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THOREX PILOT PLANT CORROSION STUDIES: II. CORROSION OF TYPES 304L, 309SCb, AND 347 STAINLESS STEEL DURING DEVELOPMENT AND PRODUCTION-DEVELOPMENT PERIODS

J. L. English

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REACTOR EXPERIMENTAL ENGINEERING DIVISION

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1. SUMMARY

Corrosion data for types 304L, 309SCb, and 347 stainless steel were obtained in a number of process vessels in the ORNL Thorex pilot plant during the development and the production-development periods of operation occurring between December 1954 and September 1956. Stressed corrosion-test specimens were exposed in the batch dissolver tank, the feed adjustment tank, the BT vapor separator, the A-column feed tank, and the BTC catch tank. Generally, types 304L and 309SCb stainless steel exhibited comparable corrosion resistance in all environments examined. Most of the studies were conducted with these two alloys. Severe corrosion damage was encountered in the vapor phase of both the batch dissolver tank, operated at a maximum temperature of 115°C, and the feed adjustment tank, operated at a maximum temperature of 155°C. Corrosion rates for types 304L and 309SCb stainless steel varied from approximately 30 to 55 mpy in the batch dissolver tank during the development and the production-development periods. Vapor-phase corrosion rates in the feed adjustment tank during the last half of the development period ranged from 85 to 100 mpy. Severe corrosion attack was experienced also in the BT vapor separator, which operated at a maximum temperature of 115°C. Rates were 30 to 55 mpy for type 304L stainless steel, 25 mpy for type 309SCb stainless steel, and a maximum rate of 150 mpy for a composite specimen of types 309SCb and 347 stainless steel.

Solution-phase corrosion rates for types 304L and 309SCb stainless steel in the batch dissolver tank ranged from 13 to 28 mpy, with the lower rates observed on the type 309SCb steel. The latter corroded at an average rate of 41 mpy in the feed adjustment tank, however. No data were available for type 304L stainless steel in the solution phase of this vessel. The corrosion of types 304L and 347 stainless steel was negligible in the A-column feed tank and the BTC catch tank; observed rates were less than 0.1 mpy.

None of the three alloys tested underwent stress-corrosion cracking in any of the process vessel environments, nor was there any indication of a stress-accelerated rate of corrosion attack. Generally, corrosion attack on flat surfaces of specimens produced uniform metal removal. Mild intergranular penetration, not exceeding 6 mils in depth, was encountered in the more corrosive environments, particularly in the vapor phase. Weld specimens of the three alloys were randomly subject to localized corrosion in the heat-affected zone immediately adjacent to weld deposits. The maximum penetration by this form of attack was 25 mils in types 309SCb and 347 stainless steel weld specimens.

Corrosion in the batch dissolver and feed adjustment tanks was significantly more severe during the development period of operation than was observed during the previously reported production period.[1] With the exception of the solution phase in the batch dissolver tank, the rates were generally well in excess of the 25-mpy maximum value tentatively established for the pilot plant. Based upon continuous operation of the pilot plant, the half-life of the type 309SCb stainless steel batch dissolver and feed adjustment

tanks was estimated to be 2.5 years each. The full life for the BT vapor separator, operating continuously, was estimated to be 1.2 years. This value was determined by the behavior of type 347 stainless steel specimens, the alloy from which the body of the separator is fabricated.

2. INTRODUCTION

This report is the second in a series describing the results of corrosion studies conducted in the ORNL Thorex pilot plant during its operation between December 1954 and September 1956. The initial report dealt with the corrosion behavior of stainless steel specimens exposed in various process vessels during the production period and the first half of the development period (December 15, 1954, to November 10, 1955).[1] The present report is concerned with the evaluation of corrosion data obtained during the second half of the development period (November 15, 1955, to September 13, 1956) and the combined production-development period (December 15, 1954, to September 13, 1956). The initial report covers in detail the history of the stainless steel test materials and the type of specimen employed. Corrosion data obtained in four process vessels, namely, the batch dissolver tank, the feed adjustment tank, the AP catch tank, and the BT vapor disengager, were presented. The present studies are a continuation of corrosion tests in the same vessels as well as in several other process vessels during the extended operational period of the pilot plant.

Table 1 shows a resumé of specimen locations and residence periods in the process vessels to be discussed. The residence period represents the total time that the specimens remained in a particular vessel; it does not represent the time that specimens were contacted by process solution or vapor.

3. EXPERIMENTAL PROCEDURE AND RESULTS

Each corrosion-specimen assembly was a conventional simple-beam, constant-strain type of stress assembly consisting of a stress specimen, a fulcrum, and a welded base plate. Auxiliary components were two sets of studs and screws for applying the desired stress. All items in a particular stress assembly were machined from the same type of stainless steel. An applied stress of 35,000 psi was used on all specimens throughout the corrosion investigation.

Upon removal from the pilot-plant process vessels, specimens were scrubbed in soapy water to remove loosely adherent corrosion products, after which they were dismantled. The individual components were cathodically defilmed in inhibited 5% H_2SO_4 solution. The defilming process, repeated several times, effectively reduced surface activities on the specimens to levels that permitted handling with negligible personnel hazard. All corrosion rates subsequently reported are based upon defilmed weight losses.

Table 1. Distribution and Residence Times for Corrosion Specimens During the Production and Development Periods of Pilot Plant Operation

Process Vessel and Identity	Operational Period	Residence Period[a]
Batch dissolver (S-1)	Development[b]	3/14/55 - 8/14/56
Feed adjustment (S-2)	Development[b]	11/15/55 - 8/14/56
BTC catch tank (P-3)	Development	3/7/55 - 8/14/56
BT vapor separator (P-2)	Development	3/4/55 - 8/14/56
A-column feed (S-4)	Development	3/11/55 - 9/13/56
Batch dissolver (S-1)	Production-development	12/23/54 - 8/14/56
BT vapor separator (P-2)	Production-development	12/17/54 - 8/14/56

(a) Does not represent the actual contact time of specimens by process solution.
(b) Specimens were exposed for approximately one half of the complete development period.

A. Corrosion During the Development Period

1. Batch Dissolver Tank. The purpose and a description of the batch dissolver tank have been reported previously.[1] The welded tank was fabricated from type 309SCb stainless steel. During the development period of operation, the tank was used primarily for the dissolution of aluminum-jacketed thorium metal slugs. The tank was also used to a lesser extent for the Neptex program involving the dissolution of MTR fuel elements. On frequent occasions, the dissolver was used merely as a storage vessel for process solutions.

   The dissolving solution was technical-grade 13 *M* HNO_3 (or 10-12 *M* HNO_3 which was recovered from the feed adjustment tank) with small amounts of mercuric nitrate and sodium fluoride to catalyze the aluminum - nitric acid and the thorium - nitric acid dissolution reactions, respectively. The solution temperature during dissolving was 110 to 115°C. The nominal composition of the solution after a dissolving cycle was: 1 *M* $Th(NO_3)_4$, 6 *M* HNO_3, 0.5 *M* $Al(NO_3)_3$, 0.0025 *M* $Hg(NO_3)_2$, and 0.0375 *M* NaF.[2]

Upon completion of dissolving operations, the dissolver tank was decontaminated with alternate passes of nitric acid and caustic tartrate solutions at temperatures from 40 to 110°C. The total decontamination time was 117 hr.

Single-specimen arrays of types 304L and 309SCb stainless steel specimens were removed from the solution and vapor phases. A resume of the exposure history appears in Table 2. It should be noted that approximately 75% of a 10,379-hr contact time by process solutions on specimens was accumulated at room temperature.

Table 2. Summary of Exposure History for Stress Specimens in Batch Dissolver Tank During Development Period

Operation	Number of Runs	Exposure Time (hr) Solution	Exposure Time (hr) Vapor
Total residence time in tank	109	12,444	12,444
Thorex dissolvings at 115°C max.[a]	74	2,490	2,490
Neptex dissolvings at 115°C max.[a]	15	99	99
Decontamination at 40 to 110°C	20	117	117
Holding time at room temperature		7,673	0[c]
Total active exposure time[b]	109	2,706	2,706

(a) Includes heating and cooling time.
(b) Holding time at room temperature not considered in total active exposure time.
(c) No vapor contact time included when process solutions were at room temperature.

The as-removed condition of the four stress assemblies indicated that appreciable corrosion had occurred, both in the solution and vapor phases. The fulcrum in each assembly was missing, and it was presumed that excessive corrosion attack had reduced physical dimensions to such a point that the fulcrum slipped from its original position. The net result was a complete release of the initially applied stress of 35,000 psi sometime during the exposure period. No evidence of cracks was found in any of the stress specimens.

Thin corrosion films were present on the solution-exposed stress and weld specimens, as indicated by film weights between 0.1 and 0.5 mg/cm^2. Heavy filming was in evidence on the vapor-exposed specimens, however; film weights varied from 2 to 6 mg/cm^2. As-removed, all specimens were a mottled, gray-brown color. A summary of the corrosion rates for the specimens appears in Table 3.

Table 3. Corrosion of Stainless Steels in Batch Dissolver Tank at 115°C Maximum During Development Period

Lab. No.	Alloy Type	Exposure Phase	Specimen Type	Total Time (hr)[a]	Corrosion Rate (mpy)
D-27	304L	Solution	Stress	2706	32.6
			Weld[b]		30.9
D-73	309SCb	Solution	Stress	2706	13.3
			Weld[c]		16.6
D-26	304L	Vapor	Stress	2706	41.8
			Weld[b]		38.8
D-72	309SCb	Vapor	Stress	2706	36.8
			Weld[c]		33.0

(a) Actual time that specimens were contacted by hot process solutions; the 7673 hr that were accumulated in contact with process solutions at room temperature were not considered in determination of corrosion rates.
(b) Heliarc-welded with type 308L rod.
(c) Heliarc-welded with type 309SCb rod.

In order to present a more realistic assessment of the corrosion behavior of the solution-exposed specimens, corrosion rates were based on an active exposure period of 2706 hr, during most of which time the specimens were contacted by process solutions at 110 to 115°C. A portion of the 2706-hr period, 338 hr, represented heating and cooling time for solutions, and 117 hr were for decontamination time. The total solution contact time was 10,379 hr. However, 7673 hr of this total represented holding time for solutions at

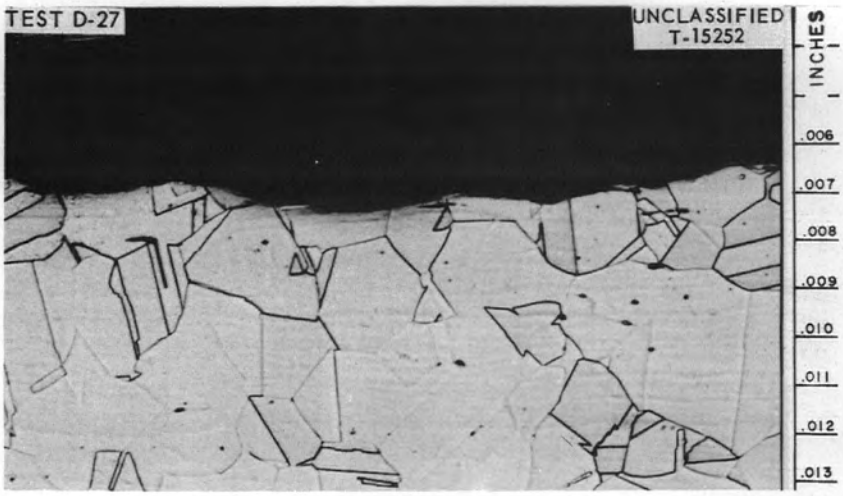
room temperature. The latter figure was not included in the determination of corrosion rate values since it has been reported that in laboratory tests with simulated conditions, corrosion rates on similar stainless steels were not in excess of 1 mpy.[3]

Corrosion of Solution-Exposed Specimens. The average corrosion rate for type 304L stainless steel stress and weld specimens was 31.8 ± 0.9 mpy during the 2706-hr exposure. There was no appreciable difference between the corrosion rate for the weld and the stress specimens. The average corrosion rate for type 309SCb stainless steel was 15.0 ± 1.6 mpy.

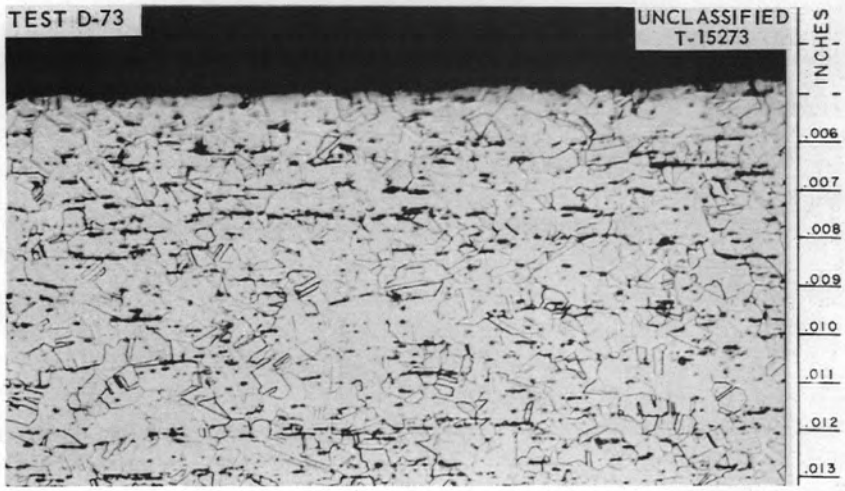
A metallographic examination was made of various sections on specimens of the two alloys. In Fig. 1 is shown the nature of the attack on flat surfaces of the stress specimens. In both cases, uniform metal removal was experienced. Such was not the case, however, on edge surfaces, as shown in Fig. 2. Severe preferential corrosion, commonly known as edge- or end-grain attack, was much in evidence. Type 304L stainless steel was more susceptible; the deepest penetration was 9 mils, compared with 3 mils for type 309SCb stainless steel. The attack was not particularly selective with respect to grain-boundary areas, inclusions in the alloys, or to the grains themselves.

The condition of weld deposits in the base-plate specimens is shown in Fig. 3. The sections were made through the as-welded face welds. The type 308L deposit was attacked in a relatively uniform manner. The type 309SCb weld metal, however, was subject to very severe localized corrosion. The attacked area shown in Fig. 3 was 18 mils in diameter and 15 mils in depth. Numerous similar-appearing pits were found in the deposit. The same weld specimen was also susceptible to pronounced knife-line attack as shown in Fig. 4. The attack occurred on both sides of the face weld in the heat-affected zone. The maximum observed penetration was 25 mils. A slight preferential interface attack, 3 mils in depth, was found in the heat-affected zones along the type 304L stainless steel face weld.

