RELEASE OF FISSION PRODUCTS FROM CANDU FUEL IN AIR, STEAM AND ARGON ATMOSPHERES AT 1500-1900°C: THE HCE3 EXPERIMENT

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ABSTRACT

Fission-product release from Zircaloy-sheathed segments of CANDU fuel was measured in the six HCE3 tests in argon, steam and air environments at peak temperatures between 1510 and 1930°C. On-line γ-spectrometry showed significant fractional releases for Xe, Kr, I, Cs, Te and Ru. Post-test deposition measurements also detected releases of Sn, Sb, Ag, Ba, Zr and Nb. The release rates of Kr, Xe, I and Cs were very low before complete sheath oxidation; their peak release rates in steam after complete sheath oxidation were not very temperature-dependent. Ru release was delayed by more than 2000 s after oxidative releases of the volatile fission products.

INTRODUCTION

This paper describes the results of a fission-product release experiment conducted in Universal Cell #3 at Chalk River Laboratories (CRL). The experiment, designated HCE3 (Hot-Cell Experiment 3), was sponsored by the CANDU Owners Group (COG) as part of its program to determine fission-product release, deposition and transport from fuel under accident conditions. The experiment was intended to measure fission-product release and transport from sheathed fuel samples at higher temperatures than previous experiments; the highest temperature previously used in sheathed-fuel tests at CRL was 1650°C [1].

Zircaloy-sheathed segments of CANDU fuel were heated to peak temperatures in the range 1500-1930°C. Air, steam and/or argon atmospheres were flowed past the heated fuel, through a deposition tube into an aerosol collection apparatus. Fission-product release data were collected using direct-viewing and gas-monitoring γ-spectrometry, and post-test γ-scanning of the apparatus.

EXPERIMENTAL APPARATUS & FUEL SAMPLES

A general schematic of the experimental apparatus is shown in Figure 1. A specialized furnace made by Kanthal Artcor Inc. employing zirconia resistive heating elements was used. Chromel pre-heaters were used to heat the zirconia heating elements to >600°C, at which temperature the zirconia heating elements conduct sufficient current to take over the heating task.

The fuel sample was positioned in the centre of the hot zone of the furnace on a thoria pedestal. The gas was flowed upward through the zirconia furnace tube. The vertical furnace tube was surrounded by a segmented zirconia guide tube. The annulus between the furnace tube and the guide tube was flooded with flowing argon or argon/hydrogen mixtures to retard the permeation of oxygen into the furnace tube at high temperatures. The furnace tube, deposition tube and aerosol collection filters were replaced after each test to allow γ-scanning measurement of released fission products.

The direct-viewing γ-spectrometer (Figure 1) monitored the fractional retention of fission products in the sample during 300 s intervals in the test, while the gas-monitoring γ-spectrometer measured the noble-gas activity in the gas stream downstream of the condenser during 300 s intervals. Zirconia oxygen sensors were used to monitor the oxygen partial pressure of the test atmosphere upstream of the furnace tube and downstream of the aerosol collection filters. Sample temperatures were measured using a pyrometer and thermocouples in the laboratory. Unfortunately, the pyrometer failed on placing the apparatus in the hot cell, so sample temperatures for hot-cell tests were inferred from measurements at a thermocouple remote from the furnace tube using sample temperature behaviour measured in laboratory tests with similar temperature histories.

All irradiated fuel specimens used in this experiment were taken from an outer element of a Darlington fuel bundle (peak linear power 46kW/m, burnup 234 MWh/kgU, 0.6% measured noble-gas gap inventory). Specimens were obtained by cutting the fuel element transversely, giving ~25-mm-long segments of fuel element. Zircaloy end-caps were press-fitted onto the segments.

TEST CONDITIONS

In each test, the sample was heated to a temperature of 1500°C or above in flowing Ar/2%H_2 (tests H01, H02 and H03) or Ar/4%H_2 (tests H04, H05 and H06) to prevent premature oxidation of the sample during the gradual heating of the furnace. The oxidizing atmosphere was added at a temperature T_{ox} for an interval of time t_{ox}; these values for each test are given in Table 1, together with the peak temperature and test atmosphere used in each test. Steam was added to the Ar/H_2 carrier gas stream in tests H01, H02 and H06 at a low enough temperature to prevent excessive formation of molten material, which might have compromised furnace tube integrity. Air was substituted for Ar/H_2 carrier gas in tests H02 and H05 at temperatures above 1500°C to prevent excessive sample degradation by U_3O_8 formation. In each test, the sample was cooled from test temperature to room temperature in flowing Ar/H_2.

In test H01, the furnace tube broke on reaching peak sample temperature. The steam flow was shut off and the flow rates of inert gas inside and outside the furnace tube were increased to maintain the inertness of the atmosphere at the sample. The furnace temperature was then reduced.

