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DP-964

AEC RESEARCH AND DEVELOPMENT REPORT

CORROSION OF EQUIPMENT IN THE HEAVY WATER COMPONENTS TEST REACTOR

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Savannah River Laboratory

Aiken, South Carolina

Printed in USA. Price $2.00
Available from the Clearinghouse for Federal Scientific
and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia

664302

DP-964

Metals, Ceramics, and Materials
(TID-4500, 41st Ed.)

CORROSION OF EQUIPMENT IN THE HEAVY WATER COMPONENTS TEST REACTOR

by

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June 1965

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CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

ABSTRACT

The corrosion experience at the Heavy Water Components Test Reactor (HWCTR) is evaluated after three years of service. Within the moderator-coolant system, corrosion caused no operating problems or equipment failures. Adherent black oxide covered all mild steel surfaces in the moderator-coolant system, and no significant pitting was observed.

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CORROSION OF EQUIPMENT IN THE HEAVY WATER COMPONENTS TEST REACTOR

INTRODUCTION

The Heavy Water Components Test Reactor (HWCTR) was operated for a three-year period from 1962 to 1964 to test candidate fuel elements for heavy water moderated and cooled power reactor systems. Operation was terminated on December 1, 1964, in keeping with an AEC decision to emphasize the organic-cooled reactor concept for its principal effort in heavy-water-moderated power reactors. Shutdown and lay-away of the HWCTR permitted thorough examination of the equipment.

One of the secondary objectives of the HWCTR program was to evaluate mild steel as a construction material for power reactors. Also, the corrosion performance and wear of other metals and components were to be evaluated. This report describes the observed corrosion and wear, as well as the procedures and techniques that were used to minimize and measure corrosion, during the period of operation. A previous report covered the preoperational period,(1) during which time a magnetite film was formed on the mild steel surfaces in the primary coolant (D_2O) system.

SUMMARY

The performance of equipment and construction materials in the HWCTR was evaluated by inspecting equipment, by analyzing the water in the primary system for corrosion products, and by inspecting corrosion coupons that were exposed inside the moderator-coolant system.

Mild steel components within the moderator-coolant system were always covered uniformly with an adherent black oxide, and experienced no measurable pitting. Based on corrosion coupon examinations, the corrosion rate (descaled weight loss) and the rate of iron release to the D_2O were very small after the first six months of exposure. No operating problems were experienced because of particulate matter in the D_2O. The purification system was operated satisfactorily without a prefilter, and activity buildup at low-flow areas and on piping caused only minor increases in radiation.

The performance of all stainless steel components, including 17-4 PH steel, was excellent. No cracks or failures occurred, and the measured corrosion rates were low.

There were no corrosion problems with Zircaloy; however, three safety rod guide tubes cracked after approximately 6000 hours of exposure in the core of the reactor. The failures were caused by high stresses (tensile and residual) and the presence of unfavorably oriented zirconium hydride.

The chemistry of the D_2O moderator-coolant was particularly adapted to the corrosion problems of mild steel. The water was maintained alkaline with lithium hydroxide at pD 10.7 ±0.5. The dissolved oxygen was kept low (<5 ppb) during nuclear operation by maintaining excess dissolved deuterium.

The secondary cooling water was treated entirely by chemical addition; that is, without deionization or deaeration. Catalyzed sodium sulfite was added to scavenge oxygen, trisodium phosphate was added for pH control, and a solution of the sodium salt of "Versene"* was added to prevent scale formation on heat transfer surfaces. Performance of mild steel surfaces was good as long as chemical controls were properly maintained. However, adequate scavenging of oxygen from the secondary cooling water was lost for several months early in 1964 because of inferior catalyzed sodium sulfite. Severe pitting (up to 85 mils) occurred on the steam generator tubes, which had minimum wall thicknesses of 109 mils; four tubes failed. An examination of one of the failed tubes revealed that this failure was caused by crevice corrosion beneath a support baffle.

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*Trademark of the Dow Chemical Company.

DISCUSSION

DESCRIPTION OF FACILITIES

The HWCTR is a pressurized reactor that is moderated and cooled with heavy water.(2) The design pressure and temperature are 1500 psi and 315°C. The maximum design power is approximately 70 MW (thermal). There are 12 test fuel positions and 24 driver fuel positions. Two of the test fuel positions were designed as isolated coolant loops (ICLs) for testing fuel under a variety of conditions. The flow diagram for the primary coolant and pressurizing gas is presented in Figure 1.

As shown in Table I, mild steels are used for all high pressure system pipe, steam generators, main system purge cooler, gas pipe, main storage tank, and some of the low pressure pipe. All secondary coolant equipment is mild steel except the heat exchangers which are either stainless or "Inconel."

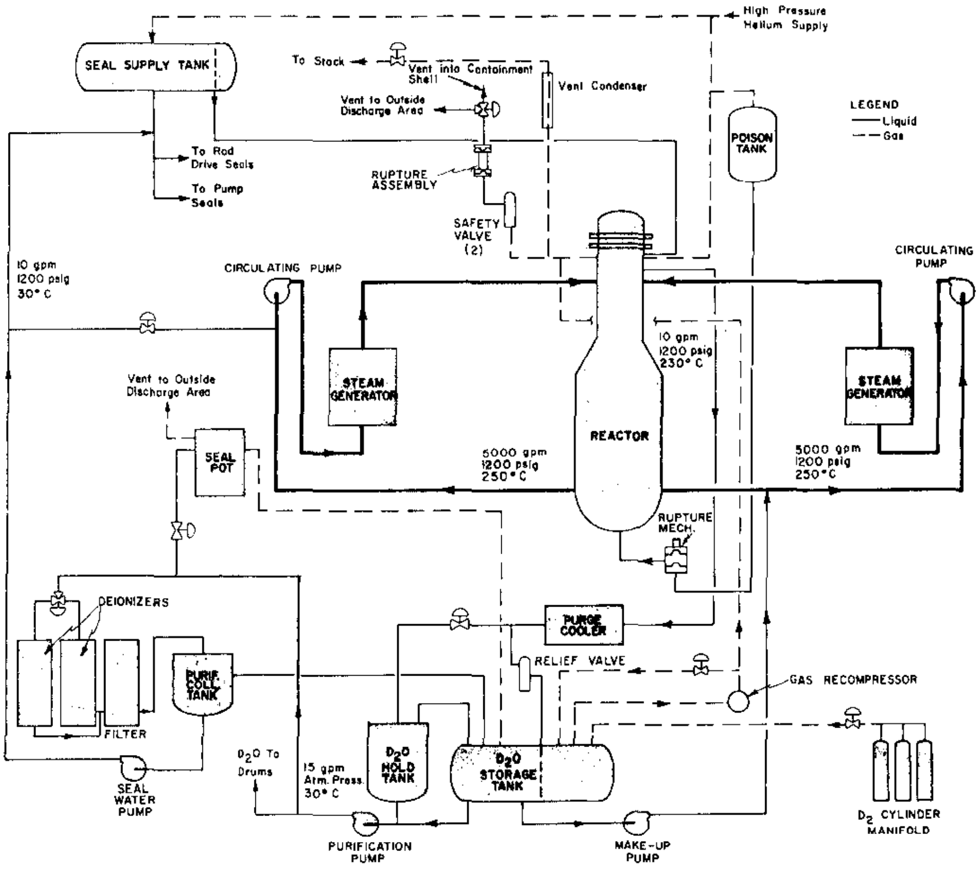

FIG. 1 MAIN COOLANT SYSTEM

TABLE I

Metals of Principal Interest in HWCTR Corrosion Studies

Metal	Use
304 SS	Reactor vessel lining, pumps, hold tank, filters deionizer, purification collection tank, seal head tanks, ICL heat exchanger shell.
316 SS	ICL pipe, surge tanks, purification pumps, ICL head tanks, ICL heat exchanger nozzles.
ASTM A-106 "B" Mild Steel	Main system pipe.
ASTM A-212 "B" Mild Steel	Reactor vessel (lined with 304 SS, 0.25 inch thick), steam generator shells.
"Inconel"(a)	ICL heat exchanger tubes and manifolds.
Zircaloy-2, -4	Fuel cladding and housings, instrument and housings, ICL pressure tube.
ASME-SA-210 Mild Steel	Steam generator tubes, purge cooler tubes.
17-4 PH SS	Control and safety rod drives, main and ICL pump shafts, impellers, casing wear rings.
ASME-SA-285	Main storage tank.
304 SS-1% boron	Control rods, safety rods.

