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BEHAVIOR OF FISSION PRODUCT TELLURIUM UNDER SEVERE ACCIDENT CONDITIONS*

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BEHAVIOR OF FISSION PRODUCT TELLURIUM UNDER SEVERE ACCIDENT CONDITIONS[a]

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ABSTRACT
Fission product release tests at Oak Ridge National Laboratory (ORNL) have provided new experimental data that help characterize the behavior of tellurium under severe light-water reactor (LWR) accident conditions. The release of tellurium from the fuel rods is dependent upon the rate and extent of cladding oxidation. Tellurium has been found to be considerably retained by metallic Zircaloy cladding at test temperatures up to 1975°C. The results indicate that the tellurium is bound by the Zircaloy cladding as zirconium telluride, but once the available zirconium metal is oxidized by the steam, tellurium is released in favor of continued zirconium oxide formation. The collection behavior of the released tellurium indicates that it is probably released from the fuel rods as SnTe and CsTe rather than as elemental tellurium.

I. INTRODUCTION

For every 100 atoms of Cs in a high-burnup LWR fuel rod, there are ~10 atoms of I, ~21 atoms of Kr, ~220 atoms of Xe, and ~19 atoms of Te. Many of the isotopes of these fission product elements are highly radioactive. Because of their high volatility, they represent a high potential for being radiological hazards in a hypothetical, severe LWR accident (less for krypton and xenon because of their chemical inertness). At the time reactor irradiation is halted by insertion of control rods, there are ~67 Ci of Te and ~65 Ci of Cs for every 100 Ci of I. The tellurium activity is very significant. In addition to being radiotoxic, the tellurium radionuclides beta decay to form radionuclides of iodine.

Over the last few years, an increased effort has been made at ORNL and other national laboratories to characterize the behavior of fission product tellurium under severe LWR accident conditions to provide experimental data for source term modeling. At ORNL, fission product release from highly irradiated PWR and BWR commercial fuel has been investigated in six tests at 1375 to 1975°C in flowing steam-helium atmospheres.[1-4] A significant amount of tellurium was released in only one of these tests — Test HI-2.[1] In that test, unlike the others, the Zircaloy cladding was totally oxidized by the steam, indicating that the steam oxidation of the Zircaloy cladding played an important role in tellurium release.

To aid in the interpretation of tellurium behavior observed in the HI test series, control test C-9 was conducted. The tellurium behavior in test C-9 was consistent with that observed in the HI tests. Tellurium was rapidly

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gettered and retained by the Zircaloy cladding but was not significantly released until the cladding was almost completely oxidized.

The tellurium results obtained in the HI tests and control test C-9 are described in the following sections.

II. HIGH-TEMPERATURE FISSION PRODUCT RELEASE TESTS (HI TESTS)

In the HI Tests, high-burnup commercial PWR and BWR fuel rod specimens (15 to 20 cm long) were heated in a flowing steam-helium atmosphere in the temperature range 1375 to 1975°C. A schematic of the experimental apparatus is shown in Fig IX.5-1. Before testing, a small 1.6-mm-diam hole was drilled through the cladding at midlength to provide an outlet for the fission products to escape. During these tests, the released fission products were carried from the furnace to the collection train, consisting of a platinum lined thermal gradient tube (TGT) with a temperature gradient from 850 to 150°C, where species condensable in that temperature range deposit. Downstream, filters collected the transported aerosol, and impregnated charcoal collected the more penetrating forms of fission products, such as elemental iodine and methyl iodide. Cold charcoal traps (-78°C) located near the end of the train were used to collect the fission gases krypton and xenon.

Several of the test parameters and fission product release values for the HI tests are given in Table IX.5-1. Note that the specimen burnups varied from 10 to 40 MWd/kg U, and the effective time at test temperature was varied from 2.5 to 33.8 min. The Kr, I, and Cs releases varied from ~2 to 59% of inventories in the test specimens and were primarily temperature and time dependent. The releases for cesium and krypton were determined by gamma spectrometry and those for iodine by neutron activation analysis.