In test H04, the atmosphere was effectively argon containing variable amounts of hydrogen and steam; oxygen entered into the annulus surrounding the furnace tube via the breaks in the segmented zirconia guide tube, then permeated through the zirconia furnace tube. Calculations using the oxygen sensor readings indicate that the $H_2O:H_2$ ratio in the outlet gas was 1:1 at a sample temperature of 1500°C and about 5:1 while the sample temperature was above 1800°C.

DATA ANALYSIS

In this experiment, the direct-viewing γ-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. To improve the counting statistics for I and Cs isotopes, spectra accumulated over 300 s periods were added together to give total spectrum collection times of ~1200 s. Release percentages were normalized using selected γ-ray peaks of La-140 and Zr-95 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 gas-monitoring γ-spectrometer detected peaks from Kr-85, Xe-131m and Xe-133. The initial calculated percentage releases of the noble-gas isotopes varied widely, and were not very similar to the Cs-134 percentage release, probably due to systematic errors in γ-spectrometer efficiency calibration. Since noble gases and cesium showed similar release behaviour and have shown similar release percentages in previous experiments [1,2], the noble-gas releases in each test were scaled to give the same final cumulative percentage release as Cs-134.

RESULTS

Ceramography of the fuel samples after high-temperature testing showed full oxidation of the sheath in all the tests including H04, which was conducted in nominally-inert atmosphere. Most of the sheath oxidation was from the outside. The only remaining metallic Zircaloy was a small island in the middle of an end-cap on the H06 sample.

The fission-product release behaviours of several isotopes are shown for tests H01 through H06 in Figures 2 through 7, respectively. The fractional release behaviours of Kr and the two Xe isotopes were almost identical to the behaviour of Cs. The beginning of rapid Xe-133 release in each test was within 300 s (one spectrum interval) of the beginning of rapid Cs-134 release. The I-131 releases exhibited most of the same characteristics as the Cs-134 releases, taking into account the poorer counting statistics of I-131 in these samples.

The release curves for the 696 keV peak (Figures 2, 3 and 4), which includes a contribution from Te-129m, have not been processed to remove the Pr-144 contribution; the curves are included only to show the timing of Te-129m releases. Most of the tellurium was probably released in tests H01 and H02 (Table 1), and statistically significant releases occurred during tests H03 and H06. Test H04, conducted in a less-oxidizing environment, and test H05, during which the oxidizing atmosphere was applied for a short time, showed less Te release. The beginning of Te release was approximately coincident with the beginning of rapid Cs release. The calculated final Te release (Table 1) in most of these tests was larger than expected (significantly greater than 100% in one case), indicating that the inventory calculations or the 696 keV γ-yield may be inaccurate for one or both of Pr-144 and Te-129m.

In the two high-temperature steam tests H01 and H03, Ru-103 showed 4% release. A large fraction of the Ru was released in the high-temperature air test H02. The very small releases of Ru in the "inert" atmosphere test H04, and the lower-temperature air tests could only be observed by deposition measurements.

Of the fission products detected by direct-viewing γ-spectrometry, releases of Y-91, Pr-144 and Eu-156 could not be observed by direct-viewing or scanning γ-spectrometry for any of the test conditions used. The releases of Zr-95 and Nb-95, and Ce-144 were <1% (Table 1). The releases of Ba were between 1% and 7% in all of the high-temperature tests (H01 through H04).

DISCUSSION

The release behaviour of iodine, cesium and noble gases exhibited considerable similarity at elevated temperatures. No significant releases of Cs were observed below ~1500°C in inert environment in the HCE3 experiment, consistent with the low gap inventory of the fuel. In previous experiments, releases of Cs in inert atmosphere at temperatures below 1400°C have been tentatively attributed to gap inventory [2]; the fuels used in those experiments had noble-gas gap inventories ranging from 4 to 24%, indicating high Cs gap inventories. The lower Cs release during inert heating may also be due to the lower heating rates in the temperature range 1000 to 1500°C (0.1 to 0.3°C/s), compared to 0.8-6°C/s in previous tests.

Rapid Cs release was delayed after the addition or ingress (*e.g.*, test H04) of oxidizing atmosphere until oxidation of the sheath was complete. The oxidative cesium release rates in steam from the HCE3 and UCE12 experiments [2] were not very temperature-dependent compared to the CORSOR-M fission-product-release correlation [5], which is used in light-water-reactor safety analysis (Figure 8). Our experimental data would be better simulated using a pair of correlations to assign different release rates before and after full sheath oxidation.

The timing of Te-129m release indicates that complete sheath oxidation is required for Te release. The final fractional releases of Te were probably similar to those of Cs, allowing for inaccuracies related to inventory calculations.

