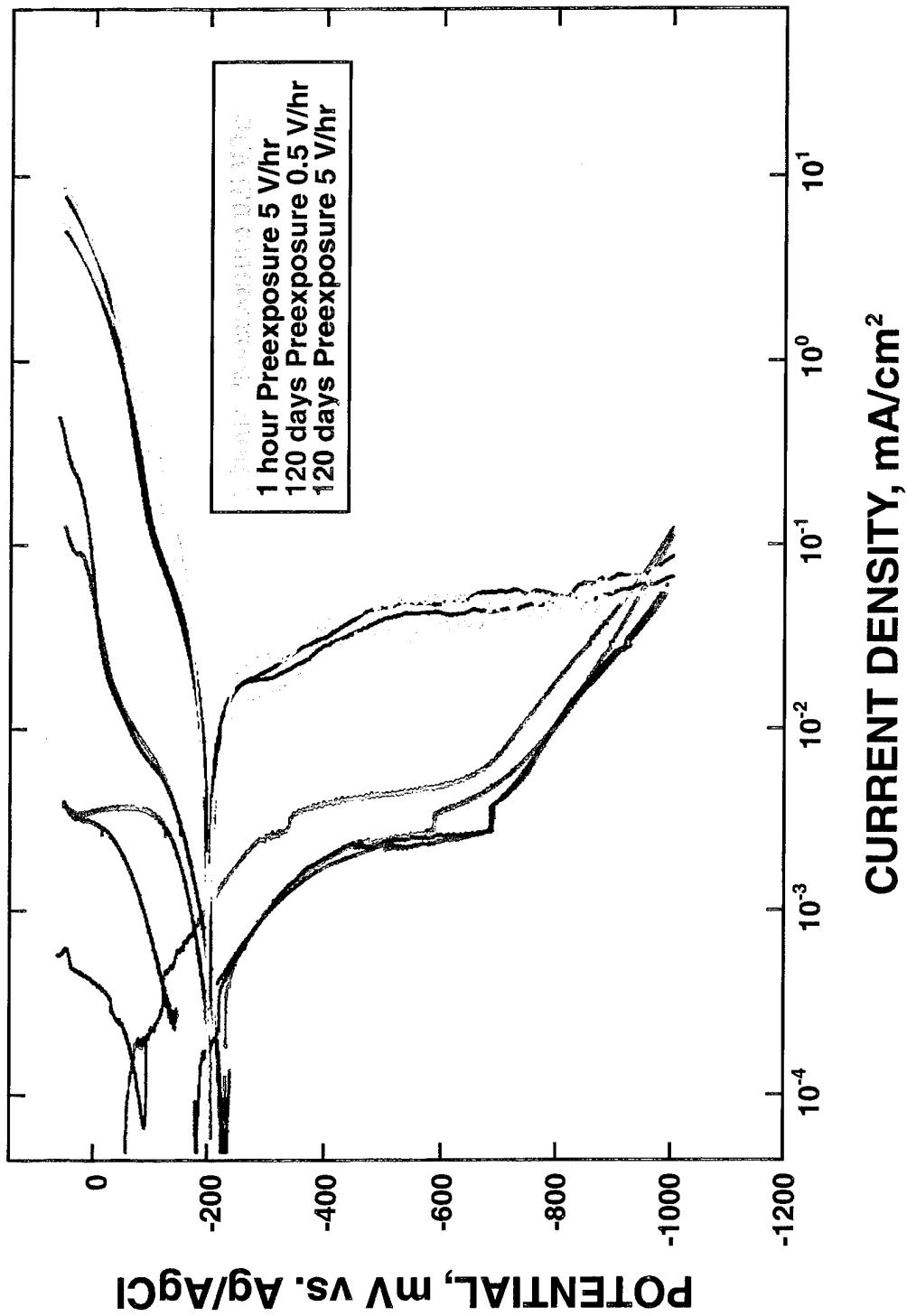
Flowing at 8.0 ft/s



APPENDIX C
POLARIZATION CURVES FROM THIS STUDY FOR 70-30 COPPER-NICKEL

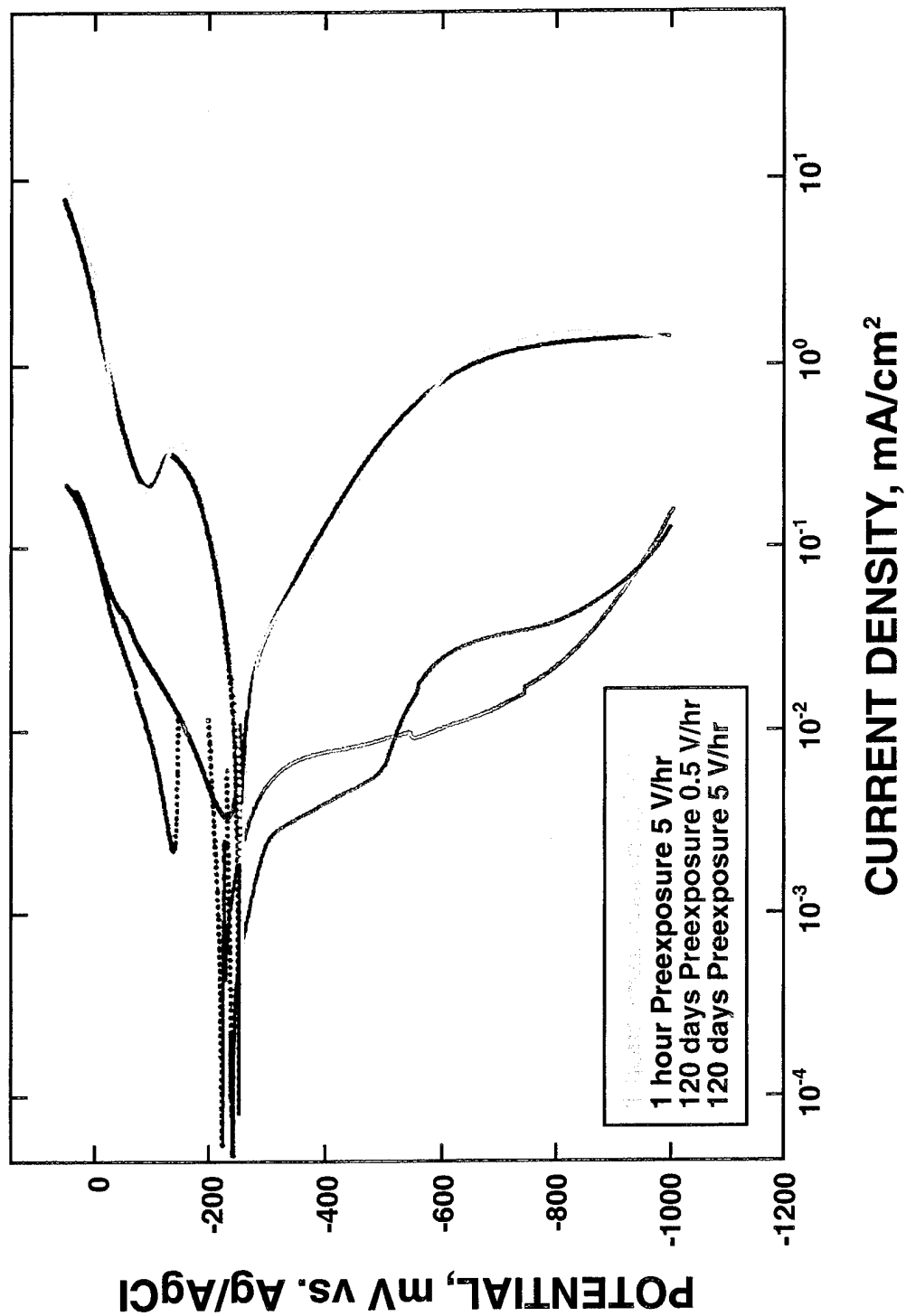
(Potentiodynamic)

70 - 30 COPPER NICKEL Quiescent Flow



(Potentiodynamic)

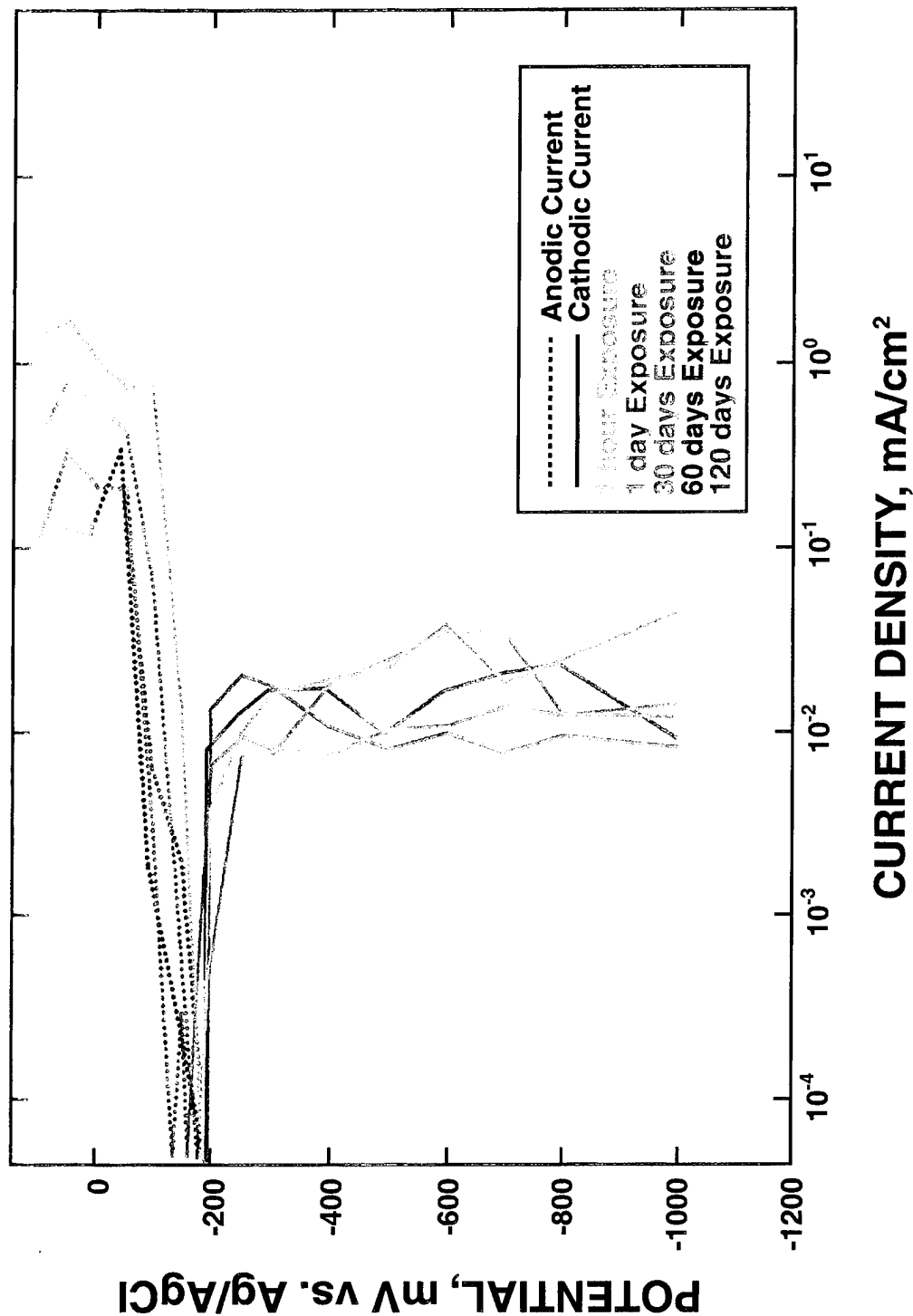
70 - 30 COPPER NICKEL Flowing at 8.0 ft/s



(Potentiostatic)

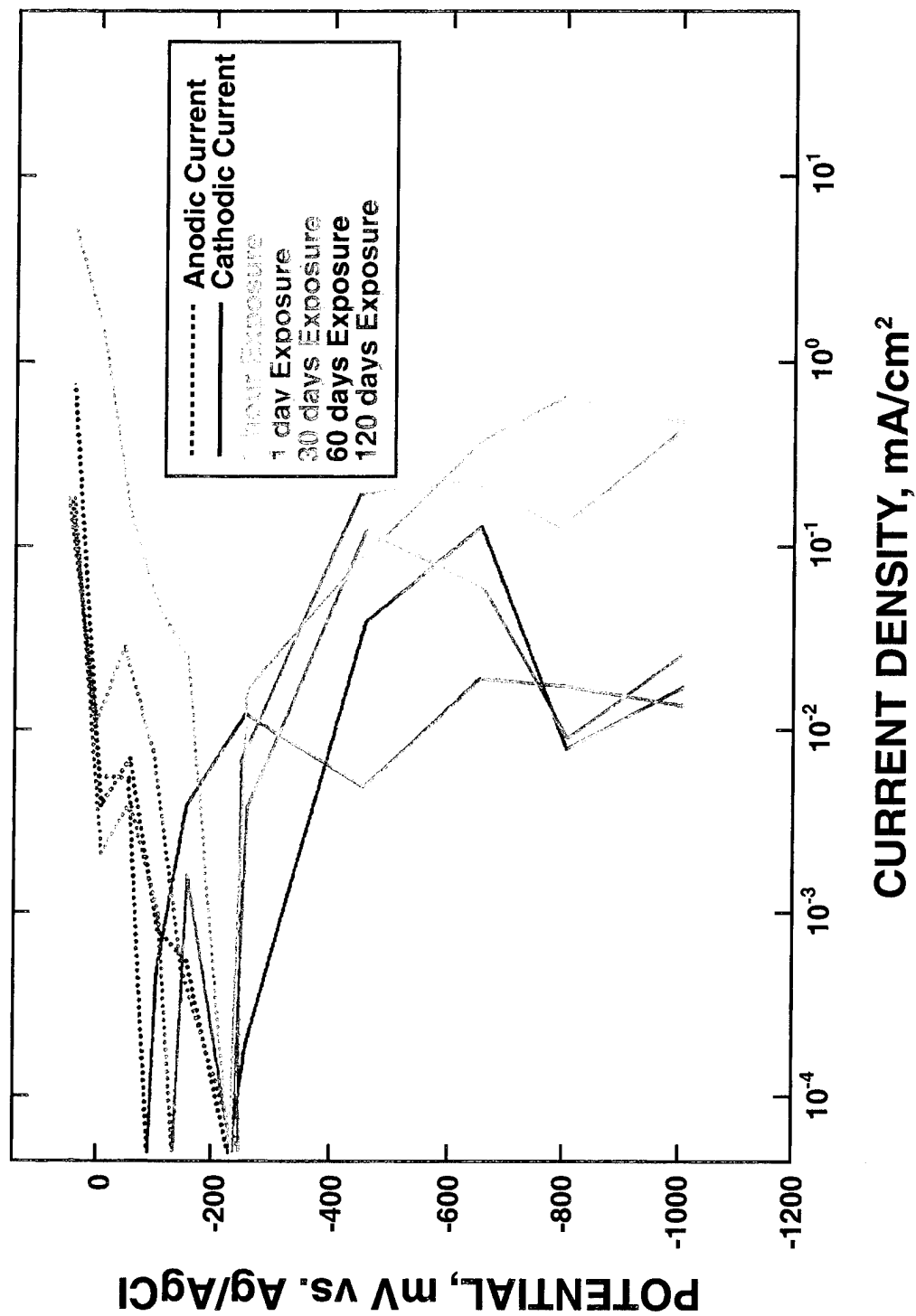
70 - 30 COPPER NICKEL

Quiescent Flow



(Potentiostatic)

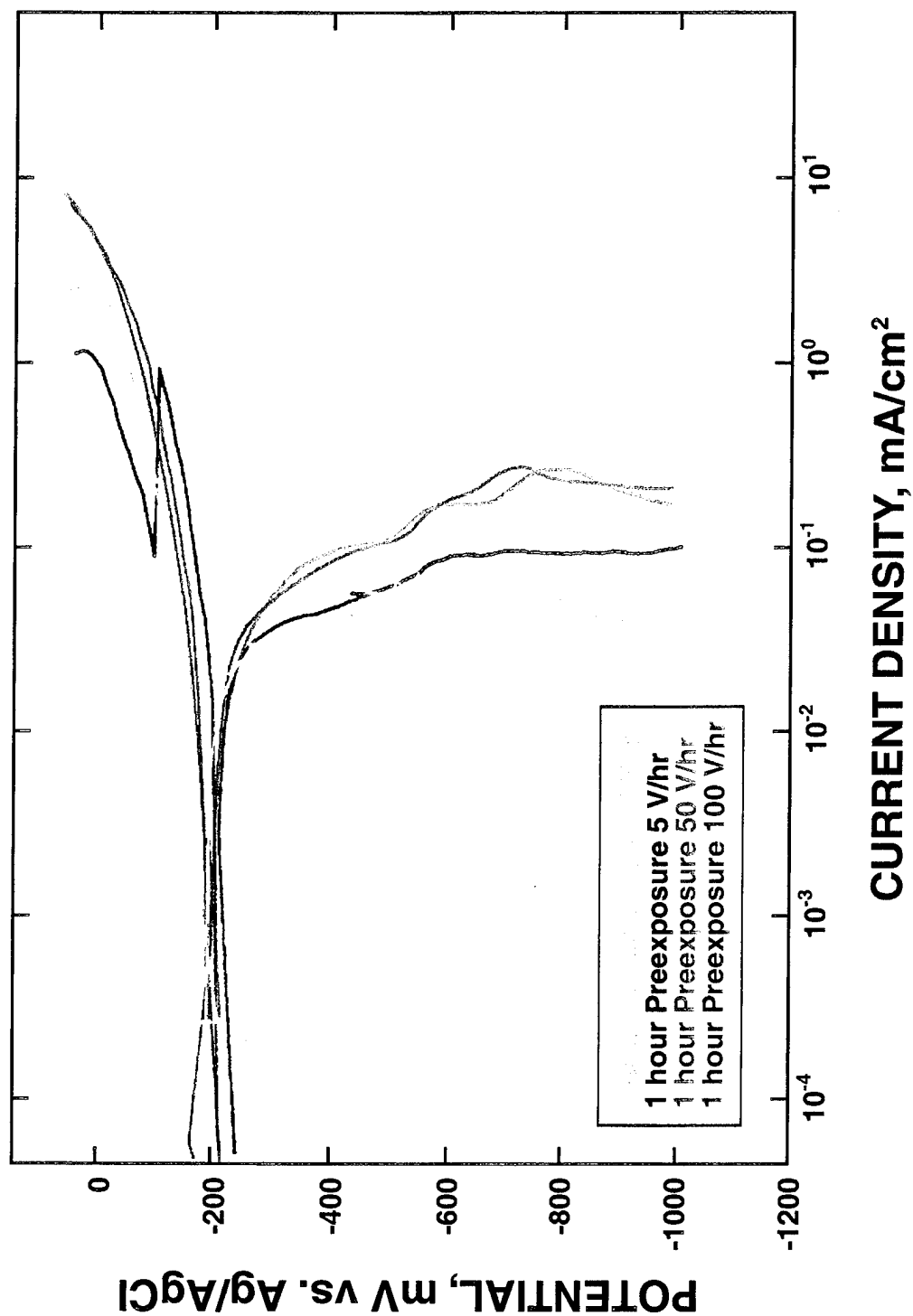
70 - 30 COPPER NICKEL Flowing at 8.0 ft/s



APPENDIX D
POLARIZATION CURVES FROM THIS STUDY FOR NAVY TYPE M BRONZE

(Potentiodynamic)

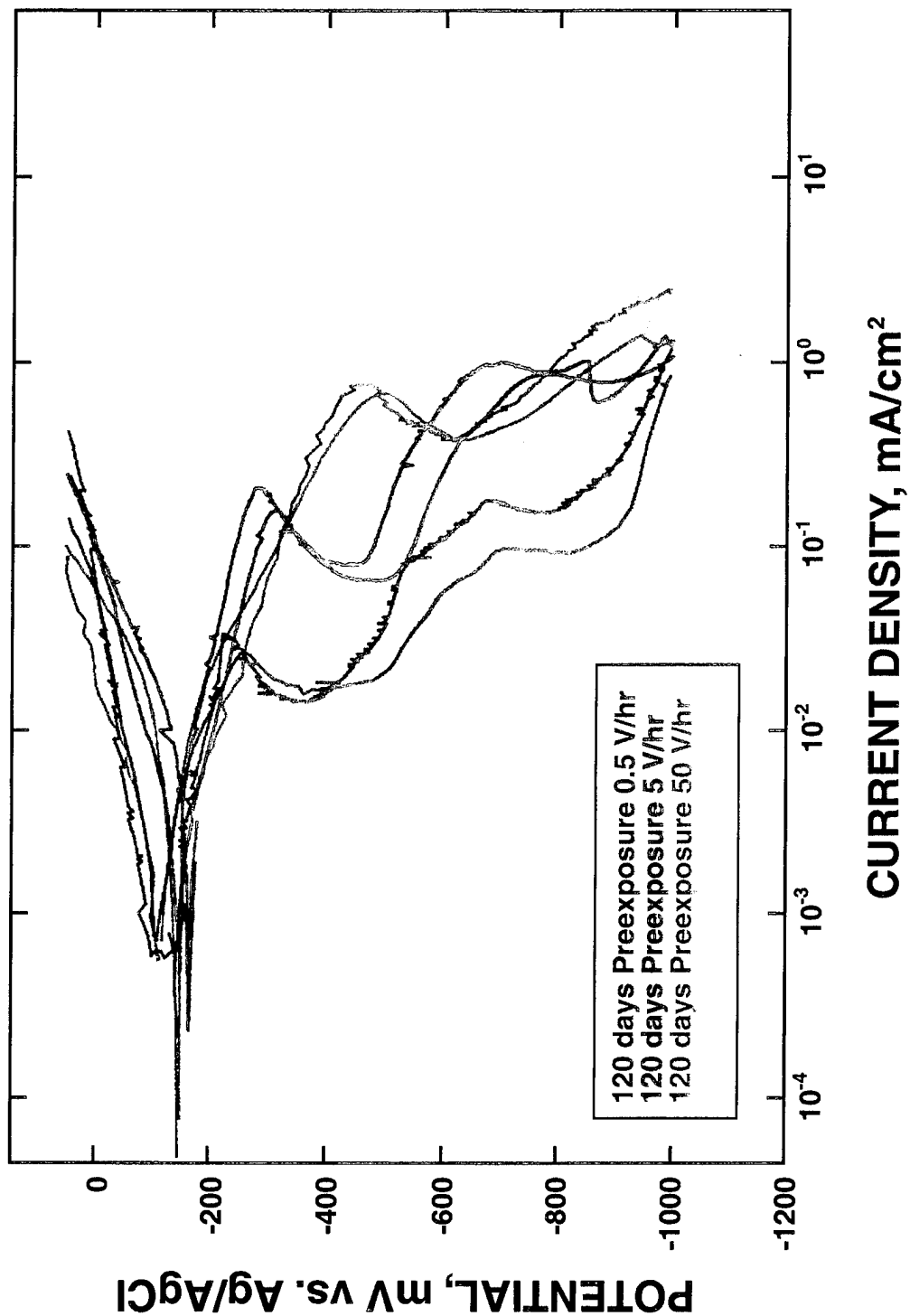
NAVY TYPE M BRONZE Quiescent Flow



(Potentiodynamic)

