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ORNL
CENTRAL FILES NUMBER

58-9-37

DATE: September 11, 1958

SUBJECT: Examinations of Specimens and Scales
Taken from the HRT Following Runs 13 and 14

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COPY NO. 111

SUMMARY

Following HRT runs 13 and 14, several metallic specimens were removed from the high pressure system and transferred to the Materials Section for examination. Samples of scale accumulation in the high pressure system were also taken after these runs and transferred to the Materials Section. Examination and analyses of these several specimens are still in progress, but some of the results are available and are reported. A possible interpretation of some of these results indicates that a considerable quantity of nickel was contained in the core scale accumulation at the end of run 13, and that part of this nickel was dissolved in solution during run 14. The amount of nickel which may have come from this source during run 14 roughly accounts for all of the increase in nickel in solution during run 14. A significant amount of uranium was also found in the scale accumulation in the core after run 13.

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EXAMINATIONS OF SPECIMENS AND SCALES TAKEN FROM THE HRT FOLLOWING RUNS 13 AND 14

I Introduction

Following HRT runs 13 and 14, several metallic specimens were removed from the HRT high-pressure system and transferred to the Materials Research Section for examination. Samples of scale accumulations in the high pressure system were also taken after these runs and transferred to the Materials Section. A list of components, specimens and samples which have been received in connection with runs 13 and 14 is given in Table I. The operations which have been performed or which are in progress with each of these samples are also shown in the table. A sketch of the reactor which shows the general location of specimens during exposure is given in Fig. 1. A brief discussion and description of some of the samples and of the sampling techniques are given below.

The results of these examinations are being reported as they become available. Some of the data which are available have not been correlated as yet. The presentation and discussion of results is limited, in this report, to the results of specimen weight measurements and of chemical analyses of scale.

II Specimen Description and Results of Examination

A. Line 103 Samples, Run 13

The line 103 coupon assembly, which was received after run 13, contained eight coupons, two each of type 347 stainless steel, 309 SCb stainless steel, Ti-75A, and Zircaloy-2. A description of the assembly and information regarding exposures prior to run 13 have been reported. To date, one coupon

of each material has been defilmed. The remaining four coupons and holder have been retained for future evaluation. A separate defilming bath was employed for each specimen, and the separate defilming solutions were transferred to the Analytical Chemistry Division for chemical and radiochemical analyses.

The results of microscopic examination of the specimens indicated that all components of the assembly retained some transported iron oxide film. There was clear evidence of solution penetration into the crevice areas between the coupons and the titanium holder. Each of the stainless steel coupons exhibited evidence of accelerated attack in some portions of the crevice region.

The results of weight measurements on these specimens are listed in Table II. The order of listing is the same as the order of arrangement of coupons in the holder with the solution flowing from H-87 to H-78. The average depth of corrosion penetration calculated from the weight losses is shown in the next to final column. The value for the 347 stainless steel coupon is about .06 mils and that for the 309 SCb coupon is 0.23 mils. For comparison, if corrosion of steel in the high pressure system only accounted for the nickel entering solution during run 13 (500 grams), and if this corrosion were uniform over the various steel surfaces, the average corrosion penetration would be about 0.5 mils. The amount of oxide removed in defilming a given specimen is shown in the final column.

The results of chemical analyses for various constituents in the different defilming solutions are given in Table III. No reliable control analysis of the defilming solution is available, but the solution, as prepared, is known to contain Ni and Cu in amounts sufficient to influence

the results. It is also known that iron is present in the defilming solution, but the concentration of this element is probably small compared with the amounts in the scale sample. No correction has been applied for the presence of any of these materials in the as-prepared solution. Chromium was sought in the scale solution but was not detected. No explanation other than experimental uncertainty is offered for the anomalously high values for iron in the H-95 sample and for the sum of iron and titanium in sample H-88.

B. Core Access Flange for Run 13

During run 13, the core access was closed with a blind flange (six threaded mounting holes were in the flange). The flange was removed after run 13 and transferred to the Materials Section.

