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THE EFFECT OF IRRADIATION ON THE CORROSION OF TYPE 347 STAINLESS STEEL BY URANYL SULFATE SOLUTIONS

F. H. Sweeton
M. D. Silverman
H. O. Day

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ORNL-2284
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Contract No. W-7405-eng-26

CHEMISTRY DIVISION

THE EFFECT OF IRRADIATION ON THE CORROSION OF TYPE 347 STAINLESS STEEL BY URANYL SULFATE SOLUTIONS

Report Written By

F. H. Sweeton, M. D. Silverman, and H. O. Day

Work Done By

S. F. Clark
H. O. Day
H. A. Fisch
B. O. Heston
W. E. Hill
Q. V. Larson
H. F. McDuffie
C. H. Secoy
M. D. Silverman
H. H. Stone
F. H. Sweeton
L. F. Woo
W. C. Yee

DATE ISSUED

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SUMMARY

Techniques have been adapted for determining the corrosion of a metal exposed to a fissioning uranyl sulfate solution. A method based on the consumption of oxygen by the metal has been found to be extremely useful for following corrosion both in and out of reactor radiation. A comparison with two other independent methods shows the technique to be reliable. Instrumental reproducibility of the order of 0.0014 mil has been shown for an oxygen measurement, and the over-all results for similar corrosion tests have differed by no more than a factor of 2.

From these exploratory experiments, it appears that reactor radiation above a power-density level of 4 w/ml causes a sharp rise in the corrosion rate. Radiation effects are not observed until after an initial induction period, which appears to depend on the amount of previous nonradiation exposure. The effect of temperature is apparently minor in the range 250 to 290° C. The pertechnetate ion at a concentration of 0,0005 m is apparently not an effective corrosion inhibitor in this system.

It is recommended that these studies be continued to improve the experimental method and to obtain a better understanding of the variables affecting corrosion in these systems.

THE EFFECT OF IRRADIATION ON THE CORROSION OF TYPE 347 STAINLESS STEEL BY URANYL SULFATE SOLUTIONS

INTRODUCTION

A major problem in the development of aqueous homogeneous reactors for industrial power purposes is the selection of suitable materials for reactor construction. These materials, in common with those used in conventional boilers, must be characterized by great strength, good corrosion resistance, ability to withstand high temperatures, and resistance to stress deformation. Other restrictions which are not encountered in conventional practice, however, are placed upon reactor materials. Such materials must resist radiation damage, exhibit good corrosion resistance during continuous exposure to reactor radiations, and in some cases possess low neutron-capture cross sections.

Type 347 stainless steel was selected as the material for the first aqueous homogeneous experimental reactor of the circulating-fuel type (the HRE), because its technology was well understood and it could be field-welded successfully. Since that selection was made, considerable data concerning the corrosion resistance of this material, both in- and out-of-pile, have been obtained. However, because of the urgent need for corrosion data on Zircaloy-2, which was selected as the material for the core vessel of the next aqueous circulating-fuel homogeneous reactor, the HRT, work on stainless steel systems was temporarily halted in the summer of 1954. This report summarizes the techniques developed and the results obtained on type 347 stainless steel over the period 1952-1954.

EXPERIMENTAL

Apparatus. The basic apparatus employed for these studies has been reported earlier[1] and has been adapted to the Low Intensity Test Reactor (LITR). A small cylindrical bomb with an internal volume of 9 ml, 0.625 in. in outside diameter and 3.75 in. in length (see Fig. 1), is machined from the material to be tested. The bottom of the bomb contains a well into which is inserted a thermocouple for measuring the temperature. The bomb is sealed by a swage pressure fitting to which is attached a stainless steel capillary, having an inside diameter of 0.020 in. and a wall thickness of 0.0075 in. Pressure is transmitted by water through approximately 20 ft of the capillary to a Baldwin strain-gage pressure cell located at the face of the LITR. Heat is supplied to the bomb by encasing it in a graphite furnace wound with resistance heating wire. Both bomb and furnace are housed in an aluminum assembly designed to permit utilization of an air stream for cooling purposes. Appropriate instrumentation for the control and recording of both temperature and pressure are available away from the face of the LITR.

Procedure. The bomb assembly, including the capillary, is filled with water and with the bomb at 270° C is tested for leaks at about 5000 psi. After satisfactorily passing the pressure test, the bomb is washed, dried, and weighed and is then loaded with approximately 5 ml of the testing solution, usually one containing uranyl sulfate and copper sulfate in varying concentrations. Oxygen is supplied to the system by adding a small volume of 30% hydrogen peroxide to the testing solution. As the temperature is raised, the peroxide decomposes to give the desired oxygen pressure. The completely loaded bomb assembly can then be either directly inserted in the LITR or "pretreated" at operating temperature before insertion in the reactor.

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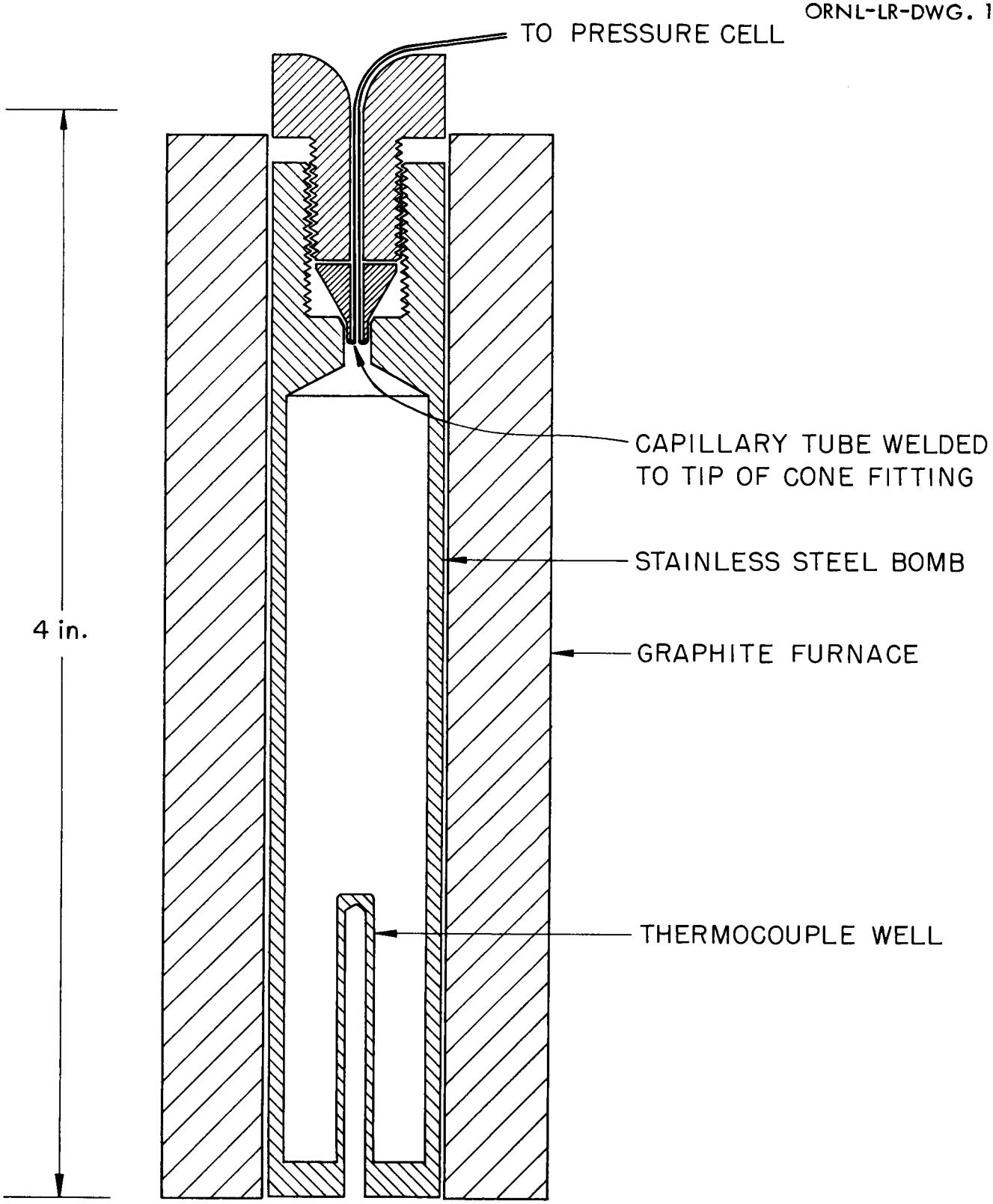

