EGG-TMI-6701
September 1984

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TELLURIUM RELEASE AND DEPOSITION DURING THE TMI-2 ACCIDENT

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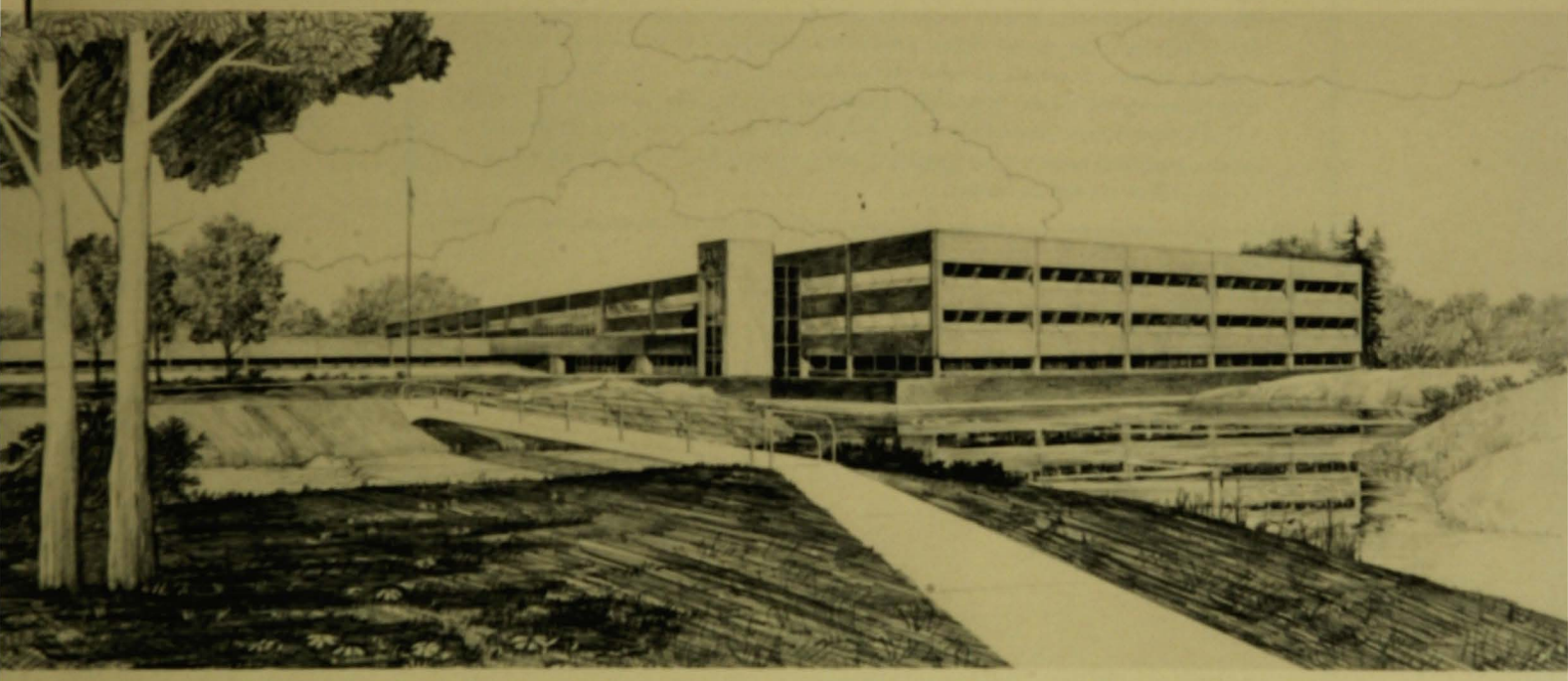
Operated by the U.S. Department of Energy



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Prepared for the
U.S. DEPARTMENT OF ENERGY
Under DOE Contract No. DE-AC07-76ID01570

EG&G Idaho

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ABSTRACT

The estimated behavior of tellurium during and after the accident at the Three Mile Island Unit-2 is presented. The behavior is based on all available measurement data for ^{129m}Te, ^{132}Te, stable tellurium (^{126}Te, ^{128}Te and ^{130}Te), and best estimate calculations of tellurium release and transport. The predicted release was calculated using current techniques that relate release rate to fuel temperature and holdup of tellurium in zircaloy until significant oxidation occurs. The calculated release fraction was low, ~7%, but the total measured release for samples analyzed to date is about 5.8%. Of the measured tellurium about 2.4, 1.8, 0.88, 0.42, 0.17 and 0.086% of core inventory were in the containment sump water, upper plenum assembly surfaces, containment solids in the sump water, makeup and purification demineralizer, containment inside surface, and the reactor primary coolant, respectively. A significant fraction (54%) of the tellurium calculated to be retained on the upper plenum surfaces (4.61% of the core inventory) was deposited during the high pressure injection of coolant at about 200 min after the reactor scram. Comparison of tellurium behavior with in-pile and out-of-pile tests strongly suggests that zircaloy holds tellurium until significant cladding oxidation occurs. Analyses of samples from the core region of TMI-2 may provide an assessment of the large fraction of tellurium retained there, thus validating the zircaloy-oxidation-dependent tellurium release models.

ACKNOWLEDGMENTS

The authors thank Mrs. Pushpa Bhatia for running the TRAP-MELT computer code and G. S. Reilly for plotting the figures. The authors acknowledge D. O. Campbell and R. A. Lorenz of ORNL for providing TMI-2 data and T. R. Lyon of WINCO for tellurium analysis.

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TELLURIUM RELEASE AND DEPOSITION DURING THE TMI-2 ACCIDENT

INTRODUCTION

Until recently, studies of tellurium release from the core were based on temperature, and its volatility in comparison with other potentially important radionuclides (I, and Cs).[1] However, tests at the core melt facility at Oak Ridge National Laboratory (ORNL), the severe fuel damage tests at the Idaho National Engineering Laboratory (INEL), and the SASCHA tests at Karlsruhe suggest that tellurium may be held up by zircaloy cladding which results in significantly lower releases from the core. These tests also demonstrated that tellurium releases increase significantly when the zircaloy cladding is oxidized and the previously held up tellurium is released. Lorenz et al.[2] emphasized that a lower-than-expected tellurium release does not necessarily mean a lower calculated release to the environment, but rather that the tellurium transport pathway is different from previously envisioned, and higher or lower releases to the environment may result depending on zircaloy oxidation during an accident progression. Also, Elrick and Sallach[3] indicate that tellurium may react with structural materials (stainless steel) and thereby be retained in the primary coolant system. Silver (from the control rods) and tin (a minor constituent of zircaloy cladding) aerosols are efficient scavengers of tellurium vapor.[3]

The tellurium behavior during and after the Three Mile Island-Unit 2 accident may shed further light on tellurium transport during a severe accident. The accident at TMI-2 on March 28, 1979, resulted in severe damage to the reactor core. As a consequence, numerous data are being gathered to study fission product behavior during and after the accident. A large data base with supporting analyses exists for noble gas, iodine, and cesium behavior. Most of the radiological and chemical analyses of the samples from TMI-2 (especially those taken soon after the accident) sparingly report tellurium levels. This lack of data is probably due to the fact that special analytical methods are required to determine the low tellurium concentrations in highly radioactive samples; and unless a special effort is made, the tellurium content is usually not measured.

Details of tellurium analytical methods being used at INEL are presented in Appendix A. Atomic emission spectroscopy using an inductively coupled plasma excitation source (ICP-AES) was used to analyze tellurium in TMI-2 leadscrew samples. A limited number of samples drawn from primary coolant water, reactor coolant bleed tank water, the containment inside surface, the containment sump water and solids, containment atmosphere, auxiliary building sump water, makeup and purification system, and upper plenum assembly surfaces were analyzed for tellurium. Examinations of tellurium on a limited number of core debris samples are underway at INEL.

The objectives of this report are to present the results of tellurium analyses performed to date on TMI-2 samples, estimate the tellurium distribution and the release and deposition fractions, and compare the data with current best estimate behavior models and data from out-of-reactor and in-reactor tests.

The following sections present: measurements and calculations of tellurium release from the TMI-2 Core, the tellurium release data from ORNL tests, tellurium releases from the PBF Severe fuel damage tests and the SASCHA tests, comparisons of the TMI-2 tellurium behavior with the above out-of-pile and in-pile tests, and conclusions reached in this investigation.

The final report on tellurium behavior is expected to be released in August 1985. It will include data on core grab samples, data from the PBF tests SFD 1-3 and SFD 1-4, any of the available tellurium data from TMI-2, tellurium chemistry and data from the TRAP-MELT computer code calculations.

TELLURIUM RELEASES

Measurements of Tellurium Released from TMI-2 Core

A summary of tellurium measured in samples to date taken from the TMI-2 plant systems and components is listed in Table 1. The systems and components included in the tellurium investigation were: (a) reactor primary coolant,[4,5] (b) reactor coolant bleed tank water,[6] (c) containment inside surface,[5,7] (d) containment sump water and solid debris,[8-11] (e) containment atmosphere,[12] (f) auxiliary building sump water,[13] (g) makeup and purification filter,[14,15] (h) upper plenum surfaces[16] (samples from the H8 and B8 leadscrews), and (i) core debris (grab samples).

Approximately 0.086% of the ^{132}Te core inventory was determined to be in the primary coolant water, based on an early analysis (March 29, 1979) of water samples.[4] This low tellurium inventory may be due to: (a) low tellurium release, (b) low tellurium solubility in water, or (c) the retention of tellurium by reaction with zircaloy cladding.

About 9×10^{-3}% of the core inventory was estimated to be in the reactor coolant bleed tank based on the data obtained on December 8, 1979, by ORNL.[6]

Plug "401" which is a painted steel disk of 7 cm (2.75 in.) diameter projecting into the containment building was gamma scanned at ORNL on August 29, 1979. It is assumed that the disk was representative of the entire inner containment surface area of 2.2×10^{8} cm^2. Analysis[5] of this indicated that ~0.045 and 0.12% of ^{127m}Te and ^{129m}Te core inventories, respectively, were deposited on containment building inside surfaces. Tellurium plateout on the hydrogen recombiner inlet spool piece was analyzed.[7] The hydrogen recombiner assembly located outside the containment is connected to the containment by piping. The inlet spool piece was analyzed for ^{129m}Te and the results indicated that 0.17% of the ^{129m}Te core inventory was deposited on containment surfaces. The effective area of the containment was estimated in a very approximate manner; the release fraction is probably no better than an order-of-magnitude estimate.

