WAPD-TM-141
AEC RESEARCH AND
DEVELOPMENT REPORT

MASTER

PICKLING OF THE ZIRCALOYS PRIOR TO CORROSION EXPOSURE

September 1958

CONTRACT AT-11-1-GEN-14

BETTIS PLANT
PITTSBURGH, PENNSYLVANIA

Operated for the
U.S. ATOMIC ENERGY COMMISSION
by BETTIS ATOMIC POWER DIVISION,
WESTINGHOUSE ELECTRIC CORPORATION

DISCLAIMER

WAPD-TM-141

UC-25: Metallurgy and Ceramics
(TID-4500, 14th Edition)

PICKLING OF THE ZIRCALOYS PRIOR TO CORROSION EXPOSURE

by

S. Kass, D. J. Fontanese, A. E. Oaks, and D. B. Scott

September 1958

Contract AT-11-1-GEN-14

Price $1.75 Available from the Office of
Technical Services, U. S. Department of Commerce,
Washington 25, D. C.

NOTE

BETTIS PLANT PITTSBURGH, PA.
Operated for the U. S. Atomic Energy Commission by
Bettis Atomic Power Division, Westinghouse Electric Corporation

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

EXTERNAL DISTRIBUTION

	Copies
UC-25: Metallurgy and Ceramics, TID-4500, 14th Edition	560
Manager, Pittsburgh Naval Reactors Operations Office, AEC	9

INTERNAL DISTRIBUTION

J. H. Bach
R. K. Birdsell
R. A. Biscoe
D. W. Bright
H. K. Browning
J. A. Chirigos
M. V. D'Auria
J. C. Eazor
D. J. Fontanese
W. L. Frankhouser
B. Francis
C. R. Garr
R. F. Gessner
J. Glatter
K. M. Goldman
J. G. Goodwin
J. H. Hart
F. W. Hassett
W. B. Haynes
E. H. Hill
H. E. Himes
W. B. Heineman
H. B. Hunter
W. J. Hurford
S. Kass (25)
C. J. Kieler
H. F. Kienzle
B. Lanker
F. J. Lennon
E. Lohr
F. R. Lorenz
E. F. Losco
W. R. McVicker
E. F. McDonough
W. L. Mudge, Jr.
A. E. Oaks
J. T. O'Connor
F. L. Orrell
N. A. Pollack
R. J. Pitzer
L. B. Prus
W. T. Ramsey
E. L. Richards
L. S. Rubenstein
P. Ruzicka
H. M. Schadel, Jr.
D. B. Scott
F. L. Shubert
F. G. Stengel
J. S. Theilacker
D. E. Thomas
H. F. Turnbull
R. T. Webster
B. S. Westerman
D. A. Wigton
W. G. Young
D. Zucker
Bettis Library (5)
NRF Library (2)

TOTAL 657

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

TABLE OF CONTENTS

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ABSTRACT

This report describes a series of investigations relative to the pickling of the Zircaloys prior to corrosion exposure. Included are studies evaluating the feasibility of utilizing common ion neutralizing and sulfuric acid rinses subsequent to pickling in order to facilitate surface cleaning and minimize acid entrapment. Investigations of various addition agents to the aqueous nitric acid-hydrofluoric acid pickling solutions were made to evaluate pickling rates, surface smoothness, ease in rinsing, and effects upon subsequent corrosion properties. The corrosion evaluations of a hydrochloric acid-hydrofluoric acid etchant and nitric and sulfuric acid-hydrofluoric acid solutions were made.

PICKLING OF THE ZIRCALOYS PRIOR TO CORROSION EXPOSURE

S. Kass
D. J. Fontanese
A. E. Oaks
D. B. Scott

INTRODUCTION

Zircaloy-2 and -3 have found extensive application in the water cooled and moderated reactors developed at the Bettis Plant, due to the excellent corrosion properties in high temperature water and steam. These excellent properties are inherent in the alloys; however, the corrosion rates of zirconium alloys are affected by the condition of the surfaces induced by machining, abrading, or chemical contamination. A truly representative surface on good quality material permits one to obtain a protective oxide and low weight gains, while a poor surface of the same material results in loose white oxide and high weight gains. Because of the sensitivity of the zirconium alloys in this respect, great care must be exercised in specimen preparation if spurious results are to be avoided.

Mechanical operations such as machining and abrading the surface of zirconium alloys give rise to a layer of disturbed metal at the surface and for an appreciable depth under it. The disturbed layer exhibits a more rapid corrosion rate than does the bulk metal, hence, must be removed prior to corrosion exposure. The effect, illustrated in Fig. 1, correlates the extent of disturbed metal under a machined surface as revealed by X-ray line-broadening measurements with the appearance of zirconium specimens after corrosion (Ref 1). The incidence of white corrosion, indicating accelerated attack, is seen to correlate with the extent of disturbed metal.

The most reliable method of pre-corrosion exposure surface preparation consists of the removal of 1 to 2 mils from each surface by bright etching in an aqueous solution containing approximately 39 v/o nitric acid (Sp.Gr.1.42), 2.5 to 3.5% hydrofluoric acid (52%). The process includes suspending the items on 18-8 type stainless steel fixtures, minimizing the contact areas between the fixtures and components. A large ratio of etchant volume to component surface area is desired as the zirconium-acid reaction is exothermic, and the etchant temperature should be maintained below 120°F. (Items pickled at temperatures in excess of the upper limit result in tapered and irregular surfaces and are more prone to be contaminated as discussed below).

Contamination occurs when the etchant is not thoroughly rinsed from the surfaces or when the etchant is permitted to dry on the specimen. In the latter case the residue is insoluble in water. Inadequate rinsing, which allows the etchant to dry on the surface, leads to the formation of white corrosion products when exposed to high temperature water. Figure 2 illustrates the corrosion behavior of Zircaloy-2 after proper and improper etching techniques (Ref 2). All specimens were corrosion tested in 680°F degassed, demineralized water after 2 mils per surface were removed by the nitric-hydrofluoric acid etchant. The first set was tested after the specimens were thoroughly rinsed. Note the black oxide surfaces with no evidences of white corrosion product. The second set was corrosion tested after the etchant was permitted to dry upon the specimens. Note that the specimens are completely covered with white corrosion product. The third set was handled in the same manner as the second set except that the specimens were vigorously scrubbed with a brush after drying. The specimens again are coated with white oxide after corrosion testing; however, the appearance indicates that some of the residual etchant was removed by the scrubbing action.

Further dramatic evidence that the corrosion resistance can be markedly deteriorated by improper etching techniques is shown in Fig. 3, a photograph of zirconium test specimens which were clamped together and exposed for 4 days in 650°F water or steam containing 200 ppm of sodium fluoride.* Under these conditions extremely deleterious corrosion is noted at the mating surfaces.

A more frequent difficulty in the corrosion testing of zirconium alloys is not the severe case of white spalling oxide, but the more subtle effects involving only weight gain values or slightly cloudy surfaces (Fig. 4). This condition is brought about during the transfer of the coupons from the etchant to the rinse bath. If the transfer is not made rapidly, the etchant clinging to the coupon becomes spent and deposits the residual reaction product upon the coupon surfaces.

Long-time process experience with simple shapes and components has shown that etching in nitric-hydrofluoric acid and rinsing can produce surfaces which accurately reflect the corrosion resistance of the base metal; however,

---

*Unpublished Research, K. M. Goldman, Bettis Plant recent experiences have demonstrated the need for new or modified procedures since accelerated corrosion was observed in spite of strict pickling and rinsing controls.

The work described in this paper constitutes a study of the pickling of the zirconium alloys prior to corrosion exposure. It presents a continuing effort to advance technology of corrosion resistant Zircaloys.

EXPERIMENTAL

Post-Etching Rinsing

Nitric Acid Rinsing After Pickling

Inasmuch as accelerated corrosion is influenced by the incomplete removal of the etchant or permitting the etchant reaction product to dry upon the zirconium alloy surfaces, the utility of common ion rinses immediately after rinsing were investigated in order to redissolve any residual reaction product from the surfaces.

Two-hundred-forty Zircaloy-2 specimens were etched in the nitric-hydrofluoric-water bath at 100°F for sufficient time to remove 2 mils per surface. The coupons were not rinsed, but permitted to drain dry for 7 days. All coupons were covered with heavy deposits of a white reaction product. (These specimens represent the extreme condition of surface contamination discussed above). The coupons were then randomly divided into groups of 10 each and rinsed in aqueous solutions containing 0, 10, 25, 40, 60, and 80 v/o nitric acid for 5, 10, and 20 min at 140° and 160°F. Upon completion of the aqueous nitric acid rinses, the specimens were thoroughly flushed in flowing tap water and static, boiling, high purity water. The coupons were then corrosion tested in 750°F steam at 1500 psi for 3 days, using procedures previously discussed (Ref 2).

Visual examination of the coupons prior to the corrosion test showed that none of the above rinsing operations completely removed the residual etchant reaction product from the surfaces, although a few areas at the tops of the coupons appeared to be free of the white deposit. Typical surfaces after rinsing are shown in Fig. 5. Post-corrosion test examination confirmed the pretest examination; none of the rinsing operations completely removed residual reaction product. Typical specimens after corrosion testing are shown in Fig. 6. Additional trends indicated were:

(a) Rinsing the contaminated surfaces in tap water did not exhibit beneficial effects. No improvement was noted with increasing rinse water temperature.

(b) Rinsing in aqueous nitric acid removed some residual reaction product; however, complete removal was not obtained. The efficiency of the removal was independent of the nitric acid concentration over the range from 10 to 80 w/o.

(c) In the low concentration range (10 to 40%) slightly improved deposit removal was obtained with increasing rinse bath temperature.

(d) At the high concentration (60 and 80%) the rinsing action was independent of time and temperature.

Inasmuch as some reaction product removal was indicated in the above experiments, a group of 40 specimens was treated to determine the value of a post-pickle rinse at room temperature in 25% nitric acid utilizing rapid transfer of the coupons from the etchant to the acid rinse. The coupons were etched 2 mils per surface at temperatures of 60° and 120°F, immediately rinsed in either 25% nitric acid at room temperature or tap water, and subsequently rinsed in high purity water.

All specimens exhibited bright lustrous surfaces with no indications of any residual reaction product.

The coupons were then corrosion tested for 3 days in 750°F steam. Visual examination of the coupons showed the following:

(a) The coupons rinsed in the aqueous nitric acid solution did not exhibit any areas of the white accelerated corrosion product. The coupons rinsed in water showed slightly cloudy films indicative of insufficient removal of the residual etchant.

(b) Little or no differences were apparent on the surfaces of the coupons which could be attributed to pickle solution temperatures.

The nitric rinse, although not a "cure-all" for surface contamination occurring during the pre-corrosion etching of zirconium alloys, is a valuable addition to the process. The chances of contaminating surfaces with residual etchant are minimized when nitric acid rinsing is employed as the time required for transfer from the pickling solution to the nitric rinse need not be as short as when water rinsing is employed.

Sulfuric Acid Rinsing After Pickling

The white precipitate formed during the dissolution of zirconium in hydrofluoric acid solutions is believed to be a hydrated zirconium fluoride (presumably $ZrF_x\,(OH)_y \cdot nH_2O$). Furthermore, it is believed that this precipitate is a cause of surface contamination and the resulting accelerated corrosion. Since preliminary experiments have shown that the precipitate is soluble in hot (100° to 140°F) aqueous sulfuric acid, a series of investigations was initiated to determine the feasibility and utility of incorporating aqueous sulfuric acid solutions after etching. It was postulated that if the precipitate were soluble in aqueous sulfuric acid, dissolution of the precipitate would remove the source of the accelerated corrosion.

Sixty-four Zircaloy-2 specimens were etched in the nitric-hydrofluoric-water etchant at 100°F for sufficient time to remove 2 mils per surface. The specimens were not rinsed but were permitted to drain-dry for 24 hours.

The specimens were covered with heavy, white deposits representing the extreme condition of surface contamination. The specimens were then randomly divided in groups of four each and rinsed in tap water 10, 25, and 50 v/o sulfuric acid for 10 and 30 min at 80° and 140°F. The specimens were then thoroughly rinsed in flowing tap water and static, boiling, high purity water. Visual examination of the specimens prior to corrosion test showed that none of the above operations completely removed all of the etchant reaction product, although gross areas of bright shiny metal were evident (Fig. 7). The dissolution of the white deposit was greater at the high temperatures than at the lower temperatures. The 25 v/o solution at 140°F removed almost all of the white deposit, but a thin, dark, blueblack smut remained.

Post corrosion test examination (Fig. 8) showed severe accelerated corrosion on all major surfaces of the specimens. Areas which appeared to be free from residual etchant prior to the test also exhibited white corrosion product. These observations indicated that although the sulfuric acid solution apparently removed all visible traces of residual etchant contamination, a secondary reaction occurred, resulting in general overall accelerated corrosion.

A group of 24 Zircaloy-2 coupons was included in a program to confirm the above indications. Coupons were processed in six groups of four each and corrosion tested for 14 days in 750°F steam. Etching temperatures of 60°, 80°, and 140°F were used, with and without subsequent rinsing in 25 v/o sulfuric acid for 30 sec at 140°F.

Pre-corrosion test examination revealed no acid stains on any of the coupons rinsed in the sulfuric acid solution, and slight stains on the coupons pickled at 140°F and water rinsed.

Post-corrosion-testing (Fig. 9) inspection showed the following:

(a) The coupons which were immediately rinsed in water exhibited shiny, black temper films. Only the coupons pickled at 140°F exhibited white corrosion product. (It should be noted that these coupons appeared stained before corrosion tests).

(b) All coupons which were rinsed in sulfuric acid exhibited general white areas, evidences of accelerated corrosion.

These experiments showed that although the reaction product formed during the etching of zirconium alloys in hydrofluoric acid solutions is soluble in hot aqueous sulfuric acid, a secondary reaction occurs at the zirconium alloy surfaces, causing a deleterious effect upon the subsequent high temperature corrosion behavior.

Caustic Rinses

The following experiment was performed to determine whether rinses performed in solutions neutralizing the residual acid clinging to the surfaces would appreciably affect the corrosion resistance and/or result in minimizing "acid stain" corrosion. Sixty-four coupons representing one Zircaloy-2 and three Zircaloy-3 ingots were etched for sufficient time to remove 2 mils per surface in the nitric-hydrofluoric solution and thoroughly rinsed in tap water. Thirty-two coupons were subsequently rinsed in a 4% solution of sodium hydroxide.

All coupons were then rinsed in hot, high purity water and corrosion tested for periods up to 168 days in 680°F water and 140 days in 750°F steam.

Precorrosion examination revealed no staining of the coupons; all surfaces were bright and lustrous.

The coupon appearances and weight gain data (Table I) showed no deleterious effects were brought about by the caustic rinse. It should be noted that although beneficial effects were not observed, caustic rinsing may be employed whenever experience has shown that water rinsing does not completely remove the entrapped etchant from the surfaces.

Additives to the Nitric Hydrofluoric Acid Etchant

The above reported experiments and long time process experience has demonstrated that the nitric-hydrofluoric etchant would be improved if the residual etchant could be removed more rapidly from the Zircaloy surfaces. Supplemental operations, nitric or caustic post-pickle rinses, fog nozzle spraying, etc., have been employed; however, these approaches are time consuming, difficult, and not completely fool-proof.

In many commercial pickling and electroplating operations, additives such as wetting agents, are often employed to facilitate metal removal, improve surface finish, increase the rinsability of etchant, etc.

A group of experiments was performed to explore the field of wetting agent additions to the nitric-hydrofluoric etchant and to evaluate their effects on the pickling rate, surface finish, corrosion behavior, and ease in rinsing.

Preliminary investigations showed the following additives were stable in the hot acid solution:

Antarox G-100	General Analine and Film
Antarox G-100 + Igepal Defoamer	General Analine and Film
Akweons 670	Swift and Company
Akweons 674	Swift and Company
Akweons 700	Swift and Company
Akweons 774	Swift and Company
Akweons 790	Swift and Company
BCO	Swift and Company
Rodine	American Chemical Paint

Antarox G-100

A series of four etchants was prepared by adding 0, 0.05 (0.55 cc/l), 0.1 (1.17 cc/l), and 0.5 w/o (5.45 cc/l) of Antarox G-100 to the 39 v/o nitric acid-3.5 v/o hydrofluoric acid-water etchant. (The addition agent readily dissolved in the acid). Ten Zircaloy-2 coupons were pickled in each of the solutions at 90°F for sufficient time to remove 2 mils per surface. During the pickling foaming was evident and the degree of foaming increased with increasing Antarox G-100 content. The coupons were thoroughly rinsed in tap water, hot (120°F) high purity water, and corrosion tested in 750°F steam.

The as-etched coupon surfaces were bright, lustrous, and exhibited no areas of staining. The corrosion tested surfaces were black, lustrous, and completely free from white corrosion product. Extended corrosion tests (84 days in 750°F steam), summarized in Fig. 10, show no deleterious effects on the corrosion resistance of Zircaloy-2 were brought about by the addition of the wetting agent to the etchant.

The preliminary weight gain data indicated that the addition of the wetting agent retarded the Zircaloy-2 corrosion and resulted in lower weight changes. Manufacturers' literature stated that the agent is a highly polar amine and tends to form tightly adherent mono-molecular layers on metallic surfaces. It was postulated that the layer would initially act as a barrier and decrease the corrosion rate; however, the barrier layer would soon be destroyed and Zircaloy-2 corrosion would proceed in the normal manner. Eighty-four days exposure in 750°F steam has confirmed the postulation. The coupons pickled in treated acid continue to show weight gains 4-6 mg/dm^2 below those etched in the "reference" etchant, but the corrosion rates are essentially identical.

When large amounts of metal (approximately 10 mils) are removed from the surfaces, a more uniform attack is obtained when the addition agent is incorporated into the etchant (Fig. 11). Furthermore, pickling rate studies (Fig. 12) have shown that the Zircaloy dissolution rate in the Antarox G-100 containing etchant is less sensitive to temperature changes than the non-Antarox G-100 containing solution.

It was hypothesized that if improved rinsability of the etchant were obtained by the addition of Antarox G-100, samples which were not immediately flushed in water after etching would not exhibit the deleterious acid stain and subsequent high corrosion rate. Accordingly, a group of twenty-four coupons was treated as follows and corrosion tested for 7 days in 750°F steam:

(a) Six coupons were etched in an 0.5 w/o Antarox solution for sufficient time to remove 2 mils per surface and immediately flushed with tap water, then high purity water.

(b) Six coupons were etched as in (a) except that the rinsing was performed 1 min after the coupons were removed from the etchant instead of immediately upon removal.

(c) Six coupons were etched in a non-Antarox G-100 etchant long enough to remove 2 mils per surface, immediately flushed with tap water, then rinsed in hot high purity water.

(d) Six coupons were etched 2 mils per surface in the non-Antarox etchant, thoroughly flushed with tap water 1 min after removal from the etchant, then rinsed in hot high purity water.

The surface appearances (Fig. 13) and the weight gain data (Table II) show that the wetting agent addition to the etchant does not eliminate the requirement for immediate rinsing after etching.

In order to minimize foaming which occurs whenever large complex components are etched in Antarox G-100 solutions, an etchant compounded of Antarox G-100 and Igepal CO-20 was employed. Foam stability was materially reduced without causing deleterious effects upon the pickling characteristics or subsequent Zircaloy corrosion.

Akweons 670

A series of four etchants was prepared by adding 0, 0.05, 0.1, and 0.5 w/o Akweons 670 to a 35% nitric acid, 5 v/o hydrofluoric acid, balance water etchant. Ten Zircaloy-2 coupons were etched in each of the solutions for sufficient time to remove 2 mils per surface, thoroughly rinsed in tap and high purity water, and corrosion tested for 14 days in 750°F steam.

During the pickling operation, excessive foaming was also noted. The as-pickled surfaces were bright and lustrous and exhibited no areas of stain. Post-corrosion-test examination indicated no adverse effects on the corrosion behavior of Zircaloy-2 were caused by the wetting agent.

Pickling rate studies, summarized in Fig. 14, again demonstrate the characteristic of a lesser dependance of pickling rate on temperature. Also lower rates were obtained with increasing agent content.

Akweons 674, 700, 774, and 790

A group of five etchants was prepared by adding 0, 0.01, 0.02, 0.04 and 0.10 w/o Akweons 674 or Akweons 700 to a 35% nitric-5% hydrofluoric acid solution. Four Zircaloy-2 coupons were etched in each of the above solutions; immediately flushed in tap water; rinsed in hot, high purity water; and corrosion tested in 750°F steam. Four additional Zircaloy-2 coupons were etched in each of the above solutions; flushed in tap water 1 minute after removal from the etchant; rinsed in hot, high purity water; then corrosion tested in 750°F steam to evaluate whether improved rinsability was obtained by the addition of wetting agent.

No acid stains were evident on any specimens thoroughly flushed immediately after etching, but stains were evident on all specimens not rinsed immediately after etching, indicating that improved rinsability was not attained.