FIGURE 1
BOMB FOR CORROSION TESTING

When the reactor is "on," the Baldwin gage indicates a pressure inside the capsule (at 250° C) which is due to the following vapors: steam (approximately 575 psi), oxygen added at the start of the experiment (usually about 250 psi), and radiolytic gas resulting from the decomposition of water by fission recoils (100-500 psi). Cupric ion in solution serves as an internal recombination catalyst[2] to reduce the radiolytic-gas pressure, allowing safer operating pressures. After the reactor is shut down, the capsule is held at 250° C long enough for the radiolytic gases to recombine in the presence of copper. Then reducing the temperature to 100° C makes it possible to obtain measurements which require only a small correction for steam to give the actual pressure of excess oxygen. Observed changes in oxygen pressure can be converted to average corrosion over the liquid-wetted metal surface.

If corrosion is allowed to proceed until all of the excess oxygen is consumed, the system goes through a pressure minimum and the later pressure increase is due to the evolution of excess hydrogen. In a few cases (H-7, H-10, and H-20) the tests were inadvertently continued into the hydrogen phase. In such a run it is questionable whether the lowest pressure observation represented excess oxygen or excess hydrogen. The double corrosion points plotted in such cases (see Fig. 2 and Fig. 8) represent the two possible situations.

Total corrosion for any experiment may be independently calculated in two other ways. The accumulation of nickel in solution has been shown by Griess and Sasmor[3] to be a measure of corrosion in out-of-pile systems. Weight changes incurred by test pin specimens, which provided about 20% of the surface area inside a bomb and were later cathodically defilmed,[4] served as the other measure of corrosion.

The first irradiation experiments were made with static bombs, but after visible indications of corrosion in the vapor phase were found in some tests, the experimental facilities were modified to permit rocking the assembly (9 cycles/min) in such a way that all the surface inside the bomb is kept wet. This technique has clarified interpretation of the data.

DATA AND RESULTS

Out-of-Pile Tests. Table 1 summarizes the results of out-of-pile rocking tests. The oxygen pressures listed in columns 2 and 3 were determined at 250° C, because more accurate temperature measurements were feasible in these out-of-pile experiments. The corrosion rates given in column 8 are the average of the data in the preceding three columns divided by the test duration. The values in column 9 were obtained by considering only the corrosion which occurred after the first 24 hr. It should be noted that the values in the last column are based on the assumption that the nickel analysis represents the true corrosion figure. Since analysis for chromium in solution gives only Cr(VI), oxygen-consumption results have been recalculated to allow for the fact that part of the chromium precipitated from the solution as Cr(III) and that the remainder was present as Cr(VI). This correction is of the order of 10% for these experiments.

In-Pile Tests. Tables 2 and 3 summarize the results of in-pile static and rocking tests, respectively. In these tables the second column lists various surface treatments (described below) that were performed on the capsules before insertion in the LITR. The values for average power density given in these tables are the best averages that have been estimated from flux measurements, activation experiments, and fission-product activity in the irradiated solutions. The test duration is expressed in terms of irradiation time, except for the first two experiments, H-2 and H-7. The difference between irradiation time and total time is seldom greater than 15%.

The figures for total corrosion for the static experiments (column 7, Table 2) are based on the oxygen-consumption measurements and have been calculated for the area wetted by the solution; the corresponding area

TABLE 1. OUT-OF-PILE ROCKING CORROSION TESTS ON 347 STAINLESS STEEL BY UO_2SO_4 SOLUTIONS

Normal Operating Conditions:[a] 0.16 m UO_2SO_4
0.01 m $CuSO_4$
pH, 2.50
temperature, 250° C

Run	Pressure of Excess Oxygen at 250°C (psi)		Test Duration (hr)	Total Corrosion (mils)			Average Corrosion Rate (mpy)		Final pH	Corrosion Products in Solution (mg/ml)		Fraction Cr Found[b] (%)
	Initial	Final		Oxygen	Nickel	Pins	Over-all	After 24 hr		Nickel	Chromium	
H-24	204	173	820	0.0145	0.0127	0.0173	0.16	0.08	3.0	0.20	0.17	51
H-26	202	156	345	.0180	.0157	.0169	0.46	0.16	2.80	0.25	0.13	33
H-36	204	172	219	.0118	.0094	.0167	0.47	0.08	2.50	0.13	0.10	47
H-37	269	231	310	.0096	.0088	.0114	0.27	0.09	2.50	0.14	0.10	44
H-38	308	285	53	.0081	.0066	.0067	1.34	--	2.68	0.10	0.06	40
H-39	255	233	167	--	.0075	.0094	0.44	--	2.50	0.10	0.10	61
H-40	273	245	289	.0095	.0082	.0142	0.29	0.09	2.60	0.11	0.11	61
H-41[c]	311	290	289	.0079	.0037	.0092	0.27	0.06	2.35	0.05	0.15	--

(a) The concentration and pH values given are for the start of the tests. At the end, U, $SO_4^{=}$, and Cu were recovered quantitatively in solution within experimental error (± 3%).

(b) Cr (VI) in solution, relative to total Cr corroded as calculated from Ni data.

(c) 185 ppm of $CrO_4^{=}$ added.