Examination of the flange showed that the interior recessed portion was covered with a reddish-brown, rustlike scale. There was some evidence of an effect of solution flow on the scale in that the rust accumulation was heavier in the center and along the outer edges of the recess than in a circular ring between these areas. There was some evidence of surface roughening in areas where the scale had flaked off. From the visual and microscopic examination, it was judged that scale thickness on the flange was about the same as that on the 347 stainless steel specimen H-70, Table II.

A sample of scale scraped from the flange surface was analysed chemically and spectrographically for several elements by members of the Analytical Division, and the results are included in Table IV. The scale was dissolved by the Analytical group, and both chemical and spectrographic analyses were made with the one solution. As may be seen in the table, the

two methods gave different results for the concentration of a given element in the scale. The scale was identified by X-ray diffraction to be predominately Fe_2O_3 .

C. Core Access Flange and Sample for Run 14

Following the run 13 flange examination, a triangular-shaped, type 347 stainless steel specimen was attached to the flange using titanium bolts and spacers. The spacers were used to offset the specimen and permit free access of solution to all surfaces. The steel specimen was pretreated in 280°C water. The titanium spacers were identified, de-greased, dried, weighed, and installed without further pretreatment. The flange was installed for HRT run 14 and, at the conclusion of the run, returned to the Materials Section for examination.

Examination of the flange and specimen assembly revealed that all surfaces exposed to the solution were heavily coated with a loosely adherent, granular, reddish-brown scale. The thickness of scale on the specimen was estimated from visual shadow-comparison to be between 5 and 10 mils.

Separate samples of scale scraped from the specimen, spacers, and a portion of the flange which had not been scraped following run 13 were analyzed chemically by the Analytical group. The results are included in Table IV.

The results of weight measurements on the installed, as-removed, and defilmed flange specimen are shown in Table II. The average corrosion penetration indicated by the loss in weight of the specimen during exposure is 0.009 mil. A penetration of this depth certainly occurred during the pretreatment of the specimen and, hence, the indicated corrosion during run 14

is extremely small. The weight lost by the specimen during defilming shows that the average weight of the scale was 12 mg/cm^2 . As mentioned above, the scale was 5 to 10 mils in thickness, hence, the indicated bulk density of the scale is 0.5 to 1.

D. Core and Line 100 Scales Following Run 13

A sample of scale from the core, mostly from the top diffuser screen, was obtained by the reactor operations group following run 13. An aspirator with a shielded Filtron filter unit as a collection chamber was employed in the recovery. A sample of scale from line 100 (the connecting line between the core and the pressurizer) was recovered by the reactor operations group using a mechanically driven auger and a catchbucket. No material was found in the catchbucket, but the flutes of the auger were coated, and a sample was thus obtained.

Visually, the scales appeared to be highly porous accumulations of rust-colored material, similar to hematite or limonite ore concentrates. The core scale was largely made up of chunks or flakes. Some large ripples were noted on this material, but none of the irregularities simulated machine marks. These materials were analyzed chemically and spectrographically by the Analytical group. The results are given in Table IV. The results for core sample I are not considered representative of the original sample since the original material was leached in dilute HNO_3 before dissolving; and, in addition, considerable splattering occurred during the dissolution step. The results are included in Table IV for comparison between the chemical and spectrographic analyses.

III Discussion of Results of Specimen Weight Measurements

The type 347 stainless steel coupon from line 103, which was examined after run 13, exhibited a weight loss which corresponds to an average corrosion penetration of 0.06 mils. The results for the similarly located 309 SCb stainless steel coupon corresponds to an average penetration of 0.23 mils. In comparison, an average penetration of about 0.5 mils would be expected if all of the probable steel corrosion in this run (500 g. Ni) was in the high pressure system with uniform attack of the different steel surfaces in this system. The only other high pressure steel surface which was examined closely after this run, that of the core access flange, showed evidence of surface roughening. Such roughening is indicative of some corrosion attack. In general, it is believed that the specimen data are not inconsistent with the postulate that the majority of the steel corrosion in run 13 was in the high pressure system with fairly general attack of the different steel surfaces, although, as shown by the data, the attack was not uniform over all steel surfaces.

The only type 347 stainless steel specimen examined after run 14 was the core access specimen. Weight results of the examination showed that the corrosion attack of the specimen during the run was negligibly small.

