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DOE RESEARCH AND
DEVELOPMENT REPORT**

CORROSION OF ZIRCALOY-4 TUBING IN 680F WATER

(LWBR Development Program)

DECEMBER 1978

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WEST MIFFLIN, PENNSYLVANIA**

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CORROSION OF ZIRCALLOY-4 TUBING IN 680F WATER
(LWBR DEVELOPMENT PROGRAM)

G. P. Marino
R. L. Fischer

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FOREWORD

The Shippingport Atomic Power Station located in Shippingport, Pennsylvania was the first large-scale, central-station nuclear power plant in the United States and the first plant of such size in the world operated solely to produce electric power. This program was started in 1953 to confirm the practical application of nuclear power for large-scale electric power generation. It has provided much of the technology being used for design and operation of the commercial, central-station nuclear power plants now in use.

Subsequent to development and successful operation of the Pressurized Water Reactor in the DOE-owned reactor plant at the Shippingport Atomic Power Station, the Atomic Energy Commission in 1965 undertook a research and development program to design and build a Light Water Breeder Reactor core for operation in the Shippingport Station.

The objective of the Light Water Breeder Reactor (LWBR) program has been to develop a technology that would significantly improve the utilization of the nation's nuclear fuel resources employing the well-established water reactor technology. To achieve this objective, work has been directed toward analysis, design, component tests, and fabrication of a water-cooled, thorium oxide fuel cycle breeder reactor for installation and operation at the Shippingport Station. The LWBR core started operation in the Shippingport Station in the Fall of 1977 and is expected to be operated for about 3 to 4 years. At the end of this period, the core will be removed and the spent fuel shipped to the Naval Reactors Expanded Core Facility for a detailed examination to verify core performance including an evaluation of breeding characteristics.

In 1976, with fabrication of the Shippingport LWBR core nearing completion, the Energy Research and Development Administration established the Advanced Water Breeder Applications (AWBA) program to develop and disseminate technical information which would assist U. S. industry in evaluating the LWBR concept for commercial-scale applications. The program will explore some of the problems that would be faced by industry in adapting technology confirmed in the LWBR program. Information to be developed includes concepts for commercial-scale prebreeder cores which would produce uranium-233 for light water breeder cores while producing electric power, improvements for breeder cores based on the technology developed to fabricate and operate the Shippingport LWBR core, and other information and technology to aid in evaluating commercial-scale application of the LWBR concept.

FOREWORD (Cont)

All three development programs (Pressurized Water Reactor, Light Water Breeder Reactor, and Advanced Water Breeder Applications) have been administered by the Division of Naval Reactors with the goal of developing practical improvements in the utilization of nuclear fuel resources for generation of electrical energy using water-cooled nuclear reactors.

Technical information developed under the Shippingport, LWBR, and AWBA programs has been and will continue to be published in technical memoranda, one of which is this present report.

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Seamless Zircaloy-4 tubing is utilized as fuel rod cladding in light water reactors. Water corrosion tests at 680F have been performed to determine the corrosion and hydriding characteristics of Zircaloy-4 tubing, fabricated by cold reduction and finished in two metallurgical conditions: a stress-relief anneal (SRA) and a recrystallization anneal (RXA). These corrosion tests revealed differences in the post-transition corrosion product weight gains of the two materials. A computer corrosion model, designated CHORT, was developed from the test data and ascribes the observed difference in material weight gain to an assumed difference in the periodicity of a postulated cyclic buckling of the oxide.

CORROSION OF ZIRCALOY-4 TUBING IN 680F WATER (LWBR Development Program)

G. P. Marino
R. L. Fischer

I. INTRODUCTION

The corrosion and hydriding behavior of Zircaloy tubing are of interest to the reactor designer because of its wide application as a cladding material for oxide pelleted fuel rods. This report presents out-of-pile, water corrosion test data representative of the Zircaloy-4 tubing utilized for the Light Water Breeder Reactor (LWBR) fuel rods.

The LWBR core has a seed-blanket configuration consisting of an inner region containing 12 movable seed assemblies each surrounded by a blanket assembly. This inner region is surrounded by an outer reflector blanket region containing 15 reflector assemblies. The seed-blanket-reflector configuration of the LWBR core contains 17,287 fuel rods comprising four different rod diameters ranging from 0.31 to 0.83 inch. Fuel rod cladding tubes of the required diameters were supplied in two metallurgical conditions:

1. Small diameter (seed rod) tubing in the recrystallized annealed (RXA) condition
2. Large diameter (blanket and reflector rod) tubing in the stress-relief annealed (SRA) condition.

