MASTER

GEAP-4025

STRESS CORROSION OF TYPE 304 STAINLESS STEEL IN SIMULATED SUPERHEAT REACTOR ENVIRONMENTS

Informal AEC Research and Development Report 568-T10-2

By
G. G. Gaul
W. L. Pearl
M. Siegler

February 26, 1962

Vallecitos Atomic Laboratory
General Electric Company
San Jose, California

UNITED STATES ATOMIC ENERGY COMMISSION • DIVISION OF TECHNICAL INFORMATION

DISCLAIMER

Printed in USA. Price $1.00. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee

GEAP-4025

METALS, CERAMICS, AND MATERIALS

STRESS CORROSION OF TYPE 304 STAINLESS STEEL IN SIMULATED SUPERHEAT REACTOR ENVIRONMENTS

February 26, 1962

Prepared For

THE U. S. ATOMIC ENERGY COMMISSION

Under

Contract No. AT(04-3)-189, Project Agreement 13

by

G. G. Gaul
W. L. Pearl
M. Siegler

Vallecitos Atomic Laboratory
Atomic Power Equipment Department
General Electric Company
San Jose, California

SUMMARY

A fuel jacket failure that occurred in May 1961 in the Type 304 stainless steel clad fuel element exposed in the Vallecitos Boiling Water Reactor superheated steam loop (SADE) was attributed to chloride stress corrosion cracking. In order to better understand the failure, a test program was carried out to try to reproduce the rapid stress corrosion attack in the simulated superheat reactor environment of the CL-1 superheat facility.

The methods of corrosion testing under heat transfer conditions reported previously (1) were modified:

1. To apply a longitudinal stress on the test sheaths to produce a 0.1 per cent elongation in 1000 hours;
2. To increase the chloride content of the moisture carryover with the steam by increasing the chloride in the recirculating water to 1.5 ppm;
3. To expose the solids deposits to various metal temperatures.

After 1000 hours of exposure, no significant attack was noted on the test sheaths.

The test procedures were further altered to simulate the significant amount of SADE fuel element exposure to saturated steam at varying temperatures with little to no superheat being generated. A 776-hour total exposure was carried out with the test conditions cycled several times in the following sequence:

1. Inlet - 546°F saturated steam; Outlet - 1050°F superheated steam;

2. Inlet --350°F saturated steam; Outlet - 360°F superheated steam;

3. Inlet - 546°F saturated steam; Outlet - 550°F superheated steam;

The entrance heater (calculated metal temperature during normal operation 800-900°F) was covered with numerous fine cracks that did not penetrate completely through the 0.030-inch sheath. The cracks were predominantly transgranular.

Discontinuities were located by ultrasonic techniques in the middle (metal temperature $\sim$ 1000°F) and exit (metal temperature $\sim$1200°F) sheaths. The discontinuities were confirmed as intergranular penetrations of 0.006 to 0.010-inch depth respectively by metallography. Both types of attack had been found on the SADE fuel element cladding failure.

Chloride salts of chromium, copper, iron and nickel have been found by X-ray diffraction in the deposit taken from the test sheaths. Some laboratory tests with unsensitized and sensitized Type 304 stainless indicated that water solutions of copper or iron chloride salts chemically attacked the sensitized material intergranularly independent of stress.

The test results indicated that chemical and chloride stress corrosion attack can act either singularly or in combination to produce the type failures experienced in the SADE and CL-1 tests.

The presence of stress had little apparent effect on the uniform corrosion rate of the test sheaths, except when the stresses were high enough to cause creep. The creep resulted in scale spalling with some accelerated corrosion in the areas of scale cracking.

STRESS CORROSION OF TYPE 304 STAINLESS STEEL IN SIMULATED SUPERHEAT REACTOR ENVIRONMENTS

INTRODUCTION

The 300 series stainless steels have been selected as the reference fuel-cladding material for utilization in several superheat reactor (SHR) systems now being designed. A report [(1)] was recently issued summarizing the results of a corrosion and corrosion-product release study of Type 304 stainless steel, exposed in out-of-pile facilities under heat transfer conditions to superheat steam containing oxygen and hydrogen representative of a typical boiling water reactor (BWR) steam source. In the tests carried out up to metal temperatures of 1300°F, intergranular attack had occurred in areas of scale fluxing and the real potential of chloride stress corrosion was indicated.

A fuel jacket failure that occurred in May 1961 in the Type 304 stainless clad fuel element exposed in the Vallecitos BWR superheated steam loop (SADE) was attributed to chloride stress corrosion cracking [(2)]. The source of the problem was indicated as a combination of abnormally high water seepage from the BWR into SADE and abnormally high chloride ion concentration in the VBWR coolant.

Because of the need to better understand the stress corrosion experience with the SADE element, the Task E out-of-pile corrosion studies of the Atomic Energy Commission sponsored Superheat Program were reoriented to try to reproduce the rapid stress corrosion attack of the Type 304 stainless steel in the simulated superheat reactor environment of the CL-1 superheat facility.

It is the purpose of this report to summarize the results of the test program carried out in the CL-1 superheat facility for simulation of a stressed fuel cladding test with heat transfer in the presence of typical BWR quantities of oxygen and hydrogen and an excessive quantity of chloride.

CONCLUSIONS

The following conclusions are based on the out-of-pile stress corrosion studies completed to date on Type 304 stainless steel:

1. The ability to reproduce the corrosion behavior of the in-reactor SADE fuel element cladding failure was demonstrated in the CL-1 superheat facility.
2. Laboratory tests indicate that water solutions of copper or iron chloride salts can chemically attack the sensitized material intergramularly independent of stress.
3. Chemical and chloride stress corrosion attack can act either singularly or in combination to produce failure in the presence of moisture.
4. The presence of stress has little apparent effect on the uniform corrosion rate, except when the stresses are high enough to cause creep. The creep can result in scale spalling with some accelerated corrosion in the areas of scale cracking.

MATERIALS

The heat transfer specimens used in the course of the portion of the program reported herein consisted of Type 304 weldrawn tubes from two commercial sources. Each test sheath was 36 3/4-inches long x 9/16 inch OD x 0.500-inch ID. The ends of the sheaths were machined to 0.560-inch OD and the last 1/4 inch on each end threaded. The sheaths were then marked, degreased in acetone, pickled for one-half hour in a 130°F 20 per cent nitric acid bath, washed, dried and weighed. No other surface treatment was performed.

The specimens for isothermal testing were purchased in 1/2-inch wide by 1/16-inch thick strips, with #1 round edges and #2 finish. They were degreased and cleaned by the same procedure used with the tubes.

The chemical composition of the test materials are listed in Table I.

TABLE I

Composition of Type 304 Stainless Steel Materials

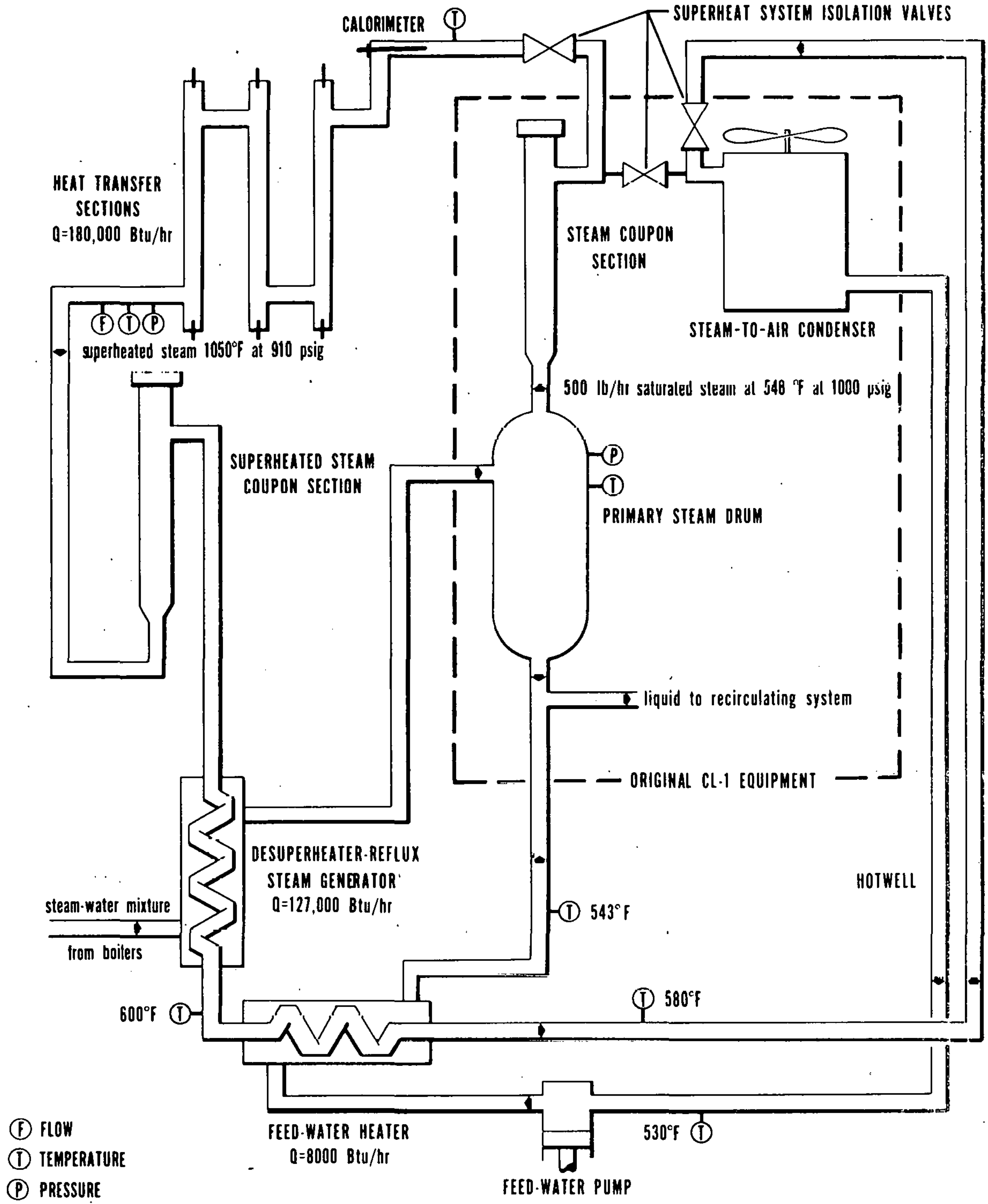
Code	C	Mn	P	S	Si	Ni	Cr	Fe	
Heat Transfer Tubes									
Q	0.048	0.88	0.021	0.021	0.45	10.75	19.02	Bal	
Y	0.05	1.08	0.016	0.006	0.73	9.32	18.52	Bal	
Coupon Strip									
Annealed	0.064	1.24	0.024	0.020	0.58	9.40	18.02	Bal	0.26 Cu
1/2 Hard*	0.08	1.12	0.034	0.015	0.56	8.89	18.05	Bal	0.17 Mo