TABLE 2. LITR STATIC CORROSION TESTS ON 347 STAINLESS STEEL BY UO_2SO_4 SOLUTIONS

Normal Operating Conditions:[a] 0.16 m UO_2SO_4
0.01 m $CuSO_4$
pH, 2.6
temperature,[b] 250° C

Run	Pretreatment	Avg Power Density[c] kw/l	Pressure of Excess O_2 at 100° C (psi) Initial	Final	Test Duration (hr)	Total Corrosion (mils)	Avg Corrosion Rate (mpy)	Final pH	Recovery in Solution (%) Initial Species U	SO_4	Cu	Corrosion Prod[c] Ni	Cr(VI)
H-2	2% CrO_3	6.0	559	220	2352	0.50	1.9	4.3	31	--	--	54	--
H-7	Etch[e]	6.1	90	117[g]	432	0.24	4.9	2.1	38	29	166	86	0.2
H-9	"	0.5	56	40	970	0.03	0.3	2.9	97	104	141	272	9.5
H-10	"	6.0	95	22	542	0.16	2.6	3.5	91	103	60	150	11.9
H-11	"	2.1	102	71	1980	0.05	0.2	3.25	84	101	90	95	6.8
H-12[b]	Electro-polished	6.3	98	17	248	0.10	3.6	3.00	98	107	100	55	--
H-13	"	3.8	102	22	151	0.13	7.4	3.65	98	96	42	35	2.4
H-18[b]	H_2O at 270° C	6.4	94	36	123	0.11	7.5	2.92	98	104	95	47	4.2
H-19	"	4.3	128	44	142	0.12	7.3	2.89	92	122	84	53	2.4
H-20[f]	"	9.7	114	41[g]	241	0.19	7.0	--Precipitation - therefore not analyzed--					

(a) The concentration and pH values given are for the start of the tests.

(b) The temperature for runs H-12 and H-18 was 290° C.

(c) Based on solution densities at 25° C.

(d) Based on total corrosion as measured by the O_2 data.

(e) Etching solution contained 20% HNO_3 and 3% HF.

(f) $KTcO_4$ added to give an initial concentration of 0.0005 m.

(g) Measured pressure at the end of experiment appeared to be hydrogen instead of oxygen. Corrosion has been calculated on this basis.

TABLE 3. LITR ROCKING CORROSION TESTS ON 347 STAINLESS STEEL BY UO_2SO_4 SOLUTIONS

Normal Operating Conditions:[a] 0.16 m UO_2SO_4
0.01 m $CuSO_4$
pH, 2.45
temperature, 250° C

Average Power Density:[b] 6.3 kw/l

Run	Pretreatment	Pressure of Excess O_2 at 100° C (psi) Initial	Final	Test Duration (hr)	Total Corrosion (mils) Oxygen	Nickel	Pins	Average Corrosion Rate (mpy) Over-all	After Break	Final pH	Recovery in Solution (%) Initial Species U	SO_4	Cu	Corrosion Prod[c] Ni	Cr
H-22	None	136	45	133	0.060	0.065	0.04	3.5	8.5	-	94	107	83	108	4.3
H-27	None	139	43	122	.061	.042	.045	4.1	9.0	3.25	93	100	86	69	0
H-28	None	139	46	97	.062	.053	.04	5.6	8.0	3.2_8	95	104	84	84	0
H-48	None	126	102	30	.016	.012	.016	4.7	--	2.5_5	98	98	90	76	0
H-49	0.7 day[d]	164	129	103	.027	.020	.019	2.3	--	2.7_5	100	101	95	--	0
H-51	1.6 days[d]	172	44	283	.083	.070	.065	2.6	7.7	2.8_0	89	95	91	86	0

(a) The concentration and pH values given are for the start of the tests.

(b) Based on solution densities at 25° C.

(c) Based on assumption that oxygen corrosion figure is exact.

(d) At 250° C after final loading but prior to irradiation.

for the rocking capsules is, of course, the total internal surface. In Table 3, since nickel analysis and pin-weight data were also available, the corrosion rates listed are an average of the three methods. The "rates after break" in the next column give an indication of the severe corrosion toward the end of the rocking experiments. The values for the species (U, $SO_4^{=}$, Cu) left in solution are relative to the amounts originally charged. The figures in the last two columns of Tables 2 and 3 are calculated on the basis of nonpreferential dissolving of the components of the stainless steel.

DISCUSSION

Pretreatments. The pressure capsules were given a variety of surface treatments before insertion into the reactor. The heavy-film technique[5] employing chromic acid was used for run H-2. In order to obtain a surface free of impurities and oxide and thereby simplify interpretation of corrosion results obtained from in-pile bombs, chemical etching and electropolishing pretreatments were employed through experiment H-13. A solution etch of HF and HNO_3 was used for experiments H-7 through H-11. The electropolishing technique employed for H-12 and H-13 was discontinued because it was doubtful that the desired surface treatment was actually being obtained. In experiments H-18 through H-20, the only surface treatment prior to loading was that due to the pressure test with water at 270° C. Subsequent capsules were pressure tested at room temperature.

The time during which the hydrogen peroxide decomposes to furnish an oxygen atmosphere has proved to be an additional form of pretreatment. During the early experiments this time amounted to several hours at 250° C. In H-7 and H-10, it was 3.5 and 16 hr, respectively, and Fig. 2 shows that the high corrosion rate was delayed in the latter case. This effect can also

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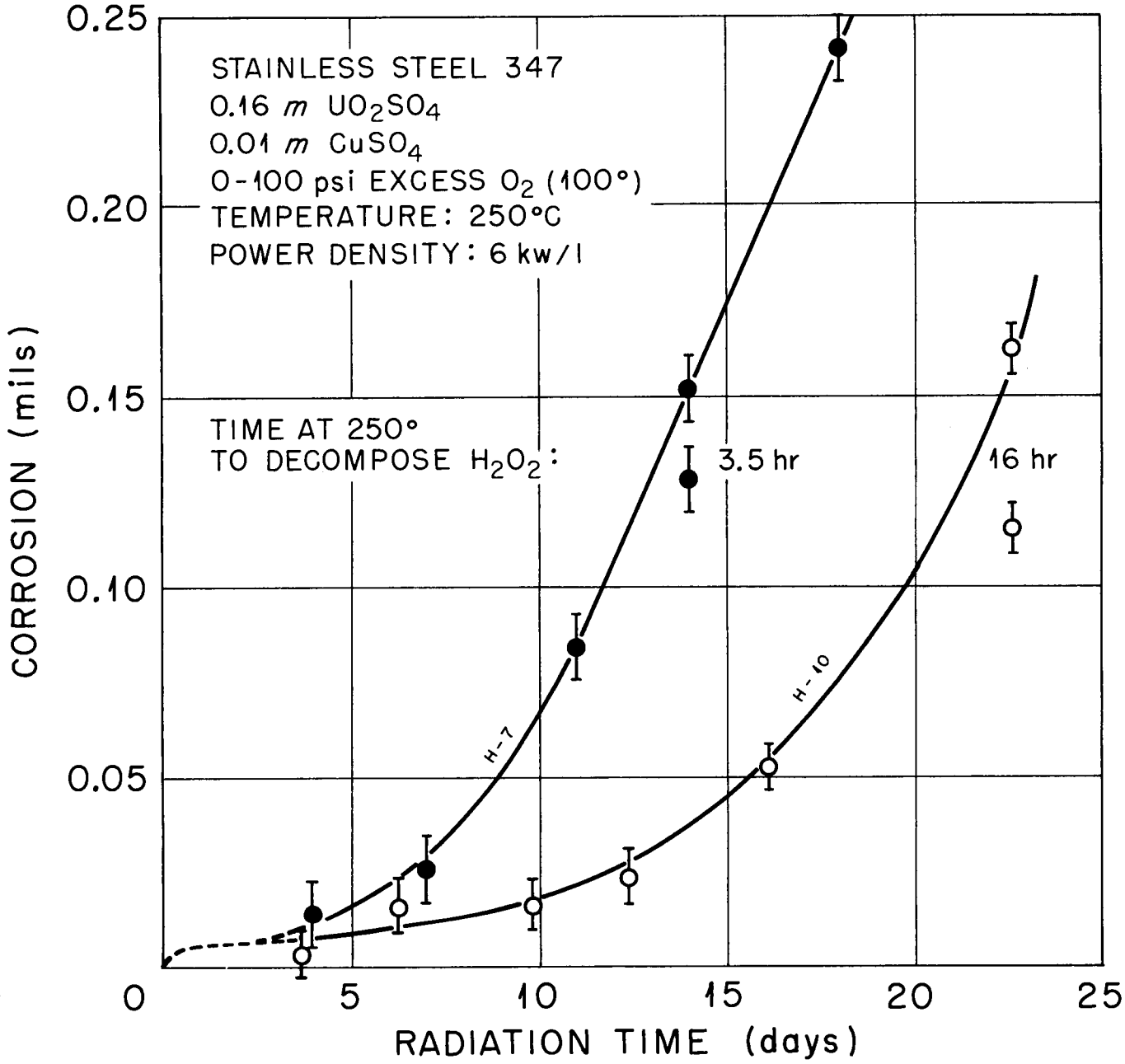

