NASA
Technical
Memorandum

NASA TM-86531

THE APPLICATION OF DIFFUSION THEORY TO THE
ANALYSIS OF HYDROGEN DESORPTION DATA AT 25°C

By Merlin D. Danford
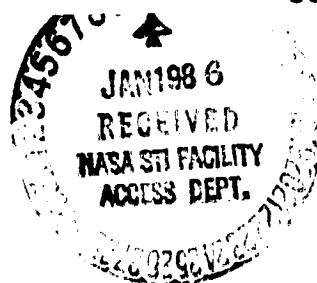
Materials and Processes Laboratory

October 1985

NASA

National Aeronautics and
Space Administration

George C. Marshall Space Flight Center

1. REPORT NO. NASA TM - 86531	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
4. TITLE AND SUBTITLE The Application of Diffusion Theory to the Analysis of Hydrogen Desorption Data at 25°C		5. REPORT DATE October 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Merlin D. Danford		8. PERFORMING ORGANIZATION REPORT #
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, AL 35812		10. WORK UNIT NO.
		11. CONTRACT OR GRANT NO.
		13. TYPE OF REPORT & PERIOD COVERED
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546		Technical Memorandum
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

Prepared by Materials and Processes Laboratory, Science and Engineering Directorate.

16. ABSTRACT.

The application of diffusion theory to the analysis of hydrogen desorption data (coulombs of H_2 desorbed versus time) has been studied. From these analyses, important information concerning hydrogen solubilities and the nature of the hydrogen distributions in the metal has been obtained. Two nickel base alloys, Rene' 41 and Waspaloy, and one ferrous alloy, 4340 steel, were studied in this work. For the nickel base alloys, it was found that the hydrogen distributions after electrolytic charging conformed closely to those which would be predicted by diffusion theory. For Waspaloy samples charged at 5,000 psi, it was found that the hydrogen distributions were essentially the same as those obtained by electrolytic charging. The hydrogen distributions in electrolytically charged 4340 steel, on the other hand, were essentially uniform in nature, which would not be predicted by diffusion theory. A possible explanation has been proposed. Finally, it has been found that the hydrogen desorption is completely explained by the nature of the hydrogen distribution in the metal, and that the "fast" hydrogen is not due to surface and sub-surface hydride formation, as was originally proposed.

17. KEY WORDS Electrochemical Methods Diffusion Theory Hydrogen Uptake Hydrogen Desorption Correlation of Experiment with Theory	18. DISTRIBUTION STATEMENT Unclassified — Unlimited

19. SECURITY CLASSIF. (of this report) Unclassified	20. SECURITY CLASSIF. (of this page) Unclassified	21. NO. OF PAGES 26	22. PRICE NTIS

MSFC - Form 3292 (May 1969)

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

TECHNICAL MEMORANDUM

THE APPLICATION OF DIFFUSION THEORY TO THE ANALYSIS OF HYDROGEN DESORPTION DATA AT 25°C

INTRODUCTION

This study was directed toward the development of theoretical methods and their application to the explanation of experimental results concerning the uptake and elimination of gaseous hydrogen at ambient temperatures by high strength alloys. It is part of a broad program aimed toward an understanding of the nature of hydrogen embrittlement. Only the concentrations and behavior of the mobile or diffusable hydrogen were studied in the present work, the experimental information being obtained by electrochemical methods which are very sensitive to the small hydrogen concentrations obtained through charging at 25°C. Further work will include study of both the mobile and trapped hydrogen, but, obviously, trapped hydrogen cannot exist at sample depths greater than those permitted by the overall hydrogen penetration.

Solutions of the Fick Law for diffusion in the X direction were employed for flat samples, with all calculations being performed with computer programs written in the FORTRAN language. Both the exact analytical solutions to the diffusion equations, obtained as given by Barrer [1], and numerical methods, as used by the computer program PDEONE [2], were investigated. The analytical methods were employed because of their greater speed of computation and greater versatility. Comparison of the analytical and numerical methods gave almost exactly the same numerical results.

THEORETICAL METHODS

Hydrogen Absorption

All of the diffusion equations employed in this work have been described by Barrer [1]. When a slab is initially free of solute, the concentration at the faces are C_1 (at $X = 0$) and C_2 (at $X = L$), one has the example of diffusion of gas into a membrane of solid free of gas. For the present case, $C_1 = C_2$ and the expression for the mean hydrogen concentration in the sample after a charging time t is given by the series

$$\bar{C} = C_1 \left[1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left\{ \frac{-D(2m+1)^2 \pi^2 t}{L^2} \right\} \right] \tag{1}$$

where L is the sample thickness and D is the hydrogen diffusion coefficient. A plot of $\bar{C}$ versus t, with $L = 0.232$ cm and $D = 4.3 \times 10^{-8}$ cm^2/sec, with $C_1 = 1.0$ ppm,

is shown in Figure 1.   Twenty-five iterations were found to be sufficient for solution of all diffusion equations. For concentration profiles, C(x) versus x, the following equation was used:

$$C(x) = S + \frac{2S}{\pi} \sum_{m=1}^{\infty} \frac{(\cos m\pi - 1)}{m} \frac{\sin \frac{m\pi x}{L}}{} \exp\left[\frac{-Dm^2\pi^2 t}{L^2}\right] \qquad (2)$$

where S is the solubility of hydrogen in the metal at a given temperature and pressure and x is depth in the sample. The mean concentration is given by:

$$\overline{C} = \frac{\int_0^L C(x)dx}{L} \qquad (3)$$

The concentration of hydrogen at the sample surfaces is immediately established at the solubility limit S for a given temperature and pressure or charging rate in the case of electrolytically charged samples. In practice the solubility S is obtained by dividing the mean (observed) hydrogen concentration by the value calculated by equation (1) for a given charge time with surfaces at unit concentration. The hydrogen concentrations versus sample depth can then be obtained using equation (2), with the mean hydrogen concentration, as obtained using equation (3), being identically equal to the observed concentration. A plot of C(x) versus X is shown in Figure 2 for a Waspaloy sample charged for 1 hr at 5,000 psi (25°C). As seen from Figure 2, penetration into the sample is appreciable, the depth of penetration being almost 0.3 mm. The solubility obtained was 1.82 ppm, with the mean concentration, as obtained by equation (3) being 0.156 ppm, the observed hydrogen concentration. Thus, the type of curve predicted by diffusion theory is that illustrated in Figure 2, and will be referred to as a non-uniform distribution. A uniform distribution type, where the hydrogen concentration versus depth is constant, is illustrated in Figure 3, with a constant hydrogen concentration of 0.156 ppm. Such distributions would not be predicted by diffusion theory except after a very long charging time.

Hydrogen Desorption

Hydrogen desorption is appreciable at room temperature for both the nickel base alloys and the 4340 steel included in this study. It is a quantity easily measured by sensitive methods, such as the EG&G-PARC corrosion measurement console, and provides important information concerning the hydrogen distribution in the metal after charging. For desorption problems, it is assumed that the concentration of hydrogen at the sample surfaces is zero for all time. The general equation for hydrogen desorption is:

$$C(x,t) = \frac{2}{L} \sum_{m=1}^{\infty} \sin \frac{m\pi x}{L} \exp\left[\frac{-Dm^2\pi^2 t}{L^2}\right] \int_0^L f(x') \sin \frac{m\pi x'}{L} dx' \qquad (4)$$

2

where t is the desorption time in seconds. For a non-uniform initial distribution, or that predicted by diffusion theory, the values of $f(x')$ are those calculated by equation (1) for a given charge time. The amount of hydrogen desorbed after a time t is given by:

$$Q(t) = Q_{HM}^{\infty} - 0.0957341d \int_{0}^{L} C(x,t) \, dx \quad .$$
(5)

Here, d is the metal density, and the conversion factor is that necessary to convert from ppm-cm to coulombs/cm^2. Q_{HM}^{∞} is the total amount of hydrogen initially contained in the sample, and is measured experimentally. It is obtained as described by Zakroczymski [3]. For a uniform initial distribution, where the membrane contains a uniform concentration of hydrogen (C_o) throughout, $C(x,t)$ is given by:

$$C(x,t) = \frac{4C_o}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \sin \frac{(2m+1)\pi X}{L} \exp \left[\frac{-D(2m+1)^2 \pi^2 t}{L^2} \right]$$
(6)

and the total amount of hydrogen desorbed after time t is again given by equation (5). In practice, $Q(t)$ versus t is measured experimentally through measurement of the current due to hydrogen desorption as a function of time, with $Q(t)$ being obtained by integration of the current-time curve. Q_{HM}^{∞} is the total amount of hydrogen desorbed after correction for cut-off at a finite time. The nature of the hydrogen distribution in the sample can be determined by fitting theoretical curves for non-uniform or uniform distributions, or a combination thereof, to the experimental curve. A typical case is illustrated in Figure 4 for 4340 steel charged electrolytically at 60 ma/cm^2 for 1 hr. The curves are those calculated after a 10,000 sec desorption time. Curves are shown for non-uniform and uniform initial distributions, with a hybrid curve representing a 59.2 percent uniform distribution, the observed quantity, also shown.

