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General Electric Company
KNOLLS ATOMIC POWER LABORATORY
Schenectady, New York

KAPL-M-GHB-1
Chemistry-General

Results of Thermal Cycling Stress Corrosion Tests of
Type-347 Stainless Steel in 500°F pH 10-11
Lithium Hydroxide

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January 8, 1959

CG Lindquist
Authorized Classifier

1/16/59
Date

*Operated for the
U.S. Atomic Energy Commission
by the
General Electric Company
Contract No. W-31-109 Eng-52

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Results of Thermal Cycling Stress Corrosion Tests of
Type-347 Stainless Steel in 500 F pH 10-11
Lithium Hydroxide.

G. H. Borrmann
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Summary.

This report describes the results of a one-month thermal cycling corrosion test of three stressed T-347 stainless bolts exposed to 500°F pH 10-11 lithium hydroxide. The bolts were heated to temperatures of 363°F, 671°F, and 700°F to produce boiling. Also, tests were made to evaluate corrosion of stressed T-347 and T-304 stainless steel under conditions of water leakage to the atmosphere using a Schroeder Embrittlement Detector.

In the bolt test, uniform black corrosion films occurred. There was no evidence of accelerated corrosion. Some small fissures were found by metallographic examination in the roots of some threads. No lithium hydroxide or other deposits occurred on the heated surfaces.

No cracking of a T-347 steel embrittlement specimen occurred in two months' exposure. No unusual corrosion of the T-304 stainless steel specimen occurred in one week of exposure to leakage.

Introduction.

D1G primary coolant water will be maintained at an elevated pH to minimize corrosion of system materials and to decrease the amount of transportable corrosion product. Lithium hydroxide will be used to raise the water pH to 9.5-10.5. Under normal conditions, no corrosion difficulties are anticipated because the hydroxide solution will be dilute. In some areas of the primary system, however, there is concern over the possibility of experiencing accelerated corrosion or

stress corrosion cracking of austenitic stainless steel due to concentration of the lithium hydroxide. The concentrating mechanisms which are of most concern are concentration by boiling in heated crevices and concentration and deposit buildup due to leakage to the atmosphere.

To study the effect of these local concentrating mechanisms on T-347 and T-304 stainless steel, corrosion tests were made which simulated the two types of concentrating conditions. Tests to evaluate solution concentration in heated crevices were conducted with three threaded bolt assemblies which were thermally cycled to various temperatures higher than the bulk water temperature to produce boiling. Concentration by leakage was evaluated with a Schroeder embrittlement detector. This device, used conventionally in the boiler industry to detect boiler water conditions conducive to caustic embrittlement, exposes a stressed specimen to a small leakage of water from the system to the atmosphere. As the water flashes to steam solids are deposited and accumulate on the surface of the test specimen.

It is the purpose of this report to describe the details of the thermal cycling tests and to present the results of examination of the test specimens for accelerated corrosion and stress corrosion cracking after four weeks' exposure. The results of similar tests conducted under steady-state conditions are reported in reference 1.

Description of Test Facility.

Tests of both types were conducted in the TF-20 carbon steel loop. A schematic diagram of the components pertinent to the tests described is shown in Figure 1. The loop is constructed of one-inch ASTM A-106 carbon steel pipe and has a water capacity of about twenty gallons. Water is recirculated at the rate of 16 gallons per minute by a canned rotor pump. A pressurizer containing immersion heaters is connected to the main loop at the pump suction and provides surge space and maintains the proper pressure during operation. Main loop heat

is supplied by immersion heaters. Purification and treatment of the bulk water is accomplished by bypassing about 0.5% of the main flow through a cooler and a column containing deionizing resin.

Throughout the test, the loop water temperature was maintained at approximately 500°F and at a pressure of 2000 psig. The pH was controlled in the range of pH 10 to 11 with Rohm and Haas Amberlite mixed bed resin No. XE-154. This is a lithium-hydroxyl form resin obtained by mixing cation resin No. XE-78 and anion resin No. XE-163.

A dissolved hydrogen content of 25 to 50 cc/liter was maintained by periodic additions of hydrogen contained in a pressurized cylinder. Specific resistance and pH measurements of the water were taken daily.

Description of Test Sections: Threaded Bolt Assembly.