IV Discussion of Results of Scale Analyses

Visual examination of the core and of line 100 by the reactor operations group and by others after run 13 indicated that a large amount of scale had accumulated in these regions. The results of scale weight measurement on line 103 coupons and of visual examination after run 13 are consistent with the postulate that the majority of the probable amount of scale formed

during the run was elsewhere than on the stainless steel surfaces in the high pressure system. Only about 20% or less was found of the amount expected if the oxide were distributed uniformly over the different high pressure steel surfaces.

The large amount of scale deposited on the core access flange and specimen array after run 14 and the negligible change in weight of the metal specimen during the run indicates that appreciable quantities of oxide were transported through the solution during the run. This scale may have come from the accumulation observed in the core after run 13. Such a transfer from the regions of high fission power density in the core to the surfaces at low power density outside the core is in accord with the results of in-pile loop experiments. In these experiments, there is evidence that bulk scale is transferred from the core to surfaces in regions external to the core.² Visual examination of the reactor core by the reactor operations group and by others after run 14 indicated that the quantity of scale in that region was less than after run 13.³

The accuracy of the data for the composition of scales which are presented in the tables is uncertain. This uncertainty is emphasized by inconsistencies between the results of chemical and spectrographic analyses. However, the data are regarded as clear evidence of a difference in composition between the scales deposited on the high pressure steel surfaces and the scale accumulation in the core and line 100 after run 13. No attempt will be made in this report to discuss all possible implications of these analytical results. Some possible implications of the Fe and Ni results are discussed below.

For purposes of this following discussion, the quantitative accuracy is assumed of the Ni/Fe ratio for the core II scale sample taken after run 13, for the Ni/Fe ratio, and for the percentage iron in the scales removed from the access flange assembly after run 14. In the two cases in which spectrographic analyses were carried out, the difference between the spectrographically and chemically determined values of the Ni/Fe ratio is a factor of two or less. In each case, the spectrographic value is the greater. The chemically and spectrographically determined values for Fe differ in about the same amount and manner in one case and are in agreement in the other. The chemically determined values are employed in the following calculations.

The constituents in the scales which make up the weight not represented by the metals have not been identified. Oxygen, water, and sulfate are probably responsible for the majority of this extra weight. Because of the dissolving technique used on these scales, no sulfate analysis has been made to date, but one will be made on a sample of the scale removed from the core after run 13. Weight loss measurements on a sample dried at varying temperatures will also be made.

V Total Amount of Steel Oxidized in Run 13 and 14 as Determined from a Possible Interpretation of Scale Data

If the above data are employed, together with a number of more or less reasonable assumptions concerning scale composition and locations in runs 13 and 14, it is possible to derive additional information regarding the amount of steel corrosion in these runs. The assumptions are as follows:

- (1) The total amount of Fe and Ni in the scales covering the stainless steel surfaces in the high pressure system after

run 13 was small compared with the total amount of these elements oxidized during the run. For convenience in the calculations, the values for Fe and the ratio for Ni/Fe in the scale from the 347 stainless steel coupon from line 103 are employed as representative of the average scale on the steel surfaces.

- (2) The remainder of the iron oxide formed during run 13 was in the scale accumulation in the core or in line 100 or elsewhere, and the average ratio of Ni/Fe in this scale was the same as that found with the core II scale sample.
- (3) In run 14, the scale deposited on all the stainless steel surfaces in the high pressure system was in the same amount, per unit area, as that on the stainless steel specimen located on the access flange.
- (4) The average ratio of Ni/Fe and the weight per cent iron in this deposited scale in run 14 were the same as that in the several samples removed from the flange array.
- (5) The deposited scale in run 14 came from scale which was located in the core or elsewhere at the end of run 13 and for which the Ni/Fe ratio was the same as that found with the core II scale sample.
- (6) The Ni/Fe ratio of the material remaining in the core after run 14, i.e., run 13 scale not transferred and deposited during run 14, was the same as that found for the core II scale sample taken after run 13.

With these assumptions as bases, values were calculated for the amount of Ni contained in the scales at the end of run 13 and 14, respectively. These and other calculated values are shown in Table V. These values indicate that about 100 g of Ni were released from the scales during run 14, a value which is in near agreement with the amount of Ni found in solution during this run. If the above assumptions are valid, this agreement indicates that steel corrosion during run 14 was very low.

