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WASTE CALCINER CORROSION

C. A. ZIMMERMAN

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Abstract

The information in this report is a compilation of corrosion data reported in the literature between 1957 and 1977 which covers the development of the waste calcination process, the operation and modifications of the Waste Calcining Facility (WCF), and the early design of the New Waste Calcining Facility (NWCF). The report shows that the selection of the austenitic stainless steels for the Waste Calcining Facilities was correct. The only persistent materials problem has been one of failure of fittings such as valves, bellows, and feed and fuel nozzles. Development work in these areas is still being done to achieve improved life and reliability of these components.

Summary

Corrosion data derived during the development and operation of the waste calcination process for solidification of aqueous nuclear wastes from reprocessing of nuclear fuels between 1957 and 1977 has been reviewed.

Early test results in laboratory and pilot-plant studies led to the selection of Type 347 stainless steel for the first Waste Calcining Facility (WCF) primary calciner vessel and Type 304L and 347 stainless steels for the aqueous feed and scrub systems. Operation history of this unit indicates that these were good choices for construction materials even after changing from aluminum nitrate to zirconium fluoride containing wastes and modification to replace the NaK heating system with "in-bed" combustion.

Problems encountered during operation have been with fittings such as valves, valve bellows, and feed and fuel nozzles. These problems continue under development with both new designs and materials being investigated and tested.

Laboratory corrosion tests and metallurgical data which have led to the selection of Nitronic-50 alloy (an austenitic stainless steel) for use in the aqueous liquid sections of the New Waste Calcining Facility (NWCF) are presented.

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I. Introduction

Materials evaluation and selection for the calcination of aqueous solutions of radioactive wastes at the ICPP began with early pilot-plant operations. Studies started with 3-inch-diameter and 6-inch-diameter calcination units that were used for corrosion testing. This early work considered only the calcination of first cycle aluminum wastes to produce an aluminum calcine. Studies later involved a 24-inch-square (sometimes referred to as the four-foot-square) calcination unit which incorporated a NaK (the eutectic alloy of 78 percent potassium and 22 percent sodium) system to provide heat for the calcination reaction. In addition to these pilot plant calcination units, special test loops were built for study of specific corrosion-erosion problems.

At a later period in the calcination studies, several other test calciners were built and operated. The 12-inch-diameter calciner and various other test loops designed to study specific problems provided initial corrosion information. Later developments included the calcination of the aqueous first cycle waste from the processing of zirconium clad fuels. This 12-inch unit is still being used to provide data for the calcination of second cycle and blended waste streams.

The Demonstration Waste Calcining Facility (DWCF) a 48-inch calciner, placed in operation in 1963, is now known as the Waste Calcining Facility (WCF). This unit was successfully operated to demonstrate the reduction of liquid radioactive waste to a dry granular solid. Additional information has been gained from continued operations of the WCF during full scale calcination of liquid waste to granular solids.

The in-bed combustion of hydrocarbon fuel was developed to replace the NaK heating system and permit higher feed rates by providing a higher heat input to the calciner bed. The effect of in-bed combustion on materials of construction was observed in pilot-plant units and special corrosion study loops.

Several processing campaigns in the 48-inch calcining unit have been completed and various parts of the unit inspected for corrosion effects between campaigns.

Corrosion during storage of the dry calcine product was investigated very early during the development of the process for calcining aluminum waste solutions. This work has continued with laboratory studies and corrosion test coupons placed in various store units. These corrosion test coupons are scheduled for removal and evaluation at various intervals over the future storage periods.

The latest development in the calcination of liquid wastes has been the development of the New Waste Calcining Facility (NWCF). Laboratory corrosion studies have provided a basis for recommending materials of construction for this unit.

II. Aluminum First-Cycle Waste Calcination

1. Calciner and Calciner Off-Gas System

1.1 Six-Inch-Diameter Pilot-Plant Calciner Corrosion Tests

Initial studies of the calcination process used a 6-inch-diameter calciner for pilot plant and service testing. Coupons of Type 347 stainless steel, Carpenter-20 alloy, and ordinary carbon steel were exposed for 436 hours at 400°C in the 6-inch-diameter calciner fluidized bed.[1] These coupons showed minor corrosion damage as demonstrated by slight weight changes (Table I). Due to the formation of scale of varying thickness, corrosion rate estimates by weight loss measurements were not made. The coupons with the scale intact were then placed in the gas stream above the fluidized bed for 242 hours. During this period a measureable weight loss was observed. It was suspected that these weight losses, at least in part, were due to attrition from the solids suspended in the gas stream. The greatest weight loss was observed on one of the Type 347 stainless steel coupons corresponding to 0.41 mils per month in the gas stream. The fact that this rate was significantly greater than the next highest observed rate might have been due to the location of the test coupon in the gas stream. The data generally indicate that only minor corrosion occurred.

Corrosion test data were collected for austenitic stainless steels immersed in the off-gas condensate stream in the pilot-plant scrubber.[1] Coupons of Nionel (now called Incoloy 825), Type 321, 329, and 347 stainless steels, and Carpenter-20 alloy were exposed in the condensate stream for 1316 hours. A tenaceous milky white salt, soluble in boiling 20 percent nitric acid, was deposited on all specimens. The test results are shown in Table II.

Although Type 347 stainless steel suffered the greatest loss, all the austenitic alloys appear to be satisfactory for off-gas service. Metallographic examination of the specimens indicated the absence of localized attack such as that associated with pitting or intergranular corrosion.

1.2 Three-Inch-Diameter Corrosion Test Calcination Unit

In early corrosion studies, a 3-inch-diameter corrosion test calcination unit was used to determine the corrosion effects of calcination reaction products under constant and controlled conditions. Corrosion data on the resistance of Type 347 and 316 stainless steels, Carpenter-20 alloy and carbon steel in heat transfer service was determined in a 1277 hour test and these data are presented in Table III.[1]

Cyclones which were used to separate entrained fines in this test unit were reported to have shown damage accompanied by only very mild corrosion.

TABLE I

Specimen Corrosion in Six-Inch Diameter Aluminum Nitrate Fluid Bed Calciner at 400°C

Specimen area= 5 in.^{2} except carbon steel which = 4 in.^{2}

Material	Initial Wt. Gr.	Wt. After 463 Hrs. in Calcine Bed	Wt. Change After 463 Hrs. in Calcine Bed	Wt. After Additional 242 Hrs. in Hot Gas Stream	Period Wt. Loss After 242 Hrs. Gas Stream	Corrosion Rate After Total Exposure (mpm)	[μm/mo]*
Carpenter-20 alloy	42.0483	42.0523	+ 0.0040	42.0460	0.0063	0.028	[0.71]
Carpenter-20 alloy	42.3134	42.3134	- 0.0002	42.3123	0.0011	0.005	[0.13]
Type 347 Stainless Steel	46.0173	46.0194	+ 0.0021	46.0182	0.0012	0.005	[0.13]
Type 347 Stainless Steel	43.8006	43.8007	- 0.0001	43.7100	0.0907	0.411	[10.4]
Carbon Steel	28.0047	28.0174	+ 0.0127	28.0142	0.0032	0.018	[0.46]
Carbon Steel	28.0834	28.1012	+ 0.0178	28.0950	0.0062	0.035	[0.89]

* 1 mil. is 25.4 μ metres

Table II

Corrosion of Austenitic Stainless Steels Immersed in Off-Gas Condensate Stream in Six-Inch Pilot-Plant Scrubber

Material	Wt. Loss in Grams After 1316 Hours	Specimen Area, In.^{2}	Corrosion Rate (mpm)	[µm/mo]*
Carpenter-20 Alloy	0.0299	5.625	0.022	[0.56]
Carpenter-20 Alloy	0.0300	5.625	0.022	[0.56]
Type 321 Stainless Steel	0.0022	2.000	0.005	[0.13]
Type 321 Stainless Steel	0.0017	2.000	0.004	[0.10]
Type 329 Stainless Steel	0.0133	7.400	0.008	[0.20]
Type 329 Stainless Steel	0.0126	7.400	0.007	[0.18]
Type 347 Stainless Steel	0.0514	5.625	0.038	[0.96]
Nionel	0.0206	7.400	0.012	[0.30]
Nionel	0.0168	7.400	0.010	[0.25]

* 1 mil is 25.4 µ metres.

Table III

Corrosion Rate of Various Alloys Used as Heat Transfer Surfaces in Aluminum-Containing Waste Calcination at 400°C

Type Alloy	Corrosion Rate MPM [µm/mo]* First 392 Hrs	Second 507 Hrs	Third 378 Hrs	Visual Observation
Carbon Steel	0.72 [18.3]	--	0.036 [0.91]	Black oxide film & flaky tuberculation
Carpenter-20	1.11 [28.2]	0.162 [4.11]	0.036 [0.91]	Some scaling
Type 347 Stainless Steel	1.15 [26.7]	0.615 [15.6]	0.154 [3.91]	Band of pits 1-2" from top of shell
Type 347 Stainless Steel	0.20 [5.08]	0.135 [3.43]	-- ---	Regular scaling
Type 316 Stainless Steel	-- --	0.196 [4.98]	0.154 [3.91]	Some irregular scaling

The observed pitting attack on the Type 347 Stainless Steel heater appear to be about 5 mils deep. Attacks of this nature demand further testing before a corrosion estimate is accomplished.

* 1 mil is 25.4 µ metres.

1.3 Corrosion of Stainless Steel in Calciner Off-Gas

A steel wire mesh was evaluated for its reaction with radioactive ruthenium in the calciner off-gas stream.[2] Test results indicated that austenitic Type 304 stainless steel mesh showed 0.10 percent weight loss after 26 days exposure at 550°C. The nature of the surface of this mesh made it difficult to determine the surface area and, therefore, corrosion rates were not calculated. The apparent high area-to-weight loss ratio suggested a low rate. Austenitic stainless steel wire mesh was judged to be sufficiently corrosion resistant for adsorption applications in the off-gas stream.

2. Feed Nozzles

2.1 3-Inch and 6-Inch Calcination Test Units

Corrosion failure occurred in the feed jet atomizer to the 3-inch-diameter corrosion test calcination unit, and a near-failure occurred in the 6-inch pilot-plant calciner test unit.[1] These jets were fabricated of Type 304 stainless steel. They handled aluminum-uranium fuel processing waste streams composed of 2.2 M aluminum nitrate, 0.008 M mercuric nitrate, 0.15 M sodium nitrate, and 1.33 M hydrogen ion. The specific gravity of this solution was 1.420. The test was run at approximately 400°C. There was a thermal gradient of nearly 350°C on these jets in this service.

The throat of the feed nozzle to the fluidized bed in the 6-inch pilot-plant calcination unit suffered intergranular attack after about 900 hours of service. The nozzle geometry promotes turbulent rather than laminar flow which may explain the highly localized attack. A metallographic analysis indicated that grain boundary attack had occurred.

The tip of the feed nozzle to the fluidized bed in the 3-inch-diameter corrosion test calcination unit also suffered severe localized intergranular attack.

A Hanford Atomic Products Operations Report indicated that austenitic stainless steels were unsatisfactory at temperatures of 114-155°C in aluminum nitrate concentrations of about 67 percent. Table IV shows rates at various temperatures in aluminum nitrate waste.

2.2 Twenty-Four-Inch Square Pilot-Plant Calciner

2.2.1 Performance of Feed Nozzle Materials

Feed nozzle tests were made in the 24-inch pilot-plant calciner. The nozzles tested were fabricated of titanium and Type 347 stainless steel.[3] Test results for flat-faced titanium nozzle tips coated with alumina and Type 440-C stainless steel nozzle tips are shown in Table V. Erosion tests of nozzle caps[5] fabricated of titanium and Type 347 and 440-C stainless steels are reported in Table VI.

Table IV

Consolidation of Corrosion Rates of heat Transfer Specimens in 70.2 Percent Aluminum Nitrate Waste Concentration

Type Stainless Steel	Temperature °C	240 Hr MPM [μm/mo]* Corrosion Rate	
304L	115	1.6	[0.04]
304L	135	8.1	[0.21]
304L	150	9.7	[0.25]
304L	165	8.4	[0.21]
309SCb	115	2.3	[0.06]
309SCb	135	14.5	[0.37]
309SCb	150	23.1	[0.59]
309SCb	165	24.1	[0.61]
Ti 75A	120-165	0.1	[0.002]

*1 mil is 25.4 μ metres.

Table V

Feed Nozzle Top Erosion Results

Nozzle	Hours Tested	Weight Loss (grams)	Volume Loss Rate (in^3/yr)	Remarks
Stainless Steel 440-C, Flat-Face, Hardened to 56 Rockwell	106	0.0315	0.0201	
Titanium, Flat-Face, 3-4 mils Alumina Facing	205	0.0124	0.00934	Losses assumed to be entirely alumina from facing

Table VI

Nozzle Cap Erosion

Cap Material	Hours in in Operation	Measured Wear grams/year
Titanium	29	2.9
Type 347 ss	99	4.0
Type 440C ss	420	0.07

2.2.2 Boron Carbide Erosion Resistance

A boron carbide nozzle cap, removed after 738 operating hours, showed no visible evidence of erosion.[6] A retaining flange on the cap broke during removal, thereby eliminating the possibility of any weight loss determination. Boron carbide is the most attrition-resistant material tested to date. However, unless design changes can eliminate installation stresses its inherent brittleness makes its use undesirable.

3. Scrub System

A corrosion-erosion study of Carpenter-20 alloy and 17-7 and 17-4 precipitation hardenable stainless steels was conducted in a slurry consisting of alumina in nitric acid at room temperature.[2] The test apparatus was designed to simulate the action of a pump impeller, and the metals were rotated at a peripheral speed of about 46,000 inches per minute. The corrosion-erosion rates were negligible in all cases.

In other studies that evaluated pump bearing materials, a pump equipped with boron carbide sleeves and Type 440-C stainless steel journals was operated 1052 hours using an alumina slurry produced at the DWCF.[6] After disassembly no measurable wear was found on the boron carbide sleeves, but up to 0.6 mil wear was found on the 440-C stainless steel journals.

Tests were carried out in a 3 percent slurry of calciner fines suspended in a 40 percent solution of nitric acid to find a bearing material[7] for the circulation pumps in the calciner scrub solution stream. The slurry was maintained at a temperature of 77°C and stirred continuously; however, the agitation was insufficient and failed to produce erosive effects. Results based on a one-week (168 hour) test are given in Table VII.

4. Miscellaneous

4.1 Gasket Materials

A test was made to determine the resistance of a calcium fluoride-impregnated Teflon gasket material (Garlock 9428) to chemical attack.[22] This material was superior to the material in use at that time if resistance to attack by chemicals was the prime consideration. It was noted, however, that the Teflon gasket would be affected adversely by high radiation fields.

4.2 Cemented Tungsten Carbide Valves

If maintenance is required, slide valves used in the WCF silica gel off-gas adsorber system may require decontamination "in place". In order to determine the possible effects of such treatment, corrosion tests were conducted[9] in hot nitric acid using pieces of the valves, made of 94 percent tungsten carbide and 6 percent cobalt.

Exposure of the valve specimens for three 48 hour periods in boiling 40 percent and boiling 10 percent nitric acids showed results presented in Table VIII. Physical examination showed the surface of the carbide to have many five mil diameter "islands" with the surrounding material corroded away. The spent nitric acid solutions from the 48-hour boiling acid test periods were rose colored, indicating that the cobalt binder was dissolving. These results indicate that decontamination conditions will have to be controlled to avoid surface roughening.

Table VII

Corrosion of Pump Bearing Materials

Metal	Corrosion Rate (Mils per Mo)	Corrosion Rate [μm/mo]**
Carboloy 608	2.3	58.4
Carboloy 608	1.8	45.7
Norbide	0.1	2.54
Norbide (Low Density)	None detected	
Carboloy 907	0.33	8.38
Carboloy 907	0.55	14.0
Stoody 1	112	2845
Colmonoy 6	160*	4064

*The rate reported for Colmonoy 6 is a maximum. The coupon was a coating of Colmonoy 6 on steel and, although efforts were made to shield this base metal, there may have been some corrosion of the steel.

**1 mil is 25.4 μmetres.

Table VIII

Corrosion Penetration of Cemented Tungsten Carbide (Based on Weight Loss Measurements During Successive 48-Hr Boiling Periods)

	Penetration in: 40% HNO_3			Penetration in: 10% HNO_3		
Boiling Period	1	2	3	1	2	3
Corrosion Rate (Mils/Mo) [μm/mo]*	64 [1626]	64 [1626]	58 [1473]	32 [813]	5 [127]	3 [76.2]

*1 mil is 25.4 μ metres.

III. Zirconium Waste Calcination

Corrosion was recognized as one of the principal problems if calcination of fluoride containing zirconium waste solutions was to be accomplished. Literature reviews and laboratory studies led to the addition of calcium to the fluoride-containing waste prior to calcination to tie-up the fluoride and promote its retention in the calciner product.

1. Calciner and Calciner Off-Gas Systems

1.1 Test Loop Studies

A corrosion-erosion recirculating test loop[10] was operated for 460 hours at 29°C and 12.5 psia using the feed solution shown in Table IX. The test loop (Figure 1) contained a silicon carbide spray nozzle and samples of Type 304, 304L, and 347 stainless steels.

Corrosion rates, based on weight loss, for various parts are given in Table X. No metal loss could be measured at the throat or orifices of the venturi scrubber although weight loss indicated some general corrosion of the equipment. The control valve was a dual-plug design constructed of Type 316 stainless steel. Measurement of the plugs and seats revealed an approximate 0.001-inch decrease in the outside diameter of the top plug while the lower plug diameter remained unchanged. The top seat increased in inside diameter by 0.0006-inch and the bottom seat increased by 0.0001-inch.

1.2 Twelve-Inch Pilot-Plant Calciner

An additional corrosion test was run in a 12-inch calciner system during the calcination of zirconium fluoride waste.[11] The materials tested and the observed corrosion results are listed in Table XI.

Corrosion rates for 1, 2, and 3 may have been biased upward since the venturi scrubber water supply was inadvertently left on during an otherwise normal shutdown of the calciner equipment. The calciner vessel temperature was 120°C when this water began flowing into the vessel. The electrical heaters and the fluidizing air were turned on to dry out the calciner vessel and off-gas lines. The temperature in the calciner vessel reached 320°C during the two-hour drying period.

