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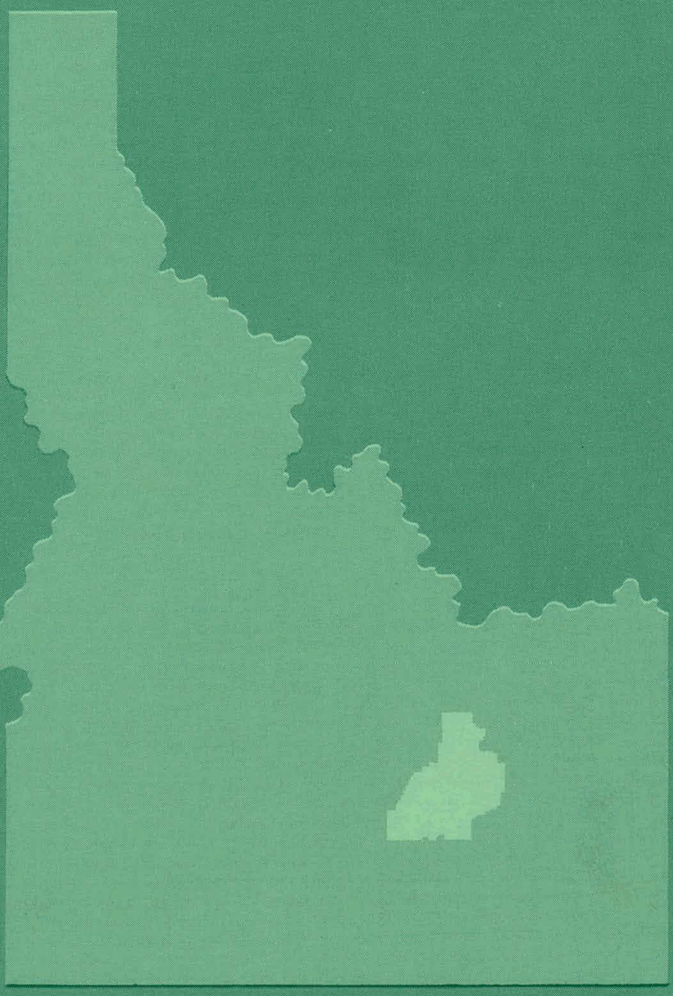
T. L. Hoffman



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Atomic Energy Division
Contract AT(10-1)-205
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ICPP HIGH-LEVEL RADIOACTIVE WASTE TANKS

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A B S T R A C T

Several 300 series stainless steels were corrosion tested in raffinate storage tanks made of the same materials at Idaho Chemical Processing Plant. After exposure to the raffinate solutions for periods of up to seven years, maximum penetration rates of 0.1 mil per year were noted.

Errata - IDO-14600

On page 8, line 5, the tank's volume is 30,000 gallons (not 300,000).

In Table I-B, page 21, the footnote to the 2nd column heading should be (2), and to the 4th column heading should be (1). (The 3rd and 5th columns are correctly headed as printed.)

PAGES 3 to 4

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CORROSION EVALUATION OF STAINLESS STEELS EXPOSED IN ICPP HIGH-LEVEL RADIOACTIVE WASTE TANKS

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CORROSION EVALUATION OF STAINLESS STEELS EXPOSED IN ICPP HIGH-LEVEL RADIOACTIVE WASTE TANKS

I. SUMMARY

Corrosion studies were conducted on welded stainless steel types 316, 316 ELC, and 348 and unwelded type 304L in four different waste solutions which result from the reprocessing of nuclear fuels at the Idaho Chemical Processing Plant. Corrosion rates were determined by immersing test specimens of the various stainless steels in the actual waste tanks for periods of up to 7 years. Maximum rates of 0.1 mil per year were observed on 304L and 348 specimens which had been exposed to acidic or acid deficient aluminum process first-cycle raffinates at about 25°C. There was no evidence of localized attack. Specimens of 304L exposed to the acid deficient aluminum nitrate raffinate from the second and third cycles showed maximum rates of 0.07 mil per year at about 25°C with minor evidence of localized attack. Spent decontaminating reagents are stored with this waste. Maximum rates for 316 ELC in zirconium fluoride-aluminum nitrate raffinate at 25°C were 0.1 mil per year. Very mild interdendritic attack was noted on the weld areas. These favorable observations at significant exposure times give indication of relatively long service life for the vessels. Continual measurements of liquid level in all tanks currently in use show that no leakage has occurred from any of the tanks due to tank failure from corrosion or other causes.

II. INTRODUCTION

Equipment is installed at the Idaho Chemical Processing Plant to recover enriched uranium from aluminum, zirconium, and Zircaloy reactor fuel materials(1,2,3,4). The fuels consist of a uranium alloy core which is clad with either aluminum, hafnium-free zirconium, or Zircaloy (1.2 to 1.7 per cent tin-zirconium alloy).