(a) Trademark of International Nickel Company.

Of particular interest is the fact that the tubes in the steam generators and main purge coolers are mild steel. They are 3/4-inch tubes with 0.109-inch minimum wall thickness.

In the reactor vessel no mild steel is exposed to moderator. All housings, fuel sheaths, and one ICL pressure tube are Zircaloy-2. The second ICL pressure tube is Zircaloy-4. The control and safety rods, and the target (burnable poison) components of the driver fuel assemblies are boronated stainless steel. The other equipment in the vessel (guide plates, thermal shields) is 304 stainless steel.

CHEMICAL CONTROL OF ENVIRONMENT

Primary Coolant

To minimize corrosion of the mild steel, the D_2O moderator-coolant was maintained alkaline at pD 10.7 ±0.5 with lithium hydroxide. By using a mixed-resin Li^+-OD^- ion exchanger in the purification system, the rate of pD change was slow and positive. A typical rate of conductivity increase was 0.35 micromhos/(cm)(month), which corresponds to a pD increase of approximately 0.25 pD unit/month. When necessary, the pD was lowered by diverting the purification stream through a D^+-OD^- mixed-resin deionizer.

Careful control of dissolved oxygen was essential because of the susceptibility of the mild steel to general corrosion and pitting. Deuterium gas was added to the pressurizing gas (helium), and controlled at 1.5 to 3.0% by volume, which gave a dissolved deuterium concentration of 10 to 20 std cc/kg of D_2O in the high pressure system. The dissolved deuterium combined radiolytically with dissolved oxygen to give a dissolved oxygen concentration of less than 0.004 std cc/kg, or approximately 5 ppb.

Figure 2 shows a gas flow diagram and typical operating conditions and gas concentrations. The gas that was dissolved in the reactor purge stream was evolved into the gas space in the hold tank when the water was cooled and depressurized. This gas flowed through a metering orifice to the storage tank, from which it was returned to the high pressure gas space over the reactor core.

A gas chromatograph was used to determine the concentrations by volume of the D_2, O_2, and N_2 in the gas that was evolved into the hold tank from the reactor purge stream. The total evolved gas flow was measured and was recorded in the control room, as was the D_2O purge flow. The concentrations of dissolved D_2, N_2, and O_2 in std cc/kg of D_2O were calculated from these three measurements.

The reactor operated at power approximately 45% of the time since the initial power operation in August 1962. During much of the time that the reactor was shut down it was necessary to have the reactor head removed. Some air dissolved in moderator during these occasions, even though attempts were made to minimize exposure to air. For this reason, the mild steel was exposed to more severe conditions than would be expected in a power reactor operating with higher on-line efficiency.

Stainless steel was protected against chloride stress corrosion by careful control of the chloride contents of the moderator and of such auxiliary materials as lubricants, gaskets, O-rings, insulation, cleaning agents, and filters.(1) The moderator chloride analyses, made three times per week with a Technicon "Autoanalyzer", showed concentrations between 5 and 25 ppb.

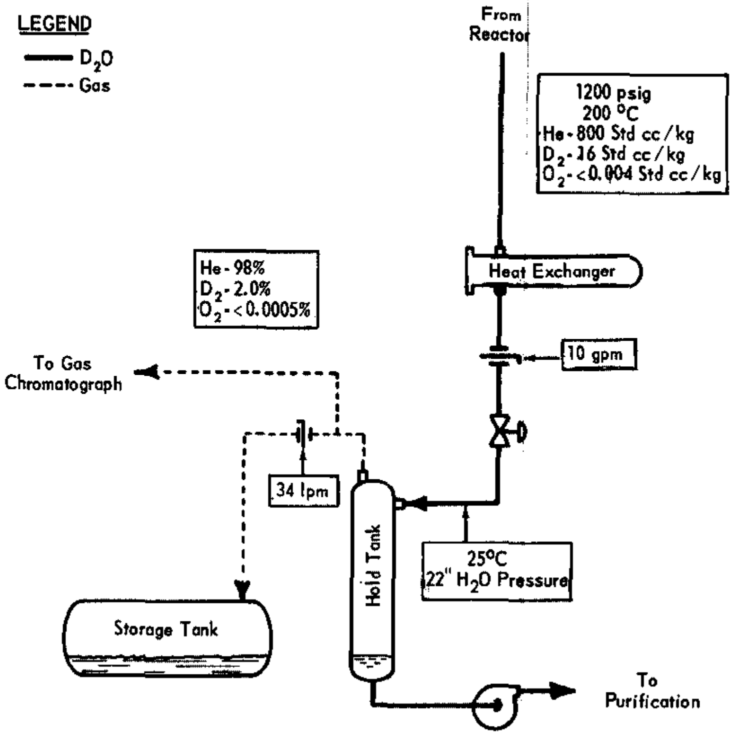

FIG. 2 REACTOR PURGE AND GAS FLOW SCHEMATIC SHOWING TYPICAL CONDITIONS

Secondary Coolant

The secondary coolant system was a once-through system. Chemically treated well water served as coolant for miscellaneous heat exchangers and as boiler feed makeup for steam generation. The steam and blowdown were discharged to the environment. Figure 3 is a simplified schematic of the secondary cooling system, showing typical concentrations of chemicals.

The well water was characterized by low solids, low pH, high carbon dioxide, and high dissolved oxygen content. Average analyses of well water are shown in Table II.

TABLE II

HWCTR Wells - Average Analyses

Determination	Concentration Well 58	Concentration Well 60	Concentration Well 67
pH	4.6	4.24	5.3
Free mineral acidity, ppm	1.9	6.3	5.3
CO_2, ppm	37.9	37.8	23.3
O_2, ppm	6.2	3.3	6.4
Hardness, ppm	2.8	2.9	3.3
Conductivity, µmho	25	55	23
Silica, ppm	8.2	8.2	5.4
Total iron, ppm	0.65	0.48	0.1
Chloride, ppm	2.3	2	-

In the HWCTR system, oxygen had to be completely removed within one minute to prevent oxygenated water from reaching process equipment.

