

# FISSION-PRODUCT RELEASES FROM CANDU FUEL AT 1650°C: THE HCE4 EXPERIMENT

L.W. DICKSON AND R.S. DICKSON

Fuel Safety Branch  
AECL, Chalk River Laboratories  
Chalk River, Ontario, Canada K0J 1J0

## ABSTRACT

The HCE4 (Hot-Cell Experiment 4) experiment was performed to study fission-product releases from CANDU fuel at 1650°C. Three sets of tests were conducted to assess the effects of fuel element length, gaseous environment, and heating rate on fission-product release. No significant effect of fuel element length was observed for most fission products released under the test conditions. Consistent with previous observations, oxidizing atmospheres increased the releases of most fission products. There was no significant effect of heating rate on fission-product releases from full-cross-section fuel fragment samples for the particular fuel and the range of heating rates studied.

## INTRODUCTION

This paper describes the results of an experiment that was performed to assess the effects of fuel element length, gaseous environment and heating rate on fission-product releases (FPR) from CANDU fuel at 1650°C. The experiment, designated HCE4 (Hot-Cell Experiment 4), was part of a research program to determine fission-product release, deposition and transport from fuel under accident conditions [1-3]. In the HCE4 experiment, sheathed and unsheathed samples of CANDU fuel were heated to peak temperatures of 1600-1650°C under controlled conditions. The tests were conducted in flowing atmospheres of air, steam and/or argon. Fission-product release data were collected using  $\gamma$ -spectrometers to view the fuel directly, and to view the effluent gases.

## EXPERIMENTAL APPARATUS AND FUEL SAMPLES

A general schematic of the experimental apparatus is shown in Figure 1. A SATEC Systems model FH-080-RA-33-3x12 split horizontal tube furnace with Super Kanthal 33 molybdenum disilicide heating elements was used for the HCE4 experiment. The furnace was mounted on a travelling track, and achieved temperature ramps of up to  $8 \text{ K}\cdot\text{s}^{-1}$  by moving the pre-heated furnace over the fuel sample. While the furnace was moved, the fuel sample (located inside an alumina furnace tube) was held stationary in the field of view of a  $\gamma$ -spectrometer by means of a magnetic pushrod assembly. The hot zone of the furnace could be moved over the fuel sample

with no loss of carrier gas or system pressure. The gas flows were controlled using Cole-Parmer type N112-02 valved rotameters and measured using Matheson model 8175 mass flow meters. The gas supply flows (Ar/2% $\text{H}_2$  or air) were  $297 \pm 14 \mu\text{mol}\cdot\text{s}^{-1}$ . A steam generator added steam to the flowing carrier gas for the tests that used steam (water supply flow  $930 \pm 50 \mu\text{mol}\cdot\text{s}^{-1}$ ). Oxygen sensors were located upstream and downstream of the fuel sample to monitor kinetics of fuel and sheath oxidation [4]. The fuel sample temperature was monitored using a type R thermocouple (measurement uncertainty  $\pm 10^\circ\text{C}$  at  $1600^\circ\text{C}$ ). One Aptec  $\gamma$ -spectrometer with an AP series high-purity germanium detector viewed the sample directly through a collimated port in the hot-cell wall, to monitor the fractional retention of fission products in the fuel sample on-line during a test. A second high-purity germanium  $\gamma$ -spectrometer was used to monitor the noble-gas activity in the gas stream downstream of a steam condenser. Deposition coupons and aerosol collectors located downstream of the fuel sample in some tests were  $\gamma$ -scanned after the experiment. The deposition and aerosol results will be reported elsewhere.

The fuel samples used in most of the tests in the HCE4 experiment were from an outer element (#16) of bundle Q53150C irradiated in channel K17 in the Darlington Unit 2 reactor at a maximum linear power of  $42 \text{ kW}\cdot\text{m}^{-1}$  to a burnup of  $\sim 210 \text{ MW}\cdot\text{h}\cdot(\text{kg U})^{-1}$ . The HCE4 experiment was conducted one to two months after the irradiation in the Darlington reactor. Fuel samples for the J07 and J08 tests were taken from a fuel element from the FDO-717 experiment (with the same diameter and sheathing as the CANDU 37-element bundle design) irradiated in the E-12 (Blowdown Test Facility) test section of the U-1 loop in the NRU (National Research Universal) reactor at a maximum linear power of  $64 \text{ kW}\cdot\text{m}^{-1}$  to a burnup of  $150 \text{ MW}\cdot\text{h}\cdot(\text{kg U})^{-1}$ . A fuel element from the same irradiation was used for the BTF-105B experiment [5]. The fuel samples for the J07 and J08 tests were cooled for about 15 months prior to the HCE4 experiment.