In general, the chromium-nickel (austenitic) grades of stainless steel showed more resistance than did the straight chromium (martensitic) grades of stainless steel. Similar corrosion results were obtained at Brookhaven National Laboratory during testing of zirconium fluoride waste calcination in a Rotary Ball Kiln.[12]

Table IX

Synthetic Feed Solution Composition

H^+	2.5 M
NO_3^-	2.5 M
Zr^{++}	0.5 g/l
Al^{+3}	0.4 g/l
F^-	0.13 g/l
Undissolved Solids	0.07 g/l

Table X

Corrosion-Erosion Test Results

Equipment Item	Corrosion-Erosion Rate (mils/mo)	[µm/mo]*
Silicon Carbide Spray Nozzle	0.03	[0.76]
Venturi Flowmeter (304)	0.08	[2.03]
Venturi Scrubber (304L)	0.31	[7.87]
Reducing Section (347-304-347)	0.00	
3/4-inch ELL in Spray Nozzle Leg (347)	0.05	[1.27]
Pump Impeller	0.01	[0.25]

*1 mil is 25.4 µmetres.

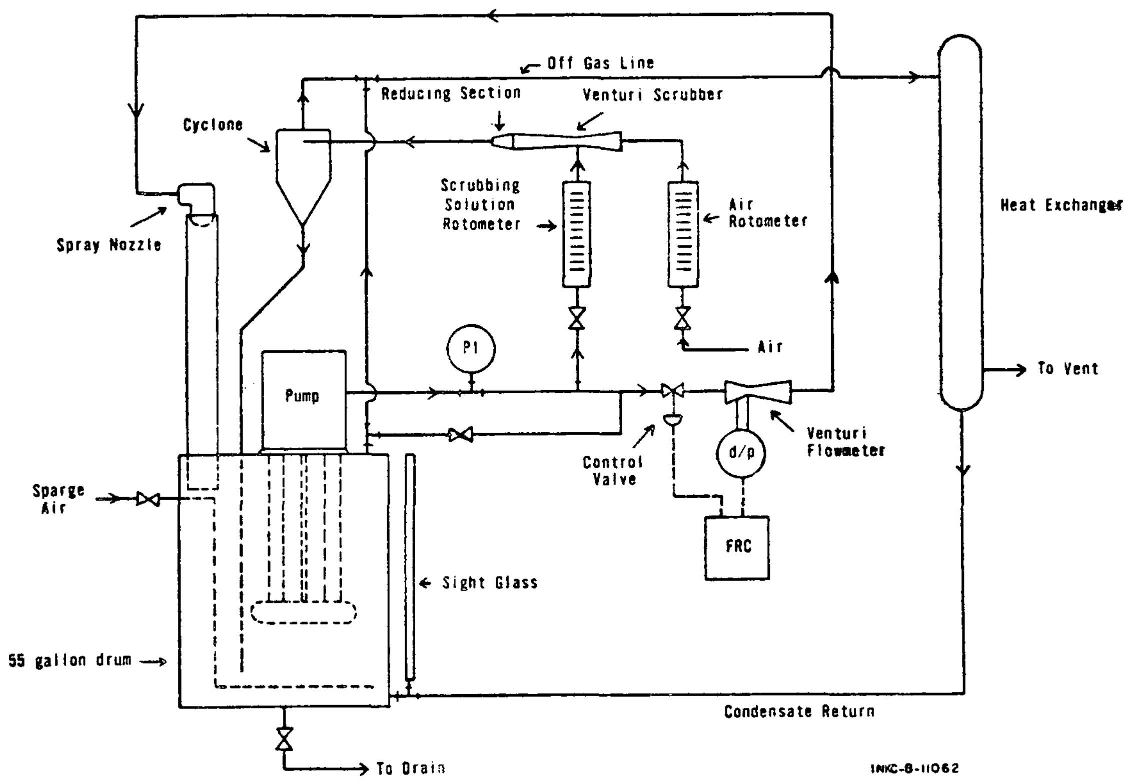


Figure 1. Schematic Diagram of Corrosion-Erosion Test Loop

Table XI

Corrosion Rates During Zirconium Fluoride Calcination
Twelve-Inch-Diameter Pilot-Plant Calciner

Type of Exposure	Material	Corrosion Rate (mils/mo) [μm/mo]*	
1. Ambient temperature feed solution with $Ca(NO_3)_2$ added	Type 304L stainless steel	0.01	[0.25]
	Type 304L stainless steel welded to Type 347 stainless steel	0.42	[10.7]
	Type 347 stainless steel welded to 17-4 PH stainless steel	0.67	[17.0]
	Type 347 stainless steel	0.60	[15.2]
2. Fluidized bed of granular product (400°C)	Type 304L stainless steel	<0.10	[<2.54]
	Inconel	0.40	[10.2]
	Type 440-C stainless steel(a)	42.50	[1080]
3. Hot calciner off-gas	Inconel - X	0.41	[10.4]
	K - Monel	0.11	[2.79]
	TimKin 16-25-6 (Cr-Ni-Mo)	0.04	[1.02]
	Nichrome (HR)	0.34	[8.64]
	Tophet "A"	0.20	[5.08]
	70% Copper - 30% Nickel	34.40	[874]
	Monel	0.08	[2.03]
	Type 310 stainless steel	0.05	[1.27]
	Type 316 stainless steel	0.03	[0.76]
	Type 329 stainless steel	0.01	[0.25]
	Boron Carbide	3.20	[81.3]
4. Hot aqueous scrubbing solution (50°C)	Type 304 stainless steel	<0.10	[<2.54]
5. Cooled aqueous scrubbing solution (30°C)	Silicon Carbide	2.50	[63.5]
	Type 304L stainless steel welded to Type 347 stainless steel	0.04	[1.02]
	Type 347 stainless steel welded to 17-4 PH stainless steel at 900°F	0.10	[2.54]
	Type 347 stainless steel welded to 17-4 PH stainless steel at 1100°F	0.11	[2.79]
	Type 347 stainless steel welded to 17-7 PH stainless steel at 900°F	0.28	[7.11]

(a) The Type 440-C stainless steel test coupons fell from their mountings above the electrical heaters and worked their way down through the bed to the air distributor plate where they were found at the end of the operating period. Therefore, the tabulated corrosion rate may be biased because of possible erosion in the neighborhood of the air distributor caps.

*1 mil is 25.4 μmetres.

1.3 Additional Material Studies

1.3.1 Service Test Corrosion Results

Three Inconel-X heater rods used in fluid-bed heat transfer service[13] corroded at an average rate of 0.4 mil/month. The observed rates in this service varied between 0.2 and 0.8 mil/month; the position of the rods in the bed could explain this rate variation.

The Type 304 stainless steel venturi throat piece in the scrubbing system completely resisted corrosion of the scrubbing solution. The Type 347 stainless steel feed nozzle port lost 0.6 mil/month. A silicon carbide nozzle in the off-gas scrubbing solution lost 2.5 mils/month due to corrosion. These service test losses are considered to be within acceptable limits.

1.3.2 Test Specimen Corrosion Results

Test specimens were mounted in various locations in the pilot-plant calcination system during the zirconium fluoride run.[13] Table XII which summarizes the tests results, compares the corrosion rates, material, and service.

1.3.3 Ruthenium Behavior on Stainless Steel Filters

The possibility of replacing the cyclone used to separate solids from the off-gas stream in the WCF by stainless steel filters was studied.[14] Corrosion of the filters in the nitric acid vapors was investigated as part of the ruthenium adsorption study.

A synthetic feed solution of 6.6 $\underline{M}$ nitric acid, containing 0.03 gram per litre ruthenium, was fed into a small laboratory-scale static bed calciner heated to 400°C. The region around the filter was maintained at 300 to 350°C. Visual observation and filter weight measurements indicated that corrosion of the filter was insignificant over the 104 hour operating period. The weight of the filter actually increased 0.04 percent because of corrosion products filtered from the off-gas stream that were not removed in a cold water wash at the conclusion of the test.

2. Scrub System

A corrosion-erosion test loop (Figure 2) was set up and operated[14] using a circulating synthetic scrub solution prepared by mixing finely divided, nonradioactive zirconia calcine product with different concentrations of nitric acid (Table XIII). The solution was replaced with fresh solution every 100 hours. Corrosion-erosion rates, calculated on the basis of weight loss, are shown in Table XIII.

After 1257 hours of operation, the corrosion-erosion rates of austenitic stainless steel equipment were found to be acceptable. Type 304, 304L, and 347 stainless steels were generally resistant to the scrubbing solution at 60°C.

Table XII

Corrosion Test Results for Various Materials During Calcination of Zirconium Fluoride Type Waste Solutions

Alloy	Location of Service	Corrosion Rate (mils/mo) [μm/m]*
304L stainless steel welded to 347 stainless steel	Calcination quench solution	0.04 [1.02]
347 stainless steel welded to 17-4 PH stainless steel	Calcination quench solution	0.10 [2.54]
347 stainless steel welded to 17-7 PH stainless steel	Calcination quench solution	0.28 [7.11]
310 stainless steel	Vapor above calciner bed	0.05 [1.27]
329 stainless steel	Vapor above calciner bed	0.01 [0.25]
316 stainless steel (modified)	Vapor above calciner bed	0.03 [0.76]
Timken 16-25-6 (Cr-Ni-Mo)	Vapor above calciner bed	0.04 [1.02]
HR Nichrome	Vapor above calciner bed	0.34 [8.64]
Tophet "A"	Vapor above calciner bed	0.20 [5.08]
Monel	Vapor above calciner bed	0.08 [2.03]
K-Monel	Vapor above calciner bed	0.11 [2.79]
Inconel-X	Vapor above calciner bed	0.41 [10.4]
Cupro-Nickel (70 Cu-30 NI)	Vapor above calciner bed	34.4 [874]
Boron carbide nozzle	Fines collection pot	3.2 [81.3]
440-C stainless steel	Lower part of bed	42.5[a] [1080]

[a] The Type 440-C stainless steel specimens came loose from the test rack and were found in the bottom of the calciner. Erosion due to location and movement in the bed could have contributed to the apparent corrosion rate.

* 1 mil is 25.4 μmetres.

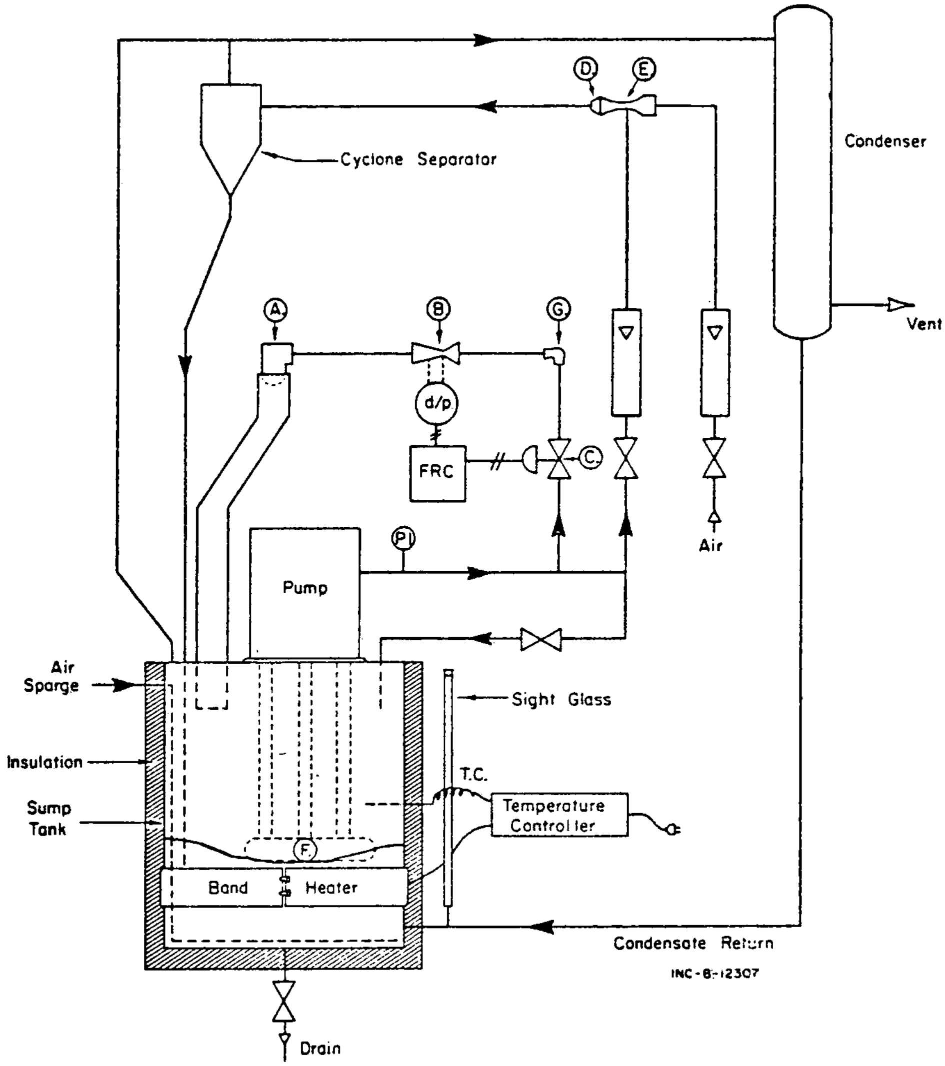


Figure 2. Corrosion-Erosion Test Loop Flowsheet

Figure 2 Call Out	Specimen Description
A	Silicon Carbide Spray Nozzle
B	Venturi Flowmeter -- Type 304 stainless steel
C	Control Valve, Double Plug, V Port
	Plug -- Type 316 stainless steel
	Seats -- Type 347 stainless steel
D	Concentric Reducer Downstream of Scrubber
	Types 347, 304, and 304L stainless steel
E	Venturi Scrubber -- Type 304L stainless steel
F	Pump Impeller -- Type 316 stainless steel
G	3/4 in. Ell -- Type 347 stainless steel

TABLE XIII

CORROSION-EROSION RATE OF VARIOUS EQUIPMENT ITEMS IN SEVERAL SYNTHETIC ZIRCONIUM SCRUB SOLUTIONS

		Operating Period I	Operating Period II		Operating Period III
			Part 1	Part 2	
Operating Time:		463 hours	125 hours	115 hours	554 hours
Scrub Solution Composition:					
Total Solids (g/l)		∿ 6	∿ 30	∿ 92	∿ 138
Undissolved Solids (g/l)		0.07	0.08	1.80	14.05
H+ (N[a])		2.5	4.2	3.5	0.9
NO_3^- (M)		2.5	4.1	5.5	3.8
Zr^{+4} (M)		0.005	0.006	0.20	0.195
Al^{+3} (M)		0.015	0.017	0.50	0.61
F^- (M)		0.13	0.06	1.00	1.30
Temperature:		29°C	55°C	58°C	60°C
Corrosion-Erosion Specimens:		Observed Corrosion-Erosion Rate (mils per month)[μm/mo]*			
Silicon Carbide Spray Nozzel	A	0.0	Weight Gain		Weight Gain
Venturi Flowmeter	B	0.1 [2.54]	0.5 [12.7]		0.3[7.62]
Control Valve	C				
Plug		<0.1 [<2.54]	2.4 [61.0]		0.5[12.7]
Seats		0.5 [12.7]	0.0		3.8[96.5]
Concentric Reducer	D	0.0	<0.1 [<2.54]		0.3[7.62]
Venturi Scrubber	E	0.3 [7.62]	0.4 [10.2]		0.1[<2.54]
Pump Impeller	F	0.0	0.9 [22.9]		0.4[10.2]
3/4" ELL	G	0.0	0.3 [7.62]		0.1[2.54]

* 1 mil is 25.4 μ metres

3. Miscellaneous

3.1 Gold-Nickel Alloy for Bellows-Sealed Valves

Experience in the WCF showed that an increased number of Type 304L stainless steel bellows on several types of valves had suffered corrosion failure following the calcining of zirconium fluoride wastes. A search was initiated for more corrosion resistant materials for seal bellows on block and control valves in the scrubbing system and for the nozzles in the feed system.[15]

Alloys that completely resist all concentrations of hydrofluoric-nitric acid mixtures at temperatures up to 100°C are unknown. The only ductile metal that is reported in the literature[16] with an acceptable corrosion rate is a 75% gold-25 percent nickel alloy. Its corrosion rate in 6 M hydrofluoric-6 M nitric acid mixture at 70°C after 382 hours was 10 microns (0.4 mil) per year.

Corrosion tests were initiated for the gold-nickel alloy as a possible replacement for Type 304L stainless steel as seal bellows in WCF service. Welds on the 75 gold-25 nickel alloy were made using electron beam techniques. The welded specimens were then subjected to heat transfer corrosion tests using various hydrofluoric-nitric acid mixtures as well as representative calciner feed solution.

The results of this work are shown in Table XIV and indicate that this alloy would be suitable for use in many hydrofluoric - nitric acid mixtures.

The alloy was insufficiently ductile for forming at room temperature. Therefore, tensile, yield, and elongation properties of this alloy at elevated temperatures were determined.[17] Room temperature tensile tests showed that it had about 2% elongation with ultimate and yield strengths of 175,000 and 87,500 psi, respectively. Welds prepared by electron beam had an ultimate strength of 107,000 psi. High temperature tensile tests at 400 and 600°C showed that the ductility of the alloy increased with increasing temperature. At 510°C the elongation of the gold-nickel alloy was about 13%.

3.2 Platinum Valve Bellow

Corrosion measurements in hydrofluoric-nitric acid solutions indicated that platinum had an acceptable corrosion rate for use in WCF service. A test bellows of Grade III platinum (99.5% minimum platinum) was purchased for testing.[18] A cyclic performance test was made in an environment of 5.9 M hydrofluoric-5.5 M nitric acid, followed by exposure in 2.0 M nitric acid at 200°C. The platinum bellows performed at 10 cycles/minute for 115,000 cycles without losing its spacing or showing significant corrosion loss. This test was conducted using a spring-loaded push rod for the tension movement and cam-actuated rod for compression.

