CORROSION BEHAVIOR
OF
ZIRCALOY

by

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INTRODUCTION

Zirconium base alloys are widely used in water cooled nuclear reactors where their high cost is offset by their low neutron cross section and relatively good resistance to corrosion in water. Although the amount of corrosion is quite small, an accurate estimate of the amount to be expected is required for good reactor design. This estimate is made by extrapolating available data to the expected life of the reactor. For valid approximations it is necessary to know the form of this corrosion rate curve.

The principle alloy in use today is Zircaloy 2 (1.5% Sn, 0.12% Fe, 0.05% Ni, 0.1% Cr, bal. Zr). Thomas[1] and Kass[2] reported the following corrosion rate equations based on weight gains which they assumed to be equal to the amount of oxygen which reacted with the alloy.

Temp. °F	Medium	Pressure psi	Equation
550	water	750	$\log \Delta m = 0.50 + 0.30 \log t$
600	water	1553	$\log \Delta m = 0.74 + 0.26 \log t$
680	water	2705	$\log \Delta m = 0.76 + 0.38 \log t$ (up to $t = 112$ days)
			$\Delta m - 34 = 0.37\,(t-112)$ (after $t = 112$ days)
750	steam	1500	$\log \Delta m = 1.10 + 0.32 \log t$ (up to $t = 41$ days)
			$\Delta m - 41 = 1.27\,(t-41)$

Where Δm is the weight gain in mg/dm^2 and t is the time in days.

Although neither Thomas nor Kass presented the data from which these equations were obtained, Kass presented a graph showing the 2 deviation of the data. This is shown in Figure 1. The times at which the curves intersected (112 days at 680°F or 41 days at 750°F) were called the transition times and were interpreted to represent a change of mechanism. The corrosion film both before and after the transition time has been identified by Schwartz, Vaughn and Cocks[3] and by Chirigos and Thomas[4] to be monoclinic zirconium dioxide.

The interpretation by Thomas and Kass of the data has been questioned. First, the data are equally well represented by equations of the form $y = mx + b$. See Figure 2. Second, there is no change in the appearance or structure of the oxide film.

A possible alternate method of measuring the amount of corrosion is to measure the capacitance of the film. This technique was used by Polling and Charlesby[5] to measure the rate of growth of films on zirconium under anodizing conditions. They calculated the dielectric constant to be 27 and used a film density of 5.67 g/cm^3. This density is in accord with a density of 5.6 g/cm^2 calculated from the crystal lattice constants for monoclinic zirconium dioxide.

Hunter and Fowle[6] working with aluminum found that the thickness of the protective film was proportional to the barrier voltage, i.e., the voltage necessary to cause anodization of the corroded specimen. This thickness was equal to the maximum thickness which could be produced by anodizing at that voltage in a solution which did not attack the oxide. Using the same general method, Polling and Charlesby[5] found that during anodization of zirconium, the maximum thickness was equal to 30 Å/v.

PURPOSE

This study was undertaken (1) to determine the kinetics of the reaction between Zircaloy 2 and water, and (2) to compare the behavior of a relatively new alloy, Zircaloy 3 (0.25% Sn, 0.25% Fe, bal Zr), with Zircaloy 2.

PROCEDURE

Corrosion Tests

Flat 0.15 cm thick specimens with a surface area of 25 cm^2 were annealed at 1425°F for 1/2 hour and etched in a 4% HF--38% HNO_3 (by volume of reagent) solution at about 110°F to remove approximately 2 mils from each surface.

Most of the specimens were tested in 1 liter stainless steel autoclaves. Sixteen specimens, supported on stainless steel holders, and approximately 450 cc of water which had been chemically deoxygenated and deionized to give a resistivity of greater than 2 meg-ohm-cm were added to each autoclave. Helium was bubbled through the water to displace the air, and the sealed autoclaves to be run with water at 680°F were placed in a furnace maintained at 680°F ± 2°; those to be run with steam at 750°F, 1500 psi, were placed in individual heating jackets where the excess water could be vented during heating.

In order to approach reactor conditions, specimens were tested at 620 and 640°F in the KAPL DT1 loop where the velocity past the specimens was 20 ft/sec. Specimens were also tested at 600°F and 30 ft/sec at Babcock and Wilcox under subcontract N101[7]. The water purity in the loop tests was not accurately controlled, but the pH was maintained at 7 and the resistivity was approximately 200,000 ohm-cm.

Each test was interrupted periodically to measure the amount of corrosion.

Weight Change Measurements

Each specimen was weighed before test and after being allowed to air dry over night at each interruption of the test. All of the weighings were made to ± 0.2 mg and are given in Table 1.

Capacitance Measurements

The corrosion film was made the dielectric in a capacitor by making the uncorroded core of the specimen one plate and a dilute solution of nitric acid the other plate, as shown in Figure 3. The capacitance measurements, listed in Table II, were made with an Electro Measurements, Inc., Model 250-DA impedance bridge which was equipped with a 1 KC oscillator.

Barrier Voltage Measurements

The corroded specimens used for barrier voltage measurements were placed in a 5% solution of boric acid to which ammonium hydroxide had been added to give a pH of 5. A schematic drawing of the system used is shown in Figure 4. DC power was supplied by a 350 volt Electronic Measurements Co. regulated power supply. The voltage was measured with a Sensitive Research Co. Model S voltmeter and the current was measured with a shunted General Electric Co. Model 8CE5DJ19A recording photoelectric potentiometer.

The barrier voltage, as shown in Table III, was determined by increasing the voltage by increments until anodization occurred. Although Hunter and Fowle[6] found the barrier voltage as a break in the current vs voltage plot, such a plot for a corroded Zircaloy specimen, as shown in Figure 5, gave a very indistinct break. However, since during anodization at constant voltage, the current decreases with time, the occurrence of anodization could be observed from current vs time chart drawn by the recording ammeter. A typical chart is shown in Figure 6.

DISCUSSION

Porosity of the Corrosion Film

In the initial stages of this work, the corrosion product was assumed to be non porous because the film was smooth and glossy and no change in weight was observed on drying. After sufficient data had been collected to suggest that the corrosion rate might be linear, film porosity was considered. Although drying of specimens at 212°F did not measurably affect the weight of the specimen, it decreased the capacitance of the specimen. If this dried specimen was allowed to stand in dilute HNO_3, the capacitance increased. A plot of the capacitance vs time of drying and time in solution is shown in Figure 7. This indicated that the film was indeed porous.

In order to estimate the extent of porosity, several corroded specimens were anodized stepwise. Before and after each anodization the capacitance of the film was measured. Since the capacitance of two capacitors in parallel is the sum of their capacitances, the capacitance of the film can be written

$$C_1 = \frac{\epsilon}{4\pi} \left(\frac{A_1}{d_1} + \frac{A_2}{d_2} + \frac{A_3}{d_3} \cdots\cdots \frac{A_n}{d_n} \right) \qquad (1)$$

where A is the area of the pore which reaches to within d cm of the metal. After the specimen has been anodized so that the thinnest portion of the film is d_2, the capacitance is

$$C_2 = \frac{\epsilon}{4\pi} \left(\frac{A_1}{d_2} + \frac{A_2}{d_2} + \frac{A_3}{d_3} \cdots\cdots \frac{A_n}{d_n} \right). \qquad (2)$$

Subtracting equation (2) from equation (1) gives

$$C_1 - C_2 = \frac{\epsilon}{4\pi} \left(\frac{A_1}{d_1} - \frac{A_1}{d_2} \right).$$

In order to get the thickness d in terms of applied voltage, several uncorroded specimens of Zircaloy were anodized and the capacitance of their oxide films measured. The reciprocal of the capacitance vs anodization voltage is shown in Figure 8. From the slope of the line, it was found that C = 7.79 A/E where C is in microfarads, A is in cm^2 and E is in volts. This agrees with the calculated relationship of C

$$C = \frac{(7.96)\,(A)}{(E)}$$

assuming $d = (30 \times 10^{-8})\,E$, and $\epsilon = 27$ as given by Charlesby and $\rho = 5.6$ g/cm^2. Therefore, equation (3) may be written

$$C_1 - C_2 = 7.79 \left(\frac{A_1}{E_1} - \frac{A_1}{E_2} \right) . \qquad (4)$$

By dividing both sides of equation (4) by A, the total area used in the capacitance measurement, the equation becomes

$$\frac{C_1 - C_2}{A} = 7.79 \quad \left(\frac{1}{E_1} - \frac{1}{E_2} \right) \left(\frac{A_1}{A} \right)$$

where A_1/A is the fraction of the film which is pores at a distance of d_1 or 30×10^{-8} E_1 cm from the metal. To obtain the value of A_1/A at various values of E, the measured capacitance per unit area was plotted against $\frac{1}{E}$ as is shown in Figure 9 for a typical specimen No. 123-8. This specimen of Zircaloy 3 had been corrosion tested for 14 days in 680°F water and had gained 0.168 mg/cm^2. From the slope of this curve, $7.79 \ \frac{A_1}{A}$, the fraction of the film which was pore area was calculated and is plotted against the applied voltage in Figure 10. The amount of void area was found to increase with applied voltage and to be about 6% of the area at the barrier voltage. Other specimens, both Zircaloy 2 and Zircaloy 3, tested in this manner, gave approximately the same void area. This indicates that the barrier voltage, rather than being a measure of the thinnest portion of the film, is a measure of the thickness at which the porosity becomes appreciable.

Mechanisms

According to the mechanism of corrosion of zirconium and Zircaloy in water proposed by Thomas and Chirigos[4], the corrosion proceeds by the diffusion of oxygen ions from the water-oxide interface to the oxide-metal interface. During the pretransition time, the oxygen ion must diffuse through the total thickness of film, and hence the corrosion rate decreases with time of corrosion (theoretically a parabolic corrosion rate). At the transition time, the film begins to rupture forming a porous outer layer and the corrosion proceeds by a linear rate.

If this is an accurate description of the mechanism, the corrosion film must be impenetrable by molecular water during the pretransition period (up to 112 days at 680°F). Thus the film should exhibit no porosity, the capacitance measurements should give a good measure of the film thickness, and the barrier voltage measured should be proportional to the film thickness. After the transition, the film should be porous; the dielectric constant of the film should increase, i.e., the apparent thickness of the film as calculated from the capacitance measurements should decrease; and the barrier voltage should drop to some constant value.

The specimens tested in this program corroded at about the same amount as those used by Thomas and Chirigos as shown in Figure 11. However, these specimens showed evidence that the film is porous and neither the capacitance measurements nor the barrier voltage measurements indicate the occurrence of a transition of mechanism. The film thickness produced in 680°F water as estimated by weight change measurements using a density of 5.6 g/cm^2 and by capacitance measurements using a dielectric constant of 27 can be seen from Figure 12 to increase fairly uniformly with time. The barrier voltage measurements as shown in Figure 13 appear to approach a maximum of 200 to 250 volts and remain constant at that value. The thickness of the protective layer is therefore approximately 6,000 to 7,500 Å which is much less than the total amount of corrosion film observed.

