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IODINE CHEMICAL FORMS IN LWR SEVERE ACCIDENTS*

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IODINE CHEMICAL FORMS IN LWR SEVERE ACCIDENTS[*]

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ABSTRACT

Calculated data from seven severe accident sequences in light-water reactor plants were used to assess the chemical forms of iodine in containment. In most of the calculations for the seven sequences, iodine entering containment from the reactor coolant system was almost entirely in the form of CsI with very small contributions of I or HI. The largest fraction of iodine in forms other than CsI was a total of 3.2% as I plus HI. Within the containment, the CsI will deposit onto walls and other surfaces, as well as in water pools, largely in the form of iodide (I^-). The radiation induced conversion of I^- in water pools into I_2 is strongly dependent on pH. In systems where the pH was controlled above 7, little additional elemental iodine would be produced in the containment atmosphere. When the pH falls below 7, it may be assumed that it is not being controlled, and large fractions of iodine as I_2 within the containment atmosphere may be produced.

1. INTRODUCTION

This study attempts to re-examine the chemical form of iodine in containment, focusing on two major effects: the form entering from the reactor coolant system (RCS) and actions that may produce volatilization within the containment. The results are based on quantitative (calculated) results of seven severe accident sequences for light-water reactor (LWR) nuclear power plants, which are listed in Table 1. These sequences represent a wide range of conditions that are significant risks; each sequence was evaluated by the Source Term Code Package (STCP) and documented in previous U.S. Nuclear Regulatory Commission (NRC) reports.[1,2] Note that this analysis does not address the ultimate disposition of various species, only the likelihood of their formation or presence in the gas phase. Thus, the effects of deposition or various engineered safety features are not considered.

The primary motivation of this study is to re-evaluate the basis for Regulatory Guides 1.3[3] and 1.4[4] which state that:

1. 50% of the maximum iodine inventory of the reactor core is released to the primary reactor containment; 25% is available for leakage; and

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Table 1. LWR accident sequences evaluated

Plant	Reactor type	Accident	Accident type	Documentation[a]
Grand Gulf	BWR — Mark III	TC (ATWS)	High pressure	BMI-2104, Vol. III
		TQUV (No makeup water)	Low pressure	BMI-2104, Vol. III
Peach Bottom	BWR — Mark I	TC2 (ATWS)	High pressure	NUREG-4624, Vol. I
		AE (LOCA, no ECCS)	Low pressure	BMI-2104, Vol. II
Sequoyah	PWR — ice condenser	TBA	Low pressure	NUREG-4624, Vol. II
Surry	PWR — large containment	TMLB' (Station blackout)	High pressure	BMI-2104, Vol V
		AB (LOCA, no ECCS) (Station blackout)	Low pressure	BMI-2104, Vol. V

[a]See refs. 1 and 2 for complete reference description.

2. of this 25% available for leakage, 91% is in the form of elemental iodine, 5% is in the form of particulate iodine, and 4% is in the form of organic iodide.

Iodine is assumed to enter containment in the forms and amounts stated above with neither physical nor chemical changes occurring in containment. However, present knowledge may not support this distribution of iodine forms and the static state throughout the duration of an accident.

It is anticipated that a more realistic representation of the chemical speciation of fission product iodine would likely result in a large proportion of particulate iodine (CsI), with smaller amounts of gaseous iodine (HI or I). In addition, a continuous revolatilization of molecular iodine might occur within containment and would include some small complement of organic iodine.

2. CHEMICAL FORMS OF IODINE ENTERING CONTAINMENT FROM THE REACTOR COOLANT SYSTEM

The chemical forms of iodine in the RCS are closely tied to the chemical forms of cesium, as illustrated by the following reactions:

$$CsI + H_2O \rightleftharpoons CsOH + HI \qquad \text{and} \tag{1}$$

$$CsI + H_2O \rightleftharpoons CsOH + I + \frac{1}{2}H_2 . \tag{2}$$
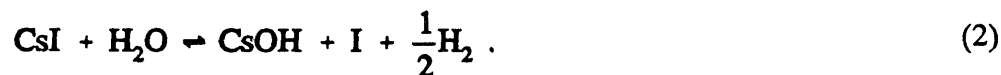
Equation (1) is the reverse of an acid-base reaction and, thus, is unlikely to proceed unless one or both products are removed. Reactions of CsOH with other materials in the RCS will tend to lower the partial pressure of CsOH. Such reactions will shift the equilibrium to the right and enhance the formation of HI. At temperatures in excess of 1800 K and at low hydrogen pressures, atomic iodine is the favored product of the reaction between CsI and H_2O, as shown in Eq. (2). Thus, in general, iodine chemical forms other than CsI are favored when steam pressures are much greater than cesium hydroxide pressures.

2.1 DATA MANIPULATION AND CALCULATIONAL TECHNIQUES

In order to evaluate the chemistry in the RCS, it is necessary to specify the thermodynamic conditions under which reactions would occur and a measure of the time span over which such conditions hold. Required quantities are temperature, pressure, volume, and molar inventories of constituent species H_2, H_2O, I, and Cs within each control volume. This evaluation has been undertaken for each of the accident sequences in Table 1 using data from the STCP calculations.[1,2] See ref. 5 for a complete description of the data manipulations and calculational procedures.

