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SUBJECT: CHEMICAL INDICATIONS OF HRT MISBEHAVIOR IN RUN 17-A

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FROM: H. F. McDuffie

SUMMARY

Examination of the results of chemical analyses of samples of the HRT fuel solution taken during run 17-A revealed significant changes in solution composition which could be correlated with changes in the power level of the reactor. For a given average reactor temperature, an increase in the power level was accompanied by decreases in the uranium and copper concentrations and increases in the sulfate and free acid concentrations.

The electrical neutrality ratio, an indication of the self-consistency of the over-all analytical results, did not show any significant relationship to the reactor power level but was strongly correlated with the serial sampling order. This effect appeared to be due largely, but not entirely, to cyclical variations in the analytical free acid determinations. Planned controls should eliminate this source of variation.

The over-all conclusion from the results is that a rise in reactor power level causes the deposition of uranium, copper, and probably nickel, in some hydrolytic process within the core circulation system in a region which is at a position between zero and average nuclear importance. This deposition requires from several minutes to several hours and is relatively easily reversible when the power is lowered.

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INTRODUCTION

At the request of S. E. Beall the writer undertook an investigation of the chemical aspects of the operation of the HRT, particularly during run 17-A, in order to search for the cause and significance of the apparent changes in chemical composition and in reactivity during operation.

It was understood that other investigators were studying various mechanical, hydrodynamic, and physical factors which might explain the sudden changes in reactivity, and this investigation was confined, therefore, to chemical information.

This report presents findings and conclusions based on the chemical analysis of samples taken during the first part of run 17, before a slight amount of extra sulfuric acid was added on August 20, 1958.

SUMMARY AND CONCLUSIONS

Summary:

1. For a given average fuel solution temperature, an increase in reactor power was accompanied by a decrease in the uranium and copper concentrations in the fuel and an increase in the free acid and the total sulfate concentrations in the fuel.
2. Higher average fuel solution temperatures required higher room temperature concentrations of uranium, copper, and total sulfate, in agreement with the expectation based on the expansion of aqueous solutions as the temperature is raised. This temperature effect was not demonstrable in the free acid data.
3. The Marshall ratio in the fuel solution decreased as the power level increased.
4. The changes in concentration were far more easily established in the fuel solution than in the blanket solution.

5. The electrical neutrality ratio (total anions:total cations) was strongly correlated with the serial sampling order and with time but was not demonstrably correlated with reactor power level.

Conclusions:

1. When the reactor power is raised uranium is removed from the circulating fuel solution but deposited (on the average) in a position of some nuclear importance (but not zero importance).

2. The importance of this position is less than the average importance of the uranium circulating in the fuel solution at zero power.

3. The nature of the deposited uranium must be such that its deposition and re-solution are easily and quickly reversible upon changes in the reactor power.

3. Some internal analytical error, which caused the cyclical change in the electrical neutrality ratio, was obscuring the expected effect of reactor temperature upon the analytical excess acid concentration.

5. Over-all analytical controls on the HRT fuel solution should be carried forward as planned.

DISCUSSION

Data Examined: Table 1 presents the analytical data for reactor fuel samples taken during run 17 before the addition of sulfuric acid. This table also presents a number of parameters calculated from the data. All the reported analytical results were converted into millimolar units of concentration.

Figures 1 through 7 present various plots of these data in order to provide bases for the discussion which follows.

Data for reactor blanket samples were examined. They were relatively fewer in number and less amenable to treatment. As will be seen later in the

discussion, there is reason to believe that the intermixing between the core and blanket regions causes the concentration changes originating in either region to be reflected in the other region via a first order process with a relatively long time constant (of the order of 5-10 hours). It further appears that the concentration changes of interest originate in the fuel solution circulating through the core region. Thus any changes in the blanket samples should be $1/3$ in magnitude compared with fuel samples and should require many hours for complete establishment. There was no indication from the blanket data examined that they were qualitatively in disagreement with the conclusions or findings based on the fuel solution samples.