## TEST CONDITIONS

Three sets of tests were conducted in the HCE4 experiment (see Table 1). The first set of tests (J01, J02, J03 and J04) was performed to assess the effect of the gaseous environment (inert, steam and air) on fission-product release from clad samples of CANDU fuel at  $1650^\circ\text{C}$ . In all of these tests, the fuel samples were heated to the test temperature in an effectively "inert" atmosphere (Ar/2% $\text{H}_2$ ), prior to being exposed to the test atmosphere. The second set of tests (J07 and J08), together with the J03 and J04 tests from the first set, was performed to assess the effect of fuel element length (20 or 100 mm) on fission-product release from sheathed samples of CANDU fuel at  $1650^\circ\text{C}$ , in a gas supply mixture containing 76 mol% steam and 0.5 mol%  $\text{H}_2$  (balance Ar). The fuel samples used in the J07 and J08 tests were heated to the test temperature in the test atmosphere. The third set of tests (J05, J06, J09 and J10) was performed to assess the effect of heating rate on fission-product release from full-pellet-cross-section fuel fragment samples in an inert (Ar/2% $\text{H}_2$ ) environment.

## DATA ANALYSIS

In this experiment, the direct-viewing  $\gamma$ -spectrometer (Figure 1) detected Y-91, Zr-95, Nb-95, Ru-103, Ru-106, Te-129m, I-131, Cs-134, Cs-137, Ba-140, La-140, Pr-144 and Eu-156. Release

percentages were normalized, using selected  $\gamma$ -ray peaks of La-140, Zr-95 and Pr-144, to correct for attenuation and sample geometry changes [1]. The release percentages for Te-129m were calculated from the count rate changes of the 696 keV peak, which contained contributions from Te-129 and Pr-144. The  $\gamma$ -ray peaks of some fission-product elements of considerable interest (e.g., I and Cs) had poor counting statistics. For the calculation of integral releases, the combined spectra obtained before the sample was inserted into the furnace were compared with those obtained after the test in order to improve the counting statistics. Table 1 shows the normalized integral fission-product releases and their statistical uncertainties ( $1\sigma$ ) for the 10 tests in the HCE4 experiment. The data processing procedure gave negative (but not statistically significant) values of fractional release for some isotopes. These non-physical negative values of fractional release were re-assigned a value of zero. The release percentage of selected isotopes as a function of time for selected tests are plotted in Figures 2-6.

The gas-monitoring  $\gamma$ -spectrometer detected peaks from Kr-85, Xe-131m, Xe-133m and Xe-133. The initial calculated percentage releases of the noble-gas isotopes varied widely, and were not very similar to the Cs-137 percentage release, probably due to systematic errors in  $\gamma$ -spectrometer efficiency calibration. Since noble gases and cesium showed similar release behaviour and have shown similar release percentages in previous experiments [1,6,7], the noble-gas releases in each test were scaled to give the same final cumulative percentage release as Cs-137.

## RESULTS AND DISCUSSION

The fuel samples were cut, polished and etched after the tests to assess the changes in the fuel and sheath microstructure. Post-test micrographs of the fuel sample from test J03 are shown in Figure 7. There was no statistically significant change in fuel grain size due to the post-irradiation temperature transient. There was some evidence of  $\text{UO}_2$ -Zircaloy interaction in the tests performed using sheathed fuel samples. The macrographs in Figure 7 show  $\text{UO}_2$ -Zircaloy alloy formation where Zircaloy came into contact with the fuel, and also show limited intrusion of molten material into some cracks. The macrographs indicate that less than 5% of the  $\text{UO}_2$  fuel interacted with the Zircaloy in these tests. Solid/solid interaction between  $\text{UO}_2$  and Zircaloy occurs locally in regions of good contact at temperatures above  $1500^\circ\text{C}$ , in the absence of an external overpressure [8]. Zircaloy reduces  $\text{UO}_2$  to metallic uranium, and the metallic uranium reacts with zirconium to form a (U,Zr) alloy which is molten at temperatures above  $\sim 1150^\circ\text{C}$ . Gaseous fission products form bubbles in the molten (U,Zr) alloy. The microstructure in the interaction zone (shown in the lower left frame of Figure 7), with its large voids and lack of apparent grain structure, is typical of previously molten (U,Zr) alloys. About 1500 s after the J03 and J04 fuel samples reached  $1600^\circ\text{C}$ , they were exposed to steam, which oxidized the Zircaloy,  $\text{UO}_2$  and material from the (U,Zr) interaction. The absence of layers in the sheath microstructure located away from the  $\text{UO}_2$ -Zircaloy interaction zones indicates that the sheath was fully oxidized, and that the oxidation occurred only from the outside in test J03.

The first set of tests (J01, J02, J03 and J04) was performed to assess the effect of environment (inert, steam and air) on fission-product release from clad samples of CANDU fuel at  $1650^\circ\text{C}$ . The releases of the volatile fission products (Kr, Xe, Cs and I) from the clad fuel samples were

low (<10%) in the Ar/2% $H_2$  environment, and were high (75-100%) in the steam and air environments. Rapid release of Kr and Xe began several hundred seconds after exposure to steam, consistent with the time required to fully oxidize the fuel sheath [1,7]. The Te-129m release in the inert atmosphere test was negligible. The Te-129m releases in the oxidizing gaseous environments varied significantly (30-80%), and did not appear to depend on the nature of the oxidant (steam or air). Some Ru release (~15%) was observed, beginning about 3600 s after the onset of rapid Cs release in the air environment. No Ru release was observed in the inert or steam atmosphere tests. No statistically significant releases of Ba, Eu, La, Nb, Nd, Pr, Y and Zr were observed in these tests.