EXPERIMENTAL

The EG&G-PARC Model 350A corrosion measurement console was employed for all measurements in this work. The sample holder employed is shown in Figure 5. It presents a sample area of 1.0 cm^2 in contact with the solution in the electrolytic cell, in this case 0.1N NaOH. Samples of Waspaloy from two different sources were used. One sample was cut from a 1.27 cm (0.5 in.) diameter Waspaloy bolt on hand in the laboratory, while the other was cut from a used turbine disk, part S/N 2279525, obtained from a Space Shuttle Main Engine. The samples were essentially of the same composition and differed only in the method of preparation (heat treatment, etc.). Samples of Rene' 41 were used as obtained (annealed) without heat treatment. The 4340 steel samples were heat treated to an ultimate tensile strength of 260,000 to

280,000 psi. All samples except that from the Waspaloy bolt were 1.59 cm (5/8 in.) in diameter, with an average thickness of about 0.200 cm.

The samples were prepared by wet sanding with 150C and 220A grit silicon carbide paper and de-greasing in boiling trichloroethylene. Sample blanks were run at a constant potential of ±0.25 V (NHE) in a 0.1N NaOH solution at 25°c. The period of measurement was 150,000 sec for each sample, with the value of the current being recorded at 500 sec intervals.

Samples of all three materials were electrolytically charged with hydrogen in 0.1N H_2SO_4 at two different charge rates, 60 ma/cm^2 and 1 ma/cm^2. In addition, two samples of Waspaloy, one from the Waspaloy bolt described previously and the other from turbine disk part S/N 2279525, were charged with hydrogen gas at a pressure of 5,000 psi at 25°C. Data for the hydrogen-containing samples were collected in the same manner as those for the blanks, with the currents due to hydrogen being obtained by subtraction.

After each run, the current versus time data were read to a computer and saved. After data from both the hydrogen containing sample and its corresponding blank were obtained, the experimental curve, Q(t) versus time, was obtained by integration of the current-time curves corresponding to the current due to hydrogen only. Values of Q_H^∞, Q_{HM}^∞, the observed concentration (C_o) and the diffusion coefficient for hydrogen (D) were obtained according to the method developed by Zakroczymski [3], and described in a previous report [4].

RESULTS AND DISCUSSION

The solubilities of hydrogen in the Rene' 41, Waspaloy and 4340 steel samples for electrolytically charged samples are shown in Table 1. As seen from the table, the solubility depends on the charge rate, being lower for the slow charge rates. This is analogous to the case for samples charged with high pressure hydrogen, where the solubility depends on the hydrogen pressure. The solubilities are about the same for the nickel-base alloys, Rene' 41 and Waspaloy, but are higher for a factor of about 4 for 4340 steel, which is known to be highly susceptible to hydrogen embrittlement [5]. The hydrogen distributions in the samples, both for high pressure charging and electrolytic charging, will be discussed separately for each metal. In all cases, theoretical curves for coulombs of hydrogen desorbed versus time will be shown for both uniform and non-uniform initial hydrogen distributions along with the curves for a hybrid distribution, if necessary, and the experimentally observed curve.

Electrolytically Charged Rene' 41

The desorption curves for a Rene' 41 sample charged for 4 hr at a rate of 1 ma/cm^2 are shown in Figure 6 and those for a sample charged for 1 hr at 60 ma/cm^2 in Figure 7. As seen from these figures, the hydrogen distribution in both cases is described very well by a non-uniform distribution which is in accord with diffusion theory.

4

Electrolytically Charged Waspaloy

The desorption curves for electrolytically charged Waspaloy at charge rates of 1 ma/cm^2 and 60 ma/cm^2, respectively, are shown in Figures 8 and 9. As shown in Figure 8, the desorption curve for the slow charge rate is described very well by a theoretical curve corresponding to a 100 percent non-uniform distribution. For the sample charged at 60 ma/cm^2, the experimental curve is best described by a hybrid curve, corresponding to a 10.2 percent uniform distribution, as shown in Figure 9. Thus, both experimental curves are essentially explained by diffusion theory, as was the case for the other nickel base alloy, Rene' 41.

Waspaloy Charged 1 Hr at 5,000 psi

The desorption curves for a Waspaloy sample cut from a used Space Shuttle Turbine Disk, part number S/N 2279525, are shown in Figure 10, while those for a sample cut from the Waspaloy bolt on hand in the laboratory are shown in Figure 11. The experimental curve for the turbine disk sample in Figure 10 is best described by a hybrid distribution which is 18.6 percent uniform, while that for the Waspaloy bolt sample in Figure 11 is completely explained by a 100 percent non-uniform distribution. Thus, the hydrogen distributions in Waspaloy, charged 1 hr at 5,000 psi at room temperature, are essentially in accord with those predicted by diffusion theory, as was the case for electrolytically charged samples. The solubility obtained for the Waspaloy bolt sample was 1.82 ppm, while that for the turbine disk sample was 1.28 ppm. Thus, the hydrogen distributions and solubilities for the samples charged at 5,000 psi are essentially the same as those obtained for electrolytically charged samples at a charge rate of 60 ma/cm^2.

Electrolytically Charged 4340 Steel

The hydrogen desorption curves for a 4340 steel sample charged 4 hr at 1 ma/cm^2 are shown in Figure 12. According to the results shown in Figure 12, the hydrogen distribution is 100 percent uniform in nature, a complete turnaround from the Rene' 41 and Waspaloy samples, and would not be predicted by the diffusion equations. While further study will be necessary to accurately explain this observation, a possible explanation might be the following.

For steady state flow, through unit area of any medium, the permeability is given by

$$P = -D \frac{\partial C}{\partial X} \quad . \tag{7}$$

Thus, the permeability depends on the concentration gradient, as shown in equation (7), which would be quite high for 4340 steel where the solubilities are relatively large. Therefore, the absorbed hydrogen could pass rapidly through the surface layers into the interior of the sample, which would result in a more uniform distribution.

The curves for a 4340 sample charged 1 hr at 60 ma/cm^2 are shown in Figure 13. The observed curve is in agreement with a hybrid curve which is 59.2 percent uniform. Since a more uniform distribution would be predicted by diffusion theory for a longer charge time, the observations of Figures 12 and 13 are consistent in that respect.

CONCLUSIONS

The hydrogen desorption curves for Rene' 41 and Waspaloy samples, both nickel base alloys, are essentially described by non-uniform distributions and are in accord with those which would be predicted by diffusion theory for both electrolytically charged samples and those charged at high pressure. The hydrogen solubility and distribution for a Waspaloy sample charged at 5,000 psi was essentially the same as that obtained by electrolytic charging at 60 ma/cm^2. The hydrogen distribution in 4340 steel charged electrolytically, was found to be uniform in nature, being 100 percent uniform for a sample charged at a slow rate for a longer period of time. This situation would not be predicted from diffusion theory, and has been explained, for the time being, by the rapid diffusion of hydrogen across the surface layers, where the concentration gradient is very large in 4340 steel due to the much higher hydrogen solubility. This is analogous to the situation occurring in steady state flow. The hydrogen solubilities for all samples are higher, in the case of electrolytically charged samples, for high charging rates. This is analogous to high pressure charging, where the solubility depends on the hydrogen pressure.

From the results of this work, it is evident that the hydrogen desorption is completely explained by the nature of the hydrogen distributions in the samples. It was originally proposed [3] that the so-called "fast" hydrogen, or hydrogen which is desorbed at a faster rate than that which would be predicted by diffusion theory, is due to the formation of surface and subsurface hydrides which are unstable at room temperature. The hydrogen desorption rate was originally calculated assuming a uniform hydrogen distribution, which resulted in the discrepancy. Thus, the "fast" hydrogen is completely explained by the nature of the hydrogen distribution, and not by the formation of hydrides.

