To: M. W. Rosenthal
From: S. S. Kirslis, F. F. Blankenship and R. A. Strehlow
Subject: Possible Tritium Containment Method

A few days ago, one of us (SS Kirslis) reported to you by phone a brief description of (1) the recent finding of sizable concentrations of tritium in the MSRE moderator graphite and (2) the idea suggested to him by this finding that tritium might be removed from a molten salt reactor fuel or coolant by chemisorption on graphite or other carbonaceous material, or by isotopic exchange with a hydrogen-containing carbonaceous material. This original idea has since been expanded in several directions by closer examination of the analytical results on tritium in MSRE graphite and by discussions among ourselves and with others who are interested in the tritium containment problem. This letter is to provide a written record of the possible invention, to report on the recent developments, and to indicate the type of information needed to evaluate the potential of these tritium trapping ideas.

Background Information on Tritium Sorption. - There is a considerable amount of literature data on the sorption and desorption of hydrogen on various types of graphite and other carbonaceous materials, and the notion of using such sorption or using exchange reactions with hydrogen-containing carbonaceous materials for trapping tritium had been casually discussed by several of us. Walt Eatherly had pointed specifically in writing to the strong chemisorption represented by hydrogen released from graphite at temperatures from 1000 to 1800°C, and speculated that tritium might be similarly sorbed. He also pointed out the possibility of strong radiation-induced chemisorption of tritium on graphite.

However, in the absence of experimental reaction rate data under actual reactor conditions, one could only guess in a qualitative way that some tritium would be sorbed on graphite. On the basis of the literature information it was certainly not possible to predict what the tritium analyses of a graphite stringer from the MSRE core showed - that about 20% of the total tritium produced during the operation of the MSRE was to be found in the moderator graphite.

Tritium analyses in MSRE Moderator Graphite. - A complete graphite stringer from the MSRE core was made available for chemical examination. In order to determine concentration profiles of various fission products from the surface of the graphite stringer to its axis, powdered samples were milled from the flat fuel channel surface at the bottom, middle, and top of the stringer. The thicknesses of the successive milled cuts in mils were 1, 2, 3, 10, 20, 30, 245, 245 and 245. A similar series of milled cuts were made on a flat...
corner surface of the stringer which had been in contact with a similar graphite surface of an adjacent stringer in the MSRE core. Also taken were deep milled cuts (62 mils) from the flat fuel channel surface.

The powdered graphite samples were weighed and dissolved in a boiling mixture of concentrated H_2SO_4 and HNO_3, with a trap to catch volatilized tritium. Aliquots of the dissolver solution and of the trap solution were analyzed for tritium, with the results reported in Table 1 for the selection of samples chosen for the first tritium analyses. Since these proved so interesting, additional samples have been submitted for tritium analysis.

**Total Tritium Retained by the MSRE Moderator Graphite.** - The most significant deduction from the tritium analyses is that a surprisingly large fraction of the total tritium produced during the operation of the MSRE was caught and retained on the moderator graphite. The calculation of tritium hold-up is given below in detail so that the assumptions and approximations made are apparent to any who would like to refine the calculation.

Inspection of the analytical data in Table 1 indicates that the tritium concentration profile dropped rapidly from about 10^{11} dpm/g at the surface to about 10^{9} dpm/g at a depth of 1/16-in. and then decreased very slowly to the center (no values below 6 \times 10^{8} dpm/g). It therefore makes sense to calculate the total tritium content by adding the amount in the outer 1/16-in., calculated as a surface contribution, to the amount in the interior of the graphite, calculated as a volume contribution.

The surface contribution was obtained by multiplying the surface concentration of tritium, dpm T/cm^2, by the total graphite area in the MSRE (∼2 \times 10^6 cm^2). The surface concentration was calculated from the data for the three 1/16-in. deep surface samples (#18, #31, and #32 in Table 1). Normally, to obtain dpm/cm^2, the analytical value of dpm/g is multiplied by the weight of milled sample and divided by the area milled. In this case, only about half of the milled sample was collected by the collection method used. However, the depth of cut was accurately known from the setting of the milling machine. Thus the weight of milled sample was essentially calculated from the known density of graphite and the known depth and area of cut:

\[
\frac{\text{dpm}}{\text{cm}^2} = \frac{\text{dpm}}{\text{g}} \times \text{density} \times \text{area} \times \text{depth} = \frac{\text{dpm}}{\text{g}} \times \frac{\text{g}}{\text{cm}^3} \times \text{cm} \]

(as is seen, the area of cut is not needed to calculate dpm/cm^2.) By this method of calculation the average surface concentration was 1.7 \times 10^9 dpmT/cm^2. Thus the total surface contribution is 1.7 \times 10^9 dpmT/cm^2 \times 2 \times 10^6 cm^2 = 3.4 \times 10^{15} dpmT for the total reactor surface.

