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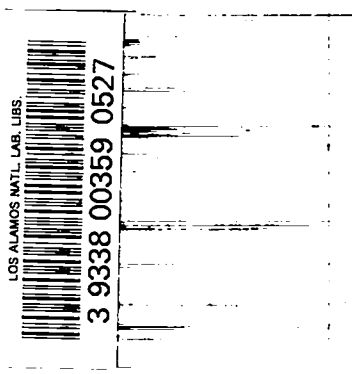
Venting Experiments with a Liquid Plutonium Alloy



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Report written: August 15, 1967
Report distributed: November 16, 1967

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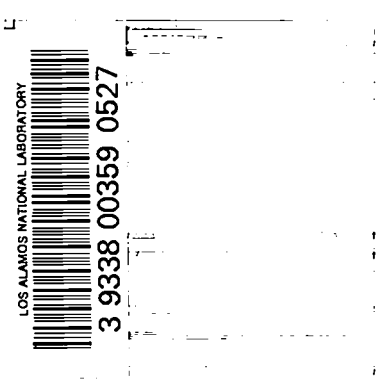
by

J. C. Clifford



VENTING EXPERIMENTS WITH A LIQUID PLUTONIUM ALLOY

J. C. Clifford

ABSTRACT

To determine the feasibility of venting fission gases from a liquid plutonium alloy fuel to sodium, open capsules containing the fuel were immersed in flowing sodium at 600°C and 650°C. In some instances the fuel and sodium were in contact; in others, a helium buffer was interposed. Container materials were tantalum and a Ta-5W alloy with and without an internal coating of TaC. Plutonium losses from capsules without a TaC layer were excessive after test times as short as 1000 h. The addition of the TaC layer reduced plutonium losses to an estimated 10^{-4} to 10^{-5} of the original inventory per year. Work on the liquid plutonium alloy fuel was terminated before in-pile experiments could be initiated.

INTRODUCTION

The experiments described here were performed during the development of liquid plutonium fuels for a sodium cooled fast reactor. In this concept, a Pu-Co-Ce alloy was contained in an array of tantalum alloy fuel pins operating in the 600° to 700°C range.

As a solution to the liquid fuel containment problem became apparent (at least out-of-pile), increased attention was given to other burnup-limiting problems. One of these is fission gas buildup in the pins, since complete gas release is anticipated (and observed) during irradiation. Increased pin wall thickness or gas reservoir volume would accommodate larger quantities of fission gases, although the additional tantalum alloy required would have detrimental effects on neutron economy. Another method for handling fission gases might be to vent the gases to the coolant.

These experiments were intended as a first step in establishing the feasibility of venting fuel pins to the primary coolant. Work on the concept was terminated before in-pile venting experiments had been initiated.

EXPERIMENT DESCRIPTION

Vented capsules containing Pu-Co-Ce alloys have been exposed to flowing sodium at 600°C and 650°C in small, hot-trapped, forced-convection loops. Both direct-contact (between fuel and sodium) and helium-buffered capsules were tested. Early experiments were conducted in a loop consisting of a 650°C test section, an air-cooled heat dump, and a plugging indicator (Fig. 1). The results of these experiments have been reported previously in more detail.[1] Later, a less complicated isothermal loop operating at 600°C was substituted (Fig. 2).

All sodium-wet sections of the loops were Type 304 or 316 stainless steel, and zirconium foil was used to control oxygen levels in the sodium. The sodium capacity of the loops was 10 lb or less, and the mass flow rate was 300-400 lb/h, providing vel-