The second set of tests (J03, J04, J07 and J08) was performed to assess the effect of fuel element length on fission-product release from sheathed samples of CANDU fuel at 1650°C in a gas-supply mixture containing 76 mol% steam and 0.5 mol%  $H_2$  (balance Ar). For most fission products released under the test conditions (Xe, Kr, Cs and I), no significant differences were found between the releases from clad fuel samples of different lengths (20 and 100 mm). The fractional Te-129m release seems to have been higher from one of the shorter fuel samples, but the uncertainty in this result is large. No firm conclusions can be drawn due to the large uncertainties, but the difference in the Te-129m releases may arise from its affinity for unoxidized Zircaloy and local differences in the extent of oxidation of the cladding. These results indicate that in CANDU safety analysis it may not be necessary to account specifically for any effect of fuel element length on releases of volatile fission products from the fuel. The possible exceptions to this conclusion are for those species that are known to have a specific chemical interaction with the cladding, and that may be affected by steam ingress into the fuel element, e.g., Te and Sb.

The third set of tests (J05, J06, J09 and J10) was performed to assess the effect of heating rate on fission-product release from full-pellet-cross-section fuel fragment samples in an inert (Ar/2% $H_2$ ) environment. The heating rates in tests J05, J09 and J10 were 0.2, 1-2 and 6  $K \cdot s^{-1}$ , respectively. In test J06, the fuel sample was subjected to two temperature ramps to ~1626°C (the first at a heating rate of 1-2  $K \cdot s^{-1}$  and the second at ~4.7  $K \cdot s^{-1}$ ). Good results were obtained on releases of volatile fission products (Cs, I) in these tests, but the noble gas (Kr, Xe) release data are not as reliable because of experimental difficulties. There appeared to be little effect of heating rates between 0.2 and 6  $K \cdot s^{-1}$  on IPR from fuel samples heated to ~1650°C in an inert (Ar/2% $H_2$ ) atmosphere. Heating rate effects are thought to be most significant for fission products located on grain boundaries. The fuel used in the HCE4 experiment had a relatively small grain-boundary inventory [3].

## CONCLUSIONS

The HCE4 (Hot-Cell Experiment 4) experiment was performed to study fission-product releases from CANDU fuel at 1650°C. Three sets of tests were conducted to assess the effects of fuel element length, gaseous environment, and heating rate on fission-product release. No significant effect of fuel element length was observed for most fission products released under the test conditions. Consistent with previous observations, oxidizing gaseous environments increased the releases of most fission products. There was no significant effect of heating rate on

fission-product releases from full-cross-section fuel fragment samples for the particular fuel and the range of heating rates studied. The data from the HCF4 fission-product release experiment are suitable for use in the validation of the SOURCE fission-product release code [9].

## ACKNOWLEDGEMENTS

The authors would like to thank R.D. Barrand, R.F. O'Connor and D.D. Semeniuk for technical assistance in the HCE4 experiment. This work was partially supported by the CANDU Owners Group (COG) Safety and Licensing R&D program under the joint sponsorship of Ontario Power Generation, Hydro Québec, New Brunswick Power and AECL.