* Room Temp. Y.S. 134,000 psi
Elongation 11 1/2%

After the test the tubes were examined by means of a stereo-microscope and weighed, descaled and sectioned as required for the particular test. The descaling was performed as described previously (1). The stressed-beam specimens were examined for cracks by means of a stereo-microscope without removing the specimens from the stress holder.

METHOD

The stress corrosion tests were carried out in the CL-1 superheat corrosion facility, previously described (1 & 3), and shown in schematic diagram in Figure 1. Earlier work (1) had shown the tendency of the solids in the moisture carried with the steam from the steam drum to deposit on



SCHEMATIC DIAGRAM OF SUPERHEAT ADDITIONS TO CL-1 TEST FACILITY

FIGURE 1

the surface of the heater sheaths. Although the recirculating coolant in the test facilities contained a total solids content of 1 - 2 ppm and chlorides of 0.03 ppm or below, a relatively heavy fan shape deposit of metal chlorides developed (~0.002 in. in 1000 hours) at the inlet to the entrance heater sheath as shown in an enlarged view in Figure 2. X-ray Diffraction (XRD) indicated the presence of $CrCl_3$, $CuCl_2$, $FeCl_2$, $FeCl_3$ and $NiCl_2$ in the deposit.

It was anticipated that Type 304 stainless steel sheaths could be made to crack in test in the CL-1 superheat facility by simulating the environmental and operating conditions to which the SADE fuel element (SH4B) had been exposed[(2)]. In particular it was considered important to simulate the following SADE characteristics:

1. Deposits exposed to various metal temperatures in the range 800 - 1300°F.
2. Applied stresses constant and near yield.
3. Heat transfer up to 175,000 Btu/ft^2-hr.
4. Increased chloride content in moisture carryover with steam.

The following equipment and system changes were made to accomplish the above characteristics in the CL-1 superheat facility:

1. A longitudinal stress was applied to the test sheaths as sketched in Figure 3. The test sheaths were extended outside the test housing, threaded and a constant tensile force applied through attached end beams by means of air cylinders. The stresses on the two higher temperature sheaths were set to produce 0.1 per cent elongation in 1000 hours.
2. The isothermal testing was accomplished by utilization of stressed

FIGURE 2 DEPOSIT ON INLET TO ENTRANCE SHEATH (5X)

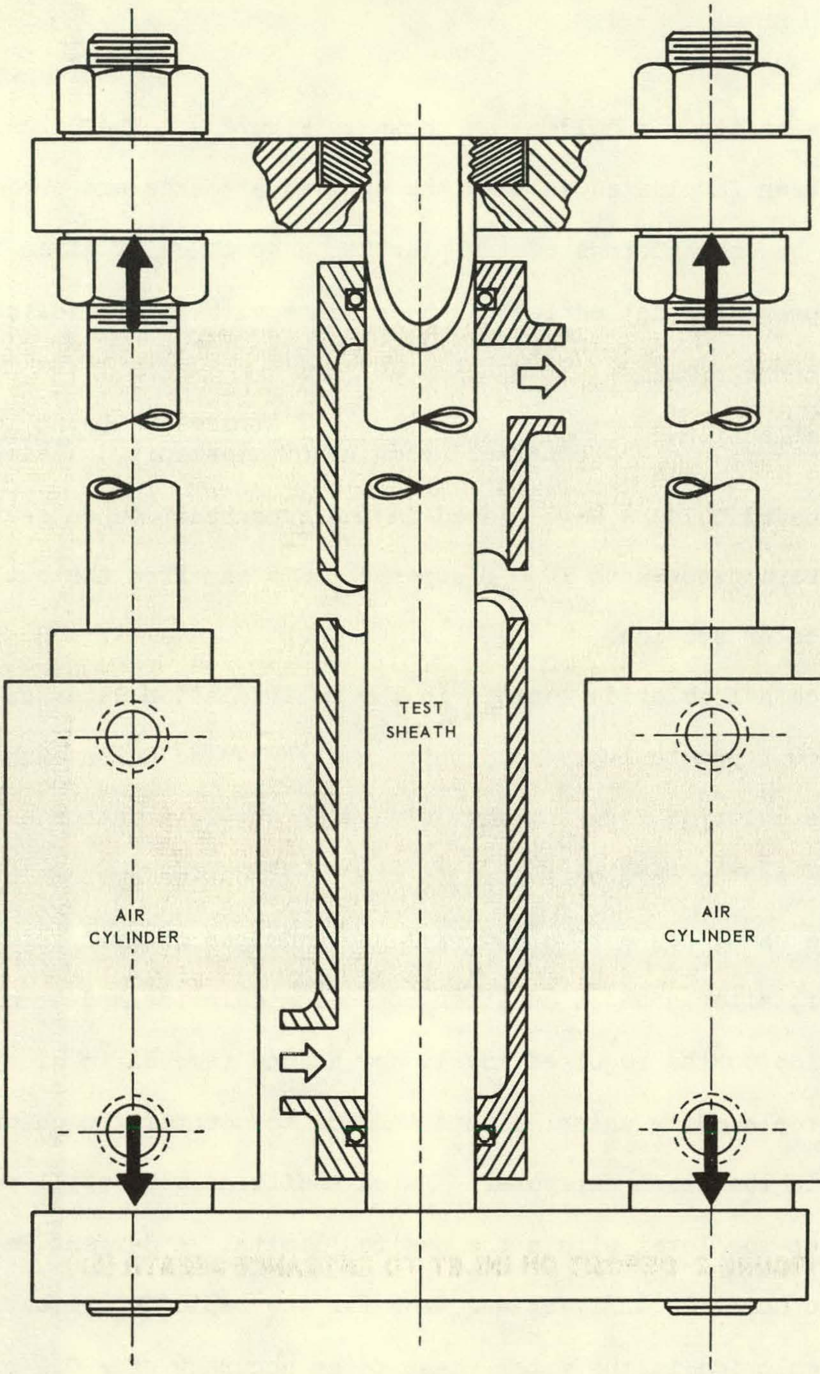


FIGURE 3 TEST SHEATH, STRESS APPLICATOR

beam specimens in holders as shown in Figure 4. The holders have been fabricated so that the applied stresses are predetermined by the spacings of the pins for a specimen of given thickness providing deflections in accordance with the following relationship:

$$\text{Deflection} = \frac{(\text{Applied stress})\ (\text{span length})^2}{\text{constant}\ (\text{modulus of elasticity})\ (\text{sample thickness})}$$

The loaded holders were placed in the superheat coupon section where they were exposed to 1050°F superheated steam from the outlet of the heater section.

3. The nominal chloride content in the recirculation water was raised from <0.1 ppm to 1.5 ± 0.5 ppm. A strong-base anion exchanger in the chloride form together with a strong-acid cation exchanger in the sodium form were used in the purification system in place of the usual respective hydroxyl and hydrogen forms. In this manner, after a batch addition of sodium chloride had brought the chloride to the required level, any anions removed in cleanup were replaced by chloride ions tending to counter the chlorides lost in the steam carryover. Batch additions were still required to keep the level within the desired limits. A Sargent Potentiometric Chloride Analyser was used for the rapid determination of the chloride in the water phase to an accuracy of $\pm$ 0.1 ppm.