Since the rate of corrosion of Zircaloy is low, it is reasonable to assume that the corrosion product is offering considerable protection even though porosity of the film has been observed. This leads to the conclusion that the film is effectively two layers, one protective and the other nonprotective. Since the porosity was observed after the shortest test periods used, it is assumed that the nonprotective film is being formed from the protective film at a constant rate. The rate of corrosion then approaches an equilibrium rate at which the rate of oxidation equals the rate of formation of the protective film which in turn is equal to the rate of conversion from protective to nonprotective film. Although no identification of the protective layer has been made, it is suggested that it may be the tetragonal form of zirconium dioxide as was observed by Schwarz, Vaughn, and Cocks[3] on zirconium specimens which had been exposed to 600°F water for less than 6 hours. The tetragonal form, although unstable at these temperatures, has a higher density, 6.1 g/cm^2, than the monoclinic 5.6 g/cm^2 and hence would have much less mechanical stress.

This study did not include the effects of alloying agents or impurities; however, their effects on the corrosion behavior could be incorporated into this mechanism by considering that they directly affect either the stability of the protective film or the rate of diffusion through the protective layer.

CONCLUSIONS

From the results obtained, it was concluded that:

1) The corrosion rate of Zircaloy in water is linear and can be described by equations as

Temperature	Equation	Type of Test
750°F steam	$\Delta W/A = 0.014\ t + 0.15$	static autoclaves
680°F water	$\Delta W/A = 0.003\ t + 0.15$	static autoclaves
640°F water	$\Delta W/A = 0.0005\ t + 0.18$	DT1 loop (20 fps)
620°F water	$\Delta W/A = 0.0005\ t + 0.22$	DT1 loop (20 fps)
600°F water	$\Delta W/A = 0.0002\ t + 0.11$	B and W loop (20 fps)

Where $\Delta W/A$ is the weight gain in mg/cm^2 and t is the time in days.

2) There is no significant difference in the corrosion rates of Zircaloy 2 and Zircaloy 3*, and

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* This statement is not meant to imply that both alloys are equally useable. Other studies, not included in this report have indicated that the corrosion of Zircaloy 2 is adversely affected by smaller quantities of impurities than is allowable in Zircaloy 2.

3) The use of capacitance measurements, although not an absolute method for measuring film thickness, is very useful in determining the nature of the oxide film.

FURTHER WORK

The study of the corrosion behavior of Zircaloy 2 is being continued. Specific areas being investigated are the rate of absorption of hydrogen and the rate at which the oxide is lost.

It is expected that the measurement of rate of oxide lost will have little effect on the results obtained on specimens tested in static water but may noticeably increase the estimate of the corrosion rate in dynamic water.

APPENDIX

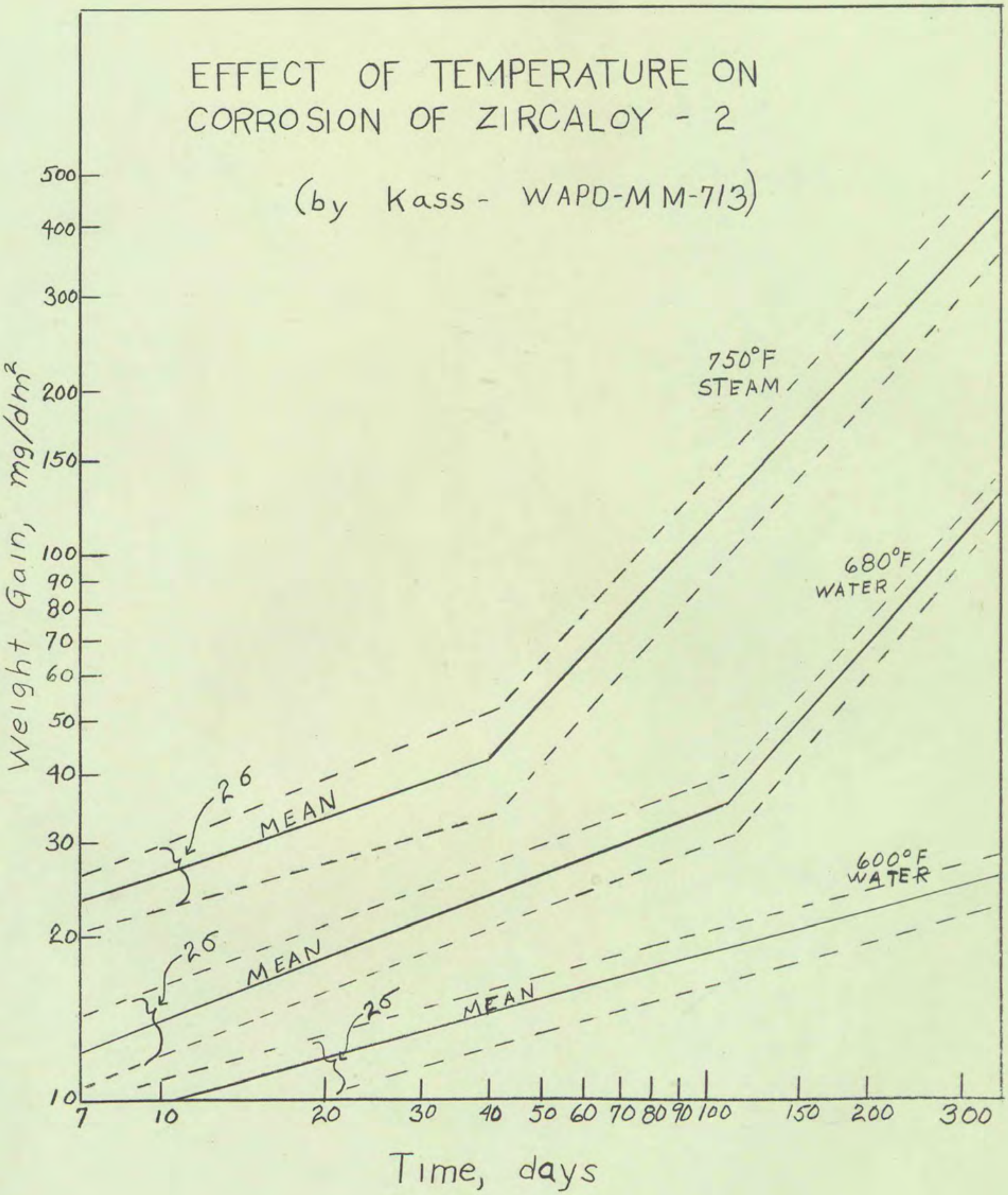

EFFECT OF TEMPERATURE ON CORROSION OF ZIRCALOY - 2
(by Kass - WAPD-MM-713)
Weight Gain, mg/dm²
500
400
300
200
150
100
90
80
70
60
50
40
30
20
10
7
10
20
30
40
50
60
70
80
90
100
150
200
300
Time, days
750°F STEAM
680°F WATER
600°F WATER
MEAN
MEAN
MEAN
2σ
2σ
2σ

Fig. 1.

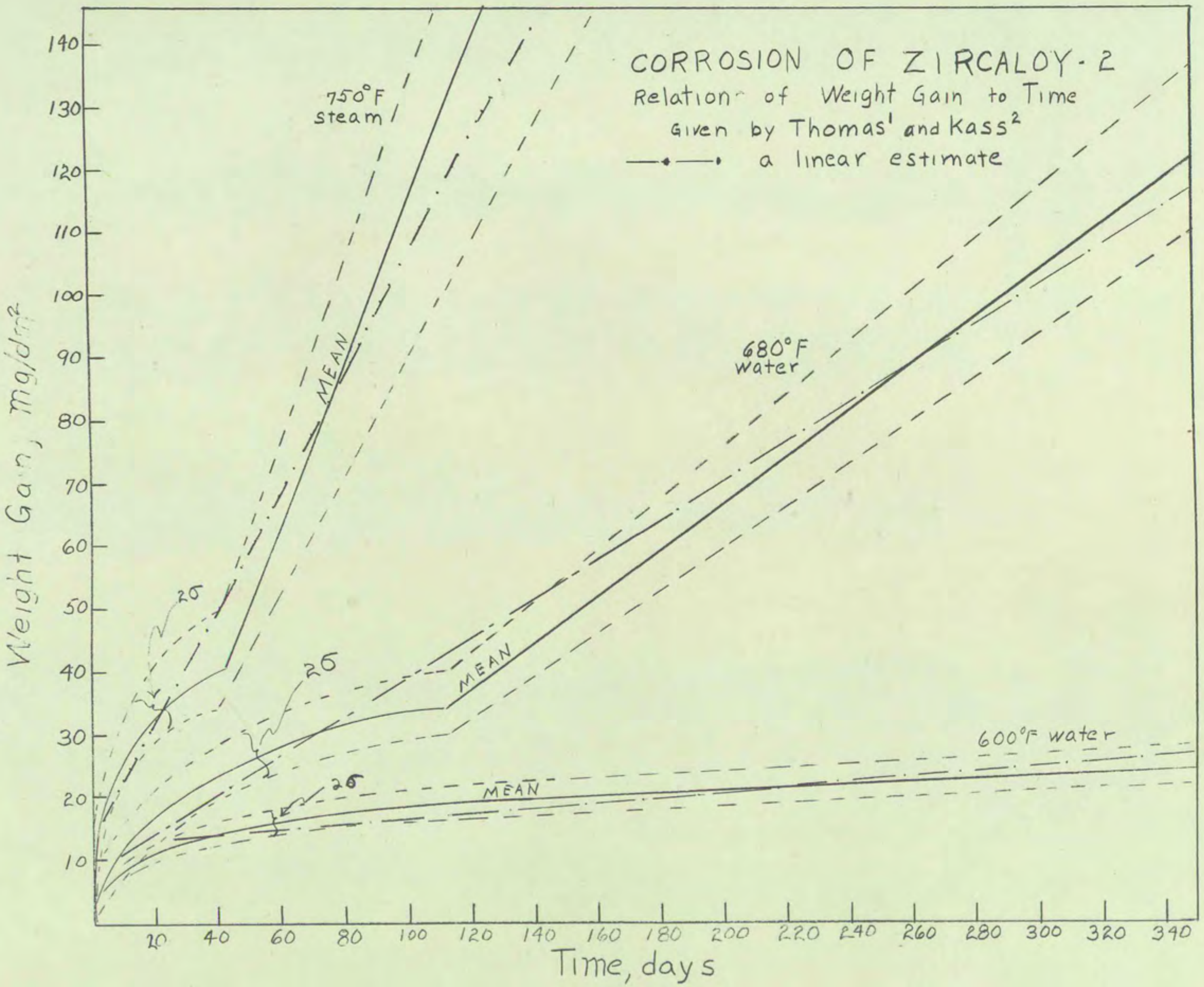

CORROSION OF ZIRCALOY-2
Relation of Weight Gain to Time
Given by Thomas¹ and Kass²
a linear estimate
750°F steam
680°F water
600°F water
MEAN
MEAN
MEAN
2σ
2σ
2σ
Weight Gain, mg/dm²
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time, days
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340

Fig. 2.

