Report No. BMI-1270
UC-25 Metallurgy and Ceramics
(TID-4500, 13th Ed., Rev.)

Contract No. W-7405-eng-92

THE NITRIC-HYDROFLUORIC ACID PICKLING OF ZIRCALOY-2

by

E. Burt Friedl
Warren E. Berry
Paul D. Miller
Frederick W. Fink

June 11, 1958

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

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HF-HNO_3 pickling solutions for Zircaloy 2 were studied. Acid concentration, bath contamination, and temperature were the parameters investigated. Pickling rates were found to be linear with time. Pickling rates increased linearly with the HF concentration, but variations in the HNO_3 concentration had little or no effect on the rate. Contamination of the bath with metal ions found in Zircaloy 2 at concentrations below saturation also had little or no effect on the pickling rate. Temperature-dependency studies in the range of 40 to 160 F indicated an activation energy of 4.95 kcal per mole for the dissolution of Zircaloy 2 in HF-HNO_3. The surface appearance of the Zircaloy 2 used in the study was found to be dependent upon both the HF and HNO_3 concentrations.

INTRODUCTION

The work-hardened surface layer formed on zirconium and its alloys by machining and other fabricating operations is known to be less resistant to corrosion by high-temperature water than the unworked base metal. It has been general practice to remove this thin layer by pickling in a nitric-hydrofluoric acid solution. The resulting surfaces exhibit the high degree of corrosion resistance required to obtain satisfactory heat-transfer properties in Zircaloy 2-clad fuel elements for pressurized-water-reactor applications.

The use of the nitric-hydrofluoric acid bath has several disadvantages. Chief among these is a loss in high-temperature-water corrosion resistance if the pickle solution is not thoroughly rinsed from the Zircaloy 2.[1] In addition, pickling of Zircaloy 2 assemblies which contain narrow channels can cause local overheating, which results in excessive pickling rates, evolution of NO_2, and staining of the alloy while it is being transferred to the rinse water. These effects are undesirable and difficult to avoid in the production of fuel-element clusters for pressurized-water reactors.

Based on present knowledge, there is not sufficient information available to predict metal-removal rate and surface finish for Zircaloy 2 pickled in a wide range of bath compositions, temperatures, and contaminant concentrations. Information on these variables could be used to define safe limits for general bath usage in production.

A program was undertaken for the Bettis Laboratory operated by Westinghouse Electric Corporation to study these variables. Acid concentrations ranging from 1 to 5 volume per cent of 49 w/o hydrofluoric acid and 20 to 80 volume per cent of 70 w/o nitric acid were investigated. The effects of temperature on pickling behavior were studied over the range of 40 to 180 F. Contamination from metal ions found in Zircaloy 2 was studied, in the amounts that would be present, if the pickle bath contained up to 20 w/o Zircaloy 2.

(1) References at end.

EXPERIMENTAL WORK

Test Procedures

Acids

The acids used in this study were concentrated cp grades normally found in the laboratory. The hydrofluoric acid was from one lot which analyzed 49.0 w/o HF. The nitric acid was taken from several lots which had a nominal concentration of 70 ± 1 w/o HNO_3.

Zircaloy 2

The Zircaloy 2 was furnished by Bettis in the form of 2 by 1 by 0.140-in. samples having a milled finish, and had the following analysis:

	Analysis, w/o		Analysis, w/o
Tin	1.45	Copper	0.0022
Iron	0.133	Magnesium	0.001
Nickel	0.044	Chlorine	0.0029
Chromium	0.080	Oxygen	0.1230
Cobalt	0.001	Hydrogen	0.0068
Titanium	0.002	Nitrogen	0.0044
Tungsten	0.002		

The Zircaloy 2 ingot was forged at 1800 F to 2-in.-thick stock. It was then rolled at 1550 F to approximately 1/8-in.-thick strip. The strip was annealed 15 min at 1550 F prior to machining the corrosion coupons.

The ingot had been corrosion tested 14 days in 750 F steam at Bettis, and exhibited an average weight gain of 31 mg per dm^2. The ingot was rejected for pressurized-water-reactor applications because of stringerlike corrosion.

Apparatus

A diagram of the test apparatus is shown in Figure 1. The pickle-bath solution was placed in a polyethylene container (A). Ten liters of solution was used in all tests except those containing additional dissolved zirconium. One liter of solution was used in the latter study because of the large amounts of zirconium required. Fresh solutions were used in each of the more than 90 experiments conducted.

The solution was stirred by means of a polyethylene propeller attached to a motor (B) rotating at approximately 100 rpm. The velocity of the solution past the specimens was not determined. The specimens (C) were alternately raised and lowered several inches in the solution at a rate of 20 cycles per minute.

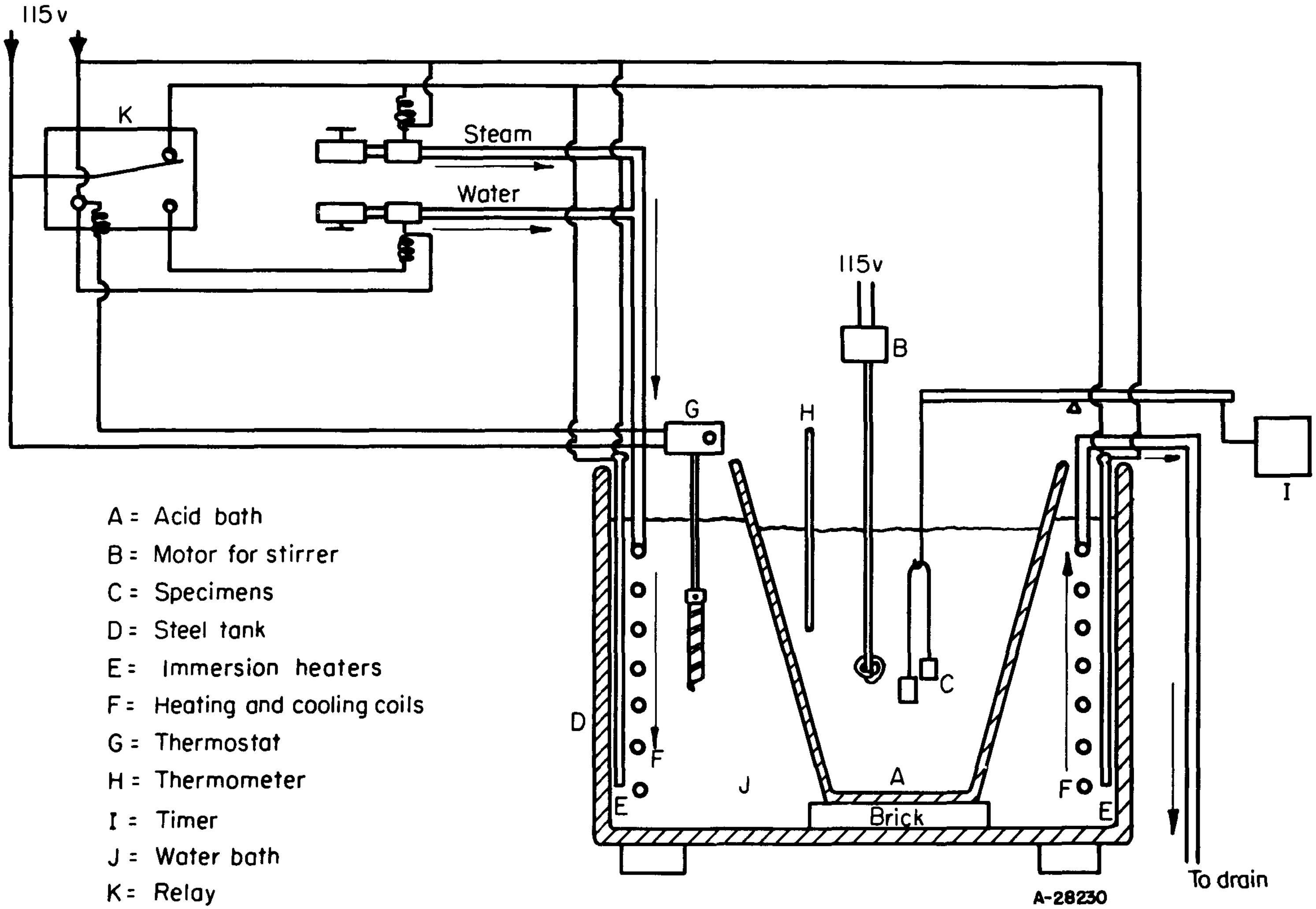


FIGURE 1. DIAGRAM OF APPARATUS USED IN NITRIC-HYDROFLUORIC ACID PICKLING OF ZIRCALOY 2

The container of pickle solution was immersed in a constant-temperature water bath contained in a 20-gal steel tank (D). Temperature was controlled to ± 1 F by means of immersion heaters (E) and cooling coils (F).

Test Results

Duplicate specimens of Zircaloy 2 were examined after being pickled a total of 1, 2, 4, and 8 min under the conditions described below. Specimens were evaluated on the basis of weight loss per unit area, thickness of metal removed, and surface appearance.

(1) 20, 40, 60, and 80 volume per cent of 70 w/o nitric acid in 3 volume per cent of 49 w/o hydrofluoric acid solution at 100 F

(2) 1, 2, 3, 4, and 5 volume per cent of hydrofluoric acid in 30 and 80 volume per cent of nitric acid at 100 F

(3) 3.5 volume per cent of hydrofluoric acid and 39 volume per cent of nitric acid at temperatures of 40, 60, 80, 90, 100, 110, 120, 140, 160, and 180 F

(4) Additions of 1, 2, 3, 5, 10, and 20 w/o zirconium to each of three baths maintained at 90 and 150 F:

  (a) 2 volume per cent HF-20 volume per cent HNO_3

  (b) 3.5 volume per cent HF-39 volume per cent HNO_3

  (c) 5 volume per cent HF to 60 volume per cent HNO_3

(5) Additions of chromium, iron, nickel, and tin singly and in combination to a 100 F 3.5 volume per cent HF-39 volume per cent HNO_3 bath in the same ratio as a solution containing 1, 2, 3, 5, 10, and 20 w/o Zircaloy 2.

Nitric Acid Concentration

Experiments conducted with 3 volume per cent HF in 20, 40, 60, and 80 volume per cent HNO_3 at 100 F revealed no marked effect on the pickling rate of Zircaloy 2 from varying the nitric acid content. As can be seen from Figure 2, the rate of dissolution was linear with time and was slightly higher in 20 and 80 volume per cent than in 40 and 60 volume per cent HNO_3 solutions. Rates of metal removal ranged from 472 to 608 mg/(dm^2)(min).

It is conceivable that the variance in results obtained represents experimental error. Work by Smith and Hill[2] has shown that solution velocity has an effect on pickling rate. In the present study, it was difficult to pickle the Zircaloy 2 specimens in exactly the same position in the container. Thus, slight differences in the velocity of the solution past the specimens could have been responsible for the observed differences in pickling rates. On the other hand, the minimum in pickling rate at 60 volume per cent HNO_3 may have been a real effect.

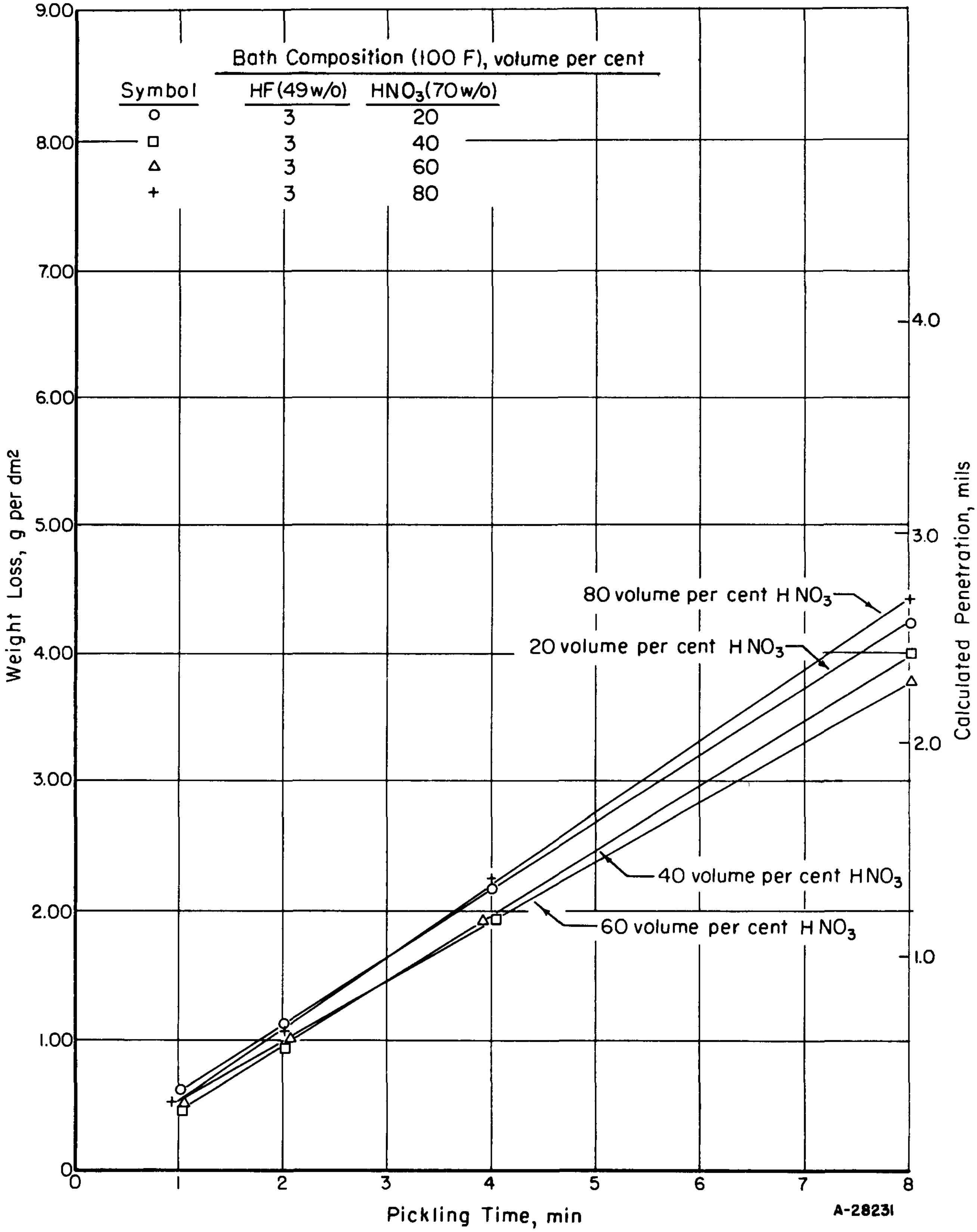
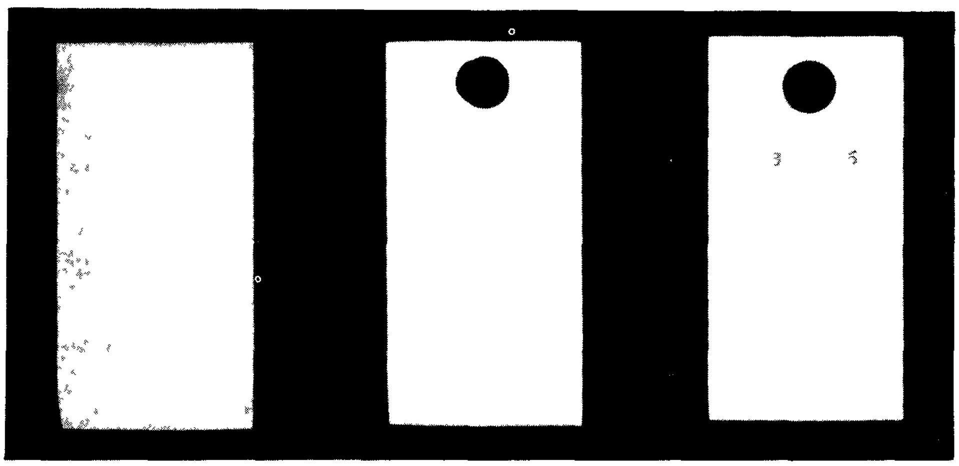