The facility operating conditions during the various test runs are summarized in Table II. The typical heavy fan shape deposit that has been noted previously on the inlet to the entrance heater (Figure 2), was allowed to form for 400 - 500 hours during the three parts of run 49. The entrance heaters and sheaths were subsequently placed in the loop in positions such that the area with the heavy deposited carry-over salts

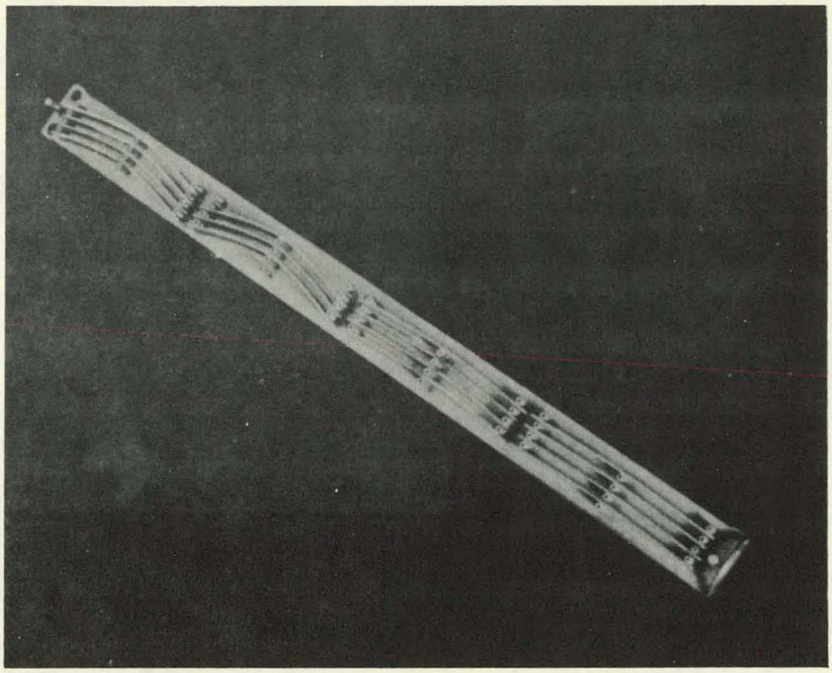


FIGURE 4 STRESSED-BEAM TEST HOLDER AND SPECIMENS

TABLE II

OPERATING CONDITIONS DURING TESTS

Run No.	49	49A	49B	50-50A	50B-50C	50D
Length of Test, Hrs.	495	447	427	210	238	242
Steam Flow, lb/hr	453	438	413	456	442	440
Moisture in inlet steam, %	1.0	1.0	-	-	-	-
Steam Temperatures, °F						
Inlet	546	546	546	546	546	546
Outlet of entrance heater	656	656	658	656	660	694
Outlet of middle heater	846	844	847	841	845	868
Outlet of exit heater	1051	1044	1041	1038	1044	1046
Inlet Steam Gas Content						
Oxygen, ppm (range)	16-28	22-34	17-42	12-29	18-25	10-26
(mean)	23.2	30	28.5	23	21.4	20.5
Hydrogen, ppm (range)	2.7-6.1	2.4-7.3	3.7-1.4	2-5	1.2-4.7	1.8-3.6
(mean)	3.8	4.7	5.4	3.8	3.3	2.69
Chloride in Recirculating Water						
Time, hrs.	378	447	296	187	235	220
ppm (range)	1.6	1.5	1.9	1.9	1.9	1.6
(mean)	0.6-2.2	0.7-2.5	1.2-2.3	1.2-2.2	1.4-2.3	1.0-2.2
Applied Stresses, psi						
Entrance Sheath	12,000	12,000	12,000	25,000	25,000	25,000
Middle Sheath	12,000	12,000	12,000	14,000	14,000	14,000
Exit Sheath	6,000	6,000	6,000	7,000	7,000	7,000
Test Sheath Location						
Entrance Heater	Q-1	Q-2	Y-3	Y-4	Y-8	Y-2
Middle Heater	Q-4	Q-4	Q-1(rev)	Y-5	Y-5	Y-5
Exit Heater	Q-3	Q-3	Q-2(rev)	Y-3(rev)	Y-3(rev)	Y-3(rev)

Average heat flux: 175,000 Btu/hr.-ft^2

Calculated metal temperatures:

Entrance Heater	800-900 F
Middle Heater	900-1100 F
Exit Heater	1100-1300 F

was exposed to a calculated metal temperature of 1100°F in the middle heater position (Q-1) or 1300°F in the exit heater position (Q-2) for run 49B. The entrance heater (Y-3) utilized in run 49B was subsequently reversed similarly and placed in the exit heater position corresponding to a 1300°F metal temperature for runs 50 and 51. The stresses applied longitudinally to the test sheaths were increased as indicated in Table II for the complete run 50.

Although the SADE fuel element SH4B had failed by stress corrosion within the first 12 days of exposure[(2)], the several steps taken in runs 49 and 50 to simulate the SADE exposure were not adequate to reproduce the stress corrosion cracking. One heater sheath did fail apparently by chloride stress corrosion cracking in the area of the test housing seal gasketing where the temperature of the essentially stagnant coolant was 200 - 250°F. The failure, however, appeared to be independent of the test conditions in the dynamic portion of the CL-1 superheat facility, (see page 25.) Further analysis of the SADE operation log revealed that the SADE fuel element was exposed to saturated steam at varying temperatures (with corresponding varying saturation pressures) part of the time. With little to no superheat being generated by the fuel, a large percentage of the total surface area of the fuel could become wetted during this period by the moisture carryover with the VBWR steam.

Based on the above considerations the mode of operation for run 51 of the CL-1 superheat facility was further modified to accomplish the following:

1. Operate at conditions similar to previous runs with full superheat for about 200 hours.
2. Decrease boiling temperature and pressure with low superheat

(power to provide ~10°F) for approximately 100 hours to permit a large area of the surface of the superheat sheaths to be wetted by the moisture carryover with the steam and to enhance the solids content therein to deposit similarly over a large area.

3. Increase boiling temperature and pressure to standard (546°F, 1000 psi) with low superheat for about 50 hours.
4. Repeat above cycle (steps 1, 2 and 3) with time units about halved.
5. End run with decreased temperature - pressure and no superheat for final exposure condition.
6. Change stress loadings during cycle to keep the heater sheaths near yield.

The attained operating conditions for the complete cycling exposure have been included in Table III.

RESULTS

Runs 49-50

Figure 5a indicates the fan-shaped deposit on the inlet to the entrance heater sheath (Y-3) after a 400-hour exposure with the recirculating coolant containing ~ 1.5 ppm chlorides. The deposit was similar in appearance to the 1000-hour exposure pictured in Figure 2 which resulted from an essentially chloride-free system. A similarly prepared sheath, Q-1, is shown in Figure 5b after having been exposed for an additional 400 hours in the middle heater location to a calculated metal temperature of 1100°F. Some of the deposit is seen to have remained in place. Heater sheath Q-2 was also exposed as the entrance heater for about 400 hours to obtain the fan-shaped deposit from the chloride bearing system and then exposed for

TABLE III

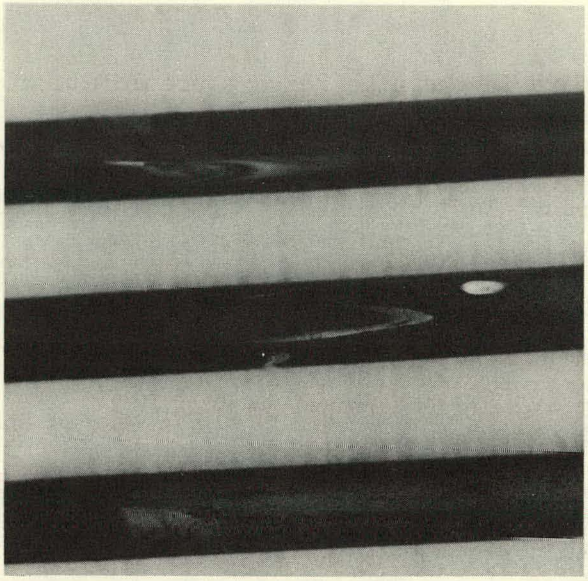
OPERATING CONDITIONS - CYCLING TEST

Run No.	50D	51			51A			
	1000 psi Full Superheat	Low Press. Low Superheat	1000 psi Low Superheat	1000 psi Full Superheat	Low Press. No Superheat**	1000 psi Low Superheat	1000 psi Full Superheat	Low Press. No Superheat**
Elapsed Time, Hours	242	96	44	120	120	20	74	60
Steam Temperature, °F								
Inlet	548*	349	546	546	357	548	547	355
Outlet of Entrance Heater (Y-2)	694	343	541	673	346	544	676	344
Outlet of Middle Heater (Y-5)	867	344	544	852	337	554	857	335
Outlet of Exit Heater (Y-3)	1046	362	550	1041	329	558	1050	325
Pressure, psig								
Outlet of Exit Heater	900	86	983	879	78	1000	894	74
Steam Drum	1000	118	1000	1000	133	1010	1006	129
Applied Stresses, psi								
Entrance Heater	25,000	25,000	25,000	25,000	25,000	25,000	25,000	25,000
Middle Heater	14,000	14,000	14,000	14,000	25,000	25,000	14,000	25,000
Exit Heater	7,000	7,000	7,000	7,000	25,000	25,000	7,000	25,000

* Steam to first heater was dried with calorimeter during Run 50D.

** Although there was no power to the superheat heaters, the middle and exit superheat sheaths were still exposed to superheated steam because of the pressure drop caused by the high steam velocities in the heater sections.

Chloride in recirculating water @ ~ 1.5 ppm.



a. 427 hours exposure as inlet end of entrance heater (Y-3)

b. 427 hours exposure as outlet end of middle heater (Q-1) after 495 hours exposure as inlet end of entrance heater.

c. 427 hours exposure as outlet end of exit heater (Q-2) after 447 hours exposure as inlet end of entrance heater.

FIGURE 5 DEPOSITS ON SHEATHS, 1.5 ppm CHLORIDE IN RECIRCULATING WATER.

an additional 400 hours in the high temperature location to a calculated metal temperature of 1300°F. Figure 5c depicts the completed exposure with the little to no deposit left in place. Considerable scale spalling was noted in the 1300°F region under the deposit, but very little on the 1100°F specimen.

