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ORNL
CENTRAL FILES NUMBER

59-8-41

DATE: August 11, 1959

COPY NO. 126

SUBJECT: Two-Liquid-Phase Temperature Limits for the Homogeneous Reactor
Fuel Solution and its Concentrates; Comments on Solid-Liquid
Equilibria.

TO: Distribution

FROM: W. L. Marshall, J. S. Gill and R. E. Moore

SUMMARY

Temperatures are given at which two liquid phases form in a synthetic homogeneous reactor fuel solution and its concentrates. The data show a two-liquid-phase boundary temperature of 332°C for the particular HRT fuel composition and a flat minimum temperature of 305°C for the initial solution concentrated between 6 and 16 times. Experiments on solid-liquid equilibria between 300 and 329°C are presented to indicate solution stability in this temperature region. Some related comments on current HRT operation are given.

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INTRODUCTION

H. F. McDuffie and W. R. Grimes have suggested that concentrating the homogeneous reactor fuel solution by local boiling should first produce a second liquid phase rather than a solid even though the pressurizer temperature is below 332°C , the two-liquid-phase boundary temperature for the HRT fuel, but not below the minimum temperature for two-liquid-phase formation at higher concentrations of the fuel solution. This investigation was initiated to test the suggestion quantitatively. The results show that, assuming the pressurizer temperature is not too far below 332°C , the second liquid phase indeed must be the first phase to appear upon concentrating the HRT fuel solution, although the ultimate product can still be a solid phase.

Both concentration and dilution of the HRT fuel may occur during reactor operation. It has been suggested that a mechanism for concentration is localized boiling either within the core solution or at certain limited locations on surfaces in the reactor core. Dilution of the fuel solution by heavy water occurs at the junction of the pressurizer and fuel system under operating conditions of the HRT. Due to the present hole in the core, dilution also occurs as fuel transfers from the core to the blanket system. It is accordingly of interest to know how the tendency toward separation into two liquid phases and also toward precipitation of solids changes with concentration or dilution of the fuel. This report deals mainly with the second liquid phase phenomenon, but possible solid precipitation is also discussed.

EXPERIMENTAL

The synthetic HRT fuel composition prepared for this study was

$$\text{UO}_3 = 0.0250 \text{ molar}$$

$$\text{CuO} = 0.0124 \text{ molar}$$

NiO = 0.0057 molar

MnO = 0.0006 molar

SO₃ = 0.0596 molar

in D₂O. The analytical results obtained for us by H. E. Zittel et al., of the Analytical Division for this solution were

UO₃ = 0.0258 molar

CuO = 0.0126 molar

NiO = 0.0058 molar

MnO = 0.000364 molar

SO₃ = 0.0612 molar.

Manganese was low probably because it was added as a solution of MnSO₄ in D₂O which had been prepared from a weighed quantity of MnSO₄·H₂O and probably contained additional water over that indicated by the formula. Since the manganese content in the fuel solution was so much lower than that of the other components, it seemed reasonable to assume that the difference in properties due to the lower manganese concentration was negligible.

Several concentrated solutions were prepared from the synthetic HRT fuel solution by evaporation of D₂O. One solution was prepared by dilution with D₂O. The temperature of the first appearance of a second liquid phase upon heating was determined for each prepared solution as well as for the synthetic HRT fuel itself. The experimental method used was visual observation of the solutions in 1 mm I.D. sealed silica tubes which were immersed in a fused salt-bath that was heated slowly while being stirred. An intermittent vibrator served for mixing the solutions in the silica tubes. Temperatures were measured by means of iron-constantan thermocouples and a Brown recorder, which was periodically checked against a Rubicon Model B potentiometer using an ice bath cold junction.

RESULTS AND DISCUSSION

Liquid-Liquid Equilibria. The liquid-liquid immiscibility boundary limits are given in Table I. The concentration factor when multiplied by the molar concentration of a component in the synthetic HRT fuel solution gives the concentration in molar units of that component in the fuel concentrate. Figure 1 is a plot of the values in the table. It can be seen that the temperature of appearance of the second liquid phase is lowered considerably upon concentration of the HRT fuel solution. After concentration by a factor of 5 or 6 there is very little further lowering of the two-liquid-phase temperature. It is possible that a minimum of 305°C is reached somewhere between concentration factors of 6 and 16. An exact determination of the concentration factor minimum would be very difficult because the curve is almost flat.

