MASTER

FISSION PRODUCT RELEASE MECHANISMS AND PATHWAYS*

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Overview

It is axiomatic that the severity of a nuclear reactor accident is determined by the extent of radioactivity escape which results. The main focus of site safety analyses is thus on fission product release and transport. Such analyses generally proceed by dividing the nuclear complex into a series of contiguous regions, or compartments, whose boundaries are usually defined by physical barriers, and then determining theoretically the behavior of the fission products within these regions, subject to the chemical and thermalhydraulic conditions which are assumed to prevail. Such considerations can be reduced to the description of three processes: (1) the introduction of fission product species into a particular region (the "source terms" for that region)· (2) attenuation mechanisms which modify the source terms in the compartment; and (3) transport across the barrier between this and the next adjacent compartment (the source terms for the adjacent region). (It is clear that the expression "source terms" can therefore have many possible meanings.)

Of all the processes involved, fission product escape from the fuel-cladding region into the primary coolant circuit is perhaps the most simple to describe; even so, it is an extremely complex function of the time/temperature history of the fuel-cladding system during an accident, since many mechanisms for release are involved. Depending upon the particular fission product species, these release mechanisms range from simple gaseous expansion processses at low temperatures to evaporation-condensation processes (aerosol formation) over molten fuel. Because of these complexities, it is convenient to subdivide the time/temperature sequence of an accident into more or less discrete phases over which specific release mechanisms dominate.

Four such phases are the periods of (1) gap release, (2) meltdown release, (3) vaporization release, and (4) oxidation release. This approach simplifies the problem considerably, although some loss of uniformity results. In addition, the methodology applies equally well to boiling water reactors and pressurized water reactors, except that the duration of each phase varies both with regard to reactor type and accident sequence.

Recommended Reading

1. G. W. Parker and C. J. Barton, pp. 525–618 in *The Technology of Nuclear Reactor Safety*, Vol. 2, T. J. Thompson and J. G. Beckerly, eds., The MIT Press, Cambridge, Massachusetts, 1973.

2. *Reactor Safety Study*, Appendix VII, WASH-1400, NUREG 75/014 (October 1975).

3. R. A. Lorenz, J. L. Collins, and A. P. Malinauskas, *Nuclear Technology* <u>46</u>, 404 (1979).

4. R. A. Lorenz, J. L. Collins, A. P. Malinauskas, O. L. Kirkland, and R. L. Towns, *Fission Product Release from Highly Irradiated LWR Fuel*, NUREG/CR-0722, ORNL/NUREG/TM-287R2 (February 1980).

5. A. P. Malinauskas, R. A. Lorenz, H. Albrecht, and H. Wild, "LWR Source Terms for Loss-of-Coolant and Core Melt Accidents," pp. 24–45 in *Proceedings of the CSNI Specialists Meeting on Nuclear Aerosols in Reactor Safety*, NUREG/CR-1724, ORNL/NUREG/TM-404, CSNI-45 (October 1980).

6. D. O. Campbell, A. P. Malinauskas, and W. R. Stratton, "The Chemical Behavior of Fission Product Iodine in Light Water Reactor Accidents," *Nuclear Technology* (May 1981).

Significance of Fission Product Release and Transport

The severity of a nuclear reactor accident is determined by the
extent to which fission products escape from the core region.

Extent of Escape	At Risk	Degree of Severity*
Leakers, normal operation	Plant	Minor
Controlled LOCA	Plant	Small
Nearly-controlled LOCA	Workers	Large
Core meltdown	General Public	Extreme

*The perceived degree of severity, due to lack of knowledge
 and/or misinformation, can be decidedly different.

Purpose of a Reactor Safety Program

Ensure the health and safety of the general public by:
1. Assessing risk from reactor accidents <u>realistically</u>
    (avoiding the "cry wolf" complex).
2. Guaranteeing that risk is minimized in a manner that
    is consistent with sound engineering practice.

This implies reasonably detailed knowledge of the mechanisms
of fission product release and transport.

Barriers to Escape

Barrier	Escape Mechanism(s)
1. Fuel Matrix	Recoil, knockout, solid state diffusion
2. Cladding	Convection, diffusion, washout
3. Primary Circuit	Convection, washout
4. Containment Structure(s)	Convection, washout

These barriers may be used to define regions or compartments for mass flow considerations.