The recovery processes for aluminum fuel consist of dissolution in nitric acid followed by solvent extraction of the uranium with, (1) methyl isobutyl ketone, the Hexone "25" process, or (2) tributyl phosphate, the TBP "25" process. The aqueous raffinate resulting from the initial solvent extraction step is the first-cycle aqueous waste which contains most of the fission products and metallic salts derived from the alloy. The first-cycle raffinates are concentrated to a minimum volume without freezing (ca. 1.7$\underline{M}$ aluminum) and are then transferred to 300,000-gallon cylindrical storage vessels. Second- and third-cycle raffinates from Hexone solvent extraction are combined and handled in a similar manner. The same second- and third-cycle process and equipment are used for all fuels. Construction materials for the tanks for both of these raffinates are either stainless steel type 348 or type 304L.

Uranium separation from zirconium or Zircaloy-2 fuels is achieved by a process which was developed by Argonne National Laboratory(4) which uses aqueous hydrofluoric acid as the fuel dissolution medium and aluminum nitrate as a complexing and salting agent to permit recovery of uranyl nitrate by solvent extraction. In this process, the aqueous feed of the first tributyl phosphate extraction column is adjusted for maximum chemical stability to a fluoride-to-zirconium mole ratio of about 5[4,5,6]. The raffinate is transferred to 300,000-gallon type 316 ELC stainless steel vessels for storage. Second- and third-cycle raffinates are combined and then transferred for storage to the same 300,000-gallon vessels used to store the second- and third-cycle raffinates from the aluminum fuel recovery processes.

Two other classes of liquid waste, which are collected separately, are the relatively low activity-level process equipment and cell-floor drain wastes. Solutions that originate from laboratory hot sinks, the solvent-recovery evaporator, and the condensers on raffinate evaporators are the major contributors to process equipment wastes (PEW). Usually, the activity level of solutions from the cell-floor drains (CFD) is low enough for direct transfer to the ground waste system. However, during cell decontamination, somewhat higher activity-level solutions are produced which are combined with the PEW stream. Both wastes are transferred to 300,000-gallon type 348 or 304L second- and third-cycle raffinate storage vessels. The original decision to use stainless steel type 348 for the aluminum raffinate storage vessel was based on process development corrosion studies that were conducted by the Oak Ridge National Laboratory (7) during the design of the ICPP.

The selection of a construction material for the zirconium first-cycle raffinate storage vessel was based upon short-term beaker-type corrosion studies[8]. In these tests, type 316 proved more resistant at 60°C than type 347 or Carpenter-20 steels. At lower raffinate temperatures, additional corrosion protection could be expected.

Due to the uncertainties associated with the materials selections for both aluminum and zirconium fuel recovery process raffinates, a long-range program was started at the ICPP to more firmly establish the expected life of the storage vessels in the various raffinates. These storage vessels contain millions of curies of fission products which, if released due to failure of a storage tank, would magnify the environmental monitoring and control problems manyfold. Thus, continued corrosion surveillance and predictions of expected tank life based on experimental data are of primary importance in the program to store the high-level radioactive wastes in underground tanks.

III. WASTE STORAGE TANKS

A. Aluminum Fuel Reprocessing Raffinates

All the raffinates from the recovery process for aluminum clad nuclear fuel are stored in 300,000-gallon vessels. Owing to their size, each vessel structure is in the "as-welded" metallurgical condition.

Every vessel is enclosed in a concrete vault which is buried under about 10 feet of earth.

The fission product heat in first-cycle raffinates is sufficiently high to require cooling for vessel corrosion control. Accordingly, submerged stainless steel coils and a reflux condenser are provided to maintain a solution temperature of less than 38°C. In the second- and third-cycle raffinates, the lower concentration of radioisotopes liberates almost no heat. It is unnecessary, therefore, to have reflux condensers or cooling coils for corrosion protection of these storage vessels.

First-cycle raffinate from the TBP "25" process is stored in 4 separate type 304L stainless steel vessels. A type 348 vessel contains all the first-cycle Hexone "25" raffinate. The second- and third-cycle raffinates from both processes are contained in two vessels, one type 348 and the other type 304L.

B. Zirconium and Zircaloy Fuel Reprocessing Raffinate

Aqueous first-cycle raffinates from the zirconium process are stored in two type 316 ELC stainless steel vessels with submerged type 316 ELC cooling coils. The second- and third-cycle raffinate is stored in the 300,000-gallon type 348 or 304L stainless steel tanks with second- and third-cycle raffinate from the aluminum fuel process.

The design of the storage vessels and composition of the wastes are summarized in Table 1. The details of the design and erection of each type of vessel, as well as the composition of the stainless steels used in the construction of the vessels and the detailed composition of the waste stored in the vessels, are given in Appendix I.

IV. TEST PROCEDURE

Corrosion specimens consisted of seamless and welded hoops, weld tabs, and sections of welded pipe. The hoops were prepared at the ICPP from sheet material. The sheet material was turned into open-seam tubes around a mandrel leaving a 1/8-inch opening. The opening was then closed in a vice and heliarc welded along the closed seam. Then, 1-inch-high hoops were cut from the tubes and all edges were machined. In the case of the stainless steel 316 tanks, the fabricator welded tabs of the sheet steel as the tanks were being erected. These tabs were cut off for corrosion testing. Samples of these are shown in Figure 1.