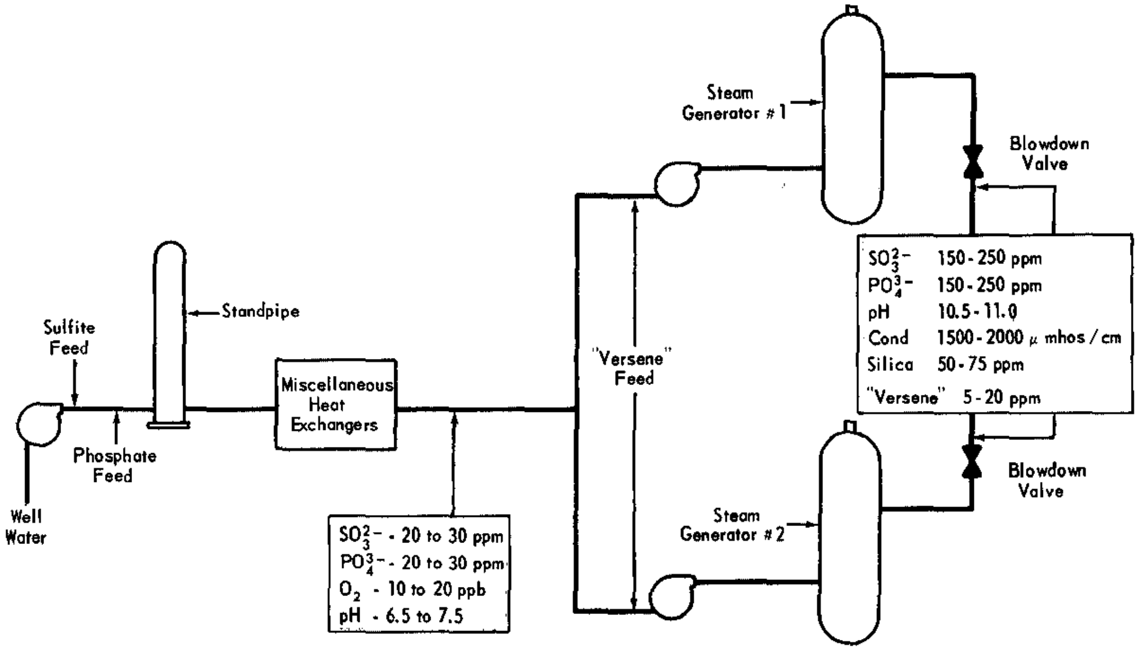

FIG. 3 COOLING WATER SYSTEM SCHEMATIC
(with typical chemical concentrations)

Treatment of the cooling water was entirely by chemical addition; that is, no deionization or deaeration was used. The basic treatment consisted of the following:

1) Sodium sulfite (catalyzed) was added for cold water reaction with dissolved oxygen.

2) Sodium phosphates were added in a "coordinated pH-phosphate control" plan to provide alkalinity for corrosion control and to prevent deposition of silica scale.

3) A chelating agent, "Versene",* was added to complex calcium and magnesium compounds to eliminate deposition of objectionable hardness scale on heat transfer surfaces.

Preliminary off-site testing of this mode of control, using small heat exchangers, indicated that it would be satisfactory. Laboratory tests, using the conventional Winkler method for the determination of dissolved oxygen, seemed to validate the assumption that the presence of residual sulfite precluded the presence of dissolved oxygen.

This system operated satisfactorily, with no evidence of oxygen corrosion pitting, until July 1964, when a tube failure occurred in one of the steam generators. Inspection of the cooling water (shell) side of the generator showed that severe pitting corrosion had occurred over the short time interval of a few months, since a recent inspection. At this time, sulfite analyses were being performed every eight hours and dissolved oxygen analyses, using the standard Winkler method, were being performed twice per month for backup protection.

A review of performance data showed that the sulfite residual in the feedwater had always been maintained greater than 10 ppm and the bimonthly analyses for dissolved oxygen had always indicated zero. However, the condition of the steel tubing clearly indicated a type of pitting characteristic of oxygen attack. Further investigation revealed that the particular brand of catalyzed sulfite that had been in use since October 1961 had been changed in early 1964. Purchase specifications for the two commercial brands of sulfite were identical. No specification of the reaction time of the sulfite with dissolved oxygen was contained in the purchase specifications.

An intensive, short-range, laboratory investigation was undertaken to determine the cause of the apparent presence of free oxygen in the feedwater, concentrating mainly on the sulfite oxygen reaction in the HWCTR well water with the two commercial sulfite products. All laboratory tests were run at room temperature. Some field tests augmented the laboratory results which indicated that the newer sulfite had indeed failed to react with all of the dissolved oxygen under the conditions of treatment.

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*Trademark of the Dow Chemical Company.

The reaction between sulfite and oxygen is catalyzed by ions of metals such as Cu, Co, Fe, Ni, and Mn, but is inhibited by materials, such as organics, that react with the catalyst or capture free radicals from the reaction chain. The two commercial sulfites used at HWCTR, denoted as Brand B for the sulfite used from October 1961 to February 1964, and Brand A for the sulfite used from February 1964 to July 1964, are special formulations that use Fe^{3+} and/or Co^{2+} as catalysts. The compositions of these products are given in Table III.

TABLE III

Sulfite Compositions
(Vendor's specifications)

	Composition, %	
	Brand B 10/61 - 2/64	Brand A 2/64 - 7/64
Sodium sulfite	91.0	91.0 min
Sodium sulfate	7.0	4.0 max
Sodium carbonate	0.85	(a)
Sodium bisulfite	0.19	(a)
Calcium sulfite	0.25	(a)
Equivalent SO_2	(a)	46.2 min
Chloride as NaCl	0.20	(a)
Ammonia as NH_4Cl	0.15	(a)
Moisture	0.20	0.2 max
Sodium phenate	0.15 max	(a)
Insoluble sulfur	0.25	(a)
Water insoluble	(a)	2.0 max
Cobalt	0.06	0.02 ±0.005
Total Fe	(a)	0.3
pH	(a)	alkaline to phenolphthalein

(a) Not included in the vendor's specifications.

Tests of the two brands of catalyzed sulfite showed a slow reaction time for Brand A. Figure 4 illustrates the two types of behavior encountered in the tests. Either the reaction time proceeded almost to completion within one minute or it required a latent period of several minutes. Other tests showed that the reaction of Brand A was affected by both the source of water and by phosphate addition but that it could be made consistently effective by addition of 0.3% Co^{2+} as a supplementary catalyst. Figure 5 illustrates the slow reaction of Brand A with HWCTR well water in the presence of 30 ppm phosphate. This curve represents conditions within HWCTR experience during the period when corrosion occurred. It was concluded that Brand A failed to remove dissolved oxygen from the water with sufficient rapidity to minimize corrosion to the steam generator.

Tests also showed that the standard Winkler method for oxygen analysis is unsatisfactory in the presence of residual sulfite. A modified Winkler method was developed in which the excess sulfite was removed by iodine as a preliminary step. Using the modified method, laboratory tests and samples taken from the HWCTR feedwater system while using Brand A sulfite showed that 2 to 5 ppm O_2 could have been in the treated feedwater going to the steam generators during the period that Brand A sulfite was used.

Based on these data, sulfite B, or sulfite A with 0.3% Co^{2+} added, was specified for use. In addition, a Hays Corporation Model 625 oxygen analyzer was installed as an independent check on the oxygen content of the feedwater. No further difficulty with water treatment occurred. The O_2 content in the feedwater indicated by the oxygen analyzer normally ranged between 0.01-0.03 ppm. Sample analyses, using the modified Winkler method, corroborated these results.

A description of the corrosion that occurred in the steam generators, and in other parts of the cooling water system, is presented in another section of this report.