Corrosion of Vapor-Exposed Specimens. Both types 304L and 309SCb stainless steel experienced greater attack in the vapor phase than in the solution phase. The average corrosion rate for type 304L stainless steel was approximately 30% higher during the 2706-hr vapor-exposure period than was observed for the similar solution-exposure period. The average rate for stress and weld specimens was 40.3 ± 1.5 mpy. As in the case of solution-exposed specimens, no significant difference was observed between the over-all corrosion behavior of the stress and weld specimens. Type 309SCb stainless steel showed a 135% increase in the average corrosion rate for vapor-exposed



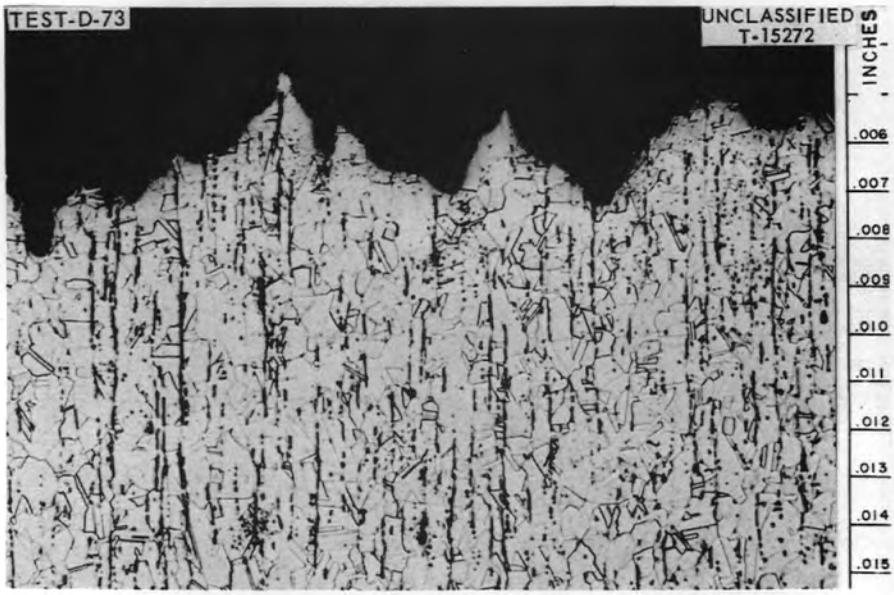
A. TYPE 304L STAINLESS STEEL



B. TYPE 309SCb STAINLESS STEEL

Fig. 1. Condition of Flat Surface on Stress Specimens After 2706 hr of Solution Exposure in the Batch Dissolver Tank. Etched in glyceria-regia. 250X.

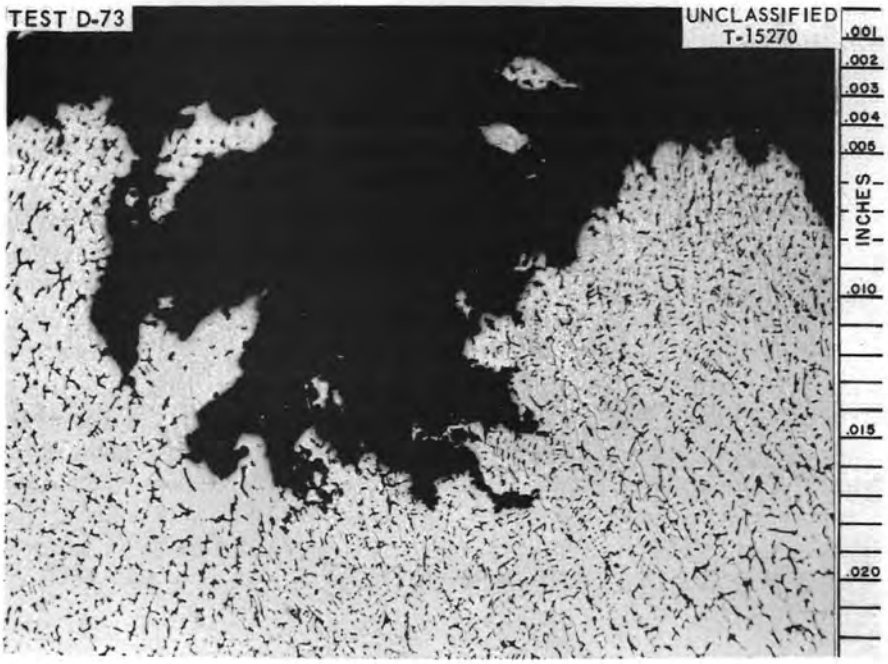
A. TYPE 304L STAINLESS STEEL



B. TYPE 309SCb STAINLESS STEEL

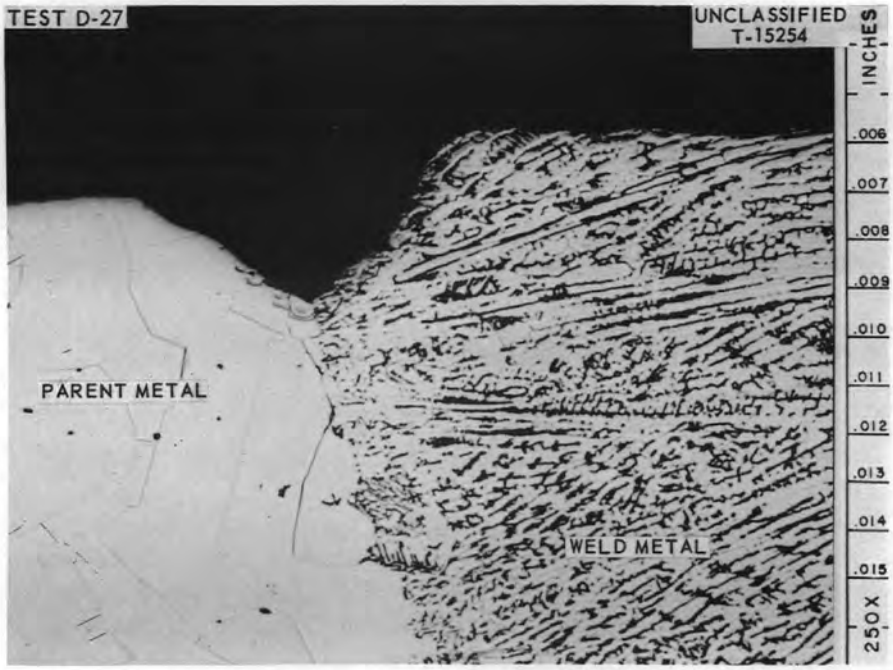
Fig. 2. Condition of Edge Surface on Stress Specimens After 2706 hr of Solution Exposure in the Batch Dissolver Tank. Etched in glyceria-regia. 250X.

A. TYPE 308L STAINLESS STEEL WELD METAL. 250X.

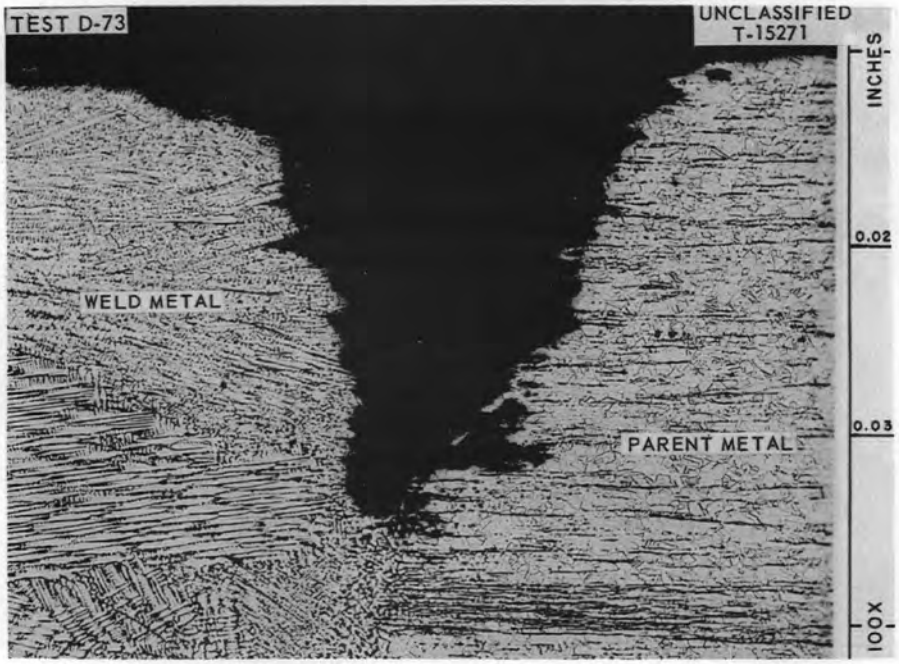


B. TYPE 309SCb STAINLESS STEEL WELD METAL. 150X.

Fig. 3. Weld Metal Attack on Stainless Steel Specimens Exposed for 2706 hr to Solution in Batch Dissolver Tank. Etched in glyceria-regia.



A. TYPE 304L STAINLESS STEEL FACE WELD. 250X.



B. TYPE 309SCb STAINLESS STEEL FACE WELD. 100X.

Fig. 4. Weld-Parent Metal Interface Attack on Stainless Steel Specimens Exposed for 2706 hr to Solution in Batch Dissolver Tank. Etched in glyceria-regia.

stress and weld specimens. The average rate was 34.9 ± 1.9 mpy, as compared with 15.0 ± 1.6 mpy for solution-exposed specimens.

Figure 5 shows the nature of the corrosion attack on the flat surface of the stress specimens. The type 304L stainless steel exhibited definite signs of intergranular attack, with the deepest penetration around 3 mils. Numerous grains were almost completely encircled by the attack. Type 309SCb stainless steel, on the other hand, underwent relatively uniform metal removal.

Edge-corrosion attack was prevalent on specimens of both alloys. The attack was similar to that shown in Fig. 2 except that the intensity was much greater. Maximum penetration resulting from the attack on type 304L stainless steel was 18 mils; on type 309SCb stainless steel it was approximately 5 mils.

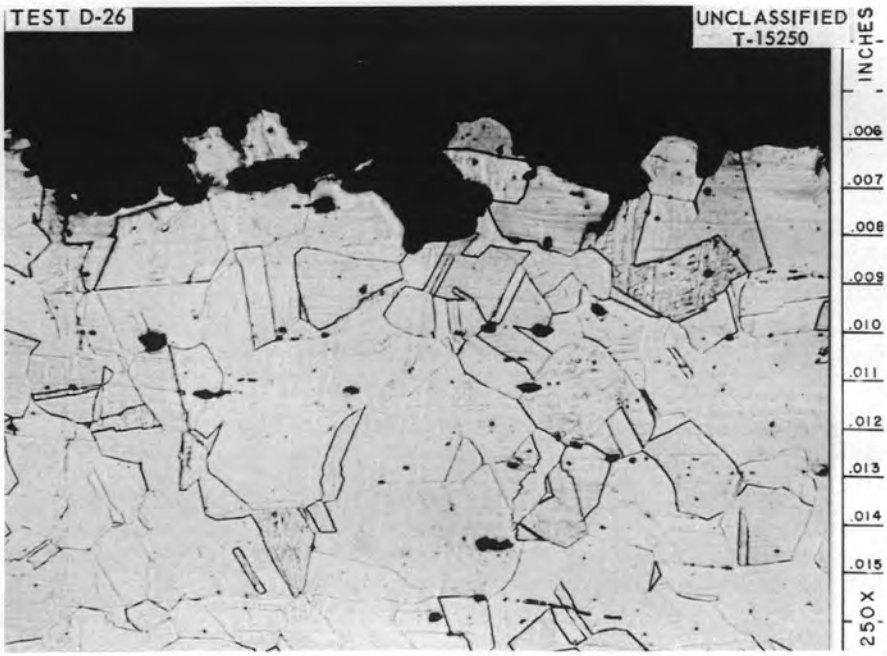
Both types 308L and 309SCb stainless steel weld deposits were subject to substantial localized corrosion. On the former, the attack was of a channeling type with grooves up to 4 mils in depth. The base and sides of the grooves were uniformly attacked. The attack on type 309SCb stainless steel was characterized by pitting, initiated by intergranular attack. The deepest pits were 6 to 7 mils in depth.

Knife-line corrosion attack was found along the face weld on type 309SCb stainless steel. No knife-line corrosion was observed at the root weld, however, as shown in Fig. 6. The intergranular nature of the attack on the type 309SCb weld deposit is readily apparent.

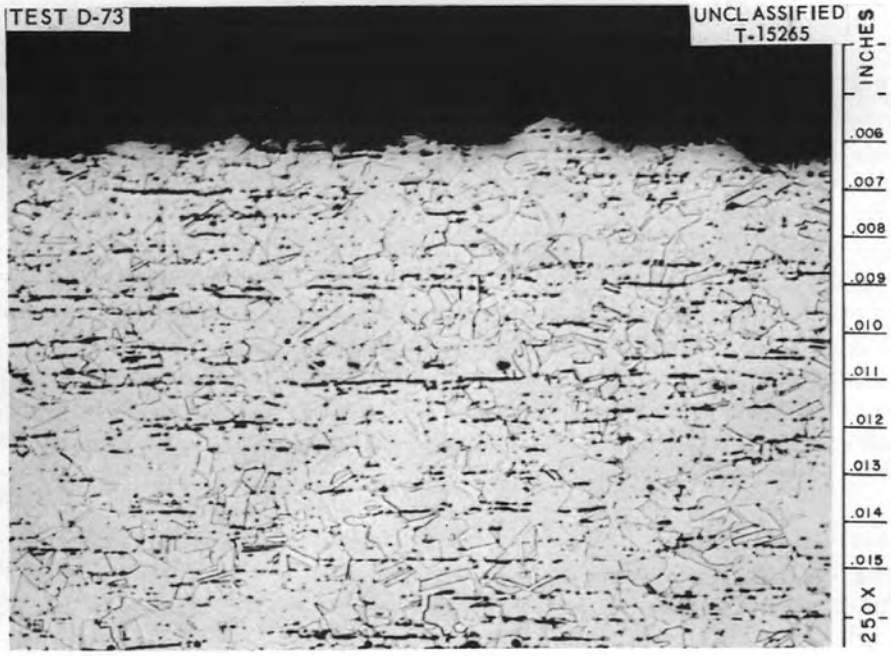
No preferential weld-parent metal interface attack was found on either the face or root welds of type 304L stainless steel. The condition of the root-weld - parent-metal interface is also shown in Fig. 6. Based upon the results of visual and metallographic examinations of solution- and vapor-exposed weld specimens in the batch dissolver tank, there was little doubt as to the superior corrosion resistance of the deposited type 308L weld metal over the type 309SCb weld metal.