Table IX.5-1. Fission product release test results

	Test No.					
	HI-1	HI-2	HI-3	HI-4	HI-5	HI-6
Specimen burnup, MWd/kg U	28	28	25	10	38	40
Test temperature, °C	1375	1700	1975	1900	1725	1950
Test time, min[a]	33.8	22.5	21.3	21.6	21.5	2.5
Cladding oxidized, %	40	100	42	27	70	40
Fission product release, % of inventory						
Krypton[b]	3.1	51.8	59.3	31.3	19.9	31.6
Iodine	2.1	53.0	35.4	24.7	22.4	24.7
Cesium	1.8	50.5	58.8	31.7	20.3	33.1
Tellurium	<0.3	>50.0	<0.6	<0.4	<0.1	<0.1

a Includes estimates for heatup and cooldown effects.
b Includes krypton released during reactor operation.

The tellurium release values in Table IX.5-1 were obtained by spark-source mass spectrometric (SSMS) analysis of test samples of deposited material taken at intervals along the platinum TGT liner and of aerosol deposited on the glass wool prefilter in the filter package. The platinum TGT liners in two key tests (HI-2 and HI-3) were analyzed by neutron activation analysis after surface deposits were removed by basic and nitric acid leaches — only trace amounts of tellurium were detected. [If elemental tellurium vapor (Te_2) had been transported to the TGT, it would have reacted with or dissolved in the platinum liner.] Those tests were chosen because of the magnitude of the releases of the other fission products and because of the significant difference in tellurium releases. With the exception of test HI-2, all the other HI tests were steam starved. Table IX.5-1 shows that the Zircaloy cladding was completely oxidized in test HI-2 , but in test HI-3, it was only ~42% oxidized.

After the test, the HI-2 fuel specimen was cast in epoxy to preserve its physical shape. It was subsequently sent to Argonne National Laboratory where posttest metallographic analysis was performed. Radial cuts through the fuel segment revealed an axial crack that ran the full length of the segment. Analyses also showed that the Zircaloy cladding was completely oxidized and had been oxidized from both the outside and the inside. This was implied because tin agglomerates were primarily found at the midwall location of the cladding. For this to have happened, the axial crack probably occurred early in the test. Since tin in the Zircaloy alloy does not oxidize as the zirconium becomes oxidized, and since it has a low melting point (mp = 232°C), liquid droplets form and grow by coalescing. As the oxide layer widens, the droplets are swept along at the oxide/metal interface.

If the axial crack did occur early in test HI-2, as believed, it helps account for the larger than expected release of fission products. The percentages of Kr, I, and Cs inventories released in test HI-2 were 2.5 times larger than those obtained in test HI-5, a similarly conducted test, and almost identical to those obtained in test HI-3, in which the test specimen was heated at 1975°C (275°C higher) for about the same time. The larger opening made it easier for the fission products to escape. Furthermore, with the inner surface of the cladding being oxidized early in the test, there was no metallic zirconium available to react with and retain the tellurium being released from the fuel pellets. Also, any tellurium that was retained before the inner surface became oxidized was probably released after the cladding became completely oxidized.

In the HI tests, as well as in previous fission product release tests conducted at ORNL in which significant releases occurred, the fractions of inventories of the released volatile fission products Kr, Cs, and I were essentially equal. It is interesting that the Te release in test HI-2 was similar to the releases of Kr, I, and Cs.

Leach data from the TGT and glass wool prefilter showed that significant portions of the deposited tellurium were soluble in basic solution. Considering the presence of Cs, Rb, and Sn (the Sn comes from the Zircaloy cladding) with the tellurium deposits, it is likely that the tellurium was present in the collection system as tellurides of these elements. All three of these tellurides are soluble in the basic leach used (NH_4OH-H_2O_2); elemental tellurium is not.

III. CONTROL TEST C-9

Control test C-9 was run to examine the behavior of tellurium in a simulated fuel specimen under test conditions similar to those used in the HI tests. The apparatus used in test C-9 was essentially the same as was used in the HI test (Fig IX.5-1), except for the addition of a hydrogen monitoring system that was used to measure the hydrogen produced from the steam-Zircaloy cladding reaction. (The cold charcoal traps were not used.) The TGT and filter package were continuously monitored by gamma detectors during the test.

