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SUBJECT: HRE-2 Corrosion Specimens - Blanket Region of Pressure Vessel (Loading No. 1) - Weight Data and Scale Analysis.

TO: E. G. Bohlmann

FROM: A. R. Olsen

SUMMARY

An array of specimens (type 347 stainless steel, zirconium alloys, and titanium alloys), exposed in the Blanket region of the HRE-2 during runs 13 and 14 as well as during some prior high temperature operations, were examined and weighed. The visual observations and weight data are presented together with the chemical analyses of scale removed from some of these specimens. The evidence indicates that the corrosion of the specimens was moderate. Some possible interpretation of the results of the scale analyses as related to core tank corrosion, are also reported.

DISCLAIMER

A set of twenty-four assorted tensile and impact specimens, designated Blanket Loading No. 1 was installed in the blanket region of the HRE No. 2 on 12-30-57 and removed on 4-8-58. A complete record of the metallurgical data and fabrication history of the specimens and array has been reported previously.[1] This report will cover only the post-exposure surface examinations, weight data and chemical analyses of the scale.

The specimen array was removed from the reactor at the completion of HRE No. 2 run 14, the second power run. During the exposure the reactor logged approximately 375 Mwhr. The specimens were exposed only to D_2O without added oxygen with the exception of a very short period of time at the end of run 14 when some core solution entered the blanket through the hole in the core. The total time at temperatures higher than 250°C was 752 hours, and at temperatures between 100°C and 250°C was 227 hours.

After removal from the reactor, the array with the specimens in place was separated without difficulty from the blanket source thimble and flange, using the equipment in the maintenance pool at the reactor site. The array was then transferred to the Corrosion Examination Facility for examination and further disassembly operations.

The array was photographed and examined, both through the cell window and with the aid of the low power magnification of the stereoscopic periscope. The holding screws were sawed off, and the specimens were removed, weighed, and re-examined. The tee mounting heads from one type 347 stainless steel, one Zircaloy-2 and one Ti-A40 titanium specimen were removed by sawing, for chemical analysis of the retained scale. Some of the specimens were then transferred to the Metallurgy group for testing and evaluation. The

remainder were stored for future examination.

Two one-inch long sections were then sawed from the center of each station along the holder. Four of these sections were transferred to the Chemical Technology Division for decontamination studies and four were stored for future examination. The remainder of the holder was sent to the burial ground. No unusual radiation or contamination difficulties were encountered during any of these operations.

Figures 1, 2, and 3 are photographs of the assembly as it was removed from the reactor. All of the specimens with one exception were covered with a very thin, dark, adherent film. The one exception, Zircaloy-2 weld specimen W-3-d, in station L position 1, was known to contain poor material on each end as evidenced by the formation of white corrosion product during pretreatment prior to installation in the holder and by metallographic examination of similar specimens.[2] The amount of white oxide was greatly increased during the in-reactor exposure. This was the only sample of the group to show a weight loss. Individual sample descriptions together with the weight data are presented in Table I. The titanium holder, webs, welds and fittings were generally covered with a dull bronze-colored adherent film with some scattered darker colored stains. There was no visual evidence of any mechanical or corrosion damage to any of the components of the array.

After weighing, the tee tips of specimens A-3-d (Zr-2), O-3-c (347 SS) and J-3-b (Ti-A40) were removed (using the abrasive saw), rinsed, dried and weighed. These tips were then transferred to the Remote Analytical Chemistry group for scale analysis. The analytical procedure, developed for in-pile corrosion test coupons, involves the pickling of the sample in a mixed, con-

centrated acid solution which dissolves scale and some base metal. The exact combination of concentrated acids (HNO_3, HCl, HF and H_2SO_4) varies with the material and the tenacity of the film. The resulting solutions are analyzed both chemically and spectrographically. The results of these analyses are reported in Table II.

Since none of these specimens were defilmed, a corrosion rate cannot be assigned. However, the weight gains and the appearance of the specimens indicate that the corrosion was very small, probably no more than would have occurred under similar conditions outside of radiation.

