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Corrosion/Erosion Tests on Candidate Voloxidizer Materials

J. G. Merkel

CONSOLIDATED FUEL REPROCESSING PROGRAM

OPERATED BY
UNION CARBIDE CORPORATION
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Consolidated Fuel Reprocessing Program

CORROSION/EROSION TESTS ON CANDIDATE VOLOXIDIZER MATERIALS

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ABSTRACT

Corrosion/erosion tests were carried out at 650°C on type 316 stainless steel and Incoloy 800H. A moist air atmosphere containing 55 ppm iodine was maintained in two rotating drums. Dimensional measurements of the walls after the test showed very small changes. After 4000 h the stainless steel drum showed a thin oxide scale. The Incoloy 800H drum had even less attack after 6000 h.

1. INTRODUCTION

Voloxidation is a proposed step in the head-end process of a fuel recycle plant. Sheared fuel elements are heated in a rotary kiln containing lifting flights and heating and cooling zones. At these conditions, the UO_2 is converted to U_3O_8 with the release of tritium and to some extent iodine and certain noble gases. Solids loading would be ~10% by volume, and the kiln will rotate at 1 rpm. With a heated zone of ~650°C, there is potential surface abrasion caused by the ceramic solids and metal hulls as well as corrosion from the iodine released from the fuel. Two candidate materials, type 316 stainless steel and Incoloy 800H, were tested at 650°C in air for several months. This experimental program by Holland[1] used two drums rotating in a furnace. The drums were loaded with solid materials, and wall thickness measurements were taken periodically during the test. Curved sections of the candidate materials were bolted together to form the experimental drums.

This report describes additional testing with the same materials exposed to a controlled atmosphere containing water vapor and iodine.

2. APPARATUS AND PROCEDURES

Each test drum was made by welding together the curved segments used in the previous program. The nominal 1/4-in.-thick plate formed 18-1/2-in.-diam cylindrical shells welded to 21-in.-diam, 1/4-in.-thick circular end plates. Each drum, one 316 SS and the other Incoloy 800H, was mounted horizontally in a furnace with 2-1/2-in.-diam SS shafts. The drive shafts extended through the furnace wall and were supported on pillow blocks (Fig. 1). The shaft was rotated at 1 rpm by a motor operating through a gear reduction unit and a V-belt pulley arrangement. Two gas lines were attached to each drum, one extending into the far end to provide an efficient atmosphere sweep.

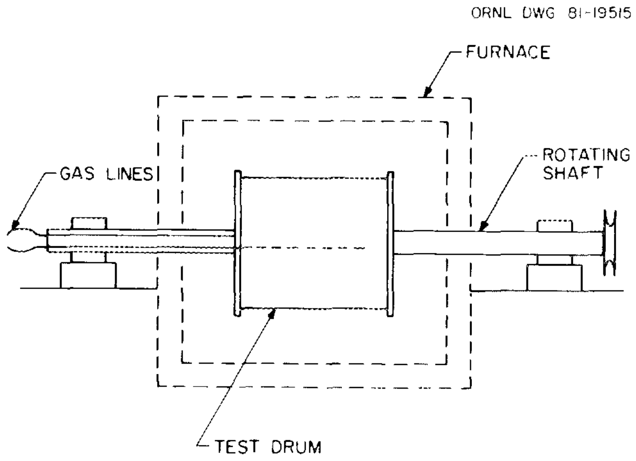

Fig. 1. Test drum configuration.

The predicted atmosphere in the voloxidizer is shown in Table 1. The mixture was simulated using moist air and iodine. The flow diagram for the experiment is shown in Fig. 2. Dry air was swept over a bed packed with iodine crystals. Moist air at the desired humidity was supplied by mixing dry and water-saturated air streams.