The solid fraction of fission-product Ru would have been present almost entirely in the metallic state at the temperatures and $P(O_2)$ values in the HCE3 experiment, and release probably occurred by oxidation to RuO_x gaseous species [6]. As observed previously for fragment samples [2], release of Ru in test H02 (and probably also in tests H01 and H03) began a significant length of time (>2000 s) after oxidative release of Cs began. This delay was due to the competition among Zircaloy, UO_2 and Ru for oxygen. Test H02 showed the largest percentage release of Ru from any complete Zircaloy-sheathed sample tested at CRL, due to the high test temperature and the comparatively long exposure to air.

Several fission products (Y, Zr, Nb, Ce, and Eu) that showed release by matrix stripping in fragment tests under these conditions [3,4] showed low (<1%) or no fractional release in the HCE3 sheathed-fuel tests. The fraction of the UO_2 volatilized and consequent fractional release by matrix stripping was much less in this experiment than in the fragment tests. The oxidized Zircaloy sheathing would also tend to decrease the amount of UO_2 volatilized by limiting the mass transport of steam and fission-product compounds.

CONCLUSIONS

In each test, the release behaviour of Cs, I and noble gases were very similar to each other. Very little Cs was released before complete oxidation of the sheath, probably because this fuel had a small Cs gap inventory; the measured gap inventory of noble gases was <1% after irradiation. These results suggest that the releases observed in inert atmosphere below 1400°C or before complete sheath oxidation in other experiments were releases of gap inventory. The release rates during UO_2 oxidation in steam showed very little temperature dependence. Release of Te began at about the same time as oxidative release of Cs. Two high-temperature steam tests (H01, 1930°C and H03, 1840°C) showed a release of ~4% of Ru. An air test at 1890°C (H02) showed the greatest release of Ru for a sheathed sample with two end-caps. Ruthenium release began well after oxidative release of volatile fission products (delay of >2000 s).

The high level of oxygen permeation into the furnace tube during the nominally-inert test H04 was probably due to the gaps in the segmented guide tube. Future apparatus should employ a singlepiece guide tube to maintain the inertness of test atmospheres at high temperatures.

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TABLE 1: EXPERIMENT CONDITIONS AND FISSION-PRODUCT RELEASES (PERCENTAGE OF INVENTORY) IN HCE3 TESTS.

Test	H01	H02	H03	H04	H05	H06
Peak T (°C)	1930	1890	1840	1830	1510	1540
T_{ox} (°C)	1500	1520	1750	(1)	1510	1540
t_{ox} (s)	8500	8740	5360	(1)	2900	8500
Oxidizing Atmosphere	90%steam/ 10% Ar/ 0.2% H_2	air	87%steam/ 13% Ar/ 0.3% H_2	steam/ 96% Ar/ H_2	air	86%steam/ 13% Ar/ 0.6% H_2
Zr-95	0.01(2)	0.36(2)	(3)	(3)	(3)	(3)
Nb-95	0.25(2)	0.81(2)	0.48(2)	0.02(2)	(3)	(3)
Ru-103	4.2	86.	3.5(2)	0.02(2)	0.02(2)	(3)
Ru-106	6	89.	3.7(2)	(3)	(3)	(3)
Ag-110m	81.(2)	14.(2)	50.(2)	13.(2)	9.5(2)	37.(2)
Sn-113	35.(2)	(3)	27.(2)	(3)	27.(2)	44.(2)
Sb-125	41.(2)	30(2)	45.(2)	(3)	6.2(2)	(3)
Te-129m	153 ± 31	198 ± 41	88 ± 29	30.(2)	13.(2)	64.(2)
I-131	86.	100.	77.	36.	14.	56.
Cs-134	85.	98.9	74.	29.	14.	56.
Cs-137	104.	98.6	73.	27.	13.	54.
Ba-140	5.1(2)	3.6(4)	2.2(2)	1.9(2)	(3)	0.02(2)
Ce-141	0.02(2)	(3)	0.01(2)	0.01(2)	(3)	(3)
Ce-144	0.06(2)	-	0.01(2)	0.02(2)	-	-

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[1] Oxidizing atmosphere was not added deliberately; significant oxygen permeation occurred at >1500°C.

[2] This value was calculated from deposition and aerosol collector observations.

[3] Deposition measurements either did not detect the isotope, or found <0.01% of the sample inventory of the isotope.

[4] The value of Ba-140 release for this test was inferred from La-140 measurements.