Future work will include the study of cylindrical samples, with the determination of both diffusable or mobile hydrogen and trapped hydrogen concentrations. Cylindrical samples will be used for a Leco Model RH-2 hydrogen analyzer and for the tensile tests to be performed on Satec Model C creep machines and, because of this, it will be necessary to study hydrogen desorption with the EG&G-PARC Model 350A corrosion measurement console using cylindrical samples of the same diameter. Computer programs for cylindrical samples, which are analogous to those for flat samples, are now being developed. In addition, recourse might be made to hydrogen charging in molten salts, where very large hydrogen concentrations can be obtained at 150°C by charging in a eutectic mixture of $NaHSO_4 \cdot H_2O$ and $KHSO_4$ [6].

6

REFERENCES

1. Barrer, R. M.: Diffusion in and Through Solids. Cambridge, 1941.

2. Sincovec, R. F. and Madsen, N. K.: Software for Nonlinear Partial Differential Equations. ACM Trans. Math. Software, Vol. 1, No. 3, 1985, p. 232-260.

3. Zakroczymski, T.: An Electrochemical Method for Hydrogen Determination in Steel. Corrosion, Vol. 38, 1982, p. 218.

4. Danford, M. D., DeRamus, G. R., Jr., and Lowery, J. R.: An Electrochemical Study of Hydrogen Uptake and Elimination by Bare and Gold-Plated Waspaloy. NASA Technical Memorandum TM-86479, October 1984.

5. Groeneveld, T. P., Fletcher, E. E., and Elsea, A. R.: A Study of Hydrogen Embrittlement of Various Alloys. Battelle Memorial Institute, Report No. DCN 1-7-54-20107 S1 (1F), January, 1969.

6. Chene, J.: Metaux Corrosion Industries, Vol. 262, 1977, p. 623-624.

TABLE 1. OBSERVED SOLUBILITIES FOR ELECTROLYTICALLY
CHARGED SAMPLES

Material	Charge Rate	Solubility (ppm)
Waspaloy	Fast[a] Slow[b]	1.28 0.75
Rene' 41	Fast Slow	1.17 0.29
4340 Steel	Fast Slow	4.97 2.30

a.   60 mA/cm^2

b.   1 mA/cm^2

8

THEORETICAL H$_2$ ABSORPTION CURVE
SURFACES AT UNIT CONCENTRATION

L = .232 cm, D = 4.3 x 10^{-8} cm^2/sec

MEAN H$_2$ CONCENTRATION, ppm

TIME OF CHARGE, HOURS
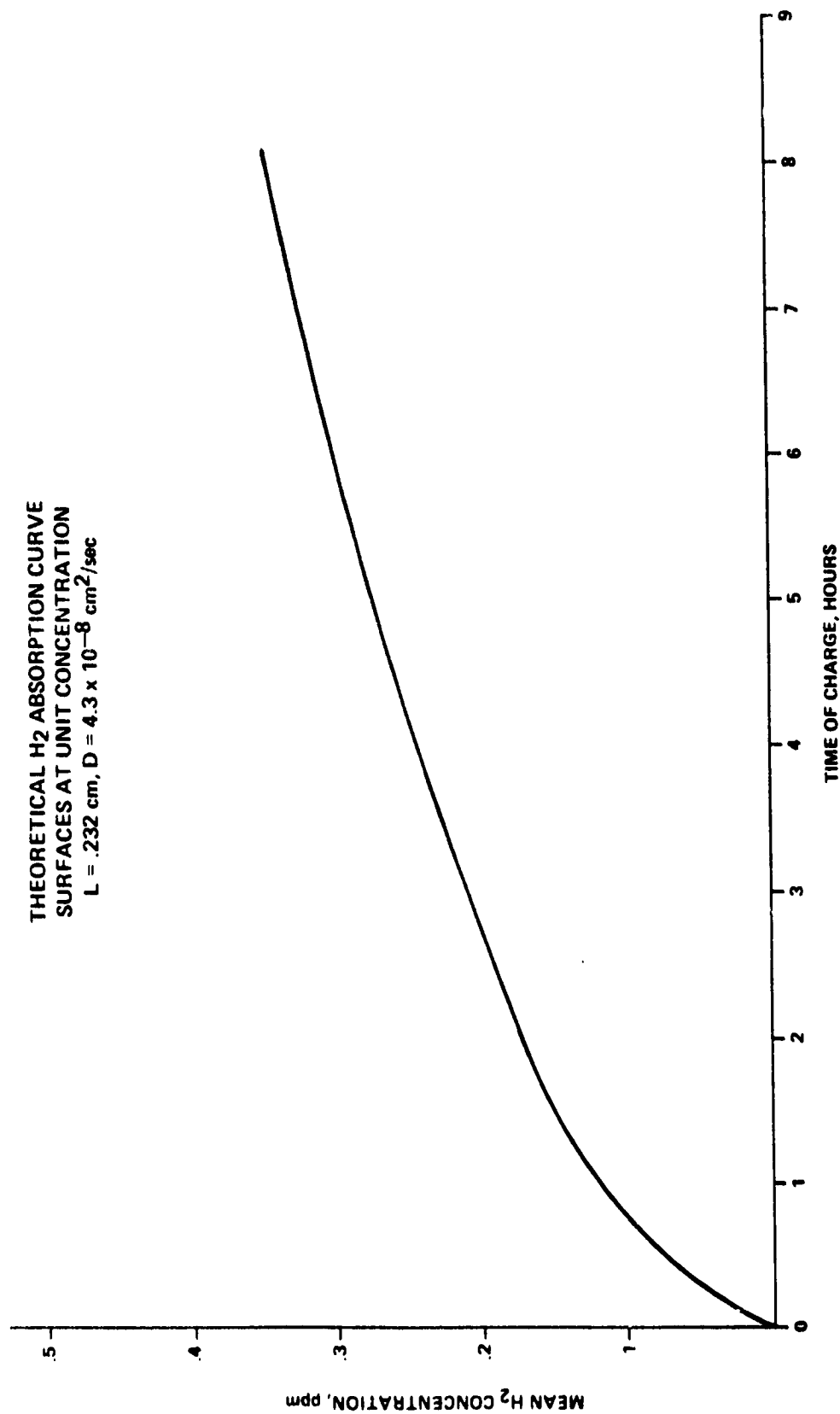
Figure 1. Theoretical absorption curve with surfaces at unit concentration.

9

WASPALOY
CHARGED 1 HOUR AT 5,000 PSI
THEORETICAL (NON—UNIFORM) DISTRIBUTION
L = .202 cm
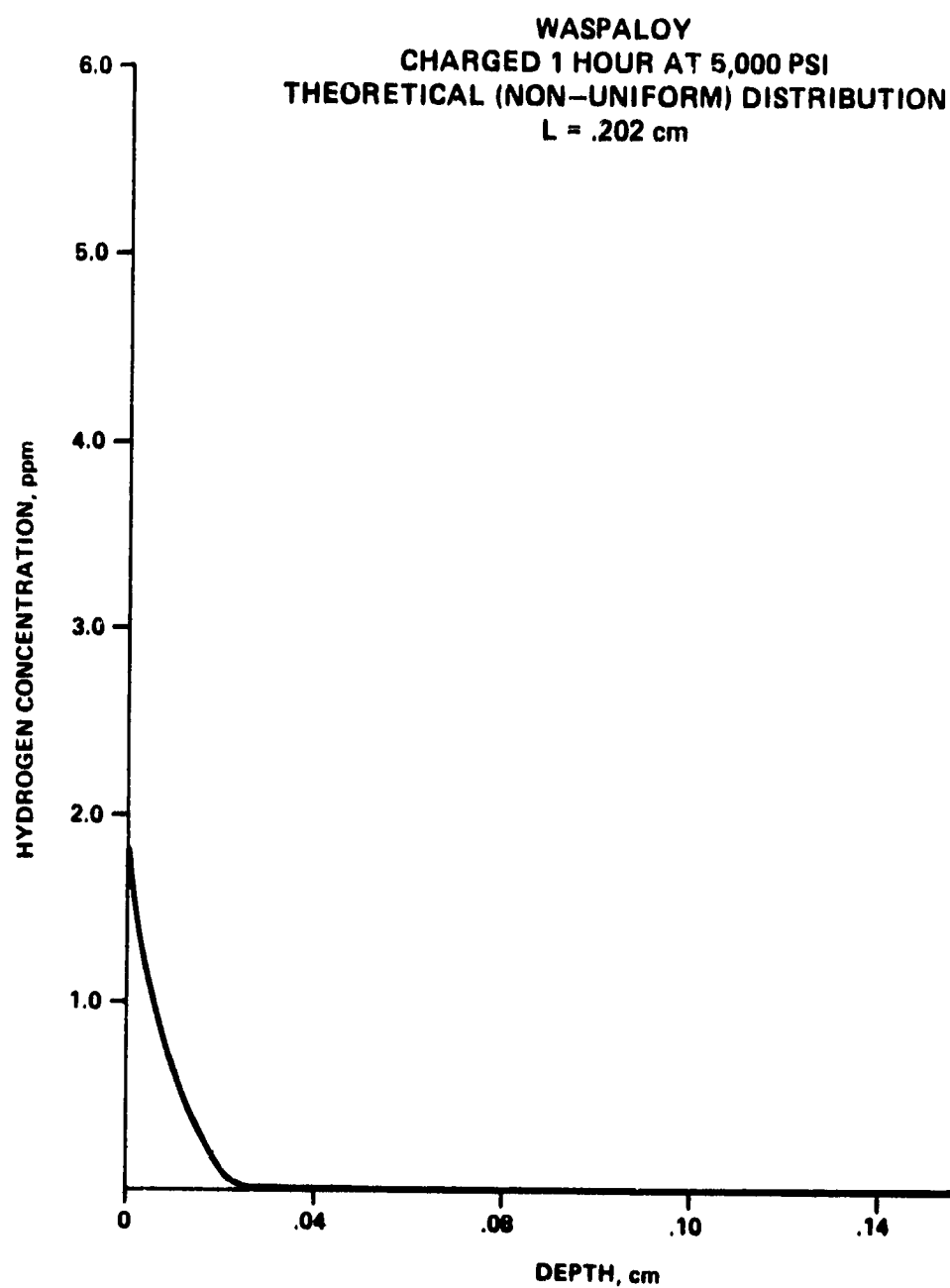
Figure 2.   Theoretical hydrogen distribution for Waspaloy
charged 1 hr at 5,000 psi.