Table 1. Voloxidizer off-gas composition

Constituent	Mole %
N_2	63.95
O_2	33.86
H_2O	2.03
HTO	Trace
Kr	0.014
Xe	0.145
Br_2	Trace
I_2	5.47×10^{-3}

By adjusting the air flows, a feed stream was provided to the drums which contained 55 ppm I_2 with 20 300 ppm H_2O. The time required to sweep out the volume of one drum (~2.2 ft^3) with a sweep flow of 0.1 scfm was determined experimentally. With the system charged with air, nitrogen was introduced, and the oxygen content of the exit gas was continuously monitored. Sweep time measurements are shown in Fig. 3 and compared with calculated values that assume perfect mixing. It can be seen that a drum could be charged with a new atmosphere in less than 1 h. The experiment was conducted with the furnace controlled at 650°C and the drums rotated at 1 rpm for up to 6000 h. Periodically (twice a week), the atmosphere was replaced by sweeping in a fresh gas mixture for a 1-h period. Feed and exit gases were checked for iodine content by bubbling through a KI solution for a known time period (i.e., 5 min) and then analyzing the solution. Because of the strong temperature dependence of the vapor pressure of iodine near room temperature, the iodine bed temperature had to be carefully monitored. A 3°C change of temperature can result in a 25% change in iodine concentration of the sweep gas.

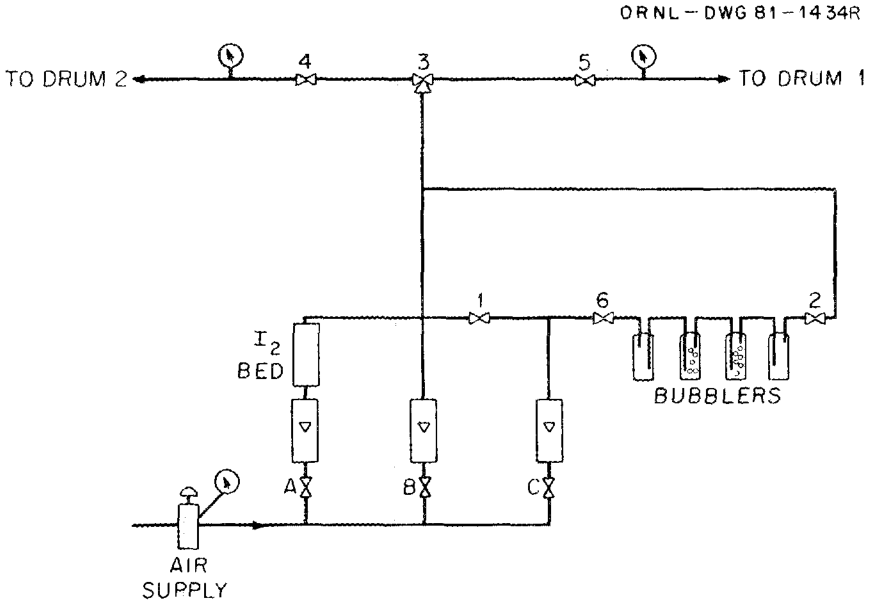

Fig. 2. Flow diagram for the voloxidation corrosion experiment.

Each drum was charged to 10% of its volume with sand and 1/4-in.-diam by 1-in.-long 304 SS slugs. Each drum had 1-in.-wide lifter blades welded to the inner surface to simulate the lifting action of the flights in a voloxidizer (which provides motion to the solids). Titanium tubing (1/8-in. OD by 0.069-in. ID) was used for the gas delivery tubes. The tubes received a slight flexing as the drum rotated at the beginning of the test. Although the tubes were bent in a spiral to relieve this action, they fractured after a few hours of operation. Stainless steel tubing (304L) was substituted for the titanium, and this proved satisfactory for the remainder of the experiment.

An interesting observation was made as the test progressed. A drum was charged with an iodine atmosphere and then swept out with air and operated with air for a few hours. When swept out again with air, the atmosphere was found to contain iodine. This was true for both drums; however, no iodine was found at room temperature. This effect might occur if an iodine compound were formed on the metal walls in equilibrium with the iodine atmosphere and then decomposed when air was substituted.