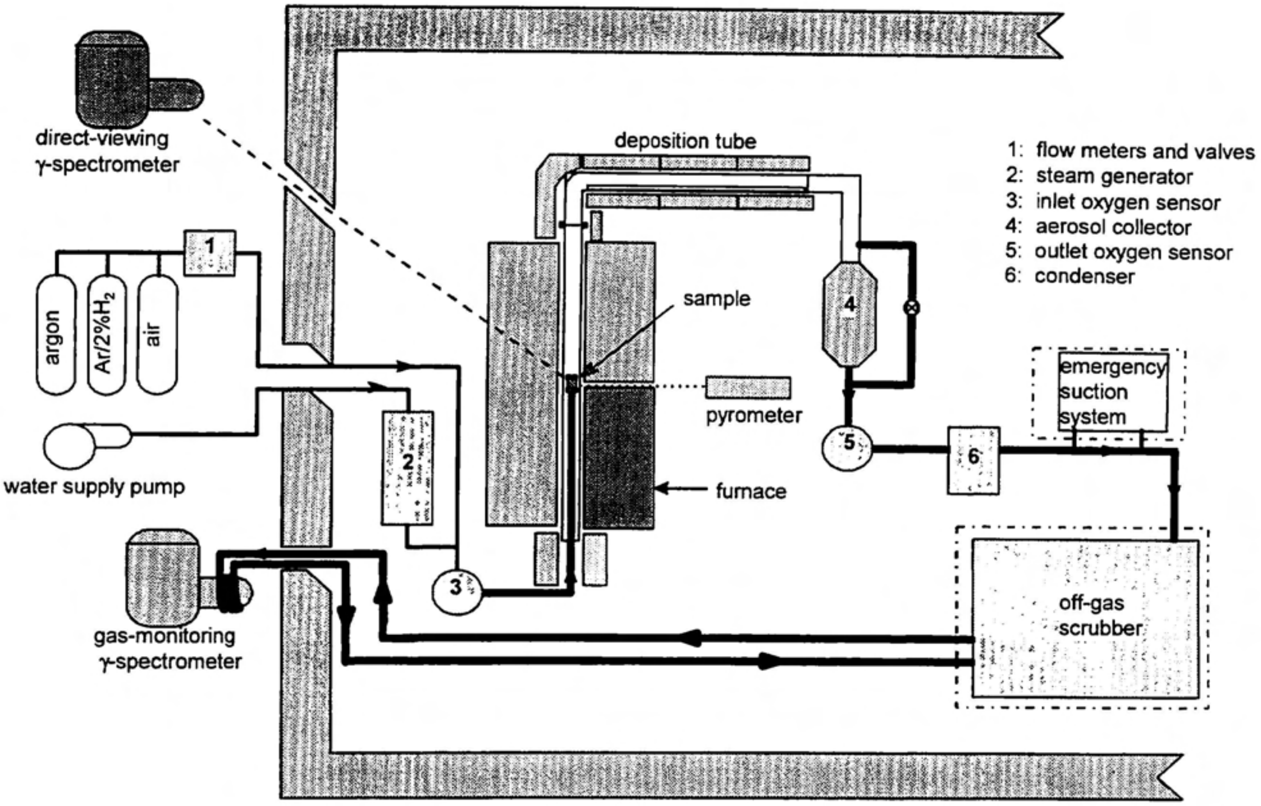

FIGURE 1. SCHEMATIC OF HCE3 HOT-CELL APPARATUS.