FIGURE 2. EFFECT OF VARYING NITRIC ACID CONTENT ON WEIGHT OF METAL REMOVED IN THE NITRIC-HYDROFLUORIC ACID PICKLING OF ZIRCALOY 2

The loss in metal thickness as measured with a micrometer closely paralleled the calculated thickness losses, which also were presented in Figure 2. The calculated thickness changes appeared to be more reliable than those which were measured. The latter were subject to some error, since the measured change in thickness represented readings on the micrometer which were estimated to the nearest 0.0001 in.

Although metal-removal rates were essentially the same over the range of nitric acid concentrations studied, the surface appearance of the Zircaloy 2 specimens used in this study was not the same for all nitric acid contents. Those pickled in 20 volume per cent HNO_3-3 volume per cent HF exhibited smooth, bright, and shiny surfaces. Those pickled in 40, 60, or 80 volume per cent HNO_3-3 volume per cent HF solutions were bright but rough. The roughness appeared as striations in the direction of rolling. The examples shown in Figure 3 illustrate the surface appearance of typical specimens. The specimen on the left is as milled. The center specimen shows the typical smooth, bright surface obtained after pickling. The specimen on the right exhibits the typical striation-type roughness after pickling.



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As Milled | Bright, Smooth Pickled Surface | Striated, Roughened Pickled Surface

FIGURE 3. TYPICAL APPEARANCE OF INERT-ATMOSPHERE-MELTED ZIRCALOY 2 SPECIMENS BEFORE AND AFTER PICKLING IN NITRIC-HYDROFLUORIC ACID

Note horizontal striated roughness on specimen at right.

The Zircaloy 2 used in this study was melted in an inert gas atmosphere. It has been shown that inert-atmosphere-melted material contains both void stringers and intermetallic stringers.[3] Vacuum-melted Zircaloy 2 contains considerably fewer stringers. In the present study, several specimens of vacuum-melted Zircaloy 2 were pickled under conditions which caused striations in the inert-atmosphere-melted material. The resulting surfaces were virtually free of striations. Thus, in addition to acid concentration, the presence of stringers in the Zircaloy 2 apparently influences the nature of the surface finish in HNO_3-HF pickling of this material.

Hydrofluoric Acid Concentration

Experiments were conducted in which Zircaloy 2 was pickled in 30 and 80 volume per cent HNO_3 containing 1, 2, 3, 4, or 5 volume per cent HF. The bath temperature was 100 F The metal loss-time curves and calculated penetrations for these experiments are presented in Figures 4 and 5. It can be seen that the pickling rates were linear with time and increased with increasing HF content The increases in pickling rate with HF content also were linear, as shown in Figures 6 and 7. The pickling rates obtained in 80 volume per cent HNO_3 were consistently lower than those obtained in 30 volume per cent HNO_3 at the same HF level. This suggests that the slight variation in pickling rates obtained in the study on the effect of HNO_3 concentration (described in the preceding section) may have been real and not a result of experimental procedure.

The measured losses in thickness from pickling in these acids were in good agreement with the calculated losses in thickness presented in Figures 4 through 7.

All alloy specimens pickled in 30 volume per cent HNO_3 at all HF levels exhibited smooth, bright, and shiny surfaces. Those pickled in 1 volume per cent HF-80 volume per cent HNO_3 also were smooth and shiny, while those pickled in 2 to 5 volume per cent HF in 80 volume per cent HNO_3 had the striated surface roughness

Additional experiments were conducted to determine whether the surface roughness was a result of the total amount of metal removed Specimens were pickled for long periods of time in 80 volume per cent HNO_3-1 volume per cent HF until the amount of metal removed was equal to that removed in 80 volume per cent HNO_3-4 volume per cent HF The surface of these specimens was bright and smooth.

Temperature

The effect of temperature on pickling behavior was studied over the range of 40 to 180 F The composition of the bath was 3 5 volume per cent HF-39 volume per cent HNO_3 This bath has been used extensively in production-line pickling of Zircaloy 2 As in other studies, pickling rates were found to be linear with time, as shown in Figure 8

The temperature dependency of the pickling rate for Zircaloy 2 in 3 5 volume per cent HF-39 volume per cent HNO_3 is shown in the conventional Arrhenius-type plot in Figure 9 The activation energy for this reaction was calculated to be 4 95 kcal per mole The pickling rate for the 180 F bath was very high and did not fall on the plotted curve. This suggests a change in the reaction mechanism near this temperature. The increase in rate cannot be fully accounted for on the basis of overheating of the specimens during pickling. If the latter had been true, a rate other than linear should have been observed, since the specimens were pickled in 1-, 2-, and 4-min increments and should have reached higher temperatures during the longer pickling times

The measured loss in thickness during pickling over the above temperature range correlated well with the calculated penetrations presented in Figure 8.

Specimens pickled at 40 and 60 F were smooth and shiny Those pickled at 160 and 180 F also were smooth and shiny but exhibited some staining. Striation-type roughness began to appear at 80 F and occurred irregularly at temperatures through 110 F

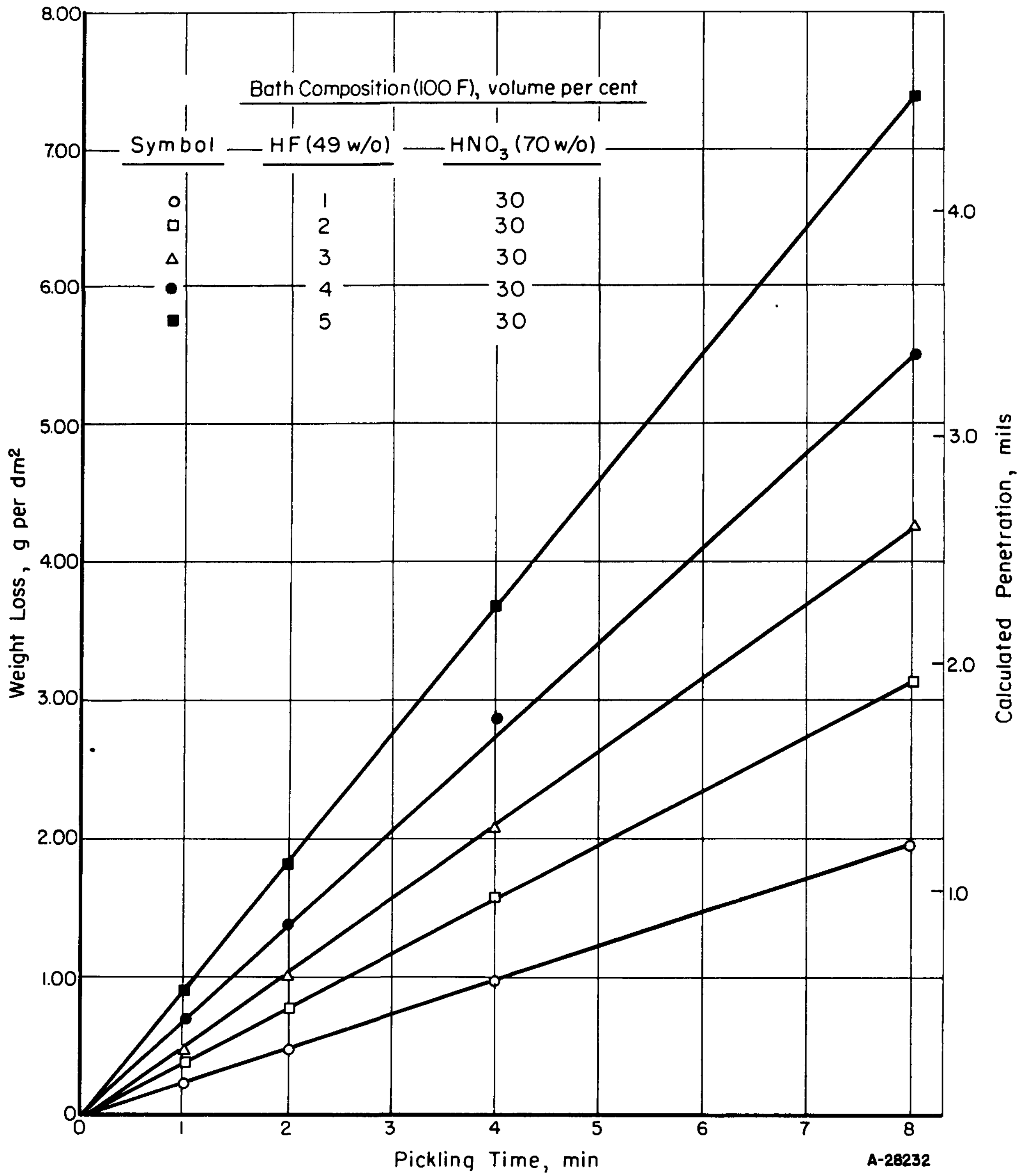

FIGURE 4. EFFECT OF VARYING HYDROFLUORIC ACID CONTENT ON WEIGHT OF METAL REMOVED IN 30 VOLUME PER CENT NITRIC-HYDROFLUORIC ACID PICKLING OF ZIRCALOY 2

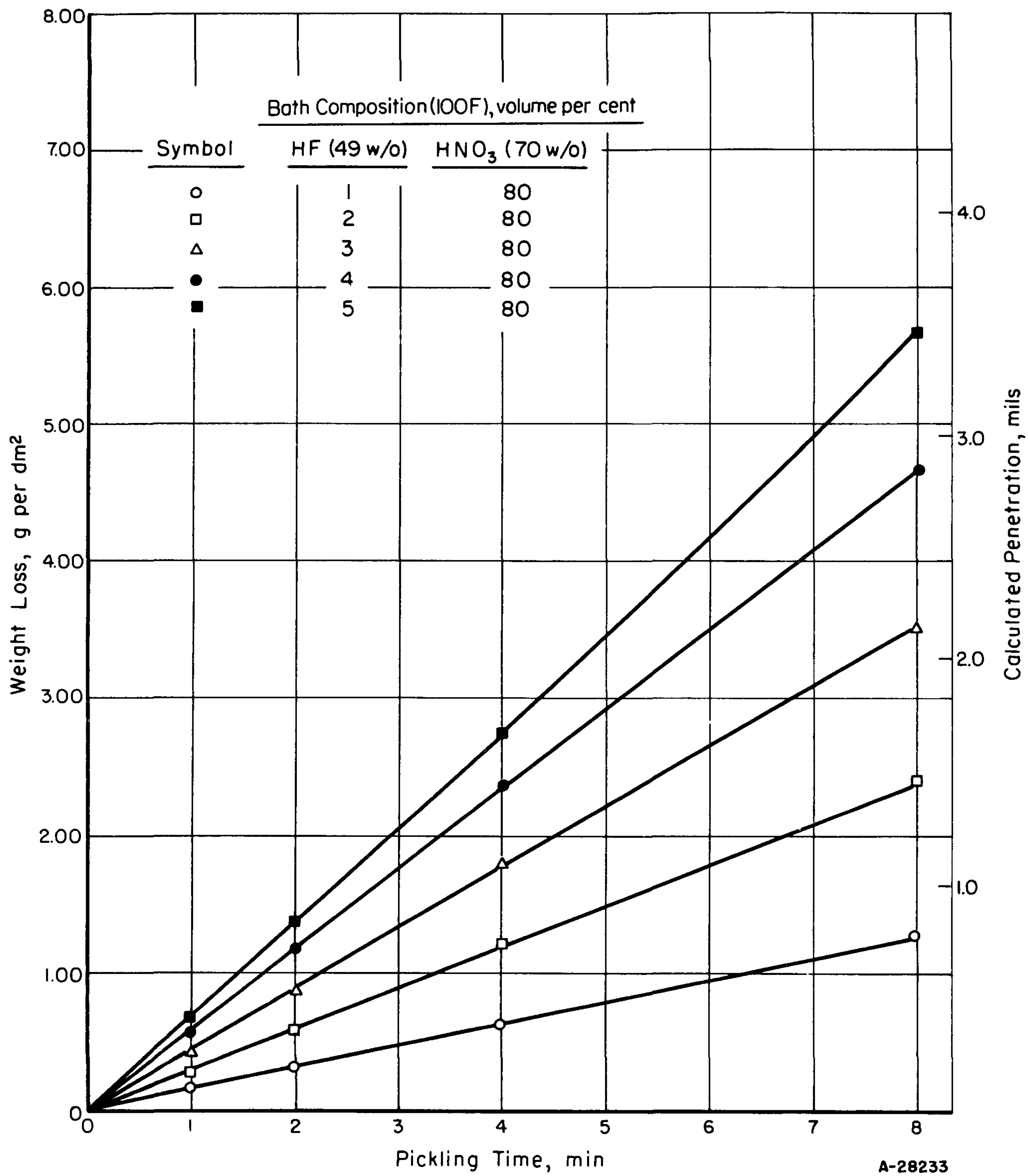

FIGURE 5. EFFECT OF VARYING HYDROFLUORIC ACID CONTENT ON THE WEIGHT OF METAL REMOVED IN THE 80 VOLUME PER CENT NITRIC-HYDROFLUORIC ACID PICKLING OF ZIRCALOY 2

