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MEASURING THE RELEASE OF SHORT-LIVED FISSION GASES DURING CAPSULE IRRADIATIONS

by

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A technique is described for the determination of the release of short-lived fission gases during capsule fuel irradiations. Sweep helium passes over the fuel specimen and carries fission gases to a delay trap located close to the capsule. Short-lived fission gases decay in the trap and deposit long-lived daughters which are assayed by radiochemical methods after trap removal. In two demonstrations of the technique the radiochemical analyses have provided information on the rate of release of 1.7-sec xenon-141, 16-sec xenon-140, 3.9 min xenon-137, and 3.2-min krypton-89. The technique should find considerable application in the irradiation evaluation of fuel materials when it is necessary to determine the contribution short-lived fission gases make to the coolant-contamination problem.

INTRODUCTION

Over the past year Battelle has used several methods to determine the release of fission gas during in-pile capsule experiments. One method consists of sweeping the fuel specimen with helium, passing this carrier gas through a refrigerated charcoal trap, and analyzing the trap radioactivity by gamma spectrometry methods. The method is satisfactory for the determination of gamma-emitting fission gases having moderately long and long half-lives. The method is not suitable for the short-lived fission gases because these species decay before the sweep helium reaches the trap. In addition, these short-lived species are frequently beta emitters which are difficult, if not impossible, to identify and measure in a mixture of fission gases.

The purpose of this report is to describe a method of determining the amount of short-lived fission gases carried in a gas stream. Two demonstrations of the method in an in-pile capsule experiment are discussed.

This work was carried out for Sanderson & Porter in support of the fuel-element evaluation program for the Pebble-Bed Reactor.

DESCRIPTION OF THE METHOD

An indirect method is used to determine the short-lived fission gases carried in the sweep helium. Sweep helium from the irradiation capsule is passed through a delay trap located near the capsule exit. The trap is filled with stainless steel mesh to provide a large surface area. Trap volume is large compared to the volume flow rate of the sweep helium. Short-lived fission gases decay in the trap, depositing long-lived daughter radioactivities which are assayed by radiochemical methods after trap removal. Decay of the fission gases outside the trap is reduced by keeping the helium transit time

between the fuel specimen and the trap entrance small. This is readily achieved by minimizing the free volume in the capsule and by using narrow-bore tubing between the capsule and the trap.

In the applications of this method described below the following fission-product chains were selected for study.

(1) Kr^{89} $\xrightarrow{3.2\ min}$ Rb^{89} $\xrightarrow{15.4\ min}$ Sr^{89} $\xrightarrow{51\ days}$

(2) Xe^{137} $\xrightarrow{3.9\ min}$ Cs^{137} $\xrightarrow{29\ years}$

(3) Xe^{140} $\xrightarrow{16\ sec}$ Cs^{140} $\xrightarrow{66\ sec}$ Ba^{140} $\xrightarrow{12.8\ days}$ La^{140} $\xrightarrow{40.2\ hr}$

(4) Xe^{141} $\xrightarrow{1.7\ sec}$ Cs^{141} $\xrightarrow{short}$ Ba^{141} $\xrightarrow{18\ min}$ La^{141} $\xrightarrow{3.7\ hr}$ Ce^{141} $\xrightarrow{33\ days}$

Radiochemical analyses of the strontium-89, cesium-137, barium-140, and cerium-141, the trap sampling time, and the residence time of the fission gases in the trap give the rate of entry of the short-lived fission gases into the trap. It is this rate which is of immediate interest in a fission-gas-release study of a fuel specimen.

$$R = \frac{A\lambda_d}{e^{-\lambda_p t}\left(1 - e^{-\lambda_p t_r}\right)\left(1 - e^{-\lambda_d T}\right)}, \qquad (1)$$

where

R = release rate of short-lived fission gas from fuel specimen, atoms per sec

A = concentration of daughter in trap at shutdown, atoms

λ_d = decay constant of daughter, sec^{-1}

λ_p = decay constant of fission gas, sec^{-1}

t = transit time between fuel specimen and trap entrance, sec

t_r = residence time of fission gas in trap, sec

T = trap sampling time, sec.