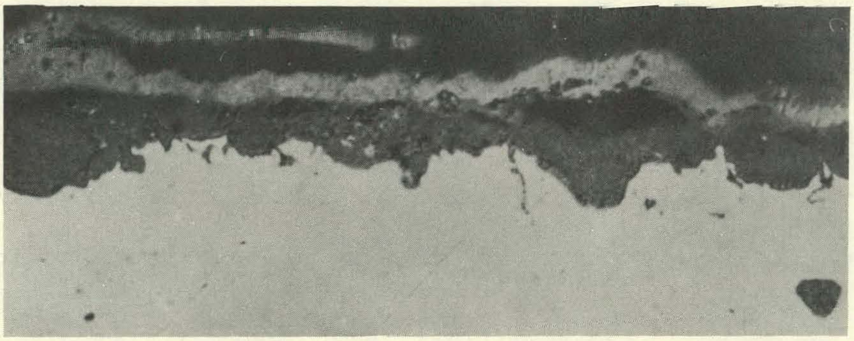
Metallographic examination of the 1300°F area, as shown in Figures 6a and 6b, indicates a much greater amount of corrosion products formed during this 400-hour exposure with deposited salts at a metal temperature of 1300°F as compared to the 2465-hour exposure without deposited salts as shown in Figure 6c. The scale was found to be porous and spalling with evidence of intergranular attack.

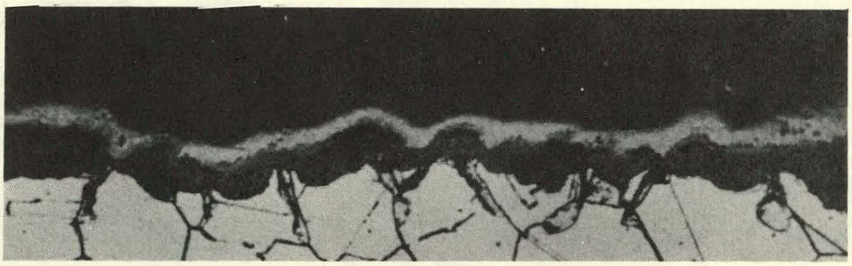
Metallographic examination of the 1100°F region (Figure 7) showed a non-typical scale with indications of spalling. Some evidence of intergranular attack was noted.

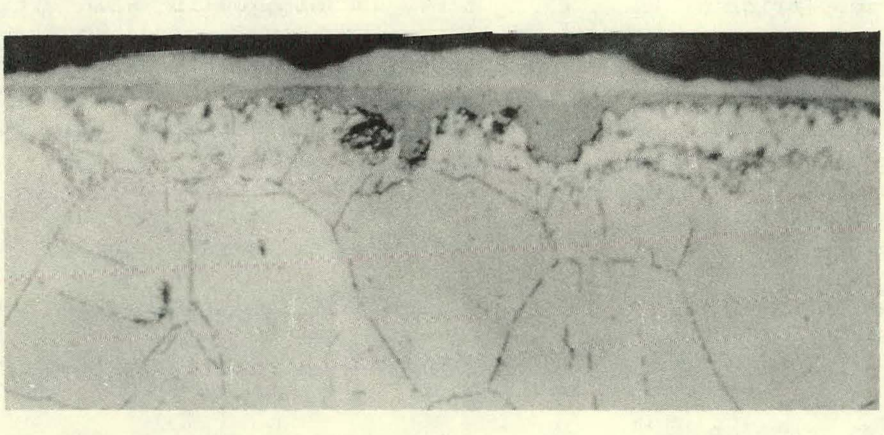
Run 51

Upon completion of the cycling test, as detailed in Table III, the entrance sheath, Y-2, was covered with numerous fine cracks as shown in Figure 8a. There was no evidence during loop operation or during the hydraulic removal of the test sheath from the heater that the cracks extended completely through the wall. The cracks examined were predominantly transgranular as shown in Figure 8b. They were similar in nature to those cracks found on the SADE SH4B element where sensitization of the Type 304 was less prevalent (2).

The middle and exit sheaths were examined by ultrasonic methods for cracks. Two indications of cracks were noted on each sheath. A 0.010-inch







c. 2465 hours exposure without stress, no chloride added, glyceregia etch.

FIGURE 6 HEAT TRANSFER EXPOSURE - TYPE 304 SS CALCULATED METAL TEMPERATURE - 1300 °F UNDESCALED (500X)

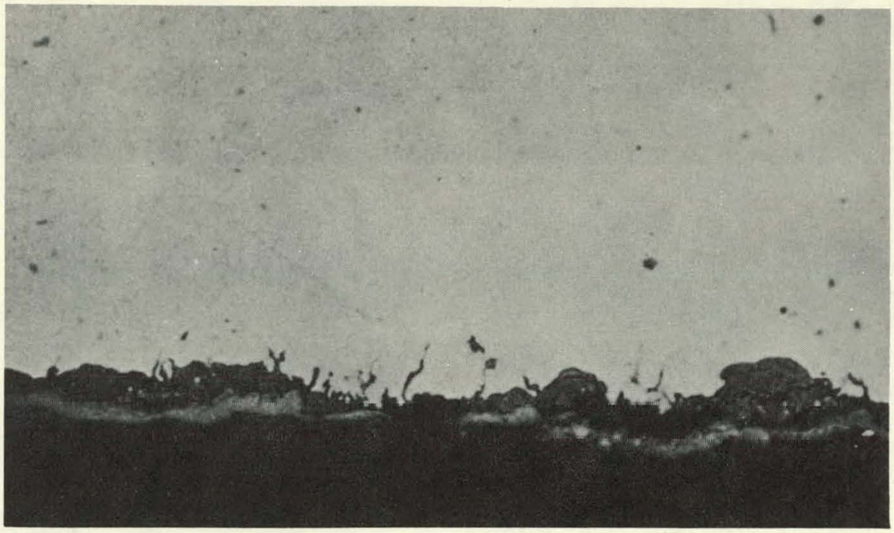
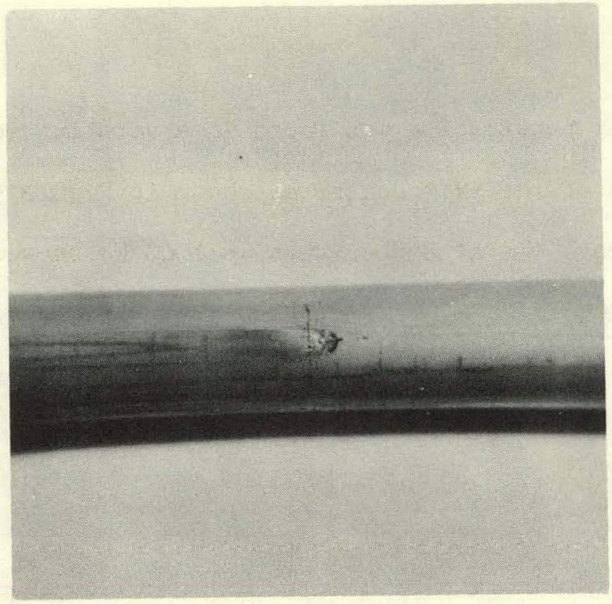
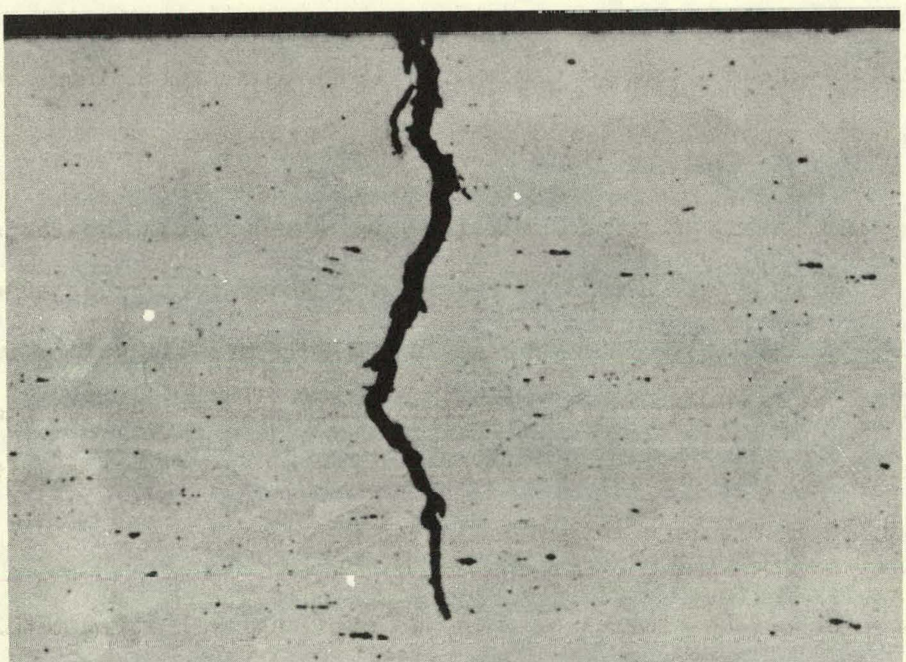


FIGURE 7 HEAT TRANSFER EXPOSURE (Q-1) - TYPE 304 SS, CALCULATED METAL TEMPERATURE - 1100 °F, 400-HOUR EXPOSURE WITH STRESS, CHLORIDE ADDED. AREA UNDER DEPOSITED SALTS. NOT ETCHED, UNDESCALED (500X)



a. Portion of sheath with several cracks (Line in middle is spacer scratch)



b. Section through typical crack (250X)

FIGURE 8 ENTRANCE HEATER SHEATH (Y-2) STRESS CRACKED, 776-HOURS EXPOSURE WITH HEAT TRANSFER - CYCLING TEST - CHLORIDE ADDED TO WATER.