2. Feed Adjustment Tank. Corrosion specimens were exposed in the feed adjustment tank during the second half of the development period, which took place between November 15, 1955, and September 13, 1956. Corrosion data for specimens exposed during the first half of the development period have been reported.[1]

The type 309SCb stainless steel feed adjustment tank and auxiliary equipment were used to prepare an acid-deficient feed solution for the uranium-thorium solvent extraction process. The first step in

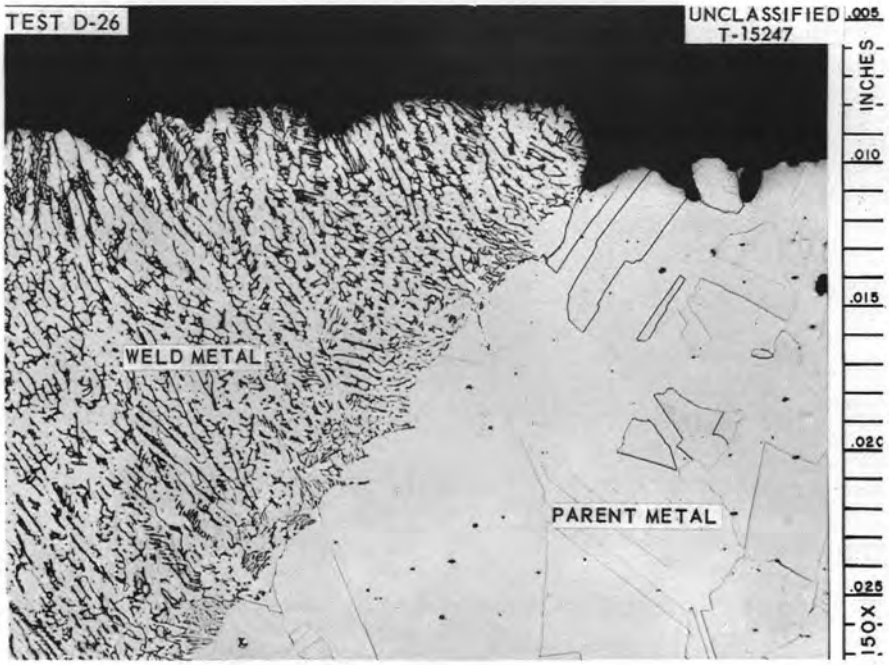


A. TYPE 304L STAINLESS STEEL

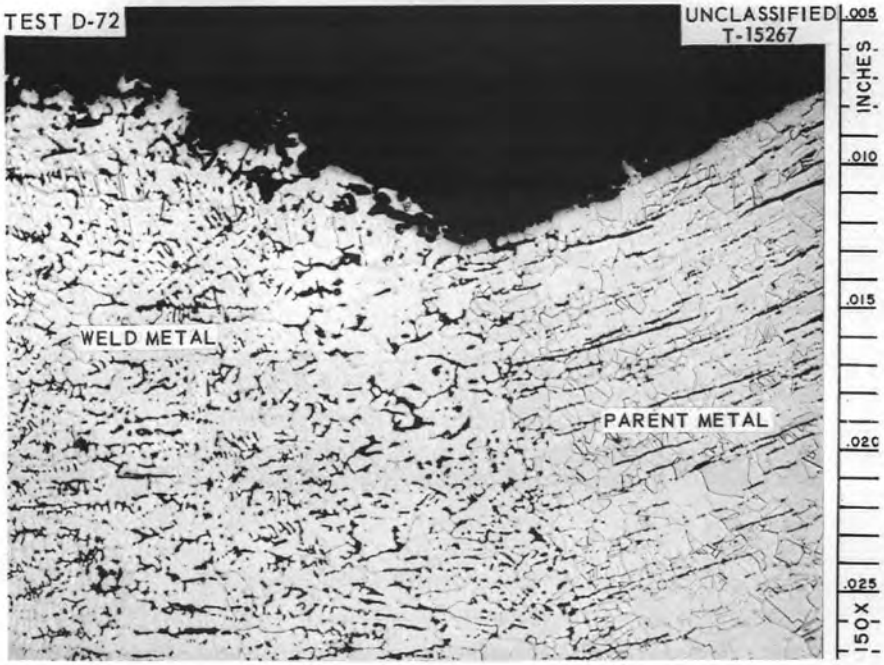


B. TYPE 309SCb STAINLESS STEEL

Fig. 5. Condition of Flat Surface on Stress Specimens After 2706 hr of Vapor Exposure in the Batch Dissolver Tank. Etched in glyceria-regia. 250X.



A. TYPE 304L STAINLESS STEEL ROOT WELD



B. TYPE 309SCb STAINLESS STEEL ROOT WELD

Fig. 6. Appearance of Weld-Parent Metal Interface of Root Welds on Stainless Steel Specimens Exposed for 2706 hr to Vapor in Batch Dissolver Tank. Etched in glyceria-regia. 150X.

the operation of the tank was an evaporation process at 110 to 115°C to remove excess nitric acid. Following this was a digestion period at 150 to 155°C to dissolve "blue" thorium oxide and to promote the destruction of the tributyl-phosphate-extractable fractions of the ruthenium fission product.

The nominal initial and final chemical compositions of process solution handled by the feed adjustment tank appear in Table 4.

Table 4. Nominal Chemical Composition of Process Solution in Feed Adjustment Tank During Development Period

Constituent	Concentration (*M*)	
	Initial	Final
HNO_3	5.0	0.5*
$Th(NO_3)_4$	1.0	4.0
$Al(NO_3)_3$	0.4	1.6
$Hg(NO_3)_2$	0.001	0.004
Fluoride	0.15	0.047

* Nitric acid deficient.

Upon completion of operations, the tank was decontaminated by the use of 58 alternate passes with nitric acid and caustic tartrate solutions. The solution temperature during decontamination was generally between 65 and 85°C. The total decontamination time, including 74 hr at room temperature, was 200 hr.

Duplicate sets of types 304L and 309SCb stainless steel were removed from the solution and vapor phases of the feed adjustment tank. A resume of the exposure history for the specimens appears in Table 5.

Table 5. Summary of Exposure History for Stress Specimens in Feed Adjustment Tank During Last Half of Development Period

Operation	Number of Runs	Exposure Time (hr)	
		Solution	Vapor
Total residence time in tank	127	6549	6549
Solution adjustment at 155°C max.[a]	53	1649	1649
Recycle solution boildown at 110°C max.[a]	16	834	834
Decontamination at 65 to 85°C	58	126	126
Holding time at room temperature		2541	0
Total active exposure time[b]	127	2609	2609

(a) Includes heating and cooling time.
(b) Holding time at room temperature not considered in total active exposure time.

The total contact time by process solutions on specimens was 5150 hr, of which 2541 hr was at room temperature and 2609 hr was with process solutions at elevated temperatures not exceeding 155°C. Corrosion rates were based upon the time at elevated temperatures rather than on the total contact time. As mentioned earlier, corrosion attack on stainless steels by simulated Thorex solutions in laboratory tests at room temperature were not greater than 1 mpy. A summary of corrosion rates is shown in Table 6.

Corrosion of Solution-Exposed Specimens. No data were available on the corrosion behavior of the solution-exposed type 304L stainless steel specimens. Upon removal of the specimen holder from the tank, it was found that the two stress assemblies were missing. Their disappearance from the holder was attributed to either a mechanical failure of the fixtures holding the assemblies or to excessive corrosion attack on the fixtures.

No stress remained on the two type 309SCb stainless steel assemblies. Release of the initially applied stress of 35,000 psi was due to loss of the fulcrum in each case, presumably as the result of severe corrosion attack. Examination of the stress specimens disclosed no indication of cracking. The stress and weld specimens were badly stained gray-brown in color. Appreciable quantities of corrosion products were in evidence;

the film weights ranged from 2 to 3 mg/cm^2. Figure 7 shows two views of one of the assemblies after defilming. The corrosion attack appeared fairly uniform with the exception of preferential attack on edge surfaces. The average corrosion rate for the duplicate sets of stress and weld specimens was 41.4 ± 4.8 mpy during the 2609-hr active exposure period. Corrosion attack on flat surfaces resulted in some roughening as shown in Fig. 8-a. There were indications of a slight preferential grain-boundary attack in a few of the examined areas, however. Severe localized attack was observed on the type 309SCb stainless steel weld metal; massive pitting and random intergranular penetration in the weld deposit are shown in Fig. 8-b. The parent metal adjacent to the weld exhibited fairly severe intergranular attack, approaching 3 to 4 mils in depth.

Table 6. Corrosion of Stainless Steels in Feed Adjustment Tank at 155°C Maximum During Last Half of Development Period

Lab. No.	Alloy Type	Exposure Phase	Specimen Type	Total Time (hr)[a]	Corrosion Rate (mpy)
D-21	304L	Solution	Assembly	2609	(b)
D-36	304L	Solution	Assembly	2609	(b)
M-45	309SCb	Solution	Stress Weld[c]	2609	46.2 36.8
M-46	309SCb	Solution	Stress Weld[c]	2609	46.3 36.4
D-3	304L	Vapor	Weld[d]	2609	95
D-10	304L	Vapor	Weld[d]	2609	100
D-55	309SCb	Vapor	Weld[c]	2609	85
M-44	309SCb[e]	Vapor	Weld[c]	2609	220

(a) Actual time that specimens were contacted by heated process solutions.
(b) Complete stress assembly missing from specimen holder.
(c) Type 309SCb stainless steel weld metal used to prepare 309SCb weld specimens.
(d) Type 308L stainless steel weld metal used to prepare 304L weld specimens.
(e) Composite specimen of types 309SCb and 347 stainless steel.

TEST M-45

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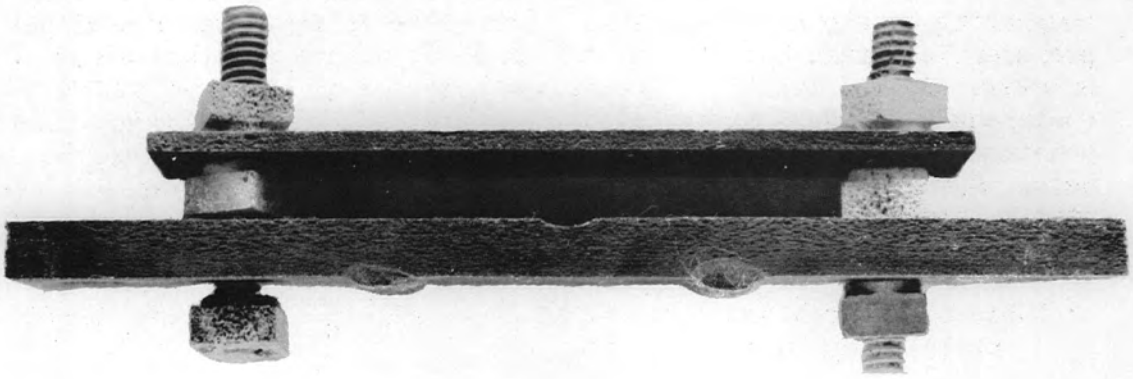
PHOTO 1737



A. SIDE VIEW

TEST M-45

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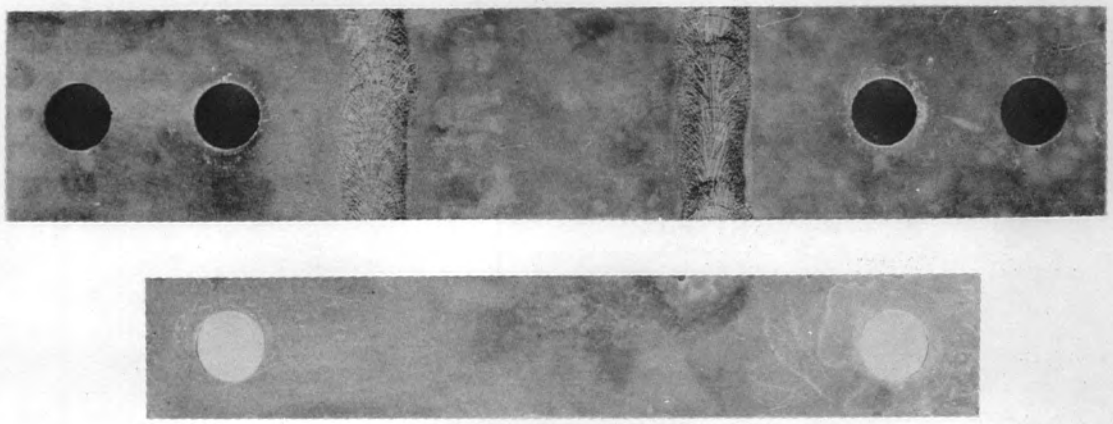
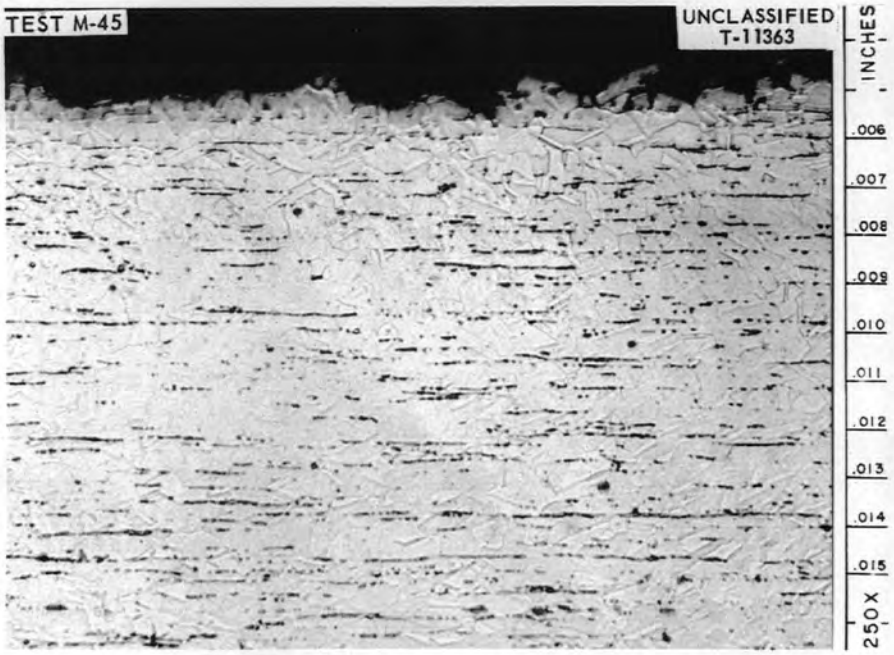
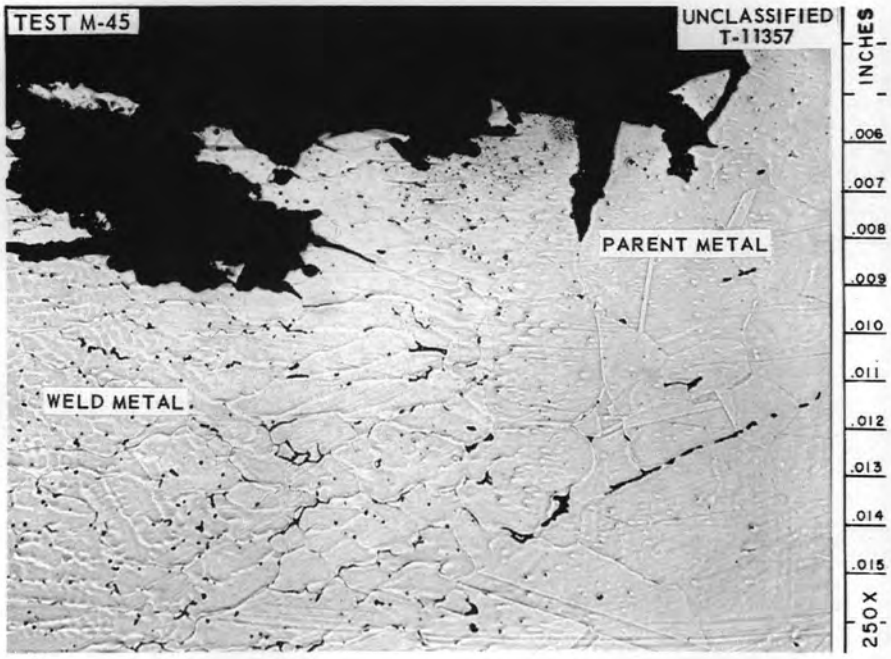


B. AS-WELDED FACE OF BASE PLATE AND TENSION SURFACE OF STRESS SPECIMEN

Fig. 7. Type 309SCb Stainless Steel Stress Assembly After 2609 hr in Solution Phase of Feed Adjustment Tank (Defilmed). 1.3X.



A. FLAT SURFACE OF STRESS SPECIMEN



B. WELD-PARENT METAL INTERFACE ON BASE PLATE

Fig. 8. Corrosion Attack on Type 309SCb Stainless Steel Exposed for 2609 hr in Solution Phase of Feed Adjustment Tank. Etched in glyceria-regia. 250X.