NAVY TYPE M BRONZE

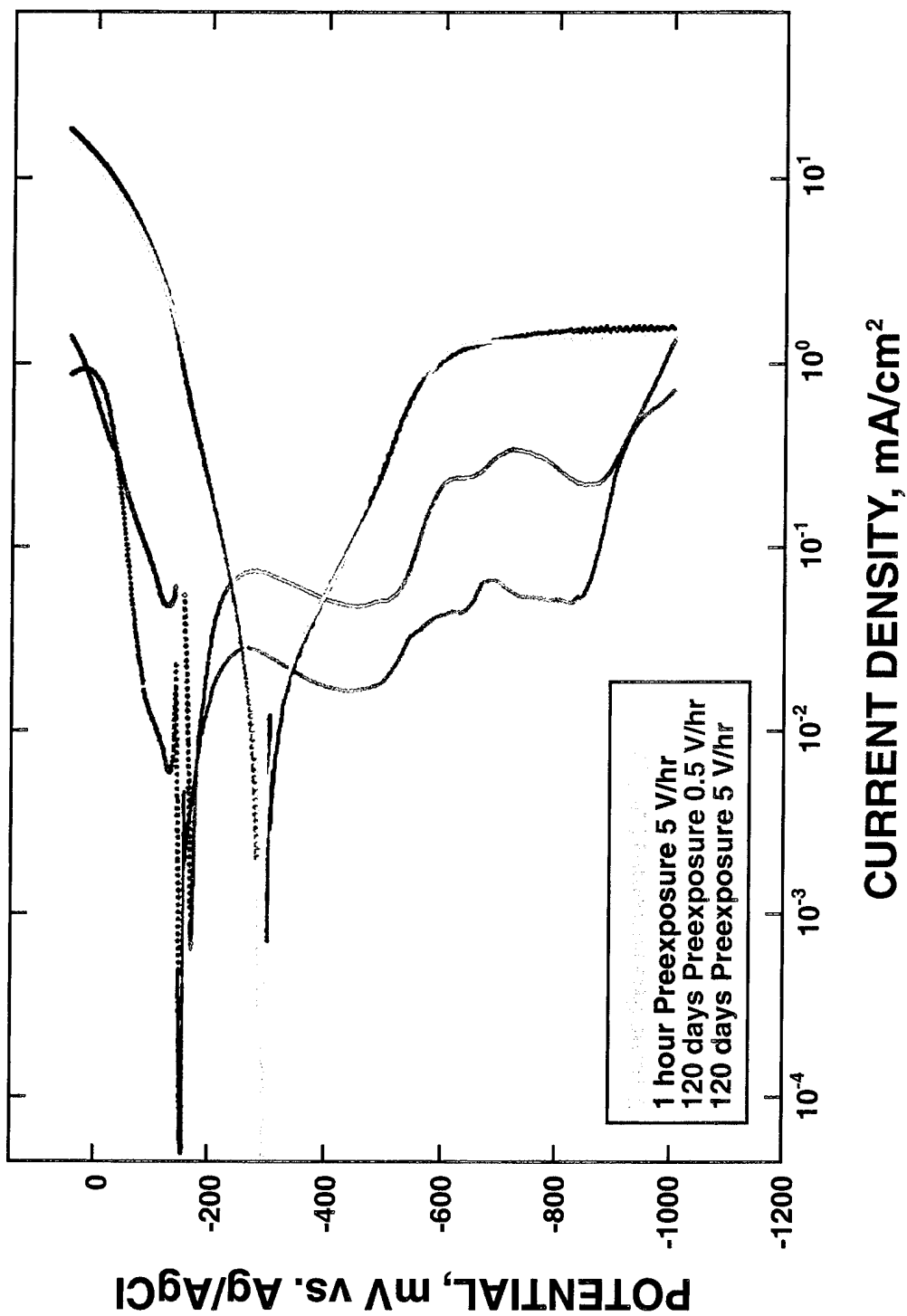
Quiescent Flow



(Potentiodynamic)

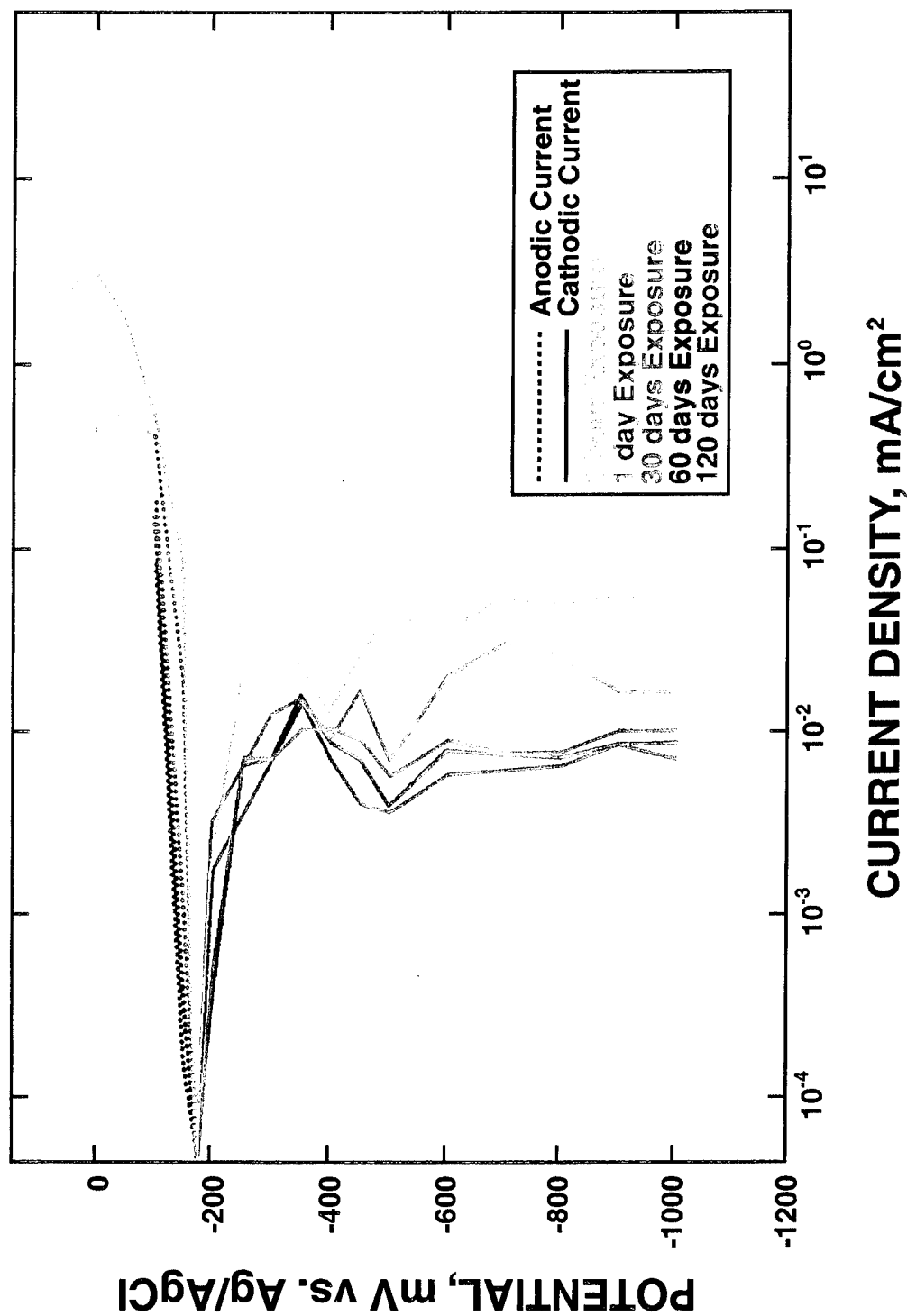
NAVY TYPE M BRONZE

Flowing at 8.0 ft/s



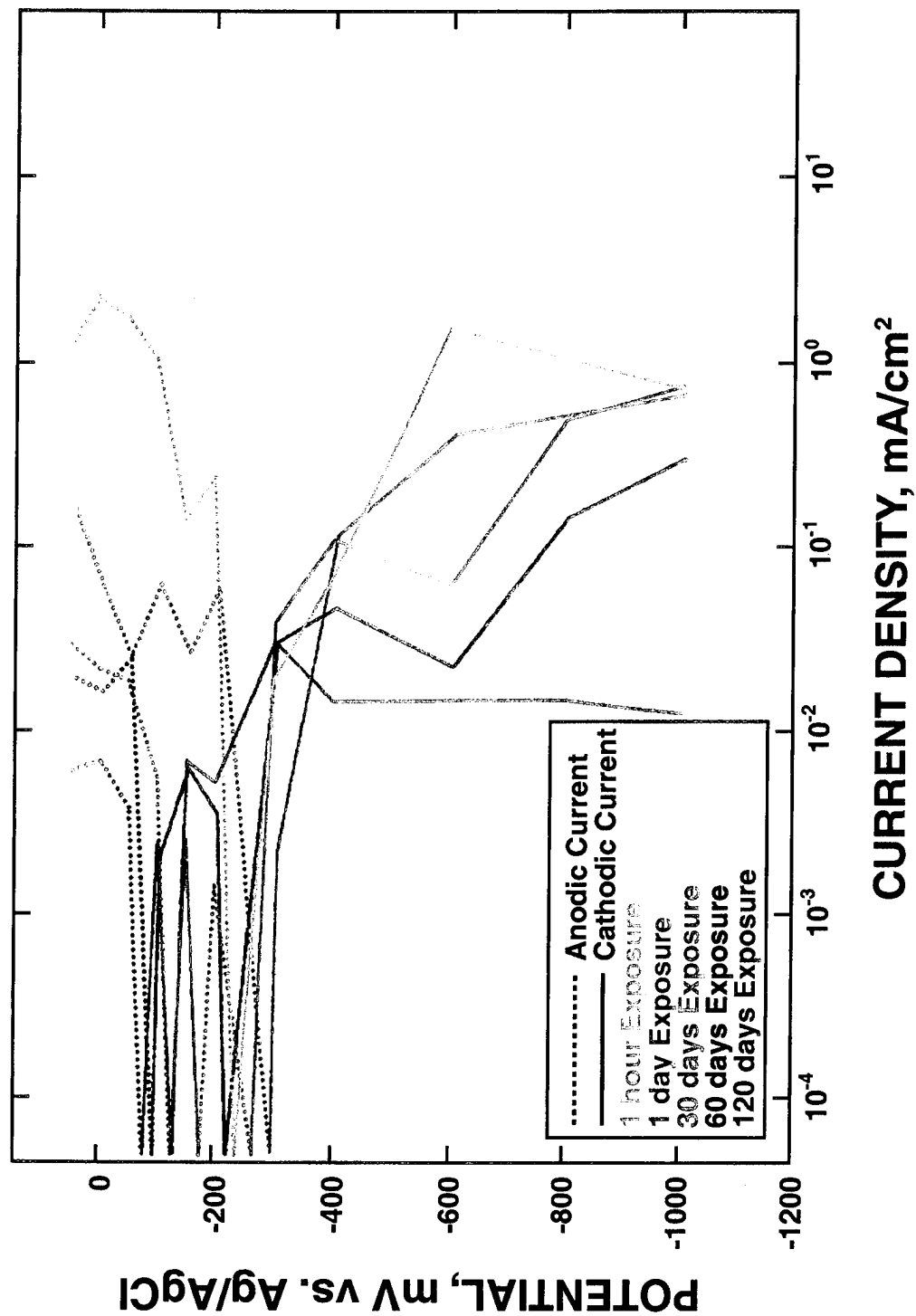
(Potentiostatic)

NAVY TYPE M BRONZE Quiescent Flow



(Potentiostatic)

NAVY TYPE M BRONZE Flowing at 8.0 ft/s

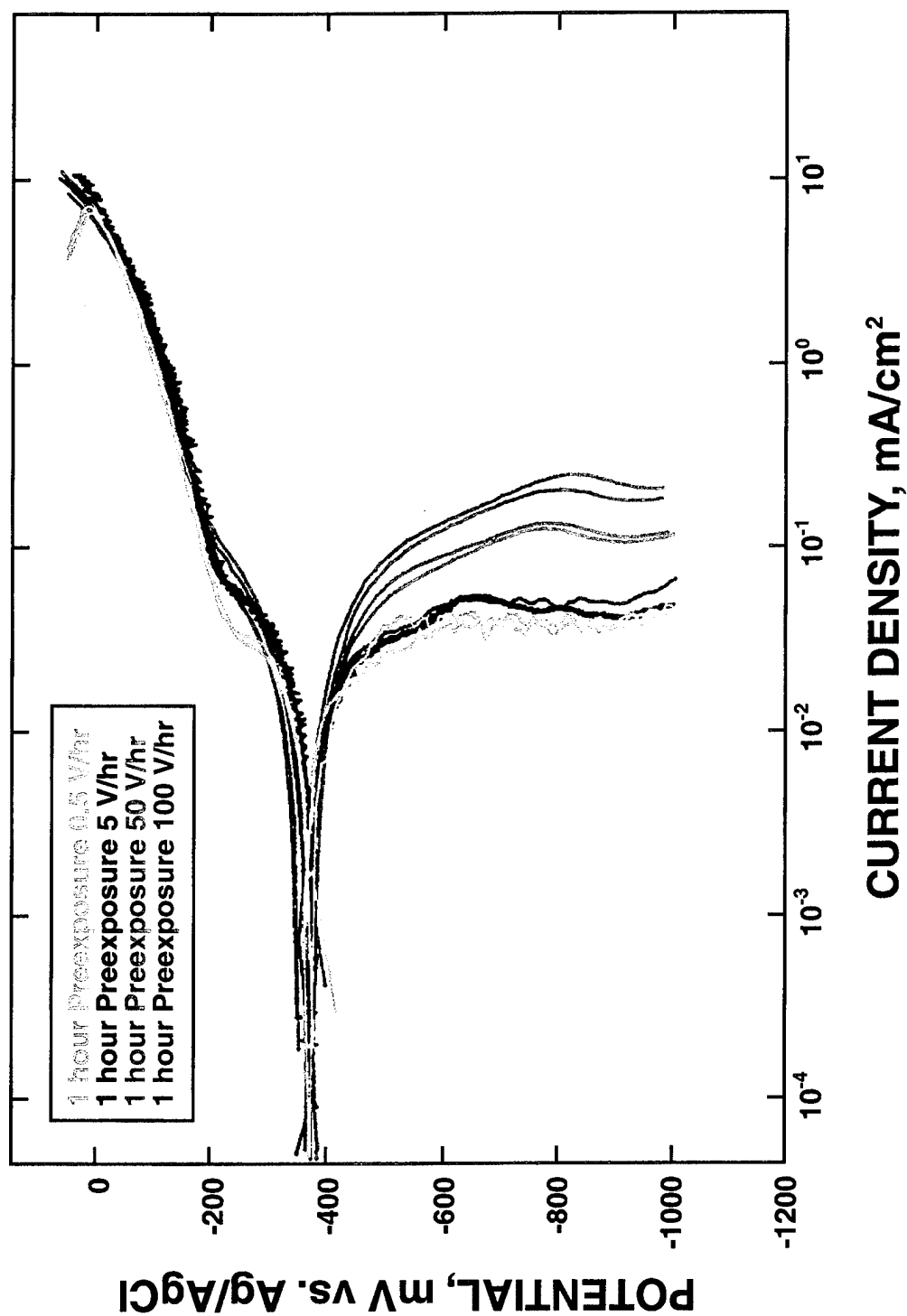


APPENDIX E
POLARIZATION CURVES FROM THIS STUDY FOR NICKEL-ALUMINUM BRONZE

(Potentiodynamic)

NICKEL - ALUMINUM BRONZE

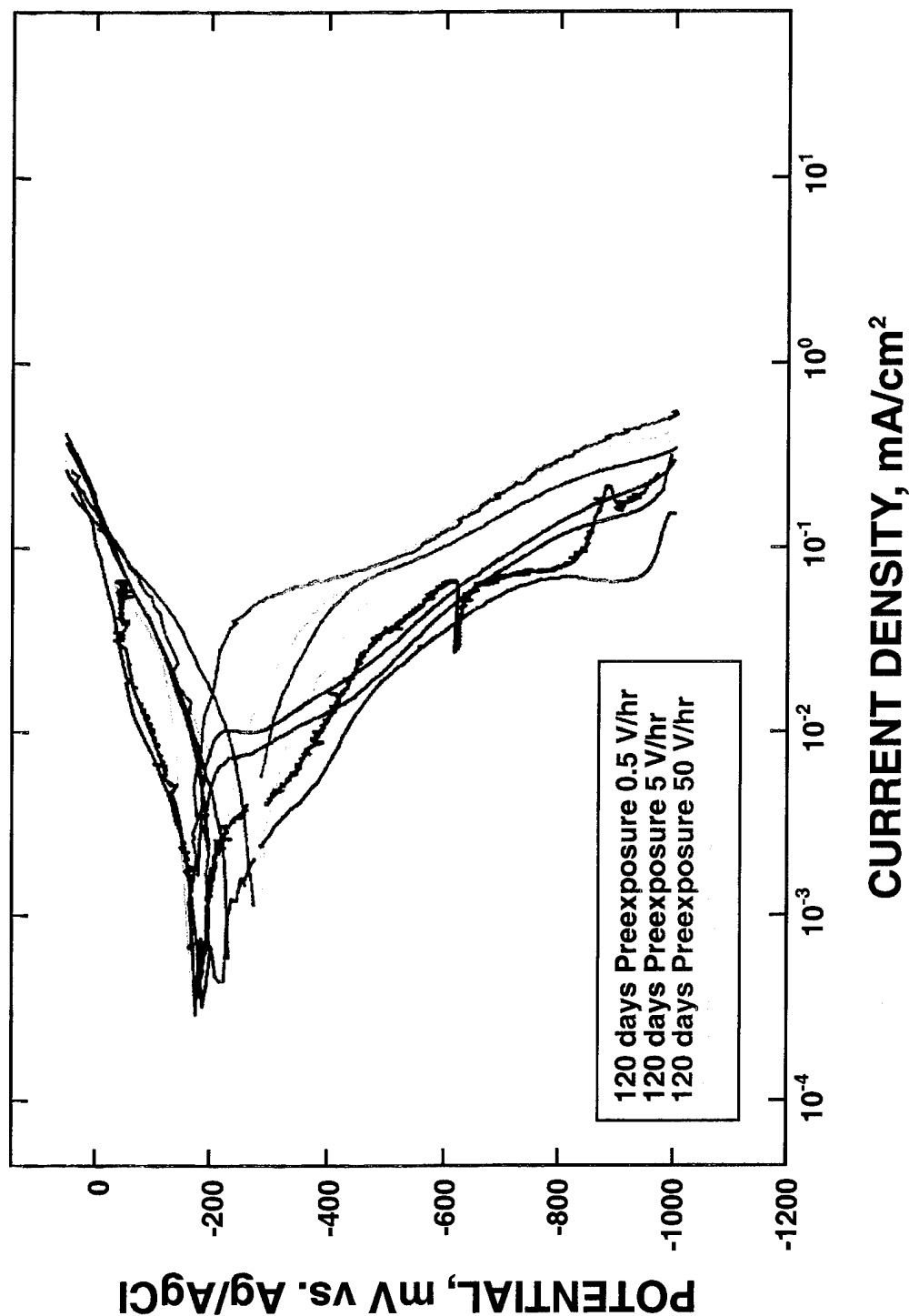
Quiescent Flow



(Potentiodynamic)

NICKEL - ALUMINUM BRONZE

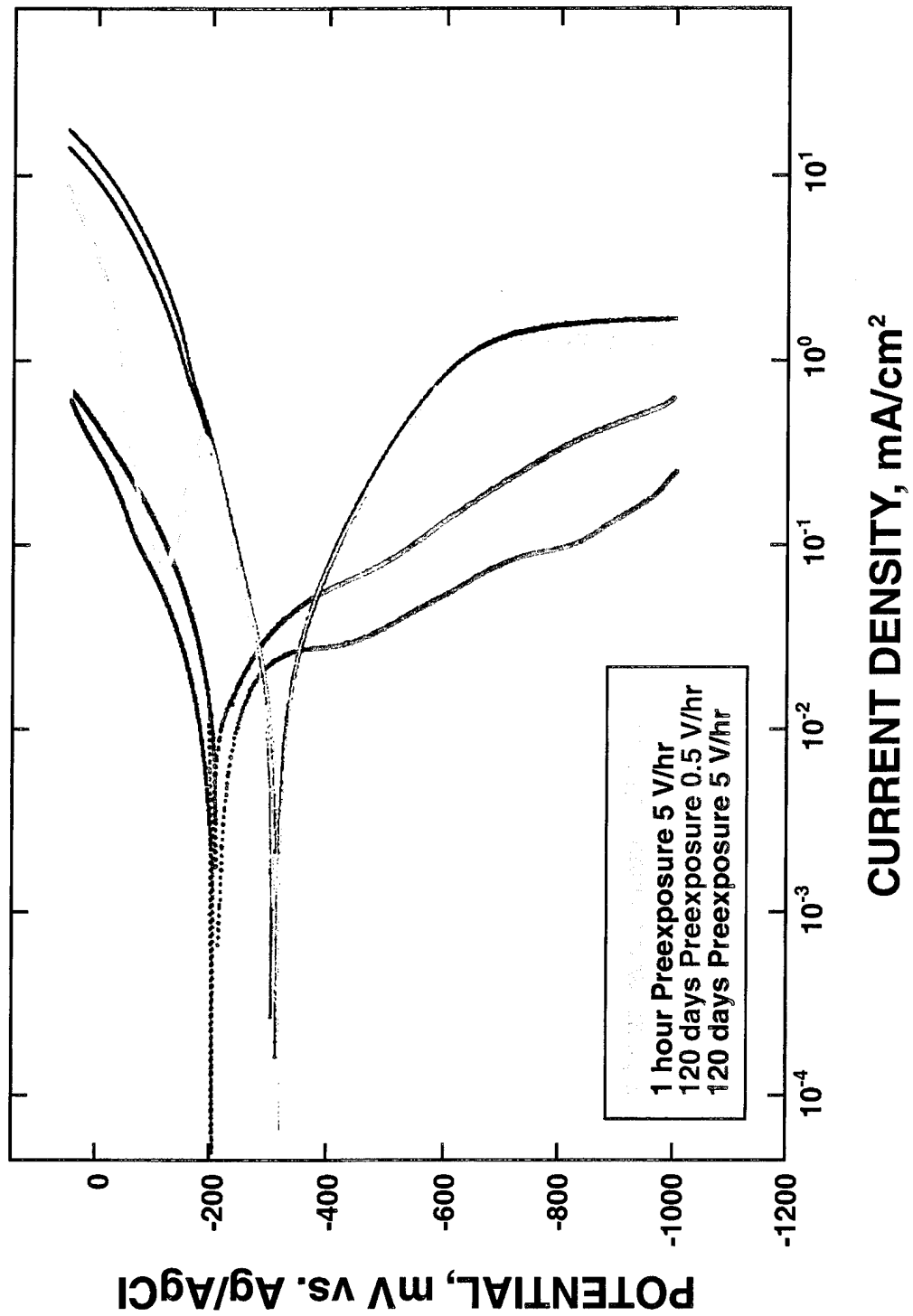
Quiescent Flow



(Potentiodynamic)

