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Behavior of Long-Lived Fission Products in Sodium[*]

by

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J. C. Clifford

ABSTRACT

Long-lived fission products have been introduced into a small, forced convection sodium loop by immersing a trace-irradiated plutonium alloy in the flowing sodium. The distribution of plutonium, ^{90}Sr, ^{137}Cs, and ^{155}Eu in the loop, over periods of 1000-3000 h, has been observed by *in situ* gamma scanning of loop components and by radiochemical analysis of traps and metal specimens removed from the loop. Hot trapping, cold trapping, and graphite adsorber experiments have been conducted.

INTRODUCTION

If the quantities involved are large, the behavior of radioactivity release to sodium coolant from failed or vented reactor fuel elements may limit access to portions of the primary coolant system and may affect the consequences of a loss-of-coolant incident. In such cases, it may be desirable to scavenge fission products (as well as uranium and plutonium) from the coolant.

The work described here is part of a program concerned with the effects of long-time contact between trace-irradiated, plutonium-containing fuels and 500-700°C sodium. Assuming that isolated fuel failures (without change of state) will occur in a large fast breeder reactor, this program is intended to supply experimental evidence relative to the following questions. (1) Could access to portions of a sodium primary coolant system be restricted because of an accumulation of long-lived, energetic, gamma-emitting fission products? (The problem of mass transport of activated corrosion products from the core area is not considered here). (2) Could fission products and plutonium present in sodium accidentally released from the primary coolant system contribute significantly to external prompt gamma dose or to inhalation dose?

Three areas of investigation have been established: (1) mechanisms for release of radioactivity to sodium from fuel at normal operating temperatures, (2) behavior of fission products in sodium, and (3) methods for concentrating activity at selected locations within the primary coolant system. Single isotopes, trace-irradiated (U,Pu)C, and irradiated Pu-Co-Ce alloys are being used in these investigations. Only experiments concerning the behavior of long-lived fission products released from Pu-Co-Ce alloy to sodium are presented here.

Because the entire spectrum of fission products could not be examined experimentally, several isotopes were selected on the basis of half-life, yield, and chemical characteristics. These are shown in Table I along with their half-lives and chemical

Table I

Isotopes of Primary Interest in Fission Product Distribution Studies

Isotope	Half-Life	Chemical Category	Sodium-Extractable
^{90}Sr	28 years	alkaline earth metal	yes
^{137}Cs	30 years	alkali metal	yes
^{131}I	8.05 days	halogen	yes
^{144}Ce	285 days	rare earth metal	no
^{95}Zr	65 days	refractory metal	no
^{106}Ru	1.0 year	transition metal	no

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groups. Some isotopes thought to be completely in-
soluble in sodium have been included, but these will
be investigated only until their lack of solubility
has been demonstrated.

EXPERIMENTAL TECHNIQUES

A high purity alloy of plutonium, cobalt, and
cerium with a melting point near 435°C is used as
the source of fission products for the experiments.
Contact of this fuel, in the molten state, with so-
dium rapidly releases the extractable isotopes and
has proved a convenient method of introducing fis-
sion products into sodium solution.

An open-mouth container partly filled with the
liquid fuel alloy is suspended in a forced convec-
tion loop, and regions of interest in the loop are
monitored using a movable scintillation detector
and a multichannel analyzer. The distribution of
pure beta emitters and low energy gamma emitters is
obtained by radiochemical analysis of metal speci-
mens, sodium, and traps removed from the system.