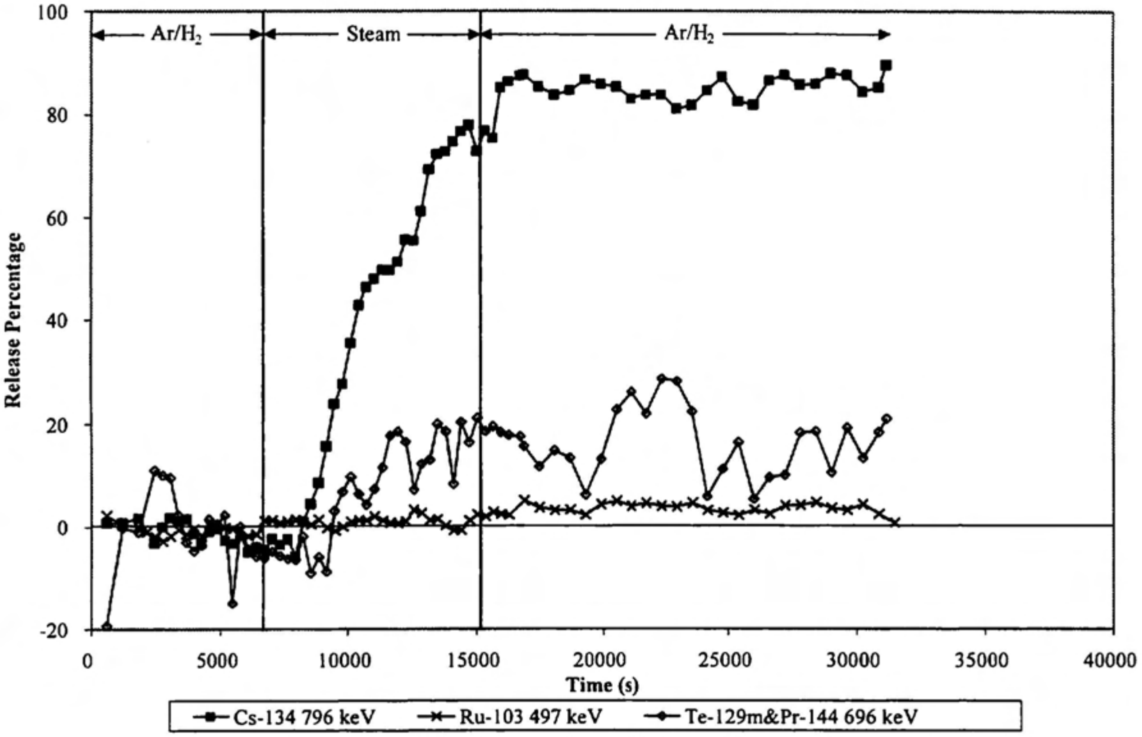

FIGURE 2: CESIUM AND RUTHENIUM RELEASE PERCENTAGES AND 696 keV "RELEASE PERCENTAGE" (Te-129m + Pr-144) FOR TEST H01 (STEAM, 1930°C).

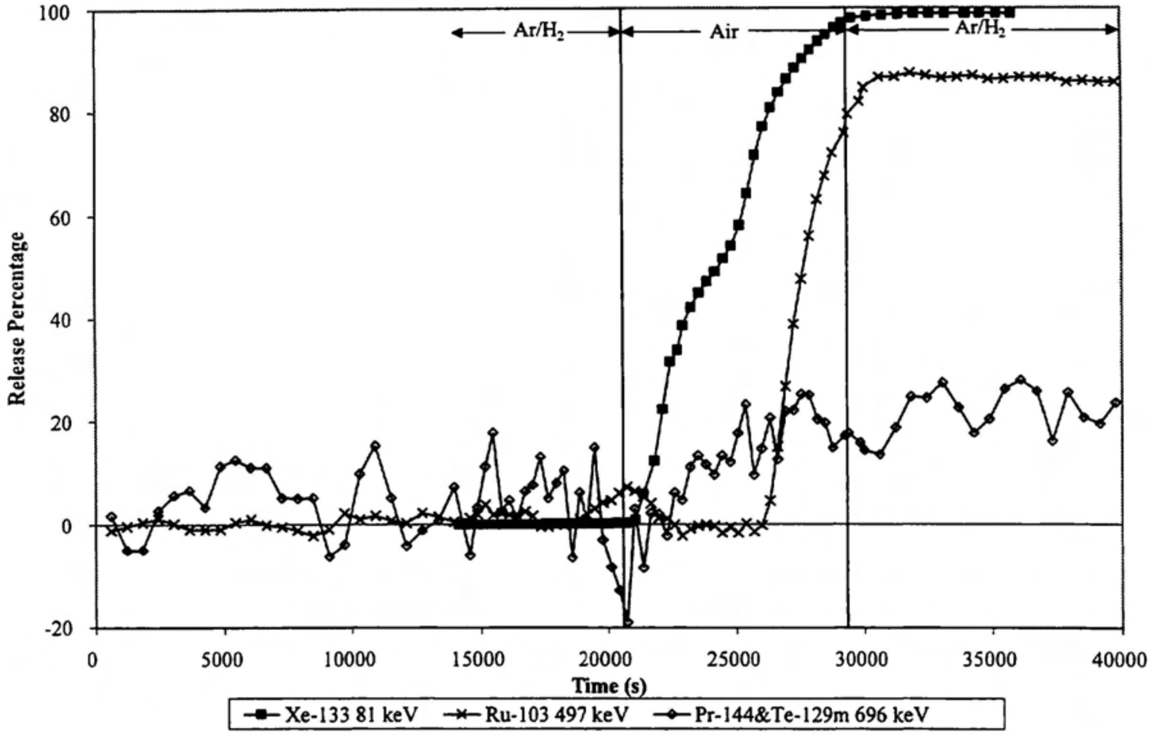

FIGURE 3: XENON AND RUTHENIUM RELEASE PERCENTAGES AND 696 keV "RELEASE PERCENTAGE" (Te-129m + Pr-144) FOR TEST H02 (AIR, 1890°C).