Another necessary quantity is the mean residence time (s) for flow through a control volume. Figure 1 shows this quantity for each of the two control volumes above core in the Surry TMLB′ sequence. A mean residence time greater than 1 s is usually sufficient to attain equilibrium for regions with a sufficiently high temperature. In Fig. 1, this condition holds for both volumes, although control volume 1 approaches this limit briefly at about 30 min.
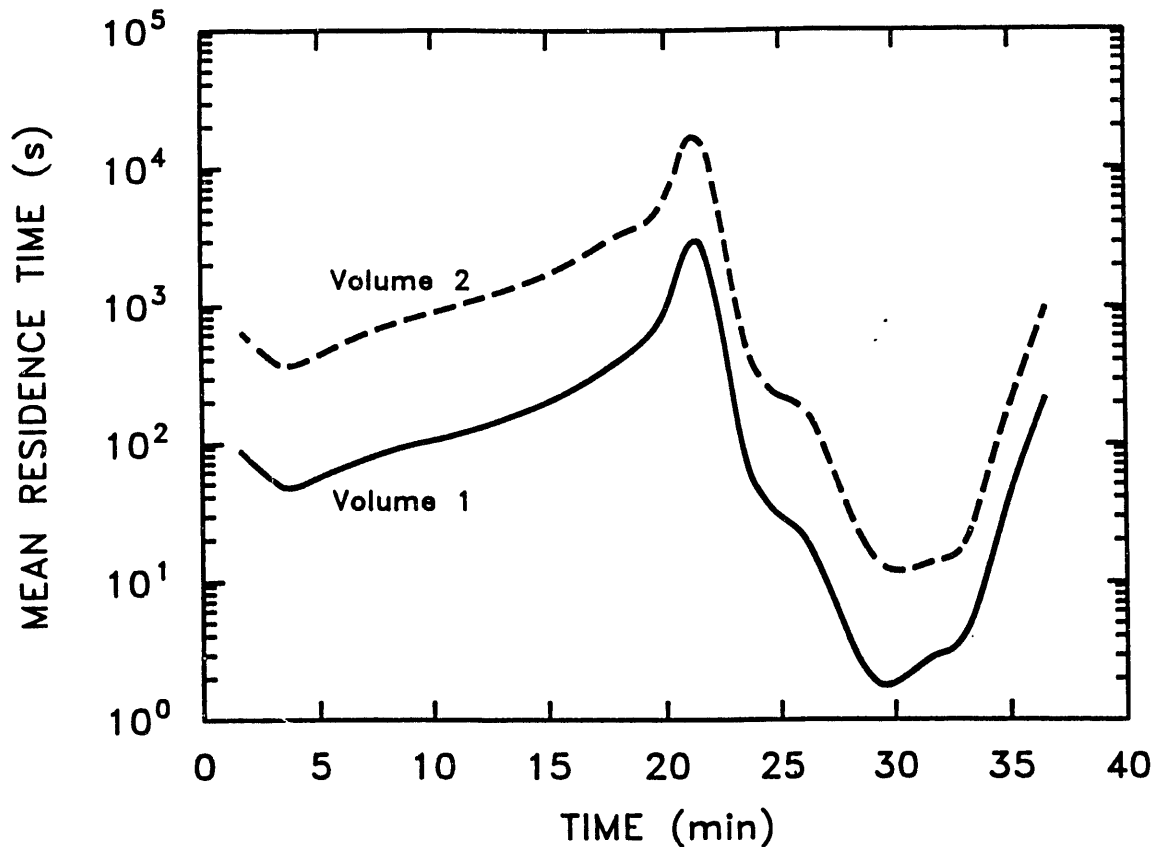
Fig. 1. Mean residence time in volumes above core for Surry TMLB'.

Fission products released from the core will undergo changes in temperature and concentration as they pass through regions of the RCS. A chemical kinetic model used 20 reactions to determine the control volume where an equilibrium of the iodine, cesium, hydrogen, and steam species becomes "frozen." This means that the temperatures and concentrations of species in subsequent control volumes are not sufficient to reach an equilibrium in the mean residence time available. Separate equilibrium calculations were run, using the FACT system,[6] to obtain the final distribution of iodine species.

2.2 OVERALL RESULTS OF CALCULATIONS

In six of seven calculations, the iodine was almost entirely in the form of CsI; the contribution of I or HI was less than 0.1% of the overall percentage of iodine. These calculations considered only reactions involving cesium, iodine, hydrogen, and water. They covered a wide range of temperatures, hydrogen concentrations, steam concentrations, and fission product concentrations. Reactions with other RCS materials were not included in these calculations, but their effects were investigated with scoping or bounding calculations as described in Sects. 2.3 and 2.4.