The denominator of Equation (1) contains terms for the decay of the fission gas before it reaches the trap, fission-gas breakthrough, and daughter buildup. In the two experiments described below the distribution of daughters in the trap shows that the breakdown correction is valid.

A large trap volume is not required if free space prior to the trap is minimized and the determination is restricted to fission gases with half-lives less than a few minutes. In a typical capsule experiment, the helium flow rate is the major factor deciding the choice of trap size.

IN-PILE EXPERIMENT

Two traps have been operated on a sweep capsule irradiated in the core of the Battelle Research Reactor. The capsule contains two fuel specimens, in separate compartments, each swept by independent helium streams. Sweep helium passes through a thin annulus separating the fuel specimen from the capsule body. The fuel specimens operate at a temperature of about 1500 F.

Equipment

The in-pile experiment is shown in Figure 1. Only one delay trap and helium system are shown. Exit helium from the capsule flows either directly to the gas train or through the trap by manipulation of the appropriate valves. Long-lived fission gases, krypton-85m, krypton-87, krypton-88, xenon-133, and xenon-135, are measured in the gas train.

Stainless steel mesh, in the form of tightly wound rolls, is stacked end to end in the trap for the deposit of the daughter radioactivities (Figure 2). The mesh is made from 6-mil wire and the mesh size is 1/8 in. The trap is fabricated from Type 304 stainless steel tubing. Before assembly, the as-received tubing and mesh are washed with soap and water, and rinsed with acetone. Important parameters in the trap experiments are listed below.

Trap wall area	2 ft^2
Surface area of mesh	32 ft^2
Volume fraction of mesh in trap	0.04
Helium pressure	~1 atm
Volume flow rate of helium	~30 ml per sec STP
Transport time of helium between fuel specimen and trap entrance	~2 sec
Residence time of helium in trap	90 to 125 sec

Radiochemical Procedures

On completion of a trap experiment, the stainless steel mesh is removed and analyzed for fission products. Radiochemical procedures for barium-140, strontium-89, cerium-141, cesium-137, iodine-131, and iodine-133 are described below. The last two species were observed in one of the trap experiments and undoubtedly escape from the fuel specimen as iodine and not as iodine precursors.