Corrosion of Vapor-Exposed Specimens. Corrosion attack on the vapor-exposed specimens in the feed adjustment tank was substantially greater than on the solution-exposed specimens for a similar exposure time, 2609 hr. In fact, of the duplicate sets of types 304L and 309SCb stainless steel stress assemblies that were originally placed in the vapor phase, only the welded base plate was recovered from each assembly. The other components, including the stress specimen, the fulcrum, and the two sets of studs and nuts in each assembly, had fallen into the tank as a result of unusually severe corrosion attack.

The general condition of the base plates was poor. Figure 9 shows the as-welded face of two of the specimens. The surfaces were very rough and grainy. The weld deposits in both specimens were severely attacked, the attack being characterized by channeling and grooving. An unusual behavior was exhibited by the type 309SCb stainless steel weld (Test M-44). The right end of the specimen shown in Fig. 9 underwent far more severe attack than did the major portion of the specimen. Since the base plate was prepared from three separate 2-in.-wide pieces of plate, the possibility existed that, inadvertently, an alloy other than type 309SCb was used for the excessively corroded section. A piece of the corroded section was submitted for chemical analysis; the results showed the material to be type 347 stainless steel. Obviously, this alloy was considerably less resistant to attack than the type 309SCb stainless steel portion of the specimen.

The average corrosion rate for the two type 304L stainless steel weld specimens was 97.5 + 2.5 mpy. The corrosion rate for the single all-type-309SCb specimen was 85 mpy. The composite specimen of types 309SCb and 347 stainless steel corroded at a rate of approximately 220 mpy.

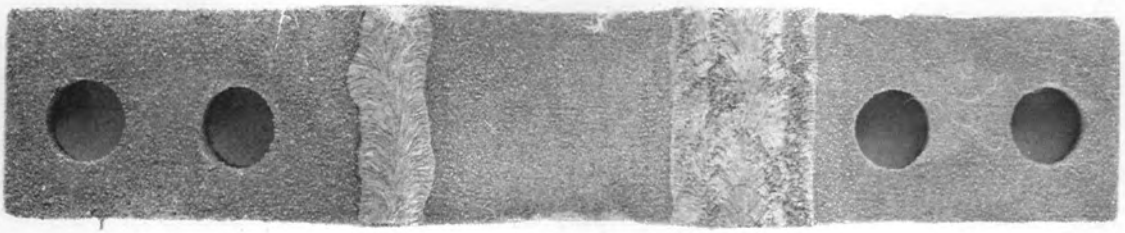
The edge surfaces of the weld specimens were severely pitted and spongy-appearing. Some preferential attack at weld-parent metal interfaces on the as-welded faces of both alloy-type specimens was observed (Fig. 10). The attack was more intense on the type 304L specimen than on the type 309SCb specimen. Preferential grain-boundary attack was found also on the parent metal adjacent to the weld deposits in both alloys.

3. BT Vapor Separator. The BT vapor separator tank is a component of the BT evaporator system, which is used to concentrate the thorium-containing solution from the uranium-thorium partition column. The separator tank is located directly above the reboiler which receives process solution containing approximately 0.25 *M* $Th(NO_3)_4$ and 0.2 *M* HNO_3. The evaporation was continued until the solution composition was about 2 *M* in $Th(NO_3)_4$ and 1.2 to 1.5 *M* in HNO_3.

The BT vapor separator is a welded tank 2 ft in diameter and 2 ft high, exclusive of the top and bottom dished heads. The body of the tank was fabricated from type 347 stainless steel; the dished top and bottom heads were made from type 304L steel.

TEST D-3

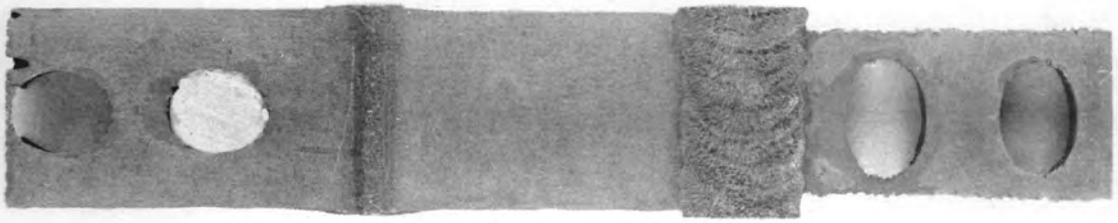
UNCLASSIFIED
PHOTO 1725



A. TYPE 304L STAINLESS STEEL

TEST M-44

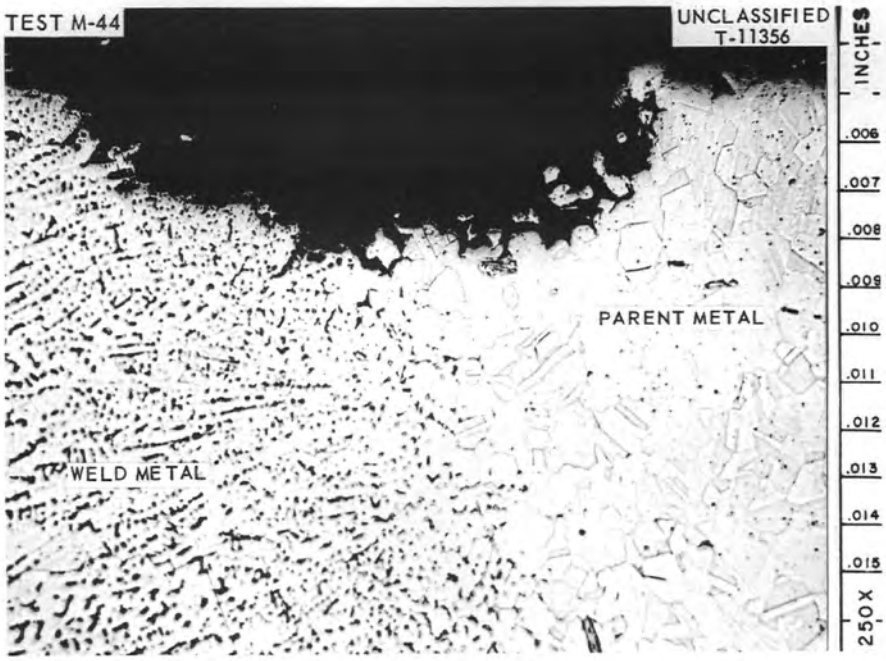
UNCLASSIFIED
PHOTO 1736



B. TYPE 309SCb STAINLESS STEEL

Fig. 9. Condition of Stainless Steel Weld Specimens After 2609 hr of Exposure in the Vapor Phase of the Feed Adjustment Tank. 1.3X.

A. TYPE 304L STAINLESS STEEL



B. TYPE 309SCb STAINLESS STEEL

Fig. 10. Weld-Parent Metal Attack on Stainless Steel Specimens Exposed for 2609 hr in Vapor Phase of Feed Adjustment Tank. Etched in glyceria-regia. 250X.

During operation, the temperature in the vapor phase was approximately 115°C. Saturated steam was the major constituent of the vapor phase. However, the vapor condensate contained, nominally, 0.05 *M* HNO_3. The total operating time for the BT vapor separator was 5788 hr, including 22 hr for decontamination. During 3312 hr of this period, the process solution contained small amounts of the fluoride and mercuric dissolver catalysts. During the remaining operational time, 2454 hr, the process solution was free of catalysts. The 22-hr decontamination period consisted of treating the tank with alternate passes of caustic tartrate and nitric acid solutions at temperatures from 70 to 115°C.

A single stress assembly of type 304L stainless steel and duplicate assemblies of type 347 steel were placed in the upper central region of the BT vapor separator. Upon completion of evaporator operation, examination of the specimen holder removed from the vessel disclosed that all components except the welded base plate in each assembly had disappeared. Loss of the components was again attributed to unusually severe corrosion attack. The base plates were dull brown in color and were very grainy. The attack was more severe on the type 304L stainless steel specimen. Figure 11 shows a low-magnification photograph of the as-welded face on the type 304L specimen and one of a type 347 stainless steel specimen.

No significant buildup of corrosion products was found on any of the specimens; film weights ranged from 0.4 to 1.2 mg/cm^2. A summary of corrosion rates for the three weld specimens appears in Table 7. The rates were based upon an operating time of 5766 hr plus a 22-hr decontamination period.

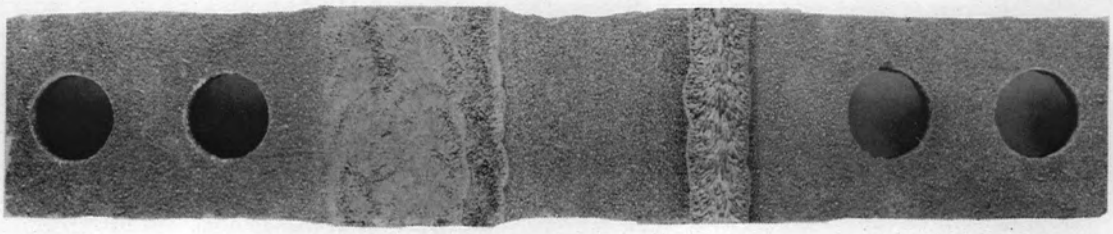
Table 7. Corrosion of Stainless Steels in BT Vapor Separator at 115°C Maximum During Development Period

Lab. No.	Alloy Type	Specimen Type[a]	Total Time (hr)	Corrosion Rate (mpy)
D-35	304L	Weld[b]	5788[c]	54.5
D-44	347	Weld[d]	5788	20.8
D-53	347	Weld[b]	5788	30.1

(a) Control and stress specimens lost due to excessive corrosion.
(b) Heliarc-welded with type 308L rod.
(c) Includes 22 hr of decontamination time.
(d) Heliarc-welded with type 347 rod.

TEST D-35

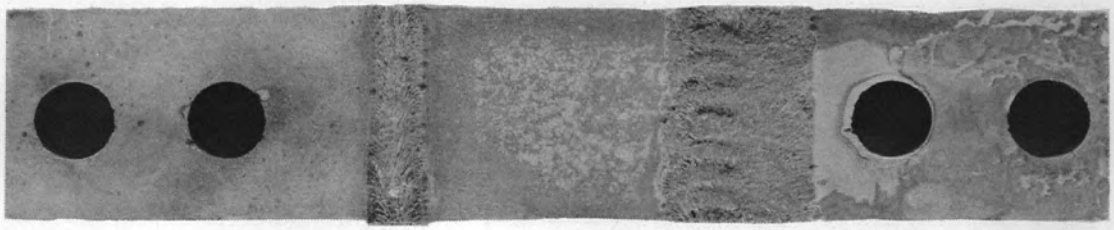
UNCLASSIFIED
PHOTO 1729



A. TYPE 304L STAINLESS STEEL

TEST D-44

UNCLASSIFIED
PHOTO 1732



B. TYPE 347 STAINLESS STEEL

Fig. 11. Stainless Steel Weld Specimens After 5788 hr Exposure in the BT Vapor Separator. 1.3X.

The single weld specimen of type 304L stainless steel corroded at a rate of 54.5 mpy. The average rate for the duplicate specimens of type 347 stainless steel was 25.4 ± 4.7 mpy.

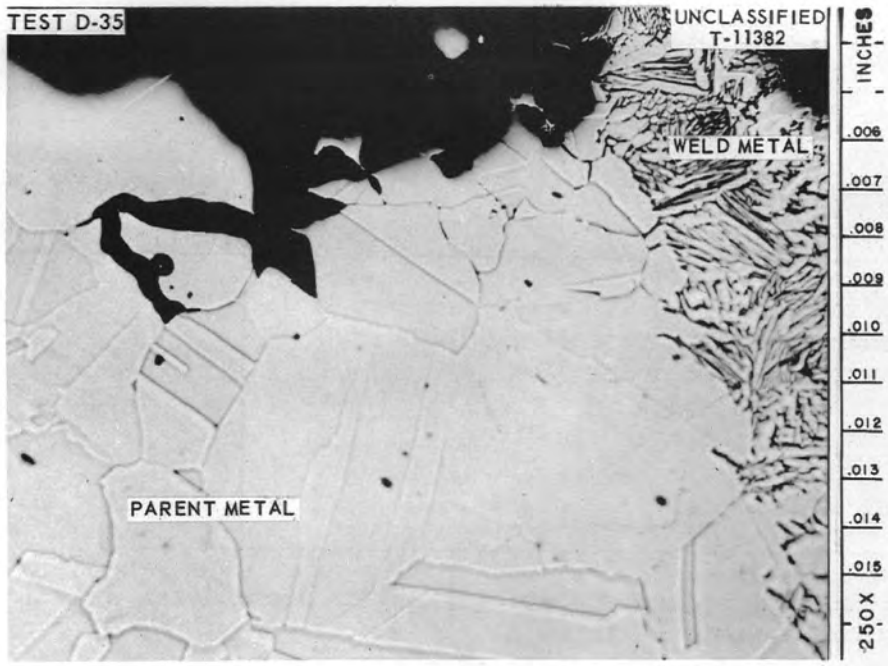
Metallographic examination of flat surfaces disclosed intergranular attack on the type 304L stainless steel which penetrated to a depth of 6 mils in some areas. The surfaces of the type 347 stainless steel exhibited slight preferential grain-boundary attack, which did not exceed 1 mil in depth. Figure 12 shows the condition of the weld-parent metal interface on the two alloys; the sections were made on the as-welded face of the specimens. No preferential attack was observed in the immediate heat-affected zone of the type 304L stainless steel; intergranular attack was found some distance away from the heat-affected zone in the parent metal, however. The weld metal, type 308L stainless steel, was badly channeled. There appeared to be a mild, knife-line attack on the type 347 stainless steel weld specimen as shown in Fig. 12; the depth of the attack was between 3 and 4 mils. By visual observation, no difference between the types 308L and 347 stainless steel weld metal used in the two 347 stainless steel weld specimens could be distinguished, both types of weld metal were severely roughened and channeled.

4. A-Column Feed Tank. The A-column feed tank, constructed of type 304L stainless steel, is used as a storage tank for feed solution to the extraction column, where the thorium-232 and uranium-233 are extracted by the tributyl phosphate solvent. The process solution entering the A-column feed tank from the feed adjustment tank, after dilution with water, had a nominal chemical composition of 0.05 to 0.2 *M* HNO_3 (acid deficient), 1.5 *M* $Th(NO_3)_4$, 0.55 *M* $Al(NO_3)_3$, 0.002 *M* $Hg(NO_3)_2$, and 0.028 *M* NaF. The latter two constituents were present only in irradiated process solutions.

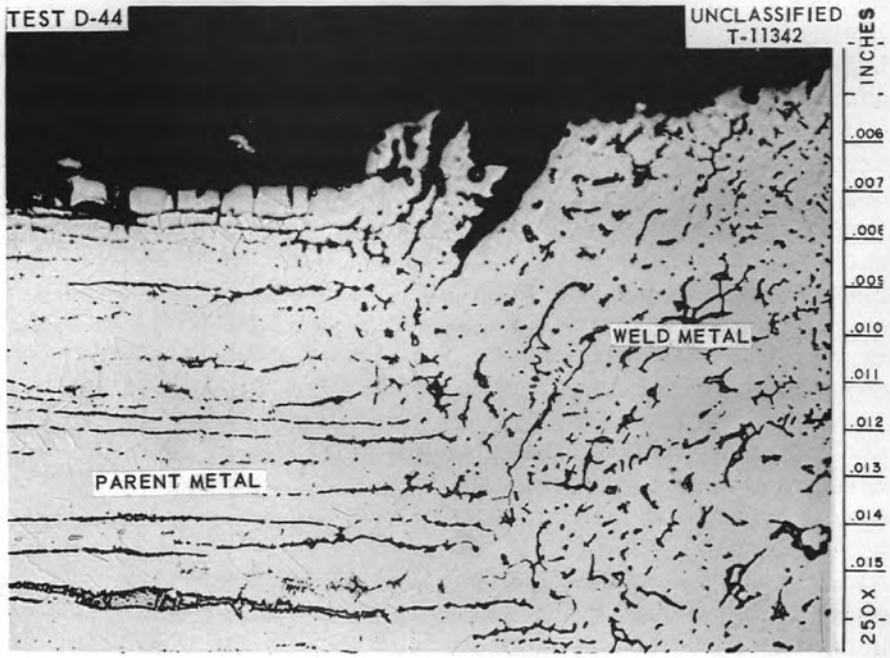
Table 8 summarizes the exposure history for specimens in the A-column feed tank. Specimens were present in the solution phase only. Generally, the temperature of the process solution ranged from 30 to 60°C; for several brief periods of operation, the tank was heated to 100°C.