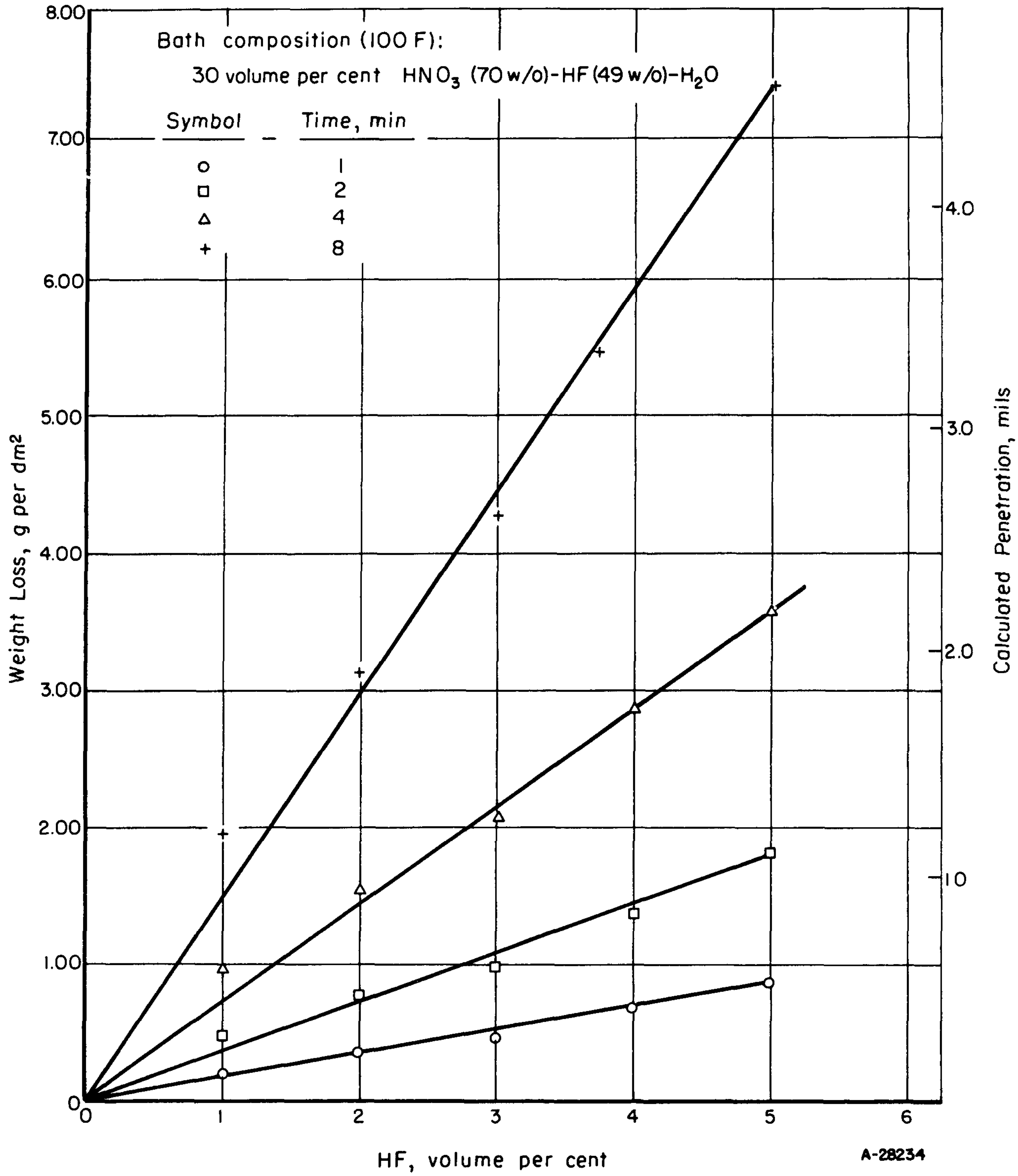

FIGURE 6. INCREASE IN PICKLING RATE OF ZIRCALOY 2 AS A FUNCTION OF HYDROFLUORIC ACID CONCENTRATION IN 30 VOLUME PER CENT NITRIC-HYDROFLUORIC ACIDS

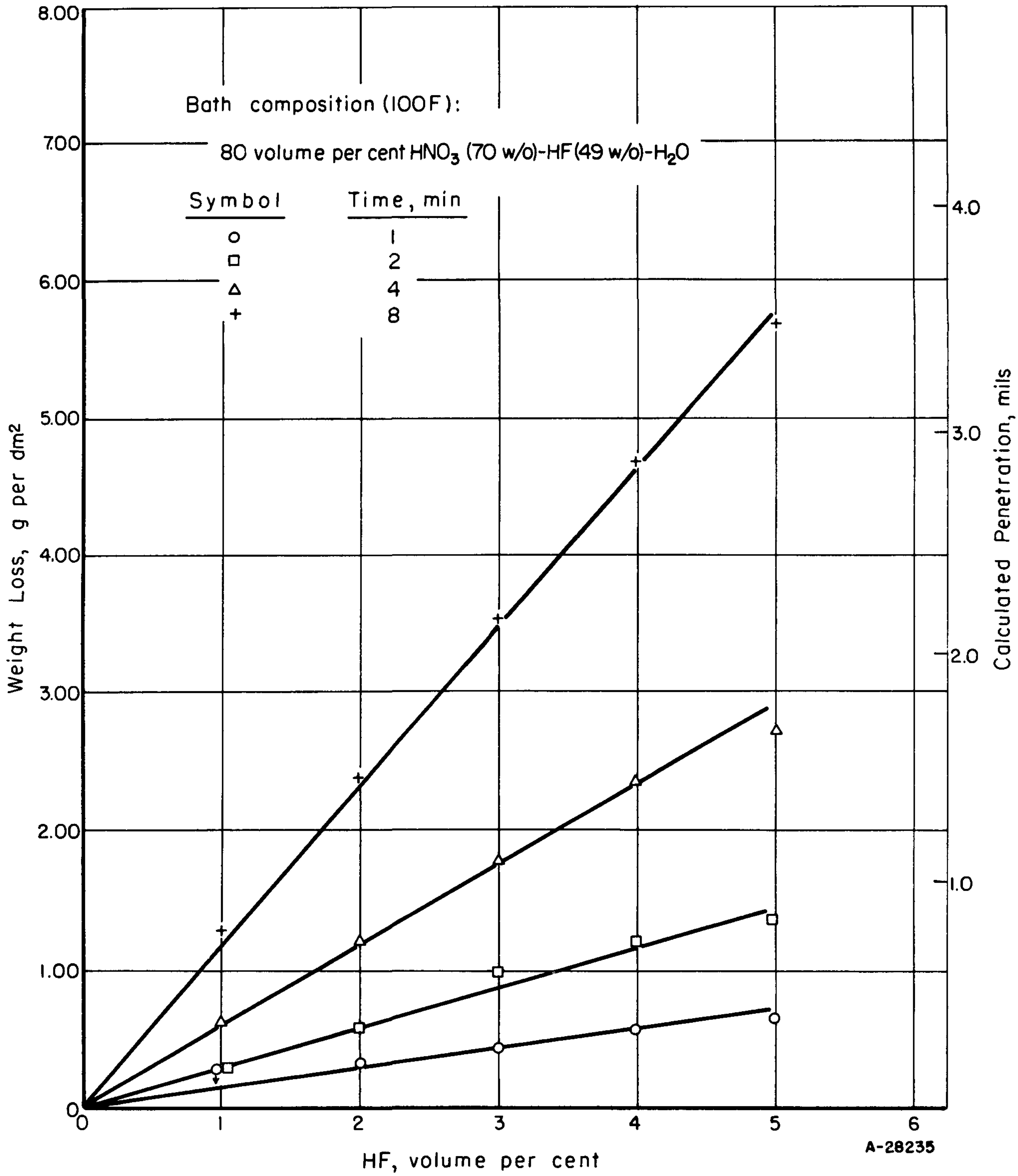

FIGURE 7. INCREASE IN PICKLING RATE OF ZIRCALOY 2 AS A FUNCTION OF HYDROFLUORIC ACID CONTENT IN 80 VOLUME PER CENT NITRIC-HYDROFLUORIC ACIDS