Post-corrosion-test examination confirmed the pretest observations. (Figs. 15 - 18). The specimens rinsed immediately after etching exhibited no deleterious corrosion attributable to the agents, while all coupons delay-rinsed exhibited white corrosion due to residual acid or reaction product.

The 750°F steam data (Tables III and IV) again reflect the deleterious corrosion effects brought about by improper rinsing after etching. The initial weight gains of the coupons etched in the Akweons containing solutions and immediately rinsed are slightly higher than the weight gains of coupons etched in the non-treated solution; however, the differences minimize as corrosion exposure is extended.

Pickling rate studies, summarized in Figs. 19 and 20, demonstrate a marked decrease in the rate of metal dissolution in treated etchants at high temperatures and with increasing addition agent.

Excessive foaming was observed when large components were pickled in Akweons 674 solutions or when air agitation was employed. Akweons 774, reported to be a nonfoaming version of Akweons 674, was investigated and exhibited behavior similar to Akweons 674.

Additional investigation showed that Akweons 790 additions to the etchant yielded nonfoaming solutions and no deleterious effects upon the corrosion behavior (Fig. 21 and Table V).

DuPont BCO

An evaluation program similar to that for Akweons was performed to determine the properties of etchants containing the addition of DuPont BCO.

All coupons properly rinsed exhibited bright lustrous surfaces while those delay-rinsed showed the usual "acid-stain". Post-corrosion inspection verified the as-etched trends; the addition agent does not relax the requirement for immediate rinsing after etching. The corrosion data (Table VI) also show the addition agent produces no ill effects upon the corrosion resistance of properly rinsed Zircaloy-2.

Pickling rate studies (Fig. 22) demonstrate that BCO also decreases the pickling rate dependency upon temperature, with a marked decrease in the rate of metal removed at high temperatures when 0.10 w/o of the addition agent is included in the etchant.

Rodine

Similar experiments were conducted using an etchant composed of 39% HNO_3, 3.5% HF, bal H_2O containing 1 oz. Rodine per liter of etchant.

The Rodine containing solutions removed metal at the same rate as the non-Rodine containing etchant; however, more uniform surfaces were obtained when the Rodine solutions were employed. In addition, the surfaces of the Zircaloy test coupons exhibited more lustrous surfaces after being etched in the Rodine solutions.

Summary of Wetting Agents

Although the presence of wetting agents in the etchants do not contribute to improved rinsability of the etchant from the metal surfaces and immediate, thorough flushing of the metal surfaces after etching must be performed, the incorporation of wetting agents in the Zircaloy pickling solutions has considerable merit. A summary of the surface metal dissolution rates (Fig. 23) shows the marked decrease in pickling rates at higher temperatures when the agents are included in the etchant. This property can be utilized for improved process control whenever large or complex Zircaloy components are pickled as the variations in the amount of surface metal removed due to minor variations in etchant temperatures will be minimized.

New Etchants

The ideal etchant for the removal of surface metal from Zircaloy-2 should possess a few basic requirements. The etch should not be harmful to corrosion resistance. It should remove surface metal in a reasonable time, should produce a clean surface, should not cause pitting, and should be easy to handle and prepare. Furthermore, it should be easily removed from the metal surfaces. The "nitric-hydrofluoric" etchant does not meet all the above specifications. The etch may be harmful to corrosion resistance and is not easy to prepare or handle. The etchant must be stored in acid resistant tanks, and hydrofluoric acid safety precautions must be strictly observed. Furthermore, material to be etched must be vigorously agitated or channeling will occur. The bath is spent after approximately 56 g per liter of solution of metal are dissolved.

Nitric-Sulfuric-Hydrofluoric Acid Etchants

Inasmuch as the above experiments showed the reaction product formed during the dissolution of zirconium in hydrofluoric acid is soluble in hot sulfuric acid, it was postulated that if the sulfuric acid were incorporated into the etchant, the reaction product would redissolve in the sulfuric acid. Thus the source of contamination would be a liquid rather than a solid, and the subsequent water rinsing action would be efficient and positive. The following group of experiments was initiated to:

(1) Determine the effect sulfuric acid concentration has on the pickling rate, surface finish, and corrosion behavior of Zircaloy-2, and

(2) determine the effect of delayed rinsing on coupons etched with a sulfuric acid containing etchant.

A series of seven etchants was prepared by substituting sulfuric acid (96%) for nitric acid in the 39 v/o nitric-3.5% hydrofluoric-water etchant. Substitutions ranging from 0 to 100% of the nitric acid were included. The water and hydrofluoric acid concentrations remained constant. Four Zircaloy coupons were etched in each of the solutions at 80° ± 10°F and 100°F ± 10°F for 8 min. After etching the coupons were rapidly transferred to tap water and then thoroughly rinsed, dried, and examined.

Figure 24 summarizes the results of the pickling rate study. The curves were prepared by calculating the average amount of metal removed per surface after each immersion period and plotting these data versus the initial sulfuric acid concentration. Very little differences in the pickling rates are observed over the range 0 to 90% substituted acid; however, the rate markedly increases at 100% sulfuric acid solution. The data further show that pickling rates of the mixed acids are less influenced by high temperatures than the completely substituted etchants. All coupons etched cleanly in each of the solutions and no evidences of white deposits, discoloration, or smudges were visible on the coupons. In general, the coupons exhibited more lustrous surfaces after etching in the "reference"* than in the substituted solutions. Coupons etched in the completely substituted acid were dull.

The coupons were corrosion tested in 750°F steam for periods up to 66 days. All coupons exhibited black, adherent, oxide films after corrosion exposure. No areas of accelerated corrosion (acid stain) were evident. Analysis of weight gain data (Figs. 25 and 26) showed small effects upon the corrosion behavior were caused by the etchants. Very slight trends of increasing weight gain with increasing sulfuric acid content were indicated.

The preceding experiment demonstrated the sulfuric acid may be substituted wholly or in part for nitric acid without seriously affecting corrosion behavior.

Another set of experiments was initiated to evaluate the sensitivity of the surfaces to the time required for transfer of the component from the etchant to the first rinse. A group of 40 Zircaloy-2 coupons was etched in the "reference" and in the 30% substituted etchant for sufficient time to remove 2 mils per surface and rinsed in tap water after various delay times of 0, 3, 10, and 30 min in the transfer to the rinse. Visual examination of the coupon surfaces after etching and rinsing revealed superior surface cleaning was attained when sulfuric acid was included in the etchant. The coupons which were rinsed immediately after etching in both solutions were bright and lustrous, showing no evidences of residual reaction product. The coupons etched in the sulfuric-acid-containing solution and held for 3, 10, and 30 min prior to rinsing exhibited bright lustrous surfaces; no residual etchant product was evident. In contrast, the coupons etched in the "reference" etchant and held for 3, 10, and 30 min

---

*39 v/o HNO_3, 3.5% HF, bal H_2O

prior to rinsing exhibited various degrees of "acid stain", the amount increasing with increasing delay time.

The coupons were then corrosion tested for 7 days in 750°F steam at 1500 psi. Visual examination (Fig. 27) of the coupons rinsed immediately in water after etching in the "reference" or the sulfuric-acid-substituted solution showed no evidences of accelerated corrosion. The surfaces were black and lustrous. In contrast, all coupons rinsed 3, 10, and 30 min after etching showed gross areas of white "acid stain" corrosion regardless of the etchant used. The amount of white oxide appeared to increase as the delay time was increased, and greater amounts of contamination appeared on coupons etched in the sulfuric-acid-containing solutions. It is of interest to note that coupons etched in the sulfuric-acid-substituted etchant and delay-rinsed appeared free from residual reaction product prior to corrosion test. This behavior confirms the indication reported previously that a secondary action, resulting in an overall corrosion, occurs when sulfuric acid dries on Zircaloy surfaces. The data furthermore confirmed the indications that sulfuric acid can be substituted for nitric acid and yields corrosion resistant surfaces, provided the transfer of the component from the etchant to the rinse bath is made very rapidly. If the transfer is not made very rapidly, secondary reaction occurs and leads to white corrosion product. For this reason it is not recommended that sulfuric-acid-containing etchants be employed for the pickling of Zircaloy prior to corrosion exposure.

Hydrofluoric-Hydrochloric Acid Etchant

The electrical resistance of the surface of Zircaloy-2 etched in the standard nitric-hydrofluoric etchant has been reported to increase markedly after a short exposure to air. This high surface contact resistance is undesirable in resistance welding. An etchant composed of 100 parts of 36% hydrochloric acid and one part 52% hydrofluoric acid was developed which results in lower surface contact resistance and retains this value for periods as long as 1 week after exposure to air at room temperature.*

To determine the feasibility of the hydrochloric-hydrofluoric etchant as an alternate or in conjunction with the nitric-hydrofluoric etchant, the following experiment was performed.

---

*Unpublished Research, E. F. Nippes, Rensselaer Polytechnic Institute

A group of Zircaloy-2 specimens was etched in the hydrochloric-hydrofluoric etchant at room temperature for 30, 60, 120, and 180 sec and thoroughly rinsed. A second set of samples was etched in a similar manner with the addition of re-etching with the nitric-hydrofluoric etchant and thoroughly rinsed. A third set of samples was etched in the hydrochloric-hydrofluoric etchant at room temperature for 30, 60, 120, and 180 sec and was permitted to drain dry. A fourth set of coupons was etched as above (hydrofluoric-hydrochloric and dried), subsequently etched in the nitric-hydrofluoric solution and thoroughly rinsed. A fifth set of coupons was etched in the reference solution and thoroughly rinsed to serve as controls. Half of each lot of coupons was then corrosion tested in 750°F steam and the remaining half in 680°F water.

In general, the coupons etched in the hydrochloric-hydrofluoric solution exhibited dull mat finished prior to corrosion exposure. Coupons etched in the nitric-hydrofluoric solution exhibited bright, specular finishes.

After exposure in either 680°F water or 750°F steam, the coupons etched in the hydrochloric-hydrofluoric solution and thoroughly rinsed exhibited dull, gray oxide films (Fig. 28). The coupons which were permitted to dry after the HCl-HF treatment exhibited general overall corrosion and white corrosion product (Fig. 29). All coupons which were etched in the hydrochloric-hydrofluoric etchant with and without rinsing prior to subsequent etching in the nitric-hydrofluoric etchant exhibited bright lustrous oxide films (Figs. 30 and 31).

Analysis of the corrosion weight gain data (Table VII) showed higher corrosion rates for coupons etched in the hydrochloric-hydrofluoric solution and thoroughly rinsed than coupons etched in the "reference" etchant and thoroughly rinsed. Coupons corrosion tested after the HCl-HF etchant was permitted to dry upon the surfaces exhibited very high weight gains or spalling and weight losses. In all cases, when coupons were etched in HCl-HF, subsequently etched in the HNO_3-HF etchant, and thoroughly rinsed, all deleterious effects of the HCl-HF etchant were removed.

The experiment demonstrated that the hydrochloric-hydrofluoric etchant is not satisfactory for the preparation of Zircaloy surfaces for corrosion exposure. The deleterious effects, however, are rendered innocuous when the surfaces are re-etched in the "reference" etchant.

Sulfuric Acid-Sodium Nitrite Etchant

A promising etch consisting of 96.2% sulfuric acid to which is added 120 g sodium nitrate per liter of acid was developed by Manufacturing Laboratories, Inc.* This solution is easier to handle than the present etch, and the safety hazard of hydrofluoric acid is eliminated. Specimen agitation is not required; however, bath agitation is recommended. With the solution maintained at 95°F and agitated, approximately 20 g of metals are dissolved per liter of solution.

The following experiment was performed to evaluate the sulfuric-nitrite etch and additional studies were performed to determine the effect upon the corrosion resistance of Zircaloy-2, to compare the corrosion rates of specimens etched by the sulfuric-nitrite solution and the nitric-hydrofluoric acid solution, and to evaluate the effects of residual etchant.

Samples of Zircaloy-2 were etched in the prescribed manner with both solutions for sufficient time to remove 2 mils per surface. After weighing, the specimens were submitted for corrosion test in 680°F degassed, deionized water. Visual examination of the coupons prior to corrosion test showed bright, lustrous surfaces. No evidences of "acid stain" were detected. After 56 days exposure in 680°F water no harmful effects attributed to the sulfuric-nitrite etch were observed. Corrosion tested surfaces of the specimens etched with the sulfuric-nitrite etch were not as black as those etched with the nitric-hydrofluoric acid solution; however, adherent lustrous, oxide films were produced.

Additional samples of Zircaloy were etched in the sulfuric-nitrite solution for sufficient time to remove 2 mils per surface. The etching solution was permitted to drain off, but no rinsing was performed. After the specimens dried they were corrosion tested in 680°F water with and without scrubbing to remove the residual product. After the corrosion test all specimens were covered with white oxide films. The films on the specimens etched in the sulfuric-nitrite solution appeared to be somewhat more adherent than those specimens etched in the nitric-hydrofluoric solution. Weight change (Fig. 32) data indicate that although the residual etchants from both solutions exhibited deleterious effects upon the corrosion resistance of Zircaloy-2, the weight losses of the unwashed sulfuric-nitrite specimens were much less than those of the unwashed

---

*272 Northampton Street, Boston, Mass.
Worked performed under Bettis Plant Subcontract No. 14-333-(1953)

nitric-hydrofluoric etchant specimens. The improvement of corrosion resistance due to scrubbing of the residual etchant product is more pronounced in the case of the sulfuric-nitrite etch than a case in the hydrofluoric-nitric etch.

These experiments have shown that there were not significant differences in the corrosion rates of Zircaloy-2 after etching with the nitric-hydrofluoric solution or the sulfuric-nitrite solution, provided the coupons were transferred rapidly from the etchant to the rinse. Incomplete removal of the residual etchant from either solution is deleterious to the corrosion resistance. This effect in the case of the sulfuric-nitrite solution is not as pronounced as in the case of the nitric-hydrofluoric solution; however, the effect is severe.

The sulfuric-nitrite etchant suffers several disadvantages:

(1) Rejuvenation of spent or partially spent etchant is not practical.

(2) Minor variation in bath composition and/or temperature result in black smutted surfaces requiring additional cleaning operations.

(3) The metal dissolution rate is low.

(4) The bath is exhausted after approximately 20 g of metal are dissolved per liter of solution, in comparison to approximately 56 g per liter when the nitric-hydrofluoric etchant is used.

SUMMARY AND CONCLUSIONS

Because of the length, diversity, and magnitude of the work covered in this report, it is felt that a general summary of the experiments will be helpful.

Rinsing Zircaloy in aqueous nitric acid after etching in nitric-hydrofluoric solutions has been demonstrated to be a valuable addition to the pickling operation as the time required for the transfer from the etchant to the rinse need not be as short as when water rinsing is employed.

Rinsing as pickled Zircaloy in aqueous sulfuric acid causes deleterious effects upon the Zircaloy corrosion properties.

Rinsing as pickled Zircaloy in caustic solution produces no harmful effects upon Zircaloy corrosion behavior; for particular application, the rinse may be beneficial in neutralizing any acid clinging to the surfaces.

The addition of wetting agents to nitric-hydrofluoric etchants has considerable merit. The agents lower the Zircaloy dissolution rate at elevated temperatures.

Nitric-sulfuric-hydrofluoric etchants have been satisfactory for pickling Zircaloy prior to corrosion exposure, provided the surfaces are immediately and thoroughly flushed to remove all traces of the etchant.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Messrs. H. E. Himes and W. R. McVicker, both of Bettis Plant, for their assistance in specimen preparation and general program follow.

Special thanks are due the Corrosion Group, Central Technical Activities, Bettis Plant, for the cooperation in the performance of the corrosion tests.

REFERENCES

1. B. Lustman and F. Kerze, Jr., "The Metallurgy of Zirconium," McGraw-Hill, New York (1955), pp. 612 to 619.
2. S. Kass, "Corrosion Testing of Zircaloy-2 and Zircaloy-3," WAPD-TM-97, October 1957.

TABLE I

CORROSION OF ZIRCALOY-2 AND ZIRCALOY-3 RINSED IN WATER OR 4% SODIUM HYDROXIDE

750°F 1500 psi Steam Tests

Exposure Time, days		Average Weight Gain, mg/dm^2									
		3	14	28	42	56	84	98	114	126	140
Alloy	Rinse										
Zircaloy-2	Water	22	27	34	45	53	65	76	84	93	106
Zircaloy-2	NaOH	17	28	33	48	56	66	75	86	91	107
Zircaloy-3	Water	17	26	30	37	37	45	48	55	56	61
Zircaloy-3	NaOH	17	25	32	38	39	47	49	56	56	61

680°F Water Tests

Exposure Time, days		Average Weight Gain, mg/dm^2					
		28	56	84	112	140	168
Alloy	Rinse						
Zircaloy-2	Water	24	30	33	35	44	59
Zircaloy-2	NaOH	25	28	31	37	43	58
Zircaloy-3	Water	24	26	28	32	35	40
Zircaloy-3	NaOH	25	27	30	34	36	40

TABLE II

7-DAY 750°F STEAM CORROSION OF ZIRCALOY-2 DELAY RINSED AFTER ETCHING ON 0.5 w/o ANTAROX-CONTAINING ETCHANT

Coupon No.	Etchant	Transfer Time, sec	Weight Gain mg/dm^2
1	0.5 w/o Antarox G-100	5	26.5
2	0.5 w/o Antarox G-100	5	27.1
3	0.5 w/o Antarox G-100	5	26.9
4	0.5 w/o Antarox G-100	5	26.9
5	0.5 w/o Antarox G-100	5	27.4
6	0.5 w/o Antarox G-100	5	22.9
Avg.			26.3
7	0.5 w/o Antarox G-100	60	29.2
8	0.5 w/o Antarox G-100	60	31.5
9	0.5 w/o Antarox G-100	60	30.2
10	0.5 w/o Antarox G-100	60	28.8
11	0.5 w/o Antarox G-100	60	33.4
12	0.5 w/o Antarox G-100	60	32.8
Avg.			31.0
13	No Antarox	5	28.3
14	No Antarox	5	30.1
15	No Antarox	5	28.7
16	No Antarox	5	29.6
17	No Antarox	5	28.7
18	No Antarox	5	29.5
Avg.			29.2
19	No Antarox	60	31.9
20	No Antarox	60	29.5
21	No Antarox	60	28.7
22	No Antarox	60	30.0
23	No Antarox	60	31.0
24	No Antarox	60	29.9
Avg.			30.2

TABLE III

750°F STEAM CORROSION OF ZIRCALOY-2 ETCHED IN AKWEONS-674-CONTAINING ETCHANT

			Weight Gain, mg/dm^2			
		Exposure Time, days	3	10	24	38
Sample No.	Etchant	Transfer Time, sec				
1	35% HNO_3	5	12.6	23	35	42
2	5% HF	5	12.6	24	37	41
3	Bal H_2	5	12.1	24	37	50
4	--	--	13.1	25	39	44
Avg.			12.6	24	37	44
5	35% HNO_3	60	19.5	33	71	83
6	5% HF	60	23.2	33	43	51
7	Bal H_2O	60	20.7	34	46	54
8	--	60	20.5	34	45	55
Avg.			20.9	34	51	61
9	35% HNO_3	5	18.4	29	31	34
10	5% HF	5	18.0	28	31	33
11	0.01% Akweons 674	5	15.7	28	30	34
12	Bal H_2O	5	16.1	29	31	34
Avg.			17.1	29	31	34
13	35% HNO_3	60	29.6	44	53	60
14	5% HF	60	31.0	45	54	61
15	0.01% Akweons 674	60	30.3	42	53	60
16	Bal H_2O	60	35.4	47	56	62
Avg.			31.6	45	54	61
17	35% HNO_3	5	19.4	32	34	36
18	5% HF	5	16.2	28	29	33
19	0.02% Akweons 674	5	17.0	30	32	35
20	Bal H_2O	5	19.3	30	31	34
Avg.			18.0	30	32	35
21	35% HNO_3	60	34.2	48	50	56
22	5% HF	60	39.0	51	54	56
23	0.02% Akweons 674	60	34.5	47	50	53
24	Bal H_2O	60	35.1	51	52	55
Avg.			35.7	49	51	55
25	35% HNO_3	5	17.0	30	32	38
26	5% HF	5	16.6	29	31	36
27	0.04% Akweons 674	5	18.0	31	34	39
28	Bal H_2O	5	16.6	29	33	36
Avg.			17.1	30	33	37

TABLE III (Cont)

			Weight Gain, mg/dm^2			
		Exposure Time, days	3	10	24	38
Sample No.	Etchant	Transfer Time, sec				
29	35% HNO_3	60	35.6	49	50	55
30	5% HF	60	35.5	50	52	60
31	0.04% Akweons 674	60	37.0	50	52	63
32	--	60	37.7	53	55	64
Avg.			36.5	51	52	61
33	35% HNO_3	5	18.8	28	34	40
34	5% HF	5	18.8	30	34	41
35	0.10% Akweons 674	5	20.5	32	35	50
36	Bal H_2O	5	16.2	29	33	42
Avg.			18.1	30	34	43
37	35% HNO_3	60	26.0	41	42	49
38	0.10% Akweons	60	37.8	53	55	61
39	5% HF	60	37.7	51	53	60
40	Bal H_2O	60	31.3	44	46	50
Avg.			33.2	47	49	55

