

## Fission-Product Effects in Molten Chloride Fast-Reactor Fuels\*

The use of the molten chlorides as fast-reactor fuels has been given consideration in the past<sup>1-3</sup>; recently, a mobile-fuel fast reactor has been proposed<sup>4</sup> consisting of 30 to 50 mole% (Pu, <sup>238</sup>U)Cl<sub>3</sub> dissolved in a molten mixture of NaCl and KCl, which is to be contained in Hastelloy-N (INOR-8, an alloy of nickel, molybdenum, iron, and chromium). Such molten chloride systems have numerous attributes, which make them attractive to the reactor physicist and engineer; however, since high fuel burnup is an ultimate goal, these systems must also be examined in the light of the chemical effects of large quantities of fission products on fuel performance and stability. Such analyses have been carried out for UO<sub>2</sub> (Ref. 5), UF<sub>4</sub> (Ref. 6), and UCl<sub>4</sub> (Ref. 7). The purpose of this technical note is to estimate these effects for fast-neutron irradiation of PuCl<sub>3</sub> in a molten chloride fuel.

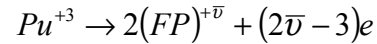
The fission-product yield distributions used in the following calculations are those estimated by Burris and Dillon<sup>8</sup> for <sup>239</sup>Pu irradiation with fast neutrons. The yield distributions presented by them are for about 2-MeV neutron irradiation of <sup>239</sup>Pu. In large ceramic-fueled fast reactors most fission events occur at energies between 1 and 100 keV; in small high-metal-density fast reactors the average fission energy is several hundred keV (Ref. 9). Comparison of mass-distribution fission-product curves<sup>10</sup> with the estimates of Burris and Dillon indicate that what error occurs from the use of higher-energy neutrons instead of those of average fission energy is undoubtedly negligible except in the mass number region between 115 and 125; even there the deviation should have little effect on the final conclusions because of the low fission yields in that region.

Robinson<sup>6</sup>, basing his argument on the requirement of electroneutrality in nuclear reactor fuels, has calculated the change in the chemical nature of the fission products as a function of irradiation time for UO<sub>2</sub> and UF<sub>4</sub> fuels. Using his procedure and fission-product yield distributions<sup>8</sup> for <sup>239</sup>Pu, one can carry through a similar analysis for PuCl<sub>3</sub> fuels. The average fission-product valency,  $\bar{\nu}$ , can be defined as

$$\bar{\nu} = \sum_i \left( \frac{y_i \nu_i}{2} \right)$$

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where  $y_i$  is the number of atoms of the  $i$ 'th fission product per fissioned plutonium atom immediately after irradiation for time  $t$ , and  $\nu_i$  is the valency of the  $i$ 'th fission product. The summation is over all fission products. The valencies in Table I were chosen for the fission products on the basis of the free energy of formation<sup>11-13</sup> of the most stable chloride at 1000K. The general reaction for the PuCl<sub>3</sub> system (all chlorine present as ions) is:



A plot of the average fission-product valency as a function of irradiation time, assuming retention of all rare gases in the system, is given in Figure 1. This plot is similar to the one for molten fluoride fuels presented by Robinson<sup>6</sup>.

Table I

Valencies of the Fission-Product Elements in Molten Chlorides	
Valency	Elements
-2	Se, Te
-1	I
0	Kr, Xe
+1	Rb, Ag, In, Cs
+2	Sr, Zr, Mo, Pd, Cd, Sn, Ba, Sm, Eu
+3	Y, Tc, Ru, Rh, Sb, La, Ce, Pr, Nd, Pm, Gd
+5	Nb

The horizontal line in Figure 1 at an average valence of 1.5 for the fission products corresponds to the maintenance of electroneutrality in a (Pu, U) Cl<sub>3</sub> fuel; this is the condition in which the total valency of the fission products is equal to the valency of the fissioned plutonium atom. Line a in the figure, which corresponds to the original choice of valencies based on chloride stability (see Figure 1 legend), is considerably above the electroneutrality line; this corresponds to a deficit of chlorine ions (or a surplus of electrons) in the melt. As indicated by Robinson<sup>6</sup>, this deficiency would most likely be adjusted by reduction of the least-stable halide to metal.

Line b corresponds to the case where ruthenium is present as the metal. Prior to the time when curve b intersects  $\bar{\nu} = 1.5$ , electroneutrality would be attained by partial reduction of the ruthenium present; beyond this point reduction of another chloride of low stability (PdCl<sub>2</sub>) is required (line c). Additional lines in the figure show the average valencies resulting from other metal

chloride reductions. The figure indicates that, up to an irradiation time of a year, all the ruthenium and a portion of the palladium present should be reduced to metal. Reduction of the fissile chloride should not occur. If the chalcogens are assumed to be zero valent, the lines are somewhat displaced but the conclusions remain essentially the same. If the long-lived rare-gas fission products are not retained in the molten chloride fuel, then alkali-metal and alkaline-earth daughters would not contribute to the calculated average valency. Under these conditions reduction of a portion of the ruthenium present occurs, but there is no necessity for palladium, technetium or molybdenum reduction.