The welded hoops were fastened to circular jigs which were in turn fastened to jig support cables. The assembly was then inserted into a tank through a riser, and the cable was fastened to the riser cover so as to suspend the samples at the desired depths. The preparation of the corrosion test specimens is described in greater detail in Appendix I.

TABLE 1

SUMMARY OF ICPP WASTE STORAGE VESSEL DESIGN

Tank No's	Waste	Temperature Range	Capacity (Gallons)	Alloy** Type	Trombone Cooling Coil Design	Wall Thickness Minimum (inches)
WM-180	Acid deficient* aluminum nitrate (1st cycle, Hexone "25" process)	30 ± 5°C	300,000	348	1 inch SCH 40	0.250
WM-182-183-185-187	Aluminum nitrate - nitric acid (1st cycle, TBP "25" process)	30 ± 5°C	300,000	304L	1½ inch SCH 80	0.250
WM-181	Aluminum (2nd cycle, Hexone "25" processes)		300,000	348	None	0.250
WM-184	Aluminum (2nd cycle, Hexone "25" processes)			304L	None	0.250
WM-103-104	Zirconium - aluminum - hydrofluoric acid (1st cycle, STR process)	17.5 ± 6.5°C	30,000	316 ELC	1 inch SCH 160	0.5625

* Ammonium hydroxide is added to aluminum nitrate solution to raise the pH.

** Tungsten Inert Gas welding process was used.

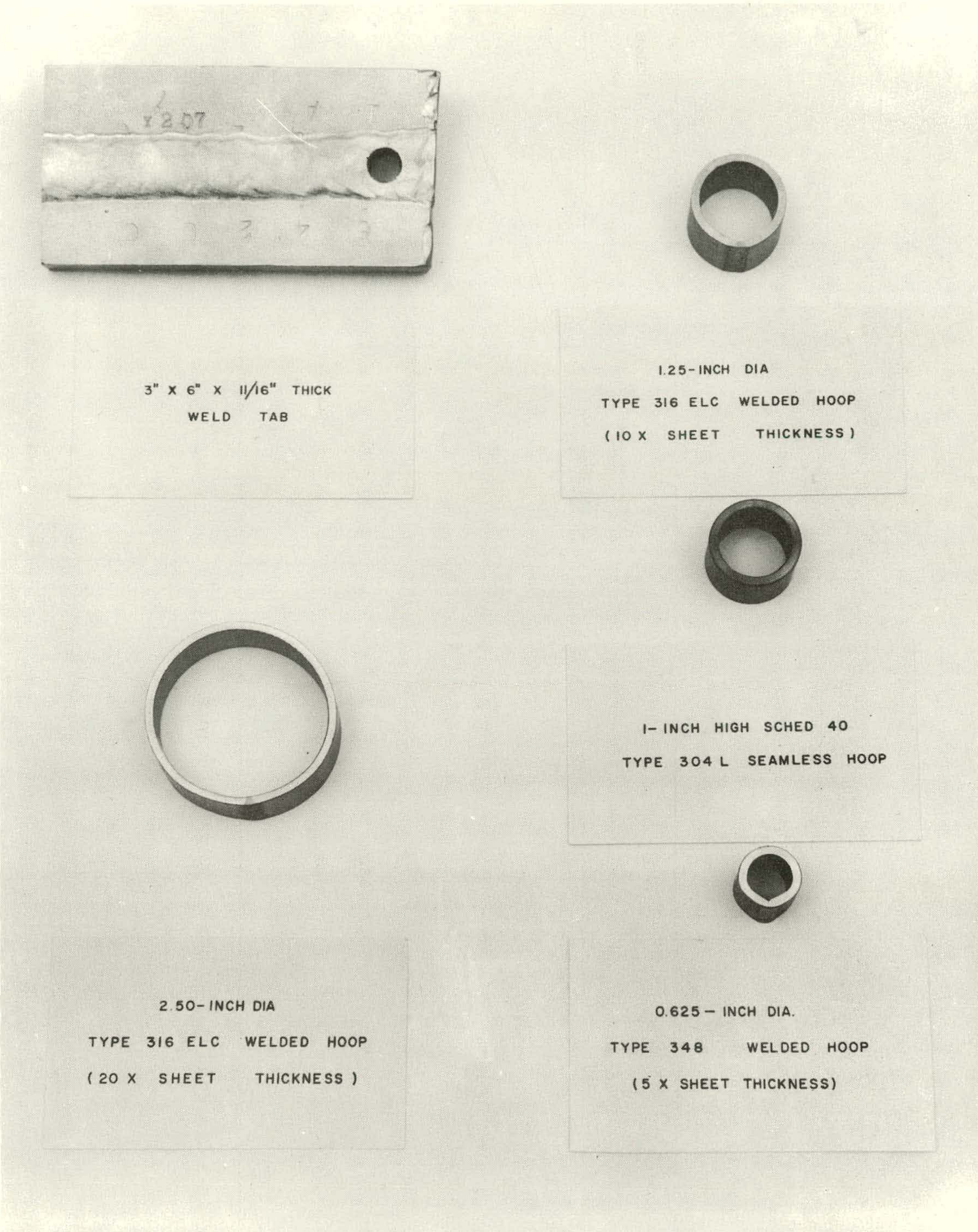

Fig. 1 Stressed, Welded Corrosion Specimens after Exposure

When the specimens were removed for examination, they were decontaminated, rinsed with water and acetone, and dried. Corrosion rates were determined by weighing the pieces. A metallurgical examination was made on each specimen and the dimensions of the pipe sections were measured.