TABLE IV

750°F STEAM CORROSION OF ZIRCALOY-2 ETCHED IN AKWEONS-700-CONTAINING ETCHANT

			Weight Gain, mg/dm^2			
		Exposure Time, days	3	10	24	38
Sample No.	Etchant	Transfer Time, sec				
1	35% HNO_3	5	12.6	23	35	42
2	5% HF	5	12.6	24	37	41
3	Bal H_2O	5	12.1	24	37	50
4	--	5	13.1	25	39	44
Avg.			12.6	24	37	44
5	35% HNO_3	60	19.5	33	71	83
6	5% HF	60	23.2	33	43	51
7	Bal H_2O	60	20.7	34	46	54
8	--	60	20.5	34	45	55
Avg.			20.9	34	51	61
9	35% HNO_3	5	15.2	25	29	34
10	5% HF	5	13.9	22	25	32
11	0.01% Akweons 700	5	14.3	25	29	33
12	Bal H_2O	5	15.2	29	30	37
Avg.			14.7	25	28	34
13	35% HNO_3	60	17.1	30	31	44
14	5% HF	60	22.0	34	51	57
15	0.01% Akweons 700	60	24.2	36	39	57
16	Bal H_2O	60	23.8	35	39	48
Avg.			21.8	34	40	51
17	35% HNO_3	5	16.1	28	29	34
18	5% HF	5	16.0	27	29	30
19	0.02% Akweons 700	5	16.6	30	30	38
20	Bal H_2O	5	17.4	29	29	34
Avg.			16.5	29	29	34
21	35% HNO_3	60	25.2	36	39	48
22	5% HF	60	26.1	37	40	51
23	0.02% Akweons 700	60	25.1	37	39	47
24	Bal H_2O	60	27.3	39	47	47
Avg.			25.9	37	41	48
25	35% HNO_3	5	16.6	28	30	36
26	5% HF	5	17.9	30	31	35
27	0.04% Akweons 700	5	18.3	32	32	36
28	Bal H_2O	5	18.3	30	31	31
Avg.			17.8	30	31	35

TABLE IV (Cont)

			Weight Gain, mg/dm^2			
		Exposure Time, days	3	10	24	38
Sample No.	Etchant	Transfer Time, sec				
29	35% HNO_3	60	33.8	47	49	56
30	5% HF	60	29.1	42	43	53
31	0.04% Akweons 700	60	27.5	39	41	44
32	Bal H_2O	60	26.0	40	41	47
Avg.			29.1	42	44	50
33	35% HNO_3	5	18.3	30	30	32
34	5% HF	5	18.8	31	30	37
35	0.10% Akweons 700	5	20.2	34	--	--
36	Bal H_2O	5	18.2	30	31	33
Avg.			18.8	31	30	34
37	35% HNO_3	60	35.3	50	50	57
38	5% HF	60	36.6	50	51	58
39	0.10% Akweons 700	60	32.2	45	46	50
40	Bal H_2O	60	35.6	49	49	57
Avg.			34.9	49	49	56

TABLE V

750°F STEAM CORROSION BEHAVIOR OF ZIRCALOY-2 ETCHED IN AKWEONS 790 SOLUTION

		Weight Gain, mg/dm^2	
	Exposure Time, days	7	14
Sample No.	Etchant		
1	35% HNO_3	21	30
2	5% HF	18	30
3	Bal H_2O	18	29
4	--	22	33
Avg.		20	31
5	35% HNO_3	20	30
6	5% HF	20	31
7	0.1% Akweons 790	22	32
8	Bal H_2O	19	31
Avg.		20	31

TABLE VI

750°F STEAM CORROSION OF ZIRCALOY-2 ETCHED IN PRODUCT-BCO-CONTAINING ETCHANTS

			Weight Gain, mg/dm^2			
		Exposure Time, days	3	10	24	38
Sample No.	Etchant	Transfer Time, sec				
1	35% HNO_3	5	12.6	23	35	42
2	5% HF	5	12.6	24	37	41
3	Bal H_2O	5	12.1	24	37	50
4	--	5	13.1	25	39	44
Avg.			12.6	24	37	44
5	35% HNO_3	60	19.5	33	71	83
6	5% HF	60	23.2	33	43	51
7	Bal H_2O	60	20.7	34	46	54
8	--	60	20.5	34	45	55
Avg.			20.9	34	51	61
9	35% HNO_3	5	13.6	25	37	44
10	5% HF	5	16.4	28	38	42
11	0.01% BCO	5	13.6	26	38	42
12	Bal H_2O	5	14.5	26	38	41
Avg.			14.5	26	38	42
13	35% HNO_3	60	23.6	36	46	57
14	5% HF	60	24.0	36	48	59
15	0.01% BCO	60	23.1	35	46	58
16	Bal H_2O	60	20.9	33	44	53
Avg.			22.9	35	46	57
17	35% HNO_3	5	11.7	24	26	32
18	5% HF	5	10.4	25	27	30
19	0.02% BCO	5	11.7	24	34	38
20	Bal H_2O	5	10.8	23	34	38
Avg.			11.2	24	30	35
21	35% HNO_3	60	20.4	33	45	41
22	5% HF	60	23.5	37	50	50
23	0.02% BCO	60	24.0	37	49	59
24	Bal H_2O	60	23.4	37	50	56
Avg.			22.8	36	49	52
25	35% HNO_3	5	12.6	24	35	39
26	5% HF	5	10.8	23	34	36
27	0.04% BCO	5	11.7	24	33	37
28	Bal H_2O	5	12.3	24	37	40
Avg.			11.9	24	35	38

TABLE VI (Cont)

			Weight Gain, mg/dm^2			
		Exposure Time, days	3	10	24	38
Sample No.	Etchant	Transfer Time, sec				
29	35% HNO_3	60	25.6	40	48	55
30	0.04% BCO	60	27.9	41	51	60
31	5% HF	60	31.9	41	52	57
32	Bal H_2O	60	26.5	39	49	56
Avg.			28.0	40	50	57
33	35% HNO_3	5	12.1	25	34	37
34	5% HF	5	12.1	24	34	35
35	0.10% BCO	5	12.1	26	34	38
36	Bal H_2O	5	12.5	24	36	38
Avg.			12.2	25	35	37
37	35% HNO_3	60	22.9	36	44	57
38	5% HF	60	23.8	37	47	52
39	0.10% BCO	60	21.5	33	43	53
40	Bal H_2O	60	21.1	37	43	52
Avg.			22.4	36	44	54

TABLE VII

CORROSION DATA OF COUPONS ETCHED IN THE HYDROCHLORIC-HYDROFLUORIC ETCHANT

	Corrosion Tested			
	680°F Water		750°F Steam	
	(Weight Gain, mg/dm^2)			
	14 Days	28 Days	3 Days	14 Days
Etched in HCl-HF for 30 sec, rinsed	22	30	29	47
	18	26	28	47
	18	26	30	50
Etched in HCl-HF for 60 sec, rinsed	17	23	26	45
	18	25	30	48
	17	22	28	46
Etched in HCl-HF for 120 sec, rinsed	17	24	27	47
	18	25	27	46
	14	23	28	45
Etched in HCl-HF for 180 sec, rinsed	15	23	26	43
	16	24	26	41
	17	25	27	44
Etched in HCl-HF for 30 sec, rinsed, Re-etched in "reference" etchant, thoroughly rinsed	12	20	16	35
	10	18	17	35
	12	19	17	38
Etched in HCl-HF for 60 sec, rinsed, Re-etched in "reference" etchant, thoroughly rinsed	11	22	18	40
	13	20	19	39
	13	22	19	38
Etched in HCl-HF for 120 sec, rinsed, Re-etched in "reference" etchant, thoroughly rinsed	11	22	19	37
	12	20	18	36
	12	21	15	34
Etched in HCl-HF for 180 sec, rinsed, Re-etched in "reference" etchant, thoroughly rinsed	11	21	15	36
	11	19	17	34
	10	20	13	32
Etched in HCl-HF for 30 sec, not rinsed	0	0	27	48
	9	10	33	53
	5	10	34	53
Etched in HCl-HF for 60 sec, not rinsed	8	14	46	65
	4	6	44	58
	12	12	40	56
Etched in HCl-HF for 120 sec, not rinsed	8	8	39	57
	14	11	40	60
	11	4	35	55

TABLE VII (Cont)

	Corrosion Tested			
	680°F Water		750°F Steam	
	(Weight Gain, mg/dm^2)			
	14 Days	28 Days	3 Days	14 Days
Etched in HCl-HF for 180 sec, not rinsed	22 17 15	6 -2 -4	44 48 41	57 65 57
Etched in HCl-HF for 30 sec, not rinsed, dried, re-etched in "reference" etchant, thoroughly rinsed	9 11 9	30 19 18	14 16 13	32 35 31
Etched in HCl-HF for 60 sec, not rinsed, dried, re-etched in "reference" etchant, thoroughly rinsed	9 13 12	18 20 20	14 17 16	32 35 34
Etched in HCl-HF for 120 sec, not rinsed, dried, re-etched in "reference" etchant, thoroughly rinsed	11 16 10	19 22 18	13 15 15	32 33 33
Etched in HCl-HF for 180 sec, not rinsed, dried, re-etched in "reference" etchant, thoroughly rinsed	10 12 11	19 21 18	14 12 13	32 29 32
Etched in Nitric-Hydrofluoric, thoroughly rinsed	9 9 10	18 18 19	13 13 12	30 33 33

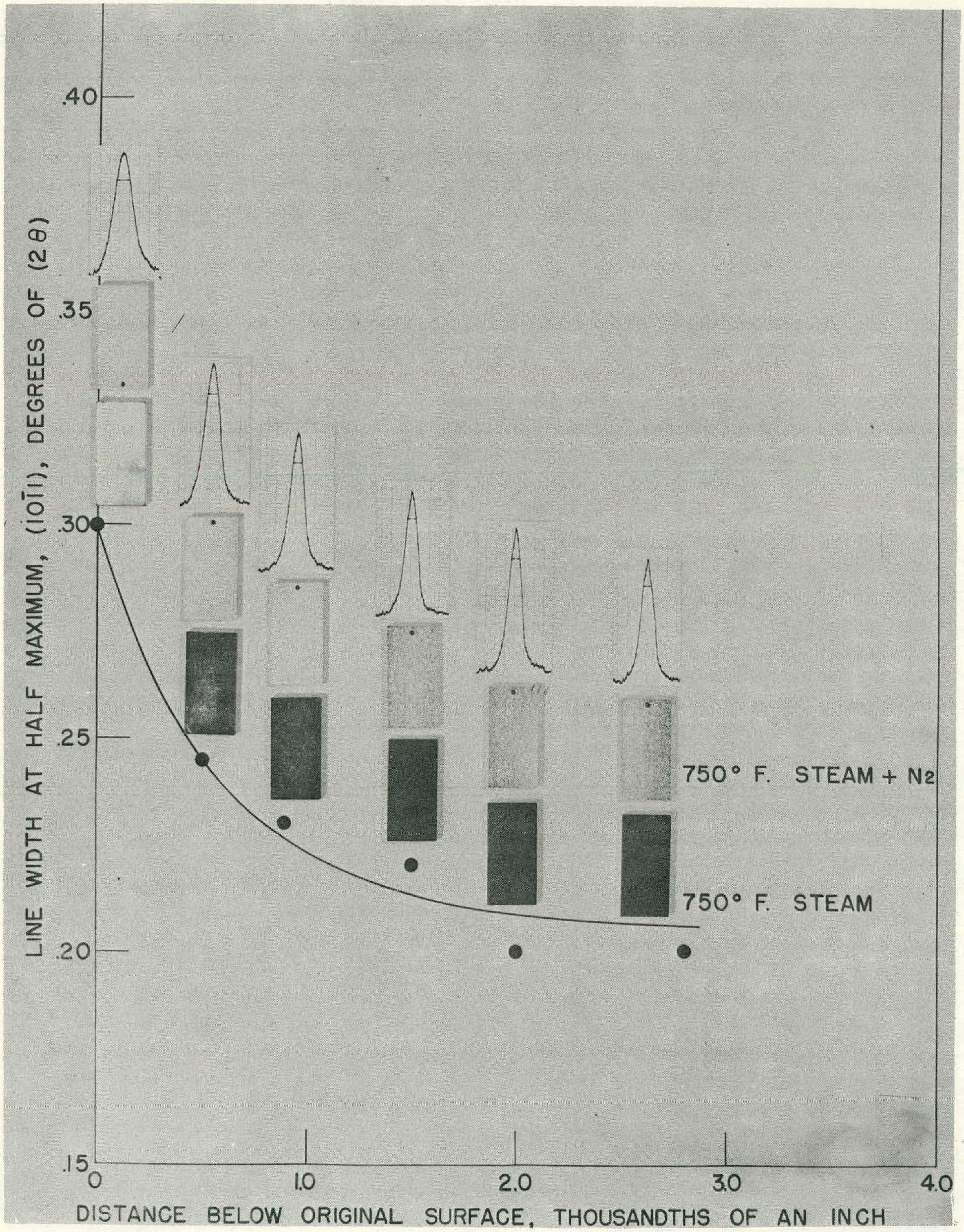
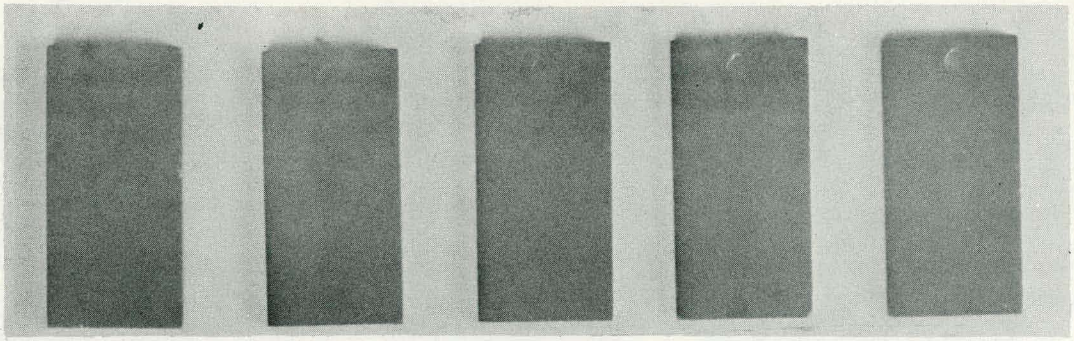
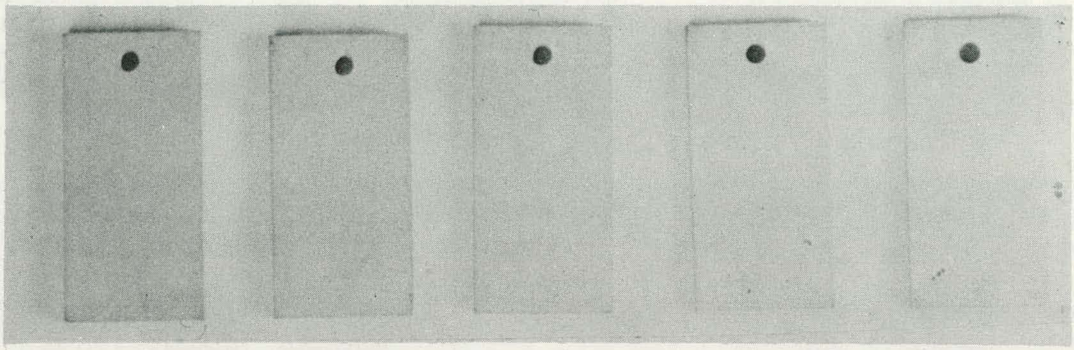


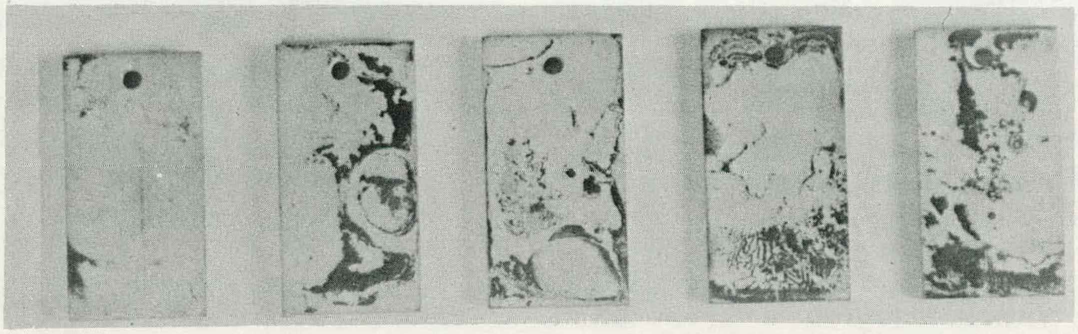
Fig. 1 Effect of Surface Condition on the Corrosion of Zirconium
(Neg 20814-6)



Specimens rinsed immediately after etching



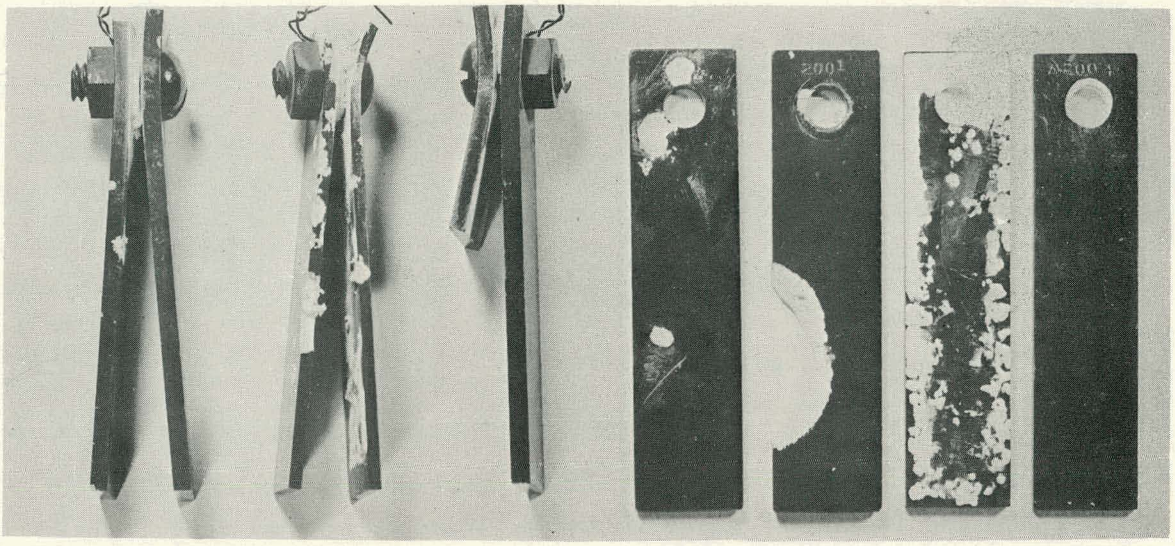
Specimens not rinsed after etching



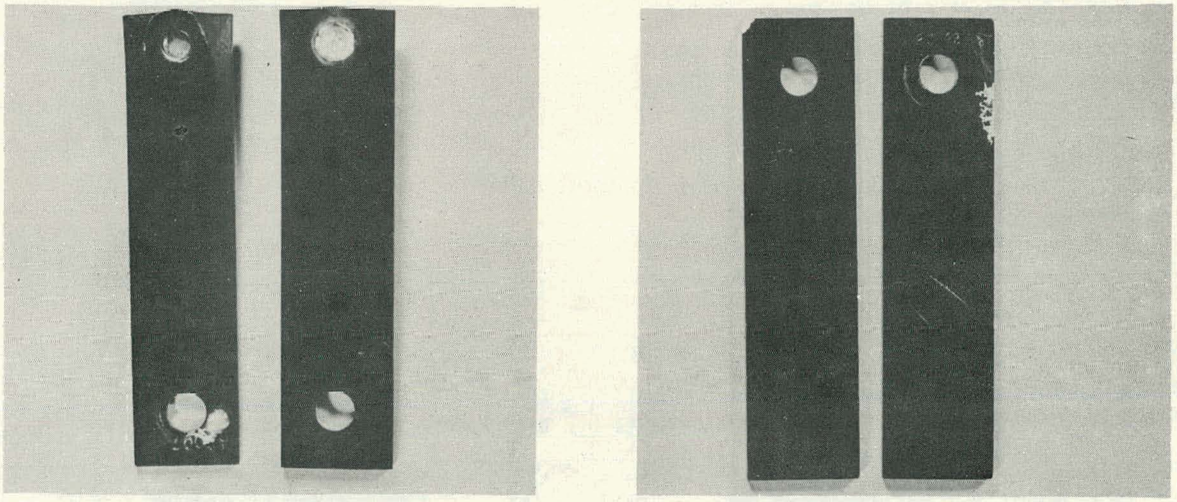
Specimens not rinsed after etching but
scrubbed before corrosion testing