10
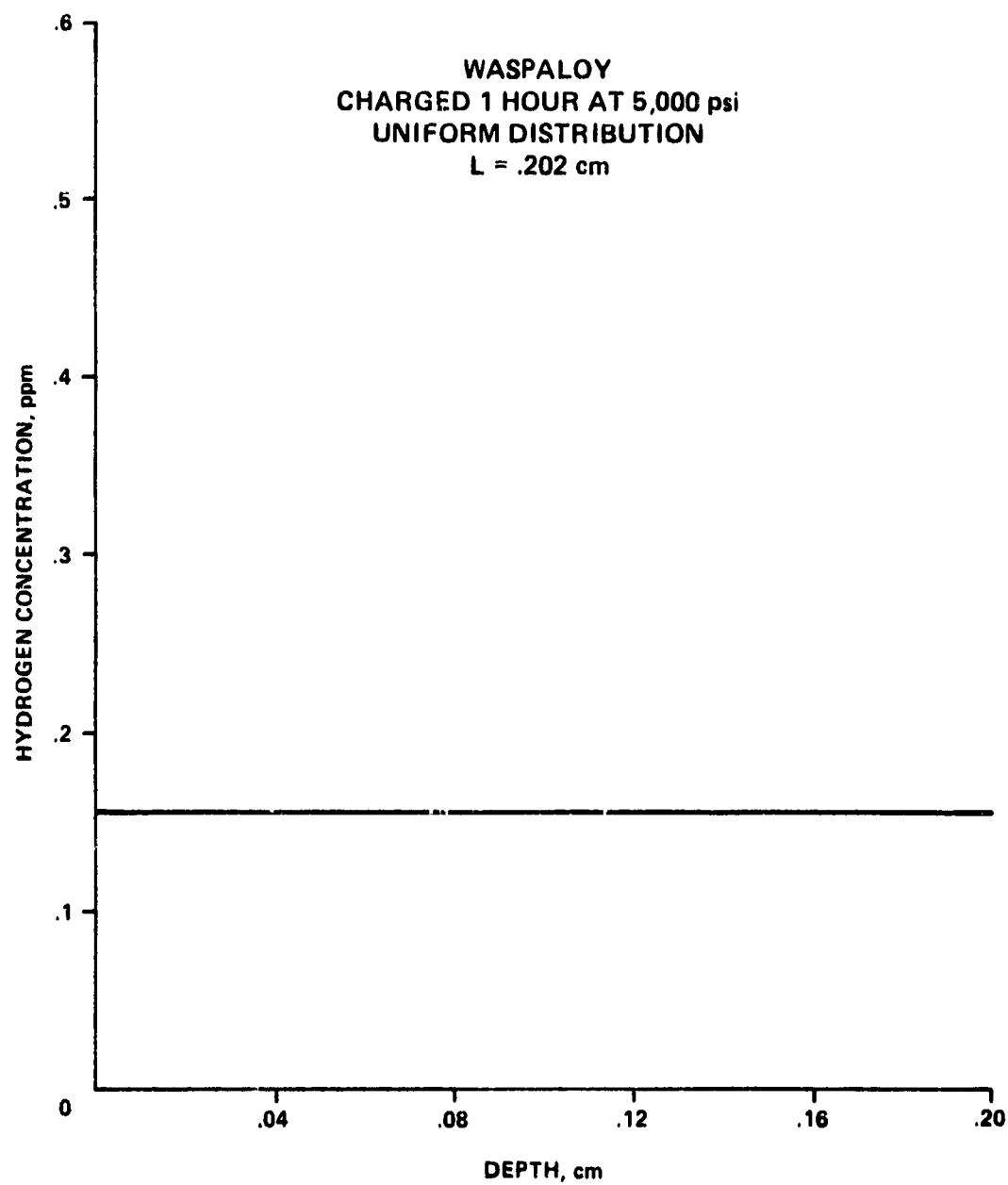
Figure 3.   Illustration for a uniform distribution.
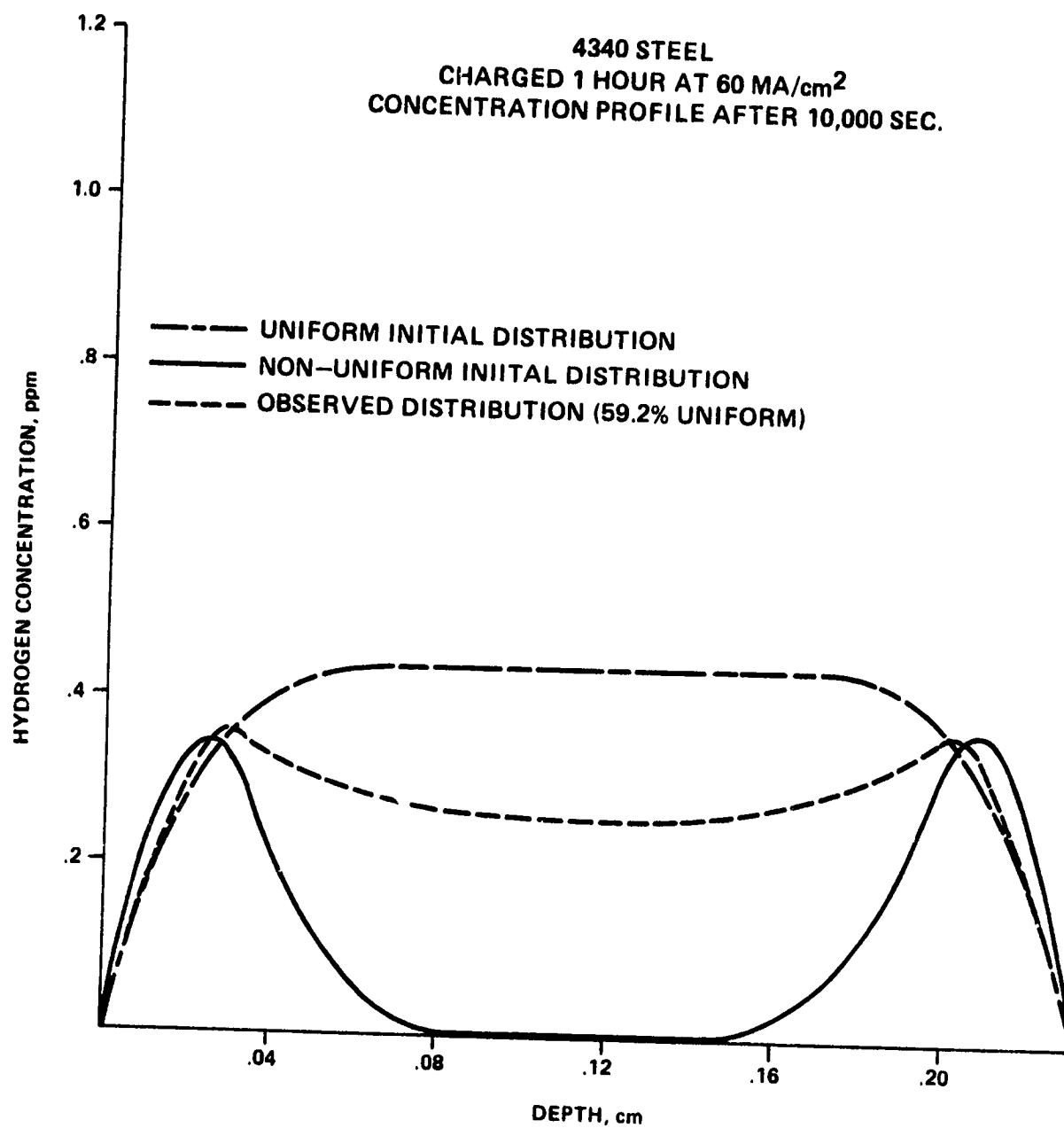
Figure 4.   Hydrogen concentration profiles for 4340 steel
after 10,000 sec.