A diagram of the threaded bolt assembly test section is shown in Figure 2*. This was constructed from carbon steel and consisted of two 1-inch flanges (2500 psi) welded to 1-inch x 2-inch reducers and three 2-inch straight tees. The threaded blocks which contained the bolt specimens were made from type-347 stainless steel. The blocks were 3.5 inches long by 2.4 inches diameter with a 1-inch, 8-threaded hole. The length of the threads from the top of the block was 1.75 inches. The remainder was reamed to a 1-inch diameter to provide a 0.082-inch annulus between the block and the shank of the bolt. The measured volume of this annulus was approximately 8 ml. The blocks were welded to the carbon steel tees with INCO-A welding rod.

After tightening the bolts into the blocks, a stainless steel seal-weld was made around the bolt head. A thermocouple tube (3/16-inch O.D. x 1/8-inch I.D. x 2.85 inches long) was welded into each bolt-block assembly. The thermocouple tube extended into the threads of each bolt between the bolt and block.

*The test of reactor materials will be reported separately by DLG Core Materials.

Each block was wound with nichrome heating wire to serve as an auxiliary heater. The heat input was controlled by adjustment of Variacs in each heating circuit and Brown Pyrovane temperature controllers.

Bolt Specimens.

The bolts used in the test were made from type-3 $\frac{1}{2}$ 7 stainless steel. These were 3.6-inch long bolts of 1-inch diameter (8 threads per inch) with a total of 12 threads ($\sim 1\frac{1}{2}$ inches). The threads were ground to better than a 32 rms microinch finish with rounded roots and crests. A 0.44-inch diameter x 3.0-inch long hole was drilled in the center of each bolt to contain a specially designed immersion heater. The heater extended about 1.0-inch (9 threads) into the threaded region of the bolt. The annulus between the root of the threads on the bolt and the crest of the threads in the blocks measured approximately 0.025-inch which was sufficient to allow entry of loop water.

The bolts were tightened into the blocks to produce a strain of 0.66×10^{-3} in/in which corresponded to a nominal stress of 20,000 psi. The elongation of the bolts was measured by dial gauges attached to the top of the bolt head and into the hole in the bolt. The thermocouple tube was installed after the bolts were tightened into the blocks.

Bolt Heaters.

The immersion type heater used in the bolts was fabricated from nichrome V heating wire supported in fired Lavite insulators. The heaters were 3 inches long x 0.425 inches diameter and consisted of four 0.120-inch diameter x 3-inch long spiral coils in parallel. The total wire length in each spiral was approximately 2 feet long and provided a cold resistance of 6 ohms. The four parallel heaters had a combined cold resistance of 1.5 ohms. During the heating cycle these were operated at approximately 110 watts.

Embrittlement Detectors.

A diagram of a carbon steel embrittlement detector is shown in Figure 3. The location of these blocks in the test loop is shown in Figure 1. The test specimens were type-347 and T-304 stainless steel. The estimated average rate of leakage during test was slightly less than one gallon per day. The embrittlement detector specimens operated at approximately 475°F.

Procedure.

Before the start of the test run, an extensive clean-up operation was performed on the loop to eliminate possible interfering substances. This operation was accomplished by means of water flushes and a deionization column. Throughout this operation, spectrographic analysis, pH, and conductivity measurements were made. The analysis of the water at the end of this operation is given in Table I.

Following the clean-up operation, the test section was installed and the loop was evacuated to 29 inches Hg to eliminate air from the threaded portions of the bolt crevices. The water used for this filling operation as well as all subsequent make-up additions was steam-condensate which was allowed to cool and then passed through deoxygenating and deionizing resin columns. After filling the loop, the water was heated to boiling at atmospheric pressure and the system vented at the pressurizer to reduce the dissolved nitrogen content of the water which was not removed by the deoxygenating resin. Venting was also performed at operating temperature and pressure. The pH of the water was regulated by continuous bypass of loop water through the lithium hydroxide resin column. After making H₂ additions, the water was sampled periodically for hydrogen, oxygen, chloride, lithium, calcium, and carbonate content. During the test run, a leaking valve necessitated shutdown and exposure of the test section to air for about six days, while the valve was replaced. The same startup procedure was employed to resume the tests.

Bolt Test.

The cartridge heaters in the bolts were turned on and allowed to reach an equilibrium temperature. These heaters raised the bolts to within 50 to 90°F of the desired operating temperatures. The auxiliary external heaters were then turned on and a temperature profile along the length of the thermocouple tubes was taken. This latter task was accomplished by extracting the thermocouple in small increments and measuring the temperatures with a Leeds and Northrup potentiometer. The temperature profiles each displayed a maximum. The external heaters were then adjusted so that these maxima were at the following temperatures.