V. RESULTS

A. Corrosion in Hexone "25" First-Cycle Raffinate

The results of measurements of corrosion specimens immersed in the waste storage tanks from about 1.5 to 7 years indicate that specimens of stainless steel 348 and 304L suffered 0.0007 mil per month maximum corrosion at about 25°C. Less than 0.001 mil per month corrosion was observed on a type 348 pipe specimen which was exposed for 7 years (2579 days). The detailed results are given in Table 2.

A microscopic examination of the 20-foot-long type 348 pipe indicated that this specimen was lightly etched but free from pits or intergranular attack. A crystalline scale was observed on the inside pipe walls at the liquid level. A comparison with a 2-inch-long unexposed control sample indicated that the 20-foot-long exposed pipe essentially completely resisted corrosion in the stored first-cycle raffinate.

B. Corrosion in TBP "25" Process First-Cycle Raffinate

The results of corrosion tests in the first-cycle raffinate are given in Table 3.

The type 304L stainless steel hoops suffered 0.01 mil per month maximum corrosion at 25°C. The maximum loss after about 2.75 years (1000 days) on 11 specimens was 0.01 mil per month. Twelve other type 304L specimens immersed for about 2.0 years suffered a maximum corrosion of 0.008 mil per month.

Microscopic examinations of the 1-inch-high hoops indicated that only slight etching occurred. Pits and grain boundary attack were not found on any of the hoops. The original machining marks were still visible on all specimens.

C. Corrosion in Second- and Third-Cycle Raffinates

Corrosion measurements were made on 5 type 304L hoop specimens after 2.75 years immersion at about 25°C. The maximum observed rate was 0.006 mil per month. These specimens suffered rather heavy etch with shallow 5-mil-deep pits. Further, most of the original machine markings were corroded away. A summary of the data is listed in Table 4.

TABLE 2

CORROSION OF TYPE 348 AS-WELDED SPECIMENS
IN HEXONE "25" PROCESS FIRST-CYCLE RAFFINATE

Date Withdrawn	Exposure Time-Days	Exposure Atmosphere	Specimen Type	Number of Specimens	A262-52T Rate mils/month	Maximum Rate mils/month
17 Jul '56	538 (1.5 yrs)	Liquid	0.625-in.-diameter welded hoops	6		3.7 x 10^{-4}
			1.25-in.-dia. welded hoops	1		2.3 x 10^{-4}
20 Nov. '56	1037 (2.8 yrs)	Liquid	0.625-in.-dia. welded hoops	5		2.7 x 10^{-4}
28 Jan '59	1462 (4.0 yrs)	Liquid	1.25-in.-diameter welded hoops	6		6.6 x 10^{-4}
19 Feb '62	2569 (7.0 yrs)	Liquid and Vapor	1-in. sch 40 welded pipe	1	1.4	Less than 1 x 10^{-3}

TABLE 3

CORROSION OF STAINLESS STEEL 304L IN TBP "25"
PROCESS FIRST-CYCLE RAFFINATE

Date		Exposure	Number of	Mils/Month
Immersed	Withdrawn	Time-Days	Specimens	Max. Rate
19 May '59	19 Feb '62	1006 (2.75 yrs)	5	1 x 10^{-2}
19 May '59	12 Feb '62	999 (2.75 yrs)	6	1 x 10^{-3}
9 Dec '59	9 Feb '62	791 (2.17 yrs)	6	2 x 10^{-3}
9 Dec '59	9 Feb '62	730 (2.00 yrs)	6	8 x 10^{-3}

TABLE 4

CORROSION OF TYPE 304L HOOPS IN HEXONE "25" PROCESS SECOND- AND THIRD-CYCLE RAFFINATES

Date		Exposure	Number of	Heat	Mils/Mo.
Immersed	Withdrawn	Time-Days	Specimens	Treatment	Max. Rate
19 May '59	19 Feb '62	1006 (2.75 yrs)	5	As received	6×10^{-3} numerous 5-mil-deep pits

D. Corrosion in Zirconium Process First-Cycle Raffinate

The test results from the exposure of specimens in first-cycle raffinate from the processing of zirconium-type fuels are listed in Table 5.

A type 316 ELC seam tab prepared by the fabricator suffered 0.01 mil per month corrosion after 13 months immersion at 25°C. Three 15-mil-deep pits were observed after 13 months on an ER 316L weld deposit of a stressed and sensitized (one-hour heat treatment at 677°C) hoop specimen. Another similarly exposed sensitized hoop and two other as-welded hoops were free of pits.