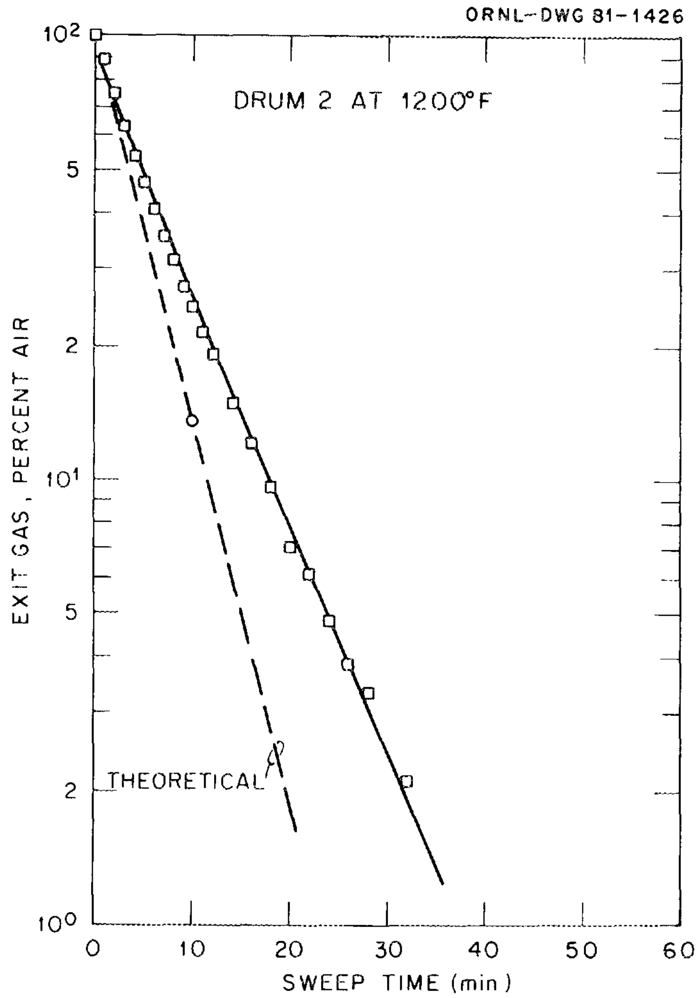

Fig. 3. Sweep time for drum 2.

3. RESULTS

3.1 Dimensional Measurements

Ultrasonic thickness measurements of the drum walls were made before and after the test. Drum 1 was Incoloy 800H and had a total time exposure to iodine of 6000 h. Thickness readings were taken at 0, 4000, and 6000 h. Drum 2 was 316 SS and operated for 4000 h. Eighty-four thickness readings were taken on each drum. A template was used to locate the same positions for each set of comparison readings. The geometry of the drums did not allow accessibility to the shell for a micrometer calibration point; therefore, a micrometer reading was made on the side plate and a velocity setting obtained from that point. The measurements were made by members of ORNL's Department of Quality Assurance and Inspection.

The test results were scattered, and it is believed more appropriate to treat the data for each test surface as a group rather than to place much emphasis on measurements at a particular point. Consequently, mean thickness changes and standard deviations were calculated for each drum. The differences are scaled by 10^3 so that a thickness change of 1 corresponds to 0.001 in. Positive differences indicate a measured thickness decrease, and negative differences indicate a measured increase in thickness at a particular point. Frequency charts were constructed showing the distribution of the 84 thickness differences measured on each surface. Figure 4 shows the thickness change for the Incoloy 800H drum after 4000 and 6000 h of testing.