FIGURE 2

EFFECT OF H_2O_2 DECOMPOSITION TREATMENT ON LATER RADIATION CORROSION

be observed qualitatively in the later rocking experiments H-22, H-27 and H-28 (Fig. 3), where the first was held at 250° for 1 hr, while the other two were heated to only 150°.

A pretreatment with the use of the testing solution itself at 250° C was specifically studied in tests H-49 and H-51. These data, also shown in Fig. 3, indicate that this type of pretreatment delays the upward break in the corrosion curve. This effect is important because it indicates that the protective film formed out-of-pile only gradually deteriorates under reactor radiation.

As noted above, some corrosion undoubtedly occurs during the period in which the temperature is raised to convert the hydrogen peroxide into oxygen. The end of this heating period is taken as the zero point in calculating corrosion for these experiments. The true zero point could be easily established if a method were developed for injecting oxygen directly into the bomb.

Comparison of Methods for Measuring Total Corrosion. Final corrosion rates were determined independently by the oxygen, nickel, and pin methods for seven out-of-pile experiments and six similar in-pile experiments. Each set of results should therefore be sufficient in number for comparing the methods statistically.

The agreement between the methods can be noted from the values given in Table 4. The average corrosion determined by any one method differs by no more than 20% from the average of the three methods. This consistency would indicate that any one of the methods is a useful tool for studying the corrosion of stainless steel.

Further information may be gained by utilizing statistical methods

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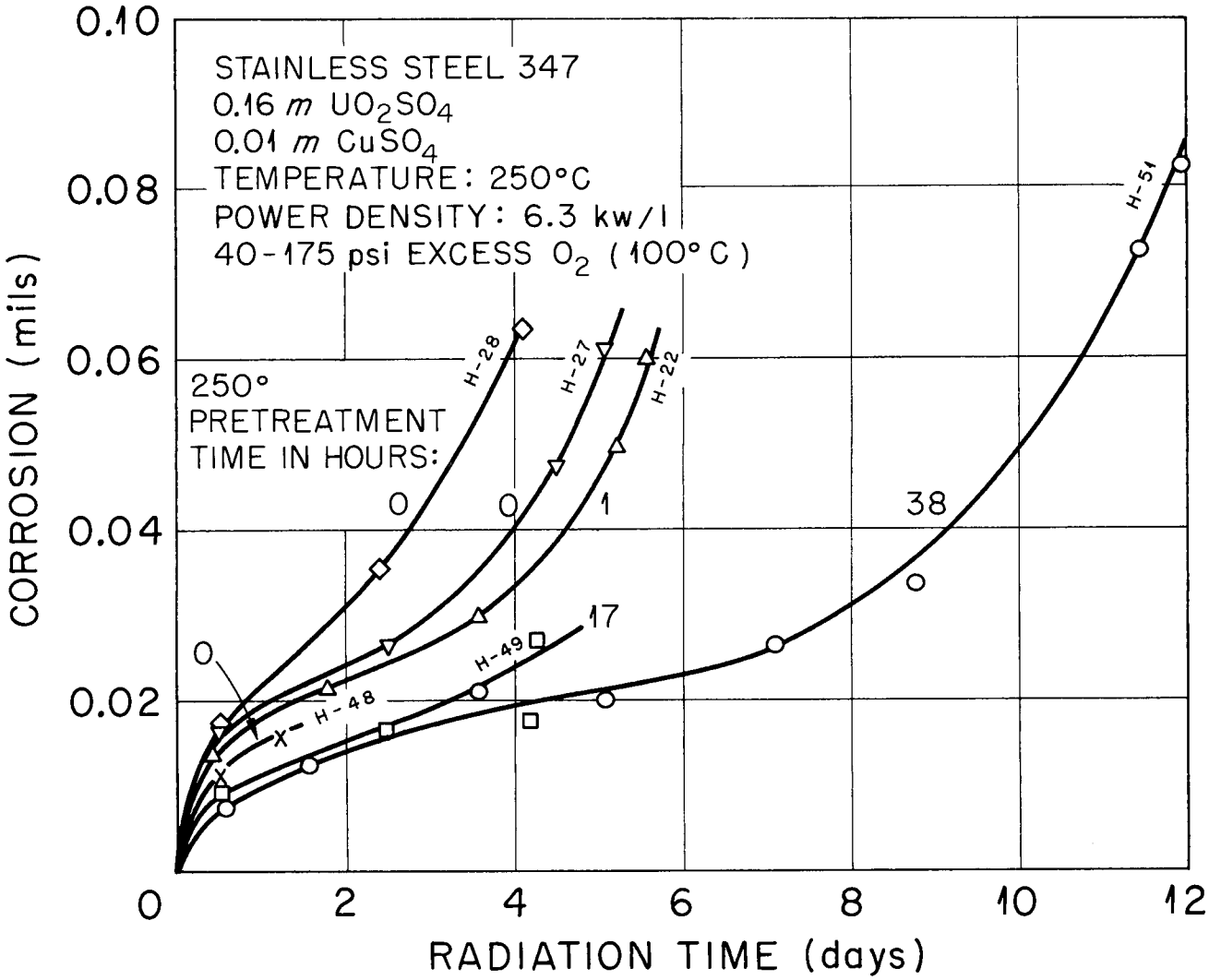

FIGURE 3

EFFECT OF PRETREATMENT BY UO_2SO_4 AND O_2

TABLE 4. AVERAGE CORROSION BY THE DIFFERENT METHODS

Method	Average Apparent Corrosion (mils x 10^3)	
	Out-of-Pile Tests	In-Pile Tests
O_2	11.3	51.5
Ni	9.3	43.7
Pin	13.2	37.5
Over-all average	11.3	44.2