A total of 43 alternate passes with nitric acid and with caustic tartrate solutions were used to decontaminate the tank. Twenty-two of the passes were conducted at room temperature; the remaining passes were made at temperatures between 70 and 100°C.

Test specimens consisted of a single stress assembly of type 304L stainless steel since the feed tank was fabricated from this alloy, and also two stress assemblies of type 347 stainless steel. The latter alloy was included to obtain corrosion data which would be applicable to the A-extraction column which was fabricated from type 347 stainless steel.



A. TYPE 304L STAINLESS STEEL



B. TYPE 347 STAINLESS STEEL

Fig. 12. Weld-Parent Metal Interface of Stainless Steel Specimens Exposed for 5788 hr in Vapor Phase of BT Vapor Separator. Etched in glyceria-regia. 250X.

Table 8. Summary of Exposure History for Solution-Exposed Stress Specimens in A-Column Feed Tank During Development Period

Operation[a]	Exposure Time (hr)
Irradiated feed solution	3513
Irradiated recovered feed solution	940
Nonirradiated feed solution[b]	1352
Water flushes, etc.	1182
Decontamination at 40 to 100°C	320
Total exposure time	7307

(a) The bulk of the operating time was accumulated with process solutions at 30 to 60°C.
(b) No fluoride or mercuric catalysts present.

The as-removed condition of the three assemblies was excellent; surfaces were lustrous and metallic-appearing. No signs of stress-corrosion cracking were observed. The assemblies were dismantled and the individual components defilmed; corrosion rates are in Table 9.

The corrosion resistance of both alloys was excellent; observed rates were not in excess of 0.1 mpy. There was no localized corrosion observed on any of the specimens. Based upon the data, it was evident that the construction materials for both the A-column feed tank and the A-column itself were completely resistant to the environment. The data also further substantiated previous laboratory corrosion data which showed near-negligible corrosion rates for the stainless alloys in simulated Thorex process solutions at or slightly above room temperature.

5. BTC Catch Tank. The thorium product from the BT evaporator system was stored at room temperature in two type 347 stainless steel catch tanks. The solution composition was approximately 2 *M* $Th(NO_3)_4$ and 1.8 *M* HNO_3.

A single stress assembly of type 304L stainless steel and duplicate specimens of type 347 stainless steel were exposed in the solution phase of one of the BTC catch tanks (P-3) for 5135 hr. A total of 183 hr of the exposure represented decontamination time with nitric acid and caustic tartrate solutions at temperatures not in excess of 85°C.

Table 9. Corrosion of Stainless Steels in A-Column Feed Tank at 30 to 60°C During Development Period

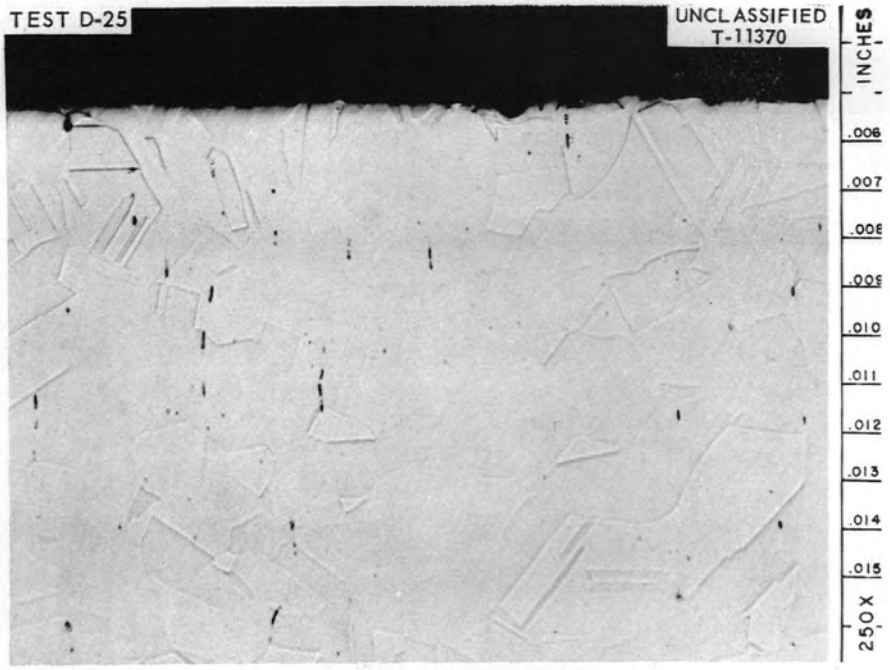
Lab. No.	Alloy Type	Exposure Phase	Specimen Type	Total Time (hr)	Corrosion Rate (mpy)
D-32	304L	Solution	Control	7307	<0.1
			Stress		<0.1
			Weld[a]		<0.1
D-43	347	Solution	Control	7307	<0.1
			Stress		<0.1
			Weld[b]		<0.1
D-52	347	Solution	Control	7307	0.1
			Stress		<0.1
			Weld[a]		<0.1

(a) Heliarc-welded with type 308L rod.
(b) Heliarc-welded with type 347 rod.

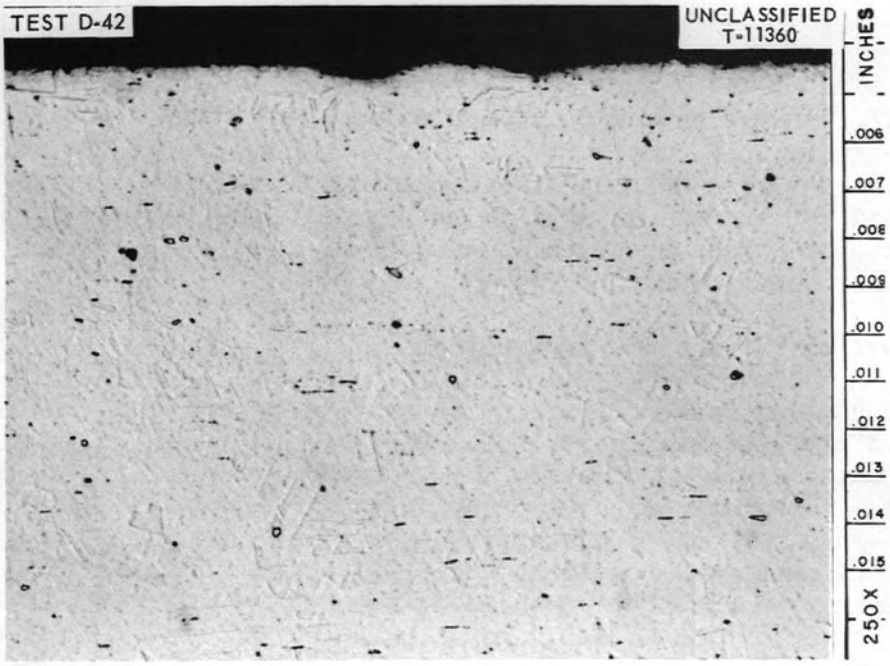
Examination of the stress specimens showed no stress-corrosion cracking. All surfaces were metallic and lustrous. The defilmed corrosion rates for the individual components in the assemblies are listed in Table 10. The corrosion rate for any of the components in the three stress assemblies did not exceed 0.1 mpy. Metallographic examination of the flat surface of a stress specimen of each alloy type disclosed the attack to be uniform as shown in Fig. 13.

B. Corrosion During the Production-Development Period

1. Batch Dissolver Tank. Duplicate stress assemblies of types 304L and 309SCb stainless steel were exposed in both solution and vapor phases of the batch dissolver tank during the production and the development periods. A summary of the exposure history for the specimens during the combined periods of operation appears in Table 11. Although for the solution-exposed specimens the total contact time by process and decontamination solutions was 11,479 hr, only 3340 hr (including 187 hr for decontamination) were accumulated at temperatures above room temperature. For previously discussed reasons, the corrosion rates were calculated on the basis of 3340 hr. The vapor-phase exposure time, likewise, was 3340 hr which included the 187 hr for decontamination. The final composition of the dissolver solution has been stated in a previous section.



A. TYPE 304L STAINLESS STEEL



B. TYPE 347 STAINLESS STEEL

Fig. 13. Condition of Flat Surface on Stress Specimens After 5135 hr of Solution Exposure in the BTC Catch Tank. Etched in glyceria-regia. 250X.

Table 10. Corrosion of Stainless Steels in BTC Catch Tank at Room Temperature During Development Period

Lab. No.	Alloy Type	Exposure Phase	Specimen Type	Total Time (hr)	Corrosion Rate (mpy)
D-25	304L	Solution	Control	5135	<0.1
			Stress		<0.1
			Weld[a]		<0.1
D-42	347	Solution	Control	5135	<0.1
			Stress		<0.1
			Weld[b]		<0.1
D-51	347	Solution	Control	5135	0.1
			Stress		<0.1
			Weld[a]		0.1

(a) Heliarc-welded with type 308L rod.
(b) Heliarc-welded with type 347 rod.

Table 11. Summary of Exposure History for Stress Specimens in Batch Dissolver Tank During Production-Development Period

Operation	Number of Runs	Exposure Time (hr) Solution	Exposure Time (hr) Vapor
Total residence time in tank	144	14,634	14,634
Thorex dissolvings at 115°C max.[a]	89	3,054	3,054
Neptex dissolvings at 115°C max.[a]	15	99	99
Decontamination at 40 to 110°C	40	187	187
Holding time at room temperature		8,139	0[c]
Total active exposure time[b]	144	3,340	3,340

(a) Includes heating and cooling time.
(b) Holding time at room temperature not considered in total active exposure time.
(c) No vapor contact time included when process solutions were at room temperature.

The four stress assemblies exhibited signs of severe corrosion damage upon removal from the tank. In each assembly, the fulcrum was missing as a result of the attack, thereby relieving the initially applied stress of 35,000 psi. None of the stress specimens were observed to have cracks. All surfaces of the assembly components were heavily stained a dark gray-brown color. There were no bulky corrosion-product deposits on the solution-exposed specimens; film weights ranged from less than 0.1 to 0.3 mg/cm^2. Corrosion-product accumulation was more pronounced on the vapor-phase specimens, with film weights varying from 1 to 9 mg/cm^2. It was speculated, however, in view of the grainy appearance of the specimens, that the high film weights may have been due in part to dislodgment of metal grains during the cathodic defilming. A summary of the corrosion rates appears in Table 12.

Table 12. Corrosion of Stainless Steels in Batch Dissolver Tank at 115°C Max. During Production-Development Period

Lab. No.	Alloy Type	Exposure Phase	Specimen Type	Total Time (hr)	Corrosion Rate (mpy)
D-5	304L	Solution	Stress Weld[b]	3340[a]	27.8 23.0
D-57	309SCb	Solution	Stress Weld[c]	3340	16.6 16.3
D-4	304L	Vapor	Stress Weld[b]	3340	54.2 53.3
D-56	309SCb	Vapor	Stress Weld[c]	3340	39.9 43.7

(a) Contact time by process solutions above room temperature.
(b) Type 308L metal used for Heliarc-welded 304L stainless steel specimens.
(c) Type 309SCb metal used for Heliarc-welded 309SCb stainless steel specimens.

Corrosion of Solution-Exposed Specimens. The corrosion resistance of type 309SCb stainless steel was approximately 50% better than that of type 304L stainless steel during the 3340-hr exposure period. The average rate for the former was 16.4 ± 0.2 mpy, as compared with a

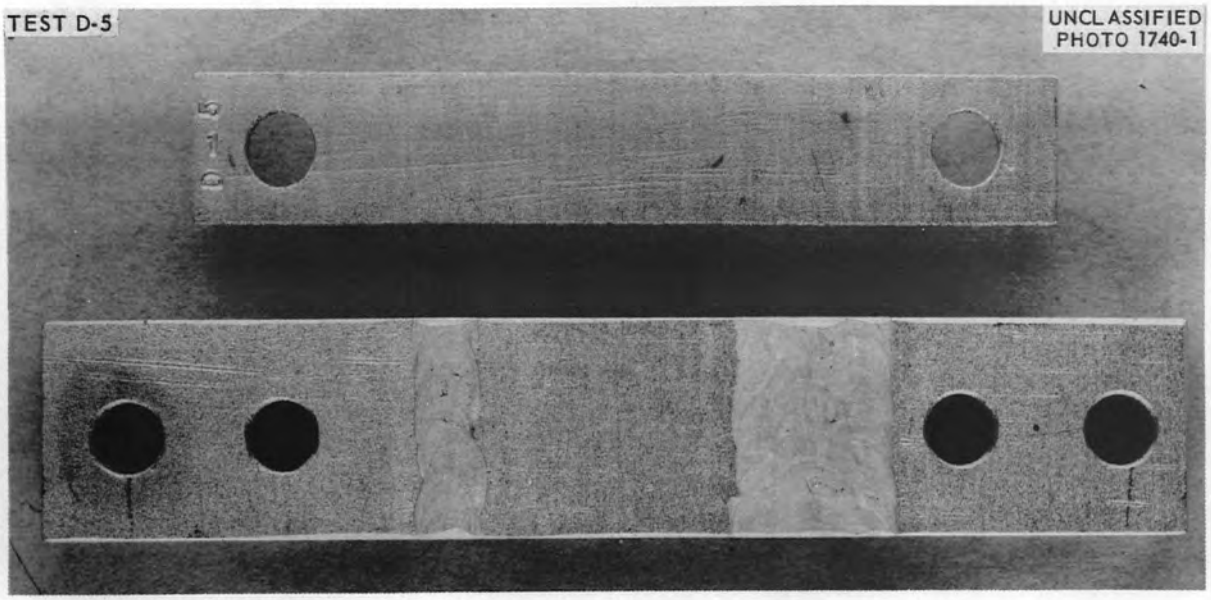
rate of 25.4 ± 2.4 mpy for the type 304L stainless steel. Figures 14 and 15 are photographs of the two alloy-type specimens after cathodic defilming. Edge corrosion was much more pronounced on the type 304L stainless steel than on the type 309SCb stainless steel. The end-grain attack on both alloys was much the same as shown in Fig. 2.

Uniform corrosion was experienced by the flat surfaces of the stress specimens as shown in Fig. 16. The surfaces were unusually smooth and free from preferential grain boundary attack.