II. DESCRIPTION OF TESTS

A. Test Materials

The seamless Zircaloy-4 tubing used in these tests was produced by cold reduction of pierced, extruded, and machined billets. Tube reduction schedules were designed to control dimensional tolerances, texture, grain size, surface finish, and mechanical properties. After each cold reduction sequence, the tubing was vacuum annealed at 1300F for four hours to effect recrystallization. For all tubing the final cold reduction exceeded 70 percent. However, the final vacuum anneal was varied to control the material strength properties. The tubing designated as RXA material was vacuum annealed five hours at 1225F. This treatment produced a fully recrystallized, fine-grained, equiaxed alpha structure. The tubing designated as SRA (stress relief annealed) material was vacuum annealed four hours at 925F. This annealing temperature is in the recovery range for highly cold-worked Zircaloy. Thus, the SRA tubing retained a significant portion of the mechanical strength produced by the final cold reduction and did not undergo recrystallization. Minimum room temperature and 700F pre-irradiation tensile properties of these two materials are compared in Table 1. The larger ultimate strength, the smaller ductility and the lower ultimate strength-to-yield-strength ratio of the SRA material are evident at both test temperatures. In Reference 1, it was demonstrated that a 550-650F coolant temperature range (normal for light water reactor operating conditions) would induce neither recrystallization of the SRA material nor additional grain growth in the RXA material over the 10,000 hours of reported test time.

The nominal composition of the Zircaloy-4 alloy used in this program is shown in Table 2. The hafnium content was limited to low values and thus was controlled by selection of the ingot feed stock.

B. Test Programs

The corrosion test program utilized 214 tube samples. These samples represented eight separate fabrication lots and eight separate Zircaloy-4 starting ingots from two separate suppliers. A fabrication lot size varied from 300 to 900 finished mill-length tubes, depending upon the tube size and manufacturing efficiency.

As illustrated in Figure 1, the two-inch long test samples were machined from mill lengths of tubing. Each sample was provided with a hanger hole for

positioning on type 300 stainless steel fixtures in the autoclave calibrated temperature zone. Each sample was identified to the starting material by a coded, engraved alphanumeric identity system.

Prior to corrosion testing, the sample outside diameter surfaces were conditioned to be representative of the surfaces of typical fuel rods as follows:

1. Vapor blast using a water slurry of number 200 alumina grit
2. Rinse in flowing tap water followed by wiping with clean cotton cloths
3. Clean in a hot detergent solution followed by a rinse in flowing tap water
4. Acid etch in a hot (100F) solution of 3.0 volume percent hydrofluoric acid, 39 volume percent nitric acid, balance water. This treatment reduced the outside diameter by a minimum of 0.003 inch.

The samples were then rinsed for a minimum of 15 minutes each in three consecutive flowing water rinse tanks. The first two rinse tanks utilized tap water; the third rinse tank utilized hot (180F), high-purity (1,000,000 ohm-centimeter resistivity) water. Upon removal from the third rinse tank, the samples were wiped dry with clean cotton cloths to preclude water staining. The time for transfer from the acid tank to the first rinse tank was restricted to three seconds maximum. The water temperature in the first rinse was restricted to 65F maximum. These restrictions were considered to be necessary precautions to preclude acid staining.

The corrosion tests were performed in electrically heated and controlled type 300 stainless steel autoclaves. In test, the samples were completely immersed in water with a pH of 7 and minimum resistivity of 1,000,000 ohm-centimeters. The water phase was maintained inside the test vessel by controlling the pressure at, or above, the saturation pressure for the test temperature. For this test program, the water temperature was controlled at $680F \pm 7F$, and the pressure was controlled at $2705 \text{ psia} \pm 100 \text{ psia}$. Autoclave pressure and temperature were continuously recorded by automatic indicating devices, and the controls were calibrated every eight hours. The autoclave operation was further monitored by insertion of Zircaloy control coupons into each run. These coupons were fabricated from a single wrought product lot for which the corrosion behavior was well characterized.