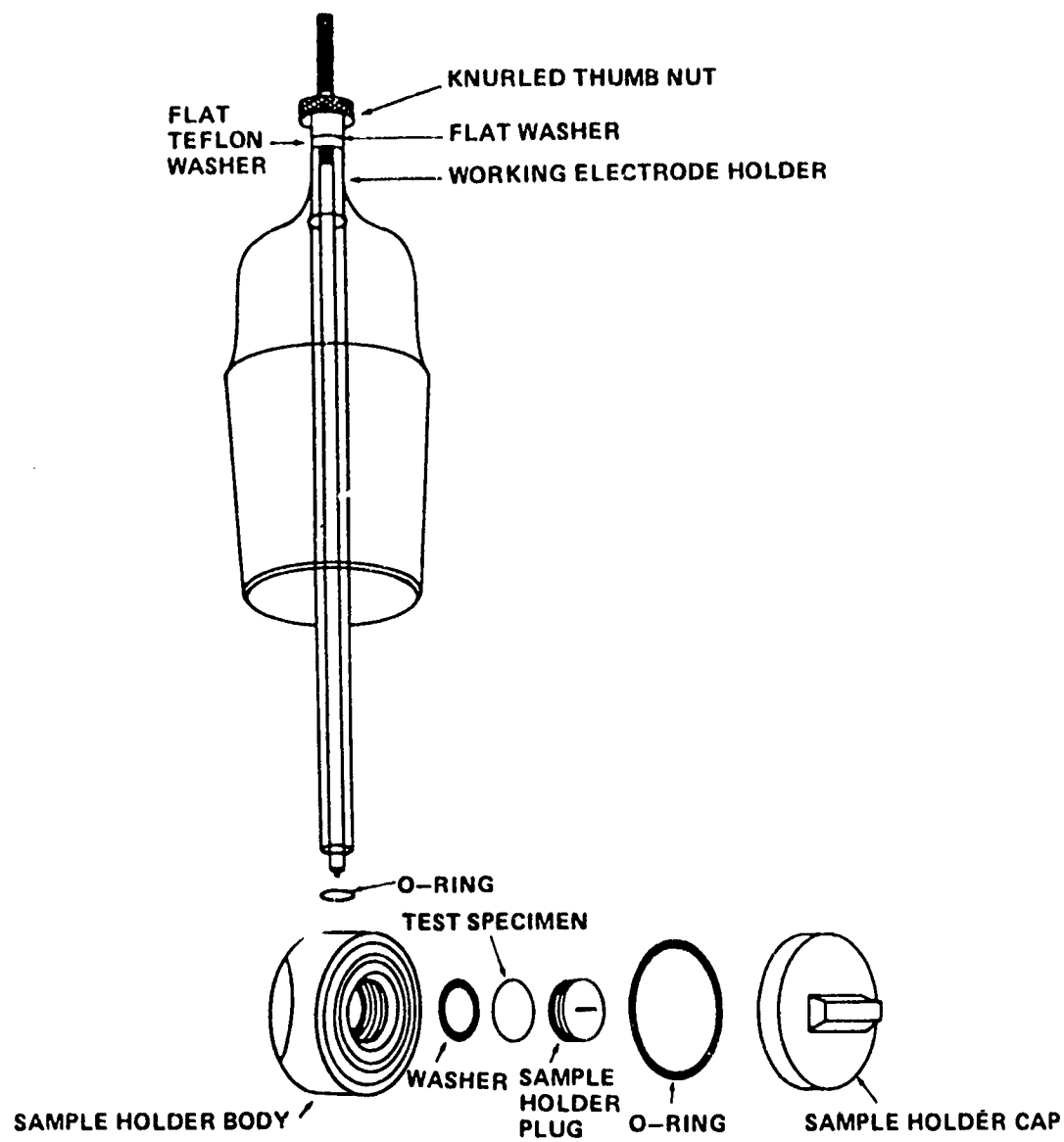
Figure 5. Exploded view of the sample holder.
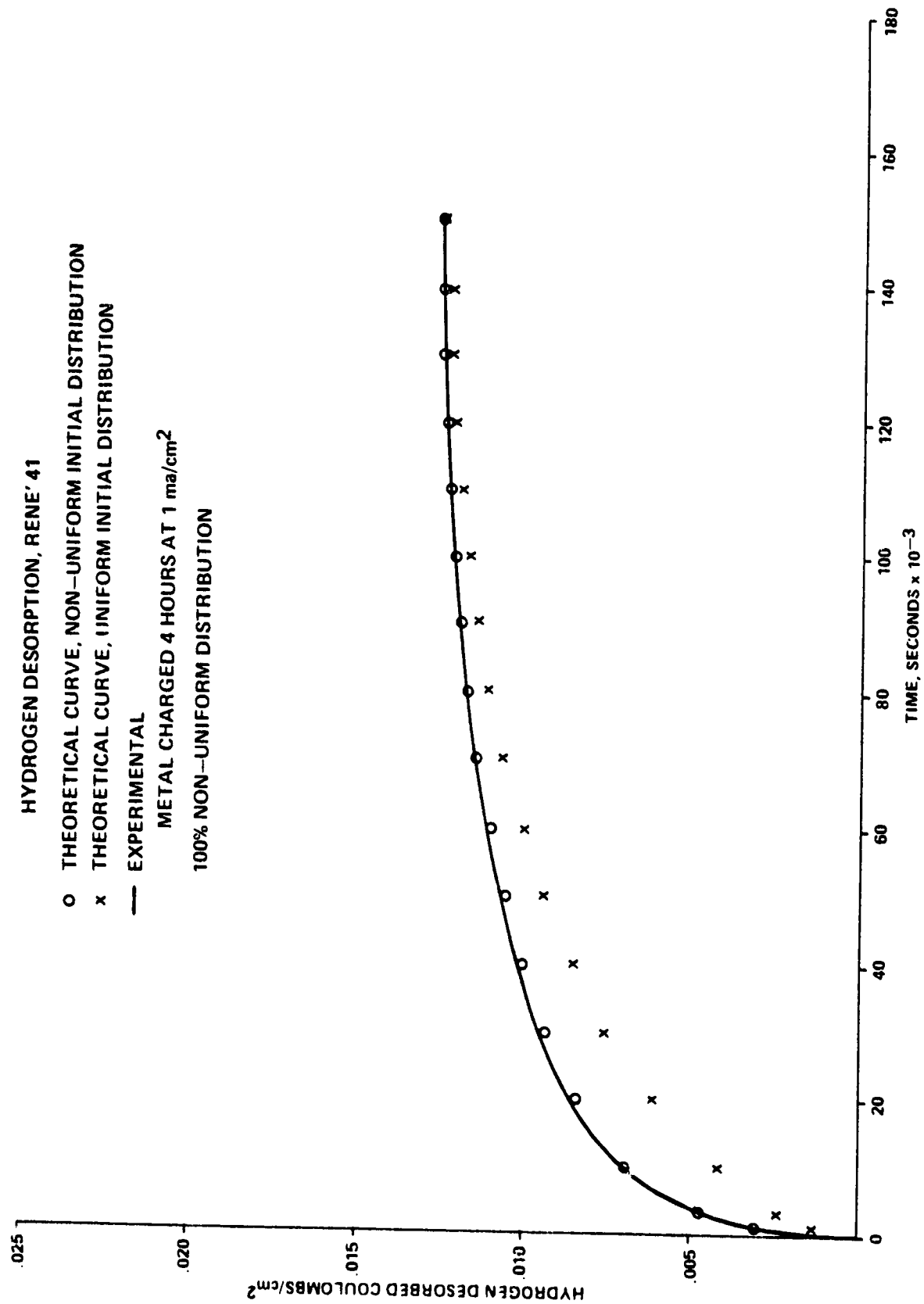
Figure 6. Coulombs of H_2 desorbed versus time for electrolytically charged Rene' 41, slow charge.