The primary purpose of the chemical analysis of the retained scale was to determine the amount of uranium in the sample. Analyses for other constituents, indicated transport of oxides from one material to another. The one uranium analysis on the titanium specimen, showing $2 \mu g/cm^2$ may or may not be significant.. This sample may have been contaminated to this low level during the remote handling.

The zirconium oxide on the stainless steel specimens represents a large portion of the weight gain. The source of this zirconium was probably the outer surface of the Zircaloy-2 core tank, which was reportedly coated with a white oxide when observed between runs 13 and 14. If one assumes that the average of $115 \mu g$ of zirconium per square centimeter of area, on these samples, is representative of all the surfaces in the blanket high-pressure system, then this scale represents approximately 58 grams of zirconium oxidized and/or transported during reactor runs 13 and 14. If uniform corrosion of the blanket side of the core vessel is assumed, this represents 0.13 mils of corrosion penetration.

On the bases that the average power level during these runs was 3 Mw, and that this corrosion occurred during radiation, the rate for 375 Mwhr would be approximately 9 mils/yr. This calculation ignores any zirconium oxidized but retained on the core wall. The 9 mpy rate is in disagreement with the reported rates of 4 to 5 mpy and 0.4 mpy for in-pile autoclave experiments ORNL 15-5[3] and Z-117[4], respectively. ORNL 15-5 was an experiment in which distilled water with an oxygen over-pressure was exposed at an estimated temperature of 295°C in a Zircaloy-2 autoclave, with machined surfaces, in a beam hole at the MTR. Z-117 was a similar experiment with oxygenated D_2O in a Zircaloy-2 autoclave, with machined surfaces, exposed at 280°C in the HB-5 facility at the LITR. The power density, due to absorption of fast neutron energy in ORNL 15-5, was estimated to be 4 w/ml while that in the HRE No. 2, at 5 Mw core power, is probably less than 0.5 w/ml and more in agreement with Z-117. Thus, the radiation enhanced corrosion rate expected for the blanket side of the core tank would have been more nearly 0.5 mpy for machined Zircaloy-2.

Since the system had been at temperatures between 250 and 300°C for approximately 1900 hours prior to run 13, the non-radiation corrosion penetration may have been significant. In-pile loop experience has shown that zirconium oxide under radiation is removed from the area of high irradiation and deposited on areas of lower irradiation. Out-of-pile corrosion data indicate that, initially at least, sandblasted Zircaloy-2 corrodes faster than as-machined Zircaloy-2 as indicated by the development of white oxides. Available data[5] on out-of-pile experiments employing good quality Zircaloy-2 with pickled surfaces show penetrations of 0.02 mils in 290°C H_2O and 0.03 mils

in H_2O at 315°C for 1900 hours. Another experiment with machined surfaces in 0.17 M UO_2SO_4 solution showed 0.02 mils penetration in 1100 hours at 250°C, and 0.025 mils penetration at 290°C in 1000 hours. In these experiments only adherent, dark colored films were formed on the metal surfaces. Thus, only a reasonable increase in rate for the sandblasted core tank could have produced most of the indicated penetration, with the remainder being produced during the 400 hours of runs 13 and 14.

It is also possible that part of the zirconium may have been derived from the phenomenon which produced the hole in the core near the end of run 14. There does not appear to be any method of evaluating this possibility at this time.