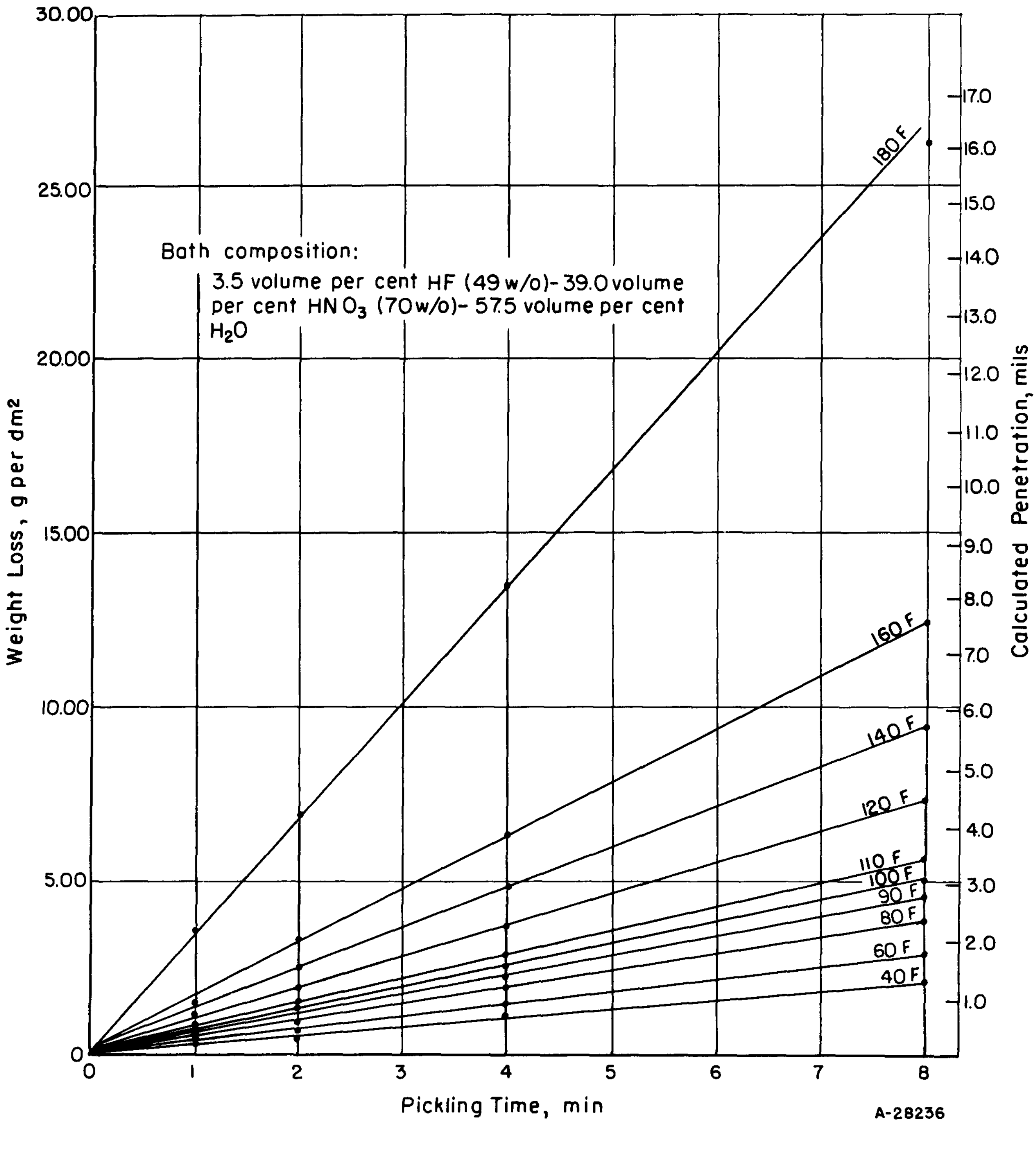

FIGURE 8. EFFECT OF TEMPERATURE ON WEIGHT OF METAL REMOVED IN THE NITRIC-HYDROFLUORIC ACID PICKLING OF ZIRCALOY 2

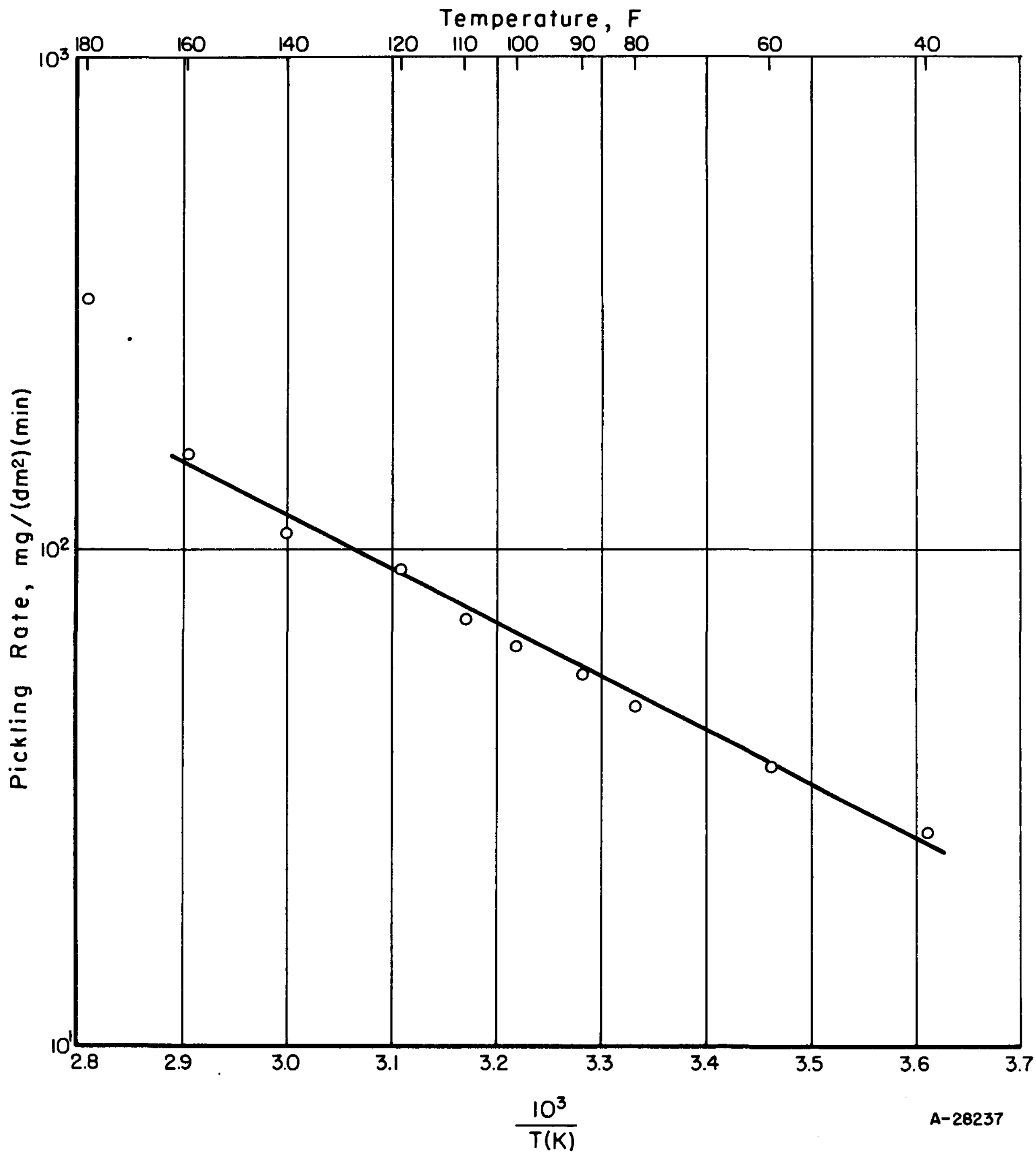

FIGURE 9. TEMPERATURE-DEPENDENCY PLOT OF PICKLING RATES FOR ZIRCALOY 2 IN 39 VOLUME PER CENT NITRIC-3.5 VOLUME PER CENT HYDROFLUORIC ACID BATH

Specimens pickled at 120 and 140 F were covered completely with striations. Some staining also was observed at 140 F. Continued pickling of specimens at 120 F until the metal removed equalled that after 8 min at 160 F failed to produce a smooth surface.

Zirconium Contamination

The effect of zirconium contamination of up to 20 w/o or saturation was investigated in three different pickle baths and at two temperatures in each bath. Crystal-bar zirconium was dissolved in excess HF and nitric acid and water were added to give the desired concentrations. Bath compositions were:

(1) 3.5 volume per cent HF-39 volume per cent HNO_3

(2) 2 volume per cent HF-20 volume per cent HNO_3

(3) 5 volume per cent HF-60 volume per cent HNO_3.

Bath temperatures were 90 and 150 F. In several baths the solubility limit of the zirconium compound was reached and precipitates formed in the solutions. The bath composition which contained the precipitate was considered saturated. No saturation was observed in 2 volume per cent HF-20 volume per cent HNO_3 containing up to 20 w/o zirconium; saturation occurred between 5 and 10 w/o zirconium in 3.5 volume per cent HF-39 volume per cent HNO_3, and between 3 and 5 w/o zirconium in 5 volume per cent HF-60 volume per cent HNO_3.

The results of the above studies are plotted in Figures 10 through 15. In some experiments, zirconium additions appeared to affect pickling rates considerably. However, it was not possible to establish a trend as to the effect of dissolved zirconium on the pickling rate of Zircaloy 2 in HF-HNO_3. The reasons for the erratic results obtained in this study are not known. The unusually high pickling rate observed in the 150 F 2 volume per cent HF-20 volume per cent HNO_3 bath containing 20 w/o zirconium could not be accounted for on the basis of bath composition, since a post test analysis of the solution revealed that the bath conditions had been met.

The pickling rates were linear with time, except for specimens pickled in 5 volume per cent HF-60 volume per cent HNO_3 at 150 F. In the latter exposure, the excessive rate of attack apparently exhausted the HF content of the solution. This resulted in a steadily decreasing pickling rate.

The measured metal-thickness changes paralleled the calculated penetrations, which also are presented in Figures 10 through 15.

With two exceptions, the surfaces of specimens which were pickled in 90 and 150 F 2 volume per cent HF-20 volume per cent HNO_3 were smooth but milky. Specimens pickled in the 150 F solutions containing 10 and 20 w/o zirconium were covered with an adherent white deposit. These white deposits were not identified because of insufficient time.

Striations were observed on surfaces of specimens pickled in the 90 F 3.5 volume per cent HF-39 volume per cent HNO_3 solutions containing 1 through 10 w/o zirconium. Specimens pickled in duplicate solutions at 150 F were smooth but stained.

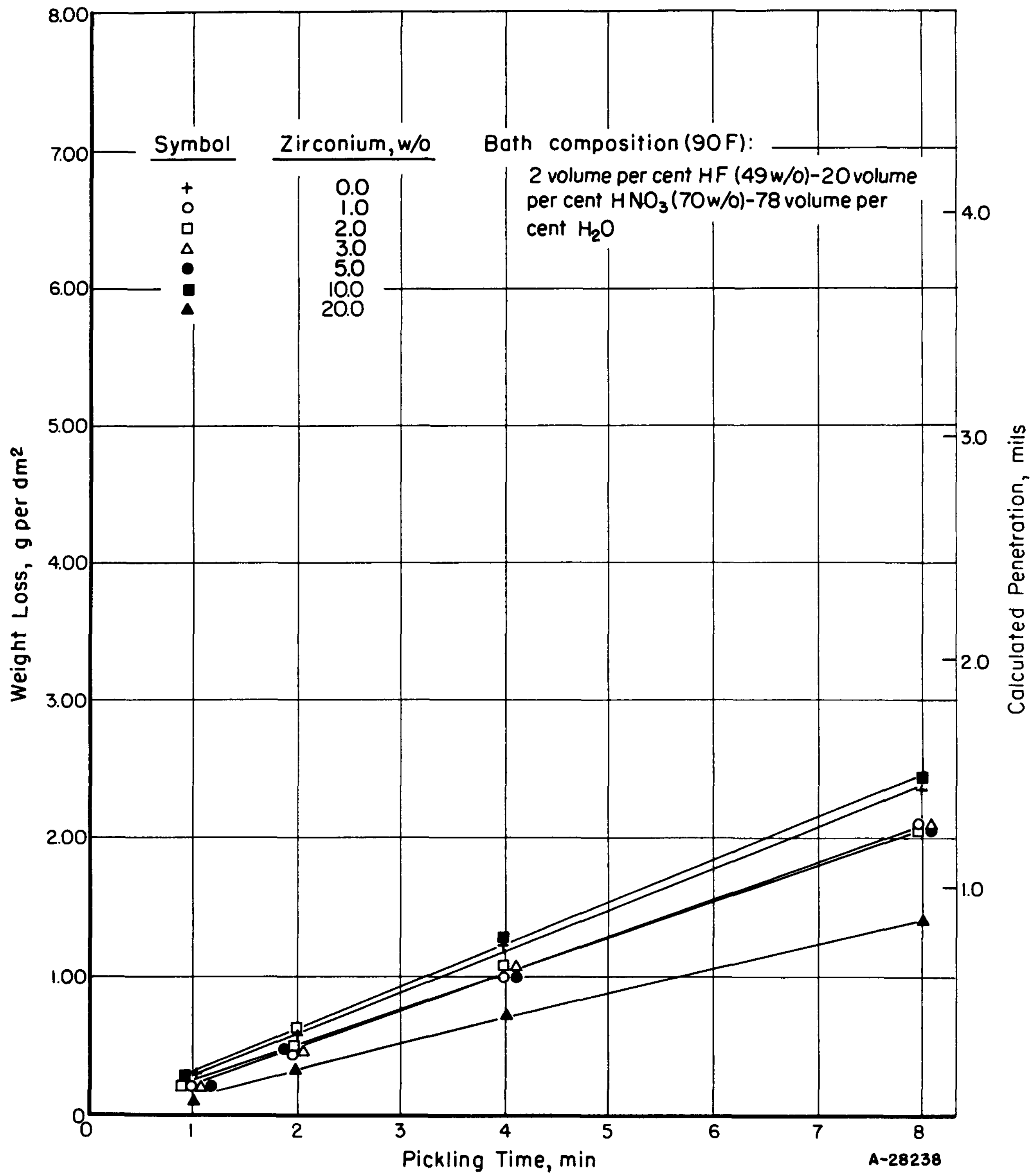

FIGURE 10. EFFECT OF ZIRCONIUM CONTAMINATION IN 90 F 20 VOLUME PER CENT NITRIC-2 VOLUME PER CENT HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

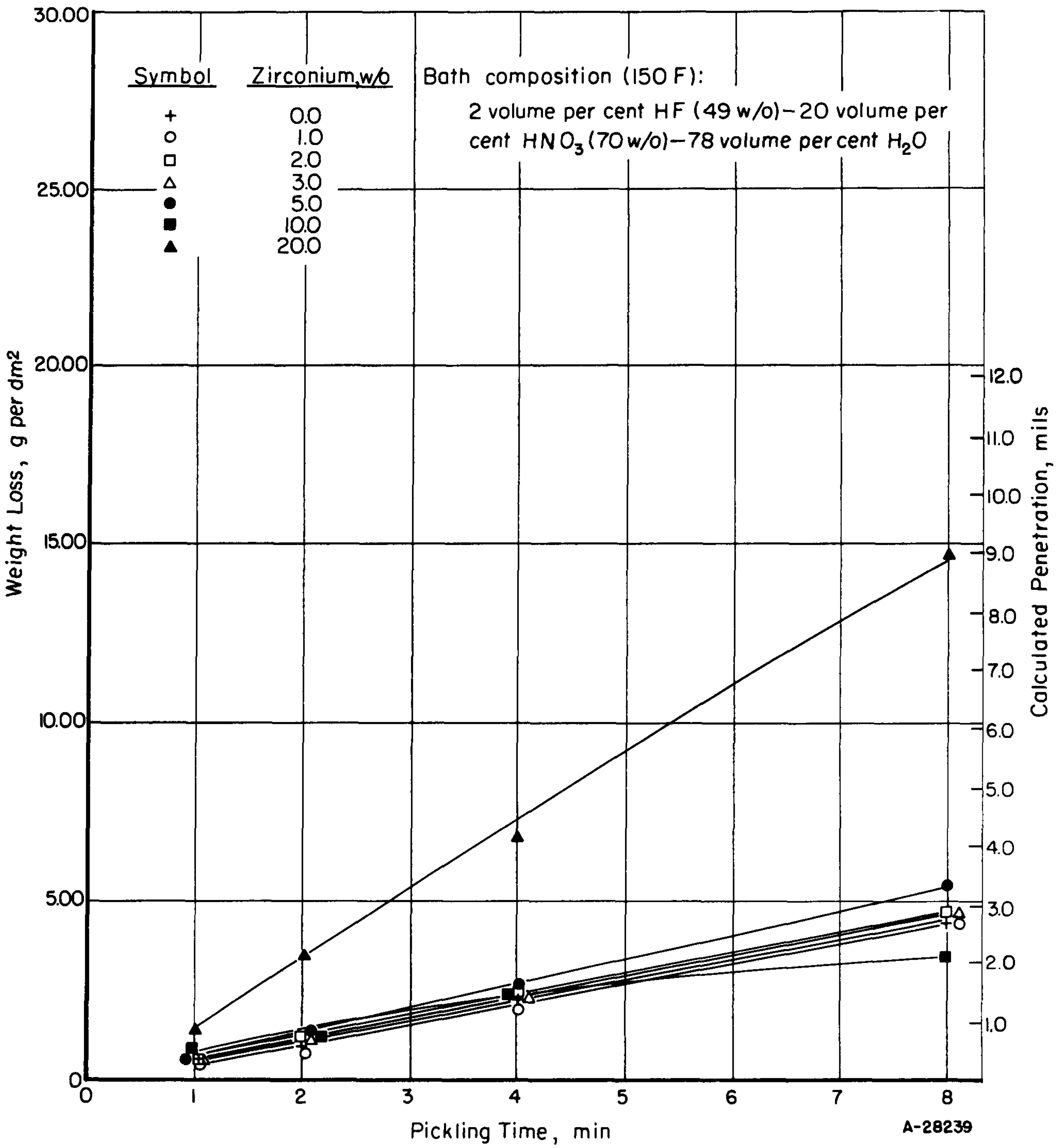

FIGURE 11. EFFECT OF ZIRCONIUM CONTAMINATION IN 150 F 20 VOLUME PER CENT NITRIC-2 VOLUME PER CENT HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