Site Safety Analysis Methodology

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             ┌──────────────┐              ┌──────────────┐
Source term  │ Compartment  │ Source term  │ Compartment  │ Source term
────────────▶│      A       │────────────▶ │      B       │────────────▶
             │    ↓  ↑      │              │    ↓  ↑      │
             └──────────────┘              └──────────────┘
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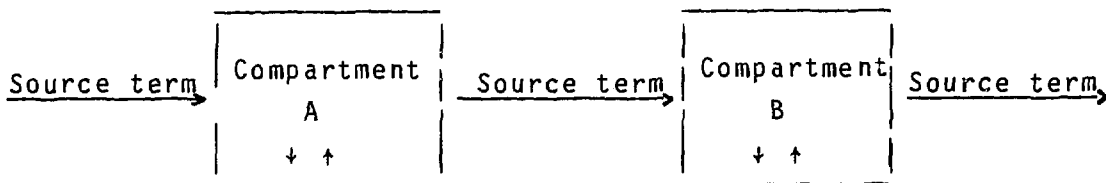
Step 1

   Quantity of fission product entering Compartment A (the
   "Source Term" for Compartment A).

Step 2

   Attenuation of the source term due to physicochemical
   processes that occur in Compartment A.

Step 3

   Quantity of fission product exiting Compartment A and
   entering Compartment B (the Source Term for Compartment B).

Characteristics of Important Fission Product Elements

Group	Elements	Probable Chemical Form in Fuel
Noble Gases	Kr, Xe	Gaseous element
Halogens	Br, I	Metal halide
Alkali Metals	Rb, Cs	Element, halide, uranate
Tellurium	Te, Se, Sb	Element
Alkaline Earths	Sr, Ba	Element or oxide
Noble Metals	Mo, Tc, Ru, Rh, Pd	Element or oxide
Refractory Oxides	Y, Zr, Nb, La, Ce, Pr, Nd, Np, Pu, etc.	Oxide

A "Generic" Release Sequence

1. Rod Failure - Burst Release (900–1100°C)
2. Gap Diffusional Release (900–1400°C)
3. Intergranular Voids Release (Oxidative Release?) (1300–1500°C)
4. Matrix Diffusional Release (1300–1900°C)
5. Meltdown Release (1800°C–2800°C)
6. Vaporization Release (2800°C–1500°C?)
7. Oxidation Release (2800°C–?) - Steam Explosion

In WASH-1400, mechanisms (1)–(4) are combined into one mode, "Gap Release."

Gap Inventories

Fission Product	Fraction of Total Inventory (Core Average)			
	WASH-1400			LCM
	ANC	BCL	ORNL	
Kr, Xe	0.06	0.10	0.08	0.02
Br, I	0.06	0.10	0.14	0.02
Rb, Cs	0.20	0.05	0.21	0.02
Te, Se, Sb	0.10 (estimate)			(0.02)
Sr, Ba	4×10^{-6}	0.02	0.02	(0.02)
Others	---	---	---	---

Gap Release - WASH-1400

$$M = M_0 f_e$$

Fission Product	f_e
Noble Gases	1
Halogens	1/3*
Alkali Metals	1/3
Tellurium	10^{-3}
Alkaline Earths	10^{-4}
Others	0

*Implies halide in fuel

Gap Release - More Recent Data

Temperature Range ($900-1300°C$):

$$M = M_B + M_D(t)$$

$M_B \ (Cs, \ I) = \alpha V_B (M_0/A)^a \ exp[-(C/T)] \simeq 2 \times 10^{-3} \ M_0 \ (950°C)$