NICKEL - ALUMINUM BRONZE

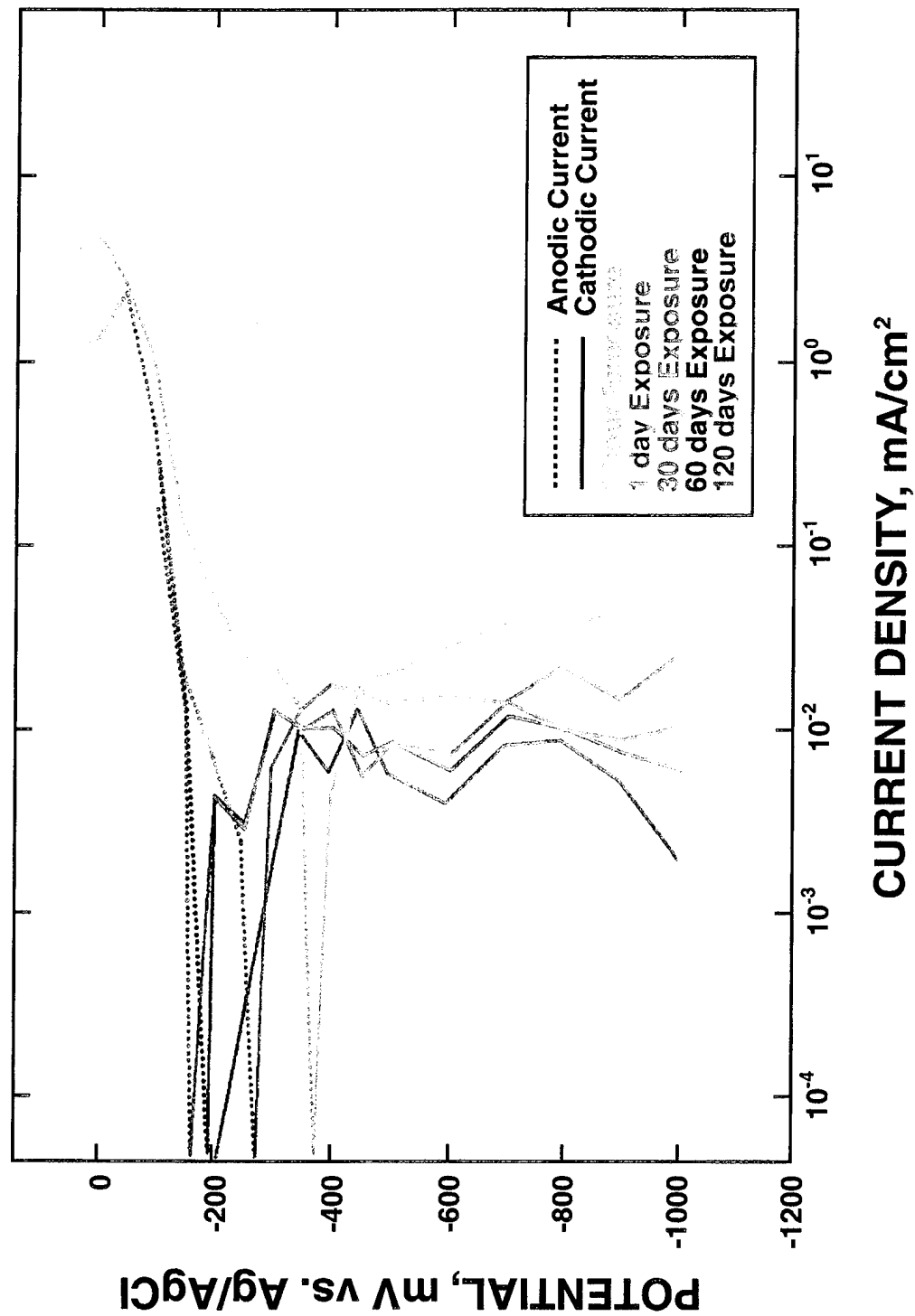
Flowing at 8.0 ft/s



(Potentiostatic)

NICKEL - ALUMINUM BRONZE

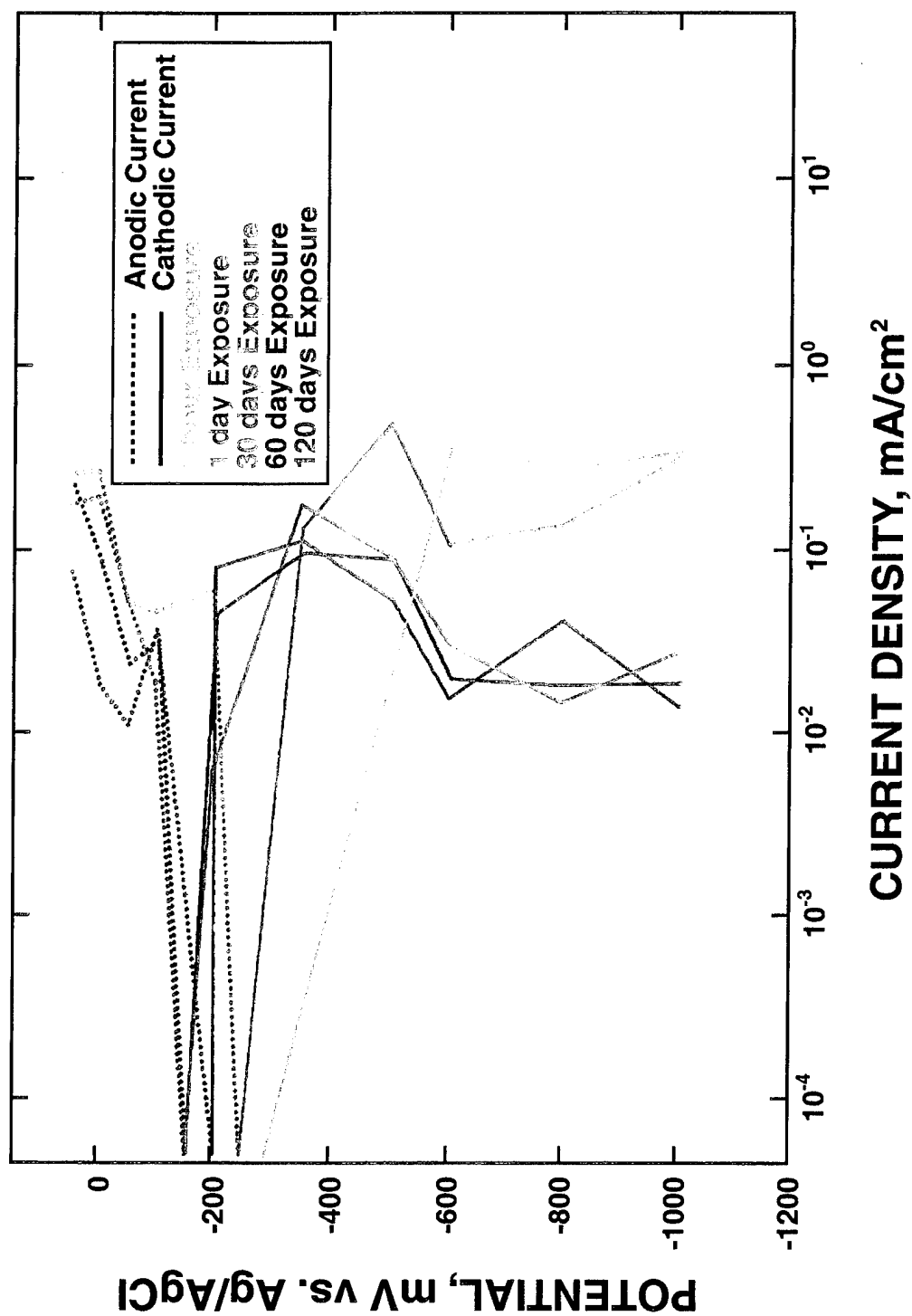
Quiescent Flow



(Potentiostatic)

NICKEL - ALUMINUM BRONZE

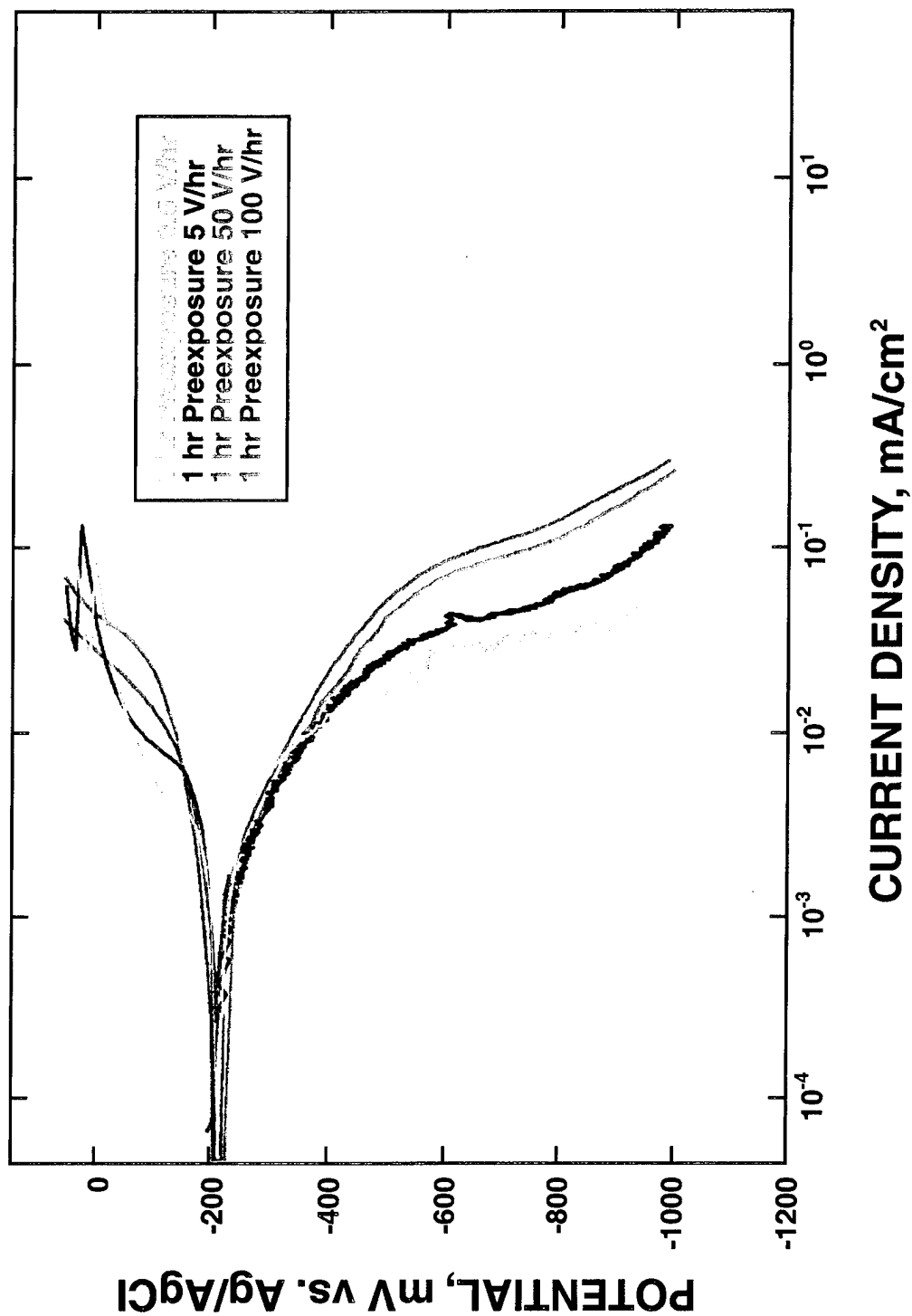
Flowing at 8.0 ft/s



APPENDIX F
POLARIZATION CURVES FROM THIS STUDY FOR MONEL

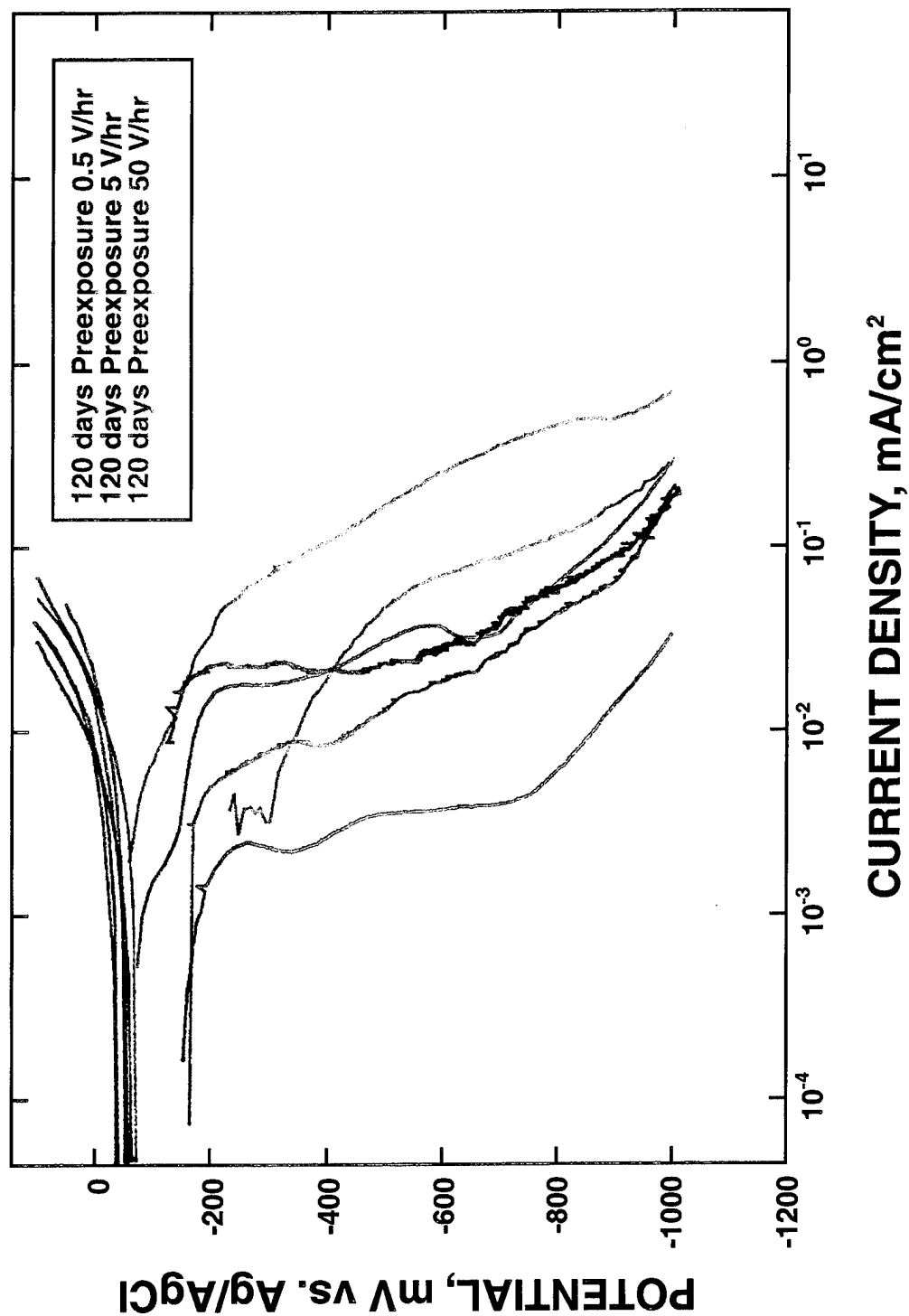
(Potentiodynamic)

MONEL Quiescent Flow



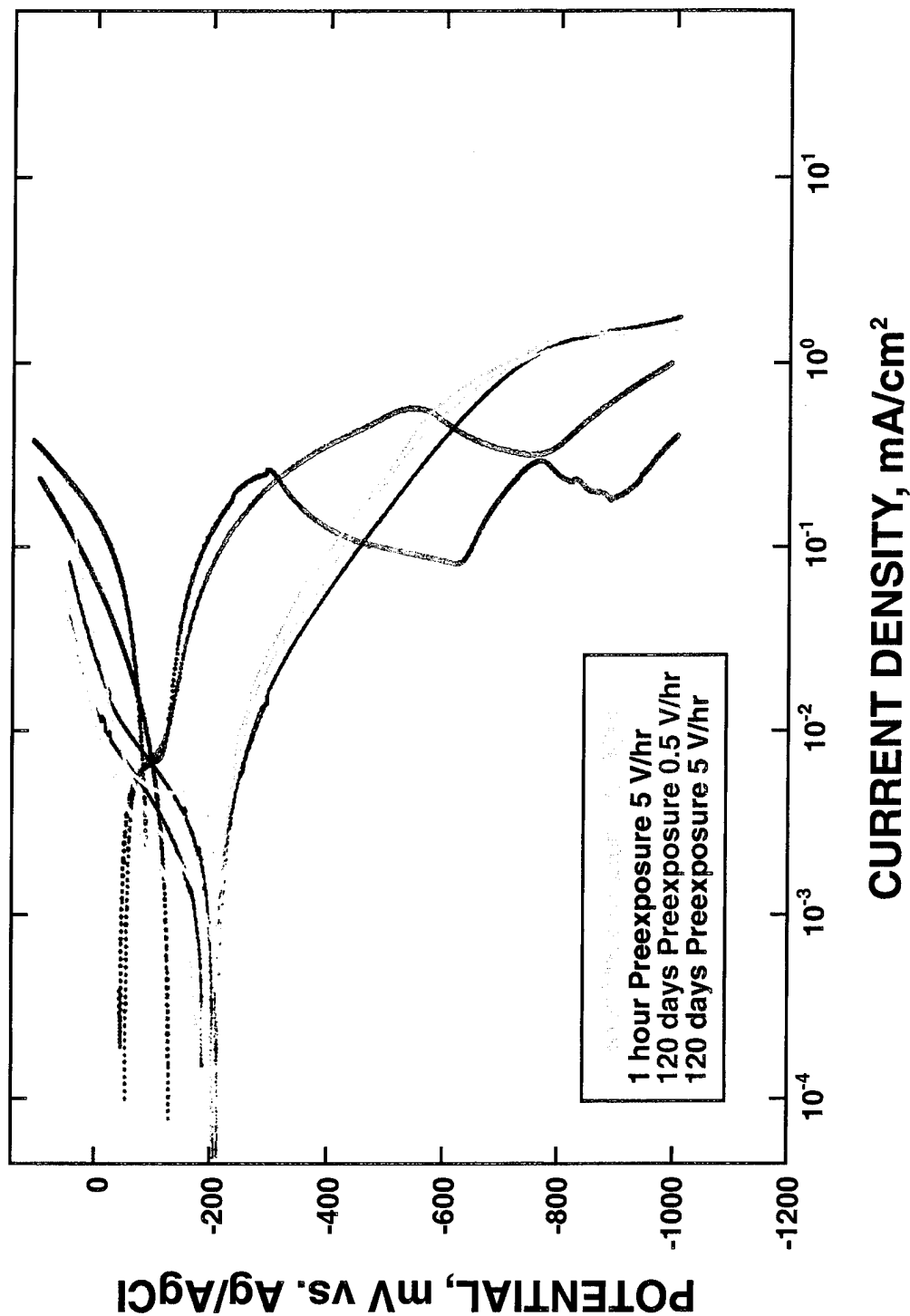
(Potentiodynamic)

MONEL Quiescent Flow



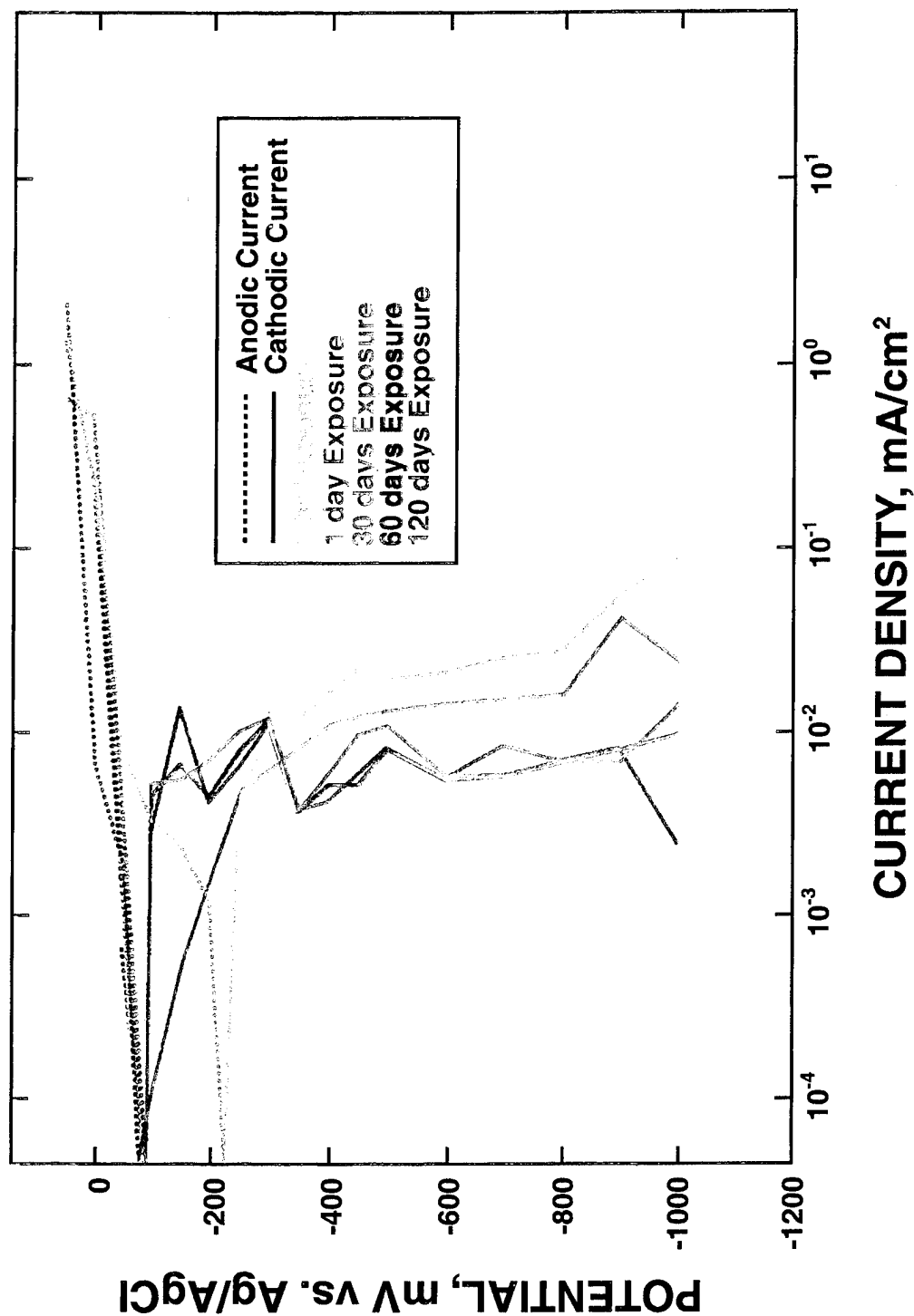
(Potentiodynamic)