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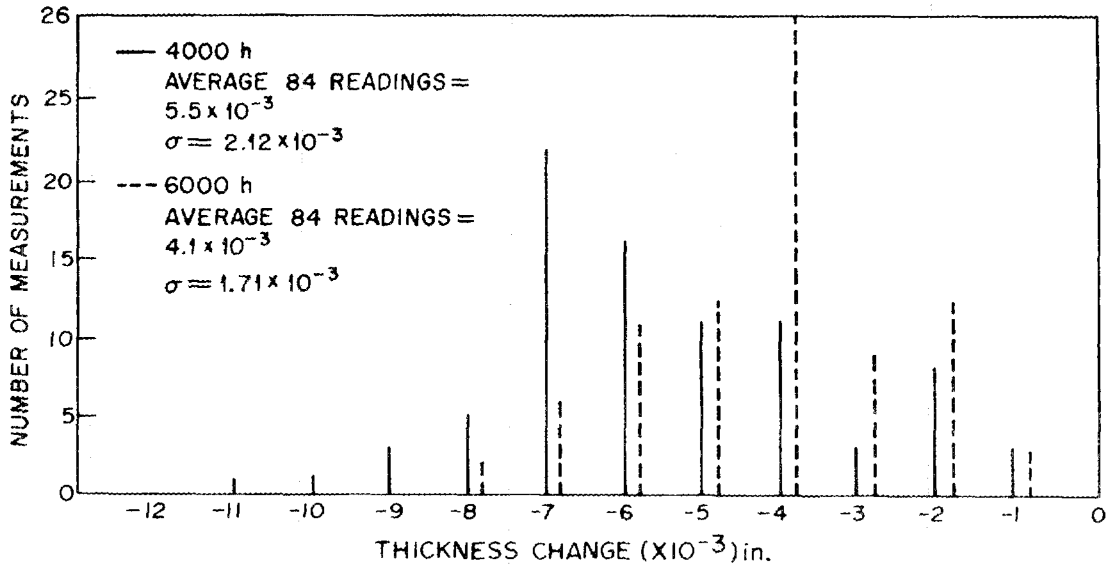

Fig. 4. Incoloy 800H drum 1 after 4000 and 6000 h of testing.

Solid lines show the distribution of data after 4000 h, and the dotted lines show the change from 0 to 6000 h. These data infer an increase in wall thickness after 4000 h but a smaller increase after 6000 h. Tightly adhering fine sand on the inside surface could have interfered with all measurements. The magnitude of the change in thicknesses was not confirmed by subsequent metallographic examination. Figure 5 shows the results of wall thickness measurements on the 316 SS drum. These data showed a very small increase in wall thickness after 4000 h.

3.2 Metallographic Examination

3.2.1 Type 304 stainless steel

A metallographic examination was made of one of the type 304 SS slugs that was tumbled with sand in drum 2. The slug had been exposed to an air (55 ppm I_2, 20 300 ppm

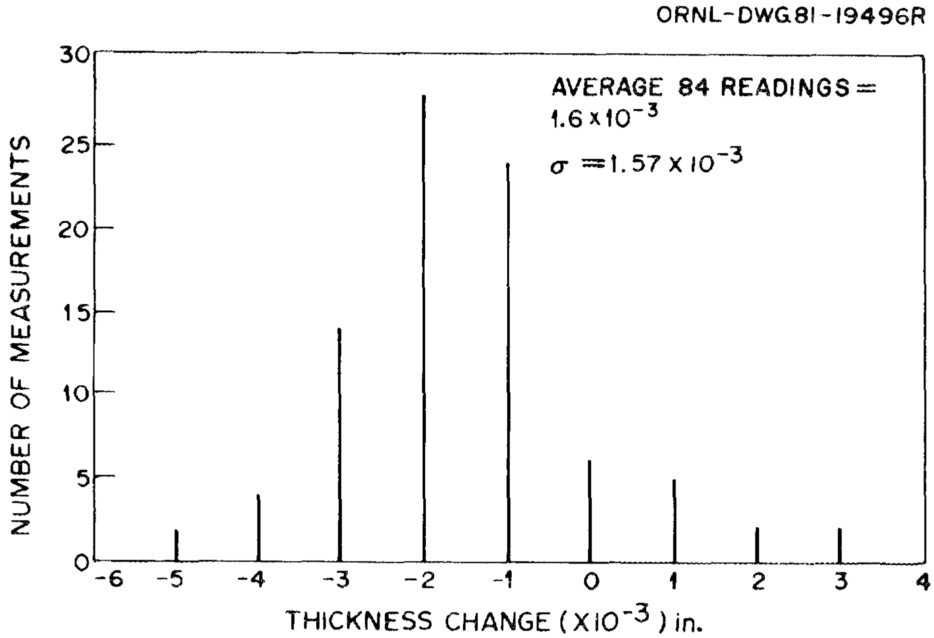

Fig. 5. Type 316 SS drum 1 after 4000 h of testing.