Fig. 2 Effect of Rinsing and Washing on the Corrosion of Zircaloy-2 Specimens Tested in 680°F Water for 58 Days

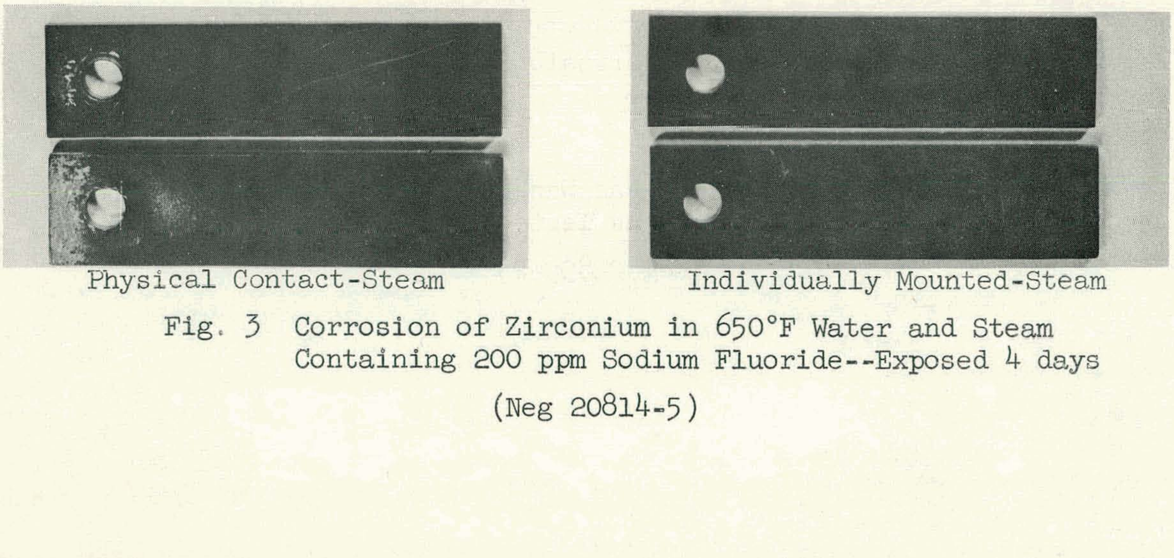
(Neg 22899-2)



Physical Contact-Water



Electrical Contact-Water Individually Mounted-Water



Physical Contact-Steam Individually Mounted-Steam

Fig. 3 Corrosion of Zirconium in 650°F Water and Steam Containing 200 ppm Sodium Fluoride--Exposed 4 days

(Neg 20814-5)

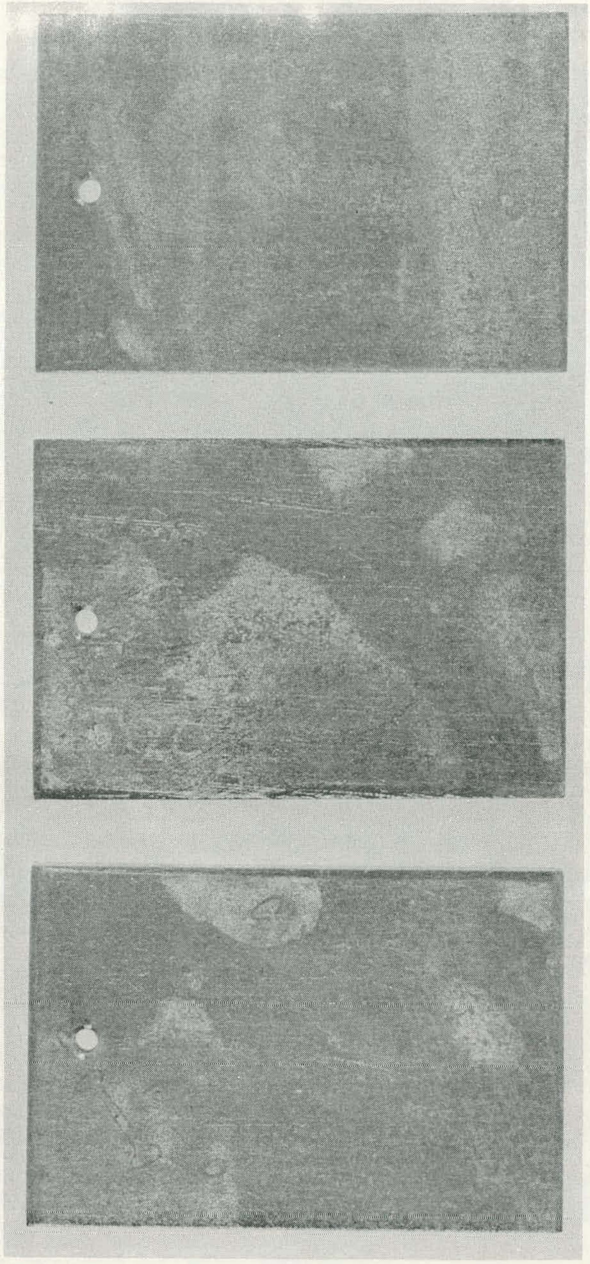


Fig. 4 Typical Surfaces after Corrosion Testing--Showing Insufficient Rinsing after Etching 2X

(Neg 22899-3)

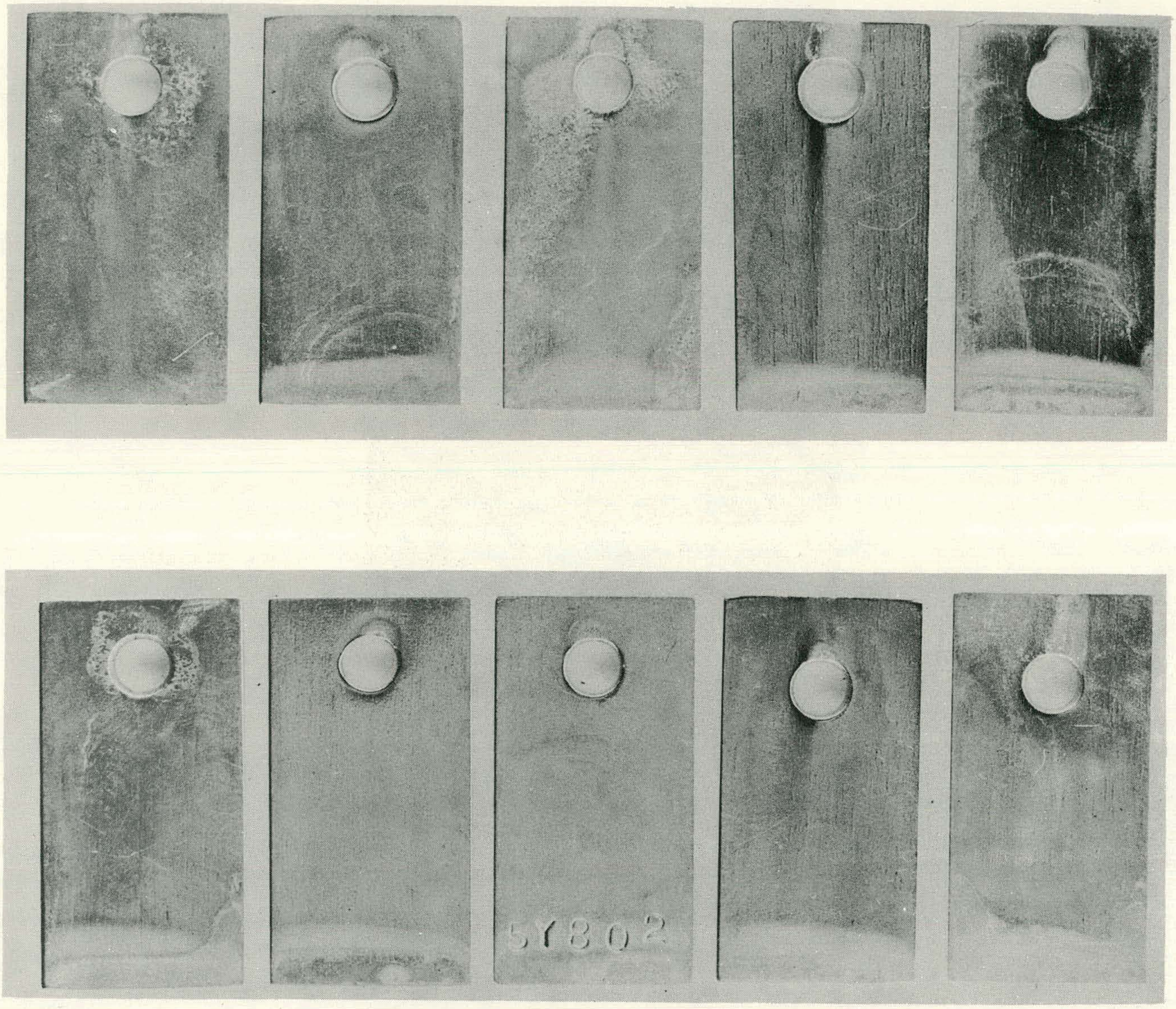


Fig. 5 Typical Surfaces of Specimens Rinsed in 25 v/o Nitric Acid at 110°F after Etching and Drying

(Neg 21798-6)

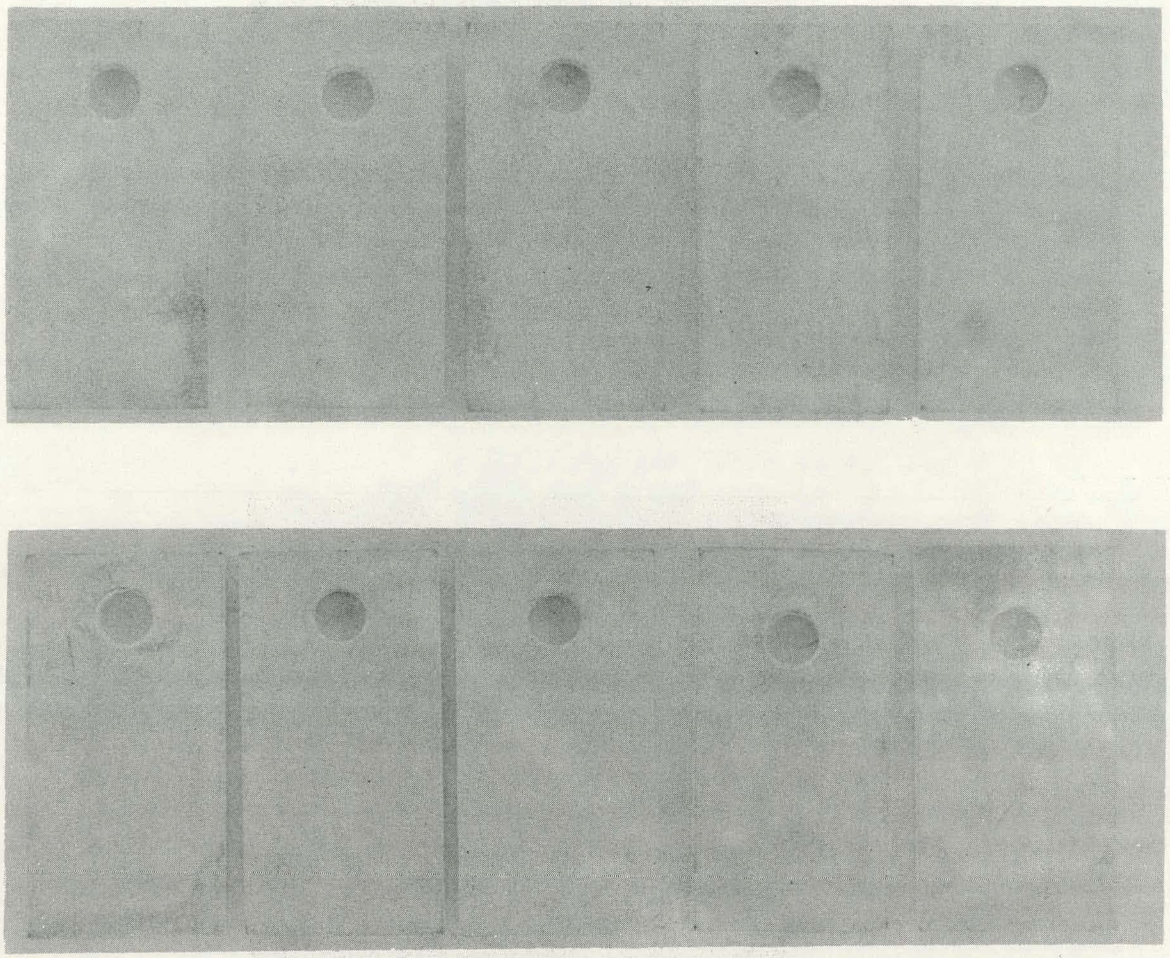
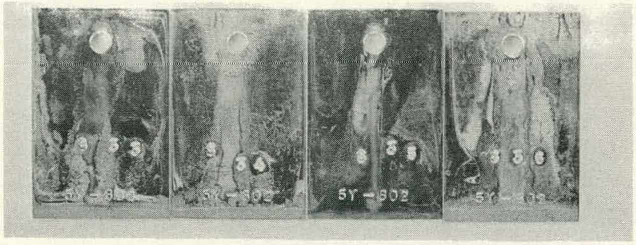
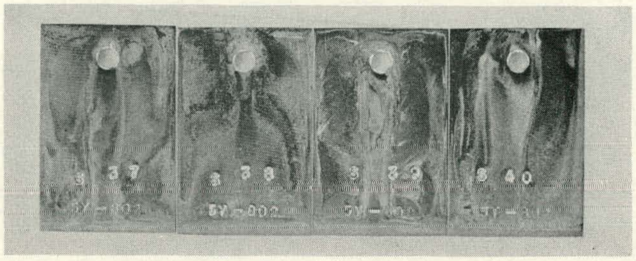


Fig. 6 Typical Surfaces of Specimens Which Were Rinsed in 25 v/o Nitric Acid at 110°F after Etching and Drying--Corrosion Tested for 3 Days in 750°F Steam

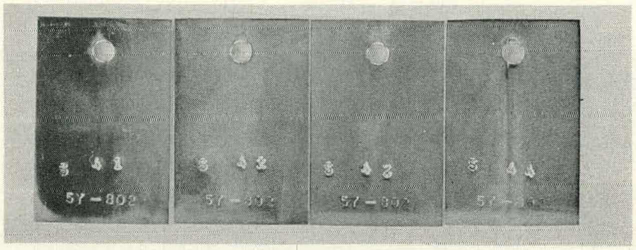
(Neg 21798-1)



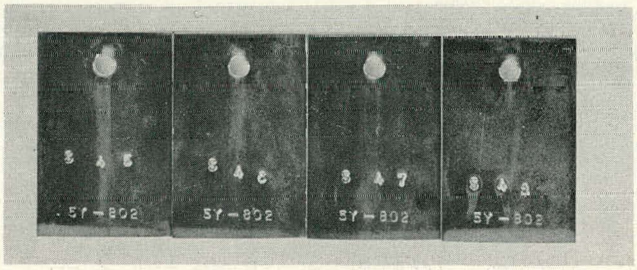
10 min at 80°F



30 min at 80°F



10 min at 140°F



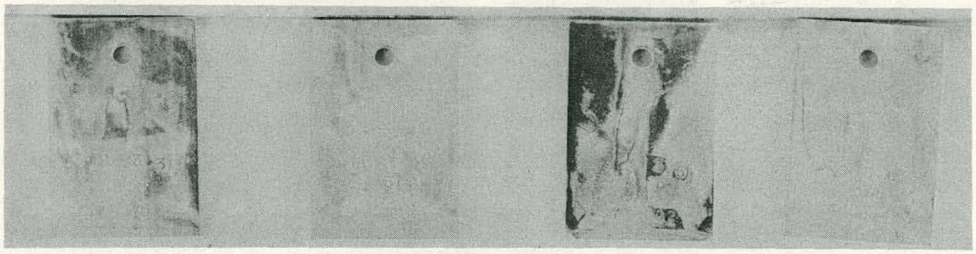
30 min at 140°F

3 in.

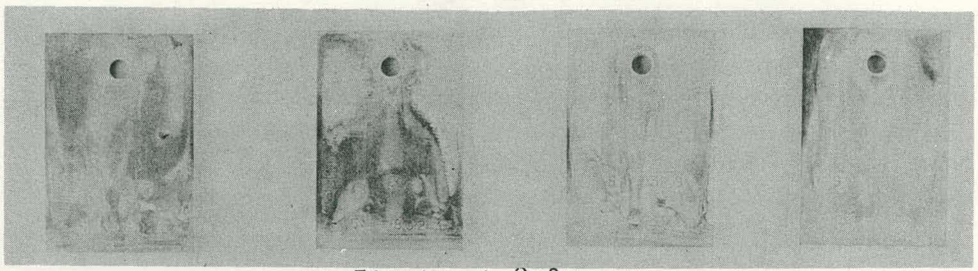
Fig. 7 Typical Surfaces of Specimens Which Were Rinsed in 25 v/o H_2SO_4 after Etching and Drying

(Neg 22657-4)

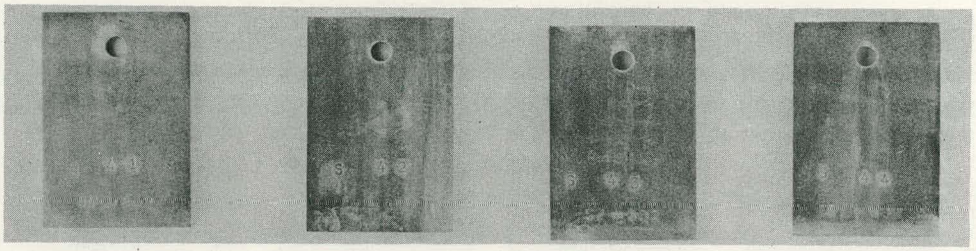
3 in.



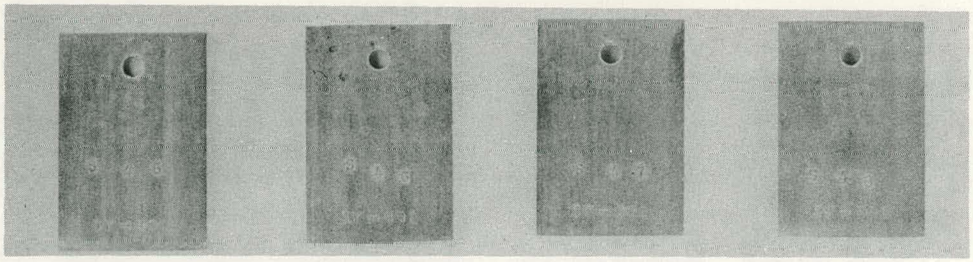
10 min at 80°F



30 min at 80°F



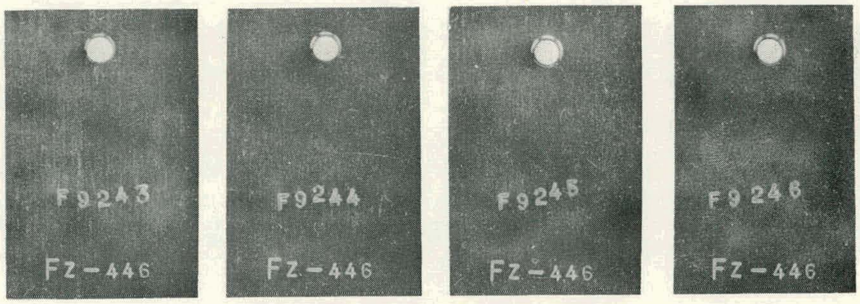
10 min at 140°F



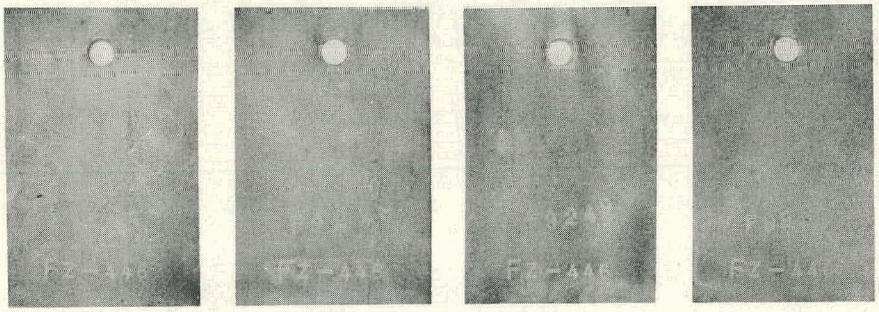
30 min at 140°F

Fig. 8 Typical Surfaces of Specimens Which Were Rinsed in 25 v/o H_2SO_4 after Etching and Drying, Subsequently Corrosion Tested for 3 days in 750°F steam