## REFERENCES

1. BARRAND, R.D., DICKSON, R.S., LIU, Z. AND SEMENIUK, D.D., "Release of Fission Products from CANDU Fuel in Air, Steam and Argon Atmospheres at 1500-1900°C: The HCE3 Experiment", Proc. 6<sup>th</sup> Int. Conf. CANDU Fuel, Niagara Falls, Canada, 1, 271-280, Canadian Nucl. Soc., Toronto, ISBN 0-919784-64-X (1999).
2. LIU, Z., DICKSON, R.S., DICKSON, L.W., BILANOVIC, Z. AND COX, D.S., "Fission-Product Release During Transient Heating of Irradiated CANDU Fuel", Nucl. Technol., 131, 22-35, July (2000).
3. DICKSON, R.S., O'CONNOR, R.F. AND SEMENIUK, D.D., "Grain Boundary Inventories of Krypton in CANDU Fuel", Proc. IAEA Seminar on Fission Gas Behaviour in Water Reactor Fuels, Cadarache, France, 337-346, ISBN 92-64-19715-X (2000).
4. COX, D.S., O'CONNOR, R.F. AND SMELTZER, W.W., "Measurement of Oxidation/Reduction Kinetics to 2100°C Using Non-Contact Solid-State Electrolytes", Solid State Ionics, 53-56, 238-254 (1992).
5. IRISH, J.D., CRAIG, S.T., BOURQUE, L.R., JONCKHEERE, M.G., KYLE, G., VALLIANT, P.J., DICKSON, L.W. AND PEPLINSKIE, R.T., "Preliminary Results of the BTF-105B Experiment: An In-Reactor Test of Fuel Behaviour and Fission-Product Release and Transport Under LOCA/LOECC Conditions", Proc. 19<sup>th</sup> Annual Canadian Nucl. Soc. Conf., Toronto, Vol. 2, Paper C-2, Canadian Nucl. Soc., Toronto, ISSN 0227-1907 (1998).
6. IGLESIAS, F.C., BRITO, A.C., LIU, Y., PETRILLI, M.A., HU, R., RICHARDS, M.J., ELDER, P., COX, D.S. AND LEWIS, B.J., "Fission Product Release Mechanisms and Groupings" Proc. 4<sup>th</sup> Int. Conf. CANDU Fuel, Pembroke, Canada, 2, 5B-23 - 5B-44, Canadian Nucl. Soc., Toronto, ISBN 0-919784-53-4 (1995).
7. IGLESIAS, F.C., LEWIS, B.J., REID, P.J. AND ELDER, P.H., "Fission Product Release Mechanisms During Reactor Accident Conditions", J. Nucl. Mater. 270, 21-38 (1999).
8. DIENST, W., HOFMANN, P. AND KERWIN-PECK, D.K., "Chemical Interactions Between UO<sub>2</sub> and Zircaloy-4 from 1000 to 2000°C", Nucl. Technol. 65, 109-124 (1984).
9. BARBER, D.H., IGLESIAS, F.C., HOANG, Y., DICKSON, L.W., DICKSON, R.S., RICHARDS, M.J. AND GIBB, R.A., "SOURCE IST 2.0: Development and Beta Testing", Proc. 6<sup>th</sup> Int. Conf. CANDU Fuel, Niagara Falls, Canada, 1, 393-402, Canadian Nucl. Soc., Toronto, ISBN 0-919784-64-X (1999).

TABLE 1: NORMALIZED INTEGRAL FISSION-PRODUCT RELEASES (%) <sup>(1)</sup> FROM FUEL SAMPLES HEATED TO ~1650°C

Test	J01	J02	J03	J04	J05	J06	J07	J08	J09	J10
Fuel Length /mm	20	20	20	100	5	5	107	20	5	5
Sheathed	Yes	Yes	Yes	Yes	No	No	Yes	Yes	No	No
Environment	Ar/H <sub>2</sub>	Air	H <sub>2</sub> O/H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub>	Ar/H <sub>2</sub>	Ar/H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub>	H <sub>2</sub> O/H <sub>2</sub>	Ar/H <sub>2</sub>	Ar/H <sub>2</sub>
Heating Rate /K.s <sup>-1</sup>	-	-	-	-	0.2	1-2 / 5	-	-	1-2	-6
Max. Temp. /°C	1620	1645	1640	1650	1629	1626	1628	1631	1627	1612
Time at Temp. /s	5733	6712	6360	6462	4840	5780	3737	4052	4240	1960
Ba-140	1 ± 3	0 ± 4	0 ± 3	0 ± 4	1 ± 2	0 ± 4			0 ± 5	2 ± 2
Cs-134	2 ± 5	75 ± 1	84 ± 1	82 ± 2	24 ± 2	19 ± 2	59 ± 1	100 - 9	24 ± 2	16 ± 2
Cs-137	0 ± 6	74 ± 2	86 ± 1	84 ± 2	24 ± 3	18 ± 3	68 ± 1	70 ± 2	18 ± 4	13 ± 4
Eu-156	6 ± 4	5 ± 5	4 ± 6	7 ± 5	10 ± 6	3 ± 9			10 ± 13	0 ± 6
I-131	11 ± 4	100 - 10	79 ± 3	100 - 10	16 ± 3	13 ± 5			6 ± 9	7 ± 4
Kr-85	8 ± 1	100 - 11	74 ± 10	73 ± 8	4 ± 1	13 ± 2	58 ± 8	57 ± 7	15 ± 2	10 ± 2
La-140	1 ± 4	1 ± 4	2 ± 4	0 ± 3	1 ± 2	3 ± 3			0 ± 6	0 ± 4
Nb-95	0 ± 6	0 ± 5	4 ± 5	0 ± 4	2 ± 3	0 ± 3	0 ± 2	0 ± 2	1 ± 2	0 ± 2
Nd-147	9 ± 8	0 ± 11	15 ± 8	12 ± 11	3 ± 9	0 ± 17			ND <sup>(4)</sup>	8 ± 10
Pr-144	0 ± 5	0 ± 5	2 ± 5	1 ± 5	0 ± 5	0 ± 5	0 ± 3	0 ± 2	0 ± 5	0 ± 4
Ru-106 <sup>(2)</sup>	0 ± 4	13 ± 3	1 ± 3	0 ± 3	0 ± 3	0 ± 3	2 ± 2	0 ± 2	0 ± 4	4 ± 2
Ru-103	0 ± 4	19 ± 3	0 ± 4	0 ± 3	0 ± 3	2 ± 3	0 ± 16	1 ± 12	0 ± 3	0 ± 2
Te-129m <sup>(3)</sup>	2 ± 17 <sup>(3)</sup>	37 ± 14 <sup>(3)</sup>	86 ± 12 <sup>(3)</sup>	34 ± 12 <sup>(3)</sup>	7 ± 8 <sup>(3)</sup>	26 ± 11 <sup>(3)</sup>			18 ± 15 <sup>(3)</sup>	0 ± 7 <sup>(3)</sup>
Xe-131m	5 ± 1	100 - 7	84 ± 7	90 ± 6	5 ± 1	11 ± 1			22 ± 2	15 ± 2
Y-91	4 ± 5	0 ± 10	17 ± 4 <sup>d</sup>	0 ± 5	4 ± 3	0 ± 12			1 ± 16	6 ± 4
Zr-95	0 ± 6	0 ± 5	7 ± 5	0 ± 3	2 ± 3	0 ± 3	0 ± 1	0 ± 1	2 ± 2	0 ± 2