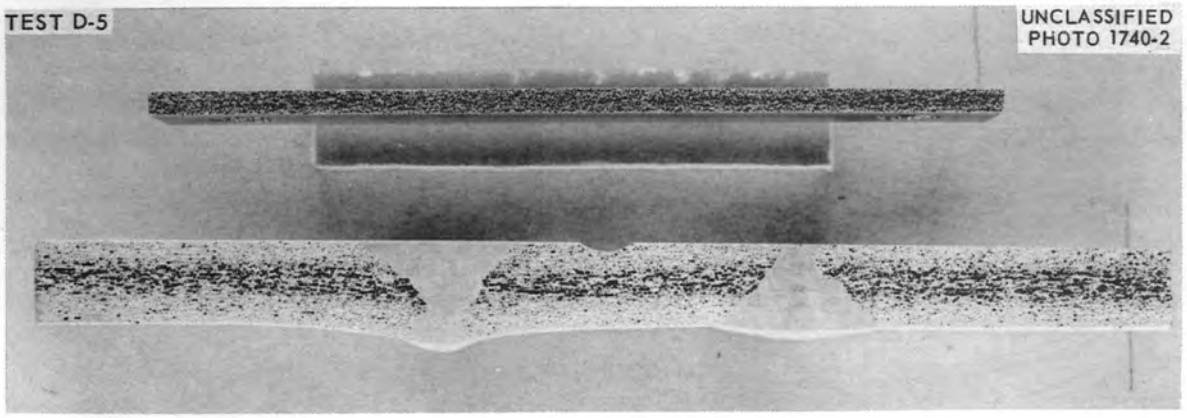
The heat-affected zones in the type 304L weld specimen were not subject to preferential corrosion attack, as indicated in Fig. 17. The metallographic examination was made on the as-welded face of the specimen. Type 309SCb stainless steel, on the other hand, was very subject to preferential corrosion at weld-parent metal interfaces, as shown in Fig. 18. In the face weld, Fig. 18-a, the attack was confined to the heat-affected zone and could be classified as knife-line corrosion. The depth of the penetration was approximately 25 mils. The attack was of a different nature in the root weld, as shown in Fig. 18-b. Some preferential attack was evident at the weld-parent metal interface. However, the weld metal was also involved in the attack as clearly shown in the photomicrograph. Both visual and metallographic examination confirmed the fact that the corrosion resistance of the weld metal was decidedly inferior to that of the parent metal. The severity of the attack on the type 309SCb stainless steel weld metal is shown in Fig. 19. Grain boundaries were highly susceptible. Type 308L stainless steel weld metal, on the other hand, was equally resistant to corrosion as was the type 304L parent metal, as shown in Fig. 17. The attack was uniform in both cases.

Corrosion of Vapor-Exposed Specimens. For a comparable exposure period at elevated temperatures, 3340 hr, the intensity of corrosion attack on the vapor-phase specimens was approximately two to three times greater than that experienced by the solution-exposed specimens. The average rate for type 304L stainless steel was 53.7 ± 0.5 mpy; the rate for type 309SCb stainless steel was somewhat lower, 41.8 ± 1.9 mpy. The type 304L stress and weld specimens exhibited extremely grainy surfaces. Edge-corrosion attack was very pronounced on both specimens. Flat surfaces of the type 309SCb stainless steel specimens showed a pickled finish but no grainy characteristics. Edge corrosion was appreciably less severe than was observed on the type 304L stainless steel specimens. The general condition of specimens of both alloys was analogous to that shown in Fig. 14 and 15 except that the attack was more intensified in all instances.

The stress specimen of each alloy was sectioned for metallographic examination of the flat surfaces; the results appear in Fig. 20. Attack on the 304L stainless steel produced a highly roughened surface.

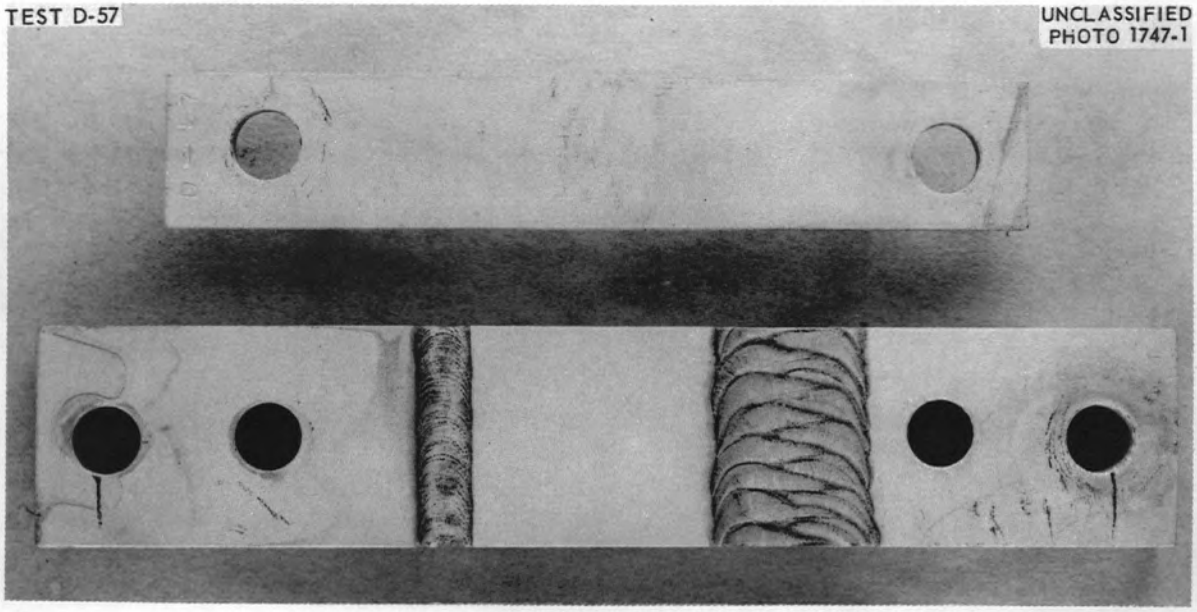


A. TENSILE SPECIMEN AND AS-WELDED FACE OF WELD SPECIMEN

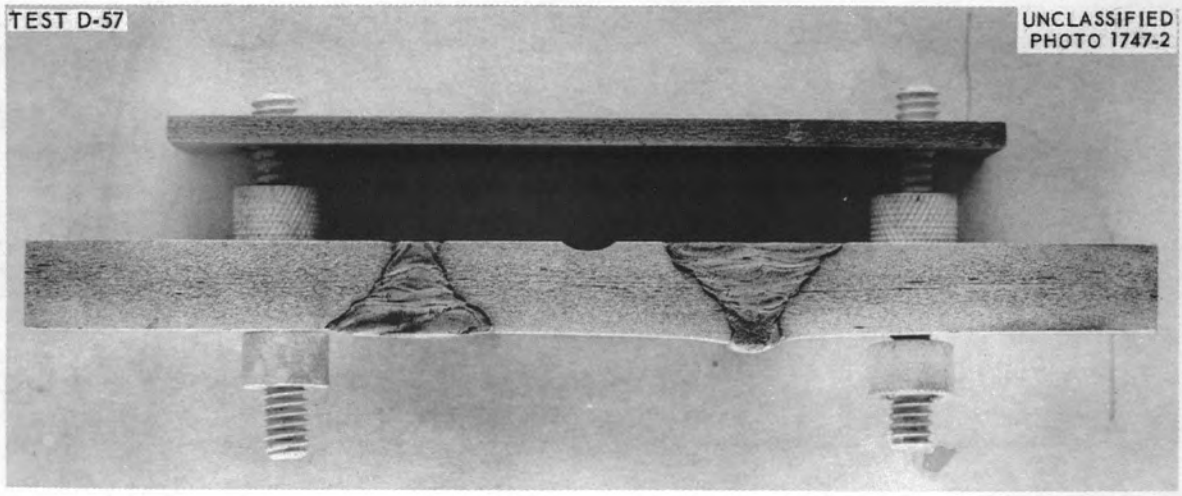


B. SIDE VIEW OF TENSILE AND WELD SPECIMENS

Fig. 14. Type 304L Stainless Steel After 3340 hr of Exposure in the Solution Phase of the Batch Dissolver Tank. 1.3X.

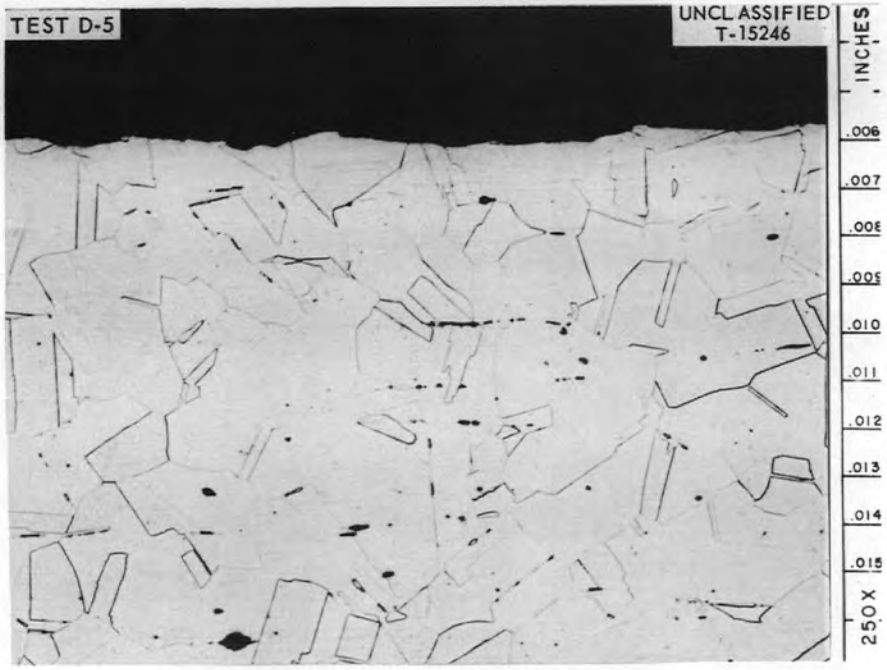


A. TENSILE SPECIMEN AND AS-WELDED FACE OF WELD SPECIMEN

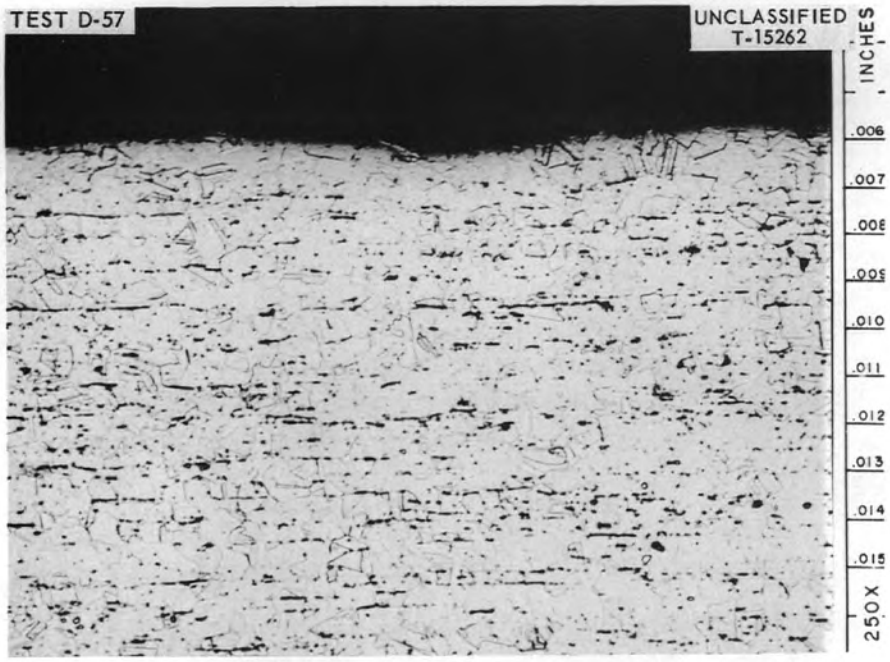


B. SIDE VIEW OF TENSILE AND WELD SPECIMENS

Fig. 15. Type 309SCb Stainless Steel After 3340 hr of Exposure in the Solution Phase of the Batch Dissolver Tank. 1.3X.

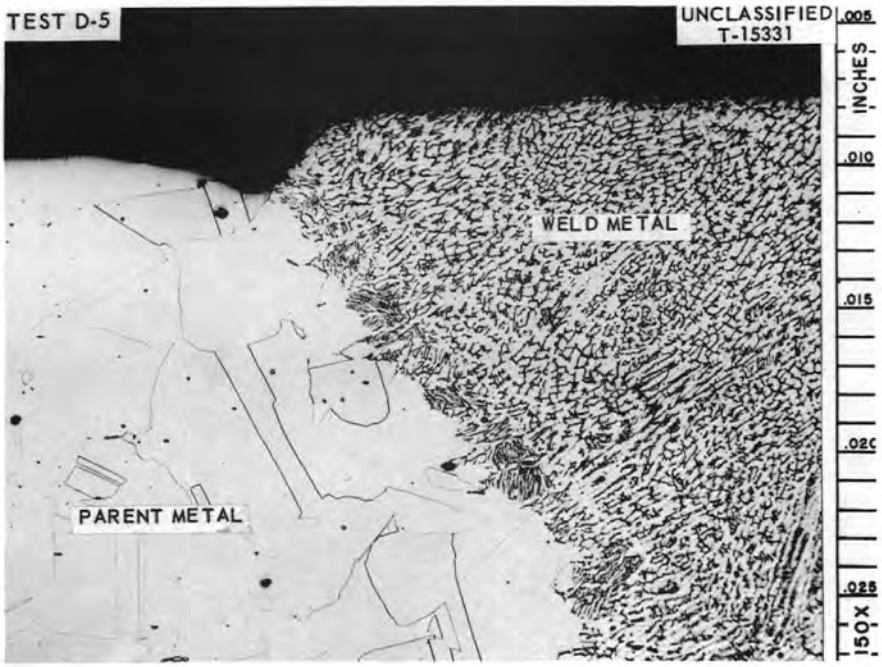


A. TYPE 304L STAINLESS STEEL

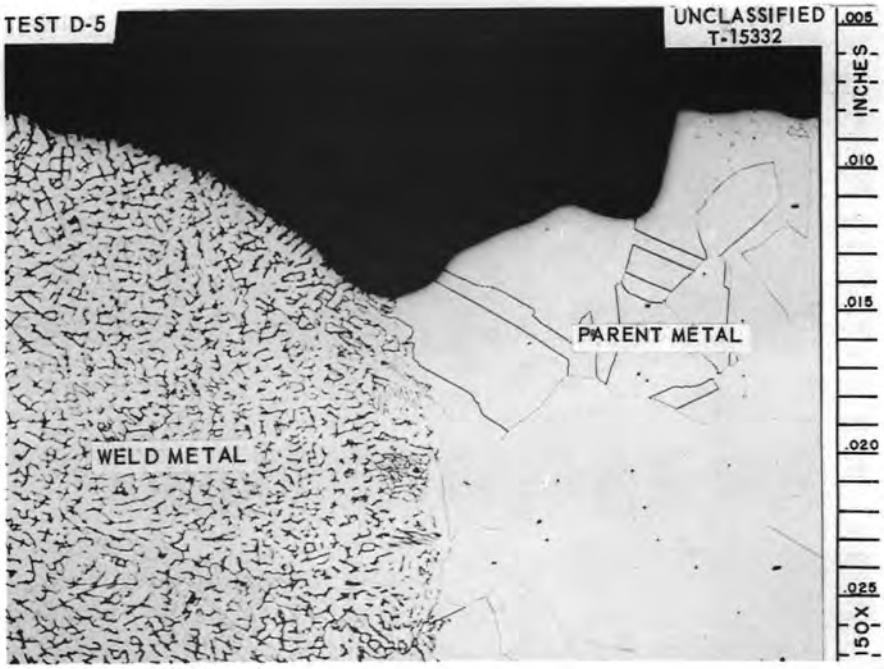


B. TYPE 309SCb STAINLESS STEEL

Fig. 16. Condition of Flat Surface on Stress Specimens After 3340 hr of Solution Exposure in the Batch Dissolver Tank. Etched in glyceria-regia. 250X.