In this test, 39.9 mg of metallic tellurium traced with ^{129m}Te were placed in a zirconia tube within a 15-cm-long simulated fuel specimen (Fig IX.5-2) that had a 1.6-mm-diam hole drilled through the cladding at the downstream end. Figure IX.5-3 shows the accumulation of tellurium in the collection apparatus (TGT plus filter package) as a function of test temperature and time. Initially, the specimen was heated in the temperature range 600 to 900°C in flowing purified helium (0.3 L/min) for a period of 45 min to allow the tellurium to vaporize from the zirconia tube and react with the Zircaloy cladding or be released via the small hole at the downstream end of the specimen. Three gamma detectors that were used to monitor the movement of tellurium in the fuel specimen indicated that it stayed at the upstream end of the test specimen. Only 0.02 mg of tellurium transported to the collection system during this period; most of the tellurium rapidly reacted with and was retained by the cladding. Because the vapor pressure of tellurium at 900°C is 0.043 MPa (0.425 atm), it would have been released rapidly in the absence of a retention mechanism.

Before steam was added to the carrier gas, the temperature of the specimen was lowered to ~445°C. After a steady flow rate of 1.5 L/min steam and 0.3 L/min helium was established, the temperature of the specimen was raised at a rate of 112°C/min to 1600°C and held there for 32 min. During this time, only 1% (0.40 mg) of the tellurium was released from the fuel specimen, an average of 0.013 mg/min.

The temperature of the test specimen was subsequently raised to 1700°C for the duration of the test. After 44 min at 1700°C, an additional 1.04 mg of tellurium was collected at a rate of 0.024 mg/min, about twice the rate observed at 1600°C. At this point in the test, only 3.6% of the tellurium had been released from the cladding of the test specimen, demonstrating good retention behavior. Thereafter, the rate of collection started increasing and, for a period of 30 min, was collected at a rate of ~1.02 mg/min, about 40 times faster than during the initial 44 min at 1700°C.

Oxidation rate calculations using Urbanic and Heidrick's data[5] predict that the thin-walled (0.064 cm) cladding tube should have been totally oxidized just before the temperature of the specimen was raised to 1700°C (Fig IX.5-3). This implies that the tellurium was being retained on the inner surface of the thick-walled Zircaloy endcap at the upstream end and on the section of tube overlapped by the endcap.

Table IX.5-2 gives an abbreviated posttest distribution of tellurium in the apparatus. A good mass balance was obtained, and about 97% of the initial tellurium was accounted for after the test. Most of the released tellurium transported to the collection system. The largest fractions were found in the TGT (56.7%) and in the filter pack (33.3%). The filter pack contained a

glass wool prefilter, two HEPA filters, and charcoal, in that order. About 99.7% of the tellurium found in the filter pack was found on the glass wool prefilter.

Table IX.5-2. Posttest distribution of tellurium in test C-9

Location	Temperature (°C)	Tellurium found in apparatus		
		(mCi)	(mg)	(%)[a]
Simulated test specimen	1700(max)	2.61	3.35	8.65
Furnace components	1700–500	0.41	0.52	1.36
Thermal gradient tube	850–150	17.10	21.94	56.72
Filter pack components	130	10.03	12.87	33.27
Total		30.15[b]	38.68[c]	100.00

a Percentage of total mass found.
b The initial ^{129m}Te activity was 31.04 mCi.
c The initial mass of tellurium was 39.9 mg; 97% of the initial tellurium was accounted for after the test.

Figure IX.5-4 shows that most of the tellurium that was collected in the TGT deposited in a peak at 600°C. Examination of a section of TGT liner from the peak location with a scanning electron microscope using an energy dispersive x-ray system (SEM/EDX) revealed that only tin and tellurium peaks were present, occurring in a 1:1 mole ratio. This implies that the tellurium deposited in the TGT as SnTe (the Sn came from the Zircaloy cladding). The absence of tellurium at the entrance end of the TGT means that the tellurium probably entered the TGT as SnTe. Had Te_2 vapor entered the platinum TGT liner, it would have reacted with the hot platinum and would have been retained. Based upon the observed behavior of cesium iodide in the TGT (which usually deposits in a peak at 500°C), we predicted that if the tellurium were transported to the TGT as SnTe, it would deposit in a similar fashion near 600°C — that was the case.

The aerosol that transported to the glass wool prefilter was determined by EDX analysis to be composed also of tin and tellurium with a slight surplus of tin.