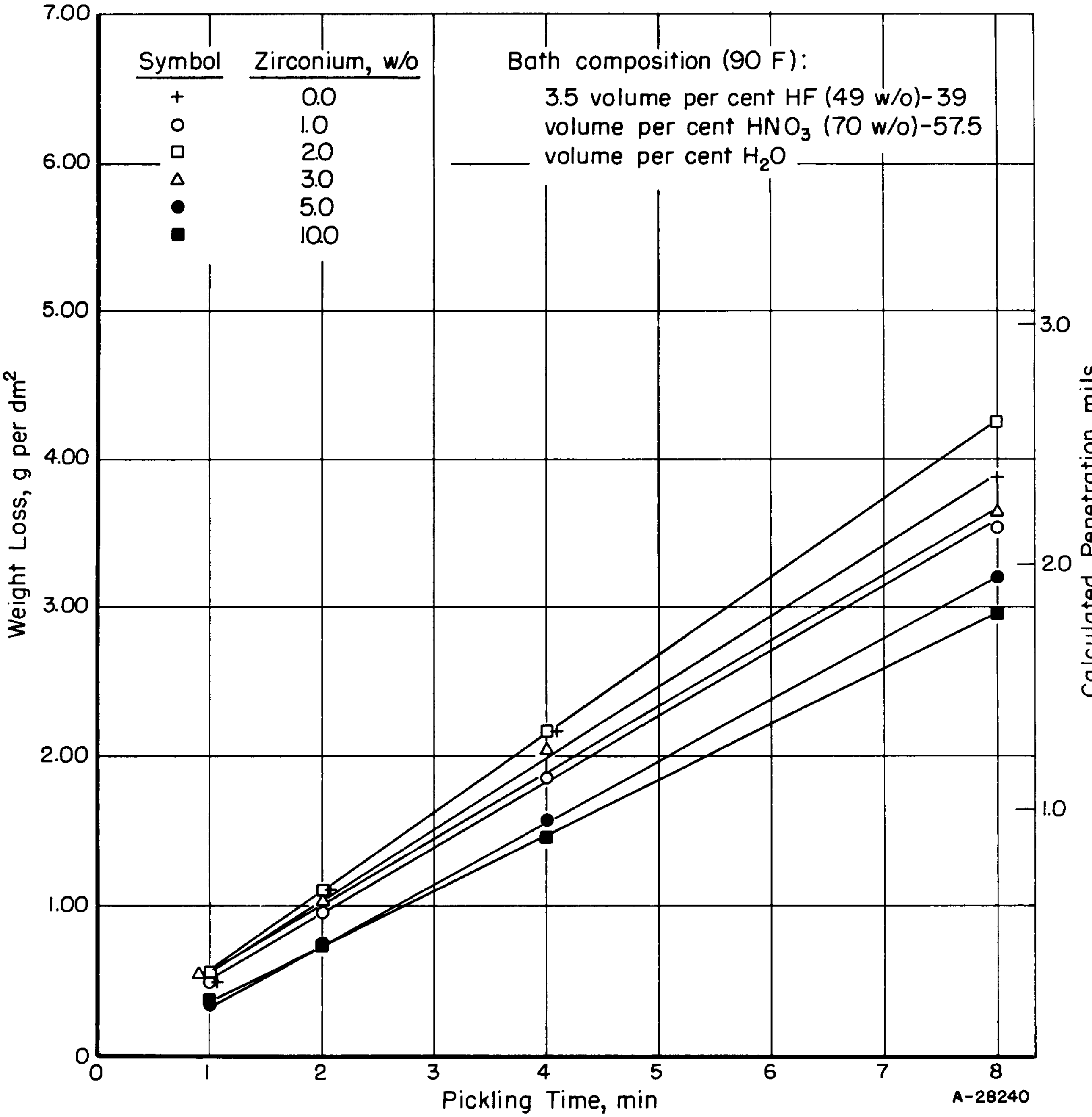

FIGURE 12. EFFECT OF ZIRCONIUM CONTAMINATION IN 90 F 39 VOLUME PER CENT NITRIC-3.5 VOLUME PER CENT HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

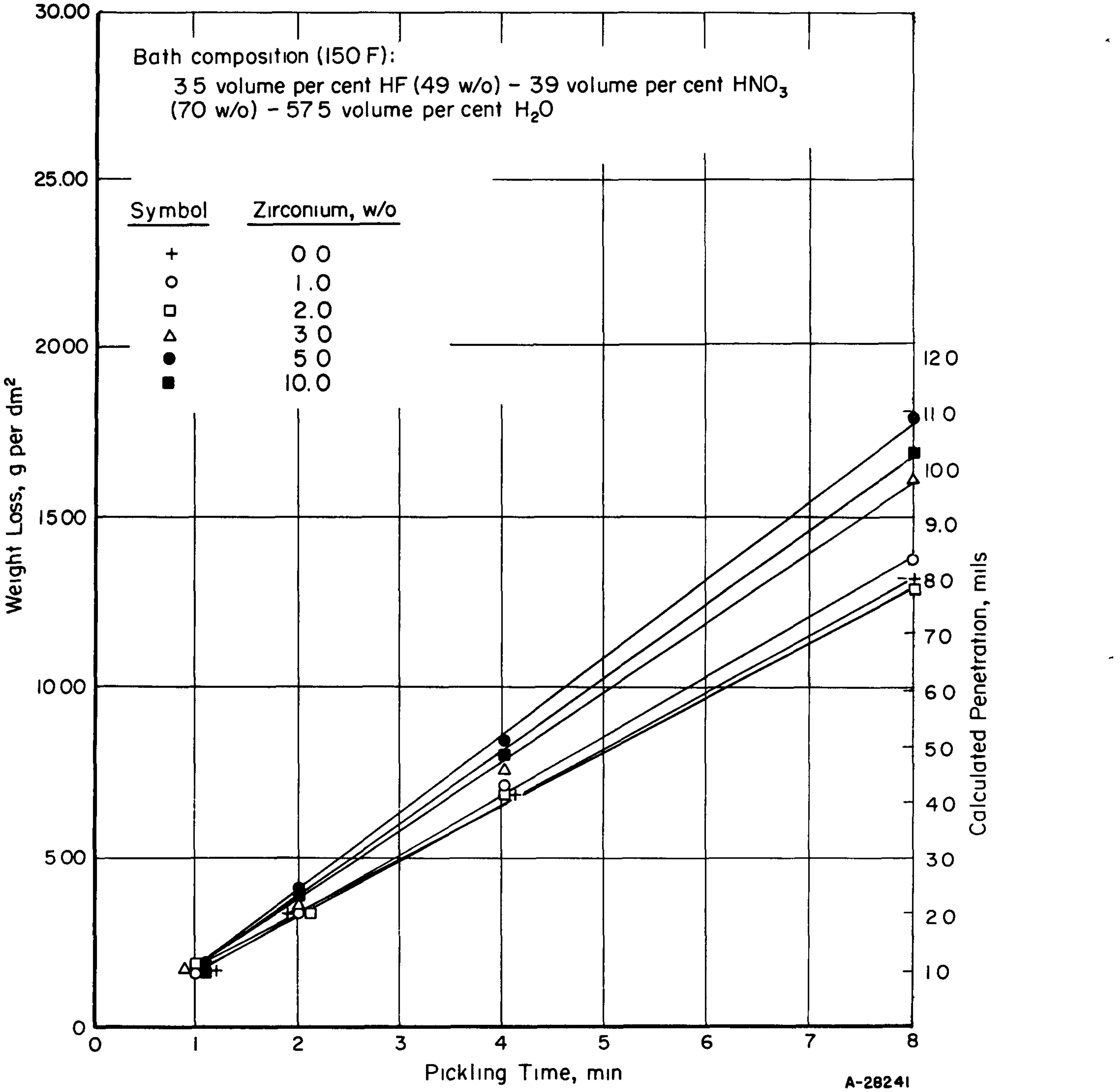

FIGURE 13. EFFECT OF ZIRCONIUM CONTAMINATION IN 150 F 39 VOLUME PER CENT NITRIC-3. 5 VOLUME PER CENT HYDROFLUORIC ACID BATH ON WEIGHT OF ZIRCALOY 2 DISSOLVED

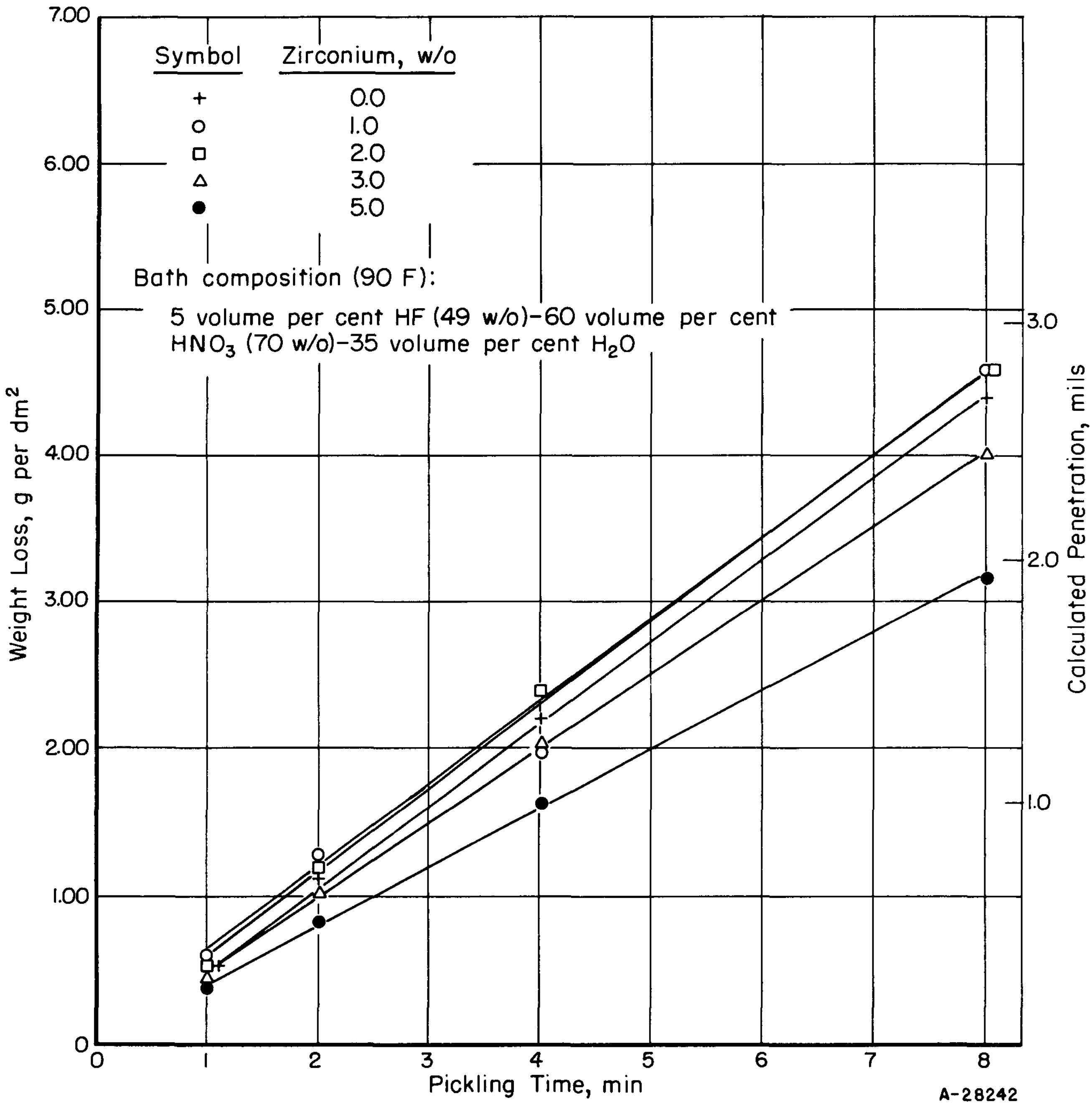

FIGURE 14. EFFECT OF ZIRCONIUM CONTAMINATION IN 90 F 60 VOLUME PER CENT NITRIC-5 VOLUME PER CENT HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

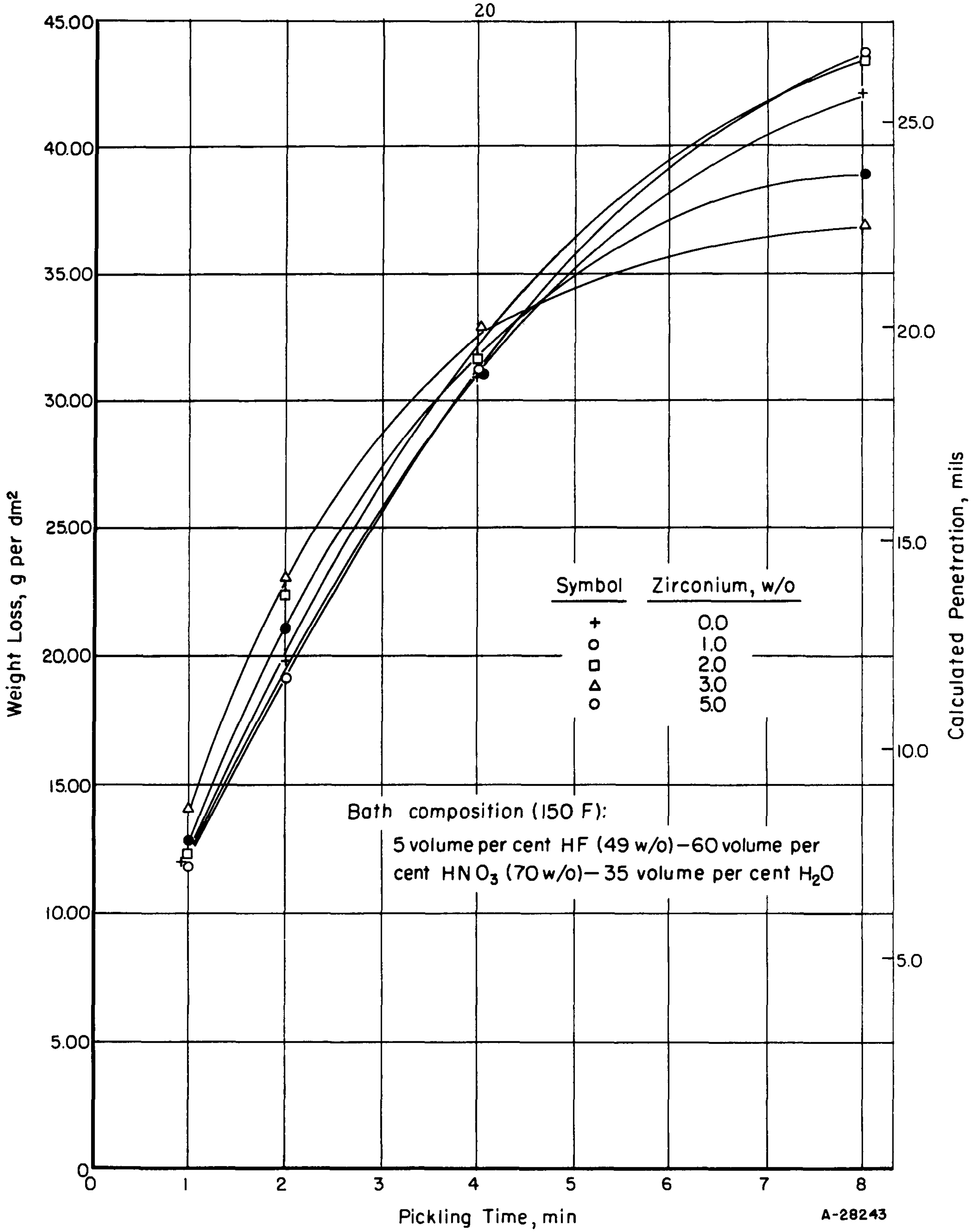

FIGURE 15. EFFECT OF ZIRCONIUM CONTAMINATION IN 150 F 60 VOLUME PER CENT NITRIC-5 VOLUME PER CENT HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