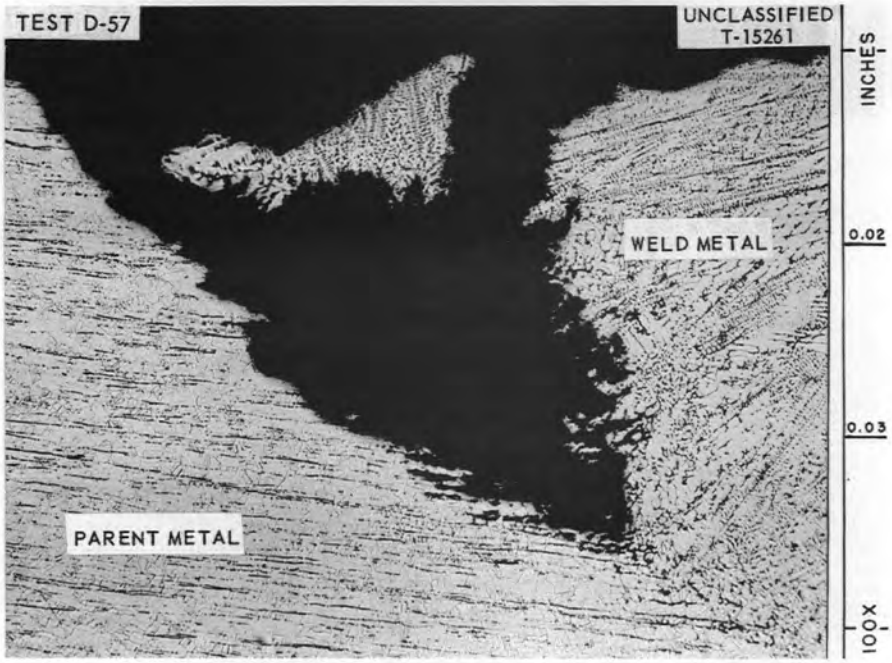


A. FACE WELD

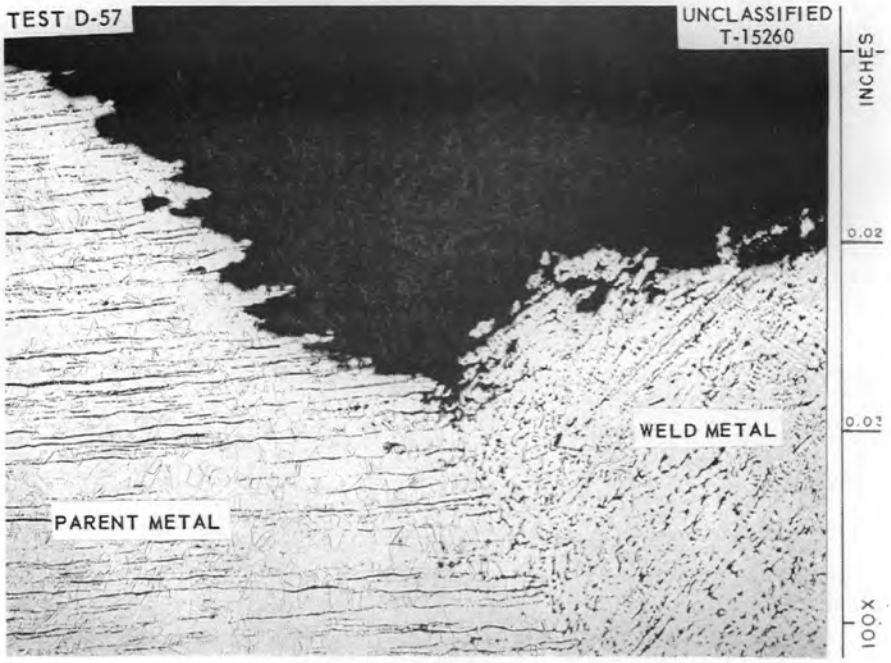


B. ROOT WELD

Fig. 17. Weld-Parent Metal Interfaces on Type 304L Stainless Steel Specimen After 3340 hr of Solution Exposure in Batch Dissolver Tank. Etched in glyceria-regia. 150X.



A. FACE WELD



B. ROOT WELD

Fig. 18. Weld-Parent Metal Interfaces on Type 309SCb Stainless Steel Specimen After 3340 hr of Solution Exposure in Batch Dissolver Tank. Etched in glyceria-regia. 100X.

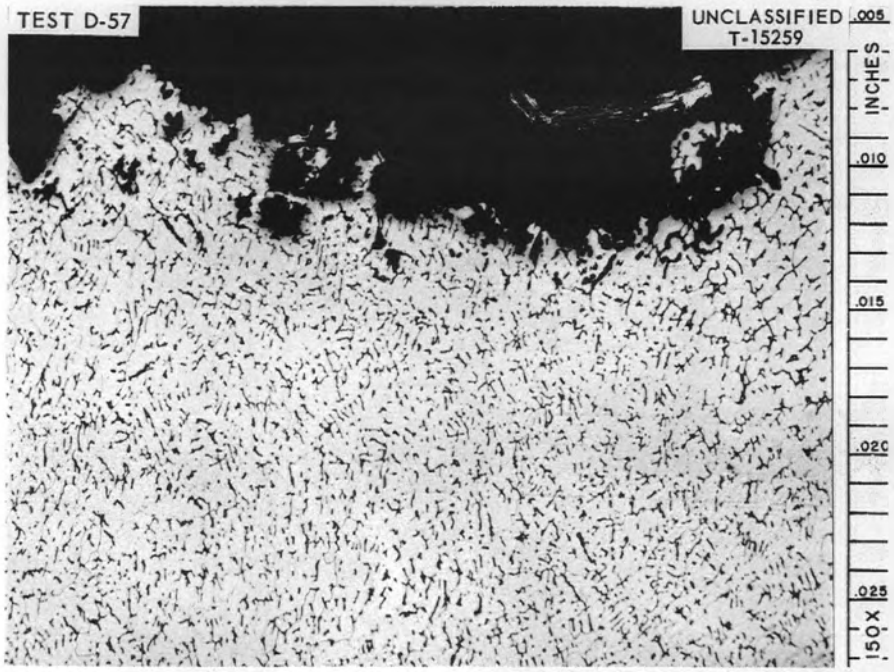
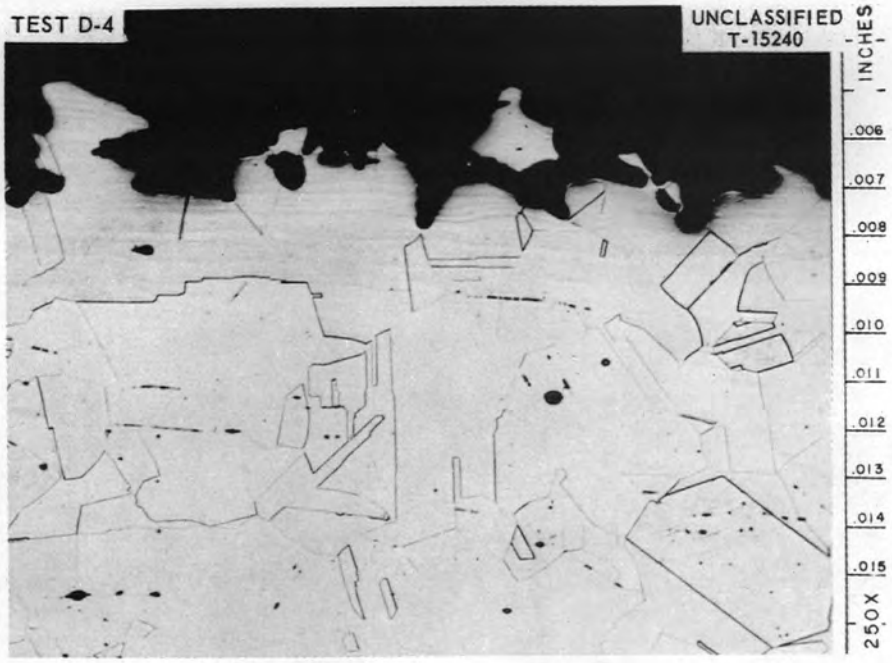
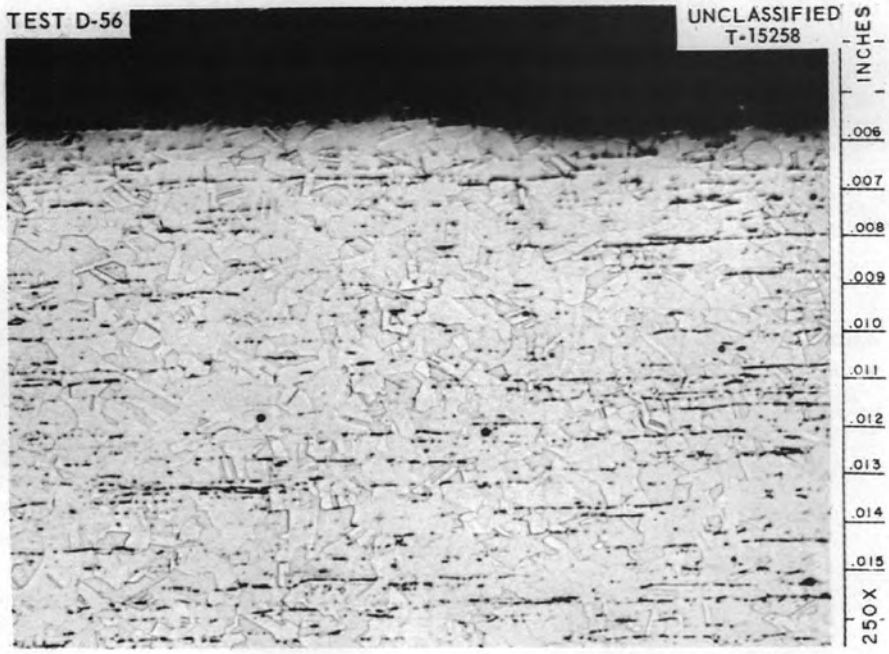


Fig. 19. Attack on Type 309 SCb Stainless Steel Weld Metal After 3340 hr Solution Exposure in Batch Dissolver Tank. Etched in glyceria-regia. 150X.



A. TYPE 304L STAINLESS STEEL



B. TYPE 309SCb STAINLESS STEEL

Fig. 20. Flat Surfaces of Stress Specimens After 3340 hr of Exposure in the Vapor Phase of the Batch Dissolver Tank. Etched in glyceria-regia. 250X.

The attack was not specifically preferential at grain boundaries, however. In many instances, the body of a grain was subject to preferential corrosion. The total penetration was between 2 and 3 mils. The finer-grained type 309SCb stainless steel was attacked uniformly on flat surfaces. Edge corrosion on the specimen produced pits up to 7 mils in depth. Pitting due to edge corrosion on the type 304L specimen was considerably more intensive, with pit depths of 20 mils common.

The weld specimens were carefully examined for signs of localized corrosion at the weld-parent metal interface. The type 304L stainless steel specimen showed a very mild preferential attack along the face weld, which involved both weld metal (type 308L) and parent metal. No preferential attack was found along the root weld. Both the face and root welds on the type 309SCb specimen were free of such attack. The type 309SCb stainless steel weld metal was heavily channeled, to a depth of 12 mils in some areas, as a result of corrosion attack. A similar but much less drastic attack was noted on the type 308L weld metal.

2. BT Vapor Separator. The function and a description of the types 304L-347 stainless steel BT vapor separator were reported in a previous section. Three stainless steel stress assemblies, one of type 304L and two of type 347, remained in the separator during the combined production-development period. Upon completion of operations, the specimens were removed for examination. The total exposure time was 6698 hr at temperatures between 100 and 115°C, including 32 hr with decontamination solutions at temperatures from 70 to 115°C. A total of 910 hr was accumulated during the production period; the remaining time was accumulated during the development period.

The three assemblies corroded so severely that the only components remaining on the support rods in the tank were the weld specimens, and they were in extremely poor condition, as shown in Fig. 21 and 22. The type 304L stainless steel specimen, welded with type 308L rod, corroded at a rate of 30.1 mpy during the 6698-hr period. The flat surfaces were very grainy in appearance, and unusually severe edge corrosion was prevalent (Fig. 21). Visually, the type 308L weld metal was more resistant than the parent metal. No preferential attack at weld-parent metal interfaces was detected.

The behavior of the two type 347 stainless steel weld specimens was most unusual, to say the least, as shown in Fig. 22. Judging from the marked difference in attack on various sections of the specimens, it was concluded that a mix-up in materials had occurred during specimen preparation. As discussed earlier, the weld specimens were prepared from three 2-in.-wide plates, each of which was 12 in. in length.

TEST D-13

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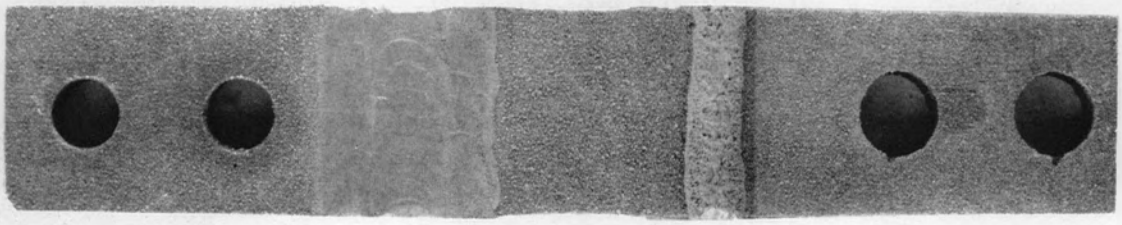

A. AS-WELDED FACE

TEST D-13

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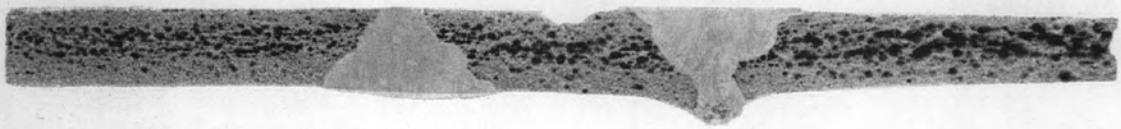

B. SIDE VIEW

Fig. 21. Type 304L Stainless Steel Weld Specimen After 6698 hr of Vapor Exposure in the BT Vapor Separator. 1.3X.