The volume contribution to the tritium hold-up in the graphite was simply calculated by choosing a typical or average interior concentration (dpm/g) and multiplying by the total grams of moderator graphite (3.6 \times 10^6 g). Taking the interior concentration as 8.4 \times 10^8 dpm (average of #11, #24, #26 and #41 in Table 1), the total volume contribution was 3.0 \times 10^{15} dpmT for the total moderator volume.
<table>
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<th>Sample No.</th>
<th>Specimen</th>
<th>Cut</th>
<th>Depth, mil</th>
<th>Weight, g</th>
<th>dpmT/g</th>
<th>Area Sample cm²</th>
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</table>

*a The number, eg. 7 3/4, is the distance from the top of the stringer to the bottom of the specimen. Each specimen was about 4 in. long. The cutter diameter was 0.619 in.

*b Up to 9 milled samples were taken cutting into the flat fuel channel surface (M) or a flat corner graphite-contacting surface (E).

*c Corrected to the date of MSRE final shutdown (12-12-69).
The rate of tritium production during full power operation of the MSRE with $^{235}\text{U}$ fuel was 24 Ci per day. The MSRE operated with $^{235}\text{U}$ for the equivalent of 376 full power days. Therefore the number of curies of tritium produced in this period was $24 \times 376 = 9030$ Ci. The MSRE operated with $^{233}\text{U}$ fuel for the equivalent of 174 full power days and generated tritium at the rate of 40 Ci per full power day for a total of 6960 Ci. In the combined operation, thus, 16,000 Ci or $3.54 \times 10^{16}$ dpm of tritium were produced.

It was estimated by an approximation procedure suggested by E. L. Compere that about 10% of the 12.26 year tritium activity produced during the total MSRE operation had decayed by the time of final reactor shutdown (12-12-69). Thus the total tritium activity remaining at reactor shutdown was about $3.2 \times 10^{16}$ dpm.

Using the corrected remaining total tritium activity, the percentage found in surface graphite was 10.6% and that in interior graphite was 9.4%, for a total of 20% of the total tritium produced during the operation of the MSRE. (These results may vary somewhat in the future as the results of more tritium analyses of MSRE graphite become available).

These are the surprisingly large trapped percentages that made it clear that MSRE moderator graphite must have been a fairly efficient tritium trap. Since tritium had a mean life in the circulating fuel of only a few minutes before it was lost to the off-gas or by diffusion through the heat exchanger wall, the graphite trapping reaction rate must have been fast to catch 20% of the tritium. Another conclusion from the size of the trapped percentage is that the tritium in the graphite could not have arisen from the presence of, say, Li impurity in the graphite. The amount of tritium found in the graphite would have required a normal lithium content of about 60 ppm. Analysis indicated only 5 ppm total ash and less than 1 ppm of lithium.

Finally, it must be pointed out that in case some of the trapped tritium at high surface concentrations could undergo a reverse reaction to leave the graphite, the fraction of tritium picked up might have been considerably higher if the tritiated surfaces had been replaced frequently with tritium-free graphite surfaces. If as much tritium diffused from the surface back out to the salt as diffused into the interior, then possibly another 9.4% of the total tritium might have been caught on rapidly renewed graphite surfaces.
Further Conclusions from the Tritium Analyses. - It was mentioned above that the tritium concentration profile dropped rapidly from about $10^{11}$ dpm/g at the surface to about $10^9$ dpm/g at a depth of 1/16-in., with a slow decrease thereafter to the center of the stringer. This type of profile indicates that the tritium was very strongly bound or immobilized at the surface where it entered the graphite and that its diffusion rate inside the graphite was very slow. This behavior is not consistent with an isotopic exchange mechanism for trapping tritium on graphite. In an exchange reaction the combined hydrogen plus tritium pressure would not change, and would have to be appreciable to result in the rapid reaction required to hold up 20% of the tritium produced on the graphite. However, the same rapid exchange reaction would cause the tritium to be distributed uniformly throughout the graphite instead of producing the observed fairly steep profiles. This is not to say that exchange would not occur if the graphite were exposed to larger amounts of hydrogen or tritium, but merely that it did not occur under MSRE conditions. In other words, the partial pressures of gaseous hydrogen, tritium, volatile hydrocarbons or volatile tritocarbons must have been exceedingly low in the graphite pores. The simplest explanation of this is that the hydrogen or tritium was very strongly chemisorbed on empty active sites on the graphite surface. As pointed out by W. Eatherly, radiation-induced chemisorption may also have been involved.