Table I. Weight Changes Observed for HRE No. 2 Corrosion Specimens Exposed in the Blanket Region of The Reactor During Runs 13 and 14

Specimen No.	Material	Station and Position	Original Weight (gm)	Pretreatment Weight (gm)	As Removed Weight (gm)	Weight Change (mgs)	Weight Change per Unit Area (mgs/cm^2)
A-3-a (T)	Zr-2 Core Tank	J-2	18.9854	18.9862	18.9917	+ 6.3	+ 0.28
A-3-b (T)	" " "	K-2	18.9818	18.9828	18.9898	" 8.0	" 0.36
A-3-c (T)	" " "	L-2	18.9120	18.9129	18.9184	" 6.4	" 0.28
A-3-d (T)	" " "	M-2	18.8886	18.8892	18.8927	" 4.1	" 0.18
B-3-a (I)	Zr-2 Allegheny Ludlum	K-6	21.0355	21.0363	21.0391	" 3.6	" 0.14
B-3-c (I)	" " "	M-6	21.0601	21.0611	21.0645	" 4.4	" 0.17
O-3-a (T)	347 SS	J-4	22.7730	22.7737	22.7769	" 3.9	" 0.17
O-3-b (T)	"	K-4	22.6657	22.6657	22.6687	" 3.0	" 0.13
O-3-c (T)	"	L-4	22.7548	22.7537	22.7566	" 1.8	" 0.08
O-3-d (T)	"	M-4	22.9327	22.9328	22.9354	" 2.7	" 0.12
W-3-d (T)	Zr-2 Weld	L-1	18.6778	18.6877	18.6705	- 17.2*	- 0.76
Y-3-a (T)	"	J-1	18.9522	18.9529	18.9577	+ 4.8	+ 0.21
Y-3-b (T)	"	M-1	19.1174	19.1183	19.1211	" 2.8	" 0.12
E-3-a (T)	Zr-15% Nb-Sponge	J-5	20.0780	--	20.1807	"102.7**	" 4.55
E-3-b (T)	" "	L-5	20.2366	--	20.2383	" 1.7	" 0.08
E-3-a (I)	" "	K-1	22.3114	--	22.3183	" 6.9	" 0.26
H-3-a (T)	" "	K-5	20.2766	--	20.2828	" 5.4	" 0.24
J-3-a (T)	Ti-A40	J-3	12.9710	--	12.9753	" 4.3	" 0.19
J-3-b (T)	"	K-3	12.9676	--	12.9737	" 6.1	" 0.27
J-3-c (T)	"	L-3	13.0308	--	13.0370	" 6.2	" 0.28
J-3-d (T)	"	M-3	13.0290	--	13.0323	" 3.3	" 0.15
J-3-a (I)	"	J-6	14.4958	--	14.4993	" 3.5	" 0.13
J-3-b (I)	"	L-6	14.4708	--	14.4757	" 4.9	" 0.18
N-3-a (T)	Ti-110AT	M-5	13.0796	--	13.0861	" 6.5	" 0.29

(T) Tensile Specimens
(I) Impact Specimens

* This sample has white corrosion product accumulations on both ends.

** There is no visual evidence for this high weight increase. The original weight may be in error.

As Removed Surface Appearance

Thin gray film with some interference colors, machine marks visible.
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" " " " " " " " " "
" " " " " " " " " "

Thin gray film with some interference colors, machine marks visible.
" " " " " " " " " "

Dark bronze covered with a thin dark gray film on all surfaces, machine marks visible.
" "
" "
" "

Streaks and patches of loosely adherent, cream white scale from each end to welds, center covered w/dark gray film.
Very dark gray film on all surfaces.
" " " " " " "

Dark gray almost black film, with occasional interference colors, machine marks visible.
" " " " " " " " " " " " " "
" " " " " " " " " " " " " "
Metallic gray film on all surfaces with some " " " " " "

Thin metallic gray film on all surfaces with some interference colors.
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Thin metallic gray film on all surfaces with some interference colors.

Table II. Chemical Analysis of Scale from Specimens in HRE No. 2 Blanket Loading No. 1 Following Run 14

Scale Source (Specimen No.)	Material	Weight[1] (mg)	Analytical Procedure	Analysis (Wt. %) U	Cu	Cr	Ni	Fe	Zr	Mn	Ti
O-3-c	347 SS	34.7	Chemical	0	0	11.4	8.6	64.1	0.9	-	-
			Spectrographic	-	1.0	12.3	8.0	51.5	0.6	1.1	ND
A-3-b	Zr-2 (Core Tank)	303.8	Chemical	0	0.07	0.07	0.2	0.2	38.5	-	-
			Spectrographic	-	ND	0.1	ND	ND	132.4	ND	ND
J-3-b	Ti-A40	31.6	Chemical	0.02	0	0	0.6	0.2	1.2	-	-
			Spectrographic	-	ND	ND	ND	ND	0.3	ND	74.9

1) The weight of sample analyzed is determined by the loss in weight of the specimens during pickling in a mixed acid solution.

