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SOME ASPECTS OF THE BEHAVIOR OF

FISSION PRODUCTS IN MOLTEN

FLUORIDE REACTOR FUELS

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OAK RIDGE NATIONAL LABORATORY

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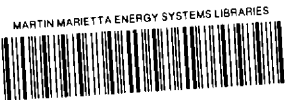
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ABSTRACT

Observations are reported on the behavior of several fission product elements in fused NaF-ZrF_4-UF_4 fuels, irradiated in capsule experiments, forced-convection in-pile loop experiments, and in the Molten Fluoride Reactor Experiment (MFRE). 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 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 hypothesis is proposed that fission product deposition may serve to reduce corrosion of metals by molten fluoride fuels.

The chemical behavior of the fission product elements is of great importance in any fluid-fueled nuclear reactor, as well as in the re-processing of nuclear fuels of any sort. Observations are reported here on the behavior of several important elements in fused fluoride fuels (1) of the type employed in the Molten Fluoride Reactor Experiment (MFRE)(2). 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 (3). 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 two in-pile forced-convection loop tests and on metal samples from one of these (4, 5).

3. The MFRE: Observations are reported on a fuel sample and on a metal sample from the MFRE (6).

Behavior of the Rare Gases

The fission monitoring technique based on Cs^{137}, developed at the Argonne National Laboratory (7), was applied to two samples of $NaF-ZrF_4-U^{235}UF_4$ (50-46-4 mole %, respectively) which had been irradiated in the MTR for 116 hrs and 325 hrs, respectively, at about 800°C, at a thermal neutron flux of $(2.36\pm0.16) \times 10^{14}$ neutrons $cm^{-2}sec^{-1}$. The results are shown in Table I. It will be observed that although agreement between the measured and calculated numbers of fissions occurring in the sample is good in the shorter irradiations, in the longer one it is very poor.

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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 3.9 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 hold the xenon. A helium gas flow rate of 15 ml/min was used 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 x 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. The capsules remained in the reactor during this period. 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

Table I

Cs^{137} Analyses in MTR-Irradiated Static Fluorides

Flux $=(2.36\pm0.16) \times 10^{14}$ neutrons cm^{-2}sec^{-1} Temp.$= 800^{\circ}$C

Time of Irradiation (hrs)	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 (7).

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

   depression.

by transferring the contents of the charcoal trap to an appropriate vessel
and counting in a 4-π 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 fused 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 MFRE (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 these
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 MFRE, an accidential leak of gases
occurred from the reactor into the pit in which it was installed (6).
This gas was dispersed by drawing it into an emergency off-gas line

Table II

Evolution of Xe^{135} from Irradiated Static Fluorides

Flux $= 7 \times 10^{11}$ neutrons $cm^{-2}sec^{-1}$ Temp $\cong$ 650 to 750°C

	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

inserted into the pit. A sample of the off-gas from this line, adsorbed on cooled charcoal, was examined by Bell, et al. (8), 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 MFRE and of one of the in-pile loops indicated the escape of less than about 20% of the Xe^{137} from these systems.

The data obtained on both static and dynamic systems demonstrates that the rare gases are evolved readily from fused 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 (9). 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. More detailed discussion of the matter is deferred here, since it is treated in another place (9).

Behavior of Ruthenium and Niobium

Samples of fluoride fuel removed from two in-pile forced-convection loops and a sample from the MFRE 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 levels of the Ru^{103} content of the fuel, especially in the LITR loop and in the FSRE, indicated the existence of an

Table III

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

	LITR Loop	MFRE	MTR Loop
Fuel Composition (mole% NaF-ZrF$_4$-U^{235}F$_4$)	62.5-12.5-25.0	53.5-40.0-6.5	53.5-40.0-6.5
Fissions/cm^3 of fuel[a] x 10^{-16}	12.9	8.7	655
Calculated Ru^{103} concn. in fuel (atoms/cm^3 x 10^{-15})	3.9	2.5	190
Observed Ru^{103} concn. in fuel (atoms/cm^3 x 10^{-15})	0.001	0.00003	104
Ratio, surface/volume (cm^{-1})	3.5	1	5
Average Ru^{103} surface concn. (atoms x 10^{-15})	1.1	2.5	17

(a) Estimated from heat generation for LITR loop and MFRE; estimated from Zr^{95} analyses for MTR loop.

an efficient means of ruthenium removal from molten fluorides. It was possible to obtain salt-free sections of Inconel pipe from the LITR loop (4) and from the reactor. These sections were selected from parts of each system which were not exposed to high thermal neutron fluxes, thus avoiding activation of the cobalt content of the 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 (10). 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 ~95% Nb^{95} (35 days) and only ~5% Zr^{95} (65 days) at the time of reactor shutdown. The relative amount of Nb^{95} expected if no segregation of the element occurred is about 5% of the total activity.

The pipe section from the MFRE 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 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 MFRE 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. 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 (11) for recovering uranium from spent fuel.

It is evident from the results reported above that ruthenium is rapidly and efficiently removed from fused fluoride fuels by Inconel container surfaces. However, the data obtained for the MTR loop experiment indicate that saturation of the walls with ruthenium was approached in that case. If this interpretation of the data is indeed correct, it seems reasonable to suggest that deposition of fission product metals may well interfere with the course of the ordinary corrosion process, (1, 12) 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 (13).

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.

Behavior of Other Fission Products

Samples of fuel drawn from the MFRE dump tank were examined by radio-
chemical 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 MFRE. The comparative
analyses of the MFRE fuel and 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} could be
interpreted to show partial loss of its parent, 2.6 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 MFRE, 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
ratios of activities of Cs^{136} and 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 MFRE 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. These results were 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} were observed. The specific gamma activity of the sample was estimated as 16 mc/gm 31 days after reactor shutdown and 3.5 mc/gm 79 days after shutdown. The average gamma-ray energies were 0.96 and 0.73 Mev, respectively.

Bell and his coworkers (8) were unable to establish the presence of iodine and bromine in the sample of MFRE 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 MFRE fuel, the question of the fate of the halogen elements in molten fluoride fuels must be left open.

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, (7b), 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 ($\sim$ 30). The yield recommended for use in fission monitoring with Zr^{95} is 0.0664± 0.0013 atoms/fission.

Table IV

Fission Product Analyses in MFRE Fuel, Compared

to a Standard Sample

Nuclide	Activity Ratio, MFRE/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

Conclusion

While most fission product elements remain in solution in molten fluoride fuels, two important classes of elements have a strong tendency to escape: the rare gases by volatilization and the noble metals, Ru and Nb, by deposition on the walls of the container. Experiments are currently in progress, which will reveal the behavior of other elements, particularly the halogens, Mo, and Zr, the latter in fuels not containing ZrF_4 as a constituent. Additional information is required concerning the extent to which metallic deposition can occur on various metals and the degree of protection which the deposited coating affords against corrosion of the container by the fuel. It must be emplasized that in choosing suitable fission monitors for use in fluid fuels, close attention must be given to the chemistry of the fission product elements. While Cs^{137} is very satisfactory for this application in solid fuel elements, the escape of its parent, Xe^{137}, makes it unreliable in fluid fuels. Similarly, Zr^{95} may be unsuitable in fused fluorides which do not contain ZrF_4 as a major constituent.

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