Table XIV

Corrosion Resistance of Valve Materials in Various Hydrofluoric-Nitric Acid Mixtures and in Zirconium Feed Solution to the Calciner

(Exposure Time: 48 hours)

Type Solutions	Temperature (°C)	Corrosion Rate: 75% Gold-25% Nickel (mils/mo)	[μm/mo]*	B_4C (mils/mo)	[μm/mo]*
Zirconium Feed Solution (0.63 M Zr, 4.1 M F, 0.427 M Al^{+++}, 2.3 N H^+, 2.27 M NO_3, 1.14 g/l Sn, 0.841 g/l Cr, 2.6 g/l B, 8.07 x 10^{-3} g/l U, 1.226 Sp gr.)	150	0.31	7.87	0.86	21.8
5.5 M HF - 5.5 M HNO_3	100	0.06	1.52	0.11	2.79
	65	0.07[a]	1.78		
3.0 M HF - 8.0 M HNO_3	150	0.11	2.79	0.08	2.03
20.0 M HF - 2.0 M HNO_3	150	0.30	7.62	0.14	3.56

a - 24-hour test

* 1 mil is 25.4 metres

3.3 Boron Carbide for Packed Valves

Packless valves with Type 304L stainless steel bellows are used in WCF service instead of packing-sealed valves because the process solutions are much more corrosive toward the usual packing than toward stainless steel bellows. Likewise, the cleanout plungers on the feed nozzle to the calciner vessel use bellows instead of packing. A search for a corrosion resistant packing material led to a study of boron carbide[15] since it was felt that this would be a material that could serve as a close-fitting stem guide and packing support that would be self-lubricating and resistant to plastic deformation.

The corrosion resistance of boron carbide was evaluated in the laboratory[15] heat transfer corrosion test apparatus using a disc-shaped specimen. Results of this work are shown in Table XIV and indicate that recrystallized boron carbide is suitable as a construction material for all concentrations of hydrofluoric-nitric acid mixtures.

IV. NaK Corrosion Studies

A NaK (78 percent potassium-22 percent sodium eutectic alloy) was evaluated during operation of the 24-inch square pilot plant calciner. The section of the NaK heat transfer loop in the oil fired furnace was constructed of Type 316 stainless steel and showed only minor corrosion damage on the fired side of the tubes after 9089 hours operation.[5] All tubes were coated with a porous, tenaceous, non-uniform scale. Numerous pits, estimated to be less than 5 mils deep, were observed under the scale. Carpenter-20 alloy heat transfer tubes in the calciner bed showed only a tarnish and no corrosion after more than 2000 hours of service.[8] Cracking failures were reported[22] in the connecting welds between Carpenter-20 alloy and Type 316 stainless steel. These failures were believed to be associated with thermal stresses due to the large number of system start-ups.

After extensive testing in pilot-plant operations, Type 316 stainless steel was selected as the material of construction for the vessels and piping in the NaK heat transfer system for the WCF.

Type 316 stainless steel was examined after 32,600 hours of calciner[17] operation. The principal effect was carbon depletion at the NaK-pipe wall interface. The presence of sigma phase formation, as evidenced by metallographic examination and accompanying embrittlement, was indicative of a fundamental change in the microstructure of the alloy due to exposure at elevated temperatures. There was no evidence of general corrosion damage.

Examination of Type 304L stainless steel in service for 15,567 hours[17] showed carbon depletion at the NaK-metal interface; there were significant amounts of carbide precipitation at the grain boundaries and only trace quantities of sigma phase formation.

A sample of Type 318 stainless steel in service for the entire 32,600 hours of loop operation was examined.[17] Most of this service (31,190 hours) had been above 600°C, the loop operating condition. The most significant effect was the almost complete absence of carbon depletion at the NaK-metal interface. Sigma phase formation was observed in this alloy and no general corrosion damage was detected.

Results indicate that Type 304L, 316, and 318 stainless steel alloys are suitable for materials of construction for nonisothermal loops containing NaK at 600 to 700°C. However, since there appeared to be a relationship between failure of pipe fittings and applied stress on the components, applied stress should be minimized in the design of future loops.[17]

V. In-Bed Combustion Corrosion Studies

The possibility of metal dusting corrosion during in-bed combustion of hydrocarbons in the WCF led to a 1200-hour laboratory test of Type 347 stainless steel in synthetic in-bed combustion gas at 500 and 600°C.[14] These tests indicated that metal dusting could be associated with the in-bed combustion process at these temperatures.

A second test[19] was conducted using the same synthetic gas composition (N_2-75, O_2-15, CO_2-7.5, and CO-2.5 mole percent) to confirm the results of the previous test and to determine the extent of metal dusting at 450°C, the anticipated operating temperature of the WCF. Welded and nonwelded specimens of Type 347 stainless steel were run for 2170 hours with specimens exposed at temperatures of 450, 500, and 535°C.

Photomicrographs indicated that carburization occurred at 500 and 535°C. The specimen exposed at 535°C showed some pitting attack, grain growth, and carbide precipitation at the grain boundaries. The specimen exposed at 500°C showed carbide precipitation and grain growth; however, it was not nearly as pronounced as in the specimen exposed at 535°C. The specimens exposed at 450°C showed slight carbide precipitation and grain growth. Both welded and non-welded specimens showed the same results.

Results of these tests indicated that low operating temperatures and complete combustion, excluding the formation of carbon monoxide, are desirable. The specimens exposed to the combustion gas for over 2170 hours indicated that corrosion of Type 347 stainless steel by metal dusting or other mechanisms is negligible at 450°C under the test conditions.

VI. Corrosion in the Waste Calcining Facility

The Waste Calcining Facility (WCF) which began operation in December 1963 as the Demonstration Waste Calcining Facility (DWCF) has also been referred to at times in the literature as the 48-inch diameter waste calciner. This facility has been operated for approximately 53,800 hours. Aluminum waste feed was used for the first and most of the second processing campaigns. Since that time, operation has been almost entirely with zirconium waste feed. In the original unit, heat supply to the calciner bed was provided by a NaK heat transfer system. This was replaced by an in-bed combustion system with the start of the fourth processing campaign.

Corrosion examination and evaluation of the WCF vessels and associated hardware have been made after the equipment was decontaminated and available for inspection.

The largest number of equipment problems associated with calciner operation are the failure of bellows seal valves and feed and fuel nozzles. Bellows material thickness was increased to attempt to alleviate this problem without any noticeable effect. Laboratory studies and literature review have failed to provide a suitable material for this application.

Feed and fuel nozzles have gone through a series of design changes and a variety of materials have been tested. The problem is very complex as a material for this application must resist high temperature oxidation, erosion, and corrosion in feed and decontamination solutions. Currently, Haynes alloys 25 and 188 (cobalt-base high temperature alloys) are under test in the calciner. The search for new materials for this service is continuing.

Failure of the deflection baffle plates in the top of the calciner vessel was discovered following the fifth processing campaign.[20] These plates were orignally made of Type 304 stainless steel and no prior indication of failure had been observed. The baffle plates were replaced with Type 310 stainless steel[18] and were failing prior to the start of the current (eighth) processing campaign. The Type 310 stainless steel baffle plates have been removed and replaced with Type 347 stainless steel plates.

Remote metallurgical examination[18,20] of the failed Type 304 stainless steel plates suggested that the failure was probably due to carburization of the metal. The appearance of the failed Type 310 stainless steel baffle plates was the same as that of the Type 304 stainless steel plates, and at this time, it is assumed that carburization was again the failure mechanism.

Six baffle plates -- two each of Carpenter-20 Cb3, Hastelloy C-276, and Nitronic-50 -- were placed under test[21] in the calciner vessel in 1975 before the seventh processing campaign. Examination prior to the eighth processing campaign showed they were in excellent condition.

A recent problem in erosion of the solids transport lines has required replacement of a few line sections. An elbow of Nitronic-50 alloy has been placed in service to determine if the high work hardening rate of this alloy will give improved erosion resistance for use in this service. Laboratory tests have shown Nitronic 50 to be superior to Type 304L stainless steel in erosion resistance.

Other corrosion problems in the WCF have generally been those associated with plant operation involving aggressive corrosive and erosive systems.

VII. Storage of Calcine

1. High Temperature Storage Tests

The initial corrosion investigation to determine materials for containment of calcine during long-term storage was done by the research division of the Fluor Corporation, Ltd.[22] At that time, high temperature (538-816°C wall temperature) storage of calciner product was under consideration.

Corrosion tests were run in which a wide range of alloys were subjected to brief but severe tests. Metal coupons, which included welds, were immersed in beds of calcined alumina, clean silica sand, San Gabriel sand, Idaho windblown and pit-run sand, and Johns Manville Sil-O-Cel insulating powder. Some coupons were protected by 1/2-inch magnesia or 1/4-inch Johns Manville Serefelt insulation. The test beds were contained in 4-inch-diameter by 12-inch-long stainless steel tubes, placed in an oven and held for periods ranging from 72 to 150 hours at temperatures varying between 510 and 927°C. Table XV includes a summary of these tests on the three most promising alloys: Incoloy (probably Incoloy 800), Inconel (probably Inconel 600), and Type 430 stainless steel.

Additional testing of these Incoloy and Inconel alloys favored Incoloy for this high temperature exposure. The results of this series of corrosion tests were summarized as follows:

1. At temperatures in excess of 816°C, all alloys showed significant damage when subjected to an environment of Idaho sand or calcined alumina. The stainless steels were considerably less resistant than the high nickel alloys, Inconel, and Incoloy. Incoloy was more corrosion resistant in sand than Inconel. The reverse was true in calcined alumina.

2. At 649°C, neither Incoloy nor Inconel was significantly attacked in sand or alumina.

3. At 732°C, Incoloy samples placed in calcined alumina for various periods of time (72 to 324 hours) showed signs of progressive attack. Inconel samples under the same conditions showed considerably less attack.

4. Of the two spiked chemicals in the calcined material, cesium and sodium nitrates, the latter caused the greater damage.

5. At 816°C, Incoloy welds were less corrosion resistant than Incoloy base metal. At 732°C, there was no noticeable difference in relative corrosion.

6. Prolonged exposure (up to 30 days) to a temperature of 635°C $\pm$ 5°C and corrosive conditions simulating the actual storage conditions did not affect the integrity of an Incoloy vessel.

Table XV

Effect of Environments on Incoloy, Inconel and Type 430 Stainless Steel

		Oven Air	Idaho Sand		Calcined Alumina	Calcined Alumina 2-1/2% $NaNO_3$ Spike	Calcined Alumina 2-1/2% $NaNO_3$ and 1/2% $CsCO_3$ Spike		
	Time (hrs)	72	72	72	72	72	72	216	324
	Temp (^{o}C)*	927	649	927	927	816	732	732	732
Oxide Film (in.)	Incoloy	0.0003	0.00025	0.0003	0.0003	0.0003	Nil	0.0003	0.0005
	Inconel	0.0003	0.00013	0.0004	0.0004	0.0006	Nil	0.0002	0.0002
	SS-430	--	0.00011	--	0.0016	0.0015	--	--	--
Grain Penetration (in.)	Incoloy	0.0008	Nil	0.0008	0.00024	0.0007	Nil	0.0004	0.0008
	Inconel	0.0005	Nil	0.0021	0.0015	0.0005	Nil	0.0003	0.0003
	SS-430	--	0.0004	--	--	0.0010	--	--	--

* Wall Temperature

It was concluded that for these test conditions, Inconel resistance to corrosion was satisfactory up to 732°C while Incoloy, as well as stainless steels, were acceptable up to 649°C. None of the materials tested were acceptable above 927°C.

Additional high temperature tests of Inconel and Inconel-X (now Inconel X-750) are reported[7] in which corrosion test coupons (welded and unwelded) were exposed in air for 2000 hours at 816°C. Results are presented in Table XVI and indicate that Inconel suffered the least attack in this exposure.

2. Long Term Corrosion Tests in Zirconia Calcine

A long term corrosion test of several construction materials (Type 304, 304L, 316ELC, 347, and 405 stainless steels, carbon steel and 6061 aluminum alloy) in zirconia calcine was initiated in 1967[14] and is continuing. The test coupons were initially exposed at 200°C (the expected maximum wall temperature during calcine storage); however, after two years the test temperature was increased to 300°C to investigate the possibility of corrosion at this higher wall temperature. After ten years of exposure, results do not indicate any severe corrosion attack. The coupons continue to show a light, tenaceous scale and a slight weight gain.

Table XVI

Corrosion of Inconel and Inconel-X in Air at 816°C

Metal	Corrosion Rate Mils per Mo	Corrosion Rate [μm/mo]*
Inconel (Unwelded)	0.022	0.56
Inconel (Unwelded)	0.020	0.51
Inconel (Unwelded)	0.019	0.48
Inconel (Welded)	0.018	0.46
Inconel (Welded)	0.017	0.43
Inconel (Welded)	0.018	0.46
Inconel-X (Unwelded)	0.084	2.13
Inconel-X (Unwelded)	0.051	1.30
Inconel-X (Unwelded)	0.039	0.99
Inconel (Welded)	0.062	1.57
Inconel (Welded)	0.045	1.14
Inconel (Welded)	0.041	1.04

* 1 mil is 25.4 μmetres.

3. Idaho Chemical Processing Plant (ICPP) Calcine Storage Bins

Final design of ICPP storage bins was based upon a requirement that the stored calcine would need to be contained for a minimum of 500 years to permit sufficient radioactive decay.[23] The stored calcine was to be maintained at a temperature below 400°C.[24] Non-metallic materials were eliminated due to possibility of fracture by cracking. A buried, single-walled, containment unit was considered, but was discarded in favor of a double containment system having a metal bin in a concrete vault. This concept has been utilized in design of all calcine storage facilities constructed or currently under design.

Corrosion data for metals over this 500 year projected time period were virtually non-existent. Analysis of the data available indicated that corrosion of the metallic bins by cooling air would be more significant than corrosion due to the contained calcined solids. Based on the limited data shown in Figure 3, the storage bins have been built of stainless steel. The first set of bins was a concentric ring type of construction using Type 405 stainless steel in contact with the stored calcine. These were contained in an outer shell of carbon steel without calcine contact with the carbon steel.[24] All subsequent bins (sets 2,3 and 4) have been construction of Type 304 stainless steel with a maximum carbon content of 0.06 percent.

For the second bin set, a corrosion allowance of 1/8-inch was allowed.[24] Corrosion test coupons were placed in two bins in this set of seven units. One of these test bins was scheduled to be filled with aluminum calcine and the other to receive zirconia calcine.

Eighty corrosion test coupons were hung on five stainless steel cables in each test bin. Each cable has sixteen coupons -- four each of Type 304, 304L, and 405 stainless steel and 1025 carbon steel. The stainless steel retaining cables are supported from blind flanges on the bin access risers. The corrosion investigation schedule calls for removal and evaluation of one set of coupons from each bin on the 5th, 10th, 20th, 40th, and 80th year of solids storage. Information from these examinations will be useful in establishing the condition of the bins and for future bin design.

Corrosion test coupons have been installed in both the third[25] and fourth[26] sets of calcine bins. These sets of corrosion coupons contain welded coupons of Type 304, 304L, and 405 stainless steels and 1025 carbon steel. Coupons are scheduled for removal and evaluation after 5, 10, 20, 40, and 80 years of exposure.

4. Calcine Storage Corrosion Test Coupon Evaluation

To date, one set of corrosion test coupons has been removed from each of the two test exposures in the second set of calcine storage bins.[24]

The results of measurements from coupons exposed for six years in alumina calcine are shown in Table XVII. These corrosion rates project

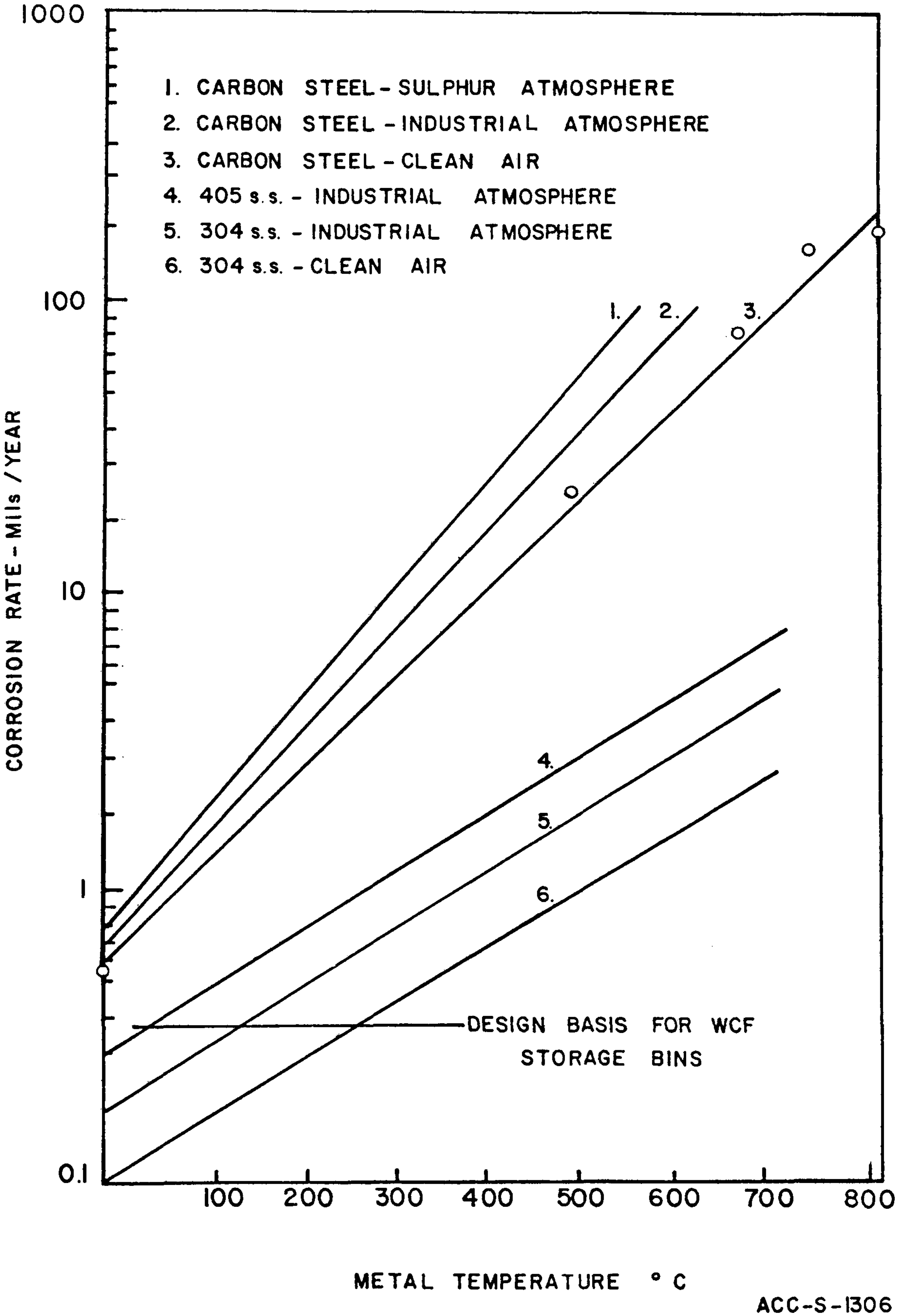


Figure 3. Corrosion Rate of Metal Alloys at High Temperature

Table XVII

Corrosion Experience in Aluminum Calcine Product

Exposure Time: 6 Years

Alloy	Average Corrosion Rate (mils per year)	[μm/y]*	Projected Corrosion After 500 Years Service (mils per year)	[μm/y]*
AISI 1025 Carbon Steel	0.024	0.61	12	305
AISI Type 405 Stainless Steel	0.014	0.36	7	118
AISI Type 304 Stainless Steel	0.003	0.08	2	50.8
AISI Type 304L Stainless Steel	0.003	0.08	2	50.8

* 1 mil is 25.4 μ metres.

a metal loss of 2 mils after 500 years for both Type 304 and 304L stainless steels, 7 mils for Type 405 stainless steel, and 12 mils for 1025 carbon steel. The mean temperature of this calcine from 1971-1973 was 60°C as determined by a thermocouple near the exposed coupons.