TABLE 1. SUMMARY OF TELLURIUM RELEASE FRACTIONS IN TMI-2 SYSTEMS

System or Component	Sampling Date	Tellurium Isotope	Percent of Initial Core Inventory[a]	Reference
Reactor primary coolant	3-29-79	^{132}Te	0.086	(4)
	3-30-79	^{132}Te	0.086	(4)
	4-10-79	^{132}Te	0.010	(4)
	6-21-79	^{132}Te	0.014	(5)
Reactor coolant bleed tank water	12-18-79	^{129}Te	0.009	(6)
Containment inside surface	8-29-79	^{127}Te	0.045	(7)
	8-29-79	^{129m}Te	0.12	(5)
	9-09-79	^{129m}Te	0.17	(7)
Containment sump water	6-20-79	^{129}Te	1.06	(8)
	6-20-79	^{132}Te	2.40	(8)
	8-29-79	^{129m}Te	0.008	(9)
Solids in water	8-28-79	^{129m}Te	0.47 0.88	(9) (10)
Sludge[b]	10-26-82	^{130}Te	765 ppm	(11)
		^{128}Te	108 ppm	(11)
		^{126}Te	27 ppm	(11)
Containment atmosphere	5-1-80	^{129m}Te	4.0×10^{-7}	(12)
Auxiliary building sump tank water sample	3-25-80	^{127m}Te	1.3×10^{-4}	(13)
		^{129m}Te	1.5×10^{-3}	(13)
Makeup and purification demineralizer	May 1983	Stable Te	4.2×10^{-1}	(14,15)
	May 1983	Stable Te	3.1×10^{-1}	(14,15)
Upper plenum surface (Leadscrew data)	September 1984	Stable Te Te impurities in stainless steel[d]	1.83	(16)

TABLE 1. (continued)

System or Component	Sampling Date	Tellurium Isotope	Percent of Initial Core Inventory[a]	Reference
Core debris	--[c]	Stable Te Te impurities in stainless steel[d]	--[c]	--
Total[e]			5.8	

a. Core inventory calculated by ORIGEN-2 code (Reference 17) and decayed to time of sample analysis.

b. Not analyzed.

c. Analysis is underway and will be reported in the final report in 1985.

d. Tellurium impurity in the stainless steel components in the core was estimated to be about 804 g and the calculated stable tellurium and ^{125m}Te inventory was about 3649 g.

e. The sum of largest tellurium releases measured in the plant system.

The containment sump water was analyzed[8] on June 20, 1979. The estimated inventory of ^{129m}Te and ^{132}Te were 2.4, and 1.69×10^{-5} µCi/mL. Based on the containment sump volume of 2.16×10^{9} mL and the core inventory on June 20, 1979 (4.9×10^{11} µCi for ^{129m}Te, and 1.53×10^{6} µCi for ^{132}Te), the estimated release fractions of ^{129m}Te and ^{132}Te are 1.06 and 2.4%, respectively.

Water samples (30 mL) from the top, middle, and bottom of the containment sump were analyzed on August 28, 1979, at ORNL.[9] About 0.035 µCi/mL of ^{129}Te was detected in the bottom sample. Two samples of solid debris collected with the bottom water sample were taken; they were centrifuged, washed, and gamma scanned. About 0.277 and 0.514 µCi/mL of ^{129m}Te was detected. Based on the containment sump water volume (2.16×10^{9} mL) and the tellurium core inventory (9.65×10^{11} µCi for ^{129}Te and 1.27×10^{11} µCi for ^{129m}Te),[10] on August 28, 1979, the estimated core release fractions from the water sample and two solid samples were 0.008, 0.47, and 0.88%, respectively. Semiquantitative spark source mass spectrometry was performed on the containment sludge sample on October 26, 1982, and identified 900 ppm (µg/g) of a stable tellurium (^{126}Te, ^{128}Te, and ^{130}Te).[11]

A containment building air sample, including associated suspended matter was analyzed during April 29 to May 2, 1980.[12] The air contained 20 µCi of ^{129m}Te, which represents 4×10^{-7}% of the core inventory of ^{129m}Te projected at this time by ORIGEN code.[17]

A water sample from auxiliary building sump tank 2B was analyzed by ORNL on March 25, 1980.[13] About 1×10^{-3} µCi/mL of $^{\beta}Te$ was identified. This analysis was accomplished by chemical separation and subsequent beta counting of the sample which contained $^{\beta}Te$ (beta emitting tellurium) which is a mixture of long lived ^{127m}Te and ^{129m}Te. Based on the auxiliary building sump tank 2B volume (5.11×10^{7} mL) and the projected core inventory of nuclides on March 25, 1980, the estimated release fractions of either ^{127m}Te or ^{129m}Te are 1.3×10^{-4} or 1.5×10^{-3}%, respectively. These release fractions are estimated assuming that the mixture of $^{\beta}Te$ contained 100% of either ^{127m}Te or ^{129m}Te.

The contents of the makeup and purification demineralizer were analyzed in May 1983.[14] The GPU has estimated[15] that 1.74×10^8 mL (46,000 gal) of highly contaminated reactor coolant passed through the demineralizer vessels during the accident. The amounts of stable Te detected in the A and B demineralizers were 10 and 30 ppm, respectively. Based on the calculated inventory of stable tellurium of 3643 g and estimated masses of solid materials in A and B demineralizers (5.1×10^5 g), the estimated release fractions are 0.14 and 0.42%, respectively.

Control rod mechanism leadscrew samples from the H8 and B8 positions were analyzed by an induction coupled plasma technique for elemental tellurium at INEL.[16] The radioactive tellurium nuclides (except ^{125m}Te) are expected to have decayed to a negligibly small amount; measured tellurium would be the stable tellurium nuclides (^{126}Te, ^{128}Te, and ^{130}Te) from the fission products, ^{125m}Te, with doped tellurium added to stainless steels as a free-machining agent. The precise quantity of doped tellurium is generally proprietary information; however, tellurium weight percentages of 0.0005 to 0.1% are typical. The estimated core inventory fraction retained on upper plenum assembly surfaces was 0.018.[16] The largest tellurium releases measured in the above plant systems and components were summed to give a total fractional release of about 5.8% of the core inventory. Analyses of core grab samples from the core are underway, but these data are not available for this report.

Calculation of Tellurium Release from TMI-2 Core

The details of the TMI-2 accident sequence have been discussed in several reports.[18-22] Some of the key events[10] in the accident sequence for the time period 100 to 213 min are shown in Table 2. The critical period of the accident sequence from the point of view of core damage and fission product release is believed to be between 113 and 208 min after the reactor scram.[10] The 113-min time corresponds to the beginning of core uncovery following phase separation in the reactor coolant when the reactor coolant pumps were turned off at about 100 min. The 208-min time corresponds to the core refill following the resumption of sustained high pressure injection at about 200 min.

TABLE 2. SUMMARY OF PERTINENT EVENTS IN THE TMI-2 ACCIDENT SEQUENCE

Time (min)	Event
100	Last Reactor Coolant (RC) pumps turned off in Loop A
113	Beginning of core uncovering
139	Pilot Operated Release Valve (PORV) closed
145	Iodine in the reactor building air sample (HP-P-227) began to increase rapidly
150	A radiation detector (in core instrument panel area monitor) showed response indicating release of activity to the primary system
174	RC pump 2B was started and ran until 193 min
192	The PORV block valve was opened and cycled several times in the next period
200	Sustained High Pressure Injection (HPI) and core reflooded
208	Core refilled

The tellurium release fraction from the core was estimated using temperatures calculated with TMIBOIL[10] and release rates calculated with the Lorenz model.[2] For these calculations, the core was divided into six 0.61-m (2-ft) axial nodes; the top four nodes were assumed to be uncovered during the accident. The core temperature history[10] and the fractional release rates (estimated from Lorenz's model)[2,5] for the three hottest nodes are presented in Table 3.

The SCDAP computer code was used to calculate the extent of zircaloy cladding oxidation.[23] The core was divided into seven axial and three radial nodes. The radial nodes are denoted by Cold (C), Average (A), and Hot (H) regions; and the axial nodes were numbered from 1 through 7. As shown in Figure 1 the cladding in nodes H6 and A6 were oxidized to >90%. The rest of the cladding in the core was oxidized to <90%. The estimated fractional releases from nodes H6 and A6, and from the rest of the core were 4.36, 1.14, and 1.46%, respectively. These estimates were made based on Lorenz's model, and weighting the core inventory according to the axial flux distribution. The total release fraction is therefore ~7%.

This low estimated tellurium release fraction is in reasonable agreement with the low measured tellurium release fraction and suggests that most of the tellurium was retained within the core, probably in the zircaloy cladding.

TRAP-MELT Calculations

The TRAP-MELT[24] is a dynamic numerical model which calculates fission product particle and vapor transport and deposition in LWR primary systems during meltdown accidents. The transport and retention of fission products within the primary coolant system during a meltdown accident are treated in terms of control volumes and flow connections. It assumes that fission product transport can be superimposed on the fluid flow without coupling to it. A radionuclide species can reside within a control volume in two states, particle and vapor form. The geometry of the system, mass flow rates of a limited number of fission products (iodine, cesium, tellurium, strontium, ruthenium, and plutonium) in each control volume, time-dependent thermal-hydraulic data, and radionuclide physical properties

TABLE 3. TMI-2 CORE TEMPERATURE AND FRACTIONAL RELEASE RATE HISTORIES

Time After Trip (min)	Core Temperature[a] (K)			Fractional Release Rate $(min)^{-1}$		
	Node 4	Node 5	Node 6	Node 4	Node 5	Node 6
153	1327	1772	2220	1.19×10^{-6}	1.33×10^{-4}	9.38×10^{-2}
158	1426	2127	2322	3.39×10^{-6}	1.44×10^{-3}	1.44×10^{-1}
163	1434	2222	2442	3.69×10^{-6}	2.37×10^{-3}	1.97×10^{-1}
168	1410	2271	2515	2.86×10^{-6}	3.06×10^{-3}	2.63×10^{-1}
173	1386	2084	2530	2.22×10^{-6}	1.15×10^{-3}	2.76×10^{-1}
178	1361	1926	2520	1.70×10^{-6}	5.05×10^{-4}	2.61×10^{-1}
183	1337	1871	2383	1.32×10^{-6}	3.08×10^{-4}	1.74×10^{-1}
188	1313	1777	2242	1.02×10^{-6}	1.41×10^{-4}	1.05×10^{-1}
193	--	1702	2104	--	6.34×10^{-5}	5.12×10^{-2}
198	--	1600	1934	--	3.81×10^{-6}	2.11×10^{-2}
203	--	1437	1716	--	6.41×10^{-7}	2.90×10^{-3}
208	--	--	1506	--	--	3.12×10^{-4}
213	--	--	1295	--	--	3.33×10^{-5}

a. Node 4 = 1.83 to 2.44 m (6 to 8 ft) from the bottom of the core. Node 5 = 2.44 to 3.05 m (8 to 10 ft) from the bottom of the core. Node 6 = 3.05 to 3.66 m (10 to 12 ft) from the bottom of the core. For Nodes 4 and 5, constants A and B (in Table 5) for oxidation <90% were used and for Node 6, constants for oxidation ≥90% were used.