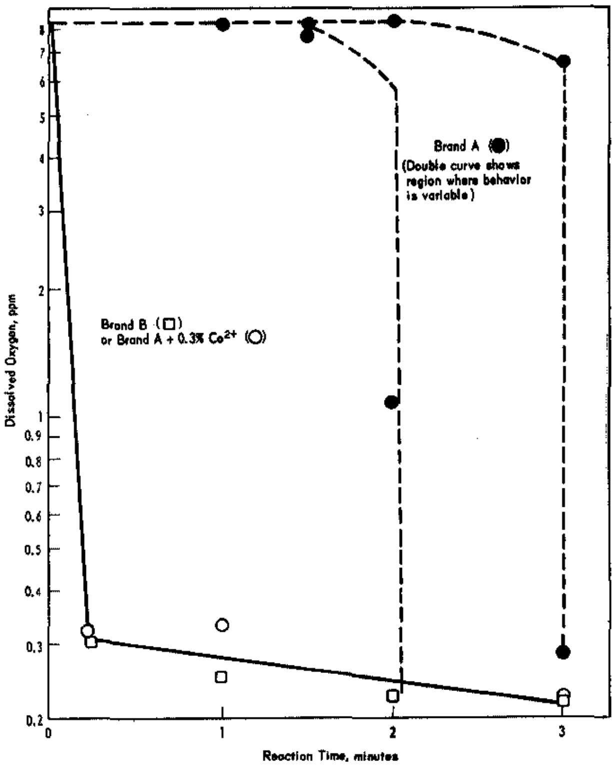


FIG. 4 RATE OF OXYGEN SCAVENGING BY CATALYZED SODIUM SULFITES IN DEIONIZED WATER

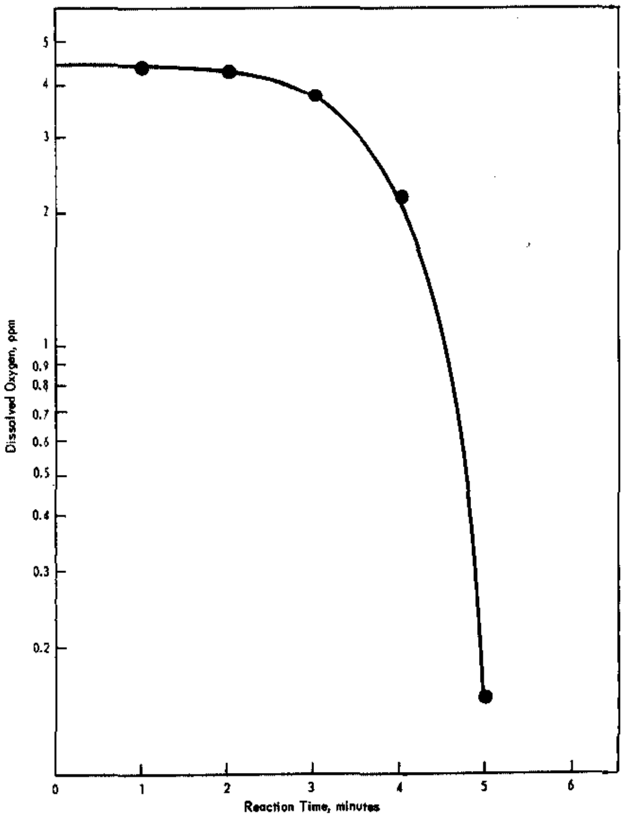


FIG. 5 OXYGEN SCAVENGING BY BRAND A SULFITE IN HWCTR WELL WATER (30 ppm PO_4^{3-} added)

MILD STEEL CORROSION

Moderator - Coolant System

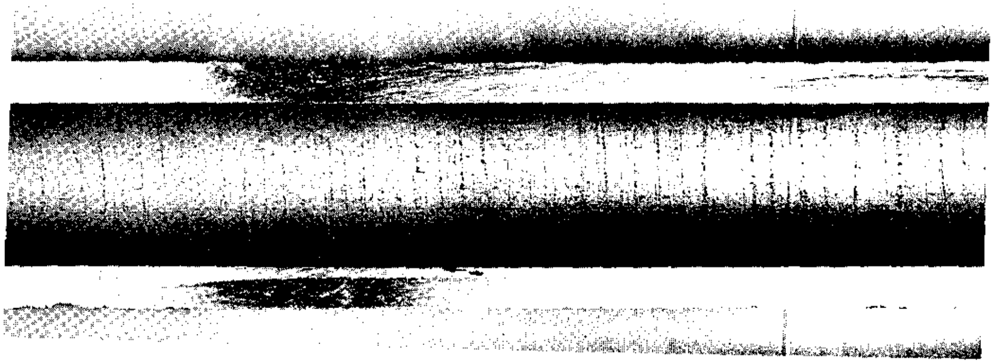
Corrosion of mild steel was monitored by inspecting corrosion coupons from the reactor (in-core and out-of-core) and storage tank, inspecting equipment, and by analyzing the moderator for corrosion products.

Numerous inspections were made of mild steel equipment and pipe, including the purge cooler heads, steam generator heads, pipe in several locations, and two sections of tube that were removed from the steam generators. Without exception, the conditions were excellent even after extended shutdowns for as long as three months, during which time considerable dissolved oxygen was in the water. All of the surfaces were covered uniformly with adherent black (magnetite) film, and showed no rusting, general corrosion, nor pitting. Figure 6 shows three views of a steam generator tube section that was removed in August 1964. The middle view shows the magnetite film, which is approximately 0.001-inch thick. The maximum corrosion penetration was also approximately 0.001-inch. Some surface roughness was present on these tubes at the time they were installed. They were rusty when received from the vendor, and were chemically cleaned before installation.(1)

Prior to initial nuclear operation, corrosion coupons were placed in the D_2O system at the following locations:

- Reactor vessel, in-core
- Reactor vessel, above core in D_2O
- Reactor vessel, at D_2O-gas interface
- Reactor vessel, in gas space
- Storage tank, in D_2O

Coupons were removed periodically and examined for weight loss, pitting, iron release to moderator-coolant, and cracking (of stressed samples). All weight losses were measured on descaled coupons. A total of 61 coupons were examined. The data on weight loss and pitting are presented in Table IV, and the weight loss data for coupons exposed to D_2O in the reactor vessel are shown in Figure 7. The period of high corrosion rates and oxide film growth apparently ended prior to 4400 hours (six months) of exposure. After 4400 hours, the corrosion rates were very low. For example, the average weight loss between 4400 and 15,240 hours of exposure was only 0.27 mg/cm^2, or 0.018 mg/cm^2 per month.



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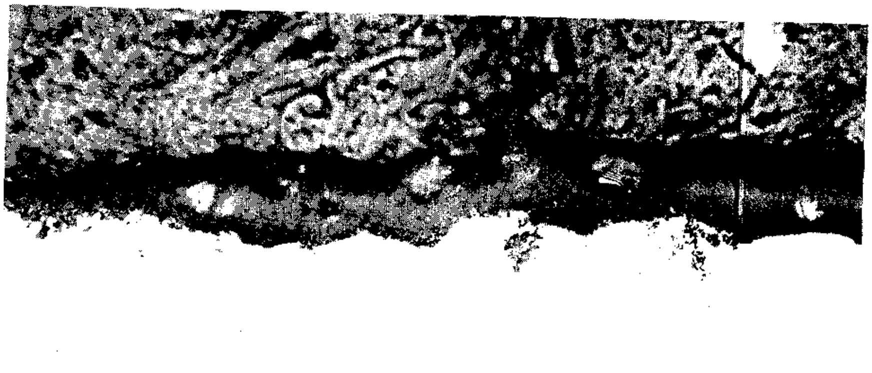
General View of Descaled Tube

2X



NEG EA23698

Before Descaling

500X

NEG EA22555

After Descaling

250X

FIG. 6 PRIMARY SIDE OF STEAM GENERATOR TUBE, AUGUST 1964

The rates of iron release to moderator are shown in Table V. During the first six months of exposure, the average release was calculated to be 0.16 mg Fe/cm^2 per month. The average "steady-state" release rate, between 6 and 33 months, was approximately 0.04 mg Fe/cm^2 per month.