The observed corrosion rates were slight on hoops that were exposed between 1.4 and 2.3 years at 17.5 ± 6.5°C. Microscopic examination of these hoops showed that no attack, either localized or general, occurred. Thus, the effect of heat treatment and stress appeared to be negligible.

After 5.1 years, type 316 ELC alloy suffered less than 0.01 mil per month corrosion while immersed in the raffinate. From a microscopic examination about 66 per cent of the original machine marks existed on the exposed specimens. Very mild interdendritic attack was present on the weld area, and pitting was found to be absent on all specimens.

VI. RECOMMENDATIONS

Stainless steel type 316 ELC is a suitable container material for the storage of zirconium fuel first-cycle raffinate at 25 ± 5°C. Specifications for tank fabrication should require that all material be tested according to the ASTM A262-577, "Boiling Nitric Acid Test for Corrosion-Resisting Steels". Further, a level of acceptability should be established at 2.0 mils penetration per month on wrought material, and 3.0 mpm on weld deposits (A262 testing of sensitized specimens). Since 316 ELC alloy is susceptible to sensitization during

TABLE 5

CORROSION OF 316ELC STAINLESS STEELS IN
ZIRCONIUM FLUORIDE-ALUMINUM NITRATE FIRST-CYCLE RAFFINATE

Type of Specimen	Number of Specimens	Heat Treatment	Date Withdrawn	Exposure Time days	Max Rate mils per month
Stressed hoop, 1.25" dia. x 0.125" wall.	1	677°C for 1 hour	2-7-58	48	0.01
American Welding Society ER-316L	2	"	2-7-58	398	0.004*
welding rod used.	1	"	5-4-59	499	0.011
	1	"	5-4-59	554	0.01
	2	as welded	5-4-59	849	0.0094
	1	"	2-8-62	1855	0.005
Stressed hoop, 2.5" dia. x 0.125" wall.	2	677°C for 1 hour	5-4-59	849	0.0068
American Welding Society ER-316L	1	"	2-8-62	1855	0.007
welding rod used	1	as welded	2-7-58	48	0.02
	2	"	2-7-58	398	0.004
	1	"	5-4-59	499	0.013
	1	"	5-4-59	554	0.012
Weld tabs 3" x 6" x 11/16"	2	677°C for 1 hour	2-8-62	1855	0.006
American Welding Society ER-316L (0.06% C) welding rod used.	2	as welded	2-7-58	389	0.01

* 15-mil-deep pits in weld.

welding, which may result in accelerated localized corrosion at stress risers, rigorous control of fabrication is required.

Future design may profitably use material for zirconium fluoride-type wastes that is thinner than the 11/16-inch-thick shells and 9/16-inch-thick dished heads which were used in existing tanks. This should be considered, especially for erecting vessels using A262 certified alloys. In addition, type 316ELC schedule 80 pipe appears to be a suitable construction material for the raffinate storage vessel cooling coils.

As a container material for first-cycle raffinate, and for aluminum fuel reprocessing second- and third-cycle combined raffinates, either type 304L or 348 alloy can be used.

The use of stainless steel types 304L or 348 does not always assure freedom from welding sensitization and stress-induced localized corrosion. The fabrication conditions should include an ASTM A262-55T, "Boiling Nitric Acid Test for Corrosion-Resisting Steels", on all materials selected for the vessels.

VII. CONCLUSIONS

The evaluation of corrosion test coupons exposed to acid deficient aluminum nitrate, acidic aluminum nitrate, and aluminum nitrate-zirconium fluoride raffinate solutions indicated that the various stainless steels used in the waste tank construction at ICPP were well chosen and that a relatively long service life can be predicted for the vessels. At this time, general corrosion rates observed are too low to allow a significant estimate of the vessel life. Those minor evidences of localized attack which have been observed are not severe enough to define the areas or mechanisms of probable ultimate failure. There is now no evidence available suggestive of any type of corrosion failure of these vessels in the next ten-year period. Careful surveillance of the test specimens in the vessels will be continued to allow early detection of accelerated localized attack or other signs of ultimate failure.

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APPENDIX I

Details of Storage Vessel Design, Corrosion Specimen Preparation, and Waste Compositions

Aluminum Process Storage Tanks

The cylindrical vessels for storage of the TBP "25" raffinates are 50 feet outside diameter x 21 feet high with 11-foot-high domed roofs. These vessels were erected by butt-welding together type 304L plates using the tungsten-inert gas process with American Welding Society classification ER 308L bare electrodes. The bottoms and 8 feet up the sides of the vessels are constructed from 5/8-inch-thick plates, and the upper 13 feet of siding from $\frac{1}{4}$-inch material. The domed roofs are made from 3/16-inch-thick plates. The cooling coils for these vessels are $1\frac{1}{2}$-inch schedule 80 type 304L pipe in a horizontal trombone configuration. An auxiliary structure is mounted inside the vessels so that the horizontal coil assemblies are supported 3 inches from the vessel bottoms.