The results of measurements from coupons exposed for two years in zirconia calcine product are presented in Table XVIII. These corrosion rates indicate a projected metal loss (after 500 years of service) of 5 mils for Type 304 and 304L stainless steels, 20 mils for Type 405 stainless steel, and 35 mils for 1025 carbon steel. The exposure temperature estimated from mean readings of a thermocouple placed near the corrosion coupons in the calcine bed was 58°C,

The following conclusions and recommendations were made based on the results from these corrosion tests:

1. A corrosion allowance independent of the thickness requirements for structural and abnormal stress must be specified as a part of the design criteria for the construction of future solids storage bins. Based upon data from the corrosion coupons that were withdrawn from the zirconium calcine storage bin, corrosion allowances for type 304L, 304, and 405 stainless steels and AISI 1025 carbon steel at 95 percent confidence level are 5, 7, 40, and 50 mils, assuming a projected 500-year service life. Accordingly, with these corrosion allowances, any of these alloys would be suitable for storage of zirconia calcine.

TABLE XVIII

CORROSION EXPERIENCE

IN ZIRCONIUM CALCINE PRODUCT

Alloy	Type Coupon	Average Corrosion Rate (Mils per Year)[µm/y]*	Projected Corrosion After 500 Years Service (Mil)[µm]*	Required Corrosion Allowance at 95% Confidence Level (Mil)[µm]*
AISI Type 304L Stainless Steel	Plates	0.010 [0.25]	5 [127]	5 [127]
	Cylinders	0.007 [0.18]	5 [127]	
AISI Type 304 Stainless steel	Plates	0.008 [0.02]	5 [127]	7 [178]
	Cylinders	0.012 [0.30]	5 [127]	
AISI Type 405 Stainless Steel	Plates	0.032 [0.81]	15 [381]	40 [1016]
	Cylinders	0.052 [1.32]	25 [635]	
AISI 1025 Carbon Steel (0.25%)	Plates	0.079 [2.01]	40 [1016]	50 [1270]
	Cylinders	0.056 [1.42]	30 [762]	

* 1 mil is 25.4 µ metres.

2. Based on data from corrosion coupons that were withdrawn from bins that contained aluminum calcine solids, corrosion allowances to provide the required 500-year life are 1, 1, 7, and 12 mils for Type 304L, 304 and 405 stainless steels and AISI 1025 carbon steel, respectively. Thus, each of these alloys is suited for aluminum calcine product storage service.

3. The existing ICPP Type 304 (0.06 percent carbon maximum) stainless steel bins for storage of dry aluminum and/or zirconium calcine solids will not exceed, at 95 percent confidence level, a metal loss of 5 ± 2 mils in 500 years service.

4. Because of the observed low corrosion rates, a revised schedule for withdrawing corrosion coupons from the storage bins to reflect observations nearing the 500-year terminal sevice life of these bins has been recommended. One cable from each bin should be withdrawn at the end of the 10th, 100th, 250th, and 450th year of solid storage service.

VIII. New Waste Calcining Facility Corrosion and Materials Study

1. Corrosion Studies

The search for improved materials of construction was initiated early in the conceptual design phases of the New Waste Calcining Facility (NWCF). A review of present and future wastes indicated that the NWCF would process solutions similiar to the first-cycle wastes currently being processed in the WCF as well as intermediate-level wastes containing varying amounts of chloride. Testing was initiated to compare materials currently in use in the WCF with candidate materials of construction to find the optimum material relative to corrosion resistance.

Corrosion testing has indicated that Nitronic 50 is the most serviceable alloy for use in the aqueous solutions to be handled in the NWCF.

1.1 Laboratory Test Apparatus

A majority of the corrosion testing was done in a heat-transfer-type test apparatus. Figure 4 is a photograph of this test apparatus, and shows the electric cone heater, the heat transfer block, the Teflon solution container, and the plastic water-cooled condenser. The test coupon fits between the heat transfer block and the Teflon solution container and is equipped with a thermocouple to permit temperature monitoring.

The heat transfer test apparatus and procedure provides an accelerated test which permits:(1) the use of very corrosive test solutions, (2) control of temperature, (3) exposure of the test sample as a heat transfer surface similar to that encountered in heat exchanger service, and (4) the use of welded or non-welded test coupons. Since the solution contacts only the test specimen and Teflon, galvanic corrosion is not possible.

Several series of corrosion tests were made in various synthetic calciner processing solutions, decontamination solutions, and other miscellaneous testing solutions.

1.2 Test Coupons

Test coupons used throughout the heat transfer corrosion tests were discs (Figure 5) of test materials that were welded using the manual Gas Tungsten Arc Weld (GTAW) process, X-rayed to assure good weld quality, then machined to shape and provided with a 125 root-mean-square (RMS) finish, unless specified otherwise. Specimens were exposed in the as-welded and as-machined condition to incorporate the induced stresses and work hardening resulting from these operations. Examples of exposed coupons are shown in Figure 6. These test coupons permitted evaluation of general corrosion as well as several different specific types of localized corrosion attack. These forms of attack may be described as follows:

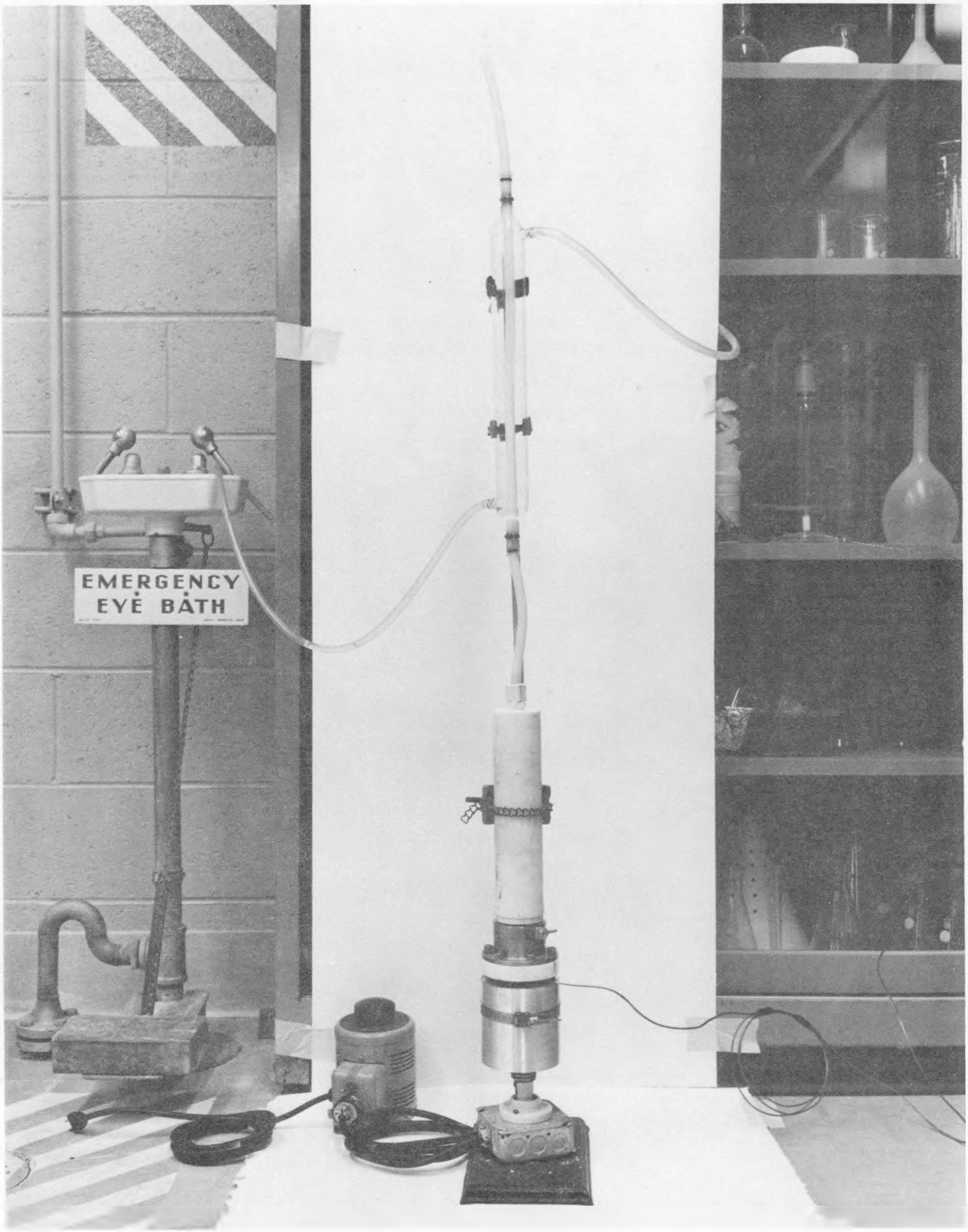


Figure 4. Heat Transfer Corrosion Test Apparatus

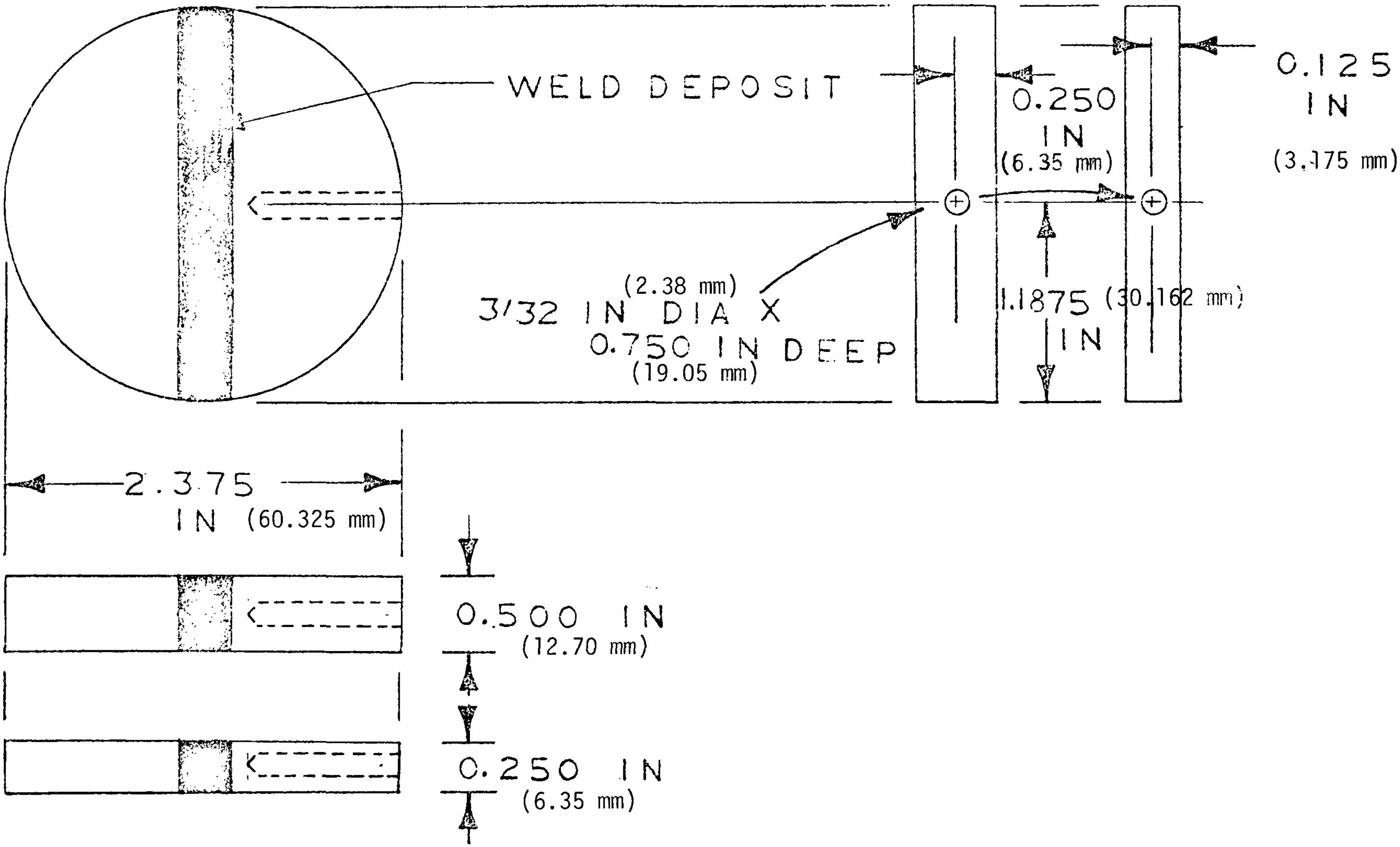
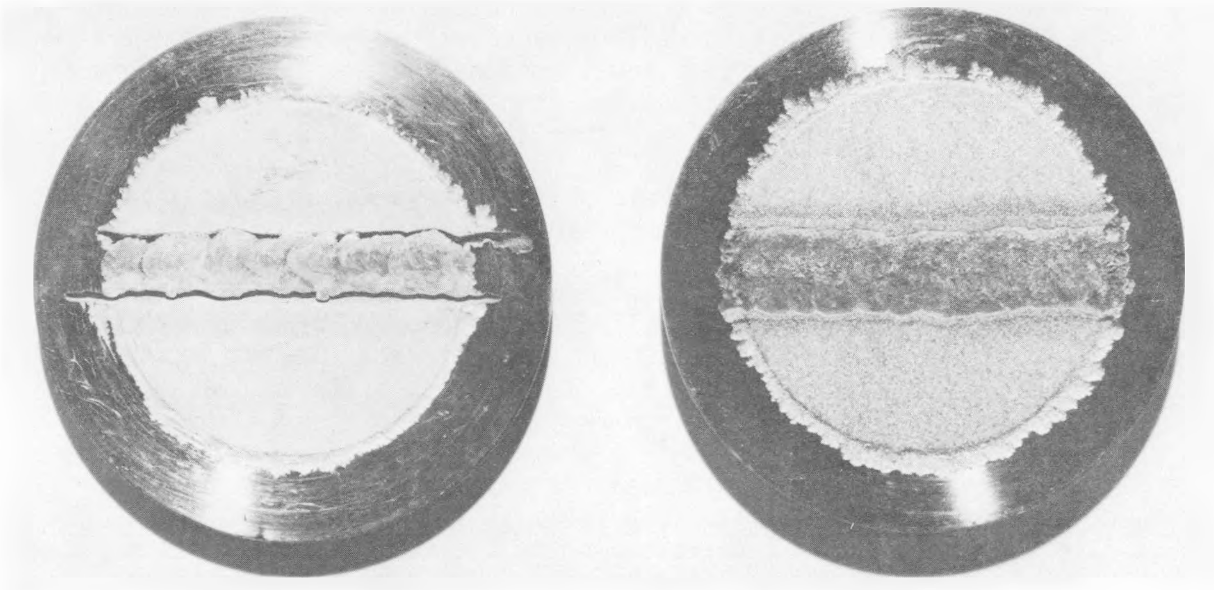


Fig. 5. Welded Heat Transfer Test Specimen

DATA FROM HEAT TRANSFER TEST COUPONS



1. GENERAL CORROSION OF WROUGHT METAL SURFACES
2. PREFERENTIAL ATTACK OF THE WELD DEPOSIT
3. WELD DECAY TYPE OF ATTACK IN THE HEAT-AFFECTED ZONE
4. KNIFELINE TYPE OF CORROSION ATTACK
5. CREVICE CORROSION ATTACK
6. CORROSION RATES CAN BE DETERMINED FROM WEIGHT LOSS AND EXPOSURE AREA MEASUREMENTS

Figure 6. Exposed Heat Transfer Test Coupons

1. General corrosion -- an overall, relatively-even, etching type of attack of the exposed test surface.

2. Preferential weld attack -- a specific attack or removal of cast weld deposit, usually an accelerated general corrosion or etching type of attack, but also may include pitting or other attack of the weld deposit. This type of attack can be sufficiently severe to obscure knife line attack.

3. Knife line attack -- preferential removal of wrought metal immediately adjacent to the weld deposit.

4. Weld decay -- preferential removal of wrought metal from the heat-affected and sensitized zone at some distance from the weld deposit which appears as a "ditch" paralleling the weld deposit. In the coupons in this series of tests, weld decay usually appeared ∿1/8-inch from the edge of the weld deposit.

5. Crevice corrosion -- metal removal where the specimen seals against the Teflon test vessel. This results from concentration of solution in the crevice and appears as a "groove" or "ditch" at the wetted juncture between the metal specimen and the Teflon container. In plant application this would be observed particularly in flanged connections between the metal and the gasket and may have a pitted appearance.

In addition to the above visual observations of specific forms of attack, the coupons were weighed and the exposed surface area was measured to permit calculation of corrosion rates and estimates of lifetime.

1.3 Corrosion Tests in Synthetic Intermediate-Level Waste Solutions

Heat transfer corrosion tests were performed using synthetic intermediate-level waste with five different alloys--Nitronic 50, Hastelloy C-276, Incoloy 825, and Type 304L and 347 stainless steels. Nominal alloy compositions are shown in Table XIX.

Tests were run using the synthetic waste solutions shown in Table XX. The four synthetic solutions were varied by providing lower and higher nitrate concentrations in each of the four compositions (Table XXI) to determine the effect of nitrate concentration on corrosion rate. The solution compositions provided an opportunity to observe the effect of varying ratios of aluminum to fluoride, and varying degrees of fluoride complexing in addition to a varying chloride-to-nitrate relationship.