Figure 1 is schematic of the stainless steel
forced-convection loop. The loop consists of three
vertical legs, a resistance heater, an air heat
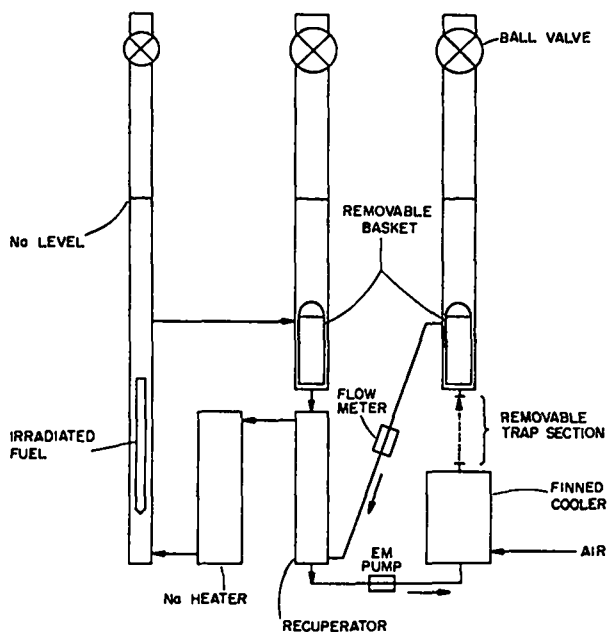dump, and a regenerative heat exchanger. The loop

contains approximately 100 in.^{3} of sodium flowing at
a maximum rate of 300 lb/h. The leg which contains
the irradiated fuel is lead-shielded, and fuel is
inserted and removed through a gas lock and shielded
handling can at its top. The other legs accept met-
al specimens, which can comprise as much as 25% of
the sodium-wet surface of the system. The loop is
operated at 150-600°C, and the maximum differential
is 300°C. A section of piping above the finned cool-
er in the cold leg is removable, allowing insertion
of traps into the loop.

Because the distribution experiments have used
irradiated, stored fuel, no data have been collected
for the shorter-lived isotopes ^{131}I or ^{95}Sr. New-
ly irradiated material has not been used because the
resolution available with the 3 x 3-in. NaI(Tl) scin-
tillation detector is not sufficient for detailed
analysis of multicomponent gamma spectra. By sub-
stituting a solid-state detector and a larger ana-
lyzer, a significant increase in resolution can be
obtained. The change in resolution is shown in
Fig. 2, which compares the spectra obtained from
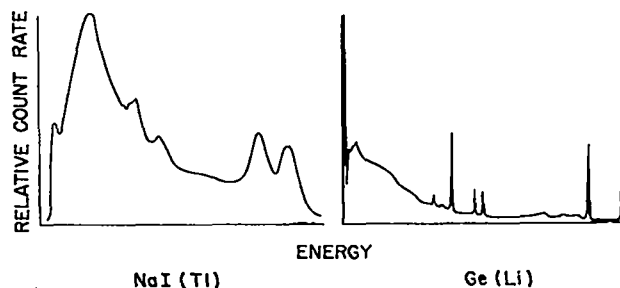
Fig. 2. Gamma spectra obtained with a 3 x 3-in.
NaI(Tl) detector and with a 5-cm^3 planar Ge(Li)
detector.

irradiated Pu-Co-Ce with the NaI system and with a
5-cm^3 Ge(Li) detector operating in anticoincidence
with an annular NaI detector. (The two peaks at the
high energy end of each spectrum are ^{60}Co). Fig-
ure 3 shows the shields, hoists, and cryostat for
the movable solid-state system which will be used
for higher resolution experiments.

EXPERIMENTAL RESULTS

A. General

The liquid-fuel alloys have provided activity
for experiments in which oxygen levels were control-
led by a zirconium hot trap, a full-flow cold trap,

Fig. 1. Forced convection sodium loop.

Fig. 3. Shields, cryostat, and hoist for Ge(Li) gamma-ray spectrometer.

or a diffusion cold trap, and for an experiment in which a graphite bed was used to scavenge residual activity from the loop. Information has been obtained for ^{90}Sr, ^{106}Ru, ^{125}Sb, ^{137}Cs, ^{144}Ce, ^{155}Eu, and total plutonium. Table II summarizes the ranges