14

Figure 7. Coulombs of H_2 desorbed versus time for electrolytically charged Rene' 41, fast charge.

15

HYDROGEN DESORPTION, WASPALOY

o   THEORETICAL CURVE, NON–UNIFORM INITIAL DISTRIBUTION

●   THEORETICAL CURVE, UNIFORM INITIAL DISTRIBUTION

—   EXPERIMENTAL

METAL CHARGED 4 HOURS AT 1 MA/cm^2
100% NON–UNIFORM DISTRIBUTION
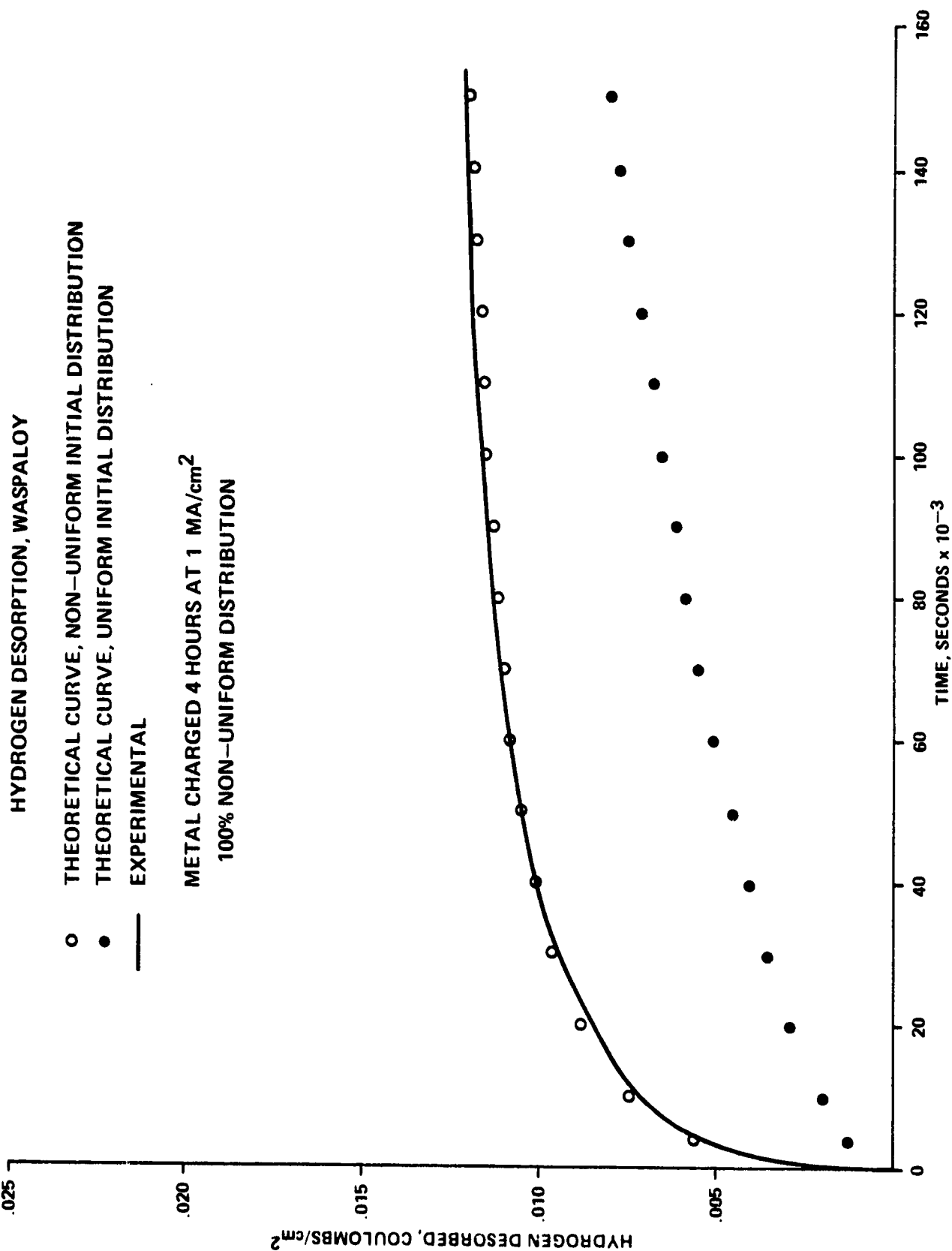
Figure 8.   Coulombs of H_2 desorbed versus time for electrolytically charged Waspaloy (S/N 22.79525), slow charge.
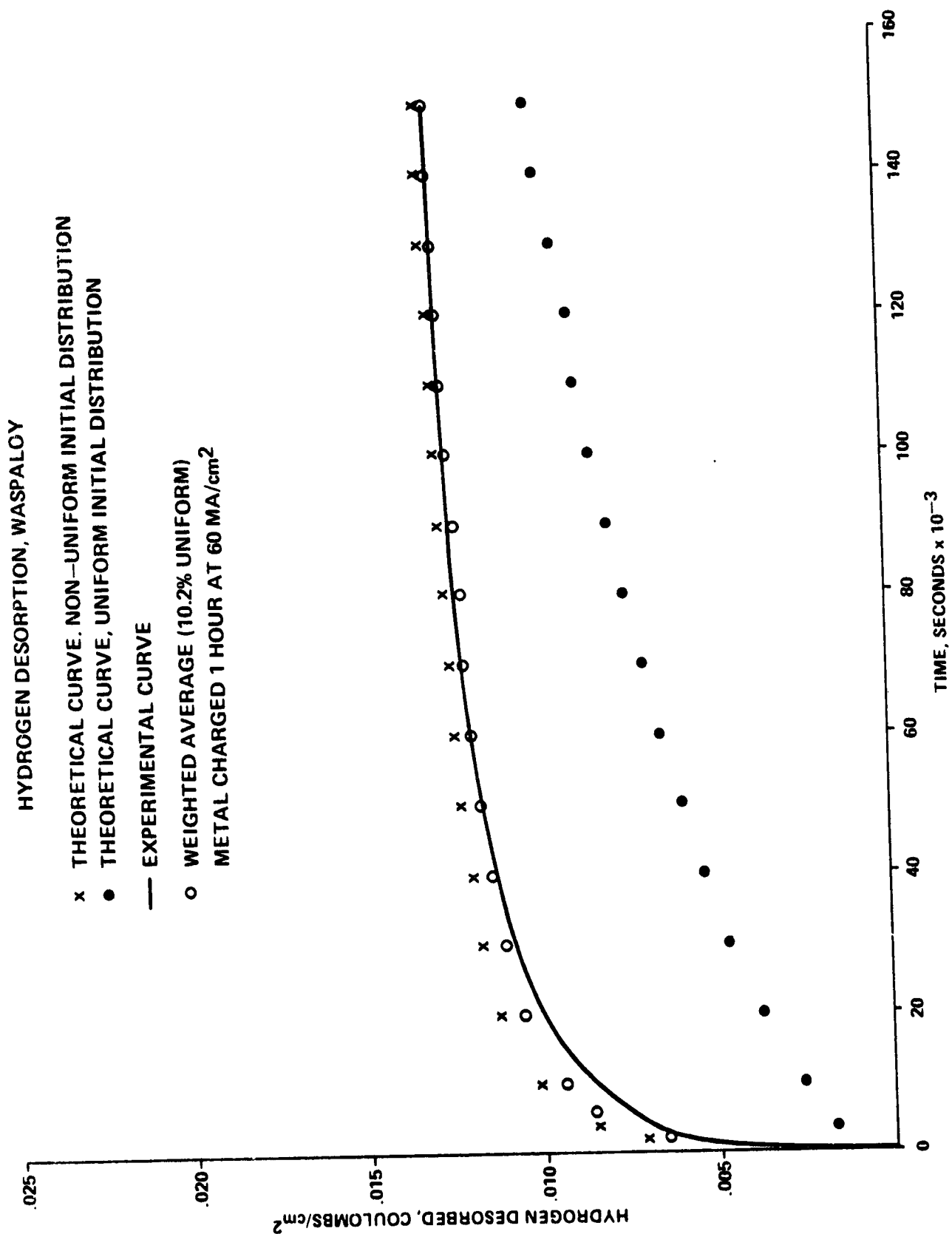
Figure 9. Coulombs of H_2 desorbed versus time for electrolytically charged Waspaloy (S/N 2279525), fast charge.