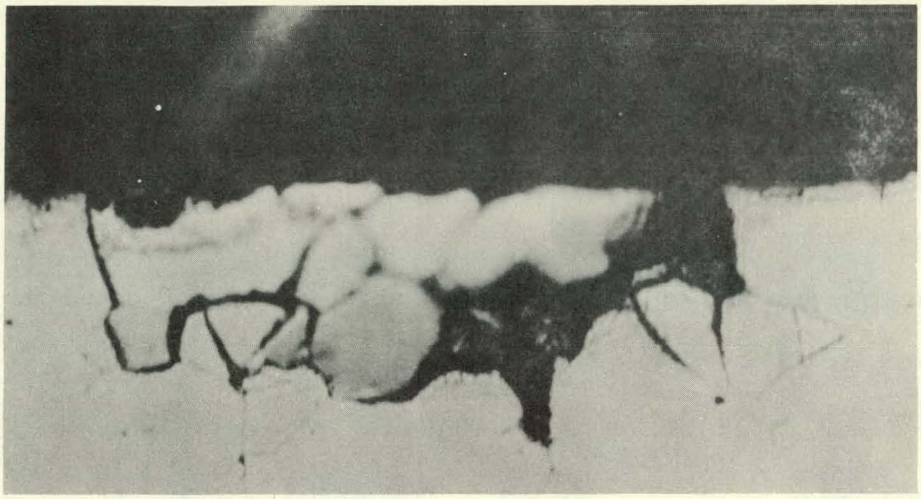
deep intergranular penetration was found in a metallurgical examination of the suspect areas of the exit heater as shown in Figure 9. Examination of the middle sheath (metal temperature ~1000°F) showed a 0.006-inch intergranular penetration ~0.006-inches wide. Figure 10 shows the typical scale formation found in the 1000 and 1125°F metal temperature areas, respectively.

Corrosion

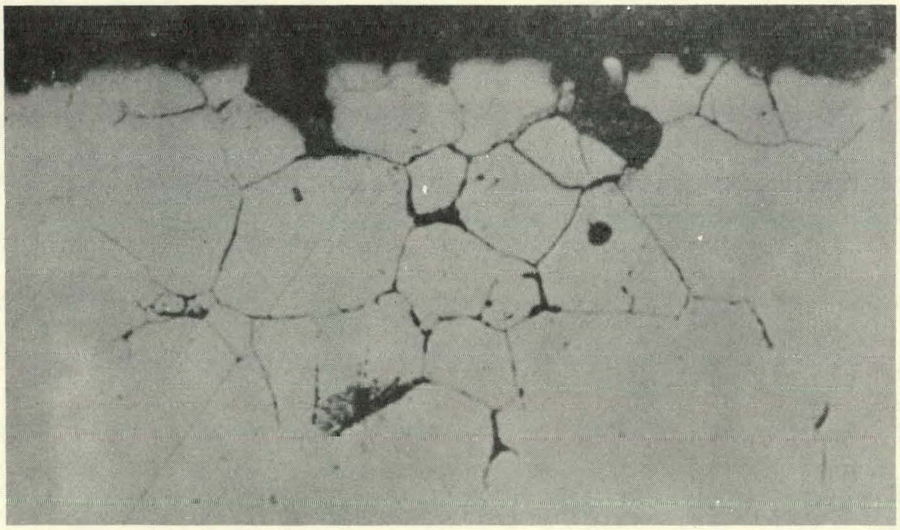
The results of a corrosion study of Type 304 stainless steel in a simulated superheat reactor environment were reported previously (1). Satisfactory performance up to 1100°F was indicated from the sheaths tested unstressed with heat transfer up to a metal temperature of 1100°F and isothermal coupons tested at 1050°F. The potential activity problem from metal-to-system losses increased in significance with increase in metal temperature above 1100°F (1).

Some further corrosion information was obtained from the tests carried out with longitudinally stressed sheaths and chlorides added to the recirculating water. The entrance and middle sheaths were normal in appearance. The high temperature exit sheaths, however, showed increasing spalling with temperature from 1200°F. The spalled end of the exit sheath, Q-3, is shown in Figure 11 after 942-hours exposure.

Since the present series of runs was aimed at evaluating metallurgical effects of chlorides, little quantitative data were obtainable. Some semi-quantitative results were obtained by weighing the exposed sheaths before and after cutting out a 1-inch piece for metallurgical evaluations. Corrosion rates were determined by correcting for the removed piece as representative, descaling the remainder of the sheath and calculating the

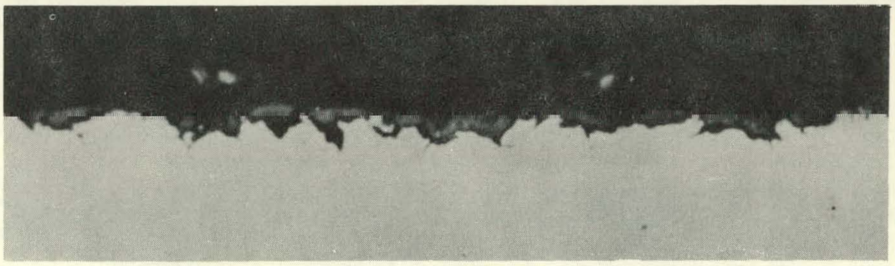


a. Near edge of attacked area. Complete boundary damage is indicated by tilted grains.

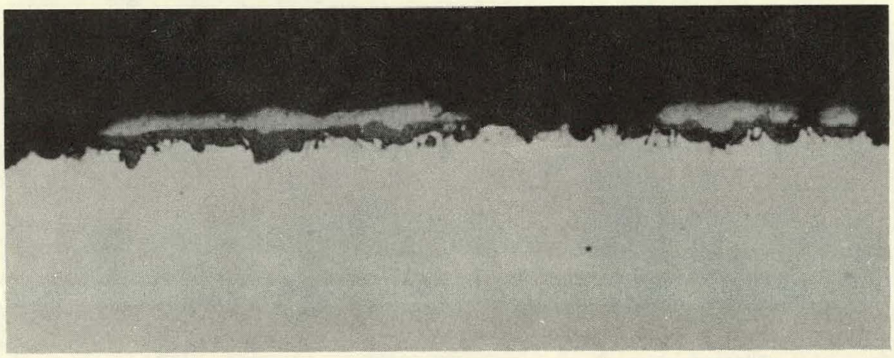


b. Near center of attacked area.

FIGURE 9 EXIT HEATER SHEATH (Y-3) SHOWING INTERGRANULAR ATTACK, 776-HOUR EXPOSURE WITH HEAT TRANSFER - CYCLING TEST - CHLORIDE ADDED TO WATER (500X)



a. Calculated metal temperature - 1000 °F(Y-5)



b. Calculated metal temperature - 1100 °F (Y-3)

FIGURE 10 TYPICAL SCALE FORMATION. HEAT TRANSFER EXPOSURE WITH STRESS CYCLING TEST - CHLORIDE ADDED TO WATER.

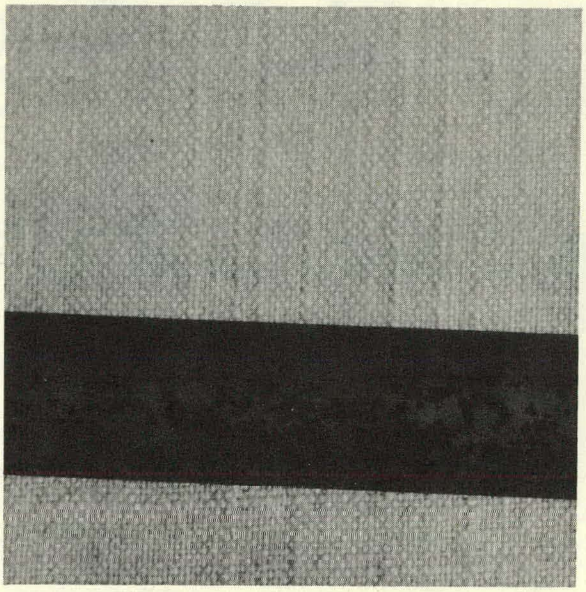


FIGURE 11 TYPICAL SPALLED CORROSION FILM ON STRESSED SHEATH (Q-3) IN 1200 - 1300 °F METAL TEMPERATURE RANGE, CHLORIDE ADDED TO WATER, 942-HOURS EXPOSURE.

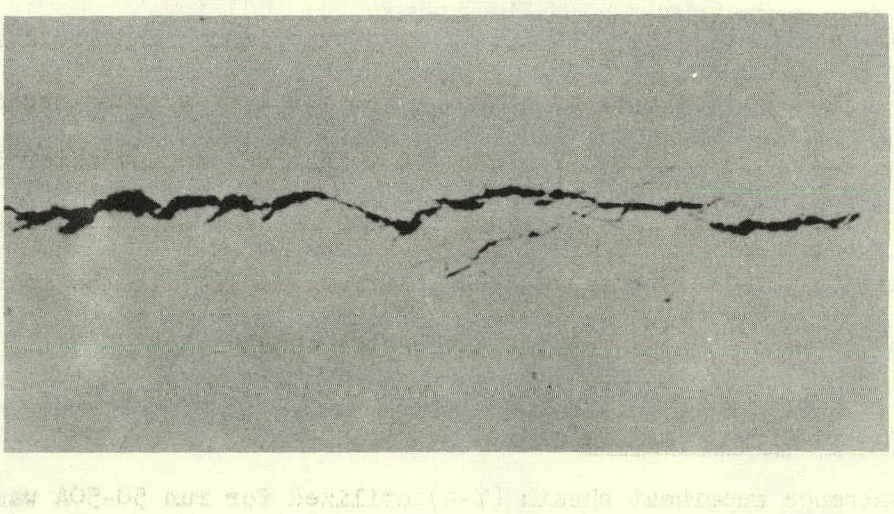


FIGURE 12 ENTRANCE SHEATH FAILURE IN TEST HOUSING END BOX FITTING, TEMPERATURE: 200-250 °F (100X)

rates therefrom. The results are reported in Table IV.