Results shown in Table XXI reveal that corrosion rates generally increase in the order of solutions 1B, 2B, 3B, 4B, and follow the decrease in the degree of fluoride complexing as calculated by the formula:

TABLE XIX

NOMINAL COMPOSITION (wt%) OF ALLOYS TESTED FOR USE IN AQUEOUS NWCF STREAMS

Alloy	C	Ni	Cr	Fe	Mn	Mo	V	Cb	N	Other
Nitronic 50	0.03-0.06	11.5-13.5	20.5-23.5	Balance	4.0-6.0	1.5-3.0	0.10-0.30	0.10-30	0.2-0.4	P 0.04 S 0.03 Si 1.00
Hastelloy C-276	0.02	Balance	14.5-16.5	4.0-7.0	1.0	15.0-17	0.35	---	---	Co 2.5 P 0.03 S 0.03 Si 0.05
Incoloy 825	0.05	38.0-46.0	19.5-23.5	Balance	1.0	2.5-3.5	---	---	---	Al 0.2 Cu 1.5-3.0 Ti 1.5-1.2 S 0.03 Si 0.5
Type 304L stainless steel	0.03	8.0-12.0	18.0-20.0	Balance	2.0	---	---	---	---	P 0.045 S 0.030 Si 1.0
Type 347 stainless steel	0.08	9.0-13.0	17.0-19.0	Balance	2.0	---	---	---	---	Cb-Ta 10xC min P 0.045 S 0.030 Si 1.0

TABLE XX

REPRESENTATIVE INTERMEDIATE LEVEL WASTE COMPOSITIONS TESTED

Component	Calciner Feed	Scrub Solution	Scrub Recycle	Condensate
Al^{+3}, M	0.58	0.53	0.58	0.03
Na—, M	0.87	0.06	0.06	0.02
Zr^{+4}, M	0.25	0.01	0.014	0.011
B, M	0.10	0.06	0.06	0.05
Hg, M	0.002	0.001	0.002	0.002
H^{+}, M	1.11	1.69	2.00	1.42
F^{-}, M	1.56	1.09	1.39	0.53
SO_4^{-2}, M	0.024	0.003	0.003	0.004
NO_3^{-}, M	3.4	2.19	2.45	1.09
Cl^{-}, ppm	670	1500	1500	150

Metals not reported as ions were calculated following analysis and reported as metals.

TABLE XXI

SUMMARY OF CORROSION TEST DATA

	1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
Solution Composition												
Al^{+3}, M	0.59	0.56	0.57	0.38	0.51	0.50	0.40	0.58	0.56	0.03	0.03	0.03
Na^{+}, M	0.86	0.90	0.96	0.06	0.06	0.06	0.06	0.06	0.06	0.02	0.02	0.02
Zr^{+4}, M	0.22	0.22	0.23	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
H^{+}, M	0.82	1.38	4.77	0.51	1.22	3.78	0.72	1.92	4.50	0.86	1.36	2.42
B, M	0.11	0.11	0.11	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.05
Hg, M	0.002	0.002	0.002	0.001	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002
F^{-}, M	1.36	1.39	1.42	0.61	1.06	1.06	0.87	1.38	1.25	0.51	0.50	0.52
NO_3^{-}, M	2.55	3.37	6.78	1.18	2.17	4.23	1.25	2.41	4.71	0.55	1.07	2.10
SO_4^{-2}, M	0.027	0.022	0.021	0.003	0.001	0.001	0.001	0.001	0.002	0.012	0.013	0.012
Cl^{-}, ppm	645	638	686	1470	1500	1500	1470	1440	1494	122	120	143
Solution Ratios and Degree of Complexing												
F/Al	2.30	2.48	2.49	1.60	2.08	2.12	2.18	2.38	2.23	17.00	16.67	17.33
NO_3/Cl	140	187	349	28	51	100	30	59	112	162	315	525
$\frac{F - 4(Zr + B)}{2\ Al}$	0.034	0.066	0.060	0.418	0.749	0.768	0.722	0.917	0.852	4.43	4.53	4.73
Free Chemical Species Calculations												
H^{+}	0.48	1.34	4.65	0.98	1.46	3.59	0.72	1.79	4.11	0.59	1.11	2.19
HF	1.92×10^{-3}	6.01×10^{-3}	1.66×10^{-2}	1.15×10^{-2}	3.48×10^{-2}	6.64×10^{-2}	0.02	6.05×10^{-2}	8.84×10^{-2}	0.13	0.19	0.18
F^{-}	1.78×10^{-6}	1.98×10^{-6}	1.58×10^{-6}	5.16×10^{-6}	1.05×10^{-5}	8.16×10^{-6}	1.30×10^{-5}	1.50×10^{-5}	9.52×10^{-6}	9.96×10^{-5}	7.44×10^{-5}	3.59×10^{-5}
HF_2^{-}	1.03×10^{-7}	3.59×10^{-7}	7.91×10^{-7}	1.78×10^{-6}	1.11×10^{-5}	1.64×10^{-5}	8.22×10^{-6}	2.73×10^{-5}	2.53×10^{-5}	3.97×10^{-4}	4.18×10^{-4}	1.92×10^{-4}
Corrosion Rate Calculated, Mils/Mo: [μm/mo]*												
Stainless Steel Type 304L	0.19 [4.83]	0.65 [16.5]	3.19 [81.0]	0.37 [9.40]	2.52 [64.0]	13.4 [340]	0.52 [13.2]	6.79 [172]	23.7 [602]	9.44 [252]	17.2 [437]	18.1 [460]
Type 347	0.12 [3.05]	0.18 [4.57]	2.74 [69.6]	0.22 [5.59]	2.52 [64.0]	7.84 [199]	0.59 [15.0]	2.89 [73.4]	15.6 [396]	7.20 [183]	9.29 [236]	16.1 [409]
Incoloy 825	0.08 [2.03]	2.00 [50.8]	1.20 [30.5]	0.15 [3.81]	1.90 [48.3]	6.70 [170]	0.30 [7.62]	3.90 [99.1]	10.6 [269]	10.9 [277]	14.5 [368]	28.4 [721]
Hastelloy C-276	0.84 [21.3]	1.78 [45.2]	21.5 [546]	0.50 [12.7]	5.43 [138]	26.0 [660]	1.68 [42.7]	8.60 [218]	71.2 [1808]	9.1 [231]	19.9 [505]	33.6 [853]
Armco 22-13-5	0.18 [4.57]	0.28 [7.11]	1.61 [40.9]	0.19 [4.83]	0.61 [15.5]	3.29 [83.6]	0.26 [6.60]	1.07 [27.2]	22.3 [566]	18.0 [457]	4.4 [112]	22.3 [566]

*1 mil is 25.4 μ metres

$$\frac{F - 4(Zr + B)}{2\ Al} = C$$

where F, Zr, B, and Al are the molar concentrations of these elements and C is indicative of the degree of complexing. The lower the value of C, the greater the degree of complexing--generally solutions with a C value less than one are acceptable for processing. In these tests, crevice corrosion cocurred in all cases where the fluoride was not complexed ($C > 1$) and was observed to decrease as the degree of complexing increased. Corrosion rates also follow the free chemical species concentrations (H^+, HF, F^-, and HF_2^-) calculated by a program developed by R. R. Hammer.[28]

The three samples within each group generally showed increasing corrosion rates as the hydrogen ion, nitrate ion, and fluoride ion concentrations increased. The nitrate-to-chloride ratios and the calculated free chemical species H^+ and HF also followed this same pattern.

Comparison of the results of visual inspection of these test coupons showed Type 304L stainless steel to have suffered knife line attack, crevice corrosion, and general attack with little weld decay or preferential weld deposit attack; Type 347 stainless steel showed a high incidence of preferential weld attack, moderate incidence of crevice corrosion and knife line attack, and low incidence of weld decay along with general corrosion. The Incoloy 825 alloy showed a low occurrence of preferential weld attack and weld decay and a moderate incidence of corrosion and knife line attack. This alloy also suffered general corrosion attack. The Hastelloy C-276 alloy suffered general corrosion attack with a low incidence of knife line attack, a moderate occurrence of preferential weld attack, and a high incidence of crevice corrosion and weld decay. Nitronic 50 alloy suffered no knife line attack and only a light discoloration band to indicate that weld decay was occurring. Nitronic 50 also showed light to moderate general corrosion with some etching of the weld deposit and some occurrence of light crevice corrosion.

Results of this series of tests indicated that the preferred material for use in the as-welded condition in this service, particularly if the uncomplexed fluoride series of tests is excluded, is Nitronic 50 with Type 347L stainless steel and Incoloy 825 next in preference followed by Type 304L stainless steel and Hastelloy C-276 in that order.

1.4 Corrosion in Synthetic NWCF Process Solutions

Heat-transfer-type tests were made by exposing Nitronic 50, Incoloy 825, and Type 304L, 347, and 310 stainless steels at approximately 110°C to synthetic process solutions, similar to these anticipated in the NWCF. Tests were also made using dissimilar alloy welding between the alloys since such dissimilar construction may be encountered--especially in flow systems where valves, pumps, etc., fabricated from the desired alloys may not be available.

The results of these tests indicate that the materials of construction for the aqueous-solution-handling parts of the NWCF process system should be Nitronic 50, Type 347 stianless steel, and Incoloy 825 in that order of preference.

Composition of the various synthetic processing streams used in these tests are presented in Table XXII. In blending these solutions, it was assumed that the zirconium waste would be reacted with 0.55 mole of calcium nitrate per mole of fluoride to form the calciner feed solution. Scrub solution is basically a nitric acid solution containing undissolved solids entrained in the wash during the cooling and scrubbing of the calciner off-gas in the quench tower and venturi scrubber, respectively.

The corrosion rate data from tests of various alloys and alloy combinations that may occur in the NWCF processing streams are presented in Table XXIII. The corrosion rates shown in this table should not be taken as absolute, but rather should be used along with the descriptive information concerning specific corrosion of each coupon.

Examination of the data shows that the Nitronic 50 alloy had a low corrosion rate and the best overall corrosion characteristics. It showed only general corrosion in all three process solutions. This alloy also appears to behave well in cases where it is welded to other alloys. The second material choice would be Type 347 stainless steel. Incoloy 825 showed a moderate corrosion rate, but suffered from knife line and crevice attack and is rated as a third choice. In contact with other alloys, Incoloy 825 shows up rather poorly since it appears to be susceptible to knife line and crevice attack. Interestingly, Type 310 stainless steel responds very well to the waste and feed solutions but does not have good resistance to the scrub solution.

Feed solution, formed by adding calcium nitrate to the waste solution, generally resulted in a slightly lower corrosion rate where dissimilar alloys were used. This lower corrosion rate appears to be the result of the availability of calcium to "tie up" any fluoride not complexed by the other complexing elements in the system.

1.5 Corrosion in Decontamination Solutions

The alloy and dissimilar alloy coupons tested in the synthetic processing streams previously mentioned were also tested in three different decontamination solutions. The results are shown in Table XXIV. As evident from the results, the Turco 4502 (an alkaline permanganate) and the 1 $\underline{M}$ nitric-acid - 0.3 $\underline{M}$ hydroxylamine sulfate (HAS) solutions were less corrosive on all materials tested than oxalic acid. Corrosion rates in oxalic acid were high for Nitronic 50. However, the alloys would see much less service in decontamination solutions than process solutions, and this finding is not considered serious.

The results of the tests in process solutions and decontamination solutions indicate a construction material order of preference for the NWCF aqueous systems of Nitronic 50, Type 347 stainless steel, and

TABLE XXII

SYNTHETIC PROCESS SOLUTION COMPOSITIONS (MOLAR)

Component	Waste Solution	Feed Solution	Scrub Solution
F^-	3.2	3.2	3.2
Al^{+3}	0.62	0.62	0.62
Zr^{+4}	0.41	0.41	0.41
B^{+4}	0.36	0.36	0.36
Fe^{+3}	0.005	0.005	0.005
Cr^{+3}	0.02	0.02	0.02
Ni^{+2}	0.0002	0.0002	0.0002
H^+	1.32	1.32	3.38
NO_3^-	1.94	5.34	7.40
Cl^-	0.012	0.012	0.014
Ca^{+2}	----	1.70	1.70

TABLE XXIII

CORROSION SUMMARY IN PROCESS SOLUTIONS (mils per mo)[μm/mo]*

Material	Waste Solution	Feed Solution	Scrub Solution
Nitronic 50 - Nitronic 50 Weld W-50	0.80 [20.3] General corrosion.	0.68 [17.3] General corrosion.	1.76 [44.7] General corrosion.
Incoloy 825 - Incoloy 825 Weld Inconel 625	1.05 [26.7] General corrosion.	0.85 [21.6] General corrosion. Possible crevice initiation.	2.86 [72.6] General corrosion. Crevice attack.
Type 310-Type 210 SS Weld 310	0.49 [12.4] Light general corrosion.	0.61 [15.5] General corrosion.	5.96[a] [151] Weld decay. Intergranular attack with grain dropping.
Type 304L - Type 304L SS Weld 308L	2.22[a] [56.4] General corrosion.	1.91 [48.5] General corrosion.	6.74 [171] General corrosion.
Type 347 - Type 347 SS Weld 347	1.56 [39.6] General corrosion.	1.27 [32.3] General corrosion.	4.09[a] [104] General corrosion. Knifeline attack initiating.
Nitronic 50 - Incoloy 825 Weld Inconel 625	0.82 [20.8] General corrosion. Possible weld decay initiating.	0.80 [20.3] General corrosion. Possible weld decay initiating.	2.63 [66.8] General corrosion preferentially of Incoloy 825. Weld decay and knifeline attack of Incoloy 825.
Nitronic 50 - Type 310 SS Weld 309 SCb	0.81 [20.6] General corrosion principally of SS 310.	0.78 [19.8] General corrosion.	3.50[a] [88.9] Light crevice attack and possible knifeline attack of Nitronic 50. Preferential weld attack SS 310 has intergranular attack with grain dropping and possible knifeline attack.
Nitronic 50 - Type 304L SS Weld W-50	1.06 [26.9] General corrosion more severe on SS 304L. Possible knifeline attack initiating.	1.00 [25.4] General corrosion. Knifeline and crevice attack starting on SS 304L.	3.86 [98.0] General corrosion. Knifeline and crevice attack on SS 304L.
Incoloy 825 - Type 310 SS Weld Inconel 625	0.76 [19.3] Light general corrosion. Knifeline attack on Incoloy 825.	0.66 [16.8] General corrosion. Knifeline attack initiating on Incoloy 825.	4.55[a] [116] General corrosion. Preferential weld attack. Knifeline attack Incoloy 825. Weld decay initiation on SS 310.
Incoloy 825 - Type 304L SS Weld Inconel 625	0.72 [18.3] General corrosion.	1.01 [25.6] General corrosion with preferential weld metal attack.	3.60 [91.4] General corrosion. Preferential weld attack. Crevice attack of 304L.
Type 310 - Type 304L SS Weld 309 SCb	1.20 [30.5] General corrosion.	0.78 [19.8] General corrosion.	2.36 [59.9] General corrosion with pitting initiation on SS 304L

a Average of 4 determinations.
* 1 mil is 25.4 μ metres

TABLE XXIV

CORROSION SUMMARY IN DECONTAMINATION SOLUTIONS (mils per mo) [μm/mo]*

Material	10% Turco 4502	8% Oxalic Acid	1 M HNO_3 - 0.3 M HAS
Nitronic 50 - Nitronic 50 Weld W-50	0.03 [0.76] Staining - Very light general corrosion.	2.40 [61.0] General corrosion.	0.04 [1.02] Very light general corrosion.
Incoloy 825 - Incoloy 825 Weld Inconel 625	0.07 [1.78] Very light general corrosion.	1.10[a] [27.9] General corrosion.	0.02[a] [0.51] Very light general corrosion.
Type 310-Type 310 SS Weld 310	0.009 [0.23] Very light general corrosion.	0.04 [1.02] General corrosion with possible crevice attack initiation.	0.03 [0.76] Very light general corrosion.
Type 304L - Type 304L SS Weld 308L	0.01 [0.25] Staining - Very light general corrosion.	2.90 [73.7] General corrosion with light crevice attack.	0.02 [0.51] Very light general corrosion.
Type 347 - Type 347 SS Weld 347	0.10 [2.54] Very light general corrosion.	2.27 [57.6] General corrosion and pitting initiation.	0.06 [1.52] General corrosion.
Nitronic 50 - Incoloy 825 Weld Inconel 625	0.10 [2.54] Light general corrosion.	1.07[a] [27.2] General corrosion.	0.02 [0.51] Very light general corrosion.
Nitronic 50 - Type 310 SS Weld SS 309 SCb	0.009 [0.23] Very light general corrosion.	1.60 [40.6] General corrosion more prominent on SS 310. Crevice attack SS 310. Knifeline attack initiation possible.	0.06 [1.52] General corrosion.
Nitronic 50 - Type 304L SS Weld W-50	0.03 [0.76] Very light general corrosion.	1.30[a] [33.0] General corrosion. Crevice attack 304L. Possible knifeline initiation 304L.	0.03 [0.76] Very light general corrosion.
Incoloy 825 - Type 310 SS Weld Inconel 625	0.02 [0.51] Very light general corrosion.	0.18 [4.57] General corrosion severe on SS 310.	0.01 [0.25] Very light general corrosion.
Incoloy 825 - Type 304L SS Weld Inconel 625	0.02 [0.51] Very light general corrosion.	1.30[a] [33.0] General corrosion more pronounced on 304L.	0.06 [1.52] Very light general corrosion.
Type 310 - Type 304L SS Weld 309 SCb	0.02 [0.51] Very light general corrosion.	2.57 [65.3] Preferential attack on SS 310. Pitting attack of SS 304L. Crevice attack initiation.	0.04 [1.02] Very light general corrosion.

a Average of 4 tests.

*1 mil is 25.4 μ metres.

Incoloy 825. Tests were run at approximately 110°C, which is higher than the anticipated operating temperature of the feed system (40°C to 65°C). The elevated temperature of these tests should provide a safety factor relative to actual process conditions.

1.6 Miscellaneous Corrosion Tests

Additional corrosion tests were made to evaluate Nitronic 50: (1) when exposed to a series of decontamination solutions following exposure in scrub solution, (2) having different surface finishes, and (3) after heat treating and cold forming.

1.6.1 Successive Exposure to Decontamination Solutions and Synthetic NWCF Scrub Solution

The processing cycle for the NWCF will be alternating cycles of exposure to process solutions and decontamination solutions. In order to rule out any detrimental synergistic corrosion effects caused by alternating exposures, a test was designed to simulate these process cycles. Corrosion tests specimens which had been previously tested through five cycles of exposure to synthetic calciner scrub solution were exposed to a series of decontamination solutions (Table XXV).