The 5 volume per cent HF-60 volume per cent HNO_3 baths containing up to 5 w/o zirconium produced striations on the alloy samples at both 90 and 150 F. The striations were very coarse and deep, and appeared more like grooves in the specimens pickled in 150 F solutions.

Contamination From Alloying Agents in Zircaloy 2

The effect on pickling behavior of bath contamination from alloying agents in Zircaloy 2 was studied in 3.5 volume per cent HF-39 volume per cent HNO_3 at 100 F. Chromium, iron, nickel, and tin ions were added singly and in combination to the bath in the same ratios as if 1, 2, 3, 5, 10, and 20 w/o Zircaloy 2 were added to the solution by pickling. Chromium, iron, and nickel were added as nitrates. Metallic tin was dissolved in HNO_3 and then added to the bath. The amounts of these additions are presented in Table 1.

The results of these experiments are plotted in Figures 16 through 20. Pickling rates were linear with time. No pronounced effect on pickling rate was observed with these minor additions, and the scatter in results obtained could well represent experimental error.

Measured metal-loss-thickness curves for the above study correlated well with the calculated penetrations as presented in Figures 16 through 20.

The surfaces of specimens pickled in solutions containing chromium, iron, or nickel ions exhibited some degree of striations. Specimens pickled in solutions containing 0.03 to 0.30 w/o tin were smooth and shiny. Specimens pickled in solutions containing all four metal ions in combination exhibited very little surface striation. Thus, it appears that tin in solution may have a beneficial effect in producing smooth, bright surfaces on Zircaloy 2 pickled in HF-HNO_3.

Surface Roughness

Surface roughness in the form of striations has been mentioned repeatedly throughout this report. Surface condition versus acid concentrations at temperatures of 90 and 100 F have been plotted in Figure 21. A curve has been drawn which separates acid concentrations according to whether a rough or smooth surface is produced on the Zircaloy 2 specimens employed in this study. The general trend is that, as HF content increases, the HNO_3 content must decrease to avoid roughened surfaces. The 3.5 volume per cent HF-39 volume per cent HNO_3 bath lies on the border line and may produce some roughening of Zircaloy 2 used in this program.

DISCUSSION

Smith and Hill have demonstrated that the rate of dissolution of zirconium in HNO_3-HF solutions is a function of the undissociated HF concentration.[2] In the presence of HNO_3 (and other acids) the fluoride-ion concentration is small and hence, for all practical purposes, the undissociated HF concentration is equal to the molarity of the HF.

TABLE 1. EFFECT OF CHROMIUM, IRON, NICKEL, AND TIN CONTAMINATION IN THE HF-HNO_3 BATHS ON THE PICKLING BEHAVIOR OF ZIRCALOY 2

	Acid Concentration					Contaminant Added		Pickling Rate	
	HF		HNO_3						
Condition	Volume Per Cent	Molarity	Volume Per Cent	Molarity	Temperature, F	Ion	w/o	Mg/(Dm^2)(Min)	Mg/(Dm^2)(Min)(Mole HF)
1	3.5	1.05	39	6.31	100	Sn	0.0150	695	662
2	3.5	1.05	39	6.31	100	Sn	0.0300	681	649
3	3.5	1.05	39	6.31	100	Sn	0.0450	662	630
4	3.5	1.05	39	6.31	100	Sn	0.0750	792	753
5	3.5	1.05	39	6.31	100	Sn	0.1500	757	722
6	3.5	1.05	39	6.31	100	Sn	0.3000	683	655
7	3.5	1.05	39	6.31	100	Fe	0.0012	732	698
8	3.5	1.05	39	6.31	100	Fe	0.0024	698	665
9	3.5	1.05	39	6.31	100	Fe	0.0036	700	666
10	3.5	1.05	39	6.31	100	Fe	0.0060	715	682
11	3.5	1.05	39	6.31	100	Fe	0.0120	742	708
12	3.5	1.05	39	6.31	100	Fe	0.0240	711	678
13	3.5	1.05	39	6.31	100	Cr	0.0010	713	679
14	3.5	1.05	39	6.31	100	Cr	0.0020	657	626
15	3.5	1.05	39	6.31	100	Cr	0.0030	699	665
16	3.5	1.05	39	6.31	100	Cr	0.0050	709	675
17	3.5	1.05	39	6.31	100	Cr	0.0100	740	705
18	3.5	1.05	39	6.31	100	Cr	0.0200	732	698
19	3.5	1.05	39	6.31	100	Ni	0.0006	718	684
20	3.5	1.05	39	6.31	100	Ni	0.0012	715	682
21	3.5	1.05	39	6.31	100	Ni	0.0018	758	722
22	3.5	1.05	39	6.31	100	Ni	0.0030	745	710
23	3.5	1.05	39	6.31	100	Ni	0.0060	757	722
24	3.5	1.05	39	6.31	100	Ni	0.0120	689	656
25	3.5	1.05	39	6.31	100	Combination of 1, 7, 13, 19, 25		718	684
26	3.5	1.05	39	6.31	100	Combination of 2, 8, 14, 20, 26		715	682
27	3.5	1.05	39	6.31	100	Combination of 3, 9, 15, 21, 27		758	722
28	3.5	1.05	39	6.31	100	Combination of 4, 10, 16, 22, 28		745	710
29	3.5	1.05	39	6.31	100	Combination of 5, 11, 17, 23, 29		757	722
30	3.5	1.05	39	6.31	100	Combination of 6, 12, 18, 24, 30		689	656