Although no pitting was found on mild steel pipe, tubes, or equipment, minor pitting did occur on the corrosion coupons, as shown in Table IV. The maximum pit depths of the last coupons examined were lower than those of three previously removed sets of coupons. Two of the mild steel coupons from the last set are shown in Figure 8, along with some stainless steel specimens.

TABLE IV

Mild Steel Corrosion Coupons from Moderator Coolant

Location Where Exposed	Exposure, hours		Descaled Weight Loss,[a] mg/cm^2				Pit Depths, mils							
							A-106		A-210		A-212		A-285	
	Total	Critical	A-106	A-210	A-212	A-285	Max	Mean	Max	Mean	Max	Mean	Max	Mean
	4,400	380	3.94 (2)[b]	2.31 (2)	3.27 (2)	3.02 (2)	<0.1		<0.1		<0.1		<0.1	
In reactor, above core	9,580	3270	3.90 (3)	2.53 (3)	3.31 (2)	3.06 (2)	3.9	2.6	3.1	1.8	4.6	2.5	3.4	2.2
	12,840	4580	3.97 (2)	2.56 (2)	3.56 (2)	2.70 (2)	7.3	3.7	6.7	3.4	7.7	3.9	6.0	3.3
	15,240	5500	3.98 (2)	3.39 (2)	3.28 (2)	3.00 (2)	7.7	3.8	5.3	3.0	6.6	3.5	6.6	3.4
	23,880	9130	7.27 (1)	4.10 (1)	-	-	3.1	1.8	2.1	1.2	2.6	1.8	-	
	14,400[c]	4580	2.54 (1)	1.52 (1)	-	-	-		-		-		-	
	12,840[d]	4580	1.38 (4)	-	-	-	6.0	2.0	-		-		-	
Main storage tank	9,860[e]	-	3.24 (1)	1.06 (1)	2.70 (1)	2.42 (1)	4.0	3.1	2.3	1.9	5.9	4.2	3.9	3.3
	24,170[e]	-	3.59 (1)	1.74 (1)	2.32 (1)	0.81 (1)	5.3	2.1	4.8	1.7	2.8	1.4	1.6	0.8
In reactor core	24,100	9130	5.44 (1)	5.89 (1)	-	-	-		-		-		-	

(a) "A-" numbers give ASTM designation of steel from which mild steel coupons were made.
(b) Numbers in parentheses are number of coupons examined to obtain values shown.
(c) Exposure includes 65 days during preoperational light water tests.
(d) Stressed coupons located approximately six inches below water-gas interface in reactor.
(e) All exposure at 20-25°C and approximately 10-inches H_2O pressure.

TABLE V

Iron Release to Moderator-Coolant From Corrosion Coupons

(mg Fe/cm^2 per month)

Period	ASTM No.→	A-106	A-210	A-212	A-285	Avg
0 to 6 months		0.20 (2)	0.14 (2)	0.17 (2)	0.15 (2)	0.165
0 to 33 months		0.091 (2)	0.070 (2)	-	-	0.080
6 to 33 months[a]		0.019	0.056	-	-	0.038

(a) By difference.

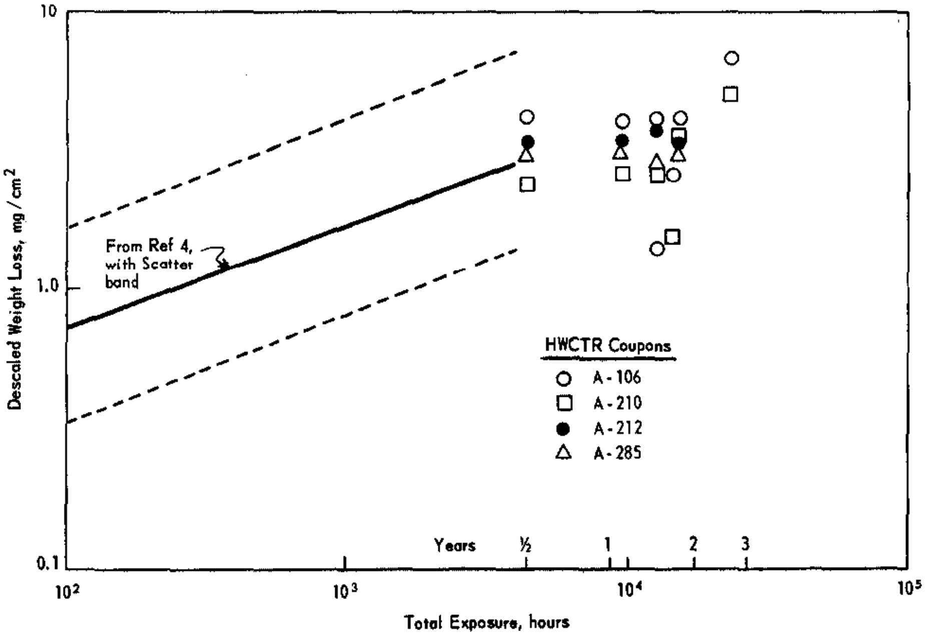


FIG. 7 WEIGHT LOSS OF DESCALED MILD STEEL COUPONS FROM MODERATOR-COOLANT

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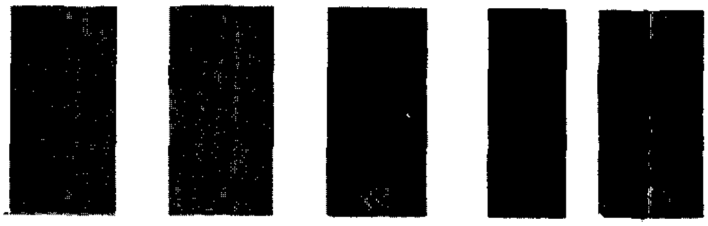
As-Removed



NEG 60826 0.67X

1 2 3 4 5

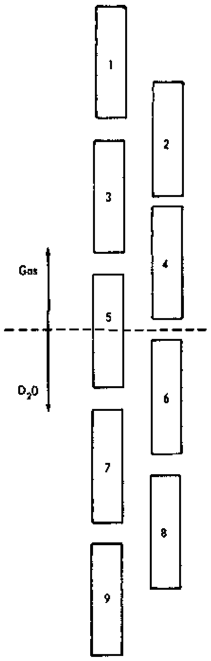
Descaled

1. A-106 Mild Steel
   Max Pit Depth = 3.0 mils
2. A-210 Mild Steel
   Max Pit Depth = 2.1 mils
3. 304 SS, Sensitized
4. 304 SS-1% Boron
5. 316 SS, Annealed

FIG. 8 CORROSION COUPONS FROM D_2O ABOVE CORE IN REACTOR
Exposure: 995 Days (23,880 hours)

Two corrosion coupons that were examined were exposed during the preoperational light-water test period and then left in the reactor for further exposure (Table IV). It may be significant that these two coupons showed less corrosion than the others that were not placed in the reactor until after the light-water test period.

One holder, containing nine stressed, mild steel (A-106) coupons, was exposed at the D_2O-gas interface in the reactor. The arrangement of the coupons and the results of the examination are shown in Figure 9. The primary purpose of this set of coupons was to determine if caustic cracking would occur on stressed mild steel surfaces where lithium hydroxide salt deposits might accumulate. No salt deposits could be seen on the coupons when they were removed, and no coupons cracked. The corrosion (descaled weight loss) of these coupons, in the D_2O, was lower than that of the other mild steel coupons, including A-106, that were exposed deeper in the D_2O for the same time period (see Table IV).