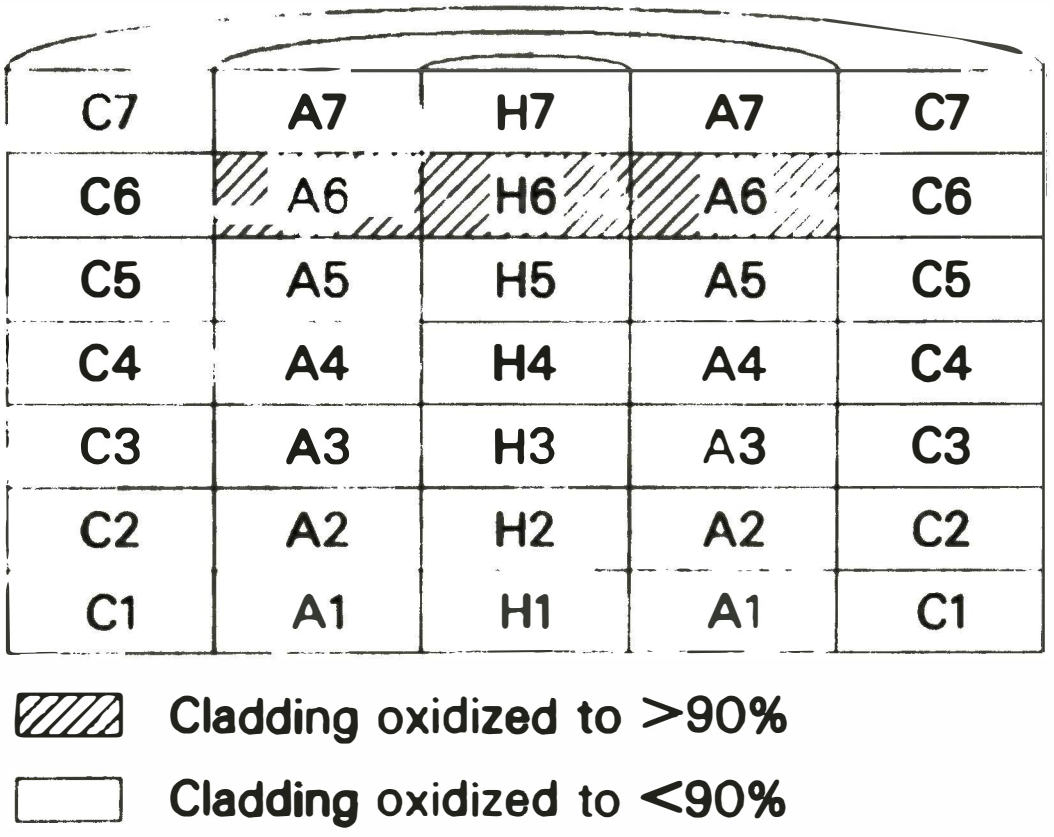

Figure 1. Extent of TMI-2 cladding oxidation.

(average radii and particle density of fission products) are required as input parameters for the code. The code calculates the deposition of these radionuclides in the control volumes at a specified time.

Preliminary calculations of tellurium transport and deposition during the TMI-2 accident were made using the TRAP-MELT computer code. Input parameters were obtained from various TMI-2 reports published[10,20,22,25] during the last five years. The primary coolant system was divided into eight control volumes as shown in Figure 2. The control volume geometries were obtained either from the Final Safety Analysis Report (FSAR)[26] or estimated. These parameters include length, hydraulic diameter, flow area, settling area, and height. Thirteen 5-min time intervals starting from 153 min and ending with 213 min were used. Steam temperatures and steam flow rates reported in Reference 22 were used and the system pressures were obtained from the measured charts reported in Reference 25. The tellurium source term (7%) estimated in the previous section was used.

The fraction of the core inventory deposited on (a) lower plenum, (b) core, (c) upper plenum, (d) upper head, (e) hot leg, (f) pressurizer, (g) steam generator, and (h) cold leg surfaces was calculated to be 1.60×10^{-4}, 0.0, 4.61, 1.46, 0.69, 0.087, 0.084, and 0.0026%, respectively. The calculated fraction of the core inventory of tellurium deposited on upper plenum surfaces versus time is shown in Figure 3. Of a total deposition of 4.6% on upper plenum surfaces, about 2.5% was calculated to be deposited after the event at 200 min, when the core was reflooded (see Table 2 for accident sequence). The large steam flow rate[22] at reflood was the principal reason for this calculated result.

The measured tellurium deposition on the upper plenum surfaces was 1.8%. The TRAP-MELT calculated tellurium deposition was 4.6%.

ORNL Review of Tellurium Release

An extensive review of available tellurium release data was performed by Lorenz et al.[2] at the ORNL. This examination of the existing tellurium release data indicates both high and low releases. High releases were observed in tests that contained no zircaloy cladding or highly

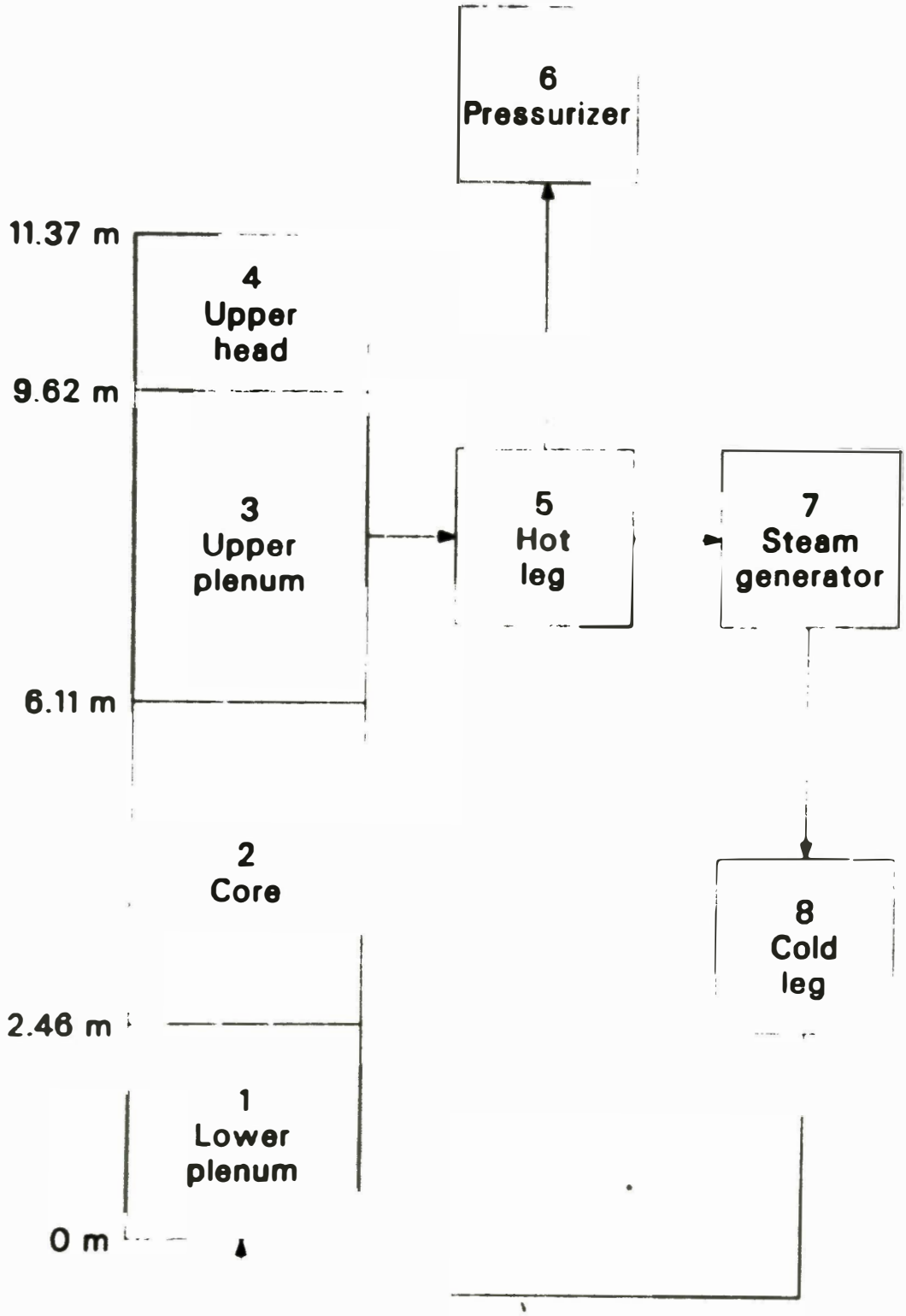

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Figure 2. TMI-2 control volumes for TRAP-MELT calculations.

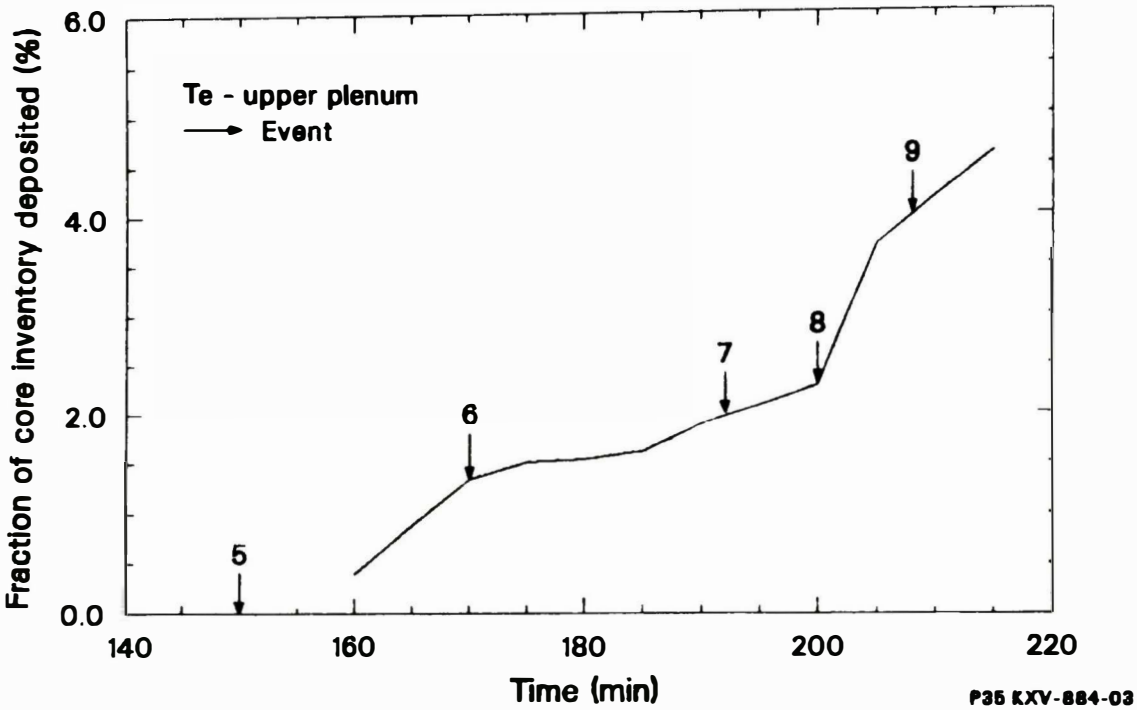

Figure 3. TRAP-MELT calculated tellurium retention on TMI-2 upper plenum surfaces.