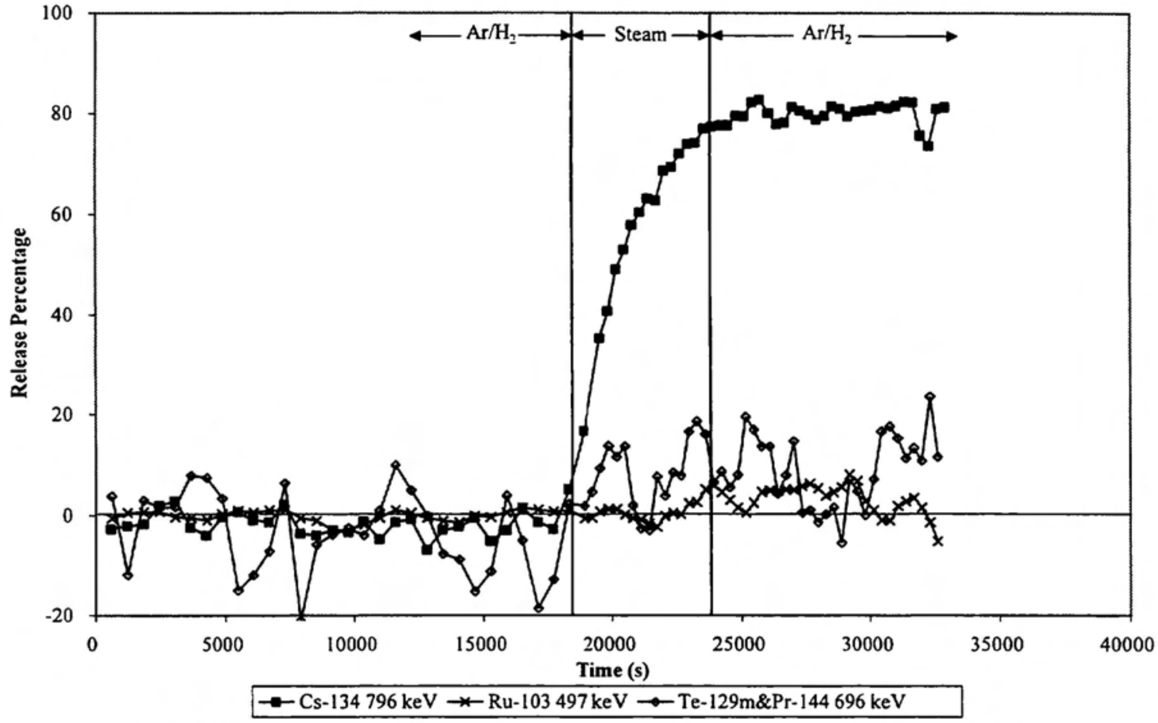

FIGURE 4: CESIUM AND RUTHENIUM RELEASE PERCENTAGES AND 696 keV "RELEASE PERCENTAGE" (Te-129m + Pr-144) FOR TEST H03 (STEAM, 1840°C).

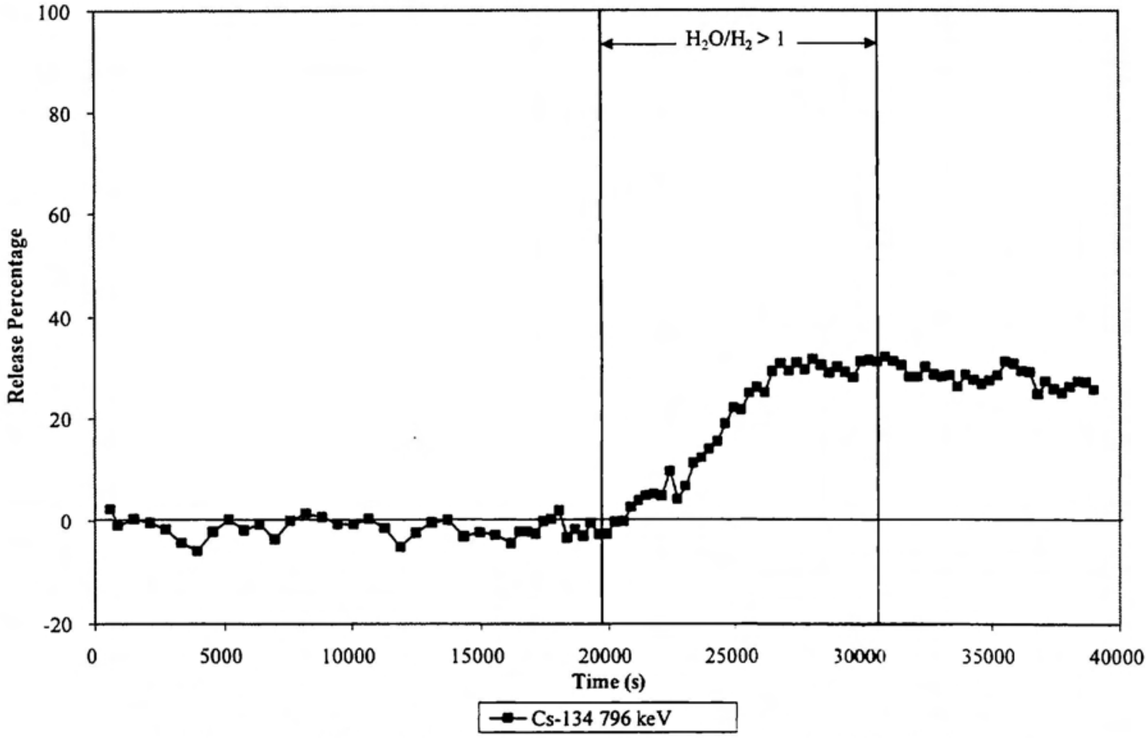

FIGURE 5: CESIUM RELEASE PERCENTAGE AS A FUNCTION OF TIME FOR HCE3 TEST H04 (SHEATHED DARLINGTON FUEL, Ar/H_2/STEAM, 1830°C).

