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SUBJECT: POSSIBILITY OF PEROXIDE PRECIPITATION WHEN THE
REACTOR CELL IS FLOODED

TO: S. E. Beall

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SUMMARY

When the reactor cell is flooded for maintenance operations, there exists the possibility that radioactive fuel solution will be cooled to temperatures which will permit peroxide precipitation of the uranium. If the flood water temperature is 30°C or above, the fission product decay heat alone will keep the temperatures in the dump tanks or storage tanks safely above that at which peroxide precipitation would be expected. If process water (instead of steam condensate) is used to flood the cell, the flood water temperature will be lower and it will be necessary to add heat through the evaporator jackets to keep the tank contents hot. Precipitation in small, uninsulated lines can be avoided by flushing out fuel solution before the cell is flooded.

INTRODUCTION

It is expected that after the HRT has operated at high power, some maintenance operations will require that the reactor cell be flooded. One of the problems involved in such a step is the peroxide precipitation of the uranium which would occur if the highly radioactive solution were cooled below some limiting temperature. In principle, at least, insulation of the tanks which will contain the active solution would insure safe temperatures, since the same activity which produces the peroxide also generates heat to keep the temperature of the fuel solution above that of the surrounding flood water.

MINIMUM SAFE TEMPERATURE

Wood¹ calculated the relation between power density and temperature necessary to prevent peroxide precipitation in the HRT fuel solution. He took into account the promoter effect of 0.005 M copper on the catalysis of peroxide decomposition by iron corrosion products. Although the HRT fuel solution is now expected to contain about twice that amount of copper, experimental results indicate the decomposition rate constant should not be significantly greater.² Therefore, the curve from Wood's memo can be used as a guide. This is the "minimum safe temperature" curve in Fig. 1.

¹P. M. Wood, Possibility of Peroxide Precipitation in HRT Dump and Sampler Lines, ORNL CF-54-11-172 (Nov. 29, 1954).

²M. D. Silverman, G. M. Watson, and H. F. McDuffie, The Decomposition of Peroxide in Aqueous Homogeneous Reactor Systems, TID-2010 (Sept. 1953) p. 60.

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ACTUAL TEMPERATURES

The temperature which will be maintained in the fuel solution by the heat source within it can be estimated as follows: Consider a vessel submerged in water and filled with solution containing a uniformly distributed heat source. Assume that the solution and the walls of the vessel are at a uniform temperature. At steady state the temperature of the solution will be

$$T = T_0 + \frac{3.413 PV}{1.8 AU} ,$$

where

T = solution temperature, °C,

T_0 = flood water temperature, °C,

P = power density, watts/liter,

V = solution volume, liters,

A = vessel surface area, ft²,

U = overall heat transfer coefficient, Btu/hr-ft²-°F.

The above equation points out that temperatures are lowest in vessels where A/V , the surface-to-volume ratio, is highest.

Temperature in Evaporator Legs

When the fuel solution is in the submerged dump tanks or storage tanks, there may not be enough convection currents to keep the entire body of solution completely mixed. It appears likely that the temperature of the solution in the evaporator legs will be lower than that in the main part of the tanks, because of the higher surface-to-volume ratio in the 4-in. legs.

For 4-in. schedule-40 pipe, $A/V = 0.48 \text{ ft}^2 \text{ liter}^{-1}$.

For flooded aluminum foil insulation, the insulation coefficient will be essentially that for conduction through the stagnant water trapped between the layers of foil. The resistance in the pipe walls will be quite low, so the overall heat transfer coefficient will be approximated by

$$U = k/t ,$$

where

k = thermal conductivity of water, 4.3 Btu/hr-ft²-°F-in.,

t = thickness of stagnant water in insulation, in.