H_2O) atmosphere for 4000 h. Figure 6 shows a gray-colored oxide scale measuring up to 25 μ in thickness on the outside surface of the slug. This view is of the as-polished (unetched) microstructure at a magnification of 500X. Figure 7 shows the microstructure after etching.* Directly beneath the surface scale can be seen a white layer 20 to 40 μ in depth. This layer was examined by an electron microprobe x-ray analyzer. No iodine was detected; however, a back-scattered electron image showed a slight depletion of chromium and a slight agglomeration of nickel.[2]

3.2.2 Incoloy 800H

The drum was sectioned and a sample obtained in the region of a girth weld. Figure 8 is a view (at 9X) of the etched wall cross section. The inner surface is at the bottom. The crack below the weld is a junction of the curved segments that form the drum. Figure 9 shows the interface area where the metal is protected from the scouring action of the solids. No corrosion or pitting is visible. A very thin oxide scale is apparent.

3.2.3 Type 316 stainless steel

A specimen similar to the Incoloy 800H sample taken from the girth-weld region was obtained from drum 2 for examination. Figure 10 shows a 316 SS drum specimen taken from the region of the girth weld, and Fig. 11 is a view (at 200X) of the interface area. No corrosive attack is evident, although there is a slightly thicker oxide scale than that seen in the Incoloy drum.

*Etchant is 50 parts HCl, 10 parts HNO_3.

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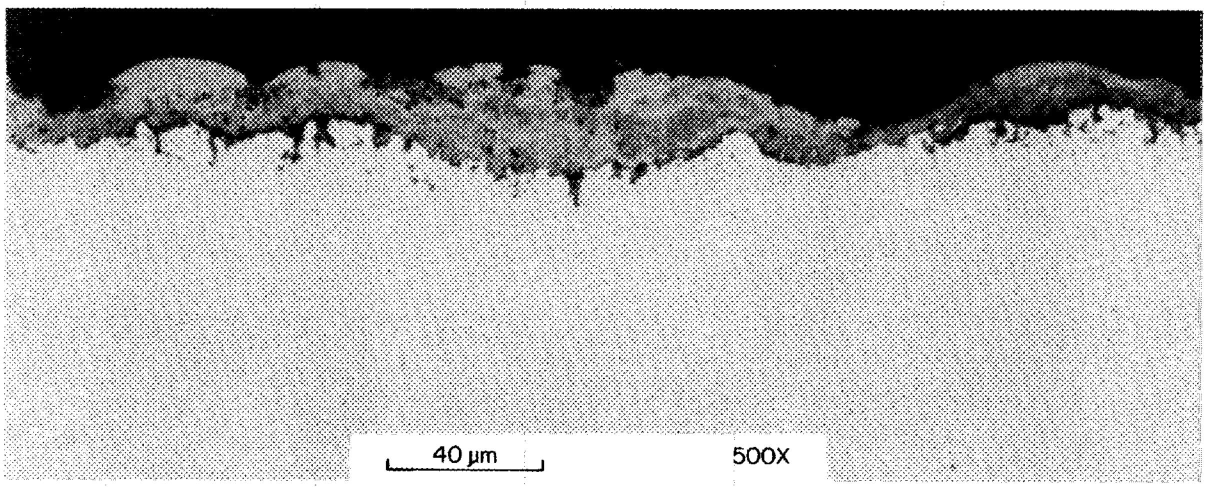

Fig. 6. Type 304 SS slug showing gray-colored oxide scale.