MONEL Flowing at 8.0 ft/s



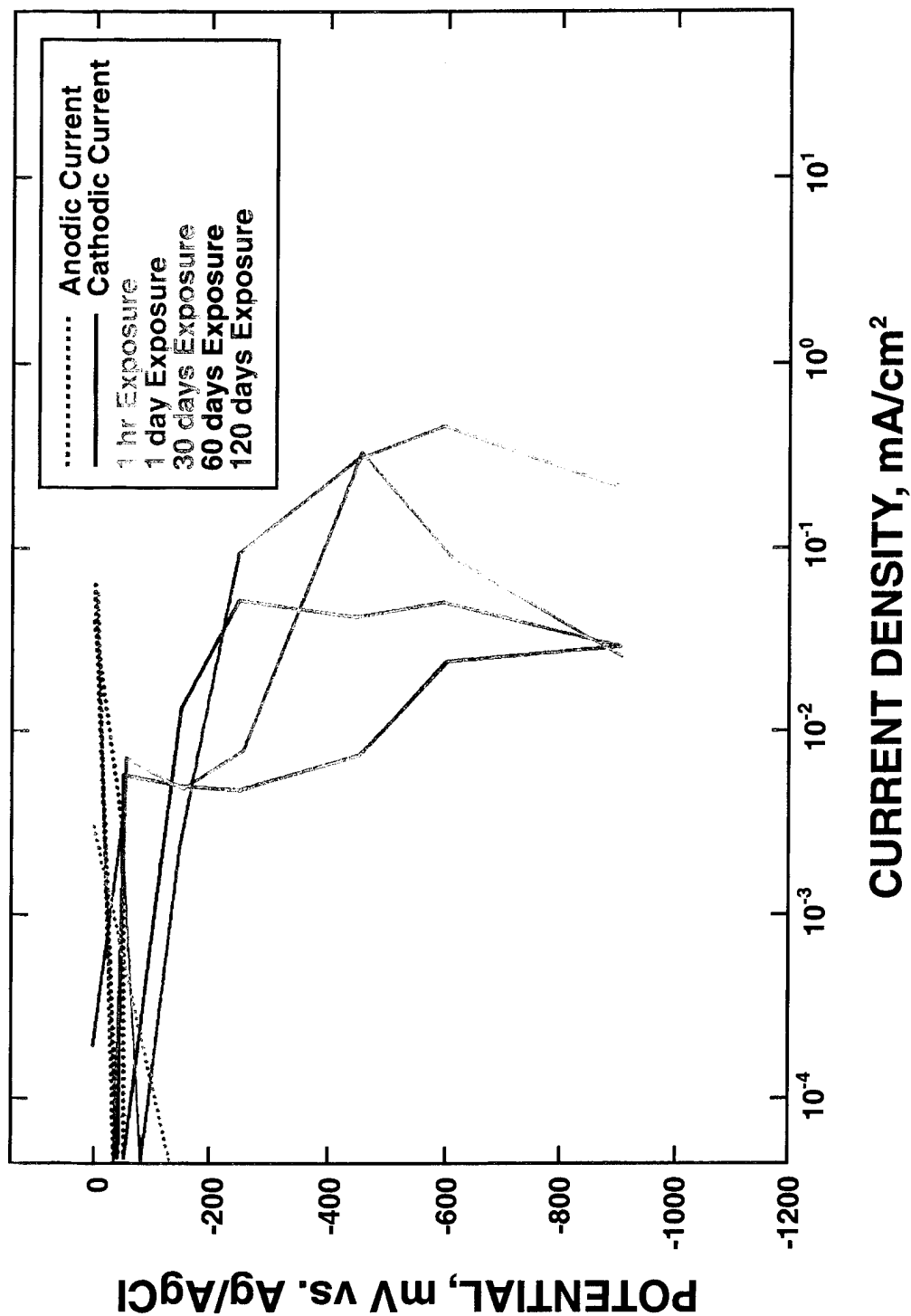
(Potentiostatic)

MONEL Quiescent Flow



(Potentiostatic)

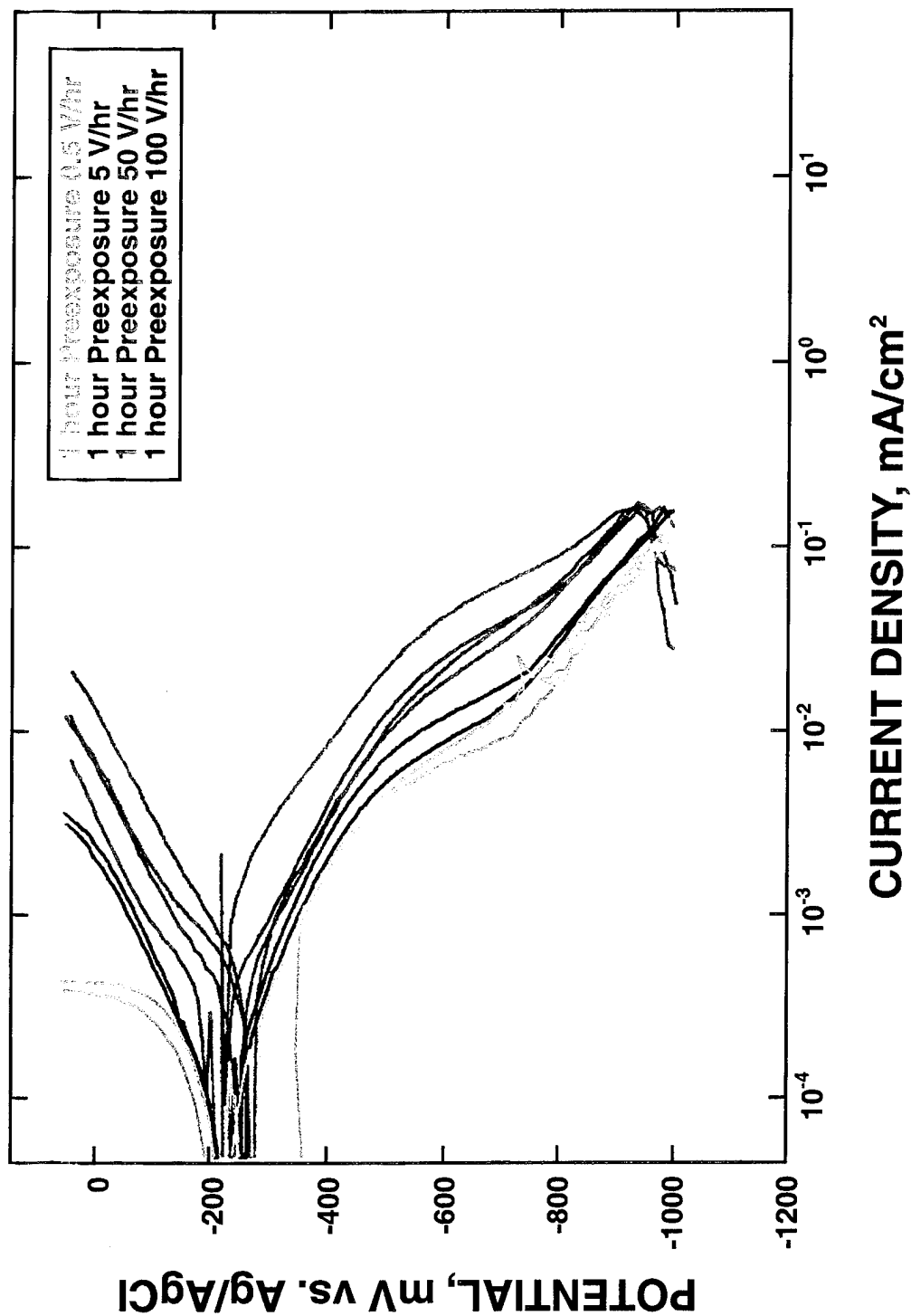
MONEL Flowing at 8.0 ft/s



APPENDIX G
POLARIZATION CURVES FROM THIS STUDY FOR ALLOY 625

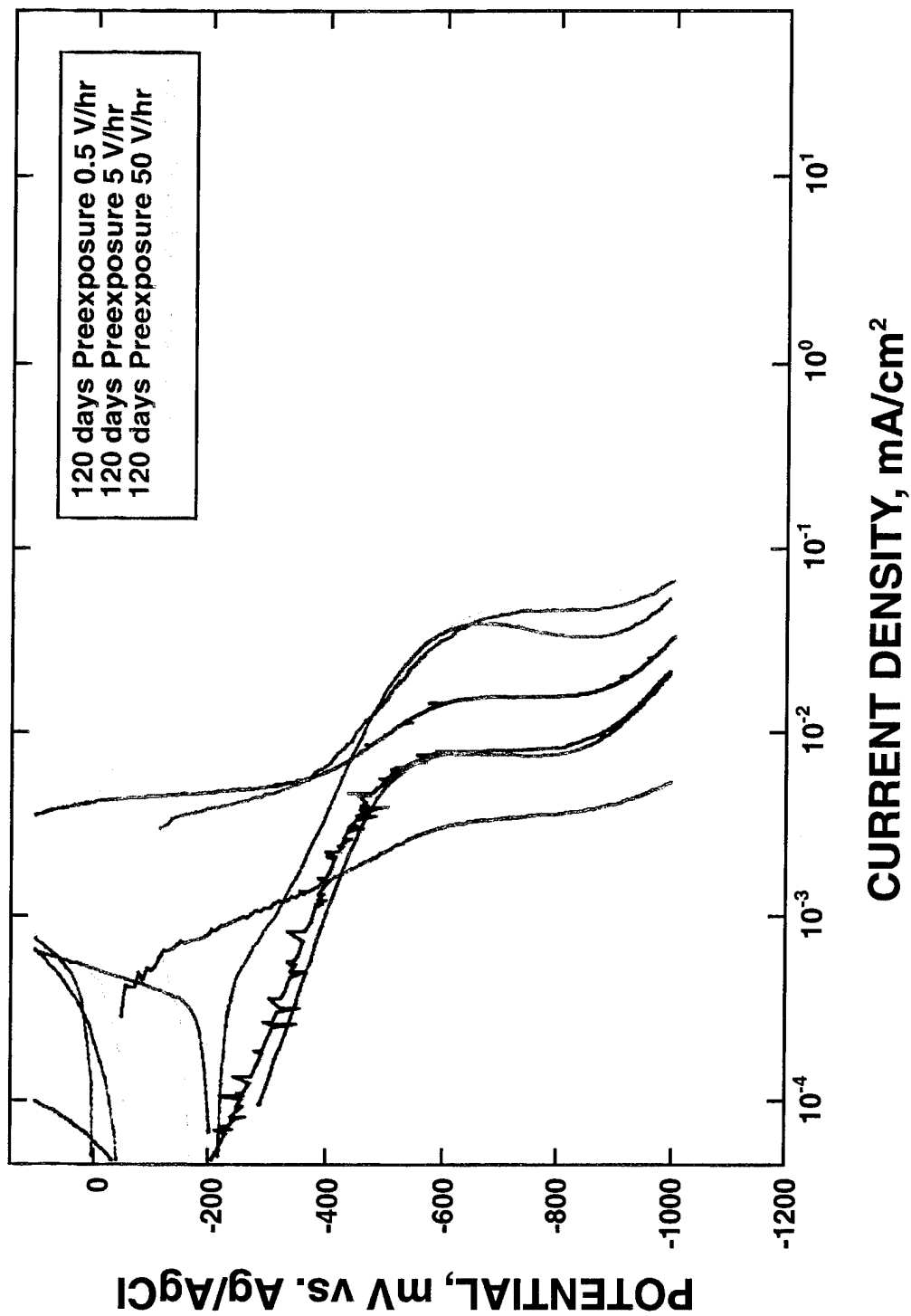
(Potentiodynamic)

ALLOY 625 Quiescent Flow



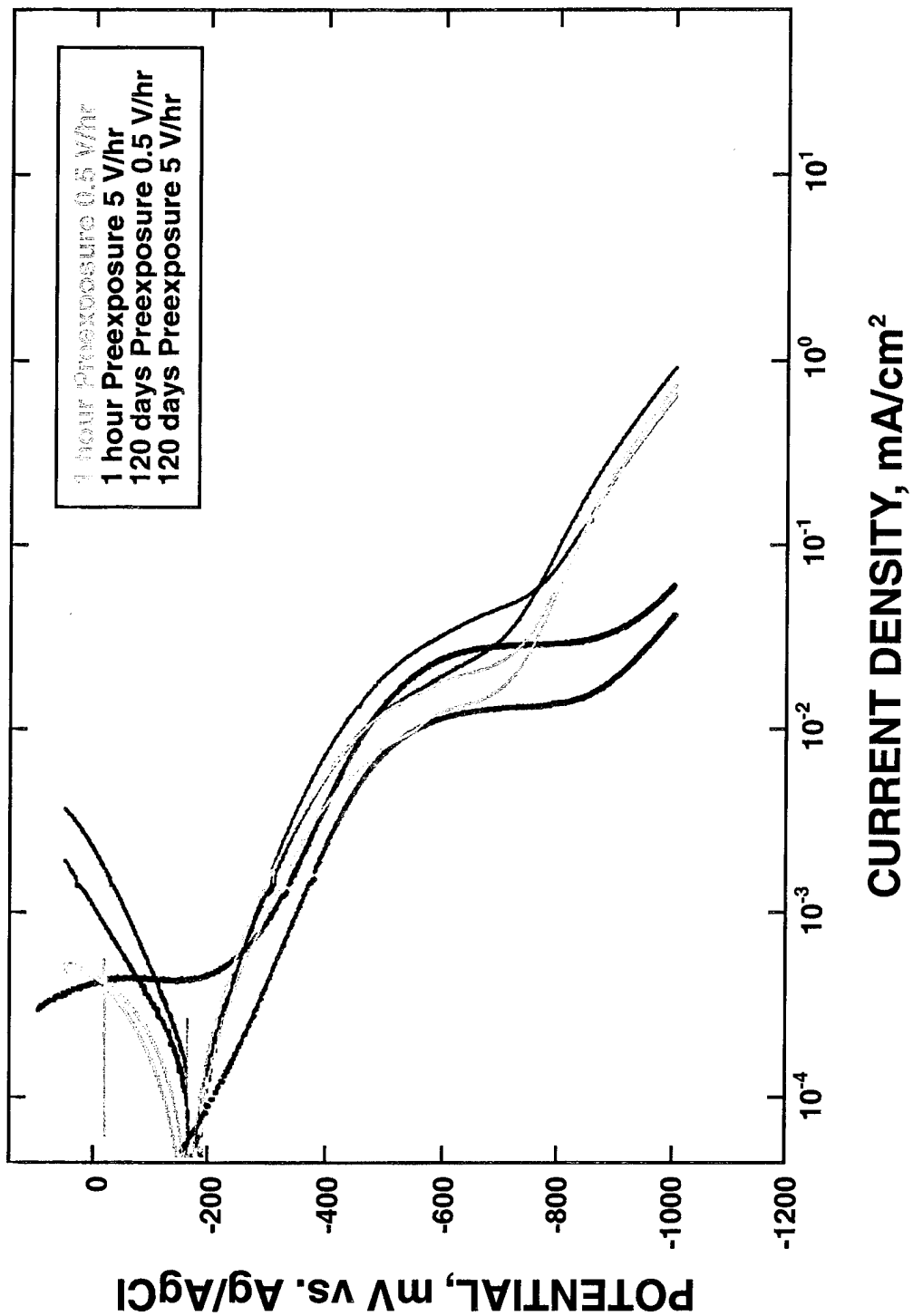
(Potentiodynamic)

ALLOY 625 Quiescent Flow



(Potentiodynamic)

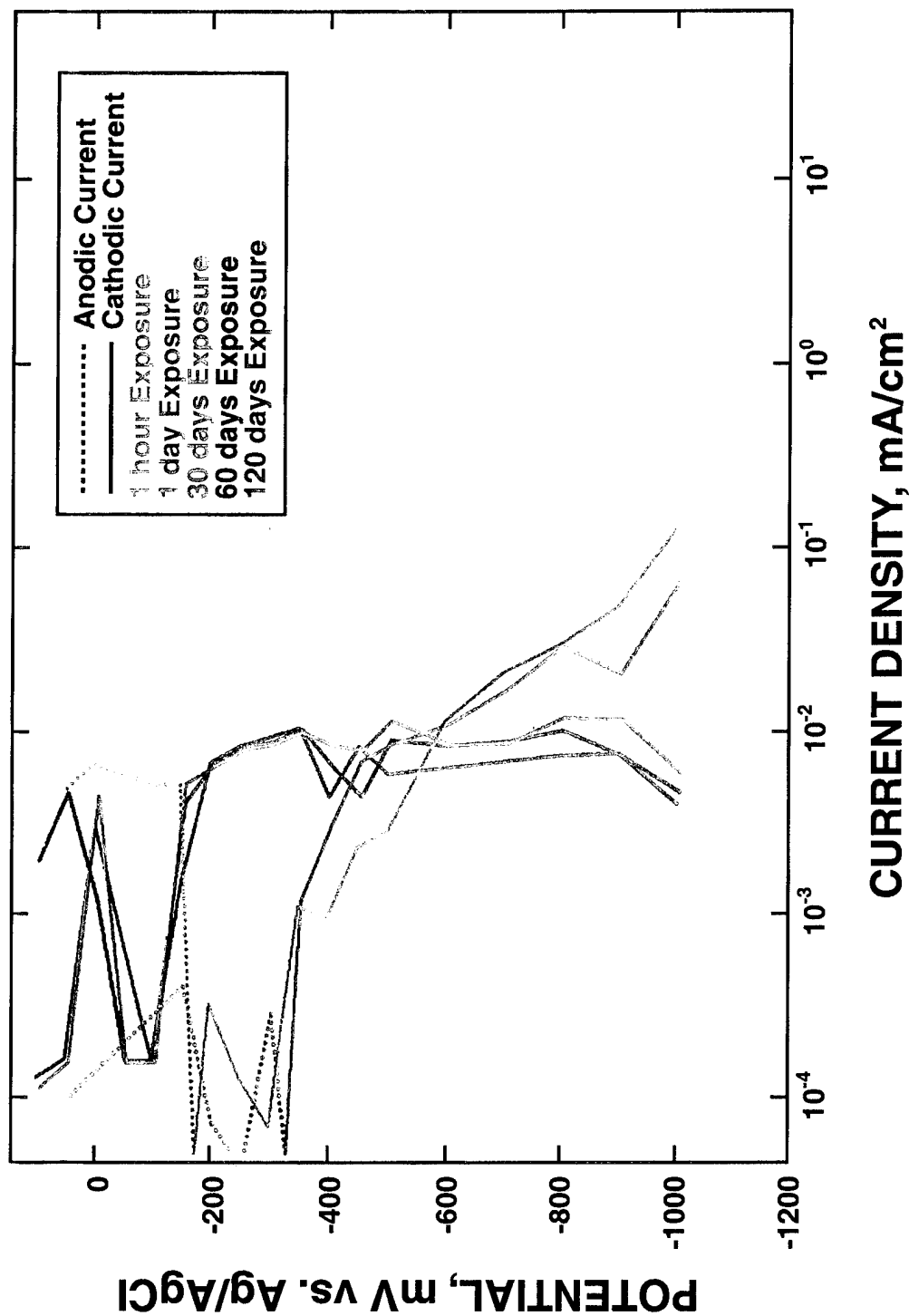
ALLOY 625 Flowing at 8.0 ft/s



(Potentiostatic)

ALLOY 625

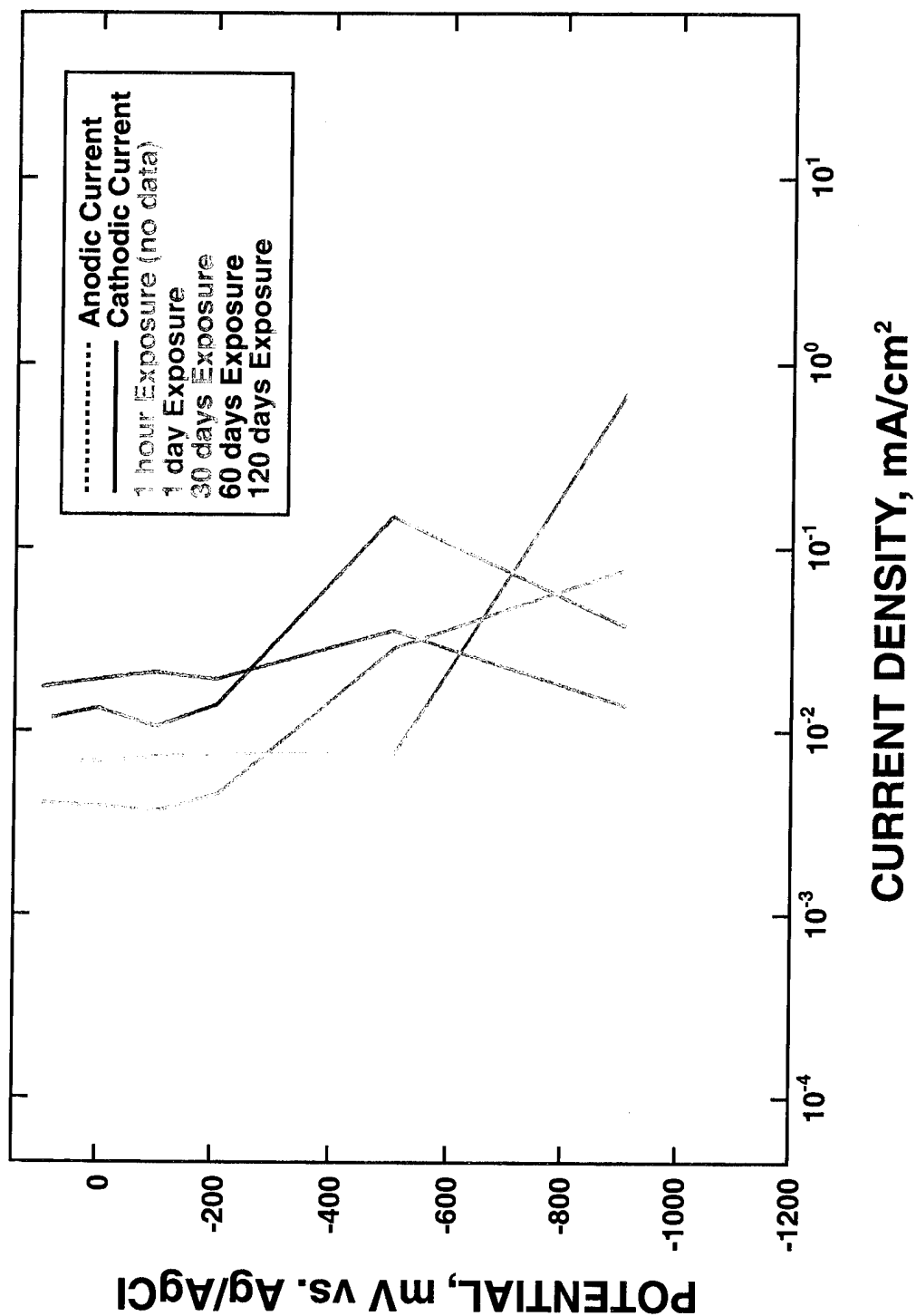
Quiescent Flow



(Potentiostatic)