Solid-Liquid Equilibria. Determination of solid-liquid equilibria in this particular system at high temperatures as a general rule cannot be accomplished by the simple procedure of observation in small-diameter, sealed, silica tubes while heating or cooling because attainment of equilibrium is often very slow and attack on the silica becomes significant after long periods of time. It is usually necessary to equilibrate solutions in bombs for a long time at constant temperature, followed by sampling of the solution at temperature for analysis. The solids in equilibrium with the liquid must then be identified.

Solid-liquid equilibria in the system $\text{UO}_3\text{-CuO-NiO-SO}_3\text{-D}_2\text{O}$ are under study by the direct sampling method.¹ The temperature for this study has

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(1) W. L. Marshall and J. S. Gill, Reported in HRP Qtly. Prog. Rep., April 30, 1959, ORNL-2743, pp. 227-229.

Table I. Second Liquid Phase Temperatures
of HRT Fuel Concentrates

Concentration Factor	Temperature (°C)
0.5	342
1.0 (Synthetic HRT Fuel)	332
2.0	323
4.9	308
8.0	305
16.0	306

thus far been restricted to 300°C. The data obtained to date, including more recent data than in reference 1, indicate that the composition of the HRT fuel is nearer to the solid solubility boundary of the red solid, $\text{CuO} \cdot 3\text{UO}_3$, than the solubility boundaries for any of the other stable solid phases such as $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{D}_2\text{O}$, $2\text{UO}_3 \cdot \text{SO}_3 \cdot 5\text{D}_2\text{O}$, $\text{NiSO}_4 \cdot \text{D}_2\text{O}$ or $\text{UO}_3 \cdot \text{D}_2\text{O}$. In order to further establish that the HRT solution is phase stable at 300°C and that the composition is near the solubility boundary for $\text{CuO} \cdot 3\text{UO}_3$, a solubility experiment was performed. After equilibrating the synthetic HRT fuel solution in a titanium bomb at 300°C for 4 days with an excess of the red solid, $\text{CuO} \cdot 3\text{UO}_3$, the sampled solution gave the following analysis:

$$\text{UO}_3 = 0.0312 \text{ molar}$$

$$\text{CuO} = 0.0140 \text{ molar}$$

$$\text{NiO} = 0.0054 \text{ molar}$$

$$\text{MnO} = 0 \text{ molar}$$

$$\text{SO}_3 = 0.0602 \text{ molar.}$$

The only solid remaining in the bomb was $\text{CuO} \cdot 3\text{UO}_3$, according to petrographic and x-ray diffraction examinations. The solubility ratio,²

$$\frac{1/2 \underline{m} \text{UO}_3 + \underline{m} \text{CuO} + \underline{m} \text{NiO}}{\underline{m} \text{SO}_3},$$

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(2) W. L. Marshall, Reported in HRP Qtly. Prog. Rep., Jan. 31, 1959, ORNL-2696, p. 205.

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for the solution in equilibrium with the solid was 0.58. This value is substantially in excess of the "safe" value of 0.5, which has been chosen as a guide for estimating stability toward solid precipitation at 300°C and with

a total SO_3 concentration of 0.06 molar. Both a lowering of the SO_3 concentration and an increase in temperature would be expected to cause a lowering of the solubility ratio for solid precipitation.

In order to determine whether the solution is stable toward solid precipitation over the temperature range from 300 to 332°C , the temperature at which the second liquid phase is produced, it was necessary to use another method. A 3 cc volume of the synthetic HRT fuel solution was sealed in a large-diameter silica tube (8 mm I.D., 2 mm wall) and held in a furnace at several temperatures in the following sequence with respect to time:

<u>T ($^\circ\text{C}$)</u>	<u>Time</u>
297	15 Min.
314	15 Min.
320	15 Min.
327	15 Min.
329	17 Hrs.

After each period of time the tube was quenched in ice water and the interior of the tube was observed with a microscope. No solids were observed as had been seen in previous similar tests with 1 mm I.D. silica tubes. Apparently the small surface to liquid volume ratio in the larger tube minimized the corrosion solubilization of SiO_2 and its detrimental effects on solution stability.