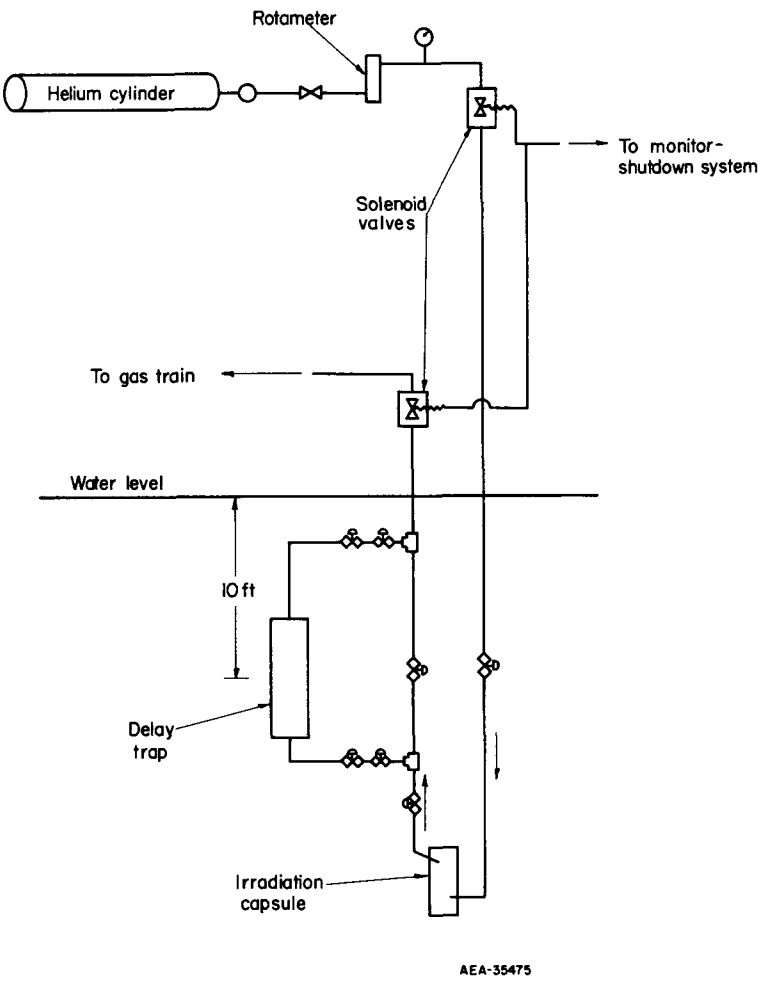

FIGURE 1. IN-PILE EXPERIMENT

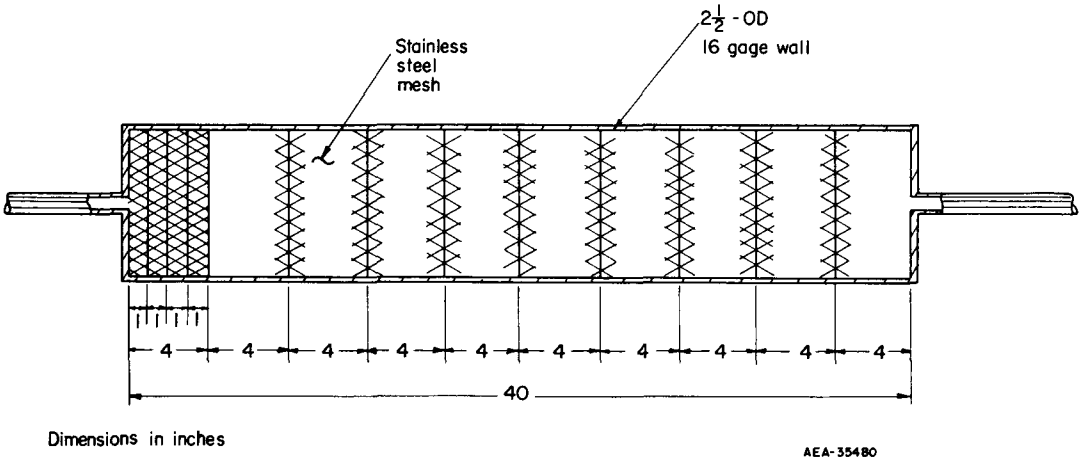

FIGURE 2. DELAY TRAP

Radiochemical Analyses

Fission products are etched from the rolls of stainless steel mesh with 75 ml of 3 N hydrochloric acid solution containing 4 mg each of cerium, strontium, barium, and cesium carriers. When iodine is to be determined, iodine carrier and 30 mg of sodium bisulfite are added. Bisulfite prevents the loss of iodine. A small addition of concentrated nitric acid to this solution will speed up the etch, but is not essential.

The etch is not selective. Several rolls were etched, and then dissolved. Gamma scans of the etch solution and the dissolved rolls were identical and showed that the same fraction of all fission products was removed by the etch. Strontium-89 analysis of both solutions showed that the etch removed 95 per cent of this fission product from the rolls.

The radiochemical separations, with the exception of cesium-137, parallel those described in the Oak Ridge Master Analytical Manual[1].

Barium-140

Twenty milligrams each of barium and strontium carriers are added to a 10-ml aliquot of the fission-product solution, and the nitrates of barium and strontium are precipitated with fuming nitric acid. This precipitation is repeated and a ferric hydroxide scavenge performed. Barium is separated from strontium by precipitation of barium chromate. The supernate is saved for the strontium analysis. The barium chromate is dissolved in hydrochloric acid, and two chloride precipitations performed with hydrochloric acid and ether. The barium chloride is weighed to determine the yield, and stored for 8 or 9 days to establish equilibrium between the barium-140 and lanthanum-140. Barium-140 is determined by measuring the 1.6-Mev gamma ray from lanthanum-140.

Strontium-89

Strontium is precipitated as the oxalate from the supernate remaining from the barium separation. The precipitate is weighed to determine the yield. Radiochemical purity of the strontium-89 is verified by a gamma scan and an aluminum-absorption curve. The strontium-89 activity is determined by counting the 1.5-Mev beta in an absolute beta counter.