<sup>(1)</sup> Statistical uncertainty values are ± 1σ. Non-physical negative release percentages that were not statistically significant were reassigned a value of zero. Release percentages of 100% were assigned negative uncertainties only.

<sup>(2)</sup> Detected as Rh-106.

<sup>(3)</sup> Non-physical Te-129m release percentages (>100%) were obtained in some tests due to Pr-144 interference with the 696 keV peak, and a large uncertainty in the relative fission and gamma yields of Pr-144 and Te-129m. The Te-129m releases quoted in this table were scaled to the Cs-137 releases in test J03.

<sup>(4)</sup> The Nd-147 gamma-ray at 531 keV was not detected in this test.

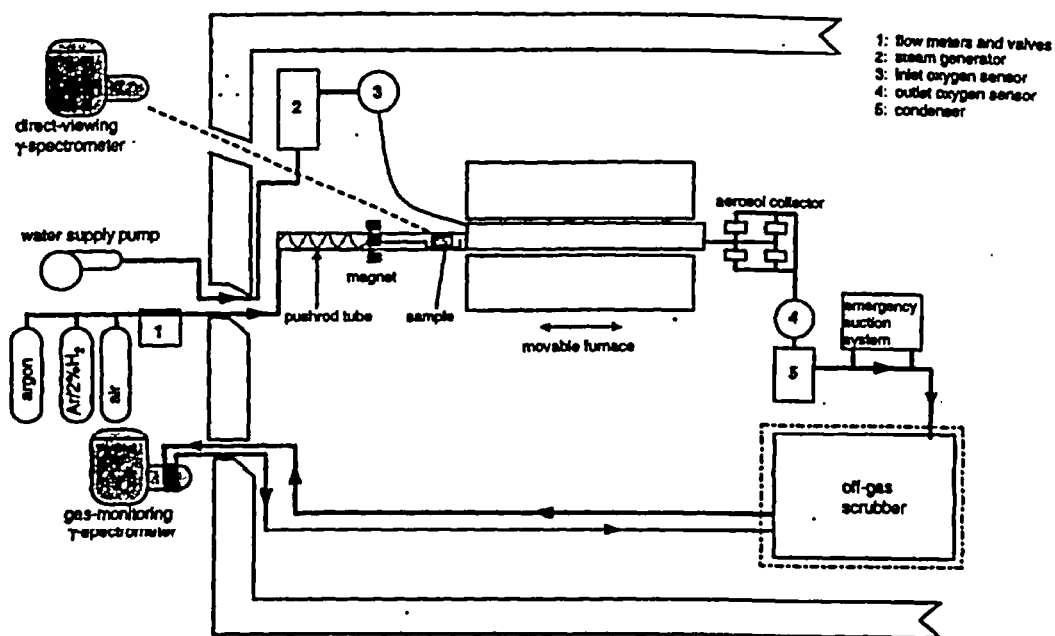


