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SOME ASPECTS OF THE BEHAVIOR OF FISSION PRODUCTS IN MOLTEN FLUORIDE REACTOR FUELS

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FISSION PRODUCTS IN FLUORIDE FUELS

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Abstract

Observations are reported on the behavior of several fission product elements in molten NaF-ZrF_4-UF_4 fuels, irradiated in capsule experiments, forced-convection in-pile loop experiments, and in the Aircraft Reactor Experiment (ARE). The rare gases have been observed to escape readily from the fuels in dynamic tests, although in static tests the rate of escape is very low. Ruthenium and niobium deposit on the Inconel walls of the fuel container, probably as metals. Other fission products studied (Sr, Zr, La, Ce) appear to remain in the fuel. The results obtained are entirely consistent with theoretical predictions. It is suggested that the observed noble metal deposit may serve to reduce corrosion of metals by molten fluoride fuels. The unsatisfactory nature of Cs^{137} as a fission monitor in such fuels is reported and the use of Zr^{95} as a substitute is discussed.

The chemical behavior of the fission product elements is of great importance in any fluid-fueled nuclear reactor, as well as in the reprocessing of nuclear fuels of any sort. Observations are reported here on the behavior of several important elements in molten fluoride fuels (1) of the type employed in the Aircraft Reactor Experiment (ARE). Most of the fuels examined have been of the NaF-ZrF_4-UF_4 type, with various compositions. The samples examined were taken from three different types of experiment:

1. Static fluoride irradiations: Observations are reported on samples of fuel from two in-pile static corrosion tests (2). Two experiments are also reported on the removal of Xe^{135} from static fluorides.
2. Dynamic fluoride irradiations: Observations are reported on fuel samples from three in-pile forced-convection loop tests and on metal samples from one of these (3, 4, 12).
3. The ARE: Observations are reported on a fuel sample and on a metal sample from the ARE.

Behavior of the Rare Gases: The fission monitoring technique based on Cs^{137}, developed at the Argonne National Laboratory (5), was applied to two samples of NaF-ZrF_4-$U^{235}F_4$ (50-46-4 mole %, respectively) which had been irradiated in the MTR for 116 hours and 325 hours, respectively, at about 800°C, at a thermal neutron flux of $(2.36 \pm 0.16) \times 10^{14}$ neutrons $cm^{-2} sec^{-1}$. The results are shown in Table I. It will be observed that although agreement between the measured and calculated number of fissions occurring in the sample is good in the shorter irradiation, in the longer one it is very poor.

Table I

Cs^{137} Analyses on Static Molten Fluorides Irradiated in the MTR

Time of Irradiation (hours)	Cs^{137} (fissions/gm x 10^{-18}) Observed (a)	Calculated (b)	Cs^{137} recovered from capsule tops (fissions/gm x 10^{-18})
116	0.085 ± 0.005	0.11 ± 0.01	0.001
325	0.091 ± 0.010	0.28 ± 0.03	0.013

(a) Based on ANL calibration of Cs^{137} flux monitoring method (5)

(b) Based on flux determined by Co activation; corrected for flux depression.

A portion of the capsule which was exposed to vapors from the molten salt was dissolved in each case and a Cs^{137} determination was performed on the resulting solution. The results (last column of Table I) show appreciable amounts of Cs^{137} to have been present on these surfaces. These results are taken as evidence of the escape from the fuel of 3.8 minute Xe^{137}, the parent of the cesium isotope.

An attempt was made to study directly the evolution of Xe^{135} from irradiated fluorides. Two runs were made under identical conditions, except that in one case the fuel was sparged by bubbling He through it, while in the other case, the carrier gas merely swept over the surface of the melt. The helium, purified by passage over hot copper turnings and magnesium perchlorate, was conducted to and from the capsule through 0.036 in. o.d. stainless steel capillary tubing. The off-gas was passed through two Dry Ice-acetone-cooled traps, the second filled with activated charcoal to adsorb the xenon. A helium gas flow rate of 15 ml/min was maintained in each experiment. The fuel sample in each case was 1 gm of NaF-KF-UF_4 (46.5-26.0-27.5 mole %, melting point 530°C), containing normal uranium. It was irradiated in the ORNL Graphite Reactor at 650 to 750°C, at a thermal neutron flux of 7×10^{11} neutrons cm^{-2} sec^{-1}, for 31 minutes. After waiting 4.5 hours for short-lived activities to decay, helium flow was started and continued for 6.5 hours. During the entire period, the capsules remained in the reactor, which had been shut down for normal refueling. The thermal neutron dose was monitored with a clip of Al-Mn-Co alloy, removed and counted immediately after the irradiation was completed. The amount of Xe^{135} was determined by transferring the contents of the charcoal trap to an appropriate vessel and counting in a 4π geometry high-pressure ionization chamber. The results are shown in Table II in terms of the response of the instrument used. No absolute calibration was made. It may be said, however, that the amount of Xe^{135} recovered in the sparging experiment was approximately that expected from the fission history of the sample. It is clear from the results of Table II that the rare gases do not diffuse extremely readily from static molten fluorides under the conditions of these experiments. Their removal is easily accomplished, however, by efficient sparging of the fuel with helium.