Interpretation of Analytical Data: D. M. Richardson had already shown that the reactor power level was positively correlated with the "calculated free acid," the difference between the sum of the uranium, copper, and nickel molarities and the total sulfate molarity. This parameter, though calculated, was believed to be more precise than the analytically observed free acid because of the nature of the procedure. Nevertheless, the analytically observed free acid was examined and also showed a strong positive correlation with power level as illustrated by Fig. 1. Although the reactor was not returned to low or zero power very frequently, those data which are available are consistent with the hypothesis that the phenomenon is reversible.

The data from sample RFH-123 are considerably at variance with all the other data, both with respect to free acid and with respect to the other parameters studied. This sample was taken almost immediately (within five minutes) after raising the power level. Two hours later at the time of sample RFH-124 there had been a substantial change in the composition of the solution, which now had adjusted itself to the higher power level. These samples indicate that the relatively rapid adjustment to an increase in power level requires a time which is longer than five minutes for completion but probably not

greater than two hours. Of course the reflection of this change into the blanket region imposes a small additional change over a longer period of time. The difference between the data of RFH-123 and RFH-124 will be noted on all the comparisons in the figures.

The uranium concentration data were then examined, and their variation with the power level is shown by Fig. 2. Two substantial effects were noted: first, as an expected effect, for a given reactor power level a higher average operating temperature required a higher concentration of uranium in the sampled fuel (the sample is analyzed at room temperature, but expansion of the liquid to the reactor operating temperature affects the total amount of uranium present in solution in the active region of the core); second, as an effect not expected in advance, the concentration of uranium at a given average temperature decreased as the power level was raised. Such a decrease in concentration would be inconsistent with the maintenance of criticality unless compensating amounts of uranium were simultaneously placed somewhere within the active region but not freely available to the circulating stream which was sampled.

If this missing uranium were placed in a position of the same average importance as that uranium which is in solution at lower power, no addition or subtraction of water would be necessary to keep the solution critical at the given temperature. The solution free acid concentration could rise if the uranium were deposited as a hydrolytic product, as uranium peroxide, or as reduced and hydrolyzed uranium; but if the nuclear importance of the uranium were unaltered the total sulfate concentration of the solution could not rise-- if the uranium were deposited along with some sulfate the circulating sulfate concentration might actually fall. However, Fig. 3 shows clearly that the total sulfate concentration rose substantially with increasing power. This

shows conclusively that the non-circulating uranium is in a position of lower nuclear importance than the average importance of circulating uranium (but still not of zero importance). The expected temperature effect on total sulfate is noted in this plot as well as in the uranium concentration plot.

Figure 4 shows that the copper concentration also decreases with increasing power. This supports the hypothesis that the copper and uranium are being lost from circulation by the same process. It could be hydrolysis, reduction and hydrolysis, or peroxide precipitation; laboratory experiments by H. H. Stone, in which a synthetic fuel solution was slightly reduced by hydrogen at 250°C and the copper found to remain in solution while the uranium disappeared, fail to lend support to the reduction hypothesis; laboratory experiments by L. O. Gilpatrick, in which a synthetic fuel solution was partially precipitated by the addition of hydrogen peroxide at around 100°C and the precipitate found to be free from copper, fail to support the peroxide precipitation hypothesis. No evidence is at hand which is incompatible with the hypothesis of some sort of hydrolytic phase-separation in which the copper is deposited along with the uranium.

Since nickel is released by corrosion in an irreversible process it would be expected that the nickel concentration would increase with time; this effect would be superimposed on any power-dependent hydrolytic process by which nickel might be lost from solution along with uranium and copper. The nickel data were examined but did not show any definite power dependence.

W. L. Marshall has examined the phase stability of systems containing uranium, copper, nickel, free acid, and sulfate as the anion; he reports that the ratio of the sum of the molarities of the three metals to the total molarity of sulfate appears to be independent of the relative quantities of the three metals present if uranium is taken to be in the form of $U_2O_5^{+2}$.