ALLOY 625

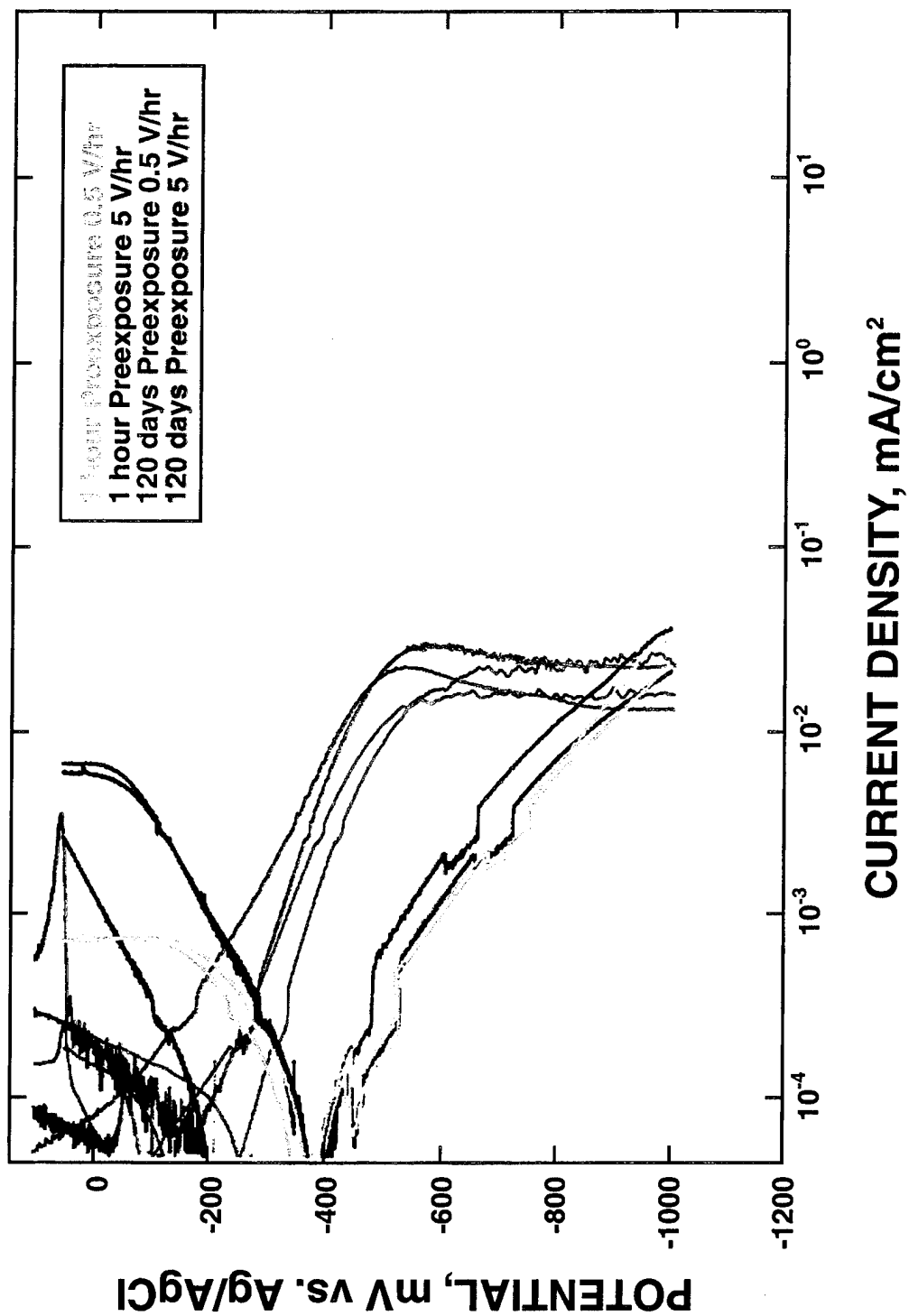
Flowing at 8.0 ft/s



APPENDIX H
POLARIZATION CURVES FROM THIS STUDY FOR TITANIUM 50

(Potentiodynamic)

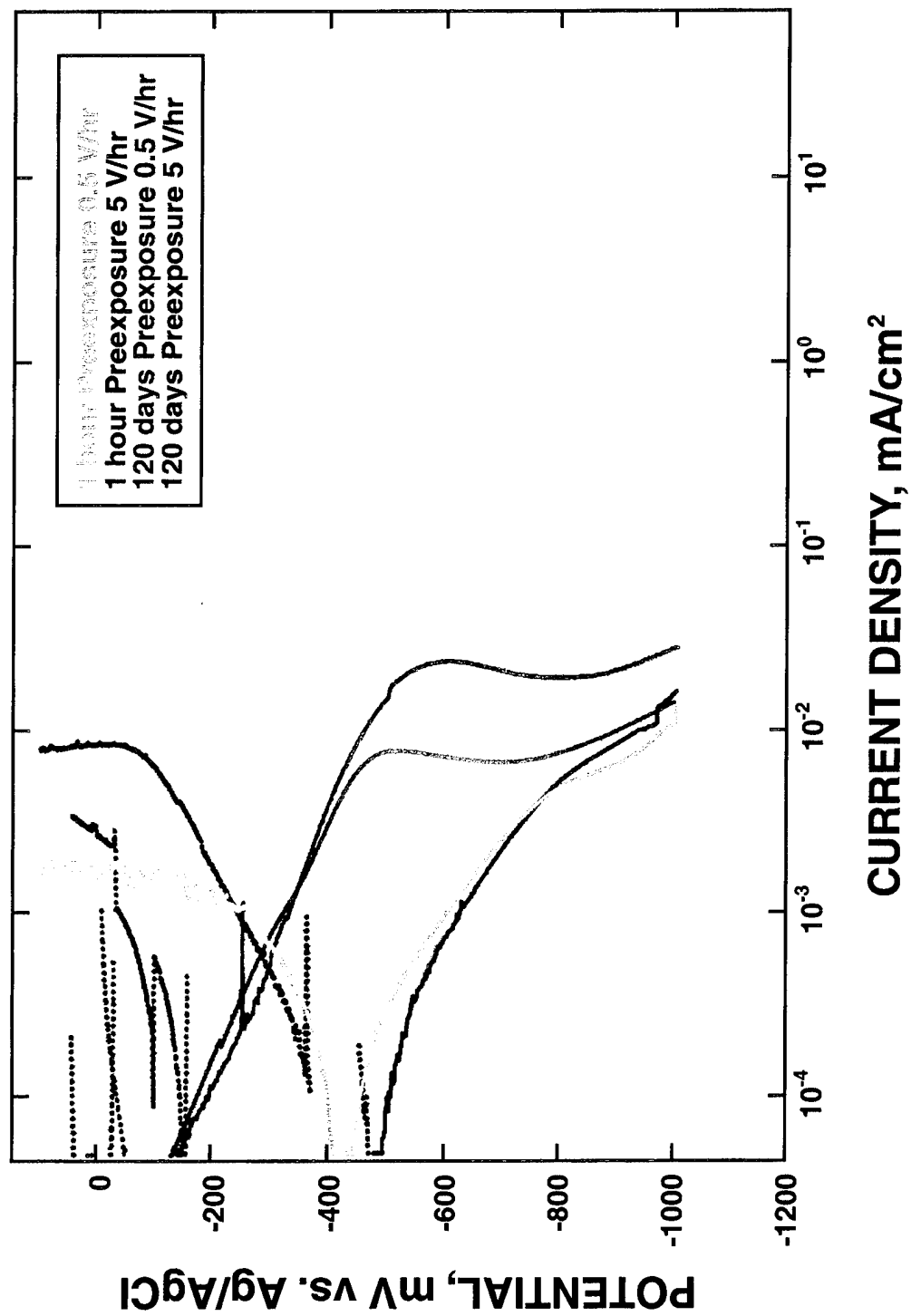
TITANIUM 50 Quiescent Flow



(Potentiodynamic)

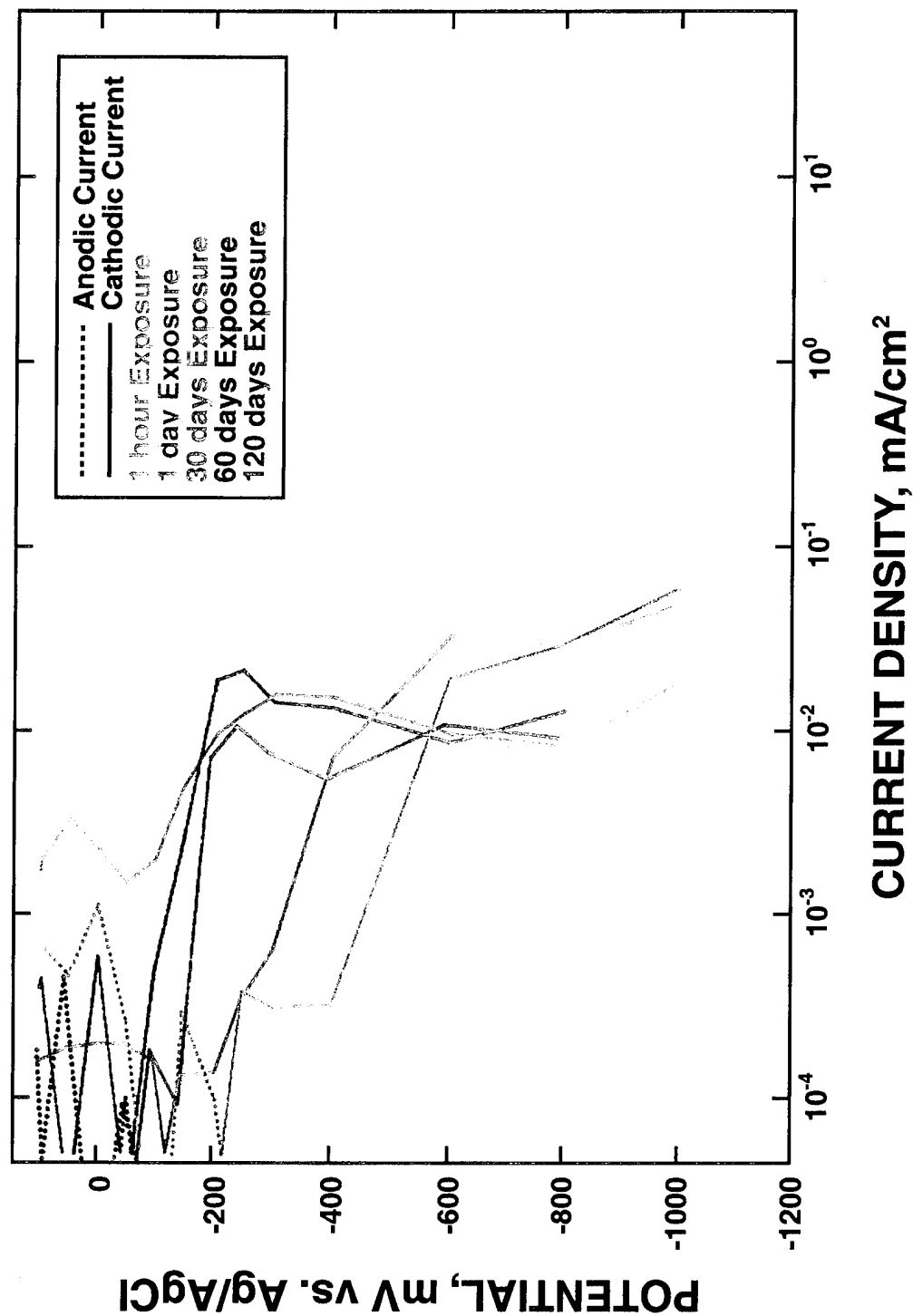
TITANIUM 50

Flowing at 8.0 ft/s



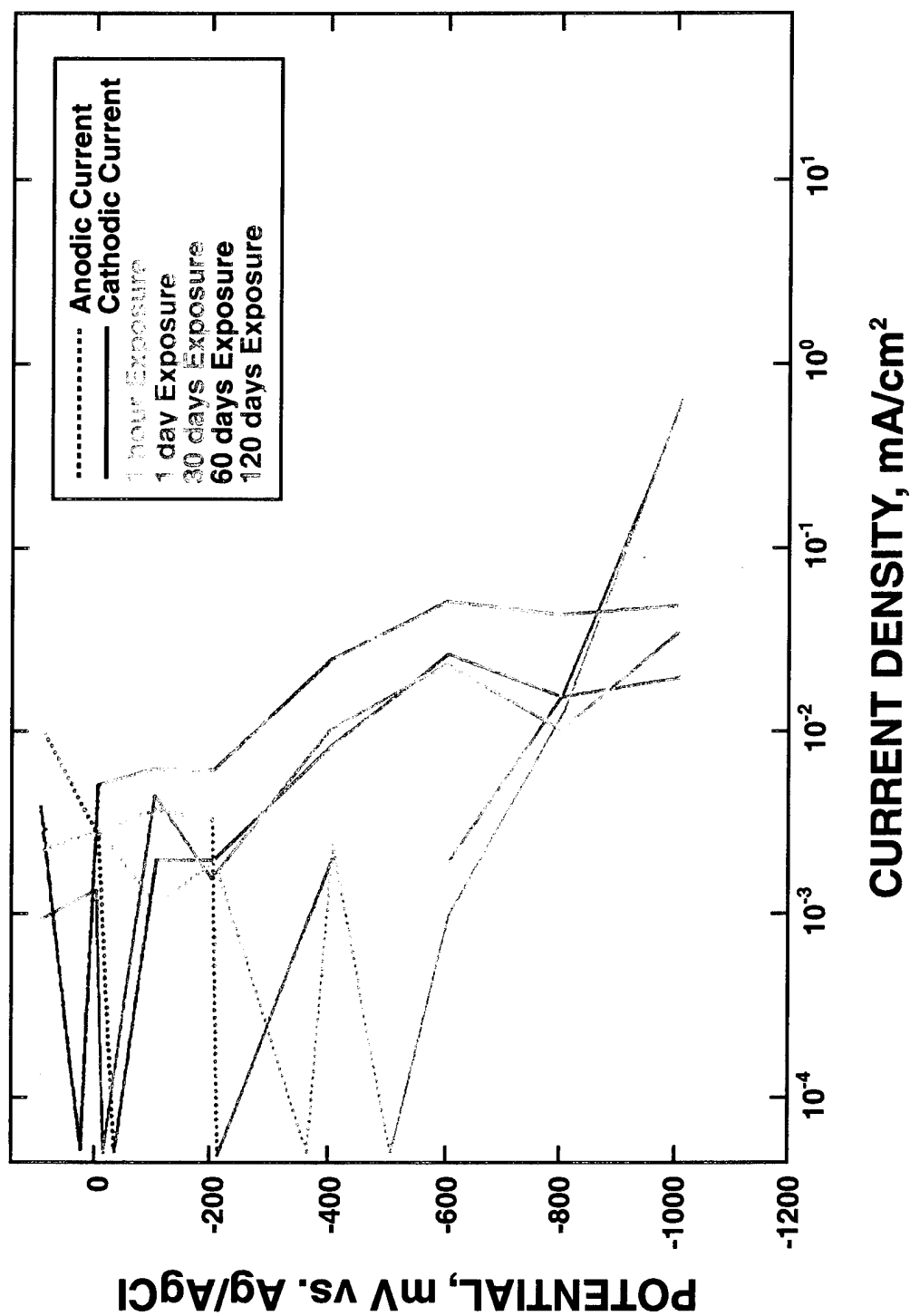
(Potentiostatic)

TITANIUM 50 Quiescent Flow



(Potentiostatic)

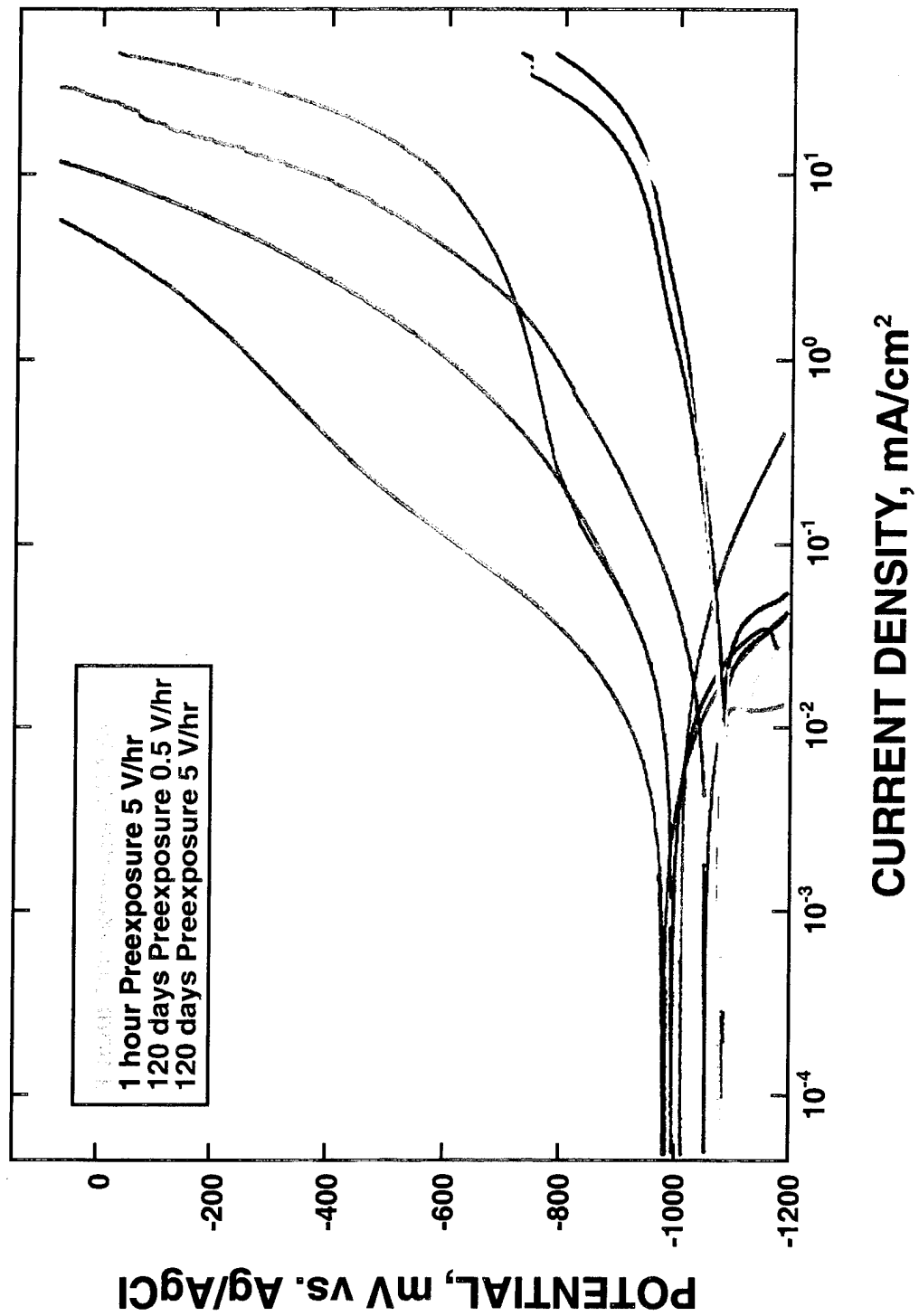
TITANIUM 50 Flowing at 8.0 ft/s



APPENDIX I
POLARIZATION CURVES FROM THIS STUDY FOR ANODE GRADE ZINC

(Potentiodynamic)

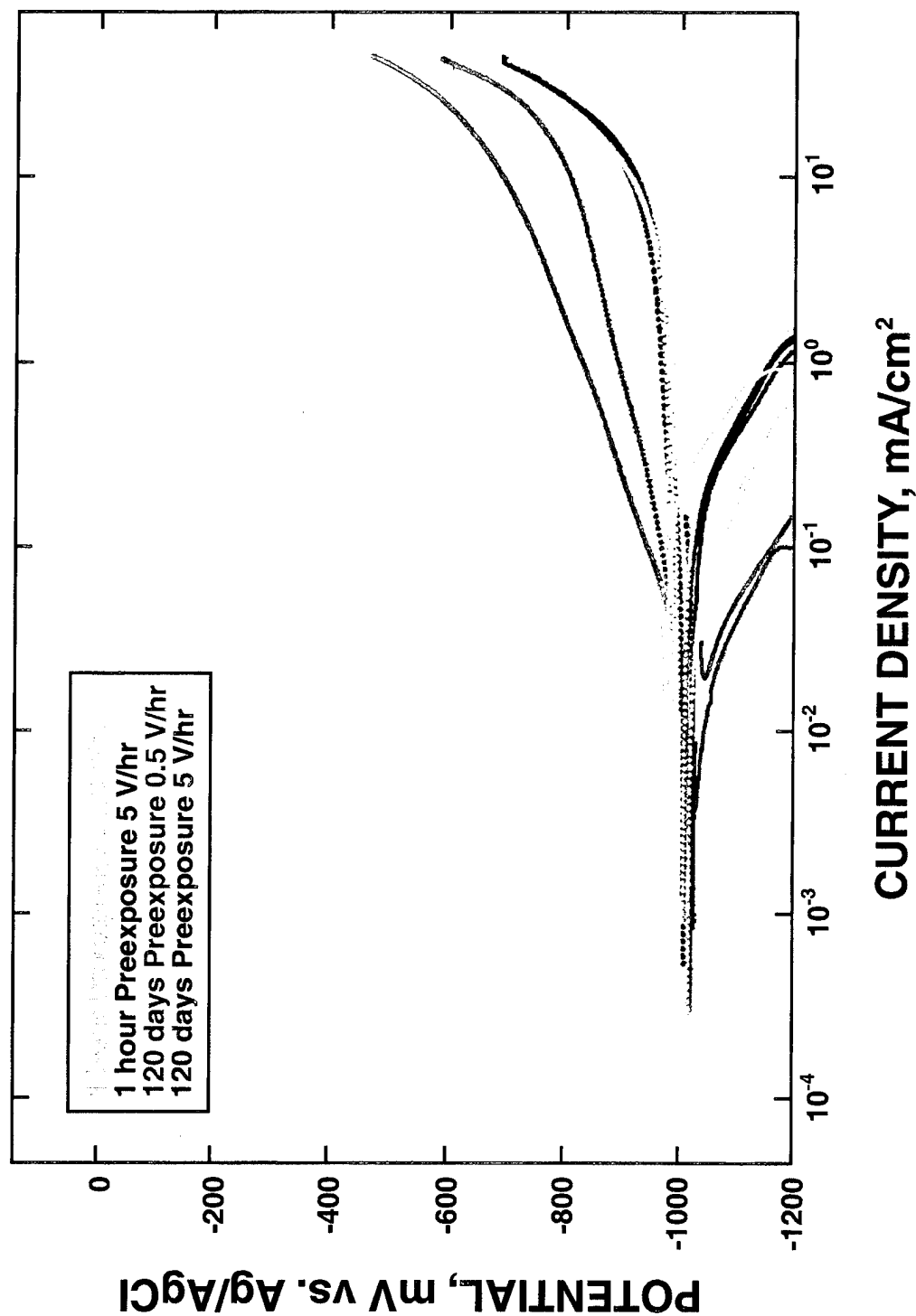
ANODE GRADE ZINC Quiescent Flow



(Potentiodynamic)