Table II

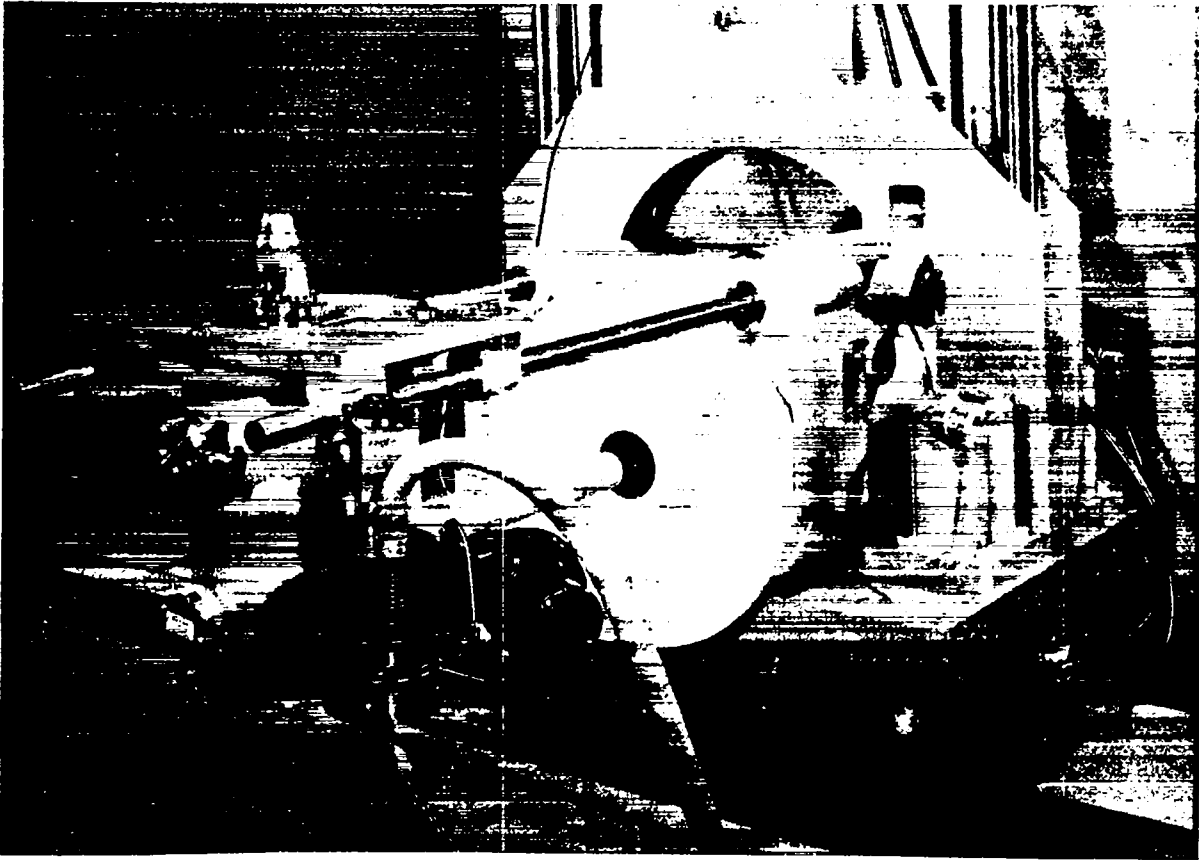Extremes of Radioactive Contamination Detected
After Distribution Experiments

Isotope	Range of Contamination	
	In Sodium (dis/min-g)	On Stainless Steel (dis/min-in²)
^{90}Sr	4×10^4 - 12×10^4	8×10^4 - 4×10^6
^{106}Ru	$\bar{<} 100$	< 200-2300
^{125}Sb	$\bar{<} 3500$	< 50-4600
^{137}Cs	2×10^4 - 1.8×10^6	2.3×10^5 - 7×10^7
^{144}Ce	$\bar{<} 2$	790-5000
^{155}Eu	290-2400	9×10^4 - 4×10^5
^{239}Pu	$< 1.4 \times 10^4$	300-3.5×10^4

of contamination levels found in sodium and on stainless steel after 2000-4000 h of operation in three experiments. The ^{137}Cs, ^{90}Sr, ^{155}Eu, and ^{239}Pu contamination levels were the highest, with ^{137}Cs levels reaching approximately 1 μCi/g in sodium and 30 μCi/in.^{2} on stainless steel. The other isotopes were detected in bulk sodium as a few hundred dis/min-g sodium, or less, and were present as surface contamination to the extent of a few thousand dis/min-in.^{2} In general, the highest surface contamination levels were observed on stainless steel in the coldest portion of the loop. The lowest levels were in high temperature regions.