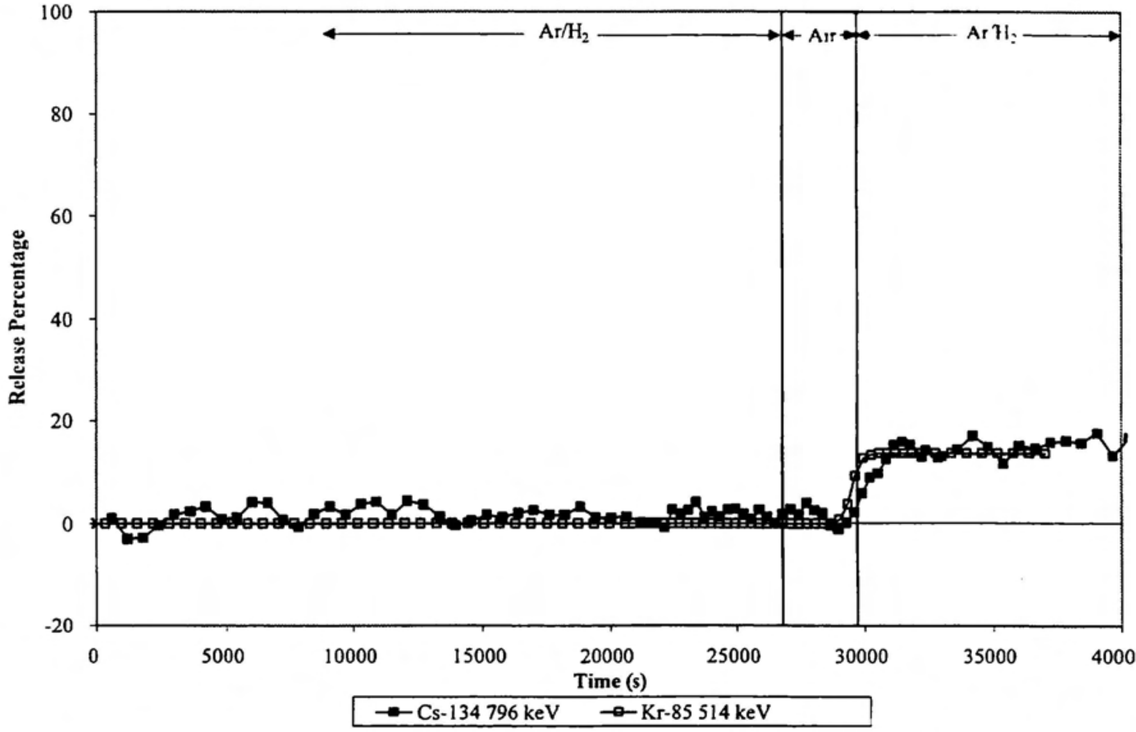

FIGURE 6: CESIUM AND KRYPTON RELEASE PERCENTAGES AS FUNCTIONS OF TIME FOR HCE3 TEST H05 (SHEATHED DARLINGTON FUEL, AIR, 1510°C).