TABLE IV

Corrosion with Heat Transfer and Stress

Sheath	Calculated Metal Temp. °F	Time Hours	Applied Stress psi	Total Corrosion mg/dm^2	Metal-to-system Loss mg/dm^2
Q-4	900-1100	942	12,000	187	65
Y-5	900-1100**	1222	14,000	157	2.1
Y-3	800-900 1100-1300**	425 1222	12,000 7,000	285	*

* Additional scale spalled off during removal of the sheath from the internal heater by means of the hydraulic heater extractor (3).

** Metal temperature varied during cycling run as listed in Table III.

The total corrosion results are comparable to those experienced in the earlier tests without stress on the sheaths and without chloride in the recirculating water (1). The metal-to-system loss for sheath Q-4 was an order of magnitude higher than previously experienced and would indicate an adverse effect of the applied stress. The metal-to-system loss during the cycling run, as calculated from exposed weight before and after de-cycling, had little significance since the mode of low superheat operation was utilized to purposely encourage the carryover solids in the moisture to deposit throughout the length of the heater sheaths.

Low Temperature Stress Failure

The entrance superheat sheath (Y-4) utilized for run 50-50A was removed after 210 hours of operation because of loss of integrity. A thorough examination revealed stress cracking in the unheated portion of the sheath opposite the gasket used for maintaining the pressure seal between the end fittings and the test housing. The sheath at the point of cracking was exposed to near stagnant water at a temperature of 200°F to 250°F and longitudinal stress of 25,000 psi. The gasketing material opposite the cracks analyzed 1280 ppm soluble chlorides and 12,700 ppm total chlorides present. Some of the chloride could have leached into the water in contact with the sheath. The cracks appeared to be transgranular in nature as indicated in Figure 12.

Isothermal Testing

Stressed specimens of annealed and one-half hard Type 304 stainless steel were exposed in stressed beam holders with the initial applied stresses as shown in the tabulation in Table V. No attempt was made to correct for the relaxation of the applied stresses with time caused by the 1050°F temperature of operation.

TABLE V

Type 304 SS Stressed Specimens in 1050°F Superheated Steam

Oxygen ~ 20 ppm.

Applied Stress, psi	No. Samples	Time Hours	No. Cracked
		Annealed	
30,000	2	500	0
60,000	2	2598	0
		One-half Hard	
60,000	2	500	0
100,000	2	2598	0

Because of the location of the superheat coupon section downstream from the superheat heaters, there is little chance for chlorides to be carried over with the superheated steam and deposited on the stressed specimens. The heated sheaths serve as excellent scavengers of any solids carried over with the steam. The specimens apparently were resistant to stress cracking in the representative quantity of oxygen present in the steam.

It should be noted further that the 1.5 ppm chloride added to the recirculating water in the CL-1 facility produced no apparent damage to the 300 series stainless steel materials of loop construction or to similarly stressed beam specimens placed in the various environments of the facility for monitoring the integrity of the facility.

DISCUSSION

The results of the investigations in SADE and in the CL-1 superheat facility are beginning to fit together to permit a better understanding of the mechanism of the type of stress corrosion encountered. The stress cracks occurring below 1000°F in SADE and the entrance superheat sheath in the CL-1 facility (calculated metal temperatures of 800-900°F) have been transgranular. In both cases the materials under test had started in the annealed condition and apparently had not been taken high enough in temperature to become sensitized.

In those cases in SADE and the CL-1 facility where the metal temperature exceeded 1000°F, the Type 304 stainless steel was found to be sensitized. In these latter instances, the attack found with most of the SADE cracks and the attack on the middle and exit superheater sheaths from CL-1were intergranular.

Some laboratory tests were carried out to study the type of attack that could be expected on sensitized and unsensitized Type 304 stainless steel in the presence of the chloride salts of chromium, copper, iron and nickel. A summary of these tests has been included in the Appendix. It was indicated on U-bend specimens at 212°F that water solutions of copper or iron chloride salts chemically attacked the sensitized material intergranularly independent of stress. The attack appeared to be of the type found with many of the SADE cracks and with the attack on the higher temperature superheater sheaths.

Some recent metallographic results from the failed SADE fuel element SH4C[(4)] further confirms the relationship. Figure 13 shows an area of the SH4C cladding away from the failed area. The intergranular attack with grains missing appears similar to the chemical attack produced in the standard chemical tests used for indicating the sensitization of 300 series stainless steels and reproduced with copper and iron chloride salts on sensitized U-bend specimens. The failure area is shown in Figure 14. Intergranular attack with complete grain removal is indicated. The missing grains indicate complete boundary attack with probable loss of the grains occurring during the preparation of the specimens.

The experience with the heavy fan shape deposit of metal chlorides formed on the inlet to the entrance heater sheaths and later moved to the high metal temperature areas in the CL-1 facility emphasizes the major role that moisture and form of deposit play in the cracking of Type 304 stainless steel in the presence of chlorides. The heavy salt deposit at the entrance effectively formed a protective coating that prevented moisture from reaching the chloride-metal interface. Under normal operating conditions the steam was completely dried before the coolant could make

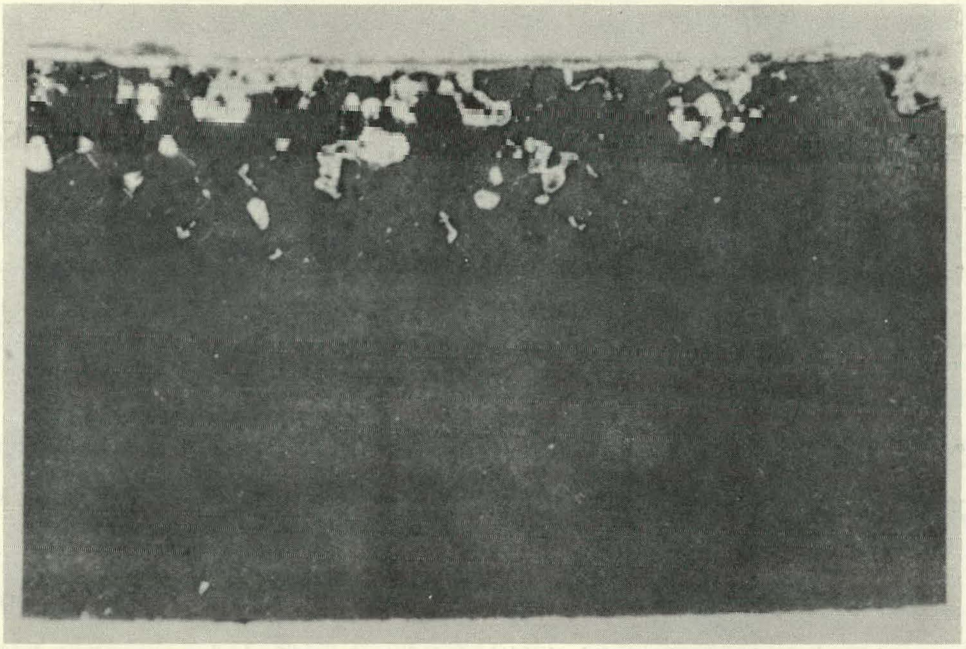


FIGURE 13 FUEL ELEMENT SH-4C INTERGRANULAR ATTACK OF CLAD AWAY FROM FRACTURE, SHOWING GRAINS MISSING FROM MATRIX. (100X) POLARIZED LIGHT

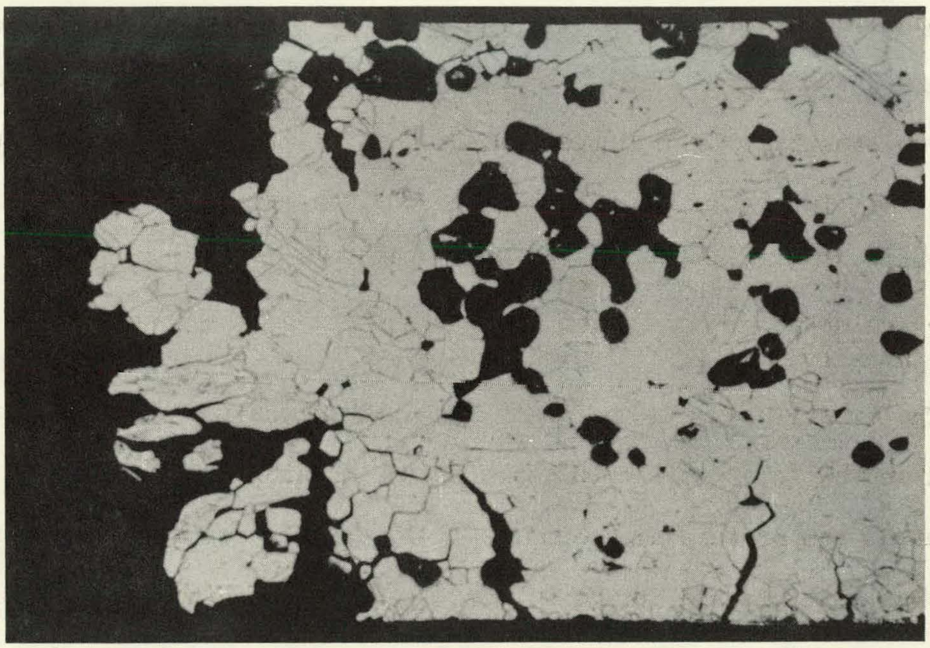


FIGURE 14 FUEL ELEMENT SH-4C SEVERE INTERGRANULAR ATTACK, AND CRACKS EMANATING FROM THE STEAM SIDE OF THE 0.028 IN. WALL. (100X)

contact with the metal. In utilizing the cycling mode of operation, which more nearly represented the environment to which the SADE fuel elements were exposed, the moisture in the steam could contact large areas of the sheaths during the period when little or no superheat was generated. Edeleanu and Snowden [(5)] have previously demonstrated that on 300 series stainless steels "........The cracking with chloride contamination is rapid only near the dewpoint and it is slow at 20°C superheat. At much higher superheat values it may not occur.........."