The general behavior indicated in the table had been anticipated in light of the chemical characteristics of the species and the results of some distribution experiments performed several years earlier. These earlier experiments consisted of encapsulating the fuel alloy with sodium and irradiating the capsules at 450 and 550°C. Radiochemical analysis

showed that approximately 99% of the ^{137}Cs extracted to the sodium phase, along with 90% of the ^{90}Sr and 95% of the ^{155}Eu. ^{106}Ru, Ce, ^{95}Zr, and ^{125}Sb remained behind.

^{90}Sr and ^{137}Cs, the species found in greatest abundance in the loop experiments, differed in behavior as shown in Table III. Here, the measured sodium contamination levels at the end of an experiment are compared with the levels which would have existed had all the released activity remained in solution. These latter values appear in the column labelled "Beginning," and were obtained by assuming that 99% of the ^{137}Cs and 90% of the ^{90}Sr from the fuel were released to the sodium at the first moment of contact. These upper limit values were compared with the sum of the experimentally determined activities in the system at the end of each test, and the agreement was satisfactory, except for ^{90}Sr in the full-flow cold trap experiment. Apparently the assumed release fractions are realistic, although the release rate, obviously, is not. For the graphite bed experiment, the initial specific activities in Table III are measured values. The time-dependent behavior of ^{137}Cs showed that very little change was occurring at the end of each experiment, and the same is assumed to hold for ^{90}Sr. Of the strontium released during the hot trap experiment, only a small fraction (less than 1/200) remained with the sodium. Essentially no change in strontium level occurred during the graphite scavenger experiment, probably because strontium had been fixed in place in the loop during the previous experiment. ^{137}Cs was not so readily removed from solution as ^{90}Sr, and the full-flow Na$_2$O trap was the least effective of the ^{137}Cs scavenging techniques. However, difficulties in controlling the trap temperature may have contributed to this condition.

By describing the individual experiments and their results in more detail it should be possible to present a better qualitative picture of the behavior of ^{137}Cs, and of ^{90}Sr as well.

B. Zirconium Hot Trap Experiment

The experiment using zirconium to control oxygen level consisted of submerging trace-irradiated fuel in the 600°C fuel leg and a stainless steel and zirconium foil assembly in each of the other legs. ^{137}Cs was identified in the coldest leg (500°C) a few hours after the fuel had been inserted. During a month at constant temperature, the ^{137}Cs level in the cold leg decreased slowly. Next, temperatures were lowered to 500°C in the fuel leg and 300°C in the cold leg, and ^{137}Cs activity continued to decrease. Rapid temperature cycling of the cold leg between 300 and 500°C had trivial effects on ^{137}Cs activity level and distribution.

As can be seen in Fig. 4, cesium lost from the sodium-filled portion of the cold leg moved into a 3-in. band above the liquid level. The activity peak coincides with the top of the thermal insulation. Similar ^{137}Cs deposits were detected in the other legs. The second ^{137}Cs deposit in the cold leg extends axially throughout a 5-in.-long tube packed with wire mesh. Cesium was detected elsewhere, but in negligible amounts (per unit surface) compared with that in the mesh.

At the end of the experiment approximately 60% of the available ^{137}Cs had transferred through the liquid/gas interfaces and had condensed on cold stainless steel walls. Approximately 5% remained in