Upon substituting the quantities above for A/V and U , the equation for the temperature in the evaporator legs becomes

$$T = T_0 + 0.93 Pt .$$

The thickness of insulation specified for the dump tanks and storage tanks is $3/4$ -in.³ For this thickness

$$T = T_0 + 0.70 P .$$

Temperatures in Main Body of Tanks

Up in the large cylindrical part of the dump or storage tanks, the surface-to-volume ratio which should be used in estimating temperatures is not clear-cut. When the solution temperature is below the boiling point, the metal surfaces above the liquid level will not be as hot as the wetted surfaces. If the solution temperature reaches the boiling point, vapor will contact the vessel walls and bring the wall temperature up to that of the solution.

The total surface area of the pair of 14-in. cylinders in a tank assembly is 118 ft². When the tanks contain about 600 liters, the cylindrical part will hold 500 liters and the wetted surface (in the cylinders) will be 73 ft². Assuming $3/4$ -in. insulation thickness and using only the wetted surface, the equation for the temperature would be

$$T = T_0 + 2.26 P .$$

Using the total surface area, the calculated temperature would be

$$T = T_0 + 1.40 P .$$

The line drawn in Fig. 1 is based on the total surface area, since this predicts the lowest temperature, hence, the most dangerous from a peroxide precipitation point of view.

Temperature in Small Lines

In small lines, where A/V is very high, the temperature of the radioactive solution will approach that of the surrounding water, even if the pipe is insulated. For example, in a $1/2$ -in. schedule-40 pipe (such as line 108 between the dump tanks and storage tanks), if it were insulated with $3/4$ -in. of foil, the temperature would be

$$T = T_0 + 0.032 P .$$

³F. C. Zapp and R. E. Schappel, Aluminum Foil Insulation Schedule, ORNL CF-55-10-126, Revision 1 (April 4, 1957).

POWER DENSITIES EXPECTED IN HRT SOLUTION

The range of power densities which might be expected in the HRT fuel solution when the cell is flooded can be found by extrapolating the curves given by Hill in CF-54-9-64. Extrapolating the curve for infinitely long operation at 5 Mw to a decay time of 24 hours gives a total power of 30 kw. Assuming all of this is uniformly absorbed in 600 liters gives a power density of 0.050 kw/liter. This power density is indicated on Fig. 1. Generally, the power density will be less than this because of somewhat shorter operating time, a longer decay time, and the escape of part of the gamma energy.

DISCUSSION

One of the uncertainties in predicting the temperature of the fuel solution is the temperature of the flood water. From the standpoint of peroxide precipitation, it would be desirable to keep the water in the cell at 30°C or above. This will be practicable if the cell is flooded with condensate made in the 7500 area, since the condensers can be regulated to produce warm condensate. If process water is used to flood the cell, the water temperature may be 20°C or less.

Figure 1 shows the calculated temperatures in the dump or storage tanks proper, in the evaporator legs and in a small pipe, all based on 30°C cell water.

It is obvious from the lower line in Fig. 1 that insulation cannot prevent low temperatures in small lines. Therefore, peroxide precipitation will almost certainly occur in small lines containing radioactive solution whenever they are submerged in water of a reasonable temperature. Trouble can be avoided by flushing lines with condensate before flooding. For example, precipitation in line 108 between the dump tanks and storage tanks could be avoided as follows: Make the transfer of fuel solution from dump to storage tanks, then drop condensate to the dump tanks and transfer that.

Figure 1 shows that if the cell water is around 30°C, the internal heat source will keep solution in the tanks safe from peroxide precipitation. In fact, this figure makes it appear that excessively high temperatures might result from fission product heating. This is not necessarily the case, however, because the curves shown are based on heat transfer through only the surfaces of the tanks proper. If the need arises, non-condensibles can be vented, allowing vapor to fill the lines and condensers above the tanks, thus providing much more surface for heat transfer to the flood water.

If the cell water is much below 30°C, as it likely will be if process water is used, the fission product decay heat alone will not keep temperatures adequately high in tanks insulated with 3/4-in. of foil. One possible answer would be to put more insulation on the tanks. A better way is to supply heat through the evaporators to help keep the

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solution hot while submerged. With the presently-installed 3/4-in. foil insulation on the steam lines to the jackets, heat losses from the steam to the flood water will not be excessive, and the steam pressure can be regulated to hold the temperature in the tanks at any desired level.

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