Because of the form of the deposit, the effect of the mixed heavy metal salts deposited on the sheaths and exposed in the CL-1 facility at 1100°F and 1300°F in oxygenated steam was mainly on the character of the scale. The accelerated tests at elevated temperature in air with an "unlimited" salt reservoir produced large amounts of loose surface scale with but minor intergranular attack. No evidence of excessive surface attack has been observed to date on SADE elements.

It can be postulated that, depending upon the ratios of the various chloride salts on the sensitized superheat sheaths, the failures can be either completely intergranular chemical attack, chloride stress corrosion cracking or a combination of both. The presence of moisture is a requisite in any case.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of the Corrosion Engineering Group who operated the CL-1 superheat facility; A. E. Pickett, who performed much of the metallography; C. N. Spalaris, who provided expert counseling throughout the program; and M. D. Fitzsimmons, who designed all special test components required.

APPENDIX

SALT ATTACK TESTING

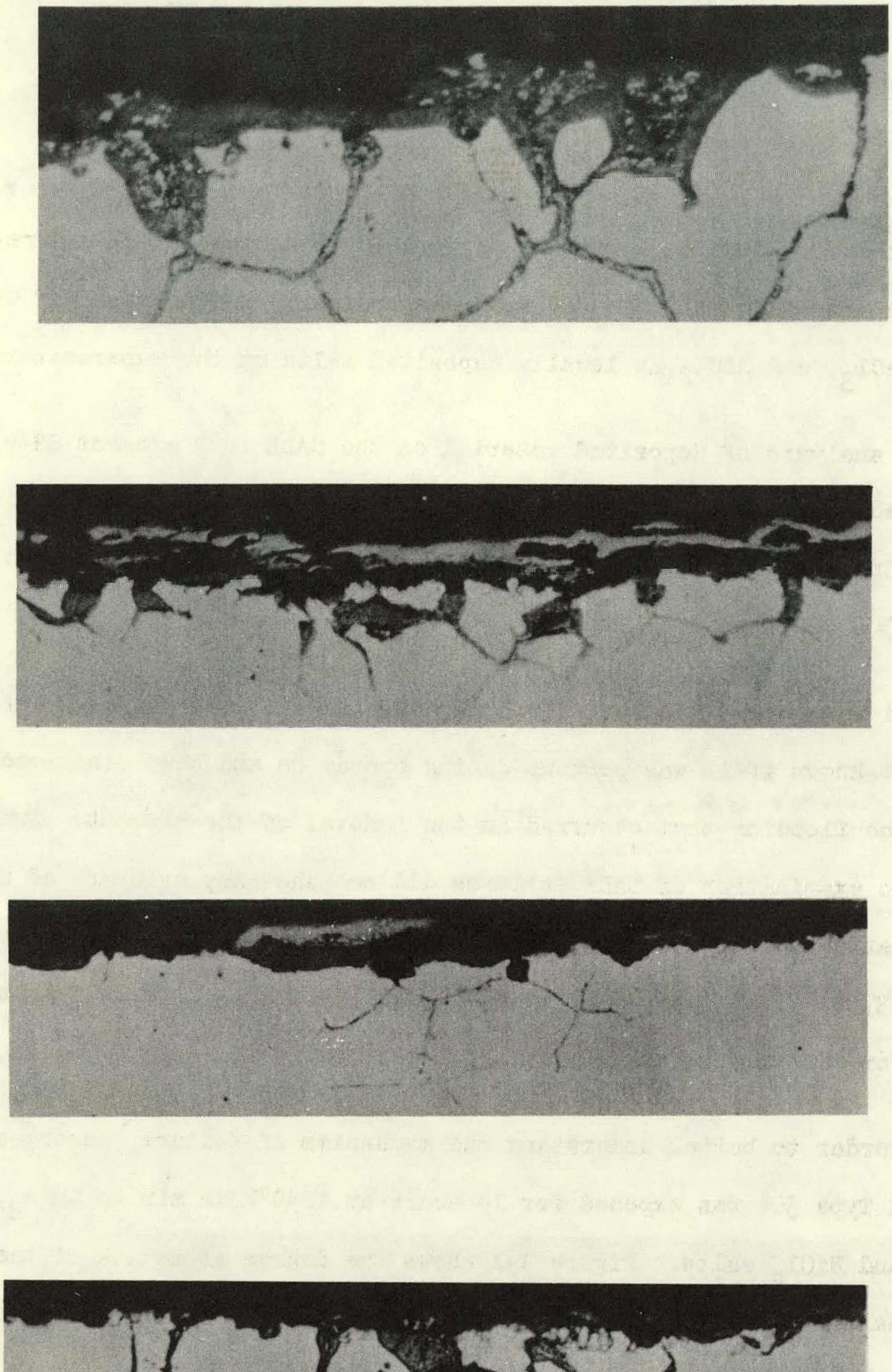
In the work done on corrosion of Type 304 stainless steel and reported in GEAP 3779 (1), the XRD analysis indicated the presence of $CrCl_3$, $CuCl_2$, $FeCl_3$, and $NiCl_2$ as locally deposited salts on the superheaters.

XRD analysis of deposited material on the SADE fuel element SH-4 also identified the lines as closely fitting the chlorides of Cu, Ni, Cr, and Fe (4). Chemical analyses of deposited material from the same element reported $>$ 9,000 ppm of chloride.

Sodium chloride was not identified in either of the above XRD analyses. It is not known if it was present during operation and then dissolved during the flooding that occurred in the removal of the element. The metallographic examination of SADE failures did not show any evidence of unusual surface attack. The attack in the case of the first failure, as reported in GEAP 3796 (2), was intergranular and spread over a wider area than seemed normal for chloride stress corrosion.

In order to better understand the mechanism of failure, unstressed, annealed Type 304 was exposed for 14 hours at 1250°F in air to $CuCl_2$, $FeCl_3$, $CrCl_3$, and $NiCl_2$ salts. Figure A-1 shows the degree of attack of the different salts. They all produced considerable surface attack with the $CuCl_2$ showing the greatest degree of intergranular attack. No attempt was made to preserve the loose scale in the mounting of the specimens.

The tests were then re-run using NaCl as the salt with annealed Type 304, RA330, Hastelloy X, Type 406, and Inconel. Figure A-2 shows the degree of attack. Considerable surface attack was noted.



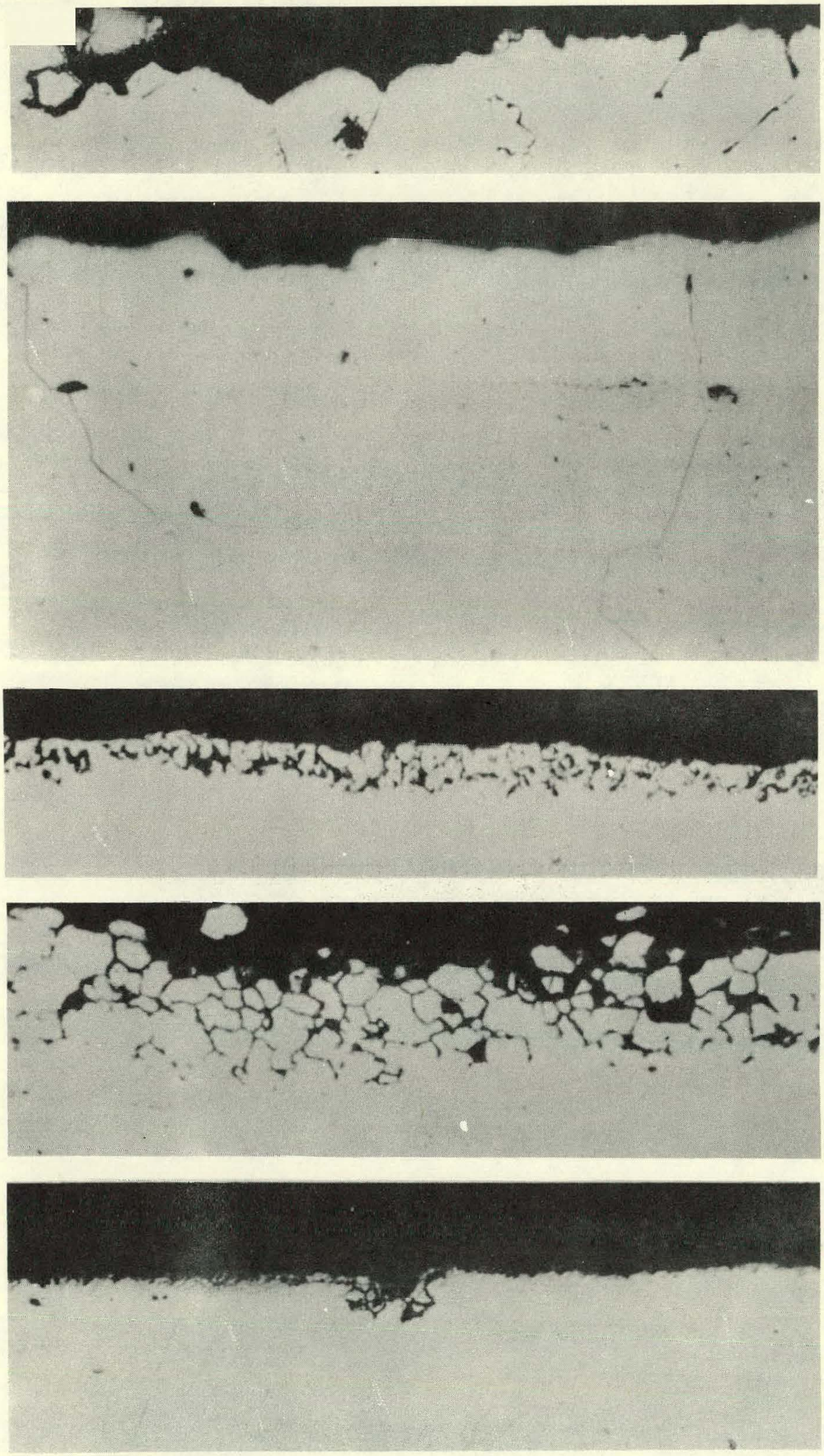
a. $CuCl_2$

b. $FeCl_3$

c. $CrCl_3$

d. $NiCl_2$

FIGURE A-1 ANNEALED TYPE 304 SS EXPOSURE TO CHLORIDE SALTS 14 HOURS, 1250 °F IN AIR. (500X)