ANODE GRADE ZINC

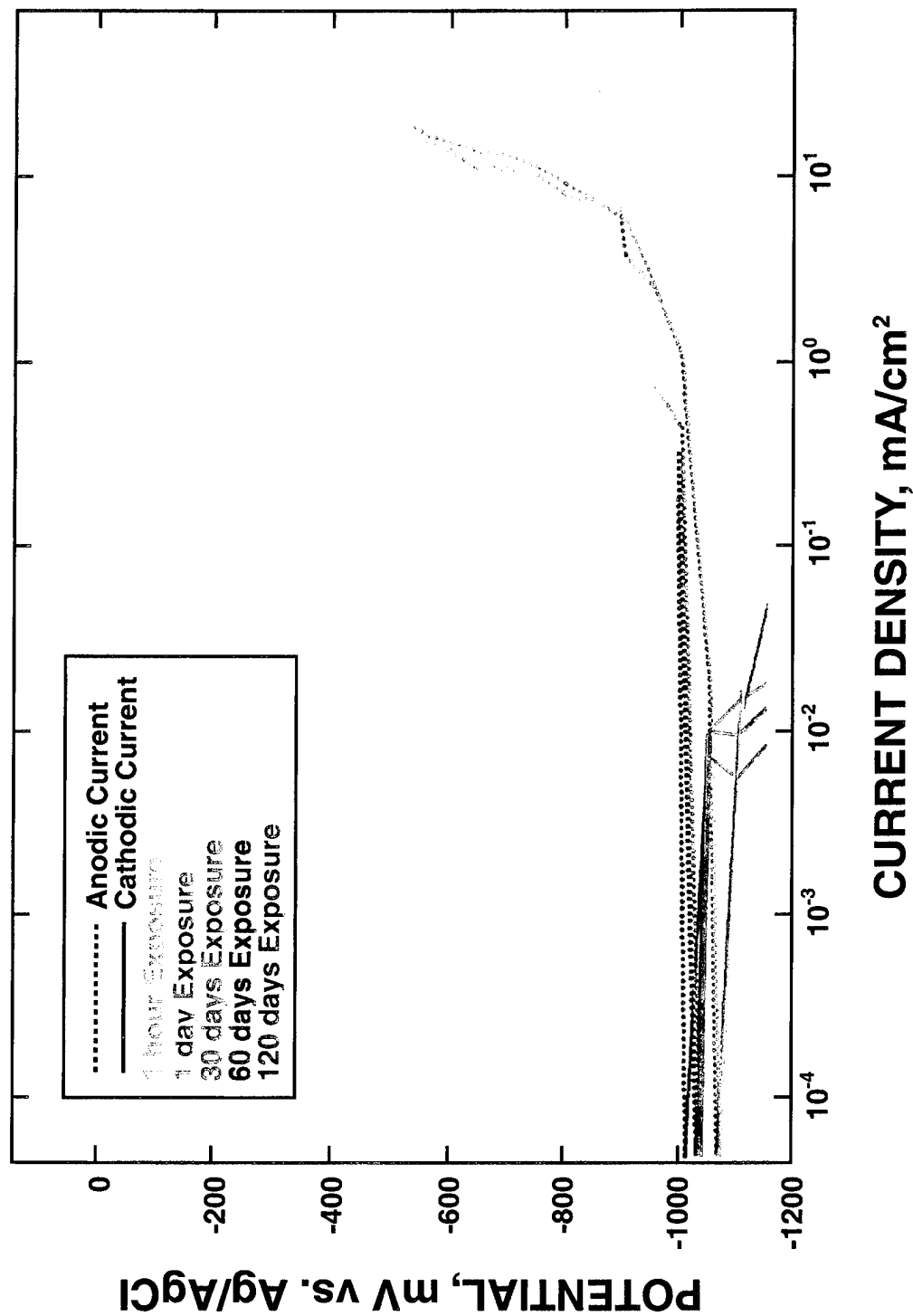
Flowing at 8.0 ft/s



(Potentiostatic)

ANODE GRADE ZINC

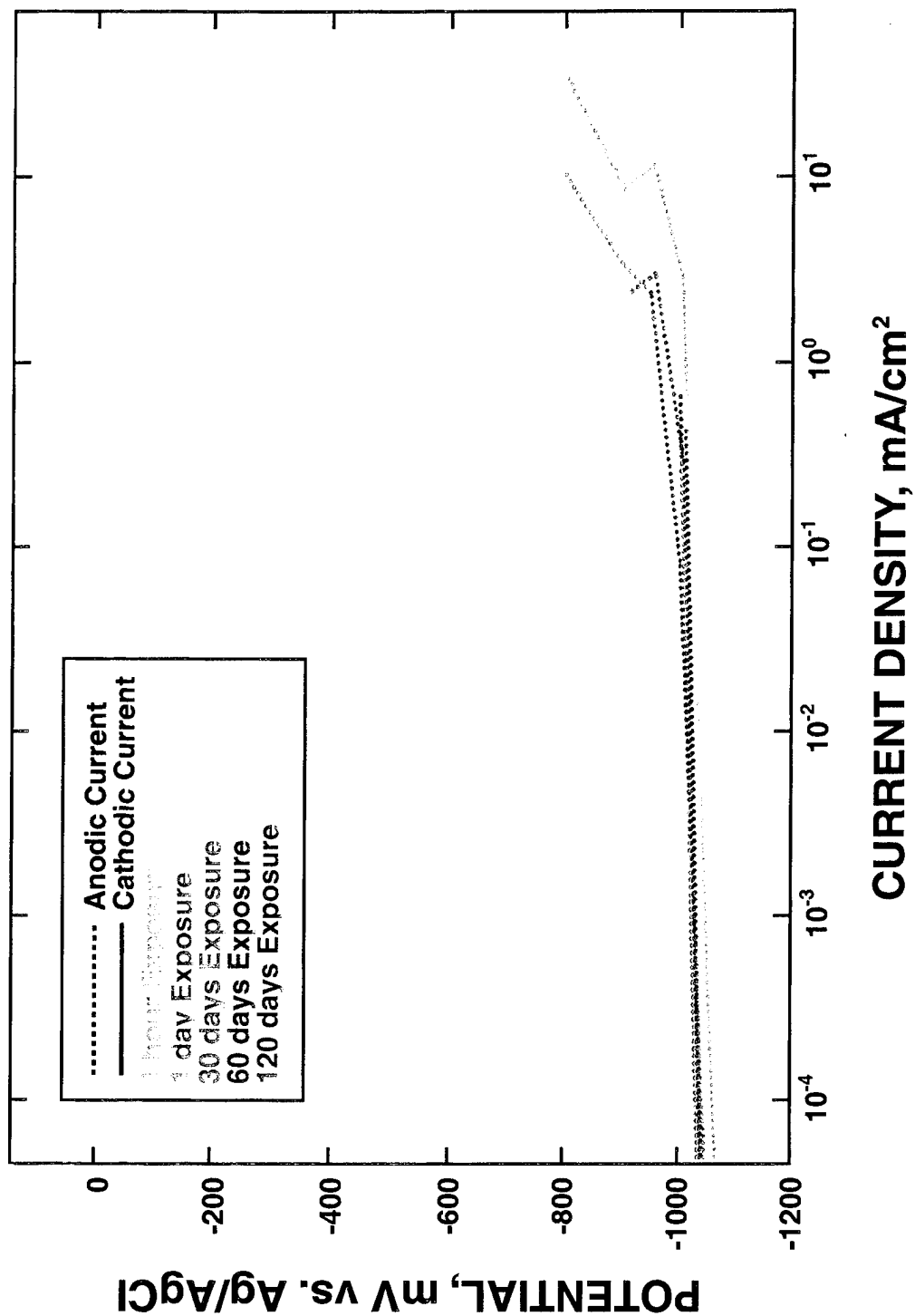
Quiescent Flow



(Potentiostatic)