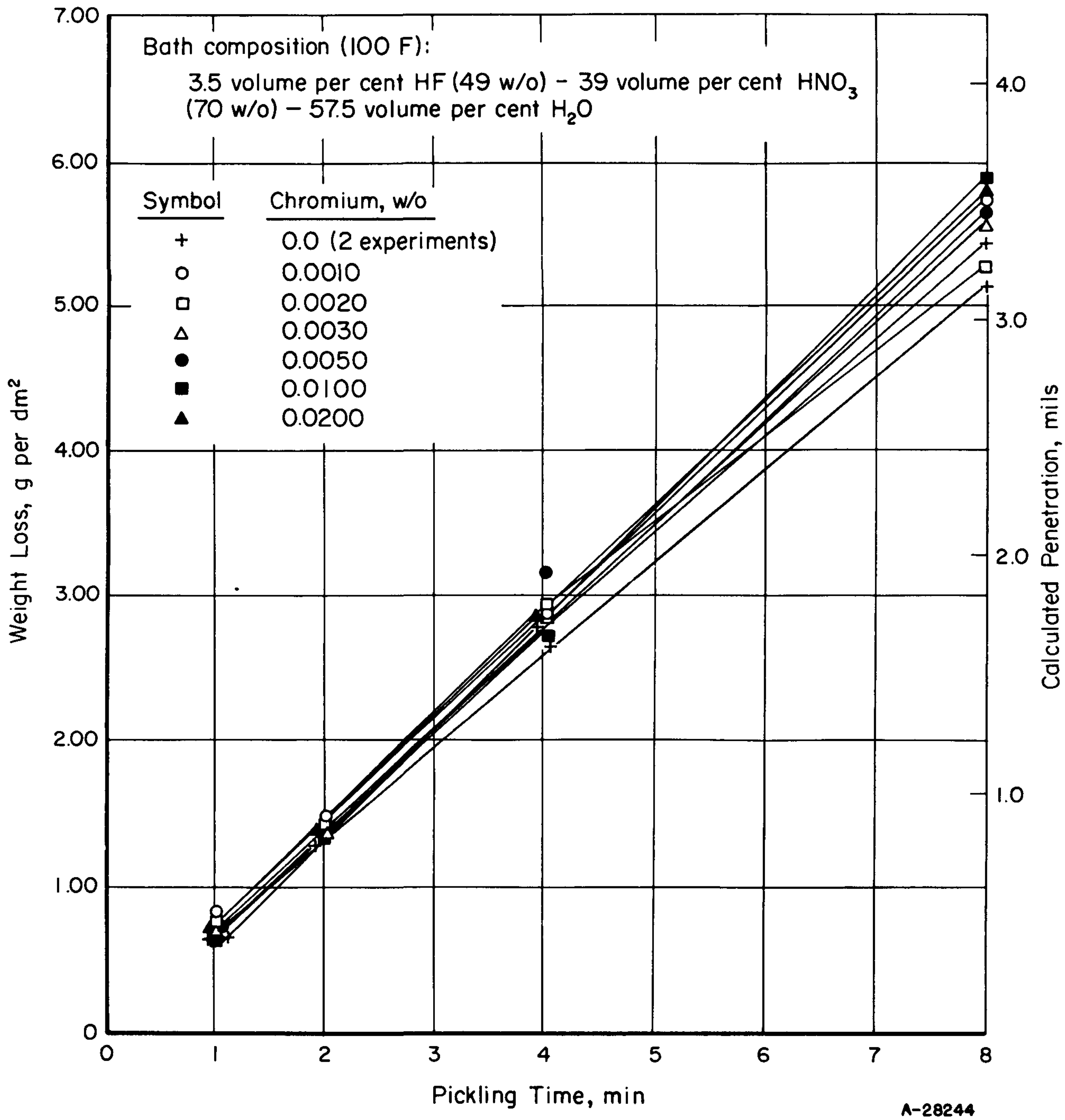

FIGURE 16. EFFECT OF CHROMIUM CONTAMINATION IN NITRIC-HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

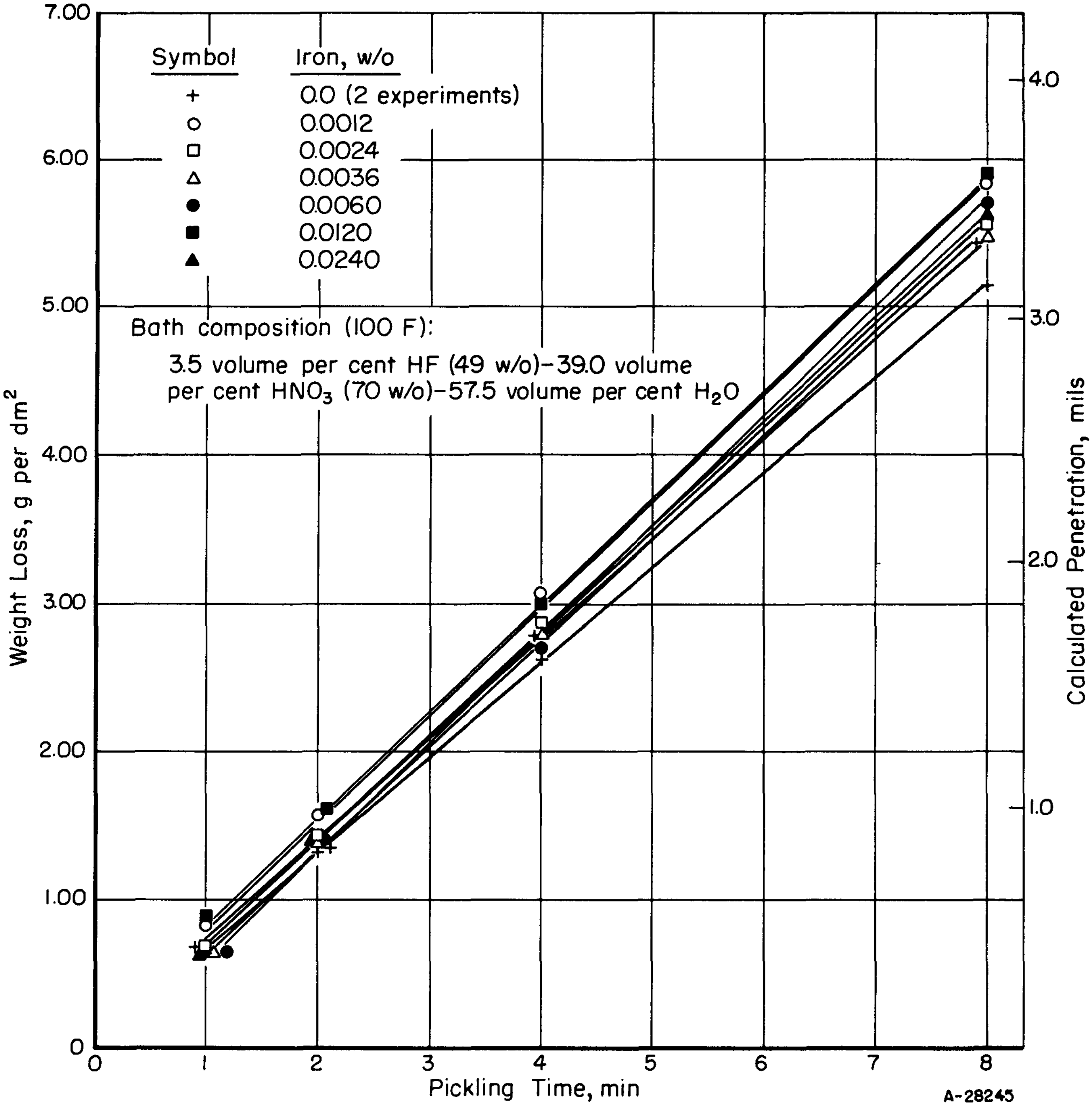

FIGURE 17. EFFECT OF IRON CONTAMINATION IN NITRIC-HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

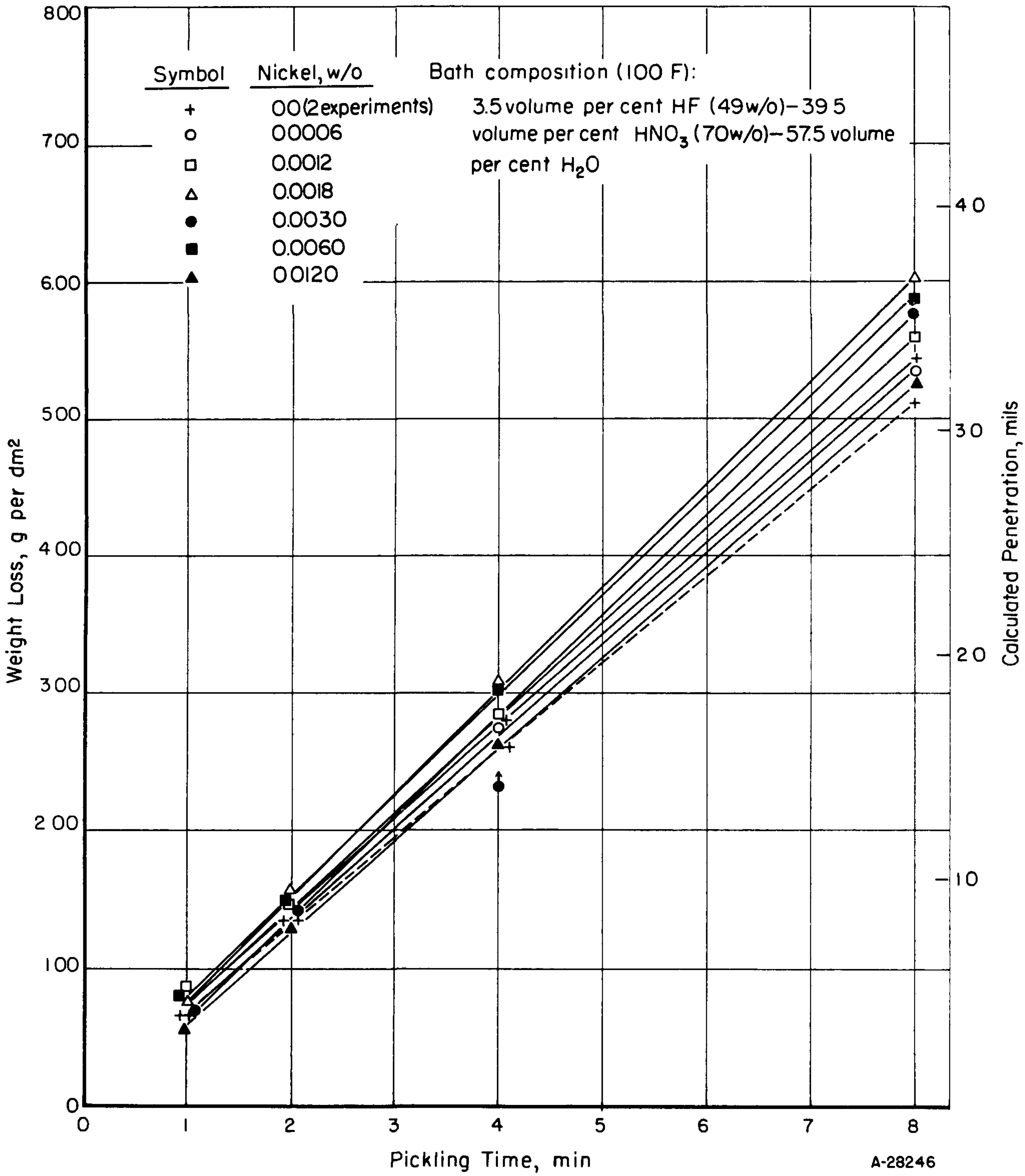

FIGURE 18. EFFECT OF NICKEL CONTAMINATION IN NITRIC-HYDROGLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

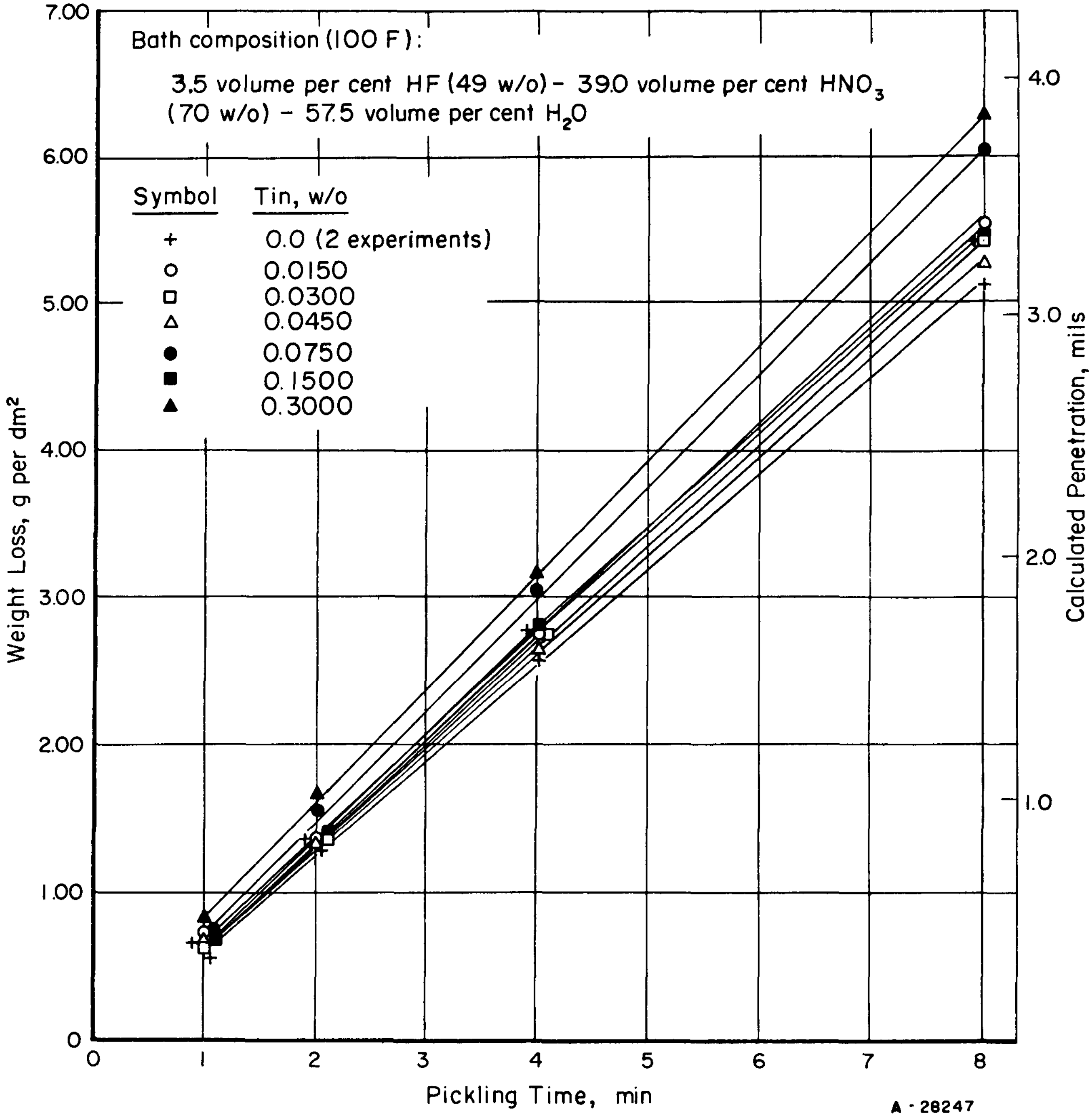

FIGURE 19. EFFECT OF TIN CONTAMINATION IN NITRIC-HYDROFLUORIC ACID BATH ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

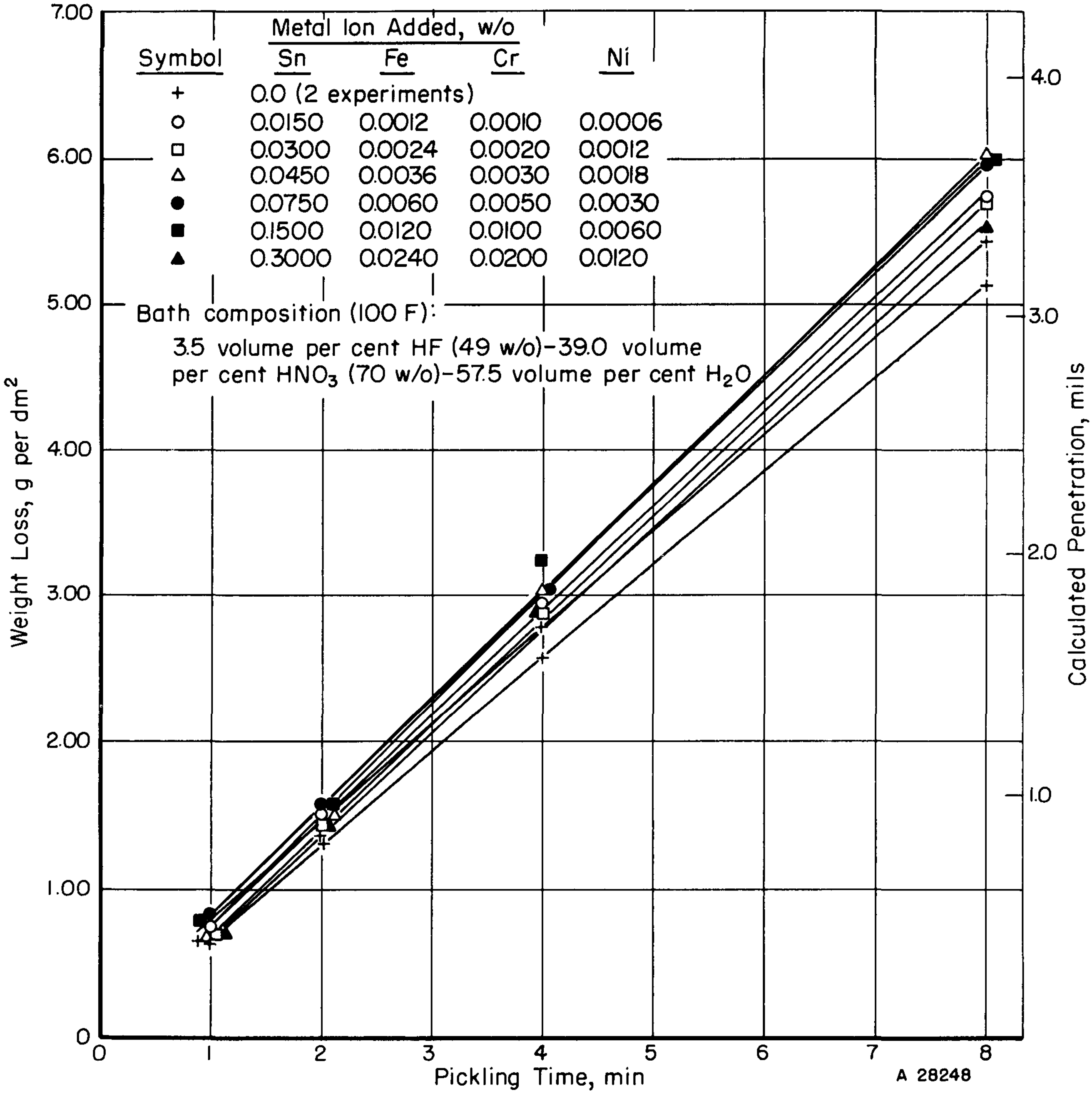

FIGURE 20. COMBINED EFFECT OF CHROMIUM, IRON, NICKEL, AND TIN IN NITRIC-HYDROFLUORIC ACID BATHS ON THE WEIGHT OF ZIRCALOY 2 DISSOLVED