17
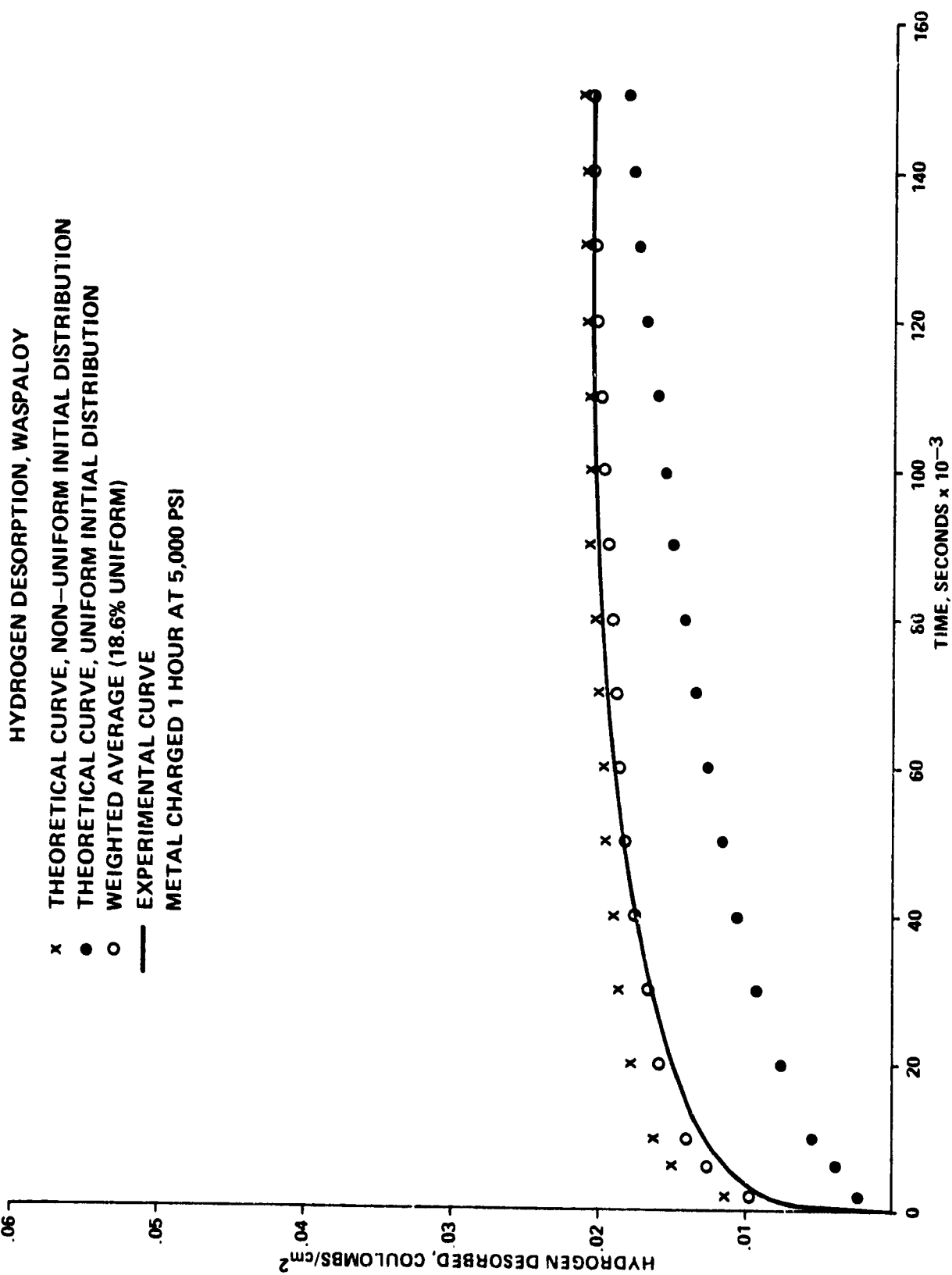
Figure 10. Coulombs of H_2 desorbed versus time for Waspaloy charged at high pressure (S/N 2279525).
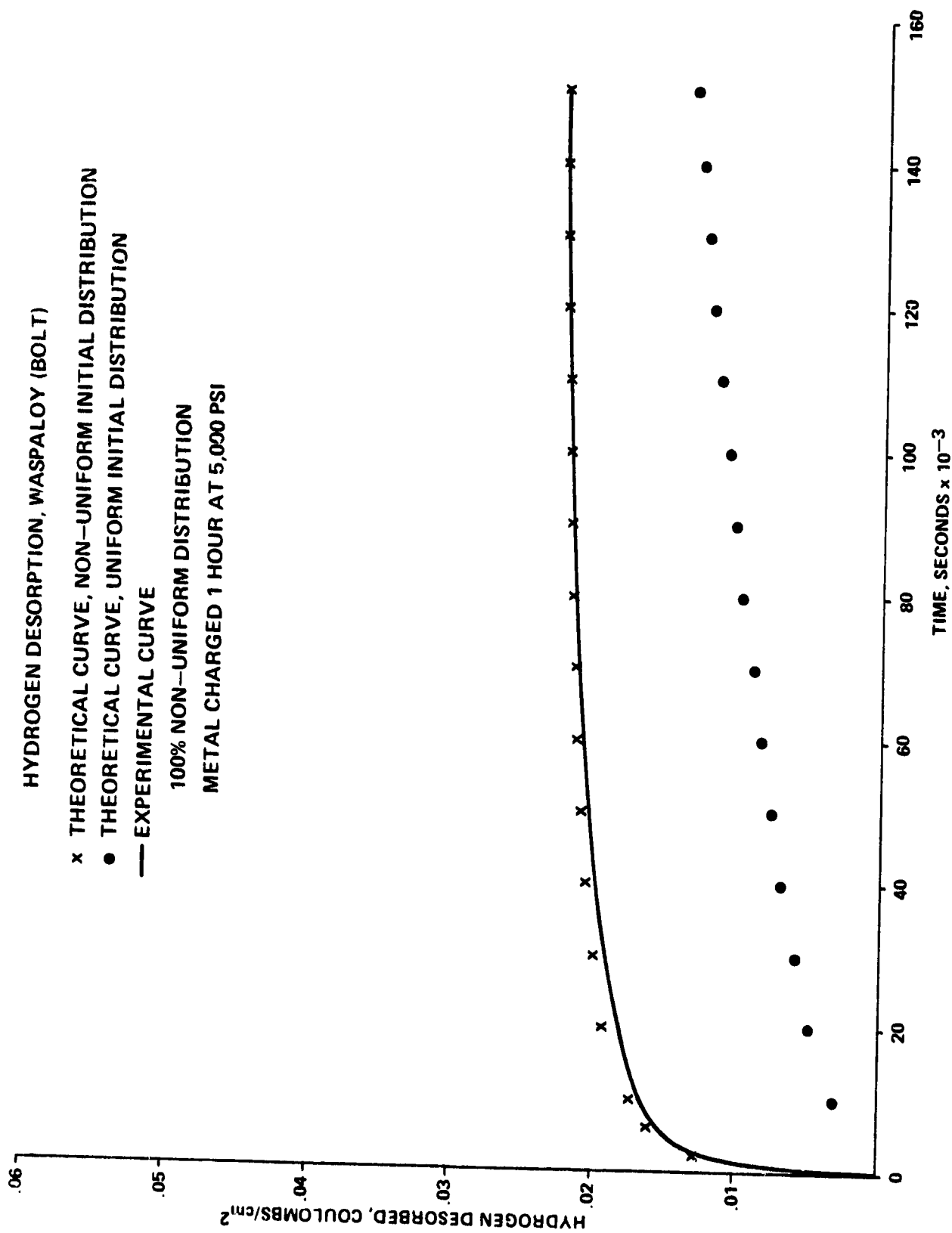
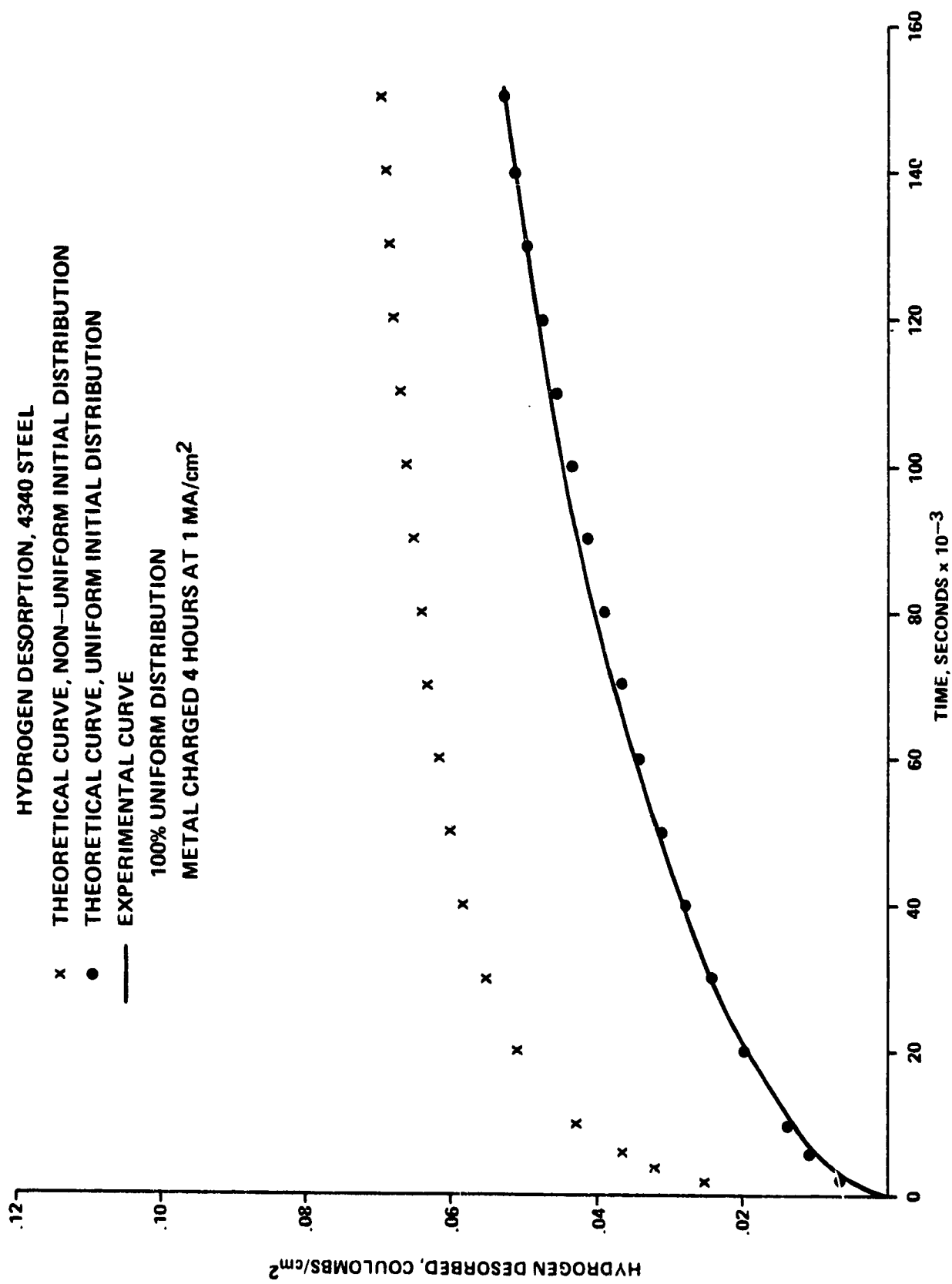Figure 11. Coulombs of H_2 desorbed versus time for Waspaloy charged at high pressure (Waspaloy bolt).