Table XXV

Corrosion Rates for a Typical Decontamination Sequence (mils per mo) [μm/mo]*

	Successive Treatments	Nitronic 50	Type 347 Stainless Steel	Type 304 Stainless Steel
1.	Five Cycles in Scrub Solution	1.76 [44.7]	4.09 [104]	6.74 [171]
2.	Turco 4502 (10%) 24 Hours	0.33 [8.38]	0.07 [1.78]	0.33 [8.38]
3.	Oxalic Acid (8%) 24 Hours	0.07 [1.78]	4.74 [120]	8.76 [222]
4.	1 M HNO_3 0.3 M HAS 24 Hours	0.01 [0.25]	0.15 [3.81]	21.94 [557]

*1 mil is 25.4 μ metres.

Three welded alloy coupons--Nitronic 50, Type 304L stainless steel, and Type 347 stainless steel--were exposed in the order shown for 24 hours in each of the boiling decontamintion solutions. The results show that the Nitronic 50 alloy is less susceptible to attach in this sequence than either Type 304L or 347 stainless steels.

1.6.2 Evaluation of Surface Finishes

Three categories of surface finishes were evaluated relative to corrosion resistance and include (1) electropolished, (2) mill standard, and (3) cold worked. The results of the associated corrosion testing are presented in the following paragraphs.

1.6.2.1 Electropolished Surfaces

Electropolishing is a surface-finishing technique which removes, by electrochemical action, active regions resulting from surface impurities and other surface imperfections and leaves a very smooth surface which has a more uniform surface-free energy. Because of the removal of the active sites, the surface should be more passive than an "as-received" surface--at least initially. In mildly aggressive media, electropolishing may significantly increase the life of a surface. In very aggressive media such as that present in waste calcination operations, the initial surface is likely to be removed rapidly, resulting in corrosion becoming a function of chemistry of the wrought material rather than the surface finish. Thus, a slight difference in corrosion rates may be observed initially with comparable rates being seen thereafter.

Two series of tests were initiated to observe the effect of complexed synthetic scrub solutions on electropolished and nonelectropolished surfaces. The effects observed with the nonelectropolished surfaces do not appear to indicate any trend toward increased corrosive attack due to repetitive cycles of exposure. The electropolished coupons tested appear to show a slight trend toward accelerated corrosive attack with repetitive cycles of exposure.

A series of corrosion test coupons were fabricated for testing in the heat transfer corrosion test apparatus. Coupons were prepared as follows:

(1) Nitronic 50 welded to Nitronic 50 using 50W (Nitronic 50) weld wire.

(2) Nitronic 50 welded to Nitronic 50 using ER-308L weld wire.

(3) Incoloy 825 welded to Incoloy 825 using Inconel 625 weld wire.

(4) Type 304L stainless steel welded to Type 304L stainless steel using ER-308L weld wire.

NOTE: All welds were completed by qualified welders using qualified gas tungsten arc welding (GTAW) procedures.

A double "V" type of weld preparation was used for all welds, and the welds were checked by X-ray to verify weld quality. The test coupons were machined to a 125 RMS surface finish. One side of the coupons was then further electropolished in the laboratory. The reverse side of the coupon was left in the nonelectropolished condition.

Electropolished and nonelectropolished sides of the these coupons were exposed for five cycles of 96 hours each in boiling synthetic scrub solution having the composition shown in Table XXVI. During the last two cycles of exposure of the electropolished coupons, the test apparatus was provided with a slight airflow to assure that the test solution was aerated. The test solutions were aerated during all five test cycles for the nonelectropolished surfaces. The results of the electropolished and nonelectropolished surface tests are presented in Tables XXVII and XVIII.

TABLE XXVI

COMPOSITION OF SYNTHETIC SCRUB SOLUTIONS

Component	Electropolished Coupon Test	Nonelectropolished Coupon Tests
Al^{+3}, M	1.49	1.16
Na^{+}, M	0.21	----
Zr^{+4}, M	0.039	0.056
Hg^{++}, M	0.008	----
B^{+3}, M	0.046	0.052
H^{+}, M	4.26	4.18
F^{-}, M	1.35	1.44
SO_4^{-2}, M	0.005	0.005
NO_3^{-}, M	5.86	7.30
Cl^{-}, mg/l	5496	4864

The data show that electropolishing does not provide any significant reduction in metal loss in this corrosive media. The metal loss during the first cycle was nearly the same as succeeding cycles, resulting in comparable corrosion rates from cycle to cycle. The increases observed from cycle to cycle are presumed to result from greater surface area due to increasing surface roughness as corrosion proceeds. The cumulative results for the 480 hours of exposure for both the electropolished and nonelectropolished surface tests indicate that Nitronic 50 suffers less metal loss than either Type 304L stainless steel or Incoloy 825.

1.6.2.2 Surface Finishes Available From Mill

Nitronic 50 can be obtained with three different surface finishes: (1) hot rolled, annealed, and pickled

TABLE XXVII

CORROSION RATES OF ELECTROPOLISHED TEST SPECIMENS

(MILS PER MO) [μm/mo]*

Cycle	Type 304L - Type 304L Stainless Steel ER-308L Wire	Nitronic 50 - Nitronic 50 W50 Wire	Incoloy 825 - Incoloy 825 Inconel 625 Wire	Nitronic 50 - Nitronic 50 ER-308L Wire
1	3.1 [78.7]	1.0 [25.4]	2.1 [53.3]	1.2 [30.5]
2	3.1 [78.7]	0.8 [20.3]	1.5 [38.1]	0.7 [17.8]
3	3.8 [96.5]	1.1 [27.9]	2.9 [73.7]	1.2 [30.5]
4	3.8 [96.5]	1.5 [38.1]	4.0 [102]	1.2 [30.5]
5	3.8 [96.5]	1.5 [38.1]	4.2 [107]	1.7 [43.2]
Cumulative Total - 480 Hr	3.5 [88.9]	1.2 [30.5]	3.0 [76.2]	1.2 [30.5]
Visual Observations	General Corrosion; Preferential weld attack; crevice attack.	General Corrosion.	General Corrosion; Preferential weld attack; light knife line attack.	General corrosion; light knife line attack.

*1 mil is 25.4 μ metres.

TABLE XXVIII

CORROSION RATES OF NONELECTROPOLISHED TEST SPECIMENS (MILS PER MO) [μm/mo] *

Cycle	Type 304L - Type 304L Stainless Steel ER-308L Wire	Nitronic 50 - Nitronic 50 W50 Wire	Incoloy 825 - Incoloy 825 Inconel 625 Wire	Nitronic 50 - Nitronic 50 ER-308L Wire
1	1.6 [40.6]	1.2 [30.5]	1.6 [40.6]	1.2 [30.5]
2	2.0 [50.8]	1.2 [30.5]	1.3 [33.0]	1.4 [35.6]
3	2.3 [58.4]	1.1 [27.9]	2.0 [50.8]	1.3 [33.0]
4	1.6 [40.6]	1.2 [30.5]	2.3 [58.4]	1.5 [38.1]
5	1.8 [45.7]	0.9 [22.9]	1.5 [38.1]	1.2 [30.5]
Cumulative Total - 480 Hr	1.9 [48.3]	1.1 [27.9]	1.7 [43.2]	1.3 [33.0]
Visual Observations	General corrosion; light preferential weld attack.	Light general corrosion; light weld attack.	General corrosion; preferential weld attackl knife line attack.	Light General corrosion; light knife line attack.

*1 mil is 25.4 μ metres.

(HRAP); (2) hot rolled, annealed, and pickled, followed by belt grinding using a 150-grit belt (HRAP - BG), and (3) hot rolled, annealed, and pickled, followed by belt grinding using a 150 grit belt, then mineral blasting (HRAP - BG - MB). Heat transfer corrosion tests were run in a synthetic scrub solution to determine if these surface finishes had any effect on corrosion.

The specimens were then exposed to a synthetic calciner scrub solution having the composition shown in Table XXIX.

TABLE XXIX

Synthetic Calciner Scrub Solution Composition Used in Testing Mill Surfaces

Component	Composition
Zr^{+4}, $\underline{M}$	0.41
Al^{+3}, $\underline{M}$	0.67
B^{+3}, $\underline{M}$	0.29
Ca^{+2}, $\underline{M}$	0.88
H^{+}, $\underline{M}$	3.47
F^{-}, $\underline{M}$	2.88
NO_3^{-}, M	5.74
Cl^{-}, ppm	475

The results of these tests are presented in Table XXX. Visual inspection of the coupons showed only light general corrosion attack.

Table XXX

Effect of Surface Finish on Corrosion Rate of Nitronic 50

Cycle	HRAP[(a)] (mils per mo)	HRAP[(a)] [μm/mo] *	HRAP-BG[(b)] (mils per mo)	HRAP-BG[(b)] [μm/mo] *	HRAP-BG-MB[(c)] (mils per mo)	HRAP-BG-MB[(c)] [μm/mo] *
1 (96 hours)	2.8	[71.1]	2.3	[58.4]	2.8	[71.1]
2 (96 hours)	2.5	[63.5]	2.4	[61.0]	2.0	[50.8]
3 (96 hours)	2.1	[53.3]	2.2	[55.9]	2.4	[61.0]
4 (96 hours)	2.4	[61.0]	2.5	[63.5]	2.4	[61.0]
5 (96 hours)	2.3	[58.4]	2.6	[66.0]	2.4	[61.0]
Cumulative: (480 hours)	2.4	[61.0]	2.4	[61.0]	2.4	[61.0]

(a) Hot rolled, annealed, and pickled.
(b) Hot rolled, annealed, and pickled, followed by belt grinding (150-grit belt.)
(c) Hot rolled, annealed, and pickled, followed by belt grinding (150-grit belt), then mineral-blasted.

* 1 mil is 25.4 μmetres.

1.6.2.3 Effect of Cold-Working Test Coupon Surfaces

Laboratory corrosion tests are usually run using coupons in the "as-welded" and "as-machined" condition. To ensure that corrosion results were not adversely influenced by coupon machining, a Nitronic 50 test specimen was run in the "as-received" condition in synthetic scrub solutions. This test indicated a cumulative corrosion rate of 2.5 mils per month after two 96-hour test periods. This compares well with the corrosion rate (2.4 mils per month) reported for "as-received" coupons having various surface finishes. Corrosion rates of 1.2, 1.3, and 1.8 have been previously reported (Tables XXV, XXVII, and XXVIII) for Nitronic 50 coupons in the "as-welded" and "as-machined" condition that have been exposed to synthetic calciner scrub solutions. The difference appears to indicate that machining (cold working) improves corrosion resistance of Nitronic 50.

Corrosion coupons were exposed at 110°C to a solution having the composition shown in Table XXXI. Results of this test are shown in Table XXXII.

Table XXXI

Synthetic Calciner Scrub Solution Composition Used in Testing Cold-Worked Surfaces

Component	Composition
Zr^{+4}, $\underline{M}$	0.44
Al^{+3}, $\underline{M}$	0.68
B^{+3}, $\underline{M}$	0.32
Ca^{+2}, $\underline{M}$	1.7
H^{+}, $\underline{N}$[a]	3.27
F^{-}, $\underline{M}$	3.4
NO_3^{-}, $\underline{M}$	7.0
Fe^{+3}, ppm	150
Cr^{+3}, ppm	1100
Ni^{+2}, ppm	18
Mn^{+2}, ppm	3

Table XXXII

Corrosion Test Results for Cold Worked Surfaces
(mils per mo) [μm/mo]*

Cycle 1 (96 hours)	2.87	[71.1]
Cycle 2 (96 hours)	2.3	[58.4]
Cumulative (192 hours)	2.5	[63.5]

*1 mil is 25.4 μ metres.

1.6.3 Corrosion of Heat-Treated Material

Nine test coupons representing Nitronic 50 and Type 304L and 347 stainless steels were heat-treated at 530°C for three different time periods to simulate sensitizing conditions during calciner operations. After heat treating in a furnace, the coupons were cleaned to remove any scale and then weighed and placed in the heat-transfer corrosion test apparatus. Corrosion testing was conducted in a synthetic scrub solution (Table XXXIII) at an average temperature of 110°C. The solution temperature varied and at times dropped below the boiling point.

Table XXXIII

Synthetic Scrub Solution for Heat-Treated Materials Tests

Component	Composition
Zr^{+4}, M	0.41
NO_3^-, M	3.98
H^+, M	3.47
Al^{+3}, M	0.67
F^-, M	2.88
B^{+3}, g/l	3.14
CL^-, mg/l	475

29.5 g of calcium nitrate trihydrate was added to each 150 ml of test solution to complex the fluoride ion (0.55 mole of calcium nitrate will complex 1 mole of fluoride).

Table XXXIV shows the duration of heat treating, the number of 96-hour exposures to scrub solution, the type of attack, and the average corrosion rate. In every test, Nitronic 50 performed better than Type 304L or 347 stainless steels.

Table XXXIV

Coupon Heat Treating and Corrosion Testing

Coupons heat-treated for 96 hours at 530°C (1000°F) and tested in 110°C (230°F) synthetic NWCF scrub solution.

Alloy	Cycles (96 hours each)	Type Attack	Average Corrosion Rate (mils/mo)	[μm/mo]*
Type 304L Stainless Steel	5	Heavy general	15.7	[399]
Type 347 Stainless Steel	2	Extreme preferential weld attack	35.9	[912]
Nitronic 50	5	Light preferential weld attack	3.3	[83.8]

Coupons heat-treated for 192 hours at 530°C (1000°F) and tested in 110°C (230°F) synthetic NWCF scrub solution.

Alloy	Cycles (96 hours each)	Type Attack	Average Corrosion Rate (mils/mo)	[μm/mo]*
Type 304L Stainless Steel	2	Heavy general attack with grain dropping	29.9	[759]
Type 347 Stainless Steel	2	Severe knife line attack	34.2	[869]
Nitronic 50	5	Preferential weld attack	4.8	[122]

Coupons heat-treated for 288 hours at 530°C (1000°F) and tested in 110°C (230°F) synthetic NWCF scrub solution.

Alloy	Cycles (96 hours each)	Type Attack	Average Corrosion Rate (mils/mo)	[μm/mo]*
Type 304L Stainless Steel	2	Heavy general attack	37.0	[940]
Type 347 Stainless Steel	2	Severe knife line attack	30.2	[767]
Nitronic 50	5	Preferential weld attack	5.6	[142]

* 1 mil is 25.4 μmetres.

1.6.4 Corrosion in a Flow Application

A corrosion test was made to evaluate the suitability of Nitronic 50, Type 304L stainless steel, and Type 347 stainless steel metal meshes in a synthetic calciner off-gas condensate. A Nitronic 50 valve was also included in this test system. Testing was conducted for 1056 hours at 72°C with a solution flow rate through the metal meshes of approximately 50 cc/min. The synthetic off-gas condensate solution composition is shown in Table XXXV.

Table XXXV

Synthetic Off-Gas Condensate Solution

Al^{+3},	0.03	Hg^{+2},	0.002 M	NO_3^-,	1.09 M
Na^+,	0.02 M	H^+,	1.42 M	Cl^-,	150
Zr^{+4},	0.018	F^-,	0.53 M		
B^{+3},	0.05 M	SO_4^{-2},	0.004 M		

The metal meshes tested were woven from 0.006-inch-OD Nitronic 50, 0.011-inch-OD Nitronic 50, 0.11-inch-OD Type 304L stainless steel, and 0.011-inch-OD Type 347 stainless steel wire. The corrosion rates of each mesh and their estimated life at 75% wastage[a] are listed in Table XXXVI.

Nitronic 50 had the best corrosion resistance of the materials tested. The 0.006-inch-OD wire is not recommended for use in this solution because 75% wastage reduces the wire size to 0.0015-inch-OD, which is too small for an effective mesh. Type 304L stainless steel mesh showed poor resistance and is not recommended for use in synthetic condensate solution. The Nitronic 50 mesh holders showed only a light general corrosion. Type 304L stainless steel flanges coupled to the holder exhibited a light etch. Type 347 stainless steel flanges had poorer resistance to the solutions and exhibited galvanic corrosion.

In addition to the mesh, a Nitronic 50 "Sno-Trik" valve with a removable valve stem tip was tested for 864 hours in the open position for corrosion resistance to the condensate solution. The valve stem tip was weighed and measured before and after the test to determine an average corrosion rate of 0.66 mil/month.

a Wastage is the decrease in mesh wire diameter.

Table XXXVI

Corrosion Rate and Expected Life in Synthetic Off-Gas Condensate Solution

Mesh Material	Corrosion Rate (mils/mo)	[µm/mo]*	Estimated Life (mo)
Nitronic 50 0.006 inch OD	0.09	[2.29]	25.0
Nitronic 50 0.011 inch OD	0.16	[4.06]	25.8
Type 304L SS 0.011 inch OD	0.21	[5.33]	19.4
Type 347 SS 0.011 inch OD	0.71	[18.0]	5.8

* 1 mil is 25.4 µmetres.

1.6.5 Miscellaneous Alloys for Special Applications

Samples of Nitronic 40, Nitronic 50 (cast), Nitronic 60, and Allegheny-Ludlum Alloy 6X having material compositions shown in Table XXXVII were exposed for five 96-hour cycles in the heat transfer corrosion apparatus. Tests were run at 110°C in a synthetic scrub solution having the composition shown in Table XXXVIII.

Corrosion rates for each alloy for each of the five cycles and the average corrosion rate over the total 480-hour exposure are presented in Table XXXIX. A brief description of the physical appearance of each test coupon is also given.

Results indicate that Nitronic 60 (>16 mils per month (mpm) corrosion) is not serviceable for calciner scrub system application. Nitronic 40 and the Allegheny-Ludlum Alloy 6X show sufficiently high corrosion rates (3.0 - 5.0 mpm) and attack to make their application in calciner liquid systems questionable. A sample of cast Nitronic 50 alloy demonstrated nearly the same corrosion rate (2.3 mpm) as was reported for this material (2.6 mpm) in a previous test (Table XXXII).

The Nitronic 40 alloy was exposed in the "as-received" and the "as-welded/as-machined" conditions. Both specimens showed only light general corrosive attack. However, both specimens demonstrated a significant corrosion rate (3.0 and 4.2 mpm), and application of this material in calciner scrub solutions would be questionable.

The Nitronic 60 alloy was also exposed in the "as-received" and the as-welded/as-machined" conditions. In this case, the corrosion rates (15.8 and 19.3 mpm) were so extreme that this material could not be used in scrub solution service.