As one part of the operation of the ARE (6), a so-called xenon experiment was performed. The control rods were calibrated during the period when the reactor was being brought to criticality by measured additions of Na_2UF_6 to the originally uranium-free salt. In the "xenon experiment", the rod position was recorded as a function of time during a 20-hour run at a nominal power of 1.5 megawatts. The rod position data were converted to $\Delta k/k$ values using the previously established calibration. When the results were corrected for Sm^{149} poisoning and for the decrease in reactivity due to U^{235} burnup, it was apparent that virtually all of the Xe^{135} had been removed from the fuel. While no certain quantitative interpretation can be given of the poisoning remaining after correction for Sm^{149} and burn-up effects, it appeared that no more than about 2% of the expected Xe^{135} remained in the reactor fuel during the period in question.

During operation of the ARE, an accidental leak of gases occurred from the reactor into the pit in which it was installed. This gas was dispersed by drawing it into an emergency off-gas line inserted into the pit.

Table II

Evolution of Xe^{135} from Static Molten Fluorides Irradiated in the ORNL Graphite Reactor

	Thermal Neutron Dose(b)	Amount of Xe^{135} (b)	
		Observed	Calculated(a)
Fuel sparged with He	0.117	1.44	-
Fuel surface swept with He	0.097	0.032	1.22

(a) Based on results obtained in sparging experiment; corrected for slight difference in uranium content of the two capsules.

(b) Arbitrary units.

A sample of the off-gas from this line, adsorbed on cooled charcoal, was examined by Bell, et al. (7), primarily by gamma-ray scintillation spectrometry. They established the presence of Rb^{88} (daughter of 2.8 hr. Kr^{88}), Xe^{135}, and Cs^{138} (daughter of 17 min. Xe^{138}), but were unable to identify many of the observed peaks in the gamma-ray spectrum.

Determination of the amounts of Cs^{137} in the fuel of the ARE and of one of the in-pile loops indicated the escape of less than about 20% of the Xe^{137} from these systems. In another loop, as much as 50 to 70% of the Xe^{137} may have escaped from the fuel.

The data obtained on both static and dynamic systems demonstrates that the rare gases are evolved readily from molten fluorides, although, in static systems, the rate of evolution is very low. The fraction of any rare gas isotope which will be removed from a fluid fuel may be estimated using a theory developed for Xe^{135} poisoning kinetics (8). This fraction depends on the geometry and flow conditions of the specific reactor, as well as on the radioactive half-life of the nuclide in question. Longer-lived nuclides will be removed to a greater extent than shorter-lived ones, very crudely in proportion to their half-lives.

Behavior of Ruthenium and Niobium: Samples of fluoride fuel removed from three in-pile forced-convection loops and a sample from the ARE were examined for the presence of Ru^{103} by radiochemical techniques. The results are shown in Table III. The very marked reduction below the expected level of the Ru^{103} content of the fuel, especially in the LITR loops and in the ARE, indicated the existence of an efficient means of ruthenium removal from molten fluorides. It was possible to obtain salt-free sections of Inconel pipe

Table III

Ru^{103} Analyses of Irradiated Molten Fluoride Fuels from Dynamic Experiments

		LITR Loops		
	ARE(b)	Horizontal(c)	Vertical(b)	MTR Loop(b)
Irradiation time (hrs.)	~75(d)	475	235	271
Fissions/cm^3 of fuel x 10^{-16} (a)	8.7	13	130	650
Ru^{103} concentration in fuel, atoms/cm^3 x 10^{-15}				
Calculated	2.5	3.9	34	190
Observed	~3×10^{-5}	$<10^{-3}$	~2×10^{-4}	100
Ratio, surface/volume (cm^{-1})	1	3.5	8	5
Average Ru^{103} surface concentration, atoms/cm^2 x 10^{-15}	2.5	1	4	17

(a) Estimated from power generation in ARE and LITR Horizontal Loop; and from Zr^{95} analyses for LITR Vertical and MTR Loops.

(b) Fuel was 53.5 mole % NaF, 40.0 mole % ZrF_4, 6.5 mole % $U^{235}F_4$.

(c) Fuel was 62.5 mole % NaF, 12.5 mole % ZrF_4, 25.0 mole % $U^{235}F_4$.