TABLE 5. STATISTICAL COMPARISON OF CORROSION DETERMINATIONS BY THE DIFFERENT METHODS

Methods Compared	σ_o^2	σ_o	σ_1	Significance Level
		Out-of-Pile		
O_2-Ni	0.61	0.8	1.4	0.003
O_2-Pin	3.16	1.8	1.1	0.10
Ni-Pin	3.54	1.9	2.7	0.009
		In-Pile		
O_2-Ni	33	5.7	5.0	0.06
O_2-Pin	35	5.9	9.5	0.010
Ni-Pin	62	7.9	3.0	0.25

for variance analysis such as outlined by Brownlee.[6] The results of such an analysis are listed in Table 5. The function σ_0, the square root of the residual variance, is a measure of the random variability which is not accounted for by known factors. In the out-of-pile tests, this random variability, shown in Table 5, is smallest when the oxygen and nickel methods are compared. Furthermore, the pin data are considerably more erratic relative to the other two. For the in-pile tests relatively poor agreement between the Ni and pin data is obtained; however, when either one is compared with the oxygen data, somewhat better consistency is noted, suggesting that the oxygen method is the most reliable of the three.

The function σ_1, the square root of the variance between methods, is a statistical measure of the difference between them. The "significance level" in the last column is a measure of the probability that the apparent difference can be explained by chance alone. It is common statistical practice to accept, as valid, differences having a significance level equal to or less than 0.050. On this basis, it is concluded that for the out-of-pile experiments the oxygen method gave results significantly higher than those obtained by the nickel method but not significantly different from those by the pin method. Also, the nickel results were significantly lower than the pin values. For the in-pile tests, the oxygen results were significantly higher than the pin values, but significant differences were not found between the oxygen and nickel methods nor between the nickel and pin methods.

The oxygen method, in addition to being the most satisfactory from the standpoint of consistency, possesses two additional advantages. It provides several corrosion determinations during the course of a single autoclave experiment, while the pin and nickel data give only one. Furthermore,

the oxygen data furnish immediate information, whereas the pin and nickel data are available only after the contents of the autoclave have been removed and analyzed.

Experimental Reproducibility of the Oxygen Method. Two reproducibility factors are involved, the measuring instruments and the sample preparation. Experiment H-11 (Fig. 4) gives the best data for instrument evaluation because it has many experimental points and an apparently simple corrosion pattern. The average deviation of the points (excluding the first three where the curvature is great) from the smoothed curve is about 0.0014 mil. This reproducibility gives considerable detail to a corrosion curve followed to at least 0.05 mil corrosion, a figure exceeded for most of the in-pile experiments. Considerably better reproducibility than this was obtained for the out-of-pile tests, in which better instrumentation was employed.

Sample-preparation reproducibility is best illustrated in Fig. 5, where the data for several essentially identical tests are shown. Although many factors may contribute to the differences between these curves, probably the most important is the assumption that the corroding surface is smooth and that its area can be calculated from the dimensions of the capsule. The error due to this assumption becomes less important, of course, with increasing penetration. Although the maximum spread between these curves amounts to about a factor of 2, the curves possess the same general shape, indicating the usefulness of this method for studying corrosion.

Power Density. Corrosion curves for H-26 and H-40, typical out-of-pile experiments, are shown in Fig. 6. In practically all out-of-pile runs, initial fast rates of about 20 mpy level off to 0.1 to 0.2 mpy within a period of 24 hr. Except for the fast initial rate, the data and curves for

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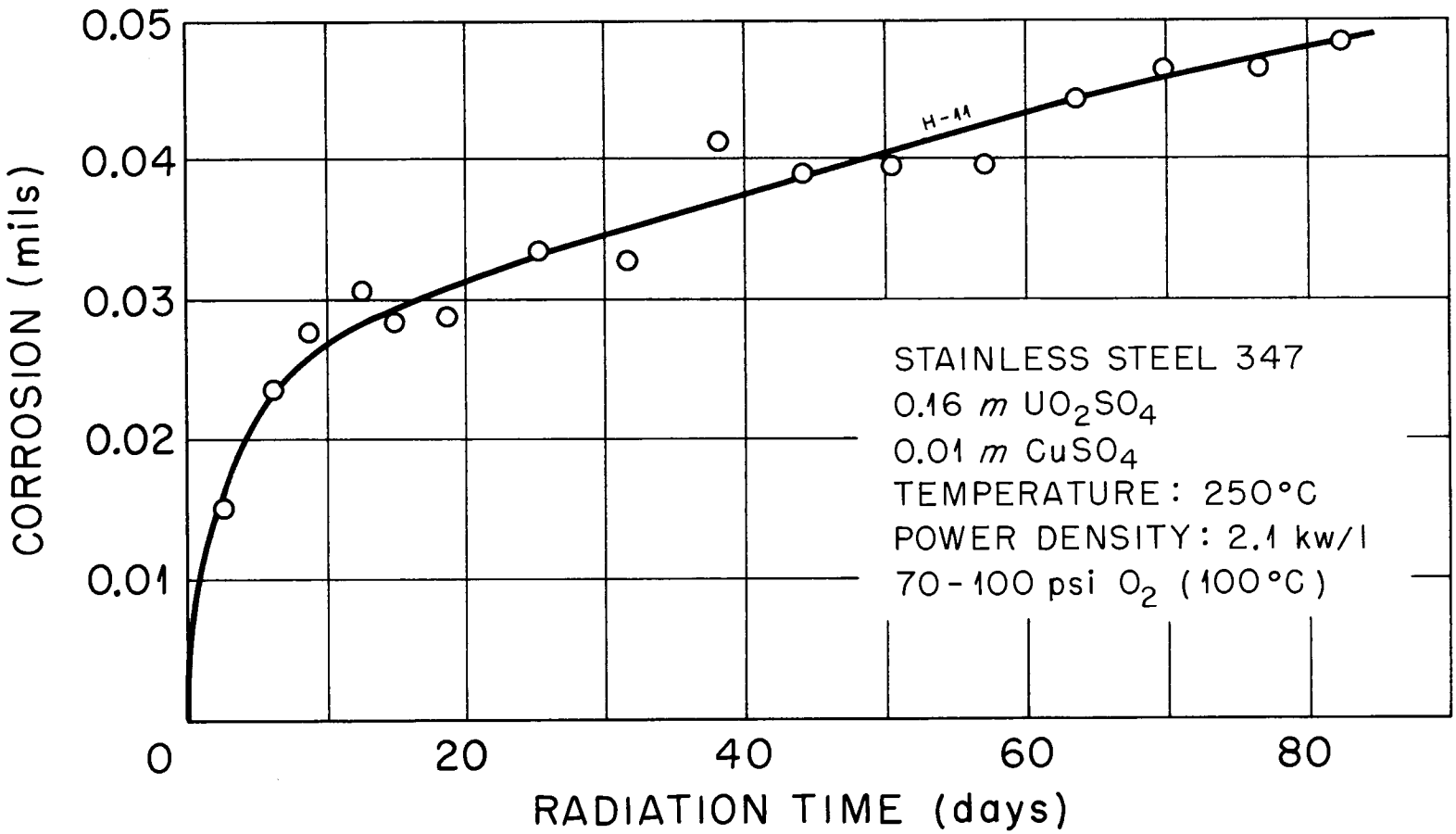