TABLE I

Weight Measurements of Corroded Zircaloy Specimens

Specimen number	Time	Initial weight	Final weight	Weight change per unit area	Calculated thickness
	days	grams	grams	mg/cm^2	cm x 10^{-4}
Zircaloy 2 tested in 680°F static water					
R-1	7	11.2153	11.2195	.168	1.15
R-2	7	11.7754	11.7796	.168	1.15
Z-7-61	9	7.6774	7.6812	.152	1.04
Z-6A-1	9½	11.0243	11.0277	.136	.93
Z-6A-3	9½	11.3955	11.3991	.144	.99
Z-6B-1	9½	11.3170	11.3213	.172	1.18
Z-6B-2	9½	11.3383	11.3426	.172	1.18
156	14	11.6568	11.6616	.186	1.28
Z-7-61	19	7.6774	7.6824	.200	1.38
Z-6A-1	20	11.0243	11.0287	.176	1.21
Z-6A-3	20	11.3955	11.3996	.164	1.13
Z-6B-1	20	11.3170	11.3222	.208	1.43
Z-6B-2	20	11.3383	11.3437	.216	1.46
R-1	21	11.2153	11.2207	.216	1.46
R-2	21	11.7754	11.7805	.204	1.43
48-4-13	30	10.8445	10.8501	.224	1.54
48-4-14	30	11.0036	11.0095	.236	1.62
48-4-15	30	11.0718	11.0788	.280	1.92
Z-7-61	50	7.6774	7.6879	.420	2.88
Z-6A-1	50	11.0243	11.0323	.320	2.20
Z-6A-3	50	11.3955	11.4039	.336	2.30
Z-6B-1	50	11.3170	11.3235	.260	1.78
Z-6B-2	50	11.3383	11.3452	.276	1.89
48-4-10	90	10.8901	10.9056	.380	2.61
48-4-11	90	11.0153	11.0247	.376	2.58
48-4-12	90	11.1370	11.1473	.412	2.83
Z-6A-1	99	11.0243	11.0342	.396	2.72
Z-6A-3	99	11.3955	11.4088	.532	3.65
Z-7-61	100	7.6774	7.6898	.496	3.40
Z-6B-1	100	11.3170	11.3254	.336	2.31
Z-6B-2	100	11.3383	11.3490	.428	2.93
Z-6B-1	130	11.3170	11.3306	.544	3.73
Z-6B-2	130	11.3383	11.3528	.580	3.98
Z-7-61	138	7.6774	7.6954	.720	4.94
Z-6A-1	148	11.0243	11.0408	.660	4.53
Z-6A-3	148	11.3955	11.4131	.704	4.83

TABLE I

(Continued)

Specimen number	Time days	Initial weight grams	Final weight grams	Weight change per unit area mg/cm^2	Calculated thickness $cm \times 10^{-4}$
Z-6B-1	160	11.3170	11.3326	.624	4.26
Z-6B-2	160	11.3383	11.3553	.680	4.66
48-4-2	160	10.7709	10.7856	.588	4.03
48-4-4	160	11.0060	11.0213	.612	4.20
48-4-6	160	11.1005	11.1157	.608	4.17
Z-6A-1	179	11.0243	11.0424	.724	4.97
Z-6A-3	179	11.3955	11.4160	.856	5.87
48-4-2	190	10.7709	10.7870	.644	4.42
48-4-4	190	11.0060	11.0225	.660	4.53
48-4-6	190	11.1005	11.1175	.680	4.66
48-4-2	220	10.7709	10.7883	.696	4.77
48-4-4	220	11.0060	11.0240	.720	4.94
48-4-6	220	11.1005	11.1196	.764	4.24
48-4-2	250	10.7709	10.7921	.848	5.82
48-4-4	250	11.0060	11.0265	.820	5.62
48-4-6	250	11.1005	11.1217	.848	5.82
48-4-2	280	10.7709	10.7955	.984	6.75
48-4-4	280	11.0060	11.0399	.956	6.50
48-4-6	280	11.1005	11.1249	.976	6.70
48-4-2	310	10.7709	10.7968	1.036	7.11
48-4-4	310	11.0060	10.0316	1.024	7.02
48-4-6	310	11.1005	11.1268	1.052	7.22
48-4-2	340	10.7709	10.8001	1.168	8.02
48-4-4	340	11.0060	11.0336	1.104	7.53
48-4-6	340	11.1005	11.1291	1.144	7.84
48-4-2	370	10.7709	10.8034	1.300	8.92
48-4-4	370	11.0060	11.0369	1.236	8.48
48-4-6	370	11.1005	11.1321	1.264	8.52
48-4-2	399	10.7709	11.8064	1.420	9.74
48-4-4	399	11.0060	11.0396	1.344	9.22
48-4-6	399	11.1005	11.1348	1.372	9.41
48-4-2	429	10.7709	10.8048	1.556	10.67
48-4-4	429	11.0060	11.0418	1.432	9.82
48-4-6	429	11.1005	11.1372	1.468	10.07

TABLE I

(Continued)

Specimen number	Time	Initial weight	Final weight	Weight change per unit area	Calculated thickness
	days	grams	grams	mg/cm^2	$cm \times 10^{-4}$
Zircaloy 3 tested in 680°F static water					
Z-1-1	8	9.3185	9.3215	.120	0.83
Z-1-2	8	9.0040	9.0073	.132	0.91
Z-7-7	9	7.7446	7.7486	.160	1.10
Z-6A-5	9½	8.6754	8.6788	.136	0.94
Z-6A-6	9½	8.6863	8.6902	.151	1.04
Z-6B-5	9½	8.5340	8.5384	.180	1.24
Z-6B-6	9½	8.7322	8.7365	.176	1.21
56-3	14	10.6851	10.6898	.188	1.29
123-8	14	11.2047	11.2089	.168	1.15
58-2	14	10.6643	10.6693	.200	1.38
Z-7-7	19	7.7446	7.7499	.212	1.45
Z-6A-5	20	8.6754	8.6794	.160	1.10
Z-6A-6	20	8.6863	8.6905	.168	1.15
Z-6B-5	20	8.5340	8.5397	.228	1.56
Z-6B-6	20	8.7322	8.7377	.220	1.51
Z-1-1	20	9.3185	9.3222	.148	1.02
Z-1-2	20	9.0040	9.0082	.168	1.15
Z-7-7	50	7.7446	7.7566	.480	3.29
Z-1-1	50	9.3185	9.3239	.216	1.48
Z-1-2	50	9.0040	9.0096	.224	1.54
Z-6A-5	50	8.6754	8.6841	.348	2.38
Z-6A-6	50	8.6863	8.6934	.284	1.95
Z-6B-5	50	8.5340	8.5424	.336	2.31
Z-6B-6	50	8.7322	8.7396	.296	2.03
Z-1-1	63	9.3185	9.3246	.244	1.67
Z-1-2	63	9.0040	9.0103	.252	1.73
Z-1-1	79	9.3185	9.3250	.260	1.78
Z-1-2	79	9.0040	9.0107	.268	1.84
Z-6A-5	99	8.6754	8.6862	.432	2.90
Z-6A-6	99	8.6863	8.6952	.356	2.42
Z-7-7	100	7.7446	7.7585	.556	3.82
Z-6B-5	100	8.5340	8.5447	.428	2.94
Z-6B-6	100	8.7322	8.7420	.392	2.69
Z-1-1	129	9.3185	9.3288	.412	2.82
Z-1-2	129	9.0040	9.0154	.456	3.14
Z-6B-5	130	8.5340	8.5516	.704	4.82
Z-6B-6	130	8.7322	8.7484	.648	4.45

TABLE I

(Continued)

Specimen number	Time days	Initial weight grams	Final weight grams	Weight change per unit area mg/cm^2	Calculated thickness $cm \times 10^{-4}$
Z-7-7	138	7.7446	7.7605	.636	4.36
Z-6A-5	148	8.6758	8.6919	.644	4.42
Z-6A-6	148	8.6863	8.7005	.568	3.90
Z-1-1	158	9.3185	9.3308	.492	3.37
Z-1-2	158	9.0040	9.0174	.536	3.69
Z-6B-5	160	8.5340	8.5527	.748	5.13
Z-6B-6	160	8.7322	8.7508	.744	5.10
Z-6A-5	179	8.6754	8.6940	.704	4.83
Z-6A-6	179	8.6863	8.7016	.612	4.20
Z-1-1	188	9.3185	9.3317	.528	3.62
Z-1-2	188	9.0040	9.0172	.528	3.62
Zircaloy 2 tested in 750°F - 1500 psi steam					
X 1	3	11.4011	11.4114	.412	2.82
Z-29-1	3	11.6930	11.6984	.216	1.48
Z-29-2	3	11.6141	11.6193	.208	1.43
R 4	8	10.4474	10.4536	.248	1.70
R 5	8	11.3816	11.3880	.256	1.76
R 6	8	11.6169	11.6224	.220	1.51
X 1B	11	11.3202	11.3278	.304	2.09
X 2B	11	11.4758	11.4859	.404	2.77
X 1C	14	11.6276	11.6366	.360	2.47
R 4	26	10.4474	10.4625	.604	4.15
R 5	26	11.3816	11.3962	.584	4.01
R 6	26	11.6169	11.6322	.612	4.20
Zircaloy 3 tested in 750°F steam					
55-8	3	10.3924	10.3984	.240	1.65
56-8	3	9.5620	9.5677	.228	1.56
51-6	3	11.5569	11.5607	.152	1.04
55-8	7	10.3924	10.3993	.276	1.89
56-8	7	9.5620	9.5689	.272	1.87
51-6	14	11.5569	11.5633	.256	1.76
55-8	14	10.3924	10.4008	.336	2.31
56-8	14	9.5620	9.5701	.324	2.22
51-6	17	11.5569	11.5642	.292	2.00
51-6	21	11.5569	11.5645	.304	2.09