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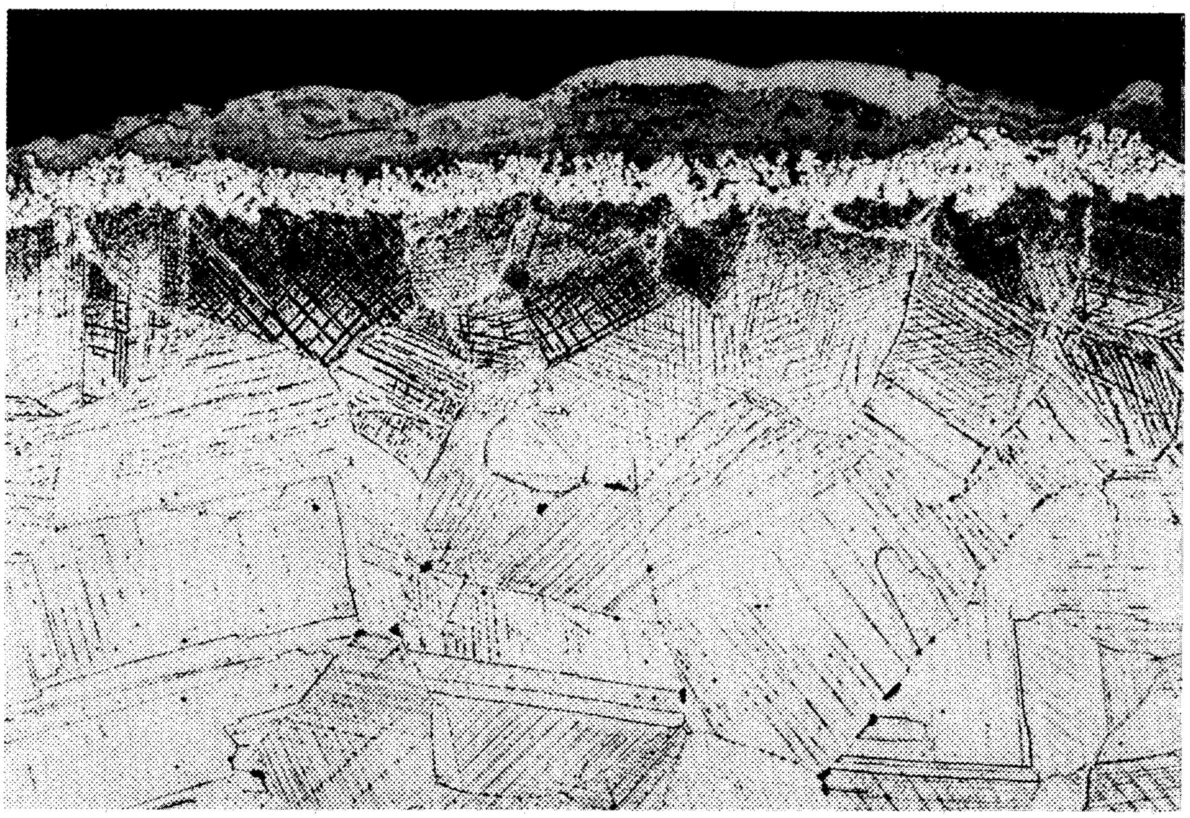

Fig. 7. Type 304 SS slug microstructure (after etching).