FIGURE 1: SCHEMATIC OF HCE4 HOT-CELL APPARATUS

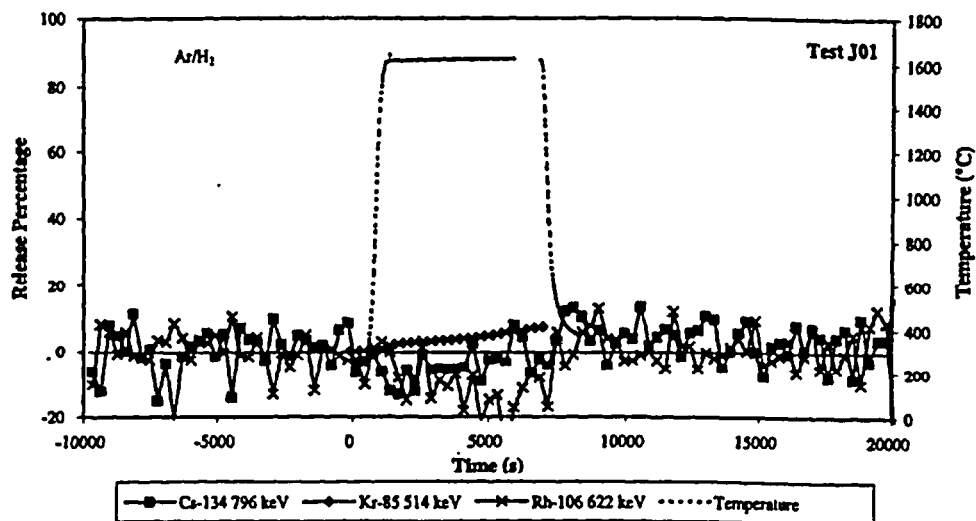


FIGURE 2: CESIUM, KRYPTON AND RUTHENIUM (AS Rh-106) RELEASE (%) AS A FUNCTION OF TIME FOR HCE4 TEST J01 (20-mm-LONG SHEATHED DARLINGTON FUEL, Ar/H<sub>2</sub>, 1620°C).

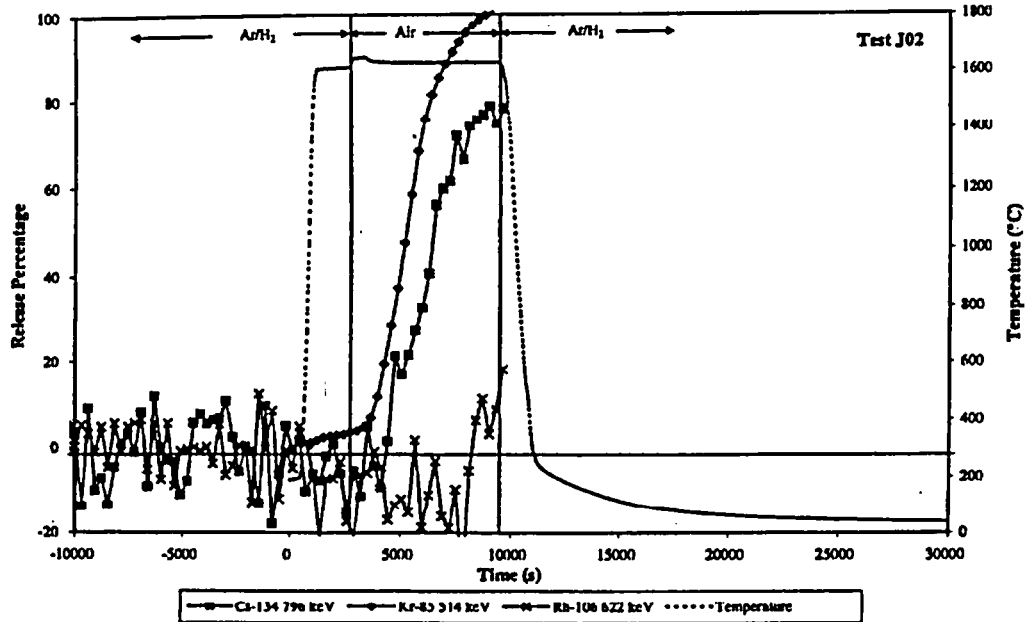


FIGURE 3: CESIUM, KRYPTON AND RUTHENIUM (AS Rh-106) RELEASE (%) AS A FUNCTION OF TIME FOR HCE4 TEST J02 (20-mm-LONG SHEATHED DARLINGTON FUEL, AIR AND Ar/H<sub>2</sub>, 1645°C).

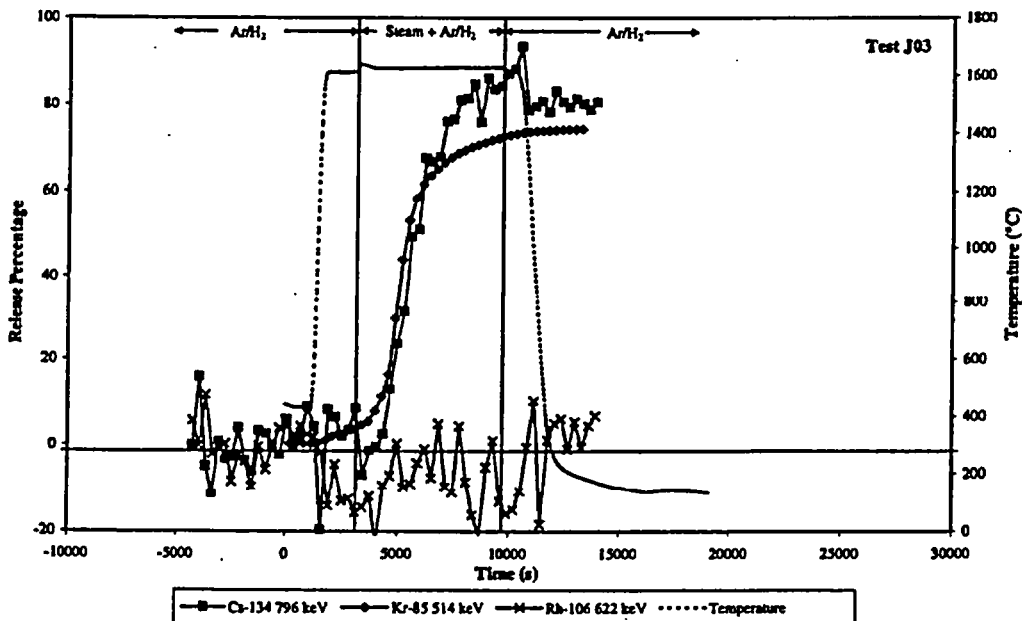


FIGURE 4: CESIUM, KRYPTON AND RUTHENIUM (AS Rh-106) RELEASE (%) AS A FUNCTION OF TIME FOR HCE4 TEST J03 (20-mm-LONG SHEATHED DARLINGTON FUEL, STEAM + Ar/H<sub>2</sub>, 1640°C).