During the second half of the Surry AB sequence, there is a period during which temperatures in the core region are in excess of 2000 K, and subsequent volumes of the upper grid

plates and guide tubes are at temperatures of only 500 K. Because of this, equilibrium compositions in the core region would be "frozen" in by the rapid decrease in temperature. For this sequence, the overall iodine distribution was 2.8% as I and 0.4% as HI, with the remainder as CsI. Thus, a total of 3.2% as I plus HI was the largest fraction of iodine in a form other than CsI in this study.

2.3 REACTION OF CsOH WITH SURFACES

Of the possible reactions of CsOH in the RCS, the reaction with structural surfaces is the most amenable to evaluation. Johnson et al.[7] have studied the deposition of CsOH on oxidized stainless steel surfaces. They used the following simple expression to relate the thermodynamic activity of CsOH to the surface concentration:

$$a = 0.5 \exp\left\{\left(98.5 - \frac{3.84 \times 10^4}{T}\right)(x - 0.28)\right\}, \qquad x < 0.28, \tag{3}$$

where a and x are the surface activity (atm) and concentration (mg/cm^2), respectively. The reaction of interest with stainless steel may be written as

$$\text{CsOH (surface)} \rightharpoonup \text{CsOH (gas)} . \tag{4}$$

Thermochemical data obtained from the FACT system[6] give the respective equilibrium constants for the reactions in Eqs. (1) and (4) as

$$K_1 = \frac{P_{CsOH}}{P_{H_2O}} \frac{P_{HI}}{P_{CsI}} = \exp\left(-1.407 - \frac{1.626 \times 10^4}{T}\right) , \tag{5}$$

$$K_4 = \frac{P_{CsOH}}{a} = \exp\left\{1.189 \times 10^1 - \frac{1.500 \times 10^4}{T}\right\} , \qquad 900 \le T \le 1263 . \tag{6}$$

Calculations using Eqs. (3), (5), and (6), together with mass balances on cesium and iodine, indicate that the amount of HI formed due to the CsOH surface reaction is less than 0.6% for each of the accident sequences studied. This is because P_{CsOH} must be very small if the ratio P_{HI}/P_{CsI} is large enough to be significant. However, if P_{CsOH} is very small, then so is x; hence, very little surface reaction could occur.

2.4 OTHER REACTIONS OF CsOH

Other reactions of CsOH may also remove it from the vapor phase, but there is generally a lack of information on the amounts and locations of other reactants. Several cesium borates may form in the reaction of CsOH with boric acid or boron oxide, which are introduced into the RCS as coolant additives. For example, the formation of cesium metaborate ($CsBO_2$) may occur by the following reaction:

$$CsOH + HBO_2 \rightarrow CsBO_2 + H_2O .$$
(7)

If sufficient metaboric acid (HBO_2) were available, it could result in a lowering of the vapor pressure of CsOH.

Two simulated core-melt tests were run by the present authors to assess boric acid volatility and the potential for vapor interactions with CsI. Two different sized simulant fuel bundles were used—nominally 1 and 10 kg. The smaller, 1 kg, fuel simulant bundle consisted of 12 zirconium tubes (10.16-cm long) with 0.247-kg end caps, 0.093-kg stainless steel grids, 0.0185-kg Inconel grids, and 0.585-kg UO_2 pellets. There were no added Cs or I species in the small bundle test. The test was performed by inductively heating the fuel bundle while injecting feed water containing 2000-ppm boric acid into the bottom of the bundle. In this test, it was found (see Table 2) that during the lower temperature heating steps up to 1600°C, ~10% of the boron transported through the bundle and was captured downstream as boron oxide. As the temperature was increased to partial melting of the bundle, the collected B_2O_3 decreased. This decrease was attributed to increased reactivity of the boron oxide with the hot fuel and clad oxides.

Table 2. Simulated core melt tests conducted in the ORNL 1-kg facility.
Boric acid addition to water injected below the bundle

Heating step	Total boron present[a] (g)	Boron collected as B_2O_3	
		Filter (%)	WASH (%)
A (1600°C)	0.034	10.37	0.0
B (1800°C)	0.088	5.5	0.68
C (2400°C)	0.142	0.024	0.009

[a]As boric acid in water used for steam generation.

The composition of the 10-kg fuel bundle is shown in Table 3. Note that in this test, CsI was added to 12 of the 60 simulant fuel rods in a limited region near the bundle centerline. Excess cesium was not added.

The 10-kg test was conducted at a bundle centerline temperature limit of 1600°C which was reached in ~30 min and maintained for an additional 30 min. During this time, 365 mL of boric acid solution containing 3.83 g of H_3BO_3 was added to the steam generator porous media below the fuel bundle. Hydrogen release measured 326 L, which would be equivalent to 72% conversion of the water and ~30% reaction of the Zircaloy in the bundle.