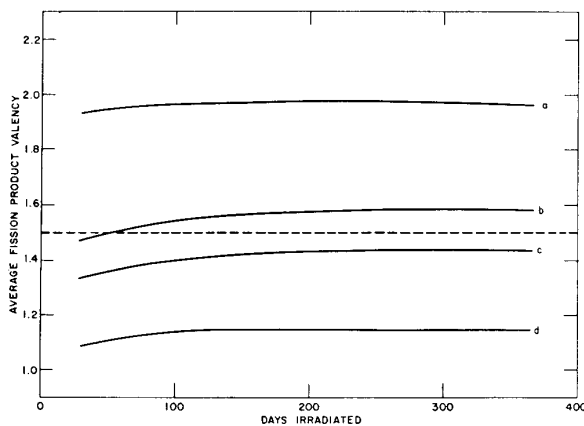


Figure 1. Fission-product average valency for  $^{239}\text{PuCl}_3$  irradiated with 2-MeV neutrons.

Rare gases retained in system.

Curve a—Valencies as in Table I

Curve b—Valencies as in Table I, except  $\text{Ru}^0$ .

Curve c—Valencies as in Table I, except  $\text{Ru}^0$  and  $\text{Pd}^0$ .

Curve d—Valencies as in Table I, except  $\text{Ru}^0$ ,  $\text{Pd}^0$ ,  $\text{Tc}^0$  and  $\text{Mo}^0$ .

One cannot neglect interaction of the fission products with the environment. Examination of thermodynamic data indicates that reaction of the fission products with the iron, nickel and chromium in alloys such as INOR-8 would be expected. The effect of such reactions would be replacement of the easily reducible noble metals by a more difficultly reducible species. The degree and speed of corrosive attack would depend greatly on the manner of deposition of the noble metals on the container. It is conceivable that corrosion may actually be reduced by noble-metal deposition on the container; such a situation may have occurred in in-pile tests of  $\text{UF}_4$  fuels contained in Inconel carried out by Robinson *et al*<sup>14</sup>.

Massive precipitation of noble metals or insoluble salts in mobile fuel would lead to serious operational difficulties, e.g. local hot spots or plugged piping. At high burnups such difficulties would be aggravated; early removal of noble-metal fission products to prevent

precipitation or efficient removal of the rare gases to reduce the amounts of noble metals precipitated would be possible aids. It is clear that in-pile corrosion testing at high burnups is necessary to clarify the effect of noble-metal deposition on interaction of the irradiated fuel with the container metal.

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1. C. GOODMAN, J.L. GREENSTADT, R.N. KIEHN, A. KLEIN, M.M. MILLS and N. TRALLI, "Nuclear Properties of Non-aqueous Fluid-Fuel Reactors," MIT-5000 (1952).
2. J.J. BULMER, E.H. GIFT, R.J. HOLL, A.M. JACOBS, S. JAYE, E. KASSMAN, R.L. McVEAN, R.G. OEHL and R.A. ROSSI, "Fused Salt Fast Breeder", CF-56-8-204 (Del) (1956).
3. M. TAUBE, *Nukleonika* **6**, 565 (1961).
4. L.G. ALEXANDER, "Molten Salt Reactor," *Proc. Conf. Breeding, Economics and Safety in Large Fast Power Reactors*, ANL-6792, p. 553 (1963), also see ORNL-3951, p. 9 (1964).
5. L.F. EPSTEIN and J. NIGRINY, "The Thermodynamics of Reducibility of Fission Product Oxides by Sodium and Other Elements," AECD-3709 (1948).
6. M.T. ROBINSON, *Nuclear Science and Engineering*, **4**, 263 (1958).
7. G. SCATCHARD, H.M. CLARK, S. GOLDEN, A. BOLTAX and R. SCHUHMAN, Jr., "Chemical Problems of Non-aqueous Fluid-Fuel Reactors," MIT-5001 (1952).
8. L. BURRIS, Jr. and I.G. DILLON, "Estimation of Fission Product Spectra in Discharged Fuel from Fast Reactors," ANL-5742 (1957).
9. D. OKRENT, *Nuclear Metallurgy* **9**, 1 (1963).
10. S. KATCOFF, *Nucleonics* **18**, 201 (1960).
11. C.J. SMITHELLS, *Metals Reference Book*, 3rd Ed., Butterworths, London, (1962).
12. A. GLASSNER, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K," ANL-5750 (1957).
13. C.E. WICKS and F.E. BLOCK, "Thermodynamic Properties of 65 Elements," Bureau of Mines Bulletin 605 (1963).
14. M.T. ROBINSON, W.A. BROOKSBANK, Jr., S.A. REYNOLDS, H.W. WRIGHT and T.H. HANDLEY, *Nuclear Science and Engineering*, **4**, 288 (1958).