Bolt No. 1	371°C	(700°F)
Bolt No. 2	336°C	(636°F)
Bolt No. 3	355°C	(671°F)

Thermal cycling was achieved by turning off both the cartridge heaters and the auxiliary external heaters and allowing the bolts to cool to an equilibrium temperature. There were three cycles during each week. For two of these the heaters were off for twenty-four hours; for the other the cooling period was of eight hours' duration.

Embrittlement Detector Test.

A T-347 stainless steel specimen tested one month in 500°F pH 10 lithium hydroxide solution in a previous test (Reference 1) was continued in this series of tests in the lower block. An annealed T-304 stainless steel specimen was tested for one month in the upper block.

The leak rate on the embrittlement detectors was adjusted by loosening the clamping nuts. The leak was adjusted until just visible by condensation of steam on a cold mirror. Tension was applied to the test specimens by tightening the adjusting screw about 1/6th turn. Once during the test, the leak in the lower specimen stopped and required readjustment. The leak in the upper test

specimen (T-304) required continual adjustment during the first week. Thereafter, it was not possible to maintain a leak in this specimen.

Specimen Examination.

Following test, the bolt-block assemblies were ground off at the weld joining the blocks to the tees. Each assembly was then cut in half lengthwise and the bolts removed from the blocks by cutting off above the seal weld. After test, each assembly was examined microscopically (36 X) for evidence of deposits in the crevices. The corrosion products were removed by electrolytic descaling and the specimens re-examined microscopically for cracks. Each bolt was again cut lengthwise and sectioned for metallographic examination. Four sections were cut from each bolt, including portions of the bolt shank as well as the threaded area. These sections were examined at magnifications up to 750 X for cracks or accelerated corrosion.

The embrittlement detector specimens were removed and examined microscopically for cracks. A portion of the lower (T-347) detector specimen was sectioned for metallographic examination at magnifications up to 750 X. The remainder of this specimen was then bent about 1/4-inch in the region where deposits were located to open any cracks present. The upper detector specimen was also bent in this manner and both were examined microscopically.

Results.

Table I summarizes the water chemistry conditions maintained throughout the test. The temperature profile measurements made on the bolt assemblies are listed in Table II.

Bolt Conditions.

All three bolts had a uniform coating of thick black corrosion product over the entire surface. There were no deposits found on any of the threads. Some areas of the threads appeared to be somewhat roughened by corrosion. The upper photo in Figure 4 illustrates some of the attack found on the thread. The

estimated depth of attack is approximately 0.001-inch. Small fissures can also be seen originating in the roots of the threads. These are approximately 0.010-inch long.

Crack Examination.

Following the removal of corrosion product by electrolytic descaling, the bolts were examined microscopically for evidence of cracks. Figure 4 shows a photomicrograph representative of the fissures observed in the roots of the threads. No other cracks were found.

Embrittlement Specimen.

The lower embrittlement detector specimen of T-347 stainless steel contained a very small amount (<10 mg) of a hard, white crystalline deposit at the end of test. The region surrounding the deposit was discolored by a blue-black corrosion film. Microscopic and metallographic examination at magnifications of up to 750 X showed that no cracks were present. There did not appear to be any excessive corrosion on the surface of this specimen. After bending, microscopic examination verified the absence of cracks.

X-ray diffraction analysis of the deposit on this specimen identified it as magnesium hydroxide. No X-ray diffraction pattern for lithium hydroxide or lithium carbonate was evident.

The lower embrittlement detector specimen of T-304 stainless steel, which stopped leaking after one week, contained no deposit. The specimen was only slightly discolored. Microscopic examination showed no cracks both before and after bending.

Discussion.

The fissures found at the thread root all followed the same pattern. During metallographic examination it was evident that the grain structure around each of these fissures was elongated in the direction of the fissure. All the fissures terminated at the end of the elongated grains. This indicates that

the areas around these fissures were subjected to considerable cold-work, possibly during thread grinding. It is difficult to state definitely whether these fissures occurred during machining or whether they are caustic stress corrosion cracks. Similar fissures were not observed in bolt specimens used in previous tests.

The uniform corrosion film found in this test differed from that observed on bolt specimens of the previous test. This may be due to the effect of thermal cycling, or it may be due to the fact that the control temperatures in this test were measured at the hottest point on the threads. These made the bolt temperatures roughly $35-60^{\circ}\text{C}$ ($60-110^{\circ}\text{F}$) lower than the corresponding bolt temperature in the previous test.

The absence of a lithium hydroxide deposit on the bolts indicates that either no deposition occurred or that it may have redissolved during the cooling portion of the thermal cycles. Although no lithium hydroxide was found in the deposit on the embrittlement detector specimen, it is also possible here that deposition did occur but that all the lithium dissolved when the water was cooled.