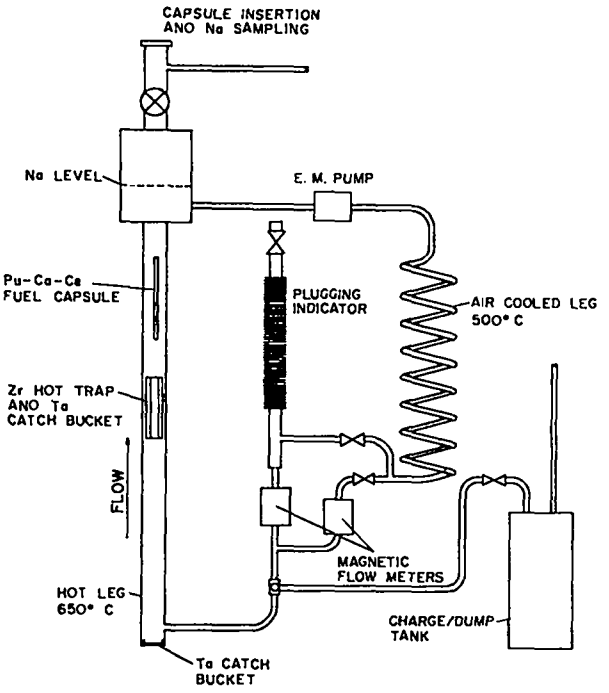


Fig. 1. Nonisothermal sodium loop for venting experiments.

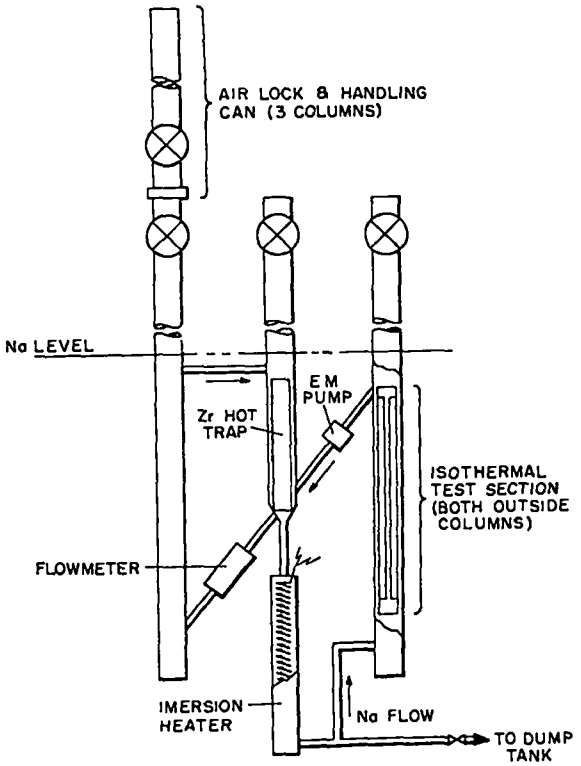


Fig. 2. Isothermal sodium loop for venting experiments.

ocities of about 1 in./sec in the fuel test sections.

The Pu-Co-Ce alloys, containing 5 to 6.2 g Pu/cm^3 fuel, were held in open tantalum or Ta-5W capsules of 3- to 16-in. length, 0.4-in. o.d., and 0.015- to 0.022-in. wall. To prevent contact of fuel and sodium in certain capsules, a cylinder, sealed at one end, was inverted and placed over the mouth and upper portion of the capsule. Helium was trapped in the top of this assembly during immersion of the capsule in sodium. Capsules were submerged singly or in groups in the test sections for 1200 to 6400 h (Table I) and were radiographed periodically to detect any gross fuel loss.

Table I

Vented Capsule Test Conditions

Capsule Number	Container Material	Time (h)	Temperature (°C)
2151	Ta	1500	650
2227	Ta	2500	650, 475*
2228	Ta	2500	650, 475*
2232	Ta	2500	650, 475*
2233	Ta	2500	650, 475*
2288	Ta	1200	650
2297	Carburized Ta	1200	650
2295	Ta	1200	650
2149	Ta	2800	650
2152	Ta	2800	650
2247	Carburized Ta	2800	650
1062	Carburized Ta-5W	2006	600
1328	Carburized Ta-5W	2006	600
1421	Carburized Ta-5W	2006	600
1321	Carburized Ta-5W	6403	600
1419	Carburized Ta-5W	6403	600

*Failure of a cooler necessitated operating the sodium system at 475°C for 1000 h.

During the initial tests, impurity levels in the sodium were determined using a plugging indicator and a dip sampler. Over an 11,000-h period plutonium, cobalt, and cerium levels did not exceed the detection limits of 0.1, 2, and 4 ppm, respectively. The plugging indicator showed a startup oxygen level of 30 ppm, which dropped to less than 10 ppm and remained below this level. Experience with other hot-trapped systems equipped with *in situ* distillation samplers,[2] and containing comparable amounts of sodium and zirconium, suggests that the oxygen level

was below 5 ppm. Impurity levels in the isothermal system were not monitored. Judging from the condition of the zirconium foil and fuel capsules at the end of the tests, the sodium was of the same quality as that from the first loop.