Following an initial pre-filming autoclave run of three days in ⁺650F water at 2208 psig, the test samples were exposed to an additional 448 cumulative days

in 680F water over four cycles of 14 days each, two cycles of 28 days, and six cycles of 56 days each. This test program produced 1600 data points. Representative samples were withdrawn after 59, 115, 227, and 395 days of cumulative exposure to preserve a record of the corrosion film appearance at these times. Prior to and following each test period, each sample was weighed to ± 0.01 milligram. Corrosion product weight gain, expressed as milligrams per square decimeter, was calculated from measured weight difference and the sample surface area. Sample dimensions were measured to ± 0.003 inch. Sample mass ranged from 4 to 20 grams. Sample surface area ranged from 23 to 64 square centimeters. Sample weight gains were a function of both the corrosion kinetics and the duration of the test cycle and ranged from three to seven milligrams. By statistical combination of the uncertainties in each of the three values, the corrosion test data are calculated to be **accurate** to within one percent.

III. DATA SUMMARY

A. Corrosion Product Weight Gain

A summary of the corrosion product weight gain measured for the Zircaloy-4 tube samples is presented in Table 3. The table is arranged in material type pairs in ascending order of their time of exposure. The Table 3 data are plotted on linear coordinates in Figure 2 along with best fit curves developed by least squares, non-linear regression analyses of the data. The most striking effect noted in Figure 2 is the difference between the post-transition corrosion behavior of the SRA and RXA materials. The SRA material weight gain is consistently a factor of 1.5 higher on the average than the RXA material weight gain.

B. Clad Hydriding

Prior experiments have demonstrated that the increase in the hydrogen content of Zircaloy during oxidation in aqueous environments is directly related to the corrosion product weight gain (Reference 2). This relationship is given by

$$\Delta H = h_1 (\Delta W)^{h_2} + h_3 + \Delta H_i, \quad (1)$$

where

ΔH = hydrogen picked up in mg/dm^2

ΔW = oxide weight gain in mg/dm^2

ΔH_i = initial hydrogen present before corrosion

h_1 , h_2 , and h_3 = environment-dependent constants.

For Zircaloy-4 in H₂O, these constants are:

$$h_1 = 0.0319$$

$$h_2 = 1.0$$

$$h_3 = -0.1824.$$

To convert ΔH to units of parts per million

$$\Delta H_{\text{ppm}} = \frac{C_3 N}{\rho t} \Delta H, \quad (2)$$

where

$$C_3 = 3.937$$

$$\rho = \text{density of Zr} = 6.545 \text{ gms/cc}$$

$$N = \text{number of corroding surfaces}$$

$$t = \text{thickness of the specimen in inches.}$$

An example of the calculated increase in hydrogen versus time of exposure to 680F water for open-ended Zircaloy-4 tube samples in the SRA condition with a nominal wall thickness of 0.0235 inch is tabulated in Table 4.

IV. DEVELOPMENT OF ANALYTICAL MODEL

A. Review of Oxidation Theories

The classical theory of oxidation or rate of growth of oxide films assumes that the rate is controlled by the diffusion of oxygen anions through the existing oxide film to the underlying metal. This theory predicts that the oxide growth on Zircaloy is self-inhibiting. As illustrated in Figure 3, the theory holds early in the corrosion process, but fails after a certain time. After this time, the data indicate an increase in the corrosion rate which is essentially constant thereafter. This phenomenon is called transition or break-away and relates to a change in corrosion kinetics. Although many theories have been put forth in the literature to explain the transition phenomenon, they can all be reduced to one common aspect, namely, a fundamental change (mechanical, chemical, or electrical) in the character of the oxide film which allows either

1. A constant-size diffusion barrier to exist, or
2. Repeated or cyclic transitions of the oxide at a given thickness causing repeated reversion to the kinetics of the beginning of the corrosion process.

In the constant diffusion barrier theory, the presence of a composite oxide layer is postulated. The outer layer is a highly permeable, cracked, previously formed oxide, and the inner layer a dense, newly formed oxide. Upon further oxidation, part of the adherent (barrier type oxide) **reverts** to permeable oxide resulting in a constant thickness of impermeable oxide as oxidation proceeds. Thus, after transition, this theory states that the kinetics are linear in time and the corrosion rate is constant. Most post-transition data can be fitted by least-squares methods to straight lines.