An extension of these calculations, in which the U/Fe ratios in the several scales are assumed to be those reported in the tables, indicates that about 700 g of U were held in the scales at the end of run 13 and that about 400 g were released during run 14.

References:

1. R. M. Warner, HRT Corrosion Sample Data and Fabrication - Circulating Lines - Addendum No. 1, ORNL CF 56-6-62, Aug. 1, 1957.
2. G. H. Jenks, et al., HRP Quar. Prog. Rep., Jan. 31, 1958, ORNL-2493, pp 120-122.
3. R. B. Briggs, Oral Communication.

TABLE I
List of Components, Specimens and Samples Removed From RRT After Runs 13 & 14 With Examinations and Operations Performed

Examinations and Operations														Scale Analysis				
Run No.	Sample Identification	As Removed			Spectrometer Scan	Weight	Scale Removal		Descaled				Metallographic or Microscopic	Induced Activity Analysis	Chemical	Radio-chemical	Specific Fe ⁵⁹ Activity	Others
		Visual	Photography	X-Ray			Mechanical	Defilming	Weight	Visual	Photography							
13	Core access flange solution side	C	C	C ¹	C ¹		C			C	C			C	C	C		
	Core access flange exterior side	C					C							C				
13	Line 103 Coupon Array	I	I	C	C	C		C ²	C	C	I	P	P	I	I	I		
13	Line 100 Scale Accumulation	C	C	C	C							P		C	C	C	Particle property determinations proposed.	
13	Core Scale	C	C	C	C							P		C	C	C	Particle property determinations proposed.	
14	Core Access Flange	C	C				C							C	C	C		
	347 SS Specimen	C	C			C	C	C	C	C	I	P	P	C	C	C		
	Ti Spacers	C	C			C	C	C	C	C	I			C	C	C		
14	Core Scale	I	I	P	P									P				
14	Blanket Corrosion Specimen Array	I	I			C		P	P			P	P	P	P		Tensile and Impact testing proposed.	

Legend: C-Completed; I-Incomplete; P-Proposed

1) Analysis of scale removed from component.

2) Only one coupon of each material 347 SS, 309 SS, Ti and Zr-2 has been defilmed to date (7-21-98).

TABLE II

Weight Data for Corrosion Coupons from HRT Holder 103 after Run 13
and for Core Access Corrosion Coupon Exposed during Run 14

Run No.	Sample Number	Material	Area (cm ²)	Initial Weight (g)	1st as Removed Weight ^a (g)	2nd as Removed Weight ^b (g)	Defilmed Weight (g)	Weight Change between Final & Initial (mg)	Corrosion Penetration (mils)	Removed Scale Weight ^c (mg/cm ²)
13	H-87	Ti-75A	20.7	16.6105	16.6115	16.6492	-	-	-	-
13	H-88	Ti-75A	20.7	16.5430	16.5438	16.5860	16.5411	- 1.9	0.008	2.17
13	H-95	Zr-2	20.7	24.0233	24.0287	24.0406	24.0290	+ 5.7	-	0.56
13	H-96	Zr-2	20.7	24.1542	24.1604	24.1693	-	-	-	-
13	H-70	347 SS	20.7	29.0756	29.0805	29.1144	29.0523	- 23.3	0.055	3.00
13	H-71	347 SS	20.7	29.0955	29.1013	29.1332	-	-	-	-
13	H-77	309 SCb SS	20.7	28.8648	28.8703	28.8587	-	-	-	-
13	H-78	309 SCb SS	20.7	28.9662	28.9714	28.9100	28.8678	- 98.3	0.23	2.04
14	Spec. A	347 SS	61.7	82.5274	-	83.2610 ^c	82.5166	- 10.8	0.009	12.1

a. Weight after HRT Run 7 Reported in ORNL CF 56-6-62 Addendum No. 1

b. Weight after HRT Run 13

c. Weight after HRT Run 14

TABLE III

Chemical Analyses of Scale Removed by Defilming Coupons from HRT Holder 103 after Run 13