Table III

Reduction in Sodium Contamination During Small Scale Loop Experiments

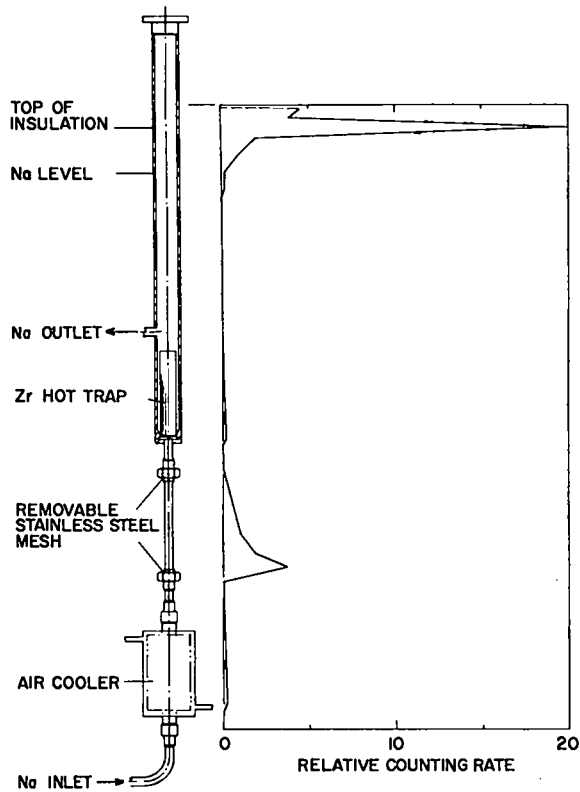| Experiment	Sodium Contamination (dis/min-g)				Reduction Factor	
	Beginning		End			
	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs	^{90}Sr	^{137}Cs
Zr Hot Trap	3.21×10^6	4.71×10^6	1.52×10^4	2.34×10^5	212	20
Graphite Scavenger	1.52×10^4	2.34×10^5	1.13×10^4	2.43×10^4	1.3	9.6
Full-Flow Cold Trap	1.74×10^6	2.59×10^6	5.18×10^3	1.79×10^6	336	1.5

Fig. 4. Distribution of ^{137}Cs in the cold leg of a zirconium-gettered sodium loop.

solution in sodium, and the remainder was distributed among the two hot traps and the other sodium-wet surfaces of the loop. Both zirconium hot traps were analyzed radiochemically. Plutonium, ^{90}Sr, and ^{137}Cs had segregated to the stainless steel portions of the trap that had operated at 300-500°C. Contamination levels here were higher, by factors of 20-50, than in corresponding sections of the trap that had operated at 500-600°C. Cesium was recovered from all metal surfaces without difficulty by alcohol rinse, while ^{90}Sr and plutonium required acid leaching.

C. Graphite Bed

To determine whether ^{137}Cs previously deposited on sodium-wetted stainless steel was recoverable, a bundle of spectroscopic-grade graphite rods was submerged in the cold leg of the loop. Figure 5 shows the activity distribution before graphite addition and a month later. The loop was operated in the 110-300°C range for a total of 50 days, and the graphite collected cesium from stainless steel tubing and mesh surfaces. The average contamination
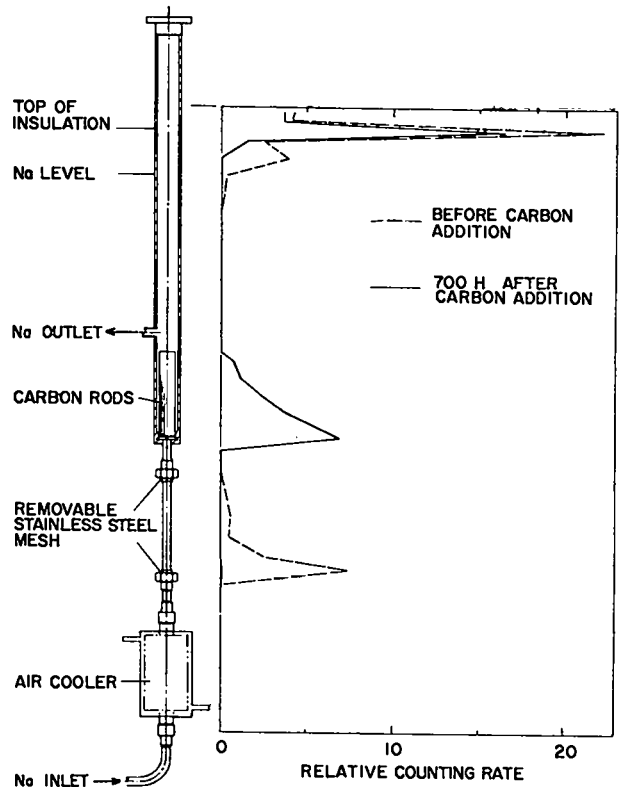

Fig. 5. Effect of graphite on the distribution of ^{137}Cs in the cold leg of a sodium loop.

level of the mesh surfaces was reduced by a factor of 40, to a final value of 3.8 x 10^5 dis/min-in^2 During this same 50-day period the cesium activity at the walls in the gas space was reduced by half.