(d) The power level of the ARE was varied frequently during its life. This time figure merely indicates the magnitude of the irradiation.

from the horizontal LITR loop (3) and from the reactor. These sections were selected from parts of each system which were not exposed to high thermal neutron fluxes, thus avoiding difficulties resulting from activation of the cobalt content of Inconel.

One pipe section was selected from a region of the LITR loop upstream from the high-flux region, another from a region an equal distance downstream. Gamma-ray spectrometry of these samples showed the presence of Ru^{103} activity and of Zr^{95}-Nb^{95} activity. The latter activity occurred to the same extent in each section, but the Ru^{103} activity in the downstream section was 40% greater than that in the upstream section. After a delay of 53 days, the two sections were re-examined. The Ru^{103} in both samples decayed with an apparent half-life of about 42 days, in good agreement with published data (9). The Zr^{95}-Nb^{95} activity, however, decayed with an apparent half-life of 40 to 43 days. This indicates that the active deposit must have contained about 95% Nb^{95} (35 days) and only about 5% Zr^{95} (65 days) at the time of reactor shutdown. The relative amount of Nb^{95} expected if no segregation of the element had occurred is about 5% of the total mass 95 activity.

The pipe section from the ARE was a ring cut out of the fuel inlet line to the reactor core. Three samples cut from this ring showed the presence of Ru^{103}, Ru^{106}, and Zr^{95}-Nb^{95}. Two of the samples were re-examined after a delay of 130 days. The apparent half-life of the Zr^{95}-Nb^{95} activity was about 50 days in each case, again suggesting that the deposit was very largely Nb^{95}. An autoradiograph of the third pipe sample showed the radioactive deposit to be well localized at the fuel-metal interface, within the rather poor resolution obtainable with beta radiation.

A pipe elbow, which served as the inlet end of the ARE emergency off-gas line, was examined for radioactivity. A very small amount of Ru^{103} was detected, which was shown by chemical treatment to be entirely on the outside of the pipe. The amount of activity was too small to estimate quantitatively; no other activity was found. It appears likely that a small amount of RuF_5 (or of RuO_4 from reaction with air that may have been introduced into the reactor when the leak occurred) volatilized from the fuel. In view of the large amount of ruthenium found on fuel container surfaces, it is felt that volatilization of this element is of very little importance in its removal from the fuel. This view is supported by experience to date with the fluoride volatility process (10) for recovering uranium from spent fuel.

The results obtained are consistent with theoretical predictions (11) that for short irradiation times (< 20 min.), ruthenium would be present in molten fluorides as Ru^{+5}, being reduced to Ru^{+3} for longer irradiations due to the necessity for conservation of valency in fission. The small yield of Ru^{103} found in the ARE emergency off-gas line presumably resulted from volatilization of RuF_5 during early reactor operations. The four experiments of Table III operated for periods of ~ 75 to 475 hours. For this interval, it was predicted that about 75 to 85% of the more noble fission product metals (particularly Ru and Mo) would be deposited on the walls of the container, the balance occurring as dispersed metal in the fuel. In the LITR loops and in the ARE, essentially all of the Ru was absent from the fuel, while in the MTR loops, only about 45% was lost. The higher removal efficiency in the first three cases may result from greater efficiency of rare gas removal than was assumed by Robinson (11). The MTR loop result is consistent with that expected for complete retention of all fission gases, but since reasonably good efficiency of gas removal is believed to have occurred during the loop operation (4), it appears more reasonable to associate the observed Ru^{103} distribution with saturation of the Inconel container with deposited fission product metals. This conclusion may be drawn also from comparison of the vertical LITR loop with the MTR loop which operated for a comparable time but at a much higher fission rate. If this interpretation of the data is indeed correct, it seems reasonable to infer that deposition of fission product metals may well interfere with the course of the ordinary corrosion process, and that long-term in-pile corrosion of metals by fluoride fuels may be significantly less than predicted from comparable out-of-pile tests. Short-term in-pile corrosion tests to date are not in disagreement with this hypothesis (12).

Niobium appears to deposit on Inconel along with ruthenium. It appears likely that molybdenum also deposits, but there has not yet been an opportunity to examine samples soon enough after irradiation to observe 67 hr. Mo^{99}, the longest-lived radioactive isotope of this element which is known in fission. It is also possible that zirconium may deposit from fuels not containing ZrF_4, but no experiments have yet been conducted on such materials.

The rate at which Ru^{103} deposits on Inconel may be estimated very crudely from the data obtained on the pipe samples from the horizontal LITR loop. From the locations of the two samples, their relative activities, and the dimensions and fuel flow rate of the loop, it was calculated that the effective half-life of Ru^{103} in the fuel was about 30 seconds. The nonuniform deposit results from this high deposition rate and from the fact that Ru^{103} is produced directly in fission (at least, no ancestor of appreciable half-life is known). Nuclides with long-lived parents, such as Nb^{95}, will form uniform deposits on the container walls, regardless of their rates of deposition.