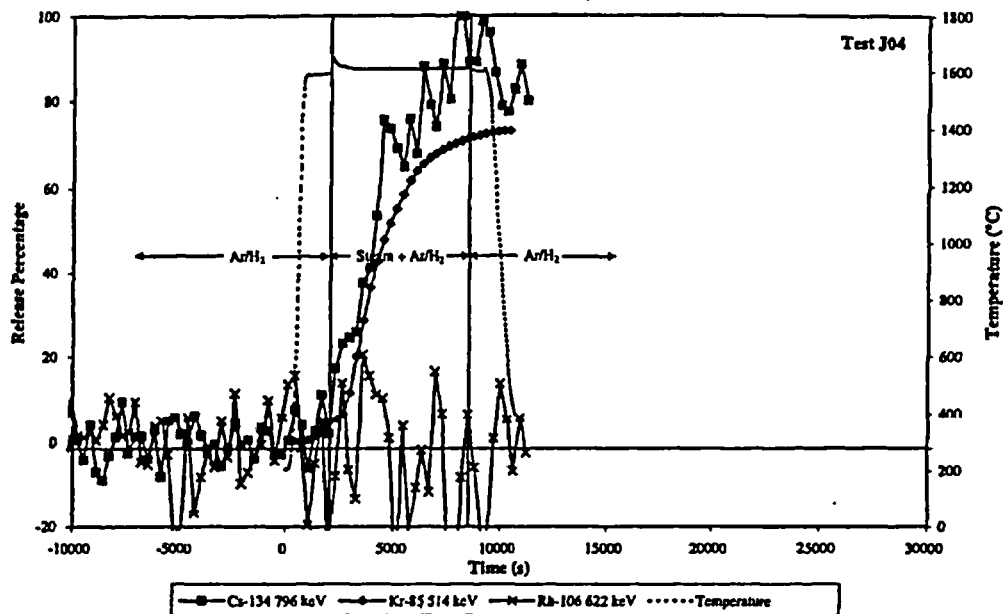


FIGURE 5: CESIUM, KRYPTON AND RUTHENIUM (AS Rh-106) RELEASE (%) AS A FUNCTION OF TIME FOR HCE4 TEST J04 (100-mm-LONG SHEATHED DARLINGTON FUEL, STEAM + Ar/H<sub>2</sub>, 1650°C).

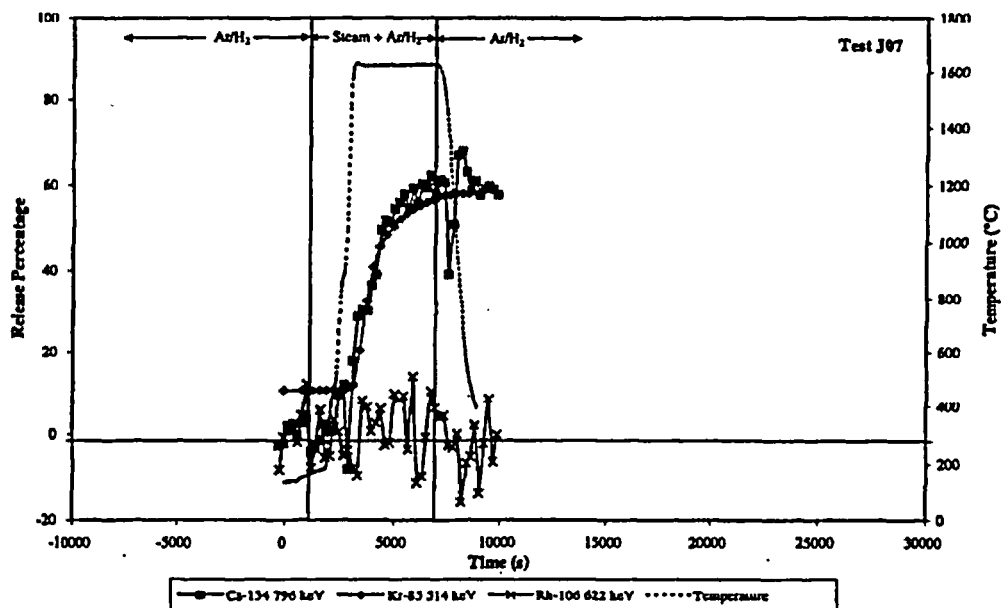


FIGURE 6: CESIUM, KRYPTON AND RUTHENIUM (AS Rh-106) RELEASE (%) AS A FUNCTION OF TIME FOR HCE4 TEST J07 (107-mm-LONG SHEATHED FDO-717 FUEL, STEAM + Ar/H<sub>2</sub>, 1628°C).