Analytical results from X-ray diffraction showed that white solids observed plated out on the quartz chimney were nearly pure CsI with no detectable B_2O_3. Chemical analysis of the washings

Table 3. Composition of 10-kg fuel bundle

Item	Weight[a] (g)
60[b] — Zircaloy tubes	2181.0
120 — Zircaloy end caps	503.6
3 — Stainless steel grids	342.0
1 — Inconel grid	112.0
4 — Stainless steel supports and screws	58.5
2 — Stainless steel lifts and screws	9.0
UO_2 pellets	(N.W.) 7464.0 (E.W.) 6739.9
UO_2 powder	(N.W.) 1201.9 (E.W.) 1059.5
$SrCO_3$	3.00
$BaCO_3$	4.05
La_2O_3	2.28
Eu_2O_3	0.21
Sm_2O_3	1.12
CeO_2	4.87
Mo	4.70
Te	0.82
Ru	5.16
CsI[c]	0.85

[a]N.W. = net weight; E.W. = uranium element weight.

[b]Twelve of these tubes each had three horizontal slits 0.010-in. wide × 1-in. long, 120° apart in their midsection.

[c]CsI mixed with 300-g UO_2, rare earths, and metal powders was added to the ~1-in. section of the 12 tubes.

from the system indicated that nearly half of the CsI had vaporized and that no boron containing materials were present. This complete failure to find any B_2O_3 downstream of the bundle was somewhat unexpected since the 1-kg test had resulted in some penetration of boron oxide. It is likely that the extra length of the 10-kg system prevented penetration by the reaction of B_2O_3 with ZrO_2. A sample analysis of a white oxide (a thin ring of mixed ZrO_2 and B_2O_3) in a very highly refractory solid solution on the oxidized clad surface was estimated to account for about one-third of the total boron added. The remainder of the boron oxide appeared to be associated with the porous ZrO_2

steam generator base at the bottom of the bundle. A test scrubber that had been operated continuously on a diverted part of the hydrogen/steam flow showed no evidence of volatile (non-particulate) iodine.

Similar results were subsequently obtained in a test with silver vaporized in a 10-kg bundle containing Ag-In-Cd alloy control rod simulants. In this later case, cadmium vapor was observed downstream, but the silver did not penetrate out of the bundle—presumedly because of interactions with Zircaloy.

Based on these results, it is highly likely that boric acid covaporized from residual water below the core in severe accidents will be tied up by the Zircaloy in the lower regions of the core and not be available airborne to affect the chemical form of the released iodine.

2.5 REVAPORIZATION OF CsI AS A SOURCE OF HI

There has been speculation that the fission product aerosols, CsI and CsOH, deposited onto the RCS surfaces under high pressure accident sequence conditions could revaporize due to heatup from their radioactive decay and from the system thermal hydraulics to become re-released into containment. Most analyses of this have considered the re-released material to remain as CsI and have focused only on the extent and timing of the revaporization. If, however, the CsOH portion of the deposited material were not available for revaporization and the revaporized CsI "saw" only steam, the question then becomes, what portion of the CsI that is revaporized gets converted to HI by the reaction in Eq. (1). To attempt to bound this, the Oak Ridge study made the following assumptions:

1. The temperature of revaporization was 1000 K (the general temperature at which equilibrium is frozen). The CsI vapor pressure was held constant according to the value predicted from the FACT system equation

$$P_{CsI} = \exp\left[\frac{-2.021 \times 10^4}{T} + 1.307 \times 10^1\right] .$$

(8)

2. The steam pressure varied in time the same as in the seven accident sequences (this was an arbitrary choice and is not intended to imply that revaporization is continuous throughout an accident sequence rather than being later in time).

3. No CsOH was present [except that made via the reaction in Eq. (1)].

4. No H_2 was present.

The integration was carried out over each sequence until an amount of CsI had been revaporized that was equivalent to the total amount of iodine released in the sequence (i.e., all of the iodine was equivalently on the surface at the start of a sequence at a location where the temperature was 1000 K).

The result of this calculation was that the largest conversion of CsI to HI in any of the sequences was 3.8%. This indicates that revaporization is not likely to produce significant amounts of volatile forms of iodine under these conditions. However, an equivalent calculation should be made for possible sequences that may have air ingress at times simultaneous with revaporization.

2.6 SUMMARY OF IODINE CHEMICAL FORMS IN THE RCS

Iodine entering containment from the RCS should be predominantly in the form of CsI. The examination of Cs-I-H$_2$O-H$_2$ interactions for seven accident sequences gave a maximum of 3.2% iodine as I plus HI, with the remainder as CsI. There are some uncertainties in the reactions of CsOH with oxides and in the revaporization of CsI that produce uncertainties to the extent in which iodine may exist in a form other than CsI. Cesium needs to be removed from reactions involving iodine if very much iodine is to be in a form other than CsI.

Based on this analysis, the chemical forms of iodine entering containment from the RCS may reasonably be described as a maximum of 5% as elemental iodine and HI, with not less than 1% as either elemental iodine or HI. The remaining ≥95% would be CsI.