Note: The area of each specimen is estimated to be 3 cm^2, ignoring the surface produced by cutting.

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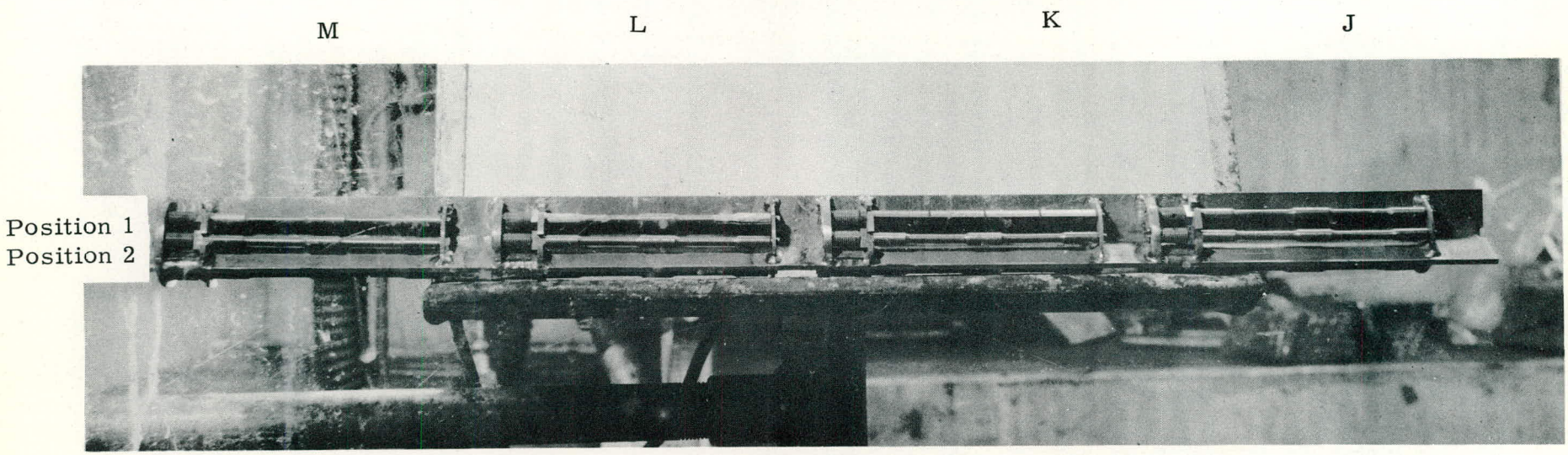

Figure 1 - HRE No. 2 Blanket Loading No. 1 as removed from the Reactor following Run No. 14.