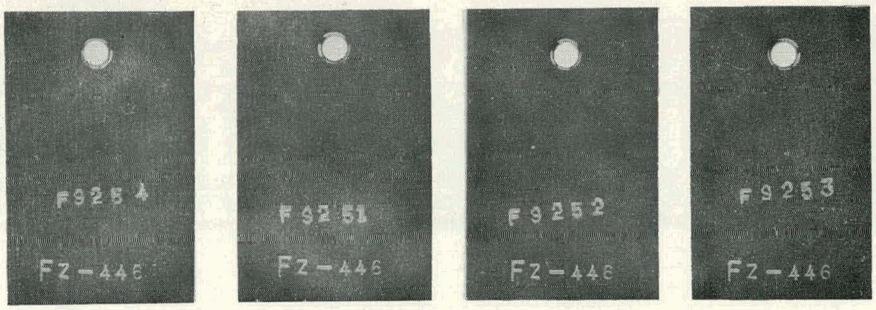
(Neg 22657-10)



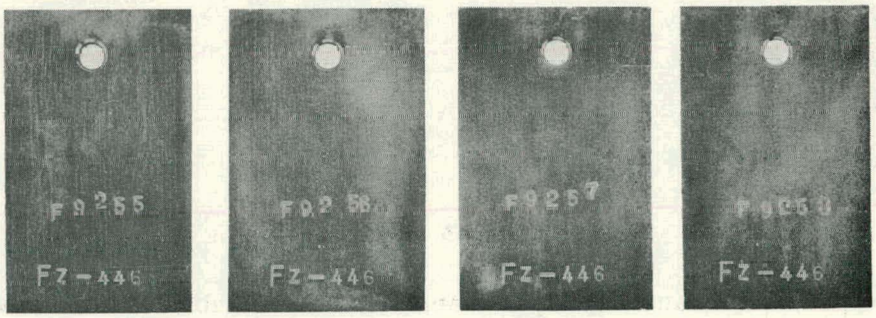
Rinsed in Water at 60°F



Rinsed in 25% H_2SO_4 at 60°F



Rinsed in Water at 100°F



Rinsed in 25% H_2SO_4 at 100°F

Fig. 9 Typical Surface Appearances of Coupons Tested for 14 Days in 750°F Steam after Rinsing in 25% Sulfuric Acid or Water

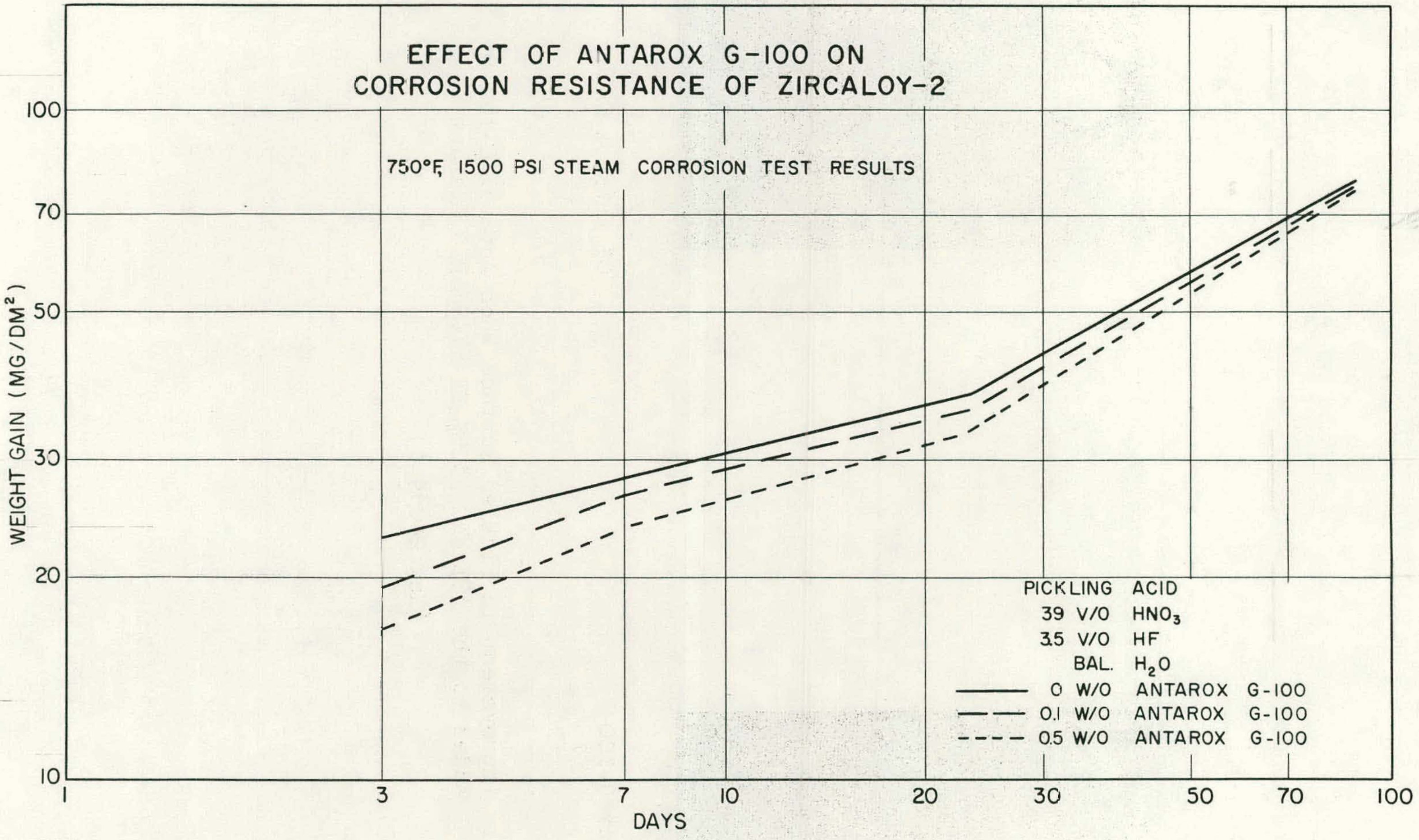
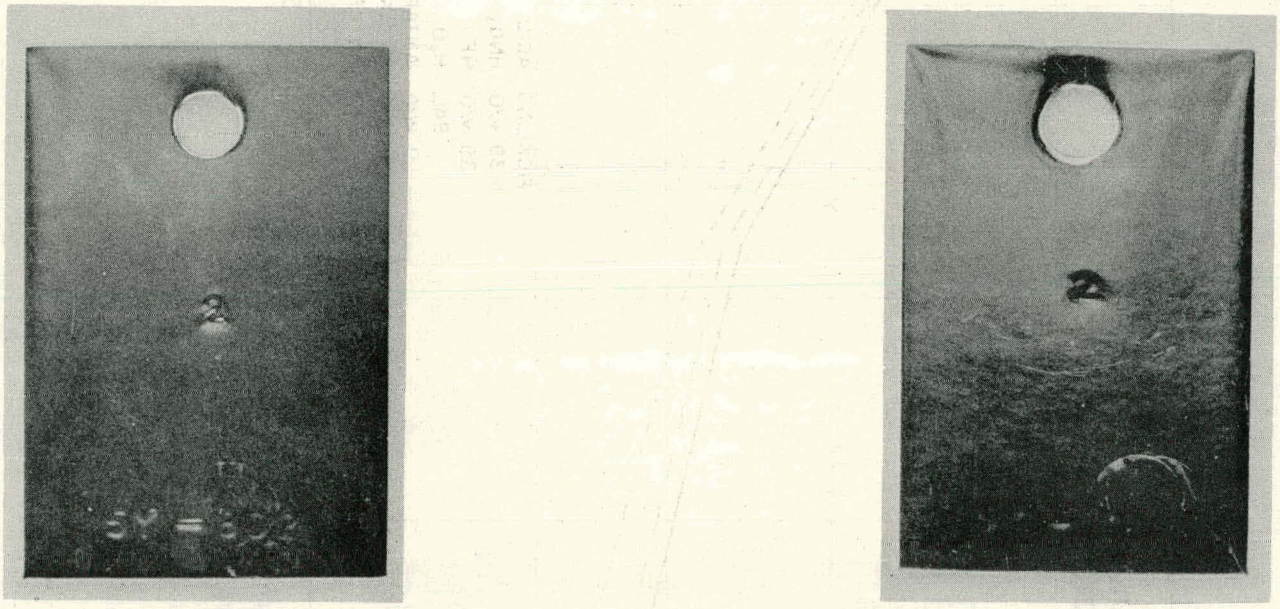


Figure 10

(Neg 24039-5)



0.5 w/o Antarox G-100

0% Antarox G-100

Fig. 11 Improvement in Pickled Surface When Antarox G-100 Is Added to the 39% HNO_3-3.5% HF-57.5% H_2O Etchant
(Neg 24039-3)

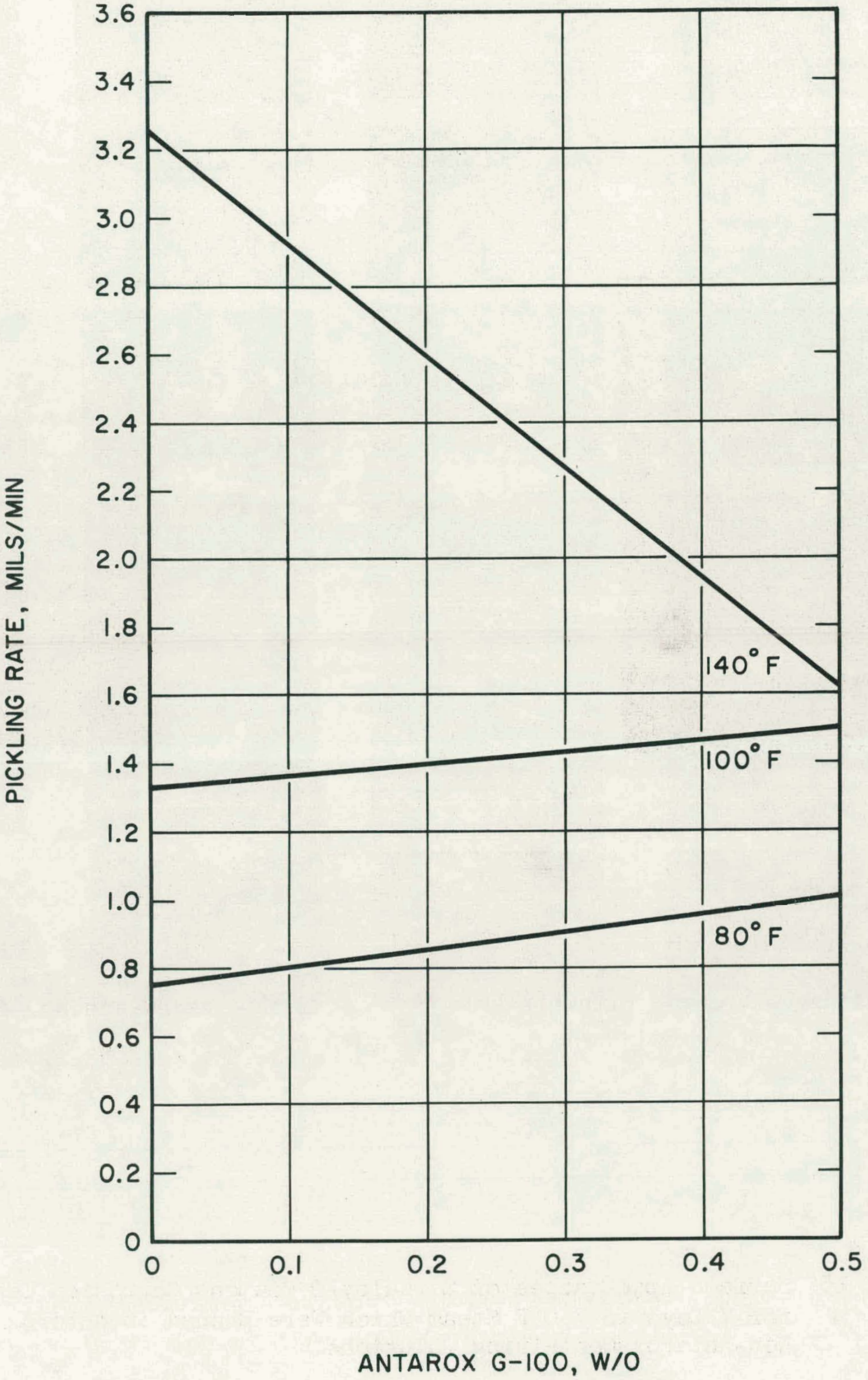


Fig. 12 Pickling Rate of Zircaloy-2 in $35\%\ HNO_3-5\%\ HF$ Plus Antarox G-100

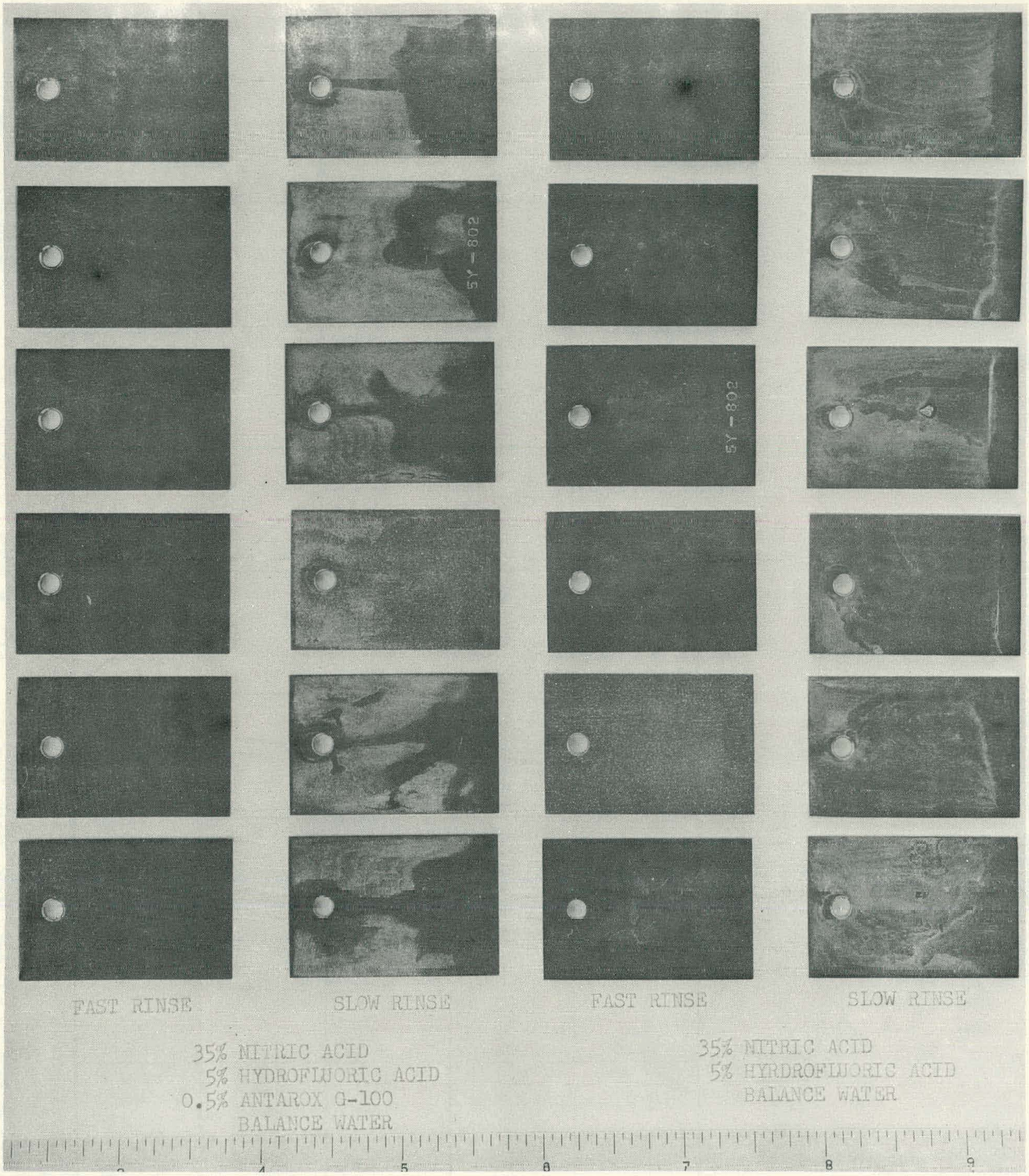


Fig. 13 Surface Appearances of Zircaloy-2 Coupons Corrosion Tested for 7 Days in 750°F Steam Which Were Etched in Antarox and Non-Antarox-Containing Solutions

(Neg 25195)

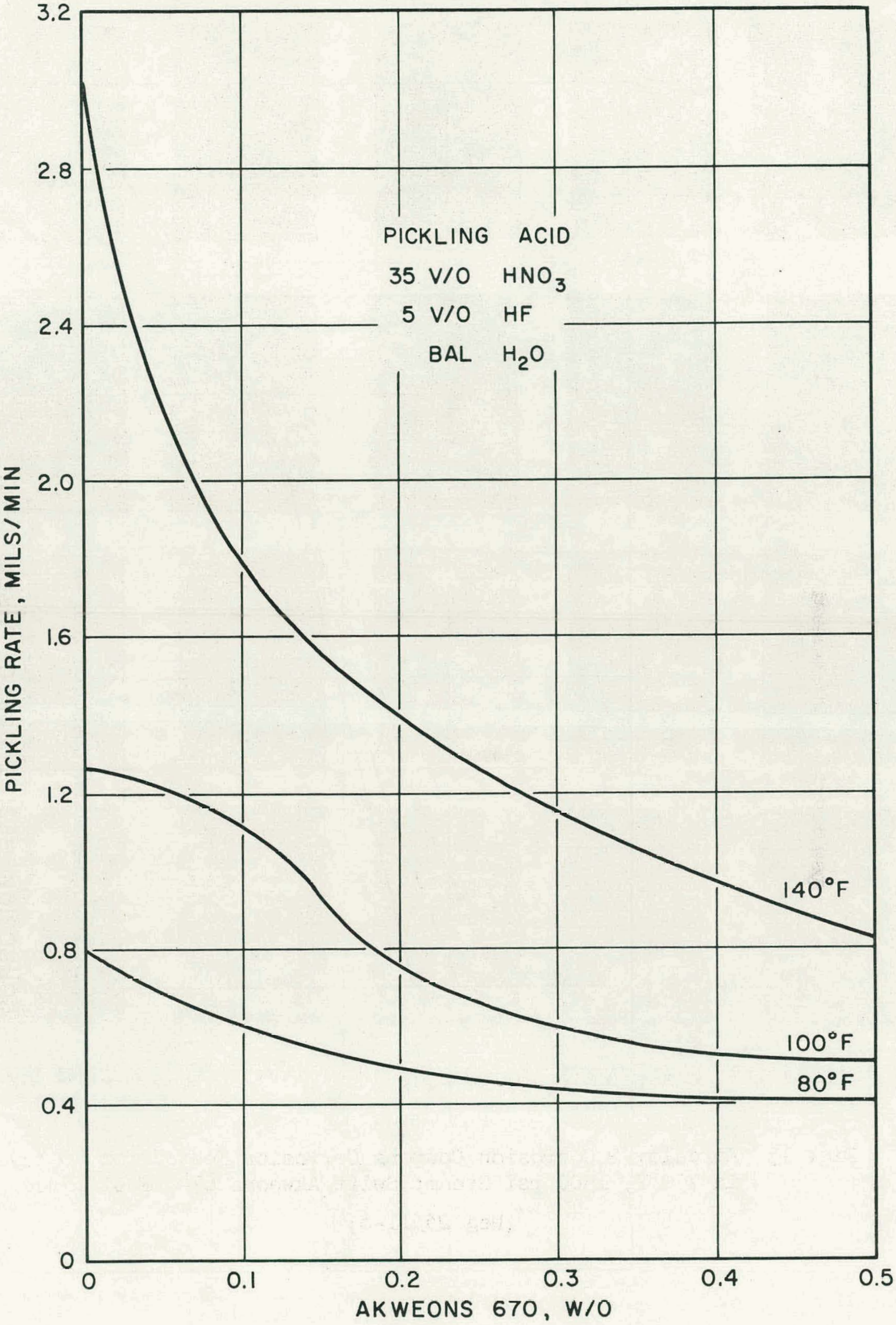


Fig. 14 Pickling of Zircaloy-2, Effect of Akweons 670
(Neg 25390-3)