At 300°C this ratio is around 0.50; it decreases with increasing temperature and may decrease very slightly with increasing total sulfate concentration. Figure 5 shows a plot of this Marshall Ratio vs fuel heat exchanger power for the fuel sample data of run 17; the strong negative relationship with the power level suggests that the solution is behaving as if it were in solubility equilibrium at progressively higher temperatures as the power level is raised. These temperatures would be much higher than the observed reactor fuel outlet temperatures. It is possible that a portion of the circulating fuel solution comes in contact with the deposited uranium at a still higher temperature and then mixes with the remainder of the circulating solution to give the observed temperature rise.

Reliability of Analytical Data: Analyses of highly radioactive solutions are admittedly difficult, and heretofore it has been impossible to study the effects of such high radiation levels upon the accuracy and precision of the analytical methods. The analytical division routinely uses control samples to monitor the procedures which are applied to the fuel solution samples. The results on the samples themselves, however, may be combined to furnish a sort of internal check upon the over-all self-consistency of the analyses; the sum of the positive ions found in the solution should equal the sum of the negative ions. An electrical neutrality ratio can be formed from these two sums and examined for deviations from the expected ratio of 1.000. Figure 6 shows that this ratio does not significantly (compared with the scatter of the data) correlate with the power level of the reactor. However, Fig. 7 reveals a very strong cyclic trend with the serial order of sampling, and the range of the variation (from 1.15 to 0.90) is much larger than the deviations about the cyclic line. Clearly there was some varying systematic bias being introduced by the analytical procedures themselves. The most likely

suspect is the free acid determination; examination of these data showed that a cyclic variation in them could explain much of the cyclic variation in the electrical neutrality ratio (but not all of it). The analytical division has been requested to institute controls based on this ratio.

Laboratory experiments by L. O. Gilpatrick have shown that the presence of peroxide can increase the apparent free acid concentration as determined by the usual procedure. In the past no determinations of the peroxide content of the fuel samples has been attempted. It has been suggested that some fuel samples might be examined for peroxide to ascertain whether routine determination or elimination of peroxide should become part of the analytical procedure.

Agreement between Analytical Chemical Behavior and Reactor Temperatures:

Normally it was expected that raising the reactor power would cause the inlet and outlet temperatures to diverge, with their average being constant. This is indeed the case for the first few seconds after the power level is raised; subsequently there is a progressive lowering of both the inlet and exit temperatures of the circulating fuel solution until the average temperature is substantially lower than it was previously. Such behavior is in agreement with the analytical indication that uranium is lost from the circulating solution soon after the power is raised; the rate of temperature decrease is an indication of the rate at which uranium is lost, and the absolute amount of temperature decrease is an indication of the absolute amount of uranium which is lost. The amount of water which must be removed from the solution in order to restore the average temperature is likewise an indication of the uranium loss.

Information from Time Dependence of Power Ratio in Core and Blanket:

It has been established that, due to the intermixing of the core and blanket regions, the concentration of uranium is about three times as high in the core

as in the blanket and the power production in the core is about 60% of the total. A sudden change in either the core or blanket uranium concentration as a consequence of a change in reactor power would be reflected by a corresponding change in the percentage of power produced in the core; as the intermixing re-established the 3:1 concentration ratio the power ratio would return to its original value, but this would require several hours. Data collected and plotted by P. N. Haubenreich showed that the ratio of core to blanket power dropped suddenly when the power was raised but then slowly increased toward its previous steady-state value. This is in agreement with the idea that the uranium is lost first from the fuel solution when the power is raised; intermixing with the blanket then slowly reduces the blanket concentration to restore the steady-state balance. Conversely, sudden lowering of the power causes a primary increase in the concentration in the fuel solution and a secondary increase in the concentration in the blanket.