TABLE I

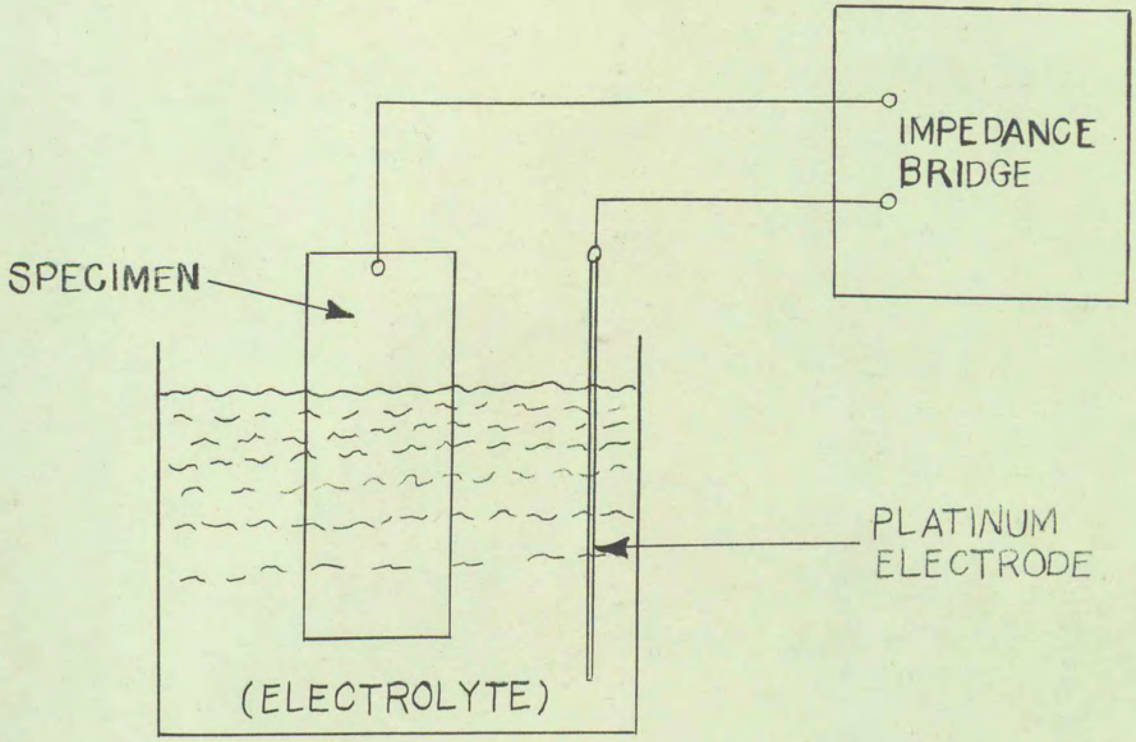
(Continued)

Specimen number	Time	Initial weight	Final weight	Weight change per unit area	Calculated thickness
	days	grams	grams	mg/cm^2	cm x 10^{-4}
55-8	32	10.3924	10.4051	.508	3.49
56-8	32	9.5620	9.5740	.480	3.29
Zircaloy 2 tested in 640°F dynamic water					
DT1-21	16	2.4673	2.4713	.160	1.10
DT1-19	21.5	2.6451	2.6503	.208	1.43
DT1-20	21.5	2.5920	2.5954	.136	.93
DT1-21	35.4	2.4673	2.4721	.192	1.32
DT1-20	37.5	2.5920	2.5957	.148	1.02
DT1-21	49.4	2.4673	2.4721	.192	1.32
DT1-20	58.3	2.5920	2.5958	.152	1.04
DT1-21	70.6	2.4673	2.4707	.136	.93
Zircaloy 3 tested in 640°F dynamic water					
DT1-10	21.5	3.4926	3.4972	.184	1.26
DT1-13	21.5	2.9781	2.9817	.144	.99
DT1-10	37.5	3.4926	3.4976	.200	1.37
DT1-13	37.5	2.9781	2.9819	.152	1.04
DT1-10	58.3	3.4926	3.4980	.216	1.45
DT1-13	58.3	2.9781	2.9823	.168	1.15
Zircaloy 2 tested in 620°F dynamic water					
DT1-3	21.5	2.1760	2.1831	.284	1.95
DT1-4	21.5	2.5121	2.5165	.164	1.13
DT1-3	37.5	2.1760	2.1835	.300	2.06
DT1-4	37.5	2.5121	2.5163	.168	1.15
DT1-3	58.3	2.1760	2.1837	.308	2.12
DT1-4	58.3	2.5121	2.5169	.192	1.32
DT1-3	70.6	2.1760	2.1838	.312	2.14
DT1-4	70.6	2.5121	2.5166	.180	1.23
Zircaloy 2 tested in 600°F dynamic water					
Z-8-5	17.9	7.7661	7.7682	.104	.71
Z-8-6	17.9	8.4191	8.4209	.072	.49

TABLE I

(Continued)

Specimen number	Time days	Initial weight grams	Final weight grams	Weight change per unit area mg/cm^2	Calculated thickness $cm \times 10^{-4}$
Z-8-7	43.4	8.3330	8.3364	.136	.93
Z-8-8	43.4	7.7912	7.8940	.112	.77
Z-8-5	83.3	7.7661	7.7700	.156	1.07
Z-8-6	83.3	8.4191	8.4233	.168	1.15
Z-8-7	128	8.3330	8.3383	.212	1.45
Z-8-8	128	7.8912	7.8953	.164	1.13
Z-8-5	137	7.7661	7.7697	.144	.99
Z-8-6	137	8.4191	8.4239	.160	1.10



EQUIPMENT FOR MEASURING CAPACITANCE

Fig. 3.

TABLE II

Capacitance Measurements of Corroded Zircaloy Specimens

Specimen number	Time days	Capacitance microfarads	Area cm^2	Capacitance per unit area $\mu f/cm^2$	Calculated thickness $cm \times 10^{-4}$
Zircaloy 2 tested in 680°F static water					
Z-7-61	9	.1857	12	.0155	1.54
Z-6A-1	9½	.3926	15	.0262	.92
Z-6A-3	9½	.4254	15	.0284	.85
Z-6B-1	9½	.2803	12	.0234	1.02
Z-6B-2	9½	.3547	12	.0295	.81
156	14	.3297	15	.0220	1.09
Z-7-61	19	.1545	10	.0155	1.54
Z-6A-1	20	.3430	17	.0201	1.19
Z-6A-3	20	.3270	16	.0204	1.17
Z-6B-1	20	.2217	11	.0201	1.19
Z-6B-2	20	.2515	11	.0229	1.04
48-4-13	30	.1955	10.9	.0179	1.33
48-4-14	30	.2192	10.9	.0201	1.19
48-4-15	30	.2621	10.9	.0240	.99
Z-7-61	50	.1625	13	.0125	1.91
Z-6A-1	50	.2110	14	.0150	1.59
Z-6A-3	50	.2120	14	.0152	1.58
Z-6B-1	50	.1138	9	.0126	1.89
Z-6B-2	50	.1292	9	.0144	1.66
48-4-10	90	.1348	10.9	.0124	1.93
48-4-11	90	.1430	11.4	.0125	1.91
48-4-12	90	.1378	10.9	.0126	1.89
Z-6A-1	99	.1378	12	.0115	2.08
Z-6A-3	99	.1435	12	.0120	1.99
Z-7-61	100	.1325	15	.0089	2.69
Z-6B-1	100	.1445	14	.0104	2.30
Z-6B-2	100	.1322	14	.0094	2.54
Z-6B-1	130	.1150	16	.0072	3.34
Z-6B-2	130	.1130	16	.0071	3.39
Z-7-61	138	.0686	13	.0053	4.53
Z-6A-1	148	.0980	16	.0061	3.90
Z-6A-3	148	.1174	16	.0073	3.26
Z-6B-2	160	.0882	18	.0049	4.88
Z-6A-1	179	.1040	20	.0052	4.58
Z-6A-3	179	.1040	20	.0052	4.58

TABLE II

(Continued)

Specimen number	Time days	Capacitance microfarads	Area cm^2	Capacitance per unit area μf/cm^2	Calculated thickness cm x 10^{-4}
48-4-2	220	.0936	19	.0049	4.88
48-4-4	220	.1347	19	.0070	3.41
48-4-6	220	.1446	19	.0076	3.14
48-4-2	280	.0470	11	.0043	5.56
48-4-4	280	.0770	11	.0070	3.41
48-4-6	280	.0748	11	.0068	3.51
48-4-2	310	.0330	9	.0037	6.45
48-4-4	310	.0558	9	.0062	3.85
48-4-6	310	.0628	9	.0070	3.41
48-4-2	340	.0536	14	.0038	6.28
48-4-4	340	.1227	14	.0088	2.71
48-4-6	340	.1080	14	.0077	3.10
48-4-2	370	.0470	16	.0029	8.22
48-4-4	370	.1050	16	.0066	3.61
48-4-6	370	.1090	16	.0068	3.51
48-4-2	429	.0391	14	.0028	8.50
48-4-4	429	.0765	14	.0055	4.35
48-4-6	429	.0811	14	.0058	4.12

Zircaloy 3 tested in 680°F static water

Specimen number	Time days	Capacitance microfarads	Area cm^2	Capacitance per unit area μf/cm^2	Calculated thickness cm x 10^{-4}
Z-1-1	8	.3367	11	.0306	.78
Z-1-2	8	.2955	11	.0269	.89
Z-7-7	9	.2596	12	.0216	1.10
Z-6A-5	9½	.4494	15	.0299	.80
Z-6A-6	9½	.3760	15	.0250	.96
Z-6B-5	9½	.3119	12	.0259	.92
Z-6B-6	9½	.3040	11	.0277	.86
56-3	14	.4400	17.1	.0257	.93
123-8	14	.3640	13.4	.0272	.88
58-2	14	.3300	16.7	.0198	1.21
Z-7-7	19	.1871	10	.0187	1.28
Z-6A-5	20	.3080	16	.0192	1.25
Z-6A-6	20	.2820	16	.0180	1.33
Z-6B-5	20	.2350	10	.0235	1.02
Z-6B-6	20	.2510	10	.0251	.95