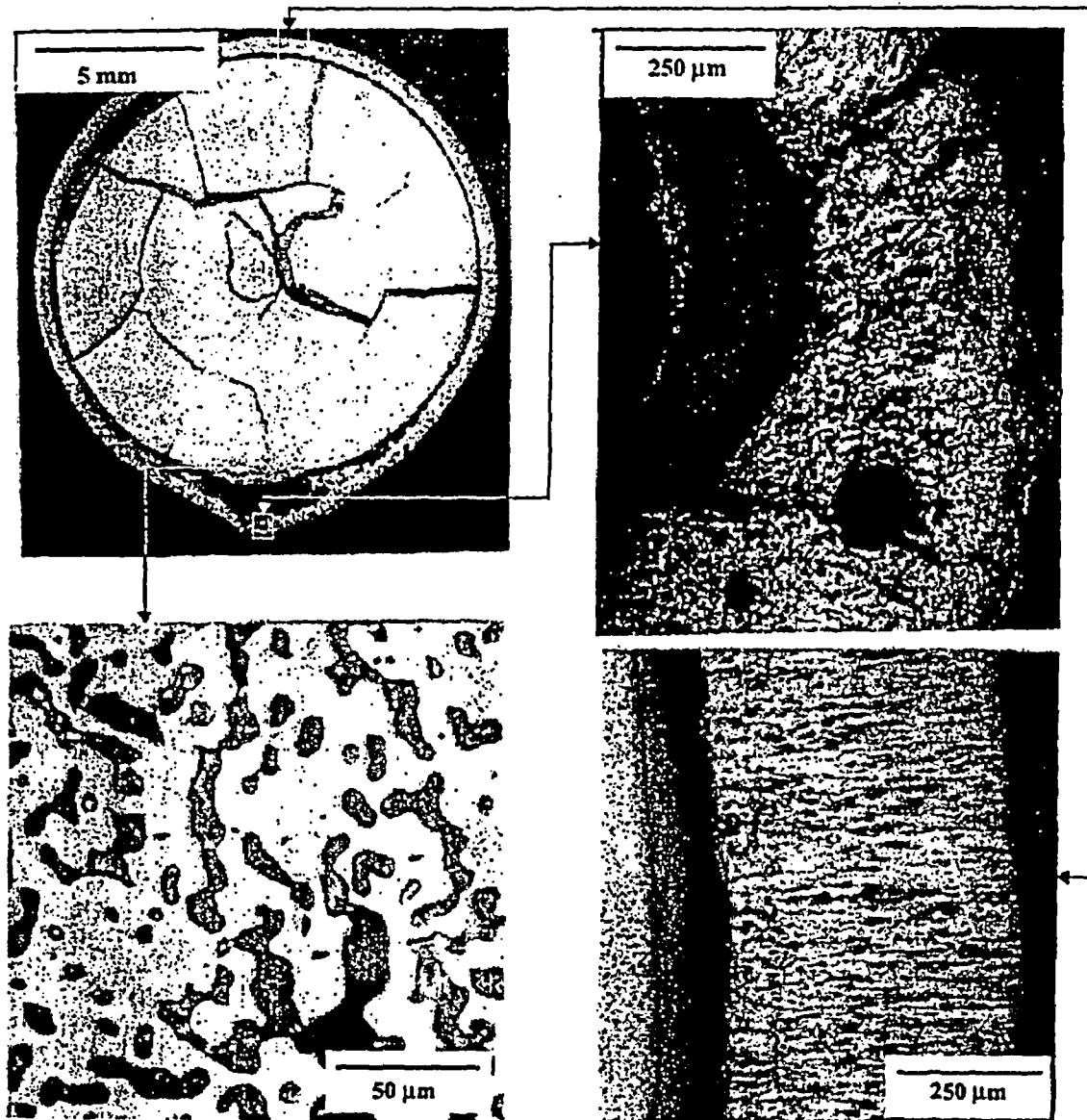


FIGURE 7: POST-TEST CERAMOGRAPHS OF THE J03 FUEL SAMPLE (1640°C, STEAM PLUS Ar/2%H<sub>2</sub>). UPPER LEFT: MACROGRAPH OF FUEL. UPPER RIGHT: MICROGRAPH OF SHEATH AT DEFORMATION, AS POLISHED. LOWER RIGHT: MICROGRAPH OF FULLY OXIDIZED SHEATH REMOTE FROM DEFORMATION, AS POLISHED. LOWER LEFT: MICROGRAPH OF FUEL PERIPHERY NEAR DEFORMED PORTION OF THE SHEATH. THIS SHOWS MICROSTRUCTURE TYPICAL OF UO<sub>2</sub>-ZIRCALOY INTERACTION.