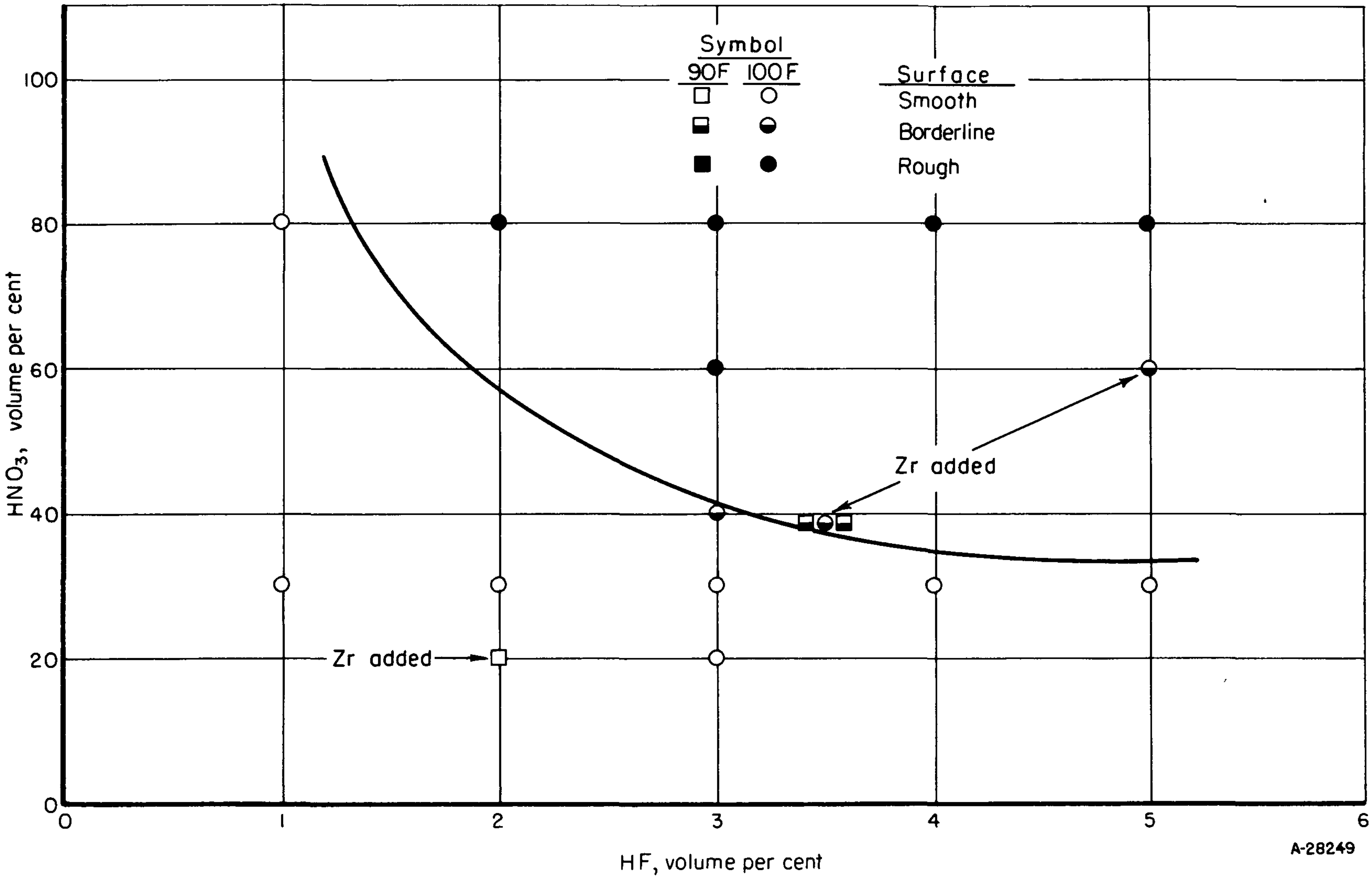

FIGURE 21. SURFACE FINSH ON ZIRCALOY 2 AS A FUNCTION OF NITRIC-HYDROFLUORIC ACID CONCENTRATIONS

The dissolution-rate data obtained for Zircaloy 2 in the present study were recalculated on the basis of undissociated HF concentration rather than volume percentages, and the results are presented in Tables 1 through 3 and are summarized in the temperature-dependency plot in Figure 22 The plotted points represent the results of the temperature-dependency study with the 3.5 volume per cent HF-39 volume per cent HNO_3 solution The curve obtained by Smith and Hill for zirconium also is included. for comparison It can be seen that the effect of temperature on the pickling rate appears greater for Zircaloy 2 than for unalloyed zirconium The activation energy was calculated to be 4 95 kcal per mole for Zircaloy 2, whereas Smith and Hill reported an activation energy of 3 34 kcal per mole for unalloyed zirconium The observed differences between Zircaloy 2 and zirconium in the temperature dependency of their dissolution rates may be real or may be an effect of stirring rate of the solution. Results reported by Smith and Hill were obtained at a stirring rate beyond the limit which produced an effect on dissolution rate

The maximum and minimum pickling rates obtained at 100 F for the studies of the effect of HNO_3, HF, and minor contaminants also are plotted in Figure 22 The small spread in results supports the theory that pickling rate is a function of HF concentration It also reflects the fact that the minor contaminants of chromium, iron, nickel, and tin have little effect on pickling rate.

The maximum and minimum pickling rates obtained in the zirconium-contaminant studies at 90 and 150 F also are plotted in Figure 22 The large spread in results points out the erratic nature of the results obtained in the zirconium-contamination study

It is interesting to note that as little as 0 03 w/o tin in solution resulted in a bright, smooth surface on the alloy specimens in pickling baths which normally produced some degree of striated roughness. The role of tin in this instance was not investigated further It may be possible that its function is to alter the anode-to-cathode ratio on the surface of the Zircaloy 2 by providing a large number of cathodes dispersed over the entire surface, thus assuring a uniform rate of attack The role of tin should be investigated further and the mechanism may provide a means of improving surface finish

Specimens pickled at temperatures above 150 F in this program consistently exhibited staining even though precautions were taken to quickly transfer the specimens to rinse water The staining results in poor corrosion resistance upon exposure in the high-temperature-water environment of pressurized-water reactors During pickling of fuel-element assemblies and clusters in the conventional bath (3 5 volume per cent HF-39 volume per cent HNO_3), it is possible that temperatures in restricted channel areas may reach or exceed 150 F. Thus, staining may occur in these areas Lowering the over-all rate of attack could conceivably result in a much lower temperature in the confined areas during pickling. Satisfactory surfaces were obtained in solutions containing as little as 1 volume per cent HF or as little as 20 volume per cent HNO_3. A further reduction in HF and/or HNO_3 concentration should be investigated to ascertain the lowest limits which result in satisfactory pickling behavior.

TABLE 2. EFFECT OF HF AND HNO_3 CONCENTRATIONS AND BATH TEMPERATURE ON THE PICKLING RATE OF ZIRCALOY 2

Acid Concentration						
HF		HNO_3			Pickling Rate	
Volume Per Cent	Molarity	Volume Per Cent	Molarity	Temperature, F	$Mg/(Dm^2)(Min)$	$Mg/(Dm^2)(Min)(Mole\ HF)$
3	0.90	20	3.23	100	608	675
3	0.90	40	6.47	100	501	555
3	0.90	60	9.70	100	472	524
3	0.90	80	12.94	100	567	629
1	0.30	30	4.85	100	246	820
2	0.60	30	4.85	100	477	795
3	0.90	30	4.85	100	536	598
4	1.20	30	4.85	100	689	524
5	1.50	30	4.85	100	933	621
1	0.30	80	12.94	100	158	528
2	0.60	80	12.94	100	299	499
3	0.90	80	12.94	100	442	492
4	1.20	80	12.94	100	587	490
5	1.50	80	12.94	100	709	472
3.5	1.05	39	6.31	40	265	252
3.5	1.05	39	6.31	60	363	345
3.5	1.05	39	6.31	80	488	474
3.5	1.05	39	6.31	90	557	531
3.5	1.05	39	6.31	100	639	608
3.5	1.05	39	6.31	110	720	686
3.5	1.05	39	6.31	120	918	825
3.5	1.05	39	6.31	140	1080	1030
3.5	1.05	39	6.31	160	1560	1485
3.5	1.05	39	6.31	180	3220	3070

TABLE 3. EFFECT OF ZIRCONIUM CONTAMINATION IN HF-HNO_3 BATHS ON THE PICKLING RATE OF ZIRCALOY 2

Acid Concentration: HF, Volume Per Cent	Acid Concentration: HF, Molarity	Acid Concentration: HNO_3, Volume Per Cent	Acid Concentration: HNO_3, Molarity	Temperature, F	Zirconium Added, w/o	Pickling Rate, Mg/(Dm^2)(Min)	Pickling Rate, Mg/(Dm^2)(Min)(Mole HF)
2	0.60	20	3.24	90	0	294	491
					1	261	435
					2	259	433
					3	260	434
					5	258	430
					10	305	509
					20	176	294
2	0.60	20	3.24	150	0	568	945
					1	568	945
					2	598	998
					3	590	985
					5	688	1148
					10	432	722
					20	1860	3100
3.5	1.05	39	6.31	90	0	485	462
					1	442	421
					2	533	508
					3	455	433
					5	402	383
					10	395	376
3.5	1.05	39	6.31	150	0	1635	1558
					1	1714	1635
					2	1613	1540
					3	2020	1925
					5	2230	2125
					10	2110	2050
5	1.50	60	9.71	90	0	549	363
					1	522	346
					2	571	378
					3	503	333
					5	394	261
5	1.50	60	9.71	150	0	5282	3495
					1	5870	3890
					2	5460	3620
					3	7610	5040
					5	4860	3220

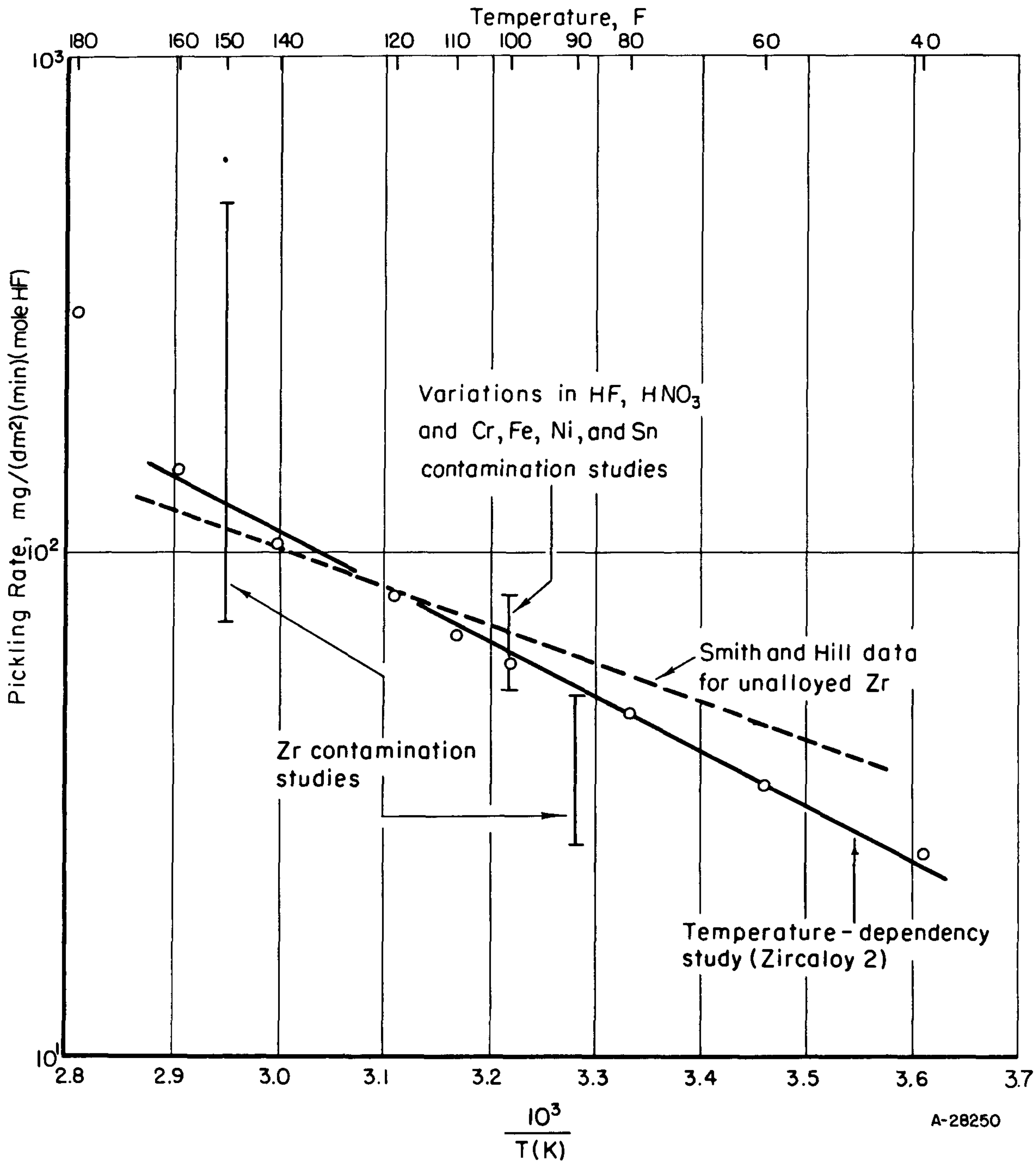

FIGURE 22. TEMPERATURE DEPENDENCY OF THE LINEAR PICKLING RATE OF ZIRCONIUM IN NITRIC-HYDROFLUORIC ACID BATHS

CONCLUSIONS

The results of this study have indicated that the pickling behavior of the Zircaloy 2 used in this program in HF-HNO_3 solutions can be described as follows:

(1) Dissolution rates, as measured by weight of metal loss or thickness decrease, are linear with time.

(2) Dissolution rates increase linearly with increases in HF content.

(3) Nitric acid content has little or no effect on dissolution rate.

(4) Minor contamination of pickling baths from chromium, iron, nickel, and/or tin has little effect on pickling rates. Tin in the range of 0.03 to 0.30 w/o improved the surface finish of the Zircaloy 2 used in this program.

(5) Zirconium contamination of up to 20 w/o or saturation in the pickling baths apparently does not affect pickling rates, based on the erratic results obtained in this study.

(6) Pickling rates increase with an increase in temperature. The increase in rate follows a typical Arrhenius plot. The calculated activation energy is 4.95 kcal per mole.

(7) Staining occurs on specimens pickled above 150 F.

(8) Zircaloy 2 surfaces in this study become roughened at HF concentrations above 2 volume per cent if the HNO_3 concentration is high (above 40 volume per cent).

ACKNOWLEDGMENT

This work was conducted under WAPD Reference No. 73 (14-3627) for the Bettis Laboratory of the Atomic Energy Commission, operated by the Westinghouse Electric Corporation. Liaison was maintained with Mr. Stanley Kass of that laboratory, whose assistance has been appreciated.

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