IV. CONCLUSIONS

Fission product tellurium was observed to be effectively retained in highly irradiated LWR fuel specimens at temperatures up to 1975°C in a flowing steam atmosphere as long as the Zircaloy cladding was not completely oxidized or severely damaged. In test HI-2, an axial crack in the Zircaloy cladding that ran the length of the specimen occurred early in the test. As a result, the inner cladding surface became oxidized early by the steam, and the tellurium being released from the fuel pellets was able to exit the specimen uninhibited. The collection behavior of the released tellurium appeared to be that of tellurides of Cs, Rb, and Sn, rather than that of elemental tellurium.

The Control Test C-9 results clearly showed that tellurium was quantitatively and rapidly gettered by the Zircaloy cladding between 600 and 900°C and that

the reacted tellurium had only a slight tendency to be released at 1700°C until oxidation of the cladding was essentially complete. Also, the results indicated that the released tellurium transported to the collection system as SnTe.

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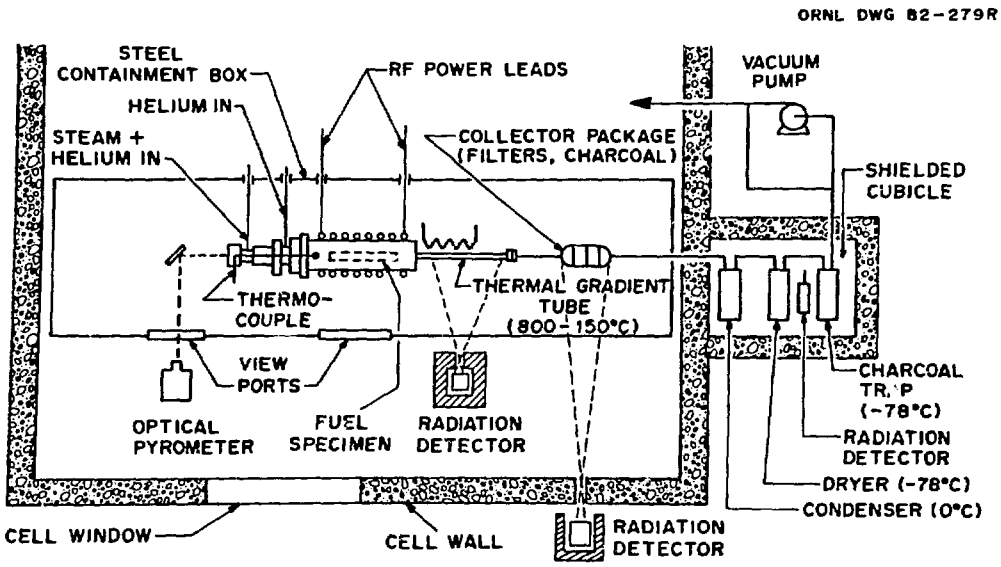

Fig IX.5-1, FISSION PRODUCT RELEASE AND COLLECTION SYSTEM.

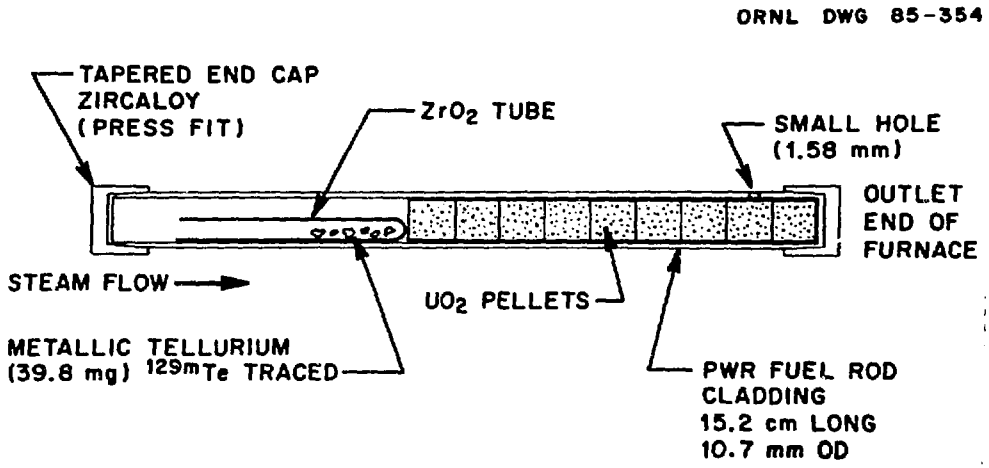

Fig IX.5-2, SPECIMEN USED IN TEST C-9.