$M_B \ (Kr, \ Xe) = M_0[1 - (P_S/P_B)]$

$M_B \ (others) \simeq 2 \times 10^{-5} \ M_T \simeq 4 \times 10^{-7} \ M_0$
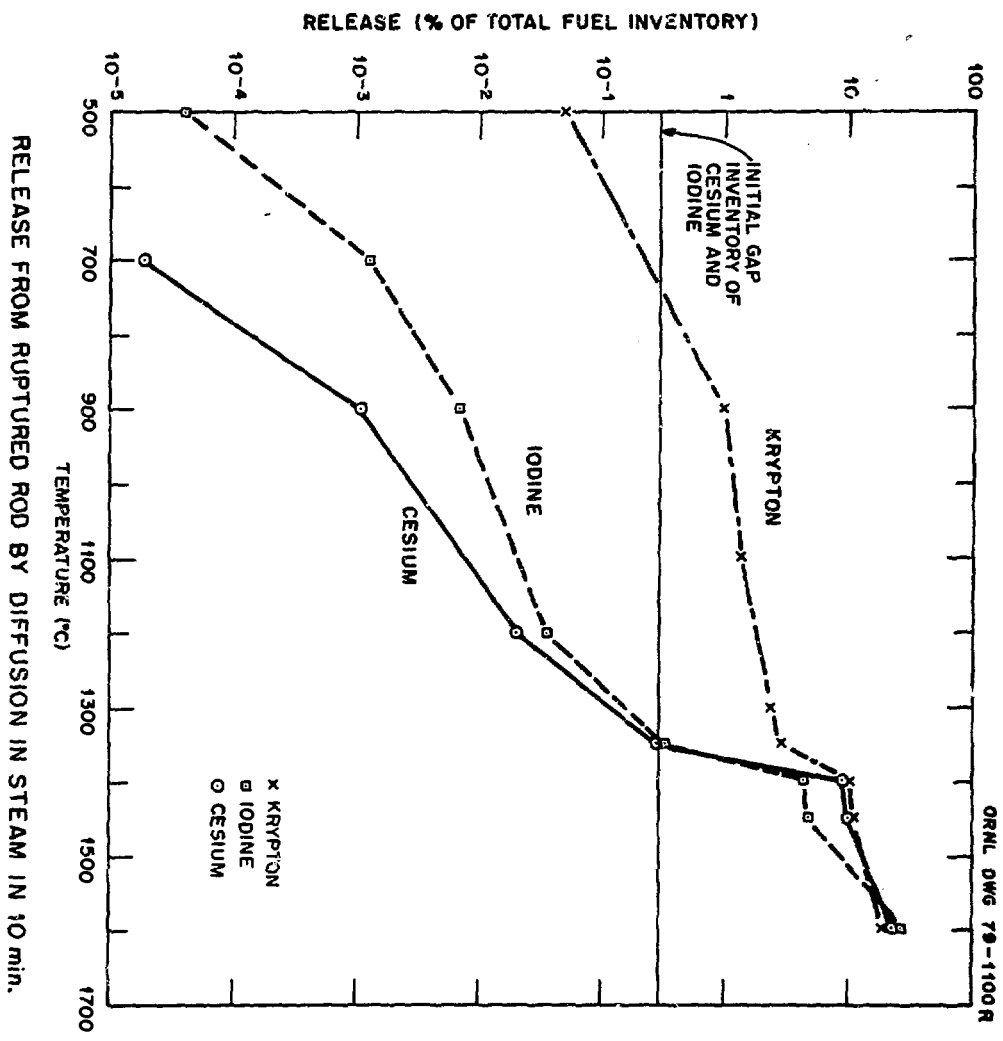
$$M_D \ (Cs, \ I) = M_0 \ \{1 - exp[-(R_0 t/M_0)]\}$$

$$R_0 = \delta(W/P_S)(M_0/A)^a \ exp[-(\gamma/T)]$$

$M_D \ (Kr, \ Xe) - GRASS \ (?)$

$M_D \ (others) - ??$

IODINE | CESIUM | TYPE OF EXPERIMENT
◁ | ◀ | IMPLANT, PREDRILLED
▷ | ▶ | IMPLANT, RUPTURED
○ | ● | CsI IMPLANT RUPTURED
□ | ■ | LOW BURNUP, PREDRILLED
△ | ▲ | HIGH BURNUP, PREDRILLED
▽ | ▼ | HIGH BURNUP, RUPTURED
+ | ✕ | HIGH GAP INVENTORY, RUPTURED

RELEASE (% OF TOTAL FUEL INVENTORY)

RELEASE FROM RUPTURED ROD BY DIFFUSION IN STEAM IN 10 min.