oxidized (>90% conversion to ZrO_2) zircaloy. Low releases were observed in tests that contained zircaloy cladding with a lower extent of oxidation (<90%). Tellurium release data from three high temperature fission product release tests (HI series tests) are presented in Table 4. In the high temperature tests HI-1, HI-2 and HI-3, high burnup commercial PWR fuel from the H. B. Robinson reactor was heated in steam at maximum temperatures of 1673, 1973, and 2273 K, respectively. Tellurium released from the 20.32-cm long fuel rod segments was measured by spark source mass spectrometry. In test HI-2, oxidation of the zircaloy cladding was complete and a larger amount of tellurium was released than in the other tests in which oxidation was limited. Lorenz et al.[2] have proposed a tellurium release rate model which is based on the extent of zircaloy oxidation. The fractional release rate, k(T) in fraction per minute, is obtained from the following expression:

$$k(T) = A\, e^{B(T-273)} \qquad (1)$$

where A and B are constants given in Table 5, and T is temperature in K. When the local degree of cladding oxidation is <90%, a low release rate is recommended. When the local degree of cladding oxidation is >90%, a high release rate is recommended. Lorenz et al. indicate that the threshold for change in release rate is a function of local oxidation and that the core average oxidation is not acceptable basis. This model was used to estimate the tellurium release during the TMI-2 accident in the previous section.

Tellurium Release from PBF Severe Fuel Damage Tests

A series of Severe Fuel Damage (SFD) tests is being conducted by EG&G Idaho Inc., in the Power Burst Facility (PBF) at the Idaho National Engineering Laboratory for the U.S. Nuclear Regulatory Commission.[27,28] A major objective of these tests is to measure the release, transport, and deposition of fission products during in-pile tests similar to the accident which occurred at the TMI-2 reactor. Four bundle experiments are presently planned for Series 1 of the SFD program. Each bundle is operated at full power for three days, and then cooled for at least eight days to build up

TABLE 4. TELLURIUM RELEASE IN HI SERIES TEST AT ORNL

Test	Temperature (K)	Time (min)	Zircaloy Oxidized (%)	Te Release (%)	Te Fractional Release Rate (fraction/minute)
HI-1	1673	30	40	0.3	7.0×10^{-5}
HI-2	1973	20	100	50 to 100	6.0×10^{-2}
HI-3	2273	20	35	0.6	2.4×10^{-4}

TABLE 5. COEFFICIENTS FOR LORENZ TELLURIUM RELEASE RATE MODEL

Cladding Condition	Temperature (K)	A	B
Zircaloy oxidation <90%	<1873	1.625×10^{-11}	1.061×10^{-2}
	1873 to 2273	9.04×10^{-8}	5.22×10^{-3}
	>2273	6.025×10^{-6}	3.12×10^{-3}
Zircaloy oxidation ≥90%	<1873	6.50×10^{-10}	1.061×10^{-2}
	1873 to 2273	3.616×10^{-6}	5.22×10^{-3}
	>2273	2.41×10^{-4}	3.12×10^{-3}

an appropriate ratio of cesium to iodine. Shortly before the transient, the bundle is irradiated for four hours to build up an adequate inventory of short-lived fission products. The inlet flow to the bundle is then reduced or the power increased to initiate the transient portion of the experiments and to force the water level to decrease, leaving the bundle cooled by steam. The bundle heats up in superheated steam to peak temperatures up to 2400 K. Parameters to be varied during the four tests are heatup rate (amount of cladding oxidation), inlet flow (hydrogen to oxygen ratio), cooldown rate (amount of fragmentation), test rod burnup, and presence of control material. Unirradiated test fuel rods were used during the first two tests, and irradiated fuel rods will be used in the third and fourth tests, with control rods included in the fourth test. The Series 1 SFD test program are summarized in Table 6. The SFD scoping test, the test SFD 1-1, and the test SFD 1-3 were completed on October 29, 1982, September 8, 1983, and August 3, 1984, respectively. Data from the SFD-ST and SFD 1-1 are presented below.

The test trains of the SFD scoping test and the test SFD 1-1 contained a 32-rod bundle of 0.91-m-long 17 x 17 pressurized-water-reactor type fresh fuel rods (6.2 wt% enriched with ^{235}U) enclosed in an insulated shroud as shown in Figure 4. During the transient, the bundle coolant entered the bottom of the fuel bundle, passed through the bundle, and then exited through an effluent steamline which connected to the sampling and monitoring system and debris filter system. Fuel behavior was monitored during the tests, with cladding surface, fuel centerline, shroud thermocouples, flow meters, steam probes, and other instrumentation.

During the SFD-scoping test, the bundle was subjected to a slow heatup (0.13 K/s) to 1700 K, and then to rapid heating (~10 K/s) to 2400 K, followed by a rapid quench. During the second test (SFD 1-1), the test bundle was subjected to a more rapid heating (~0.45 K/s) to 1300 K, 1.3 K/s to 1700 K and then more rapid heating (~30 K/s) to 2400 K. The SFD 1-1 test was slow-cooled rather than quenched. Considerable cladding oxidation (virtually all zircaloy in the test bundle), cladding melting, fuel liquefaction (18% of the bundle), and fuel fragmentation (60% of the

TABLE 6. PBF SEVERE FUEL DAMAGE TESTS

PBF Test No.	Heating Rate (K/s)	Inlet Flow (g/s)	Test Rods	Cooling	Date of Completion
SFD-ST	0-15	20.0	Fresh fuel	Quench	10/29/82
SFD-1-1	TMI-2[a]	0.6	Fresh fuel	Slow	9/08/83
SFD-1-3	TMI-2[a]	0.6	Irradiated fuel	Slow	8/3/84
SFD-1-4	TMI-2[a]	0.6	Irradiated fuel and control rod material	Slow	1985

a. Characterized by slow heating rate up to 1700 K and rapid heating rate above 1700 K, driven by metal-water reaction.

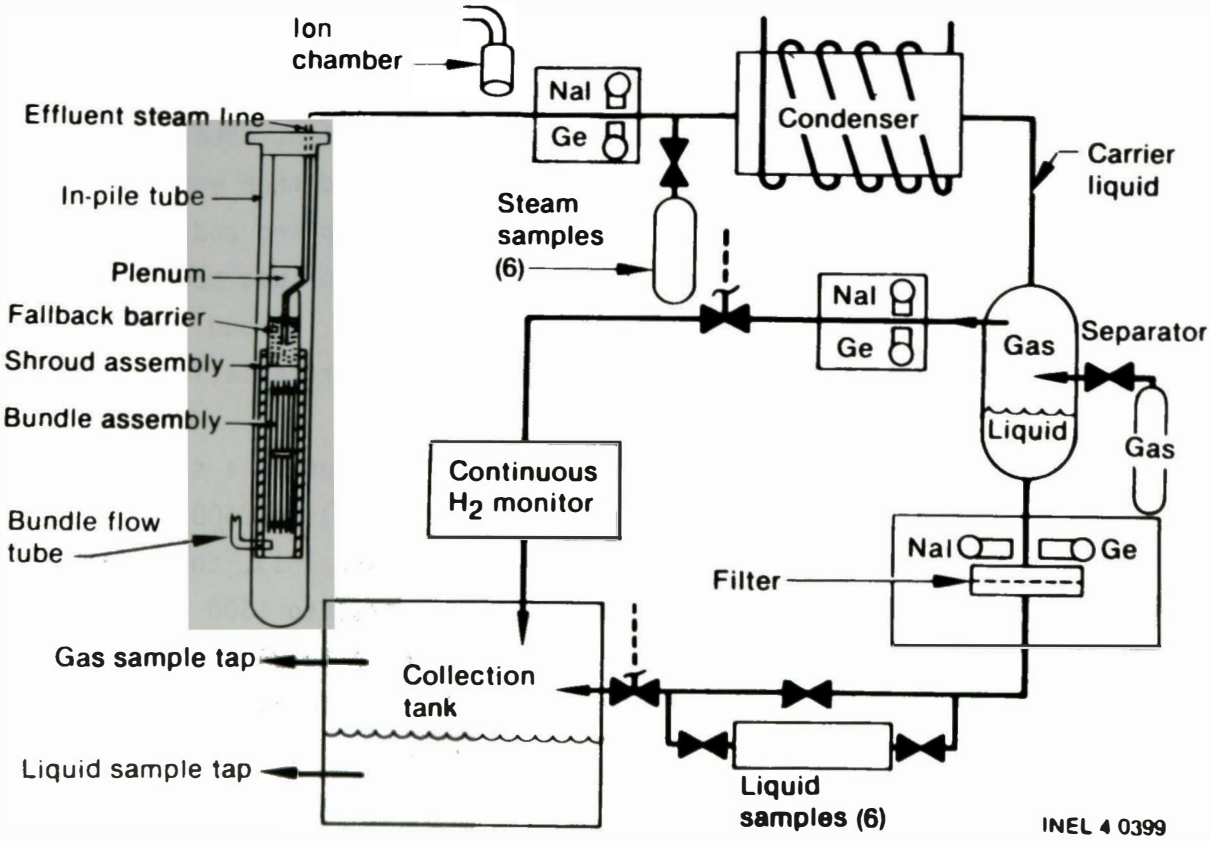

Figure 4. SFD fission product monitoring system.

bundle) occurred during the SFD-ST. Limited cladding oxidation (30%) and significant cladding melting and fuel liquefaction occurred during Test SFD 1-1.

Different types of effluent samples were collected during these SFD tests and analyzed by a variety of analytical techniques.[29] The types of samples include: (a) six steam samples, (b) six liquid grab samples, (c) filter debris samples, (d) several steamline pipe samples, and (e) liquid and gas samples from the collection tank as shown in Figure 4.

The fractional release rates (fraction of the bundle inventory released per minute) were calculated from the gas and liquid grab samples. The data are presented in Table 7.

The high tellurium release rate measured in SFD-ST compared to SFD 1-1 are probably due to extensive oxidation of the cladding, and the high steam flow rate and the steam plentiful conditions that existed during the SFD-ST. In SFD 1-1, plateout of the tellurium may have occurred in the steamlines due to much slower flow rates, and the zircaloy cladding may have held tellurium, because the extent of cladding oxidation was so low.