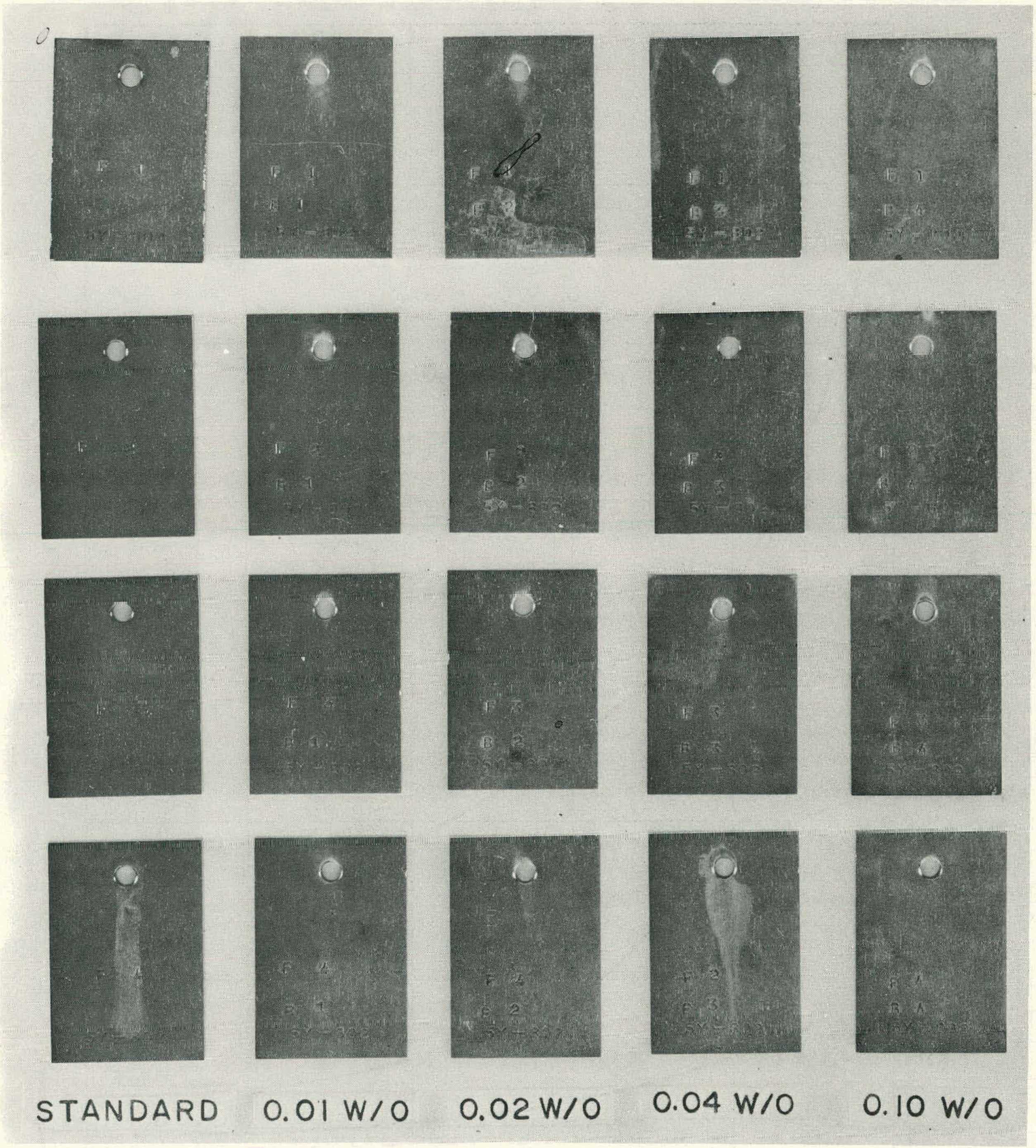


Fig. 15 Zircaloy-2 Corrosion Coupons Corrosion Tested for 10 Days in 750°F, 1500 psi Steam; Swift Akweons 674, Fast Rinse

(Neg 23311-6)

Fig. 16 Zircaloy-2 Corrosion Coupons Corrosion Tested for 10 Days in 750°F, 1500 psi Steam; Swift Akweons 674, Slow Rinse

(Neg 23311-2)

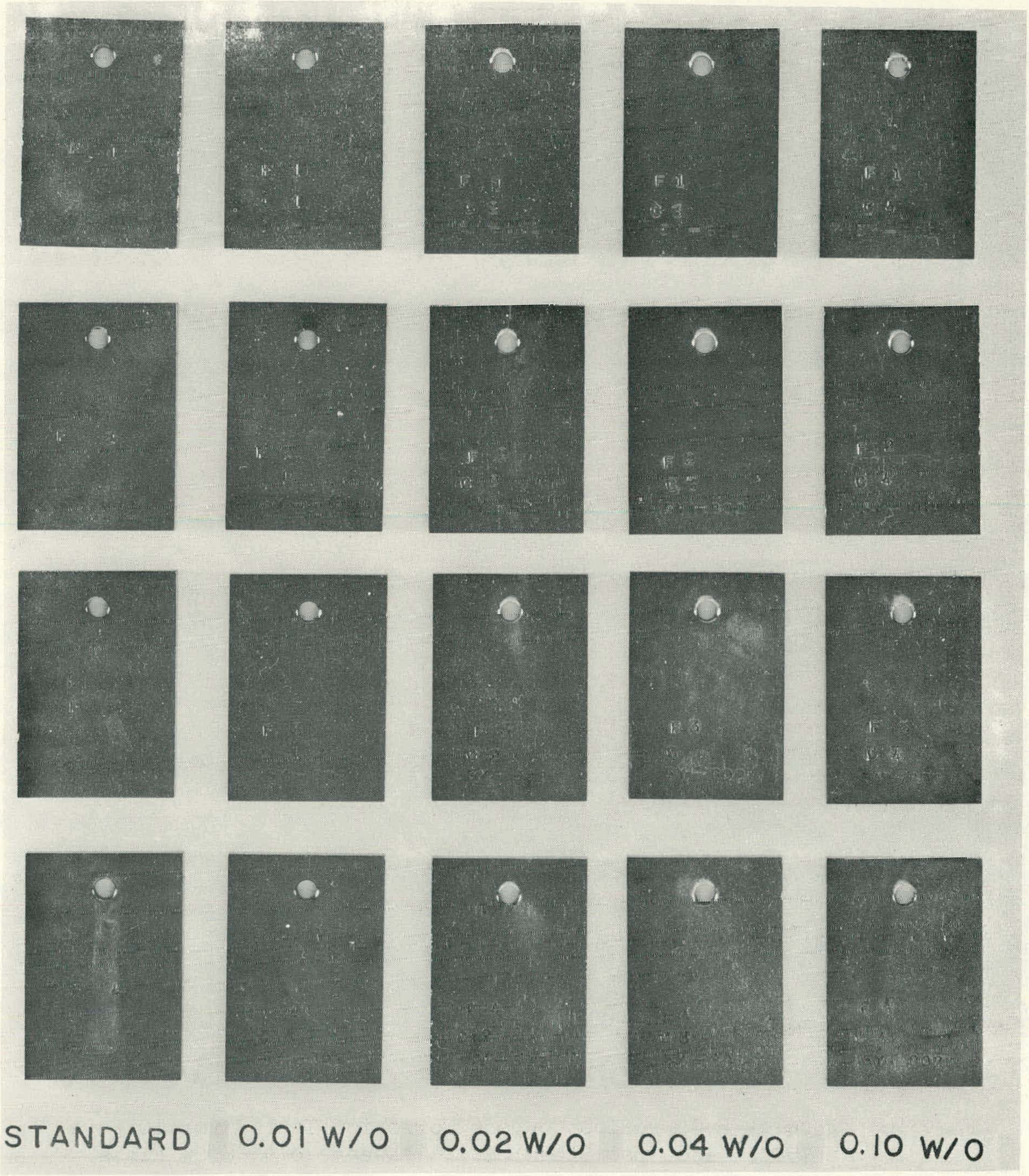


Fig. 17 Zircaloy-2 Corrosion Coupons Corrosion Tested for 10 Days in 750°F, 1500 psi Steam; Swift Akweons 700, Fast Rinse

(Neg 23311-3)

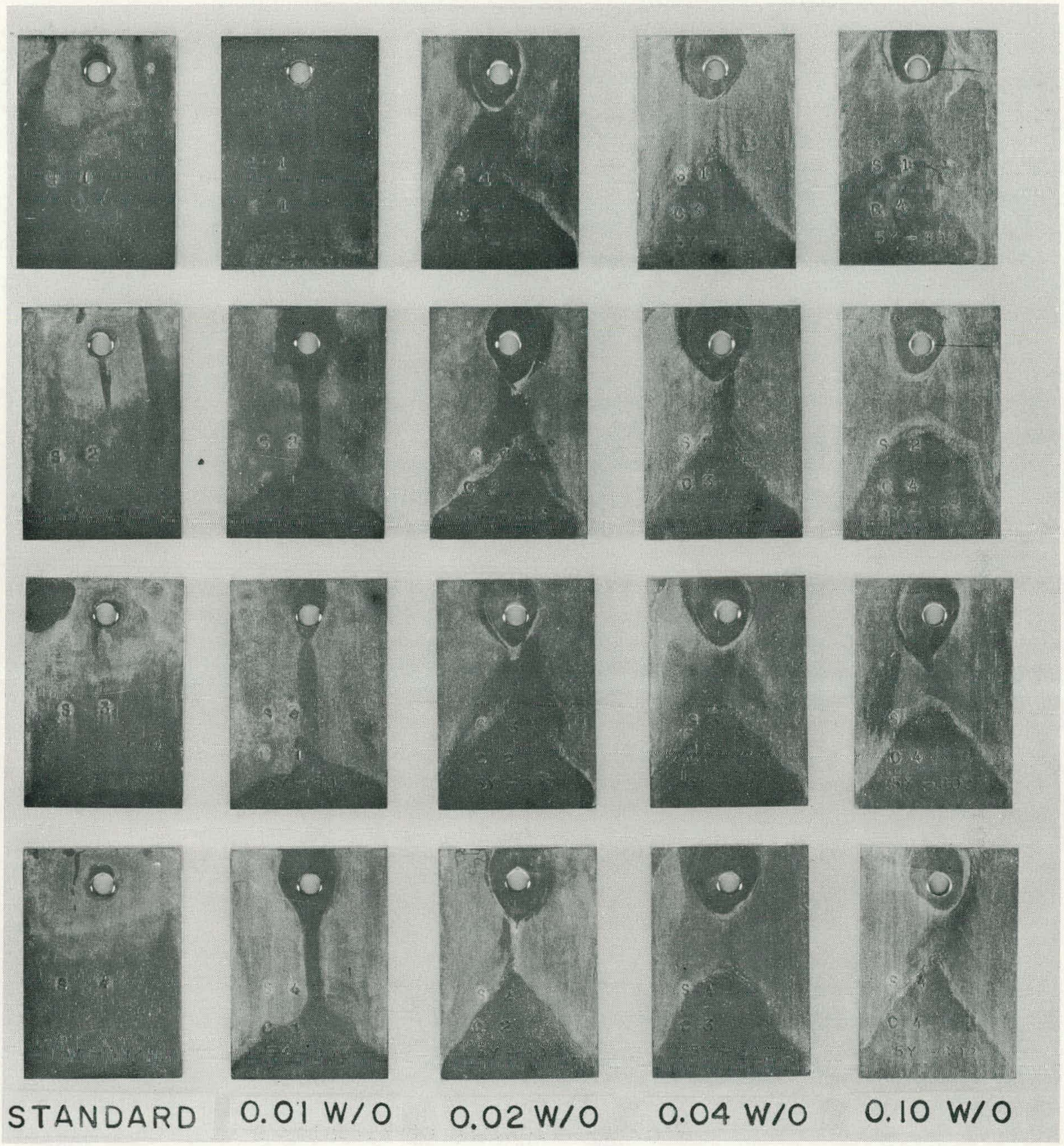


Fig. 18 Zircaloy-2 Corrosion Coupons Corrosion Tested for 10 Days in 750°F, 1500 psi Steam; Swift Akweons 700, Slow Rinse

(Neg 23311-5)

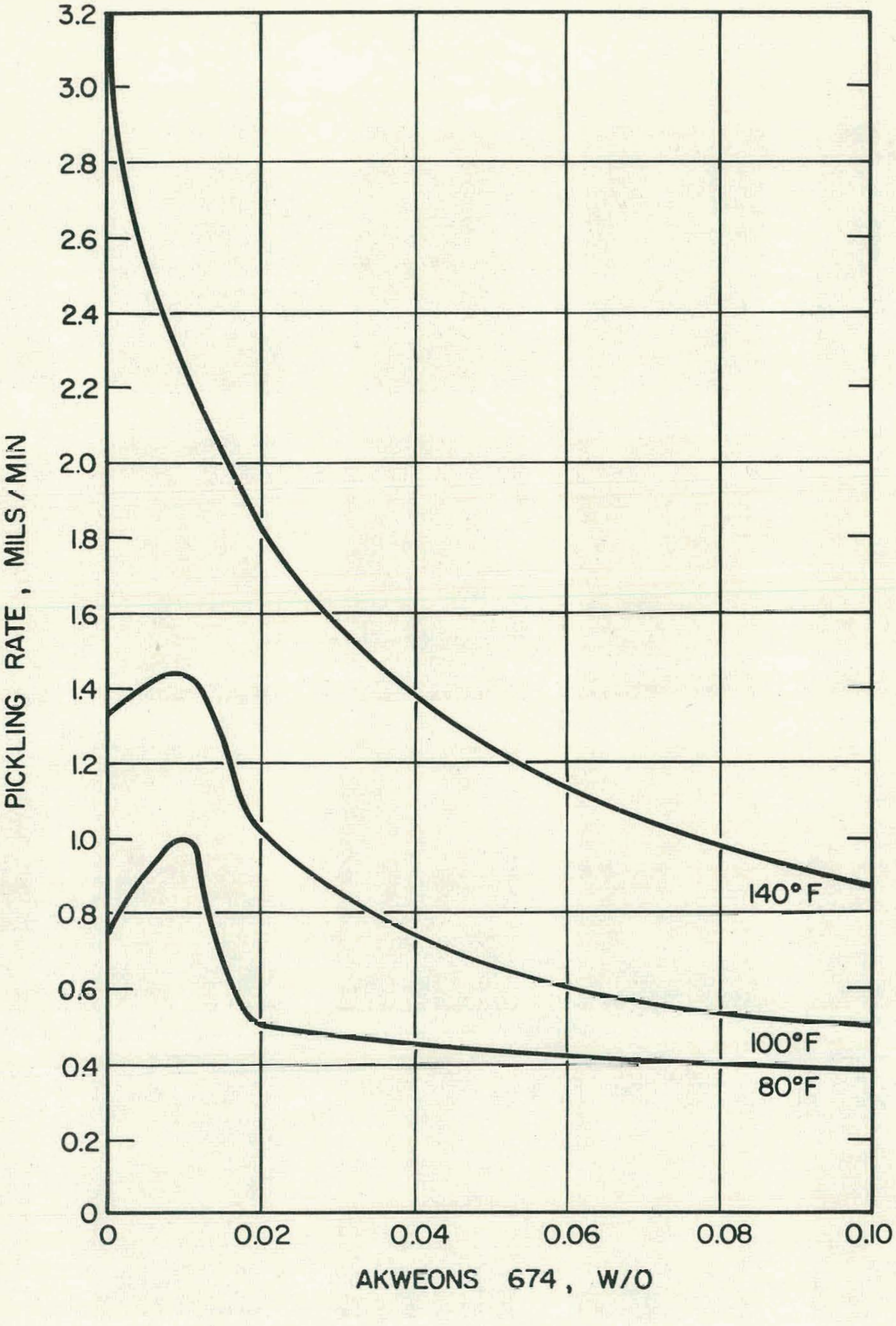


Fig. 19 Pickling of Zircaloy-2 in $35\% \ HNO_3$-5% HF Plus Akweons 674

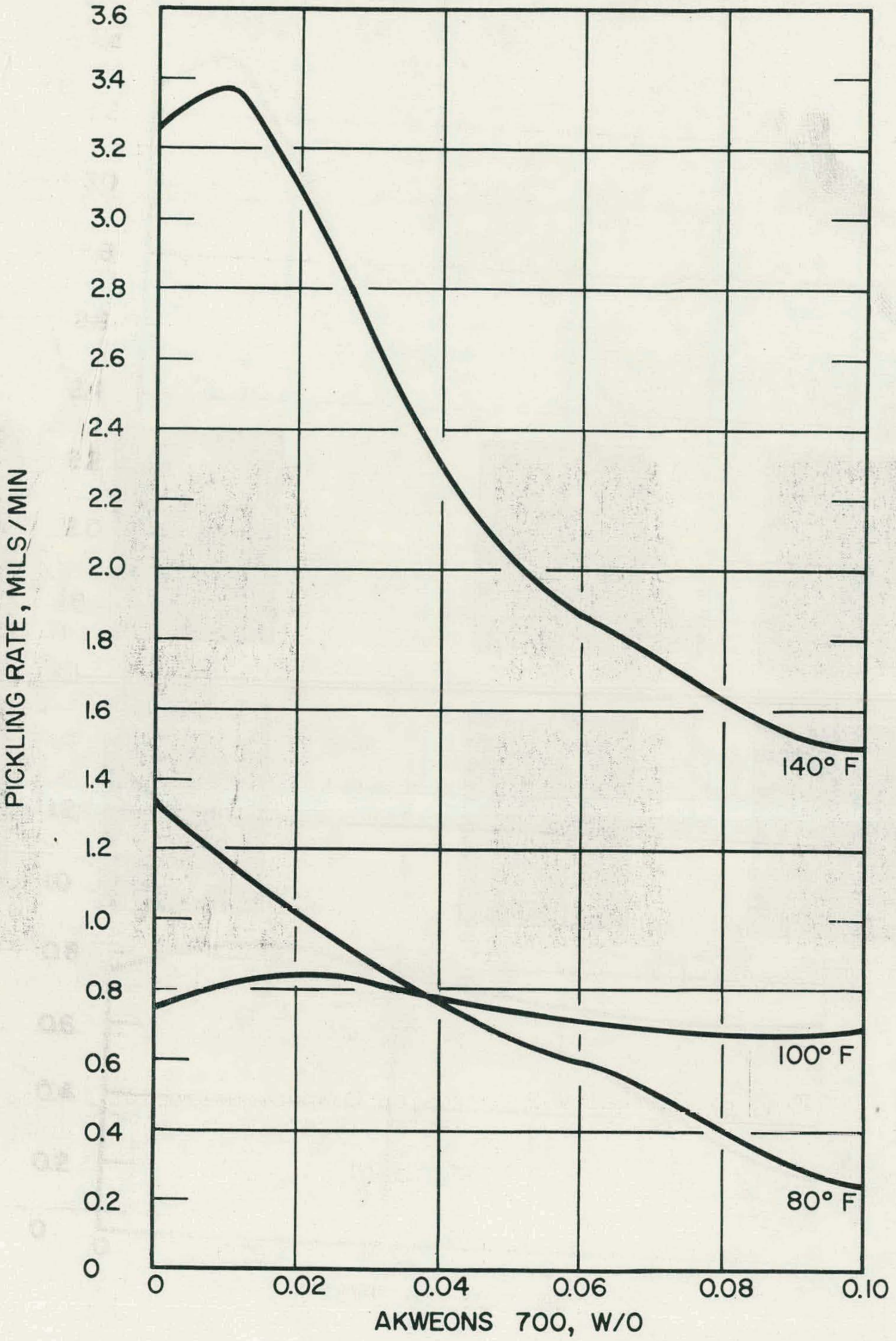
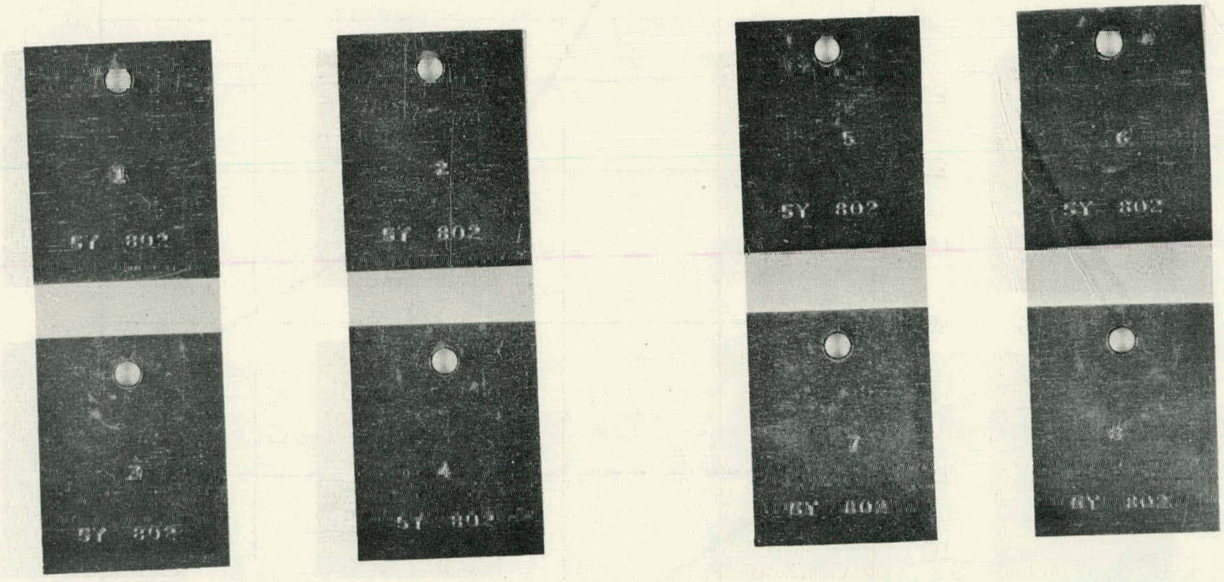