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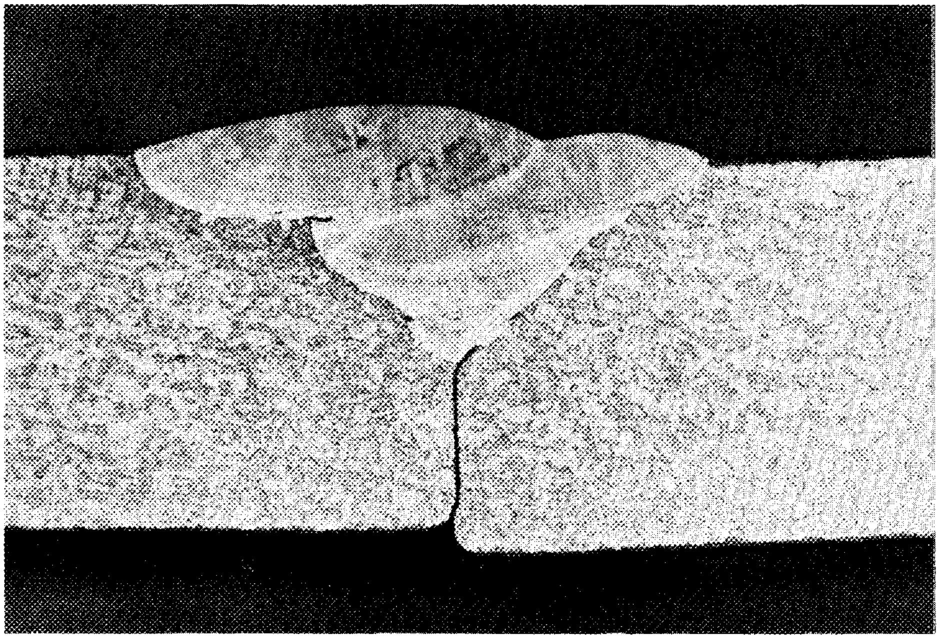

Fig. 8. Incoloy 800H drum wall specimen (9X), etched.

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Fig. 9. Interface area of Incoloy 800H drum specimen.

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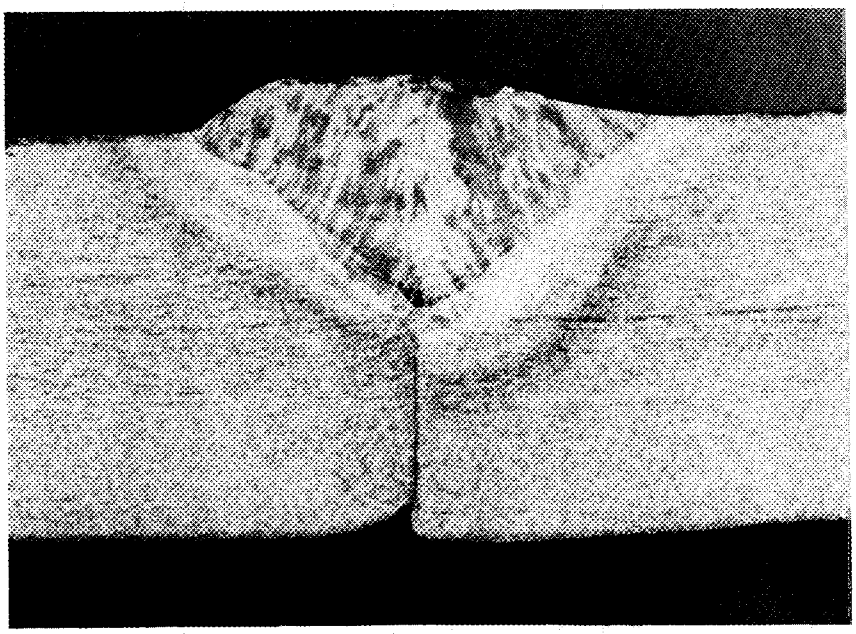

Fig. 10. Type 316 SS drum wall specimen (9X), etched.