ORNL DWG 79-1100R
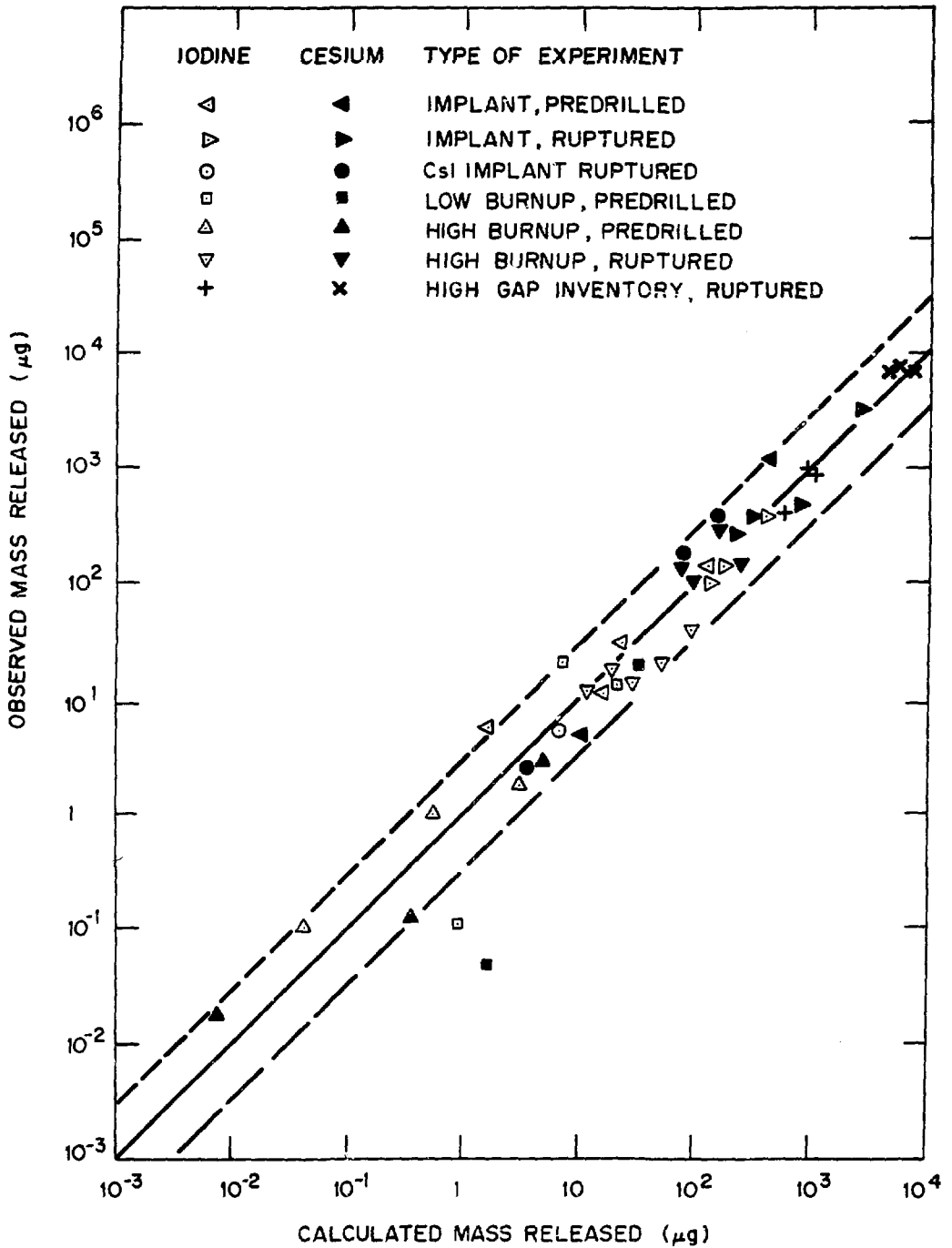
Is the WASH-1400 Release Model Conservative?

From 900–1800°C ,

$$M = M_0 f_e$$

Controlled LOCA

    1.   Burst at 950°C

    2.   Temperature rises to 1200°C for 10 minutes

Fission Product	Escape Fraction f_e	
	WASH-1400	Best Estimate
Noble Gases	1	1.02
Iodine Species	0.33	0.003
Cesium Species	0.33	0.003
Tellurium	0.001	0.003?*
Others	$<10^{-4}$	$<10^{-6}$

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*Te boils at 1390°C, CsI at 1280°C

For a controlled LOCA -- yes

Is the WASH-1400 Release Model Conservative?