3. PROCESSES THAT ALTER THE CHEMICAL FORMS OF IODINE IN CONTAINMENT

3.1 RADIOLYSIS

In the presence of radiation, the equilibrium formation of I$_2$ from I⁻ is strongly dependent on pH and less dependent on temperature and concentration. Ignoring the last two effects, this dependence can be written as

$$F(pH) = equilibrium\ fraction = \frac{[I_2]}{[I_2] + [I^-]} ,$$ (9)

where [x] is concentration of I$_2$ or I⁻ (g-atom/L). Data from Lin,[9] as shown in Fig. 2, illustrate this effect for several initial concentrations and pH values using solutions that were at ambient temperature and had been irradiated for 1 h at 4.5 Mrad/h. The final pH values were not indicated but probably decreased slightly because no mention is made of buffering in the experiment. The values of pH >6 may not be quantitatively useful since the very small conversion fractions are probably incorrect due to measurement error. As seen in Fig. 2, F is near 0 for pH >7 and near 1 for pH <2 but experiences a drastic change in the range 3 < pH < 4. This can be effectively modeled by the functional form

$$F = [1 + e^{\alpha\ pH + \beta}]^{-1} ,$$ (10)

that was fit to Lin's data using nonlinear least squares, yielding α = 1.72, β = -6.08.

If the pH is maintained sufficiently high through buffering or addition of sufficient basic material, very little conversion will occur. In this case, most iodine remains dissolved as I⁻. A quantitative treatment is more difficult. Lin's data generally indicate less than 1% conversion at
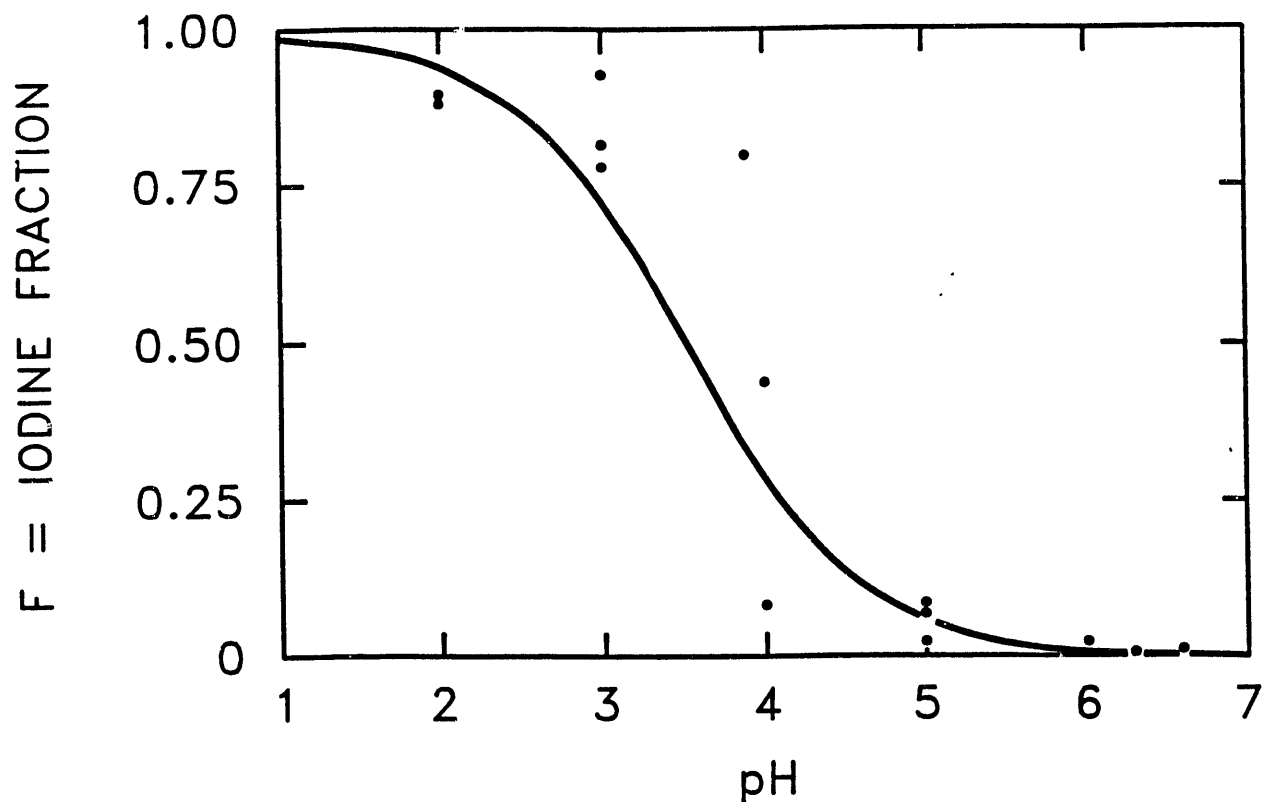
Fig. 2. Radiolytic conversion of I⁻ to I₂ [data from C. C. Lin, *J. Inorg. Nucl. Chem.* **42**, 1101 (1980)].

pH = 7. This value declines as the total iodine concentration decreases. ORNL data indicate that for a dose rate of 0.35 Mrad/h and an iodine concentration of 10^{-4} mol/L, conversion was 0.003% after 4 h of irradiation and 0.03% after 24 h. The last value, 0.03%, has been used in the present work.