The distribution (mass balance) of tellurium in various components of the system is presented in Table 8. About 40% of the core inventory of ^{129m}Te was released during SFD-ST; in contrast, <1% was released in SFD 1-1. The principal reason for this differences is believed to be holdup of tellurium by Zircaloy in SFD 1-1.

Tellurium Release from SASCHA Tests

Experiments have been performed[30-32] in the SASCHA facility in Karlsruhe, West Germany, to investigate fission product release under severe damage and core meltdown conditions. The major objectives were (a) to determine the release fractions of radiologically important fission products in the temperatures range 1773 to 3073 K (1500 to 2800°C), and (b) to characterize the physical and chemical behavior of the released material in the primary coolant system. The SASCHA test facility consists of a high frequency induction furnace, a crucible, and devices for aerosol

TABLE 7. FRACTIONAL RELEASE RATES FROM PBF SFD TESTS (fraction/minute)

Test	Heatup 2000 K	Heatup 2400 K	Quench 600 K
SFD-ST	7.0×10^{-6}	5.42×10^{-3}	2.9×10^{-3}
SFD 1-1	3.0×10^{-8}	--	3.8×10^{-5}

TABLE 8. OVERALL MASS BALANCE OF ^{129m}Te IN PBF SFD TESTS (fraction of total bundle inventory)

Samples	Tests: SFD-ST[a]	Tests: SFD 1-1[b]
304 SS Steam Lines	1.02×10^{-1}	5.30×10^{-3}
Grab Samples	7.60×10^{-5}	5.10×10^{-7}
5 μm 304 SS Filter	1.96×10^{-1}	6.10×10^{-4}
Collection Tank	9.80×10^{-2}	3.10×10^{-3}
Total Release Fraction	3.96×10^{-1}	9.01×10^{-3}

a. Slow heatup and quench, high steam flow rate (20 g/s), steam plentiful, and 100% cladding oxidation.

b. Fast heatup, slow cooldown, low steam flow rate (0.6 g/s), steam starved, and 30% cladding oxidation.

collection and analysis. The fuel rods were composed of zircaloy cladding and UO_2 pellets with a simulated burnup of 44 GWd/t. Stainless steel and absorber materials were included to obtain a representative core melt composition. The integral melt mass was about 200 to 250 g. The released material was collected on glass fiber filters. The filters and the walls of the transport tube were analyzed.

The earlier tests were conducted in air at maximum temperatures ranging from 1773 to 3073 K (1500 to 2800°C) and in steam at 2173 to 2673 K (1900 to 2400°C). The flow rate and pressure were 10 to 30 L/min and 0.21 MPa (two bars), respectively. The fractional release rates (fraction of the inventory released per minute) are presented in Table 9. The fractional release rates in air and steam were essentially the same. During these early tests, the heating rates were normally ≤473 K/min, the zircaloy cladding was almost completely oxidized and the total estimated tellurium fraction was 0.81.

Experiments were also conducted with a reduced steam supply (28 L/min Ar 1.5 L/min steam) and with a purely reducing atmosphere (28 L/min Ar 1.5 L/min of H_2). The release fractions are shown in Figures 5 and 6. Lower tellurium release was measured for a reduced steam supply. Although the temperature in Test S-281 (Ar + 5% H_2) was 200 to 400 K higher for some minutes, the tellurium release in Test S-229 (steam) was about a factor five lower. In Test S-282 (Ar + 5% steam) a low steam supply resulted; tellurium release between the two cases has been discussed above. Tellurium releases in high and low steam supply tests are compared in Figure 6. Tellurium release in low steam supply test, S-282 (1.5 L/min steam + 28 L/min Ar), was about 30% and in the high steam supply test, S-250 (30 L/min steam), tellurium release was about 70%. Albrecht and Wild[31] suggest that the low degree of oxidation causes tellurium to be retained in the melting crucible due to chemical reactions with the zircaloy cladding and (probably) with the stainless steel components. As the oxidation increases, the resulting tellurides are destroyed in favor of metal oxide formation which, in turn, accelerates the release of tellurium.

TABLE 9. FRACTIONAL RELEASE RATES FROM SASCHA TESTS IN AIR AND STEAM (fraction/minute)

Temperature (K)	2073	2173	2273	2473	2673
Air[a]	4.8×10^{-3}	--	--	3×10^{-2}	7.3×10^{-2}
Steam[a]	--	1.8×10^{-2}	--	--	7.1×10^{-2}
Ar + 5% H_2	--	1.8×10^{-3}	--	--	--

a. Flow rate = 10 to 30 L/min, Pressure = 0.2 MPa (2 bars).

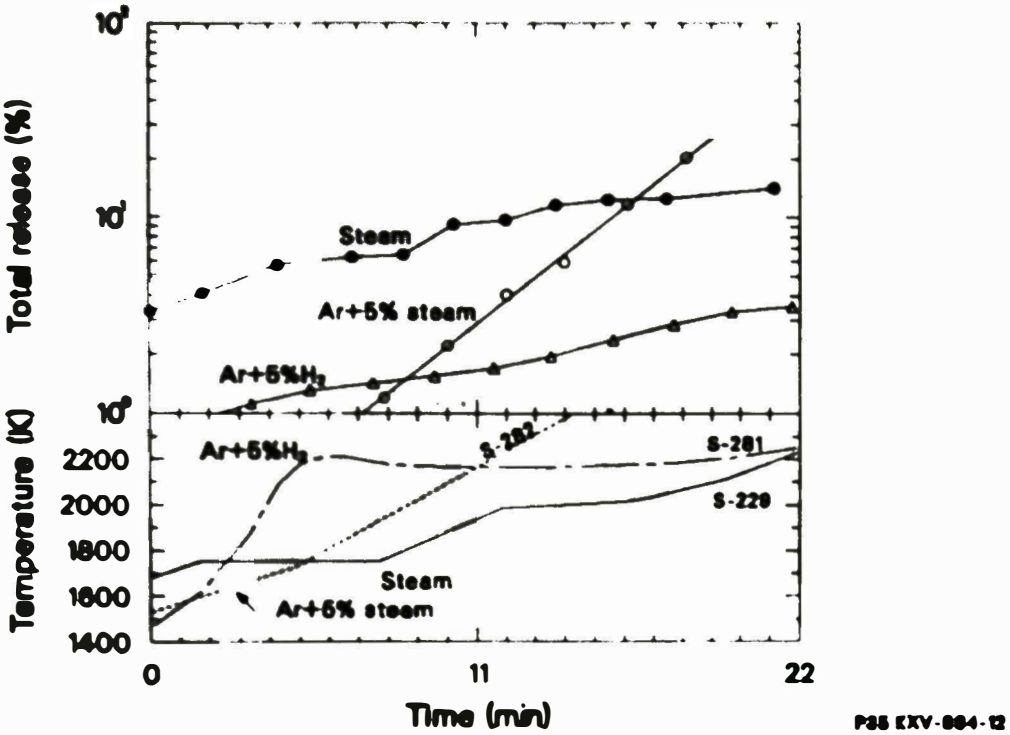

Figure 5. Dependence of tellurium release on steam supply in SASCHA tests.

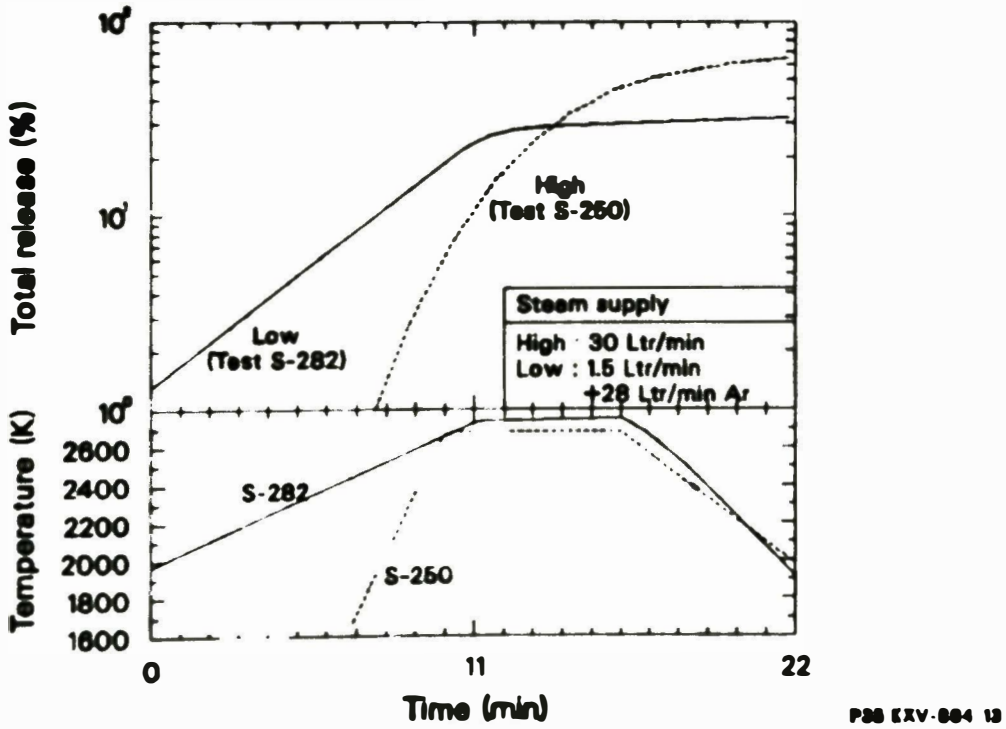

Figure 6. Tellurium release in SASCHA tests with high and low steam supply.

COMPARISON OF TMI-2 TELLURIUM BEHAVIOR WITH IN-PILE AND OUT-OF-PILE TESTS

In this section, the fractional release rates and release fractions estimated and measured during the TMI-2 accident are compared with measurements from the two PBF Severe Fuel Damage Tests, and the ORNL and SASCHA out-of-pile tests. The modified tellurium release model of Lorenz et al. was used to estimate the fractional release rates for TMI-2 in the temperature range of 1300 to 2550 K for two regions in the core: 3.05 to 3.66 m (10 to 12 ft) and 2.44 to 3.05 m (8 to 10 ft) from the bottom of the core, where the cladding oxidation was >90 and <90%, respectively. The fractional release rates versus temperature are shown in Figure 7 and compared with the data from the PBF tests (SFD-ST and SFD 1-1), ORNL tests (HI-1, HI-2, and HI-3) and the SASCHA tests. The PBF SFD-scoping Test result at 2400 K, the ORNL Test HI-1 and the SASCHA tests lie above the lower line calculated for TMI-2 with the Lorenz model for <90% cladding oxidation but below the upper line calculated for >90% oxidation. The SFD-ST results at 2000 K, the SFD 1-1, and the ORNL Test HI-3 show low tellurium release rates below the <90% oxidation curve. This result is probably indicative of low zircaloy cladding oxidation in the tests and holdup of tellurium by zircaloy. The release rate measured in Test HI-2 is in reasonable agreement with the curve calculated for cladding oxidation >90%.