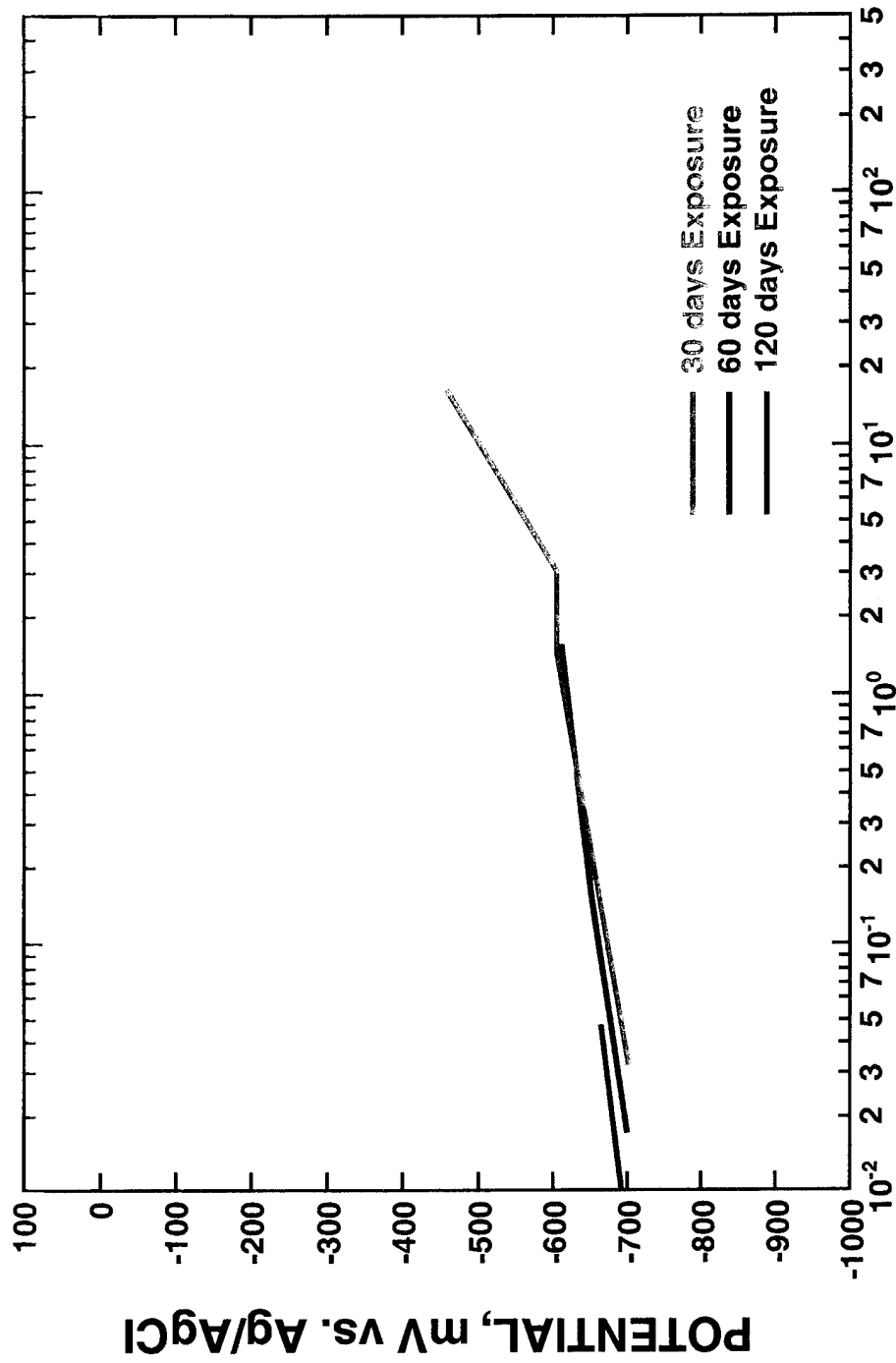
ANODE GRADE ZINC

Flowing at 8.0 ft/s



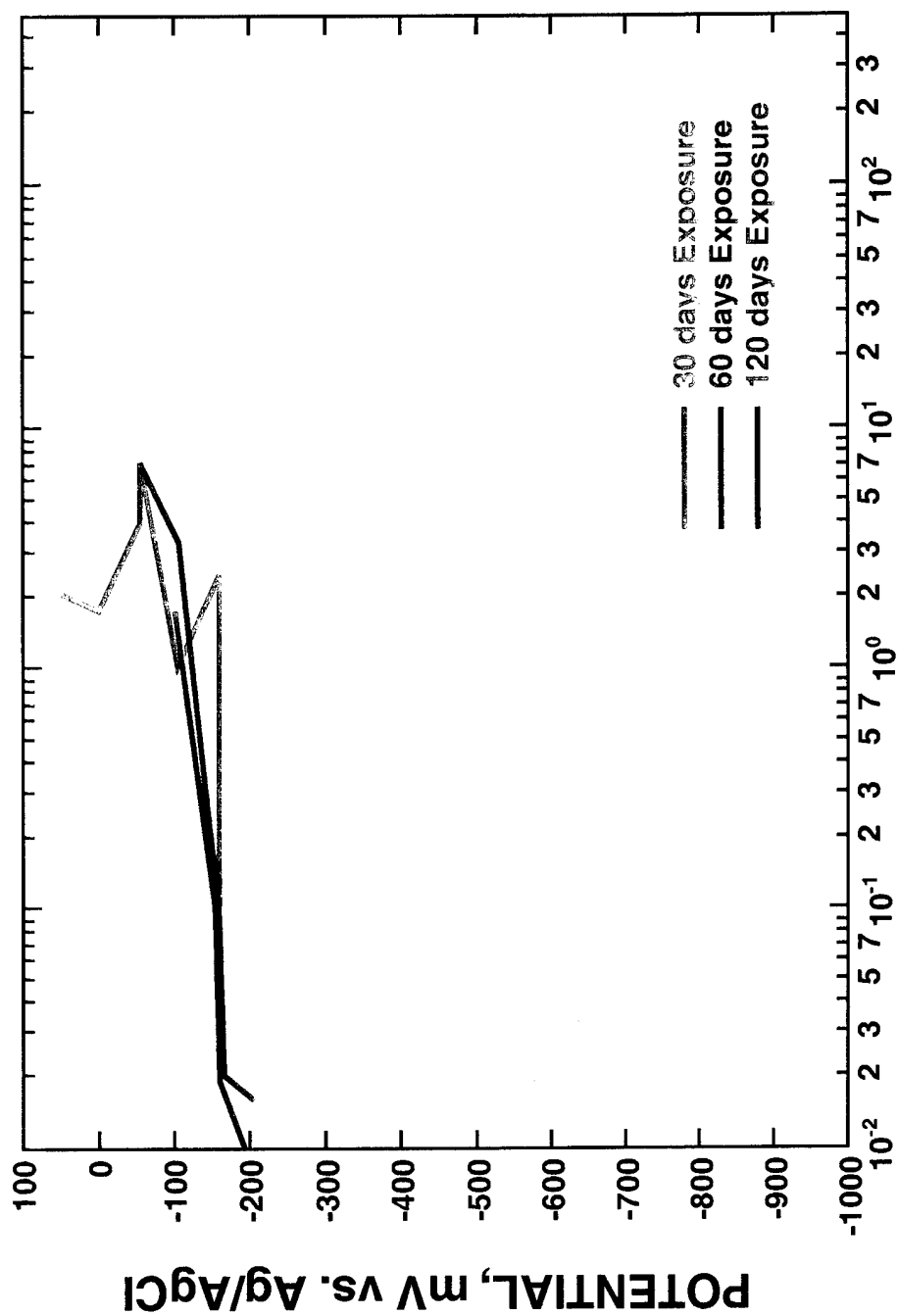
APPENDIX J
CORROSION RATES FROM POTENTIOSTATIC TESTS IN THIS STUDY

CORROSION OF HY-80 STEEL



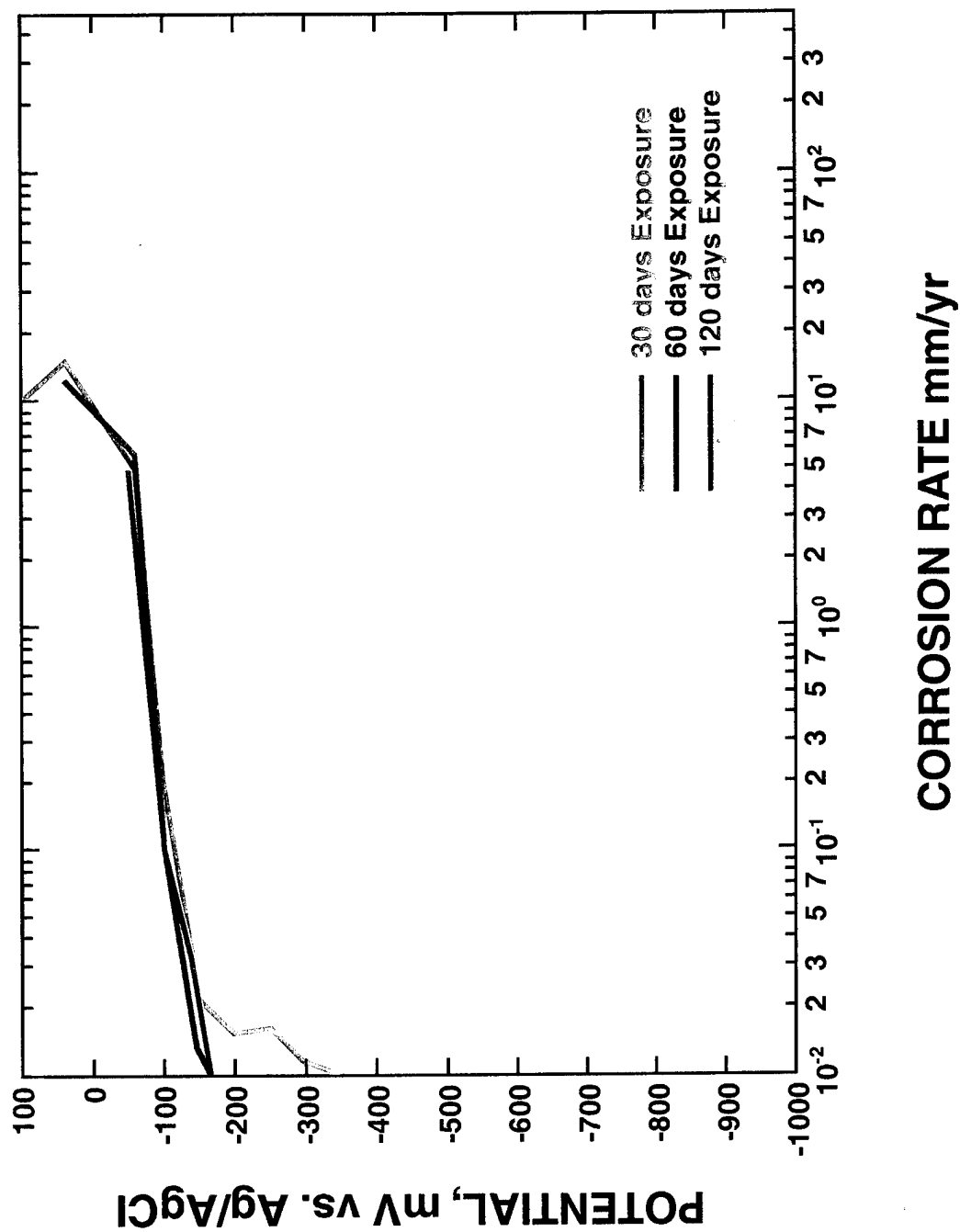
CORROSION RATE mm/yr

CORROSION OF 90 - 10 COPPER NICKEL

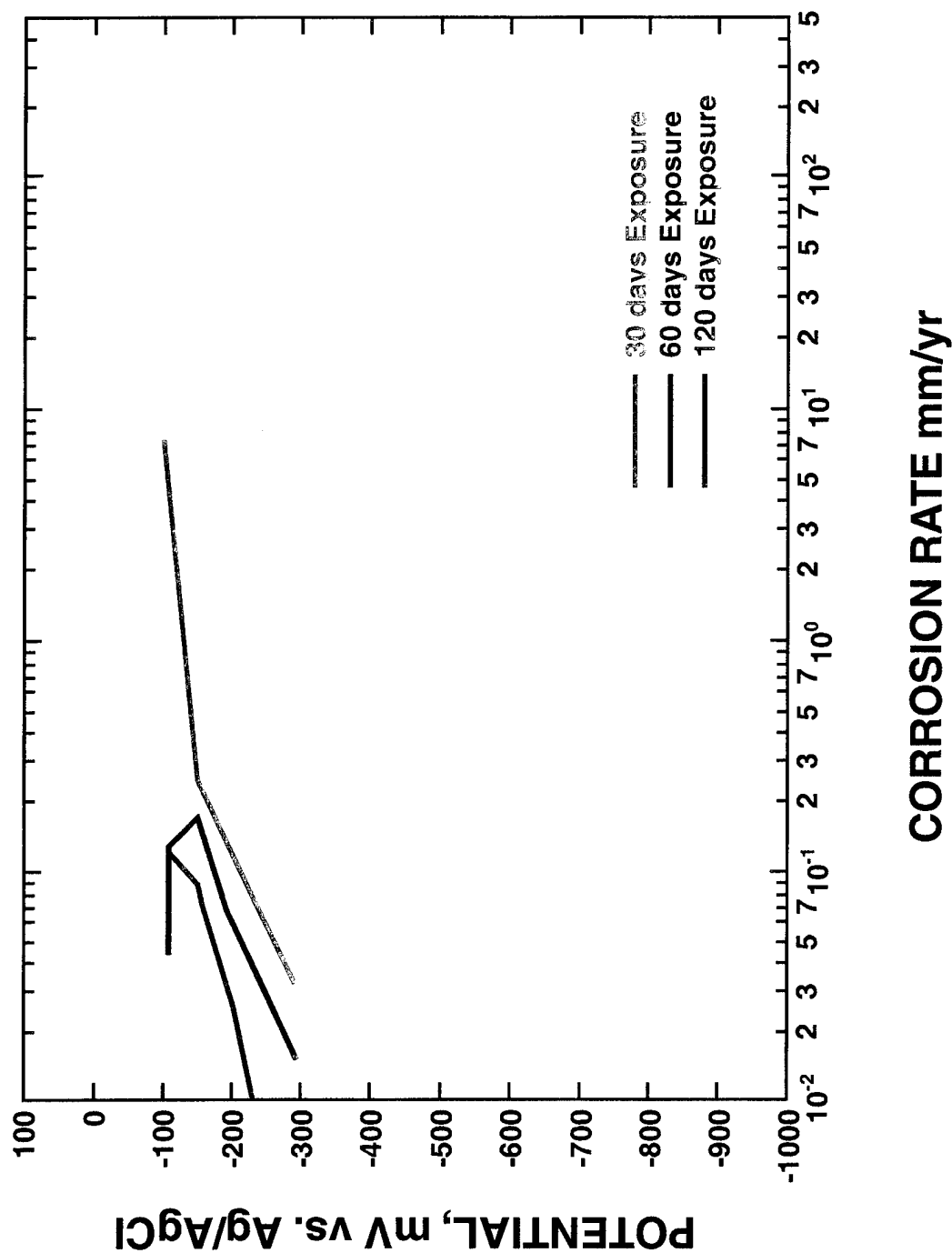


CORROSION RATE mm/yr

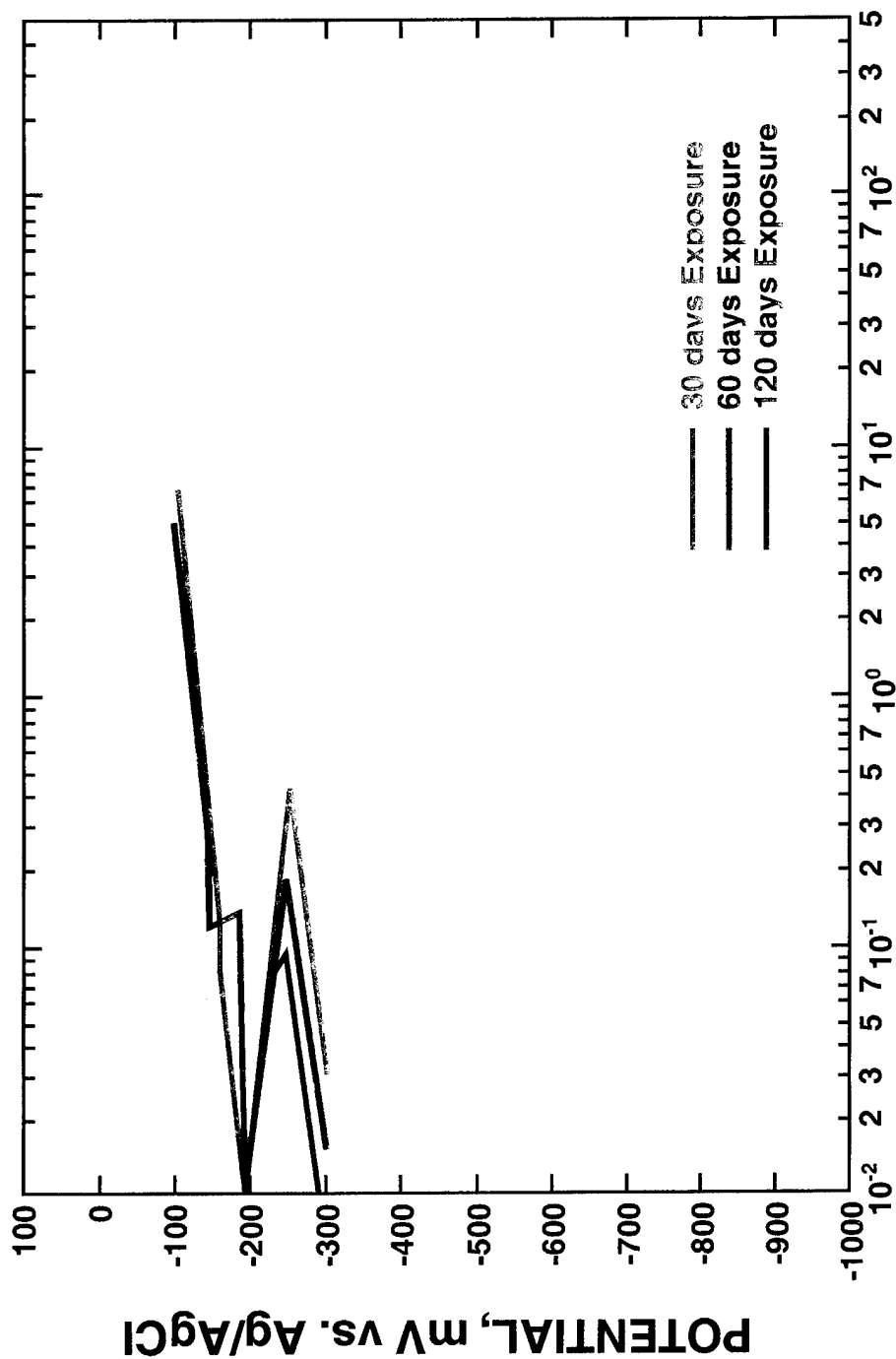
CORROSION OF 70 - 30 COPPER NICKEL



CORROSION OF M BRONZE

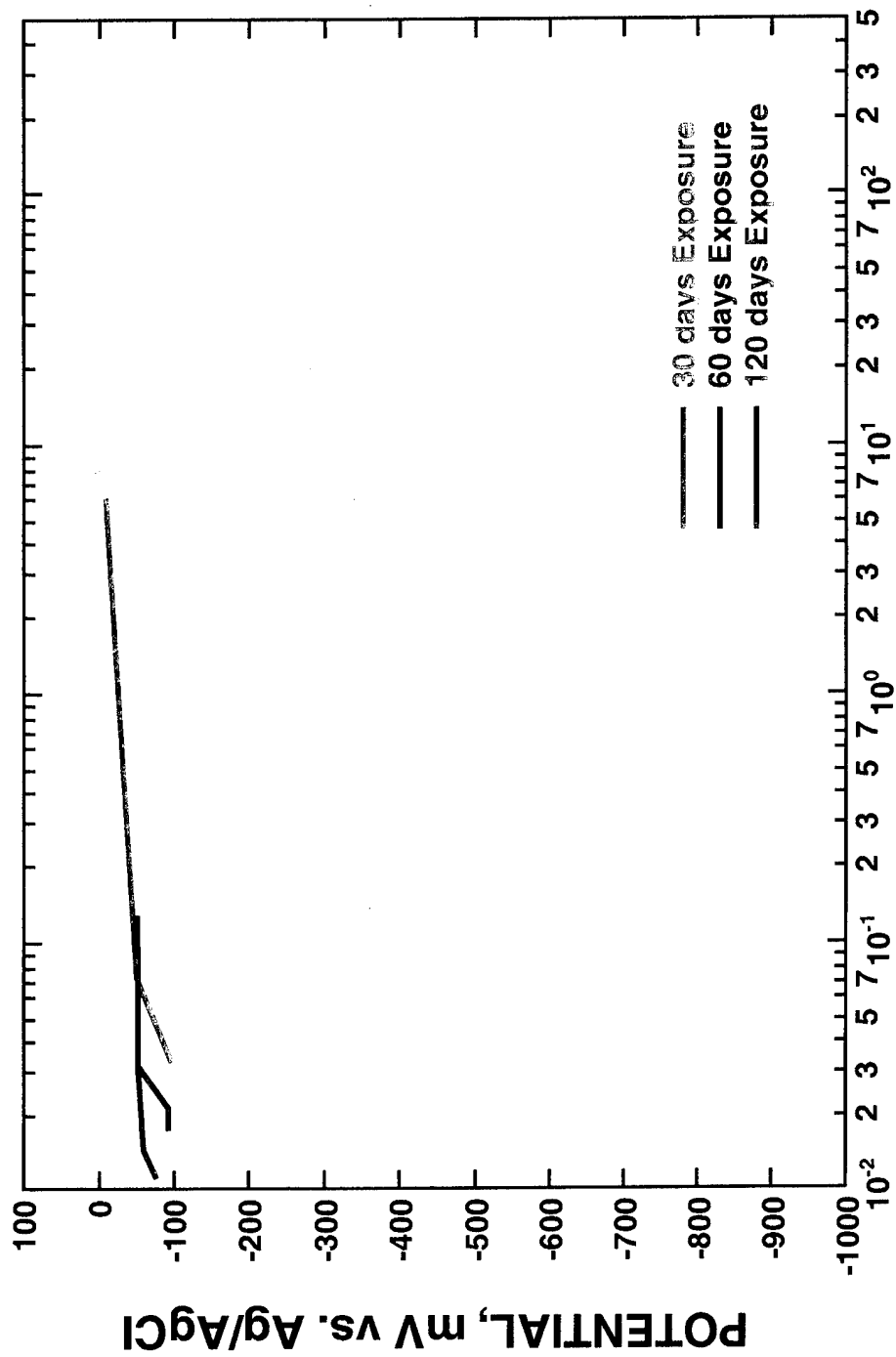


CORROSION OF Ni-Al-BRONZE



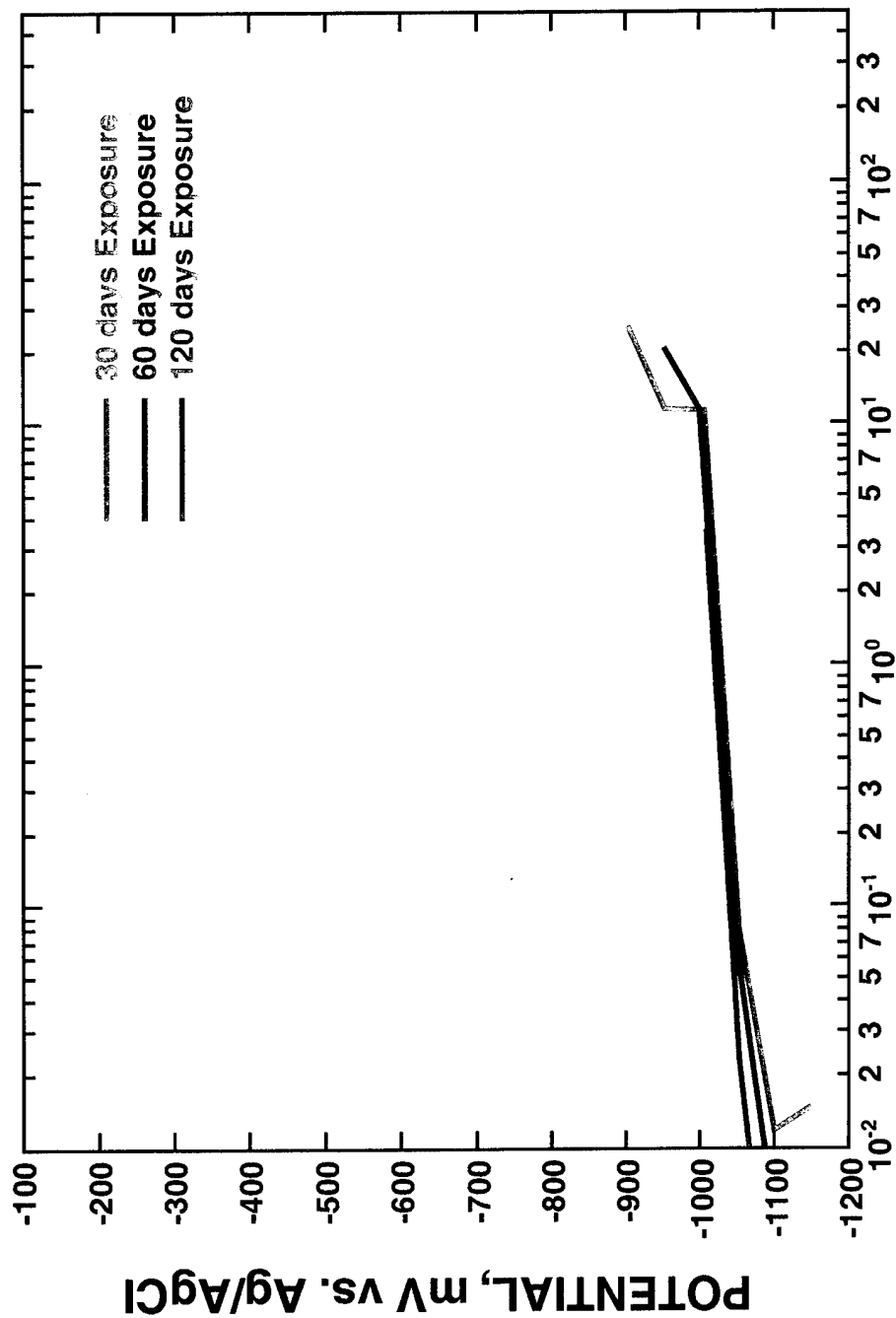
CORROSION RATE mm/yr

CORROSION OF MONEL 400



CORROSION RATE mm/yr

CORROSION OF ANODE GRADE ZINC

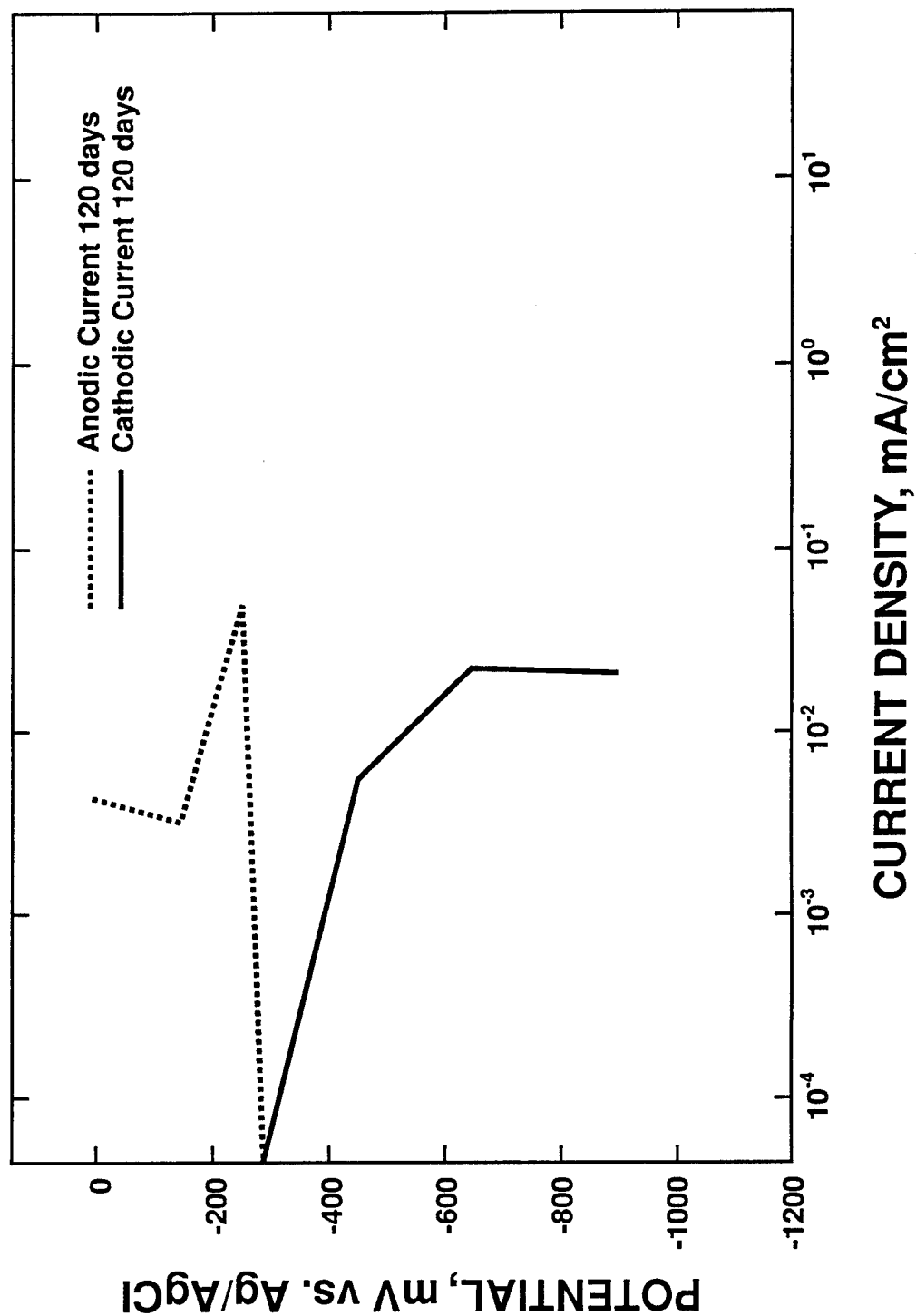


CORROSION RATE mm/yr

APPENDIX K
SMOOTHED POLARIZATION CURVES USED IN BOUNDARY ELEMENT STUDY

90 - 10 COPPER NICKEL

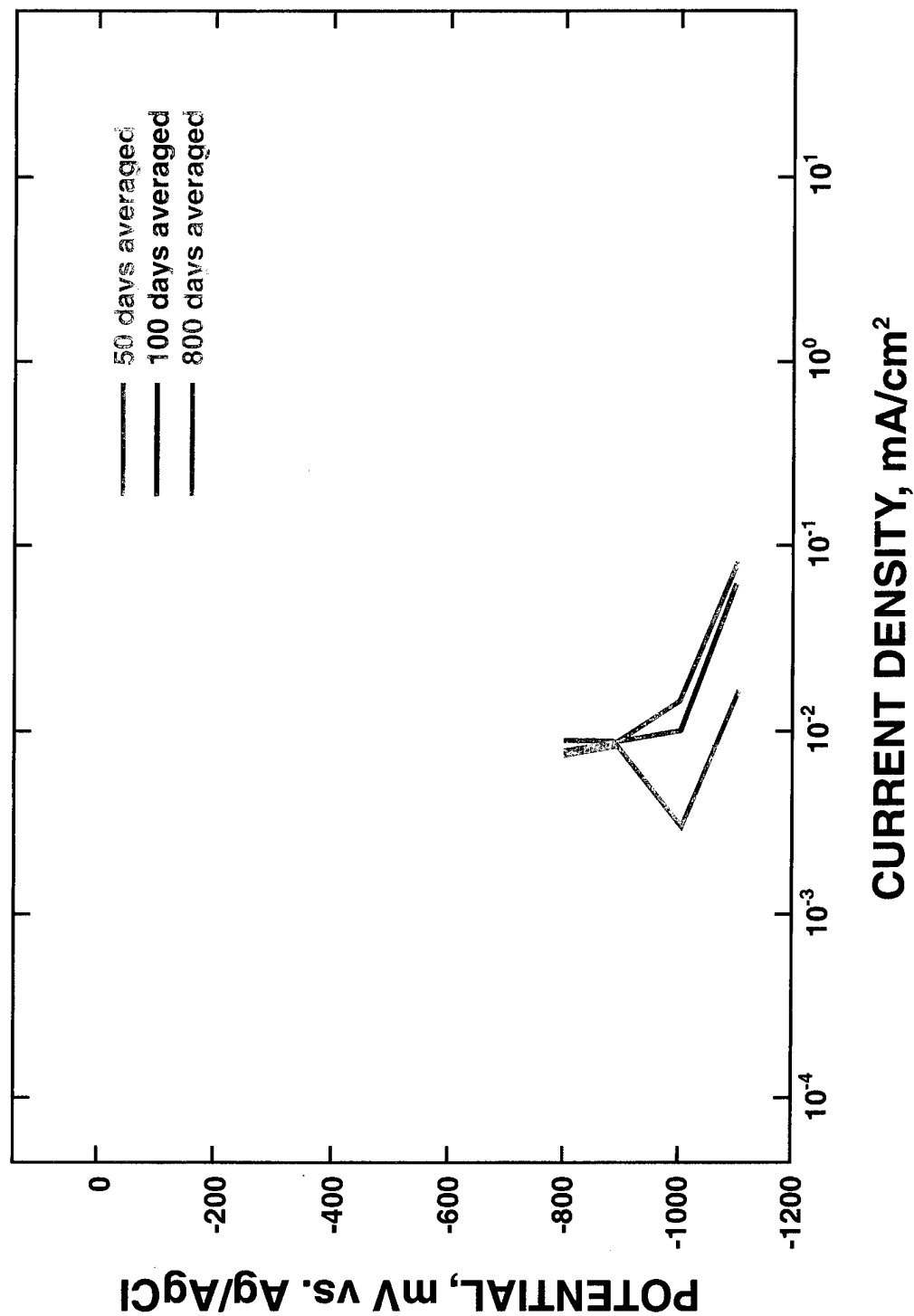
Quiescent Flow - Boundary Element Curve



APPENDIX L
FOSTER AND MOORES' 800-DAY POLARIZATION DATA

(Potentiostatic)