BEHAVIOR OF ANNEALED TANTALUM CONTAINERS

The capsules shown in Fig. 3 are typical of

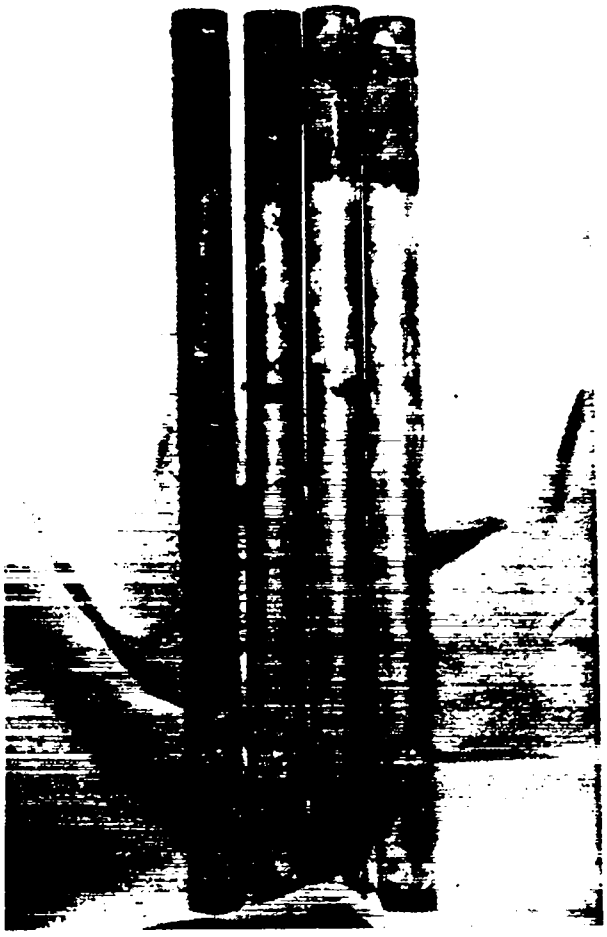


Fig. 3. Vented capsules after 2500 h in 650°C sodium.

the annealed tantalum capsules tested. The black, roughened appearance of the upper ends was caused by a fuel film that spread over the walls from the fuel-sodium interfaces. The light colored markings are sodium oxide, and the darker discolorations just above the capsule centers and near the tips are points of contact between capsule and holder. The fuel-spread phenomenon is further illustrated by the condition of a 3-in.-long tantalum capsule which rested inside a larger diameter, 5-in.-long tantalum tube sealed at the bottom (Fig. 4). Originally, the small capsule contained Pu-Co-Ce alloy to a level marked by the deposit highest on the capsule wall. The assembly was immersed in 650°C sodium