If the pH level is not deliberately controlled, it may decrease sufficiently to allow considerable conversion of I⁻ to I₂. The primary mechanism is radiolytic generation of nitric acid. If the pH is neutral initially, then this effect soon dominates, resulting in

$$[H^+] = 10^4 \ g(HNO_3) \ \frac{E_{dep}}{V_L N_a} \ , \tag{11}$$

where

$[H^+]$ = concentration of H^+ (mol/L),
$g(HNO_3)$ = rate of HNO_3 production due to irradiation (molecules/100 eV),
E_{dep} = total energy deposition due to fission product decay (MeV),

$$V_L \qquad = \text{ volume of water (L), and}$$
$$N_a \qquad = 6.022 \times 10^{23} \text{ (molecules/mol)}.$$

ORNL measurements of pH change and nitrate ion formation at $30°C$ gave:

$$g(HNO_3) = 0.007 \text{ molecules/100 eV} .\tag{12}$$

This relationship is based on radiation absorption by the aqueous phase. The actual mechanism for the formation of nitric acid is not known. It may occur in the aqueous phase, in the gas phase, or at the gas-surface interface.

The energy deposition over a time, Δt, is

$$E_{dep} = \dot{E}_{dep} \, \Delta t = \Delta t \sum m_j \, \dot{e}_j , \tag{13}$$

where

$$\Delta t \quad = \text{ time (h)},$$
$$\dot{E}_{dep} \quad = \text{ total energy deposition rate (MeV/h)},$$
$$m_j \quad = \text{ mass of nuclide group } j \text{ in pool (g), and}$$
$$\dot{e}_j \quad = \text{ energy deposition rate per unit mass of nuclide group } j \text{ (MeV/s} \cdot \text{g)}.$$

A grouping of fission products and actinides compatible with that used in STCP accident studies was selected and is shown in Table 4. The specific energy deposition rate $\dot{e}_j$ for each group was determined from a detailed analysis of Browns Ferry [a large boiling-water reactor (BWR) with Mark I containment] accident sequences using the ORIGEN2 code.[10,11] These group energy deposition rates for the Browns Ferry BWR are assumed applicable to all plants and sequences considered in the present study.

The group masses (m_j) are obtained by multiplying the total core inventory $(\bar{m}_j)$ by the estimated fractional release into containment:

$$m_j = f_j \, \bar{m}_j . \tag{14}$$

Total core inventories for the plants are those identified in previous reports.[1,2] Various estimates of the fractional releases f_j can be obtained from a study by Nourbakhsh.*

Finally, Δt in Eq. (13) is the time needed to reach the approximate steady state. In general, the first phase of an accident can be considered to reach steady state in 10 to 15 h; the latter is the time value used for Δt in this work. Combining Eqs. (10) through (13), the fractional conversion takes the form

$$F = \left[1 + e^{\beta} [H^+]^{-\frac{\alpha}{\ln 10}} \right]^{-1} = \left[1 + 5.55 \times 10^{13} \left(\frac{V_L}{E_{dep}} \right)^{0.747} \right]^{-1} . \tag{15}$$

_____

*H. P. Nourbakhsh, presentation to NRC staff, October 4, 1990.

Table 4. Nuclide groupings and group-specific energy deposition rates

Group index, j	Characteristic element	Included nuclides	Energy deposition rate, $\dot{e}_j \times 10^{-13}$ (MeV/s · g)
1	I	I, Br	111.2
2	Cs	Cs, Rb	1.006
3	Te	Te, Se	3.497
4	Sr	Sr	7.879
5	Ba	Ba	2.348
6	Ru	Ru, Tc, Rh, Mo	1.706
7	Ce	Ce, Pu, Np	0.407
8	La	La, Am, Cm, Y, Pr, Nd, Pm, Sm, Eu, Zr,[a] Nb	6.523
9	Xe	Xe, Kr	0.721

[a]Includes only fission products.

Thus, when pH is not controlled, fractional conversion is directly dependent on the liquid volume (V_L) in which radiolysis occurs; the energy deposition E_{dep}, which itself depends on the amounts of radioactive species in water; and the time (Δt) allowed for radiolysis processes to reach steady-state conditions.

3.2 GAS-LIQUID PARTITIONING

The equilibrium distribution of a single volatile specie such as I_2 is represented by the partition coefficient:

$$P = \frac{[I_2\ (aq)]_{eq}}{[I_2\ (g)]_{eq}} \ . \tag{16}$$

This quantity is inversely related to the Henry's Law constant K (i.e., $P = 1/K$) and should not be confused with the overall iodine partition coefficients often used in reactor safety studies. In this study, partition coefficients for I_2 were calculated from the equation:

$$\log_{10} P = 6.29 - 0.0149\ T \ . \tag{17}$$

This relationship gives the experimental value reported by Eguchi et al.[12] and by Sanemasa et al.[13] at 298 K. Extrapolation of the experimental results of these investigators to 373 K yielded a partition coefficient of 3. Furrer et al.[14] reported a calculated partition coefficient at 373 K of 9. Some of the data used in his calculation were based on estimated parameters. Equation (17) gives a partition coefficient of 5.3 at 373 K, a reasonable average of these values.