The release fractions measured and estimated from TMI-2 are compared with the in-pile and out-of-pile tests in Table 10. The calculated and measured tellurium release fractions for TMI-2 were low. The measured tellurium fraction in the TMI-2 accident simulation test (SFD 1-1) in the PBF was even lower. The PBF SFD 1-1 test closely approximated the thermal hydraulic conditions of the TMI-2 accident, and the results of this test indicate very small tellurium release (~0.9%), which may be attributed to the holdup of tellurium by unoxidized zircaloy in the test bundle. The SFD 1-1 result is consistent with ORNL tests, where the cladding oxidation was low and tellurium was tied up with the zircaloy cladding. The tellurium release in SASCHA test (Ar + 5% H_2) was consistent with TMI-2. Also in SASCHA tests, the tellurium release was higher in a test where the

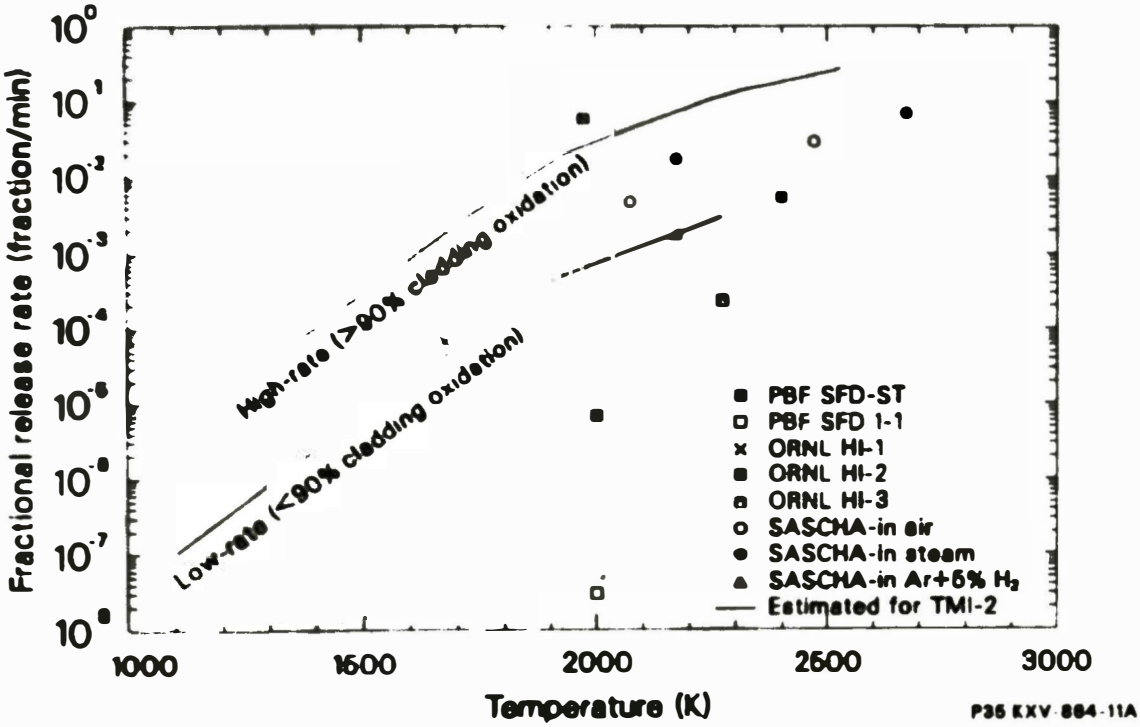

Figure 7. Comparison of fractional release rates.

TABLE 10. COMPARISON OF TMI-2 Te RELEASE FRACTIONS WITH IN-PILE AND OUT-OF-PILE TESTS

Event	Maximum Fuel Temperature (K)	Cladding Oxidation (%)	Release Fraction	Reference
TMI-2 Accident	2600	Low	5.8×10^{-2} (measured) 7.0×10^{-2} (estimated)	Present Study
PBF Tests				
SFD-ST	2400	100	4.0×10^{-1}	
SFD 1-1	2400	30	9.0×10^{-3}	
ORNL Tests				
HI-1	1673	40	3.0×10^{-3}	2
HI-2	1973	100	0.5 to 1.0	
HI-3	2273	35	6.0×10^{-3}	
SASCHA Tests				
Low Steam Flow (1.5 L/min)	2573	Low	3.3×10^{-1}	2
High Steam Flow (30 L/min)	2733	High	6.5×10^{-1}	
Ar + 5% H_2	2173	0	3.6×10^{-2}	
Ar + 5% Steam	2200	Low	2.0×10^{-1}	

steam flow was high. The availability of unoxidized zircaloy in the TMI-2 core during the accident is expected to be the cause for holdup of the tellurium and ultimate low release fractions. Analyses of samples from the core region may provide an assessment of the large fraction of tellurium retained in the core, thus validating the zircaloy-oxidation dependent tellurium release models.

CONCLUSIONS

A number of available TMI-2 samples were analyzed, best estimate calculations were performed, and the data were compared with in-pile and out-of-pile tests. The following conclusions are drawn from the analysis:

1. Very little (~5.8%) tellurium was released and transported from the TMI-2 core, probably as a result of holdup by zircaloy cladding and structural materials. Analyses of samples from core region may provide an assessment of the large fraction of tellurium retained there.

2. Best estimate calculations suggest that a significant fraction of the total tellurium was deposited on the upper plenum surfaces due to the high pressure injection at about 200 min after the reactor scram, resulting in high steam flow.

3. Comparison of tellurium release fractions and fractional release rates from the TMI-2 accident, with in-pile and out-of-pile test results, suggests that zircaloy holds tellurium until the cladding is oxidized significantly.

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APPENDIX A
TELLURIUM ANALYTICAL METHODS

J. S. Jessup

APPENDIX A
TELLURIUM ANALYTICAL METHODS

INTRODUCTION

The Idaho National Engineering Laboratory (INEL), as part of the broad core activities research program, will be conducting chemical analyses on a variety of samples obtained from the damaged Three Mile Island (TMI) Unit-2 reactor. The 1979 accident at TMI-2 resulted in the release of significant quantities of fission products from the damaged core to the reactor coolant system and containment building. Radioactive tellurium, as a radioiodine precursor, can constitute a significant health hazard if released to the environment. Also, the chemical interaction of tellurium with other reactor materials, principally zircaloy and stainless steel during severe core damage accidents, is not well understood. To date, there are very limited data available for tellurium in TMI-2 samples. Also, radioactive tellurium present in the fuel (except ^{125m}Te) at the time of the accident has now decayed to less than detectable concentrations. For this reason, attention has been focused on the postaccident measurement of stable fission product tellurium concentrations on reactor plant surfaces and core debris to determine tellurium retention and transport behavior.

Interpretation of quantitative tellurium data in TMI-2 samples is complicated by the fact that natural tellurium is routinely added to stainless steels as a free-machining agent.[1] The precise quantity of doped tellurium in a given sample of alloy is generally proprietary information; however, tellurium weight percentages of 0.0005 to 0.1% (5.0 to 1000 ppm) are typical. This interference requires that elemental analyses on all TMI-2 samples be screened for relative ratios of stainless steel components and tellurium (Fe/Ni/Cr/Te). In those cases in which tellurium and Fe/Ni/Cr are present in ratios which indicate the presence of doped steels, it will probably not be possible to extract any information relating to fission product tellurium. However, for those samples in which stainless steel components are not present in significant quantities, and for samples in which tellurium concentrations far exceed doped levels, tellurium analytical data may provide information on the behavior of fission product tellurium.

This Appendix provides a summary of analytical methods and procedures for the separation and analysis of tellurium in TMI-2 samples from the following areas:

- Leadscrews
- Makeup filter debris
- Reactor building basement debris and liquids
- Core debris (fuel, cladding, and structural materials).

The major elemental constituents of these core region materials include: iron, nickel, and chromium (304 and 17-4 PH stainless steel, inconel 718 and x-750, zircaloy-4); zirconium (zircaloy-4); silver, cadmium and indium (absorber alloy); aluminum and boron (burnable poison rod); and uranium (fuel).

In some cases, a determination of tellurium concentration may be performed directly on a dissolved sample, without any preliminary treatment. However, this requires that: (a) the sample be adequate in size, with a tellurium concentration above instrumental detection limits; (b) no significant elemental interferences are present; and (c) the exposure rate of the sample is low enough to allow its use with the present radioactive exhaust system (currently 200 mR/h). For those samples where elemental interferences are present, or when preconcentration of the tellurium is necessary, the tellurium must be isolated from the bulk of the sample matrix.

EXPERIMENTAL METHODS

Analytical methods have been developed for the separation and analysis of tellurium in various sample matrices. Tellurium separation procedures have been evaluated, with ion-exchange resins, reductions, and precipitations providing the most effective means of separating tellurium from complex matrices. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is the method of choice for the determination of total tellurium concentration.

Dissolution Methods

The TMI-2 samples from the core region have been brought into solution at the INEL through either a bisulfate fusion or a HNO_3/HF dissolution. The dissolution procedures for specific samples are described in detail in an analytical procedures report,[2] but a brief description of the dissolution procedures is reported here.

Bisulfate Fusion

Decomposition of a sample by the use of fluxes is a common method for breaking up and/or oxidizing the components of a sample. A potassium bisulfate fusion has been successfully applied for the dissolution of a number of TMI-2 samples. The sample is slowly heated in a fusion chamber containing $Sr(NO_3)_2$ and $KHSO_4$, until the material fuses. After cooling, a known volume of deionized water is added to the melt. The insoluble $SrSO_4$ is removed by centrifuging and decanting the supernatant. An aliquot of the aqueous solution is available for ICP-AES analysis of tellurium.

HNO_3/HF Dissolution

Dissolution of metals and alloys containing tellurium presents no serious difficulties when carried out in HNO_3/HF solution at moderate temperatures (<100°C). A 1:1:1 volume mixture of water, nitric acid, and

hydrofluoric acid is quite effective in the dissolution of high temperature alloys. Volatilization of tellurium is only a problem when a sample is warmed in the presence of a halogen, HCl, or HBr vapors.

In some cases, the HNO_3/HF dissolution procedure was used to leach and solubilize surface deposits from a base alloy sample. The dissolution was not allowed to proceed to the point where the base metal was significantly attacked. However, the HNO_3/HF solutions typically can be expected to contain varying amounts of base metals along with the surface adherents. In these cases, the overall mass of the solubilized sample is not known. Analytical data on these samples will not provide absolute elemental concentrations (such as µg Te/g sample), but rather relative elemental constituents (such as wt%, normalized to a given major elemental component.