TABLE II

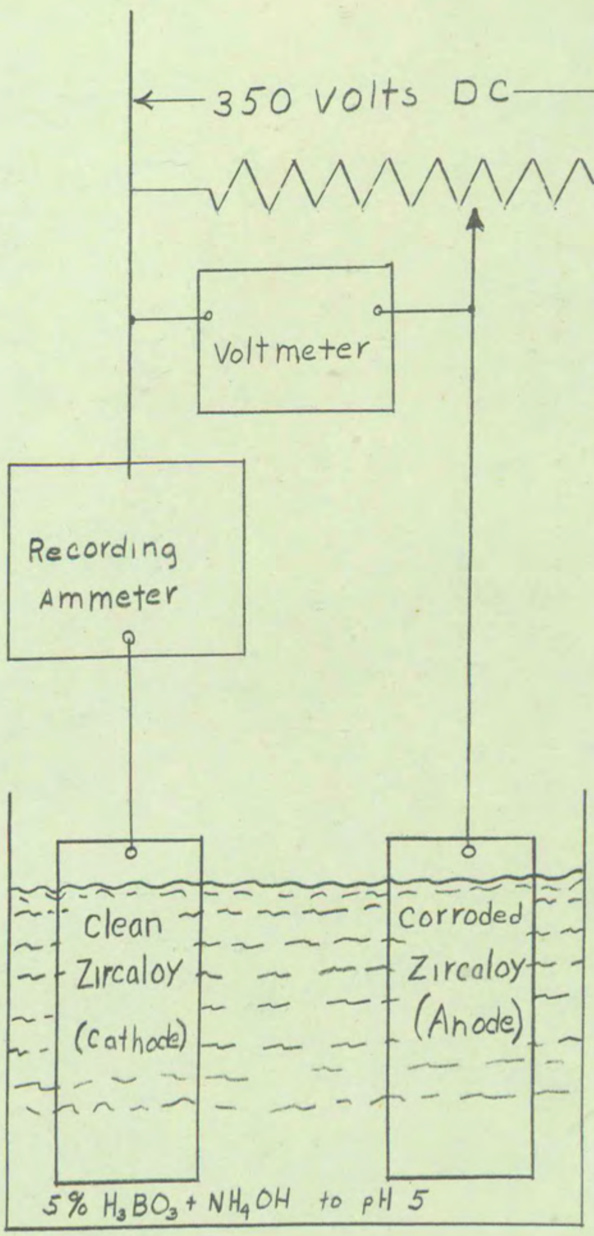
(Continued)

Specimen number	Time	Capacitance	Area	Capacitance per unit area	Calculated thickness
	days	microfarads	cm^2	μf/cm^2	cm x 10^{-4}
Z-1-1	20	.4073	19	.0240	1.00
Z-1-2	20	.3893	19	.0205	1.16
Z-7-7	50	.1780	13	.0137	1.74
Z-1-1	50	.1916	13	.0147	1.63
Z-1-2	50	.1905	13	.0147	1.63
Z-6A-5	50	.1965	14	.0141	1.69
Z-6A-6	50	.2020	14	.0144	1.66
Z-6B-5	50	.1290	9	.0144	1.66
Z-6B-6	50	.1350	9	.0150	1.59
Z-1-1	63	.1848	14	.0132	1.81
Z-1-2	63	.1887	14	.0134	1.78
Z-1-1	79	.1815	14	.0130	1.84
Z-1-2	79	.1754	14	.0125	1.91
Z-6A-5	99	.1405	12	.0117	2.04
Z-6A-6	99	.1315	12	.0110	2.17
Z-7-7	100	.1265	15	.0084	2.84
Z-6B-5	100	.1570	14	.0112	2.13
Z-6B-6	100	.1480	14	.0106	2.26
Z-1-1	129	.1330	16	.0083	2.88
Z-1-2	129	.1237	16	.0077	3.10
Z-6B-5	130	.1220	16	.0076	3.14
Z-6B-6	130	.1220	16	.0076	3.14
Z-7-7	138	.0897	13	.0069	3.46
Z-6A-5	148	.1440	16	.0090	2.66
Z-6A-6	148	.1296	16	.0081	2.95
Z-1-1	158	.1375	17	.0081	2.95
Z-1-2	158	.1060	17	.9962	3.85
Z-6A-5	179	.1220	20	.0061	3.92
Z-6A-6	179	.1280	20	.0064	3.74
Z-1-1	188	.0810	16	.0051	4.68
Z-1-2	188	.0740	16	.0046	5.20
Zircaloy 2 tested in 640°F dynamic water					
DT1-19	21.5	.4135	15	.0276	.87
DT1-20	21.5	.4941	15	.0329	.73
DT1-21	49.4	.2858	17	.0168	1.42
DT1-20	58.3	.3817	15	.0254	.95

TABLE II

(Continued)

Specimen number	Time	Capacitance	Area	Capacitance per unit area	Calculated thickness
	days	microfarads	cm^2	$\mu f/cm^2$	cm x 10^{-4}
Zircaloy 3 tested in 640°F dynamic water					
DT1-10	21.5	.4815	17	.0283	.84
DT1-13	21.5	.4406	15	.0294	.81
DT1-10	58.3	.3134	17	.0184	1.30
DT1-13	58.3	.2909	15	.0194	1.23
Zircaloy 2 tested in 620°F dynamic water					
DT1-3	21.5	.4750	17	.0280	.85
DT1-4	21.5	.4150	15	.0276	.87
DT1-3	58.3	.3135	17	.0185	1.29
DT1-4	58.3	.2730	15	.0182	1.31



EQUIPMENT FOR MEASURING BARRIER VOLTAGE
Fig. 4.

TABLE III

Barrier Voltage Measurements of Zircaloy Specimens Corroded in 680°F Water

Specimen number	Material	Time (days)	Barrier voltage (volts)
R 1	Zirc 2	7	28
R 2	Zirc 2	7	30
56-2	Zirc 3	14	2
58-2	Zirc 3	14	3.8
123-8	Zirc 3	14	12
R 1	Zirc 2	21	30
R 2	Zirc 2	21	25
48-4-13	Zirc 2	30	50
48-4-14	Zirc 2	30	27
48-4-10	Zirc 2	90	57
Z-6B-5	Zirc 3	160	115
Z-6B-2	Zirc 2	160	230
Z-6A-1	Zirc 2	179	210
Z-6A-3	Zirc 2	179	190
Z-1-2	Zirc 3	188	190
48-4-2	Zirc 2	429	245
48-4-4	Zirc 2	429	245

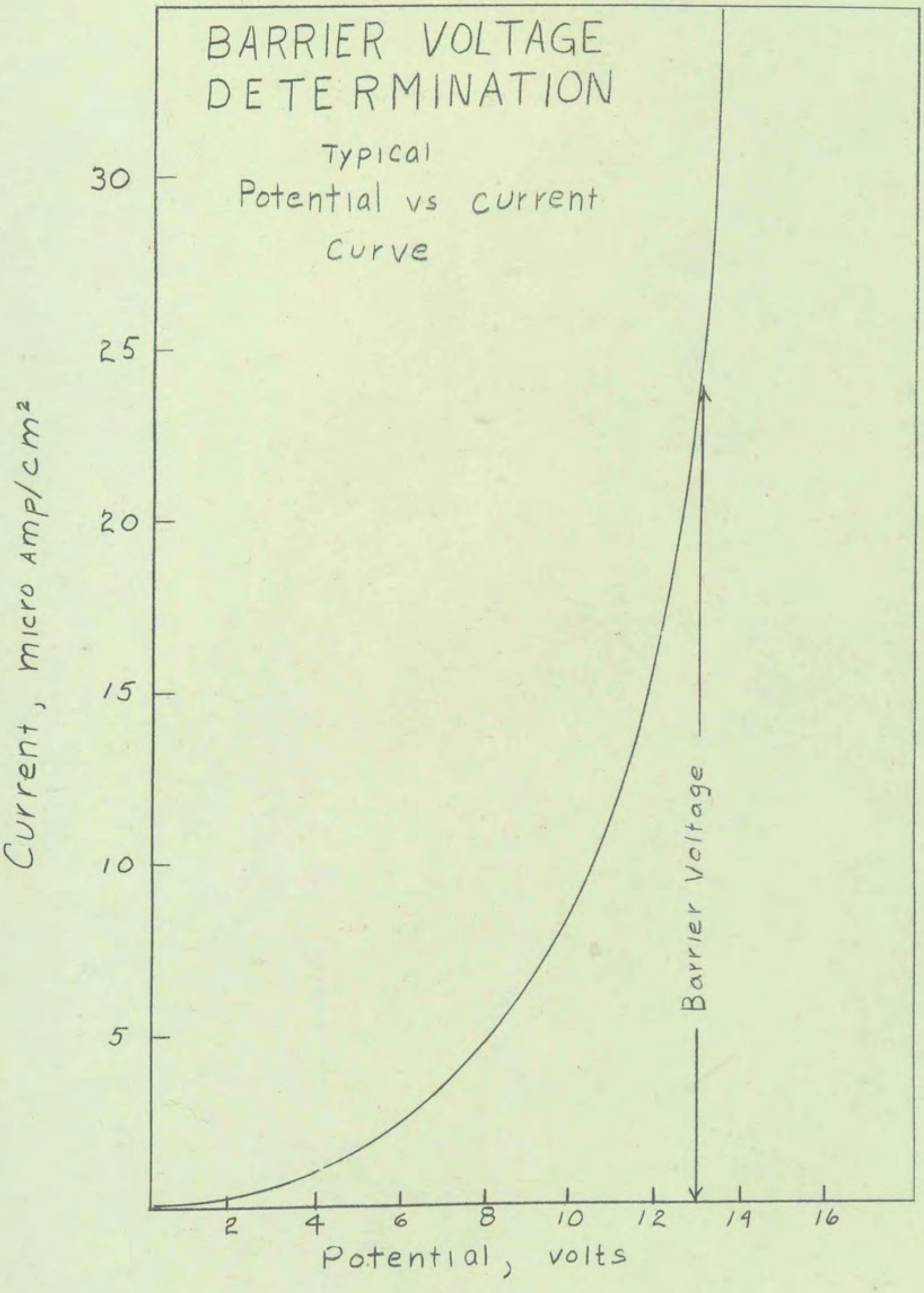

BARRIER VOLTAGE
DETERMINATION
Typical
Potential vs current
Curve
Current, micro amp/cm²
30
25
20
15
10
5
2
4
6
8
10
12
14
16
Potential, volts
Barrier Voltage