Even though it may take considerable time to approach such equilibration in a large system such as a reactor containment, Eq. (16) can still be used to estimate I_2 volatility. In fact, instant equilibration is a conservative assumption since considerable holdup could be expected in real-life situations.

3.3 GAS-PHASE REACTIONS: FORMATION OF ORGANIC IODIDES

The process of converting I_2 into organic iodides (chiefly CH_3I) is still not fully understood. Postma and Zavodoski[15] reviewed production rates from about 70 containment tests and determined that the asymptotic steady-state conversion to CH_3I was

$$\% \ I_2 \text{ converted} = 0.19 \ C_{mo}^{-0.26} \ , \tag{18}$$

where C_{mo} = initial I_2 concentration (mg/m^3). In a more recent review, Beahm et al.[16] described the steady-state organic iodide concentration (mg iodine/m^3) using the form

$$C^* = 0.0189 \ C_{mo}^{0.82} \tag{19}$$

in place of Eq. (18). This equation was based on containment experiments performed with irradiated fuel rather than simulated materials, resulting in a percent conversion somewhat greater than that obtained from simulant materials (cf Fig. 4, ref. 17). By converting units to g-atom/L, Eq. (19) can be rewritten as

$$[CH_3I] = \beta \ [I_2]^{0.82} \ , \tag{20}$$

where $\beta = 0.0189 \ (10^6 \cdot MW)^{-0.18}$, MW being the molecular weight of I. For MW = 130, then $\beta = 6.55 \times 10^{-4}$, which indicates that generally less than 1% of gaseous iodine will be organic.

3.4 OVERALL BEHAVIOR

As described in the previous sections, the distribution of species throughout the gas and liquid phases can be estimated from models for three basic processes: radiolytic conversion of I^- to I_2 in water, evaporation of I_2, and gas-phase formation of organic iodides. Defining the desired quantities as concentration variables (g-atom/L),

$$C_1 = [I_2(aq)], \quad C_2 = [I_2(g)], \quad C_3 = [I^-(aq)], \quad C_4 = [CH_3I(g)] \ , \tag{21}$$

Eqs. (16), (9), and (20) can be rewritten as

$$C_1 = PC_2 \ , \quad C_3 = \frac{(1 - F)}{F} \ C_1 \ , \quad \text{and} \quad C_4 = \beta \ C_2^{0.82} \ . \tag{22a,b,c}$$

In addition, the total iodine inventory N_T (g-atom) is equal to the initial I^- entering the containment, and remains constant throughout the distribution process:

$$N_T = V_L (C_1 + C_3) + V_g (C_2 + C_4) .$$ (22d)

These four equations, (22a) through (22d), can be solved in a straightforward manner to obtain the four unknown concentrations in Eq. (21).

Because organic iodide is such a small part of the total, it is helpful to examine the distribution behavior without considering organic iodide. By ignoring Eq. (22c), it is possible to combine and rearrange Eqs. (22a), (22b), and (22d) to get

$$\frac{N_2}{N_T} = \left(1 + \frac{V_L P}{V_g F} \right)^{-1} ,$$ (23)

where $N_2 = V_g C_2$ = g-atom of I_2 in gas. Equation (23) is a convenient expression of the fraction of iodine that is volatilized. (Consideration of organic iodide will increase this fraction very slightly.) For the case of uncontrolled pH, substitution of Eq. (15) into Eq. (23) yields

$$\frac{N_2}{N_T} = \left\{ 1 + \frac{V_L P}{V_g} \left[1 + 5.55 \times 10^{13} \left(\frac{V_L}{E_{dep}} \right)^{0.747} \right] \right\}^{-1} .$$ (24)

Equations (23) and (24) are in particularly convenient form to quickly estimate iodine volatility.

3.5 CALCULATIONAL RESULTS AND DISCUSSION

The analysis described in this section has been applied to each of the seven accident sequences mentioned in Table 1. The gas volumes used for BWRs include all primary containment space, although it may sometimes be appropriate to use only wetwell airspace, depending on sequence considerations. The various data and the quantities calculated from them are described for each accident sequence in ref. 5.

The conversion data of Lin[9] were taken at a dose rate of 4.5 Mrad/h—in the range of PWR rates. The data taken at ORNL are generally in the range of BWR dose rates (i.e., 0.35 to 0.6 Mrad/h). Both sets of data indicate that conversion is dominated by pH effects. In this study, two scenarios were evaluated: (1) control of pH above 7 and (2) uncontrolled pH with resulting drops below 7 due to nitric acid formation. For this calculation, it was not necessary to specify the material that was used to control the pH at 7 or above.

If the pH is controlled so that it stays above 7, the system of equations (22) is solved to yield the species distributions in Table 5. These results indicate a small production of volatiles for PWRs but virtually none for BWRs. Such results are strongly dependent on the aqueous conversion fraction of $F = 3 \times 10^{-4}$, which represents a best estimate of the maximum from ORNL data. Thus, if pH is maintained at 7 or above, only a small additional amount of I_2 is expected in the gas phase of PWR systems.