The water chemistry data summarized in Table I show that throughout most of the tests the water conditions were within the limits specified. The data show that very close water chemistry control was possible. The pH generally stayed near the lower specified limit with an average pH of 10.38. The continuous flow through the lithium hydroxide resin did not result in a pH greater than 10.5. This indicates that very little dissolved substances were available for exchange in this test.

The lithium content of the loop water calculated from pH measurement agreed quite closely with the lithium content determined by chemical analysis. In general, the calculated lithium content averaged about 0.2 ppm lithium less than the measured lithium.

Very good agreement (except for 7/28/58) was obtained between the measured resistivity and resistivity calculated from the measured pH assuming pure lithium hydroxide solution. This good agreement indicates that the main dissolved constituent was lithium hydroxide.

Throughout the test the chloride, oxygen, calcium, and carbonate contents were below the maximum specified amounts.

Conclusions.

1. The results of these tests indicate that short-time exposure of stressed T-347 stainless steel bolts to boiling conditions in 500°F pH 10-11 lithium Hydroxide does not produce severe corrosion.

2. Exposure of stressed T-347 stainless steel to conditions of leakage investigated in this test does not appear to induce stress corrosion cracking.

Acknowledgment.

Loop operations were performed by P. Angerami and W. Paulus of
Experimental Engineering.

Reference.

KAPL-M-GEG-11, dated May 2, 1958, by G. E. Galonian: Results of Stress Corrosion Tests of Type-347 Stainless Steel in 500°F pH 10-11 Lithium Hydroxide.

Table I

Summary of Water Chemistry Conditions
During Second Lithium Hydroxide Stress Corrosion
Tests in TF-20 Loop.

Date Sampled	pH	Resistivity Ohm-cm	Li ⁺ ppm	CO ₃ ⁼ ppm	Cl ⁻ ppm	O ₂ ppm	H ₂ cc/liter	Ca ⁺⁺ ppm
Specified	10-11	-	0.7-7.0	< 1.0	< .5	< .1	25-50	< .2
7/1/58*	-	-	1.5	< .2	-	-	-	.01
7/7/58	10.3	24,200	1.7	< .2	< .25	.11	-	< .5
7/14/58	10.4	17,300	2.0	.3	< .1	.02	27	< .5
7/18/58	-	-	1.8	.2	-	-	-	< .1
7/23/58	10.0	43,600	.7	.4	< .1	.03	0.5	< .1
7/25/58	-	-	1.2	.2	-	-	-	< .1
7/28/58	10.5	28,000	1.5	.7	< .1	.02	77	.1
8/1/58	10.3	23,300	1.6	.3	-	-	-	.1
8/7/58	10.3	21,100	1.5	.2	.1	.01	26	.1
8/8/58	-	-	1.5	.4	-	-	-	.1
8/11/58	10.3	27,000	1.6	.3	.1	-	43.5	.1
8/15/58	-	-	1.5	.14	-	.02	-	.1
8/18/58	10.2	31,000	1.5	.2	.1	.01	51	.1

* Analysis at end of clean-up operation. Contents of other impurities from spectrographic analysis are:
Mg-.03 ppm, Al-.09 ppm, Fe-.05 ppm, all other metals-.02 ppm.

Doc 9-1

Temperature Variation Along Beated
Bolts Tested in 260°C Lithium Hydroxide.

Distance Away From End of T. C. Well (Inches)	Temperature (°C)		
	<u>Bolt No. 1</u>	<u>Bolt No. 2</u>	<u>Bolt No. 3</u>
Control Temperature	371°C	336°C	356°C
0	331	310	329
1/4	343	322	338
1/2	353	329	344
3/4	360	334	350
1	367	336	354
1 1/4	371	336	356
1 1/2	370	334	355
1 3/4	368	329	350
2	360	326	342
2 1/4	345	317	325
2 1/2	324	292	303
2 3/4	242	230	262
3	188	172	202

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SCHEMATIC DIAGRAM TF-20 LOOP

FIG. 1

HEATED CREVICE TEST SECTION ASSEMBLY

FIG. 2

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EMBRITTLEMENT DETECTOR

FIG. 3

Thread Surface of T-347 Stainless Steel Bolt No. 1
Thermally Cycled Between 400-700°F
Four Weeks in pH 10-11 Lithium Hydroxide. (25X).

Photomicrograph of Crack in Above Thread Root. (500X).

Figure 4