Although the bed collected activity during the entire test period, an apparent redistribution of activity began 2/3 of the way through the test.

The use of graphite to recover significant fractions of the ^{137}Cs previously spread throughout a sodium system (in solution and on stainless steel surfaces) might be effective if it could be established that negligible carbon were introduced into solution and transported to surfaces where carburization could not be tolerated.

D. Full-Flow Na$_2$O Cold Trap

To investigate the effect of cold trapping on ^{90}Sr and ^{137}Cs levels in sodium, a small full-flow cold trap was inserted in place of the removable trap section of the loop (Fig. 1).

A schematic of the trap appears in Fig. 6. The trap consists of a regenerative cooler and a thin-walled bulb filled with stainless steel mesh. With
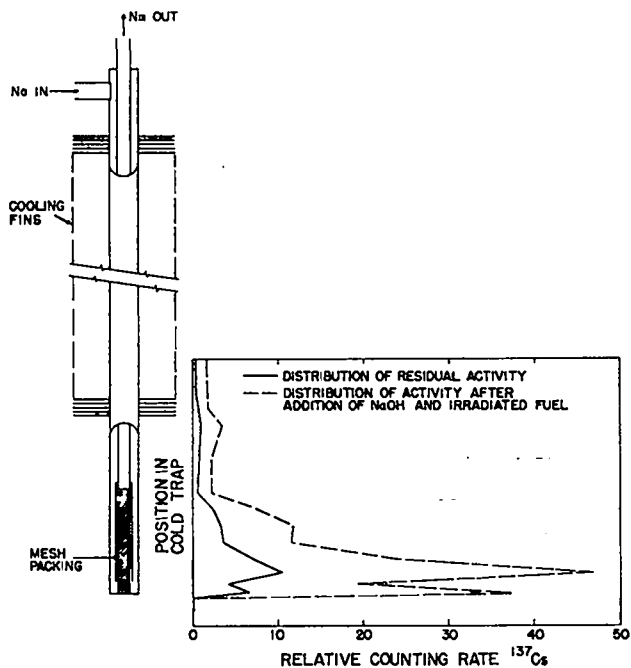
Fig. 6. Distribution of ^{137}Cs in cold trap.

the trap bulb operating at 175°C, oxygen (as NaOH) was added to the loop. The solid line on the graph (Fig. 6) shows the axial distribution of ^{137}Cs scavenged from the loop during this period.

After the cold trap had stopped scavenging ^{137}Cs, specimens of stainless steel mesh and additional trace-irradiated Pu-Co-Ce were placed in the loop. The fuel and one mesh specimen were held at 500°C, and the other mesh specimen was held at 300°C. The axial distribution of ^{137}Cs in the cold trap 12 days after addition of fuel is represented by the dashed line in Fig. 6. The two distributions have the same characteristics; in each case the largest peak is associated with a spider used to maintain spacing between the concentric tubes in the bulb. The second peak is aligned with the inside bottom plate of the cold trap. The lowest peak occurs in the region where the shell covering the cooling fins is attached to the recuperator. Whether the ^{137}Cs distribution is patterned after the distribution of sodium oxide is unknown. The distribution of activity did not change appreciably during the remaining 2-1/2 months of operation. However, the total ^{137}Cs activity in the trap was affected by small changes in trap temperature so that a steady-state condition was not attained.

The distribution of ^{137}Cs and ^{90}Sr at the end of the test is shown in Table IV. The agreement be-

Table IV

Distribution of ^{90}Sr and ^{137}Cs After
Full-Flow Cold Trap Experiment

	^{90}Sr (dis/min)	^{137}Cs (dis/min)
Na$_2$O Trap Bulb	2.69 x 10^7	2.52 x 10^9
Na$_2$O Trap Bleed Valve	0.02 x 10^7	0.60 x 10^9
Cold Leg Mesh (downstream)	1.60 x 10^7	0.48 x 10^9
Hot Leg Mesh (upstream)	0.68 x 10^7	0.02 x 10^9
Loop Sodium	0.88 x 10^7	3.14 x 10^9
Total	5.87 x 10^7	6.76 x 10^9
Fuel Pin Inventory before Test	3.25 x 10^9	7.64 x 10^9
% Activity Accounted for	1.8%	88.5%

tween the ^{90}Sr recovered and that available from the fuel is poor, and the only appropriate observation seems to be that strontium segregated to the cold trap. Per unit area of stainless steel surface, the cold trap mesh contained about eight times more ^{90}Sr than the mesh operated at 500°C.