General significance. The results have shown that the particular HRT synthetic fuel solution is stable toward hydrolytic solid precipitation at temperatures up to 332°C where the second liquid phase is produced. The higher acidity of solutions more concentrated than the HRT fuel should place these solutions even further from the solid-liquid solubility boundary than

the HRT fuel solution. Therefore, upon concentrating the HRT fuel solution at temperatures above 305°C , a second liquid must be the first phase to appear, although this second liquid phase could convert rapidly to solid as its temperature rises to very high levels. This increase in temperature, due to the increase in fission density within the heavy-liquid phase, would quickly boil away water (D_2O) from the heavy phase, cause decomposition and ultimately produce solid oxides. The boundary limit for second liquid phase formation must be the important limit rather than the solid-liquid boundary limit if boiling concentration either on the core wall or within the solution is indeed the mechanism by which loss of uranium from solution occurs.

Since the minimum temperature in Figure 1 for liquid-liquid immiscibility is 305°C , it is evident that HRT solutions which would boil and concentrate below 305°C would ultimately form a solid phase or phases instead of a second liquid phase. However, to precipitate these solid phases the fuel solution would have to be concentrated by a factor of 150 or greater in molar units and the solid phases in all probability would be stoichiometric or acid salts rather than hydrolytic solids. There is very much less probability of concentrating the HRT fuel solution to a factor of 150 than to factors of 2 to 6; in either event, fuel components would be lost from solution.

If the HRT fuel solution is diluted with D_2O at some point in the reactor system, the solution will become less acidic, and consequently the hydrolytic precipitation of a solid becomes more likely. Since there is a concentration gradient in the reactor system at the junction of the pressurizer and fuel system due to dilution of the fuel at this location, a solid might precipitate there. Increased temperature at the junction would also favor

precipitation of solid. Indeed, D. M. Richardson³ has reported finding

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- (3) D. M. Richardson, "Composition of Solids from HRT Mockup Pressurizer," ORNL CF-56-6-56.
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crystals of a material with an analysis corresponding approximately to that of $\text{CuO} \cdot 3\text{UO}_3$, but containing small amounts of other metals such as nickel, iron and manganese in the horizontal pipe connecting the steam pressurizer (340°C) and the main loop of the HRT mockup. Also, Richardson⁴ found approxi-

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- (4) D. M. Richardson, "Composition of Solids from HRT Pressurizer Line," ORNL CF-57-5-36.
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mately 20 gms of the same material in the horizontal pipe and flange which connect the HRT fuel pressurizer with the outlet from the reactor core vessel after HRT Run No. 7 with depleted fuel solution. The x-ray diffraction patterns of the solids reported by Richardson are essentially identical to that for the red solid, $\text{CuO} \cdot 3\text{UO}_3$.

SIGNIFICANCE WITH RESPECT TO

CURRENT OPERATION OF THE HRT⁵

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- (5) This section was added to the report during the revision process. The experimental data and partial conclusions have been mentioned previously in ORNL Project and Status Report for June, 1959. ORNL-2781, p. 4 (1959).
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Upon lowering the pressurizer temperature to 301°C the HRT has been operated at 5.0 megawatts without any apparent fuel stability problems.⁶

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- (6) S. E. Beall, E. G. Bohlmann, D. M. Richardson and R. B. Briggs,
"Operations of the HRT over the Period July 4 to August 4, 1959."
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In previous operations over the past month the pressurizer temperature was varied from 314 to 324°C. At these higher temperatures the threshold power of operation, established by loss of uranium from solution, was inversely proportional to pressurizer temperature. The minimum two-liquid-phase temperature of 305°C may be very significant in that it may establish a maximum temperature limit for operation of the pressurizer. In other words, at pressurizer temperatures below approximately 305°C the formation of the second liquid phase and consequent loss of uranium from solution may not be possible. The reduced temperature of the pressurizer should also make it less likely that the hydrolytic precipitation of solids such as $\text{CuO} \cdot 3\text{UO}_3$ would occur at the junction of the pressurizer and fuel system where the fuel is undergoing dilution. Additional acidity of the fuel can both raise the two-liquid-phase temperature minimum and inhibit hydrolytic solid precipitation at locations in the system where the fuel is undergoing substantial dilution, thus making higher pressurizer temperatures possible for operation.

Figure 1
THE TEMPERATURE OF THE APPEARANCE OF THE SECOND
LIQUID PHASE AS A FUNCTION OF DILUTION AND
CONCENTRATION OF THE HRT FUEL

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