Table 1. Analytical and Reactor Data for Fuel Solution Samples from Run 17-A

RFH-17 No.	Date	Time	FHX Power MW	Avg. Temp. $1/2(T_{O_2} + T_1)$ °C	Analytical Data					Electrical Neutrality Ratio	Marshall Ratio
					U +6 m M	Cu+2 m M	Ni+2 m M	SO ₄ ⁼ m M	Free H ₂ SO ₄ m M		
10	7-31	21:13	0	259	25.88	13.22	5.11	56.21	~10	1.142	.556
13	8-1	06:32	0	275	29.54	13.90	3.14	61.42	~10	1.085	.517
16	8-1	21:35	0	269	26.05	13.41	3.75	58.19	13.50	1.026	.518
23	8-2	14:45	1.2	270	25.21	13.17	3.19	66.36	25.00	0.996	.436
26	8-2	17:50	1.2	270	24.54	12.80	3.15	66.00	20.75	1.077	.427
33	8-3	01:44	1.2	270	26.11	13.61	4.24	69.22	24.00	1.018	.446
42	8-3	17:25	1.5	270	24.79	12.42	3.13	66.83	25.50	1.015	.418
47	8-4	06:15	1.8	268	23.24	11.30	2.62	62.40	27.75	0.961	.409
51	8-4	14:55	2.2	271	22.25	12.14	3.09	66.05	28.50	1.001	.398
57	8-5	05:40	0.9	272.5	26.28	13.79	3.83	63.03	20.00	0.986	.488
73	8-5	21:25	2.5	275	25.84	12.53	2.94	77.29	32.50	1.047	.367
81	8-6	09:40	2.1	271	22.90	12.23	2.76	64.23	26.75	0.993	.411
93	8-7	05:25	2.1	270	22.75	12.35	2.73	66.36	24.25	1.068	.398
120	8-9	01:35	0.3	270	29.33	13.97	3.01	62.51	11.00	1.090	.506
123	8-9	10:18	2.1	268	28.11	13.83	4.01	62.67	13.125	1.060	.509
124	8-9	12:14	2.1	258	19.58	9.74	3.03	59.80	22.25	1.095	.377
133	8-10	03:58	2.3	264	21.26	11.48	3.26	64.70	19.75	1.16	.394
139	8-10	13:05	2.5	273.5	24.73	12.28	3.07	73.80	30.75	1.04	.375
143	8-10	20:48	2.5	274.5	24.54	12.50	3.65	71.77	25.50	1.084	.395
146	8-11	03:09	3.1	274.5	27.65	12.61	3.41	77.97	26.50	1.111	.382
152	8-11	13:20	3.1	270.5	21.93	11.02	2.87	69.01	26.50	1.107	.360
168	8-12	05:07	3.1	274	24.56	11.90	3.30	69.95	28.00	1.032	.392
181	8-12	11:33	3.1	272	23.53	11.38	3.87	67.87	30.75	0.976	.398
184	8-12	13:05	3.1	272	22.75	11.79	3.81	68.03	25.00	1.074	.396
208	8-13	23:50	2.1	268	22.94	12.47	3.97	61.26	28.5	0.903	.455
211	8-14	05:20	2.1	269	24.12	13.44	5.07	74.95	32.32	1.000	.407
220	8-14	22:19	2.1	267.5	21.85	15.91	3.41	64.75	25.00	0.978	.467
224	8-15	01:20	2.1	268.5	21.76	11.55	4.79	66.41	-		.409
240	8-16	06:43	2.1	267	23.24	13.17	4.38	60.48	24.50	0.926	.482
249	8-16	18:24	2.1	266.5	23.00	12.81	3.19	64.07	24.00	1.016	.429
256	8-17	14:52	2.1	269	22.39	12.53	3.42	62.35	29.50	0.919	.435
271	8-18	22:25	2.1	266.5	21.93	12.72	3.68	61.36	26.00	0.961	.446
272	8-19	01:29	2.1	266	22.69	11.71	3.54	60.48	25.00	0.9609	.439
275	8-19	03:35	2.1	266	21.09	11.74	3.29	60.74	25.50	0.9857	.4211

Figure 1. Effect of Power Level on Free Acid

Figure 2. Effect of Power Level on Uranium Concentration

Figure 3. Effect of Power on Total Sulfate Concentration

Figure 4. Effect of Power Level on Copper Concentration

Figure 5. Effect of Power on Marshall Ratio

Figure 6. Effect of Power on Electrical Neutrality Ratio

Figure 7. Effect of Serial Sample Order on Electrical Neutrality Ratio

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