Cerium-141

Twenty milligrams each of cerium, lanthanum, and zirconium carriers are added to 10 ml of the fission-product solution, and the rare-earth fluorides precipitated with hydrofluoric acid. The precipitate is dissolved in a boric acid-nitric acid mixture, and cerium (IV) iodate precipitated in the presence of bromate. This precipitate is dissolved in a hydrochloric acid-hydrogen peroxide mixture and the iodate precipitation repeated. The iodate is dissolved, zirconium carrier added, and a zirconium iodate scavenge performed. Cerium (III) is precipitated twice as the hydroxide, followed by a final

(1) Reference at end.

precipitation as the oxalate. The cerium oxalate is weighed to obtain the yield, and the cerium-141 activity determined by measuring the 0.14-Mev gamma ray.

Iodine-131 and Iodine-133

Twenty milligrams of iodide carrier is added to 10 ml of the fission-product solution. Iodine is separated from other fission products by oxidation to periodate with sodium hypochlorite, followed by reduction to iodine with hydroxylamine hydrochloride, and extraction of the iodine into carbon tetrachloride. The iodine is back-extracted into aqueous sodium bisulfite, and the extraction and back-extraction repeated. Iodine is precipitated finally as silver iodide and weighed to determine the yield. Iodine-131 and Iodine-133 activities are determined by measuring the 0.364- and 0.530-Mev gamma rays, respectively.

Cesium-137

A tetraphenylboron precipitation is used to determine cesium-137. Ten milligrams of cesium carrier is added to 10 ml of the fission-product solution. Cesium tetraphenylboron is precipitated by addition of 4 ml of 0.03 M sodium tetraphenylboron. The precipitate is dissolved in acetone, and two ferric hydroxide scavenges performed. The tetraphenylboron precipitation is repeated and the precipitate weighed to determine the chemical yield. A beta counter is used to determine the cesium-137.

Results

One trap was operated for 24 hr. The residence time of the helium sweep gas was 90 sec. The second trap was operated for 2 hr and the residence time was 125 sec. Selected rolls of mesh from both traps were analyzed for strontium-89, barium-140, and cerium-141. In addition, the first trap was analyzed for iodine-131 and iodine-133 and the second was analyzed for cesium-137. Results are shown in Figures 3, 4, 5, and 6.

If the only source of strontium-89, barium-140, cerium-141, and cesium-137 in the trap is the decay of 3.2-min krypton-89, 16-sec xenon-140, 1.7-sec xenon-141, and 3.9-min xenon-137, and every daughter sticks where it is formed, the daughters should follow the predicted distributions (solid lines) in Figures 3, 4, and 5. The points are experimental values, corrected for decay between trap shutdown and analysis. Good agreement shows that very little, if any, of the strontium-89, barium-140, cerium-141, and cesium-137 escape the fuel specimens in this capsule experiment.

It is interesting to note that 3.2-min krypton-89, instead of 4.5-sec bromine-89, determines the distribution of strontium-89 in the trap. This is to be expected because, for any trapping efficiency, this short-lived species is concentrated near the trap entrance and decays rapidly to krypton-89 which is not absorbed in the trap. Accordingly, bromine-89 will have very little effect on the half-life of the strontium-89 distribution in the trap.

Very little of the daughters deposit on the inside wall of the trap. The wall of one trap was etched in several areas and the gross activity of these etch solutions