The stainless steel 348 vessel for storage of Hexone "25" process raffinate is 50 feet outside diameter x 23 feet high plus an 11-foot-high domed roof. During the erection of this vessel, the TIG welding process with ER 347 bare electrodes was used for butt-welding together the stainless steel 348 plates. The lower 8 feet of the vessel side and its bottom were constructed from 5/8-inch-thick plates. One-quarter-inch-thick material was used to erect the upper 15 feet of the cylindrical vessel sides, and 3/8-inch-thick plates to fabricate the roof. The vessel cooling coil is designed from 1-inch schedule 40 stainless steel 348 pipe in a horizontal trombone configuration. This coil is supported 3 inches from the bottom of the vessel. In addition, 22 peripheral coils, which are spaced on 1-foot centers, traverse the inside walls of the vessel. The cooling coil condenser is made from stainless steel 348 alloy except for about 1 dozen brass valves and a few carbon steel parts which can be serviced by direct maintenance.

Zirconium Process Storage Tanks

Two separate type 316ELC stainless steel vessels contain all the STR process raffinate. A hollow cylindrical shell was first constructed by butt-welding together pre-formed 11/16-inch-thick plates. Two spherically dished 9/16-inch-thick heads were then welded to the open ends of the shells. The dimensions of the erected vessels are $11\frac{1}{2}$ feet outside diameter x 42 feet long. The "sigma" welding process (inert gas, automatic metallic arc) with American Welding Society ER 316L bare weld wire was specified. Because the actual weld deposits contained about 0.06 per cent carbon, and were therefore regarded as potential sources of failure, 316ELC 3/8-inch-thick plates were then welded over the inside surface of the original weld seams by the vessel fabricator using the metal-arc process with coated ER 316L wire. These 316ELC stainless steel vessels are in the as-welded metallurgical condition, and are provided with submerged stainless steel type 316ELC 1-inch, schedule 160 cooling coils and a stainless steel type 316ELC condenser.

Second- and Third-Cycle Storage Tanks

The aqueous raffinates from the second- and third-cycle Hexone extraction columns are stored in a 300,000-gallon stainless steel type 304L vessel. The vessel was welded by the tungsten inert-gas welding process with ER 308L wire. The dimensions of this cylindrical vessel are 50 feet outside diameter x 21 feet high with an additional 11 feet to accomodate a domed roof. The bottom and 8 feet up the shell side is constructed by butt-welding together 5/8-inch-thick plates. The remaining upper 13 feet of the shell is erected with $\frac{1}{4}$-inch-thick plates. The roof is fabricated from 3/16-inch plate. No cooling coils are provided.

Solution and Metal Compositions

The compositions of the materials of construction of the tanks and the corrosion specimens are given in Appendix Table I-A. The compositions of the waste solutions in storage are given in Appendix Table I-B.

Corrosion Test Specimens

For the Hexone "25" first-cycle raffinate, a stainless steel 348 welded pipe that was 20 feet long, and stainless steel 348 welded hoops were immersed as corrosion specimens. The 1-inch schedule 40 pipe was selected from warehouse stock, and was in the as-received, annealed metallurgical condition. The hoops were prepared locally from sheet material. Samples of type 348 wrought material were turned into open seam tubes from 0.125-inch-thick plates. Each tube was formed around a mandrel having a diameter either 5 or 10 times the sheet thickness which left a 1/8-inch opening. The tubes were then closed in a vice and heliarc welded along the seam with American Welding Society classification ER 347 uncoated wire. Next, 1.000 ± 0.0005 inch high hoops were cut from the tubes and all the edges were machined to a 1/32-inch radius. These hoops were in the as-welded condition.

Circular jigs and jig support cables were used as auxiliary experimental equipment. Stainless steel type 348 alloy was the construction material for the jigs and 3/16-inch-diameter stainless steel 410 for the cables. A polyethylene coated cable was employed for first-cycle Hexone "25" raffinate and zirconium process studies; bare cable was used for the other equipment.

Stainless steel 304L seamless hoops were corrosion evaluated in the stored raffinates from both the first-cycle TBP "25" process and the second- and third-cycle raffinates. These specimens were cut into 1-inch-high sections from 1-inch schedule 40 seamless pipe. The pipe was annealed at the mill and hoops were cut and machined at the ICPP.

TABLE I-A

COMPOSITIONS OF METALS USED IN
ICPP WASTE STORAGE TANKS AND CORROSION TESTS

Type Stainless Steel	%C Max	% Cr	% Ni	%Mn Max	%P Max	%S Max	%Si Max	% Mo	% Cb & Ta
304L Plate and Sheet	0.03	18.00 20.00	8.00 12.00	2.00	0.045	0.030	1.00		
ER 308L Bare and Electrode	0.03	19.50@ 22.00	9.00 11.00	2.50	0.030	0.030	0.60		
316L Plate and Sheet	0.03	16.00 18.00	10.00 14.00	2.00	0.045	0.030	1.00	2.00 3.00	
ER 316L Bare Electrode	0.03	18.00 20.00	12.00 14.00	2.50	0.030	0.030	0.60	2.00 2.50	
E 316L Coated Electrode	0.04	17.00 20.00	11.00 14.00	2.50	0.040	0.030	0.90	2.00 2.50	
348 Plate and Sheet	0.08	17.00 19.00	9.00 13.00	2.00	0.045	0.030	1.00		10 x C min, 1.10 max (Ta 0.10 Max)
ER 347 Bare Electrode	0.08	18.50@ 21.00	8.50 10.50	2.50	0.030	0.030	0.60		10 x C 1.00 max