FIGURE 4
CONSISTENCY OF IN-PILE CORROSION DETERMINATIONS BY OXYGEN METHOD

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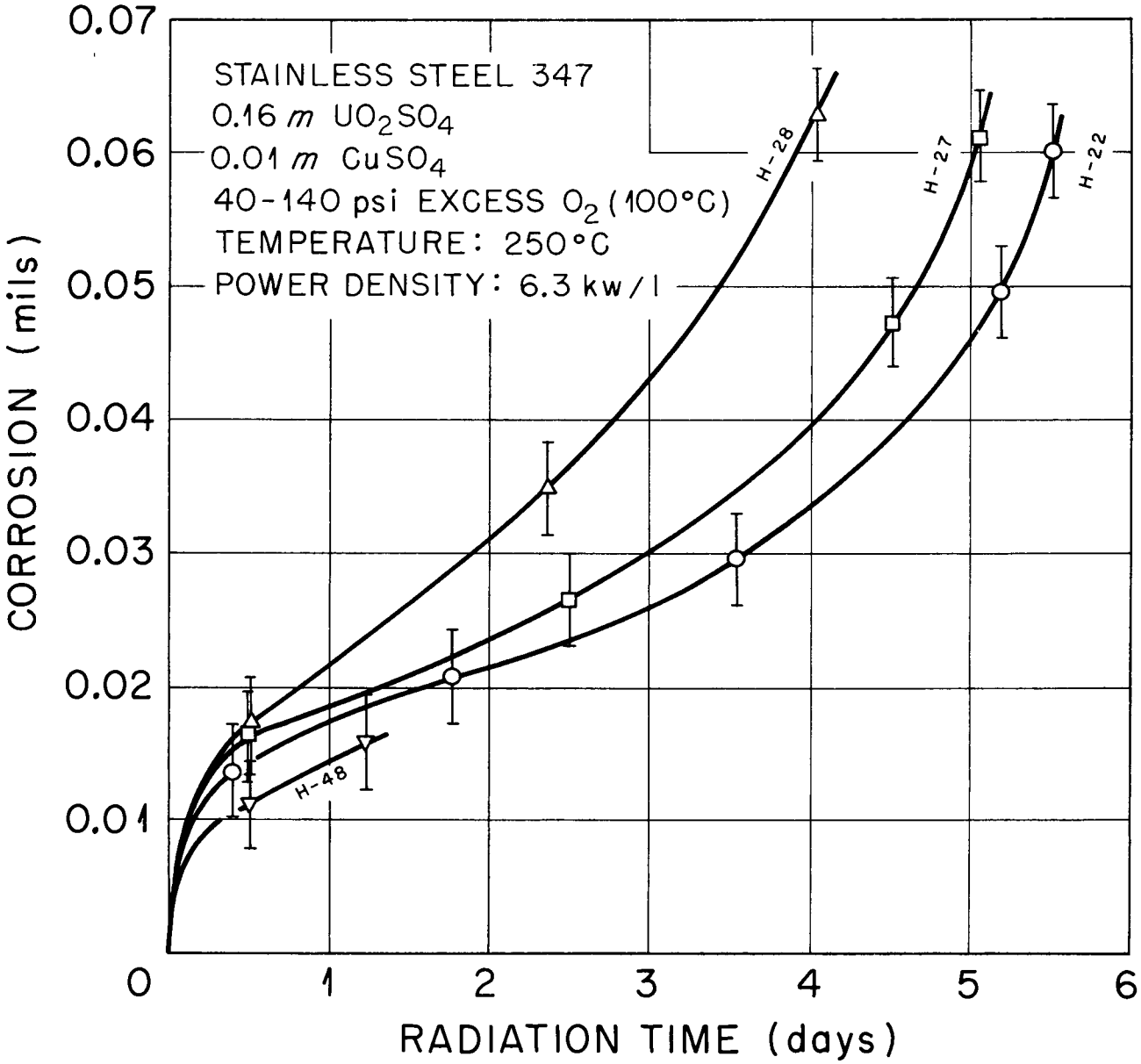

FIGURE 5

REPRODUCIBILITY OF IN-PILE CORROSION MEASUREMENTS

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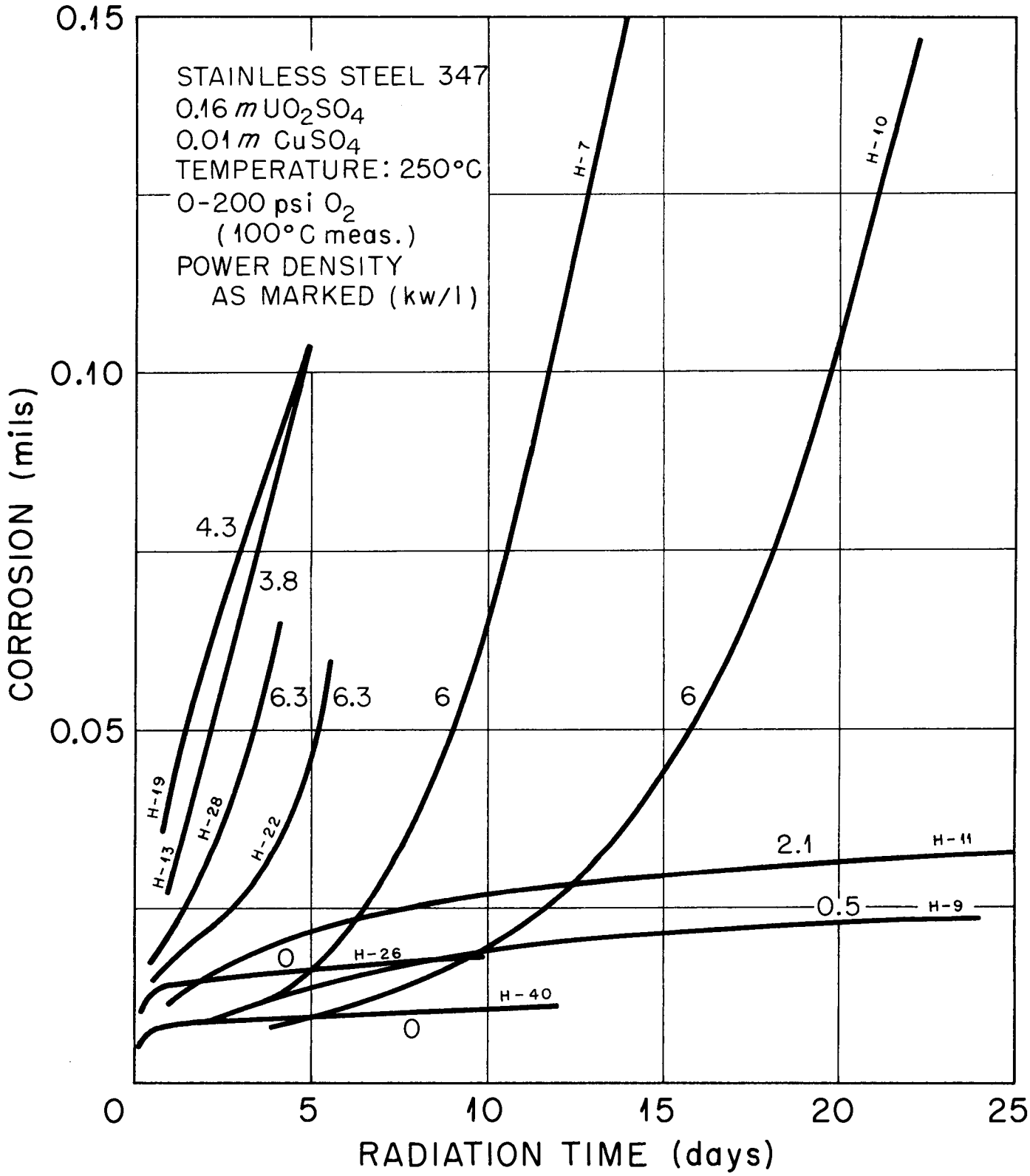