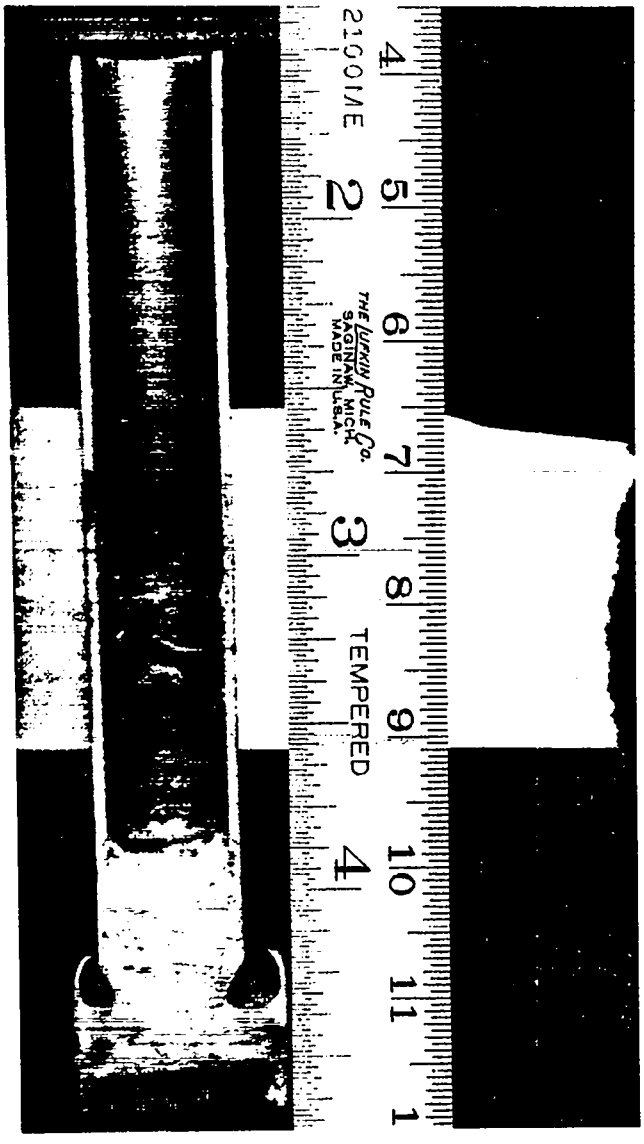


Fig. 4. Fuel climb on tantalum after 2800 h in 650°C sodium.

for 2800 h, and examined metallographically. The capsule showed no sign of penetration in the original fuel zone, consonant with past behavior of annealed tantalum and Pu-Co-Ce alloys.[2] Apparently all fuel transfer from the inner to the outer container took place up the wall and over the top.

The capsules shown in Fig. 3 exhibited evidence of isolated fuel-container reaction below the

fuel-sodium interfaces. At the interfaces, this reaction layer changed to a thicker, duplex structure consisting of a diffusion zone and crystalline precipitate (Fig. 5 and 6). Electron beam microprobe

Fig. 5. Start of continuous Ta-Co reaction layer at fuel-sodium interface; unetched, 100X.

examination showed that the layer below the liquid level, as well as the diffusion layer of the duplex structure, contained tantalum and cobalt as the major constituents, and smaller amounts of plutonium and cerium. The crystalline material contained only cobalt and tantalum in the approximate ratio Ta_2Co. The dark region adjoining the crystalline material was a Pu-Co-Ce mixture. These reaction layers have been observed regularly when tantalum is used to contain Pu-Co-Ce alloys,[3] and the mechanics of their formation is discussed elsewhere in detail.[4] At increasing distances from the fuel-sodium interface, the reaction layer thinned, and only intermittent reaction occurred near the capsule mouth and on outside surfaces. The black, roughened portions of the outside surfaces (Fig. 3) corresponded to areas of intermittent reaction. The discolorations resulting from contact of capsules and holder could not be associated with any microstructural feature.

An increase in capsule exposure time from 1500

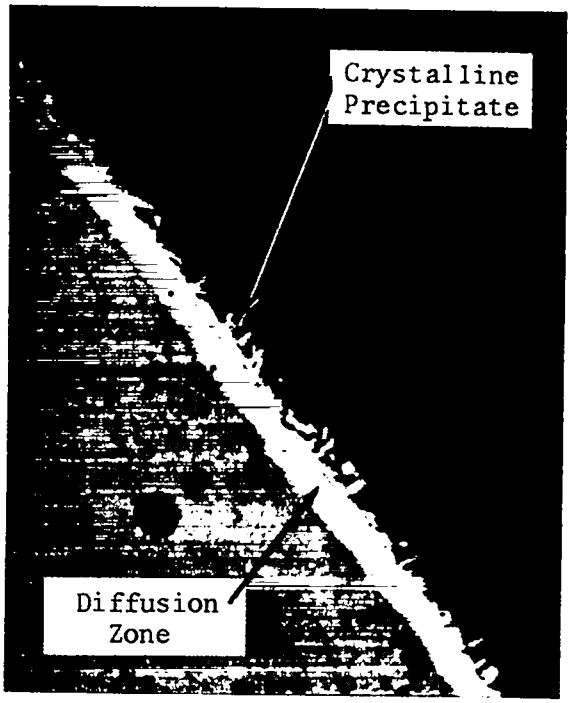


Fig. 6. Fuel and duplex Ta-Co layer in sodium phase near sodium-fuel interface; unetched, 400X.

to 2800 h resulted in greater fuel loss and thicker, more extensive Ta-Co reaction layers.