TABLE XXXVII

COMPOSITION OF ALLOYS (WT%)

Alloy	C	Mn	P	S	Si	Cr
Nitronic 40	0.033	8.76	0.019	0.012	0.70	19.99
Nitronic 50	0.040	5.00	0.013	0.013	0.46	21.18
Nitronic 60	0.071	8.43	0.027	0.005	4.00	16.85
Allegheny-Ludlum Alloy 6X	0.027	1.46	0.023	0.004	0.56	20.32

Alloy	Ni	Mo	N	Cu	Cb	V
Nitronic 40	6.92	---	0.30	---	---	---
Nitronic 50	12.70	2.27	0.26	---	0.15	0.13
Nitronic 60	8.62	0.35	0.12	0.23	---	---
Allegheny-Ludlum Alloy 6X	24.17	6.42	0.030	---	---	---

Table XXXVIII

Synthetic Scrub Solution Used for Testing Miscellaneous Alloys

Component	Composition
Al^{+3}, M	0.68
B^{+3}, M	0.32
Zr^{+4}, M	0.44
H^{+}, M	3.27
F^{-}, M	3.40
NO_3^{-}, M	3.86

The Allegheny-Ludlum Alloy 6X samples were overlays made with 6X weld rod on Nitronic 50 base metal. The couples were then machined to provide a smooth, flat test surface. One specimen was tested in the "as-received" and "as-machined" condition. The second specimen was welded, machined, and then heat-treated at 1121°C (2050°F) in argon for 1/2-half hour and water-quenched before being tested. The heat-treated specimen demonstrated a slightly higher corrosion rate (4.5 mpm) than the non-heat-treated specimen (3.4 mpm). In addition, because of corrosion, each weld pass was identifiable on the surface of the non-heat-treated specimen. This specimen also appeared to have less uniform surface attack than the heat-treated specimen. Based on these results, the application of this alloy to the calciner scrub system would be questionable.

The cast Nitronic 50 sample corrosion rates repeated a previous test in which an average corrosion rate of 2.6 mpm was observed after five cycles. In this test, the specimen demonstrated an average corrosion rate of 2.3 mpm after five cycles of exposure. This compares with a corrosion rate for wrought Nitronic 50 alloy of 2.4 mpm reported in Table XXX.

1.6.6 Laboratory Test Vessel

A laboratory test vessel was fabricated of 1/4-inch-thick Nitronic 50 plate.

The plate was rolled to form a cylinder 10 inches high by 8-3/4 inches in diameter. This cylinder was then machined longitudinally into two parts which were welded back together to form a corrosion test vessel. One weld was made using Nitronic 50 weld wire (50W), and the second weld was made using ER-308L weld wire. The welds were made by a

TABLE XXXIX

HEAT TRANSFER CORROSION TEST RESULTS (MILS PER MO) [μm/mo]*

Nitronic 40

Cycle	"as-received"[a]		"as-welded and "as-machined"[b]	
1	3.2	[81.3]	3.1	[78.7]
2	2.8	[71.1]	4.5	[114.]
3	3.2	[81.3]	4.6	[117.]
4	2.4	[61.0]	4.2	[107.]
5	3.5	[88.9]	4.8	[122.]
Cumulative (480 hr)	3.0	[76.2]	4.2	[107.]
Visual observations	Light general etching		light general attack with light crevice attack and weld decay	

Nitronic 60

Cycle	"as-received"[a]		"as-welded" and "as-machined"[b]	
1	9.9	[251]	20.5	[521]
2	15.2	[386]	18.2	[462]
3	13.5	[343]	Discontinued	
4	14.7	[373]		
5	26.0	[660]		
Cumulative (480 hr)	15.8	[401]	19.3 (193 hr)	[490]
Visual observations	General attack with light crevice attack		General attack with preferential weld attack and severe weld decay	

6-X Overlay

Cycle	"as-welded" and "as-machined"[b]		"as-welded" and "as-machined"[a] heat-treated[c]	
1	3.5	[88.9]	5.1	[129]
2	3.6	[91.4]	4.6	[117]
3	1.9	[48.3]	4.5	[114]
4	5.4	[137]	3.9	[99.1]
5	2.7	[68.6]	4.3	[109]
Cumulative (480 hr)	3.4	[86.4]	4.5	[114]
Visual observations	Light general attack with specific attack of weld deposit, leaving the deposit w/rather porous appearance		Light general attack	

Cast Nitronic 50

Cycle	"as-machined"[b]	
1	2.6	[66.0]
2	2.0	[50.8]
3	2.3	[58.4]
4	1.8	[45.7]
5	2.7	[68.6]
Cumulative (480 hr)	2.3	[58.4]
Visual observations	Light general corrosion with some small pitlike flaws in the casting	

a Standard synthetic scrub solution - Table XXXVIII- containing 0.90 M calcium nitrate.

b Standard synthetic scrub solution - Table XXXVIII - containing 1.63 M calcium nitrate

c Heat-treated at 1121°C (2050°F) in argon for 1/2 hr, then water-quenched.

* 1 mil is 25.4 μmetres

qualified welder using a procedure qualified per the requirements of Section IX of the ASME Code. The test vessel was provided with flanged ends which could be isolated from the body of the vessel by gaskets of Teflon sheet, thus allowing the test solution to contact only the Nitronic 50 vessel walls.

The vessel was equipped with two welded Nitronic 50 pipe stubs, one above the other and about 8 inches apart. These stubs were connected to an air lift to ensure circulation and aeration of the test solution. The test vessel was also equipped with cooling condensers to reduce the loss of test solution by evaporation. The test solution was a synthetic calciner scrub solution having the average composition shown in Table XL. The vessel was exposed to the solution for 1900 hours. At the end of this period, visual examination of the test vessel showed only a light etch of the wrought metal and light general corrosion of both weld deposits. The ER-308L weld bead showed slightly more corrosive attack.

Table XL

Composition of Synthetic Scrub Solution Used for Testing Laboratory Test Vessel

Component	Composition
F^-, M	2.83
NO_3^-, M	3.46
Al^{+3}, M	0.16
Zr^{+4}, M	0.38
B^{+3}, M	0.38
Fe^{+3}, M	0.0045
H^+, N[a]	2.39
Cr^{+3}, mg/l	1050
Ni^{+2}, mg/l	15.8
Mn^{+2}, mg/l	3.3
Cl^-, mg/l	494

In addition to visual observations, samples of test solutions were analyzed after each period of exposure. Based on the composition of the Nitronic 50 alloy materials used, the increase in chromium content of the test solution, and the area of Nitronic 50 surface exposed to liquid, a calculation was made to determine an apparent corrosion rate. These calculated rates are presented in Table XLI.

Table XLI

Calculated Corrosion Rates of Nitronic 50 Test Vessel

Sample No.	Length of Exposure (hours)	Corrosion Rate (mils per mo)	[μm/mo]*
1[a]	96	2.7	68.6
2[a]	120	1.6	40.6
3[a]	96	2.1	53.3
4	96	1.6	40.6
5	--	Test Solution Lost	
6	145	1.2	30.5
7	336	1.3	33.0
8 (new solution)	198	2.0	50.8
9	360	1.1	27.9
10	354	1.2	30.5
Average	--	1.6	40.6

(a) Volumes were not obtained at the end of these test periods to allow correcting back to original volume in determining chromium removed from the vessel wall as was done in all other tests. The test vessel has subsequently been exposed an additional 1056 hours in synthetic off-gas condensate solution. Visual examination after this exposure shows only light general corrosion of the vessel and the two weld seams. The results of these tests provided confirmation that Nitronic 50 was a suitable material of construction for use in the calciner process system.

* 1 mil is 25.4 μ metres.

2. Metallurgical Considerations

The major metallurgical consideration associated with Nitronic 50 was the development and qualification of welding procedures. Procedures were developed and qualified for the Gas Tungsten Arc Welding (GTAW) and Shielded Metal Arc Welding (SMAW) processes as discussed in the following sections.

Another important consideration was Nitronic 50's resistance to chloride stress corrosion cracking.

2.1 Development of Nitronic 50

The basis for any stainless steel's corrosion resistance is its chromium content, which must be in excess of 11.5%. The basic austenitic stainless steel, Type 302 stainless steel (sometimes called 18-8), has an addition of nickel which further improves corrosion resistance in some media and improves the alloy's ductility and high temperature strength. With the development of welding techniques, observation showed that the carbon content of Type 302 stainless steel must be reduced to prevent intergranular corrosive attack (sensitization) in the weld area. This resulted in the Type 304/304L stainless steel formulations. Addition of 2 to 3% molybdenum to the Type 304 stainless steel composition was found to give greater corrosion resistance and high temperature strength. This resulted in the Type 316 stainless steel alloy.

The following design objectives were established by Armco Steel to improve Type 316 stainless steel:[29] (1) improve corrosion resistance, (2) improve strength, and (3) improve resistance to intergranular attack after sensitizing conditions.

An alloy with some of the attributes of the desired alloy was Armco's Nitronic 40, which has a higher chromium level and a higher strength than Type 316 stainless steel. Nitronic 50 is the result of combining the attributes of Type 316 stainless steel and Nitronic 40 into one alloy.

Nitronic 50 has the following features as compared with Type 316:

(1) Higher chromium level for increased corrosion resistance and resistance to intergranular attack.

(2) A maximum carbon content of 0.06% and additional columbium to serve as a stabilization element to improve resistance to intergranular corrosion after sensitizing treatments.

(3) Additional nitrogen to function as a solid solution strengthening element and as an austenite phase stabilizer.

(4) Increased nickel and manganese content to stabilize the austenitic structure.

(5) Additional vanadium to increase strength and resistance to intergranular attack.

The typical chemical compositions for several alloys are shown in Table XLII, and typical mechanical properties are shown in Table XLIII. High-temperature mechanical properties for these alloys are shown in Table XLIV which also shows Nitronic 50's excellent strength characteristics at high temperatures.

2.2 Welding Armco Nitronic 50

Butt-welded joints were successfully made with Nitronic 50 using the GTAW and SMAW processes. Weld procedures were qualified to Section IX of the ASME Boiler and Pressure Vessel Code.

2.2.1 Gas Tungsten Arc Welding

For the GTAW process, the 1/4-inch test plates were manually welded using direct-current straight polarity with argon torch and backup gas. A 0.062-inch-diameter Nitronic 50W weld filler wire was used. Liquid penetrant and radiographic examinations were performed when welding was completed.

The first weld samples did not pass the bend test because a highly-cold-worked plate (RC-40) had been inadvertently supplied for test purposes. No bending was observed in the base plate; all bending occurred in the weld itself.

TABLE XLII

TYPICAL ALLOY CHEMICAL COMPOSITIONS

Alloy	C	Mn	P	S	Si	Cr	Ni	Mo	Other
Type 304L SS	0.035 max	2.0 max	0.04 max	0.03 max	0.75 max	18/20	8/13	-	N - 0.15/0.40
Type 316 SS	0.08 max	2.0 max	0.04 max	0.03 max	0.75 max	16/18	11/14	2/3	N - 0.2/0.4
Nitronic 40	0.08 max	8/10	0.06 max	0.03 max	1.0 max	19/21.5	5.5/7.5	-	Cb - 0.1/0.3
Nitronic 50	0.06 max	4/6	0.04 max	0.03 max	1.0 max	20.5/23.5	11.5/13.	1.5/3	Va - 0.1/0.3

Table XLIII

Typical Alloy Mechanical Properties

Alloy	Yield Strength (ksi)	Tensile Strength (ksi)	Elongation (%)	Reduction of Area (%)
Type 304L Stainless Steel	30	75	60	55
Type 316 Stainless Steel	35	80	65	77
Nitronic 40	65	99	48	70
Nitronic 50	60	120	50	70

Table XLIV

Typical Alloy Short-Time Elevated Tensile Properties

Alloy	Test Temp (°F)	Ultimate Tensile Strength (ksi)	0.2% Yield Strength (ksi)
Type 304L Stainless Steel[a]	Room		
	400	53.2	17.5
	600	51.8	15.5
	800	50.4	14.5
	1000	46.2	12.9
	1200	37.1	11.2
Nitronic 50,[b]	Room	121.0	65
1-inch bar	400	--	--
2050°F anneal	600	104.5	46.5
	800	98.0	45.5
	1000	91.5	41.5
	1200	83.0	41.5
Hastelloy X,[c]	Room	114.0	53.5
1/2-inch plate	400	91.5	38.0
2175°F anneal	600	94.0	35.0
	800	92.5	36.0
	1000	89.5	39.5
	1200	83.5	40.0

(a) ASTM Data Series DS 5S2, 1969.
(b) Armco Steel Corp. Bulletin S-45C.
(c) Cabot Corp. Stellite Division

A second test plate was obtained in the solution annealed condition and was welded successfully. The mechanical properties obtained are shown in Table XLV.

Table XLV

Mechanical Properties for GTAW Process Weldments

Sample	Ultimate Tensile Strength (ksi)	% Elongation (2-inch Gage Length)
1	120.0	22
2	122.0	22

2.2.2 Shielded Metal Arc Welding

A 1/2-inch Nitronic 50 plate was welded using a 5/32-inch Nitronic 50W electrode with direct-current reverse polarity. The samples were inspected as in the GTAW tests.

The mechanical properties obtained are shown in Table XLVI. The samples did not pass radiographic inspection because of nonuniform root reinforcement and slag inclusions. These defects can probably be attributed to the rather large diameter weld rod (5/32 in.), which causes control problems. A recommended method of making a joint with the SMAW process would be to make the root pass with the GTAW process, then use the SMAW process to fill the joint.

Table XLVI

Mechanical Properties for SMAW Process Weldments

Sample	Ultimate Tensile Strength (ksi)	% Elongation (2-inch Gage Length)
1	128.2	21
2	126.6	21

2.3 Resistance to Sensitization

The quench tower is a vessel in the NWCF process system. The vessel's function is to cool the calciner off-gas to its dewpoint. The quench tower will operate at an inlet gas temperature of 900 to 1000°F and a scrubbing solution temperature of 100°F. The solution will have the composition shown in Table XLVII. These severe conditions frequently have detrimental effects on metals. To assure that no problems existed, the effects of this temperature and corrosive environment were tested on Nitronic 50 and Type 304L, and 347 stainless steels.

Table XLVII

Typical NWCF Scrub Solution Composition

H^+, M	0.9 - 2.5
NO_3, M	2.5 - 5.0
F^-, M	0.9 - 1.7
Ca^{+2}, M	0.5 - 0.9
AL^{+3}, M	0.25 - 0.45
Zr^{+4}, M	0.15 - 0.3
Na^+, M	---
Cl^-, ppm	---
Sp. Gr.	1.15 - 1.27
Undissolved Solids, g/l	10 - 40

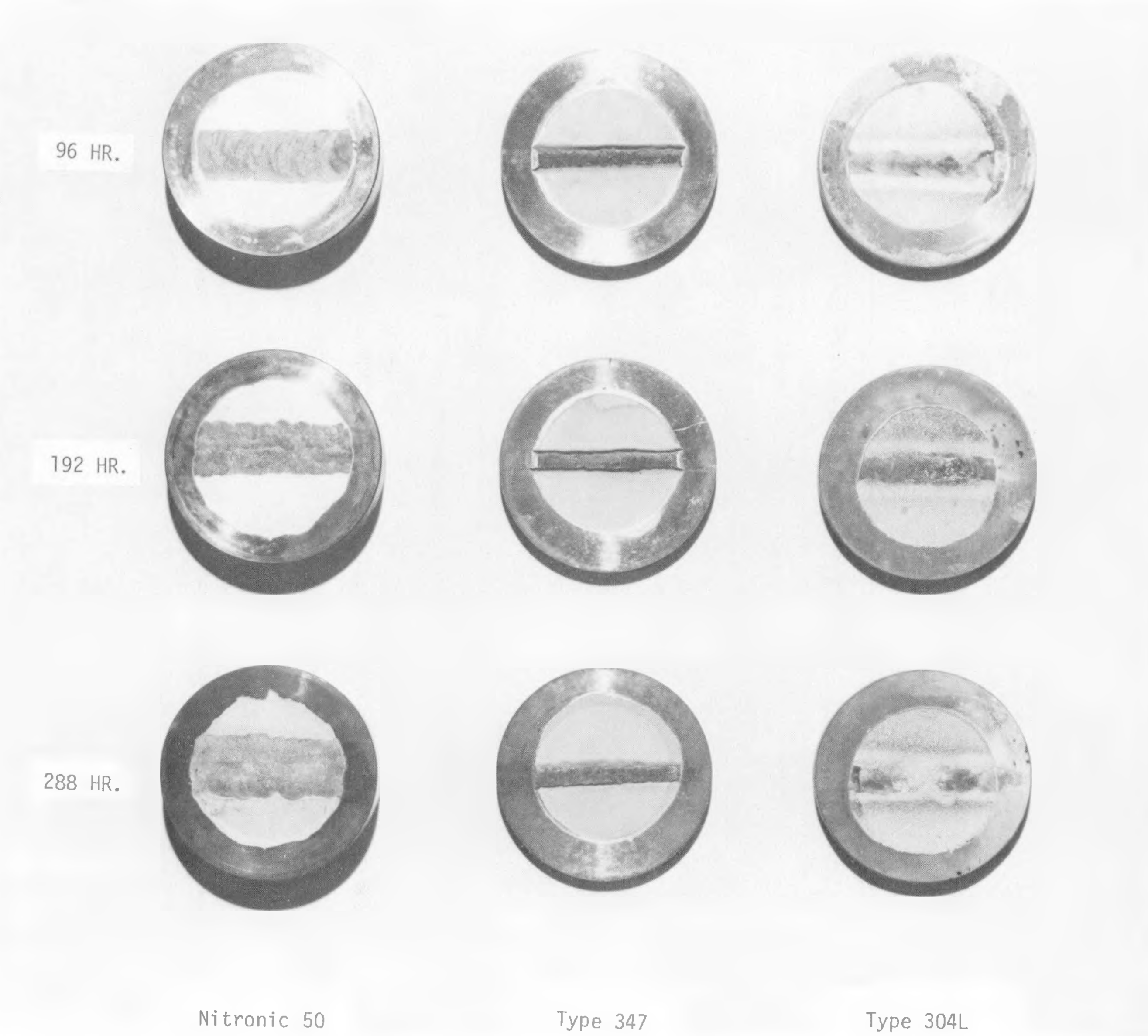
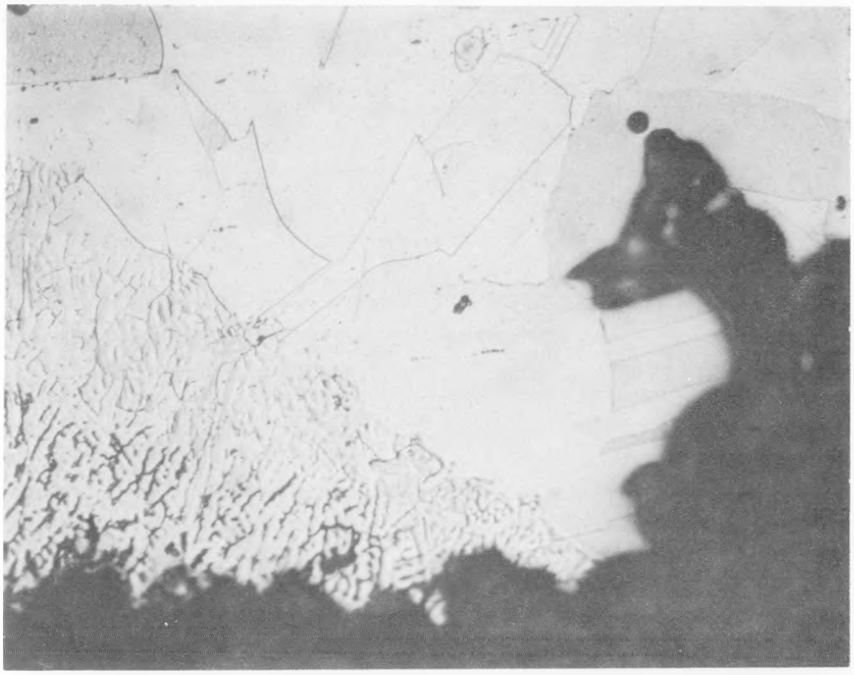
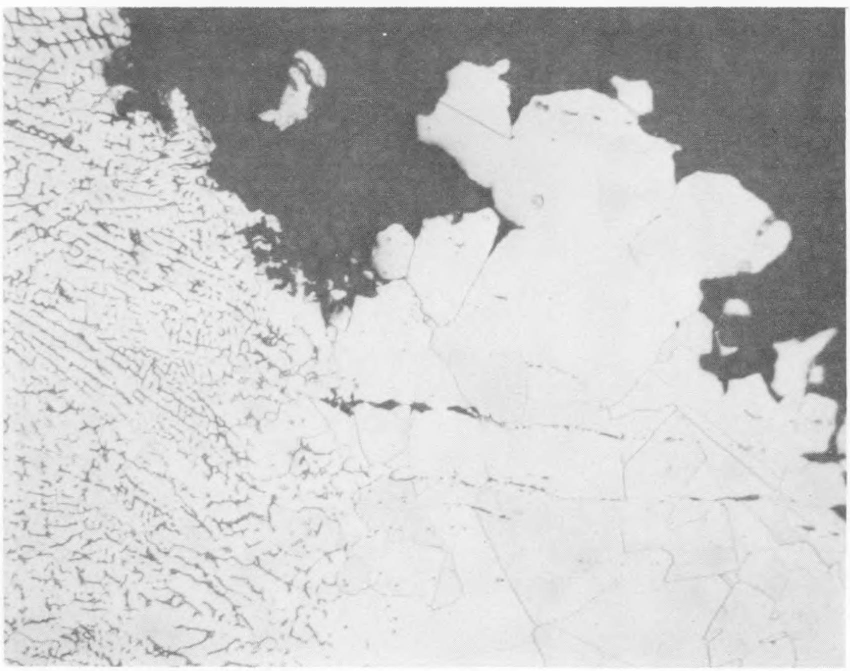