The cyclic transition theory assumes that at a given oxide thickness, the entire oxide film cracks (buckles) and somehow allows the permeation of oxidant directly from the environment resulting in a restart of the corrosion at high initial rates. This effect is illustrated in Figure 3 by the broken or cyclic pre-transition type curves in the post-transition region.

B. Development of the CHORT Computer Program

Evaluation of the Table 3 data demonstrated that prior to transition, both the RXA and the SRA materials corrode at essentially the same rate. Pre-transition data for both materials were adequately predicted by the equation

$$W^n = Ae^{Q/T}(t^m) + C/T + D \quad , \quad (3)$$

where

W = corrosion product weight gain

T = test temperature

t = test time

e = base 2.7183 of Napierian logarithms

and A, Q, n, m, C, and D are constants. From the Table 3 pre-transition corrosion data, the values of these constants were determined to be:

$$A = 6.357 \times 10^{11}$$

$$Q = -13636$$

$$n = 3$$

$$m = 1$$

$$C = 0$$

$$D = 0$$

From the Table 3 data, the weight gain to transition (W_{TR}), was calculated to be 31.00 milligrams per square decimeter for the RXA material and 27.53 milligrams per square decimeter for the SRA material. The reason for the

difference in the weight gain to transition is not known but may be related to the effects of residual cold work. The effect of residual cold work on the corrosion behavior of Zircaloy-4 has been previously observed and reported (Reference 3).

The CHORT program assumed the occurrence of cyclic transitions due to oxide buckling. It is noted that the mechanics of the oxide fracture remain obscure.

The CHORT program further assumed that the weight gain to transition, and therefore the time period of each transition, are constant and equal to that of the initial corrosion cycle. In the absence of sufficient data to better characterize the cyclic nature of the corrosion, the uniform cycle was chosen for assessment of the tubing data. The parameters selected allow the use of the pre-transition constants shown in Equation (3). Finally, the CHORT program is also based on the assumption that the weight gain at transition was independent of the temperature of the corrosion environment.

The program allows variation of the time to transition so that various weight-gain-time plots could be made for each transition time chosen. The CHORT model was used to fit both the RXA and the SRA tube material by using the Equation (3) constants and by changing only the weight gain to transition, W_{TR} . Since the weight gain at transition and hence the time to transition are lower for the SRA material than for the RXA material, the cyclic periodicity is lower. This resulted in an increase in the average corrosion kinetics of the SRA material after the first cycle. The CHORT program formulation is appended.

V. COMPARISON OF CHORT PREDICTION TO TEST DATA

A. Corrosion Product Weight Gain

CHORT predictions and the Table 3 experimental data for out-of-pile corrosion product average weight gain of the tubing samples in 680F water are plotted in Figure 4. Note the excellent fit achieved by CHORT for the SRA material. A weight gain at transition (W_{TR}) of 27.53 mg/dm² and a time to transition (t_{TR}) of 74 days were used. For the RXA material, the CHORT predictions were consistently higher than the experimental data, since the CHORT weight gain constants to best reproduce the higher values of the range of the experimental data were selected. The chosen CHORT constants were $W_{TR} = 31.00$ mg/dm² and $t_{TR} = 107$ days. The results of CHORT calculations performed to extrapolate the corrosion behavior of both materials in 680F and 2000 days exposure are given in Figure 5. Calculations using the CHORT program for 640F, 600F, and 550F water are plotted in

Figures 6, 7, and 8, respectively. These predictions compared well with prior reported work (Reference 4) on RXA material and were considered to support the selection of a constant weight gain to transition of 31.00 milligrams per square decimeter for the RXA material, independent of the exposure temperature. These data also support the selection of a constant weight gain to transition of 27.53 milligrams per square decimeter for the SRA material in 680F water and increase confidence in using this W_{TR} value at lower temperatures where no prior data existed.

B. Clad Hydriding

Two samples of SRA tubing were removed from test, one after 31 days and the other after 283 days exposure to 680F water. These samples were analyzed for hydrogen content by hot vacuum extraction techniques. The analytical values averaged 38 ppm for the 31-day exposure and 179 ppm for the 283-day exposure. Samples of this tubing lot had also been analyzed for hydrogen prior to corrosion test. The lot average was 12.7 ppm. Thus, the increase in hydrogen content due to corrosion was 25.3 ppm after 31 days and 166.3 ppm after 283 days exposure to 680F water. The Table 4 CHORT calculated values for the increase in hydrogen content at these exposure times were 23.8 and 167.3 ppm, respectively. The agreement between the calculated and experimental data is considered to be excellent.