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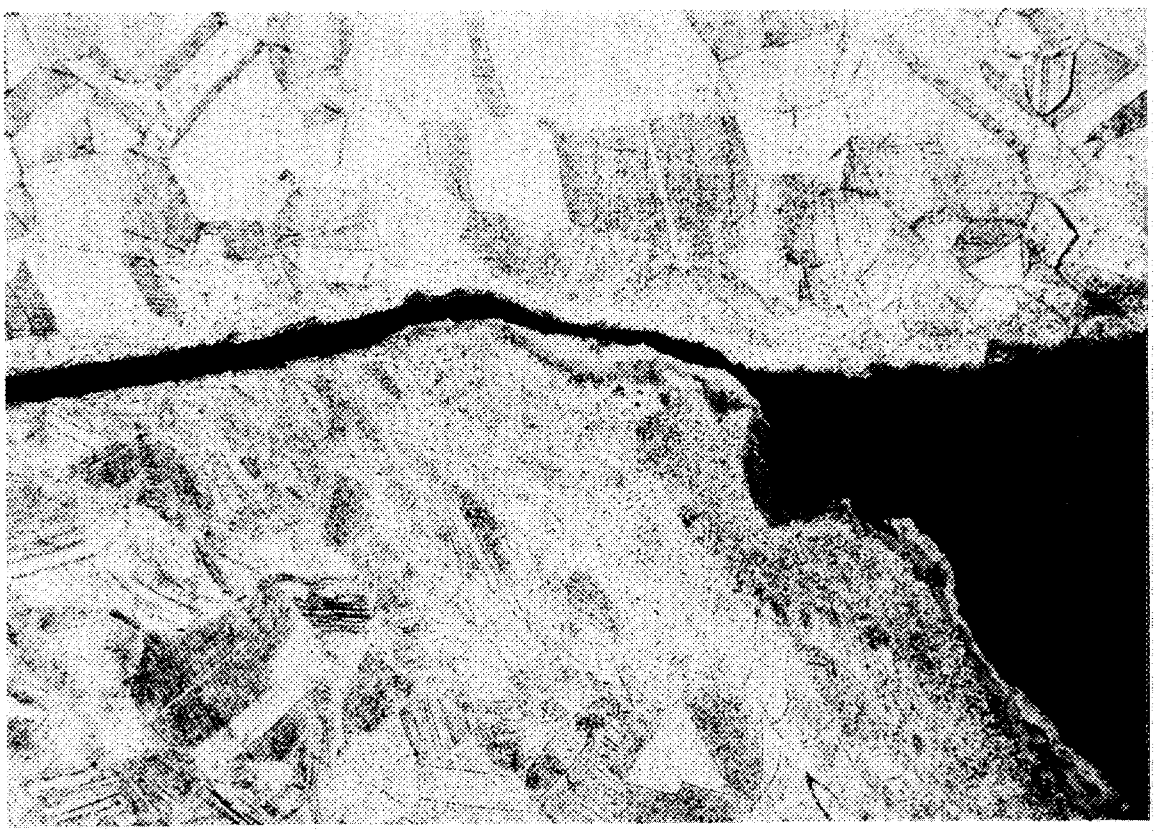

Fig. 11. Interface area of type 316 SS drum specimen.

4. CONCLUSIONS

Most of the reported corrosion studies involving iodine have been at higher concentrations, without water vapor, and were extrapolations from short-term tests. Horsley[3] reported corrosion rates of stainless steel at 350°C to be ~7 mil/year at 15 mm I_2. The tests in this study had an iodine partial pressure of 0.04 mm Hg. Fukuda and Omorr[4] studied the dependence of iodine vapor pressure at 700°C on the corrosion of stainless steel for 1-h exposure. In 100-h tests in humidified air at 40°C, Beavers et al.[5] found ~3-μm-deep pitting in Incoloy 800. The iodine concentration was comparable to our tests. A corrosion rate, calculated from weight loss, was reported to be 100 μm/year (40 mil/year). The tests here were designed to determine the structural integrity of candidate metals under prototypical voloxidizer operating conditions. It should be emphasized that the drum surfaces had a preoperation history of exposure to air at 650°C for several months (156 d) prior to the start of the tests. The thin oxide layer may have helped protect against attack from the moist iodine atmosphere. No corrosive attack was detected on either the 316 SS or the Incoloy 800H drum surfaces. The erosion action of the solids rotating in the drum was minimal, although sharp edges of the tumbling metal slugs were rounded, and finely powdered Fe_2O_3 was detected in the sand.

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