Fuel losses also were higher, and Ta-Co reaction layers were more extensive in capsules when a helium atmosphere was maintained over the fuel during testing. Performance of the first helium-buffered capsules was so poor that these tests were suspended until fuel climb had been eliminated in the direct-contact capsules.

EFFECT OF TANTALUM CARBIDE LAYERS

Tantalum carbide layers were applied to the inside surfaces of fuel capsules by packing the capsules with activated carbon granules and heating them to 1700°C in the presence of hydrogen. The technique, as finally adopted, produced continuous, 2- to 4-μ-thick TaC layers without increasing the hydrogen content of the base metal. While the carburizing technique was being investigated, two tantalum capsules with rather crude, discontinuous TaC layers were tested at 650°C. Fuel climb was reduced, and Ta-Co reaction was prevented in regions where the carbide layer had no defects.

When the final carburizing technique was adopted, a Ta-5W alloy was substituted for the original tantalum container material, the fuel capsule length

and lower tip configuration were altered, and the experiments were transferred to an isothermal sodium system (Fig. 2) operating at 600°C. As far as can be determined, only the addition of the TaC layer affected the results of subsequent experiments.

Figure 7 shows two internally carburized Ta-5W capsules and their stainless steel rack after a 6400-h exposure to 600°C sodium. In one capsule, sodium-fuel contact was allowed, while in the other

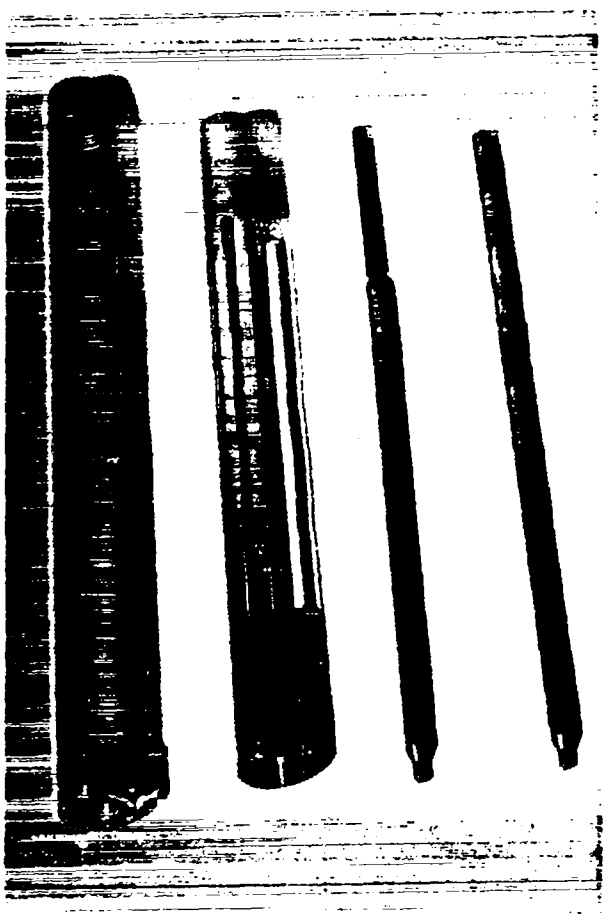


Fig. 7. Vented Ta-5W alloy fuel capsules and stainless steel rack after immersion in 600°C sodium for 6400 h.

a helium atmosphere was maintained above the fuel. In contrast to the behavior shown in Fig. 3, only traces of plutonium ($\leq$ 400 dis/min/in.^{2}) were detected on the outside surfaces of the carburized capsule and on the stainless steel rack.

The capsules were sectioned and examined metallographically, but no attack was seen in either. Figure 8 shows the sodium-fuel interface from the 6400-h, direct-contact capsule. This is the area of heaviest attack in uncarburized capsules (Fig. 5). The carbide layer at this point is indistinguishable