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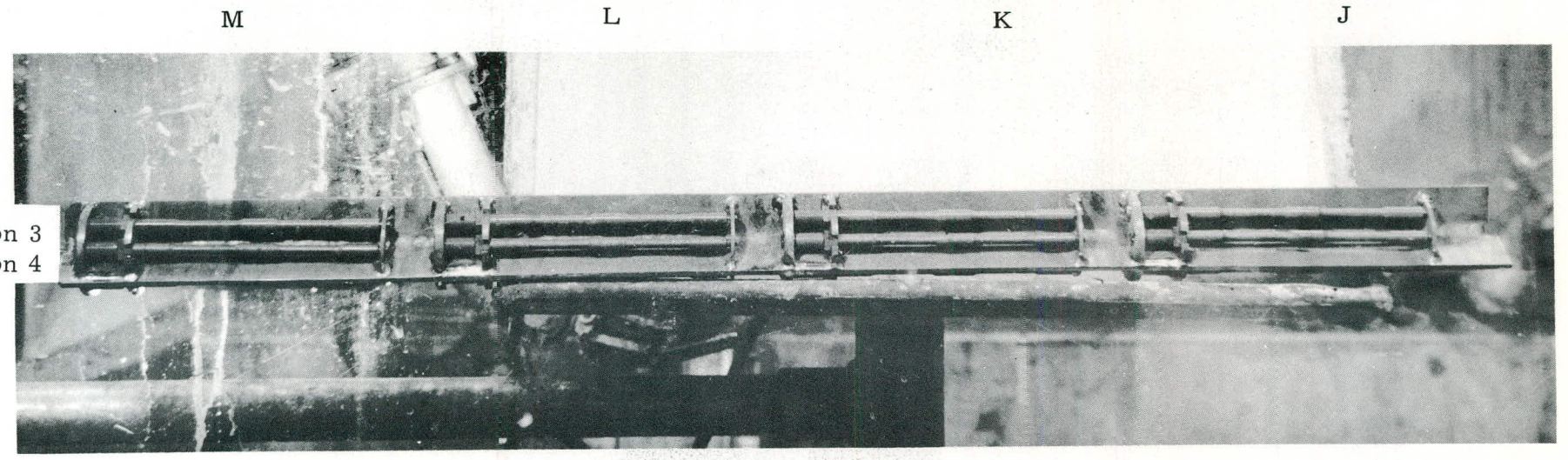

Figure 2 - HRE No. 2 Blanket Loading No. 1 as removed from the Reactor following Run No. 14.

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STATION

M L K J

Position 5
Position 6

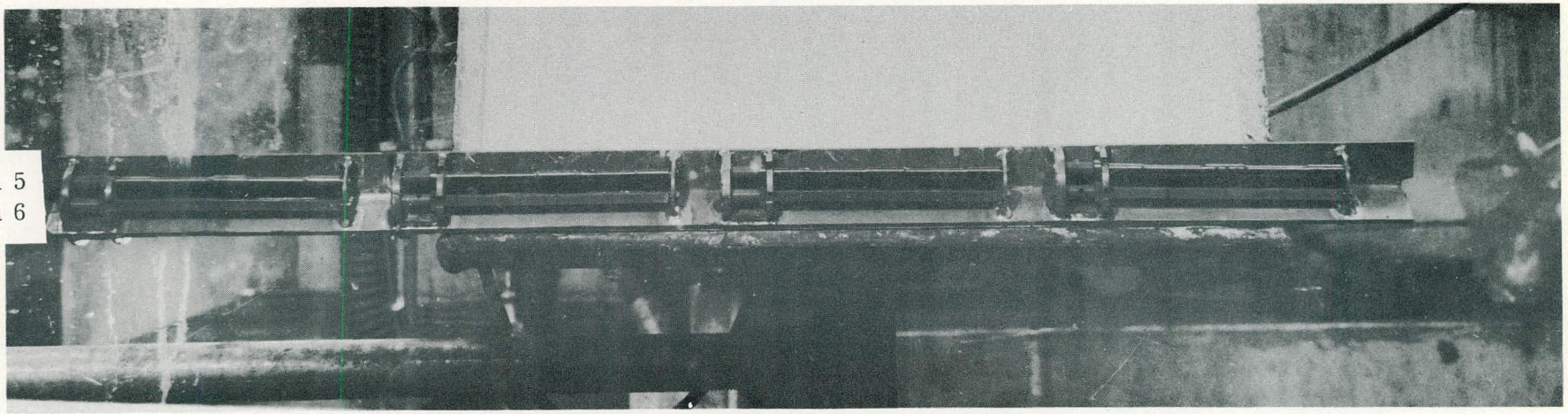

Figure 3 - HRE No. 2 Blanket Loading No. 1 as removed from the Reactor following Run No. 14.

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