Analysis Method

A number of analytical methods are available for the determination of tellurium in a variety of inorganic materials. However, the convenience, sensitivity, and interferences of any given technique must be evaluated with consideration given to the samples of interest. The analyses method for the TMI-2 samples should: (a) allow for rapid qualitative elemental analyses (to screen for stainless steel content); (b) allow for rapid multielement quantitative analysis (to determine Fe/Ni/Cr/Te ratios); and (c) exhibit maximum sensitivity (to limit preconcentration in small samples). Gravimetric methods are inappropriate for the analysis of TMI-2 samples for several reasons, including limited accuracy and serious interference from heavy metals. Volumetric methods for tellurium determinations generally are based on direct or indirect redox titrations. However, they are most applicable for tellurium concentrations in the milligram range. Electrochemical methods for the determination of tellurium can be quite sensitive, but they require rigorous control of elemental oxidation states; lead and other metals pose serious interferences. X-ray fluorescence is capable of estimating tellurium concentration in alloys down to the 1-ppm range. However, the presence of selenium in the sample can dramatically affect the detection limit. Atomic

adsorption spectroscopy is a convenient method for the analysis of small amounts of tellurium, but convenience is sacrificed for samples requiring multielement analysis.

Atomic emission spectroscopy utilizing an inductively coupled plasma excitation source (ICP-AES) is a particularly useful method for the rapid qualitative or quantitative analyses of multiple elements in a variety of sample matrices. The ICP-AES instrument utilizes an inductively coupled argon plasma as an excitation source for the sample. Because of the high temperatures and high excitation power of plasmas, plasma emission spectra are extremely line rich. Qualitative analysis is accomplished by an analysis of the wavelengths of the emitted light; quantitative analysis relates the intensity of emitted light to the concentration of a given element. The ICP-AES instrument to be used for analyses of TMI-2 samples is a Leeman Labs Plasma-Spec.[3] This instrument has the following capabilities which make it appropriate for use with TMI-2 samples:

- Qualitative Analysis Mode--The use of this mode allows for rapid screening of a sample for up to 20 user-selected elements. This will allow an initial determination of sample matrix (dissolved stainless, zircaloy, control rods, etc.) in order to identify necessary background corrections.

- Quantitative Multielement Mode--The use of this mode allows for the rapid, sequential scanning of up to 20 wavelengths for user-selected elements. Concentrations of individual elements are calculated based on previously entered calibration curves. For most elements, the signal intensity exhibits excellent linearity over 3 to 5 orders of magnitude. This mode will allow for rapid quantitative analysis of all the elements of interest (Fe, Ni, Cr, Te, Zr, U, Cu, Sn, and Mo).

- Detection Limits--ICP-AES detection limits for elements to be analyzed in TMI-2 samples are presented in Table A-1. The detection limit for tellurium (15 ng/mL, 0.015 ppm) is the most critical, since trace quantities may be present in some samples.

TABLE A-1. ICP-AES DETECTION LIMITS

Element	Detection Limit (ng/ml)
Tellurium (Te)	15.0
Iron (Fe)	0.09
Nickel (Ni)	0.2
Chromium (Cr)	0.08
Zirconium (Zr)	0.06
Uranium (U)	1.5
Tin (Sn)	3.0
Copper (Cu)	0.04
Molybdenum (Mo)	0.2

The concentration of natural tellurium doped in stainless steels (typically 5 to 1000 ppm) is well within the instrumental detection limit.

A number of the TMI-2 grab samples available for Te analysis are in the 10 to 200-mg size range. The dissolution procedure brought the total volume of these sample solutions to 20 mL. In order for the tellurium in solution to be detectable without preconcentration, a minimum of 300 ng Te must be present. For the 10 to 200 mg samples, this requires approximately 1.5 to 300 ppm tellurium. Those samples in which the tellurium concentration is below the detection limit (as evidenced by the qualitative scans) will be retained for subsequent tellurium separation/concentration.

Separation Methods

The direct determination of TMI-2 samples may be prohibited by one or more of the following factors. First, the sample size and/or analyte concentration may be too small to reach the Te detection limit. Individual samples from the same bulk fraction may be consolidated if sample size is the limitation. A series of separations designed to concentrate the tellurium might be sufficient to alleviate the problem of analyte concentration. A second factor which might preclude the direct determination of tellurium would be the presence of significant quantities of interfering elements. Despite the fact that tellurium has 764 emission lines, only a limited number are appropriate for analytical use. High concentrations of elements with strong emission lines in the immediate vicinity of Te emissions might require that the tellurium be isolated from the interfering species prior to analysis. The final factor which may limit the direct determination of tellurium in TMI-2 samples is the effective radiation dose rate. A typical sample volume for multielement qualitative and quantitative analysis is approximately 5 to 10 mL. The majority of the total sample volume is released to a drain storage, and the remaining sample in the torch compartment is vented through a chimney to the radioactive exhaust system. The effective dose rate for an individual sample is limited to 200 mR/h. This may require that the tellurium be separated from some of the radioactive sample constituents, prior to analyses.

The most effective procedures for the separation and/or concentration of tellurium in TMI-2 samples are based on precipitations, reductions, and ion-exchange techniques. The most appropriate separation or concentration methods for a given sample can be selected based on the dose rate of the sample and the results of any preliminary qualitative scans.

Ion-Exchange

A method which makes use of a Dowex anion exchange resin is particularly useful for the separation of many of the species which may be present in TMI-2 samples.[4] The separation is carried out using a column of Dowex I x 8, 200 to 400 mesh, chloride form resin. The sample is taken up in an HF/HNO_3 solution (1:2 by volume) with a total fluoride concentration of 0.6 to 1.0 M. The pH of the resulting solution is adjusted to between 5 and 6 with a dilute solution of NH_4OH. Following a neutral wash of the column, the sample solution is introduced. A flow rate of 0.5 $mL/min/cm^2$ allows for adequate separation of individual species. A diagram of the separation scheme for individual elements is shown in Figure A-1, and efficiencies for selected elements are given in Table A-2.

Sn (II) Reduction

Microgram quantities of tellurium in aqueous acidic solution are very effectively reduced to the zero valent state by freshly prepared Sn (II) solutions.[5,6] This is widely used as a preconcentration method for ultimate tellurium determinations.

In order to minimize air oxidation of Sn (II), the following solution must be prepared daily. 100 mL of concentrated hydrochloric acid is added to 250 g of stannous chloride ($SnCl_2 \cdot 2H_2O$), and the solution is warmed until clear. When cool, the solution is diluted to 250 mL with concentrated hydrochloric acid.

Approximately 10 mL of the freshly prepared $SnCl_2$ solution is added to the warm acidic sample solution containing tellurium. The resulting solution is mixed, cooled to room temperature, and allowed to stand

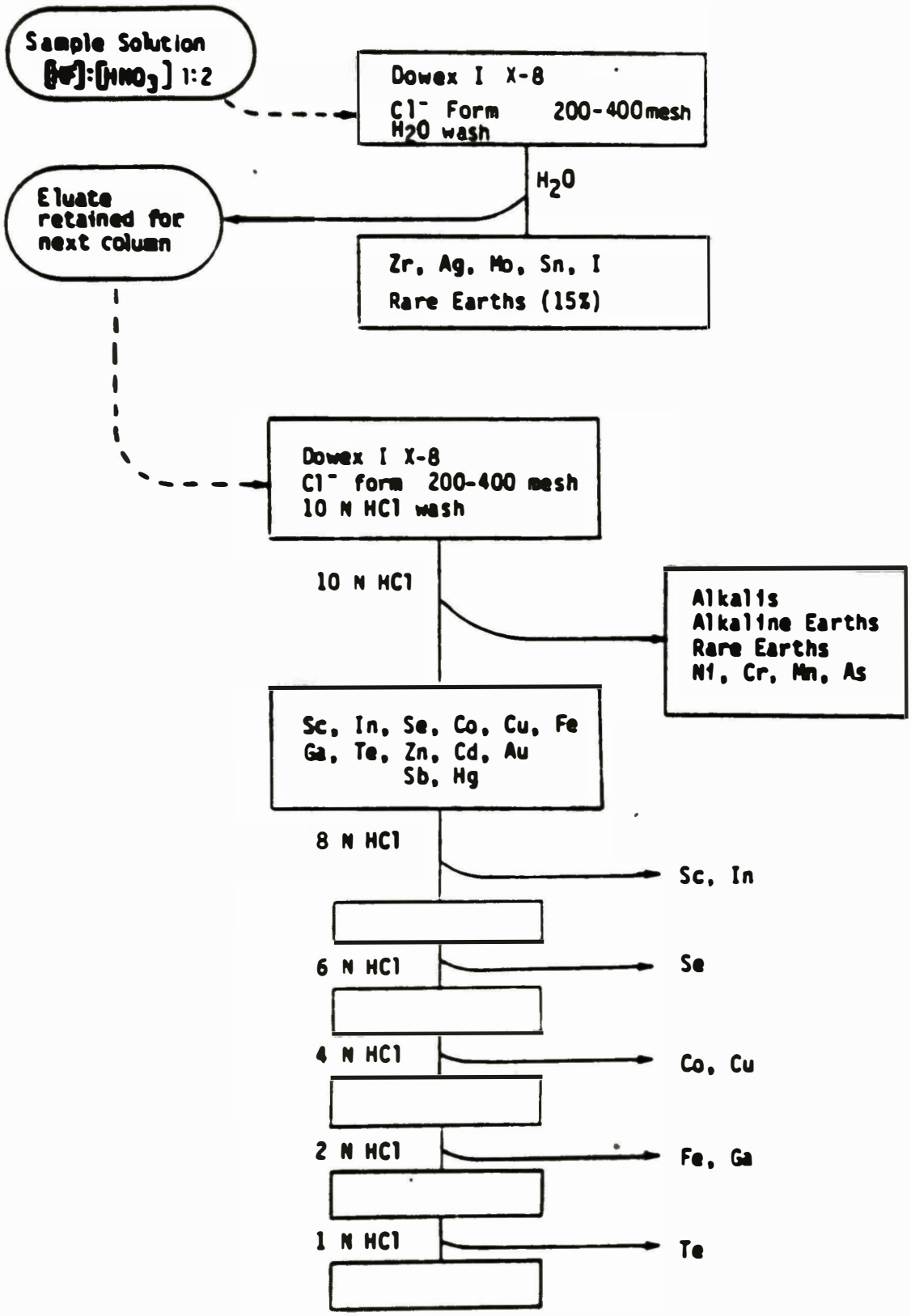

Figure A-1. Dowex separation scheme.