An ingenious alternative theory was suggested by E. G. Bohlmann and E. L. Compere who observed that the heavy carbonaceous deposits on and inside the mist shield in the MSRE pump bowl contained tritium concentrations even higher than those measured on the graphite stringer surfaces. They are speculating that the thermal and radiolytic decomposition of pump oil leaking into the MSRE pump bowl may have had much to do with the appearance of tritium on reactor surfaces. The charred carbonaceous decomposition products, containing non-volatile strongly bound hydrogen and tritium, may have circulated in the MSRE fuel circuit and left deposits on the graphite surfaces. Diffusion of tritium from such deposits into interior graphite would be slow.

It should be emphasized that hydrogen exchange provides a completely independent mechanism by which tritium may be abstracted from a salt or gas phase into a carbon phase. For this mechanism to operate rapidly it is desirable that the carbon phase be rich in hydrogen which is stably bound at 650°C and that the hydrogen pressure be appreciable. R. A. Strehlow has pointed out that carbonaceous materials are available which stably hold 5 to 8 atom % hydrogen at 650°C. E. L. Compere predicts that exchange reaction rates should be rapid, since in his own experience thermal cracking of heavy oil fractions proceeds rapidly at 600°C, and similar free radical mechanisms are probably involved.

The practical choice between the chemisorption and the exchange methods will depend upon relative reaction rates, capacities and other special characteristics. For example, if radiation-induced chemisorption was mainly responsible for the trapping of tritium on MSRE moderator graphite, then the chemisorption method may not be effective in the coolant salt. Also it may develop that both mechanisms may be applied even with the same material. The chemi-
sorption method could sorb hydrogen and tritium until the active sites were saturated; then the hydrogen pressure would build up in the pores and the exchange mechanism would take over.

It was pointed out by R. A. Strehlow that HF and TF may be involved in the tritium trapping reactions. An appreciable fraction of the total gaseous and dissolved tritium in a molten salt reactor fuel is present as TF. It is known that HF is a powerful catalyst for cracking and reforming hydrocarbons. Therefore a particularly strong effect of HF partial pressure on exchange reactions should be expected.

Information Needed.—In order to evaluate the potentialities of the two suggested methods of trapping tritium from molten salt reactor fuel or blanket salt circuits, laboratory confirmation of a number of critical points is urgently needed.

1. Measurement of the rate of chemisorption of tritium at 500-650°C from the gas phase on graphite and other carbonaceous materials which have been thoroughly degassed at 650 to 1000°C. Half-lives greater than a few minutes are not of practical interest.
   a. Effect of radiation or gaseous discharge treatment of graphite on above.
   b. Effect of other activation methods.

2. Measurement of the rate of exchange of gaseous tritium with hydrogen containing carbonaceous materials at 500-650°C.
   a. First measure exchange rate of hydrogen with MSRE graphite which already contains tritium. (Suggested by W. R. Grimes).
   b. Measure effects of hydrogen pressure and hydrogen content of graphite on exchange rate.

3. Repetition of above experiments in metal systems containing molten fluorides at various oxidation potentials to provide various HF partial pressures.

Acknowledgments.—The authors gratefully acknowledge the encouraging comments and helpful suggestions of many individuals in the Reactor Chemistry and Reactor Divisions with whom the ideas in this letter were discussed. We want to express particular appreciation to E. L. Compere and E. G. Bohlmann for many useful consultations, and to E. G. Bohlmann and W. P. Eatherly for the foresight to insist on obtaining tritium analyses on graphite samples exposed in the MSPE. Without these analyses, it would have been difficult to take seriously the idea of trapping tritium on carbonaceous materials.

References