Table 5. Distribution of iodine species for pH controlled above 7

Plant	Accident	Fraction of total iodine (%)[a]			
		$I_2(g)$	$I_2(L)$	$I^-(L)$	$CH_3I(g)$
Grand Gulf	TCγ	0.05	0.03	99.92	0.001
	TQUVγ	0.01	0.03	99.96	0.0003
Peach Bottom	AEγ	0.002	0.03	99.97	0.0001
	TC2γ	0.002	0.03	99.95	0.0004
Sequoyah	TBA	0.21	0.03	99.97	0.004
Surry	TMLB'γ	1.9	0.03	98.0	0.03
	ABγ	2.4	0.03	97.5	0.03

[a]Assuming an equilibration time of $\Delta t = 15$ h.

If the pH falls below 7, a system for controlling pH is not being used and the decreased pH results in a larger fraction of aqueous I^- being converted to I_2. Evaporation of this volatile species to maintain equilibrium partitioning will result in greater atmospheric I_2. This, in turn, yields higher organic iodide concentrations. Results for this case are shown in Table 6 for the equilibrium species distributions. As expected, the levels of airborne volatiles are much higher than in the controlled case, indicating almost complete conversion for PWRs.

Table 6. Distribution of iodine species for uncontrolled pH

Plant	Accident	Fraction of total iodine (%)[a]			
		$I_2(g)$	$I_2(L)$	$I^-(L)$	$CH_3I(g)$
Grand Gulf	TCγ	24.1	13.9	61.8	0.20
	TQUVγ	6.0	16.6	77.7	0.05
Peach Bottom	AEγ	1.6	20.5	77.9	0.01
	TC2γ	10.1	16.7	73.2	0.06
Sequoyah	TBA	67.3	9.6	22.6	0.40
Surry	TMLB'γ	97.2	1.5	0.7	0.60
	ABγ	97.7	1.2	0.6	0.60

[a]Assuming an equilibration time of $\Delta t = 15$ h.

The gaseous I_2 fraction is considerably higher in PWRs than in BWRs because the large water volumes in the latter both lower the dose rate and retain greater quantities of dissolved I_2. This last effect also depends on the gas volume and the ratio of gas to liquid volumes. It is ironic that the relatively small gas space in the Peach Bottom reactor (generally a safety liability) permits noticeably less evaporation than other reactors, resulting in the lowest gaseous I_2 fractions.

The other principal effect is due to temperature—the I_2 partition coefficient changes markedly over the range of temperatures used. This effect of temperature is most noticeable in the BWR sequences where different sequences at the same plant show large differences in the airborne I_2 fraction. Thus, an increase in containment temperature (at the gas-liquid interface) from 60 to 115°C produces nearly an order of magnitude increase in the airborne fraction.

The organic iodide is present in PWRs at about 0.5% of core inventory. In BWRs, this concentration is closer to 0.1%. The I_2 generated by the radiolytic conversion of I^- dominates the amount released as I_2 from the RCS. Further, based on the equilibrium assumption, the presence of some I_2 already airborne will result in less evaporation of I_2 formed radiolytically. Hence, for the case of uncontrolled pH, the cumulative total is well represented by the equilibrium amount formed within containment.

4. TECHNICAL FINDINGS

This study assumed that iodine forms in containment can be delimited by an examination of the seven severe accident sequences in LWR plants, along with an evaluation of associated processes. The associated processes include the deposition of CsOH on RCS surfaces and the effects of radiolysis. The issue is the chemical form of iodine that may be produced in the RCS and in containment—not the ultimate disposition of the various chemical forms. For example, it is likely that much of the gaseous I_2 in containment would be removed by engineered safety features or would deposit on painted or metal surfaces.

4.1 ASSESSMENT OF IODINE CHEMICAL FORMS IN THE RCS

The maximum iodine as I plus HI calculated for the seven severe accident sequences is 3.2%. Iodine in all forms other than I, HI, and CsI is estimated to be less than 1%. Although this analysis only considered seven sequences at four plants, it is reasonable to consider that a maximum of 5% of the iodine would be present as elemental iodine and HI for all accident sequences. A minimum value would not be expected to be less than 1%. The remaining 95% of the iodine would be as CsI.

The gaseous forms of iodine that entered containment from the RCS were given in terms of both elemental iodine and HI, which are related by the reaction

$$I + \frac{1}{2}H_2 \rightleftharpoons HI. \tag{25}$$

Lower temperatures and higher hydrogen pressures tend to favor HI over I, with the opposite conditions favoring I over HI.

The major uncertainty is the extent to which CsOH will react with oxide materials and reduce its vapor pressure. If the reaction of CsOH is to have a major impact on the iodine chemical forms, most of it (certainly more than 90%) must be fixed at a very low vapor pressure.

4.2 ASSESSMENT OF IODINE CHEMICAL FORMS IN CONTAINMENT

The production of I_2 in containment will be directly related to the pH levels of the water pools. Failure to control the pH at or above 7 could result in a dramatic increase in atmospheric I_2. Essentially all of the I_2 could become gaseous in the PWRs without pH control. For BWRs, as much as 25% of the core inventory could become gaseous. However, maintaining the pH above 7 results in negligible volatilization.

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