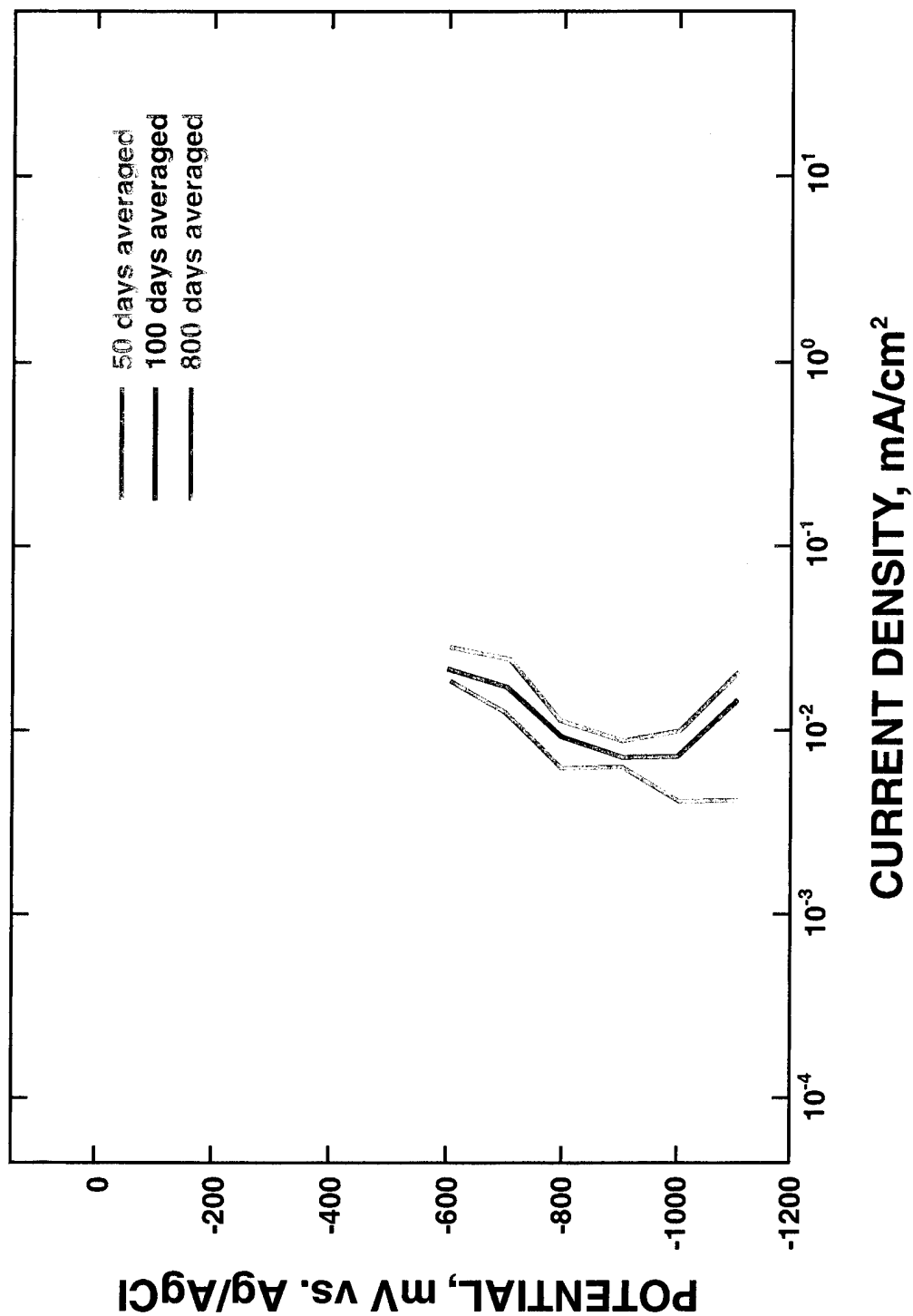
STEEL Quiescent Flow 9°C*



* after Foster and Moores

(Potentiostatic)

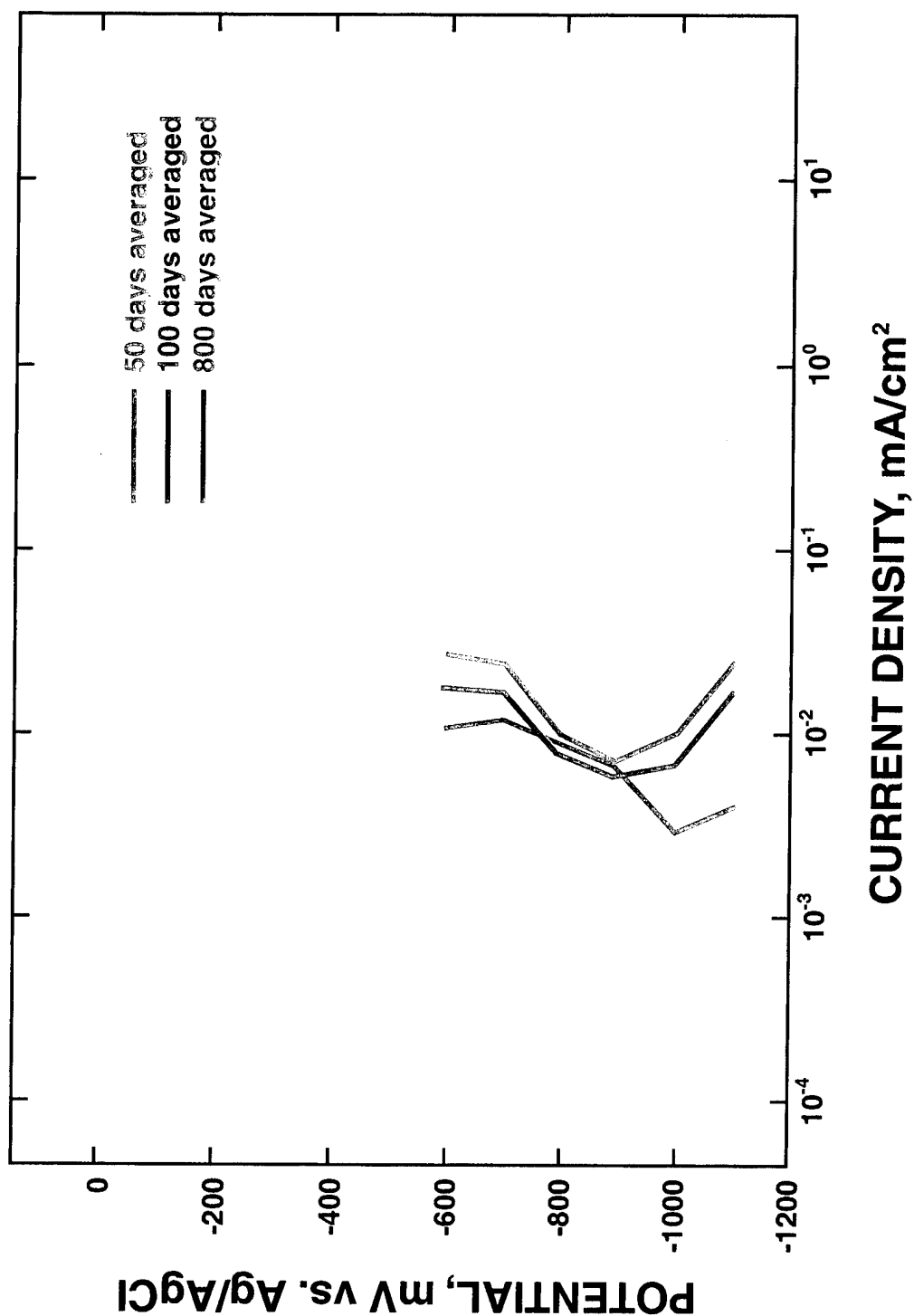
90 - 10 COPPER NICKEL Quiescent Flow 9°C*



* after Foster and Moores

(Potentiostatic)

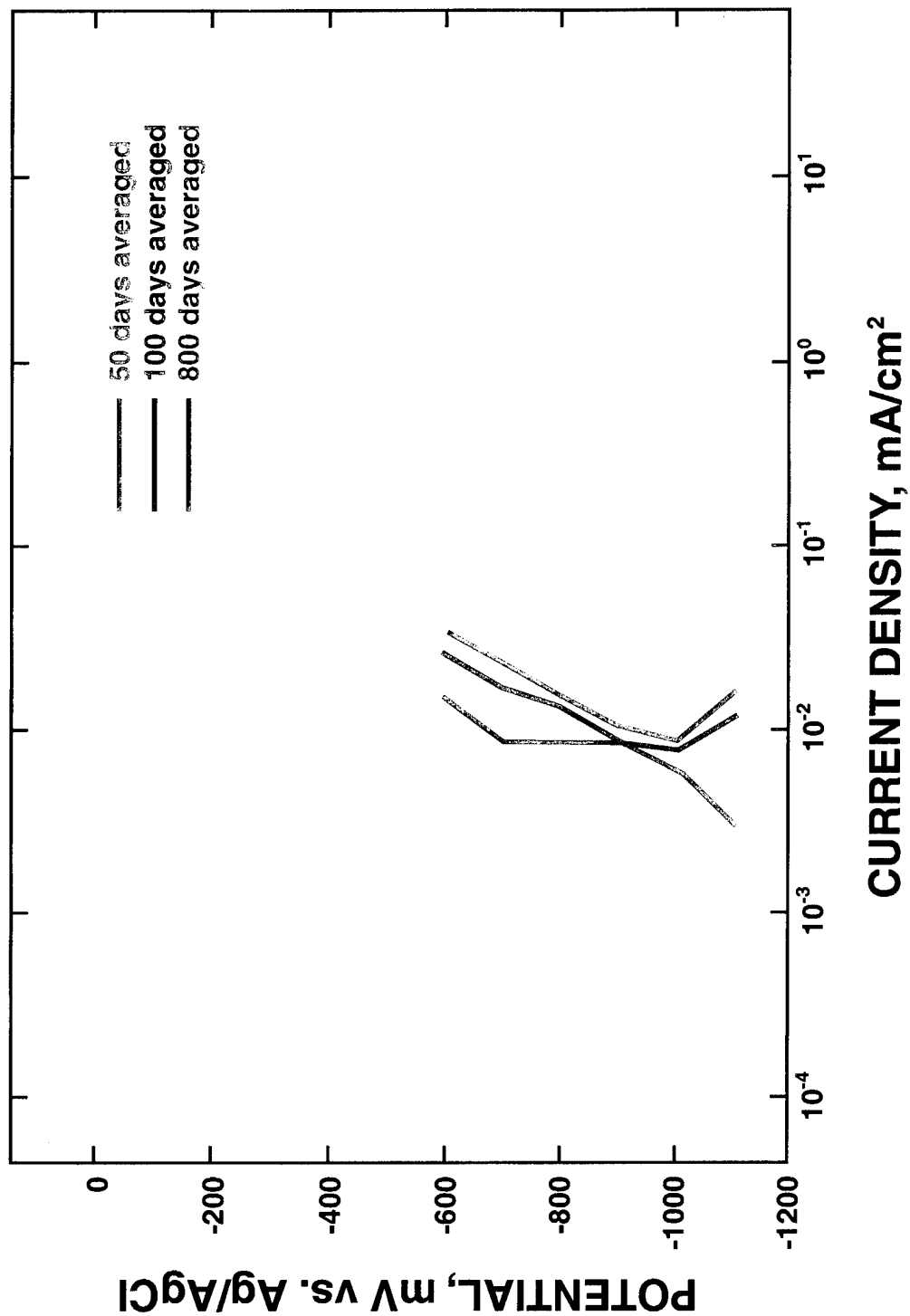
70 - 30 COPPER NICKEL Quiescent Flow 9°C*



* after Foster and Moores

(Potentiostatic)

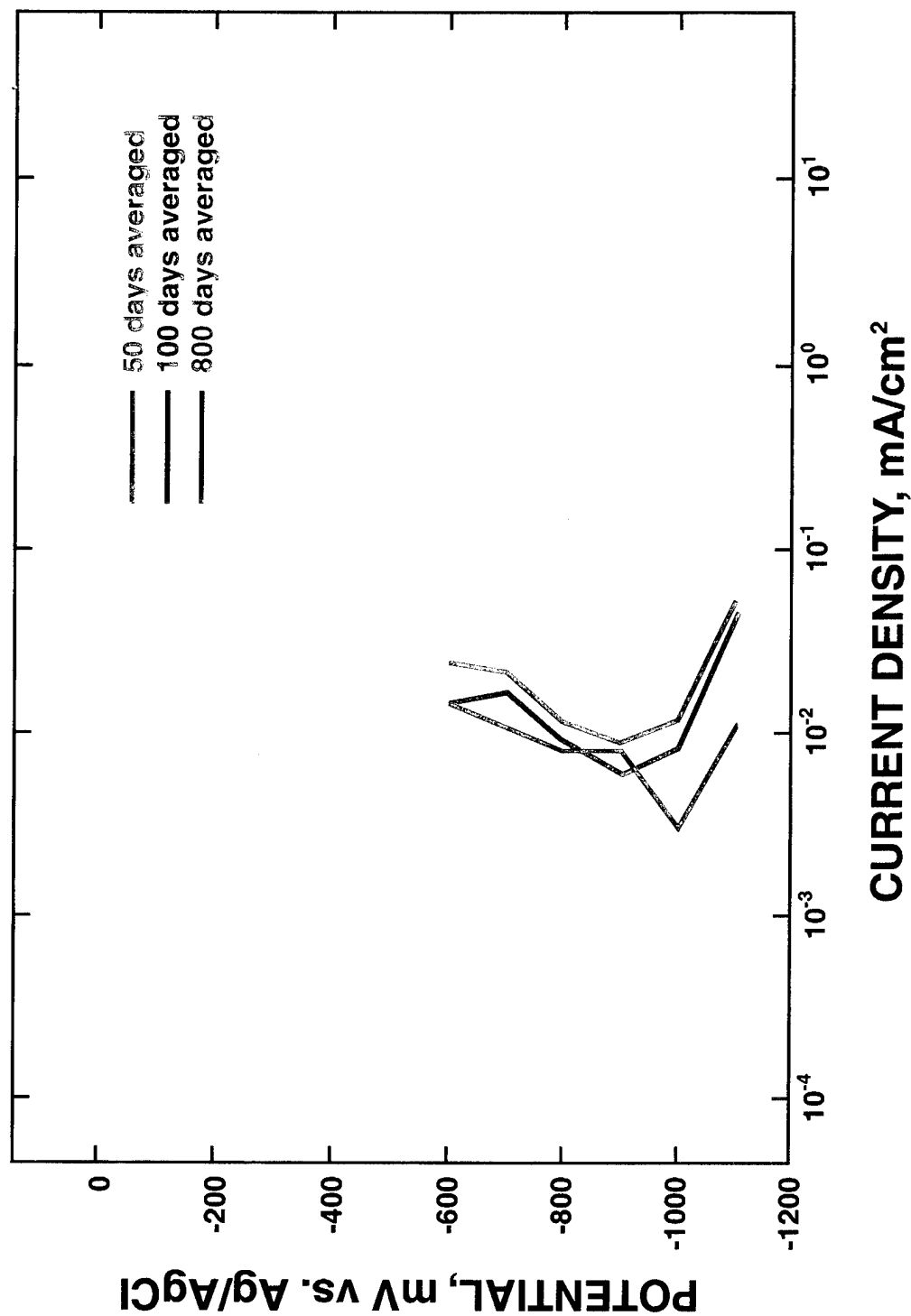
ALUMINUM BRONZE Quiescent Flow 9°C*



* after Foster and Moores

(Potentiostatic)

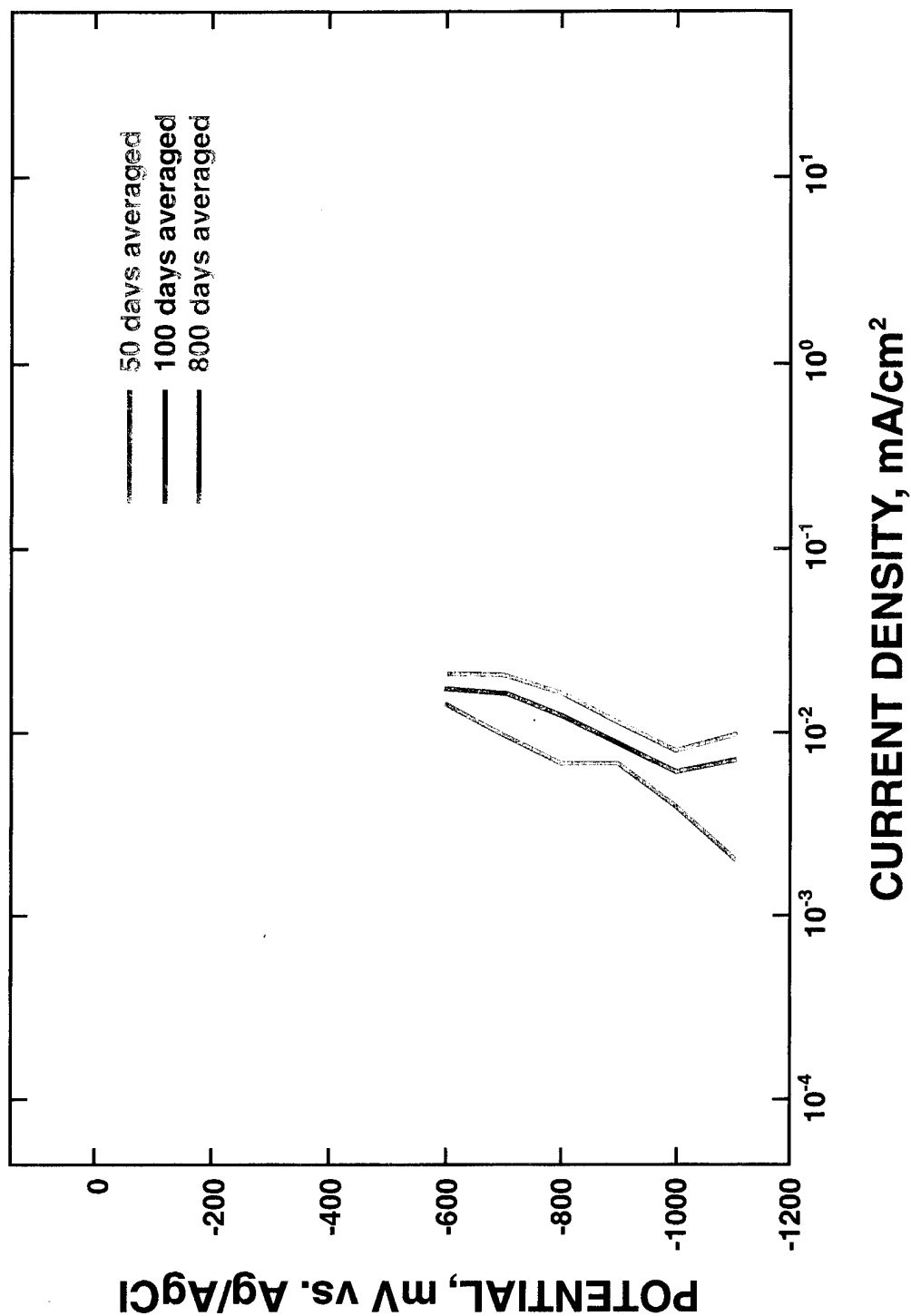
MONEL Quiescent Flow 9°C*



* after Foster and Moores

(Potentiostatic)

TITANIUM Quiescent Flow 9°C*

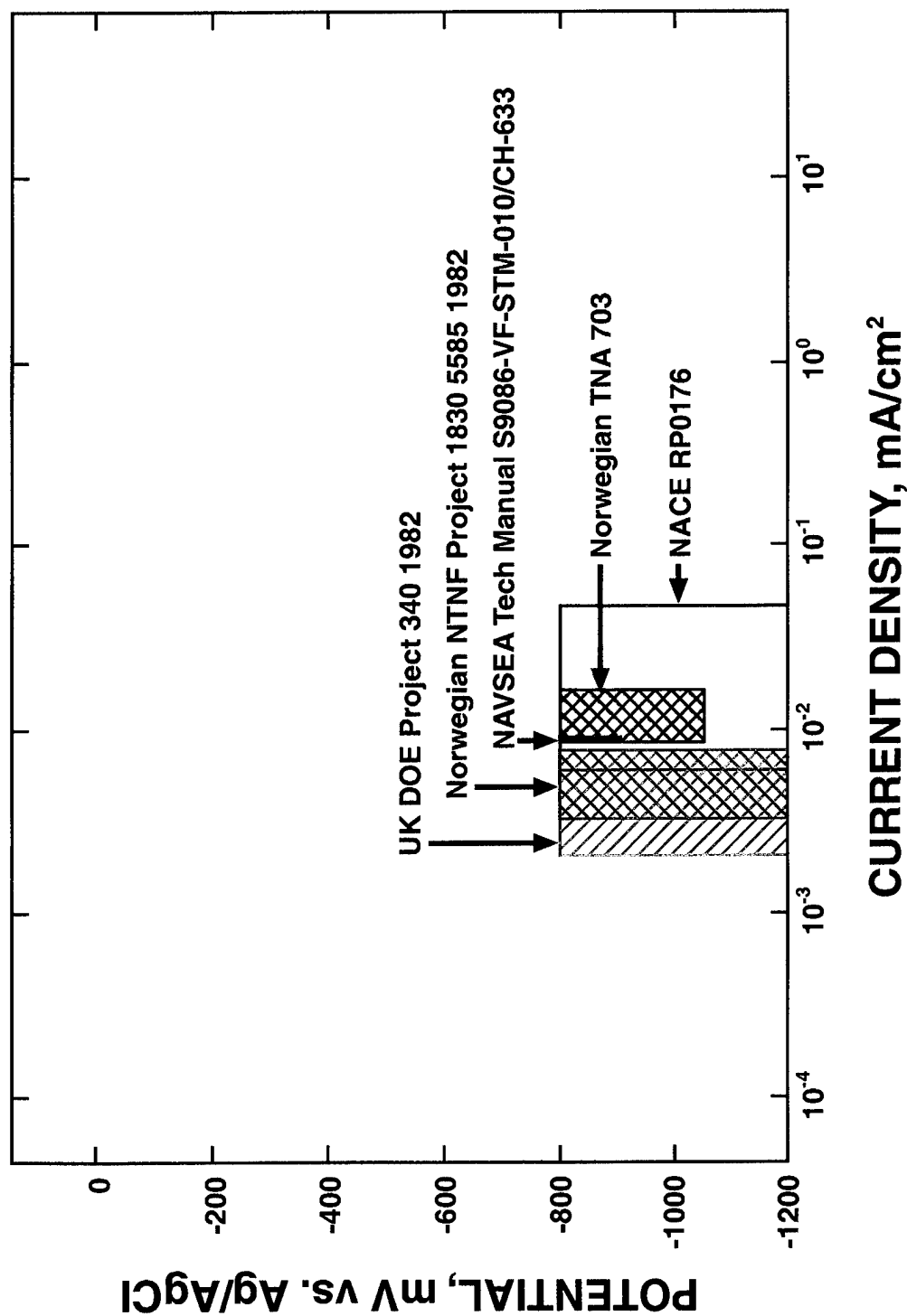


* after Foster and Moores

APPENDIX M
CATHODIC PROTECTION DESIGN DATA FOR STEEL

STEEL

Design Guidelines for Cathodic Protection*



* after Wyatt

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 1995		3. REPORT TYPE AND DATES COVERED Final
4. TITLE AND SUBTITLE Atlas of Polarization Diagrams for Naval Materials in Seawater			5. FUNDING NUMBERS Program Element 62761N Task Area SF61541-591 Work Units 1-2803-162; 1-2803-164	
6. AUTHOR(S) Harvey P. Hack				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Carderock Division Naval Surface Warfare Center Bethesda, Md. 20084-5000			8. PERFORMING ORGANIZATION REPORT NUMBER CARDIVNSWC-TR-61-94/44	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, Va. 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Polarization curves were developed in seawater at low (quiescent) flow and at 2.4 m/s flow for nine structural alloys. Potentiostatically generated curves for up to 120 days are compared with potentiodynamically generated curves at four scan rates with freely corroding pre-exposures of 1 or 120 days. Smoothed curves successfully used in computer model predictions of cathodic protection current and potential distributions are also presented. These curves are compared with previously published data available for 800 days exposure and with cathodic protection current density design guidelines. Corrosion rate data as a function of potential after up to 120 days exposure are also presented.				
14. SUBJECT TERMS Polarization curves, Seawater, Cathodic protection, Galvanic corrosion, Corrosion rate, Corrosion, Computer modeling, Stray current corrosion, Steel, Copper-nickel, Bronze, Titanium, Alloy 625, Zinc			15. NUMBER OF PAGES 162	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Same as Report	