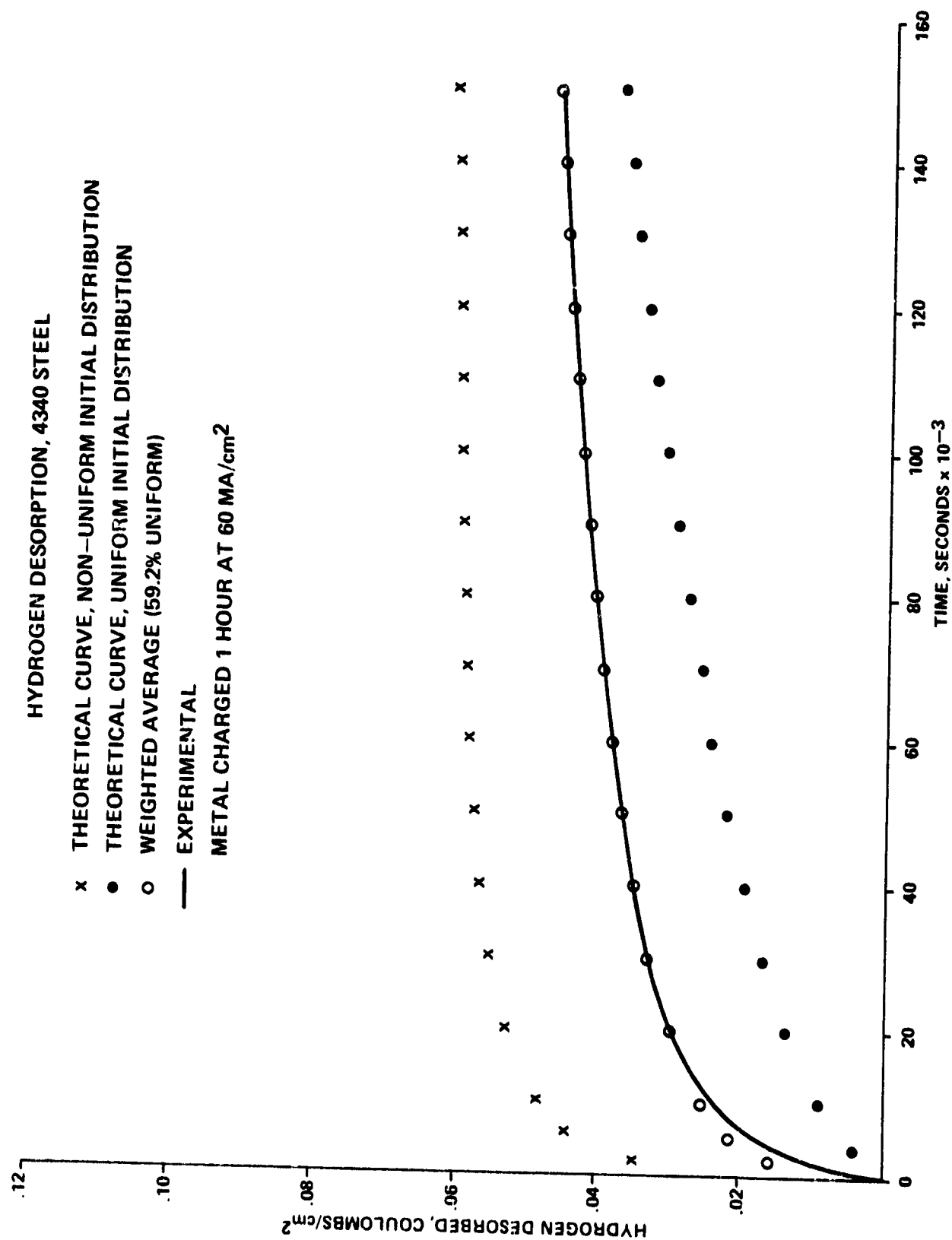Figure 12. Coulombs of H_2 desorbed versus time for electrolytically charged 4340 steel, slow charge.
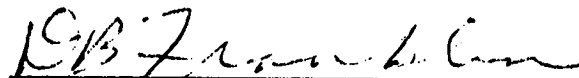
Figure 13. Coulombs of H_2 desorbed versus time for electrolytically charged 4340 steel, fast charge.

21

APPROVAL

THE APPLICATION OF DIFFUSION THEORY TO THE ANALYSIS OF HYDROGEN DESORPTION DATA AT 25°C
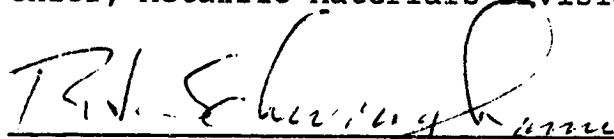
By Merlin D. Danford

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

D. B. Franklin
Chief, Corrosion Research Branch

Herman L. Gilmore
Chief, Metallic Materials Division

R. J. Schwinghamer
Director, Materials & Processes Laboratory