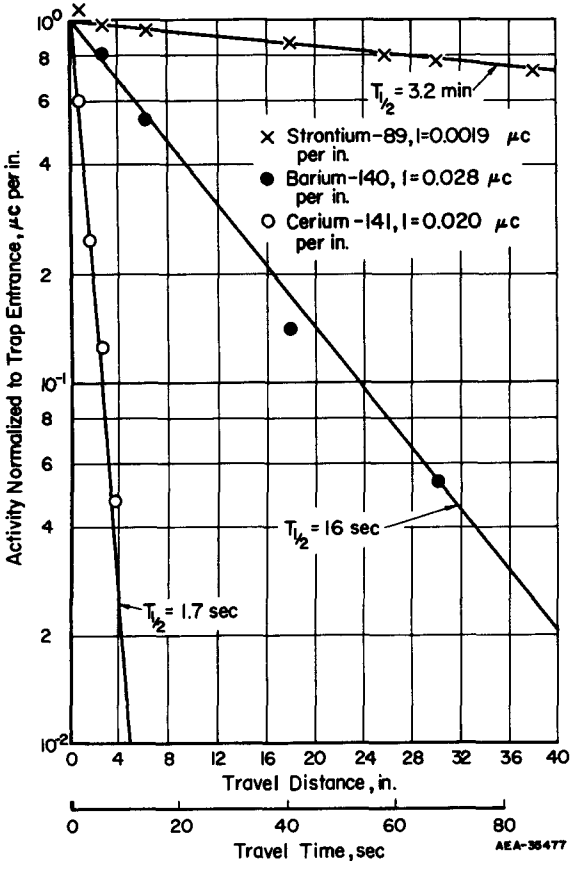

FIGURE 3. DISTRIBUTION OF STRONTIUM-89, BARIUM-140, AND CERIUM-141 IN FIRST TRAP EXPERIMENT

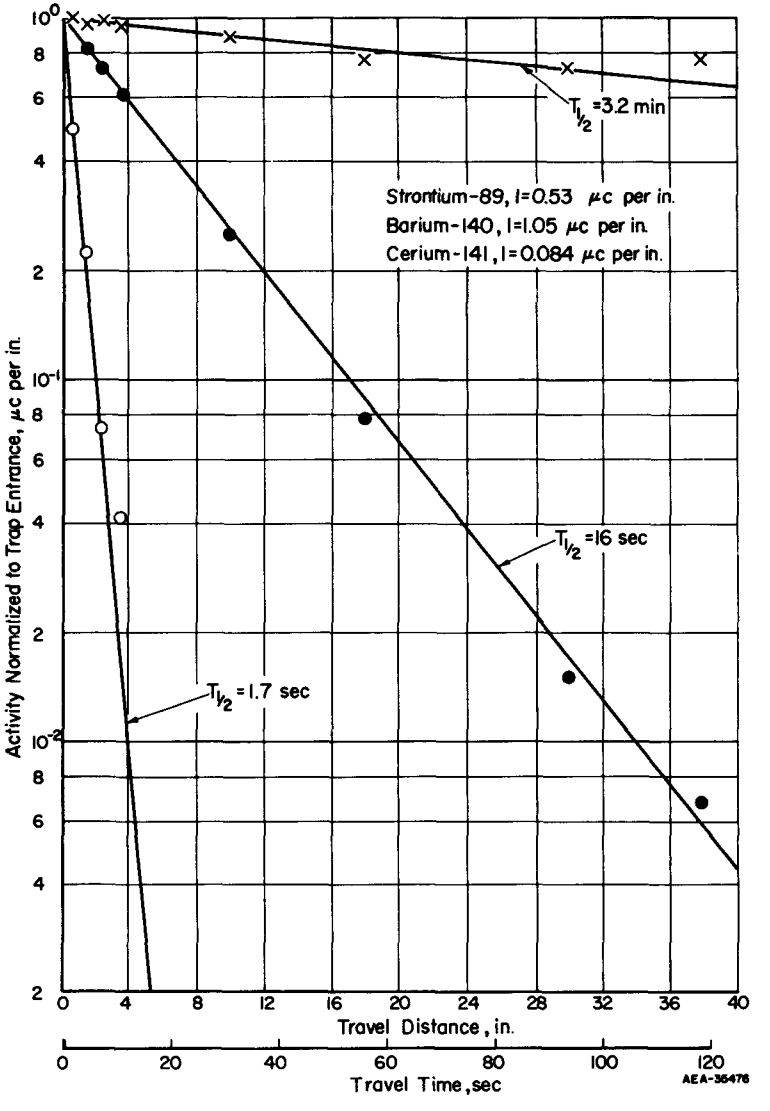

FIGURE 4. DISTRIBUTION OF STRONTIUM-89, BARIUM-140, AND CERIUM-141 IN SECOND TRAP EXPERIMENT

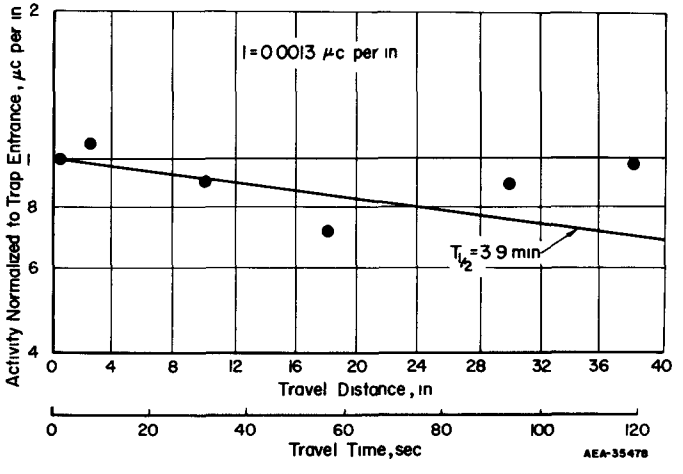

FIGURE 5. DISTRIBUTION OF CESIUM-137 IN SECOND TRAP

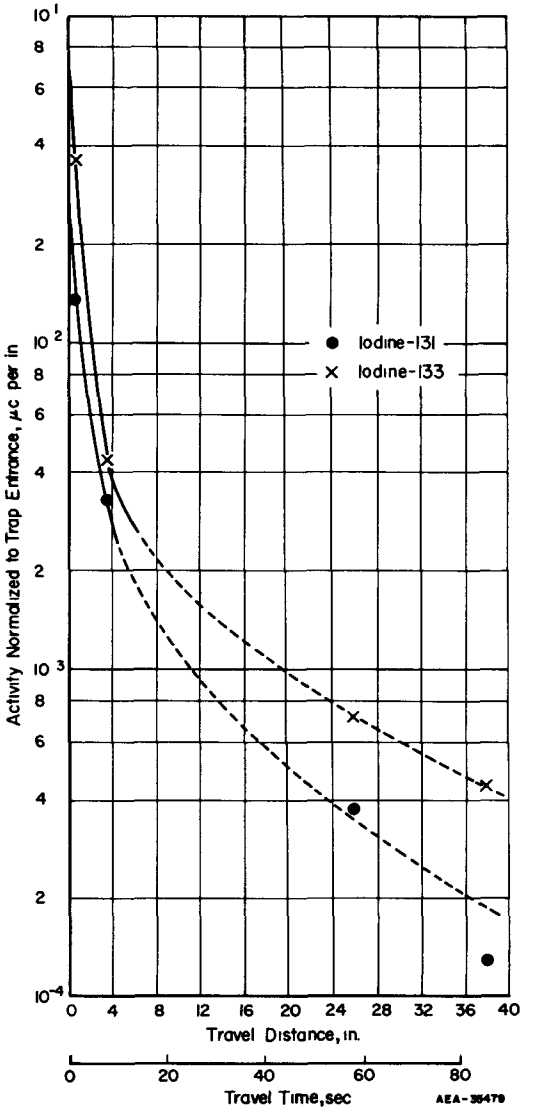

FIGURE 6. DISTRIBUTION OF IODINE-131 AND IODINE-133 IN FIRST TRAP

compared with the activity etched from rolls adjacent to these wall areas. Less than 2 per cent of the activity on the roll at the entrance of the trap was found on the adjacent wall. A negligible amount of activity was found on the wall next to the second roll.

Iodine-133 and -135 results are presented in Figure 6. Below 10^{-3} μc per in. counting statistics are poor and the shape of the curve in this region is uncertain. The iodine-131/iodine-133 ratio in the trap is the same as this ratio in the fuel specimen. This is evidence that iodine escapes the fuel specimen as iodine and not in the form of iodine precursors alone.

DISCUSSION

The delay trap has proven to be a good solution to the problem of measuring the release of short-lived fission gases during fuel-capsule experiments. Data of this type are very helpful in a study of fission-gas-release mechanisms and provide valuable information on the coolant-contamination problem. This latter feature is important in view of the increasing emphasis on higher fuel temperatures where diffusion release alone can present a coolant-contamination problem.

One final remark on the delay trap seems appropriate here. There appear to be cases where traps in series can be used with advantage. Traps of various sizes (residence times) can be used in series to separate the daughters of short-lived fission gases into groups. The smallest trap is located next to the capsule.

REFERENCE

(1) Master Analytical Manual, Section 2, Oak Ridge National Laboratory, TID-7015 (1957).

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