@ Chromium min = 1.9 x nickel

TABLE I-B

COMPOSITION OF STORED RAFFINATES

Element	Al Fuel First-Cycle Hexone "25"(1)	Al Fuel First-Cycle TBP "25" (2)	Second-Cycle (2)	Zr-Fuel 1st-Cycle STR (2)
Aluminum, M	1.65	1.65	1.2	0.61
Ammonia, M	1.37	> 0.05	0.20	
Mercury (ic), g/l	5.52	3.42	--	
Ruthenium, g/l	0.019	0.034	--	
Nitrate, M	7.10	5.38	--	
Iron, g/l	0.07	0.35		
Chloride, M	> 0.005	> 0.005	0.003	
Tellurium, g/l	0.0022	0.0073		
Molybdenum, g/l	0.0161	0.0687		
Zirconium, M				0.83
Sodium, g/l	0.22	1.46	1.64	
Acidity, H^+ N	0.13N-Basic	0.89	0.055	0.97
Sp. GR 25°C	1.286	1.291	1.280	1.166
Ferrous Ammonium Sulfamate M			0.02-0.04	
Tin				0.53
Fluoride M	0.009			2.61
Oxalic Acid			0.009	
Tartaric Acid			0.03	
Periodic Acid			0.009	
Turco 4324 and 4182A			3750 pound	

(1) Calculated concentrations

(2) Measured concentrations

Weld tabs prepared by the erector of the vessels and other specimens prepared locally were used for the studies of the zirconium raffinate solution. Samples of 316ELC wrought material were turned into two 13-inch-long open seam tubes from 0.125-inch-thick plates. One tube was formed around a mandrel having a diameter 10 times the sheet thickness, and the other 20 times its thickness. This operation left a longitudinal opening which was about 1/8-inch wide. The longitudinal edges of the two tubes were squeezed together, and heliarc welded along the seam with ER 316L uncoated wire. Twelve 1.000 ± 0.005-inch-high hoops were then cut from each of the 12-inch-long tubes. Next, all the edges of the hoops were machined to 1/32-inch radius. One-half of the hoops from each of the two different diameter tubes were heat treated at 1250°F for 1 hour. The remainder were given no post-weld thermal treatment which could affect the alloy metallurgy.

The vendor tabs were made from extensions of the vessel shell seams of the 11/16-inch-thick, 316ELC, first-cycle raffinate storage vessel. These tabs were prepared at the vessel erection site by the fabricator using the "sigma" welding process that was used to erect the vessel. Accordingly, ER 316L weld deposits join pairs of 316L wrought plates forming 3 inch x 11/16-inch-thick samples.

Type 304 stainless steel was the material of construction for six 4.5-inch-diameter specimen jigs. The jig supports were made from polyethylene-coated, 3/16-inch-diameter, type 304 cables.

APPENDIX II

Details of Tank Usage and Sampling Procedure

First-Cycle Hexone

On January 26, 1955, twelve 1.25-inch inside diameter and twelve 0.625-inch inside diameter stressed hoops, and two 20-foot-long pipe pieces were immersed into the first-cycle Hexone raffinate storage vessel. On that date, the depth of the liquid raffinate was 48 inches; it had reached a volume of 274,000 gallons and a depth of 219 inches by January 15, 1956. No changes have occurred since that time. All the hoops were mounted on three 8-inch-diameter circular jigs that were supported from an access riser cover by a polyethylene-coated type 410 stainless steel support cable. The jigs were fabricated from type 348 alloy. The three jigs were bolted to the cable so as to rest 18, 48, and 72 inches from the bottom of the vessels. The 20-foot long pipes were supported on separate type 410 coated stainless steel cables. These pipes were inserted into the vessel from the same access riser as the hoops. The vessel was closed by bolting the cover to the access riser.

Prior to insertion of the pipes into the storage vessel, a 2½-inch-long section was cut from each pipe. These sections were preserved as control specimens. In addition, a 1-inch-long section was cut from each pipe to determine the resistance in an ASTM A262-52T Huey Test, using 65 per cent boiling nitric acid.

On July 17, 1956, six hoops were withdrawn for a corrosion evaluation. Subsequent withdrawls of six hoops occurred on November 20, 1957, and January 28, 1959. On February 19, 1962, one of the two 20-foot-long pipes was removed from the stored raffinate for evaluation.

During January 1957, it was decided to erect additional storage facilities for the aluminum fuel raffinates. Plant experience with type 348 alloy after 538 days in the first-cycle aluminum raffinate at 30°C suggested that any austenitic stainless steel would be a satisfactory material. Since type 304L was the cheaper alloy, it was chosen as the construction material.