FIGURE 6
EFFECT OF POWER DENSITY

typical irradiation experiments (H-7, 10, 22, and 28, shown in Fig. 6) are in direct contrast to those obtained in out-of-pile work. Over-all corrosion rates are as high as 7.5 mpy, and during the latter portion of the in-pile experiments the rate is even higher than this figure. Thus there is no doubt that radiation can accelerate the corrosion of stainless steel.

However, the corrosion rate is not a simple function of the power density. Experiments H-9 and H-11 (shown in the same figure), run at power densities of 0.5 and 2.1 kw/liter, respectively, show corrosion rates of approximately 0.1 mpy. This is roughly the figure obtained for out-of-pile tests after the initial fast growth period. Experiments H-7 and H-10, run at about 6 kw/liter, show much greater over-all rates of corrosion, especially near their termination, when the rates were as high as 8 mpy. Experiments H-13 and H-19, in which the power density was about 4 kw/liter, also exhibited high corrosion rates. Thus there is a strong indication that the mechanism of corrosion changes sharply in the power-density region of 2 to 4 kw/liter.

It is interesting to note that experiment H-11 was continued until the total corrosion was greater than that at which the sharp rise in rate occurred in experiments H-7 and H-10. Thus the sharp increase in corrosion rate cannot be easily correlated with any simple acceleration mechanism based on cumulative corrosion such as the thickness of oxide film. In addition, total fission was greater in test H-11 than in the other two, which implies that the mechanism is not a simple function of either radiation dosage or the buildup of fission products.

Temperature. Only two experiments, H-12 and H-18 (only one experimental point was obtained for the latter), were conducted at a temperature

other than 250° C, and both of these were at 290° C. From the data shown in Fig. 7 it appears that the effect of temperature on the corrosion of type 347 stainless steel under irradiation is minor in the region between 250 and 290° C.

Solution Stability. It may be noted from Tables 2 and 3 that high pH values (≥ 3.0) obtained at the end of the experiments are consistent with low copper recovery; this is also true to some extent with uranium recovery, although to a lesser degree. These effects are in agreement with the results of phase-rule studies,[7] which indicate that in many cases copper precipitates before uranium at 250° C. Lack of oxygen in H-7 undoubtedly caused the reduction and precipitation of uranium, accounting for its low recovery. An effort was made to terminate subsequent experiments before the excess oxygen was consumed.

The high radioactivity levels encountered have made it difficult to evaluate solution stability accurately. Some idea of the uncertainty of these results can be obtained by noting the reported recoveries over 100%; however, experimental procedures and analyses were apparently improved during the course of these experiments, since the later data appear to be more consistent.

Corrosion Inhibitors. Cartledge has shown[8] that, in the absence of radiation, potassium pertechnetate in low concentration (0.0005 m) is extremely effective for passivating carbon steel exposed to aqueous solutions containing small concentrations of chloride ion. Experiment H-20 was run to determine whether the pertechnetate would appreciably lower the corrosion of type 347 stainless steel by uranyl sulfate solution under reactor conditions. The corrosion data are given in Fig. 8. Unfortunately, only

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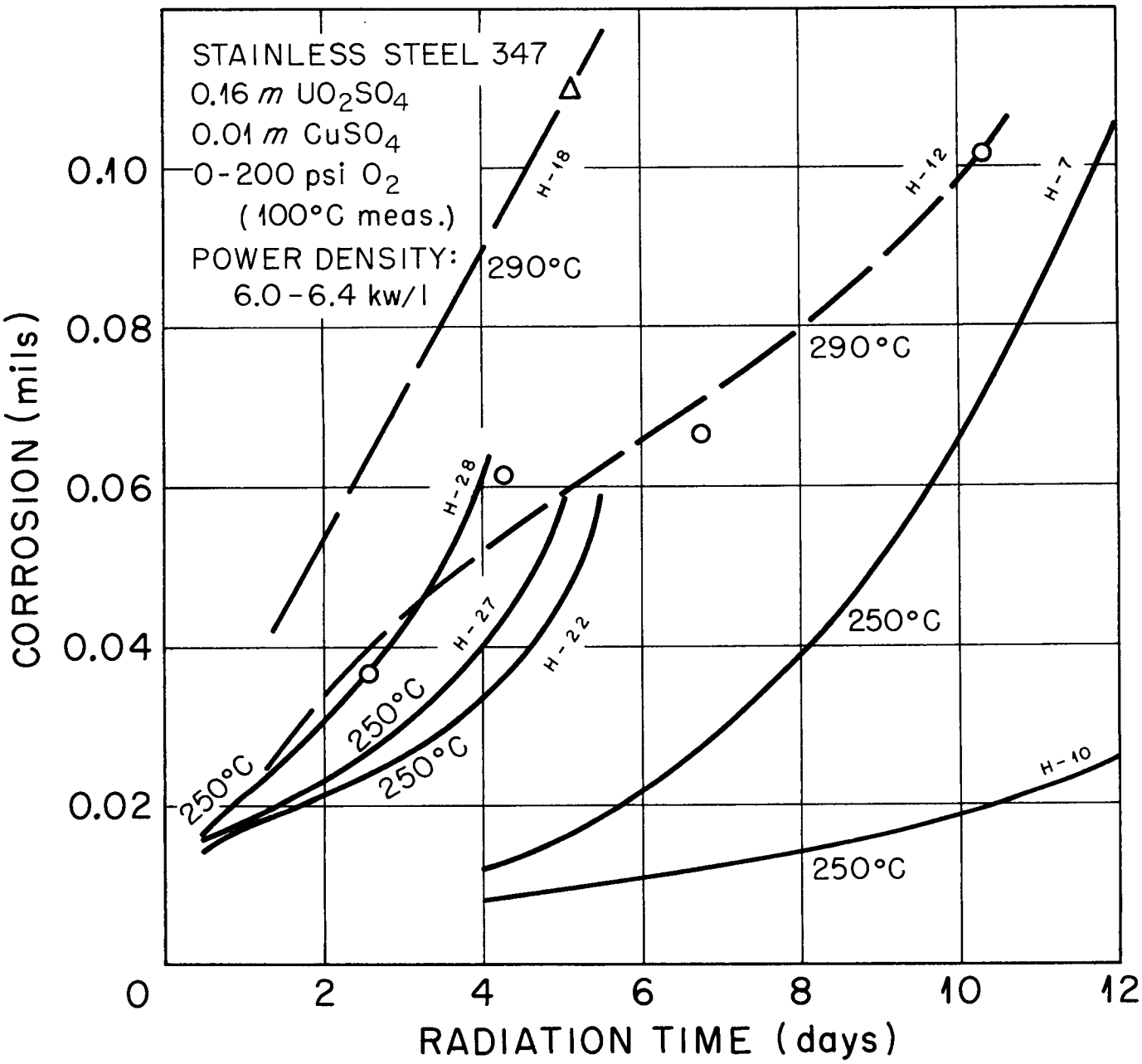