Coupons	Descaled Weight Loss, mg/cm^2	Pit Depths, mils	
		Max	Mean
1	0.87	4.3	2.1
2	1.14	7.0	1.8
3	0.97	1.9	2.1
4	0.95	2.8	1.3
5	0.95	3.9	1.7
6	1.29	4.5	2.0
7	1.40	5.0	2.0
8	1.37	5.1	2.1
9	1.46	6.0	2.1

Note: No cracks were found

FIG. 9 STRESSED MILD STEEL (A-106) COUPONS FROM D_2O - GAS INTERFACE
Exposure: 12,840 hours

Samples of circulating particulate matter ("crud") were filtered periodically from the reactor purge stream with 0.45-micron filters. These samples were analyzed to determine particulate concentration, iron content, and radionuclide activities. The analytical results are shown in Tables VI and VII. All of these samples were taken during steady power operation.

TABLE VI

Concentrations of Particulate Matter in Moderator-Coolant[(a)]

Date Sample Taken	Concentration, ppb	Percent Fe
7/24/63	85	15.6
10/16/63	68	3.4
1/11/64	89	-
1/21/64	61	3.3
6/23/64	7.3	58
6/25/64	3.4	-
11/13/64	7.6	53
11/20/64	4.8	43

(a) Samples were air dried to obtain weight.

TABLE VII

Radionuclide Activities in Particulates Filtered From Moderator-Coolant,(a) d/m/mg

Radionuclide	Date Sample Taken →	7/24/63	10/16/63	1/21/64	6/23/64	11/13/64	11/20/64
^{239}Np		-	5.4×10^{5}	2.3×10^{5}	3.3×10^{7}	4.4×10^{6}	1.3×10^{7}
^{140}Ba-La		3.5×10^{4}	1.3×10^{5}	6.8×10^{5}	3.6×10^{5}	1.9×10^{6}	6.5×10^{6}
^{51}Cr		3.8×10^{5}	3.6×10^{5}	1.8×10^{5}	3.3×10^{5}	3.0×10^{6}	4.0×10^{6}
^{60}Co		8.3×10^{4}	7.0×10^{4}	3.1×10^{4}	3.5×10^{5}	7.6×10^{5}	8.1×10^{5}
^{95}Zr-Nb		2.3×10^{5}	4.7×10^{4}	1.5×10^{5}	1.2×10^{6}	1.1×10^{6}	7.2×10^{5}
^{59}Fe		-	-	2.2×10^{4}	-	6.8×10^{5}	5.3×10^{5}
^{141}Ce		1.2×10^{4}	9.9×10^{4}	7.3×10^{4}	-	7.3×10^{5}	5.0×10^{5}
^{132}Te		-	7.7×10^{4}	-	-	2.3×10^{5}	2.7×10^{5}
^{54}Mn		-	-	-	-	2.4×10^{5}	2.1×10^{5}
^{137}Cs		-	3.9×10^{4}	-	-	2.3×10^{5}	-
^{124}Sb		-	-	-	-	1.2×10^{5}	-
^{58}Co		-	-	-	-	1.7×10^{5}	-
^{46}Sc		-	-	-	-	7.8×10^{4}	6.0×10^{4}
$^{103-106}$Ru		3.3×10^{4}	7.5×10^{4}	4.4×10^{4}	-	-	-
^{65}Zn		4.2×10^{4}	7.9×10^{3}	-	-	-	-

(a) Corrected for decay to time sample was taken.

From Table VI it is evident that the particulate concentration and iron content changed markedly between January and June 1964. During this interval the reactor was shut down for nearly three months, and for much of that time the moderator was exposed to the atmosphere. It is believed that this extended exposure to relatively high oxygen concentrations caused a more protective layer of γ-Fe_2O_3 (haghemite) to form over the magnetite film on the mild steel surfaces.(5,6) However, the oxide was not identified.

Radionuclides that deposit on surfaces of pipe and equipment cause radiation to increase from these surfaces. The rate of activity buildup is undoubtedly influenced by the concentration of particulates in the moderator-coolant and the specific activities of the long-lived radionuclides in this suspended material. Radiation measurements were made periodically at selected locations to determine activity buildup. Typical results are shown in Table VIII.

TABLE VIII

	Typical Radiation From Pipe, mr/hr at 3"					
Location	12/62	1/63	6/63	5/64	10/64	12/64
10" pipe at main pump suction	12	16	17	25	39	30
10" valve body in reactor inlet pipe	5	10	11	10	22	30

Oxide films from mild steel coupons that were exposed in the reactor D_2O (above core) were dissolved and analyzed for radionuclides to determine sources of the radiation. Results are shown in Table IX. These coupons were installed prior to initial nuclear operation and removed after termination of operation. Analyses were made 45 days after reactor shutdown; therefore radionuclides with short half-lives were not determined. All results were corrected for decay to the time of reactor shutdown.

Although ten, or possibly eleven, fuel failures occurred in the HWCTR, most of the radiation from these mild steel surfaces was from activated corrosion products. For comparison, the typical radionuclide activities in the moderator are shown in Table X.

TABLE IX

Radionuclides in Oxide Films of Mild Steel Corrosion Coupons, d/m/mg Fe

Radionuclide	ASTM No. →	A-210	A-106	Average
^{60}Co		6.0×10^4	5.2×10^4	5.6×10^4
^{59}Fe		3.8×10^4	5.9×10^4	4.8×10^4
^{95}Zr-Nb		1.1×10^4	7.3×10^3	9.2×10^3
$^{103-106}$Ru		7.2×10^3	5.6×10^3	6.4×10^3
^{141}Ce		6.9×10^3	2.6×10^3	4.8×10^3
^{58}Co		2.3×10^3	7.0×10^3	4.6×10^3
^{54}Mn		5.6×10^3	1.4×10^3	3.5×10^3
^{51}Cr		8.7×10^3	$<2 \times 10^3$	$<5.4 \times 10^3$
^{46}Sc		$<1 \times 10^3$	1.6×10^3	$<1.3 \times 10^3$

TABLE X

Radionuclide Activities in Moderator

(Average Results at Full Power Operation
July through November 1964)

Radionuclide	Activity, d/m/ml
^{18}F	1.1×10^5
^{24}Na	3.0×10^4
^{132}I	1.0×10^4
^{56}Mn	8.9×10^3
^{135}Ir	7.2×10^3
^{133}I	3.6×10^3
^{122}Sb	5.5×10^2
^{99}Mo - ^{141}Ce	4.0×10^2
^{131}I	3.8×10^2
^{124}Sb	3.0×10^2
^{95}Zr-Nb ^{239}Np ^{59}Fe ^{60}Co	$<1 \times 10^2$ (Usually not detectable)

Secondary - Coolant System

As indicated in the section on Chemical Control of Environment, oxygen control of the secondary coolant was lost for several months early in 1964. Prior to that accident, very little corrosion had been found. Inspection in May 1963 showed that the steam generator tubes in good condition, and the maximum pit depth was approximately 5 mils. On February 4, 1964, the first tube failed and a thorough inspection was made. The maximum pit depth was 15 mils, but the pits were clean (without tubercles) and existance of a corrosion problem was not recognized.