Figure 7. Sensitized Coupons after Exposure to Scrub Solution



220X
Figure 8. Type 304L Stainless Steel Weld-Base Metal Interface



220X
Figure 9. Type 347 Stainless Steel Weld-Base Metal Interface

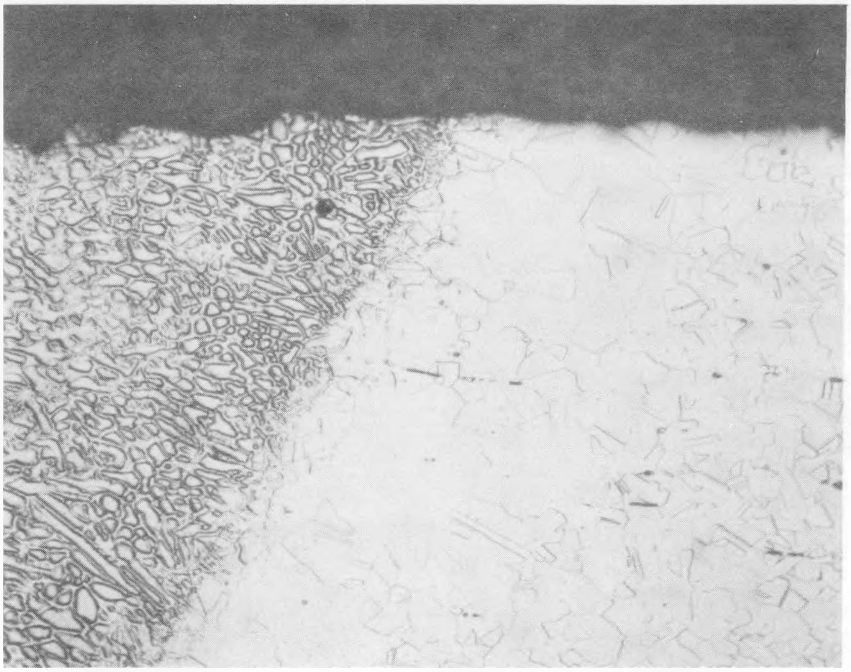


Figure 10. Nitronic 50 Weld-Base Metal Interface

To simulate the vessel environment, metal samples were heat-treated at 1000°F for time periods of 96, 192, and 288 hours. Samples were then tested in the heat transfer corrosion apparatus described in Section VIII-1.1 . Corrosion rates are shown in Table XLVIII. Figure 7 shows all coupons after their exposure.

The Type 304L and 347 stainless steels exhibit differing forms of intergranular attack due to metallurgical changes brought about by the 1000°F heat-treating temperature. The resistance of Nitronic 50 to these temperature effects is also shown.

The Type 304L stainless steel coupons suffered intergranular attack due to sensitization as shown in Figure 8. Numerous theories to explain this phenomenon have been advanced such as the chromium depletion theory, the strain theory,[30] the electrochemical theory,[31] and a solute segregation theory. The most reasonable theory is the chromium depletion theory. According to this theory, the influence of temperature in the 800 to 1500°F range causes carbon that is held in a supersaturated condition in the metal lattice to diffuse to the grain boundary area. The carbon then preferentially combines with chromium to form a carbide of the form $(Cr, Fe)_{23}C_6$, leaving a chromium-depleted area near the grain boundary. This depleted area will then not have enough chromium to form a passive film, which results in a drastic reduction in corrosion resistance. The Type 304L stainless steel composition has a reduced carbon level to eliminate sensitization effects in weld areas, but will suffer intergranular attack after longer times in the sensitization range.[30,34-37]

The Type 347 stainless steel shows a type of intergranular attack called "knife line" as shown in Figure 9. This steel has added columbium, which is a strong carbide former, to tie-up the carbon before it has a chance to combine with chromium. The knife line attack occurs in a narrow area adjacent to the weld bead. This area is at a high temperature during welding, which places all carbides, both columbium and chromium, in solution. At a temperature of 1000°F the chromium carbide will preferentially form.[36,38-41] This will then promote intergranular attack due to chromium depletion as occurred in Type 304L stainless steel.

The Nitronic 50 alloy shown in Figure 10 shows no sign of intergranular attack, only some light attack of the weld area. The alloy shows effective stabilization. The small increase in corrosion rates for the longer heat-treat times shows a slight susceptibility to intergranular attack in process solutions, but the alloy proved to be far superior to Type 304L and 347 stainless steels in this respect.

2.4 Resistance to Chloride Stress Corrosion Cracking (CSCC)

An investigation was conducted to determine the possibility of chloride stress corrosion cracking (CSCC) with Nitronic 50. The NWCF Nitronic 50 equipment will operated up to 162°F metal wall temperature with hot calciner gas scrubbed with a water solution containing 1.5 M HNO_3, 4.5 M NO_3, 1.5 M F^- (complexed with Al and Zr), and about 500 ppm CL^-. The relatively high operating temperature with chlorides present in acid solution makes any austenitic stainless steel subject to scrutiny for resistance to CSCC. There are several factors present in this material and the particular service which appear to be beneficial in repressing the CSCC type of attack:

(1) Nitronic 50, which contains molybdenum and somewhat higher nickel than Type 304L or 347 stainless steels, is superior to both alloys in CSCC resistance. Nitronic 50 has approximately the same resistance as Type 316 stainless steel.

(2) The tendency for austenitic stainless steels to crack in hot, highly acidic chloride solution is somewhat remote. Immunity has been reported in boiling HCl solution (pH <5) and in boiling HNO_3 solutions (pH < 2). The presence of some free (uncomplexed) fluoride ions accelerates general corrosion in HNO_3, which should provide further assurance against CSCC. The reasons for this resistance to cracking are somewhat obscure but probably lie in the areas of passive film morphology, adsorption (chemisorption) kinetics, and the tendency of relatively active corrosion to keep the metal surface free of crack-initiating sites.

(3) The presence of significant amounts of NO_3^- is known to inhibit CSCC. The role of nitrate ion in promoting immunity to CSCC is discussed in the following section.

According to Uhlig,[42] the critical cracking potential of austenitic alloys in boiling 42% $MgCl_2$ (-0.145 V vs. a standard hydrogen electrode) is considered to be the potential above which Cl^- can chemisorb on surface imperfections and below which they desorb. Inhibiting ions such as NO_3^-, by the process of competitive absorption, shift the critical potential in the noble direction. At a concentration corresponding to the critical cracking potential exceeding the corrosion potential, CSCC no longer takes place.

A study by Bryant and Green[43] discusses the susceptibility of austenitic stainless steels to cracking and boiling 42% $MgCl_2$ and inhibition of Type 304 and 316 stainless steels by NO_3^- additions with or without carbonates. As a result of tests conducted on stressed specimens, the study concludes that inhibitions by nitrate additions can be effected for Type 304 and 316 stainless steels in boiling $MgCl_2$ at 155°C. About 4% $NaNO_3$ or KNO_3 (2.46 - 2.92% NO_3^-) is required to inhibit Type 316 stainless steel without addition of carbonate. A change in crack morphology from CSCC which penetrates the metal, to surface corrosion which prevents CSCC, is associated with inhibition.

Successful inhibition is further supported in a paper by A. S. Couper.[44] In boiling 42% $MgCl_2$ test, nitrates were the only inhibitors that effectively stopped CSCC in Type 304 stainless steel. At least 2% nitrate ion was required. The successful operation of the Type 347 stainless steel quench tower in the WCF for many thousands of hours under similar conditions without any reported cracking is reassuring. Although records are not available to show whether the WCF quench tower was stress-relieved or not, it is quite unlikely.

Based on the foregoing evidence, Nitronic 50 should perform satisfactorily in the service intended without stress relief. In addition, the risk of possible intergranular stress corrosion cracking in the aggressive, acidic environment if any sensitization occurs during heat treatment is greater than any possible advantage.

If the operating Type 347 stainless steel vessel was postweld heat-treated, the absence of reported intergranular corrosion is most likely explained by the larger amounts of stabilizing element present in Type 347 stainless steel (columbium 10 times carbon in Type 347 stainless steel vs. 5 times carbon in Nitronic 50).

IX. CONCLUSIONS AND RECOMMENDATIONS

The selection of the 300 series austenitic stainless steels for use in the WCF was a sound decision. The use of Type 347 stainless steel in the primary calcining vessel has proven successful in withstanding not only the original design for handling of aluminum wastes, but has provided a satisfactory unit, after process modifications, for solidifying zirconium fluoride wastes and using the in-bed combustion system. The use of Type 304L and 347 stainless steels in the feed, aqueous off-gas, and waste systems has proven satisfactory for these systems, although corrosion damage has been observed.

Corrosion testing of the newly developed Nitronic-50 alloy has indicated that it has superior chemical corrosion resistance in present and anticipated future waste solutions, and it has been recommended for the liquid handling units in the NWCF.

Recommended future work includes the following:

1. Literature review and laboratory testing to attempt to improve materials used in fittings such as valves, bellows, feed and fuel nozzles, etc. to improve the service life and reliability of these items.

2. Laboratory and pilot-plant corrosion studies will continue to evaluate the effect of any change in calciner feed composition on corrosion of the feed, calcination and scrub system equipment.

3. Baffle plates currently under test in the WCF will continue to be examined and evaluated and test plates will be placed in the NWCF calciner vessel to permit evaluation of corrosion in that unit.

4. Corrosion test coupons will be installed in any additional sets of storage bins as they are built to provide a means of monitoring the condition of the bins in the future.

5. Studies to determine improved materials for areas of high erosion-corrosion will be continued as needed.

References

1. C. E. Stevenson, Technical Progress Report for July through September 1957, Idaho Chemical Processing Plant, IDO-14422, (December 1957).

2. C. E. Stevenson, Technical Progress Report for July through September 1958, Idaho Chemical Processing Plant, IDO-14457, (February 1959).

3. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, October-December 1960, IDO-14553, (May 1961).

4. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, January-March, 1961, IDO-14560, (August 1961).

5. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, April-June 1961, IDO-14567, (November 1961).

6. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, October-December 1961, IDO-14583, (March 1962).

7. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, April-June 1960, IDO-14534, (December 1960).

8. C. E. Stevenson, Technical Progress Report for April through June 1959, Idaho Chemical Processing Plant, IDO-14494, (March 1960).

9. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, January-March, 1963, IDO-14616, (September 1963).

10. J. R. Bower, Ed., Chemical Technology Branch Annual Report Fiscal Year 1967, IN-1087, (October 1967).

11. J. C. Petrie, et al, Fluidized-Bed Calcination of Simulated Zirconium Fluoride Waste in Exploratory Pilot-Plant Tests, IDO-14653, (July 1965).

12. R. F. Domish and L. P. Hatch, Continuous Calcination of High Level Radioactive Wastes by Means of a Rotary Ball Kiln, BNL-832, (November 1963).

13. J. R. Bower, Ed., Chemical Processing Technology Quarterly Progress Report, April-June 1964, IDO-14646, (January 1965).

14. J. R. Bower, Ed., Chemical Technology Branch Annual Report Fiscal Year 1968, In-1201, (October 1968).

15. J. R. Bower, Ed., Chemical Programs Division Annual Report Fiscal Year 1970, IN-1457, (March 1971).

16. C. I. Whitman, "New Approaches to Fuel Processing," Nucleonics, Vol. 16, #11, p. 158 (1958).

17. J. R. Bower, Ed., Idaho Chemical Programs Annual Technical Report Fiscal Year 1971, ICP-1006, (May 1972).

18. J. R. Bower, Ed., Idaho Chemical Programs Annual Technical Report Fiscal Year 1973, ICP-1047, (June 1974).

19. J. R. Bower, Ed., Chemical Technology Branch Annual Report Fiscal Year 1969, IN-1314, (October 1969).

20. J. A. Wielang and W. A. Freeby, The Fifth Processing Campaign in the Waste Calcining Facility, FY-1972, ICP-1021, (June 1973).

21. J. R. Bower and R. T. Struhs, Eds., Idaho Chemical Programs Annual Technical Report Fiscal Year 1975, ICP-1086, (June 1976).

22. J. I. Stevens, Ed., Idaho Chemical Processing Plant-Technical Progress Report-Radioactive Waste Disposal Projects, July-September 1959, IDO-14514, (July 1960).

23. C. L. Bendixsen and G. E. Lohse, Storage Facilities for Radioactive Calcined Waste Solids at the Idaho Chemical Processing Plant, IN-1155, (July 1958).

24. T. L. Hoffman, Corrosion Monitoring of Storge Bins for Radioactive Calcine, ICP-1071, (October 1975).

25. D. P. Wright and C. L. Bendixsen, Design Criteria for ICPP Third Solids Storage Facility for Radioactive Calcined Waste Solids, CI-1129, (March, 1968).

26 R. E. Schindler, Design Criteria for ICPP Fourth Calcined Solids Storage Facility, ACI-146, (February 1974).

27. R. R. Thomas, et.al., Materials of Construction for the New Waste Calcining Facility Process System, ACI-196, (March 1977).

28 R. R. Hammer, A Correlation of Calculated Fluoride Species with Corrosion and Precipitation in Process Solutions, ACI-143.

29. R. R. Gaugh, E. E. Denhard, Jr., and D. C. Perry, ASM Technical Report No. C 70-24.2.

30. T. Z. Moore, Welding Research Supplement, May 1960, pp 199-S to 204-S.

31. R. Stickler and A. Vinckier, Transactions, American Society for Metals TASEA, Vol. 54, 1961, pp 362-380.

32. J. S. Armijo, Corrosion, NACE, Vol. 24, No. 1 (January 1968).

33. A. Joshi and D. F. Stein, Corrosion, NACE, Vol. 28, No. 9, (September 1972).

34. J. R. Auld, Proceedings, Second International Congress on Metallic Corrosion, NACE, 1963, pp 445-461.

35. J. O. Edstrom and L. L. Jungberg, Chemical Engineering (December 21, 1964) pp 114-120.

36. Intergranular Corrosion of Chromium-Nickel Stainless Steel - Final Report. Bulletin, Welding Research Council, WRCBB, No. 138, (1969) New York.

37. S. Polgary, ESAB, Vol. 8, No. 1-2, 1972.

38. H. F. Ebling and M. A. Scheil, Metal Progress, August 1959, pp 87-91.

39. M. Henthorne, Process Industries Corrosion, NACE, 1975, pp 66-89.

40. C. H. Samans, K. Kingshita, and I. Matsushima, Corrosion 76, NACE, 1976, Paper #159.

41. V. Cihal, Localized Corrosion, NACE, 1974.

42. H. H. Uhlig, "Factors Affecting Susceptibility to Stress Corrosion Cracking" (Abstract), Proceedings, Fourth International Congress on Metallic Corrosion, 1972, p 128.

43. R. E. Bryant and J. B. Green, "Inhibition of Chloride Stress Corrosion Cracking of Stainless Steels," Materials Protection and Perfection, (November 1970) pp 19-23.

44. A. S. Couper, "Testing Austenitic Stainless Steels for Modern Refinery Applications," Materials Protection and Performance (October 1969) pp 21-22.