Sample Number	Material	Weight ^a (mg)	Per Cent Scale Represented by Constituents	Amount of Constituent in Scale (Weight Per Cent) and Mass Ratio of Element to Iron in Scale									
				Fe	U	U/Fe	Zr	Zr/Fe	Ni	Ni/Fe	Cu	Cu/Fe	Ti
H-70	347 SS	62.1	35	30	1.5	0.05	2.0	0.07	1	0.03	1	0.03	--
H-78	309 SCb SS	42.1	80	75	0.5	0.007	1.0	0.01	2	0.03	4	0.05	--
H-88	Ti-75A	44.9	--	80	1.0	0.01	2.0	0.03	3	0.04	5	0.06	34
H-95	Zr-2	11.6	--	120	0.5	0.004	7.0	0.06	6	0.05	5	0.04	--

a. The weight of the material analyzed was determined by the difference between the as-removed and defilmed coupon weights.

TABLE IV

Analyses of Scale Removed from HRT after Runs 13 and 14

Run No.	Source of Scale	Sample Weight (g)	Analytical Technique	Per Cent of Scale Represented by Constituents	Amount of Constituent in Scale (weight per cent) and Mass Ratio of Element to Iron in Scale										
					Fe	U	U/Fe	Ni	Ni/Fe	Cu	Cu/Fe	Cr	Cr/Fe	Zr	Zr/Fe
13	Core I ^a	1.7329	Chemical Spectrographic		18.2	0.32	-	0.18	0.010	0.09	-	0	-	0.01	
					18.5	-	-	0.35	0.019	0.15	-	2.3	-	0.17	
13	Core II	1.2033	Chemical	13.5	10.4	2.0	0.2	0.6	0.06	0.4	0.04	0.1	0.01	0	0
13	Line 100	0.4437	Chemical	12.0	7.7	2.5	0.3	0.8	0.10	0.2	0.03	0.8	0.10	0	0
13	Core Access Flange, Fuel Side	0.0655	Chemical Spectrographic	36.0	34.6	0.4	0.01	0.5	0.015	0	0	0	0	0.2	0
				75.0	65.0	-	-	1.3	0.020	0.2	0.003	7.1	0.11	1.5	0.023
14	Access Flange	0.0292	Chemical	43.9	36	0.14	0.004	0.6	0.016	0.7	0.019	6.5	0.18	nil	
14	Core Access 347 Sample A	0.0658	Chemical	41.6	39.5	0.11	0.003	0.4	0.010	0.6	0.015	1.0	0.025	nil	
14	Ti Spacer Employed with 347 Sample A	0.0489	Chemical	42.7	40.2	0.23	0.006	0.6	0.015	0.6	0.015	1.1	0.027	nil	

a. This sample splattered during the dissolving process after a dilute HNO_3 leach. The contents of the leach solution were not included in this sample.

SKETCH: SHOWING LOCATION OF METAL AND SCALE SPECIMENS EXAMINED

AFTER HRT RUNS NO. 13 AND NO. 14

FIGURE 1

TABLE V

Total Fe and Ni Content of Scales after Runs 13 and 14 Calculated from Composition of Scale Samples, and Values Employed in Calculations or Used for Comparison

Factor	Value	Source of Value
Area of stainless steel in high pressure system, cm ²	4.2 x 10 ⁵	Results of measurements
Iron in HRT stainless steel, w/o	66.0	
Nickel in HRT stainless steel, w/o	12.5	
Nickel entering solution in run 13, g	500	
Nickel entering solution in run 14, g	100	
Total amount of stainless steel oxidized during run 13, g	5,700	Calculated from available data with several assumptions as bases as described in text.
Total amount of iron oxidized during run 13, g	3,770	
Total amount of nickel oxidized during run 13, g	714	
Total Fe and Ni on high pressure steel surfaces after run 13		
Fe, g	378	
Ni, g	11	
Increase during run 14 measured after run		
Fe, g	1,960	
Ni, g	27	
Total Fe and Ni in scale collection in core		
after run 13		
Fe, g	3,390	
Ni, g	200	
after run 14		
Fe, g	1,430	
Ni, g	86	
Decrease in Ni content of scales during run 14	Ni, g	91

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