Fig. 5

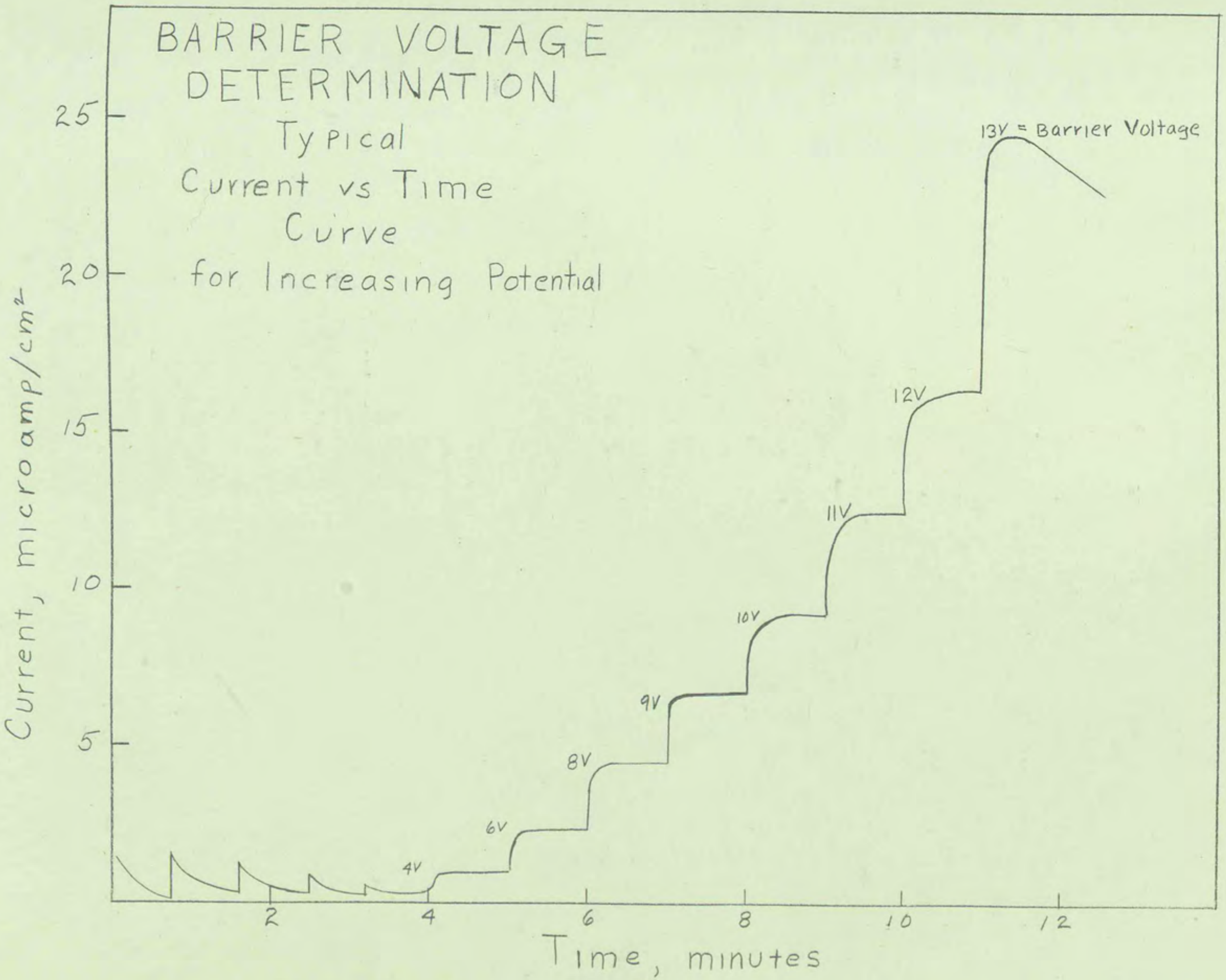

BARRIER VOLTAGE DETERMINATION
Typical
Current vs Time
Curve
for Increasing Potential
13V = Barrier Voltage
12V
11V
10V
9V
8V
6V
4V
25
20
15
10
5
2
4
6
8
10
12
Current, microamp/cm²
Time, minutes

Fig. 6.

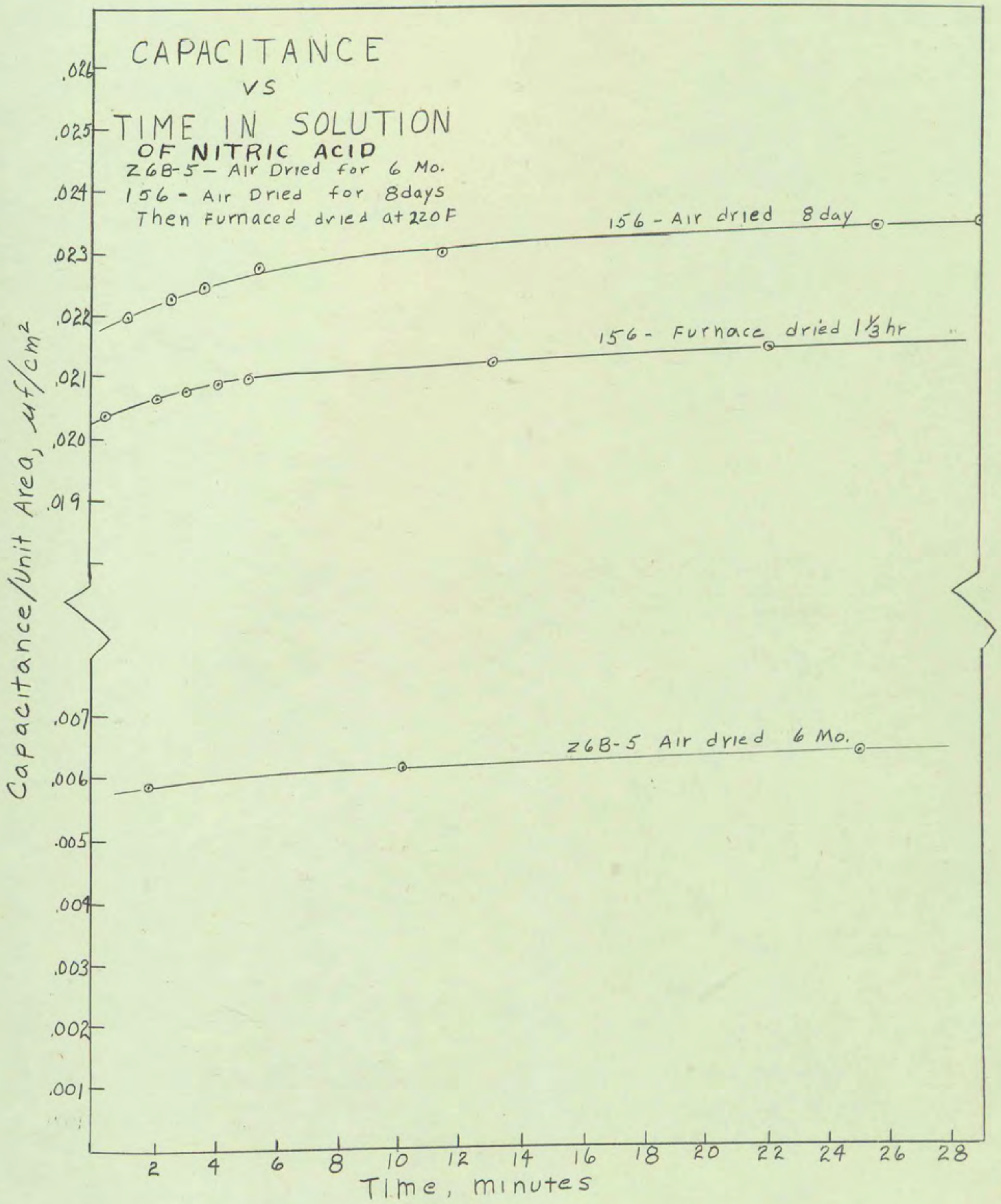

CAPACITANCE
VS
TIME IN SOLUTION
OF NITRIC ACID
Z6B-5 – Air Dried for 6 Mo.
156 - Air Dried for 8days
Then Furnaced dried at 220F
156 - Air dried 8 day
156 - Furnace dried 1 1/3 hr
Z6B-5 Air dried 6 Mo.
Capacitance/Unit Area, uf/cm²
.026
.025
.024
.023
.022
.021
.020
.019
.007
.006
.005
.004
.003
.002
.001
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Time, minutes

Fig. 7.

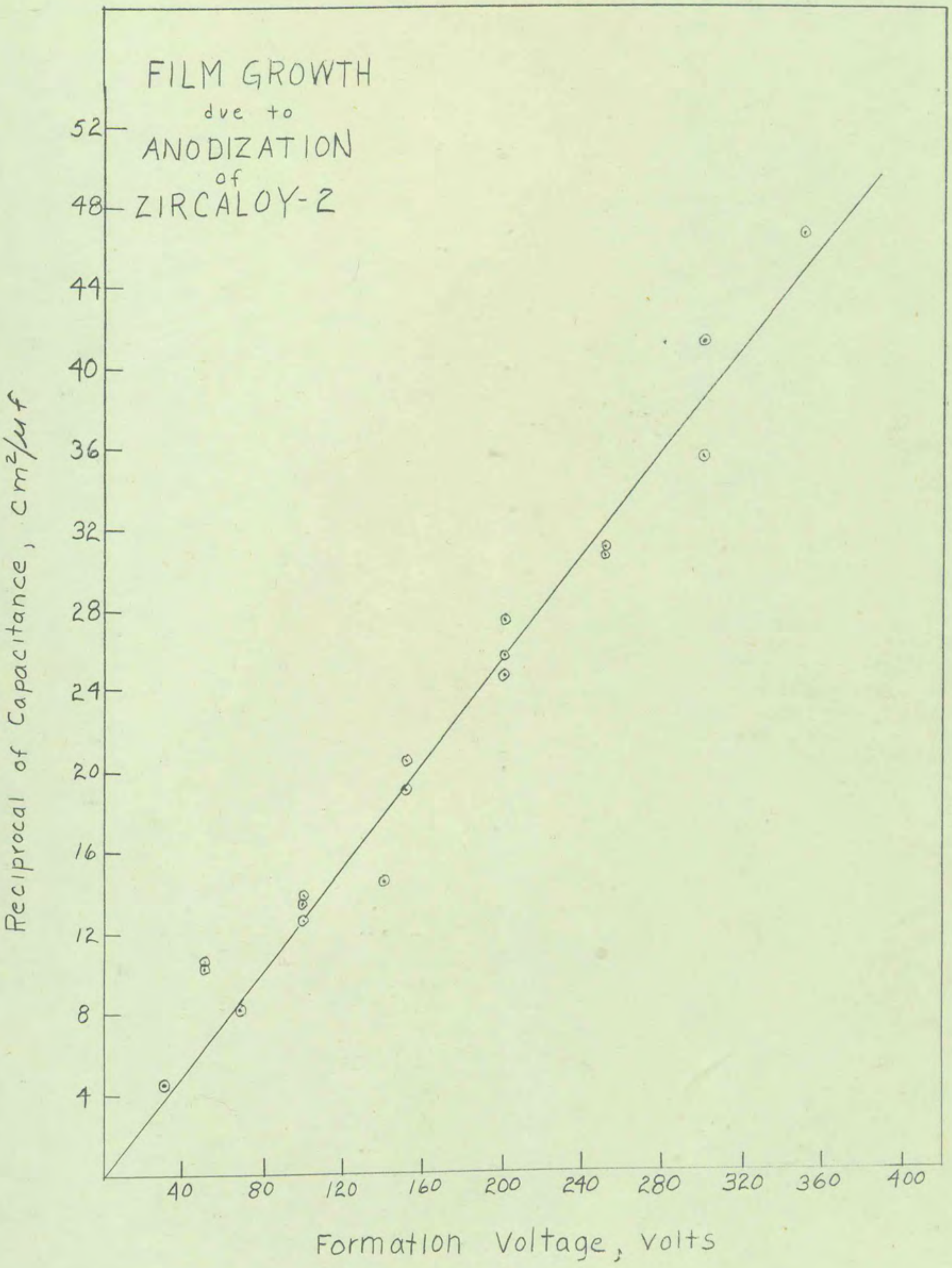

FILM GROWTH
due to
ANODIZATION
of
ZIRCALOY-2
Reciprocal of Capacitance, cm²/μf
52
48
44
40
36
32
28
24
20
16
12
8
4
40
80
120
160
200
240
280
320
360
400
Formation Voltage, volts