TEST D-47, D-38

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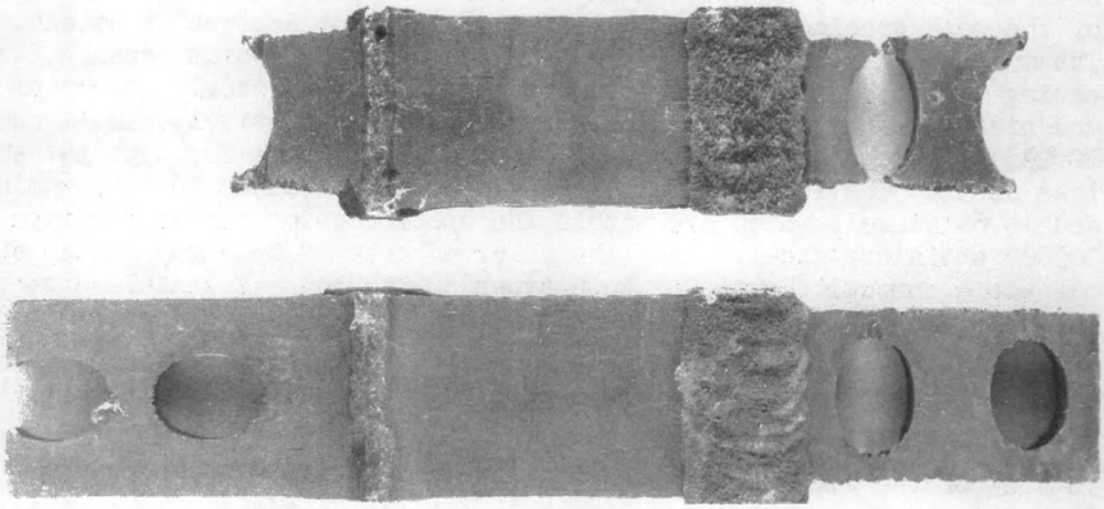

A. AS-WELDED FACE

TEST D-47, D-38

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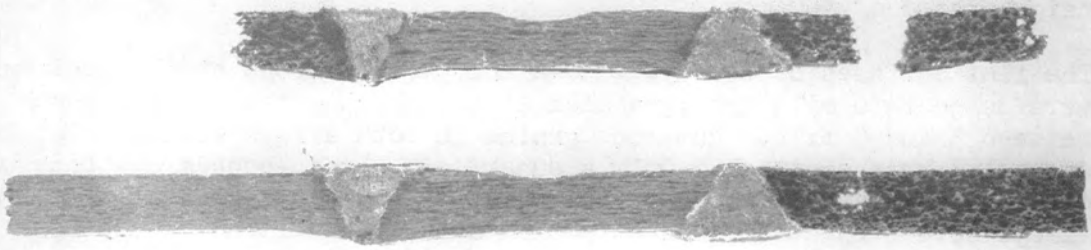

B. SIDE VIEW

Fig. 22. Type 347 Stainless Steel Weld Specimens After 6698 hr of Vapor Exposure in the BT Vapor Separator. 1.3X.

During welding, the plates were placed side by side, lengthwise. After welding, 1-in.-wide specimens were cut across the 6-in.-width dimension. Weld specimens of type 304L, 309SCb, and 347 stainless steel were prepared at the same time, and it is conceivable that a number of the 2-in.-wide strips could have become mixed prior to welding.

Sections for spectrographic analysis were therefore cut from portions of the weld specimen (D-38) that showed different degrees of attack. The more heavily corroded section was shown to be niobium-bearing, indicating the alloy to be type 309SCb or 347 stainless steel. Chromium and nickel contents of the same section were, respectively, 18.1% and 10.2%; both results are within the composition ranges for type 347 stainless steel. The less severely attacked metal contained 22.8% chromium and 14.6% nickel, which are within the specification ranges for type 309SCb stainless steel. Thus the observed rate of 63.5 mpy on the specimen was a composite rate for both types 309SCb and 347 stainless steel. The rate would have been significantly higher had the weld specimen been fabricated entirely from type 347 stainless steel, and appreciably lower had the specimen been prepared exclusively from type 309SCb stainless steel.

In view of the similarity of the companion specimen (test D-47 in Fig. 22), it was concluded that a material mix-up had occurred also in the preparation of this specimen. Both ends were attacked severely and were therefore assumed to be type 347 stainless steel. The center portion underwent less drastic attack, and it was assumed to be type 309SCb stainless steel. As shown in Fig. 22, a portion of the type 347 stainless steel end was missing as received from the pilot plant; the corrosion rate, determined by the weight-loss method, was placed in the neighborhood of 150 mpy.

The flat surfaces of the types 304L and 347 stainless steel specimens were subject to mild intergranular attack which extended to a depth between 3 and 5 mils. Numerous grains in both alloys were completely encircled by the attack. Only a superficial grain-boundary attack was observed on flat surfaces of the type 309SCb stainless steel. The alloys were subject to edge-corrosion attack, the least severe of which was experienced by the type 309SCb stainless steel portions of the specimens.

Knife-line corrosion attack was not observed on any of the weld specimens, and in all cases, as shown in Figs. 21 and 22, the weld metal appeared more resistant to attack than the base metal.

4. DISCUSSION OF RESULTS

A summary of the average corrosion rates for types 304L and 309SCb stainless steel, and in a few cases type 347 stainless steel, exposed in the various Thorex pilot plant process vessels is given in Table 13. The reported exposure periods include the time at operating temperature for the particular process vessel, the time required for heating and cooling process solution, and the time required to decontaminate the vessel.

One consistent behavior exhibited by both types 304L and 309SCb stainless steel was that, in those process vessels where both solution- and vapor-phase corrosion was examined, the attack in the vapor phase was generally about twice as intense as it was in the solution phase. This was the case for the batch dissolver and feed adjustment tanks during the development period and the batch dissolver tank during the production-development period. Vapor-phase rates higher than solution-phase rates were obtained also for the feed adjustment tank during the production period of operation.[1] In the present study, vapor-phase specimens were not exposed in the A-column feed tank or in the BTC catch tank. However, since the operating temperature for both tanks was not above 60°C and since solution-exposed specimens corroded at rates less than 0.1 mpy, it was believed that vapor-phase attack would not be significant in the two vessels. There was no solution-phase environment in the BT vapor separator.

The present investigation as well as the previous one for the Thorex pilot plant[2] disclosed that of the vessels containing corrosion specimens, substantial attack was encountered in the batch dissolver tank, the feed adjustment tank, and the BT vapor separator. Figure 23 presents a graph of the maximum corrosion rates of specimens in the three vessels during the production, development, and the combined production-development periods of operation (December 15, 1954, to September 13, 1956). In most cases, the maximum generalized corrosion rate occurred during the development period. Generally, the corrosion rates for both types 304L and 309SCb stainless steel exposed in the solution phase in the batch dissolver tank and in the feed adjustment tank decreased slightly with increased exposure time. The maximum rate observed was about 47 mpy for type 309SCb stainless steel in the feed adjustment tank during the development period. In the same two process vessels, vapor-phase corrosion attack increased with increased exposure time. Again, the highest corrosion rates occurred during the development period in the feed adjustment tank. Maximum rates of 100 and 85 mpy were obtained, respectively, on types 304L and 309SCb stainless steel specimens.

In the third process vessel experiencing aggressive corrosion attack, the BT vapor separator, the vapor-phase corrosion rates for both types 304L and 347 stainless steel increased with increased exposure time. The maximum rate for type 304L was 54 mpy during the development period and 150 mpy for a specimen of type 347 welded to type 309SCb stainless steel during the combined production-development period.

Table 13. Summary of Corrosion Rates for Types 304L and 309SCb Stainless Steel Exposed in ORNL Thorex Process Pilot Plant from December 17, 1954, to September 13, 1956

Period of Operation	Process Vessel	Operating Temperature (°C)	Specimen Location	Exposure Time (hr)[a]	Corrosion Rate (mpy)	
					304L	309SCb
Development	Batch dissolver tank	110-115	Solution	2706	31.8 ± 0.9	15.0 ± 1.6
			Vapor	2706	40.3 ± 1.5	34.9 ± 1.9
Development[b]	Feed adjustment tank	110-115	Solution	2609	(c)	41.4 ± 4.8
			Vapor	2609	97.5 ± 2.5	85
Development	BT vapor separator	115	Vapor	5788	54.5	25.4 ± 4.7[d]
Development	A-column feed tank	30-60	Solution	7307	<0.1	<0.1[d]
Development	BTC catch tank	15-30	Solution	5135	<0.1	<0.1[d]
Production-Development	Batch dissolver tank	110-115	Solution	3340	25.4 ± 2.4	16.4 ± 0.2
			Vapor	3340	53.7 ± 0.5	41.8 ± 1.9
Production-Development	BT vapor separator	115	Vapor	6698	30.1	107 ± 43[e]

(a) Holding time for process solution at room temperature not considered as part of active exposure period.

(b) Data are for last half only of development period.

(c) Specimens lost from support rod in tank.

(d) Reported rates are for type 347 stainless steel.

(e) Represents a composite rate for types 309SCb and 347 stainless steel.

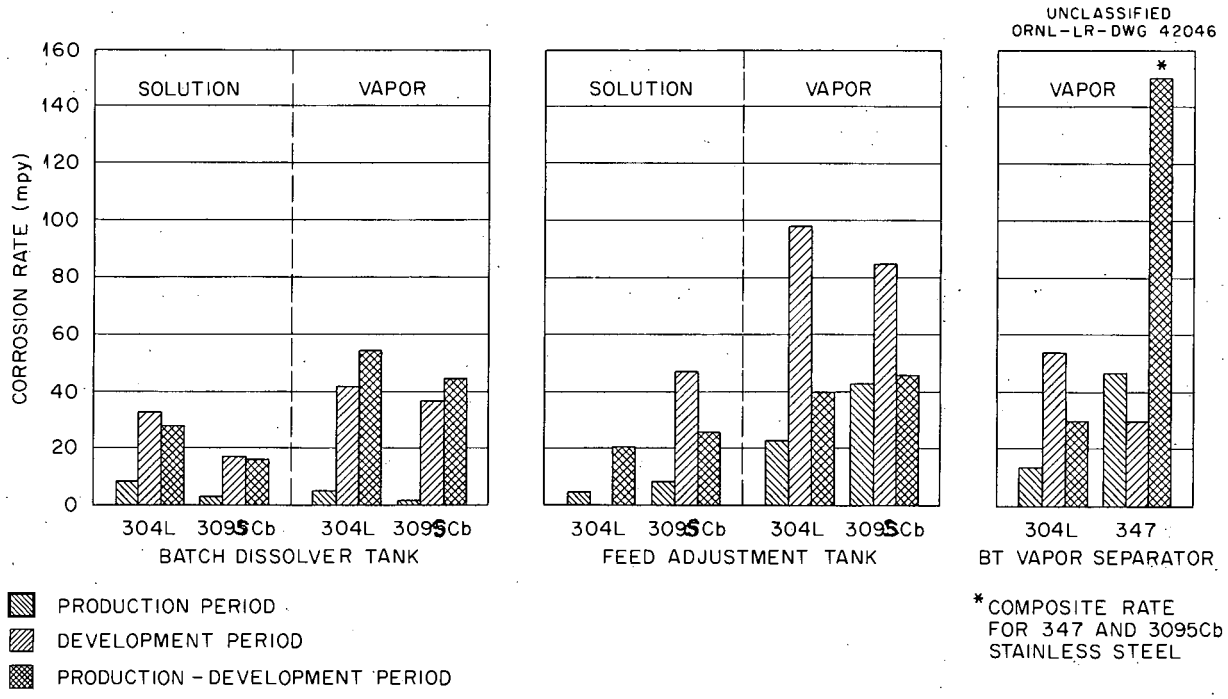

Fig. 23. Maximum Corrosion Rates Observed on Stainless Steel Specimens in Thorex Pilot Plant During Production and Development Periods of Operation.

In general, attack on flat surfaces of specimens of the three stainless alloys, types 304L, 309SCb, and 347, was uniform, although a mild form of intergranular attack occurred in a number of the more corrosive environments. The deepest observed penetration was 6 mils, which occurred on type 304L stainless steel exposed in the BT vapor separator. Edge corrosion was pronounced on all alloys in environments producing corrosion rates of 25 mpy and greater. It has been reported previously, based upon the results of laboratory tests with a simulated Thorex process solution, that the attack resulting from edge corrosion did not contribute significantly to the total attack observed on stainless steel specimens.[1]

Another form of localized corrosion observed on a number of test specimens was preferential attack in the heat-affected zone near welds. This type of attack was not observed consistently on all weld specimens of the three stainless alloys. The intensity of the attack varied, with maximum penetration up to 25 mils.

Corrosion attack in other process vessels was negligible. Types 304L and 347 stainless steel corroded at rates less than 0.1 mpy during periods in excess of 5000 hr in both the A-column feed tank and the BTC catch tank.

A maximum tolerable rate of 25 mpy has been tentatively set for process vessels in the Thorex pilot plant.[4] As shown by the results from the present investigation, areas exist in the pilot plant where this value is exceeded by factors ranging from slightly less than two to four.

From the available corrosion data, it is possible to estimate the service life of the process vessels in which substantial corrosion attack was encountered. Such information is shown in Table 14 in the form of half-life service; i.e., the useful service life is based upon one-half of the wall thickness of the respective vessels. The half-life times are based upon the maximum observed corrosion rates (uniform corrosion) for specimens of the same alloy type as the tank material plus the penetration due to localized forms of corrosion attack on the specimens. The half-life values are based upon a full-time operating schedule for the pilot plant. The maximum corrosion rates used to determine service life times occurred in the vapor phase of each of the three process vessels.

Both the batch dissolver tank and the feed adjustment tank have an estimated half-life of 2.5 years of continuous operation. The projected full service life of 1.2 years for the BT vapor separator was based upon the severe attack on the type 347 stainless steel specimens. The wall of the separator is fabricated from this alloy type. The full service life based upon the type 304L stainless steel top and bottom dished heads was estimated to be 1.6 years.

Table 14. Estimated Half-Life Times for Process Vessel in Thorex Pilot Plant[a]

Vessel	Material	Wall Thickness (mils)	Operating Time (hr)[b]	Maximum Penetration (mils)			Half-Life	
				Uniform	Localized	Total	(hr)	(yr)
Batch dissolver tank	309SCb	375	3340	17	12[c]	29	21,640	2.5
Feed adjustment tank	309SCb	500	2609	25	5[d]	30	21,730	2.5
BT vapor separator	304L-	188	5788	36	6[e]	42	13,960[g]	1.6[g]
	347	188	6698	115	5[f]	120	10,495[g]	1.2[g]

(a) Based upon vapor-phase exposure where most severe attack was encountered.

(b) Actual operating time at temperatures above room temperature.

(c) Preferential weld metal corrosion.

(d) Knife-line attack.

(e) Preferential weld metal corrosion and intergranular attack.

(f) Intergranular corrosion attack.

(g) Based upon entire wall thickness of 188 mils.

In view of the fact that the maximum desirable rate of 25 mpy is being exceeded, substantially in some cases, in the batch dissolver tank, the feed adjustment tank, and the BT vapor separator, it appears that the possibility of using other materials of construction for the Thorex pilot plant should be considered. Titanium, for example, may be attractive from a corrosion-resistance viewpoint. Some preliminary studies by the Battelle Memorial Institute[5] have indicated that titanium looks promising in a Thorex dissolving solution containing aluminum to complex the fluoride catalytic agent. If the tests continue to show favorable behavior, titanium specimens should be placed in various process vessels of the Thorex pilot plant to evaluate its corrosion resistance to the process solutions.

5. ACKNOWLEDGMENTS

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Appreciation is also expressed to C. M. Boyd of the ORNL Metallography Group and to H. L. Barker and L. L. Fairchild of the Solution Materials Corrosion Section.

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(4) A. C. Jealous, Thorex Information Meeting Summary, ORNL CF-54-11-145, November 26, 1954, p 66.

(5) Communication from F. W. Fink, Battelle Memorial Institute, to W. E. Clark, Oak Ridge National Laboratory, February 26, 1959.

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