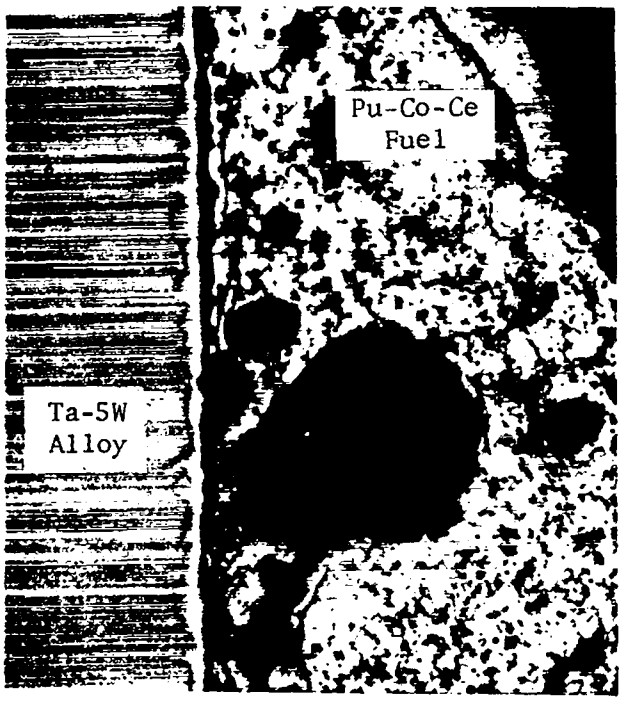


Fig. 8. TaC layer on Ta-5W alloy in region of fuel-sodium interface after 6400 h at 600°C, as polished, 300X.

from the control specimens and is typical of all inside surfaces from both the direct-contact and helium-buffered capsules.

The appearance of carburized Ta-5W capsules tested for 2000 h was identical to that of the 6400-h capsules.

FUEL LOSSES

As a check on the effectiveness of TaC layers in preventing fuel spread, several capsules were sectioned, and 1-in.-long, half-cylinder segments of surface between the fuel meniscus and the capsule mouth were leached to recover any fuel present. In Table II, the results from four carburized Ta-5W capsules are compared with similar results (where available) from a bare tantalum capsule and a carburized tantalum capsule.

Although there were variations in operating temperature, time, and capsule length from test to test, the effectiveness of the carbide layer in preventing fuel spread is obvious. The bare tantalum

Table II

Fuel Climb in Carburized and Bare Ta and Ta-5W Capsules

Capsule	Operating Conditions: Time (h)	Temp. (°C)	Configuration	Fuel Recovered from Segment (mg): Distance of Segment Center from Fuel Meniscus: 1 in.	2.5 in.	4 in.	5.5 in.	7 in.	8.5 in.	10 in.
Ta-5W, Carburized D-1062	2000	600	He buffer	17.11	0.062	0.042	0.039	0.038	---	---
Ta-5W, Carburized D-1421	2000	600	Direct Contact	8.1	0.055	0.040	0.038	0.045	0.072	0.078
Ta-5W, Carburized D-1419	6400	600	He buffer	141	0.075	0.052	0.034	0.062	---	---
Ta-5W, Carburized D-1321	6400	600	Direct Contact	4.64	0.079	0.032	0.046	0.107	0.032	0.040
Ta, Carburized D-2297	1200	650	Direct Contact	3960	---	4.55	---	0.223	---	---
Ta D-2288	1200	650	Direct Contact	1388	---	---	---	18.92	---	---

capsule (D-2288) contained appreciable quantities of fuel along the wall at the 7-in. level. This fuel had lost 80% of its original cobalt to the TaCo intermetallic compound layer along the walls.

In comparison, the 7-in. segment removed from an imperfectly carburized tantalum capsule (D-2297) contained approximately 1/100th of the fuel recovered from the corresponding segment of D-2288. (Since both capsules were part of the same test assembly, the results are comparable.) Cobalt depletion in this case was approximately 15% and resulted from TaCo intermetallic compound formation at breaks in the carbide layer.

Although the carburized Ta-5W capsules were tested approximately 2 and 5 times longer than the imperfectly carburized tantalum capsule, they contained less than one-half of the fuel found in the latter capsule (at the 7-in. level). Comparing one Ta-5W capsule with another, there are no large differences in the quantities of fuel recovered from comparable segments, regardless of operating time or whether a helium buffer was used.

On the basis of metallographic examination of the capsules and the amount of fuel recovered from the walls, it appears that the fuel spread encountered on tantalum surfaces was eliminated by the addition of a TaC layer. Carburized capsules were operated both with a helium buffer and with fuel-sodium contact without any appreciable differences in behavior.

With the elimination of fuel spread, there appears to be no mechanism by which fuel will be lost (except for capsule failure) from an inert gas-buffered capsule. In a direct-contact capsule, however, losses will occur because of diffusion of plutonium up the stagnant column of sodium separating fuel from bulk coolant.