FIGURE 7
EFFECT OF TEMPERATURE

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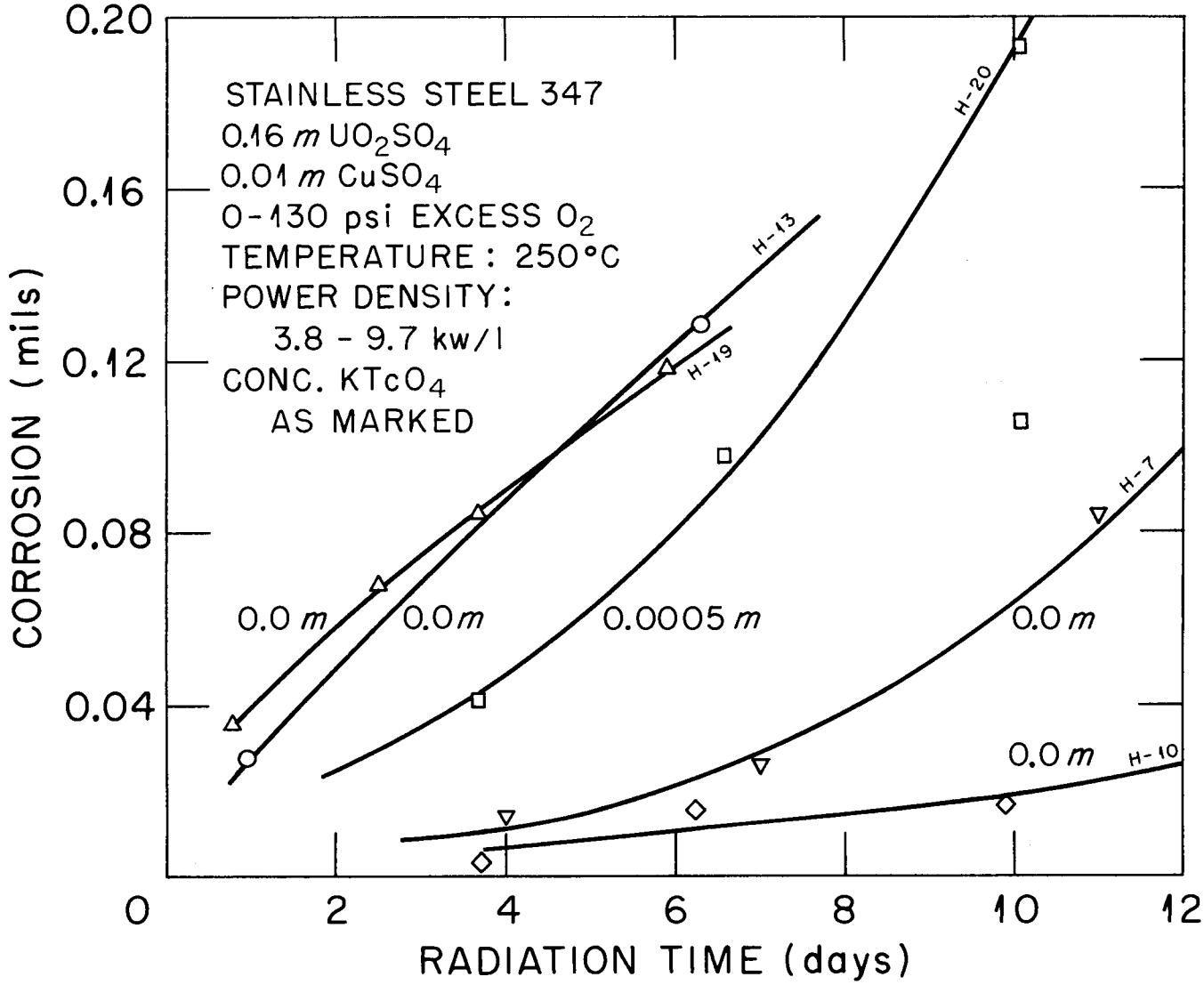

FIGURE 8
EFFECT OF POTASSIUM PERTECHNETATE

three corrosion points were obtained before termination of the run, and no solution analyses are available because of precipitation. However, a high corrosion rate was observed, indicating that the inhibitor was ineffective under these conditions.

Cartledge has recently found[9] that the effectiveness of pertechnetate ion as an inhibitor depends qualitatively on the relative concentrations of the pertechnetate ion and other anions present ion the solution. This fact suggests that corrosion tests with considerably higher concentrations of pertechnetate ion should be made, since the test solutions have a relatively high concentration of sulfate ion.

Suggestions for Future Work. The present techniques should be improved and expanded. The development of a satisfactory method for oxygen injection should give more accurate corrosion data in the early stages of an experiment. Improvements in sampling and analytical technique could result in better evaluation of solution decomposition during irradiation. The development of physical and chemical methods for analyzing the highly radioactive corrosion films should aid in characterizing corrosion processes.

Present corrosion studies should be continued in an effort to elucidate mechanisms. The effect of power density should be investigated fully, particularly in the critical region of 2 to 4 kw/liter. Out-of-pile experiments performed under special conditions, such as at higher temperatures or with added chloride ion, may prove useful in elucidating in-pile corrosion mechanisms. Other variables which obviously should be studied are oxygen pressure, temperature, solution concentration, and different types of radiation. Additives may be useful in testing tentative corrosion mechanisms.

ACKNOWLEDGMENT

The authors are indebted to S. F. Hluchan, J. F. Potts, and J. T. Delorenzo for their help in the design of the instrumentation used in these experiments; to the Analytical Chemistry Division for the necessary chemical analyses; to W. D. Reel for editorial assistance in the preparation of this report; and to B. S. Dunlap for preparing the final graphs.

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8. G. H. Cartledge, Corrosion, 11, 335t, (1955).

9. G. H. Cartledge, Private Communication, Jan. 22, 1957.

SOURCES OF ORIGINAL DATA

Experiment No.	ORNL Notebook Numbers
H-2	1784, 2251, 2395
H-7	2250
H-9	2251, 2905
H-10	2251, 2905
H-11	2904, 2905
H-12	2904, 2905, 2959
H-13	2904, 2905, 2959
H-18	2905, 2959
H-19	2905, 2957, 2959
H-20	2905, 2960
H-22	2905, 2960
H-24	3294
H-26	3294
H-27	3469, 4431
H-28	2960
H-36	3294
H-37	3294
H-38	3294
H-39	3294
H-40	3541
H-41	3541
H-48	3469
H-49	3469
H-51	3469