The ^{137}Cs agreement in Table IV is better. At the end of the test, 88.5% of the activity available from the fuel was recovered. Sodium in the loop contained 46% of the ^{137}Cs recovered, and the Na$_2$O trap accounted for an additional 38%. A 1/4-in.-diameter bleed line on the downstream side of the cold trap contained 9% of the activity, although there was no flow in this line during the experiment. The net amount of ^{137}Cs transferred from sodium to gas-filled sections was trivial.

The fact that a small diameter bleed line (whose activity pickup was diffusion-limited) contained 1/4 as much ^{137}Cs as the larger full-flow cold trap located upstream indicates that the full-flow trap was not a particularly effective scavenger. Whether the small amount of ^{137}Cs transferred to the gas-filled section in this experiment (contrasted with the amount transferred in the hot trap experiment) results from lower sodium-gas interface temperatures or from the presence of a cold trap is unclear. (The transport of ^{137}Cs from sodium to the vapor phase is being investigated in another portion of the program).

E. Na$_2$O Diffusion Cold Trap Experiment

Because of the difficulty in maintaining close temperature control over the Na$_2$O full-flow cold

trap, a diffusion cold trap was substituted to determine whether Na_2O affects the distribution of ^{137}Cs or whether the distribution is determined by temperature alone. The experiment consists of: (1) establishing an equilibrium with respect to ^{137}Cs before significant Na_2O has been added to the trap, (2) adding large amounts of NaOH to the system in an attempt to upset this equilibrium and, (3) adding zirconium foil to the high temperature section of the loop to remove oxygen from the cold trap and observing any ^{137}Cs redistribution. At present the experiment is in the second phase.

SUMMARY AND CONCLUSIONS

1. The phenomena observed here are not novel. They have been reported in conjunction with reactor experiments in this country and abroad. The fact that similar behavior has been seen in these experiments adds weight to the belief that small scale studies can be useful.

2. The results of these experiments are interesting enough that a more systematic investigation of fission product distribution and trapping is being undertaken, including determination of the shorter-lived isotopes ^{131}I, ^{95}Zr, ^{140}Ba. The immediate goals are to identify sodium-soluble isotopes and to examine the effects of primary coolant system construction materials, design features, and operating conditions on these isotopes.

3. All isotopes for which data were obtained had segregated to the cold portions of the sodium system under all operating conditions. Appreciable fractions of the activities released to the sodium system were removed from solution by one means or another, although the effects of such variables as temperature, temperature gradient, and sodium purity are unknown. Of the isotopes considered, only ^{90}Sr and ^{137}Cs appear to be of any consequence in the experiments.

4. The difficulty with which ^{90}Sr has been recovered from metal specimens, the low levels of ^{90}Sr contamination in sodium, and the lack of evidence for any redistribution of ^{90}Sr in the sodium system indicate that strontium, once deposited from sodium solution, is fixed in place. No attempt has yet been made to identify deposition mechanisms or rates.

5. The ease with which ^{137}Cs has been recovered from analytical specimens, together with the migration of cesium from liquid to gas phase and its recovery within the sodium system by several techniques, suggests that it is very weakly adsorbed on sodium-wet surfaces. In these experiments cold trapping was the least effective method for reducing the ^{137}Cs content of contaminated sodium. No attempt has been made, as yet, to identify ^{137}Cs deposition mechanism or rates. Although some rate data have been obtained for ^{137}Cs, they are influenced to such a degree by the type of fuel used (i.e., liquid metal) and the experimental configurations that they have not been reported.

6. In interpreting these observations, it should be remembered that the source of activity was a liquid metal in which all fission products probably existed in the fully reduced state. Departures from this condition, brought about by substitution of oxide and carbide fuels for the liquid Pu-Co-Ce alloy, have not been discussed.