About this same time the solvent used to separate the uranium from fission products and the alloy metal salts was changed from Hexone to tributyl phosphate (TBP). The proposed composition of the aqueous raffinates from the TBP extraction appeared to be compatible with either type 304L or 348 alloys for long term storage.

Since the construction material for one of the storage vessels for second- and third-cycle raffinates and all of the first-cycle raffinates from the TBP "25" process is stainless steel type 304L, specimens of that alloy were studied in the as-received metallurgical condition except that machining was necessary to prepare the specimens. Seventy-two stainless steel type 304ELC seamless hoops were immersed into each of 2 first-cycle raffinate storage vessels on May 19, 1959. One vessel had been filled by July 13, 1958, and another during February, 1959. On December 9, 1959, 72 type 304ELC hoops were immersed into each of 2 additional first-cycle storage vessels. One was filled during November 1959, and one was empty. Filling of the empty vessel with first-cycle raffinate began on December 26, 1959; and on February 28, 1960 the liquid depth was observed to be 40 inches. Gradual filling continued during the next two years, so that the liquid levels were 64.8 inches in May 1961, and 82.1 inches on February 27, 1962.

Periodic inspection and the retirement of selected hoop specimens from the tanks was started in 1962. During February 9 to 19, 1962, 6 hoop specimens were withdrawn and retired from each of the four first-cycle TBP "25" raffinates. The remaining 68 hoops were reimmersed.

All hoops and pipes removed for examination were decontaminated, rinsed with water and acetone, and dried. Corrosion rates on the hoops were determined by weighing, and a metallurgical examination of each specimen was made. An optical examination of representative sections was made on the 20-foot-long pipe, and its dimensions were measured to estimate corrosion resistance.

Second- and Third-Cycle Raffinates

For second- and third-cycle raffinate studies, 72 type 304ELC hoops were inserted into the storage vessel on May 19, 1959. The depth of the liquid on that date was 76.8 inches which is equivalent to 96,075 gallons. Filling continued slowly until August 22, 1960, at which time the depth was 107 inches. Between then and October 17, 1960, the vessel was filled to 228 inches by adding 151,280 gallons of second- and third-cycle concentrate. On February 19, 1962, 6 hoop specimens were withdrawn, decontaminated, and their corrosion rates determined. The remaining 68 test hoops were again immersed for further study.

Zirconium Raffinates

Tests were conducted for about 61 months to determine the corrosive effects of the first cycle zirconium raffinate on various grades of 18-8 Mo stainless steels. The raffinate solution during the first 11 months was a tin-free zirconium first-cycle raffinate, but during the remaining 50 months the raffinate was a composite of the tin-free and tin-bearing zirconium raffinates.

On December 18, 1956, twenty-four stressed hoops and 4 tabs prepared by the vendor were immersed into 1 of the 3 vessels which were provided for storing zirconium first-cycle raffinates. The liquid level in the vessel on that date was only a few inches. By January 5, 1957, the level was about 18 inches, but by October 27, 1957 and December 21, 1957, the liquid level was 37.8 inches and 68 inches respectively.

Twelve stressed hoops were prepared from a 2.50-inch-diameter tube whose wall thickness was 0.125 inches. Six of these were heat treated at 1250°F for 1 hour, thus sensitizing these specimens. An additional 12 stressed hoops were made from another 1.25-inch-diameter tube with a 0.125-inch nominal wall thickness. One-half of these hoops were heat treated at 677°C after accomplishing the last fabrication steps.

The vendor seam tabs, which were 3 inch x 6 inch x 11/16 inch thick, were immersed in the as-welded condition which is quite representative (except for stress levels) of the raffinate storage vessel seams.

Prior to immersing the hoops and tabs into the first-cycle zirconium raffinate, all specimens were descaled, passivated, weighed, and inspected visually for weld fissures. Hot 3 per cent hydrofluoric - 20 per cent nitric acid mixture was used as the descaling solution, and boiling 30 per cent nitric acid solution was used to passivate these hoops and tabs.

The specimens were fitted onto 6 circular jigs which were supported from riser covers on the raffinate storage vessel by 2 jig support cables. Each coated type 304 cable was first secured to the riser covers so that the running end was 27 feet long. Then 3 jigs (SS 304) were bolted to the cables so as to rest 18, 36, and 60 inches from the bottom of the vessel. Next, the 24 hoops and 4 tabs were evenly distributed on the two cable-jig assemblies and lowered into the storage vessel. The riser covers were then bolted to the risers. By reversing this procedure and withdrawing the jig-cable assemblies, periodic inspections of the specimens were accomplished.

Two vendor tabs and 6 hoops were withdrawn for corrosion evaluation on February 7, 1958. Eight hoops were withdrawn on May 4, 1959, and on February 8, 1962, two hoops and 2 tabs were removed. Each specimen that was withdrawn for corrosion evaluation was first decontaminated. The corrosion rates were calculated from weight loss data and metallurgical examination of the coupons was made.

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