Fig. 20 Pickling of Zircaloy-2 in
35% HNO_3-5% HF Plus Akweons 700



Standard

0.1 w/o Swift Akweons 790

Fig. 21 Zircaloy-2 Corrosion Coupons Corrosion Tested for 7 Days in 750°F, 1500 psi Steam; Fast Rinse

(Neg 23431)

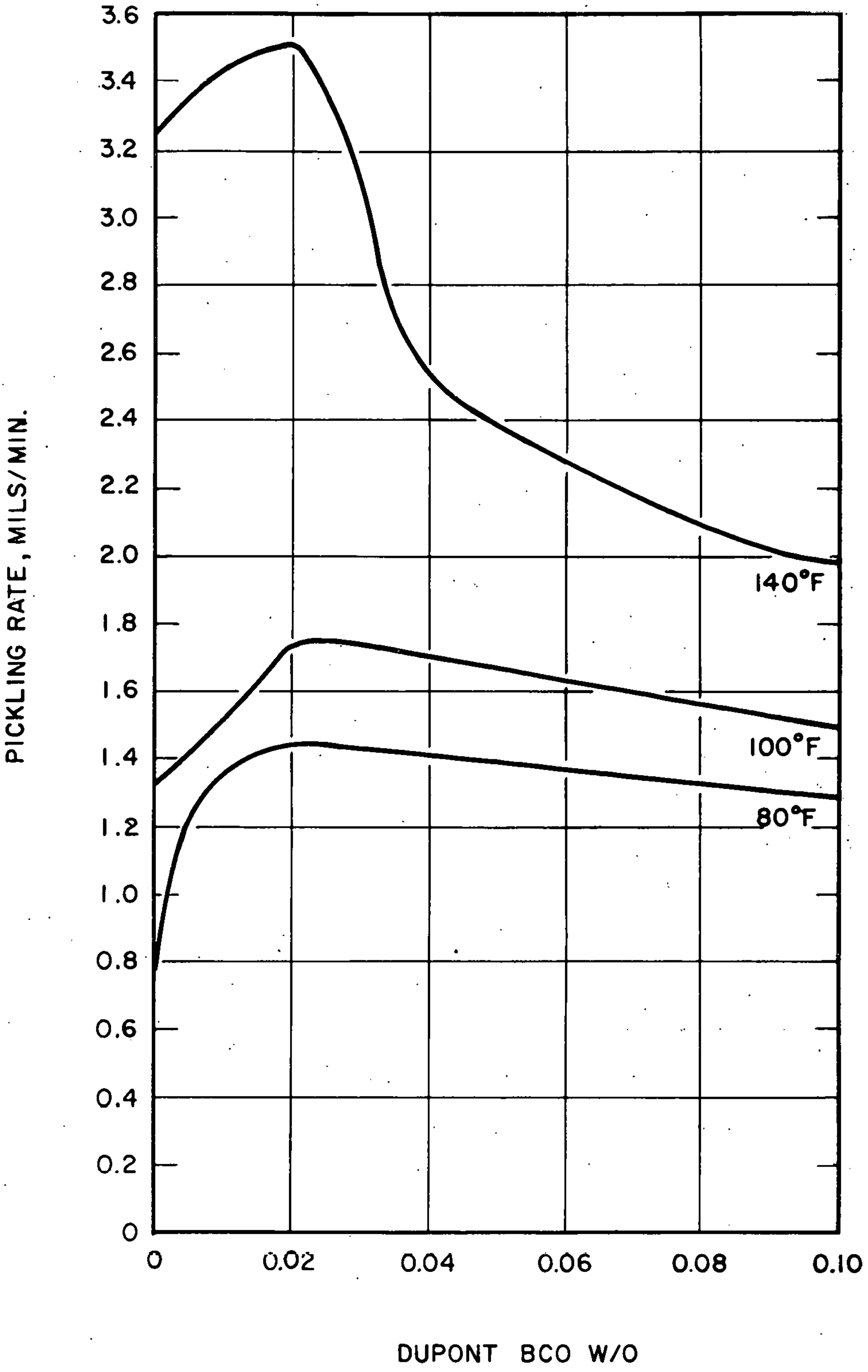


Fig. 22 Pickling of Zircaloy-2 in
35% HNO_3-5% HF Plus DuPont BCO

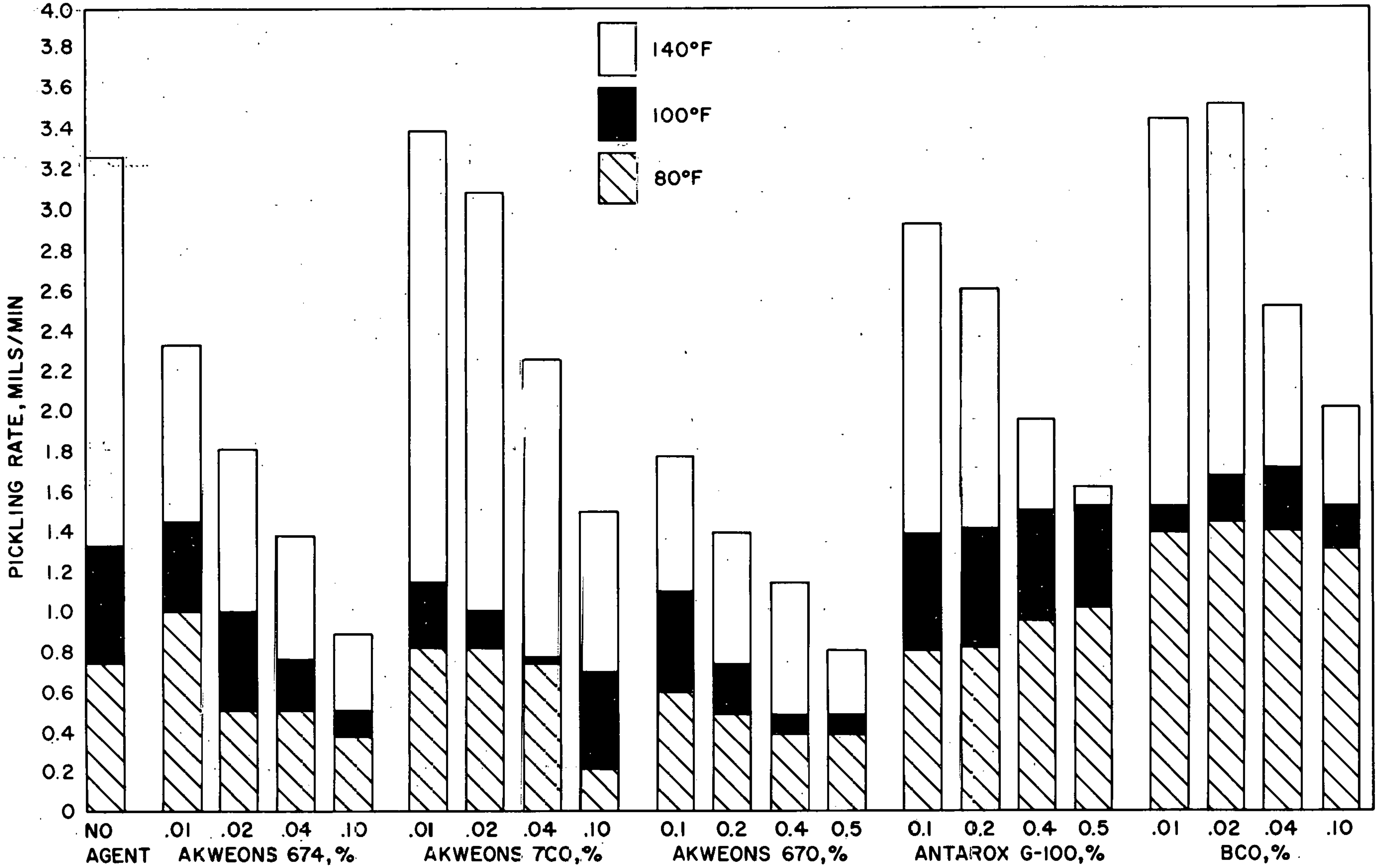


Fig. 23 Pickling Rates of Zircaloy-2 in 35% HNO_3-5% HF Solutions with Agents Added

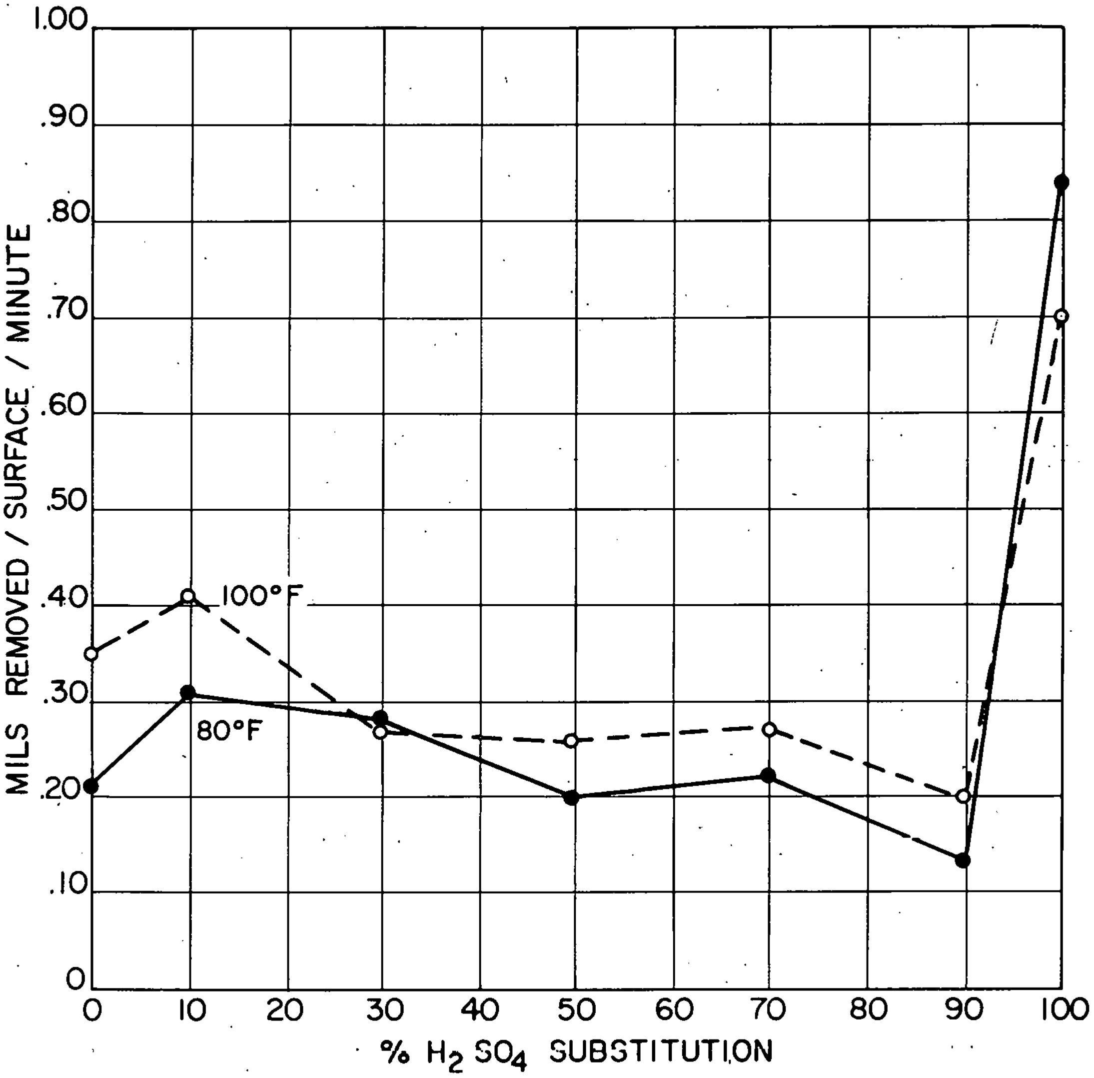


Fig. 24 Pickling Rates of Sulfuric-Acid-Substituted Etchant
(Neg 23700-11)

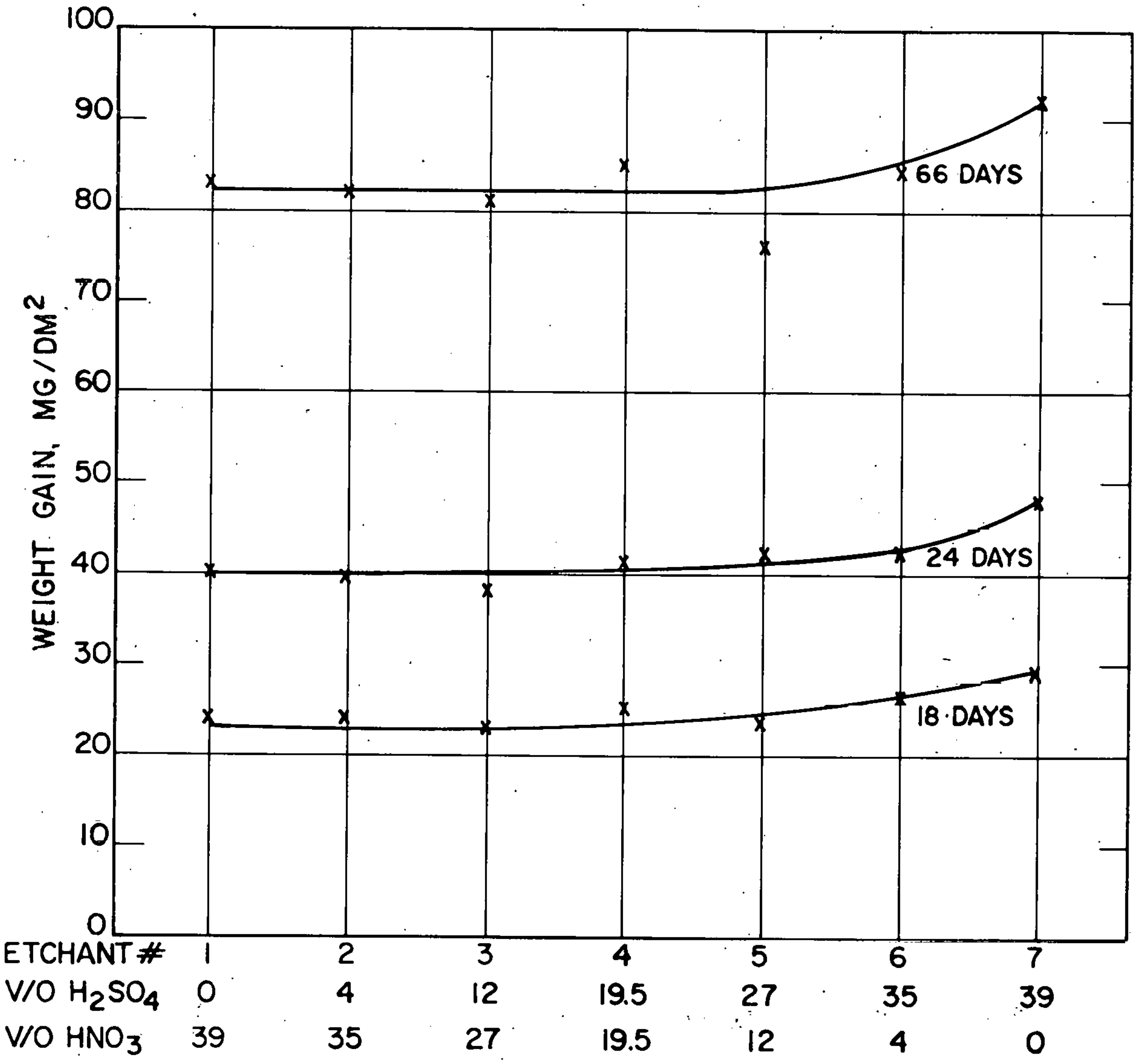


Fig. 25 750°F Steam Corrosion of Zircaloy-2 Etched at 80°F in Various Sulfuric Acid Solutions

(Neg 23700-13)

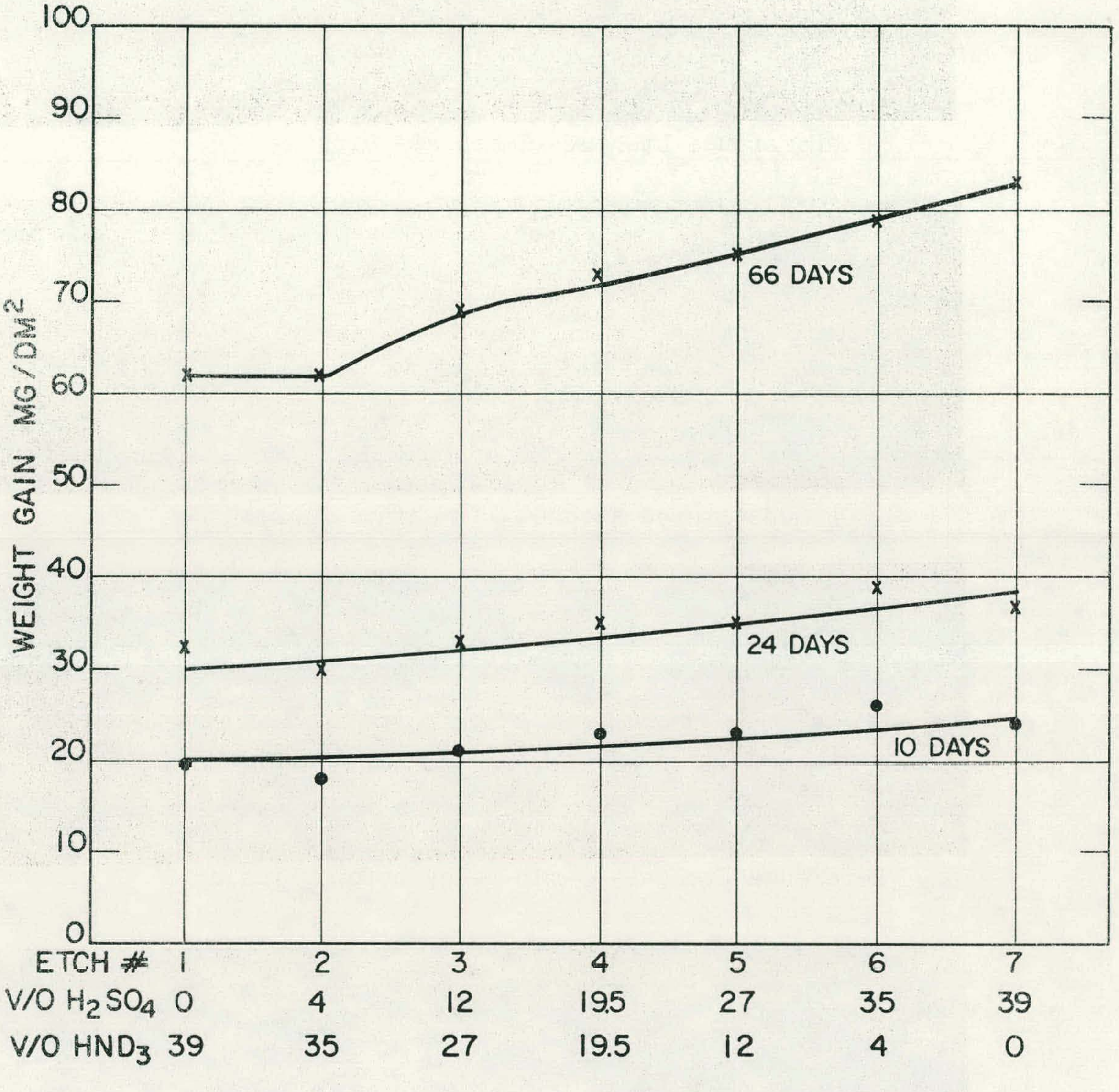
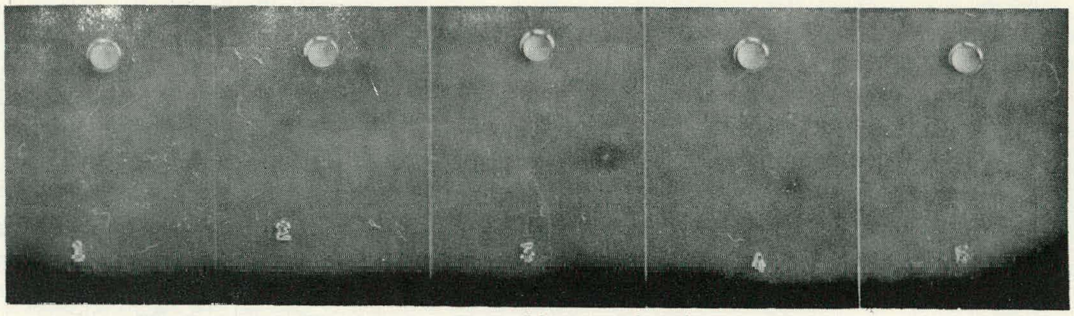
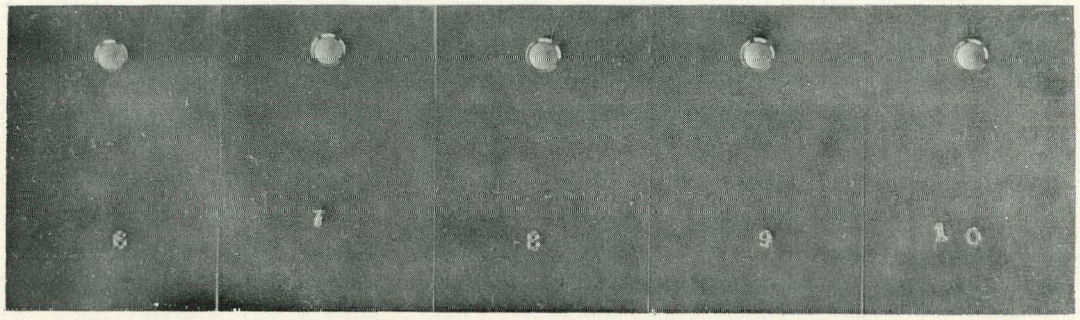