ORNL DWG 85-353R3

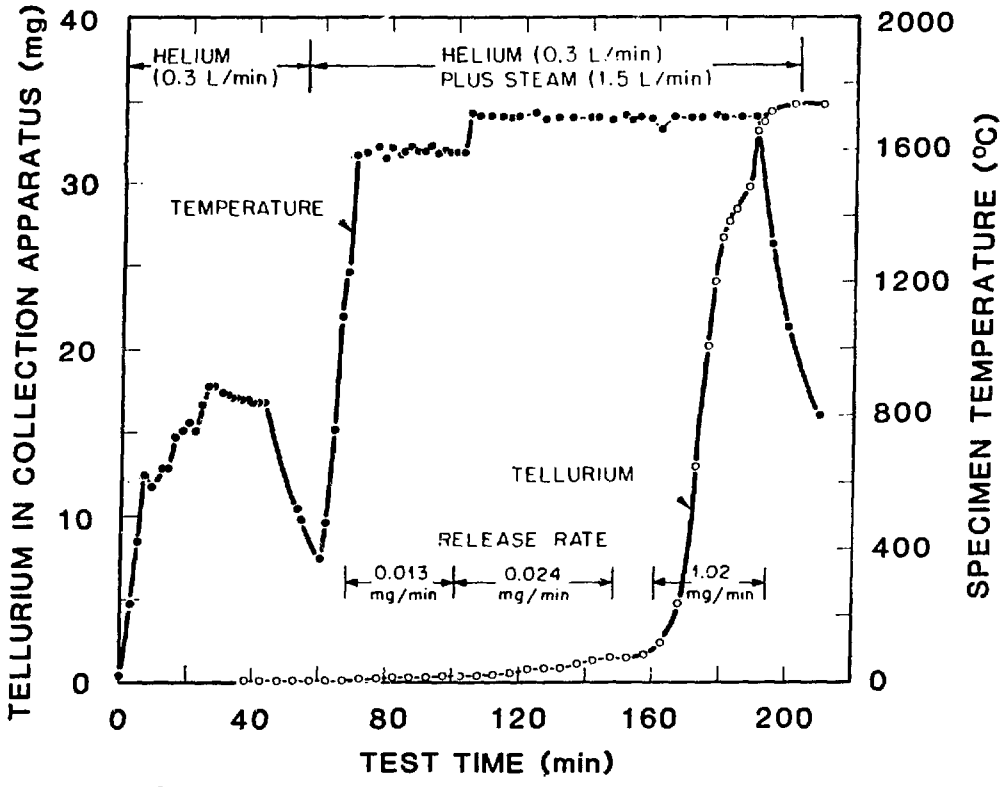

Fig IX.5-3, ACCUMULATION OF TELLURIUM IN THE COLLECTION APPARATUS AS A FUNCTION OF TEST TEMPERATURE AND TIME IN TEST C-9.

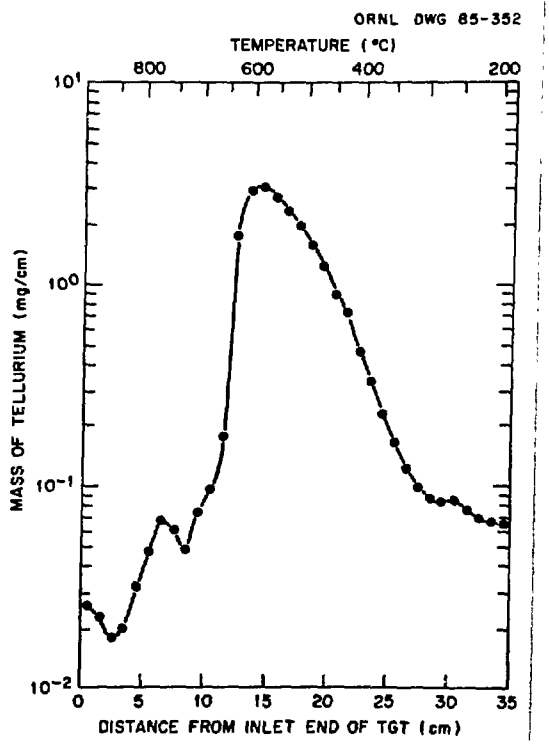

Fig IX.5-4, DISTRIBUTION OF TELLURIUM IN THE TGT IN TEST C-9.