a. Type 304 SS

b. RA 330

c. Hastelloy X

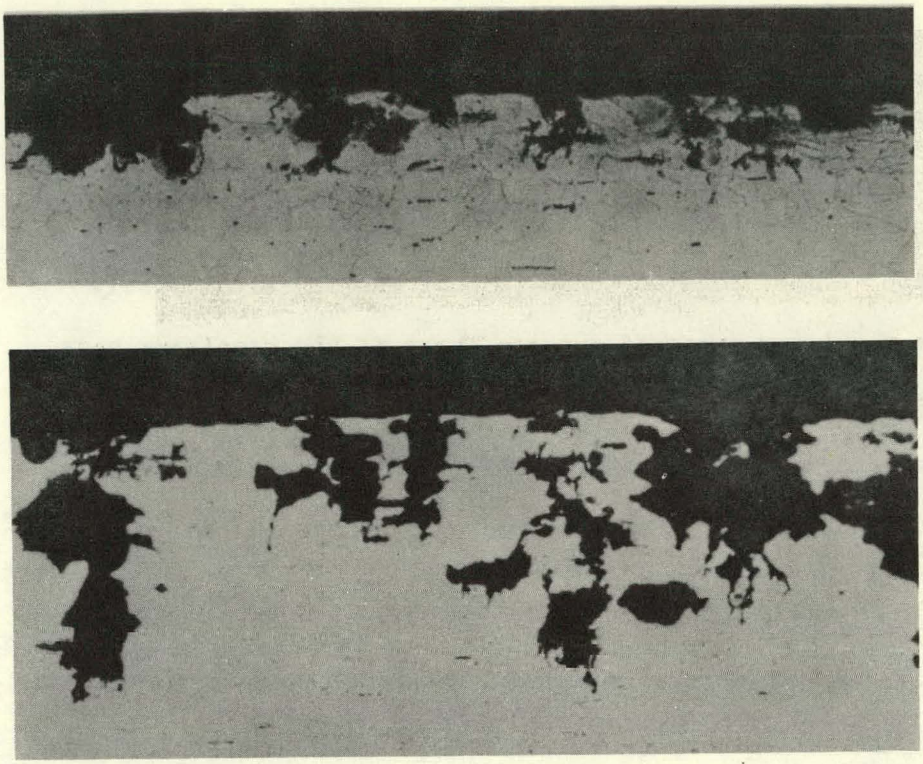
d. Type 406 SS

e. Inconel

FIGURE A-2 METAL EXPOSURES TO SODIUM CHLORIDE 14 HOURS, 1250 °F IN AIR, ANNEALED (500X)

Four U-bend specimens of Type 304 were exposed to $CuCl_2$ salts for 14 hours at 1250°F. There was consideralbe scale spalling in the areas stressed in tension, almost none on those in compression, with loosely adherent scale on the lower stressed areas. Three of the specimens had additional stress applied and were exposed to 550°F oxygenated water for 168 hours. There were no failures and metallographic examination showed no noticeable effect of the $CuCl_2$ salt corrosion products in the grain boundaries.

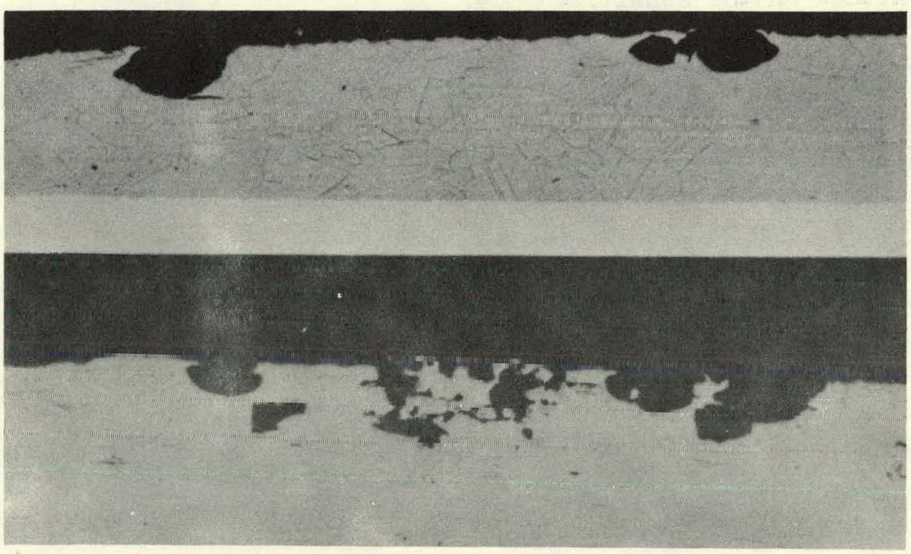
Sensitized U-bend specimens were exposed to 20,000 ppm chloride in solutions of $CuCl_2$, $CrCl_3$, $NiCl_2$, $FeCl_3$, and NaCl at 200-212°F. The specimens were examined after exposures of 30 minutes and two hours. The metallographic examinations showed no attack by the NaCl or the $NiCl_2$. Figures A-3 to A-5, magnified to 100x, show the degree of attack by the other solutions. These salts, expecially the $FeCl_3$ and $CuCl_2$ produce an intergranular chemical attack on the sensitized 304.



a. 30-minute exposure

b. 2-hour exposure

FIGURE A-3 SENSITIZED TYPE 304 SS U-BEND, EXPOSED TO CUPRIC CHLORIDE SOLUTION, 200-212 °F, 20,000 ppm CHLORIDE (100X)



a. 30-minute exposure

b. 2-hour exposure

FIGURE A-4 SENSITIZED TYPE 304 SS U-BEND, EXPOSED TO FERRIC CHLORIDE SOLUTION, 200-212 °F, 20,000 ppm CHLORIDE (100X)

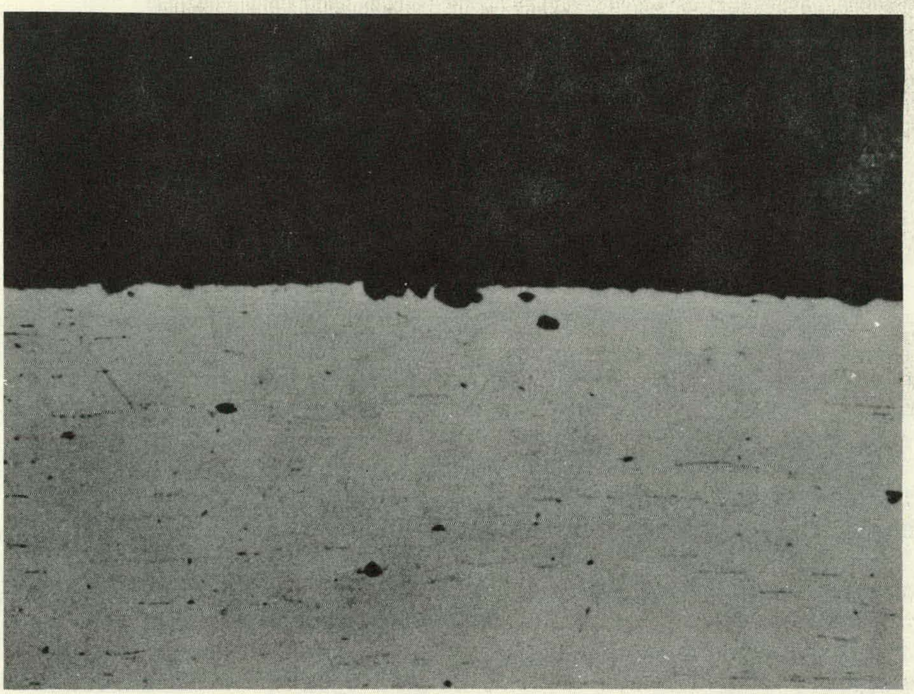


FIGURE A-5 SENSITIZED TYPE 304 SS U-BEND, EXPOSED TO CHROMIC CHLORIDE SOLUTION, 200-212 °F, 20,000 ppm CHLORIDE, 2-HOUR EXPOSURE (100X)

REFERENCES

1. Gaul, G. G., and Pearl, W. L., Corrosion of Type 304 Stainless Steel in Simulated Superheat Reactor Environment, GEAP-3779, October 16, 1961.

2. Spalaris, C. N., Boyle, R. F., Evans, T. F., and Esch, E. L., Design, Fabrication, and Irradiation of Superheat Fuel Element SH-4B in VBWR. GEAP-3796, September 1, 1961.

3. Fitzsimmons, M. D., Pearl, W. L., and Siegler, M., A Simulated Superheat Reactor Corrosion Facility, GEAP-3778, August 14, 1961.

4. Pennington, R. T., Nuclear Superheat Project Tenth Quarterly Progress Report, October-December 1961, GEAP-4024.

5. Edeleanu, C., and Snowden, P. P., Stress Corrosion of Austenitic Stainless Steels in Steam and Hot Water Systems, Journal of Iron and Steel Institute, 186: 406-422, 1957.