Fig 8

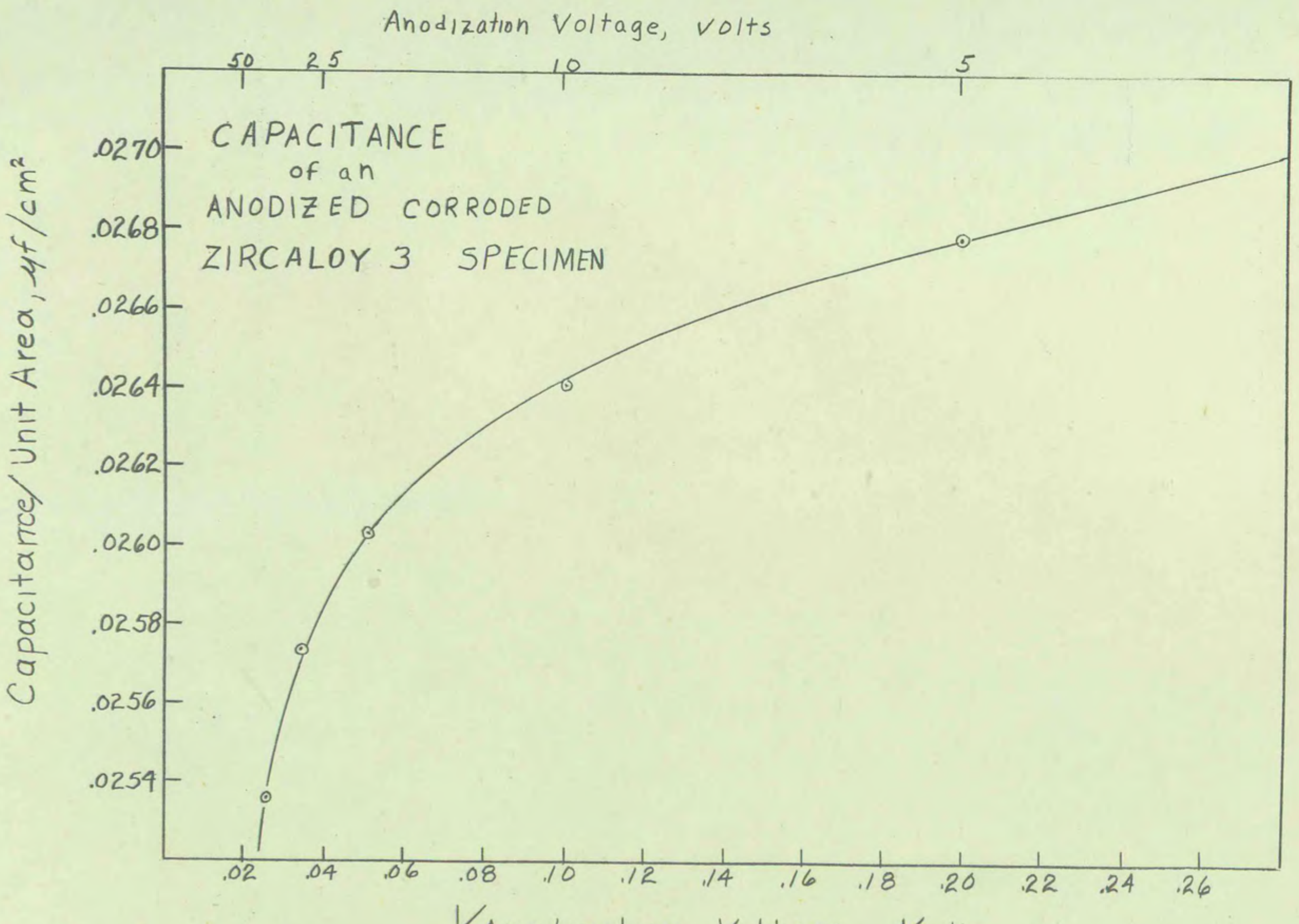

Anodization Voltage, volts
50
25
10
5
CAPACITANCE
of an
ANODIZED CORRODED
ZIRCALOY 3 SPECIMEN
Capacitance/ Unit Area, μf/cm²
.0270
.0268
.0266
.0264
.0262
.0260
.0258
.0256
.0254
.02
.04
.06
.08
.10
.12
.14
.16
.18
.20
.22
.24
.26
1/Anodization Voltage, 1/volts

Fig.9.

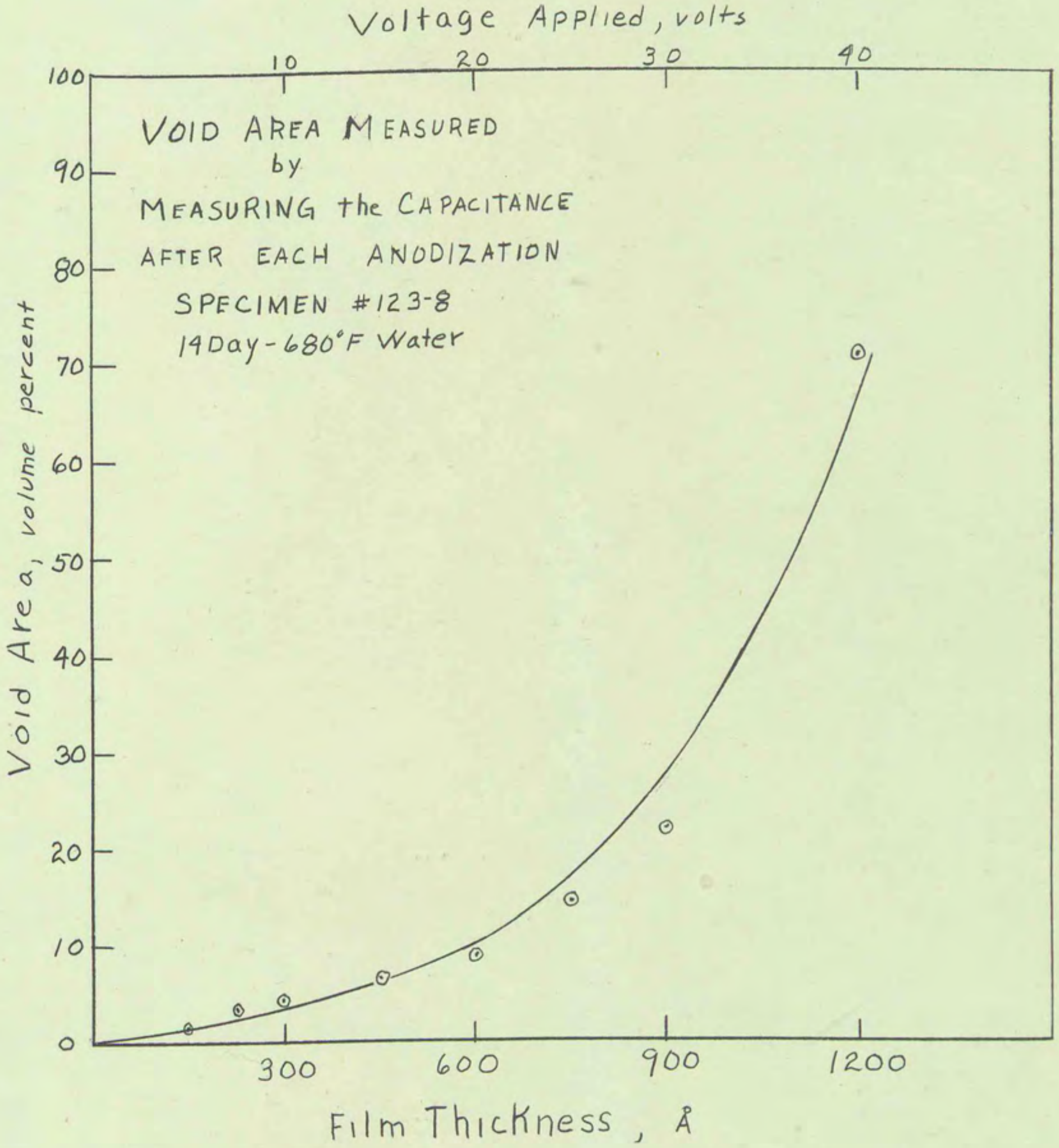

Voltage Applied, volts
10
20
30
40
100
90
80
70
60
50
40
30
20
10
0
VOID AREA MEASURED
by
MEASURING the CAPACITANCE
AFTER EACH ANODIZATION
SPECIMEN #123-8
14Day-680°F Water
Void Area, volume percent
300
600
900
1200
Film Thickness, Å

Fig. 10.