As an order of magnitude estimate of diffusion losses from direct contact pins, consider the case of a vented core of the size intended as a reference design for the Molton Plutonium Burnup Experiment (MPBE). The MPBE has been detailed previously,[5] so that it suffices to describe the experiment as a 20-MWt, sodium-cooled array of sealed Ta-5W pins fueled with a Pu-Co-Ce alloy. The core consists of 637 fuel pins containing approximately 96 kg of plutonium. Fuel pins are 0.400-in. o.d., 0.022-in. wall, and 24- to 30-in. long. The liquid fuel alloy occupies the lower 13 in. of each pin; the rest of the pin serves as a fission gas reservoir whose size is set by allowable hoop stresses in the pin. The mixed-mean coolant outlet temperature is 600°C, and the pin maximum temperature is 700°C.

To estimate diffusion losses from this core, the following assumptions were made.

1. Fuel pin length is 24 in., and fuel occupies the lower 13 in.
2. Fuel pin material is inert to plutonium.
3. The initial period of transient diffusion is short compared to an assumed operating time of 1 year, and this initial period can be neglected.
4. The plutonium concentration in sodium at the fuel-sodium interface of a pin is constant and equal to the equilibrium solubility of plutonium in sodium.

5. The plutonium concentration in the bulk coolant is zero (the rate of plutonium removal from solution in bulk coolant is much larger than its rate of introduction into the coolant).

6. The temperature of fuel and bulk coolant is 700°C.

7. The diffusivity of plutonium is unaffected by small changes in concentration of plutonium in sodium or by the presence of additional species in dilute solution in sodium.

For this case the Fickian diffusion equation,

$$J = -D \frac{\partial C}{\partial X} ,$$

describing isothermal, unidirectional diffusion of one species in another reduces to

$$J = -D \frac{\Delta C}{\Delta X} .$$

At 700°C the diffusivity of most species in liquid metals lies in the range 10^{-4} to 10^{-5} cm^2/sec.[6] The solubility of plutonium in sodium equilibrated with a Pu-Co-Ce alloy has been reported as $\leq$ 2 ppm at 700°C.[7] The height of the stagnant column of sodium is approximately 11 in. (28 cm). Using the higher value for the diffusivity, the flux of plutonium across a unit surface at the mouth of a pin is

$$J = (10^{-4} \text{ cm}^2/\text{sec}) \frac{2 \times 10^{-6} \text{ g/cm}^3}{28 \text{ cm}}$$

$$= 7.15 \times 10^{-12} \text{ g/cm}^2\text{-sec},$$

and the plutonium loss from 637 pins during a year is

$$(7.15 \times 10^{-12} \text{ g/cm}^2\text{-sec})(3.16 \times 10^7 \text{ sec})\ (410 \text{ cm}^2)$$

$$\cong 0.1 \text{ g Pu},$$

compared to an initial inventory of approximately 96 kg. If the height of the sodium column is reduced to 5 cm (approximately 2 in.), the plutonium losses are increased to approximately 0.6 g/yr.

Based on these low loss rates alone (which could be increased two orders of magnitude without significant effect on reactor operation), the use of direct-contact vented fuel elements appears feasible. However, experiments indicate that 90 to 100% of the ^{90}Sr and ^{137}Cs produced in a liquid fueled pin would transfer to the sodium coolant within a few days of its production, and that ^{137}Cs would be difficult to remove from sodium solution.[8] ^{140}Ba and the iodine isotopes also are expected to be extractible. The potential safety and maintenance problems associated with coolant containing large amounts of long-lived gamma emitters (in comparison to ^{24}Na) have not been evaluated.

CONCLUSIONS

Considering fission product release as well as fuel loss, it appears that attention should be directed toward gas-buffered, vented pins. An in-pile study of the release of fission gases and other fission products whose precursors are gaseous or volatile would represent the next step in determining the feasibility of venting liquid plutonium alloy fueled pins to sodium.

ACKNOWLEDGMENTS

Acknowledgment is gratefully made to J. H. Bender and L. R. Bergamo for preparation of metallographic specimens, and to W. J. Baughman, R. G. Bryan, T. K. Marshall, L. E. Thorn, and G. R. Waterbury for analytical assistance.

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