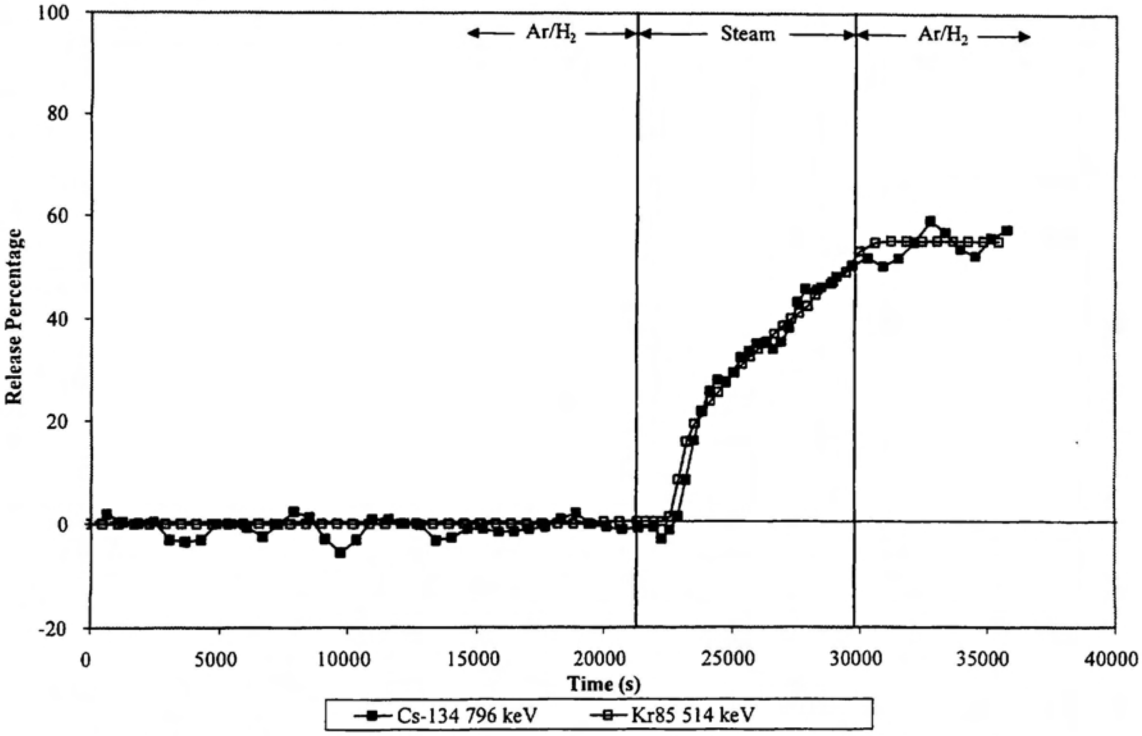

FIGURE 7: CESIUM AND KRYPTON RELEASE PERCENTAGES AS FUNCTIONS OF TIME FOR HCE3 TEST H06 (SHEATHED DARLINGTON FUEL, STEAM, 1540°C).

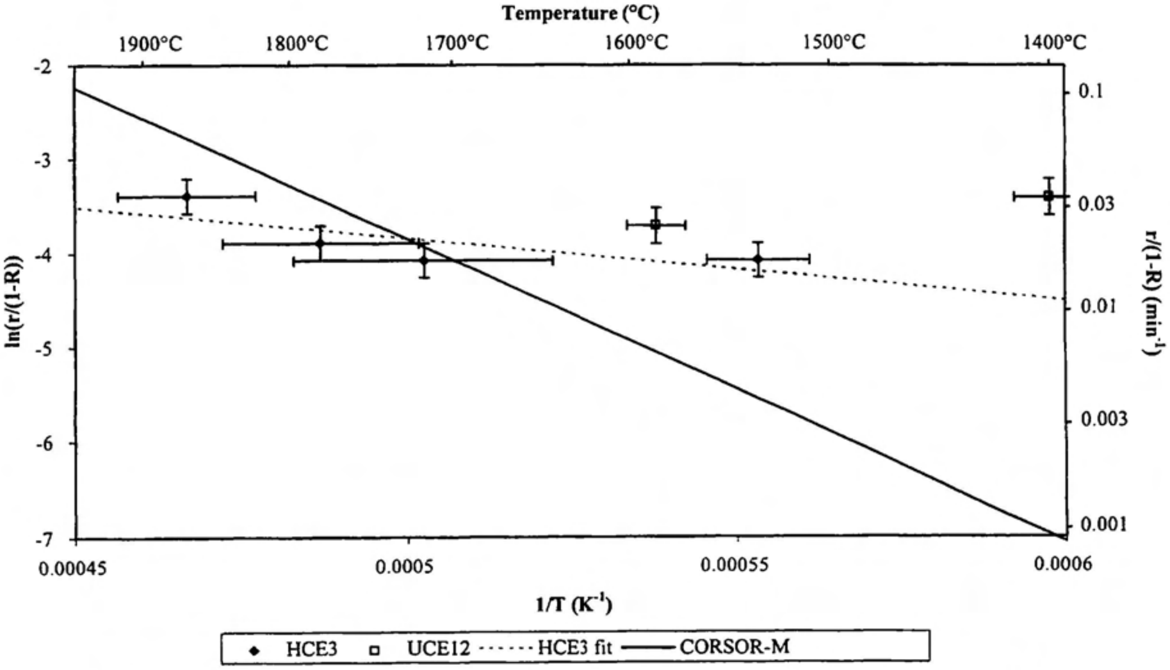

FIGURE 8: ARRHENIUS PLOT OF Cs RELEASE RATE AFTER FULL SHEATH OXIDATION (r) DIVIDED BY REMAINING FRACTION OF Cs INVENTORY (1-R) FOR SHEATHED-FUEL STEAM TESTS (HCE3 and UCE12 EXPERIMENTS)