From 900–1800°C,

$$M = M_0 f_e$$

Nearly-Controlled LOCA (TMI-2)
1. Burst at 950°C
2. Temperature maintained between 1200–1800°C for prolonged periods

Fission Product	Escape Fraction f_e		
	WASH-1400	Best Estimate	TMI-2
Noble Gases	1	(0.7)	0.7
Iodine Species	0.33	0.7	0.6
Cesium Species	0.33	0.7	0.6
Tellurium	0.001	(0.7)	?
Others	$<10^{-4}$	---	$>10^{-4}$

WASH-1400 presumes that the temperature range 1200–1800°C (i.e., up to the onset of melting) is traversed rapidly, and that significant melting occurs thereafter.

Release From Molten Fuel

$$M = M_M^* f = M_T^* f_M f$$

Fission Product	f	Uncertainty Range
Noble Gases	0.9	0.5–1
Halogens	0.9	0.5–1
Alkali Metals	0.8	0.4–0.9
Tellurium Group	0.15	0.05–0.25
Alkaline Earths	0.1	0.02–0.20
Noble Metals	0.03	0.01–0.10
Refractory Oxides	0.003	0.0001–0.01

Vaporization Release

Release due primarily to the sparging action of concrete decomposition gases on the molten mass.
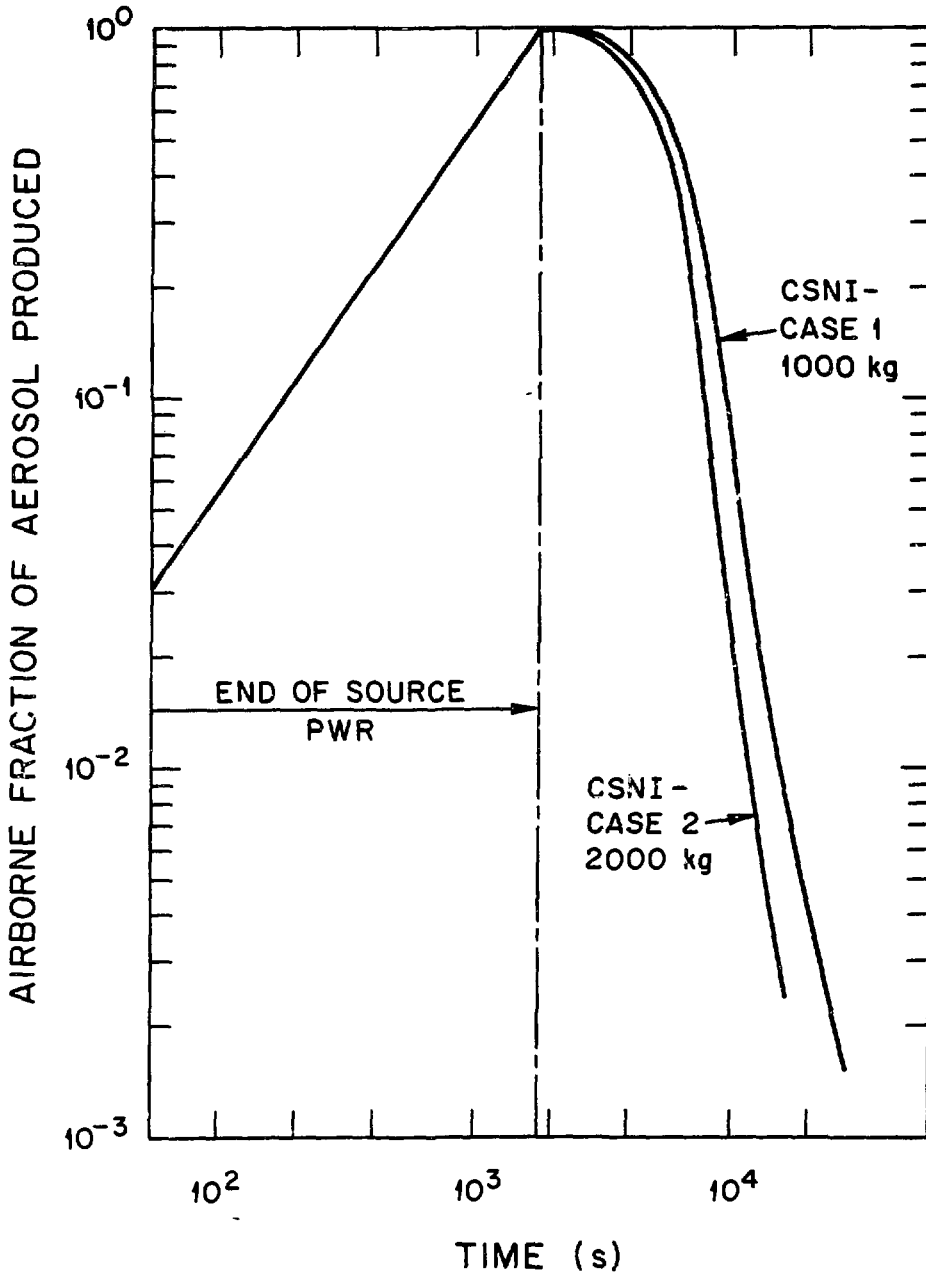
$$M = M''_T (VLF)_\infty [1 - \exp(-0.6935t/\tau)]$$