VI. CONCLUSIONS

Samples of cold-worked Zircaloy-4 tubing were corrosion tested in 680F water. The test tubing was representative of two metallurgical conditions which resulted from the vacuum annealing treatments employed after the final cold working. These conditions were designated as SRA for tubing stress-relief annealed at 925F and RXA for tubing recrystallize-annealed at 1225F. Analysis of the corrosion test data revealed distinct differences in the corrosion behavior of the two materials. These differences were a lower weight gain at transition and a higher post-transition corrosion rate for the SRA material. A computer program, designated CHORT, was developed and qualified to the test data. This model assumed that oxide buckling, at a constant oxide weight gain increment, occurs at each cyclic transition. The lower oxide weight gain experienced by the SRA material at the initial transition occurred in a shorter time cycle. The assumption of a constant weight gain to each subsequent transition thus results in shorter cycle times and, hence, an increase in the average corrosion kinetics of the SRA material after the initial transition.

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REFERENCES

- (1) O. M. Katz, "Recovery and Recrystallization Kinetics of Cold-Worked Zircaloy-4 Plate and Tubing," WAPD-TM-590, February 1968.
- (2) S. Kass, "Development of the Zircaloys," ASTM Special Technical Publication #368, 1964.
- (3) C. R. Woods, Editor, "Properties of Zircaloy-4 Tubing," WAPD-TM-585, December 1966.
- (4) S. Kass, "Aqueous Corrosion of the Zircaloys at Low Temperatures," Journal of Nuclear Materials, 29 (1969) 315-321.

TABLE 1. TENSILE PROPERTIES OF ZIRCALOY-4 CLADDING TUBES

A. Room Temperature Tests

<u>Material Type</u>	<u>95/95 Minimum Values</u>		
	<u>UTS (ksi)</u>	<u>UTS/TYS Ratio</u>	<u>% Elong.</u>
RXA ⁽¹⁾	69.9	1.40	27.0
SRA ⁽²⁾	69.4	1.31	20.4

B. 700F Tests

<u>Material Type</u>	<u>95/95 Minimum Values</u>		
	<u>UTS (ksi)</u>	<u>UTS/TYS Ratio</u>	<u>% Elong.</u>
RXA ⁽¹⁾	32.5	1.87	32.2
SRA ⁽²⁾	57.9	1.21	18.8

NOTES:

(1) RXA = Annealed 5 hours at 1225F after >70% cold work

(2) SRA = Annealed 4 hours at 925F after >70% cold work

TABLE 2. THE COMPOSITION OF ZIRCALOY-4 ALLOY

<u>Alloying Element</u>	<u>Acceptance Range (%)</u>	
	<u>Minimum</u>	<u>Maximum</u>
Tin	1.20	1.70
Iron	0.18	0.24
Chromium	0.07	0.13

<u>Impurity Element</u>	<u>Limit (PPM, max.)</u>
Aluminum	75
Boron	0.5
Carbon	270
Cadmium	0.5
Cobalt	20
Copper	50
Hydrogen	25
Hafnium	35
Manganese	50
Nickel	70
Niobium	100
Nitrogen	80
Oxygen	1600
Samarium	10
Silicon	120
Tantalum	200
Thorium	7
Titanium	50
Uranium	3.5
Vanadium	50
Zinc	100