Behavior of Other Fission Products: A sample of fuel drawn from the ARE dump tank was examined by radiochemical methods. In order to estimate the efficiency of retention of some typical fission products, these analyses were compared with similar results obtained on a sample of NaF-ZrF_4-UF_4 (50-46-4 mole %) irradiated in the solid state in the ORNL Graphite Reactor. The irradiation time was matched approximately to the high power operating time of the ARE. The comparative analyses of the ARE fuel and of the standard are shown in Table IV. It is clear that, with the exception of Ru^{103}, there is no gross loss of the fission product nuclides listed. The ratio obtained for Sr^{89} can be interpreted to show partial loss of its parent, 3.2 min. Kr^{89}, but no explanation can be offered for the value obtained for Zr^{95}. It is likely that no loss occurred of any of these fission product elements from the fuel of the ARE, and that the variation from 0.3 to 1.6 is a reflection of experimental errors, such as inhomogeneous samples, chemical difficulties in the complex fluoride system, etc. A determination was also made of the ratio of the activities of Cs^{136} and of Cs^{137} in the two samples. The result indicated the loss of less than 20% of the Xe^{137} parent of the latter nuclide.

Analysis of the gross gamma-ray spectrum of a 7 mg. sample of fuel from the ARE was continued through the period from 31 to 81 days after shutdown of the reactor. The total activity of the sample was determined in a high-pressure ionization chamber. This result was combined with gamma-ray spectral data to yield both total photon emission rates and differential decay data. The only activities detected were Ba^{140}-La^{140}, Ce^{141} and Zr^{95}-Nb^{95}. Neither Ru^{103} nor I^{131} was observed. The specific gamma activity of the sample was estimated as 16 mc/mg 31 days after reactor shutdown and 3.5 mc/mg 79 days after shutdown. The average gamma-ray energies were 0.96 and 0.73 Mev, respectively.

Table IV

Fission Product Analyses in ARE Fuel, Compared to a Standard Sample

Nuclide	Activity Ratio, ARE/Standard
Sr^{89}	0.6
Zr^{95}	0.3
Ru^{103}	1.6×10^{-5}
La^{140}	1.5
Ce^{141}	1.6
Mean (Omitting Ru^{103})	1.0 ± 0.5

Bell and his coworkers (7) were unable to establish the presence of iodine and bromine in the sample of ARE off-gas which they examined. Since 8 day I^{131} could not be detected in the analysis of the gross gamma-ray spectrum of the ARE fuel, the question of the fate of the halogen elements in molten fluoride fuels must be left open.

A series of radiochemical analyses performed on fuel from the vertical LITR loop gave similar results, summarized in Table V. The low activity obtained for Sr^{89} indicates the escape of its krypton ancestor. The low result for Ce^{144} is not understood and may reflect either experimental errors or non-representative sampling. The Cs^{137} result probably reflects loss of its xenon parent.

Use of Zr^{95} as a Fission Monitor: Uncertainties as to the applicability of Cs^{137} as a fission monitor in fluid reactor fuels led to the adoption of Zr^{95} as a substitute, at least for fuels containing macroscopic amounts of normal zirconium. In order to calibrate the use of this nuclide, two samples of enriched uranium were irradiated as solutions for 2.375 days in the ORNL Graphite Reactor. One solution was prepared from U_3O_8, the other from a typical NaF-ZrF_4-UF_4 fuel. After 10 days decay, radiochemical determinations were made of Cs^{137} and Zr^{95}. Comparison of these results, using the ANL Cs^{137} standards (5b), gave a fission yield for Zr^{95} of 0.0664 ± 0.0013 atom/fission. Using the integrated neutron dose, measured with a cobalt monitor, the yield is 0.0632 ± 0.0021 atom/fission. The discrepancy between the two results is removed when the cobalt activation flux is corrected for the cadmium ratio prevailing in the irradiation facility ($\backsim$ 30). The yield recommended for use in fission monitoring with Zr^{95} is 0.0664 ± 0.0013 atoms/fission.

Table V

Radiochemical Analyses of Fluoride Fuel from a Vertical LITR Loop

Nuclide	Activity Ratio[a]
Sr^{89}	0.13
Sr^{90}	1.14
Zr^{95}	0.86
Ru^{103}	5×10^{-5}
Cs^{137}	0.34
Ce^{144}	0.39

(a) The activities listed are corrected for the different fission yields of the several nuclides and are normalized so that the values for Zr^{95} and Sr^{90} average unity.

In other systems, it may prove necessary to employ other nuclides as fission monitors. It is essential that attention be given to the chemistry of the more important fission products at an early stage in the development of new fuel materials if accurate monitoring of in-pile experiments is to be obtained.

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