$\tau = 30$ min, to $t = 90$ min

Fission Product	$(VLF)_\infty$
Noble Gases	1
Halogens	1
Alkali Metals	1
Tellurium Group	1
Alkaline Earths	0.01
Noble Metals	0.05
Refractory Oxides	0.01

Mass Release During Core Meltdown

Fission Products	Inventory (kg)	Release (kg)
Noble Gases	299	270
All Others	2,015	185
Structural Materials	167,600	1,065

AEROSOL RELEASE AND DEPOSITION
IN REACTOR CONTAINMENT

Iodine

A Special Fission Product Element

Its many forms:

I^- Iodide (CsI, HI, ZrI_2 ...)

I_2 Uncombined Iodine

IO_3^- Iodate

HOI Hypoiodous Acid (Existence Questionable)

RI Organic Iodides

Two Views of Iodine Behavior

1. Present NRC Position
    Regulatory Guides 1.3 and 1.4 ... Of the iodine
    released into the containment building, 91% is to be
    considered as the uncombined form, 5% as organic
   iodine, and 4% associated with particulates.

    Basis - The Windscale Accident

2. The New Position
    Fission product iodine is released into the primary
    circuit as iodide (probably CsI), and will remain
    as iodide under the reducing conditions character-
    istic of all LWR accidents until and unless
    oxidizing conditions are encountered.

    Basis - The Three Mile Island Accident
    Further, at Windscale
    $$4CsI + O_2 = 2Cs_2O + 2I_2$$
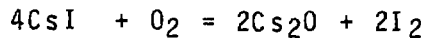
Differences in the Two Views

A. Volatility
1. Boiling point of I_2 - 184°C
2. Boiling point of CsI - 1280°C
(Fuel cladding temperature is about 300°C)

B. Solubility
1. I_2 - 0.78 g/L @ 50°C
2. CsI - 1500 g/L @ 50°C
(note that, in the gas phase @ 50°C, I_2
density is 0.03 g/L; whence $D_{I_2} = n_l/n_g = 26$)

C. Control Strategy
1. Trap I_2 .
2. Prevent oxidation of iodide (at least until
it becomes aqueous)

Reactor Accidents

| Reactor	Noble Gases (Ci)	Iodine
Windscale	3×10^5	2×10^4
TMI-2	8×10^6	15

Core Meltdown Accident Scenario
Present View

1. Rods burst around 900–1100°C. Iodine must therefore be released to the same extent as the noble gases, since its boiling point is 184°C. (This is contrary to experiment and to WASH-1400.)

2. Reaction with primary circuit surfaces may or may not occur while the iodine is transported to the primary circuit breach. (TRAP code calculations indicate negligible interaction.)

3. If I_2 contacts liquid water before entering the containment building (as at TMI or in a BWR) significant attenuation occurs because of solubility considerations. If not, the I_2 enters the containment building as a gas, which then distributes between the aqueous and gaseous phases, and deposits or reacts with various surfaces (particulates, paint, etc.). Some organic iodides are formed.