TABLE A-2. SEPARATION DATA USING DOWEX I X 8

Eluting Solvent	(Volume)[a]	Elute	Efficiency (%)[b]
8 N HCl	(12)	In	100
6 N HCl	(5)	Se	100
4 N HCl	(6)	Co,Cu	100
2 N HCl	(8)	Fe	95
1 N HCl	(5)	Te	100

a. The number in parentheses represents the number of column volumes of eluting solvent necessary to effect the separation.

b. The efficiency is reported as the percentage of the total element eluted by the solvent at the moment of elution (+0.1%).

undisturbed for 3 to 4 h. The precipitated tellurium is filtered on a 0.6 μ micropore filter. The precipitation yield is 90% for samples containing <140 μg of tellurium.

A potential interference in the Sn (II) reduction method is the simultaneous reduction of As, Bi, Cu, Au, Hg, Se, and Ag to their metallic states. This technique is not generally appropriate for the separation of analytically pure tellurium, but is very useful for the preconcentration of microgram quantities.

SO_2 Reduction

The reduction of tellurium by SO_2 in acidic solution is the preferred method for obtaining analytically pure tellurium metal.[7] Although the reduction can be carried out with SO_2 alone, this requires that no HNO_3 be present in solution, and all the tellurium be in the +4 oxidation state. The limitation can be avoided by the use of SO_2 and hydrazine, which effectively reduces either the +4 tellurite or the +6 tellurite to the zero valent metal.[8]

Fifteen mL of a saturated SO_2 solution is added to a warm HCl solution (2.0 to 5 N) containing tellurium. The reducing agent can be added by bubbling SO_2 through the solution, however this results in the loss of significant quantities of $TeCl_2$ through volatilization. Approximately 10 mL of 15% $N_2H_4 \cdot HCl$ is added to the SO_2/Te solution, followed by another 25 mL of saturated SO_2 solution. The resulting solution is brought to a boil, and allowed to boil until the Te precipitate settles out of solution (typically less than 5 min). The slow precipitation of tellurium from a warm solution allows for the formation of a more crystalline precipitate, which is more resistant to air oxidation.

This reduction procedure results in the quantitative precipitation of elemental tellurium if the solution HCl concentration is 2.0 to 5.0 N.[9] The tellurium does not precipitate from >8 N HCl solutions. Mercury may be coprecipitated along with the tellurium.

Fe (III) Coprecipitation

Coprecipitation of tellurium with metal hydroxides is a very effective means of concentrating small amounts of tellurium in acidic solution.[10] The method is equally effective for Te (IV) and Te (VI), and is best accomplished in solutions containing less than 400 mg of iron. Tellurium can be precipitated from HNO_3 by this method, but the solution must not contain more than 3% (by volume) HNO_3.

The slightly acidic sample solution containing 100 to -200 mg of $Fe(NO_3)_3$ is poured into an excess of NH_4OH solution (pH 9.7) with constant stirring. As the $Fe(OH)_3$ precipitates, up to 0.5 mg of tellurium is quantitatively precipitated. The precipitation yield lowers to 65-80% for samples containing less than 0.1 mg of tellurium. Also, the coprecipitation efficiency of tellurium is dramatically affected by pH. For example, only a 65% efficiency is attained at a pH of 8.0. Because of this, it is important that the acidic sample be added to an excess of base solution, and the pH of the mixture be monitored during the course of the precipitation.

The presence of Zn, Cd, and Mo in large amounts does not interfere with tellurium coprecipitation, however, more than 400 mg of iron causes difficulty in the filtration of the hydroxide precipitate. Lead may be coprecipitated along with the tellurium.

Metal Sulfide Precipitation

The precipitation of tellurium sulfide affords a convenient means of separating tellurium from those elements which form soluble sulfides, including Fe, Ni, Cs, and Sr. The major interference in the method is presented by copper, so an initial qualitative test for its presence must be run. If necessary, copper can be removed by precipitation with hydroquinone.

Te (IV) is very readily reduced by H_2S, but Te (VI) is considerably slower. In order to convert all the Te (VI) in acid solution to the +4 oxidation state, the solution is taken up in dilute (<6 N) HCl and

warmed (at <100°C). This acidic solution of Te (IV) is then saturated with H_2S by slowly bubbling the gas through the solution. It is important that the TeS_2 precipitation be done cold, in order that the resulting precipitates are reasonably soluble.

Discussion

The tellurium analytical methods described in this appendix have been selected for their applicability toward tellurium determinations in a series of samples from the damaged TMI Unit-2 reactor. The materials which will be analyzed for tellurium content include stainless steels, inconels, zircaloy-4, control rod alloy, burnable poison, fuel, and coolant. These matrices are found in samples from leadscrews, makeup filter debris, reactor building basement debris and liquids, and core debris (fuel, cladding, and structural materials).

The direct application of tellurium analytical data toward an explanation of fission product deposition is complicated by the fact that there may be serious contamination of TMI-2 samples by natural tellurium. Tellurium is routinely present in stainless steels in weight percentages of 0.00050 to -0.1%. As a consequence, all elemental analyses for TMI-2 samples must be screened for relative amounts of stainless steel components. Analytical tellurium data from samples which do not contain significant quantities of stainless steel components (Fe/Ni/Cr) may be interpreted as arising from fission product tellurium with a reasonable degree of certainty. Those samples which contain appreciable quantities of stainless steel components must be carefully evaluated to determine the significance of any tellurium data in terms of fission product behavior. If the tellurium and Fe/Ni/Cr are present in ratios which approximate those found in doped steels, it will not be possible to extract any information about fission product tellurium. However, if the tellurium concentration far exceeds the 0.1 wt% maximum for doped steels, some qualitative information about fission product tellurium can be inferred. In this case quantitative fission product tellurium information is not possible since the concentrations of doped tellurium can vary over three orders of magnitude.

The analytical method to be used for the determination of tellurium in TMI-2 samples is Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The instrumental detection limits for the elements of interest (Table A-1) are within the ranges necessary for the analysis of most of the TMI-2 samples. In some cases, when tellurium concentrations are below instrumental detection limits, a series of separations can be used which are designed to preconcentrate the tellurium.

ICP-AES interferences generally consist of spectral overlap or matrix effects. In most cases, serious interferences arising from spectral overlap can be avoided by using alternate analytical lines. For example, the determination of iron in the presence of uranium requires that a somewhat unusual iron line be selected in order to avoid spectral interferences from uranium at other wavelengths.[11] It is important that potential spectral interferences be evaluated in any given sample based on the known elemental composition, or a qualitative survey of individual constituents.

In general, ICP-AES systems are comparatively free from matrix effect, at least when compared to atomic absorption spectroscopy. In most cases, matrix matching samples with standards will reduce the interferences to acceptable levels. For the TMI-2 samples a series of high purity multielement ICP standards containing Fe, Ni, Cr, and Te have been prepared, as well as standards containing Fe, Ni, Cr, and Te in acid solutions of UO_2 and zirconium. In this way, standards will be matrix matched with the major elemental constituents present in core region materials. The standard calibration curves will be selected for a matrix based on the qualitative elemental scan. This should essentially eliminate any matrix interferences in the TMI-2 samples.

The individual separation procedures described in this appendix are applicable toward a variety of analysis problems, however, the most effective selection of appropriate methods for an individual sample can be based on specific factors. A summary of the individual analysis steps would include the following:

1. Determination of effective radioactive dose rate for a sample solution.

   Sample solutions for ICP-AES analysis (typically about 5 mL) are limited to a 200 mR/h dose rate. Samples which exceed this value will require some preliminary separations to isolate the tellurium from the bulk of the sample activity. The Dowex ion-exchange method, Sn (II) reduction, or iron hydroxide coprecipitation might be appropriate for such an initial separation.

2. Perform a rapid qualitative elemental scan for elements of interest (Te, Fe, Ni, Cr, Zr, Cu, Sn, Mo).

   A rapid qualitative scan of the sample serves several purposes. First, it provides a quick evaluation of whether the tellurium concentration is above or below the instrumental detection limit. The absence of a tellurium signal indicates that preconcentration of the solution may be necessary. Alternatively, in the case of very small samples, it may be possible to consolidate several small samples from the same bulk fraction.

   Another purpose of a qualitative sample analysis is the evaluation of individual sample matrices. The identification of the major elemental constituents in a sample serves to target the origin of the material [zircaloy is indicated by tin, 17-5 PH (stainless steel) is indicated by copper, inconel is indicated by molybdenum], and provide the sample matrix for the evaluation of elemental interferences in subsequent procedures.

   Based on the results of the qualitative analysis, a sample is either targeted for preconcentration/separation, or available for quantitative analysis.

3. Perform a sequential multielement quantitative analysis for elements of interest.

Quantitative data for tellurium, iron, nickel, and chromium should be obtained for each sample in which the tellurium concentration is above the instrumental detection limit. Samples which contain significant quantities of fission product tellurium (as determined by the Te scan and Fe/Ni/Cr ratios) may be more comprehensively analyzed by performing quantitative analyses for those elements which comprise the sample matrix.

Experimental molar ratios of selected elements for individual samples can be compared with nominal ratios in core materials to determine the origin of a given sample matrix. A summary of elemental composition for selected core materials is tabulated in Table A-3.

4. Perform tellurium separation or preconcentration procedures as necessary.

Separation of tellurium from individual elements may be necessary for two reasons. First, the dose rate of the sample may be too high (>200 mR/h) to allow its use in the ICP-AES system. The major contributing isotopes to the sample activity can be identified, and separation schemes selected which will effectively isolate the tellurium from the bulk of the sample activity. In most cases, separation of the Cs and Sr would probably be sufficient to lower the dose rate to acceptable levels.

Separation or preconcentration of tellurium from the bulk of the sample matrix may also be necessary when its concentration is below the instrumental detection limit. The experimental procedures described in this appendix are applicable toward many sample matrices. However, selection of the individual method is most effectively based on the results of a qualitative elemental scan. For example, the Fe (III) coprecipitation method is only effective for samples containing less the 400 mg of iron. This probably precludes use of this technique for samples containing

TABLE A-3. MATERIAL COMPOSITION OF TMI-2 CORE REGION COMPONENTS (wt %)

Material	Fe	Ni	Cr	Cu	Sn	Mo
304 SS	Major	8-10.5	18-20	--	--	--
17-4 Ph	Major	3-5	15.5-17.5	3-5	--	--
Zircaloy-4	0.2	--	0.1	--	1.5	3

	Ag	Cd	In	Al_2O_3	B_4C
Control Rod	80	5	15	--	--
Burnable Poison	--	--	--	98	1.5

large amounts of steels. Also, the ion-exchange method is limited in its application to large samples by the loading capacity of the resin.

Because of the relatively high efficiencies of the separation techniques (65 to -100% depending on the experimental conditions), these methods should serve to isolate tellurium in quantities necessary for ICP-AES analysis.

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