TABLE 3. CORROSION OF ZIRCALOY-4 TUBING IN 680F WATER

<u>Material Condition</u>	<u>Corrosion Time (Days)</u>	<u>Average Weight Gain (mg/dm²)</u>	<u>Range of Data</u>	<u>Number of Specimens</u>	<u>Variability* Factor (Positive)</u>
RXA	3 (650F)	8.34	6.08- 12.22	152	1.47
SRA	3 (650F)	8.09	7.47- 9.24	62	1.14
RXA	17	15.18	14.30- 16.68	104	1.10
SRA	17	15.14	13.87- 16.46	61	1.09
RXA	31	19.62	18.04- 22.07	145	1.12
SRA	31	19.71	18.31- 22.16	61	1.12
RXA	45	22.23	21.58- 23.41	21	1.05
SRA	--	--	--	0	--
RXA	59	24.58	22.20- 26.59	121	1.08
SRA	59	24.66	23.55- 28.01	52	1.14
RXA	87	28.31	26.55- 30.74	123	1.09
SRA	87	29.83	27.19- 34.65	52	1.16
RXA	115	31.04	29.04- 33.23	102	1.07
SRA	115	48.56	43.75- 50.65	42	1.04
RXA	171	53.19	47.72- 56.37	102	1.06
SRA	171	60.23	57.69- 66.61	43	1.11
RXA	227	63.02	57.09- 66.77	82	1.06
SRA	227	86.25	82.35- 88.51	34	1.03
RXA	283	75.39	63.41- 87.74	70	1.16
SRA	283	108.96	94.40-115.66	34	1.06
RXA	339	81.50	74.41- 91.25	17	1.12
SRA	339	--	--	0	--
RXA	395	107.85	95.04-119.96	61	1.11
SRA	395	159.35	140.15-168.24	25	1.06
RXA	451	132.93	131.29-134.19	9	1.01
SRA	451	179.36	158.91-199.47	25	1.11

*Calculated by: $VAR = \frac{\text{Max. Value}}{\text{Average}}$

TABLE 4. CHORT CALCULATED INCREASE IN HYDROGEN CONTENT
FOR ZIRCALOY-4 SRA TUBING⁽¹⁾ IN 680F WATER

Corrosion Test Time (days)	Corrosion Product Weight Gain (mg/dm ²)	Increase In Clad Hydrogen (ppm)
3	7.79	3.38
17	16.41	17.46
31	20.30	23.81
59	25.33	32.03
87	42.39	59.88
115	49.88	72.13
171	73.32	110.40
227	92.60	141.88
283	108.19	167.35
395	136.00	212.76
451	176.71	279.25

⁽¹⁾ CHORT input for tubes 0.527-inch diameter, 23.5 mil wall thickness, corroding on two sides (open ends).

***NOTE: DEPTH CONTROLLED TO ± 0.003
BY MANUFACTURING PRACTICE**

Figure 1. Zircaloy-4 Tubing Samples Used in 680F Water
Out-Of-Pile Corrosion Tests

Figure 2. Corrosion of Zircaloy-4 Tubing in 680F Water

Figure 3. Schematic of Typical Corrosion - Time Data for Zr

Figure 4. Corrosion Data. Zircaloy-4 Tubing in 680F Water
Versus Chort Predictions

Figure 5. Chart Predictions of Corrosion Product Weight Gain,
Zircaloy-4 Tubing in 680F Water

Figure 6. Chort Predictions of Corrosion Product Weight Gain,
 Zircaloy-4 Tubing in 640F Water

Figure 7. Chart Predictions of Corrosion Product Weight Gain for Zircaloy-4 Tubing in 600F Water

Figure 8.. Chort Predictions of Corrosion Product Weight Gain for Zircaloy-4 Tubing in 550F Water

APPENDIX A - CHORT PROGRAM FORMULATION

CHORT assumes that cyclic transitions occur at constant corrosion product weight gains (W_{TR}) equal to 27.53 mg/dm² for SRA Zircaloy, and 31.00 mg/dm² for RXA material. Thus, after each transition, the corrosion kinetics of the initial cycle are repeated. Hence, the computer was programmed to solve the generalized corrosion equation

$$(\Delta W)^3 = [6.357 \times 10^{11} \exp(-13,636/T)]t \quad (1)$$

where

ΔW = corrosion product weight gain

T = temperature (K) of the corrosion environment, and

t = exposure time (days).

The time intervals between each solution of Equation (1) is input as a variable. After each weight gain calculation the calculated value is compared to the experimentally determined limit value W_{TR} , which is the weight gain at transition, and the calculations are repeated. When transition occurs within a time step, its occurrence is noted in the print-out. Weight gains are additive over the chosen time period for corrosion exposure.

Based on the calculated weight gain, the associated increase in hydrogen is also calculated from the equation

$$\Delta H = 0.0319 (\Delta W)^{1.0} - 0.1824 \quad (2)$$

This value is then converted to parts per million (ppm) by the formula

$$\Delta H_{ppm} = 3.937N/6.545t \quad (3)$$

where

N = the number of corroding surfaces, and

t = the material thickness in inches.