In July 1964, the tube failure occurred that led to the discovery of severe pitting. The appearance of the tubes at that time is shown in Figure 10. The deepest pits were 85 mils in the No. 1 generator, and 55 mils in the No. 2 generator. Tubercles were evident on and around the pits. The appearance of the pits indicated the cause to be excessive concentration of oxygen, and the cause was subsequently identified, as described on page

Inspections were made to assess the corrosion damage to the other parts of the cooling water system. No significant corrosion occurred in pipe and equipment that was always cold (less than 30°C). The No. 1 purge cooler was pitted to a maximum depth of 30 mils on the hottest (D_2O inlet) tubes. On the coldest tubes there was general surface roughness up to 3 to 5 mils deep.

The final inspection of the steam generator tubes was made in December 1964. The tubes were clean. All of the large tubercles that were present in July had been dissolved, presumably by the "Versene" that was added to the generator feedwater. The rigorous oxygen control that was instituted in July had evidently arrested the corrosion.

STAINLESS STEEL CORROSION

Inspections were made periodically of 304 and 316 stainless steel equipment, including reactor vessel lining, pipe, pumps, and internal components of the reactor vessel. Without exception, all surfaces were uniformly covered with a grey-black oxide film. No cracks or other defects were found. A number of 304 and 316 stressed corrosion coupons, sensitized and annealed, were examined after exposures up to 24,100 hours in-core and out-of-core. No cracks were found. The corrosion rates of some unstressed coupons are given in Table XI. No significant difference was seen between in-core and out-of-core specimens.

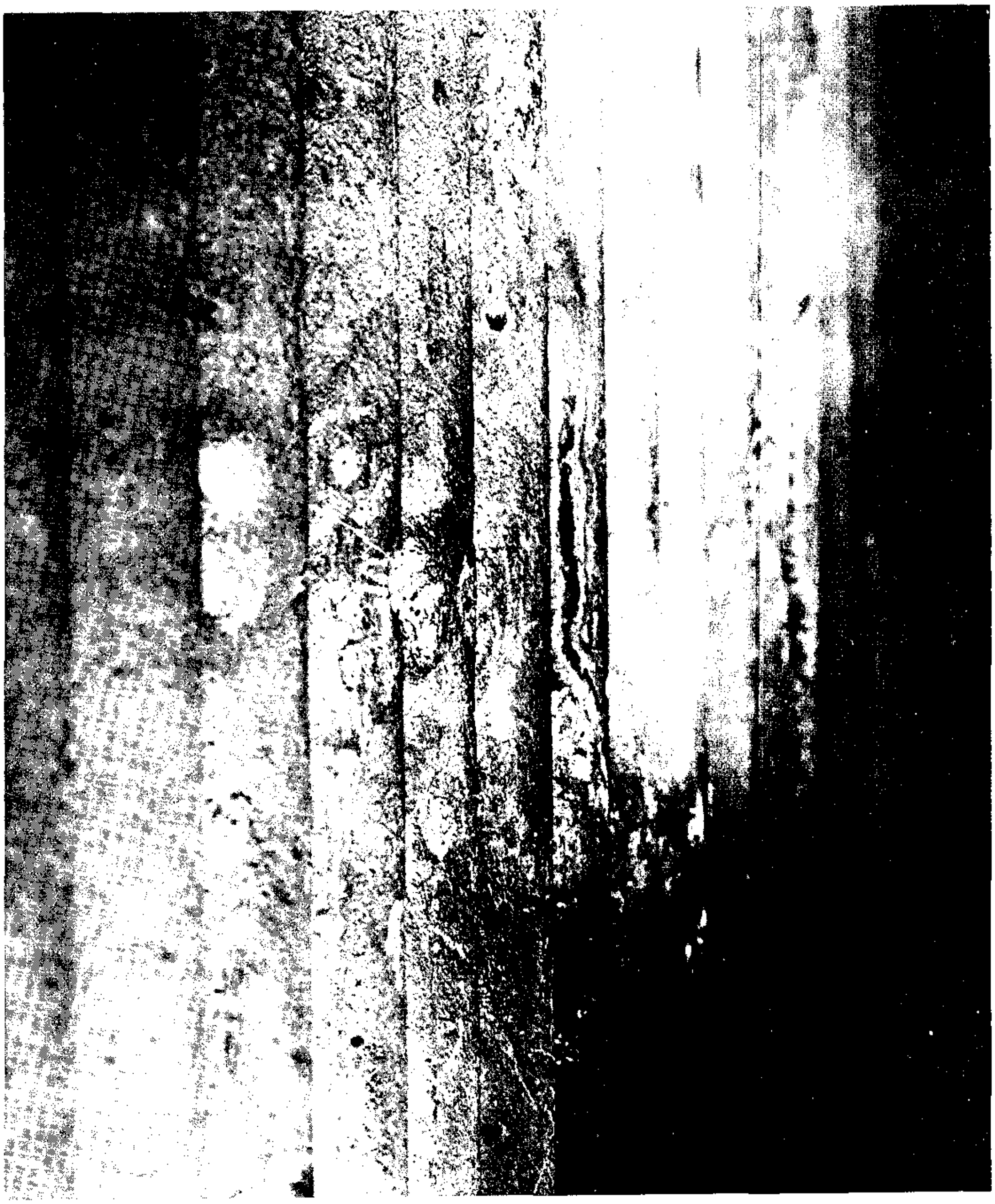


FIG. 10 VIEW OF THE COOLING WATER SIDE OF STEAM GENERATOR TUBES, JULY 1964

TABLE XI

Corrosion Rates of Stainless Steel Coupons

Material	Weight Loss, mg/cm^2 Above Core 12,840 hr	Above Core 23,800 hr	In-Core 15,700 hr[a]	In-Core 24,100 hr
304 SS, annealed	0.11[b]	-	0.19	-
304 SS, sensitized	0.013[b]	0.23	0.23	0.29
304 SS - 1% boron	0.017	0.15	0.0064	-
316 SS, annealed	0.13	0.32	0.15	0.09

(a) Includes 1560 hr in the preoperational light water test period.
(b) Total exposure was 14,400 hr, including 1560 hr in the preoperational light water test period.

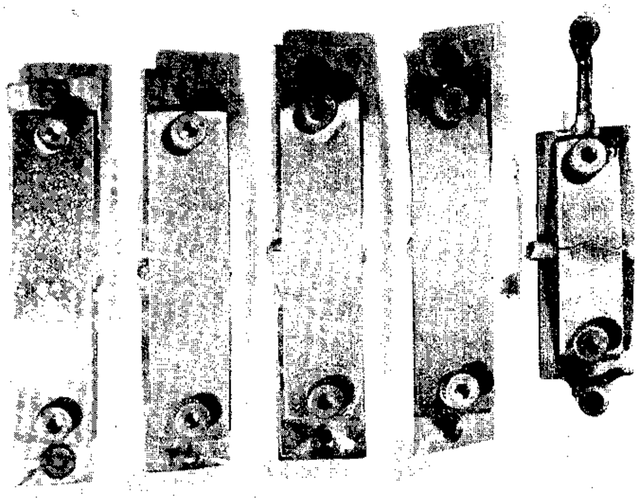
All of the 17-4 PH stainless steel used in the HWCTR was heat treated at 1100°F, which is believed to be the best treatment for prevention of stress-corrosion cracking. No failures occurred on equipment or corrosion coupons that were heat treated in this manner. Results of corrosion coupon examinations are in Table XII. Three coupons cracked, all of which had been heat treated at 900°F, and two of which were exposed during the preoperational light water test period and then returned to the reactor. Two of the cracked coupons were located in the reactor gas space (see Figure 11), and one was in the D_2O above the core.