4. Escape into the environment occurs through water leakage and (primarily) gas leakage.

Core Meltdown Accident Scenario
More Recent View - The Core Region

1. Rods burst around 900–1100°C. Small amounts of CsI and Cs
   are released at this time, as given by the burst release
   model.

2. Both Cs and CsI continue to slowly diffuse from the failed
   fuel rods, as given by the diffusional release model, as
   the cladding temperatures rise. During this period,
   extensive steam-zircaloy reaction occurs.

3. Around 1300–1400°C, sudden release of Cs and CsI occurs;
   the core inventories of these two species are virtually
   exhausted before zircaloy-urania eutectic formation appears.
   During this period, the core is probably steam-starved;
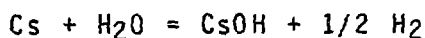   release occurs primarily into a hydrogen atmosphere.
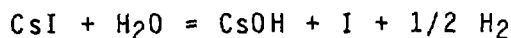
Equilibria to be Considered

Decomposition of CsI:

$$CsI = Cs + I$$
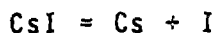
$$K_1 = \frac{p_{Cs}\, p_I}{p_{CsI}}$$

Cesium-Steam Reaction:

$$Cs + H_2O = CsOH + 1/2\ H_2$$

$$K_2 = \frac{p_{CsOH}\sqrt{p_{H_2}}}{p_{Cs}\, p_{H_2O}}$$

Cesium Iodide-Steam Reaction:

$$CsI + H_2O = CsOH + I + 1/2\ H_2$$

$$K_3 = \frac{p_{CsOH}\, p_I\, \sqrt{p_{H_2}}}{p_{CsI}\, p_{H_2O}}$$

	K_1 (atm)	K_2 (atm)$^{-1/2}$	K_3 (atm)$^{1/2}$	(p_{CsI}/p_I)*
T = 1300K	7.7×10^{-10}	6.6×10^1	5.1×10^{-8}	1.0×10^5
T = 2000K	7.1×10^{-5}	4.4×10^0	3.1×10^{-4}	1.7×10^1

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*Assuming: $p_{H_2}/p_{H_2O} \approx 10$; $p_I/p_{H_2O} \approx 10^{-3}$;
   $\sum p_{Cs}/\sum p_I \approx 10$; $p_{\leqslant 45} \approx 2$ atm

Core Meltdown Accident Scenario
More Recent View - The Primary Circuit

1. In the early stages of the accident, most of the CsI will
    deposit on surfaces which are less than 400—600°C or, if
    contacted by water, will dissolve and be transported in
    this manner.

2. As the surface temperatures rise, the deposited CsI will
    re-evaporate, and be transported as vapor. Depending upon
    the location of the primary system breach, and the nature
    of the accident, the condensation-evaporation process can
    be repeated several times.

3. Finally, the CsI emerges through the primary circuit
    breach. At this period into the accident, a significant
    amount of particulates are present.

Core Meltdown Accident Scenario
More Recent View - The Containment Building

1. The "Dry" Accident - If the CsI is introduced directly into the containment building at high temperature (700–800°C), oxidation can occur, yielding uncombined iodine. If oxidation does not occur, the CsI distributes among the water, the particulates, and various other surfaces. The only airborne form would be as particulate, probably as a minor radioactive component.

2. The "Wet" Accident - The CsI is assumed to contact water and to be transported in this form into the containment building. Oxidation can occur, according to the equilibrium

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+ .$$
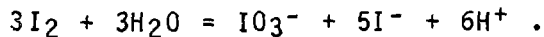
At room temperature,

$$K = \frac{[IO_3^-][I^-]^5[H^+]^6}{[I_2]^3} = 8 \times 10^{-48} \ (mole/L)^9 .$$

But

$$[IO_3^-] \approx [I^-] = 10^{-4} \ \underline{M}$$

$$[H^+] = 10^{-7} \ \underline{M}$$

so

$$[I_3] = \left\{ \frac{(10^{-4})(10^{-4})^5(10^{-7})^6}{(10^{-47})} \right\}^{1/3} = 5 \times 10^{-7} \ \underline{M} .$$

Thus, major iodine releases must be along aqueous pathways.

Concluding Remarks

1. It is insufficient to identify the nuclide being released; chemical form is equally important.

2. The extent of release of several significant fission products are critically determined by physicochemical aspects.