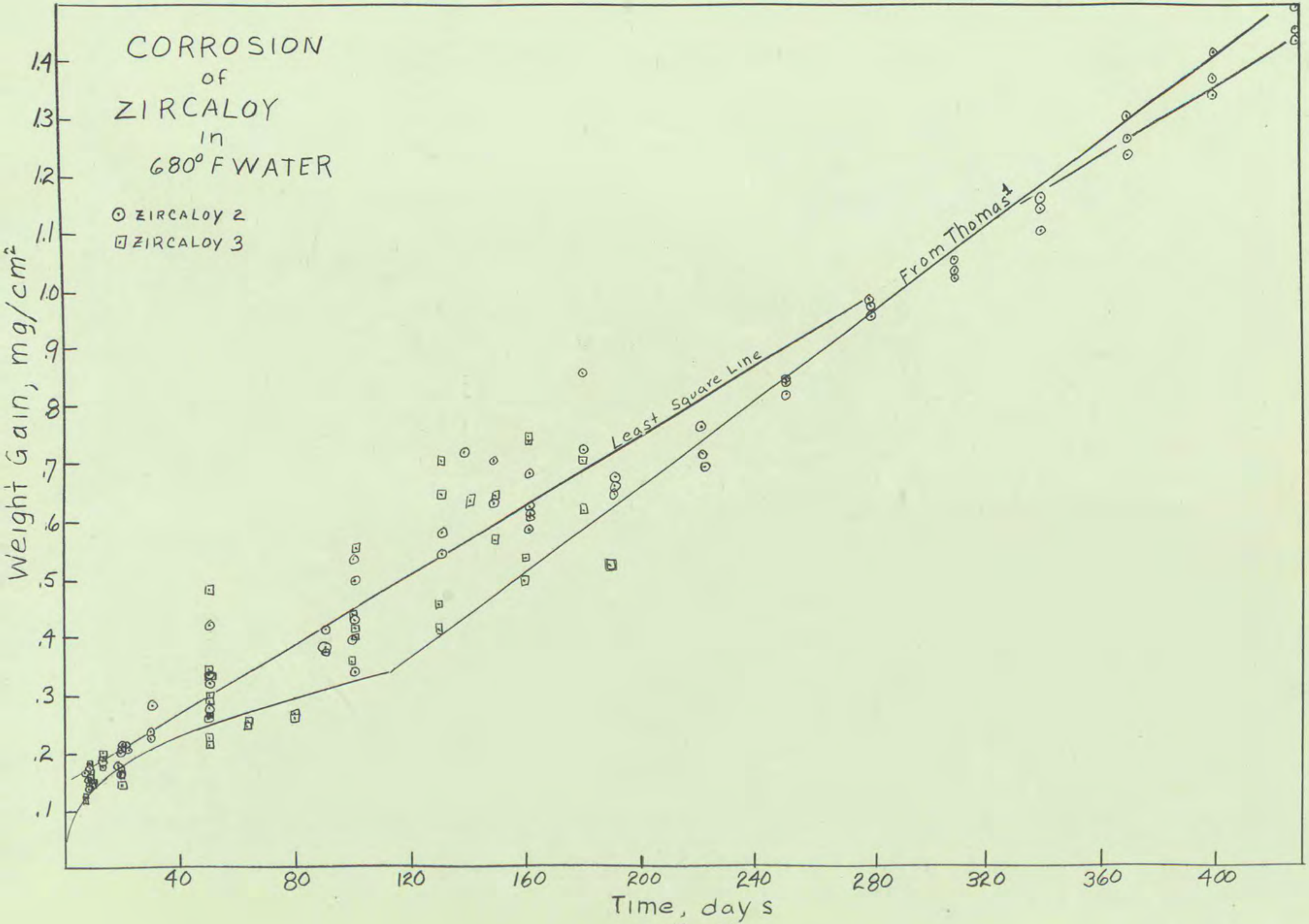

CORROSION
of
ZIRCALOY
in
680° F WATER
⊙ ZIRCALOY 2
⊡ ZIRCALOY 3
Least Square Line
From Thomas1
Weight Gain, mg/cm²
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
40
80
120
160
200
240
280
320
360
400
Time, days

Fig. 11.

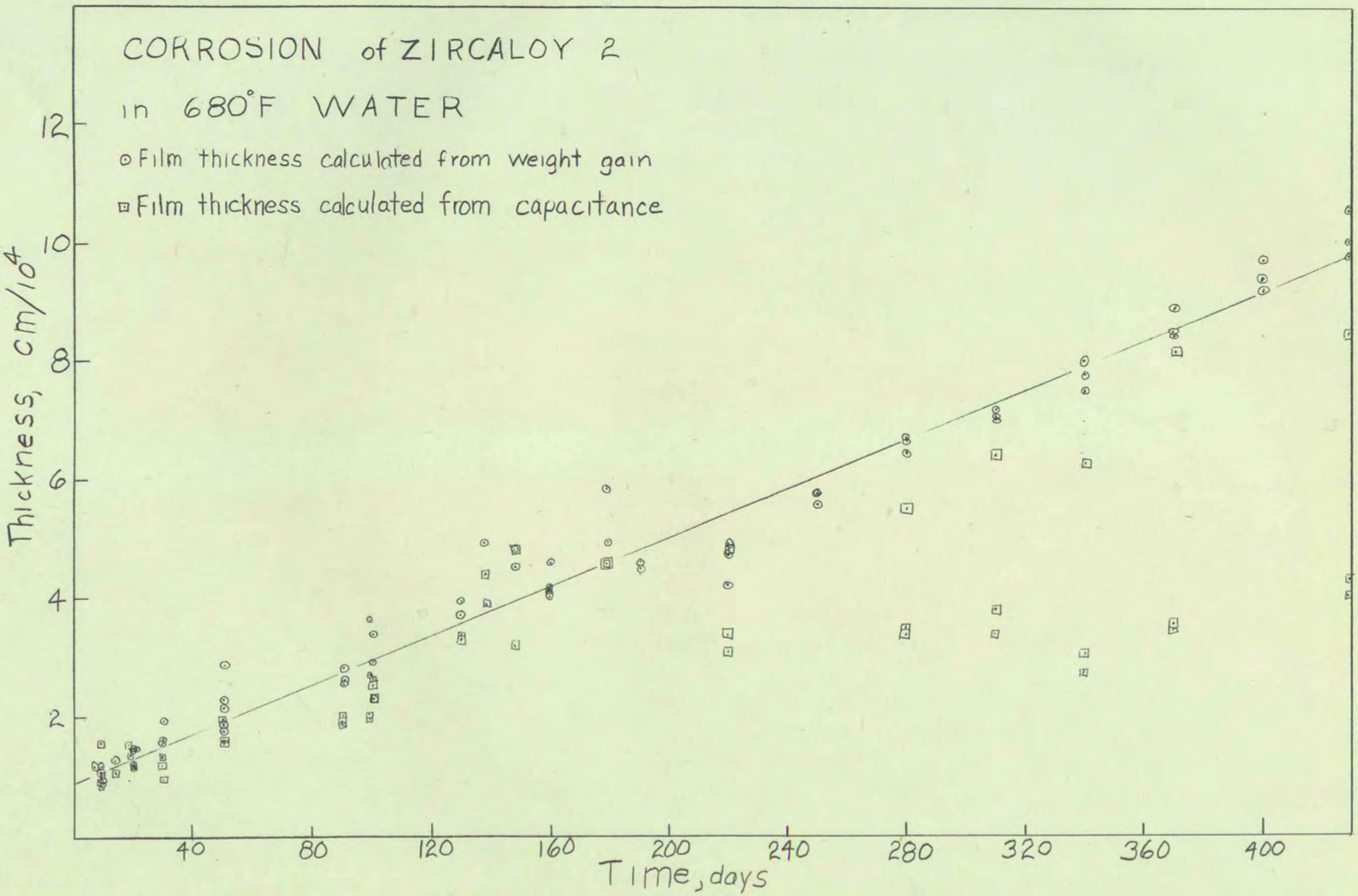

CORROSION of ZIRCALOY 2
in 680°F WATER
⊙ Film thickness calculated from weight gain
⊡ Film thickness calculated from capacitance
Thickness, cm/10⁴
12
10
8
6
4
2
40
80
120
160
200
240
280
320
360
400
Time, days

Fig. 12.

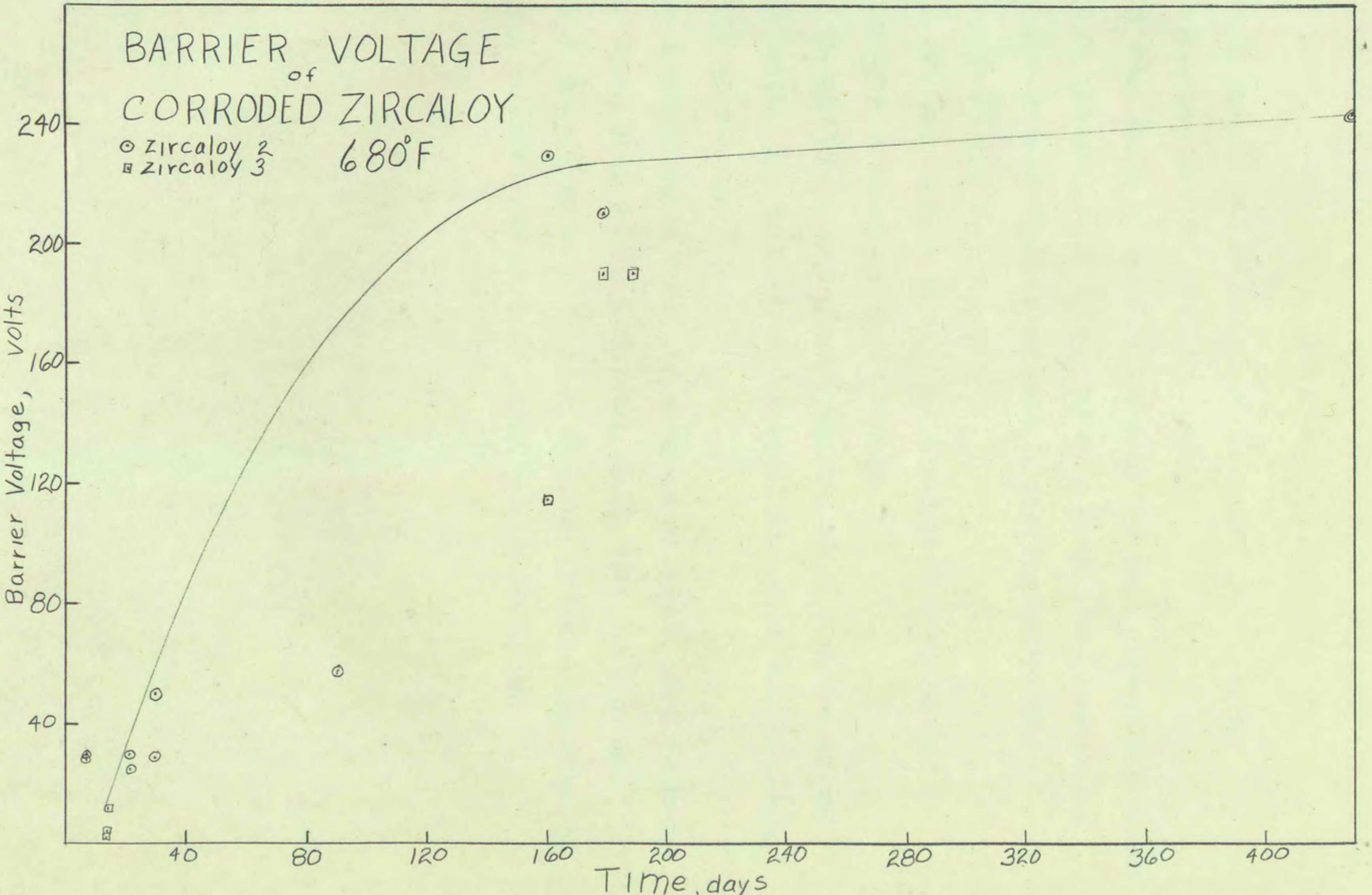

BARRIER VOLTAGE of CORRODED ZIRCALOY
680°F
Zircaloy 2
Zircaloy 3
Barrier Voltage, volts
240
200
160
120
80
40
40
80
120
160
200
240
280
320
360
400
Time, days

Fig. 13.

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