TABLE XII

Corrosion of Stressed 17-4 PH Stainless Steel Coupons

Condition	In D_2O Above Core 12,840 hr	In D_2O Above Core 23,880 hr	In Reactor Gas Space 12,840 hr	In Reactor Gas Space 23,880 hr
48% cold worked, 8 hr at 1100°F	No cracks	No cracks	No cracks	No cracks
8 hr at 1100°F	No cracks	No cracks	No cracks	No cracks
48% cold worked, 1 hr at 900°F	No cracks	No cracks	No cracks	Cracked
1 hr at 900°F	No cracks	No cracks	No cracks	No cracks
1 hr at 900°F[a]	Cracked	-	-	Cracked

(a) These coupons received an additional 1560 hr of exposure during the preoperational light water test period.



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1X

1 - Cold Worked 48%, 8 hr at 1100°F

2 - 8 hr at 1100°F

3 - Cold Worked 48%, 1 hr at 900°F

4 - 1 hr at 900°F

5 - 1 hr at 900°F, exposed an additional 1560 hrs during light water test period

FIG. 11 STRESSED 17-4 PH STAINLESS STEEL COUPONS FROM REACTOR GAS SPACE
Exposure : 23,880 hours

ZIRCALOY CORROSION

Numerous inspections were made of Zircaloy equipment and corrosion coupons. None of the equipment showed the white oxide that is indicative of "breakaway" corrosion. Two coupons, simulating a Zircaloy-2 tubing-to-forging weld in the isolated loop pressure tube, showed breakaway corrosion around the weld. The weld on the pressure tube did not show this corrosion.

In April 1964, three of the six safety rod guide tubes were found to have failed. Metallurgical examination of one of the failed tubes led to the conclusion that the failures were caused by a combination of excessive tensile stresses during safety rod drop tests and appreciable residual stresses at the outer surface of the tubes. Contributing factors were (1) an abrupt change in guide tube diameter (for hydraulic snubbing) in the region of maximum stress, (2) high hydrogen content resulting from tube fabrication technique and accelerated corrosion from the high fast neutron exposure (7×10^{19} n/cm^2), and (3) radially oriented platelets of zirconium hydride. Detailed discussions of these failures and the subsequent analyses are given in references 7, 8, and 9.

CONTROL ROD DRIVE AND SEAL ASSEMBLIES

A detailed description of the control rod drive and seal assemblies is presented in reference 10. One assembly was disassembled and inspected in April 1963, and again in December 1964.

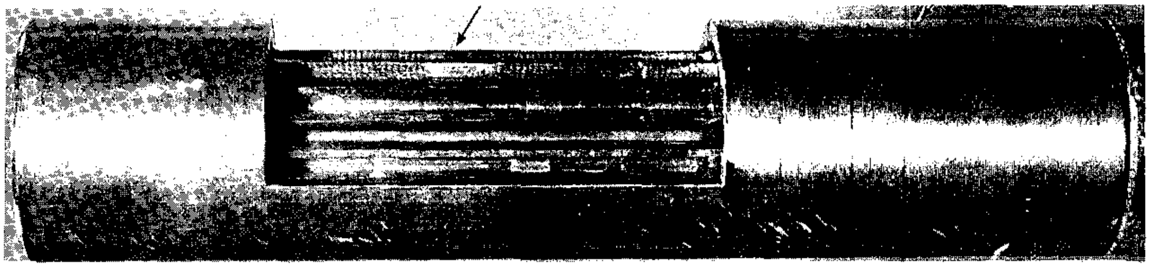
The April 1963 inspection revealed three minor problems:

1) Wear on teeth of delatch pinion gear.
2) Minor corrosion under O-ring on seal bushing.
3) General corrosion of upper extension.

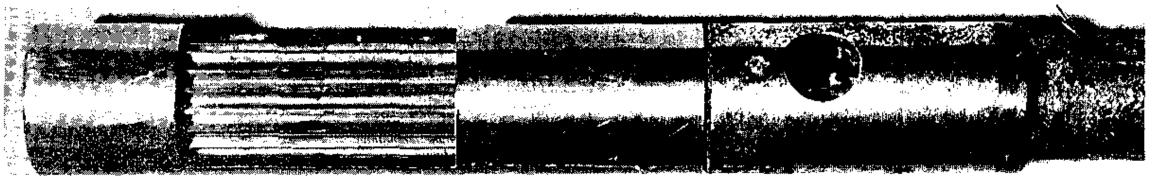
The December 1964, inspections revealed no new problems, and showed that the problems listed above had not worsened during the 20 months since the first inspection. Comparative photographs of the delatch pinion gear and the seal bushing are shown in Figures 12 and 13.

Figure 12 also shows the general corrosion on the upper extension. The appearance of the O-ring groove in the seal bushing is better in December 1964, than in April 1963, because this surface was polished after the first inspection (Figure 13).

Many of the components were examined by the dye-penetrant method, and no cracks were found. Also, the floating-ring labyrinth seals were inspected for evidence of buildup of particulate matter, and none was found.

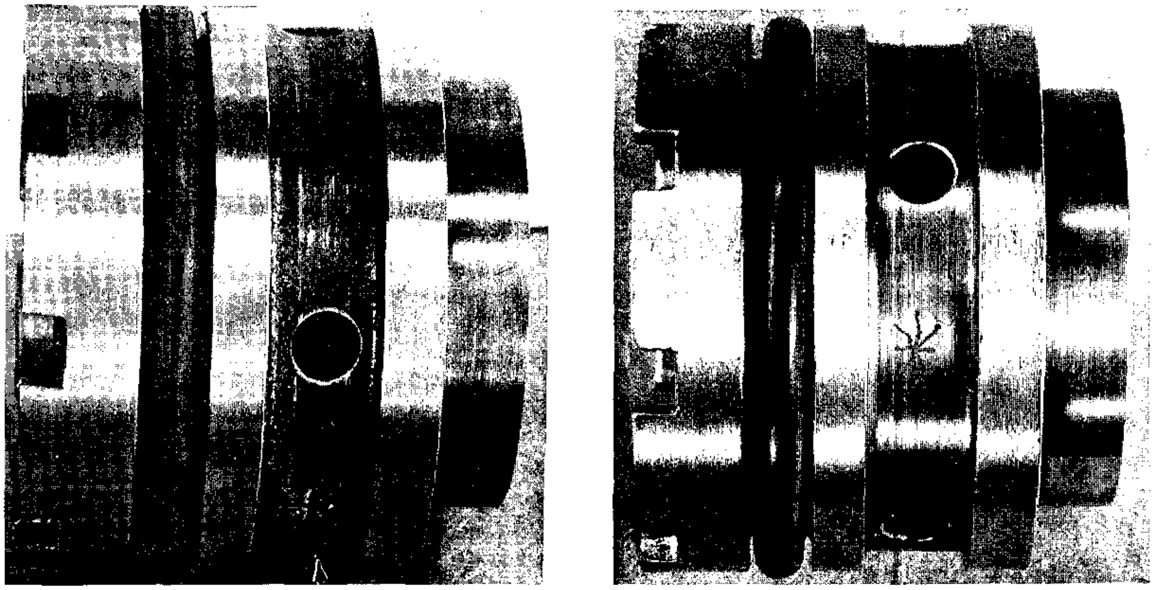


April 1963



December 1964

FIG. 12 CONTROL ROD DELATCH PINION GEAR



April 1963 (Note corrosion)

December 1964

FIG. 13 CONTROL ROD SEAL BUSHINGS, 17-4 PH SS