Fig. 26 750°F Steam Corrosion of Zircaloy-2 Etched at 100°F in Various Sulfuric Acid Solutions

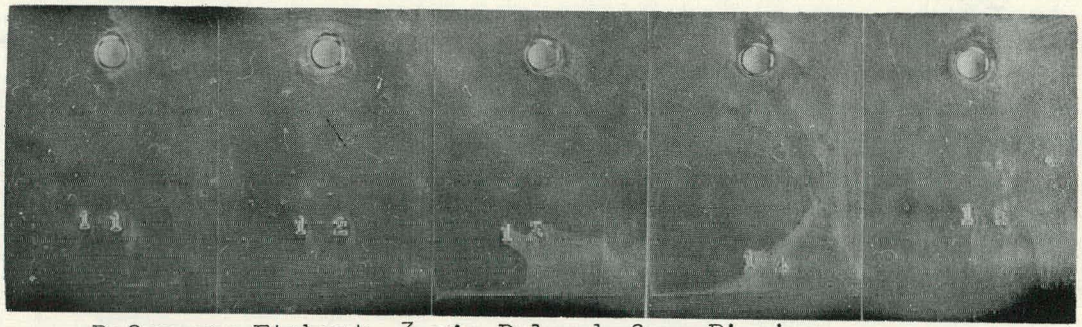
(Neg 23700-12)



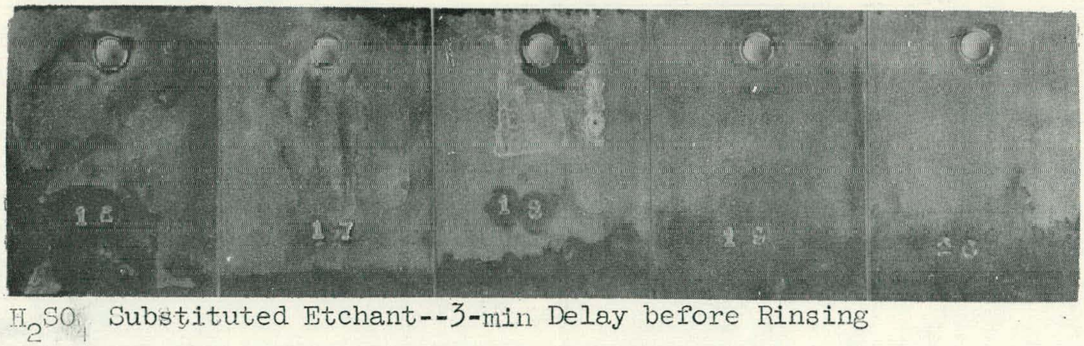
Reference Etchant--Immediate Rinsing



H_2SO_4 Substituted Etchant--Immediate Rinsing



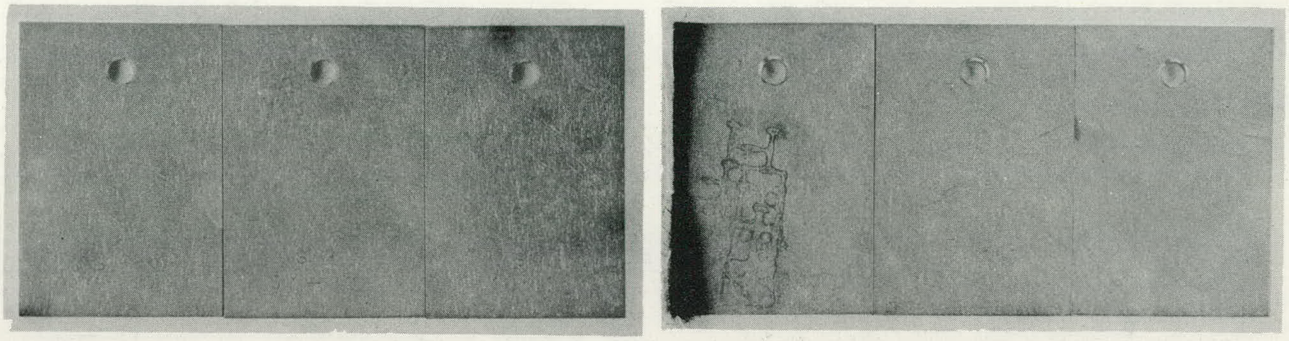
Reference Etchant--3-min Delay before Rinsing



H_2SO_4 Substituted Etchant--3-min Delay before Rinsing

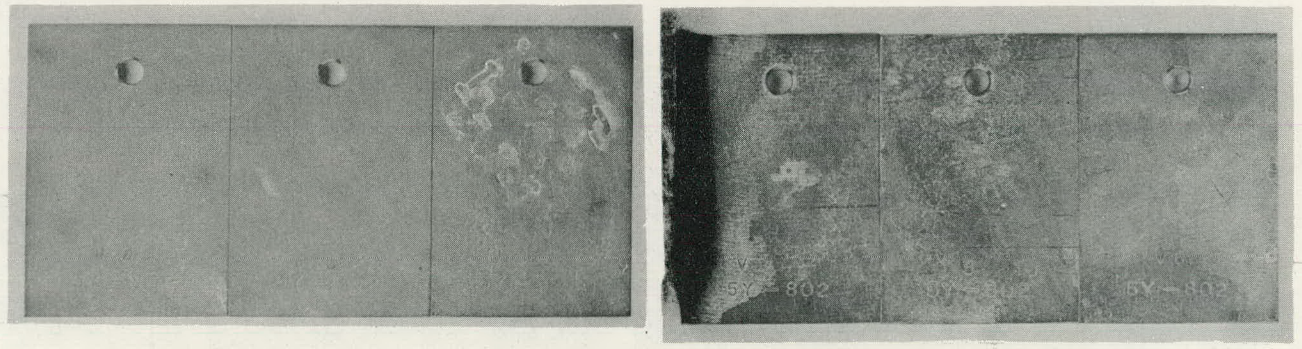
Fig. 27 Surface Appearance after 7 Days Exposure in 750°F Steam of Coupons Rinsed with and without Delay in Transfer

(Neg 23700)



30-sec etch (Neg 23146-10)

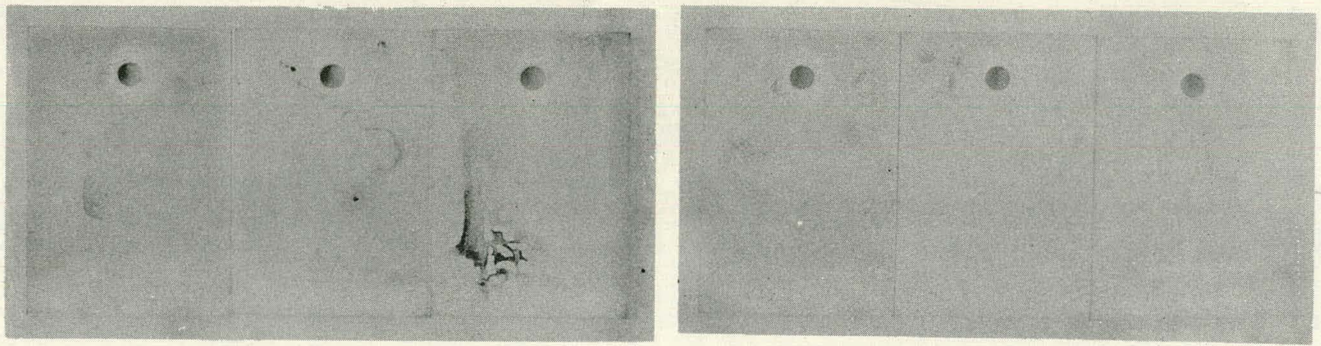
60-sec etch (Neg 23146-15)



120-sec etch (Neg 23146-4)

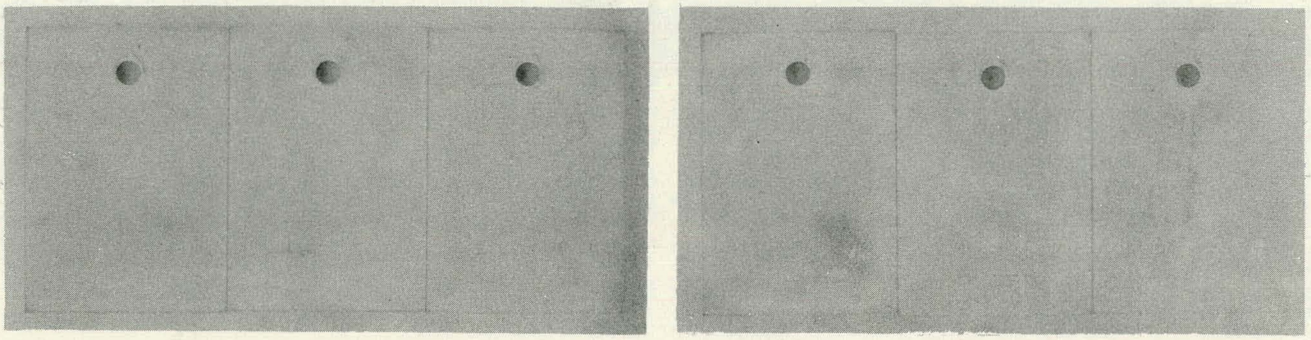
180-sec etch (Neg 23146-8)

Fig. 28 Corrosion of Zircaloy Coupons Exposed for 14 Days at 750°F after Being Etched in HCl-HF for Varying Lengths of Time and Thoroughly Rinsed



30-sec etch (Neg 23146-12)

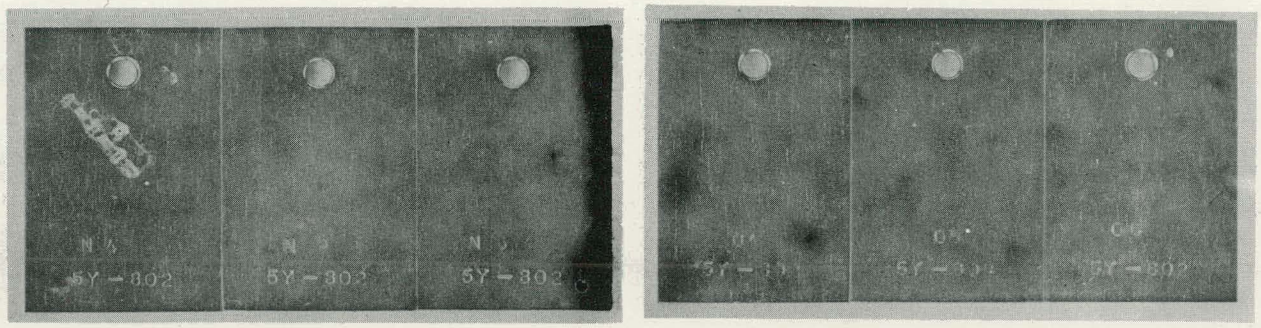
60-sec etch (Neg 23146-5)



120-sec etch (Neg 23146-14)

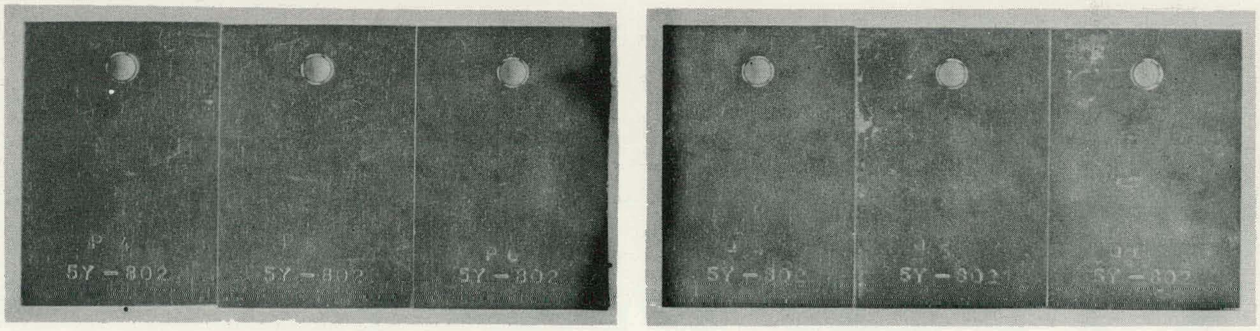
180-sec etch (Neg 23146-11)

Fig. 29 Corrosion of Zircaloy Coupons Exposed for 14 Days at 750°F after Being Etched in HCl-HF For Varying Lengths of Time. Coupons Were Not Rinsed Prior to Corrosion Exposure.



30-sec etch (Neg 23146-13)

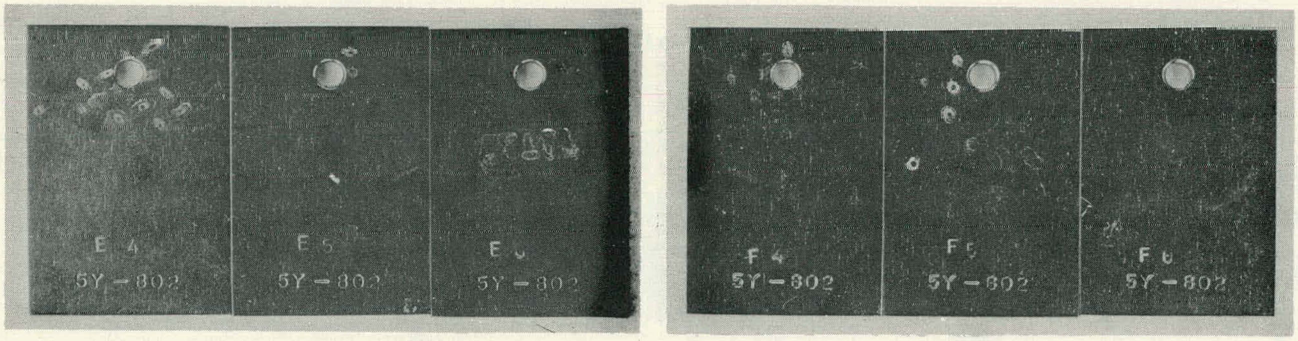
60-sec etch (Neg 23146-6)



120-sec etch (Neg 23146-9)

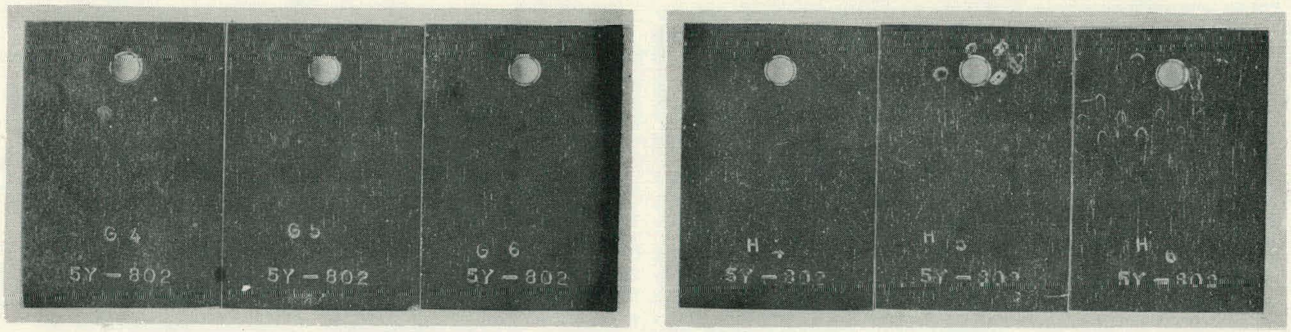
180-sec etch (Neg 23146-2)

Fig. 30 Corrosion of Zircaloy Coupons Exposed to 750°F Steam after Being Etched in HCl-HF for Varying Lengths of Time, Not Rinsed, Permitted to Dry, Then Re-Etched in HNO_3-HF to Remove 2 mils per Surface and Thoroughly Rinsed



30-sec etch (Neg 23146-1)

60-sec etch (Neg 23146-16)



120-sec etch (Neg 23146-17)

180-sec etch (Neg 23146-3)

Fig. 31 Corrosion of Zircaloy Coupons Exposed for 14 Days in 750°F Steam after Being Etched in HCl-HF for Varying Lengths of Time, Rinsed, and Re-Etched in HNO_3-HF to Remove 2 mils per Surface. Coupons Were Thoroughly Rinsed Prior to Corrosion Exposure.

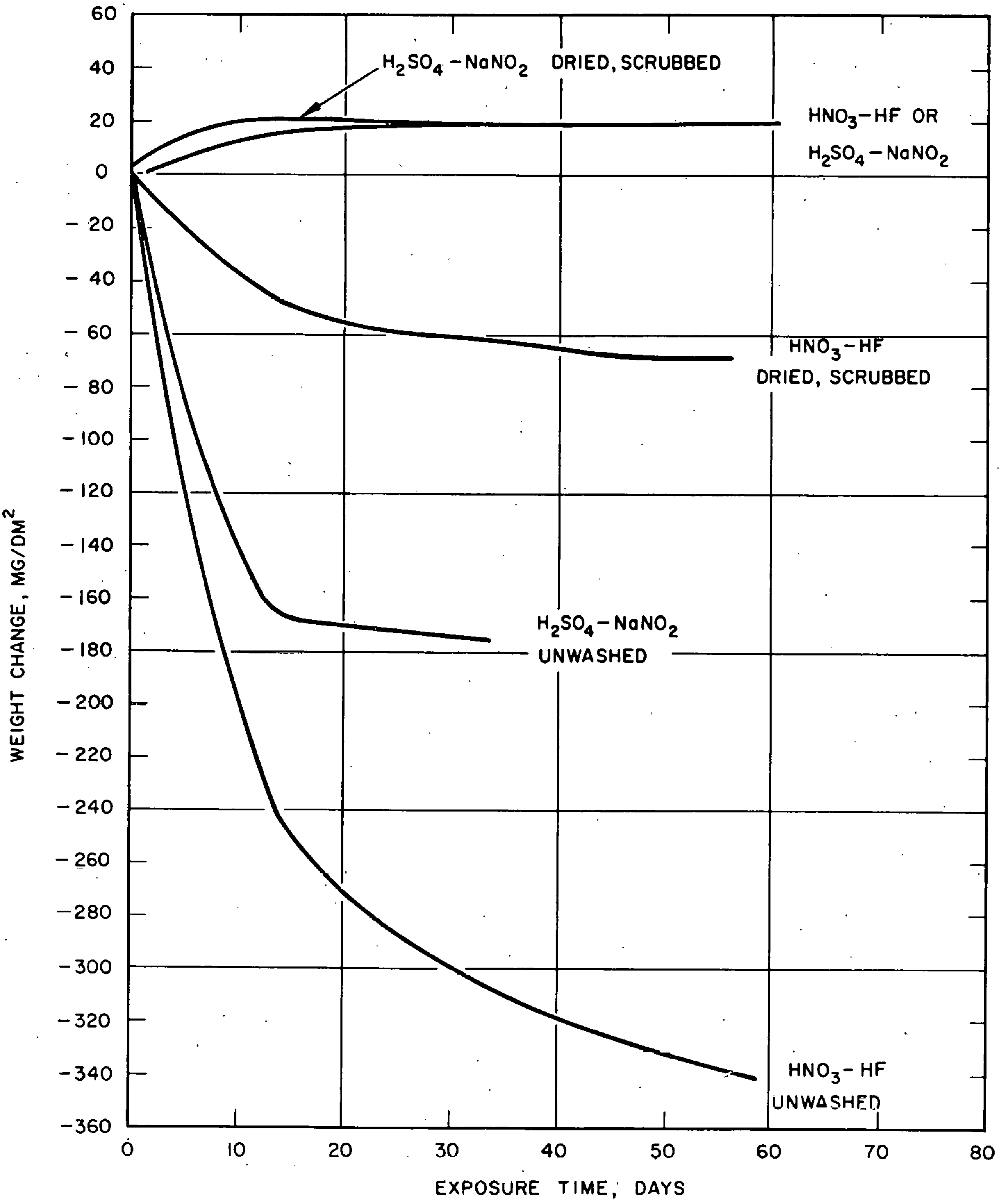


Fig. 32 Corrosion of Zircaloy-2 in 680°F Water after Being Etched in HNO_3-HF and H_2SO_4-$NaNO_2$